Inorg. Chem. **2001,** *40,* 2147−2155

Bimetallic Reactivity. Preparation and Properties of Bimetallic Complexes Formed by Binucleating Ligands Bearing 4- and 6-Coordinate Sites

Louise M. Liable-Sands, Christopher Incarvito, and Arnold L. Rheingold*

Department of Chemistry and Biochemistry, University of Delaware, Newark, Delaware 19716

C. Jin Qin, Anna L. Gavrilova, and B. Bosnich*

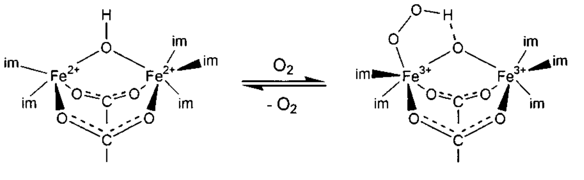
Department of Chemistry, The University of Chicago, 5735 South Ellis Avenue, Chicago, Illinois 60637

Received September 26, 2000

Four binucleating ligands bearing 4- and 6-coordinate sites employing phenolate bridges have been prepared. Bimetallic copper(II) and nickel(II) complexes of some of these ligands have been isolated and characterized. Crystal structures of two of the copper(II) complexes have been determined. A monometallic manganese(II) complex of one of these ligands was isolated. Upon exposure to dioxygen, acetonitrile solutions of the complex in the presence of chloride ions lead to the formation of a manganese(IV) complex. The crystal structure of this complex is reported, and it is shown that the metal is in the 4-coordinate ligand site and is bound to two chloride ions.

Introduction

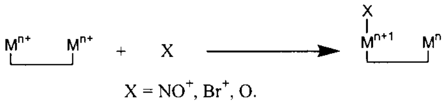
The respiratory protein, hemerythrin,[1] has as its active site two contiguous iron atoms that are bridged by two carboxylate ligands and a hydroxyl group. The other ligands are imidazoles (im), one iron atom is 6-coordinate, and the other is 5-coordinate, **1**.



1 **2**

Dioxygen binds to the 5-coordinate iron atom, and two electrons are transferred, one from each iron atom, to the dioxygen. During this process,[2] the hydroxyl proton is transferred to the emerging peroxide ligand to give a hydroperoxide unit, **2**. A number of realistic structural models for the diiron center of hemerythrin have been reported,[3,4] but as yet, no dioxygen adduct resembling the hemerythrin structure has been isolated, although spectroscopic evidence has been presented suggesting similar dioxygen binding for a structural analogue in solution.[5]

Our interest in the functioning of hemerythrin is both specific and general. Whereas our ultimate aim is to reproduce the specific dioxygen binding of hemerythrin, we have a general interest in the oxidative addition phenomenon displayed by the protein. There are two generally recognized forms of oxidative addition. The more common case is where the substrate adds to a single metal and raises its oxidation state by two units; the other, which is common among dioxygen adducts, is where the reduced substrate bridges two metals after raising the oxidation state of each metal by one unit. The case of oxy-hemerythrin, **2**, is quite distinct; it represents a one-site addition two-metal oxidation phenomenon,[6] a process which, as far as we are aware, has not been reproduced in a synthetic system. In principle, such additions could be extended beyond the substrate, dioxygen, and could include other two-electron oxidants such as NO$^+$, Br$^+$, and O. Thus, in a suitably designed bimetallic system, it may be possible to observe the one-site addition two-metal oxidation reactions depicted in eq 1.



(1)

There are, of course, other substrates that can be envisioned.

The search for systems that would undergo one-site addition two-metal oxidation reactions led us to study the systems **3** and **4**. In these systems, one metal is in a 6-coordinate site and the other is in a 4-coordinate site, or if a ligand Y is coordinated, this site can be made 5-coordinate.[7]

The links A and B were varied and, generally, consisted of two or three aliphatic carbon atoms. Most of the work concerned the reactivities of di-Co(II) complexes, but the results observed apply to other metals and combination of metals. Inspection of

---

(1) Stenkamp, R. E. *Chem. Rev.* **1994**, *94*, 715 and references therein.

(2) (a) Solomon, E. I.; Brunold, T. C. *J. Am. Chem. Soc.* **1999**, *121*, 8277. (b) Solomon, E. I.; Brunold, T. C. *J. Am. Chem. Soc.* **1999**, *121*, 8288.

(3) Wieghardt, K.; Pohl, K.; Gebert, W. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 727.

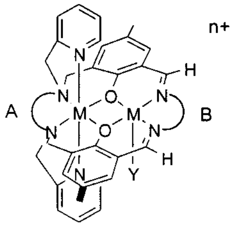
(4) Armstrong, W. H.; Lippard, S. J. *J. Am. Chem. Soc.* **1983**, *105*, 4837.

(5) Mizoguchi, T. J.; Lippard, S. J. *J. Am. Chem. Soc.* **1998**, *120*, 11022.

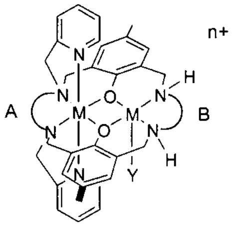
(6) Bosnich, B. *Inorg. Chem.* **1999**, *38*, 2554.

