

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

Synthesis and Characterization of Binuclear Schiff Base Complexes of Nickel, Copper, and Manganese¹

BRYAN C. WHITMORE and RICHARD EISENBERG*

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Binuclear complexes of Ni, Cu, and Mn have been synthesized and characterized. The reaction of bis(salicylaldehyde) complexes of nickel(II) and copper(II) with *m*-xylylenebis(2-(1,3-propanediamine)) (3) result in the formation of Ni^{II}L (5) and Cu^{II}L (7), respectively, where L = *m*-xylylenebis(2-(1,3-propanedisalicylaldehyde)) (2-). The reaction of manganese(II) acetate with salicylaldehyde and 3 results in the formation of Mn^{II}L (6a). The nickel complex, 5, undergoes a quasireversible two-electron transfer at -1.47 V vs. SCE attributable to the nickel(II)-nickel(I) couple. Complex 5 is diamagnetic and has been characterized by ¹H NMR spectroscopy while the binuclear nickel(I) complex (11) is paramagnetic. The binuclear nickel(I) complex can be generated from 5 both electrochemically and chemically and has been shown by infrared analysis to form adducts of CO, MeNC, and *n*-BuNC. The EPR spectrum of a frozen THF solution of the bis(nickel(I)) complex (11) is consistent with the existence of noninteracting metal-centered radicals. The carbonyl and *n*-BuNC adducts of 11 are EPR silent. Magnetic susceptibility measurements by the Faraday method show the manganese and copper complexes (6a and 7) have solid-state room-temperature moments of 5.47 and 1.92 μ_B/metal center, respectively, while the solution magnetic moment of the binuclear copper complex (7) is found by the Evans method to be 1.49 μ_B/copper center. This reduced magnetic moment relative to the moment for mononuclear Cu(salprn) (1.79 μ_B) may indicate a weak magnetic interaction between the two copper centers in the binuclear copper complex 7.

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.² 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 that hold the metals in close, fixed arrangements, as in the case of molecular A-frames,³ cofacial diporphyrins,⁴ side-by-side macrocycles,⁵ and macrocyclic inclusion complexes.⁶ 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",⁷ "earmuff" com-

plexes,⁸ and other similar complexes⁹ that are based on ligands having bridging xylylene moieties. The binuclear complexes that 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 that 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. Indeed, Martell and co-workers have shown that interactions of the type we envisioned do occur in a dioxygen adduct of a cobalt(II) wishbone complex, where the dioxygen molecule bridges two cobalt centers in an intramolecular fashion.^{7b} Complexes of this type, thus, have the potential to serve as two-center, multielectron catalysts.

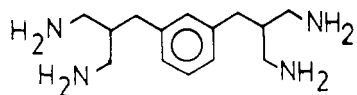
In the present paper we report the synthesis and characterization of binuclear nickel, manganese, and copper complexes of the ligand *m*-xylylenebis(2-(1,3-propanedisalicylaldehyde)). Drawings of the binuclear complexes, along with the nomenclature used throughout this paper, are presented in Figure 1.

Experimental Section

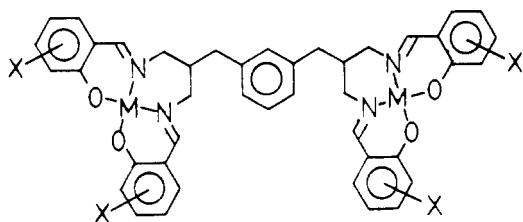
Manipulations involving air-sensitive materials were performed under nitrogen by using modified Schlenk techniques. Elemental

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3, *m*-xylylenebis(2-(1,3-propanediamine))



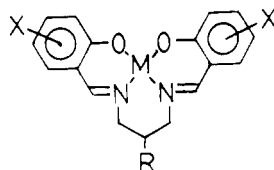
5, M = Ni(II), X = H: *m*-xylylenebis(Ni(salprn))

6a, M = Mn(II), X = H: *m*-xylylenebis(Mn(salprn))

6b, M = Mn(II), X = 3-MeO: *m*-xylylenebis(Mn(MeO-salprn))

6c, M = Mn(II), X = 5-NO₂: *m*-xylylenebis(Mn(NO₂-salprn))

