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BINUCLEAR SCHIFF BASE COMPLEXES OF
M-XVLYLENEBIS(2-(13-PROPANE)DI (2-PYRID. (U) ROCHESTER
UNIV NY DEPT OF CHEMISTRY B C WHITMORE ET AL.

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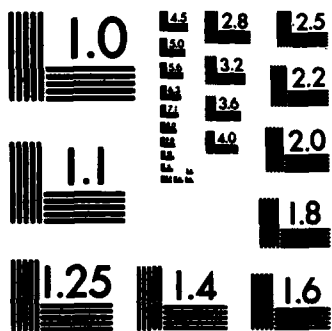
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Binuclear Schiff Base Complexes of m-Xylylenebis(2-(1,3-propanedi(2-pyridinealdimine))) and m-Xylylenebis(2-(1,3-propanedi(2-pyrrolealdimine)))

by

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2-4 exhibit electronic spectra consistent with tetragonally distorted square planar complexes. The binuclear nickel complex 2a exhibits a molar conductance of $\Lambda_{m, 182} = 182 \text{ cm}^2 \text{ ohm}^{-1}$ in methanol while its mononuclear analogue, Ni(1,3-propanedi(2-pyridinealdimine))Cl₂, has a conductance of $\Lambda_{m, 160} = 160 \text{ cm}^2 \text{ ohm}^{-1}$, both typical of 2:1 electrolytes. In DMF solution, complex 2c exhibits a molar conductance of $\Lambda_{m, 87} = 87 \text{ cm}^2 \text{ ohm}^{-1}$, typical of a 1:1 electrolyte, while the mononuclear nickel complex, Ni(1,3-propanedi(2-pyrroloaldimine))(SCN)₂, has a molar conductance in DMF of $\Lambda_{m, 75} = 75 \text{ cm}^2 \text{ ohm}^{-1}$, also in the range expected for a 1:1 electrolyte. The room temperature magnetic susceptibilities were determined for complexes 2a, 2b, 2c, 3 and 4, and all were found to be paramagnetic ($S = 1$ ground states for 2, 3, 4 and 5, $S = \frac{1}{2}$ for 3 and 4). The condensation of 2-pyrroloaldehyde with *m*-xylidenebis(2-(1,3-propanedi(2-pyridinealdimine))) followed by the addition of nickel(II) or copper(II) acetate leads to the formation of the neutral, nonconducting complexes, Ni₂(L)₂(S) and Cu₂(L)₂(S), respectively (L = *m*-xylidenebis(2-(1,3-propanedi(2-pyrroloaldimine)))(2-)). The electronic spectra of 5 and 6 are consistent with square planar coordination geometries. While complex 6 is paramagnetic, complex 5 is diamagnetic and has been characterized by ¹H NMR spectroscopy. A complete assignment of all the resonances of 5 is given and the conformation of the propanediamine chelate ring is discussed based on the coupling constants in the observed spectrum.

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($S = 1$ ground states for $\underline{2}$, $S = \frac{1}{2}$ for $\underline{3}$ and $S = \frac{3}{2}$ for $\underline{4}$). The condensation of 2-pyrroledialdehyde with *m*-xylylenedis(2-(1,3-propanediamine)) followed by the addition of nickel(II) or copper(II)acetate leads to the formation of the neutral, nonconducting complexes, $\text{Ni}_2\text{L}'(\underline{5})$ and $\text{Cu}_2\text{L}'(\underline{6})$, respectively (L' = *m*-xylylenedis(2-(1,3-propanedi(2-pyrroledialdime))) (2-)). The electronic spectra of $\underline{5}$ and $\underline{6}$ are consistent with square planar coordination geometries. While complex $\underline{6}$ is paramagnetic, complex $\underline{5}$ is diamagnetic and has been characterized by ^1H NMR spectroscopy. A complete assignment of all the resonances of $\underline{5}$ is given and the conformation of the propanediamine chelate ring is discussed based on the coupling constants in the observed spectrum.

Contribution from the Department of Chemistry
University of Rochester, Rochester, New York 14627

Bimuclear Schiff Base Complexes of *m*-Xylylenedis(2-(1,3-propanedi(2-pyridinedialdime))) and *m*-Xylylenedis(2-(1,3-propanedi(2-pyrroledialdime)))

Bryon C. Whitmore and Richard Eisenberg*

Received

Abstract

Bimuclear complexes of Ni, Cu, and Co have been synthesized and characterized. The reaction of nickel(II)-, copper (II)-, or cobalt(II)chloride with a solution of 2-pyridinedialdehyde and *m*-xylylenedis(2-(1,3-propanediamine)) results in the formation of $\text{Ni}_2\text{LCT}_4(\underline{2a})$, $\text{Cu}_2\text{LCT}_4(\underline{3})$ and $\text{Co}_2\text{LCT}_4(\underline{4})$, respectively, where L = *m*-xylylenedis(2-(1,3-propanedi(2-pyridinedialdime))). The bimuclear nickel complexes, $\text{Ni}_2(\text{NH}_3)_5(\underline{2b})$ and $\text{Ni}_2(\text{SCN})_4(\underline{2c})$ are prepared by metathesis of the chloride ion of complex $\underline{2a}$ using the appropriate sodium salt. These complexes, $\underline{2}$ - $\underline{4}$, exhibit electronic spectra consistent with tetragonally distorted six-coordinate complexes. The bimuclear nickel complex $\underline{2a}$ exhibits a molar conductance of $\Lambda_{\text{MH}} = 182 \text{ cm}^2 \text{ ohm}^{-1}$ in methanol while its mononuclear analogue, $\text{Ni}(\text{1,3-propanedi(2-pyridinedialdime)})\text{Cl}_2$, has a conductance of $\Lambda_{\text{MH}} = 140 \text{ cm}^2 \text{ ohm}^{-1}$, both typical of 2:1 electrolytes. In DMF solution, complex $\underline{2c}$ exhibits a molar conductance of $\Lambda_{\text{MH}} = 87 \text{ cm}^2 \text{ ohm}^{-1}$, typical of a 1:1 electrolyte, while the mononuclear nickel complex, $\text{Ni}(\text{1,3-propanedi(2-pyridinedialdime)})(\text{SCN})_2$, has a molar conductance in DMF of $\Lambda_{\text{MH}} = 75 \text{ cm}^2 \text{ ohm}^{-1}$, also in the range expected for a 1:1 electrolyte. The room temperature magnetic susceptibilities were determined for complexes $\underline{2a}$, $\underline{2b}$, $\underline{2c}$, $\underline{3}$ and $\underline{4}$, and all were found to be paramagnetic

