BINUCLEAR SCHIFF BASE COMPLEXES OF
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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)))

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Binuclear complexes, oxidation-reduction, conductivity, magnetic moments, chelates, chelate ring conformation

Bioluminescence

Binuclear complexes of Ni, Cu, and Co have been synthesized and characterized. The reactions of Ni(II), Cu(II), or Co(II) with a solution of 2-phenyldiamine and ethylenebis(2,2'-pyridylamine) results in the formation of NiCl₂(2,2'-pyridylamine)NiCl₂ (2) and CuCl₂(2,2'-pyridylamine)CuCl₂ (3), respectively, where 2,2'-pyridylamine is (2,2'-pyridylamine). The binuclear nickel complexes NiCl₂(2,2'-pyridylamine)NiCl₂ (2) and NiCl₂(SR)₂ (3) are prepared by metathesis of the chloride ion of complex 2 with the appropriate sodium salt. These complexes,

$\delta \cdot 4$ exhibit electronic spectra consistent with a trigonally distorted axial-coordinate complex. The binuclear nickel complex 2 exhibits a molar conductance of $A_m = 182$ cm$^2$ mol$^{-1} \cdot$ cm$^{-1}$ in methanol while its mononuclear analogue, Ni(1,3-propyldiamine)Cl₂, has a conductance of $A_m = 140$ cm$^2$ mol$^{-1} \cdot$ cm$^{-1}$, with typical of 2:1 electrolytes. In DMF solution, complex 2 exhibits a molar conductance of $A_m = 87$ cm$^2$ mol$^{-1} \cdot$ cm$^{-1}$, typical of a 1:1 electrolyte, while the mononuclear nickel complex, Ni(1,3-propyldiamine)Cl₂, has a molar conductance in DMF of $A_m = 75$ cm$^2$ mol$^{-1} \cdot$ cm$^{-1}$, 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 state for 2a, S = 1/2 for 3, and S = 3/2 for 4). The condensation of 2-phenyldiamine with Ni(1,3-propyldiamine) followed by the addition of nickel(II) or copper(II) acetate leads to the formation of the neutral, nonconducting, binuclear nickel complexes NiCl₂(L)(NiCl₂) (4) and CuCl₂(L)(CuCl₂) (5), respectively (L = 2-phenyldiamine). The electronic spectra of 4 and 5 are consistent with square-planar coordination geometries. While complex 4 is paramagnetic, complex 5 is diamagnetic and has been characterized by $\mu$ NMR spectroscopy. A complete assignment of all the resonances of 5 is given and the conformation of the propyldiamine chelate ring is discussed based on the coupling constants in the observed spectrum.
Dinuclear Schiff Base Complexes of m-Xylylenediaz(2-(1,3-propanedi-2-pyridinaldiamine)) and m-Xylylenediaz(2-(1,3-propanedi-2-pyridinaldiamine))

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Received

Abstract

Dinuclear Schiff base complexes of Ni, Co, and Cu have been synthesized and characterized. The reaction of nickel(II)-, copper (II)-, or cobalt(II) chloride with a solution of 2-pyridinaldehyde and m-xylylenediamine(2-(1,3-propanediamine) results in the formation of Ni₂L₂Cl₄ (2a), Co₂L₂Cl₄ (3) and Cu₂L₂Cl₄ (4), respectively, where L = m-xylylenediamine(2-(1,3-propanediamine)). The dinuclear nickel complexes, Ni₂L₃(S₂) (2b) and Ni₂L₃(SCH₂) (2c) are prepared by metathesis of the chloride ion of complex 2a using the appropriate sodium salt. These complexes, 2b-4, exhibit electronic spectra consistent with tetragonally distorted six-coordinate complexes. The dinuclear nickel complex 2c exhibits a molar conductance of \( \lambda_{\text{M}} = 102 \, \text{cm}^2 \text{M}^{-1} \text{ohm}^{-1} \) in methanol while its mononuclear analogue, Ni(1,3-propanediamide(2-pyridinaldiamine))Cl₂, has a conductance of \( \lambda_{\text{M}} = 140 \, \text{cm}^2 \text{M}^{-1} \text{ohm}^{-1} \), both typical of 2:1 electrolytes. In DMSO solution, complex 2c exhibits a molar conductance of \( \lambda_{\text{M}} = 87 \, \text{cm}^2 \text{M}^{-1} \text{ohm}^{-1} \), typical of a 1:1 electrolyte, while the mononuclear nickel complex, Ni(1,3-propanediamide(2-pyridinaldiamine)(SCH₂), has a molar conductance in DMSO of \( \lambda_{\text{M}} = 75 \, \text{cm}^2 \text{M}^{-1} \text{ohm}^{-1} \), 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.
Introduction

