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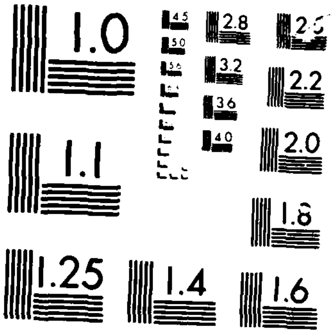

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TRANSITION METAL (II) COMPLEXES OF DITHIACYCLOPHANES

FINAL TECHNICAL REPORT

EARL DOOMES, THORNTON RHODES AND DERALD CHRISS

25 March 1986

U. S. ARMY RESEARCH OFFICE

DAAG29-82-G-0013

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

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20. ABSTRACT

This investigation is related to our recent report on the synthesis and characterization of cobalt (II), copper (II), and nickel (II) complexes of the new macrocyclic ligand, 7-oxa-2,12-dithia[13] (2,6)pyridinophane (1). [1] The coordination chemistry of a series of structurally related macrocylclic ligands (1-8) was investigated. Macrocycles studied include oxa-, dioxa-, and thia- dithiapyridinophanes (2a, 2b, and 3a, respectively), oxa-, dioxa-, trioxa- and polymethylene-dithiaparacyclophanes (4a and 5, 4b, 4c and 6) and 2,10-dithia[3.3](2,6)pyridinophane (9). The pyridinophanes (2a, 2b, 3a and 9) formed stable crystalline complexes when treated with methanol solutions of cobalt (II), copper (II), and nickel (II) salts. However, cobalt (II) and nickel (II) salts did not form crystalline complexes when combined with the paracylcophanes (4, 5, and 6). Electronic spectra, electrolytic conductivities and magnetic susceptibilities data, and elemental analyses were utilized in the characterization of these complexes. Solution and solid state effective magnetic moments were identical for each complex derived from the oxapyridinophane 1, indicating that the same species exists in both phases. Overall, physical data support monomeric structures of general formula M(II)LX2 (where M(II) = the transition metal (II) cation, L= macrocycle, and X = halogen or thiocyanate) for all complexes studied.

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ABSTRACT

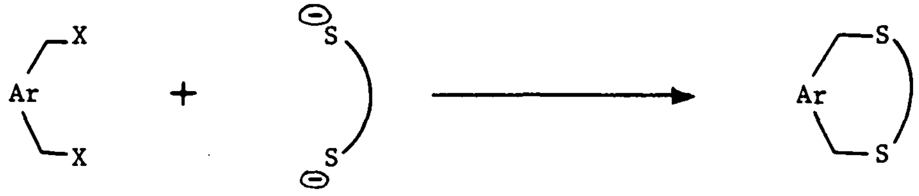
This investigation is related to our recent report on the synthesis and characterization of cobalt (II), copper (II), and nickel (II) complexes of the new macrocyclic ligand, 7-oxa-2,12-dithia[13] (2,6)pyridinophane (1). [1] The coordination chemistry of a series of structurally related macrocylclic ligands (1-8) was investigated. Macrocycles studied include oxa-, dioxa-, and thia- dithiapyridinophanes (2a, 2b, and 3a, respectively), oxa-, dioxa-, trioxa- and polymethylene-dithiaparacyclophanes (4a and 5, 4b, 4c and 6) and 2,10-dithia[3.3](2,6)pyridinophane (9). The pyridinophanes (2a, 2b, 3a and 9) formed stable crystalline complexes when treated with methanol solutions of cobalt (II), copper (II), and nickel (II) salts. However, cobalt (II) and nickel (II) salts did not form crystalline complexes when combined with the paracylcophanes (4, 5, and 6). Electronic spectra, electrolytic conductivities and magnetic susceptibilities data, and elemental analyses were utilized in the characterization of these complexes. Solution and solid state effective magnetic moments were identical for each complex derived from the oxapyridinophane 1, indicating that the same species exists in both phases. Overall, physical data support monomeric structures of general formula M(II)LX2 (where M(II) = the transition metal (II) cation, L= macrocycle, and X = halogen or thiocyanate) for all complexes studied. However, the series includes some non-electrolytes and some 1:1 electrolytes. Tentative structures have been proposed for the various coordination compounds. We have been unable to obtain crystals of any of these complexes that would be suitable for X-ray crystallographic structural analyses. The electrochemistry of this series will be examined within the next three months in order to complete our characterizations. A significant achievement during the grant support period was development of a general scheme for synthesis of trithiapyridinophanes utilizing diisothiorouium salts (derived from simple n-haloalkanols) as key intermediates.

