SYNTHESIS AND CHARACTERIZATION OF BINUCLEAR SCHIFF BASE COMPLEXES OF NICK. (U) ROCHESTER UNIV NY DEPT OF CHEMISTRY B C WHITMORE ET AL. 04 NOV 83
OFFICE OF NAVAL RESEARCH
Contract NO0014-83-K-0154
Task No. NR 634-742
TECHNICAL REPORT NO. 1

Synthesis and Characterization of Binuclear
Schiff Base Complexes of Nickel, Copper, and Manganese
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Prepared for Publication
in
Inorganic Chemistry

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November 4, 1983

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Synthesis and Characterization of Binuclear Schiff Base Complexes of Nickel, Copper and Manganese

Dyan C. Whitmore and Richard Eisenberg

Received

Binuclear complexes of Ni, Cu and Mn have been synthesized and characterized. The reaction of bis(salicylddehyde) complexes of nickel(II) and copper(II) with p-xylylenebis(2-(1,3-propanediamine)) results in the formation of 1 and 2, respectively, while the reaction of manganese(II) acetate with salicylddehyde and 3 results in the formation of 4a. The nickel complex, 3, undergoes a quasi-reversible two-electron transfer at -1.47 V vs SCE attributable to the nickel(II)-nickel(I) couple. The binuclear nickel(I) complex can be generated from 3 both electrochemically and chemically, and has been shown by infrared analysis to form adducts of CO and NO. Magnetic susceptibility measurements by the Faraday method show the manganese and copper complexes (4a and 2) have solid state room temperature moments of 5.47 and 1.92 B.M. per metal center, respectively, while the solution magnetic moment of the binuclear copper complex (2) is found by the Evans method to be 1.49 B.M. per copper center. This reduced magnetic moment relative to the moment for mononuclear DPP (1.79 B.M.) suggests a weak magnetic interaction between the two copper centers in the binuclear copper complex 2.

Introduction

The synthesis of binuclear complexes in which a ligand structure maintains the metal centers in close proximity represents an important current objective in the study of transition metal systems. The interest in these complexes derives in part from their ability to serve as simple models for multi-metal-centered catalysts. Many binuclear complexes of this type have been reported in recent years with the orientation of the metal centers, and hence, the nature of the metal-metal interactions, controlled via the selection of appropriate bridging ligands. Several series of complexes utilize ligands which hold the metals in close, fixed arrangements, as in the case of molecular A-frames, cofacial dipyrroles, side-by-side macrocycles and macrocyclic inclusion complexes. A different series of complexes employs more flexible ligands, which provide a less restricted environment for each metal relative to the second metal center. Examples of this series include so-called "wishbone complexes," "ear-muff" complexes and other similar complexes, which are based on ligands having bridging xylene moieties. The binuclear complexes which we report in the present paper also belong to this last group of flexibly bridged binuclear metal systems.

By design, the metal centers in the binuclear complexes reported herein are separated by distances which vary from a minimum of 4 Å to a maximum of 12 Å. At the smallest of these values we expect no direct metal-metal bonding, although magnetic interactions between the metals in these complexes may be observable. More importantly, the complexes are constructed so that interactions between the two metal centers and a single substrate molecule, or between two metal-bound substrates are possible. These complexes, then, have the potential to serve as two-center, multielectron catalysts.

In the present paper we report the synthesis and characterization of
Experimental Section

Manipulations involving air sensitive materials were performed under
nitrogen using modified Schlenk techniques. Elemental analyses were performed
by Galbraith Laboratories Inc., Knoxville, Tennessee.

Physical Measurements. Melting points were determined using a Mel-temp
apparatus and are uncorrected. 1H NMR were recorded on a JESOL-CO WP00 100
MHz instrument, a Varian EM-390 90 MHz instrument or a Bruker WH600 400 MHz
instrument with chemical shifts reported in ppm relative to TMS as an internal
standard. Deuterated solvents were purchased from Aldrich. Infrared spectra
were recorded on a Perkin-Elmer model 467 grating spectrophotometer. Samples
were either mull on NaCl plates or KBr pellets. Electronic spectra
were recorded on a Perkin-Elmer model 330 spectrophotometer or a Cary model
110 spectrophotometer using 1 cm quartz cells. Extinction coefficients are
given in 1 m⁻¹ cm⁻¹. Solid state magnetic moments were determined by the
Faraday method using a Cahn electrobalance and HgCo(NCS)₂ as a calibrant.
Diamagnetic corrections were made using Pascals constants. Solution
magnetic moments were determined using the Evans NMR method in DMSO.

