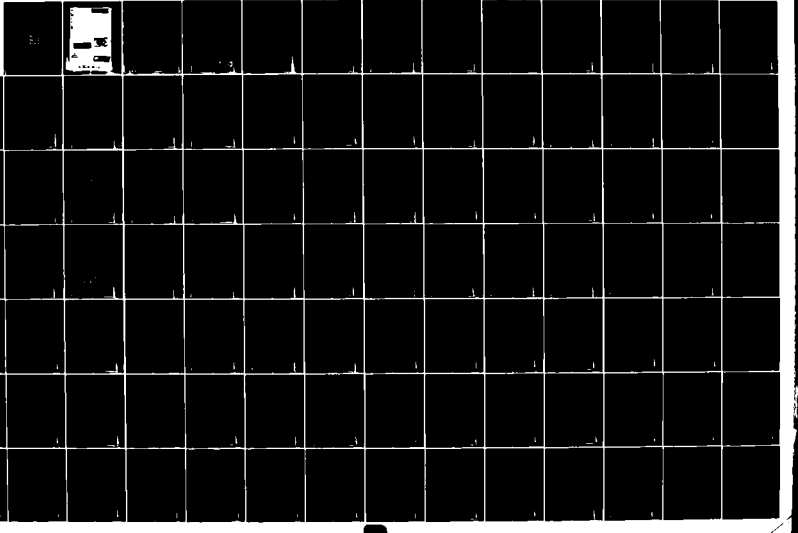
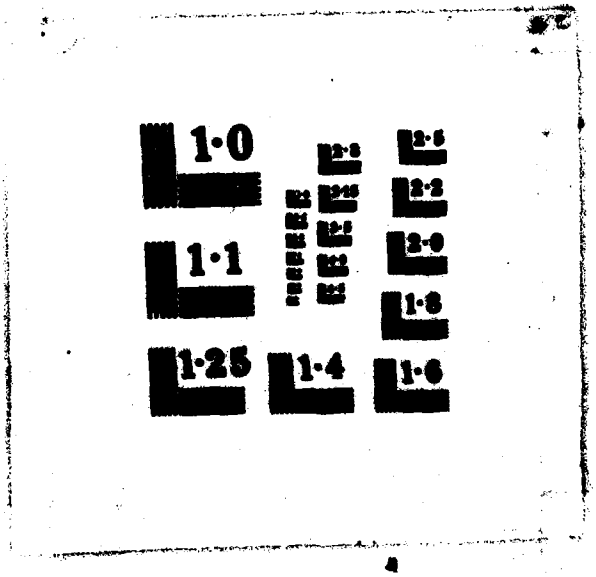
AD-A148 190 INTERNATIONAL CONFERENCE ON COORDINATION CHEMISTRY (23RD) HELD AT BOULDER..(U) COLORADO UNIV AT BOULDER E L KING ET AL. 03 AUG 84 ARO-21423.1-CH-CF 1/2

UNCLASSIFIED DAAG29-84-M-0199 F/G 7/4 NL




1·0
1·1
1·25
1·4
1·6
1·8
2·0
2·2
2·5



Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER ARO 21423.1-CH-CF	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Twenty-Third International Conference on Coordination Chemistry. Abstracts of Papers		5. TYPE OF REPORT & PERIOD COVERED 22 Feb 84-21 Feb 85 Final Report 6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Robert E. Sievers		8. CONTRACT OR GRANT NUMBER(s) DAAG29-84-M-0199
9. PERFORMING ORGANIZATION NAME AND ADDRESS University of Colorado		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS U. S. Army Research Office Post Office Box 12211 Research Triangle Park, NC 27709		12. REPORT DATE 13. NUMBER OF PAGES 681
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

The view, opinions, and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Coordination Chemistry
Catalysis
Synthesis
Reaction Kinetics
Thermodynamics
Electrochemistry

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Abstracts are presented in this book in the following areas: Energetics and Dynamics, Catalysis, Bioinorganic, Synthesis and Techniques and Applications.

21423.1-CH

TWENTY-THIRD INTERNATIONAL CONFERENCE ON COORDINATION CHEMISTRY

ABSTRACTS OF PAPERS

University of Colorado
Boulder, Colorado, U.S.A.
July 29 - August 3, 1984

Editors: Edward L. Blinn, Dwight H. Busch and Robert E. Stevens

DTIC
ELECTE
S D

Published by:
Cooperative Institute for Research
in Environmental Sciences
University of Colorado
Campus Box 449
Boulder, Colorado USA 80309

XXIII ICCC

Table of Contents

		Page
Sponsors and Supporters		v
Organizing Committee Members		vi
General Information		vii
Time Schedule		xiii
Plenary Lectures		1
Abstracts*		
I.	ENERGETICS AND DYNAMICS	
A.	Photophenomena in Coordination Chemistry	(1)65; (16)174; (34)254
B.	Reactivity and Redox Pathways--Theory and Experiment--Unusual Oxidation States	(48)477; (50)553; (61)691
C.	Kinetics and Mechanism of Transition Metal Compound Reactions	(1)9; (2)18; (9)95; (17)185; (18)195; (25)262
D.	Electrochemistry, Thermodynamics	(32)327; (48)482; (49)496; (50)496; (57)563
II.	CATALYSIS	
A.	Coordination Chemistry of Surfaces	(26)272
B.	Promoted Oxygenation	(3)27; (10)103
C.	Activation of Small Molecules	(33)337; (41)418; (51)588
III.	BIOINORGANIC	
A.	Nitrogenase	(11)117
B.	Metalloenzyme Coordination Chemistry	(42)427; (52)514; (58)571; (62)612; (63)634
C.	Coordination Chemistry of Iron Transport	(34)345; (48)486
IV.	SYNTHESIS	
A.	Ln and An Derivatives	(55)545; (60)634
B.	Complexes with Special Ligands-Macrocyclics Schiff Bases, Cryptates, Compartmental Ligands	(4)40; (12)123; (19)204; (26)213; (37)281; (38)302; (48)444
C.	Metals in Polymers-Catalysis and Electrochemistry	(28)291
D.	Multiple Metal-Ligand Bonds	Lecture 408; (59)594
E.	Metal Clusters	(42)409; (50)502; (58)575; (62)612
F.	General	(35)35; (39)448; (52)504; (62)622
V.	TECHNIQUES AND APPLICATIONS	
A.	Mass Spectrometric Techniques Applied to Coordination Compounds	(21)204

B.	Electronic Properties and Structure	(6)63; (14)154; (22)234; (29)290; (37)376
C.	Environmental Coordination Chemistry	(28)282; (45)461
D.	Applications in Medicine	(38)368; (39)397; (47)469; (59)583
E.	Coordination Chemistry in the Curriculum	(12)145
F.	General	(7)73; (23)242; (31)318

Author Index 665

The number in parenthesis is the session number; the abstracts for that session are to be found on the indicated pages.

Sponsors & Supporters

Sponsored by:

Division of Inorganic Chemistry of the American Chemical Society and the International Union of Pure and Applied Chemistry

Supported by:

ACS Petroleum Research Fund
Air Force Office of Scientific Research
Air Products and Chemicals, Inc.
Army Research Office
B.F. Goodrich Company
E.I. duPont de Nemours & Company, Inc.
Exxon Corporation
Monsanto Company
National Institutes of Health
Polaroid Corporation
Procter and Gamble Company
Rhone-Poulenc, Inc.
Standard Oil Company of Ohio
UOP, Inc.
Union Oil Company
University of Colorado

Accession For
NTIS GRA&I
DTIC TAB
Unannounced
Justification
Distribution/
Availability Codes
Dist | Avail and/or Special
A1

XXIII INTERNATIONAL CONFERENCE ON COORDINATION CHEMISTRY

John C. Bailar, Jr. and Henry Taube
Co-Presidents

Organizing Committee Members

Executive Committee

Robert E. Sievers
Conference Chairman
Cortlandt G. Pierpont
Conference Secretary
Daryle H. Busch
Program Chairman
Stanley Kirschner
Permanent ICCC Secretary
Mary C. Rakowski DuBois
Treasurer
Edward L. King
Publications Chairman

Advisory Committee

Arthur W. Adamson
Fred Basolo
F. Albert Cotton
Russell S. Drago
Mary L. Good
Harry B. Gray
Jack Halpern
M. Fred Hawthorne
Dale W. Margerum
Arthur E. Martell
Earl L. Muetterties(dec.)
Robert W. Parry
George W. Parshall
Norman Sutin

Program Committee

Daryle H. Busch
John Burgess
John P. Fackler
Thomas J. Meyer
Kenneth Raymond
Mark S. Wrighton

Local Arrangements Committee

Robert M. Barkley
Kenneth C. Brooks
Helena L. Chum
Daniel L. DuBois
Gareth R. Eaton
Sandra S. Eaton
Brenly B. Fleischer
Christine N. Elmslie
Pamela J. Keel
Carl A. Koval
Adam D. Norman
James C. Smart
Steven H. Strauss
Harold F. Walton

XXIII INTERNATIONAL CONFERENCE ON COORDINATION CHEMISTRY

General Information

The Opening Session and Plenary Lectures will be held in Macky Auditorium. Detailed information about the location of lecture and discussion rooms and other aspects of the meeting is provided in the on-site program.

Posters will be displayed in the Glenn Miller Ballroom of the University Memorial Center. Poster Discussions, in which all poster presenters participate, will be held in several small meeting rooms in the University Memorial Center and Chemistry 270.

Abstracts in this book are presented in the following arrangement: Abstracts for plenary lectures are presented first on the day given. Abstracts for Session Lectures and Poster Presentations for each half-day period are grouped together by symposium topic. Underlined names indicate the presenting author.

At the top of each abstract is given a designation of the half day, the session number, and the abstract number, e.g., Ma1-5, meaning Monday a.m., Session 1, Paper 5.

Session lectures have an "0" after the session number, e.g., TUp8-02.

Each abstract page is numbered at the bottom, and the Author Index gives this page number for the abstract of a paper by each author and co-author(s).

Time Schedule

The detailed schedule with the locations and times for all sessions is given in the on-site program. Only an outline of the program is presented here.

Five Plenary lectures are scheduled: one each on Tuesday, Thursday and Friday mornings starting at 9 a.m., and two on Wednesday morning starting at 8:30 a.m.

Morning Poster Meetings last from 10 a.m. to noon (posters will be on display during this two-hour period). Poster authors will be at their posters from 10:30 - 11 a.m. and in their assigned Poster Discussion rooms from 11:30 to noon. Associated Session Lectures will be from 11 - 11:30 a.m.

Afternoon Poster Meetings last from 1:30-3:30 p.m.; associated session lectures are scheduled for 2-2:30 p.m. and 2:30-3 p.m. Poster authors will be at their posters from 1:30 - 2 p.m., and in the assigned Poster Discussion rooms from 3 - 3:30 p.m.

Evening Poster Meetings last from 7:30-9:30 p.m.; associated Session Lectures are scheduled for 7:30 - 8 p.m. and 8 - 8:30 p.m. Poster authors will be at their posters from 8:30 - 9 p.m., and in the assigned Poster Discussion rooms from 9 - 9:30 p.m.

Session Lectures and Poster Discussions are classified under the following emphasis topics. The time periods for sessions in each of these areas are given below with the designated session numbers; if there is a Session Lecture associated with a session or group of sessions under the same topic, there is a designation "L".

	Monday		Tuesday		Wednesday		Thursday		Friday	
	Morn	Aft	Morn	Eve	Morn		Morn	Eve	Morn	Aft
I. ENERGETICS AND DYNAMICS										
A. Photochemistry		8 L,(2)	16 L	24 L						
B. Reactivity and Redox Pathways								48 L	56 L	61 L,(2)
C. Kinetics and Mechanisms	1,2 L	9	17,18 L	25 L						
D. Electrochemistry, Thermodynamics					32 L		49	48,50 L	57	
II. CATALYSIS										
A. Coordination Chemistry of Surfaces				26 L,(2)						
B. Promoted Oxygenation	3 L	10 L,(2)								
C. Activation of Small Molecules					33 L		41 L	51 L,(2)		
III. BIOINORGANIC										
A. Nitrogenase		11 L,(2)								
B. Metalloenzymes							42	52 L	58 L	62,63 L,(2)
C. Iron Transport					34 L		43 L			
IV. SYNTHESIS										
A. Ln and An Derivatives								53 L		64 L
B. Special Ligands	4 L	12 L	19,20	27 L	35		44			
C. Metals in Polymers				28 L,(2)						
D. Multiple Metal-Ligand Bonds							45 L	5 L,(2)		
E. Metal Clusters							46	54	59 L	65 L,(2)
F. General	5	13			36					66
V. TECHNIQUES AND APPLICATIONS										
A. Mass Spectrometry			21 L							
B. Electronic Structure	6 L	14	22 L	29	37					
C. Environmental Chemistry					38 L		46 L			
D. Applications in Medicine				30 L	39		47		60 L	
E. Coordination Chemistry in the Curriculum		15 L								
F. General	7		23	31						

PLENARY LECTURES

CHEMISTRY OF SQUARE PLANAR ORGANOMETALLIC COMPLEXES OF THE NICKEL GROUP RELEVANT TO CATALYSIS

Akio Yamamoto, Takakazu Yamamoto, Sanshiro Komiya, and Fumiyuki Ozawa

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 227, JAPAN

Square planar dialkyl complexes of Ni, Pd, and Pt exhibit intriguing difference in their reactivities. Their thermolysis pathways vary depending on the nature of metal, ligands, alkyl groups, geometry and added ligand. Kinetic studies on the thermolysis and trans-cis isomerization reactions of PdR_2L_2 (L = tertiary phosphine) complexes indicate the involvement of 3-, 4-, and 5-coordinate intermediates.



Constraints of these geometries on the reaction pathways to induce reductive elimination or β-hydrogen elimination are discussed.

Reactions of these complexes with carbon monoxide give different products depending on the metal, geometry and the alkyl groups. Reaction courses of PdR_2L_2 type complexes with CO can be accounted for consistently by assuming the alkyl migration to the coordinated CO ligand.

Based on the information obtained through these basic studies on the reactivities of square planar d^8 complexes, novel catalytic systems promoted by palladium complexes converting organic halides (RX), CO and amines into α-keto amides have been developed:

$$RX + 2CO + HNR_2' \xrightarrow{[Pd]} RCCNR_2'$$

The α-keto amides can be converted into a variety of useful compounds including α-amino acids.

The role of the palladium complexes involved in the catalytic double carbonylation is discussed.

Plenary II

COMMENTS ON THE INTERACTION OF DIOXYGEN SPECIES & METAL IONS

Henry Taube

Department of Chemistry, Stanford University, Stanford, California.

A survey will be made of data bearing on the interaction of metal ion complexes with dioxygen and the reduction products superoxide and peroxide. Equilibrium data, and, as well, kinetic data will be considered. The survey will better serve to identify effects which challenge our understanding than to provide explanations.

STRUCTURE AND REACTIVITY OF SOME TRANSITION METAL COMPLEXES

Günther Wilke

Max-Planck-Institut für Kohlenforschung,
Kaiser-Wilhelm-Platz 1, D-4330 Mülheim-Ruhr, West-Germany

Recent investigations on the structure of bis η^3-allylnickel will be discussed in addition to some remarkable reactions involving this system. The interactions of organometallic main group metal species with olefin nickel complexes have been investigated by NMR-spectroscopy and, in the cases of stable complexes, by x-ray crystallography. The acceptor strength of the nickel atom depends upon the coordinated π-ligands as does the polarity of the bonds between nickel and complexed groups from main group organometallics. In this context a very effective catalytic transalkylation of aluminum trialkyls with olefins will be described which has also been observed for an organo-lithium species.

Plenary IV

ENCAPSULATED METAL IONS

Alan M. Sargeson

The Research School of Chemistry, Australian National University, G.P.O. Box 4, Canberra A.C.T. 2601 Australia

The metal ion complexes of sexidentate macropolycyclic aza- and thia-aza ligands have displayed a variety of interesting properties. They include: extraordinary stability, surprisingly rapid electron transfer rates between the encapsulated metal ions despite the saturated organic insulating cage, sensitive communication between substituents on the ligand and the metal ion leading to substantial variations in the redox potential and interesting reactivity of the bound ligands.

The origin of the rapid electron transfer, attributed to strain in the bound ligand, has implications in general for electron transfer reactions both for simple complex ions and metalloenzymes. The effect should also be reflected in redox potentials and spectroscopic phenomena. Aspects of the cage chemistry pertaining to these phenomena and effects will be discussed. What happens to the electron transfer rates and redox potentials when the cage is compressed for example? Can two metal ion cages be dimerised and do the metal ions then communicate? How does the metal ion enter and leave the cage? What are the general structural, spectroscopic and photochemical features of the cage complexes?

Finally, some new developments and prospects for the use of such complexes will be outlined.

MONONUCLEAR ACTIVE SITES OF MOLYBDOENZYMES: CHEMICAL APPROACHES TO STRUCTURE AND REACTIVITY

R. H. Holm and Jeremy M. Berg

Department of Chemistry, Harvard University, Cambridge, Massachusetts, USA 02138

One of two general classes of molybdoenzymes contains mononuclear catalytic sites and effects oxidation or reduction of substrate X/XO by oxygen atom transfer: X + (O) $\rightleftharpoons$ XO. The reaction $L_nMoO_2 + X \rightarrow L_nMoO + XO$ is well established in synthetic systems, and is frequently accompanied by dimerization of Mo(VI,IV) complexes to $[L_nMo(V)O]_2O$. A general kinetic analysis allowing determination of oxo-transfer rate constants in systems with μ-oxo dimer formation is outlined. EXAFS results for several enzymes indicate the minimal coordination spheres $Mo(VI)O_2(SR)_{2,3}$ and $Mo(IV)O(SR)_{3,4}$ for oxidized and fully reduced forms, respectively. In a synthetic approach to these sites, the ligand pyridine-2,6-bis(1,1-diphenylethanethiol) was prepared. Reaction with $MoO_2(acac)_2$ afforded the 5-coordinate trigonal bipyramidal complex $MoO_2(L\text{-}NS_2)$, which was converted to $MoO(L\text{-}NS_2)(DMF)$ with Ph_3P in DMF. In this and other oxo-transfer reactions of these complexes, the gem-diphenyl groups sterically suppress dimerization to a Mo(V)-O-Mo(V)O complex. This reaction is blocked in enzymes by protein structural constraints. $MoO(L\text{-}NS_2)(DMF)$ and Me_3NO react to produce $MoO_2(L\text{-}NS_2)$ and Me_3N. Substrate saturation kinetics are observed at sufficient Me_3NO concentrations. The two reactions were coupled to generate a catalytic sulfoxide reduction/phosphine oxidation cycle. In a related reaction d-biotin-d-sulfoxide is reduced by $MoO(L\text{-}NS_2)(DMF)$ to d-biotin. Inasmuch as d-biotin-d-sulfoxide reductase is a Mo enzyme-dependent enzyme, this reaction provides a meaningful model for an enzymatic oxo-transfer reaction. Kinetic data for various oxo-transfer reactions are presented and their relevance to enzymatic processes is discussed.

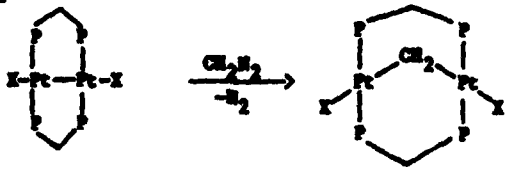
MONDAY MORNING

KINETICS AND MECHANISMS OF "MOLECULAR A-FRAME" FORMATION

James K. Hoyano and S. Muralidharan

Iowa State University, Ames Laboratory and Department of Chemistry, Ames, Iowa 50011 USA

The dimuclear platinum(I) complexes $X_2Pt_2(\mu\text{-dppm})_2$[dppm = bis-(diphenylphosphino)methane, X = halide] are converted to so-called molecular A-frame structures.[1] In a typical example, shown in eq 1, CH_2N_2 inserts into the metal-metal bond.



(1)

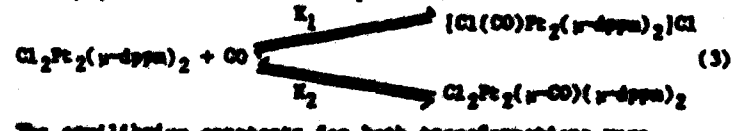
Analogous transformations occur to insert such groups as SO_2, CO, S(from S_8), and H^+(from HCl). Similar albeit slower transformations are observed for cationic complexes $[L_2Pt_2(\mu\text{-dppm})_2]^{2+}$ and $[L(X)Pt_2(\mu\text{-dppm})_2]^{+}$ (L = CO, pyridine, PPh_3).

A general rate law applicable to the reactions in CH_2Cl_2 of all of the complexes, $(Pt^1)_2$, with all of the reagents (R), is:

$$\frac{d[\text{A-frame}]}{dt} = \frac{k_1[(Pt^1)_2][R]}{\kappa + [R]} \qquad (2)$$

In some cases only the condition $\kappa >> [R]$ prevails, and second-order kinetics apply. In others, the full rate equation is found, a situation realized for $(PPh_3)_2Pt_2(\mu\text{-dppm})_2^{2+}$ and R = CH_2N_2, SO_2, CO, S_8, and HCl. These reactions all attain the same limiting rate at sufficiently high [R], characterized by $k_1 = (2.78 \pm 0.08) \times 10^{-2}$ $M^{-1}s^{-1}$ at 25 °C in CH_2Cl_2 ($\Delta H_1^{\ddagger} = 25.1 \pm 0.4$ kcal mol^{-1}, $\Delta S_1^{\ddagger} = 18.5 \pm 1.3$ cal mol^{-1} K^{-1}). These and other data suggest a two-step mechanism, the first step being unimolecular heterolysis of the metal-metal bond.

The reaction of $Cl_2Pt_2(\mu\text{-dppm})_2$ with CO forms not only the A-frame product, but also (and more rapidly) a metal-metal bonded monocarbonyl, both in reversible equilibria:



(3)

The equilibrium constants for both transformations were evaluated by ^{31}P NMR (eq 3, $K_1 = 38.1 \pm 0.2$ M^{-1}, $K_2 = 10.9 \pm 0.3$ M^{-1} in CH_2Cl_2 at 25 °C). The kinetics of the forward and reverse of the separate reactions have also been determined. In the forward direction, each follows a rate law like eq 2. Mechanisms have been proposed to account for these observations.

1. Puddephatt, R. J. Chem. Soc. Reviews, 1983, 12, 99.

REACTIVITY OF Ni(Me_4-14-ane)$^+$ TOWARD ALKYL HALIDES AND HYDROPEROXIDES. OXIDATIVE ADDITION VS. RADICAL ABSTRACTION

Andreja Bakač and James H. Espenson

Ames Laboratory, Iowa State University, Ames, Iowa 50011, U.S.A.

(1,4,8,11-Tetramethyl-1,4,8,11-tetraazacyclotetradecane)-nickel(I) ion, Ni(Me_4-14-ane)$^+$, reacts with methyl iodide in alkaline aqueous solution according to eq 1

$$2\ Ni(Me_4\text{-}14\text{-}ane)^+ + MeI \longrightarrow MeNi(Me_4\text{-}14\text{-}ane)^+ + I^- + Ni(Me_4\text{-}14\text{-}ane)^{2+} \qquad (1)$$

The new organonickel complex MeNi(Me_4-14-ane)$^+$ is also produced in the reaction of Ni(Me_4-14-ane)$^+$ and $MeC(Me)_2OOH$, eq 2

$$2\ Ni(Me_4\text{-}14\text{-}ane)^+ + MeC(Me)_2OOH \longrightarrow MeNi(Me_4\text{-}14\text{-}ane)^+ + Ni(Me_4\text{-}14\text{-}ane)^{2+} + CMe_2O + OH^- \qquad (2)$$

At pH 12.5 and 0.10 M ionic strength, MeNi(Me_4-14-ane)$^+$ decomposes according to eq 3 with $k_3 = 4.09 \times 10^{-3}\ s^{-1}$.

$$MeNi(Me_4\text{-}14\text{-}ane)^+ + H_2O \longrightarrow Ni(Me_4\text{-}14\text{-}ane)^{2+} + CH_4 + OH^- \qquad (3)$$

Higher alkyl halides also react with Ni(Me_4-14-ane)$^+$ producing short-lived organonickel complexes. The assignment of the mechanisms of the formation and decomposition reactions is based on the kinetics, stoichiometry and product analysis data.

Ma1-2

VOLUME OF ACTIVATION AS MECHANISTIC CRITERION FOR COMPLEX FORMATION AND AQUATION REACTIONS OF TRANSITION METAL IONS

R. Mohr and R. van Eldik

Institute for Physical Chemistry, University of Frankfurt, Robert Mayer Str. 11, 6000 Frankfurt/Main, FRG

The application of high pressure kinetic measurements in the elucidation of intimate reaction mechanisms of transition metal complexes has made significant progress in recent years[1,2]. With the general availability of equipment capable of handling the study of fast reactions under pressures up to 3 kbar, systematic data sets become available which enable volumes of activation to be employed as an important mechanistic criterion. It is along these lines that we have studied the effect of pressure on a series of complex formation and the reverse aquation reactions of some first row transition metal ions. Preliminary results [3,4] demonstrated that complex formation of Mn(II), Fe(II), Co(II) and Ni(II) with bipyridine and terpyridine in general follows the pattern observed for the solvent exchange reactions of these species[5]. A gradual mechanistic changeover from I_a to I_d substitution processes occurs along these metal ions.

We have now completed this series of studies and have volume of activation data for the complex formation reactions (excess metal ion and excess ligand) as well as the reverse aquation processes. These results will be discussed in detail and the value of $\Delta V^{\ddagger}$ as mechanistic criterion will be emphasized.

1. R. van Eldik and H. Kelm, Rev. Phys. Chem. Jpn., 50, 185 (1980).
2. D.A. Palmer and R. van Eldik, Coord. Chem. Rev., 36, 89 (1981).
3. R. Dose and R. van Eldik, Inorg. Chem., 21, 4108 (1982).
4. R. van Eldik, E.L.J. Breet, R. Dose, R. Mohr and H. Kelm, AIRAPT meeting, Albany (1983).
5. A.E. Merbach, Pure Appl. Chem., 54, 1479 (1982) and references cited therein.

Mal-3

FORMATION AND STABILITY OF PALLADIUM(II) CARBONATO COMPLEXES

G. Mahal and R. van Eldik

Institute for Physical Chemistry, University of Frankfurt,
Robert Mayer Str. 11, 6000 Frankfurt/Main, FRG

In contrast to the numerous data available on the formation and aquation reactions of octahedral carbonato complexes[2], very little is known concerning the corresponding reactions of square planar complexes. Our recent activities in the area of substitution reactions of Pd(II) complexes[2-4] have emphasized the important role of spontaneous aquation reactions occurring in aqueous solution[5]. Such aquated species have now been found to react very rapidly with dissolved CO_2 to produce the corresponding carbonato complexes. A systematic study of the kinetics of such complex formation reactions as well as the reverse acid- and base-catalysed aquation reactions was undertaken, and the results will be presented.

The aquo complexes studied are all of the type $Pd(L)OH_2^{2+}$, where L = dien; 1,1,7,7-Me_4dien and 1,1,7,7-Et_4dien (dien = diethylenetriamine). Typical CO_2 uptake rate constants are 80 and 5300 $M^{-1} s^{-1}$ at 25°C for L = Et_4dien and Me_4dien, respectively. The acid-catalysed decarboxylation of $Pd(Et_4dien)OCO_2$ has a rate constant of 2 s^{-1} at 25°C, which is in good agreement with that found for octahedral complexes. The base-catalysed aquation rate constant strongly depends on the steric crowding on the dien ligand and presumably involves rate-determining substitution by water (i.e. solvolysis) via metal-oxygen bond breakage on the carbonate ligand. The significance of these results in relation to the general substitution behaviour of such complexes will be discussed in detail.

1. D.A. Palmer and R. van Eldik, Chem. Rev., in press.
2. E.L.J. Breet, R. van Eldik and H. Kelm, Polyhedron, in press.
3. R. van Eldik, E.L.J. Breet, M. Kotowski, D.A. Palmer and H. Kelm, Ber. Bunsenges. Phys. Chem., 87, 984 (1983)
4. E.L.J. Breet and R. van Eldik, Inorg. Chem., in press.
5. M. Kotowski and R. van Eldik, prepared for publication.

Ma1-4

KINETIC AND STRUCTURAL INVESTIGATIONS OF Fe^{III} EDTA CATALYSED DECOMPOSITION OF HYDROGEN PEROXIDE

Keith C. Francis, Diane Cummins and John Oakes

Unilever Research Port Sunlight Laboratory, Quarry Road East, Bebington, Wirral, Merseyside, L63 3JW, England

A detailed kinetic analysis is given of hydrogen peroxide decomposition catalysed by Fe^{III} EDTA. Structural investigations have been made using nmr and electronic absorption spectroscopy. It is demonstrated that the monohydroxy Fe^{III} EDTA complex is the primary active catalyst and this reacts with the perhydroxyl anion to produce the well known purple complex. Decomposition of hydrogen peroxide conforms to Michaelis-Menten kinetics, the rate determining step involving breakdown of this complex. In contrast to earlier reports, it is shown that the HO_2^- ion displaces a carboxyl group from the monohydroxy Fe^{III} EDTA complex rather than the hydroxyl group. The dihydroxy Fe^{III} EDTA complex is also shown to form a purple peroxy complex with HO_2^-, but its breakdown occurs at a much slower rate. The results are consistent with formation of radicals either upon breakdown of the peroxy complex or in subsequent reactions, but these are not rate determining.

NMR STUDIES OF CATALASE AND MODELS

J. Oakes

Unilever Research Port Sunlight, Quarry Road East, Bebington, Wirral, Merseyside, L63 3JW, England

The rate at which catalase can decompose hydrogen peroxide into oxygen and water is one of the highest recorded for enzyme reactions - 1 molecule of catalase can decompose 2½ million molecules of peroxide in 1 minute at 0°C. This poster will dwell upon recent NMR and x-ray investigations and how they have shed light upon the way nature has specifically designed the active centre of catalase and determined its mechanism of action. One topic of recent interest is whether a water molecule is accessible to the active site. It will be demonstrated somewhat surprisingly, that water does not actually coordinate to Fe(III) but is strategically situated some 3.8Å away. This has important consequences mechanistically and will be discussed in some detail.

THE CORRELATION OF SUCCESSIVE STABILITY CONSTANTS FOR METAL COMPLEXES-ANTICOOPERATIVITY AND COOPERATIVITY

Edward L. King
Department of Chemistry, University of Colorado, Boulder, Colorado, USA 80309

Successive replacement of one type of ligand, H_2O, by another, X, in the first coordination shell of a hydrated metal ion conforms to the statistical pattern, the Langmuir isotherm,

$$\bar{n}/N = \kappa[X] \; / \; (1+\kappa[X])$$

in very few systems. For most systems, particularly those involving anionic ligands, the range of concentration of X over which the value of $\bar{n}/N$ changes by a particular amount (e.g. from 0.25 to 0.75) exceeds the statistical value, e.g. for a change of $\bar{n}/N$ from 0.25 to 0.75 requires a ligand concentration change that is larger than the statistical nine-fold range. For such systems the addition of an X ligand to the coordination shell of the metal ion reduces the tendency for the successive stages of ligation; this type of system is said to be anticooperative. For some metal complex ion systems, however, the opposite is observed. The change of ligation from $\bar{n}/N$ = 0.25 to 0.75 occurs over a smaller than statistical range of concentration of ligand, and such systems are called cooperative. Models for the correlation of data from systems displaying each of these types of behavior will be presented, as will be their application to literature data. Of particular interest is application of the Monod-Wyman-Changeux allosteric model[1] to data for those systems displaying cooperativity. The essential features of this model as it pertains to metal complex ion systems are the existence of the hydrated metal ion in two or more forms coupled with the undominant of these forms having the greater ligation tendency. The two forms for the hydrated metal ion may be two coordination numbers (e.g. four and six for zinc(II)) or two different spin states (e.g. high spin and low spin nickel(II)).[2]

1 J. Monod, J. Wyman, and J.-P. Changeux, J. Mol. Biol. 12 88(1965)

2 E. L. King, Inorg. Chem. 20,2350(1981)

Ma1-7

PRESSURE EFFECT ON THE RATE OF LIGAND ISOTOPIC EXCHANGE OF SOME METAL ACETYLACETONATO COMPLEXES IN ACETYLACETONE

Akira Nagasawa, Hiroaki Kido, Tomoko M. Hattori, Hideaki K. Tanaka and Kazuo Saito

Chemistry Department, Faculty of Science, Tohoku University, Sendai, 980 Japan

Our studies of ligand isotopic exchange of tris(acetylacetonato) complexes of ter- and quadrivalent metal ions have been extended to the following systems under high pressures up to 300 MPa by the isotope labelling method.(1)

$$[Al(acac^*)_3] + Hacac \rightleftharpoons [Al(acac)_3] + Hacac^*$$

$$[Mo^{VI}O_2(acac^*)_2] + Hacac \rightleftharpoons [MoO_2(acac)_2] + Hacac^*$$

The McKay R is expressed by the following equations for both.

$$R = -2[Mo]\ln(1 - F)/t \quad \text{and} \quad R = -3[Al]\ln(1 - F)/t$$

$$R = [complex](k_1 + k_2[H_2O])$$

Complex		Rate const.	k_H/k_D	$\Delta H^{\ddagger}$ [b]	$\Delta S^{\ddagger}$ [c]	$\Delta V^{\ddagger}$ [d]
$[Al(acac)_3]$	k_1	9.07×10^{-5}	1.5	85.1	-36.6	+9.1 ± 1.4
	k_2	1.47×10^{-3} [a]	1.6	80.3	-31.9	+5.3 ± 0.4
(in EtOAc) (2)	k_1	0.11×10^{-5}	—	89.5	-51.0	—
	k_2	0.46×10^{-3} [a]	—	89.5	+0.1	—
$[MoO_2(acac)_2]$	k_1	1.05×10^{-3}	1.9	64.4	-85.5	0 ± 1
	k_2	8.27×10^{-3} [a]	1.5	63.9	-70.6	0 ± 1

[a] Second order rate const. in $dm^3 mol^{-1} s^{-1}$ [b] $kJ\,mol^{-1}$
[c] $J\,mol^{-1}K^{-1}$ [d] $cm^3 mol^{-1}$

Common steps of the ligand exchange are written as:



Since the deuterium isotope effect is significant, the proton transfer must play an important role in determining the rate of exchange. By considering a stationary state of the intermediate with an added Hacac, the rate formula for k_1 is written as follows.

$$k_1 = k_a k_p/(k_{-a} + k_p)$$

The observed $\Delta V^{\ddagger}$ is analyzed to consist of $(\Delta V_a^{\ddagger} + \Delta V_{-a}^{\ddagger} + \Delta V_p^{\ddagger})$, while k_{-a} should be much larger than k_p. Since the proton transfer does not seem to involve big volume change, the observed $\Delta V^{\ddagger}$ should reflect the activation volume of the first step.

Observation of volume of activation for substitution reactions involving chelate ligand is quite novel, and useful for discussing the reaction mechanism.

(1) K.Saito, Pure and Applied Chem., 1974, 38, 325; A.Nishikawa, H. Kido, K.Saito, Inorg. Chem., 1981, 20, 1107 and the references.
(2) K.Saito, K.Umeda, Bull.Chem.Soc.Jpn., 1968, 41, 304.

DYNAMICS OF EQUILIBRIA IN AQUEOUS SOLUTION OF PARAMAGNETIC TRANSITION METAL COMPLEXES

István Nagypál

Department of Chemistry, Lajos Kossuth University, H-4010 Debrecen, Hungary

The NMR relaxation study of the ligand exchange processes has received considerable attention since the laying of the foundation of the method by Swift and Connick[1]. Their method - used to study the rate of water exchange from the first coordination sphere of the paramagnetic metal ions - has later been extended to other solvents and to the metal-ligand systems.

The most important condition for studying the dynamics of equilibria is to know the composition and stability of the complexes formed in the systems under exactly the same condition which is used for NMR relaxation studies. This condition, however, was taken into account only in some exceptional cases earlier. Moreover, the effect of the ligand exchange between the paramagnetic sites has been completely ignored.

Our - partly published - recent equilibrium and relaxation studies in aqueous solution of more than twenty copper(II), vanadyl and chromium(II) complexes led to the following results:

a. The exchange of ligands between the paramagnetic sites must be considered. Its ignorance led to the misinterpretation of the earlier studies.

b. The rate of proton exchange between the diamagnetic sites (for example $NH_3 \rightleftharpoons H_2O$) must also be considered; even their rate constants could be calculated in a number of systems.

c. The ligand exchange takes always place through the formation and dissociation of the successive complexes. This is supported by T-jump studies in some systems.

d. The results indicate that the NMR relaxation and chemical relaxation methods are closely inter-related. The reason of the almost independent development of these methods is that the NMR results for ligand exchange processes were not interpreted correctly earlier.

1. T.J. Swift and R.E. Connick, J. Chem. Phys. 1962, 37, 307.

THE RATES OF EXCHANGE BETWEEN THE FREE AND BOUND CARBONATES OF $UO_2(CO_3)_3^{4-}$ ION

B.M. Alqaadi

Department of Chemistry, College of Education, University of Baghdad, Baghdad, Iraq.

The rates of exchange between free and bound carbonates of the tris-carbonate dioxouranate(VI) ion at various temperatures (8°-70°C) and hydrogen ion concentrations (pH=7.9-10.3) are measured. ^{13}C-NMR measurements were performed on a Bruker wp-200 spectrometer equipped for variable temperature operation. The rates of exchange were calculated using line-shape analysis with the aid of a computer program.

Carbonate-bicarbonate mixtures give a singlet spectrum whose apparent chemical shift is a weighted average of the composition. Titration against NaOH of a solution of 0.09M $NaHCO_3$ and 0.3M $NaNO_3$ with a 90% label in 90%-5% H_2O—D_2O results in a pK_a of 9.70±0.02 at 20°C.

INTRAMOLECULAR TWO-ELECTRON-TRANSFER IN THE OXIDATION OF *cis*-DIAQUABIS(OXALATO)CHROMATE(III) BY PERIODATE

Nader A. Al-Jallal and Yousif Sulfab

Department of Chemistry, University of Kuwait, P.O. Box 5969, Safat, Kuwait, State of Kuwait

There are very few reports on the oxidation of the chromium (III) ion or complexes. The oxidation of *cis*-$[Cr(OX)_2(H_2O)_2]^-$ by IO_4^- gives Cr(VI) as the final product. The kinetics of this reaction in presence of a large excess $[IO_4^-]$ obeyed first-order dependence on $[Cr^{III}]_T$. The dependence of k_{obs}, the pseudo-first-order rate constant, on $[IO_4^-]$ is not linear and obeyed eq.(1) at fixed reaction conditions.

$$k_{obs} = \frac{2k[IO_4^-]}{1 + K[IO_4^-]} \qquad (1)$$

From linear plots of k_{obs}^{-1} *vs* $[IO_4^-]^{-1}$, the values of k and K were determined at various reaction conditions.

Equation (1) is consistent with complex formation between the two reactants in a step preceding the intramolecular electron-transfer step. The hydroxo-form of the complex, $[Cr(OX)_2(H_2O)(OH)]^{2-}$, is the reactive Cr(III) species where hydroxo ligand labilizes the *cis* H_2O and facilitates substitution by periodate and lowers the redox potential of the Cr(III,V) couple.

Chromium(V) is believed to be the primary product of oxidation as evidenced from the lack of initiation of polymerization of acrylonitrile. The stoichiometry of the reaction was investigated and from it a "dead end" chromium(III)-periodate complex is believed to be formed.

KINETICS AND MECHANISM OF THE REACTIONS BETWEEN ACETATOPENTAAMMINECOBALT(III) AND RUTHENIUM(II)-AMMINE SPECIES IN AQUEOUS SOLUTION.

Edward A. Alozie, J. Folorunso Ojo and Olusegun Olubuyide.

Department of Chemistry, University of Ife, Ile-Ife Nigeria.

The reactions between acetatopentaamminecobalt(III) and ruthenium(II)ammine species ($Ru(NH_3)_6^{2+}$ and $Ru(NH_3)_5H_2O^{2+}$) have been investigated in aqueous solution at I = 0.20 mol.dm^{-3}(LiCl), [H$^+$] = 0.01-0.04 mol.dm^{-3}(HCl) and t = 25°C. Electron-transfer occurs in this acid concentration range between hexaammine-ruthenium(II) and acetatopentaamminecobalt(III) by an acid-catalysed path, and outer-sphere mechanism. The protonated and unprotonated cobalt(III) species undergo electron-transfer with hexaammine-ruthenium(II) with second-order specific rate constants k = 35.2 dm^{3}mol^{-1} sec^{-1} and 0.10 dm^{3}mol^{-1}sec^{-1} respectively at 25°C. No electron-transfer occurs in this acid concentration range between acetatopentaamminecobalt(III) and aquapentaammineruthenium(II) species, but a stable complex in which acetate forms a bridge between cobalt(III) and ruthenium(II) is formed. The UV and visible spectra of the resulting complex are:

UV : λ_{max} = 330nm, ε_{max} = 1.51x10^{3}dm^{3}mol^{-1}cm^{-1}
Visible: λ_{max} = 516nm, ε_{max} = 70 dm^{3}mol.$^{-1}$cm^{-1}

The specific rate constant (k) for the formation of the complex at 25°C, I = 0.20mol.dm^{-3}(LiCl), [H$^+$] = 0.01-0.04 mol.dm^{-3} (HCl) is (0.63 ± 0.06)dm^{3}mol^{-1}sec^{-1}.

Recently, aquapentaammineruthenium(II)[1] was shown to undergo electron-transfer reaction by innersphere mechanism with some cobalt(III) complexes, for the first time. The investigation reported here is also the first of its type in which the electron-transfer power of ruthenium(II) towards cobalt(III) species is masked, by complex formation.

References:

1. Oboyega Daramola, J. Folorunso Ojo, Olusegun Olubuyide, and Fidelis Oriaifo, J. Chem. Soc. (Dalton Trans.) 1982, 2137; other references therein.

HIGH-PRESSURE OXYGEN-17 NMR WATER EXCHANGE STUDIES ON THE Ti^{3+}, V^{3+}, Al^{3+} AND Ga^{3+} HEXAAQUATED METAL IONS.

Alain Hugi, Deirdre Hugi, Lothar Helm and André E. Merbach.

Institut de Chimie Minérale et Analytique, Université de Lausanne, 3, Place du Château, CH-1005 Lausanne, Switzerland.

We have recently built high pressure multinuclear magnetic resonance probe heads, for electro-[1] and superconducting magnets,[2] with the high spectral resolution ($1 \cdot 10^{-8}$ and $0.5 \cdot 10^{-9}$ ppm, respectively) and the good stability (± 0.2 K) and accuracy of temperature required for kinetic applications. This technique has been used to study the effect of pressure on the exchange rate of solvent molecules between the first coordination sphere of a metal ion or complex, and bulk solvent.

The most striking results were obtained for the divalent high spin first row hexasolvated transition metal ions. Contrary to earlier belief (Eigen-Wilkins mechanism) there is a gradual changeover in substitution mechanisms along the series. The early members show I_a behaviour and the later ones I_d behaviour, the change in activation mode occurring after the d^5 configuration.[3]

In this communication we report the results of a variable temperature and variable pressure oxygen-17 NMR study of water exchange on the Ti^{3+}, V^{3+}, Al^{3+} and Ga^{3+} hexaaquated ions. The study was performed in solutions of variable acid concentration and with non-coordinating counter-ions. For the first two ions the water exchange rates are strongly accelerated with pressure, whereas for the latter two ions the rates are decreased with pressure, allowing assignment of associative and dissociative activation modes, respectively. The dissociative behaviour of gallium is to be stressed because it is in contradiction with claims for an associative transition state for complex formation reactions on this ion.[4]

Along the first row transition metal series, the progressive increase in activation volume (from negative values to a small positive values) for the high spin trivalent metal ions leads to the conclusion that there is a changeover in mechanism after the d^3 configuration :

Ti^{3+} (I_a), V^{3+} (I_a), Cr^{3+} (I_a), Fe^{3+} (I_a), Ga^{3+} (I_d).

1. W.L. Earl, H. Vanni and A.E. Merbach, J. Magn. Reson. 29, 11 (1978).

2. D.L. Pisaniello, L. Helm, P. Meier and A.E. Merbach, J. Am. Chem. Soc. 105, 4628 (1983).

3. A. Merbach, Pure & Appl. Chem. 54, 1479 (1982).

4. R. Cerioli, F. Secco, M. Venturini, Inorg. Chem. 21, 2992 (1982).

Ma2-4

CORRELATION BETWEEN REACTIVITIES AND STRUCTURES OF Ni(II)-ETHYLENEDIAMINE AND -GLYCINATE COMPLEXES IN SOLUTION

Mitoshi Ohtaki

Department of Electronic Chemistry, Tokyo Institute of Technology at Nagatsuta, Nagatsuta-cho, Midori-ku, Yokohama, 227 JAPAN

Structures of $[Ni(H_2O)_n(en)_m]^{2+}$ (n=2, m=2 and n=0, m=3) and $[Ni(H_2O)_n(gly)_m]^{(2-m)+}$ (n=4, m=1 and n=0, m=3) complexes have been determined by the X-ray diffraction method for solutions containing these complexes, and the structure data are compared with thermodynamic and kinetic ones of the complex formation reactions in order to discuss reactivities of the complexes.

The X-ray diffraction analysis of the $[Ni(H_2O)_6]^{2+}$ 1) and $[Ni(H_2O)_n(en)_m]^{2+}$ 2) complexes in solution reveals that the Ni-OH_2 bond lengthens from 2.04 Å in $[Ni(H_2O)_6]^{2+}$ to 2.10 Å in $[Ni(H_2O)_2(en)_2]^{2+}$ when ethylenediamine molecules are introduced to the coordination sphere of Ni(II) ion. The Ni-N bond within the $[Ni(H_2O)_n(en)_m]^{2+}$ complexes also elongates from 2.10 Å in $[Ni(H_2O)_2(en)_2]^{2+}$ to 2.20 Å in $[Ni(en)_3]^{2+}$. Thus, we can conclude that the Ni-OH_2 and Ni-N bonds lengthen, and therefore, weaken with increasing number of ethylenediamine molecules within the complexes. The decrease (i.e., more negative) in the ΔS°_n value of stepwise formation reactions of the $[Ni(H_2O)_n(en)_m]^{2+}$ complexes is responsible for the decrease in the ΔG°_n value of the complexes, although the ΔH°_n value becomes more negative with the increase in the number, n, of ethylenediamine molecules within the complexes. The results indicate that the Ni-OH_2 bond more and more weakens and becomes easier to be broken in a higher complex than a lower one, and therefore, velocity constants should be larger at the stage of formation of a higher complex than a lower one, even the entropy of activation may act slightly unfavorably at the former step than the latter.

A similar consideration may be made for the formation reactions of $[Ni(H_2O)_n(gly)_m]^{(2-m)+}$. However, the situation may be more complicate and interpretation of the thermodynamic quantities of the complex formation reactions may be more difficult in the glycinate system than in the ethylenediamine one, because in the former the Ni-O distance between the central nickel(II) ion and an oxygen atom within the carboxylate group of glycinate ion shortens from 2.09 Å in $[Ni(H_2O)_4(gly)]^+$ (through 2.06 Å in $[Ni(H_2O)_2(gly)_2]$ (solid)) to 2.03 Å in $[Ni(gly)_3]^-$, and on the other hand, the Ni-N and Ni-OH_2 bonds lengthen from 2.09 Å in $[Ni(H_2O)_4(gly)]^+$ to 2.14 Å in $[Ni(gly)_3]^+$ and from 2.04 Å in $[Ni(H_2O)_6]^{2+}$ to 2.10 Å in $[Ni(H_2O)_2(gly)_2]$ (solid), respectively, 3) with increasing number of glycinate ions, m, within the complexes. Thus, we can expect that, independent of the change in the length of the Ni-O(COC) and Ni-N bonds, the Ni-OH_2 bond weakens in the course of the complex formation reactions, and thus, the velocity constant of the complex formation reactions should be increased with the number of glycinate ions within the complexes.

1) M. Ohtaki, T. Yamaguchi and M. Maeda, Bull. Chem. Soc. Jpn., 49, 701 (1976).
2) T. Fujita and M. Ohtaki, Bull. Chem. Soc. Jpn., 55, 458 (1982).
3) R. Tsuchiya and M. Ohtaki, Bull. Chem. Soc. Jpn., 56, 3635 (1983).

SYNTHESES AND KINETIC ASPECTS OF THIOCYANATO AND ISOTHIOCYANATO LINKAGE ISOMERS OF COBALT(III) COMPLEXES LIGATING AMINOPOLYCARBOXYLATES

Hiroshi Ogino and Hiroaki Isago

Department of Chemistry, Tohoku University, Sendai 980, Japan

We attempted to prepare unknown species $[Co(NCS)(edta)]^{2-}$.[1] An aqueous 1 M $HClO_4$ solution containing $Na[Co(edta)]\cdot 4H_2O$ was heated at 60 °C for 10 min[2] and, then, NaSCN was added. The solution was heated at 90 °C for 1 min. Chromatographic separation for the resulted solution afforded the desired species $[Co(NCS)(edta)]^{2-}$ as well as an unexpected product $[Co(SCN)(edta)]^{2-}$. Similarly, when an aqueous solution containing $[Co(H_2O)(hedtra)]$ and NaSCN was heated, $[Co(NCS)(hedtra)]^-$ and $[Co(SCN)(hedtra)]^-$ formed simultaneously. All four species could be isolated as solids and characterised by elemental analyses and electronic, infrared absorption, and ^{13}C-NMR spectroscopic measurements.

In aqueous solutions at room temperature, the *N*-bonded isomers are stable, while the *S*-bonded isomers are unstable. $[Co(SCN)(edta)]^{2-}$ and $[Co(SCN)(Hedta)]^-$ ($pK_a = 3.3$) liberate SCN^- and change to $[Co(edta)]^-$.

$$[Co(SCN)(edta)]^{2-} \xrightarrow{k_1} [Co(edta)]^- + SCN^-$$

$k_1 = 2.6 \times 10^{-4}\ s^{-1}$ at 47.6 °C and $I = 1.0$ ($LiClO_4$)

$$[Co(SCN)(Hedta)]^- \xrightarrow{k_2} [Co(edta)]^- + H^+ + SCN^-$$

$k_2 = 1.2 \times 10^{-4}\ s^{-1}$ at 47.6 °C and $I = 1.0$ ($LiClO_4$)

No linkage isomerization of $[Co(SCN)(edta)]^{2-}$ was observed. This means that $[Co(NCS)(edta)]^{2-}$ formed in the reaction of $[Co(H_2O)(Hedta)]$ and SCN^- is not derived from $[Co(SCN)(edta)]^{2-}$, but from the direct substitution of the aqua ligand in $[Co(H_2O)(Hedta)]$ by SCN^-. On the other hand, simultaneous occurrence of both linkage isomerization and aquation was observed for $[Co(SCN)(hedtra)]^-$.

$$[Co(SCN)(hedtra)]^- \begin{cases} \xrightarrow{k_{is}} [Co(NCS)(hedtra)]^- \\ \xrightarrow{k_{aq}} [Co(H_2O)(hedtra)] + SCN^- \end{cases}$$

$k_{is} = 8 \times 10^{-5}\ s^{-1}$ and $k_{aq} = 1.7 \times 10^{-4}\ s^{-1}$ at 70.0 °C and $I = 0.50$ ($LiClO_4$)

It was also found that the direct reaction of $[Co(H_2O)(NH_3)_5]^{3+}$ with SCN^- gave $[Co(NCS)(NH_3)_5]^{2+}$ and $[Co(SCN)(NH_3)_5]^{2+}$.

The simultaneous formation of the thiocyanato and isothiocyanato linkage isomers appears to be a more common phenomenon than has previously been appreciated for the reactions between SCN^- and cobalt(III) complexes containing water molecule(s).

1. Abbreviations : EDTA = ethylenediaminetetraacetate; HEDTRA = *N*-hydroxyethylethylenediaminetriacetate.
2. Under this condition, nearly half part of $[Co(edta)]^-$ changes to $[Co(H_2O)(Hedta)]$.

SOLID STATE REACTIONS OF COPPER(II) COMPLEXES

P. O'Brien

Department of Chemistry, Chelsea College, University of London, Manresa Road, London SW3 6LX, United Kingdom.

The copper(II) complex of N-acetyl-B-alanine (naba) exists in two forms, of empirical formula $[Cu(naba)_2]\cdot 2H_2O$, a monomeric blue complex and a dimeric green form with a structure similar to copper(II) ethanoate monohydrate[1]. On thermal dehydration the blue complex is quantitatively converted into a dimeric green anhydrous complex. An identical (by X-ray powder diffraction, I.R. spectroscopy and elemental analysis) anhydrous complex is obtained by thermally dehydrating the green complex. This unusual solid-state rearrangement has been studied in some detail.

The isothermal rate of dehydration of both green and blue complexes has been measured using a thermobalance. The rate of dimerization of the monomeric complex can be monitored by EPR spectroscopy. All rates are best described by a one-half order rate law; this corresponds to phase-boundary control in two dimensions. The rates of dehydration and rearrangement are not equal for the blue complex. Visual observations of the dehydration of crystals of the blue complex confirm that rearrangement occurs subsequent to dehydration. This suggests that water is not involved in this reaction at the molecular level.

The reaction has also been studied by DTA. This and other geometric rearrangements for other copper complexes are discussed, in terms of the reaction mechanism at a molecular level and the observed kinetics of reaction.

1. Battaglia, L.P., A. Bonamartini Coradi, G. Marcotrigiano, L. Menabu, and G.C. Pellacani, *Inorg. Chem.*, *20*, 1075, 1981.

KINETICS AND MECHANISM OF ANATION OF AQUOPENTAAMMINE RHODIUM(III) BY MALONATE IN WEAKLY ACIDIC MEDIA

C. Chatterjee and A.S. Bali

Chemistry Department, Indian Institute of Technology, Powai, Bombay 400076, INDIA

The kinetics of the anation reaction of aquopentaammineRhodium(III) ion by malonic acid, bimalonate and malonate dianion to form the hitherto unknown malonato pentaammineRhodium(III) have been studied as a function of $[H^+]$ for the acidity range $1.4 \leq pH \leq 5.0$ for total malonate concentration upto 0.3M in the temperature range 60-80°C and at ionic strength 1.0M adjusted with sodium perchlorate. Experimental acidity range includes acidic and its conjugate basic forms of the anating ligand. Ion pairing is not significant between the complex ion and malonic acid but kinetically identifiable with bimalonate and malonate ions. The anation by basic forms involve formation of ion-pairs in a preequilibrium step followed by rate determining interchange of the aquo by carboxylate ligands. The observed pseudo-first-order rate constants fit the equation:

$$k_{obs} = \frac{k_0[H_2Mal] + k_1Q_1[HMal^-] + k_2Q_2[Mal^{2-}]}{1 + Q_1[HMal^-] + Q_2[Mal^{2-}]}$$

where k_0 is the second order rate constant of $(NH_3)_5Rh\text{-}OH_2^{3+}$ by malonic acid; k_1, Q_1 and k_2, Q_2 are the rate and stability constants of the bimalonate and malonate dianion ion-pairs respectively. Typical experimental results at 60°C are:

$k_0 = 3.04 \times 10^{-5} M^{-1} sec^{-1}$, $k_1 = 1.73 \times 10^{-4} sec^{-1}$, $k_2 = 3.46 \times 10^{-4}$ sec^{-1}, and the essentially temperature independent parameters Q_1 and Q_2 are 1.8 M^{-1} and 7.5 M^{-1} respectively. The activation parameters for k_0, k_1 and k_2 paths are: $\Delta H^{\ddagger}$ = 18.86(±0.7), 25.7(±0.8), 23.0(±1.4) kcal mol^{-1} and $\Delta S^{\ddagger}$ = -23.18(±0.36), 0.92(±0.1) and -5.92(±2.2) cal $deg^{-1} mol^{-1}$ respectively. A comparison with the analogous reaction of Co(III) suggests a significant participation of the incoming ligand in the transition state for rhodium system.

KINETICS AND MECHANISM OF AQUATION AND FORMATION OF CHROMATOPENTA-AMMINECOBALT(III) ION.

Novelette P. Palmer and Tara P. Dasgupta

University of the West Indies, Chemistry Department, Mona, Kingston 7 Jamaica.

The complex ion chromatopentaamminecobalt(III) undergoes aquation rapidly in acidic solution to form aquopentaamminecobalt(III) and chromate ions. The reaction has been followed by stopped-flow spectrophotometry within the acidity range 0.01 M < H^+ < 1 M between 20° and 30° C and at an ionic strength of 1.0M. The following mechanistic scheme has been proposed to explain the variation of pseudo-first-order rate constants with acidity.

$$(NH_3)_5CoCrO_4^+ + H_3O^+ \underset{}{\overset{K_1}{\rightleftharpoons}} (NH_3)_5CoHCrO_4^{2+} + H_2O$$

$$(NH_3)_5CoHCrO_4^{2+} + H_3O^+ \overset{K_2}{\rightleftharpoons} (NH_3)_5Co\,H_2CrO_4^{3+} + H_2O$$

$$(NH_3)_5CoHCrO_4^{2+} + H_2O \xrightarrow{k_1} (NH_3)_5CoH_2O^{3+} + HCrO_4^-$$

$$(NH_3)_5CoH_2CrO_4^{3+} + H_2O \xrightarrow{k_2} (NH_3)_5CoH_2O^{3+} + H_2CrO_4$$

The kinetics of the formation of title complex ion by reaction of chromate with the ion $Co(NH_3)_5OH_2^{3+}$ has also been studied as a function of acidity in the range 6.0 < pH < 8.0 and of chromate concentration 0.01 M < $[CrO_4]_T$ < 0.04 over the temperature range 15° <t < 26°. Under these conditions the rate data suggest that both the complex ions $(NH_3)_5CoOH^{2+}$ and $(NH_3)_5CoOH_2^{3+}$ react with $HCrO_4$ to form $(NH_3)_5CoCrO_4^+$. Computerised least square analysis has been performed to get best fit of all the rate constants. The results will be discussed in relation to the similar types of reactions of aquopentaamminecobalt(III) ions with other oxyanions[1,2].

1. T.P. Dasgupta and G.M. Harris, J.Am.Chem.Soc., 1977, 99, 2490.

2. R.S. Taylor, Inorg.Chem. 1976, 16, 116.

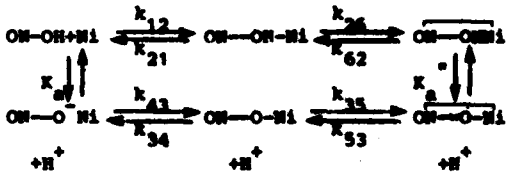
KINETICS OF CHELATION OF NICKEL(II) BY NITROSO-NAPHTHOL SULFONATES

S.A. Bajue, P. Dasgupta, R.B. Jordan, G.C. Lalor

University of West Indies, Kingston, Jamaica; University of Alberta, Edmonton, Alberta, Canada T6G 2G2.

The kinetics of formation of various nitroso-naphthol-nickel(II) complexes have been studied from pH 4 to 7, and the dissociation of the complexes has been studied in ~0.02 to 0.1 M H^+. The acid dissociation constants of the ligands (K_a), and formation constants of the complexes (K_z) have been determined also.

The kinetic results are consistent with the following reaction scheme:



With a steady state for the monodendate intermediates, the observed pseudo-first-order rate constants is given by

$$k_{obs} = \left\{ \frac{k_{12}[H^+] + k_{43}K_a}{1 + \dfrac{k_{12}[H^+] + k_{43}K_a}{k_{12}\dfrac{k_{26}}{k_{21}}[H^+] + k_{43}\dfrac{k_{35}}{k_{34}}K_a}} \right\} \left\{ \frac{[Ni]}{K_a + [H^+]} + \frac{K_a''}{K_a K_z (K_a'' + [H^+])} \right\}$$

The kinetic data for the formation and dissociation reactions have been fitted to this equation. The results for the 1-nitroso-2-naphthol 7-sulfonate are typical: at 25° in 0.10 M $LiClO_4$; k_{12} = 4.4 x 10^3 M^{-1} s^{-1}; k_{43} = 5.8 x 10^4 M^{-1} s^{-1}; k_{26}/k_{21} = 0.17; k_{35}/k_{34} = 31; k_{53} = 0.23 s^{-1}; k_{62} = 8 x 10^2 s^{-1}; K_a'' = 0.44 M. This wealth of kinetic information for the various ligands studied will be compared, and discussed with regard to the rate controlling steps under various conditions, and the relationship between K_z and K_a and the kinetic results.

Ma3-01

HYDROCARBON OXIDATION BY TRANSITION METAL COMPLEXES

C.A. Tolman

Du Pont Central Research and Development Department, Wilmington, DE 19898

The oxidation of hydrocarbons in the liquid phase by soluble transition metal catalysts is an important class of industrial reactions for the preparation of organic chemicals. In spite of their importance, the roles of the transition metal complexes are not particularly well understood in most cases. Several roles have been proposed. Part of the difficulty is that many of the roles may be played at the same time, and occur in reactions alongside other purely organic reactions which do not involve metals. Proposed roles include: (1) formation of MO_2 complexes, followed by hydrogen abstraction, (2) one electron oxidations by inner sphere or outer sphere electron transfer processes, with electron donation by either diamagnetic or free radical species, (3) catalytic decomposition of hydroperoxides, (4) epoxidation of olefins by transfer of O from MOOR, and (5) reactions of MO species to abstract hydrogen or insert oxygen into C-H or C=C bonds.

The various roles of transition metals will be illustrated with examples from the literature and from our own work on the oxidations of alkylaromatics and cyclohexane.

OXIDATION OF BIS(L-SERINATO)COPPER(II) GIVING AN ALDEHYDE FUNCTION AND HYDROGEN

Manuel CASTILLO and Elias RAMIREZ

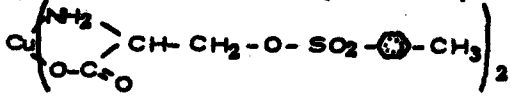
Departamento de Química Inorgánica y General.
Facultad de Química.Universidad de Sevilla.Spain.

The reactions of α-amino-β hydroxyacids have received much attention by inorganic chemists because the related nonenzymatic reactions are usually strongly catalysed by metal ions,(1,2).

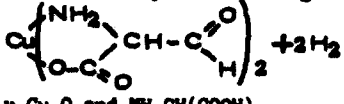
We report here that serine oxidation occurs by degradation of bis(L-serinato)copper(II). The presence of reduced copper suggests that some reacting species is involved in oxidation-reduction reactions and we are trying to characterise all the products of serine degradation,aldehide,acid carboxylic and hydrogen.

Experimental

Upon heating at 90°C for a few hours an aqueous solution of bis(L-serinato)copper(II) and 4-toluensulfonyl chloride precipitation of



occurs.
This compound is descomposed evolving



and finally Cu_2O and $NH_2CH(COOH)_2$.

A mechanism for these reactions is proposed,and the Cu(II) ion catalyzes oxidation of L-serine.

The complexes of Cu(II) have been characterized by i.r. and e.s.r. spectroscopy.

The i.r. and ^{1}H-nmr spectra of $NH_2CH(COOH)_2$ have been studied and the volume of hydrogen measured elsewhere.

References

1- L.Casella,Inorg.Chim.Acta, 1981,55, L-9.

2- P.Sharrock,Polyhedron,1983,2, 111.

STRUCTURAL AND METAL CATALYTIC EFFECTS IN THE DECOMPOSITION OF SECONDARY ALKYL HYDROPEROXIDES

J. D. Druliner, U. Klabunde, M. Mappa and C. A. Tolman

Central Research and Development Department, Experimental Station
E. I. du Pont de Nemours and Company, Wilmington, DE, USA 19898

It is well known that metal-catalyzed hydroperoxide bond cleavage can be classified as following homolytic or heterolytic pathways. Little has been reported about the effects of metal catalysts and alkyl group structure on control of the decomposition mechanism of secondary alkyl hydroperoxides. We have found, using the criterion of high ketone/alcohol ratio and oxidation of the solvent, that secondary alkyl hydroperoxides decompose with varying extents of both heterolytic and homolytic reactions depending on alkyl group structure and choice of metal. Three secondary alkyl hydroperoxides studied were: cyclohexyl hydroperoxide, α-tetralin hydroperoxide, and ethylbenzene hydroperoxide. Metal salts which favored heterolytic reaction (Cr, V, and Mo) were those which also are preferred for olefin epoxidation. Salts of Co and Mn, which are known to epoxidize olefins poorly owing to preferential decomposition into free radicals, decomposed the peroxides studied mostly homolytically.

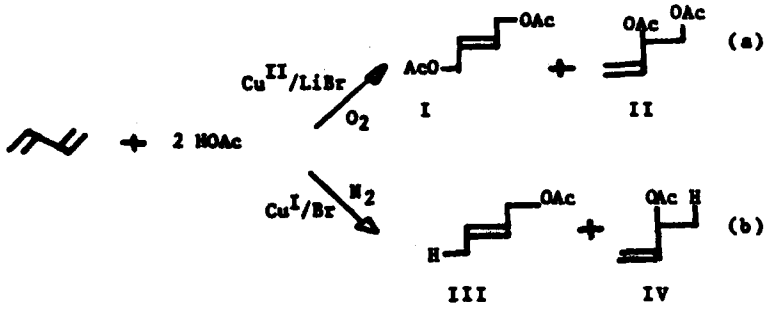
In the cyclohexyl hydroperoxide experiments, use of [U-^{14}C]-labelled solvent cyclohexane or labelled cyclohexyl hydroperoxide permitted the amounts of ketone and alcohol products produced from the solvent or from the hydroperoxide to be independently measured. In the ethylbenzene hydroperoxide experiments, ϕ-CH(OH)C_2H_5 spiking studies allowed measurements to be made of the amounts of ϕ-$COCH_3$ formed by stepwise formation of ϕ-CH(OH)CH_3 opposed to direct formation of ϕ-$COCH_3$ from the hydroperoxide. Control of product ratios by structural effects was pronounced in the case of α-tetralin hydroperoxide.

COPPER CATALYZED ACETOXYLATION OF BUTADIENE

I.N. Mamalis, A.F. Noels, A.J. Hubert and Ph. Teyssié.

Laboratory of Macromolecular Chemistry and Organic Catalysis, University of Liège, Sart Tilman, 4000 Liège, Belgium.

Butadiene reacts with acetic acid in the presence of copper salts under oxidative conditions to afford diacetoxybutenes. (1)



The present communication reports on the factors governing the efficiency and the selectivity of the catalytic system : the I/II (or III/IV) ratios appeared to depend on different factors such as the presence of added salts and ligands, whereas the catalytic system was studied by EPR(Cu) and ^{7}Li NMR spectroscopy.

Moreover kinetics stressed the key role of halogenated intermediates in the reaction together with the importance of oxygen : the reaction follows a different course under anaerobic conditions (path b).

Competition with cyanide ion showed the preferential participation of the latter in the reaction; the implication of these results in relation with the copper catalysed hydrocyanation reaction (2) will be therefore discussed.

1) P.R. Stapp. J.Org.Chem., 44, 3216 (1979).
2) E. Puentes, I. Mamalis, A.F. Noels, A.J. Hubert and Ph. Teyssié. J. Catal., 82, 365-372 (1983).

Ma3-4

NEW VANADIUM AND MOLYBDENUM PEROXO COMPLEXES WITH POLYCARBOXYLIC AND AMINO ACIDS

Cirila Djordjevic, Myunghi Lee, Nikola Vuletic and Sandra A. Craig

The College of William and Mary, Williamsburg, Virginia, USA 23185

New compounds of the general formula $M^{I}[VO(O_2)L]$, L = iminodiacetate, ethylendiaminetetraacetate, tartrate, malate, and citrate, respectively, were synthetized. These orange, stable and crystalline substances are soluble in aqueous solutions, where peroxovanadium charge transfer bands occur between 300-450 nm, showing dependence upon the heteroligand and the pH. The potentials of peroxo group oxidation with strong oxidants depend upon the heteroligand as well.

Molybdenum forms diperoxo compounds of the formula $M_2^{I}[MoO(O_2)_2L]$, L = malato, malonato and citrato, respectively. These yellow, stable and crystalline compounds are soluble in water and absorb strongly in near UV. An important difference between vanadium and molybdenum is the reaction with amino acids in the presence of hydrogen peroxide. V(V) seems to form complex peroxides which cannot be separated from aqueous solutions, and the reduction to V(IV) occurs in the absence of hydrogen peroxide. Mo(VI), on the other hand, forms stable Mo(VI) complexes. Crystalline compounds of the formula $MoO(O_2)_2AA$, AA= glycine, valine, and proline, were synthetized so far.

IR spectra of all these complexes show characteristic differences in comparison to the spectra of free ligand ions. In the 1700-1600 cm^{-1} region shifts of 50-100 cm^{-1} occur, indicating the presence of coordinated carboxylato oxygens. Strong additional bands appear in the 1000-850 cm^{-1} region assigned to MO and (O-O) stretchings. Peroxide analysis was done by two independent methods, and metal, carbon, hydrogen and nitrogen analyses agreed well with the proposed formulae. Some of the compounds contain water. X-Ray structure analysis of some of these complexes is in progress.[1]

Peroxo heteroligand complexes of vanadium and molybdenum are of interest in catalytic oxidation of organic substrates.[2] Besides serving as model systems for biochemistry, these complexes bring insight into vanadium and molybdenum interactions with numerous peroxo species existent in living matter.[3]

1. E. Sinn, C. Djordjevic, et al, to be published.

2. H. Mimoun, L. Saussine, E. Daire, M. Postel, J. Fischer and R. Weiss, J. Am. Chem. Soc. 1983, 105, 3101.

3. C. Djordjevic, L.G. Gensher and M.A. Bynum, Inorg. Chim. Acta 1983, 77 (B7), 301.

REDUCTIVE OXYGEN-OXYGEN BOND CLEAVAGE IN η^2-PEROXOTITANIUM(IV) PORPHYRINS

Tadeusz Malinski[a,d], D. Chang[a], Karl M. Kadish[a], Alain Giraudeau[b], Maurice Gross[b], Jean-Marc Latour[c], and Jean-Claude Marchon[c].

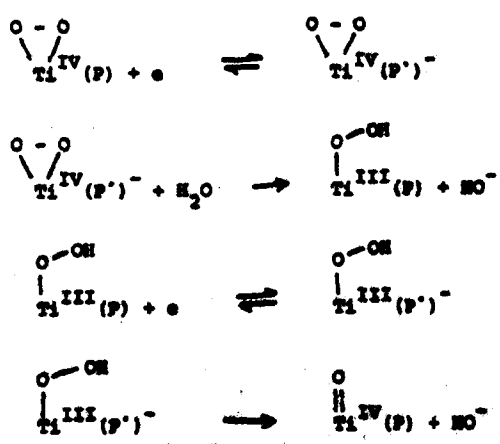
(a) Department of Chemistry, University of Houston, Houston, Texas 77004, USA

(b) Laboratoire d'Electrochimie et de Chimie Physique, Université Louis Pasteur, 4, rue Blaise Pascal, 67000 Strasbourg, France.

(c) Laboratoires de Chimie (LA CNRS 321), Département de Recherche Fondamentale, Centre d'Etudes Nucléaires de Grenoble, 85 X, 38041 Grenoble, France.

(d) Present address : Oakland University, Rochester, Michigan 48063, USA.

The two-electron reduction of $Ti(O_2)(tpp)$ and $Ti(O_2)(oep)$, leading to TiO(tpp) and TiO(oep) respectively, was investigated by spectroscopic and electrochemical techniques in dichloromethane and tetrahydrofuran solutions. Experimental results are accounted for by an ECEC mechanism which is summarized in the following scheme :



The initially produced species is the porphyrin anion radical complex $Ti(O_2)(tpp')^-$, which is stable under strictly anhydrous conditions. Protonation of the peroxo ligand by trace water leads to a hydroperoxo-titanium(III)porphyrin complex by internal electron transfer. Cleavage of the O-O bond of the hydroperoxo ligand takes place after a second electron has been stored in the porphyrin.

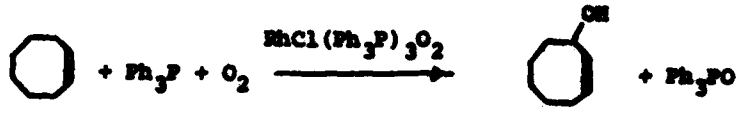
The first intermediate, $Ti(O_2)(tpp')^-$, is a very unusual species : it contains in the same molecular framework a two-electron oxidant and a strong one-electron reductant, but these apparently cannot react with each other in the absence of a proton source, and the complex is stable in anhydrous solution. Reaction with a proton donor destroys this fragile equilibrium, however, by providing a pathway for the two-reduction electron of the coordinated peroxide.

STUDIES ON THE CATALYTIC CO-OXYGENATION OF CYCLO-OCTENE

Gordon Read and Janet Shaw
University of Exeter, Exeter, EX4 4QD, Devon, U.K.

In reactions promoted or catalysed by rhodium and iridium complexes at temperatures close to ambient, cyclo-octene is the exception to the generalisation that alkenes undergo oxygenative attack at the olefinic bond. James[1] and Holland and Milner[2] report oxygenation at allylic hydrogen which suggests, at least superficially, a different mode of oxygenation to that detected in terminal alkenes[3] and 1,5-cyclo-octadiene[4].

We report (a) factors influencing the catalytic conversion of cyclo-octene to cyclo-oct-1-en-3-ol in the heterogeneous-oxygenation :-



and (b) the utilisation of β-isotopic shifts in the ^{13}C n.m.r. of deuterated cyclo-oct-1-en-3-ol to distinguish between oxygenation by :-

(i) direct allylic attack,
(ii) vinylic attack followed by double bond migration,
(iii) attack on an intermediate η^3-allyl species.

1. B.R. James, F.T.T. Ng, and E. Ochiai, Canad. J. Chem., 1972, 50, 590.
2. D. Holland and D.J. Milner, J.C.S. Dalton, 1979, 2440.
3. G. Read and P.J.C. Walker, J.C.S. Dalton, 1977, 883; E. Mimoun, M.M.P. Mignard and I. Sérée de Roch, J. Amer. Chem. Soc., 1978, 100, 5437.
4. M.T. Atlay, M. Preece, G. Strukul, and B.R. James, J.C.S. Chem. Comm., 1982, 406; L. Carlton, G. Read, and M. Urquhart, J.C.S. Chem. Comm., 1983, 585.

Ma3-7

REACTIONS OF OXOMOLYBDENUM COMPLEXES WITH REDOX SUBSTRATES

Joseph Topich and James T. Lyon, III

Virginia Commonwealth University, Department of Chemistry, Richmond, Virginia, USA 23284

The oxygen atom transfer reactions for MoO_2(5-X-SSP) and MoO_2(5-X-SSE) (where 5-X-SSP^{2-} = N-(5-X-salicylidene)-2-aminobenzenethiolate, 5-X-SSE^{2-} = N-(5-X-salicylidene)-2-aminoethanethiolate and X = Br, Cl, H, CH_3O) with $PEtPh_2$ were studied in detail between 30 and 60°C. The applicable rate law is $-d[Mo^{VI}O_2L]/dt = k_1[Mo^{VI}O_2L][PEtPh_2]$. The specific rate constants span the range from 8.4×10^{-4} $M^{-1}sec^{-1}$ (X = CH_3O) to 19.6×10^{-4} $M^{-1}sec^{-1}$ (X = Br) for MoO_2(5-X-SSP) at 30°C and from 21.4×10^{-4} $M^{-1}sec^{-1}$ (X = CH_3O) to 34.8×10^{-4} $M^{-1}sec^{-1}$ (X = Br) for MoO_2(5-X-SSE) at 60°C. Only oxo-Mo(IV) complexes are observed as products of these reactions. A linear dependence is observed between log (k_{1X}/k_{1H}) and the Hammett σ_p parameter for the ligand X-substituents for the two series MoO_2(5-X-SSP) (ρ=+0.75) and MoO_2(5-X-SSE) (ρ=0.42). Activation parameter data were obtained for MoO_2(5-H-SSP) (E_a = 67.9 kJ/mol, $\Delta H^{\ddagger}$ = 65.2 kJ/mol and $\Delta S^{\ddagger}$ = -86.5 J/mol-°K) and MoO_2(5-H-SSE) (E_a = 72.0 kJ/mol, $\Delta H^{\ddagger}$ = 70.3 kJ/mol and $\Delta S^{\ddagger}$ = -82.6 J/mol-°K). In addition, the reactions and reactivity patterns of the oxo-Mo(IV) complexes with NO_3^-, activated acetylenes (RC≡CR) and diazenes (RN=NR) will be described.

NICKEL(II) AND MANGANESE(II) ION CATALYZED OXIDATION OF o-PHENYLENE-DIAMINE WITH MOLECULAR OXYGEN

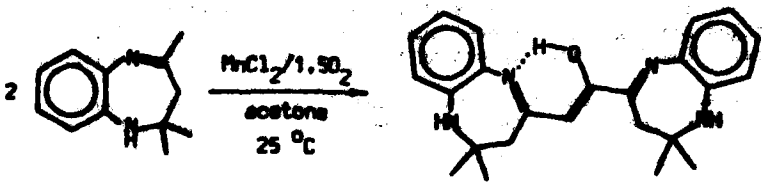
Zoltan Szeverenyi, Peter Viski and Laszlo I. Simandi

Central Research Institute for Chemistry,
H-1025 Budapest, Pusztaszeri ut 59/67, Hungary

Recent studies have shown that cobalt(II) ion catalyzes the oxidation of o-phenylenediamine (OPD) to 2,3-diaminophenazine (DAP) or to substituted benzimidazoles, depending on the type of solvent used[1]. The key intermediate was found to be a reactive μ-peroxodicobalt complex[2].

It has now been found that nickel(II) perchlorate and manganese(II) chloride are also effective catalysts for OPD oxidation. Methanol solutions of OPD, containing these salts, absorb molecular oxygen under ambient conditions, leading to the formation of DAP (yield 30-40 %). Nickel(II) nitrate does not catalyze the reaction.

In acetone solvent a different reaction pattern is observed. In nitrogen atmosphere OPD undergoes condensation with acetone, catalyzed by metal salts such as $Ni(ClO_4)_2$, $MnCl_2$, $CaCl_2$ and $Zn(OAc)_2$. The condensation product is 2,3-dihydro-2,2,4-trimethyl-1H-1,5-benzodiazepine (I). In oxygen atmosphere, O_2 is absorbed when the solution contains $Ni(ClO_4)_2$ or $MnCl_2$. Remarkably, $Ni(NO_3)_2$ catalyzes the condensation but does not lead to dioxygen absorption. The $MnCl_2$ catalyzed condensation/oxidation has been studied in detail. The major product is 1,2-bis(2,3-dihydro-2,2-dimethyl-1H-1,5-benzodiazepine-4-yl)-1-hydroxyethene (II). The first intermediate in the oxidation of I is the 4-carboxaldehyde, which condenses with unreacted I to produce an aldol. Dehydrogenation of the aldol yields II.



(I) (II)

The kinetics of O_2-uptake has been investigated and interpreted.

1. S.Nemeth and L.I. Simandi, J. Mol. Catal., 1982, 14, 241

2. S.Nemeth and L.I. Simandi, Inorg. Chem., 1982, 22 (in press)

MECHANISMS OF Co(III) INITIATED HYDROCARBON OXIDATION

Allan E. Nader

Petrochemicals Department, E. I. du Pont, Experimental Station, Wilmington, Delaware 19898, USA.

The cobaltic acetate oxidation of hydrocarbons has been the subject of much synthetic, mechanistic, and industrial interest[1]. Nevertheless many features of the initial Co(III)-substrate reaction remain obscure. The Co(III) oxidation of methylbenzenes ($C_6H_{6-n}(CH_3)_n$, n=1-5), alkylaromatics (ArR, R=Me, Et, iPr) and alicyclics (C_nH_{2n}, n=6,7) were examined in acetic acid under anaerobic conditions to define the nature of the initial steps.

Kinetic analysis revealed two Co(III) reduction pathways, (1) hydrocarbon oxidation and (2) acetate ligand oxidation. The rate of Co(III) consumption is first order in [Co(III)] and [substrate], but *inversely dependent on* [Co(II)]. Methylarene reaction rates correlate with hydrocarbon ionization potential (IP), whereas alkylaromatic rates are consistent with α-hydrogen C-H bond strength ($3^\circ > 2^\circ > 1^\circ$). Deuterium kinetic isotope measurements reveal a monotonic increase in k_H/k_D with methylarene IP, while alkylaromatics exhibit significantly greater k_H/k_D values with decreasing α C-H bond energy. These findings indicate the operation of two competing Co(III)-hydrocarbon processes, (1) direct electron transfer (ET) and (2) ligand mediated hydrogen abstraction. Low IP aromatics (hexamethylbenzene) react mainly by ET, whereas high IP substrates (toluene, cyclohexane) or reactive hydrogen bearing hydrocarbons (cumene) favor the H-abstraction route. Kinetic models supporting these pathways will be presented.

1. R. A. Sheldon and J. K. Kochi, "Metal-Catalyzed Oxidation of Organic Compounds," Ch. 5. Academic Press, New York, 1981.

Ma3-10

COBALT COMPLEXES OF NO_x

Robert D. Feltham, Clemente Vallenilla, Richard Ortega, and Trevor Bailey

Chemistry Department, University of Arizona, Tucson, AZ 85721 USA

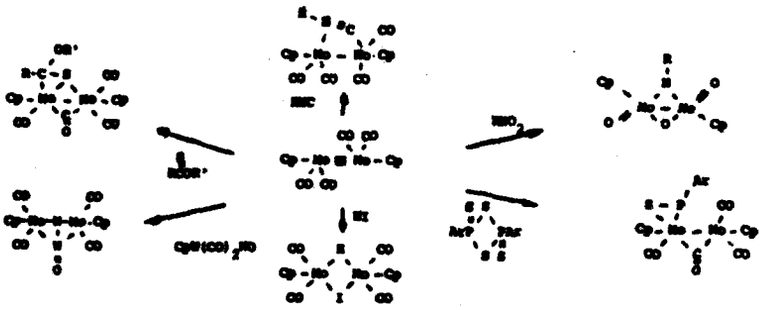
Cobalt complexes of NO, NO_2, and NO_3 comprise an important and interesting family of compounds. At least five different types of 18 electron complexes with NO and NO_2 ligands are possible: $Co(NO_2)_3L_3$ A, $Co(NO)(NO_2)_2L_2$ B, $Co(NO)_2(NO_2)L$ C, $Co(NO)_3$ D, and $Co(NO)L_3$ E. Prior to this work, examples of B and C have not been reported. We have now prepared numerous tertiary phosphine derivatives of $Co(NO)(NO_2)_2L_2$, $Co(NO)_2(NO_2)L$, $Co(NO_2)_2L_3$, $Co(NO_2)_2L'_2$ and $Co(NO_3)_2L'_2$, where L = PPh_3, $PMePh_2$, PMe_2Ph, $PEtPh_2$, $Ph_2P(CH_2)_3PPh_2$, and L' = $O{=}PPh_3$ and $O{=}PMePh_2$. These compounds have been characterized by elemental analyses, ir spectroscopy, NMR spectroscopy, ESR spectroscopy, ^{15}N-substitution and by X-ray crystallography. Among the many novel features found for the diamagnetic compounds is the presence of both N-bound and semi-chelating -ONO ligands in $Co(NO)(NO_2)_2L_2$ and $Co(NO)_2(NO_2)L$. $Co(NO)(NO_2)_2(PMePh_2)_2$ and $Co(NO)(NO_2)_2(PMe_2Ph)_2$ have square pyramidal geometry with strongly bent Co-N-O groups (129°) and a weakly interacting oxygen atom from the chelating -ONO group trans to the nitrosyl ligand. The -ONO ligand in $Co(NO)_2(NO_2)(PPh_3)$ is also semi-chelating, but has a significantly longer Co---O distance of 2.782(4)Å. The $-NO_2$ and $-NO_3$ ligands in the paramagnetic complexes also exhibit a variety of stereochemistries from N-bound $-NO_2$ groups in $Co(NO_2)_2(PMePh_2)_3$ to chelating NO_2 and NO_3 groups in $Co(NO_2)_2(O{=}PPh_3)_2$, c-$Co(NO_3)_2(O{=}PPh_3)_2$, and t-$Co(NO_3)_2(O{=}PMePh_2)_2$. The interconversion reactions of these cobalt-NO_x complexes using oxidants such as O_2 and NO and reductants such as CO and olefins have been investigated. Oxidation of $Co(NO)(NO_2)_2L_2$ and $Co(NO)_2(NO_2)L$ by O_2 produces $Co(NO_3)_2(O{=}PR_3)_2$ as the final product. Reaction of $Co(NO)(NO_2)_2(Ph_3)_2$ with benzoyl chloride produces $Co(NO)_2Cl(Ph_3)$. The reaction of $Co(NO)(NO_2)_2(PPh_3)_2$ with NO produced $Co(NO)_2(NO_2)(PPh_3)$ in good yields, while its reaction with CO produced $Co(NO)(CO)(Ph_3)_2$ in good yields. Under some conditions, intermediates from these reactions have been isolated and characterized and will be discussed.

Ma3-11

REACTION OF PEROXYDIC COMPOUNDS WITH MULTIBONDED MOLYBDENUM COMPLEXES

Henri Arzoumanian, Richard Lai, Jacques Metzger, Jean François Petrignani, IPSOI, Univ. Aix-Marseille III, Rue H. Poincaré, 13013 Marseille

The reactivity of multibonded molybdenum complexes towards electron rich or electron poor compounds has aroused numerous recent investigation (1-6).



Results of the interaction of organic or metallic peroxides with these multibonded complexes will be presented. The similarity with the previously described systems including oxygen transfer will be discussed. Implications of these observations on the oxygen activation process catalysed by heterobimetallic systems will be proposed.

1.Curtis M.D. ; Messerle, L. ; Fotinos, N.A. In "Reactivity of Metal-Metal Bonds" ; Chisholm M.H., Ed. ; Am. Chem. Soc. : Washington, 1981 ; ACS Symp. Ser. N° 155.
2.Feaney, H.D. ; Knox, S.A.R., J. Chem. Soc., Chem. Commun. 1982, 1062.
3.Adams R.D. ; Katahira D.A. ; Yang L.W. Organometallics 1982, 1, 231.
4.Alper H. ; Petrignani, J.F. ; Einstein, F.W.B. ; Willis, A.C. J. Am. Chem. Soc., 1981, 105, 1783.
5.Alper H. ; Einstein F.W.B. ; Nagai R. ; Petrignani, J.F. ; Willis, A.C. ; Organometallics 1983, 2, 1291.
6.Alper H. ; Einstein F.W.B. ; Petrignani, J.F. ; Willis A.C. Organometallics 1981, 2, 1422.

PEROXOFLUOROCOMPLEXES OF NONTRANSITIONAL ELEMENTS

E.G. Ippolitov and B.N. Chernyshov

Institute of Chemistry of the Far Eastern Center of the Academy of Sciences of the USSR

Hitherto unknown hydrogenperoxofluoro complexes of elements of main groups III and IV have been studied by ^{19}F, ^{11}B, and ^{119}Sn NMR methods (1,2). *Octahedral species* $MF_n(OOH)_{6-n}^{2-}$ (M=Ge, Sn) and tetrahedral species $BF_m(OOH)_{4-m}^{-}$ five upfield ^{19}F signals. All isomers in these series of species have been identified, and quantitative correlations established. The σ and π donor properties of OOH cause a cis effect of M-F bonds in the hydrogenperoxofluorocomplexes.

The nature of ^{19}F, ^{11}B chemical shifts in the hydrogenperoxofluoroborates is examined in terms of quantochemical nuclei magnetic screening. In addition, their stability constants (3) and the chemical shifts dependences on the complexes' substitutors number, n, are determined.

NMR spectroscopy had advantages in the nontransitional elements heteroligand complexes investigation in solutions in presence of fluorine compounds.

1. Chernyshov, B.N., G.P. Shetinina, E.G. Ippolitov, *Koord. Khimia*, *6*, 1520, 1980.
2. Chernyshov, B.N., N.A. Didenko, E.G. Ippolitov, *Doklady Academii Nauk SSSR*, *262*, 626, 1982; *Koord. Khimia*, *9*, 210, 1983.
3. Chernyshov, B.N., G.P. Shetinina, E.G. Ippolitov, *Surnal Neorg. Khimii*, *10*, 2692, 1982.

Ma4-01

BIS-MACROCYCLES. THE COORDINATING BEHAVIOUR OF DOUBLE-RING OCTA-AZA LIGANDS

Luigi Fabbrizzi

Dipartimento di Chimica Generale, Università di Pavia, via Taramelli 12, 27100 Pavia, Italy

Bis-macrocycles are molecules in which two cyclic sub-units are linked together, for instance by an aliphatic chain. Each sub-unit may incorporate a metal ion and the two encircled cations display independent or mutually dependent activity depending upon the length of the joining segment.

We have recently developed a synthetic method for the preparation of bis-macrocycles, whose sub-units are tetra-aza systems containing two amino groups and two amido groups. The two-subunits may be linked through amine nitrogen atoms or through carbon atoms of the aliphatic backbone. Each ring can incorporate a metal ion (e.g. Cu^{II}) with simultaneous deprotonation of the two amido groups.

Ring-to-ring effects will be discussed with special regard to: i) the stepwise incorporation of two Cu^{II} ions followed by equilibrium studies; ii) the metal-metal interaction monitored by ESR; iii) the electrochemically reversible oxidation behaviour of the two metal centres (Cu^{II}/Cu^{III} redox change) in aqueous solution.

SYNTHESES, STRUCTURES, AND MAGNETIC PROPERTIES OF μ-CARBOXYLATO DICOPPER(II) COMPLEXES WITH SCHIFF BASES DERIVED FROM 1,3-DIAMINO-2-PROPANOL AND VARIOUS β-DIKETONES OR SALICYLALDEHYDE.

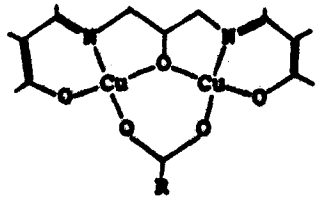
Sigeo Kida, Masataka Takeuchi, Kazuhiro Takahashi and Yuzo Nishida

Department of Chemistry, Faculty of Science, Kyushu University 33, Hakozaki, Higashiku, Fukuoka 812, Japan

Alkoxo- and carboxylato-bridged binuclear copper(II) complexes newly synthesized here are unique in bearing a very large Cu-O-Cu angle(109 ~ 134°). The complexes were prepared by reacting the Schiff base(H_2L-a, H_2L-j, or H_2L-s), copper(II) acetate(or benzoate), and triethylamine in methanol in 1:2:3 mole ratio, where H_2L-a, H_2L-j, and H_2L-s represent Schiff bases derived from 1,3-diamino-2-propanol and acetylacetone, 2-acetyl-1,3-pentanedione, or salicylaldehyde, respectively.

Single-crystal X-ray analyses have revealed that all the complexes consist of binuclear unit shown in Fig. 1. In the case of Cu_2(L-j)CH_3COO the binuclear units are further linked by the weak coordination of the acetyl oxygen to a copper atom of a neibouring molecule, froming infinite linear chains.

It has been widely accepted that antiferromagnetic interaction increases with increasing Cu-O-Cu angle in dialkoxo- or dihydroxo-bridged copper(II) complexes. However, in the present complexes, despite the large Cu-O-Cu angles, the magnetic moments(listed in the Table) are showing only weak antiferromagnetism in contrast to the strong spin-coupling in conventional dialkoxo-bridged copper complexes. Especially, in the case of Cu_2(L-j)-CH_3COO the magnetic moment at room temperature is nearly normal and the Weiss constant is -2°K. In order to give a reasonable explanation of the weak antiferromagnetism in the present complexes, some improvement seems to be necessary for present superexchange theories.



Cu_2(L)RCOO

complex	Cu-O-Cu	μ_{eff}
Cu_2(L-a)CH_3COO	133°	1.64
Cu_2(L-j)CH_3COO	109	1.77
Cu_2(L-s)CH_3COO	139	1.55
Cu_2(L-s)C_6H_5COO	133	1.65

BINUCLEAR METAL COMPLEXES OF N,N',N'',N'''-TETRAKIS(2-AMINOETHYL)CYCLAM

Ichiro Murase, Hiroshi Sonoda, Masahiro Mikuriya, and Sigeo Kida
College of General Education, Kyushu University, Fukuoka 810, Japan

We have synthesized the titled ligand(TAEC) by the reaction of N-tosylaziridine with cyclam followed by acid hydrolysis. TAEC·6HBr or free TAEC reacted with excess copper(II), nickel(II), and cobalt (II) ions to give binuclear complexes. The complexes obtained were $[Cu_2(taec)]Br_x(ClO_4)_y$ (x=4, y=0; x=1, y=3; x=0, y=4), $[Ni_2(taec)](ClO_4)_4$, and $[Co_2(taec)]OH\cdot X_3$ ($X=ClO_4$, PF_6).

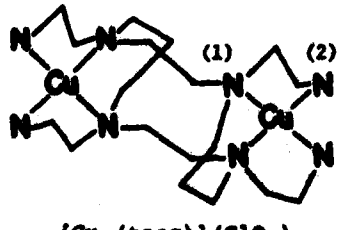
The crystal structure of $[Cu_2(taec)](ClO_4)_4$ has been elucidated by the X-ray analysis as shown in the figure. The cyclam moiety in the complex takes a folded conformation and the copper(II) ions are not in the ring but located outside to form square-planar N_4 chelates with the pendant amino groups. The d-d band is at 19,200 cm^{-1} in solid and 17,700 cm^{-1} in water.

$[Cu_2(taec)]Br(ClO_4)_3$ and $[Cu_2(taec)]Br_4$ showed absorptions both at 16,300 cm^{-1} in water as well as in solid suggesting the coordination of a bromide ion. For $[Cu_2(taec)]Br(ClO_4)_3$, the magnetic susceptibilities obeyed the Curie-Weiss low in the range 297-87 K with θ=-24 K, indicating that an antiferromagnetic *spin-exchange* interaction is operating between the copper(II) ions through the bromide ion. Thus the structure of these complexes may be different from the figured one. The X-ray analysis is under way.

$[Ni_2(taec)](ClO_4)_4$ was diamagnetic and showed the d-d band at 22,000 cm^{-1} in solid, which indicates a square-planar environment around the nickel(II) ions and probably takes a similar configuration to the figured one.

For $[Co_2(taec)]OH(ClO_4)_3$, ν_{OH} appeared at 3,560 cm^{-1} and μ_{eff}=4.1 B.M. at room temperature which is a little lower than those for ordinary high spin cobalt(II) complexes. Some interaction is expected between the two cobalt ions.

Synthesis of analogous tetraazamacrocycles and their complexes will be presented.



$[Cu_2(taec)](ClO_4)_4$

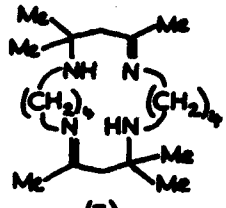
Cu-Cu	5.479(1)Å
Cu-N(1)	2.066(4)Å
Cu-N(2)	2.000(6)Å

COMPLEXES OF LARGE RING MACROCYCLIC DIENES

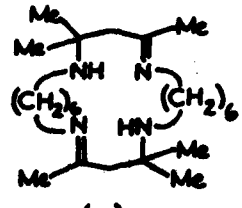
Robery W Hay and Mahesh P Pujari

Chemistry Department, University of Stirling, Stirling FK9 4LA, UK

The synthesis of ligands such as Me$_6$[16]dieneN$_4$(I)[1,2] and Me$_6$[22]dieneN$_4$(II) as their hydroperchlorate salts $LH_2^{2+}(ClO_4)_2$ will be described. The free base forms have also been isolated and M.W.'s obtained by vapour pressure osmometry. The ligand (I) gives



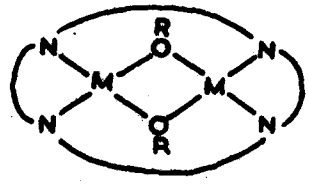
(I)



(II)

mononuclear complexes with Cu(II) and Ni(II), which are kinetically labile in acid and base, and the dissociation kinetics will be discussed.

Binuclear copper (II) and nickel (II) complexes are formed by (II) as shown in (III) where R = Me. X-ray data[3] indicates a



(III) M = Ni(II), or Cu(II)

Cu---Cu separation of 3.034Å and there is a relatively strong anti-ferromagnetic interaction between the copper centres. Reduction of the dienes with NaBH$_4$ gives the saturated C-meso and C-racemic macrocycles which can be separated by fractional crystallisation.

The coordination chemistry of the reduced ligands will also be discussed in detail.

1. J W L Martin, J H Timmons, A E Martell and C J Willis, Inorg Chem 1980, 19, 2328.

2. R W Hay and R Bembi, Inorg Chim Acta 1982, 62, 89.

3. M Yamashita, H Ito and T Ito, Inorg Chem 1983, 22, 2102.

FROM POLYNUCLEAR TO TRINUCLEAR HETEROMETALLIC ORDERED CHAINS BY USE OF A DISSYMETRIC BISBIDENTATE LIGAND, THE DITHIOOXALATE ANION

Jean-Christian Trombe, Catherine Frasse, Alain Gleizes and Jean Galy

Laboratoire de Chimie de Coordination du CNRS associé à l'Université Paul Sabatier, 205, route de Narbonne, 31400 Toulouse, France

Due to its dissymetric configuration, the dithiooxalate anion possesses the capacity for bridging two different metal ions according to their comparative oxophilic or sulfophilic character, and for consequently generating solid molecular complexes built of *ordered bimetallic infinite or finite chains*:

$$\ldots(O_2C_2S_2)M(S_2C_2O_2)M'(O_2S_2C_2)\ldots$$

(M = Ni(II), Pd(II), Pt(II), Cu(II); M' = Ca(II), Zn(II), Mn(II), In(III), Th(IV)) (Ln: lanthanide).

The number of metal centers of a chain is governed by the electroneutrality rule and therefore depends on the respective oxidation state of the metals involved and on the presence of additional anionic ligands.

When both M and M' are in the same oxidation state - here II - infinite chains are obtained. This ability was used to create the first one-dimensional ferrimagnetic compounds with Cu(II) (s = 1/2) and Mn(II) (s = 5/2) as spin carriers*. In this series, the [MnM] and the [CaNi] derivatives are isostructural in spite of a coordinence change on M': Mn is heptacoordinated (additional ligand: H_2O) while Ca is octacoordinated. In both cases, the Mn or Ca coordination geometry constrains the chains to adopt a zigzag shape.

With M = Cu(II), Ni(II), Pd(II), Pt(II) and M' = Ln(III), centrosymmetric pentanuclear entities are formed. Again, the chains are zigzag shaped, but the crystal packing is dramatically changed when the coordinence of the lanthanide goes from nine to eight.

The association of Ni(II) and Th(IV) gives rise to trinuclear entities.

Experiments are currently developed to build chains with original numbers of metal centers and with more than two different metals as well, in order to get varied magnetic properties.

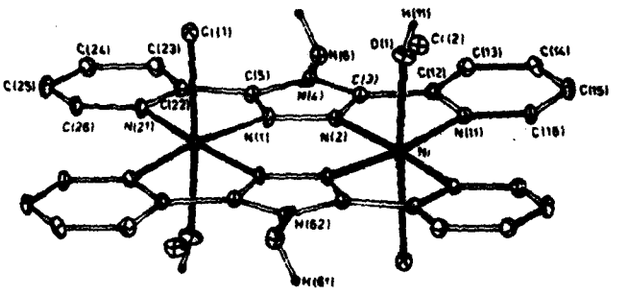
* See communication at the present Conference, M. Verdaguer, A. Gleizes, J.-P. Renard and J. Seiden.

DINUCLEATING TRIAZOLE LIGANDS. THE STRUCTURE OF COORDINATION COMPOUNDS OF 3,5-BIS(PYRIDIN-2-YL)-4-AMINO-1,2,4-TRIAZOLE

Fennegien S. Keij, Rob Prins, Jaap G. Haasnoot and Jan Reedijk

Department of Chemistry, State University Leiden, Gorlaeus Laboratories, P.O. Box 9502, 2300 RA Leiden, the Netherlands

3,5-bis(pyridin-2-yl)-4-amino-1,2,4-triazole, bpat, prepared from hydrazine monohydrate and cyanopyridin-2-yl[1], acts as a strongly chelating ligand. Bpat reacts with transition-metal(II) salts, MX_2 with M = Mn, Fe, Co, Ni, Cd and X = Cl, Br, NO_3, yielding dinuclear coordination compounds. An X-ray structure of a Nickel(II) compound was performed. $[Ni_2(bpat)_2Cl_2(H_2O)_2]Cl_2(H_2O)_4$ crystallizes in the triclinic space group $P\bar{1}$ with a = 6.840(2), b = 10.199(4), c = 12.480(3) Å, α = 78.62(3), β = 76.47(2), γ = 84.17(3)°, Z = 1. Refinement based on 4015 independent reflections yielded R_w = 0.034. The dinuclear $Ni_2(bpat)_2$ unit (figure) is almost planar.



The nickel ions are coordinated by four nitrogen atoms of the two tetradentate ligands, with N-Ni-N-angles of 93.00(4), 76.74(4), 113.67(4) and 76.47(4)° and Ni-N distances of 2.013(1), 2.029(1), 2.155(1), 2.164(1) Å. The axial ligands are a water molecule and a chloride ion. The coordination of the metal centers is rhombically distorted tetragonal. Such a distorted geometry has been described for a Cu(II) compound of a related ligand[2]. The uncommon ligand-field spectrum of the nickel(II) compound is interpreted along with these findings. Variable temperature magnetic susceptibility measurements on a group of bpat compounds revealed that a relatively weak antiferromagnetic exchange is present. The exchange in a group of copper compounds with the related ligand bpt[2] has been found to be much stronger antiferromagnetic. The origin for the differences will be discussed.

1. J.F. Geldard and F. Lions, J. Org. Chem. 30 (1965), 318.
2. R. Prins, J.G. Haasnoot and J. Reedijk, Proc. Int. Conf. Coord. Chem. 22 (1982), 656.

Ma4-6

DICOBALT AND DICOPPER COMPLEXES OF A MACROCYCLIC LIGAND

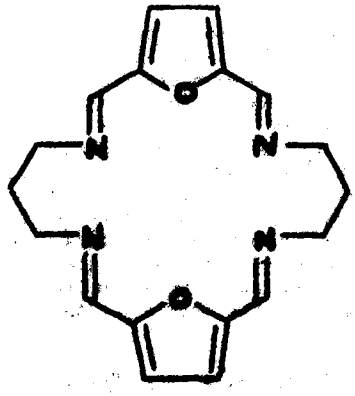
S.M. Nelson

Department of Chemistry, Queen's University, Belfast BT9 5AG, N. Ireland.

The Ca^{2+}, Sr^{2+} and Ba^{2+} ions are templates for the cyclic (2+2) condensation of 2,5-diformylfuran with 1,3-diaminopropane to afford complexes of the 20-membered tetra-imine macrocycle L in high yield.[1] The alkaline earth ions are readily replaced by Co(II), Cu(I) or Cu(II) to give dinuclear complexes in which, in most cases, the metal ions are intramolecularly linked via two single-atom bridges (e.g. CN^-, OR^-, SR^-, N-bonded-only NCS^-, S-bonded-only NCS). Magnetic susceptibility and e.s.r. measurements confirm that the dinuclear di-Co(II) and di-Cu(II) complexes are antiferromagnetically coupled, the degree of interaction depending on the nature of the bridging groups and the coordination geometry of the metal.

The di-Cu(II) complexes undergo ready reduction to di-Cu(I) with accompanying oxidation of the bridging ligand or other available substrate, e.g. catechols, thiols, amines. When carried out in the presence of dioxygen several of the oxidations are catalytic reflecting the value of the complexes as models for certain Type 3 copper proteins.[2]

1. M.G.B. Drew, F.S. Esho, and S.M. Nelson, J. Chem. Soc., Dalton Trans., 1983, 1653.
2. S.M. Nelson, F.S. Esho, A. Lavery and M.G.B. Drew, J. Am. Chem. Soc., 1983, 105, 5693.



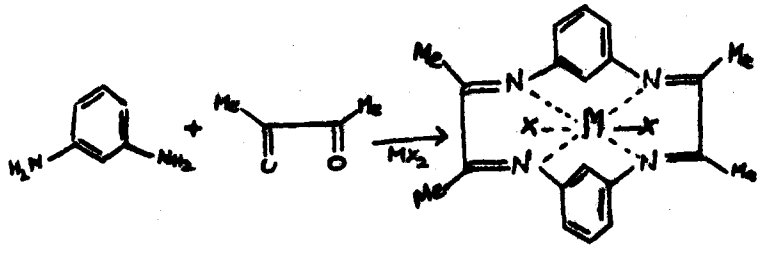
L

DIVALENT METAL CHELATES OF N_4 MACROCYCLIC LIGAND

V.B. Rana and V.K. Chauhan

Department of Chemistry, Meerut College, Meerut, India

Divalent oxovanadium, manganese, iron, cobalt, nickel and copper salts react with m-phenylenediamine and 2,3-butanedione to form metal chelates of a 14-membered N_4 macrocyclic ligand: dibenzo-(e,1)-2,3,8,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-[14]-1,3,8,10-tetraene. The chelates are of the type $[M(Me_4\ [14]\ 1,3,8,10\text{-tetene}N_4)X_2]$; where M=VO(II), Mn(II), Fe(II), Co(II), Ni(II) or Cu(II) and X=Cl, Br, NO_3 or NCS. The ligand coordinates through all the four azomethine nitrogens which are bridged by 2,3-butanedione moieties. The analytical, conductance, magnetic, electronic and infrared spectral studies indicate them to be distorted octahedral. The amount of distortion is calculated in terms of DT/DQ by applying NSH theory. The reaction can be shown as:



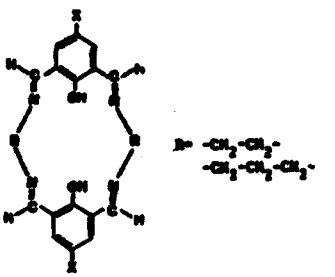
Ma4-8

NEW CYCLIC AND ACYCLIC SCHIFF BASES DERIVED FROM 2,6-DIFORMYL-4-CHLOROPHENOL AND THEIR INTERACTION WITH URANYL(VI), COPPER(II) AND NICKEL(II) IONS

U. Casellato, D. Fregona, S. Sitran, S. Tamburini, and P.A. Vigato

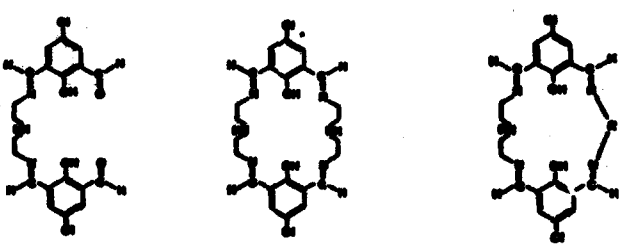
Istituto di Chimica e Tecnologia dei Radioelementi-C.N.R., Padova, Italy

It was well established, some years ago, that cyclic Schiff bases of the type:



can act as binucleating ligands towards transition metal ions, and homo- and heterobinuclear complexes have been synthesized.

We have prepared the acyclic and cyclic compartmental ligands:



and the corresponding nickel(II), copper(II) and uranyl(VI) mononuclear homo- and heterobinuclear complexes.

Their physico-chemical properties have been established by i.r., u.v. and magnetic data. The catalytic behavior of some binuclear complexes prepared, towards the oxidation of phenols, has been tested and compared with that of the corresponding mononuclear complexes.

Ma4-9

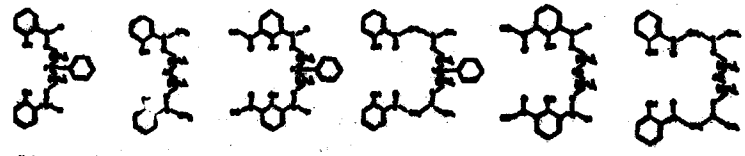
PREPARATION AND PROPERTIES OF NEW HEPTADENTATE COMPARTMENTAL LIGANDS AND RELATED MONO AND BINUCLEAR COMPLEXES.

U.Casellato, D.Fregona, S.Sitran, S.Tamburini and P.A.Vigato
Istituto di Chimica e Tecnologia dei Radioelementi -C.N.R.- PADOVA

Many papers have been published, in these last few years, dealing with the synthesis and physico-chemical properties of binucleating ligands. These ligands have two adiacent site, one, inner, containing the O_2O_2 coordination set and the second, outer, containing the O_2O_2 set. These ligands can thus coordinate two similar or dissimilar metal ions in close proximity in order to give rise to an interaction between the two ionic centres.

We have enlarged the internal site by means of a hydrocarbon chain containing a fifth donor atom, by reaction of p-acetoacetylphenol or 3-formylsalicylic acid with amines of the type: $H_2N-(CH_2)_n-X-(CH_2)_n-NH_2$ (n=2,3; X=N-H, P-C_6H_5).

The Schiff bases:



H_2L_a H_2L_b H_2L_c H_2L_d H_2L_e H_2L_f

have been synthesized, which have been used for the preparation of mononuclear and dinuclear complexes of copper (II), nickel (II) and uranyl (VI) ions.

For a better knowledge of the properties of these complexes, the ligands H_2L_a and H_2L_b and the related copper (II), nickel (II) and uranyl (VI) complexes have been prepared.

The catalytic activity of copper (II) complexes in the oxidation reaction:



+ other products

has been also studied.

'DISLOCATION' DISCRIMINATION AND THE RELATIVE STABILITIES OF MACROCYCLIC LIGAND COMPLEXES OF Zn(II) AND Cd(II)

Leonard F. Lindoy and Anthony J. Leong

Department of Chemistry and Biochemistry, James Cook University, Queensland 4811, Australia

Peter A. Tasker

School of Chemistry, Polytechnic of North London, London, N7 8DB.U.K.

Cyclic ligands are particularly suitable for use as metal-ion selective reagents since, in addition to the usual parameters which influence the affinity of an open-chain ligand for a particular ion (e.g. donor atom type, chelate ring sizes etc), the macrocyclic hole size can be 'tuned' to provide a donor atom cavity which exhibits an optimum fit for a given metal ion.

We present here examples which illustrate an additional mechanism by which macrocyclic ring-size discrimination may occur. *Such discrimination involves a dislocation in the complexation behaviour of a particular metal ion along a series of closely related macrocyclic ligands.* Such a dislocation occurs when the gradation of properties along the ligand series triggers a substantial change in coordination geometry or ligand conformation in adjacent complexes in the series. The changes in thermodynamic stability which accompany a dislocation may be used to achieve metal-ion discrimination.[1] This type of macrocyclic-ligand discrimination differs from the previously mentioned type since it is not necessarily dependent on the close fit of the metal ion for the macrocyclic hole. Discrimination may occur, for example, even when the macrocyclic ring sizes are considerably larger than are required to tightly surround the metal ion involved. Discrimination of this type has now been achieved for a number of ligand types and the subtle factors underlying such discrimination have been elucidated using a combination of solution equilibrium, NMR, force-field,[2] and X-ray diffraction[3] techniques. Dislocation discrimination will be illustrated by outlining the behaviour of Zn(II) and Cd(II) with a range of O_6, and N_4-donor macrocyclic ligands.

Little emphasis has been given to a systematic study of this discrimination mechanism in the past. Apart from the implications for the design of new metal-ion specific reagents, studies of the present type will undoubtedly contribute to a more general understanding of metal-ion recognition by organic substrates.

---

[1] K.R. Adam, A.J. Leong, L.F. Lindoy, H.C. Lip, B.W. Skelton and A.H. White. J.Am.Chem.Soc., 1983, 105, 4645-4651.

[2] K.R. Adam, L.F. Lindoy and P.A. Tasker, unpublished work.

[3] In collaboration with E.P. Dancey, K. Henrick, and M. McPartlin, Polytechnic of North London.

STUDIES IN ALKYLTHIO DERIVATIVES OF INDIUM

Shuvendu Chatterjee[1], and D.D. Bhatnagar[2]

[1]Department of Chemists, Tata College, Chaibasa-833 202, District Singhbhum, Ranchi University, Bihar, and [2]Chemical Laboratories, University of Rajasthan, Jaipur-302 004, India.

A novel series of alkylthio derivatives (EtS) In.1.5EtSH, $In(SPr)_3$, $In(SBu)_3$ and phenylthio derivative $(PhS)_2InPhSH$ possessing In-S-C bonds[2], has been isolated from hydrated indium trichloride to establish a comparative survey with In-O-C bonded[1] highly hydrolysable $In(OR)_3$ (where R=Me, Et, Pr, Pr^i, Bu, Bu^s, Bu^t or Pent). $In(OPr^i)_3$ was found to yield tri to tetrameric species in boiling parent alcohol, whereas $In(SR^n)_3$ were insoluble in all common organic solvents, except in boiling pyridine, in which these were found monomeric ebullioscopically. The i.r. studies were found inconsistent with their formulations and the following three probable steps were found in the pyrolyses studies:

$$2\ In(SR)_3 \rightarrow In_2S_3 + 2RSR\uparrow.$$

$$In_2S_3 + O_2 \rightarrow 2\ InS + SO_2\uparrow.$$

$$1\ InS + 7/2\ O_2 \rightarrow In_2O_3 + 2\ SO_2\uparrow.$$

The hydrolysable $In(SBu^t)_3$ [dimeric in boiling benzene] could be synthesized by the thiolysis of $In(OPr^i)_3$ under rigorous moisture-free conditions.

Acknowledgement: We express our deep sense of gratitude to Professor R.C. Mehrotra, FRSC.

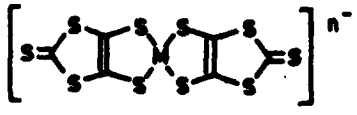
1. Chatterjee, S., S.R. Bindal, and R.C. Mehrotra, *J. Indian Chem. Soc.*, *LIII*, 897, 1976, and references therein.
2. Chatterjee, S., paper no. IIb8, Proceedings, XVIII Int. Conf. on Coord. Chem., Sao Paulo, Brazil, July 18-23, 1977, pp88.
3. Chatterjee, S., *J. Asiatic Society*, August 1978, communicated.

UNUSUAL SOLID STATE PROPERTIES OF NEW COMPLEXES DERIVED FROM THE 4,5-DIMERCAPTO-1,3-DITHIOLE-2-THIONE LIGAND

Michèle Bousseau*, Patrick Cassoux*, Mary Garbauskas**, Leonard Interrante**, John Kasper**, Jean-Pierre Legros* and Lydie Valade*

* LCC Cnrs, 205 Route de Narbonne, 31400 Toulouse, FRANCE
** General Electric R&D, P.O.Box 8, Schenectady, N.Y. 12301, USA

The metal complexes of the 4,5-dimercapto-1,3-dithiole-2-thione ligand (or dimercaptoisotrithione = dmit)[1] can be used as a source of new compounds exhibiting unusual solid state (electric, magnetic,...) properties[2,3].



The $[M(dmit)_2]^{n-}$ complexes (n = 0, 1, 2)

These new compounds are of two main types : (i) "ion-radical salts" $[M(dmit)_2]C_x$, where C^+ is a countercation with $0<x<1$, and (ii) π-donor.acceptor compounds $D.[M(dmit)_2]_y$, where D is a π-donor molecule with $y>1$.

The synthesis, structural characterization, transport properties and the results of magnetoresistance, magnetic susceptibility and E.S.R. studies will be described for new compounds of both types with M = Ni, Pd, Pt,..., and/or $C^+ = NBu_4$, $AsPh_4$,..., and/or D = substituted derivatives of tetrathiafulvalène.

These results will be discussed in terms of the electronic structure, the crystal structure, the "fractional" oxidation state in the ion-radical salts, the degree of charge-transfer between the donor and the acceptor molecules and the extent of intrastack and interstack electronic coupling. From the latter viewpoint, it will be shown that the use of sulfur atoms on the periphery of the molecular unit as a means of extending the π-electron systems and promoting interstack electronic coupling is an effective strategy in realizing the objective of a "true 3-D molecular metal".

1. G. Steimecke, H.J. Sieler, R. Kirmse and E. Hoyer, Phosphorus and Sulfur, 1979, 7, 49.
2. L. Valade, M. Bousseau, A. Gleizes and P. Cassoux, J. Chem. Soc. Chem. Commun., 1983, 110.
3. M. Bousseau, L. Valade, M-P. Brunigel, P. Cassoux, M. Garbauskas, L. Interrante and J. Kasper, Nouv. J. Chim., 1984, 8, in press.

SYNTHESIS AND COORDINATION CHEMISTRY OF SOME NEW ANIONIC TRIPOD LIGANDS

Samuel O. Grim,[a] Samuel A. Sangokoya,[a] Richard D. Gilardi,[b] Ian J. Colquhoun[c] and William McFarlane[c]

[a]Department of Chemistry, University of Maryland, College Park, Maryland 20742

[b]Naval Research Laboratory, Washington, D.C. 20375

[c]Department of Chemistry, City of London Polytechnic, London EC3N 3EY, U.K.

We have recently shown that tris(diphenylthiophosphinoyl)-methane, $[Ph_2P(S)]_3CH$, $HTrisS_3$, can be deprotonated to give the mesomerically stabilized anion, $TrisS_3^-$, which has been isolated as the stable Li^+ and $n\text{-}Bu_4N^+$ salts.[1-2] Some preliminary coordination chemistry with Hg(II) has been reported[3-4] and we report additional ligand syntheses and coordination chemistry here.

$TrisS_3^-$ reacts with Zn, Cd, and Hg(II) halides to give complexes of the type $TrisS_3MX$ in which $TrisS_3^-$ behaves as a uninegative tripodal sulfur-bonded six-electron donor. The resulting complexes are cages with carbon and the metal as bridgeheads in the six-membered chelate rings and are similar to the polypyrazolylborate complexes. $TrisS_3^-$ also reacts with Cu(I) halides, or $AgNO_3$ in the presence of a neutral ligand L, or with R_3PAuCl to form complexes of the type $TrisS_3ML$. The x-ray crystallographic determination of $TrisS_3AgP(\underline{n}\text{-}Bu)_3$ reveals a cage complex in which the three sulfur atoms are bonded to silver. Comparisons of structural and NMR data among $HTrisS_3$, $TrisS_3^-$, and $TrisS_3AgP(\underline{n}\text{-}Bu)_3$ will be made.

Further, the analogous compounds $[Ph_2P(O)]_n[Ph_2P(S)]_{3-n}CH$, where n=1,2 or 3 and their respective anions $TrisOS_2^-$, $TrisO_2S^-$ and $TrisO_3^-$ have been synthesized and some of their coordination chemistry is presented. Whereas $TrisS_3^-$ with its "soft" donor sulfur atoms favors "soft" metals such as Ag(I) and Hg(II), the $TrisO_3^-$ favors "harder" metals such as those of the first transition series.

1. S.O. Grim, S.A. Sangokoya, I.J. Colquhoun and W. McFarlane, J. Chem. Soc., Chem. Commun. 1982, 930.
2. S.O. Grim, R.D. Gilardi and S.A. Sangokoya, Angew. Chem. Int. Ed. Engl. 1983, 22, 254.
3. S.O. Grim, P.H. Smith, L.C. Satek, I.J. Colquhoun and W. McFarlane, Polyhedron 1983, 1, 137.
4. S.O. Grim, S. Mittelo, M.L. Aumon, P.H. Smith, I.J. Colquhoun, W. McFarlane and J.R. Holden, Inorg. Chim. Acta 1983, 77, L217.

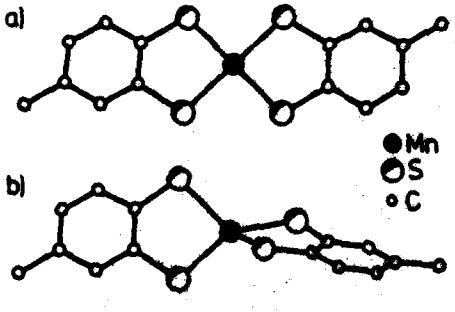
THE REACTION OF Mn WITH TOLUENE-1,2-DITHIOLATE (tdt)$^{2-}$: SYNTHESIS AND STRUCTURES OF $[Mn(tdt)_2]^{2-}$, $[Mn(tdt)_2]^-$ AND $[Mn(tdt)_2MeOH]^-$

Klaus Greiwe*, Bernt Krebs and Gerald Henkel

Anorganisch-Chemisches Institut der Universität Münster
Corrensstr. 36, D-4400 Münster, Federal Republic of Germany

In contrast to iron the chemistry of manganese in the oxidation states +2 and +3 with sulfur-containing ligands such as thiolates or dithiolenes is not well developed though both metals are direct neighbors of the periodic table. Structurally identified manganese complexes with complete thiolate coordination have been limited to the monomeric anion $[Mn(SPh)_4]^{2-}$ [1] and the dimeric compound $[Mn_2(S(CH_2)_2S)_4]^{2-}$ [2] (1) both of which exhibit the structural characteristics of their iron counterparts.

During our investigations on manganese-sulfur compounds we have isolated the mononuclear complex $[Mn(tdt)_2]^{2-}$ (2) (tdt = toluene-1,2-dithiolate) as well as its oxidized analog $[Mn(tdt)_2]^-$ (3). From methanolic solutions 2 can be isolated as $[Ph_4P]_2[Mn(tdt)_2]\cdot 2MeOH$ (4), whereas 3 crystallizes together with $[Mn(tdt)_2MeOH]^-$ (5) as mixed Ph_4P^+ salt.



The X-ray structure determination of 4 demonstrates an extremely distorted sulfur tetrahedron (mean Mn(II)-S 2.418 Å, S-Mn-S 88.7 to 124.6°, see figure b), whereas for 3 a square-planar sulfur arrangement (mean Mn(III)-S 2.281 Å) is observed (see figure a). The structure of 5 derives from 3 by addition of a methanol molecule whose oxygen atom expands the coordination sphere of manganese towards a square pyramid (mean Mn(III)-S 2.340 Å). In contrast to 1 the structure of 3 does not reflect the architecture of the iron derivative though some similarities between the mononuclear MnS_4 units of 3 and the FeS_4 subunits of the binuclear $[Fe_2(tdt)_4]^{2-}$ [3] anion are obvious.

The manganese-sulfur chemistry may also play an important role in biological systems as the presence of manganese in various biomolecules is firmly established[4]; e.g., a Mn(III)-S(cys) bond is discussed as a structural element of the active protein center of acid phosphatase[5].

1. B. Swanson, N.C. Stephenger and B. Coudouvanis, J. Am. Chem. Soc. 1978, 100, 1952.
2. G. Christou and J. Huffman, J. Chem. Soc., Chem. Commun. 1983, 558.
3. G. Henkel, W. Tremel, U. Kuhlmann and B. Krebs, "Abstracts of Papers", XXI ICCC, Toulouse, 1988, p. 351.
4. G.D. Lawrence and D.T. Sawyer, Coord. Chem. Rev. 1978, 27, 173.
5. H. Kawaba, Y. Sugiura and H. Tanaka, Inorg. Chim. Acta 1983, 79, 112.

SOFT CHEMISTRY IN THE LAMELLAR MPS_3 SERIES : EXAFS CHARACTERIZATION OF $Mn_{1-x}Ni_xPS_3$ HETEROMETALLIC LAYERS.

Rene CLEMENT[a], Yves MATHEY[a] and Alain MICHALOWICZ[b]

a - Lab. de Physicochimie Minérale and ERA 672 , Université PARIS SUD 91405 ORSAY - FRANCE .

b - Lab. de Physicochimie Structurale, Université de PARIS Val de Marne, 94000 CRETEIL FRANCE and LURE , 91405 ORSAY FRANCE

Transition metal hexathiohypodiphosphates MPS_3 form a class of lamellar semiconductors which give rise to a rather uncommon intercalation chemistry. Indeed , beside intercalating electron donor species through guest→ host electron transfer (a mechanism which has led to the realization of lithium batteries)and thus resembling the transition metal dichalcogenides , several MPS_3 are also able to take up cationic species in the interlamellar space to give intercalation compounds where the positive charge of the inserted species is balanced by a corresponding loss of intralamellar M^{2+} cations (a mechanism so far unknown in intercalation chemistry[1]). Alkali metal cations inserted this way are solvated and highly mobile , and they can be exchanged against a variety of other cationic species as bulky as the tris(2-2'bipyridyl)Ru(II) complex[2] .

The aim of the present work is the search for a soft and general method for synthesizing heterometallic layered materials possessing paramagnetic ions in strong interaction . The key idea relies on the possibility that labile inserted transition metal species would be able to jump back into the available intralamellar voids.

The obtained single phased material has been characterized by powder X ray diffraction , magnetic measurements and EXAFS spectroscopy at both manganese and nickel edges. The reaction process first involves the exchange of the hydrated K^+ ions by hydrated nickel species, followed by a dehydration step , whereupon the nickel ions leave the interlamellar space and go into the intralamellar manganese vacancies. The material obtained in this soft way appears practically identical to a material of the same composition prepared by a conventional high temperature technique. A reaction mechanism is suggested to account for such a surprisingly high mobility of cations in a lamellar structure at room temperature. It assumes the existence of a dynamical equilibrium in the close vicinity of the layers, between the solid host structure and the solvated M^{2+} and $P_2S_6^{4-}$ species.

(1) R. Clement, J.C.S. Chem. Commun.,1980, 647.
(2) R. Clement, J.Am.Chem.Soc.,1981,103, 6998.

METAL COMPLEXES WITH STERICALLY ENCUMBERED THIOLATE LIGANDS: MODELS FOR METAL-SULFIDE HETEROGENEOUS CATALYSTS

Michelle Millar* and Stephen A. Koch

Department of Chemistry, New York University, New York, N.Y. USA 10003; Department of Chemistry, State University of New York at Stony Brook, Stony Brook, N.Y. USA 11794

We have been using sterically hindered thiolate ligands to prepare coordinatively unsaturated metal-sulfur complexes to serve as simple models for the active sites of metal-sulfide heterogeneous catalysts. $[M(SR)_4(CH_3CN)]$ [M= Ru, Os; RS = 2,3,5,6-tetramethylbenzenethiolate ($C_{10}H_{13}S$) and 2,4,6-triisopropylbenzenethiolate ($C_{15}H_{23}S$)] react rapidly with CO at room temperature and atmospheric pressure to give $[M(SR)_4(CO)]$. The formula and molecular structure of $[Ru(SC_{10}H_{13})_4(CO)]$ were confirmed by an X-ray crystal structure determination. The CO ligand occupies an axial position of the trigonal bipyramidal coordination center. These $[M(SR)_4(CO)]$ compounds provide rare examples of compounds containing a CO molecule coordinated to a metal in the formal +4 oxidation state. Reactivity studies with RNC, NO, H_2S, thiophene, alkynes and alkenes will also be discussed. The ability of sulfur ligands to increase the π-basicity of high oxidation state metal centers may be a key feature in the mechanism of heterogeneous metal-sulfide catalysts.

PALLADIUM AND PLATINUM COMPLEXES OF IMIDAZOLE-THIONE MOLECULES

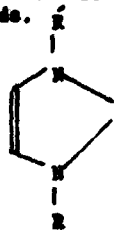
Linda M. Butler, Eric S. Raper and William R. Tomlinson

School of Chemical & Life Sciences, Newcastle Polytechnic, Newcastle upon Tyne, NE1 8ST, England

Complexes of Palladium (II) and Platinum (II) with Imidazoline-2-thione (Imt),1-Methylimidazoline-2-thione (MImt) and 1,3-Dimethylimidazoline-2-thione (DMImt) have been prepared. Both neutral and acid media have been used in the syntheses in order to establish whether the coordination chemistry of the molecules, with these metals, is pH-dependant.

Compound stoichiometries have been established by chemical (C,H,N) and thermal analysis methods, the latter showing the extent of hydration in the complexes. Further characterisation has been obtained by X-ray Powder Diffraction Methods, Infrared and Electronic Spectroscopy and Electronic Conductivity Measurements.

The crystal structures of $(M(MImt)_4)Cl_2.2H_2O$ (M = Pd(II) or Pt(II)) (1,2) have also been obtained from single crystal X-ray studies, confirming the presence of uncoordinated H_2O molecules, ionic chloride ions and square-planar MS_4^{2+} entities linked by H-bonds.



R = R^1 = H = Imidazoline-2-thione (Imt)

R = H, R^1 = CH_3 = 1-Methylimidazoline-2-thione (MImt)

R = R^1 = CH_3 = 1,3-Dimethylimidazoline-2-thione (DMImt)

1. M.E. O'Neill, R.S. Raper, J.A. Daniels and I.W. Nowell Inorg. Chim. Acta 66(3) (1982) 79-84

2. L.M. Butler, J.R. Creighton, R.E. Oughtred, R.S. Raper and I.W. Nowell Inorg. Chim. Acta 75(2) (1983) 149-154

SYNTHESIS AND CHARACTERIZATION OF THE COORDINATION POLYMERS OF COPPER(II) AND NICKEL(II) WITH PSEUDOTHIOHYDANTOIN (PTH)

L.J. Paliwal and N.S. Bhave

Chemistry Department, Nagpur University Campus, Nagpur, India.

In the present communication attempts have been made to synthesize and characterize the number of coordination polymers of copper(II) and nickel(II) with Pesudothiohydantoin (PTH) in varied solvent media and at different temperatures.

It has been observed that, in case of nickel(II)-PTH polymers (prepared at different temperature and in different solvent media), Ni(II) ion is surrounded by octahedral environment. Whereas in copper(II)-PTH polymers two types of geometries can be predicted: (i) Coordination polymers of copper(II), synthesized below temperature 75°C and in different solvent systems, are found to be octahedrally surrounded copper(II) ions. (ii) Copper(II)-PTH polymers obtained above 75°C are assumed to be square planar.

Characterization of the coordination polymers has been undertaken with the help of electronic, IR spectra and magnetic susceptibility measurements.

On the basis of elemental analysis, composition of the coordination polymers are suggested as $(Ni(PTH)\cdot 2H_2O)_n$, $(Cu(PTH)\cdot 2H_2O)_n$ and $(Cu(PTH))_n$.

SYNTHESIS AND REACTIVITY OF POLYSULFIDE RING COMPLEXES OF NICKEL(II)

Sabyasachi Sarkar and K.N. Udupa

Department of Chemistry, Indian Institute of Technology, Kanpur 208 016, India

Recently, nickel joined the group of transition metals relevant in biological redox reactions parallel to iron-sulfur proteins.[1] The occurrence of CN^-, S^{2-} on primordial earth suggests that there may be the importance for the evolution of these enzymes on the chemistry of $Ni^{2+}/CN^-/S^{2-}$. It is well known that cyanide ion readily removes sulfur from sulfur chains with the formation of thiocyanate. Of interest to us, then, is the reaction of the readily formed $Ni(CN)_4^{2-}$ with polysulfide. Quite unexpectedly this reaction led to the isolation of a new nickel(II) polysulfide chelate, NiS_{10}^{2-}. When the same reaction is carried out in DMF medium using S_8/KOH, instead of aqueous polysulfide, complex of the type $(CN)_2NiS_5^{2-}$ is formed. These complexes were isolated as tetraphenylphosphonium/tetraphenylarsonium salts and were characterized by elemental analysis, IR, Raman, NIR/VIS/UV and XPE spectroscopy. The redox chemistry of these complexes was followed by cyclic voltametry. Oxidation of NiS_{10}^{2-} with oxygen resulted in the isolation of a new species, $NiS_{10}O_2^{2-}$. Such reactions are relevant to the metabolism of phototropic microorganisms which oxidise S^o or S^{2-} and are effective in the sulfur cycle.[2] Complete structural characterization of this oxidized species is under investigation and the results will be discussed.

1. A.V. Xavier, M. Teixeira, I. Moura, J.J.G. Moura and J. LeGall, Inorg. Chim. Acta, 1983, 79, 13.

2. (a) H. Bothe and A. Trebst: Biology of Inorganic Nitrogen and Sulfur, Springer-Verlag, Berlin, 1981. (b) B. Meyer: Sulfur, Energy and Environment, Elsevier, Amsterdam, 1977.

SPECTROSCOPY INVESTIGATION OF SOME p- AND d-ELEMENT COMPLEXES WITH SULPHUR-CONTAINING LIGANDS

Kh.M.Yakubov, Ye.N.Bakhus, Ye.Ya.Kalonterova
Tadjik State University, Lenin st.,17, Dushanbe, USSR

As a result of p- and d-element complexes (Mn, Cr, V, Pb, Bi, Hg) investigation with macromolecular sulphur-containing ligands by KFA, IR, KPR-spectroscopy methods it has been concluded about metal coordination process in polymer matrix and macromolecule coordination centre composition.

Fibrous macromolecule ligands are thioamidated copolymer PVA with polyakrilonitrile (PAN) and polyakrilonitrile, functional groups of which ($-C\lesssim^{SH}_{NH_2}$ ⇌ $C\lesssim^{S}_{NH_2}$; COOH; OH; $CONH_2$) contain oxygen, sulphur and nitrogen donor atoms.

Investigating complexes element analysis has shown, that sulphur and p-element containing ratio is 2:1 for Hg(II), Pb(II) and 3:1 for Bi(III), that indicates of these metal coordination with sulphur atom, while d-element containing (Cr, V) in polymer does not depend on sulphur concentration.

Absorption spectra analysis of the investigating samples in the interval 3323, 3218 [ν (NH_2)] and 1630 [σ (NH_2)] makes it possible to exclude the bond formation Me - N, as far as after metal injection into polymer matrix neither the absorption lines shift nor their intensity change takes place. The absorption line at 1752 sm^{-1}, typical for stretching vibrations and observing in the ligand after metal injection, shifts to long-wave interval, that is explained by ligand coordination by the metals through oxygen of CO group.

KR-spectroscopy data obtained for iron(III) complex samples with the investigated macromolecular ligands proves the conclusion about coordination through oxygen atom of carbonal group.

Oxidation degrees of the studied paramagnetic metals in the studied complexes being determined by KPR method are Cr(III), Mn(II), V(VI). Vanadium sample spectra have the parameters typical for ванадиум compounds (VO^{2+}).

PREPARATION OF ISOCYANIDE COMPLEXES WITH THE DINITROGEN-BINDING METAL CENTRE $\{Re(S_2CNEt_2)(PMe_2Ph)_3\}$

Armando J.L. Pombeiro

Centro de Química Estrutural, Complexo I,
Instituto Superior Técnico, Av. Rovisco Pais, Lisboa, Portugal

Raymond L. Richards
School of Molecular Sciences, University of Sussex, Falmer, Brighton, England

Dinitrogen complexes may constitute a convenient source of electron-rich transition metal centres which may activate ligands such as isocyanides (CNR) towards electrophilic agents[1], and a similarity in the chemical behaviour of the methyl isocyanide and the dinitrogen ligand has been recognized in a few cases, usually involving group VI (Mo and W) phosphinic complexes of the type $[ML_2L'_4]$ (L' = tertiary monophosphine or 1/2 diphosphine) where any of the ligand types ($CNMe$ or N_2) may undergo attack by a protic or a Lewis acid.

In order to study the influence of the metal and co-ligands on the activation of isocyanides by dinitrogen-binding centres we are extending the preparation of isocyanide complexes from dinitrogen parent compounds to group VII transition metals with different sulphur ligands.

The molecular structure of mer-$[Re(\eta^1\text{-}S_2PPh_2)(N_2)(CNMe)L_3]$ has recently been confirmed[2] by X-rays and the preparation of related species with a different dithioligand, e.g., $[Re(\eta^2\text{-}S_2CNEt_2)(CNMe)L_3]$ (A, L=PMe_2Ph, reaction 1) and mer-$[Re(\eta^1\text{-}S_2CNEt_2)(N_2)(CNMe)L_3]$ (B, reaction 2), is now presented.

$$[Re(\eta^2\text{-}S_2CNEt_2)(N_2)L_3] + CNMe \rightarrow [Re(\eta^2\text{-}S_2CNEt_2)(CNMe)L_3] + N_2 \quad (1)$$

$$[Re(\eta^2\text{-}S_2CNEt_2)(N_2)L_3] + CNMe \rightarrow \text{mer-}[Re(\eta^1\text{-}S_2CNEt_2)(N_2)(CNMe)L_3] \quad (2)$$

A strong activation of the isocyanide ligand towards electrophiles is expected for complex A in view of the observed low i.r. $\nu(CN)$ value (1810 cm^{-1}).

Complex B presents both N_2 and $CNMe$ ligands and a direct comparison between these species may thus be possible.

These reactions will be discussed as well as the relative behaviour of the $\{Re(S_2CNEt_2)L_3\}$, $\{Re(S_2PPh_2)L_3\}$ and $\{ReCl_4\}$ dinitrogen-binding centres.

References: 1 - A.J.L. Pombeiro, "Reactions of ligands analogous to dinitrogen on dinitrogen binding sites", Ch.10 in "New Trends in the Chemistry of Nitrogen Fixation", J.Chatt, L.M.D.Pina, R.L. Richards, eds., Academic Press, 1980.

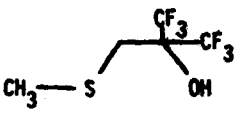
2 - A.J.L.Pombeiro, P.B.Hitchcock, R.L.Richards, Inorg. Chim. Acta, 1983, 71, L21.

Acknowledgements: The support given by the JNICT (contract Nº 215.80.58), the INIC (Portugal) , the British Council and the Calouste Gulbenkian Foundation is gratefully acknowledged.

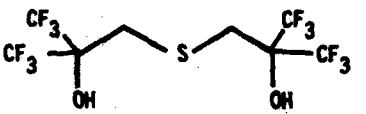
HYBRID MULTIDENTATE LIGANDS: STUDIES ON FIRST-ROW TRANSITION METAL, Pd(II), AND Pt(II) COMPLEXES OF ALKOXY-THIOETHER LIGANDS

René T. Boeré, W. Mark Brown, and Christopher J. Willis
The University of Western Ontario, London, Canada N6A 5B7
and Douglas W. Stephan
The University of Windsor, Ontario, Canada N9B 3P4

The compounds 1 and 2 will coordinate (in the deprotonated form) to give transition metal complexes of, respectively, a bidentate, uninegative ligand and a tridentate, dinegative ligand:



1 (deprotonated = L^1)



2 (deprotonated = L^2)

In each case, a hard alkoxy-donor site, $-C(CF_3)_2O^-$, is combined with a soft thioether donor, and ligands of this type are therefore capable of coordination to a variety of transition metal ions.

With L^1, we have prepared neutral complexes $M(L^1)_2$, where M = Cu, Ni, Pd, or Pt, and $M(L^1)ClPR_3$, where M = Pd or Pt. Using a variety of phosphines as coligands, cationic complexes of the type $[M(L^1)(PR_3)_2]BF_4$ have been prepared, and structural determinations have been made for M = Pt, PR_3 = PPh_3 and PR_3 = Ph_2PMe. NMR studies, particularly in relation to inversion at the CH_3-S site in the chelate ring, are discussed in conjunction with the structural results on the Pt systems.

The range of first-row transition metal complexes accessible with ligand 1 is much smaller; $M(L^1)_2$ is a moisture-sensitive, purple compound for M = Cu^{2+}, but for M = Ni^{2+} or Co^{2+}, only polymeric, hydrated, materials were obtained. By contrast, ligand 2 gives a range of stable, generally five-coordinate, neutral complexes of the type $M(L^2)(N\text{-}N)$, where M = Co^{2+}, Ni^{2+}, or Cu^{2+} and N-N = $(pyr)_2$, dipy, or $Me_2NCH_2CH_2NMe_2$. A structural determination on $Co(L^2)(pyr)_2$ shows TBP geometry about the metal ion, with axial S and N, equatorial O, O, and N donors resulting from a facial coordination of the ligand. Steric hindrance from the bulky $-C(CF_3)_2O^-$ donors appears to inhibit the coordination of an additional molecule of pyridine which would have produced the more common six-coordinate environment for Co^{2+}.

Ma6-01

EXCHANGE-COUPLED COORDINATION COMPLEXES STUDIED BY NEUTRON SCATTERING AND OPTICAL SPECTROSCOPY

Hans U. Gudel

Institut fur anorg. und phys. Chemie, Freiestrasse 3, CH-3000 Bern 9, Switzerland

Inelastic neutron scattering (INS) and optical spectroscopy are useful complements to the more common magnetochemical techniques for the study of exchange-coupled complexes. Experimental exchange splittings are obtained without using theoretical models.

The temperature dependence of exchange as well as the role of biquadratic exchange can be studied by INS. A separation of intra and intermolecular exchange effects is possible. Nearest-neighbor vs. second-nearest-neighbor exchange effects can be investigated in complexes containing more than two magnetic centers.

Optical spectroscopy allows the study of ground and excited state properties. High-resolution low-temperature luminescence and absorption spectroscopy is used for probing exchange splittings in the electronic ground state. Transitions to singly and doubly excited states are observed in the absorption spectra. Orbital exchange parameters, containing information about the dominant exchange pathways, are deduced from excited state splittings. Spin-crossover phenomena can be observed by Zeeman absorption spectroscopy. Energy transfer as a consequence of intermolecular interactions is studied by time-resolved luminescence and excitation spectroscopy.

SYNTHESIS, CRYSTAL STRUCTURE AND MAGNETIC PROPERTIES OF 1D LINEAR-CHAIN ORGANIC INTERCALATED Cr(II): $[(CH_3)_4N]CrX_3$, (X=Cl, Br)

C. Bellitto, G. Dessy, V. Fares, D. Fiorani, and S. Viticoli

Istituto di Teoria, Struttura Elettronica Composti di Coordinazione del C.N.R., Area della Ricerca di Roma, 00016 Monterotondo Staz., Italy.

The magnetic and thermal properties of 1D transition metal ion complexes have been of great interest in the last few years from both a theoretical and experimental point of view. Recently, we focused our attention of the chemistry and magnetic properties of organic-intercalated low-dimensional Cr(II) compounds[1], and we have found a new method of synthesis and crystal growth of these interesting materials[2]. Hexagonal $ACrX_3$, (A=unipositive cation, X=halogen) are good experimental examples, because their magnetic properties are mainly resulting from exchange interaction in one direction, and because they contain a Jahn-Teller ion. By far, while $ACrX_3$ with A=Cs, Rb, K, have been extensively studied, there is a lack of information on similar organic-intercalated compounds: $[(CH_3)_4N]CrX_3$, X=Cl, Br, I (TMCrX hereafter); compounds where the inter-chain distance is greater than in the corresponding inorganic ones, due to the bulkiness of the cation. To this Conference we wish to present the crystal structure and the magnetic properties of TMCrC and TMCrB.

TMCrC crystallizes in the space group $P6_3/m$, (C_{6h}^2) of the hexagonal system, Z=2, with unit-cell dimensions: a=b=9.129(3) and c=6.512(2) Å. The structure consists of linear one-dimensional chains of Cr atoms with three bridging chlorine atoms between them. It is a linear-chain antiferromagnet, (J/k=-15.25 K), showing a 3D magnetic order at T_N=7 K.

TMCrB has been synthesized and it crystallizes as yellow-olive microcrystalline powder. Preliminary magnetic susceptibility measurements do not show any evidence of long-range order down to 4.2 K. The physical properties and the chemistry of both compounds will be reported and discussed.

1. Bellitto, C., and P. Day, *J. Chem. Soc., Dalton*, 1207, 1978.
2. Bellitto, C., and P. Day, *J. Cryst. Growth*, *58*, 641, 1982.

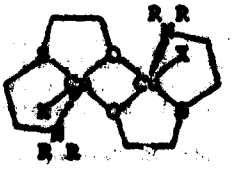
TEMPERATURE DEPENDENCE OF STRUCTURE AND MAGNETIC INTERACTION IN DIALKOXO-BRIDGED BINUCLEAR COPPER(II) COMPLEXES WITH 2-[2-(DIALKYLAMINO)ETHYLTHIO]ETHANOL

M. Mikuriya [a], K. Toriumi [b], T. Ito [b], and S. Kida [a]

[a]Department of Chemistry, Faculty of Science, Kyushu University, Fukuoka 812, JAPAN

[b]Institute for Molecular Science, Okazaki National Research Institutes, Okazaki 444, JAPAN

The temperature dependence of magnetic susceptibility has been explained in terms of the Van Vleck's equation based on the Heisenberg model for most of the binuclear copper(II) complexes so far reported. Recently, however, we have prepared a series of dialkoxo-bridged copper(II) complexes, Cu(R-nso)X (HR-nso = 2-[2-(dialkylamino)ethylthio]ethanol; R = CH_3, C_2H_5, n-C_3H_7, n-C_4H_9; X = Cl, Br, NO_3, NCS), which could not be interpreted by the equation based on the Heisenberg model except the cases of Cu(C_2H_5-nso)Cl and Cu(n-C_4H_9-nso)Cl.[1] There are two possible explanations for this result based on the assumptions, 1) variation of the structure with temperature and 2) anisotropic spin exchange model. In order to settle the controversy we have carried out the X-ray crystal structure analysis of Cu(n-C_3H_7-nso)Cl at 120 K. Although the structure is fundamentally the same as that at room temperature and the Cu-O-Cu angle which has been generally thought to be the most important factor to determine the degree of magnetic interaction received no appreciable effect by temperature, a substantial change was observed in the planarity of the bonds incorporating the bridging oxygen atom. The increase of deviation from the plane is a suitable magnitude for the decrease of $-2J$ value (340 cm^{-1} → 230 cm^{-1}) on the basis of the comparison of the magnetic and structural data of many dialkoxo-bridged copper(II) complexes.



Cu(R-nso)Cl

1. M. Mikuriya, H. Ōkawa, and S. Kida, Bull. Chem. Soc. Jpn. 1980, 53, 2871; 1981, 54, 2979; 1982, 55, 1086.

SEARCH FOR SPIN-PEIERLS TRANSITIONS IN PARAMAGNETIC LINEAR CHAIN COMPLEXES OF TRANSITION METALS

William E. Hatfield and Leonard W. ter Haar

Department of Chemistry 045A, University of North Carolina, Chapel Hill, North Carolina, USA, 27514

Spin-Peierls transitions in antiferromagnetic uniformly-spaced chain compounds was predicted theoretically more than twenty years ago. Since then, more than 150 uniformly-spaced, antiferromagnetically-exchange coupled, transition metal chains have been synthesized and characterized, yet, up to now, there have been no reports of such chains exhibiting the characteristic magnetic suscepti- bility behavior reflecting spin-Peierls transitions.

An examination of the theory for SP transitions suggests that the phenomenon may be found in those systems in which structural features leading to strong three-dimensional interchain phonon interactions are maximized, and those features that permit interchain magnetic interactions are minimized. A compound that meets these structural criteria is [N-(salicylaldiminato)glycinato]-aquocopper(II) hemihydrate, $[Cu(C_9H_7NO_3)(H_2O)]\cdot\frac{1}{2}H_2O$, Cu-NSG.

Formula units of Cu-NSG stack in the b-direction to form a uniformly-spaced chain with the intrachain superexchange network being Cu-O-C-O-Cu.[1] In addition, neighboring chains pack antiparallel in the crystal structure with an interleaving of molecular units which promotes interchain phonon interactions. There are no obvious interchain superexchange pathways, and interchain magnetic interactions are minimized.

Magnetic susceptibility data clearly show the distinctive fingerprint of a magnetoelastic SP transition in Cu-NSG. There is a chain-like maximum near 4 K, and an SP-knee near 2.2 K. Above the SP transition, the magnetic susceptibility data may be fit by Heisenberg S = 1/2 theory with $J = -1.55$ cm^{-1} and $g = 2.14$. The exchange coupling constant is temperature dependent below 5.5 K as a result of the large spin-phonon coupling [$T(SP)/2|J| = 0.48$]. The magnetic susceptibility in the SP phase may be fit by the expression

$$\chi_M = (Ng^2\mu_B^2/kT)(A)\exp[-2J(1-T/T_c)/kT]$$

where the temperature parameter T_c accounts for the characteristic progressive dimerization of formula units in the chain. Theoretical implications of these results will be discussed, and data for additional compounds will be presented.

1. T. Ueki, T. Ashida, Y.Sasada, M. Kakudo, Acta Crystallogr. 1967, 22, 870.

MAGNETIC INTERACTIONS IN HOMO- AND HETERO-BINUCLEAR INORGANIC AND BIOINORGANIC COMPLEXES

Ekk Sinn, Greg A. Brewer
University of Virginia, Charlottesville, Virginia 22901, U.S.A.

John de Jersey and Burt Zerner
University of Queensland, St Lucia, Queensland, Australia

Complexes with oxygen bridges between first-row transition metals have been synthesized in order to examine the magnetic interactions that can occur when the metals are paramagnetic. Most of these have been characterized by X-ray crystallography. Both homo- and hetero-binuclear (and polynuclear) systems have been examined, e.g. Cu-Cu, Ni-Ni, Cu-Mn, Cu(II)-Fe(II and III). Similar systems have also been examined with imidazole bridges built into the ligand. These will be compared with models that have been proposed for cytochrome oxidase, in which a Cu-Fe interaction is presumed.

The homobinuclear complexes can be either ferro or antiferromagnetic, but all the heterobinuclears are found to be antiferromagnetic. Theoretical arguments are presented for the preponderance of antiferromagnetic interactions with dissimilar metal atoms: the case for non-existence of ferromagnetic coupling is made for the Cu(II)-Fe(III) couple, regardless of how the metals are linked, and from this it is extrapolated to show that ferromagnetic interaction in any heterobinuclears are at least improbable, and need not normally be considered in model complexes.

Purple iron phosphatase, e.g. from porcine allantoic fluid, in the oxidized form contains magnetically coupled Fe(III) species, evidently in a Fe^{III}-O-Fe^{III} unit, with considerable analogy to hemerythrin. In the reduced form it contains Fe^{III}-Fe^{II}. In metal-substituted forms, Cu^{II}-Fe^{III} is strongly coupled, while Fe-Mg and Fe-Zn are strongly magnetic, due to elimination of the coupling. Interpretation of EXAFS of the Fe-N form of the enzyme is facilitated by comparison with heterobinuclear complexes, containing the same metal atoms at precisely known distances (X-ray) which have therefore been synthesized.

MOLECULAR ENGINEERING OF THE COUPLED BINUCLEAR COMPLEXES.

O. Kahn, Y. Journaux, I. Morgenstern, M. Verdaguer and P. Lacroix

Laboratoire de Spectrochimie des Eléments de Transition, ERA 672, Université de Paris-Sud, 91405 Orsay, France.

In the last few years, we laid the foundations of a molecular engineering of the polymetallic systems. Our goal is to know the metal ions and the ligands we have to choose, the whole symmetry we have to design in order to obtain a complex exhibiting expected magnetic properties. For that we proposed a model of the interaction between the metal ions in which the main concept is that of natural magnetic orbitals and of overlap density between these magnetic orbitals. Recently, we extended this model by taking into account the spin polarization effects induced by the bridging ligands with an highest occupied molecular orbital close in energy to the magnetic orbitals.

Among the results obtained in this frame, we can mention :
(i) the design of the first binuclear complexes in which the coupling is purely ferromagnetic;
(ii) the achievement of a large interaction between metal ions far away from each other;
(iii) the possibility to tune the magnitude of the interaction in a given bridging network by playing on the nature of the terminal ligands;
(iv) the exaltation of the spin polarization effects in μ-azido copper (II) complexes;
(v) the synthesis of cationic coupled complexes with potentially electron donor counteranions.

According to the available place, we shall present some of these results by focusing on the newest developments.

The first papers in this field are listed in ref.[1-3]

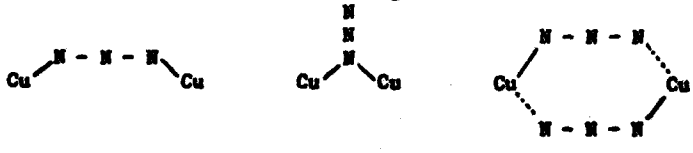
1. O. Kahn, J. Galy, Y. Journaux, J. Jaud and I. Morgenstern-Badarau, J.Am.Chem.Soc., 1982, 104, 2165.
2. Y. Journaux, O. Kahn, I. Zarembowitch, J. Jaud, J. Galy, J.Am.Chem.Soc., in press.
3. M. Julve, M. Verdaguer, A. Gleizes, M. Philoche-Levisalle and O. Kahn, Submitted to J.Am.Chem.Soc.

SPIN POLARIZATION EFFECTS IN μ-AZIDO COPPER (II) BINUCLEAR COMPLEXES

Olivier Kahn[a], Marie-Laure Boillot[a], Yves Jeannin[b] and I. Morgenstern-Badarau[b]

a : Université de Paris-Sud, 91405 Orsay, France
b : Université P. et M. Curie, 75230 Paris, France

The most fascinating aspect of the chemistry of the μ-azido copper (II) binuclear complexes is likely the versatility of their magnetic properties. When N_3^- bridges in an end-to-end fashion as in 1, the coupling is strongly antiferromagnetic. When N_3^- bridges in an end-on fashion as in 2, this favors the ferromagnetic coupling. Finally, the coupling is negligible or very weakly antiferromagnetic when the metal ions are semi bridged as in 3 :



1 2 3

To understand the mechanism of the phenomenon in a thorough manner :
(i) we extensively developed the chemistry of the μ-azido and μ-cyanato copper (II) complexes. In most of the cases, the molecular structures were refined by X-ray diffraction;
(ii) we investigated the magnetic properties and the powder and single crystal EPR spectra of the compounds;
(iii) we performed ab initio calculations with large CI on model systems (in collaboration with french theoreticians) and proposed the concept of spin polarization effects due to the nature of the π_g MOMO's of N_3^-.

The first papers corresponding to this work are listed in Refs [1-3].

1. I. Morgenstern-Badarau, S. Sikorav and O. Kahn, J.Cryst.Spec. Research 1983, 13, 1.
2. O. Kahn, S. Sikorav, J. Gouteron, S. Jeannin and Y. Jeannin, Inorg.Chem. 1983, 22, 2877.
3. S. Sikorav, O. Kahn and I. Morgenstern-Badarau, Inorg.Chem., in press.

$CuMn(S_2C_2O_2)_2$, 7.5 H_2O AND RELATED COMPOUNDS. MAGNETIC PROPERTIES, EXPERIMENTAL AND THEORETICAL CHARACTERIZATION OF THE FIRST QUASI-ONE-DIMENSIONAL ferrimagnetic CHAIN

Michel Verdaguer[1], Alain Gleizes[2], Jean-Pierre Renard[3], and Joseph Seiden[3]

[1]Laboratoire de spectrochimie des elements de transition, E.R.A. 672, Universite de Paris-Sud, 91045 Orsay, [2]Laboratoire de chimie de coordination du C.N.R.S., 205 Route de Narbonne, 31400 Toulouse, [3]Institute d'electronique fondamentale, Laboratoire associe au C.N.R.S., Universite de Paris-Sud, 91405 Orsay, France.

The quasi-one-dimensional compound $CuMn(S_2C_2O_2)_2$. 7.5 H_2O (CuMnDTO) and related compounds (where Cu is replaced by Ni, Pd, Pt) were synthesized, their crystallographic structures were refined, and their magnetic susceptibilities were measured in the temperature range 1.3-240 K.

The curve X_MT versus T for CuMnDTO presents a minimum at 130 K and a maximum at T=7.5 K where three-dimensional ordering occurs. Magnetization data at 1.3 K and 4.2 K in the field range 0-5 T are consistent with an antiferromagnetic interaction between Cu(II) and Mn(II) ions through the dithiooxalato bridge and weak ferromagnetism in the ordered phase.

Different theoretical models accounting for isotropic exchange interaction between quantum spins S1=1/2 (Cu++) and quantum or classical S2=5/2 (Mn++) reproduce well experimental data, allowing the determination of the coupling constant -J.S1.S2 as J=-30 cm^{-1}. Extended Huckel calculations allow to visualize the σ-exchange pathway through the dithiooxalate anion.

The antiferromagnetic interaction between Cu(II) and Mn(II) metallic ions lead to ONE-DIMENSIONAL FERRIMAGNETIC behavior characterized for the first time, both theoretically and experimentally, in a fully structurally characterized compound.

Gleizes, A., M. Verdaguer, *J. Am. Chem. Soc. 103*, 7073-7074, 1981.
Verdaguer, M., A. Gleizes, J.-P. Renard, and J. Seiden, *Phys. Rev.*, B, in press.
Gleizes, A., M. Verdaguer, submitted to *J. Am. Chem. Soc.*

INTERACTION THROUGH BIS-BIDENTATE LIGANDS IN COPPER(II) BINUCLEAR COMPLEXES: FROM THE UNDERSTANDING OF THE EXCHANGE PATHWAY TO THE SYNTHESIS OF COMPOUNDS WITH EXPECTED MAGNETIC PROPERTIES

Michel Verdaguer[1], Marie-France Charlot[1], Yves Journaux[1], Olivier Kahn[1], and Miguel Julve[2]

[1]Laboratoire de spectrochimie des elements de transition, E.R.A. 672, Universite de Paris-Sud, 91405 Orsay, France; [2]Facultad de ciencas quimicas, departamento de Quimica Inorganica, Universitad de Valencia, Burjasot, Valencia, Espana

In our attempts to understand the mechanism of interaction of two copper(II) ions through pluriatomic bridges, we synthesized binuclear complexes with bridging ligands such as oxalato (1), oxamato (2), oxamido (2), and dithiooxamido (3) and we measured their magnetic susceptibilities in the temperature range 4.2-300 K.

By varying the terminal ligands, we modified the copper(II) coordination spheres in symmetrical as well as in asymmetrical complexes, and in so doing, we were able to tune the coupling constant J ($H=-J\,S_1 S_2$) from J=0 to J=-800 cm^{-1}. In all the compounds, a σ-pathway is operating: the less electronegative the atoms of the bridge are, the greater J. This is qualitatively reproduced by Huckel calculations (4).

An ab-initio calculation performed on a slightly modelized μ-oxalato compound $(Cu(NH_3)_2OH_2)_2C_2O_4$ allowed us to find a theoretical J value (-295 cm^{-1}) close to the experimental one (-385 cm^{-1}) (5) and to describe the various contributions to the singlet-triplet gap in terms of kinetic and potential exchange, following Anderson's model (6).

It is possible to give a unified picture of the interaction in these compounds and to use it to synthesize new complexes with expected magnetic properties.

1. Julve, M., M. Verdaguer, O. Kahn, A. Gleizes, and M. Philoche-Levisalles, *Inorg. Chem.*, *22*, 368-370, 1983, and submitted to *J. Am. Chem. Soc.*
2. Journaux, Y., M. Julve, M. Verdaguer, and O. Kahn, unpublished work.
3. Girerd, J.J., S. Jeannin, Y. Jeannin, and O. Kahn, *Inorg. Chem.*, *17*, 3034-3040, 1978.
4. Verdaguer, M., Thesis, Orsay, 1984.
5. Charlot, M.F., M. Verdaguer, Y. Journaux, P. De Loth, J.P. Daudey, submitted to *Inorg. Chem.*
6. Anderson, P.W., *Solid State Physics*, *14*, 99-211, 1963.

HETEROBINUCLEAR COMPOUNDS : OPTICAL, MAGNETIC AND MAGNETIC CIRCULAR DICHROISM STUDY OF $Cs_3CrRuCl_9$

Bernard Briat, Jean-Claude Canit, Jacques Darriet* and Marc Drillon*

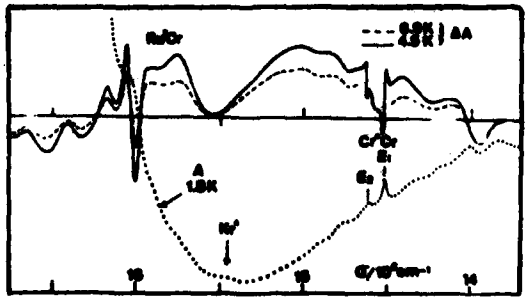
Laboratoire d'Optique Physique, ESPCI, 10, rue Vauquelin, 75231 Paris-Cedex 05 - France,

* Laboratoire de Chimie du Solide, Université de Bordeaux I, 351 Cours de la Libération, 33405 Talence - France, and :

* Sciences des Matériaux, ENSC, 1, rue Blaise Pascal, 67008 Strasbourg Cedex - France.

Clusters of transition metal ions serve as molecular models for checking physical concepts. Among those clusters, the confacial, bi-octahedral anions $M_2Cl_9^{3-}$ can be stabilized as isolated units of high symmetry (D_{3h}) with, e.g., Cs as the countercation and M = Cr, Ti, V. Single crystals of $Cs_3M_2Cl_9$ can easily be grown for spectroscopic and magnetic measurements. Previous studies of our own include the chromium and titanium derivatives /1,2/.

We report here on a study of $Cs_3CrRuCl_9$ single crystals. Our problem was to demonstrate whether they contain both Cr-Cr, Cr-Ru and Ru-Ru pairs or whether one has chains of alternating ions Cr-Ru-Cr... MCD data show very clearly that the first statement does apply. The amount of Cr-Cr pairs can be monitored by the derivative-like $\mathcal{A}_0$ terms at E_1 and E_2, associated with the S=0 ground state. The rest of the spectrum shows $\mathcal{B}_0$ terms which are correlated with the presence of paramagnetic Cr-Ru pairs. This magnetism results from the antiferromagnetic coupling of S = 3/2 (Cr^{3+}) and S' = 1/2 (Ru^{3+}).



1. B. Briat, M.F. Russel, J.C. Rivoal, J.P. Chapelle and O. Kahn, Mol. Phys. 1977, 34, 1545.
2. B. Briat, O. Kahn, I. Morgenstern-Badarau and J.C. Rivoal, Inorg. Chem. 1981, 20, 4193.

STRUCTURE AND PROPERTIES OF THALLIUM(I) FORMATE SOLUTION

Hitoshi Ohtaki*, Kazuhiko Ozutsumi* and Asao Kusumegi**

*Department of Electronic Chemistry, Tokyo Institute of Technology at Nagatsuta, Nagatsuta-cho, Midori-ku, Yokohama, 227 JAPAN
**Institute for High Energy Physics, Ōho-cho, Tsukuba-gun, Ibaragi Prefecture, 305 JAPAN

Some thallium(I) carboxylates are extremely soluble in water, and the solutions can be used as heavy liquids for gravity concentration of minerals. Since the solutions have also very large absorptivities for high energy particles, they may be used as absorbers of radiation beams. In the present work we studies the structure and some physicochemical properties of thallium(I) formate solutions.

The structure of an aqueous solution of thallium(I) formate of 10.77 mol dm^{-3} (density; 3.189 g cm^{-3}, Tl:H_2O mole ratio; 1:2.59), which is an almost saturated solution at room temperature, is determined by the X-ray diffraction method by using a θ-θ type diffractometer at 25 °C. From the analysis of the radial distribution curve and the structure factors of the solution, it was found that thallium(I) ions combined with formate ions to form the tetramer, $Tl_4(HCOO)_4$, in the solution. The structure of the tetramer is shown in Fig. 1. The interatomic distances within the complex thus determined are as follows: Tl_1-O_1: 2.79 Å, $Tl_1 \cdots C_1$: 3.33 Å, $Tl_1 \cdots O_8$: 3.50 Å, $Tl_1 \cdots Tl_2$: 3.92 Å, $Tl_1 \ldots Tl_3$: 4.34 Å, $Tl_1 \cdots O_3$: 4.31 Å, $Tl_1 \cdots O_7$: 4.34 Å, and $Tl_1 \cdots Tl_4$: 4.79 Å.

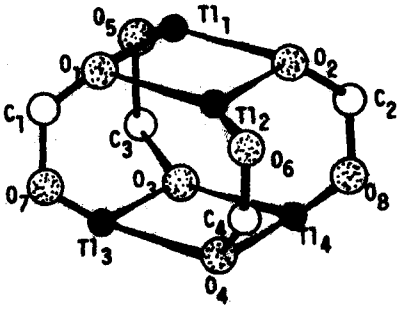


Fig. 1. The structure of $Tl_4(HCOO)_4$ complex in solution.

Densities, refractive indices, viscosities and conductivities of thallium(I) formate solutions of varying concentrations have been measured at 25 °C. The former three quantities monotonously increase with the concentration of thallium(I) formate, but the conductivity of the solution first increases and then decreases with the concentration. Therefore, the Walden product, $\Lambda \cdot \eta$ (Λ denotes the molar conductivity and η the viscosity) of the solution decreases with increasing concentration and then becomes a plateau in the range 6 - 12 mol dm^{-3} of thallium(I) formate solutions (Fig. 2).

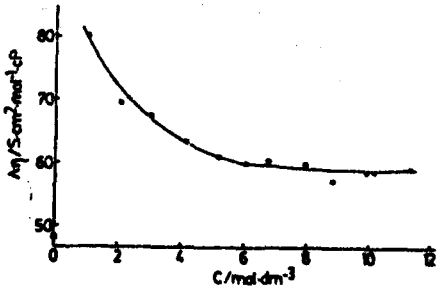


Fig. 2. Walden products of thallium(I) formate solutions at 25 °C.

POLARIZED X-RAY ABSORPTION EDGE SPECTROSCOPY

James E. Penner-Hahn, Britt Hedman, Teresa A. Smith, Edward I. Solomon and Keith O. Hodgson

Department of Chemistry, Stanford University, Stanford, CA, USA 94305

X-ray absorption spectroscopy has proven extremely useful in elucidating the metal ion coordination environment in metalloproteins. Much of this work has utilized extended X-ray absorption fine structure (EXAFS) spectroscopy. EXAFS, while extremely useful in determining the radial distribution of ligands around a metal, can provide only very limited information regarding the angular distribution of these ligands. X-ray absorption edge structure, in contrast, is reasonably sensitive to the geometrical arrangement of ligands around the absorbing (metal) atom.

Currently, the detailed relationship between molecular structure and X-ray absorption edge structure is poorly understood. The polarization dependance of the X-ray absorption edge of an oriented sample can be used to unambiguously determine the symmetry properties of the different edge transitions[1,2]. The determination of transition symmetries is important for testing different theories of edge structure. In addition, polarized X-ray absorption edge measurements frequently reveal directionally-specific structure which is not apparent in the absorption edge for the amorphous sample[3].

Recent polarized measurements of the X-ray absorption edge structure for a variety of transition metal complexes will be presented. The different theoretical predictions of X-ray absorption edge structure will be compared with the experimentally observed structure. In particular, the application of polarized X-ray absorption measurements to biological systems will be discussed.

1. J.E. Hahn and K.O. Hodgson, ACS Symposium Series, 1983, 211, 431-444.
2. J.E. Hahn, R.A. Scott, K.O. Hodgson, S. Doniach, S.R. Desjardins, and E.I. Solomon, Chem. Phys. Lett., 1982, 88, 595-598.
3. R.A. Scott, J.E. Hahn, S. Doniach, H.C. Freeman, and K.O. Hodgson, J. Amer. Chem. Soc., 1982, 104, 5364-5369.

ADVANCES IN THE STRUCTURAL COORDINATION CHEMISTRY BY LAXS TECHNIQUE
(LAXS : Large Angle X-ray Scattering)

Jean GALY, Alain MOSSET and Pierre LECANTE

Laboratoire de Chimie de Coordination CNRS,
205, route de Narbonne, 31400 TOULOUSE, France.

A new integrated system, based on X-ray scattering by molecular liquids, complexes in solution or amorphous compounds, has been designed and realized in our laboratory to investigate their structure ; it is named LASIP (Liquid and Amorphous Structure Investigation Package).

- The LAXS pattern produced by the sample is quickly recorded by a micro-computer controlled goniometer with position-sensitive detection installed on a classical X-ray source (2 kW generator).
- The interactive software of LASIP allows both experimental data processing and simulation from structural models. LASIP makes possible the experimental structural study in less than half-day and allows the searcher to test directly his hypotheses about the structure of his sample.
- Applications of the system will be presented, i.e. :
  . LAXS investigation of the local structure and correlation with the magnetic behaviour of the amorphous compounds of the family $MM'(EDTA)(H_2O)_4 . 2H_2O$ with MM' = Ni, Co, Mn, Cu ...
  . Structural investigation of the rubeanate complex $Ni_4(S_2C_2N_2)_5.(H_2O)_{0.25}$...

The latest investigations will also be presented.

EXAFS AND X-RAY DIFFRACTION OF AQUEOUS SILVER PERCHLORATE AND NITRATE SOLUTIONS

Toshio Yamaguchi

Department of Electronic Chemistry, Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama 227 Japan

During the past few decades, X-ray diffraction technique has been widely applied to structural investigations of electrolyte solutions. The information obtained by the X-ray diffraction technique is, however, the sum of all the atomic pair correlation functions in the solutions. Hence, it is sometimes difficult to separate the different components. A recently developed extended X-ray absorption fine structure (EXAFS) technique overcomes the above difficulty associated with X-ray diffraction analysis. It gives information on the short-range structure around an absorbing atom itself and not of the solvent structure. Comparative EXAFS and X-ray diffraction studies have proved to give a more accurate structure of electrolyte solutions.[1]

In the present study, we applied both EXAFS and X-ray diffraction methods to aqueous 3 M and 9 M silver perchlorate and nitrate solutions.[2,3] EXAFS spectra were measured at SSRL.

The analysis of EXAFS and X-ray diffraction data revealed the hydration structure of Ag(I) ions, in which about four oxygen atoms coordinated to the Ag(I) ion with an Ag-O distance of about 2.4 A. In the nitrate solutions, the anions are bound to Ag(I) as monodentate ligands. In the perchlorate solutions, ion-pairs are formed only in the very concentrated solution, when the number of water molecules is not sufficient to fill out the inner coordination sphere of the Ag(I) ion. The Fourier transform of the EXAFS data of the aqueous 9 M silver nitrate solution indicates the presence of Ag...Ag interactions at around 3.84 A.

Short-range structures in the aqueous solutions, in $AgNO_3$ melt and in crystals of $AgClO_4$ and $AgNO_3$ are compared and discussed.

Accuracies and limitations in application of both methods to solutions are also discussed.

1. T. Yamaguchi, O. Lindqvist, T. Claeson and J. B. Boyce, Chem. Phys. Letters, 1982, 91, 528.

2. T. Yamaguchi, O. Johansson, B. Holmberg, M. Maeda and H. Ohtaki, To appear in Acta Chem. Scand. Ser. A.

3. T. Yamaguchi, O. Lindqvist, J. B. Boyce and T. Claeson, To appear in Acta Chem. Scand. Ser. A.

STRUCTURAL STUDIES ON MANGANESE(II) ACETYLACETONE IN THE SOLID AND GAS PHASES

S. Shibata, S. Onuma and K. Iijima

Department of Chemistry, Shizuoka University
Oya, Shizuoka, Japan 422

We have been studying structures of metal complexes in the gas and solid phases by both electron and X-ray diffraction methods. In Budapest, the structures of metal β-diketonates in the gas phases were summarized and they were discussed in comparison with those in the solid phases. As the extensive research, we present here the structures of manganese(II) acetylacetone in the solid and gas phases. This compound is the remaining divalent iron-group metal complex that has not been determined until now.

Manganese(II) acetylacetonate has been prepared by sublimation. A three-dimensional analysis of the crystal structure yielded that the crystal belong to the triclinic, space group $P\bar{1}$, and the molecule is trimeric with two trigonal-prisms and one antiprism in which a manganese ion is surrounded by six oxygen atoms. The average distances of the non-bridged and bridged Mn-O are 2.10 and 2.20 Å respectively, and the Mn-Mn distance is 3.11 Å. The acetylacetone ligands are coplanar and the average OMnO angle is 90°. The trimeric form of manganese(II) acetylacetonate has been suggested by Graddon and Mockler[1] from molecular weight determination. It is very interesting to see the difference of the trimeric form between Mn(II) and Ni(II)[2] acetylacetonates.

On the other hand, a study by gas electron diffraction gave the results that the molecule is monomeric and four coordinated with a tetrahedral configuration in contrast with the polymeric form with the six coordinated ion in the solid phase. The least-squares analysis gave Mn-O = 2.06 Å and OMnO = 91°. The structures of manganese(II) acetylacetonate in the solid and gas phases will be discussed in connection with those of other complexes in this series.

1. D.P. Graddon and G.M.Mockler, Aust. J. Chem., 1964 17, 1119.
2. G.J. Sullen, M.Mason and P. Pauling, Inorg. Chem., 1965, 4, 456.

EXAFS STUDIES ON SOME MIXED AMINOACID CHELATES OF COPPER (II)

Alok Kumar and A.N. Vishnoi
Physics Department, Allahabad University, Allahabad

and

U.C. Srivastava
Chemistry Department, C.M.P. Degree College, Allahabad.

Extended X-ray (K) absorption fine structure (EXAFS) Spectra of copper in some chelates involving mixed amino acids (CuLL'vide Table) have, for the first time, been recorded photographically using 400 mm radius curved crystal spectrograph. The results are correlated with the spectra obtained for the parent single amino-acid chelates.

It is found that the measured energies of the principal absorption maxima (E_A) for the parent chelates add up and get subtracted in mixed chelates containing nta and leu respectively. Within the mixed chelates the E_A and edge-shift values exceed by 10-15 eV over the latter group. The edge structures conform to the stereochemistry. The results are explained in terms of m.o. theory[1].

The recent stern's graphical method[2,3] based on EXAFS energies (upto 150 eV) is used to estimate the radius of the coordination sphere. The results agree with X-ray diffraction data where available.

1. U.C. Srivastava and H.L. Nigam, Coord. Chem. Rev., 1973, 9, 275.
2. E.A. Stern, D.E. Sayers and F.W. Lytle, Phys. Rev., 1975, B11, 4825.
3. F.W. Lytle, D.E. Sayers and E.A. Stern, Phys. Rev., 1975, B11, 4836.

Table E_A energies and stern bond lengths of Cu-Chelates

Ligands	nta	gly	ala	val	leu	asp	nta gly	nta ala	nta val	leu gly	leu asp
E_A(eV)	8.8	13.7	13.9	15.6	20.2	15.3	20.8	25.1	25.8	9.9	8.2
(R-α) (Å)	1.42	1.57	1.63	1.64	1.46	-	1.43	1.63	1.73	1.64	1.43
R(Å)	1.85	2.00	2.06	2.07	1.89	-	1.86	2.06	2.16	2.07	1.86

AN EXAFS STUDY OF THE COBALT(II) AND IRON(III) COMPLEXES OF ETHYLENEDIAMINETETRAACETIC ACID AND ETHYLENEDIAMINETETRA (METHYLENEPHOSPHONIC) ACID

Eileen M. Wardell[†], Diana Cummins[*], John G. Chambers[*], C. David Garner[†] and Craig D. Adam[*]

† University of Manchester, Manchester, England
* Unilever Research Laboratory, Port Sunlight, Wirral, England

EXAFS is a structural technique which, although available for a long time, has only recently received wide application through the availability of Synchrotron Radiation Sources[1]. It is especially valuable for structural analysis of chemical or biological systems where conventional diffraction methods are not applicable. Biological systems have enjoyed the more intense study, to date. One reason for this has been that the sensitivity of the absorption technique has been insufficient to allow EXAFS detection for dilute solution samples. However, the recent commissioning of a fluorescence detection system at the Daresbury SRS has allowed an increase in sensitivity of some 500-fold. Solution spectra may now be obtained at concentrations as low as 100μ molar[2].

We have used the Daresbury SRS EXAFS facility to study the complexation of cobalt (II) and iron(III) by the multidentate ligands EDTA and EDTMP. Spectra have been recorded for crystalline samples using the conventional absorption detectors, and solution samples have been studied in the fluorescence detector mode.

The data and their computer analyses will be presented, and structures for the complexes proposed. The solid state structures will be compared to those obtained from X-Ray diffraction analysis whilst the solution structures will be compared with those obtained from electronic absorption spectroscopy and other spectroscopic techniques.

1. B-K Teo, Acc. Chem. Res., 13, 412, 1980.

2. S.S. Hasnain, P.D. Quinn, G.P. Diakun, E.M. Wardell and C.D. Garner, submitted for publication.

E.X.A.F.S. AND RAMAN STUDIES OF A NEW CLASS OF LAYER-TYPE IONIC CONDUCTORS $M^{I}_{2-x}M^{II}PS_3$ – (M^{I}=Cu,Ag),(M^{II}=Mn,Cd).

Y. Mathey[a], R. Clement[a], A Michalowicz[b], O. Poizat[c] and C. Sourisseau[d]

a) Laboratoire de physicochimie minerale et E.R.A. 672, Universite de Paris-Sud, 91405 Orsay; b) Laboratoire de physicochimie structurale, Universite de Paris-Val-de-Marne, 94000 Creteil, and Lure, Universite de Paris-Sud, 91405 Orsay; c) Laboratoire de spectrochimie infrarouge et Raman, C.N.R.S., 94320 Thiais; d) Laboratoire de spectrochimie infrarouge, Universite de Bordeaux I, 33405 Talence, France.

Layered metal phosphorus trichalcogenides MPS_3 (where M is a transition metal) constitute an interesting series of systems able to intercalate a large variety of guest species. Investigations carried out in our groups during the last four years have shown that the most unexpected feature of these compounds is probably their aptitude (at least with M=V, Mn, Fe, Zn, Cd) to lead to intralamellar metallic vacancies (up to 50%) through the uptake of cationic species including coordination complexes (1).

Recent synthetic work led us to study the new systems $M^{I}_{2-x}M^{II}PS_3$ derived from the parent compounds through the replacement of one M^{II} by two M^{I}. E.x.a.f.s. proved to be an invaluable technique in solving the problem of structural disorder encountered in these new two-dimensional host lattices (2). Simultaneously Raman scattering spectroscopy gave clear-cut evidence for the existence of low-frequency, temperature-dependent translational modes $T_u(M^{I})$. The relationship between these Raman data and the onset of a weak ionic conductivity is well established in the particular case of the $Mn_{0.80}Cu_{0.40}PS_3$ compound (3). Further studies on several analogs with M^{II}=Cd, M^{I}=Cu or Ag and x=0.5 will be presented.

1. Clement, R., *J. Chem. Soc. Chem. Commun.*, 647, 1980, and *J. Amer. Chem. Soc.*, *103*, 6666, 1981.
2. Mathey, Y., A. Michalowicz, F. Toffoli, and G. Vlaic, to be published in *Inorganic Chemistry*.
3. Mathey, Y., R. Clement, J.P. Audiere, D. Poizat, and C. Sourisseau, to be published in *Solid State Ionics*.

DETERMINATION OF THE CHARGE STATE AND THE METAL-LIGAND BOND STRENGTH OF TRANSITION METAL COMPLEXES FROM $L\beta_2$ X-RAY SPECTRA

A.A. Voityuk and E.A. Kravtsova

Institute of Inorganic Chemistry, Siberian Branch of the USSR Academy of Sciences, Novosibirsk, USSR

X-ray $L\beta_2$ emission spectra were obtained for a series of Ru, Rh and Pd complexes with a coordination number of 6. The electronic structure of the complexes was calculated by semiempirical INDO method. The dependence of the profile of the X-ray spectra on the extent of the metal-ligand interaction and the relative positions of the 4d levels of the metal was studied. It is shown that the increase in the positive charge on the central atom with increasing formal oxidation number or due to the d-density transfer from the metal to a π-acceptor ligand leads to an appreciable increase of the relative intensity in the long wave region of the spectrum. The established relationship between the form of the spectra and the charge state on the metal makes it possible to use the experimental $L\beta_2$ spectra for determination of the charge state in analogeous compounds.

By comparing the spectra of $K_2Ru(NO)Cl_5$ and hexacomplexes of Ru(III) and Ru(IV) it was found that the charge state on the metal in the $Ru\text{-}NO^{3+}$ fragment corresponds to the oxidation state of 4.

The calculated and experimental results show that the increase in the long wave relative intensity must be accompanied by a strengthening of the metal-ligand σ-bond. Introduction of a π-acceptor substituent CO or NO into the octahedral complex $[RuL_6]$ with L = NH_3, CN^-, Cl^- increases the long wave maximum intensity which suggests a stronger Ru-L bond in the substituted compound in agreement with the theoretical results.

The studies of mono-, bi- and polynuclear chlorocomplexes of Rh(III) showed that the charge on the metal and the Rh-Cl bond strength in polynuclear compounds are smaller than in the mononuclear complex.

Ma7-10

THE MECHANISM OF MUTUAL INFLUENCE OF LIGANDS IN RUTHENIUM COMPLEXES WITH π-ACCEPTOR LIGANDS

L.N. Mazalov, A.A. Voitenk, E.A. Kravtsova

Institute of Inorganic Chemistry, Siberian Branch of the USSR Academy of Sciences, Novosibirsk, USSR

Transition metal complexes with π-acceptor ligands are widely used as homogeneous catalysts and also represent important materials for the studies of photochemical conversions. In this connection, it would be desirable to have a detailed knowledge of the electronic density redistribution upon introduction of π-acceptor ligands. The present work deals with the results of a quantum-chemical and X-ray spectral study of t the electronic mechanism of action of π-acceptor ligands in ruthenium complexes.

1. Analysis of the X-ray $K\alpha_{1,2}$ and $K\beta_{1,3}$ spectra of nitrosyl and carbonyl complexes showed that the transfer of the d_π-density from the metal to a π-acceptor ligand leads to an increase in the σ-accepting ability of the ligand.