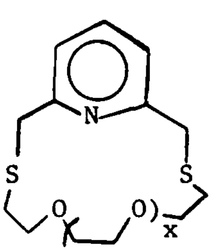
Outline of Research Findings

Statement of Problem: Physical data on transition metal (II) complexes of macrocyclic ligands containing the donor sets SNSO, SNSOO, SNSOOO, SNS, SNSN, SOS and SS will be collected. We shall utilize these data to assess whether geometrically restricted macrocycles with selected donor sets generate unusual ligand fields (e.g., similar to the ligand field in blue copper proteins).

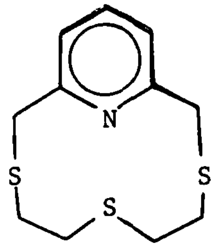
a. Synthesis of Ligands. Previously, we utilized the high dilution method of Vogtle to synthesize a series of dithiaparacyclophanes. [2,3] The general method for synthesis of cyclophane ligands is through the high dilution reaction of the appropriate bis-(halomethyl)arene with a 1,n-alkalenedithiolate (0.040 mole scale in two liters of solution). The

1,n-alkanedithiolates are generated conveniently from the corresponding diisothiouronium dihalides, providing an excellent method for handling exact quantities of precursors of the dithiacyclophanes. This approach has been utilized in the synthesis of several known dithia- and trithiapyridinophanes (2 and 3a, respectively) and the new trithiapyridinophane 3b.

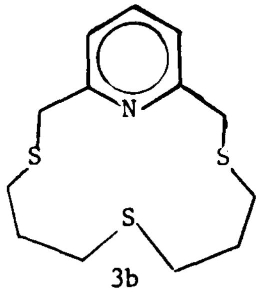




2a x = 0
2b x = 1
2c x = 2



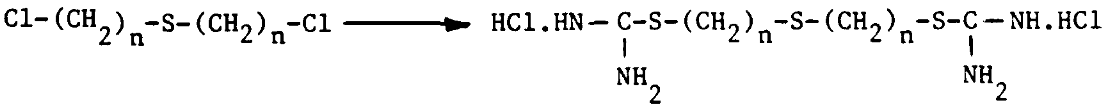
3a



3b

A significant achievement during this period of support is the development of an approach for conversion of n-haloalkanols to the corresponding thiaether dithiols via diisothiouronium dihalides. The n-haloalkanol is treated with sodium sulfide in aqueous alcohol to yield the dihydroxy thiather. The dihydroxy thiather is allowed to react with excess thionyl chloride to yield the bis-(chloroalkyl) thiather. These intermediate compounds were not isolated, and the latter was treated with two molar equivalents of thiourea in ethanol to yield the crystalline diisothiouronium dichlorides. The overall scheme is outlined in the equations that follow. The availability of the thialkane-1,n-ditholates opens the possibility for synthesis of a wide range of trithiacyclophanes. The various new dithiacyclophanes that were synthesized by this gereral method will be described under the section that deals with the associated coordination chemistry.