Binuclear transition metal complexes have received much attention in recent years. 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, oxygen activation and photosynthetic water reduction. Binuclear complexes have also been utilized in the study of electron transfer processes and metal-metal interactions. The interest in these systems also arises from their ability to serve as simple models for multi-metal centered catalysts. 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 xylene moiety. 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-xylene systems. Martell and co-workers have reported the formation of a dioxygen adduct of a cobalt(II) "wishbone" complex, where the dioxygen molecule bridges two cobalt centers in an intramolecular fashion. A binuclear copper "ear-muff" complex, 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-xylenebis(2-(1,3-propanedi(2-pyridinediamine))) and m-xylenebis(2-(1,3-propanedi(2-pyridine)aldimine)) (2-). Drawings of the binuclear complexes, along with their nomenclature are presented in Figure 1.

Experimental Section

The following abbreviations are used for the tetradeinate ligands: pya, 1,3-propanedi(2-pyridinediamine); pyrr, 1,3-propanedi(2-pyridinealdimine) (2-). Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

Physical Measurements. 1H NMR were recorded on a Bruker WH000 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. Electrochemical measurements were made at room temperature with a PAR 113 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-700 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 N eq. KCl with the literature value of 0.002768 ohm⁻¹cm⁻¹ at 25°C. Typically, equivalent conductances for the complexes in solution were determined at five concentrations ranging from 5 mM-0.1 mM. The equivalent conductances at 1 mM were then determined from an Onsager plot of equivalent conductance vs. (concentration)¹².

Reagents. All solvents used were analytical reagent grade except where otherwise noted. m-Xylenebis(2-(1,3-propanediamine)), was prepared as described previously. Ni(pya₂)Cl₂, Ni(pyrr₂)Ni(pya₂)Cl₂, Cu(pyr₂)Cl₂, Ni(pyr₂), and Cu(pyr₂)Cl₂ were all prepared by literature methods.
2-Pyridimethaldehyde and 2-pyrrrolealdehyde were purchased from Aldrich and used without further purification.

m-Xylylenedibis[(NI(pz2-prm)](H)[CN]4·2H2O (2a). 2-Pyridimethaldehyde (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 NiCl2·6H2O (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 C33H34N3O5: C, 48.18; H, 5.40; N, 11.09; Cl, 14.04. Found: C, 48.49; H, 5.41; N, 11.10; Cl, 14.09. IR (KBr): 1645, 1596, 1478, 1445, 1306, 1019, 776 cm⁻¹.

m-Xylylenedibis[(NI(pz2-prm)](H)[NC]4·2H2O (2b) is prepared by the metathesis of Cl⁻ in 2a using an excess of NaN₃ in H₂O and is recrystallized from H₂O/acetonitrile.

Anal. Calcd for C32H34N4O4H: C, 49.16; H, 4.57; N, 30.18. Found: C, 49.10; H, 4.40; N, 30.37. IR (KBr): 2020, 1640, 1598, 1476, 1445, 1306, 1018, 777 cm⁻¹.

m-Xylylenedibis[(NI(pz2-prm)](NCS)4·H₂O (2c) is prepared by metathesis of Cl⁻ in 2a using an excess of NaSCN in methanol. Anal. Calcd. for C42H40N20·5·H₂O: 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-Xylylenedibis(Co(pz2-prm)]Cl₂·2H₂O (3). This complex is made following the procedure for synthesizing 2a but using CoCl₂·6H₂O as the metal salt and is isolated as a green solid in 64% yield. Anal. Calcd for C38H₄₂N₄O₂Co·Cl₂·2H₂O: 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, 1224, 775 cm⁻¹.

m-Xylylenedibis(Co(pz2-prm)]Cl₂·7H₂O (4). This complex is made by the same procedure used to prepare 2a using CoCl₂·6H₂O 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 C38H₄₂N₄O₂Co·Cl₂: C, 45.98; H, 5.29; N, 11.29; Cl, 14.29. Found: C, 45.31; H, 5.34; N, 10.92; Cl, 14.25. IR (KBr): 1645, 1600, 1479, 1446, 1308, 1022, 777 cm⁻¹.