2. The possibility of a qualitative determination of the metal-π-acceptor bond strength from the $K\beta_{1,3}$ spectra of the complexes is demonstrated.

3. The introduction of a π-accepting substituent X into complexes ML_6 was found to strengthen the σ-bonding between the metal and cis- and trans-ligands. The directivity of the influence is thus pronounced. The change in the π-bonding depends on the properties of ligand L; for π-bond is stronger, thereof when L is a π-donor and weaker when L is a π-acceptor.

Ma7-11

X-RAY SPECTROSCOPIC STUDY OF THE ELECTRONIC STRUCTURE OF VANADIUM CATALYSTS FOR THE OXIDATION OF SO_2 to SO_3 AND A NUMBER OF MODEL SYSTEMS

L.N. Mazalov, S.B. Erenburg, D.I. Kochubey, V.A. Chernov, K.I. Zamarayev

Institute of Inorganic Chemistry of the Siberian Branch of the USSR Academy of Sciences, Novosibirsk, USSR

Institute of Catalysis of the Siberian Branch of the USSR Academy of Sciences, Novosibirsk, USSR

X-ray spectroscopic technique was employed to study the electronic structure of vanadium catalysts for production of H_2SO_4. VL_4 , OK_1 , SK_α and SK_β spectra were obtained for a number of model systems : V_2O_5, metavanadates, oxide vanadium bronzes, alloys of V_2O_5 with potassium sulfates as well as for catalysts before and after their treatment by reaction medium.

It was found that most of the alkali metal vanadates do not differ significantly in O2p-electron density distribution, whereas for oxosulfovanadates these differences are more pronounced. It was suggested that for the samples prepared by alloying V_2O_5 with$KHSO_4$, $K_2S_2O_7$ and K_2SO_4 oxide groups (of the type SO_3-O-O-V) are formed independently of the initial sulfates whose structure is similar to that of the $S_2O_8^{2-}$ anion. It was found that although the general character of the 3d-electron density distribution is not changed in going from vanadium bronzes to alloyed model compounds, there is some increase in the 3d-density in the upper part of the valence band and the deeper part of the valence band shows splitting. The form of the SK_β -line for the catalyst samples studied corresponds to a slightly distorted tetrahedral oxygen environment of the sulfur.

MONDAY AFTERNOON

INTERMOLECULAR PHOTOREDOX REACTIONS OF COORDINATION COMPOUNDS

A. Vogler
Universität Regensburg, Institut für Anorganische Chemie
D-8400 Regensburg, Federal Republic of Germany

Intermolecular photoredox reactions can occur by different mechanisms. A resonance transfer takes place if both redox partners are in contact, exhibiting an intermolecular charge transfer absorption band. Metal-to-metal and metal-to-solvent charge transfer transitions are examples of this resonance transfer mechanism. Light-induced electron transfer can also occur via internal excited states of one of the redox partners. This may involve intermediate formation of charge transfer exciplexes. Higher energy excited states of complexes can participate in intermolecular electron transfer when the electron acceptor is solvent.

Mp8-02

APPLICATIONS OF METAL TO LIGAND CHARGE TRANSFER EXCITED STATES

Thomas J. Meyer

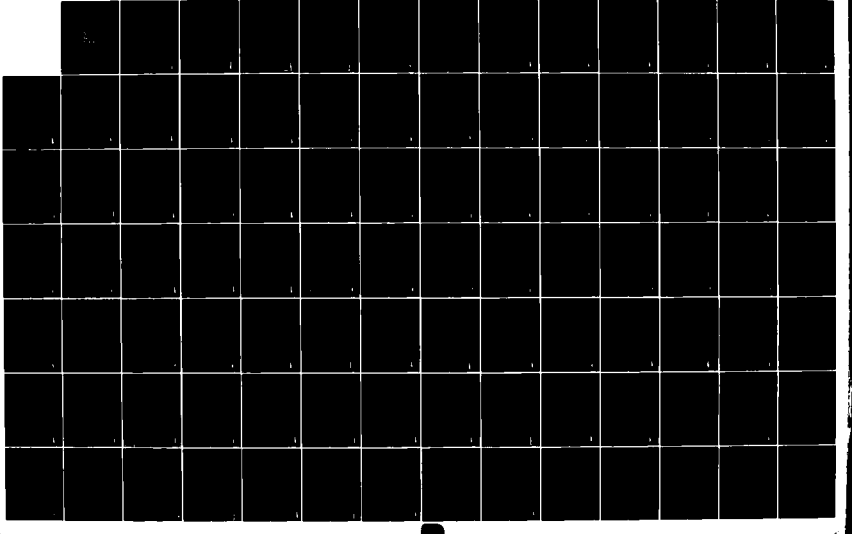
Department of Chemistry, Unviersity of North Carolina, Chapel Hill NC 27514

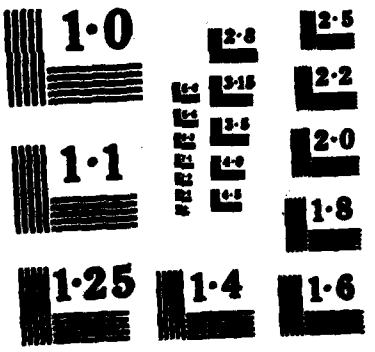
The photochemical and photophysical properties of a series of polypyridyl-based MLCT excited states have been studied in detail. The properties of these states can be understood based on available information concerning excited state structure and dynamics. More recently, this class of excited states has found application in a number of areas including: 1) Charge transfer splitting in chromophore-quencher complexes and metal-metal dimers; 2) Photoelectrochemical current responses in polymeric films containing both chromophores and quenchers; 3) Photochemical reactions based on organometallic chromophores including the reduction of CO_2 to CO.

AD-A146 190 INTERNATIONAL CONFERENCE ON COORDINATION CHEMISTRY (23RD) HELD AT BOULDER..(U) COLORADO UNIV AT BOULDER E L KING ET AL. 03 AUG 84 ARO-21423.1-CH-CF

UNCLASSIFIED DAAG29-84-G-0199 F/G 7/4 NL

2/8




1·0
1·1
1·25
1·4
1·6
2·0
2·2
2·5

PHOTOCATALYTIC SPLITTING OF WATER USING TWO PHOTOSENSITIZERS CADMIUM(II)TETRA-N-METHYL-PYRIDINO PORPHYRAZINE AND CADMIUM(II)(TRIMETHYL AMINO-PHENYL)PORPHYRIN

Ramaiah, S. Ramasamy and Laurence. K. Thompson

Department of Chemistry, Memorial University, St. Johns, Newfoundland, Canada, A1B 3X7.

Cd(II)-tetra-N-methyl-3,4-pyridino-porphyrazine, Cd(II)tmppa^{4+}, and Cd(II)(trimethylaminophenyl)porphyrin, Cd(II)TAPP^{4+}, were prepared and investigated for their properties as photocatalysts in the oxidation and reduction of water. The visible and luminescence spectra of both the compounds were very similar to the corresponding phthalocyanine and porphyrin respectively. The fluorescence of Cd(II)tmppa^{4+} occuring at 710nm was very efficiently quenched by TEOA, cysteine, EQ, EDTA and a wide range of Mn(II) complexes but not by methylviologen, MV^{2+}. The phosphorescence of Cd(II)TAPP^{4+} occuring at 680nm was quenched efficiently by MV^{2+} but not other donors. These results suggest that the Cd(II)tmppa^{4+}/Cd(II)tmppa^{4+*} couple has the potential to oxidise water whereas the Cd(II)TAPP^{3+}/Cd(II)TAPP^{4+*} couple has the potential to reduce water. The photocatalytic splitting of water with a two sensitiser system was therefore investigated. Photolysis of a solution containing Cd(II)tmppa^{4+}, a donor like TEOA or a Mn(II) complex and visible light in the 500-700nm range did lead to the oxidation of the Mn(II) complex. However the initial reaction was fast but further photolysis leads to bleaching. The sequence of reactions may be written as

$$Cd(II)tmppa^{4+} + h\nu \longrightarrow Cd(II)tmppa^{4+*}$$
$$Cd(II)tmppa^{4+*} + Mn(II) \longrightarrow Cd(II)tmppa^{3+} + Mn(III)$$
$$2\ Cd(II)tmppa^{3+} \longrightarrow Cd(II)tmppa^{4+} + Cd(II)tmppa$$

The Cd(II)tmppa^{3+} is the reduced dianion and causes the bleaching effect. Simple acceptors as scavengers were not able to overcome bleaching. This is the first instance of a photooxidation reaction with a porphyrazine complex.

Cd(II)TAPP^{4+} photoreduces methylviologen catalytically at pH 7 in the presence of TEOA very efficiently. Use of Cd(II)tmppa^{4+}, Cd(II)TAPP^{4+}, MV^{2+} and Mn(II) at pH 6.5 did suggest that both a photooxidation and photoreduction reaction were going on simultaneously followed by the inefficient combination of Cd(II)tmppa^{3+} and Cd(II)TAPP^{3+} to give the initial photosensitisers. However there was also some bleaching observed. Further investigations are in progress to verify the reactions occuring and to establish that two different photosensitisers can be efficiently used to mimic photosynthesis.

1. A. B. P. Lever, S. Licoccia, P. C. Minor, K. Magnall and B. S. Ramaswamy, Adv. Chem. Ser., 1982, 201,237.

MIXED LIGAND COMPLEXES OF RUTHENIUM(II), CONTAINING 2,2'-BIPYRIDINE AND CYCLOMETALLATING LIGANDS.

J. Selbin, F. Reveco, J. H. Medley and N. S. Bhacca

Louisiana State University, Baton Rouge, LA 70803, USA and University of South Carolina, Columbia, S.C. 29208, USA (JHM)

Recently a large number of complexes of the type $[Ru(bpy)_{3-x}L_x]^{n+}$, where x is 1,2 or 3 and L is either a substituted bipyridine or bipyridine-like molecule or a non-bipyridine-like but bidentate unsaturated nitrogen donor ligand, have been synthesized and generally subjected to spectroscopic and electrochemical studies. The impetus, as is the case in our work, is usually to try to understand better why $[Ru(bpy)_3]^{2+}$ is a solar energy conversion catalyst (sensitizer) and to find related species which might improve on such catalytic behavior.

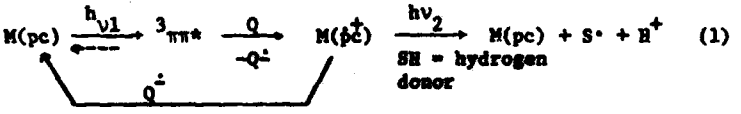
We are preparing new types of ruthenium(II) complexes in which the ligand L is a cyclometallating ligand, such as 2-phenylpyridine. Here, for example, we shall describe the preparation and the detailed two-dimensional Fourier transform proton NMR (which allows the unambiguous assignment of 23 distinguishable protons), and the (300° and 77°K) visible-ultraviolet absorption, excitation and emission spectra of $[Ru(bpy)_2L]PF_6$, where L is 2-(4'-nitrophenylpyridine). The presence of the carbon-ruthenium normal covalent bond has altered the spectral properties in both expected and unexpected ways from the tris-bipyridine complex and these will be detailed in the paper.

SEQUENTIAL BIPHOTONIC PHOTOCHEMISTRY OF TRANSITION METAL PHTHALOCYANINES

G. Ferraudi

Radiation Laboratory, University of Notre Dame, Notre Dame, Indiana USA 46556

Long lived intermediates in photochemical reactions, namely excited states or radicals, can be made to absorb enough light in order to produce their photochemical conversion into new species. These sequential biphotonic processes have been induced by using the lowest lying $^3\pi\pi^*$ state of transition metal phthalocyanines as the recipient of the second photon in irradiations with high intensity monochromatic light. Also phthalocyanine radicals, generated by electron transfer quenching of the $^3\pi\pi^*$, have been used as receptors of the second photon in experiments where the photolyte was irradiated at two different wavelengths with pulses of monochromatic light and frequencies ν_1 and ν_2.



Since the photochemical reactions of the phthalocyanine radical, namely those shown in eq.1, are different from their thermal reactions, the sequential biphotonic excitation can be used for modifying the overall photoreactivity of these systems. Mechanisms for the sequential biphotonic processes, with excited states and radicals as in intermediates, will be presented.

PHOTOCHEMISTRY OF POLYMETALLIC, MIXED-METAL COMPLEXES

John D. Petersen, Ronald R. Ruminski, Eva C. Eberle, Herbert W. Behlow, Jr., and Karen J. Brewer

Clemson University, Department of Chemistry, Clemson, South Carolina, USA 29631

In 1979[1], our group reported the first example of intramolecular energy transfer in a mixed-metal bimetallic complex. These bimetallic species utilize one metal center as a photon absorbing (antenna) fragment and the second metal center as a reactive fragment. Our initial studies[1,2] involved model systems where the antenna fragment was $Fe^{II}(CN)_5L$, $Ru^{II}(NH_3)_5L$ or $Ru(bpy)_2XL$ (L=pyrazine, 4-cyanopyridine or 4,4'-bipyridine) and the reactive fragment was $L\,Rh^{III}(NH_3)_5$ or $L\,Co^{III}(CN)_5$. These studies suggested modifications of the absorbing fragment to minimize photochemical reactivity of that metal center and modifications of the bridging ligand to enhance communication between the metal centers and resiliency between the two fragments.

Recently, we have prepared a series of bimetallic complexes using 2,2'-bipyrimidine (bpym) as the bridging ligand[3]. This ligand, when used to prepare $Ru(NH_3)_4(bpym)^{2+}$, $Fe(bpym)_3^{2+}$, $Fe(CN)_4(bpym)^{2-}$, $Fe(CN)_2(bpym)_2$, $W(CO)_4(bpym)$, $Cr(CO)_4(bpym)$, $V(CO)_4(bpym)^+$ and $Ru(bpy)(bpym)Cl_2$ and combined with a second metal center display intense metal-to-ligand charge transfer (MLCT) transitions in the visible region of the spectrum. The reactive metal centers currently under study are metal dihydride systems which potentially undergo photoelimination of H_2. However, these systems by themselves usually require UV photons to drive these reactions. The covalent coupling of visibly absorbing metal fragments to these metal hydrides could potentially drive the photochemical production of H_2 with visible light.

The monometallic photochemistry of such complexes as $Co(bpym)(PR_3)_2H_2^+$ and Rh(III) analogs will be discussed in terms of their efficiency for H_2 production. The preparation, characterization, and photochemistry of the bimetallic complexes will be discussed in terms of the ability to drive these reactions with visible light. Some additional comments will be made regarding the integration of the H_2 producing reaction into a water splitting scheme.

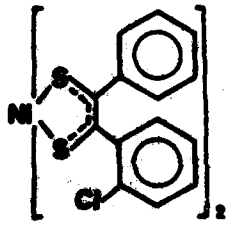
1. J. A. Gelroth, J. E. Figard, and J. D. Petersen, J. Am. Chem. Soc. 1979, 101, 3649.
2. K. J. Moore, L. Lee, J. E. Figard, J. A. Gelroth, A. J. Stinson, H. D. Wohlers, and J. D. Petersen, J. Am. Chem. Soc. 1983, 105, 2274.

PHOTOCHEMICAL HYDROGEN PRODUCTION FROM WATER INDUCED BY A NICKEL DITHIOLENE COMPLEX, ACTING BOTH AS A PHOTOSYNTHESIZER AND AS A CATALYST

E. Vrachnou-Astra, E. Heatzopoulos, J. Konstantatos, and D. Katakis

Chemistry Department, Nuclear Research Center "Democritos", Aguia Paraskevi Attikis, Athens, and Inorganic Chemistry Laboratory, Athens University, Navarinous 13A, Athens, Greece.

2-Chloro-bisdithiobenzil nickel(II), 1 (Figure) was synthesized for the first time in our laboratory and was tested as a potential photosensitizer for the photochemical cleavage of water. It absorbs strongly in the UV, VIS, and NIR regions and in the absence of electron donors or acceptors it is stable under illumination, even with UV light, in various solvents.



1

The photochemical experiments were performed in acetone-water solutions (70:30); in pure water the complex is insoluble. In the presence of a reversible electron acceptor (dimethyiviologen, MV^{2+}) and of a sacrificial electron donor (amine), illumination with visible light leads to dihydrogen evolution, while 1 is transformed into its monoion, 1^-. The monoion is stable under illumination for a long time. At later stages the blue free radical $MV^{\cdot+}$ starts accumulating. Hydrogen evolution gradually slows down. The turnover number for H_2 is ~100, depending upon the relative concentrations of 1, $MV^{\cdot+}$, and the amine, the nature of the amine and finally the wavelength of the incident light.

No catalyst is needed for the formation of hydrogen. This shows that 1 acts also as a catalyst for the electron transfer reaction from $MV^{\cdot+}$ to H^+. A study of the thermal reaction of 1 with $MV^{\cdot+}$ that was prepared by reduction of MV^{+} with zinc, showed that 1 is first quickly transformed into its monoanion, 1^-, which in turn acts as a catalyst on the excess of $MV^{\cdot+}$ to give dihydrogen equivalent to the excess of $MV^{\cdot+}$.

In the photochemical studies both 1 and 1^- act as photosensitizers but they are unique for their catalytic action.

PHOTOELECTROCHEMISTRY BASED ON POLYMER FILMS

Stephen J. Parus, Joseph P. Otruba, Thomas J. Meyer

Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27514

Polymeric films containing M(II-polypyridyl complexes (M=Os,-Ru) have been prepared on electrode surfaces by electropolymerization or chemical binding. In the polymeric films the photophysical properties of the chromophores are modified compared to model monomeric compounds in solution. The most striking feature is the appearance of non-exponential decays. The chromophoric sites in the films have reactivity properties similar to those of related chromophores in solution including oxidative and reductive quenching and energy transfer to lower-lying acceptores. Photolysis of the films in the presence of irreversible quenchers such as complexes of Co(III) lead to the build up of the expected redox product in the film and the appearance of photocurrents. However, most interesting is the appearance of the sustained photocurrents in the presence of reversible redox quenchers. In particular attachment of metal chromophores to thin films of chlorosulphonated polystyrene leads to films in which a concentration gradient of chromophore exists from the outside of the film to the electrode surface. In the presence of oxidative or reductive quenchers photolysis leads to sustained reductive or oxidative photocurrents, respectively. The origin of the photocurrents will be discussed as will the possible application of such devices in photochemical energy conversion schemes.

PHOTOREACTIONS OF RUTHENIUM COMPLEXES

Ronald A. Krause and Kirsten Krause

Department of Chemistry, University of Connecticut, Storrs, CT, USA, 06268

We have found the well known complex $[Ru(DMSO)_4Cl_2]$ (1) (DMSO=dimethylsulfoxide) to be photolabile. This was anticipated since the lowest energy band in this complex appears to be predominantly of ligand field origin (ε=90). Photosubstitution reactions of 1 promise a new route to a variety of complexes.

Photolysis of 1 is both wavelength and solvent dependent. In dichloromethane visible photolysis (pyrex filters) produces a green complex, formulated as $[Ru(DMSO)_3Cl_2]_2$(2), the O-bonded DMSO being last. UV photolysis leads to different products.

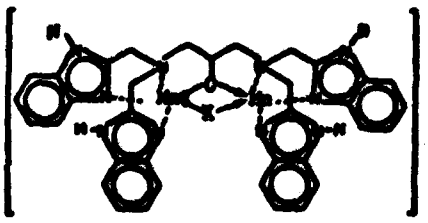
Photolyzing a dichloromethane solution of 1 in the presence of 2-(phenylazo) pyridine at room temperature leads to the known isomers of $[Ru\ L_2\ Cl_2]$ at a rate much faster than the dark reaction. At-60°C photolysis yields only 2 and a new, rose colored complex, presumably $[Ru\ L\ (DMSO)_2\ Cl_2]$. At 0°C all components are detected.

The thermal reaction of 1 with 2,2'-bithiazole (3) yields a new orange complex, $[Ru(3)\ (DMSO)_2Cl_2]$ as anticipated. Visible photolysis of 1 and 3 in dichloromethane rapidly produces this compound followed by a second reaction (not observed thermally) to produce a new, blue complex. This compound contains DMSO and 3, and may be oligomeric.

BINUCLEAR MANGANESE COMPLEXES AS MODELS FOR THE CATALYTIC SITE FOR WATER OXIDATION IN THE PHOTOSYNTHETIC O_2 EVOLVING ENZYME

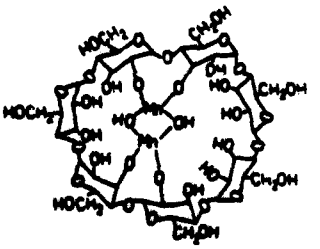
Balachandran Vani Nair and G. Charles Dismukes, Frick Chemical Laboratory, Princeton University, Princeton, N.J. USA 08544

Synthetic manganese dimers are essential for a clear interpretation of the complex spectroscopic and biochemical properties of the catalytic site for photosynthetic water oxidation. This process involves four intermediate oxidation states. One of the sites includes a cluster of two, or possibly four, interacting Mn ions that exhibit a characteristic multiline EPR signal identified with a mixed valence oxidation state of the Mn. Although a complete functioning enzyme has never been isolated, a subunit which binds two Mn ions in a binuclear site has been characterized (G. C. Dismukes, et al. 1983, in "The Oxygen Evolving System of Green Plant Photosynthesis", Y. Inoue, editor, Academic Press, Tokyo, 145-159.). EPR of the Mn site shows superhyperfine coupling to magnetic ligands which is altered upon substitution of F^- for Cl^- in the intact membrane complex. A site for Cl^- binding on the enzyme is thus indicated and probably accounts for the reversible loss of oxygen evolution upon removing Cl^-. Several polydentate ligand systems which bind 2 Mn atoms have been studied, two of which are shown below. The benzimidazole complex (A) has been prepared starting with Mn^{2+} and having Cl^- or CH_3COO^- as bridging ligands. These are ferromagnetic dimers in the Mn_2(II,II) oxidation state, according to magnetic susceptibility and EPR analysis. A mixed valence, antiferromagnetic, CH_3COO^- bridged dimer is formed when Mn^{3+} is the starting material. These oxidation states exhibit EPR features which correlate with those observed in two states of the OEC. β-cyclodextrin forms isolable, binuclear Mn_2(II,II) and Mn_2(III,III) complexes (B) which are antiferromagnetic and EPR silent in solution. When Mn_2(II,II) reacts with 1 equivalent or less of O_2 it exhibits intense EPR characteristic for an even-spin, ferromagnetic dimer containing equivalent Mn ions. This is presumed to occur via formation of a peromo or superomo bridge between the two Mn ions. Reaction with excess O_2 yields the Mn_2(III,III) complex, irreversibly. This work is supported by the National Science Foundation, grant number CHE82-27920.



$X = CH_3COO^-$, Cl^-

A



B

KINETICS AND MECHANISMS OF INVERSION AT ASSYMMETRIC NITROGEN CENTERS IN TETRAAMINE MACROCYCLIC LIGAND COMPLEXES OF COPPER(II)

Bih-Fong Liang, Chung-Shin Lee and Chung-Sun Chung
National Tsing Hua University, Hsinchu, Taiwan 300, Republic of China

The extreme kinetic inertness and very high thermodynamic stability of tetraamine macrocyclic ligand complexes are significant for inorganic stereochemistry, since they greatly enhance the number of potentially isolable isomers. In aqeuous solution, meso-5,5,7,12, 12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (tet a) or rac-5, 5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (tet b) reacts with copper(II) to form initially a blue complex which is readily converted into the more stable red isomer.[1] The crystal structure determinations of the complexes indicate inversions at asymmetric nitrogen centres are required for the blue-to-red interconversion.[1,2] Two pathways of this interconversion, protonation pathway and coordinated base pathway, have been proposed in our previous papers.[3,4] In strongly acidic media, this reaction is acid catalyzed due to the required cleavage of the copper-nitrogen bond. In neutral or slightly basic media, the main reaction pathway is via a hydroxide ion which is coordinated to the copper. In the current investigation, we have extended our study of these blue-to-red reactions to the highly basic region. Under these conditions, both coordinated base-catalyzed pathway and free base-catalyzed pathway contribute to the observed rate.[5] The detailed mechanisms for these pathways are proposed and discussed. The important factors affecting the reactivity of these reactions are considered.

References

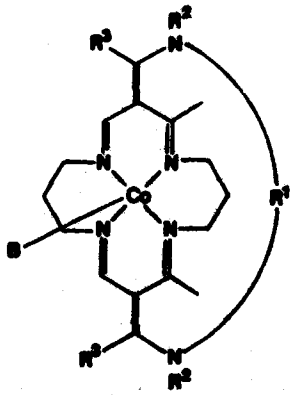
1. B. F. Liang, D. W. Margerum, and C. S. Chung, Inorg. Chem., 1979, 18, 2001.
2. R. M. Clay, P. Murray-Rust, and J. Murray-Rust, J. Chem. Soc., Dalton Trans., 1979, 1135.
3. B. F. Liang and C. S. Chung, Inorg. Chem., 1980, 19, 1867.
4. B. F. Liang and C. S. Chung, Inorg. Chem., 1981, 20, 2152.
5. C. S. Lee and C. S. Chung, Inorg. Chem., in press.

STUDY OF THE AUTOXIDATION REACTIONS OF COBALT(II) LACUNAR COMPLEXES

Dennis L. Nosco, Wayne E. Evans, and Daryle H. Busch

Department of Chemistry, The Ohio State University, 140 West 18th Avenue, Columbus, Ohio, USA, 43210

The rates of autoxidation of cobalt(II)-lacunar complexes (structure I) have been examined as a function of substitution at the R^1, R^2, and R^3 positions and as a function of solvent. For example, when $R^2 = R^3 = CH_3$ and $R^1 = (CH_2)_5$ the observed rate constant is 1.8×10^{-4} s^{-1} (30.0°C, P_{O_2} = 650 torr, 2.0 M 1-methyl imidazole in acetonitrile). The reaction exhibits a complicated dependence on the concentration of external axial base and on the partial pressure of dioxygen. The dependence of the rate on the type of base present and the nature of the autoxidation product will also be discussed. Candidate mechanisms are to be compared with the results of earlier studies on the autoxidation of cobalt(II) complexes.



REACTIONS OF COBALT(II) COMPLEXES CONTAINING 8-QUINOLINOLATE ION OR ITS DERIVATIVES WITH NITROGEN MONOXIDE

Eiichi Miki, Kazuomi Ishimaru, Katsunori Saito, Toshiaki Maejima, Kunihiko Mizumachi, Tatsujiro Ishimori, and Mikio Tanaka*
Department of Chemistry, College of Science, Rikkyo(St. Paul's) University, Nishi-Ikebukuro, Toshima-ku, Tokyo 171, JAPAN
* Laboratory of Chemistry, Nippon Medical School, Kosugi, Nakahara-ku, Kawasaki 211, JAPAN

Transition-metal complexes react with nitrogen monoxide, NO, causing the NO to disproportionate, or to give nitrosyls or hyponitrito-complexes. NO also reacts with transition-metal nitrosyls to bring about electrophilic attack by the NO on the coordinating NO or disproportionation of the NO, or to give the hyponitrito- or further nitrosylated complexes. These reactions proceed separately or simultaneously, as the case may be.[1)]

In the present work, using several organic media, we have examined the reactions with NO of cobalt(II) complexes containing 8-quinolinolate ion (qn) or its derivatives (2-methyl- (2mqn), 4-methyl- (4mqn), 5-chloro- (5cqn), or 5-nitro-8-quinolinolate ion (5nqn)), CoL_2, or their nitrosyls.

The stoichiometries of the reactions were determined by mass analysis of the gaseous product, N_2O, and the residual NO. ^{15}NO and the ^{15}N-nitrosyls were used for examining the reaction mechanisms. The solid products were characterized by NMR and IR (including ^{15}N-isotopic effects) spectrometries.

The main reactions were as follows:

(1) Nitrosylation followed by electrophilic attack of NO on the coordinating NO group, and by a new type of disproportionation of NO: $Co^{2+} + 9NO \longrightarrow Co^{3+} + NO^+ + NO_3^-(c) + NO_2^-(c) + 3N_2O$ ($Co^{2+} + {}^*NO \longrightarrow Co^{3+} + {}^*NO^-(c)$, ${}^*NO^-(c) + 2NO \longrightarrow {}^*NO_2^-(c) + N_2O$, $6NO \longrightarrow NO^+ + NO_3^-(c) + 2N_2O$) (L = qn; in CH_2Cl_2; *N, labelled nitrogen; c, coordinating). Also, $Co^{2+} + 5NO \longrightarrow Co^{3+} + NO_3^-(c) + 2N_2O$ ($Co^{2+} + {}^*NO \longrightarrow Co^{3+} + {}^*NO^-(c)$, ${}^*NO^-(c) + 2NO \longrightarrow NO_2^- + N{}^*NO$, $NO_2^- + 2NO \longrightarrow NO_3^-(c) + N_2O$) (L = qn, 5cqn, or 5nqn; in py or 10%(v) py-DMF).

(2) New type of disproportionation of NO, and nitrosylation: $Co^{2+} + 11NO \longrightarrow Co^+ + 3NO^+ + NO_3^-(c) + NO_2^-(c) + 3N_2O$, $Co^{2+} + 2NO \longrightarrow Co^0 + 2NO^+(c)$ (L = 2mqn; in CH_2Cl_2).

(3) Nitrosylation: $Co^{2+} + NO \longrightarrow Co^{3+} + NO^-(c)$ (L = 4mqn, 5cqn, or 5nqn; in CH_2Cl_2 or DMF).

Nitrogen monoxide disproportionated to give invariably N_2O and NO_3^-, sometimes together with nitrosyl cation, NO^+. The electrophilic attack was also observed.

The solid products obtained, the disproportionations of NO involved in the formation of NO_3^-, and the reaction mechanisms will be discussed.

1. J.A. McCleverty, Chem. Rev. 1979, 79, 53; K.K. Pandey, Coord. Chem. Rev. 1983, 51, 69.

KINETIC STUDY OF AXIAL LIGATION IN HEMIN BY THE STOPPED-FLOW METHOD

Hiroshi Tomiyasu and Hiroshi Fukutomi
Research Laboratory for Nuclear Reactors, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo, 152 Japan

Various ligand substitutions at the axial positions of protoporphyrin(IX) Fe(III) complex have been investigated by the stopped flow method. In the reaction between bis(pyridine)complex hemin$(py)_2$ and tert-butylamine (TBA), it was found that the rates are markedly dependent on free TBA concentrations and k_{obs} [1] can be given by $k_{obs} = k_1[TBA]$ in low TBA concentrations ($[TBA] < 0.12$ M) and $k_{obs} = k_2[TBA]^2$ in high TBA concentrations ($[TBA] > 0.2$ M[2]). The values of k_1 and k_2 are determined to be 0.095 $M^{-1}s^{-1}$ and 0.48 $M^{-2}s^{-1}$ at 20°C, respectively. We propose that the substitution proceeds from low-spin hemin$(py)_2$ to low-spin hemin$(TBA)_2$ through a low-spin intermediate hemin(py)(TBA) in high TBA concentrations, while the reaction undergoes a spin change through a pathway from hemin(py)(TBA) to high-spin hemin(TBA) in low TBA concentrations.

In the reaction between dimethyl sulfoxide (dmso) complex and cyanide ion,

$$\text{hemin(dmso)}^{+} + 2CN^{-} \longrightarrow \text{hemin}(CN)_2^{-} + \text{dmso} \quad [3]$$

we observed two distinct stopped-flow traces. The results suggest a consecutive mechanism passing through a high-spin monocyano intermediate, hemin(CN). However, under the condition of low CN^- concentrations such as $[CN^-]/[\text{hemin}] < 2$, an additional very slow reaction trace was observed. This corresponds to the breaking of Fe-CN^- bond in hemin(CN). Because of the thermodynamical unstability of hemin(CN) compared with low-spin hemin$(CN)_2^-$, hemin(CN) undergoes a ligand rearrangement resulting in the formation of hemin$(CN)_2$ and hemin(dmso).

1) $-d[\text{hemin}(py)_2]/dt = k_{obs}[\text{hemin}(py)_2]$
2) M = mol/dm^3
3) Charges of hemin are omitted except for this equation.

EXCHANGE AND DISSOCIATION KINETICS OF OXAAZA- AND OXATHIA-CRYPTATES

Mary Zoe Baker, Mary E. Springer and Richard W. Taylor

University of Oklahoma, Department of Chemistry, Norman, OK, USA 73019

The effects of donor atom substitution on the dissociation kinetics of the Tl^+, Pb^{2+} and Ca^{2+} complexes of cryptands $2_O2_O2_S$, $2_O2_S2_S$ and $2_O2_O2_{NH}$ have been studied using stopped-flow and conventional techniques. Cryptands 2.2.2 and $2_B.2_B.2$ have been included for purposes of comparison. When $HClO_4$ is employed as the scavenger species, a mechanism involving parallel acid-catalyzed (k_H) and uncatalyzed (k_d) pathways, consistent with the following rate law:

$$\text{rate} = (k_d + k_H[H^+])[\text{MCryp}],$$

is sufficient to describe the dissociation of most of the cryptates in water or 90:10 methanol-water mixtures. However, the $Tl(2.2.2)^+$ and $Pb(2_O2_S2_S)^{2+}$ cryptates exhibit saturation type behavior at high acid concentrations consistent with a shift in the rate determining step from proton attack to one involving a conformational change of the complex. The $Pb(2_O2_O2_{NH})^{2+}$ cryptate exhibits a mixed first- and second-order hydrogen ion dependence indicating proton attack on at least one of the bridge nitrogens.

Exchange reactions of some cryptates were studied using excess Na^+, Tl^+, 2.2.2 or EDTA as the scavenger species. In most cases the rate of exchange was independent of the concentration of the scavenger. However, the reaction of $Pb(2_O2_S2_S)^{2+}$ with 2.2.2 showed a nonlinear dependence on [2.2.2] at pH = 9.0 consistent with the rate law:

$$\text{rate} = \frac{k_d + k_L[2.2.2]}{1 + K_{MCL}[2.2.2]}\ [Pb(2_O2_S2_S)^{2+}$$

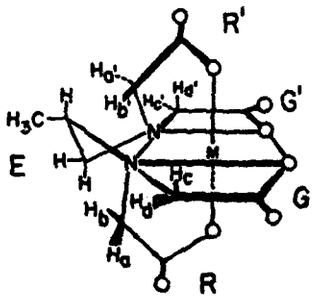
The reactions of $Pb(2.2.2)^{2+}$ and $Pb(2_B{\cdot}2_B{\cdot}2)^{2+}$ with EDTA in the pH range 8.7-10.5 exhibit a first order dependence on $[EDTA]_{TOT}$.

HYDROGEN-DEUTERIUM ISOTOPIC EXCHANGE KINETICS OF Δ-(+)$_{546}$-Cs[Co(R(-)PDTA)] AND Λ-(-)$_{546}$-Cs[Co(S(+)PDTA)]

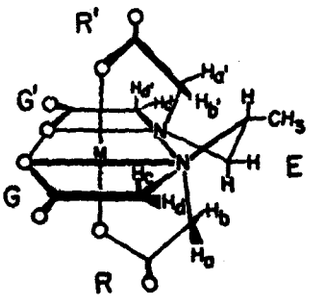
Lila H. O'Connor, Alfons J. Schermaier, and Karl H. Pearson

Department of Chemistry, Cleveland State University, Cleveland, OH 44115

Using a computerized Perkin-Elmer 241 polarimeter, the observed rotations of the base-catalyzed solution of Δ-(+)$_{546}$-Cs[Co(R(-)PDTA)] and Λ-(-)$_{546}$-Cs[Co(S(+)PDTA)] in deuterium oxide were monitored at 60 second intervals for seven days at a single wavelength (436 nm) using a Hg lamp. The sample temperature was controlled with a thermostatted cell holder; solution temperature in the quartz ORD cell was maintained at 20.0°C and monitored using a calibrated digital thermometer.



Δ-(+)$_{546}$-Cs[Co(R(-)PDTA)]



Λ-(-)$_{546}$-Cs[Co(S(+)PDTA)]

The observed rotation for the Δ-(+)$_{546}$-Cs[Co(R(-)PDTA)] complex increased and then decreased, which indicated that first one methylenic proton, H_a, and then a second methylenic proton, $H_{a'}$, were undergoing isotopic exchange. Opposite rotational changes but similar results were obtained for the Λ-(-)$_{546}$-Cs[Co(S(+)PDTA)] complex. The optical rotation data obtained indicated that initially the H_a site was mainly undergoing isotopic exchange and that after $\sim$ 1-4 h, depending on the pD value, this isotopic exchange was nearly complete and then the second proton, $H_{a'}$, was mainly undergoing hydrogen-deuterium exchange.

The values of the observed pD dependent pseudo-first order rate constants, $k_{1(obs)}$, in the pD range of 10.3 to 10.8 are $\sim 4.4 \times 10^{-4}$ sec^{-1} to 1.4×10^{-3} sec^{-1} with the corresponding specific rate constants, k_{D_a}, $\sim$ 25.0 M^{-1} sec^{-1} for the initial hydrogen-deuterium exchange. The value for the second specific rate constants, $k_{D_{a'}}$, is approximately 275 times slower than k_{D_a} and has a value of $\sim 9.0 \times 10^{-2}$ M^{-1} sec^{-1}. These results were supported by C^{13} NMR and CD measurements.

EXOTIC KINETIC PHENOMENA INVOLVING METAL COMPLEXES

M.T. Beck, Gy. Bazsa, Gy. Rabai and I. Fabian

Department of Chemistry, Kossuth Lajos University, Debrecen, 4010, HUNGARY

There is an increasing number of reactions in which the concentration of one or more components exhibit more than one extrema in time. Our investigations showed that in some of these exotic kinetics metal complexes are involved.

1. OLIGO-OSCILLATORY REACTION IN THE Mn(VII) - OXALIC ACID - MALONIC ACID SYSTEM. The absorbance of the reaction mixture exhibits three extrema in time at 260 nm. The two sub-systems exhibit one maximum only at 260 nm. The most likely explanation of the three extrema is that Mn(III) is a relatively stable intermediate of these reactions, and the three extrema in the absorbance vs time curves correspond to extrema in the Mn(III) concentration vs time curve. Similar kinetic behavior can be expected by the reduction of Cr(VI) with certain pairs of reducing agents.

2. SUCCESSIVE COMPLEX FORMATION AS MODEL OF THE OVERSHOOT-UNDERSHOOT. The A+B⇌C⇌D⇌ type reactions were analysed by Denbigh et al,[1] and they pointed out that at most n-2 extrema can be exhibited at the concentration vs time curves for any of the components, if n is the number of components. When the ligand is in high excess, the stepwise complex formation can be considered as such type of reaction. The study of the Cr^{3+} - SCN^- system revealed an overshoot with the complex $CrSCN^{2+}$, $Cr(SCN)_2^+$ and $Cr(SCN)_3$, but the calculations showed that - although there is a no monotonous change in the rate constants of formation and dissociation of stepwise complexes - no more than one extremum may appear in the concentration versus time curves at any arbitrary initial concentration conditions. It seems unlikely that any real system of this type shows more than one extremum.

3. DEGENERATION OF OSCILLATING REACTIONS. The number of the extrema in the concentration versus time curves be as high as several hundreds in a closed system in the bromate oxidation of malonic acid catalysed by ferroin or cerium(IV). The number of extrema decreases with increasing concentration of catalyst. With ferroin the oscillatory behavior disappears completely over a certain concentration of ferroin, however, even the extreme increase of the concentration of cerium(IV) leads to a limiting number of periods. The possible differences in the mechanisms of the effects of the two catalysts are analysed.

4. OLIGO-OSCILLATORY REACTIONS INVOLVING COORDINATED LIGANDS AS SUBSTRATES. It was discovered recently[2] that the oxidation of hydroxylamine with iodate or periodate is a genuine oligo-oscillatory reaction: there are at most three extrema in the iodide concentration versus time curves. Experiments are in progress on the halogenate oxidation of of different hydroxylamine - metal complexes.

1. K.G. Denbigh, M. Hicks and F.M. Page, Trans.Faraday Soc. 1949, 44, 479.

2. M.T. Beck and Gy. Rabai, J.Chem.Soc.Dalton Trans, 1982, 1678.

KINETIC AND EQUILIBRIUM STUDIES OF METALLOPORPHYRINS

K.R. Ashley

Chemistry Department, East Texas State University, Commerce, TX 75428.

The ligand substitution reactions of metalloporphyrins have been studied for the past ten years in this laboratory. The metals that have been used in these complexes have been cobalt, chromium, and rhodium. Various porphyrins have been used. In all of the complexes, the metals have been labilized to axial ligand substitution. This paper will summarize and compare the results of these studies. New kinetic and equilibrium data for the reactions of (*meso*-tetrakis(*p*-sulfonatophenyl)-porphyrinato)diaquochromate(III) with pyridine and imidazole and (hematoporphyrinato)-diaquocobaltate(III) with cyanide will be presented.

This research is supported by the Robert A. Welch Foundation, Houston, Texas.

Mp10-01

OXYGEN TRANSFER PROCESSES CATALYZED BY OXOMETAL SPECIES

Roger A. Sheldon and Jaroslaw M. Sobczak

Oce Andeno B.V., Postbox 81, 5900 AB Venlo, The Netherlands

The combination of cheap, readily available, single oxygen donors, such as hydrogen peroxide, alkyl hydroperoxides, amine oxides, hypochlorite, etc, with metal catalysts provides a range of selective oxidants with broad scope in organic synthesis. These reactions generally involve oxometal species as the active catalyst and, from a mechanistic viewpoint, can be divided into two types: (a) oxometal-oxygen donor complex as the active oxidant, and (b) oxometal complex as the active oxidant. In the latter example the single oxygen donor is said to act as a terminal oxidant.

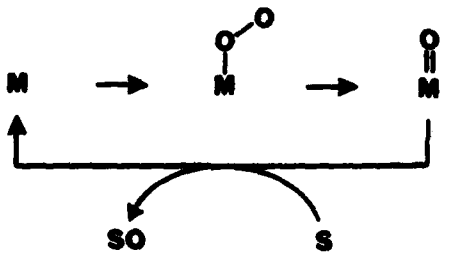
Mechanistic and synthetic aspects of these reactions will be reviewed and results will be presented from the study of a novel system.

METAL-OXO AND METAL-PEROXO INTERMEDIATES IN OXIDATIVE CATALYSIS

John T. Groves

The University of Michigan, Department of Chemistry, Ann Arbor, Michigan 48109

The reactivity of transition metal oxides toward hydrocarbons is now clearly established. Aliphatic hydroxylation has been shown to proceed *via* a hydrogen abstraction-radical recombination pathway. The mechanism of olefin epoxidation must also be stepwise, at least for oxo-manganese porphyrin complexes, since significant loss of stereochemistry accompanies epoxidation in this case. Recent results regarding the general catalytic scheme for oxygen activation and transfer outlined below will be presented. The data indicated that the O-O bond cleavage step and the oxygen transfer to substrate have the characteristics of electron transfer reactions. Related reactions for the activation and transfer of nitrogen will also be described.



1. J. T. Groves, T. E. Nemo, J. Am. Chem. Soc. 1983, 105, 5786, 6243.

2. J. T. Groves, T. Takahashi, J. Am. Chem. Soc. 1983, 105, 2073.

3. J. T. Groves, Y. Watanabe, T. McMurry, J. Am. Chem. Soc. 1983, 105, 4489

THE PROFOUND EFFECT OF GEOMETRY UPON REDOX PROPERTIES OF LOW-SPIN RUTHENIUM(II) COMPLEXES OF THE TYPE, DIHALORUTHENIUM(SULFOXIDE)$_n$-(THIOETHER)$_{4-n}$. IMPLICATIONS FOR MOLECULAR OXYGEN CATALYSIS.

Dennis P. Riley

The Procter & Gamble Company, Miami Valley Laboratories, P.O. Box 39175, Cincinnati, Ohio USA 45247

In recent studies we have reported that $RuX_2(DMSO)_4$ complexes act as sulfide oxidation catalysts using molecular oxygen to give sulfoxides in high yield with good selectivity. The actual catalyst is generated in situ in the presence of excess thioether in alcoholic solvents from the cis- or trans-$RuX_2(DMSO)_4$ complexes. From studies designed to aid in the determination of the structure of the catalytic species in these systems, we have synthesized and characterized a large number of new dihaloruthenium(II) complexes containing both sulfoxide and thioether ligands. The electrochemistry of these complexes have been investigated to determine the effect of structure and the degree of substitution on the redox chemistry.

We have observed under conditions simulating the catalytic situation that complexes of the type $RuX_2(DMSO)_{4-n}(SR_2)_n$ (where n = 1 to 4) readily form from $RuX_2(DMSO)_4$. The degree of substitution is dependent upon the steric bulk of the substrate; i.e., when SR_2 is small most of the ruthenium is present as $RuX_2(SR_2)_4$, but when SR_2 is very bulky as in $(t\text{-Bu})_2S$, then only one complex forms, $RuX_2(t\text{-Bu}_2S)(DMSO)_3$. Cyclic voltammograms for the complexes, $RuX_2(\text{sulfoxide}_2)_n(SR_2)_{4-n}$, reveal that the S-bound sulfoxide ligand is an excellent π-acceptor ligand for the low-spin d^6 metal center. A plot of $E_{1/2}$ vs n is linear with a slope of +0.21 v; indicating that each replacement of a thioether ligand by a sulfoxide lowers the energy of the HOMO (d_π) by approximately 4.8 kcal. When n=2, five different structural isomers are possible. Four of these isomers have been synthesized and characterized. Their $E_{1/2}$ values range from +0.75 v to +1.45 v. This large range of potentials can also be explained in terms of Ligand Additivity.[2] From these electrochemical studies the structure of the actual catalyst has been elucidated.

1. D. P. Riley, Inorg. Chem., 1982, 22, 1965.
2. B. E. Bursten, J. Amer. Chem. Soc., 1982, 104, 1299.

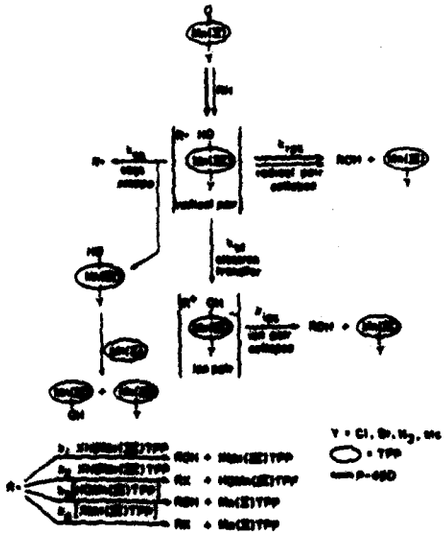
MULTIPLE MECHANISMS OF ALKANE C-H BOND HYDROXYLATION BY BIOLOGICAL AND ABIOLOGICAL OXOMETALLOPORPHYRINS

Craig L. Hill and John A. Smegal

Emory University, Atlanta, GA. 30322 and the University of California, Berkeley, CA. 94720

The cytochrome P-450 enzymes are one of the two or three most kinetically potent oxidizing agents in the biosphere. A high-valent oxoFe form of the heme active site of cytochrome P-450 appears to be the species responsible for the oxygenation of unactivated alkane C-H bonds in physiological systems. We have found that synthetic high-valent Mn porphyrins that constitute analogs for the active form of the active site of cytochrome P-450 are capable of facilitating all the oxygenation processes seen with the enzymes and some unprecedented alkane functionalization processes in addition.[1]

A thorough investigation of the mechanism of alkane functionalization by our Mn porphyrin based systems using several purified extremely reactive complexes and variety of physical methods produced the results summarized in the figure.



We believe that most if not all alkane oxygenations by oxometal species involve one or a combination of the processes shown in the figure with the appropriate oxo species substituted for the oxo Mn(V) porphyrin complex.

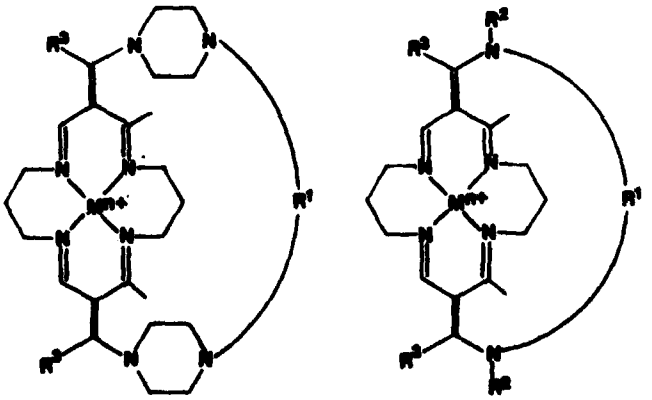
1. J.A. Smegal and C.L. Hill J. Am. Chem Soc. (1983) 105, 3515 and references cited therein.

A STUDY OF THE USE OF NOVEL MACROBICYCLIC COMPLEXES WITH LARGE PERSISTENT VOIDS AS DIOXYGEN ACTIVATION AND SELECTIVE OXIDATION CATALYSTS

Bradley K. Coltrain, and Daryle H. Busch

Department of Chemistry, The Ohio State University, 140 West 18th Avenue, Columbus, Ohio, USA, 43210

Macrobicyclic transition metal complexes of I have been designed and synthesized to model the selective oxidation chemistry of cytochrome P450. These complexes (I) permit hydrophobic binding of organic substrates near the metal center suggesting their possible use in modeling ternary complex formation (metal:substrate:O_2). Chromium, manganese, and iron complexes of I and the similar macrobicyclic complexes II have been shown to react with monooxygen transfer reagents such as iodosobenzene, sodium hypochlorite, and m-chloroperoxybenzoic acid and effect catalytic oxidation of substrates such as styrene and cyclohexane. The product distribution of the oxidation of toluene utilizing Fe(III) complexes of I and II and H_2O_2 has been found to vary with changing bridge size R^1. Attempts have been made to identify any intermediates that occur during the oxidation process. Attention ha been given to those intermediates in proposed dioxygen activation mechanisms.



OXIDATION OF PHENOLIC COMPOUNDS BY O_2 CATALYZED BY COBALT AND MANGANESE MACROCYCLIC COMPLEXES.

Maryvonne Frostin, Martine Perrée-Fauvet, Claude Bied-Charreton, Dany Pujol and Alain Gaudemer.

Laboratoire de Chimie de Coordination Bioorganique. Université de Paris-Sud. 91405 Orsay (France).

Aromatic compounds (indoles, phenols) are readily oxidized by molecular oxygen in the presence of cobalt(II) Schiff base or porphyrin complexes. Manganese(III) porphyrin ClMnTPP has proved also to be a good catalyst for the oxidation of indole (1), phenols and ethylenic derivatives (2): the last reaction must be performed in the presence of a co-reductant ($Bu_4N\ BH_4$). A comparative study of the mechanisms of the cobalt - and manganese - catalyzed oxidation of 2,4,6-tritertbutylphenol was undertaken. Peroxydic intermediates have been detected during the reactions catalyzed by cobalt complexes: an alkylperoxo-cobalt complex was isolated and fully characterized and it could be converted to the 4-hydroperoxy derivative of the phenol. This hydroperoxide, which is the direct precursor of the major oxidation product: 2,6 ditertbutylbenzoquinone, appears also to be an intermediate during the Mn-catalyzed reaction. The multiple roles of the metal during these oxidation will be discussed and extension to other phenolic derivatives will be presented.

1) M.N. Dufour, G. Johnston, A.L. Crumbliss and A. Gaudemer, J. Mol. Catal., 1980, 7, 277.

2) M. Perrée-Fauvet and A. Gaudemer, J. Chem. Soc. Chem. Comm., 1981, 874.

METAL ION-MEDIATED EPOXIDATION OF OLEFINS BY IODOSYLBENZENE

Joan S. Valentine, Catherine C. Franklin, Reuel B. VanAtta, and Alice Fan Tai

Department of Chemistry and Biochemistry and Molecular Biology Institute, University of California, Los Angeles, California, 90024, USA

We have initiated a study of metal-ion mediated oxygenations using a variety of oxygen atom sources in an attempt to observe and characterize some of the intermediates in these reactions and to relate them back to the biological systems.

Metalloenzymes that catalyze the incorporation of oxygen atoms derived from dioxygen into organic substrates usually contain either iron or copper. Our understanding of the mechanisms involved in the reactions of the iron-containing heme oxygenases has been substantially advanced by the characterization of high-valent metalloporphyrin oxo complexes, typically prepared by reactions using single oxygen atom sources such as iodosylbenzene, which are capable of epoxidation or hydroxylation of organic substrates. In the case of the copper oxygenase enzymes, by contrast, our understanding is much more limited and synthetic analogues of active intermediates have not been prepared.

Reaction of iodosylbenzene with trans-stilbene in the presence of either cupric or cobaltous nitrate in acetonitrile gave trans-stilbene oxide and benzaldehyde with yields of approximately 75% and 10% respectively. The analogous reaction with cis-stilbene was observed initially to give isomerization to trans-stilbene which then reacted to give the products already described. 2,3-Dimethyl-2-butene, cyclohexene, and 1-hexene were also epoxidized under the same conditions. In the case of the reaction with cupric nitrate, spectroscopic evidence suggests that a copper-iodosylbenzene complex was formed.

These results indicate that a metalloporphyrin is not required for activation of iodosylbenzene to give substrate oxygenation. Evidence concerning the mechanism and its relationship to possible biological processes will be described.

ACTIVATION OF MOLECULAR OXYGEN AT BINUCLEAR COPPER SITES

William E. Summers, III and John E. Bulkowski

University of Delaware, Department of Chemistry, Newark, Delaware, USA 19711

Our approach to the activation of molecular oxygen for the selective oxidation of aromatic substrates has employed discrete dicopper complexes of binucleating 20-, 22-, and 24- membered hexaamine macrocyclic ligands as the catalytic species. Dicopper(I) compounds of the hexaamines, stabilized as the bis CO derivatives, have been synthesized and are very O_2 sensitive in solution. They show a high selectivity for the catalytic oxidation of phenols to o-quinones at 25°C and O_2 partial pressures of ca. one atm. Mononuclear copper analogs of diethylenetriamine, although reactive under similar conditions, are not selective. The selectivity is a direct consequence of the structural integrity and geometry enforced on the binuclear copper site by the ligand framework.

During the course of this work, a dioxygen-bridged dicopper compound of the 20- membered macrocycle, 1,4,7,11,14,17-hexaazacycloeicosane, was isolated and structurally characterized by x-ray crystallography. This dimeric complex consists of two dicopper-containing macrocycles connected via two intermolecular dioxygen bridges between copper centers in adjacent macrocycles. Based on charge and structural considerations, the O_2-bridged copper atoms are formulated as μ-superoxo bridged dicopper(II) units with O-O bond distances of 1.20 Å and Cu-O-O bond angles of ca. 160°. The coordination geometries of all four copper centers are nearly square pyramidal with three nitrogens of the macrocycle and an oxygen of dioxygen in the basal plane. An oxygen atom from water occupies the axial position. Several of the structural features at the copper sites are similar to those determined for dioxygen binding in the dicopper metalloproteins hemocyanin and tyrosinase. The structural constraints imposed on the metals by the ligand and the unique redox properties of the dicopper unit resulting from the close proximity of the copper atoms appear to be important for formation and stability of the O_2-Cu_2 bridge. This structural result may be particularly important to understanding the mechanism of molecular oxygen activation in such systems.

The isolation and structural characterization of the copper complexes will be discussed, and a mechanism for the selectivity of the oxidation reactions will be proposed.

ZEOLITE ENCAPSULATED TRANSITION METAL COMPLEXES AS OXIDATION CATALYSTS

Norman Herron, Chadwick A. Tolman, and Galen D. Stucky

Central Research and Development Department
E. I. du Pont de Nemours & Co., Wilmington, Delaware, USA, 19898

While zeolitic materials have found widespread application in petroleum refining areas such as hydrogenation, hydrocracking, etc., their potential as catalysts for selective oxidation reactions has been largely overlooked. The work to be presented has sought to develop novel zeolite encapsulated metal complexes and to explore their use as oxidation catalysts seeking shape selection of both reactants and product distribution.

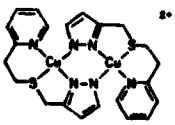
A cobalt(II) Schiff-base complex has been prepared inside a zeolite pore structure and is shown to catalyze the autoxidation of phenols to quinones. However, the catalytic turnover of this species is dramatically reduced compared to the corresponding homogeneous solution phase reaction; possible reasons for this difference will be presented. Attempts to define an oxidation reaction, useful as a probe of new zeolite catalysts, will be described - including catalytic oxidations of phenols, toluene, anisole and alkenes.

BINUCLEAR COPPER CHELATES FOR THE CATALYTIC AUTOXIDATION OF 3,5-DI-t-BUTYLCATECHOL

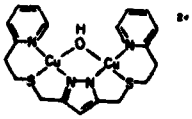
P. L. Urbach, D. F. Gervasio, Jong-Pyng Chyn and Michael D. McDevitt

Department of Chemistry, Case Western Reserve University, Cleveland, Ohio, USA 44106

The redox catalysis of two different types of high redox potential binuclear copper(II) chelates (1,2) toward the autoxidation of 3,5-di-t-butylcatechol (TBC) to the corresponding quinone (TBQ) has been investigated. The capability of these



1



2

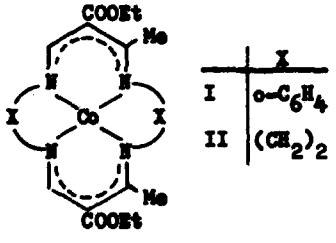
binuclear chelates to act as two-electron oxidants for TBC and then be reoxidized by O_2 via a multi-electron pathway makes them ideal candidates for this redox catalysis. The structural characterization of 1 and the chloro-bridged analog of 2 by x-ray diffraction reveals the anticipated geometries with Cu-Cu distances of 3.70 and 3.65 A, respectively. The d-d and charge transfer spectra of the chelates have been interpreted fully. Of particular interest are the ligand to metal charge transfer (LMCT) transitions arising from the thioether donors (325 nm) and from the bridging hydroxide in 2 (405 nm, 345 nm). Evidence suggests that the hydroxide bridge is lost upon reduction to the Cu(I)...Cu(I) state and that it is restored upon reoxidation in aqueous solution. Electrochemical characterization of the chelates by cyclic or differential pulse voltammetry shows complicated redox behavior attributed to the Cu(II)/Cu(I) couple in the range +50-100 mV versus SCE.

In the absence of O_2, the chelates rapidly oxidize TBC to TBQ with a 1:1 stoichiometry in acetonitrile solution. The formation of TBQ is monitored by its absorption band at 410 nm. In the presence of O_2 in 50:50 methanol:water, the oxidation of TBC becomes catalytic for both chelates with 2 being a much more effective catalyst than 1. The O_2:TBC ratio is found to be 0.5 in the reaction catalyzed by 2. The nature of the catalysis by the two chelates is apparently different. Preliminary initial rate studies indicate the reaction is first order in O_2 and the catalyst for 1. For 2, the reaction appears to be first order in O_2,catalyst and TBC. The relationship between the structures of the catalysts, changes which occur upon reduction to Cu(I)...Cu(I), and the mode of catalysis will be discussed.

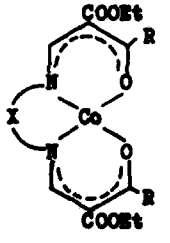
A NEW KIND OF ELECTROCHEMICAL REDUCTION OF DIOXYGEN IN THE PRESENCE OF TRICYCLIC OR MACROCYCLIC SCHIFF BASE COBALT COMPLEXES

Ernst-G. Jäger, Manfred Rudolph, Michael Rost and H. Hennig
Universität Jena, Sektion Chemie, DDR-6900 Jena, Steiger 3, GDR

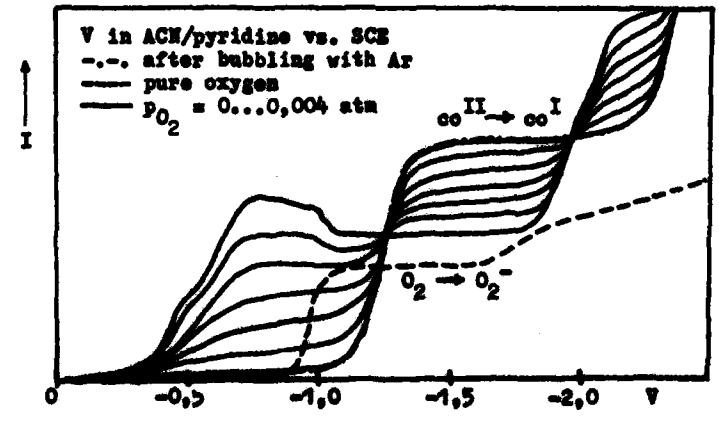
Comparing the effect of the cobalt complexes I - V on the electrochemical reduction of dioxygen in aprotic solvents, three kinds of dc-polarograms have been observed: (1) With I and II the polarographic curves are nearly the sum of those for the pure reductions O_2/O_2^- and Co^{II}/Co^{I}. (2) With III and IV a constant limiting current occurs in the region of the complex reduction, as described earlier by Costa[1] for CoSalen. (3) With V a polarographic spectrum with two "iso-current" points is observed, as shown in the figure, indicating the formation of a species with a lower diffusion coefficient (probably by the reaction $O_2 + 2\ co \xrightarrow{2\,e} (co_2O_2)^{2-}$). The results will be discussed with respect to the ESCA orbital energies, the redox potentials and the Lewis acidity of the complexes, their ability to form superoxo and peroxo derivatives respectively, and their catalytic activity in air oxidation of para-phenylenediamine derivatives.



	X
I	o-C_6H_4
II	$(CH_2)_2$



	X	R
III	o-C_6H_4	Me
IV	$(CH_2)_2$	Me
V	o-C_6H_4	OEt



1. A. Puneddu, G. Tauzher and G. Costa, Gazz. Chim. Ital. 1980, 110, 69

STERIC AND ELECTRONIC CONTROL OF METALLOPORPHYRIN CATALYZED HYDROCARBON OXIDATION

M. J. Nappa and C. A. Tolman

Central Research and Development Department,
E. I. du Pont de Nemours and Company, Experimental Station,
Wilmington, Delaware, USA 19898

Cytochrome P-450 are a class of enzymes which catalyze the mono-oxygenation of a variety of organic substrates using dioxygen and NADH as well as single oxygen donors such as iodosoarenes. The use of synthetic metalloporphyrins as models for the enzyme is now firmly established, however, these models give relatively low yields and poor selectivity. We are attempting to more effectively mimic the enzyme using phenyl-substituted metalloporphyrins as catalysts to probe steric and electronic effects in oxidations of hydrocarbons using oxygen transfer agents. Some of our recent work in this area will be described.

Mp10-11

SHAPE SELECTIVE ALKANE HYDROXYLATION

Kenneth S. Suslick, Bruce R. Cook, Mary M. Fox, and Thomas R. Reinert

School of Chemical Sciences, University of Illinois, Urbana, Illinois, USA, 61801

A series of manganese porphyrins with sterically protected pockets are shown to be shape selective alkane hydroxylation catalysts. With iodosylbenzene as oxidant, good selectivity is observed for terminal hydroxylation of the least hindered C-H; for a number of alkanes with 5,10,15,20-tetrakis(2',4',6'-triphenylphenyl)porphyrinatomanganese(III) acetate ("bis-pocket" porphyrin[1]) as catalyst. These results are reminiscent of the terminal hydroxylation activity shown by some cytochrome P-450 isozymes. Lessened selectivity is observed with 5,10,15,20-tetrakis(2',4',6'-trimethoxyphenyl)porphyrin, as expected due to the much shallower pocket, and essentially no regioselectivity is found with the unprotected 5,10,15,20-tetraphenylporphyrin The presence of such shape selectivity conclusively demonstrates the intimate involvement of the manganese porphyrin as the active site of hydroxylation of the alkanes, when iodosylbenzene is the oxidant. In direct contrast, the use of alkylhydroperoxides (e.g., t-butylhydroperoxide) does not produce any shape selectivity, and thus must proceed through a radical chain mechanism which uses the metalloporphyrin only for initiation.

Further work with the "bis-pocket" porphyrin iron(II) O_2 adducts and attempts to use O_2 with hydridic reductants as an oxygenation system will be discussed. As a part of this effort, various CO and O_2 affinities have been determined[2] for both an unprotected, "flat" porphyrin (5,10,15,20-tetraphenylporphyrinatoiron(II)) and a "bis-pocket" porphyrin(5,10,15,20-tetrakis(2',4',6'-triphenylphenyl)porphyrinatoiron(II)) as a function of 1) steric hindrance of a bound imidazole, 2) hydrogen bonding to the bound imidazole, and 3) solvent polarity. Increased steric hindrance beyond a simple 2-methyl substituent has little effect on CO binding. Hydrogen bonding of 1,10-phenanthroline to the bound imidazole has little effect on CO binding, contrary to suggestions made from imidazolate ligation. Solvent polarity enhances O_2, but diminishes CO affinities, which provides a new mechanism for CO/O_2 discrimination, an important function in O_2carrying heme proteins to prevent poisoning from endogenously produced CO.

1. K. S. Suslick and M. M. Fox J. Am. Chem. Soc. 1983, 105, 3507.
2. K. S. Suslick, M. M. Fox, and R. R. Reinert J. Am. Chem. Soc. 1984, 106, XXXX.

THE CATALYTIC PROPERTIES OF THE TRANSITION METAL TETRAAZAMACROCYCLIC COMPLEXES

K.B.Yatsimirskii, L.P.Tikhonova, Ja.Labuda, Ja.D.Lampeka, L.N.Zakrevskaja

The L.V.Pisarzhevsky Institute of Physical Chemistry of the Ukrainian SSR Academy of Sciences, Prospekt Nauki, 31, 252028 Kiev, USSR

The catalytic properties of the transition metal tetraazamacrocyclic complexes depends on the possibility of realization of central ion different redox states in these complexes.

We observed the catalytic action of a number of nickel(II) tetraazamacrocyclic complexes in oscillating chemical reactions with bromate-ion as oxidant. It is determined /1/ that oscillation of concentration ratio $[NiL^{3+}]/[NiL^{2+}]$ are observed at any degree of ligand unsaturation and does not depend from manner of double bonds location.

The kinetics of ascorbic acid oxidation by dioxygen which is catalysed by tetrabenzotetraaza macrocyclic copper(II) complex $Cu(TAAB)^{2+}$ have been studied /2/. The proposed mechanism involves reduction of $Cu(TAAB)^{2+}$ by ascorbic acid with generation of $HAsc^{\cdot}$ radicals followed by rapid interaction of these radicals with dioxygen and oxidation of $Cu(TAAB)^{+}$ by superoxoradicals $HO_2^{\cdot}$.

1. K.B.Yatsimirskii, L.P.Tikhonova, L.N.Zakrevskaja, Ja.D.Lampeka, Teor.Eksp.Khim., 1982, 18, 439.
2. K.B.Yatsimirskii, Ja.Labuda, Zh.Neorg.Khim., 1980, 25, 2464.

STRUCTURAL STUDIES ON THE METAL CLUSTERS IN NITROGENASE

W. H. Orme-Johnson, M. Nelson, M. Levy, M. Walters, P. Lindahl, S. Chapman, B. Hoffman[1], and E. Münck[2]

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts, USA

[1]Department of Chemistry, Northwestern University, Evanston, Illinois, USA

[2]Gray Freshwater Biological Institute, University of Minnesota, Navarre, Minnesota, USA

Nitrogenase catalyzes the reduction of dinitrogen to ammonia, and this activity results from electron transfer, MgATP hydrolysis, and substrate binding properties of two proteins, the Fe protein and the MoFe protein. A combination of EXAFS and Mössbauer studies suggest that in contrast to the currently accepted hypothesis, the Fe protein contains a center other than the classical $Fe_4S_4(RS)_4$ cluster found in ferredoxins. Combined EPR, Electron Spin Echo, and ENDOR studies reveal that the paramagnetic centers in the MoFe protein bind substrates, depending on the oxidation state of the protein. These experiments and those using EXAFS and mass spectroscopic measurements allow us to refine our picture of the M centers, which contain Mo, Fe, and S and which are responsible for the paramagnetism of the MoFe protein as isolated. We also have new information on the structure of P and S centers, Fe clusters in the MoFe protein. The use of mutations in the 18 genes of the *nif* region of the *Klebsiella pneumoniae* chromosome, to further examine the synthesis and structure of these inorganic components of nitrogenase, will also be discussed.

(Supported by NIH (GM30943, NSF (8205764-PCM), and USDA (59-2253-722-1.)

Structural Studies of Molybdenum Sites in Metalloenzymes

Keith O. Hodgson

Department of Chemistry, Stanford University
Stanford, California 94305

There are a number of now well characterized molybdenum-containing enzymes that are involved in a variety of biological processes. Among these are nitrogenase, xanthine oxidase, nitrate reductase and sulfite oxidase. Over the past few years, the active sites of these enzymes have been studied extensively by x-ray absorption spectroscopy. The work, both in our laboratories and outside, has resulted in the definition of two classes of active site. The method of x-ray absorption spectroscopy will be reviewed and the results of studies on molybdenum enzymes discussed. Of particular emphasis will be recent studies on the nitrogenase MoFe cofactor in the presence and absence of selenophenol and on various states of the MoFe protein.

MOLYBDENUM CHEMISTRY RELATED TO NITROGENASE: REACTIONS OF Mo(VI), Mo(V) AND Mo(IV) COMPLEXES WITH REDUCIBLE SUBSTRATES AND WITH ALKYLATING AGENTS

G.N.Schrauzer
Department of Chemistry, University of California at San Diego,
Revelle College, La Jolla,
Calif. 92093

Remarkably stable organometallic derivatives of oxomolybdate(VI) are obtained by the reaction of $Br_2Mo(O)_2(bpy)$ with organomagnesium halides. The purple complexes of composition $R\text{-}Mo(Br)(O)_2(bpy)$ are readily hydrolyzed to anionic organomolybdate species, $R\text{-}MoO_3^-$. These colorless ions are remarkably resistant to hydrolysis of the Mo-C bond; R may be alkyl, alkenyl or aralkyl. In most reactions, R exhibits carbanionic properties. A number of group transfer reactions have been observed. The Mo-C bonds are highly sensitive to reductive cleavage. In acidic media, β-elimination reactions are observed if R has hydrogen in β-position.

Substitution of both Br^- ions in $Br_2Mo(O)_2(bpy)$ by organic residues yields complexes of the type $R_2Mo(O)_2(bpy)$. Their stability is highly dependent on the presence of β-hydrogen in the R-residues. Until recently, only the complexes with $R = CH_3$, neopentyl or benzyl could be prepared. A modification of the synthesis has since permitted the preparation of a number of bis-n-alkyl derivatives. While the complex with $R = CH_3$ is stable enough to be sublimed, the complex with $R=C_2H_5$ decomposes in solution during recrystallization, affording reduced Mo-bpy derivatives plus a 1:1 mixture of C_2H_4 and C_2H_6. Properties of a number of related complexes will be discussed.

Reactions of Mo(V) and Mo(IV) species with reducible substrates such as C_2H_2, C_2H_4 and N_2 will be delineated and interpreted mechanistically in relation to previous work with nitrogenase model systems.

SULFUR-CONTAINING CHELATES OF MOLYBDENUM. REACTIONS OF HYDRAZINES WITH OXOMOLYBDENUM(VI) THIOHYDROXAMATE AND HYDROXAMATE ANALOGS

M. Fitzroy, K.S. Murray

Chemistry Department, Monash University, Clayton, Victoria, 3168, Australia.

J. Frederiksen, E. Horn, M.R. Snow

Department of Physical and Inorganic Chemistry, University of Adelaide, Adelaide, South Australia, 5001, Australia.

Oxo- and sulfido-molybdenum complexes are currently of much interest both from the bioinorganic and technological points of view.[1] EXAFS studies have shown the presence of MoO_2^{2+} and $MoOS^{2+}$ entities, coordinated to S-donor (cysteinate) residues, in the active sites of enzymes such as xanthine oxidase.[2] The present study is concerned with a systematic approach to try to understand the effect of varying the co-ligand donors (S vs. O) on the reactivity of the oxomolybdenum moiety. Two related groups of complexes of the thiohydroxamate, $O_2Mo(RCS.NR'O)_2$, and hydroxamate, $O_2Mo(RCO.NR'O)_2$, types have been prepared and their reactivities towards hydrazines such as $RNHNH_2$, R_2NNH_2 and $R(C{=}X)NHNH_2$ (X = O,S) are being investigated. X-ray diffraction studies on representative examples of the resulting oxomolybdenum hydrazido(2-) and diazenidomolybdenum compounds will be discussed.

Some rather unusual Mo-catalysed transformations of hydroxamic acids to amides have also emerged from this work.

1. "Some Recent Developments in the Chemistry of Chromium, Molybdenum and Tungsten", Ed. J.R. Dilworth, M.F. Lappert, (University of Sussex, July 1983).

2. S.P. Cramer, R. Wahl, K.V. Rajagopalan, J. Amer. Chem. Soc., 1981, 103, 7721.

COMPARISON OF NifV⁻ AND WILD-TYPE NITROGENASES AND THEIR IRON MOLYBDENUM COFACTORS

Barry E. Smith, Chen Guan-Xiong, Timothy R. Hawkes, Liang Yin-Chu and Paul A. McLean

AFRC Unit of Nitrogen Fixation, University of Sussex, Brighton, BN1 9RQ, U.K.

NifV mutants of *Klebsiella pneumoniae* can reduce C_2H_2 but not N_2.[1] This phenotype is associated with the MoFe protein (NifV⁻Kp1) which contains the site that binds reducible substrates. Unlike wild-type nitrogenase, nitrogenase containing NifV⁻Kp1, also has its H_2-evolution activity approx. 70% inhibited by CO.

MoFe protein prepared by reacting NifB⁻Kp1 (which lacks the iron-molybdenum cofactor, FeMoco) with cofactor (NifV⁻FeMoco) extracted from NifV⁻Kp1, also had the NifV⁻ phenotype, i.e. the modified substrate-reducing properties of NifV⁻Kp1 are associated with its FeMoco.[2] These data provide strong evidence that FeMoco includes the site for binding N_2 and CO.

Nitrogenase containing NifV⁻Kp1 is more effective at reducing HCN than is the wild-type enzyme.[3] The apparent K_m (CH_4 production) is lower and the percentage of electrons going to HCN reduction (rather than H_2 evolution) much higher with NifV⁻ nitrogenase compared to the wild-type enzyme. These and other data on substrate reduction by NifV⁻ nitrogenase can be rationalised in terms of it functioning at a higher potential than the wild-type enzyme.

The ratio of Fe to Mo in FeMoco is generally accepted as 7±1:1.[4] However reports on its sulphur content vary from four[5] to nine[6] per Mo and although there seems to be general agreement on the absence of amino acids[5,7] the presence of other organic ligands[5,8] is more contentious. Recent data on both of these aspects of cofactor structure will be presented.

1. P.A. McLean and R.A. Dixon, Nature (London) 1981, 292, 655.
2. T.R. Hawkes, P.A. McLean and B.E. Smith, Biochem.J., 1984, in the press.
3. Liang Y.-C. and B.E. Smith, in Advances in Nitrogen Fixation Research, 1984 (eds. C. Veeger and W.E. Newto· Nijhoff and Junk, The Hague, in the press.
4. B.E. Smith in Nitrogen Fixation: The Chemical-Biochemical-Genetic Interfaces, 1983 (eds. A. Müller and W.E. Newton) p.23, Plenum Press, New York and London.
5. S.-S. Yang, W.-H. Pan, G.D. Friesen, B.K. Burgess, J.L. Corbin, E.I. Stiefel and W.E. Newton, J.Biol.Chem., 1982, 257, 8042.
6. M.J. Nelson, M.A. Levy and W.H. Orme-Johnson, Proc.Natl.Acad. Sci.U.S.A., 1983, 80, 147.
7. B.E. Smith in Molybdenum Chemistry of Biological Significance, 1980 (eds. W.E. Newton and S. Otsuka) p.179, Plenum Press, New York and London.
8. L.A. Levchenko, O.S. Roschupkina, A.P. Sadkov, S.A. Marakushev, G.M. Mikhailov, and Yu.G. Borod'ko, Biochim.Biophys.Res.Comm., 1980, 96, 1384.

CRYSTALLOGRAPHIC STUDIES OF NITROGENASE IRON PROTEIN

John J. Kornuc, Nguyet Tran and Douglas C. Rees

Department of Chemistry and Biochemistry, University of California, Los Angeles, California USA 90024.

The nitrogenase iron protein is responsible for the transfer of reducing equivalents to the molybdenum-iron protein, and the coupling of this process to the hydrolysis of ATP. We have crystallized the iron protein from Azotobacter vinelandii nitrogenase in the reduced form. The needle-shaped crystals are in space group $P2_12_12$ (a=94.6A, b=179.9A, c=74.1A) and diffract to at least 3.5A resolution. Density measurements indicate that 5 or 6 Fe-protein monomers are present in the asymmetric unit.

Low resolution data (8A) has been collected on a diffractometer from native and derivative Fe-protein crystals. High resolution data is being obtained using oscillation camera techniques. We are in the process of locating heavy atom sites necessary to provide phase information and to identify the non-crystallographic symmetry operations relating the Fe-protein monomers. Current progress on the structure determination will be described, with emphasis on the symmetry of the Fe-protein dimer; location and characterization of the metal centers; location of the MgATP binding site, and the relationship of this site to the metal center.

CHEMISTRY OF SOME IRON-MOLYBDENUM-SULFUR COMPLEXES

John W. McDonald, Botao Zhuang, Laurence D. Rosenhein, and William E. Newton

Charles F. Kettering Research Laboratory, Yellow Springs, Ohio USA 45387

The discovery that the molybdenum site of nitrogenase is part of an iron-molybdenum-sulfur cluster unit has prompted the syntheses of a large number of metal complexes of this type in recent years. Although the synthetic analog for this enzyme site has not yet been isolated, significant progress has been made toward its preparation via this chemical approach. Three different Fe-Mo-S systems which are under investigation in our laboratory will be described in this poster.

1) The Fe-Mo-S site of nitrogenase gives rise to an S=3/2 EPR signal which is unique among biological systems. Because antiferromagnetic coupling between an S=1/2Mo(V) and an S=2 Fe(II) should yield a net S=3/2 state, we have prepared $[Et_4N]_2$ $[(o\text{-}xyl\text{-}S_2)FeS_2MoS_2]$ whose reversible electrochemical reduction suggested that we could use it to prepare the $[(o\text{-}xyl\text{-}S_2)FeS_2MoS_2]^{3-}$ ion which formally contains the desired electronic configuration. This species, prepared either chemically or electrochemically, indeed displays an S=3/2 EPR signal with g values very similar to the Mo-Fe protein of nitrogenase. Synthetic procedures and characterization data, as well as detailed EPR parameters, for this system will be presented.

2) The reaction of the known[1] $Mo(RNC)_4(S\text{-}t\text{-}Bu)_2$ with FeX_2 (X=Cl,Br) yields the new heterometallic species $X_2Fe(S\text{-}t\text{-}Bu)_2Mo(RNC)_4$ which formally contain Fe(II) and Mo(II). These complexes exhibit reversible electrochemistry and this facet of their behavior, along with preparative methods and spectroscopic data, will be described.

3) A new Fe-Mo-S species has been formed by reaction of $FeCl_3$ with a mixture of $LiOMe$, Li_2S, MoS_4^{2-}, and t-BuSH in MeOH. The synthetic procedure will be described in detail and the spectral properties of the new cluster will be presented. The current elemental analytical data for this complex indicates that it should be formulated as $[Fe_6MoS_{11}]^{4-}$ making it the first species with an Fe/Mo ratio similar to the iron-molybdenum cofactor of nitrogenase.

1. S. Otsuka, M. Kamata, K. Hirotsu, and T. Higuchi, J. Am. Chem. Soc., 1981, 103, 3014.

MODELS FOR THE FeMo-COFACTOR OF NITROGENASE: A NEW SYNTHETIC STRATEGY

B.A. Averill, K.S. Bose, P.E. Lamberty, J. Kovacs, G.L. Lilley, and E. Sinn

Department of Chemistry, University of Virginia, Charlottesville, Virginia 22901 USA

Two basic types of synthetic Mo-Fe-S cluster have now been prepared as potential models for the FeMo-cofactor of nitrogenase: single and double "cubane" clusters containing the $MoFe_3S_4$ unit (e.g., $Mo_2Fe_6S_8(SR)_9]^{3-}$, and "linear clusters containing the MoS_2Fe unit (e.g., $[S_2MoS_2FeS_2Fe(SR)_2]^{3-}$). Physical and chemical studies have shown that neither cluster type is a detailed model for the FeMo-cofactor, and to date it has not been possible to transform these materials into other, more realistic models.

The synthesis of all known examples of Mo-Fe-S cluster relies on reaction of MoS_4^{2-} with an iron complex, that is, the sulfide in the cluster products is originally bonded to Mo. We have begun to explore alternative synthetic routes that will produce new cluster types, and in particular are interested in strategies in which the sulfide orginates with the iron reagent.

We have found that the $[Fe_2S_2(CO)_6]^{2-}$ ion[1] reacts with molybdenum sources to produce several clusters containing the novel MoS_2Fe_2 unit (in which each Fe is also coordinated by 3 CO's), as well as several new iron-sulfur-carbonyl clusters. The preparation, properties, and structures of these new clusters will be described, together with oxidative decarbonylation reactions that result in replacement of carbonyl ligands by thiolates.

1. D. Seyferth, R.S. Henderson, and L.-C. Sung, Organometallics 1982, 1, 125.

ACTIVATION OF DINITROGEN

J.R. Dilworth, R.A. Henderson, G.J. Leigh, C.J. Pickett, and R.L. Richards

A.F.R.C. Unit of Nitrogen Fixation, University of Sussex, Brighton, BN1 9RQ, U.K.

Although dinitrogen is now known to bind to almost all the transition elements, the factors controlling its activation are only now becoming clear. They are not simple, and it is necessary to specify the kind of reaction for which activation is required, and the products. The situation has been reviewed fairly recently.[1]

Activation to hydronation occurs when dinitrogen is bound end-on to transition elements to the left side of the transition series. These elements, though often considered electron-deficient, are strongly electron-releasing. The consequence is considerable π-bonding, and a build up of charge on the amo-nitrogen. The amo-nitrogen is then susceptible to attack by electrophiles, such as the hydron and Lewis acids. In the former case, attack leads, via diazenido-complexes, to hydrazido(2-)-complexes, and ammonia and hydrazine, but hydrazide(2-) appears very stable and how it degrades further is not at all clear. In the latter case, one may write structures such as below.

M-N-N-M

These hydrogenate to give hydrazine, indeed this is apparently characteristic of bridging, activated dinitrogen.

The alkylation of end-on dinitrogen by alkyl halides is apparently a radical process. It requires paramagnetic intermediates, but the necessary conditions for such alkylations are not clear. The subsequent alkylation (to dialkylhydrazide(2-)) is a nucleophilic substitution. Degradation routes to amines and dialkylhydrazines have been established.

1. R.A. Henderson, G.J. Leigh, and C.J. Pickett, Adv. Inorg. Chem. Radiochem., 1983, 27, 197.

STRUCTURAL AND REACTIVITY PROBES OF THE FEMO COFACTOR OF NITROGENASE.

W.E. Newton, S. Lough, F.A. Schultz, J.F. Rubinson, S.F. Gheller, J.W. McDonald, B.K. Burgess, S.D. Conradson and K.O. Hodgson

C.F. Kettering Research Laboratory, 150 East South College St., Yellow Springs, Ohio 45387, USA, and Department of Chemistry, Stanford University, Stanford, CA 94305, USA.

Structural, compositional and reactivity insights concerning the iron-molybdenum cofactor (FeMoco) from the molybdenum-iron protein of nitrogenase of Azotobacter vinelandii have been obtained through a variety of physiochemical studies.

X-ray absorption spectroscopic studies at the Mo edge have produced high quality X-ray absorption near edge spectra (XANES) and extended X-ray absorption fine structure (EXAFS) data sets which suggest limits on possible atomic arrangements and stoichiometrics.

Related controlled chemical reactions, involving oxygen and metal-chelating agents, have also indicated the presence of at least two environments for Fe and a Mo coordination sphere consisting of S and O donors.

Electrochemical studies have produced insights into the redox properties of FeMoco, which have been further utilized in reactions with chemical reductants and oxidants including organic reagents and iron-sulfur clusters. These last reactions have suggested possible electron-transfer pathways to FeMoco within the molybdenum-iron protein of nitrogenase.

IDENTIFICATION OF Mo-S-Cu CLUSTERS BY ^{95}Mo NMR SPECTROSCOPY

Martin Minelli and John H. Enemark
Department of Chemistry, University of Arizona, Tucson, AZ 85721

John R. Nicholson and C.D. Garner
Department of Chemistry, University of Manchester, Manchester M13 9PL U.K.

There is considerable current interest in the preparation and study of Mo-S-Cu clusters[1]. This is stimulated by the significant recent developments in metal-sulfur chemistry and by the desire to provide a chemical interpretation of the copper-thiomolybdate interactions which are responsible, at least in part, for copper deficiency in ruminant animals[2,3].

As part of our ^{95}Mo NMR studies we have look at the ^{95}Mo NMR chemical shifts of a variety of Mo(VI)-S-Cu(I) clusters, notably the series $[MoS_4(CuX)_n]^{2-}$ (n = 1 or 2; X = Cl, CN or PhS; n = 3, Z = Cl or Br, n = 4, X = Br). The chemical shifts provide a clear indication of the cluster type. For the above series, the attachment of each Cu(I) moiety to the central $[MoS_4]^{2-}$ unit results in an apparent increase in the shielding experienced at the ^{95}Mo nucleus of ca. 300 ± 50 ppm. A similar perturbation of the ^{95}Mo resonance has been observed for Cu(I) and Ag(I) complexes of $[MoOS_3]^{2-}$.

1. W. Clegg, C.D. Garner, J.R. Nicholson and P.R. Raithby, Acta Cryst. 1983, C39, 1007 and references therein.

2. C.F. Mills, Philos, Trans. R. Soc. Lond Ser. B 1979, 288, 51.

3. C.F. Mills, I. Bremner, T.T. El-Gallad, A.C. Dalgarno and B.W. Young, Trace Element Metabolism in Man and Animals, edited by M. Kurchgessner, 1978, 150; Freising-Weihenstephan: Institut fuer Ernaehrungsphysiologie.

NITROGENASE REACTIVITY: AZIDE REDUCTION

Barbara K. Burgess, Judith F. Rubinson, James L. Corbin and Michael J. Dilworth[a]

Charles F. Kettering Research Laboratory, 150 East South College St., Yellow Springs, OH, 45387, USA. [a]Murdoch University, Murdoch Western Australia, Australia 6153.

We have recently investigated the reduction of azide by Azotobacter vinelandii nitrogenase. Previous studies (1) have shown that azide is reduced by two electrons to $N_2 + NH_3$, by six electrons to $N_2H_4 + NH_3$, and by eight electrons to $2NH_3$. We have performed azide concentration dependence experiments as a function of pH in order to determine if all reactions occur at the same site, via a common mechanism, and if HN_3 or N_3^- is the species being reduced. The data show that the two electron reduction to $N_2 + NH_3$ is pH independent indicating N_3^- is the substrate for this reaction. In contrast, the six electron reduction to $N_2H_4 + NH_3$ is markedly pH dependent indicating HN_3 as the substrate with an extremely low K_m. Competition experiments with N_2 and C_2H_2 strongly suggest that the latter reaction occurs at the N_2 reduction site and that HN_3 reduction may be a good model for N_2 reduction. The two electron reduction of N_3^-, however, appears to occur at a different site. Another interesting feature of this reaction is that at infinite azide only about 75% of the electrons are being used to reduce azide, with the remainder going to H_2 evolution. Although for N_2 this 75%/25% (NH_3/H_2) distribution would be stoichiometric, for azide, which can be reduced by two, six or eight electron pathways, it represents much less than one (0.43) H_2 evolved per azide reduced. N_2 and azide are the only substrates so far investigated which cannot eliminate H_2 evolution by nitrogenase. The relevance of this phenomenon to redox states of the enzyme reactive toward different substrates will be discussed.

1. M. J. Dilworth and R. N. F. Thorneley, Biochem. J., 1981, 193, 971.

A BIS(DINITROGEN) COMPLEX OF MOLYBDENUM: A CHEMICAL RESEMBLANCE TO NITROGENASE?

T. Adrian George and Lenore M. Koczon

University of Nebraska, Lincoln, Nebraska U.S.A. 68588-0304

Daniel B. Howell

Nebraska Wesleyan University, Lincoln, Nebraska, U.S.A. 68504

Trans-$Mo(N_2)_2$(triphos)(PPh_3), 1, where triphos=$PhP(CH_2CH_2PPh_2)_2$ reacts with anhydrous HBr to produce ammonia and/or hydrazine. In tetrahydrofuran (THF) solution ammonia is the sole nitrogen hydride product and $MoBr_3$(triphos) is the metal-containing product. On the other hand, in less polar solvents such as benzene, hydrazine becomes the predominant nitrogen hydrid product. In both of these reactions the initial steps lead to a mixture of two isomeric hydrazido(2-) complexes.[1] In the ammonia-forming reaction (THF/HBr) one of the hydrazido(2-) complexes reacts rapidly, with the loss of PPh_3, to form an intermediate (presently uncharacterized) during the first hour of reaction. If the reaction is allowed to react to completion (ca. 60 h)>99% of the nitrogen can be accounted for as dinitrogen and ammonia. However, if a CH_2Cl_2/H_2O mixture is added after about 1h of reaction a significant amount of hydrazine is detected.[2] In separate experiments hydrolysis was conducted at different time intervals. The yields of hydrazine correlated well with the disappearance of the reactive hydrazido(2-) isomer. At 12 h, hydrolysis resulted in the detection of only a trace amount of hydrazine.

It is the formation of hydrazine upon hydrolysis of the ammonia-forming reaction mixture early in the reaction that appears to provide an analogy with one of the properties of nitrogenase.

From the reaction of 1 with HBr in benzene a single, new molybdenum(III) complex, 2, has been isolated. This complex exhibits a ν(P-H) at 2250 cm^{-1}, has a μ(eff) of 4.00 B.M., and analyses for [$MoBr_4(Ph_2PCH_2CH_2PPhCH_2CH_2PHPh_2)$]. One of the Mo-P bonds has been cleaved and the phosphorus atom protonated. We do not believe that 2 is the molybdenum-containing product in the hydrazine-forming reaction. Instead 2 is formed in the reaction of the actual product with acid. $MoBr_3$(triphos) reacts with HBr to produce 2.

1. Boseard, G.E.; George, T.A.; Howell, D.B.; Koczon, L.M.; Lester, R. K. Inorg. Chem. 1983, 22, 1968-1970.

2. George, T. A.; Koczon, L.M. J. Am. Chem. Soc., 1983, 105, 6334-6335.

ENDOR OF THE NITROGENASE MoFe PROTEIN

R.A. Venters, M. Nelson, W.H. Orme-Johnson and B.M. Hoffman

Department of Chemistry, Northwestern University, 2145 Sheridan, Evanston, Illinois, USA 60201

In ENDOR spectra of the catalytic center (FeMo-Co) of MoFe, we observe six different and distinct irons, at least six types of structural protons, one molybdenum and several sulfur atoms per cofactor.[1,2] Changes in these various resonances upon addition of the inhibitory substrate, methyl isocyanide (MIC), provide unique information about substract binding.

MIC binding perturbs only one of the six observed irons. The iron which shifts frequency is the one most strongly coupled to the spin system (#6); other ENDOR data suggest that it can be considered to be in the more reactive Fe^{2+} state. Along with our molybdenum ENDOR measurements, the result suggests that one iron, probably along with molybdenum, forms the MIC binding site.

Binding of MIC does not cause major changes in the proton ENDOR spectra, indicating that no structural protons (probably on cysteine residues) are displayed upon substrate binding. However, the difference spectrum indicates small changes in the coupling of two protons, which presumably are associated with cysteines at the binding site.

In order to obtain a more complete characterization of the metal atoms in the EPR-visible center of MoFe, we have now performed a preliminary ^{33}S ENDOR study. The initial results, which show several well-resolved ^{33}S resonances, are very encouraging.

1. "^{95}Mo and ^{1}H Endor of the Nitrogenase MoFe Protein," Brian M. Hoffman, James E. Roberts, and W.H. Orme-Johnson, J. Am. Chem. Soc., 104, 860 (1982).

2. "^{57}Fe Endor of the Nitrogenase MoFe Protein," B.M. Hoffman, R.E. Venters, J.E. Roberts, M. Nelson, and W.H. Orme-Johnson, J. Am. Chem. Soc., 104, August (1982).

Molybdenum and Tungsten/Sulfur Cluster Chemistry and Induced Redox Processes

Thomas R. Halbert, Steven A. Cohen and Edward I. Stiefel

Corporate Research Science Laboratories
Exxon Research and Engineering Company
Clinton Township, Route 22E, Annandale, N.J. 08801

A primary goal of recent research in our group has been to establish and explore general patterns of reactivity in transition metal/sulfur chemistry. Such patterns, along with the new molecular species which result from extensions of these patterns, will be of use in unraveling the complexities of a variety of metalloenzymes and industrial catalysts which involve transition metals in a sulfur coordination environment.

Prior work has clearly established two types of redox reaction associated with Mo/S complexes. In one type, redox is centered at the sulfide/polysulfide ligands, and no change in metal oxidation state occurs. In the other, redox is centered at the metal, and no change in ligand oxidation level occurs. A recent example of the former type is the reaction of $Mo_3S_7^{4-}$ with the sodium salt of 1,2-ethanedithiol (edt), which leads to the new trinuclear anion $Mo_3S_4(edt)_3^{2-}$. The structure of this complex is layered, and its relationship to the structure of MoS_2 will be pointed out. Reversible reactions with S and trisulfides will be related to the creation and filling of sulfur vacancies in the heterogeneous catalysts. Further, resonance Raman spectra show an interesting correspondence to the spectra of Fe_3S_4 clusters in enzymes.

In addition to the two types of redox reaction mentioned above, we have now discovered a new type of redox reaction, in which an M/S (M=Mo,W) complex reacts with an oxidant to yield a product with the Mo in a lower oxidation state. This counter-intuitive process involves an "internal electron transfer" wherein the external oxidant induces reduction of the metal by the coordinated sulfide ligands. Several new examples of this class of reaction will be given.

THE PERPETUAL SCHIFF BASE

David E. Fenton

Department of Chemistry, The University, Sheffield S3 7HF, U.K.

The Schiff base must be regarded as a fundamental building block in coordination chemistry. This year, 1984, sees the *sesquicentenary of the birth of* Hugo Schiff and this lecture is presented in commemoration of this event.

Schiff (1834-1915) was educated in Germany but left because of his liberal political views and spent his life in Italy, where he carried out his major scientific work. His studies were predominantly in organic chemistry, although he first prepared $SOCl_2$ from SO_2 and PCl_5 and later devised the nitrometer bearing his name. In 1864 he discovered the condensation products of aldehydes and amines now collectively known as Schiff bases.

$$RCHO + R'NH_2 \longrightarrow RC(H)=NR'$$

Metal complexes of such bases have been known for more than 100 years - and actually pre-date Schiff. However it was he who established the synthetic technique of preparing salicylaldimine complexes by the reaction of primary amines with preformed metal salicylaldehyde complexes. The subsequent development of this area, through Combes (acen, 1889), Delepine, Morgan, Dubsky and Sokol (salen, 1931) and Pfeiffer, whose contributions (1931-1942) gave us the foundation for much contemporary work, will be outlined.

Post-Pfeiffer, the development of macrocycles, the use of metal complexes as ligands, and the introduction of binucleating and compartmental ligands has given access to the strategic synthesis of models for metal sites in biomolecules, and to materials suitable for studying the electron transfer and magnetic exchange processes available in oligometallic arrays. These areas will be emphasised *in order to show* the perpetuality of the Schiff base and the salient role which it plays in contemporary coordination chemistry.

MANGANESE(II)-MANGANESE(III) MIXED-VALENCE COMPLEX WITH A STRATI-BIS SCHIFF BASE

Hisashi Ōkawa and Sigeo Kida

Department of Chemistry, Faculty of Science, Kyushu University 33, Hakozaki, Higashiku, Fukuoka 812, Japan

1,2,3,4-Tetrakis(salicylideneamino)-2,3-dimethylbutane (abbreviated as H_4(sata)) has been shown to form strati-bis bimetal complexes.[1] In this study we have isolated and characterized a mixed-valence Mn(II)-Mn(III) complex with this ligand.

An yellow dichloromethane solution of the manganese (II) complex, Mn_2(sata), was air-oxidized to a red-brown solution, from which were isolated black-red prisms of the composition $Mn_2(sata)(OH)\cdot H_2O$. The magnetic moment per molecule is 7.0 BM at room temperature and 5.9 BM at 80K. Cryomagnetic behabior can be well interpreted by the susceptibility equation for the (S=5/2)-(S=2) system based on the Heisenberg model, suggesting the formation of a Mn(II)-Mn(III) complex. The exchange integral was evaluated to be -6.0 cm^{-1}. The superexchange through the Mn-OH-Mn bridge is supposed for the complex.

Electronic spectrum was characterized by an absorption in the near IR region (7700 cm^{-1} in CH_2Cl_2, ε~100 $dm^3M^{-1}cm^{-1}$), which can be assigned to the inter-valence transition band. The solvent dependence of the band frequency may be interpreted by Hush's theory.[2] Electron delocalization factor, α^2, was evaluated to be 0.005, which is consistent with the Class II type of the classification by Robin and Day.[3]

Cyclic voltammetry and polarography, coupled with controlled-potential electrolyses, revealed the quasi-reversible processes:

$$[Mn^{III}_2(sata)(OH)]^+ \underset{}{\overset{-0.25V}{\rightleftharpoons}} [Mn^{II}Mn^{III}(sata)(OH)] \overset{-0.75V}{\rightleftharpoons} [Mn^{II}(sata)(OH)]^-$$

1) The present authors, Chem. Lett., 1981, 483; Bull. Chem. Soc. Jpn., 55, 2122 (1982); ibid., 56, 149 (1983); Inorg. Chim. Acta, 75, 9 (1983).
2) N. S. Hush, Prog. Inorg. Chem., 8, 391 (1967).
3) M. B. Robin and P. Day, Advan. Inorg. Chem. Radiochem., 10, 247 (1967).

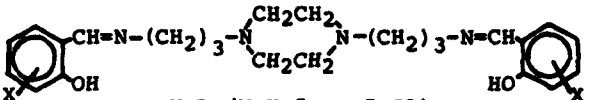
3D METAL COMPLEXES OF POLYDENTATE LIGANDS
——PSEUDO-TRIGONAL-PRISMATIC COMPLEXES——

Hiro Kuma[a], Yoshiyuki Namba[b], and Shoichiro Yamada[a]

a College of General Education, Osaka Univ., Toyonaka, Osaka 560

b Osaka Kyoiku University, Tennoji, Osaka 560, JAPAN

In the course of studies on polydentate ligands, we have isolated metal complexes having a pseudo-trigonal-prismatic structure.



H_2L (X=H,5-Br,5-Cl)

Reactions of H_2L with several metal salts yielded complexes of the following types: [Co L] and $[ML]ClO_4$ (M(III)=Mn, Fe, Co). Electronic spectra and magnetic properties of the complexes [Co L] show that their structure is neither octahedral nor tetrahedral. The crystal structure of one of them (X=5-Cl) has been determined by X-ray methods. The crystal consists of a mononuclear molecule [Co L] having a distorted-trigonal-prismatic structure. Two oxygen and two imine nitrogen atoms of the ligand are coordinated with a cobalt(II) ion in a distorted square-planar geometry (Co-O: 2.014, Co-N:2.174A), the other two tertiary nitrogen atoms being bound at further distances (2.297, 2.332A) with the metal ion.

The iron(III) complexes $[Fe\ L]ClO_4$ are of a high-spin type (=5.9-6.0 BM). The structure analysis with one of them (X=H) shows that the mononuclear complex $[Fe\ L]^+$ in the crystal also has a distorted trigonal-prismatic structure.

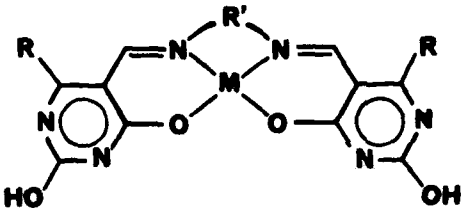
The pseudo-TP structure in these complexes seems to be favoured by the steric condition produced by the ligand, in combination with the constraint imposed on the tertiary nitrogen atoms. The structure of the cobalt(III) complex, which is expected to approach the octahedral structure, is now under investigation. The structures of the present complexes are discussed in comparison with those of the related complexes.

SYNTHESIS AND COMPLEXING PROPERTIES OF SCHIFF BASE LIGANDS DERIVED FROM PYRIMIDINE BASES.

Isabelle Sasaki, Marie-Noelle Dufour and Alain Gaudemer.

Laboratoire de Chimie de Coordination Bioorganique - Université de Paris-Sud - 91405 Orsay - (France).

Schiff-base Cobalt(II) complexes are able to catalyse the oxidation of various organic compounds by dioxygen. Recently we have been interested in the synthesis of new complexes of that type which might induce oxidative strand-scission of deoxyribonucleic acids: such molecules should be able not only to convert O_2 into reactive species but also to bind strongly to DNA. For that purpose we have developed the synthesis of metal complexes of Schiff-base ligands derived from pyrimidine bases such as 1 (1).



1 R: H,OH
M: Cu,Co

Uracil and barbituric acid were converted to the corresponding 5-formyl derivatives which were condensed with di- or triamines to give the expected diimines in good yields. The structures of the corresponding Cu(II) and Co(II) complexes were determined by X-ray cristallography and spectroscopic methods and found to be simular to those of the corresponding Salen-type complexes. A comparative electrochemical study showed that the ligands present in complexes 1 are less electron-donating than Salen. Introduction of a hydroxyl group at C-6 decreases both the Cu(II)/Cu(I) and Co(III)/Co(II) half-wave potentials by ca. 200mV and futhermore gives the Co(II) complexes catalytic activity for the oxidation of phenols.

1) I. Sasaki, M.N. Dufour and A. Gaudemer, Nouv. J. Chimie, 6, 341, (1982).

UNUSUAL PROPERTIES OF SOME IRON (II) COMPLEXES WITH SALICYLALDEHYDE DERIVATIVES.

L. Araya*, R. Latorre*, J. Costamagna

* Universidad de Chile, Casilla 653, Santiago, Chile
** Universidad de Santiago, Casilla 5659, Santiago, Chile

New complexes if iron(II) with bidentate ligands derived from 5-bromo-salicylaldehyde (5BrSA) and substituted anilines (Y-anil, Y=H,2Cl, 3Cl, 4Cl, $2CH_3$, $3CH_3$, $4CH_3$) have been synthesized and characterized by analysis and conventional spectroscopies.

The Table shows room temperature data of Mössbauer spectra and molar magnetic susceptibilities (χ). For planar complexes with coordination number four with salicylaldehydes an isomer shift (IS) and a quadrupole splitting (QS) of those magnitude for low spin complexes are expected to be observed (1). The effect of substituent is not clearly significative from Mössbauer results.

Nevertheless, a ferromagnetic behaviour is observed for all the complexes at room temperature in solid state while in chloroform solution they show a magnetic moment of 3.3-3.5 Bohr magnetons. In addition, the Mössbauer spectra at 14 K show an hiperfine pattern (six lines) and a doublet which can be attributed to ferromagnetic interactions with two sites for the iron atoms.

These unusual facts could tentatively be interpreted in terms of the existence of (a) planar complexes with a $d_{x^2-y^2} > d_{xy} > d_{z^2} > d_{xz} = d_{yz}$ energy orbital d levels and (b) a triplet state due to the proximity of d_{xy} and d_{z^2} orbitals (2,3).The Mössbauer spectra at room temperature would be due to fast relaxation.

COMPLEXES	Mössbauer (mm/s) IS(a)	QS	$\chi Fe \times 10^6$ (cgs)
$Fe(5BrSA\text{-}Anil)_2$	0.41	0.74	4470
$Fe(5BrSA\text{-}2ClAnil)_2$	0.40	0.77	4164
$Fe(5BrSA\text{-}3ClAnil)_2$	0.41	0.80	2971
$Fe(5BrSA\text{-}4ClAnil)_2$	0.43	0.77	2416
$Fe(5BrSA\text{-}2CH_3Anil)_2$	0.41	0.68	1476
$Fe(5BrSA\text{-}3CH_3Anil)_2$	0.41	0.72	1875
$Fe(5BrSA\text{-}4CH_3Anil)_2$	0.38	0.75	3458

(a) related to sodium nitroprusside.

1. E. Fluck, in "Chemical Applications of Mössbauer Spectroscopy", Academic Press, New York, 1968, p. 279.

2. F.A. Cotton, G. Wilkinson, "Advanced Inorganic Chemistry", J. Wiley, 4th Ed., New York, p. 757.

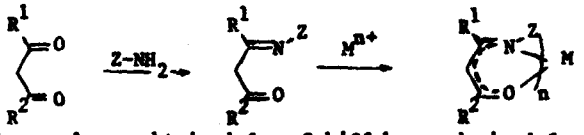
3. E. König, G. Rotter, H.A. Goodwin, Inorg. Chem. 1981, 20, 3677

SYNTHESIS OF NEW SCHIFF BASES AND SCHIFF BASE COMPLEXES VIA METAL CONTROLLED STEREOSPECIFIC CONDENSATIONS OF COPPER(II) β-DIKETONATO COMPLEXES WITH Z-NH_2 (Z = OH, NHAr, -$(CH_2)_n$-NH_2)

Dosten Baluch, Ronald Bennett, John Charalambous, Nigel J Harris, L Ian B Haines

School of Chemistry, The Polytechnic of North London, London N7 UK

Schiff base complexes of type 1 are usually prepared directly from the Schiff base.



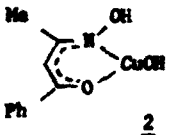
1

In complexes obtained from Schiff bases derived from unsymmetrical β-diketones the position of condensation is determined by the nature of groups R^1 and R^2 in the diketone and is the same in both ligands.

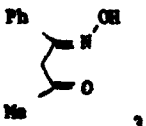
Condensation of Z-NH_2 (Z = e.g. OH, aryl, NHAr) with metal β-diketonates provides an alternative route to Schiff base complexes. We report that in such reactions in addition to the effect of groups R^1 and R^2 some metals have a pronounced effect on the position of condensation.

Our studies of the reaction of copper(II) β-diketonates demonstrate the role of the metal and its control on the stereospecifity of the condensation. Thus, for example, Cu(bzac)$_2$ (bzacH = 1-phenyl-1,3-butanedione) on treatment with NH_2OH affords two condensation products 2 and 3 in equimolar amounts in which condensation occurs at different carbonyl groups of the diketone moeity. This contrasts the behaviour of bzacH towards NH_2OH which involves condensation of the carbonyl group adjacent to methyl to give 4. Similarly 5 has been obtained from Cu(bzac)$_2$ and 1,2-diaminoethane whereas the 1:2 reaction between bzacH and the diamine gives the symmetrically condensed product 6.

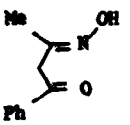
The novel behaviour of the copper complexes is rationalised in terms of their ability to undergo Lewis base induced internal redox reactions. Detailed mechanistic proposals will be presented and discussed.



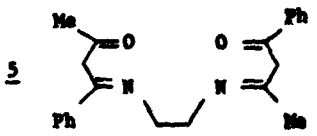
2



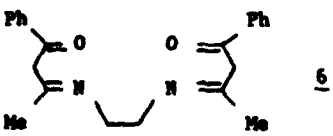
3



4



5



6

A SINGLY CONDENSED SCHIFF-BASE DERIVATIVE : PREPARATION, CHARACTERIZATION AND PROPERTIES.

Jean-Pierre COSTES, Gérard GROS and Jean-Pierre LAURENT

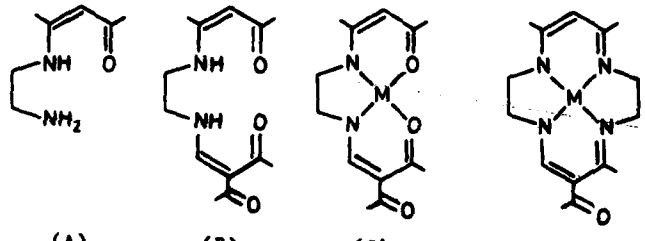
Laboratoire de Chimie de Coordination du CNRS, 205, route de Narbonne, 31400 TOULOUSE (France).

Among the metal complexes of Schiff bases, a particular attention has been paid to the complexes derived from tetradentate diimino ligands resulting from the condensation of two molecules of keto-precursor with one molecule of diamine. However, by using suitable exprimental conditions, a singly condensed ligand, AEH, may be isolated from the reaction of pentane-2,4-dione with 1,2-diaminoethane.

This "half-unit" A (figure) has been fully characterized by NMR (^{1}H and ^{13}C) and X-ray structural determination in the case of its copper(II) complex.

The potentialities of this compound have been investigated with regard to the following items :

- formation of metal complexes, $M^{II}(AE)_2$ and $M^{II}(AE)X$;
- non-template synthesis of non-symmetric tetradentate Schiff bases and related metal complexes such as B and C (figure) ;
- template synthesis ;
- preparation of non-symmetric macrocyclic complexes, for instance D (figure).



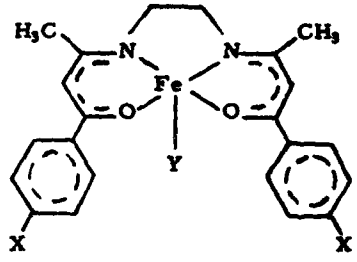
(A) (B) (C) (D)

SYNTHESIS AND CHARACTERIZATION OF KETOIMINATO FE(III) COMPLEXES WITH CHLORO AND BROMO COUNTERIONS

J. Michael Gregory and Sue C. Cummings

Department of Chemistry, Wright State University, Dayton, Ohio, USA 45435

Two series of Fe(III) complexes of formulation [Fe-p-X-(benacen))Y], where p-X(benacen) is the tetradentate Schiff base ligand derived from the condensation of ethylenediamine and various para-X substituted benzoylacetones, and Y is Cl^- or Br^-, have been prepared in hot methanol by reaction of anhydrous $FeCl_3$ and $FeBr_3$ with the deprotonated ligands. The new complexes have been characterized as five-coordinate Fe(III) monomers of the type illustrated.



Conductivity measurements in CH_2Cl_2 on the maroon or purple microcrystalline products establish that the complexes are nonelectrolytes. Infrared spectral evidence indicates that the N_2O_2 donor atoms of the ketoiminato ligands adopt a square-planar configuration about the iron ions as in the analogous Co(II) chelates previously prepared in these laboratories.[1] Also, an intense, low energy band (360 cm^{-1}) in the ir spectra of all of the chloro derivatives has been assigned to an Fe-Cl stretching mode. Values of the magnetic moments are consistent with a high spin d^5 configuration. Very intense electronic spectral bands in the visible region between 558 and 460 nm (ϵ = 10^3 - 10^4 L/mol-cm) are attributed to M-L charge transfer transitions and provide little information on the coordination geometry. Closer analysis and comparison of the physical data with those published on similar Fe(III) systems suggests that the complexes are monomeric; however, additional studies are underway to provide confirmation of the proposed structures.

1. L. S. Chen and S. C. Cummings, Inorg. Chem. 1978, 17, 2358.

COPPER(II) COMPLEXES OF SCHIFF BASE LIGANDS DERIVED FROM PYRROLE-2,5-DICARBOXALDEHYDE AND FROM 2-ACETOACETYLPYRROLE

Harry Adams, Neil A. Bailey, David E. Fenton, Martha S. Leal Gonzalez, Colin H. McLean, Richard Moody, Stephen Moss, Cecilia O. Rodriguez de Barbarin, and Patrick B. Roberts

Department of Chemistry, The University, Sheffield S3 7HF, U.K.

The use of pyrrole-2,5-dicarboxaldehyde and of 2-acetoacetylpyrrole in the preparation of novel macrocyclic, acyclic and compartmental Schiff bases will be presented. The discussion will centre on the complexation of copper(II) by these ligands and will be accompanied by salient crystal structures of complexes derived from each type of ligand. The complexes prepared include mono-, and μ-alkoxy bridged homodi-nuclear copper(II) derivatives of the macrocycles, and mononuclear copper(II) complexes of the compartmental ligands. In the latter the metal moves from compartment to compartment, as the length of the bridging diamine is varied, in order to retain a square coplanar geometry. At long chain lengths an unusual 'fly-over' complex is formed in which the bridging chain acts as a cap for the metal site.

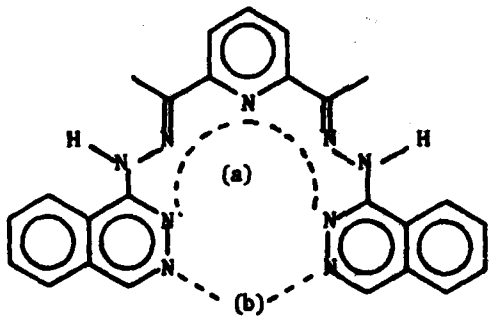
2,6-DIACETYLPYRIDINE-BIS(1'-PHTALAZINYL)HYDRAZONE. A USEFUL LIGAND FOR THE SYNTHESIS OF MONO-, DI-, AND TRI-(HOMO AND HETERO)NUCLEAR COMPLEXES OF TRANSITION METALS.

G. Paolucci(1), G. Rossetto(2), P. Zanella(2), and M. Casarin(2).

(1) Dipartimento di Chimica, Facoltà di Chim. Ind.le, Università di Venezia, Calle Larga S.Marta 2372, Venezia, ITALY.

(2) Istituto di Chimica e Tecnologia dei Radioelementi, Area di Ricerca C.N.R., Corso Stati Uniti, 35100 Padova, ITALY.

The title ligand (I) has been synthesized with the aim to study the possibility of obtaining poly-nuclear transition metal complexes, according to the presence of two different chelating sites (a) and (b):



(I)

Due to the acidity of hydrazonic hydrogen, mono-nuclear neutral species have been obtained from Cu^{II}, Ni^{II}, Co^{II} and Zn^{II} acetates. By reacting some of these mono-nuclear neutral complexes with transition metal halides MX_2, some binuclear species have been obtained. Moreover by using transition metal perchlorates, some homo- and hetero-trinuclear species have been isolated.

The spectroscopic and magnetic behaviours of the complexes are discussed.

EXPLOITATION OF $[Ni(CN)_4]^{2-}$ AS LIGAND : GENERATION OF HETEROMETAL CORES OF BIOLOGICAL RELEVANCE

S.B.S. Mishra* and A. Pant

Department of Chemistry, M.G. Degree College (MKP University) Gorakhpur-273001 (India)

Nickel has recently joined the group of transition metals relevant in biological redox processes and has been shown to be a structural component of hydrogenases.[1] The importance of 'Spontaneous Self Assembly' of metal aggregates in biological system has also recently been emphasised[2] because the directed synthesis of desired metal aggregates is difficult to achieve, moreso when multimetal systems are to be synthesised.

Exploiting the ligational potential of $[Ni(CN)_4]^{2-}$ the synthesis of multimetal aggregates of biological importance could be achieved. One report of the formation of a trimetaller nickel complex [trans $Ni(NC)_2Ni(CN)_2Ni$ trans] had earlier appeared in literature where $[Ni(CN)_4]^{2-}$ acts as a ligand.[3] Following cores could be synthesised, however, utilising the ligational ability of $[Ni(CN)_4]^{2-}$:

$[L\ Cu(NC)_2Ni(CN)_2]^-$ (I) ; $[L_2Fe(NC)_2Ni(CN)_2]^{2-}$ (II)

$[L\ Cu(NC)_2Ni(CN)_2CuL]$ (III) ; $[L_2Fe(NC)_2Ni(CN)_2FeL_2]^{2-}$ (IV)

and $[L\ Cu(NC)_2Ni(CN)_2FeL_2]^-$ (V). L = phen; X = Cl^-/PhS^-

The $[Ni(CN)_4]^{2-}$ anion serves as a bidentate ligand in I and II whereas a quadridentate ligand in III, IV and V in which the CN^- are coordinated to Fe(II) and/or Cu(I) through the N end.

The existence of such multimetal cores in the biological system could be responsible for the connected role of these metal ions in various biological processes like electron transfer, catalysis, oxidation-reduction, storage and transport.

1. A. V. Xavier, M. Teixeira, I. Moura, J.S. Moura and J. LeGall, Inorg. Chim. Acta, 1985, 79, 13 and references therein.

2. R. H. Holm, Chem. Soc. Rev., 1981, 10, 455.

3. K. R. Mann, D.N. Duggan and D.N. Hendrickson, Inorg. Chem., 1975, 14, 2577.

REACTION OF ALIPHATIC AMINES WITH TIN TETRACHLORIDE-PART I "SYNTHESIS OF TRICHLORO-(METHYLAMINO)-BIS-(METHYL-AMINE) TIN(IV). METHYLAMINE HYDROCHLORIDE."

DR. RAJA HUSSEIN ABU-SAMN
Associate Professor, Chemistry Department,
College of Science, King Saud University
Riyadh, Saudi Arabia

Abstract:

By passing an excess of dried pure monomethylamine gas into a solution of water-free tin tetrachloride in carbon tetrachloride, an exothermic reaction takes place, resulting in the formation of a white precipitate, whose structure is time-dependent.

After two hours the complex trichloro-(methylamino)-bis-(methylamine)tin(IV). methylamine hydrochloride (I) is formed with the formula $SnCl_4.4CH_3NH_2$.

The paper describes the preparation of complex (I), the apparatus used for purifying the gas CH_3NH_2 and the mechanism of the reaction. Also the i.r. and ^1H-nmr spectra of the complex are given and interpreted.

SYNTHESIS AND COORDINATION CHEMISTRY OF 4,7-BIS-(DICYANOMETHYLIDENE)-1,4,7,10-TETRAHYDRO-1,10-PHENANTHROLINE

Leonard V. Interrante and Arlene G. Williams

General Electric Corporate Research and Development, Schenectady, NY, USA 12301

Martin N. Ackermann

Department of Chemistry, Oberlin College, Oberlin, OH, USA 44074

The synthesis, structural characterization, and the results of a preliminary investigation of the coordination properties of the new organic ligand system, 4,7-bis-(dicyanomethylidene)-1,4,7,10-tetrahydro-1,10-phenanthroline (BDCHP) will be described. This ligand is obtained[1] as the crude disodium salt starting from 4,7-dichloro-1,10-phenanthroline by reaction with excess $NaHC(CN)_2$. The disodium salt can be converted to mixed tetraethylammonium/alkali metal ion derivatives (i.e., $[(C_2H_5)_4N]_2Na(BDCHP)$ and $(C_2H_5)_4NLi(BDCHP)$) by solution in tetraethylammonium hydroxide followed by addition of a solution of the alkali metal salt. These tetraethylammonium derivatives, which are crystalline and readily soluble in organic solvents, serve as convenient sources of the BDCHP ligand for the preparation of transition metal complexes. In this manner the mono-BDCHP complex of Ru(II), $[Ru(phen)_2(BDCHP)]$, was prepared starting from $Ru(phen)Cl_2$. The same complex was also prepared by reaction of the coordinated Cl_2phen ligand in $[Ru(phen)_2(Cl_2phen)]^{2+}$ with $NaHC(CN)_2$. This reaction has also been carried out on the tris-Cl_2phen Ru(II) complex to yield the corresponding red-violet tris-BDCHP Ru(II) complex, $[Ru(BDCHP)_3]^{4-}$. These Ru(II) complexes are strongly absorbing in the visible region and have long-lived charge transfer excited states which emit at >600nm. The mono-BDCHP complex shows five, apparently reversible, redox processes between -2.2V and +1.8V vs. SCE in acetonitrile, including two one-electron oxidations attributable to the coordinated BDCHP ligand. This complex is soluble in strong acid media in which it exhibits absorption, emission, and NMR spectra indicative of the reversible protonation of the dicyanomethylene groups of the coordinated BDCHP ligand.

Preliminary work has also been carried out on complexes of BDCHP with Ir(I) and Cu(II) of the type, $R^+[Ir(CO)_2(BDCHP)]^-$ and CuL(BDCHP), where L = bipy and phen. The former complexes are semiconductors in the solid state and show a strong dependence of the conductivity on the nature of the cation, R. Partial oxidation with iodine results in enhancement of the conductivities by several orders of magnitude. Both the Ir(I) and Cu(II) complexes absorb strongly in the visible region and emit at >600nm.

1. M.N. Ackermann and L.V. Interrante, J. Org. Chem. 1983, 184, 382.

MIXED LIGAND COMPLEXES OF Mg(II), Ca(II), Sr(II) AND Ba(II)

Raghu N. Prasad, Ram P. Sharma and Mithlesh Jindal

Department of Chemistry, University of Rajasthan, Jaipur - 302 004 (INDIA)

Due to weaker complexing ability and lack of convenient physico-chemical properties to detect the weak metal-ligand interaction the coordination chemistry of alkali and alkaline earth metals remained neglected. Only recently, complexation studies of these metal ions with conventional as well as macrocyclic ligands have been undertaken following the recognition of various important roles of these metal ions in biological systems. However, the mixed ligand complexes of these metal ions have not yet been reported and the present paper describes the synthesis of the mixed ligand complexes of the type, $[MLL'(H_2O)_2]$ (where HL and HL' are two different carbonyl compounds such as salicylaldehyde, o-hydroxyacetophenone or 2,4-pentanedione and M = Mg(II), Ca(II), Sr(II) and Ba(II)).

These complexes have been characterized by elemental analyses, TLC, TGA, IR and electronic spectra. In TLC the mixed complexes showed single spot with R_f value being the intermediate of the two corresponding bis-complexes indicating that they are mixed complexes rather than a mixture of two bis-complexes. A split band at ~1650 cm^{-1} in the IR spectra of mixed complexes indicates the presence of two different coordinated carbonyl groups. The presence of two coordinated water molecules is supported by TGA and IR spectra.

The electronic spectra exhibit a number of additional bands in the mixed ligand complexes as compared to the corresponding bis-complexes, which is in accord with the lower symmetry of the mixed ligand complexes. As the symmetry of the complex is lowered the number of bands in the electronic spectrum is expected to increase because the crystal field states are further split, allowing more transitions.

Synthesis: To the ethanolic solution of the metal chloride an ethanolic solution of the two different carbonyl compounds was added (1:1:1 molar ratio). The pH of the reaction mixture was raised to 8.5 by adding ammonia drop by drop. The crystalline solid obtained was filtered, washed with ethanol and dried in vacuo.

The mixed complexes could also be prepared by adding ethanolic solution of two ligands to freshly prepared metal hydroxide suspension and heating the contents on a water-bath for about 15 minutes.

MIXED - LIGAND COMPLEXES OF COPPER(II) WITH 2,2',2" TERPYRIDINE AND SOME MONOSUBSTITUTED PHENOLS

WHEI-LU KWIK and KOK-PENG ANG

Department of Chemistry, National University of Singapore, Lower Kent Ridge Road, Singapore 0511, REPUBLIC OF SINGAPORE

A series of twelve mixed-ligand complexes, [Cu(tpy)L]Cl, where tpy = 2,2',2" - terpyridine and L = a monosubstituted phenol RC_6H_4OH [R = NO_2, CH_3, CH_3O, F, Cl, Br] has been synthesized and characterised. Unlike the mixed ligand complexes of copper(II) with 2,2'-bipyridyl and an oxygen donor ligand, these complexes can be isolated satisfactorily only by the reaction of $[Cu(CH_3CN)_4]^+$ with tpy and phenol in acetonitrile-ethanol. The Cu(I) complex ensued rapidly oxidises to yield the Cu(II) form. The X- band EPR spectra in 5:1 methanol : water at 77°K are well resolved, indicating that these complexes are monomeric in the solvents used. The spin Hamiltonian parameters [$g_{\parallel}$, $g_{\perp}$, $A_{\parallel}$ ($^{63/65}$Cu)] are typical of tetragonal Cu(II) complexes[1]. Results from electronic spectral, conductivity and magnetic susceptibility measurements are in accord with the above structural conclusions. The relative stabilities of these complexes in solution as determined by a study using the Method of Continuous Variation, demonstrate that the phenolic substituents have substantial influence on the ease of formation of these mixed ligand complexes. The spectral (IR, electronic, EPR) and electrochemical data will be discussed and compared with those of copper(II) complexes containing 2,2' bipyridyl and oxygen-donor ligands[2,3].

1. B.A. Goodman and J.B. Raynor, Adv. Inorg. Chem. Radiochem. 1970, 13, 135-362.
2. F.A. Walker, H. Sigel and D.B. McCormick, Inorg. Chem. 1972, 11, 2756.
3. W.L. Kwik and K.P. Ang, Aust. J. Chem., 1978, 31, 459.

ATTEMPTS TO SYNTHESIZE 5-COORDINATE DIMETHYL SULFOXIDE COMPLEXES OF PLATINUM(II)

Luther E. Erickson, Douglas R. Wright, and Gregory E. Vignoul

Grinnell College, Grinnell, Iowa, USA, 50112

Van der Poel, et al. have succeeded in making a wide variety of stable 5-coordinate mixed olefin-diamine or olefin-diimine complexes of general structure I.[1] The compounds were all prepared by the simple reaction of the nitrogen chelating agent with Zeise's salt analogs in a dry, non-polar solvent, Eqn. (1).

(1) $K[Pt(olefin)Cl_3]$ + :N:N →  + KCl

I

Recognizing the similarities in DMSO and olefins as ligands for platinum, we have attempted to prepare analogous 5-coordinate DMSO complexes by the reaction of nitrogen chelates with $K[Pt(DMSO)Cl_3]$ in non-polar solvents. The results obtained with several different nitrogen chelates will be described.

In general, reactions with the DMSO complexes are much slower than corresponding reactions with Zeise's salt and the products are much less stable. Though nmr evidence suggests initial formation of the 5-coordinate species in some cases, subsequent work-up of reaction mixtures usually led to isolation of the 4-coordinate species, $Pt(N\text{-}N)Cl_2$.

The reactions with N,N'-t-butyldiamine and N,N'-t-butyldiimine were particularly smooth and provide an interesting contrast. For the diamine, though the 5-coordinate species is the initial product of the reaction, a stable equilibrium is reached between 5-coordinate and 4-coordinate species in a few hours at room temperature. By contrast, for the diimine, a bridged dimer with two 4-coordinate Pt moieties per diimine, was obtained as the only significant product. An nmr study of the dimer suggests that its structure is drastically different from that of the analogous phosphine and arsine bridged complexes reported by Van der Poel et al.[2] for N,N'-t-butyldiimine.

1. H. Van der Poel, G. Van Koten, M. Kookes, C.H. Stam, Inor. Chem. 1981, 20, 2941.

2. H. Van der Poel, G. Van Koten, K. Vrieze, M. Kokkes, C.H. Stam, Inorg. Chim. Acta, 1980, 39, 197.

ORGANOMETALLIC CHEMISTRY OF METAL CYANIDE COMPLEXES

Louis S. Stuhl, R. del Rosario and S.J. Carter

Brandeis University, Department of Chemistry, Waltham, MA USA 02254

We have developed a crown-ether based technology for carrying out reactions on the heretofore essentially intractable low-valent metal cyanides.[1] This has enabled us to carry out the first detailed study of the reactivity of $K_4Ni(CN)_4$ (1). This compound reacts with alkynes and electron deficient alkenes to yield novel π-bonded organonickel cyanide complexes. Compound 1 reacts with diphenylacetylene to give $(K\cdot 18\text{-CROWN-6})_2[(\eta^2\text{-PhCCPh})Ni(CN)_2]$ (2). Compound 2 is inert to excess diphenylacetylene, but reacts with CO to provide the first synthesis of a completely pure salt of the $Ni(CN)_2(CO)_2^{2-}$ anion. Benzyl halides are coupled by reaction with 2. Benzaldehyde undergoes condensation with acetonitrile solvent during reaction with 1 and crown ether producing a cinnamonitrile complex. 1 plus crown ether is unreactive to H_2, CO_2 or simple alkenes and dienes. Curiously, unlike $K_4Ni(CN)_4$, $K_4Ni_2(CN)_6$ reactions are not substantially facilitated by added crown ether.

Reduction of $(K\cdot crown)_3\ Co(CN)_5$ in the presence of alkynes gives several organometallic products in low yield, depending on the alkyne. Diphenylacetylene is catalytically trimerised to hexaphenylbenzene under these conditions. Cyclopentadienylcobalt systems are more tractable. $C_5H_5Co(CO)_2$ cleanly substitutes one CO thermally or photolytically with (K·crown)CN to give $(K\cdot crown)[C_5H_5Co(CO)(CN)]$ (3). Attempts to substitute the second carbonyl by cyanide lead to decomposition. Compound 3 reacts with PhCCPh to give $(\eta^4\text{-}C_4Ph_4CO)Co(C_5H_5)$ and several minor products with negligible alkyne trimerization. 3 is not simply alkylated by benzyl bromide; a complex product mixture results. Efforts to synthesize $[C_5H_5Co(CN)_2]^{2-}$ salts will also be discussed.

1. R. del Rosario and L.S. Stuhl, submitted for publication.

CYANO-BRIDGED MIXED VALENCE COPPER(I,II) SPECIES

Oren P. Anderson, Joseph H. Reibenspies, and Susan K. Laird

Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523, USA

Stoichiometric mixtures (1:2) of the $Cu(CN)_3^{2-}$ anion and the copper(II) complex cation of ligand 1 (1 = the monoanion of 3,9-dimethyl-4,8-diazaundeca-3,8-diene-2,10-dione dioxime) yield the trinuclear cyano-bridged mixed valence complex 2, $[Cu(1)]_2[Cu(CN)_3]$. A structural study of 2 shows it to consist of a trigonal planar tricyanocuprate(I) anion which employs two cyano ligands to bridge to two $Cu(1)^+$ complex cations. The third cyano ligand is nonbridging. The structural study clearly shows that the bridging cyano ligands are bound to copper(I) through carbon and to copper(II) through nitrogen. The two bridging interactions are not equivalent, one being nearly linear (Cu(II)-N-C=172.6°) while the other is distinctly nonlinear (Cu(II)-N-C=157.2°). This difference in bridge geometry results in significant differences in the coordination geometries about the copper(II) atoms in the two nonequivalent $Cu(1)^+$ complex units.

Addition of $Cu(1)^+$ to a solution in which the dicyanocuprate(I) monoanion is the predominant Cu(I) species results in isolation of species 3, formulated as $[Cu(1)][Cu(CN)_2]$. Structural study of two different crystalline forms of 3 show both to consist of long polymeric chains in which copper(I) atoms are bridged by cyano ligands. These polymeric chains can serve as polymeric ligands, since only one cyano group is used for bridging between Cu(I) atoms. In both structures the second cyano ligand on each Cu(I) is also bound (through nitrogen) to the copper(II) atom of a $Cu(1)^+$ unit. The two crystalline forms of 3 are shown to arise from a different pattern of linear/nonlinear cyanide bridging modes in the two cases. Distinct spectroscopic differences between the two polymeric ligand systems can be shown to reflect the observed differences in structure.

THE ISOLATION OF TWO, SINGLY BRIDGED, DIMERIC SPECIES IN THE O_2 OXIDATION OF $Cr(H_2O)_6^{2+}$ to $[Cr(H_2O)_4(OH)]_2^{4+}$

James E. Finholt, Arthur Glasfeld, Elizabeth Bent, Jane Weier

Carleton College, Northfield, Minnesota, USA, 55057

When 0.05 M $Cr(H_2O)_6^{2+}$ in 0.05 M $HClO_4$ is treated with excess O_2 the solution turns green. After about an hour at 24 °C the solution is blue and is almost 100% $[Cr(H_2O)(OH)]_2^{4+}$. Analysis of spectral, ion exchange, acid-base, and redox properties of the green solution suggest that 99% of the chromium is present as an equilibrium mixture of two, singly bridged, dimers.

$$(H_2O)_5Cr^{H}{}^{O}Cr(OH)(H_2O)_4^{4+} + H^+ = (H_2O)_5Cr^{H}{}^{O}Cr(H_2O)_5^{5+}$$

Preliminary results indicate that the equilibrium constant for this reaction is between 20 and 40.

Mp13-10

FORMATION OF DOUBLE ZINC-COBALT ORTHOPHOSPHATES AND THEIR NATURE

M.M.Antroptseva and L.N.Shchegrov

Ukrainian agricultural Academy, Kiev, USSR

Synthesis conditions of double zinc-cobalt orthophosphates are determined of $Zn_{3-x}Co_x(PO_4)_2 \cdot 4H_2O$ ($0<x \leq 1.00$) composition with the structure of orthorhombic hopeite and $Zn_{1-x}Co_x(H_2PO_4)_2 \cdot 2H_2O$ ($0<x<1.00$) crystallising in monoclinic system (space group $P\,2_1/n$, $Z=2$).

The former represent solid solutions on the basis of $Zn_2Zn(PO_4)_2 \cdot 4H_2O$ and are formed as the result of a partial or complete isomorphic substitution of zinc in the coordinational polyhedron (octahedron) by cobalt. Their individuality is proved and limiting of formation is explained by production of the extremely saturated solid solution of $Zn_2Co(PO_4)_2 \cdot 4H_2O$ composition.

$Zn_{1-x}Co_x(H_2PO_4)_2 \cdot 2H_2O$ dihydrophosphates are deposited as mixed crystals being structurally similar to $Zn(H_2PO_4)_2 \cdot 2H_2O$ and $Co(H_2PO_4)_2 \cdot 2H_2O$. Unlike $Zn_{3-x}Co_x(PO_4)_2 \cdot 2H_2O$, they form a continuous series of solid solutions of substitution. Formation of double isostructural orthophosphates takes place without a change of the main structural motive of the crystalline lattice. The space group of crystal symmetry is preserved.

Physical and chemical properties of the produced compounds are investigated. The state of water is studied and the influence is evaluated of cation's nature on the energy of hydrogen bonds being realised in the structure of double orthophosphates. Chemism of their thermolysis is stated and the change of the crystalline structure of initial compound and cation coordinational number, accompanying it. It is noted that dehydratation of dihydrophosphates proceeds with the formation of free phosphoric acids, as an intermediate thermal treatment products.

Mp13-11

THE CHEMISTRY OF $CoX(PMe_3)_3$ COMPLEXES : REACTION WITH LEWIS BASES

M.Dartiguenave, B.Capelle, L.C.Ananias de Carvalho, Y.Peres, Y.Dartiguenave ,*A.L.Beauchamp

Laboratoire de Chimie de Coordination, 205 Rte de Narbonne Toulouse 31400 France

Département de Chimie, Université de Montréal, C.P. 6210 ,Succ.A , Montréal, Qué H3C 3V1 Canada *

The coordination chemistry of $CoX(PR_3)_3$ complexes with nucleophiles is still not well known when compared to rhodium and irridium analogs. One reason is the variety of species present in solution when these compounds are dissolved in an organic solvent. The number and the nature of these species are dependent on the solvent, the temperature, the nature of X, of PR_3 and on the added nucleophilic ligand.

We report here the reaction of $CoBr(PMe_3)_3$ with Lewis Bases such as ethylene, substituted ethylenes, diphenylacetylene, dienes.

The first step of the reaction appears to be addition of the nucleophile giving rise to a diamagnetic five coordinate species which is identified at low temperature by NMR spectroscopy. Depending on the solvent, molecular or cationic species are obtained.

In toluene, molecular $CoBr(L)(PMe_3)_3$ compounds have been characterized by their A_2B or ABC ^{31}P NMR patterns, but have never been isolated pure.

In acetone, methanol , acetonitrile, the cationic species $\{Co(L)(PMe_3)_3\}^+$, $\{Co(L)_2(PMe_3)_3\}^+$, $\{Co(L)(MeCN)(PMe_3)_3\}^+$ have been identified by ^{13}C, ^{31}P, ^1H NMR spectroscopy. They have been isolated in the solid state as tetraphenylborate salts. Their molecular structure, together with the characteristics of the coordinated Lewis base have been confirmed by their crystal structure determination when L = C_2H_4 , C_2Ph_2, C_4H_6 (1).

Two other Co(I) species are also present in the solution : $\{Co(PMe_3)_4\}^+$ which gives rise to $\{Co(L)(PMe_3)_4\}^+$ complexes and $\{Co(PMe_3)_2\}^+$ isolated and characterised as $\{Co(PMe_3)_2BPh_4\}$ by NMR and X-ray structure.

All these results will be compared and discussed in relation with the reactivity of these cobalt(I) species.

1. B.Capelle, A.L.Beauchamp, M.Dartiguenave, Y.Dartiguenave, H.F.Klein J.Amer.Chem.Soc. 1982, 104, 3891

B.Capelle, M.Dartiguenave, Y.Dartiguenave, A.L.Beauchamp, J. Amer. Chem.Soc. 1983, 105, 4662

CATION-SOLVATED COMPLEXES OF ALKALI AND ALKALI EARTH HALIDES WITH TRIS(2-HYDROXYALKYL)AMINES

M.G. Voronkov and V.P. Baryshok
Institute of Organic Chemistry, Siberian Division of the USSR Academy of Sciences, 664033 Irkutsk, USSR

The interaction of alkali and alkali earth halides (MX and MX_2) with tris(2-hydroxyalkyl)amines, $N(CH_2CHROH)_3$ (R = H, CH_3) in acetonitrile, methanol or their mixture has been studied.

Fluorides of higher alkali metals (M = K, Rb, Cs) form with triethanolamine (TEA) 1:2 adducts (I). Halides with M = Li, Na, K (X = Cl, Br, I) afford with TEA 1:1 cation-solvated complexes (II) if the ion radii ratio (r_M/r_X) ranges within 0.35-0.60.

The complexes (I) and (II) are hygroscopic crystalline substances with the melting point below 130°C.

In methanole or its mixture with acetonitrile, 1:1 MX_2-TEA complexes (III) are formed. However, the possibility of their formation is not determined by a simple r_M/r_X ratio.

The MX and MX_2 complexing with tris(2-hydroxypropyl)amine (TIPA) is not identic to that with TEA. The adducts formed (IV) are more readily soluble in organic solvents than (I-III).

The ^1H and ^{15}N NMR and IR spectra of (I-IV) and the stability constants have been studied and determined. It is suggested that the cation M in (I) displays a cubic geometry, the fluorine anion being in the outer coordination sphere.

The complexes (I-IV) can be used in anion-exchange reactions instead of crown ethers and for the creation of transporting systems controlling the ion-exchange in cell membranes.

DIFFERENTIAL POLARIZED ABSORPTION IN CRYSTALLINE COORDINATION COMPOUNDS

Hans Peter Jensen

Chemistry Department A, Building 207, Technical University of Denmark, DK-2800 Lyngby, Denmark

Differential polarized absorption methods based on phase modulation have in the last decade become rather popular as a mean of assigning electronic and conformational states of molecules and complex ions.[1]

The success rests on considerations based on optical calculus[2] and use of a photoelastic modulator.[3] As far as use of optical calculus is concerned this allows us to show how mixed phenomenological effects can be understood in terms of non-commutivity of spin matrices and how the pure effects may subsequently be extracted from a series of experiments with varying setting in the optical train.

Thus in principle it is possible to measure e.g. the circular dichroism of a linear anisotropic medium. The molecular interpretation, however, may very well present a series of problems. One problem is that the electric field vector in a crystal is not normally transvers to the direction of propagation. Another problem rise from the internal field on a molecule in a crystal, so that one in general do not observe the absorption spectrum of a molecule to be the same in the crystal and in isolation. If furthermore the crystal is linear anisotropic the relationship between the electric field and a molecule is given by a tensor rather than by a numerical factor.

The paper will demonstrate how these problems are overcome for a series of cobalt(III) trisdiamine complexes.

1. H.P. Jensen, Appl. Spectrosc. Rev. 1982-83, 18, 305.
2. H.P. Jensen, J.A. Schellman and T. Troxell, Appl. Spectrosc. 1978, 32, 192.
3. J.C. Kemp, J. Opt. Soc. Am. 1969, 59, 950.

SINGLE-CRYSTAL POLARIZED SPECULAR REFLECTANCE SPECTROSCOPY ON INTENSE ELECTRONIC TRANSITIONS

Ronald L. Musselman

Principia College, Elsah, Illinois, U.S.A. 62028

Specular reflectance spectroscopy is a useful technique for obtaining polarized single-crystal spectra in the UV through IR ranges when high transition intensities render other techniques difficult.

Traditional absorption data may be obtained from reflection values through a Kramers-Kronig transformation based upon Fresnel's equation for the absorption coefficient, $k = -2r \sin\theta / 1 + r^2 - 2r\cos\theta$. The Kramers-Kronig relationship, $\theta(\omega) = \frac{2\omega}{\pi} \int_0^{\infty} \frac{\ln r}{\omega^2 - \omega'^2} d\omega'$, provides the phase change upon reflection. Good estimates of electrical conductivity when present may be obtained through applying the optical constants to Drude theory for electrons in metals.

The instrumentation for determining reflectance is based upon a polarizing microscope for ease in crystal handling and light imaging[1], with standard light sources and detectors, and is computer-controlled.

Spectra of crystalline monomers, dimers, and interacting chains have shown well-defined spectra having ε_{max} values from 5×10^2 to 8×10^4, as well as metallic reflection with plasma edges rising to 95%.

Polarizations of single-molecule charge transfer transitions have been obtained, for example in the tetracyanonickelate anion where the cesium-potassium salt provided a non-interacting crystalline arrangement and the sum of the in-plane and out-of-plane polarizations matched closely the solution spectrum[2].

The spectra of the dimeric complex $KCuCl_3$ have been compared with the $CuCl_4$ monomer[3], and show an interesting, intense new "dimer" band. Observation at reduced temperature (78K) gives a pronounced improvement in resolution.

Interacting chains of tetracyano nickelates,-palladates, and -platinates provide an excellent probe of delocalization through a prominent red-shifted peak with intensities as high as $\varepsilon_{max} = 8 \times 10^4$. Extreme interaction, as in mixed-valence tetracyanoplatinates leads to one-dimensional conductivity with values measured optically in the same range as those measured by the four-probe technique[5].

1. Anex, B.G., Mol. Cryst 1960, 1, 1.
2. Musselman, R.L.; Stocher, L.C.; Watkins, S.F., Inorg. Chem., 1980, 19, 3400.
3. Desjardins, S.R.; Penfield, K.W.; Cohen, S.L.; Musselman, R.L.; Solomon, E.I.; J. Am. Chem. Soc., 1983, 105, 4590.
4. Anex, B.G.; Musselman, R.L., J. Phys. Chem, 1980, 84, 883.
5. Musselman, R.L.; Williams, J.M., J. Chem Soc., Chem. Commun. 1974, 186.

ELECTRONIC TRANSITION PROBABILITIES IN OPEN-SHELL METAL COORDINATION COMPOUNDS

Stephen F. Mason

Chemistry Department, King's College, London WC2R 2LS, U.K.

The Laporte-forbidden d-d or f-f transitions of open-shell metal ions in largely ionic complexes acquire an electric dipole probability by two localised-systems *mechanisms*, where metal-ligand charge overlap is neglected. A first-order electric dipole transition moment arises, either from the mixing of the parity-forbidden with parity-allowed electron promotions under the electrostatic field of the ligands, or from transient dipoles induced in the ligand groups by an allowed even-multipole electric moment of the d-d or f-f excitation.

The electrostatic field and the ligand polarization mechanisms make complementary intensity contributions to the parity-forbidden transitions of a given metal complex, dependent upon the rank of the leading electric multipole moment. The polarization intensity contribution is larger for electric 2^2-pole than 2^4-pole transitions and, in the case of Ln(III) complexes, is negligible for 2^6-pole transitions, where the electrostatic intensity contribution is predominant. Cross-term intensity contributions, positive or negative, between the electrostatic and the polarization mechanisms are significant for 2^2-pole and 2^4-pole transitions.

The ligand polarization mechanism covers the ligand-hypersensitive *f-f* oscillator strengths of Ln(III) complexes, and the large d-d dipole strengths, with an abnormal *negative* temperature coefficient, of tetrahedral transition metal complexes. For the latter complexes of Co(II), the otherwise-anomalous *negative* sign of the electric dipole moment ratio of t_2-t_2 to e-t_2 d-electron transitions, obtained from the Faraday MCD strengths, B and C, is additionally accommodated by the polarization mechanism, as are the d-d rotational strengths of chiral Co(III) six-coordinate complexes.

Applied initially to complexes containing monoatomic ligands, with an effective isotropic polarizability, the ligand polarization mechanism is found to depend, on extension to polyatomic ligand cases, upon the anisotropy of the ligand polarizability tensor in complexes with the higher non-centric symmetries. The polarizability anisotropy gives non-zero transition-probability contributions which vanish in the mean-polarizability approximation, accounting for the d-d rotational strengths of chiral five-coordinate Cu(II) complexes, and some f-f dipole strengths in dihedral Eu(III) complexes.

S.F. Mason, Struct. Bonding, 39 (1980) 55;
J. Less Common Metals, 93 (1983) 45.

CIRCULAR DICHROISM SPECTRA IN THE SPIN-FORBIDDEN d-d TRANSITIONS OF $Cr^{III}(N)_6$ TYPE COMPLEXES

Sumio Kaizaki

Nara Women's University, Nara 630, Japan

The understanding of chiroptical spectra in the spin-forbidden d-d transitions of tris(diamine)chromium(III) complexes has much advanced in experiments and theories the last decade, still there have remained some ambiguous elucidations.[1-4] In order to study this subject, we examine the room-temperature solution circular dichroism (CD) spectra in the ^2E_g, $^2T_{1g} \leftarrow {}^4A_{2g}(O_h)$ transitions of the diastereomers, Λ-$[Cr(en)_x(R\text{-diamine})_y(S\text{-diamine})_z]^{3+}$ ($x + y + z = 3$) and Δ-, Λ-cis-$[Cr(NH_3)_2(R\text{-diamine})_2]^{3+}$, where the diamines used are (R)- and (S)-propylenediamine or (1R,2R)- and (1S,2S)-1,2-cyclohexanediamine.

The differences in observed CD spectra between each pair of the diastereomers are accounted for by separability and additivity of the configurational effect due to chiral arrangements of three or two diamines and the vicinal one due to puckered diamine rings and/or asymmetric carbons. The configurational CD curves in the spin-forbidden transitions of the tris- and bis(diamine) complexes give three peaks with alternate signs; (+), (-), (+) for Λ-type complexes as similarly observed for Λ-tris(en) and Λ-cis-diammine-bis(en) complexes. Meanwhile, the vicinal CD curves in the corresponding region exhibit four peaks; (-), (+), (-), (+) from the lower frequency side for the (R-diamine) complexes. The former two peaks are covered under the band envelope of the lowest frequency ^2E_g configurational CD as observed in $[Cr(L\text{-aminoacidato})(en)_2]^{2+}$ system.[5] The latter two correspond to the $^2T_{1g}$ configurational CD peaks associated with the $^2A_2$ and $^2E \leftarrow {}^4A_2(D_3)$ transitions in view of the peak positions. Consistent assignments of these configurational and vicinal CD peaks to the doublets $\leftarrow$ quartet electronic transitions in D_3 or D_3' field are made in connection with the CD in the first spin-allowed $^4T_{2g} \leftarrow {}^4A_{2g}$ transitions on the basis of the theoretical relation[1] between the rotational strengths for the spin-forbidden transitions and those for the first spin-allowed transitions. The CD behavior in the spin-forbidden transitions of $[Cr(NH_3)_4(R\text{-diamine})]^{3+}$ and the related complexes will also be discussed in a similar manner to the case of the tris- and bis(diamine) complexes. Through the present discussions, it will be demonstrated that the ^2E_g split components due to the electronic transitions to the Kramers doublets (2A and E) with a small spacing of less than 100 cm^{-1} can be observed by room-temperature CD measurements in solutions.

1) Kaizaki, S.; Hidaka, J.; Shimura, Y. Inorg. Chem. 1973, 12, 142.
2) Hilmes, G. L.; Brittain, H. G.; Richardson, F. S. Inorg. Chem. 1977, 16, 528.
3) Harnung, S. E.; Leier, T. Acta Chem. Scand. 1978, A42, 41.
4) Geiser, Urs; Güdel, Hans U. Inorg. Chem. 1981, 20, 3013.
5) Kaizaki, S.; Ito, M. Bull. Chem. Soc. Jpn. 1981, 54, 2499.

DETAILED CORRELATIONS BETWEEN THE LIGAND TO METAL CHARGE-TRANSFER (LMCT) SPECTRA OF Cu(II)- AND Ru(III) -IMIDAZOLES AND IMIDAZOLATES. ELECTRONIC STRUCTURES OF CARBON BOUND Ru(III)-IMIDAZOLES AND IMIDAZOLATES

Karsten Krogh-Jespersen and Harvey J. Schugar

Department of Chemistry, Rutgers, The State University of New Jersey, New Brunswick, New Jersey, USA 08903

The published[1] LMCT spectra of Ru(III)-imidazole and Ru(III)-imidazolate species are more fully interpreted. Intensity and energy shifts resulting from (a) ligand alkylation at ring carbon atoms, (b) linkage isomerism of the imidazole ligand (Ru-C vs. Ru-N bonding), and (c) deprotonation of either the N- or C- bound ligand are accounted for. On the basis of semiempirical MO calculations, a rationalization for this novel linkage isomerization reaction of Ru(II)-imidazole complexes is proposed. A number of poorly explored aspects of LMCT in model and native Cu(II)-imidazole and Cu(II)-imidazolate chromophores are better illuminated by the results and analysis of the Ru(III) analogs. LMCT spectra for the Cu(II) and Ru(III) complexes consist of excitations from upper occupied ligand σ,π-orbitals to the sole accessible metal ion d-vacancy and thus reflect the electronic structure of the ligands.

1. M.F. Tweedle and H. Taube, Inorg. Chem. 1982, 21, 3361.

OPTICAL ACTIVITY OF TRANSITION METAL COMPLEXES: AN ANGULAR OVERLAP MODEL FRAMEWORK FOR COMPUTER MODELING

Patrick E. Hoggard

Department of Chemistry, North Dakota State University, Fargo, ND 58105

The Angular Overlap Model is a particularly convenient vehicle for optical activity calculations because of the ease with which the exact geometry may be used to express the ligand field potential. Our work concentrates on the five narrow line components of the (O_h) ^2E_g and $^2T_{1g}$ bands of Cr(III) complexes, because of the unambiguous assignments of sign and magnitude which are possible. Broad band CD spectra are invariably composed of several overlapping components, often with opposite signs, making detailed interpretation difficult.

Our treatment includes full configuration interaction within the d^3 manifold, and allows evaluation of spin-orbit coupling and other ligand field parameters on optical activity. Of particular interest is the overall question of dissymmetry. There are actually two factors of importance here: the dissymmetric arrangement of the entire molecule, and that of the atoms bound to the metal ion(which are the only ones appearing in the ligand field potential). Both may contribute to the creation of nonzero electric dipole matrix elements, but the latter causes extensive mixing, which appears to have an even larger effect on rotatory strengths of the bands in question. Thus a $Cr(L\text{-}L)_3$ complex is calculated to (and of course, does) possess optical activity even when the L-Cr-L bond angle is 90°. But the rotatory strengths increase, especially for the spin-forbidden bands, with departure from orthoaxiality. Conformational isomerism can also be explicitly handled.

The broad spin-allowed bands can be well enough fit with a first-order perturbation expression for the rotatory strength, but a second order expansion is necessary to approach a good fit to the signs and magnitudes of the spin-forbidden bands.[1] Unfortunately, this has as a consequence the proliferation of fitting parameters.

1.F.S. Richardson, Inorg. Chem. 1972,11,2366.

FOURIER TRANSFORM ELECTRONIC CIRCULAR DICHROISM USING PHOTOTHERMAL DEFLECTION (MIRAGE) DETECTION

Richard A. Palmer, A. Claude Boccara and Danièle Fournier

Department of Chemistry, Duke University, Durham, North Carolina, USA, 27706, and Laboratoire d'Optique Physique, Ecole Supérieure de Physique et de Chimie Industrielles, 10, rue Vauquelin, 75005 Paris, France.

The measurement of the electronic circular dichroism (CD) of strongly absorbing and/or light scattering solids using the combined advantages of Fourier transform interferometry and photothermal deflection will be described. Results using both laboratory constructed and commercial interferometers will be given. In this work low frequency (ca. 20 hz) circular modulation of the interferometer output is achieved using tandem beat frequency photoelastic modulators.[1] Samples are immersed in an inert transparent liquid and the photothermal deflection of the probe laser beam is monitored by a position sensitive detector using standard lock-in amplification circuitry. This work brings together the strengths of previous efforts[2,3] and illustrates the potential of the method for obtaining optical activity data otherwise difficult to measure.

CD spectra have been measured of transition metal compounds in single crystals and in powders and the data compared where possible to those obtained by transmission techniques using dilute samples. Application to surfaces and surface supported materials will be discussed.

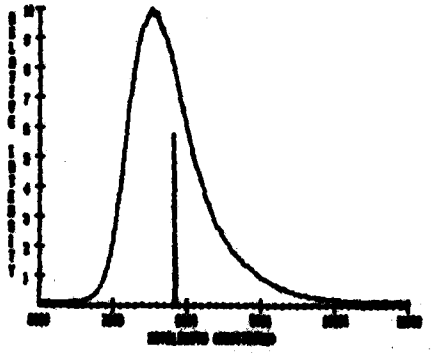
1. R. A. Palmer, J. C. Roark and J. C. Robinson, ACS Symposium Series, No. 119, p 375, 1980.
2. D. Fournier, A. C. Boccara and J. Badoz, Appl. Opt. 1982, 21, 74.
3. D. Déberre, A. C. Boccara and D. Fournier, Appl. Opt. 1981, 20, 4281.

TUNABLE SOLID STATE LASERS BASED ON Cr(III) $^4T_2$–$^4A_2$ FLUORESCENCE

Leonard J. Andrews

GTE Laboratories Incorporated, 40 Sylvan Road, Waltham, Massachusetts, USA 02254

When the Cr^{3+} ion is placed in a sufficiently low octahedral ligand field, broad infrared photoluminescence from the $^4T_2$ electronic level can often be observed. In many ionic crystals, this $^4T_2$–$^4A_2$ transition is purely radiative; that is, the fluorescence quantum efficiency is unity. In 1978, this transition was used to demonstrate the first tunable Cr^{3+} laser, $BeAl_2O:Cr^{3+}$ (the mineral alexandrite).[1] The alexandrite laser operates well in spite of the fact that the ligand field strength at the Cr^{3+} site causes the $^4T_2$ level to lie 800 cm^{-1} above the ^2E and have only 2% thermal population at 300 k. Since the announcement of alexandrite, we[2] and others[3] have been developing hosts in which the $^4T_2$ lies energetically lower than the ^2E. The figure below shows spontaneous fluorescence and untuned stimulated emission from such a host, $Gd_3Sc_2(GaO_4)_3$ or GSGG:Cr^{3+}.[3] We have been developing two types of



GSGG:Cr^{3+} spontaneous $^4T_2$–$^4A_2$ fluorescence and lasing output at 786 nm in an untuned resonator.

low field hosts, the germanium garnet $Ca_3Sc_2(GeO_4)_3$ and the fluoride elpasolite K_2NaScF_6. Spectroscopic, photophysical, and crystal growth properties of these Cr^{3+} doped hosts will be discussed.

1. J.C. Walling, O.G. Peterson, H.P. Jenssen, R.C. Morris, and E.W. O'Dell, IEEE J. Quant. Elec. QE-16, 1302 (1980).

2. P.T. Kenyon, L. Andrews, B. McCollum, and A. Lempicki, IEEE J. Quant. Elec. QE-18, 1180 (1982).

3. D. Pruss, G. Huber, A. Beimoroski, V.V. Laptev, I.A. Shcherbakov, and Y.V. Zharikov, Appl. Phys. B 28, 355 (1982).

CHROMIUM(III) BROAD-BAND QUARTET-QUARTET LUMINESCENCE IN GLASS CERAMICS WITH HIGHER YIELD THAN IN COMPLEXES

Renata Reisfeld*and Christian K.Jørgensen**

*Enrique Berman Professor of Solar Energy,Department of Inorganic Chemistry,Hebrew University,Jerusalem,Israel
**Section de Chimie,Université,CH1211 Geneva4,Switzerland

A-third of the 120 states of $3d^3$ have S=3/2.In octahedral symmetry,the groundstate is $^4A_{2g}$,and the excited quartets $^4T_{2g}$ and $^4T_{1g}$ provide rather intense,spin-allowed absorption bands. The transitions to the two lowest doublets ^2E_g and $^2T_{1g}$ (almost coiciding;they may also produce a complicated $^4T_{1g}$ structure of $^4T_{2g}$ in the red)are weak,but narrow[1]. The fluorescence of ^2E_g in the ruby and in $Cr(CN)_6^{-3}$ is well-known,and has almost the quantum yield 1 under favorable conditions.In the Tanabe-Sugano diagram,the crossing of $^4T_{2g}$ (the centre of the broad band indicates the sub-shell energy difference Δ also called 10Dq)and ^2E_g occurs at the ratio(called"ligand field strength"by Schäffer[3]) Δ/B close to the value 21 predicted for well-defined t_{2g}^3 and $t_{2g}^2e_g$.

Some Cr(III)complexes show emission from $^4T_{2g}$ for ligand field strengths below the crossing-point (or slightly above,allowing for vibrational de-excitation) but it is very weak[2] and usually only observed by strong cooling. The broad emission band would be quite useful for planar luminescent concentrators of solar energy[3,4] combined with photovoltaic silicon.Octahedral chromophores $Cr(III)O_6$ in glasses do not show quantum yields of $^4T_{2g}$ above 0.17 in lithium calcium silicate[5] and 0.22 in lithium lanthanum phosphate glass[4].The mechanism of non-radiative de-excitation is not similar to trivalent lanthanides[6] and seems related to vibrational amplitudes of the quartets.In collaboration with Drs.M.Ish-Shalom and A.Buch,Israel Ceramics and Silicate Institute,Haifa,0.02molar Cr(III) in glasses[7] (mole %)$58.7SiO_2$:$16.7Al_2O_3$:$17.8MgO$:$6.7TiO_2$ and $70.2SiO_2$:$15.0Al_2O_3$:$4.4ZnO$:$7.1Li_2O$:$1.5TiO_2$:$1.5ZrO_2$:$0.3As_2O_3$ molten together at 1570°C were shown,by appropriate treatment,to form transparent glass ceramics containing microcrystallites of spinel $MgAl_{2-x}Cr_xO_4$ and gahnite $ZnAl_{2-x}Cr_xO_4$,respectively.The relative intensity of $^4T_{2g}$ (around 800 nm)and (weaker) ^2E_g emission(at 700 nm) depends on exciting wavelength(due to differing glass sites)but is very high.

1. C.K.Jørgensen,Oxidation Numbers and Oxidation States, Springer-Verlag,Berlin and New York,1969.
2. H.L.Schläfer,H.Gausmann&K.Witzke,J.Chem.Phys.1967,46,1423.
3. R.Reisfeld&C.K.Jørgensen,Struct.Bond.1982,49,1.
4. R.Reisfeld,J.Less-Common Metals 1983,93,243.
5. L.J.Andrews,A.Lempicki&B.C.McCollum,J.Chem.Phys.1981,74, 5526.
6. R.Reisfeld&C.K.Jørgensen,Lasers and Excited States of Rare Earths,Springer-Verlag,Berlin and New York,1977.
7. R.Reisfeld,A.Kisilev,E.Greenberg,A.Buch & M.Ish-Shalom, Chem.Phys.Lett.,submitted.

SPECTROSCOPIC STUDIES OF THE ELECTRONIC STRUCTURE OF $CuCl_4^=$ AND ITS PARALLELS TO THE BLUE COPPER ACTIVE SITE

Kevin W. Penfield, S. R. Desjardins, S. L. Cohen, Andrew A. Gewirth, Edward I. Solomon

Stanford University, Department of Chemistry, Stanford, California 94305, USA

Our group has been extremely interested in electronic theoretical, and spectral studies of the $CuCl_4^=$ complex because of the relative simplicity of its geometric and electronic structure and for its utility as a spectral analog to the Blue Copper Active Site. This d^9, one hole complex is found in a variety of geometries ranging from flattened tetrahedral (D_{2d}) to square planar (D_{4h}); Dimeric units ($Cu_2Cl_6^=$) are also structurally defined. These highly symmetric complexes provide excellent systems for correlating changes in electronic structure with changes in geometry. A combination of polarized single crystal optical absorption, reflectance and X-ray absorption spectroscopy, variable energy photoelectron spectroscopy, EPR, variable temperature MCD, and SCF-Xα-SW theoretical studies have been used to study the ground state wavefunction, and d-d and CT excited states of a variety of $CuCl_4^=$ complexes.[1,2] Parallel results on the electronic structure and bonding in the blue copper active sites will also be presented.[3,4]

References:

1. S. R. Desjardins, K. W. Penfield, S. L. Cohen, R. L. Musselman and E. I. Solomon, J. Am. Chem. Soc., 105, 4590 (1983).

2. J. E. Hahn, R. A. Scott, K. O. Hodgson, S. Doniach, S. R. Desjardins and E. I. Solomon, Chem. Phys. Lett. 88, 595 (1982).

3. K. W. Penfield, R. R. Gay, R. S. Himmelwright, N. C. Eickman, V. A Norris, H. C. Freeman, and E. I. Solomon, J. Am. Chem. Soc. 103, 4382 (1981).

4. K. W. Penfield, A. A. Gewirth, E. I. Solomon, to be published.

THEORETICAL STRUCTURE ELUCIDATION OF SHORT LIVED TRANSIENTS GENERATED BY PULSE RADIOLYSIS OR FLASH PHOTOLYSIS OF PLATINUM CHLORIDE COMPLEXES

H.CHERMETTE[1], A.GOURSOT [2], E.PENIGAULT [2], M.CHANON [3] and W.L.WALTZ [4]

1- Inst.de Phys.Nucléaire,43 Bd du 11 Novembre 1918, F-69622 Villeurbanne Cédex, France

2- Ecole Nat.Sup.Chimie, 3,rue Werner, F-68093, Mulhouse Cédex, France

3- Université d'Aix Marseille, rue H.Poincaré, F-13397 Marseille Cédex,France

4- Université of Saskatchewan, Saskatoon, Sask, S7N OWO, Canada

Relativistic MSXα calculations have been performed on Pt (III) models of transients generated either by pulse radiolysis of $PtCl_4^{2-}$ in water or in NaCl solutions, or by pulse radiolysis or flash photolysis of $PtCl_6^{2-}$. Calculated electronic structures and charge transfer absorption spectra have been obtained for $PtCl_4O^{3-}$, $PtCl_4(OH)^{2-}$, $PtCl_5(OH)^{3-}$, $PtCl_4(OH)_2^{3-}$, $PtCl_4(OH)(H_2O)^{2-}$, $PtCl_5^{2-}$, $PtCl_6^{3-}$ and $PtCl_4^-$ with, when necessary, different geometries and/or bond lengths.

The comparison of the theoretical values with experiment suggests :

i) the common species generated by pulse radiolysis or flash photolysis of $PtCl_6^{2-}$ is probably $PtCl_4^-$ (D_{4h}) although the possibility of weakly coordinated apical ligands cannot be ruled out.

ii) the short lived transient generated by pulse radiolysis of aqueous solutions of $PtCl_4^{2-}$ is best described as $PtCl_4(OH)^{3-}$, while the transient species observed in chloride medium (neutral or acidic) may be $PtCl_6^{3-}$ with moderate axial bond lenghts elongation.

Mp15-01

COORDINATION CHEMISTRY IN THE CURRICULUM IN PORTUGAL

J. O. CABRAL

Faculdade de Ciências, Universidade do Porto
4000 Porto, Portugal

Coordination Chemistry is taught at practically all the Portuguese Universities, although with large differences in breath and depth among Universities.

At the bachelor's level (first three years) it is generally included in Inorganic and in Analytical Chemistry courses; at the licenciate's level (following one or two years) it can appear as an independent optional subject, thus including formal teaching and an appropriate research project.

At the graduate level (M.Sc. or Ph.D.), students will join a research group. It is at this level that Coordination Chemistry finds its strength in Portugal, where there are several groups engaged in research of good standard.

The main features of Coordination Chemistry in the curriculum in Portuguese Universities will be described, with special emphasis on the University of Porto.

COBALT(II) AMMINE COMPLEXES AS REVERSIBLE ABSORBER OF OXYGEN — STUDENT EXPERIMENTS IN HIGH SCHOOLS

Kazuko Ogino, Isamu Otsuki, Kou Ishiyama and Kazuo Saito

College of Medical Sciences and Department of Chemistry, Faculty of Science, Tohoku University, Sendai 980 Japan

Cobalt(II) ions in aqueous ammoniacal solutions are readily oxidized by molecular oxygen to binuclear cobalt(III) complexes:

$$2\,Co(NH_3)_5^{2+} + O_2 \rightleftharpoons [Co(NH_3)_5O_2Co(NH_3)_5]^{4+} \quad (1)$$

which are decomposed in basic solutions containing EDTA to give Co(II)EDTA and O_2:[1]

$$[Co(NH_3)_5O_2Co(NH_3)_5]^{4+} + 2\,Hedta^{3-} \rightarrow 2\,Coedta^{2-} + 8\,NH_3 + 2\,NH_4^+ + O_2 \quad (2)$$

We have attempted to utilize these reactions for student experiments in high schools.

Estimation of oxygen content in atmosphere: The uptake of atmospheric oxygen by the aqueous mixture of $CoCl_2$, NH_3 and NH_4Cl according to eq 1 was measured volumetrically by the use of a syringe and a disposable 3-way stopcock. The reaction was quick and reproducible. The remaining gas in the syringe was collected and tested for the absence of oxygen. The solution in the syringe was then mixed with an EDTA solution in another syringe and the liberated amount of oxygen (eq 2) was measured. The experiments were performed by ca. 200 students in classes and in club activities in 2 junior and 6 senior high schools. The results are as follow:

1. The oxygen content in atmosphere thus determined was in the range of 19 ± 2 %, and the recovery of oxygen by Reaction 2 was in the range of 100 ± 6 %.
2. The reaction sequence 1 and 2 is understandable to students and arouses their interest to transition metal complexes.
3. The experiments are easy to handle, involve no danger, can be completed within 50 min, and seem to be very much suited for student experiments.

Application to subjects involving reactions of biological interest: The above-mentioned procedure for the estimation of oxygen content can be applied to various other subjects:

1. Evolution of oxygen by the photosynthesis of green plants: Sprays of some needle-leaf trees in a polyethylene bag filled with CO_2 are irradiated by an electric lamp. After 30 min, the oxygen content of the gas in the bag is measured.
2. The catalytic evolution of O_2 from H_2O_2 by catalase of animal livers: The catalytic reaction can be followed by measuring the volume of oxygen.
3. The oxygen content of the gas left after combustion: A candle is burned in a stoppered flask. After the flame has gone out, the oxygen content of the gas left in the flask is determined.

1) R. G. Wilkins, Advan. Chem. Ser. 1971, 100, 111.

THE IMPORTANCE OF COORDINATION CHEMISTRY AS A DISCIPLINE PROMOTING THE INTEGRATION OF THE UNDERGRADUATE CURRICULUM

Ernesto Giesbrecht, Ana Maria C. Ferreira and Henrique E. Toma

Instituto de Química, Universidade de São Paulo, CP 20780, São Paulo, SP, Brazil

Coordination chemistry can have an exceptional role as a discipline, by promoting the integration of the undergraduate curriculum. Because of its interdisciplinary character, many of the fundamental concepts in chemistry can be dealt with in a broad sense, providing an unified view of the problems.

Symmetry, stereochemistry, electronic structure, magnetism, spectroscopy, thermodynamics, equilibrium, kinetics and photochemistry are typical subjects which have been taught in this way, in a coordination chemistry course, at the University of São Paulo (Brazil). Scheduled regularly at the third year level, the course offers an unique opportunity of teaching and practing synthetic, analytical and instrumental techniques. Theory and laboratory have followed an unified approach, covering the basic aspects of coordination chemistry, metal ion catalysis and bioinorganic chemistry.

The limitations faced by the third world have required the development of simple and convenient techniques, using inexpensive materials. Research in this area have improved the teaching of coordination chemistry, generating new, alternative experimental approaches. Some typical successful examples have been recently described in the literature.[1,2]

1. A.M.C. Ferreira and H.E. Toma, Química Nova, 1982, 5, 131.
2. H.E. Toma, A.M.C. Ferreira and V.K.L. Osório, J. Chem. Ed., 1983, 60, 600.

THE CONCEPT OF VIBRONIC INTERACTIONS IN THE CURRICULUM OF COORDINATION CHEMISTRY

I.B.Bersuker

Institute of Chemistry, 277028 Kishinev USSR

Among the achievements of the theory of electronic and molecular structure in the past quarter of the century the development of a new concept, the concept of vibronic interactions[1], which gets over the separate description of the motions of electrons and nuclei in the adiabatic approximation by means of taking into account explicitely the mixing of electronic states by nuclear displacements, seems to be of primary importance. It is most essential for systems with relatively (but absolutely not necessarily) close in energy electronic states,e.g coordination compounds (or when there are changes in electronic population of molecular orbitals (MO), e.g. by coordination), and allows to explain from a common point of view (and to predict new) effects and laws in all the areas of modern chemistry and physics of molecules and crystals, including recently discussed problems of stereochemistry and crystal chemistry, reactivity and chemical activation, electron-conformational transitions in biologic systems. The usual presentation of electronic and molecular structure in the Curriculum is based on the adiabatic approximation resulting in a restricted stereotype thinking in which the origin of important details concerned the influence of electrons on the nuclear configuration, dynamics and transformations is lost. The concept of vibronic interactions is devoid of this fault and gives a key to the correct understanding and formation of a more adequate way of thinking in chemistry most important in the Curriculum.

1. I.B.Bersuker,The Jahn-Teller Effect and Vibronic Interactions in Modern Chemistry, Plenum Press,N.Y.,1983.

PRACTICAL APPLICATIONS OF COORDINATION COMPOUNDS

Ronald D. Archer

Department of Chemistry, University of Massachusetts, Amherst, MA 01003

Metal coordination compounds are important throughout chemistry, both basic and applied. Too often chemical educators get so involved with discussions on the basic aspects of the subject (e.g., varied stereochemistries, isomer possibilities, simplified theories, thermodynamic stabilities, and reaction dynamics) that the practical aspects of the subject are not covered at all. Students appreciate knowing that the chemistry which they are studying has importance outside of the classroom, too.

Preformed chelates are utilized in a wide variety of applications.[1] To illustrate, lanthanide β-diketonates have found uses as lasers, antiknock petroleum additives, and NMR shift reagents. Coordination compounds serve as catalysts, both enzymatically and in organic synthesis; and new metal-containing enzymes and catalytically-active synthetic coordination compounds are reported frequently. The latter include both homogeneous and anchored catalysts of both mononuclear and metal-cluster types, as well as zeolites and photoactive catalysts. Coordination compounds are used as therapeutic agents, bactericides, fungicides, dyes, pigments, photographic and lithographic reagents, moisture indicators, and petroleum additives; for polymer stabilization, electroplating formulations, and ion-selective electodes. Potential applications include complexes for artifical blood, solar energy conversion, etc. The list could be expanded further.

Ligands have practical applications, too. A number of pharmaceutical drugs are available which can extract metal ions from biological tissue. Other ligands are used as bactericides, fungicides, and disinfectants. Metal deactivators include ligands which can prevent gum formation in gasoline or rancidity in butter. Many analytical methods involve the selectivity of ligands for metal ions. Again the list could be expanded.

Conversely, metal ions can interact with natural or synthetic chemicals which have ligating functional groups. Metal ions, either as compounds or complexes, often stabilize or otherwise modify polymers, dyes, and other organic and inorganic species through coordination.

1. R. D. Archer, "Coordination Compounds," in Kirk-Othmer: Encyclopedia of Chemical Technology, 3rd Edition, John Wiley and Sons, Inc., New York, 1979, Vol. 6, pp. 784 - 797.

COORDINATION CHEMISTRY IN THE CURRICULUM
WHAT SHOULD BE TAUGHT WHEN?

Stanley Kirschner

Department of Chemistry, Wayne State University, Detroit, Michigan 48202, U.S.A.

One of the major problems facing those concerned with developing curricula for courses that will include topics in coordination chemistry is the selection of appropriate topics for the various levels of instruction. In the USA topics in coordination chemistry are usually included in the first-year (freshman) chemistry course, as well as in advanced undergraduate (third or fourth year) courses in inorganic chemistry. Coordination chemistry is also included in advanced courses given at the graduate level in most US universities.

At the First-Year Level.- (About 5 lectures + qualitative analysis + two 4-hour laboratories + qualitative analysis lab.)

Included in the first-year course in general chemistry are introductory topics in coordination chemistry, including nomenclature, definitions of important terms, bonding in complexes, structure, isomerism, and elementary A.O. and C.F. concepts.

At the Junior-Senior Undergraduate Level (3rd-4th year).- (About 45 lectures + 80 hours of lab.)

Usually included in the courses at this level are an historical introduction, bonding theories (A.O., M.O., LFT, VSEPRT, etc.), optical activity (ORD, CD), spectra and structure, thermodynamics, stability, reaction rates and mechanisms, and a few special topics (e.g., biocoordination chemistry, "sandwich complexes", metal-metal bonding and cluster complexes, etc.)

At the Graduate Level.- (About 45 lectures)

Included in the courses at this level are advanced topics in coordination chemistry, including absolute configuration and conformation, MCD, pi-complexes, bridge complexes, catalysis, spectra interpretation,, nmr, epr, group theoretical concepts, bioinorganic topics, etc.

The Laboratory.

Syntheses normally constitute the most important part of laboratory courses that include coordination chemistry, as well as the resolution of racemic mixtures of dissymmetric complexes, determination and interpretation of spectra of various kinds (ORD, CD, nmr, ir, x-ray, uv-vis, etc.). Further, the synthesis of various types of ligands may also be included, as well as a special project, such as synthesizing a complex and its ligands, determining its various spectra, and determining its structure.

COORDINATION CHEMISTRY IN THE CURRICULUM OF INDIAN UNIVERSITIES

H.L. Nigam

A.P.S. University, Rewa (M.P.) 486003, India

Coordination compounds are finding increasing use in biological, medicinal and industrial catalytic processes. Coordination chemistry, therefore, has of necessity become an integral part of Chemistry curriculum at the university level. It is being taught as a special/optional/course paper in every Indian university at the post graduate level.

To the normal contents of coordination chemistry relating to structure, synthesis and reaction dynamics, topics like reactivity of coordinated ligands, the study of metallo enzymes, the study of metal encapsulates using macrocyclic ethers and cryptands have widened the scope enormously.

The ideas like that of vertical bonds, sandwich bonds and/or bonding of a whole molecule have posed a challenge to the ingenuity of the theoretical chemist. It is this multifaced growth of the subject that has led to some confusion as to proper scope of the subject of coordination chemistry. Whether Group theory and Graph theory should necessarily form a part of a course in coordination is not clear.

In the Indian universities' curriculum there is a lot of disparity in course content. The situation shall be analyzed in detail.

A NEW ASPECT OF HYDROLYSIS OF METAL IONS

Michael Ardon and Avi Bino

Department of Inorganic and Analytical Chemistry,
The Hebrew University of Jerusalem, Jerusalem 91904, Israel

In 1907 Alfred Werner defined the hydrolysis of metal ions as a dissociation of a water ligand into a hydrogen ion and a hydroxo ligand.[1] Accordingly, the product of hydrolysis of a diaqua metal salt such as *trans*-$[Co(en)_2(H_2O)_2]Br_2$ was formulated as a *hydroxoaqua* complex, *trans*-$[Co(en)_2(H_2O)(OH)]Br_2$. This universally accepted formulation requires the existence of two distinct oxygen ligands, OH and H_2O. One should be able, at least in principle, to distinguish between the OH ligand and the H_2O ligand in the structure of crystalline hydroxoaqua complexes.[1] Werner distinguished between *mononuclear* and *polynuclear* products of hydrolysis. In the latter the metal atoms are bridged by oxygen atoms that are always coordinated *directly* to two (or three) metal atoms. This O atom may, or may not, be protonated, forming a μ-hydroxo or a μ-oxo bridge respectively. All polynuclear hydrolytic species investigated or proposed since 1907 possessed this direct M-O-M bridge.

We discovered a new type of polynuclear hydrolytic products of metal ions. In these species neighboring metal atoms are not bridged by one O atom but by a *hydrogen oxide* ligand $H_3O_2^-$. This ligand is formed by a strong (>100 KJ) symmetric hydrogen bond between an OH ligand of one metal atom and an H_2O ligand of the other metal atom. It was first discovered in trinuclear clusters of Mo and W [2] and later in classical hydroxoaqua metal ions.[3] We conclude that Werner erred in assigning a mononuclear structure to "hydroxoaqua" ions in the crystalline state. The socalled *cis*-hydroxoaqua ions are dimers bridged by two H_3O_2 bridges and the socalled *trans*-hydroxoaqua ions are polynuclear chains of metal atoms bridged by single H_3O_2 ligands. Such dimers and polymers also exist in aqueous solutions of "hydroxoaqua" ions. "Olation" reactions in the solid state and in aqueous solutions proceed by elimination of water molecules from H_3O_2 bridges, accompanied by formation of OH bridges between metal ions. Some *redox* reactions in aqueous solution may proceed by cleavage of an H_3O_2 ligand bridging the oxidizing and the reducing ions. The net result of such a process is an "H atom transfer" mechanism proposed by Silverman and Dodson over 30 years ago.[4]

1. A. Werner, Ber. 1907, 40, 272-287; 2103-2125; 4434-4441; 4834-4844.
2. A. Bino and D. Gibson, J. Am. Chem. Soc. 1982, 104, 4383-4388.
3. M. Ardon and A. Bino, J. Am. Chem. Soc. 1983, 105, 7747-7748.
4. J. Silverman and R.W.J. Dodson, J. Phys. Chem. 1952, 56, 846-852.

TUESDAY MORNING

TUa16-01

LOW-TEMPERATURE PHOTOCHEMISTRY AND SPECTROSCOPY USING POLARIZED LIGHT

J.J. Turner and M. Poliakoff

Department of Chemistry, University of Nottingham, Nottingham, UK.

Low-temperature techniques such as matrix isolation and the use of liquid noble gas as solvents have been shown to be of value for the investigation of photochemical organometallic intermediates.[1] Most studies have involved mononuclear species (e.g. $Cr(CO)_6$); binuclear species present increased difficulties for interpretation. Thus techniques which provide additional information on photochemical mechanisms are welcome.

We have demonstrated[2] the value for organometallic and organic photochemistry of a combination of matrix isolation with photochemistry and spectroscopy using polarized light. In this technique - a development of Albrecht's 'photoselection' - randomly oriented matrix-isolated species are photolysed with plane polarized light; both parent compound and photoproduct are then examined in the infrared and UV/visible regionswith plane polarized light. Evidence is often found for 'dichroic photodepletion', 'dichroic photoproduction' and photoreorientation'; this lecture will show how these effects can lead to important deductions concerning photochemical mechanisms.

Recently we have been extending the technique to polynuclear species and the results of these experiments will be described.

1. see e.g. J.J. Turner and M. Poliakoff, "Photochemical Intermediates" in Inorganic Chemistry Towards the 21st Century, ed. M.H. Chisholm, Amer. Chem. Soc., 1983.

2. e.g. J.K. Burdett, J.M. Grzybowski, R.N. Perutz, M. Poliakoff, J.J. Turner and R.F. Turner, Inorg. Chem., 1978, 17, 147; M.S. Baird, I.R. Dunkin, N. Hacker, M. Poliakoff and J.J. Turner, J. Am. Chem. Soc., 1981, 103, 5790.

LIGAND-TO-METAL CHARGE-TRANSFER EXCITED STATE REACTIVITY OF METAL COMPLEXES

David R. Tyler, Alice E. Bruce, Mitchell R.M. Bruce, and Wad Silavwe.

Columbia University, Department of Chemistry, New York, N.Y. 10027

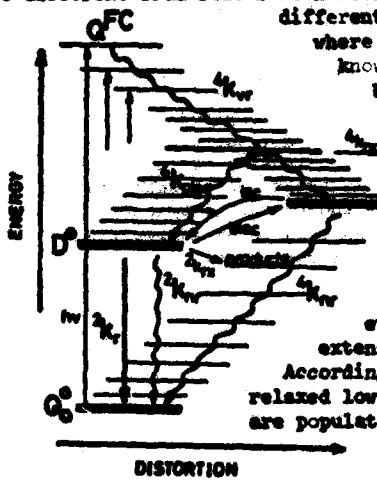
The ligand-to-metal charge-transfer (LMCT) excited state reactivities of the following complexes were studied: Cp_2MO (M=Mo,W; $Cp=\eta^5-C_5H_5$), Cp_2TiX_2 (X=Cl, Br, I), Cp_2MoS_2, Cp_2TiSi_5, $(CpMoS_2)_2$, and $(CpMoO)_2S_2$. The LMCT absorption bands in these complexes were identified with the aid of self-consistent field-Xα-scattered-wave molecular orbital calculations. The following results are general for the complexes above: (1) LMCT excitation leads to intermediates or products in which reduction of the metal center has occured; (2) L→M charge-transfer excitation leads to cleavage of the M-L (single) bond; (3) L→M charge-transfer excitation does not lead to M=L (double) bond cleavage; and (4) LMCT excitation (in which the ligand is a chelating ligand) leads to inefficient cleavage of the M-chelate bonds. In complexes with M=L double bonds, the L atom is susceptible to nucleophile attack in the excited state. For example, in the reaction of Cp_2MoO with PR_3, the products are $(Cp_2Mo)_2$ and OPR_3. Useful oxygen atom transfer reactions utilizing this principle will be discussed. Although electrophilic attack at the metal center is suggested by the charge distribution in the LMCT excited state, we have not found this to be an important process in the reactivity of the complexes above.