Electrochemical measurements were made at room temperature using a PAR 173
potentiostat, PAR 175 universal programmer, and a PAR 179 Digital coulometer.
The three electrode cell utilized a saturated calomel reference electrode with a
0.1 N KClaq salt bridge, and a platinum auxiliary electrode. For cyclic
voltammetry the working electrode was either glassy carbon, platinum or a
hanging mercury drop. Controlled potential coulometry required either a
mercury pool or a platinum bashed working electrode.

Reagents. Isophthalaldehyde was purchased from Tridom Fluka. Malononitrile
was purchased from Aldrich and was distilled from P2O5 at reduced pressure prior to use. Dicyclohexylammonium thiocyanate (1 M solution in THF) and salicylaldehyde were purchased from Aldrich. Benzaldehyde, 13 Mitsui, 14 Hisaoka, 15 and 16 Cupel were all prepared by the literature methods and gave satisfactory elemental analyses. Triethylammonium formate anhydride (TEAF) 17 was prepared by the literature method. All solvents used were analytical reagent grade except where otherwise noted. THF was distilled from sodium-lithium alloy and benzophenone under nitrogen.

o-Xylylenediamine (1). Malononitrile (2.64 g, 0.06 m) dissolved in ethanol (10 ml) is added to a solution of isophthalaldehyde (2.76 g, 0.02 m) in hot ethanol (35 ml). The solution is heated 10 minutes, cooled to room temperature and filtered yielding 1 as a white crystalline solid (4.3 g, 93%), mp 177-179°C. Anal. Calc'd for C14H12N2: C, 73.60; H, 6.33; N, 24.84. Found: C, 72.96; H, 2.80; N, 24.36. 1H NMR ((CD3)2CO): 8.2-8.6 (m, 5H, vinyl, 4,5,6-aromatics), 7.7-8.0 (m, 1H, 2-aromatic). IR (KBr): v =CH, 2225 cm⁻¹.

Mass spectrum m/e 230 (M⁺).

o-Xylylenediamine (2). A DMF solution (40 ml) of 1 (2.3 g, 0.01 m) and TEAF (5.2 g) is stirred at 35°C for two hours, added to ice water (40 ml) and extracted with benzene (3x100 ml). The benzene extracts are washed with water (200 ml), dried over MgSO4 and reduced in volume to 10 ml. The resulting precipitate is then recrystallized from hot ethanol (50 ml) giving 2 as a white crystalline solid (1.9 g, 81%), mp 120.5-122°C. Anal. Calc'd for C14H12N2: C, 71.77; H, 4.31; N, 23.92. Found: C, 71.64; H, 4.56; N, 23.87. 1H NMR ((CD3)2CO): 7.4 (s, 5H, aromatic), 4.5 (t, J = 7 Hz), 2H, CH(2CH3), 3.4 (d, J = 7 Hz), 4H, benzyllic. IR: v =CH 2255 cm⁻¹. Mass spectrum m/e 234 (M⁺).