Introduction

Binuclear transition metal complexes have received much attention in recent years.¹ The interest in such systems is stimulated by a number of factors. Bimetallic coordination complexes may serve as models for a variety of biological reactions, such as oxygen transport,² oxygen activation³ and photosynthetic water reduction.⁴ Binuclear complexes have also been utilized in the study of electron transfer processes⁵ and metal-metal interactions.⁶ The interest in these systems also arises from their ability to serve as simple models for multi-metal centered catalysts.⁷ Many types of binuclear complexes have been reported in recent years with the orientation of the metal centers and hence the nature of the metal-metal interactions controlled through the selection of bridging ligands.

We recently reported a series of binuclear Schiff base complexes based on a ligand containing a bridging xylylene moiety.⁸ This type of complex belongs to a series of complexes employing flexible bridging ligands which provide relatively independent and unrestricted environments for each complexed metal ion relative to the second metal center. Complexes of this type are also flexible enough to allow interactions between the two metal centers and a single substrate molecule, as has been demonstrated in complexes of related p-xylylene systems. Martell and co-workers have reported the formation of a dioxygen adduct of a cobalt(II) "wishbone" complex,⁹ where the dioxygen molecule bridges two cobalt centers in an intramolecular fashion. A binuclear copper "ear-muff" complex,¹⁰ intramolecularly bridged by a single hydroxyl group has also been reported and crystallographically characterized.

In the present paper we report the synthesis of binuclear transition metal complexes of Ni, Cu and Co based on the new Schiff base ligands m-xylylenebis(2-(1,3-propanedi(2-pyridinealdimine))) and m-xylylenebis(2-(1,3-propanedi(2-pyridinealdimine))) and m-xylylenebis(2-(1,3-propanedi(2-pyridinealdimine))) (2-). Drawings of the binuclear complexes, along with their nomenclature are presented in Figure 1.

Experimental Section

The following abbreviations are used for the tridentate ligands: py₂-pm, 1,3-propanedi(2-pyridinealdimine); pyr₂-pm, 1,3-propanedi(2-pyrrolealdimine) (2-). Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

Physical Measurements. ¹H NMR were recorded on a Bruker WM400 400-MHz instrument with chemical shifts reported in ppm relative to Me₄Si. Infrared spectra were recorded on a Perkin-Elmer Model 467 grating spectrophotometer. Electronic spectra were recorded on a Perkin-Elmer Model 330 spectrophotometer using 1-cm quartz cells. Extinction coefficients are given in M⁻¹cm⁻¹. Solution magnetic moments were determined using the Evans NMR method.¹¹ Electrochemical measurements were made at room temperature with a PAR 173 potentiostat, a PAR 175 universal programmer, and a PAR 179 digital coulometer. The three-electrode cell consisted of a saturated calomel reference electrode with a 0.1 M KCl (aq) salt bridge, a platinum auxiliary electrode and either a glassy carbon, platinum or hanging mercury drop working electrode. Conductance measurements were made with a Barnstead DM-70CB conductivity bridge equipped with a Barnstead B-10 1.0cm cell. A working cell constant was determined from the ratio of the observed specific conductance of 0.02 M aq. KCl with the literature value of 0.002768 ohm⁻¹cm⁻¹ at 25°C.¹² Typically, equivalent conductances for the complexes in solution were determined at five concentrations ranging from ca. 5 x10⁻⁴ to 0.1 M. The equivalent conductances at 1 M were then determined from an Onsager plot of equivalent conductance vs. (concentration)^{1/2}.

Reagents. All solvents used were analytical reagent grade except where otherwise noted. m-xylylenebis-(2-(1,3-propanediamine)), ¹, was prepared as described previously.⁸ Ni(py₂-pm)Cl₂,¹³ Ni(pyr₂-pm)(N₃)₂,¹³ Cu(py₂-pm)(ClO₄)₂,¹⁴ Ni(pyr₂-pm),¹⁵ and Cu(pyr₂-pm)¹⁶ were all prepared by literature methods.

2-Pyridinealdehyde and 2-pyrrolinealdehyde were purchased from Aldrich and used without further purification.

m-Xylylenebis(N(py₂prn)Cl₄·2H₂O (2a)) 2-Pyridinealdehyde (0.413 g, 3.86 mm) dissolved in isopropanol (5 ml) is added dropwise over 2 min to a stirred solution of 1 (0.241 g, 0.965 mm) in isopropanol (5 ml) at 0°C. The reaction mixture is stirred at room temperature for 1 h, and the ligand solution then added to HCl₂·2H₂O (0.46 g, 1.93 mm) dissolved in hot ethanol (10 ml). The resulting dark green solution is reduced in volume by one-half and then cooled to 0°C. The resulting precipitate is filtered, washed with diethyl ether (20 ml) and dried in vacuo yielding 2a as a pale yellow-green solid (0.39 g, 40%). Further reduction in volume of the filtrate yields another crop of 2a (0.34 g, 35%). Total yield, 75%. Anal. Calcd for C₃₈H₅₄N₈Cl₄O₈: C, 45.18; H, 5.40; N, 11.09; Cl, 14.04. Found: C, 45.49; H, 5.41; N, 11.10; Cl, 14.09. IR (KBr): 1645, 1596, 1478, 1445, 1306, 1019, 776 cm⁻¹.

m-Xylylenebis(N(py₂prn))(N₃)₄·2H₂O (2b) is prepared by the metathesis of Cl⁻ in 2a using an excess of NaN₃ in H₂O and is recrystallized from H₂O/acetone. Anal. Calcd for C₃₈H₄₂N₂₀O₂: C, 49.16; H, 4.57; N, 30.18. Found: C, 49.10; H, 4.60; N, 30.37. IR (KBr): 2020, 1640, 1596, 1478, 1445, 1308, 1018, 777 cm⁻¹.