7, M = Cu(II), X = H: *m*-xylylenebis(Cu(salprn))



8a, M = Ni(II), R = X = H: Ni(salprn)

8b, M = Ni(II), R = C₆H₅CH₂, X = H Ni(sal-bz-prn)

9a, M = Mn(II), R = X = H: Mn(salprn)

9b, M = Mn(II), R = H, X = 5-NO₂: Mn(NO₂-salprn)

9c, M = Mn(II), R = H, X = 3-MeO: Mn(MeO-salprn)

10, M = Cu(II), R = X = H: Cu(salprn)

Figure 1. Labeling scheme and nomenclature.

analyses were performed by Galbraith Laboratories Inc., Knoxville, TN.

Physical Measurements. Melting points were determined with a Mel-temp apparatus and are uncorrected. ¹H NMR were recorded on a JEOLCO MH100 100-MHz instrument, a Varian EM-390 90-MHz instrument, or a Bruker WH400 400-MHz instrument with chemical shifts reported in ppm relative to Me₄Si 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 Nujol mulls on NaCl plates or KBr pellets. Electronic spectra were recorded on a Perkin-Elmer Model 330 spectrophotometer or a Cary Model 118 spectrophotometer using 1-cm quartz cells. Extinction coefficients are given in M⁻¹ Cm⁻¹. EPR spectra were recorded on a Bruker ER-200 EPR spectrometer. Solid-state magnetic moments were determined by the Faraday method with a Cahn electrobalance and HgCo(NCS)₄ as a calibrant. Diamagnetic corrections were made with use of Pascals constants.¹⁰ Solution magnetic moments were determined by using the Evans NMR method¹¹ in Me₂SO.¹² 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 utilized a saturated calomel reference electrode with a 0.1 N KCl(aq) 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-based 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. The BH₃·THF complex (1 M solution in THF) and salicylaldehyde were purchased from Aldrich. Benzylmalononitrile,¹³ Ni(salprn),¹⁴ Mn(salprn),¹⁵ and Cu(salprn)¹⁶ were all prepared by the literature methods and gave satisfactory elemental analyses. Triethylamine-formic acid azeotrope (TEAF)¹⁷ was prepared by the literature method. All solvents used were analytical reagent grade except where otherwise noted. THF was distilled from sodium-lead alloy and benzophenone under nitrogen and then stirred over sodium amalgam.

***m*-Xylylidenebis(malononitrile) (1).** Malononitrile (2.64 g, 0.04 mol) dissolved in ethanol (10 mL) is added to a solution of isophthalaldehyde (2.76 g, 0.02 mol) in hot ethanol (35 mL). The solution is heated 10 min, cooled to room temperature, and filtered, yielding **1** as a white crystalline solid (4.3 g, 93%), mp 177–179 °C. Anal. Calcd for C₁₄H₆N₄: C, 73.03; H, 2.63; N, 24.34. Found: C, 72.96; H, 2.80; N, 24.36. ¹H NMR ((CD₃)₂CO): 8.2–8.5 (m, 5 H, vinyl, 4,5,6-aromatics), 7.7–8.0 (m, 1 H, 2-aromatic). IR (KBr): ν_{CN} 2225 cm⁻¹. Mass spectrum: *m/e* 230 (M⁺).

***m*-Xylylbis(malononitrile) (2).** A DMF solution (40 mL) of **1** (2.3 g, 0.01 mol) and TEAF (5.2 g) is stirred at 35 °C for 2 h, added to ice water (40 mL), and extracted with benzene (3 × 100 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. Calcd for C₁₄H₁₀N₄: 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, 4 H, aromatic), 4.6 (t(*J* = 7 Hz), 2 H, CH(CN)₂), 3.4 (d(*J* = 7 Hz), 4 H, benzylic). IR: ν_{CN} 2255 cm⁻¹. Mass spectrum: *m/e* 234 (M⁺).

