1624 *Inorg. Chem.* **1984**, *23*, 1624-1629

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Binuclear Schiff Base Complexes of *m*-Xylylenebis[2-(1,3-propanediylbis(2-pyridinecarbaldimine))] and *m*-Xylylenebis[2-(1,3-propanediylbis(2-pyrrolecarbaldiminate))(2−)]

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Received June 21, 1983

Binuclear 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-pyridinecarbaldehyde and *m*-xylylenebis[2-(1,3-propanediamine)] results in the formation of Ni_2LCl_4 (**2a**), Cu_2LCl_4 (**3**), and Co_2LCl_4 (**4**), respectively, where L = *m*-xylylenebis[2-(1,3-propanediylbis(2-pyridinecarbaldimine))]. The binuclear nickel complexes $Ni_2L(N_3)_4$ (**2b**) and $Ni_2L(SCN)_4$ (**2c**) are prepared by metathesis of the chloride ion of complex **2a** using the appropriate sodium salt. These complexes, **2**–**4**, exhibit electronic spectra consistent with tetragonally distorted six-coordinate complexes. The binuclear nickel complex **2a** exhibits a molar conductance of $\Lambda_{mM} = 182$ cm² M⁻¹ Ω⁻¹ in methanol while its mononuclear analogue, Ni(1,3-propanediylbis(2-pyridinecarbaldimine))Cl_2, has a conductance of $\Lambda_{mM} = 140$ $cm^2\ M^{-1}\ \Lambda^{-1}$, both typical of 2:1 electrolytes. In DMF solution, complex **2c** exhibits a molar conductance of $\Lambda_{mM} = 87$ $cm^2\ M^{-1}\ \Omega^{-1}$, typical of a 1:1 electrolyte, while the mononuclear nickel complex, Ni(1,3-propanediylbis(2-pyridinecarbaldimine))$(SCN)_2$, has a molar conductance in DMF of $\Lambda_{mM} = 75$ $cm^2\ M^{-1}\ \Omega^{-1}$ also in the range expected for a 1:1 electrolyte. The room-temperature magnetic susceptibilities were determined for complexes **2**–**4**, and all were found to be paramagnetic ($S = 1$ ground states for **2**, $S = {}^1/_2$ for **3**, $S = {}^3/_2$ for **4**). The condensation of 2-pyrrolecarbaldehyde with *m*-xylylenebis[2-(1,3-propanediamine)] followed by the addition of nickel(II) or copper(II) acetate leads to the formation of the neutral, nonconducting complexes Ni_2L' (**5**) and Cu_2L' (**6**), respectively (L′ = *m*-xylylenebis[2-(1,3-propanediylbis(2-pyrrolecarbaldiminate))(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 on the basis of the coupling constants in the observed spectrum.

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 activation,[3] and photosynthetic water reduction.[4] Binuclear complexes have also been utilized in the study of electron-transfer processes[5] and metal–metal interactions.[6] The interest in these systems also arises from their ability to serve as simple models for multimetal-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 that 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 hydroxo 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-propanediylbis(2-pyridinecarbaldimine))] and *m*-xylylenebis[2-(1,3-propanediylbis(2-pyrrolecarbaldiminate))(2−)]. Drawings of the binuclear complexes along with their nomenclature are presented in Figure 1.

Experimental Section

Abbreviations are as follows: $(pya)_2prn$ (1,3-propanediylbis(2-pyridinecarbaldimine)); $(pyrr)_2prn$ (1,3-propanediylbis(2-pyrrolecarbaldiminate)(2−)); *m*-Xyl (*m*-xylylene). Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