2-Benzyl-1,3-diaminopropane (4). BMI/THF (82 ml, 0.082 m) is added over a ten-minute period to a refluxing solution of benzaldehyde (5.3 g, 0.094 m) in THF (20 ml) under a nitrogen atmosphere. The reaction solution is refluxed for four hours. Reaction workup is similar to the workup of BMI using HCl (4.1 m) and 16 H NaOH (20 ml). After basic hydrolysis and filtration, the aqueous phase is extracted with ether (3x30 ml) and the organic phase dried over magnesium sulfate and removed in vacuo. The remaining oil is vacuum distilled yielding 4 as a colorless oil. (0.9 g, 16%), bp 130-135°C (4 mm Hg). 1H NMR (CDCl3): 7.1 (s, 5H, aromatic), 2.4-2.7 (overlapping doublets, 6H, methylene, benzyllic), 1.5-1.8 (m, 1H, methine), 1.1 (s, 3H, NH). IR: v =NH 3265 3345 cm⁻¹.
m-Xylylenediamine(Hisalpyn) (8a). A suspension of bis(salicyalddehyde)nickel(II) dihydrate (0.95 g, 2.87 mm) and \( \Delta \) (0.36 g, 1.4 mm) in 90% ethanol (100 ml) is refluxed 24 hours. The solvent is removed and the resulting olive green solid is dissolved in CHCl\(_2\) and filtered to remove unreacted Ni(sal). Removal of CHCl\(_2\) yields \( \Delta \) as a brown solid (0.91 g, 83%). Anal. Calcd for C\(_4\)H\(_9\)NO\(_2\): C, 61.79; H, 5.20; N, 6.87; Ni, 14.38. Found: C, 61.27; H, 5.15; N, 6.52; Ni, 14.14. IR(KBr): \( \nu_{\text{O-H}} \) 1610 cm\(^{-1}\); \( \nu_{\text{Ketonic}} \) 1535 cm\(^{-1}\). UV/VIS(THF): \( \lambda_{\text{max}} \) 600 nm (shoulder) (c 136), 416 nm (c 8000), 368 nm (c 9800), 320 nm (c 9800). \( \nu_{\text{eff}} \) 0.31 B.M. (Fareday) (uncorrected). \( \text{IH NMR (CDCl}_3\): 6.4-7.5 \( \text{m, CH, aromatic, \( \text{NH}_3\))}, \ 3.3-3.9 \( \text{m, CH}_2\), 2.6-2.8 \( \text{m, CH}_2\), 2.3-2.6 (m, \( \text{CH}_2\), methine). \( \text{J}_{\text{NH}} \) 8.4Hz, \( \text{J}_{\text{CH}} \) 5.8Hz, \( \text{J}_{\text{CH}} \) 7.1Hz, \( \text{J}_{\text{CH}} \) 7.6Hz, \( \text{J}_{\text{CH}} \) 6.2Hz. See Figure 2 and Results Section for more detailed assignments.

m-Xylylenediamine(Nisalpyn) (8a). An aqueous solution (10 ml) of \( \Delta \) (0.53 g, 2.12 mm) is added dropwise to a stirred solution of manganese(II) acetate dihydrate (1.04 g, 4.24 mm) and salicyalddehyde (1.03 g, 8.48 mm) in methanol (30 ml) under a nitrogen atmosphere. The resulting yellow precipitate is filtered under nitrogen and dried in vacuo yielding 8a as a yellow solid (1.0 g, 60%). Anal. Calcd for C\(_4\)H\(_9\)NO\(_2\): C, 61.01; H, 5.38; N, 6.78; Mn, 13.19. Found: C, 60.70; H, 5.33; N, 6.25; Mn, 12.68. IR(KBr): \( \nu_{\text{C=H}} \) 1615, \( \nu_{\text{O-H}} \) 1535 cm\(^{-1}\); \( \nu_{\text{eff}} \) 5.47 B.M./metal center (Fareday)

m-Xylylenediamine(Cosalpyn) (2). A methanolic solution of \( \Delta \) (1.25 g, 5 mm) (20 ml) is added to a refluxing solution of bis(salicyalddehyde)copper(II) dihydrate (3.06 g, 10 mm) in methanol (100 ml). The solution is refluxed twenty hours, cooled and filtered yielding \( \Delta \) as a green solid (2.0 g, 50%). Anal. Calcd for C\(_4\)H\(_9\)NO\(_2\): C, 62.43; H, 5.00; N, 6.94; Cu, 15.73. Found: C, 62.68; H, 5.00; N, 6.90; Cu, 15.42. IR: \( \nu_{\text{C=H}} \) 1605; \( \nu_{\text{Ketonic}} \) 1533 cm\(^{-1}\).

VIS (CHCl\(_3\)): \( \lambda_{\text{max}} \) 600 mm (c 495). \( \nu_{\text{eff}} \) 1.92 B.M./metal center (Fareday), 1.49 B.M./metal center (Evans).