WAVELENGTH-DEPENDENT PHENOMENA IN CHROMIUM(III) PHOTOCHEMISTRY

Mary A. Jamieson, Mauro Maestri[1], and Nick Serpone

Department of Chemistry, Concordia University, 1455 deMaisonneuve Blvd. West, Montréal, Québec, CANADA, H3G 1M8

A continuing controversy in the photochemistry and photophysics of chromium(III) complexes centres around the specific role(s) played by the excited quartet and doublet excited states in defining the photochemical behaviour.[2] The issue is further complicated by the questions of prompt reaction from unrelaxed excited states and back intersystem crossing from the vibrationally relaxed doublet to the relaxed quartet (see SCHEME). Reactivity modes may or may not be different from states with different spin multiplicities and different extents of thermalisation. Only where the photochemical behaviour is known in sufficient detail would it be possible to make photophysical distinctions.



SCHEME

In the case of $Cr(bpy)_3^{3+}$ (bpy = 2,2'-bipyridine) in aqueous solution, a model has evolved[3] to account for a rather extensive array of experimental results. According to this model, the vibrationally relaxed lowest excited doublet states ($^2T_1/^2E$) are populated by nearly quantitative intersystem crossing from the short-lived quartet state ($^4T_2$) with back intersystem crossing not being an important process.

In a study of the photochemistry of $Cr(en)_2(NCS)_2^+$, Balzani et al.[4] noted that in the range 350-570 nm both ϕ_{NCS^-} and ϕ_{H^+} are independent of wavelength of excitation, but ϕ_{phen} decreases at ca. 530 nm. This was taken to mean that NCS^- aquation and H^+ uptake occur entirely from the THEXI quartet state.

We have recently investigated the wavelength dependence (313-640 nm) of the quenchable ($^2\phi_{rx}$) and unquenchable ($^4\phi_{rx}$) quantum yields as well as $^2\phi_r$. These studies indicate that the photoreaction from the short-lived, elusive $^4T_2$ state occurs from an unrelaxed level in competition with vibrational relaxation and prompt isc.

(1) Visiting Scientist, University of Bologna, Italy.

(2) A. D. Kirk, Coord. Chem. Rev., 39, 225 (1981).
(3) M.A.Jamieson, N.Serpone, and M.Z.Hoffman, Coord.Chem.Rev., 39, 121 (1981).
(4) V.Balzani et al., J.Am.Chem.Soc., 100, 1463 (1978).

PHOTOISOMERIZATION AND PHOTOCHEMICAL AMMINE LIGAND AQUATION AND WATER EXCHANGE OF THE ISOMERIC AMMINEAQUA-CHROMIUM(III) COMPLEXES

L. Mønsted and O. Mønsted

The Royal Veterinary and Agricultural University,
and
University of Copenhagen, Copenhagen, Denmark

All 10 members of the series of ammineaquachromium-(III) complexes, $[Cr(NH_3)_x(OH_2)_{6-x}]^{3+}$ x = 6,5,cis-4, trans-4, fac-3, mer-3, cis-2, trans-2, 1 and 0, are known. This series of complexes is well suited for a systematic study of influences from the non-reacting ligands on the kinetic behaviour of octahedral complexes, and we have earlier studied the thermal reactions.[1-3]

The photoinduced reactions of these species have been studied by irradiation in the ligand field bands, and the complex mixtures of isomers, which results have been identified by the combined use of ion exchange chromatography, visible absorption spectroscopy and mass spectrometry. This type of data have been used to evaluate quantum yields by a new numerical method involving integration of coupled photochemical differential equations. This approach has allowed a reliable determination also of minor products, and this has been of value particularly for a characterization of the complicated reactivity pattern of the tetraammines-, triammines and diammines. For these species photo-isomerization and photochemical water exchange dominates but loss of coordinated ammonia is also significant.

The data will be presented in detail and implications for current theoretical approaches to a detailed mechanism for these reactions will be discussed.

1. L. Mønsted and O. Mønsted, Acta Chem. Scand. 1980, A34, 259, and references therein.
2. L. Mønsted and O. Mønsted, Acta Chem. Scand. 1982, A36, 365.
3. L. Mønsted and O. Mønsted, Acta Chem. Scand. 1982, A36, 555.

PHOTOSOLVOLYSIS REACTIONS OF RHODIUM(III) COMPLEXES: MECHANISTIC INFORMATION FROM THE EFFECT OF PRESSURE

U. Kuester, S. Wieland, W. Weber, R. van Eldik and H. Kelm

Institute for Physical Chemistry, University of Frankfurt, Robert Mayer Str. 11, 6000 Frankfurt/Main, FRG

Photosolvolysis reactions of pentaammine complexes of Rh(III) generally occur according to the reactions

$$Rh(NH_3)_5L^{(3-n)+} + S \xrightarrow{h\nu} \begin{cases} Rh(NH_3)_5S^{3+} + L^{n-} \\ trans\text{-}Rh(NH_3)_4(L)S^{(3-n)+} + NH_3 \end{cases}$$

where S = H_2O, DMSO, DMF, PMA; L^{n-} = NH_3, DMF, py, Cl^-, Br^-, I^- and SO_4^{2-}. The quantum yields for these processes exhibit very characteristic pressure dependencies, from which apparent volumes of activation can be determined[1,2]. These volumes of activation are composite quantities of the effect of pressure on the photochemical and photophysical processes involved. Studies[3] on the effect of pressure on the luminescence life times of the ligand field excited states of such complexes make it possible to extract the pressure dependence of the photochemical process. It turns out that the non-radiative deactivation process exhibits no meaningful pressure dependence[4,5], whereas the ligand solvolysis reaction exhibits a characteristic dependence from which mechanistic conclusions can be drawn[4-7].

This work has now been extended to a series of systems in which L is a neutral leaving group. In addition, the solvolysis reaction of the cis-$Rh(bpy)_2Cl_2^+$ in different solvents is presently under investigation. A detailed discussion of the available results and their mechanistic interpretation will be presented.

1. W. Weber, Ph.D. thesis, University of Frankfurt, 1982.
2. U. Kuester, Diplomarbeit, University of Frankfurt, 1983.
3. P.C. Ford and co-workers, University of California at Santa Barbara.
4. W. Weber, R. van Eldik, H. Kelm, J. DiBenedetto, Y. Bencsmun, H. Offen and P.C. Ford, Inorg. Chem., 22, 623 (1983).
5. W. Weber, J. DiBenedetto, H. Offen, R. van Eldik and P.C. Ford, Inorg. Chem., in press.
6. W. Weber and R. van Eldik, Inorg. Chim. Acta, in press.
7. W. Weber, U. Kuester, R. van Eldik and H. Kelm, AIRAPT meeting, Albany 1983.

THE PHOTOCHEMICAL BEHAVIOUR OF MIXED-VALENCE CYANOMETALLATES

H.Hennig, A.Rehorek, D.Rehorek, and Ph.Thomas

Karl-Marx-Universität, Sektion Chemie, Liebigstr. 18, DDR-7010 Leipzig, G.D.R.

Within the framework of our investigations of photocatalytic systems based on light-sensitive coordination compounds [1], [2] and their spectral sensitization our interest is focused especially on possibilities to realise the concept of static spectral sensitization [3], [4]. The concept of static sensitization consists in the combination of the sensitizer S and the complex C to be spectrally sensitized in a closed unit. Among the experimental possibilities to realize the concept of static sensitization mixed-valence compounds of the class II within the ROBIN-DAY classification are of considerable interest because they allow in principle the generation of optical windows ranging from the ultraviolet up to the near infrared caused by inter-valence (IT) transitions. However, the well known fact of fast back electron transfer processes is to take into account as a strong restricting factor concerning efficient electron transfer from one metal center to the other photochemically induced by IT excitation.

Cyanometallates like octacyanomolybdate(IV), octacyanotungstate(IV), hexacyanoruthenate(II), and hexacyanoferrate(II) form mixed-valence compounds with appropriate copper(II), iron(II), uranium(VI), and vanadium(IV) compounds. Detailed spectroscopic investigations in solutionshow that these mixed-valence compounds are characterised by more or less intensive IT transitions. The IT behaviour can be described within the framework of the conceptual approach of HUSH. Photochemical investigations of mixed-valence cyanometallates show low photoreactivity only, caused by fast back electron transfer processes. Both physical and chemical scavenging processes, the latter in form of a new type of sequential two-photon processes may be helpfully in quenching the back electron transfer.

[1] H.Hennig, Ph.Thomas, R.Wagener, D.Rehorek and K.Jurdeczka, Z. Chem. 1977, 17, 241.
[2] H.Kisch and H.Hennig, EPA NEWSLETTER, in press.
[3] H.Hennig, Ph.Thomas, R.Wagener, M.Ackermann, R. Benedix and D.Rehorek, J. Signal AM 1981, 9, 269.
[4] H.Hennig, D.Rehorek and R.D.Archer, Coord. Chem. Rev., in preparation.

Effects of High Pressure on the Photophysical Kinetics of d^6 Metal Complexes

DiBenedetto, J. ; Goodwin, H.; Arkle, V.; Offen, H.; Ford, P.C.; University of California at Santa Barbara, Santa Barbara CA 93106

High pressure photophysical and photochemical measurements on several Rh(III)ammine complexes have provided evidence for a dissociative mechanism for the substitution reactions of ligand field (LF) excited states[1] through the interpretation of volumes of activation. Reported here are continuations of such investigations into the pressure dependence of the excited state dynamics of additional rhodium(III) complexes and of other d^6 group VIII metal complexes.

The iron(II) chelate complexes FeL_3^{2+} (L = pyim) and FeL'_2^{2+} (L' = phenmethoxa) each exist in fluid, ambient temperature solution as an equilibrium of the high (quintet) and low (singlet) spin states. The equilibrium concentration of the two states are shown to vary with pressure, and from these measurements a ΔV^0 value of -10 cm^3/mole was measured for FeL_3^{2+}. Pulsed laser flash photolysis show the high spin-low spin relaxation to occur on the 10^2 nanosecond time scale and have proven to be modestly pressure dependent in the case of the FeL'_2^{2+} complex.

The equilibria between the metal center (LF) and charge transfer (CT) or ligand centered (π-π^*) excited states of $IrL_2Cl_2^+$ complexes (L = bipyridine, 5,6-dimethylphen) have been probed as a function of pressure. For each of these complexes, two low lying excited states luminesce in fluid solution with identical lifetimes[2]. The ratios of the intensities of emission from these two states vary with pressure with the charge transfer or ligand localized emission becoming a larger fraction of the total intensity at higher pressures. These data will be interpreted in terms of the volumes of the relevant excited states and the photophysical dynamics involved.[3]

1) W. Weber, R. van Eldik, H. Kelm, J. DiBenedetto, Y. Ducommun, H.Offen, and P.C. Ford. Inorganic Chemistry, 1983, 22 ,623
2) R. J. Watts, Inorg. Chem., 1981, 20 ,2302
3) These studies were supported by an NSF grant to PCF

PHOTOCHEMICAL PERTURBATION OF $^1A \rightleftharpoons {}^5T$ EQUILIBRIA IN IRON(II) COMPLEXES AND DETERMINATION OF ACTIVATION VOLUMES FOR THE SPIN-STATE INTERCONVERSION IN SOLUTION

Ian Lawthers and John J. McGarvey

Department of Chemistry, Queen's University of Belfast, Belfast BT9 5AG, N. Ireland

Karel Heremans

University of Leuven, B3030, Heverlee, Belgium

Hans Toftlund

Odense University, DK5230, Odense, Denmark

Investigation of the dynamics of interconversion between thermally populated spin states in transition metal complexes is important for understanding the influence of intersystem crossing phenomena on the excited state reactivity of such systems[1].

We have shown recently[2] that perturbation of the low-spin $\rightleftharpoons$ high-spin equilibria in a range of Fe(II) complexes can be brought about photochemically by pulsed laser irradiation in the MLCT bands of the low-spin isomer, permitting a study of the intersystem crossing dynamics in a range of solvents. We have now extended this investigation by studying the relaxation kinetics as a function of pressure in order to determine activation volumes for the spin interconversions. The corresponding enthalpies and entropies of activation have also been measured.

Results will be presented for several complexes containing either α-diimines or aliphatic amines and substituted pyridines as ligating groups. The activation volumes exhibit a considerable degree of solvent and ligand dependence. The trends in these data and in the corresponding activation entropies will be discussed.

1. R.A. Binstead, J.K. Beattie, T.G. Dewey and D.H. Turner, J. Am. Chem. Soc. 1980, 102, 6442 and references therein.
2. J.J. McGarvey and I. Lawthers, J.C.S. Chem. Comm. 1982, p.906.

PHOTOAQUATION OF NEW COMPLEXES OF RHODIUM(III) WITH HETEROCYCLIC LIGANDS

Mariel M. Muir, Serigio Sanchez, Rodrigo Díaz, and Nancy Joyner

University of Puerto Rico, Department of Chemistry, Río Piedras, Puerto Rico, USA 00931

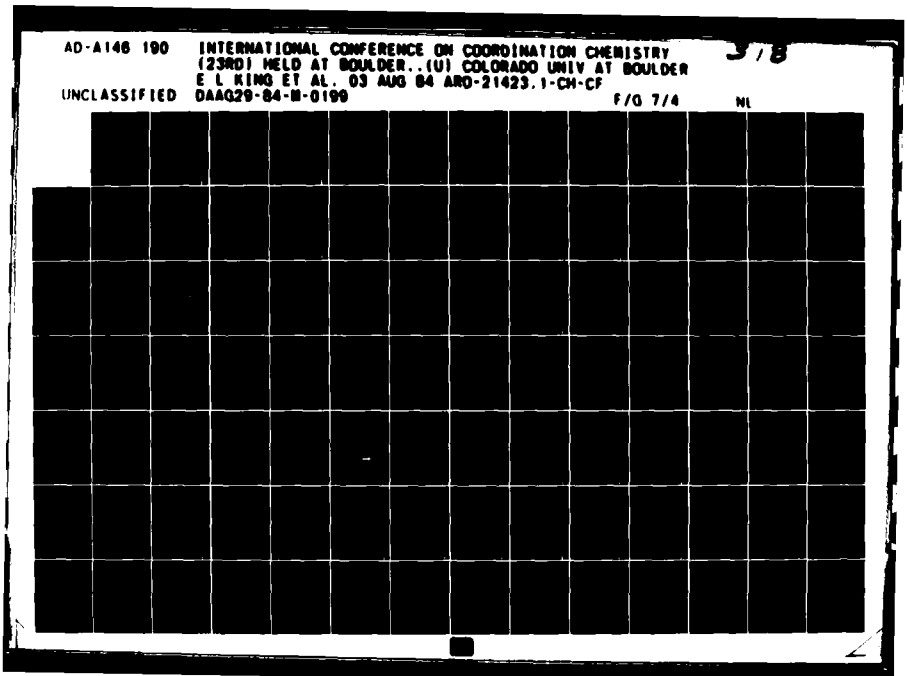
Complexes of Rh(III) of the type $Rh(L)_4X_2^+$, where L is NH_3 or amine and X is Cl^-, Br^-, I^-, H_2O, OH^-, or CN^-, undergo photoaquation reactions upon irradiation into the ligand field bands. The ligand which is replaced by water has been shown to vary as the nature of L and X are varied. In several cases, when L is NH_3, the photoaquation reaction is accompanied by stereochemical change. No such stereochemical change has been observed, however, when the ligand L is pyridine or other heterocyclic amine.

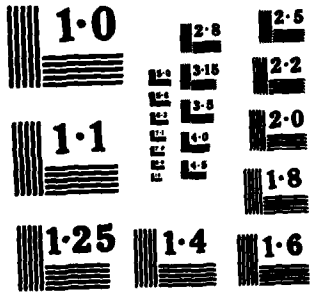
The approach of Vanquickenborne using the AOM to predict the labilized ligand has been very successful in accounting for the published observations for the complexes of Rh(III) in which L is NH_3 or aliphatic amine. However, significant differences in behavior observed for the complexes with pyridine have not been rationalized.

In order to better understand these photoaquation reactions, several new complexes of the type trans-$Rh(L)_4XY^+$ have been prepared with derivatives of imidazole and thiazole. The results of ligand field photolyses of these new complexes will be presented. For several of the complexes, parameters for use in the Vanquickenborne approach have been estimated, so that comparison of the experimental results can be made with theory. Efforts to include proper parameters for pi-bonding of the heterocyclic ligands have been made.

AD-A146 190 INTERNATIONAL CONFERENCE ON COORDINATION CHEMISTRY (23RD) HELD AT BOULDER..(U) COLORADO UNIV AT BOULDER E L KING ET AL. 03 AUG 84 ARO-21423.1-CH-CF

UNCLASSIFIED DAAG29-84-M-0190 F/G 7/4 NL




1·0
1·1
1·25
1·4
1·6
2·8
3·15
3·5
4·0
4·5
2·5
2·2
2·0
1·8

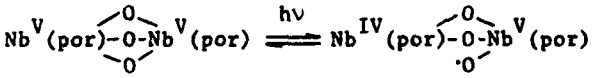
PHOTOREDOX CHEMISTRY OF PORPHYRIN COMPLEXES OF MOLYBDENUM AND NIOBIUM

Yukito Murakami, Yoshihisa Matsuda, and Shuji Sakamoto

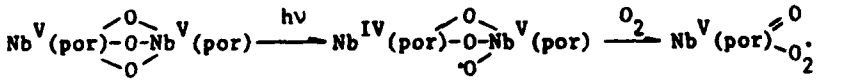
Department of Organic Synthesis, Faculty of Engineering, Kyushu University, Fukuoka 812, Japan

MOLYBDENUM COMPLEXES. Mo(O)(OX)(por) gives a radical species, OX$^{\cdot}$ upon irradiation with the visible light in benzene, accompanied with simultaneous reduction of Mo(V) to Mo(IV), where OX and por denote alcoxy and porphyrin ligands, respectively. The photoreduction takes place less readily for the complexes with polar axial coordination bond, Mo-OX. For the complexes with bulky axial ligands, the reduction rate depends on the bulkiness of the ligands. These observations lead to the conclusion that the photoreduction involves two competitive processes, photochemical homolysis of the axial coordination bonds and release of generated radical species from the reaction site.

NIOBIUM COMPLEXES. The tri-μ-oxo dimer, Nb(V)(por)(O)$_3$Nb(V)-(por), is not subjected to the photoreduction under anaerobic conditions in benzene, while it is subjected to the photoreduction in the presence of a small amount of ethanol affording Nb(IV) and ethoxy radical species. This observation clearly indicates that a monomer species formed upon addition of ethanol is reduced by irradiation in a similar manner as observed with the molybdenum complexes, and that the tri-μ-oxo dimer is not reduced because of rapid recombination of Nb(IV) and -O$^{\cdot}$ radical species even if homolysis of one of the oxo bridges takes place.



The tri-μ-oxo dimer gives an ESR signal due to a radical species containing a Nb nucleus upon irradiation with the visible light under aerobic conditions. This ESR signal vanishes upon interruption of the irradiation, addition of a radical scavenger, or removal of oxygen. The reaction is consistent with the homolytic cleavage of one of the oxo bridges upon irradiation followed by oxidation with molecular oxygem.



In conclusion, the porphyrin complexes of molybdenum and niobium can be considered to be effective photochemical activators for oxygen and oxygen containing ligands.

PHOTOCHEMISTRY OF SINGLY- AND DOUBLY-BRIDGED PEROXO-DICOBALT(III) COMPLEXES

Helmut R. Mäcke

Institute of Inorganic Chemistry, University of Basel, Spitalstrasse 51, 4056 Basel, Switzerland

Co(II) complexes with polyamine ligands react reversibly with molecular oxygen. Due to the fact that this reaction attracted the interest of many groups, a good kwowledge of the ground state chemistry of this family of complexes exists. The interest in the excited states of these compounds is documented by many investigations of the electronic spectra.[1] It remains a need to study the excited-state reactivity.

The dominant spectral features of these compounds are high intensity bands, which are due to $O_2 \longrightarrow Co(III)$ transitions. Three types of spectra have been observed.
1. *μ-Peroxo,μ-hydroxo-dicobalt(III)* complexes exhibit 2 CT bands of about equal intensity in the near uv.
2. Singly-bridged complexes of the type $(N_5)CoO_2Co(N_5)^{4+}$ (N_5 being 5 NH_3 or polyamines) show only one band at ~300 nm. They exclusively have been shown to have a transplanar CoO_2Co unit.[2]
3. Singly-bridged complexes of the type $(L_5)CoO_2Co(L_5)$ (L_5 being aminoacid ligands) show 2 CT bands between 300 and 400 nm.

A model[1], assuming that the number and energies of the bands are a function of the torsion angle of the CoO_2Co unit, explains the spectral differences.

The photochemistry of the 3 classes is reported. Only little photoactivity is found upon irradiation into the CT bands. This is due to the kinetic and thermodynamic instability of the primary photoproducts which causes rapid restauration of the starting complex. Addition of a scavenger like edta, which scavenges the photochemically produced Co(II), causes a photoaccelerated decay. The photoreaction is very clean and consists of a reductive elimination of O_2 and formation of Co(II) in all cases. Most interestingly the wavelength variation of the quantum yield is different for the three groups of complexes.

μ-O_2,μ-OH-complexes show a sharp rise of the quantum yield at the onset of the higher energy CT band. This suggests that the first CT band is not or much less photoactive or may not even be a $O_2 \longrightarrow Co(III)_4$ CT band. The quantum yield of the type $(N_5)CoO_2Co(N_5)^{4+}$ is independent of wavelength throughout the near uv- and visible region. This is explained assuming a low lying, nonspectroscopic CT state. So far one singly-bridged complex with 2 CT bands was investigated. It was shown that both bands are photoactive.

1. A.B.P.Lever & H.B.Gray, Acc.Chem.Res. 11, 348 (1978)
2. W.P.Schaefer, Inorg.Chem. 7, 725 (1968)

TUa17-01

BINUCLEAR COPPER COMPLEXES AND THEIR INTERACTION WITH MOLECULAR OXYGEN

Marie-Thérèse Youinou, Wolfgang Petri and John A. Osborn

Institut Le Bel, Université Louis Pasteur, 4, rue Blaise Pascal, 67000 Strasbourg, France

Binuclear copper sites have been implicated in several copper enzymes particularly those involving oxygen transport, storage and reactivity. Model studies on binuclear copper complexes in which the copper sites are in close proximity will be described. The properties (spectroscopic, electrochemical, magnetic) and the reactivity (in particular with molecular oxygen) of such species will be described.

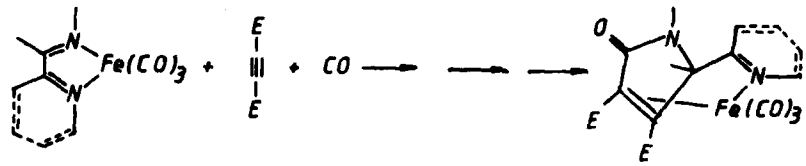
C-C CONNECTING REACTIONS OF COORDINATED 1,4-DIAZA-1,3-DIENES (DAD): 3-PYRROLINE-2-ONES FROM (DAD)Fe(CO)$_3$ AND ALKYNE

Hans-Werner Frühauf, Frank Seils and Richard J. Goddard

Universität Duisburg, FB 6, Organische Chemie, Bismarckstr. 90, D-4100 Duisburg 1;
MPI für Strahlenchemie, Stiftstr. 34-36, D-4330 Mülheim a. d. Ruhr;
MPI für Kohlenforschung, Lembkestr. 5, D-4330 Mülheim a. d. Ruhr, W.-Germany

Reactions of 1,4-diaza-1,3-dienes (DAD) coordinated to transition metals in which C-C bonds are formed have hitherto only been observed for some binuclear complexes, and in particular for those containing ruthenium, e. g., (DAD)Ru$_2$(CO)$_6$ /1/. It has been claimed that the unsymmetrical 6e coordination mode of the DAD system in these complexes, which we first described for the corresponding iron complexes /2/, is crucial for the activation of DAD for C-C bond formation.

As will be described, treatment of (DAD)Fe(CO)$_3$ (1) with dimethyl acetylene dicarboxylate under an atmosphere of CO gives 3-pyrroline-2-ones as their Fe(CO)$_3$-complexes 2 /3/.



1 E = COOMe 2

This synthetically very useful reaction clearly demonstrates that C-C bond formation is also feasible for DAD coordinated solely through the nitrogen lone pairs, and the 6e coordination mode, which involves the π-electrons of one C=N moiety, is not a necessary prerequisite.

Mechanistic details of this interesting stepwise cyclization in the metal coordination sphere will be discussed on the basis of spectroscopic and structural information obtained for two intermediates that could be isolated in the case of two special DAD ligands, and of 13-CO labeling experiments involving these intermediates.

/1/ G. van Koten and K. Vrieze, Adv. Organomet. Chem. 1982, 21, 151 - 239.
/2/ H.-W. Frühauf, A. Landers, R. Goddard and C. Krüger, Angew. Chem. 1978, 90, 56 - 57; Angew. Chem. Int. Ed. Engl. 1978, 17, 64 - 65.
/3/ H.-W. Frühauf, F. Seils, M. J. Romao and R. Goddard, to be published in Angew. Chem.

KINETIC DETERMINATION OF THE COBALT-CARBON BOND DISSOCIATION ENERGY OF ADENOSYLCOBALAMIN

Richard G. Finke and Benjamin P. Hay

Department of Chemistry, University of Oregon, Eugene, Oregon, USA 97403

Reaction product, kinetic, $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and Co-C BDE (bond dissociation energy) data are reported for the thermolysis of adenosylcobalamin. The radical scavenger 2,2,6,6-tetramethylpiperidine-1-oxy was used to establish that the cleavage of the Co-C bond to yield free radicals was the rate determining step of the reaction. The temperature dependence of the rate of homolysis was measured from 90 to 120°C to yield $\Delta H^{\ddagger}$ = 29.8 $\pm$ 0.4 kcal/mol and $\Delta S^{\ddagger}$ = .8 $\pm$ 1.1 e.u. From this information and other data the base-on Co-C BDE of adenosylcobalamin is estimated to be $\simeq$ 29 kcal/mol. The above activation parameters, upon comparison to those obtained for B_{12}-dependent enzymes, suggest that the enzymes provide a net, $\gtrsim$ 13 kcal/mol lowering of the free energy barrier for Co-C bond homolysis, resulting in a rate acceleration of > 10^9.

THE EFFECT OF A CO LIGAND ON THE REACTIVITY OF Co_2^+ TOWARDS C-H BONDS IN ALKANES

R. B. Freas III and D. P. Ridge

University of Delaware, Chemistry Department, Newark, Delaware 19711, U.S.A.

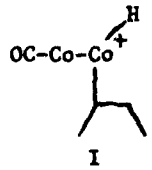
As isolated gas phase species, Fe^+, Co^+ and Ni^+ efficiently attack C-C and C-H bonds in alkanes, but Co_2^+ is unreactive.[1,2] (Reaction 1). Addition of a CO ligand, however, activates Co_2^+

$$Co_2^+ + \text{butane} \longrightarrow \text{no reaction} \qquad (1)$$

$$Co_2CO^+ + \text{butane} \longrightarrow Co_2COC_4H_6^+ + 2H_2 \qquad (2)$$

dramatically. Co_2CO^+ reacts at essentially the collision rate with butane to produce $Co_2COC_4H_6^+$.

It is suggested that the effect is a consequence of the energetics of the oxidative addition transition state I. Bonds to



I

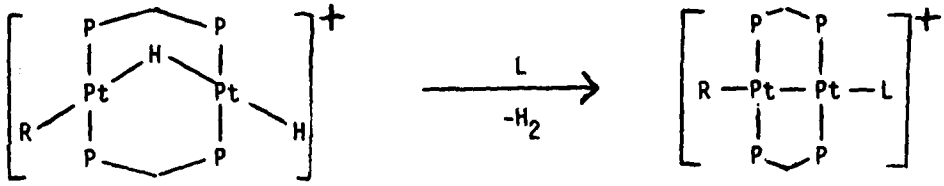
hydrogen and alkyl carbons are much stronger for Co^+ than for Co as evidenced by the reactivity of Co^+ towards alkanes. The energy of I is lowered by concentrating positive charge on the Co bound to alkyl carbon and hydrogen. The resulting decrease in the positive charge on the other Co strengthens the bond to CO. The effect of the CO ligand then is to support a polarization of charge in the Co_2^+ dimer that enhances its reactivity. Evidence pertinent to this hypothesis will be presented.

1. J. Allison, R. B. Freas and D. P. Ridge, J. Amer. Chem. Soc., 1979, 101, 1332.
2. R. B. Freas and D. P. Ridge, J. Amer. Chem. Soc., 1980, 102, 7129.

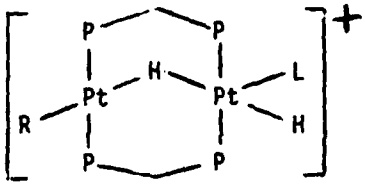
MECHANISM AND ENERGETICS OF REDUCTIVE ELIMINATION OF HYDROGEN FROM BINUCLEAR HYDRIDOPLATINUM COMPLEXES

Ross H. Hill and Richard J. Puddephatt University of Western Ontario, London, Ontario, Canada N6A 5B7

Reactions of binuclear hydridoplatinum (II) complexes with soft ligands, such as tertiary phosphines, give diplatinum (I) complexes and hydrogen (equation, R=Me or H, L=PR_3, P P=$Ph_2PCH_2PPh_2$).



Intermediates are formed of structure



A detailed study of the equilibrium constants for formation of the intermediates and of the rates of the overall reaction shows a strong correlation between these two parameters. It is suggested that the reductive elimination involves coupling of H atoms across the two platinum centers.[1,2]

1. R.H. Hill and R.J. Puddephatt, J.Am.Chem.Soc., 1983, 105, 5797.

2. K.A. Azam, M.P. Brown, R.H. Hill, R.J. Puddephatt and A. Yavari, Organometallics, submitted for publication.

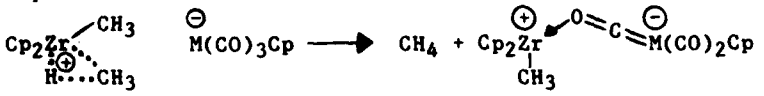
MECHANISMS OF REACTIONS OF TRANSITION-METAL HYDRIDES: PROTON TRANSFER, HYDROGEN ATOM TRANSFER, AND M-H DONOR LIGAND

Robin T. Edidin, Jeffrey M. Sullivan, Keith E. Warner, and Jack R. Norton

Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523, USA

Reactions of transition-metal hydrides, including concerted reactions, may be classified according to whether zero, one, or two electrons are transferred to the substrate along with the hydrogen atom. Examples of all three mechanisms can be found in elimination reactions which form C-H bonds and heterobimetallic complexes.

The reaction of Cp_2ZrMe_2 with $HM(CO)_3Cp$ (M = Cr, Mo, W) proceeds by a proton transfer mechanism.[1]



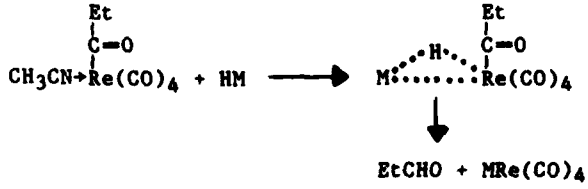
The relative rates (Cr>Mo>W) and entropies of activation all agree with those found for a known proton transfer reaction, the reaction of $HM(CO)_3Cp$ with aniline.

The reaction of CH_3AuPPh_3 with $H_2Os(CO)_4$ proceeds by the radical

$$2CH_3AuPPh_3 + H_2Os(CO)_4 \longrightarrow 2CH_4 + (Ph_3PAu)_2Os(CO)_4$$

chain oxidative addition of $H\text{-}OsH(CO)_4$ to CH_3AuPPh_3. The chain carrier, $\dot{H}Os(CO)_4$, can be generated independently, and the reaction initiated, by the photolysis of $H_2Os_2(CO)_8$. Phosphine substitution on $H_2Os(CO)_4$ ($R_3P + H_2Os(CO)_4 \rightarrow H_2Os(PR_3)(CO)_3 + CO$) involves the same chain carrier, as is shown by the fact that both reactions can be initiated simultaneously.

The elimination of aldehydes from the reaction of metal hydrides (HM, M = $Re(CO)_5$, $Mn(CO)_5$, $CpCr(CO)_3$, $CpW(CO)_3$) with a solvated rhenium acyl complex involves nucleophilic displacement of solvent by the M-H bond of the hydride complex - which thus functions (at least transiently) as a ligand for the acyl complex.



The order of reactivity of HM in those reactions (e.g., $HW(CO)_3Cp$ > $HCr(CO)_3Cp$, and $HRe(CO)_5$>$HMn(CO)_5$) is substantially the reverse of that found in proton transfer reactions.

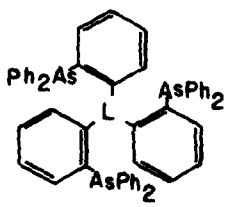
1. "The Synthesis, Structure and Reactions of Dinuclear Compounds Containing Early and Late Transition Metals", R.T. Edidin, B. Longato, B.D. Martin, S.A. Matchett, and J.R. Norton*, Organometallic Compounds: Synthesis, Structure and Theory, Shapiro, B.L., editor, Texas A & M University Press, 1983, pp. 260-280.

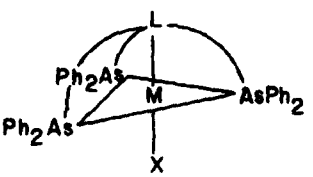
KINETICS AND MECHANISMS OF MONODENTATE LIGAND REPLACEMENT REACTIONS IN TRIGONAL BIPYRAMIDAL NI(II) AND PD(II) COMPLEXES CONTAINING THE TETRADENTATE LIGANDS QAS AND PTAS

Nancy J. MacNeill and Eugene Grimley

Mississippi State University, Drawer CH, Mississippi State, Mississippi, USA 39762

Nickel(II) and Palladium(II) form 5 coordinate trigonal bipyramidal complexes with the tetradentate ligands QAS and PTAS, as shown below. The change in the apical donor atom from phosphorus to arsenic results in an increase in the metal - apical donor atom bond length and hence an elevation of the geometrical positioning of these ligands in the nickel(II) and palladium(II) complexes.





The stoichiometry observed for reactions conducted in anhydrous methanol at an ionic strength of 0.050 M is given by the equation $MX(LTAS)^+ + Y^- \rightleftharpoons MY(LTAS)^+ + X^-$, where M = Ni or Pd and L = P or As. At 25° C, kinetic experiments for three systems provide second order rate constants as a function of the nucleophilic character of the entering ligand.

	n^o_{Pt}	k_2, $M^{-1}s^{-1}$		
		$NiBr(PTAS)^+$	$NiBr(QAS)^+$	$PdBr(PTAS)^+$
NO_2^-	3.22	0.11	2.81	8.2
I^-	5.42		23.1	1180
SCN^-	5.65	6.7	157	2090
N_3^-	3.58	8.9	192	86
CN^-	7.0	24	230	12 300
$SC(NH_2)_2$	7.17	154	850	40 100
PPH_3	8.79	NR	NR	slow

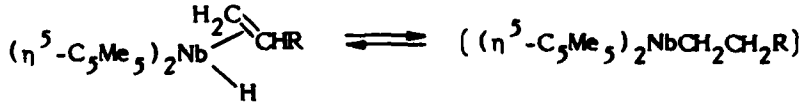
Low sensitivities of the rates to the nature of the entering ligands, steric control of rates of replacement by the geometrically constraining tetradentate ligands, and relatively consistent activation parameters of $\Delta H^{\ddagger}$ = 6-10 kcal/mol and $\Delta S^{\ddagger}$ = 20-28 eu are factors consistent with an associative interchange mechanism.

KINETICS AND MECHANISM OF OLEFIN INSERTION INTO THE TRANSITION METAL HYDRIDE BOND

John E. Bercaw and Nancy M. Doherty

Department of Chemistry, California Institute of Technology, Pasadena, California 91125, USA

Bis(pentamethylcyclopentadienyl)niobium(III) olefin hydride complexes, $(\eta^5\text{-}C_5Me_5)_2Nb(CH_2{=}CHR)(H)$, have been prepared by the reaction of $(\eta^5\text{-}C_5Me_5)_2NbH_3$ with olefins or the reaction of $(\eta^5\text{-}C_5Me_5)_2NbCl_2$ with alkyl grignards. The product of insertion of the olefin into the niobium hydride bond is trapped by carbon monoxide and isocyanide to give the bis(pentamethylcyclopentadienyl)niobium(III) alkyl CO and CNR derivatives. The kinetics of the insertion have been studied by dynamic NMR techniques for a series of olefin complexes (R = H, Me, Ph, p-$Me_2NC_6H_4$, p-$MeOC_6H_4$, p-MeC_6H_4, p-$CF_3C_6H_4$).



The steric and electronic effects of the substituents on this reaction provide information on both the ground and transition states for the insertion process. Our current thoughts on the mechanism of olefin insertion into the metal-hydride bond will be presented.

CHROMIUM FORMYL COMPLEXES IN AQUEOUS SOLUTIONS

Haim Cohen, Dan Meyerstein, Alan Shusterman and Mathania Weiss

Chemistry Departments, Ben-Gurion University of the Negev
and Nuclear Research Centre Negev, Beer-Sheva, Israel

The radical $\cdot CH(OH)_2$ (which is produced by the reaction of hydroxyl radicals, OH, with hydrated formaldehyde) reacts with chromous ions in aqueous solutions to form a complex with a chromium carbon bond. The specific rate of formation of $(H_2O)_5CrCH(OH)_2^{2+}$ is 1.0×10^8 $M^{-1}s^{-1}$ in acidic solutions. The latter complex in acidic solutions has a spectrum with λ_{max} = 305 nm (ϵ=2300 $M^{-1}cm^{-1}$) and a shoulder at 375 nm (ϵ=410 $M^{-1}cm^{-1}$). In acidic solutions pH 1.0, and 0.1 M $CH_2(OH)$, $(H_2O)_5Cr\text{-}CH(OH)_2^{2+}$ or $(H_2O)_5Cr\text{-}CHO^{2+}$ whichever is the intermediate observed, decomposes in a pseudo first order process with $k = 0.034$ s^{-1}. At pH 6.0 the formation of $(H_2O)_5Cr\text{-}CH(OH)_2^{2+}$ is followed by two consecutive reactions obeying pseudo first order rate laws, with $k = 1.5 \times 10^2$ s^{-1} and $k = 0.35$ s^{-1} respectively. The first reaction is probably the dehydration reaction $(H_2O)_5Cr\text{-}CH(OH)_2^{2+} \rightarrow (H_2O)_5Cr\text{-}CHO^{2+}+H_2O$ as the spectrum of the second intermediate indicates that the chromium-carbon bond is kept intact. In the second reaction the chromium carbon bond decomposes yielding $chromium(III)_{aq}$. Carbon monoxide is a final product at both pH's though no dihydrogen is observed. The mechanism of decomposition is discussed.

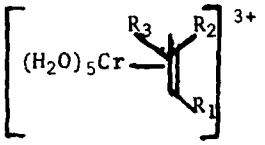
Acknowledgement. This study was supported in part by the U.S.-Israel Binational Science Foundation, B.S.F., Jerusalem, Israel.

KINETICS AND MECHANISM OF THE β-HYDROXYL ELIMINATION FROM $[(H_2O)_5Cr\text{-}CHR_1CR_2R_3OH]^{2+}$ IN AQUEOUS SOLUTIONS

Haim Cohen, Dan Meyerstein, Alan J. Shusterman and Mathania Weiss

Chemistry Departments, Ben Gurion University of the Negev and Nuclear Research Centre Negev, Beer-Sheva, Israel

The alkyl chromium complexes $[(H_2O)_5Cr\text{-}R]^{2+}$, where $R = CH_2CH_2OH$, $CH(CH_3)CH_2OH$, $CH(CH_3)CH(OH)CH_3$ and $CH_2C(CH_3)_2OH$ decompose to yield $Cr(H_2O)_6^{3+}$ and the corresponding alkene. For the latter two alkyl residues the reaction proceeds via a relatively stable intermediate. This intermediate is identified as



formed by an acid catalysed β elimination reaction. The identification of the intermediate as the electron-deficient $d \rightarrow \pi^*$ complex and not as $[(H_2O)_5Cr\text{-}CR_2{=}CR_2R_3]^{2+}$ or $[(H_2O)_5Cr\text{-}CHR_1\text{-}CR_2{=}CH_2]^{2+}$ as earlier suggested is based on the observation that the 2 methyl propene formed in D_2O, for $R = CH_2C(CH_3)_2OH$, contains no deuterium above the natural abundance level. (Measurements for $R = CH(CH_3)CH(OH)CH_3$ are in progress). For $R = CH_2CH_2OH$ and $CH_2CH(OH)CH_3$ the same mechanism is proposed and the lack of observation of an intermediate is attributed to the fact that the β elimination reaction becomes the rate determining step in the reaction sequence. The factors, affecting the rate of the β elimination reaction and the relative stability of the chromium(III)-alkene $d \rightarrow \pi^*$ complex are discussed.

Acknowledgement. This study was supported in part by the U.S.-israel Binational Science Foundation, B.S.F., Jerusalem, Israel.

KINETICS AND MECHANISM OF AQUATION OF $[Cr(C_2O_4)_2(pyridoxamine)]^-$ ION

Ewa Kita and Premyslaw Kita

Institute of Chemistry, N. Copernicus University, 87-100 Torun, Poland.

Previously,[1,2] the mixed $[Cr(C_2O_4)_2(L\text{-}L)]^-$ type complexes, where L-L = pyridoxine, pyridoxal, pyridoxamine (PM) and histamine, were synthesized as model quasi-enzyme compounds. In acidic aqueous media PM is chelated through the phenolate and adjacent 4-aminomethyl groups with the pyridine nitrogen protonated. In the pH range 2-3, the rate of $[Cr(C_2O_4)_2(PM)]^-$ ion aquation is independent of $[H^+]$. The reaction products are H_2PM^{++} and cis-$[Cr(C_2O_4)_2(OH_2)_2]^-$. The intermediate compound $[Cr(C_2O_4)_2(OH_2)(HPM)]$ was isolated. The Cr-PM chelate ring opening, as a result of the Cr-N bond breaking, is the rate controling stage. Activation parameters for the first step of the aquation have been determined: $\Delta H^{\ddagger}$ = 98.2 ± 2.1 kJ/mol and $\Delta S^{\ddagger}$ = -34.4 ± 6.7 J/K mol at I = 0.25 M.

1. P. Kita and E. Kita, Polish J. Chem., in press.
2. P. Kita, ibid., in press.

KINETICS AND MECHANISMS OF THE REACTIONS BETWEEN CHROMIUM (II) AND DIPYRIDYLETHYLENES IN ACIDIC AQUEOUS SOLUTIONS

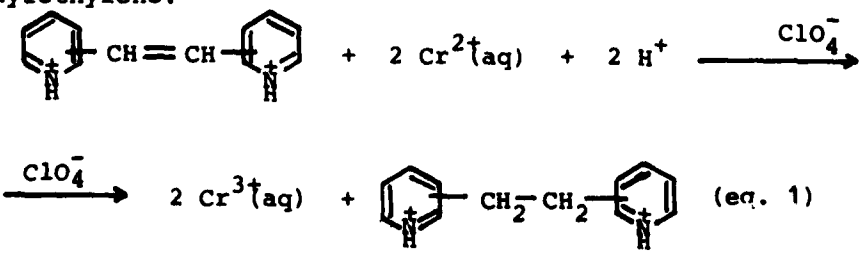
A.Koutselos and A.Petrou*
University of Athens, Inorganic Chemistry Laboratory
Navarinou 13A, Athens, Greece.

The reduction of Dipyridylethylenes by Chromous ion in $HClO_4$ acidic solutions to the saturated Dipyridylethanes (eq.1) takes place through the formation of an Organochromium intermediate in the case of the 2,2'-Dipyridyl ethylene and a radical in the case of the 4,4'-Dipyridylethylene.

The acidolysis of the Organochromium occurs in two stages the first of which follows first order kinetics with an acid-independent and an acid-dependent term.

The formation and decomposition of the radical were studied as a function of the concentrations of 4,4'-Dipyridylethylene, Chromium (II) and H^+.

The experimental results for the two substrates are compared and discussed in terms of the nature of their Lowest Excited States, "ethylenic" in 2,2'- and ethylenic with a strong mixing of "pyridinic" in 4,4'-Dipyridylethylene.[1]



(eq. 1)

(1) G.Orlandi, G.Poggi and G.Marconi, J.C.S.Faraday II, 1980, 76 , 598.

KINETICS AND MECHANISM OF THE FORMATION AND INTRAMOLECULAR REDOX REACTIONS OF AQUOSULFITO- AND DISULFITOBIS-(ORTHOPHENANTHROLINE)COBALT(III) COMPLEXES IN AQUEOUS SOLUTION

Gordon M. Harris and Vijay K. Joshi

Department of Chemistry, State University of New York at Buffalo, Buffalo, NY 14214.

Diaquobis(orthophenanthroline)cobalt(III) complex reacts with aqueous sulfite to produce as the first identifiable product the S-bonded mono-sulfitoaquo species, according to the expression:

$$\text{Rate} = k_o\{[Co(phen)_2(OH_2)(OH)^{2+}] + [Co(phen)_2(OH)_2^+]\}[SO_2] + k_1[Co(phen)_2(OH_2)(OH)^{2+}]\{[HSO_3^-] + [SO_3^{2-}]\} + k_2[Co(phen)_2(OH)_2^+]\{[HSO_3^-] + [SO_3^{2-}]\}.$$

It is noteworthy that the diaquo complex is inactive toward SO_2, as found in other studies of this kind, and that the hydroxo species do not discriminate between HSO_3^- and SO_3^{2-} in the replacement process. The rate constants k_o, k_1, and k_2 are respectively 4.4×10^7, 5.8, and 0.15 $M^{-1}s^{-1}$ at 25°, demonstrating the expected very large advantage of direct SO_2 addition as compared to substitution by HSO_3^- or SO_3^{2-}. Below pH 6, the formation process is too rapid to record by stopped-flow technique. However, a second sulfite addition to the species $Co(phen)_2(SO_3)(OH_2)^+$ is observable, according to the expression: $\text{Rate}=k_1^1[Co(phen)_2(SO_3)(OH_2)^+]\{[HSO_3^-] + [SO_3^{2-}]\}$ to yield the complex anion $Co(phen)_2(SO_3)_2^-$ (k_1^1=131 $M^{-1}s^{-1}$ at 25 °). Above pH 7.5, the addition of the second sulfite does not occur, the only stable product being $Co(phen)_2(SO_3)(OH)$. At moderate acidities ($0.1<[H^+]<1.0M$), both mono- and disulfito complexes undergo slow internal redox according to a proton pre-equilibration mechanism (k_{mono} and k_{di} are 8.3×10^{-6} and $1.8\times10^{-6}s^{-1}$, respectively, at 45°), to yield Co_{aq}^{2+} and SO_4^{2-} in the expected 2:1 stoichiometric ratio. Decomposition of the sulfito species by sulfite elimination only becomes observable when $[H^+]>2$ M at 45°.

Parallel studies with the bis(bipyridyl) congener yield entirely analogous data, differing only in the magnitude of the rate constants. Contrary to a previous report, none of our work provided evidence for chelated monosulfito complexes involving either the $Co(phen)_2$ or $Co(bipy)_2$ moiety. Our presentation will provide details of the experimental procedures and of the data obtained, and will include justification of the mechanistic conclusions.

COMPLEXATION OF URANIUM(VI) BY SULFOSALICYLATE : A KINETIC STUDY

S.Gangopadhyay, M.N.Bishnu, R.N.Banerjee & D.Banerjea

Chemistry Department, University College of Science, Calcutta 700009, India

Kinetic study of complexation of uranium(VI) by sulfosalicylate (L^{3-}) has been made by stopped-flow spectrophotometric technique at pH 7-8.5 (NH_3+NH_4NO_3 buffer) and I = 1M (KNO_3+NH_4NO_3). A brownish-red 1:2 complex (λ_{max} = 460 nm) is formed[1]. Results are in conformity with the following:

$$UO_2^{2+} + OH^- \overset{K'}{\rightleftharpoons} UO_2(OH)^+ ; \quad UO_2(OH)^+ + OH^- \overset{K''}{\rightleftharpoons} UO_2(OH)_2$$

$$UO_2(OH)^+ + \text{HO}\diagup\!\!\diagdown C_6H_3(SO_3^-) \overset{K}{\rightleftharpoons} O_2U\!\!\diagup\!\!\diagdown \begin{matrix}\text{OH HO}\\ O_2C\end{matrix} C_6H_3(SO_3^-)$$

$$\text{Slow (k)} \downarrow \quad -H_2O$$

$$UO_2(L)_2^{4-} + H_2O \xleftarrow[\text{Fast}]{LH^{2-},\ OH^-} O_2U\!\!\diagup\!\!\diagdown \begin{matrix}O\\ O_2C\end{matrix} C_6H_3(SO_3^-)$$

The proposed fast equilibrium step K and the fast rate step are in conformity with known lability of U(VI)-OH_2 bond[2]; monomeric $UO_2(OH)^+$ is well-known[3] and in its case further labilisation of H_2O bound cis to OH group is expected. The scheme leads to,

$$k_{obs} = kK\left[LH^{2-}\right] / \left\{1 + K\left[LH^{2-}\right] + K''\left[OH^-\right]\right\}$$

At 25°C, K = 1×10^4, K'' = 1.4×10^7 (cf. literature data[4]) k = 41 sec^{-1}, $\Delta H^{\ddagger}$ = 51.7 kJ mol^{-1}, $\Delta S^{\ddagger}$ = -42.4 $JK^{-1}mol^{-1}$. Significant negative $\Delta S^{\ddagger}$ value agrees with rate determining ring closure. Effect of substituents is under investigation.

References:

1. C.V.Banks & R.S.Singh, J.Inorg.Nucl.Chem., 15, 125 (1960)
2. V.Frei & H.Wendt, Ber.Buns.Phys.Chem., 74,593 (1970)
3. C.F.Baes & N.J.Meyer, Inorg.Chem., 1, 780 (1962)
4. J.Stary, Coll. Czech.Chem.Comm., 25, 890 (1960)

HIGH-PRESSURE STOPPED-FLOW STUDIES ON THE MECHANISTIC DIFFERENCE OF THE INDIUM(III) COMPLEXATION IN DIFFERENT SOLVENTS

Koji Ishihara, Shigenobu Funahashi, and Motoharu Tanaka

Laboratory of Analytical Chemistry, Faculty of Science, Nagoya University, Nagoya 464, Japan

We have recently exploited a high-pressure stopped-flow apparatus with spectrophotometric detection which enables us to follow fast reactions in solution at pressures up to 200 MPa.[1] We are studying with this apparatus the mechanism of formation of various metal complexes. The formation and dissociation of the 1:1 nickel(II) complex and the solvent exchange on nickel(II) ion in various solvents have been shown to be accommodated within the framework of similar I_d mechanism.[2] More recently we have shown, on the other hand, that in organic solvents much bulkier than water the mechanism of the complexation of hexasolvated iron(III) changes from an associative to a dissociative process, depending on the steric factors of solvent molecules and entering ligands.[3] In order to extend this idea and to obtain additional data, it was decided to measure the activation volume for the complexation of indium(III) ion in bulkier solvents. The negative value of activation volume ($\Delta V^{\ddagger}$ = -23 cm^3 mol^{-1})[4] is consistent with an associative mode of activation operative in the trimethyl phosphate exchange on the indium(III) hexasolvate.

The formation rate of the 1:1 indium(III) complex with 4-isopropyltropolone (Hipt) has been studied spectrophotometrically at various temperatures and at various pressures up to 200 MPa by the high-pressure stopped-flow technique in nonaqueous solvents such as N,N-dimethylformamide (DMF), dimethyl sulfoxide (Me_2SO), trimethyl phosphate (TMP), triethyl phosphate (TEP), and tributyl phosphate (TBP). The rate is first order with respect to indium(III) and Hipt. Activation parameters were determined from temperature and pressure dependences of the second-order rate constants.

Activation volumes for the indium(III) complexation depend indeed on the bulkiness of coordinated solvent molecules (TBP > TEP > DMF ≃ Me_2SO > TMP). We observed hardly parallel relations between $\Delta V^{\ddagger}$ and $\Delta S^{\ddagger}$.

1. K. Ishihara, S. Funahashi and M. Tanaka, *Rev. Sci. Instrum.* 1982, *53*, 1231.
2. K. Ishihara, S. Funahashi and M. Tanaka, *Inorg. Chem.* 1983, *22*, 2564.
3. K. Ishihara, S. Funahashi and M. Tanaka, *Inorg. Chem.* 1983, *22*, December, in press.
4. A.E. Merbach, *Pure Appl. Chem.* 1982, *54*, 1479.

TRANS EFFECT AND TRANS INFLUENCE ON TRANS - $|Ru(NH_3)_4P(OR)_3(H_2O)|^{2+}$, (R=Me, Pr, ^{i}Pr and But)

Jose Cardoso do Nascimento Filho and D. Wagner Franco

Universidade Federal do Rio G. Norte-59000 Natal/RN. Instituto de Fisica e Quimica de S. Carlos, Sao Carlos-SP 13560 C.P. 369, Brasil.

Trans- $|Ru(NH_3)_4P(OR)_3(H_2O)|^{2+}$, (R=Me, Pr, ^{i}Pr and But) reacts with isonicotinamide at second order specific rates k^1 of 1.16, 2.33, 7.42 and 8.09 M^{-1} sec^{-1} (25°C, μ=0,10 $NaCF_3COO/CH_3COOH$) respectively for R=Me, Pr ^{i}Pr and But. The products trans-$|Ru(NH_3)_4P(OR)_3isn|(PF_6)_2$ have been isolated and characterized by micro analysis, cyclic voltammetry and electronic spectra data. The aquation rates k_{-1} for the isonicotinamide derivatives are 5.2×10^{-2}, 5.9×10^{-2}, 1.99×10^{-1} and 3.4×10^{-1} sec^{-1} for R=Me, Pr, But and ^{i}Pr, respectively. The activation parameters for the forward reactions indicate the same mechanism for all of them. The substitution proceeds by a dissociative mechanism with a significant outer-sphere of trans-$|Ru(NH_3)_4P(OR)_3(H_2O)|^{2+}$ with isn. Assuming k_1 as indicative of the lability of the coordinated water molecule on the monophosphite complexes, the following sequence of increment of the trans-effect may be proposed: $P(OMe)_3<P(OPr)_3<P(O^iPr)_3<P(OBut)_3$. The affinity of the monophosphite complexes for isn increases according to $P(OMe)_3\approx P(O^iPr)_3<P(OEt)_3<P(OPr)_3\approx P(OBut)_3$.

CARBON DIOXIDE COMPLEXES OF COPPER(II) ALKOXIDES

John C. Cooper

Inorganic and Electrochemistry Branch, Naval Research Laboratory, Washington, D.C., USA 20375

Although reactions of carbon dioxide with metal complexes such as copper(II) methoxide have been known for some time, lack of mechanistic studies of ligand exchange and complex formation, and of structural data have limited the evaluation of carbon dioxide as a ligand.

In mixed solvents of methanol and aromatic nitrogen bases such as pyridine, carbon dioxide reacts rapidly with copper(II) alkoxides to form an O-bonded mono-dentate carbon dioxide complex. The reaction is first order in carbon dioxide at low concentrations (k_1=1100 to 3000 $M^{-1}S^{-1}$) and is rate limited by copper--ligand dissociation at high carbon dioxide concentrations. This initial fast, reversible reaction is followed by a slower CO_2-independent rearrangement to a carbon dioxide bridged complex. The resulting complexes have high formation constants ($K_1 \sim 10^3$ M^{-1} for the bridged complexes).

Elucidation of solution and solid structures will be described and the details of the kinetics and mechanisms of ligand exchange in these complexes will be presented. The differences in ligand strength, bonding modes, and subsequent reactions observed for carbon dioxide and carbon disulfide will be discussed.

FORMATION AND DISSOCIATION OF CU(II) AND NI(II) COMPLEXES OF ETHYLENEDIAMINE-BIS-ACETYLACETONATE($enba^{2-}$)

S. Gangopadhyay, R. N. Banerjee and D. Banerjea

Chemistry Department, University College of Science, Calcutta 700009, India.

Rates of acid catalysed dissociation of M(enba) (M = Cu, Ni) in water-dioxan and water-ethanol media have been measured by stopped-flow spectrophotometric method. The results conform to,

$$k_{obs} = k_1 [H^+] + k_2 [H^+]^2$$

Cu(enba) is more labile than Ni(enba) as expected; at 25°C, $[H^+]$ = 0.01M, I = 0.1M in water-dioxan(10%) media $k^{Cu}_{obs}/k^{Ni}_{obs}$ = 2.33. Both k_1 and k_2 decrease with increased proportion of the co-solvent. log k (k = k_1, k_2) varies linearly with 1/D, Y and Z values of the solvent mixture; negative slopes of log k vs. 1/D and small positive slopes of log k vs. Y and log k vs. Z plots suggest dissociative process for both the concurrent paths; strongly negative ΔS^* values suggest significant solvent (H_2O) participation in the transition state. ΔH^* and ΔS^* values corresponding to k_1 and k_2 for the Cu(II) and Ni(II) complexes as well as of several other similar systems conform to an iso-kinetic trend implying similar mechanism. Rates of formation of M(enba) from $M^{2+}.aq$ and excess $enbaH_2$ in water-dioxan(10%) at pH 7.5 have also been measured; the copper complex is formed considerably much faster than the nickel complex under these conditions. The results are in conformity with outer-sphere association followed by transformation of the outer-sphere complex to the product in a one-step process.

LIGAND EXCHANGE REACTIONS OF CUPROUS IONS

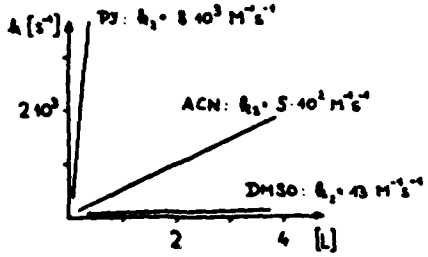
U. Ochsenbein and C.W. Schläpfer

Institute of Inorganic Chemistry, University of Fribourg
CH-1700 Fribourg (Switzerland)

The ligand exchange reaction (1) of α-diimine (L-L) ligands on $Cu(L\text{-}L)_2^+$ complexes have been studied by ^1H-NMR spectroscopy.[1]

$$Cu(L\text{-}L)_2^+ + L\text{-}L \underset{0.1M\ NEt_4ClO_4}{\overset{L'}{\rightleftharpoons}} Cu(L\text{-}L)_2^+ + L\text{-}L \qquad (1)$$

Reaction (1) is slow on the NMR time scale in $CHCl_3$, a non coordination solvent. Addition of a coordinating solvent or a good ligand L for cuprous ions accelerates the exchange. The rate is linear dependent on the concentration of L. The slope is a measure for the affinity between cuprous ions and L.



The activation parameters of the exchange reaction have been determined at intermediate concentrations of L.

L-L	L	$\Delta H^{\neq}$ (kJ Mol^{-1})	$\Delta S^{\neq}$ (J $Mol^{-1}K^{-1}$)	$V^{\neq}$ ($cm^3 Mol^{-1}$
	PY	36±1	-55±3	5.75±.16
	ACN	40±2	-64±5	10.34±.60

$$Cu(L\text{-}L)_2^+ + 2ACN \xrightarrow[0.1M\ NEt_4ClO_4]{} Cu(L\text{-}L)ACN_2^+ + L\text{-}L \qquad (2)$$

If the rate constant of dissociation (2) is interpreted assuming a pseudo first order mechanism ([ACN])=19.02M) the same activation parameters as for the exchange reaction (1) are obtained.

This result indicate that ligand exchange and dissociation reaction proceeds through the same transition state, with an additionale monodentate ligand L' in the coordination sphere. Prelinimary results show, that the activation parameters are strongly influenced by the ligand L-L.

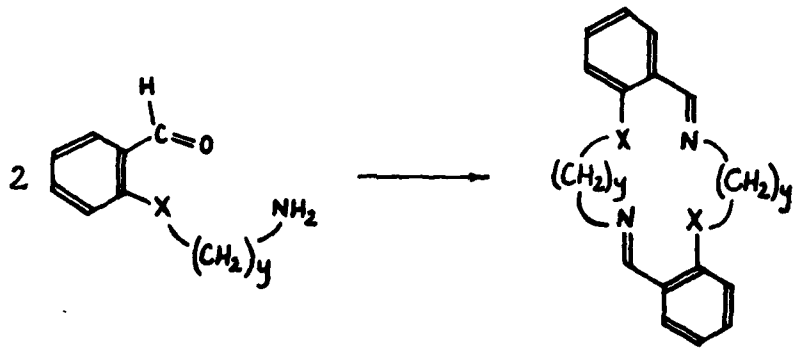
1. U. Ochsenbein, Diss. Nr. 828, University of Fribourg (1981)

A GENERAL SYNTHESIS FOR A VARIETY OF TRANS-N_2X_2 MACROCYCLES

John W.L. Martin, Kevin P. Wainwright, K.D. Vinindra Weerasuria and S. Bruce Wild

Research School of Chemistry, The Australian National University, P.O. Box 4, Canberra, A.C.T., 2600, Australia

Investigations into the complexation properties of trans-N_2X_2 macrocycles (X = O,S,N,As) have been inhibited by the absence of a satisfactory synthesis for this type of macrocycle. We have established a suitable method (Scheme) which is based upon the observation that certain ortho-substituted amino-benzaldehydes spontaneously cyclise to give trans macrocyclic di-imines in better than 80% yield.



Compound	x	y
(a)	O	2
(b)	O	3
(c)	S	2
(d)	S	3
(e)	NH	2
(f)	AsMe	2
(g)	AsMe	3

In order to generate the precursor amino-aldehyde we have found it sufficient in the cases where X = O,S or NH, to stir the corresponding ortho-substituted benzyl alcohol in methylene chloride with barium manganate. The macrocycle is isolated from solution 24h later without isolating the intermediate aldehyde. In the case where X = AsMe oxidising conditions cannot be used. Here the aldehyde is formed first and is protected with N,N^1-dimethylethylenediamine. Introduction of the aminoethylmethylarsine substituent leads to spontaneous cyclisation accompanied by elimination of the N,N^1-dimethylethylenediamine.

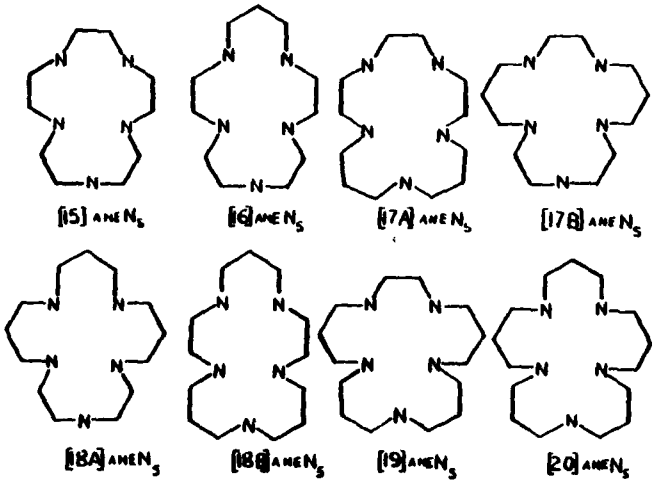
COBALT(II) AND COBALT(III) COMPLEXES OF THE PENTAAZAMACROCYCLES [15]aneN$_5$–[20]aneN$_5$

Peter Osvath and David C. Weatherburn

Chemistry Department, Victoria University of Wellington, Wellington, New Zealand.

Cobalt(III) complexes of the pentaazamacrocycles [15]aneN$_5$, [16]aneN$_5$, [17]aneN$_5$, [17B]aneN$_5$, [18A]aneN$_5$ and [18B]aneN$_5$ have been prepared and characterized.

Cobalt(III) complexes of [19]aneN$_5$ and [20]aneN$_5$ could not be prepared but cobalt(II) complexes were prepared which are believed to be five-coordinate.



Co[15]aneX^{n+} complexes exist as either the racemic or as one of the meso isomers; the other meso isomer is not observed. Co[16]aneX^{n+} complexes have been prepared as only one isomeric form, a meso isomer with the six membered ring in the middle of the three chelate rings in the plane containing four nitrogen atoms. Co[17A]aneX^{n+} also exist in one isomeric form, the racemic isomer with both six membered rings in the plane containing the four nitrogen atoms. Co[17B]aneN$_5$X^{n+} exists in two isomeric forms, one meso, one racemic of the geometric isomer with the 6,5,6 arrangement of chelate rings in the plane of the four nitrogen atoms. Co[16]aneN$_5$X^{n+} and Co[17A]aneN$_5$X^{n+} undergo induced aquation (Hg^{2+}, Ag^{+}) and base hydrolysis with retention of configuration. Co[15]aneN$_5$X^{n+} and Co[17B]aneN$_5$X^{n+} react under those conditions with some inversion of configuration.

LANTHANIDE IONS AS NMR PROBES FOR POLYAZA POLYCARBOXYLIC MACROCYCLES: STABILITY, STRUCTURE AND CONFORMATIONAL EQUILIBRIA.

J.F. Desreux and M.F. Loncin.
Analytical and Radiochemistry, University of Liège, Sart Tilman (B6), B-4000 Liège, Belgium.

Further studies on the complexation of lanthanide ions (Ln) by functionalized azamacrocycles have now been completed. Competition methods led to the determination of reliable stability constants of some LnDOTA and LnTETA complexes. DOTA forms the most stable Ln complexes known.

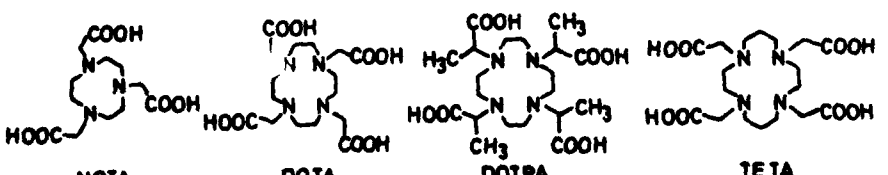
Moreover, ^{1}H and ^{13}C NMR studies showed that the LnNOTA complexes are non-rigid: the conformation of the ethylenediamine groups is inverting rapidly. On the contrary, the conformation of the cycle is frozen at room temperature in the case of DOTA[1] and of the optically active DOTPA. The latter remains rigid up to 100°C. Also, the solid and solution structures of LnDOTA are identical and axially symmetric[2]. A different conformational process takes place in the TETA complexes. In the solid, the coordination polyhedron is a distorted dodecahedron. This structure is maintained in solution but the two trapezoidal planes of the dodecahedron exchange their position and the NMR spectra are modified accordingly.

In each case, the conformation of the polyaza ring is identical to the conformation of the corresponding free polyoxa macrocycle. The coordination polyhedron of the Ln ions could have been deduced directly from the structure of these polyethers in the solid state.

Finally, the twelve-membered macrocycles exist in solution in two forms. For DOTA, the major form is axially symmetric and the ligand is octadentate while in the minor form, it is heptadentate, one carboxylic group being uncoordinated. The reverse is found for DOTPA: the axially symmetric form accounts for only 8.7% of the total concentration. The differences in coordination mode of the ligands are very well reflected in the values of the crystal field coefficients.

These NMR data are most unusual for Ln complexes which are known to be higly labile.

[1] J.F. Desreux, Inorg. Chem. 1980, 19, 1893.
[2] M.R. Spirlet, J. Rebizant, J.F. Desreux and M.F. Loncin, Inorg. Chem., in press.



[14]TETRAENEN$_4$ MACROCYCLES: SYNTHESIS OF THE PROTONATED METAL-FREE LIGAND AND PREPARATION, CHARACTERIZATION, AND ELECTROCHEMISTRY OF THE MANGANESE COMPLEX

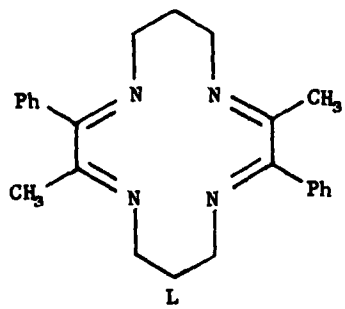
Susan C. Jackels and Brian A. Anderson

Wake Forest University, Department of Chemistry, Winston-Salem, North Carolina, USA 27109

Most complexes of substituted [14]tetraeneN$_4$ macrocycles are prepared by template condensation of α-diketones with 1,3-diaminopropane in the presence of divalent metal. This general method is successful for all of the later first row transition metals except Zn and Mn. The Zn complex of L has been prepared by reductive transmetalation of the CuL^{2+} complex with Zn metal. Neither of the above methods leads to the Mn complex. In order to make possible the preparation of Mn and other metal complexes of L we have isolated the protonated metal-free ligand salt of L. This ligand salt is made by treatment of the Cu(II) complex with anhydrous HCl in CH_3CN.

$$CuL^{2+} + 4H^+ \xrightarrow[CH_3CN]{LiBr} L\cdot 4HBr + Cu^{2+}$$

This ligand salt was used to prepare the Mn complex by reacting it with $Mn(OAc)_2$ in absolute EtOH. Addition of PF_6^- yields the product $[MnLBr]PF_6$. The Br^- axial ligand could be removed from the 5-coordinate complex by treatment with Ag^+. Other axial ligands were substituted including Cl^-, I^-, OH^- and nitrogenous neutral ligands. The complexes were characterized by elemental analyses, conductivity, IR, UV-Visible, and magnetic susceptibility measurements. All are 5-coordinate having high-spin Mn(II). The electrochemistry of the complexes was investigated using cyclic voltammetry. In CH_3CN at a glassy carbon electrode the halide derivatives undergo a reversible one-electron reduction at about -1.1 Volt versus $Ag^+/0.1\,\underline{M}$ $AgNO_3$. Compared to other Mn macrocyclic complexes, those of L are remarkably stable toward oxidation to Mn(III).



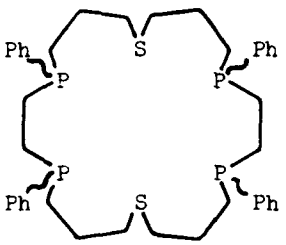
L

MACROCYCLIC POLYPHOSPHANE LIGANDS: A NOVEL TETRAPHOSPHADITHIA [22]-MEMBERED RING AND ITS COBALT(II) AND NICKEL(II) COMPLEXES

M. Ciampolini, S. Mangani, N. Nardi, P.L. Orioli and F. Zanobini

Department of Chemistry, University of Florence, Florence, Italy, Department of Chemistry, University of Siena, Siena, Italy and ISSECC (CNR), Florence, Italy

As part of our continuing studies[1] on polyphosphane macrocycles we synthesised the new compound 5,8,16,19-tetraphenyl-1,12-dithia-5,8,16,19-tetraphosphacyclodocosane, L. Such a macrocycle, containing a 22-membered ring, should allow one to investigate the effect of ring size on the coordinative behaviour when compared with the previously studied 18-membered rings.[2] The synthesis of L was carried out by reacting bis(3-chloropropyl)sulfide with the dilithium salt of 1,2-bis(phenylphosphino)ethane. The yield was about 15% and three diastereoisomers, out of the five obtained, were isolated in the pure state. They are 5RS,8RS,16RS,19SR (L_α), 5RS,8RS,16SR,19SR (L_β), and 5RS,8RS,16RS,19RS (L_δ).



(L)

These diastereoisomers react with cobalt(II) and nickel(II) to give 1:1, 2:1, and 3:2 metal to ligand complexes. An X-ray crystal structure analysis shows that the L_β nickel(II) complex, $[Ni_2Br_2(L_\beta)][BPh_4]_2 \cdot MeOH$, consists of dinuclear $[Ni_2Br_2(L_\beta)]^{2+}$ cations, $[BPh_4]^-$ anions and disordered lattice MeOH molecules. The dinuclear cation is centrosymmetric and each nickel ion displays a square-planar geometry achieved by coordination of two phosphorus atoms, one sulfur atom and one bromide anion. The Ni···Ni distance (5.13 Å) is very long ruling out any direct interaction. Electronic and $^{31}P\{^1H\}$ spectra as well as conductivity measurements show that the same structure holds in solution for this complex.

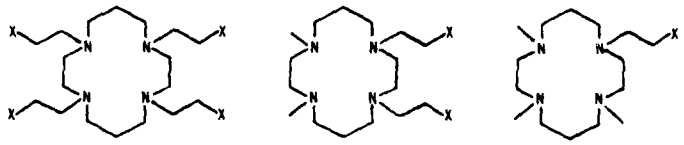
1. M. Ciampolini, P. Dapporto, N. Nardi, and F. Zanobini, J. Chem. Soc. Chem. Commun. 1980, 177; M. Ciampolini, P. Dapporto, A. Dei, N. Nardi, and F. Zanobini, Inorg. Chem. 1982, 21, 489; M. Ciampolini, P. Dapporto, N. Nardi, and F. Zanobini, *Inorg. Chem.* 1983, 22, 13; M. Ciampolini, N. Nardi, F. Zanobini, R. Cini, and P.L. Orioli, Inorg. Chim. Acta 1983, 76, L17.
2. M. Ciampolini, N. Nardi, P. Dapporto, P. Innocenti, and F. Zanobini, J. Chem. Soc. Dalton Trans. in the press; M. Ciampolini, P. Dapporto, N. Nardi, and F. Zanobini, J. Chem. Soc. Dalton Trans. in the press.

COMPLEXES OF TETRA-N-ALKYLATED CYCLAM LIGANDS CONTAINING FUNCTIONALIZED NITROGEN SUBSTITUENTS: SYNTHESIS, ISOMERIZATION, N-DEALKYLATION

E. Kent Barefield, Gary M. Freeman, Donald G. Van Derveer and Keith A. Foster

School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia, USA 30332

Metal complexation reactions of ligands of types I-III have been investigated. (Synthesis of Ib, IIa-d and IIIa-e, which have not



Ia-d IIa-d IIIa-e

a: X = CN, b: X = $C(O)NH_2$, c: X = CO_2CH_3, d: X = CH_2NH_2, e: X = CO_2H

been previously reported, will be described.) With Ni(II) the products obtained under kinetic control all appear to have the trans I stereochemistry. This has been firmly established for the complex of Ia by an x-ray structure. The kinetic products of Ni(II) and Ia, Ib or IIb isomerize upon heating in a suitable solvent (Ia, CH_3CN; Ib and IIb, H_2O). X-ray structures on the isomerized products of Ia and Ib show them to have the trans III stereochemistry. These isomerizations occur more rapidly than those of Ni(tetramethylcyclam)$^{2+}$ (Moore, et. al., Chem. Commun., 522 (1983).

When either isomer of the Ni(II) complex of Ia is heated in water (18-20 h) a complex of 1,8-bis(2-carbamoylethyl)-4-(2-cyanoethyl)-1,4,8,11-tetraazacyclotetradecane is formed in about 40% yield. An x-ray structure on this complex shows that the nickel ion is six-coordinate with the macrocycle folded such that the 1 and 8 nitrogens are cis and in the same plane as the carbamoyl oxygens, which act as the fifth and sixth donors. Ni(cyclam)$^{2+}$ (5%) and a complex of 1,8-bis(2-carbamoylethyl)-1,4,8,11-tetraazacyclotetradecane (15%) were also isolated from the hydrolysis reaction. These are apparently formed by an independent pathway from the major product since it did not undergo any reaction after 96 h of additional heating. Dealkylation of nickel complexes of carbamoylethyl substituted ligands has not been observed so far; however, the Cu(II) complex of IVb undergoes dealkylation upon heating in acetonitrile with sodium methoxide. Facile dealkylation has also been observed for the Cu(II) complexes of IIIc (CH_3O^-/CH_3CN) and IIIe (H^+/H_2O).

Our results indicated that the possibility of dealkylation and isomerization must be considered in future studies of macrocyclic tertiary amine ligands that contain functionalized N-alkyl groups. When retro-Michael reactions are possible, high temperatures and acidic or basic conditions should be avoided. Such dealkylation reactions may also be sensitive to the nature of the metal ion.

OLIGOMERIC OXO-/HYDROXO-BRIDGED CLUSTERS OF Mo AND W IN OXIDATION STATES III,IV AND V FROM MONOMERIC 1,4,7-TRIAZACYCLONONANE AND ITS TRIMETHYL DERIVATIVE COMPLEXES

P.Chaudhuri, G.Backes-Dahmann, K.Wieghardt

Ruhr-Universität Bochum, P.O.B.102148, D-4630 BOCHUM, FRG

Br_2-oxidation of $M(CO)_3L$ [1] [M=Mo,W] affords mononuclear $O^{V}MLBr_3$ (I). I dimerises in aqueous solution resulting yellow cis $[W_2O_4L_2]^{2+}$ (II).

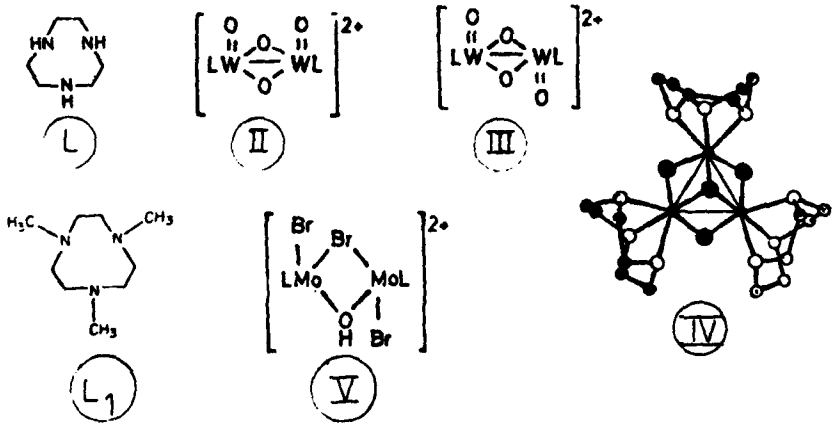
The corresponding brick-red trans-isomer(III), has also been prepared. Both isomers are diamagnetic suggesting a direct W-W interaction.

Reduction of I with Zn in acidic solution results a deep green solution which on oxidation by air yields deep-red trinuclear complex $[M_3O_4L_3]^{4+}$ (IV). W-W single bonds are postulated according to its short W....W distances (~ 2,52 Å) and diamagnetism.

Above mentioned green solution (containing Mo) afforded Mo(III) dimer. Single crystal X-ray structural determinations of the green W(III) complex is in progress.

Oxidation of $Mo(CO)_3L_1$ [2] with HNO_3 yields yellow crystals (characterised by chemical analysis, IR and magnetic measurements) of a probably oxo-bridged tetranuclear Mo(V) complex. X-ray structure (inprogress) will be presented.

The electrochemistry of the complexes will also be presented.



1. P.Chaudhuri, K.Wieghardt, Yi-Hung Tsay and C.Krüger. Inorg.Chem.,in Press.

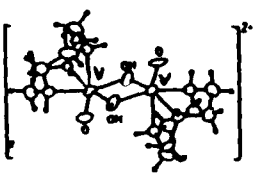
2. K.Wieghardt, P.Chaudhuri, B.Nuber, J.Weiss. Inorg.Chem., 1982, 21, 3086.

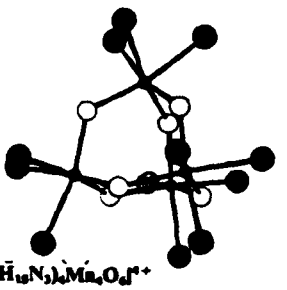
1,4,7-TRIAZACYCLONONANE - A VERSATILE LIGAND FOR THE SYNTHESIS OF NOVEL OLIGOMERIC OXO-/HYDROXO BRIDGED COMPLEXES

Karl Wieghardt, Klaus Pohl, Martin Koeppen

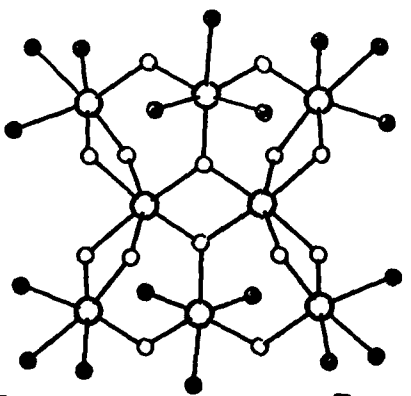
Ruhr-Universität Bochum, P.O.B.102148, D-4630 BOCHUM, FRG

The tridentate ligand 1,4,7-triazacyclononane (L) and its N-methylated analog form stable monomeric, octahedral complexes of the type LMX_3 (M=Ti,V,Cr,Mn,Fe,Co,Mo,Ru; X=Br,Cl). The controlled hydrolysis of these complexes leads to a variety of dimeric, trimeric and oligomeric complexes with oxo- and/or hydroxo bridges. For example the following structural types have been identified by X-ray cyrstallography

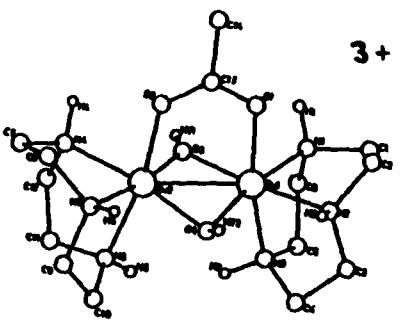




$[(C_9H_{15}N_3)_4Mn_4O_6]^{4+}$



$[L_6Fe_8(\mu_3\text{-}O)_2(\mu_2\text{-}OH)_{12}]Br_8 \cdot 9H_2O$



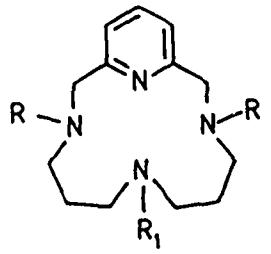
3+

The electrochemistry and magnetic properties of these complexes have been investigated. The diamagnetic $Ru^{III}Ru^{III}$ species containing a metal-metal bond is reversibly reduced to the Ru^{II}/Ru^{III} mixed valence species. The V(IV) V(IV) species exhibits strong antiferromagnetic coupling (d^1-d^1); it represents the first u-hydroxo complex of V(IV).

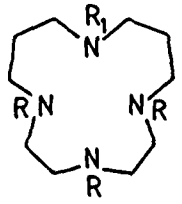
COORDINATION CHEMISTRY OF AZAMACROCYCLIC LIGANDS INCLUDING SOME WITH PENDANT COORDINATING ARMS

Nathaniel W.Alcock, Peter Moore, Colin Pierpoint & John Sachinidis

Department of Chemistry, University of Warwick, Coventry, CV4 7AL.UK.



(A)



(B)

New Pendant-Arm Macrocyclic Ligands: Synthesis of (A) and (B) (R_1 = $(CH_2)_xNMe_2$; x = 2 or 3; R = H or Me) will be described. These quinquedentate ligands (L) give 5-coordinate trigonal bipyramidal complexes of the type $[M(L)](ClO_4)_2$ confirmed, by the crystal structure of a Ni^{2+} complex. Cu^{2+} and Zn^{2+} complexes have also been isolated and characterised. In acidic solution these trigonal bipyramidal complexes (M = Ni^{2+} or Cu^{2+}) form square-planar complexes by protonation of the pendant-arm:

$$\underset{\text{tbp}}{[M(L)]^{2+}} + H^{+} = \underset{\text{square planar}}{[M(LH)]^{3+}}$$

For the Cu^{2+} complexes a high acidity is required to force this equilibrium to the right, but for Ni^{2+} the square-planar complex forms readily at low pH, and at a rate too fast to measure by stopped-flow.

Isomerisation Reactions Isomerisation of complexes formed by tetraazamacrocyclic ligands occurs in the presence of donor solvents or ligands. For example $[Ni(TMC)]^{2+}$ (TMC = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane) can be interconverted between R,S,S,R- and R,S,R,S-geometries in DMSO or DMF, and quite rapidly in the presence of n-propylamine. Other isomerisation reactions will be reported.

1. P. Moore, J.Sachinidis and G.R.Willey, J.Chem.Soc.,Chem.Comm., 1983, 522.
2. N.W. Alcock, C.Pierpoint & P.Moore, J.Chem.Soc.Dalton.Trans., (in press).

NEW COORDINATION CHEMISTRY INDUCED BY BULKY DIORGANOPHOSPHIDO LIGANDS

Richard A. Jones, Anthony L. Stuart, Mark H. Seeberger and Thomas C. Wright

Department of Chemistry, University of Texas at Austin, Austin, Texas 78712

The use of the di-tert-butyl phosphido ligand ($^tBu_2P^-$) and other bulky phosphido groups has enabled the isolation and characterization of a number of new complexes which exhibit interesting new geometries, stoichiometries and chemical behavior.[1-4] Five main areas will be discussed: (a) The synthesis and substitution chemistry of dinuclear complexes of nickel(I) of formula $(Ni(\mu\text{-}^tBu_2P)PR_3)_2$. Of interest here is the isolation of unusual asymmetric, stable, carbonyl complexes of stoichiometry $LNi(\mu\text{-}^tBu_2P)Ni(CO)_2$ (L = CO, PR_3). In these complexes one nickel(I) atom is trigonal planar while the other has a pseudotetrahedral geometry. (b) Dimers of the cobalt triad which have the general formula $[M(\mu\text{-}R_2P)L_2]$ (M = Co, Rh, Ir; L = two-electron donor; CO, PR_3, etc.). The interesting feature in this family of complexes is the observation of three different types of isomer. On the basis of bond length considerations the approximate geometry about each metal (tetrahedral or planar) may be correlated with the bond order of the metal-metal interaction. Thus, two planar metals have a bond of order zero while two tetrahedral metals have a bond of order two. The intermediate case, with one tetrahedral and one planar metal also exists, and the bond order here is one. Factors which affect the formation of a particular isomer will be described as will a Rh(I) system which exhibits the unusual feature of a facile, reversible, metal-metal bond cleavage which is accompanied only by a geometrical isomerism. (c) Mixed metal systems which are stabilized by a single $\mu\text{-}^tBu_2P$ bridge, including dinuclear complexes of Cr-Co, Cr-Ni and Cr-Rh. (d) The synthesis, characterization and X-ray structure of $Mo_2(\mu\text{-}^tBu_2P)_2(^tBu_2P)_2$ which is the first reported binary transition metal diorganophosphide. (e) The synthesis, characterization and X-ray structure of $[Li_2(\mu_3\text{-}^tBu_2P)(\mu_2\text{-}^tBu_2P)C_4H_8O]_2$ which is, so far, the only lithium diorganophosphide to have been structurally characterized. The structure has an unusual staggered, planar Li_4 unit.

1. R.A. Jones, A.L. Stuart, J.L. Atwood, W.E. Hunter and R.D. Rogers, Organometallics 1982, 1, 1721.
2. R.A. Jones, T.C. Wright, J.L. Atwood and W.E. Hunter, Inorg. Chem. 1983, 22, 993.
3. R.A. Jones, T.C. Wright, J.L. Atwood and W.E. Hunter, Organometallics 1983, 2, 470.
4. R.A. Jones, A.L. Stuart, J.L. Atwood and W.E. Hunter, Organometallics 1983, 2, 874.

OPENING OF THE P_4 MOLECULE: TETRAPHOSPHORUS CHAIN $P^{P}_{P}{}^{P}$ AS A PART OF AN EIGHT-PHOSPHORUS CONTAINING LIGAND IN A COBALT COMPLEX

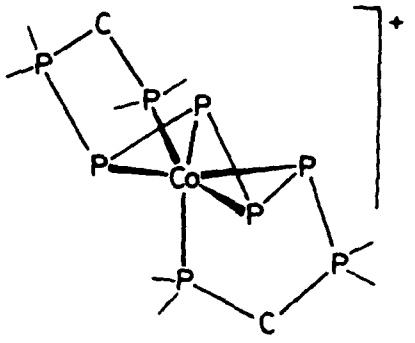
Franco Cecconi, Carlo A. Ghilardi, Stefano Midollini and Annabella Orlandini

Istituto per lo Studio della Stereochimica ed Energetica dei Composti di Coordinazione, CNR, Firenze, Italy

Little is known of reactivity of white phosphorus towards organometallic species. Indeed although a breaking off of the P_4 molecule generally occurs, only sometimes complexes containing the fragments cyclo-P_3, P_2 or P atoms metal-coordinated have been isolated.[1,2,3]

Now, by reacting cobalt(II) tetrafluoroborate with bis(diphenylphosphino)methane (dpm) and white phosphorus, we have succeeded in the synthesis of the complex $[Co(Ph_2PCH_2PPh_2PPPPPh_2PCH_2PPh_2)]BF_4$, which can hopefully represent an important novel contribution to the understanding of the P_4 molecule breaking off.

The X-ray structure of the complex has showed that the novel ligand $Ph_2PCH_2PPh_2PPPPPh_2PCH_2PPh_2$ arising from the opening of a P_4 molecule and the attack of two dpm ligands is formed. This ligand coordinates the metal through the four phosphorus atoms of the zigzag $P^{P}_{P}{}^{P}$ fragment and two phosphorus atoms belonging to the dpm ligands.



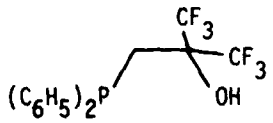
Investigations about the reactivity of this compound, which are in progress, have now achieved the following results: (i) the phosphorus atoms of the $P^{P}_{P}{}^{P}$ fragment are coordinatively unsaturated, the present complex reacting with $W(CO)_6$ to form the derivative $[Co(Ph_2PCH_2PPh_2PPPPPh_2PCH_2PPh_2)W(CO)_5]BPh_4$, (ii) the complex can be used in the place of white phosphorus to form cyclo-P_3 derivatives.

1. M. Di Vaira, C.A. Ghilardi, S. Midollini, and L. Sacconi, J. Am. Chem. Soc. 1978, 100, 2550.
2. C.F. Campana, A. Vizi-Orosz, G. Palyi, L. Markò, and L.F. Dahl, Inorg. Chem. 1979, 18, 3054.
3. G.L. Simon and F. Dahl, J. Am. Chem. Soc. 1973, 95, 382.

MULTIDENTATE HYBRID LIGANDS: STUDIES ON A BIDENTATE ALKOXY-PHOSPHINO LIGAND; AN INSTANCE OF CIS-TRANS ISOMERISM IN A SQUARE-PLANAR Ni^{2+} COMPLEX

René T. Boeré, Craig Montgomery, and Christopher J. Willis
The University of Western Ontario, London, Canada N6A 5B7

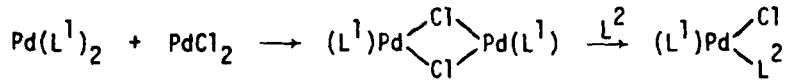
We have prepared compound 1, which (in its deprotonated form) acts as a bidentate, uninegative, ligand in which the hard alkoxy-donor group, $-C(CF_3)_2O^-$, is coupled with the soft phosphino donor



1 (deprotonated = L^1)

This ligand gives neutral complexes $M(L^1)_2$, where M = Co^{2+}, Ni^{2+}, Pd^{2+}, and Pt^{2+}, together with the copper(I) complex $(L^1)Cu(PPh_3)_2$ and the rhodium(III) anionic complex $K[Rh(L^1)_2Cl_2]$. NMR studies on the Pt^{2+} complex show only a cis-square-planar geometry, but for M = Ni^{2+}, solution NMR show that two isomers are present in a solvent- and temperature-dependent equilibrium. These are assigned as cis- and trans-forms of the square-planar complex $Ni(L^1)_2$ and thermodynamic parameters for their interconversion have been evaluated. By a suitable choice of solvent, the solid complex has been obtained in two crystalline forms, and structural studies are in progress to correlate these with the solution behaviour.

The palladium system has been extended by the preparation and subsequent cleavage of chloro-bridged dinuclear species:

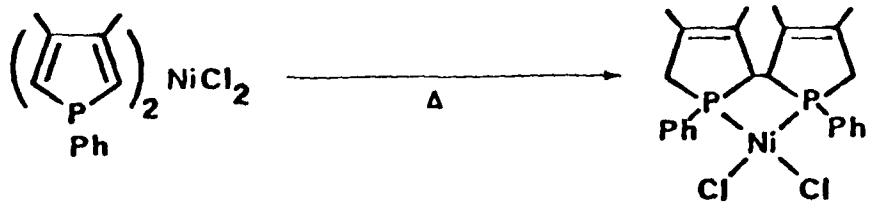


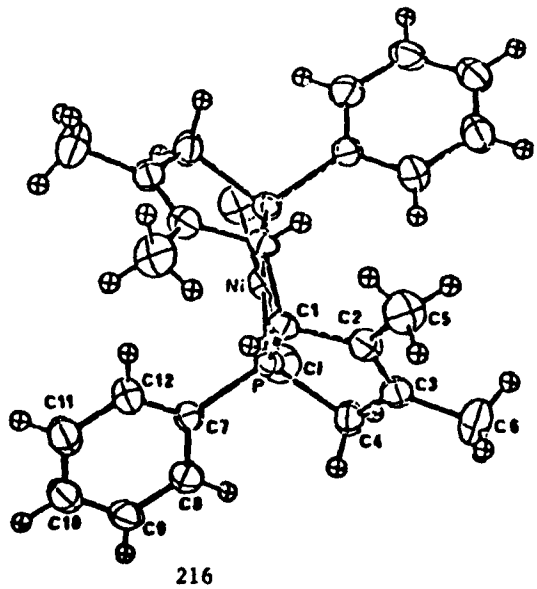
$L^2 = R_2S$, etc.

ENANTIOMERIC DIPHOSPHOLENES BY NICKEL(II) PROMOTED THERMAL DIMERIZATION OF PHOSPHOLES

F. Mercier and F. Mathey, Laboratoire CNRS/SNPE, 94320 Thiais France, J. Fischer, Universite' Louis Pasteur, 67070 strasbourg, France and J.H. Nelson, Department of Chemistry, University of Nevada, Reno, Nevada 89557

Thermolysis in alcoholic solvents between 140 and 170°C of 1-phenyl-3,4-dimethylphosphole in the presence of anhydrous Nickel (II) chloride leads to the synthesis of racemic dichloro-2,2'-bis[3,4-dimethylphosphole-3-ene] Nickel (II) chloride in reasonable yield. This reaction represents the first synthesis of a diphospholene and occurs with remarkable stereoselectivity. This ligand has been transferred from Ni(II) to Pd(II), Pt(II), and Ru(II) without epimerization. The mechanism of the formation of the diphospholene will be discussed. The complexes have been characterized by a variety of spectroscopic techniques, e.g., ^{1}H, $^{13}C\{^{1}H\}$, $^{31}P\{^{1}H\}$ and $^{1}H\{^{31}P\}$ NMR, infrared spectroscopy, electrochemistry and for the Ni(II) and Pd(II), single crystal x-ray crystallography.





REACTIONS OF Co(II) WITH $NaBH_4$ IN THE PRESENCE OF BIDENTATE PHOSPHINES

David G. Holah,[a] Alan N. Hughes,[a] Stanislaw Maciaszek,[a] Kenneth O. Parker[b] and Vincent R. Magnuson[b]

[a]Department of Chemistry, Lakehead University, Thunder Bay, Ontario, Canada, P7B 5E1

[b]Department of Chemistry, University of Minnesota, Duluth, Duluth, Minnesota, USA, 55812

Reactions between Co(II) and $NaBH_4$ in the presence of $Ph_2P(CH_2)_nPPh_2$ (n=1-6) lead to the formation of a variety of complexes. These include the very recently structurally characterized $[Co(Ph_2P(CH_2)_5PPh_2)(BH_4)]_2$ [1] (which contains both bridging phosphines and tridentate bridging BH_4^- groups) and $CoH[Ph_2P(CH)_3PPH_2]_2$ (which contains 5- coordinated Co(I) with chelating phosphines and a terminal hydride.

The chemistry of the Co(II)/BH_4^- system with Dppm (n=1) as the phosphine ligand is reported in this paper and the differences in the resulting Dppm complexes as compared to $Ph_2P(CH_2)_nPPh_2$ (n=2-6) complexes will be noted. The actual product formed in reactions between $CoCl_2$, $NaBH_4$ and Dppm is markedly dependent upon the ratio of the reactants, the rate of addition of the $NaBH_4$ and the time of reaction; very careful control of these parameters is necessary to obtain reproducible results. Two of the first complexes to form are the green, paramagnetic Co(I) complexes [CoCl(Dppm)] (I) and $CoCl(Dppm)_2\cdot$Solvent (II), with I being convertible into II under certain conditions. Along with the formation of II, a yellow crystalline Co(III) complex, $CoHCl_2(Dppm)_2\cdot 2EtOH$ (III) can be isolated from this strongly reducing environment. The ^{31}P nmr signal at δ-15 ppm is consistent with chelating Dppm ligands and the ^1H nmr spectrum, with an upfield quintet at δ-17.2 ppm (J_{PH} = 52 Hz), confirms the presence of the terminal hydride.

Different reaction parameters lead to the formation of a red Co(I) hydride complex, $[CoH(Dppm)_2]$ (IV). The ^{31}P nmr signal at δ57.2 ppm strongly suggests the presence of bridging Dppm ligands and accordingly a dimeric structure. This is in contrast to the stoichiometrically similar monomeric n=3 complex mentioned earlier. Extending the reaction time leads to an as yet unidentified extremely air-sensitive crystalline complex (V), which appears to contain boron. This complex is also produced when (II) or (III) react with additional $NaBH_4$. Recrystallization of (V) leads to the coprecipitation of a very dark paramagnetic complex (VI).

Results of further synthetic, chemical and physical studies and x-ray diffraction studies, as available, will be reported.

1. D. G. Holah, A. N. Hughes, S. Maciaszek and V. R. Magnuson, J. Chem. Soc. Chem. Commun., 1983, in press.

SYNTHESIS AND CHARACTERIZATION OF TUNGSTEN CARBONYL COMPOUNDS WITH TRIMETHYLENEMETHANE LIGANDS

Agnes A. Alich* and Nancy S. Mills**

*College of St. Scholastica, Duluth, Minnesota, USA 55811
**Trinity University, San Antonio, Texas, USA 78284

Tungsten carbonyl derivatives containing the dianion of isobutylene and ligands such as bis-(diphenylphosphino)-ethane (DIPHOS) have been synthesized. Preliminary results suggest that the C_4H_6 ligand acts as a six-electron donor, bonded as trimethylenemethane, rather than as a four-electron donor, which would yield a metallocyclobutane. Confirming evidence will be presented.

The steps in the synthesis may be summarized as follows:

$$Mo(CO)_6$$

$$\downarrow$$

$$W\left[(C_6H_5)_2PC_2H_4P(C_6H_5)_2\right](CO)_3Br_2$$

$$\downarrow$$

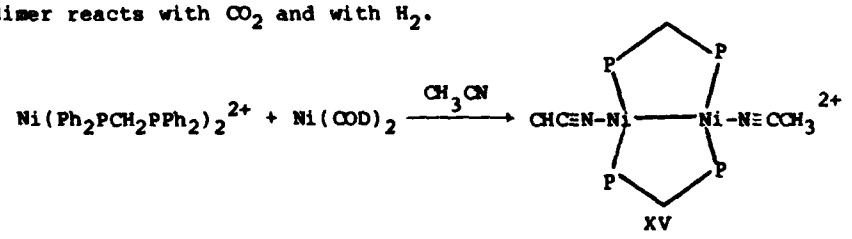
$$W\left[(C_6H_5)_2PC_2H_4P(C_6H_5)_2\right](C_4H_6)(CO)_2$$

Nickel(II), Nickel (I), and Nickel(0) Complexes of Polydentate Phosphine Ligands

Daniel L. DuBois

Solar Energy Research Institute, 1617 Cole Boulevard, Golden, CO 80401

The reaction of $Ni(CH_3CN)_6^{2+}$ with a variety of bidentate, tridentate, and tetradentate ligands results in the formation of $Ni(Ph_2PCH_2PPh_2)_2^{2+}$ (I), $Ni(Ph_2PCH_2CH_2PPh_2)_2^{2+}$ (II), $Ni(Ph_2PCH_2CH_2CH_2PPh_2)_2^{2+}$ (III), $Ni(Ph_2PCH_2CH_2Py)_2^{2+}$ (IV), $Ni[PhP(CH_2CH_2PPh_2)_2](CH_3CN)^{2+}$ (V), $Ni[PhP(CH_2CH_2Py)_2](CH_3CN)^{2+}$ (VI), $Ni[Ph_2PCH_2CH_2P(Ph)CH_2CH_2P(Ph)CH_2CH_2PPh_2]^{2+}$ (VII), and $Ni[P(CH_2CH_2PPh_2)_3](CH_3CN)^{2+}$ (VIII) (where Py is 2-pyridyl). The electrochemistry of these complexes will be discussed. Similarly reaction of $Ni(COD)_2$ with various ligands leads to the formation of the known $Ni(Ph_2PCH_2CH_2PPh_2)_2$ (IX) and $Ni(Ph_2PCH_2CH_2CH_2PPh_2)_2$ (X) complexes and the new complexes $Ni(Ph_2PCH_2CH_2Py)_2$ (XI) and $[NiP(CH_2CH_2PPh_2)_3]_2$ (XII). Reaction of $Ni(COD)_2$ with various tridentate ligands results in the formation of intractable mixtures of complexes. Reaction of (II), (III), and (IV) with IX, X, and XI, respectively, results in the formation of the corresponding Ni(I) complexes. Reaction of VIII and XII in acetonitrile results in the formation of a new Ni(I) dimer formulated as $[NiP(CH_2CH_2PPh_2)_3]_2^{2+}$ (XIII). The same reaction carried out using tetrahydrofuran as the solvent results in the formation of the known nickel(I) monomer $[NiP(CH_2CH_2PPh_2)_3]^+$ (XIV). Another nickel(I) dimer, XV, can be formed as shown in reaction (1). This dimer reacts with CO_2 and with H_2.



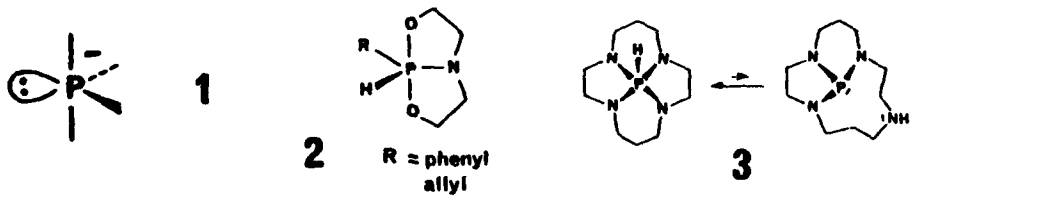
XV

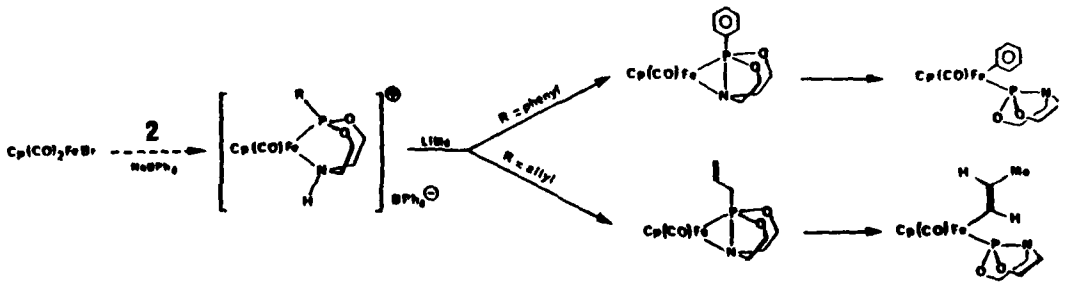
SOME INTER-REACTIONS BETWEEN TRANSITION METALS AND CYCLIC PHOSPHORUS/NITROGEN LIGANDS

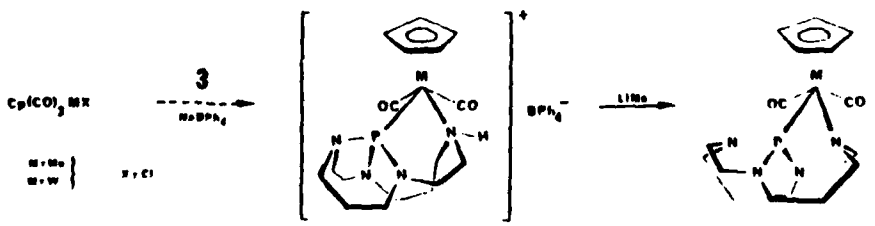
Pierre Vierling, Jean-Marc Dupart, and Jean G. Reiss

Laboratoire de Chimie Minerale Moleculaire, Equipe de Recherche Associee au CNRS, Parc Valrose, 06034 Nice, France.

Phosphorus ligands are commonly used as tools to provoke given electronic and geometric structures in metal complexes and modulate their properties. But the metal does not stay innocent with respect to the ligand; it may perturb it profoundly and induce new phosphorus chemistry. Such inter-reactions have led to the unveiling of tautomeric forms, the production of new types of ligands such as phosphoranides (1) and their complexes, to the observation of original group migration and bond activations, etc. Examples will be taken from the chemistry of bicyclic aminophosphoranes (2) and from cyclamphosphorane (3) in the presence of transition metal derivatives:







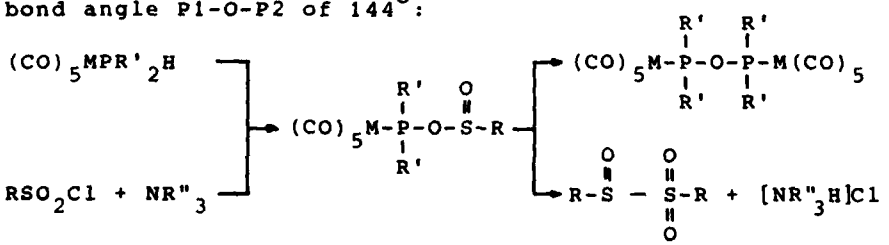
SYNTHESIS, CRYSTAL STRUCTURE AND COMPLEX CHEMICAL BEHAVIOUR OF METAL-COORDINATED PHOSPHINITE DERIVATIVES

Christina Zeiher and Ingo-Peter Lorenz

Institute for Inorganic Chemistry of the University, Auf der Morgenstelle 18, D-7400 Tübingen (F.R.G.)

The phosphorus homologues of sulfonamides are hitherto unknown because of the extremely unstable atomic combination $R'_2P{-}S(O)_2R$. In our endeavour to find suitable methods of preparation for these compounds we have reacted some metal-coordinated phosphanes with the corresponding sulfonyl derivatives.

For instance, the diphenylphosphane complexes $(CO)_5M{-}P(C_6H_5)_2H$ (M = Cr, Mo, W) react with sulfonyl chlorides RSO_2Cl via the not isolable sulfinyldiphenylphosphinito-P metal complexes $(CO)_5M[P(C_6H_5)_2OS(O)R]$ to give the homogeneous anhydrides, the tetraphenyldiphosphoxane complexes $[(CO)_5MP(C_6H_5)_2]_2O$ and the sulfinylsulfones $R(O)S{-}S(O)_2R$. The crystal structure determination for M = Cr shows two nearly octahedral configurated $(CO)_5CrP(C_6H_5)_2$-moieties joined by an unsymmetrical oxygen bridge and the bond angle P1-O-P2 of 144°:



As a result of the reaction of the bifunctional dianion $[(CO)_4MnP(C_6H_5)_2]^{2-}$ with SO_2Cl_2 we surprisingly obtained tetracarbonyl-hydrogenbis(diphenylphosphinito-P)-manganese instead of the expected mono- or dimeric complex $[(CO)_4MnP(C_6H_5)_2S(O)_2]_n$ (n = 1, 2) with the intact sulfonyl and phosphido function. In addition to simple substitution, also complicated redox reactions must take place.

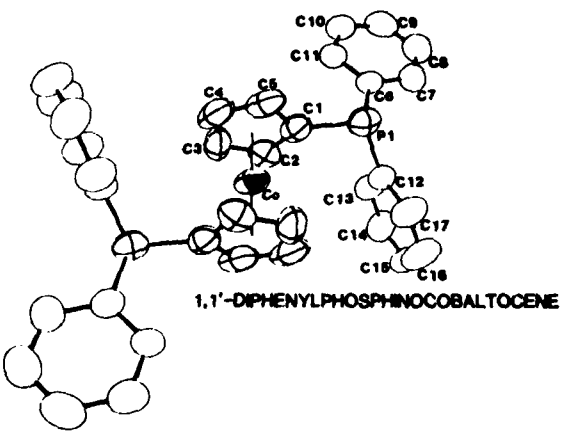
According to the x-ray structure analysis four carbonyl and two phosphinito-P ligands are bound in cis-positions to the octahedral coordinated manganese atom. The two oxygen atoms are linked together by an unsymmetrical hydrogen bridge forming the nearly planar six-membered ring system Mn-P1-O5-H-O6-P2. The compound can be transformed by $N(C_2H_5)_3$ to the corresponding salt indicating an interesting complex chemical behaviour.

Synthesis, X-Ray Structural Characterization, and Reactions of 1,1'-Diphenylphosphinocobaltocene

Charles W. Eigenbrot, Jr., Daniel L. DuBois and James C. Smart

Solar Energy Research Institute, Golden, Colorado, 80401, USA

The use of symmetrically disubstituted metallocenes as novel bidentate ligands[1] has been hampered by a lack of general synthetic routes for the introduction of donor groups such as diarylphosphines. Reaction of $TlC_5H_4PPh_2$ [2] with anhydrous $CoCl_2$ gives the neutral complex, $Co(C_5H_4PPh_2)_2$, in good yield. This paramagnetic (μ_{eff} = 1.73 B.M.) Co(II) metallocene exhibits structurally significant variations in Co-C_1 and intraring C-C distances due to electronic effects of diphenylphosphine substituents. Extended Hückel molecular orbital calculations indicate the degeneracy of the e_g orbital set in a symmetrical metallocene is lifted by a bonding interaction between a d orbital on phosphorus and a p orbital on C_1. The metal d_{xz} orbital interacts in an antibonding fashion with C_1, C_3 and C_4. The strongest interaction was calculated to be with C_1, which is consistent with the observed variations in metal-to-ring carbon distances of the order $C_1 > C_3, C_4 > C_2, C_5$. The electrochemistry, and reaction chemistry of this redox active bidentate ligand will be discussed.



1,1'-DIPHENYLPHOSPHINOCOBALTOCENE

1. A. W. Rudie, D. W. Lichtenberg, M. L. Katcher and A. Davison, Inorg. Chem., 1978, 17, 2859-2863.

2. M. D. Rausch, B. H. Edwards, R. D. Rogers and J. L. Atwood, J. Amer. Chem. Soc., 1983, 105, 3882-3886.

DISPLACEMENT REACTIONS OF THE DINITROGEN COMPLEX trans-$[ReCl(N_2)(dppe)_2]$. PREPARATION OF A TETRAHYDROBORATE COMPLEX OF Re(I), $[Re(BH_4)(dppe)_2]$

Armando J.L. Pombeiro

Centro de Química Estrutural, Complexo I,
Instituto Superior Técnico, Av. Rovisco Pais, Lisboa, Portugal

Raymond L. Richards
School of Molecular Sciences, University of Sussex, Falmer, Brighton, England

Although dinitrogen is usually a labile ligand, complex trans-$[ReCl(N_2)(dppe)_2]$, (A), presents a strong metal-N_2 bond which is stabilized by the electron donor halide co-ligand. However, an unsaturated species, $[ReCl(dppe)_2]$, has recetly been isolated[1] upon photolysis of the parent N_2 complex, and it may be involved in the replacement reactions of dinitrogen by isocyanides[2] or carbon monoxide.

The chloride ligand in complex(A)may be displaced by an abstractor such as Tl^+, and new complexes may be derived upon coordination of an anionic species with, or without, N_2 loss.

Hence, e.g., the tetrahidroborate complex cis-$[Re(BH_4)(dppe)_2]$, (B), and the thiolate species $[Re(SC_6H_4CH_3)(dppe)_2]$ are prepared according to reactions (1) and (2) with N_2 evolution, whereas the unstable dinitrogen-ethoxide complex $[Re(OEt)(N_2)(dppe)_2]$ appears to be formed in reaction (3).

$$[ReCl(N_2)(dppe)_2]\ (A) \xrightarrow[thf]{TlBF_4, BH_4^-} cis\text{-}[Re(BH_4)(dppe)_2] \quad (1)$$

$$[ReCl(N_2)(dppe)_2]\ (A) \xrightarrow[thf]{TlSC_6H_4CH_3\text{-}4} [Re(SC_6H_4CH_3\text{-}4)(dppe)_2] \quad (2)$$

$$[ReCl(N_2)(dppe)_2]\ (A) \xrightarrow[thf]{TlOEt} [Re(OEt)(N_2)(dppe)_2] \quad (3)$$

The bonding of the BH_4^- ligand to the metal in complex (B) will be discussed in terms of the available spectroscopic data.

The effect of the co-ligand trans to dinitrogen on the stabilization of the Re-N_2 bond and the application of complex(A) to generate reactive unsaturated species will also be object of discussion.

References: 1-D.L.Hughes,A.J.L.Pombeiro,C.J.Pickett,R.L.Richards, J.Organometal.Chem.,1983, 248,C26. 2-A.J.L.Pombeiro, C.J.Pickett, R.L.Richards, J.Organometal.Chem., 1982, 224, 285

Acknowledgements: The support given by the JNICT (contract Nº 216.80.56), the INIC (Portugal) and the British Council are gratefully acknowledged.

THERMOCHEMISTRY AND STABILITY OF ION-MOLECULE COMPLEXES FROM GAS PHASE ION MOLECULE EQUILIBRIA

Jan Sunner. Tom Magnera. Gary Caldwell. Ram Sharma and P. Kebarle

Chemistry Department, University of Alberta, Edmonton, Canada, T6G 2G2

Ion molecule equilibria (n-1,n) can be measured with a pulsed ionization high pressure mass spectrometer.

$$M^+ + L = M^+L \qquad (0,1)$$

$$M^+L_{n-1} + L = ML_n \qquad (n-1,n)$$

$$M^+ + {}_nL = ML_n \qquad (0,n)$$

Determination of the equilibrium constants at different temperatures leads via van't Hoff plots to the corresponding enthalpy, free energy and entropy changes. $\Delta H^\circ_{n-1,n}$, $\Delta G^\circ_{n-1,n}$ and $\Delta S_{n-1,n}$. Summation of the stepwise changes (n-1,n) leads to (0,n) data. Values up to n = 6 can generally be obtained.

Recent results that will be presented include the alkali positive ions M^+ and the halide ions X^- complexing with the ligands H_2O, CH_3OH, Me_2CO, MeCN, Me_2SO, dimethylformamide, dimethylacetamide, SO_2, CS_2. Data with a much larger variety of ligands is available for the potassium ion and the chloride and fluoride ion. Quantum mechanical calculations when performed with a large basis set predict binding energies in good agreement with the experimental results. The binding energies, particularly as the size of the ion increases are dominated by electrostatic interactions. To understand the changes of binding with nature of ligand one must take into account the detailed charge distribution in the ligand (which adds up to the ligand dipole seen at larger distances). Similar account must be taken of the distribution of the polarizability. Such considerations provide more rigorous explanation of stabilities of complexes than the concepts of the hard and soft acids and bases theory.

Thermochemical results for multidentate ligands can be also obtained. Recent results for the complexes of H^+, H_3O^+, $CH_3OH_2^+$ and NH_4^+ with crown ethers will be presented.

ELECTRON, NEGATIVE ION AND RADICAL INTERACTIONS AT TRANSITION METAL CENTRES UNDER NEGATIVE CHEMICAL IONISATION CONDITIONS

Glen W. Dillow, Ian K. Gregor and Michael Guilhaus

University of New South Wales, P.O. Box 1, Kensington, N.S.W., Australia 2033

Transition metals when appropriately complexed by bidentate or quadridentate ligands present highly specific reactive centres for gaseous reactions to occur under negative chemical ionisation (NCI) conditions. Electron attachment leading to the formation of long-lived molecular negative ions is related to the availability of an accessible metal or ligand-based LUMO and also the stability of the metal oxidation state with respect to reduction. If coordinatively unsaturated, the metal is capable of entering into reactions with negative ions generated by ionisation of reagent gases within the ion source. Numerous factors influence such reactions which take place unencumbered by complicating solvation phenomena. These include the hard-soft acid-base properties of the metal, its stereochemistry and preferred coordination number, the ligand donor atom sets together with the Lewis and Brønsted base properties of the reagent negative ions. In certain cases such reactions are competitive with electron attachment processes. Reactions which involve the participation of radicals derived from hydrocarbon or halocarbon reagent gases can also occur at metal centres and can be identified by appropriate metal chelate selection and emmision current variations. Illustrations of these various types of reactions will be given.

EARLY-STAGE THERMAL DECOMPOSITION OF AN EXPLOSIVE COORDINATION COMPOUND BY MASS SPECTROMETRIC AND ANCILLARY TECHNIQUES*

M. L. Lieberman, W. J. Andrzejewski and R. O. Yelton

Sandia National Laboratories, P.O. Box 5800, Albuquerque, NM 87185, USA and Monsanto Research Corporation, Mound Facility, P.O. Box 32, Miamisburg, OH 46342, USA

The coordination compound 2-(5-cyanotetrazolato)pentaammine-cobalt(III) perchlorate, designated CP, has been shown to be an explosive that rapidly undoes deflagration-to-detonation transition. As a result, thermal decomposition studies of such a material must focus attention on early and/or late stages of reaction. In the present investigation the early stages of CP decomposition have been examined through the use of the following techniques: mass spectrometric analysis of species generated under ultrahigh vacuum and flowing helium using electron impact ionization; mass spectrometric analysis of species generated under flowing helium and subjected to chemical ionization; combined differential scanning calorimetric and mass spectrometric analysis; and ^{1}H, ^{2}H and ^{15}N nmr analysis of isotopically exchanged materials. Analyses were also performed on related compounds, including the cyanotetrazole ligand and complexes in which the perchlorate anion had been replaced by bromide, tetrafluoroborate, or nitrate ion.

The experimental results are compared with bond lengths available from a single crystal structure determination[1] in order to propose specific mechanistic steps in the decomposition. Mass spectrometric analyses clearly identify ammonia as the initial gaseous decomposition product. Its formation corresponds to the endothermic reaction that precedes the exothermic stage of decomposition in which various redox reactions occur. The nmr analyses indicate that the equitorial ammines are replaced preferentially to the trans ammine. The absence of a pronounced cyanotetrazole mass spectrum during CP decomposition indicates that this ligand is strongly bonded to the cobalt. Identification of cyanogen, however, suggests the occurrence of ring opening.

1. E.J. Graeber and B. Morosin, Acta Cryst. (1983) C39, 567.

*Work supported by the U.S. Department of Energy under Contract No. DE-AC04-76DP00789.

GAS PHASE ION MOLECULE REACTIONS OF ALKYNEHEXACARBONYLDICOBALT COMPOUNDS WITH ALKENES.

Paola Michelin Lausarot, Lorenza Operti, Gian Angelo Vaglio, Mario Valle e Paolo Volpe

Istituto di Chimica Generale ed Inorganica, Università di Torino, Corso Massimo d'Azeglio 48, 10125 Torino (Italy)

The possibility to obtain information about the gas phase reactivity of classes of organometallic compounds by mass spectrometry has recently aroused increasing interest.[1,2]

Alkynehexacarbonyldicobalt complexes, $Co_2(CO)_6L$ (L = ligand), in the chemical ionization ion source of a mass spectrometer at about 0.5 torr react with propene (P) and give substitution products, together with $[M]^+$, originated by charge exchange processes, and their fragments.

When the ligand of $Co_2(CO)_6L$ is 1,1-dimethyl-2-propyn--1-ol the reaction product is $[Co_2(CO)_6P]^+$. On the contrary, $Co_2(CO)_6L$ complexes where L is butyne, phenylacetylene, diphenylacetylene and 1-dimethylamino-2-propyne, give $[Co_2(CO)_4LP]^+$ ions, which fragment by successive loss of the four CO groups and of P. When L is 2-propyn-1-ol the substitution product is not identified, as the two pathways give ions with the same nominal mass.

It is suggested that the substitution processes involve charged metal containing species and neutral propene molecules.

The main fragmentation process of $Co_2(CO)_6L$ (L = $HC_2C(CH_3)_2OH$, HC_2CH_2OH) is the elimination of H_2O from the protonated molecular ion to give the base peak $[M + H - H_2O]^+$ and an abundant $[M + H - H_2O - CO]^+$ ion. Similarly the corresponding $[M + H - NH(CH_3)_2]$ ion is observed in the $Co_2(CO)_6HC_2CH_2N(CH_3)_2$/propene system. $[M + H]^+$ is also observed in the spectrum of $Co_2(CO)_6HC_2CH_2N(CH_3)_2$, whereas it is absent in the spectra of all the other compounds examined.

The alkynehexacarbonyldicobalt complexes show the same behavior when they react with trans-2-pentene at 0.5 torr.

The factors affecting the observed gas phase reactivity will be discussed in detail.

1. L.F. Halle, R. Houriet, M.M. Kappes, R.H. Staley and J.L. Beauchamp, J. Am. Chem. Soc. 1982, 104, 6293.
2. G.A. Vaglio, P. Volpe and L. Operti, Org. Mass Spectrom. 1982, 17, 617.

MULTIPHOTON IONIZATION MASS SPECTROMETRY IN THE STUDY OF ELECTRONIC SPECTRA AND FRAGMENTATION PROPERTIES OF COORDINATION COMPOUNDS

Jeffrey B. Morris and Murray V. Johnston

University of Colorado, Campus Box 215, Boulder, Colorado, USA 80309

Supersonic jet spectroscopy utilizing multiphoton ionization detection has become a popular technique for spectroscopic studies of large molecules. By this method, gas phase molecules are cooled to very low temperatures in the supersonic jet to yield greatly simplified electronic absorption spectra. This simplification allows detailed spectroscopic investigations to be performed.

We have chosen to apply this technique to the study of coordination compounds having metal centered d-d or f-f transitions. Through the use of multiphoton ionization mass spectrometry as a detection method, we are able to probe the electronic spectra of jet cooled metal complexes and elucidate photochemical pathways. Optical and mass spectroscopic data will be presented for a variety of complexes. The utility of the technique will be demonstrated for various fluorinated acetylacetonate chelates of the transition metals and for 2,2,6,6-tetramethyl-3,5-heptanedionate chelates of the lanthanides. Applications to transition metal porphorin complexes and their photochemistry will also be discussed. Finally, the potential analytical applications of volatile chelates to highly selective metal ion isotopic determinations will be considered.

ANALYSIS OF METAL DIETHYLDITHIOCARBAMATES BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY

C. Moynihan and P. Fennessey

University of Colorado Health Sciences Center, 4200 E. 9th Avenue Box C232, Denver, Colorado, USA 80262

Although metals have been gas chromatographed as volatile metal chelates since the early 1960's, there are still many problems with these techniques which prevent their wide-spread use for the separation and analysis of metals. Mass spectrometry, coupled with gas chromotography can be a powerful tool to analyze the problems associated with the chromatography of metal chelates.

Using metal complexes of diethyldithiocarbamate, metal exchange has been observed. Data gathered from work using various metal transfer lines between the gas chromatograph and the mass spectrometer will be discussed. Ligand exchange has been observed using the perfluoro analog of diethyldithiocarbamate. Investigation of these phenomena may lead to a more complete understanding of the coordination properties of metal alkylcarbamates.

Coates et al[1] have reported that zinc diethyldithiocarbamate ($Zn(DDC)_2$) is a 5-coordinate structure which reacts 1:1 with amines. This knowledge has allowed us to add NH_4OAc to the extracted zinc chelate and alleviate the exchange problems.

1. E. Coates, B. Rigg, B. Saville and D. Skelton, J. Chem. Soc., 1965, 5613.

THE STUDY OF TRANSITION METAL CLUSTERS AND THEIR REACTIVITIES USING FOURIER TRANSFORM MASS SPECTROMETRY

DonnaJean Anderson and David H. Russell

Texas A&M University, Department of Chemistry, College Station, Texas, USA 77843

Investigations into the chemical and physical properties of transition metal clusters is rapidly expanding. In part, the rapid growth in catalysis studies can be traced to the development of new experimental techniques which allow for more detailed studies than do bulk methods. A major emphasis of our research program is the synthesis of gas phase transition metal clusters by ion-molecule reactions using Fourier transform mass spectrometry (FT/MS). The objectives of these studies include the study of the reactivities of metal ions with other metal containing species, characterizing these clusters using both spectroscopic methods and chemical reactivities and utilizing these clusters as models for catalytic reactions, e.g., C-H and C-C bond insertion reactions.

The sequence of cluster ion formation for a number of transition metal carbonyl systems have been studied. The overall cluster formation sequence is highly sensitive to the initial reactant ion, e.g., M^+, $M(CO)^+$, etc., and the reactivities of the initial reactants ion differ significantly. These investigations are simplified by the use of ion ejection techniques in which the reacting metal ion is mass selected and allowed to react with the neutral molecule. Using this approach it is possible to compare relative reactivities and to follow the sequence of reactions leading to cluster formation. This technique coupled with pulsed valve sample introduction allows us to study the reactivity of these clusters with small hydrocarbons in an effort to model catalytic reactions. We have also studied the influence of Lewis acids on the reactivities of these clusters using ion desorption techniques.

We will discuss the use of FT/MS to determine the sequence of reaction in the transition metal carbonyls, the reactivities of these clusters with small hydrocarbons, and the influence that Lewis acids have on the reactivities of these clusters.

MECHANISMS OF REARRANGEMENT OF Fe(OLEFIN)$^+$ COMPLEXES

Michael L. Gross and David A. Peake

University of Nebraska, Dept. of Chemistry, Lincoln, Nebraska USA, 68588.

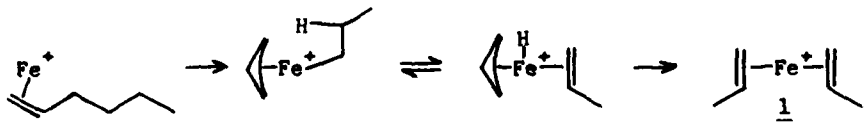
Douglas P. Ridge

University of Delaware, Dept. of Chemistry, Newark, Delaware USA, 19711.

Organometallic reactions are often influenced by the effects of solvent molecules and coordinated ligands. Reactions may be studied in the absence of these effects in the gas phase. For example, simple models of reaction intermediates may be synthesized in the source of a mass spectrometer and their structures probed by tandem mass spectrometry (MS/MS) in order to elucidate reaction mechanisms.

Fe(olefin)$^+$ complexes, formed by reaction of $FeCO^+$ with the olefin in a high pressure source, rearrange to a bis-olefin complex by a mechanism first proposed by Beauchamp[1] (Scheme I).

Scheme I



1

Oxidative addition of the allylic C-C bond of 1-hexene to Fe^+, followed by transfer of a β-H and reductive elimination results in a bis-propene complex, 1. The collisionally activated decomposition (CAD) spectrum of Fe(1-hexene)$^+$ is dominated by $FeC_3H_6^+$ formed by the loss of propene from 1. In fact, the $FeC_3H_6^+$ product can be shown to be Fe(propene)$^+$ by an MS/MS/MS experiment[2], providing further support for the proposed mechanism.

The generality of the allylic insertion mechanism was tested by examining a series of $FeC_8H_{16}^+$ formed from isomeric octenes and methylheptenes. In addition, the structures of product ions formed by collisional activation of the stable $FeC_8H_{16}^+$ were determined by comparing their CAD spectra with those of reference iron-olefin complexes. The C-C triple bond of alkynes also reacts with Fe^+ by this mechanism, resulting in an alkene-alkyne-iron complex.

1. P. B. Armentrout, L. F. Halle and J. L. Beauchamp, J. Am. Chem. Soc., 1981, 103, 6624.

2. D. J. Burinsky, R. G. Cooks, E. K. Chess, and M. L. Gross, Anal. Chem. 1982, 54, 295.

GAS PHASE ION CHEMISTRY AND PHOTOCHEMISTRY OF Group 8 (Fe, Co, Ni) MX^+(X=H, O, S, CH_2, and CH_3)

D. B. Jacobson, C. J. Cassady, T. C. Jackson, and B. S. Freiser

Purdue University, Department of Chemistry, West Lafayette, Indiana USA 47907

Activation of C-H and C-C bonds by transition metals is an important fundamental process in catalysis. Gas phase studies of the reactions of atomic metal ions with hydrocarbons represents a method to obtain the inherent reactivity of these ions in the absence of solvent or ligand interferences. Findings for the group 8 metals, for example, indicate that the order of reactivity is $Fe^+ > Co^+ > Ni^+$ and that, in direct contrast to solution behavior, oxidative insertion into C-C bonds not only occurs but is often the dominant mode.[1]

A logical extension of this research is to study the effects of small ligands on metal reactivity. With the exception of MCO^+ which is readily obtained from electron impact on the parent carbonyl complexes, however, difficulty in generating the desired species has delayed work in the area. Using Fourier transform mass spectrometry, which we have dubbed the "complete gas phase chemical laboratory", we have launched into this area over the past year with systematic studies on the chemistries of MX^+ where X = H, O, S, CH_2, and CH_3. Illustrative of this work is our study on the group 8 hydride ions.[2] The results of these studies indicate that metal hydrides activate C-H bonds in contrast to the bare metal ions which activate C-C bonds. Furthermore, the order of reactivity, $NiH^+ > CoH^+ > FeH^+$ contrasts sharply with the bare metal ion reactivity and emphasizes the complexity of the nature of catalysis and underlines the possibility of fine tuning catalytic processes through an improved understanding of the fundamentals.

Finally, preliminary results on the photodissociation of MX^+ complexes will be presented. Photodissociation spectra yield information on the electronic and geometric structure of ions, as well as information on the bond dissociation energies, $D(M^+ - X)$.

1. D. B. Jacobson and B. S. Freiser, J. Am. Chem. Soc., 1983, 105, 5197.

2. T. J. Carlin, L. Sallans, C. J. Cassady, D. B. Jacobson, and B. S. Freiser, J. Am. Chem. Soc., 1983, 105, 6320.

NMR SOLUTION STRUCTURAL STUDIES OF AXIALLY SYMMETRIC Ln(NOTA) CHELATES AND THEIR COMPLEXES WITH CYCLOPROPANE CARBOXYLIC ACID.

A. Dean Sherry,* Mangal Singh,* and C.F.G.C. Geraldes+

* The University of Texas at Dallas, P. O. Box 688, Richardson, Texas, 75080, U.S.A. and

+ The University of Coimbra, 3000 Coimbra, Portugal

The macrocyclic ligand, 1,4,7-triazacyclononane-N,N´,N´´-triacetate (NOTA) and its complexes with the trivalent lanthanide cations have been examined by proton and carbon magnetic resonance. The proton spectra of La(NOTA) and Lu(NOTA) show singlets for the acetate protons and overlapping doublets (quartet) for the ethylene protons, indicative of labile Ln-O bonds and long-lived Ln-N bonds similar to those observed in the corresponding EDTA complexes. Lanthanide induced shifts (LIS) have been measured for all proton and carbon resonances in nine paramagnetic Ln(NOTA) complexes at 25°C and 70°C. At both temperatures the ethylene protons are paramagnetically shifted into two pairs of resonances with $J_{gem} \approx 8{\cdot}8$ Hz (measured in the Eu(NOTA) complex) while the acetate protons remain a singlet. The direction and magnitude of the ^{1}H and ^{13}C shifts indicate they are dominated by contact interactions in most of the Ln(NOTA) complexes. The contact and pseudocontact contributions to each of the observed LIS have been separated and the resulting pseudocontact shifts agree well with those calculated using an axially symmetric molecular model.

We have also examined the binding of cyclopropane carboxylic acid with nine Ln(NOTA) chelates using the LIS method. Previous studies on this carboxylic acid binding with the Ln(EDTA) chelates[1] and on L-proline binding with the aquo Ln^{3+} cations[2,3] suggested that the measured pseudocontact shifts in the C_o and C_α resonances contain a non-axial shift component. Using these same analyses, the ^{1}H and ^{13}C shifts in cyclopropane carboxylic acid resonances bound to the axially symmetric Ln(NOTA) complexes fit the axial symmetry model rather well suggesting that the previously observed non-axial shifts arose from an asymmetry in the $Ln(H_2O)_x^{3+}$ and Ln(EDTA) ligand fields.

1. Mangal Singh and A. Dean Sherry, J. Less-Common Met., 1983, 94, 351.

2. Mangal Singh, Joe J. Reynolds, and A. Dean Sherry, J. Am. Chem. Soc., 1983 105, 4172.

3. A. Dean Sherry and Mangal Singh, J. Less-Common Met., 1983, 94, 343.

TUa22-01

MÖSSBAUER CHARACTERIZATION OF THE RATE OF ELECTRON TRANSFER IN MIXED-VALENCE TRANSITION METAL COMPLEXES.

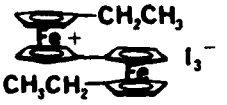
David N. Hendrickson, Seung M. Oh and Michelle J. Cohn

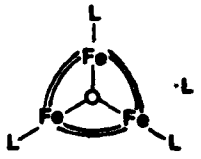
University of Illinois, School of Chemical Sciences, 505 S. Mathews, Urbana, Illinois 61801, U.S.A.

The study of discrete mixed-valence transition metal complexes is proving to be useful in characterizing the factors controlling electron transfer between transition metal ions. By employing the intrinsic timescales associated with various physical techniques, it has been possible to bracket the electron-transfer rates for a number of mixed-valence complexes. Very recently the electron-transfer rate has been observed to be temperature dependent for a few mixed-valence complexes.

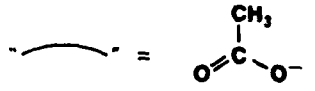
Variable-temperature Mössbauer results are presented to characterize the rate and nature of electron transfer in the following mixed-valence biferrocenes and trinuclear $Fe_2^{III}Fe^{II}$ acetates with the composition $[Fe_3(\mu_3\text{-}O)(O_2CCH_3)_6L_3]\cdot L$, where L is a pyridine.

(I) 

(II) 

(III) 

where 



Two doublets are present in the spectra for complexes I, II, and III at low temperature. The components of the two doublets for I broaden and coalesce into one doublet as the temperature of I is increased. The data can be approximated by a two-site relaxation model. The variable-temperature behavior of complexes II and III are different; in general, two doublets convert into one doublet as the temperature is increased but there is no line broadening. Furthermore, changing the "extra" solvate L molecule in (III) from a pyridine to benzene, toluene or a void leads to dramatic changes in the Mössbauer characteristics. A model will be advanced to account for these observations in terms of electron-phonon interactions, order-disorder, and the stacked arrangement of these complexes in the solid state.

HEXAKIS N,N'-DI-PROPYLTHIOUREA IRON(II) TETRAFLUORBORATE: DYNAMIC PROPERTIES.

J. Granifo*, R. Latorre*, J. Costamagna**

* Universidad de Chile, Casilla 653, Santiago, Chile
** Universidad de Santiago, Casilla 5659, Santiago, Chile

The behaviour of Fe(N,N'-propylthiourea)$_6$(BF$_4$)$_2$ by Mössbauer effect with temperature was studied. Results are shown in the Table. It is possible to see that the isomer shift (IS) and the quadrupole splitting (QS) do not change significatively and are in the range observed for analogous compounds (1). On the other hand, the complex does not show absorption above ca. 202 K and the linewidth ($\Delta\Gamma$) increases with temperature.

Shapiro's model (2) explains the absorption phenomena with temperature but it is necessary to take into account diffusion of the iron atom to explain the widening of the line (3). In this case, the iron atom, placed in an essentially octaedral environment("box"), is supposed to have a "sudden jump" to equivalent positions inside the box. These jumps would simulate a diffusion phenomena. With this model (3), it is possible to calculate the time the atom remains in each position, τ and a diffusion coefficient, D. The $\Delta\Gamma_o$ =0.30 mm/s, obtained by extrapolation, allow to get D and τ values. From these values an activation energy of 1100 cal/mol and a mean displacement of the atom (0.34 A°) for all temperatures were obtained. When the mean time life of the excited state of ^{57}Fe, $\sim 7 \times 10^{-8}$ s, is greater than τ, the probability of getting Mössbauer effect is low. This fact is consistent with the experimental results.

A similar behaviour is observed for the perchlorate derivative. Its results will be compared and discussed.

T (K)	IS[a] (mm/s)	QS (mm/s)	Absorption(Linewidth) Line 1[b] (% (mm/s))	Line 2 (% (mm/s))	Dx10^9 (cm^2/s)	τx10^8 (s)
90	1.31	3.47	11.1(0.31)	10.1(0.31)	7	275
108	1.30	3.50	9.2(0.32)	8.4(0.32)	14	137
140	1.29	3.49	6.0(0.42)	5.7(0.42)	69	28
170	1.27	3.50	4.0(0.50)	3.9(0.48)	137	14
202	1.25	3.50	1.9(0.60)	1.8(0.58)	206	9
295	-	-	0.0(-)	0.0(-)	-	-

(a) related to sodium nitroprusside; (b) line at lower velocity

1. R. Latorre, J.A. Costamagna, C.R. Abeledo, E. Frank, R.B. Frankel, J. Inorg. Nucl. Chem., 1979, 41, 649.
2. N.N. Greenwood, T. Gibb, "Mössbauer Spectroscopy", Chapman and Hall, London, 1971, p. 348.
3. (a) C. Janot, "L'effect Mössbauer et ses applications" Masson, Paris, 1972, Ch.5.; (b) V.I. Goldanskii, E.F. Makarov, in "Chemical Applications of Mössbauer Spectroscopy", Academic Press, New York, 1968, p. 44

MAGNETIC PROPERTIES OF IRON(III) PHTHALOCYANINES

G. Brain, B.J. Kennedy, K.S. Murray

Chemistry Department, Monash University, Clayton, Victoria, 3168, Australia.

H. Homborg, W. Kalz

Institute for Inorganic Chemistry, University of Kiel, D-2300, Kiel, Germany.

New and improved methods of synthesis[1] of iron(III) phthalocyanines of types Fe Pc(-2) X (X = F, Cl, Br, I, N_3)

Fe Pc(-1) X_2 (X = Cl, Br)

[Fe Pc(-2) L_2]$^-$ (L = OH, OR, CN, N_3, NCS)

(Fe Pc(-2))$_2$O

have allowed us to explore the electronic features of these interesting molecules by means of magnetic susceptibility, esr and Mössbauer techniques. Previous reports of the characterization and magnetic properties of some of them, e.g. FePc(-2)Cl, are contradictory and somewhat incomplete. This chloro-complex displays a spin-admixed S = 3/2 / 5/2 ground state similar to that found in iron(III) porphyrins of the type FeTPP($OClO_3$) but different to the S = 5/2 analogue Fe(TPP)Cl.[2] Comparisons will be made of axial ligation and *in-plane* chelate effects on the spin-states and electronic structures of the present species and related Fe(III) porphyrins.

Despite recent clarification of the nature of the μ-oxo dimer (FePc(-2))$_2$O by Ercolani *et al*,[3] we show that this compound still has some secrets to divulge.

1. W. Kalz and H. Homborg, Z. Naturforsch, 1983, 38b, 470.

2. W.R. Scheidt and C.A. Reed, Chem. Rev., 1981, 81, 543.

3. C. Erconali, M. Gardini, F. Monacelli, G. Pennesi and G. Rossi, Inorg. Chem., 1983, 22, 2584.

ELECTRONIC STRUCTURE OF SOME NOVEL SPIN-MIXED AND SPIN-CROSSOVER IRON(III) PORPHYRINS

L.B. Dugad, V.R. Marathe, and S. Mitra

Chemical Physics Group, Tata Institute of Fundamental Research, Colaba, Bombay 400005, India.

Perchlorato iron(III) porphyrins are of considerable interest as they seem to stabilize predominantly the unusual intermediate-spin ground state admixed extensively with the high-spin character[1,2]. This unusual electronic structure manifests through very novel magnetic and spectroscopic properties of these complexes. Our recent detailed studies show that nitrogenous-base adducts of these complexes also exhibit very unusual magnetic and spectroscopic properties.

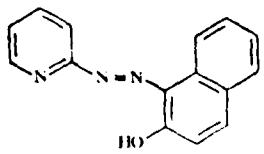
In this paper we present and quantitatively discuss solid state magnetic susceptibility (1-300K), magnetization (1-20K and 10-50 kOe) and solution isotropic proton shift (340-230K) results on a series of perchlorato iron(III) porphyrins and their adducts. We present definitive evidence of the long-speculated spin-mixed ground state as well as spin-crossover phenomena in these iron porphyrin complexes.

1. Mitra, S., V.R. Marathe, and R. Birdy, *Chem. Phys. Lett.*, *96*, 103, 1983, and references therein.
2. Mitra, S., in "Iron Porphyrins", Vol. 2, A.B.P. Lever and H.B. Gray, eds., Addison-Wesley Publishing Company, Massachusetts, 1983.

IRON(III) COMPLEXES INVOLVING SPIN-CROSSOVER AND SPIN-EXCHANGE INTERACTION: A MÖSSBAUER STUDY

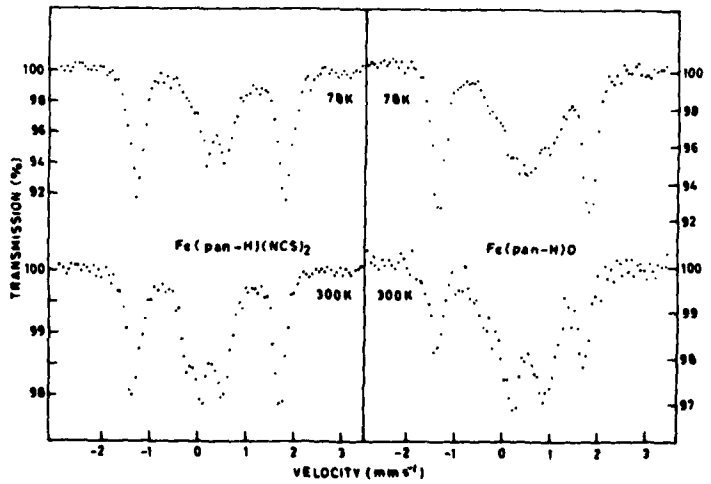
Krishna B. Pandeya and Mohammad Nadeem Alam
Department of Chemistry, University of Delhi, Delhi, INDIA

Chandra Prakash and Jagdish S. Baijal
Department of Physics, University of Delhi, Delhi, INDIA



[I]

We have reported[1] magnetic and Mössbauer properties of a low spin iron(III) complex $Fe(pan\text{-}H)_2C\ell O_4$ of pan I, a terdentate chelating agent and have now prepared two new iron(III) complexes of pan; Fe(pan-H)O (μ_{eff}, 3.25 BM at 300K), by reaction between iron(III) chloride and pan in aquo-ethanolic medium and $Fe(pan\text{-}H)(NCS)_2$ (μ_{eff}, 3.57 BM at 300K), by similar reaction in presence of NH_4NCS. Both complexes show the presence of spin-exchange interaction and also exhibit the phenomenon of spin-crossover as evidenced by their Mössbauer spectra (Figure below).



The low-spin component of the Mössbauer spectrum is a clear doublet in each case, while the high-spin component shows structurer (clearer at LNT) attributable to magnetic hyperfine splitting. The results are of immense theoretical interest from the "spin-flipping" considerations.

1. K.B.Pandeya, R.P.Singh, G.L.Sawhney and J.S.Baijal, Solid State Commun. 1979, 32, 823.

^{57}Fe MÖSSBAUER AND ^{31}P NMR SPECTROSCOPIC CHARACTERIZATION OF $Fe(CO)_4L$ COMPLEXES (L = PHOSPHINE AND PHOSPHITE)

Hidenari Inoue, Tsuneo Shirai, and Ekkehard Fluck†

Department of Applied Chemistry, Keio University, Yokohama 223, Japan
†Gmelin-Institut der Max-Planck-Gesellschaft, Varrentrappstr. 40/42, D-6000 Frankfurt am Main 90, FRG

A variety of monosubstituted iron tetracarbonyls with phosphine and phosphite ligands have been synthesized by the elimination reaction of a carbonyl ligand from iron pentacarbonyl or iron dodecacarbonyl. Particularly the phosphine and phosphite ligands in which the groups attached to the phosphorus atom are bulky and electronegative tend to favor the trigonal bipyramidal structure. Although these iron carbonyl complexes provide a good opportunity for studing the Fe-P bond, there have been relatively few systematic investigations by ^{57}Fe Mössbauer and ^{31}P NMR spectroscopy.

All the ^{57}Fe Mössbauer spectra obtained here showed a relatively large quadrupole splitting doublet characteristic of trigonal bipyramidal $Fe(CO)_4L$ complexes. The quadrupole splitting as well as the isomer shift fall into the range typical of monosubstituted iron carbonyls with C_{3v} symmetry. The increasing tendency in the isomer shift is interpreted by the ligand-to-iron σ donation and iron-to-ligand π back donation.[1] The linear dependence of the quadrupole splitting on the isomer shift with a positive slope has revealed that the σ-donor capability is offset by the π-acceptor capability.

The $^{31}P\{^1H\}$ NMR spectra of $Fe(CO)_4L$ complexes showed sharp signals in most cases. As expected, the signals of phosphite complexes exhibited larger down-field shifts than those of phosphine ones. There was a linear correlation between the ^{31}P chemical shift for the free phosphine and the change in the chemical shift on coordination. This correlation is interpreted in terms of the change in the cone angle rather than electronic effect, since the larger the cone angle of the free ligand, the smaller the coordination shift. Unfortunately no good correlation could not be found between the ^{31}P chemical shift for the free phosphine and the coordination shift for the corresponding phosphite complexes.

The ^{57}Fe Mössbauer isomer shift is a measure of the total electron density at the iron nucleus, while the ^{31}P NMR chemical shift reflects the electron density around the phosphorus atom. In view of this feature a combination of ^{57}Fe Mössbauer and ^{31}P NMR spectroscopy is very attractive to elucidate the Fe-P bond. A correlation between the isomer shift and the chemical shift will be discussed in detail for $Fe(CO)_4L$ complexes.

1. B. A. Sosinsky, N. Norem, and R. G. Shong, Inorg. Chem., 21, 4229 (1982).

Fe(2,2'-BIPYRIDYL)F_2 - A SPIN-TRIPLET IRON(II) SPECIES?

Diana L. Sedney and William M. Reiff

Williams College, Williamstown, MA, USA, 01267
Northeastern University, Boston, MA, USA, 02115

The controlled thermolysis of dihalidebisdiimineiron(II) compounds typically yields monodiimine products that exhibit a variety of structural, electronic and magnetic behavior. For example, Fe(bipy)Cl_2 (bipy = 2,2'-bipyridyl) occurs in two isomeric forms, a tetrahedral monomer and octahedral polymer where the six coordinate isomer is a ferromagnet below 4.2 K. When the anion is thiocyanate, an octahedral polymer is again observed but with antiferromagnetic interactions.[1]

This paper presents the preparation and characterization of the fluorine analog, Fe(bipy)$F_2 \cdot 2H_2O$. The Mössbauer and magnetic properties (δ_{78K} = 0.50, ΔE_Q = 0.85 mm/sec, μ_B(300 K) = 4.51) are consistent with a triplet (S=1) spin state. The bisbipyridyl precursor was also thought to exist in a triplet spin state since the synthesis, Mössbauer, and magnetic parameters are identical to the data for Fe(1,10-phenanthroline)$_2F_2 \cdot 4H_2O$.[2] However, further investigation of the Mössbauer spectra of some bisdiimine complexes in applied magnetic fields by Koenig, et al., has shown that these species are actually low-spin iron(II) cation/high-spin iron(III) double salts.[3] The results of the high field Mössbauer spectra for both the mono- and bis-bipyridyl fluorine species will therefore be considered in the determination of the ground state electron configurations.

1. W.M. Reiff, B. Dockum, M.A. Weber and R.B. Frankel, Inorg. Chem., 14, 800 (1975); B. Dockum, Ph.D. Thesis, Northeastern University, 1977.
2. E. Koenig and K. Madeja, Inorg. Chem., 7, 1848 (1968).
3. E. Koenig, G. Ritter and H.A. Goodwin, Inorg. Chem., 20, 3677 (1981).

STABILIZATION OF Me (III) OXIDE ELECTROPHYSICAL PROPERTIES FOR TYPE $MeTaO_4$ TANTALATES

F.A.Rozhdestvenskii
Ural Polytechnic Institute, 620002, Sverdlovsk, USSR

A series of tantalate electrical and magnetic parametres is determined to conform to those of initial oxides Me (III). Correlation of Me (III) oxides electrical conductivity with synthesized on their basis tantalates is evident from Table I.

Table I. Electrical conductivity of Me (III) oxides and related tantalates

Oxides	ρ,(Ohm^{-1} cm^{-1}			Tantalates	ρ,(Ohm^{-1} cm^{-1})		
Ti_2O_3	2,51	10^{-6}	[1]	$TiTaO_4$	2,14	10^{-6}	[2]
V_2O_3	0,81	10^{-4}	[1]	$VTaO_4$	1,03	10^{-4}	[2]
Cr_2O_3	1,58	10^{-6}	[1]	$CrTaO_4$	1,54	10^{-6}	[2]
Fe_2O_3	1,0	10^{-5}	[1]	$FeTaO_4$	1,7	10^{-5}	[2]

Calculated and experimental values of the effective magnetic moment for Me (III) initial ions and for Me(III) tantalates are given in Table 2.

Table 2. Magnetic data for Me (III) oxides and $MeTaO_4$ tantalates

Ions Me^{3+}	Therm	μeff.(M.B.), calculated		μeff.(M.B.), experiment.		μeff.(M.B.) $MeTaO_4$		T(K), exp.
Ti^{3+}	$^2D_{3/2}$	1,73	[3]	1,77-1,79	[3]	1,59	[2]	90-300
V^{3+}	$^3F_2$	2,83	[3]	2,76-2,85	[3]	1,55	[2]	90-300
Cr^{3+}	$^4F_{3/2}$	3,87	[3]	3,68-3,86	[3]	3,68	[2]	90-300
Fe^{3+}	$^6S_{5/2}$	5,92	[3]	5,4-6	[3]	4,83	[2]	200-300
Ce^{3+}	$^2F_{5/2}$	2,56	[4]	2,39-1,51	[4]	2,48	[2]	90-300
Pr^{3+}	$^3H_4$	3,62	[4]	3,59	[5]	3,91	[2]	90-300
Nd^{3+}	$^4I_{9/2}$	3,68	[4]	3,66	[5]	3,66	[2]	90-300
Sm^{3+}	$^6H_{5/2}$	1,55-1,65	[6]	1,540	[6]	1,66	[2]	300
Eu^{3+}	$^7F_0$	3,40-3,5	[6]	3,615	[6]	3,22	[2]	300

Yet, unlika Me_2O_3, the Me_2O_3-based tantalates are more thermo- and corrosion resistant, since compounds formed by Me(III) and Ta(V) oxides crystallize in the structural types which admit 3d- and 5d-elements disposition in the octahedral fields.

References

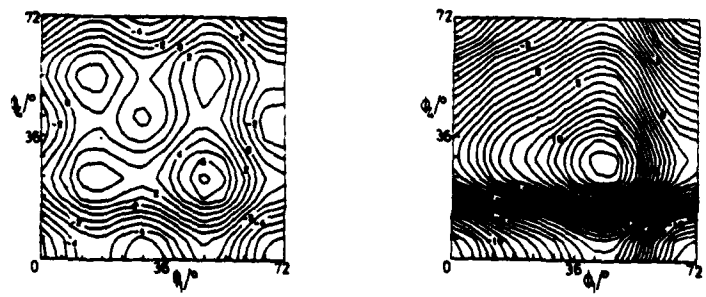
1. F.I.Morin. Bell Syst. Techn. Journ. 1958, N 4, 1047. 2. F.A.Rozhdestvenskii, e.a. VINITI, Deposited Doc. 1983, N 5, 112. 3. P.W.Selwood, Magnetochemistry, New York, 1943. 4. J.G.Dorfman, Magnetic Properties and Structure of Matter, Moscow, Izd GITL, 1955. 5. K.N.R.Taylor, M.I.Darby, Physics of Rare Earth Solids. - London, Charman and Hall ZTD, 1972. 6. Van Vleck and F.Amelia, Phys. Rev., 1929, v. 34, p. 1625.

THE MOLECULAR CONFORMATION AND ROTATIONAL DISORDER IN CRYSTALLINE FERROCENE AND NICKELOCENE

Jan C.A. Boeyens and Demetrius C. Levendis

Department of Chemistry, University of the Witwatersrand, Johannesburg, South Africa.

Ferrocene and nickelocene have pseudo-isomorphous structures at room temperature but only ferrocene undergoes a second-order phase transformation on cooling. This difference in behaviour can be explained in terms of rotational disorder due to packing effects. Intermolecular interactions associated with molecular reorientation can only be simulated correctly provided translational symmetry is preserved during all allowed rotations. Contour maps of environmental potential energy as a function of independent ring rotations are significantly different for ferrocene (1) and nickelocene (2).



Whereas the rings in ferrocene molecules in the crystal can rotate like a set of smoothly mating gears, any rotation in the nickelocene crystal leads to high-energy clashes between hydrogen atoms. The results readily account for the disorder in the room-temperature ferrocene structure, suggest a mechanism for the phase transition and predict the correct low-temperature structure.

STRUCTURAL STUDIES ON COPPER(II) COMPLEXES WITH TRIS(HYDROXYMETHYL)AMINOMETHANE (TRIS)

Carlo Mealli, Michal Sabat, Antonio Sabatini, and Alberto Vacca

Dipartimento di Chimica dell'Università di Firenze, and I.S.S.E.C.C., CNR, Florence, Italy

The compound tris(hydroxymethyl)aminomethane of the formula $NH_2C(CH_2OH)_3$ (TRIS) is widely used as a biochemical buffer. Since many of biochemical reactions involve metal ions it is important to know how TRIS interacts with metals. It has been shown[1] that TRIS forms complexes with a number of transitions metal ions, usually through deprotonation of one of the hydroxyl groups.

In reaction with copper(II) halides two different compounds were isolated and on the basis of spectroscopic and magnetic measurements they were characterized as (1) Cu(TRIS H_{-1})(TRIS)Br and (2) Cu(TRIS H_{-1})Cl_2, where (TRIS H_{-1}) stands for the deprotonated form of the ligand.

X-ray structure analysis performed for both compounds revealed that the compound (1) may be described as a hydrogen-bonded dimer held together by strong O-H ... O interactions. The donor-acceptor distances (2.50(2) Å) between the O atoms of the two units of the dimer are rather similar to those found in transition metal complexes with other aminoalcohols,[2] where the cooperative hydrogen bonding is one of the most important factors determining their crystal structure. The Cu(II) central ion has a square-plane coordination sphere with a cis arrangement of the TRIS chelate ligands.

The compound (2) exhibits a step-like geometry of the central core. Each of the two binuclear units held together by weak Cu-O interactions consists of two square-planar Cu(II) atoms. The distorted squares share the side defined by two bridging oxygen atoms. The Cu_2O_2 bridging framework is not planar. One of the bridging O atoms is weakly coordinated to the Cu atom of another binuclear unit with Cu-O separation of 2.407(6) Å.

The results of the structure analysis indicate that the TRIS buffer can be involved in formation of various polynuclear complexes with transition metal ions.

1. E.B. Fischer, U.K. Haering, R. Tribolet, and H. Sigel, Eur. J. Biochem. 1979, 94, 523; L. Bologni, A. Sabatini, and A. Vacca, Inorg. Chim. Acta 1979, 69, 71, and references therein.
2. J.A. Bertrand and P.G. Eller, Prog. Inorg. Chem. 1976, 21, 29.

THE CRYSTAL STRUCTURE OF BIS(TRIMETHYLAMMONIUM) DECABROMOTETRACUPRATE(II) AND GENERAL OBSERVATIONS REGARDING STACKED HALOCUPRATE OLIGOMERS

Roger D. Willett and Urs Geiser

Department of Chemistry, Washington State University, Pullman, WA 99164-4630, USA

Slow evaporation of an aqueous solution of copper(II) bromide and trimethylammonium bromide (ca. 2:1 molar ratio) yields dark purple needle-like crystals of $[(CH_3)_3NH]_2Cu_4Br_{10}$ (in the following TRCB). The crystal structure, as examined by single crystal X-ray diffraction, consists of tetrameric essentially planar $Cu_4Br_{10}^{2-}$ units. There are four crystallographically independent metal ions, three with 4+2, and one with 4+1 coordination. The shorter bonds, within the tetramers are in the range 2.3-2.5 Å, the longer ones, between tetramers, 2.85-3.4 Å. The tetramers stack in such a way that bromine atoms of subsequent units alternatingly cover 3 or 4 copper ions.

This is different than in the corresponding chloride salt, where the stacking is uniform and the tetramers centrosymmetric, with two 4+2 and two 4+1 coordinated copper ions. Both salts show hydrogen bonding between the trimethylammonium ions and the terminal halides.

The factors governing the existance of $Cu_nX_{2n+2}^{2-}$ or $Cu_nX_{2n}L_2$ (n = 2,3,4,5, x = Cl,Br) oligomers, and the manner in which they stack, are not completely known. The size of the halogen, as well as the size and shape of the counter ion are important factors. Except for the smallest ions, the counter ion has to provide for some hydrogen bonding to stabilize the stacked oligomers structure type. Not all $ACuCl_3$ salts form dimers. If A is a medium-size compact ion incapable of hydrogen bonding (e.g. tetramethylammonium) or a large, flat ion and with many acidic hydrogens (e.g. substituted aminopyridimium), chain structures are found. On the other hand, large cations without hydrogen bonding (e.g. $(C_6H_5)_4P^+$) favor isolated non-planar dimers.

A nomenclative scheme to classify stacked oligomes structures is presented.

TRANSITION METAL COMPLEXES OF NITROXYL RADICAL LIGANDS

Robert J. Doedens, Leigh C. Porter and Michael H. Dickman

Department of Chemistry, University of California, Irvine, California 92717

To date, only a very limited number of complexes containing a nitroxyl radical covalently bound to a transition metal ion have been isolated.[1] We have now prepared and characterized two new series of such compounds. Copper(II) trihaloacetate adducts of stoichiometry $Cu(O_2CR)_2L$ have been obtained for all combinations of R=CF_3, CCl_3, CBr_3 and L=2,2,6,6-tetramethylpiperidinyl-1-oxy (tempo) or 2,2,5,5-tetramethylpyrrolidinyl-1-oxy (proxyl). Crystal structures of the two trichloroacetate adducts show them to have a dimeric structure which is an unusual variant of the classic copper (II) acetate monohydrate structure.[2] All of these dimers are diamagnetic, probably because of strong coupling of the Cu(II) and nitroxyl free spins.

A second series of complexes is $M(hfac)_2L_2$, where hfac=hexafluoroacetylacetonato, M=Mn^{2+}, Co^{2+}, Ni^{2+}, and L=tempo or proxyl. Crystal structures of four of these complexes show that all have a centrosymmetric octahedral structure with oxygen-bound nitroxyl ligands. There are, however, differences in structural details. Magnetic susceptibility measurements show coupling of intermediate strength between metal and ligand free spins. For the Mn^{2+} complexes, the susceptibility data (6-300K) are well-represented by a spin-only model with J(Mn-nitroxyl) = -79 cm^{-1} and -105 cm^{-1} for L=proxyl and tempo, respectively. For both Mn complexes, J(nitroxyl-nitroxyl) is essentially zero. These J-values correspond to a ground state with $S=^3/_2$ and a first excited level with $S=^5/_2$ displaced by 5 J (Mn-nitroxyl) from the ground state. The Co^{2+} and Ni^{2+} complexes have qualitatively similar susceptibility curves.

Additional novel metal-nitroxyl complexes have been prepared and generalizations concerning their stabilities, structures, and magnetic properties are beginning to emerge.

1. M. H. Dickman and R. J. Doedens, Inorg. Chem., 20, 2677 (1981) and references therein.

2. For preliminary communication of structural results for one of these complexes, see L. C. Porter, M. H. Dickman, and R. J. Doedens, Inorg. Chem., 22, 1962 (1983).

ELECTRONIC AND MOLECULAR STRUCTURE OF DL VANADYL(IV) TARTRATE(4-) AND METHYL-SUBSTITUTED TARTRATE(4-) BINUCLEAR COMPLEXES

Harold D. Beeson, Robert E. Tapscott, and Eileen N. Duesler

Dept. of Chemistry, University of New Mexico, Albuquerque, NM 87131

In order to explain structural changes accompanying methyl substitution of binuclear vanadyl(IV) DL-tartrate(4-), as observed in a recent crystal structure determination on sodium μ-(+)-dimethyltartrato(4-)-μ-(-)-dimethyltartrato(4-)bisoxovanadate(IV) dodecahydrate (1), an X-ray structure determination on a second crystal form, a hexahydrate, has been completed and several Fenske-Hall type molecular orbital calculations on model systems have been carried out. The latter not only provide evidence for the causes of the structural changes accompanying methyl substitution but they allow an assignment of the visible spectra of vanadyl(IV) DL-tartrate and other cis vanadyl(IV) α-hydroxycarboxylate complexes.

The salt $Na_4[(VO)_2((+)\text{-dmt})((-)\text{-dmt})].6H_2O$, "dmt" = dimethyltartrate(4-), $[OOCC(CH_3)(O)C(CH_3)(O)COO]^{4-}$, crystallizes in the monoclinic space group $P2_1/c$ with $\underline{a}$ = 10.624, $\underline{b}$ = 11.621, $\underline{c}$ = 11.719 Å, β = 124.07°, Z = 2. Like the blue dodecahydrate studied earlier, the pink hexahydrate exhibits a decreased V-V distance, a dropping of the vanadium atom into the plane of the four equatorial oxygen ligators, an increased vanadium-tartrate hydroxyl oxygen atom distance (all relative to the nonmethylsubstituted complex), and sixth site coordination by an ionized tartrate hydroxyl oxygen atom in the other half of the binuclear complex. Unlike the dodecahydrate structure, however, the complex present in the hexahydrate is severely distorted from the idealized D_{2h} geometry (though a crystallographic center of symmetry is maintained).

The molecular orbital calculations confirm an energy level ordering for the HOMO and the lowest four LUMOs of a'($d_{x^2-y^2}$), a"(d_{xz}), a"(d_{yz}), a'(d_{xy}), and a'(d_{z^2}) in C_s localized symmetry with the a"(d_{xz}),a"(d_{yz}) pair having nearly the same energy. This is essentially the same ordering determined for vanadyl(IV) pentahydrate by Ballhausen and Gray (2).

The MO calculations also indicate that the vanadium atom drops into the plane of the four equatorial oxygen atoms (decreasing the V-V distance) when there is methyl group substitution in order to acquire sixth-site bonding to offset loss in bonding with other ligators as a result of decreased ligand basicity. Vanadyl to tartrate hydroxyl oxygen atom bond orders decrease as a result of this sixth-site coordination.

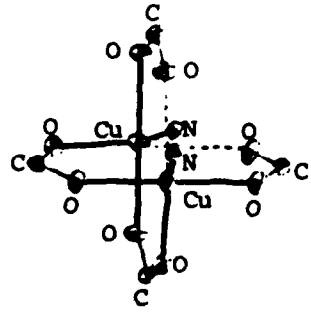
1. S. K. Hahs, R. B. Ortega, R. E. Tapscott, C. F. Campana, and B. Morosin, Inorg. Chem. 1982, 21, 664.
2. C. J. Ballhausen and H. B. Gray, Inorg. Chem. 1962, 1, 111.

A DIMERIC COPPER(II) CARBOXYLATE COMPLEX WITH DISTORTED TRIGONAL BIPYRAMIDAL GEOMETRY AROUND COPPER. THE STRUCTURE AND MAGNETIC PROPERTIES OF $[Cu(O_2CCPh_3)_2 \cdot py]_2 \cdot C_6H_6$ AND $Cu(O_2CCPh_3)_2 \cdot 2py$

O.W. Steward[a], M. Kato[b], S.-C. Chang[a], M. Sax[c], C.-H. Chang[c], T. Taura[b], C.F. Jury[a], Y. Muto[d], T. Tokii[d], J. Pletcher[c], C.S. Yoo[c]

(a) Departments of Chemistry and Physics, Duquesne University, Pittsburgh, PA 15282 USA, (b) Department of Chemistry, Aichi Prefectural University, Nagoya 467, Japan, (c) Biocrystallography Laboratory, V A Medical Center, Pittsburgh, PA 15240 and Department of Crystallography, University of Pittsburgh, Pittsburgh, PA 15260 USA, (d) Department of Chemistry, Saga University, Saga 840, Japan

$[Cu(O_2CCPh_3)_2 \cdot py]_2 \cdot C_6H_6$, 1, has been found to have a very unusual structure[1], a distortion of the copper(II) acetate monohydrate type structure, which undoubtedly arises as a result of crystal packing forces, cf. Fig. One can visualize the cage as being formed by the bonding together of two crystallographically independent copper(II) ions by four triphenylacetato ligands, with each copper(II) having a distorted trigonal bipyramidal geometry; the dihedral angle between the equatorial planes is 88.8°. Two of the Cu-O bonds are very long, 2.458(3)Å and 2.349(3)Å, (Fig., dotted lines), and the Cu-Cu distance, 3.086(1)Å, is considerably larger than reported for the classical dimer structure. The dihedral angle between the py rings is 49.1°. A structurally related cage recently has been reported by Porter, et al.[2] The parallel alignment of the py rings and the intermolecular distances between the rings, 3.415(7)Å and 3.474(2)Å, on adjacent dimer units indicate that intermolecular forces are responsible for the observed distortions. Mutual inter-dimer repulsions between the py rings generate clefts in the neighboring molecules allowing for a more compact crystal structure. The ESR spectrum (X-band) of 1 is different from other copper(II) carboxylate dimers, $D < h\bar{\nu}$: $D = 0.204\ cm^{-1}$, $g_\perp = 2.07$, $g_{||} = 2.29$. ESR spectra of seven related complexes, $[Cu(O_2CCR_3)_2 \cdot L]_2$ (R = Me, Ph; L = α-pic, γ-pic, α,α′-lut), indicate the classical dimer structure. Magnetic data (Faraday, 80°-300°K) on 1 gave the following parameters: $-2J = 184\ cm^{-1}$, $\bar{g} = 2.173$, $N\alpha = 85.1 \times 10^{-6}$ cgs.



$Cu(O_2CCPh_3)_2 \cdot 2py$ is monomeric with the usual distorted octahedral structure: ESR $g_\perp = 2.063$, $g_{||} = 2.276$, $A_{||} = 0.0077\ cm^{-1}$; Faraday $\bar{g} = 2.145$, $N\alpha = 64.9 \times 10^{-6}$ cgs, ($\mu = 1.85$ BM, 24°).

1. C.-H. Chang, PhD Thesis, University of Pittsburgh, Pittsburgh, PA, 1982; Diss. Abstr. B 1982, 43, 1467B.
2. L.C. Porter, M.H. Dickman, and R.J. Doedens, Inorg. Chem. 1983, 22, 1962.

NITROXYDE SPIN-LABELS AS LIGANDS FOR COPPER (II) HALOGENOCARBOXYLATES

Patrick Sharrock and Milan Melnik*

Department of Chemistry, Université de Sherbrooke, SHERBROOKE (Québec) CANADA J1K 2R1

* Department of Inorganic Chemistry, Slovak Technical University, CS 81237, Bratislava, Czechoslovakia.

Much of the interest in free radical compounds of nitroxyl type stems from their utility as spin labels in the study of biological or complex systems. There is also current interest in the interaction of organic free radicals with various metal ions. Only few coordination compounds of such unusual ligands with paramagnetic metal ions have been studied[1], and a wide range of magnetic properties have been found.

Tempo (2,2,6,6-tetramethyl-piperidinyl-1-oxy) forms a dimeric adduct with Copper(II) trichloroacetate[2]. The crystal structure shows the Cu-Cu and Cu-O bond lengths are different from those of other dimeric Copper(II) carboxylates[3]. This prompts us to report on the synthesis and characterization of a series of compounds formed with Tempo or substituted analogues and of general formula CuX_2L (X = $ClCH_2CH_2COO^-$, CCl_3COO^- or CF_3COO, L = Tempo, 4-hydroxytempo or 4-oxotempo). These grass-green compounds are obtained by reaction of the nitroxyl ligands with the appropriate Copper(II) carboxylate in pentane or methylene chloride.

Electronic absorption spectra show two bands centered at ≈ 720 nm and ≈ 380 nm. Significant changes in the IR absorptions are found in the COO^- and N-O• stretching frequencies. EPR spectra of the complexes nitroxydes do not show features typical of triplet state cupric dimers nor do they reveal classical nitroxyde signals near g ≈ 2. The electronic structures of these complexes will be discussed in terms of their spectral and magnetic properties.

1. G.R. Eaton and S.S. Eaton, Coord. Chem. Rev. 1978, 26, 207.
2. L.C. Porter, M.H. Dickman and R.Y. Doedens, 1983, 22, 1962.
3. M. Melnik, Coord. Chem. Rev. 1982, 42, 259.

* Present address: Department of Chemistry, Université de Sherbrooke, Sherbrooke (Québec) CANADA J1K 2R1

MONOMERIC, DIMERIC AND POLYMERIC PEROXO VANADATES

Cirila Djordjevic and Ekk Sinn

Departments of Chemistry, College of William and Mary, Williamsburg, Virginia 23185, and University of Virginia, Charlottesville, Virginia 22901, USA.

Investigating the peroxo heteroligand complexes of the early transition metals, we have recently synthetized and determined the structure of three peroxo vanadates(V): $K_2[VO(O_2)NTA]2H_2O$, $K[VO(O_2)(citrato)]H_2O$, and $NH_4[VO(O_2)IDA]$, NTA=nitrilotriacetate, IDA=iminodiacetate. These structures turned out to be interesting: the first is monomeric, the second dimeric, and the third polymeric. With five structures of V(V) peroxo complexes reported by others previously, we now can draw a few generalizations and single out some salient structural features displayed by this type of compounds.

Monomeric or dimeric, monoperoxo or diperoxo, seven coordinated complexes exit, in which vanadium polyhedra can be viewed as a distorted pentagonal bipyramid. Monomeric arrangements are more common, occuring for heteroligands L = oxalate, NTA, picolinate, and dipicolinate, respectively. Dimeric anions exist in $(NH_4)_4[O\{VO(O_2)_2\}_2]$, and $K_2[V_2O_2(O_2)_2(citrato)_2]2H_2O$. In the former complex bridging occurs via a single nonlinear μ-oxo group and a long bond to an adjacent peroxo oxygen.[1] The monoperoxo citrato V(V) polyhedron, however, is connected to another polyhedron by two alkoxy oxygens. $NH_4[VO(O_2)IDA]$ represents the only polymeric peroxo heteroligand complex found so far. Pentagonal bipyramidal V(V) polydedra are linked by carboxylato groups with a relatively weak interionic V-O bond to form a polymeric anion chain.

Peroxo ligands turn out in the equatorial plane of the pentagonal bipyramid in all the structures. The (O-O) bond length stays in a relatively narrow range of 1.43-1.44 Å for complexes containing aminocarboxylato heteroligands. V=O group invariably occupies the apical position with the bond length ranging from 1.58 to 1.62 Å.

The structural analyses show that the coordination of peroxides to vanadium is fairly flexible. Peroxo groups can be coordinated to vanadium symmetrically or nonsymmetrically, by two almost equal V-O bonds or with bond lengths differing up to 0.11 Å. They can be accomodated in monomeric, dimeric or polymeric environments.

1. I. B. Svensson and R. Stomberg, Acta Chem. Scand., 1971, 25, 898.

THE JAHN-TELLER EFFECT OF π-ANTIBONDING T_{2g} GROUND STATES - STRUCTURAL, MAGNETIC AND SPECTROSCOPIC INVESTIGATIONS ON Ti^{3+} CHLORO-COMPLEXES

Dirk Reinen, Stefan Kremer and Heiner Wächter

Fachbereich Chemie der Philipps-Universität, Hans-Meerwein-Strasse, D - 3550 Marburg (G.F.R.)

While the Jahn-Teller effect of transition metal ions with σ-antibonding E_g ground states in octahedral coordination is well established (1), experimental studies of compounds with T ground states are scarce so far. We have investigated octahedrally coordinated Ti^{3+} ions in chlorides of the ordered perovskite type by means of X ray and neutron diffraction, by susceptibility measurements and by various spectroscopic methods (EPR, Raman, IR, UV/Visible) in the temperature region from 4 - 300 K. The specific lattice was chosen, because it provides a host site of regular O_h symmetry for Ti^{3+} and hence allows to study vibronic coupling effects of the Jahn-Teller type without significant disturbance from packing forces. At 298 K the compounds $A_2A'TiCl_6$ [A,A': alkaline ions] are cubic, but undergo transitions to lower symmetry phases with decreasing temperature. The π-antibonding $^2T_{2g}$ ground state is split by the combined action of LS coupling and symmetry reduction by about 200 to 300 cm^{-1}, as can be deduced from the magnetic and 5 K single crystal EPR data. The orbital contributions to the g tensor are largely quenched by vibronic interaction between the electronic ground state and the e_g vibrational mode [Ham effect (2)]. The excited E_g state is split by 1500 ± 300 cm^{-1} and gives further evidence for the presence of T ⊗ e coupling. Finally experimental results on TiF_6^{3-} polyhedra in various host structures are given for comparison.

1. D. Reinen and C. Friebel, Structure and Bonding 1979, 37, 1.

2. F. S. Ham, Phys. Rev. 1969, 166, 307.

ON THE SYMMETRY OF RARE EARTH METAL TANTALATE BASED CONCENTRATED CRYSTALS

M.G.Zuev, A.A.Fotiev
Inst. Chem., Ural Sci. Centre, GSP-145, Sverdlovsk, USSR

Polytantalate based $LnTa_7O_{19}$ rare earth metal concentrated crystals are of certain interest for integral optics (1). However their structure is not well understood at present. The aspects of (Ce, Ta)Ta_6O_{19} disorded crystal symmetry space group are still debatable. X-ray diffraction shows them to be $P6_3$ /mcm, while according to electron diffraction they are to be $P\bar{6}c2$ (2).

Vibration spectroscopy application makes possible identification of the crystal space group. On the basis of hexagonal syngony diffraction classes factor-group analysis of atom vibration in crystals (Ce, Ta)Ta_6O_{19} have been made. Presentations for atom optical vibrations have been given. Infrared absorption and Ramanspectra of polytantalates have been recorded on Perkin-Elmer-457, UR-20 and DFS-24 spectrometre, respectively.

Preferable polytantalate symmetry space group has been singled out and commented on.

References

1. F.A.Rozhdestvenskii, M.G.Zuev, J.Lumin. 1983, (being published).
2. W.S.Johnson, L.M.Gatehouse, Acta Cryst. 1980, B 36, 523.

THE ACCOUNT OF THE STRUCTURAL DIFFERENCE BETWEEN $RbMnCl_3$ AND $RbMnBr_3$

by E.M. ALI Faculty of Science, King Saud University, Riyadh, Saudi Arabia.

The crystal structure of $RbMnCl_3$ was determined by the author and others(Acta Cryst.(1977) B33, 256) to be hexagonal $P6_3/mmc$ a = 7.16(1), C = 17.83(4)A, D_o =3.09, D_x =3.11 g cm^{-3}) , Z = 6; the unit cell accommodates six close-packed layers of composition $RbCl_3$ with Mn ions situated between the layers, being octahadrally coordinated by CL ions.

The crystal structure of $RbMnBr_3$ was determined by the author and others (Acta Cryst.(1980) B36 671) to be hexagonal $P6_3/mmc$ a = 7.56(2)A, C = 6.35(2)A D_o = 3.97, D_x = 4.01 gcm^{-3}, Z = 2. The unit cell consists of two hexagonally close-packed $RbBr_3$ layers with Mn actahedrally coordinated by Br ions. The differences between these two structures are that in $RbMnCl_3$. We have six close-packed layers while there are two close-packed layers in $RbMnBr_3$. Moreover in the latter structure the Mn-Br octahedra share opposite faces to form infinite chains of composition ($MnBr_3$) parallel to the c-axis while in the $RbMnCl_3$ structure that infinite chain does not exist.

The reasons put forward to account for these differences are that the cation/anion ratio in $RbMnCl_3$ is too large to permit the formation of infinite chains of Mn-Cl face sharing octahedra. The second reason is the polarization effect: the extra polarization of the bromine compared with the chlorine made $RbMnBr_3$ isomorphous with $CsNiCl_3$, which has two close-packed layers, while $RbMnCl_3$ is not.

TUESDAY EVENING

THE PHOTOCHEMISTRY OF TRIRUTHENIUM DODECACARBONYL, $Ru_3(CO)_{12}$, AND OTHER TRINUCLEAR CLUSTERS.

Peter C. Ford and Marc F. Desrosiers
Department of Chemistry, University of California
Santa Barbara, California, USA, 93106

Summarized will be quantitative continuous and flash photolysis studies of the trinuclear cluster $Ru_3(CO)_{12}$ and various derivatives $Ru_3(CO)_{12-x}L_x$ (L= a phosphine or phosphite ligand, x= 1-3) in several different media. The focus will be on the elucidation of mechanisms for the photofragmentation reactions (e.g. eq. 1)[1-4] and for the photosubstitution reactions of these clusters. Irradiation wavelength studies indicate that these two photoreactions occur from two different excited states, the lower energy state being principally responsible for the photofragmentation.

(1) $Ru_3(CO)_{12} + 3L \longrightarrow 3Ru(CO)_4L$

(2) $Ru_3(CO)_{12} + L \longrightarrow Ru_3(CO)_{11}L + CO$

(L=CO, Ph_3P or $(CH_3O)_3P$)

Similar photoreaction studies of the trinuclear osmium carbonyl cluster $Os_3(CO)_{12}$ and substituted derivatives have also been carried out. For the unsubstituted dodecacarbonyl photofragmentation is at most a very minor pathway when lowest states are excited, but short wavelength irradiation leads to substituted clusters as in eq. 2. However the substituted derivatives $Os_3(CO)_9L_3$ are much more susceptible to photofragmentation.[5]

1. Johnson, B.F.G.; Lewis; J; Twigg, M.V.; J. Organomet. Chem., 1974. 67 C75-76.
2. Wrighton, M.S.; Geoffroy, G.L., Organometallic Photochemistry, Academic Press: New York, 1978 and references therein.
3. Desrosiers, M.F.; Ford, P.C.; Organometallics 1982. 1 1715-1716.
4. Malito, J. Markiewicz, S.; Poe, A; Inorg. Chem. 1983, 21, 4337.
5. Other individuals who have contributed to these experimental investigations are David Wink, Valerie Arkle, Ray Trautman and Allen Friedman, all of UCSB. This research has been supported by a grant from the U.S. National Science Foundation.

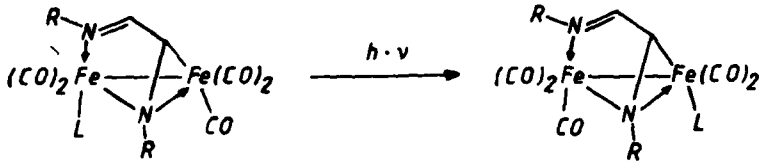
AN UNUSUAL PHOTOCHEMICAL REARRANGEMENT: THE ENERGY SINK IN HEXACARBONYL (1,4-DIAZA-1,3-DIENE)DIIRON PRECLUDING PHOTOSUBSTITUTION OF CO?

Hans-Werner Frühauf, Dieter Meyer and Joachim Breuer

Universität -GH- Duisburg, FB 6, Organische Chemie, Bismarckstr. 90, D-4100 Duisburg, W.-Germany

As we now know, the 1,4-diaza-1,3-diene (DAD) ligand system, -N=C-C=N-, may donate from 2 to 8 any even number of electrons for coordination to transition metals /1/. The unsymmetrically bridging 6e coordination mode in the binuclear title complexes 1a was the first example where, in addition to the four nitrogen n-electrons, the π-electrons of one C=N moiety were shown to be involved /2/. Beyond this interesting coordinative and structural feature, compounds 1a chemically appeared rather barren. In particular, we found it impossible in 1a photochemically to substitute CO for other ligands, e. g. π-systems, a behavior sharply contrasting that of $(DAD)Fe(CO)_3$ with chelating σ-N, σ-N' 4e coordination of the DAD /3/.