m-Xylylenebis(N(py₂prn))(NCS)₄·H₂O (2c) is prepared by metathesis of Cl⁻ in 2a using an excess of NaSCN in methanol. Anal. Calcd. for C₄₂H₄₀N₁₂O₄S₄: C, 51.76; H, 4.15; N, 17.25; S, 13.16. Found: C, 51.42; H, 4.25; N, 17.02; S, 13.09. IR (KBr): 2065, 1640, 1598, 1477, 1445, 1307, 1018, 774 cm⁻¹.

m-Xylylenebis(Cu(py₂prn)Cl₄·2H₂O (3)). This complex is made following the procedure for synthesizing 2a but using CuCl₂·6H₂O as the metal salt and is isolated as a green solid in 64% yield. Anal. Calcd for C₃₈H₄₂N₈O₂Cu₂Cl₄: C, 50.05; H, 4.65; N, 12.29. Found: C, 50.12; H, 4.78; N, 12.06. IR (KBr): 1638, 1600, 1478, 1446, 1305, 1226, 775 cm⁻¹.

m-Xylylenebis(Co(py₂prn)Cl₄·7H₂O (4)). This complex is made by the same procedure used to prepare 2a using CoCl₂·H₂O in place of NiCl₂·6H₂O and is isolated as an olive green solid containing orange microcrystals which when crushed become olive green. Yield, 74%. Anal. Calcd for C₃₈H₅₅N₈O₇Co₂Cl₄: C, 45.98; H, 5.29; N, 11.29; Cl, 14.29. Found: C, 46.31; H, 5.34; N, 10.92; Cl, 14.25. IR (KBr): 1645, 1600, 1479, 1446, 1308, 1022, 777 cm⁻¹.

Co(py₂prn)Cl₂·H₂O. 2-Pyridinealdehyde (1.07 g, 10 mm) and 1,3-propanediamine (0.37 g, 5 mm) are combined in isopropanol (5 ml) at 0°C and stirred at room temperature for 9 h. The solution is then added to CoCl₂·H₂O (1.19 g, 5 mm) in hot ethanol (5 ml), refluxed 10 min, and then cooled to room temperature. After 1 h, the solution is filtered and the orange crystalline solid washed with isopropanol (10 ml), and diethyl ether (20 ml) and dried in vacuo (yield 1.0 g, 50%). Additional precipitate forms upon addition of diethyl ether to the reaction solution, and after filtration the precipitate is washed with ether and dried in vacuo (yield 0.81 g, 41%). Total yield, 91%. The orange solid can be recrystallized from hot acetonitrile, yielding orange crystals. Anal. Calcd for C₁₅H₁₈N₄OCoCl₂: C, 45.01; H, 4.54; N, 14.00; Cl, 17.72. Found: C, 45.17; H, 4.44; N, 14.16; Cl, 17.98. IR (KBr): 1642, 1595, 1475, 1430, 1375, 1305, 1018, 782, 433 cm⁻¹.

m-xylylenebis(Ni(pyrr₂pm))(5). 2-Pyrrolealdehyde (0.307 g, 3.23 mm) and 1 (0.203 g, 0.61 mm) are refluxed in isopropanol (30 ml) for 2 h and added to a hot solution of Ni(OAc)₂·H₂O (0.604 g, 1.62 mm) in ethanol (20 ml). This is refluxed another hour and chilled to 0°. The resulting solid is filtered, washed with ethanol (10 ml) and dried in vacuo yielding 5 as an orange solid (0.33 g, 66%). Anal. Calcd for C₃₄H₃₄N₄H₂O: C, 60.76; H, 5.10; N, 16.67. Found: C, 61.02; H, 5.60; N, 16.42. IR (KBr): 1669, 1440, 1369, 1312, 1043, 790 cm⁻¹. ¹H NMR (CDCl₃): 7.25 (1 H, m, aromatic), 7.17 (4 H, s, imine), 7.07 (3 H, m, aromatic), 6.89 (4 H, s, pyrrolic), 6.57 (4 H, m, pyrrolic), 6.08 (4 H, m, pyrrolic), 3.21 (4 H, d, methylene), 2.95 (4 H, dd, methylene), 2.85 (4H, d, benzylic), 2.16 (2 H, m, methine).

m-xylylenebis(Cd(pyrr₂pm))(6) is prepared by the above procedure using Cu(OAc)₂ in place of Ni(OAc)₂ and is isolated as a green solid in 58% yield. Anal. Calcd for C₃₄H₃₄N₄Cd₂: C, 59.90; H, 5.03; N, 16.44. Found: C, 60.10; H, 5.14; N, 16.21. IR (KBr): 1594, 1440, 1373, 1310, 1036, 746 cm⁻¹.

Results and Discussion

Ligand Syntheses. The ligands used to prepare the binuclear complexes examined in this paper are made by the Schiff base condensation of 1 equiv of m-xylylenebis(2-(1,3-propanediimine)) (1)⁶ with 4 equiv of either 2-pyridinealdehyde or 2-pyrrolealdehyde, and are used immediately without isolation. The binuclear complexes are then prepared using these ligand solutions following minor modifications of the reported synthetic procedures for their mononuclear analogues.

Pyridinealdimine complexes.

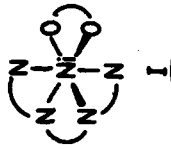
Synthesis. The reaction of NiCl₂·6H₂O with the ligand solution of m-xylylenebis(2-(1,3-propanedi(2-pyridylimine))) produces the binuclear nickel complex m-xylylenebis(Ni(py₂pm))Cl₄, 2a, as a yellow-green solid. This complex is soluble in water, methanol and ethanol but insoluble in chloroform, Me₂SO, ether and hydrocarbon solvents. Its mononuclear analogue, Ni(py₂pm)Cl₂ is a green crystalline solid and exhibits similar solubility properties. The copper and cobalt binuclear complexes, 3 and 4, are prepared similarly to 2a and also show similar solubility properties. The copper(II)¹⁴ and nickel(II)¹³ complexes of the tetradentate chelating agent py₂pm have been reported previously, but the mononuclear cobalt complex, Co(py₂pm)Cl₂, is reported here for the first time. It is synthesized by a modification of the procedure used to make Ni(py₂pm)Cl₂,¹³ and is isolated as air stable orange crystals which appear olive-green when crushed.