7,2'-[2-benzyl-1,3-propanediybis(salicyl)imido]-bis(hexamethylene)nickel.
(Hisal-pa-pro) (H). Salicyalddehyde (0.3 g, 2.4 mm) and \( \Delta \) (0.2 g, 1.2 mm) are refluxed in ethanol (10 ml) for fifteen minutes. NiCl\(_2\)·6H\(_2\)O (0.20g, 1.2 mm) is then added and the solution refluxed 15 hours. The solution is cooled and filtered yielding \( \Delta \) as brown crystals (0.20 g, 39%). Anal. Calcd for C\(_4\)H\(_9\)NO\(_2\): C, 67.17; H, 5.17; N, 6.53. Found: C, 67.26; H, 5.41; N, 6.60. IR (KBr): \( \nu_{\text{C=H}} \) 1610; \( \nu_{\text{Ketonic}} \) 1535 cm\(^{-1}\). \( \text{IH NMR (CDCl}_3\): 6.3-7.3 \( \text{m, CH, aromatic, \( \text{NH}_3\))}, 3.1-3.7 \( \text{m, CH}_2\) (J\(_{\text{NH}}\) = 13 Hz), 2.5-2.6 (m, \( \text{CH}_2\), benzyl (J\(_{\text{benzyl}}\) = 7 Hz), 2.1-2.4 (m, \( \text{CH}_2\), methine).

Formation and observation of nickel(II) complexes.

(m-Xylylenediamine(Hisalpyn))\(_2\). A suspension of m-xylene diamine(Hisalpyn), \( \Delta \), (0.25 g, 0.32 mm) in dry, deoxygenated THF (50 ml) is placed over sodium amalgam under a nitrogen atmosphere. The yellow suspension gradually becomes deep blue and is transferred using cannulae to a second flask under nitrogen. This blue THF solution is then used in subsequent experiments. UV/VIS(THF): \( \lambda_{\text{max}} \) 675 nm (c 2000), 470 nm (c 1700), 360 nm (c 12,000).

CO adduct. Carbon monoxide is bubbled through the blue nickel(II) solution for two minutes causing the solution to turn green. IR(THF): \( \nu_{\text{C=O}} \) 2045 cm\(^{-1}\).

CN adduct. Addition of excess methyl isocyanide to the blue nickel(II) solution results in the formation of yellow solution. IR(THF): \( \nu_{\text{CN}} \) 2165, 2070 cm\(^{-1}\).
Results and Discussion

Ligand Synthesis. The ligand used to prepare the binuclear complexes studied in this paper is made by the Schiff base condensation of four equivalents of salicylaldehyde with \(\text{m-xylylenbam}(2-(1,3\text{-propandiamine}), 3\). The synthesis of this new tetra-amine \(\text{m}\) is accomplished by the following route. The condensation of salicylaldehyde with two equivalents of malononitrile produces \(\text{m-xylylenbenzamalenitrite}\) \(\text{m}\). The reduction of \(\text{m}\) by TFAH, followed by NaO-TNF reduction produces the desired compound, \(\text{m-xylylenbam}(2-(1,3\text{-propandiamine}))\). Infrared analysis of the product shows the presence of a primary amine (2Hg, 3350 cm\(^{-1}\), 3260 cm\(^{-1}\)). The amine is soluble in water and alcohol but relatively insoluble in other organic solvents. Distillation at reduced pressure (0.001 mm Hg, 150°C) yields \(\text{m}\) as a colorless oil. Although not analytically pure, the formation of \(\text{m}\) is confirmed by its proton NMR in either D2O or D6-methanol along with the isolation of binuclear complexes prepared from this tetra-amine compound. The binuclear complexes \(\text{m}\) and \(\text{m}\) are prepared by minor modifications to the reported synthetic procedures for their mononuclear analogues, \(\text{m}\) and \(\text{m}\), respectively.