Physical Measurements. ^1H NMR were recorded on a Bruker WH400 400-MHz instrument with chemical shifts reported in ppm relative to Me_4Si. Infrared spectra were recorded on a Perkin-Elmer Model 467 grating spectrophotometer. Electronic spectra were recorded on a Perkin-Elmer Model 300 spectrophotometer using 1-cm quartz cells. Extinction coefficients are given in units of $M^{-1}\ cm^{-1}$. Solution magnetic moments were determined by 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 N 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 1.0-cm cell. A working cell constant was determined from the ratio of the observed specific conductance of 0.02 N KCl(aq) with the literature value of 0.002 768 $\Omega^{-1}\ cm^{-1}$ at 25 °C.[12] Typically, equivalent conductances

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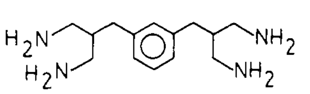
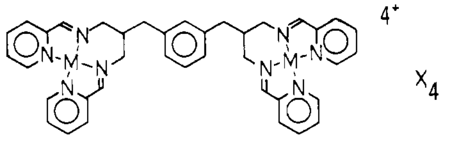


1, m-Xylylenebis(2-(1,3-propanediamine))



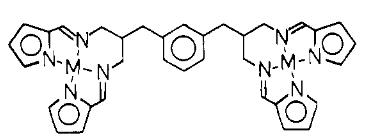
2a, M = Ni(II), X=Cl^-: m-Xylylenebis(Ni(pya_2prn))Cl_4

2b, M = Ni(II), X = N_3^-: m-Xylylenebis(Ni(pya_2prn))$(N_3)_4$

2c, M = Ni(II), X = NCS^-: m-Xylylenebis(Ni(pya_2prn))$(NCS)_4$

3, M = Cu(II), X = Cl^-: m-Xylylenebis(Cu(pya_2prn))Cl_4

4, M = Co(II), X = Cl^-: m-Xylylenebis(Co(pya_2prn))Cl_4



5, M = Ni(II): m-Xylylenebis(Ni($pyrr_2prn$))

6, M = Cu(II): m-Xylylenebis(Cu($pyrr_2prn$))

Figure 1. Labeling scheme and nomenclature.

for the complexes in solution were determined at five concentrations ranging from ca. 5–0.1 mM. The equivalent conductances at 1 mM were then determined from on 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((pya)$_2$prn)Cl_2,[13] Ni((pya)$_2$prn)$(N_3)_2$,[13] Cu((pya)$_2$prn)$(ClO_4)_2$,[14] Ni((pyrr)$_2$prn),[15] and Cu(((pyrr)$_2$prn)[16] were all prepared by literature methods. 2-Pyridinecarbaldehyde and 2-pyrrolecarbaldehyde were purchased from Aldrich and used without further purification.

***m*-Xyl[Ni((pya)$_2$prn)]$_2$Cl$_4$·8H$_2$O (2a).** 2-Pyridinecarbaldehyde (0.413 g, 3.86 mmol) dissolved in isopropyl alcohol (5 mL) is added dropwise over 2 min to a stirred solution of **1** (0.241 g, 0.965 mmol) in isopropyl alcohol (5 mL) at 0 °C. The reaction mixture is stirred at room temperature for 1 h and the ligand solution then added to $NiCl_2·6H_2O$ (0.46 g, 1.93 mmol) dissolved in hot ethanol (10 mL). The resulting dark green solution is reduced in volume by 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 is 75%. Anal. Calcd for $C_{38}H_{54}N_8Ni_2Cl_4O_8$: 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*-Xyl[Ni((pya)$_2$prn)]$_2$(N$_3$)$_4$·2H$_2$O (2b)** is prepared by the metathesis of Cl^- in **2a**, using an excess of NaN_3 in H_2O and is recrystallized from H_2O/acetone. Anal. Calcd for $C_{38}H_{42}N_{20}O_2Ni_2$: C, 49.16; H, 4.57; N, 30.18. Found: C, 49.10; H, 4.60; N, 30.37. IR (KBr): 2020, 1640, 1598, 1478, 1445, 1308, 1018, 777 cm^{-1}.