Co(pz2-prm)]Cl₂·H₂O. 2-Pyridimethaldehyde (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-xyleneamidbis(NH(pyrpy_prn))(6). 2-Pyrrrolealdehyde (0.307 g, 3.23 mm) and 1
(0.282 g, 0.81 mm) are refluxed in isopropanol (30 ml) for 2 h and added to
a hot solution of Ni(OAc)2·H2O (0.404 g, 1.12 mm) 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 6 as an orange solid
(0.33 g, 66%). Anal. Calcld for C30H40N4O2Ni: C, 60.76; H, 5.10; N, 16.67.
Found: C, 61.02; H, 5.20; N, 16.42. IR (KBr): 1580, 1440, 1380, 1312, 1043,
740 cm⁻¹. 1H NMR (CDCl₃): 7.25 (1 H, m, aromatic), 7.17 (4 H, s, tosylm),
7.07 (3 H, m, aromatic), 6.80 (4 H, s, pyrrolic), 6.57 (4 H, m, pyrrolic),
6.00 (4 H, m, pyrrolic), 3.21 (4 H, d, methylene), 2.95 (4 H, dd, methylene),
2.86 (4 H, d, benzyllic), 2.16 (2 H, m, methin). m-xyleneamidbis(Cu(pyrrpy_prn))(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. Calcld
for C30H40N4Cu: C, 60.90; H, 5.03; N, 16.44. Found: C, 60.10; H, 5.14;
N, 16.21. IR (KBr): 1590, 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-xyleneamidbis(2-(1,3-propanediamine)) (1) with 4 equiv of either 2-pyrindine-
aldehyde or 2-pyrrrolealdehyde, 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.

Pyridinaldehyde complexes.

Synthesis. The reaction of NiCl₂·H₂O with the ligand solution of m-xylene-
amidbis(2-(1,3-propanediamine(2-pyrindine)) produces the binuclear nickel complex
m-xyleneamidbis(NH(pyrpy_prn))Cl₂, 26, as a yellow-green solid. This complex is
soluble in water, methanol and ethanol but insoluble in chloroform, Na₂SO₄.
ether and hydrocarbon solvents. Its mononuclear analogue, Ni(pyrpy_prn)Cl₂ is
a green crystalline solid and exhibits similar solubility properties. The copper
cobalt binuclear complexes, 3 and 4, are prepared similarly to 26 and also
show similar solubility properties. The copper(II) and nickel(II) complexes
of the tetradentate chelating agent pyrpy_prn have been reported previously, but
the mononuclear cobalt complex, Co(pyrpy_prn)Cl₂, is reported here for the first
time. It is synthesized by a modification of the procedure used to make
Ni(pyrpy_prn)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 pyridinaldehyde group exhibit bands typical of 2-substituted
pyridines 10 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, 27, shows in addition to the above
bands, an azide stretch at 2200 cm⁻¹, which can be assigned to a terminal azide
bonding mode. The nickel(II) thioctyanate derivative, 28, exhibits an infrared
stretch at 2005 cm⁻¹ assignable to νCN, but the C=S stretch and NCS bending
modes are obscured by the chelating ligand bands. The mononuclear nickel complex,
Ni(pyrpy_prn)(NCS)₂, 13 which is proposed to contain N-bonded thioctyanate ligands
based on the observed C=S stretching and NCS bending frequencies, has its νCN
at 2092 cm⁻¹. On the basis of the similarity between νCN for the nickel complex
26 and for Ni(pyrpy_prn)(NCS)₂, we propose the presence of N-bound thioctyanate ligands
in 26.
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, Zₙ, 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 3A₂g - 3T₂g and 3A₂g - 3T₁g transitions. In addition, the weak band which appears at 780 nm can be assigned to the spin forbidden transition 3A₂g - 1E₉. The low energy band, 3A₂g - 3T₂g, contains splitting (815 (s7) and 1060 (s7)) similar to that observed for its mononuclear analogue, Ni(npy₂prn)Cl₄.²⁰ Typical of tetragonally distorted nickel(II) complexes.²⁰ The splitting can be assigned to the 3A₂g - 3T₂g and 3A₂g - 3T₁g 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 Zₙ are thus formulated as [m-xylimelos (Ni(npy₂prn))(Cl)₄(S)₄-x][S-x], where S = H₂O or CH₃OH, 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 Zₙ.