The observation of the photo-rearrangement 1b → 2b, details of which will be reported, now offers an explanation:



1 a: L = CO b: L = P(OMe)3 2

Though seemingly involving mutual exchange of L and CO across the Fe-Fe bond, the reaction rather proceedes by way of the two DAD halves interchanging their identity. Upon electronic excitation of 1b the excitation energy is trapped in the DAD ligand, and no Fe-CO antibonding states are populated. Relaxation may go to either 2b or 1b ground state, 2b being favored with bulky groups R. For R = t-Bu, the photostationary state is fully to the side of 2b.

Very likely, this process is also operating in 1a, then merely waisting energy by being degenerate. New results of ongoing 13-CO labeling studies with 1a and 1b will be included.

/1/ G. van Koten and K. Vrieze, Adv. Organomet. Chem. 1982, 21, 151-239.

/2/ H.-W. Frühauf, A. Landers, R. Goddard and C. Krüger, Angew. Chem. 1978, 90, 56-57; Angew. Chem. Int. Ed. Engl. 1978, 17, 64-65.

/3/ H.-W. Frühauf and G. Wolmershäuser, Chem. Ber. 1982, 115, 1070-1082.

METATHESIS OF 2-PENTENE CATALYZED BY $W(CO)_6$-HALIDE PHOTOSYSTEMS

Dorota Borowczak, Teresa Szymanska-Buzar and Józef J. Ziółkowski

Institute of Chemistry, University of Wroclaw, 50-383 Wroclaw, Poland

Donor-acceptor interactions between $W(CO)_6$ (donor) and different halides (acceptors) (i.e. CBr_4, CCl_4, $AlCl_3$, BF_3) under influence of light (λ_{max}=350nm) leads to the formation of the system which is catalytically active in metathesis reaction of 2-pentene. When electron affinity of halide (A) is higher than 1.95 eV., the formation of charge-transfer complex in reaction mixture is observed according to the scheme:

$$W(CO)_6 + A \Leftrightarrow [W(CO)_6....A] \xrightarrow{h\nu} \dot{W}^{(+)}(CO)_6....\dot{A}^{(-)}]$$

The charge-transfer complex formation could be concluded from the correlation of the downfield shift of absorption band at about 34650 cm^{-1} (corresponding to the electron transfer $^1A_{1g} \rightarrow {}^1T_{1u}$ in $W(CO)_6$) with the electron affinity (E_A) values of halides used. Further evidence of C.T. complex formation was found from IR spectra in which the low frequency band in the 1600-1700 range could be assigned to the carbonyl group interacting via oxygen with the electron acceptor (A) $(CO)_5 W-C \equiv O \rightarrow A$.

The product of donor-acceptor interaction in the system: $[W(CO)_6 \cdots CCl_4]$, namely $\cdot CCl_3$ radical, was ESR identified as the spin adduct with nitrosodurene. Alternative interaction leading to another charge transfer complex formation may proceed between 2-pentene (donor) and halides A (acceptors):

$$C_2H_5CH = CHCH_3 + A \Leftrightarrow [C_2H_5CH = CHCH_3 \cdots A] \rightarrow h\nu$$
$$\rightarrow [C_2H_5CH-{}^{(+)}CHCH_3 \cdots \dot{A}^{(-)}]$$

The presence of this interaction was evidenced by the appearance of the new electronic absorption band as well as by the lowering of the ν(C=C) (1647 cm^{-1}) frequency in IR spectrum of 2-pentene.

The product of this interaction (allyl radical) was ESR identified. The results obtained allowed description of the formation mechanism of the active form of metathesis reaction catalyst derived from $W(CO)_6$ under irradiation.

PROPERTIES OF THE LOWEST EXCITED STATES OF TRANS-$(N_2)_2W(DIPHOS)_2$

J. G. Brummer and G. A. Crosby

Department of Chemistry, Washington State University, Pullman, WA 99164-4630

The trans dinitrogen complex of zerovalent tungsten with bis-(diphenylphosphinoethane) has both spectroscopic and photochemical interest.[1,2] When irradiated with UV light in fluid solution at room temperature it rapidly loses N_2, but, when confined in a glass at low temperature (<100 K), the molecule emits an intense luminescence and is photochemically stable.[3] The emission is structured, which strongly implicates a charge-transfer (CT) excited state lying lowest; the efficient loss of N_2, however, points toward a ligand field assignment.

To clarify the nature of the lowest excited state manifold we have initiated a thorough spectroscopic investigation. Comparisons of the T-dependent spectra (77-4 K) clearly show that the emission arises from at least three electronic transitions, a dominant one with origin at 564 nm, a second one peaking at ∿578 nm that dies out as T → 4 K, and a third component at ∿564 nm that is clearly due to an impurity. Resolution of the spectra via box-car techniques discriminates against the impurity emission that decays in the nanosecond range, whereas the measurements confirm that the other two bands arise from the same species, presumably the title compound. They decay in the microsecond range.

We have studied the decay time of the total emission vs temperature in the 85-4 K range. Below 50 K the measured decay time becomes shorter, although the intensity increases substantially. The decay times remain exponential at all temperatures.

From our measurements we infer that:

(a) the lowest excited (emissive) manifold arises from a triplet term, presumably CT in nature,
(b) the lowest two components of this triplet are split, via spin-orbit coupling, by ∿10 cm^{-1},
(c) the lowest component has a greater radiative rate constant than the next one up in energy,
(d) these lowest emitting states are not responsible for the photochemistry, and
(e) the observed photochemistry is due to a higher manifold of states that we infer to be ligand field in nature.

1. Caruana, A.; Hermann, H.; Kisch, H. J. Organomet. Chem. 1980, 187, 349.
2. George, T. A.; Busby, D. C.; Allen Iske, S. D. "Inorganic and Organometallic Photochemistry", Wrighton, M. S., Ed.; Advances in Chemistry Series No. 168, 1978; Chap. 9, p 147.
3. Caruana, A.; Kisch, H. Angew. Chem. Int. Ed. Engl. 1979, 18, 328.

PHOTOINDUCED REACTIONS OF METAL CARBONYL DIMERS WITH ORGANIC DISULFIDES

Kathryn L. Brandenburg and Harmon B. Abrahamson

Department of Chemistry, University of Oklahoma, Norman, Oklahoma, USA 73019

Metal carbonyl dimers such as $[(\eta^5\text{-}C_5H_5)(CO)_3W]_2$ react with organic disulfides under visible or ultraviolet irradiation to produce metal carbonyl thiolate complexes in excellent yields.[1] In contrast to analogous thermal reactions which give dinuclear complexes with bridging thiolates, the photoreactions give mononuclear complexes exclusively. Potential ligating sites on the side chain that could lead to chelated complexes are not bound except in secondary reactions of the primary photoproducts. Judicious choice of irradiation wavelengths and solution temperatures thus permits the synthesis of monodentate complexes of normally chelating ligands such as dialkyldithiocarbamates.

Visible light, which is not absorbed by the disulfides, is fully capable of causing the reaction, indicating that the primary photoprocess involves the metal dimer. Carbonyl-loss intermediates can be ruled out because of the lack of chelated complexes among the primary photoproducts. This leaves homolytic metal-metal bond cleavage as the most likely primary photoprocess. However, unlike other photoreactions proceeding through metal carbonyl radical intermediates, such as halogen abstraction, the disappearance quantum yields in the disulfide reactions approach unity in some cases. This indicates that there is likely a radical chain component to this reaction.

Details of the preparative reactions and spectroscopic parameters of the newly synthesized complexes will be presented, along with the results of quantum yield determinations and mechanistic conclusions.

1. H. B. Abrahamson and M. L. Freeman, Organometallics, 1983, 2, 679-681.

THERMAL AND PHOTOCHEMICAL PHOSPHINE SUBSTITUTION REACTIONS OF THE TETRACOBALT CLUSTER, $Co_4(CO)_8(\mu\text{-}CO)_2(\mu_4\text{-}PC_6H_5)_2$

Richard P. Schmidt, Jr. and Larry M. Cirjak

The Standard Oil Company (Ohio), 4440 Warrensville Center Rd., Cleveland, Ohio USA 44128

The thermal and photochemical reactivity patterns of $Co_4(CO)_8(\mu\text{-}CO)_2(\mu_4\text{-}PC_6H_5)_2$ I, with a variety of phosphine ligands (including L = $P(C_6H_5)_3$, P(o-tolyl)$_3$, P(t-butyl)$_3$ and P(i-propyl)$_3$) have been investigated.

The reactions of I with L proceeds in a stepwise manner to produce the mono-(II) and di-substituted (III) clusters of general formula $Co_4(CO)_{8-x}L_x(\mu\text{-}CO)_2(\mu_4\text{-}PC_6H_5)_2$ (x = 1,2). The concentration and temperature dependence of the rate of these reactions were monitored by HPLC. The kinetic behavior of this cluster is consistent with the following two term rate law.

$$\text{Rate} = k_1[I] + k_2[I][L]$$

At lower temperatures (<50°C) the contribution of the ligand-independent (first-order) term is negligible. We ascribe this first-order term to rate determining CO dissociation followed by rapid reaction with incoming ligand. The activation energy associated with this process requires temperatures >50°C before significant rates of reaction are observed. In contrast, moderate rates of reaction related to the ligand-dependent (second-order) term are observed below 50°C as long as the steric bulkiness of the incoming ligand in this S_N2-type process is limited. Thus, at 20°C a significant rate is observed for the reaction of I with P(n-Butyl)$_3$ while no reaction with $P(C_6H_5)_3$ is observed. Subsequent reaction of II with additional phosphine to form III appears to go by a mechanism involving CO dissociation in the rate-determining step regardless of the steric bulkiness of the incoming ligand.

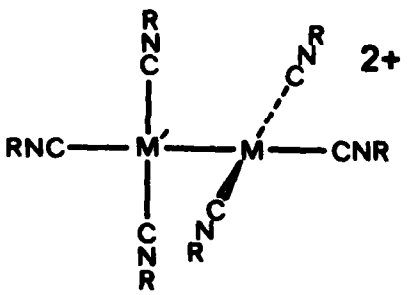
We have also found that substitution reactions of this tetracobalt cluster can also be induced photochemically. Photolysis of I in the presence of $P(C_6H_5)_3$ (at 20°C, 366nm) produces mixtures of II and III with moderate efficiency and no measurable cluster decomposition. Absorption of light by I or II apparently results in the expulsion of carbon monoxide followed by rapid reaction with incoming ligand. Geometric disposition of the phosphine ligands for disubstituted cluster synthesized thermally or photochemically is the same, which suggests that both processes utilize the same intermediate for substitution.

PHOTOCHEMISTRY OF UNSUPPORTED METAL-METAL BONDS: REACTIVITY OF PHOTOGENERATED $\cdot M(CNMe)_3^+$ (M = Pd, Pt) RADICALS

A. R. Cutler, M. K. Reinking, C. P. Kubiak

Department of Chemistry, Purdue University, West Lafayette, IN, USA 47907.

The photochemistry of M-M σ-bonded Pd and Pt hexakis-isocyanide complexes are being investigated.



M = M' = Pd, Pt
M = Pd; M' = Pt

The homo- and heteronuclear Pd and Pt complexes of this study possess Structure I. The observed photochemistry of MeNC derivatives can be interpreted in terms of the clean photogeneration of reactive $\cdot M(CNMe)_3^+$ radicals. Photolysis of an equimolar mixture of the two homonuclear complexes, $[Pd_2(CNMe)_6]^{2+}$ and $[Pt_2(CNMe)_6]^{2+}$ yields a statistical mixture of the starting materials and the heteronuclear species, $[PdPt(CNCH_3)_6]^{2+}$ as determined by 470 MHz ^{1}H-NMR spectroscopy. Similarly, irradiation of the heteronuclear species leads to a statistical mixture of the homonuclear species. Crossover has been followed by ^{195}Pt-NMR and found to be the only observable photoprocess in acetonitrile solvents. In the presence of halogen atom donors, CX_4 (X = Cl, Br), irradiation leads to halogen atom abstraction yielding $MX(CNMe)_3^+$ (M = Pd, Pt; X = Cl, Br). The quantum efficiencies for this process are high. In CCl_4, the values range from Φ_{diss} = 0.09 for $[Pt_2(CNCH_3)_6]^{2+}$ to Φ_{diss} = 0.42 for $[Pd_2(CNCH_3)_6]^{2+}$. Studies of quantum yield dependence on $[CCl_4]$ mitigate against a radical chain mechanism. Photolysis of $[Pt_2(CNCH_3)_6]^{2+}$ in a low temperature glass yields a spectrum displaying characteristic ^{195}Pt splitting and provides strong additional support for metal-metal bond homolysis upon irradiation. Analysis of the product ratios for the photoreaction of $[PdPt(CNMe)_6]^{2+}$ in CCl_4 yields a relative reactivity of the photogenerated radicals $k[Pt(CHCH_3)_3]^+/k[Pd(CNCH_3)_3]^+$ of 4.6. The higher reactivity of the platinum based radical is in contradiction with the relative quantum efficiencies for halogen atom abstraction. This may reflect efficient quenching of the excited state in $[Pt_2(CNCH_3)_6]^{2+}$ or slow escape of the photogenerated $[Pt(CNCH_3)_3]^+$ radicals from the solvent cage.

The nature of the primary photoprocess in the observed photochemistry is still uncertain. A critical double label crossover between $[Pd_2(CNCD_3)_6]^{2+}$ and $[Pt_2(CNCH_3)_6]^{2+}$ provides a direct means of assessing M-M vs M-CNMe labilization in the excited states of these complexes. Results of these studies will be presented.

PHOTOINDUCED NITROSYL DISSOCIATION FROM CARBONYLNITROSYLBIS(TRIPHENYLPHOSPHINE)IRIDIUM

Mitsuru Kubota and Michael K. Chan

Harvey Mudd College, Claremont, California USA 91711

The formation of the metal isocyanate (MNCO) moiety from the reaction of NO and CO previously reported for complexes of Pt, Ir, and Mo[1] is important since MNCO species have been suggested as intermediates in the metal catalyzed pollution removal reaction of CO and NO as NH_3 and CO_2. We have observed that the photoreaction of $[Ir(PPh_3)(CO)(NO)]$ (1) and PPh_3 previously reported to give $[Ir(PPh_3)_3NCO]$[2], instead proceeds with dissociation of NO. Photolysis of 1 with PPh_3 in CH_2Cl_2 at 360, >300, or 254 nm results in formation of $[Ir(PPh_3)_2(CO)Cl]$, N_2O, and Ph_3PO. The thermal reaction leads to the formation of $[Ir(PPh_3)_3(NO)]$. The photolysis of $[Ir(PPh_3)(CO)N_3]$ and PPh_3 likewise does not lead to $[Ir(PPh_3)_3NCO]$, but proceeds with Ir-N bond cleavage. The consequence of M-NO bond homolysis in reactions of $[Rh(PPh_3)_2(CO)(NO)]$, $[Rh(PPh_3)_3(NO)]$, and $[(Ir(PPh_3)_2(CO)(NO)X_2]$ will be described.

1. S. A. Bhaduri, I. Bratt, B. F. G. Johnson, A. Khair, J. A. Segal; R. Walters, C. Zuccaro, J. Chem. Soc. Dalton Trans., 1981, 234.

2. S. A. Bhaduri, B. F. G. Johnson, C. J. Savory, J. A. Segal, J. Chem. Soc. Chem. Commun. 1974, 809.

C-H ACTIVATION REACTIVITY OF SATURATED AND UNSATURATED HYDROCARBONS WITH LANTHANIDE COMPLEXES

P. L. Watson

E. I. du Pont de Nemours & Company, Central Research and Development Dept., Experimental Station 328/330, Wilmington, Delaware 19898

Variation of both hydrocarbon substrates and the metal center in the CH activation reaction:

$$(C_5Me_5)_2M\text{-}CH_3 + R\text{-}H \rightleftharpoons (C_5Me_5)_2M\text{-}R + CH_4$$

(M=Sc, Y, Lu) lead to differences in reaction rate of many orders of magnitude. Effects of steric crowding, prior coordination, hydrocarbon acidity and metal electrophilicity are important in controlling reaction rates and equilibria. Current understanding of this type of C-H bond activation will be compared with other organometallic systems which also activate hydrocarbon substrates.

KINETICS OF THE DISPLACEMENT OF PYRIDINE-2-CARBOXYLATE AND PYRIDINE-2-CARBINOLATE FROM THEIR CHELATED GOLD(III) COMPLEXES.

Lucio Cattalini, Gianpaolo Marangoni, and Martin L. Tobe

Università di Venezia, Calle Larga - S. Marta 2137, 30123 Venezia, Italy, and University College London, 20 Gordon Street, London WC1H OAJ, England.

The kinetics and mechanism of the displacement of two N,O donor chelates from their Au(III) complexes have been compared. The reaction,

$$Au(N{-}{-}O)Cl_2 + 2Cl^- \xrightarrow{H^+} AuCl_4^- + N{-}{-}OH \text{ or } H\overset{+}{N}{-}{-}OH$$

(N——O = pyridine-2-carboxylate, (I); pyridine-2-carbinolate, (II).) in 5% aqueous methanol at 30°C, takes place in two stages. In (I) there is a relatively rapid reversible ring opening at nitrogen with the free nitrogen protonated, followed by a slow displacement of the carboxylate group that is not acid catalysed. In (II) there is an irreversible acid catalysed ring opening at the alkoxide oxygen followed by a slow uncatalysed displacement of the nitrogen. In both cases the associative reaction with chloride offers the main pathway but there can be a substantial contribution from an associative solvolysis at low chloride concentrations.

The rate of displacement of the heterocyclic nitrogen is governed by its basicity[1] and the change in the position of ring opening is due (a) to the effect of the change in the substituent in the 2-position from $-COO^-$ to $-CH_2O^-$ (or their conjugate acids) on this basicity and (b) to the relative labilities of the $-COO^-$ and $-CH_2O^-$ (or CH_2OH). In the latter case protonation only increases the lability by two orders of magnitude.

1. L. Cattalini and M.L. Tobe, Inorg. Chem. 1966, 5, 1145.

REACTIONS OF COBALT(II)PROTOPORPHYRIN(IX) DIMETHYL ESTER (Co(II)P) IN COORDINATING APROTIC SOLVENTS

Dušanka Pavlović, Bujar Domi, Zdravko Dokuzović, Mira Sertić, Blaženka Jurišić, and Smiljko Ašperger

Department of Chemistry, Faculty of Pharmacy and Biochemistry, University of Zagreb, Zagreb, Croatia, Yugoslavia

Co(II)P (5×10^{-6}M), dissolved in a coordinating aprotic high dielectric solvent (air), rapidly gives Co(II)P(solvent) and Co(II)P(solvent)(O_2) at equilibrium. The solutions' Soret maxima gradually shift bathochromically, due to the formation of solvento Co(II)P μ-peroxo dimers. (Soret shifts, and k(obs,25°): DMSO, 403→427, $2.6\cdot10^{-6}$; DMF, 404→424, $3.4\cdot10^{-6}$; hexamethylphosphoramide, 402→426, $3.0\cdot10^{-5}$; CH_3CN, 399→424, $1.3\cdot10^{-5}$; pyridine (py), 402→426 nm, $1.5\cdot10^{-4}s^{-1}$). On the other hand, ligands(L), added to the solutions of Co(II)P in protic solvents (MeOH, EtOH, PrOH, ethylene glycol, formamide) in air, yield[1] Co(III)PL_2^+. However, MeOH, a poor electron donor, yields Co(III)$P(MeOH)_2^+$ in acidified methanolic solution (HCl(g), p-toluenesulfonic, perchloric, acetic, acids, $\geq 10^{-5}$M). With increasing acidity k(obs) reaches a limiting value, $5\cdot10^{-2}s^{-1}$. Addition of py to a Co(II)P solution in MeOH (air) accelerates the formation of Co(III)$P(py)_2^+$ (and Co(II)P disappearance) but only until k(obs,25°)=$1.5\cdot10^{-3}s^{-1}$ is attained. Further increase of [py] changes the solvent's nature. The disappearance of Co(II)P is then slowed down because solvent-py favors the formation of corresponding μ-peroxo dimer which is slower than diligando-complex formation.(In py k(obs,25°) = $1.5\times10^{-4}s^{-1}$.) Analogous rate maxima appear with all alcohols used and with formamide. The dramatic influence of solvents on Co oxidation states is also seen when Co(III)P(Cl) is dissolved in MeOH; oxidation state is retained, but rapid formation of Co(III)P-$(MeOH)_2^+$ and Co(III)P(MeO)(MeOH) ensues. In DMSO Co(III)P(Cl) yields (24h, 25°) (Co(II)P(DMSO) and (DMSO)-Co(II)P(O_2) (Soret 403 nm).

1. Z. Dokuzović, Xh. Ahmeti, D. Pavlović, I. Murati, and S. Ašperger, Inorg.Chem. 1982, 21, 1576.

TUp25-3

KINETIC AND SPECTROSCOPIC STUDIES OF THE SUBSTITUTION REACTIONS OF $Rh(acac)(CO)_2$ WITH TRIPHENYLPHOSPHITE

R. van Eldik[a], S. Aygen[a], H. Kelm[a], A.M. Trzeciak[b] and J.J. Ziolkowski[b]

[a]Institute for Physical Chemistry, University of Frankfurt, Robert Mayer Str. 11, 6000 Frankfurt/Main, FRG

[b]Institute of Chemistry, University of Wroclaw, 14 Joliot Curie St., 50-383 Wroclaw, Poland

Square-planar complexes of Rh(I) are known to be very reactive during substitution and oxidative-addition reactions largely due to their 16-electron d^8 configuration. Rh(I) complexes containing phosphorous ligands are particularly of interest because of their catalytic activity in many important organic reactions, viz. hydrogenation, carboxylation and hydroformylation. Although many of these complexes are already used in industrial applications, there is still a lack of fundamental information on the reaction mechanism and corresponding structural features of such complexes in real catalytic systems.

Recently, some of us[1,2] reported synthetic and structural data on the Rh(I) species produced during the reaction

$$Rh(acac)(CO)_2 + 2P \longrightarrow Rh(acac)P_2 + 2CO$$

where acac = acetylacetonato and $P = P(OPh)_3$. We have now undertaken a detailed kinetic investigation of this reaction using stopped-flow and high pressure techniques. In addition, we have employed uv-visible and ^{31}P-NMR techniques to characterize reaction intermediates, as well as subsequent substitution products when an excess of phosphite is used, viz. $Rh(acac)P_3$ and $Rh(acac)P_4$. A detailed discussion of the kinetic and structural data will be presented, and the nature of the catalytic mechanism will be emphasized.

1. A.M. Trzeciak and J.J. Ziolkowski, Inorg. Chim. Acta, 64, L267 (1982).
2. A.M. Trzeciak and J.J. Ziolkowski, J. Mol. Catal., 19, 41 (1983).

KINETICS OF LIGAND SUBSTITUTION IN Pt(II) AND Pd(II) COMPLEXES: THE ROLE OF THE DONOR ATOMS IN cis-POSITION

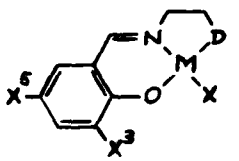
M. Becker, E. Hilms, G. Tiedtke, H. Volz and H. Elias

Anorganische Chemie III, Eduard-Zintl-Institut,
Technische Hochschule Darmstadt, 6100 Darmstadt,
Federal Republic of Germany

The kinetics of ligand substitution according to (1)

$$MLX + Y \rightleftharpoons MLY + X \qquad (1)$$

have been studied spectrophotometrically and conductometrically at constant ionic strength (0.2 M $NaClO_4$) in the solvent methanol for M = Pt(II) and Pd(II) and for L representing a monobasic tridentate O,N,N or O,N,S chelate ligand.



≡ MLX

D = $-N(Et)_2$, -S-Et

X = NO_3^-, Cl^-

The complexes MLX are of square-planar coordination geometry[1].

For a variety of neutral and anionic monodentate entering nucleophiles Y reaction (1) follows rate law (2):

$$\text{rate} = k_Y[Y][MLX] \qquad (2)$$

Conductivity measurements prove that for X = NO_3^- the complex MLX dissociates, thus forming the solvento species MLS^+ (S = solvent molecule).

For a given combination of ligands X and Y the complex carrying the donor groups D = $-N(Et)_2$ reacts considerably slower than the one with D = -S-Et.

The attempt to fit the data obtained for the second-order rate constant k_Y to relationship (3) reveals a very poor correlation (S = nucleophilic discrimination factor).

$$\log k_Y = S \cdot n^o_{Pt} + c \qquad (3)$$

The rate data and the kinetic effects observed for various substituents X^3 and X^5 are compared to the n^o_{Pt} values characteristic for the standard substrate trans-$Ptpy_2Cl_2$ and are related to the specific influence exerted by the cis donor groups O and $-N(Et)_2$ or -S-Et.

1. H. Elias, E. Hilms and H. Paulus
Z. Naturforsch. 1982, 37b, 1266

HIGH PRESSURE NMR STUDIES ON TRANSITION METAL COMPLEXES

Ron L. Batstone-Cunningham, Harold W. Dodgen, John P. Hunt and D. Max Roundhill

Washington State University, Pullman, Washington, USA 99164

The complexes $[Pd(2\text{-methallyl})Cl]_2$ and $Pd(2\text{-methallyl})Cl(PPh_3)$ mixed in $CHCl_3$ solution show syn-anti exchange of the allyl hydrogens in the mono-nuclear species and apparent 2-methallyl exchange between the mono and di-nuclear species[1].

Proton NMR studies at pressures up to 230 MPa were carried out on these systems and apparent volumes of activation for the above exchange processes were obtained. For the syn-anti exchange $\Delta V^{\ddagger} = 0 \pm 2$ cc/mol and for 2-methallyl exchange $\Delta V^{\ddagger} = 11 \pm 2$ cc/mol.

These values are believed to be composites due to the probable multi-step mechanisms involved. The mechanisms will be discussed in the light of this and previous work including the role played by solvent.

In another study, the equilibrium and water exchange kinetics in the high spin-low spin system of Ni(II) 1,4,8,11-tetraazaundecane in aqueous solution is investigated at high pressure using 17-O NMR[2]. The major goal of this study is to find ΔV^{o} for the high spin-low spin conversion which involves loss of two water molecules. This value will be useful in testing ideas concerning volume changes in water exchange reactions[3].

1. For example see: K. Vrieze, P. Cossee, A.P. Praat and C.W. Hilbers, J. Organomet. Chem. 1966, 11, 353.
2. R.J. Pell, H.W. Dodgen and J.P. Hunt, Inorg. Chem. 1983, 22, 529.
3. T.W. Swaddle, Inorg. Chem. 1983, 22, 2663.

STEREOCHEMISTRY AND REARRANGEMENTS OF EIGHT-COORDINATE TANTALUM(V) AND NIOBIUM(V) DITHIOCARBAMATES AND MONOTHIOCARBAMATES

John R. Weir and Robert C. Fay

Cornell University, Ithaca, New York, USA 14853

Stereochemical nonrigidity is a pervasive feature of the chemistry of higher coordination complexes. The first example of an eight-coordinate tetrakis chelate that is stereochemically rigid on the NMR time scale was the tetrakis(N,N-dimethyldithiocarbamato)-tantalum(V) cation, $[Ta(Me_2dtc)_4]^+$.[1] In this complex the bidentate dtc ligands span the m edges of a D_{2d} dodecahedron.[2] Reported herein are variable temperature ^1H NMR studies of related tetrakis-(dithiocarbamato)- and (monothiocarbamato)-complexes of Ta(V) and Nb(V), $[Ta(R_1,R_2dtc)_4][TaX_6]$ (R_1,R_2 = Me,Me; i-Bu,i-Bu; Me,i-Pr; Me,Ph, Me,C_6H_{11}; Me,CH_2Ph; X = Cl or Br), $[Nb(Me_2dtc)_4]Cl$, $[Ta(Me_2mtc)_4][TaCl_6]$, and $[Nb(Me_2mtc)_4][NbCl_6]$. The complexes were prepared by reaction of the metal pentahalides with anhydrous $Na(R_1,R_2dtc)$ or $Na(Me_2mtc)$. They were characterized by elemental analysis, conductance measurements, and by IR and NMR spectroscopy.

Low-temperature ^1H NMR spectra of $[Ta(Me_2dtc)_4][TaCl_6]$ and $[Nb(Me_2dtc)_4]Cl$ exhibit two methyl resonances of equal intensity, consistent with the dodecahedral mmmm structure found in the solid Ta compound.[2] The complexes that contain unsymmetrical dtc ligands also display two methyl resonances, but the relative intensities deviate from unity increasingly as R_2 varies in the series $[Ta(Me,-R_2dtc)_4][TaX_6]$ (R_2 = C_6H_{11}, i-Pr, CH_2Ph). These latter spectra indicate an equilibrium mixture of mmmm stereoisomers that differ in the distribution of methyl groups between the dodecahedral A and B sites. Separate resonance lines for the various stereoisomers are not observed; only the local environment of the methyl groups (A- or B-site) can be distinguished. However, the population of methyl groups in A or B sites is influenced by the nature of R_2.

The low-temperature ^1H NMR spectrum of $[Ta(Me_2mtc)_4][TaCl_6]$ exhibits four methyl resonances of equal intensity, consistent with the dodecahedral mmmm-C_{2v} stereoisomer found in the solid state for $[M(Et_2mtc)_4]$ (M = Ti or Zr).[3] In this isomer, the four sulfur atoms are clustered in all-cis positions. Surprisingly, $[Nb(Me_2-mtc)_4][NbCl_6]$ displays four methyl resonances of relative intensity 3:1:3:1, indicative of one of the two mmmm-C_s stereoisomers.

At higher temperatures, the NMR lines coalesce owing to a metal-centered rearrangement process that exchanges methyl groups between the A and B sites. Coalescence temperatures are -52 to -76°C for the dtc complexes [$\Delta G^*(-60°C) \approx 11$ kcal mol^{-1}] and -2 to -15°C for the mtc complexes [$\Delta G^*(25°C) \approx 14$ kcal mol^{-1}]. Activation parameters have been determined by total line-shape analysis. The higher rearrangement barriers for the mtc complexes point to a polytopal rearrangement mechanism.

1. R. C. Fay, D. F. Lewis, and J. R. Weir, J. Am. Chem. Soc., 1975, 97, 7179.
2. D. F. Lewis and R. C. Fay, Inorg. Chem. 1976, 15, 2219.
3. W. L. Steffen and R. C. Fay, Inorg. Chem. 1978, 17, 2120.

DISSOCIATIVE SUBSTITUTION IN 4-COORDINATE PLANAR PLATINUM(II) COMPLEXES. THE KINETICS OF SULFOXIDE EXCHANGE AND DISPLACEMENT BY BIDENTATE LIGANDS IN THE REACTIONS OF CIS-DIARYLBIS(DIMETHYLSULFOXIDE-PLATINUM(II) IN CHLOROFORM AND BENZENE

Santo Lanza, Domenico Minniti, Peter Moore, John Sachinides, Raffaello Romeo, Martin L. Tobe.

Dipartimento di Chimica Inorganica e Struttura Moleculare, Universita di Messina, Via dei Verdi, 98100 Messina, Italy; Department of Chemistry and Molecular Sciences, University of Warwick, Coventry CV4 7AL, England; Chemistry Department, University College London, 20 Gordon St., London, WC1H OAJ, England.

The kinetics of the exchange of dimethylsulfoxide with cis-$[Pt(C_6H_5)_2(Me_2SO)_2]$ in $CDCl_3$ have been followed by stopped-flow ^1H nmr and the rate law, Rate = $(k_1 + k_2[Me_2SO])[complex]$, established. At 300 K, $k_1 = 7.9 \times 10^{-2} s^{-1}$ and $k_2 = 1.0 \times 10^{-1} M^{-1} s^{-1}$; the latter pathway making a minor contribution that may be due to changes in the bulk solvent. The reaction, cis-$[Pt(C_6H_5)_2(Me_2SO)_2]$ + bipy = $[Pt(C_6H_5)_2(bipy)]$ + $2Me_2SO$ in chloroform takes place in a single observable step whose rate is determined by the displacement of the first sulfoxide and the kinetic form is consistent with competition between Me_2SO and the chelate for a reactive intermediate. The reactions of the bis(sulfoxide) complex with 2,2'-bipyridyl, 1,10-phenanthroline and 1,2-bis(diphenylphosphino)-ethane have been studied spectrophotometrically in benzene. The sulfoxides are displaced in a single observable step and the rate law, $-d \ln[complex]/dt = k_1k_3[L\text{-}L]/(k_{-1}[Me_2SO] + k_3[L\text{-}L]) + k_2[L\text{-}L]$, established. Only in the case where L-L is bis(diphenylphosphino)ethane does the k_2 path make any significant contribution to the rate. k_1 is independent of the nature of the entering group, $1.9 \times 10^{-2} s^{-1}$ at 298 K, $\Delta H^{\ddagger} = 15$ kcal mol^{-1}; $\Delta S^{\ddagger} = -16$ cal $K^{-1}mol^{-1}$, while the ratio k_3/k_{-1} is very sensitive to the nature of L-L = 0.055, 0.23, and 5.12 for L-L = bipyridyl, phenanthroline and bis(diphenylphosphino)ethane respectively at 298 K. The reactions of cis-$[Pt(4\text{-}CH_3\text{-}C_6H_4)_2(Me_2SO)_2]$ are similar. A mechanism in which the loss of the first sulfoxide is rate determining and takes place without assistance from L-L or the solvent is proposed. The labile intermediate thereby generated is partitioned between L-L and dimethylsulfoxide in the ratio k_3/k_1. In the case of the diphosphine nucleophile there is a parallel associative attack with rate constant $k_2 = 10\ M^{-1}s^{-1}$. The ring closing reaction displacing the other sulfoxide is fast.

TUp25-8

MOLECULAR MECHANICAL ANALYSIS OF NON-DISSOCIATIVE INTRAMOLECULAR REARRANGEMENTS IN MX_6 AND MX_5 SYSTEMS

John F. Geldard and H. Keith McDowell

Clemson University, Clemson, SC, USA 29631, Los Alamos National Laboratory, Los Alamos, NM, USA 87545

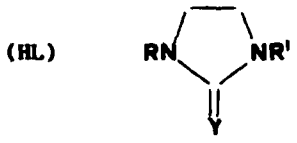
The interconversion of the thirty isomers of MX_6 and the twenty isomers of MX_5 is being studied by the use of Smart Monte Carlo molecular mechanical calculations.[1] The object of the study is to determine the most probable trajectories for isomer interconversions, and the activation parameters as functions of the M-X bond distance and strength, and of the X group size. The calculations simulate gas phase behavior. Rate constants are calculated from the median time of interconversion among statistically averaged ensembles of molecules. The valence force field uses a pair-wise multipotential function of angle about the M atom, as well as M-X bond restoring forces. The multipotential function simulates Leonard-Jones repulsion to X-X close approach. The force constants are calibrated by a normal mode calculation to give vibrational frequencies appropriate to the different types of MX_6 and MX_5 molecules, from the very rigid to the very loose.

1. P. J. Kossky, J. D. Doll, and H. L. Friedman, J. Chem. Phys. 1978, 69, 4628.

OsO_4 REDUCTION BY SOME IMIDAZOLIDINE-2-THIONE AND -2-SELONE LIGANDS

Franco Cristiani, Francesco A. Devillanova, Angelo Diaz and Gaetano Verani. -Istituto di Chimica Generale Inorganica ed Analitica; Via Ospedale 72, 09100 Cagliari, ITALY.

In $HClO_4$ solutions, OsO_4 reacts with the following imidazoline-2-thione and -2-selone[1]



(HL)	R	R'	
	H	H	Y = S, Se
	H	Me	
	H	Et	

to give Os(III) complexes , according to the reaction

$$2\,OsO_4 + 22\,HL + 6\,H^+ \longrightarrow 2\,[Os(HL)_6]^{3+} + 5\,L_2 + 8\,H_2O \qquad (1)$$

where HL is the ligand and L_2 its oxidation product, i.e. the disulphide or diselenide. Reaction (1) takes place through several elementary processes, among which the rate-determining step involves one molecule of substrate, one of perchloric acid and one of ligand.

The use of N,N'-dialkylimidazolidine-2-thione (R=R'=Me, Et) as reducing-complexing agents[2,3] allowed us to stop the reduction at Os (VI) and then to prepare the osmyl complexes $[OsO_2L_4]^{2+}$, where L is the disubstituted imidazolidine. On this basis, we also hypothesized that (1) can occur via an Os(VI) intermediate, i.e. $[OsO_2(HL)_4]^{2+}$, although this species was never isolated. This hypothesis[2,2] was confirmed on studying the reduction of $[OsO_2L_4]^{2+}$ by means of HL in presence of $HClO_4$. The specific rate constants obtained for this reaction are very close to those found for reaction (1), thus suggesting that the rate-determining step is the same in the two reactions and that it regards the Os(VI) $\longrightarrow$ Os(III) reduction.

Casually, by standing $[OsO_2L_4](ClO_4)_2$ in the reaction medium, we verified a further reduction with formation of new Os(IV) complexes[3] of formula trans-$[OsCl_2L_4](ClO_4)_2$. It is interesting to point out that the reduction Os(VI) $\longrightarrow$ Os(IV) takes place with a simultaneous reduction of ClO_4^- to Cl^-, since no Cl^- ion was added in the reaction medium. However, in order to understand the mechanism of $[OsCl_2L_4]^{2+}$ formations, we separated different compounds having formula $OsL_4(ClO_4)_4$, which may be hypothesized as the precursors of the trans-$[OsCl_2L_4](ClO_4)_2$.

At present, we are considering the opportunity of carrying out reaction (1) in different monoprotic acids, in order to clarify further aspects of this complicated reduction.

1. F.Cristiani, F.A.Devillanova, A.Diaz and G.Verani, Phosphor Sulfur Relat.Elem., 12, 305 (1982). 2. F.Cristiani, F.A.Devillanova, A.Diaz and G.Verani, Inorg.Chim.Acta, 68, 213 (1983). 3. F.Cristiani, F.A.Devillanova, A.Diaz, G.Verani and L.Antolini, Transition Met.Chem, 8, 236 (1983); J.C.S. Dalton, 1261 (1983).

COORDINATION CHEMISTRY OF CO ON ZnO SURFACES

Edward I. Solomon

Stanford University, Department of Chemistry, Stanford, California 94305, USA

We have been generally interested in the application of photoelectron spectroscopy as a probe of the interactions of small molecules with metal oxide surfaces. Emphasis thus far has been placed on ZnO, an active catalyst for methanol synthesis. ZnO is also unusual from a spectroscopic viewpoint due to the observation that upon chemisorption to powders, the CO stretching frequency increases by 70 cm^{-1} compared to its gas-phase value, 2143 cm^{-1}, in sharp contrast to the decrease which occurs on most transition metal surfaces and inorganic complexes.

The wurtzite crystal structure of ZnO provides several chemically different low index surfaces which have been characterized by LEED. The (10$\bar{1}$0) is a "dimer" face with Zn^{2+} and O^{2-} ions arranged in pairs with their coordinatively unsaturated directions 19° off normal, while the "polar" faces, (0001) and (000$\bar{1}$), are ideally viewed as planes of Zn^{2+} or O^{2-} ions, respectively, with their coordinatively unsaturated positions normal to the surface.

Our studies thus far on the interaction of CO with ZnO have combined the techniques of angle-integrated and angle-resolved UPS and High Resolution Electron Energy Loss Spectroscopy (HREELS). These studies clearly demonstrated that CO binds carbon end down to the unsaturated Zn^{2+} site on all three faces, forming approximately linear Zn-C-O complexes.

These studies are all consistent with an electronic picture of CO acting as a 5σ donor by transferring electron density from this weakly antibonding orbital, with little or no π backbonding to the CO 2π^* orbital. This results in a net donation of charge to the surface zinc. Hence, the CO bond order is increased and the CO molecule is polarized with some positive charge at the carbon.

This geometric and electronic structure picture of CO on ZnO has implications concerning its reactivity, in particular with respect to the synthesis of methanol. The polarized molecule has a strengthened CO bond, initiallty making C-O bond rupture less probable, but making the molecule susceptible to heterolytic attack by dissociated H_2, which is known to adsorb as $Zn\text{-}H^-$ and OH^+.

ANALOGIES IN SURFACE-CHEMICAL ELEMENTARY PROCESSES AND THE BEHAVIOR OF COORDINATED COMPLEXES

John T. Yates, Jr., University of Pittsburgh, Department of Chemistry, Pittsburgh, Pennsylvania, USA 15260

Structural and spectroscopic studies of the behavior of adsorbed molecules on transition metal surfaces have shown that concepts in coordination chemistry may often apply to ligand behavior in chemisorption. Two examples of this relationship will be discussed:

NH_3 Chemisorption on Ni(110) (1).

The Ni(110) surface is a ridged surface containing slightly electropositive ridge atoms and slightly electronegative valley atoms. A molecular imaging technique, ESDIAD(2), has been used to image the N-H bond directions in the oriented adsorbed NH_3 molecules by observing H^+ emission directions in space when NH_3(ads) is bombarded by electrons. The results indicate that the N-lone pair donor electrons form the chemisorption bond with single Ni ridge atoms. All azimuthal orientations of the NH_3 molecule about the normal C_{3v} axis are allowed on this site. The NH_3 molecule is either rotating or librating on its site about C_{3v}; low temperature studies indicate that any barrier to rotation is below 1.8 kcal/mole.

CO Chemisorption on Pd(3,4).

By using infrared techniques to study chemisorbed CO species on small (75Å) Pd particles, we have studied the chemisorption of terminally-bound CO molecules onto a field of chemisorbed 2-fold bridged-CO species. This process results in a stoichiometric conversion of two bridged-CO species into terminal CO's for each additional terminal-CO chemisorbed. A model involving competition between strong π-acceptor species (2-fold CO bridges) and weaker π-acceptor species (terminal-CO) is proposed as the controlling factor in carbonyl rehybridization locally on the surface. The addition of CO to a surface region containing bridged-CO triggers bridged CO → terminal CO conversion.

1. C. Klauber, M. Alvey, and J. T. Yates, Jr., submitted, Chem. Phys. Letters.

2. T. E. Madey and J. T. Yates, Jr., Surface Science, 63, 203 (1977).

3. P. Gelin and J. T. Yates, Jr., Surface Science Letters, 136, L1-L8, (1984).

4. P. Gelin, A. Siedle, and J. T. Yates, Jr., submitted, J. Phys. Chem.

TUp26-1

CHEMISORPTION BOND ENERGY AND BOND ACTIVATION ON TRANSITION METAL SURFACES: CRUCIAL ROLE OF ANTIBONDING ADSORBATE ORBITALS

Evgeny M. Shustorovich and Roger C. Baetzold

Research Laboratories, Eastman Kodak Company, 1669 Lake Avenue, Rochester, New York, USA 14650

An analytical and tight-binding-type computational model has been developed to treat periodic trends of chemisorption bond energies and adsorbate stereochemistries on transition-metal surfaces.[1] The striking finding is that the antibonding adsorbate orbitals play the dominant role in chemisorption, so that even saturated molecules such as H_2 or CH_4 will typically behave as acceptors. The major physical reasons for this are the higher donor ability of surfaces (compared with metal clusters) and larger overlap with the σ^* orbitals (compared with σ orbitals). Another striking effect is the adsorbate-induced sp-d orbital rehybridization of the metal surface atoms. These conclusions have been nicely corroborated in the recent work by Saillard and Hoffmann.[2] Various applications of the general findings[1] to bond activation, work function changes, surface core shifts, heats of adsorption, adsorbate registries, and surface diffusion barriers will be discussed.

1. E.M. Shustorovich, R.C. Baetzold, and E.L. Muetterties, J. Phys. Chem., 1983, 87, 1100, and references therein.

2. J.Y. Saillard and R. Hoffmann, submitted, J. Am. Chem. Soc.

ATOM VS CLUSTER REACTIVITIES: CLUSTER ORGANOMAGNESIUM AND CALCIUM REAGENTS

Alan Whetten, Yuzo Imizu, and Kenneth J. Klabunde

Department of Chemistry, Kansas State University, Manhattan, Kansas USA 66506

In order to understand organic reaction chemistry on metal surfaces, an understanding of free atoms and small metal clusters becomes imperative. The basic question breaks down to, "What free metal particle is the most chemically reactive, atoms (M), dimers (M_2), or larger clusters (M_x)?"

By employing modern matrix isolation techniques in combination with infra red and UV-visible spectroscopy, it is now possible to study low temperature oxidative addition reactions of isolated atoms and clusters. In the present study the reactions of Mg atoms, Mg_2, Mg_3, $(Mg)_x$ and Ca atoms, Ca_2, $(Ca)_x$ with CH_4, CH_3F, CH_3Cl, CH_3Br, and CH_3I were monitored at 9K. Infra red spectroscopy indicated that $CH_3(M)_nX$ products were formed with all of the halides. No reactions occurred with CH_4, however. UV-visible spectroscopy indicated that for CH_3F, CH_3Cl, and CH_3Br atoms were not the reacting species. All of the evidence indicates that M_2, M_3, and $(M)_x$ were the reacting species to form $CH_3(M)_nX$ where $n>1$. In the case of CH_3I both atoms and clusters reacted. These experiments constitute the first examples where σ-bond breaking reactions took place on a cluster but not a single atom. Mechanistically this allows a clearer understanding of the basic C-X bond cleavage. A discussion of possible mechanistic features will be presented dealing with initial electron transfer,[1] bond energies, etc.

Theoretical work predicts that the reaction $Mg_2 + CH_3X \rightarrow CH_3Mg_2X$ would be more exothermic than the analogous Mg atom reaction.[2] This is apparently the result of the Mg-Mg bond being extremely weak in the free dimer, but relatively strong in the CH_3Mg_2X product.

1. Y. Tanaka, S. C. Davis, and K. J. Klabunde, J. Am. Chem. Soc., 1982, 104, 1013.

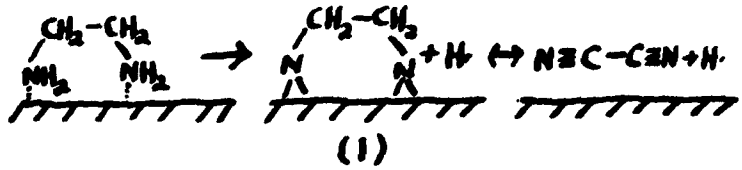
2. P. G. Jasien and C. E. Dykstra, J. Am. Chem. Soc., 1983, 105, 2089.

COADSORPTION CHEMISTRY OF H_2 AND C_2N_2 ON Pt(111): A COMMON INTERMEDIATE IN THE HYDROGENATION OF CYANOGEN AND THE DEHYDROGENATION OF ETHYLENEDIAMINE ON Pt(111).[1]

J.R. Kingsley, David Dahlgren[2], and John C. Hemminger

University of California, Irvine, Department of Chemistry, Irvine, California, USA 92717

The adsorption of C_2N_2 on Pt(111) results in two desorption states (α,β). The α state, T_{max}=368 K, is due to the desorption of molecularly adsorbed C_2N_2. The β state, T_{max}=780 K, is most likely due to the recombination of adsorbed CN groups. Coadsorption of H_2 and C_2N_2 results in a surface nitrene (1) which decomposes to give back H_2 and C_2N_2 at 430 K. Decomposition of ethylenediamine results in the same species. Dehydrogenation of ethylene-d_4-diamine shows that the amine hydrogens are removed first in this process followed at 430 K by the removal of the hydrogens from the carbons liberating C_2N_2 as the final product. This is summarized in the reaction scheme below. Under ultra-high-vacuum conditions the reaction step dinitrene ↔ cyanogen is reversible while the diamine → dinitrene is not.



(1)

1. Supported in part by the Office of Naval Research.

2. Present address: MMRD, Lawrence Berkeley Laboratory, Berkeley, California 94720.

COORDINATION AND CATALYSIS ON AMMONIA SYNTHESIS IRON CATALYSTS

K. R. Tsai Dai-wei Liao Zhong-quan Wang Hong-bin Zhang
Department of Chemistry and Institute of Physical Chemistry,
Xiamen (Amoy) University, Xiamen, China

The proposed cluster structural model of active site for ammonia synthesis on α-Fe(111) surface and coordination modes of $(N_2)_{ads}$ are discussed together with the results of observation using *in situ* laser Raman spectroscopy. The Raman peaks at 1940 and 2040 cm^{-1}, which have been observed under actual reaction conditions for ammonia synthesis at 450 C on doubly promoted iron catalyst (one of typical industrial ammonia synthesis catalysts), may be due to N≡N stretching, corresponding to symmetrically chemisorbed $(N_2)_{ads}$ species (i.e., double-end-on coordination of N≡N to Fe's in the outermost surface layer, and multiple-side-on to other Fe's in lower surface layers) and to unsymmetrically chemisorbed $(N_2)_{ads}$ species (i.e., single-end-on to an outermost surface Fe, and multiple-side-on to other Fe's in lower surface layers), respectively; the Raman peak being found at 423 cm^{-1} may be attributed to $(Fe)_s$—N stretching, corresponding to the $(N_2)_{ads}$ species. The *in situ* Raman spectroscopic investigations have also indicated that the chemisorbed dinitrogen, $(N_2)_{ads}$, rather than $(N)_{ads}$, or $(NH)_{ads}$, appeared to be the predominant intermediates under actual reaction conditions for ammonia synthesis on iron catalysts at 450 C and under atmospheric pressure. The plausibilities of proposed coordination modes of $(N_2)_{ads}$ and its hydrogenated transition state on 7-Fe cluster-structural active site have also been examined using approximate quantum-chemical calculation (EHMO), the results of which showed that with the flat-lying symmetrical coordination mode, the total energy of the system was much lower and the overlapping population between the two N atoms was less than that with other single-end-on-plus-multiple-side-on coordination modes, thus favoring chemisorption of N_2 and activation of N≡N bond. These above results and the known inverse isotopic effect of dueterium seem to favor the associative mechanism for ammonia synthesis reaction. The intimate relation between coordination and catalysis on ammonia synthesis iron catalysts is pointed out.

TUp26-5

STRUCTURE OF ADSORBED BENZENE MONOLAYERS ON THE RH(111) CRYSTAL FACE

B. E. Koel*, J. E. Crowell, C. M. Mate a l G. A. Somorjai

Materials and Molecular Research Division, Lawrence Berkeley Laboratory, and Department of Chemistry, University of California, Berkeley, California 94720

Benzene adsorption on the Rh(111) crystal surface has been studied using HREELS, LEED and TPD. The vibrational spectra establish that benzene adsorbs molecularly at 300K and is π-bonded to the surface with the molecular ring plane parallel to the metal surface plane. Benzene chemisorbs with a similar geometry for all of the ordered and disordered monolayers studied up to the temperature of decomposition. Benzene adsorption is only partially reversible; less than twenty percent of the adsorbed benzene desorbs molecularly upon heating. The remaining benzene irreversibly decomposes, evolving hydrogen and leaving a carbon-covered surface. The nature of these hydrocarbon fragments is discussed elsewhere.[1]

Recent dynamic LEED calculations[2] together with the angle-dependent HREELS studies reported here establish a $C_{3v}(\sigma_d)$ bonding symmetry for the c(2$\sqrt{3}$x4)rect-C_6H_6 structure. Several other ordered benzene overlayers can be formed between 300-400K depending on the benzene coverage. No large changes occur in the chemisorption bonding mode or geometry coincident with the two-dimensional ordering phase transitions in this temperature range. Two adsorption sites are observed, and the relative population of these depends on both temperature and coverage. Near saturation coverages a dominant fraction of benzene molecules occupy hcp hollow sites with $C_{3v}(\sigma_d)$ symmetry. Similar adsorption behavior and surface chemistry is seen for benzene chemisorbed on several other transition metal surfaces, including evidence for two adsorption sites with $C_{3v}(\sigma_d)$ symmetry.

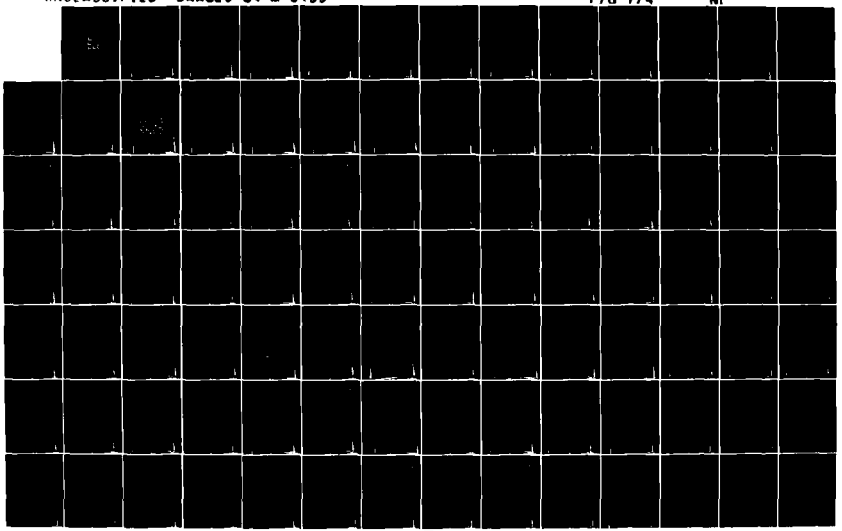
The frequency of the CH out-of-plane bending mode (γ_{CH}) is an indirect indication of the extent of interaction between benzene and the metal surface. For the several transition metal single crystal surfaces studied so far, the strength of the metal-benzene bonding estimated by the metal-ring vibrational frequencies or the molecular desorption temperatures is correlated reasonably well with the frequency shifts of the γ_{CH} vibration and also with the work function of the clean metal surface. However, the γ_{CH} mode is shown to be sensitive to the nature of the adsorption site, in addition to the chemisorption bond strength.

1. B. E. Koel, J. E. Crowell, and G. A. Somorjai, Surface Sci., submitted.
2. M. A. Van Hove, R. F. Lin, and G. A. Somorjai, Phys. Rev. Lett. 51, 778 (1983).

*Miller Institute Postdoctoral Fellow, Present Address: CIRES, Department of Chemistry, University of Colorado, Boulder, CO 80309

AD-A146 190 INTERNATIONAL CONFERENCE ON COORDINATION CHEMISTRY (23RD) HELD AT BOULDER..(U) COLORADO UNIV AT BOULDER E L KING ET AL. 03 AUG 84 ARO-21423.1-CH-CF 4/8

UNCLASSIFIED DAAG29-84-M-0199 F/G 7/4 NL



1·0
1·1
1·25
1·4
1·6
2·0
2·2

TUp26-6

ETHYLENE COORDINATION AND OXIDATION ON PALLADIUM SINGLE CRYSTALS (Pd(100))

E. Stuve and R.J. Madix

Stanford University, Department of Chemical Engineering, Stanford, California 94305

The coordination and reaction of C_2H_4 with clean and oxygen covered Pd(100) was studied with temperature programmed reaction spectroscopy (TPRS) and high resolution electron energy loss spectroscopy (HELS). Both di-σ- and π-bonded forms of C_2H_4 were stable at 80 K on clean Pd(100). The bond energy of the π-bonded form ranged from 6 to 18 kcal/mol. The di-σ-bonded form dehydrogenated to form bound atomic hydrogen and a stable intermediate inferred to be a vinyl species ($CHCH_2$). This intermediate in turn reacted further between 275 and 300 K to produce CH groups. Atomic hydrogen recombined to form gaseous H_2 at its normal temperature of 360 K, while condensation and dehydrogenation of CH groups occurred from 350 to 500 K. A p(2×2)O overlayer, corresponding to an oxygen-palladium surface coverage ratio of 0.25, was sufficient to completely block the reaction of ethylene. Some ethylene dehydrogenation and reaction with atomic oxygen was observed for lower oxygen coverages. It was found that the extent of dehydrogenation decreased in a 2:1 ratio with increasing oxygen coverage, as expected for complete inhibition of dehydrogenation by p(2×2) islands of oxygen. Only the π-bonded form of C_2H_4 was stable on the surface with greater than 0.25 monolayer of atomic oxygen.

TUp26-7

HYDROCARBON CHEMISTRY ON MODIFIED W(100) SURFACES

C. M. Friend and K. A. Pearlstine

Department of Chemistry, Harvard University, 12 Oxford Street, Cambridge, Massachusetts, USA 02138

Oxygen-treated and carbided surfaces of tungsten have been shown to catalyze reactions of hydrocarbon molecules involving C-H and C-C bond activation.[1,2] We have initiated a program the objective of which is to identify key factors controlling catalytically important C-H and C-C bond scission/formation processes occurring on tungsten-based surfaces. These studies primarily focus on C-H bond activation in C_2H_2, C_2H_4 and C-C bond activation in cycloheptatriene on W(100), W(100)-(5x1)-C, and W(100)-(2x1)-O.

Thermal treatment of ethylene (C_2H_4) yielded C_2H_4 and H_2 as desorption products on all surfaces studied. The C_2H_4 desorbed in two poorly resolved maxima at 190K, 250K on clean W(100), 195K and 225K on W(100)-(2x1)-O, and 160K, 200K and 230K on W(100)-(5x1)-C.

Isotopic exchange experiments were performed to probe for reversible C-H bond activation in ethylene. A significant degree of isotopic mixing, indicative of facile, reversible C-H bond activation, was observed on the clean W(100) surface following coadsorption of C_2H_4 and C_2D_4 with exchange primarily occurring in the higher temperature desorption maxima. No significant exchange was observed on the -(2x1)-O and -(5x1)-C surfaces.

Thermal desorption spectra obtained following acetylene desorption yielded H_2 and C_6H_6, with H_2 being the primary product. Coadsorption of excess H with C_2H_2 on W(100) yielded C_2H_4; the hydrogenated products originated from a C_2H_2 surface intermediate based on isotopic exchange reactions. No ethylene hydrogenation was observed on the -(5x1)-C or -(2x1)-O surfaces.

Cycloheptatriene formed benzene on W(100)-(5x1)-C at ~450K. Cycloheptatriene and H_2 were the only other desorption products. No benzene formation was observed on the W(100)- or W(100)-(2x1)-O surfaces.

1. F. Kapteijn and J. C. Mol, J. Chem. Soc., Farad. Trans. I 1982, 78, 2583.

2. See, for example, J. B. Benziger, R. I. Ko, and R. J. Madix, J. Cat. 1980, 64, 132.

TUp27-01

SYNTHETIC ION CARRIERS TAILORED AFTER NATURAL IONOPHORES

ABRAHAM SHANZER[a], JACQUELINE LIBMAN[a] and FELIX FROLOW[b],
Departments of Organic Chemistry[a] and of Structural Chemistry[b] The Weizmann Institute of Science, Rehovot, Israel.

In the search for artificial ion carriers, macrocyclic carbonyl compounds were synthesized that bear deliberate resemblance to naturally occuring ionophores and their conformations examined. The compounds studied include lactones, amides, thiolactones and thionelactones that vary in the number of functional groups, in ring size and in ring symmetry.

Structural analyses of the compounds prepared led to identify two basic structures that mimik the arrangements of the natural iron carriers Enterobactin and Nocardamin. These structures differ in their binding and transport properties, functioning either as 'one way shuttle' (Enterobactin) or as reversible carriers (Nocardamin). The synthesis of structural analogs of both types of compounds will be described and their binding and transport characterization discussed.

MOLECULAR MECHANICS CALCULATIONS AS AN AID IN LIGAND DESIGN

Robert D. Hancock, V.J. Thom, Jan C.A. Boeyens, and M.J. van der Merwe
University of the Witwatersrand, Johannesburg, South Africa.

The Molecular Mechanics approach for the prediction of the geometry of polyamine complexes of Co(III) and Ni(II) is briefly described. Apart from the prediction of molecular geometry, these calculations are useful in predicting the thermodynamics of complex-formation of Ni(II) with polyamines. An important consideration here is that account must be taken of the fact that the M-N bond is stronger when the nitrogen is secondary than when it is primary.

The molecular mechanics calculations show the interesting result that the strain free Co-N bond in Co(III) complexes is 1.925 Å, which is shorter than actually observed in any Co(III) complexes with polyamines. The reason for the fact that the observed bond length is longer than the strain-free bond length is that v.d. Waals repulsions between the hydrogens on adjacent nitrogen donors and alkyl groups cause the Co-N bond to be stretched out from the strain-free value of 1.925 Å to the values of 1.94 to 2.04 Å observed in polyamine complexes of Co(III). This is similar to the familiar idea of radius ratios in solids, where too large anions cannot approach a too small cation sufficiently closely.

The small size of Co(III) thus demonstrated has important design consequences. Thus, in order to stabilise Co(III) relative to the large Co(II) ion, polyamine ligands must be selected which have a low packing density, i.e. they can approach the small Co(III) ion as closely as possible. Molecular mechanics are thus used to rationalise the Co(II)/Co(III) redox potentials. It is also demonstrated that the Ni(III) ion is very small, and it is shown how Ni(II)/Ni(III) redox potentials may be similarly rationalised. The synthesis of the novel complex of Ni(III) with the low packing-density ligand 1,4,7-triazacyclononane-N,N',N''-triacetate is described, and its stability is rationalised in terms of the above concepts.

ORGANIC-PHASE COORDINATION OF METAL IONS BY MACROCYCLIC COMPOUNDS

W. J. McDowell and B. A. Moyer

Oak Ridge National Laboratory, P. O. Box X, Oak Ridge, Tennessee 37831, USA

Organophilic crown ethers and similar macrocyclic compounds enhance the extraction or phase transfer of metal ions from an aqueous to organic phases by organophilic cation exchangers such as alkyl phosphoric acids, alkyl-aryl sulfonic acids, carboxylic acids, and β-diketones. The enhancement is synergistic; that is, the effect of the mixture is greater than the sum of the separate effects of the reagents used alone. Ions examined include the alkali and alkaline earths and some of the first-row transition elements. Characterization of the organic-phase complexes indicate that the organic-phase-soluble salt of the metal ion is coordinated by the macrocycle with part or all of the coordination being supplied by that ligand. The extraordinary strength of these complexes appears to be derived from the pre-positioned nature of the coordination sites in the macrocyclic ligand and to the more positive entropies of formation as compared with monodentate ligands. In most cases the metal ion appears to be surrounded by the macrocycle. Synergistic effects are much weaker when steric effects prevent this or when size-correspondence between the ion and macrocycle cavity is poor. Bonding strength is also affected by the flexibility of the macrocycle ring suggesting that compliance of the position of the coordinating atoms with the preferred three-dimensional bonding requirements of the metal ion is important. Studies of such complexes may contribute to the understanding of bonding geometries of ions in solution.

STRUCTURE OF BENZO-15-CROWN-5 COPPER(II) COMPLEX

You Xiao-Zeng[1], Li Zhong-De[1], Yang Xing-Shui[1], Li Cun[1], Wang Ding-Nang[1], and Huang Jin-Shun[2]

[1]University of Nanking, Nanking, and [2]Fujan Institute of Research on the Structure of Matter, China.

The model system for copper(II) situated in metalipretains has aroused much interest recently. The structure of the title complex has not been studied yet.

By photospectroscopic method, it was found that $Cu(ClO_4)_2 \cdot 6H_2O$ formed a stable complex with benzo-15-crown-5 in acetone solution. The metal to ligand ratio of the complex is 1:1 and the formation constant is 15.4. The IR spectra were obtained by use of Nujol mulls and ^1H NMR spectra were obtained in CD_3COCD_3 solutions, which showed that copper(II) ion was directly coordinated to crown ether oxygens and was a little farther from the benzo-ring.

A brown crystal complex was prepared. The composition of the complex was found to be $\{[Cu(C_{14}O_5H_{20})(H_2O)_2](ClO_4)_2\} \cdot 3H_2O$. Its structure has been determined by single crystal X-ray diffraction. It belongs to monoclinic system, $P2_1/a$ space group with a=16.142(8)Å, b=20.233(5)Å, c=7.822(3)Å, β=95.58(3), V=2677.8Å^3, Z=4. The structure was refined by least-squares and the value of R was 0.040.

Our results reported here differ significantly from those previously reported of different coordination geometry. Here the crystal structure contains discrete $(Cu(C_{14}O_5H_{20})(H_2O)_2$ ion, ClO_4 anions and H_2O molecules. There is hydrogen bonding between coordination H_2O and crystal H_2O. The angle between the benzo plane and ether plane is 29.0°. The Cu(II) ion almost sits in the center of the ether oxygens and is coordinated with the oxygens of two H_2O molecules. This is a new transition-metal-crown complex with a coordination number of seven.

1. Lehn, J.M., M.R. Truter, et al., *Struct. Bonding*, *16*, 1, 1973.
2. Bereman, R.D., J.R. Wasson, and S.N. Choi, *J. Inorg. Nucl. Chem.*, *37*, 2087, 1975.
3. Izatt, R.M., *J. Am. Chem. Soc.*, *98*, 7626, 1976.
4. Mukai, K., T. Yano, and K. Ishizu, *Tetrahedron Lett.* *46*, 4661, 1981.
5. Holt, E.M., *Acta Crystal., Sec. B*, *37*, 1060, 1981.

THE INFLUENCE OF CROWN ETHERS AND CRYPTS ON THE FORMATION OF Au^- IN NON-AQUEOUS SOLVENTS

David B. Wallace, R. Jagannathan and J.J. Lagowski

Department of Chemistry, The University of Texas, Austin, Texas, U.S.A., 78712

Crown ethers and cryptands assist the dissolution of alkali metals in amines and ethers to produce solvated electrons and metal anions. The reaction of solvated electrons with gold metals to produce Au^- has been performed in various solvents, e.g., methylamine, ethylamine, ethylenediamine, THF, glyme. The characterization of the Au^- species by its ultraviolet charge transfer to solvent (CTTS) spectrum will be presented.

Au^- can also be obtained in some of the above solvents electrochemically using cryptated alkali metal trifolates as supporting electrolytes. The cyclic voltammetry of such solutions reveals the peak potentials for oxidation of Au^- and reduction of Au.

Attempts to find a cosolvent for the precipitation of a complexed amide salt from the stable CS/Au/18-crown-6 ammonia solutions will be discussed.

TUp27-5

SYNTHESIS AND CHARACTERIZATION OF SOME METAL MACROCYCLE COMPLEXES

C. Martinez, R. Jagannathan, J.N. Ramsden and J.J. Lagowski

Department of Chemistry, The University of Texas, Austin, Texas, U.S.A., 78712

Complexes of cryptands (C_{22}, C_{21}, C_{222}, C_{221}), cyclam, tetramethylcyclam, 1,10, dithio-18-crown-6 with a series of metal ions, e.g., Cr, Mn, Cu, Ag, Zn, Cd, Hg have been prepared and characterized. The nature of the binding of the ligand to the metal ion has been investigated using IR and NMR (^{13}C and ^{14}C) spectroscopy. The electrochemistry of these complexes in non-aqueous solvents (CH_3CN, CH_2Cl_2, SO_2) is discussed in terms of unusual oxidation states.

Attempts to prepare gold complexes of macrocyclic ligands as precursors for electrochemical generation of Au^- in non-aqueous solvents are described.

BIOINORGANIC ASPECTS OF ALKALI AND ALKALINE EARTH CATIONS – X-RAY STRUCTURAL ANALYSIS OF Na(picrate)(benzo-15-crown-5)

N.S. Poonia

Chemistry Department, University of Indore, Khandwa Road, Indore 452001, India

D.L. Ward and A.I. Popov

Chemistry Department, Michigan State University, East Lansing, MI 48824, USA

With the ultimate aim to throw light on the chemical principles related to the discrimination between Na and K, and Mg and Ca ions in biological systems we have undertaken the X-ray crystallographic investigations of a long list of related (cation)(anion)(B15C5)$_n$ (B15C5 = benzo-15-crown-5) systems so as to follow the anion/ligand preferences of the different cations under common conditions. In the present report we discuss the structural aspects of Na(Pic)(B15C5) (where pic is picrate) vis-a-vis those of the other (cation)(pic)(B15C5)$_n$ systems studied by us.

Na(pic)(B15C5) has been found to be an anion-paired 1:1 complex wherein the crown chelates through all the five oxygens (Na-O, 2.40 to 2.50 A) and pic acts as a bidentate through phenoxide (Na-O$^-$, 2.35 A) and an ortho-nitro oxygen (Na-ONO, 2.51 A). The Ca(pic)(B15C5) system, interestingly, presents also a comparable picture instead of the expected sandwich, with the only additional feature in that the cation becomes chelated through the para-nitro function of the pic belonging to the adjacent molecule of the complex in the lattice. The Lewis acid status of Na will be discussed along with that of the other cations to explain the results.

TUp27-7

THE EFFECT OF SOLVENT ON METAL ION FLUX THROUGH MACROCYCLE MEDIATED MEMBRANES.

Reed M. Izatt, Don W. McBride, Jr., Philip R. Brown, and James J. Christensen

Brigham Young University, Provo, Utah 84602

We have incorporated various parameters associated with the macrocycle-mediated flux of metal ions through liquid membranes into a mathematical model of the transport process.[1-3] Four of these parameters, the partition coefficient of the species present, log K for metal ion-macrocycle interaction, the diffusivity of the various species and the thickness of the unstirred boundary layers, are affected directly by the solvent used to form the membrane. We have conducted transport experiments using several halocarbon solvents so that the physical characteristics of the solvents can be analyzed in relation to flux rates.

Dicyclohexano-18-crown-6 was used to mediate the flux of sodium, potassium, rubidium, cesium, calcium, strontium, and barium through membranes made of dichloromethane, trichloromethane, tetrachloromethane, 1,2-dichloroethane, 1,1,2-trichloroethane, and 1,1,2,2-tetrachloroethane. The relative flux rates for these membranes were found to have distinctive patterns for monovalent and divalent cations. The flux rates have been compared with various physical properties of the solvents to examine possible correlations between these properties and the flux of the metal ions.

1. J.D. Lamb, J.J. Christensen, J.L. Oscarson, B.L. Nielsen, B.W. Asay, and R.M. Izatt, J. Am. Chem. Soc., 102, 6820-6824 (1980).

2. J.J. Christensen, J.D. Lamb, P.R. Brown, J.L. Oscarson, and R.M. Izatt, Sep. Sci. Technol., 16, 1193-1215 (1981).

3. D.W. McBride, Jr., R.M. Izatt, J.D. Lamb, and J.J. Christensen, in Inclusion Compounds, J.L. Atwood, J.E.D. Davies, and D.D. MacNicol, eds., Academic Press, in press.

MACROCYCLE-MEDIATED CATION TRANSPORT FROM METAL ION MIXTURES USING A TOLUENE EMULSION MEMBRANE SYSTEM

Reed M. Izatt, David V. Dearden, Evan R. Witt, Don W. McBride, Jr., and James J. Christensen

Brigham Young University, 204 ESC, Provo, Utah, U.S.A. 84602

Metal separations from various mixtures of alkali metal, alkaline earth metal, Cu^{2+}, Zn^{2+}, Ag^{+}, Tl^{+}, and Pb^{2+} nitrates were studied in an emulsion membrane system similar to that described earlier.[1-4] The membrane consisted of a water in oil emulsion composed of 0.050 M $Li_4P_2O_7$ in H_2O and 0.020 M dicyclohexano-18-crown-6 (DC18C6) in toluene with sorbitan monooleate serving as surfactant. The emulsion was placed into an aqueous source phase solution of the metal nitrates of interest. Of the cations studied, Pb^{2+} was transported most rapidly and selectively. The selectivity of the system for particular cations is governed by the relative M^{n+}-DC18C6 and M^{n+}-$P_2O_7^{4-}$ complex stabilities. Formation of a sufficiently stable M^{n+}-DC18C6 complex is necessary to partition cations into the toluene membrane, and formation of a more stable M^{n+}-$P_2O_7^{4-}$ complex is necessary to strip cations from the membrane into the receiving phase.

1. M.P. Biehl, R.M. Izatt, J.D. Lamb, and J.J. Christensen, Sep. Sci. Technol., 17, 289-294 (1982).

2. R.M. Izatt, M.P. Biehl, J.D. Lamb, and J.J. Christensen, Sep. Sci. Technol., 17, 1351-1360 (1982).

3. J.J. Christensen, S.P. Christensen, M.P. Biehl, S.A. Lowe, J.D. Lamb, and R.M. Izatt, Sep. Sci. Technol., 18, 363-373 (1983).

4. R.M. Izatt, D.V. Dearden, D.W. McBride, Jr., J.L. Oscarson, J.D. Lamb, and J.J. Christensen, Sep. Sci. Technol., in press.

ELECTROSTATIC AND REDOX EFFECTS IN AQUEOUS COMPLEX IONS WITH CHARGED SIDE GROUPS

George I.H. Hanania
American University of Beirut, Beirut, Lebanon.

Complex ions containing ligands with acidic side groups provide convenient models for the study of intramolecular charge effects. Two aspects to consider are: the effect of coordination to the metal on the acid strength of ionizing side groups, and the thermodynamically corresponding effect of side group ionizations on the redox properties of complex ions. Systems that we have investigated include the iron, and some copper, complexes of N-coordinating heterocyclic ligands, as well as the imidazole complex of ferrimyoglobin and cobalt derivatives of vitamin B_{12}.

The acid dissociation data show very marked increase in the acid strength of side groups resulting from coordination of the ligand to a central cation. The effect is characterized by two main features: it is essentially an enthalpy effect, the entropy of ionization being substantially the same in the free ligand as in the complex; and it is cumulative, in that its magnitude depends on the electrostatic charge of the metal, and on the extent of enhanced stabilization, through electron delocalization, of the conjugate base of the group in the complex.

The pH variation of reduction potentials for iron(III-II) systems of the above type gives a measure of the difference in free energy of ionization of acidic side groups in oxidant and reductant ions, which is itself the cumulative effect of electronic and electrostatic factors. The latter factor can be theoretically evaluated by applying the Tanford-Kirkwood model of intramolecular electrostatic interactions, as modified by Shire, Hanania & Gurd (Biochemistry, 13, 2967 (1974)), for calculations on globular proteins. This discrete-charge model enables the computation of electrostatic contributions to the observed pH variation of reduction potential at given ionic strength and temperature. From these results, the electronic contribution can then be assessed.

We have recently extended the above treatment to three types of N-coordinating ligands: hydroxy-1,10-phenanthrolines, 2-pyridinealdoxime and 2,6-pyridinedialdoxime, and 2,2'-pyridylimidazoline, the last being a less strongly conjugated system than the others. The results of reduction potential measurements and electrostatic calculations show that the electronic factor is dominant in complex ions where the ligand is highly conjugated. Electrostatic differences which appear among the various complexes can be interpretated in terms of the number and position of ionizing side groups, as well as the degree of electron delocalization involved.

TUp28-01

"METAL-LIKE" MOLECULAR ASSEMBLIES COMPOSED OF COFACIAL METALLOMACROCYCLES. CHEMICAL AND PHYSICAL STUDIES

Tobin J. Marks

Department of Chemistry, Northwestern University, Evanston, Illinois 60201 USA

This lecture outlines an efficacious approach to the control of molecular stacking interactions in low-dimensional mixed valence materials by locking partially oxidized metallomacrocycles together in a face-to-face orientaton. For example, doping of the cofacially joined polymers $[M(Mac)O]_n$ (M = Si,Ge,Sn; Mac = macrocycle such as phthalocyanine) with halogen (I_2,Br_2), nitrosyl ($NOBF_4$, $NOPF_6$, $NOSbF_6$), or high-potential quinoid (TCNQ, DDQ) electron acceptors, or employing anodic electrochemical techniques, results in a broad family of robust, soluble, environmentally stable, electrically conductive macromolecules with a substantial range of "tunable" chemical and physical characteristics. The new materials have been characterized by a battery of physical techniques, including X-ray diffraction, EPR, static magnetic susceptibility, solid state NMR, specular reflectance, transmission ir and optical spectroscopy, photoacoustic Raman, Hall effect, thermoelectric power, and variable temperature four-probe dc electrical conductivity. What is emerging is an intriguing picture of how tight-binding conduction bandwidth and optical, magnetic, and charge transport collective phenomena are intimately connected with the architecture of the metallomacrocyclic assembly, the identity of lattice guests, and the degree of partial oxidation.

In related work, we describe several new approaches to the synthesis of macromolecular/macromolecular and molecular/macromolecular hybrid "alloys." These metallomacrocycle-based materials can be fabricated into strong, flexible, oriented, environmentally stable, electrically conductive films and fibers.

TUp28-02

ELECTROCHEMICAL POLYMERIZATION, ELECTRON TRANSFER CHEMISTRY, AND ELECTROCHEMISTRY OF VINYL SUBSTITUTED RU AND OS POLY-PYRIDINES

C. R. Leidner, P. G. Pickup, W. Kutner, K. Wilbourn, & Royce W. Murray

University of North Carolina at Chapel Hill, Department of Chemistry, 17-21 Venable Hall, 045A, Chapel Hill, NC 27514

Abstract

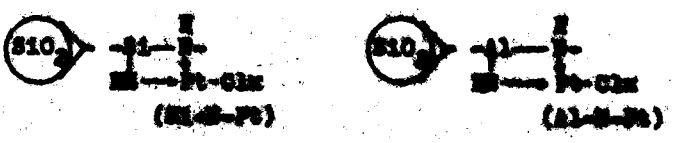
Electrochemical reduction of vinyl-substituted Ru or Os polypyridine complexes in aprotic media leads to polymerization-coupling reactions between the complexes. Under appropriate conditions, adherent, insoluble, electrochemically reactive films coat the electrodes used for the polymerization reduction. These films are useful models for investigation of electron transfer self-exchange reaction kinetics in polymeric media, where the kinetics are conceivably limited by intrinsic electron transfer barriers, polymer microdynamic motions, or charge compensating counterions diffusion. The films have also been employed for electron transfer cross-reaction kinetic studies with analogous complexes in the solution, where kinetics of polymer-solution reactions thermodynamically unfavorable by as much as 0.5 V have proven measurable. The films are, furthermore, useful for studies of spatially organized electron transport rates in bilayers and sandwich electrodes. Under appropriate conditions in the electrochemical polymerization, soluble oligomers can also be formed in the electrochemical cells, which are useful in investigating the polymerization reaction chemistry.

INORGANIC POLYMER-PLATINUM COMPLEX CATALYSTS FOR OXIDATION AND HYDROGENATION

Mei-Yu Huang, Chang-Yu Ren, You-Xue Yuan and Ying-Yan Jiang

Institute of Chemistry, Academia Sinica, Zhongguancun, Peking 100080 China

Two silica-supported inorganic polymer-platinum complexes: silica-supported polysiloxane-platinum complex (abbreviated as Si-O-Pt) and silica-supported polyaluminoxane-platinum complex (Al-O-Pt) have been prepared.



(Si-O-Pt) (Al-O-Pt)

Si-O-Pt has been found to catalyze the oxidation of isopropanol to acetone and phenol to benzoquinone in 90 % yields respectively at room temperature under an atmospheric oxygen pressure.

Al-O-Pt has been found to catalyze the hydrogenation of aromatic rings as benzene and phenol to cyclohexane and cyclohexanol, and hydrogenation of propanal to propanol-1 in 100 % yields respectively at room temperature under an atmospheric pressure of oxygen.

Si-O-Pt and Al-O-Pt are more active than any other catalysts reported before for the oxidation of alcohols, and the catalysis of Al-O-Pt for the hydrogenation of aromatics are similar to those of alkane-supported polymer-platinum complexes.

Since the supports are very stable inorganic oxides, the catalysts can be prepared directly from without any expensive loss of the catalytic activities.

In general, all polymer ligands in polymer-metal complex catalysts are organic and easily oxidized in the catalytic process, but the polymer ligands of Si-O-Pt and Al-O-Pt are inorganic and very stable in the catalytic processes.

(1) Y.-Y.Jiang, Y.-Z. Wang and Y.-T.Jiang, J. Mol. Catal., 1985, 29, 85.

INORGANIC POLYMERS AS CHEMICAL DERIVATIZATION AGENTS OF OXIDATIVELY UNSTABLE METAL ELECTRODES: THE NICKEL ELECTRODE

Andrew B. Bocarsly, Sujit Sinha, and Brian D. Humphrey

Princeton University, Department of Chemistry, Frick Laboratory, Princeton, New Jersey 08544 - USA

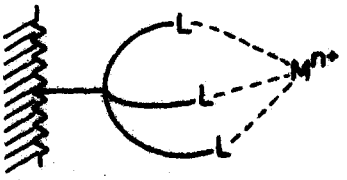
Anionic metallocyanide complexes of the form $[M(CN)_{6-x}L_x]^{n-}$ (M=Fe,Ru,Mn) (L=H_2O,NO,CN, Histidine, 2,2' bipyridine, 1,2-cyclohexyldiamine) can be immobilized on Ni electrodes by potentiostating the electrode in aqueous solutions of the anions. The surface coverage obtained is shown to be a function of composition of derivatizing solution, nickel surface pretreatment, electrode potential, and the reaction time. Diffuse reflectance (FTIR and U.V.-visible) spectra of derivatized Ni surfaces show a cyano bridged bimetallic structure indicative of a Ni^{2+} substituted prussian blue like polymer. The cyclic voltammogram of surface immobilized $M(CN)_6^{-3}$(M=Fe,Ru) shows close to ideal electrochemical behavior. These surfaces are very stable with ~10% loss on > 18,000 potential cycles between Fe^{II} and Fe^{III} state. The $E_{\frac{1}{2}}$ value and the shape of the surface cyclic voltammetric wave are shown to depend strongly on the supporting electrolyte cation. Further, these coatings show a cation selectivity, indicating an ordered structure. Such surface layers stabilize the Ni electrode surface against oxide formation while allowing various solution redox couples to react at the electrode. Thus, both reaction specificity and in certain cases electrocatalytic behavior can be induced by this type of derivatization.

IMIDAZOLES AND PYRAZOLES ON POLYMERS: NEW ROUTES TO SELECTIVE ION-EXCHANGE RESINS

Suresh K. Sahni, Willem L. Driessen and Jan Reedijk

Department of Chemistry, State University Leiden, Gorlaeus Laboratories, P.O. Box 9502, 2300 RA Leiden, the Netherlands

The development of new economic and efficient methods to trap toxic and precious metals has increased recently. The low degree of selectivity, large loss of material and limited possibility of recycling, associated with the more commonly used methods of conventional ion-exchange resins and solvent extraction involving the use of chelating ligands are responsible for this. Chelating ion-exchange resins, offering many advantages over the existing methods, appear to be better tools to deal with these problems of depleting resources of precious metals and increasing pollution of environment with toxic metal ions. The ligating behaviour of several multidentate imidazole and pyrazole derivatives towards transition metal ions has been studied in detail, in recent years. In view of their versatile chelating properties and marked ability to bind certain metal ions strongly, several of such ligands have been anchored onto cross-linked styrene-divinylbenzene copolymers to evaluate their selective ion-exchange characteristics. New synthetic routes have been developed to obtain chelating ion-exchange resins devoid of possible inter- and intra-strand cross-linkings and having varied degree of steric constraints, contributing to their high capacity and selectivity, respectively.



Schematic structure of a metal chelated by a polymeric ligand. L = pyrazole, imidazole or related ligand.

The so-developed chelating ion-exchange resins and their metal complexes (studied both in aqueous and non-aqueous media) have been characterised on the basis of their analytical properties and by means of spectral (infrared, ligand field and epr) methods in conjunction with their elemental analysis. An attempt has been made to develop a possible relationship between the selectivity of chelating ion-exchange resins and geometry of their metal complexes and the role played by the steric factors has also been evaluated. The chelating resins so far studied have been found to be selective for copper(II) ions in the pH range 3-7 and possess capacity which is comparable with some of the commercially available chelating ion-exchange resins.

SYNTHESIS AND PROPERTIES OF POLYNUCLEAR ARENE-METAL PI-COMPLEXES

B. Bush and J.J. Lagowski

Department of Chemistry, The University of Texas, Austin, Texas, U.S.A., 78712

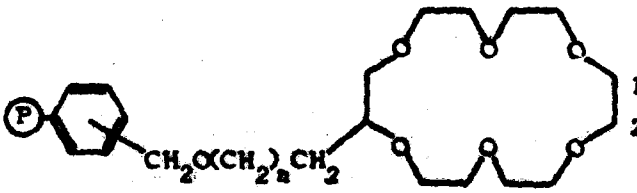
Synthetic routes for the formation of polynuclear arene-metal pi-complexes are discussed. These complexes are basically bisbenzenechromium moieties connected by groups which have exhibited a potential in other contexts to transmit electronic effects; e.g., $-SiR_2-$ and -PR-. Among the more interesting properties of these species is their ability to communicate electronic effects between the metal sites. Experimental results that address this question include electrochemical (c-v experiments) and e.s.r. measurements.

PHASE-TRANSFER CATALYTIC ACTIVITY OF CROWN-ETHERS BONDED TO A POLYSTYRENE MATRIX

Pier Lucio Anelli, Fernando Montanari and Silvio Quici

Centro C.N.R. and Istituto di Chimica Industriale dell'Universita', Via C. Golgi 19, 20133 Milano, Italy

Polymer-supported crown-ethers 1a-d and 2a-d (4.5-62% ring substitution) have been obtained by reaction of 1% cross-linked chloromethylated polystyrenes with (hydroxymethyl) and (ω-hydroxynonyl)-18-crown-6, respectively.



1a-d n = 0
2a-d n = 8

Their phase-transfer catalytic activity has been tested in anion promoted nucleophilic aliphatic substitutions (eq. 1), and compared with that of structurally similar soluble crown-ethers, and of polymer-supported and soluble phosphonium salts.

$$n\text{-}C_8H_{17}OMes + Y^- \longrightarrow n\text{-}C_8H_{17}Y + MesO^- \qquad \text{(eq. 1)}$$

Y = I, Br, CN, SCN.

The results indicate that catalytic activity of 1a-d and 2a-d strongly depends on the combination of three parameters: the nature of nucleophile, the pernant ring substitution, and the presence of a spacer chain.

As for the related quaternary salts, phase-transfer reactions promoted by polymer-supported crown-ethers follow a mechanism identical with that observed for soluble catalysts: the reactions occur in the organic shell surrounding a complexed crown-ether; anions are exchanged at the water-organic solvent interface, the exchange not requiring the concomitant transfer of cationic counterparts.

DETERMINATION OF THE SOLUTION STRUCTURE OF Cr^{3+} AND Mo^{3+} COMPLEXES BY ^2H NMR SPECTROSCOPY

J. Ivan Legg, Robert J. Bianchini, Charles A. Green, Sumio Kaizaki,* Norio Koine+ and W. Douglas Wheeler

Wash. State Univ., Dept. of Chemistry, Pullman, WA 99164; *Nara Women's Univ., Nara 630, Japan; +Ehime Univ., Ehime 790, Japan

It is not uncommon to hear or read statements about the inability to do NMR studies on Cr^{3+} systems. In a recent chapter on organochromium(III) complexes Espenson wrote, "Most of the methods used to detect CrR^{2+} and to follow its reactions are based on UV-visible spectrophotometry. It has played a much more prominent role in the experimental studies than in many organometallic systems owing to the paramagnetism of these complexes which have three unpaired electrons and are thus not amenable to study by nmr techniques."[1] The long electron-spin relaxation times associated with Cr^{3+} cause extreme broadening of the ^1H NMR resonances.[2]

However, we have recently demonstrated that ^2H NMR is an effective probe of Cr^{3+} stereochemistry. We have found that in comparison to ^1H NMR spectra, much narrower (by a factor of ~30) and better resolved resonance signals are observed when ^2H NMR spectra are obtained for Cr^{3+} complexes. For example, we have shown that ^2H NMR will resolve geminal deuterons on a chelate ring.[3]

A comprehensive study of multidentate amine-carboxylate and amino acid complexes has been initiated to determine the potential of ^2H NMR as a structural probe. Stereospecifically deuterated ligands have been synthesized by reported procedures.[4] We have found that some previously accepted solution structures which form the basis of extensive studies are most likely incorrect. For example, we have found that between pH 3.5 and pH 6.5 Cr(edta)$^-$ is sexadentate, a structure not currently widely accepted. We have also demonstrated that ^2H NMR can be used to effectively probe the structure of Mo^{3+} complexes. These exploratory studies suggest that ^2H NMR will be of considerable value to many investigations involving Cr^{3+} and Mo^{3+} chemistry.

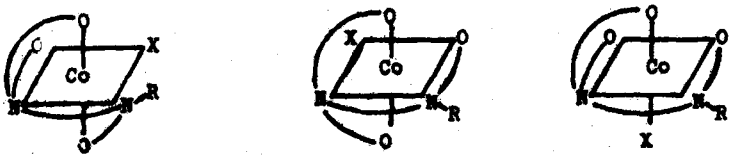
1. Espenson, J.H. In "Advances in Inorganic and Bioinorganic Mechanisms;" Sykes, A.G., Ed.; Academic Press: New York and London, 1982; p. 4.
2. Holm, R.H.; Hawkins, C.J. In "NMR of Paramagnetic Molecules;" La Mar, G.N.; Horrocks, W. DeW., Jr.; Holm, R.H., Eds.; Academic Press: New York and London, 1973; Chapt. 8, pp. 243-286.
3. Wheeler, W.D.; Kaizaki, S.; Legg, J.I. Inorg. Chem. 1982, 21, 3248.
4. Kapus, W.E.; Legg, J.I. J.Am.Chem.Soc. 1976, 98, 4970 and references therein.

THE STEREOCHEMISTRY OF COBALT(III) COMPLEXES OF ed3a AND SUBSTITUTED ed3a USING NMR SPECTROSCOPY

Shunji Utsuno[1], Chris Maricondi, Dusan J. Radanović[2], S. R. Trifunovic[2], and Bodie Douglas

Department of Chemistry, University of Pittsburgh, Pittsburgh, PA, 15260, USA

Ethylenediamine-N,N',N'-triacetic acid, ed3a, is a quinquedentate ligand that can form three isomeric Co(III) complexes with the 6th position occupied by a unidentate ligand such as H_2O, NO_2^- or CN^-.



cis-equatorial trans-equatorial cis-polar

Which isomer results depends upon the substituent on the secondary donor nitrogen and the ligand in the 6th position. Generally, when R = alkyl only the cis-equatorial isomer forms in any abundance and when R = H both the cis-equatorial and the trans-equatorial can be isolated. So far the only cis-polar isomer reported has been the one with R = $-CH_2COOH$ and X = Br^-, [Co(edta)Br]. We report here the results of a study of the stereochemistry of both the cis-equatorial and the trans-equatorial isomers of ed3a with Co(III) and CN^- and the cis-equatorial isomer of N-methyl-ed3a with Co(III) and CN^-. Our results are compared with those already obtained by other groups for similar complexes with NO_2^- and H_2O in the 6th position. Notable differences are discussed in terms of the known structural parameters for the $[Co(ed3a)NO_2]^-$ ion and attributed largely to the different coordinating abilities of CN^- and NO_2^-. Neutral and acidic H_2O solutions were run and both selectively and completely decoupled spectra were recorded. The analysis of the ^{13}C spectra were facilitated to a degree by obtaining ^1H spectra beforehand which showed completely resolved AB patterns for the three different glycinate rings and partially resolved splitting patterns for the ethylenediamine backbone. Data were collected using a Bruker WH-300 NMR spectrometer.

1. Department of Chemistry, Shimane University, Shimane-Ohi 422, Japan.
2. Department of Chemistry, Svetozar Markovic University, 34000 Kragujevac, Jugoslavia.

ISOTROPIC AND ANISOTROPIC EXCHANGE INTERACTIONS BETWEEN TRANSITION METAL IONS

A. Bencini, I.S.S.E.C.C., C.N.R., Florence, Italy
C. Benelli, D. Gatteschi, C. Zanchini, University of Florence, Florence, Italy
A.C. Fabretti, G.C. Franchini, University of Modena, Modena, Italy

Isotropic exchange interactions are reasonably well understood for dinuclear copper complexes[1], but much less is known about couples of different metal ions and about tri- and tetranuclear complexes. Another field where still our understanding does not go very deep is that of anisotropic exchange.

In fact it has long been known that the anisotropic exchange term, which is present in the spin hamiltonian for couples of metal ions, is determined by the interaction between one ion in its ground state and the other ion in one of its excited states[2], but up to the present, no systematic attempt has been made to obtain reliable estimates of these interactions in series of homologous complexes. Recently we reported some results regarding di-μ-hydroxo[3] and di-μ-azido[4] bridged copper(II) complexes, in which some useful correlations were made on the electronic structure of the complexes and the principal values and directions of the zero-field splitting tensor, obtained through single crystal EPR spectroscopy.

We wish to report other data on several series of di- and tri-nuclear complexes involving copper(II) and also other ions, with a variety of bridging ligands, some of which were especially designed to provide asymmetric bridges, thus favouring the formation of heterodinuclear species. The experimental data will be discussed within the frame of existing theories, and also Xα calculations will be used in order to relate the observed isotropic and anisotropic exchange contribution to the electronic structure of the complexes.

1. D.J. Hodgson, Progr. Inorg. Chem. 1975, 19, 173; W.E. Hatfield, ACS Symp. Ser. 1975, No. 5, 108.
2. J. Kanamori "Magnetism"; G.T. Rado and H. Suhl, Eds.; Academic Press, New York, 1963; Vol. 1, p. 161.
3. L. Banci, A. Bencini and D. Gatteschi, J. Am. Chem. Soc. 1983, 105, 761.
4. L. Banci, A. Bencini and D. Gatteschi, Inorg. Chem. in press.

A TENTATIVE INTERPRETATION OF ESR SPECTRA OF THE "PLATINUM BLUES"

Philippe ARRIZABALAGA*, Paule CASTAN**, Michel GEOFFROY* and Jean-Pierre LAURENT**.

* Departement de Chimie Physique, 30 Quai Ernest Ansermet, 1211 GENEVE 4 (Suisse).

** Laboratoire de Chimie de Coordination du CNRS, 205, route de Narbonne, 31400 TOULOUSE (France).

"Platinum blues" are one of the most curious species belonging to the platinum family complexes. Indeed, independently of their unusual blue color, they exhibit paramagnetic properties in contrast to the diamagnetic behaviour of the platinum(II) and platinum(IV) complexes.

Several reports of ESR spectra appeared in the literature[1-5]. One of them[2] was related to the only monocrystalline species yet isolated and allowed the determination of the corresponding g-tensor, the hyperfine structure being only observed on the solution spectra.

We succeed in observing a well-resolved spectrum related to a powdered sample of a blue complex prepared from 1-methylhydantoin, that offers the possibility of probing various structural models. A good agreement between the experimental and the calculated spectra is obtained by assuming that the hyperfine structure would be attributed to coupling of a single electron with four ^{195}Pt nuclei involved in a tetrameric unit, the electron being delocalized over the four nuclei.

Moreover this model may be generalized to account for the spectra of all blue complexes displaying an hyperfine structure.

(1) B. LIPPERT, J. Clin. Hemat. Onc. 7, 26, 1977.

(2) J.K. BARTON, J.J. DANNA, H.N. RABINOWITZ, J.V. WASZCZAK and S.J. LIPPARD, J. Amer. Chem. Soc., 101, 1434, 1979.

(3) J.K. BARTON, C. CARAVANA and S.J. LIPPARD, J. Amer. Chem. Soc., 101, 7269, 1979.

(4) M. SEUL, H. NEUBACHER and W. LORMANN, Z. Naturforsch. 36b, 272, 1980.

(5) J.P. LAURENT, P. LEPAGE, P. CASTAN and P. ARRIZABALAGA, Inorg. Chim. Acta, 67, 31, 1982.

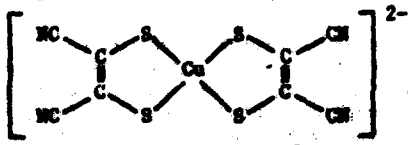
SINGLE-CRYSTAL ^{13}C ENDOR AND TRIPLE RESONANCE ON BIS(MALEONITRILEDITHIOLATO)CUPRATE(II), $Cu(mnt)_2^{2-}$

R. Kirmse, J. Stach, U. Abram, R. Böttcher*, M. Gribnau** and C.P. Keijzers**

Departments of Chemistry and Physics*, Karl-Marx-University, 7010 Leipzig, Liebigstrasse 18, GDR
Department of Molecular Spectroscopy**, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands

Dithiolene complexes attracted much interest because of their interesting bonding properties: highly covalent metal-ligand bonds have been found. Ligand hyperfine interactions provide direct information about delocalization of unpaired spin density over the ligand orbitals. However, ^{33}S interactions have been observed only in a few cases because of the very low natural abundance of ^{33}S (the isotope with a non-zero nuclear spin).

We report the ^{13}C (and ^{1}H) ENDOR spectra of $Cu(mnt)_2^{2-}$



doped into $Ni(mnt)_2^{2-}$ and $Zn(mnt)_2^{2-}$, which have totally different structures: the arrangement of the NiS_4 unit is almost planar, that of ZnS_4 is close to tetrahedral[1]. Interestingly, the isotropic parts of the ^{13}C couplings of the CN groups are larger than those of the C=C carbons. For $Cu/Ni(mnt)_2^{2-}$ these couplings are calculated, including all two- and three-centre contributions, and the importance of these multicentre contributions will be shown. The signs of A^C were determined by TRIPLE resonance (C=C is "-", C-N is "+") and appear to be of key importance for the calculated results. The C=C carbons are found to lie almost in a nodal plane of the MO of the unpaired electron, which explains the negative sign. The influence of the different symmetries of the host complexes on the spin hamiltonian parameters will be discussed.

1. The $Zn(mnt)_2^{2-}$ structure was solved by J. Stelzer (K.M.U. Leipzig).

EPR STUDIES ON PAIRS OF JAHN-TELLER DISTORTED HEXAKIS-PYRIDINE-N-OXIDE COPPER(II), $Cu(C_5H_5NO)_6^{2+}$, IONS

C.P. Keijzers, E. de Boer and J.S. Wood*

Department of Molecular Spectroscopy, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands
Department of Chemistry*, University of Massachusetts, Amherst, Mass 01003, USA

The hexakis-pyridine-N-oxide metal(II) complexes, $M(pyO)_6X_2$, with $X^- = ClO_4^-$, BF_4^- or NO_3^- and M^{2+} a transition metal ion (Mn to Zn) are a class of isomorphous compounds (space group $R\bar{3}$). The copper complexes have been studied in the pure as well as in a dilute form, doped into the zinc host. The reason for this interest is the Jahn-Teller (JT) activity of the complex ion, in which the CuO_6 moiety forms a nearly perfect octahedron. This leads to static distortions at low temperatures (≤ 60 K), i.e. tetragonal elongations of the octahedra[1]. One might anticipate a random orientation of nearest neighbour (n.n.) complexes but this is not the case. The BF_4^- complex turns out to be *ferrodistortive*, i.e. all axes of elongation are parallel, whereas the ClO_4^- and NO_3^- salts are *antiferrodistortive*, i.e. the axes of elongation of n.n. ions are mutually orthogonal. The change of magnetic properties on passing the JT phase transition is quite striking. In the BF_4^- case it leads to two-dimensional antiferromagnetism, and in the ClO_4^- and NO_3^- cases to pseudo-one-dimensional antiferromagnetic behaviour[2,3]. These properties are explained by the structural ordering of the elongated octahedra[1]. In order to elucidate the nature of the coupling between two neighbouring $Cu(pyO)_6^{2+}$ ions, the present EPR study has been undertaken on "semi-dilute" (5-10%) ^{63}Cu:$Zn(pyO)_6X_2$ single crystals. Below the transition from dynamic to static JT distortion, pairs of $Cu(pyO)_6^{2+}$ ions are observed in all systems. In the ClO_4^- and NO_3^- salts, antiferrodistortive *and* a small amount of ferrodistortive pairs are detected. For both types of pairs all types of configurations are found, except the one with largest possible exchange interaction. The latter ferrodistortive configuration is not present in both salts whereas the antiferrodistortive configuration with maximum exchange is only just detectable in the NO_3^- salt. In the BF_4^- salt ferro- and antiferrodistortive configurations do appear with similar intensities, but also here the antiferrodistortive arrangement with maximum exchange is missing. The above conclusions could be drawn from a comparison between experimental and calculated spectra[4]. This comparison enabled also the determination of the weak exchange interactions in the ferrodistortive pairs.

1. J.S. Wood, C.P. Keijzers, E. de Boer and A. Buttafava, Inorg. Chem. 1980, 19, 2213.
2. H.A. Algra, L.J. de Jongh and R.L. Carlin, Physica B, 1978, 93, 24.
3. D. Beinan and S. Krause, Solid State Commun. 1979, 29, 691.
4. G. van Kalkeren, C.P. Keijzers, R. Srinivasan, E. de Boer and J.S. Wood, Mol. Phys. 1983, 48, 1.

SOLVENT NMR RELAXATION STUDIES ON IRON(III) PORPHYRINS IN METHANOL

S.C. Chopra and R. B. Jordan

Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2G2

Proton NMR relaxation rates and chemical shifts have been measured for the solvent resonance of solutions of the trifluoromethanesulfonate salts of iron(III) protoporphyrin(IX), and iron(III) tetraphenylphorphyrin in CH_3OD in the temperature range from -60°C to +60°C. The longitudinal (R_1) and transverse (R_2) relaxation rates have been used to obtain the activation enthalpy and entropy for solvent exchange: the values for iron(III) protoporphyrin(IX) are 10.4 kcal/mol and 6.7 cal/mol/deg respectively, and for iron(III) tetraphenylporphyrin 11.3 kcal/mol and 8.5 cal/mol/deg respectively. Measurements in 50:50 and 80:20 mixtures of CD_2Cl_2:CH_3OH indicate that the solvent exchange rate is independent of the CH_3OD concentration for iron(III) protoporphyrin(IX).

It will be shown that measurements of the rotating frame relaxation rate ($R_{1\rho}$) are related to R_2, the solvent exchange rate (r_m), and the chemical shift of the coordinated solvent ($\Delta\omega_m$) by the equation

$$R_{1\rho} = R_{1\rho}^{\infty} + S_\rho^2(R_2 - R_{1\rho})\omega_1^{-2}$$

where ω_1 is the precessional frequency in the spin-locking field, $R_{1\rho}^{\infty}$ is the limiting $R_{1\rho}$ as $\omega_1 \to \infty$ and

$$S_\rho^2 = \{(R_{2m}+r_m)^2 + \Delta\omega_m^2\}(R_{1m}+r_m)/(R_{2m}+r_m).$$

The $R_{1\rho}$ - ω_1 measurements can be used to determine $\Delta\omega_m$. This value can be combined with bulk solvent chemical shift values to calculate the solvation number of the paramagnetic metal ion species. The method will be demonstrated for $Co(CH_3OD)_6^{2+}$ and $Ni(CH_3CN)_6^{2+}$, and used to determine if one or two solvent molecules are coordinated to the iron(III) porphyrins.

TUp29-8

ELECTRON-ELECTRON SPIN-SPIN INTERACTION IN COMPLEXES OF Fe(III), Ni(II), AND Mn(II) WITH NITROXYL-CONTAINING LIGANDS

Lee Fielding, K. Douglas Kiesler, Kundalika More, Jyoti S. More, Gareth R. Eaton, and Sandra S. Eaton

Departments of Chemistry, University of Denver, Denver, CO 80208 and University of Colorado at Denver, Denver CO 80202

When slowly relaxing S=1/2 transition metals interact with a nitroxyl radical on a coordinated ligand, AB patterns are observed in the EPR spectra in fluid solution[1], frozen solution[2], and in doped single crystals.[3] In this poster the interaction of nitroxyl radicals with transition metals with S>1/2 and faster relaxation times will be discussed.

The effect of Fe(III) on the EPR spectrum of a nitroxyl radical is dependent on the spin state of the Fe(III) and the bonding pathway between the iron center and the nitroxyl radical. Several examples will be discussed. The interaction between paramagnetic Ni(II) and a nitroxyl radical is strongly dependent on the coordination environment of the Ni(II). The importance of the metal relaxation time will be discussed.

When nitroxyl-containing ligands are coordinated to Mn(II) complexes of hexafluoroacetylacetonate or trifluoroacetylacetonate, resolved electron-electron coupling is observed in the fluid solution EPR spectra. The coupling constants are about an order of magnitude smaller than have been observed for copper(II) and vanadyl complexes of the same ligands. However, since interaction with an S=5/2 metal splits each nitroxyl line into a sextet while interaction with an S=1/2 metal splits each nitroxyl line into a doublet, the impact of the Mn(II) on the nitroxyl spectrum is substantial even for values of J which might be considered small for an S=1/2 metal.

The effect of intermolecular metal-nitroxyl collision interactions on the nitroxyl EPR spectra will also be discussed.

1. S.S. Eaton, K.M. More, G.R. Eaton, Can. J. Chem. 1982, 60, 1392 and references therein.

2. S.S. Eaton, K.M. More, B.M. Sawant, P.M. Bagnal, and G.R. Eaton, J. Magn. Reson. 1983, 52, 435.

3. R. Ramasseul, K.M. More, G.R. Eaton, and S.S. Eaton, J. Am. Chem. Soc. 1983, 105, 5147.

MULTIFREQUENCY EPR SPECTROSCOPIC STUDY OF SITE STRUCTURE AT METAL CENTERS

R. Linn Belford and Mark J. Nilges

University of Illinois, Schools of Chemical and Medical Sciences, 505 South Mathews ave., Urbana, Illinois, USA 61801

By varying frequency and thus magnetic field one to two orders of magnitude, one can drastically change the relative importance of Zeeman (electronic and nuclear) terms with respect to field-independent (exchange, hyperfine, zero-field splitting, nuclear quadrupole) terms in the spin Hamiltonian. By so doing, one can suppress or amplify certain transitions, optimize resolution, detect noncoincident orientations among principal axes of the various coupling matrices at a metal site, and eliminate confusion caused by overlapping lines. Frequencies from 1 to 300 GHz are feasible. The use of another experimental variable, orientation of the oscillating magnetic field, allows further control over relative intensities of the various spectral transitions. These experimental variables provide especially powerful aids to the interpretation of EPR spectra of powders, glasses, and frozen solutions.

Examples of use of frequency variation and oscillating-field direction variation to study structure at a variety of metal sites are shown. The metals include Cu, Mo, Co, Mn, Ru, and Ni. Systems range from inorganic polyions to aqueous solutions of metal-complexed antibiotics.

The authors thank several collaborators, including J. S. Hyde of the National Biomedical ESR Center, Milwaukee (National Institutes of Health 5-P41-RR01008) for valuable contributions and the National Science Foundation for support.

SUPER HYPERFINE STRUCTURE FROM HALOGEN ATOMS IN MIXEDLIGAND COPPER (II) COMPLEXES

Protr M. Soloshenkin, Alexander V. Ivanov, Nikolay I. Kopitsya and Philipp A. Shvengler

V.I.Nikitin Institute of Chemistry, Tajik Academy of Sciences, Ainy - 299, Dushanbe, Tajik SSR, USSR, 734063

Mixedligand halogen-containing complexes, which have covalent bonds copper - halogen: Cu-Cl; Cu-Br; Cu-I, were obtained by oxidising dissolving of metallic copper in the halogen-containing solvents medium in presence of some nitro- and sulphurchemicals with successive addition of the derivatives of sulphhydrilic reagents into the reaction mixture.

For synthesis of the complexes the following reagents were used: O-butyl-N-methylthionocarbamate (BMTC); N,N-hexamethylene-N'-phenylthiourea (PhTU); 2,9-dimethyl-1,10-phenantroline (Phen); tetraethylthiuramdisulphide $(DTC)_2$; bis-(diethyldiselenocarbamate) $(DSC)_2$ and others.

The comparative analyses of the ESR spectra and observation of the super hiperfine structure from nuclei of nitrogen, phosphorus, chlorine, bromine and iodine atoms enabled us to find the composition and structure of the complexes formed, as well as evaluate the spin density of halogen atoms on ns- and np-orbitals includingly. It was found out, that there are ~10,5 % of spin density on chlorine atoms; ~11,4 % on bromine atoms and ~12,0 % on iodine atoms. σ-atomic orbital of halogen atoms consists of ~5,5 % on ns-orbital and of~94,5 % on np-orbital.

Bonds copper - halogen with the increase of covalent are in following line: Cu-Cl; Cu-Br; Cu-I.

THE DESIGN OF METAL COMPLEXES AS CHEMOTHERAPEUTIC AGENTS

Peter J. Sadler
Department of Chemistry, Birkbeck College, University of London, Malet Street, London WC1E 7HX

A survey of the Periodic Table will be made to identify areas where coordination chemistry is likely to be of particular future interest in chemotherapy. The design features which can be incorporated into complexes will be discussed.

These features will be illustrated with reference to anticancer and gold antiarthritic drugs. Examples from our own work will include, for platinum, dynamic processes on coordinated ligands, unusual ring closure reactions, isomerizations, steric interactions, enhancement of amine displacement and the incorporation of additional redox centres in ligands for radiosensitization work. For gold we have studied the reactivity of gold thiolate clusters and phosphine transfer reactions outside and inside cells. Methods for enhancing the stability of Au(III) and unusual stereochemistries of Au(I) have emerged.

Multinuclear NMR mapping approaches have been particularly informative, and often allow the direct observation of coordination chemistry in intact biological media.

TUp30-1

METAL COMPLEXES WITH POTENTIAL DIAGNOSTIC AND SPECIFIC ANTI-TUMOR ACTIVITY

Michael Cais, Dori Zwickel and Tamar Kimel

Department of Chemistry, Technion - Israel Institute of Technology, Technion City, Haifa, Israel 32000

Estrogens are taken up selectively and retained by estrogen target tissues and certain tumors derived from these tissues, by virtue of their high affinity binding to the estrogen receptors present in these tissues. Because of this selective, receptor-mediated uptake, an estrogen could be used as a carrier for targeting chemotherapeutic anti-tumor metal complexes such as cis-Pt(II) derivatives.

This concept formed the basis of our studies which led, inter alia, to the development of a new diagnostic system designated METALLOIMMUNOASSAY (MIA)[1] and new liquid-liquid and solid-liquid separation techniques for non-centrifugation immunoassay procedures[2].

Studies on the antigenicity of metalloheptens in metalloimmunoassays indicated that immunorecognition by appropriate anti-estrogen antisera for mercurated estrogens was retained to a reasonable degree, despite the stereoelectronic effects of the substituents. In vivo studies with rats indicated that ^{203}Hg-labelled estradiol was preferentially accumulated in mammary tumors compared to healthy mammary glands[3]. These results provided the incentive to synthesize estrogen derivatives bearing the cis-Pt(II) moiety. In preliminary results we have encountered solubility problems with Pt- labelled estradiol derivatives and work currently in progress is aimed at overcoming these difficulties.

1. M. Cais, Methods in Enzym., 1983, 92, 445
2. M. Cais, Methods in Enzym., 1983, 92, 336
3. J. Shani, L.M. Lieberman, A. Sammi, T. Schlesinger and M. Cais, Int. J. Nucl. Med. Biol., 1982, 9, 251

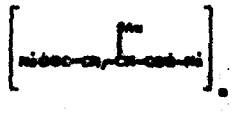
ADVANCES IN CHRYSOTHERAPY (GOLD CONTAINING THERAPEUTIC AGENTS)

Blaine M. Sutton, Deborah L. Bryan, Judith C. Hempel, Gerald R. Girard and David T. Hill

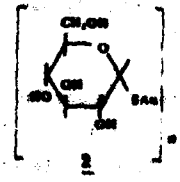
Medicinal Chemistry Department, Smith Kline and French Laboratories, P.O. Box 7929, Philadelphia, Pa. 19101

Gold has been used in medicine since antiquity. However, use of gold(I) coordination compounds for the treatment of rheumatoid arthritis (RA) has evolved in modern medicine as the most successful application of chrysotherapy (treatment with gold compounds). Gold(I) compounds have been accepted as first line disease modifying drugs for treatment of RA since 1960; specifically, disodium aurothiomalate (Myochrysine, 1), aurothioglucose (Solganal, 2), sodium 3-aurothio-2-propanolsulfonate (Allochrysine, 3). These agents must be administered by injection in order to be effective therapeutically. Auranofin, [(2,3,4,6-tetra-O-acetyl-1-thio-β-D-glucopyranosato-S)(triethylphosphine)gold(I), 4] is a new chrysotherapeutic agent effective in the treatment of RA when administered orally. Although the antiarthritic gold drugs are all gold(I) thiolates, the biological profile of orally administered auranofin differs from that of the injectables. Oral administration allows a lower gold level dosage regimen which promises safety and provides convenience benefits over injectable agents.

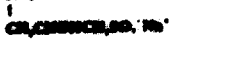
Since transition metal complexes are in dynamic equilibrium in the biological milieu, investigations of the metabolism, site and mechanisms of action of these agents are complicated. Nevertheless a variety of physical and spectroscopic methods have provided information about the structure, gold oxidation state, coordination number and ligand exchange properties of gold containing biological agents. Results which relate to the biology of chrysotherapeutic drugs will be highlighted.



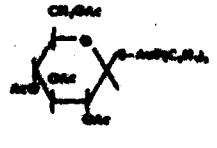
1



2



3



4

SYNTHESIS AND CHARACTERIZATION OF PHOSPHITE AND PHOSPHONITE COMPLEXES OF TECHNETIUM(I)

Dennis W. Wester, David H. White, Fred W. Miller and Richard T. Dean

Medical Products Group, Mallinckrodt, Inc., 675 McDonnell Blvd., St. Louis, MO 63134

John A. Schreifels and Alan F. Berndt

Chemistry Department, University of Missouri - St. Louis, St. Louis, MO 63121

Jerry E. Bunt

Chemistry Division, Argonne National Laboratory, Argonne, IL 60439

Phosphite complexes of transition metals have received much attention in recent years due to their application in catalysis and their formal analogy to carbonyl complexes. Binary metal-phosphite complexes are known for most of the later transition metals, manganese and technetium being notable exceptions. We now report the synthesis and characterization of a series of technetium(I)-phosphite complexes, $Tc[P(OR)_3]_6^+$, as well as complexes with closely related phosphonites.

Synthesis of the complexes is achieved by reacting $NaTcO_4$ with the ligand either in alcoholic solution or in neat ligand. This reaction is remarkable because the phosphite is able to reduce Tc(VII) to Tc(I) and act as a stabilizing ligand for the reduced metal. Addition of $NaB(C_6H_5)_4$ precipitates the hexakis(ligand) Tc(I) ion in all cases. Recrystallization gives analytically pure compounds.

NMR (^{99}Tc and ^{31}P) of the complexes show the expected patterns for an octahedral $Tc-P_6$ molecule. The technetium resonance consists of a septet and the phosphorus signal is a doublet. The chemical shifts and coupling constants are compared to those for other metal-phosphorus species.

Mass spectra (fast atom bombardment and plasma desorption) in positive and negative ion modes show parent peaks corresponding to $Tc[P(OR)_3]_6^+$ and $B(C_6H_5)_4^-$, respectively. For the cation, successive loss of one, two or three ligands gives rise to a series of peaks.

X-ray crystal structure studies of the trimethyl-phosphite complex are nearing completion. Two formula units comprise the asymmetric unit in a triclinic cell. Each $Tc[P(OCH_3)_3]_6^+$ ion has octahedral geometry. The $B(C_6H_5)_4^-$ ions are tetrahedral around B.

X-ray photoelectron spectra of several Tc compounds show a linear shift of binding energy with oxidation state. The binding energies of the phosphite and phosphonite complexes fall in the region expected for Tc(I).

Infrared spectra contain the bands expected for $P(OR)_3$ and $RP(OR)_2$ ligands. The absorptions of the $B(C_6H_5)_4^-$ ion are relatively unchanged from $NaB(C_6H_5)_4$. A low energy band is tentatively assigned as a Tc-P vibration.

POLAROGRAPHIC INVESTIGATIONS ON METAL DETOXICATION USING SOME IONOPHORIC CRYPTANDS

H.L. Nigam, Jagdish Prasad, and Pushpendra Kumar

A.P.S. University, Rewa (M.P.) 486 003, and Department of Chemistry, University of Allahabad, Allahabad (U.P.) 211 002, India.

The ability of ionophores to complex with various metal ions may help in selective removal of the toxic metal ions from biological systems. While ionophoric activity for maintaining the cell balance of alkali and alkaline earth metal ions is well studied and documented, little attention seems to have been paid to toxicologically more important heavy metal ions, e.g.:

Target ions: Co^{++}, Ni^{++}, Cd^{++}, Pb^{++}, Cu^{++}.

Non-target ions: Zn^{++}

Many techniques have been used to study such complexation processes but polarographic data on such systems are very scanty. The present investigation is, therefore, devoted to the study of mechanism and kinetic parameters in the electroreduction of binary complexes of these heavy metal ions with cryptands like, 4,7,13,16,21-pentaoxa-1,10-diazobicyclo (8.8.5) tricosane and 4,7,13,18-tetraoxa-1,10-diazobicyclo (8.5.5) dicosane.

The systems studied are Metal: Ligand :: 1:1, 1:2, and 1:3 in 50% DMSO - water mixture using tetramethyl ammonium chloride as base electrolyte. Morphological characteristics, $E_{\frac{1}{2}}$ values, rate contents, and activation energies have been evaluated following standard procedures. All the systems were found to be irreversible. pH effects have also been studied. The results shall be presented and their bearing on metal detoxication in biological systems shall be discussed.

TUp30-5

METALLOTHIONEIN - STUDIES OF ITS METAL-SULFUR CLUSTERS AS THEY RELATE TO ESSENTIAL, TOXIC AND THERAPEUTIC METAL METABOLISM IN EHRLICH TUMOR CELLS.

D. Petering, A. Kraker, S. Krezoski, G. Bachowski, D. Lehn, D. Stone, C.F. Shaw and J. Otvos

Department of Chemistry, University of Wisconsin-Milwaukee, Milwaukee, Wisconsin USA

Ehrlich cells contain a Zn-binding protein with properties of metallothionein (Mt). Because the biological function of Mt is not understood, studies of the inorganic properties of Mt have been combined with examination of its role in metal metabolism in this cell line. The seven zinc ions bound to Mt exist in two Zn-sulfhydryl clusters. Estimates of the apparent equilibrium constants for the binding of zinc in either cluster were obtained using a bis(thiosemicarbazone) and NTA as competitive ligands. The values of K^{Zn}_{ZnMt} at pH 7.4 and 25° for either cluster are $2\pm1\times10^{11}$. The metal sites are kinetically reactive as well. However, there is an apparent kinetic selectivity to the ligand exchange. For example, the rates of reaction of EDTA and NTA with ZnMt are similar, while iminodiacetic acid fails to react under favorable thermodynamic conditions. Of interest, amino acids are unreactive with ZnMt. ApoZn proteins also react with ZnMt. ZnMt donates zinc to Apocarbonic anhydrase in a bimolecular process with $k=1.5\times10^{3}M^{-1}sec^{-1}$ at pH 7.4 and 25°. It is proposed that ZnMt is a reactive intermediate in zinc metabolism in the Ehrlich cells. A number of treatments of Ehrlich cells halt cell growth and under the same conditions rather specifically cause the loss of zinc from ZnMt: (1) host zinc deficiency; (2) exposure of cells in culture to EDTA, NTA, 1,10 phen. and chelex resin, all of which are thought to target cellular zinc; and (3) displacement of zinc from ZnMt by the toxic metal Cd^{2+}, and by antitumor drugs such as 3-ethoxy-2-oxobutyraldehyde bis(thiosemicarbazonato) Cu(II), and cis-diaminedichloro Pt(II). All three classes of treatments suggest that Zn in ZnMt is linked to cell proliferation. One and two demonstrate that ZnMt is the major, kinetically reactive form of Zn in this cell. The rapidity of loss of Zn from ZnMt in 2-chelex(t1/2-1 hr), suggests that direct exchange reactions in the cell between ZnMt and other cellular ligands may be occurring, thereby supporting the hypothesis set forth above. This idea is supported by experiments with sonicated cell supernatants plus apocarbonic anhydrase, in which, within small error, ZnMt is the only donor source of zinc in the system. In (3) it is demonstrated that ZnMt is a major binding site for Cd^{2+} and two metallodrugs. Whether such reactions are important for cytotoxicity or protect the cells from metal toxicity is under study.(This research was supported by NIH grant GM-25083).

CLEAVAGE REACTIONS OF SOME DISULFIDES BY BIS-PHOSPHINE GOLD(I) SALTS: SYNTHETIC AND MECHANISTIC ASPECTS

David T. Hill and Gerald R. Girard

Medicinal Chemistry Department, Smith Kline & French Laboratories, P.O. Box 7929, Philadelphia, Pennsylvania 19101

The gold(I) phosphine coordination complexes, auranofin (1), Et_3PAuCl (2) and $(Et_3P)_2Au^+Cl^-$ (3), are active against adjuvant-induced arthritis in rats upon oral administration. Although the gold(I) atom in each complex is at least 2-coordinate, the nature and disposition of the surrounding ligands while similar, markedly affects the chemical and physical properties of each complex. For example, coordination of a second phosphine in complex 2 to form 3 renders the complex ionic in polar solvents while 2 is undissociated. In studying the effect of gold compounds on disulfide-sulfhydryl interchange reactions 3, but not 2, was found to react directly with Ellman's reagent.[1] ^{31}P nmr studies[2] with whole blood indicate that 2 binds the SH groups of glutathione and hemoglobin while 3 denatures albumin. The latter reaction occurs presumably via attack of 3 on the S-S linkages. Incubation of 2 with red blood cells resulted in the formation of the bis-phosphine cation, $(Et_3P)_2Au^+$ as shown by ^{31}P nmr[3], but 3 did not appear to enter the red cells. These diverse bioinorganic observations prompted us to explore the synthetic and mechanistic aspects of the reaction of bis-phosphine coordinated gold(I) salts with disulfides.

In halocarbon media, 3 was found to cleave a variety of symmetrical disulfides to give as the major gold products the phosphine-coordinated gold(I) thiolates: Et_3PAuSR (R=CH_3, C_6H_5, CN, COC_6H_5, etc.). Sterically hindered disulfides (e.g. t-Bu) were unreactive. $[(CH_3)_3P]_2Au^+Cl^-$ (4) and $[(C_6H_5)_3P]_2Au^+Cl^-$ (5) were also found to cleave disulfides. The products of the reaction of 3 with $(C_6H_5COS)_2$ were isolated and found to include $Et_3PAuSOCC_6H_5$, Et_3PAuCl, $(C_6H_5CO)_2S$ and Et_3PS. Et_3PAuCl (2) failed to react with disulfides unless Et_3P was added. A mechanism requiring formation of a free phosphine from the bis-salt is proposed. Additional details will be discussed.

Auranofin (1) = Et_3PAuSR, R= 2,3,4,6-tetra-O-acetylglucopyranose

1. M. DiMartino, SK&F Laboratories, Personal Communication.
2. Sadler et al., J. Inorg. Biochem., 12, 317 (1980).
3. Sadler et al., Platinum, Gold and Other Metal Chemotherapeutic Agents, S. Lippard ed., ACS Symposium Series 209, 371 (1983).

TUp30-7

CHARACTERIZATION OF METABOLITES OF AURANOFIN, AN ORAL, ANTI-ANTHRITIS, GOLD-BASED DRUG

R.C. Elder, K.G. Tepperman and Jon D. Doi

University of Cincinnati, Mail Location #172, Cincinnati, Ohio, USA 45221

Auranofin, an orally-administered, experimental, gold-based, anti-arthritis drug is in the final stages of testing under a new drug application with the US FDA. The drug, triethylphosphine-ß-d-tetraacetylthioglucose-gold(I), has been approved for human use in several other countries; however, little is known about its metabolism. We have used an everted gut experiment to show, first that drug metabolites containing gold pass through the intestinal wall and second to characterize several of these metabolites. To examine the metabolites in detail we have developed HPLC (high performance liquid chromatography) procedures which allow us to quantify and separate the drug and its metabolites. In this process we have utilized, first, a 214 nm uv detector since these materials have rather low extinction coefficients at 254 nm. Second, we have coupled HPLC to an atomic absorption (AA) spectrophotometer to produce a gold specific HPLC detector. Gold sensitivity is near 5 ppm with our current AA detector.

Initial experiments at the Stanford Synchrotron Radiation Laboratories (SSRL) using X-ray absorption near edge spectroscopy established that the material passing through the gut wall maintained the gold-phosphorus bond, whereas subsequent HPLC experiments demonstrated that this material was not the drug auranofin but rather a series of metabolites. We have isolated the principal metabolite and shown it to be the desacetyl form of the drug, namely, triethylphosphine-ß-d-thioglucosegold(I). Experiments characterizing these metabolites in hamsters and rats will be detailed.

Support for this work is from the NSF (PCM8023763), the Kroc Foundation and Smith Kline and French Laboratories. SSRL is operated by DOE and maintains a biotechnology laboratory under support from the NIH.

AUROTHIONEINS - TWO DISTINCT MODES OF GOLD COORDINATION TO METALLOTHIONEIN

C. Frank Shaw III,* J. Laib,* R. C. Elder† and M. K. Eidsness†

*Department of Chemistry, University of Wisconsin-Milwaukee, Milwaukee, Wisconsin, USA 53201
†Department of Chemistry, University of Cincinnati, Cincinnati, Ohio, USA 45221

Metallothioneins are important proteins in the homeostasis of the essential metals, zinc and copper; and in the metabolism of one inorganic pollutant, cadmium; and the medicinally-used heavy metals, gold and platinum. In vivo up to 30% of the gold in renal cell cytosol may be bound to metallothionein although the latter accounts only for 2-3% of the cellular thiol groups.

Three gold-containing thioneins (Au,Zn,Cd-Th, Au,Cd-Th and $(TmSAu)_xTh$, where Th=thionein and TmS=thiomalate) have been prepared by the reactions of horse kidney Zn,Cd-thionein with aurothiomalate (AuSTm). When thionein was present in excess the thiomalate ligand was displaced and the protein chelated the gold in a bidentate fashion. Primarily zinc, and some cadmium, was displaced to form Au,Zn,Cd-Th or Au,Cd-Th. When AuSTm was present in excess, monodentate coordination of the protein to the gold thiomalate lead to the product, $(TmSAu)_x$Thionein, with essentially complete removal of the zinc and cadmium. EXAFS/XANES studies of Au,Zn,Cd-Th and $(TmSAu)_xTh$ established that the oxidation states and coordination environments of gold were $Au(I)S_2$ and that the gold-sulfur bond distances were 2.29 and 2.30, respectively. A chromophoric method to measure the rates of zinc and cadmium displacement was developed. Using Zincon, a zinc-specific chromophore, a single first order rate was obtained with limiting or excess AuSTm. Using a cadmium and zinc chromophore, 4-(2-pyridylazo)resorcinol, a fast step comparable to the rates measured with Zincon and a slower first order reaction were obtained with limiting or excess AuSTm.

$(TmSAu)_x$-Thionein was unstable and readily transferred gold to cytosolic proteins. Even in the absence of other reagents, it spontaneously rearranged to a more compact structure. Radioimmunoassay (performed by Professor Garvey, Syracuse University) established that the aurothioneins retained their antigenicity to native metallothionein antibodies. $(C_2H_5)_3PAuCl$ reacted with excess metallothionein to displace zinc and incorporate gold, but the tetraacetyl-1-β-D-thioglucose analogue, $(C_2H_5)_3PAu$-SATg, did not react.

GOLD-SERUM ALBUMIN COMPLEXES

C. F. Shaw III,* N. A. Schaeffer,* M. C. Carlock,* R. C. Elder,† M. K. Eidsness,† and G. Calis@

*Department of Chemistry, University of Wisconsin-Milwaukee, Milwaukee, Wisconsin, USA 53201
†Department of Chemistry, University of Cincinnati, Cincinnati, Ohio, USA 45221
@Department of Chemistry, University of Neijmegen, The Netherlands

Serum albumin transports most of the extracellular gold present in the blood. Because it is probably the most labile form of gold in blood, the formation, structures and reactions of the complexes are essential to a molecular understanding of chrysotherapy and the pharmacokinetics of gold drugs.

The reaction of bovine serum albumin (BSA) with sodium gold(I) thiomalate (AuSTm) and the resulting complexes were examined. Gold and [^{35}S]-thiomalate are incorporated into the resulting complex in approximately 1:1 ratio. The amount of AuSTm which binds increases with the mercaptalbumin (Alb-SH) content of the BSA preparation. Three preparations, $BSA(AuSTm)_n$, where n=0.44, 1.30 and 2.65, were isolated for spectroscopic characterization. The first reported ^{197}Au Mössbauer and also XANES and EXAFS spectra of gold-protein complexes demonstrate their utility for elucidating the environments of gold bound to macromolecules. The Mössbauer spectrum of $BSA(AuSTm)_{1.30}$ (corresponding to $AlbS(AuSTm)_{2.0}$) was resolved into two quadrupole doublets, IS_1=1.88; QS_1=6.68; IS_2=1.70; QS_2=6.50 mm/sec, consistent with two slightly different $Au(I)S_2$ environments. The EXAFS/XANES spectra of $BSA(AuSTm)_{0.44}$ demonstrate that gold(I) is coordinated by two sulfur atoms at a distance of 228±2 pm. In $BSA(AuSTm)_{2.65}$, the gold atoms were in indistinguishable AuS_2 coordination environments with an average bond distance of 230±2 pm. The binding of AuSTm to albumin increased its electrophoretic mobility. AuSTm did not compete with dansylamide or dansylsarcosine for drug binding sites I or II. It is proposed that gold binds tightly to Cys-34 to form AlbSAuSTm and that additional weaker binding occurs via bridging thiomalates (e.g. $AlbS(AuSTm)_n$ or $AlbSAu_n(STm)_{n-1}$ or by non-covalent interactions at remote sites on the protein $[AuSTm]_n$·AlbSAuSTm.

Chromatographic and ^{31}P NMR studies of the reaction of Auranofin (triethylphosphine-2,3,4,6-tetra-O-acetyl-8-1-thio-D-glucopyranosoto-S-gold(I)) with albumin demonstrate that it binds preferentially at Cys-34 with loss of the acetylthioglucose moiety. A second weaker class of binding sites may be present. Et_3PAuCl also reacts preferentially at Cys-34, but other gold binding sites, which are altered by chromatographic separation from unreacted complex and free Cl^-, are also important. Further studies of the latter compounds are in progress.

PARA- AND META-SUBSTITUTED BENZENESELENINATO COMPLEXES OF OSMIUM(III) HALIDES

Fabrizia Forghieri, Gianni Graziosi, Carlo Preti and Giuseppe Tosi

Istituto di Chimica Generale ed Inorganica, University of Modena, 41100 Modena, Italy

New complexes of osmium(III) with meta- and para-substituted benzeneseleninic acids of the type $XC_6H_4SeO_2H$ (X= H, p-Cl, m-Cl, p-Br, m-Br, p-Me) are reported. The compounds, of the type $Os(XC_6H_4SeO_2)_3$, $Os(XC_6H_4SeO_2)_2Y$, $Os(XC_6H_4SeO_2)Y_2$ (Y= Cl, Br) and $Os_2(XC_6H_4SeO_2)_3Cl_3$, have been studied through spectroscopic techniques (i.r., far-i.r. and electronic spectra), magnetic susceptibility measurements, thermogravimetric studies and conductivity measurements. The wavelengths of the principal electronic absorption peaks have been accounted for quantitatively in terms of the crystal field theory; the nephelauxetic parameter is indicative of an appreciable metal-ligand covalency.

It is worth noting that among the present complexes the highest Dq values are related to the $Os(XC_6H_4SeO_2)_3$ derivatives in which OsO_6 chromophores are present; the Dq values decrease on passing to the 1:2 and 1:1 metal:ligand molar ratio complexes according to the presence of chlorine and bromine containing chromophores.

The i.r. data point to a O,O'-seleninato coordination for all the complexes; in particular the presence of three SeO bands with the irreducible representation A_2+2E in the i.r. spectra of the trisderivatives suggests an octahedral configuration with D_3 symmetry. The complexes of the type $Os(XC_6H_4SeO_2)_2Y$ and $Os(XC_6H_4SeO_2)Y_2$ (Y= Cl, Br) are polymeric octahedral with bridging halide atoms.

The magnetic moment values lie in the expected range for the trisbenzeneseleninato derivatives, while they decrease on passing to halo-complexes.

The results will be discussed in detail and the stereochemistries of the complexes are related to the experimental data.

PREPARATION AND SPECTROSCOPIC CHARACTERIZATION OF THE PURE BONDISOMERS $[OsCl_5(NCS)]^{2-}$ AND $[OsCl_5(SCN)]^{2-}$

Wilhelm Preetz and Udo Horns

Institut für Anorganische Chemie der Universität,
D-2300 Kiel, Olshausenstr. 40

The oxidation of $[OsCl_5I]^{2-}$ with $(SCN)_2$ in CH_2Cl_2 yields the bondisomers $[OsCl_5(NCS)]^{2-}$ and $[OsCl_5(SCN)]^{2-}$, which are isolated as pure compounds by ion exchange chromatography on DEAE-cellulose. Only the salts of the N-isomer show significant shifts in the vibrational and electronic spectra caused by polarization of the terminal S depending on the size of the cations and the polarity of the solvents. In the IR- and Raman spectra $\nu_{CN(S)}$, $\nu_{CS(N)}$ and δ_{NCS} are found at higher wavenumbers than $\nu_{CN(N)}$, $\nu_{CS(S)}$ and δ_{SCN}. In the optical spectrum of the red $[OsCl_5(SCN)]^{2-}$ the charge-transfer S$\rightarrow$Os is nearly constant at 538 nm, but the N$\rightarrow$Os transition of the yellow to violet coloured N-isomer shifts from 480 nm in organic solvents or in presence of large alkylammonium cations to 516 nm in aqueous solution and to 544 nm in the solid Cs-salt. The optical electronegativities are calculated to $\chi_{opt}(-SCN) = 2,6$ and $\chi_{opt}(-NCS) = 2,6-2,8$. According to spin-orbit coupling and to lowered symmetry (C_{4v}) the splitted intraconfigurational transitions are observed at 10K as weak peaks in the regions 600, 1000 and 2000 nm. The 0-0 transitions are calculated from the vibrational fine-structure. The lowest level of both isomers is confirmed by peaks in the electronic raman spectra. With the parameters $\zeta(Os^{IV}) = 3200\ cm^{-1}$ and $B(-SCN) = 316\ cm^{-1}$ or $B(-NCS) = 288\ cm^{-1}$ there is a good fit of calculated and experimental data, resulting in the nephelauxetic series: $F^- > Cl^- > \underline{S}CN^- > Br^- > \underline{N}CS^- > I^-$.

THE MCD SPECTROSCOPY - A POWERFUL TOOL FOR ELUCIDATING THE ELECTRONIC STRUCTURE OF ORGANO-F-ELEMENT COMPOUNDS

Hanns-Dieter Amberger

Institut für Anorganische und Angewandte Chemie der Universität Hamburg, Martin-Luther-King-Platz 6, D-2000 Hamburg 13, Federal Republic of Germany

Norman M. Edelstein

Materials and Molecular Research Division, Lawrence Berkeley Laboratory, Berkeley, California, 94720 USA

Organometallic complexes of the f-elements don't crystallise into single crystals which are suitable for optical measurements. Therefore they can only be studied in solution and the additional information obtained from polarized optical single crystal measurements is missing. In solution comparable information may be obtained by performing magnetic circular dichroism (MCD) measurements.

By studying the MCD and absorption spectra of adducts of rare earth tricyclopentadienides (= $Cp_3Ln \cdot add$; Ln = Pr, Nd; add = methyltetrahydrofuran, cyclohexylisocyanide) dissolved in methyltetrahydrofuran and mixtures of methylcyclohexane/toluene at 300, 90 and 30 K, respectively, many transitions could be assigned. Assuming an effective crystal field of C_{3v} symmetry good agreement between calculated and experimental crystal field splitting patterns of the above-mentioned compounds could be achieved by fitting the appropriate parameter set.

On the basis of the calculated eigenvectors the experimentally determined temperature dependence of the paramagnetic susceptibility and the temperature dependence of the isotropic shifts of some protons of the cyclohexylisocyanide ring of $Cp_3Pr \cdot CNC_6H_{11}$ and $Cp_3Nd \cdot CNC_6H_{11}$, respectively, could be explained.

H.-D. A. would like to thank the Deutsche Forschungsgemeinschaft for financiating his research scholarship at the Lawrence Berkeley Laboratory.

This work was supported in part by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

BIVALENT METAL ION - BIPYRIDINES INTERACTIONS IN AQUEOUS SOLUTIONS AT 25°C

Mostafa M. Emara*, Nazik A. Farid†, and Mohie M. Bahr*

*Department of Chemistry, Faculty of Science, Nasr City, Cairo, and †Egyptian Institute of Petroleum Research, Nasr City, Cairo, Egypt.

The molecular charge-transfer complexes between 2,2' and 4,4'-bipyridines as donors and bivalent metal ions as V-acceptors have been investigated in aqueous solutions. Measurements are carried out at 25°C in different ionic strengths. The electronic absorption spectra is carried out at λ=280 nm with 2,2' bipyridine and λ=245 nm with 4,4' bipyridine.

The experimental conditions are carried out in such a way to assume 1:1 complex between the bivalent metal ions M^{2+} and the two types of bipyridines. In case of 2,2' bipyridine the band at 280 nm was split into two bands on addition of the complexing bivalent metal ions, and the band itself shifted to a longer wavelength (290 nm). However, in case of 4,4' bipyridine no split is observed and practically the λ_{max} has not changed. Stability constants with 4,4' bipyridine isomer are generally higher than those with 2,2' isomer.

Comparison of the results for 4,4' bipyridine to that of 2,2' isomer are discussed in terms of the structure of each ligand[1].

1. Emara, M.M., and M.M. Bahr, *Bull. De La Soc. Chimique De France*, 1-2, 1-25, 1963.

STRUCTURE AND ELECTRONIC PROPERTIES OF (BENZYLIDENEACETONE)$Fe(CO)_2L$ COMPLEXES WITH L=CO, TERTIARY PHOSPHINES AND TERTIARY PHOSPHITES.

Eduardo J.S. Vichi[a], Fred Y. Fujiwara[a], Edison Stein[a], Vania M. Nogueira[a], Assis V. Benedetti[b] and Elisa B. Saitovich[c].

[a]Instituto de Química-UNICAMP, Campinas - SP - Brasil.

[b]Instituto de Química-UNESP, Araraquara - SP - Brasil.

[c]Centro Brasileiro de Pesquisas Físicas-CNPq, Rio de Janeiro - RJ - Brasil.

The structure and the electronic effects in the title complexes were studied by ^{13}C NMR and Mössbauer spectroscopies, and by electrochemical techniques. The X-ray crystal structures of the complexes with L=PEt_3 and $PPhMe_2$, previously reported[1], show that the Fe atom adopts a distorted octahedral coordinated geometry in which three of the sites are occupied by the benzylideneacetone, BDA.

The ^{13}C resonances of the CO ligands show that, contrary to the tricarbonyl derivative, the complexes containing phosphorus ligands are not fluxional. This is attributed to an increase in the "six coordinated character"[2] due to an increase in the π-back donation from the filled metal d orbitals (or hybrid orbitals) to the LUMO of BDA, induced by the better σ-electron donor and poorer π-acceptor phosphorus ligands, compared to CO. This hypothesis is supported by the Mössbauer results.

The ^{13}C resonances of coordinated BDA shows a very large upfield shift of the carbons directly bonded to iron, as expected on the basis of the electron-donor nature of the $Fe(CO)_2L$ moieties. This electron-donor capacity increases with the basicity of L as shown by the electrochemical results. A linear correlation was observed between the ratio δC terminal/δC central of the heterodiene function of coordinated BDA and the Tolman electronic parameter[3], ν, of the phosphorus ligands. Correlations were also observed between isomer shifts, σ, quadrupole splitings, ΔEq, iron oxidation potentials and chemical shifts, δC.

The results are interpreted on the basis of a bonding scheme in which the coordinated BDA acts as a "sink" for the negative charge placed in the iron atom by the phosphorus ligands via $\sigma_P \rightarrow Fe \rightarrow$ BDA mechanism.

The authors thank CNPq and FAPESP for financial support.

1 - R.J.S. Vichi, P.R. Raithby and M.Mc Partlin, J. Organomet. Chem. 1983, 00.

2 - L. Kruczinsky and J. Takats, Inorg. Chem. 1976, 12, 3140.

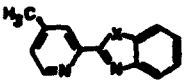
3 - C.A. Tolman, Chem. Revs. 1977, 77, 313.

TUp31-6

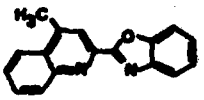
COPPER(II) CHLORIDE COMPLEXES WITH SOME 2-(4'-METHYL-2'-PYRIDYL AND 4'-METHYL-2'(OR 8')-QUINOLYL)BENZ-X-AZOLES

G. Devoto
Cattedra di Chimica A, Facoltà di Medicina, Università di Cagliari, 09100 Cagliari, Italy
M. Massacesi, G. Ponticelli
Istituto di Chimica Generale, Fisica e Analitica, Università di Cagliari, 09100 Cagliari, Italy
G. Micera and P. Piu
Istituto di Chimica Generale e Inorganica, Università di Sassari, 07100 Sassari, Italy.

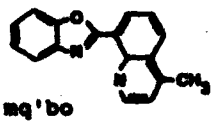
In the course of a systematic study on the coordination properties of some benz-X-azole (X = NH, O and S) derivatives we have prepared and characterized the copper(II) complexes of the following liganda:



X = NH, mpbi
X = S, mpbt
X = O, mpbo



mqbo



mq'bo

Compounds of formula $CuLCl_2$ have been obtained, whose spectral data indicate bidentate N-bonded ligands and terminal metal-halogen bonds. The complexes $CuLCl_2$ (L = mpbt, mqbo and mq'bo), in both solution and solid-state, have pseudotetrahedral CuN_2Cl_2 chromophores, whereas $Cu(mpbo)Cl_2$ has a flattened tetrahedral geometry, as shown by electronic and e.s.r. spectra. Two isomeric (yellow and green) compounds of stoichiometry $Cu(mpbi)Cl_2$ have been characterized. It is suggested that both involve similar N_2Cl_2 donor sets, but differ as regard to the degree of tetrahedral distortion.

A complex of formula $Cu(mpbi)_2N_2O$, displaying properties typical of five-coordinate chromophores, has been also obtained. Plausible structures for this compound in both solution and the solid state are proposed on the basis of the spectral results.

THERMAL ANALYSIS AND VIBRATIONAL SPECTRA OF SOME COBALT - PYRIDINE COMPLEXES

P. Verhoeven and D.A. Thornton

University of Cape Town, Dept. of Inorganic Chemistry, Rondebosch 7700, Cape Town, South-Africa

H. Hofmans and H.O. Desseyn

Universiteit Antwerpen (RUCA), Lab. Anorganische Scheikunde, Groenenborgerlaan 171, B2020 Antwerpen, Belgium

The thermal properties of a number of monomeric tetrahedral and polymeric octahedral Cobalt complexes with general formula CoL_2X_2 (L = pyridine or substituted pyridine; X = Cl or Br) were investigated. The thermogravimetric (TG) and Differential Scanning Calorimetric (DSC) results are related to the position of the metal - ligand stretching vibrations.

General Decomposition Scheme

$$CoL_2X_2 \longrightarrow CoL_{5/3}X_2 + 1/3\ L \quad (1a)$$

$$CoL_{5/3}X_2 \longrightarrow CoLX_2 + 2/3\ L \quad (1bc)$$

$$CoLX_2 \longrightarrow CoL_{2/3}X_2 + 1/3\ L \quad (2a)$$

$$CoL_{2/3}X_2 \longrightarrow CoL_{1/3}X_2 + 1/3\ L \quad (2b)$$

$$CoL_{1/3}X_2 \longrightarrow CoX_2 + 1/3\ L \quad (2c)$$

Where 1 and 2 indicate the loss of the first and second pyridine ligand (L) respectively and a b and c indicate the partial decompositions of the ligand.

For some complexes reactions a b and c occur simultaneously without formation of stable intermediates. For the stable intermediates, infrared spectra clearly indicate that $CoLX_2$, $CoL_{2/3}X_2$ and $CoL_{1/3}X_2$ exist as polymers. The halogen atoms form bridges between the Cobalt atoms resulting in the formation of double and triple layers.

CoL_2X_2 complexes with ligands as 4 MO-py and 4 H_2N-py having a strong electron-inducing effect on the Co-N(py) bond are more stable than those with ligands having electron-acceptor properties such as 3 Cl-py and 3 Br-py. A relation can be made between the heat of decomposition (ΔH_{dec}) and the decomposition temperature of the polymeric octahedral CoL_2X_2 complexes with L = 3 Cl-py or 3 Br-py and X = Cl or Br.

SPECTROSCOPY (ELECTRONIC, MASS-, RADIO- AND VIBRATIONAL) OF β-DIKETONATE METAL-COMPLEXES IN THE GAS PHASE

S.V. Volkov and Y.A. Mazurenko

Institute of General and Inorganic Chemistry, Ukr. SSR Academy of Sciences, 252601 Kiev, USSR

The investigation of metal complexes in the gas phase is a new and important stage in the chemistry of coordination compounds due to the possibility to obtain information on the structure and properties of individual molecules under conditions which (1) are not complicated by additional interactions of condensed phase and (2) permit direct comparison with the data of quantum-chemical calculations.

The use of a complex of spectroscopic methods: electronic and IR spectroscopies, mass-spectrometry, ESR a.o. allowed us to study in detail the state of sufficiently volatile and thermally stable 3d-metal β-diketonates in conjugated gas phase-melt-solid phase systems.

The IR, electronic and ESR spectra, taken for the first time, and mass-spectrometric data allowed us to characterize the structure of complexes in the individual state (vapour phase), to elucidate the mode of intermolecular interaction in the condensed state (molten and solid phases), to determine stability and the pathways of dissociation and fragmentation with β-diketonate (pentanedionates-2,4; 1,1,1-trifluoro-; 1,1,1,5,5,5-hexafluoropentanedionates-2,4; 1,1,1,2,2,3,3-heptafluoroheptanedionates-4,6 a.o.) complexes of chromium(III), manganese(II), iron(II and III), cobalt(II), nickel(II), copper(II). The effect of the nature of the metal and α-substituents in diketonate, additionally coordinated donor molecules and phase transitions on the structure and stability of complexes is discussed.

WEDNESDAY MORNING

Wa32-01

New Media for Electrochemical Investigations of Inorganic Compounds

Alan M. Bond

Division of Chemical and Physical Sciences,

Deakin University, 3217 Victoria, Australia.

Abstract

Electrochemical techniques, such as voltammetry, are now widely used to study reaction mechanisms in inorganic chemistry. In comparison to spectroscopy, there are still many limitations with respect to the temperature range, solvents and flexibility. Recently, new techniques based on platinum microelectrodes have enabled the electrolyte to be eliminated in organic solvents such as acetonitrile, benzene and dichloromethane. Such electrodes also allow the possibility for undertaking measurements in very low temperature glasses. New instrumental methods combined with these electrodes also offer possibilities for undertaking voltammetric measurements in hydrocarbons. The elimination of electrolyte and the new range of solvents allows substantial simplification of electrode processes and data can be more readily compared with other techniques of physical measurement. In addition to providing details of the new techniques, examples of electrode processes of carbonyl compounds, coordination compounds and a range of organometallics in the new media for electrochemical investigations will be discussed.

INFLUENCE OF Cl^- ON RATE AND MECHANISM OF THE ELECTRODE REACTIONS Cu(I)/Cu(Hg) AND Hg(II)/Hg IN DIMETHYLSULFOXIDE OR ACETONITRILE SOLUTIONS

Sture Fronæus and Carl Lennart Johansson

Inorganic Chemistry 1, Chemical Center, University of Lund, P.O.Box 740, S-220 07 Lund, Sweden

The electrode reactions have been studied at the equilibrium potential by the faradaic impedance method and a cyclic current-step method. In the DMSO solutions the supporting electrolyte was 1 M NH_4ClO_4, whereas in AN it was 0.1 M $(C_2H_5)_4NClO_4$. Double-layer data have been obtained from electrocapillary measurements.

In DMSO and AN Cu^+ can exist as the solvated ion, because its disproportionation constant is much lower than in water. In the DMSO solutions kinetic measurements could be performed only at $[Cl^-] > 15$ mM, and the rate law obtained indicates that Cu^+ and the binuclear complexes Cu_2Cl_2 and $Cu_2Cl_3^-$ predominate as oxidants in the ion-transfer step $Cu(I) + e^- \rightleftarrows Cu(Hg)$. On the other hand, the mononuclear complexes, that are the main Cu(I) species in the solutions used, do not take part detectably. This result can be correlated to the negative ΔH^o-values at the formation of $CuCl_j^{1-j}$ (j = 1 and 2), as a participation of these complexes would involve breaking of fairly strong Cu(I)-Cl bonds.

The results from measurements on AN solutions at $[Cu^+] < 1$ mM show that Cu^+ as well as the complexes $CuCl$ and $CuCl_2^-$ contribute to the ion-transfer, and there is a large increase in the rate constant of the electrode reaction on formation of CuCl. This effect can primarily be correlated to the large and positive ΔH^o and ΔS^o, accompanying this complex formation and indicating a pronounced decrease in the inner-sphere solvation[1]. Ligand bridging at the electrode via the coordinated Cl^- could also contribute to the high rate constant.

From the rate low obtained in the kinetic measurements on the Hg(II)/Hg electrode reaction in DMSO solutions it can be concluded that the reaction proceeds step-wise with $Hg(II) + e^- \rightleftarrows Hg(I)$ as the rate-controlling step. The solvated Hg^{2+} and Hg_2^{2+} as well as the complexes $HgCl_j^{2-j}$ (j = 1-4) and the dinuclear Hg_2Cl^{3+} take part in the overall charge transfer. The rate constant of the step $HgCl_j^{2-j}/Hg(I)$ (j = 0-4) increases with the number of Cl^- coordinated. The primary cause of the large increase on formation of $HgCl^+$ most probably is a change from octahedral to tetrahedral coordination[2], and the further increase for j > 1 can be correlated to the steady lengthening of the Hg(II)-Cl bond.

1. S. Fronæus, C.L. Johansson and B. Palm, J. Electroanal. Chem. 1978, 88, 1.

2. I. Persson and J. Hahn, To be published.

STANDARD REACTION ENTROPIES of REDOX REACTIONS of MIXED-VALENCE COMPLEXES

J.E.J. Schmits, P.J. Koonen, J.G.M. van der Linden and J.J. Steggerda
Department of Inorganic Chemistry, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands.

An intriguing feature of this class of complexes is the status of the unpaired electron i.e. can the system be described as valence delocalised or as valence trapped. With respect to this we studied the Creutz-Taube ion $[I]^{5+}$ and the related complexes $[II]^{4+}$ and $[III]^{3+}$, further biferrocinium $[IV]^{2+}$ and the bis(fulvalene) diiron $[V]^{+}$.

$[(NH_3)_5Ru(pyz)Ru(NH_3)_5]^{5+}$; $[I]^{5+}$ $[(NH_3)_5Ru(pyz)RuCl(bpy)_2]^{4+}$; $[II]^{4+}$

$[(bpy)_2ClRu(pyz)RuCl(bpy)_2]^{3+}$; $[III]^{3+}$

pyz = pyrazine bpy = 2,2'-bipyridine.

We determined ΔS° of the two successive oxidation steps of the complexes $[I]^{4+}$, $[II]^{3+}$, $[III]^{2+}$, $[IV]^{o}$ en $[V]^{o}$ and electron transfers of the related mono-Ru complexes $[Ru(NH_3)_5pyz)]^{2+}$, $[RuCl(bpy)_2(pyz)]^{+}$ and $[Ru(bpy)_3]^{3+}$ and ferrocene. ΔS° was calculated from the temperature dependence of $E_\frac{1}{2}$ as determined in a non-isothermal cell according to Weaver who showed this to be a reliable method.[a] Half-wave potentials were taken as $E_\frac{1}{2} = \frac{1}{2}(E_{p,a}+E_{p,c})$ measured by cyclic voltammetry under reversible conditions and in the temperature range -20° - $+30^\circ$ C in acetone solutions.

a Yee, E.L.; Cave, R.J.; Guyer, K.L.; Tyma, P.D.; Weaver, M.J. J. Am. Chem. Soc. 101, 1131 (1979).

Table Standard Reaction Entropy (ΔS°) in $cal.mol^{-1}\ K^{-1}$

$RuCl(bpy)_2(pyz)$	2+/+	: 24 ;	1+/0	18	
$Ru(NH_3)_5(pyz)$	3+/2+	: 44			
I	6+/5+	: 43 ;	5+/4+	: 44	
II	5+/4+	: 23 ;	4+/3+	: 42	
III	4+/3+	: 23 ;	3+/2+	: 22	
ferrocene	1+/0	: 19			
IV	2+/1+	: 24 ;	1+/0	: 18	
V	2+/1+	: 33 ;	1+/0	: 18	

From these data and the more general experience that these redox entropies are dominated by rearrangements in the solvation sphere, it is concluded that I, II, III and IV show "trapped" valency in that the time between two intramolecular electron transfers is long compared to the relaxation time of the solvent dipoles (10^{-11} s). For V the valence is found to be "delocalised" on that time scale.

D.M.E. BEHAVIOUR OF NICKEL(II)-ETHYLENEDIAMINE-AMINO ACID TERNARY SYSTEMS

Anita Rani Aggarwal, Krishna B. Pandeya and R. P. Singh

Department of Chemistry, University of Delhi, Delhi, INDIA

We report here the results of polarographic investigations on nickel(II)-ethylenediamine-amino acid ternary systems with four amino acids, viz., glycine, α-alanine, β-alanine and valine. Fixed concentrations of nickel(II) (0.2mM) and amino-acids (~3mM) were used and ethylenediamine concentration was varied from 0.0716 to 0.716mM. The studies were made at constant temperature (303k), constant pH (8.0) and constant ionic strength (0.3M KNO_3), with 0.005% gelatin solution as maxima suppressor. The reduction is irreversible and diffusion controlled throughout. Transfer coefficient (α_n) and formal rate constant ($k^\circ_{f,h}$) have been evaluated by Oldham and Parry method[1]. Some results are presented in the Table below.

[en] $\times 10^4$M	$-E_{\frac{1}{4}}$ (v)	α_n	$D^{\frac{1}{2}} \times 10^3$ (cm/sec^2)	$k^\circ_{f,h}$ (cm/sec)	$-\alpha E_{\frac{1}{4}}$ (v)
	(a) Glycine (2.95mM)				
0.716	1.2995	0.8299	1.56	1.54×10^{-18}	0.5392
7.160	1.2296	0.9500	1.05	9.76×10^{-20}	0.5841
	(b) α-alanine (2.82mM)				
0.716	1.1708	0.7739	1.47	7.05×10^{-16}	0.4530
7.160	1.1092	0.9540	1.20	8.40×10^{-18}	0.5291
	(c) β-alanine (3.06mM)				
0.716	1.5030	0.6810	1.45	4.58×10^{-13}	0.3585
7.160	0.9841	0.8684	1.32	1.53×10^{-14}	0.4273
	(d) valine (2.99mM)				
0.716	1.9086	0.7521	0.93	8.24×10^{-15}	0.4131
7.160	1.0438	0.9384	0.90	9.70×10^{-17}	0.4921

The trends in $-E_{\frac{1}{4}}$ and $k^\circ_{f,h}$ are in accordance with the relative stability and reducibility of the complexes as expected from the steric considerations.

1. R.B.Oldham and R.P.Parry, Anal.Chem. 1968, 40, 65.

ELECTROCHEMICAL STUDIES OF METAL-METAL σ BONDED (P)In-Mo(CO)$_3$Cp PORPHYRINS

P. Cocolios[a], O. Vittori[a], C. Moise[b], R. Guilard[b] and K.M. Kadish

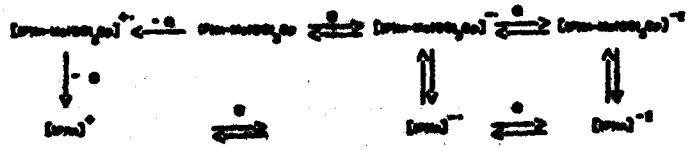
[a]Department of Chemistry, University of Houston, TX 77004 USA

[b]Laboratoire de Synthese et d'Electrosynthese Organometallique associe au CNRS (LA33), Faculte des Sciences "Gabriel", 6, Bd. Gabriel 21100 Dijon FRANCE

The titled indium(III) porphyrins[1], where P = tetraphenyl or octaethylporphyrin containing a binuclear framework were studied in benzonitrile and methylene chloride, 0.1 M TBAP, using variable temperature cyclic voltammetry.

Both complexes undergo two single electron reductions and one two electron oxidation. At fast scan rates (>0.100 V/s) the first reduction is reversible at all temperatures. At scan rates <0.100 V/s the electron transfer is followed by a rapid chemical reaction characterized by elimination of the $[Cp(CO)_3Mo]^-$ anion. A similar process occurs upon addition of a second electron. The produced $[(P)In]^{-\bullet}$ and $[(P)In]^{-2}$ species are in equilibrium with the electrogenerated (dimeric) monoanion and dianion. Lowering the temperature results in a higher stabilization of the starting complex. The generated $[Cp(CO)_3Mo]^-$ anion is oxidized at -0.08 V yielding the corresponding radical which dimerizes giving rise to the stable $[Cp(CO)_3Mo]_2$ derivative.

The two electron oxidation of (P)In-Mo(CO)$_3$Cp occurs at about +0.80 V and irreversibly leads to formation of $[(P)In]^+$ and $[Cp(CO)_3Mo]^+$. The porphyrin cation is associated with a perchlorate anion and undergoes three additional oxidative quasireversible electron transfers, as evidenced by a study of genuine (P)InClO$_4$ derivatives. The $[Cp(CO)_3Mo]^+$ cation is reduced at -0.40 V yielding the corresponding radical which rapidly reacts to give the $[Cp(CO)_3Mo]_2$ dimer. The behavior of the electrogenerated molybdenum anion and cation was ascertained by cyclic voltammetric measurements of commercial $[Cp(CO)_3Mo]_2$ samples. The overall electron transfer reaction of the title compound is summarized in the scheme below.



Scheme I

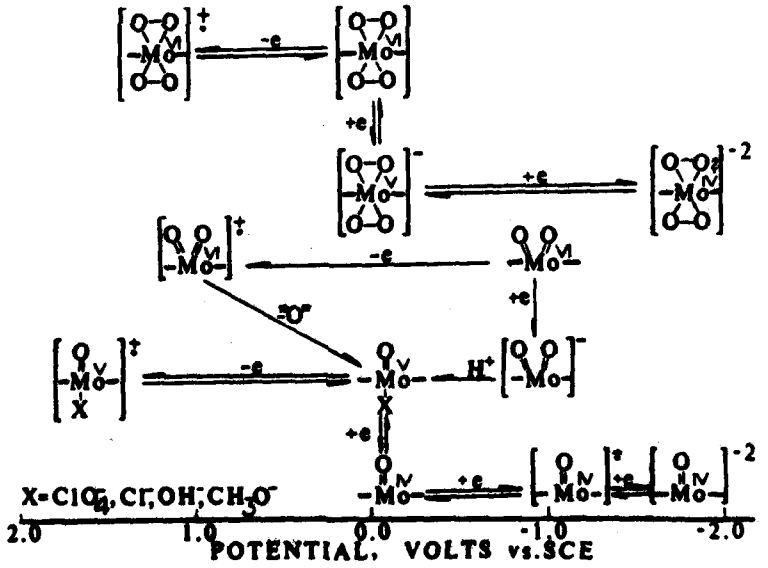
1. P. Cocolios, C. Moise and R. Guilard, J. Organomet. Chem., 1982, 288, C43.

ELECTRON TRANSFER PATHWAY IN ELECTROCHEMICAL REACTIONS OF CIS-DIOXO AND BISPEROXO-MOLYBDENUM (VI) AND OXO-MOLYBDENUM (IV), (V)

Tadeusz Malinski and Karl M. Kadish

Oakland University, Rochester, Michigan 48063 and
University of Houston, Houston, Texas 77007, U.S.A.

The electrochemical reduction and oxidation of (5, 10, 15, 20-teraphenylporphinato) cis-dioxo- and bisperoxo-molybdenum (VI) and oxo-molybdenum (IV), (V), was investigated. These complexes were studied in dichloromethane solution containing either TBAP or TBACl as supporting electrolyte by dc polaragraphy, cyclic voltammetry, coulometry and controlled potential electrolysis. ESR and spectro-electrochemical techniques were used for investigating the products of each electron transfer reaction. The electron transfer pathway for oxidation and reduction of the Mo (IV), (V) and (VI) species is shown in the following scheme.



ELECTROCHEMICAL STUDIES OF MULTIELECTRON TRANSFER IN POLYNUCLEAR COMPLEXES

Richard L. Lintvedt and Barry A Schoenfelner
Wayne State University, 123 Chemistry, Detroit, Mich., 48202, USA

The potential capability of polynuclear metal complexes to transfer two or more electrons at closely spaced potentials makes them attractive candidates for reagents and/or catalysts in a variety of reactions involving small molecules. In previous studies we have discussed the fact that several binuclear Cu(II) 1,3,5-triketonates and their diamine Schiff-bases exhibit cyclic volt m-metry consistent with two reversible, sequential one-electron transfers at very nearly the same potentials in the presence of excesses of small cations such as Na^+ and Li^+.[1,2] In the absence of such cations, one-electron reversible CV behavior is observed. These studies have been carried out with a hanging mercury drop electrode (HMDE) in dimethyl formamide. These conclusions have been substantiated by determining current functions from simulations of CV waves in the scan range 0.020 to 50.00 V/sec. On this basis, the difference in potential for the sequential one-electron steps in the presence of Na^+ is on the order of 10-50mV. This is inspite of the fact that magnetic studies show that the two Cu(II) ions are strongly interacting, i.e. the compounds are nearly diamagnetic at room temperature.

These systems have also been investigated by chronoamperometry which can be used to quantify kinetic phenomena in electrochemical reactions. For times less than 1 sec., after a potential step to well beyond E^o, a HMDE appears as a planar electrode. The Cottrell equation holds for a non-kinetically complicated system. For two electron systems that follow the ECE mechanism:

$$O + 1e^- \rightleftharpoons R' \xrightarrow{k} R'' + 1e^- \rightleftharpoons R'''$$

then,

$$i(t) = nFAC_o^* \sqrt{\frac{D_o}{\pi t}} (2 - e^{-kt})$$

Current-time data for these binuclear complexes has been fit to this function using a non-linear least squares program.

The Cu(II) triketonate and Schiff-base complexes exhibit simple Cottrell equation currents with n=1 in the absence of small cations like Na^+ or Li^+. When small cations are introduced, ECE behavior is observed. At short time (~2-4 msec) the observed current corresponds to a $1e^-$ reduction, however, at long time (~400 msec) the current is exactly twice the value observed in the absence of small cations. Since the value of k depends on which cation is used, we propose that the intervening chemical reaction in the ECE mechanism is related to small cation association with the singly reduced complex. Such association apparently results in the two redox potentials being very similar. An analogous electrochemical treatment of bis (1,3,5-trihetonato) dinickel(II) complexes will be discussed.

1. Lintvedt, R.L., Kramer, L.S., Inorg. Chem., 1983, 22, 796.
2. Lintvedt, R.L., Ranger, G., Schoenfelner, B.A., Inorg. Chem., scheduled to appear Jan. 1984.

HETERODINUCLEAR PORPHYRIN COMPLEXES

C. Michael Elliott, R.R. Krebs, and J.K. Arnette

Colorado State University, Department of Chemistry,
Fort Collins, Colorado 80523

The special reactivity exhibited by many catalysts, ranging from metalloenzymes to supported heterogeneous metal catalysts, has been attributed to the ability of substrate to simultaneously interact with multiple transition metal sites. Studying discrete hetero- and homodinuclear metal complexes provides a means to probe how metal sites, within such complexes, interact with each other and with substrate molecules.

meso-α,α,α,α-Tetrakis(*o*-nicotinamidophenyl)porphyrin (Figure 1) is a ligand capable of binding two metals in square-planar coordi-

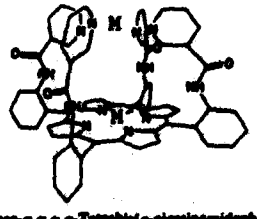


Figure 1. *meso*-α,α,α,α-Tetrakis(*o*-nicotinamidophenyl)porphyrin. Multiple bonds have been omitted for clarity.

nation sites oriented in parallel planes coaxial to one another. Metal complexes of 1 have been the subject of several reports that are of interest because of, among other things, their potential utility as models for cytochrome *c* oxidase.[1-3]

We have observed that complexes having M = Ru^{+2} and M′ = some first row transition metal have unusual coordination, spectral, and redox properties when compared to analogous simple *meso*-tetraphenylporphyrin complexes. For example, the Ru/Co complex of 1 exhibits Co(III) axial binding constants (for a variety of ligands) that are many orders of magnitude larger than for the analogous tetraphenylporphyrin complex.

The complexes Ru/Mn, Ru/Fe, and Ru/Co are most likely to possess properties of interest.

The results of electrochemical and spectral studies of these heterodinuclear porphyrins will be presented along with preliminary consideration of their utility as electrode bound species in modified electrode systems.

1. D.A. Buckingham, M.J. Cleaver, and I.M. Wender, J. Am. Chem. Soc., 100, 2899 (1978).

2. C.M. Elliott, J. Chem. Soc., Chem. Commun., 399 (1980).

3. C.M. Elliott and R.R. Krebs, J. Am. Chem. Soc., 104, 4301 (1982).

CORRELATIONS BETWEEN CHARGE TRANSFER ENERGIES AND ELECTROCHEMICAL REDOX COUPLES

Elaine S. Dodsworth, Masa-Aki Haga and A.B.P.Lever

York University, Downsview (Toronto), Ontario, Canada M3J 1P3

Charge transfer transitions occur generally between an orbital localised mainly on the metal, and an orbital localised mainly on the ligand. These orbital energies can often be probed by electrochemistry. It is possible to establish relationships between electrochemical redox potentials and optical ligand to metal (LMCT) or metal to ligand charge transfer (MLCT) transition energies. The redox couples involve equilibria between the solvated ground states of different configurations. Optical transitions involve Franck-Condon excited states which may be stabilised or destabilised by solvation, and may also be vibrationally excited. Correlation between redox potentials and optical transition energies provides a means of probing inner-sphere reorganisational energies and outer-sphere, solvation, energies.

An excellent correlation between metallophthalocyanine LMCT optical energies and redox couples, was reported[1] In circumstances where the effects of both differential solvation and vibrational excitation are minimal. Systems where these effects are not minimal will now be presented.

The $M(CO)_4(BPZ)$ (BPZ = bipyrazine) system exhibits two strongly solvatochromic MLCT bands. In addition to exploring correlations between the MLCT transition energies and various solvent parameters, the oxidation and reduction electrochemical potentials were recorded in a range of solvents of widely varying polarity.

The optical transition shifts to higher energy with increasing polarity of the solvent. Surprisingly, the difference between the potentials of oxidation and reduction, formally related to the HOMO-LUMO gap, actually decreases with increasing solvent polarity. This is explained in terms of extreme destabilisation of the excited MLCT state probably as a consequence of the dipole moment changing sign. Values for the inner and outer sphere re-organisation energies have been estimated.

A series of $[Ru(bipy)_2(LL')]^{2+}$ complexes (bipy = bipyridine) in a range of different formal oxidation levels display rich electrochemical activity and rich optical spectra comprising MLCT, MLCT and, probably, LL'CT spectra. They provide an excellent opportunity to relate optical and electrochemical data, and details will be presented.

1. A.B.P.Lever, E.R.Dockal, J.C.Minor, S.Licoccia, B.S.Ramaswamy and K.Kassyncki, J.Am.Chem.Soc., 1981, 103, 6800.

THE ELECTRON TRANSFER REACTIONS IN THE ELECTROCHEMISTRY OF THE COORDINATION COMPOUNDS

Herman C. Budnikov and Olga Yu. Kargina
Kazan State Ulyanov-Lenin University, Kazan, USSR, 420008

The electrode reactions of the inert metal (Cu,Ni) chelates of new organic reagents related to β-diketones: fluorinated β-ketoamines, β-thioketoamines, monothio-β-diketones are summarized. The chelates were shown to undergo one-electron reversible reduction in DMF by d.c. a.c., cyclic, commutated polarography and ESR. $E_{1/2}$-values of reversible steps represent the thermodynamic ones, i.e. the measure of the LVMO of the complexes.

The reduction of the fluorinated β-ketoaminates occurs at more positive potentials than that of the ligands bearing proton instead of metal, $E_{1/2}$ depending both on the nature of the central ion and the ligand structure. $E_{1/2}$ of the complexes correlate with Hammet constants for R located in para-position of the benzene ring of the ligand. ρ_π-Values for the complexes are less than those for the ligands, with the tendency being caused by the decrease of the LVMO sensitivity to the substituent effect.

ESR data show the unpaired electron in the reduction product of nickel β-ketoaminates and monothio-β-diketonates is sited on nickel atom. The geometry of Ni(I) intermediates and the donor atom effect are discussed.

One-electron reversible reduction both of nickel β-thioketoaminates and β-thioketoamines occurs at close potentials, the reduction product being regarded as a complex of Ni(II) with the ligand anion-radical according to ESR data.

Electrochemistry of the complexes studied and β-diketonates as well as dithio-β-diketonates is compared.

ACTIVATION OF CARBON DIOXIDE BY METAL COMPLEXES

Donald J. Darensbourg

Department of Chemistry, Texas A&M University, College Station, Texas 77843, USA

The insertion of CO_2 into M-H and M-C bonds to afford metalloformates or metallocarboxylates represents potential steps in catalytic cycles of the reduction of carbon dioxide. We report herein on the mechanistic aspects of the C-H and C-C bond forming processes involving CO_2 mediated by anionic group 6b transition metal species.

Observations on the intimate details of CO_2 insertion into $CH_3W(CO)_5^-$ to generate $CH_3CO_2W(CO)_5^-$ are consistent with a concerted (I_d) mechanism. The reaction was found to be first order in both metal substrate and carbon dioxide. In addition, the activation parameters measured for this process in tetrahydrofuran were determined to be $\Delta H^{\ddagger} \sim -39$ kjoul-mol^{-1} and $\Delta S^{\ddagger} = -167$ joul-mol^{-1}. Congruously, carbon dioxide insertion is not retarded by the presence of carbon monoxide.

A significant acceleration of CO_2 insertion was noted in the presence of alkali metal counterions which serve to neutralize the buildup of negative charge on the incipient carboxylate ligand. Reactions subsequent to the CO_2 insertion process, i.e. alkali metal assisted displacement of the carboxylate ligand by other nucleophiles (e.g., equation 1), will be discussed.

$$M\text{-}O\text{-}\overset{O}{\overset{\|}{C}}\text{-}R^- \xrightarrow{LiCl} M\text{-}Cl^- + RO_2C^-\ Li^+ \qquad (1)$$

Substitution at the metal center by phosphorus donor ligands was found to greatly enhance the rate of CO_2 insertion into the metal-carbon bond. For example, whereas $CH_3W(CO)_5^-$ undergoes reaction with CO_2 to afford $CH_3CO_2W(CO)_5^-$ at ambient temperature and pressure over several days, cis-$CH_3W(CO)_4PPh_2^-$ reacts with CO_2 in a matter of 1-2 hours to yield cis-$CH_3CO_2W(CO)_4PPh_2^-$. A similar rate enhancement was noted for CO_2 insertion into the W-C bond in the chelating $(CO)_4W(CH_2CH_2CH_2PPh_2)^-$ derivative. This latter species was prepared by deprotonation of the $(CO)_4W(CH_2CH_2CH_2PPh_2H)$ derivative derived from reaction (2).

$$(CO)_5W^{2-} + Ph_2P(CH_2)_3Cl \rightarrow (CO)_5W(CH_2CH_2CH_2PPh_2H)^- + (CO)_5WC(O)CH_2CH_2CH_2PPh_2^- \qquad (2)$$

X-ray structural investigations of several of these metal-alkyl derivatives will be presented along with the role of CO_2 insertion reactions in catalytic cycles involving the conversion of carbon dioxide, hydrogen and alkenes, to alkyl formates in the presence of anionic metal carbonyl derivatives.

VIBRONIC ACTIVATION OF SMALL MOLECULES IN CATALYSIS

I.B.Bersuker and S.S.Budnikov

Institute of Chemistry, 277028 Kishinev, Grosula 3,USSR

The vibronic theory of chemical activation by coordination in the elementary act of catalysis is based on the concept of vibronic interaction explicitely including, by means of orbital vibronic constants, the detailed influence of changes in the electronic shell on the nuclear framework resulting in a change of the activation energy of chemical reactions with the coordinated molecule [1]. In the semiempirical version the main parameters of the theory are the changes of the frequency of vibrations and interatomic distances (by coordination) in the direction of the reaction path directly coupled to the changes of the electronic MO population numbers (orbital charge transfers).In the case of diatomics and localised double bounds (say, in olefines) a one-parameter version of the theory was worked out, this parameter being the change of the frequency of streching vibrations. For H_2, NO, CO, O_2, C_2H_4, C_2D_4, C_3H_6 molecules coordinated to mono and polynuclear complexes and to solid state surfaces the parametrisation procedure was worked out, and vibronic constants, orbital charge transfers and resulting changes of the activation energy of chemical reaction with these molecules due to coordination were calculated. These results are in direct or indirect agreement with experimental data and allow to predict, at least qualitatively or semiquantitatively,the expected activation of small molecules by coordination to various active centers.

1. I.B.Bersuker, The Jahn-Teller Effect and Vibronic Interactions in Modern Chemistry, Plenum Press, New York, 1983.

FORMATION AND REACTIVITY OF $(CO)_4FeCO_2H^-$ IN THE GAS PHASE. IMPLICATIONS FOR THE $Fe(CO)_5$-CATALYZED WATER-GAS SHIFT REACTION.

Kelley Lane, Larry Sallans and Robert R. Squires

Purdue University, West Lafayette, Indiana USA 47907

The properties and reactivity of $(CO)_4FeCO_2H^-$, 1, produced in a flowing afterglow apparatus are described. The title ion is the sole product of a rapid gas phase reaction between $Fe(CO)_5$ and hydrated-hydroxide ion clusters $HO(H_2O)_n^-$ n=1,2,3 (eq. 1). This contrasts the reaction with bare, unsolvated hydroxide which yields exclusively $(CO)_3FeOH^-$ by CO ligand expulsion.

$$(1)\qquad HO(H_2O)_n^- + Fe(CO)_5 \longrightarrow \begin{cases} \xrightarrow{n=1,2,3} (CO)_4FeCO_2H^- + nH_2O \\ \xrightarrow{n=0} (CO)_3FeOH^- + 2CO \end{cases}$$

Assignment of the iron hydroxy-carbonyl (metallocarboxylic acid) structure to 1 is based upon several lines of chemical and thermodynamic evidence. For example, ion 1 undergoes facile hydrogen-deuterium exchange in the presence of CH_3CO_2D as does its deuterated analog with HCO_2H and H_2S. Furthermore, no oxygen-18 incorporation is observed in reactions of 1 with $H_2{}^{18}O$ and only a single oxygen-18 appears in the product of reaction between $Fe(CO)_5$ and $H^{18}O(H_2{}^{18}O)_n^-$ n=1,2,3. The results of these studies and the thermochemical information which they provide are discussed in terms of the postulated role of $(CO)_4FeCO_2H^-$ in the $Fe(CO)_5$-catalyzed water-gas shift reaction.

PHOTODECOMPOSITION OF WATER WITH SUPPORTED NOBLE METAL CLUSTERS

Virginia H. Houlding and Arthur J. Frank
Solar Energy Research Institute, 1617 Cole Boulevard, Golden, CO 80401 USA

Noble metal catalysts deposited onto microparticulate semiconductor materials are effective electron transfer mediators in the photodecomposition of water (1). In an effort to increase catalytic efficiency and introduce redox specificity, methods are being sought for the deposition of very small (<20 Å) metal clusters onto semiconductor supports.

Clusters of the type $[Pt_3(CO_6)_n]^{2-}$ where n = 2-10 were synthetized according to the method of Longoni and Chini (2) and used to functionalize several semiconductor materials. Details of catalyst synthesis and characterization will be reported, and the performance of these catalysts in water photodecomposition will be compared to that of analogous catalysts prepared by previously published methods.

1. M. Grätzel, Acc. Chem. Res. 1981, 14, 376-384.
2. G. Longoni and P. Chini, J. Am. Chem. Soc. 1976, 98, 7225-7231.

SYNTHESIS AND REACTIVITY OF COBALT AND RUTHENIUM COMPLEXES OF 1,4,7 TRIAZACYCLONONANE (TACN) AND 1,4 BIS(1,4,7 TRIAZACYCLONON-1-YLMETHYL)BENZENE (PXBCN).

John M. Lyon and Stephan S. Isied

Dept. of Chemistry, Rutgers, The State Univerasity of New Jersey, New Brunswick, New Jersey USA 08903

The ligand, PXBCN, was synthesized and characterized in our laboratory to investigate its binucleating properties, especially for the oxidation of metal-coordinated H_2O molecules to molecular oxygen (eq 1)

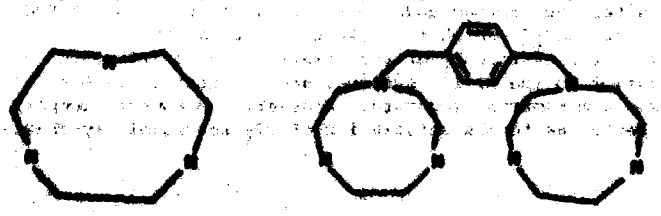


The advantage of PXBCN over other binucleating ligands is that the metals are held far enough apart so that μ-oxo formation within the same ligand is prevented. However, formation of μ-peroxo complexes is possible. To demonstrate the formation of μ-peroxo complexes with this ligand, cobalt(III)-μ-peroxo complexes with PXBCN and TACN were prepared and characterized by elemental analysis, UV-Vis spectra, and cyclic voltammetry. Oxidation to the corresponding superoxo complexes resulted in species with characteristic UV-Vis and EPR spectra. In order to study the oxidation of coordinated water, the ruthenium complexes of PXBCN and TACN were synthesized starting with $K[Ru(bipy)Cl_4]$. Chloro and aquo complexes of the type

$[Ru(bipy)(TACN)Cl]PF_6$ $[Ru(bipy)(TACN)(OH_2)](PF_6)_2$

$[(RubipyCl)_2PXBCN](PF_6)_2$ $[(Rubipy(H_2O)_2)_2PXBCN](PF_6)_4$

were characterized by elemental analysis, UV-Vis spectra, and electrochemical behavior. Significant differences exist between the oxidation properties of the chloro and aquo species. Whereas, the chloro species of both mono and binuclear complexes undergo reversible one electron transfer corresponding to the Ru(II/III) couple, the aquo complexes are further oxidized to form Ru(IV) species. Studies on modification of the chemical reactivity of these complexes by replacing the bipy ligands are in progress.



TACN PXBCN

CO_2 FIXATION BY ZINC(II) AND NICKEL(II) COMPLEXES WITH TETRAAZACYCLOALKANES

Tasuku Ito, Masako Kato, and Haruko Ito

Institute for Molecular Science,
Okazaki National Research Institutes, Okazaki 444, JAPAN

Certain four-coordinate Zn(II) and Ni(II) complexes with tetraazacycloalkanes take up CO_2 in solution very easily under mild conditions to fix it into the resulting complexes as RCO_2^-, $R_2NCO_2^-$, or HCO_2^- under given conditions. The following compounds have been synthesized in this way and characterized.

$M(L)(O_2COR)ClO_4$: $M=Zn^{2+}, Ni^{2+}$; L=[14]aneN$_4$, [15]aneN$_4$, Me$_2$[14]aneN$_4$, Me$_4$[14]aneN$_4$; R=Me, Et, n-Bu (not all the combinations).

$Ni(rac\text{-}Me_6[14]aneN_4)(H_2O)(O_2COR)ClO_4$: R=Me, Et.

$Ni(rac\text{-}Me_6[14]aneN_4)(O_2CHR_2)ClO_4$: R=Me, Et, n-Bu.

$M(L)(O_2COH)ClO_4$: (M,L)= Zn^{2+}, Me$_4$[14]aneN$_4$; Ni^{2+}, rac-Me$_6$[14]aneN$_4$.

It has been found by X-ray analyses of five structures that compounds adopt a variety of coordination modes including five-coordination of the square-pyramidal or trigonal-bipyramidal type, as well as pseudo octahedral type, assuming a linear chain structure by bridge coordination, trimeric or monomeric structures.

Particularly fascinating characteristics of the present systems are : (i) The up-take reactions proceed under very mild conditions --- in some cases, CO_2 is fixed spontaneously in the air; (ii) The up-take reactions are mostly reversible; (iii) Resultant complexes are stable in the air; (iv) For example, in $CDCl_3$ solution of Zn([15]aneN$_4$)(O_2COCH_3)ClO_4, there exists an equilibrium between the $CH_3OCO_2^-$ and CH_3O^- complexes, that involves reversible absorption-desorption of CO_2.

Viewed from the observed structural features and chemistries, the CO_2 fixations by the present complexes are considered to be accomplished in the following way. Four nitrogens of the tetraazacycloalkane occupy firmly four coordination sites out of possible five- or six-sites at either square-planar or trigonal bipyramidal positions, giving rise to reactive vacant site(s). The vacant sites thus formed undergo the fixation reaction of RCO_2^-, $R_2NCO_2^-$, or HCO_2^-, which is present in the solution.