Nickel Complexes. The reaction of nickel(II) bis(salicylaldehyde) with \(\text{m}\) in refluxing methanol produces the binuclear nickel complex \(\text{m}\) in 83% yield. Complex \(\text{m}\), isolated as a brown solid, analyzes correctly for the dithrahydride, and is soluble in tetrahydrofuran, dichloromethane, chloroform, and dimethylsulfoxide, giving yellow-to-light brown solutions. The mononuclear analogue, \(\text{m}\), which is also a brown solid, gives similarly colored solutions.

A second mononuclear analogue, complex \(\text{m}\) (Nisal-bz-prn), is prepared by the addition of nickel(II) chloride to an ethanolic solution of salicylaldehyde and 2-benzyl-1,3-diaminopropane, and is isolated as a brown crystalline solid in 39% yield.

All these nickel complexes, \(\text{m}\), \(\text{m}\) and \(\text{m}\), have similar spectral properties. The infrared spectra of Nisal-bz-prn \(\text{m}\) and m-xylylenbamis-(Nisalprn) \(\text{m}\) both show strong absorption bands at 1610 and 1535 cm\(^{-1}\) (KBr) while Nisalprn \(\text{m}\) exhibits IR bands at 1616 and 1543 cm\(^{-1}\) (KBr).14 The visible absorption spectrum of m-xylylenbamis(Nisalprn) has an absorption maximum at 600 nm (shoulder) while Nisalprn has a similar maximum of 595 nm.10 The extinction coefficients of the two complexes are both small (ε = 136 for \(\text{m}\) and ε = 80 for \(\text{m}\)) typical of d-d transitions. Solid state susceptibility measurements show that \(\text{m}\) is diamagnetic.

The 400 MHz proton NMR spectrum of m-xylylenbamis(Nisalprn) \(\text{m}\), is shown in Figure 2. The aromatic protons appear as a series of multiplets in the 6.5 to 7.3 ppm region along with a 7.10 ppm singlet due to the imine CH. Decoupling experiments allow the unambiguous assignment of each of the aromatic resonances. In addition, the benzyl hydrogens appear as a doublet (J = 7.6 Hz) at 2.65 ppm, split by the methine hydrogen, \(\text{m}\). The inequivalent methylene hydrogens, \(\text{m}\) and \(\text{m}\), of the propanediamine chelate ring appear at 3.57 and 3.26 ppm as doublets of doublets, split by each other \((J_{	ext{geminal}} = 13.1 Hz)\) and by \(\text{m}\) \((J_{	ext{geminal}} = 6.2, 6.4 Hz)\). The methine hydrogen, \(\text{m}\), appears as a multiplet at 2.32 ppm. The proton NMR spectrum and the detailed spectral assignments thus provide conclusive evidence for the binuclear structure of complex \(\text{m}\), m-xylylenbamis(Nisalprn). Additional support is also found in the proton NMR spectrum of Nisal-bz-prn \(\text{m}\), which closely resembles that of the binuclear nickel complex \(\text{m}\). The aromatic and imine CH resonances appear in the 6.3 to 7.4 ppm region. The benzyl hydrogens appear at 2.55 ppm split into a doublet by the methine hydrogen \((J = 7 Hz)\). The methylene hydrogens of the propanediamine ring are once again inequivalent and appear as two doublets.
of doublets at 3.8 and 5.5 ppm (Axial) = 15 Hz, (Equatorial) = 8 Hz), while the
manganese spectrum appears as a multiplet at 2.3 ppm.

Both m-Alanyl and m-Kylenaminos(m-Alanyl) [3] exhibits
quasireversible reduction in DMSO as demonstrated by cyclic voltammetry.
(See Table 1.) Complex 5A shows a reduction wave at -1.66 V while the
binuclear nickel complex exhibits a reduction wave at -1.47 V. Each wave is
due to the nickel(III)-nickel(III) couple. Controlled potential coulometry of 5A
in DMSO at -1.66 V shows that one electron per metal center is passed. It has
been reported that reduced macrocyclic nickel complexes react with CO to give
Ni(II)-CO adducts.19 Reduction of 5A to 3A using 15 medium amperes produces a
deep blue solution. The visible spectrum of this nickel(II) solution shows a
strong absorption and 670 nm (e 2000) compared to the weak absorption at 600
nm (e 120) for the nickel(II) complex 5A. When the blue nickel(II) solution
is placed under an atmosphere of carbon monoxide, the solution becomes green
and its IR spectrum shows a stretch at 2045 cm⁻¹ indicating the formation of a
nickel(II) carbonyl adduct. In a separate experiment, the introduction of
excess methyl isocyandate to the blue nickel(II) solution causes the color to
change to yellow, and the infrared spectrum exhibits stretches at 2166 and
2070 cm⁻¹ corresponding to free and coordinated methyl isocyandate,
respectively.