The addition of other weak donors, such as Na₂SO₄, to an aqueous solution of Zₙ 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 Zₙ in water produces significant changes in its electronic spectrum. When Na₂CO₃ is added to an aqueous solution of Zₙ, a new band appears in the near-IR region at 910 nm (s33) (3A₂g - 3T₂g), replacing the 800 and 1005 nm bands of complex Zₙ. 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(ethylendiamine) nickel(II) complexes containing cis-chelated nitrate ligands.²¹ When Na₂C₂O₄ is added to complex Zₙ, spectral changes similar to those seen upon the addition of carbonate are observed (λ_max 980 nm(s11)). In addition to the changes seen for the 3A₂g - 3T₂g transition, there is an increase in the extinction coefficients of the 3A₂g - 3T₁g transitions (s45 and s46 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 diatomic ligands, CO₃²⁻ and C₂O₄²⁻, to the nickel(II) centers and a reduction of symmetry about the metal centers from D₄h to C₂v-distorted octahedral structures shown as L₂²⁰,²²

The cobalt complexes exhibit electronic spectra typical of pseudo-octahedral symmetry.²⁰ The complex, Co(npy₂prn)Cl₂ has weak ligand field bands at 950 nm (c 5) and at 660 nm (c 100) assignable to the 4T₁g - 4T₂g and 4T₁g - 4E₉ (p) transitions. The binuclear cobalt complex, ₂, exhibits a broad transition centered at 970 nm (c 7) (4T₁g - 4T₂g) and a band at 460 nm (c 132) (4T₁g - 4E₉ (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, ₂, contains a weak band assignable to a d-d transition at 750 nm (c 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
Magneto 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 $\text{Ni}^{II}$ in aqueous solution using the Evans NMR method gives a value of $\mu_{\text{eff}} = 3.05 \mu_B$/metal center while a value of 3.07 $\mu_B$/metal center is obtained for $\text{Ni}(\text{pya}_{2}\text{pr})\text{Cl}_2$ as shown in Table II. The azide and thiocyanate complexes, $2a$ and $2b$, yield values of 3.06 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 $4a$ 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 $4a$ possesses a magnetic moment of 4.57 $\mu_B$/metal center, while its mononuclear analogue, $\text{Co}(\text{pya}_{2}\text{pr})\text{Cl}_2$, 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 quasi-reversible 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, $\text{Co}(\text{pya}_{2}\text{pr})\text{Cl}_2$. The binuclear nickel complex and its mononuclear counterpart, $\text{Ni}(\text{pya}_{2}\text{pr})\text{Cl}_2$, exhibit quasi-reversible 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, $\text{Ni}(\text{pya}_{2}\text{pr})\text{Cl}_2$, 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, $\text{m-xylylendiim}(\text{Ni}(\text{pya}_{2}\text{pr}))\text{Cl}_2$, 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 $\text{Ni}(\text{pya}_{2}\text{pr})\text{Cl}_2$. 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 DMSO. Unfortunately a suitable solvent to examine both $2b$ and $\text{Ni}(\text{pya}_{2}\text{pr})(\text{N}_3)_2$ could not be found. However, complexes similar to the azide derivatives were prepared, namely the thiocyanate complexes. In dimethylformamide solution, the mononuclear nickel complex, $\text{Ni}(\text{pya}_{2}\text{pr})(\text{SCN})_2$ 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 $5a$, 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.

Pyroloimidazolium Complexes.