Infrared Spectra. The infrared spectra of the binuclear schiff base complexes containing the pyridinealdimine group exhibit bands typical of 2-substituted pyridines¹⁹ and also display a band near 1640 cm⁻¹ assigned to the stretching vibration of the C-H group. The reported mononuclear analogues have similar infrared spectra. The azide derivative, 2b, shows in addition to the above bands, an azide stretch at 2020 cm⁻¹, which can be assigned to a terminal azide bonding mode. The nickel(II) thiocyanate derivative, 2c, exhibits an infrared stretch at 2085 cm⁻¹ assignable to ν_{CN}, but the C-S stretch and NCS bending modes are obscured by the chelating ligand bands. The mononuclear nickel complex Ni(py₂pm)(NCS)₂,¹³ which is proposed to contain N-bonded thiocyanate ligands based on the observed C-S stretching and NCS bending frequencies, has its ν_{CN} at 2092 cm⁻¹. On the basis of the similarity between ν_{CN} for the nickel complex 2c and for Ni(py₂pm)(NCS)₂ we propose the presence of N-bound thiocyanate ligands in 2c.

Electronic Spectra. The binuclear complexes exhibit electronic spectral bands similar to their mononuclear analogues in both wavelength and extinction coefficient (Table I). The binuclear nickel complex, $\bar{2}a$, contains two principle bands in the near-infrared and visible regions in both methanol and aqueous solution. These bands have low extinction coefficients typical of d-d transitions and appear in the region where the first two spin allowed transitions for an octahedral nickel(II) complex are expected. The parent octahedral bands are the ${}^3A_{2g} \rightarrow {}^3T_{2g}$ and ${}^3A_{2g} \rightarrow {}^3T_{1g}$ transitions. In addition, the weak band which appears at 760 m can be assigned to the spin forbidden transition ${}^3A_{2g} \rightarrow {}^1E_g$. The low energy band, ${}^3A_{2g} \rightarrow {}^3T_{2g}$, contains splitting (815 (c17) and 1050 (c7)) similar to that observed for its mononuclear analogue, $Ni(py)_2(pyridine)Cl_2$, typical of tetragonally distorted nickel(II) complexes.²⁰ The splitting can be assigned to the ${}^3A_{1g} \rightarrow {}^3E_{2g}$ and ${}^3A_{1g} \rightarrow {}^3E_g$ transitions. The first tetragonal component occurs at higher energy and is a measure of the in-plane donor strength, while the second, lower energy component reflects the donor strength of the axial ligands. The species present in aqueous or methanolic solutions of $\bar{2}a$ are thus formulated as $[N\text{-xylylenbis} (Ni(py)_2(pyridine))Cl]_x(S)_y]^{(4-x)+}$, where $S = H_2O$ or CH_3OH , with the weaker field ligands Cl^- and solvent S occupying axial coordination positions. From the conductivity data it appears that $x = 1$ for aqueous solutions and $x = 2$ for methanolic solutions of complex $\bar{2}a$.

The addition of other weak donors, such as Mg_2CO_3 , to an aqueous solution of $\bar{2}a$ causes no change in its electronic spectrum, indicating the continued presence of the tetragonally distorted solvated species. However, the addition of either carbonate or oxalate to complex $\bar{2}a$ in water produces significant changes in its electronic spectrum. When Mg_2CO_3 is added to an aqueous solution of $\bar{2}a$, a new band appears in the near-IR region at 910 m (c33) (${}^3A_{2g} \rightarrow {}^3T_{2g}$), replacing the 800 and 1005 m bands of complex $\bar{2}a$. The lack of splitting of this band indicates formation of a nickel (II) species which no longer contains

a tetragonally distorted ligand field. The electronic spectrum is similar to spectra observed for bis(ethylenediamine) nickel(II) complexes containing cis-chelated nitrate ligands.²¹ When Mg_2CO_3 is added to complex $\bar{2}a$, spectral changes similar to those seen upon the addition of carbonate are observed (λ_{max} 990 m(c31)). In addition to the changes seen for the ${}^3A_{2g} \rightarrow {}^3T_{2g}$ transition, there is an increase in the extinction coefficients of the ${}^3A_{2g} \rightarrow {}^3T_{1g}$ transitions (c45 and c40 for carbonate and oxalate, respectively). All of these spectral changes (i.e. - lack of splitting and intensity enhancement) are consistent with the chelation of the dianionic ligands, CO_3^{2-} and $C_2O_4^{2-}$, to the nickel(II) centers and a reduction of symmetry about the metal centers from D_{4h} to C_{2v} -distorted octahedral structures shown as $\bar{1}$,^{20,22}



The cobalt complexes exhibit electronic spectra typical of pseudo-octahedral symmetry.²⁰ The complex, $Co(py)_2(pyridine)Cl_2$ has weak ligand field bands at 950 m (c5) and at 460 m (c100) assignable to the ${}^4T_{1g} \rightarrow {}^4T_{2g}$ and ${}^4T_{1g} \rightarrow {}^4T_{1g}(P)$ transitions. The binuclear cobalt complex, $\bar{2}$, exhibits a broad transition centered at 970 m (c7) (${}^4T_{1g} \rightarrow {}^4T_{2g}$) and a band at 460 m (c132) (${}^4T_{1g} \rightarrow {}^4T_{1g}(P)$). The broadness of the low energy bands for the cobalt complexes may indicate some splitting of the transitions into more than one component, consistent with tetragonal distortion of these complexes.²⁰ The binuclear copper complex, $\bar{3}$, contains a weak band assignable to a d-d transition at 730 m (c211) with a long tail into the near-IR region. The assignment of this band is uncertain due to its broadness. It most likely contains several unresolved transitions, a common feature of tetragonally distorted copper(II) complexes.²⁰

Magnetic and Electrochemical Data.