Manganese Complexes. m-Kylenaminos(m-Alanyl), 5A, is prepared by the reaction
of manganese acetate and salicylaldehyde with 5 under a nitrogen atmosphere,
and is isolated as a yellow solid in 60% yield. The reaction must be carried
out under an inert atmosphere since the resulting manganese Schiff base
complex is easily oxidized in solution. Once the complex is filtered and
dried, it is moderately stable towards air oxidation, but does gradually
darken over a period of several weeks. The binuclear manganese complex
analyzes correctly for the trihydrate, and is paramagnetic both in solution
and in the solid state. Measurement of the magnetic moment of 5A in DMSO
solution using the Evans UNK method gives a value of μeff = 4.76 B.M. per
metal center, consistent with a high spin manganese(III) complex, thus
providing evidence for the ease of air oxidation of the manganese center
in solution. Using the same method, a magnetic moment of 5.81 B.M. is obtained
for m-Alanyl, 5A. Determination of the solid state magnetic moment by the
Faraday method gives μeff = 4.47 B.M. per metal center for 5A and μeff = 6.01
B.M. for 5A (μeff = 5.93 B.M.).20 The larger magnetic moment of 5A as
determined by this method may be due to increased interactions between the
Mn(II) centers in 5A resulting from its binuclear structure. However, other
factors such as partial oxidation of 5A in the solid state relative to 5A
cannot be ruled out at this time.

The manganese complexes 5A and 5A have similar infrared spectra typical
of transition metal Schiff base complexes. Quasireversible oxidations in DMSO
are observed for 5A and 5A when examined by cyclic voltammetry. m-Alanyl
exhibits a quasireversible wave at -0.24 V (E1/2) while
m-Kylenaminos(m-Alanyl), 5A, has a wave at -0.25V. These waves are due to
the manganese(III)-manganese(II) couple.

Two other binuclear manganese complexes have been synthesized21 and
examined electrochemically. Electrochemical properties of these manganese
complexes are shown in Table 1. The reduction potentials for complexes 5A and
5A are similar while 5A is shifted significantly more positive. This
observation is readily explained by the electron withdrawing properties of the
nitro-substituent of 5A, which causes a decrease in electron density at the
metal centers thereby stabilizing the manganese(II) oxidation state relative
to that of manganese(III).
Copper Complexes.  α-xylylenediamine(bisalprn), Z, is prepared by the reaction of copper(II) dimethylglyoxime with Z and is obtained as a green solid in 60% yield. Its yield was reported for Casalpin (9). The bimetallic complex analyses correctly for the monohydrate and is paramagnetic both in the solid state and in DMF solution. Measurement of the magnetic moment of Z in the solid state gives a value of $\mu_{\text{eff}} = 1.92$ B.M. per metal cation consistent with copper(II). The solid state moment, $\mu_{\text{eff}}$, determined for Casalpin is 1.85 B.M. The solution magnetic moments were determined in DMF by the Evans method yielding values of $\mu_{\text{eff}} = 1.49$ B.M. and 1.79 B.M. for Z and 10 respectively. The reduced moment for the bimetallic system Z relative to the mononuclear complex 10 again suggests the possibility of increased magnetic interactions for the former, presumably due to the closer average proximity of two metal centers in a bimetallic complex relative to the separation of two mononuclear complexes in solution. The copper complexes Z and 10 exhibit similar infrared spectra which are consistent with copper Schiff base complexes. The visible spectra show similar absorption maxima. For the bimetallic complex, $\lambda_{\text{max}} = 605 \text{ nm}$ (ε 495) while for Casalpin, $\lambda_{\text{max}} = 603 \text{ nm}$ (ε 240). Cyclic voltammetry of Z in DMF shows the presence of a poorly defined irreversible reduction wave at $-1.4 \text{ V}$. Similar behavior is exhibited by its mononuclear analogue Casalpin, 10 (E$_{1/2, \text{irrev}}$ = -1.3 V).