Synthesis. The reaction of nickel($\text{II}$) and copper($\text{II}$) acetate with the ligand solution $\text{m-xylylendiim}(2-(1,3\text{-propanedi}(2\text{-pyrroloidine}))$, prepared in situ, results in the formation of $\text{m-xylylendiim}(\text{Ni}(\text{pyr}_{2}\text{pr}))(\text{5})$ and $\text{m-xylylendiim-(Cu(pyrr}_{2}\text{pr}))(\text{5})$, respectively. The binuclear nickel complex, $\text{5a}$, is an orange
solid, as is its mononuclear analogue, Ni(pyrr$_2$prn). Both copper complexes, Cu(pyrr$_2$prn)$_2$ and Cu$_2$ 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.  

Electronic Spectra. The UV-Visible spectra of the binuclear complexes 5 and 6 are nearly identical to the spectra reported for the analogous mononuclear complexes. The spectral bands assigned to the $\pi-\pi^*$ transition for the mononuclear nickel and copper complexes appear at 318 and 285 nm respectively, while these bands appear at 318 and 299 nm for the binuclear nickel and copper complexes, so it appears that the major ligand $\pi-\pi^*$ 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, 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 (c 280)), it is most likely the $^1A_g \rightarrow ^1A_g$ transition of square planar Ni(II) corresponding to $d_{3z^2}$-$d_{xy}$, $d_{xz}$-$d_{yz}$. The copper complexes, 5 and Cu(pyrr$_2$prn)$_2$, exhibit single broad transitions in the same region as other square planar copper(II) complexes. While several d-d transitions are expected, they are often unresolved as is typical of many other square planar Cu(II) complexes. 

The magnetic moment of the binuclear copper complex, 5, was determined in Me$_2$SO solution using the Evans NMR method and gives a value of $\mu_{eff} = 1.67$ $\mu_B$/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 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 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-xylidiimnes(Ni-sal$_2$prn), 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(pyrr$_2$prn)$_2$. In addition, the benzylic hydrogens, $H_n$, appear as a doublet (J=7.77) at 2.83 ppm, split by the methine hydrogen, $H_o$. 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, $H_o$, 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 ($J_{ef}=13.7$ Hz) and a doublet of doublets ($J_{ef}$, $J_{ef}=6.85$ Hz). Two possible staggered conformations of the six-membered chelate ring are shown below. One would expect that the bulky alkyl
The crystal structure of this complex reveals

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 H₆ and H₇ in complex I, we can calculate the respective coupling constants, J₇₈ and J₆₇, 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 I.

We previously reported the synthesis and ¹H NMR spectrum of the binuclear nickel complex, (m-xylidenebis(2-(1,3-propanediamino)salicylaldimine)) bis nickel(II) (2). If we compare the proton NMR spectrum of complex I with that of complex II, we see a marked difference between their methylene resonances (see Figure 3). While the methylene hydrogens in complex I, H₆ and H₇, appear as a doublet and a doublet of doublets, respectively, the same methylene groups in the salicylaldimine complex (2) give rise to two doublets of doublets. The methylene protons in complex II 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 I. If the carbon-carbon bond of the chelate ring is twisted so that H₆ approaches H₇, as shown in equation (1), we expect.
according to the Karplus relationship, that the coupling between $H_e$ and $H_g$ should increase as the dihedral angle between them approaches $0^\circ$. In addition, the coupling between $H_e$ and $H_g$ should decrease as a result of the decrease in their dihedral angle from $180^\circ$ towards $120^\circ$. When $\phi$ reaches $30^\circ$ the predicted coupling constants, $J_{eg}$ and $J_{eb}$, 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 $\mathcal{Z}$ with a similar copper chelate which has been analyzed by x-ray crystallography. The crystal structure of III, (bis(2-hydroxycetophenone)trimethylenedimino)copper(II) shows that the six-membered copper-propanediamine ring takes a twisted boat conformation. If the nickel complex, $\mathcal{Z}$, were to adopt the same conformation, the dihedral angle, $\phi$ (see equation (1)), between $H_e$ and $H_g$ would be approximately $30^\circ$, which is the value obtained from the $^1H$ NMR results using the Karplus equation. Thus, in going from the fused 6,6,6-membered chelate rings in complex $\mathcal{Z}$ to the 5,6,5-membered rings in complex $\mathcal{S}$, 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 $\mathcal{S}$ and $\mathcal{Z}$.