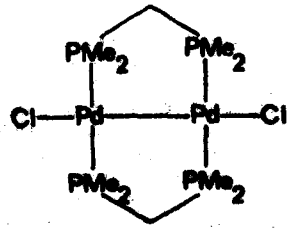
As to the efficiency of the fixation, the Zn(II) complexes are superior to the Ni(II) systems, and a linear chain structure surpasses a monomeric structure. However, a monomeric complex is likely better as to the utilization of CO_2 in organic syntheses.

THE ROLE OF WATER SOLUBLE BIS-(DIMETHYLPHOSPHINO) METHANE BRIDGED DI-PALLADIUM COMPLEXES IN THE HOMOGENEOUS CATALYSIS OF THE WATER GAS SHIFT

Marc L. Kullberg and Clifford P. Kubiak

Department of Chemistry, Purdue University, West Lafayette, IN, USA 47907

New dipalladium complexes bridged by bis-(dimethylphosphino) methane have been prepared. The parent complex, $Pd_2Cl_2(dmpm)_2$, 1, reacts with a variety of small molecules including CO, SO_2, CS_2, CH_3NC and C_2H_2. The structure of $Pd_2Cl_2(\mu\text{-}CO)(dmpm)_2$, 2, has been determined by X-ray diffraction and is of the "A frame" type.



1

A most surprising feature of the chemistry of these compounds is their high solubility and stability in aqueous solutions. UV-Vis, ^1H and $^{31}P[H]$-NMR spectral data, conductivity measurements, and pH titrations collectively point to the identity of 1 in water as the dihydroxyl species $Pd_2(OH)_2(dmpm)_2$, 3. The substitution of chloride by hydroxide is reversible in aqueous media.

Complex 1 is a catalyst precursor for water gas shift (WGS) catalysis in aqueous solutions. Heating 1 in H_2O under CO leads to the evolution of CO_2 and H_2 at an initial turnover rate of >2/hr decreasing over 1 week to ~.2/hr. The major species found in solution are $Pd_2(\mu\text{-}CO)(OH)_2(dmpm)_2$, 4, and $Pd_2(\mu\text{-}CO)H_2(dmpm)_2$, 5. The mechanism of CO_2 evolution and formation of the hydride 5 is interpreted in terms of CO insertion into the Pd-OH bonds of 4. Support for this contention is derived from related phenoxide complexes. Addition of CO to $Pd_2(OPh)_2(dmpm)_2$ results in initial CO insertion into the Pd-Pd bond followed by insertion into Pd-OPh bonds to give $Pd_2(\mu\text{-}CO)(\text{-}C(O)OPh)(dmpm)_2$. Upon heating, CO_2 is evolved to give the diphenyl complex, $Pd_2(\mu\text{-}CO)Ph_2(dmpm)_2$. The corresponding dibenzoate, $Pd_2(\mu\text{-}CO)(\text{-}OC(O)Ph)(dmpm)_2$, does not decarboxylate upon heating. These data suggest that CO insertion into the Pd-OH bonds of 4 is responsible for CO_2 evolution in water gas shift catalysis. New studies of insertions of olefins and acetylenes into the Pd-OR bonds of complexes related to 1 will be presented.

CATALYTIC OXIDATION OF WATER BY μ-OXO-RUTHENIUM COMPLEX ON COLLOIDAL SUPPORTS

Kenji Honda and Arthur J. Frank
Solar Energy Research Institute, 1617 Cole Boulevard, Golden, CO 80401 USA

Catalytic films of RuO_2 powder dispersed in a polymer support attached to the surface of CdS photoanodes have been shown to be effective in stabilizing the semiconductor against photooxidative corrosion while affording the catalytic oxidation of water.[1,2] The effectiveness of the catalytic films, however, depend on the weight ratio of RuO_2-to-polymer. In principle, increased catalytic activity, selectivity, and stability can be achieved with homogeneous catalysts.

As an alternative to the microcrystalline RuO_2 particles, we have investigated the μ-oxo-binuclear system $[(bpy)_2(H_2O)\text{-}Ru^{III}\text{-}O\text{-}Ru^{III}(H_2O)(bpy)_2]^{4+}$ as a water oxidation catalyst.[3] The μ-oxo-ruthenium dimer can be rapidly oxidized electrochemically to higher valence states. Over a period of hours, the higher valenced ruthenium dimeric complex brings about the four-electron oxidation of water and reverts to the original valence state. The amount of O_2 produced is stoichiometric during the initial stages. Depending on the applied potential and other experimental conditions, the ruthenium dimeric system decomposes irreversibly. The stability of the dimeric system to oxidative degradation can be markedly enhanced while permitting the oxidation of water to occur by immobilizing the complex on various colloidal supports. These results and others will be discussed.

1. A. J. Frank and K. Honda, J. Phys. Chem. 1982, 86, 1933.
2. A. J. Frank and K. Honda, J. Electroanal. Chem. 1983, 150, 673.
3. S. W. Gersten, G. J. Samuels, and T. J. Meyer, J. Am. Chem. Soc. 1982, 104, 4029.

Acknowledgment

The support of the Division of Chemical Sciences, Office of Basic Science, U.S. Department of Energy, is greatly appreciated.

Wa34-01

ASPECTS OF THE COORDINATION CHEMISTRY OF IRON TRANSPORT PROTEINS

Philip Aisen

Department of Physiology and Biophysics, Albert Einstein College of Medicine, Bronx, New York 10461, USA

The transferrins comprise a class of two-sited iron-binding proteins, which arose during the course of biochemical evolution through duplication and fusion of a gene specifying a primitive single-sited protein. A variety of spectroscopic, thermodynamic and kinetic studies have demonstrated differences between the sites of human transferrin, but whether these differences are mapped into the physiological domain is still an unsettled and controversial question. The transferrin molecule serves a vehicle for iron transport, interacting with cells which require the metal for the biosynthesis of essential iron proteins (notably hemoglobin) as well as cells in which iron is absorbed, stored or recovered from hemoglobin for recycling. In the absence of transferrin, noxious reactions involving the catalytic capacity of iron in electron transport may occur to the detriment or destruction of cells. However, some of these reactions, involving a form of transferrin known as lactoferrin which is found within specific granules of microbe-destroying white blood cells (polymorphonuclear leukocytes), may exploit the catalytic capacity or iron to generate oxygen radicals capable of microbial killing.

Originally thought to be a single-sited "half-transferrin," and named accordingly, uteroferrin is now known to be a protein with a binuclear, tyrosine-ligated iron center. The protein exists in interconvertible pink and purple forms, the iron existing as an Fe(III)-Fe(III) couple in the purple variety, and as an Fe(III)-Fe(II) pair in the pink species. Spectroscopic features of the iron center change in response to a variety of anions and protein-perturbing agents. Found in the uterine fluid of pigs (and certain other vertebrates), uteroferrin may function as an intermediate in iron exchange between circulating transferrins of maternal sow and fetal pig. Additionally, it displays acid phosphatase activity which may be important in regulating cellular metabolism. Both phosphatase and iron-transfer activities are sensitive to the redox state of the protein, suggesting that uteroferrin may be a sensor of oxidative metabolism.

1. B.C. Antanaitis and P. Aisen, Uteroferrin and the Purple Acid Phosphatases Advances in Inorganic Biochemistry (H.C. Theil, G.L. Eichhorn and L.G. Marzilli, Eds.) 5, 113-136, 1983.

2. O. Zak, A. Leibman, and P. Aisen, Metal-binding Properties of a Single-sited Transferrin Fragment, 742, 490-495.

THE DESIGN, SYNTHESIS, AND EVALUATION OF NEW MULTIDENTATE LIGANDS FOR TRIVALENT METAL IONS

Arthur E. Martell, Ramunas J. Motekaitis and Christina Hasserodt

Department of Chemistry, Texas A&M University, College Station, Texas, USA, 77843

Because of the well known affinity of phenolate oxygen donors for the ferric ion, several new multidentate ligands containing one or more monodentate phenolate-type donor groups have been synthesized and evaluated. The variation of parent EDTA structure represented by EHPG (ethylenebis-o-hydroxyphenylglycine) and HBED (bis-(o-hydroxybenzyl)ethylenediaminediacetic acid) has been further extended by changing the number of phenolate donors, replacing acetate groups by phosphonate and phosphonate half ester groups, by using heterocyclic (pyridine) rings in place of phenyl rings, and by extending the polyamine backbone to three and four nitrogens. These new ligands offer a range of very high affinities for Fe(III), and for other trivalent metals such as Ga(III) and In(III). In most cases the stabilities of the trivalent metal chelates are too high to be determined by direct potentiometric measurement of hydrogen ion concentration. The equilibria involving these ligands were measured by competition with other multidentate ligands such as EDTA and TTHA (triethylenetetraaminehexaacetic acid). The ligands with phosphonate groups were found to be superior to those containing acetate groups with respect to stabilities of the complexes formed, but suffer from insolubility of the complexes in the neutral and weakly acid pH range. A potentially inexpensive and effective ligand was obtained through a Mannich reaction involving p-cresol, formaldehyde, and glycine as starting materials. Work now in progress is directed toward the synthesis and study of macrocyclic polyamines substituted with phenolate and carboxylate donors, and which seem to offer promise of high stability and selectivity for trivalent metal ions.

BORON ANALOGS OF HYDROXAMATES: SYNTHESIS, CHARACTERIZATION, AND REACTION WITH METALS.

Karen W. Morse and Verrill M. Norwood

Department of Chemistry and Biochemistry, Utah State University, Logan, Utah 84322

Reaction of borano-amino acids, $(R_{3-x}\overset{+}{N}H_x)\bar{B}H_2COOH$, with $NH_2OH \cdot HCl$ in aqueous acidic solution produces boranohydroxamates $(R_{3-x}\overset{+}{N}H_x)\bar{B}H_2CONHOH$ in good yield. The solids are characterized by IR, ^1H and ^{11}B NMR, and by their reaction with iron. Absorptions characteristic of an iron hydroxamate complex are obtained at varying pH. These absorptions in the visible region are directly comparable to the ranges for those for hydroxamate iron complexes. The reactions between the borano-amino acids and substituted hydroxylamine derivatives have also been studied. One example is the reaction between $(CH_3)_3\overset{+}{N}HCH_2CO_2H$ and $NH_2OCH_2Ph \cdot HCl$. Studies on the hydrogen ion-catalyzed boranohydroxamic acid formation will also be reported.

MODELS FOR THE IRON BINDING SITE IN THE TRANSFERRINS

Kevork Spartalian, Joseph Bonadies, Christopher Bailey and Carl J. Carrano

Departments of Physics and Chemistry, University of Vermont, Burlington, Vermont, USA 05405

The quinquedentate ligand, N,N', ethylene salicylaldiamine hydroxyphenylglycine, (H3HG) has been studied as a model for the iron binding site in the transferrins. The Fe(H3HG) contains an open coordination site that binds water in aqueous solution and can undergo hydrolysis at near neutral pH as has been recently suggested to occur in the protein.[1] The complex is monomeric and has been characterized by elemental analysis, magnetic susceptibility, optical spectroscopy and electrochemistry. A crystal structure of the methanol solvate has been completed. In aqueous solution Fe(H3HG) undergoes hydrolysis as evidenced by optical spectroscopy. Analysis of spectra indicate a pKa for the coordinated water of ca. 6.7. The occupation of the sixth ligand position can be followed by *Mossbauer spectroscopy*. At low pH there is a single iron species assigned as the aquo complex which has a very low zero field splitting, D. At high pH the water is deprotonated to form a hydroxo complex. At intermediate pH both the aquo and hydroxo forms coexist as well as a new species that shows fast electronic relaxation. These spectra are significant in terms of transferrin models because transferrin is known to have a very low D value.[2] In light of results obtained with this model, a new interpretation of the binding site in the transferrins is suggested.

1. V.L. Pecoraro, W.R. Harris, C.J. Carrano and K.N. Raymond, Biochemistry, 1981, 20, 7033.

2. K. Spartalian, and W.T. Oosterhuis, J. Chem. Phys. 1973, 59, 617.

STRUCTURE AND METAL BINDING SITES IN FERRITIN

G.C.Ford, E. Godbehere, T.H.Lilley, D.W. Rice, A.Treffry, J.L.White and P.M. Harrison

Departments of Biochemistry and Chemistry, The University, Sheffield S10 2TN, U.K.

The three dimensional structure of horse spleen apoferritin has recently been refined at 2.8Å resolution and refinement at higher resolution is underway. The three dimensional structure will be described and features emphasised which are thought to be of importance in relation to ferritin's iron storage function. Although the chemical constitution of ferritin iron-cores has been identified, iron binding sites on apoferritin are at present unknown and difficult to determine. To understand mechanism of iron incorporation and mobilisation in ferritin we need to identify the iron binding ligands and their positions in the three dimensional structure. One approach to this problem is to examine sequence homologies in relation to functionally important regions of the structure. A second approach is the use of spectroscopic methods to study the binding of iron and other metals to the apoferritin shell. Results of such studies will be outlined.

1. D.W. Rice, G.C. Ford, J.L. White, J.M.A. Smith and P.M. Harrison Advanc.Inorg.Biochem. 1983 5, 39.

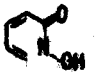
HYDROXYPYRIDINONES: HIGHLY EFFECTIVE BIDENTATE IRON CHELATORS

Robert C. Scarrow, Walter P. Kwan and Kenneth N. Raymond

Department of Chemistry, University of California, Berkeley
California 94720 USA

Siderophores (oligopeptides secreted by microbes to solublize environmental iron) have provided useful models for synthetic ferric ion chelators.[1] Such molecules have potential medical value in the treatment of acute or chronic iron overload. Many of these synthetic chelates can rapidly remove iron from serum transferrin (a mammalian iron-transport protein), as desired for iron-removal drugs.[2,3]

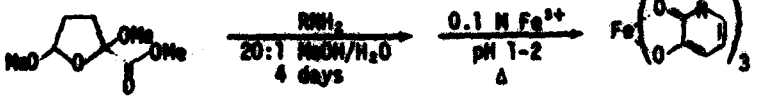
The hydroxypyridinones ("Hopo's") shown below are ligands similar to the catecholate and hydroxamate groups common in siderophores. Changes in the visible spectra of iron(III)/hydroxypyridinone solutions as functions of pH and added EDTA have been used to obtain the identity and formation constants of complexes in dilute aqueous solution (25°, μ = 0.1 M). The oxypyridonate anions form 1:1, 2:1, and 3:1 complexes with ferric ion; the latter have log(β) = 26.9, 29.6, and 35.0 for 1,2-, 3,2- and 3,4-Hopo respectively. The simple hydroxypyridinones bind iron best between pH 5 and 8; in this range they bind iron(III) better than catecholates or hydroxamates. The ability of hydroxypyridinones to remove iron from transferrin will be described.

1,2-Hopo: 

3,2-Hopo: 

3,4-Hopo: 

Attachment of several hydroxypyridinone groups to an organic "backbone" increases the iron affinity in dilute solution. One method of attachment is the following modification of a literature[4] synthesis of 3,2-Hopo:



1. K. N. Raymond, V. L. Pecoraro and F. L. Weitl, in Design of New Chelating Agents, Elsevier/North Holland, New York, 1981, pp 165-187.
2. K. N. Raymond and T. P. Tufano, in The Biological Chemistry of Iron, D. Reidel Publishing Co., Holland, 1982, pp 85-105.
3. K. N. Raymond, T. D. Y. Cheung, V. L. Pecoraro and C. J. Carrano, in The Biochemistry and Physiology of Iron, Elsevier Biomedical, New York, 1982, pp 649-662.
4. N. Clausen-Haas and P. Nedenskov, Acta Chem. Scand. 1966, 9, 14.

THERMODYNAMIC BINDING CONSTANTS FOR DIVALENT CATIONS TO HUMAN SERUM TRANSFERRIN

Wesley R. Harris

Laboratory for Energy-Related Health Research, University of California, Davis, California USA 95616.

The difference uv spectrum of nickel-transferrin shows the characteristic maxima at 256 and 297 nm arising from the binding of the metal ion to tyrosine phenolate groups at the metal binding sites. However, at pH 7.4 the binding of nickel to serum transferrin is so weak that less than one equiv of nickel is bound even with a 6-8 fold excess of free metal ion. Based on difference uv titration curves, the nickel transferrin binding constant is calculated to be $10^{3.5}$. Even though less than one equiv of metal ion is bound, studies on the two forms of monoferric transferrin indicate that both metal binding sites of the protein are involved. There does not appear to be a strong preference for nickel binding to one site over the other.

In a previous study,[1] the zinc(II)-transferrin binding constants have been used to estimate the iron(II)-transferrin binding constants using a linear free energy relationship (LFER) between the zinc and ferrous ion stability constants with a series of low molecular weight ligands. The zinc LFER predicted ferrous constants of $10^{6.7}$ and $10^{6.4}$, which are much larger than the value of $10^{3.5}$ estimated by Kojima and Bates.[2] A new LFER has been prepared for the binding of nickel and ferrous ion which can be described by the equation

$$\log K_{Fe} = 0.76 \times \log K_{Ni} + 0.07$$

This equation predicts a ferrous constant of $\log K = 2.7 \pm 0.8$, which is much more consistent with the results of Kojima and Bates. Zinc is a d^{10} ion with no crystal field stabilization energy, so it can readily assume distorted coordination geometries. Both nickel and ferrous ion have a strong preference for regular octahedral geometry. Thus if the protein imposed a distorted coordination geometry upon the metal ion, this might not have a significant impact on the zinc constants, but would be expected to reduce the binding affinities for both iron(II) and nickel(II). Thus the nickel LFER is considered the more reliable estimator of a true binding affinity for ferrous ion.

1. W.R. Harris, Biochemistry 1982, 21, 3820.
2. M. Kojima and G.W. Bates, J. Biol. Chem. 1981, 256, 12034.

COPPER(II) COMPLEXES OF NOVEL UNSYMMETRICAL MULTIDENTATE AZOMETHINES

Raghu N. Prasad and Ram P. Sharma

Department of Chemistry, University of Rajasthan, Jaipur-302004 (INDIA)

Transition metal complexes of symmetrical multidentate azomethines have been widely studied, but owing to the difficulty in the synthesis of unsymmetrical azomethines bearing two >C=N- groups, the complexes of the latter have not been studied so far. Investigations on such complexes have been undertaken in our laboratory and Ni(II) complexes of such ligands have been reported(1,2). In the present paper the synthesis of Cu(II) complexes of the following unsymmetrical multidentate azomethines is described:

$HOC_{10}H_6CH{:}NXN{:}C(R)C_6H_4OH$, $HOC_{10}H_6CH{:}NXN{:}C(CH_3)CHC(CH_3)OH$, $HOC_6H_4CH{:}NXN{:}C(CH_3)C_6H_4OH$ and $HOC_6H_4C(R){:}NXN{:}C(CH_3)CHC(CH_3)OH$ (where R = H or CH_3 and X = $-(CH_2)_3-$, $-(CH_2)_4-$, $-(CH_2)_6-$, $-o-C_6H_4-$, $-(CH_2)_2NH(CH_2)_2-$ or $-(CH_2)_2NH(CH_2)_2NH(CH_2)_2-$)

These complexes have been synthesized by the reactions of the preformed mixed imine complexes of Cu(II) of the type CuLL' (where HL and HL' are two different imines) with diamines such as 1,3-diaminopropane, 1,4-diaminobutane, 1,6-diaminohexane or o-phenylenediamine and polyamines such as diethylenetriamine or triethylenetetramine and have been characterised by elemental analyses, TLC, magnetic measurements and IR and electronic spectra. The data indicate square planar geometry for all the complexes. Thus in the penta- and hexadentate ligands only azomethine nitrogens coordinate whereas the nitrogen atoms of NH groups of the amine residue remain uncoordinated.

1. R. P. Sharma and R. N. Prasad, Synth. React. Inorg. Met.-Org. Chem. 1982, 12, 547.
2. R. P. Sharma and R. N. Prasad, Acta Chim. (Budapest), in press.

SYNTHESIS AND CHARACTERISATION OF TRANSITION METAL COMPLEXES OF TETRADENTATE N_6-MACROCYCLIC LIGAND

W.U. Malik, Ramesh Bembi and Randhir Singh
Department of Chemistry, University of Roorkee,
Roorkee-247667 INDIA

There has been recent interest in the study of macrocyclic complexes which are considered as possible synthetic models for naturally occurring macrocyclic systems like biochemically important proteins, vitamin B_{12}, chlorophyll etc. Tetraaza macrocycles have attracted substantial interest in the design and preparation among inorganic chemists in the recent past (1-5). An intriguing feature of these systems is that the size of the ligand can be changed with relative ease by synthetic means which can have the effect that the enclosed metal ion behaves in quite different ways.

In the present communication we report the synthesis and characterisation of 16-membered N_6-macrocyclic complexes of nickel(II), cobalt(II), and copper(II) obtained via template reactions, using 2,6-diaminopyridine and 1-phenyl 1,3-butanedione. These macrocyclic complexes were characterised by magnetic, conductance, electronic and infra red spectral studies. The far I.R. spectra support that only four azomethine nitrogens coordinate which are bridged by diketone moieties and no evidence for coordination of pyridine nitrogens. These macrocycles are, on the basis of the above studies, considered to have a distorted octahedral configuration. This distorted octahedral environment arises due to the steric interaction of the 2,6-diaminopyridine ring with methyl and phenyl substituents on the macrocyclic ring.

1. D.H.Busch, Helv.Chim.Acta, Fasciculus Extraordinarius Alfred Werner,174(1967).
2. L.F.Lindoy,L.J.Dehayes,I.J.Zompa and D.H.Busch, J.Am. Chem.Soc.,96,4046(1974).
3. J.W.L.Martin,J.H.Johnton and N.F.Curtis, J.Chem.Soc. Dalton Trans.,68(1967).
4. D.V. Cook and N.F.Curtis, J.Chem.Soc.,Dalton Trans., 1076,(1973)
5. N.F.Curtis, Coord.Chem.Rev.,3.3 (1968).

POLYMERIC BIPOSITIVE METAL COMPLEXES OF MULTIDENTATE SCHIFF BASE LIGANDS

Badri V. Agarwala, Pyare L. Maurya and Arun K. Dey
Chemical Laboratories, University of Allahabad, Allahabad 211002, India

Multidentate Schiff bases are potential catenating ligands for obtaining polymeric complexes which have been investigated for their spectral, magnetic and thermal properties. The coordination occurs both with keto- and enolic forms of the ligand and often leads to the formation of oxygen-bridged bi- and trinuclear complexes (1-3).

Polymerization reactions carried out by the condensation of bis(salicylaldehydo)metal(II) chelate with diamines 1,4-diaminobenzene(DAB) and 4,4'-diaminodiphenyl(DADP) are described. Two salicylaldehyde molecules are linked to each bipositive metal ion through the oxygen atoms of the phenolic and aldehydic oxygens to form the initial monomeric chelate. On interaction with diamines, the nitrogen atom of one of the amino groups replaces the aldehydic oxygen to form the polymeric metal complex. Evidence for the substitution of H atom of the OH group of salicylaldehyde to form M-O bond on complexation, disappearance of bands at 1625 and 3400 cm^{-1} in the spectra of Schiff base complexes and appearance of new bands at ~ 1560 and ~ 1600 cm^{-1} due to the formation of -C = N bonds is observed from i.r. spectra. DAB or DADP molecule acts as a bridging unit between the two bis(salicylaldehydo)metal(II) units.

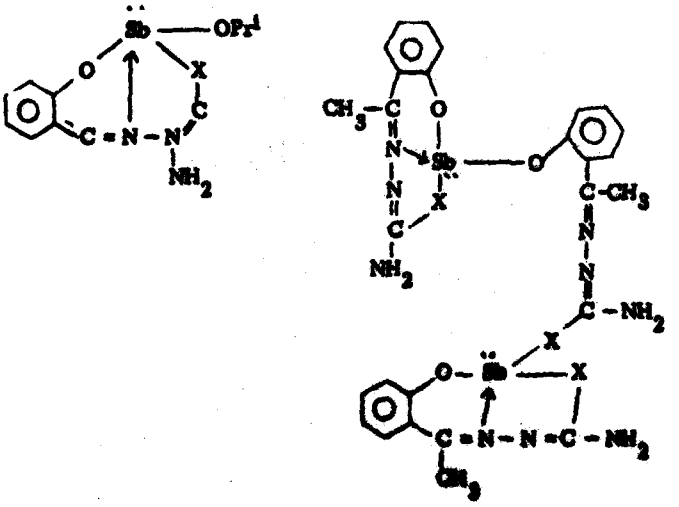
The geometry of the molecule is demonstrated by magnetic data and reflectance spectra, and their relative order of thermal stabilities is discussed.

1. S. Sinn and C.M. Harris, Coord. Chem. Revs. 1969, 4, 391.
2. P.L. Maurya, G.P. Dube and B.V. Agarwala, J. Ind. Chem. Soc. 1982, 59, 1400.
3. D. Khanna, V. Banerjie, B.V. Agarwala and A.K.Dey, Ind. J. Chem. 1982, 21A, 609.

X-RAY DIFFRACTION, MÖSSBAUER SPECTRAL AND RELATED STUDIES ON SOME Sb(III) COMPLEXES

Anil Saxena*, Ashok Kumar* and J. P. TANDON
Department of Chemistry University of Rajasthan, JAIPUR, INDIA.
*School of Molecular Sciences, University of Sussex, Brighton, U.K.

The bonding and structural features of some antimony (iii) complexes of the type, $(OPr^i)SbL_2$, Sb_2L_3 and $SbCl_3.L$ are described (where L is the dianion of semicarbazones, thiosemicarbazones and Schiff base of δ-benzyl dithiocarbazate). The Mössbauer spectra are typical of Sb(iii) complexes in which the non bonding pair of electrons is stereochemically active. The thiosemicarbazone complexes show more negative isomer shifts compared to the semicarbazone complexes as well as they are more readily oxidised to Sb (v) as evidenced by the presence of small amount Sb(v) species in Mössbauer spectra.



These complexes adopt [illegible] lattice on crystallization. All the complexes [illegible] antifungal- and antibacterial activities.

Wa35-5

BINUCLEAR DIVALENT PALLADIUM AND PLATINUM METAL CHELATES BRIDGES BY AROMATIC DIAMINES

M.P. Tantia and D.P. Singh

Department of Chemistry, Meerut College, Meerut, India

Divalent palladium and platinum chlorides react with m-phenylenediamine or 2,6-diaminopyridine and acetylacetone to form complexes of tetradentate ligands. The complexes are characterized to be dimeric square planar with diamine moieties acting as bridges, of the type: $[M(C_{19}H_{19}N_2O_2)]$ and $[M(C_{15}H_{17}N_3O_2)]$; where M=Pd(II) or Pt(II). The structures of complexes are established by the help of analyses, conductance, magnetic, electronic and infrared spectral studies. The ligands coordinate through all the azomethine nitrogens and carbonyl oxygen atoms by deprotonation, however, in 2,6-diaminopyridine complexes, pyridine-nitrogen does not take part in coordination.

STUDIES ON Cu(II), Ni(II), Co(III) COMPLEXES WITH 1,4,8,11-TETRAAZACYCLOHEXADECANE AND CYCLOHEPTADECANE

Ramesh Bembi, Randhir Singh, and Wahid U. Malik

Chemistry Department, University, Roorkee, India.

Two new macrocyclic ligands, 1,4,8,11-tetraazacyclohexadecane and 1,4,8,11-tetraazacycloheptane and their copper(II), Ni(II), and Co(III) complexes which carry 8- and 9-membered chelate rings, have been synthesized. The square planar copper(II) complexes show rapid acid catalyzed dissociation which has been studied by the stopped flow technique. A general mechanism proposed for the acid catalyzed dissociation of their polyamine complexes may be adopted for these complexes. The breaking of the second copper-nitrogen bond appears to be rate determining. The acid catalyzed path leading to dissociation is consistent with the following kinetic scheme:

$$[CuL]^{2+} + H^+ \overset{K}{\rightleftharpoons} [CuLH]^{2+}$$

$$[CuLH]^{2+} + H^+ \overset{k}{\rightleftharpoons} Cu^{2+} + [LH_2]^{2+}$$

and the rate expression is given by

$$k_{obs} = k_o + \frac{Kk[H^+]}{1+K[H^+]}$$

Electronic spectral data shows that the ligand field strength decreases with increasing ring size. The 5,6,5-chelate ring sequence is the stabilizing factor since it holds the macrocycle in a synthetically pre-oriented geometry suitable for coordination.

The yellow nickel(II) complexes in aqueous solution show an equilibrium between the four coordinate square planar and six coordinate diaquo octahedral species. The equilibrium constants and the thermodynamic parameters for this equilibrium have been evaluated by studying the temperature dependent electronic spectra.

The 6-coordinate cobalt(III) complexes are very stable and undergo facile axial substitution reactions. It has been possible to prepare cis-cobalt(III) complexes with acetylacetone and glycine as axial ligands. In these complexes the macrocycles attain a folded conformation with a C_2 axis.

THE INTERACTION OF 2,6-DIACETYLPYRIDINE-BIS (p-TOLUENSULFONYL)HYDRAZONE WITH Cu^{II}, Co^{II}, Ni^{II}, Zn^{II}, UO_2^{+2}, and U^{IV}.

G. Paolucci(1), G. Rossetto(2), and P. Zanella(2).

(1) Dipartimento di Chimica, Facoltà di Chim. Ind.le, Università di Venezia, Calle Larga S.Marta 2372, Venezia, ITALY.

(2) Istituto di Chimica e Tecnologia dei Radioelementi, Area di Ricerca C.N.R., Corso Stati Uniti, 35100 Padova, ITALY.

The title compound behaves as tetra- and penta-dentate chelating ligand depending on the nature of the metal ions. In addition the very high acidity of the hydrazonic hydrogens affords neutral complexes also in alcoholic neutral medium, indicating that the very low basicity of the alcohols is sufficient to deprotonate the intermediate ionic complexes. Thus a series of new complexes has been obtained, in which the ligand is present in its very unusual tautomeric form.
In the Table are summarized the analytical and spectroscopic data of the new complexes obtained.

TABLE

Compound	Calcd.				Found				I.R(cm^{-1})	
	C	H	N	S	C	H	N	S	$\nu_a SO_2$	$\nu_s SO_2$
H_2TSDAP	56.31	5.01	14.03	12.82	56.05	4.85	13.90	12.76	1391	1163
TSDAPCo	49.65	4.14	12.59	11.51	49.25	4.20	12.50	11.25	1210	1072
TSDAPZn H_2O	47.55	4.31	12.06	11.02	47.80	3.85	12.10	10.85	1272	1089
TSDAPZn	49.07	4.09	12.45	11.38	48.68	4.25	12.25	11.05	1212	1072
TSDAPNi H_2O	48.12	4.36	12.20	11.52	48.00	4.30	12.30	11.35	1262	1102
TSDAPNi	49.67	4.14	12.80	11.52	49.90	4.20	12.75	11.35	1224	1082
TSDAPCu H_2O	47.70	4.32	12.10	11.06	48.05	4.05	12.25	10.85	1263	1098
TSDAPUO$_2$	35.98	3.00	9.13	8.34	35.65	3.25	9.10	8.20	1265	1083
(TSDAP)$_2$U	44.80	3.73	11.36	10.39	44.05	3.50	10.85	9.95	1264	1075

MAKING AND BREAKING BONDS ON Ni CENTRES BONDED TO THE RIGID TERDENTATE LIGAND $[C_6H_3(CH_2NMe_2)_2\text{-}2,6]^-$

Gerard van Koten, David M. Grove and Rob Zoet
University of Amsterdam, Department of Inorganic Chemistry, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands.

As a result of both the special steric (planar NCN arrangement) and electronic (trans positioned hard N donor atoms) constraints of the anionic NCN ligand the nickel centres in complexes of type I show a varied and sometimes extraordinary chemical reactivity. Examples are:-

1. In the presence of water the equilibrium:

$$I + H_2O \rightleftharpoons [(NCN)Ni(H_2O)]^+ + X^-$$

is important and $[(NCN)Ni^{II}(H_2O)]^+BF_4^-$ has been isolated.

2. The reaction of I (X = Cl) with electrophiles (e.g. $Cu^{II}Cl_2$) results in the quantitative formation of $(NCN)Ni^{III}Cl_2$ via a ligand transfer oxidation route. Products originating from C-Ni^{II} bond cleavage are not formed. $(NCN)Ni^{III}I_2$ has a square planar pyramidal structure (X-ray: Ni-I 2.62 (mean) Å) and ESR spectra point to a d^7 electronic configuration of Ni. [1] The interconversion $Ni^{II} \rightleftharpoons Ni^{III}$ (X = Br) and vice versa occure at a surprisingly low $E_{1/2}$ of +0.38 V (vs. SHE; cyclovoltammetry in MeCOMe and Bu_4NBr) and parallels that recently found for the Ni site in hydrogenase. [2]



$(NCN)Ni^{II}X$ (I)

3. Of the great variety of $(NCN)Ni^{II}X$ complexes, the compounds with $X = NO_2$ (nitro form) and O_2CH (O-bonded formate, X-ray) are particularly notable. Whereas analogous $(NCN)Pt^{II}O_2CH$ eliminates CO_2 at room temperature to give "(NCN)Pt-H", $(NCN)Ni^{II}O_2CH$ is stable in boiling toluene. These and other species (X = RS, aryl etc.) are now being studied with particular regard to the identification of their unusual Ni^{III} oxidation products.

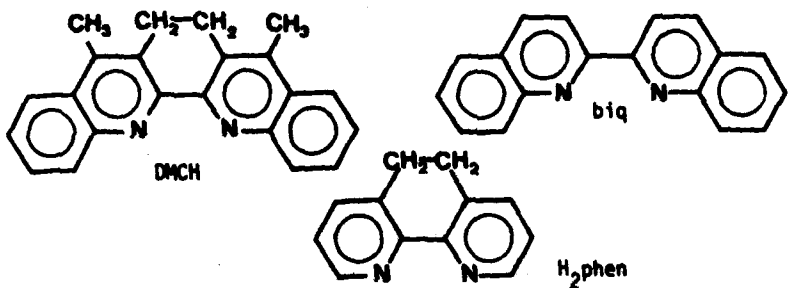
1. D.M. Grove, G. van Koten, R. Zoet, N.W. Murrall and A.J. Welch, J. Am. Chem. Soc. 1983, 105, 1379.
2. S.P.J. Albracht, E.G. Graf and R.K. Thauer, FEBS Lett. 1982, 140, 311.

STERICALLY CROWDED RUTHENIUM-POLYPYRIDYL COMPLEXES. LIGAND CONFORMATION AND PHOTOSUBSTITUTION.

Alex von Zelewsky and Peter Belser

Institute of Inorganic Chemistry, University of Fribourg, CH-1700 Fribourg (Switzerland)

Several sterically crowded polypyridyl ligands yield ruthenium(II)-complexes with interesting photophysical properties.[1-3] The structure of the complex $Ru(DMCH)_3^{2+}$ in its PF_6-salt has been determined



by X-ray methods.[4] The extreme crowding of the ligands in this complex leads to a relatively long Ru-N distance (2.115 A as compared to 2.056 A in $Ru(bpy)_3^{2+}$) and a pronounced puckering in the $-CH_2-CH_2-$ bridge caused by inter ligand repulsion. The conformations of the non-aromatic six-membered rings are identical for all three ligands yielding a $\Delta(\lambda,\lambda,\lambda)$, $\Lambda(\delta,\delta,\delta)$ enantiomeric pair. NMR-spectroscopy allows for an analysis of the ring motion also in the mixed $Ru(bpy)_{3-n}(DMCH)_n^{2+}$ complexes and in the related series $Ru(bpy)_{3-n}(H_2phen)_n^{2+}$, which contains the sterically much less demanding ligand H_2phen.

Photosubstitution reactions of the type (1)

$$Ru(bpy)_2(biq)^{2+} \xrightarrow[H^+]{H_2O} Ru(bpy)_2(H_2O)_2^{2+} + biq \qquad (1)$$

for the various members of the series indicate the consequences of the steric crowding for the reactivity in the excited state. The latter is determined mainly by two factors:

- The ligand field strength determined by the metall-ligand distance and
- The inherent ability of a coordinated ligand to undergo a ring closure reaction, once the chelate ring has been opened.

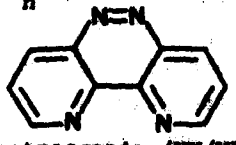
1. A. Juris, F. Barigelletti, V. Balzani, P. Belser and A. von Zelewsky, Israel J. of Chem. 22, 87 (1982).
2. P. Belser, A. von Zelewsky, A. Juris, F. Barigelletti, A. Tucci and V. Balzani, Chem. Phys. Letters, 89, 101 (1982).
3. F. Barigelletti, A. Juris, V. Balzani, P. Belser and A. von Zelewsky, Inorg. Chem. 22, 3335 (1983).
4. M. Zehnder, 12th Int. Cong. of Cryst., August 1981, Ottawa.

NEW RUTHENIUM(II) COMPLEXES WITH 4,5,9,10-TETRA-AZAPHENANTHRENE AS LIGAND

Peter Belser

University of Fribourg, Pérolles, CH-1700 Fribourg, Switzerland

A series of new ruthenium complexes, $Ru(bpy)_{3-n}(taphen)_n^{2+}$ with n = 1,2,3 has been prepared.



= taphen[1]

The spectroscopic (UV/VIS (absorption and emission), IR, NMR), electrochemical and photochemical properties were studied.

$Ru(taphen)_3^{2+}$ shows many similarities to $Ru(bpy)_3^{2+}$.

The MLCT-absorption (ε = 15000) is shifted to 436 nm and the emission lies at 660 nm (25°C).[2]

The ligand centered π-π^* transitions of taphen are easily discernible in the complex and in the free ligand.

Emission is observed for all the ruthenium complexes.

Protonation of the complexes at the azo-bridge is studied in the ground- and in the excited state.[3]

Chemical reactivity of the coordinated taphen is explored with respect to several transformations, particularly quaternization at the azo-bridge.

1. S. Kanoktanaporn and J.A. Hugh MacBride, J. Chem. Soc., Perkin 1, 1978, 1126.

2. P. Belser and A. von Zelewsky, Helv. Chim. Acta, 1980, 63, 1675.

3. R.J. Crutchley, N. Kress and A.B.P. Lever, J. Am. Chem. Soc., 1983, 105, 1170; R.J. Crutchley and A.B.P. Lever, Inorg. Chem., 1982, 21, 2276.

HALIDE COMPLEXES OF MOLYBDENUM(V)

Zelentsov V.V., Subbotina N.A., Kazin P.E.,
Zhirov A.I., Felin M.G.

Moscow State University, Moscow, USSR, 117234

A new series of anionic complexes A_2MoX_6 and $A_3Mo_2X_9$ (X - Cl or Br, A - protonated molecules of 8-oxyquinoline, 2-amino-4,6-dioxypyrimidine, mono- and diethanolamine) have been prepared. The complexes were caracterised by elementary analysis, UV-, VS- and IR-spectroscopy, X-ray powder analysis and magnetic susceptibility measurements of samples.

Bi-nuclear complexes possess low values of effective magnetic moments due to the presence of Mo-Mo bonds; the values of magnetic moments for mono-nuclear complexes are close to the spin values. A correlation of μ_{eff} to the size and the structure of organic cations had been observed. The presence of ammonium groups in the hexahalomolybdates had been proved.

An investigation of possibility of synthesis of molybdenum(V) complexes with organic ligands by isothermic dehydrohalogenation of corresponding halomolybdates in solide state had been carried.

By thermolysis of halomolybdates of 8-oxyquinolinium the coordination of organic ligand to the metal atom occures. By process of thermal decomposition of anionic halide complexes of ethanolamines the partial destruction of amine take place simultaneously with the ligand coordination. An analogous processes for the hexahalomolybdates of 2-amino-4,6-dioxypyrimidinium the dissociation without coordination of amine had been observed.

Wa35-12

SYNTHESIS AND STRUCTURE OF URANYL AMIDOXIME COMPLEXES

E.G. Witte and K. Schwochau

Institute of Chemistry, Nuclear Research Centre (KFA) Jülich,
D-5170 Jülich, Federal Republic of Germany

G. Henkel and B. Krebs

Anorganisch-Chemisches Institut der Universität
D-4400 Münster, Federal Republic of Germany

Our investigations on the extraction of uranium from seawater[1-4] revealed hydroxylamine derivatives of poly(acrylonitriles), so-called poly(acrylamidoximes), to be capable of accumulating uranium from natural seawater by more than 3600 ppm corresponding to a concentration factor of $1.1 \cdot 10^6$. Thus we have studied the complexing behaviour of the amidoxime functional group toward uranyl ions, in particular the coordination symmetry and the kind of donor atoms in monomeric uranyl amidoxime model complexes.

The uranyl complexes $[UO_2(\text{acetamidoxime})_4](NO_3)_2$ and $[UO_2(\text{benzamidoxime})_4](NO_3)_2 \cdot x\delta$ (δ=nitromethane or 1,2-dichloroethane, $x < 1$) were prepared by the reaction of uranyl nitrate with the corresponding amidoxime in ethanolic solution and characterized by infrared spectroscopy and thermal anlysis. The crystal structures of the acetamidoxime complex and the 1,2-dichloroethane containing benzamidoxime complex were determined by single crystal x-ray diffraction measurements. $[UO_2(\text{acetamidoxime})_4](NO_3)_2$ crystallizes in the monoclinic space group I 2/c with $a = 14.929(3)$, $b = 8.946(2)$, $c = 16.790(4)$ Å, $\beta = 96.01(2)^\circ$ and $Z = 4$ whereas crystals of $[UO_2(\text{benzamidoxime})_4](NO_3)_2 \cdot x$ 1,2-dichloroethane are triclinic, space group $P\bar{1}$ with $a = 9.890(4)$, $b = 14.826(6)$, $c = 15.227(6)$ Å, $\alpha = 75.76(3)$, $\beta = 87.13(3)$, $\gamma = 81.22(3)^\circ$ and $Z = 2$. In both complexes the linear uranyl group is equatorially surrounded by four oxygen atoms of monodentate amidoxime ligands, the mean bond lengths in $[UO_2(\text{acetamidoxime})_4](NO_3)_2$ and $[UO_2(\text{benzamidoxime})_4](NO_3)_2 \cdot x$1,2-dichloroethane being U=O = 1.775 and 1.778 Å and U-O = 2.320 and 2.326 Å, respectively. In accordance with infrared spectroscopic results the nitrate ions are not coordinated to uranium but interact with the ligand molecules via hydrogen bonds.

1. K. Schwochau, L. Astheimer, H.-J. Schenk, and E.G. Witte, Z.Naturforsch. 27b, 214 (1982)

2. H.-J. Schenk, L. Astheimer, E.G. Witte, and K. Schwochau, Sep. Sci. and Technol. 17, 1293 (1982)

3. L. Astheimer, H.-J. Schenk, E.G. Witte, and K. Schwochau, Sep. Sci. and Technol. 18, 307 (1983)

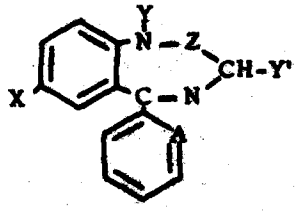
4. K. Schwochau, L. Astheimer, H.-J. Schenk, and E.G. Witte, Chemiker-Zeitung 107, 177 (1983)

SYNTHESES AND STRUCTURAL STUDIES OF SOME 1,4-BENZODIAZEPINE COMPLEXES

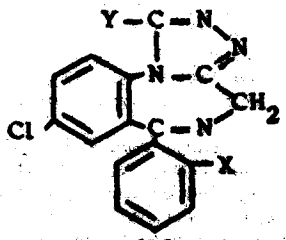
Adriano Benedetti*, Carlo Preti and Giuseppe Tosi

Centro Strumenti* and Istituto di Chimica Generale ed Inorganica, University of Modena, 41100 Modena, Italy

Following our interest in the chemistry of 1,4-benzodiazepines (1,2) owing to their biological and other applications, we report the results of the study of many d-block metal derivatives with the following ligands



(a)



(b)

(a)	Z-C(O), A-CH, X-Cl, Y-H, Y'-OH	Oxazepam
	Z-C(O), A-CH, X-Cl, Y-CH_3, Y'-OH	Temazepam
	Z-C(O), A-CH, X-NO_2, Y-CH_3, Y'-H	Nimetazepam
	Z-C(O), A-N, X-Br, Y-Y'-H	Brotizolam
	Z-CH_2, A-CH, X-Cl, Y-CH_3, Y'-H	Medazepam
(b)	X-Y-H	Estazolam
	X-Cl, Y-CH_3	Triazolam

The obtained complexes have been characterized through vibrational and electronic spectra, ^1H and ^{13}C n.m.r. studies, conductivity measurements, magnetic susceptibility data, thermogravimetric (TG and DTG) and crystal and molecular structure studies.

The results will be discussed in detail and compared each other for the same metal atoms along the series of the different benzodiazepines and for the different metals with the same benzodiazepines.

References

1. C.Preti and G.Tosi, J.Coord.Chem. 1979, 8, 233 and ref. therein quoted.
2. A.Benedetti, C.Preti and G.Tosi, J.Mol.Struct., in press.

Wa36-2

SYNTHESIS AND CHEMICAL BONDING IN HALOGEN CHALCOGENIDE COMPLEXES OF GOLD (III)

Z.A. Fokina and V.F. Lapko
Institute of General and Inorganic Chemistry, Ukr. SSR Academy of Sciences, 252601 Kiev, USSR

Gold chloride coordination compounds with chalcogen chloride ligands of the general formula $AuCl_3L$, where L = SCl_4, $SeCl_4$, TeCl, SCl_2, $SeCl_2$, have been synthesized in nonaqueous solvents.

The structure of the new coordination compounds has been studied by vibrational spectroscopy (IR, Raman), nuclear quadrupole resonance (^{35}Cl NQR) and electronic absorption spectroscopy (EAS) in the solid state, in molecular chalcogen halide melts and in nonaqueous solvents.

In $AuCl_3ECl_2$ complexes (where E = S, Se) (type I), the ligand is in the dichloride form and attaches itself to the central gold atom via the chalcogen atom. In $AuCl_3ECl_4$ (type II) complexes, the ligand is in the tetrachloride form and attaches itself to the gold atom via the chlorine atom.

In complexes of both types, a distortion of the square planar environment of the central gold atom and a decrease in the symmetry of the coordination centre to C_{2v} (IR, Raman) are observed. The symmetrical structure of $AuCl_4$ was established only for nonaqueous solutions of the $[SCl_2^+][AuCl_4]^-$ complex (EAS). In all other cases of type-II complexes, the ligand is coordinated via the chlorine bridge Au-Cl-E.

The differences in the nature of the chemical bonding of chlorine atoms to the central gold atom in $AuCl_3ECl_4$ are confirmed by the considerable quadrupole splitting in ^{35}Cl NQR spectra.

The diversity of the coordinated forms of gold complexes with chalcogen chlorides is due to the ambivalent nature of the ligands.

SPECTROSCOPIC STUDIES OF TRANSITION METAL ION COMPLEXES OF DIETHYLENE TRIAMINE PENTA-ACETIC ACID (DTPA) AND DIETHYLENE TRIAMINE PENTA-METHYLENE PHOSPHONIC ACID (DTPMP)

J Oakes and C G van Kralingen

Unilever Research Port Sunlight Laboratory, Quarry Road East, Bebington, Wirral, Merseyside, L63 3JW, England

The structures of DTPA and DTPMP complexes of transition metal ions in aqueous solution have been investigated by nmr, esr and electronic adsorption spectroscopy. It is shown that DTPA complexes are much less hydrated than corresponding EDTA complexes, consistent with the increase in stability constants. The most marked reduction in water binding on replacing EDTA by DPTA occurs with Fe^{3+} and Mn^{2+} and it is demonstrated, using esr, that there is a change in overall stereochemistry from 7- to a predominantly 6- coordinate structure for Fe^{3+}. Other DTPA complexes adopt octahedral symmetry as do all the DTPMP complexes. Complexes of DTPMP with Co^{2+}, Ni^{2+} and, to a lesser extent, Cu^{2+} have lower hydration numbers than the corresponding EDTMP counterparts, due to simultaneous binding of three nitrogen donors in DTPMP. The Fe^{III} DTPMP complex has one water bound similar to the Fe^{III} EDTMP complex, but the Mn^{2+} complex of DTPMP is more hydrated than the corresponding EDTMP complex. Finally, it is concluded that phosphonate groups produce a less effective crystal field than carbonyl groups.

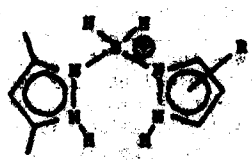
CHIRAL POLYPYRAZOLYL-BORATE LIGANDS AND COMPLEXES.

Erich Frauendorfer and Giuseppe Agrifoglio.

Escuela de Quimica, Facultad de Ciencias, Universidad Central de Venezuela, Caracas, Venezuela.

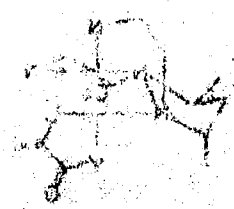
A new method for the synthesis of unsymmetrical dihydro-bispyrazolyl-borates using boron cations as intermediates has been developed.

A tetrahedral complex of boron with less than three negative ligands exhibits a positive charge. The synthesis of boron cations with two hydrides as negative ligands and two pyrazoles as neutral ligands will be described.



The reduction of these boron cations with sodium hydride or sodium powder gives the corresponding polypyrazolylborates Na $[H_2B(R\text{-}Pz)(R'\text{-}Pz)]$. Complexes with cobalt, nickel and zinc have been obtained and characterized. The X-ray structure of the complex $[H_2B(3,5\text{-}Me_2Pz)(3,5\text{-}Ph_2Pz)]_2Zn$ confirms a structure of essentially C_2-symmetry.

Reaction of $Na[H_2B(3,5\text{-}Me_2Pz)(Pz)]$ with 4-chloropyrazole produces the first chiral polypyrazolyl-borate $Na[H(3,5\text{-}Me_2Pz)(Pz)(4\text{-}ClPz)]$.



STEREO SPECIFIC INFLUENCES OF AN AXIAL C-METHYL GROUP IN CIS-β 2,3,2-TET CO(III) SYSTEM

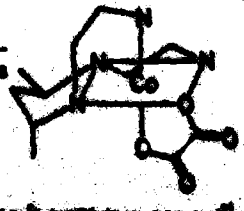
Morio Yashiro, Masanobu Ajioka, Shigenobu Yano and Sadao Yoshikawa

Department of Synthetic Chemistry, Faculty of Engineering, University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113, JAPAN

In the asymmetric synthesis, how to design an asymmetric environment is the most important subject. It has been reported that the cis Co(III) complex containing a tetramine of 2,3,2-type which has an optical active 2R,4R-pentanediamine moiety takes Λ-β geometry stereo specifically[1] (figure). We applied the specificity in developing an asymmetric synthesis of α-amino acids.[2] X-ray studies of these cis complexes show a central six-membered ring adopts chair conformation with one methyl group axial and the other equatorial.[2,3] Because the six-membered ring, which has the origin of the stereo specificity, takes symmetrical chair conformation, it is difficult to explain why Λ-β was the only product and Δ-β form was not obtained. Here, in order to elucidate the factor to present these remarkable specificity, we have newly synthesized a cis Co(III) oxalato complex with 5R-Me-2,3,2-tet, which has only one methyl group, and have examined the stereo selectivity.

5R-Me-2,3,2-tet was added to an aqueous solution of $K_3[Co(ox)_3]$ and stirred in the presence of activated charcoal at 50°C for 3 h. ^1H and ^{13}C NMR spectra of the reaction mixture shows the existence of the two isomers of [Co(ox)(5R-Me-2,3,2-tet)]$^+$. We have succeeded to separate them by column chromatography on a Dowex 50W-X8 cation exchange resin (0.2M $NaClO_4$-H_2O eluent, 70cm x 4.5cm). Red crystals from each band have been characterized by elemental analysis, NMR, AB and CD spectra and the molecular model studies. The two isomers was identified as Λ-β- and Δ-β-[Co(ox)(5R-Me-2,3,2-tet)]$^+$, in which each central six-membered ring takes a chair conformation with an equatorial methyl group. At a thermodynamic equilibrium using the method of Dwyer et al.[4] at 20°C, the isomers ratio of Λ-β and Δ-β was found to be a 47/53.

We have performed the strain energy minimization calculation of the related structures including Λ-β- and Δ-β-[Co(ox)(5R,7R-Me_2-2,3,2-tet)]$^+$(using the CONFAN2 program[5]). The results obtained well corresponded to the experimental data. Thus, the results suggested that the equatorial methyl group is not significant and the axial methyl plays an important role to obtain the stereo specificity of 2,3,2-tet Co(III) system.



1. F. Hirayama, Bull. Chem. Soc. Jpn., 1973, 46, 472.
2. M. Ajioka, et al., J. Am. Chem. Soc., 1981, 103, 2459.
3. S. Yano, et al., Inorg. Chem., 1978, 17, 16.
   S. Yano, et al., XXII I.C.C.C., Budapest, abstracts.
4. F. P. Dwyer, et al., J. Am. Chem. Soc., 1965, 87, 901.
5. M. Yamagami, et al., Inorg. Chem. 1980, 19, 2435.

ETHYLENEDIAMINE(TETRAMETHYLENEPHOSPHONIC) ACID: A NOVEL TRANSITION METAL COMPLEXING AGENT?

D. Cummins

Unilever Research Laboratory, Port Sunlight, Wirral, England

EDTMP is a strong complexing agent for a number of transition metals. Preliminary investigations of its equilibria with Cu(II), Ni(II), Co(II), Zn(II), Mg(II), Ca(II) and Fe(III) have been published, but little work has been carried out subsequently on the nature of its transition metal complexes. Its importance as a sequestering agent for metal ions has, however, been noted and its sequestering ability has been compared with that of EDTA[1]. We have studied the binding of Co(II) and Fe(III) by EDTMP and have compared the complexes formed with their carboxylate analogues.

In the solid state, both Co(II) and Fe(III)-EDTMP are six-coordinate complexes[2]. Their electronic absorption spectra show bands at 1250, 625 and 550(s), 505, 475 nm and at 1065 and 760 nm, typical of Co(II)[3] and Fe(III)[4] respectively.

In the solution state, however, different structures are observed. For Fe(III)-EDTMP these bands are shifted to 960 and 690 nm, respectively. Two alternative structures can be proposed to explain these observations: the first is a seven-coordinate structure analogous to that of Fe(III)-EDTA, the second is an "expanded" six-coordinate structure in which either 5 or 6 ligand groups are bound to the Fe(III). These structures will be discussed and additional spectroscopic evidence will be presented to support the proposed structure.

The spectrum of the Co(II) complex in solution is markedly different from its spectrum in the solid state, the lowest energy band being split and shifted to lower wavelength (920 and 800 nm) and the higher energy band (580(s), 545, 500 nm) being of considerably higher intensity (by a factor of >3). The spectrum is characteristic of Co(II) in a five-coordinate high-spin environment[5]. That Co(II)-EDTMP is high spin is confirmed by solution nmr measurement of the magnetic susceptibility; the magnetic being 4.8 BM.

1. R.J. Motekaitis, I. Murase and A.E. Martell, Inorg Chem., 15, 2303, 1976.

2. D. Cummins and T.C. van Soest, Proc XXI ICCC, Toulouse, 1980.

3. E.V.B. Stuttgallich, T.E. Michaeli, J.A. Muir, E.C. Lingafelter and E.J. Rose, Inorg. Chem., 17, 1978.

4. E. Garbatt, G. Long and R.J.P. Williams, [illegible], 1411, 1971.

5. [illegible]

DERIVATOGRAPHIC STUDY OF [illegible] COMPLEXES OF TRANSITION METALS WITH SALICYLIC ACID

H.C. Mishra and R.R. Jha

Department of Chemistry, Ranchi University, Ranchi 834 008, India.

The complexes were prepared by interaction of metal carbonate and hot aqueous solution of salicylic acid in 1:2 molar ratio. In case of Ti(III), Cr(III), Fe(III) and Fe(III) freshly prepared hydroxides were used. The composition of the complexes obtained were represented by [illegible] (n=2 in case of Ti(III) and Zn(II) and n=4 in case of Fe(II), Co(II), Ni(II) and Cu(II)). [illegible] in case of Cr(III) and [illegible] in case of Zn(II) which were established by elemental analysis, electronic, i.r., nmr spectra and chemical tests. The magnetic susceptibility measurements and electronic reflectance spectra indicate six coordinated distorted octahedral arrangement. X-ray results confirm octahedral structure and mode of binding of multiple ligand.

The general trend of T.G.A. curve is that the dehydration starts at 80±10°C and terminates at 150±20°C and is shown by endothermal peak in D.T.A. curve. The second step starts at 240±10°C and ends at 340±15°C and is shown by exothermal peak in D.T.A. curve. This step is due to the oxidation of salicylic acid moieties. This step is shown by endothermal peak in D.T.A. curve. The decomposition of [illegible] starts at 240±10°C and ends at [illegible] and is shown by exothermal peak in D.T.A. curve. [illegible]

ALUMINUM(III) ALIZARIN RED S COMPLEXES

John C. Cooper, Sharon Livingston, and Nancy S. Bowen

Inorganic and Electrochemistry Branch, Naval Research Laboratory, Washington, DC 20375

Aluminum is an extremely reactive metal but rapidly becomes coated with an oxide layer which protects it from further reaction with its environment. As part of studies of ligands that will remove this oxide coating, we have characterized complexes of 3,4-dihydroxy-9,10-dioxo-2-anthracenesulfonic acid (Alizarin Red S) and aluminum(III) in solution over a wide range of pH's. Alizarin Red S has a pK_{a_2} of 5.76 and pK_{a_3} of 10.79. Because the complexes formed are colored, uv-vis spectroscopic methods can be used.

Molar ratio method and continuous variation studies have shown that at pH 4.0 Alizarin Red S forms a complex with Al^{3+} which has an absorbance maximum at 475 nm and an Alizarin Red S to Aluminum ratio of 2 to 1. The complex follows Beer's law for an aluminum concentration range of 1×10^{-4} to 6×10^{-4} M. At pH 8.3 the λ-max of the complex shifts to 485 nm and the intensity increases. Here molar ratio and continuous variation plots have shown that the Alizarin Red S to Al^{3+} ratio is 3 to 1. The solutions are mixed at pH 4 and then the pH is raised to 8.3 with concentrated tris buffer. The complex precipitates in the 6 to 7.5 region and a change in λ-max and intensity occurs above pH 7.5. No complex forms with the Alizarin Red S above pH 11.5.

An earlier study had shown from both the method of continuous variation and from electrical conductance studies that a 2:1 Alizarin Red S to Aluminum(III) complex with λ-max = 470 nm formed at pH 8.5 and that the intensity and absorbance maximum changed as the pH was increased. The log of the equilibrium constant at pH 8.5 was determined to be 7.2 by these workers and they suggest that the aluminum is bound to the phenolic oxygens.[1] Others have suggested that it is bound to a quinone oxygen and a phenolic oxygen.[2] Elemental analyses and infrared spectrum, combined with other characterization methods of the isolated solid complexes helped to characterize the coordination site. These results will be discussed.

1. E. L. Roth and A. K. Roy, J. prakt. Chem. 1963, 4, 239.

2. E. G. Kiel and P. H. Hoeritjes, J. Soc. Dyers. Colourists, 1963, 79, 21.

SYNTHESIS AND CHARACTERIZATION OF 5-(SUBSTITUTED AZO)-BARBITURIC ACID COMPLEXES

Mamdouh S. Masoud, Tahany M. Salem, and Zenat Zaki

Chemistry Department, Faculty of Science, Alexandria, Egypt.

Different azo ligands of the biologically active compounds derived from barbituric and thiobarbituric acids are synthesized. The ligands are characterized by spectral methods (NMR, IR, UV and VIS). Some of the compounds are in the azo form and others are in the hydrazo structure. The pK's values, evaluated by spectrophotometric and potentiometric methods, are highly affected by the electronic character of the substituent. The azo-hydrazo equilibria is highly affected by changing the physical properties of the solvent to affect the phenomena of tautomerism. The synthesized complexes of Co(II), Ni(II) and Cu(II) salts of the entitled ligands gave different stoichiometries, but mainly with the 1:2 mole ratio. The mode of bonding is determined by IR where in most complexes the azo moiety is not in the coordinated environment. The geometry of the complexes is determined by recording the electronic spectra; there are 4-, 5- and 6-coordinated systems. The electron spin resonance of the copper complexes at different temperatures is done. The magnetic properties at variable temperatures are evaluated where Curie-Weiss law is obeyed. The stability constants of some complexes are computed where a relationship between log β and pK_L is constructed.

COPPER(II) HALIDE COMPLEXES OF NITRO-SUBSTITUTED PYRIDINE N-OXIDES

Margaret Farago and Sossi Dichakjian

Chemistry Department, Royal Holloway and Bedford Colleges,
Egham Hill, Surrey TW20 OEX, U.K.

Complexes of 4-nitro 2,6 Lutidine N-oxide (L), and 3- nitro 2,6-Lutidine N-oxide (L') with $CuCl_2$ and with $CuBr_2$ have been prepared and studied by a number of techniques.

Compounds of the type CuL_2X_2 and CuL'_2X_2 are green and have magnetic moments of about 1.75 BM at 85K, rising to 1.8 BM at room temperature. In addition to the green CuL_2Br_2, a brown isomer can be prepared, which has a magnetic moment of 1.06 BM, independent of temperature between 85 and 300K.

The crystal structure of CuL'_2Cl_2, as representative of the green compounds, shows that the complex is four-coordinate, trans-planar and monomeric, where the CuL'_2Cl_2 units are well separated from each other. The Cu-O and Cu-Cl bond lengths are 1.941(1) and 2.229(0) A respectively. The two independent cis Cl-Cu-O angles are 85.73(4) and 92.27(4)°, while the trans O-Cu-O' and Cl-Cu-Cl' are 179.98(6) and 179.97(3)° respectively. The ring planes are inclined at an angle of 117.83(7)° to the basal plane containing the central metal atom. This orientation brings the two methyl groups into positions which hinder axial approach to the Cu(II) ion, and therefore prevents formation of dimeric or plymeric species. The structure is not novel in the series of copper(II) pyridine N-oxide halide complexes, except for its more distorted nature, which is probably brought about by steric crowding near the donor site.

The brown isomer CuL_2Br_2 may also be described as square planar, since the Br-Cu-O bond angles are 90.00°. However, the Cu-Br bond lengths are shorter (2.272 A) than the Cu-O bonds (2.689 A). The dihedral angle between the plane of the coordinated atoms and the pyridine ring is 97.1° placing the two methyl groups in the axial positions. However, the relatively long Cu-O (N-oxide) distance allows some interaction to take place between the nitro-oxygen and the next copper ion. Thus another way of describing the complex would be to consider a linear Br-Cu-Br structure with four semi-coordinated ligands on the other axes of a grossly distorted tetragonal. Thus instead of coordination with one strong bond through the oxygen of the N-oxide group (as is expected in the green isomer), two weak bonds between Cu(II) and two donor sites are formed. The magnetic behaviour and its relation to the structure of the complex will be discussed.

CHROMATOGRAPHIC AND SPECTROMETRIC INVESTIGATION OF SOME TRANSITION METAL COMPOUNDS WITH UNSYMMETRICAL β-DIKETONES

Bernd Wenclawiak und Peter Schultze

Anorganisch Chemisches Institut der Universität, Corrensstr. 36, D-4400 Münster, FRG

Like other not fluorinated unsymmetrical β-diketonates [1], the octahedral Cobalt and Chromium Tris-2,2,7-trimethyloctane-3,5-dionates show fac and mer isomers, which can be seperated by reversed phase liquid chromatography [2]. They were identified by spectrometric methods such as NMR (for Co(tod)$_3$), MS and UV-VIS (for Co(tod)$_2$ and Cr(tod)$_3$) [3].

The Bis-2,2,7-trimethyloctane-3,5-dionates of Mercury and Palladium have been investigated. Pd(tod)$_2$ is coordinated like a chelate. High resolution 300 MHz ^{1}H-NMR however produces more signals than expected. This gives evidence for structural isomers as cis- and trans-square planar coordination.

The metal-tod chelates are easily dissolved in unpolar solvents. Hg(tod)$_2$ needs a more polar solvent. Spectra of IR and ^{13}C-NMR show free carbonyl groups and MS and SIMS show different fragmentation compared with other metal-bis-β-diketonates. This indicates no chelate conformation.

Additionally we will discuss the spectrometric investigations on other unsymmetrical aliphatic metal-β-diketonates and the liquid chromatographic separation of all geometrical isomers of tris coordinated metal ions with two different β-diketone ligands.

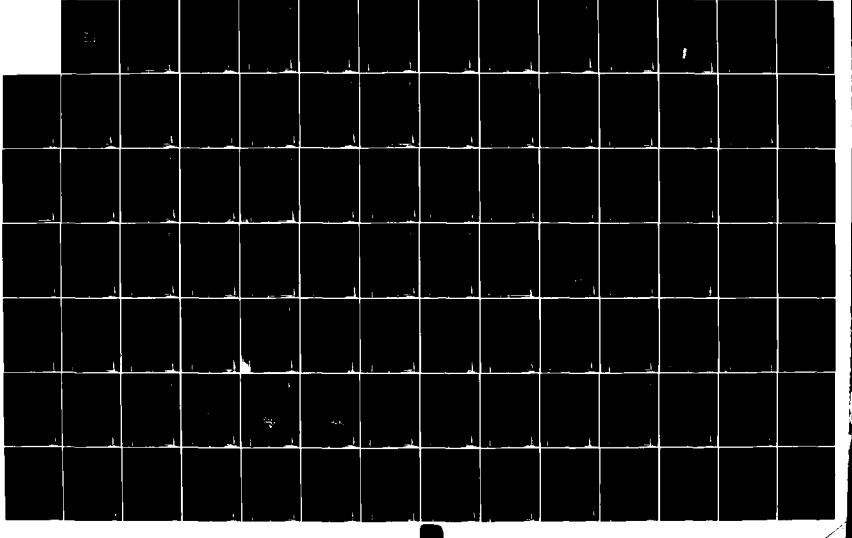
1. R.C. Fay and T.S. Piper, J. Am. Chem. Soc. 1962, 84, 2303
2. B. Wenclawiak and R.E. Sievers, Fres. Z. Analyt. Chem. 1983, 314, 682
3. B. Wenclawiak; R.M. Barkley; E.J. Williams and R.E. Sievers, submitted for publication

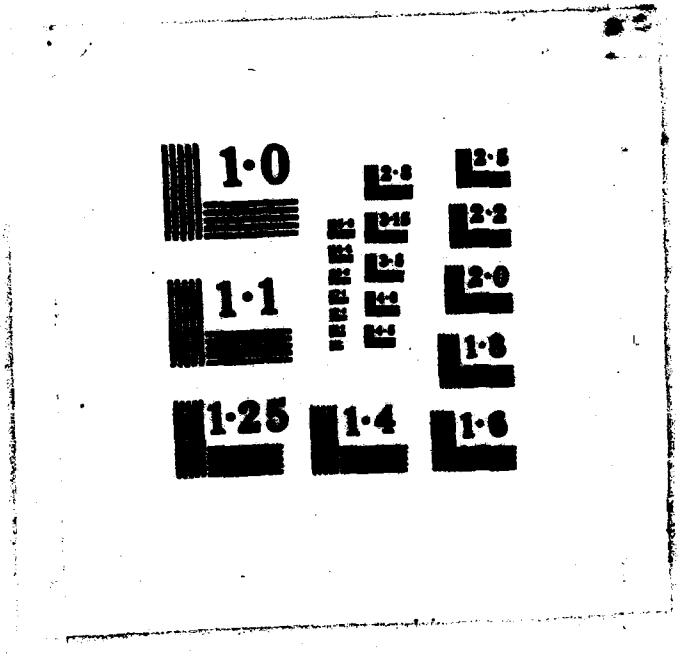
AD-A148 190 [INTERNATIONAL CONFERENCE ON COORDINATION CHEMISTRY (23RD) HELD AT BOULDER..(U) COLORADO UNIV AT BOULDER E L KING ET AL. 03 AUG 84 ARO-21423.1-CH-CF

UNCLASSIFIED DAAG29-84-M-0109 F/G 7/4

5/8

NL




1·0
1·1
1·25
1·4
1·6
1·8
2·0
2·2
2·5

STRUCTURE OF METAL COMPLEXES WITH UNSTABLE CHALCOGEN HALIDES AS LIGANDS

S.V. Volkov, N.I. Timoshchenko and V.L. Kolesnichenko

Institute of General and Inorganic Chemistry, Ukr. SSR Academy of Sciences, 252601 Kiev, USSR

Until now, coordination compounds of III-V groups elements and gold with unstable, under normal conditions, sulphur tetrachlorides, which is coordinated via the bridge chlorine up to its entire detachment and formation of SCl_3^+ and complex MCl_n^- (n = 1, 2), have been known.

Recently, we have synthesised coordination compounds of palladium and platinum: $PdCl_2(SeCl_2)_2$, $PtCl_4(SeCl_2)_2$ with selenium dichlorides, which is stable only in pairs (> 200 °C) and brings about coordination via the selenium atom over the transpositions of the complex[1,2].

At the present time, new thioselenchalide complexes of molybdenum and tungsten (M): MS_2SeX_2 (X = Cl, Br) have been obtained and investigated. Their composition was determined by chemical analysis, the individuality was confirmed by X-ray study, and the structure was studied by NMR, NQR on halogen atoms and vibrational (IR, Raman) spectroscopy.

The presence of a disulphide group bound to metal atoms in the $M\langle^{S}_{S}$ fragment has been established. It has been shown that selenium dihalide splits out, and a metal thiohalide forms by thermal decomposition.

Thus, molybdenum and tungsten thioselenchalides are metal thiohalide and selenium dihalide complexes $S_2\text{-}\overset{X}{\underset{SeX_2}{M}}\text{-}X_2$. Coordination of selenium dibromide, which is unstable under normal conditions, has been established for the first time.

1. S.V. Volkov, Z.A. Fokina and N.I. Timoshchenko, Proc. XXth IUPAC, Moscow, 1973, p. 207.
2. S.V. Volkov, Z.A. Fokina and N.I. Timoshchenko, Rev. Chim. Minerr. (in press).

ELECTRONIC STRUCTURE OF METAL CLUSTERS. A NOVEL APPROACH.

Mauro Bacci

Istituto di Ricerca sulle Onde Elettromagnetiche del CNR,
Via Panciatichi 64, 50127 Firenze, Italy.

During last years many efforts have been devoted to the understanding of the electronic structure of multinuclear metal clusters. However the theoretical results are very sensitive to the utilized approach and often just the same method of analysis provides different results depending on the approximations, which were introduced in the calculations.

In the present communication it is proposed that the electronic structure of highly symmetrical metal clusters can be profitably described by considering, before the inclusion of ligand field effects, the valence electron cloud to be subject to a spherical potential and delocalized over the whole complex. As a matter of fact the problem reduces itself to the evaluation of the electronic levels in a quite similar fashion as in free atoms or ions.

The usefulness of the approach is shown for several classes of metal clusters such as the Fe_4S_4 centers in iron-sulfur proteins and the metal clusters series, which are encountered in Chevrel phases.

PREDICTABLE COMPLEX CHEMISTRY OF UNSATURATED QUARKS

Christian K.Jørgensen
Section de Chimie,Université,CH1211 Geneve4,Switzerland

Like the century between Boyle and Lavoisier consolidated the concept of elements,the last 20 years have seen established that matter with positive rest-mass consists of quarks(electric charges a small multiple of e/3)and of leptons(such as electrons).Chemists might leave the internal structure of nuclei(with charge Ze)to physicists,if it was not that Fairbank(U.Stanford)consistently finds fractional charges of niobium balls suggesting one unsaturated quark per 10^{20} nucleons(0.16mg),the higher limit of the concentration ranges predicted by Wagner and Steigman 1979 of survival after the Big Bang,when the condensation to nucleons happened at a dew-point 2 teraKelvin.Systems containing unsaturated quarks cannot be fully neutralised by electrons,and introduced atomic numbers(Ze+1/3)intercalated in the Periodic Table.They have high affinity to metallic samples,and to materials with pronounced chemical polarizability and non-innocent ligands.They must have undergone extensive geochemical [illegible] and whereas the mere mobile carriers in niobium are likely to have Ze+1/3 or 1/3(diquark adjwith loosely bound electrons,the fixed carriers may be fission products with Z close to 45,73,91,105,...and the calculated photon of the ridge(above more than 10^{-30} nucleons)changing to the heat curve,at high atomic weights.Concentration from solution may occur on Prussian blue or heteropolyanion-resins relevant to varying oxidation number of by [illegible] chemistry in a deoxygenated non-oxidising solution.[illegible] (I) and [illegible] Organic acid extraction of [illegible] oxidising after collidal [illegible] [illegible] followed by [illegible]

1. C.K.
2. C.K.
3. C.K.
4.
5.
6.

METAL d-ORBITAL SPIN AND CHARGE POPULATIONS COMPARED

Brian N. Figgis and Philip A. Reynolds
School of Chemistry, University of W.A., Nedlands, Australia 6009

For three compounds both spin density distribution from polarised neutron diffraction (p.n.d.) and charge density distribution from accurate low temperature X-ray diffraction are available. It is of interest to compare the metal d-orbital populations which can be obtained from each by modelling the covalent distributions in terms of atomic orbital occupation numbers.

Manganese phthalocyanine[1]: the moderate quality p.n.d. data set gives $a_g^{2.3}\ b_{2g}^{0.7}\ a_{1g}^{0.8}\ b_{1g}^{-0.2}$ spin units, while a moderate quality X-ray data set gives $a_g^{1.3}\ b_{2g}^{1.5}\ a_{1g}^{0.9}\ b_{1g}^{0.1}$ charge units. With simple assumptions and guidance from theory, the spin populations may be used to deduce a charge population set $a_g^{2.0}\ b_{2g}^{1.3}\ a_{1g}^{0.8}\ b_{1g}^{0.2}$, agreeing semi-quantitatively with the X-ray set.

trans-tetraamminedinitronickel(II)[2]: the good quality p.n.d. and X-ray data sets yield respectively $t_{2g}^{6.0}\ e_g^{1.7}$ spin units and $t_{2g}^{5.0}\ e_g^{2.6}$ charge units (using octahedral notation for clarity). The simple assumptions yield charge populations $t_{2g}^{6.0}\ e_g^{2.3}$ from the spin results, again showing fair agreement between the two techniques.

bis(n-propylcyclopentadienyl)iron(III) tetrachloroferrate(III)[3]: the accurate but somewhat limited p.n.d. data set yields $t^{4.4}$ and $e^{4.0}$ spin units respectively for the cation and the anion, it not being possible to distinguish between the t_{2g} and the a_g orbitals. The good quality X-ray data give for the cation charge $t_{2g}^{3.9}\ a_g^{1.7}$ ($e^{5.6}$) and for the anion $t_{2g}^{3.8}\ e^{3.2}$ ($e^{3.2}$). If it is accepted that the d-orbital population is indeed greater than the free-iron Fe^{3+} value of 5, the spin results yield charges $t^{4.4}$(tet) and $t^{4.0}$(oct), giving satisfactory agreement between the methods.

1. (a) B.N. Figgis, G.A. Williams, J.B. Forsyth and E. Sinn, J. Chem. Soc. Dalton Trans., 1981, 1837; (b) B.N. Figgis, E.S. Kucharski and G.A. Williams, J. Chem. Soc. Dalton Trans., 1980, 1515.
2. G.E. Chandler, B.N. Figgis, E.S. Kucharski, P.A. Reynolds and E. Sinn, J. de Physique, 1982, 43, C7-323.
3. (a) B.N. Figgis, P.A. Reynolds and E. Sinn, Inorg. Chem., 1982, in press; (b) B.N. Figgis, P.A. Reynolds and A.H. White, to be published.

ELECTRONIC STRUCTURE OF ALKYNE OLIGOMERIZATION COMPLEXES BY UV PHOTOELECTRON SPECTROSCOPY AND AB INITIO CALCULATIONS

G. Granozzi[a], G. Biscontin[a], D. Ajò[b], M. Casarin[b] and S. Aime[c]

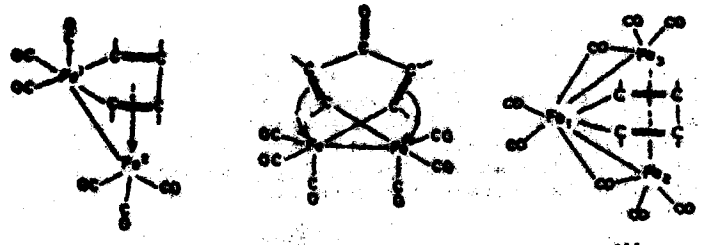
[a]Istituto di Chimica Inorganica, University of Padova (Italy),

[b]Istituto di Chimica e Tecnologia dei Radioelementi CNR,Padova(Italy)

[c]Istituto di Chimica Inorganica, University of Torino (Italy)

Reactions between iron carbonyls and acetylenes give rise to several bi- and tri-nuclear compounds where the alkyne group undergoes various type of oligomerization pathways (1). In these compounds both the metal-metal interactions and the bridging role of some carbonyls are in discussion (2,3).

We report here the gas-phase He(I) and He(II) excited photoelectron spectra of compounds I, II and III together with the results of minimal basis set ab initio pseudopotential calculations (4).



I II III

The results will be compared with those of a previous study on the related $Fe_2(CO)_6$(butatriene) molecule (5).
For compounds I and III we have been able to detect distinct ionization events which are to be related to the in-phase and out-of-phase combinations of the two "radical" lobes of the butadienyl fragment representing the two Fe-C σ bonds.

(1) H. Bönnemann in "Organic Synthesis via Metal Carbonyls", eds. I. Wender and P. Pino, Interscience, New York 1968, vol. 1.
(2) F.A. Cotton and J.M. Troup, J.Amer.Chem.Soc., 96 (1974) 1233.
(3) F.A. Cotton, Prog. Inorg. Chem., 21 (1976) 1.
(4) J.C. Barthelat, M. Pelissier and A. Serafini, Mol. Phys., 33(1977) 159.
(5) G. Granozzi, M. Casarin, S. Aime and D. Ajò, Inorg.Chem. 21 (1982) 4005.

AB INITIO MO STUDIES OF THE ELECTRONIC PROPERTIES AND STRUCTURES OF FOUR-COORDINATED DIVALENT ZINC(II), COPPER(II) AND NICKEL(II) ACETYLACETONATES

S. Shibata and F. Hirota

Department of Chemistry, Shizuoka University
Oya, Shizuoka, Japan 422

Ab initio SCF MO calculations were carried out on the four-coordinated acetylacetone complexes of Zn(II), Cu(II) and Ni(II) complexes. Gas electron diffraction experiments gave that the Zn(II) complex is tetrahedral[1] and Cu(II) and Ni(II) complexes are square-planar. The present studies have been undertaken to explain the experimental results by the theoretical calculation.

The calculations were performed using the library program JAMOL 3.[2] The Gaussian sets of (7s3p) contracted to (2s1p) were used for carbon and oxygen and the sets of (12s6p4d) contracted to (5s2p1d) were used for the metals. A diffuse p orbital was added to represent a 4p orbital of the metal. In the calculations the preference of the conformation, D_{2h} of D_{2d} was checked and most of molecular parameters were fixed in the experimental values.

The calculations gave the results that the Zn(II) complex takes a tetrahedral conformation D_{2d} of A_1, and the Cu(II) and Ni(II) complexes take square-planar conformation D_{2h} of $^2B_{2g}$ and ^1A_g, respectively, in agreement with the observed results. The calculation could also explain successfully the observed d-d absorption spectra of the Cu(II) complex.

According to the calculations the overlap population of the metal-oxygen bond is about 0.3 in all of the complexes. About one electron is transferred to the non-bonding π orbital of the ligand from the metal. Thus the metal-oxygen bonding is essentially ionic. The latter also support the experimental results that the structure of the ligand part in the complex is nearly the same as that of acetylacetone itself.

1. S. Shibata and M. Onto, J. Mol. Struct., 1981, 77, 269.
2. M. Kashiwagi et. al., Library program of the Institute of Molecular Science.

MOLECULAR ORBITAL STUDIES OF SOME BINUCLEAR PLATINUM DIPHOSPHITE COMPLEXES

Edward A. Boudreaux

University of New Orleans, Department of Chemistry, Lakefront, New Orleans, LA. 70148 USA

Molecular orbital calculations according to the SC-MEH method[1] have been carried out on the bis-platinum diphosphite dimers, $Pt_2(P_2O_5H_2)_4X_2^{n-}$, where the platinum atom are in the (II) or (III) oxidation states and X=Cl^-, Br^-, H_2O, or vacant.

The fact that a surprisingly substantial negative charge (ca.-0.6 to -0.7) resides on the Pt atoms will be discussed in relation to the uniqueness of the chemical bonding, and its relationship to the photoredox behavior of these complexes. The significance of the platinum 6p orbital involvement in bonding relative to the 5d orbitals, is a key feature in rationalizing the nature of the metal-metal bonding in these systems.

Calculated Pt-Pt bond energies and uv-visible spectra will also be presented and discussed.

1. T.P. Carsey and E.A. Boudreaux, Theoret Chim. Acta, 1980, 56 211, and references quoted therein.

FUNDAMENTAL ELECTRONIC PROPERTIES OF TRANSITION-METAL COMPLEXES: THE CORRELATION OF CORE AND VALENCE IONIZATION ENERGY SHIFTS IN METHYL-SUBSTITUTED FERROCENES

Dennis L. Lichtenberger and Gary P. Darsey

Department of Chemistry, University of Arizona, Tucson, Arizona, USA 85721

Knowledge of the relationship between metal core ionization energies and localized metal valence ionization energies can be a valuable aid in evaluating the nature of the bonding and the distribution of electrons in metal complexes. The relative shifts of core and valence ionizations are useful because both are sensitive to charge distributions and relaxation energies, but only the valence ionizations are sensitive to orbital overlap interactions[1]. Ferrocene and its methyl-substituted derivatives are excellent molecules for studying the relative core and valence ionization energy shifts because the valence metal $a_{1g}(d_{z^2})$ ionization energy band is one of the sharpest known for metal complexes, indicating that the $a_{1g}(d_{z^2})$ orbital is largely non-bonding and localized on the metal.

A gas-phase core and valence photoelectron spectroscopic study is reported for a series of symmetrically and unsymmetrically methyl-substituted ferrocenes. Examples include ferrocene, 1,2,4,1',2',4',-hexamethylferrocene, decamethylferrocene, and 1,2,3,4,5-pentamethylferrocene.

A consistent trend in the observed core [$2p_{3/2}$ Fe and 1s C] and valence [$a_{1g}(d_{z^2})$ and e_{1g}(ring pi)] ionization energy shifts is found, and this trend reveals several surprising results. First, the $2p_{3/2}$ Fe core and $a_{1g}(d_{z^2})$ valence ionization energies show almost equivalent shifts upon methyl group substitution. However, the 1s C core and e_{1g} (ring pi) valence ionization energy shifts are not at all equivalent, with the valence shifts being at least four times as large as the core shifts. This difference in shifts is due to the overlap of methyl group orbitals with the ring pi orbitals[2]. It is also interesting that both the core and valence shifts are found, in all cases, to be additive with respect to the number of methyl groups on the cyclopentadienyl ligands. These observed shifts provide a quantitative measure of the effect of methyl group substitution on the electronic structure of metallocenes.

1. W.L. Jolly, Acc. Chem. Res. 1968, 1, 376.

2. D.C. Calabro, J.L. Hubbard, C.H. Blevins II, A.C. Campbell, and D.L. Lichtenberger, J. Am. Chem. Soc. 1981, 103, 6839.

ELECTRONIC PROPERTIES AND STRUCTURES OF TRANSITION METAL COMPLEXES FROM GAS PHASE PHOTOELECTRON SPECTROSCOPY

Dennis L. Lichtenberger and Louis S. Pang

Department of Chemistry, University of Arizona, Tucson, Arizona, USA 85721

This research program is directed at obtaining detailed experimental information on the electronic mechanisms by which metals bond and activate small organic molecules. A major feature of the program is the continued aplication and development of our high-resolution HeI/HeII valence and high precision X-ray core photoelectron spectroscopy instrumentation utilizing a 36 cm radius hemispherical analyzer.

Most of our studies are concerned with the interactions of small molecules with metals in organometallic molecules that are sufficiently stable and volatile for investigation in the gas phase. Recent results on the interactions of acetylene and other alkynes with different metal centers will be used to illustrate the techniques and information available from these studies. The research also involves the synthesis of new organometallic molecules that are particularly significant for these studies. The characterization of these new molecules includes X-ray crystal structure determinations and variable temperature NMR investigations of fluxionality. The precise structures and fluxionality have been very informative in relation to the results of the electron spectroscopy.

The alkyne molecules that have been prepared and investigated are of the general form $CpM(CO)_2(alkyne)$, where Cp represents different methylated cyclopentadienyl rings and the metal is manganese, rhenium, or vanadium. Of particular interest are ionizations from the two alkyne pi bonds. When the alkyne is coordinated to metal these ionizations undergo a splitting because of different bonding interactions with the metal in comparison of the symmetric combination of the alkynes. These splitting observations also have important influences on the metal cyclopentadienyl ionizations. When the metal is manganese the alkyne acts as a two-electron donor and the coordination of the alkyne is parallel to the Cp ring. When the metal is rhenium the alkyne acts as a four-electron donor, the coordination of the alkyne is perpendicular to the Cp ring, and the different orientation of the alkyne is much more favorable

THE ELECTRONIC STRUCTURE OF cis-DIAMMINEPLATINUM α-PYRIDONE BLUE AND THE CRYSTAL STRUCTURE OF THE BLUE ETHYLENEDIAMINE ANALOGUE: METAL-METAL BONDING AND CHARGE TRANSFER IN FOUR ATOM Pt(2.25) CHAINS

Thomas V. O'Halloran,[a,b,c] Alvin P. Ginsberg,[b] Phillip E. Fanwick,[d] Michael M. Roberts,[a,c] L. Steven Hollis,[c] and Stephen J. Lippard[a,c]

[a]Massachusetts Institute of Technology, Cambridge, MA 02139; [b]Bell Laboratories, Murray Hill, NJ 07974; [c]Columbia University, New York, NY 10027; [d]University of Kentucky, Lexington, KY 40506

Polarized single-crystal optical spectroscopy, together with a scattered wave Xα analysis, provides an understanding of the intriguing blue color and the metal-metal interactions in the Pt(2.25) chain complex cis-diamminebis(α-pyridonato) blue (PPB), cis-[Pt(NH$_3$)$_2$(C$_5$H$_4$NO)]$_2$(NO$_3$)$_2$·H$_2$O. Pt-Pt bonding is found to be mainly due to σ overlap between Pt d_{z^2}, a hybrid orbitals. The PPB HOMO and LUMO are Pt-Pt σ* in character and are delocalized over all four Pt atoms (Figure 1). PPB is therefore a Robin-Day class III-A compound. Immediately below the HOMO are two orbitals with Pt-pyridone oxygen π* character. These orbital characteristics are used to rationalize the polarized absorption spectra of PPB. The blue color of PPB is due to the intense symmetry-allowed transitions at 1.82 eV (680 nm) and 2.38 eV (521 nm), which may be described, respectively, as inner Pt-Pt σ → inner Pt-Pt σ* and outer Pt-Pt σ → outer Pt-Pt σ*. Single crystals of the blue ethylenediamine analogue of PPB have recently been isolated and the crystal structure has been determined (Figure 2). Expanding downward Pt(1)···Pt(2) and Pt(2)···Pt(1') distances. Optical spectra show that the low-energy absorption bands are shifted to lower energy in this ethylenediamine analogue. These differences are rationalized by the results of the Xα calculations.

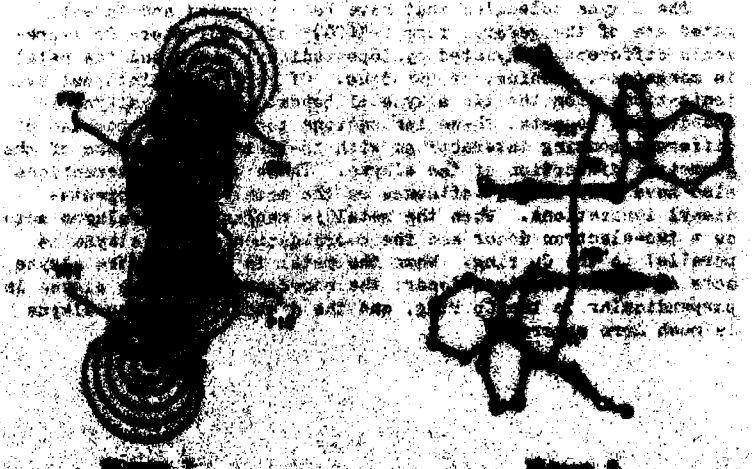


Figure 1

Figure 2

THE ELECTRONIC STRUCTURE OF METAL-HETEROATOM TRIPLE BONDS

Edward M. Kober and Dennis L. Lichtenberger

Department of Chemistry, University of Arizona,
Tucson, AZ 85721

Complexes containing metal-heteroatom triple bonds have been reported to be important for a wide variety of catalytic processes. For example, metal-oxo species appear to be effective as olefin metathesis catalysts and metal-nitride or -imido species are probably intermediates for nitrogen fixation. Quite recently, the species RC≡W(OCMe$_3$)$_3$ have been shown to function as active acetylene metathesis catalysts. The comprehension of the electronic structure of such species could well prove important in understanding the mechanism of and designing improvements to these catalytic schemes. Here, this problem is addressed using core and valence photoelectron spectroscopy.

The complexes chosen for study are of the stoichiometry Y$_3$MX$_n$ where M=Mo,W; X=Cl,OCMe$_3$; and Y=O (n=4) or Y=E,CR (n=3). For X=OCMe$_3$, the first ionization occurs in the range 7-10 eV and can be ascribed to the metal-heteroatom π-bond. Vibrational structure with $\Delta\omega$~1,000 cm^{-1} (corresponding to the M≡Y stretch) can be resolved on this ionization for many of the complexes. The ionizations from the XO($p\pi$) orbitals are found to occur at 10-11 eV, consistent with the concept that alkoxide ligands can function as strong π-donors. For the WECR alkylidyne species, the data indicates a considerable build-up of negative charge on the carbon atom. Implications regarding the mechanism of acetylene metathesis by RCW(OCMe$_3$)$_3$ are discussed.

For X=Cl, there appears to be considerable mixing between the orbitals of all of the atoms such that an ionization from the M≡Y π-bond cannot be cleanly identified. It is found that chloride functions as a much weaker electron donor than alkoxide. In none of the above systems could the M≡Y σ-bond ionization be identified. Fenske-Hall MO calculations suggest that this ionization should occur at >11 eV where it would be obscured by other bands.

THE STUDY OF THE ELECTRONIC STRUCTURE OF Ni(II), Pd(II), Pt(II) COMPLEXES BY SCF X_α-SW METHOD

K.M. Neyman, A.V. Kondratenko, L.N. Mazalov, L.V. Molchanova, V.A. Naslusov

Institute of Inorganic Chemistry, Siberian Branch of the USSR Academy of Sciences, Novosibirsk, USSR

Institute of Chemistry and Chemical Technology, Siberian Branch of the USSR Academy of Sciences, Krasnoyarsk, USSR

The methods of X-ray and photoelectron spectroscopy are most effectively used when employing, at least for some of the complexes under study, reliable quantum-chemical calculations of highly excited states. This is particularly true for transition metal compounds where small splittings between the electron levels do not allow obtaining of spectra with resolved molecular-orbital structure.

The present work gives the results of SCF- X_α SW calculations of the electronic structure of the square complex anions ML_4^{2-} (M = Ni, Pd, Pt ; L = Cl^-, CN^-). The calculated energies and intensities of the X-ray emission, absorption and photoelectron spectra are used to interpret the experimental data. It was found that qualitatively true results are obtained both for touching and overlapping atomic spheres, the quantitative correlation with experiment being achieved by introducing overlapping. The Madelung field generated by the crystal environment in MCl_4^{2-} presicely taken into account was not found to lead to any substantial changes in splittings and intensities as compared with the results of the crystal field calculations by means of Watson sphere. The fine structure of the absorption spectra is accounted for by self-emission effects.

THEORETICAL DESCRIPTION OF Ag^+ IMPURITY ION DIMERS IN Na Cl

H.CHERMETTE [1], B.ATOUSSI [2] and C.PEDRINI [2]

1- Institut de Physique Nucléaire (et IN_2P_3)

2- Physico Chimie des Matériaux Luminescents (ERA 1003-CNRS)

Université C.Bernard Lyon-1 43 Bd du 11 Novembre 1918 , F-69622 Villeurbanne Cédex, France

Ag^+ impurity ion pairs $(Ag^+)_2$ have been recently studied in strongly doped Na Cl crystals. They are characterized by absorption and emission bands quite different from those assigned to single ion impurities. The bands are shifted towards lower energies and their temperature and impurity concentration dependances are typical of dimer centers. According to recent results of the study of polarization of luminescence, it was clearly established that the axes of the two identified dimers (violet and green emission) are parallel to the C_4 axis of the crystal.

The electronic structure of such systems are theoretically studied for the first time by means of MSXα molecular orbital calculations. The dimers are described by $(Ag_2 Cl_{11})^{3-}$ (D_{4h} symmetry) and $(Ag_2 Cl_{10})^{8-}$ (D_{2h} symmetry) clusters embedded in Na Cl potential.

In agreement with experiment, the calculated transition energies are shifted towards lower values in going from monomers to dimers, independantly of symmetries (D_{4h} or D_{2h}), of Ag - Cl distances, and/or of embedding potentials.

Finally, the importance of the role played in the covalent bonding between the two Ag^+ ions by bridging chlorides is depicted through wave functions contours.

ION SPECIFICITY: A BACTERIAL VIEW OF THE PERIODIC TABLE

Simon Silver and Tapan K. Misra

Washington University, St. Louis, Missouri 63130 USA

The specificity with which microbial cells interact with the cations and anions that form from the elements of the Periodic Table is so great that it can only be determined by coordination bonding between the ions and the macromolecules (generally proteins) that govern these specificities. Bacterial cells divide inorganic ions into three groupings: (a) Good ions required for growth; (b) Abundant ions that are generally not needed; and (c) Bad toxic ions of no biological utility. K^+, Mg^{2+}, Fe^{3+}, PO_4^{3-}, and SO_4^{2-} are examples of required nutrients for all living cells. Ca^{2+}, Na^+, and Cl^- are abundant ions that are not required by most microbial cells; these can be "coupled" to specialized growth processes and then become essential for certain types of cells. Hg^{2+}, Cd^{2+}, AsO_4^{3-}, AsO_2^- and Ag^+ are examples of toxic ions of no physiological use.

For "good ions" bacterial cells have highly specific membrane transport systems, consisting of membrane proteins coded for by chromosomal genes. These serve to discriminate, for example, in favor of K^+ and against Na^+, and in favor of Mg^{2+} and against Ca^{2+}, so that the cells concentrate the required nutrient to a high intracellular concentration. For abundant but unessential ions there are also membrane transport proteins governed by chromosomal genes. These generally regulate intracellular concentrations by actively pumping, for example Ca^{2+} and Na^+, from the cell to the outside at the expense of metabolic energy.

Resistances to bad toxic ions are governed by genes on small DNA molecules called plasmids, which also harbor the genes governing antibiotic resistance mechanisms and toxins involved in disease. These genes produce proteins that may also be parts of membrane transport systems. AsO_4^{3-} resistance is due to an ATPase membrane pump specific for arsenate (and discriminating against phosphate) that lowers the intracellular AsO_4^{3-} level. Cd^{2+} resistance is due to a separate membrane pump that appears to remove Cd^{2+} by an electroneutral exchange for H^+. But Cd^{2+} efflux is dependent on the membrane $\Delta\psi$, which is in turn generated by the proton pumping membrane ATPase involved in oxidative phosphorylation. Hg^{2+} resistance involves a specific Hg^{2+} transport protein, but only in order to move the Hg^{2+} ions into the cells for exposure to the detoxifying enzyme mercuric reductase. This NADPH-dependent FAD-containing sulfo-reductase converts Hg^{2+} to Hg^0, which diffuses out from the cell and is rapidly volatilized from stirred systems. For organomercurials such as phenylmercuric acetate and methylmercuric chloride, a second enzyme, an organomercurial lyase, first splits the C-Hg bond, which is followed by mercuric reductase action. Protein purification and DNA sequencing studies are beginning to identify the active sites of these highly specific proteins, which must in principle provide the ligand bonding specificity characteristic of the intact bacterial cells.

HIDDEN INDUCTIVE EFFECTS AS A FACTOR IN LIGAND DESIGN.

Robert D. Hancock, Fabrizio Marsicano, and Bandile S. Nakani,
University of the Witwatersrand, Johannesburg, South Africa.

The pK_a values of ligands in water have traditionally been regarded as a measure of the intrinsic basicity of ligands. Thus, the fact that pK_a values of primary amines along the series RNH_2 as R is changed from methyl to ethyl, isopropyl, and then t-butyl remain constant is taken to indicate that the inductive effects of these alkyl groups is constant. We have found[1] that logK values for Ag(I) complexes with this series of amines increases as the degree of C-methylation of the α-carbon atom increases. It has been shown[2] that in the gas-phase the proton basicity increases strongly along this series, and the constancy of the pK_a values is then interpreted as steric hindrance to solvation of the proton as R is changed from methyl through t-butyl. The response of the Ag(I) ion to the increasing inductive effect is then interpreted[1] in terms of a lower susceptibility of the linear Ag(I) ion to steric hindrance than is found for the solvated proton. Since these inductive effects are not apparent in the pK_a values of these amines, we have called them "hidden" inductive effects.

Hidden inductive effects are also present in ethylenediamine complexes as the degree of C-alkyl substitution increases[1]. In square-planar Cu(II) and Ni(II) complexes the susceptibility to steric hindrance is sufficiently low that as the amount of C-alkyl substitution is increased, so there is a marked increase in logK, coupled with a strong increase in ligand field strength, depending also on the position of the C-alkyl substituents on the ethylene bridge. Again, these inductive effects are "hidden", since, as with the primary monoamines, they are not evidenced in the ligand pK_a values.

The macrocyclic effect in N-donor macrocycles also has a component of the extra stability of the complexes of the macrocycles associated with a hidden inductive effect. The macrocycle has only secondary nitrogens, where the open-chain ligand has some primary as well. The pK_a values of primary and secondary nitrogens are in general very similar, but in the gas-phase the secondary are much stronger proton bases, so once again we are dealing with a hidden inductive effect. As with C-alkyl substitution of amines, there is an increase in complex stability, as well as a dramatic increase in ligand field strength[3].

1) R.D. Hancock, B.S. Nakani, and F. Marsicano, Inorg. Chem., 1983, 22, 2531.

2) R.W. Taft in "Kinetics of Ion-molecule reactions", P. Ausloos, Ed., Plenum Press, New York, 1979.

3) R.D. Hancock and W.J. McDougall, J. Am. Chem. Soc., 1980, 102, 6551.

THE COORDINATION CHEMISTRY OF FULVIC ACID

J. A. Marinsky, J. Ephraim, A. Mathuthu and S. Alegret*

Chemistry Department, State University of New York at Buffalo, Buffalo, New York 14214 and *Analytical Chemistry Department, The Autonomous University of Barcelona, Barcelona, Bellaterra, Spain

The protonation of a fulvic acid (FA) source (the Armadale Horizons Bh FA) has been examined potentiometrically in aqueous and non aqueous media. Three different carboxylic acid units characterized by pK_a values of ~2.6, ~3.6 and ~4.6, respectively, appear to be principle constituents of this FA source. A fourth acidic group encountered (pK_a value of ~6.2) can be attributed to either an alcohol or enol moiety. By extension of these protonation studies to FA samples containing Eu(III) and Cu(II) the presence of phenolic, and in significantly smaller quantity, amine functional units has been demonstrated. The total hydrogen ion neutralized by standard base, in their presence, is a factor of 25% to 35% greater than in their absence. Such potentiometric behavior can only be attributable to release of hydrogen ion, not otherwise available for detection, by complexation of these metals by weakly acidic ligands ($pK_a > 9$) present as constituents of the FA.

From the formation constants resolvable for the two principle chelated species formed at high pH (5.5 to 7.5), the chelating groups are assigned to, respectively a phenolic group ($pK \sim 13$) ortho to a carboxylic acid moiety ($pK \sim 3.6$) and an amine group ($pK \sim 10$), also contiguous to a carboxylic acid group ($pK \sim 4.6$). At lower pH values (3.0-5.0) the major species is the positively charged $Cu(RCOO)^+$ formed with the separate carboxylic acid units.

The coordination chemistry of FA, in the presence of trace and macro quantities of Co(II), Zn(II), Cd(II) and Ni(II) has also been investigated in parallel experiments. The results obtained are consistent with the model developed above.

BEHAVIOR OF PLUTONIUM IN MARINE SYSTEMS

Gregory R. Choppin[1] and John W. Morse[2]

[1]Department of Chemistry, Florida State University, Tallahassee, FL 32306; [2]Department of Oceanography, Texas A&M University, College Station, TX 77843.

Plutonium can exist in marine systems in IV, V, and VI oxidation states. Laboratory experiments are described which confirm the stability of the V oxidation state in the solution phase of sea water. The implications of this observation in terms of the redox and complexation behavior of the IV, V and VI oxidation states are discussed. Particular emphasis is given to the possible significance of the reduction of Pu(VI) by the humic materials present in sea water. The absorption of the various oxidation states onto solid materials in the marine environment has also been measured. Kinetic data is presented for the rate of adsorption on carbonate and oxide surfaces. The role of various complexing agents in sea water and their effects on the sorption and resuspension of plutonium from the marine sediment is described.

This research was supported by the U.S.D.O.E. Office of Health and Environmental Research.

INTERACTION OF NEPTUNIUM(V) WITH SELECTED ORGANIC LIGANDS AND A SURFACE WATER FULVIC ACID.

Terry F. Rees[a], Garon C. Smith[b], Patrick MacCarthy[b], and Stephen R. Daniel[a]
[a]U. S. Geological Survey, Lakewood, Colorado, 80225, USA
[b]Colorado School of Mines, Golden, Colorado, 80401, USA

Understanding the interactions of neptunium with naturally-occurring ligands is of paramount importance in assessing the long-term safety of various radioactive waste disposal methods. The role of natural organic ligands such as fulvic and humic acids in increasing trace metal solubilities has long been recognized, and numerous models have been proposed to quantify these interactions. The MacCarthy-Smith model for multiligand systems (1) has been advanced as potentially useful in treating such cases; however, complete experimental verification of the model has not yet been demonstrated.

The interactions at pH 7.5 and ionic strength 0.1 of Np(V) with salicylate, phthalate, citrate, and phosphate, with mixtures of these ligands, and with a surface water fulvic acid were investigated via the Schubert method (2). These ligands were selected as representative of structures and acidities of functional groups present in fulvic acids. The experimental conditions simulate those in natural waters. Salicylate was found not to react significantly with Np(V), while phthalate and citrate formed 1:1 complexes with conditional stability constants of 2.7×10^{3} and 6.9×10^{3}, respectively, at 25°C. Free energies, enthalpies, and entropies of complexation were obtained via measurement of the conditional constants at 10°, 25°, and 35°C. Based on these values, it was concluded that both ligands form inner-sphere complexes with Np(V). In addition, mixtures of citrate, phthalate, and phosphate were studied, and conformity to the MacCarthy-Smith model for multiligand systems under Schubert conditions was demonstrated.

Noninteger slopes in Schubert plots were obtained for the Np(V)-fulvic acid system. Interpretation of noninteger slopes in terms of the formation of discrete complexes, as often reported in the literature, is shown to be erroneous through rigorous theoretical analysis.

1. P.MacCarthy and G. C. Smith, in Chemical Modeling in Aqueous Systems, Jenne, E.A., editor, ACS Symposium Series, no. 93, pp 281-292

2. J. Schubert, J. Phys. and Coll. Chem., 1948, 52, 340

THE COORDINATION CHEMISTRY OF A NEW CLASS OF CHELATING PYRAZOLE DERIVATIVES

Willem L. Driessen and Jan Reedijk

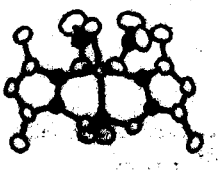
Department of Chemistry, State University Leiden, Gorlaeus Laboratories, P.O. Box 9502, 2300 RA Leiden, the Netherlands

Recently an efficient synthetic route to new pyrazole containing compounds has been developed (1). This method is based on the replacement of amine-hydrogens by N-methylpyrazole groups, whereby the pyrazole ring may or may not contain substituents. A wide variety of chelating systems, differing in structural complexity, can be obtained in this way. These systems cover a large field of possible applications. Examples are:

i) Coordination compounds of these chelating pyrazole-amine derivatives may function as model compounds for metalloproteins. In upgrading the complexity, and also by incorporating other donor atoms like sulfur, model compounds can be designed and tested which mimick the properties of metallo-enzymes gradually better, thus rendering insight in the relation between structure and function.

ii) By anchoring such pyrazole derivatives to polymeric matrices, chelating ion-exchangers are obtained with a higher potential for the specific separation of metal ions.

iii) The pyrazole derivatives can be designed in such a way that they are capable of bridging more than one metal ion at varying distances. The polynuclear coordination compounds obtained in this way can be of interest for catalytic or magnetochemical properties.



So far coordination compounds have been prepared and characterized - by analytical spectroscopical and X-ray structural methods - of chelating ligands which are N-methylpyrazole derivatives of ammonia, of aminoethane, of aminobenzene, and of 1,2-diaminoethane. The coordination chemistry of these relatively simple ligand systems already rendered some interesting - even surprising - results. For instance: A binuclear cobalt compound in which the metal ions are bridged by an extended water-ethanol-fluoride bridge. A nickel-nitrate compound in which the two anions are bonded to the metal ion: one monodentate and the other bidentate (see the figure; the ligand is the 3,5-dimethylpyrazole derivative of aminoethane).

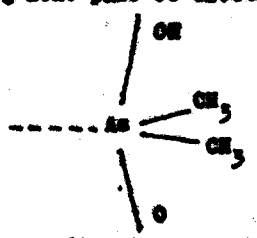
A number of seven-coordinate transition metal compounds. The details of the latest results will be presented.

1. W.L. Driessen, Recl. Trav. Chim. Pays Bas 101 (1982), 441.

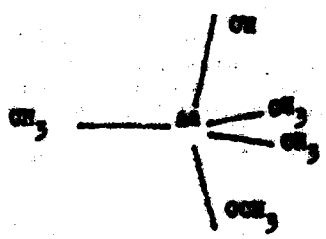
ARSENIC COMPLEX WITH COORDINATION NUMBERS FOUR AND FIVE

A. A. Antonow
Institute of Low Temperature and Structure Research,
Polish Academy of Sciences, Wroclaw, Poland

Arsenic a toxic metalloid element exiting in several reactions of living organisms.
A mode of four coordination structure is found for $(H_3C)_2AsO(OH)$ compound, this same as for some main group compounds, for example $AsCl_4^-$ and $SbCl_4^-$ anions.
The coordination geometry here may be regarded as derived from trigonal bipyramidal five-coordination by omitting one of the three "equatorial" ligands. The "empty" coordination position of the trigonal bipyramid is occupied by a non-bonding lone pair of electrons of the arsenic as central atom.



The trigonal bipyramidal coordination structure is found for $(H_3C)_3As(OCH_3)(OH)$ compound. The $SbCl_5^{2-}$ anion provides of square pyramidal coordination.



THE CONDENSATION OF DNA BY CHROMIUM(III) IONS

Dan Persson[x], Ragnar Österberg[+] and Gunnar Bjursell[x].

x) Department of Medical Biochemistry, University of Göteborg, S-400 33 Göteborg, Sweden
+) Department of Chemistry and Molecular Biology, Swedish University of Agricultural Sciences, S-750 07 Uppsala, Sweden

Chromium(III), one of the most potent inorganic carcinogens[1], induces condensation of DNA into a very compact product at 37°C and 30 mM ionic strength, as shown by electron microscopy. The condensation occurs at such a low Cr(III)/DNA-P molar ratio as 1.5:1. Under these conditions, Cr(III) inhibits the interaction between ethidium and DNA as shown by absorption and fluorescence spectra. Analysis of non-bound Cr(III) indicates that the specific chemistry of Cr(III) rather than the unspecific charge effect of Cr(III) plays an important role for the Cr(III)-DNA interactions. Due to this strong Cr(III)-DNA interaction *in vitro*, it is tempting to speculate that Cr(III)-DNA complexes will interfere seriously with the *in vivo* function of DNA such as, for instance, the DNA binding of regulatory proteins.

1. International Agency for Research on Cancer (1980), Chromium and chromium compounds. In Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Humans. Vol. 23. Lyon: I.A.R.C. p.205.

GENETIC TOXICITY OF TRANSITION METAL COMPLEXES

Edwin H. Abbott, Guylyn Warren and Samuel Rogers

Department of Chemistry, Montana State University, Bozeman, MT 59717.

Transition metal ions can interfere with the fidelity of DNA replications under certain circumstances. We have studied a large number of complexes principally by means of differential lethality bioassays[1]. In this approach, strains of bacteria are selected deficient in one or more DNA repair modes. The toxic concentration of a potential mutagen is determined on each strain. This toxic concentration is compared to the concentrations observed on the repair proficient wild type. Increased toxicity on a repair deficient strain is presumed to be due to genetic damage which cannot be repaired. Thus one cannot only determine mutagenicity but also infer the mechanism by which it occurs.

The comparative genetic toxicity of complexes of Rh, Cr, Co, Pt, Ni, Cu, Zn and In have been studied. Complexes with half lives for ligand exchange of about 2 hours are often mutagens. Labile complexes are not mutagens nor are most of the very inert complexes. The ligands are important determinents of mutagenic activity. In six coordinate complexes, those with good leaving groups adjacent to one another tend to be more active. Using optically active complexes, it can be demonstrated that the mutagenic step occurs within the first two ligand substitutions. The stereochemical requirements, ligand requirements, and mechanisms of mutagenicity of these transition metal complexes will be presented and discussed.

1. Warren, G., *Short-term Bioassays in the Analysis of Complex Environmental Mixtures.* Edited by S. Sander, L. Claxton, and S. Nesnow. Plenum, New York, 101-117, 1980.

KINETICS OF INTERACTIONS OF PORPHYRINS WITH NUCLEIC ACIDS

Robert F. Pasternack and Esther J. Gibbs

Swarthmore College, Swarthmore, Pennsylvania, USA 19081
and Goucher College, Towson, Maryland, USA 21204

The interactions of nucleic acids with water-soluble porphyrins and metalloporphyrins have been investigated by stopped-flow and temperature-jump techniques. Both natural DNA (calf thymus) and synthetic copolymers (poly(dG-dC) and poly(dA-dT)) have been employed. The porphyrins studied belong to the tetrakis (4-N-methylpyridyl)porphine series and can be divided into two groups: i) those which have no axial ligands when bound to nucleic acids (e.g., Ni(II), Cu(II), and the non-metallo derivatives) and ii) those which maintain axial ligands upon binding (e.g., Mn(III), Fe(III), Co(III), and Zn(II) derivatives). The reaction of both axially and non-axially liganded porphyrins at AT sites is too rapid to be measured by the kinetic methods utilized; whereas at GC sites, the interaction of the non-axially liganded porphyrins is in the millisecond time range and can be monitored by both stopped-flow and temperature-jump techniques. These results corroborate previous static studies, utilizing visible spectroscopy and circular dichroism, which indicate that the formation of an intercalated complex occurs only at GC base pair sites with porphyrins which do not possess axial ligands. With all the porphyrins investigated, the complexes formed at AT sites are envisioned as being of an "external" type involving some degree of overlap between the porphyrin and the bases of the duplex.

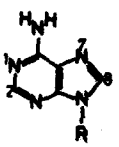
In relaxation experiments of poly (dG-dC) with H_2TMpyP-4, a large, reproducible effect is observed which can be analyzed as a single exponential. Rate constants for association and dissociation of the H_2TMpyP-4/poly (dG-dC) complex are 3.7 x 10^7 M^{-1} sec^{-1} and 1.8 s^{-1}, respectively. This interaction process is too rapid to require base pair opening in the intercalation mechanism. With calf thymus DNA and H_2TMpyP-4, a multiphasic relaxation profile is observed. Both the amplitude and concentration dependencies of these kinetic effects indicate that the processes being observed involve the redistribution of porphyrin among the various sites on the nucleic acid.

INTRAMOLECULAR EQUILIBRIA IN COMPLEXES OF ADENINE-NUCLEOTIDES

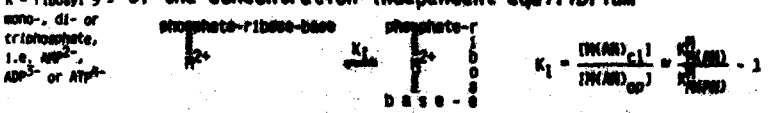
Helmut Sigel

Institute of Inorganic Chemistry, University of Basel, Spitalstrasse 51, CH-4056 Basel, Switzerland

Metal ion complexes of adenine-nucleotides (AN) act as substrates in enzymic processes. Their structure in solution has fascinated chemists for many years.[1] However, the un-awareness of the metal ion promoted self-association of adenine-nucleotides via base-stacking[2,3] has hampered studies and led to conflicting views. ^{1}H NMR shift experiments[2,3] and UV absorption measurements[4] show that macrochelates are formed through an intramolecular coordination of the metal ion to the phosphate moiety and to N-7. The position of the concentration-independent equilibrium



R = ribosyl 5'-mono-, di- or triphosphate, i.e. AMP^{2-}, ADP^{3-} or ATP^{4-}



$$K_I = \frac{[M(AN)_{cl}]}{[M(AN)_{op}]} \approx \frac{\%\,M(AN)_{cl}}{\%\,M(AN)_{op}} - 1$$

between this macrochelate ($M(AN)_{cl}$) and the *open* isomer ($M(AN)_{op}$) may be estimated[2-4] from stability constants by including the data of pyrimidine-nucleotides (PN) which undergo *no* base-metal ion interaction.[1-4] The extent of macrochelation in the complexes of the adenine-nucleotides (I = 0.1; 25°C)[2,3,5]

	Mn^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
% $[M(AMP)]_{cl}$	28	34	79	44	38
% $[M(ADP)^-]_{cl}$	55	60	80	58	67
% $[M(ATP)^{2-}]_{cl}$	36	57	74	76	82

depends on the number of phosphate groups present in these nucleotides: % $M(AMP)_{cl}$ < % $M(ADP)^-_{cl}$ > % $M(ATP)^{2-}_{cl}$. It should be added that (i) replacement of the adenine moiety by the 1,N^6-ethenoadenine moiety[6] increases the concentration of the 'closed' isomers considerably,[5] and that (ii) in ternary M(ATP)(amino acid)$^{3-}$ complexes with tryptophanate or leucinate the adenine moiety is also able to undergo stacking or hydrophobic interactions with the indole or isopropyl residues.[7]

Supported by the Swiss National Science Foundation.

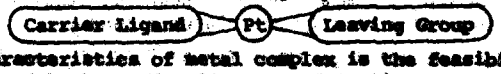
1. R. B. Martin and Y. H. Mariam, *Met. Ions Biol. Syst.* 1979, 8, 57.
2. K. H. Scheller, F. Hofstetter, P. R. Mitchell, B. Prijs, and H. Sigel, *J. Am. Chem. Soc.* 1981, 103, 247.
3. K. H. Scheller and H. Sigel, *J. Am. Chem. Soc.* 1983, 105, 5991.
4. Y. H. Mariam and R. B. Martin, *Inorg. Chim. Acta* 1979, 35, 23.
5. H. Sigel and K. H. Scheller, *Eur. J. Biochem.* 1984, in press.
6. K. H. Scheller and H. Sigel, *J. Am. Chem. Soc.* 1983, 105, 3005.
7. (a) H. Sigel, *Coordination Chemistry - 20*, D. Banerjea (Ed.), 1980, p. 27. (b) H. Sigel et al., *Inorg. Chem.* 1983, 22, 925.

AN ATTEMPT TO DEVICE ORGAN-SPECIFIC ANTITUMOR PLATINUM COMPLEXES OF 1R,2R-CYCLOHEXANEDIAMINE

Masahide Noji, Kenji Inagaki and Yoshinori Kidani

Faculty of Pharmaceutical Sciences, Nagoya City University
Tanabe-dori, Mizuho-ku, Nagoya, JAPAN 467

Since the discovery of antitumor activity of cis-Platin by B. Rosenberg in 1969, various attempts have been made to develop more antitumor active and less toxic platinum complexes. Among the carrier ligands of the Pt complexes, 1,2-cyclohexanediamine(=dach) has been found one of the best carrier ligands, and varieties of Pt dach complexes have been prepared by the modification of leaving groups. Among three dach isomers---cis and trans geometrical isomers and trans-d and -l optical isomers---trans-l-dach(=1R,2R-dach) has been found the most effective ligands.



The characteristics of metal complex is the feasibility of the modification of both carrier ligands and leaving groups. In order to show physiological activity, organic drugs usually bind with biological ligands by chemical reactions. The products thus formed will not be reduced to the original drugs any more. However, metal complexes bind with biological ligands to form mixed ligand complexes. They may be reduced to the initial drugs under the living conditions, such as pH, concentrations and coexisting substances.

The toxicity of Pt(1R,2R-dach)Halogen$_2$ is decreased, shown in the Table below. Antitumor animal tests against leukemia L 1210 were carried out according to the NCI Pt Analog Study Protocol.

Halogens	Toxic Dose, mg/kg	Optimum Dose, mg/kg	T/C% (cured)
Cl	12.5	6.25	215
Br	25	12.5	229 (1/6)
I	200	25	159

And the solubility is decreased in the following order: Cl>Br>I

Pt 1R,2R-dach complexes of mono- and bis-(sugar carboxylates) are very soluble in water. They are rather hygroscopic. The antitumor activity is: mono-D-glucuronate showed its optimum dose, 6.25 mg/kg, and T/C% 335, 5 mice out of 6 were cured; bis-D-glucuronate showed its optimum dose, 50 mg/kg and T/C% 330 and 2 mice were cured.

Pt complexes of mono- and bis-(O-acetyl sugar carboxylates) are also prepared. Mono Pt complexes are soluble in both water and alcohol, while bis Pt complexes are not soluble in water. They are soluble in alcohol, benzene and chloroform. They showed higher antitumor activity.

The authors believe that modification of leaving groups of Pt dach complexes afford

1. more antitumor active Pt complexes than cis-Platin,
2. less toxic Pt complexes,
3. water-soluble Pt complexes,
4. lipo-soluble Pt complexes, and
5. Pt complexes which provide specific affinity to the certain organs. This coordination chemical approach may develop active and promising agents against slow-growing tumors.

BINDING SITES AND STABILITIES OF TRANSITION METAL IONS WITH NUCLEOSIDES.

R. Bruce Martin

Chemistry Department, University of Virginia, Charlottesville, Virginia 22901

It is to the everlasting embarrassment of organic chemistry that in early 1953 it has not described definitively the dominant tautomeric structures that occur in the four nucleic bases of DNA. Thirty years later the predominant tautomeric forms and proton binding sites are generally agreed upon. The problem of metal ion binding sites in the nucleic bases remains. In the purine bases there is a metal ion binding dichotomy between N1 and N7.[1] The problem is resolved by comparison of linear log stability constant versus pK_a plots for a variety of related ligands.

Stability constant logarithms for Ni^{2+}, Cu^{2+}, and Zn^{2+} binding at pyridine or purine N1 type nitrogens and imidazole or purine N7 type nitrogens display a linear relationship with pK_a for each metal ion and nitrogen type. The slopes of all lines vary only from 0.3 to 0.5. For all three aqueous metal ions and $dienPd^{2+}$, at the same pK_a, the stability constant for N7 binding is 0.8 to 1.2 log units stronger than for N1 binding. For neutral adenosine the N1 site is intrinsically 320 times more basic than the N7 site. However, for the above three aqueous metal ions the ratio of N1 to N7 bound adenosine complexes is projected to be 3, 2.5, and 1, respectively. Thus solutions of neutral adenosine and these aqueous metal ions contain comparable amounts of N1 metalated and N7 metalated complexes. Intrinsic protonation and metal ion stability constants are compared for adenosine, guanosine and inosine. N7 coordination in purine bases predominates at low pH and gives way to favored N1 coordination for $dienPd^{2+}$, Cu^{2+}, and Zn^{2+} between pH 1.5 to 2.7 for adenosine, pH 6.1 to 6.7 for inosine, and pH 6.9 to 7.5 for guanosine.[2]

1. R.B. Martin and Y.H. Mariam, Metal Ions in Biological Systems, 1979, 8, 57-124.

2. S-H. Kim and R.B. Martin, Inorg. Chim. Acta, 1984, 91, 19-24.

ANTITUMOR PROPERTIES OF Ru,Rh,Pd,Ir AND Pt COMPLEXES WITH EDTA AND RELATED LIGANDS

M.G.Basallote,J.Benitez,R.Vilaplana,E.J.G.Consejero and F.González

Departamento de Química Inorgánica, Facultad de Ciencias, Apartado 40, Puerto Real, Cádiz, Spain

From the first report by Rosenberg et al.(1) of coordination compounds with antitumor properties,there is an increasing interest in this topic, specially in those aspects dealing with structure-activity relationships and the mechanism of action (2,3). In this contribution recent results of a systematic study of closely related compounds will be reported.

Dichloro complexes of Ru(III),Rh(III),Pd(II),Ir(III) and Pt(II) with several chelating agents have been synthesized by both new and previously described procedures.Because of the special stability of chelate rings,EDTA-type compounds(EDTA,PDTA,GDTA,EDBA,IDA) have been chosen as inert ligands.

The compounds are characterized by elementary analyses,infrared and electronic spectra,and ^{1}H and ^{13}C NMR spectra. Their antitumor properties are tested at several schedules in mice bearing Ehrlich ascites tumor.cis-DDP was used as positive control and results were treated according to N.C.I. rules(4).Some compounds were also tested against L1210 and P388 leukemia.Results indicate that some of them are active against Ehrlich tumor but their T/C values are lower than those of cis-DDP.

Although the nature of DNA-Pt interactions remains unclear,the mechanism of action of platinum compounds seems to imply their fixation to guanine-rich DNA fragments.A previous step consisting of the hydrolysis in the cell of platinum compounds is also suggested (3).In accordance with the tentative mechanism outlined above, the hydrolysis and reactivity towards guanine of the compounds reported here has been studied.Solid products isolated from these reactions have been studied using the same techniques described above for the starting products.

1. B.Rosenberg,L.VanCamp,J.E.Trosko and V.H.Mansour, Nature 1969 222 , 385
2. "Cisplatin,current status and new developments", A.W.Prestayko, S.T.Crooke and S.K.Carter eds.,Academic Press,1980
3. ACS Symp.Ser. 1983 , 209
4. Cancer Chemother. Rep. 1972 , 3

CIS-DIAMMINEDICHLOROPLATINUM(II) CROSSLINKS HIGH MOBILITY GROUP 1 AND 2 PROTEINS TO DNA IN MICROCOCCAL NUCLEASE ACCESSIBLE REGIONS OF CHROMATIN.

William M. Scovell, Nancy Muirhead and Lee R. Kroos

Bowling Green State University, Bowling Green, Ohio, USA 43403

The anti-neoplastic agent, cis-$(NH_3)_2PtCl_2$ (cis-DDP), covalently modifies both DNA and proteins and is found to crosslink these components in cellular chromatin, although the identity and location of the proteins involved has not been determined. The proteins providing the integrity to chromatin are of two types - the histone proteins contained in the repeating nucleosome unit, in addition to the non-histone chromosomal proteins (NHCP) which are non-randomly distributed in the genome and are thought to contribute to both the structural and functional heterogeneity of chromatin. To gain further insight into chromatin structure and the mode of action of cis-DDP in undistrubed chromatin packaged in nuclei, we reacted cis-DDP with nuclei and monitored the character of the soluble nuclear proteins as a function of cis-DDP reaction time. We observed a progressive decrease in the proteins bands for (1) the low mobility group (LMG) proteins and also (2) the high mobility group (HMG) proteins 1,2 and E. These findings suggested that these proteins are extensively crosslinked to DNA and/or other proteins. Chemical reversal of the cis-DDP binding verified that virtually all these proteins were clearly crosslinked in the reaction. Micrococcal nuclease digestion of the cis-DDP treated nuclei, however, released only HMG 1,2 and E proteins. These findings imply that the HMG 1,2 and E proteins interact directly with or are in very close proximity to DNA segments which are sensitive to limited micrococcal nuclease digestion. It has been proposed by others that the HMG 1 and 2 proteins are DNA binding proteins which may be associated with DNA replication and/or transcription.

These data are of interest on at least two counts. First, they may reveal a novel mechanism by which cis-DDP inhibits DNA replication and other biological functions. Second, the data provide new insights into chromatin structure and specifically the location of the HMG 1 and 2 proteins in chromatin. A proposed model for the protein-DNA interaction which we are currently evaluating will be presented and discussed.

Wa39-7

Binding of $(NH_3)_5Ru$ to DNA and Metal Ion Induced Oxidation of dG

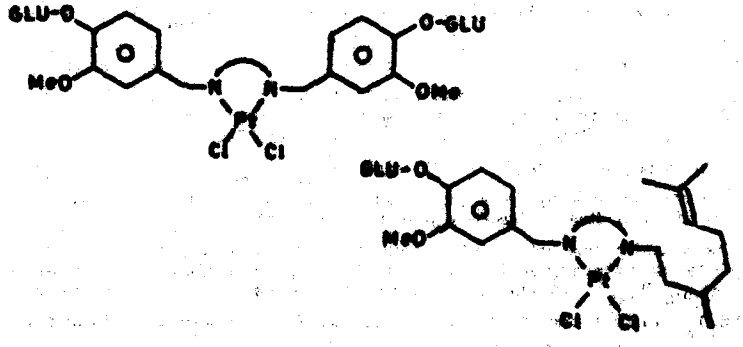
M.J. Clarke, P.E. Morrissey and B. Jansen
Department of Chemistry, Boston College, Chestnut Hill, MA 02167
K.A. Marx and R. Kruger
Department of Chemistry, Dartmouth College, Hanover, NH 03755

The reaction of $[(H_2O)(NH_3)_5Ru]^{2+}$ with calf thymus DNA has been studied under approximately equilibrium conditions over a reactant molar ratio range of $0.1 < [Ru(II)]/[P_{DNA}] < 50$. For covalently bound Ru levels up to 0.26 Ru_{DNA}/P_{DNA} the predominant binding site is N-7 of dG. Kinetic studies revealed a multiphasic reaction with an initial fairly rapid coordination of the metal ion being followed by slower reactions. Reactions were quenched after the initial reaction reached its pseudo-equilibrium point and before subsequent reactions had progressed substantially. HPLC of oxidized, acid-hydrolyzed samples of Ru(III)-DNA, prepared from helical DNA, revealed the presence of only $[(Gua)(NH_3)_5Ru(III)]$ for $0.1 < [Ru(II)]/[P_{DNA}] < 0.5$, which was verified by UV-Vis identification of the isolated chromatographic band. At $[Ru(II)]/[P_{DNA}] > 0.5$ or when single stranded DNA was used, UV-vis spectra suggested additional binding to dA and dC residues. HPLC and individual spectrophotometric identification of these samples revealed $[(Gua)(NH_3)_5Ru(III)]$ and $[(Ado)(NH_3)_5Ru(III)]$. The UV and CD spectra of Ru(III)-DNA with $Ru_{DNA}/P_{DNA} = 0.26$ indicated no extensive destacking or alteration in geometry (B family) compared to unsubstituted DNA. Samples prepared at $[Ru(II)]/[P_{DNA}] > 0.6$ appear to have undergone counterion induced condensation, since these were rapidly sedimenting and unable to electrophorese into an agarose gel. At $Ru_{DNA}/P_{DNA} > 0.26$ the appearance of spectral characteristics due to $[(NH_3)_5Ru(III)]$ coordination to the exocyclic amines of dA and dC is indicative of double helix disruption. Scatchard plots with helical DNA yielded a binding constant of 5.1×10^3 with a 60% availability of dG(7) sites, while similar plots with single stranded DNA gave $K = 7.8 \times 10^3$ with 100% of the dG(7) sites available. Studies with calf nuclei indicated essentially the same level of binding to dG(7) sites in nucleosomal and internucleosomal linker DNA. The observed rate constant for the hydrolysis of the sugar-purine bond in $[(dG)(NH_3)_5Ru(III)]$ was 5.4×10^{-6} sec^{-1} over the pH range 6-7.0, but decreased in the range of the pK_a (7.6) for proton loss from N(1). $[(NH_3)_5Ru(III)]$ is a factor of 1850 and 185 less efficient at catalyzing this reaction than the proton or methyl group, respectively; however, the hydrolysis of Ru-dG at 56° and pH 7.4 is approximately 1000 to 10,000 times more rapid than that of free dG or dG residues in DNA. The observed rate constants for oxidation of the coordinated nucleoside to 8-hydroxydeoxyguanosine increased with pH (from 2.1×10^{-5} sec^{-1} at pH 6 to 1.1×10^{-4} sec^{-1} at pH 7), indicating this reaction to be base catalyzed. This suggests that oxidation of the nucleoside is preceded by deprotonation of C-8 followed by hydroxide or water attack at this site. The metal-induced hydrolysis and oxidation of dG sites may be evidence for potential new mechanisms for the mutagenic and chemotherapeutic properties of platinum group metal ions.

PLATINUM (II) COMPLEXES WITH DIAMINES CONTAINING GLUCOSIDES.

Juan M. Fernández-G., Instituto de Química, Universidad Nacional Autónoma de México, México D.F.

Several substituted diamines with radicals containing a glucoside were prepared and reacted with K_2PtCl_4 obtaining the corresponding cis-Dichloro Platinum (II) complexes.



The complexes have been characterized by chemical analysis, infrared spectroscopy and molar conductivity.

PURINE DERIVATIVES OF BICYCLOPENTADIENYL TITANIUM 2+, 3+ AND 4+ METALLOCENE COMPLEXES

Daniel Cozak and Adelakhim Mardhy

Département de chimie, Faculté des sciences et de génie, Université Laval, Québec, Québec, Canada, G1K 7P4.

A few years ago Köpf and Maier reported high biological activities for the treatment of tumors for several metallocene compounds including $(\eta^5\text{-}C_5H_5)_2TiCl_2$[1]. The following reports on this subject indicated that the biochemical activity of the titanocene agent is probably similar to that of the well known platinum(II) amino class of compounds, e.g. cis-$Cl_2Pt(NH_3)_2$[2]. This prompted us to examin model reactions involving nucleic acid bases and titanocene complexes. Hence, we which to report on the observed chemical reactions of purine (PuH), $C_5H_4N_4$, and adenine (AdH), $C_5H_5N_5$, base units of DNA, with these complexes.



I II III

The reactivity of PuX and AdX, X= H or alkali metal, with the titanocene complexes I, II and III were studied under different conditions.

We have isolated and characterized different addition and substitution products depending on the oxidation state of the titanium reactant, e.g. $[(\eta^5\text{-}C_5H_5)_2Ti^{III}]_2Ad$, $(\eta^5\text{-}C_5H_5)_2Ti^{III}ClPuH$. However, in the adenine reactions, the nature of the products were not predictable. For the latter case, decomposition of the metallocenic structure was often observed. The reaction of complexes I, II and III with the corresponding anionic ligands, Pu^- and Ad^-, gave the expected products in good yields for the purinato ligand only.

The elemental analysis, ir, esr and nmr data will be presented for the isolated complexes together with the X ray diffraction crystal structure for the $(\eta^5\text{-}C_5H_5)_2Ti^{IV}ClPu$ complex.

1. P. Köpf-Maier, H. Leitner, R. Voigtländer and H. Köpf, Z. Naturforsch. 34b (1979) 1174.

2. P. Köpf-Maier and H. Köpf, Naturwissenschaften 67 (1980) 413.

CHEMICAL PROPERTIES AND PHARMACOKINETICS OF SOME PLATINUM COMPOUNDS IN THE KIDNEY TISSUE

N.N. Zheligovskaya, V.K. Brovtsyn, and E.P. Krasovskaya

Moscow State University, Department of Chemistry, Oncological Research Center of AMN of USSR, Moscow, USSR.

Pharmacokinetics of the platinum compounds with different thermodynamic stability and kinetic lability is compared in this paper. Three platinum derivatives, $[Pt(NH_3Cl)_2]$(DDP), $[Pt(NH_3Cl)_2(OH)_2]$ and $[Pt(NH_3)_4]Cl_2$ were each administered in single doses of 7 mg/kg, 40 mg/kg and 15 mg/kg respectively to male rats. The research was performed by means of instrumental neutron activation analysis. At 24 hours after administration of $[Pt(NH_3Cl)_2]$ drug concentration in the kidneys decreases according to power dependence $c=At^{-b}$, where "c" is concentration, "t"-time, "A", "b"-constants. At 72 hours after administration of antitumoral compound $[Pt(NH_3Cl)_2(OH)_2]$, the average pharmacokinetic curve corresponds to exponential dependence with $T_{1/2}$=5d. The pharmacokinetic curve of non-antitumor compound $[Pt(NH_3)_4]Cl_2$ can be resolved into three exponential components with $T_{1/2}$=12min, 3,6h and 4d. The differences of pharmacokinetic curves can be explained by different reactionability of platinum compounds to innersphere substitution with electrondonor fragments of the proteins. The labile compounds DDP rapidly and strongly are bound to proteins; this implies indirectly the power dependence of platinum elimination from kidney parenchyma on time. The Pt(IV) complex $[Pt(NH_3Cl)_2(OH)_2]$ is about 10 times more inert than DDP: the great bulk of $[Pt(NH_3Cl)_2(OH)_2]$ is eliminated from the body through kidneys before it reacts with protains. This is why $[Pt(NH_3Cl)_2(OH)_2]$ as well a strength compound $[Pt(NH_3)_4]^{+2}$ comes into comparatively weak interaction with biosubstrate of the kidney tissue. It results in the exponential pharmacokinetic curve.

THURSDAY MORNING

MULTIPLE METAL-CARBON AND METAL-PHOSPHORUS BONDS INVOLVING GROUP 8 METALS

George R. Clark, D. Scott Bohle, Simon V. Hoskins, Clifton E.F. Rickard and Warren R. Roper.

Department of Chemistry, University of Auckland, Auckland, New Zealand.

The reactivity of metal-carbon double bonds is discussed in terms of the nature of the substituents on the carbene carbon atom. Complexes of the simple ligand, difluorocarbene, can be derived from various CF_3-complexes.[1,2] $Cd(CF_3)_2DME$, (DME = dimethoxyethane) reacts directly with several zerovalent complexes of Ru and Os to form CF_2-complexes. Examples of these new molecules are $Os(=CF_2)(CO)_2(PPh_3)_2$, $Ru(=CF_2)(CO)_2(PPh_3)_2$ and $Os(=CF_2)Cl(NO)(PPh_3)_2$. The crystal structures and typical reactions of these compounds will be described. The reactions indicate that while it is still possible to have substitution reactions at the carbene carbon atom in these zerovalent complexes an alternative reaction is with electrophiles, e.g. HCl and $Os(=CF_2)(CO)_2(PPh_3)_2$ give $Os(CF_2H)Cl(CO)_2(PPh_3)_2$. The difluoromethyl-complex with BCl_3 yields an intermediate $CBCl_2$-complex which undergoes electrophilic addition to the benzene ring of a triphenylphosphine ligand so forming a novel chelate.

$Cd(CF_3)_2DME$ also reacts with $OsCl(=CCl_2)(CO)(PPh_3)_2$ to give $OsCl_2(=CFCl)(CO)(PPh_3)_2$. Reactions of this mixed dihalocarbene-complex will be described.

Possible routes to compounds with multiple metal-phosphorus bonds have been explored and the chemistry of $Os(PHPh)Cl(CO)_2(PPh_3)_2$ is described. In this molecule the PHPh-ligand acts as a 1-electron donor and the geometry about P is pyramidal from X-ray crystal structure determination. However, in certain reactions the PHPh-ligand behaves as a phosphenium-cation, e.g. reaction with methoxide gives the zerovalent compound $Os(PH(OMe)Ph)(CO)_2(PPh_3)_2$.

1. G.R. Clark, S.V. Hoskins and W.R. Roper, J.Organomet.Chem. 1982, 234, C9.

2. G.R. Clark, S.V. Hoskins, T.C. Jones and W.R. Roper, J.Chem.Soc. Chem.Commun., 1983, 719.

LINEAR ENTHALPY RELATIONSHIPS: BINARY AND TERNARY COMPLEXES OF COPPER(II) WITH AMINOACIDS AND 1,10-PHENANTHROLINE/2,2'-BIPYRIDYL

Y.T. Chen, H.K. Lin, Z.S. Gu and H.Q. Liu

Department of Chemistry
Nankai University
Tianjin, P.R.C.

Over two decades ago the senior author predicted on theoretical ground that there should exist a linear relationship between the enthalpy of formation of complex compound and the enthalpy of dissociation of the ligand in solution(1), i.e.,

$$\Delta H_{ML} = Q - \beta \Delta H_{HL} \qquad (1)$$

where ΔH_{ML} denotes the heat of formation of the complex compound while ΔH_{HL}, the heat of ionization of the ligand, and Q and β are constants. Equation (1) was first tested in the Cu(II)-N-(meta-substituted phenyl)glycines system by temperature coefficient method(2).

In this communication we report the existence of linear enthalpy relationships in binary and ternary complexes of copper (II) with some aminoacids and 1,10-phenanthroline/2,2'-bipyridyl whose enthalpies were determined calorimetrically. All these systems conform nicely to equation (1) and the results are shown below (ΔH values are expressed as Kj/mole; r denotes correlation coefficient; substituting groups are Cl, H, CH_3, CH_3O. Experimental conditions: 25°C, 0.1M $NaClO_4$, 30% (V/V) ethanol).

1. Cu(II)-N-(para-substituted phenyl)glycines
   $\Delta H_{ML} = -10.700 + 0.448\Delta H_{HL}$ r = 0.992
2. Cu(II)-N-(para-substituted phenyl)glycines-1,10-phenanthroline
   $\Delta H_{MLL'} = -22.562 - 0.202\Delta H_{HL}$ r = -0.997
3. Cu(II)-N-(meta-substituted phenyl)glyines
   $\Delta H_{ML} = -9.667 + 0.637\Delta H_{HL}$ r = 0.991
4. Cu(II)-N-(meta-substituted phenyl)glycines-2,2'-bipyridyl
   $\Delta H_{MLL'} = -20.085 - 0.592\Delta H_{HL}$ r = -0.999

This is believed to be the first report on the test of equation (1) by calorimetric measurement.

REFERENCES

(1) Y.T. Chen, Z. Phys. Chem., 220, 231 (1962)
(2) Y.T. Chen and H.K. Lin, Acta Chimica Sinica, 41, 103 (1983).

THERMODYNAMICS OF COMPLEX HALIDE FORMATION

Douglas P.Graddon and Cheong Khoo

School of Chemistry, University of New South Wales, P.O.Box 1, Kensington, N.S.W.2033, Australia

We are using the technique of calorimetric titration to obtain thermodynamic data for complex halide ion formation in acetonitrile solution

Mercury halides, HgX_2, react with halide ions in two steps forming HgX_3^- then HgX_4^{2-}, except that in the case of HgI_2 an additional intermediate ion, $Hg_2I_5^-$ is also observed. Enthalpy data parallel those reported in aqueous solution, but are more negative by some 20 kJ/mol, reflecting the smaller enthalpy of solvent displacement in acetonitrile. The overall enthalpy change increases from X = Cl to I as the Hg-X bonds formed increase in strength. For the chloride most of the enthalpy change occurs in the second step, for the iodide most in the first, suggesting that solvent displacement occurs mainly in step 1 for the chloride and in step 2 for the iodide; this conclusion is supported by increasingly more positive entropy terms for step 1 in the order Cl, Br, I.

Zinc halides, ZnX_2, also react with halide ions in two similar steps, except that with ZnI_2 only the first step can be observed. The much less negative enthalpies of complex ion formation than with HgX_2 can be correlated with the known formation of stoichiometric acetonitrile solvates and consequently large enthalpies of solvent displacement. Enthalpy changes are about 5 kJ/mol more negative for step 1 than for step 2, consistent with displacement of one molecule of solvent at each step; this is supported by entropy changes which are positive for step 1 and near zero for step 2.

Study of $CdCl_2$ was prevented by low solubility in acetonitrile. The results for CdI_2 are consistent with successive formation of CdI_3^- and CdI_4^{2-}. A smaller enthalpy change in the first step, together with a higher formation constant, implies that solvent displacement takes place mainly in step 1. Results obtained for the bromide require the assumption of $CdBr_3^-$ as an intermediate ion, but it is not possible to evaluate $CdBr_3^-$ as an additional intermediate. The enthalpy change is almost wholly associated with the final step in the reaction, again implying that solvent displacement occurs at an early stage; such solvent displacement could account for the formation of a dimeric intermediate anion.

REACTIONS OF 2- AMINOMETHYLPYRIDINE WITH TRANSITION METAL IONS IN AQUEOUS SOLUTION: $\Delta G°$, $\Delta H°$, $\Delta S°$, AND VISIBLE SPECTRA

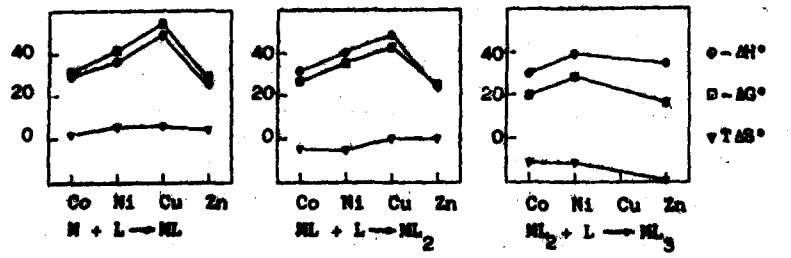
Adriana Baseggio, Lucia Bologni, Antonio Sabatini, and Alberto Vacca

Dipartimento di Chimica dell'Università di Firenze and I.S.S.E.C.C. CNR, Florence, Italy

The 2-aminomethylpyridine ligand has two non equivalent donor atoms. Upon coordination to a metal ion it forms five membered chelate rings in analogy with ligands such as etylenediamine and bipyridil. A comparison of the specific chemical behaviours is interesting.

Several results are available about the thermodynamics of formation of the complexes of ampy[1]. However some of these results are contradictory and to be regarded critically in a systematic approach. We have studied the formation equilibria of the ampy complexes with Mn, Co, Ni, Cu, Zn in 0.15 M NaCl solution at 25°C having in mind the following goals: (i) determination and characterization of the main species in the various systems, (ii) obtainement of thermodynamic quantities $\Delta G°$, $\Delta H°$ and $\Delta S°$. Potentiometric, calorimetric and spectrophotometric techniques have been used. Experimental data have been elaborated by developing computer programs in order to optimize the agreement between the observed and calculated quantities. It is to be pointed out that the imput to the program is comprehensive of experimental data of different nature which are all exploited properly in order to individuate the chemical species present at the equilibrium.

The systems under investigation have shown the presence of protonated and oxydrilated species beside the simple complexes $M(ampy)_n$ (n = 1,2,3). The thermodynamic functions $\Delta G°$, $\Delta H°$ and $T\Delta S°$ shown in the diagrams refer to the stepwise formation of the simple complexes and are expressed in kJ mol^{-1}.



1. Y. Couturier, C. Petitfaux, Bull. Soc. Chim. Fr. 1974, 885; P.R. Huber, R. Griesser, H. Sigel, Inorg. Chem. 1971, 10, 945; A.M. Goeminne, Z. Eeckhaut, Bull. Soc. Chim. Belg. 1971, 80, 605 and references therein.

USE OF EPR SPECTROSCOPY FOR THE INVESTIGATION OF KINETICS AND EQUILIBRIA OF CUPRIC COMPLEXES IN SOLUTION

Harald Gampp

University of Basel, Spitalstrasse 51, CH-4056 Basel, Switzerland

The EPR spectra of paramagnetic ions strongly depend on the ligand environment and EPR spectroscopy therefore should be a useful method for investigating both kinetics and equilibria of complexes in solution.

However, EPR plays only a minor role among the methods used for determining stability constants and moreover is mostly restricted to simple systems, which can be described by a single equilibrium constant.

In kinetics, solution EPR is widely applied for the study of reactions of organic radicals but is only rarely used in the field of of coordination chemistry.

The mayor reason is, that transition metal complexes very often give rise to broad solution spectra. Therefore overlapping in multicomponent systems prevents the straightforward data analysis, which is possible in the case of organic radicals, where the observed signals consist of rather narrow lines.

These problems could be successfully overcome[1,2] by the use of appropriate mathematical methods. (i) Representation of the measured spectra in their eigenvector space gives the number of absorbing species and also significantly reduces the amount of data to be handled in the subsequent numerical treatment. (ii) Rate or stability constants as well as spectra can be calculated using a procedure, that does not need any information with regard to the spectra of the complexes. This makes the method particulary useful in cases, where several complexes are formed simultaneously and if their spectra are unknown and/or strongly overlapping.

The pH-dependent complexation of Cu(II) by 3,6,9-triazanonanedioic acid diamide and the hydrolysis of the cupric complex of 3,6,9-triazaundecane-1,11-dinitrile in aqueous NaOH are chosen as examples to illustrate the use of solution EPR in equilibria and in kinetical systems, respectively.

1. H. Gampp, M. Maeder, and A.D. Zuberbühler, Talanta 1980, 27, 1037.
2. M. Maeder and H. Gampp, Anal. Chim. Acta 1980, 122, 303.

SPECFIT: A COMPREHENSIVE AND USER-FRIENDLY FORTRAN PROGRAM FOR THE DETERMINATION OF STABILITY CONSTANTS FROM SPECTROSCOPIC DATA.

Harald Gampp, Marcel Maeder, Charles J. Meyer, and Andreas D. Zuberbühler.

University of Basel, Spitalstrasse 51, CH-4056 Basel, Switzerland.

The use of spectrophotometric and related spectroscopic data should in principle be ideal for the elucidation of complicated equilibria. Contrary to potentiometry, spectroscopy provides an internal check of the chemical model chosen to explain the data, i.e. the spectra of the individual species. In addition, these spectra can give valuable structural information.

Difficulties in realization of this goal arise from
- frequently strong overlap of individual spectra
- correlation of absorptivities and equilibrium constants
- the large number of unknown molar absorptivities
- the large body of data (typically 1000 data points).

A comprehensive, reliable, and user-friendly program, written in standard FORTRAN 77, has been developed to overcome these difficulties. By elimination of the molar absorptivities from the iterative refinement of the non-linear parameters the number of unknowns is reduced to the number of equilibrium constants, i. e.,[1] the same as in corresponding potentiometric titrations[1]. Principal component analysis reduces[2] the amount of raw data typically by a factor of five[2]. The use[3] of analytical instead of numerical derivatives[3] speeds up the algorithm and increases numerical safety. The handling of the program is extremely simple and as input only the data and a definition of the chemical model by means of the stoichiometric composition of the complex species and a rough estimate of the equilibrium constants are needed.

The program has been tested on several rather complicated equilibrium systems and has given results comparing favorably with those obtained potentiometrically. The reproducibilities of the two methods are equal, but the discriminatory power between two different chemical models is consistently superior with the spectrophotometric method.

1. H. Gampp, M. Maeder, and A.D. Zuberbühler, Talanta 1980, 27, 1037.
2. M. Maeder and H. Gampp, Anal. Chim. Acta 1980, 122, 303.
3. A.D. Zuberbühler and T.A. Kaden, Talanta 1982, 29, 201.

THE ERROR PROPAGATION IN THE CALCULATION OF FREE LIGAND CONCENTRATION USING THE OSTERBERG AND RELATED METHODS

Lucien C. Van Poucke

Limburgs Universitair Centrum, Universitaire Campus, B 3610 Diepenbeek, Belgium

The determination of the stability constants of ternary systems from potentiometric titration curves can be very difficult when polynuclear, protonated and hydroxocomplexes are present. The knowledge of very precise pH, pL and pM data is required. pH and in most cases pM data can be obtained from direct measurements. pL data can be calculated using methods introduced by Hedstrom[1] and developed by other workers, i.a. Osterberg[2]. In these methods no assumption is made about the stoichiometric composition of the metalion complexes. The pL are obtained by a graphical method using an integration and a differentiation. The graphical method can easily be computerised. Although a number of good results using this method have been reported, in some cases error propagation leads to unreliable results.

In this investigation one searches for objective criterions about the reliability of the pL data. Therefore a number of simulations are performed. The error propagation is calculated and the ranges in which the method gives unreliable results is fixed in function of known experimental variables such as the volume of the solution, the total concentrations and the pH and/or pM data.

1. B. Hedstrom, Acta Chem. Scand. 9, 613 (1955).

2. R. Osterberg, Acta Chem. Scand. 14, 471 (1960).

THa40-7

STUDIES ON MIXED-LIGAND COMPLEXES OF CADMIUM WITH SOME AMINO ACIDS AND 2,2'-BIPYRIDYL

Miss Rajani, P.C. Gupta, C.P.S. Chandel, and C.M. Gupta

Department of Chemistry, University of Rajasthan, Jaipur-302004, India.

The mixed ligand complexes of cadmium with some amino acids (glycine, alanine, isoleucine, glutamic acid and aspartic acid) and 2,2'-Bipyridyl have been studied at the dropping mercury electrode. The cadmium amino acid simple systems were studied in aqueous medium while the cadmium 2,2'-Bipyridyl system was studied in 50% (V/V) Dioxane-water medium. The stability constants were determined with the help of Deford and Hume's method. The mixed systems were studied by keeping the concentration of amino acid constant. The $F_{\bar{n}}$ functions were evaluated by the method of Schaap and McMasters and extrapolation method was used to calculate A, B, C and D.

In all the systems, a single well-defined wave was obtained, the reduction process was reversible and diffusion controlled. Cadmium being hexa coordinated metal ion, three mixed ligand complexes were formed which are Cd(amino acid) (Bipyridyl), Cd(amino acid)(Bipyridyl)$_2$ and Cd(amino acid)$_2$(Bipyridyl). Steric, electrostatic and statistical factors have also been discussed.

THERMODYNAMIC AND SPECTROSCOPIC INVESTIGATION OF METAL COMPLEXES WITH LIGAND-LIGAND INTERACTION

Paola Amico[a], Raffaele P. Bonomo[b], Rosario Calì[b], Vincenzo Cucinotta[b], Pier G. Daniele[a], Giorgio Ostacoli[a], Enrico Rizzarelli

[a]Istituto di Analisi Chimica Strumentale, Università di Torino, Italy

[b]Dipartimento Chimico, Università di Catania, Italy

Stacking or solvophobic interactions have been found to exist in metal complexes with mixed ligands and their possible implications for biological systems have been widely stressed.[1] We have previously shown that the thermodynamic parameters of complex formation are diagnostic of the presence of ligand-ligand interaction in some ternary complexes of copper(II) and zinc(II) with bifunctional ligands.[2,3] This report concerns with a thermodynamic and spectroscopic study (EPR and NMR) of mixed complexes of copper(II) and zinc(II) with monosubstituted malonates and 2,2'-bipyridyl as ligands in aqueous solution. Preliminary results have shown that some peculiar differences between dimethyl- and di-n-butyl-malonates can be accounted for by the presence of an intraligand interaction in the Zn(bipy)(n-DiBuMal) complex.[3] The formation of this complex was more enthalpically and less entropically favoured than the analogous complex with dimethylmalonate. In order to correlate the extent of the solvophobic interaction with the length and the ramification of the alkylic side chains, we have investigated a series of mono-alkylic derivatives of malonate with n- and iso-alkyl side chains containing up to five carbon atoms. The experimental results pointed out that only in zinc(II) complexes this "secondary" bond is present. Besides the influence on the thermodynamic parameters, as a consequence of the ternary complex formation, an upfield shift in the terminal side chain methyl(s) peak is observed in the PMR spectra.

1. H. Sigel, B.E. Fischer, and E. Farkas, Inorg. Chem., 1983, 22, 925.
2. G. Arena, R. Calì, V. Cucinotta, S. Musumeci, E. Rizzarelli, and S. Sammartano, J.C.S. Dalton, 1983, 1291.
3. E. Rizzarelli, Inorg. Chim. Acta, 1983, 78, 91.

THa40-9

LOG K, ΔH AND TΔS VALUES FOR M^{n+} INTERACTION WITH SEVERAL BENZO AND DIBENZO CYCLIC POLYETHER DERIVATIVES IN CH_3OH AT 25°C

Glen A. Clark, Reed M. Izatt, James E. King, John D. Lamb, and James J. Christensen

Brigham Young University, Provo, Utah, U.S.A. 84602

Log K, ΔH and TΔS values have been determined calorimetrically in methanol at 25°C for the interaction of Na^+, K^+, Rb^+, Cs^+, Sr^{2+}, Ba^{2+}, Ag^+, Tl^+, and Pb^{2+} with benzo-15-crown-5, benzo-18-crown-6, dibenzo-18-crown-6, dibenzo-21-crown-7, dibenzo-24-crown-8, and dibenzo-27-crown-9. Generally, log K values decrease in the series unsubstituted, monobenzo substituted, dibenzo substituted macrocycle. Log K values in the cases of large ring macrocycles, i.e., 24-crown-8 and 27-crown-9 types, are lower than are those where the fit between cation and macrocycle cavity diameter is best. Interpretation of the log K values is made in terms of the corresponding ΔH and TΔS values. Comparisons are made between the results and those obtained earlier[1,2] for unsubstituted crown ethers and for crown ether diesters.

1. J.D. Lamb, R.M. Izatt, C.S. Swain, and J.J. Christensen, J. Am. Chem. Soc., 102, 475-479 (1980).

2. J.D. Lamb, R.M. Izatt, C.S. Swain, J.S. Bradshaw, and J.J. Christensen, J. Am. Chem. Soc., 102, 479-482 (1980).

ACTIVATION OF HYDROGEN BY SULFIDO BRIDGED DIMERS OF MOLYBDENUM(IV) AND TUNGSTEN(V)

O. A. Rajan, R. Weberg, and M. Rakowski DuBois

University of Colorado, Department of Chemistry, Campus Box 215, Boulder, Colorado, USA 80309

The incorporation of deuterium into certain alkynes and alkenes is catalyzed by the molybdenum dimer $(CpMoS)_2S_2CH_2$ ($Cp=C_5H_5$ or $CH_3C_5H_4$). Reduction of the alkyne is also catalyzed.[1] For example, under an atmosphere of deuterium, 2-butyne is converted into d_x-cis-2-butene where x ranges from 2 to 8. A mechanism which involves an intermediate with bridging hydrosulfido ligands is proposed. Efforts to increase the selectivity of this deuterium exchange will be discussed.

A series of new cyclopentadienyl tungsten dimers bridged by sulfur ligands have been synthesized and characterized. Some of these complexes have also been found to activate hydrogen. For example, under an atmosphere of hydrogen at 40°, $(CpWS)_2(SC_2H_2S)_2$ is converted into $(CpW)_2S_2(SC_2H_2S)$. The reaction involves the hydrogenation of a terminally chelated ethenedithiolate ligand followed by the elimination of ethylene and elemental sulfur. A third tungsten dimer $(CpWS)_2(SC_2H_4S)$ serves as a catalyst for the hydrogenation of azocompounds under mild conditions.

The reactivity of the above systems suggests that the interaction of sulfur ligands with hydrogen may be observed in various structural and electronic environments. In order to investigate this possibility, we have synthesized dimeric cyclopentadienyl derivatives of iron and rhenium which contain bridging sulfur ligands. The X-ray diffraction studies of the complexes will be discussed, and their reactivities will be compared to that of the molybdenum and tungsten derivatives.

1. M. McKenna, L. L. Wright, D. J. Miller, L. Tanner, R. C. Haltiwanger, and M. Rakowski DuBois, J. Am. Chem. Soc. 1983, 105, 5329.

METALLOPHTHALOCYANINES AS HYDROGENATION CATALYSTS

Laurence J. Boucher and D. Ross Spears

Western Kentucky University, Bowling Green, Kentucky, USA, 42101

Metallophthalocyanines, [M(PC)], show activity in the catalytic hydrogenation of nitrogen containing heterocycles. The [M(PC)] used include those where M equals Mg(II), V(IV), Cr(III), Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Al(III), Si(IV), Mo(II), Ru(II), Ag(II), Sn(II), Sn(IV), Pt(II), and Pb(II). The catalysts were supported on silica, alumina, silica-alumina and titania. The batch hydrogenations, in decane, hexadecane, xylenes and 2,6 lutidine, were carried out at 150-350°C and 500-3000 psi H_2. The catalysts are effective in the selective hydrogenation of quinoline to 1,2,3,4-tetrahydroquinoline. The conversion is dependent on the metal derivative. At 250°C and 1000 psi H_2 the order of activity for [M(PC)]/SiO_2 is

Ru > Sn > Mo > Ag > Ni > Co > Cu > Pt > Si > Al > Zn > Mn > Mg > Fe > V > Pb.

The metal free derivative shows no activity.

The kinetics of the hydrogenation of quinoline with supported [Co(PC)] have been determined. The rate is first order in quinoline and in hydrogen pressure. The reaction is slow with a typical half life of 20 hours at 250°C and 1000 psi H_2 and pseudo first order rate constants in the range of 10^{-5} to 10^{-4} sec^{-1}. The rate is dependent on the solvent, support and temperature. The solvent order is: decane > xylenes > 2,6 lutidine while the support order is: SiO_2-Al_2O_3 > SiO_2 > Al_2O_3 > TiO_2. The variation in rate is small, being a factor of five for solvent and a factor of three for the support. The rate increases with temperature quite slowly and the apparent activation energy is ~11 Kcal/mole for decane solutions and all supports.

Other nitrogen heterocycles are hydrogenated at different rates. With the common solvent, 2,4 lutidine, the order of substrate reactivity at 250-350°C and 1000 psi H_2 pressure is: acridine >> quinoline > quinaldine > indole > carbazole = 0. The hydrogenations are selective with quinaldine yielding 1,2,3,4-tetrahydroquinaldine, acridine yielding 9,10 dihydroacridine and indole giving indoline. No hydrogenolysis is noted during the reactions.

In general the supported [Co(PC)] catalysts show deactivation upon use. Metal analysis shows that the loss of cobalt from the catalyst depends on the support. The catalysts supported on silica-alumina are appreciably more stable than those supported on silica or alumina. While the SiO_2-Al_2O_3 catalysts show little or no metal loss from 200-350°C in the absence of quinoline, the SiO_2 and the Al_2O_3 catalysts show substantial losses under reaction conditions. The metal loss increases with increase in reaction temperature, increase in metal content and increase in reaction time. ESR spectra indicate that metal loss from the catalyst occurs with phthalocyanine macrocycle hydrogenation.

CHARACTERIZATION OF $W(CO)_3(PPr^i_2)_2(\eta^2\text{-}H_2)$, THE FIRST EXAMPLE OF A MOLECULAR HYDROGEN COMPLEX*

G. J. Kubas, R. R. Ryan, P. J. Vergamini, H. J. Wasserman, and B. I. Swanson

Los Alamos National Laboratory, University of California, Los Alamos, New Mexico 87545 U.S.A.

The discovery[1] of isolable 16-electron complexes, $M(CO)_3(PR_3)_2$ (M = Mo, W; R = Cy, Pr^i), has led to an exceptionally rich and unique small molecule coordination chemistry. Facile reversible binding of H_2, N_2, C_2H_4, H_2O, and ROH has been found, as well as irreversible bonding of CO, SO_2, NH_3, and η^2-CH_2O. Addition of H_2 (1 atm) to $M(CO)_3(PR_3)_2$ yields stable yellow crystalline solids mer,trans-$M(CO)_3(PR_3)_2(H_2)$ which have been shown by spectroscopic and crystallographic means to contain a coordinated dihydrogen molecule. The H_2 is extremely labile and reversibly dissociates upon exposure to vacuum. Raman and ir spectra of the H_2, D_2, and HD forms of $W(CO)_3(PCy_3)_2(H_2)$ have been found to be consistent with side bonding of H_2 to the metal and modes at 2690, 2360, and 1900 cm^{-1} have been assigned to be ν(HH), ν(HD), and ν(DD), respectively. $\nu_s(WH_2)$, $\nu_a(WH_2)$, and $\delta(WD_2)$ were observed at 1570, 953, and 319 cm^{-1}. Proton nmr of $W(CO)_3(PPr^i_2)_2(H_2)$ showed a single broad resonance at τ 14.2 for the H_2 ligand but gave a 1:1:1 triplet with J(HD) = 33.5 Hz for the HD species (cf., 43.2 Hz in gaseous HD). Crystal structure analyses of $W(CO)_3(PPr^i_2)_2(H_2)$ demonstrate the presence of the η^2-H_2 ligand; pertinent distances are W-H(avg) = 1.95(23) Å (X-ray), 1.89(1) Å (neutron) and H-H = 0.75(16) Å (X-ray), 0.82(1) Å (neutron).[2]

The H_2 ligand axis is parallel to the P-W-P direction and the H-H separation is slightly larger than that in free H_2 (0.74 Å). This remarkable structure may represent an arrested form of oxidative addition. Theoretical studies,[3] carried out after the discovery of the complex, were found to predict the η^2-H_2 tungsten bonding, which is considered to be primarily a 2-electron, 3-center, σ-type interaction. Further studies, including the reactivity of the H_2 complex, are in progress.

1. Kubas, G. J., Chem. Commun. 1980, 61.
2. Single crystal neutron diffraction studies were carried out at both the Los Alamos Pulsed Neutron Source and Brookhaven National Laboratory, in collaboration with Dr. Thomas Koetzle.
3. Hay, P.J., submitted for publication.

* Research sponsored by U.S. Department of Energy, Office of Energy Research, Chemical Sciences Division.

KINETICS OF HOMOGENEOUS HYDROGENATION OF CYCLOHEXENE CATALYSED BY Rh(I) AND Ir(I) ARSINE COMPLEXES

M.M.Taqui Khan, Nadar T. Khan, Safia and Nasseruddin

University College of Science, Department of Chemistry, Osmania University, Hyderabad-500 007 INDIA

The complexes of the type $MClL(CH_2CH_2AsPh_2)_2$ (where M = Rh(I) or Ir(I)) have been synthesised[1] and characterised by elemental analysis, ir, nmr and conductivity data. These complexes are used as catalysts in the present investigation for the homogeneous hydrogenation of cyclohexene in the temperature range 20-50° and at 0.4 to 1 atms of partial pressure of hydrogen. The dependence of rate of reduction of cyclohexene, on the substrate concentration, catalyst concentration and hydrogen concentration in solution, and temperature is reported. A mechanism has been proposed, in which the catalyst activate molecular hydrogen by forming a dihydrido species of the type $MClL(H)_2$ (where $L = HN(CH_2CH_2AsPh_2)_2$) followed by the transfer of hydrogen to the olefin to form cyclohexane. The kinetic data follows the following rate law:

$$\text{Rate} = \frac{k' K_1 [H_2][C][S]}{(1+K_1[H_2])(1+K_2[S])}$$

k' = rate constant for the rate determing step.

K_1 and K_2 = equilibrium constant.

$[H_2]$, $[C]$ and $[S]$ = hydrogen, catalyst and substrate concentration in solution respectively.

The rate law is in accordance with experimental observations. The order of the reaction with respect of $[H_2]$ and $[S]$ is fractional and that of $[C]$ is pseudo first order. The activation parameters of the reaction ΔH^* and ΔS^* have also been evaluated.

THs41-4

HOMOGENEOUS HYDROGENATION OF 1-HEPTENE CATALYSED BY BIS(DIPHENYLPHOSPHINOETHYLAMINE)CHLORORHODIUM(I)

M.M.Taqui Khan, Badar T. Khan, Safia and Nagaraja Rao

University College of Science, Department of Chemistry, Osmania University, Hyderabad-500 007 INDIA

In the present investigation bis(diphenylphosphinoethylamine)chlororhodium(I) is used as the catalyst for the homogeneous hydrogenation of 1-heptene. The dependence of rate of hydrogenation on factors such as catalyst and substrate concentration at 20° and 30° and 1 atmosphere of hydrogen pressure is reported. One mole of hydrogen is absorbed per mole of the catalyst. The following probable mechanism is proposed for the hydrogenation reaction.

$$MClL + H_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} MClL(H)_2$$

$$MClL + S \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} MClL(S)$$

$$MClL(H)_2 + (S) \xrightarrow[slow]{k'} MClL(H)_2(S)$$

$$MClL(S) + H_2 \xrightarrow[slow]{k''} MClL(H)_2(S)$$

$$MClL(H)_2(S) \xrightarrow{fast} MClL + \text{heptane}$$

$$MClL = RhCl(NH_2CH_2CH_2PPh_2)_2$$

The above tentative mechanism involves the activation of molecular hydrogen by the catalyst to form the dihydride species which then undergoes to form the mono-olefinic species. Further reaction followed by the transfer of hydrogen to the olefin which dissociates off to give the catalyst and the paraffin.

REACTION OF CHROMIUM ATOMS WITH STYRENE AS A SUBSTRATE

Michael C. Shepherd and J.J. Lagowski

Department of Chemistry, The University of Texas at Austin, Austin, Texas, U.S.A., 78712

Cocondensation of chromium atoms with styrene in a heptane matrix at -196°C yields a variety of products. Oligomerized hydrocarbon products include several identifiable (by NMR and mass spectroscopy) dimers and several trimers. The dimers include diphenylbutanes, diphenylbutenes, and diphenylbutadienes. These products vary significantly from those obtained by thermal, acid catalyzed, and other oligomerization processes.

Also present in the reaction mixture is a chromium-containing organometallic complex. The reaction mixture at room temperature is a red-brown color characteristic of bis-arene chromium(0) complexes. The red-brown color changes to a dark blue upon freezing with liquid nitrogen, but returns to the original red-brown upon warming. The color change is tentatively assigned to changes in the mode of coordination of the styrene ligands on the chromium center. The course of the reaction is discussed from the product analyses and other physical chemical data.

THa41-6

TITANOCENE SUPPORTED ON CHRYSOTILE ASBESTOS FIBERS. SELECTIVE HYDROGENATION OF OLEFINS.

Daniel Cozak

Département de chimie, Faculté des sciences et de génie. Université Laval. Québec, Québec. Canada. G1K 7P4.

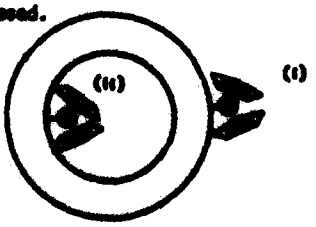
Some aspects of the catalytic properties of supported titanocene reduced by n-buthyllithium has been examined for the hydrogenation of some linear and cyclic olefins at NTP[1,2]. The solid support used is the highly structured brucite-silicate mineral, chrysotile [$Mg_3Si_2O_5(OH)_4$].

The supported titanocene precursor examined (0.9-5.7 w%, Ti) were prepared by reacting $(C_5H_5)_2TiCl_2$ or $(C_5H_5)_2TiCl$ with selected chrysotile short fibres (1-10 μm long) in toluene. A brief account of the chemical and spectroscopic data for the isolated fibre will be given.

The catalytic H_2 gas uptake was measure for several linear olefins (e.g., 1-hexene, 1-octene, 1,3-octene, ...). These results indicate that the activity of the system is comparable to other metal and ligand anchored titanocene complexes. However, the measured H_2 uptake for cycloolefins was significantly slower (ca. 10^{-2}) compared to those measured for the corresponding linear molecules. Moreover, cyclohexene is not hydrogenated by the catalyst under these conditions.

Evidence will be given showing that fibre structure is preserved in the catalyst and titanium is bonded to the fibre's surface. The novel high selectivity reported here for the titanocene catalyst is believed to be caused by the serpentine crystal structure of the support. Hence, models where the titanium is either anchored to the magnesium layer, -Mg-O-$Ti(C_5H_5)_2$ (structure I), or to the silicate layer, ≡Si-O-$Ti(C_5H_5)_2$ (structure II), of the fibre will be discussed.

Cross section of a chrysotile fibre showing possible anchoring sites



1. D. Cozak, C. Barbeau, F. Gauvin, J.-P. Surry, C. Dallaire, R. DeWolf and F. Kimmerle, Can. J. Chem. 61 (1983) 0000.
2. D. Cozak and C. Dallaire, Can. J. Chem., in press.

CARBON MONOXIDE HYDROGENATION ON COBALT BASED * CATALYSTS : THE PROBLEM OF OXYGENATES PRODUCTION.

J.L. Costa, A. Damonceau, J. Drapier, A.J. Hubert, A.F. Noels and Ph. Teyssié.

Laboratory of Macromolecular Chemistry and Organic Catalysis, University of Liège, Sart Tilman, 4000 Liège, Belgium.

Cobalt-based catalysts have been investigated by focusing on the production of oxygenates (particularly alcohols and C_2-oxygenates) in Fischer-Tropsch reactions. It appeared that some Co(I) complexes were in some cases, precursors of catalytic species displaying significant selectivities in alcohols production relatively to other oxygenates (mainly aldehydes). The activity is relatively low under the used conditions (autoclave, no trapping of the products, p=150 bars, T=200-250°C).

The selectivities are very sensitive to support effects and to the presence of cocatalysts. However, the addition of a second metal leads to a strong increase of efficiency in some cases but without improvement of the selectivity : the hydrocarbons remaining the main reaction products. The pressure is an important factor as practically no oxygenates are formed under low pressure (~1 bar).

A comparison between a liquid phase system [1] and a supported catalyst has been realized when using a circulating device allowing the continuous trapping of the products and operating under low pressure (1.4 bar) conditions. Significant production of olefins relatively to alkanes was observed under these conditions. Moreover the influence of different factors (supports, catalyst aging ...) on the selectivities (distribution of hydrocarbons relatively C-atom number, distribution of isomers) and on the yield has been investigated in some typical examples.

Finallly, the factors governing these effects will be disclosed together with the mechanistic implications of our results (e.g. the importance of the oxidation state of cobalt).

* This work was sponsored by the Commission of European Communities (CEE)(Contract n°EE-D-2-326-B).

1) M. Blanchard, D. Vanhove, F. Petit and A. Mortreux. J.Chem.Soc.Chem.Comm.,908 (1980) and Ref.therein.

CATALYTIC PROPERTIES OF IMIDAZOLE-CONTAINING SYSTEMS

T.N.Shahtahtinsky, U.A.Narimanbekov, A.Ye.Smolyar, A.R.Abramov, I.Z.Aliyev, F.M.Ibragimova

Institute of Theoretical Problems of Chemical Technology, pr.Narimanova 29, Baku, USSR, 370143

The quantum chemical investigation of imidazole models with hydrogen donors and π-electronic systems indicates the possibility of catalytic effect by imidazole-containing systems in hydrogen transport and Michael type addition reactions.

The π-complexation of imidazole with unsaturated systems leads to the formation of donor-acceptor pairs with subsequent electron distribution depending upon the nature of unsaturated compounds.

The experimental evidence of the theoretical predictions becomes obvious from the experimental data on the liquid phase catalytic hydrogen exchange between alcohols and carbonyl compounds as well as cyanoethylation of organic substances with activated hydrogen atom using imidazole, hystidine and trypsin as catalysts.

The first type reactions take place in acidic media (pH < 5), while the Michael type reactions are catalyzed by imidazole and its derivatives at pH > 8.

In all cases in the temperature range 25–40 °C the rates of the reactions are comparativily slow.

It is suggested that the hydrogen exchange reactions occur through the simulteneous migration of two protons and the charge distribution along the bond distribution chain with participation of two molecules of imidazole, while the cyanoethylation reaction goes through the four-centre cyclic intermediate arrangement.

The possibility of such slow chemical reactions catalysed by imidazole derivatives in the living matter is proposed.

METHYLMERCURY(II) INTERACTIONS WITH SELENIUM-CONTAINING LIGANDS PERTINENT TO THE ACTIVE SITE OF GLUTATHIONE PEROXIDASE

Alan P. Arnold, Khoon Sin Tan and Dallas L. Rabenstein

University of Alberta, Edmonton, Alberta, Canada T6G 2G2

The mammalian enzyme Glutathione Peroxidase (GSHPx) catalyses the conversion of organic hydroperoxides to alcohols and contains selenium at the active site. Selenium exists as selenocysteine in the reduced form, and as the corresponding selenenic acid (RSeOH) or seleninic acid ($RSeO_2H$) in the oxidised form of the enzyme.[1]

Inhibition of GSHPx by heavy metal ions may result in increased oxidative damage of cellular membranes and thereby be linked to the toxic effects of these metals. We have determined the formation constants for MeHg(II) with $HSe(CH_2)_nCOOH$, n=1-3; selenocysteine, selenocysteamine, selenopenicillamine and $HSeCH_2CH_2OH$. The displacement equilibrium constants for these selenols with the MeHg(II) complex of mercaptoacetic acid were determined by measuring the exchange-averaged ^1H NMR mercaptoacetate resonance as a function of pH in D_2O solution. The selenols form complexes which are more stable by 0.3 to 0.9 logK units than their thiol analogs.[2,3]

By following the conversion of ^tBuOOH to ^tBuOH in hemolysed human erythrocytes by spin-echo and transfer of saturation ^1H NMR experiments, it is apparent that MeHg(II) does not significantly inhibit the peroxidase activity of GSHPx. Species distribution calculations show that under toxic conditions, at most 3% of MeHg(II) is complexed by the enzyme selenohydryl sites at physiological pH, the remainder being bound in rapid exchange to hemoglobin and to substrate glutathione.[4,5]

In the presence of intracellular thiols, insignificant binding is expected to occur at seleninic acid sites of the oxidised form of GSHPx. Equilibrium studies by ^1H NMR with model seleninic acids formed during MeHg(II) cleavage of diselenides in aqueous solution, show only weak binding to seleninic and carboxylic sites of these molecules.

1. R.J. Shamberger, "Biochemistry of Selenium", Plenum Press, New York 1983.
2. R.S. Reid and D.L. Rabenstein, Can. J. Chem. 1981, 59, 1505.
3. A.P. Arnold and A.J. Canty, Can. J. Chem. 1983, 61, 1428.
4. D.L. Rabenstein, A.A. Isab and R.S. Reid, Biochim. Biophys. Acta, 1982, 696, 53.
5. R.S. Reid and D.L. Rabenstein, J. Am. Chem. Soc., 1982, 104, 6733.

A COMPARATIVE STUDY OF Cu(II) AND Ni(II) TERNARY COMPLEXES INVOLVING HETEROAROMATIC N-BASE AND HISTIDINE OR HISTAMINE

Vibha K. Patel and Pabitra K. Bhattacharya

Chemistry Department, M.S. University, Baroda, India.

Cu(II) is known to form two types of complexes with histidine in aqueous medium, [Cu(H.Hist)] with coordination from aminocarboxylate end, imidazole nitrogen being free and protonated and [Cu.Hist], with coordination from amino nitrogen and imidazole nitrogen with free carboxylate. It was thought of interest to study the nature of coordination in ternary complexes [MAL] where M=Cu(II) or Ni(II), A=2,2'-bipyridyl, 1,10-phenanthorline and L=Histidine or Histamine.

The formation constants of the ternary complexes were determined by using SCOGS computer technique. It is observed that two ternary complexes [CuA.H.Hist] and [CuA.Hist] are formed. As expected $\Delta\log k$ is found to be less negative for O^-–N coordinating [CuA.H.Hist] species and more negative for N-N coordinating [CuA.Hist] species. In case of ternary complex involving Ni(II), only one species [NiA.Hist] with coordination from amino nitrogen and imidazole nitrogen is formed and $\Delta\log k$ is negative.

It is interesting to observe that unlike normal observation, $\Delta\log k$ for [NiA.Hist] complex is less negative than for [CuA.Hist] complex. Similar observation is made in cases in [MA.Histamine] complexes also. The probable reason could be that as in the case of $[Cu(bipy)_2(H_2O)_2]$ complex, $[CuA.L(H_2O)_2]$ (L=Hist or Histamine, coordinating from aromatic nitrogen as bipyridyl) also has a cis structure. Hence in the formation of [Cubipy L] from $[Cu(bipy)(H_2O)_3]$, the ligand L gets coordinated at one equatorial and one axial position. Due to Jahn Teller effect, the ligand L is strained and the value of $\log k_{CuA}$ is lowered, resulting in more negative $\Delta\log k$ value than in case of [NiAL], wherein this effect is not operative.

This may be extended as a probably reason why Ni(II) is not preferred in the metalloenzymes, involving a ligand with Histidine like coordination and another O^-–N coordinating peptide or O^-–O^- coordinating phenolate.

NEW MODEL COMPLEXES FOR THE STUDY OF CADMIUM BINDING SITES IN PROTEINS

Robert A. Bulman, Denise Higham, Jeremy K. Nicholson and Peter J. Sadler*

*Department of Chemistry, Birkbeck College, University of London, Malet Street, London WC1E 7HX, UK.

^{113}Cd NMR studies at 44 and 88 MHz of a new amino acid derivative of EDTA will be presented. The ligand is highly unusual in providing a wide variety of binding sites for cadmium ions which are in relatively slow exchange on the NMR timescale. Further curiousity arises from the observation that three of the ^{113}Cd nmr signals exhibit similar chemical shifts to those of the naturally-occuring cadmium-binding protein metallothionein. Moreover they also show homonuclear ^{113}Cd-^{113}Cd spin-spin coupling : the first example in a model system.

MIXED-LIGAND BIOMETAL COMPLEXES WITH CATECHOLAMINES AND NUCLEOTIDES ESSENTIAL IN THE MECHANISM OF NEUROTRANSMITTER ACTION

A.S.Grigoriva, N.P.Konakhovich, L.I.Budarin, V.G.Golovaty and V.V.Shabelnicov

The L.V.Pisarzhevsky Institute of Physical Chemistry of Ukrainian SSR Academy of Sciences, Kiev, USSR, 252150

Recently, a complexation has been suggested to be essential in normal functioning of neurotransmitters, catecholamines (CA), i.e. the CA binding, storage and transport are effected in the form of the complexes with biometals and nucleotides capable of existing in brain fractions rich in CA, metal ions and ATP.

A mixed-ligand complexation in vitro for ternary systems containing biometals (Ca, Mg, Zn, Mn, Fe, Cu), exogeneous CA (H_2L^+) and ATP has been revealed by field desorption mass spectrometry (FDMS), pH-potentiometry and EMR.

A precise calculation of complexation equilibria has indicated that for ternary systems, in the pH range 3-6, a metal is bound to ATP and with increasing pH up to physiologic values, CA coordinates to a metal-ATP complex to produce mainly a 1:1:1 mixed-ligand complex.

The formation constants for ternary chelates have been calculated. Their magnitude depends regularly on the nature of metal, the structure ofcatecholamine and acid-basic properties of catecholamine donor groups.

In FDMS, for ternary solution system, at pH 8, an intensive line corresponding to a mixed-ligand ion, $[M(HL)ATP^{3-}]$ is observed and a wide temperature range. A mode of ligand coordination in the ternary chelate has been established by the type molecular ion fragmentation, i.e. via the donor oxygen atoms of an ATP phosphoric acid fragment, nitrogen and oxygen of the CA side chain.

Our findings provide a direct evidence for the existence of ternary chelates of biometals with nucleotides and catecholamines responsible for the metabolism of neurotransmitters in vivo.

THE REDUCTION OF OCTAETHYL- AND TETRAPHENYL-PORPHINATO, PLATINUM(IV) CHLORIDE BY PIPERDINE

Barry Schwartz and Saul I. Shupack

Villanova University, Villanova, Pa., USA, 19085

Synthetic metal porphyrins are useful models for the study of the redox and coordination chemistry of biological porphyrins such as hemoglobin and chlorophyll. The reaction between six coordinate octaethyl- or tetraphenyl-porphinato platinum (IV) chloride (Pt(IV)OEPCl$_2$ and Pt(IV)TPPCl$_2$) and piperidine results in the reduction to the corresponding four coordinate Pt(II) porphyrin, a two electron transfer. The reaction is first order in both reactants in the initial stages, but after the reaction is about 50% complete the kinetic's become complex. The second order rate constants are about 3×10^{-4} M^{-1} sec^{-1} and 6×10^{-4} M^{-1} sec^{-1} respectively. Temperature studies showed the reaction to be endothermic, with $\Delta H^{\ddagger}$ = 12 kcal/mole for both complexes.

ESR studies failed to show any evidence of a Pt(III) intermediate or a piperidine radical. In addition no initial porphyrin-piperidine molecular complex was observed. The entropy of activation is -33 eu for both complexes which is indicative of an outer sphere reaction.

Mass spectrometry identified pyridine as the oxidation product of piperidine for the Pt(IV)OEPCl$_2$ reaction. Thus, the reduction of three molecules of Pt(IV)OEPCl$_2$ will oxidize one piperidine molecule. The intermediate oxidation products of piperidine are thought to increase the complexity of the reduction during the later stages. This process is different from that observed for the Fe(III)TPPCl reduction[1].