***m*-Xyl[Ni((pya)$_2$prn)]$_2$(NCS)$_4$·H$_2$O (2c)** is prepared by metathesis of Cl^- in **2a** using an excess of NaSCN in methanol. Anal. Calcd for $C_{42}H_{40}N_{12}OS_4Ni_2$: 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): 2085, 1640, 1598, 1477, 1445, 1307, 1018, 774 cm^{-1}.

***m*-Xyl[Cu((pya)$_2$prn)]$_2$Cl$_4$·2H$_2$O (3).** This complex is made by following the procedure for synthesizing **2a** but using $CuCl_2·6H_2O$ as the metal salt and is isolated as a green solid in 64% yield. Anal. Calcd for $C_{38}H_{42}N_8O_2Cu_2Cl_4$: 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*-Xyl[Co((pya)$_2$prn)]$_2$Cl$_4$·7H$_2$O (4).** This complex is made by the same procedure used to prepare **2a** using $CoCl_2·H_2O$ in place of $NiCl_2·6H_2O$ and is isolated as an olive green solid containing orange microcrystals, which when crushed become olive green; yield 74%. Anal. Calcd for $C_{38}H_{55}N_8O_7Co_2Cl_4$: 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((pya)$_2$prn)Cl$_2$·H$_2$O. 2-Pyridinecarbaldehyde (1.07 g, 10 mmol) and 1,3-propanediamine (0.37 g, 5 mmol) are combined is isopropyl alcohol (5 mL) at 0 °C and stirred at room temperature for 1 h. The solution is then added to $CoCl_2·H_2O$ (1.19 g, 5 mmol) in hot ethanol (5 mL), and the resultant mixture is refluxed 10 min and then cooled to room temperature. After 1 h, the solution is filtered and the orange crystalline solid washed with isopropyl alcohol (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 is 91%. The orange solid can be recrystallized from hot acetonitrile, yielding orange crystals. Anal. Calcd for $C_{15}H_{18}N_4OCoCl_2$: 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*-Xyl[Ni((pyrr)$_2$prn)]$_2$ (5).** 2-Pyrrolecarbaldehyde (0.307 g, 3.23 mmol) and **1** (0.203 g, 0.81 mm) are refluxed in isopropyl alcohol (30 mL) for 2 h and added to a hot solution of $Ni(OAc)_2·H_2O$ (0.404 g, 1.62 mmol) in ethanol (20 mL). This is refluxed another hour and chilled to 0 °C. The resulting solid is filtered, washed with ethanol (10 mL), and dried in vacuo, yielding **5** as an orange solid (0.33 g, 60%). Anal. Calcd for $C_{34}H_{34}N_8Ni_2$: C, 60.76; H, 5.10; N, 16.67. Found: C, 61.02; H, 5.50; N, 16.42. IR (KBr): 1589, 1440, 1380, 1312, 1043, 740 cm^{-1}. ^1H NMR ($CDCl_3$): δ 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), 2.86 (4 H, d, benzylic), 2.16 (2 H, m, methine).

***m*-Xyl[Cu((pyrr)$_2$prn)]$_2$ (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 $C_{34}H_{34}N_8Cu_2$: 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, 1038, 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-propanediamine)] (**1**)[8] with 4 equiv of either 2-pyridinecarbaldehyde or 2-pyrrolecarbaldehyde and are used immediately without isolation. The binuclear complexes are then prepared by using these ligand solutions following minor modifications of the reported synthetic procedures for their mononuclear analogues.