***m*-Xylylenebis(2-(1,3-propanediamine)) (3).** BH₃·THF (135 mL, 0.135 mol) is added to a refluxing solution of **2** (6.38 g, 0.027 mol) in THF (100 mL) under a nitrogen atmosphere over a period of 90 min. The solution is refluxed 9 h more and then cooled to room temperature. Concentrated HCl (12 mL) is cautiously added to the reaction solution, and the solvent is removed in vacuo. To the solid residue is slowly added 16 M aqueous NaOH (45 mL). The solution is placed on a hot water bath 45 min, followed by cooling and filtration. Upon standing, the filtrate forms two layers. The top layer is removed, dissolved in methanol (150 mL), and filtered. Removal of solvent then yields crude **3** (5.8 g). Bulb-to-bulb distillation at 0.001 mm and 150 °C yields **3** as a colorless oil (0.68 g, 10%). ¹H NMR (CD₃OD): 7.04 (m, 4 H, aromatic), 2.6 (m, 12 H, all methylenes), 1.8 (m, 2 H, methine). IR: ν_{NH₂} 3265, 3350 cm⁻¹.

2-Benzyl-1,3-diaminopropane (4). BH₃·THF (82 mL, 0.082 mol) is added over a 10-min period to a refluxing solution of benzylmalononitrile (5.3 g, 0.034 mol) in THF (20 mL) under a nitrogen atmosphere. The reaction solution is refluxed 4 h. Reaction workup is similar to the workup of **3**, using HCl (4.1 mL) and 16 M NaOH (20 mL). After basic hydrolysis and filtration, the aqueous phase is extracted with ether (3 × 30 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 mmHg). ¹H NMR (CDCl₃): 7.1 (s, 5 H, aromatic), 2.4–2.7 (overlapping doublets, 6 H, methylene, benzylic), 1.5–1.8 (m, 1 H, methine), 1.1 (s, 4 H, NH₂). IR: ν_{NH₂} 3265, 3345 cm⁻¹.

***m*-Xylylenebis(Ni(salprn)) (5).** A suspension of bis(salicylaldehyde)nickel(II) dihydrate (0.95 g, 2.87 mmol) and **3** (0.35 g, 1.4 mmol) in 95% ethanol (100 mL) is refluxed 24 h. The solvent is removed, and the resulting olive green solid is dissolved in CH₂Cl₂ and filtered to remove unreacted Ni(sal)₂. Removal of CH₂Cl₂ yields **5** as a brown solid (0.91 g, 83%). Anal. Calcd for

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$C_{42}H_{38}N_4O_4Ni_2 \cdot 2H_2O$: C, 61.79; H, 5.20; N, 6.87; Ni, 14.38. Found: C, 61.27; H, 5.15; N, 6.52; Ni, 14.16. IR (KBr): $\nu_{C=N}$ 1610, $\nu_{aromatic}$ 1535 cm^{-1} . UV-vis (THF): λ_{max} 600 nm (shoulder) (ϵ 136), 416 nm (ϵ 8000), 360 nm (ϵ 9800), 320 nm (ϵ 9000). $\mu_{eff} = 0.31 \mu_B$ (Faraday) (uncorrected). 1H NMR (CD_2Cl_2): 6.4–7.5 (m, 24 H, aromatic, imine CH), 3.3–3.9 (m, 8 H, CH_2N), 2.6–2.8 (m, 4 H, benzylic), 2.3–2.6 (m, 2 H, methine) ($J_{ab} = 8.6$ Hz, $J_{bc} = 5.6$ Hz, $J_{cd} = 7.1$ Hz, $J_{gh} = 7.6$ Hz, $J_{ijk} = 6.2, 6.4$ Hz, $J_{kl} = 7.6$ Hz). See Figure 2 and Results and Discussion for more detailed assignments.

***m*-Xylylenebis(Mn(salprn)) (6a)**. An aqueous solution (10 mL) of **3** (0.53 g, 2.12 mmol) is added dropwise to a stirred solution of manganese(II) acetate dihydrate (1.04 g, 4.24 mmol) and salicylaldehyde (1.03 g, 8.48 mmol) in methanol (30 mL) under a nitrogen atmosphere. The resulting yellow precipitate is filtered under nitrogen and dried in vacuo, yielding **6a** as a yellow solid (1.0 g, 60%). Anal. Calcd for $C_{42}H_{38}N_4O_4Mn_2 \cdot 3H_2O$: 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): $\nu_{C=N}$ 1615, $\nu_{aromatic}$ 1535 cm^{-1} . $\mu_{eff} = 5.47 \mu_B$ /metal center (Faraday).