The solution magnetic moments for the binuclear complexes are also nearly the same as their mononuclear analogues. The nickel complexes have magnetic moments consistent with high spin d^8 systems. Measurement of the magnetic moment of 2a in aqueous solution using the Evans NMR method gives a value of $\mu_{\text{eff}} = 3.06 \mu_B$ /metal center while a value of $3.07 \mu_B$ /metal center is obtained for $\text{Ni}(\text{pyr}_2\text{prn})\text{Cl}_2$ as shown in Table II. The azide and thiocyanate complexes, 2b and 2c, yield values of 3.08 and $3.07 \mu_B$ /metal center, respectively. These magnetic moments fall within the expected range for octahedral nickel(II) complexes. 23a The binuclear copper complex 3 has a magnetic moment of $1.86 \mu_B$ /metal center indicating a single unpaired electron and consistent with non-interacting d^9 metal centers. 23b And finally, the binuclear cobalt complex 4 possesses a magnetic moment of $4.57 \mu_B$ /metal center, while its mononuclear analogue, $\text{Co}(\text{pyr}_2\text{prn})\text{Cl}_2$, has a value of $\mu_{\text{eff}} = 4.04 \mu_B$ /metal center. These values indicate three unpaired electrons per metal center in each cobalt complex consistent with high spin d^7 systems. 23c All magnetic moments were determined in solution using the Evans NMR method. ¹¹

Both copper complexes exhibit quasireversible reductions at a platinum electrode in acetonitrile as demonstrated by cyclic voltammetry. Complex 3a shows a reduction wave at -0.24v as does its mononuclear analogue, $\text{Cu}(\text{pyr}_2\text{prn})\text{Cl}_2$. The binuclear nickel complex and its mononuclear counterpart, $\text{Ni}(\text{pyr}_2\text{prn})\text{Cl}_2$, exhibit quasireversible reductions at -0.92v (vs SCE) in acetonitrile at the platinum electrode.

Conductivity.

The molar conductivity values and assigned electrolyte types of the nickel complexes are given in Table III. These assignments were made by comparing the observed conductivities with values reported for other complex ions. ²⁴ The mononuclear complex, $\text{Ni}(\text{pyr}_2\text{prn})\text{Cl}_2$, exhibits molar conductances in both methanol and

water typical of a 2:1 electrolyte, indicating dissociation of both chloride ions from the nickel center in these polar solvents. If the binuclear nickel complex, $m\text{-xylylenebis}(\text{Ni}(\text{pyr}_2\text{prn})\text{Cl})_2$, were also to dissociate all its chloride ions then it would be expected to exhibit molar conductances typical of a 4:1 electrolyte in these same solvents. The binuclear nickel complex, 2a, however, shows reduced equivalent conductances compared to $\text{Ni}(\text{pyr}_2\text{prn})\text{Cl}_2$. In water, 2a is a 3:1 electrolyte and in methanol, only a 2:1 electrolyte. The azide derivative of the binuclear complex (2b) was also examined and it was determined to be a 2:1 electrolyte in DMF. Unfortunately a suitable solvent to examine both 2b and $\text{Ni}(\text{pyr}_2\text{prn})(\text{N}_3)_2$ could not be found. However, complexes similar to the azide derivatives were prepared, namely the thiocyanate complexes. In dimethylformamide solution, the mononuclear nickel complex, $\text{Ni}(\text{pyr}_2\text{prn})(\text{SCN})_2$ is a 1:1 electrolyte. If the binuclear nickel complex behaved in an analogous fashion one would expect it to be a 2:1 electrolyte. Complex 2c, however, exhibits a molar conductance typical of a 1:1 electrolyte, lower than the expected value.

The molar conductances, then, for all of the binuclear complexes examined are typically lower than would be expected when compared with their mononuclear analogues. This may originate from a decrease in the successive anion dissociation constants, reflecting the difficulty in forming highly charged species in solution. It may also be the result of enhanced ion pairing or even bridge formation in the binuclear complexes due to the proximity of the metal centers. Attempts to prepare and isolate such intramolecularly bridged species are in progress.

Pyrrolealdimine Complexes.

Synthesis. The reaction of nickel(II) and copper(II) acetate with the ligand solution $m\text{-xylylenebis}(2\text{-}(1,3\text{-propanedi}(2\text{-pyrrolidimine}))$, prepared in situ, results in the formation of $m\text{-xylylenebis}(\text{Ni}(\text{pyr}_2\text{prn}))(\underline{5})$ and $m\text{-xylylenebis}(\text{Cu}(\text{pyr}_2\text{prn}))(\underline{6})$, respectively. The binuclear nickel complex, 5, is an orange

Figure 2. The detailed assignment of resonances provides conclusive evidence for the binuclear structure of 5. The high field NMR spectrum also provides an accurate measurement of the coupling constants in the propanediamine ring. By applying the Karplus relationship²⁴ to these values, we can obtain information concerning the conformation of the chelate ring. If we compare the ¹H NMR spectrum of complex 5 with that of the previously reported complex, m-xylenebis(Ni(sal₂pm)),⁸ we see a marked difference in their methylene resonances. This difference can be explained readily by the presence of different chelate ring conformations.

The ¹H NMR of complex 5 contains the following resonances. The aromatic and pyrrolyl protons appear as a series of multiplets in the 6.0 - 7.3 ppm region along with a 7.14-ppm singlet due to the imine CH. Assignments were made based on decoupling experiments and by comparison with Ni(pyr₂pm).²⁵ In addition, the benzylic hydrogens, H_b, appear as a doublet (J=7.77) at 2.83 ppm, split by the methine hydrogen, H_g. The inequivalent methylene hydrogens, H_e and H_f, of the propanediamine chelate ring appear at 3.15 and 2.88 ppm as a doublet and a doublet of doublets, respectively. The geminal coupling is 13.70 Hz and only one of the methylene hydrogens, H_f, exhibits coupling to the methine hydrogen (J=6.85 Hz). The methine hydrogen, H_g, then appears as a complex multiplet at 2.09 ppm.