Pyridinecarbaldimine Complexes. Synthesis. The reaction of $NiCl_2·6H_2O$ with the ligand solution of *m*-xylylenebis[2-(1,3-propanediylbis(2-pyridylimine))] produces the binuclear nickel complex *m*-Xyl[Ni((pya)$_2$prn)]$_2$Cl$_4$ (**2a**) as a yellow-green solid. This complex is soluble in water, methanol, and ethanol but insoluble in chloroform, Me_2SO, ether, and hydrocarbon solvents. Its mononuclear analogue, Ni((pya)$_2$prn)Cl_2, 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 pya$_2$prn have been reported previouly, but the mononuclear cobalt complex, Co((pya)$_2$prn)Cl_2, is reported here for the first time. It is synthesized by a modification of the procedure used to make Ni(pya)$_2$prn)Cl_2[13] and is isolated as air-stable orange crystals,

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(17) Magnetic moment was determined in 2% *t*-BuOH(aq).
(18) Magnetic moment was determined in Me_2SO.

Table I. UV-Visible Spectral Data

complex[a]	solvent	λ_{max}, nm (ϵ, L mol^{-1} cm^{-1})
$Ni_2LCl_4 \cdot 8H_2O$	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)
$Ni((pya)_2prn)Cl_2 \cdot H_2O$[b]	CH_3OH	1064 (4), 820 (10), 794 sh, 763 sh, 575 (7)
$Ni_2L(N_3)_4 \cdot 2H_2O$	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_2LCl_4	CH_3OH	730 (211), 285 (20 000)
$Cu((pya)_2prn)Cl_2$	CH_3OH	720 (127), 288 (14 100)
$Co_2LCl_4 \cdot 7H_2O$	H_2O	970 (7), 460 sh (132), 320 (3670), 280 (35 600)
$Co((pya)_2prn)Cl_2 \cdot H_2O$	H_2O	950 (5), 460 sh (100), 320 (2225), 280 (17 700)
Ni_2L'	$CHCl_3$	510 ± 20 sh (280 ± 50), 436 (8750), 393 (14 000), 318 (43 100), 271 (9210)
$Ni((pyrr)_2prn)$[c]	$CHCl_3$	437 sh (5700), 396 (9400), 380 sh (8900), 318 (27 400), 270 sh (6200)
Cu_2L'	$CHCl_3$	530 sh (85), 357 (33 100), 289 (24 700)
$Cu((pyrr)_2prn)$[d]	$CHCl_3$	560 (128), 426 sh (900), ~345 (12 000–19 000), ~278 (12 000–26 000)

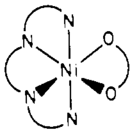
[a] L = *m*-Xyl($(pya)_2prn)_2$; L' = *m*-Xyl($(pyrr)_2prn)_2$. [b] Reference 13. [c] Reference 15. [d] Reference 16.

which appear olive green when crushed.

Infrared Spectra. The infrared spectra of the binuclear Schiff base complexes containing the pyridinecarbaldimine group exhibit bands typical of 2-substituted pyridines[19] and also display a band near 1640 cm^{-1} assigned to the stretching vibration of the C=N 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($(pya)_2prn)(NCS)_2$,[13] which is proposed to contain N-bonded thiocyanate ligands on the basis of 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($(pya)_2prn)(NCS)_2$ 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, **2a**, contains two principal 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 that appears at 760 nm 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 nm (ϵ 17) and 1050 (ϵ 7)) similar to that observed for its mononuclear analogue, Ni(($(pya))_2prn)Cl_2$,[13] typical of tetragonally distorted nickel(II) complexes.[20] The splitting can be assigned to the $^3B_{1g} \rightarrow {}^3B_{2g}$ and $^3B_{1g} \rightarrow {}^3E_g$ 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 **2a** are thus formulated as [*m*-Xyl[Ni($(pya)_2prn)]_2(Cl)_x(S)_{4-x}]^{(4-x)+}$, where S = H_2O or CH_3OH, with the weaker field ligand 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 **2a**.