***m*-Xylylenebis(Cu(salprn)) (7)**. A methanolic solution of **3** (1.25 g, 5 mmol) (20 mL) is added to a refluxing solution of bis(salicylaldehydato)copper(II) dihydrate (3.06 g, 10 mmol) in methanol (100 mL). The solution is refluxed 20 h, cooled, and filtered, yielding **7** as a green solid (2.0 g, 50%). Anal. Calcd for $C_{42}H_{38}N_4O_4Cu_2 \cdot H_2O$: 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: $\nu_{C=N}$ 1605, $\nu_{aromatic}$ 1533 cm^{-1} . Vis ($CHCl_3$): λ_{max} 600 nm (ϵ 495). $\mu_{eff} = 1.92 \mu_B$ /metal center (Faraday), 1.49 μ_B /metal center (Evans).

[2,2'-(2-Benzyl-1,3-propanediylbis(nitrilomethylidene))bis(phenolato)nickel(Ni(sal-bz-prn)) (8b). Salicylaldehyde (0.3 g, 2.4 mmol) and **4** (0.2 g, 1.2 mmol) are refluxed in ethanol (10 mL) for 15 min. $NiCl_2 \cdot 6H_2O$ (0.28 g, 1.2 mmol) is then added and the solution refluxed 15 h. The solution is cooled and filtered, yielding **8b** as brown crystals (0.20 g, 39%). Anal. Calcd for $C_{24}H_{22}N_2O_2Ni$: C, 67.17; H, 5.17; N, 6.53. Found: C, 67.26; H, 5.41; N, 6.60. IR (KBr): $\nu_{C=N}$ 1610, $\nu_{aromatic}$ 1535 cm^{-1} . 1H NMR ($CDCl_3$): 6.3–7.3 (m, 15 H, aromatic, imine CH), 3.1–3.7 (m, 4 H, CH_2N) ($J_{geminal} = 13$ Hz, $J_{N-CH_2-CH} = 6$ Hz), 2.5–2.6 (d, 2 H, benzylic) ($J_{benzyl-methine} = 7$ Hz), 2.1–2.4 (m, 1 H, methine).

Formation and Observation of Nickel(I) Complexes. [*m*-xylylenebis(Ni(salprn))]²⁻ (11). A suspension of *m*-xylylenebis(Ni(salprn)) (**5**) (0.25 g, 0.32 mmol) 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 with use of cannulae to a second flask under nitrogen. This blue THF solution is then used in subsequent experiments. UV-vis (THF): λ_{max} 665 nm (ϵ 5415), 470 nm (sh), 360 nm (ϵ 12000).

CO Adduct. Carbon monoxide is bubbled through the blue nickel(I) solution for 2 min, causing the solution to turn yellow. IR (THF): ν_{CO} 2045 cm^{-1} .

CH₃NC Adduct. Addition of excess methyl isocyanide to the blue nickel(I) solution results in the formation of a yellow solution. IR (THF): ν_{CN} 2165, 2070 cm^{-1} .

***n*-C₄H₉NC Adduct**. Two equivalents of *n*-butyl isocyanide is added to a THF solution of complex **11** under a nitrogen atmosphere, producing a green solution. IR (THF): ν_{CN} 2060 cm^{-1} .

[Ni(salprn)]⁻. A solution of Ni(salprn) (**8a**) in dry degassed THF is placed over sodium amalgam under a nitrogen atmosphere. The yellow-brown solution gradually becomes deep blue. The blue solution is used in subsequent EPR experiments.

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 4 equiv of salicylaldehyde with 1 equiv of *m*-xylylenebis(2-(1,3-propanediamine)) (**3**). The synthesis of this new tetraamine (**3**) is accomplished by the following route. The condensation of isophthalaldehyde with 2 equiv of malononitrile produces *m*-xylylidenebis(malononitrile) (**1**). The reduction of **1** by TEAF, followed by $BH_3 \cdot THF$ reduction produces the desired compound, *m*-xylylenebis(2-(1,3-propanediamine)). Infrared analysis of the product shows the presence of a primary amine (ν_{NH_2} 3350, 3280 cm^{-1}). The amine is soluble in water and alcohol but relatively insoluble in other organic solvents. Distillation at reduced pressure (0.001 mmHg, 150 °C) yields **3** as a colorless oil. Although

the product is not analytically pure, the formation of **3** is confirmed by its proton NMR spectrum in either D_2O or methanol-*d*₄ along with the isolation of binuclear complexes prepared from this tetraamine compound. The binuclear complexes **5–7** are prepared by minor modifications to the reported synthetic procedures for their mononuclear analogues, **8a–10**, respectively.