Further analysis of the methylene resonances, H_e and H_f, provide information concerning the conformation of the 1,3-propanediamine ring. As previously mentioned, these protons give rise to a doublet (H_e, J_{ef} = 13.7 Hz) and a doublet of doublets (H_f, J_{fg} = 6.85 Hz). Two possible staggered conformations of the six-membered chelate ring are shown below. One would expect that the bulky alkyl

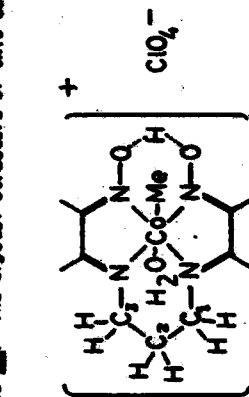
solid, as is its mononuclear analogue, Ni(pyr₂pm).¹⁵ Both copper complexes, Cu(pyr₂pm)¹⁶ and 5, are brown solids. The infrared spectra of the binuclear nickel and copper complexes exhibit C-H stretches at 1589 and 1594 cm⁻¹ respectively, similar to those reported for their mononuclear analogues.^{15,16}

Electronic Spectra. The UV-Visible spectra of the binuclear complexes 5 and 6 are also nearly identical to the spectra reported for the analogous mononuclear complexes.^{15,16} The spectral bands assigned to the π→π* transition for the mononuclear nickel and copper complexes appear at 318 and 286 nm, respectively, while these bands appear at 318 and 289 nm for the binuclear nickel and copper complexes, so it appears that the major ligand π→π* transition is unaffected by the presence of the second metal center in the binuclear complexes. The positions of the remaining UV-visible bands for the binuclear complexes correlate well with those of their mononuclear counterparts. The nickel complex, 5, exhibits a band in the region expected for d-d transitions in square planar nickel(II) complexes,²⁰ appearing as a shoulder on a higher energy transition. While the exact energy and intensity of this band are not certain (estimated values are 510 nm (ε 280)), it is most likely the ¹A_{1g} → ¹A_{2g} transition of square planar Ni(II) corresponding to d_{xy} → d_{x²-y²}. The copper complexes, 6 and Cu(pyr₂pm), exhibit single broad transitions in the same region as other square planar copper(II) complexes.²⁰ While several d-d transitions are expected, they are often unresolved as is typical of many other square planar Cu(II) complexes.²⁰

The magnetic moment of the binuclear copper complex, 6, was determined in Me₂SO solution using the Evans NMR method and gives a value of μ_{eff} = 1.67 μ_B/metal center.

Ring Conformation by NMR Analysis. Unlike the nickel pyridinealdimine complexes 2a, 2b and 2c, the nickel(II) pyrrolealdimine complexes are diamagnetic and thus amenable to NMR analysis. The 400-MHz ¹H NMR spectrum of complex 5 is shown in

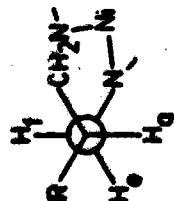
perchlorate ²⁷ shown as II. The crystal structure of this complex reveals



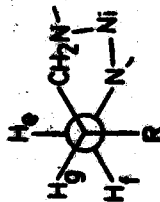
II

torsional angles about the C₁-C₂ and C₂-C₃ bonds of -67.6° and 66.7° respectively. If we use a value of 67° as the dihedral angle between H_b and H_g in complex I we calculate the respective coupling constants, J_{bg} and J_{fg}, to be 0.8 and 9.1 Hz. These calculated values are in agreement with those obtained experimentally and indicate a half-chair conformation for the propanediamine chelate ring of complex I.

We previously reported the synthesis and ¹H NMR spectrum of the binuclear nickel complex, (m-xylene)bis(2-(1,3-propanediamine)) bis perchlorate(III) (7).⁸ If we compare the proton NMR spectrum of complex 5 with that of complex 7 we see a marked difference between their methylene resonances (see Figure 3). While the methylene hydrogens in complex 5, H_b and H_f, appear as a doublet and a doublet of doublets, respectively, the same methylene groups in the salicylidimine complex (7) give rise to two doublets of doublets. The methylene protons in complex 7 have a geminal coupling constant of 13.1 Hz and are both split by the methine proton with couplings of 6.2 and 6.4 Hz. These spectral differences can readily be explained in terms of conformational differences in the propanediamine ring from that of complex 5. If the carbon-carbon bond of the chelate ring is twisted so that H_b approaches H_g, as shown in equation (1), we expect,



i



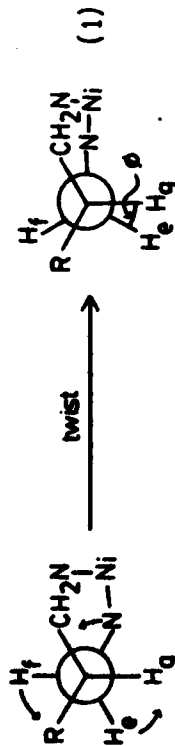
ii

group, R = (-CH₂-H_g-CH₂-), would prefer the less sterically crowded equatorial position as in conformation (i). An estimation of the coupling constants of this conformation can be obtained from the Karplus relationship,²⁶ and then compared to those measured experimentally. The dihedral angle between protons H_b and H_g would be 60° giving rise to an expected coupling constant of 1.7 Hz, while the angle between H_f and H_g would be 180°, giving rise to a large coupling of 9.2 Hz. Although no coupling is observed between H_b and H_g, a small, unresolved coupling of 1-2 Hz may be present. Both dihedral angles in conformation (ii) would be 60°, yielding equal and small couplings of 1.7 Hz. The qualitative results, thus, strongly favor conformation (i). The combination of fused chelate rings having 5, 6 and 5 members which is present in complex 5 also exists in the cobalt complex (1-diacetylmonoximate)imino-3-diacetylmonoximate(methyl) aquocobalt(III)

boat conformation. If the nickel complex, 7, were to adopt the same conformation, the dihedral angle, ϕ (see equation (1)), between H_f and H_g would be approximately 30° , which is the value obtained from the 1H NMR results using the Karplus equation. Thus, in going from the fused 5,6,6-membered chelate rings in complex 7 to the 5,6,5-membered rings in complex 5, there is a change in the conformation of the central chelate ring, which shows itself by the observed difference in the 1H NMR spectra of 5 and 7.