1. J. Del Gaudio and G.N. LaMar, J. Am. Chem. Soc., 100, 1112 (1978).

THs42-6

THE ELECTRONIC STRUCTURE OF PLANAR PALLADIUM COMPLEXES AND THEIR BIOLOGICAL ACTIVITY

L.N. Mazalov, E.A. Kravtsova, A.A. Voityuk

Institute of Inorganic Chemistry, Siberian Branch of the USSR Academy of Sciences, Novosibirsk, USSR

FThe results of a quantum-chemical and X-ray spectral study of cis- and trans-isomers $Pd(NH_3)_2Cl_2$, $Pd(glH)_2Cl_2$ and $Pd(gl)_2$ and of the compounds Pd(gl)(glH)Cl , $Pd(NH_3)_4Cl_2$ and K_2PdCl_4 are considered. The electronic structure calculations were performed by the semiempirical INDO method. The profile of the X-ray ClKβ -spectrum was found to depend on the mutual arrangement of the Cl atoms and can be used to establish the cis- or trans-configuration of the com - pounds. According to the calculations, the change in the short wave intensity of the spectrum corresponds to the change of the Cl 3p AO contribution to the occupied antibonding MO and, hence, can be used for prediction of changes in the Pd-Cl bond strength in other complexes.

The PdLβ_2 spectrum characterizes the extent of participation of the 4d AO of the metal in the MO of the complex. The profile of the spectrum depends markedly on the charhe on the central atom. The obtained experimental and calculated results show the charge on the metal in the complexes to increase on going from a cis- to a trans-isomer.

On the basis of these results the relationship between the biological activity of the complexes and their electronic structure is considered.

CHROMIUM(III) COMPLEXES OF GLUTATHIONE

M. Abdullah, J. Barrett, and P. O'Brien

Department of Chemistry, Chelsea College, University of London, Manresa Road, London, SW3 6LX, United Kingdom.

The Glucose Tolerance Factor (GTF)[1] is a chromium(III) complex believed to enhance the activity of insulin by acting as a cofactor. It has been isolated from a number of systems but most notably Brewer's yeast. Analysis of material from yeasts indicates the major components to be chromium(III), glycine and cysteine together with glutamic and nicotinic acids. The amino acids involved are the components of the naturally occurring tri-peptide glutathione (GSH or H_3L^+).

The effectiveness of GTF is usually assessed in an isolated adipocyte cell system[2]. Glucose uptake by the cells is measured in the presence and absence of GTF and/or insulin. Active GTF preparations stimulate glucose uptake by the cells in the presence of insulin; but it is important to note that in the absence of insulin metabolism is unaffected. *GTF is* thus not insulin mimetic but insulin potentiating. The mechanism of this process is at present unknown and studies are hampered by the fact that little is known of the structure of GTF. Although complexes of chromium(III) showing GTF behavior have been *synthesized*, none of these have been characterised. An uncharacterised chromium(III) complex of glutathione and nicotinic *acid shows remarkable* activity in *in vitro* test systems[2]. We wish to report the synthesis and characterisation of a number of GSH/Cr(III) complexes; these are the first such complexes to be prepared.

Three different kinds of complex have been synthesized: a bis-glutathione complex $K_3[Cr(H_2L)(H_3L)]$, mixed complexes with the amino acid L-cysteine, L-glutamic acid and L-aspartic acid $K_3[Cr(H_2L)(A(2-)]$ (A(2-) is the dianion of the amino acid) and a mixed complex with glycine $K_3[Cr(H_2L)(gly^0-(OH))]$. All these complexes exhibit an intense UV charge transfer band which is characteristic of a Cr-S bond. The sulphydryl to chromium linkage undergoes an acid-catalysed hydrolysis. The complexes have been characterised by elemental and thermogravimetric analysis, electronic and infra-red spectroscopy and circular dichroism. Comparison of these properties with those of known chromium(III) complexes leads to the conclusion that glutathione is bound to chromium(III) by the C-terminal glycine group (N,O) and the deprotonated sulphur of cysteine. The glutamic acid residue does not apparently interact with the chromium center in these complexes.

Preliminary testing indicates that these complexes may show some biological activity both in cultures of yeast cells and isolated rat adipocytes.

1. Mertz, W., *Nutrition Reviews*, *31*, 148, 1973.
2. Anderson, R.A., J.E. Brenner, and M.M. Polansky, *J. Agric. Food Chem.*, *28*, 1216, 1978.

ELECTROSTATIC EFFECTS IN METALLOPROTEIN ELECTRON TRANSFER: A COMPUTER GRAPHICS STUDY OF THE INTERACTION BETWEEN PLASTOCYANIN AND CYTOCHROME c

Hans C. Freeman,[1] Elizabeth D. Getzoff[2] and John A. Tainer[2]

[1] Department of Inorganic Chemistry, University of Sydney, N.S.W. 2006, Australia. [2] Department of Molecular Biology, Research Institute of Scripps Clinic, La Jolla, CA 92037, U.S.A.

The Cu-protein, plastocyanin (M.W. = 10,500), has an essential role in photosynthesis as an electron carrier between Photosystems II and I. The biological electron donor to plastocyanin is a membrane-bound heme protein, cytochrome f (M.W. = 30,000). Electron-transfer from a related protein, cytochrome c (M.W. = 12,400), to plastocyanin in aqueous solution has some shortcomings as a model for the biological system, but is a well documented reaction.

In order to test the hypothesis that electrostatic effects play an important role in electron-transfer between metalloproteins, we have made calculations of the electrostatic potential and field at various distances from the molecular surfaces of plastocyanin and cytochrome c. We have used the results to direct a computer graphics search for orientations which are likely to favour electron transfer between the molecules.

The calculations comprise (i) the definition of the 'surface' of a molecule as that surface which is accessible to a probe sphere with a 1.4Å radius, (ii) the assignment of partial charges to the atomic positions, using a data-base of quantum-mechanically derived partial charges for various types of amino-acid residue, and (iii) the calculation of the electrostatic potential and field at closely spaced points on the 'surface' of the molecule and at various distances - 6Å, 8Å ....12Å - from it. The results of the calculations are displayed as computer-generated stereoscopic diagrams in which colour-coded arrows represent the magnitudes and directions of the electrostatic field vectors at various distances from the molecule.

The calculations have shown that electrostatic field effects are significant even at distances of 12Å from the molecular surfaces. Representations of the molecules and their electrostatic field vectors may be manipulated by means of computer graphics to produce orientations in which the complementarity between the electrostatic fields, as well as the opportunities for hydrogen-bonds and for electrostatic interactions between side-chains, are plausible.

A number of computer-generated stereoscopic colour diagrams will be displayed.

THE PROLINE RESIDUE AS A 'BREAK-POINT' IN COMPLEXES OF OLIGOPEPTIDES WITH COPPER(II)

Henryk Kozlowski, Grazyna Formicka-Kozlowska and Leslie D. Pettit.

Institute of Chemistry, University of Wroclaw, 50-383 Wroclaw, Poland,
Department of Inorganic and Structural Chemistry, The University, Leeds, LS2 9JT, U. K.

Insertion of a proline residue into the second or third position of a tetrapeptide chain divides the molecule into two fragments which are potentially able to co-ordinate independently with a metal ion. What is more, the proline residue encourages a beta-turn in the peptide chain, particularly when in the second position, with the result that the two ends of the chain are encouraged to adopt a conformation favourable to joint chelation to a metal ion such as copper(II). This means that copper can lock the peptide into the biologically important 'bent' conformation.[1] This could provide a role for copper in the activity of some neuropeptides and endomorphins.

To establish the chemical basis of these suggestions we have studied the copper complexes of the following families of ligands, using potentiometry and UV, visible, CD and EPR spectroscopy:

Pro-GlyGlyGly, Gly-Pro-GlyGly, GlyGly-Pro-Gly and GlyGlyGly-Pro;
Sar-GlyGlyGly, Gly-Sar-GlyGly, GlyGly-Sar-Gly and GlyGlyGly-Sar;
Phe-Pro-GlyGly, Gly-Pro-Phe-Gly and Gly-Pro-Gly-Phe;
Tyr-Pro-GlyGly, Gly-Pro-Tyr-Gly and Gly-Pro-Gly-Tyr together with the naturally occuring peptides melanostatin (Pro-Leu-Gly-NH_2), thyrotropin releasing factor (Pyr-His-Pro-NH_2) and neuromedin[2,3] (Tyr-Pro-Phe-Pro-Gly) together with its component peptides.

The results confirm the specific effect of a proline residue on a peptide chain. Co-ordination starts with the nitrogen of the terminal amine group and the first peptide proton to ionise is generally the peptide proton of the C-terminal amino acid to form a large chelate ring spanning the two ends of the tetrapeptide chain.

The results and their implications will be discussed.

1) P. Y. Chou and G. D. Fasman, J. Mol. Biol., 1977, 115, 135.
2) G. Formicka-Kozlowska, H. Kozlowski and L. D. Pettit, J. Inorg. Biochem., 1983, 18, 315.
3) H. Kozlowski, H. Kozlowski, L. D. Pettit, M. Bataille and B. Becquet, J. Inorg. Biochem., 1983, 18, 231.

THE COORDINATION CHEMISTRY OF MICROBIAL IRON TRANSPORT

Kenneth N. Raymond

Department of Chemistry, University of California, Berkeley, California 94720 USA

Iron is the only transition metal for which well-defined biological uptake and transport processes have been characterized. The need for such processes is due both to the ubiquitous role of iron in biology and to its *profound* insolubility as the hydroxide of aqueous Fe(III). For bacteria, fungi and other microbes, the solubilization and cellular absorption of iron takes place using a class of Fe(III)-specific complexing agents called siderophores. The coordination chemistry and function of several of these agents will be reviewed.[1]

There are many different siderophores known and several types of transport behavior have been characterized. We have used metal-substituted [Cr(III) for Fe(III)], kinetically inert siderophore complexes to probe some of the mechanistic features of Fe(III) transport into the microbial cell. We have also used Ga(III) substitution to probe the possible involvement of reduction in the release of iron by the siderophore. Recently synthetic siderophores have been prepared in which certain molecular fragments are the same as the modeled siderophore. Complexes of these ligands are then used to determine how the molecular recognition process works for those siderophores for which there are specific receptors on the microbial membrane surface.

The solution equilibria and exchange kinetics of siderophore complexes are being studied in order to determine the intrinsic limitations of iron exchange processes as they relate to microbial iron transport.[2]

1. K. N. Raymond, G. Müller and B. F. Matzanke, Topics in Current Chemistry, Vol. 123, 1984.

2. V. L. Pecoraro, W. R. Harris, C. B. Wong, C. J. Carrano and K. N. Raymond, J. Am. Chem. Soc. 1983, 105, 4623.

CHEMICAL AND BIOLOGICAL PROPERTIES OF RETROHYDROXAMATE FERRICHROME

Thomas Emery and Richard K. Olsen

Utah State University, Department of Chemistry & Biochemistry, Logan, Utah 84322

Ferrichrome is a trihydroxamate peptide type siderophore for several microorganisms. We have now obtained retrohydroxamate ferrichrome by chemical synthesis. In this molecule, the three -CO- and -NOH- functions have been reversed in the hydroxamate containing side-chains. Examination of molecular models suggested that this derivative might mimic the biological action of ferrichrome.

The retro derivative was compared to ferrichrome in three independent assays. It was indistinguishable from ferrichrome as a growth factor for the auxotroph, Arthrobacter terregens, over a thousand-fold concentration range. No detectable difference in the two compounds was observed in their ability to antagonize the antibiotic action of albomycin against Bacillus subtilis. Finally, the Fe-59 labelled compounds were compared in their effectiveness as ferric ionophores for the fungus, Ustilago sphaerogena. Although the shapes of the uptake curves were somewhat different, the retro derivative was as least as effective as ferrichrome during the initial phase of uptake. The rate of iron uptake was not diminished upon addition of ferrichrome A, demonstrating that the retro compound utilizes the ferrichrome uptake system.

In contrast, desmethylretrohydroxamate ferrichrome, in which the three methyl groups surrounding the iron are replaced by hydrogens, showed no activity with A. terregens and was not an effective siderophore for U. sphaerogena, demonstrating that the methyl groups are essential for biological activity.

In spite of the biological activity of retrohydroxamate ferrichrome, we unexpectedly found significant differences in chemical properties when compared to ferrichrome. In particular, it appears to be a much weaker chelator of iron(III) as shown by the sensitivity of the visible spectrum to pH and the ability of 0.02M ethylenediaminetetraacetate to compete for its iron, which is not the case for ferrichrome.

In conclusion, retrohydroxamate ferrichrome is the first chemically synthesized substance that exactly mimics the biological activity of ferrichrome, and this work offers a route to the synthesis of other analogues that may be orally effective in the treatment of iron storage diseases.

THERMODYNAMIC AND MECHANISTIC STUDIES OF IRON(III) HYDROXAMIC ACID COMPLEXES RELATING TO IRON BIOAVAILABILITY

A. L. Crumbliss and L. Fish

Duke University, Department of Chemistry, Durham, NC, USA, 27706

Although iron is the fourth most abundant element in the earth's crust, its bioavailability is limited due to the low solubility of the aquo ion in neutral medium caused by hydrolysis. In order to acquire this essential element aerobic and facultative aerobic microorganisms utilize iron(III)-specific chelating agents, called siderophores. The function of these siderophores is to solubilize the iron by forming an iron(III) complex which is transported to the cell where the iron is released. Two classes of siderophores have been identified based on the structure of the iron binding site: catechols and hydroxamic acids. There is some evidence that thiohydroxamic acids may be a potential member of the class of siderophores.

Kinetic and thermodynamic data will be presented for iron chelation by synthetic hydroxamic acids, $R_1C(O)N(OH)R_2$, and thiohydroxamic acids, $R_1C(S)N(OH)R_2$, and for complex dissociation. Direct comparisons will be made to determine the influence of the >C=S donor group in the thiohydroxamic acids relative to the >C=O donor group in the hydroxamic acids on the kinetics and mechanisms of complex formation and dissociation. These results will be related to possible bioavailability pathways available to the natural siderophores and to the potential efficiency of the thiohydroxamate moiety as a biological iron transport binding site. For example, the kinetics and thermodynamics of iron(III) chelation and complex dissociation for p-(CH_3O)-C_6H_4-$C(X)N(OH)H$ (X = S,O) have been investigated. Comparative results between the O and S hydroxamate systems may be summarized as follows: 1) the thiohydroxamic acid ligand forms a more stable complex in acid medium; 2) formation rates on $Fe(H_2O)_6^{3+}$ and $Fe(H_2O)_5OH^{2+}$ are comparable for both ligands; 3) iron(III) complexes of both ligands undergo aquation via parallel acid dependent and acid independent paths; and 4) aquation by either path is 100 times slower for the thiohydroxamic acid complex. The mechanistic implications of these and other data will be discussed.

Kinetic data for iron exchange reactions between hexadentate chelators (siderophores and aminocarboxylates) will be presented along with evidence for catalysis of these exchange reactions by mono- and bidentate ligands of biological relevance. These results will be discussed in relationship to possible mechanisms for iron exchange related to siderophore mediated iron bioavailability.

RECOGNITION AND TRANSPORT OF COORDINATION ISOMERS OF SIDEROPHORES IN FUNGI

Günther Winkelmann and Hans-georg Huschka

University of Tübingen, Institut für Biologie I, Mikrobiologie I, Auf der Morgenstelle 1, D-7400 Tübingen, FRG, Germany

Our understanding of the mechanism of iron uptake, mediated by sid-rophores is still in a rudimentary state, partly because of the insufficient knowledge concerning the the conformation and configuration of siderophores and partly because of the inherent difficulties in working with such a complex structure as the cell membrane.

Although the designation " siderophore " might suggest an analogy to the classical ionophores, which penetrate membranes by enhancing the lipophilicity after ligation, there is considerable evidence that siderophore uptake is a receptor-mediated uptake process requiring a structure-function relationship between siderophores and membrane " carriers". Recent studies from our laboratory have demonstrated that uptake of siderophores into fungal cells involves highly specific recognition of siderophores by membrane located transport systems(1, 2).

In these studies a correlation between structure and recognition was established by the use of *enantiomeric* siderophores: The chemically synthesized Δ-cis-*enantio*-ferrichrome, containing D-ornithine, was excluded from transport, whereas the natural Δ-cis-ferrichrome was rapidly transported.

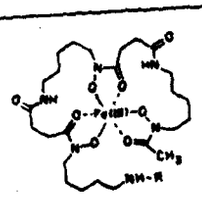
In order to decide which part of the siderophore molecule - peptide moiety or coordination center - is of above importance for uptake, we compared binding and transport of Δ-cis-*enantio*-ferrichrome, Δ-cis-*enantio*-ferrichrome with Δ-coprogen, and ferrichrome with [illegible] (3)

1. G. Winkelmann, FEMS Lett. 1979, 5, 93.
2. G. Winkelmann and V. Braun, FEMS Microbiol. Lett. 1981, 11, 239.
3. G. Winkelmann, H. Voigt, G. Duhy and G. Winkelmann (in press).

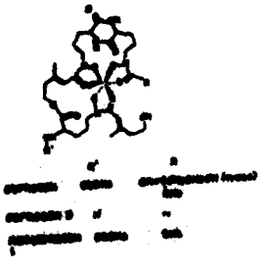
THE MOLECULAR STRUCTURES OF TWO LINEAR SIDEROPHORES: (1) FERRIOXAMINE D_1 and (2) NEOCOPROGEN I, A NOVEL COPROGEN ANALOG, BY X-RAY DIFFRACTION

M. Bilayet Hossain, M. A. F. Jalal, Beverly Benson, Charles L. Barnes and Dick van der Helm

Department of Chemistry, University of Oklahoma, Norman, Oklahoma 73019 USA



FERRIOXAMINE B : R = H
FERRIOXAMINE D_1 : R = $COCH_3$



(1) Ferrioxamine D_1, $C_{27}H_{47}N_6O_9Fe$: The ferrioxamine family of siderophores (iron sequestering and transport agents) is produced by several species of Streptomyces and Nocardia. Ferrioxamine D_1 is a member of the linear ferrioxamines and is an N-acetyl derivative of Ferrioxamine B (Figure). The compound was purified by reversed phase chromatography and crystallized from methanol-ether system under anhydrous conditions.

Ferrioxamine D_1 crystallizes in the triclinic system, space group $P\bar{1}$ with a = 15.036(20), b = 16.240(17), c = 7.861(8) Å, α = 89.30(9), β = 100.01(11), γ = 101.82(10), V = 1847.4 Å^3, Z = 2. The structure was determined from 5131 diffractometer data measured at 138K using MoKα radiation (2θ(max.) = 48°). Final R factor is 0.066. The crystal structure contains a racemic mixture of Δ-cis and Λ-cis isomers. Details of structural features will be discussed in comparison with other related structures.

(2) Neocoprogen I, $C_{31}H_{47}N_6O_{12}Fe$, a novel siderophore was isolated from iron-deficient cultures of Curvularia pallulata, which also produces coprogen and a number of other minor siderophores. The compound was purified by reversed phase chromatography using C_{18} bonded silica gel as the stationary phase and methanol-water gradient as the mobile phase. It was crystallized from ethanol solution equilibrated with acetonitrile at 4° C.

Crystal data: Orthorhombic $P2_12_12_1$, a = 8.80(1), b = 26.33(4), c = 36.84(4) Å, V = 8085.1 Å^3, Z = 8. Structure was determined by direct methods using 4288 reflections measured at 138K using MoKα radiation (2θ(max.) = 48°). The R factor at this stage of refinement is 0.129. Neocoprogen I assumes Δ-trans isomer, and is the first example of a [illegible] coordination of a [illegible] in the solid state.

COORDINATION ISOMERIZATION IN THE GALLIUM COMPLEX OF DESFERRIFERRIOXAMINE B

Brandan A. Borgias and Kenneth N. Raymond

Department of Chemistry, University of California, Berkeley, California 94720 USA

Desferriferrioxamine B (Desferal®) is a natural ferric ion complexing agent or siderophore[1] produced by Streptomyces pilosus, and is currently used in the clinical treatment of individuals with either acute or chronic iron overload. It is a trihydroxamic acid that yields a cationic, six-coordinate complex upon metal binding at neutral pH. It had been shown that the Cr^{3+} complex of desferriferrioxamine B exists as a mixture of two (or more) geometrical isomers.[2] It was also suggested that only five of the eight possible geometric isomers were sterically possible. However, an additional isomer has recently been isolated and it has been shown that eight, not five, isomers are actually possible.[3] The ferric complex presumably exhibits the same coordination isomerism but, due to the kinetic lability of high-spin ferric complexes, these isomers cannot be isolated.

We have performed ^{13}C-NMR measurements on the Ga^{3+} and Al^{3+} complexes of desferriferrioxamine B and have found that only two significant isomers are observed in both cases. Possible assignments of these isomers are discussed based on the observed chemical shift data. Furthermore, the observed rate of interconversion between the isomers of the Ga^{3+} complex was determined in MeOH solution: k_{obs} = 75(6) s^{-1} with $\Delta H^{\dagger}$ = 17(1) kcal/mol, and $\Delta S^{\dagger}$ = 9(3) e.u.

Additional experiments, aimed at identification of the isomers and elucidation of the imerization mechanism in aqueous solution, will be discussed.

1. K. N. Raymond, G. Müller and B. F. Matzanke, Topics in Current Chemistry, Vol. 123, Springer-Verlag, 1984.

2. J. Leong and K. N. Raymond, J. Am. Chem. Soc. 1975, 97, 293.

3. G. Müller, W. Keller-Schierlein and K. N. Raymond, submitted to J. Bacteriology.

IRON(III) COORDINATION CHEMISTRY OF LINEAR DIHYDROXYBENZOYL-SERINE POLYMERS DERIVED FROM ENTEROBACTIN

David J. Ecker, Sylvia C. Liu, Chiu Y. Ng and Kenneth N. Raymond

Department of Chemistry, University of California, Berkeley, California 94720 USA

Under conditions of nutritional iron stress enteric bacteria produce enterobactin, a low molecular weight iron chelating agent (siderophore), for the purpose of solubilizing extracellular iron. Enterobactin is a cyclic trimer of dihydroxybenzoylserine (DHBS) residues linked by ester bonds. Sequential hydrolysis of enterobactin gives DHBS linear trimer, dimer and monomer, all of which are capable of complexing ferric ion. These products were isolated from the culture supernatant of E. coli by DEAE sephadex chromatography and preparative electrophoresis. The iron(III) coordination chemistry of each compound was studied by CD spectroscopy, spectrophotometric and potentiometric pH titrations and EDTA competition experiments. The CD spectrum of the ferric linear trimer agreed in all major features with the CD of ferric enterobactin, suggesting the same (Δ) metal ion absolute configuration. Protonation constants for the ferric linear trimer are 7.1, 5.2 and 3.9; higher than the values for ferric enterobactin.

THa43-7

SIDEROPHORE ACTIVITY OF FERRIC HYDROXAMATE COMPLEXES

Samuel J. Goldman, Peter J. Lammers, and Joann Sanders-Loehr
Portland State University, Portland, Oregon, USA 97207

Jeffrey E. Plowman and Thomas M. Loehr
Oregon Graduate Center, Beaverton, Oregon, USA 97006

Schizokinen, a dihydroxamate derivative of citric acid, is the siderophore produced by several strains of Anabaena cyanobacteria.[1-3] In the ferric schizokinen complex the iron appears to be chelated via the α-hydroxycarboxylate group of the citrate moiety as well as the two hydroxamate groups.[4] Evidence for this hexadentate structure comes from comparisons of the behavior of ferric schizokinen and ferric acetylschizokinen, a compound in which the citrate hydroxyl group has been modified by acetylation. At neutral pH, ferric schizokinen has an absorption spectrum characteristic of a citrate dihydroxamate; its molecular weight and electrophoretic mobility are characteristic of a 1:1 complex. Ferric acetylschizokinen, on the other hand, has an absorption spectrum characteristic of a trihydroxamate; its molecular weight and electrophoretic mobility are indicative of the formation of a $(\text{ferric})_2(\text{acetylschizokinen})_3$ complex. Thus, carboxylate coordination is only favored when the α-hydroxy group can provide a chelate ring.

Different ferric hydroxamate complexes vary in the effectiveness with which they promote iron uptake in Anabaena. Acetylschizokinen is active in the same concentration range as schizokinen.[4] Aerobactin, a citrate dihydroxamate with two additional carboxylates, requires a 10-fold higher concentration to approach the siderophore activity of schizokinen.[3] Ferrioxamine B, a ferric trihydroxamate, is essentially inactive. A comparison of the structures of these four compounds indicates that a common feature required for siderophore recognition may be the presence of two $-N(OH)-C(O)-CH_3$ groups in the iron coordination environment.

1. P.B. Simpson and J.B. Neilands, J. Phycol. 1976, 12, 44.

2. P.J. Lammers and J. Sanders-Loehr, J. Bacteriol. 1982, 151, 288.

3. S.J. Goldman, P.J. Lammers, M.S. Berman, and J. Sanders-Loehr, J. Bacteriol. in press.

4. J.E. Plowman, T.M. Loehr, S.J. Goldman, and J. Sanders-Loehr, J. Inorg. Biochem., in press.

PH-METRIC EVIDENCE ON METAL-PEPTIDE NITROGEN LINKAGE IN THE COMPLEXES OF SOME OLIGOPEPTIDE DERIVATIVES

Ram Nayan

Department of Chemistry, Hindu College (Rohilkhand University), Moradabad-244001, India

Elucidation of structures of metal peptide complexes in aqueous solution is of considerable attraction in view of their importance as model systems in biological studies. Investigations on some oligopeptide derivatives (H_2L), diglycine-N,N-diacetic acid (2GDA), triglycine-N,N-diacetic acid (3GDA), and tetraglycine-N,N-diacetic acid (4GDA) with transition metal ions, Co^{2+}, Ni^{2+}, and Cu^{2+}, carried out in solution using pH-metric measurements and ir spectral studies, have yielded interesting informations. The pH vs moles of alkali used per mole of ligand($\bar{n}$) curves of 1:1 metal-ligand systems (below $\bar{n}$=3) and the ir spectra have indicated the formation of MHL (with terminal unionized carboxylate) and ML^- species (where M=is the transition metal ion), involving the amine nitrogen-diacetic acid carboxylates (and amido carbonyl with some metal ions) in coordination.

An increase in $\bar{n}$ values beyond 3.0 may be expected due to, either complex hydrolysis or proton removal from the peptide nitrogen (free dissociation or displacement due to complexation). On the basis of ir spectra, the authors[1] have suggested the metal-peptide nitrogen binding in the complexes formed above $\bar{n}$=3 (except in Ni^{2+}-2GDA system where they observed the existence of $NiL(OH)^{2-}$), while the association of OH^- ion with the complexes appears to be more reasonable because of high pK values of peptide hydrogen. Thus, applying the previously described method[2], a modified pH-metric evidence has been presented to examine metal-peptide nitrogen bindings in such systems. The study has been extended, also, to those complex systems where ir spectra were not measured due to, incomplete formation of the complex species or the other reasons. The results obtained, confirm the participation of peptide nitrogen in coordination with metal ions and show the formation of $NiH_{-1}L^-$ instead of $NiL(OH)^{2-}$ [with 2GDA], $NiH_{-1}L(OH)^{2-}$ [with 3GDA], and $CoH_{-1}L(OH)^{2-}$, $CoH_{-1}L(OH)^{4-}$ [with 4GDA] involving one or two peptide nitrogens.

1. R.J. Motekaitis and A.E. Martell, Inorg. Chem. 1974, 13, 591.
2. R. Nayan and A.K. Dey, Transition Metal Chem. 1977, 2, 110.

PREPARATION AND SPECTRAL CHARACTERISATION OF Cu(II) COMPLEXES OF SOME BIOLOGICALLY ACTIVE ORGANIC CHELATING AGENTS

Bhagwan S. Garg and Satendra K. Jain

Department of Chemistry, University of Delhi, Delhi-110007, India

Cu(II) complexes of biologically active ligands, such as 2-acetylpyridine-4,4'-dimethyl-3-thiosemicarbazone and 2-acetylpyridine-4(4-methylpiperidinyl)-3-thiosemicarbazone, have been synthesized. The general formula of the complexes prepared is CuLX, where X=F^-, Cl^-, Br^-, I^-, CH_3COO^- and NO_3^- and L=deprotonated form of the above thiosemicarbazones. Complexes have been duly characterized by the elemental analysis, magnetic measurement, infrared spectra, electronic spectra, conductivity measurements and epr spectra. The conductivity data for the complexes in DMF point them to be non-electrolytic in nature. Infrared data for both the series of compound provide the information that ligands behave as deprotonated tridentate (coordinating through NNS set of donor atoms) in these complexes, fourth position being occupied by anion 'X'. Monodentate nature of polyatomic anion, i.e. nitrate and acetate, has also been ascertained through ir data. Electronic spectra in nujol mull, $CHCl_3$ and DMF suggest the planar geometry of the complexes. The epr data for solids, powders and solutions at RT and LNT point towards the axial $d_{x^2-y^2}$ ground state and suggest coordination through sulphur, which is in agreement with ir results. A little change in 'g' value upon lowering in temperature indicates no significant change in planarity of these species. epr studies in solution at RT and LNT also point that ligand provides a strong covalent environment with strong in plane sigma- and pi-bonds.

XANTHINE COMPLEXES WITH FIRST ROW TRANSITION METAL IONS

Chester M.Mikulski, Matthew Kurlan

Department of Chemistry and Physics, Beaver College, Glenside, Pennsylvania, USA 19038

and Nicholas M.Karayannis

Amoco Chemicals Corporation, P.O.Box 400, Naperville, Illinois, USA 60566

During previous studies in these laboratories, a complex of the $Cu(xn)_2 \cdot 2HClO_4$ type was isolated, by refluxing for a week a mixture of xanthine (xnH) and hydrated copper(II) perchlorate in ethanol-triethyl orthoformate (teof), and characterized [1]. Analogous synthetic reactions between xnH and the perchlorates of several 3d dipositive (M = Mn, Fe, Co, Ni, Zn) and tripositive (M = Cr, Rh) metal ions were performed during the work herein described.

Mixtures of the ligand and the hydrated metal perchlorate in either ethanol-teof or ethyl acetate were refluxed for periods ranging from five to twenty five days, depending on the speed of accumulation of substantial quantities of each particular solid metal complex. Under these preparative conditions, manganese(II) and iron(II) perchlorates behave in the same manner as copper(II) perchlorate, yielding $Mn(xn)_2 \cdot 2HClO_4$ and $Fe(xn)_2$ complexes. However, the metal(III) and the rest of the metal(II) (M = Co, Ni, Zn) perchlorates formed adducts with neutral xnH, of the $M(xnH)_2(ClO_4)_3 \cdot 2H_2O$ (M = Cr, Rh) and $M(xnH)_2(ClO_4)_2 \cdot 3HClO$ (M = Co, Ni, Zn) types.

The C=O stretching bands of free xnH (1700, 1660 cm^{-1}) are not significantly shifted upon formation of any of the new metal complexes. This indicates that none of these compounds involves O(2)- or O(6)-coordinated xanthine. The M(III) complexes are apparently isomeric with two terminal xnH, two aqua and two $-OClO_3$ ligands coordinated to the metal ion, and one ionic ClO_4^- group. The M(II) complexes are bi- or poly-nuclear. Among these, $Fe(xn)_2$ is magnetically ordered at room temperature, and probably involves multiple xn bridges between adjacent Fe(II) ions. The rest of the M(II) complexes show near-normal room temperature magnetic moments and are considered to be linear chainlike polymers with single xanthine bridges between adjacent metal ions (M = Mn, Co, Ni, Zn). These complexes contain also terminal monodentate xanthine and ethanol ligands, xnH, for M = Co, Ni, Zn, octahedrally bonds perchlorate, bidentate xanthine probably coordinates through N(9), while bidentate hydroxyl ethanol is most likely coordinating through the N(7) and N(9) heterocyclic nitrogens [2].

1. C.M.Mikulski, M.Kurlan, L.Antonucci and N.M.Karayannis, Inorg. Chim. Acta, 1975, [illegible] in Pr.

2. P.E.Fjeldsted and S.Altshuler, Inorg. Chim. Acta, 1975, [illegible] 169.

CRYSTAL STRUCTURE OF A COPPER COMPLEX OF 2-C-CARBOXY PENTONIC ACID; A DECOMPOSITION PRODUCT OF ASCORBIC ACID.

Richard E. Norman, Ronald E. Stenkamp, and Norman J. Rose

University of Washington, Seattle, Washington, USA 98195

The crystal structure of the title complex contains two different copper sites. The copper atoms in one site are components of an alternating Cu-O six membered ring. Each copper atom in this ring is bound to four oxygen atoms; a square pyramidal coordination is completed by a weakly bound chlorine atom. The other copper environment is a 4 + 2 arrangement involving three oxygen atoms from one ligand and their symmetry related mates from another.

The ligand is a dicarboxylic acid and has hydroxy groups on carbon atoms 2-5. It binds to copper through all four carboxylate oxygen atoms, the 2-C oxygen atom, and the 3-C oxygen atom. The Cu-O-Cu linkages of the six membered ring contain the 2-C oxygen atoms; a pattern observed with [Cu(C6H8O8)]-2.[1]

The ligand and copper atoms form two dimensional polymeric sheets held together by hydrogen bonds.

The complex is prepared from ascorbic acid and cupric salts in the presence of glycine. The ligand is a known decomposition product of dehydroascorbic acid, the two electron oxidation product of ascorbic acid [2].



1. A. [illegible]

2. L. [illegible]

CIRCULAR DICHROISM AND STRUCTURAL STUDIES OF NICKEL(II) COMPLEXES WITH N-GLYCOSIDES DERIVED FROM KETOSES

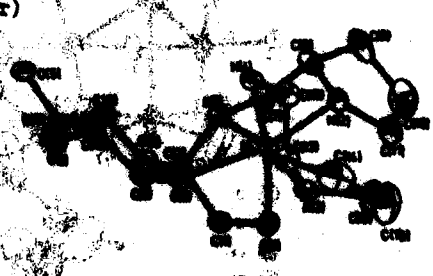
Taro Tsubomura, Shigenobu Yano, and Sadao Yoshikawa

The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113, Japan

Carbohydrates have long been known to form complexes with metal ions, however only a few transition metal complexes were characterized. Recently we reported the synthesis and characterization of new nickel(II) complexes containing N-glycoside ligand(s).[1,2] In the series of the study, we determined the structures of two ketose containing complexes; $[Ni(en)(D\text{-fru-}en)]^{2+}$(1) and $[Ni(en)(L\text{-sor-}en)]^{2+}$(2).[3] They were obtained from the reaction between $[Ni(en)_3]^{2+}$ and D-fructose or L-sorbose. It revealed that an N-glycoside ligand from a ketose and a diamine coordinates to the nickel(II) ion through the two oxygen atoms of hydroxy-groups on C-1 and C-3 of the sugar residue, and through the two nitrogen atoms of the diamine residue.

To examine the relationships between the structures and their CD spectra, we have prepared and characterized nickel-ketose complexes containing an N-glycoside derived from a ketose and a diamine (propylenediamine, aminomethylpyrrolidine(ampr), aminomethylpiperidine, etc.). All these complexes were synthesized by the reaction between $[Ni(diamine)_3]^{2+}$ and L-sorbose or D-fructose in methanol. The mother liquor was refined by gel chromatography and blue crystals were obtained. Analytical data indicated that each of these complexes has a diamine ligand and an N-glycoside ligand. Effective magnetic moments are in the range of 3.14-3.27μB.

We have undertaken an X-ray crystal structure determination of one of the product, $[Ni(S\text{-ampr})(L\text{-sor-}S\text{-ampr})]Cl_2\cdot CH_3OH\cdot H_2O$, where L-sor-S-ampr is 2-[(pyrroridilmethyl)amino]-2-deoxy-L-sorbose. As shown in Figure, it revealed that nickel atom is octahedrally coordinated with a bidentate diamine (S-ampr) and a tetradentate N-glycoside (L-sor-S-ampr). The ketose takes α-$^2C_5$ pyranose form as in the case of complex 1 and 2.



The CD spectra of these complexes have similar pattern in the second and third absorption region. Therefore it is deduced that 1) this type of structure obtained is considerably preferable for the complexes containing N-glycosides derived from a ketose and a diamine, 2) the CD patterns observed in the second and third absorption [illegible]

References

1. Tsubomura, T. et al. [illegible]
2. Yasui, M. et al. [illegible]
3. [illegible]

SYNTHETIC AND NMR STUDIES OF NOVEL DIAMAGNETIC CO(III) COMPLEX CONTAINING AN N-GLYCOSIDE DERIVED FROM D-MANNOSE

Shigenobu Yano, Katsuaki Ishida, and Sadao Yoshikawa

Department of Synthetic Chemistry, Faculty of Engineering,
University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113, JAPAN

The interaction of carbohydrates with transition metals is of current interest for coordination chemistry and bioinorganic chemistry. Despite a wide interest in complexes with sugars, very little is known about the structural details of the complexes. Recently, we have reported the synthesis and X-ray structure determination of novel type of nickel(II) complexes containing N-glycosides derived from the reaction of a diamine and a monosaccharide.[1-3] Since these complexes are paramagnetic compounds, it is difficult to examine coordination behaviour of sugars in a solution by means of the high resolution NMR spectroscopy.

We wish to report the first isolation and NMR study of novel diamagnetic cobalt(III) complex containing a N-glycoside derived from ethylenediamine (*en*) and D-mannose (D-man). A methanol solution of $CoCl_2 \cdot 6H_2O$ (5mmol) was added over 40 min to a methanol solution containing D-man (10 mmol) and *en* (10 mmol). The solution was refluxed for 30 min. In the presence of activated charcoal, air was bubbled into the solution for 3 h. Filtration yielded a wine red solution. The major coumarins product was developed as a wine red band by column chromatography on a Dowex SCW-X8 cation exchange resin (0.1 N $NaClO_4$-H_2O eluent). Desalting was accomplished by gel permeation chromatography on Sephadex G-15. Concentration followed by addition of excess ethanol yielded wine red crystalline solid. Wine red crystals were obtained for open recrystallization from a 1:2 water-ethanol solution. This product has been characterized by elemental analysis, conductivity measurements, IR, CD, and ^{1}H NMR spectra. The analytical, molar conductivity, and spectroscopic data indicate that the complex is coordinated with a bidentate ethylenediamine and a tetradentate 1-[(2-aminoethyl)amino]-1-deoxy-D-mannose (D-man-*en*) ligands as shown in Figure. Thus it can be denoted *cis*-(O-4)-[Co(*en*)(D-man-*en*)]Cl_2·$2H_2O$. In the ^{1}H NMR spectrum (400 MHz, D_2O) of the complex, all of the signals from the sugar residue could be assigned completely employing the double and triple resonance techniques. The obtained vicinal coupling constant values indicated that the six-membered ring of the sugar moiety is in the expected $^4C_1$ conformation (Figure).



1. S. Yano, S. Tanaka, K. Ueno, and S. Yoshikawa, J. Am. Chem. Soc., 1980, 102, 7512.
2. S. Yano, K. Ishida, S. Tanaka, T. Ito, and S. Yoshikawa, Inorg. Chem., 1981, 20, 1115.
3. S. Yano, K. Ishida, S. Tanaka, T. Ito, and S. Yoshikawa, J. Chem. Soc., Chem. Comm., 1981, 1081.

THE REACTIVITY OF ALCALOIDS WITH COPPER(II) PROPIONATE

Milan Melnik[1] and Patrick Sharrock[2]

[1] Department of Inorganic Chemistry, Slovak Technical University, CS 81237, Bratislava, Czechoslovakia.

[2] Department of Chemistry, Université de Sherbrooke, SHERBROOKE (Québec) CANADA J1K 2R1

The binding of metal ions to alcaloïds is a subject of interest because of the biological importance of these compounds. In our effort to better understand the nature of metal-alcaloid interactions, we have investigated ternary complexes formed by Copper(II) propionate with nicotine, papaverine, caffeine, theophylline and theobromine. The alcaloids react with copper propionate in methanolic solution to yield adducts which were characterized by elemental and thermal analyses, IR, electronic and EPR spectra, as well as by magnetic measurements as a function of temperature.

The green compounds obtained have the general formula $Cu(CH_3CH_2COO)_2 \cdot L$ (L = nicotine, papaverine or caffeine). A grey-green hydrated bis(theophilline)Copper(II) can be isolated, but theobromine does not exhibit adduct formation under the above experimental conditions.

The solid state electronic spectra of $Cu(CH_3CH_2COO)_2 \cdot L$ shows a band at 14 μm^{-1} and a shoulder at 17 μm^{-1}. Room temperature EPR spectra for the powdered samples are consistent with the expected spin of S = 1 for dimers. The exchange interaction parameters - 2 J are near 300 cm^{-1}. We will present a correlation which we found between 2J values and the pKa of axial ligands.

The Copper(II) compounds with theophylline and theobromine show broad and unsymmetrical EPR bands with gi = 2.00. These compounds have strong antiferromagnetic exchange interactions. The structure of these complexes and the general mechanism of reaction of purine alcaloïds with Copper(II) will be discussed.

* Present address: Department of Chemistry, Université de Sherbrooke, Sherbrooke (Québec) CANADA J1K 2R1

OXOVANADIUM(IV), MANGANESE(II), IRON(III), AND COPPER(II) COMPLEXES OF 1H-HEXAHYDROAZEPINE-1-THIOCARBOXYLIC ACID 2-[1-(2-PYRIDINYL)-ETHYLIDENE]HYDRAZIDE: SPECTRAL, MAGNETIC, ESR, AND X-RAY STUDIES

Y.K. Bhoon

Sri Venkateswara College, Dhaula Kuan, New Delhi-110 021 (India)

John P. Scovill and Daniel L. Klayman

Division of Experimental Therapeutics, Walter Reed Army Institute of Research, Washington, DC 20307 (USA)

Judith L. Flippen-Anderson

Laboratory for the Structure of Matter, Naval Research Laboratory, Washington, DC 20307 (USA)

1H-Hexahydroazepine-1-thiocarboxylic acid 2-[1-(2-pyridinyl)-ethylidene]hydrazide [LH][1] has been shown to react with transition metal ions to give stable complexes.[2] With salts of Mn(II), Cu(II), Fe(III), and O=V(IV), the complexes $[Mn(II)\ 2L^-]$, $[Cu(II)\ L^-X^-]$, $[Fe(III)\ 2L^-]^+$ $[Fe(III)\ Cl_4]^-$, and $[O=V(IV)\ 2L^-]$, respectively, were obtained. These compounds were characterized by magnetic measurements which were performed in the range of -195°C to room temperature. ESR spectral studies were carried out in the polycrystalline state and in $CHCl_3$ solution at -195°C and at room temperature. Consideration of the magnetic moments derived for these compounds suggests that the Mn(II) complex is octahedral, whereas the Cu(II) complex has square planar geometry. An X-ray study established the structure of the $[Fe(III)\ 2L^-]^+$ ion as octahedral, with tetrahedral $[Fe(III)\ Cl_4]^-$ as a counter ion. Previously, this complex had been assigned the square pyramidal structure, $[Fe(III)\ L^-2Cl^-]$.[3] In contrast to the above mentioned complexes, where L^- acts as a singly charged tridentate ligand, in the oxovanadium(IV) complex L^- appears to be bidentate, with the pyridine N-atom noncoordinating. IR spectral correlations will also be discussed.



LH

1. D.L. Klayman, J.P. Scovill, J.F. Bartosevich, C.J. Mason, J. Med. Chem., 22, 1367 (1979).

2. J.P. Scovill, D.L. Klayman, C.F. Franchino, J. Med. Chem. 25, 1261 (1982).

3. Y.K. Bhoon, S. Mitra, J.P. Scovill, D.L. Klayman, Trans. Met. Chem., 7, 264 (1982).

CHARACTERIZATION OF SOME METAL COMPLEXES OF 4-PHENYL-1-DIACETYLMONOXIME-3-THIOSEMI-CARBAZON (BMPTS)

Mohsen M. Mostafa, Kamal M. Ahmed, Ahmed A-El-Asmy, and Magdy M. Beckhiet

Chemistry Department, Faculty of Science, Mansoura University, Egypt.

New metal complex of the title ligand were prepared using alcoholic solution of MX_2 (M=Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II); X=Cl or Br). The nature of the solids that have been isolated, as well as the method of bonding, has been ascertained using spectral (UV, IR, NMR) and magnetic measurements. Four different structures, $[M(BMPTS)X_2]$; $[M(BMPTS-H)X\cdot H_2O]$; $[M(BMPTS-2H)\cdot H_2O]$; and $[Co(BMPTS-H)_2]$ have been isolated and characterized. The ligand coordinated is both a bidentate and/or tridentate depending on the nature of the metal salt used and the method of preparation. The bonding sites have been confirmed by IR and NMR techniques. Results of molecular weight determination support a monomeric structure for the complexes under investigation. Also, the results have been compared to the analogy ligands and its metal complexes which have been reported [1,2] earlier from our laboratory.

1. El-Asmy, A.A., and M.M. Mostafa, *Polyhedron*, *2*, 691, 1983.
2. Mostafa, M.M., and A.A. El-Asmy, *J. Coord. Chem.*, *12*, 197, 1983.

A GOLD(I) COMPOUND CONTAINING AN INFINITE ARRAY OF SHORT METAL-METAL BONDS

Sten Ahrland, Bertil Norén and Åke Oskarsson

Inorganic Chemistry 1, Chemical Center, University of Lund, Box 740, S-220 07 Lund, Sweden

In solvents solvating via soft donor atoms, the monovalent states of the coinage metals copper, silver and gold are strongly stabilised both relative to the metallic and to the higher oxidation states, i.e. the d^{10} electron configurations are highly preferred. If also the anions present are soft, this tendency is further strengthened.

Gold(I) is therefore highly stabilised in solvents coordinating via the soft sulfur atom as has indeed been confirmed by our preparation of iodo-tetrahydrothiophene-gold(I). This compound is formed when a gold foil is treated with a solution of iodine in tetrahydrothiophene (THT). The reaction proceeds quite rapidly to completion even at room temperature. The conditions are thus very different from those encountered in aqueous solution. Besides the strong solvation of gold(I) in THT, the strong coordination of the I^- formed contributes to the easy oxidation of the metal.

The light yellow crystals formed have the stoichiometric composition Au(THT)I. The structure determination, by X-ray diffraction at 200 K, reveals, however, two Au atoms of very different coordination. One is bonded to two iodide ions, the other to two THT molecules; the I-Au-I and S-Au-S entities are both almost linear. These units alternate through the structure forming a zig-zag chain. The Au-Au distances within the chain are quite short, 2.967(2) and 2.980(2) Å, i.e. only slightly longer than the interatomic distance of 2.877 Å in metallic gold. This indicates fairly strong metal-metal bonds, inasmuch as there are no ligand bridges to force the Au atoms together. Only van der Waals forces act between the chains.

This compound seems to be the first one found where gold atoms are joined by very short metal-metal bonds to an infinite array. A similarly short Au-Au distance (2.998(1) Å) involving no bridging ligands has been found before[1], but only within a discrete complex, viz. $Au_4(Pyridine)_4I_4$. Also, a compound containing infinite arrays of Au atoms is known[2], but in this case the non-bridged Au-Au distances are all much longer, half of them even as long as 3.109(6) Å.

1. A.-M. Adams, W. Hiller and J. Strähle, Z. anorg. allg. Chem. 1982, 485, 81.

2. S.L. Lawton, W.J. Rohrbough and G.T. Kokotailo, Inorg. Chem. 1972, 11, 2227.

REACTIONS OF GOLD CLUSTER COMPOUNDS

J. Bour, W. Bos and J. Steggerda

Department of Inorganic Chemistry, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands.

Gold cluster compounds with 3-13 Au atoms have been prepared with phosphines (P) and/or halides or pseudohalides like CN and SCN (X) coordinated to the periphery of the cluster. They show chemical reactivity in dissociation and association of AuP^+ or AuX. Some clusters show reversible electron transfer in electrochemical studies, in this way the unique paramagnetic $Au_9P_8^{2+}$ was prepared. Further substitution reactions and complicated fragmentation and growth can occur.[1]

Recently[2] isonitril was introduced as a ligand and $Au_9P_6(RNC)_2^{3+}$ was isolated and its X-ray structure and properties studied. With amines it yields gold cluster carbene compounds.

In striking contrast with so many stable carbonyl clusters of the platinum metals, CO does not form stable gold cluster compounds. There is, however, a reaction of gold nitrate compounds with CO which yield a variety of products. Structures and properties of these will be reported.

1. J.J. Steggerda, J.J. Bour and J.W.A. van der Velden, Recl. Trav. Chim. Pays Bas 101, 164 (1982).

2. W. Bos, J.J. Bour, J.W.A. van der Velden, J.J. Steggerda, A.L. Casalnuovo and L.H. Pignolet, J. Organometallic Chemistry 253, C64-C66 (1983).

THa45-3

SYNTHESIS AND CHEMISTRY OF RHODIUM CLUSTERS WITHIN ZEOLITES

Brian E. Hanson, Dennis Taylor, Edward Rode, and Mark E. Davis

Virginia Polytechnic Institute and State University, Departments of Chemistry and Chemical Engineering, Blacksburg, Virginia, USA 24061

Rhodium carbonyl complexes are readily synthesized within zeolites. Typically, rhodium is introduced via cation exchange and carbonyl synthesis is achieved simply by introducing carbon monoxide. The synthesized carbonyl complex depends on temperature, pressure, and the zeolite support. Surprisingly, the two faujasites, 13X and 13Y, stabilize different rhodium carbonyl complexes; $Rh(CO)_2^+$(ads) on 13X and $Rh_6(CO)_{16}$(ads) on 13Y. These zeolites are isostructural and differ only in the Al/Si ratio and, thus, in the cation exchange ratio.

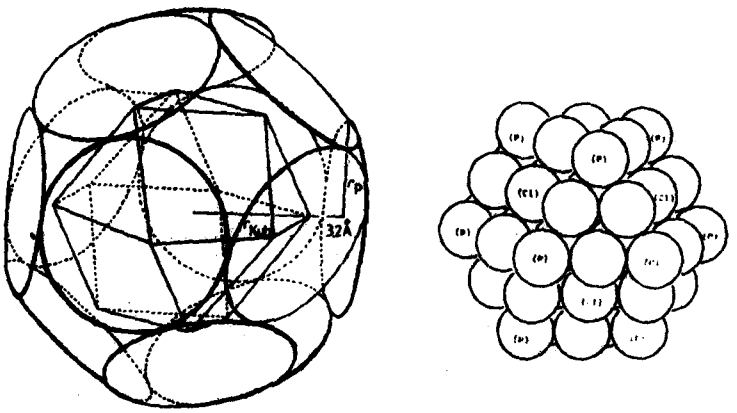
The synthesis of $Rh_6(CO)_{16}$(ads) on 13Y has been monitored by *in situ* fourier transform infrared spectroscopy. Preliminary results suggest that $Rh_4(CO)_{12}$ is formed as a transient species in the synthesis of the hexanuclear cluster. This is consistent with the homogeneous synthesis of $Rh_6(CO)_{16}$. Reactions of intrazeolitic rhodium clusters with nucleophiles will be presented.

$Rh_6(CO)_{16}$(ads) on 13Y is an active catalyst for the gas phase hydroformylation of propylene. *In situ* infrared spectroscopy data acquired during hydroformylation will also be presented.

SYNTHESIS AND INVESTIGATION OF LARGE TRANSITION METAL CLUSTERS

Günter Schmid and Wilfried Huster

Institute for Inorganic Chemistry, University of Essen, Essen, West-Germany



$M_{55}L_{12}$ Cluster Model

The synthesis of transition metal clusters of the type $M_{55}L_{12}X_n$ succeeds by reaction of B_2H_6 with appropriate transition metal phosphine or arsine complexes. The formation of two-shell structures with 55 closest-packed metal atoms depends extremely on the ligand geometry and the reaction conditions. Ideal conditions are shown in the figure. Twelve ligands envelope the cluster nucleus in such a manner as to touch each other. The areas between the phosphine or arsine ligand circles can be occupied by smaller ligands as chlorine and carbon monoxide. Using 'wrong ligands' the formation of M_{55} clusters failes. The direct connection between the metal nucleus and the ligand size could be shown by the synthesis of the clusters $Au_{55}(PPh_3)_{12}Cl_6$, $Rh_{55}(PPh_3)_{12}Cl_6$, $Rh_{55}[P(tert\text{-}Bu)_3]_{12}Cl_{20}$, $Ru_{55}[P(tert\text{-}Bu)_3]_{12}Cl_{20}$, and $Pt_{55}[As(tert\text{-}Bu)_3]_{12}Cl_{20}$.

The cluster solutions show a super mobile behavior of the ligands, so that the expected coupling, e.g. in $Rh_{55}(PPh_3)_{12}Cl_6$ and $Rh_{55}[P(tert\text{-}Bu)_3]_{12}Cl_{20}$ are completely averaged in the ^{31}P NMR spectra, leading to a sharp singlet. By means of high resolution transmission electron microscopy we succeeded in proving the correct size of the Au_{55} cluster (1). This method allows the observation of ideal crystal growth starting with 55 metal atoms.

1) Dr. J.-O. Bovin, Lund, Sweden

UNUSUAL BONDING MODES OF CARBONYL METALATE ANIONS

Robert Bender, Pierre Braunstein and Michel Pfeffer

Laboratoire de Chimie de Coordination, ERA 670 du CNRS, Université Louis Pasteur, 4 rue Blaise Pascal, F-67070 Strasbourg (France)

Recent examples have been reported in the literature where group 6 carbonylmetalate anions act as formal 4 electron donor bridging ligands between two transition metals. (1-3) We present a further example of this type involving now the $Co(CO)_3PPh_3^-$ anion. Thus, the triangulo cluster $CoPt_2(\mu\text{-}PPh_2)(\mu\text{-}CO)_2(CO)(PPh_3)_3$ has been prepared and can be described as a $Ph_3P\text{-}Pt\text{-}Pt\text{-}PPh_3$ unit bridged by the PPh_2 and the metalate fragments*.(4) Isolobal analogies relate this cluster to $Pt_2(\mu_2\text{-}PPh_2)_2(PPh_3)$ and to $Pt_2[\mu\text{-}m(CO)_3Cp]_2(PPh_3)_2$ (m=Cr,Mo,W). We have now observed the following reaction

$$[(\overset{\frown}{N\,C})Pd]_2(\mu\text{-}M)(\mu\text{-}Cl) + [(\overset{\frown}{N\,C})Pd(MeCN)_2]^+ \rightarrow \{[(\overset{\frown}{N\,C})Pd]_3(\mu_3\text{-}M)(\mu_3\text{-}Cl)\}^+$$

where N⌢C = cyclometalated ligand (8-methylquinoline-8C,N or dimethylaminotoluene-2C,N)

M = $Mo(CO)_3(\eta^5\text{-}C_5H_5)$.

The tetrametallic cationic cluster thus obtained represents the first example where an organometallic anion is symmetrically bridging 3 transition metals, therefore behaving as a formally 6 electron donor anionic moiety (5).

The cubane-like structure of this new cation will be presented.* The role of the ancillary N⌢C chelates will be discussed together with our attempts to generalize this reaction to other systems.

1. M. Pfeffer, J. Fischer, A. Mitschler and L. Ricard, J. Am. Chem. Soc., 1980, 102, 6338.

2. R. Bender, P. Braunstein, J.M. Jud and Y. Dusausoy, Inorg. Chem., 1983, 22, 3394.

3. H. Werner and P. Thometzek, Angew. Chem. Int. Ed. Engl., 1982, 21, 692.

4. R. Bender, P. Braunstein, B. Metz and P. Lemoine, Organometallics 1984, 3, ...

5. P. Braunstein, J. Fischer, D. Matt and M. Pfeffer J. Am. Chem. Soc., 1984, 106, ...

* Crystal structure determined in the Laboratoire de Cristallochimie, ULP, Strasbourg.

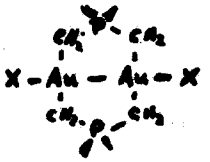
PROPERTIES OF DINUCLEAR GOLD YLIDE COMPLEXES

John P. Fackler,Jr., A. M. Mazany, H. H. Murray,III, J. Tocher, J. Basil, H. Knachel, B. Trozinska, R. Niera, D. Dudis,

Department of Chemistry, Texas A&M University, College Station Texas, 77840.

Dinuclear gold(II) ylide complexes ,I, show changes in the metal-metal bond length and the symmetric Raman stretch consistent with expected influences of the ligand substituents on the metal-metal bond. In particular as the terminal ligand atom substitutent is changed from O to S to Cl to Br to I, the Au-Au stretch is found to decrease in frequency as the Au-Au distance increases.

I



X = Cl, Br, I, -SR, -OR, etc.

The product formed from oxidation of the gold(I) ylide dimer with benzoyl peroxide (benzoate terminal ligands) displays a very active metal-metal bond. This complex reacts at room temperature in solution with CH_3NO_2 to form an adduct in which a bond is ruptured. The structure of this unusual product will be described.

Dinuclear gold(I) ylide complexes react with alkyl halides(1) in a reversible manner to form gold(II) products. This reaction appears to involve an electron transfer initiation step. Although the chemical reaction is reversible, the electrochemical oxidation in THF is not. While two single electron waves are observed in the oxidation of the gold(I) dimers, the process in not electrochemically reversible. Reorganization apparently occurs after the initial electron transfer. Electrochemical reduction of the gold(II) dimers similarly involve irreversible processes except with the iodide and a mixed sulfur-carbon ylide complex.

Examination of the properties of the dinuclear gold(I) ylide complexes of $CH_2P(S)Ph_2$ demonstrated that geometric isomers can be obtained either with gold-gold bonds or mixed valent Au(III)/Au(I) oxidation states. Structures of both types of complex have been obtained and will be described.

1. Fackler, J. P., Jr.; Basil, J. D.; ACS Symposium Series, 1983, 211, 201-208

PHYSICO-CHEMICAL INVESTIGATION OF IRON(III) AND CHROMIUM(III) CLUSTER COMPOUNDS WITH UPPER FATTY ACID ANIONS

M.M.Mansurov, Kh.M.Yakubov, G.L.Semyenova
Tadjik State University, Lenin st.,17, Dushanbe, USSR

The results on the investigation of iron(III) and chromium(III) μ_3-oxoclusters with anions of capric, pentadecoic, palmitic, oleanolic and stearic acids of the next composition: $[Fe_nCr_{3-n}(RCOO)_6(H_2O)_3]NO_3$, where n = 0, 1, 2, 3; R - C_9H_{19}, $C_{14}H_{29}$, $C_{15}H_{31}$, $C_{17}H_{33}$, $C_{17}H_{35}$ are cited in the report. These compounds have been synthesized according to the methods /1/ by the reaction of interaction in non-aqueous solvents of iron(III) and chromium(III) nitrates with the noted acids. Compositions and properties of the obtained compounds have been established by electronic, infra-red, gamma-resonance spectroscopy, static magnetic susceptibility and derivatography.

Electronic absorption spectra and diffuse reflection of homo- and heteronuclear iron(III) and chromium(III) carboxilates develop a series of typical lines indicating of individual compound formation. The lines corresponding to stretching vibrations ν(M-O) in the interval 400-500 sm^{-1}, ν(M-H_2O), at 600-660 sm^{-1} have been revealed in IR spectra. Position and distance between the lines ν_s(COO) and ν_{as}(COO) are typical for bridged carboxil groups.

Synthesized compound Mössbauer spectra analysis made it possible to establish, that, in the noted compounds, iron(III) ions are in a high-spin state.

Quadrupole splitting dependence on the number of chromium(III) ions in the molecule composition indicates in favour of heteronuclear complex formation with the fragment $\{Fe_nCr_{3-n}\}$.

Magnetic property measurements of the compounds have shown, that the effective magnetic moment at room temperature is lower than "spin" value for s = 5/2 and is decreasing by the temperature fall, that is conditioned by antiferromagnetic interaction in the isolated trinuclear (M_3O) cation interval.

The investigations carried out by us made it possible to conclude, that 3d-elements (iron, chromium) with the upper fatty acids form μ_3-oxocarboxilates of the known composition.

References:

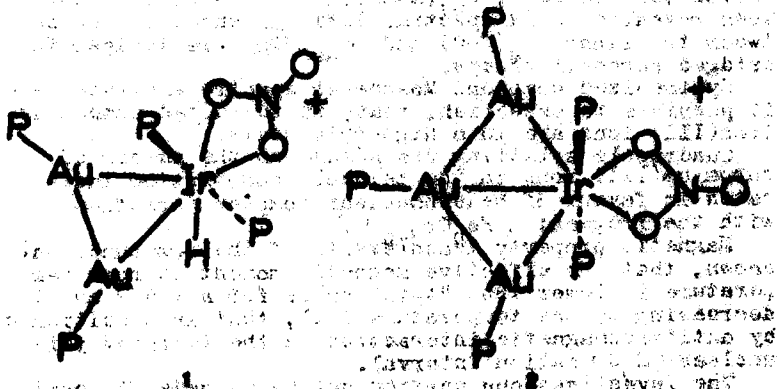
1. Mansurov M.M., Semyenova G.L., Yakubov Kh.M., Zhemchuzhnikova T.A. - J.neorgan.khimii, 1983, t.28, №6. - 1460s.

MIXED METAL GOLD-IRIDIUM CLUSTER COMPOUNDS: SYNTHESIS, STRUCTURE AND REACTIVITY.

Al L. Casalnuovo, Jeff Olofson, Tim Laska, and Louis. H. Pignolet

Department of Chemistry, University of Minnesota, Minneapolis MN USA 55455

The reaction of cationic iridium hydrides such as $[Ir(H)_2(PPh_3)_2]^+$ with $AuPPh_3NO_3$ in acetone solution leads to the formation of several new mixed-metal clusters. Compounds observed during this reaction at low temperature include Au-H-Ir bridged intermediates and $[IrAu_2(H)(PPh_3)_2NO_3]^+$,1. At room temperature the primary product of this reaction is $[IrAu_3(PPh_3)_2NO_3]^+$, 2. Compounds 1 and 2 have been characterized by single crystal x-ray diffraction and by ^{31}P and ^1H NMR spectroscopy. These complexes react with small molecules such as H_2 and CO to give new mixed metal clusters. For example, the reaction of 2 with H_2 leads to the formation of a larger cluster which is tentatively formulated as $Ir_2Au_6(PPh_3)_6(H)_2(NO_3)_2$. Experiments have been carried out which give some information about the mechanism of reaction between $Au(PPh_3)^+$ and simple metal hydrides. These results will be presented along with the structural details of other mixed metal gold clusters. Reference 1 below will serve as an introduction to this work.



1 2

(1) A. L. Casalnuovo, L. H. Pignolet, J. W. A. van der Velden, J. J. Bour, and J. J. Steggerda, J. Am. Chem. Soc. 1983, 105, 5957.

THE COORDINATION CHEMISTRY OF THE SOLID WATER INTERFACE AS A MAJOR CONTROL IN AQUATIC GEOCHEMISTRY

Werner Stumm, Herbert Motschi and Laura Sigg
Swiss Federal Institutes of Technology, Zurich

Almost all the problems associated with understanding the processes that control the composition of our environment concern interfaces. Oxides especially those of Si Al Fe and Mn are abundant components of the earth's crust. The oxygen donor atoms present on the hydrous oxide surfaces tend to undergo protolysis, and to form complexes with metal ions, and to become exchanged for other ligands (anions or weak acids).

With the help of spectroscopic measurements, especially (ESR and ENDOR) insight into the structure of some of these complexes was gained; it could be shown that they often consist of inner sphere complexes.

The tendency to form surface complexes at the oxide water interface is comparable to that to form corresponding soluble metal complexes in solution.

The rates of processes occurring at the hydrous oxide surface such as precipitation (heterogeneous nucleation on oxide surfaces) of minerals and dissolution of minerals are important in the shattering of rocks, in the formation of soils and sediments - are critically dependent on the coordinative interactions taking place on oxide surfaces. Surface coordination reactions at the particle/water interface are consequently important in determining the residence time and ultimate fate of reactive elements in oceans and lakes.

PROTON AND METAL ION BINDING TO NATURAL ORGANIC POLYELECTROLYTES
I. STUDIES WITH SYNTHETIC MODEL COMPOUNDS

J. A. Marinsky (1) and M. M. Reddy (2)
(1) Chemistry Department, State University of New York at Buffalo, Buffalo, New York.
(2) U. S. Geological Survey, Denver, Colorado

Ion binding by natural organic polyelectrolytes is a topic of much recent research interest. Unfortunately data interpretation often obscures fundamental processes involved in ion-polyion binding reactions and confounds attempts to generalize experimental findings. In this paper we discuss application of standard solution chemistry techniques to characterize ion-binding reactions with well-defined and uniform synthetic weak acid polyelectrolytes and their cross-linked gel analogues. A unified physico-chemical model for the analysis of ion complexation reactions involving charged polymeric systems is presented and verified. This model is based on a modified Henderson-Hasselbalch equation, $pH = pK + p(\Delta K) + \log(\alpha/1-\alpha)$, where pK is the intrinsic acid dissociation constant of the ionizable functional groups on the polymer, $p(\Delta K)$ is the deviation of the intrinsic constant due to electrostatic interaction between the hydrogen ion and the polyanion, and alpha (α) is the polyacid degree of ionization. In two phase systems (i.e. those containing a gel matrix permeable to solvent) a Donnan membrane potential term is needed to calculate the ionic concentrations within the gel phase.

Using this approach pK values for repeating acidic units of polyacrylic (PAA) and polymethacrylic (PMA) acids were found to be 4.25 +/- 0.03 and 4.8 +/- 0.1, respectively. These intrinsic constants are similar to the values for the monomer carboxylic acids (propanoic acid, pK = 4.236 (25°C, zero ionic strength) for PAA, and 2-methyl propanoic acid, pK = 4.849 (25°C, zero ionic strength) for PMA) they resemble. The polyion electrostatic deviation term derived from the potentiometric titration data (i.e. $p(\Delta K)$) is used to calculate metal ion concentration at the complexation site on the surface of the polyanion assuming that: (1) the electrostatic deviation term for hydrogen ion and metal ions are the same and, (2) the concentration of metal ions at the complexation site can be calculated using the Boltzmann distribution equation. The intrinsic cobalt-polycarboxylate binding constants (7.8 for PAA and 3.0 for PMA) obtained using this procedure are consistent with the range of published binding constants for simple monomeric carboxylate analogues. In two phase systems incorporation of a Donnan membrane potential term allows determination of the intrinsic pK of a cross-linked PAA gel, pK = 4.45, in excellent agreement with the value obtained for the linear polymer in soln and the monomer. Similarly, the intrinsic proton binding constant for cobalt ion binding to a PAA gel (degree of [illegible]) was found to be in agreement with the linear polyelectrolyte analogue and the monomeric acid for cation-carboxylate complexation.

SPECIATION OF METAL COMPLEXES IN THE ENVIRONMENT

Arthur E. Martell, Ramunas J. Motekaitis and Robert M. Smith

Department of Chemistry, Texas A&M University, College Station, Texas, USA, 77843

A large fraction of the 50,000 organic chemicals manufactured in the U.S.A. ultimately turn up in the environment. Many of these are complexing ligands and many others are partially oxidized or hydrolyzed or otherwise converted by chemical, photochemical, and microbiological process to ligands capable of combining with the 30-40 metal ions introduced into environmental waters by natural processes or by environmental pollution. Thus a case may be made for the possible presence of the order of a million metal complexes in environmental aqueous systems. Since the mobilities and toxicities of metals depend on the nature of the complexes formed (speciation), the assessment of environmental hazard depends on identification of the complexes formed and determination of their concentration levels. Because the determination of stability constants of about ~1 million complexes, plus a large number of mixed ligand and mixed metal species, is obviously impossible, it is necessary to develop indirect methods of estimating metal speciation in complex multicomponent systems.

Methods now being employed for expansion of the incomplete data base provided by Critical Stability Constants[1] involve a combination of three general procedures- 1, interpolation between known values to provide missing data; 2, the use of linear free energy relationships (LFER's) to extrapolate known thermodynamic constants to related systems that have not been measured experimentally, and 3, the use of known values for functional group metal ion affinities, or combinations of functional groups, for empirical estimation of metal ion affinities of ligands that have not been measured experimentally. Examples of how these procedures work will be described by the use of previously measured values for the prediction of unknown constants measured subsequently. A critical analysis of methods of estimating stability constants has been described recently[2].

Correlations used thus far have been employed for the completion of expanded data bases for mono- and dicarboxylic acids with metal ions likely to be found in environmental systems. Graphical relationships illustrating the predictability of stability constants for the alkaline earth and lanthanide metal ions will be presented.

The expanded data base consisting of measured and estimated stability constants has now been employed to calculate, by means of the computer program SPE[3], the speciation of metal complexes formed in multicomponent systems of the type that may be found in environmental waters. Several examples involving large numbers of ligands and metal ions will be described.

1. R. M. Smith and A. E. Martell "Critical Stability Constants" Vols.1-5, Plenum Press, New York, 1974, 1975, 1976, 1977, 1982.
2. A. E. Martell, R. J. Motekaitis and R. M. Smith in "Environmental Inorganic Chemistry", Verlag Chemie, in press.
3. R. J. Motekaitis and A. E. Martell, J. Coord. Chem., submitted.

SPECIATION AND SOLUBILITIES IN THE H^+-Al^{3+}-OXALIC ACID SYSTEM

Staffan Sjöberg,[1] Halka Bilinski,[2] Laszlo Horvath,[2] Lars-Olof Öhman[1] and Nils Ingri[1]

1) Dept. of Inorg. Chem., University of Umeå, Sweden
2) Dept. of Phys. Chem., "Ruder Boskovic", Zagreb, Yougoslavia

At present much attention is paid to the environmental chemistry of aluminium. Elevated concentrations of Al(III) have been found, not only in acidified lakes and streams, but also in waters with high content of organic matter. Speciation, solubilities as well as the coordination of aluminium in these waters are at present not fully understood.

The object of the present study is to give composition and stability of complexes and solid phases formed in the title system. The coordination of Al is also interpreted.

Experiments were performed as a series of potentiometric (glass electrode) titrations combined with ^{27}Al-NMR measurements (25 °C, 0.6 M Na(Cl) medium). Precipitation ranges were determined from tyndallometric and pH measurements.

The results show that besides a series of binary complexes AlL^+, AlL_2^- and AlL_3^{3-}, two mixed hydroxo species $Al_2(OH)_2L_2$ and $Al_2(OH)_2L_4^{4-}$ are formed. The Al-solubility is given by two crystalline phases depending on oxalate to aluminium ratio, which have been characterized by IR, X-ray powder spectra and chemical analysis. Complex formation constants and solubility products have been determined. The significance of the results will be discussed in connection with conditions existing in natural waters.

THE ROLE OF SURFACE COORDINATION IN THE DISSOLUTION OF δAl_2O_3.

Gerhard Furrer, Herbert Motschi, Werner Stumm

Swiss Federal Institute for Water Resources and Water Pollution Controll (EAWAG), Zürich, Switzerland

Chemical processes at the hydrous-oxide solution interface - protonation of surface OH-groups and surface coordination with ligands (anions) - are important for understanding the dissolution of solid oxid phases.
For most slightly soluble minerals the rate of dissolution is controlled by reactions at the surface (and not by transport processes) and thus depends on its coordination chemistry.
In a case study we have evaluated the effects of various complex forming organic anions (oxalate, salicylate, citrate and benzoate) and of protons on the dissolution kinetics of δAl_2O_3 (pH 2.5 - 6).
The results can be generalised into a simple rate law which shows that the dissolution rate depends on the degree of surface protonation and the concentration of anionic surface complexes.

1. G. Furrer and W.Stumm, Chimia 1983, 37 , 338.

IONIC STRENGTH DEPENDENCE OF FORMATION CONSTANTS

Pier G. Daniele[a], Alessandro De Robertis[b], Carmelo Rigano[c] and Silvio Sammartano[b]

[a] Istituto di Analisi Chimica Strumentale dell'Università, via Bidone 36, 10125 Torino, Italy

[b] Istituto di Chimica Analitica dell'Università, via dei Verdi, 98100 Messina, Italy

[c] Seminario Matematico dell'Università, viale A. Doria 6, 95125 Catania, Italy

Since Davies[1] found the well known equation for the calculation of activity coefficients up to I=0.1 mol dm^{-3}, no substantial advance has been made towards finding an equation valid for I > 0.1 mol dm^{-3}.

In order to check the possibility of obtaining a general equation for the ionic strength dependence of formation constants, we studied several aqueous systems containing different ligands and metal ions[2]. These investigations showed that formation constants are, with a fairly good approximation, independent of background in the range 0.01 ≤ I ≤ 1 mol dm^{-3}, if taking into account all the interactions among the various ions in solution, even including ion-pair formation between the ligands and the alkali metal ions of the background.

Very recently we have further investigated this topic by considering the dissociation of cationic acids and the complexation of lanthanide(III) with some mono-, di- and tricarboxylic acids.

The analysis of previous and present results allow us to describe the ionic strength dependence of formation constants (for I ≤ 1 mol dm^{-3}) with a simple general equation.

1 C.W. Davies "Ion Association", Butterworths, London, 1962

2 P.G. Daniele, C. Rigano, S. Sammartano, Ann. Chim.(Rome) 73, 761 (1983) and refs therein

A NEW APPROACH TO THE RECOVERY AND REUSE OF INORGANIC MATERIALS FROM INDUSTRIAL WASTES.

U.Croatto, G.F.Piovan and P.A.Vigato.
Università - C.N.R. - Centro Tecnochimico - PADOVA (Italy)

It is known that tannery industries utilize, in their treatment, various inorganic compounds as sulfides, chromium salts (almost exlusively chromium (III), ammonia, water, etc. In addition, in the purification of waste water, other inorganic products are employed, among which are iron (II) sulfate, aluminium (III) sulfate, manganese (II) and nickel (II) salts.

In the view of environmental protection and the reuse of materials it was necessary to study new purification system of waste water in order to remove inorganic compounds having toxicity and/or scarce availability in our planet.

Chromium, owing to its toxicity, the continuous dwindling of its mineral sources and the never-ceasing increase of its cost, has the unavoidable need for recovery and reuse. Such an operation, besides being well established, is also highly rewarding.

We have carried our studies on the most suitable technology also from an environmental standpoint.

Sulfide also, due to its toxicity, must be eliminated from wastes in any event and possibly recovered. It can conveniently be recovered from liquid wastes segregated from limepit tanks by diffusion through permeable membranes; its recovery is however less rewarding than that of chromium.

Alternatively, sulfide can be removed biologically by treating limepit wastes as reported below.

We have recently studied, more economic and efficient processes for the recovery and reuse of chromium and for sulfide disposal.

The waste water from chrome tanning is segregated from the other wastes and treated for the separation and purification of chromium with subsequent reuse as tanning material by dissolution in sulfuric acid to obtain a solution with the requisite basic exchange degrees. It is possible, in addition, to effect further purification of the recovered product, if this is required for the tanning of particularly valuable hides. The recovery of chromium, as $Cr(OH)_3$, is almost complete and owing to the high price and the considerable concentrations of chromium in the waste water, it represents a remunerative problem.

As regards the sulfides, we have studied a biological system that are partially incorporated in the formation of microbial suspending matter and partially converted into sulfur and sulfates by means of bacteria.

LIGAND SORPTION BY COORDINATIVELY UNSATURATED METAL CHELATES IN GAS CHROMATOGRAPHIC ANALYSIS

J. N. Gillis, E. J. Williams, and R. E. Sievers

University of Colorado, Campus Box 449, Boulder, Colorado, USA 80309

The ability of some metal chelates to form adducts with nucleophilic compounds has been exploited by our research group for use in two areas of analytical chemistry. We have used metal chelate-containing polymers as selective sorption media for collection and concentration of ligands in air analysis and as gas chromatographic stationary phases for the separation of oxygen from nitrogen at room temperature.

Stable metal chelates that carry oxygen reversibly at ambient temperature have been the objective of many studies. A new metal chelate, [[5,5'-(1,2-ethanediyldinitrilo)bis[2,2,7-trimethyl-3-octanato]]N,N',O,O']cobalt(II), Co(todon), has been bonded to a copolymer of divinylbenzene, ethylvinylbenzene and 4-vinylpyridine, and studied as a selective sorbent for complexation of O_2. The selective and reversible interaction of this stationary phase with molecular oxygen results in an increase in retention time for oxygen relative to that of nitrogen and argon. Baseline resolution of oxygen and nitrogen is achieved at 25°C with little distortion of peak symmetry. The oxygen-carrying polymer is stable to repeated injections of air and may be useful for separation of oxygen from air by parametric pumping.

A new cross-linked europium(III)-containing porous polymer has been synthesized in our laboratory for use as a sorbent in the preconcentration of trace levels of nucleophilic species from air. This sorbent material was prepared by the acetylation of phenyl moieties in a styrene-divinylbenzene copolymer, followed by a Claisen condensation with a fluorinated ester. Europium(III) was then bonded to the β-diketonate moieties to form sites for complexation. In frontal gas chromatography the Eu-containing polymer shows greatly enhanced retention of nucleophilic compounds, such as aldehydes, ketones and nitriles, relative to that exhibited by the underivatized polymer. Increases in breakthrough volumes (a measure of how strongly a compound is retained) were: acetaldehyde, 0.5 to 7.6 L/g (15-fold); acetone, 4.3 to 31 L/g (7-fold); and acetonitrile, 2.6 to 15 L/g (7-fold). The Eu-containing polymer exhibits good thermal stability and releases complexed nucleophiles upon heating to 210°C for 15 minutes in a flowing He stream. Ligands are trapped cryogenically, then analyzed by temperature programming a fused silica capillary column. This new polymer has been used as a selective sorbent for the preconcentration and subsequent gas chromatographic-mass spectrometric analysis of volatile, nucleophilic organic compounds in coffee aroma, human urine, and urban air.

COORDINATION CHEMISTRY USED TO DESIGN MEDICAL LIGANDS TO REMOVE METAL IONS

David R. Williams

Department of Applied Chemistry, University of Wales Institute of Science and Technology, Cardiff CF1 3NU, UK.

It is well established that industrial metals and excesses of essential biological metals displace equilibria *in vivo* away from optimal complexing and detract from health. The competition between an exogenous metal and an *in vivo* metal for a particular ligand donor site is often not proportional to their respective formation constants because several other factors are involved.

However, the advent of large computer simulation models of important biological fluids such as blood plasma and milk has permitted a quantitative comparison to be made between different metal ions and different ligands *in vivo* and for the mobilising powers of an administered ligand to be assessed. Such models assume that, for efficiency reasons, many *in vivo* solutions approximate to equilibrium or steady states.[1]

When the offending metal is situated within tissues it is necessary to employ synergistic chelation therapy whereby two drugs are administered. The first is lipophilic and can proceed to the interior of cells whence it extracts the metal concerned and takes it, as a complex, into blood plasma. Then, the second agent administered takes over the metal and forms a charged complex which is useful for renal excretion. This concept has been successfully developed for removing cadmium and lead.

No exogenous agent is absolutely specific for metals *in vivo*. Usually, it is necessary to top-up or, at any rate, monitor the concentrations of closely related metals. Coordination chemistry can, however, increase the margin of safety between the selectivity of an agent for an offending metal versus that of the essential metals. This has led us to suggest N,N'-bis-(2-aminoethyl)-1,3-propanediamine as a new agent for removing copper ions[2] and tetraethylenepentamine as a new agent for removing nickel from nickel carbonyl poisoned species.[3] Agents more specific for lead have also been studied.[4]

1. D.R.Williams, Proc. 2nd Int.Conf.Clin.Chem. & Chem. Toxicol. (1984), Ed. S.Kaye, Academic, London.
2. P.H.May, D.C.Jones & D.R.Williams, Lancet, 1982, May 15, 1147.
3. P.H.May, D.C.Jones, D.R.Williams, H.W.Dunkelman Jr., and M.A.Kuhn-Plaisance, in press.
4. M.J.Miller and D.R.Williams, Inorganica Chimica Acta, 1983, 80, in press.

EQUILIBRIUM AND REACTION MECHANISM OF Pd(II) COMPLEXES WITH ETHIONINE

Mohamed S. El-Ezaby, Najeeb A. Al-Salem and Husam M. Abu Soud

Department of Chemistry, Kuwait University, P.O. 5969, Kuwait

Ethionine(Eth) analog of the amino acid, methionine is produced by several organisms(1). Its hepatotoxic and hepatocarcinogenic actions in rats were the subject of many reports (2,3). Ethionine likely forms s-adenosylethionine and acts as methionine antagonist. Recently (4), it has been shown that some Pd(II) complexes with vitamin B_6 inhibit strongly cell divisions of organism, E. coli B-766. We have also found (5) that ethionine inhibits slightly the cell divisions of the same microorganism, E. coli. However, the presence of Eth in the medium containing Pd(II) complexes with vitamin B_6 stops the inhibitory power of these complexes (5).

Equilibrium study has been carried out on the interaction of *DL.Ethionine with Pd(II) in* aqueous solution at I=.16M(Cl^-) and at 25°C. From the potentiometric methods used, it has been concluded that five complexes exist in the pH range 2.8-4.8. The species are $PdCl_3EthH^o_2$, $PdCl_2Eth^-$, $PdClOHEth^-$, $Pd(Eth)_2H_2$ and $Pd(Eth)_2$. In addition, the stopped flow method has been used to study the reaction kinetics of Pd(II) with Eth. Four kinetic steps were observed in the pH range 1.0-5.5. These steps are dependent on the total concentration of Eth(T_{Eth}) as well as on the pH of the medium. The observed pseudo first order rate constants (k_{obs}) for the four reaction kinetic steps at constant pH are expressed empirically by,

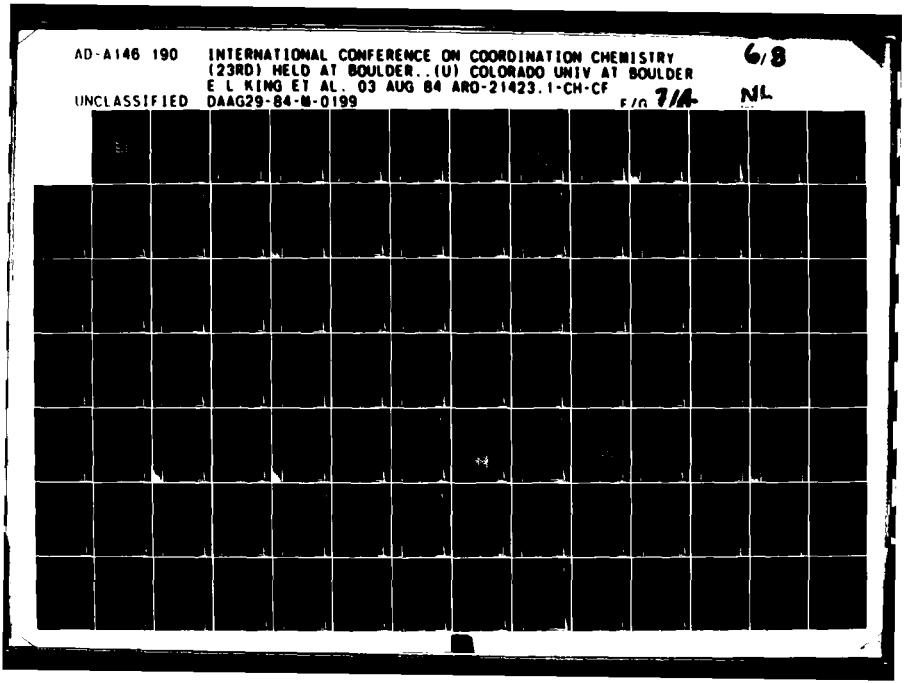
$$k^i_{obs} = m_i + m_i' T_{Eth}$$

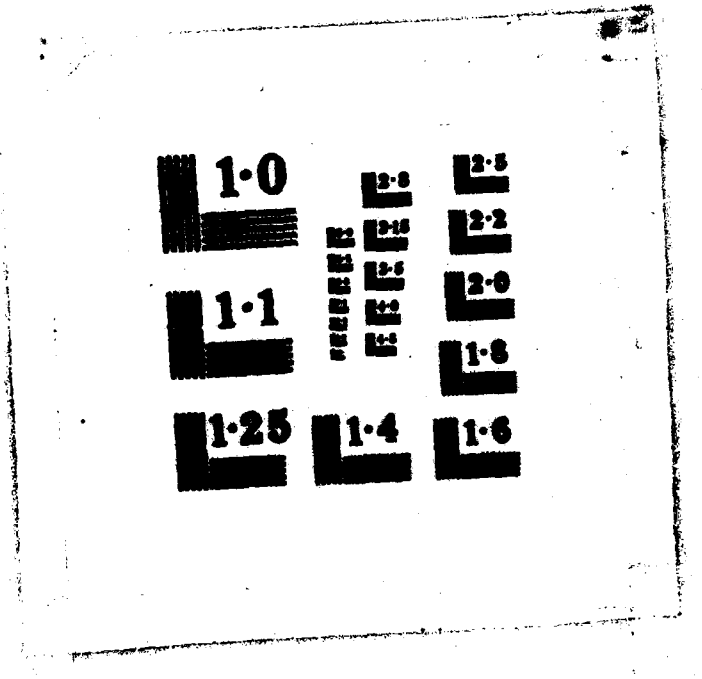
where m_i and m_i' denotes the backward and forward rate constants. These parameters are pH dependent. It has been concluded that hydrolysed Pd(II) species play an important role in the complex formation reactions with Eth. The kinetic data were interpreted in terms of the complex species obtained from the equilibrium study. The cis-trans substitution reactions has been suggested to account for some kinetic stpes.

1. J.F. Fisher and M.F. Mallate, J. Gen. Physiol. 1961, 45, 1.
2. E. Farber, Adv. Cancer Res. 1963, 7, 383.
3. P.F. Swann, A.E. Pegg, A. Hawks, E. Farber and P.N. Magee, Biochem. J. 1971, 123, 175.
4. N.M. Moussa, A. Lahham, M.S. El-Ezaby, N.A. Al-Salem, M.E. Abu Zaid, G.S. Mahmoud, A. Kabarity and S. Mazrooei, J. Inorg. Biochem. 1982, 17(3), 185.
5. N.M. Moussa, A. Kabarity and M.S. El-Ezaby, submitted for publication.

AD-A146 190 INTERNATIONAL CONFERENCE ON COORDINATION CHEMISTRY (23RD) HELD AT BOULDER..(U) COLORADO UNIV AT BOULDER E L KING ET AL. 03 AUG 84 ARO-21423.1-CH-CF 6/8

UNCLASSIFIED DAAG29-84-M-0199 F/G 7/4 NL




1·0
1·1
1·25
1·4
1·6
1·8
2·0
2·2
2·5

IMMOBILE AND MOBILE PHASE ESR SPECTROSCOPY STUDIES ON BIOLOGICALLY INTERESTING CuKTSM$_2$

William E. Antholine, Riccardo Basosi, James S. Hyde, Suzanne Lyman* and David H. Petering*

National Biomedical ESR Center, Medical College of Wisconsin, Milwaukee, Wisconsin 53226 and *University of Wisconsin-Milwaukee, Milwaukee, Wisconsin 53201.

Although changes in the ESR spectrum with varying pH for the antitumor agent 3-ethoxy-2-oxobutyraldehyde bis(thiosemicarbazonato) copper II (CuKTS), and closely related analogs have been previously observed, present room temperature ESR data versus pH for 3-ethoxy-2-oxobutyraldehyde bis (N^4 dimethylthiosemicarbazonato) copper (II) (CuKTSM$_2$) clearly characterized a low pH and a high pH form. Computer simulations of these spectra and spectra from published data are interpreted utilizing a superposition of only these two distinct pH forms.

Since previous work had indicated that CuKTSM$_2$ localizes in the membrane while CuKTS localizes in the cytoplasm and is rapidly reduced by thiols, it was not surprising that the room temperature ESR signal was stable for CuKTSM$_2$ and rapidly disappeared for CuKTS after incubation in Ehrlich ascities tumor cells. It is surprising that at low concentrations CuKTSM$_2$ is essentially immobilized in its association with Ehrlich cells. This observation can only be made at room temperature and not in frozen solutions. At higher concentrations more CuKTSM$_2$ is found in the mobile phase and, at this transition point, CuKTSM$_2$ is also considerably more toxic against Ehrlich cells than previously suspected.

Supported by National Institutes of Health Grants CA-22184 and RR-01008.

CATECHOLAMIDES AS PLUTONIUM CHELATORS

R. Vann Bynum and James D. Navratil

Rockwell International, Rocky Flats Plant, P. O. Box 464, Golden, Colorado 80401

Raymond J. Bergeron and Howard Seligson

University of Florida, Department of Medicinal Chemistry, Gainesville, Florida 32610

Plutonium in aqueous solution is most commonly found in the IV oxidation state, having a charge-to-radius ratio similar to Fe(III) (4.4 vs. 4.7).[1] The chemistry of the two metal ions is similar. For example, although Pu(IV) prefers octadentate ligands, it, like Fe(III), can form very stable chelates with hexadentate ligands. The design of plutonium chelators, unlike iron chelators, is based on the assumption that octacoordinate ligands represent the optimum situation for plutonium binding.

A series of structurally novel compounds, referred to as 1-octadentate catecholamides, have been synthesized. Preliminary complexation studies[2] have been conducted on these compounds showing them to be efficient decorporation agents. "Flute", an octacoordinate catecholamide, was found to remove 98.3 percent plutonium from waste streams which were heavily loaded with many metals.

The results of optimization of the octadentate catecholamides as plutonium chelators will be presented along with stability constants for some of the complexes.

1. F. A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, John Wiley and Sons, New York, NY 1980.

2. R. J. Bergeron, E. J. Kline, J. D. Navratil, and C. M. Smith, Radiochimica Acta, in press.

METAL IONS, AGING AND ALZHEIMER'S DISEASE

Gunther L. Eichhorn and Stephen J. Marlik

Laboratory of Cellular & Molecular Biology, National Institutes of Health, National Institute on Aging, Gerontology Research Center, Baltimore, Maryland, USA 21224

The aging process is affected by both genetic and environmental factors. A variety of evidence indicates that the basic aging phenomenon is genetically determined. Consequently, age changes are observed in various aspects of genetic information transfer, e.g. replication and transcription of DNA and protein synthesis. The likelihood that these phenomena can be controlled in a beneficial matter appears remote.

Environmental effects are also important in aging, and metal ions are among the most important of environmental agents. The concentrations of these metal ions in cells change with age, and we have recently found that the permeability of the cells to metal ions changes dramatically as a result of aging. Since the metal ions are required for all genetic information transfer steps, but can also produce errors in these steps, it is evident that the age-dependent changes in cellular concentrations of metal ions may impact on genetic information transfer in such a way as to modify the aging process. We have previously studied a number of ways in which metals produce deleterious effects on nucleic acids, such as crosslinking, degradation and mispairing. Recently we and others have studied the changes in DNA conformation produced by metals, and we have shown that different DNA conformers have different abilities to sustain DNA synthesis.

Alzheimer's disease is the most prevalent form of senile dementia, and the presence of this disease has been correlated with the accumulation of Al(III) ions specifically. Al(III) concentration in brain has also been related to the number of neurofibrillar tangles, which are associated with the disease. There is also evidence that Al(III) concentration in the brain increases with age. Al has been shown to concentrate in the chromatin of the nucleus. We have shown that the Al(III) forms a number of complexes with DNA, and one of these involves Al crosslinks of DNA strands. Preliminary evidence indicates the Al also causes DNA degradation in chromatin; studies are under way to determine if such degradation has occurred in chromatin obtained from brains of deceased Alzheimer's patients. Al is implicated in a host of other neurological disorders, and we have therefore carried out DNA studies of a variety of Al(III) complexes that may be responsible for the toxic effects. The complexing of Al with ATP is suspected in the progress of dialysis dementia; we have characterized four different Al(III) ATP complexes.

Metal ions and other environmental substances clearly do not bear primary responsibility for aging and the diseases like Alzheimer's disease. The effects of the various agents from whole organisms which the substances that are primarily responsible for these phenomena. The importance of studying the metal effects lies in the fact that they are much more likely to be subject to control than the primary genetic determinants.

EFFECT OF CYTOCHROME P-450 AND GLUTATHIONE ON DNA DAMAGE BY CHROMATE IN CHICK EMBRYO HEPATOCYTES

Karen E. Wetterhahn and Doreen Y. Cupo

Department of Chemistry, Dartmouth College, Hanover, New Hampshire, 03755, USA

Chromate, a known carcinogen, was found to cause DNA strand breaks, DNA-protein cross-links and interstrand cross-links in chick embryo hepatocytes. Rapid repair of DNA strand breaks and interstrand cross-links was observed after removal of cells from chromate exposure. However, DNA-protein cross-links were observed to be very persistent.

Reduction of chromate has been found to be catalyzed by the cytochrome P-450 electron transport system *in vitro*.[1] Glutathione has also been found to react with chromate *in vitro* through formation of a chromium(VI)-thioester which subsequently undergoes reduction.[2] The role of cytochrome P-450 and glutathione in chromate-induced DNA damage was investigated in chick embryo hepatocytes since glutathione and different families of cytochrome P-450 are inducible in these cells. Inducers varied in their ability to effect the DNA lesions caused by chromate. These results will be discussed in relation to chromate metabolism and carcinogenicity.

1. J.D. Garcia and K.W. Jennette, J. Inorg. Biochem. 1981, 14, 281.
2. P.H. Connett and K.E. Wetterhahn, Structure and Bonding, 1983, 54, 93.

Cr(III) PHOSPHATES AS MODELS FOR BREWER'S YEAST CHROMIUM COMPOUNDS

Enrique Gonzalez-Vergara, Douglas Held, and Harold M. Goff

Department of Chemistry, University of Iowa, Iowa City, Iowa 52242 USA

Nearly 25 years have passed since the discovery of chromium as an essential trace element in the diet of animals. Human deficiencies have been documented, and the element apparently participates in control of sugar metabolism. However, such fundamental questions as mechanism of action and chemical structure remain to be answered. Brewers yeast is reportedly high in chromium, and this source has been utilized for a number of clinical and nutritional studies. Extensive chromatographic fractionation of the soluble components of brewers yeast reveals that major chromium compounds present do not stimulate adipocyte glucose oxidation, but that at least two organic components are responsible for previously-observed bioactivity. Nevertheless, the major anionic chromium fraction of brewers yeast may represent the primary source of a stable, absorbable chromium species in animal and human trials. The anionic fraction of brewers yeast has been the subject of extensive purification and spectroscopic characterization in this laboratory. The [illegible] is green in color and absorption maxima in the visible region occur at 422, 595, and 686 (spin forbidden) nm. This visible spectrum is well simulated by the spectra from synthetic chromium complexes of orthophosphate, pyrophosphate, tripolyphosphate, glycolytic phosphates, and ATP. Facile formation of these synthetic complexes is observed under mild aqueous conditions. Although d-d transitions are very similar for the anionic yeast chromium component and various phosphate complexes, the broad g = 4 EPR signal is best simulated by the ATP complex. A chelated polyphosphate derivative may thus define the ligand environment for the native yeast species. The favorable solubility and stability of some of the chromium phosphate complexes at physiological pH make them good candidates for additional nutritional and metabolic studies.

THURSDAY EVENING

TMp48-01

PROTIC CONTROL OF REDOX EQUILIBRIA AND UNUSUAL OXIDATION STATES OF NICKEL AND COPPER

Animesh Chakravorty

Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Calcutta, India 700032

The coupling of redox and protic equilibria is electrochemically examined in oxime complexes of nickel[1] and copper[2]. The concerned ligands are :

$RC(=NOH)C(R')=N(CH_2)_2NH(CH_2)_2NH(CH_2)_2N=C(R')C(=NOH)R$, ($H_2L$)

$RC(=NOH)C(R')=N(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_2$, (HY)

$RC(=NOH)C(R')=N(CH_2)_2NH_2$, (HT)

$RC(=NOH)C(R')=N(R'')$, (HB); $HC(=NOH)C_6H_4N$, (HP)

where R, R' and R'' are alkyl or aryl groups.

The nickel species $Ni^{II}(H_2L)^{2+}$, $Ni^{II}(HT)_2^{2+}$, $Ni^{II}(HY)^{2+}$, $Ni^{III}(HL)^{2+}$, $Ni^{III}(HT)(T)^{2+}$, $Ni^{III}L_2^{2+}$, $Ni^{IV}L^{2+}$, $Ni^{IV}T_2^{2+}$ have been isolated as perchlorates. In the H_2L and HT complexes protic equilibria control the metal redox potentials (0.7V to 0.9V vs SCE). The reversible 2e Ni(II)/Ni(I) couple at low pH splits into two discrete 1e couples, Ni(II)/Ni(III) and Ni(III)/Ni(II), at higher pH. In aqueous media the experimental Ni(III)/Ni(II) formal potential drops to -0.2V. Complexes $Ni^{II}(HY)^{2+}$ and $Ni^{III}(HY)^{3+}$ are also interconverted by proton-controlled electron transfer; here Ni(IV) is not formed.

In the binuclear trimers $Cu^{II}_2(X)^{4+}$ and $Cu^{II}_2(X)^{6+}$ (X = B or BH; B = 1 or 2), the Cu_2^{II} and Cu_2^{III} moieties respectively undergo pH dependent and pH independent reductions:

$$Cu^{III}Cu^{II}(X)^{5+} + e \rightleftharpoons Cu^{II}_2(X)^{4+} \quad (pH > 4)$$

$$Cu^{II}_2(X)^{6+} + e \rightleftharpoons Cu^{II}Cu^{III}(X)^{5+} \quad (pH < 4)$$

The [illegible] of the redox-[illegible] control of [illegible] has been [illegible] in a Cu_2^{II} complex.

1. [illegible]

2. [illegible]

STABILIZATION OF COPPER(II) AGAINST REDUCTION TO COPPER(I) IN ACETATE COPPER(II) COMPLEXES WITH TRIPHENYLPHOSPHINE

Gregor Ondrejovič, Dušan Valigura and Marian Koman
Department of Inorganic Chemistry, Slovak Technical University, 812 37 Bratislava, Czechoslovakia

Ligands L as CN^-, I^-, SCN^-, thiourea, triphenylphosphine (PPh_3) usually cause reduction of Cu(II) to Cu(I). In comparatively many known Cu(II) complexes with L, Cu(II) becomes stabilized against the reduction by the effect of chelate ligands. Structure analysis of such complexes and ESCA measurements of Cu(II) bipyridyl complexes with L show the stabilization of Cu(II) relative to Cu(I) especially in cases when L is bonded in equatorial positions in a trigonal bipyramid or compressed octahedron, and further in axial positions in a tetragonal pyramid and an elongated octahedron[1].

We have found that dimeric structure of copper(II) acetate acts as a stabilizing factor of Cu(II) against reduction to Cu(I) in reaction of $CuAc_2$ with PPh_3 from solvents with a high concentration of dimeric species Cu_2Ac_4. The complex $Cu_2Ac_4(PPh_3)_2$ was separated while from those with a low concentration of dimeric species Cu(I)-Cu(II) complex, $Cu_2Ac_4(PPh_3)_2$ was declared. The X-ray structure analysis[2] showed that the molecule of $Cu_4Ac_8(PPh_3)_4$ consists of a dimeric structure unit, as known in the structure of $Cu_2Ac_4(H_2O)_2$, in which to the axial positions of both Cu(II) atoms two tetrahedral structure units of $Cu_2Ac_4(PPh_3)_2$ are coordinated through bridging oxygen atoms of the acetate groups.

[illegible] in the dimeric [illegible] complex, in the case of this Cu(II) complex a soft PPh_3 ligand is bonded to the soft Cu(I) atom as expected.

1. V.I. [illegible]
2. M. Koman, D. Valigura, J. Moravec and G. Ondrejovič, J.C.S. Chem. Comm., submitted for publication.

HIGH OXIDATION STATE PALLADIUM COMPLEXES OF AMIDATE CHELATING LIGANDS

Chih Ho and Arlene Hallburg

University of Houston-University Park, 4800 Calhoun, Houston, Texas, USA 77004

The amidate nitrogen in chelating ligands is known to stabilize uncommon trivalent complexes of copper and nickel.[1] We are exploring the utility of the electron-rich amidate nitrogen donor in stabilizing high oxidation state complexes of other copper and nickel family transition metals. In particular, we have oxidized the palladium(II) complex of a tetradentate ligand di(α-aminoisobutyryl)-α-aminoisobutyric acid, Aib_3, 1, to form relatively stable trivalent or tetravalent palladium species in aqueous solution. The oxidation state achieved appears governed by the identity of the anions present during controlled potential electrolysis of $Pd^{II}(H_2Aib_3)^-$, 2, where the subscript on the hydrogen symbol indicates the number of amidate nitrogen donors to the central metal ion.

Differential pulse voltammetry of 2 in an aqueous chloride medium gives an irreversible anodic peak with $E_{p,a}$ = 1.11 V vs. NHE in 1 M NaCl whereas in the absence of chloride two irreversible oxidation waves are seen at 1.40 V and 1.80 V. Controlled potential electrolysis of 2 in a chloride-free medium at E_{appl} = 1.30 - 1.65 V (species 3) or in an aqueous chloride medium at E_{appl} = 1.50 V (species 4) gives different chemical species as determined by uv-vis spectroscopy, kinetic stability, and chemical reduction. Chemical reduction of 3 with either iodide or $Co^{II}(H_2Aib_3)^-$ shows 3 to be two equivalents more oxidized than 2. Under the conditions for chemical reduction, 2 does not react with iodide. In contrast, chemical reduction of 4 with iodide shows it to be only one equivalent more oxidized than 2. Addition of bromide to 3 gives a uv spectrum identical to 4 in the presence of bromide but with one half of the expected intensity of 4 prepared in an aqueous bromide medium.

These facts suggest that the formation of either palladium(III) (species 4) or palladium(IV) (species 3) depends on the anions present in aqueous media. Oxidation of 2 giving 3 is thought to disproportionate to 2 and 4 in solutions of halide (either Br^- or Cl^-).

[1] T. Ito, [illegible], J.A. Bertrand, and D.G. Margerum, J. Am. Chem. Soc., [illegible], 1981.

THE ROLE OF INTERMEDIATES IN ELECTRON-TRANSFER REACTIONS INVOLVING Cu(II)/(I) REDOX COUPLES

D. B. Rorabacher, M. J. Koenigbauer, B. Westerby, and J. F. Endicott

Department of Chemistry, Wayne State University, Detroit, Michigan USA 48202

Among common redox couples, Cu(II)/(I) systems are generally distinguished by differences in the coordination numbers of the two oxidation states as well as large differences in the preferred coordination geometries. As a result, the transfer of an electron to or from a copper atom is usually accompanied by the rupture or formation of one or two coordinate bonds resulting in anharmonicities which could jeopardize the application of the Marcus square root relationship to outer-sphere cross reactions. In investigating Cu(II)/(I) systems involving varying degrees of steric constraints, we have previously observed electrochemical evidence suggesting the existence of two different $Cu^{I}L$ species which are presumed to differ conformationally. We now wish to report the direct observation of two $Cu^{I}L$ species of differing kinetic behavior as manifested in cross reactions in aqueous solution. The energy barrier between these two $Cu^{I}L$ species is sufficiently large that the conversion of the more stable species to the metastable species can be kinetically characterized. The demonstration of the existence of such metastable species brings into question the interpretation of most other Cu(II)/(I) kinetic studies and suggests that the theoretical approaches need to be modified accordingly.

THp48-4

EVALUATION OF INNER- vs. OUTER-SPHERE EFFECTS UPON THE SUBSTITUTIONAL LABILITY OF SOLVATED COPPER(II) ION IN MIXED SOLVENT MEDIA

D. B. Rorabacher and L. H. Wheeler

Department of Chemistry, Wayne State University, Detroit, Michigan USA 48202

Simple complex formation reactions of solvated metal ions in mixed solvent media frequently exhibit unusual kinetic trends as a function of solvent composition which are attributable to the differing substitutional lability of the various mixed solvated species. Evaluation of the specific rate constants for the individual solvated species is of great value in understanding the subtle influences of slight changes in the inner-coordination sphere upon substitutional lability. However, such evaluations are hampered by the unknown contributions of competing bulk solvent effects arising from preferential outer-sphere solvation. We have observed that the latter effects can be investigated independently by studying the substitution kinetics of solvated Cu(II) in mixed solvent media, at least in those cases where water is one of the solvent components. Due to the influence of Jahn-Teller distortions, $Cu(H_2O)_6^{2+}$ is exceptionally labile toward substitution. However, the replacement of one inner-sphere water molecule by a different coordinating solvent molecule (e.g., $Cu(H_2O)_5(CH_3OH)^{2+}$) removes the electronic degeneracy of Cu(II) and, thus, eliminates (or at least greatly diminishes) the Jahn-Teller effect. As a result, mixed solvated species are not kinetically competitive with the pure solvated species. The presence of only a single reactive species allows bulk solvent effects to be investigated independently when varying the solvent composition. Reactions with multidentate ligands, in which first-bond formation is not the rate-determining step, exhibit distinctly different behavioral trends whose solvent dependent characteristics may be useful for mechanistic interpretation.

MIXED VALENCE COMPOUNDS CONTAINING THE $V_2O_3^{3+}$ CORE.

Jean-Pierre LAUNAY, Yves JEANNIN and Maria DAOUDI

Laboratoire de Chimie des Métaux de Transition, CNRS-ERA 608,
Université Pierre et Marie Curie, 4 place Jussieu,
75230 PARIS Cedex 05, FRANCE

The mixed valence compounds $\left[V^{V}V^{IV}O_3(pmida)_2\right]^{-}$ (pmida = pyridylméthyliminodiacétate)[1] and $\left[V_5^{V}V_4^{IV}O_{16}(bdta)_4\right]^{7-}$ (bdta = butanediaminetétraacétate) have been prepared and characterized by X-ray cristallography, UV-Visible spectroscopy, magnetic measurements and electrochemistry.

The structure of the pmida complex in the acid form $H\left[V_2O_3(pmida)_2\right].4H_2O$ shows the $V{=}O{-}V{=}O$ core first described by Saito et al[2]. Small deviations with respect to centrosymmetry have been observed. However, they are assigned to an asymetric disposition of the H^{+} ion rather than to an electronic localization. A single crystal spectroscopic study reveals the presence of an extra band at 1200 nm (not seen in solution) which has the polarization of an intervalence band. The electrochemical behaviour in acetonitrile shows two reversible systems: $V^{IV}{-}V^{V} + e^{-} \rightleftarrows V^{IV}{-}V^{IV}$ and $V^{IV}{-}V^{V} - e^{-} \rightleftarrows V^{V}{-}V^{V}$. The comproportionation constant is very large ($\sim 10^{24}$).

The structure of the bdta complex in $K_7\left[V_9O_{16}(bdta)_4\right].27H_2O$ is very unusual. The anion is organized around a $V^{V}O_4$ tetrahedron from which four $V^{V}{-}V^{IV}$ mixed valence "arms" expand giving an overall S_4 symmetry. The mixed valence groups exhibit the usual V_2O_3 stereochemistry and are connected by the bdta ligands in a complicated way. The presence of four coupled mixed valence units is apparent in the optical and electrochemical behaviour.

1. P. Bebonneau, C. Sanchez, J. Livage, J.P. Launay, M. Daoudi and Y. Jeannin. Nouv. Journ. Chimie 1982,6,353

2. M. Nishizawa, K. Hirotsu, S. Ooi and K. Saito. J. Chem. Soc. Chem. Comm. 1979,707. A. Kojima, K. Okazaki, S. Ooi and K. Saito. Inorg. Chem. 1983,22,1169.

THE EFFECT OF THE CHANGE FROM SQUARE PLANAR TO OCTAHEDRAL COORDINATION ON THE pKa OF THE LIGAND IN CONJUGATED UNSATURATED TETRAAZA-MACROCYCLIC NICKEL COMPLEXES

Haim Cohen, Mordechi Nutkovich, Dan Meyerstein and Alan Shusterman

Chemistry Departments, Ben-Gurion University of the Negev and Nuclear Research Centre Negev, Beer-Sheva, Israel

The pKa's for the ligand in the di- and tervalent nickel complexes with 11,13 dimethyl-1,4,7,10-tetraazacyclotrideca-10,13 diene, L_1, and 11-methyl-13-trifluoromethyl-1,4,7,10-tetraazacyclotrideca-10,13 diene, L_2, were measured. The results are 6.55 and 8.8 for NiL_1^{2+} and $NiL_1(H_2O)_2^{3+}$ and 0.84 and 5.1 for NiL_2^{2+} and $NiL_2(H_2O)_2^{3+}$ respectively. These results are surprising as one expects that due to the larger inductive effect the ligands of the tervalent nickel complexes should be more acidic. A plausible explanation of this unexpected result is that the HOMO of the π system of the deprotonated ligand is differently stabilized by the interaction with the nickel $4p_z$ orbital in the di- and tervalent complexes. In the planar divalent complexes the $4p_z$ orbital is non-bonding whereas it is antibonding in the octahedral tervalent complexes. Thus it is plausible that the $4p_z$ orbital is higher in energy in the tervalent complexes if the change from non-bonding to antibonding more than compensates the change in charge. In this case the π system formed due to deprotonation will be more stabilized in the divalent complexes thus explaining the experimental observations. The spectra and kinetics of dimerization of the tervalent complexes are reported.

Acknowledgement. This study was supported in part by the U.S.-Israel Binational Science Foundation, B.S.F., Jerusalem, Israel.

STUDIES ON THE REACTIVITY OF TRANSITION METAL COMPLEXES CONTAINING O-QUINONE LIGANDS

Marion E. Cass and Cortlandt G. Pierpont

University of Colorado, Campus Box 215, Boulder, Colorado, USA

Transition metal complexes containing chelated o-quinone ligands have been under investigation in our research program for several years. Studies carried out primarily with metals of the first transition series on neutral bis and tris quinone complexes have shown that metal and quinone electronic levels are similar in energy but remain localized. Redox chemistry can, therefore, be carried out on quinone ligands or on the complexed metal ion, independently. Reduction of neutral tris (semiquinone)chromium(III) complexes occurs at the ligands while reduction of the vanadium analog with one unit of charge results in dramatic reorganization of charge within the molecule. Further reduction occurs at the metal ion.

$$Cr^{III}(SQ)_3^{\bullet} \overset{e^-}{\rightleftharpoons} Cr^{III}(SQ)_2(Cat)^- \overset{e^-}{\rightleftharpoons} Cr^{III}(SQ)(Cat)_2^{2-} \overset{e^-}{\rightleftharpoons} Cr^{III}(Cat)_3^{3-}$$

$$V^{III}(SQ)_3^{\bullet} \overset{e^-}{\rightleftharpoons} V^{IV}(Cat)_3^- \overset{e^-}{\rightleftharpoons} V^{IV}(Cat)_3^{2-} \overset{e^-}{\rightleftharpoons} V^{III}(Cat)_3^{3-}$$

While the neutral chromium complexes are air stable, the vanadium and analogous molybdenum complexes are quite oxygen sensitive. Both complexes appear to react with O_2 by a common mechanism and reactions have been followed using epr (V) and NMR (Mo). Many of the complexes formed during the O_2 reactions have been isolated in crystalline form and characterized crystallography. The net reaction is catechol oxidation to benzoquinone with oxygen reduction to water. Further studies are being carried out on the addition of other molecules to the $V(SQ)_3$ complexes including CH_3I, acetylenes, olefins and sulfur.

STERIC INFLUENCES ON THE ELECTRON TRANSFER PROPERTIES OF SOME NICKEL(II)/NICKEL(III) MACROCYCLIC COMPLEXES

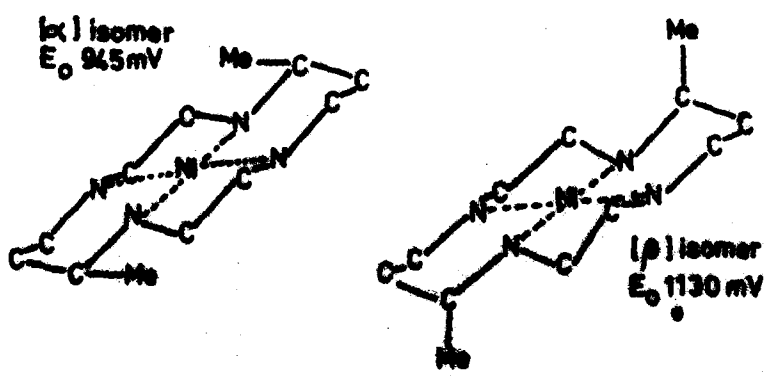
M. Fairbank, A. McAuley and P.R. Norman

Chemistry Department, University of Victoria, Victoria, B.C. V8W 2Y2 Canada

Extensive kinetic, potentiometric and e.s.r. studies have been made recently(1) on the redox behaviour of nickel(II)/(III) macrocyclic complexes, with a view to better understanding the mechanisms of electron transfer involving low spin d^7 ions. Substituent effects on the redox reactions have been noted in several investigations.(2) In general, substitution on the macrocyclic ring raises the E° and reduces the self-exchange electron transfer rate, in some cases by several orders of magnitude. We report here the results of a study on nickel complexes with the ligand (Me$_2$ cyclam); (5,12-dimethyl, 1, 4, 8, 11-tetraazacyclotetradecane). Several conformations of these complexes have been isolated (including two C-meso isomers) and characterised by X-ray, ^{13}C, ^1H nmr, kinetic and electrochemical methods. Marked differences in the redox behaviour are observed within the conformers. (For the isomers indicated above quasi-reversible potentials of 945 and 1130 mV have been obtained). The data demonstrate the effects of stereochemical change proximate to that occurring within the primary coordination sphere during the oxidation process. Other systems displaying similar behaviour will be described.

1. R.I. Haines and A. McAuley, Coord. Chem. Revs., 1981, 39, 77

2. E. Zeigerson, G. Ginsburg, J.Y. Becker, L.J. Kirschenbaum, N. Cohen and D. Meyerstein, Inorg. Chem. 1981, 20, 3988.



CONTROL OF STRUCTURE OF METAL PI-COMPLEXES THROUGH MULTI-ELECTRON-TRANSFER REACTIONS

William E. Geiger

University of Vermont, Burlington, VT, U.S.A. 05405

In many cases the structure of a metal pi-complex can be altered by changing the electron count of the complex. Examples will be discussed in which reversible alteration of metal-ligand bonding has been achieved by electrochemical methods. Emphasis will be placed on systems which display multiple electron-transfer processes, especially those which reduce or oxidize through apparent two-electron processes:

1) the pseudo triple-decker sandwich compunds $[(\eta^5\text{-}C_5R_5)M]_2(\eta^8\text{-}C_8H_8)$, R=H or Me, oxidize through a two electron oxidation to a dication in which the C_8 ring adopts a twisted conformation; 2) Metal-arene compounds of the type $(\eta^5\text{-}C_5Me_5)M(\eta^6\text{-arene})^{2+}$ reduce in either two one-electron steps (M=Rh) or a single two-electron process (M=Ir) to apparent η^4-arene containing neutral compounds. The rate of the process is markedly dependent on solvent.

REDOX CHEMISTRY ASSOCIATED WITH ELECTRON-RICH METAL-METAL TRIPLE BONDS.

Kim R. Dunbar, Stephen H. Tetrick and Richard A. Walton

Department of Chemistry, Purdue University, West Lafayette, Indiana 47907, U.S.A.

Complexes containing the electron-rich metal-metal triple bond configuration $\sigma^2\pi^4\delta^2\delta^{*2}$ have been isolated for the isoelectronic Re_2^{4+} and Os_2^{6+} cores.[1] In the case of dirhenium species, the interconversion between complexes possessing the Re_2^{4+} (B.O.= 3), Re_2^{5+} (B.O.= 3.5) and Re_2^{6+} (B.O.= 4) cores is readily accomplished. For example, the quadruply-bonded dirhenium(III) complexes $Re_2Cl_6(PR_3)_2$ (PR_3 = PEt_3, P-n-Pr_3, $PEtPh_2$, $PMePh_2$), are easily reduced to the corresponding mono-anions using $Co(C_5H_5)_2$ as the reducing agent in acetone solution. The paramagnetic products, which possess Re-Re bond orders of 3.5, have been isolated as the cobaltocenium salts and have been studied electrochemically using the cyclic voltammetry technique. ESR spectral measurements confirm that the reaction products arise from simple one-electron transfer processes. The salts $[(C_5H_5)_2Co^+][Re_2Cl_6(PR_3)_2^-]$ undergo non-redox substitution reactions with PR_3 to yield $Re_2Cl_5(PR_3)_3$. The complexes $Re_2Cl_5(PR_3)_3$ may in turn be reduced to diamagnetic $[(C_5H_5)_2Co]^+[Re_2Cl_5(PR_3)_3]^-$ by cobaltocene. The conversion of the $[Re_2Cl_5(PR_3)_3]^-$ anions to $Re_2Cl_4(PR_3)_4$ occurs upon treatment with PR_3. The anion $[Re_2Cl_6(PR_3)_2]^-$ is isoelectronic with both $Re_2Cl_6(PR_3)_3$ and $[Re_2Cl_4(PR_3)_4]^+$, the latter being prepared by the one-electron oxidation of $Re_2Cl_4(PR_3)_4$ using $NOPF_6$.[2]

The dicesium(III) acetate $Cs_3(O_2CCH_3)_4Cl_2$ has been prepared by the reaction of $[Os_2Cl_8]^{2-}$ with acetic acid-acetic anhydride.[3] Cyclic voltammetric studies on solutions of $Os_2(O_2CR)_4Cl_2$ (R = Et or n-Pr) in 0.2M tetra-n-butylammonium hexafluorophosphate-dichloromethane show that these complexes possess a very accessible one-electron reduction at $E_{\frac{1}{2}}$ +0.3V vs. SCE. Chemical reduction of these complexes using acetone solutions of cobaltocene affords the paramagnetic salts $[Cp_2Co][Os_2(O_2CR)_4Cl_2]$, which are derivatives of the Os_2^{5+} core. These species appear to possess different electronic ground state configurations from their dirhenium analogues $[Re_2(O_2CR)_4Cl_2]^-$; the details of these differences will be discussed. The complexes $Os_2(hp)_4Cl_2$ and $Os_2(mhp)_4Cl_2$, derived from the bridging ligands 2-hydroxypyridine (Hhp) and 6-methyl-2-hydroxypyridine (Hmhp), exhibit redox behaviour closely related to that of their carboxylate analogues.

1. F. A. Cotton and R. A. Walton, "Multiple Bonds Between Metal Atoms", J. Wiley & Sons, New York, 1982.
2. F. A. Cotton, N. E. Dunbar, L. R. Falvello, M. Tomas and R. A. Walton, J. Am. Chem. Soc., 1983, [illegible], 4060.
3. T. Behling, G. [illegible], T. A. [illegible], D. A. Tocher and M. B. [illegible], J. Chem. Soc., Dalton Trans., 1983, 2189.

ELECTROCHEMICAL AND SPECTROSCOPIC STUDIES OF MANGANESE COMPLEXES AS MODELS FOR THE PHOTOSYSTEM II CO-FACTOR IN GREEN PLANT PHOTOSYNTHESIS

Donald T. Sawyer and Kenneth Yamaguchi

Department of Chemistry, University of California, Riverside, California 92521, U.S.A.

The water-oxidation process ($2H_2O \rightarrow O_2 + 4H^+ + 4e^-$; $E^{\circ\prime}_{pH\ 7}$ = +0.81 V vs NHE) of green-plant photosynthesis apparently makes use of a multinuclear-manganese catalytic center. With the goal to model this process in terms of the requisite redox thermodynamics, ligand stability, and biological relevance, a series of manganese(III) complexes ($Mn^{III}L_3$; L = 8-quinolinate, acetylacetonate, picolinate, and 2,2′-bipyridine-N,N′-dioxide) have been synthesized. The oxidation-reduction processes for each of these complexes have been characterized in aprotic media by cyclic voltammetry, UV-visible spectroscopy, and magnetic measurements. In the case of the picolinate and acetylacetonate complexes, electrochemical oxidation yields a transiently stable $Mn^{IV}L_3^+$ species that rapidly oxidizes H_2O_2 and OH^-. The redox thermodynamics for the Mn(III)/Mn(IV) and Mn(III)/Mn(II) couples for this group of $Mn^{III}L_3$ complexes and their hydrolytic derivatives will be discussed in relation to the water-oxidation process of photosystem II.

METAL-AND LIGAND-CENTERED ELECTROCHEMISTRY OF OXOMOLYBDENUM COMPLEXES CONTAINING A SINGLE CATECHOLATE LIGAND.

Julie R. Bradbury and Franklin A. Schultz

Charles F. Kettering Research Laboratory, 150 E. South College St., Yellow Springs, Ohio 45387, USA

We have prepared seven-coordinate monooxo Mo(VI) complexes containing a single catecholate ligand by two synthetic routes: oxidative addition of o-quinones *to oxo* molybdenum(IV)

$$MoO(S_2CNEt_2)_2 + Q \rightarrow MoO(cat)(S_2CNEt_2)_2 \qquad (1)$$

and neutralisation of dioxo Mo(VI) with protonated catechol

$$MoO_2(S_2CNEt_2)_2 + H_2cat \rightarrow MoO(cat)(S_2CNEt_2)_2 + H_2O \quad (2)$$

These complexes undergo two metal-centered and two ligand-centered electron transfers corresponding to Mo(VI) → Mo(V) → Mo(IV) reductions and catecholate → semiquinone → quinone oxidations. The oxidation potentials of the catecholate are shifted positively by about 1.8V upon coordination to the electropositive Mo^{4+} center. The catecholate to semiquinone oxidation is reversible. The product of this oxidation with 3,5-di-t-butylcatecholate ligand exhibits an EPR spectrum with g=2.00[illegible] and hyperfine coupling constants of A(1H)=3.6G and A([illegible])=2.1G, which indicates that unpaired spin density is located predominantly on the ligand in the one-electron oxidized state of the molecule. The oxomolybdenum center undergoes a change in coordination number from seven to five upon reduction from Mo(VI) to Mo(IV). This change results in closely spaced or overlapping potentials for the Mo(VI)/Mo(V) and Mo(V)/Mo(IV) redox steps. The position of these waves and the extent of overlap is influenced by the dynamics of the ligand dissociation reactions coupled to the electron transfer steps. The potentials of the metal- and ligand-based electron transfers are influenced by substituents on the catecholate and by the remaining ligands in the molybdenum coordination sphere, but to different extents. The possibility of controlling the site of electron transfer (metal versus catecholate) by varying the auxiliary ligands in the coordination sphere of these complexes is discussed.

ELECTROCHEMISTRY AND SPECTROELECTROCHEMISTRY OF FIVE-COORDINATE σ BONDED IRON-ARYL PORPHYRINS. INTERACTIONS WITH PYRIDINE AND NITRIC OXIDE.

K. M. Kadish[a], D. Lancon[a], P. Cocolios[a], and R. Guilard[b]

[a]Department of Chemistry, University of Houston, TX 77004 USA

[b]Laboratoire de Synthese et d'Electrosynthese Organometallique associe au CNRS (LA 33). Faculte des Sciences "Gabriel" 6, Bd. Gabriel, 21100 Dijon FRANCE

The low spin S=1/2 five-coordinate iron(III)-aryl σ bonded porphyrins (OEP)Fe(C_6H_5) and (TPP)Fe(C_6H_5) were studied by electrochemical and spectroelectrochemical techniques. Under appropriate conditions both complexes undergo one reversible single electron reduction and two reversible single electron oxidations. However at low scan rates the first oxidation process is followed by an irreversible chemical reaction producing a new electroactive species. This species may be further oxidized by one electron to yield the corresponding iron(III)-N-phenyl derivative. The latter species is reversibly reduced by one electron to give [N-C_6H_5P]Fe^{II}P. This couple undergoes an overall two electron irreversible reduction involving back migration of the phenyl group from the nitrogen to the iron atom, thus generating the starting material in its reduced form.

Upon addition of pyridine to benzonitrile or CH_2Cl_2 solutions new six-coordinate cationic, neutral, and anionic species were generated. Formation constants for these ligand additions were calculated. Further characterization of the neutral (P)Fe(C_6H_5)(Py) complexes was provided by ^{1}H NMR measurements. Coordination by pyridine of the five-coordinate derivatives leads to stabilization of the neutral and oxidized forms thus lowering the rate of the reaction processes. In addition, under reductive electrolysis of the aryl group leading to (P)Fe^{II}(C_6H_5)$_2$ is obtained upon displacement of [(P)Fe(C_6H_5)]$^-$ by pyridine.

Cyclic voltammograms of (P)Fe(C_6H_5) recorded under various pressures of nitric oxide revealed the formation of new six-coordinate nitrosyl, nitrato and hydroxonitrosyl iron porphyrin species, depending on the NO pressure. On the basis of electronic absorption spectra the former complexes were identified as the same species previously reported by Ballard et al.[1]. The formal Fe(II)/Fe(III) oxidation in these derivatives is anodically shifted by up to 1.60 V when compared to their precursors.

The effect of the σ bonded aryl group and the sixth NO axial ligand on the oxidation-reduction potentials and the thermodynamic stability of the newly formed nitrosyl iron porphyrins is discussed.

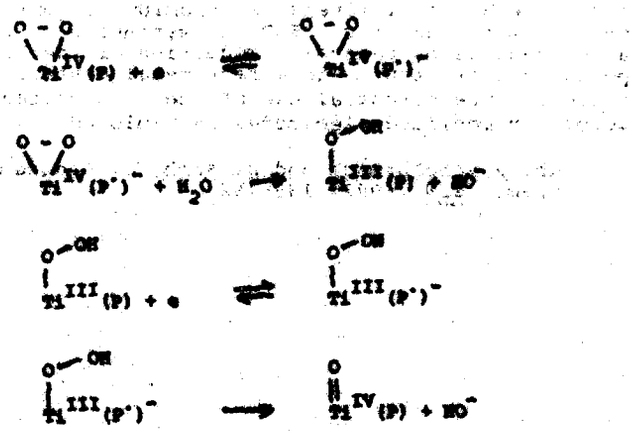
1. G. Lagrange, P. Cocolios and R. Guilard, J. Organomet. Chem., in press.

REDUCTIVE OXYGEN-OXYGEN BOND CLEAVAGE IN η^2-PEROXOTITANIUM(IV) PORPHYRINS

Tadeusz Malinski*‡, D. Chang*, Keri M. Kadish*, Alain Giraudeau**, Maurice Gross*, Jean-Marc Latour†, and Jean-Claude Marchon†

* Dept. of Chemistry, Oakland University, Rochester, MI 48063; **Laboratoire d'Electrochimie et de Chimie Physique, Universite Louis Pasteur, 4 rue Blaise Pascal, 67000 Strasbourg, France; †Laboratoires de Chimie (LA CNRS 321), Departement de Recherche Fondamentale, Centre d'Etudes Nucléaires de Grenoble, 85 X, 38041 Grenoble, France; ‡Present Address: Oakland University, Rochester, MI 48063.

The two-electron reduction of $Ti(O_2)(tpp)$ and $Ti(O_2)(oep)$, leading to TiO(tpp) and TiO(oep) respectively, was investigated by spectroscopic and electrochemical techniques in dichloromethane and tetrahydrofuran solutions. Experimental results are accounted for by an ECEC mechanism which is summarized in the following scheme:



The initially produced species is the porphyrin anion radical complex $Ti(O_2)(tpp)^-$, which is stable under strictly anhydrous conditions. Protonation of the peroxo ligand by trace water leads to a hydroperoxotitanium(III)porphyrin complex by internal electron transfer. Cleavage of the O-O bond of the hydroperoxo ligand takes place after a second electron has been stored in the porphyrin.

The first intermediate, $Ti(O_2)(tpp)^-$, is a very unusual species: it contains in the same molecular framework a two-electron oxidant and a strong one-electron reductant, but these apparently should react with each other in the absence of a proton source, and the complex is stable in anhydrous solvents. Besides that, a future theory should explain this fragile equilibrium between an oxidant and a reductant, which is responsible for the one-electron reactivity of the complexes presented.

THp49-6

ELECTROCHEMICAL AND ^{13}C NMR STUDY OF BIS(ARENE) CHROMIUM(0) AND MOLYBDENUM(0)

C. Mark Seymour and J. J. Lagowski

University of Texas at Austin, Dept. of Chem.
Austin, Texas 78712

Cyclic voltammetric and ^{13}C NMR measurements have been made for a series of bis(arene)M(0) compounds, where M= Cr, Mo. The stability of tetrahydrofuran in highly reducing environments make it an ideal solvent for electrochemical study of these organometallic complexes. The anion radical generation and kinetics of bis(trimethylsilyl-η^6benzene)chromium(-I) are observed by cyclic voltammetry. ESR and synthesis[1] of this anion radical by potassium reduction of the Cr(0) compound is consistent with a rare metal-centered anion radical. The potential use of the bis(arene)Cr $^{+/o}$ couple in modified electrodes is explored.

1. Ch. Elschenbroich and J. Koch, J. Organometal. Chem., 229 (1982) 139-158

SYNTHESIS, STRUCTURAL AND ELECTROCHEMICAL STUDIES OF SOME MOLYBDENUM, IRON AND RUTHENIUM COMPLEXES WITH FERROCENE-CONTAINING LIGANDS.

Pierre GOUZERH, Yves JEANNIN and Véronique MARECHAL.

Laboratoire de Chimie des Métaux de Transition, CNRS-ERA 608, Université Pierre et Marie Curie, 75230 PARIS cedex 05, FRANCE.

In view of our interest in the chemistry of compounds with multiple metallic redox sites, we have synthesized a number of complexes with ferrocene based ligands, with the aim of investigating the feasibility of intervalence transfer through a bridging metal center. The following complexes : $[MoO_2L_2]$, $[MoO_2L'_2]$, $[N(Et)_4][MoOCl_3L]$, $[Ru(CO)_2L_2]$, $[FeL_2(acac)]$ and $[FeL'_3]$ have been prepared from the reactions of $[MoO_2(acac)_2]$, $[N(Et)_4][MoOCl_4(H_2O)]$, $[Ru_3(CO)_{12}]$ and $[Fe(acac)_3]$ with the ferrocenylidene derivatives of benzoylhydrazine (HL) and thiobenzoylhydrazine (HL'). The monooxo-bridged dimers $[Mo_2O_3L_4]$ and $[Mo_2O_3L'_4]$ have been obtained by the reactions of $[MoO_2L_2]$ and $[MoO_2L'_2]$ with PPh_3, and the condensation reactions of $[MoO_2L_2]$ and $[MoO_2L'_2]$ with phenylhydrazine have yielded the bis(phenyldiazenido) derivatives.

The crystal and molecular structure of $[MoO_2L_2]$. solv (solv = 0.20 CH_2Cl_2, 0.18 C_6H_{14}) has been determined by single-crystal X-ray diffraction methods : $P2_1/n$, a = 11.149(7), b = 20.463(3), c = 15.541(5) Å, β = 90.40(5)° ; R = 0.063 for 3861 reflections ; the ligand coordinates through the oxygen and the azomethine nitrogen atom ; the nitrogen donor atoms are trans to the terminal oxo groups. The μ-oxo Mo(V) dimers and the bis(phenyldiazenido) compounds have been characterized by IR spectroscopy and the compound $[Ru(CO)_2L_2]$ has been assigned as the cis-isomer on the basis of IR data. The S = 5/2 high-spin $[FeL_2(acac)]$ and S = 1/2 low-spin $[FeL'_3]$ compounds have been characterized by variable-temperature magnetic studies.

All the compounds have been studied by electrochemical techniques with particular attention to the oxidation of the ferrocenyl groups and to the redox chemistry of the molybdenum center. The two-electron reduction process for $[MoO_2L_2]$ has been found by cyclic voltammetry to be quasi-reversible, an unusual feature for a bis(chelate)dioxomolybdenum(VI) complex.

ELECTROCHEMICAL REMOVAL OF AN ELECTRON FROM $M(CO)_4bpy$ LABILIZES THE COORDINATION SPHERE MORE THAN ITS ACCEPTANCE

D.Miholová, L.Pospíšil, A.A.Vlček

The J.Heyrovský Institute of Physical Chemistry and Electrochemistry, Czechoslovak Academy of Sciences, Vlašská 9, 118 40 Prague 1, Czechoslovakia

Redox orbital concept[1] requires that the change of electron number in π-orbitals influences the stability of the system. To test this implication, $M(CO)_4bpy$ (M = Cr,Mo, W) were studied electrochemically in THF and CH_3CN. These series of complexes form a suitable model system as they undergo both oxidation and reduction.

The reduction is predominantly localized on the bpy ligand, whereas the oxidation results in the removal of one electron from orbitals predominantly of metal origin. Both in the radical anion and cation, primarily formed, labilization of coordination sphere was observed. In the cation substitution already by the solvent molecules proceeds, whereas the anion requires presence of a nucleophile. The rate of substitution is by several orders of magnitude higher in the cation than in the anion. The electrochemical behaviour separating the effect of a hole in the d-electrons and that of an electron in the bpy π-orbitals, implies that the removal of one d-electron has a greater labilizing effect than addition of one electron into bpy π-system.

Analogous labilization was observed to result in the MLCT process[2]. Comparison of electrochemical and photochemical processes makes it possible to deduce differencies in properties of redox and MLCT states.

1. A.A.Vlček, Electrochim.Acta 1968, 13, 1063; Rev.Chim. Minérale 1967, 4, 611.
2. K.W.Hein, J.Ondrej, D.J.Stufkens and A.Oskam, Inorg.Chem. 1980, 19, 3013.

TRANSITION METAL COMPLEXES AS THE ELECTROCATALYZERS OF HYDROGEN EVOLUTION

Herman C. Budnikov, Nicholas A. Ulakhovich and Elvina P. Medyantseva

Kazan State Ulyanov-Lenin University, Kazan, USSR 420008

The processes of the catalytic evolution of hydrogen in solution of metal complexes with organic ligands can be subdivided into groups. It is reasonable to suppose that the oxidation state of the central atom in the catalytically active compound is the basis of this subdivision. In the electrochemical reactions of the first group, complexes with a central atom in the 2+ oxidation state are involved in the protonation process. The catalytic hydrogen wave is observed before the discharge of this complex, in which the rupture of the metal-ligand bond occurs. The evolution of hydrogen in solutions of the transition metal complexes with some thiosemicarbazones, xanthogenates and dithiocarbamates. In the case where the metal forming a complex is in the 3+ oxidation state, the hydrogen wave, as a rule, is preceded by a reversible one-electron reduction wave due to the transition M (III) $\xrightarrow{e}$ M (II).[1]

Electrochemical reactions occurring at more negative potentials (preferably in alkaline solutions) form the second group of transition metal complexes with sulphur-containing ligands to provoke this type of reactions. As in these cases catalytic waves follow the stages in which the central chelate ion is reduced, involvement of complexes with the low oxidation state of the metal in the catalytic effect may be assumed.

References

1. V.F.Surovov, H.C.Budnikov, N.A.Ulakhovich and E.P.Medyantseva, J. Electroanal. Chem. 1989, 264, 1.

STABILITY CONSTANTS FOR Mg(II) and Cd(II) ADENOSINE PHOSPHOROTHIOATE COMPLEXES USING 31P NMR SPECTROSCOPY

Vincent L. Pecoraro, Jeffrey D. Hermes and W. W. Cleland

Department of Biochemistry, University of Wisconsin-Madison, Madison, Wisconsin, USA 53706

Determination of the screw sense specificity for metal nucleotides by kinases is important in deducing a three dimensional picture of an enzyme's active site. Nucleotide phosphorothioates have been used to elucidate this screw sense specificity[1]. In these complexes sulfur is substituted for oxygen on one of the internal phosphorous atoms, generating a chiral center. Magnesium (II) prefers to coordinate to the oxygen atom of such complexes, while Cd(II) is bound predominantly to the sulfur atom. Thus by choosing the proper metal one can generate either screw sense isomer with the same chiral thiophosphate and use these in enzymatic assays to define the enzyme's specificity. An assumption of this method is that Mg(II) and Cd(II) bind exclusively to oxygen and sulfur, respectively. To test this hypothesis we are determining the stability constants of ATP, ADP, ATPαS, ATPβS and ADPαS with Mg(II) and Cd(II) using 31P NMR spectroscopy. We have also completed pH titrations to determine the pK's of the ligands. Our studies, which are in agreement with previously reported values[2], have shown that the pK values for ATP and ADP are 6.63 and 6.66, respectively (30°, μ=0.1M). Moreover, these pK values are not perturbed for ATPαS, ATPβS or ADPαS (6.64, 6.65, 6.77). The stability constants for CdATP and CdADP (log K=4.36, 3.53) are of the same magnitude as the Mg(II) complexes (log K=4.06, 3.17). We will also report the stability constants for the Mg(II) and Cd(II) phosphorothioate species. From these data we can estimate the percentage of Cd-O versus Cd-S coordination. The 31P NMR spectra also indicate to which phosphates the metal ion is bound (e.g., bidentate versus tridentate coordination). These data will be discussed with emphasis on enzymatic studies using these compounds.

1. M. Cohn, Accts. Chem. Res. 1982, 15, 325.

2. A.E. Martell and R.M. Smith, Critical Stability Constants, vol. 2, 281.

EMF EQUILIBRIUM STUDIES OF POLYTUNGSTATE IONS IN FRESHLY ACIDIFIED AQUEOUS TUNGSTATE SOLUTIONS, 3 M $LiClO_4$ MEDIUM AT 25°C

Karl-Heinz Tytko

Institute of Inorganic Chemistry, University of Göttingen, Göttingen, West Germany

The polytungstate system, ionic medium 3 M $LiClO_4$ at 25°C, has been investigated in the entire range of acidification by means of the equilibrium data (Z, log c_{H^+}, $C_{WO_4^{2-}}$)[1] and their mathematical analysis. Measuring range: $C_{WO_4^{2-}}$ = 0.2 to 0.001562 M, Z = 0 to 1.61, 287 data points. Each data point was individually obtained by a "point titration" performing an extrapolation of the H^+ concentration to zero time.

As has been shown for the polymolybdate system[2,3], a definite interpretation of the (Z, log c_{H^+}, $C_{WO_4^{2-}}$) data of systems as complex as polymetalate systems is impossible on the basis of these data solely. Therefore, as in case of the polymolybdate system[2], a reaction scheme for the hydrolysis of the tungstate ion WO_4^{2-} in aqueous media derived from theoretical investigations on the formation mechanisms and structures of polymetalate ions was taken as a basis for the interpretation of the data, comprising the species $W_7O_{24}^{6-}$ (8,7)[1] and $W_8O_{26}^{4-}$ (12,8) and their protonated forms (9,7), (10,7), (11,7), and (13,8) as well as the species $W_{10}O_{32}^{4-}$ (16,10). The latter species, occurring at the border of the range of our theoretical investigations, has been shown to exist by other experiments before, as well as the species (8,7). This reaction scheme gives a good description of the (Z, log c_{H^+}, $C_{WO_4^{2-}}$) measuring data with the following (preliminary) formation constants: $\beta_{8,7} = 10^{64.75}$, $\beta_{9,7} = 10^{69.13}$, $\beta_{10,7} = 10^{72.51}$, $\beta_{11,7} = 10^{74.38}$, $\beta_{12,8} = 10^{84.14}$, $\beta_{13,8} = 10^{86.27}$, $\beta_{16,10} = 10^{108.70}$.

The special merits of the species (8,7) and (12,8) are their unique thermodynamic stability and kinetic inertia depending on geometric qualities of their structures[4]. Their protonated forms occur in virtue of the basicity of the species as also determined by the geometry of the structures and, furthermore, by the charge number of the ions[5]. The reasons for the occurrence of the species (16,10) are discussed as well as the reasons of the dissimilar behavior of the polymolybdate system at this point.

If the measuring data are analyzed without any assumptions concerning the species, species (8,7) can be detected unambiguously by the spacing of the Z(log c_{H^+}) curves for the different tungstate concentrations and the species (16,10) and (13,8) by the final plateau at Z = 1.61 in the (Z, log c_{H^+}, $C_{WO_4^{2-}}$) diagram. For the intermediate species there are different possibilities of interpretation just as in case of the polymolybdate system.

1. Z: H^+ consumed per WO_4^{2-}; (p,q): $H_{p-2r}W_qO_{4q-r}^{(2q-p)-}$.
2. K.H. Tytko and others, Z. Anorg. Allg. Chem. 1983, 503, 43.
3. J. Aveston and others, Inorg. Chem. 1964, 3, 735.
4. K.H. Tytko, Chem. Scr. 1983, 22, 201.
5. K.H. Tytko et al., Adv. Inorg. Chem. Radiochem. 1976, 19, 239.

EQUILIBRIUM ANALYSIS OF THE AQUEOUS MOLYBDOPHOSPHATE SYSTEM. A COMPLEMENTARY EMF AND ^{31}P-NMR STUDY

Lage Pettersson, Ingegärd Andersson and Lars-Olof Öhman

Department of Inorganic Chemistry, University of Umeå, S-901 87 Umeå, Sweden

Equilibria in the H^+-MoO_4^{2-}-HPO_4^{2-} system have earlier been studied by our research group by emf[1] (glass electrode, 25 °C, 3.0 M $Na(ClO_4)$ medium) and combined emf-spectrophotometric[2] methods. Using the results from the equilibrium analysis as a firm base; information from single crystal structure determinations, large-angle X-ray scattering (LAXS) on solutions[3,4] and Raman measurements on solids and solutions[5], made it possible to establish the structures of the predominant aqueous species. Two main series of complexes were found: One colourless with three (5,2)-species having the formulas $Mo_5P_2O_{23}^{6-}$, $HMo_5P_2O_{23}^{5-}$, $H_2Mo_5P_2O_{23}^{4-}$ and one yellow with the five Mo/P = 9/1 species $H_3Mo_9PO_{34}^{6-}$, $H_4Mo_9PO_{34}^{5-}$, $H_5Mo_9PO_{34}^{4-}$, $H_6Mo_9PO_{34}^{3-}$ and the dimer $Mo_{18}P_2O_{62}^{6-}$. The $H_6Mo_9PO_{34}^{3-}$-species was found to have the $Mo_9PO_{31}(OH_2)_2^{3-}$ structure in the solid phase[6,7] and LAXS studies showed the other three 9,1 to have essentially the same structure[4]. The combined emf-spectrophotometric data[2] indicated additional complex(es) having a higher Mo/P ratio than 9. An extended emf study gave no decisive answer and had therefore to be complemented with another experimental method. ^{31}P-NMR spectroscopy was considered most suitable and it is the results from this complementary emf and NMR study that will be presented in the poster. At Mo/P < 2.5 the existence of the (5,2)-species were firmly established and at pH > 1.5 no other complexes could be detected. At higher Mo/P ratios NMR data show that besides the (9,1)-species additional complexes are formed. One of these, a species with a Mo/P ratio of 12:1, becomes predominating in very acidic solutions (pH < 1).

1. L. Pettersson, Chem. Scr. 1975, 7, 145.
2. L. Lyhamn and L. Pettersson, Chem. Scr. 1980, 15, 62.
3. G. Johansson, N. Ingri and L. Pettersson, Acta Chem. Scand. 1974, A 28, 1119.
4. G. Johansson, N. Ingri and L. Pettersson, Acta Chem. Scand. 1978, A 32, 497.
5. L. Lyhamn and L. Pettersson, Chem. Scr. 1977, 12, 142.
6. A. Strandberg, Acta Chem. Scand. 1978, A 32, 217.
7. B. Hedman, Acta Chem. Scand. 1978, A 32, 239.

AN IRON(II) MACROCYLIC COMPLEX WHICH ACTS AS A SELECTIVE HOST FOR DISSOLVED CARBON MONOXIDE AND THEREBY FACILITATES THE TRANSPORT OF GASEOUS CO THROUGH LIQUID MEMBRANES

C.A. Kayal*, R.D. Noble**, J.D. Way**,
D. Louie**, Z. Reyes*, B. Bateman**

*University of Colorado, Boulder, Colorado, USA 80309
**National Bureau of Standards, Boulder, Colorado, USA 80303

The Fe(II) complex ion derived from the macrocyclic ligand 2,3,9,10-tetramethyl-1,3,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene[1], Fe(II)(TIM)$(C_6H_5CN)_2^{2+}$, reversibly binds carbon monoxide in benzonitrile. The 1:1 complexation reaction $Fe(II)(TIM)(C_6H_5CN)_2^{2+} + CO = Fe(II)(TIM)(C_6H_5CN)(CO)^{2+} + C_6H_5CN$, which is believed to proceed by a dissociative mechanism[2], has an equilibrium constant $K/[C_6H_5CN] = 460\ M^{-1}$ at 298K. The forward rate constant for the reaction is $0.17\ M^{-1}s^{-1}$ while the reverse rate constant is $3.7 \times 10^{-4}\ s^{-1}$.

Rising energy and operating costs have underscored the need for efficient and selective separation processes for gaseous mixtures. Carbon monoxide is a potential raw material in synthesis routes for several major chemical products and an abundant source of CO would enhance growth of CO as a raw material for chemical industry. A promising separation method which utilizes reversible chemical complexation is facilitated transport in liquid membranes. The reaction of Fe(II)(TIM)$(C_6H_5CN)_2^{2+}$ with CO affords facilitated transport across benzonitrile liquid membranes and, since the complex does not bind N_2, O_2, CO_2 or H_2, the facilitated transport is relatively selective for CO. Depending upon the membrane thickness and the complex concentration, the transport rate is 20-30% greater than the purely diffusional rate. Results of experiments involving competitive transport of CO in the presence of CO_2 are also reported.

The rate constants for CO-binding and the diffusion coefficients for the Fe(II) complexes can be used as input parameters for a mathematical model[3] which predicts the magnitude of the facilitated transport. Furthermore, the model indicates that reversibility of the complex, as opposed to the thermodynamics or kinetics of the complexation reaction, limits the facilitated transport. The measurement and mathematical procedures described can be applied to any 1:1 complexation reaction between a non-volatile carrier and dissolved gas molecule in order to predict the magnitude of facilitated transport and how the facilitation can be improved via molecular engineering. The effect of photochemistry and electrochemistry on carrier-induced facilitated transport will also be discussed.

1. D.A. Baldwin, R.M. Pfeiffer, D.W. Reichgott, N.J. Rose, J. Am. Chem. Soc. 1973, 95, 5152.
2. L. Vaska and T. Yamaji, J. Am. Chem. Soc. 1971, 93, 6673.
3. C.A. Kolbner and R.D. Noble, J. Memb. Sci. 1980, 7, 189.

THp50-5

EVALUATION OF COOPERATIVITY EFFECTS FROM THERMODYNAMIC DATA OF METAL-LIGAND AND MACROMOLECULE-LIGAND EQUILIBRIA

A.Braibanti, F.Dallavalle, E.Fisicaro, G.Mori and M.Pasquali
University of Parma, I-43100 Parma (Italy)

It has been shown[1] how cooperativity and chelate effects both in metal-ligand and macromolecule-ligand complexes can be evaluated on a common scale by means of dimensionless parameters. The parameters K_ϵ, K_η refer to homotropic chelate effect and $K_{\epsilon'}$, $K_{\eta'}$ to heterotropic chelate effect. The parameter $K_\gamma=\beta_{MA_2}^{1/2}/\beta_{MA}$ for *bis*-complexes, or $K_\gamma=\beta_n^{1/n}/\beta_{MA}$ for *n*-ligand complexes indicate the extent of homotropic cooperativity. On the other hand the heterotropic cooperativity can be evaluated by $K_{\gamma'}=\beta_{MAB}^{1/2}/(\beta_{MA}\cdot\beta_{MB})^{1/2}$, $K_{\gamma'}=\beta_{MA_2B}^{1/3}/(\beta_{MA}^2\cdot\beta_{MB})^{1/3}$, etc. The parameter K_γ ($K_{\gamma'}$) allows to calculate the chemical potential change $\Delta\mu_\gamma^\circ=-RT\ln K_\gamma$ ($\Delta\mu_{\gamma'}^\circ$). The parameters are obtained as ratios between operational equilibrium constants expressed in reciprocal concentration units, the same as the activity coefficients. Therefore the changes in chemical potentials due to cooperativity effects can be compared with changes due to the ionic strength. This relationship is particularly significant because the cooperativity effect is mainly due to external ligand-ligand interactions, where the solvent plays an important role.

The correctness of this thermodynamic treatment can be demonstrated on the Bjerrum plane ($\bar{n}$, $-\ln[A]$). The usefulness of these parameters will be shown by means of sets of data taken from potentiometric and calorimetric measurements on metal-ligand systems obtained in this laboratory and from data in the literature. Also ligand-ligand interactions in macromolecular compounds can be evaluated and come out to be of the same order of magnitude as the interactions in metal complexes[2].

1. A.Braibanti, F.Dallavalle, G.Mori and M.Pasquali, Inorg. Chim. Acta 91, 000 (1984)
2. G.Weber, Adv. Protein Chem. 29, 1 (1975)

FORMATION CONSTANTS OF HOMO- AND HETERODINUCLEAR METAL PORPHYRINS DETERMINED THROUGH EPR SPECTROSCOPY

Lucia Banci

Department of Chemistry, University of Florence, Florence, Italy

In the frame of investigation tending to characterize the heterodinuclear metal porphyrin complexes, the problem of the role of the metal ion and of the stereochemistry of the porphyrin complex on the dimerization equilibrium has been faced.

The constants for the formation of the copper(II)-copper(II) and copper(II)-iron(III) dinuclear species according to the following equilibria have been evaluated at room temperature

$$2CuMPD \rightleftharpoons (CuMPD)_2$$

$$CuMPD + FeMPDCl \rightleftharpoons CuMPD \cdot FeMPDCl$$

where MPD is mesoporphyrin IX dimethyl ester.

The EPR spectra of $CHCl_3$ solutions containing the above species are sensitive only to the monomeric CuMPD one; therefore the intensity of the signals are only proportional to the concentration of the above species.

By measuring the intensities of EPR spectra of solutions containing the copper(II) porphyrin complex a value of $66 \pm 10\ M^{-1}$ has been obtained for the dimerization constant. The formation constant of the heterodimer, obtained from EPR spectra of solution containing the copper and iron complexes, has been found to be $36 \pm 5\ M^{-1}$; the equilibrium constant for the iron(III) porphyrin chloride dimerization is estimated from the same EPR data to be negligibly small.

The formation constants of both the homo- and heterodimers are consistent with the reported values of 62 and $31\ M^{-1}$ for the nickel(II) complex and the pure porphyrin[1]

The fitting of the data in the assumption that only monomeric and dimeric species are present in solution is rather satisfactorily, as found in previous studies on similar systems.[1]

The square pyramidal configuration of Fe(III)Clporphyrin apparently strongly disfavours dimerization but not the formation of the mixed species.

1. Doughty, D.A.; Dwiggins, C.W., Jr. J. Phys. Chem. 1969, 73, 423

THE STABILITY OF PALLADIUM(II) COMPLEXES WITH N-LIGANDS

G. Anderegg, Yan Qing Yu, and H. Wanner

Laboratorium für Anorganische Chemie, ETHZ, CH-8092 Zurich

The investigation of the equilibria involved in metal complex formation is generally limited to cases in which these processes occur in the pH range from 3 to 10. For this reason many authors have used the direct pH method exclusively and consider it as sufficiently sensitive for the determination of all stability constants of metal complexes. This is true for the complexes of the divalent 3d cations with a large number of ligands.

In the case of the 4d divalent cation of palladium, the situation is different. The above given method can be of some help to obtain the constants $K_n(=[ML_n]/([ML_{n-1}][L]))$, for n = 3 and 4, only for unidentate ligands such as ammonia[1]. For polydentate ligands, in a millimolar solution of the metal ion and of the ligand and in 1N $HClO_4$, the 1:1 complex is completely formed and the equilibrium concentration of Pd^{2+} can be very low, e.g., between 10^{-5} and 10^{-14}M. It is therefore apparent that this given method cannot be used to obtain the required constants.

Thiocyanate and bromide anions (X^-) form stable Pd(II) complexes and their stability constants are known[2]. In solutions containing a polyamine and the unidentate X^-, the complex PdX_4^{2-} is the more stable even in strong acidic medium, while that of the former ligand prevails at pH > 7. Thus, with a change of pH, the ligand-ligand exchange occurs with large changes of the optical density of the solution. The complexes with aliphatic amines show d-d band maxima at wavelengths which depend on the number of coordinated N atoms, but the intense absorption of the aromatic amines cover the d-d band of their complexes.

The constant of the exchange equilibrium (I) can be determined

$$PdX_4^{2-} + H_jL^{j+} + PdL^{2+} + 4X^- + jH^+ \qquad (I)$$

by spectrophotometry or by alkalimetric titrations of solutions with equimolar amounts of the metal ion and protonated ligand in presence of an excess of the anion X^-. Mixed complexes $PdLX_n^{(2-n)+}$ have to be considered. The bipyridyl complexes undergo ligand exchange with protonated triethylenetetramine in the pH range 3-6 allowing the determination of the equilibrium constants involved.

Data for ethylenediamine, 2,2'-bipyridyl, 1,10-phenanthroline, and different aliphatic and aromatic tetraamines will be presented. Also hydrolytic decomposition of the complexes and pentacoordination of Pd(II) will be considered.

1. L. Rammussen and C.K. Jörgensen, Acta Chem.Scand. 1965,22,2313.
2. G. Anderegg and S.C. Malik, Helv. Chim. Acta 1976, 59, 1888.

TRp51-01

THE ACTIVATION AND CATALYTIC FUNCTIONALISATION OF SATURATED HYDROCARBONS BY SOME SOLUBLE TRANSITION METAL SYSTEMS

Denise Baudry, Michel Ephritikhine, Hugh Felkin, Tauqir Fillebeen-Khan, Yvonne Gault, Rupert Holmes-Smith, and Janusz Zakrzewski.

Institut de Chimie des Substances Naturelles, Centre National de la Recherche Scientifique, 91190 Gif-sur-Yvette, France.

A number of soluble transition metal polyhydrides (e.g., L_2ReH_7, L_3RuH_4, $L_3Ru(H_2)H_2$, L_2IrH_5; L = tertiary phosphine), in the presence of an olefin (e.g., 3,3-dimethylbutene) as a hydrogen acceptor, have been found to bring about the "activation" of C-H bonds in saturated hydrocarbons under mild conditions.

The following selective (> 95%) homogeneous reactions will be described:

(a) The one-pot conversion of linear alkanes C_nH_{2n+2} (n = 5, 6, 7, 8) into the corresponding 1-alkenes.

(b) The catalytic conversion of cycloalkanes C_nH_{2n} (n = 6, 7, 8) into the corresponding cycloalkenes.

The mechanism of these reactions will be discussed; it is thought to involves the insertion of coordinatively unsaturated (14e) intermediates (e.g., L_2ReH_3) into a C-H bond of the hydrocarbon.

IRIDIUM COMPLEXES IN THE ACTIVATION OF ALKANES AND CYCLOALKANES

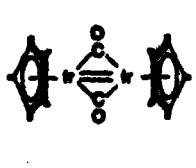
William A.G. Graham, James K. Hoyano, and Alexander D. McMaster

Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2G2

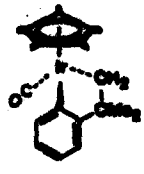
Under UV irradiation, the complex $(\eta\text{-}C_5Me_5)Ir(CO)_2$ (1) forms a coordinatively unsaturated intermediate which can oxidatively add carbon-hydrogen bonds of all kinds in intermolecular fashion.[1] The X-ray structure of 1 provides no clue to this remarkable reactivity, which is so far limited to structurally similar Rh and Ir complexes, including $(\eta\text{-}C_5H_5)Ir(CO)_2$.[2]

The primary products of these photochemical reactions are alkyl- or aryl-iridium hydrides $(\eta\text{-}C_5Me_5)Ir(CO)(H)R$ (2), with aromatic C-H reacting 4-5 times faster than aliphatic C-H. Isolation of the very sensitive complexes 2 is possible, but they are normally converted to the robust halogeno derivatives, several of which have been structurally characterised.

Complexes 2 by subsequent thermal, photochemical, or chemical processes provide access to new mononuclear or binuclear species. Various mixed-ligand complexes of the type $(\eta\text{-}C_5Me_5)Ir(CO)(\text{olefin})$ can be obtained from halide derivatives of 2. Warming 2 (R = cyclohexyl) at 90°C affords the previously unreported 3. Irradiation of 2 (R = neophyl, $CH_2CMe_2C_6H_5$) forms



3



4



5

the benzometallacycloheptene complex 4 in an orthometallation process. In the aryl series, continued irradiation of 1 in benzene leads to several products, among them the μ-σ-phenylene complex 5. Reactions of these binuclear complexes will be discussed.

---

1. J.K. Hoyano and W.A.G. Graham, *J. Am. Chem. Soc.*, 1982, 3723.
2. J.K. Hoyano, A.D. McMaster, and W.A.G. Graham, *ibid*, 1983, 105, 7190.

H/D-EXCHANGE REACTIONS BETWEEN ALKANES AND DEUTERIUM CATALYZED BY SUPPORTED ORGANORHODIUM COMPLEXES

Nobumasa Kitajima and Jeffrey Schwartz

Princeton University, Princeton, New Jersey, USA 08544

Transition metal-catalyzed exchange reactions between alkanes and D_2 are simple examples of C-H bond cleavage, and the elucidation of mechanisms for such processes may lead to the development of selective transformations of alkanes to other organic products. We have noted H/D exchange between butane and D_2 catalyzed by (silica)-OMh(allyl)H, **1**; an equilibrium mixture of deuterium-incorporated alkane was noted after long reaction times.[1] Details of this alkane-D_2 exchange procedure have been determined; two different mechanisms operate for it.

Many metal particles catalyze exchange between alkanes and D_2:[2] for an alkane (C_nH_{2n+2}) the number of C-H bonds exchanged for C-D ones initially observable is close to $2n+2$. In contrast, sequential H/D exchange (for various alkanes) was noted when **1** was used as a catalyst. Decomposition of **1** (heat at 400°C under H_2 for 4 hrs) gives **2** which is black in color and does not show IR absorptions attributable to Rh-H stretching modes. Not surprisingly **2** shows catalytic activity different from that of **1**. Tris(allyl)-rhodium mixed with KBr (no chemical deposition) and treated with H_2 instantly gives black material (no IR transmission, likely Rh metal) which behaves analogously with **2**, as does Rh/SiO_2. Characteristic H/D exchange profiles may, therefore, be of use in distinguishing metallic Rh (initially high d_n) from Rh complexes (initially high d_1, low d_n) in these oxide-bonded catalysts. Activation of linear alkanes by **1** occurs more rapidly than does that for branched species implying the importance of steric factors in the rate-determining step. Methane and [illegible] undergo H/D exchange much less rapidly than do ethane or other linear alkanes.

We propose that alkane activation occurs in a fashion analogous to that of hydrogen,[1] the initial electrophilic attack upon a C-H bond. In the case of ethane or neopentane, only "α" C-H bonds are present, and H/D exchange may occur through a ligand edgewise ("hydridic") pathway (A); when "β" C-H bonds are present, deprotonation may yield olefinic intermediates, and exchange may occur, as well, through a "protonic" pathway (B) in which acidic OH groups of the support and H_2 undergo exchange, catalyzed by **1**, to give -OD units. Proton transfer from -OD to the olefinic intermediate leads to product in which the "β" C-H bond and D_2 have been exchanged. Exchange through (B) is suggested by occur at a rate much higher than that for (A). That these two exchange pathways exist was supported by experiments involving specifically deuterated analogs of **1**.

1. M. D. Ward and J. Schwartz, Organometallics, 1982, 1, 1030.

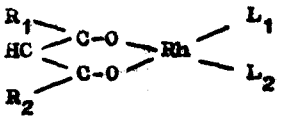
2. G. Rothall, Adv. Catal., 1956, 11, 233.

EFFECT OF LIGAND STRUCTURE ON REACTIVITY OF Rh(I) COMPLEXES

Anna M. Trzeciak and Józef J. Ziółkowski

Institute of Chemistry, University of Wrocław, 50-383 Wrocław, Poland

Sixteen-electron, square Rh(I) complexes whose structure could be modified by the ligands of different σ-donor/π-acceptor properties are convenient model systems to the study of substitution and/or oxidative addition reactions. The following compounds:



R_1=CH_3; C_6H_5; CF_3; $C_{10}H_7$, C_4SH_4
R_2= CH_3; CF_3
L_1=PPh_3; $P(OPh)_3$
L_2=CO; $P(OPh)_3$

were synthesized and spectroscopically (^1H, ^{13}C, ^{31}P NMR, IR, UV-Vis) examined. All complexes were obtained as the mixture of isomers. The trans-effect of asymmetric β-diketones was found to be too weak to form a given isomer of the Rh(AA)(CO)P complex (AA=β-diketone, P=PPh_3, $P(OPh)_3$).

The weaker donor properties of $P(OPh)_3$ compared with those of PPh_3 allow one to obtain complexes of the $Rh(AA)[P(OPh)_3]_2$ [I] type, unknown with the phosphine ligand. Considerable delocalization of the electron density in these complexes leads to equalization of the electron properties of the substituent R in β-diketonate and is the cause for greater electrophilicity of rhodium in [I] types complexes than in the $Rh(AA)(CO)(PPh_3)$[II] ones.

The phosphite complexes exhibit the great reactivity versus CO, H_2 under mild conditions, while the phosphine complexes require the enhanced pressure. Different is the behavior of both types of complexes in the presence of the appropriate phosphorus ligand in excess. In the system [II] + PPh_3 there proceeds the fast exchange of the free and the coordinated phosphine, according to the S_N2 mechanism. In the system [I] + $P(OPh)_3$ the formation of pentacoordinated $Rh(AA)[P(OPh)_3]_3$ complex was observed, instead. That complex readily undergoes the substitution or oxidative addition reaction in the presence of CO, H_2 or their mixture. Both [I] and [II] type complexes catalyze the olefin hydroformylation reaction under relatively mild conditions (p=1-12 atm.; t=60-80°C) and were used in model mechanistic studies.

MOLECULAR STRUCTURES OF CYCLOPENTADIENYL- AND CARBOMETHOXYCYCLOPENTADIENYL-COBALTACYCLOPENTADIENE, AND CARBOMETHOXYCYCLOPENTADIENYL(DIMETHYL)COBALT —— COMPLEXES WHICH ARE RELEVANT TO COBALT-CATALYZED SYNTHESIS OF PYRIDINES FROM ACETYLENES AND NITRILES

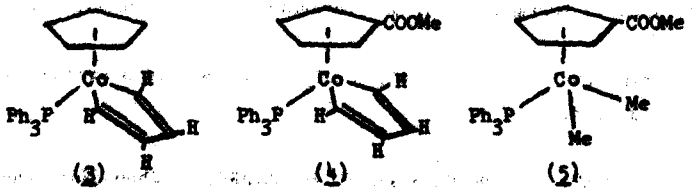
Yasuo Wakatsuki and Hiroshi Yamazaki

The Institute of Physical and Chemical Research, Wako-shi, Saitama, 351, Japan

We have utilized the outstanding reactivity of the cyclopentadienylcobalt unit towards alkynes in the synthesis of heterocyclic compounds [1]. One of the examples is the co-cyclotrimerization of alkynes with nitriles, mediated by the $(C_5H_5)Co$ [2]. The unit can be generated from many precursors such as CpCo(diene), $CpCo(CO)_2$, CpCoCp, $CpCo(PPh_3)$(alkyne), $CpCo(PPh_3)_2$ (1) etc. It appears almost certain that the reaction includes a cobaltacyclopentadiene which reacts further with nitriles via an intermediate like $(C_5H_5)(RCN)Co\text{-}CH\text{=}CH\text{-}CH\text{=}CH$ (2) [3].

It was found recently that the introduction of a carbomethoxy group in the cyclopentadienyl ring, $(ZC_5H_4)Co$ (Z=CO_2Me), greatly enhances the catalytic activity. For example, when MeC≡CH and MeC≡N were reacted at 95°C in the presence of $(C_5H_5)Co(COD)$, the amount of trimethylpyridines formed was 250 mole/g.atom Co : The value increased to 1150 when $(ZC_5H_4)Co(COD)$ was used. In the hope that we could get some informations on the role of the carbomethoxy group in the Cp-ring, we prepared cobaltacyclopentadienes (3) and (4) by the reaction of (1) or its carbomethoxy analog with RC≡CH, and carried out their single crystal X-ray analyses. Complexes (3) and (4) may be regarded as a model for intermediate (2). An alkyl cobalt complex (5) was also analyzed for comparison.

The distance between the (ZC_5H_4) ring and Co, 1.723(3) Å, is shorter than that in (C_5H_5)-Co, 1.741(3) Å. Also the C(metallocycle)-Co bond length in (4), 1.931(6) Å, appears to be shorter than in (3), 1.945(6) Å. These findings suggest stronger interaction of cobalt with the organic moieties in (4) than in (3). In (5), a contribution of the fulvene type resonance form of the cyclopentadienyl ring was observed.



(3) (4) (5)

1. Y.Wakatsuki and H.Yamazaki, J.C.S. Chem. Commun., 1973, 280: Y.Wakatsuki, T.Kuramitsu, and H.Yamazaki, Tetrahedron Lett., 1974, 4549.
2. Y.Wakatsuki and H.Yamazaki, Tetrahedron Lett., 1973, 3383. H.Bönnemann and R.Brinkmann, Synthesis, 1975, 600.
3. Y.Wakatsuki and H.Yamazaki, J.C.S. Dalton trans., 1978, 1278.

THp51-4

ACTIVATION OF C-H BONDS BY NOVEL RUTHENIUM COMPLEXES RuH_4L_3 (L = PCy_3, PPr_3, $P(NEt_2)_3$)

Bruno Chaudret and René Poilblanc

Laboratoire de Chimie de Coordination du CNRS associé à l'Université Paul Sabatier, 205, route de Narbonne, 31400 Toulouse, France

The reaction between Ru(COD)(COT) and phosphines under hydrogen has been shown to be a convenient route to mono and polynuclear polyhydrido complexes[1]. In the presence of three equivalents of the phosphine (L = PCy_3, PPr_3, $P(NEt_2)_3$) the new complexes RuH_4L_3 have been obtained and characterized by analytical and spectroscopic data.

These complexes when dissolved in deuterated aromatic solvents (C_6D_6, C_7D_8) show a remarkable reactivity in exchanging the protons of the phosphine ligands with the deuterium atoms of the solvent[2]. This reaction is spontaneous - it occurs readily in the dark at room temperature under argon - and high yields of deuteration have been obtained. A mechanism involving dissociation of a phosphine followed by subsequent oxidative additions and reductive eliminations of the arene solvent and of the coordinated phosphine ligand is proposed.

The most outstanding feature of this system is a similar ability both to intramolecular and intermolecular C-H activations.

Experiments on C-H activation of saturated hydrocarbons will also be reported.

1. B. CHAUDRET, G. COMMENGES and R. POILBLANC, J. Chem. Soc. Chem. Comm. 1982, 1386.
2. B. CHAUDRET, submitted for publication.

THp51-5

RHODIUM(I) CATALYZED COOLIGOMERIZATION OF CARBON MONOXIDE WITH OLEFINS

Jeffrey S. Brumbaugh and Ayusman Sen

Department of Chemistry, Pennsylvania State University, University Park, PA 16802, USA

Rhodium(I) compounds such as $HRh(CO)(PPh_3)_3$ and $ClRh(CO)(PPh_3)_2$, when dissolved in ROH-HOAc mixture (ROH = MeOH, EtOH, Me_2CHOH), were found to catalyse the cooligomerization of C_2H_4 and CO to a mixture of $H\{CH_2CH_2CO\}_nOR$ and $H\{CH_2CH_2CO\}_nCH_2CH_3$ (n = 1-4). In the case of monosubstituted olefins such as propene and 1-butene, only the isomeric monoketones and esters (i.e., n = 1 products) were observed. Using a new mathematical model, a quantitative analysis of the products of the C_2H_4-CO oligomerization reaction indicated that this reaction proceeded through a single mode of chain growth involving alternate insertions of CO and C_2H_4 with the concomitant alcoholysis and reduction of the resulting metal-acyls and -alkyls respectively. The alcoholysis of the metal-acyls was found to proceed 1.8 times faster in MeOH than in EtOH. In addition, a significant deuterium isotope effect (k(MeOH)/k(MeOD) = 2.6) was observed for the alcoholysis step. The source of the hydrogen required for the formation of the ketones in H_2O. For example, the cooligomerization of C_2H_4 and CO also occurred in MeOH-H_2O and Me_2CO-H_2O. In the latter case, since no alcohol is present, the only products were the oligomeric ketones. Thus, it was possible to rationally control the product distribution in the cooligomerization reaction.

HOMOGENEOUS CATALYTIC DICARBONYLATION OF 1,4-DIFUNCTIONALIZED-2-BUTENES, A POTENTIAL ROUTE TO ADIPIC ACID.

Albert S. C. Chan
Monsanto Company, 800 N. Lindbergh Blvd, St. Louis, MO, USA 63167.

Although the catalytic carbonylation of allylic species has been extensively studied in the last two decades and fairly good results have been obtained for the carbonylation of allyl chloride and allyl methyl ether,[1] the selective dicarbonylation of 1,4-difunctionalized-2-butenes has been relatively unsuccessful. Side reactions such as isomerization and hydrogenolysis appeared to be the biggest problems.[2] Since the linear, dicarbonylated products from 1,4-difunctionalized-2-butenes can be easily converted to adipic acid,

$$XCH_2CH{=}CHCH_2X + 2CO \longrightarrow X\overset{O}{\overset{\|}{C}}CH_2CH{=}CHCH_2\overset{O}{\overset{\|}{C}}X \xrightarrow{H_2} \xrightarrow{H_2O} HO_2CCH_2CH_2CH_2CH_2CO_2H ,$$

a catalyst system for the selective dicarbonylation of these compounds is highly desirable.

In this paper we will describe a highly effective palladium catalyst system which offers high yields of linear, dicarbonylated products. The effects of solvent, catalyst promoters and inhibitors will be discussed. The kinetics and possible mechanisms will also be discussed.

1. D. Medema, R. van Helden and C.F. Kohll, Inorg. Chim. Acta., 3(1969)255.
2. S. Imamura and J. Tsuji, Tetrahedron, 25(1969)4187.

HOMOGENEOUS PALLADIUM CATALYZED CARBONYLATION OF ORGANIC HALIDES UNDER LOW CARBON MONOXIDE PRESSURE: SYNTHESIS OF AROMATIC ALDEHYDES

I. Pri-Bar and O. Buchman

Radiochemistry Department, Nuclear Research Center, Negev P.O. Box 9001 Beer-Sheva 84190, Israel.

Formylation of halobenzenes catalyzed by palladium complexes is known to proceed under high pressures (approx. 100 atm.) of CO and H_2[1,2] (eq. 1). Such conditions obviously reduce the values of the reaction as a preparative tool.

$$Ar - X + H_2 + CO \xrightarrow[\text{Base}]{\substack{H_2,CO\ \ 100\ atm. \\ Pd\ catalyst}}{}_{100 - 150^{\circ}C} Ar - \overset{O}{\overset{\|}{C}} - H \qquad (1)$$

We wish to report a novel palladium catalyzed formylation reaction which takes place at low CO pressure (3-4 atm.) using polymethylhydrosiloxane (PMHS) as the hydrogen source (eq. 2).

$$Ar - X + CO + PMHS \xrightarrow[\text{base}]{\substack{CO\ \ 4\ atm. \\ Pd\ catalyst}}{}_{80 - 130^{\circ}C} Ar - \overset{O}{\overset{\|}{C}} - H \qquad (2)$$

The reaction is highly chemoselective: benzaldehyde was obtained in 96% yield from the reaction of iodobenzene, while bromobenzene was converted to benzaldehyde in 72% yield under the same conditions. Chlorobenzene was found to be practically unreactive under these reaction conditions. Using milder reaction conditions 4-bromoiodobenzene was formylated to give 4-bromobenzaldehyde in 93% yield.

1. Schoenberg, A., and R.F. Heck, *J. Amer. Chem. Soc.*, *96*, 7761, 1974.
2. Yoshida, H., N. Sugita, K. Kudo, and Y. Tsuzaki, *Bull. Chem. Soc. Japan*, *49*, 1661, 1976.

THE ACTIVATION OF DI-OLEFINS AND DIENES BY METALS: THE PHOTOELECTRON SPECTROSCOPY OF $CpM(C_2H_4)_2$ AND $CpM(C_4H_6)$

Dennis L. Lichtenberger, Glen Eugene Kellogg, and John J. Coffey II.

Department of Chemistry, University of Arizona, Tucson, Arizona, USA 85721.

A core and valence photoelectron spectroscopic study using MgKα, HeI, and HeII radiation is reported for a series of $CpML_2$ complexes (Cp = cyclopentadienyl or pentamethylcyclopentadienyl, M = Co or Rh, L = ethylene or L_2 = butadiene). These molecules exhibit complex valence spectra: sixteen of the eighteen EAN electrons appear below 12 eV. The multi-technique approach (HeI, HeII, XPS, and chemical structure perturbation) provides clear, unambiguous band assignments for all orbitals.

The activation of olefins by metals is currently being vigorously investigated. The photoelectron spectroscopy reported here provides unique bonding information for this $CpM(C_2H_4)_2$ system. Each of the four linear combinations of pi orbitals available from the parallel di-olefin geometry are especially informative when activated by the metal orbitals of the CpM moeity. Four important questions regarding metal/ligand interactions in this system are to be addressed: (1) What is the extent of the ligand / Cp pi delocalization? (2) What is the nature of the HOMO? (3) What is the effect of replacing Co with Rh? (4) How does replacing the parallel diethylene pi system with butadiene affect orbital quantizations?

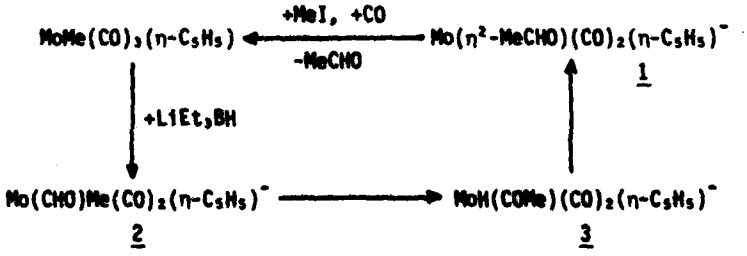
A significant degree of pi delocalization is found. By comparing the band positions of the cyclopentadienyl and pentamethylcyclopentadienyl analogs and calculating shifts, it is found that both ligand and Cp pi ionization bands shift equivalently although the perturbation is specific to the Cp ring. Delocalization in this case indicates a high degree of electron fluidity. The questions of the HOMO character and effect of Rh substitution are complementary as the HOMO in the Co complexes is metal based whereas that of the Rh complexes shows a significant amount of ligand character in the HeI/HeII comparisons of band intensities. Two major effects are observed when butadiene replaces two ethylenes. The first is a decrease in ligand character of the HOMO for the Rh complexes. Secondly, the d_{xy} and $d_{x^2-y^2}$ orbitals become degenerate. Both these effects underscore the significance of the parallel olefin geometry.

A STOICHEIOMETRIC ACETALDEHYDE SYNTHESIS INVOLVING ORGANO-MOLYBDENUM COMPLEXES

J. Trevor Gauntlett and Mark J. Winter

Department of Chemistry, The University, Sheffield S3 7HF, U.K.

We present a stoicheiometric acetaldehyde synthesis from MeI, CO and H^- based upon the attack of a hydride donor upon a methyl molybdenum carbonyl complex. Addition of $LiEt_3BH$ to a tetrahydrofuran solution of $MoMe(CO)_3(\eta\text{-}C_5H_5)$ (itself readily available from $Mo(CO)_3(\eta\text{-}C_5H_5)^-$ and MeI) results in a sequence of reactions leading ultimately to the spectroscopically characterised anionic acetaldehyde complex 1. The initial product is the formyl complex 2 [partial data: ^1H n.m.r. δ(THF), 14.30 (s, 1H, formyl) p.p.m., ^{13}C n.m.r. δ(THF), 287.7 (CHO) p.p.m.] which readily isomerises to the anionic hydrido acyl 3 [partial data: ^1H n.m.r. δ(THF), -5.15 (s, 1H, Mo-H) p.p.m., ^{13}C n.m.r. δ(THF), 306.9 (COMe) p.p.m.]. In turn the hydrido acyl 3 rearranges to the anionic acetaldehyde complex 1. It is necessary to perform appropriate ^2H and ^{13}C isotopic labelling experiments to unambiguously assign n.m.r. spectra. For comparison the ^{13}C n.m.r. resonance of the aldehyde carbon of the anion 1 [^{13}C n.m.r. δ(THF), 56.2 (MeCHO, $^1J_{CH}$ 156 Hz) p.p.m.] may be related to the corresponding signal for the neutral $Mo(CO)(\eta^2\text{-}PhCHO)[\eta^2\text{-}Ph(C_6H_4N)CNHMe](\eta\text{-}C_5H_5)$ at 81.6 p.p.m.[1]



Subsequent treatment of a solution of 1 with MeI under a CO atmosphere results in formation of $MoMe(CO)_3(\eta\text{-}C_5H_5)$ together with acetaldehyde (g c. and g.c.m.s), thus completing a stoicheiometric cycle. The latter reaction probably proceeds by nucleophilic attack of 1 upon MeI to give the neutral $MoMe(CO)_2(MeCHO)(\eta\text{-}C_5H_5)$ from which acetaldehyde is evolved through replacement by CO.

In related reactions reaction of 1 with MeI in the presence of PPh_3 leads to acetaldehyde and $MoMe(PPh_3)(CO)_2(\eta\text{-}C_5H_5)$ while allyl bromide with 1 apart from acetaldehyde produces $Mo(CO)_2(\eta^3\text{-}C_3H_5)(\eta\text{-}C_5H_5)$.

1. H. Brunner, J. Wachter, I. Bernal, and M. Creswick, Angew. Chem. Int. Ed., 1979, 18, 861.

THp52-01

COBALT(II) AS A SPECTROSCOPIC PROBE OF METAL SITES IN METALLOPROTEINS

Ivano Bertini, Department of Chemistry, University of Florence, Florence, Italy.

Cobalt(II) has been introduced in the place of zinc(II) in Carbonic Anhydrase, Carboxypeptidase A, and Liver Alcohol Dehydrogenase, as well as in the iron(III) site of siderophillins. The paramagnetic properties of the ion (S=3/2) have allowed us to investigate the interaction with coordinated water molecules through water ^1H NMRD. The theory of the interaction between the S=3/2 spin and the proton spin has been developped to account for the effects of zero field splitting.

^1H NMR spectra have also been measured of the whole proteins with particular care devoted to the isotropically shifted signals due to protons of the donor groups. The experiments have been carried out also in presence of substrates and inhibitors. Detailed information have been obtained as far as the structure and function of the metalloproteins are concerned. A reflection is due to the possible differences between zinc and cobalt enzymes.

COBALT(III) PEPTIDES WITH RELEVANCE TO ENZYMES

Clifford J. Hawkins[a], Jill Martin[a] and Michael R. Snow[b]

a University of Queensland, St Lucia, Queensland 4067, Australia
b University of Adelaide, Adelaide, Sth Australia, 5001, Australia

The imidazole group of histidine is one of the main coordinating side-groups in metalloenzymes. Metal complexes of tripeptides with histidine as the C-terminal residue or the central amino acid have been reported in the literature for labile metals, and, for the former peptide, for cobalt(III).[1] In these complexes the modes of coordination are NH_2,N^-,N^-,Im and NH_2,N^-,Im, respectively, with these donor groups in the same plane. With histidine as the N-terminal residue in L-his-gly-gly, two cobalt(III) complexes have been synthesised by the 'peroxo dimer' method[2] in which the imidazole is coordinated in an apical position. Structural and spectroscopic studies of these complexes will be described.

In cytochrome c oxidase and the superoxidedismutases, the imidazole group acts as a bridging ligand. Coordination is believed to be via the N atoms. An imidazolate bridged cobalt(III) dimer has been prepared in which there are two different forms of coordination. In one complex the coordination is symmetric via the two nitrogens. In the other, the coordination is unsymmetric possibly through one nitrogen and side-on via the π-electrons of the ring. This form of imidazole coordination has been implicated in the interconversion of 4-methyl- to 5-methylimidazole while bound to cobalt(III).[3] The structure of the unsymmetric dimer is currently under investigation and the results of this investigation will be presented.

A study of the $\alpha\beta$-elimination of H_2S and H_2O from the side-groups of coordinated cysteine and serine peptides will also be reported.

1. C.J. Hawkins and J. Martin, *Inorg. Chem.*, 1983, **22**, in press.

2. E.J. Evans, J.E. Grice, C.J. Hawkins and M.R. Heard, *Inorg. Chem.*, 1980, **19**, 3496.

3. M.F. Haq, C.E. Johnson, S. Peden and R.E. Shepherd, *Inorg. Chem.*, 1983, **22**, 2693-2700.

RESONANCE RAMAN STUDIES OF O_2 STRETCHING VIBRATIONS IN OXYGEN ADDUCTS OF COBALT PORPHYRINS.