The addition of other weak donors such as Na_2SO_4 to an aqueous solution of **2a** 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 **2a** in water produces significant changes in its electronic spectrum. When Na_2CO_3 is added to an aqueous solution of **2a**, a new band appears in the near-IR region at 910 nm (ϵ 33) ($^3A_{2g} \rightarrow {}^3T_{2g}$), replacing the 800- and 1005-nm bands of complex **2a**. The lack of splitting of this band indicates formation of a nickel(II) species that 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 $Na_2C_2O_4$ is added to complex **2a**, spectral changes similar to those seen upon the addition of carbonate are observed (λ_{max} 890 nm (ϵ 31)). 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 (ϵ 45 and ϵ 40 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 I.[20,22]



I

The cobalt complexes exhibit electronic spectra typical of pseudooctahedral symmetry.[20] The complex Co($(pya)_2prn)Cl_2$ has weak ligand field bands at 950 nm (ϵ 5) and at 460 nm (ϵ 100) assignable to the $^4T_{1g} \rightarrow {}^4T_{2g}$ and $^4T_{1g} \rightarrow {}^4T_{1g}$(P) transitions. The binuclear cobalt complex, **4** exhibits a broad transition centered at 970 nm (ϵ 7) ($^4T_{1g} \rightarrow {}^4T_{2g}$) and a band at 460 nm ($\epsilon$ 132) ($^4T_{1g} \rightarrow {}^4T_{1g}$(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, **3**, contains a weak band assignable to a d–d transition at 730 nm (ϵ 211) 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 μ_{eff} =

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Table II. Magnetic Moments in Solution

complex[a]	magn moment,[b] μ_B/metal center	complex[a]	magn moment,[b] μ_B/metal center
$Ni_2LCl_4 \cdot 8H_2O$ (**2a**)	3.06	Cu_2LCl_4 (**3**)	1.86
		$Cu((pya)_2prn)Cl_2$	1.74
$Ni_2L(N_3)_4 \cdot H_2O$ (**2b**)[c]	3.00	$Co_2LCl_4 \cdot 7H_2O$ (**4**)	4.57
		$Co((pya)_2prn)Cl_2 \cdot H_2O$	4.04
$Ni_2L(NCS)_4 \cdot H_2O$ (**2c**)[c]	3.07	Cu_2L' (**6**)[c]	1.64
		$Cu((pyrr)_2prn)$[c]	1.67
$Ni((pya)_2prn)Cl_2$	3.07		

[a] L = *m*-Xyl($(pya)_2prn)_2$; L′ = *m*-Xyl($(pyrr)_2prn)_2$. [b] Determined in 2% $(CH_3)_3COH$(aq) solution. [c] Determined in $(CH_3)_2SO$ solution.

Table III. Molecular Conductivity Data

complex	solvent	Λ,[a] 10^{-3} M	electrolyte type[b]
m-Xyl[$Ni((pya)_2prn)]Cl_4 \cdot 8H_2O$	H_2O	431	3:1
	CH_3OH	182	2:1
$Ni((pya)_2prn)Cl_2$	H_2O	228	2:1
	CH_3OH	140	2:1
m-Xyl[$Ni((pya)_2prn)]_2(N_3)_4 \cdot 2H_2O$	DMF	152	2:1
$Ni((pya)_2prn)(N_3)_2$	H_2O	198	2:1
m-Xyl[$Ni((pya)_2prn)]_2(SCN)_4$	DMF	87	1:1
$Ni((pya)_2prn)(SCN)_2$	DMF	75	1:1

[a] Equivalent conductances are reported for 10^{-3} M solutions and are reported in Ω^{-1} cm^2 mol^{-1}. [b] Reference 24.