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 $\mathcal{S}$. In addition, it has allowed a conformational analysis to be performed for the binuclear nickel complexes through the use of the Karplus relationship. Further studies of these and related binuclear complexes are in progress.
Acknowledgment. We wish to thank the Office of Naval Research and the National Science Foundation (CHE83-08064) for support of the research. BCM gratefully acknowledges a Sherman Clarke Fellowship.

References.


17. Magnetic moment was determined in 2% t-BuOH("aq).

18. Magnetic moment was determined in Me2SO.


(26) The coupling constants are obtained from the equation $J_{ab} = 4.22 - 0.5 \cos \phi + 4.5 \cos 2\theta$, where $\phi$ is the dihedral angle. Karplus, R. J. Am. Chem. Soc. 1963, 85, 2870.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Solvent</th>
<th>$\lambda_{max} (cm^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni$_2$Cl$_4$·H$_2$O</td>
<td>CH$_3$OH</td>
<td>1000(7), 815(17), 760(15), 560(11), 380 sh(364), 280(25,300).</td>
</tr>
<tr>
<td>Ni$_2$Cl$_2$·H$_2$O</td>
<td>H$_2$O</td>
<td>1005(7), 800(21), 760(18), 540(12), 375(297), 280(25,000).</td>
</tr>
<tr>
<td>Ni(pyr$_2$pm)$_2$Cl$_2$·H$_2$O</td>
<td>DMF</td>
<td>955(28), 823 sh(21), 460 sh(319), 315(5360), 275(14,900).</td>
</tr>
<tr>
<td>Ni$_2$(SCN)$_4$·H$_2$O</td>
<td>DMF</td>
<td>675(38), 785 sh(19), 525(33), 400 sh(530), 278(27,500).</td>
</tr>
<tr>
<td>Cu$_2$Cl$_4$</td>
<td>CH$_3$OH</td>
<td>730(211), 285(20,000).</td>
</tr>
<tr>
<td>Cu(pyr$_2$pm)$_2$Cl$_2$</td>
<td>CH$_3$OH</td>
<td>720(127), 288(14,100).</td>
</tr>
<tr>
<td>Co$_2$Cl$_2$·7H$_2$O</td>
<td>H$_2$O</td>
<td>970(7), 460 sh(132), 320(3670), 280(35,600).</td>
</tr>
<tr>
<td>Co(pyr$_2$pm)$_2$Cl$_2$·H$_2$O</td>
<td>H$_2$O</td>
<td>950(5), 460 sh(100), 320(2225), 280(17,700).</td>
</tr>
<tr>
<td>Ni$_2'^+$</td>
<td>CHCl$_3$</td>
<td>510 sh(280-50), 436(8750), 393(14,000), 318(45,100), 271(9320).</td>
</tr>
<tr>
<td>Ni(pyr$_4$pm)$_2$</td>
<td>CHCl$_3$</td>
<td>437 sh(5700), 396(9400), 380 sh(6900), 316(27,400), 270 sh(6200).</td>
</tr>
<tr>
<td>Cu$_2'^+$</td>
<td>CHCl$_3$</td>
<td>530 sh(85), 357(33,100), 289(24,700).</td>
</tr>
<tr>
<td>Cu(pyr$_4$pm)$_2$</td>
<td>CHCl$_3$</td>
<td>560(128), 426 sh(900), -345(12,000-9,000), -275(12,000-26,000).</td>
</tr>
</tbody>
</table>

*L = 2,2'-xylidenebis(pyr$_2$pm), L' = 2,2'-xylidenebis(pyr$_4$pm)