Krzysztof Bajdor, Kazuo Nakamoto and James Kincaid

Chemistry Department, Marquette University, Milwaukee, Wisconsin 53233 and University of Kentucky, Lexington, Kentucky 40506

The nature of dioxygen binding to myoglobin and hemoglobin has been a subject of intense study during the past decade and many model systems have been developed in an effort to understand the factors which control oxygen binding in the native protein systems. Historically, vibrational spectroscopy offers great potential for detection of slight alterations in bonding which are associated with minor structural perturbations. However, Resonance Raman (RR) spectroscopy has not been shown to be a useful probe of $\nu(O\text{-}O)$ in the iron model compounds or native systems since this mode is not enhanced with the laser lines which have been used thus far.[1] On the other hand, strong enhancement of both $\nu(O\text{-}O)$ and $\nu(Co\text{-}O)$ has been observed in the cases of O_2 complexes of cobalt myoglobin and hemoglobin[2] and cobalt model systems.[3,4]

Interpretation of the RR spectra of O_2 adducts of cobalt porphyrins in the 1000-1200 cm^{-1} region is often complicated by the presence of core vibrations of the macrocycle, axial ligand vibrations and solvent bands. In an attempt to provide a better understanding of these complicated vibrational spectral patterns, we have undertaken a comprehensive study of a number of model compounds. Specifically, we have carried out strategic isotopic labeling studies in order to demonstrate that certain multiplets arise from vibrational coupling and thus to distinguish this effect from other, steric or electronic factors which might give rise to multiple bands. Evidence is presented for vibrational coupling between $\nu(O_2)$ and internal modes of axial ligands. The utility of mixed isotope ($^{16}O\text{-}^{18}O$) experiments for determining the geometry of the Co-O-O linkage and in detecting vibrational coupling is explored. Results, using a limited number of axial ligands, and several different porphyrins in high and low polarity solvents, indicate that the largest effects on $\nu(O_2)$ frequencies are brought about by interactions with solvent molecules and are consistent with stabilization of charge separation in the $Co^{3+}\text{-}O_2^{3-}$ formulation.

1. M.A. Walters and T.G. Spiro, Biochem., 1982, 21, 6984.

2. M. Tsubaki and N. Yu, Proc. Natl. Acad. Sci. USA, 1981, 78, 3581.

3. K. Bajdor, K. Nakamoto, and J. Kincaid, J. Am. Chem. Soc., 1983, 105, 678.

4. H. Mackin, M. Tsubaki, and N. Yu, Biophys. J., 1983, 41, 349.

ARTIFICIAL HEMOGLOBIN: EFFECTS OF CENTRAL METAL AND AXIAL LIGAND ON COOPERATIVITY

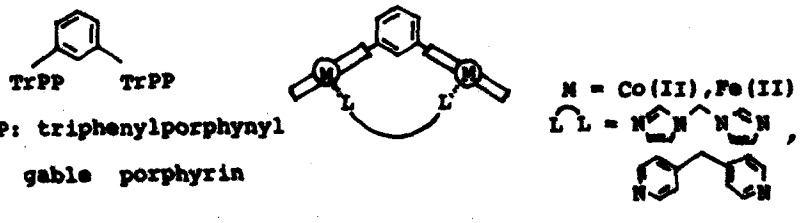
Iwao Tabushi and Tomikazu Sasaki

Kyoto University, Yoshida, Sakyo-ku, Kyoto 606, Japan.

Hemoglobin is a typical example of allosteric enzymes, binding dioxygen molecule cooperatively. We have been developing a new concept of "chemical allosterism" in which allosterism is understood as a "coupling" between active sites of locally same (or very similar) structure. The simplified chemical model systems, therefore, is necessary to elucidate the "coupling" mechanism involved.

As reported by us previously, dicobalt(II) complex of gable porphyrin (Figure) binds dioxygen cooperatively. The observed cooperativity (n=1.5, K_2/K_1 = 8.6±0.8) is satisfactorily large enough to compare with that of hemoglobin (n=3.0, $(K_{i+1}/K_i)_{av}$ = 8~10).

To gain further insights into "chemical allosterism", we investigated the effects of central metal and axial ligand on cooperative O_2 binding. For the purpose, Fe or Co was used as the central metal ion and 4,4-dipyridylmethane or N,N-diimidazolylmethane was used as a bridging ligand. Using these systems, cooperative CO binding was studied by measuring electronic spectrum change and CO partial pressure (GLC). Important findings in the present study are: (1) considerably larger Hill's coefficient (stronger cooperativity) for Fe than Co, (2) cooperativity sensitive to structure of a bridging ligand, and (3) cooperativity sensitive to ligand concentration.



TrPP: triphenylporphynyl

gable porphyrin

1. Tabushi, I., and T. Sasaki, *J. Am. Chem. Soc.*, *105*, 2901, 1983.

SPECTROELECTROCHEMICAL STUDIES OF BEEF HEART CYTOCHROME C OXIDASE

W. R. Ellis, D. F. Blair, H. Wang, H. B. Gray, and S. I. Chan

California Institute of Technology, Pasadena, California, USA 91125

As part of our effort to elucidate the thermodynamic properties of beef cytochrome c oxidase, we have undertaken anaerobic spectroelectrochemical experiments using both long-path stirred cells and optically transparent thin-layer electrode (OTTLE) cells. Attention has been focused on the Cu_A and cytochrome$_a$ sites in the native enzyme, as well as in the cyanide and carbon monoxide derivatives. The enthalpic and entropic contributions to the redox processes associated with these metal centers have been determined via measurement of the temperature dependences of their redox potentials. In contrast to single-site metalloproteins studied thus far, the temperature dependences for the redox potentials of Cu_A and heme$_a$ are markedly nonlinear, indicating a substantial change in ΔCp° upon reduction of these metal sites, as might be expected for a multisubunit electron-transfer protein. Evidence for metal-metal interactions as well as manifestations of pulsed vs. resting behavior will also be presented. These spectroelectrochemical results on cytochrome c oxidase will be compared with data previously reported for blue copper proteins and cytochromes.

THp52-5

ATP HYDROLYSIS PROMOTED BY AQUO-AMINE COBALT(III) COMPLEXES

Salah S. Massoud, Fikru Tafesse, Ronald M. Milburn and Markus Hediger

Department of Chemistry, Boston University, Boston, MA 02215, USA

Certain cobalt(III) complexes of type $N_yCo(H_2O)_{6-y}^{3+}$ [N_y = amine ligand(s)] are highly effective in promoting the hydrolysis of ATP [adenosine 5'-triphosphate] to ADP and P_i [orthophosphate]. Hydrolysis rates at a given temperature depend particularly on the nature of N_y, the Co to ATP ratio, pH, the ATP concentration, and methods of preparing reaction solutions.

Earlier studies[1] with N_y = tn_2 have now been extended to N_y = dpt, cyclen, and trpn [tn = $H_2N(CH_2)_3NH_2$; dpt = $H_2N(CH_2)_3NH(CH_2)_3NH_2$; cyclen = $HN(CH_2CH_2NH)_3CH_2CH_2$; trpn = $N(CH_2CH_2CH_2NH_2)_3$]. Reactions utilizing the latter two ligands can be especially effective. For example, reaction of 10^{-3}M $trpnCo(H_2O)(OH)^{2+}$ with 10^{-3}M trpnCoATP or tn_2CoATP (β,γ-chelates) at pH $\sim$ 6.8 and 25°C produces P_i at initial rates corresponding to $k_i \sim 4 \times 10^{-3}\ s^{-1}$; the rate enhancement over the unpromoted reaction is here $\sim 5 \times 10^5$. At higher Co to ATP ratios, and at higher ATP concentrations the rate enhancements are significantly greater.

Features of the proposed mechanism for the trpnCo/ATP system in the pH region where $trpnCo(H_2O)(OH)^{2+}$ predominates, which we give as an example, are as follows: Addition of $trpnCo(H_2O)(OH)^{2+}$ to ATP at a 1:1 molar ratio results in rapid water substitution to form monodentate-complexed ATP; this complex then undergoes the competitive reactions of (1) ring closure to produce the six-membered (predominantly β,γ) chelate trpnCoATP (I) [$\sim$95% product], and (2) attack by coordinated hydroxide on a β- or γ-phosphorus to produce ADP and P_i [in part complexed, $\sim$5% product]. The 1:1 chelate I exhibits very low reactivity toward hydrolysis of the ATP, with reaction presumably requiring ring opening to provide coordinated hydroxide. When additional $trpnCo(H_2O)(OH)^{2+}$ is added to I, rapid reaction occurs to produce a 2:1 complex which can provide an appropriately positioned coordinated hydroxide. Subsequent attack on a phosphorus can lead to ADP and P_i. At this overall 2:1 trpnCo to ATP stoichiometry rate saturation occurs, which can be attributed to formation of the double six-membered chelate. At higher trpnCo to ATP ratios, where the rates are significantly greater and rate saturation is less important, additional $trpnCo(H_2O)(OH)^{2+}$ is available to facilitate ATP hydrolysis through formation of transient 3:1 trpnCo to ATP complexes.

1. M. Hediger and R.M. Milburn, J. Inorg. Biochem. 1982, 16, 165-182.

TERNARY COBALT(III) COMPLEXES CONTAINING IMIDAZOLE AS A LIGAND

Jayanta K. Das and Kailash C. Dash

Department of Chemistry, Utkal University, Vani Vihar, Bhubaneswar-751004, India

Binary complexes of cobalt(III) with imidazole (or derivatives) are not formed. But a number of ternary cobalt(III) complexes have been synthesized where imidazole is bonded to this metal ion.

Three main groups of compounds are reported. They are (a) *cis*-$[Co(en)_2(Im)Cl]Cl_2$; (b) *trans*-$[Co(acac)_2(Im)(NO_2)]$; and (c) *trans*-$Co(dmg)_2(Im)Cl]$ where acac=acetylacetonate ion, en=ethylenediamine, dmg=dimethylglyoximato anion, and Im=imidazole or its N- or C-substituted derivatives. They are characterized by IR, NMR (^1H and ^{13}C) and mass spectra as well as by X-ray crystal structure analysis. Structural interconversion from the trans-configuration of the original compound to the cis-configuration in $[Co(en)_2(Im)Cl]Cl_2$ has been detected, but not for the $[Co(acac)_2(Im)(NO_2)]$ or $[Co(dmg)_2(Im)Cl]$ complexes. However, in case of $[Co(acac)_2(Im)(NO_2)]$ complexes, slow isomerization during a course of several days in $CHCl_3$ solution is detected, as indicated by NMR spectra.

COPPER EXAFS OF CYTOCHROME c OXIDASE

Robert A. Scott, Stephen P. Cramer, S. Arif Kazmi, and James R. Schwartz

School of Chemical Sciences, University of Illinois, Urbana, Illinois, USA 61801

We have examined the copper extended x-ray absorption fine structure (EXAFS) of cytochrome c oxidase (a two-heme, two-copper containing enzyme) from beef heart mitochondria. A comparison was made of resting state data on cytochrome c oxidase prepared by a number of different procedures, with emphasis placed on the examination of the first coordination sphere.

We observe very significant differences in the copper first coordination sphere among the various enzyme preparations, indicating that differences among these preparations extend to the detailed active site structures. This observation can explain the confusion that exists concerning the lack of agreement between the published data of two groups.[1,2] In addition, these structural differences may reflect the molecular heterogeneity of resting state cytochrome c oxidase identified by other techniques.

1. Scott, R. A. In "The Biological Chemistry of Iron," Dunford, H. B.; Dolphin, D. H.; Raymond, K. N.; Sieker, L. C., Eds.; Reidel: Boston, 1982; pp 475-84.

2. Chance, B.; Powers, L.; Ching, Y. In "Mitochondria and Microsomes," Lee, C. P.; Schatz, G.; Dallner, G., Eds.; Addison-Wesley: London, 1981; pp 271-92.

3. Brudvig, G. W.; Stevens, T. H.; Morse, R. H.; Chan, S. I. Biochemistry 1981, 20, 3912-21.

^{1}H NMR SPECTRA OF MAGNETICALLY COUPLED SYSTEMS: Co_2Cu_2 SUPEROXIDE DISMUTASE AND A Cu^{II}-Fe^{III} INORGANIC COMPLEX

I. Bertini, G. Lanini, C. Luchinat, R. Monnanni and A. Scozzafava, University of Florence, Department of Chemistry, Florence, Italy

Cobalt(II) has been inserted in the zinc(II) site of superoxide dismutase, and the derivatives have been investigated through ^{1}H NMR spectroscopy both in the absence (Co_2E_2SOD) and in the presence (Co_2Cu_2SOD) of copper(II) in the catalytic site. The 60 MHz ^{1}H NMR spectra show isotropically shifted signals arising from the interaction of ligand protons with the unpaired electrons. The spectra of Co_2E_2SOD are relatively ill-resolved and typical of pseudotetrahedral cobalt(II) in protein environments with similar ligands, while the spectra of Co_2Cu_2 SOD show numerous and well resolved (sharper) signals. A possible explanation is that in the latter derivative signals from both the cobalt(II) and copper(II) sites are observed, the signals from the latter site being detected owing to the reduced nuclear relaxing efficiency of copper(II) when magnetically coupled with cobalt(II). The problem of effects of metal-metal magnetic coupling on the nuclear relaxation rates have been addressed by throughly investigating the behaviour of the 1:1 adduct between bis(ethylenediamine)copper(II) and hexacyanoferrate(III) in 1,2 ethanediol solutions. The longitudinal relaxation rates of the solvent protons in solutions of the above adduct measured in the frequency range 0.01-60 MHz are sizeably lower than in solutions of the analogous adduct between the copper complex and the diamagnetic hexacyanocobaltate(III) anion.

Theoretical treatments have been developped to extract the correlation time from NMRD data in order to understand the relationship between the extent of magnetic coupling in ethero atomic systems and the nuclear relaxation parameters.

THp52-9

AN INVESTIGATION OF THE INTERACTION OF PHOSPHATE ANION AND BOVINE SUPEROXIDE DISMUTASE

Elena Borghi

Istituto per lo Studio della Stereochimica ed Energetica dei Composti di Coordinazione, CNR, Firenze, Italy

Bovine Superoxide Dismutase(SOD) is a dimeric metalloenzyme of Mw 32,000 containing, in its oxidized form, a zinc(II) and a copper(II) ion in each subunits[1]. The copper and zinc centers in each subunit are bridged by an imidazolate ion from histidine-61[1]. SOD efficiently catalyzes the dismutation of superoxide[2]. One of the caracteristic properties of SOD is its high affinity for anions[3]. Several anions bind to copper(II)[3] and substitute for a histidine nitrogen[4,5]. Phosphate anion shows unusual effects on SOD and its derivatives[6]; it interferes with affinity of other anions, has an inhibitory effects on the SOD activity, but it seems not to bind to copper(II). In the same way the affinity of anions is reduced for the phenylglyoxal modified-SOD, and phenylglyoxal binds arginine 141, which lies within 6 Å of the active site copper, close to the ligand histidine 118[1,7]. Arginyl residues play a role in anion binding in certain enzyme and are a good binder for phosphate ion[8].

Spectroscopic evidence concerning the nature of the interaction between phosphate and Cu,ZnSOD has been obtained. The hypothesis that the guanidino group of arginine 141 may be the site of phosphate interaction with the SOD enzyme has been tested by an NMR relaxation investigation. Model compounds have also been investigated.

1. J.A. Tainer, E.D. Getzoff, K.M. Beem, J. S. Richardson, D.C. Richardson, J. Mol. Biol., 1982, 160, 181.
2. J.M. Mc Cord, I. Fridovich, J.Biol.Chem., 1969, 244, 6049.
3. J.A. Fee, B.P. Gaber, J.Biol.Chem., 1972, 247, 60; G. Rotilio, L. Morpurgo, C. Giovagnoli, L. Calabrese, B. Mondovì, Biochemistry, 1972, 11, 2187.
4. I. Bertini, C.Luchinat, A. Scozzafava, J.Am.Chem.Soc., 1980, 102, 7349.
5. I. Bertini, E. Borghi, C. Luchinat, A. Scozzafava, J.Am.Chem.Soc., 1981, 103, 7779.
6. A. Rigo, P.Viglino, G.Rotilio,R.Tomat, FEBS Lett.,1975,50,?86; L. Calabrese, D. Cocco, A. Desideri, FEBS Lett., 1979,106, 142; K.G. Strothkamp, S.J. Lippard, Biochemistry, 1981, 20, 7488.
7. D.P. Malinowski, I. Fridovich, Biochemistry, 1979, 18, 5909.
8. L.G. Lange, J.F. Riordan, B.L. Vallee, Biochemistry, 1974, 13, 4361.

THp53-02

NITRIDO, OXO, PEROXO AND IMIDO COMPLEXES

William P. Griffith, Neil T. McManus and Alastair J. Neilson*

Dept. of Chemistry, Imperial College, London SW7, England.

*Dept. of Chemistry, University of Auckland, Auckland, New Zealand.

(a) Nitrido and related species. The symmetrically-bound u-nitrido complexes containing the $M_2^{IV}N$ unit[1] (M=Os,Ru) have been further investigated. It is shown that in these species the metal behaves as though it is in the III or II state, forming stable complexes with such ligands as CN^-, CO, NO, NCS^-, halide, NO_2^-, en, NH_3, PR_3, py, bipy etc. This behaviour is consistent with the strong π-donor properties of the nitrido ligand. Vibrational, ^{99}Ru NMR and ESCA spectroscopy together with cyclic voltammetry and single crystal X-ray results on these complexes have been studied. Attempts to prepare mixed complexes containing MNM' units have been made. Data are also presented on complexes containing the linear $M_3N_2^{n+}$ units[2], and related complexes containing oxo[3] and peroxo ligands will also be discussed.

(b) Imido complexes. The results of some studies on the vibrational spectra of rhenium, tungsten and osmium alkyl- and arylimido complexes will be briefly presented.

1. M.J. Cleare and W.P. Griffith, J. Chem. Soc. (A), 1970, 1117.
2. J.P. Hall and W.P. Griffith, J. Chem. Soc. (Dalton) 1980, 2410.
3. J.R. Campbell, R.J.H. Clark, W.P. Griffith and J.P. Hall, J. Chem. Soc. (Dalton) 1980, 2228.

HYDRAZIDO(1-), 1,2-HYDRAZIDO(2-), AND HYDRAZIDO(4-) COMPLEXES OF TUNGSTEN (VI)

Richard R. Schrock, Lauren Blum, and Klaus H. Theopold

Department of Chemistry 6-331, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

In an effort to prepare Mo and W μ-N_2 complexes analogous to those known for Nb and Ta (e.g., $[MCl_3(THF)_2]_2(\mu\text{-}N_2)$, best described as a hydrazido(4-) complex), we have been adding hydrazine to d^0 complexes. $W(NPh)Me_4$ reacts with N_2H_4 to give a hydrazido(1-) complex, $W(NPh)Me_3(N_2H_3)$, believed to be dimeric. A 1,2-hydrazido complex, $[W(\eta^5\text{-}C_5H_5)(CCMe_3)Cl]_2(\mu\text{-}N_2H_2)$, is the product of the reaction between $W(\eta^5\text{-}C_5H_5)(CCMe_3)Cl_2$ and N_2H_4. The reaction between $W(C_2Ph_2)(OCMe_3)_4$ and N_2H_4 produces a hydrazido(4-) complex, $[W(C_2Ph_2)(OCMe_3)_2]_2(\mu\text{-}N_2)$. Each of these species is unique, we propose largely because of extensive π-bonding between tungsten and the nitrogen ligand.

NEW CONCEPT OF VALENCE IN COORDINATION CHEMISTRY AND STRUCTURAL RULES FOR THE TRANSITION METAL CLUSTERS

Guang-Xian Xu (K.H.Hsu)

Department of Chemistry,Peking University
Beijing,People's Republic of China

The valence of metals in inorganic chemistry usually refers to the oxidation states.However,many coordination compounds,organometallics and clusters are covalently bonded,but there still lacking a precise definition of covalence of metal atoms in these compounds. In this paper,the covalence of an atom or a molecular fragment in a molecule is defined as the number of electrons accepted in its valence orbitals during the formation of the molecule.Thus for a coordinate covalent bond A→B,in which the ligand B donates two electrons to the vacant orbital of A,the covalence of A is therefore two, while that of B is zero.For an η^x hapto-bond to metal M, the covalence of M is x.

The covalence of a molecular fragment is defined as the number of vacancies in the valence orbitals of the fragment.Some examples are given as follows:

Monovalent fragments: $Mn(CO)_5$,$Re(PR_3)_5$,$Co(CO)_4$

Divalent fragments: $Fe(CO)_4$,$Ru(PR_3)_4$,$W(CO)_5$

Trivalent fragments: NiCp,$Co(CO)_3$,$TaCp_2$,Fe(CO)Cp

Tetravalent fragments:$Fe(CO)_3$,CoCp,$Os(PR_3)_3$,MoAcPy

Pentavalent fragments:$Ir(PR_3)_2$,FeCp,$Mn(CO)_3$,Ni(NO)

Hexavalent fragments: $Pt(PR_3)$,$Fe(CO)_2$,MnCp,$Os(PR_3)_2$

Heptavalent fragments:$Re(PR_3)_2$,Fe(NO),Co(CO),$IrPR_3$

Octavalent fragments: $Cr(CO)_2$,$W(CO)_2$,VCp,Mn(NO)

Nonavalent fragments: $V(CO)_2$,$Ta(CO)_2$,Cr(NO),Mn(CO)

Decavalent fragments: Cr(CO),W(CO),V(NO),Fe,MnH

Relevant structural rules were derived based on these definitions. These rules may be used to explain the structure and bonding capability of many transition metal clusters,which are exceptions of the famous Wade's rule and to predict many new cluster compounds.

1. Guang-Xian Xu(K.H.Hsu),The Second China-Japan-U.S.A. Symposium on Organometallic and Inorganic Chem.,1982.
2. Guang-Xian Xu,Chem.J.Chinese Univ.,1982,Spec.Issue,114
3. Guang-Xian Xu,J.Molecular Science,1983,1,1.

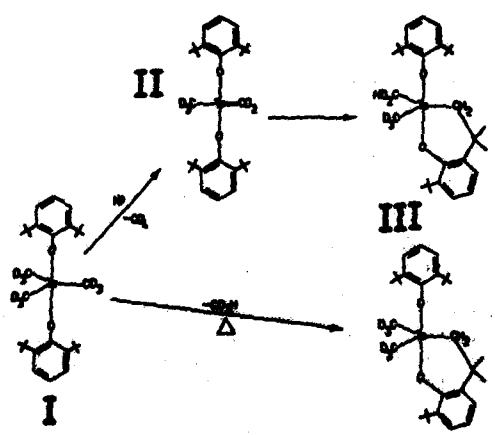
PHOTOCHEMICALLY INDUCED α-HYDRIDE ABSTRACTIONS

Linda R. Chamberlain, Arlene P. Rothwell and Ian P. Rothwell

Purdue University, Chemistry Department, West Lafayette, Indiana, USA 47907

The sterically crowded molecule $Ta(OAr')_2Me_3$ (OAr' = 2,6-di-tertbutyphenol) (I)[1] has been found to undergo the smooth loss of one equivalent of methane and formation of a methylidene complex $Ta(OAr')_2(=CH_2)(CH_3)$(II).[2] On standing at 25°C for four hours, (II) converts to the cyclometallated complex (III) in which an aliphatic CH bond of the tert-butyl group has been added to the $Ta=CH_2$ function.[3] Complex (III) may also be synthesized directly from (I) by thermolysis.[4] Labelling studies have clearly differentiated the thermal and photochemical routes to (III)(Scheme).

The nature of the photochemical process leading to (II) and other reactivity studies will be presented.



1. Chamberlain, L.; Rothwell, I. P.; Huffman, J. C., Organometallics, 1982, 1, 1538.

2. Chamberlain, L.; Rothwell, I. P.; Huffman, J. C., J. Am. Chem. Soc., 1982, 104, 7338.

3. Chamberlain, L.; Rothwell, A. P.; Rothwell, I. P., J. Am. Chem. Soc., submitted.

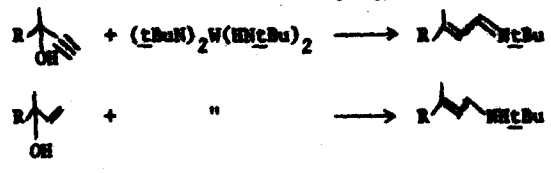
NEW ORGANIC CHEMISTRY OF d^0 TRANSITION METAL IMIDO COMPLEXES

Dominic M. T. Chan, W. A. Nugent, D. C. Roe and T. H. Tulip

Central Research & Development Department, Experimental Station, E. I. du Pont de Nemours & Company, Wilmington, Delaware 19898

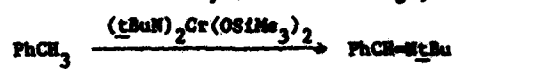
Four previously unreported reactions of early transition metal organoimido (i.e., M=NR) complexes will be discussed:

- Amination of Allylic and Propargylic Alcohols. e.g.,

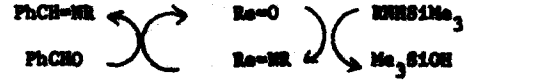


R=$(CH_3)_2C{=}CHCH_2CH_2$

- Ammoxidation of Hydrocarbons. e.g.,



- Catalytic Heterometathesis of Unsaturated Carbon-Heteroatom Double Bonds. e.g.,



- Direct Observation of o-Hydrogen Exchange in a Novel Perfluoropinacolate Tungsten Imido Complex.

In addition to having considerable synthetic utility, these homogeneous reactions of monomeric imido complexes provide excellent models for a number of discrete steps in the heterogeneous ammoxidation of propylene to acrylonitrile.

THE EFFECT OF BULKY GROUPS ON THE STABILITY AND RATE OF FORMATION OF AZAPLATINACYCLOBUTANE RINGS

Michael Green and Jamil K. K. Sarhan

Department of Chemistry, University of York, York, YO1 5DD, UK.

Treatment of alkene-platinum complexes, 1, with amine, am, leads to neutral σ-alkanide compounds, 2. Excess am converts these to either cyclic compounds[1,2], 3, or cationic σ-alkanide acyclic species[3], 4. The former are stabilised thermodynamically relative to the latter if bulky substituents are present.

cis-$[PtCl_2(\eta^2\text{-}RR'C{=}CH_2)Y]$ + am ⇌ cis-$[Pt(CH_2CRR'am)Cl_2(Y)]$ (i)

1 2

2 + am ⇌ $[PtCH_2CRR'am^{-H}(Cl)Y]$ or $[Pt(CH_2CRR'am)Cl(am)Y]$ (ii) or (iii)

3 4

(i) The compound formed in $CDCl_3$ after ca. 30 minutes is

R	R'	Y	am	Product
H	H	dmso	secondary am	2
			primary am	3
Et			secondary am/t-$BuNH_2$	2
H		PPh_3	secondary am/t-$BuNH_2$	2
			$MeNH_2$/$EtNH_2$/n-$PrNH_2$/n-$BuNH_2$	3
H		Me_2NH/4Me-py	Me_2NH	2
Me/Et			Me_2NH	2

(ii) Nearly all the examples of 3 that have been characterised as solids are derived from am = Me_2NH or piperidine.

(iii) When Y=dmso, ν(Pt-N) rises as the R and R' become larger, viz R,R' : H,H, 568; Me,H, 572; Et,H, 575; Me,Me, 578 cm^{-1}.

(iv) When Y=PPh_3, the equilibrium constant, K_1K_{11}, for the formation of 3 from 1 rises: am=Me_2NH<Et_2NH<n-Pr_2NH<n-Bu_2NH.

From the point of view of kinetics, ^{1}H-n.m.r. shows that the rate of cyclisation to form 3 is increased by bulky groups, rising:

(a) Y=dmso, R=R'=H: Me_2NH < Et_2NH < n-Pr_2NH < n-Bu_2NH

(b) Y=dmso, am = Me_2NH; R=R'=H < R=Me,R'=H < R=Et, R'=H < R=R'=Me.

1. I.M. Al-Najjar, M. Green, S.J.S. Kerrison & F.J. Sadler, J.Chem.Soc., Chem. Comm., 1979, 311.
2. A. De Renzi, A. Panunzi & A. Vitagliano, Gazz. Chim. Ital., 1978, 108, 45.
3. J.K.K. Sarhan, M. Green & I.M. Al-Najjar, J. Chem. Soc., Dalton Trans., 1984 (in April).

LOW VALENT METAL COMPLEXES OF TEFLATE ($OTeF_5$) DERIVATIVES

Steven H. Strauss, Kent D. Abney, Kim M. Long, and Michael J. Pawlik

Colorado State University, Fort Collins, CO 80523

The pentafluoroorthotellurate ($OTeF_5$), or teflate, group has been substituted for fluorine or chlorine in a wide variety of main group and high valent transition metal complexes.[1,2] By using various physicochemical criteria, it has been repeatedly demonstrated that the electronegativity of the teflate group and fluorine are practically equal. We now report that teflate can serve as a ligand in a variety of low valent metal complexes. For example, spectroscopic data (NMR, IR, VIS) on $Mn(CO)_5(OTeF_5)$ show that teflate is lightly bound to manganese. The data also show an absence of any pi bonding between O and Mn, in harmony with the structure of this molecule, which displays a staggered conformation (i.e. teflate is staggered with respect to the carbonyl ligands). Significant pi bonding between O and Te is evidenced by a high Te-O stretching frequency (841 cm^{-1} in CH_2Cl_2) and a short Te-O bond distance (1.754(12)Å). This distance is shorter by 0.05Å than in any other teflate structure determined to date. We will also present results on other low valent complexes containing one or more teflate ligands.

We have also been exploring the use of $P(OTeF_5)_3$ and $As(OTeF_5)_3$ as extremely bulky substitutes for carbon monoxide in metal complexes. We will present a variety of spectroscopic data for $M(CO)_nL$ complexes that show that our bulky ligands (L) rival PF_3 in pi acidity. We will discuss the unusual reactivity of the metal complexes that is a consequence of the steric requirements of these bulky pi-acid ligands. We will also present data that show that $As(OTeF_5)_3$ is a Lewis acid (sigma acid) towards bases such as CH_3CN and Cl^-. The occurrence of both sigma and pi acidity in the same molecular species is rare.

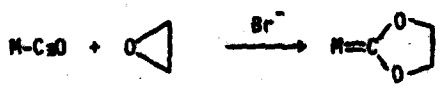
1. K. Seppelt, Angew. Chem., Int. Ed. Engl., 1982, 21, 877.
2. A. Engelbrecht and P. Sladky, Adv. Inorg. Chem. Radiochem., 1961, 24, 189.

SYNTHESIS OF DIOXOCARBENE COMPLEXES BY THE REACTION OF METAL CARBONYLS WITH ETHYLENE OXIDE

Robert J. Angelici and Mono M. Singh

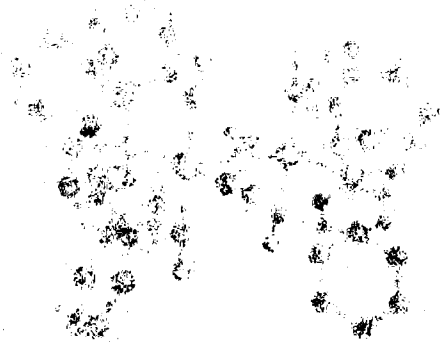
Department of Chemistry and Ames Laboratory, Iowa State University, Ames, Iowa, USA 50011

We previously reported[1] the room temperature reaction of cationic metal carbonyl complexes (e.g., $CpFe(CO)_3^+$, $CpMn(NO)(CO)_2^+$ and $CpRu(CO)_3^+$) with ethylene oxide in the presence of Br^- to yield the dioxocarbene complexes according to the equation:



Neutral carbonyl complexes are less reactive; however, at 100°C $Fe(CO)_5$, $Mn_2(CO)_{10}$, $Re_2(CO)_{10}$, and $Ru_3(CO)_{12}$ react with ethylene oxide to give the dioxocarbene complexes: $Fe(CO)_4(\overline{COCH_2CH_2O})$ $Mn_2(CO)_9(\overline{COCH_2CH_2O})$, $Re_2(CO)_9(\overline{COCH_2CH_2O})$, $Re_2(CO)_8(\overline{COCH_2CH_2O})_2$ and $Ru_3(CO)_{10}(\overline{COCH_2CH_2O})_2$. Structures, some reactions, and the mechanism of formation of these new complexes will be discussed.

1. M. M. Singh and R. J. Angelici, Angew. Chem. Int. Ed. Engl. 1983, 22, 163.



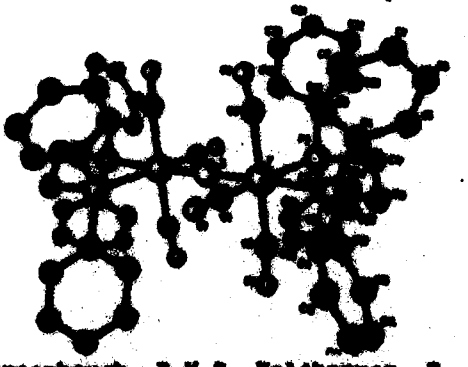
μ_2-E[V(CO)$_3$dppe]$_2$, E = S, Se, Te, COMPLEXES WITH LINEAR VEV MULTIPLE BONDS

Erwin Weiss, Jan Schiemann and Peter Hübener
Universität Hamburg, Institut für Anorganische und Angewandte Chemie, Martin-Luther-King-Platz 6, D-2000 Hamburg, Germany (F.R.G.)

Several transition metal-main group element compounds containing multiple bonds have been known in recent years, e.g. $(\eta^5\text{-}C_5H_5)(CO)_2Cr{\equiv}Cr(CO)_2(\eta^5\text{-}C_5H_5)$ [1], $(\eta^5\text{-}C_5H_4Me)(CO)_2Mn{\equiv}Ge{\equiv}Mn(CO)_2(\eta^5\text{-}C_5H_4Me)$ and $[(\eta^5C_5H_4Me)Mn(CO)_2]_3$ [2]. The synthesis of vanadium-chalcogen compounds with multiple bonds in linear VEV groups (E = S, Se, Te) has now been accomplished. The sulfur compound 1 has been prepared via routes (a) and (b) and the selenium (2) and tellurium (3) compounds so far only via route (a).

$$Na[V(CO)_4dppe] \xrightarrow{Na_2EO_3/H^+} \mathbf{1}, \mathbf{2}, \mathbf{3}\ (E = S, Se, Te) \quad (a)$$
$$Na[V(CO)_4dppe] \xrightarrow{Na_2S/H^+} \mathbf{1} \quad (b)$$

An X-ray structure analysis of 1 reveals a centrosymmetric molecule with very short V-S distances (217.2 pm). The V-S bond order is assumed to be between 2 and 3. This is consistent with the occurence of rotamers in solution as observed by IR.



1

[1] T.J. Greenhough, B.W.S. Kolthammer, P. Legzdins, J. Trotter, Inorg.Chem. 18(1979)3543
[2] W. Gädo, H. Weiss, J.Organomet.Chem. 213(1981)451.

THE METAL LIGAND BOND IN VARIOUS COORDINATE COMPOUNDS OF SILICON AND PHOSPHORUS, A STUDY BASED ON X-RAY EMISSION SPECTRA

M.A. Mohammed Al-Kadier

Department of Chemistry, College of Education, University of Mosul, Mosul, Iraq.

A series of penta and hexacoordinate silicon derivatives are prepared from a series of aliphatic diols and 4-tert-butyl catechol.

The $SiK_{\beta1,3}$ X-ray emission spectra from these complexes have been recorded using Philips PW 1410 X-ray fluorescence spectrometer. The results are compared with the corresponding X-ray emission spectra from tetracoordinate silicon compounds $Si(OC_2H_5)_4$[1] and silica, and are interpreted using a simple molecular orbital model[2].

With saturated ligands the main $SiK_{\beta1,3}$ peak shows no splitting, whereas in the case of unsaturated ligands, the main peak is split into two, reflecting the presence of both σ- and π-character in the Si-ligand bond.

This study is also extended to cover some of the phosphorus compounds, $(C_6H_5)_3P$ and $(C_6H_5)_3PO$ for which $PK_{\beta1,3}$ X-ray emission spectra are measured.

A peak splitting is observed in both $PK_{\beta1,3}$ spectra, confirming the involvement of the ligand π-orbitals in the P-ligand bond.

It is found that neither the overall charge of the complex nor the coordination number of the silicon or the phosphorus had any observable effect upon the spectra.

1. Al-Kadier, M.A.M., Thesis, University of London, 1978.
2. Urch, D.S., *Adv. X-ray Analysis*, *14*, 250, 1971.

NEW COMPOUNDS OF RHODIUM (II) WITH METAL-METAL BOND

A.P. Kotchetkova, L.B. Sveshnikova, V.M. Stepanovitch

N.S. Kurnakov Inst. of General and Inorg. Chem. Academy of Sciences, USSR, II707I Moscow, Leninsky prospect 3I

The information about the synthesis and properties of compounds with Rh (II) - Rh (II) bond and with various terminal and bridging ligands, including "lantern" type, continue to be comparatively scarce.

The reduction of the complex Rh (III), containing in the inner sphere strong-bonded bidentate ligand (for example, bipyridine), leads to formation of $[Rh_2X_4(L_2)]$



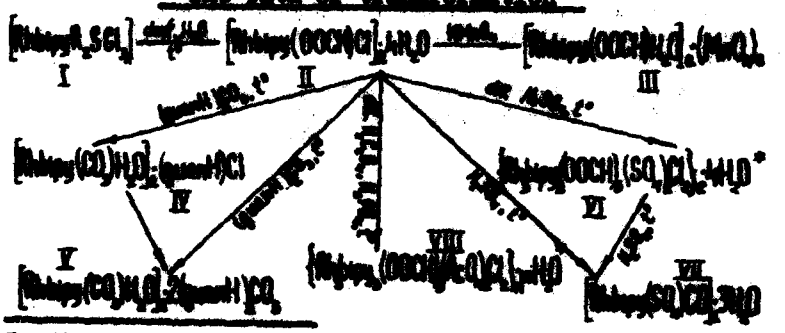
X= OOCH

A= bipy

L= Cl

By the substitution of the formic groups were obtained the other compounds of the same type.

The path of transformation



R= CH_3-, C_2H_5-; dmf= dimethylformamide; bipy= bipyridine; guan= guanidine; ACO_4= $C_2O_4^{2-}$, HPO_4^{2-} bipy=bipyH

Interaction II with dilute H_2SO_4, H_3PO_4 and $H_2C_2O_4$ leads to polymerization of binuclear fragments with formation of polymers VI, VIII.

Investigation results lead to conclusion about presence of Rh (II) - Rh (II) bond in synthesized complexes and about "semi-lantern" structure of the compound II - VIII.

I. A.P. Kotchetkova, L.B. Sveshnikova, V.M. Stepanovitch and V.I. Sokol, Coord. Chem. 1982, 8, 389

THp53-10

DISTORTIONAL ISOMERISM IN OXO AND NITRIDO COMPLEXES

Barry L. Haymore[a], William A. Goddard III[b] and Janet N. Allison.[b]

a. Monsanto Company, Corporate Research Laboratory, St. Louis, Missouri 63167; b. California Institute of Technology, Noyes Laboratory of Chemical Physics, Pasadena, California 91125.

The low temperature (-160°C) structure of the unstable green isomer of $MoOCl_2(PMe_2Ph)_3$ has been determined. Although the structure is disordered, the Mo-O distance in one model refined (R_w=0.055) to a value of 1.80(2)Å which closely resembles the unusually long Mo-O bond length of 1.801(9)Å in the stable green complex $MoOCl_2(PEt_2Ph)_3$[1] and contrasts the more normal Mo-O bond length (1.676(7)Å) in the stable blue isomer of $MoOCl_2(PMe_2Ph)_3$.[2]

Short and long M-O bonds have also been documented[3] for $[MoO(OH_2)(CN)_4]^{2-}$, and long M-N bonds in certain rhenium and molybdenum nitrido complexes suggest that nitrido complexes behave similarly. This unusual type of isomerism, though sterically controlled, is new and fundamentally different from ordinary steric distortions. The underlying factors governing the bonding in these isomers will be discussed with reference to oxo, nitrido and imido ligands.

1. L. Manojlovic-Muir and K. W. Muir, J. Chem. Soc., Dalton Trans., 1972, 686.
2. L. Manojlovic-Muir, J. Chem. Soc. A, 1971, 2796.
3. V. K. Wieghardt, G. Backes-Dahmann and W. Holzbach, Z. Anorg. Allg. Chem., 1983, 499, 44.

A SPONTANEOUS REDUCTION OF $[Ta_6Cl_{12}]^{4+}$ TO $[Ta_6Cl_{12}]^{3+}$ IN ACID MEDIA; PREPARATION, PROPERTIES AND CRYSTAL STRUCTURE OF $(CH_3)_4N[(Ta_6Cl_{12})(H_2O)_6]Br_4$

Nevenka Brničević and Živa Ružić-Toroš
"Rudjer Bošković" Institute, Zagreb, Croatia, Yugoslavia

The treatment of air oxidized methanol-water alkaline solutions[1] of $[Ta_6Cl_{12}]^{4+}$ with concentrated HCl or HBr in the presence of tetramethylammonium or tetraethylammonium cations results in spontaneous, unexpected, reduction of the cluster unit $[Ta_6Cl_{12}]^{4+}$ to the unit $[Ta_6Cl_{12}]^{3+}$. An isomorphous, paramagnetic series of 3+ clusters, $M[(Ta_6Cl_{12})(H_2O)_6]X_4$ with $M=(CH_3)_4N^+$, $(C_2H_5)_4N^+$; X=Cl, Br, have been prepared. At higher concentrations of acids the 4+ clusters $[Ta_6Cl_{12}]X_4.6H_2O$ have been isolated. Aspects of reduction of the $[Ta_6Cl_{12}]^{4+}$ unit in acid media are discussed.

The structure of $(CH_3)_4N[(Ta_6Cl_{12})(H_2O)_6]Br_4$ has been determined by three-dimensional single crystal X-ray analysis. The compound crystallizes in cubic space group Fd3m with the unit cell dimension a=19.926(5)Å. The structure has been determined by Patterson and Fourier methods and refined by full-matrix least-squaers to R=0.042. The structure is composed of discrete $[(Ta_6Cl_{12})(H_2O)_6]$ octahedra, $(CH_3)_4N^+$ and Br^- ions. The Ta-Ta distance is 2.9054(8)Å. The Ta-Cl and Ta-O distances are 2.449(3) and 2.22(2)Å respectively.

1. N. Brničević, Š. Mesarić and H. Schäfer, Croat. Chem. Acta, in press.

SYNTHETIC AND STRUCTURAL STUDIES ON ORGANOIMIDOTUNGSTEN COMPLEXES

Donald C. Bradley, R. John Errington, Michael B. Hursthouse and Richard L. Short.

Department of Chemistry, Queen Mary College, Mile End Road, London E1 4NS, U.K.

Recently we reported the synthesis and characterization of $[W_3(NPh)_3(\mu_2\text{-}O)_3Me_6(PMe_3)_3]$[1], $[W(NR)Cl_4(THF)]$[2], $[W(NR)Cl_3(L)_2]$[2], $[W(NR)Cl_2(L)_3]$[2] and $[W_2(NBu^t)_2(\mu_2\text{-}NPh)_2Cl_4(NH_2Bu^t)_2]$[3] from reactions involving tetrachloro-organoimidotungsten(VI) complexes $[W(NR)Cl_4]$ A. Further work has shown that A reacts with chloride giving the octahedral anion $[W(NR)Cl_5]^-$ as the triphenylbenzylphosphonium salt B (R = p-tolyl. In the presence of a reducing agent (Na/Hg) the binuclear tungsten(V) anion $[W_2(NR)_2Cl_7]^-$ was isolated as the tpbp-salt C (R = Et, Ph). An X-ray structure determination of C (R = Ph) showed a metal-metal bonded (W-W = 2.835Å) μ_3-trichloro-bridged dimer with terminal phenylimido groups. The trinuclear W(VI) anions $[W_3(NBu^t)_3(\mu_2\text{-}NR)_3Cl_7]^-$ have been obtained as tpbp-salts D (R = Ph, p-tolyl) by treatment of the dimeric $[W_2(NBu^t)_2(NR)_2Cl_4(NH_2Bu^t)_2]$ complexes with tpbp-chloride. The tert.-butylammonium salt of D (R = Ph) was also isolated from the reaction of $W(NPh)Cl_4$ with $Bu^tNH(SiMe_3)$. Preliminary X-ray studies have shown the trinuclear anions to contain a triple-bridging chloride, μ_2-arylimido groups and terminal tert.-butylimido groups. In attempting to prepare a W(III) organoimido compound from the reaction of WCl_4 with Bu^tNH_2 the novel dimeric tert.-butylamido compound $[W_2Cl_4(NHBu^t)_2NH_2Bu^t)_2]$ E was isolated. The crystal structure showed that the unbridged tungsten atoms are strongly bonded (W-W = 2.29Å). Spectroscopic and X-ray crystallographic data on these and other new compounds currently under investigation will be presented.

1. D.C. Bradley, M.B. Hursthouse, K.M. Abdul Malik, and A.J. Nielson, J.Chem.Soc.Chem.Commun., 1981, 103.

2. D.C. Bradley, M.B. Hursthouse, K.M. Abdul Malik, A.J. Nielson and R.L. Short, J.Chem.Soc.Dalton Trans., 1983, 2631.

3. D.C. Bradley, R.J. Errington, M.B. Hursthouse, A.J. Nielson and R.L. Short, Polyhedron, 1983, 2, 849.

SYNTHESIS, ELECTROCHEMISTRY AND SPECTROSCOPIC STUDY OF DIRHODIUM(II) COMPLEXES WITH AMIDATO BRIDGING LIGANDS

J.L. Bear, R. Lifsey, M. Ahsan, M. Chavan, and K.M. Kadish

Department of Chemistry, University of Houston, TX 77004 USA

Studies involving the effect of various bridging ions on the properties of dirhodium(II) complexes have been in general confined to bridging ligands with only oxygen donor atoms such as CO_3^{2-}, SO_4^{2-} and $RCOO^-$. With these types of ligands it is difficult to find bridging groups which increase the electron density on the dirhodium(II) moiety beyond that produced by the pivalate ion. Also in these complexes the equatorial bonding symmetry around each rhodium is always the same. However, the situation is quite different for amidato bridged dirhodium(II) complexes with respect to both the σ and π donor ability of the bridging ligand and equatorial bonding symmetry.

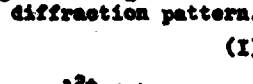
Dirhodium(II) complexes of the general formula $[Rh_2(OOCCH_3)]_{4-n}(RNOCR')_n$ with n=1 to 4, are obtained from the reaction of $Rh_2(OOCCH_3)_4$ with amides. Several geometric isomers of the different substitution products have been isolated. The number of isomers produced for each of the substitution products depends on the amide substituents R and R'. The potentials for the redox reactions of $Rh_2(Ac)_{4-n}(RNOCR')_n$ and λ_{max} of the bands in the visible spectra show sensitivity to the number of amidato ligands, the substituents R and R', and the nature of the axial ligands. Potentials were measured using cyclic voltammetry and electrode processes were characterized by spectroelectrochemistry and EPR. With the more basic amidato ligands, two reversible one electron oxidations were observed for complexes where n = 3 and 4. This is unlike the tetracarboxylato bridged dimer which shows only a single one electron oxidation at a much higher potential. The amidato bridged complexes appear to be better π donors than the corresponding carboxylato complexes with respect to their axial bonding characteristics and react readily with CO and NO to form adducts. These adducts were characterized by UV-visible, IR, and EPR spectroscopy as well as by electrochemical techniques.

GENERATION OF S,S BRIDGED $\{W_2^{V}O_2S_2\}^{2+}$ MOIETY DIRECTLY FROM WO_4^{2-}: SYNTHESIS OF HITHERTO UNKNOWN $[W_2O_2S_2(S_2)_2]^{2-}$ AND $[W_2O_2S_2(dtc)_2]$ (dtc = diethyldithiocarbamate anion) COMPLEXES

R.G. Bhattacharyya and A. Rai Chaudhuri
Department of Chemistry, Jadavpur University, Calcutta 700032, India.

Molybdenum and tungsten, the 4d and 5d congeners of the subgroup VI elements, have much of a common chemistry, but, while interactions of NH_2OH or S_x^{2-} ion with MoO_4^{2-} gave way to a rich Molybdenum-nitrosyl or Molybdenum-sulphur Chemistry (including Mo-S clusters) respectively, this area in case of tungsten is totally undeveloped. The basic reason, of course, is the very unfavourable redox potential of W^{VI}-W^{V} couple (compared to Mo^{VI}-Mo^{V}, where it is quite favourable), so that the potential generated by the oxidative degradation of NH_2OH or the oxidative reaction, viz., $S_x^{2-} \rightarrow xS+2e$, is not sufficient to reduce WO_4^{2-} to a suitable tungsten(V) (possibly WO^{3+}) species which may be the initial and necessary step for the above mentioned reactions.

Herein is made an inaugural report of the generation of the S,S bridged $\{W_2O_2S_2\}^{2+}$ moiety by firstly reducing the WO_4^{2-} to the W(V) stage using NCS^- in acidic medium[1] and then treating the green solution with polysulfide ion (S_x^{2-}). Addition of large cations on the above solution precipitates the species $R_2[W_2O_2S_2(S_2)_2]$ [R=Me_4N (1), Et_4N (2), n-Bu_4N (3), Ph_4P (4), Ph_3MeP (5) and Ph_4As (6)], which is the only example of a complex where W(V) (or, in any oxidation state) is linked with a S_2^{2-} ligand. (1) may be considered to be isostructural with the corresponding Mo analogue[2] as is evident by comparing their X-ray powder diffraction pattern.

(I) 

That $\{W_2O_2S_2\}^{2+}$ (I) is the fundamental building block of these types of complexes is evident by reacting the polysulfide treated W(V) solution with $NaEt_2dtc.3H_2O$, instead of the counter ions when neutral and dimeric complex $[W_2O_2S_2(dtc)_2]$ (7) also isostructural with the Mo analogue[3] could be obtained. The infrared spectra of the $[W_2O_2S_2(S_2)_2]^{2-}$ as well as that of $[W_2O_2S_2(dtc)_2]$ are almost superimposable with their respective Mo analogue.

The common feature of the RAS of (1)-(6) as well as that of (7) is a shoulder at ca 300 nm which may be due to $d(W) \rightarrow \pi^*(S)_2$ transition and an unique band at 430 nm in (7) may be due to $d(W) \rightarrow S_2^{\pi^*}$ transition. The observed diamagnetism indicates that the complexes contain a single W-W bond.

1. H. Funk and H. Böhland, Z. Anorg. Allg. Chem. 1962, 318, 169; R.G. Bhattacharyya, unpublished work.
2. W. Clegg, N. Mohan, A. Müller, A. Neumann, W. Rittner and G.M. Sheldrick, Inorg. Chem. 1980, 19, 2066.
3. A. Müller, R.G. Bhattacharyya, N. Mohan and B. Pfefferkorn, Z. Anorg. Allg. Chem. 1979, 454, 118.

TRINUCLEAR TRANSITION METAL COMPOUNDS, CONTAINING TRIAZOLES AND SMALL ANIONS AS BRIDGING LIGANDS

Frits J. Rietmeijer, Adrianus J. den Hartog, Gerard A. van Albada, Jaap G. Haasnoot and Jan Reedijk

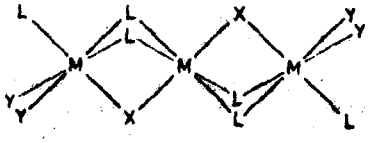
Department of Chemistry, State University Leiden, Gorlaeus Laboratories, P.O. Box 9502, 2300 RA Leiden, the Netherlands

Reports on 4-alkyl substituted 1,2,4-triazoles show a preference of these ligands to form polynuclear metal compounds with triple bidentate triazole bridges[1].

With 3,5-dialkyl subatituted triazoles steric reasons apparently prevent the ligands from triple bridging, producing structures with two 1,2-coordinating ligands and small anions (F^-, NCS^-, N_3^-).

Ligands used in the present study are 3,4,5-trimethyl-1,2,4-triazole (L1), 3,5-dimethyl-4-amino-1,2,4-triazole (L2) and 3,5-diethyl-1,2,4-triazole (L3). As a source of metal ions, mixtures of metal salts were used containing at least one small anion. As an example, L1 and mixture of CuF_2 and $Cu(BF_4)_2$ dissolved in ethanol gave $Cu_3F_2(L1)_8(BF_4)_4$.

Other compounds studied are for example: $Cu_3F_2(L2)_8(CF_3SO_3)_4$, $Co_3F_2(L3)_6(NCS)_4$ and $Ni_3(NCS)_2(L3)_6(NCS)_4$. This last compound has terminal, as well as the uncommon N-bridging thiocyanate. The structure is schematically shown in the figure.



Schematic structure of the triazole compounds L = ligand, X = bridging anion, F^-, NCS^- or N_3^-. Y = terminal anion (NCS) or ligand (L).

The X-ray structures of some of these compounds will be described and discussed in conjunction with spectroscopic and magnetic data. The magnetic exchange interactions between the metal atoms are small, but significant. The manganese, cobalt and copper compounds are antiferromagnetically coupled, but - surprisingly - the nickel tripers are ferromagnetic.

1. G. Vos, R.A. le Fèbre, R.A.G. de Graaff, J.G. Haasnoot and J. Reedijk, J. Am Chem. Soc. 105 (1983), 1682, and references cited therein.

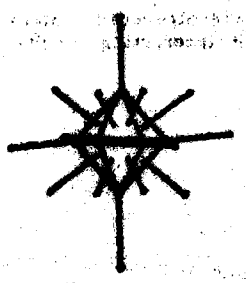
THE STRUCTURES OF TWO TETRANUCLEAR[illegible]

Thomas C. Zietlow, Harry B. Gray and William P. Schaefer

California Institute of Technology, Division of Chemistry and Chemical Engineering, Pasadena, California, USA 91125

Many oxidation-reduction reactions of great industrial or biological significance involve the transfer of 2, 4 or more electrons in one step. It is possible to model some of these reactions using metal cluster complexes as a source or sink for electrons. We have been particularly interested in clusters that can participate in photochemical energy storage reactions without requiring relay molecules or separate catalysts. One class of complexes that we have identified as having attractive excited state properties, i.e., having a geometrically stable excited state that is a better oxidant or reductant than the ground state, has the t_{2g}^6 electronic configuration $(d^6)_6$ and is exemplified by $Mo_6Cl_{14}^{2-}$ or W_6Br_{14}.

Simple theoretical considerations suggest that the excited state of these M_6X_{14} ions should resemble the ground state of an $M_6X_{14}^-$ anion. In order to test this conjecture, as well as to provide a framework for interpreting the electronic spectra of these ions, we have determined the crystal structures of compounds containing the W_6Br_{14} anion and dianion. Both are highly regular octahedral metal clusters, with 6 axially and 8 facially coordinated bromide atoms. The anion has a slightly enlarged tungsten octahedron with slightly shorter W-Br (axial) bonds, and shows marginally larger deviations from regularity. EPR experiments on the anion at 4 K show a significant distortion that is not apparent at room temperature with X-rays. The anion is a powerful oxidizing agent and may be useful in photochemical water-splitting processes.



$W_6Br_{14}^{2-}$ and $W_6Br_{14}^-$

	Bond Distances (Å)	
	$W_6Br_{14}^{2-}$	$W_6Br_{14}^-$
W-W	2.624(7)	2.649(9)
W-W'	3.716(14)	3.747(11)
W-Br (axial)	2.508(4)	2.539(11)
W-Br (facial)	2.630(10)	2.613(10)

HETEROBIMETALLIC ALKOXIDES: MODEL COMPOUNDS FOR MIXED METAL OXIDES

Nemi C. Jain* and Gyanendra K. Parashar

Department of Chemistry, University of Delhi, Delhi 110007, India. *Present address: University of Virginia, Charlottesville, VA.

Metal alkoxides have been proposed and thought to act as models for metal oxides, which provide the most versatile class of heterogeneous catalysts in a large number of organic and organometallic reactions. Comparing metal oxides with mixed metal oxides, we believe that there may be important contributions in the later system from two or more different metal atoms acting collectively to bring about activation that wouldn't be possible in the former case. It is with this view, attempts have been made to develop models for mixed metal oxides by synthesizing new compounds of the type $MM'_x(OR)_y$; an analysis of the published and unpublished observations on the properties of heterobimetallic isopropoxides suggests that these complexes have a covalent nature and thus can be used to obtain mixed metal oxides, $MM'_xO_{y/2}$, in pure state.

In contrast to non-hydrocarbon soluble, polymeric and non-volatile nature of metal isopropoxides (e.g., the transition metals), some of the heterobimetallic isopropoxides have shown quite remarkable properties. One of such exciting examples is cited here: It is now well established that aluminum isopropoxide is a tetramer in solid state while chromium(III), whose size (0.98Å) is close to aluminum(III) (0.53Å), forms a non-volatile and completely insoluble (in organic solvents) isopropoxide, which has a polymeric structure, $Cr(3+)O_6$. However, heterobimetallic isopropoxide, $CrAl_3(OPr^i)_{12}$, is a green volatile liquid which is soluble in organic solvents. Synthesis of this versatile complex stimulated the synthesis of a large number of such derivatives of bi-, tri- and tetravalent metals (e.g., Mn(II), Fe(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II), Be(II), Sn(II), $Bu^nSn(IV)$, Zr(IV)). These compounds are, in general, a highly reactive groups of complexes; common reactions involving substrates with acidic hydrogens include hydrolysis with H_2O, alcoholysis with other alcohols and substitution reactions with β-diketonates.

We do like to mention that attempts to synthesize complexes of the type $LiCr(OR)_{3+x}$, $Li_xM(OR)_{3+x}$, $NaAs(OR)_6$, $M'Sb(OR)_6$ (where R=Me, Et or Pr^i; M'=Li, Na or K), $SbAl_3(OPr^i)_{18}$ etc., however, couldn't be materialized.

Finally it should be emphasized that heterotrimetallic alkoxides, whose chemistry is still unknown, may provide interesting results; this point is clearly worthy of investigation.

SYNTHESIS AND PROPERTIES OF THE DINUCLEAR HALOGENOFORMATE Re(III) COMPLEXES

Telman Kh. Kurbanov, Ada S. Kotelnicova and Nasib S. Osmanov

Institute of Inorganic and Physical Chemistry, Narimanov Prospect 29, Baku - 370143, USSR.

In this report the result of the synthesis and properties of a number of neutral types of halogenoformate Re(III) complexes $Re_2X_4(HCOO)_2L_2$, $Re_2X_6(HCOO)_2$ and $Re_2X_5(HCOO)_4$, where X=Cl, Br and L-organic bases, are presented. The chemical, magnetic, X-ray structure analysis, IR and Raman spectroscopies were applied and the multiple Re-Re bond in these compounds was shown.

The reactions of $(NH_4)_2Re_2Cl_6(HCOO)_2$ with aliphatic and aromatic amines, DPFA, DPA and others resulted in formation of the compounds with protonated amines in outersphere or neutral type complexes with the axial substituents. The transformation of the diformate complexes Re(III) to each other (neutral ⇔ ionic) are investigated.

DPA interacts with $(NH_4)_2Re_2Cl_6(HCOO)_2$ in formic acid and transforms to DPFA and neutral type complex with DPFA molecules in axial positions are formed. The structure of $Re_2Cl_4(HCOO)_2(DPFA)_2$ is investigated by X-ray analysis and different values of Re-O axial bonds (2.38(2)Å and 2.45(2)Å) are established. It was the first report[1] indicating the different bond lengths in dimeric carboxylate complexes of VI and VII groups metals.

The investigation of the reaction between halogenoformate Re(III) complexes and the mixture of HCOOH and HBr acids indicated disproportionation of Re_2^{6+}(III) to Re(I) and Re(IV), which is the first observation for the compounds with the Re_2^{6+} coordination center.

The temperature behavior of the prepared compounds has been investigated and the formation of the pentacarbonylhalides and rhenium dioxide was shown. The amount of the groups in complexes increases from di to tetraformate Re(III). At the temperatures higher than 500°C the pure metallic rhenium is observed.

In addition we note the different properties of the halogenoformate complexes Re(III) and other halogenocarboxylatodirhenium(III) complexes as the original group of the complexes with multiple metal-metal bond.

1. Kuznetsov, P.A., M.D. Surazhskaya, T.B. Larina, A.S. Kotelnicova, and N.S. Osmanov, *Coord. Chem. (Russian)*, 5, 1868, 1979.

THERMAL DECOMPOSITION PROCESS STUDIES OF HETERONUCLEAR MIXED-VALENT μ_3-OXOCARBOXILATES OF SOME 3d-ELEMENTS ON THE BASIS OF IRON

K. M. Yakubov, V.A. Logvinenko, T.A. Zhemchuzhnikova, Sh.Kh. Abdullaev, and G.V. Gavrilova

Tadjik State University, Lenin Street, 17, Dushanbe, USSR, 734018

Investigation results on thermal decomposition process study of heteronuclear mixed-valent acetate μ_3-oxoclusters with the general formula:

$$Fe_2^{III}M^{II}O(CH_3COO)_6(H_2O)_3\ nH_2O\ ,$$

where M=Mn, Fe, Co, Ni and n=1 or 2 are presented in the report.

Noted compound derivatographic investigation carried out in temperature interval 20-800°C in ceramic crucibles have proved that heteronuclear μ_3-oxoacetates thermolysis process consists of a few steps.

On the basis of preparative analysis, mass-spectrometry of solid and gaseous complex decomposition products, it has been determined that the first step, that with endothermal effect, is combined with supersphere water molecule loss. The second step is also endothermal, and corresponds to withdrawal process of two coordinated H_2O molecules and CH_3COOH molecule. The next steps, largely, with exothermal effects should be related not only to the rest CH_3COOH ligand splitting from the complex, but to the acid molecule destruction.

The second, $Fe_2^{III}M^{II}O(CH_3COO)_6(H_2O)_3 \xrightarrow{110-170°C} Fe_2^{III}M^{II}O(CH_3COO)_5OH+2H_2O+CH_3COOH$ thermal destruction step has been studied in detail. Its parameters are shown to be more sensitive to variated heterometal M nature. Mass-spectrometrically measured temperature H_2O and CH_3COOH concentration dependences in gaseous phase turned out to be a sophism. Therefore, for this considered thermolysis step, gross gas addition curves obtained on running reactor with conductivity detector were used for kinetic parameters (E and lg A) calculation.

Mathematical gas emission data processing by /1/ programme on ECM has shown that the curves are described by comprehensive sphere equation, and activation energy and lg A of the process are increasing in the series: Fe Mn Co Ni.

1. Nikolaev, A.V., V.A. Logvinenko, Y. Shestak, V. Shilvera, *Dokl AN SSSR*, 232, 148, 1976.

COORDINATION IN THE SOLID STATE, ESPECIALLY IN METAL-METAL BONDED STRUCTURES

John D. Corbett

Department of Chemistry and Ames Laboratory-DOE, Iowa State University, Ames, Iowa 50011

Coordination of nonmetals to metals is a significant component in the structures of a wide variety of nonmolecular binary compounds of the early transition metals. The structures often represent not just coulombically advantageous ways to pack anions about cations but also substantial covalency and specific coordination. The nature of the bonding in traditional four- and six-coordinate environments characteristic of close-packed systems often proves to be the most ambiguous. On the other hand, the perseverance of unusual coordination polyhedra, i.e., trigonal prismatic, is clear evidence of strong interactions. Some of the most interesting examples exhibit an admixture of ionic, covalent and metallic (delocalized) bonding, and most examples will be drawn from this class.

Theoretical evidence for covalency has been well documented by band calculations, e.g., for ScS, TiO and many hydrides. XPS and UPS results for the valence regions of hydrides such as YH_2 provide direct experimental proof for metal-hydrogen covalency. Interstitial nonmetals in metals are presumably similar.

The early 4d, 5d, 4f and 5f elements exhibit a nontraditional behavior on reduction in that the added electrons are usually not localized on specific metal atoms but delocalized in a cluster or into a one-, two- or three-dimensional metal-metal bonding. Metal-nonmetal distances in these remain close to those in the normal-valent compound since the added electrons are not screening. Although the coordination role of the nonmetal is sometimes similar, phosphides, etc., in one class, sometimes quite complex, are relatively simple, elements of the essential coordination polyhedra about the metal in the normal-valent solid being present in the reduced. In some cases, the reduced phases, such as [illegible] or clusters exhibit very specific [illegible] for the [illegible] Normally, the [illegible] bonding [illegible] of rods or [illegible] as the [illegible] of the [illegible] [illegible] to [illegible] the [illegible] [illegible] [illegible]

SYNTHESIS OF HYDRIDE-BRIDGED HETEROPOLYMETALLIC TRANSITION METAL-LANTHANIDE AND YTTRIUM COMPLEXES

William J. Evans and Timothy P. Hanusa

University of California, Irvine, Department of Chemistry, Irvine, California 92717, USA

In the course of investigating the first crystallographically-characterized organometallic lanthanide and yttrium hydrides $[(C_5H_4R)_2LnH(THF)]_2$ (R=H, CH_3; Ln=La, Nd, Y, Yb; J. Am. Chem. Soc., 1982, 104, 2008), we discovered an unusual class of trimetallic tetrahydrides, $\{[(C_5H_5)_2Ln(\mu_2\text{-}H)]_3(\mu_3\text{-}H)\}^-$ (J. Am. Chem. Soc., 1982, 104, 2015). The μ_3-H in the trimers is in a unique metallic coordination environment in that it is both centered within and coplanar with the three metal atoms. Analysis of the possible mechanisms for formation of the trimetallic tetrahydrides suggests that species such as $(C_5H_5)_2LnH_2^-$ may be involved. Attack by $(C_5H_5)_2LnH_2^-$ on $[(C_5H_5)_2LnH(THF)]_2$ with the displacement of THF could readily generate the observed trimers.

These ideas have been tested using transition metal dihydrides, L_2MH_2, and these experiments have resulted in the synthesis of new heteropolymetallic species involving hydrogen bridges. The stability of the new complexes appears to be quite sensitive to the electronic and steric properties of the transition metal reagent. Thus, although $[(C_5H_4CH_3)_2YH(THF)]_2$ reacts rapidly at room temperature with $[(C_5H_4CH_3)_2ZrH_2]_2$ to generate the thermally-stable trimer $\{[(C_5H_4CH_3)_2Y(\mu_2\text{-}H)]_2[(C_5H_4CH_3)_2Zr(\mu_2\text{-}H)]\}(\mu_3\text{-}H)$, the yttrium dimer does not react with $(C_5H_5)(PPh_3)ZrH_2$ even at elevated temperatures and produces only tractable heterometallic species with $(PPh_3)_2ZrH_2$. The factors affecting the reactivity of yttrium and lanthanide hydride dimers with a variety of metal hydride reagents will be discussed.

DIVALENT LANTHANOID SYNTHESIS IN LIQUID AMMONIA

A. L. Wayda and J. L. Dye

AT&T Bell Laboratories, 600 Mountain Avenue, Murray Hill, New Jersey, USA 07974

R. D. Rogers

Northern Illinois University, DeKalb, Illinois, USA 60115

By the use of new vacuum line technology and rigorous handling techniques, exclusively divalent europium and ytterbium pentamethylcyclopentadienides can be prepared in high yield via the reaction of the respective metals in liquid ammonia with pentamethylcyclopentadiene (C_5Me_5H). Using this synthetic scheme, the unusual ammoniate $(\eta^5\text{-}C_5Me_5)_2Yb(NH_3)(OC_4H_8)$ has been isolated and crystallographically characterized. $(\eta^5\text{-}C_5Me_5)_2Yb(NH_3)(OC_4H_8)$ crystallizes in the orthorhombic space group $Pca2_1$ with unit cell dimensions $a = 22.877(5)$, $b = 15.488(3)$, $c = 11.018(3)$ Å and $D_{calc} = 1.33_8$ gm^{-3} for $Z = 8$. Least squares refinement resulted in a final R value of 0.069 based on 3150 independent observed reflections. There are two molecules in the asymmetric unit. One molecule exhibits disorder between the NH_3 and THF sites resulting in an overlap of the N and O positions, while the other shows disorder only of the THF ring. In the second molecule, ammonia is coordinated to the metal center via a Yb(2)-N bond length of 2.55(3) Å. The Yb(2)-O distances and average Yb(2)-C(Cp) bond lengths are 2.45(3) Å and 2.77(4) Å, respectively. The reaction chemistry of lanthanoid metal solutions with alcohols to yield well-characterized divalent alkoxides will also be presented.

ON THE CHEMISTRY OF TRIS(CYCLOPENTADIENYL)URANIUM(IV)TETRAPHENYL-BORATE AND OTHER f-ELEMENT COMPLEXES INVOLVING THE $B(C_6H_5)_4$-LIGAND

Kenan YÜnlÜ, HÜseyin Aslan and K. Dieter Fischer

Institut fÜr Anorganische und Angewandte Chemie der UniversitÄt Hamburg, Martin-Luther-King-Platz 6, D-2000 Hamburg 13, W.-Germany

Recently, the first example of a cationic $[Cp_3UX_2]^+$-system ($X = NCCH_3$[1]) of trigonal bipyramidal coordination has been verified and crystallographically confirmed, however, the homologous diaqua-complex ($X = H_2O$) could so far only be trapped outside an aqueous solution in the metastable solid $[Cp_3U(OH_2)_2]NO_3$[2]. While the attempted precipitation of other type B salts from aqueous solutions according to

$$Cp_3UCl \xrightarrow[NaX]{H_2O} Cp_3UY\downarrow \quad \text{or} \quad [Cp_3U(OH_2)_n]X\downarrow$$
$$\text{(A)} \qquad\qquad \text{(B)}$$

leads mainly to anhydrous type A systems (e.g. $X = BF_4^-$ or PF_6^-; $Y = F$), the novel type B representative 1 with $n \approx 12$ could be prepared with $X = B(C_6H_5)_4^-$. Alternatively, in the presence of CH_3CN, the rather stable compound $[Cp_3U(NCCH_3)_2][B(C_6H_5)_4]$ 2 is obtained.

The metastable species $[Cp_3U(H_2O)_{12}][B(C_6H_5)_4]$ readily loses H_2O to give the previously reported[3] complex $Cp_3UB(C_6H_5)_4$, 3. From this latter compound, $B(C_6H_5)_3$ may be liberated quantitatively in vacuo at about 100 °C. The brown product 4 appears to be analytically pure $Cp_3UC_6H_5$, although this complex is expected to undergo pyrolysis at elevated temperatures.

Complex 3 is most probably not a genuine salt, but, according to its NIR/VIS-spectrum, a pseudotetrahedral Cp_3UX-derivative in which the $B(C_6H_5)_4$-ligand is bonded to the uranium ion via one or more C-atoms of a C_6H_5-group. The same argument holds for the previously reported organouranium polymer $[U[B(C_6H_5)_4]_4)^3$. The reaction pattern: 3 → 4 + $B(C_6H_5)_3$ appears to be exemplaric for the behaviour of a number of other $R_nMB(C_6H_5)_4$-systems (e.g. M = U, Yb, Zr, Hf, Sn; R = Cp or alkyl).

1. G. Bombieri, F. Benetollo, R. Kliehne and K.D. Fischer, J. Chem. Soc. Dalton Trans. 1983, 1115.
2. K.D. Fischer, H. Kliehne and G.R. Siemel, J. Organomet. Chem. 1982, 228, 99.
3. H. Bornberger, R. Kienze and B. Kanellakopulos, Inorg. Nucl. Chem. Lett. 1978, 14, 319.

THE CHEMISTRY OF A URANIUM-CARBON MULTIPLE BOND

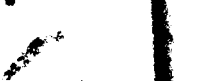
Roger E. Cramer, Kelvin Higa, K. Panchanatheswaran and John W. Gilje

University of Hawaii, 2545 The Mall, Honolulu, Hawaii, USA 96822

Reaction of Cp_3UCl with a lithiated phosphoylide $Li(CH_2)(CH_2)PR_2$ produces $Cp_3U{-}CHP(CH_2)R_2$ (I). The availability of two electron pairs on the carbon bound to both uranium and phosphorus suggests a possible uranium-carbon double bond, confirmed by the very short uranium-carbon distance, 2.29(3)Å.

In contrast to Fischer type carbene complexes which have an electrophilic carbon, I is a powerful nucleophile, even capable of nucleophilic displacement on CCl_2F_2.

Compound I also reacts with polar, unsaturated bonds, of molecules such as CO, RNC and RCN. Carbon monoxide inserts into the uranium-carbon multiple bond to produce



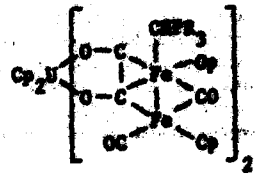
while RNC inserts to produce an analogous product

The nitrile MeCN inserts into the uranium-carbon



multiple bond to form $Cp_3U{-}N{=}C{=}C{-}PR_2$. In this compound the uranium-carbon bond length, 2.06(1)Å, suggests a uranium-nitrogen bond with substantial multiple bond character.

Compound I reacts with $[CpFe(CO)_2]_2$ to effect the coupling of bridging and terminal carbonyls to produce an $\eta^1{:}\eta^3$ allyl iron complex,



It also reacts with $CpMn(CO)_3$ to produce



which upon heating additionally produces a product which appears to be Cp_3UCN and produces a crystalline product whose structure shows it to be



In the reaction with $[CpFe(CO)_2]_2$ the oxygen seeking character of uranium has served to activate the CO's so that they can be coupled. In the reaction with $CpMn(CO)_3$ the strong oxygen-uranium bond has led to the complete removal of oxygen from CO and its replacement with a carbon to form an acetylide.

SYNTHESIS AND STRUCTURAL STUDIES OF METALLOCENES DERIVATIVES OF BIVALENT LANTHANIDES

Kurbanov T.Kh., Suleimanov G.Z., Beletskaya I.P.

The Institute of Inorganic and Physical Chemistry of the Academy of Sciences of the Azerbaijan SSR, Baku, USSR

It is known that certain lanthanides may yield various organic derivatives in a bivalent state. C- and B-carboranyl and bimetallic derivatives belong to the such classes of compound (1).

Continuation of the investigation in the area of synthesis and studies of the properties of organic derivatives of bivalent lanthanides was the extension of the reaction of $(C_5H_5)_2Hg$ with Ln^0 (2) to π-cyclopentadienyl mercury organic derivatives of the transition metals. Having mercury derivatives of ferrocene and cymantrene with Ln^0 (Ln=Sm,Eu,Yb) as an instance we have produced the first specimen of metallocenes derivatives of bivalent lanthanides



$M = Mn$, $L = 3CO$, $n = 1$, $m = 4(5)$; $M = Fe$,

$L = C_5H_5$, $n = 0$, $m = 4(5)$, $Ln = Sm, Eu, Yb$.

The nature of interaction of the atoms of Yb with a cyclopentadiene ring in the derivatives of ferrocene(Cymantrene)has been studied by the method of NMR-spectroscopy and it has been estimated that introduction of an atom of Yb into the cyclopentadiene ring in these derivatives resulted in change of the chemical shift of α-protons towards a weak field and that indicates electronoacceptor abilities of Yb.

1. H.Schumann, Proc. NATO, Adv.Study, Inst. Sogesta, Urbino, 1978,Dordrect, 1979, p.81.
2. G.Z. Suleimanov, L.F.Rybakova, A.Nuriev, T.Kh.Kurbanov, I.P.Beletskaya, J.Organometal.Chem., 235(1982) C.19.

THE BULKINESS OF X-LIGANDS IN THE SYNTHESIS OF Cp_2UX_2 SYSTEMS. THE REACTIVITY OF $Cp_2U(NEt_2)_2$ TOWARDS ALIPHATIC ALCOHOLS AND PHENOLS WITH DIFFERENT STERIC HYNDRANCES.

G. Paolucci(') , G. Rossetto(") , P. Zanella(") . and A. Berton(") .

(') Dipartimento di Chimica, Facolta di Chim. Ind.le, Università di Venezia, Calle Larga S.Marta 2372, Venezia, ITALY.

(") Istituto di Chimica e Tecnologia dei Radioelementi, Area di Ricerca C.N.R., Corso Stati Uniti, 35100 Padova, ITALY.

The reaction of aliphatic alcohols and phenols with Cp_3U-R systems has been reported[1] to produce mixtures of products, due to the substitution either of R or Cp groups by the reagents. In addition the possibility of obtaining stable Cp_2UX_2 derivatives, i.e. without any ligands redistribution, has been related to the bulkiness either of Cp'(Cp'= polysubstituted cyclopentadienyl)[2] or X[3] ligands. Moreover the reactivity of $Cp_2U(NEt_2)_2$ towards mono- and bi-functional thioalcohols and thiophenols has been briefly described[4].

In this communication we report the behaviour of $Cp_2U(NEt_2)_2$ towards aliphatic alcohols and phenols containing different steric hyndrances, and the synthetic approach to Cp_3U-OR or $Cp_2U(OR)_2$ derivatives.

$$Cp_2U(NEt_2)_2 + 2\ HO\text{-}R' \xrightarrow{R.T.} \underset{(I)}{Cp_2U(OR')_2} \longrightarrow \tfrac{1}{3}\ \underset{(II)}{Cp_3U\text{-}OR'} + \tfrac{1}{3}\ U(OR')_4$$

IIa , R' = C_2H_5

IIb , R' = i-C_3H_7

Ic and IIc , R' = t-C_4H_9

IId , R' = $-C(CH_3)(CH(CH_3)_2)-CH_2-CH=CH_2$

IIe , R' = phenyl

IIf , R' = 2-isopropyl-phenyl

Ig, R'=2,6-diisopropyl-phenyl

REFERENCES

1)T.J.Marks, A.M.Seyam, and J.R.Kolb, J.Am.Chem.Soc., 1973, 95, 5529; T.J.Marks and W.A.Natcher, J.Am.Chem.Soc., 1976, 98, 703.
2)T.J.Marks and R.D.Ernst in "Comprehensive Organometallic Chemistry" G.Wilkinson Ed., Pergamon Press, 1982, Vol.3.
3)G.Paolucci, P.Zanella, G.Rossetto and O.Traverso, Abstracts of XIth ICOMC, Atlanta, 1983, 24.
4)J.D.Jamerson and J.Takats, J.Organomet.Chem., 1974, 78, C23.

FRIDAY MORNING

EXPERIMENTAL PROBES OF ELECTRONIC MATRIX ELEMENT CONTRIBUTIONS TO ELECTRON TRANSFER REACTIONS

John F. Endicott and T. Ramasami

Department of Chemistry, Wayne State University, Detroit, Michigan, USA 48202

An important current problem in the dynamics of electron transfer systems is elucidation of factors contributing to reactivity patterns in weakly coupled systems. Assuming the donor acceptor interactions are sufficiently weak, the nuclear and electronic contributions may be treated separately in the reactant and product wave functions, and the rate constant becomes,

$$k = K_o \langle \psi_P^o | \hat{H}_C | \psi_R^o \rangle^2 \text{ (FC)}$$

where (FC) is the nuclear overlap or Franck-Condon term and

$$V = \langle \psi_P^o | \hat{H}_C | \psi_R^o \rangle$$

is the electronic matrix element. A number of lines of observation indicate that the first order coupling of the zero-order electronic wave functions can be described by the electron exchange operator ($H_C \sim H_{exch} + \ldots$).

Contributions of V^2 to reactivity patterns have been found to be largest in reactions of Co(III)-(II) couples; possibly owing to the large changes in coordination sphere bond length or/and in spin multiplicity that accompany electron transfer. The rates of several reactions of Co(III)-(II) couples have now been found sensitive to environmental C-T perturbations[1,2] and there are similar effects of low energy charge transfer states involving coordinated ligands. Systematic studies of $Co(sep)^{2+}$ reductions of $Co^{III}(NH_3)_5X$ and $Co^{III}(en)_2AmX$ complexes have shown that the reaction rates are increased by the following factors: (a) LMCT perturbations; (b) MLCT perturbations; (c) increasing similarity in energy of electronic states of reactants and products. The contributions of low energy CT excited states to the reaction rates are interpreted as "superexchange" contributions to the exchange interaction. The dependence on LF excited states (c) can be interpreted as a "resonance" effect in V, and relates to more adiabatic self-exchange than cross-reactions. Both effects couple nuclear and electronic coordinates.

There is also a tendency of V to decrease as the reactants are surrounded by bulkier ligands. This effect has been systematically probed in related energy transfer studies, for which $V = A\exp(-\alpha r_{DA})$ and $\alpha^{-1} \approx 1.8 \pm 0.4$ Å.[3]

1. J. F. Endicott, T. Ramasami, D. C. Gaswick, R. Tamilarasan, M. J. Heeg, G. R. Brubaker, and S. C. Pyke. J. Am. Chem. Soc. 1983, 105, 5301.
2. T. Ramasami and J. F. Endicott. Inorg. Chem. 1984, 23, 0000.
3. J. F. Endicott, R. Tamilarasan, G. R. Brubaker, and D. C. Gaswick. J. Phys. Chem. 1984, 88, 0000.

THE REDUCTION OF IRON(III) BINUCLEAR COMPLEXES

Abbas A. El-Awady,* Patricia C. Harrington and Ralph G. Wilkins

*Department of Chemistry, Western Illinois University, Macomb, Illinois 61455 and Department of Chemistry, New Mexico State University, Las Cruces, New Mexico 88003, USA

The reduction of iron(III) binuclear complexes of the type $L(H_2O)Fe^{III}OFe^{III}L(H_2O)^{n}$ is being currently explored. The ligands L represent 1,10-phenanthroline or 2,2'-dipyridyl (n=4+) and tetra-(4-sulphonatophenyl)porphine[1] (n=8-) and are abbreviated phen, bipy and TPPS respectively.

Electron reduction. All undergo rapid interaction with e_{aq}^- with rate constants k_1 shown in Table. These rates are observed at both 600 nm (electron loss) and 350 nm or 475 nm (gain of iron-electron adduct). The product of the electron reaction undergoes further changes in all cases, with first-order rate constants k_2 and k_3 slightly dependent on the concentrations of dimers used (10-100μM).

Ligand	pH	$k_1 M^{-1}s^{-1}$	k_2, s^{-1}	k_3, s^{-1}	$k_4 M^{-1}s^{-1}$	k_5, s^{-1}
phen	8.2	9×10^{10}	2.3×10^4	3.6×10^3	$> 10^6 (S_2O_4^{2-})$	0.17
dipy	8.2	9×10^{10}	1.5×10^4	1.4×10^3	$> 10^6 (S_2O_4^{2-})$	1.6
TPPS	9.0	1.1×10^{11}	2.2×10^4	2.1×10^3	$2.6 \times 10^8 (SO_2^-)$	0.013

The absorbance characteristics of the intermediate suggest that, at least with dipy, the e_{aq}^- reaction has produced a coordinated ligand radical which then in the k_2 and k_3 steps loses the electron to solution (to return to the original ion) or undergoes an intramolecular electron transfer resulting in $Fe(H_2O)_2(dipy)_2^{2+}$ and $Fe(H_2O)_2(dipy)_2^{3+}$. At the end of the k_3 step, the spectra of dipy and phen complexes are similar to the original. Pronounced differences between initial and final spectra are observed with TPPS.

Dithionite reduction. The kinetics were studied by stopped-flow. The very rapid reduction (k_4) was complete within mixing time for phen and dipy complexes but measurable for TPPS (SO_2^- reductant). This step was followed by first-order transformations (k_5, independent of dithionite concentration and observation wavelength). With phen and dipy, these are disproportionation of $FeL_2(H_2O)_2^{2+}$ to FeL_3^{2+} and Fe^{2+} which are the final products. With TPPS, the nature of the first-order transformation is uncertain. It is a single reaction with clean isosbestic points at 408 nm, 446 nm, 500 nm and 603 nm. The final product is the iron(II) binuclear complex, which is rapidly oxidized by O_2 to $Fe(CN)_6^{3-}$ to the original iron(III) binuclear complex. Stopped-flow rapid scan has been used to characterize the intermediates spectrally.

1. E.B. Fleischer, J.M. Palmer, T.S. Srivastava and A. Chatterjee, J. Am. Chem. Soc. 1971, 93, 3162.

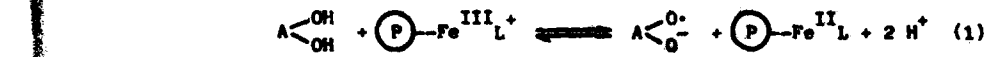
This work was supported by National Science Foundation and National Institutes of Health grants. Some of the experiments were performed at the Center for Fast Kinetics Research on the University of Texas at Austin (supported jointly by the Biotechnology Branch of the Division of Research Resources of NIH and UT at Austin).

STEREOSELECTIVE ELECTRON TRANSFER IN ASYMMETRIC COUPLES

B. Pispisa and A. Palleschi

Dipartimento di Chimica, Università di Napoli, 80134 Napoli and
Dipartimento di Chimica, Università di Roma, 00185 Roma (Italy)

Electron transfer (eq 1) from optically active catecholamines (L-dopa and L-adrenaline) to Iron(III) in $[Fe(tetpy)(OH)_2]^+$ complex ions anchored to poly(L-glutamate) (FeL) or poly(D-glutamate) (FeD) proceedes stereoselectively when extensive and possibly specific interactions between substrates molecules and the peptidic residues of the ordered polymer in the close environment of the active sites occur (tetpy = 2,2',2",2"'-quaterpyridyl). This ensures different steric constraints for the two diastreomeric precursor complexes, which affect differently the separation and orientation of the redox centers.



(1)

For instance, preliminary conformational calculations indicate that the closest catecholic-O·····Fe separation distance in the case of L-dopa is 5.0 Å in DL and 6.5 Å in LL adduct and that the redox centers in the two diastereoisomers experience a different mutual orientation as well. The specific rates for the intramolecular electron-transfer step (k_{et}), as obtained by kinetic data in the steady-state conditions, are $(1.9 \pm 0.2)\cdot10^{-2}$ and $(0.7 \pm 0.1)\cdot10^{-2}$ s^{-1}, respectively (25°, pH 7, Tris buffer 0.05 M), whereas the equilibrium constant for the formation of the precursor complexes is $K_{o_{DL}} = (1.95 \pm 0.61)\cdot10^3$ and $K_{o_{LL}} = (1.18 \pm 0.33)\cdot10^3$ M^{-1}. From the results, $k = k_{et}\cdot K_o = 37.1 \pm 12.0$ and 8.3 ± 2.5 $M^{-1}\cdot s^{-1}$, respectively [1], to be compared with $k_{obsDL} = 33.4 \pm 2.1$ and $k_{obsLL} = 7.9 \pm 0.4$ $M^{-1}\cdot s^{-1}$ (eq 1; 25°).

The estimated values of K_o by the potential energy data at the closest separation distance of the redox centers result to be in satisfactory agreement with the foregoing data. This gives further confidence in the potential functions used for conformational analysis. Similar findings were obtained with L-adrenaline [2].

The overall results shall be discussed in the light of a few general considerations concerning the stereoselective pathway in electron transfer processes between asymmetric redox species.

1) B.G.Gamsiek and A. Naim, J. Am. Chem. Soc., 1971, 93, 7347; A. Naim and N. Sutin, Inorg. Chem., 1976, 15, 476.
2) B. Pispisa and A. Palleschi, Inorg. Chim. Acta, 1983, 78(87), 97; B. Pispisa, M. Berteri and A. Farinella, Inorg. Chem., 1983, 22.

A UNIFIED TREATMENT FOR A VARIETY OF TYPES OF KINETIC BEHAVIOR OBSERVED IN RUTHENIUM(III)- TITANIUM(III) INNER-SPHERE ELECTRON-TRANSFER REACTIONS

Joseph E. Earley and Patrizia Barone
Department of Chemistry, Georgetown University,
Washington, D.C. 20057

Consider ET reactions that follow the general mechanism:

$$A_nRu(III)X_j^{+} + Ti(III)Y_i \xrightarrow{kK} A_nRu(III)X_jTi(III)Y_i^{+}$$

$$A_nRu(III)X_jTi(III)Y_i^{+} \rightleftharpoons A_nRu(III)X_jTi(III)Y_iOH + H^{+}$$

$$A_nRu(III)X_jTi(III)Y_iOH \xrightarrow{et} A_nRu(II)X_jTi(IV)Y_i'$$

$$A_nRu(II)X_jTi(IV)Y_i' \xrightarrow{k''} A_nRu(II)X + Ti(IV)^{+} + Y_i'$$

The steady-state rate law corresponding to this mechanism is:

$$k_{obs} = \frac{k_{et}\ k\ K\ K''\ [A_nRu(III)X_j]\ [Ti(III)]}{(k' + [H^{+}])\ (k'' + [Ti(III)])\ (k''' + [H^{+}] + [Ti(III)])}$$

(Where k', k'' and k''' are combinations of constants). Depending on the nature of the ligands A_n, X_j and Y_i one or another of the rate-law-terms would be expected to determine the observed kinetics. We have observed all the expected limiting cases.

If X has an open coordination-position and also a suitable pi-electron system (unless the stability of the intermediate is quite low, as it is when X is SSO_3^{2-}) then the rate of formation of the multinuclear complex is rate-determining (this is seen for carboxyato and thiocyanato-oxidants). Deprotonation and follow-up reactions of the products of ET are often significant, especially when overall free energy-change is small. Two classes of oxidants give rise to reactions with rates limited by ET. In one of these classes, the kinetics indicate formation of remarkably stable intermediates.

The pattern of reactivity we observe in the Ru(III)-Ti(III) is quite different from the pattern observed in other redox pairs. The single most significant factor is difference in symmetry of the ET process (pi-pi vs. sigma-sigma and pi-sigma).

No other redox pair gives rise to as large a variety of types of redox behavior as does the Ru(III)-Ti(III) system. By the use of the single unified mechanism given above, all this variety of mechanism can be understood by a single coherent conceptual framework.

SPECTRA, KINETICS AND ELECTROCHEMISTRY OF VANADIUM(II)-TRIS(PICOLINATE): A NEW STRONGLY REDUCING PROBE FOR ELECTRON TRANFER PROCESSES

Henrique E. Toma and Fernando T.P. Lellis

Instituto de Química, Universidade de São Paulo, CP 20780, São Paulo, SP, Brasil

Vanadium(II) ions form with the pyridine-2-carboxylate ligand, a series of successive complexes, exhibiting strong CT bands in the visible region. The stability constants β_1, β_2, and β_3 were determined potentiometrically as 7.2×10^4 M^{-1}, 2.5×10^9 M^{-2} and 7.6×10^{13} M^{-3}, respectively, at 25°C, and 0.43 M $LiOAcP_3$. The tris-substituted complex absorbs at 660 nm ($\varepsilon=7.2\times10^3$ $M^{-1}cm^{-1}$), with a shoulder around 445 nm. Reversible CV were observed using gold electrodes, with $E_{1/2}$ = -0.451 V vs NHE, and $D = 4.8\times10^6$ $cm^2.s^{-1}$.

Because of its strongly reducing properties, $V(pic)_3^-$ was used as a ptobe in electron transfer kinetics with poorly oxidising complexes such as $Co(NH_3)_6^{3+}$, $Co(en)_3^{3+}$, $Co(bis)_2^+$, $Ru(NH_3)_6^{3+}$ and Eu^{3+} ions. The self exchange constant for the $V(pic)_3^{+/0}$ couple based on the $Co(en)_3^{3+/2+}$ couple was 3.7×10^3 M^{-1} s^{-1} (I=1M). This value, compared with k_{11}= 1.0×10^{-2} M^{-1} s^{-1} for $V(H_2O)_6^{3+/2+}$, indicates that the picolinate ligand plays an important role in electrons transfer, lowering the inner sphere and outer sphere reorganisation energies.

The self exchange rate constant calculated for the $Co(bis)_2^{+/0}$ complex was 5.6×10^{-5} $M^{-1}s^{-1}$ (I=1M). The estimated k_{11} value for $Co(NH_3)_6^{3+/2+}$, assuming E^0 = - 0.1 V, was 2×10^{-9} $M^{-1}s^{-1}$. For Eu^{3+} ions, the kinetics were strongly inhibited by the picolinate ligand in excess. The effect was negligible in the presence of acid, where the formation of europium-picolinate complexes is precluded. The calculated k_{11} for Eu^{3+} ions was 5.3 $M^{-1}s^{-1}$. This value indicates a non adiabatic mechanism, fitting an approximate linear behavior of k_{11} versus the reaction driving energy.

FAPESP, CNPq

ELECTRON SELF-EXCHANGE BY $Mn(CNR)_6^{+/2+}$: R=METHYL, ETHYL, ISOPROPYL, t-BUTYL, CYCLOHEXYL, AND BENZYL

Roger Nielson and Scot Wherland

Washington State University, Pullman, WA 99163-4630, USA

The electron self-exchange of the title compounds has been measured by ^{55}Mn NMR line broadening as a function of concentration, temperature, and added $n\text{-}Bu_4NBF_4$. The rate constant has been found to vary by more than a factor of 300 over the range of compounds studied. Conductivity studies on the methyl and cyclohexyl complexes have shown that they are not ion-paired under the experimental conditions. Thus the increase in rate which occurs as the electrolyte concentration is increased has been analyzed as an electrostatic work term effect. Previous studies[1] have shown different behavior in solvents which promote ion pairing.

The observed self-exchange rate constants ($M^{-1}s^{-1}$) at 26 °C in acetonitrile with 0.1M $n\text{-}Bu_4NBF_4$ are: methyl, 2.0 X 10^7; ethyl, 1.9 X 10^6; cyclohexyl, 4.4 X 10^5; isopropyl, 2.5 X 10^5; t-butyl, 6.4 X 10^4; benzyl, 1.3 X 10^6.

These data, except benzyl, follow the order expected if steric bulk near the manganese is rate controlling. The extent to which the variation in rate constant can be attributed to an electron transfer distance effect will be discussed by separating the activation process into several components as suggested by Marcus theory. The electrostatic work required to bring the complexes together is calculated from the salt dependence. The range of inner-sphere reorganization is analyzed using Raman and infrared measurements on the complexes in both oxidation states.[2] The outer-sphere reorganization term is discussed by reference to the solvent dependence previously measured for the cyclohexyl compound.[1] The problem of the extent of interpenetration of the coordination spheres and solvent displacement from the intervening sphere will be considered and the possible significance of activation volume measurements to this question presented. This discussion of the contributions to the activation process will be used to interpret the activation parameters. Whether the observed deviation from the steric bulk correlation by the benzyl complex can be attributed to a superexchange path or is better interpreted as a special pre-cursor complex stability will also be discussed.

1. Roger Nielson and Scot Wherland, Inorganic Chemistry, in press.
2. Roger Nielson and Scot Wherland, in preparation.

Electron Transfer Reactions of Nickel(IV) Oxime-Imine Complexes

A. Graham Lappin
Department of Chemistry, University of Notre Dame, Notre Dame, IN 46556 USA

In aqueous media, complexes of nickel(IV), $Ni(IV)L^{2+}$, are readily prepared in the sexidentate oxime-imine chromophore, H_2L.



H_2L

They are moderately powerful oxidants which can be reduced to nickel(II) with a potential around a volt. Mechanistic studies indicate that reduction by both one- and two-electron reagents takes place predominantly in two consecutive one-electron steps, with formation of nickel(III) intermediates.[1,2] Under conditions of high pH, these nickel(III) species are thermodynamically stable and can be prepared and studied as independent reagents.

The nickel(IV) complexes are inert to substitution and can be optically resolved.[3] They have been shown to react by outer-sphere mechanisms while the nickel(III) species exhibit both outer-sphere and inner-sphere behavior. Self exchange rates for the Ni(IV)/(III) interconversion, estimated using Marcus theory, are around 4×10^3 $M^{-1}s^{-1}$. Optically resolved nickel(IV) and nickel(III) complexes have been shown to act as stereoselective oxidants.[4]

Recent aspects of the chemistry of these nickel(IV) and nickel(III) complexes will be presented.

References

1. Lappin, A.G.; Laranjeira, M.C.M. J. Chem. Soc., Dalton Trans., 1982, 1961.

2. Lappin, A.G.; Laranjeira, M.C.M.; Youde-Owei, L. J. Chem. Soc., Dalton Trans., 1981, 721.

3. Meaney, P.J.; Lappin, A.G.; Peacock, R.D.; Stewart, R. J. Chem. Soc., Chem. Commun., 1980, 789.

4. Lappin, A.G.; Laranjeira, M.C.M.; Peacock, R.D. Inorg. Chem. 1980, 19, 766.

REACTIONS OF SILVER(III) WITH ONE-ELECTRON REDUCING AGENTS

Louis J. Kirschenbaum, Edward T. Borish, and James D. Rush.

Department of Chemistry, University of Rhode Island, Kingston, Rhode Island, USA 02881

The tetrahydroxoargentate(III) ion is a low spin d^8 system which is stable for several hours in 1 M NaOH at room temperature. The square planar geometry of $Ag(OH)_4^-$ permits inner sphere electron transfer reactions to occur either within a five-coordinate intermediate or in a four-coordinate complex after replacement of a hydroxyl group by the reductant. Previous studies of the two-electron reduction of $Ag(OH)_4^-$ by ethylenediamine,[1] NO_2^-,[2] arsenite ion,[3] N_3^- [4] and $S_2O_3^{2-}$ [5] indicate that silver(III) can react by either of these paths. There is no correlation between redox potential and reaction rate for this series.

This paper will present results for the reaction of $Ag(OH)_4^-$ with MnO_4^{2-}, $Fe(CN)_6^{4-}$, and $Mo(CN)_8^{4-}$. These substrates commonly react by simple, one-electron transfer mechanisms. In each case, two consecutive reactions are observed which we attribute to the successive one-electron reduction of Ag(III) to Ag(I). Bimolecular rate constants for the first step obey a linear free energy correlation indicating a common mechanism for these three reactions. The second redox step seems to involve silver(II) disproportionation. Subsequent polymerization and precipitation of AgO causes a change in stoichiometry as the concentration of reductant is lowered. The possibility that the reduction of $Ag(OH)_4^-$ by silver(II) proceeds by an outer sphere process will be discussed.

1. L.J. Kirschenbaum, *J. Inorg. Nucl. Chem.*, 1976, 38, 681.
2. E.T. Borish; L.J. Kirschenbaum, *J. Chem. Soc. Dalton Trans.*, 1983, 749.
3. L.J. Kirschenbaum; J.D. Rush, *Inorg. Chem.*, 1983, 22, 1304.
4. E.T. Borish; L.J. Kirschenbaum, submitted to *Inorg. Chem.*
5. J.D. Rush; L.J. Kirschenbaum, submitted to *Inorg. Chem.*

ELECTRON TUNNELING IN TRANSMEMBRANE EXCHANGE REACTIONS BETWEEN VESICLE-BOUND 4-ALKYLPYRIDINEPENTAAMMINERUTHENIUM$^{2+/3+}$ IONS

Lester Y. C. Lee and James K. Hurst

Oregon Graduate Center, 19600 N.W. Walker Road, Beaverton, Oregon, USA 97006

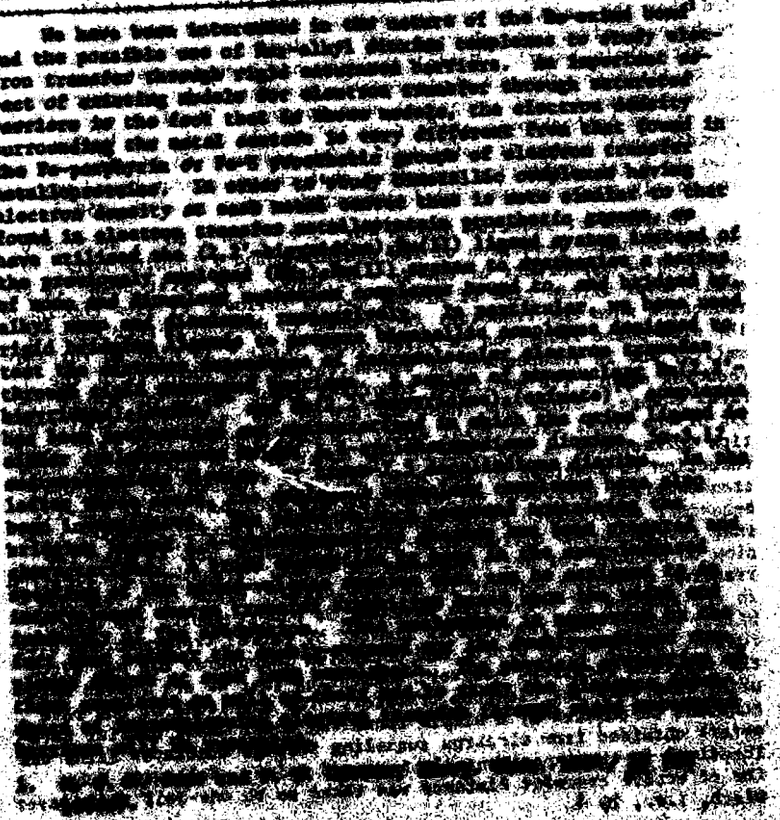
Amphiphilic 4-alkylpyridinepentaammineruthenium ions bind strongly to monolamellar vesicles prepared from egg lecithin, provided that the length of the hydrocarbon chain is greater than ten methylene units. For shorter chains, binding decreases progressively with chain length. Vesicle binding has been demonstrated by ultrafiltration through semipermeable membranes, by chromatography on dextran gels, and by optical spectroscopy. The last method makes use of the bathochromic shift from 398 to 415 nm in the Ru(II) $\rightarrow$ pyridine(π^*) charge transfer band which accompanies binding. Quasi-elastic light scattering indicates that the ruthenium-bound vesicles are nearly monodisperse with hydrodynamic radii of about 250 Å.

Addition of reducing agents (Cr^{2+}, V^{2+}, Cu^{+}, Ru^{2+}, ascorbate) causes biphasic reduction of the vesicle-bound ruthenium ions, as measured by appearance of the Ru $\rightarrow$ py band. The first phase is generally over within time of mixing and is followed by slow continued reduction when the reductant is present in stoichiometric excess. The slow phase reduction is first order (t$_{1/2}$ = 15 min) in ruthenium(III) and is independent of concentration and identity of the reducing agent; its amplitude comprises about 30% of the total optical change. Since the inner surface of the vesicle is also about 35% of the total interfacial area, the data suggest that fast reduction corresponds to reaction on the outer vesicle surface and slow reduction to reaction on the inner surface. Kinetically controlled transmembrane diffusion of reductants was confirmed by the classic behavior[illegible] [illegible] slow to equilibrate for ions of lower permeability. Electron transfer appears to be tunneling. Since this process in this system is electrogenic, the observed permeability ratios [illegible] [illegible] fusion. [illegible] [illegible] [illegible]

MODELS FOR ELECTRON TRANSFER THROUGH SATURATED BARRIERS. THE INTERACTION OF ALKYL CHAINS AND DIOLEFIN LIGANDS WITH CIS-DICHLOROBIS(2,2'-BIPYRIDYL)RUTHENIUM (II): SYNTHESIS, SPECTRA, AND ELECTROCHEMISTRY OF THE RUTHENIUM (II) COMPLEXES FORMED

Maureen J. Kendrick Gene[illegible] and John H. Dunsm[illegible]

University of South Carolina, Columbia, South Carolina USA 29208



EXPERIMENTAL DETERMINATION OF ENERGY DIFFERENCES BETWEEN ISOMERIC COBALT(III) COMPLEXES

Morten J. Bjerrum and Erik Larsen
The Royal Veterinary and Agricultural University
and The H.C. Ørsted Institute, Copenhagen, Denmark

Reversed phase high performance chromatography (RP HPLC) has been used to achieve separations of isomers in some tris diamine cobalt(III) systems. Mixtures of isomers have been made acording to preparative routes from cobalt(II) and ligand after oxidation and also from isolated pure isomers equilibrated by means of active charcoal in aqueous solutions. Cobalt(III) forms robust (inert) complexes and therefore the equilibrium composition can be "frozen" by the addition of excess acid and removal of the catalyst by filtration. Analysis of such equilibrium mixtures by means of RP HPLC (with heptanesulfonate in methanol/water as eluent) has given information about the free energy differences between the isomers.

Many cobalt(III) complexes and also the tris diamine complexes react very fast with sulfide ions to produce the same black cobalt sulfide precipitate and an amount of heat.[1] When the reaction takes place in a calorimeter under specified conditions it is possible to obtain enthalpy differences between isomers. We have attached a microcomputer to an LKB precision microcalorimeter and used this equipment to study the cobalt(III) systems mentioned above, and four bis[(2-aminoethyl)(3-aminopropyl)sulfide]cobalt(III) isomers.

The results will be discussed in the poster.

1. S. Gøgger, O. Gang and F. Woldbye, Acta Chem. Scand. A30 (1976) 98.

INTERACTION OF VO(IV) WITH SOME L-AMINO ACIDS IN AQUEOUS SOLUTION

K.P. Kariya and N.S. Bhave

Chemistry Department, Nagpur University Campus, Nagpur 440010, India

The interaction between VO(IV) and amino acids has become of considerable interest as coordination phenomena, as models for metal-protein reactions and as models for biological systems.

Present paper deals with the equilibria studies between VO(IV) ions and some L-amino acids like L-Aspartic acid, L-Cysteine, L-Glutamic acid, L-Threonine, L-Phenylalanine, and L-Histidine in aqueous solution for the pH range 2-11 at 25° and at an ionic strength of 0.15M KNO_3. L-Aspartic acid and L-cysteine forms 1:2 complex while L-Histidine, L-Phenylalanine, L-Glutamic acid and L-Thronine forms 1:1 complex. The values of log K for VO(IV) chelates with L-Glutamic acid, L-Threonine, L-Histidine, and L-Phenylalanine have been found to be 8.90, 8.08, 9.80 and 7.80 respectively. For VO(IV)-L-Cysteine and VO(IV)-L-Aspartic acid chelates log K_1 and log K_2 values have been found to be 3.10, 5.80 and 9.90, 5.13. The order of stability is found to be L-Aspartic acid > L-Cysteine > L-Histidine > L-Glutamic acid > L-Threonine > L-Phenylalanine.

LATTICE PROPERTIES OF CESIUM HEXACHLOROTHORIUM (IV)

L. Thakur and Awad El-Hossadi
Faculty of Science, Garyounis University,
P.O.BOX:9480 Benghazi, Libya (SPLAJ)

Thakur and co-workers[1,2] have proposed an empirical form of lattice energy equation which yields reliable values for diatomic, polyatomic and complex ionic solids. Lattice energy of Cs_2ThCl_6 calculated using the same procedure assuming a spherical distribution of charge about the complex anion has been found to be 1355 kJ mol^{-1}. The standard heat of formation of the complex ion in the gaseous state, ΔH_f^o Th Cl_6^{2-} (g) calculated was -1712 kJ mol^{-1}. The two-stage chloride-ion affinity for thorium tetrachloride and the hydrational enthalpy of $ThCl_6^{2-}$ (g) calculated were -295 kJ mol^{-1} and -937 kJ mol^{-1} respectively. The sum of first through fourth ionization energies of thorium calculated was 6970 kJ mol^{-1} from which ΔH_f^o Th^{4+} (g) = 7568 kJ mol^{-1}. The metal-ligand coordination bond-energy ($Th^{4+} \longleftarrow Cl^-$) was found to be 1310 kJ mol^{-1}. The above data compare well with some of the literature values reported earlier.

1. L. Thakur, and A. K. Sinha, Indian J. Pure & Appl. Phys., 1977, 15, 794.
2. L. Thakur, B. B. Sandwar and A. K. Sinha, Indian J. Chem., 1979, 17A, 1.

HEATS OF COMBUSTION OF SOME THORIUM DICARBOXYLATES

L. Thakur, F. Gaber and Awad El-Hossadi
Faculty of Engineering, University of Garyounis,
P.O.BOX: 9476, Benghasi, LIBYA. (SPLAJ)

With an ionic radius of 0.99 Å and a charge of 4+ thorium (IV) fulfils the optimum conditions required for high coordination. At the elution stage, carboxylic acids are used for the separation of thorium from other elements. Thermodynamic properties of thorium carboxylates offer an interesting field for investigation in view of the use of thorium as a reactor fuel in the future generation of breeder reactors.[1] In this work we report the heats of combustion of some crystalline thorium dicarboxylates using oxygen bomb-calorimeter. From the standard heats of combustion, ΔH_c, the standard heats of formation of the crystalline compounds, ΔH_f°(c), have been calculated using the auxiliary thermochemical data. Table below lists the values with their limits of error in each case.

Table

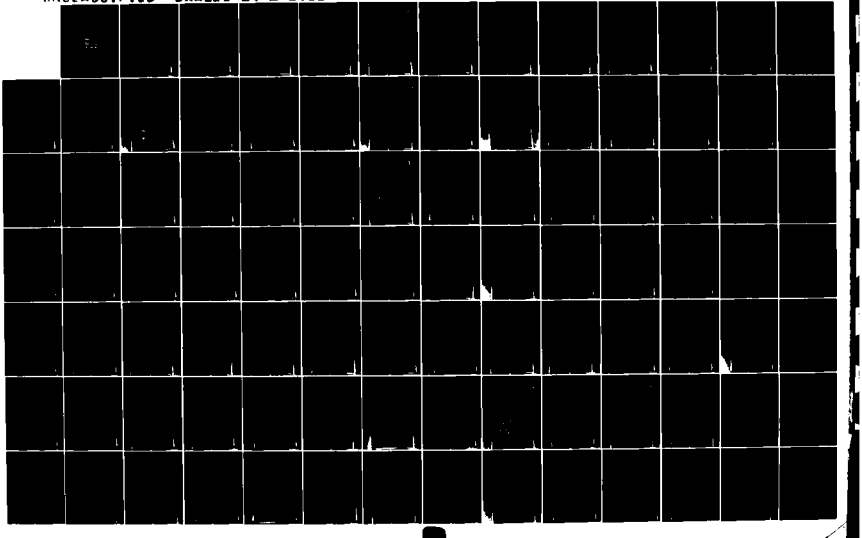
Compounds	$-\Delta H_c$ (kcal mol^{-1})	$-\Delta H_f^\circ$(c) Kcal mol^{-1}
$Th(C_2O_4)_2 \cdot 6H_2O$ (c)	107.4 ± 10	971.8 ± 20
$Th(C_2O_4)_2 \cdot 4H_2O$ (c)	110.5 ± 10	832.1 ± 20
$Th(CH_2C_2O_4)_2 \cdot 3H_2O$ (c)	529.7 ± 10	805.7 ± 20

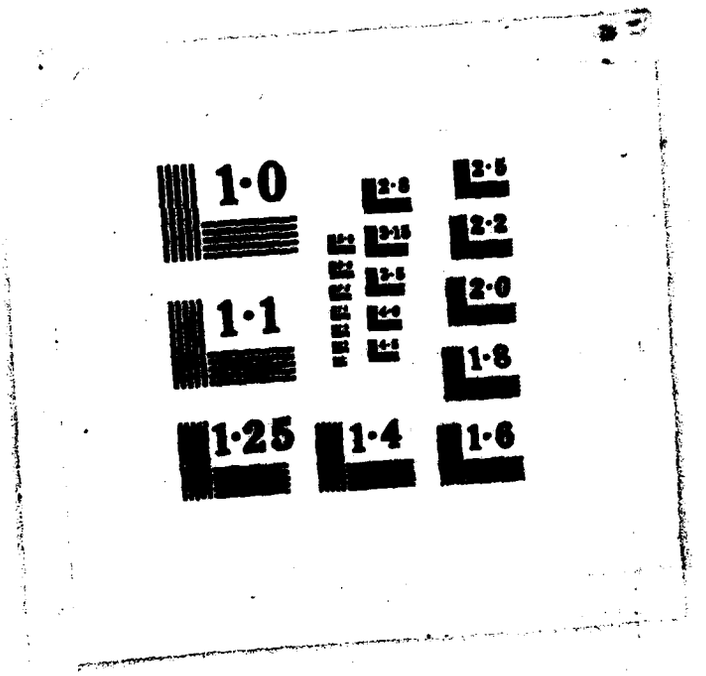
The standard heats of formation of anhydrous thorium oxalate calculated from the above data is -532.1 ± 20 Kcal mol^{-1}: The compounds were prepared from Analar-grade materials and purity assessed from elemental analysis.

1. L. Thakur, A. K. Thakur and M. F. Ahmad, Indian J. Chem. 1980, 19 A, 793.

AD-A148 190 INTERNATIONAL CONFERENCE ON COORDINATION CHEMISTRY (23RD) HELD AT BOULDER..(U) COLORADO UNIV AT BOULDER E L KING ET AL. 03 AUG 84 ARO-21423.1-CH-CF 7/8

UNCLASSIFIED DAAG29-84-M-0199 F/G 7/4 NL




1·0
1·1
1·25
1·4
1·6
1·8
2·0
2·2
2·5

REACTION BETWEEN I_2 AND SOME 5,5-DIMETHYLHYDANTOIN DERIVATIVES WITH SULPHUR AND/OR SELENIUM

Franco Cristiani, Francesco A. Devillanova, Angelo Diaz and Gaetano Verani. Istituto di Chimica Generale Inorganica ed Analitica; Via Ospedale 72, 09100 Cagliari, ITALY

In these last years, we have focused our interest on the coordinating ability of molecules with general formula:



R = H, Me, Et
X = O, S, CH_2, NH, NMe, NEt
Y = S, Se

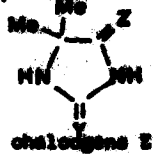
both towards molecular iodine and towards some transition metal ions. Although these ligands possess several potentially coordinating centres, we have found that the coordinative bond occurs only through Y, whose ability in coordinating depends both on X and R.

The Y donor ability has been measured by evaluating the stability constants (K) of the reaction

$$L + I_2 \rightleftharpoons LI_2$$

where L is one of the above molecules. By changing R, X and Y, the K values spread over a wide range, thus indicating that the determination of K is a powerful tool, which is also able to enhance small charge changes on Y[1]. More recently, we have used this reaction to measure the influence on Y of a benzene ring condensed with the above molecules[2].

Now, we wish to use the adduct formation with I_2 to study the donor properties of the following molecules:



Y , Z = O, S, Se

where two chalcogens Z and Y are present as exo-atoms. The choice of molecules having two methyl groups on C(5) is made in order to obtain compounds soluble enough in low polar solvents.

Preliminary experiments, carried out on the derivatives of hydantoin containing the following exo-atoms (Y , Z) = (O , S), (S , O), (S , S) and (Se , S), have shown that:

i) only one atom binds the molecular iodine;
ii) the exo-atom near C(2) is a better donor than the one near C(4), when Y ≠ Z;
iii) selenium atoms have slightly more sulphur than oxygen.

1. F.A.Devillanova and G.Verani, [illegible], 1803 (1981)
2. F.Cristiani, F.A.Devillanova, A.Diaz and G.Verani, J.C.S.Perkin II, in press.

THERMODYNAMICS OF VANADIUM COORDINATION COMPOUNDS

S.M.Cheshnitskiy, V.L.Koshevnikov, A.A.Potiev
Institute of Chemistry of Ural's Scientific Center, AS USSR, GSP-145, Pervomajskaja St., 91, Sverdlovsk, USSR

Vanadium coordination compounds have a number of valuable properties which are connected with the nature of their electronic and crystal structure. Vanadates of MVO_4-type, the basic structural elements of which are chains of VO_4-tetrahedra connected by MOn-polyhedra, are of particular interest.

In the present study the heat capacity of orthovanadates $FeVO_4$, $CrVO_4$ and $AlVO_4$ in the temperature range between 3 and 300K was determined in the adiabatic cryostat. On the $C_p(T)$ dependence for $AlVO_4$ a Shottkey anomaly caused by the presence of V^{+4} centers in the sample, which are formed during the synthesis of the compound in air, was found. Analysis within the limits of the two-level model permits to evaluate their concentrations. On the $C_p(T)$ dependence for $FeVO_4$ there are two λ-peaks with maxima at 15,7 and 21,2, and for $CrVO_4$ - at 50$\pm$ 1K caused by magnetic ordering of Fe^{+3} and Cr^{+3} ions.

By the drop-calorimetry method the enthalpy changes for reactions of direct synthesis of MVO_4 (M = Fe, Cr, Al) from oxides were measured using a high-temperature Kalve-type calorimeter. They allowed to calculate the standard enthalpies of formation.

Analysis of different contributions to the heat-capacity and the enthalpies of formation of these compounds made possible to determine the connection between their thermodynamic properties and structural characteristics.

COORDINATION COMPOUNDS OF ALIPHATIC AND AMINOACIDS IN IRON(II) AND IRON(III) AQUEOUS SOLUTIONS

Kh.M.Yakubov, Yo.Ya.Offengenden

Tadjik State University, Lenin Street, 17, Dushanbe, USSR, 734016

Thermodynamic investigations of complexforming reactions in iron(II) and iron(III) aliphatic and aminoacids aqueous-perchlorate solutions by ozrsdmetry, NM-relaxation and electronic spectroscopy methods have being carried out by us for ricent years made it possible to reveal the next:

1). Dominance regions and stability constants natural change of monomolear FeA^{2+}, $FeAOH^{+}$, FeA_2^{+}, FeA_3 and polymolear $Fe_xA_y(OH)_z$ of acid and hydroxoacid mixed coordination iron compounds in the series of monobasic aliphatic acids: formic - acetic - propionic - butyric.

2). Start-up complexing pH shift to the more acid region of the solution and interval reduction of the compounds existence with increase of complexforming ion concentration, ligand, temperature and ionic strength of the solution.

3). Correlation dependence of salt medium nature influence on iron complexforming processes.

4). Heat effects of complexforming reactions of iron(II) and iron(III) monomolear coordination compounds determined by the methods of temperature coefficient and dilution calorimetry are in direct dependence on the length of carbonil radical chain.

5). Simultaneous formation of monomolear [illegible] compounds in [illegible] aminoacids solutions (glycine, alanine, aminobutyric, diaminopropionic).

6). The formation of [illegible] coordination compounds [illegible] aminoacids occurs in dependence on acid solutions of aliphatic series as well as aminoacids.

CONTRIBUTION TO THE STUDY OF METAL-SULFUR BOND ENERGIES IN METAL--DITHIOCARBAMATE COMPLEXES

Manuel A.V. Ribeiro da Silva, Ana M.M.V. Reis and G. Pilcher

Departamento de Química, Faculdade de Ciências, Universidade do Porto, 4000 PORTO, PORTUGAL

Dialkylammonium dialkyldithiocarbamate $(R_2NH_2)^+(S_2CNR_2)^-$ are useful reagents for producing metaldithiocarbamates complexes.

Standard enthalpies of formation of several dialkylammonium dialkyldithiocarbamates (see Table), were determined at 298.15 K, by solution-reaction calorimetry, from the enthalpy of reaction

$$2R_2NH(\ell)+CS_2(\ell) \rightarrow (R_2NH_2)^+(S_2CNR_2)^-(c)$$

The enthalpies of decomposition

$$R_2NH_2S_2CNR_2(c) \rightarrow R_2NH(g) + \begin{matrix} NR_2 \\ S \end{matrix}\!\!>\!C\!-\!S\!-\!R \quad (g)$$

were measured by high temperature microcalorimetry, being the products of decomposition confirmed by mass spectrometry. The results lead to the standard enthalpies of formation of dialkyldithiocarbamic acids, in the gaseous phase (see Table), which would not be possible to obtain for such compounds containing the group

$$NR_2\!-\!C\!<\!\begin{matrix} S \\ S \end{matrix}$$

by conventional methods, since these compounds are unstable in the condensed phase.

The results are discussed in terms of structure.

Values of standard enthalpies of formation for metal-dialkyldithiocarbamate complexes will be presented and discussed in terms of metal-sulfur bond energies.

RESULTS (in kJ mol^{-1})

R	$\Delta_f H^\circ_m$(R$_2$NH$_2$S$_2$CNR$_2$, c)	$\Delta_f H^\circ_m$(R$_2$NCS$_2$H, g)
Et	-366.9 ± 2.1	-89.8 ± 4.2
n-Pr	-368.2 ± 3.2	-88.8 ± 5.2
iso-Pr	-363.3 ± 2.9	-84.3 ± 5.0
n-Bu	-452.2 ± 3.6	-
iso-Bu	-446.9 ± 3.6	-79.4 ± 5.7

Fa58-01

THE ACTIVE SITE IN THE CATECHOL DIOXYGENASES

Lawrence Que, Jr.

Department of Chemistry, University of Minnesota, 207 Pleasant St. Southeast, Minneapolis, MN 55455

The catechol dioxygenases are iron enzymes which catalyze the oxidative cleavage of catechols to *cis,cis*-muconic acids with the incorporation of the elements of dioxygen.[1,2]



The high-spin ferric center in the active site is involved in neither a heme complex nor an iron-sulfur cluster but is coordinated to ligands on the polypeptide chain. These enzymes and many of their complexes have been studied by a variety of spectroscopic methods including Mossbauer, EPR, resonance Raman, NMR, and x-ray absorption spectroscopies. Together they provide a picture of the iron active site and how substrates and inhibitors interact with it. Comparisons with synthetic inorganic complexes have been essential for developing this picture.

1. L. Que, Jr., Coord. Chem. Rev. 1983, 50, 73-108.
2. L. Que, Jr., Adv. Inorg. Biochem. 1983, 5, 167-199.

PHENOLATE VIBRATIONS IN COPPER AND IRON PROTEINS

Joseph W. Pyrz[a,b] and Lawrence Que, Jr.[b]

Departments of Chemistry, Cornell University[a], Ithaca, New York 14853, and University of Minnesota[b], Minneapolis, Minnesota 55455

Resonance Raman spectroscopy has proven useful in recent years as a probe for charge transfer transitions. Excitation within the electronic absorption envelope results in enhancement of vibrational modes associated with the ligand responsible for the charge transfer. Metalloproteins containing bound tyrosinate are particularly amenable to this technique since phenolate to metal charge transfer transitions are usually found in the visible region of the spectrum and enhancement factors of phenolate vibrational modes are large.

Hemocyanin and tyrosinase are binuclear copper proteins that bind molecular oxygen. Chemical and spectroscopic studies have elucidated much of the coordination chemistry of these copper systems.[1] One aspect of the coordination chemistry yet to be determined is the nature of the endogenous ligand. Solomon has suggested that this bridge may be tyrosine on the basis of low temperature visible spectroscopy.[1] Resonance Raman spectra of synthetic Cu-O (phenolate) model complexes have been studied to serve as a basis for comparison with these proteins.

The involvement of phenolates in charge transfer transitions is manifested by enhancement of characteristic vibrations at ca. 1170, 1270, 1500, and 1600 cm^{-1}. These vibrations are associated with phenolate ring deformation modes. In binuclear copper complexes the 1270 cm^{-1} peak is shifted to ca. 1300 cm^{-1} with $^{16}O/^{18}O$ isotopic shifts unequivocally assigning this to ν_{CO}. The observation of such a value for the ν_{CO} may serve as a marker for bridging systems.

Iron tyrosinate proteins also show enhanced vibrations in the 1100-1700 cm^{-1} region typical of phenolate ring deformation modes. The low frequency region has been less well characterized; in particular, various tentative assignments for the feature near 570 cm^{-1} have been suggested.[2,3]

In order to ascertain the nature of the vibration, the model compound Fe(salen)OC_6H_4-4-CH_3 has been studied where the axial p-cresolate ligand serves as a model for tyrosinate. The complex indeed exhibits a peak at 568 cm^{-1} which can be assigned to the p-cresolate. Polarization experiments show that the peak is polarized, as is found in the proteins. Isotopic shifts found for $^{54}Fe/^{56}Fe$ and $^{16}O/^{18}O$ substitution and ring deuteration indicate that the vibration can be assigned as predominantly the $6a^b$ symmetric stretch of tyrosine rather than an Fe-O stretch.

1. N.C. Eickman, R.S. Himmelwright and E.I. Solomon, Proc. Natl. Acad. Sci. U.S.A. 1979, 76, 2094.
2. K. Nagai, T. Kitagawa, A. Morishima, F. Tuboto and T. Kitagawa, Biochemistry 1980, 22, 1305.
3. B.C. Antanaitis, T. Strekas and P. Aisen, J. Biol. Chem. 1982, 257, 3766.
4. G. Varsanyi, "Vibrational Spectra of Benzene Derivatives," Academic Press: New York 1969.

PARAMAGNETIC ^{1}H NMR SPECTRA OF HEMERYTHRIN

Michael J. Maroney[a], Randall B. Lauffer[b], Donald M. Kurtz, Jr.[c] and Lawrence Que, Jr.[a]

Departments of Chemistry, University of Minnesota[a], Minneapolis, Minnesota 55455, Cornell University[b], Ithaca, New York 14853, and Iowa State University[c], Ames, Iowa 50000, USA

The binuclear iron site of the respiratory protein hemerythrin has been characterized by a variety of spectroscopic techniques as well as x-ray crystallography.[1] These studies have primarily focused on oxyhemerythrin and the various met forms to reveal an active site which consists of two high-spin ferric centers in a confacial bioctahedron. The two irons are strongly antiferromagnetically coupled and bridged by an oxo group and two carboxylates from glutamate and aspartate. The remaining coordination sites are occupied by five histidines, with the sixth site available for the binding of oxygen and other ligands. It is also possible to prepare mixed-valent Fe(III)-Fe(II) forms of the protein which exhibit EPR signals with g-values <2, indicating the persistence of the antiferromagnetic coupling in these states.[1,2] Whether the cluster structure remains in deoxyhemerythrin (Fe(II)-Fe(II) state) is not known presently. Recent EXAFS data indicate that the iron-iron distance is shorter in the deoxy form; however, the temperature dependent appearance of the Fe-Fe vector suggests the loss of the oxo bridge.[3]

We report the observation of paramagnetically shifted resonances in the ^{1}H NMR spectra of hemerythrin. Resonances due to histidine N-H's can be unequivocally assigned due to their solvent exchangeability. From the observed isotropic shifts and their temperature dependence,[4] we can obtain insights into the ligand environments and magnetic properties of the iron centers in all three oxidation states.

1. R.G. Wilkins and P.C. Harrington, Adv. Inorg. Biochem. 1983, 5, 51-85.
2. D.M. Kurtz, Jr., J.T. Sage, M. Hendrich, P.G. Debrunner, and G.B. Lukat, J. Biol. Chem. 1983, 258, 2115-2117.
3. W.T. Klose, E.A. Stern, J.D. McCallum, and J. Sanders-Loehr, J. Am. Chem. Soc. 1983, 105, 1919-1923.
4. R.B. Lauffer, B.G. Antanaitis, P. Aisen, and L. Que, Jr., J. Biol. Chem. 1983, 258, in press.

Fa58-3

REDOX REACTIONS IN AQUEOUS SYSTEMS CONTAINING IRON CHELATE COMPOUNDS, DYES AND NADH

Kazuko Tanaka and Reita Tamamushi

Inorganic Chemistry Lab., The Institute of Physical and Chemical Research, Wako-shi, Saitama, 351 Japan

In microbial fuel cells, the electron transfer from microorganisms to electrode is performed with the aid of redox mediators(1). Several kinds of dyes(2) and Fe(III) chelate compounds(3) have been found to be effective mediators in microbial fuel cells; especially Fe(III) chelate compounds worked effectively in the presence of a small amount of thionine(4). The purpose of this study is to get an information concerning the reduction mechanism of mediators by microorganisms and coupled reaction mediator mechanisms of Fe(III) chelate compounds and thionine.

Assuming that the redox activity of microorganisms is attributed to the NAD^+/NADH couple, we studied the reduction rates of thionine and Fe(III)EDTA by NADH in pH 7.0 phosphate buffer solutions using spectrophotometric and polarographic methods.

The reduction rate of thionine by NADH obeyed the first order kinetics with respect to the concentration of thionine and NADH. The reduction rate of Fe(III)EDTA by NADH was found to be very slow, but it was accelerated by the addition of a small amount of diaphorase. The reduction rate of thionine by NADH in the presence of Fe(III)EDTA, and that of Fe(III)EDTA by NADH in the presence of thionine were determined and discussed with the knowledge of the above reactions and electron transfer rate constants of oxidized thionine/Fe(II)EDTA and reduced thionine/Fe(III)EDTA redox couple.

1. H. P. Bennetto, J. L. Stirling, K. Tanaka, and C. A. Vega, Biotechnol. Bioeng., 25, (1983), 559.
2. S. D. Roller, H. P. Bennetto, G. M. Delany, J. R. Mason, J. L. Stirling, C. F. Thurston, in preparation.
3. K. Tanaka, C. A. Vega and R. Tamamushi, Bioelectrochem. Bioenergetics, in print.
4. K. Tanaka, C. A. Vega and R. Tamamushi, ibid.

A PLANT-TYPE FERREDOXIN MODEL COMPLEX FROM A SYNTHETIC 20-PEPTIDE LIGAND WITH A CHARACTERISTIC PEPTIDE SEQUENCE

A. Nakamura,[a] N. Usyama,[a] T. Ueno,[a] T. Tsukihara,[b] H. Kumagai,[c] S. Sakakibara,[c] K. Wada[a] and H. Matsubara[a]

[a]Faculty of Science, Osaka University, Osaka 560,
[b]Faculty of Engineering, Tottori University, Tottori 680, and
[c]Protein Research Foundation, Osaka 562, Japan

Based upon the peptide sequence and the X-ray structure of plant-type ferredoxins, we have designed and prepared a new peptide (20-peptide) capable of binding $[Fe_2S_2]^{2+}$ core. Incorporation of the $[Fe_2S_2]^{2+}$ core is accomplished by the reaction of the 20-peptide with $Fe_2S_2Cl_4^{2-}$ in DMF. The spectroscopic data (visible, CD, and MCD) indicated formation of $[Fe_2S_2(20\text{-peptide})]^{2-}$ together with other iron-sulfur-peptide species.

Structure of 20-peptide:

Ac-Pro-Tyr-Ser-Cys-Arg-Ala-Gly-Ala-Cys-Ser-Thr-Cys-Ala-Gly-Pro-Leu-Leu-Thr-Cys-Val-NH_2

(abbreviated as 20-peptide)

Synthetic reaction:

$$\text{20-peptide} \xrightarrow[\text{in DMF under Ar}]{[Fe_2S_2Cl_4]^{2-}} \begin{cases} [Fe_2S_2(\text{20-peptide}(-4H))]^{2-} \\ \text{other species} \end{cases}$$

SYNTHESIS AND PROPERTIES OF HEXANUCLEAR Fe/Se/SR-CLUSTERS AND THE X-RAY STRUCTURE OF $[Fe_6Se_6(SMe)_2]^{4-}$

Henry Strasdeit, Bernt Krebs and Gerald Henkel

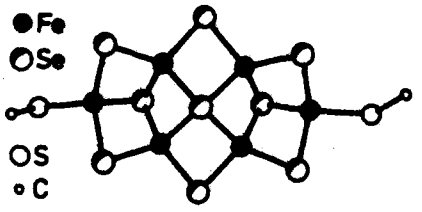
Anorganisch-Chemisches Institut der Universität Münster
Corrensstr. 36, D-4400 Münster, Federal Republic of Germany

Different procedures have been developed for the preparation of $[Fe_6S_6(SR)_2]^{4-}$ clusters [1-4]. Here we report on analogous $[Fe_6Se_6(SR)_2]^{4-}$ complexes (R = Me, CH_2Ph) which can be synthesized according to the dichalcogenide method [1,2] by using Na_2Se_2 instead of Na_2Se:

$$6\ Fe(SR)_3 + 6\ Na_2Se_2 \longrightarrow Na_4[Fe_6Se_6(SR)_2] + 7\ RSSR + 2\ NaSR + 3\ Na_2Se.$$

From the deep-brown MeOH/DMF solutions the hexanuclear anions were precipitated as black crystalline compounds $(Et_3NCH_2Ph)_4[Fe_6Se_6(SMe)_2]$ (1) and $(Et_4N)_4[Fe_6Se_6(SCH_2Ph)_2]$ (2), respectively.

1 crystallizes in the monoclinic space group $P2_1/c$ with 4 formula units per unit cell. In the crystal isolated $[Fe_6Se_6(SMe)_2]^{4-}$ anions (see Figure) are separated by $Et_3NCH_2Ph^+$ cations. The structural characteristics of the $[Fe_6Se_6]^{2-}$ core are closely related to those of the sulfur-containing derivatives though the expected differences are obvious. The six tetrahedrally coordinated Fe atoms form a planar arrangement defining a central square as well as two triangles. The metal atoms of the square are surrounded exclusively by Se atoms while a thiolate-S atom is located within the coordination sphere of each of the two remaining Fe atoms.



Selenide is present in three different bridging modes: as μ_2-, μ_3-, and μ_4-Se. The Fe-Fe and Fe-Se distances (mean values at the present state of refinement: 2.79 and 2.37 Å, respectively) are significantly larger than the corresponding ones in the sulfur analogs.

The ^1H NMR spectra of $[Fe_6X_6(SR)_2]^{4-}$ complexes show larger downfield shifts for protons attached to α-carbon atoms for X = Se than for X = S, probably indicating higher paramagnetism of the selenium compounds.

S/Se replacement, also known for $[Fe_2X_2]^{2+}$ and $[Fe_4X_4]^{2+}$ cores [5], is of biochemical interest as biologically active selenium homologs of certain Fe/S enzymes have been synthesized [6].

1. G. Henkel, H. Strasdeit and B. Krebs, Angew. Chem., Int. Ed. Engl. 1982, 21, 201; Angew. Chem., Suppl. 1982, 489.
2. H. Strasdeit, B. Krebs and G. Henkel, Inorg. Chem., in press.
3. G. Christou, M. Sabat, J.A. Ibers and R.H. Holm, Inorg. Chem. 1982, 21, 3581.
4. K. S. Hagen, A.D. Watson and R.H. Holm, J. Am. Chem. Soc. 1983, 105, 3905.
5. J.M. Berg and R.H. Holm in "Iron-Sulfur Proteins"; T.G. Spiro, Ed.; Wiley: New York, 1982; Chapter 1.
6. T.C. Stadtman, Science 1974, 183, 915.

Fa58-6

THE SYNTHESIS, STRUCTURE AND SPECTROSCOPIC PROPERTIES OF A MIXED LIGAND μ-OXO IRON(III) DIMER

Ray J. Butcher, M.V. Walker, E. Sinn, C.J. O'Connor, and W.M. Reiff

Chemistry Departments, Howard University, Washington, D.C., 20059; University of Virginia, Charlottesville, VA 22901; University of New Orleans, New Orleans, LA; Northeastern University, Boston, MA.

The synthesis, structure, magnetism and Mössbauer spectroscopy of a novel mixed ligand μ-oxo dimer of iron(III) will be presented. The title complex was obtained from the reaction of iron(III) chloride, salicylaldehyde and 2-aminoethylpiperazine and has the formula; $[Fe(C_7H_5O_2)(C_{13}H_{17}ON_3)]_2O$. Both halves of the dimer are related by a crystallographic 2-fold axis passing through the oxygen bridge. The coordination shell about each iron atom is completed by two oxygen donors from a salicylaldehyde moiety, an oxygen and two nitrogen donor from an N-2-aminoethylpiperazinesalicylaldimine moiety and the μ-oxygen atom. Variable temperature magnetic and Mössbauer data have been obtained for this compound and will be discussed in terms of the structure as determined by X-ray diffraction.

METAL-THIOLATE COMPLEXES: MODELS FOR METAL-CYSTEINE COORDINATION IN METALLOPROTEINS

Stephen A. Koch* and Michelle Millar

Department of Chemistry, State University of New York at Stony Brook, Stony Brook, N.Y. USA 11794; Department of Chemistry, New York University, New York, N.Y. USA 10003

Metal-cysteine coordination is a common ligation mode in a wide range of metalloproteins. The synthesis and structural characterization of thiolate complexes of Fe, Co, Mo, Cu and Ni will be presented. Particular emphasis will be given to the use of sterically hindered thiolate ligands to control the coordination geometry at the metal center and to the use of methods to inhibit auto redox reactions (i.e. $M^n + RS^- = M^{n-1} + 1/2\ RSSR$).

CHEMICAL PROPERTIES AND REDOX REACTIONS OF BACTERIAL PROTEINS CONTAINING LARGE IRON CLUSTERS

Gerald D. Watt

Charles F. Kettering Research Laboratory, Yellow Springs, Ohio USA 45387

Iron is an essential element in metabolic reactions. In many enzymes single iron atoms function as electron transfer centers but in the iron-sulfur redox proteins 2Fe, 2S, 3Fe, 3S and 4Fe, 4S clusters act as electron transfer centers. Recently we have described a protein isolated from the bacterium Azotobacter vinelandii which contains heme and 2000-4000 Fe atoms in a tightly bound core in the center of the protein shell. The similarity of this protein to Mammalian ferritin (an iron storage protein) has been discussed.[1] The most notable difference between ferritin and the newly discovered protein is the presence of heme in the latter and its ability to undergo reversible redox reactions involving each Fe atom in the core. Each Fe^{3+} in the core rapidly accepts an electron at -440 mv without losing Fe^{2+} after reaction. The protein is thus able to store 2000-4000 e/mole and at a later time transfer them to other electron transfer reagents. We have studied the redox properties of both the heme and the core Fe atoms along with magnetic properties of the core Fe atoms. The Mossbauer spectra of the core Fe atoms have been determined at various states of reduction and will be discussed in terms of Fe valence state and possible structures present.

1. E.I. Stiefel and G.D. Watt. Nature, 279 81 (1979)

RESONANCE RAMAN SPECTROSCOPIC STUDIES OF THE μ-OXO-BRIDGED BINUCLEAR IRON CENTER IN OXYHEMERYTHRIN AND IN THE MODEL COMPLEX, $[Fe_2O(o\text{-Phen})_4(H_2O)_2](NO_3)_4 \cdot 5H_2O$.

Andrew K. Shiemke, Jeffrey E. Plowman, Joann Sanders-Loehr, Thomas M. Loehr, Cynthia K. Schauer, and Oren P. Anderson.

Department of Chemistry & Biochemical Sciences, Oregon Graduate Center, Beaverton, OR 97006 (AKS, JEP & TML); Department of Chemistry, Portland State University, Portland, OR 97207 (JSL); and Department of Chemistry, Colorado State University, Fort Collins, CO 80523 (CKS & OPA).

Oxyhemerythrin (oxyHr), the respiratory protein of the marine sipunculid, Phascolopsis gouldii, was investigated by resonance Raman spectroscopy. The presence of a μ-oxo-bridged binuclear iron center was established by locating ν_{symm}(Fe-O-Fe) at 486 cm^{-1} using UV-excitation. In $H_2{}^{18}O$, this frequency shifts to 475 cm^{-1}. The magnitude of this shift is similar to that observed for other μ-oxo-bridged Fe(III)-proteins, such as ribonucleotide reductase [1] and several metHr's [2]. The enhancement profile for this mode in oxyHr maximizes at ≈360 nm, suggesting that the strong absorption band in this region has considerable oxo → Fe(III) charge transfer character. The asymmetric Fe-O-Fe vibration has been observed for the first time in these binuclear iron proteins, also using UV-excitation. In oxyHr, this mode is at 757 cm^{-1} and shifts by ≈40 cm^{-1} to lower energy in O-18 water.

We have structurally characterized the μ-oxo-bridged Fe(III) complexes with o-phenanthroline, $[Fe_2O(phen)_4(H_2O)_2]X_4$. The NO_3^- salt crystallizes in space group P$\bar{1}$ (Z=2) with a = 13.828 A, b = 15.122 A, c = 15.890 A, α = 84.44°, β = 64.99°, and γ = 68.46°. This complex has Fe-O-Fe bond lengths typical of oxo-bridged dimers [3], and shows a bridge angle of 155.1°. Vibrational and electronic spectroscopic studies on this complex have shown that it is an excellent model for the RR spectral data obtained on the binuclear iron proteins. As with the proteins, strong resonance enhancement has been observed for ν_{symm}(Fe-O-Fe) at 395 cm^{-1} (390 cm^{-1} in $H_2{}^{18}O$). The asymmetric vibration of the Fe-O-Fe cluster was recorded both in the ir-spectrum, where the absorption is strong, and in the Raman spectrum, where the intensity is weak, but with nearly coincident values of 827 cm^{-1} (786 cm^{-1} in $H_2{}^{18}O$). Thus, the RR behavior of the μ-oxo-bridged binuclear iron proteins can be appropriately modeled by the binuclear iron complexes containing a single oxo-bridge.

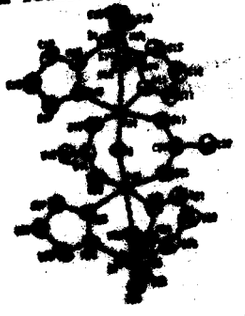
[1] B.M. Sjöberg, T.M. Loehr, & J. Sanders-Loehr, Biochemistry 21, 96 (1983).
[2] S.M. Freier, L.L. Duff, D.F. Shriver, & I.M. Klotz, Arch. Biochem. Biophys. 202, 449 (1980).
[3] J.A. Thich, D.N. Toby, D.A. Powers, J.A. Potenza, & H.J. Schugar, Inorg. Chem. 20, 3314 (1981).

SYNTHESIS, STRUCTURE, AND PROPERTIES OF A MODEL FOR THE DIIRON SITE OF HEMERYTHRIN, $[Fe_2O(O_2CR)_2(HBpz_3)_2]$

William H. Armstrong, Alan Spool, and Stephen J. Lippard

Massachusetts Institute of Technology, Cambridge, Massachusetts, USA, 02139

The binuclear iron complexes $[(HBpz_3)FeO(O_2CR)_2Fe(HBpz_3)]$ ($HBpz_3$ = tri-1-pyrazolylborate anion, R = H, 1; CH_3, 2; Ph, 3), which are good models for the physical and redox properties of the hemerythrin diiron center, have been synthesized either from simple ferric salts in aqueous solution (1, 2) or from $[Cl_3FeOFeCl_3]^{2-}$ in acetonitrile solution (3).[1,2] X-ray diffraction studies of 1 and 2 revealed molecular structures in which the two iron atoms are bridged by an oxygen atom and two bidentate carboxylate groups and are each capped by the tridentate ligand, $HBpz_3^-$ (see figure below). The complexes have Fe-O(oxo) distances in the range 1.776-1.787 Å, Fe-O-Fe angles of 125.3° (1) and 123.5° (2), and Fe···Fe separations of 3.168 Å (1) and 3.145 Å (2). These model complexes were further characterized by magnetic measurements (J = -125 cm^{-1}), electronic absorption spectroscopy (262 nm, ϵ_{Fe} = 3400 $M^{-1}cm^{-1}$; 339 nm, ϵ_{Fe} = 4600 $M^{-1}cm^{-1}$; 457 nm, ϵ_{Fe} = 510 $M^{-1}cm^{-1}$; 492 nm, ϵ_{Fe} = 460 $M^{-1}cm^{-1}$; 695 nm, ϵ_{Fe} = 70 $M^{-1}cm^{-1}$; ~990 nm, ϵ_{Fe} = 1.5 $M^{-1}cm^{-1}$), Mössbauer spectroscopy (δ = 0.48 mm/sec; ΔE_Q = 1.64 mm/sec), resonance Raman (Fe-O-Fe, ν_s = 528 cm^{-1}, ν_a = 283 cm^{-1}) and infrared (ν_{as} = 751 cm^{-1}) spectroscopies, electrochemical measurements (irreversible reduction at -0.76 V vs. SCE followed by formation of $Fe(HBpz_3)_2$), and ^1H nuclear magnetic resonance spectroscopy (acetate CH_3 at ~0.5 ppm).[1,2] X-ray absorption spectra of 2 are practically superimposable upon spectra of metazidomyohemerythrin, emphasizing the congruence of the iron atom coordination spheres in the model and native species.[3] A thorough discussion of these physical properties along with a comparison to hemerythrin and other proteins that contain oxo-bridged diiron units (ribonucleotide reductase, purple acid phosphatases) will be presented.



1. W.H. Armstrong and S.J. Lippard, J. Am. Chem. Soc., 1983, 105, 4837.
2. W.H. Armstrong, A. Spool, G.C. Papaefthymiou, R.B. Frankel, and S.J. Lippard, submitted for publication.
3. W.H. Armstrong, A. Spool, S.J. Lippard, M.E. Cox, K.O. Hodgson, J.L. Smith, and W.A. Eisenbrandson, submitted for publication.

SULFIDE DERIVATIVES OF THE BINUCLEAR IRON SITE OF HEMERYTHRIN AT BOTH MET AND SEMI-MET OXIDATION LEVELS. EVIDENCE FOR REPLACEMENT OF THE μ-OXO BRIDGE BY SULFIDE

Gudrun S. Lukat,[‡] Donald M. Kurtz, Jr.,[‡] Andrew K. Shiemke,[§] Thomas M. Loehr,[§] and Joann Sanders-Loehr[¶]

[‡]Iowa State University, Ames, Iowa, USA 50011, [§]Oregon Graduate Center, Beaverton, Oregon, USA 97006 and [¶]Portland State University, Portland, Oregon, USA 97207.

Preparation and characterization of sulfide derivatives of the non-heme iron, oxygen-carrying protein, hemerythrin (Hr) at both met and semi-met oxidation levels are reported. A combination of Mossbauer, EPR, UV-vis, resonance Raman and analytical data are consistent with replacement of the μ-oxo bridge between the irons with a single sulfide.[1,2] MetsulfideHr can be prepared only via oxidation of semi-metsulfideHr. Under anaerobic conditions metsulfideHr is stable for at least several hours at room temperature and much longer at 4°C. Under anaerobic conditions metsulfideHr slowly decomposes to the semi-met oxidation level. That this decomposition is initiated by attack of OH^- at iron is suggested by experiments in which a large excess of N_3^- causes conversion of metsulfideHr to semi-metazideHr as judged by UV-vis and EPR spectroscopy. Under aerobic conditions the product of metsulfideHr decomposition is metHr and no EPR spectrum is observed during this transformation. Unlike met and semi-metHr, the sulfideHrs do not form anion adducts. This result can be rationalized on the basis of steric and electronic changes at the iron site upon replacement of a μ-oxo by a μ-sulfido bridge. Our results support the idea that a μ-oxo bridge persists at the iron site of semi-metHr in the absence of sulfide but that it is more labile in the semi-met form. Our work demonstrates that a stable iron-sulfur center can exist in a protein without thiolate ligation to iron and raises the possibility that such centers naturally occur in as yet undiscovered proteins.

1. D. M. Kurtz, Jr., J. T. Sage, M. Hendrich, P. G. Debrunner and G. S. Lukat, J. Biol. Chem. 1983, 258, 2116.

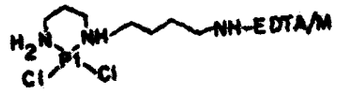
2. G. S. Lukat, D. M. Kurtz, Jr., A. K. Shiemke, T. M. Loehr and Joann Sanders-Loehr, submitted for publication.

cis-DIAMINOALKANEDICHLOROPLATINUM(II) COMPLEXES CONTAINING TETHERED NICKING AND INTERCALATING FUNCTIONALITIES: NEW REAGENTS FOR STUDYING PLATINUM ANTICANCER DRUG - DNA INTERACTIONS

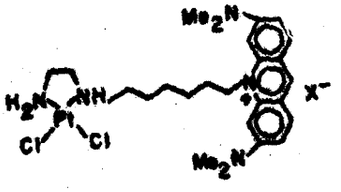
John P. Caradonna, Bruce E. Bowler, L. Steven Hollis, Matthew Eichner, and Stephen J. Lippard

Massachusetts Institute of Technology, Cambridge, Massachusetts, USA, 02139

The synthesis and characterization of the two new platinum complexes, 1 and 2 shown below, will be described. Compound 1 was prepared to address a fundamental dichotomy in platinum/DNA biochemistry, namely: Are the nuclease detectable platinum binding sites[1,2] the same as all platinum binding sites? Compound 2 was inspired by our discovery that intercalators can switch the nuclease detectable binding sites of cis-diamminedichloroplatinum(II) (cis-DDP) on a DNA restriction fragment.[3] The results of studies of the binding and reactivity of these new cis-DDP analogs with DNA will be presented.



1 M = Fe, Co, etc.



2 X = Cl, NO_3

1. G.L. Cohen, J.A. Ledner, W.R. Bauer, H.M. Ushay, C. Caravana, and S.J. Lippard, J. Amer. Chem. Soc. 1980, 102, 2487.
2. T.D. Tullius and S.J. Lippard, J. Amer. Chem. Soc. 1981, 103, 4620.
3. T.D. Tullius and S.J. Lippard, Proc. Natl. Acad. Sci. U.S.A. 1982, 79, 3489.

X-RAY STRUCTURE OF CIS-DICHLORO BIS(GLYCYL LEUCINE METHYL ESTER) PLATINUM(II).ANTITUMOR ACTIVITY CIS-PLATINUM(II) WITH PEPTIDE ESTERS AND CIS-PALLADIUM(II) WITH α-AMINOACIDS CHLORIDE COMPLEXES.

MANUEL CASTILLO and ELIAS RAMIREZ

Departamento de Quimica Inorgánica y General.
Facultad de Quimica. Universidad de Sevilla.Spain.

Introduction

In recent years there has been considerable interest in Pt(II) and Pd(II) complexes that show antitumor activity (1,2) but there are few papers on antitumor activity of the Pt-peptide complexes(3). We now report our studies of the antitumor activity of the following compounds:

CIS-$PdCl_2$(glyOCl)$_2$(I),CIS-$PtCl_2$(gly-leuOMe)$_2$(II) and

CIS-$PtCl_2$(gly-gluOMe)$_2$(III)

on Ehrlich ascites and Leukaemia L-1210.

Experimental

The complexes were prepared in our chemistry laboratories (4,5)and they were characterized by chemical analysis,molecular weight determination and i.r. and ^{1}H-nmr spectroscopy.

X-ray analysis

Were report here on the crystalline structure of the (II) complex, derived from a X-ray single crystal structure analysis.

Antitumor activity

We first determined the level of the complexes which would be tolerated by the mices (LD_{50} doses) and then whether below these levels,they would inhibit the growth of transplantable tumors in these animals. The tests were with Ehrlich ascites and Leukaemia L-1210.

The results showed that the activity of (I) complex is less than (II) and (III) complexes.

The structural features of these complexes will be discussed and correlated to their antitumor activity.

References

1- B.Rosenberg,Naturwissenschaften,1973,60,399.
2- M.J.Clear, Coord.Chem.Rev.,1974,12, 349.
3- W.Beck,H.Biesinger,M.Dirnth,B.Purucker,G.Thiel,H.Seidenberg, B.Wappes and N.Schönenberg,Chem.Ber.,1982,115, 2286.
4- M.Castillo,A.Romero,and E.Ramirez,Trans.Met.Chem.,1983,(in press).
5- M.Castillo,A.Romero and E.Ramirez,Inorg.Chem.,(in press).

CHEMISTRY OF MODEL NUCLEOBASE COMPLEXES OF CISPLATIN

Rut Beyerle-Pfnür, Bernhard Lippert, Gabriele Raudaschl, Helmut Schöllhorn, and Ulf Thewalt

Anorganisch-Chemisches Institut, Technische Universität München, 8046 Garching, and
Sektion für Röntgen- und Elektronenbeugung, Universität Ulm, 7900 Ulm, F.R.G.

The paper will focus on structural, spectroscopic, and reactivity aspects of three groups of compounds of cis-$(NH_3)_2Pt(II)$, and their possible relevance to the mode of action of platinum antitumor agents.

(1) N1 Binding to 6-Oxopurines.

Complexes of cis-$(NH_3)_2Pt(II)$ with 7,9-dimethylguanine and 7,9-dimethylhypoxanthine with Pt coordination through N1 have been prepared and the basicity of O6 has been assessed by use of potentiometric pH titration and reaction with additional cis-Pt(II) and heterometals.

(2) Reaction Products from the Treatment of Nucleobase Complexes with Cyanide.

The study of the solution behavior of model nucleobase (B) complexes of the type cis-$(NH_3)_2PtB_2$ in the presence of excess CN^- may provide an explanation for the inability to completely remove Cisplatin from DNA by CN-treatment. Reaction products obtained from solutions containing nucleobase complexes and CN^- have been isolated and characterized.

(3) Diplatinum(III) Complexes of 1-Methyluracil.

A series of dinuclear Pt(III) complexes $[X(NH_3)_2Pt(1\text{-MeU})_2Pt(NH_3)_2Y]^{n+}$, containing bridging uracil ligands in head-tail and head-head arrangement and a variety of different axial ligands X and Y, have been prepared, structurally characterized, and studied in solution.

INTERACTION OF PLATINUM(II) COMPOUNDS WITH DNA AND DNA-FRAGMENTS

Jan Reedijk, Anne Marie J. Fichtinger-Schepman,
Jeroen H.J. den Hartog and Johannis L. van der Veer

Department of Chemistry, State University Leiden, Gorlaeus Laboratories, P.O. Box 9502, 2300 RA Leiden, the Netherlands

Cis-diamminedichloroplatinum(II) and several analogues are in frequent use as cytostatic compounds. Reaction of such compounds with DNA is believed to be the main cause of the cytostatic properties[1] at the cellular level. Binding of the platinum compounds (or their hydrolysis products) is known to take place mainly at the guanine-N7 atoms of the DNA. Because the active Pt compounds have two potential binding sites, the reaction with DNA occurs potentially into two steps. Recent work has made clear that also the second step is likely to be a binding to a (second) guanine-N7 atom on the same DNA strand[2].

Biochemical evidence is available that chelation of the cis-Pt compounds to adjacent guanine pairs in DNA is frequently occurring, although binding to fragments with an intermediate base cannot be excluded[3]. Our present research is directed toward the study of the distortion in the DNA, after reaction with cis-Pt compounds, and the influence of neighbouring bases on the structure of the DNA adduct, with special attention to changes in the H-bonding pattern.

When salmon sperm DNA is treated with cis-Pt compounds and afterwards analyzed using enzymatic digestion, HPLC and NMR, we have found that the major product is a chelate of structure cis-Pt(pGpG) in which two guanine N7 atoms from neighbouring bases are binding to a cis-Pt group. Minor products are found to be cis-Pt(pApG) and products containing trinucleotides.

Binding of cis-Pt to trinucleotides GpXpG (X=C,A) indicates that in all cases chelation occurs through the N7 guanine atoms. In the case of pGpGpG, however, cis-Pt coordinates mainly to two adjacent guanines. These results suggest that chelation through both neighbouring guanines, and through guanines separated by a third base can indeed occur. When a neighbouring guanine is available, however, this chelation is more frequently occurring.

Binding of cis-$Pt(NH_3)_2Cl_2$ to a decanucleotide TCTCGGTCT- results in a similar chelate with binding through the guanine-N7 Pt-binding, results in complete formation of a double helix (as in the case when the free decanucleotides are added together), with a decreased melting temperature and a significant distortion in the central part of the duplex, as revealed by proton NMR studies in D_2O and H_2O.

1. S.J. Lippard, Science, 218 (1983), 1075-1082 and references cited.
2. A.T.M. Marcelis and J. Reedijk, Recl. Trav. Chim. Pays-Bas, 102 (1983), 121.
3. J. Brouwer, P. van de Putte, A.M.J. Fichtinger-Schepman and J. Reedijk, Proc. Natl. Acad. Sc. (USA), 78 (1981), 7010.

Ru(III) AND Rh(III) PERCHLORATE COMPLEXES OF PURINE AND PYRIMIDINE BASES

Badar Tauqi Khan and Ahmed Gaffuri

University College of Science, Department of Chemistry, Osmania University, Hyderabad-500 007 INDIA

Interaction of $M(ClO_4)_3$, [where M = Ru(III) or Rh(III)] with purine and pyrimidine bases in aqueous or aqueous methanolic solution resulted in the formation of neutral or cationic complexes. Conductivity data indicate that these complexes are 1:3 or 1:2 electrolytes except adenine complexes of Ru(III) or Rh(III) and thymine complex of Rh(III) which are non-electrolytes. These complexes are characterized by elemental analysis, ir, nmr and electronic spectra.

The presence of unidentate coordinated perchlorates in the adenine complexes and Rh(III) thymine complex is exhibited by a triply split ν_3 and ν_4 modes. In the case of guanine, hypoxanthine, cytosine, uracil and thymine complexes, the presence of exclusively ionic perchlorates is indicated by a single peak for ν_3 and ν_4 modes of perchlorate which are the fundamental vibrations of this group[1,2]. Rest of the complexes exhibit the presence of both ionic and coordinated perchlorates. The electronic spectral data exhibit the d-d transition and the LMCT bands that are in good agreement with the tentative geometry proposed for the complexes. The ir and the nmr spectra of the complexes indicate that the soft platinum group metal ions preferentially coordinate to the purine bases through N_7 and the pyrimidine bases through N_3. In none of the purine complexes the ligand coordinates through CO oxygen or the NH_2 nitrogen which is in accordance with our previous findings[3].

1. B.J.Hathaway and A.E.Underhill, J. Chem. Soc., 1961, 3091.

2. A.S.Nikumbe and R.A.Krause, Inorg. Chem., 1965, 4, 404.

3. S.T.Khan and A.Mahmood, J. Inorg. Nucl. Chem., 1978, 40, 1938.

PLATINUM GROUP METAL COMPLEXES OF HYPOXANTHINE AND GUANINE

Badar T. Khan, Aneesa Mehmood, Akbar Ali & Murali Mohan

University College of Science, Department of Chemistry, Osmania University, Hyderabad-500 007 INDIA.

Interaction of MCl_3 [M = Ru(III), Rh(III) and Ir(III)] dichlorotetrakisdimethylsulphoxideruthenium(II) and hexammineruthenium(III) chloride with guanine (2-NH_2, 6-OH purine) and hypoxanthine (6-OH purine) gave different complexes depending on the pH of the solution as well as the starting material.

In hypoxanthine complexes of Ru(III) and Ir(III), the ligand acts as a monodentate ligand, the site of metal binding being N_7 of the imidazole ring, whereas in Ru(II) and Rh(III) complexes, it acts as a bridging bidentate ligand coordinating through N_3 and N_9.

In acidic medium guanine is protonated at N_1 and the site of metal [Ru(II), Ru(III), Rh(III) and Ir(III)] binding is N_7 whereas, in basic medium N_7 and the exocyclic oxygen (C_6=O) is also involved in coordination forming a bidentate chelate.

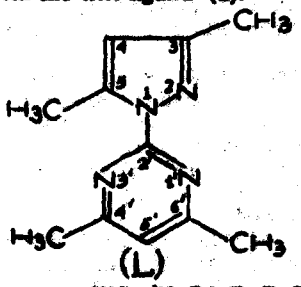
Guanine fails to react with $[Ru(NH_3)_6]Cl_3$, on contrary to hypoxanthine, that interacts with hexammine ruthenium(III) or chloropentammine ruthenium(III) replacing one ammonia or chloride ion from the coordination sphere of the metal ion. However no apparent effect of the $-NH_2$ group at the C_2 position can be attached to the varied behaviour of the ligands. These findings have been substantiated by elemental analysis, conductivity data, ir, nmr and electronic spectra.

MODEL COMPLEXES OF PALLADIUM(II) AND PLATINUM(II) WITH 3,5-DIMETHYL-1-(4',6'-DIMETHYL-2'-PYRIMIDYL) PYRAZOLE AS POTENTIAL ANTI-TUMOUR DRUGS

Nityananda Saha and Durgadas Mukherjee

Department of Chemistry, Calcutta University, Calcutta 700009, India.

The promising anti-tumour activity among some Cis-platinum(II) complexes has been the major factor in stimulating viable research in the design of "model complexes" which could mimic the interaction of metal ions with DNA. As a part of our programme[1], this communication reports the synthesis and spectroscopical characterization of twelve new Pd(II) and Pt(II) complexes with the title ligand[2] (L).



All the complexes analyzed as ML_2X_2 (M=Pd, X=Cl, Br, I, SCN, NO_2, NO_3, ClO_4, $\frac{1}{2}SO_4$; M=Pt, X=Cl, Br, SCN, NO_3) and proved to be non-electrolytes (Λ_m<80 $ohm^{-1}cm^2mole^{-1}$ at 25°C) in DMF solution. The diamagnetism of the species is authenticated by magnetic susceptibility measurements at 28°C and a square planar structure is indicated. Diffuse reflectance spectral bands in the region 17.86-21.75 and 28.6-31.2 kK are assigned to $^1A_{1g} \rightarrow {}^1A_{2g}$ and $^1A_{1g} \rightarrow {}^1E_g$ transitions respectively in square planar Pd(II) and Pt(II) complexes; spectral bands between 31.25-42.5 kK ($\epsilon = 10^4$ 1 $cm^{-1}mole^{-1}$) in DMF solutions are attributed to $M \leftarrow L_\pi$ CT bands coupled with possibly inter/intra ligand transitions. IR spectra indicate ^2N and $1'N$ heteroatoms of the ligand in metal coordination sites [ν(C=N(Pym) and ν(C=N(Pz) appearing at ~640 and ~550cm^{-1} respectively]; ^1H NMR spectra of the complexes compared with that of the ligand also supportive to this view. Coordinated nature of the counteranions (X) is evidenced by IR. spectra, and the cis-geometry of the chloro complexes is confirmed with strong νPd-Cl (at 305 and 295cm^{-1}) and νPt-Cl (at 325 and 295cm^{-1}) stretching vibrations (A_1 and B_1 in C_{2v} symmetry).

1. Saha, N., D. Bhattacharyya, and S.K. Kar, *Inorg. Chim. Acta.*, *67*, 157, 1982.
2. Saha, N., and D. Mukherjee, *Polyhedron*, *2*, 47, 1983.

COMPLEXATION OF THE ADENINE WITH CIS-DICHLOROBIS-(DIMETHYLSULFOXIDE)PLATINUM(II) IN DMSO

I. I. Volchenskova, N. N. Maidanevich, L. I. Budarin

The L. V. Pisarzhevsky Institute of Physical Chemistry of the Ukrainian SSR Academy of Sciences, Prospect Nauki, 31, 252028 Kiev (USSR)

The reactions of adenine (Ad) with platinum compounds are of interest for biology and pharmacology in modelling the possible types of interaction of antitumor platinum complexes with nucleic acids and their monomeric fragments.

The complexation of Ad with cis-$PtCl_2(DMSO)_2$ in DMSO was studied by spectrophotometric and conductometric techniques. UV spectra and conductivity for the solutions were measured at constant metal and increasing ligand concentrations. Spectral bands induced by $\pi - \pi^*$, $\pi - \pi^*$ transitions for Ad and by d - d transitions for the metal were analysed.

The dependence of the optical density of solution on a ligand-metal ratio indicates to the unteraction of components to give 2:1, 1:1, 1:2, 1:3 and 1:4 stable Pt-Ad complexes. The formation of the 2:1 Pt-Ad complex leads to a shift of absorption maximum for Ad to a long wave region by 900 cm^{-1}. With increasing the number of coordinate Ad molecules, a long wave shift value decreases. For the 1:1 and 1:2 complexes it is 500 cm^{-1} and for 1:3 and the 1:4 complexes only 100 cm^{-1}. When the ligand environment of the original complex, cis-$PtCl_2(DMSO)_2$ substituted by Ad a hypochromic effect is observed for a d - d band of the central atom.

The reaction between cis-$PtCl_2(DMSO)_2$ and Ad at Pt-Ad ratio below 2:1 proceeds without changes in the conductivity. On further addition of Ad the conductivity gradually increases. It should be noted that the conductivity increases even at Pt/Ad higher than when the interaction between these components was not detected spectrophotometrically. The conductometric data suggest the formation of the stable ionic pairs or complexes with higher coordination numbers.

The low unaffected conductivities observed in the formation of 2:1 Pt-Ad complex undicate to the absence of trans-labilised effect of DMSO and Ad on the chlorine ions in a binuclear complex μ-adenine-bis(cis-dichlorodimethylsulfoxideplatinum)(II).

MECHANISM OF ACTION OF PLATINUM(IV) ANTITUMOR AGENTS

J. F. Vollano, E. E. Blatter, R. E. Brandon
and J. C. Dabrowiak

Department of Chemistry, Syracuse University,
Syracuse, New York 13210

The platinum(IV) complex cis-trans-cis $Pt(IV)((CH_3)_2CHNH_2)_2(OH)_2Cl_2$. CHIP, 1, is currently undergoing clinical trials in the United States as a potential second generation analogue of cis dichlorodiammine platinum(II), CDDP, 2. Mechanistic studies on 1 have indicated that the compound is capable of cleaving DNA.[1] We have found that reaction of 2 with excess H_2O_2 to produce the ammonia analogue of 1 yields a pale yellow crystalline solid, 3, containing a hydrogen peroxide moiety (ir, 860 cm^{-1}, O-O str). Spin trapping experiments with PBN in water revealed that thermal decomposition of 3 results in the production of hydroxyl radical (g, 2.005; A(H), 3.6G; A(N), 15.9G) and a bright yellow solid, 4. Subsequent analysis identified 4 as cis-trans-cis $Pt(IV)(NH_3)_2(OH)_2Cl_2$ (ir: 3520 cm^{-1}, OH str; 330 cm^{-1}, Pt-Cl str. Pt-195 nmr: , 885 ppm; $J^{195}Pt-^{14}N$, 194 Hz). Incubation of PM2-DNA (37°C; Drug/DNA, 4; 20 mM TRIS-NO_3; pH, 8.0) with 1, 3 and 4 followed by agarose gel electrophoresis and ethidium bromide staining showed that of the three compounds only 3 can cleave DNA. Unaltered electrophoretic mobilities of Form I, covalently closed circular, Form II, open circular, and Form III, linear PM2-DNA in the gel matrix further suggests that none of the compounds bind to DNA. X-Ray crystallographic analysis of 3 to determine the disposition of the peroxide moiety, ultimately revealed a hydrogen peroxide molecule symmetrically bridged, via hydrogen bonding, between two cis-trans-cis $Pt(IV)(NH_3)_2(OH)_2Cl_2$ units in the crystal lattice. The above observations strongly suggest that neither DNA cleavage nor DNA binding (without reduction to Pt(II)) have important roles in the mechanism of action of the platinum(IV) based antitumor agents.

1. S. Mong, P. C. Eubanks, A. W. Prestayko and S. T. Crooke, Biochemistry, 1982, 21, 3174.

Fa60-01

REACTIONS OF FUNCTIONAL MAIN GROUP ELEMENT AND ORGANIC COMPOUNDS WITH TRIMETAL CLUSTERS

Heinrich Vahrenkamp
Institut für Anorganische und Analytische Chemie, Universität Freiburg, Albertstr. 21, D - 7800 Freiburg, Germany

Three possible entries to the chemistry of new M_3 cluster derivatives will be dealt with:

1. Capping.
   The preferred formation of $M_3(CO)_9(\mu_3\text{-}L)$ systems allows to predict many $RuCo_2(CO)_9L$ compounds with four-electron ligands L to be generated from $RuCo_2(CO)_{11}$ and appropriate precursors of RN, RP, RAs, C_2, C_4, and CN units. Likewise, starting from $Ru_3(CO)_{12}$, six-electron ligands L have to be introduced to form $Ru_3(CO)_9L$, which has been attempted with C≡C, C≡N, and C≡P containing precursors.
2. Reactions of anionic clusters.
   By our cluster construction procedures we have obtained several hydrido metal clusters. We have started to investigate the reactions of these or their anions with cationic main group element compounds or molecular main group element halides. First results will be reported.
3. Substitution with functional ligands.
   It is easy to introduce functional $AsMe_2X$ ligands with As-N, As-O, and As-ML_n units into trimetal clusters. The reactive substitution derivatives can be converted to polycyclic and cage compounds built from metal and arsenic units.

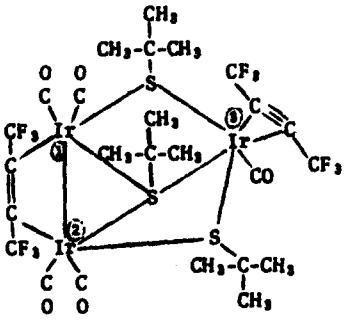
STRUCTURAL NOMENCLATURE FOR COORDINATION COMPOUNDS

T. E. Sloan and D. H. Busch

Chemical Abstracts Service, P.O. Box 3012, Columbus, Ohio 43210 and The Ohio State University, Department of Chemistry, 140 West Eighteenth Avenue, Columbus, Ohio 43210.

A topologically exact notation for coordination compounds that contain ambidentate and flexidentate ligands was proposed in 1978.[1] This notation introduced the κ (kappa) ligating atom indicator and illustrated its use for complex ligands in mononuclear coordination compounds. The κ notation is extended to polynuclear noncluster complexes, and principles for numbering central metal atoms in polynuclear noncluster complexes are presented. Examples are provided to illustrate the use of central atom numbering with the κ coordination indicator and with bridging ligands, and to designate the structure of unsymmetrical polynuclear complexes. A superscript multiplier is used with the κ, e.g., κ^2C, to provide an economical but exact structural coordination name. The bridged metal atoms are indicated by m:n, or m:n:p.

Example:[2]



μ-[1,2-Bis(trifluoromethyl)-1,2-ethenediyl-1κC^1:2κC^2]-pentacarbonyl-1κ^2C,2κ^2C,3κC-bis-μ-(1,1-dimethylethanethiolato-1:3κS,2:3κS)-μ$_3$-(1,1-dimethylethanethiolato-1:2:3κS)-[3(η^2)-1,1,1,4,4,4-hexafluoro-2-butyne]triiridium-1,2(*Ir-Ir*)

1. Sloan, T. E. and Busch, D. H. *Inorg. Chem.*, 1978, 17, 2043.

2. Devillers, J.; de Montauzon, D.; and Poilblanc, R. *Angew. Chem., Int. Ed. Engl.*, 1981, 20, 287.

NEW CLUSTERS OF Ni AND Co WITH PHOSPHINE LIGANDS

Dieter Fenske, Ramazan Basoglu, Hans Hachgenei and Friedhelm Rogel

Institute for Inorganic Chemistry, University of Karlsruhe, D-7500 Karlsruhe, FRG

$NiCl_2$ reacts with $PhP(SiMe_3)_2$ and PPh_3 to form an unknown compound. After addition of CH_3COCl, a mixture of two species were obtained, which are clusters of the following composition:

$Ni_8(CO)_4\ (\mu_4\text{-}PPh)_6\ (PPh_3)_4$; $Ni_8Cl_4\ (\mu_4\text{-}PPh)_6\ (PPh_3)_4$

1 2

1 obeys with 120 valence electrons the noble gas rule, 2 contains 116 valence electrons. The X-ray crystal structure demonstrates that both compounds contain a Ni_8-cluster. 1 is observed to be diamagnetic, whereas 2 shows paramagnetic behaviour. Therefore 2 can be regarded as a mixed valenced cluster composed of 4 Ni^{1+} and 4 Ni^0. Under reducing conditions the Cl-ligands in 2 can be replaced by CO. The oxidation of 2 with Br_2 leads to $[2]^+Br_3^-$. A Br^- containing cluster was prepared by reaction of 1 with Br_2.

The reaction of $CoCl_2 \cdot 2\ PPh_3$ and $PhP(SiMe_3)_2$ leads to $Co_4\ (\mu_3\text{-}PPh)_4\ (PPh_3)_4$ (3). This compound contains a Co_4-cluster pertaining to T_d-symmetrie and can be oxidized to $[3]^+$ and $[3]^{2+}$. With CH_3COCl 3 reacts to $[3]^+[CoCl_3PPh_3]^-$.

SYNTHESES, MULTINUCLEAR NMR STUDIES, AND STEREOCHEMICAL CONSEQUENCES OF CHELATED, BRIDGING PHOSPHINO-PHOSPHIDO LIGANDS

Devon W. Meek, Robert Glaser, Dennis J. Kounts, Robert D. Wald, Judith C. Gallucci, and Loren Chen

Department of Chemistry, The Ohio State University, Columbus, Ohio, USA 43210

Tertiary-secondary diphosphine ligands of the type $R_2PCH_2CH_2$-$CH_2P(Ph)H$ provide rational and controlled routes to phosphido-bridged bimetallic complexes. The ^1H, $^{31}P\{^1H\}$, and $^{195}Pt\{^1H\}$ NMR data on a series of phosphido-bridged diplatinum(II) and dipalladium(II) complexes and the crystal and molecular structures of two phosphido-bridged platinum(II) dimers will be reported. The compound d,l-$[PtCl\{PhP(CH_2)_2P(C_6H_{11})_2\}]_2$ was synthesized from $PtCl_2$-$\{Ph(H)PCH_2CH_2CH_2P(C_6H_{11})_2\}$ in THF and crystallized from dichloromethane ethanol as chiral crystals belonging to the orthorhombic space group D_2^1-$P2_12_12_1$. The structure was refined to an R index on F of 0.027 for 4667 observed reflections ($F_o^2 > 3[\sigma(F_o^2)]$ and 368 variables. By use of the Bijvoet method, the data crystal was found to have the (S_P,S_P)-absolute configuration. The two nonbonded platinum atoms ($Pt\cdots Pt$ = 3.5454(5) A) are bridged by two phosphido groups, the tetra-atomic Pt-μP-Pt-μP core is bent [dihedral angle = 19.1(2)°], and the two phenyl groups are *cis*. The structure of the corresponding *meso* complex was refined to an R index on F of 0.026 for 4385 observed reflections ($F_o^2 > 3[\sigma(F_o^2)]$) and 227 variables. In the *meso*-diplatinum complex, two nonbonded platinum atoms [$Pt\cdots Pt$ = 3.5771(2) A] are bridged by two phosphido groups, the tetra-atomic core is planar, and the two phenyl groups are *trans*. In a comparison of phosphido-bridged Pt(II) and Pd(II) dimers differing in core geometry, the ^{31}P chemical shift of the phosphido P-atom is shifted -22 to -41 ppm in the planar diastereomer *vis-a-vis* the corresponding bent-core isomers. The magnitudes of some $^{31}P\{^1H\}$ and $^{195}Pt\{^1H\}$ NMR coupling constants (e.g., $^2J_{\mu P-\mu P'}$, $^1J_{Pt-P}$, $^2J_{Pt-Pt'}$; $J_{meso} > J_{d,l}$) appear to be sensitive to the planar-/bent-core stereochemistry. Comparisons of the $^{31}P\{^1H\}$ data between analogous Pt(II) and Pd(II) complexes, as well as with the planar $Pt_2(\mu\text{-}PPh_2)_2$ core in other complexes, will be presented.

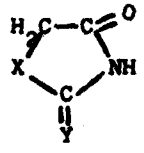
In an attempt to prepare a different type of phosphido-bridged bimetallic complex, treatment of cobaltacene, $Co(Cp)_2$, with two equivalents of secondary phosphines (*e.g.*, Ph_2PH, Et_2PH, $PhMePH$, $(C_6H_{11})_2PH$ or Me_2PH) leads to the dicobalt complexes $CpCo(\mu\text{-}PR_2)_2$-CoCp, which contain Co-Co bonds. Analogously, one equivalent of the di-secondary phosphines $PhHP(CH_2)_nPHPh$ (n = 2,3) produce similar dicobalt complexes in which the bridging phosphido groups are linked *via* the $(CH_2)_n$ chain. Sulfur dioxide breaks the Co-Co bond in both types of complexes (*i.e.*, $CpCo(\mu\text{-}PR_2)_2CoCp$ and $CpCo(\mu\text{-}PhP(CH_2)_nPPh\text{-}\mu)$-CoCp), whereas HBF_4 solutions and electrochemical studies show different behavior between the two types of phosphido ligands. Proton and P-31 NMR studies will be correlated with X-ray structural results on the dicobalt complexes.

COPPER COMPLEXES WITH PENTA-ATOMIC HETEROCYCLIC LIGANDS CONTAINING NITROGEN,OXYGEN AND SULPHUR.

Carla Cauletti,Claudio Furlani and Luisa Sestili

Dipartimento di Chimica, Università "La Sapienza" di Roma, Italia.

Ligands of general formula:



X = NH, S
Y = NH, O, S

are of great interest in the chemistry of coordination compounds.In fact in the complexes these ligands may act or as neutral molecules or as anions, having lost an hydrogen. Furthermore they possess in both formes more than one donor atoms,having therefore the possibility of being mono- or polydentate in the complexes.In the latter case then they may give rise or to a chelate structure, each ligand molecule being coordinated to only one metal atom, or to a polynuclear structure, in which the ligand is bridging between two metal ions .

With the aim of performing an extended investigation on the coordinating properties of several transition metals towards these ligands, we started with the preparation and characterization of copper complexes.

The compounds were synthesized in non-aqueous media and were not soluble in the most common organic solvent. They were characterised by means of elemental analysis, solid state UV-vis. and IR spectroscopy,magnetic measurements and, in case of the compound with X = Y = S, also gas-phase UV photoelectron spectroscopy.The results obtained indicated that in all the complexes copper is present as Cu(I), with sp hybridization giving rise to oligomeric units. For the ligands with X = Y = S and X = NH, Y = S this unit is represented by the formula $[Cu_4L_2(LH)_2]A_2$ (A = p-toluensulphonate anion), where the anion L acts as bidentate whilst the neutral molecule LH acts as monodentate. The ligand with X = S, Y = NH hydrolyses upon coordination giving rise to the complex containing the anion of the ligand with X = S, Y = O. The resulting compound has formula $[Cu_4L_2]A$, in which the ligand exhists only in the anionic bidentate forme.

STRUCTURAL STUDIES OF DIMERIC(μ-THIOLATO)OXOTUNGSTEN(V) COMPLEXES

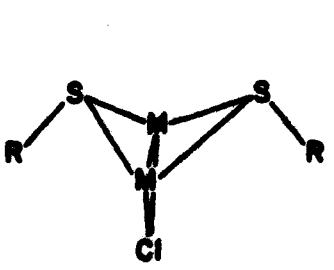
Joanne M. Ball, P. Michael Boorman and John F. Richardson
University of Calgary, Calgary, Alberta, Canada T2N 1N4

There has been extensive recent interest in the chemistry of metal thiolate complexes, as a result of the recognition of the importance of these species in biological systems. We have been interested in the structures of μ-thiolato tungsten complexes and the perturbations to these structures, and probably to their reactivities, caused by terminal oxo ligands.

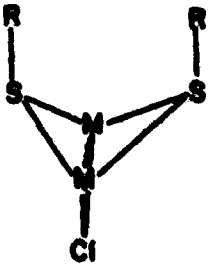
We now report the preparation and crystallographic structures of the compounds $[Ph_4P][Cl_2OW(\mu\text{-}Cl)(\mu\text{-}SPh)_2\ WOCl_2]$, (1), and $[Ph_4As][Cl_2OW(\mu\text{-}Cl)(\mu\text{-}S(p\text{-}tolyl))_2\ WOCl_2]$, (2).

These structures will be compared in detail with $[Ph_4P][Cl_2OW(\mu\text{-}Cl)(\mu\text{-}S^iBu)_2\ WOCl_2]$[1], (3) and $[(S_2CNEt_2)OMo(\mu\text{-}Cl)(\mu\text{-}SPh)_2\ MoO(S_2CNEt_2)]$[2], (4). In general the structures are found to have a greatly distorted confacial bioctahedral arrangement. The presence of very long M-Cl_{br} bonds (~2.61Å) relative to W-Cl_t bonds (~2.37Å), however, allows for an alternative description of the structures, namely that the complexes consist of two distorted square pyramidal species sharing an edge with the μ-Cl ion loosely coordinated to both W atoms.

Two types of geometry are found at the μ-SR atoms, *ee* and *aa*.



ee



aa

A discussion of the preference for the *aa* configuration, which would not be expected to be as stable as the *ee* form, on steric grounds, will be presented.

1. V.D. Patel, P.M. Boorman, K.A. Kerr, and K.J. Moynihan, Inorg. Chem., 1982, 21, 1383.

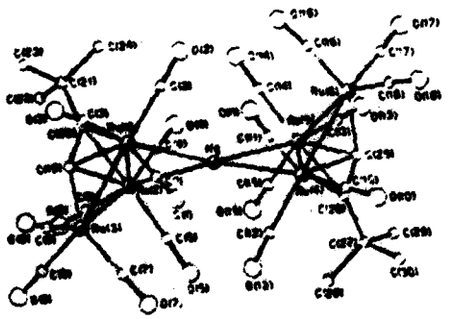
2. G. Bunzey, J.H. Enemark, J.I. Gelder, K. Yamanouchi and W.E. Newton, J. Less-Common Met., 1977, 54, 101.

STEREOCHEMISTRY AND LIGAND DYNAMICS OF A SKELETALLY CHIRAL METAL CLUSTER

Bruce Novak and Edward Rosenberg
California State University, Northridge, CA 91330

The solid state structure of $(\mu_4\text{-Hg})[Ru_3(CO)_9(\mu_3\text{-}C_2{}^tBu]_2$ (I) reveals that double butterfly cluster to be a skeletally chiral molecule. We have synthesized the mono, di, and tri-substituted phosphine derivatives of (I) by thermolysis of $P(C_6H_5)_3$ by Pt and Pd promoted substitution using $Pt(P(C_6H_5)_3)_4$ and $Pd(P(C_6H_5)_3)_4$. Substitution occurs at each wing tip first to give $(\mu_4\text{-Hg}\ [Ru_3(CO)_9(\mu_3\text{-}C_2{}^tBu)]](Ru_3(CO)_8(\mu_3\text{-}C_2{}^tBu)P(C_6H_5)_3$ (II) and $(\mu_4\text{-Hg})[Ru_3(CO)_8(\mu_3\text{-}C_2{}^tBu)P(C_6H_5)_3]_2$ (III) and then at one of the ruthenium atoms bridged by mercury to give $(\mu_4\text{-Hg})[Ru_3(CO)_7(\mu_3\text{-}C_2{}^tBu)(P(C_6H_5)_3)_2 - [Ru_3(CO)_8(\mu_3\text{-}C_2{}^tBu)(P(C_6H_5)_3)]$ (IV). The VT-^{31}P-nmr of II shows that there are three populated conformers for the phosphine, while only one radial conformer is found for $Ru_3(CO)_8(\mu_3\text{-}C_2{}^tBu)(P(C_6H_5)_3)$. This indicates that that skeletal chirality of II is conserved in solution, at least at low temperature (-80°C); and that the chirality has stereochemical consequences for bulky substituents at the ruthenium atoms. The results of further VT-^{1}H-, ^{13}C- and ^{31}P-nmr studies which demonstrate the relative rigidity of the chiral skeleton of metal atoms in I-IV will be presented.