$$\mathrm{HO\text{-}(CH_2)_n\text{-}X \longrightarrow HO\text{-}(CH_2)_n\text{-}S\text{-}(CH_2)_n\text{-}OH \longrightarrow}$$



$$\mathrm{Cl\text{-}(CH_2)_n\text{-}S\text{-}(CH_2)_n\text{-}Cl \longrightarrow HCl.HN-\underset{\underset{NH_2}{|}}{C}\text{-}S\text{-}(CH_2)_n\text{-}S\text{-}(CH_2)_n\text{-}S\text{-}\underset{\underset{NH_2}{|}}{C}-NH.HCl}$$

$$\mathrm{\longrightarrow HS\text{-}(CH_2)_n\text{-}S\text{-}(CH_2)_n\text{-}SH}$$

b. Characterization of Transition Metal (II) Complexes of 5-Oxa-2,8-dithiapyridinophane (2a) and 2,5,8-Trithiapyridinophane (3a). The previously synthesized [3,4] ligands, 2a and 3a, were synthesized in high yield by the high dilution reaction of bis-2,6-(chloromethyl)pyridine with the appropriate 1,n_dithiolate. Physical data for 2a and 3a were identical to those reported for these substances in the literature. [3,4] The transition metal (II) halide complexes and the cobalt (II) thiocyanate complexes were synthesized as outlined in Scheme I. The designations for ligands (see below) indicate the potential donor set and bridge size between the methanethio groups of the cyclophanes. Specific transition metal (II) complexes synthesized, and their properties are listed in Table I.

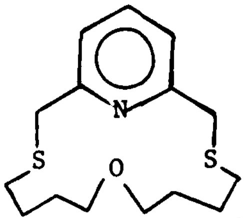
Scheme I

$$\mathrm{L} \quad + \quad \mathrm{M(II)X_2} \xrightarrow[\text{methanol}]{\text{hot}} \mathrm{MLX_2}$$

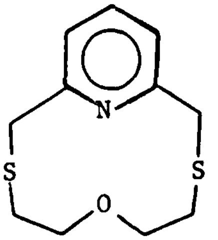
M(II) = Co(II), Ni(II) or Cu(II)

X = Cl, Br or SCN

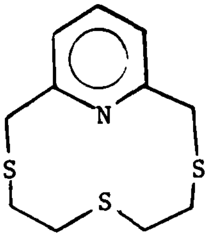
L = 1, 2a or 3a



1 = SNSO-9



2a = SNSO-5



3a = SNSS-5

Electrolytic conductivity data (equivalent conductances equaling 38-89 ohm-1 cm2 mole-1) indicate that complexes of 2a and 3a investigated are 1i1 electrolytes or non-electrolytes. Also, magnetic moments for this series of complexes fall within the expected range for the central metal cations (Table I). Ultraviolet-visible spectra for the series of SNSO-5 complexes are reported in Table II. The analogous data for complexes of SNSS-5 are reported also. Although the affinities of the metal (II) cations for a thiather sulfur atom would be expected to be greater than their affinities for ether oxygen, the complexes of SNSO-5 and SNSS-5 appear to have analogous structures. These data suggest that each ligand is tetradentate, and that one of the halide ions enter the inner coordination sphere. Spectral and electrolytic conductivity data (~25 ohm-1 cm2 mole-1) indicate that the thiocyanate complexes are six coordinate wherein both monodentate thiocyanate ligands enter the inner coordination sphere. The ultraviolet-visible spectra of previously reported polymethylene dithiapyridinophanes (SNS ligand) show maxima at different wavelengths than the oxa- and thia- dithiapyridinophanes reported here [6].