a Ref. 13.
b Ref. 15.
c Ref. 16.
**Table II. Magnetic moments in solution.**

<table>
<thead>
<tr>
<th>Complexa</th>
<th>Magnetic Momentb (B.M./Metal center)</th>
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<tbody>
<tr>
<td>H(_2)Cl(_2\cdot3)H(_2)O (2a)</td>
<td>3.06</td>
</tr>
<tr>
<td>H(_2)L(H(_2)O)(_4) (2b)c</td>
<td>3.00</td>
</tr>
<tr>
<td>H(_2)L(NCS)(_4\cdot3)H(_2)O (2c)c</td>
<td>3.07</td>
</tr>
<tr>
<td>H(_2)L(py2prn)Cl(_2)</td>
<td>3.07</td>
</tr>
<tr>
<td>Cu(_2)Cl(_4) (3)</td>
<td>1.86</td>
</tr>
<tr>
<td>Cu(py2prn)Cl(_2)</td>
<td>1.74</td>
</tr>
<tr>
<td>Co(_2)Cl(_4\cdot7)H(_2)O (4)</td>
<td>4.57</td>
</tr>
<tr>
<td>Co(py2prn)Cl(_2\cdot2)H(_2)O</td>
<td>4.04</td>
</tr>
<tr>
<td>CuL' (6)c</td>
<td>1.64</td>
</tr>
<tr>
<td>Cu(py2prn)c</td>
<td>1.67</td>
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</tbody>
</table>

**Table III. Molecular conductivity data.**

<table>
<thead>
<tr>
<th>Complex</th>
<th>Solvent</th>
<th>(\Lambda_{10^{-3}})c</th>
<th>Electrolyte typed</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\eta)xylylenobis((\text{H}(\text{py2prn})\text{Cl}))(_4\cdot)BM(_2)O</td>
<td>H(_2)O</td>
<td>431</td>
<td>3:1</td>
</tr>
<tr>
<td>(\eta)xylylenobis((\text{H}(\text{py2prn})\text{Cl}))(_4\cdot)2H(_2)O</td>
<td>CH(_3)OH</td>
<td>182</td>
<td>2:1</td>
</tr>
<tr>
<td>(\eta)xylylenobis((\text{H}(\text{py2prn})\text{Cl}))(_4\cdot)2H(_2)O</td>
<td>H(_2)O</td>
<td>228</td>
<td>2:1</td>
</tr>
<tr>
<td>(\eta)xylylenobis((\text{H}(\text{py2prn})\text{Cl}))(_4\cdot)2H(_2)O</td>
<td>CH(_3)OH</td>
<td>140</td>
<td>2:1</td>
</tr>
<tr>
<td>(\eta)xylylenobis((\text{H}(\text{py2prn})\text{Cl}))(_4\cdot)2H(_2)O</td>
<td>DME</td>
<td>152</td>
<td>2:1</td>
</tr>
<tr>
<td>(\eta)xylylenobis((\text{H}(\text{py2prn})\text{Cl}))(_4\cdot)2H(_2)O</td>
<td>H(_2)O</td>
<td>190</td>
<td>2:1</td>
</tr>
<tr>
<td>(\eta)xylylenobis((\text{H}(\text{py2prn})\text{Cl}))(_4\cdot)(SCN)(_4)</td>
<td>DME</td>
<td>87</td>
<td>1:1</td>
</tr>
<tr>
<td>(\eta)xylylenobis((\text{H}(\text{py2prn})\text{Cl}))(_4\cdot)(SCN)(_4)</td>
<td>DME</td>
<td>75</td>
<td>1:1</td>
</tr>
</tbody>
</table>

aEquivalent conductances are reported for \(10^{-3}\)M solutions and are reported in ohm\(^{-1}\) cm\(^2\) mole\(^{-1}\). b Ref. 24.
Figure 1. Labelling scheme and nomenclature.

Figure 2. 400-MHz $^1$H NMR spectrum of m-xylylenebis(Ni(pyr$_2$prn)) (5).

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

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

2a. $M = $ Ni(II), $X = $Cl$^-$: m-Xylylenebis(Ni(pyr$_2$prn))Cl$_4$
2b. $M = $ Ni(II), $X = $H$_3^+$: m-Xylylenebis(Ni(pyr$_2$prn))(H$_3$)$_4$
2c. $M = $ Ni(II), $X = $NCS$^-$: m-Xylylenebis(Ni(pyr$_2$prn))(NCS)$_4$
3. $M = $ Cu(II), $X = $Cl$^-$: m-Xylylenebis(Cu(pyr$_2$prn))Cl$_4$
4. $M = $ Co(II), $X = $Cl$^-$: m-Xylylenebis(Co(pyr$_2$prn))Cl$_4$
5. $M = $ Ni(III): m-Xylylenebis(Ni(pyr$_2$prn))
6. $M = $ Cu(II): m-Xylylenebis(Cu(pyr$_2$prn))