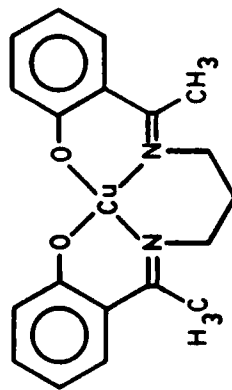
Summary

The physical and spectral properties of the binuclear complexes reported here parallel those of their mononuclear analogues. The visible spectra of the binuclear complexes are nearly identical to those of the corresponding mononuclear complexes. A comparison of the magnetic moments determined in solution of the binuclear complexes with their mononuclear counterparts reveals nearly identical values suggesting the metal centers in the binuclear complex are sufficiently insulated from one another to prevent significant electronic interactions between them. While conductivity measurements suggest some metal-ligand-metal interactions in the pyridine-aldimine complexes, studies are continuing in order to obtain more direct evidence for this type of interaction. The use of high field NMR has provided conclusive evidence for the binuclear structure of complex 5. In addition, it has allowed a conformational analysis to be performed for the binuclear nickel complexes through the use of the Karplus relationship.²⁶ Further studies of these and related binuclear complexes are in progress.



according to the Karplus relationship,²⁶ that the coupling between H_f and H_g should increase as the dihedral angle between them approaches 0° . In addition, the coupling between H_f and H_g should decrease as a result of the decrease in their dihedral angle from 180° towards 120° . When ϕ reaches 30° the predicted coupling constants, J_{fg} and $J_{fg'}$ would be 6.0 and 6.9 Hz, which are close to the experimentally observed couplings.

We can compare the predicted conformation for the propenediamine ring in complex 7 with a similar copper chelate which has been analyzed by x-ray crystallography. The crystal structure of III, (bis(2-hydroxyacetophenone)trimethylenediimine) copper(II)²⁸ shows that the six-membered copper-propenediamine ring takes a twisted



III

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Table I. UV-Visible Spectral Data

Complex ^a	Solvent	$\lambda_{max, nm} (\epsilon, l \text{ mol}^{-1} \text{ cm}^{-1})$
$Ni_2Cl_4 \cdot 8H_2O$	CH_3OH	1050(7), 815(17), 760(15), 560(11), 380 sh(364), 280(29,300).
	H_2O	1005(7), 800(21), 760(18), 540(12), 375(297), 280(29,000).
$Ni(pyv_2pm)Cl_2 \cdot H_2O^b$	CH_3OH	1064(4), 320(10), 794 sh, 763 sh, 575(7).
$Ni_2L(H_2O)_4 \cdot 2H_2O$	DMF	955(28), 823 sh(21), 460 sh(319), 315(5360), 275(14,900).
$Ni_2L(SCN)_4 \cdot H_2O$	DMF	875(38), 785 sh(19), 525(33), 400 sh(530), 278(27,500).
Cu_2Cl_4	CH_3OH	730(211), 285(20,000).
$Cu(pyv_2pm)Cl_2$	CH_3OH	720(127), 288(14,100).
$Co_2Cl_4 \cdot 7H_2O$	H_2O	970(7), 460 sh(132), 328(3670), 280(35,600).
$Co(pyv_2pm)Cl_2 \cdot H_2O$	H_2O	950(5), 460 sh(100), 320(2225), 280(17,700).
Ni_2L^c	$CHCl_3$	510/20 sh(280/50), 436(8750), 393(14,000), 318(43,100), 271(9210).
$Ni(pyrr_2pm)^c$	$CHCl_3$	437 sh(5700), 396(9400), 380 sh(8900), 318(27,400), 270 sh(6200).
Cu_2L^d	$CHCl_3$	530 sh(85), 357(33,100), 289(24,700).
$Cu(pyrr_2pm)^d$	$CHCl_3$	560(128), 426 sh(900), -345(12,000-19,000), -278(12,000-26,000).

^aL = m-Xylylenebis(pyv₂pm), L' = m-Xylylenebis(pyrr₂pm)

^bRef. 13.

^cRef. 15.

^dRef. 16.

Table II. Magnetic moments in solution.

Complex ^a	Magnetic Moment ^b (B.M./Metal center)
$\text{Ni}_2\text{Cl}_4 \cdot 4\text{H}_2\text{O}$ (2a)	3.06
$\text{Ni}_2\text{L}(\text{H}_3)_4 \cdot \text{H}_2\text{O}$ (2b) ^c	3.00
$\text{Ni}_2\text{L}(\text{NCS})_4 \cdot \text{H}_2\text{O}$ (2c) ^c	3.07
$\text{Ni}(\text{pya}_2\text{prm})\text{Cl}_2$	3.07
Co_2Cl_4 (3)	1.86
$\text{Cu}(\text{pya}_2\text{prm})\text{Cl}_2$	1.74
$\text{Co}_2\text{Cl}_4 \cdot 7\text{H}_2\text{O}$ (4)	4.57
$\text{Co}(\text{pya}_2\text{prm})\text{Cl}_2 \cdot \text{H}_2\text{O}$	4.04
$\text{Cu}_2\text{L}'$ (5) ^c	1.64
$\text{Cu}(\text{pyrr}_2\text{prm})$ ^c	1.67

^aL = m-Xylylenebis(py_a₂prm), L' = m-Xylylenebis(pyrr₂prm). ^bDetermined in 25 aqueous (CH₃)₃COH solution. ^cDetermined in (CH₃)₂SO solution.

Table III. Molecular conductivity data

Complex	solvent	$\Lambda \cdot 10^{-3}$ ^a	electrolyte type ^b
m-Xylylenebis(Ni(py _a ₂prm))Cl ₂ · 4H ₂ O	H ₂ O	431	3:1
	CH ₃ OH	182	2:1
Ni(py _a ₂prm)Cl ₂	H ₂ O	226	2:1
	CH ₃ OH	140	2:1
m-Xylylenebis(Ni(py _a ₂prm))(N ₃) ₄ · 2H ₂ O	DMF	152	2:1
Ni(py _a ₂prm)(N ₃) ₂	H ₂ O	198	2:1
m-Xylylenebis(Ni(py _a ₂prm))(SCN) ₄	DMF	87	1:1
Ni(py _a ₂prm)(SCN) ₂	DMF	75	1:1

^aEquivalent conductances are reported for 10⁻³M solutions and are reported in $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$. ^b Ref. 24.

Figure 1. Labelling scheme and nomenclature.