Table I. Physical Properties of Transition Metal (II) Complexes of 2a and 3a (SNSO-5 and SNSS-5, respectively)

Compound (a)	Color	μ_{eff} (b)	Λ (c)
Co(SNSO-5)2Cl	bright purple	5.1	53
Co(SNSO-5)2(SCN)	purple	5.0	38
Ni(SNSO-5)2Cl	bright green	3.3	62
Ni(SNSO-5)2Br	green	3.3	54
Cu(SNSO-5)2Cl	dark green	1.6	35
Cu(SNSO-5)2Br	pale green	2.3	54
Co(SNSS-5)2Cl	purple	5.3	34
Co(SNSS-5)2(SCN)	dark purple	4.8	17
Ni(SNSS-5)2Cl	blue-green	3.3	(d)
Ni(SNSS-5)2Br	blue	3.2	81
Cu(SNSS-5)2Cl	greenish-brown	1.7	42
Cu(SNSS-5)2Br	olive green	1.7	69
Co(SNSO-9)2(SCN)	purple	5.0	55

(a) the ligands are designated by donor set and number of members between methanethio groups, (b) Bohr magnetons, room temperature, (c) in ohm-1 cm2 mole-1 for 2 x 10-4 M nitromethane or dimethylformamide solutions, (d) insoluble.

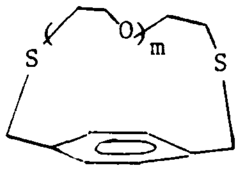
TABLE II. Electronic Spectral Data of Complexes of 5-Oxa-2,8-dithiapyridinophane (2) and of 2,5,8-Trithiapridinophane (3)

Complex	Absorption Bands, Frequencies, kK (ε)
	In nitromethane
Cu(SNSO-5)2Cl	15.2 (300)
Cu(SNSO-5)2Br	14.9 (370)
Ni(SNSO-5)2Cl	15.7 (40), 25.1 (93), 27.0 (82)
Ni(SNS-5)2Br	15.9 (62), 24.2 (116), 26.8 (184)
Co(SNS-5)2CL	15.3 (307), 16.9 (308), 19.0 (73), 26.8 (228)
Cu(SNSO-5)2Cl	14.5 (228)
	In acetonitrile
Cu(SNSO-5)2Br	14.3 (305)
Ni(SNSO-5)2Cl	15.6 (55), 25.6 (98), >30 (strong)
Ni(SNSO-5)2Br	15.6 (69), 26.6 (150), >30 (strong)
Co(SNSO-5)2(SCN)	15.2 (198), 16.0 (150), 17.6 (209), >30 (strong)
	In dimethylformamide
Cu(SNSS-5)2Br	16.9 (94), 262 (1,073)
Ni(SNSS-5)2Br	15.2 (98), 35.1 (7,680)
Co(SNSS-5)2Cl	14.8 (296), 16.4 (190)
Co(SNSS-5)2(SCN)	16.0 (221), 32.8 (811)
Co(SNSO-9)2(SCN)	16.0 (608), 16.7 (355)

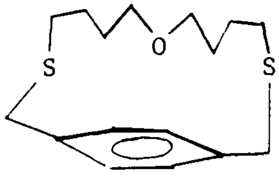
Co(SNSO-5)2(SCN), Cu(SNSS-5)2Cl, and Ni(SNSS-5)2Cl were synthesized also.

c. Characterization of Copper (II) Complexes Derived from Oxa-, Dioxa-, Trioxa- and Polymethyleneparacyclophanes (4a, and 5, 4b, 4c, and 6, respectively).

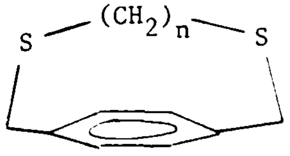
Dithiaparacyclophanes were synthesized in good yield (40-80%) by adapting the high dilution method of Vogtle. The 1,n-alkane-dithiolates and oxaalkane-1,n-dithiolates were generated conveniently in situ from the corresponding diisothiouronium dihalides. Reaction of the dithiolates with appropriate bis-(halomethyl)arenes yield the ligands outlined below. We synthesized five new oxacyclophane ligands (4, 5 and 7) along with four previously reported polymethylene cyclophanes.