1. E. Rosenberg, K. King, K.I. Hardcastle, A Tirripichio, Inorg. Chem., 22, 1339(1983).

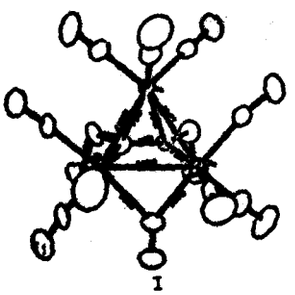


I

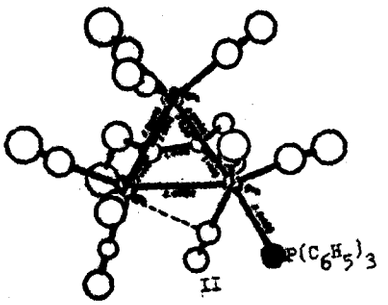
THE EFFECTS OF PHOSPHINE SUBSTITUTION OF THE STRUCTURE, DYNAMICS AND REACTIVITY OF ORGANOMETAL CLUSTERS

Julia Bracker, Edward Rosenberg and Robert W. Gellert
California State Univerasity, Northridge, CA 91330

The structure of the cluster $(\mu_3\text{-}CH_3CH_2C{\equiv}CCH_2CH_3)(\mu\text{-}CO)Os_3(CO)_9$ (I) has been determined and shows the organic ligand to be exactly parallel to the carbonyl-bridged edge of the metal triangle. The solid state structure of the phosphine-substituted derivative $[(C_6H_5)_3P]Os_3(CO)_9(\mu_3\text{-}CH_3CH_2C{\equiv}CCH_2CH_3)$ (II) has also been done and shows only one semibridging carbonyl and a shift of the organic ligand toward a perpendicular orientation. The ligand dynamics and relative reactivity of these complexes toward forther rearrangement of the organic ligand on the trimetallic site will be discussed.



I



II

FRIDAY AFTERNOON

Fp61-01

MOLECULAR STRUCTURE AND CHEMICAL REACTIVITY OF RUTHENIUM COMPLEXES

Andreas Ludi

Institut für Anorganische Chemie, Universität Bern, CH-3000 Bern 9, Switzerland.

The results of a comprehensive study of the self exchange reaction

$$*Ru(H_2O)_6^{2+} + Ru(H_2O)_6^{3+} \xrightarrow{k} *Ru(H_2O)_6^{3+} + Ru(H_2O)_6^{2+}$$

are presented and discussed in terms of the Marcus approach. The investigation of this unique low-spin d^6-d^5 couple among transition metal aqua ions comprises the determination of the crystal and molecular structures for both aqua salts, the normal coordinate analysis of the infrared and Raman spectra of the hydrated ions, and the measurement of the water exchange kinetics based on ^{17}O-NMR data. ^{17}O- and ^{99}Ru-NMR spectroscopy is employed to directly determine the self exchange rate: $k = 44\ M^{-1}s^{-1}$. The structural and kinetic data of the aqua ion are compared to the analogous properties of the ruthenium ammine complexes.

Solid salts of $Ru(H_2O)_6^{2+}$ are demonstrated to be very versatile reagents in synthetic coordination chemistry affording facile and efficient preparative routes to a wide variety of classical complexes as well as organoruthenium compounds.

Fp61-02

ELECTROCHEMISTRY AND ORGANOMETALLIC RADICALS

B.A. Narayanan, P.M. Zizelman, C. Amatore, and J.K. Kochi

Department of Chemistry, Indiana University, Bloomington, IN 47405

The use of transient electrochemical techniques as a tool for the study of organometallic and catalytic reactions will be presented. The ligand substitution kinetics of a series of carbonylmanganese cation radicals $MeCpMn(CO)_2L^+$ with L=3- and 4-substituted pyridine ligands are measured for a variety of phosphine nucleophiles N of differing steric and electronic properties. The unified free energy relationship is shown for the first time to accommodate all the extensive rate data, if the steric effect is evaluated by Tolman's cone angles for the phosphines, and the electronic effects are evaluated by the acid-base dissociation constants of the pyridine ligands and the phosphine nucleophiles. The range of second-order rate constants k_1 for ligand substitution of $MeCpMn(CO)_2L^+$ extends over four decades from 3.0 to 2×10^4 $M^{-1}s^{-1}$. The measurement of the fast rates of ligand substitution by transient electrochemical techniques is based on the novel electrocatalysis of the neutral precursor $MeCpMn(CO)_2L$ in the presence of added phosphine nucleophiles. The analysis of the electrochemical kinetics for this mechanism by Feldberg's method for the computer simulation of the cyclic voltammograms and by Saveant's adimensional evaluation of the CV peak currents is described in detail. Quantitative electrochemical methods can also be applied to the reduction of carbonylmetals to formylmetals and hydridometal intermediates and finally to methylmetalcarbonyls.

ORGANIC REACTIONS OF TRISBIPYRIDYLTITANIUM(O)

Alberto Flamini and Anna M. Giuliani

C.N.R., I.T.S.E., Area della Ricerca di Roma, Casella Postale 10, 00016 Monterotondo Stazione, Roma, Italy

$Ti(bpy)_3$ (bpy= ) is a well-known compound, first made by Herzog after the reaction:

$$2\ Li_2bpy + TiCl_4 + bpy \longrightarrow Ti(bpy)_3 + 4\ LiCl$$

It is a diamagnetic, very air-sensitive, thermally stable, blue, crystalline solid, to which a monomeric octahedral (D_3) molecular structure can be assigned.

We have found (UV, ^1H NMR) that $Ti(bpy)_3$ in solution mantains the same molecular structure as in the solid and it is stable in well deareated dry solvents.

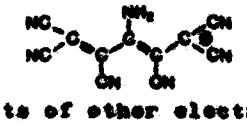
Although potentially capable of a very interesting chemistry, as the metal is in a low oxidation state (formally zero), it has not been studied so far. In the course of a research project on the use of coordination compounds for organic syntheses, we have recently focussed our attention on the reactions of $Ti(bpy)_3$ with suitable electrophiles; some preliminary results are summarized here (reaction products with benzophenone (1, Φ_2CO) and tetracyanoethylene (2, TCNE):

(1) $Ti(bpy)_3 + 4\ \Phi_2CO \longrightarrow Tibpy(\Phi_2CO)_4 + 2\ bpy$

Evidence has been obtained that the benzophenone in the final product has been reduced to pinacol.

(2) $Ti(bpy)_3 + TCNE \longrightarrow Ti(bpy)_2TCNE + bpy$

The reaction product can be further transformed by treatment with an oxidizing proton source (O_2/H_2O or (CH_3NO_2)), to the ionic species $[Ti(bpy)_2 O_m^{2-}]nC_{11}N_7H_2^-$. The anion $C_{11}N_7H_2^-$ has been fully characterized (^1H and ^{13}C NMR, IR and mass spectrum of the conjugated neutral acid $C_{11}N_7H_3$), and it has been identified as the 1,1,-2,4,5,5-hexacyano-3-amino-pentadienide:



Reaction products of other electrophiles with $Tibpy_3$ or with the analog $Ti(phen)_3$ (phen=o-phenantroline) will be presented and discussed.

A PULSE-RADIOLYSIS STUDY OF TRANS-DIAQUA-, TRANS-AQUAHYDROXO- AND TRANS-DIHYDROXO-(1,4,8,11-TETRAAZACYCLOTETRADECANE)CHROMIUM(III).

Gwyneth M. Nord and Ole Mønsted

Department I, Inorganic Chemistry, H.C.Ørsted Institute, University of Copenhagen, DK-2100 Copenhagen Ø, Denmark;

Palle Pagsberg, Anne Nielsen and Eva Floryan-Løvborg, Chemistry Department, Risø National Laboratory, DK-4000 Roskilde, Denmark.

Reaction of hydroxyl radicals with the title complexes leads to the stepwise formation of intermediates in which the metal center is oxidized. The reactant complexes are finally regenerated so that the overall process is the catalysis by the Cr(III) complexes of the disproportionation of oxygen species which are partly derived from coordinated water. Rate constants for the individual steps will be included in a description of the overall mechanism.

GAS PHASE OXIDATION OF TRANSITION METAL CARBONYL ANIONS

Kelley Lane, Larry Sallans, Robert R. Squires

Purdue University, West Lafayette, Indiana, USA 47907

The gas phase reactions between several transition metal carbonyl anions $M(CO)_n^-$ (M=Fe, Cr, Mo, Co, Mn; n=4, 5) and dioxygen have been investigated in a flowing afterglow apparatus at 300K. Extensive oxidation of the metal occurs with accompanying decarbonylation to yield a variety of novel metal oxides and dioxygen cluster anions $M(CO)_nO_m^-$, n=0-4, m=1-6 . Bimolecular reaction rates and primary product distributions have been determined in order to characterize the complex oxidation mechanisms. For instance, while most of the primary oxidation product ions from $Fe(CO)_4^-$ are rapidly converted in subsequent O_2-collisions to the observed terminal ions FeO_2^-, FeO_3^- and FeO_4^- (eq. 1), the $Fe(CO)_3O_2^-$ anion appears to be relatively unreactive even in the presence of relatively high flows of O_2 reactant.

(1) $$Fe(CO)_4^- + O_2 \begin{cases} \xrightarrow{75\%} Fe(CO)_2O^- \\ \xrightarrow{15\%} Fe(CO)_3O_2^- \\ \xrightarrow{10\%} Fe(CO)_3O^-,\ Fe(CO)_2O_2^- \end{cases} \xrightarrow{O_2} \begin{matrix} FeO_2^-, \\ FeO_3^-, \\ FeO_4^-, \\ Fe(CO)_3O_2^- \end{matrix}$$

Furthermore, the hundred-fold greater reaction rates measured for the 17-electron metal anions $Fe(CO)_4^-$, $Cr(CO)_5^-$ and $Mo(CO)_5^-$ relative to those for the 18-electron species $Co(CO)_4^-$ and $Mn(CO)_5^-$ illustrate the radical nature of these oxidations.

Reactions of several of the metal oxide anions with selected neutral molecules are also described.

KINETIC STUDIES OF TRIS (4,4,4-TRIFLUORO-1-PHENYL-1,3-BUTANEDIONATO) RUTHENIUM(III) REDUCTION IN ALCOHOLS

R. Grobelny[1] and B. Banas[2]

[1]Rivers State University of Science and Technology, Department of Chemistry, P.M.B. 5080, Port Harcourt, Nigeria; [2]Institute of Chemistry, University of Wroclaw, 50-383 Wroclaw, Poland.

Fluorinated β-diketonates of ruthenium(III) with general formula $Ru(\beta\text{-diketone})_3$ easily undergo reduction in alcoholic and other non-water solution containing strong base. The reduced form is oxidized reversibly after acidification according to:

$$Ru(\beta\text{-diketone})_3 + \bar{e} \quad \underset{H^+}{\overset{OH^-}{}} \quad Ru(\beta\text{-diketone})_3^-$$

We have carried out our kinetic investigation of reduction of $Ru(BTA)_3$, where BTA is 4,4,4-Trifluoro-1-*phenyl*-1,3-butanedione, in methanol and ethanol solution containing KOH by spectroscopic means. Results show that reaction is pseudo first order with respect to ruthenium complex or reducing agent. Reducing agents are CH_3O^- and $C_2H_5O^-$, respectively. The reaction of reduction of $Ru(BTA)_3$ in the range of concentration of base 0.00-0.20 mol dm^{-3} may be described by following kinetic equation:

$$-\frac{d[Ru(BTA)_3]}{dt} = k[Ru(BTA)_3][RO^-]$$

where R=$-CH_3$, $-C_2H_5$. At 25°C, experimentally determined values of k and activation energy E_A are:

$$k_{methanol} = 3.9 \cdot 10^{-4}\ dm^3\ mol^{-1}\ sec^{-1}$$

$$k_{ethanol} = 17.0 \cdot 10^{-4}\ dm^3\ mol^{-1}\ sec^{-1}$$

E_A (methanol) = 88.70 kJ mol^{-1}, E_A (ethanol) = 66.76 kJ mol^{-1}

1. Gordon, G., M.J. O'Connor, R.H. Holm, *Inorg. Chim. Acta.*, *5*, 381, 1971.
2. Patterson, G.S., R.H. Holm, *Inorg. Chem.*, *11*, 2285, 1972.
3. Trzeciak, A.M., R. Grobelny, J.J. Ziolkowski, *React. Kinet. Catal. Lett.*, *17*, 121, 1981.

OBSERVATIONS ON THE $IrCl_6^{2-}/IrCl_6^{3-}$ SYSTEM IN NITROUS ACID

M. S. Ram and David M. Stanbury

Rice University, Department of Chemistry, P. O. Box 1892, Houston, Texas, USA 77251

A remarkable variety of phenomena are observed in the aqueous $IrCl_6^{2-}/IrCl_6^{3-}$/N(III) system at 25° (μ = 1.0 M, $LiClO_4$). In alkaline media $IrCl_6^{2-}$ is reduced by excess N(III) with simple bimolecular kinetics. At pH 3 the reaction becomes second order with respect to [N(III)]. At pH 2 the reaction is accelerated, and the dependence on [N(III)] is fairly complex; at pH 1 the reaction is slower and no longer *pseudo-first* order.

When $IrCl_6^{2-}$ is mixed at pH 0 with excess N(III) a prompt absorbance increase occurs which is attributed to $IrCl_6^{2-}$ and which is dependent upon the age and concentration of the acidified N(III) solution. This is followed by a pseudo-first order absorbance increase which is second order in [N(III)]. At [N(III)] > 1 x 10^{-3} M this is followed by a slower non-first order loss of absorbance. The yield of $IrCl_6^{2-}$ decreases with decreasing acidity, becoming effectively zero at pH > 1; the rates, however, are independent of pH. When the reaction is performed with $IrCl_6^{2-}$ in excess, the yield of $IrCl_6^{2-}$ is strongly enhanced by dissolved O_2; in degassed solutions a limiting yield of 1:1 $AIrCl_6^{2-}/ANO_2$ is obtained; the rate law is $d[IrCl_6^{2-}]/dt = k[H^+][IrCl_6^{3-}][HNO_2]$ with k = 0.8 $M^{-2}s^{-1}$. The mechanism for this last rate law is proposed to involve rate-limiting reduction of NO^+ to NO by $IrCl_6^{3-}$. This is the first example where reduction of NO^+ by a substitution-inert reducing agent is substantially less than diffusion controlled; the dynamics are comparable with those involving the O_2/O_2^- redox couple.

MECHANISM OF THERMAL DIHYDROGEN FORMATION IN HOMOGENEOUS AQUEOUS SOLUTIONS AT pH VALUES AROUND NEUTRAL; THE SPECIAL ROLE OF SULFUR LIGANDS AND SOME BIOLOGICAL IMPLICATIONS

D. Katakis*, J. Konstantatos†, G. Kalatzis†, and E. Vrachnou-Astra†

*Inorganic Chemistry Laboratory, University of Athens, Navarinou 13A, Athens; †Chemistry Department, Nuclear Research Center "Democritos", Aguia Paraskevi Attikis, Athens, Greece.

The system investigated is the couple V^{II}/V^{III} in the presence of cysteine and other thiolo-compounds. The large excess is necessary for avoiding precipitation of insoluble hydroxides (pH 8.0-9.5). There are no complications due to heterogeneous effects. The equilibria are complex, but the overall kinetics simple. Equilibrium mixtures are investigated spectrophotometrically and polarographically. At certain pH ranges the couple V^{II}/V^{III} is reversible.

The overall kinetics of complexation of V^{II} or V^{III} with the ligands used are controlled by the first step. The mechanism is investigated in detail.

In the case of V^{II}, complexation is followed by dihydrogen formation. V^{II}-cys is one of the very few homogeneous metal ion systems known to give dihydrogen thermally under mild conditions. Compared, for example, to V^{II}-serine, which was also investigated, V^{II}-cys is more efficient. Half-wave potentials under reversible conditions do not differ much. The origin in the difference of efficiency is mainly kinetic. The study of the factors affecting the kinetics provides information about the pathways of the electron transfer from the ground state of the reductant (which can be regarded as a sacrificial donor) eventually (if no other oxidants are present) to the solvent. In this sense this study is helpful in understanding the analogous reactions of the transient and the more difficult to study excited states produced photochemically. It is also helpful in understanding some aspects of the action of biological redox systems, and especially the role of the cysteines in the active enzyme center.

BIS(BIPYRIDINE) DICARBONYL COMPLEXES OF MOLYBDENUM(II) AND TUNGSTEN(II)

Joseph A. Connor, E. Joyce James, Colin Overton, Josephine M.A. Walshe

Chemical Laboratory, University of Kent, Canterbury, Kent CT2 7NH, England

Oxidation of cis-$[M(CO)_2(bpy)_2]$ with silver(I) in coordinating solvents produces the stable metal(II) cationic complexes cis-$[Mo(CO)_2(bpy)_2(solvent)]X_2$ and cis-$[W(CO)_2(bpy)_2]X_2$ ($X=BF_4$).

Reactions with neutral two-electron donor ligands, L, such as tertiary phosphines or isocyanides, result in preferential substitution of the CO ligands at seven-coordinate molybdenum(II) to give $[Mo(CO)_2L(bpy)_2]^{2+}$, $[Mo(CO)L_2(bpy)_2]^{2+}$ and $[MoL_3(bpy)_2]^{2+}$, which contrasts with preferential substitution of the bpy ligands at six-coordinate tungsten(II) to give $[W(CO)_2L_2(bpy)]^{2+}$. Further substitution at molybdenum(II), to give $[MoL_5(bpy)]^{2+}$ has been observed. Further substitution at tungsten(II) may lead to either $[W(CO)_2L_4]^{2+}$ or $[WL_4(bpy)]^{2+}$, depending on the nucleophile.

A variety of neutral (sulphide, amine, phosphine, isocyanide, alkene, alkyne, aromatic) and anionic (oxyanion, alkoxide, thiolate amide, alkyl) nucleophiles have been investigated. The results generally emphasize the distinction between molybdenum(II) and the superior π-base tungsten(II) in these systems.

LIGAND OXIDATIVE DEHYDROGENATION OF α,ω-DIAMINE-BRIDGED COMPLEXES

Patricia A.M. Williams and Pedro J. Aymonino.

Área de Química Inorgánica (programa QUINOR), Facultad de Ciencias Exactas, Universidad Nacional de La Plata, 47 y 115, 1900 La Plata, R. Argentina.

Bidentate ligands such as ethylenediamine and 2- and 4-picolylamine coordinated to two $[Fe(CN)_5]^{3-}$ groups are readily oxidized to the coordinated diimines leading to the chromophore $[(CN)_5Fe\text{-}N\text{=}C\text{-}(C\text{=}C\text{-})_n C\text{=}N\text{-}Fe(CN)_5]^{6-}$ with n=0 and 1[1]. Examples of ligands with n=2 and 3 are 4,4'-bipyridine[2] and trans-1,2-bis(4-pyridil)ethylene[2].

All the complexes exhibit strong absorption in the visible region attributable to metal-to-ligand electron transfer. Absorption maxima are between 452 and 520 nm and show no clear correlation with n. Molar absorptions increase from 3.30 to 4.15 (log ε) with the lengthening of the bridge.

The kinetics of oxidation of $[Fe_2(CN)_{10}(4\text{-picam})]^{6-}$ (4-picam: 4-picolylamine) by peroxodisulphate, according to the following stoichiometry, has been investigated spectrophotometrically:

$$[Fe_2(CN)_{10}(4\text{-picam})]^{6-} + S_2O_8^{=} = [Fe_2(CN)_{10}(4\text{-picim})]^{6-} + 2\ HSO_4^{-}.$$

(4-picim: 4-picolylimine).

This reaction seems to be a chain reaction which obeys the following rate equation:

$$\frac{d[(Fe_2(CN)_{10}(4\text{-picim}))^{6-}]}{dt} = k[S_2O_8^{=}] ,$$

which is in accordance with the accepted mechanism of oxidation reactions by peroxodisulphate[3]. At 25°C, I=1M (NaCl), pH=9.4 ($NaHCO_3$+NaOH), k_{exp} = 9.1x10^{-3} min^{-1}.

1. This work.
2. F. Félix and A. Ludi, Inorg. Chem. 1978,17,1782.
3. D.A.House, Chem. Rev. 1962,62,185.

SOLID-STATE IRON(II/III) ELECTRON TRANSFER

Ladda Montri[1], Roderick D. Cannon[1*], David B. Brown[2], Kerry M. Marshall[3] and C. Michael Elliott.[3]
[1]School of Chemical Sciences, University of East Anglia, Norwich NR4 7TJ, England; [2]Department of Chemistry, University of Vermont, Burlington, Vermont 05405; [3]Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523.

Mixed-valence tri-μ-oxo iron acetates, $[Fe(III)_2Fe(II)O(OOCCH_3)_6L_3]$, L = H_2O or pyridine, are considered from the standpoint of their intramolecular electron transfer rates.

Infrared spectra of the mixed-metal analogues $[Fe(III)_2M(II)O(OOCCH_3)_6L_3]$, M = Mn, Co, Ni are used to identify vibrations of the planar Fe_2MO unit, and to show that the mixed-valence compound (M = Fe) has distinct valency states on the infrared time scale.

Data from Mössbauer spectra and solution redox chemistry, however, indicate appreciable electron delocalisation.

Adiabatic potential energy surfaces are calculated and fitted to the physical data available for the mixed-valence iron trimers. It is concluded that these complexes are valence trapped at room temperature, but intermediate between Robin and Day Classes II and III, with the pyridine complex particularly close to the border line.

AZOLE-CONTAINING COPPER CHELATES AS MODELS FOR THE ACTIVE SITES IN COPPER PROTEINS

Jan Reedijk

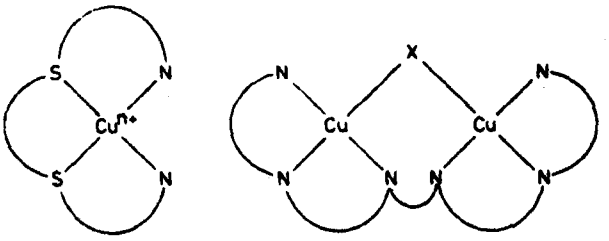
Department of Chemistry, State University Leiden, Gorlaeus Laboratories, P.O. Box 9502, 2300 RA Leiden, the Netherlands

All structurally characterised active sites of copper proteins are known to contain at least one copper-imidazole bond. This is proven to be the case for type I (or blue) copper (*e.g.* azurin and plastocyanin), type II copper (superoxide dismutase) and type III (hemocyanin), using X-ray crystallography[1].

The varying spectroscopic properties of the copper proteins are believed to originate from:
- stereochemical constraints, resulting in unusual geometries,
- presence of other ligands (such as thiolate).

Our approach to the field consists of the design, synthesis, catalytic properties, spectroscopic studies, magnetic characterisation and structure determination of coordination compounds containing copper and chelating ligands with imidazole groups (or other azole ligands)[2].

The so-designed compounds can be viewed as derivatives of the following two generalised structures:



Details of the observed structures, their spectral properties and their catalytic behaviour in oxidation reactions will be presented.

1. For a review: see H. Beinert, Coord. Chem. Rev. 33 (1980), 55.
2. P.J.M.W.L. Birker and J. Reedijk, Copper Coordination Chemistry, Biochemical and Inorganic Perspectives. K.D. Karlin and J. Zubieta (eds), Adenine Press, New York, 1983.

THE INTERACTION OF COBALT(II) AND ZINC(II) COMPLEXES WITH APOARSANILAZOTYROSINE-248 CARBOXYPEPTIDASE A

Junzo Hirose and Ralph G. Wilkins

Faculty of Pharmaceutical Sciences, Nagoya City University, Nagoya 467, JAPAN and Department of Chemistry, New Mexico State University, Las Cruces, New Mexico 88003, USA

Increasing interest is being shown in the general system (1)

$$(Apo)P + ML \rightleftharpoons PML \rightleftharpoons PM + L \qquad (1)$$

where (Apo)P represents demetallated protein and ML is a metal-ligand complex. The forward direction represents the final steps in the biosynthesis of some metalloproteins. In the reverse step, ligand L removes the metal ion M from the metalloprotein PM to produce apo, important in producing a variety of metallo-protein derivatives. A start has barely been made on studying the influence of ligand L on (1).

We have previously measured the kinetics of interaction of metal ions with apocarbonic anhydrase and apocarboxypeptidase and examined the influence of ligands on the cobalt(II)-apocarbonic anhydrase system.[1] In the present study we describe the kinetics of reaction of a variety of cobalt(II) and zinc(II) complexes with apoarsanilazotyrosine-248 carboxypeptidase A at pH 8.2, I = 1.0M (NaCl) and 25°C using stopped flow. The very rapid completion of the metal-azotyrosine-248 link at this pH[2] is used to monitor spectrally the uptake of the metal by apoprotein. Only the 1:1 metal ligand complexes were reactive and interact *in toto* with the protein. This has been observed in the transfer of metal from zinc and copper thionein to a number of apoproteins.[3]

The second order rate constants ($M^{-1}s^{-1}$) were measured for the following 1:1 cobalt-ligand complexes (zinc in parenthesis): 1,10-phenanthroline 3×10^6 (4×10^6); 1,10-phenanthroline-5-sulfonate 2.4×10^6; 2,2',2"-terpyridine 1.2×10^6; water (aqua ion) 7.7×10^5 (5.0×10^6); 8-hydroxyquinoline-5-sulfonate 9.5×10^4 (7.0×10^5); pyridine-2,6-dicarboxylate 9×10^4; batho-phenanthroline-disulfonate $< 10^5$. The sequence is quite different from that previously measured for apocarbonic anhydrase. The varied effects of ligands on the metal ion entry suggest that metal ion entry proceeds in two or more steps.

1. K. Gerber, F.T.T. Ng and R.G. Wilkins, Bioinorg. Chem. 1975, 4, 153; E.J. Billo, K.K. Brito and R.G. Wilkins, Bioinorg. Chem. 1978, 8, 461; P.C. Harrington and R.G. Wilkins, Bioinorg. Chem. 1980, 12, 107.

2. L.W. Harrison and B.L. Vallee, Biochemistry, 1978, 17, 4359.

3. F.O. Brady, Trends Biochem. Sci. 1982, 7, 143.

This work was supported by a National Science Foundation grant.

AMINOACIDATE DECHELATION UPON PEPTIDE, AMIDE, AND ALCOHOL DEPROTONATION IN Cu(II) CHELATES

C. R. Krishnamoorthy, David P. Paar, and Robert Hakon

West Virginia University, P. O. Box 6045, Morgantown, WV 26506-6045

The potentially three strongest σ-donor groups present at the active site of metalloenzymes, amide: asparagine, glutamine; alcohol: serine, threonine; and peptide groups have been shown upon deprotonation to labilize aminoacidate binding to Cu(II). The bis(N-acetamidoiminodiacetato)- and the bis(N,N-bis-(2-hydroxyethyl)glycinato)copper(II) chelates have been shown to undergo aminoacidate dechelation upon amide (eq. 1) and alcohol (eq. 2) proton ionization, respectively.

$$[Cu(ADA)_2^{3-}] \rightleftarrows [Cu(H_{-1}ADA)H_2O^-] + ADA^{2-} + H^+ \quad (1)$$

$$[Cu(bicine)_2] \rightleftarrows [Cu(H_{-1}bicine)H_2O] + bicine^- + H^+ \quad (2)$$

The mixed ligand chelate, (N,N-bis(carboxymethyl)glycylglycinato)-glycinatocopper(II), $Cu(DGDA)gly^{2-}$, has been shown to lose glycine upon peptide proton ionization (eq. 3).

$$[Cu(DGDA)gly^{2-}] \rightleftarrows [Cu(H_{-1}DGDA)^{2-}] + gly^- + H^+ \quad (3)$$

Potentiometric, visible, and electron spin resonance studies have been employed to study the above and other similar reactions. The logarithm of the equilibrium constants for eq. 1-3 are $-11.34 \pm .02$, $-12.36 \pm .02$, and $-11.68 \pm .02$, respectively.

Since reactions 1-3 are instantaneous, involve the loss of a strongly coordinated aminoacidate group in a facile manner, and contain functional groups found at the active site of metalloproteins, the systems could serve as models for substrate removal in metalloenzymes. The mechanism of the substitution reactions (eq. 1-3) appear to be of the S_N1CB variety with the conjugate base ($^-NHC(=O)-$, HO^-, and $-O-C(=O)-$, respectively) as the major substitution product and not a transient intermediate.

DISULFUR COMPLEXES OF MOLYBDENUM AND TUNGSTEN

John A. Broomhead

Chemistry Department, Faculty of Science, Australian National University, Canberra A.C.T. 2601, Australia.

Some form of sulfur ligation is known to be a feature of certain molybdoenzymes and there is considerable interest in the synthesis and reactions of both Mo and W in sulfur environments. In this paper, new complexes in which these metals are completely ligated by three different types of S donors are described.

Passage of SO_2 through a solution of $W(CO)_3(S_2CNR_2)_2$ (R = Me, Et, ^iPr, C_6H_5-CH_2, pyrrolidyl) in dichloromethane under N_2 gives a mixture which can be separated on a silica-gel column into green and red-brown products. Analyses and a variety of physical measurements support the formulation of the green product as $WS(S)_2(S_2CNR_2)_2$ and the red-brown product as $WO(S)_2(S_2CNR_2)_2$.

The same green complexes may be prepared by reaction of S_8 with $M(CO)_3(S_2CNR_2)_2$ (M = Mo, W). The properties and reactions of these compounds will be discussed.

PEROXIDE BINDING TO A CU(II) CENTER FORMED BY REACTION OF DIOXYGEN WITH A PHENOXO-BRIDGED BINUCLEAR CU(I) COMPLEX

Kenneth D. Karlin, Richard W. Cruse, Y. Gultneh, J.C. Hayes, and J. Zubieta

Department of Chemistry, SUNY Albany, Albany, NY, 12222

The reactions of dioxygen and subsequent reactivity with mono- and binuclear Cu(I) centers are of interest because of their relevance to the copper enzymes (e.g. hemocyanin and tyrosinase) involved in oxygen transport and activation. Here, we describe the synthesis and structural characterization of a novel new phenoxo-bridged binuclear Cu(I) complex, $Cu_2(XYL\text{-}O)^+$. Each Cu(I) ion is tetracoordinate with ligation to the bridging phenoxo oxygen, two pyridyl nitrogen atoms and an amino N atom. Reaction of this complex with dioxygen at -80°C in dichloromethane gives rise to a stable peroxo-Cu(II) complex which is characterized by a strong peroxo → Cu(II) CT band at 505 nm. Confirmation of the complex's formulation also comes from resonance Raman spectroscopy where a band at 803 cm^{-1} (O-O stretch) shifts to 750 cm^{-1} when isotopically labelled ^{18}-dioxygen is used to form the complex.

TERNARY COPPER(II)- L-GLUTAMATO COMPLEXES

Luciano Antolini, Giuseppe Marcotrigiano*, Ledi Menabue and Gian Carlo Pellacani

Istituto di Chimica Generale e Inorganica, University of Modena, 41100 Modena and (*) Istituto di Chimica, Facoltà di Medicina-Veterinaria, University of Bari, 70126 Bari, Italy.

Recent works on copper(II)-aspartate complexes have demonstrated that, although the coordination mode of the amino acid varies, the square-pyramidal geometry of the copper(II) ion is always preferred (1).

In order to verify if this tendency is peculiar to this type of amino acids, in this paper we report a structural, magnetic and spectroscopic investigation on some amine (imidazole, 2,2'-bipyridile, 1-10-ortophenantroline) adducts of the copper(II)-glutamato complex.

The structure of the imidazole adduct consists of neutral Cu(glu)(im) units bridging glutamato anions to give polymeric linear chains. The copper ion involves a four coordinate CuN_2O_2 chromophore in a slightly distorted square-planar geometry.

First structural results performed on the other adducts suggest different environments for the copper(II) ions.

The magnetic and spectroscopic properties of the compounds are also discussed and interpreted in the light of their known crystal structures.

The results are discussed in comparison with those of the aspartate analogues and are used to provide support for structural hypotheses based upon magnitude of equilibrium constant.

1. L.Antolini, G.Marcotrigiano, L.Menabue and G.C.Pellacani, Inorg. Chem., 22, 141 (1983) and references cited therein.

NICKEL(III) PEPTIDE COMPLEXES

Dale W. Margerum, C. Robert Dennis, Stephen A. Jacobs, William R. Kennedy, George E. Kirvan, Krishan Kumar, Mark T. Nemeth, and Thomas L. Pappenhagen

Department of Chemistry, Purdue University, West Lafayette, Indiana 47907, USA

Bis(dipeptide) and bis(tripeptide) complexes of nickel(III) are characterized in regard to the stability of the complexes, ESR spectra, electrode potentials, electron-transfer and decomposition reactions. Ternary complexes of bipyridyl, terpyridyl, and other ligands with nickel(III) peptide complexes also are characterized in solution. The trivalent oxidation state of nickel is stabilized by the bis(peptide) or ternary complexes. Electron transfer rate constants are many orders of magnitude smaller for reactions that are forced to be outer-sphere compared to reactions that can proceed by inner-sphere mechanisms via bridging ligands in the axial coordination positions of nickel(III). The coordination geometry of nickel(III) and nickel(II) complexes are compared.

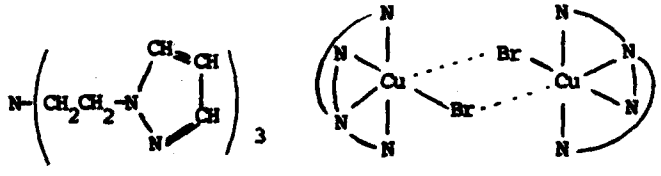
STRUCTURAL CHARACTERIZATION OF A COPPER COMPOUND WITH THE FORMULA $Cu_4Br_7L_3 \cdot 3H_2O$ (L = TRIS(1-PYRAZOLYLETHYL)AMINE)

A. Bencini* and F. Mani**

*I.S.S.E.C.C., C.N.R., Florence; **University of Florence, Department of Chemistry, Via J. Nardi, 39, Florence, Italy

Copper complexes with specially designed polydentate ligands containing pyrazole as donors are widely studied for the possible implication they may have in clarifying the structures of some metalloenzymes.

In an attempt to prepare dimeric copper complexes, $CuBr_2$ and the tetradentate ligand tris(1-pyrazolylethyl)amine, TPyEA, have been reacted in an acetone-ethanol solution. A compound with a formula $Cu_4Br_7(TPyEA)_3 \cdot 3H_2O$



has been obtained and its structure has been determined by means of a X-ray analysis.

The compound contains three non-equivalent five-coordinate $[CuBr(TPyEA)]^+$ cations, a $[CuBr_3]^{2-}$ anion, one Br^- and H_2O molecules. Two copper(II) complex cations are close to each other (see scheme) in an arrangement which resembles the structure of the dinuclear $[CoBr(TPyEA)]_2^{2+}$ complex(1), apart the two intermolecular Cu...Br distances which are distinctly longer than the intramolecular Cu-Br bond distances (370 vs. 250 pm). The third $[CuBr(TPyEA)]^+$ cation is separated by the two aforementioned cations by an interposed $[CuBr_3]^{2-}$ anion. In the discrete $[CuBr_3]^{2-}$ anion the copper(I) exhibits an almost trigonal planar coordination. This coordination is unprecedented in copper(I) halide complexes, most of which have a polynuclear structure and a tetrahedral coordination.

The $Cu_4Br_7(TPyEA)_3 \cdot 3H_2O$ compound when dissolved in acetone catalyses the formation of mesityl oxide.

1. M. Di Vaira and F. Mani, Inorg. Chim. Acta, 1983, 70, 99.

NEW MIXED-VALENCE Mn^{II}-Mn^{III} COMPLEXES. POSSIBLE ROLE OF SUCH UNITS IN THE MANGANESE WATER SPLITTING ENZYME.

Jean-Pierre Tuchagues,[†] Yeong T. Hwang[††] and David N. Hendrickson[††]

[†]Laboratoire de Chimie de Coordination-CNRS et Université Paul Sabatier, 205, route de Narbonne, 31400 Toulouse, France.

[††]University of Illinois, School of Chemical Sciences, 505 S. Mathews, Urbana, Illinois 61801, U.S.A..

The neutral molecular complexes Mn^{II}(saldien) and $Mn^{(II)}$(5-NO_2 saldien) prepared first by Taylor et al.[1] result, respectively, from the coordination of the N_3O_2 pentadentate ligands saldien and 5-NO_2saldien to manganese(II). EPR and variable-temperature magnetic susceptibility data are presented to show the presence of an intramolecular antiferromagnetic Mn^{II}-Mn^{II} exchange interaction in Mn^{II}(saldien). The magnetic behavior of Mn^{II}(5-NO_2saldien) suggests intermolecular associations in the solid state and the intramolecular Mn^{II}-Mn^{II} interactions in non coordinating solvents.

Mixed-valence Mn^{II}-Mn^{III} dimers originating from these complexes have been characterized and studied in the solution state using EPR techniques. The EPR spectra of these mixed-valence manganese II/III species exhibit a 16 line pattern identical to those described by Dismukes et al.[2] and Andreasson et al..[3]

The EPR simulation of the spectra is consistent with an antiferromagnetically coupled pair having a total spin S = 1/2 and nearly isotropic hyperfine and g tensors: $g_x = g_y = 2.006$; $g_z = 2.000$; $|A_{x,1}| = |A_{y,1}| = 170$ G; $|A_{z,1}| = 156$ G; $|A_{x,2}| = |A_{y,2}| = |A_{z,2}| \simeq 82$ G assuming a gaussian linewidth which increases with the nuclear spin quantum number.

The presence and function of such Mn^{II}-Mn^{III} mixed-valence units versus the Mn^{III}-Mn^{IV} sites suggested earlier for the manganese water splitting enzyme of photosystem II will be discussed.

1. W.M. Coleman, R.K. Boggess, J.W. Hughes and L.T. Taylor, Inorg. Chem. 1981, 20, 700.
2. G.C. Dismukes and Y. Siderer, Proc. Natl. Acad. Sci. USA 1981, 78, 274.
3. O. Hansson and L.E. Andreasson, Biochim. Biophys. Acta 1982, 679, 261.

X-RAY ABSORPTION STUDIES ON TYPE 2 COPPER PROTEINS

G.P. Diakun*, S.S. Hasnain*, L. Alagna*, and N.J. Blackburn†

*SERC Daresbury Laboratory, Warrington, Cheshire, WA4 9AD; † Department of Chemistry, University of Manchester Institute of Science and Technology, P.O. Box 88, Manchester, M60 1QD, United Kingdom.

EXAFS and XANES data have been collected for concentrated aqueous solutions of oxidised, reduced and cyanide bound bovine superoxide dismutase (SOD), native dopamine monooxygenase (DβM), and native and azide bound plasma monoamine oxidase (MAO). The copper site of SOD is found to change upon reduction to a three coordinate structure with 3 Cu-N (imidazole) groups at the shorter distance of 0.194 nm, compared to 0.199 nm in the oxidised enzyme. This result provides the first direct confirmation and is fully consistent with previous proposals that an essential step in the enzyme mechanism is the dissociation of an imidazole ligand upon reduction.

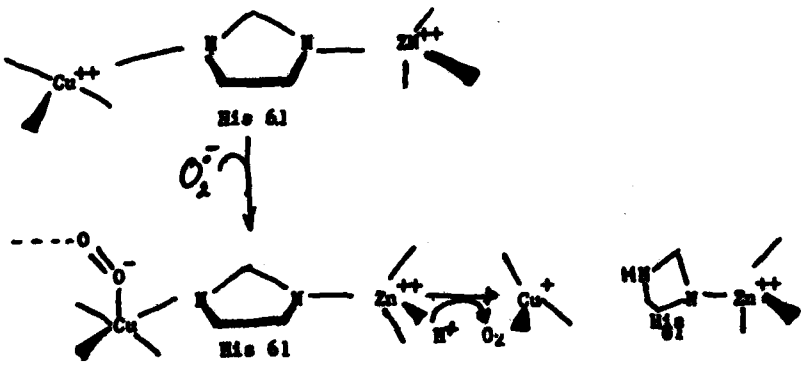


Fig. 1 Schematic mechanism and proposed structural changes around the Cu and Zn sites of superoxide dismustase during the reduction step.

Interpretation of the data for cyano-SOD suggests that CN^- displaces one imidazole ligand from the equatorial plane and leads to a decrease in Cu-N distances of the other three.

For DβM and MAO, in view of the limited quality of data, our conclusions must remain tentative. However, the EXAFS study clearly shows that in each case Cu is coordinated to > 3 imidazoles and the structures of the catalytic sites in all three enzymes are thus closely related. For DβM, Cu is surrounded by 4 imidazoles at 0.201 nm and one or two solvent molecules at 0.23 nm.

Progress has also been made in extracting angular information from the near edge structure of native SOD using multiple scattering calculations which show that most of the features can be accounted for if the imidazole rings lie above the equatorial plane at an angle of 25-30°. These calculations are being extended to the other enzymes and their derivatives.

EFFECT OF pH ON THE RATE OF LONG-DISTANCE, INTRAMOLECULAR ELECTRON TRANSFER IN RUTHENIUM-MODIFIED AZURINS

Nenad M. Kostić, David F. Blair, Huey-jeun Chiang, Joan B. Shelton, J. Rogert Shelton, Walter A. Schroeder, and Harry B. Gray

Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91126 U.S.A.

The reaction between $a_5RuH_2O^{2+}$ (a is NH_3) and *Pseudomonas aeruginosa* azurin, followed by oxidation, yields two modified proteins, containing covalently bound a_5Ru^{3+} groups. The locations of these labels were determined by peptide mapping, absorption spectroscopy, and EPR spectroscopy. One modified azurin, designated AzRu, contains a single Ru label at the imidazole ring of His-83. The other modified protein, designated $AzRu_2$, contains a label at His-83 and an additional a_5Ru^{3+} group elsewhere on the peptide chain. Both AzRu and $AzRu_2$ were examined by various spectroscopic methods (UV-VIS, CD, EPR, and resonance Raman) and the reduction potentials of the $Cu^{2+/+}$ and $Ru^{3+/2+}$ centers in the proteins were determined by thin-layer spectroelectrochemistry and cyclic voltammetry.

The modified azurins are well suited for the study of kinetics, mechanism, and thermodynamics of long-distance electron transfer. The Cu and Ru redox centers are embedded in the rigid protein matrix and held at a fixed and known distance in each protein. We have used microsecond flash photolysis to effect intramolecular electron transfer from $a_5Ru(His\text{-}83)^{2+}$ to the Cu^{2+} site in both AzRu and $AzRu_2$. The rate constant for the electron transfer is markedly pH-dependent in the former protein, but pH-independent in the latter one. We will discuss these contrasting results from mechanistic and thermodynamic points of view.

X-RAY ABSORPTION STUDIES ON TYPE 2 COPPER PROTEINS

G.P. Diakun*, S.S. Hasnain*, L. Alagna*, and N.J. Blackburn†

*SERC Daresbury Laboratory, Warrington, Cheshire, WA4 9AD; † Department of Chemistry, University of Manchester Institute of Science and Technology, P.O. Box 88, Manchester, M60 1QD, United Kingdom.

EXAFS and XANES data have been collected for concentrated aqueous solutions of oxidised, reduced and cyanide bound bovine superoxide dismutase (SOD), native dopamine monooxygenase (DβM), and native and azide bound plasma monoamine oxidase (MAO). The copper site of SOD is found to change upon reduction to a three coordinate structure with 3 Cu-N (imidazole) groups at the shorter distance of 0.194 nm, compared to 0.198 nm in the oxidised enzyme. This result provides the first direct confirmation and is fully consistent with previous proposals that an essential step in the enzyme mechanism is the dissociation of an imidazole ligand upon reduction.

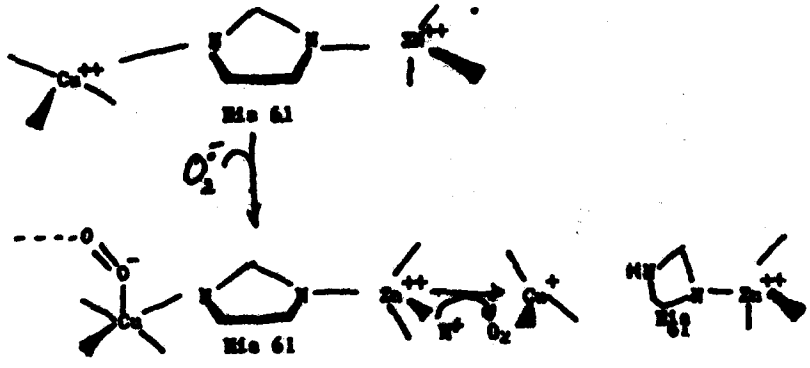


Fig. 1 Schematic mechanism and proposed structural changes around the Cu and Zn sites of superoxide dismutase during the reduction step.

Interpretation of the data for cyano-SOD suggests that CN^- displaces one imidazole ligand from the equatorial plane and leads to a decrease in Cu-N distances of the other three.

For DβM and MAO, in view of the limited quality of data, our conclusions must remain tentative. However, the EXAFS study clearly shows that in each case Cu is coordinated to > 3 imidazoles and the structures of the catalytic sites in all three enzymes are thus closely related. For DβM, Cu is surrounded by 4 imidazoles at 0.201 nm and one or two solvent molecules at 0.23 nm.

Progress has also been made in extracting angular information from the near edge structure of native SOD using multiple scattering calculations which show that most of the features can be accounted for if the imidazole rings lie above the equatorial plane at an angle of 25-30°. These calculations are being extended to the other enzymes and their derivatives.

Fp63-01

STRUCTURE, SPECTRAL PROPERTIES AND REACTIONS OF DIOXYGEN-MERCAPTO-IRON-PORPHYRIN COMPLEXES. MODELS FOR THE ACTIVE SITE OF P 450 CYTOCHROMES.

Raymond WEISS,

Laboratoire de Cristallochimie et de Chimie Structurale (E.R.A. 08), Institut Le Bel - Université Louis Pasteur - 4, rue Blaise Pascal - 67070 STRASBOURG Cedex, FRANCE.

Use of picket-fence porphyrin and weakly reducing thiolates have allowed the isolation and characterization of dioxygen adducts of mercapto-iron-porphyrins. Spectral and structural data of two such adducts will be presented. The reactivity of such adducts towards different reducing agents will be discussed. Structural data on the peroxo-iron III intermediate will be presented as will be spectral data on the reaction products of this intermediate with electrophillic species. Analogies between the spectroscopic properties, the structure and reactivity of these model compounds and those of the heme containing monooxygenase, cytochrome P 450, will be described.

CHARACTERIZATION OF FIVE-COORDINATE IMIDAZOLE-LIGATED IRON(III) PORPHYRINATES

W. Robert Scheidt, David K. Geiger and Young Ja Lee

Department of Chemistry, University of Notre Dame, Notre Dame, Indiana, USA 46556

In the course of investigations of the interaction of iron(III) porphyrinates with sterically hindered nitrogenous bases, we have isolated and structurally characterized both five-coordinate species, $[Fe(P)(L)]^+$, and six-coordinate species $[Fe(P)(L)_2]^+$. L is either 2-methylimidazole or 1,2-dimethylimidazole and P is the dianion of octaethylporphyrin. These species are high-spin in the solid state. The *five-coordinate species* are the first definitively characterized species of iron(III) porphyrinates having a neutral axial ligand. Two crystalline modifications of [Fe(OEP)(2-MeIm)]ClO_4 have been structurally characterized using X-ray diffraction data collected at 100 K. The first crystalline form contains two molecules in the asymmetric unit of structure. These two molecules form a π-π complex. A completely satisfactory analysis of this form was not possible owing to crystallographic disorder. A second crystalline form was subsequently obtained and analyzed. Structural parameters for the iron(III) coordination group are, at the current state of refinement, Fe-N(porph) = 2.038 Å and Fe-N(axial) = 2.067 Å with the iron(III) atom displaced 0.55 Å from the mean plane of the porphinato core. The corresponding structural parameters of the first, less precisely determined derivative are similar. These parameters are significantly smaller than those of other high-spin iron(III) porphyrinates having an anionic axial ligand (average Fe-N(porph) = 2.069 Å, Fe(III) displacement = 0.51 Å). This FeN_5 coordination group is, of course, closely related to the five-coordinate ferric hemoproteins having histidine as the proximal ligand.

The second derivative also forms a π-π complex between two adjacent porphinato cores with a mean planar separation of just over 3.3 Å. The occurrence of π-π complexation in these two complexes (and presumably in an isomorphous 1,2-dimethylimidazole derivative) suggests that the π-π interaction stabilizes these five-coordinate species in the solid and solution; we have been unable to prepare analogous tetraphenylporphinato species.

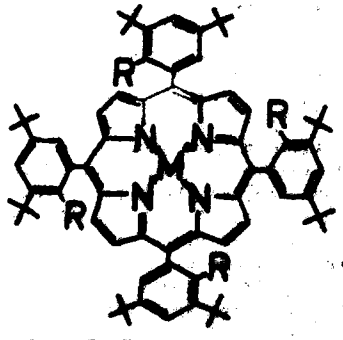
Crystal data: Form I, monoclinic, $C2/c$, a = 22.786 (6) Å, b = 15.828 (4) Å, c = 49.974 (12) Å, β = 101.70 (2), Z = 16. Form II, monoclinic, $P2_1/n$, a = 15.059 (3) Å, b = 19.040 (4) Å, c = 15.098 (3) Å, β = 98.40 (1), Z = 4.

SYNTHESES AND PROPERTIES OF NEW "BIS-POCKET" PORPHYRINS

T. Ken Miyamoto and Yukiyoshi Sasaki

Department of Chemistry, Faculty of Science, The University of Tokyo, Tokyo 113, Japan

A variety of protected porphyrins have so far provided much information relating to dioxygen reactivity. For a more complete understanding of the structure-function relationship of hemoproteins, exploitation of other protected porphyrins are obviously required. Among others, "bis-pocket" type porphyrinal[1] are the most promising candidate for the possible unsymmetrical protection to both faces of the molecular plane. We present here the examples of such a class of synthetic porphyrins 1-M and 2-M.



1-M, R = H.

2-M, R = NO_2.

M = 2H, FeBr, FeOH or $FeO_{\frac{1}{2}}$.

1-2H and 2-2H were synthesized by the Rothemund procedure and four atropisomers of 2-2H were separated by alumina column chromatography. Each isomer of 2-2H has relatively high conformational stability to light and prolonged heating.

Three protected porphyrins, 1-2H, $2\text{-2H}_{\alpha\alpha\alpha\alpha}$ and $2\text{-2H}_{\alpha\beta\alpha\beta}$, showed varying degrees of Fe incorporation as listed in Table. The resulting bromocomplexes, 1-FeBr and 2-FeBr, were converted to hydroxy iron(III) species. 1-FeOH and 2-FeOH are stable at room temperature. At higher temperature (61°C), however, 1-FeOH changes to the μ-oxo dimer, $\frac{1}{2}$-$FeO_{\frac{1}{2}}$, while four complexes, 2-FeOH, are stable for at least 8 h. Thus thermal stability of 1-FeOH is less secured than that of 2-FeOH.

All these facts clearly demonstrate that steric bulk of new porphyrins leads to the inhibitory Fe incorporation, and to stabilization of hydroxy iron(III) species. These properties make sharp contrast to those of unprotected porphyrins such as TPP or OEP system.

Practical use of 1-CoO_2 toward an antineoplastic agent will be also discussed.

Table. Fe incorporation

Free base	Conversion % *
TPP	80
1-2H	60
$2\text{-2H}_{\alpha\alpha\alpha\alpha}$	40
$2\text{-2H}_{\alpha\beta\alpha\beta}$	0

* Reaction conditions: free base 0.08 m mol; 2,6-lutidine 0.4 m mol; $FeBr_2$ 0.4 m mol; THF 20 ml; 30°C; 3h; under N_2.

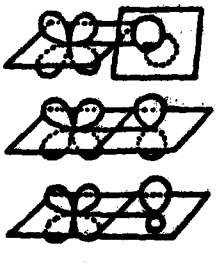
1. K. S. Suslick and N. H. Fox, J. Am. Chem. Soc., 105, 3507 (1983).

DESIGN AND SYNTHESIS OF STABLE DIOXYGEN ADDUCTS OF IRON(II) COMPLEXES ON THE BASIS OF THE NOVEL PROPOSAL ON ELECTRON TRANSFER PATHWAY

Yasuo Yamamoto, Kuninobu Kasuga, and Keiichi Tsukahara

Department of Chemistry, Shimane University.
1060 Nishikawatsucho, Matsue, 690 Japan.

The principle of oxidation- and oxygenation- mechanisms of heme iron(II) does not seem to be well established. For the thorough explanation, a hypothesis on electron transfer pathway(Fig. 1), which has been proposed by one of us(Y.Y.) and which is not in conflict with the various facts involving electron transfer, is introduced. On the basis of this hypothesis, the stable oxygenation of myoglobin and picket fence porphyrin are interpreted by the schemes of Fig. 1(c) and Fig. 1(a) types, respectively. In the present paper we report dioxygen adducts of several iron(II) complexes which have $-NH_2$ group(s) close to coordinated dioxygen(N – O(1): ~3.4 Å; N – O(2): ~2 Å), so that the electron transfer, i. e., the autoxidation of oxygenated iron(II) does not occur by the schemes of Fig. 1(a) and/or Fig. 1(c) types.



(a) Electron transfer does not occur, because the nodal planes are not coplanar. (stable oxygenation)[1)]

(b) It does. (autoxidation)[1)]

(c) It does not, because the p orbital is distorted from the reflection symmetry.[2)] (stable oxygenation)[1)]

Fig. 1

Hypothesis of electron transfer pathway.(electron is not transferred through σ bond.)
1) In the case of $Fe-O_2$ system, p orbital of this figure may be replaced by π^*orbital(electron-acceptor orbital).
2) An orbital can be distorted by, for instance, hydrogen bond.

BIOLOGICALLY RELEVANT DIFFERENCES (STRUCTURAL, THERMODYNAMIC, AND KINETIC) BETWEEN IRON(II, III) PORPHYRINS, CHLORINS, AND ISOBACTERIOCHLORINS

Steven H. Strauss, Kim M. Long, Robert V. Hudgens, Susan E. Elmore, Dennis M. Jonsrud, and J. Rory Kennedy

Colorado State University, Fort Collins, CO 80523

A variety of heme-containing oxidoreductase enzymes do not contain iron porphyrins but instead contain iron complexes of chlorins or isobacteriochlorins (hereafter collectively refered to as hydroporphyrins). The discovery of iron hydroporphyrins in these enzymes has prompted us to examine the properties of series of iron porphyrins, chlorins, and isobacteriochlorins having identical or very similar peripheral substitution. To ascertain whether a given prosthetic group is optimally suited for a particular chemical task, it is necessary to discover what features of the chemistry of iron hydroporphyrins differ from iron porphyrins.

We will present results that demonstrate that ligand affinities of Fe(P) and Fe(P)(NCS) (P = OEP, OEC, and OEiBC)[1] can vary by several orders of magnitude when the ligated five- or six-coordinate complexes, respectively, are high spin. Our hypothesis is that hydroporphyrins can more readily accomodate high spin Fe(II) and Fe(III) because they are structurally more compliant (they are more flexible and have larger cores). Our proposed structural basis for the observed ligand affinity differences is supported by the molecular structures of new iron hydroporphyrins, which we will also present.

We will also present results from our initial studies of electron transfer and ligand exchange kinetic differences between iron porphyrins and hydroporphyrins.

1. S. H. Strauss, M. E. Silver, and J. A. Ibers, J. Am. Chem. Soc., 1983, 105, 4108.

THE ACTIVE SITE STRUCTURE AND LIGAND BINDING PROPERTIES OF CHLOROPEROXIDASE

John H. Dawson, Masanori Sono
Department of Chemistry
University of South Carolina
Columbia, SC USA 29208

and Lowell P. Hager
Department of Biochemistry
University of Illinois
Urbana, IL USA 61801

Chloroperoxidase (CPO) is a unique heme-iron metalloenzyme that catalyzes both peroxide-dependent oxidations as well as halogenations of organic substrates. Spectral similarities between CPO and cytochrome P-450 have previously been cited as evidence for endogenous thiolate ligation to the CPO heme iron as has been well established for P-450. In particular, both enzymes exhibit substantially red shifted Soret UV-visible absorption maxima (~450 nm) in their ferrous CO states. However, no free sulfhydryl groups available for ligation to the heme iron have been detected in chemical studies of CPO. In order to obtain additional information about the active site structure of CPO, we have carried out extensive UV-visible absorption and magnetic circular dichroism (MCD) spectroscopic studies of both ferric and ferrous CPO in the presence of various exogenous ligands. Whenever possible, direct comparison has been made between the spectral properties of analogous states of CPO and P-450. The following major conclusions have been reached:

1. Close UV-visible absorption and MCD spectral similarities are almost always observed between analogous ligand adducts of CPO and P-450 involving over twenty-five examples of carbon, nitrogen, oxygen, sulfur and phosphorus donors to the ferric and ferrous enzymes. This is most consistent with essentially identical coordination structures for both enzymes, i.e., endogenous axial thiolate ligation trans to the site of exogenous ligand binding.
2. Most importantly, coordination of an exogenous thiolate ligand to ferric CPO yields a very red-shifted Soret UV-visible absorption maximum together with the appearance of a very prominent peak in the near-UV region. This unusual "split Soret" spectrum has only been observed in ferric porphyrin complexes with biomimetic ligands in the bis-thiolate ligated case (both model complexes and thiolate-bound ferric P-450). These data provide compelling evidence for endogenous thiolate ligation in ferric CPO.
3. Halide ions (I^-, Br^-, Cl^-, F^-) directly compete with cyanide for binding to the ferric iron of CPO. Thus the halide ions, themselves, serve as ligands to the heme iron of CPO.
4. Analysis of the binding affinities of acidic ligands to CPO as a function of pH requires that the ligands bind to the enzyme in their neutral form (HX) and then dissociate to the metal-bound anion and the protein-bound proton. These observations are consistent with analogous data on other peroxidases and catalases. In contrast, with P-450, an ionic ligand may bind directly.
5. Alkyl carboxylate ligands bind directly to the heme iron of CPO (in competition with cyanide) but yield complexes that are a mixture of high and low-spin. This contrasts directly to the P-450 case where all exogenous ligands produce exclusively low-spin complexes.

INFRARED SPECTRA OF THE INTERMEDIATE SPIN Fe(octaethylporphyrin)ClO_4

Bennett Hutchinson and Steve Sample

Abilene Christian University, Box 8208 ACU, Abilene, Texas, USA 79699

Because of their biological significance, iron porphyrin complexes have been extensively investigated. Previous work has shown the importance of the spin state of the iron in these systems.[1] This work examines Fe^{+3} in the intermediate spin state, S=3/2, in the Fe(OEP)ClO_4[2] complex using vibrational spectroscopy. The results of this study locate the position of the Fe-N and Fe-O stretching bands and indicate the symmetry of the ClO_4 in this covalent environment.

Stable isotopic substitution using $^{16}O/^{18}O$ and $^{54}Fe/^{57}Fe$ was used to identify and assign the infrared spectra. The Fe-N stretching band was placed at 270 cm^{-1} based on a $^{54}Fe/^{57}Fe$ shift of 3 cm^{-1}. Comparison of this intermediate spin result with that of the high-spin Fe(OEP)Cl Fe-N stretching band assignment of ~265 cm^{-1} shows little change.[3] Assignment of the Cl-O modes in the ν_3 and ν_4 regions were based on the $^{16}O/^{18}O$ shifts. Three intense and one weak absorption appear in the ν_3 region at 1183, 1169, 1159, and 995 cm^{-1} while three bands and a shoulder occur in the ν_4 region. These bands show isotopic shifts from 12 to 30 cm^{-1}. The C_{3v} symmetry ClO_4 predicts only two infrared active bands in each of these regions, so the ClO_4 is in a less symmetrical configuration.

The Fe-O(ClO_4) stretching band in the Fe(OEP)ClO_4 is hidden by a broad porphyrin ligand absorption between 335-365 cm^{-1}. Support for this assignment is obtained from the infrared spectra of Fe(TPP)ClO_4 which shows an absorption not present in the ligand at 362 cm^{-1} which is suggested as a Fe-O(ClO_4) absorption.

1. W. Schlodt and C. Reed, Chem. Rev. 1981, 81, 395.

2. OEP is octaethylporphyrin.

3. M. Ogoshi, R. Watanabe, Z. Yoshida, J. Hanada, and H. Watanabe, J. Am. Chem. Soc. 1973, 95, 2845.

SYNTHESIS AND PROPERTIES OF IRON(III) PORPHYRIN COMPLEXES WITH HIGHLY OXIDIZING OXYANION LIGANDS

Harold M. Goff, Gregory M. Godziela, and Lisa A. Ridnour,
Department of Chemistry, University of Iowa, Iowa City, Iowa 52242
USA

A variety of new oxyanion complexes of iron(III) porphyrins have been prepared and isolated from nonaqueous media. Oxyanion ligands include IO_3^-, ReO_4^-, WO_4^{2-}, and CrO_4^{2-}. The complexes are synthesized either by a metathesis reaction between the chloro-iron(III) porphyrin complex and the silver oxyanion salt, or by reaction of the oxyacid with the oxoiron(III) porphyrin dimer. Reactions are monitored by optical and proton NMR spectroscopy. Proton NMR spectra of iron(III) tetraphenylporphyrin complexes reveal a hyperfine-shifted pyrrole proton signal in the far downfield region diagnostic of a high-spin iron(III) configuration. The chromate complex is particularly novel in view of the limited coordination chemistry known for this strolgly oxidizing ion. The chromate complex is assumed to have a bridged dimeric structure on the basis of a 2:1 iron to chromate analysis, and proton NMR spectra which show large chemical shift differences for non-equivalent meta-phenyl proton resonances. Reactions of the complexes with organic substrates are under investigation.

ELECTRONIC EFFECTS IN TRANSITION METAL PORPHYRINS. THE EFFECT OF SYMMETRICAL vs. UNSYMMETRICAL AND PARA vs. META PHENYL SUBSTITUTION ON THE FORMATION CONSTANTS OF A SERIES OF TETRAPHENYLPORPHINATO-IRON(III)-BIS-N-METHYLIMIDAZOLE COMPLEXES

F. Ann Walker and Virginia L. Balke

Department of Chemistry, San Francisco State University, 1600 Holloway Ave., San Francisco, California, USA 94132

We have previously shown that all Zn(II) tetraphenylporphyrins form complexes with the axial ligand, 3-picoline, whose stabilities are rationalized on the basis of the Hammett equation,[1]

$$\log \frac{K_X}{K_H} = (\Sigma\sigma_X)\,\rho \qquad (1)$$

irrespective of whether the phenyl substituents are symmetrically or unsymmetrically arranged, or whether they are attached at the meta or para positions of the phenyl rings. In contrast, Fe(III) tetraphenylporphyrins exhibit a more complex behavior. For the general reaction

$$PFeCl + 2\ N\text{-}MeIm \underset{CHCl_3,\ 25^{\circ}C}{\overset{B_2}{\rightleftharpoons}} PFe(N\text{-}MeIm)_2^{+}Cl^{-} \qquad (2)$$

tetra-para-substituted TPP complexes have previously been shown to behave according to equation (1), with $\rho = -0.39$.[2] (The negative sign is due to the necessity of stabilizing a positive charge on Fe(III) in the product.[2]) However, tetra-meta-substituted TPP complexes and unsymmetrically para-substituted TPP complexes, $(p\text{-}X)_n(p\text{-}Y)_{4-n}TPPFeCl$, have recently been found to behave according to equation (1) with identical values of $\rho = -0.18$. These results lead to a re-evaluation of the Fe(III) porphyrin bis-axial ligand complex formation system, in which tetra-para-substituted TPPs are now viewed as behaving anomalously. The reason for this "anomalous" behavior is believed to be the forced conjugation of the fourth phenyl ring in the product, $(p\text{-}X)_4TPPFe(N\text{-}MeIm)_2^{+}Cl^{-}$, in order to remove the formal positive charge on Fe(III). That this is an unfavorable process is seen by the fact that it does not occur until the fourth identical substituent is added.

Amide-containing TPPFeCl derivatives exhibit their own type of "anomalous" behavior, in that they form complexes significantly more stable than predicted by their Hammett substituent constants. This effect is explained in terms of ion-pair stabilization of the product through H-bonding of the amide to the displaced chloride.

The implications of these findings to the redox potentials of heme proteins and the properties of the Picket Fence porphyrin will be discussed.

1. G. A. McDermott and F. A. Walker, Inorg. Chim. Acta, in press.
2. F. A. Walker, M.-W. Lo and M. T. Ree, J. Am. Chem. Soc., 98, 5552(1976).

Fp63-9

RESONANCE RAMAN SPECTRA OF CHLORINS AS MODELS FOR THE PROSTHETIC GROUPS OF "GREEN" HEME PROTEINS

Laura A. Andersson, Thomas M. Loehr, Chi K. Chang, Anthony R. Lim, and A. Grant Mauk

Department of Chemistry & Biochemical Sciences, Oregon Graduate Center, Beaverton, OR 97006 (LAA & TML); Department of Chemistry, Michigan State University, East Lansing, MI 48824 (CKC); and the Department of Biochemistry, University of British Columbia, Vancouver, BC V6T 1W5.

Resonance Raman spectra of iron chlorin complexes have been investigated as models for the prosthetic groups of the "green" heme proteins. The RR spectra of Fe(III)-photoprotoporphyrin IX and Fe(III)-deuterochlorin, in which ring B of their porphyrin macrocyles are reduced, show several new bands above 1000 cm^{-1} that are not observed in porphyrin spectra. Furthermore, the pattern of relative intensities is strikingly different and there is a significant increase in the number of totally-symmetric (i.e., polarized) RR modes in the chlorin spectra.

Sulfmyoglobin (SMb) is an example of a "green" heme protein. This protein exhibits an anomalous electronic absorption spectrum after reaction of myoglobin with certain sulfur-containing reagents, and has been postulated to result in reduction of the porphyrin moiety [1]. The RR spectra of oxidized and reduced SMb are diagnostic of a chlorin-containing prosthetic group. The increased number of spectral lines and the greater number of polarized RR bands are consistent with a general loss of symmetry of the chlorins vs. the porphyrins.

Both Fe(II)SMb and Fe(III)SMb show two strong spectral features near 1360 cm^{-1}. Porphyrin complexes exhibit only a single, strong band at this frequency, the well-characterized oxidation-state marker band [2]. However, two polarized RR bands are also evident in the spectra of Ni(II)-, Cu(II)-, and Fe(III)-octaethylchlorins [3], as well as in the RR spectra of the chlorin-containing heme cd_1 from Pseudomonas aeruginosa [4].

[1] T. Brittain, C. Greenwood, & D. Barber, Biochim. Biophys. Acta, 136, 121 (1982).
[2] T.G. Spiro, in "Iron Porphyrins," Pt. II, A.B.P. Lever & H.B. Gray, Eds., Addison-Wesley, 1983, Chap.3.
[3] Y. Ozaki, T. Kitagawa, & H. Ogoshi, Inorg. Chem. 18, 1772 (1979).
[4] T.M. Cotton, R. Timkovich, & M.S. Cork, FEBS Lett. 133, 39 (1981).

Fp64-01

PHOSPHINE COMPLEXES OF TRI- AND TETRAVALENT URANIUM

Richard A. Andersen
Chemistry Department, University of California
Berkeley, California 94720

The coordination chemistry of tri- and tetravalent uranium compounds with tertiary phosphines will be described. Traditionally actinide metals are classified as class a or hard acceptors. The principal reason for this classification was the non-existence of phosphine complexes of these metals. We have recently prepared the eight coordinate (idealized D_{2d}-symmetry) complexes, $UX_4(Me_2PCH_2CH_2PMe_2)_2$, where X is Cℓ, Br, Me, or OPh. We have prepared the related nitrogen and arsenic complexes, $UCℓ_4(Me_2NCH_2CH_2NMe_2)_2$ and $UCℓ_4(1,2\text{-}(Me_2As)_2C_6H_4)_2$. Equilibrium constant measurements show that the affinity of these complexes is in the order N < P > As. Thus, the phosphine ligand is a stronger donor than either the amine or arsine ligand towards $UCℓ_4$. The same pattern of affinity is observed in the trivalent complexes of the type Cp_3UL, where L is PMe_3 or pyridine. Hence, phosphine ligands are better donors than amine ligands towards tri- or tetravalent uranium, in contrast to previously held views.

THE DIRECT ELECTROCHEMICAL SYNTHESIS OF THORIUM AND URANIUM COMPOUNDS

N. Kumar, L. Matassa and Dennis G. Tuck

Department of Chemistry, University of Windsor
Windsor, Ontario, Canada N9B 3P4

The electrochemical oxidation of a metal into a non-aqueous solution phase provides a simple one-step room temperature synthetic route to neutral and anionic metal halide complexes.[1] With thorium and solutions of halogen (X_2; X = Cl,Br) in acetonitrile[2], the products are $ThX_4.4CH_3CN$, which can be easily transformed into other neutral adducts, or by heating in vacuo to the uncomplexed ThX_4. In the presence of X_2+R_4NX, the products are $[R_4N]_2[ThX_6]$. Solutions of I_2 in CH_3CN give rise to $ThI_2.2CH_3CN$, from which ThI_2, ThI_2.bpy, or $ThOI_2$ are easily obtained.[3] All these syntheses have many advantages over earlier high temperature routes.

With uranium $|X_2|CH_3CN|$ cells under a nitrogen atmosphere, the products are again $UX_4.nCH_3CN$ compounds, from which related derivatives can be formed, but in the presence of oxygen one obtains analogous neutral or anionic UO_2X_2 species.

The β-diketonate derivatives ThL_4 (L = $acac^-$ and analogues) can be prepared by similar routes,[4] as can UL_4 and UO_2L_2.

Thorium(IV) nitrate species can be obtained by oxidising the metal electrochemically into either $N_2O_4|EtOAc|CH_3CN$ or $HNO_3|$tri-n-butyl phosphate solutions. The uncomplexed $Th(NO_3)_4$,its neutral adducts, and salts of $[Th(NO_3)_6]^{2-}$ have all been prepared in good yield by such methods.

1. C. Oldham and D.G. Tuck, J. Chem. Ed., 1982, 59, 420.
2. N. Kumar and D.G. Tuck, Can. J. Chem., 1982, 60, 2579.
3. N. Kumar and D.G. Tuck, Inorg. Chem., 1983, 22, 1951.
4. J.J. Habeeb, D.G. Tuck and F.H. Walters, J.Coord. Chem., 1978, 8, 27.

SYNTHETIC AND STRUCTURAL CHEMISTRY OF GADOLINIUM AND OTHER LANTHANIDE CATECHOLATE COMPLEXES

Gwen E. Freeman and Kenneth N. Raymond

Department of Chemistry and Materials and Molecular Research Division, Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720 USA

Several lanthanide(III) complexes with catechol (1,2-dihydroxybenzene) have been prepared and characterized by structural, analytical, and spectroscopic techniques. Only 1:1 complexes are observed at low pH, but bis-, tris-, and tetrakiscatecholato lanthanide complexes have been prepared in basic (pH > 12) solutions.

The structures of tris- and tetrakiscatecholato gadolinium compounds have been determined by single crystal X-ray diffraction. The $Na_5Gd(catecholate)_4 \cdot 19.2H_2O$ has D_{2d} dodecahedral molecular symmetry and the structure is nearly isomorphous with the previously characterized[1,2] series $Na_4M(IV)(catecholate)_4 \cdot 21H_2O$, M = U, Th, Ce, and Hf. The triscatecholato Gd complex is a dimer, $Na_6[Gd(catecholate)_3]_2 \cdot 20H_2O$. Each gadolinium atom is seven-coordinate and coupled by two bridging catecholate ligands.

Analytical and crystallographic data tentatively indicate the formulation $Na_2[Gd(catecholate)_2]_2 \cdot 20H_2O$ for the biscatecholate complex.

The solution composition/product interdependence of the synthetic chemistry of these compounds will be presented and compared to the solution chemistry[3] of other lanthanide catecholates.

1. S. R. Sofen, K. Abu-Dari, D. P. Freyberg and K. N. Raymond, J. Am. Chem. Soc. 1978, 100, 7882.

2. S. R. Sofen, S. R. Cooper and K. N. Raymond, Inorg. Chem. 1979, 18, 1611.

3. D. Zhu, M. Kappel and K. N. Raymond, manuscript in preparation.

SIMPLE AND BIMETALLIC LANTHANIDE (ACTINIDE) ALKOXIDES AS SYNTHONS IN INORGANIC CHEMISTRY

Ram C. Mehrotra
University of Rajasthan, Jaipur 302004 (India)

Simple and bimetallic isopropoxides of lanthanides (actinides), $Ln(OPr^i)_3$ and $Ln[Al(OPr^i)_4]_3$, can be synthesized easily by the reactions of their anhydrous chlorides alcoholates with requisite quantities of sodium isopropoxide or potassium tetraisopropoxy-aluminate.

All these can be easily purified by crystallization or volatilisation(particularly the latter). They react with considerable facility with water and a variety of hydroxy organic compounds(ROH) like alcohols, phenols, fluoroalcohols ; glycols, ethanolamines, organic and silyl esters, β-diketones, fluoro-β-diketones, β-ketoesters, salicylaldehyde ; β-ketoamines, β-salicylaldimines, carboxylic, fluoro and hydroxy carboxylic acids to yield a variety of simple and mixed derivatives:

$$Ln(OPr^i)_3 + n\ ROH \xrightarrow{C_6H_6} Ln(OPr^i)_{3-n}(OR)_n + n\ Pr^iOH\uparrow$$

$$Ln[Al(OPr^i)_4]_3 + 3n\ ROH \longrightarrow Ln[Al(OPr^i)_{4-n}(OR)_n]_3 + 3n\ Pr^iOH\uparrow$$

These products are proving of great interest from a number of points of view like catalysis (pure oxides and mixed oxides), laser properties (anhydrous pure β-diketonates, for which this is the only convenient route in a number of cases), shift reagents, gas chromatography (fluorinated derivatives) and structure (coordination, association and 'f' orbital participation).

A number of very interesting mixed ligand derivatives have been synthesized by the reaction of the type:

$$Ln(OPr^i)_x(A)_{3-x} + x\ HB \longrightarrow Ln(B)_x(A)_{3-x} + x\ Pr^iOH$$

Structural features of the derivatives are being investigated in detail.

1. D.C.Bradley, R.C.Mehrotra and D.P.Gaur, ' Metal Alkoxides', Academic Press, 1978.
2. R.C.Mehrotra, et al., Coord. Chem. Rev., 1980, 31,67.
3. R.C.Mehrotra, 'Recent Adv.Inorg.Radiochem.',Vol.XXVI, Academic Press.1983.

ACTINIDE AND LANTHANIDE EXTRACTION CHEMISTRY WITH NEUTRAL BIFUNCTIONAL ORGANOPHOSPHORUS COMPOUNDS

Anthony C. Muscatello and James D. Navratil

Rockwell International, Rocky Flats Plant, P. O. Box 464, Golden, Colorado 80401

Research on actinide and lanthanide extraction chemistry with neutral bifunctional organophosphorus compounds (such as carbamoylmethylphosphonates) has been slow developing compared to monofunctional compounds.[1] In the last few years however, with increased applications of these reagents in the nuclear field,[2-6] there has been a renaissance in the chemistry of these compounds. Applications have been primarily with the reagents dihexyl-N,N-diethylcarbamoylmethylphosphonate (DHDECMP) and to a lesser extent, the dibutyl analog (DBDECMP). Both DHDECMP and DBDECMP extract actinides and lanthanides appreciably from nitric acid solutions whereas few other elements are extracted. The extraction mechanisms of some actinides and lanthanides have been reported.[1] Addition of tributylphosphate to both DHDECMP and DBDECMP has been found to synergistically enhance the extraction of plutonium and americium.[6,7] The chemistry of these reagents with selected lanthanide and actinide elements will be reviewed with emphasis on recent work in the authors' laboratory.

1. W. W. Schulz and J. D. Navratil in N. N. Li (Ed.) Recent Developments in Separation Science, Vol. 7, CRC Press, Boca Raton, FL, 1982, p. 31.

2. W. W. Schulz and L. D. McIsaac in W. Muller and R. Linder (Eds.) Transplutonium Elements, North Holland Pub. Co., Amsterdam, 1976, p. 433.

3. J. D. Navratil and G. H. Thompson, Nucl. Technol., 43, (1979), 136.

4. L. L. Martella, J. D. Navratil and H. T. Saba, in J. D. Navratil and W. W. Schulz (Eds.) Actinide Recovery from Waste and Low Grade Sources, Harwood Academic Publishers, New York, 1982.

5. W. I. Yamada, L. L. Martella and J. D. Navratil, J. Less-Common Metals, 86, (1982), 211.

6. J. D. Navratil and L. L. Martella, Sep. Sci. Technol., 16, (1981), 1147.

7. A. C. Muscatello, J. D. Navratil and M. E. Killian, Sol. Extr. Ion Exch., 1, (1983).

URANYL COORDINATION POLYMERS

Christopher J. Hardiman, Ryszard Grybos and Ronald D. Archer

Department of Chemistry, University of Massachusetts, Amherst, MA 01003

Metal ions coordinated with bridging ligands can form polymers with properties quite different from analogous organic polymers without metals. However, intractability is a serious problem in such polymers where the metal is an integral part of the backbone. In order to minimize this problem, we are using three approaches: (1) oxo metal ions, (2) bulky ligands, and (3) non-rigid coordination centers. We have previously reported on the latter approach[1] for eight-coordinate zirconium and tungsten(IV).

Uranyl polymers have been synthesized through solution reactions and by interfacial methods for a wide variety of ligands, including aliphatic, olefinic, acetylinic, and aromatic dicarboxylates; bis-8-quinolinols; bis-Schiff-bases; bis-β-diketones; and quinones. Pyridine and dimethylsulfoxide solvate the growing polymers and solubilize them until the molecular weights reach the maximum allowed by reagent stoichiometry. The reactions are forced through distillation of acetic acid and the solvent under reduced pressure when uranyl acetate is used as the reagent. Interfacial syntheses involve uranyl nitrate in diethyl ether and the ligand anions in water.

Rigorous molecular weight evaluations of these and other coordination polymers have been made with N-methyl-2-pyrrolidone solutions on Superstyrogel gel permeation columns, with viscosity measurements, and by end group analyses. The results indicate number-average molecular weights of up to 30,000 for some of the film forming uranyl polymers.

The polymer films have interesting properties. Excellent glass adhesion and good lithographic sensitivity are two which we have investigated.

1. R. D. Archer, W. H. Batschelet and M. L. Illingsworth, J. Macromol. Sci.-Chem., 1981, A16, 261.

SYNTHESIS AND IDENTIFICATION BY X-RAYS DIFFRACTION AND I.R. SPECTROSCOPY OF MIXED ALKALINE AND RARE EARTH POLYPHOSPHATES

Dalila Ben Hassan, Mokter Farid, Najia Ariguib and Malika Trabelsi

Ecole Normale Supérieure, Zarzouna, Bizerte, Tunisie.

The condensed phosphates have acknowledged a great evolution since the discovery of luminescent properties of Neodym ultraphosphate ($Nd P_5O_{14}$) in 1972(1). These properties might be extended to mixed monovalent and rare earth polyphosphates(2), (3).

So the study of mixed monovalent (M^I=Li, Na, K, Rb, Cs, NH_4^+) and rare earth (La, Sm,...) polyphosphates gives a double interest. It permits-to study a fundamental problem which may lead to the identification of new compounds, - to obtain compounds with "a high added value".

Two types of mixed coumpounds $M^ILn(PO_3)_4$ and $M^I_2Ln(PO_3)_5$ have been synthetized for the first time:

$LiLn(PO_3)_4$
$NaLn(PO_3)_4$
$K Ln(PO_3)_4$; $K_2Ln(PO_3)_5$—$(NH_4)Ln(PO_3)_4$; $(NH_4)_2Ln(PO_3)_5$

$RbLn(PO_3)_4$; $Rb_2Ln(PO_3)_5$—$TlLn(PO_3)_4$; $Tl_2Ln(PO_3)_5$

$CsLn(PO_3)_4$; $Cs_2Ln(PO_3)_5$

$AgLn(PO_3)_4$

(Ln=La, Sm)

The new coumpounds have been isolated and characterized by X-Rays diffraction and I.R. Spectrum.

Two methods for the preparation of these new coumpounds have been stated.

Crystal unit cell parameter as well as the space group, of the different varieties have been difined.

The I.R. spectra of these coumpounds indicate if phosphate anions are chain phosphates or cyclic phosphates.

1. H.G. Danielmeyer and H.P. Weber, J. Quant. Elect., 1972, 8 , 805.
2. D.Bimberg,D.J. Robbins, D.R. Wight and J.P. Jeser, Appl. Phys.Lett., 1975, 27, (2), 67.
3. K. Otsuka, T. Yamada, M. Saruwaterie and T. Kumura, IEEE J. Quant. Elect., 1975, QE-11, 330.

SYNTHESIS AND ANALYTICAL APPLICATIONS OF STEREOCHEMICALLY RIGID LANTHANIDE CHELATE COMPLEXES

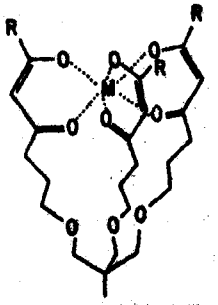
K. C. Brooks, B. A. Medeiros, D. M. Walba, R. W. Siergiej, R. M. Barkley, and R. E. Sievers

University of Colorado, Campus Box 449, Boulder, Colorado, USA 80309

An important property of six-coordinate lanthanide complexes is the ability to expand their coordination sphere to form seven- or eight-coordinate species. This property is exploited in the use of lanthanide chelates as shift reagents for NMR spectroscopy and as complexing sorbent gas chromatography stationary phases.

Two classes of stereochemically rigid tulip-shaped hexadentate ligands have been synthesized. One class is based on the Schiffs' base condensation of tris(2-aminoethyl)amine with a variety of β-diketone compounds. The Eu(III) and Yb(III) complexes can function as NMR shift reagents.

A more stable hexadentate ligand, tris(2-oxo-9,9,9-trifluoro-6,8-nonanedione)ethane, H_3tfne (R=CF_3), has been synthesized in two major synthetic steps.



TULIP LIGANDS

The first step is a Williamson ether synthesis affording 1,1,1-tris-(2-oxo-6-pentanone)ethane. A condensation reaction with ethyltrifluoroacetate then yields H_3tfne. Positive ion fast atom bombardment mass spectrometry of the europium(III) complex of H_3tfne in thiodiglycerol exhibits M + 1 ions at m/z = 809 and 811 (with isotope patterns characteristic of europium). The use of a different ester in the condensation allows for the introduction of different substituents at the end of the tripod legs.

The application of lanthanide complexes as NMR shift reagents and their use in GC stationary phases will be presented.

NICKEL AND BIMETALLIC COBALT-NICKEL CARBIDE CLUSTERS

Giuliano Longoni, Alessandro Ceriotti and Mario Manassero

Dipartimento di Chimica Inorganica e Metallorganica e Centro del CNR, via G. Venezian 21, 20133 Milano, Italy

Carbide carbonyl clusters are known for several transition metals (Re, Fe, Ru, Os, Co, Rh).[1] In contrast, analogous compounds of nickel subgroup metals, other than bimetallic derivatives such as $[Fe_4Ni_2C(CO)_{14}]^{2-}$, $[Fe_5NiC(CO)_{15}]^{2-}$ and $Fe_5MC(CO)_{16}$ (M=Ni, Pd),[1] were unknown. The absence in the literature of nickel carbide molecular clusters was rather surprising when considering the existence of a Ni_3C binary phase.[2]

We will report the synthesis and structural characterization of a series of carbide clusters of Co-Ni and Ni containing up to four interstitial carbon atoms. Species so far characterized by X ray include $[Co_3Ni_9C(CO)_{20}]^{3-}$, $[Co_3Ni_7C_2(CO)_{18}]^{3-}$, $[Co_6Ni_2C_2(CO)_{16}]^{2-}$, $[Ni_8C(CO)_{16}]^{2-}$, $[Ni_9C(CO)_{17}]^{2-}$, $[Ni_{10}C_2(CO)_{16}]^{2-}$ and $[Ni_{16}C_4(CO)_{23}]^{4-}$.

Several of the above compounds are labile under carbon monoxide atmosphere; when degradation reactions were carried out under mixtures of CO and H_2, hydrocarbons were detected in the gas phase. Mixtures of hydrocarbons (C_1-C_4) result also from reaction of these derivatives with acids. Metal-carbide binary phases show similar behaviors.[2] Whether simple hydrolysis and/or proton-induced reduction of cluster-bound CO[3] is at the origin of hydrocarbons is being investigated.

1. M. Tachikawa and E.L. Muetterties, Prog. Inorg. Chem., 28 (1981) 203.
2. A.F. Wells, Structural Inorganic Chemistry, 5th ed., Clarendon Press, London, 1975.
3. R.H. Whitmire and D.F. Shriver, J. Am. Chem. Soc., 1980, 102, 1456.

SUBSTITUTION REACTIONS OF PHOSPHORUS LIGANDS ON TRI-RUTHENIUM CLUSTER COMPLEXES; CATALYSIS BY HALIDE IONS.

Carsten E. Kampe, Guy Lavigne and Herbert D. Kaesz

University of California, Los Angeles, California, USA 90024

Edge double-bridged tri-ruthenium carbonyl complexes undergo facile substitution of a carbonyl group by a phosphorus ligand at 25 °C in benzene solution. When a bridging acyl group is present substitution occurs exclusively on the ruthenium atom to which the acyl oxygen atom is bonded. The starting materials undergo rapid exchange with ^{13}CO permitting their enrichment for ^{13}C NMR studies.

$Ru_3(\mu\text{-}H,\mu\text{-}O{=}C(Me))(CO)_{10}$ reacts within 4 hr with one molar equivalent of triphenylphosphine to give the substitution product $Ru_3(\mu\text{-}H,\mu\text{-}O{=}C(Me))(CO)_9PPh_3$, in 48% yield. 25% of starting material and some 10% of the complex $Ru_3(CO)_{11}PPh_3$, are also obtained. With excess triphenylphosphine less of the monosubstituted acyl hydrido complex is obtained. Reaction with $P(OMe)_3$ requires an excess of phosphite but then only a 15% yield of $Ru_3(\mu\text{-}H,\mu\text{-}O{=}C(Me))(CO)_9P(OMe)_3$ is isolated along with $Ru_3(CO)_{11}P(OMe)_3$, (5%).

The complexes $Ru_3(\mu\text{-}H,\mu\text{-}X)(CO)_{10}$ react within 10 min with one equivalent of triphenylphosphine to yield the products $Ru_3(\mu\text{-}H,\mu\text{-}X)(CO)_9PPh_3$, X=Cl, Br or I, respectively. When X=I a carbonyl group is readily lost from the product to give $Ru_3(\mu\text{-}H,\mu,\text{-}I)(CO)_8PPh_3$. This transformation is reversible.

The complexes $Ru_3(\mu\text{-}X,\mu\text{-}O{=}C(Et))(CO)_{10}$, X=Cl, Br or I, react in less than 1 min with triphenylphosphine to give nearly quantitative yields of $Ru_3(\mu\text{-}X,\mu\text{-}O{=}C(Et))(CO)_9PPh_3$ (98, 95 and 93%, respectively) or trimethylphosphite to give $Ru_3(\mu\text{-}X,\mu\text{-}O{=}C(Et))(CO)_9P(OMe)_3$ (78, 75 and 68%, respectively). Exposure of $Ru_3(\mu\text{-}Cl,\mu\text{-}O{=}C(Et))(CO)_{10}$ in benzene solution to an atmosphere of ^{13}CO leads to instantaneous specific enrichment at four atoms equilibrating to two additional sites within 2 hr. The remaining four carbonyl groups are enriched on a much longer time scale.

Halide ions in the form of their salts have been found to catalyze the substitution of PPh_3 into $Ru_3(CO)_{12}$ in tetrahydrofuran. Polysubstituted complexes are obtained within 1 hr reflux at 25 °C. The catalysis is more effective in producing polysubstituted complexes than the radical ion catalysis discovered by M.I. Bruce and co-workers.[1] The degree of substitution is controlled by the amount of PPh_3 added to the system.

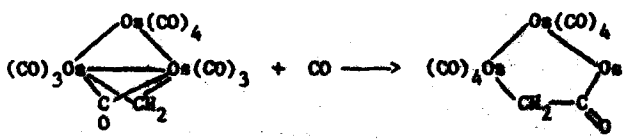
1. M.I. Bruce, J.G. Matisons and B.K. Nicholson, J. Organomet. Chem. 1983, 247, 321.

PRODUCTS FROM THE REACTIONS OF $Os_3(CO)_{11}(\mu\text{-}CH_2)$ WITH CO, SO_2, Cl^-, AND OTHER NUCLEOPHILES

Eric D. Morrison and Gregory L. Geoffroy

Department of Chemistry, Pennsylvania State University, University Park, PA 16802

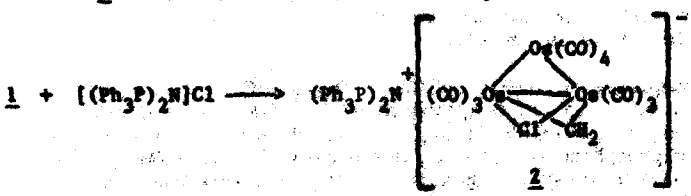
The methylene-bridged cluster $Os_3(CO)_{11}(\mu\text{-}CH_2)$, 1,[1] has a rich derivative chemistry. It reacts with CO to give the new ketene substituted cluster $Os_3(CO)_{12}(\mu\text{-}CH_2CO)$ whose structure as determined by an x-ray diffraction study is that shown in eq 1. The mechanism



(1)

1

of formation of this ketene substituted cluster will be discussed as well as its reactions with H_2, H_2O, and CH_3OH. Complex 1 also reacts rapidly with $[(Ph_3P)_2N]Cl$ to yield the new chloride-bridged cluster 2 which has also been structurally characterized, eq 2.



(2)

This $\mu\text{-}CH_2$ cluster 2 also reacts with CO to give new products which will be described. The reactions of the $\mu\text{-}CH_2$ cluster 1 with SO_2, $[(Ph_3P)_2N]NO_2$, $[(Ph_3P)_2N]N_3$, and other nucleophiles will also be presented.

1. Steinmetz, G. R.; Geoffroy, G. L., J. Am. Chem. Soc., 1981, 103, 1278.

HETERO-TETRAMETALLIC Ni_2Fe_2 CLUSTERS WITH ALKYNE-DERIVED SUBSTITUENTS.

Arthur J. Carty and Carl Westerhall, Department of Chemistry, University of Waterloo, Ontario, Canada.

Enrico Sappa, Institute of Inorganic Chemistry, University of Turin, Italy.

Antonio Tiripicchio, Institute of Inorganic Chemistry, University of Parma, Italy.

We synthesized and characterized several tri- to hexa-nuclear heterometallic clusters containing nickel and metals of the iron triad. When $Fe_3(CO)_{12}$ is reacted with $(Cp)_2Ni_2(RC_2R')$, the square planar clusters $(Cp)_2Ni_2Fe_2(CO)_6(\mu_4\text{-}\eta^2\text{-}RC_2R')$ are obtained[1].

For R=H, R'=isopropenyl, besides to the above structure, a spiked triangular isomer $(Cp)_2Ni_2Fe_2(CO)_5(\mu_3\text{-}CO)[C.C(H)C(=CH_2)\text{-}CH_3]$ can be obtained[2].

Cluster expansion and contraction reactions for the above clusters have been attempted with success, and will be discussed; the observed cluster core isomerism can be explained on these bases.

By using molecular hydrogen as reaction gas, a considerable increase in the yields of the square planar $(Cp)_2Ni_2Fe_2(CO)_6(C_2Ph_2)$ is observed; the structure of the complex has been studied by X-rays and will be discussed together with its reactivity.

Extension of the same preparative method to the reaction of $Fe_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}\eta^2\text{-}C_2Ph)$[3] with $[(Cp)Ni(CO)]_2$ leads to very high yields of a new Ni_2Fe_2 cluster, the phosphido-bridged $(Cp)_2Ni_2Fe_2(CO)_5(PPh_2)(C_2Ph)$, which has been characterized by i.r., ^1H, ^{13}C and ^{31}P n.m.r. and F.A.B. mass spectrometry. An X-ray structural investigation on this complex is in progress.

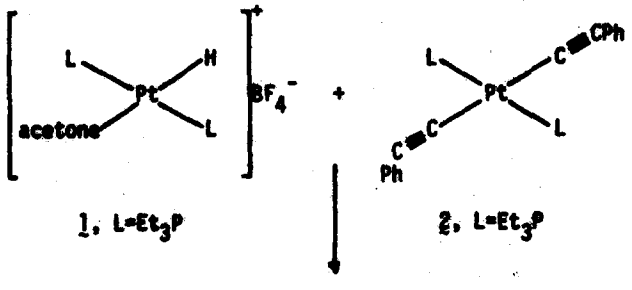
1. E. Sappa, A. Tiripicchio and M. Tiripicchio Camellini, J. Organometal. Chem., 198 (1980) 243.
2. M.L. Nanni Marchino, E. Sappa, A.M. Manotti Lanfredi and A. Tiripicchio, J. Chem. Soc. Dalton Trans., in the press.
3. H.A. Patel, R.G. Fischer, A.J. Carty, D.V. Naik and G.J. Palenik, J. Organometal. Chem., 90 (1973) C 49.

ADDITION OF M-H BONDS ACROSS METAL-ACETYLIDE C-C TRIPLE BONDS: A DIRECT ROUTE TO DINUCLEAR μ_2-VINYLIDENE COMPLEXES.

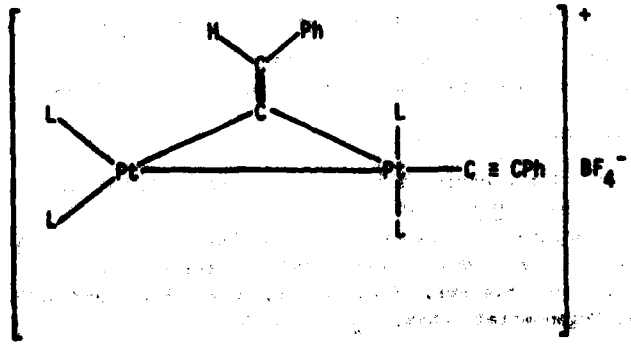
Dawood Afzal, P. G. Lenhert and C. M. Lukehart
Vanderbilt University, Department of Chemistry,
Nashville, Tennessee, USA 37235

There is considerable current interest in discovering direct preparative methods for the synthesis of complexes containing unusual types of ligands and for the synthesis of dinuclear complexes. We have discovered that reactive M-H bonds can add across the C-C triple bonds of metal-acetylide ligands to give dinuclear μ_2-vinylidene complexes. As an example, the cationic Pt-H complex, 1, reacts with the acetylide complex , 2, to give the μ_2-vinylidene complex, 3, as shown below.

The x-ray structure of 3 will be presented. At current refinement, the Pt-Pt distance in 3 is 2.750(1) Å. The reaction of 1 with other metal-acetylide complexes will be discussed also.



1, L=Et_3P 2, L=Et_3P



3, L=Et_3P

TOWARDS A FIELD MODEL OF TRANSITION-METAL CLUSTERS

Arnold J. Ceulemans
University of Leuven, Laboratory of Quantum Chemistry,
Celestijnenlaan 200F, Leuven, Belgium B-3030

Several important concepts of coordination chemistry derive from Ligand-Field Theory which provides a versatile model of the electronic structure of transition-metal complexes. Currently two rival forms of the theory are in use, based either on a global or a local parametrization scheme. Whereas the global scheme offers a complete description of the symmetry of the ligand-field hamiltonian as a whole, its local counterpart rests upon the elementary unit of a metal ion and a single ligand. In a typically chemical way of thinking, the complex is assembled from these elementary building blocks, assuming straightforward ligand additivity.

Both models necessarily are limited to mononuclear compounds, containing one central metal ion, which provides a predominant central field. Quite in contrast polynuclear clusters lack such a field, since all important interactions are tangential rather than radial. This so called heterarchical electronic structure of clusters challenges well established bonding concepts. As an alternative to most recent treatments, which focus on the local interactions between neighbouring nuclei, an attempt will be made to develop a cluster-field theory of the global type. Following the methodology of the global ligand-field models, the covering group of simple polynuclear clusters is identified, suitable hamiltonian forms are adduced, and fundamental parameters are proposed.

VIBRATIONAL STUDY AND CRYSTAL STRUCTURE OF (μ_4-η_2 ACETYLENE) DECACARBONYL TETRACOBALT, (μ_4-η_2 C_2H_2)$Co_4(CO)_8(\mu CO)_2$.

Giuliana Gervasio, Rosanna Rossetti and Pier Luigi Stanghellini

Istituto di Chimica Generale ed Inorganica, Università di Torino (ITALY)

The title compound and its deuterium and ^{13}C isotopic derivatives have been prepared from the reactions of $Co_4(CO)_{12}$ and C_2H_2, C_2D_2 and $^{13}C_2H_2$, respectively. Infrared data on the acetylene ligand vibrational modes were collected and assigned on the basis of the frequency shifts by the isotopic labelling and of the comparison with appropriate models. The very low value of the C-C stretching frequency suggests a large π-back--bonding donation from the Co_4 unit, which lowers considerably the C-C bond order. Comparison of the acetylene frequencies with those of the acetylene adsorbed on Ni (111) faces[1] shows good correspondence.

The molecule structurally consists in a butterfly arrangement of cobalt atoms, which coordinate the C_2H_2 ligand in such a way that the C-C axis is nearly parallel to the hinge of the butterfly. The C-C bond length (1.399(7)Å) and the great back-bending angle (53°) of the acetylene confirm the strong decrease of the "acetylenic" character of the ligand. Each Co atom bears two terminal CO groups, whereas two asymmetric CO's bridge two opposite edges of the butterfly. The Co-Co distances are: 2.559 Å (hinge), 2.464 Å av. (unbridged edge), 2.450 Å av. (bridged edge); the dihedral angle of the butterfly is 116°. The entire molecule possesses an approximate C_2 symmetry.

The complex crystallizes in the monoclinic space group $P2_1/c$ with a = 11.228(2) Å, b = 8.514(2) Å, c = 17.793(3) Å, β = 94.35(2)°, Z = 4. All the atoms, hydrogens included, were located with the final index R = 0.044 for 2750 observed reflections.

1) J.E. Demuth and I. Ibach, Surf. Sci. 1979, 85, 365.

NITROGEN-HYDROGEN BOND FORMATION FROM NITRIDO AND NITROSYL METAL CARBONYL CLUSTERS

Wayne L. Gladfelter, Margaret L. Blohm, Joanne Smieja, and Douglas E. Fjare

Department of Chemistry, University of Minnesota, Minneapolis, MN 55455

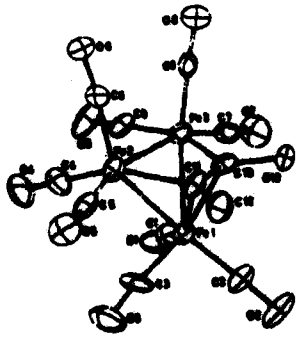
New imido (NH) and amido (NH_2) complexes of metal carbonyl clusters have been formed using coordinated N atoms or NO as the source of the nitrogen. The results of the reaction of the nitrido clusters $[FeRu_3N(CO)_{12}]^-$, $[FeRu_3N(CO)_{10}[P(OCH_3)]_2]^-$, and $[Ru_4N(CO)_{12}]^-$ with strong acids will be reported. With $[FeRu_3N(CO)_{12}]^-$ and $[FeRu_3N(CO)_{10}[P(OCH_3)_3]_2]^-$ quantitative formation of the conjugate acid occurs via intensely colored intermediates. While the proton ultimately bridges the hinge metal-metal bond of the butterfly clusters framework the intermediate has been identified as an imido cluster. Spectroscopic characterization of the unusual species will be presented. The protonation of $[Ru_4N(CO)_{12}]^-$ with CF_3SO_3H also proceeds through a deep purple species. The final product mixture contains $[Ru_5N(CO)_{14}]^-$, $HRu_4N(CO)_{12}$, and the new imido cluster $Ru_3(NH)(CO)_{10}$. When CO is added to the reaction immediately after formation of the purple intermediate, the color is quenched and $Ru_3(NH)(CO)_{10}$ can be isolated in 50% recrystallized yield.

The reaction of $HOs_3(CO)_{10}(NO)$ with hydrogen generates the amido cluster $HOs_3(NH_2)(CO)_{10}$ in 26% yield. Further reaction with H_2 leads to $H_4Os_4(CO)_{12}$. Details of this reaction and its ruthenium analog will be presented.

CARBON MONOXIDE ETHYLIDYNE COUPLING INDUCED BY ONE-ELECTRON REDUCTION OF $(\mu_3\text{-CO})(\mu_3\text{-CCH}_3)Fe_3(CO)_9\ P(C_6H_5)_4$: X-RAY CRYSTAL STRUCTURE OF THE RESULTING COMPOUND $(CH_3CCO)Fe_3(CO)_9\ P(C_6H_5)_4$ 2 CONTAINING A PROPYNOLATE ANION $\mu_3\text{-}\eta^2$ BONDED AND STUDY OF ITS TRANSFORMATION INTO $(\mu_3\text{-C}\equiv\text{CCH}_3)Fe_3(CO)_9\ P(C_6H_5)_4$ BY CARBON OXYGEN SCISSION

Dominique de Montauzon, Françoise Dahan and René Mathieu
Laboratoire de Chimie de Coordination du CNRS associé à l'Université Paul Sabatier, 205 route de Narbonne, 31400 Toulouse, France

We have recently found[1] that the electrochemical one-electron reduction of $(\mu_3\text{-CO})(\mu_3\text{-CCH}_3)Fe_3(CO)_9\ P(C_6H_5)_4$, 1 leads to a paramagnetic complex which analyses as $Fe_3(CO)_{10}CCH_3\ P(C_6H_5)_4$ 2. This compound is protonated by weak acids giving $(\mu_3\text{-C}\equiv\text{CCH}_3)Fe_3(CO)_9\ P(C_6H_5)_4$ formally resulting from carbon-oxygen breaking and coupling of the generated carbide with the ethylidyne ligand. We have now isolated 2 and the X-ray crystal structure (Fig. 1) gives evidence that the one-electron reduction has induced the coupling of the ethylidyne ligand and carbon monoxide. The CH_3CCO unit is $\mu_3\text{-}\eta^2$ bonded and can be described as a propynolate anion. The mechanism of carbon-oxygen breaking will be discussed in the light of these results.



1. D. de Montauzon and R. Mathieu, J. Organomet. Chem. 1983, 252, C83.

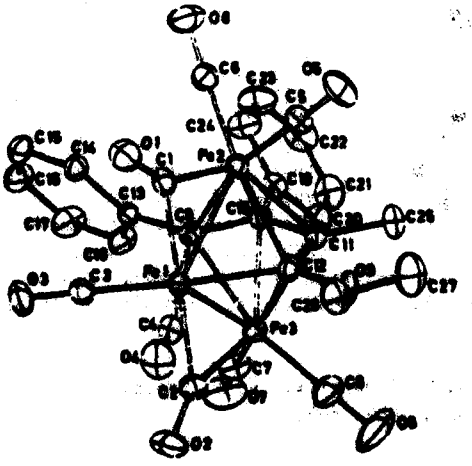
INTRAMOLECULAR CARBYNE-CARBYNE COUPLING INDUCED BY THE ACTION OF HYDROGEN OR DIPHENYLACETYLENE ON THE TRINUCLEAR BIS CARBYNE IRON CLUSTER $(\mu_3\text{-}CCH_3)(\mu_3\text{-}COC_2H_5)(Fe_3(CO)_9$

Didier Nuel, Mohamed Lourdichi, Françoise Dahan and René Mathieu
Laboratoire de Chimie de Coordination du CNRS associé à l'Université Paul Sabatier, 205 route de Narbonne, 31400 Toulouse, France

At 70°C and under 20 atmosphere pressure of hydrogen, the title cluster is destroyed. Gas chromatography analysis of the solution shows that the main product of the reaction is $C_3H_7OC_2H_5$ i.e. the product resulting from the coupling and hydrogenation of the two carbyne fragments. A further example of induced intramolecular carbyne-carbyne coupling results from the action of diphenylacetylene on the same cluster in refluxing toluene. The reaction products analyzes as $Fe_3(CO)_8((C_6H_5)C)_2(CCH_3)(COC_2H_5)$.

An X-ray crystal structure determination shows that the molecule contains a ferracyclopentadiene ring resulting from the coupling of diphenyl acetylene with the fragment formed by the coupling of the two carbyne ligands (Figure 1).

The mechanism of this novel reaction will be discussed and the reactivity of $(\mu_3\text{-}CCH_3)(\mu_3\text{-}COC_2H_5)Fe_3(CO)_9$ toward other unsaturated molecules will be presented.

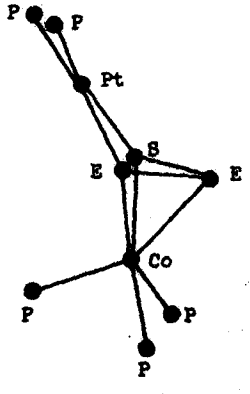


INSERTION OF THE $Pt(PPh_3)_2$ UNIT INTO INORGANIC TRIATOMIC RINGS COORDINATED TO METAL-LIGAND MOIETIES

Massimo Di Vaira, Simonetta Moneti, Maurizio Peruzzini, Luigi Sacconi, and Piero Stoppioni

Dipartimento di Chimica, Università, Via J. Nardi, 39, 50132 Firenze Italia

We have recently synthesized and characterized cobalt complexes of formula $[(triphos)Co(E_2S)]BF_4$ (triphos = 1,1,1-tris(diphenylphosphinomethyl)ethane; E = As, P) containing the heterocyclic diphosphorus sulfur or diarsenic sulfur units tribapto(η^3)-coordinated to the metal atom. We now report that on reaction of the $[(triphos)Co(E_2S)]BF_4$, E = P, As, compounds with $(C_2H_4)Pt(PPh_3)_2$ complexes of formula $[(triphos)Co(E_2S)Pt(PPh_3)_2]BPh_4$ are obtained, formed by insertion of the $Pt(PPh_3)_2$ unit into a bond of the triatomic ring. The structures of the two compounds, which are isomorphous to each other, have been established by single-crystal X-ray diffraction analysis. The cobalt atom (see scheme) in the two derivatives is coordinated by the three phosphorus atoms of the triphos ligand and by the atoms of the P_2S or As_2S unit. The latter is considerably distorted from the regular triangular shape it has in the parent $[(triphos)Co(E_2S)]^+$ cation,[1] since the bond where insertion occurs lengthens considerably (P_2S, 2.81; As_2S, 3.03 Å) whereas the other two bonds in the ring have normal values. The platinum atom is in a nearly planar arrangement formed by the two PPh_3 phosphorus atoms and by the two atoms defining the long side of the distorted P_2S or As_2S group. This is a novel type of reaction for coordinated triatomic inorganic rings.



1. M. Di Vaira, M. Peruzzini, and P. Stoppioni, J. Chem. Soc. Chem. Commun., 1982, 894.

METALLO-LIGAND COMPLEXES OF METAL CARBONYLS

Elliott L. Blinn, Irene S. Cihon, Mark R. Mason, Maria L. Poor, Paul M. Treichel and Marvin H. Tegan

Bowling Green State University, Bowling Green, Ohio, USA, 43403
and University of Wisconsin, Madison, Wisconsin, USA, 53706

Metal complexes containing either terminal oxygen or sulfur atoms are known to coordinate to other metal(II) or metal(III) ions. We have prepared, characterized, and studied the physical and chemical properties of a variety of heterometallic complexes that were prepared from metallo-ligands and organometallic compounds. In effect, a low oxidation state complex and a typical oxidation state complex are fused into a single molecular species.

The reactions of $Mn(CO)_5Br$ or $Mn(CO)_3(CH_3CN)_2Br$ with Msalen (where M is Cu, Co, Fe, Zn and salen is the condensation product salicylaldehyde and ethylenediamine) in a variety of solvents resulted in the substitution products having the general formula $[Mn(CO)_3Msalen]Br$. The $Mn(CO)_3Cusalen$ complex could be decarboxylated by heating the complex at 155°C under vacuum. During the reaction of $Mn(CO)_5Br$ with Cusalen a band at 1730 cm^{-1} in the infrared region appears and disappears. The 1730 cm^{-1} infrared band suggests that a bridging carbonyl between the Mn and Cu exist in the intermediate. (The other $[Mn(CO)_3Msalen]Br$ complexes have not yet been investigated to order to determine whether similar chemistry occurs.) The reactions of Cosalen and Cusalen with $Mn(CO)_5Br$ in xylene resulted in a polynuclear complex that does not contain carbonyl groups.

The reactions of biacetyl-bis-(mercaptoethylimino)-nickel(II), NiBe, or 2,3-pentanedione-bis-(mercaptoethylimino)-nickel(II), NiPe, with $Mo(CO)_6$ or $Mo(CO)_4C_7H_8$ resulted in the product $Mo(CO)_4NiBe$ and $Mo(CO)_4NiPe$. Both compounds showed the expected four bands in the carbonyl region. The magnetic moment for $Mo(CO)_4NiPe$ is 0.980 BM. These reactions are sensitive to the nature of the solvent. Hexane, toluene and 2-propanol appeared to be most effective. A similar product occurs upon reaction of bis-acetylacetone-ethylenediimino nickel(II), Ni(acacen), and $Mo(CO)_4C_7H_8$. $Mo(CO)_4Ni(acacen)$ is formed. The reaction of $(NH_4)_2MoS_4$ with $Mo(CO)_6$ in refluxing DMF resulted in complete decarboxylation. The nature of the product has not yet be ascertained. No reaction occurred between MnCosalen or Cosalen with either $Mo(CO)_6$ or $Cr(CO)_6$.

ANIONIC THIONITROSYL COMPLEXES OF RUTHENIUM(II) AND OSMIUM(II)

Krishna K. Pandey

Department of Chemistry, Devi Ahilya Vishwavidhyalaya Indore-452 001, India

The synthesis, structure and bonding of transition metal thionitrosyl complexes has been provocative subject for few years.[1] I report here for the first time the synthesis of anionic thionitrosyl complexes of ruthenium(II) and osmium(II).

Trithiazyltrichloride reacts with hydrated ruthenium trichloride and osmium trichloride in tetrahydrofuran to give a brown product $Ru(NS)Cl_3$, ν(NS) 1295 cm^{-1} and a green product $Os(NS)Cl_3$, ν(NS) 1290 cm^{-1} respectively. The complexes $A_2[M(NS)Cl_5]$ (A = NH_4, PPh_4; M = Ru, Os) are prepared by the addition of an aquous solution of ACl to an aquous solution of $M(NS)Cl_3$. The recrystallization of $(PPh_4)_2[M(NS)Cl_5]$ in H_2O-CH_3OH (1:1) mixture yields red crystals $(PPh_4)[Ru(NS)Cl_4(H_2O)]$ and green crystals $(PPh_4)[Os(NS)Cl_4(H_2O)]$. The NS stretching frequency in these complexes appears in the range 1255-1300 cm^{-1}.

In the complexes $(PPh_4)[M(NS)Cl_4(H_2O)]$, ruthenium (or osmium) is octahedrally coordinated with H_2O trans to the NS group. The M-N-S group is approximately linear with an Ru-N-S angle 170.9(4)° and Os-N-S angle 171.8(2)° (Table). The shortening of bond trans to NO^+ ligand[2] and the lengthening of bond trans to NS^+ ligand have been observed.

Table : Bond angle (°) and bond lengths (Å) for $(PPh_4)[M(NS)Cl_4(H_2O)]$

Complex	M-N-S	N-S	M-N	M-O
$[Ru(NS)Cl_4(H_2O)]^{-1}$	170.9(4)	1.504(4)	1.729(4)	2.112(3)
$[Os(NS)Cl_4(H_2O)]^{-1}$	171.8(2)	1.502(2)	1.747(4)	2.178(3)

1. H.W. Roesky and K.K. Pandey, Adv. Inorg. Radiochem. 1983, 26, 337.
2. R.D. Feltham and J.H. Enemark, Topics Inorg. Organomet. Stereochem., 1981, 12, 155.

SYNTHESIS AND PROPERTIES OF PENTACARBONYLTRIFLUOROMETHANESULFANATO MANGANESE(I) AND RHENIUM(I)

Steven P. Schmidt, Jay Nitschke, and William C. Trogler

Department of Chemistry, Northwestern University, Evanston, Illinois, USA 60201

The complexes $M(CO)_5(O_3SCF_3)$, where M = Mn and Re, were prepared by the reaction between $M(CO)_5Br$ and $Ag(O_3SCF_3)$ in CH_2Cl_2 solvent. Infrared spectra show that the triflate $(O_3SCF_3)^-$ ligand is coordinated to the metal center. These complexes readily substitute the triflate ligand stoichiometrically with weak nucleophiles such as ether or THF. Multiple ligand substitution is observed with an excess of nucleophile. In addition, the reactions of the complexes $M(CO)_5(O_3SCF_3)$ with carbonylmetalates will be discussed.

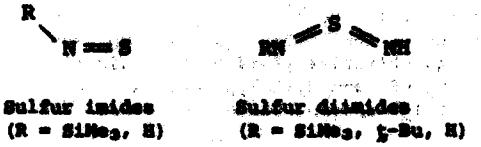
In the super acid solvents HO_3SCF_3, HO_3SF, and HO_3SCF_3/SbF_5, and HO_3SF/SbF_5, the triflate derivatives will react with CO to yield $M(CO)_6^+$ and this reaction proceeds dramatically faster upon SbF_5 addition. Addition of SbF_5 to a HO_3SCF_3 solution of $Re(CO)_5(O_3SCF_3)$ causes a specific shift in the ^{13}C NMR resonance trans to the triflate ligand. Solutions of the $M(CO)_5(O_3SCF_3)$ complexes can also be generated in nearly quantitative yield by the oxidation reaction between anhydrous HO_3SCF_3 and $M_2(CO)_{10}$ complexes, or by protonation reactions of $Mn(CO)_5B$ species where B = a base such as pyridine, Br^-, or H^-.

The $M(CO)_5(O_3SCF_3)$ complexes exhibit a low energy electronic absorption (380 nm for Mn and 322 nm for Re) in CH_2Cl_2 solution. SCF-Xα-DV calculations for $Mn(CO)_5^+$ predict the d-d transition $8e \rightarrow 10a_1$ to occur at 409 nm. In HO_3SCF_3 solvent $Mn(CO)_5(O_3SCF_3)$ exhibits an absorption $\varepsilon = 1400\ cm^{-1}M^{-1}$, at 396 nm.

STABILIZATION OF SMALL SULFUR-CONTAINING MOLECULES IN TRANSITION METAL COMPLEXES

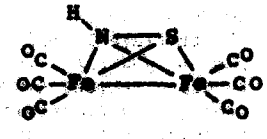
M. Herberhold, W. Jellen and W. Bühlmeyer
Laboratorium für Anorganische Chemie der Universität Bayreuth
West Germany

Small sulfur-nitrogen molecules (a, b) which are either unknown or difficult to obtain under normal conditions, can be generated starting from the salt K_2SN_2 or from substituted sulfur diimides, $S(NR)_2$ (R = $SiMe_3$, t-Bu), and stabilized in metal complexes.



Sulfur imides (R = $SiMe_3$, H)

Sulfur diimides (R = $SiMe_3$, t-Bu, H)



(a) (b) (c)

A typical example is the preparation of the first complex of unsubstituted sulfur imide, $(\mu\text{-HNS})Fe_2(CO)_6$ (c), which contains HNS in a bridging position.

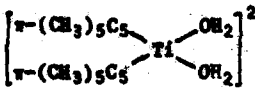
Sulfur diimides (b) react with hydrido metal compounds such as $CpW(CO)_3H$ to give adducts in which the reactive sulfur-nitrogen molecules have become part of a metallocycle.

STRUCTURAL CHEMISTRY OF SOME COMPLEXES CONTAINING Cp_2M^{IV} AND CpM^{IV} UNITS (Cp = C_5H_5 OR $(CH_3)_5C_5$; M = Ti OR Zr)

Wiltraud Lasser, Ulf Thewalt and Brigitte Wolf

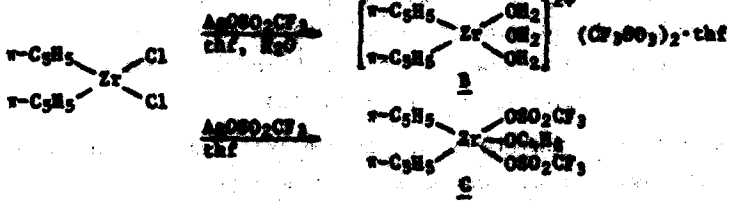
Sektion Röntgen- und Elektronenbeugung, Universität Ulm, Oberer Eselsberg, D-7900 Ulm, F.R.G.

With the hope to obtain salts with the two-coordinate cation $[(\pi\text{-}(CH_3)_5C_5)_2Ti]^{2+}$ we reacted $(\pi\text{-}(CH_3)_5C_5)_2TiCl_2$ with silver trifluoromethanesulfonate in tetrahydrofuran containing traces of water. The compound actually formed was the tetra-coordinate diaqua complex A, however. So the reaction takes the same course as for the sterically less crowded $(\pi\text{-}C_5H_5)_2Ti^{IV}$ unit.

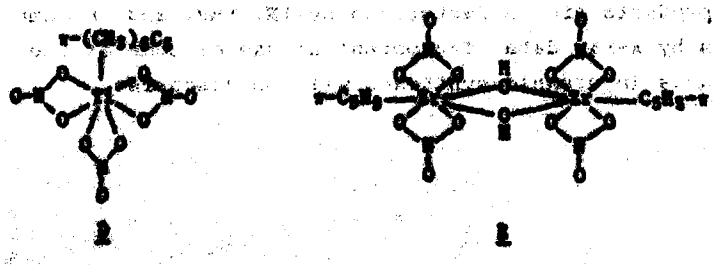


A

In the analogous reaction starting with $(\pi\text{-}C_5H_5)_2ZrCl_2$ the ionic triaqua complex B was obtained. When water was excluded the neutral complex C was isolated. Both, B and C, are rare examples of $(\pi\text{-}C_5H_5)_2Zr^{IV}$ complexes with a coordination number of five. Both correspond to the eighteen-electron rule.



Complexes D and E containing only one Cp group and in addition chelating nitrate ligands correspond also to the eighteen-electron rule. These compounds form in the reaction of $(\pi\text{-}(CH_3)_5C_5)_2TiCl_2$ and $(\pi\text{-}C_5H_5)_2ZrCl_2$ with aq. HNO_3 in $CHCl_3$:



D E

Complexes A to E were characterized by X-ray structure

UNUSUAL REACTIONS OF ACETYLENE COMPLEXES

Helmut G. Alt and Heidi I. Hayen

Laboratorium für Anorganische Chemie, Univ. Bayreuth
Universitätsstraße 30, D-8580 Bayreuth, West-Germany

In the acetylene complexes $CpW(CO)(C_2H_2)Me$ (1) and $CpW(CO)(C_2H_2)COMe$ (2) (Cp = η^5-cyclopentadienyl, Me = methyl) the alkyne acts as a four electron ligand. The reactions of 1 and 2 with alkylating agents, nitric oxide, oxygen, nitrosyl chloride, trimethylphosphane, trimethylphosphite and carbonmonoxide are described:

The reaction of 1 with Et_3OBF_4 leads to the first cationic acetylene carbene complex $[CpW(CO)(C_2H_2)(C(OEt)Me)]BF_4$, (Et = ethyl).

The reactions of 1 and 2 with NO yield $CpW(CO)(C_2H_2)NO$, $CpW(CO)(HC{\equiv}CCOMe)NO$ and the oxo complex $CpW(O)(C_2H_2)Me$. PMe_3 and 2 give the new yields metallacyclopropane complex $CpW(CO)(PMe_3)[(PMe_3)HC-C(H)COMe]$.

NOCl and 2 form $CpW(CO)(NO)(HClC-CHCOMe)$, the first carbonyl nitrosyl olefin complex of this type.

In the reaction of 2 and CO or $P(OMe)_3$ five-membered vinyl ketone metallacycles can be obtained which are able to add another alkyne to form eight-membered rings. All products are characterized by IR, NMR, and in some cases by x-ray data. The potential use of some of the products in organic syntheses will be discussed.



X

Q

DISUBSTITUTED ARENE-CHROMIUM-TRICARBONYL COMPLEXES

EricROSE,Jean-Charles BOUTONNET and Jacques LEVISALLES

Université P.et M.Curie,Laboratoire de Chimie Organique,4 Place Jussieu,75230 PARIS Cedex 05,FRANCE

Different disubstituted arene-chromium-tricarbonyl complexes are studied in solution(NMR) and in the solid state in order to predict the regioselectivity of the addition of a nucleophile(1-2) on these complexes.

The regioselectivity of the lithiation and the addition of nucleophiles on these complexes are discussed.

The chromium can be recovered from the reaction as $Cr(CO)_6$ when the arene-chromium-tricarbonyl complex is treated with a nucleophile and then with H^+ under CO atmosphere(3).This reaction is applied in order to synthesize organic molecules having pharmaceutical properties.

(1) R.J.CARD and W.S.TRAHANOVSKY.Tetrahedron Letters 1973,22,1823.

(2) M.F.SEMMELHACK,Ann.N.Y.Acad.Sci.1977,295,36.

(3) J.C.BOUTONNET,J.LEVISALLES,J.M.NORMANT and E.ROSE J.Organomet.Chem.1983,255,C21.

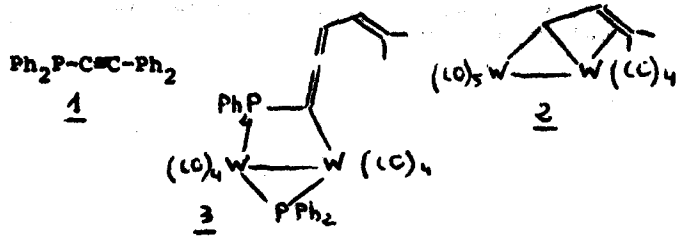
UNUSUAL REACTIVITY OF A DIPHOSPHINO ALKYNE TOWARDS μ-ALKYLIDENE COMPLEXES.

J.LEVISALLES, F.ROSE-MUNCH, H.RUDLER
Université P.et M.Curie, Laboratoire de Chimie Organique
4 Place Jussieu, 75230, PARIS Cedex 05, FRANCE.

J.C.DARAN and Y.JEANNIN
Université P.et M.Curie, Laboratoire de Chimie des métaux de transition, 4 Place Jussieu, 75230 PARIS Cedex 05, FRANCE.

The diphosphino alkyne, $Ph_2P-C{\equiv}C-PPh_2$ 1 reacts with μ-alkylidene complex[1] 2 to give a new phosphido complex 3 after insertion of the alkyne into one of the C-W bonds of the bridge and an unusual C-P bond rupture. X-Ray crystallography verified the structure.

A comparison of the reactivity of the alkyne 1 towards another μ-alkylidene complex is done.



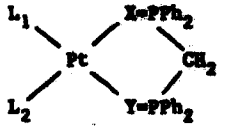
1- J.LEVISALLES, F.ROSE-MUNCH, H.RUDLER, J.C.DARAN, Y. DROMZEE et Y.JEANNIN.
J.Chem.Soc.Chem.Commun.1981,152.

NOVEL LIGANDS DERIVED FROM DEPROTONATED ORGANO-PHOSPHINE CHALCOGENIDES

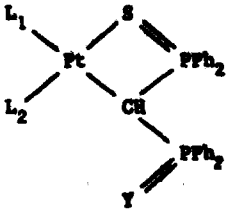
Keith R. Dixon, Jane Browning and Gordon W. Bushnell

University of Victoria, P. O. Box 1700, Victoria, B.C., Canada V8W 2Y2

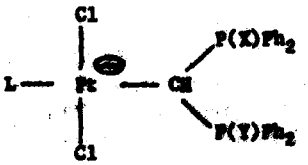
The coordination chemistry of $Ph_2P(X)CH_2P(Y)Ph_2$ and $(Ph_2P(X))_2CH$ and more especially the derived anions $[Ph_2P(X)CHP(Y)Ph_2]^-$ and $[(Ph_2P(X))_2C]^-$ (X, Y = O or S) is remarkably varied. The structural types I-IV have been characterised by ^{31}P NMR (and in several cases by x-ray diffraction) and unusual fluxional processes involving rapid exchange of free and co-ordinated sulphur have been identified for complexes II and IV (X = S). In some instances the fluxional process involves essentially a "bimolecular" reaction controlled by pivotal motion about a strong metal-ligand bond, rather than the more common simple exchange of coordination sites in a "dangling" ligand. This offers the possibility of selective control of reactive sites in connection with catalyst modelling.



I (X,Y = O,S)



II (Y = O or S)



III (X = Y = O or S)



IV (X = S)

Fp66-11

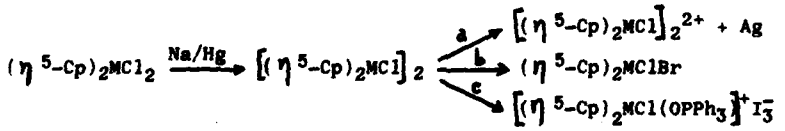
NEW CATIONIC AND NEUTRAL η^5-CYCLOPENTADIENYL ZIRCONIUM AND HAFNIUM COMPLEXES

Tomás Cuenca and Pascual Royo

Departamento de Química Inorgánica. Facultad de Ciencias. Universidad de Alcalá de Henares. (Spain).

Zirconium and hafnium(III) complexes of the type $[(\eta^5\text{-Cp})_2MCl]_2$ (M=Zr,I ; Hf,II) have been prepared in high yield by reduction of $(\eta^5\text{-Cp})_2MCl_2$ with one equivalent of sodium amalgam. The behaviour observed in the isolation of the Zr(III) complex is different from that previously described for this compound[1]. Both are diamagnetic at room temperature and stable in the solid under dry argon but are easily oxidized in the presence of air.

The oxidation of complexes I and II with one equivalent of $AgClO_4$ gives metallic silver and yellow solutions which on evaporation yield the cationic dimer species $[(\eta^5\text{-Cp})_2MCl]_2^{2+}$ (M=Zr, III; Hf, IV). The addition of different ligands to solutions of III and IV gives cationic mononuclear complexes of the type $[(\eta^5\text{-Cp})_2MClL]^+$ when L is a monodentate ligand (M=Zr, L=$OPPh_3$, V; $NHPh_2$, VI and M=Hf, L=$OPPh_3$, VII). When L is a bidentate ligand, dimer cationic species with the ligand bridging both metal atoms are isolated $\{[(\eta^5\text{-Cp})_2MCl]_2(\mu\text{-L-L})\}^{2+}$ (M=Zr, L-L=dppe, VIII; 2,2'-bipy, IX and M=Hf, L-L=2,2'-bipy, X).



(a) $AgClO_4$, (b) 1 mol Br_2, (c) 3 mol I_2

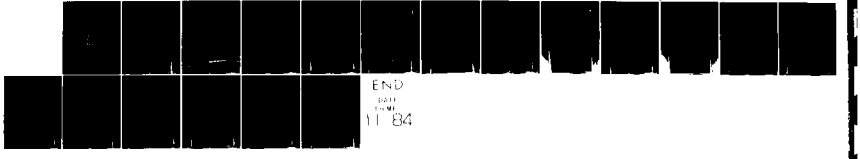
The oxidation of complexes I and II with one equivalent of Br_2 gives the mixed halocomplexes $(\eta^5\text{-Cp})_2MClBr$ (M=Zr, XI; Hf, XII). The same oxidation with I_2 gives a solid which could not be characterized as the pure iodocomplex. However, in the presence of $OPPh_3$ and with an excess of I_2, the cationic complex $[(\eta^5\text{-Cp})_2ZrCl(OPPh_3)]^+ I_3^-$ was obtained.

All complexes described were characterized by analysis, conductivity measurements and ir and ^1H nmr spectroscopy.

(1) P.C.Wailes, H.Weigold; J.Organomet.Chem. 28, 91, (1971)

AD-A146 190 INTERNATIONAL CONFERENCE ON COORDINATION CHEMISTRY (23RD) HELD AT BOULDER..(U) COLORADO UNIV AT BOULDER E L KING ET AL. 03 AUG 84 ARO-21423.1-CH-CF 8/8

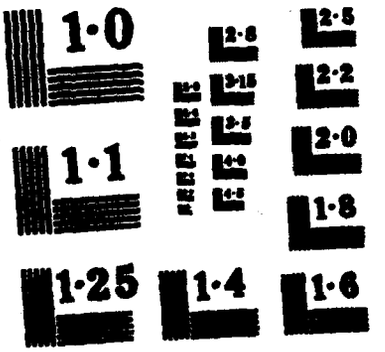
UNCLASSIFIED DAAG29-84-M-0199 F/G 7/4 NL



END

DATE FILMED

11 84


1·0
1·1
1·25
1·4
1·6
1·8
2·0
2·2
2·5

POLYMER IRON CARBONYL COMPLEXES IN ORGANIC SYNTHESIS

G. Cainelli, F. Manescalchi, M. Panunzio, A. Umani Ronchi

Istituto Chimico "G. Ciamician" Universita di Bologna and C.S.F.M.-C.N.R.

The tetracarbonylhydridoferrate anion, prepared in hydroalcoholic solution from iron pentacarbonyl and potassium hydroxide according to the equation:

$$Fe(CO)_5 + 3\ KOH \rightarrow KHFe(CO)_4 + K_2CO_3 + H_2O$$

has been supported on a polystyrene matrix by an anion exchange process using macroporous ion exchange resins (for instance Amberlyst A 26) in the chloride form.

The hydride I, rapidly and quantitatively exchanges under inert atmosphere with the chloride ion by simple stirring the resin with a solution of the anion:

$$P - N(CH_3)_3\ ^+Cl^- + KHFe(CO)_4 \rightarrow \quad P\quad N(CH_3)_3\ ^+HFe(CO)_4^- + KCl$$

The reagent so prepared was directly utilized to convert alkyl halides to homologous aldehydes, aromatic nitro-compounds to corresponding amines, and acid chlorides into aldehydes:

$$RX + 1 \rightarrow RCHO$$

$$ArNO_2 + 1 \rightarrow ArNH_2$$

$$RCOCl + 1 \rightarrow RCHO$$

AUTHOR INDEX

Author Index

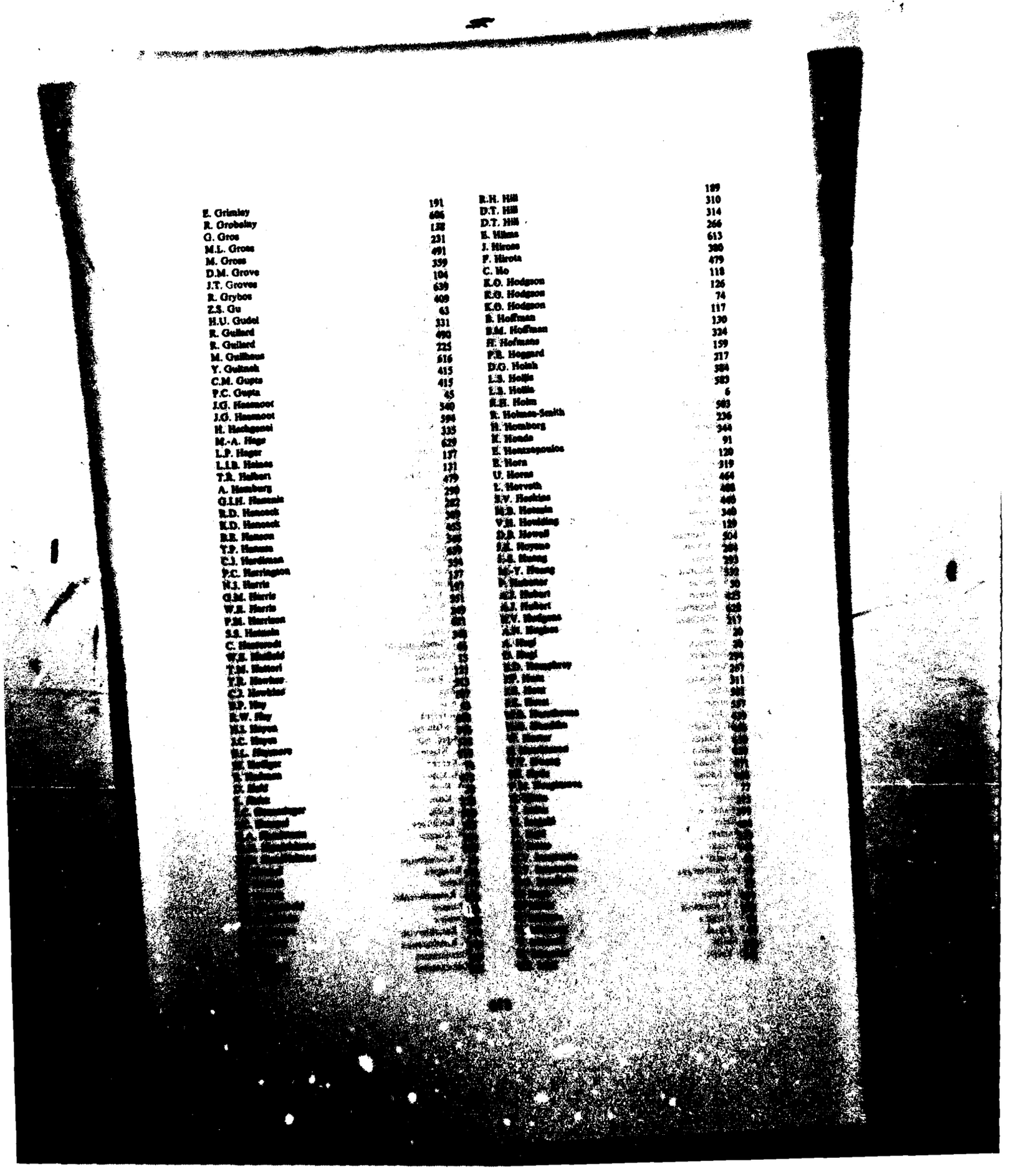
A. A-El-Aamy 452
E.H. Abbott 396
S.K. Abdullaev 544
M. Abdullah 433
K.D. Abney 530
H.B. Abrahamson 258
U. Abram 302
A.R. Abramov 426
H.M. Abu Soud 470
R.H. Abu-Sama 143
M.N. Ackermann 144
C.D. Adam 79
H. Adams 140
D. Afital 646
B.V. Agarwala 354
A.R. Aggarwal 330
G. Agrifoglio 367
K.M. Ahmad 452
S. Ahrland 453
M. Ahsan 538
S. Aime 379
P. Aisen 345
M. Ajioka 368
D. Ajo 379
N.A. Al-Jalili 18
M.A.M. Al-Kadier 533
N.A. Al-Salem 470
L. Alagna 621
M.N. Alam 200
N.W. Alcock 212
S. Alegret 390
A. Ali 588
E.M. Ali 252
A.A. Alich 218
I.Z. Aliyev 426
J.N. Allison 535
S.A. Alessi 19
S.M. Alsadi 17
H.G. Alt 658
C. Amatore 602
H.-D. Amberger 320
P. Amico 416
G. Anderegg 502
R.A. Andersen 634
O.P. Andersen 149
B.A. Anderson 207
D. Anderson 230
I. Anderson 498
O.P. Anderson 589
L.A. Anderson 633
L.J. Andrews 161
W.J. Andrzejewski 226
P.L. Anelli 297
E.-P. Ang 146
E.J. Angelici 521
W.B. Anthalina 471
L. Antolini 617
A.A. Antonov 394
N.M. Antropiusova 151
L. Anyo 136
R.D. Archer 169
R.D. Archer 639
M. Ardon 172
N. Ariguib 640
V. Arkle 180
W.H. Armstrong 581
J.K. Arnette 334
A.P. Arnold 427
P. Arrizabalaga 301
H. Arsoumanian 38
K.R. Ashley 102
H. Aslan 548
S. Asperger 264
B. Atoumi 387
B.A. Averill 124
S. Ayas 265
P.J. Aymonino 610
M. Bacci 376
G. Bachovski 313
G. Backes-Dahmann 210
R.C. Bastsold 274
N.M. Bahr 321
J.S. Bajaj 238
N.A. Bailey 140
C. Bailey 348
T. Bailey 37
K. Bajdor 516
S.A. Bajac 26
A. Balog 9
M.Z. Baluk 99
Y.N. Bakhus 60
A.S. Bali 24
V.L. Balke 632
J.M. Ball 597
D. Baluch 137
B. Banar 606
L. Banci 501
D. Banerjea 198
D. Banerjea 202
R.N. Banerjee 198
R.N. Banerjee 202
R.K. Barefield 209
R.M. Barkley 641
C.L. Barnes 440
P. Barone 556
J. Barret 433
V.P. Baryshok 153
M.G. Basallote 401
A. Battaglia 411
J. Bau 458
R. Battaglia 594
R. Battai 471
B. Bauman 499
R.L. Bautista-Cunningham 267
D. Bawley 503
G. Bazin 101
J.L. Bear 538
A.L. Beauchamp 152
M.T. Beck 101
M. Becker 266

M.M. Bakhtin 452
N.D. Basov 246
H.W. Bakker, Jr. 90
I.P. Bakushkin 550
R.L. Ballard 306
C. Ballou 64
P. Baker 360
P. Baker 361
R. Bambi 353
R. Bambi 357
D. Ban Hanson 648
A. Banchini 300
A. Banchini 619
R. Bander 457
A.V. Bandyopadhyay 322
A. Bandyopadhyay 364
C. Banelli 300
J. Banker 401
R. Bannert 137
B. Banner 448
B. Bant 150
J.B. Barnes 192
R.J. Bargeron 472
A.F. Barnett 311
I.B. Barnhart 168
I.B. Barnhart 338
I. Barnini 514
I. Barnini 522
A. Barton 551
R. Bayerle-Pfaar 385
N.B. Bhasin 68
D.D. Bhatnagar 51
P.R. Bhattacharyya 428
B.G. Bhattacharyya 539
N.S. Bhave 564
N.S. Bhave 58
Y.K. Bhoon 451
R.J. Bianchini 298
C. Bird-Cherreton 168
H. Bilimoria 464
A. Bino 172
G. Biocanin 379
M.N. Bishnu 198
M.J. Bjerrum 583
G. Bjornal 392
I. Blaauboer 69
N.J. Blackburn 621
D.P. Blair 512
D.F. Blair 602
B.E. Blaiser 391
E.L. Blau 653
M.L. Bleiler 649
L. Bleus 332
A.B. Bonnely 304
A.C. Bonnen 140
R.T. Bonti 62
R.T. Bonn 213
J.C.A. Boogaart 342
J.C.A. Boogaart 282
D.S. Bobbs 498
M.-L. Bollier 99
L. Bologni 477
J. Bonaffini 348
A.M. Bond 227
R.P. Bonham 498
P.M. Boorman 597
E. Borghi 523
B.A. Borgino 441
E.T. Borish 560
D. Borowczak 256
W. Bos 454
K.S. Bose 124
R. Botcher 302
L.J. Boucher 419
E.A. Boudreaux 381
J. Bour 454
M. Bourgeois 52
J.-C. Bourgenaut 659
B.E. Bowler 583
J. Brother 599
J.R. Bradbury 489
D.C. Bradley 537
A. Brahanti 500
O. Brain 236
K.L. Brandenburg 258
R.R. Brandon 591
P. Brannstein 457
J. Brauer 255
G.A. Brewer 67
K.J. Brewer 90
B. Briet 72
N. Brnicevic 536
K.C. Brooks 641
J.A. Broomhead 615
V.K. Brovtsyn 406
D.B. Brown 611
P.R. Brown 288
W.M. Brown 62
J. Browning 661
A.R. Bruce 175
M.R.M. Bruce 175
J.S. Brumbaugh 509
J.G. Brummer 527
D.L. Bryan 510
O. Buchanan 511
L.I. Budnin 480
L.I. Budnin 500
H.C. Budnikov 386
H.C. Budnikov 495
S.I. Budnikov 388
W. Buhlmeyer 490
J.S. Bukowski 110
R.A. Bulman 480
R.E. Burgess 126
R.H. Burgess 128
D.H. Burch 107
D.B. Burch 398
D.H. Burch 98
B. Burk 286
G.W. Burkhard 481
R.A. Butcher 397
L.H. Butler 97
J.H. Cabral 469
G. Cabrelli 488
M. Cain 389
G. Caldwell 395
R. Call 484
G. Calo 397
J.C. Cash 78
E.B. Cannon 481

B. Capello 152
J.P. Cardenas 583
M.C. Carlock 317
C.J. Carrano 348
S.J. Carter 148
A.J. Carty 645
A.L. Casimovo 460
M. Casrin 141
M. Casrin 379
U. Casilao 40
U. Casilao 49
M.E. Cass 486
C.J. Cassidy 232
P. Cassoux 52
P. Casso 301
M. Castillo 28
M. Castillo 504
L. Catalini 263
C. Cavioni 595
P. Cavoni 214
A. Cavioti 642
A.J. Cavisamos 647
A. Chakravorty 476
L.B. Chamberlain 527
J.G. Chambers 79
M.K. Chan 261
A.S.C. Chan 510
S.I. Chan 518
D.M.T. Chan 528
C.P.S. Chandel 415
C.-H. Chang 247
S.-C. Chang 287
D. Chang 491
C.K. Chang 633
M. Chanon 164
S. Chapman 117
J. Charalambous 137
M.-F. Charles 71
S. Charlesjos 51
C. Charlopoulos 28
P. Chaudhuri 210
A.B. Chaudhuri 589
B. Chaudhuri 265
V.K. Chauhan 48
M. Chavan 530
G.-K. Chen 221
Y.T. Chen 489
L. Chen 265
H. Chenausu 105
H. Cheniaux 58
V.A. Cheney 60
S.H. Cheraghchi 28
S.H. Cheraghchi 265
H.J. Cheng 265
G.A. Chepin 265
S.C. Chepin 265
J.J. Chichesamos 265
J.J. Chichesamos 265
J.J. Chichesamos 265
C.A. Chieng 265
J.F. Chin 265
M. Chiropolos 265
H.S. Chisti 265
L.M. Chisti 265
G.A. Chisti 48
G.R. Clark 488
M.J. Clarke 483
W.W. Cleland 496
R. Clement 55
R. Clement 80
P. Cocolios 331
P. Cocolios 490
J.J. Coffey, II 512
S.A. Cohen 131
S.L. Cohen 165
H. Cohen 193
H. Cohen 194
H. Cohen 483
M.J. Cohn 234
I.J. Colquhoun 53
B.E. Colvin 187
E.J.G. Conjoro 481
J.A. Connor 489
S.D. Conradson 126
B.B. Cook 115
J.C. Cooper 201
J.C. Cooper 371
J.D. Corbett 565
J.L. Corbin 128
J.L. Corn 425
J. Cornenagas 136
J. Cornenagas 225
J.-F. Cornu 136
D. Cosak 485
D. Cosak 494
S.A. Craig 31
S.P. Crozier 521
R.E. Cramer 549
F. Cristini 271
F. Cristini 367
U. Crosio 487
G.A. Crosby 257
J.E. Crowell 278
A.L. Cruzalbo 498
R.W. Crum 665
V. Cuniberto 416
T. Cuonn 682
S.C. Cummings 139
D. Cummins 52
D. Cummins 300
D. Cummins 7
B.Y. Cupo 531
A.E. Cutler 532
J.C. Dabrowiak 536
P. Dahan 538
P. Dahan 651
B. Dahlgren 654
P. Dalmasso 656
S.F. Dalton 658
P.G. Danielo 660
P.G. Danielo 662
B. Darwish 664
J. Darwish 666
J. Darwish 668
C. Daszkiewicz 670
C. Daszkiewicz 672
S. Davies 674
T. Davies 676
A. Davies 678
R.A. Davis, Jr. 680

T.P. Dasgupta 25
P. Dasgupta 26
K.C. Dash 520
M.E. Davis 433
J.H. Dawson 362
J.H. Dawson 630
A. De Roberts 466
E. de Boer 308
C.G.B. de Barbarin 140
L.C.A. de Carvalho 132
J. de Jersey 67
D. de Montmorcn 650
R. del Rosario 148
A.H.J. den Hartog 140
J.H.J. den Hartog 506
R.T. Dunn 311
D.V. Dawton 209
A. Dumoncaux 433
C.B. Dumis 618
S.R. Dunjardin 163
J.P. Dupuis 286
M.P. Dumoulin 234
H.O. Dunyn 329
G. Duny 44
F.A. Duvillanova 271
F.A. Duvillanova 507
G. Duvoto 328
A.E. Day 304
J. Dilluendeno 108
M. Di Vaio 402
E. Díaz 182
G.P. Diakun 481
A. Díaz 371
A. Díaz 507
S. Diakolihn 373
M.H. Diekman 245
G.W. Dillow 225
J.R. Dilworth 135
M.J. Dilworth 136
G.C. Dimoulas 94
E.E. Dixon 451
C. Djordjevic 249
C. Djordjevic 34
H.W. Dodgen 257
E.S. Dodsworth 188
E.S. Dondoss 495
N.H. Doherty 182
J.B. Doi 315
Z. Dokmanovic 255
E. Domi 255
E. Donaho 200
J. Donnel 45
W.C. Dohmen 255
W.L. Dohmen 255
M. Dollins 75
J.B. Donahue 85
D.L. Dobbs 200
M.J. Dobbs 200
D. Dodd 200
C.G. Dodson 200
W.C. Dodson 200
J.W. Dodson 200
A.C. Dow 200
J.R. Earley 526
G.R. Eaton 285
S.S. Eaton 285
R.C. Eberle 99
D.J. Eder 442
N. Edelstein 320
R.T. Eddin 190
G.L. Eichhorn 473
M. Eshner 283
M.K. Eidemon 316
M.K. Eidemon 317
C.W. Eisenbrot, Jr. 222
A. El Dassuky 25
A.A. El-Awady 554
M.A. El-Beshy 470
A. El-Hennidi 565
A. El-Hennidi 566
R.C. Elder 315
R.C. Elder 316
R.C. Elder 317
H. Elias 266
C.M. Elliott 334
C.M. Elliott 611
W.B. Ellis 518
S.E. Elmore 638
M.M. Emery 331
T. Emery 457
J.F. Endicott 638
J.P. Endicott 233
J.H. Enemark 127
J. Epheian 308
M. Ephrikhian 308
S.B. Erenberg 83
L.E. Erickson 147
B.J. Errington 597
J.E. Epperson 0
J.E. Epperson 0
W.J. Evans 316
W.E. Evans 16
L. Fabbrini 0
J. Fabian 88
A.C. Falconi 308
J.D. Fallin, Jr. 638
M. Fallmyer 638
F.S. Fanwick 308
M. Farago 38
V. Garza 0
N.A. Farid 308
M. Farid 638
E.C. Fay 638
Abdi Fazio 638
E. Fazio 638
E.S. Feldman 638
F. Fennessy 638
[illegible] 638
[illegible] 638
[illegible]

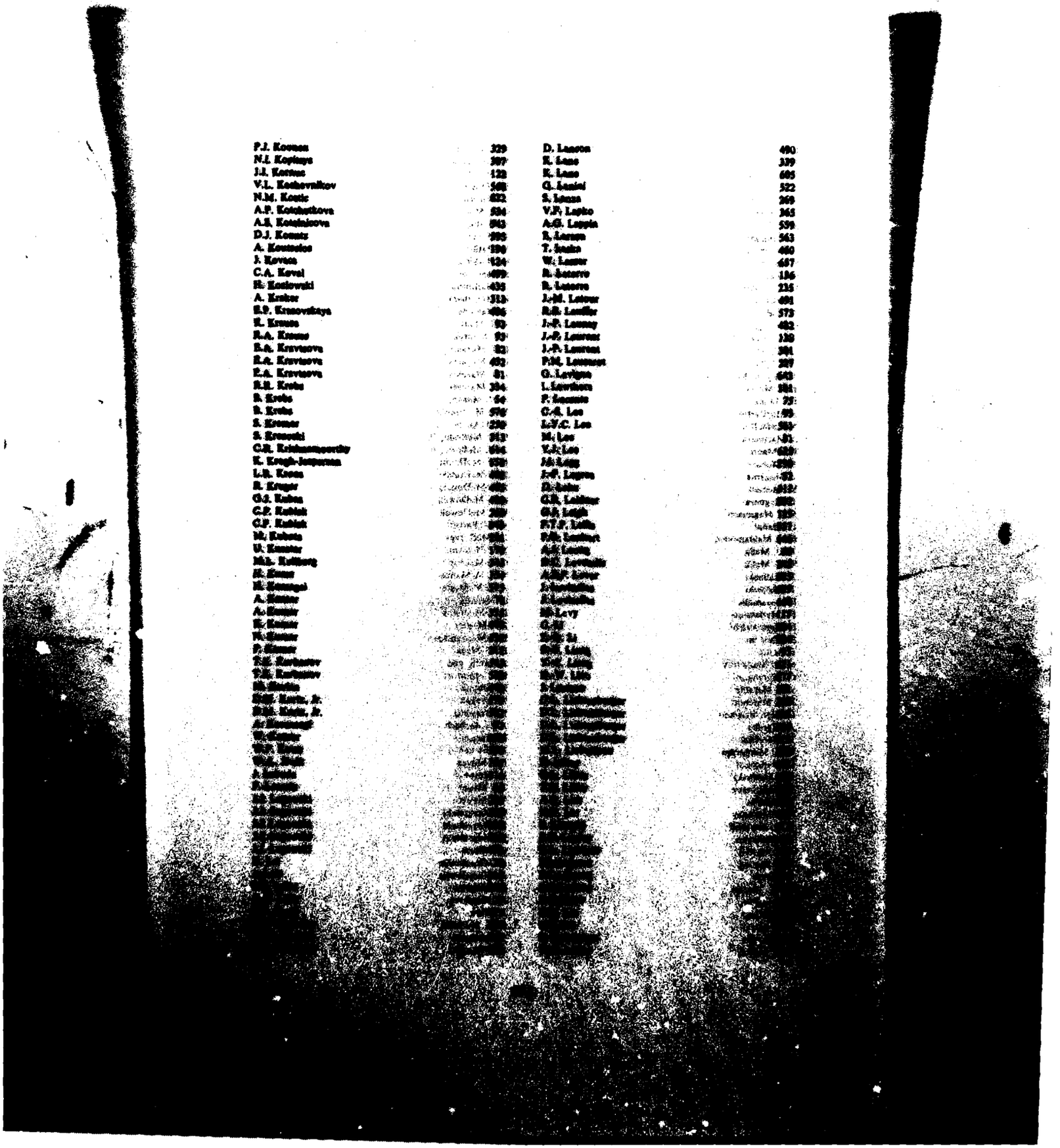
J.E. Pinholt 150
R.G. Pinks 187
D. Pierani 64
J. Pischer 216
R.D. Pischer 548
L. Pish 436
E. Pisicaro 500
M. Pitzroy 120
D.E. Pjare 649
A. Plumini 603
J.L. Pippen-Anderson 451
E. Pluck 239
Z.A. Potina 365
P.C. Pord 189
P.C. Pord 254
G.C. Pord 349
F. Porghieri 318
G. Pormicka-Kozlowska 435
K.A. Poster 209
A.A. Potiev 251
A.A. Potiev 568
D. Pournier 160
M.M. Pox 115
G.C. Pranchini 309
K.C. Prancis 12
D.W. Prasco 280
A.J. Prank 340
A.J. Prank 344
C.C. Prankfin 100
C. Prauss 46
E. Preamdorfer 307
R.B. Press, III 350
J. Prederiksen 120
G.E. Preeman 626
G.M. Preeman 389
H.C. Preeman 450
D. Pregosa 46
D. Pregosa 49
B.S. Preiser 382
C.M. Priend 350
F. Prelov 488
S. Prenesos 350
M. Prentis 350
H.-W. Prohnef 600
H.-W. Prohnef 545
R. Pokotomi 90
S. Prankoski 600
C. Pirlini 350
G. Pisser 400
P. Piter 350
A. Pitlini 350
J.C. Pottmer 400
J. Pitly 400
J. Pitly 400
R. Pitzroy 400
R. Pitzroy 400
S. Pitzsimmons 400
S. Pitzsimmons 400
M. Pitzsimmons 400
R. Pitzsimmons 400
C. Pitzsimmons 400
C. Pitzsimmons 400
P. Pitzsimmons 400
A. Pitzsimmons 400
A. Pitzsimmons 400
Y. Poult 505
J.T. Poustiet 513
G.V. Povrilova 544
W.E. Poiger 486
D.E. Poiger 525
U. Poiser 344
J.P. Poldard 270
R.W. Pollert 399
M.J.E. Pone 362
M. Poodfroy 301
G.L. Poodfroy 644
T.A. Porge 120
C.F.G.C. Poraldon 203
D.F. Porvasio 112
G. Porvasio 648
E.D. Potneff 434
A.A. Powirth 160
S.F. Phaller 126
C.A. Philardi 214
E.I. Phbs 397
E. Phubrodt 167
E.D. Pilardi 53
J.W. Pilo 549
J.N. Pilin 488
A.P. Pimberg 304
G.E. Pinard 310
G.E. Pinard 314
A. Pinardino 491
A.M. Pinfini 488
W.L. Pinfisher 660
E. Pinar 395
A. Pinfeld 120
A. Pining 44
A. Pining 70
E. Pinfinino 340
E.J. Poddard 396
W.A. Poddard, III 585
G.M. Podstein 631
H.M. Poff 475
H.M. Poff 535
S.J. Pollman 440
V.A. Polovay 440
M.S.L. Pomalez 440
P. Pomalez 440
E. Pomalez-Vargas 475
E. Pomfrin 180
A. Pomirez 350
P. Pomirez 440
D.A. Pomkins 440
W.H.D. Pomson 440
I. Pomith 440
G. Pomrani 440
R.B. Pony 440
R.B. Pony 440
R.B. Pony 440
C. Ponfield 440
C.A. Ponn 440
M. Ponn 440
P. Ponnigan 440
J. Ponnigan 440
P. Ponnigan 440
P. Ponnigan 440
P. Ponnigan 440
P. Ponnigan 440
P. Ponnigan 440



E. Grimley 191
R. Grobelny 606
G. Gros 138
M.L. Gross 231
M. Gross 491
D.M. Grove 359
J.T. Groves 104
R. Grybos 639
Z.S. Gu 408
H.U. Gudel 63
R. Guilard 331
R. Guilard 490
M. Guilheus 225
Y. Gultneh 616
C.M. Gupta 415
P.C. Gupta 415
J.G. Hanmoot 65
J.G. Hanmoot 540
H. Hashgawi 504
M.-A. Hage 335
L.P. Hager 623
L.I.B. Haines 137
T.R. Halbert 121
A. Hamberg 479
G.I.H. Hanania
R.D. Hancock
R.D. Hancock
R.E. Hansen
T.P. Hansen
C.J. Hardman
P.C. Harrington
N.J. Harris
G.M. Harris
W.E. Harris
P.M. Harrison
S.S. Hattalia
C. Hauswirth
W.E. Hazfeld
T.M. Heberl
T.B. Hawkins
C.J. Hawkins
S.P. Hay
R.W. Hay
H.I. Hayes
J.C. Hayes
W. Hedges
T. Hedges
R. Heil
L. Heil

R.H. Hill 189
D.T. Hill 310
D.T. Hill 314
E. Hilsa 266
J. Hirose 613
F. Hirota 300
C. Ho 479
K.O. Hodgson 118
K.O. Hodgson 126
K.O. Hodgson 74
B. Hoffman 117
B.M. Hoffman 130
H. Hofmann 324
P.B. Hoggard 159
D.G. Holah 217
L.B. Hollis 304
L.B. Hollis 583
R.H. Holm 6
R. Holmes-Smith 583
H. Homberg 236
K. Honda 344
E. Hontzopoulos 91
R. Hora 120
U. Horna 319
L. Horvath 464
R.V. Hoskins 468
R.B. Hotmin 440
V.H. Houlding 340
D.B. Howell 120
F.E. Hoyano 504
S.S. Hsieh
M.-Y. Hsieh
K. Hubener
A.J. Hubert
A.J. Hubert
R.V. Hudgins
A.M. Hughes





T.M. Loehr 500
T.M. Loehr 582
T.M. Loehr 633
V.A. Logvinenko 544
M.F. Loncin 206
K.M. Long 530
K.M. Long 628
G. Longoni 642
L.-P. Lorenz 221
S. Lough 126
B. Louie 499
M. Lourdichi 651
C. Luchinat 522
A. Ludi 680
G.S. Lukat 582
C.M. Lukehart 646
S. Lyman 471
J.M. Lyon 341
J.T. Lyon, III 34
H.R. Mäcke 184
E. Mänck 117
P. MacCarthy 392
N.J. MacNeill 191
S. Macieszak 217
R.J. Madix 279
M. Maeder 413
T. Maejima 97
M. Maestri 176
T. Magnera 284
V.R. Magnuson 217
G. Mahé 11
N.N. Maidanovich 990
W.U. Malik 353
W.U. Malik 357
T. Maliński 392
T. Maliński 491
I.N. Mamalis 30
M. Manassero 648
P. Manassaldi 663
S. Mangani 206
F. Mani 819
M.M. Manorov 499
G. Marangoni 365
V.R. Marathe 227
J.-C. Marchon 401
G. Marcotrigiano 617
A. Mardby 485
V. Marechal 490
D.W. Margerum 618
C. Marinangeli 209
J.A. Marinsky 208
J.A. Marinsky 402
T.J. Marks 294
M.J. Maroney 393
R.M. Marshall 611
P. Martinez 208
A.E. Martell 365
A.E. Martell 469
J. Martin 515
J.W.L. Martin 2067
R.B. Martin 406
G. Martinez 208
E.A. Martz 408
S.P. Mason 406
M.R. Mason 406
M.S. Masoud 372
M. Massacesi 323
M. Massoud 23
S.S. Massoud 519
L. Matassa 635
C.M. Mate 278
F. Mathey 216
Y. Mathey 55
Y. Mathey 89
R. Mathieu 650
R. Mathieu 651
A. Mathuthu 390
H. Matsubara 575
Y. Matsuda 183
A.G. Mauk 633
P.L. Maurya 354
L.N. Mazalov 306
L.N. Mazalov 432
L.N. Mazalov 82
L.N. Mazalov 83
A.M. Mazany 458
Y.A. Mazurenko 325
A. McAuley 485
D.W. McBride, Jr. 288
D.W. McBride, Jr. 289
M.D. McDevitt 112
J.W. McDonald 123
J.W. McDonald 126
H.E. McDowell 270
W.J. McDowell 283
W. McFarlane 53
J.J. McGarvey 181
F.A. McLean 121
C.H. McLean 140
N.T. McManus 524
A.D. McMaster 504
C. Meali 243
B.A. Medieros 641
J.H. Medley 88
E.P. Medyantseva 495
D.W. Meek 395
A. Mehmood 508
R.C. Mehrotra 637
M. Melník 248
M. Melník 450
L. Menabue 617
A.E. Merbach 20
P. Merdor 816
J. Metzger 38
G.S. Meyer 419
D. Meyer 285
T.J. Meyer 93
T.J. Meyer 92
D. Meyerstein 193
D. Meyerstein 194
R. Meyerstein 483
G. Mezei 323
A. Michalowicz 55
A. Michalowicz 89
S. Mikhailov 284
H. Mikkelsen 404
R. Mikulski 97
G.G. Mikuliski 440
M. Mikuriya 42
M. Mikuriya 68

R.M. Milburn 519
M. Millar 56
M. Miller 578
P.W. Miller 311
N.S. Mills 218
M. Minelli 127
D. Minniti 269
S.B.S. Mishra 142
H.C. Mishra 370
T.K. Misra 388
S. Mitra 237
T.K. Miyamoto 626
K. Mizumachi 97
M. Mohan 588
R. Mohr 10
C. Moise 331
L.V. Molchanova 386
S. Monsti 652
R. Monsanni 522
L. Monsted 177
O. Monsted 177
O. Monsted 604
F. Montanari 297
C. Montgomery 215
L. Montri 611
R. Moody 140
P. Moore 212
F. Moore 269
J.K. More 305
K. More 305
I. Morgenstern 68
G. Mori 500
J.B. Morris 228
R.D. Morrison 644
P.E. Morrissey 403
K.W. Morse 347
J.W. Morse 391
S. Moss 140
A. Mosset 75
M.M. Mostafa 452
R.J. Motekaitis 346
R.J. Motekaitis 463
H. Motschi 461
H. Motschi 465
B.A. Moyer 283
C. Moynihan 229
M.M. Muir 182
N. Muirhead 402
D. Mukherjee 589
Y. Murakami 183
S. Muralidharan 8
I. Murase 42
H.H. Murray, III 458
K.S. Murray 120
K.S. Murray 256
R.W. Murray 292
A.C. Mussatello 638
R.L. Musselman 195
Y. Muso 349
A.E. Nader 36
A. Nagasawa 15
I. Nagypal 16
B.U. Nair 94
K. Nakamoto 516
A. Nakamura 579
B.S. Nakani 389
R. Nakao 614
Y. Namba 134
M.J. Nappa 114
M. Nappa 29
B.A. Narayanan 602
N. Nardi 208
O.A. Narimanbekov 426
V.A. Nasiusov 386
J.D. Navratil 472
J.D. Navratil 638
R. Nayan 444
M.K. Nazeeruddin 421
A.J. Neilson 524
R. Neilson 558
M. Nelson 117
M. Nelson 130
J.H. Nelson 216
S.M. Nelson 46
M.T. Nemeth 618
W.E. Newton 123
W.E. Newton 126
K.M. Neyman 386
C.Y. Ng 442
J.R. Nicholson 127
J.K. Nicholson 429
R. Niera 458
H.L. Nigam 171
H.L. Nigam 312
M.J. Nilges 306
Y. Nishida 41
J. Nitschke 655
R.D. Noble 499
A.F. Noels 30
A.F. Noels 425
V.M. Nogueira 322
M. Noji 399
G.M. Nord 604
B. Noren 453
R.B. Norman 447
P.R. Norman 485
J.R. Norton 190
V.M. Norwood 347
D.L. Nosco 96
B. Novak 598
D. Nsel 651
W.A. Nugent 528
M. Nutkovich 483
P. O'Brien 23
P. O'Brien 433
L.H. O'Connor 100
C.J. O'Connor 577
T.V. O'Halloran 304
J. Oakes 12
J. Oakes 13
J. Oakes 366
U. Ochsenbein 283
H. Offen 180
Y.Y. Offengenden 589
K. Ogino 166
H. Ogino 22
S.M. Oh 234
L.-O. Ohman 464
L.O. Ohman 498
R. Ohuchi 21

H. Ohtaki 73
J.F. Ojo 19
H. Okawa 133
J. Olofson 460
R.K. Olsen 437
O. Olubuyide 19
G. Ondrejovic 478
S. Onuma 77
L. Operti 227
P.L. Orioli 208
A. Orlandini 214
W. Orme-Johnson 117
W.H. Orme-Johnson 130
R. Ortega 37
J.A. Osborn 185
A. Oskarsson 453
N.S. Ostanov 543
G. Ostacoli 416
R. Osterberg 395
P. Ovrath 285
J.P. Otruba 92
I. Otsuki 166
J. Otvos 313
C. Overton 609
F. Ozawa 2
K. Ozutsumi 73
D.P. Paar 614
L.J. Palmal 58
A. Palmeri 555
R.A. Palmer 168
N.P. Palmer 25
K. Panchanatheswaran 549
K.K. Pandey 654
K.B. Pandeya 238
K.B. Pandeya 330
L.S. Pang 383
A. Pant 142
M. Panunzio 663
G. Paolucci 141
G. Paolucci 558
G. Paolucci 551
G. Paolucci 618
T.L. Pappenhagen 542
G.K. Parasher 217
K.O. Parker 86
V.N. Parmon 92
S.J. Parus 588
M. Pasquali 397
R.F. Pasternack 428
V.K. Pasul 264
D. Pavlovic 500
M.J. Pawlik 231
D.A. Peake 289
K.A. Pearlstine 109
E.H. Pearson 406
V.L. Pecoraro 287
C. Pedrini 617
G.C. Pellacani 160
R.W. Penfield 164
E. Pentgrath 74
J.R. Penner-Hahn 152
Y. Perez 108
M. Perrin-Pecvet 388
D. Persson 652
M. Pervanini 310
D. Petering 471
J.D. Peterson 90
W. Petri 185
J.F. Petrignani 38
A. Petrou 196
L. Pettersson 498
L.D. Pettit 435
M. Pfeffer 457
C.J. Pickett 125
P.G. Pickup 292
C. Pierpont 212
C.G. Pierpont 484
L.H. Pignolet 460
G. Pilcher 570
G.F. Piovan 467
B. Plapiac 555
P. Pla 323
J. Pletcher 247
J.E. Plowman 443
J.E. Plowman 500
K. Poki 211
R. Polibinac 508
O. Polzat 80
M. Poliakoff 174
A.J.L. Pombeiro 223
A.J.L. Pombeiro 61
G. Pontiroli 323
N.S. Poonia 287
M.L. Poor 653
A.I. Popov 287
L.C. Porter 245
L. Pospisil 494
C. Prakash 228
R.N. Prasad 145
J. Prasad 312
R.N. Prasad 352
W. Preetz 319
C. Prati 318
C. Prati 364
I. Pri-Bar 511
R. Prins 45
R.J. Puddephatt 189
M.P. Pujari 43
D. Pujol 108
J.W. Pyrz 572
L. Que, Jr. 572
L. Que, Jr. 572
L. Que, Jr. 573
S. Quici 297
G. Rabai 101
D.L. Rabenstein 427
D.J. Radanovic 299
O.A. Rajan 418
Ma. Rajni 413
M. Rakowski-DuBois 418
M.S. Ram 609
T. Ramasami 353
T. Ramasami 87
B.S. Ramaswamy 22
R. Ramirez 284
R. Ramirez 286
J.N. Ramsden 286
V.B. Rana 47
N. Rao 402
S.S. Raper 57
G. Randaccio 505

K.N. Raymond 350
K.N. Raymond 436
K.N. Raymond 441
K.N. Raymond 442
K.N. Raymond 636
G. Reed 33
M.M. Reddy 462
J. Reedijk 295
J. Reedijk 393
J. Reedijk 45
J. Reedijk 540
J. Reedijk 586
J. Reedijk 612
D.C. Rees 122
T.F. Rees 392
A. Rehorek 179
D. Rehorek 179
J.H. Reibenspies 149
W.M. Reiff 240
W.M. Reiff 577
D. Reinen 250
T.R. Reinert 115
M.K. Reinking 260
A.M.M.V. Reis 570
R. Reisfeld 162
C.-Y. Ren 293
J.-P. Renard 70
P. Reveco 88
Z. Reyes 499
P.A. Reynolds 378
D.W. Rice 340
R.L. Richards 125
R.L. Richards 223
R.L. Richards 61
J.F. Richardson 597
D.P. Ridge 188
D.P. Ridge 231
L.A. Ridnour 631
J.G. Reiss 220
P.J. Riemsdijr 540
C. Rigano 466
C.E.F. Rikard 443
D.P. Riley 105
R. Rizzarelli 416
P.B. Roberts 140
M.M. Roberts 284
R. Rodo 455
D.C. Roe 528
P. Rogel 504
S. Rogers 396
R.D. Rogers 547
R. Romeo 509
A.U. Rondhi 643
W.R. Roper 488
D.B. Rorabacher 480
D.B. Rorabacher 481
M.J. Rose 547
R. Rose 650
F. Rose-Munch 648
E. Rosenberg 398
E. Rosenberg 509
L.D. Rosenhein 555
E. Rosenvil 638
G. Rossetto 543
G. Rossetto 551
G. Rossetto 551
M. Rost 113
A.P. Rothwell 527
I.P. Rothwell 527
D.M. Roundhill 267
N.S. Rowan 371
P. Royo 662
F.A. Rotzdestvenskii 241
J.P. Rubinson 126
J.P. Rubinson 128
H. Rudler 660
M. Rudolph 113
R.R. Ruminski 90
J.D. Rush 560
D.H. Russell 230
Z. Ruzic-Toros 536
R.R. Ryan 420
Michel Sabat 243
A. Sabatini 243
A. Sabatini 411
L. Sacconi 652
J. Sachnaidze 269
J. Sachnaidze 212
P.J. Sadler 388
P.J. Sadler 429
B. Saha 421
B. Saha 422
N. Saha 589
S.K. Sahni 295
K. Saito 166
K. Saito 97
K. Saito 15
E.B. Saitovich 322
S. Sakakibara 575
S. Sakamoto 183
T.M. Salem 372
T.M. Salem 23
L. Salkas 339
L. Salkas 605
S. Sammartano 466
S. Sample 630
S. Sanchez 182
J. Sanders-Loehr 443
J. Sanders-Loehr 588
J. Sanders-Loehr 582
S.A. Sangokoya 53
R. Sappa 665
A.M. Sargeson 5
I.K.K. Sarkan 320
S. Sarkar 98
I. Sasaki 122
T. Sasaki 217
Y. Sasaki 606
D.T. Sawyer 606
K. Sax 247
A. Sazatsu 322
E.C. Sciriven 320
W.P. Schaefer 242
R.A. Schaefer 327
G.E. Schauer 320
W.R. Schaub 320
A.J. Schmeider 320
J. Schneeman 320
C.W. Schläpfer 320
G. Schmid 320

R.P. Schmidt 299
S.P. Schmidt 655
J.E.J. Schmitz 329
R.A. Schoenfeiner 333
H. Schollhorn 585
G.N. Schrauzer 119
J.A. Schreifels 311
R.R. Schrock 525
W.A. Schroeder 622
H.J. Schugar 158
F.A. Schultz 126
F.A. Schultz 489
P. Schultze 374
B. Schwartz 431
J. Schwartz 505
J.R. Schwartz 521
K. Schwochau 563
R.A. Scott 521
W.M. Scovell 402
J.P. Scovil 451
A. Scozzafava 522
D.L. Sedney 240
M.H. Seeberger 213
J. Selden 70
F. Sells 186
M.A. Sekkine 23
J. Selbin 88
H. Seligson 472
G.L. Semyonova 459
A. Sen 389
N. Seppoe 176
M. Sertic 364
L. Sestili 396
C.M. Seymour 492
V.V. Shabalnikov 436
T.N. Shabalnikaty 436
A. Shamir 281
R.P. Sharma 145
R. Sharma 224
R.F. Sharma 252
P. Sharrock 248
P. Sharrock 458
C.F. Shaw, III 313
C.F. Shaw, III 316
C.F. Shaw, III 317
J. Shaw 33
L.N. Shchegrov 151
R.A. Sheldon 168
J.E. Sheldon 622
J.E. Sheldon 622
M.C. Shepherd 223
A.D. Shevy 223
S. Shibata 340
S. Shibata 77
A.E. Shilnikov 111
A.E. Shilnikov 111
T. Shimi 111
R.L. Shoer 111
S.I. Shupack 111
A.L. Shuvalova 111
A.L. Shuvalova 111
L. Shuvalova 111
V.M. Shvedenkov 111
V.A. Shvetsov 111
E.W. Siegel 111
R.E. Sievers 111
R.E. Sievers 111
H. Sigel 111
L. Sigl 111
N. Silavwe 111
S. Silver 111
L.I. Simandi 111
D.P. Singh 111
M. Singh 111
M.M. Singh 111
R.P. Singh 111
R. Singh 111
R. Singh 111
J. Sinha 111
E. Sinn 111
S. Sinn 111
S. Sinn 111
S. Sinn 111
S. Sitran 111
S. Sitran 111
S. Sjoberg 111
T.E. Sloan 111
J.C. Smart 111
J.A. Smegal 111
J. Smith 111
B.E. Smith 111
G.C. Smith 111
R.M. Smith 111
T.A. Smith 111
A.Y. Smolyar 111
M.R. Snow 111
M.R. Snow 111
J.M. Sobczak 111
R.I. Soloman 111
R.I. Soloman 111
R.I. Soloman 111
P.M. Solodovnikov 111
G.A. Somorjai 111
M. Sone 111
N. Sonoda 111
C. Sourisseau 111
E. Spartalian 111
D.R. Spears 111
A. Spasi 111
M.E. Spivagin 111
R.R. Squires 111
R.R. Squires 111
U.C. Srivastava 111
J. Stach 111
D.M. Stanbury 111
P.L. Stanghellini 111
J.J. Steggerda 111
J.J. Steggerda 111
E. Stein 111
V.M. Stepanov 111
V.M. Stepanovich 111
G.V. Stepetat 111
M. Stiefel 111
G. Stucky 111
F. Stuqlund 111
E. Suchocki 111
G.M. Sumner 111
G.M. Sumner 111
V. Sundaram 111
A.L. Sunset 111

G.D. Stucky 111
L.S. Stuhl 148
W. Stumm 465
E. Stuve 279
N.A. Subbotina 362
G.Z. Suleimanov 550
Y. Sultab 18
J.M. Sullivan 190
W.B. Summers, III 110
J. Sunner 224
K.S. Suslick 115
B.M. Sutton 310
L.B. Svedmikova 534
B.J. Swanson 420
Z. Szeverenyi 35
T. Szymanska-Buzar 256
I. Tabushi 317
F. Tafesse 519
A.F. Tai 109
J.A. Taimr 434
K. Takahashi 41
M. Takeuchi 41
R. Tamamushi 374
S. Tamburini 48
S. Tamburini 49
K.S. Tan 427
H.K. Tanaka 15
M. Tanaka 199
K. Tanaka 574
M. Tanaka 97
J.P. Tandon 355
R.E. Tapscott 346
H. Taube 3
T. Taura 247
D. Taylor 455
R.W. Taylor 99
M.H. Tegan 653
M.P. Teotia 396
K.O. Tepperman 315
L.W. ter Haar 66
S.M. Terrick 487
P. Teyssié 30
P. Teyssié 425
L. Thakur 565
L. Thakur 566
K.H. Theopold 525
U. Thewalt 585
U. Thewalt 657
V.J. Thom 282
P. Thomas 179
L.K. Thompson 87
D.A. Thornton 324
G. Tiddia 266
L.P. Tikhonova 116
N.I. Timoshenko 375
A. Tiripicchio 645
M.L. Tobe 283
M.L. Tobe 580
J. Tonker 608
R. Toftlund 591
T. Tokii 349
C.A. Tolman 111
C.A. Tolman 114
C.A. Tolman 27
C.A. Tolman 29
H.E. Toma 167
H.B. Toma 557
H. Tomiyasu 98
W.R. Tomlinson 57
J. Topich 34
K. Toriumi 65
G. Tosi 318
G. Tosi 364
M. Trabelsi 640
N. Tran 122
B. Trzcinska 458
A. Treffry 349
P.M. Treichel 653
S.R. Trifunovic 299
W.C. Trogler 655
J.-C. Trombe 44
A.M. Trzeciak 265
A.M. Trzeciak 506
K.R. Tsai 277
T. Tsubomura 448
K. Tsukahara 627
T. Tsukihara 575
J.P. Tuchagues 620
D.G. Tuck 635
T.H. Tulip 528
J.J. Turner 174
D.R. Tyler 175
K.H. Tytko 497
K.N. Udupa 59
T. Ueno 575
N. Ueyama 575
N.A. Ulakhovich 495
F.L. Urbach 112
S. Utsuno 290
A. Vacca 243
A. Vacca 411
G.A. Vaglio 227
H. Vahrenkamp 592
L. Valade 52
J.S. Valentine 109
D. Valigura 478
M. Valle 227
C. Valzanlia 37
R.B. VanAtta 109
R.Vann Bynum 472
D.G. Van Derveer 289
L.C. Van Poucke 414
G.A. van Albada 540
R. van Eldik 10
R. van Eldik 11
R. van Eldik 178
R. van Eldik 265
G. van Koten 359
C.G. van Kralingen 366
D. van der Helm 440
J.G.M. van der Linden 220
M.J. van der Meeve 482
J.L. van der Veer 186
R.S. Vemuri 130
G. Vemuri 591
G. Vemuri 593
M. Verdaguer 68
M. Verdaguer 70
M. Verdaguer 72
P.J. Vergamini 480

P. Verhoeven 324
E.J.S. Vichi 322
P. Vierling 228
P.A. Vigato 457
P.A. Vigato 46
P.A. Vigato 49
P.A. Vigato 147
G.E. Vignoni 481
R. Vilaplana 78
A.N. Vishnevi 35
P. Vitali 64
S. Vitiosi 131
O. Vitori 494
A.A. Vlcek 35
A. Vogler 432
A.A. Volkyuk 51
A.A. Volkyuk 52
A.A. Volkyuk 398
I.I. Volshonkova 223
S.V. Volkov 375
S.V. Volkov 391
J.F. Volkmo 227
P. Volpe 226
R. Volz 208
A. van Zoonsky 153
M.G. Voronkov 698
E. Vrashnov-Astro 91
E. Vrashnov-Astro 31
N. Vukvic 209
R. Wachter 575
E. Wada 282
R.D. Wald 286
E.F. Walsworight 287
Y. Wakatsuki 641
D.M. Walba 577
M.V. Walker 282
F.A. Walker 698
D.S. Wallace 117
J.M.A. Wallabe 467
M. Wallace 164
R.A. Wallace 277
W.L. Wallis 208
Z.-Q. Wang 515
D.-N. Wang 282
H. Wang 357
H. Wanker 79
D.L. Ward 196
E.M. Wardell 282
E.E. Warner 282
G. Warren 282
H.J. Wasserman 282
P.L. Watson 282
G.B. Watt 282
J.D. Way 282
A.L. Wayda 282
C. Wazeriski 282
D.C. Wazeriurbam 282
W. Weber 282
E. Weberg 282
E.D.V. Wassmuth 282
J. Weber 282
J.E. Weir 282
E. Weiss 282
H. Weiss 282
M. Weiss 282
E. Weiss 282
B. Wenderink 374
D.W. Werter 311
B. Westerby 488
K.E. Westerhuis 474
W.D. Wheeler 238
L.H. Wheeler 481
S. Whetland 338
A. Whetton 275
D.H. White 311
J.L. White 349
E. Wieghardt 210
K. Wieghardt 211
S. Wieland 178
E. Wilkocen 232
S.S. Wild 284
G. Wilke 4
R.G. Wilkins 554
R.G. Wilkins 613
R.D. Wilott 344
A.G. Williams 144
D.R. Williams 488
E.J. Williams 488
P.A.M. Williams 488
C.J. Wills 215
C.J. Wills 62
G. Winkelmann 45
M.J. Winter 23
E.E. Wit 38
E.G. Wite 265
E. Wolf 657
J.E. Wood 157
D.R. Wright 213
T.C. Wright 226
Y. Xiao-Zong 126
G.-X. Xu 59
E.E. Yakubov 59
E.E. Yakubov 114
E.E. Yakubov 8
E.E. Yakubov 2
S. Yamada 2
S. Yamaguchi 2
T. Yamaguchi 15
A. Yamamoto 57
T. Yamamoto 18
Y. Yamamoto 19
H. Yamauchi 19
X.-S. Yang 19
S. Yano 19
S. Yano 19
S. Yano 19
M. Yashiro 19
J.T. Yates, Jr. 19
E.E. Yeskinskii 19
R.G. Yates 19
C.S. Yeo 19
S. Yoshikawa 19
S. Yoshikawa 19
S. Yoshikawa 19
M.-T. Youinou 19
Y.S. Yu 19
Y.-L. Yuan 19
K. Yuzik 19
S. Zaki 19
L.E. Zakharchuk 19
J. Zakrzewski 19

K.I. Zamaraev 86
C. Zanchini 360
P. Zanella 141
P. Zanella 358
P. Zanella 551
F. Zanobini 208
C. Zelter 221
V.V. Zelentsov 362
B. Zerner 67
H.-B. Zhang 277
N.N. Zheligovskaya 486
T.A. Zhemchuzhnikova 544
A.I. Zhirov 362
B. Zhang 123
T.C. Zielinski 541
J.J. Zielkowski 226
J.J. Zielkowski 506
J.J. Zielkowski 265
P.M. Zieleman 682
R. Zoet 359
A.D. Zuberbuhler 413
J. Zubieta 616
M.G. Zuev 251
D. Zwiebel 369