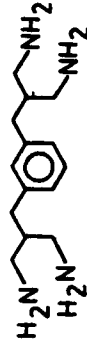
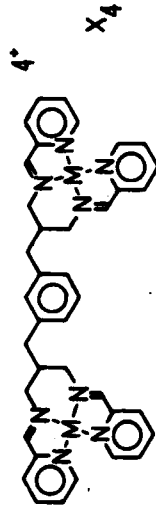


Figure 2. 400-MHZ ^1H NMR spectrum of *m*-xylylenebis(Ni(pyrr₂pm)) (5).

Figure 3. ^1H NMR methylene resonances for complexes 5 (a) and 7 (b).

1. *m*-Xylylenebis(2-(1,3-propanediamine))



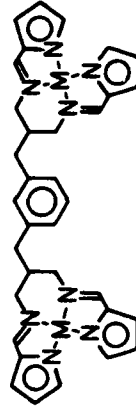
2a. M = Ni(II), X = Cl⁻: *m*-Xylylenebis(Ni(pyrr₂pm))Cl₄

2b. M = Ni(II), X = H₃⁻: *m*-Xylylenebis(Ni(pyrr₂pm))(H₃)₄

2c. M = Ni(II), X = NCS⁻: *m*-Xylylenebis(Ni(pyrr₂pm))(NCS)₄

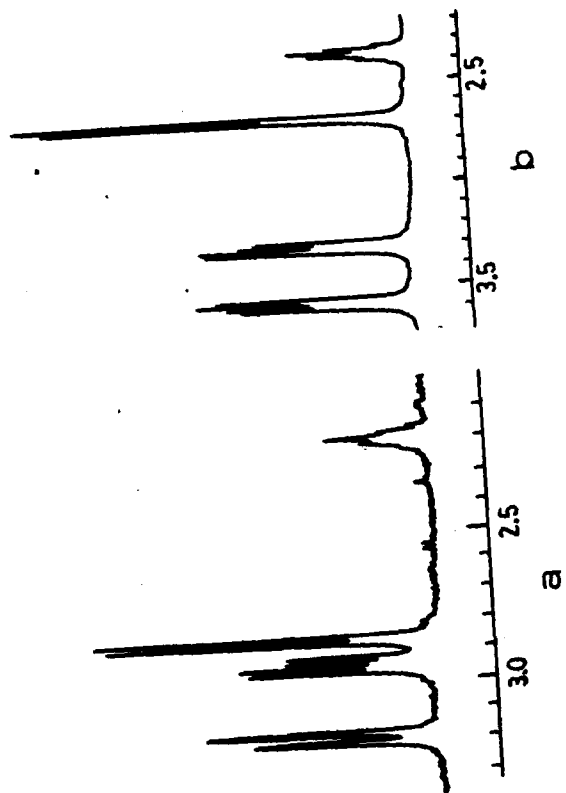
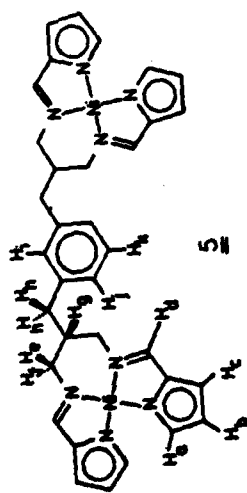
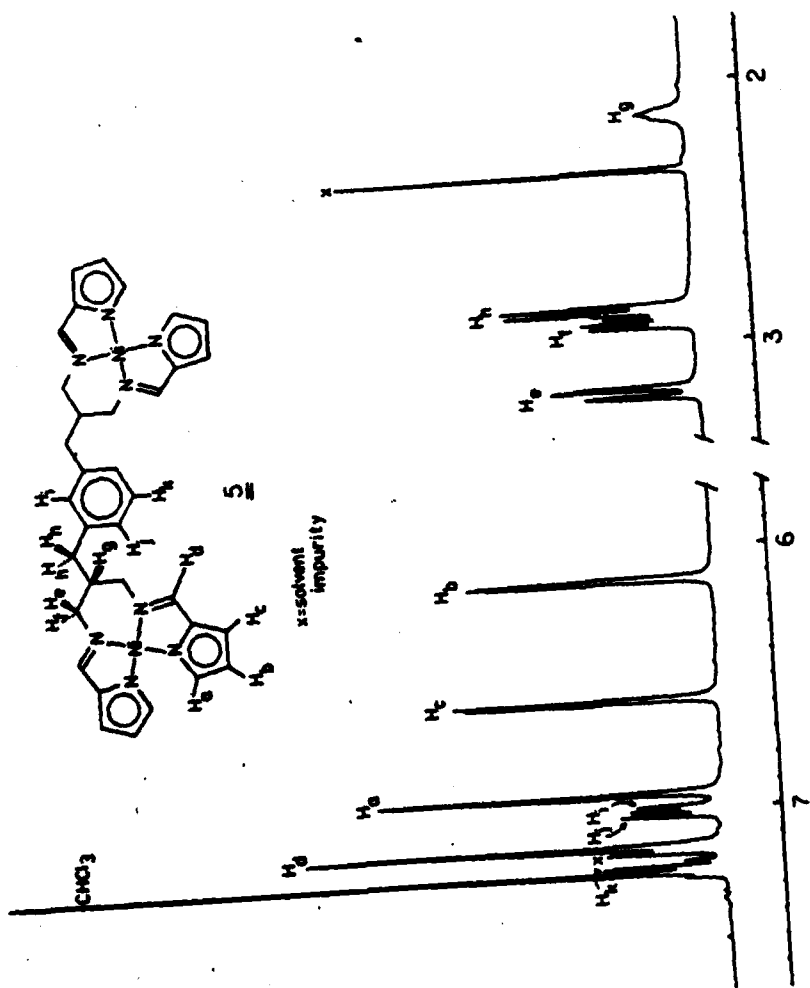
3. M = Cu(II), X = Cl⁻: *m*-Xylylenebis(Cu(pyrr₂pm))Cl₄

4. M = Co(II), X = Cl⁻: *m*-Xylylenebis(Co(pyrr₂pm))Cl₄



5. M = Ni(II): *m*-Xylylenebis(Ni(pyrrr₂pm))

6. M = Cu(II): *m*-Xylylenebis(Cu(pyrrr₂pm))



film
feet
Boys
Race
Miss
The
of
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Le
rich
by
These
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