(7) (a) Fraser, C.; Johnston, L.; Rheingold, A. L.; Haggerty, B. S.; Williams, C. K.; Whelan, J.; Bosnich, B. *Inorg. Chem.* **1992**, *31*, 1835. (b) Fraser, C.; Ostrander, R.; Rheingold, A. L.; White, C.; Bosnich, B. *Inorg. Chem.* **1994**, *33*, 324. (c) Fraser, C.; Bosnich, B. *Inorg. Chem.* **1994**, *33*, 338. (d) McCollum, D. G.; Hall, L.; White, C.; Ostrander, R.; Rheingold, A. L.; Whelan, J.; Bosnich, B. *Inorg. Chem.* **1994**, *33*, 924. (e) McCollum, D. G.; Fraser, C.; Ostrander, R.; Rheingold, A. L.; Bosnich, B. *Inorg. Chem.* **1994**, *33*, 2383. (f) McCollum, D. G.; Yap, G. P. A.; Liable-Sands, L.; Rheingold, A. L.; Bosnich, B. *Inorg. Chem.* **1997**, *36*, 2230. (g) McCollum, D. G.; Yap, G. P. A.; Rheingold, A. L.; Bosnich, B. *J. Am. Chem. Soc.* **1996**, *118*, 1365.

10.1021/ic0012625 CCC: $20.00



3



4

3 (Y absent and A and B are derived from ethylenediamine, M = Co(II)) suggests that dioxygen might add to the 4-coordinate, salen-like site[8] and that the superoxide intermediate might be further reduced to peroxide by oxidation of the Co(II) in the 6-coordinate site. It was found that neither the di-Co(II) nor di-Fe(II) complexes of **3** reacted with O_2, suggesting that the individual components of analogous monometallic complexes cannot necessarily be transferred to bimetallic analogues. Di-Co(II) complexes of the type **4**, however, are readily oxidized with O_2 and with ferrocenium (fc$^+$) ions but mixed valence species are formed. Dioxygen oxidizes the Co(II) in the 5-coordinate site (Y = Cl), but fc$^+$ oxidizes the Co(II) in the 6-coordinate site. Once one of the sites is oxidized, however, it is not possible to oxidize the other Co(II) with fc$^+$ ions.

We have ascribed the deactivation to metal oxidation in bimetallic complexes to three effects; through-space electrostatic interactions due to increases in positive charge, to through-bond covalent interactions where the oxidation of one metal leads to poorer electron donation of the bridging atoms to the other metal and to mechanical coupling. Mechanical coupling is the oxidative deactivation that accompanies conformational rearrangements that ensue after the first of the metals is oxidized. We believe that mechanical coupling is decisive in the oxidative deactivation of the metals in **3** and **4** and is partly a consequence of the macrocylic nature of the ligands where the degrees of conformational freedom are restricted. The restrictions are greater in **3** than in **4** because of the presence of the rigid imine groups in the former.

If the macrocylic nature of the ligands in **3** and **4** is one of the major factors contributing to mechanical coupling deactivation, it would be useful to investigate analogous bimetallic complexes where the chelate rings, B in **3** and **4**, were removed. A number of these ligands were prepared but it was found that the metals in the 4-coordinate sites were unstable with respect to dissociation. Molecular models suggest that, in the absence of the B ring, the four donor atoms are misaligned for coordination. Because of this, we designed a new, nonmacrocylic binucleating ligand bearing 4- and 6-coordinate sites, which models suggested would provide less deactivating mechanical coupling than **3** and **4**. Although these new binucleating ligands brought with them new complexities which did not allow us to investigate one-site addition two-metal oxidation reactions, they provided a number of interesting results which we report.

Experimental Section

General Methods. Infrared spectra were recorded on a Nicolet 20SXB FTIR spectrometer using Nujol mulls on NaCl disks for solid samples. Electronic absorption spectra were obtained with a Perkin-Elmer Lambda 6 UV/vis spectrophotometer. Cyclic voltammetric measurements were carried out at 25 °C in dry acetonitrile under argon using a BAS 100 electrochemical analyzer (Bioanalytical Systems, Inc.). The supporting electrolyte was tetrabutylammonium hexafluorophosphate ($TBAPF_6$, 0.1 M). A three-electrode assembly consisting of a platinum disk working electrode, a platinum auxiliary electrode, and a Ag/AgCl reference electrode was used. Elemental analyses were performed by Desert Analytics Laboratory, Tuscon, AZ. Magnetic susceptibilities were measured at 25 °C on powdered samples using a Johnson Matthey magnetic susceptibility balance and in solution by Evans method in deuterated acetonitrile with TMS as a reference. Conductance measurements were made at 25 °C in dry acetonitrile using 1.0×10^{-3} M samples and a YSI Scientific Model 35 conductance meter. ^{1}H NMR and ^{13}C NMR spectra were recorded on either a Bruker DRX400 or a DMX500 Fourier transform spectrometer using $CDCl_3$ as a solvent and TMS as an internal standard unless otherwise stated. Chemical shifts (δ) are given in ppm, coupling constants (J) in hertz. Melting points are uncorrected. Ethanol refers to absolute ethanol. Acetonitrile was dried over CaH_2, THF was dried over potassium/benzophenone ketyl, and ethyl ether was dried over sodium/benzophenone ketyl. TLC was carried out on precoated silica gel (Whatman, PE SIL G/UV) or aluminum oxide (J. T. Baker, aluminum oxide IB-F). Silica gel 60 Å (Merck, 230−400 mesh) or aluminum oxide 58 Å (Aldrich, activated, basic, 150 mesh) was used for flash chromatography.