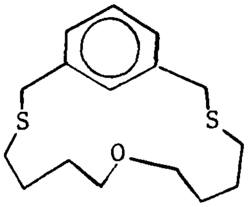
4a m = 1, SOS-5
4b m = 2, SOOS-8
4c m = 3, SOOOS-11



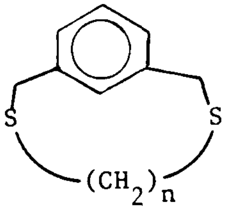
5, SOS-9



6 n = 7 or 9
SS-7 or SS-9



7



8 n = 7 or 8

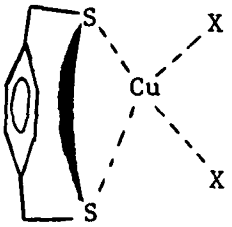
The coordination chemistry of the new oxadithiametacyclophane 7 and of the previouslv reported dithiamethcyclophanes (8) were investigated in order to examine structural effects on the ease of formation and stability of copper (II) complexes within the series. Neither oxadithiaparacyclophene 4a (containing a nine membered bridge) nor dithiametacyclophanes (7 and 8) yielded solid insolable copper (II) chloride complexes in methanol solution. On the other hand, oxadithiaparacyclophanes (4b, 4c, 5 and 6) and polymethylenedithiaparacyclophanes (6, containing bridges of ten or more members) yielded green crystalline complexes that are sparinglyl soluble in anhydrous methanol. Complexes may be formulated as shown in Table III. These copper (II) complexes exhibit relatively low melting points, and their equivalent conductances suggest neutral molecular structures. The failure of 4a and of 7 and 8 to form stable crystalline complexes indicate a steric requirement in the ligand structure. In the absence of x-ray crystallographic data on a representative complex, a folded structure (A) is proposed wherein copper (II) is in its usual square planar geometry. An interesting alternate structure (B), although unlikely, is one in which copper (II)

Table III. Physical Data for Copper (II) Complexes of Dithiaparacyclophanes (4b, 4c, 5 and 6)

Compound (a)	mp, °C	Λ (b)	UV-visible, kK (c)
Cu(SOS-9)2Cl	137-138	17	22.8 (288)
Cu(SOOS-8)2Cl	136-137	17	22.8 (285)
Cu(SOOS-8)2Br	120-122	30	16.8 (196)
CU(SOOOS-11)2Cl	143-145	20	22.9 (278)
Cu(SOOOS-11)2Br	125-127	30	16.9 (157)
Cu(SS-7)2Cl	140-141	15	22.9 (244)
Cu(SS-9)2Cl	142-143	27	22.9 (249)

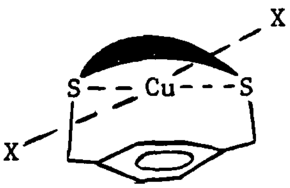
(a) See previous page for structures; notation indicates potential donor set. (b) In ohm-1 cm2 mole-1 for 1 x 10-3 M solutions in dimethylformamide. (c) spectra were determined in dimethylformamide solution.

$CuCl_2$ + Ligand $\longrightarrow$ Cu(Ligand)2Cl, green solid would occupy the cavity between the aliphatic bridge and the aromatic nucleus. A tetrahedral structure for copper (II) as shown in structure C appears remote.