Nickel Complexes. The reaction of nickel(II) bis(salicylaldehyde) with **3** in refluxing methanol produces the binuclear nickel complex (**5**) in 83% yield. Complex **5**, isolated as a brown solid, analyzes correctly for the dihydrate and is soluble in tetrahydrofuran, dichloromethane, chloroform, and dimethyl sulfoxide, giving yellow-to-light brown solutions. The mononuclear analogue, **8a**, which is also a brown solid, gives similarly colored solutions.

A second mononuclear analogue, complex **8b** (Ni(sal-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, **5**, **8a**, and **8b**, have similar spectral properties. The infrared spectra of Ni(sal-bz-prn) (**8b**) and *m*-xylylenebis(Ni(salprn)) (**5**) both show strong absorption bands at 1610 and 1535 cm^{-1} (KBr) while Ni(salprn) (**8a**) exhibits IR bands at 1616 and 1543 cm^{-1} (mull).¹⁴ The visible absorption spectrum of *m*-xylylenebis(Ni(salprn)) has an absorption maximum at 600 nm (shoulder) while Ni(salprn) has a similar maximum at 595 nm.¹⁸ The extinction coefficients of the two complexes are both small ($\epsilon = 136$ for **5** and $\epsilon = 80$ for **8a**), typical of d-d transitions. Solid-state susceptibility measurements show that **5** is diamagnetic.

The 400-MHz proton NMR spectrum of *m*-xylylenebis(Ni(salprn)) (**5**) is shown in Figure 2. The aromatic protons appear as a series of multiplets in the 6.5–7.3 ppm region along with a 7.18-ppm singlet due to the imine CH. Decoupling experiments allow the unambiguous assignment of each of the arene resonances. In addition, the benzylic hydrogens appear as a doublet ($J = 7.6$ Hz) at 2.65 ppm, split by the methine hydrogen, H_k . The inequivalent methylene hydrogens, H_i and H_j , of the propanediimine chelate ring appear at 3.57 and 3.28 ppm as doublets of doublets, split by each other ($J_{geminal} = 13.1$ Hz) and by H_k ($J_{vicinal} = 6.2, 6.4$ Hz). The methine hydrogen, H_k , 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 **5**, *m*-xylylenebis(Ni(salprn)). Additional support is also found in the proton NMR spectrum of Ni(sal-bz-prn) (**8b**), which closely resembles that of the binuclear nickel complex **5**. The aromatic and imine CH resonances appear in the 6.3–7.4-ppm region. The benzylic hydrogens appear at 2.55 ppm, split into a doublet by the methine hydrogen ($J = 7$ Hz). The methylene hydrogens of the propanediimine ring are once again inequivalent and appear as two doublets of doublets at 3.2 and 3.5 ppm ($J_{geminal} = 13$ Hz, $J_{vicinal} = 6$ Hz), while the methine hydrogen appears as a multiplet at 2.24 ppm.

Both Ni(salprn) (**8a**) and *m*-xylylenebis(Ni(salprn)) (**5**) exhibit quasireversible reductions in Me_2SO as demonstrated by cyclic voltammetry. (See Table I.) Complex **8a** shows a reduction wave at -1.46 V while the binuclear nickel complex exhibits a reduction wave at -1.47 V. Each wave is due to the nickel(II)–nickel(I) couple. Controlled-potential coulometry of **5** in Me_2SO at -1.65 V shows that one electron per metal center is passed. Reduction of **5** in THF using 1% sodium amalgam produces a deep blue solution of complex **11**, which is confirmed to be a nickel(I) complex by its EPR spectrum in frozen THF solution ($g_{\parallel} = 2.298$, $g_{\perp} = 2.081$).