3.06 μ_B/metal center while a value of 3.07 μ_B/metal center is obtained for $Ni((pya)_2prn)Cl_2$ as shown in Table II. The azide and thiocyanate complexes, **2b** and **2a**, yield values of 3.00 and 3.07 μ_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 μ_B/metal center, indicating a single unpaired electron and consistent with noninteracting d^9 metal centers.[23b] And finally, the binuclear cobalt complex **4** possesses a magnetic moment of 4.57 μ_B/metal center, while its mononuclear analogue, $Co((pya)_2prn)Cl_2$, has a value of μ_{eff} = 4.04 μ_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 by using the Evans NMR method.[11]

Both copper complexes exhibit quasi-reversible reductions at a platinum electrode in acetonitrile as demonstrated by cyclic voltammetry. Complex **3a** shows a reduction wave at −0.24 V as does its mononuclear analogue, $Cu((pya)_2prn)Cl_2$. The binuclear nickel complex and its mononuclear counterpart, $Ni(pya)_2prn)Cl_2$, exhibit quasi-reversible reductions at −0.92 V (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, $Ni((pya)_2prn)Cl_2$, 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*-Xyl[$Ni((pya)_2prn)]_2Cl_4$, 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 $Ni((pya)_2prn)Cl_2$. 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 $Ni((pya)_2prn)(N_3)_2$ could not be found. However, complexes similar to the azide derivatives were prepared, namely the thiocyanate complexes. In dimethylformamide solution, the mononuclear nickel complex $Ni((pya)_2prn)(SCN)_2$ 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.

Pyrrolecarbaldimine Complexes. Synthesis. The reaction of nickel(II) and copper(II) acetate with the ligand solution *m*-xylylenebis[2-(1,3-propanediylbis(2-pyrrolecarbaldimine))], prepared in situ, results in the formation of *m*-Xyl[$Ni((pyrr)_2prn)]_2$ (**5**) and *m*-Xyl[$Cu((pyrr)_2prn)]_2$ (**6**), respectively. The binuclear nickel complex, **5**, is an orange solid, as is its mononuclear analogue, $Ni((pyrr)_2prn)$.[15] Both copper complexes, $Cu((pyrr)_2prn)$[16] and **6**, are brown solids. The infrared spectra of the binuclear nickel and copper complexes exhibit C=N 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 $\pi \rightarrow \pi^*$ 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 $\pi \rightarrow \pi^*$ 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 $^1A_{1g} \rightarrow {}^1A_{2g}$ transition of square-planar Ni(II) corresponds to $d_{xy} \rightarrow d_{x^2-y^2}$. The copper complexes, **6** and $Cu((pyrr)_2prn)$, 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 Me_2SO solution by using the Evans NMR method, and a value of μ_{eff} = 1.67 μ_B/metal center is given.

Ring Conformation by NMR Analysis. Unlike the nickel pyridinecarbaldimine complexes **2a–c**, the nickel(II) pyrrolecarbaldimine complexes are diamagnetic and thus amenable to NMR analysis. The 400-MHz ^1H NMR spectrum of complex **5** is shown in 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 relationship[24]

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[23] Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 3rd ed.; Interscience: New York, 1972: (a) p 894; (b) p 916; (c) p 882.

[24] Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81.

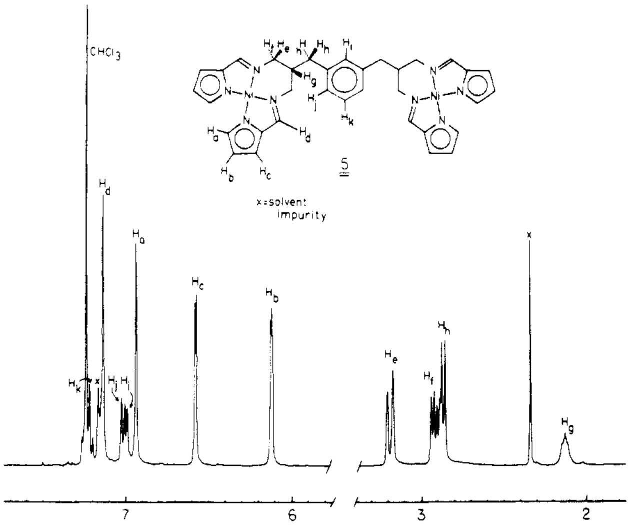
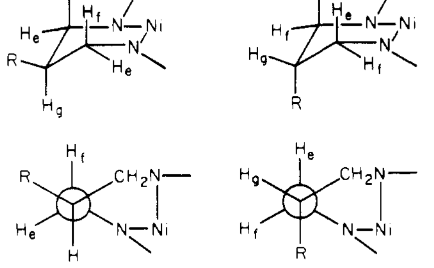