Summary

From the preceding discussion it is seen that the spectral and physical properties of the bimetallic complexes are very similar to those of their mononuclear analogues. The visible spectra of the nickel and copper bimetallic complexes are nearly identical to the corresponding mononuclear nickel and copper complexes. Electrochemical studies show that the redox properties of the bimetallic nickel and manganese complexes (10, 26-29) are very similar to the mononuclear complexes of nickel and manganese (9, 26-29). The presence of two metal centers in the bimetallic complexes does not appear to affect the reduction potentials of the nickel or manganese complexes, but the peak separations do appear to be slightly larger for the bimetallic complexes compared to their mononuclear analogues (see Table 1). However, no splitting of the waves into two components is observed for the bimetallic complexes.

This observation leads us to two possible conclusions. (1) The metal centers are sufficiently insulated from one another to prevent significant electronic interactions between them. (2) While weak electrostatic interactions between the metal centers may exist in the bimetallic complex, their effects are not observable by cyclic voltammetry. Theory predicts that even in the case of molecules containing multiple, noninteracting redox centers, the successive electron transfers should follow a statistical separation of formal potentials. For a two center system this separation should be 36 mV. We might therefore expect a slight broadening of the cv waves of the bimetallic complexes compared to their mononuclear analogues which is in fact the case. These observations suggest that for the bimetallic complexes reported here, the two metal centers are for the most part electronically insulated. There does, however, seem to be enough conformational flexibility in the ligand framework to allow a "face-to-face" approach of the two metal centers. This may be evidenced by the reduced magnetic moments in solution of the bimetallic complex Z relative to its mononuclear analogue 10. Attempts to obtain more direct evidence of the conformational flexibility of these bimetallic systems, such as through the formation of adducts in which a common substrate is coordinated to both metal centers, are in progress. We expect
that bimetallic complexes of the type reported here will be capable of storing
storing two units of charge (electrons or holes) via one electron redox
processes for each metal center, and then transferring these units of charge
to a commonly bound substrate as redox activated catalysts.

Acknowledgments

We wish to thank the National Science Foundation (Grant CHE80-11574) and
the Office of Naval Research for support of this research. W.C.N. gratefully
acknowledges a Sherman Clarke Fellowship.

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therein.

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2396.

Table I. Electrochemical Data for the Binuclear and Mononuclear Complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>$E_{1/2}$, V</th>
<th>$n_{sp}$, mF</th>
<th>$i_{p}/i_{a}$</th>
<th>scan rate, mV/s</th>
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<tr>
<td>m-xylylenediaminabis(4-salpin)</td>
<td>-1.47</td>
<td>160</td>
<td>1.04</td>
<td>200</td>
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<tr>
<td>4-salpin $AA$</td>
<td>-1.66</td>
<td>130</td>
<td>.97</td>
<td>200</td>
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<td>1.07</td>
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<tr>
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<td>100</td>
<td>.95</td>
<td>90</td>
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<td>110</td>
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<td>90</td>
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<td>91</td>
<td>1.08</td>
<td>100</td>
</tr>
<tr>
<td>m-xylylenediamine(4-NH$_2$-salpin) $AA$</td>
<td>-1.46</td>
<td>--</td>
<td>--</td>
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</tr>
<tr>
<td>Cu(II) $AA$</td>
<td>-1.93</td>
<td>--</td>
<td>--</td>
<td>500</td>
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</tbody>
</table>

$^a$ DMF solution, complex concentration $10^{-3}$ M, supporting electrolyte TBAPF$_6$ (0.1 M), platinum electrode (298 K). $^b$ Reference 21. $^c$ Irreversible wave, glassy carbon electrode, supporting electrolyte TBP (0.1 M). $^d$ The cyclic voltammetric peak-to-peak separation.
Figure 1: Labeling scheme and nomenclature.

Figure 2: 400-MHz 1H NMR spectrum of α-xylylenbis(hisalpyr).