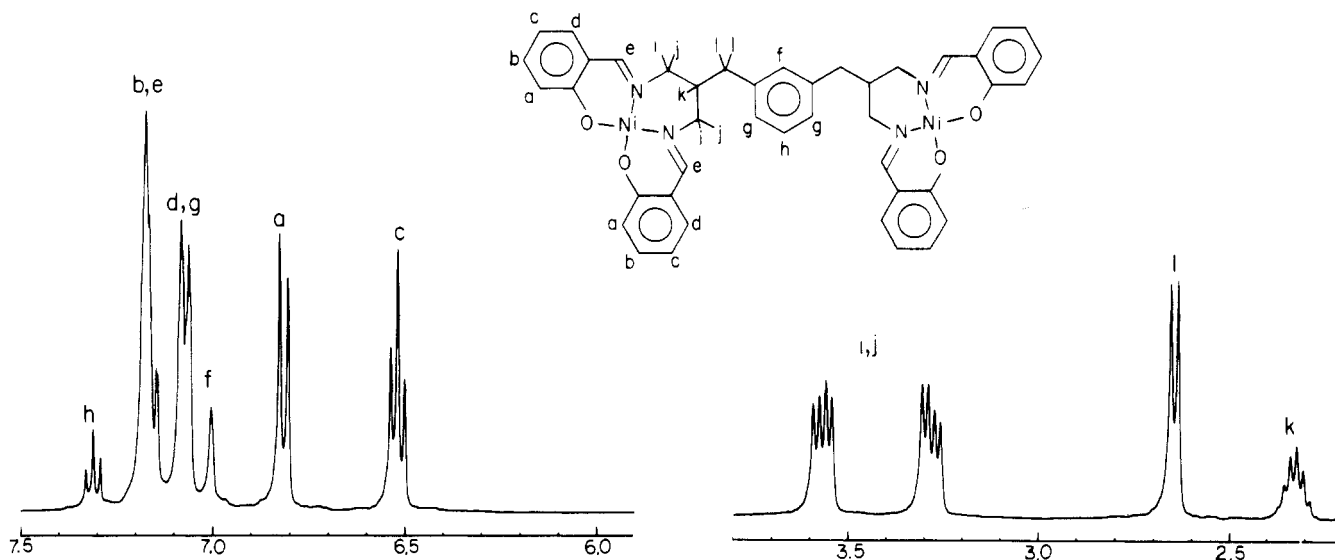


Figure 2. 400-MHz ^1H NMR spectrum of *m*-xylylenebis(Ni(salprn)) (5).

Table I. Electrochemical Data for the Binuclear and Mononuclear Complexes^a

complex	$E_{1/2}$, V	ΔE_p , ^d mV	i_p^c/i_p^a	scan rate, mV/s
<i>m</i> -xylylenebis(Ni(salprn)) (5)	-1.47	160	1.04	200
Ni(salprn) (8a)	-1.46	130	0.97	200
<i>m</i> -xylylenebis(Mn(salprn)) (6a)	-0.25	130	1.07	200
Mn(salprn) (9a)	-0.24	90	1.03	200
<i>m</i> -xylylenebis(Mn(NO ₂ -salprn)) (6b) ^b	-0.11	180	0.95	50
Mn(NO ₂ -salprn) (9b)	-0.12	105	1.00	50
<i>m</i> -xylylenebis(Mn(MeO-salprn)) (6c) ^b	-0.20	110	1.13	50
Mn(MeO-salprn) (9c) ^b	-0.23	91	1.08	100
<i>m</i> -xylylenebis(Cu(salprn)) (7)	-1.4 ^c			500
Cu(salprn) (10)	-1.3 ^c			500

^a Me₂SO solution; complex concentration $\sim 10^{-3}$ M; supporting electrolyte (TBA)BF₄ (0.1 M); platinum electrode (296 K).

^b Reference 21. ^c Irreversible wave; glassy carbon electrode; supporting electrolyte TEAP (0.1 M). ^d The cyclic voltammetric peak-to-peak separation.