Figure 2. 400-MHz ^{1}H NMR spectrum of *m*-Xyl[(Ni(pyrr)$_2$prn)]$_2$ (5).

to these values, we can obtain information concerning the conformation of the chelate ring. If we compare the ^{1}H NMR spectrum of complex **5** with that of the previously reported complex, *m*-Xyl[Ni((sal)$_2$prn)]$_2$,[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 ^{1}H 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 on the basis of decoupling experiments and by comparison with the spectrum of Ni((pyrr)$_2$prn).[25] In addition, the benzylic hydrogens, H_h, appear as a doublet (J = 7.77 Hz) 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, provides 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.



i ii

One would expect that the bulky alkyl group, R = $CH_2C_6H_4CH_2$, 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_e 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_e 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 [*N*,*N*′-propane-1,3-diylbis(biacetyl imine oximato)(1–)]methylaquocobalt(III) perchlorate[27] (II). The

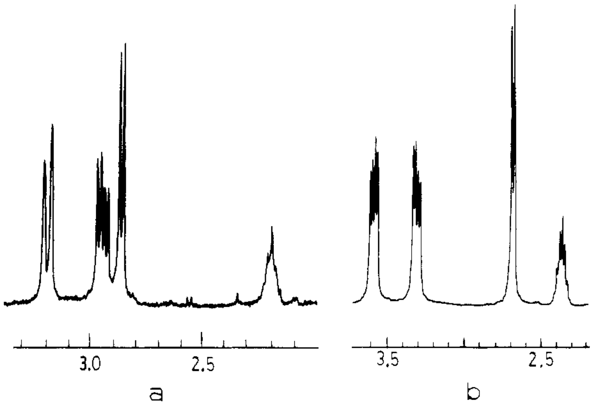
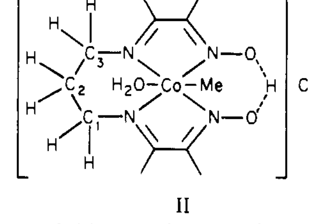


Figure 3. ^{1}H NMR methylene resonances for complexes **5** (a) and **7** (b).



II

crystal structure of this complex reveals torsional angles about the C_1–C_2 and C_2–C_3 bonds of −67.6 and 65.7°, respectively. If we use a value of 67° as the dihedral angle between H_e and H_g in complex **5**, we calculate the respective coupling constants, J_{eg} and J_{fg}, to be 0.9 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 **5**.

We previously reported the synthesis and ^{1}H NMR spectrum of the binuclear nickel complex [*m*-xylylenebis(2-(1,3-propanediylbis(salicylaldiminato)))]dinickel(II) (**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_e and H_f, appear as a doublet and a doublet of doublets, respectively, the same methylene groups in the salicylaldimine 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_e and approaches H_g, as shown in eq 1, we expect, according to the Karplus, relationship,[26] that the

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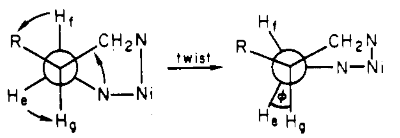
[25] Jones, C. J.; McLeverty, J. A. *J. Chem. Soc. A* **1971**, 1052.

[26] The coupling constants are obtained from the equation $J_{HH'} = 4.22 - 0.5 \cos \phi + 4.5 \cos (2\phi)$, where ϕ is the dihedral angle: Karplus, M. *J. Am. Chem. Soc.* **1963**, *85*, 2870.