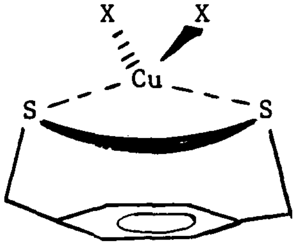
A

square planar, *cis* X groups



B

square planar, trans X groups

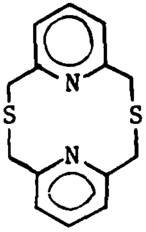


C

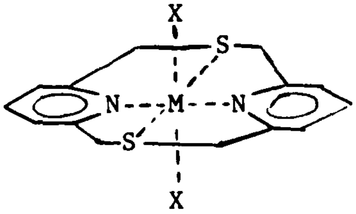
tetrahedral

While effective magnetic moments for this series of complexes are relatively low (μeff = 1.4-1.7 B.M.), the experimental values support monomeric structures (as apposed to polymeric or cluster complexes) for these crystalline substances. Characteristics of visible spectra within this series of copper (II)-dithiaparacyclophane complexes (in dimethylformamide) depended on the monodentate halide ions primarily, as shown in the data summary in Table III. Since conductivity and electronic spectral data were obtained in the same solvent, identical species were examined in each case. Thus the electrolytic conductivity data assures us that complexes do not dissociate in dimethylformamide (complexes are non-electrolytes).

d. Complexes of 2,10-Dithia[3.3](2,6) pyridinophane (9). The pyridinophane 9 was reported previously. However, we are unaware of any reports on the coordination chemistry of this tetradentate ligand. The bipyridyl ligand (9) reacted with metal (II) salts in methanol solution to yield crystalline complexes with high melting points (>300 degrees Celsius) and low solubilities in polar aprotic solvents (nitromethane and dimethylformamide). Electrolytic conductivity on dilute solutions indicate that the series of complexes are non-electrolytes, suggesting a six-coordinate octahedral structures (10). Elemental analyses on these complexes support the general formula, M(SNSN)X2.



9
designated SNSN



M(II) = Cu(II)
= Co(II)
= Ni(II)
X = Cl
= Br
= SCN

10 $M(SNSN)X_2$

Table IV. Transition Metal (II) Complexes of 2,10-Dithia[3.3](2,6)pyridinophane (1).

Compound	μ_{eff}	Λ, ohm-1 cm2 mole-1	UV-Visible
Cu(SNSN)2Cl	2.0	27	(b)
Cu(SNSN)2Br	1.4	47	(b)
Co(SNSN)2Cl	4.8	13	(b)
Co(SNSN)2(SCN)	4.5	23	(b)

(a) obtained on 2 x 10-4 M dimethylforamide solutions, (b) no significant absorption was observed in the visible spectra at these concentrations.

We have begun the preparation of two manuscripts for publication of portions of this work. The comparative chemistry of structurally related ligands and the physical properties of their complexes will be discussed. Measurement of the oxidation-reduction potentials of the complexes will allow us to determine whether ligand structure (as well as donor set) can alter significantly the ease of reduction of copper (II). We have the equipment and reagents on hand to make these measurements. Our efforts to obtain crystals suitable for x-ray crystallographic analyses continue. We have made arrangements with the crystallography group at Lousiana State University for determination of crystal structures of representative examples within our series of complexes, and they provided tips on how suitable crystals may be grown. The critical literature review connected with our experimental findings will be included in forthcoming manuscripts. We plan to complete two manuscripts based on data included in this report by August, 1986.

PUBLICATIONS: None

SCIENTIFIC PERSONNEL:

Earl Doomes, Principal Investigator, 20 Septimber 1982 through 19 September 1985.

Thornton Rhodes, Co-principal Investigator, 20 September 1982 through 5 November 1984 (unable to continue due to illness).

Derald Chriss, Research Associate, 20 January 1984 through 17 May 1985.

Sylvester Burton, Graduate Student, 19 August 1983 through 19 September 1985; Mr. Burton will receive an M. S. degree in chemistry in May 1986.

Verlinda Allen, Undergraduate student, 20 August 1984 through 17 may 1985; Ms. Allen expects to receive a B. S. degree in chemistry in May 1986.

Batool Tadayoni, Research Assistant, 1 June through 8 August 1985. Ms. Tadayoni is now a graduate student who is supported by a Chemistry Department assistantship, and expects to receive an M. S. degree in May 1986 (organic research problem).

Depaak Mohanty, Undergraduate Research Assistant, 20 September through 19 December 1983.

Hillary Wynn, Research Assistant, 9 June through 18 August 1983.

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6. See references 1 and 2 for a brief discussion of this point.

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