The visible spectrum of this nickel(I) solution shows a strong absorption at 665 nm (ϵ 5415) compared to the weak absorption at 600 nm (ϵ 136) for the nickel(II) complex (5). When the blue nickel(I) solution is placed under an atmosphere of carbon monoxide, the solution becomes yellow and its IR spectrum shows a stretch at 2045 cm^{-1} , indicating the formation of a nickel carbonyl adduct. The infrared stretching frequency is similar to those of previously reported nickel(I)-CO adducts of macrocyclic ligands.¹⁹ However, the carbonyl adduct of complex 11 is EPR silent. The reversibility of carbon monoxide adduct formation was tested by attempting to restore the original blue color of the starting nickel(I) complex. If the yellow solution is either purged with nitrogen or placed in vacuo, there is no observable color change, indicating that an irreversible addition of CO and possible redox reaction has taken place. The stoichiometry of this addition was monitored by the infrared stretching frequency of the CO ligand, and it was determined that two CO's are added per binuclear nickel(I) complex, presumably one CO to each metal center. In a separate experiment, the introduction of excess methyl isocyanide to the blue nickel(I) solution causes the color to change to yellow, and the infrared spectrum exhibits stretches at 2165 and 2070 cm^{-1} corresponding to free and coordinated methyl isocyanide, respectively.

Similarly, the addition of 2 equiv of *n*-butyl isocyanide to a THF solution of complex 11 produces a green solution, which exhibits an infrared absorption at 2060 cm^{-1} due to coordinated isocyanide. When up to 2 equiv of *n*-butyl isocyanide is added to 1 equiv of complex 11, only one IR stretch is observed between 2000 and 2300 cm^{-1} . If more than 2 equiv is added, a new IR band appears at 2155 cm^{-1} , which is due to free isocyanide. (A THF solution of *n*-butyl isocyanide has an IR band at 2155 cm^{-1} .) The *n*-butyl isocyanide adduct, as in the case of the carbonyl adduct, is EPR silent.

The mononuclear nickel complex, 8a, behaves similarly to the binuclear nickel complex, 5. Reduction of Ni(salprn) in THF using sodium amalgam produces a deep blue solution, confirmed to be a nickel(I) complex by its EPR spectrum in frozen THF ($g_{\parallel} = 2.295$, $g_{\perp} = 2.074$). The addition of either CO or *n*-BuNC to the blue solution causes the color change to yellow, and as in the case of the binuclear nickel complex, these solutions become EPR inactive. Results from the IR experiments suggest the formation of five-coordinate nickel complexes when carbon monoxide or alkyl isocyanides are added to solutions of the nickel complex, 11. However, one would expect to observe EPR signals for these complexes if simple 1:1 adducts were formed. Only speculations can be made at present to explain the disappearance of the EPR signals in the reactions of the nickel(I) species, so further studies of these systems are in progress.

Manganese Complexes. *m*-Xylylenebis(Mn(salprn)) (6a) is prepared by the reaction of manganous acetate and salicylaldehyde with 3 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 toward 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 6a in Me₂SO solution using the Evans NMR method gives a value of $\mu_{\text{eff}} = 4.84 \mu_{\text{B}}$ /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. With the same method, a magnetic moment of 5.01 μ_{B} is obtained for Mn(salprn) (9a). Determination of the solid-state magnetic moment by the Faraday method gives $\mu_{\text{eff}} = 5.47 \mu_{\text{B}}$ /metal center for 6a and $\mu_{\text{eff}} = 6.01 \mu_{\text{B}}$ for 9a (lit.²⁰ $\mu_{\text{eff}} = 5.93 \mu_{\text{B}}$).

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The lower magnetic moment of **6a** as determined by this method may be due to increased interactions between the Mn(II) centers in **6a** resulting from its binuclear structure. However, other factors such as partial oxidation of **6a** in the solid state relative to **9a** cannot be ruled out at this time.