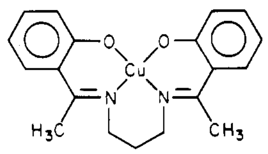
[27] Brükner, S.; Calligaris, M.; Nardin, G.; Randaccio, L. *Inorg. Chim. Acta* **1969**, *3*, 278.



(1)

coupling between H_e 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 to 120°. When ϕ reaches 30°, the predicted coupling constants, J_{eg} 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 propanediamine ring in complex **7** with a similar copper chelate that has been analyzed by X-ray crystallography. The crystal structure of III [bis(2-hydroxyacetophenone) trimethylenediiminato]copper(II),[28] shows that the six-membered copper-propanediamine ring takes a twisted-boat conformation. If the nickel complex, **7**, were to adopt the same conformation, the dihedral angle, ϕ (see eq 1), between H_e and H_g would be approximately 30°, which is the value obtained from the ^1H NMR results using the Karplus equation. Thus, on going from the fused 6-, 6-, and 6-membered chelate rings in complex **7** to the 5-, 6-, and 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**.



III

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 with 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 pyridinecarbaldimine 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] relationship.[26] Further studies of these and related binuclear complexes are in progress.

Acknowledgment. We thank the Office of Naval Research and the National Science Foundation (Grant CHE83-08064) for support of the research. B.C.W. gratefully acknowledges a Sherman Clarke Fellowship.

Registry No. **1**, 70865-15-5; **2a**, 89178-09-6; **2b**, 89178-10-9; **2c**, 89178-11-0; **3**, 89178-12-1; **4**, 89178-13-2; **5**, 89178-14-3; **6**, 89178-15-4; $Co((pya)_2prn)Cl_2$, 89178-16-5; $Ni((pya)_2prn)Cl_2$, 39489-09-3; $Cu((pya)_2prn)Cl_2$, 89178-17-6; $Cu((pyrr)_2prn)$, 16389-93-8; $Ni((pya)_2prn)(N_3)_2$, 39489-05-9; $Ni((pya)_2prn)(SCN)_2$, 39489-04-8; 2-pyridinecarbaldehyde, 1121-60-4; 2-pyrrolecarbaldehyde, 1003-29-8.

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The Four-Electron Oxidation of a Novel μ-Oxo Dimer, $[((p\text{-}Et_2N)TPP)Fe]_2O$

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Received September 19, 1983

The oxidation of $[((p\text{-}Et_2N)TPP)Fe]_2O$ (**1**) and $((TPP)Fe)_2O$ (**2**) was investigated in CH_2Cl_2 by electrochemical and spectral techniques. Contrary to expectation, four, and not three, electrons were abstracted from each dimer. The first electron transfer (at 0.34 V vs. SCE for **1** and 0.84 V vs. SCE for **2**) involved formation of a cation radical delocalized on both of the porphyrin rings. The most anodic two-electron oxidation of **1** (at 0.76 V) was consistent with a reaction involving oxidation of two noninteracting equivalent reaction sites. This is the first example of such a reaction with iron porphyrins. A similar two-electron oxidation was also observed for **2**, but in this case, the reaction sites appear to be interacting and the half-wave potentials were separated by 90 mV. The one- and two-electron-oxidized complexes of **1** were chemically generated and isolated in the solid state as the mono- and diperchlorate salts. ^1H NMR and IR spectroscopic methods were used to identify the initial reactants while IR, ESR, and electronic absorption spectroscopy and rotating-disk voltammetry were used to characterize the oxidation products of each electron-transfer step.

Introduction

The electrochemical and chemical oxidation of $((TPP)Fe)_2O$ has been reported in nonaqueous media.[1-5] Both the singly and doubly oxidized complexes have been isolated,[5] and after a great deal of controversy,[6] there is now little doubt that initial electron abstraction involves orbitals of the porphyrin ring to

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