The manganese complexes **6a** and **9a** have similar infrared spectra typical of transition-metal Schiff base complexes. Quasi-reversible oxidations in Me₂SO are observed for **6a** and **9a** when examined by cyclic voltammetry. Mn(salprn) exhibits a quasi-reversible wave at -0.24 V ($E_{1/2}$) while *m*-xylylenebis(Mn(salprn)) (**6a**) has a wave at -0.25 V. 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 I. The reduction potentials for complexes **6a** and **6c** are similar while **6b** is shifted significantly more positively. This observation is readily explained by the electron-withdrawing properties of the nitro substituent of **6b**, 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. *m*-Xylylenebis(Cu(salprn)) (**7**) is prepared by the reaction of copper(II) bis(salicylaldehyde) with **3** and is obtained as a green solid in 50% yield. No yield was reported for Cu(salprn) (**10**).¹⁶ The binuclear complex analyzes correctly for the monohydrate and is paramagnetic both in the solid state and in Me₂SO solution. The EPR spectrum of **7** in CHCl₃ at room temperature exhibits a four-line isotropic signal ($g_{\text{iso}} = 2.109$, $A = 8.25 \times 10^{-3} \text{ cm}^{-1}$). Measurement of the magnetic moment of **7** in the solid state gives a value of $\mu_{\text{eff}} = 1.92 \mu_{\text{B}}$ /metal center, consistent with copper(II). The solid-state moment, μ_{eff} , determined for Cu(salprn) is $1.85 \mu_{\text{B}}$. The solution magnetic moments were determined in Me₂SO by the Evans method, yielding values of $\mu_{\text{eff}} = 1.49$ and $1.79 \mu_{\text{B}}$ for **7** and **10**, respectively. The reduced moment for the binuclear system **7** 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 binuclear complex relative to the separation of two mononuclear complexes in solution. The copper complexes **7** and **10** exhibit similar infrared spectra that are consistent with copper Schiff base complexes. The visible spectra show similar absorption maxima. For the binuclear complex, $\lambda_{\text{max}} = 605 \text{ nm}$ ($\epsilon = 495$) while, for Cu(salprn), $\lambda_{\text{max}} = 603 \text{ nm}$ ($\epsilon = 240$). Cyclic voltammetry of **7** in Me₂SO shows the presence of a poorly defined irreversible reduction wave at -1.4 V. Similar behavior is exhibited by its mononuclear analogue Cu(salprn) (**10**) ($E_{\text{red}}^{\text{irrev}} = -1.3 \text{ V}$).

Summary

From the preceding discussion it is seen that the spectral and physical properties of the binuclear complexes are very

similar to those of their mononuclear analogues. The visible spectra of the nickel and copper binuclear complexes are nearly identical with those of the corresponding mononuclear nickel and copper complexes. Electrochemical studies show that the redox properties of the binuclear nickel and manganese complexes (**5**, **6a-c**) are very similar to those of the mononuclear complexes of nickel and manganese (**8a**, **9a-c**). The presence of two metal centers in the binuclear 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 binuclear complexes compared to those for their mononuclear analogues (see Table I). However, no splitting of the waves into two components is observed for the binuclear 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 binuclear 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.²² For a two-center system this separation should be 36 mV. We might therefore expect a slight broadening of the CV waves of the binuclear complexes compared to those of their mononuclear analogues, which is in fact the case. These observations suggest that, for the binuclear 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 binuclear complex **7** relative to its mononuclear analogue **10**. Attempts to obtain more direct evidence of the conformational flexibility of these binuclear 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 binuclear complexes of the type reported here will be capable of 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.

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Registry No. **1**, 17239-70-2; **2**, 83416-72-2; **3**, 70865-15-5; **4**, 83416-73-3; **5**, 83416-74-4; **6a**, 83416-75-5; **7**, 83416-76-6; **8a**, 21268-28-0; **8b**, 83416-77-7; **9a**, 24323-08-8; **9b**, 83416-78-8; **10**, 21051-65-0; **11**, 83416-79-9; **11**, CO adduct, 83416-80-2; **11**, CH₃NC adduct, 83416-81-3; **11**, *n*-C₄H₉NC adduct, 83416-82-4; [Ni(salprn)]⁻, 77023-89-3; malonitrile, 109-77-3; isophthalaldehyde, 626-19-7; benzyl malonitrile, 1867-37-4; bis(salicylaldehydato)-nickel(II), 14263-01-5; salicylaldehyde, 90-02-8; bis(salicylaldehydato)copper(II), 14523-25-2.

(21) Complexes **6b** and **6c** are prepared by minor modification of the procedure used for the synthesis of **6a**, substituting 3-methoxy- or 5-nitrosalicylaldehyde. Similarly, complexes **9b** and **9c** are prepared by the same method used to prepare **9a**, using the substituted salicylaldehyde in place of salicylaldehyde. These complexes have been synthesized but not obtained analytically pure.

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