Ligand Synthesis. 2-Acetoxybenzaldehyde (5) was made by a modification of the preparation described by Fürstner and Jumbam.[9] In a 500-mL two-neck flask were dissolved salicylaldehyde (0.20 mol, 21.30 mL) and pyridine (0.25 mol, 20.20 mL) in 200 mL of methylene chloride. To the stirred clear light yellow solution was added acetyl chloride (0.24 mol, 17.10 mL) dropwise over 10 min under N_2. The solution was stirred at 25 °C for 20 h, during which time a white suspension formed. To the mixture was added aqueous HCl (0.1 M, ∼200 mL) to adjust the pH to ∼3. The methylene chloride layer was separated, and the aqueous layer was extracted with methylene chloride (2 × 50 mL). The combined organic fractions were washed with 200 mL of saturated aqueous solution of $NaHCO_3$ and then with water (2 × 100 mL). The methylene chloride extracts were dried over Na_2SO_4. Filtration and evaporation yielded the product as light orange oil. The product was purified by distillation (bp110−115 °C, ∼5 Torr) to give colorless oil, 30.50 g (93%). ^{1}H NMR ($CDCl_3$): δ 2.40 (s, 3 H), 7.19 (d, $J = 8.3$ Hz, 1H), 7.40 (t, $J = 7.6$ Hz, 1 H), 7.64 (t, $J = 7.9$ Hz, 1 H), 7.89 (d, $J = 7.7$ Hz, 1 H), 10.11 (s, 1H).

2-Dimethoxymethylphenol (6) was made by a modification of the preparation described by Liepa and Morton.[10] In a 2-L two-neck flask was dissolved 2-acetoxybenzaldehyde (0.2 mol, 32.84 g) in 800 mL of toluene. To the solution was added dropwise a solution of sodium methoxide (prepared from sodium (0.21 mol, 4.83 g) and 300 mL of methanol) with vigorous stirring over 30 min under N_2. The resultant gelatinous solution was stirred at 25 °C under N_2 for 12 h to give a light orange solution. The reaction was quenched by pouring the solution slowly into an aqueous solution of NH_4Cl (21.2 g in 1 L) with vigorous stirring. The organic layer was separated, and the water fraction was extracted with ether (3 × 300 mL). The combined organic layers were dried over $MgSO_4$, filtered, and then concentrated first by rotary evaporation and then under high vacuum (∼0.1 Torr, 2 h) to yield the product as a light yellow oil, which was sufficiently pure for the next reaction. Yield: 32.08 g (95%). ^{1}H NMR ($CDCl_3$): δ 3.40 (s, 6 H), 5.56 (s, 1 H), 6.87 (m, 2 H), 7.16 (d, $J = 7.3$ Hz, 1 H), 7.24 (t, $J = 9.3$ Hz, 1 H), 8.07 (s, 1 H). ^{13}C NMR ($CDCl_3$): δ 52.74, 104.51, 116.95, 119.66, 120.80, 128.36, 130.24, 155.67.

1-Dimethoxymethyl-2-methoxymethoxybenzene (7) was prepared following a procedure similar to that reported by Van Heerden et al.[11] To a solution of 2-dimethoxymethylphenol (0.12 mol, 20.19 g) in 120 mL of methylene chloride, was added methyltrialkyl(C_8−C_{10})-ammonium chloride (Aldrich, Adogen 464 phase-transfer catalyst, 8.5 mol %, 0.011 mol, 5.54 g) and aqueous NaOH (11.5 g in 60 mL) with stirring at 25 °C. After the mixture was stirred for 20 min, chloromethyl methyl ether (0.17 mol, 13.0 mL) was added dropwise to the vigorously stirred solution over 10 min under N_2. The stirred solution was maintained at 25 °C in a water bath. The reaction was monitored for

---

(8) Floriani, C.; Calderazzo, F. *J. Chem. Soc. A* **1969**, 946.

(9) Fürstner, A.; Jumbam, D. N. *Tetrahedron* **1992**, *48*, 5991.

(10) Liepa, A. J.; Morton, T. C. *Aust. J. Chem.* **1986**, *39*, 1747.

(11) Van Heerden, F. R.; Van Zyl, J. J.; Rall, G. J. H.; Brandt, E. V.; Roux, D. G. *Tetrahedron Lett.* **1978**, *7*, 661.

completion by observing a color change from bright yellow to colorless; otherwise, more chloromethyl methyl ether was added until a colorless solution was achieved. The layers were separated, and the aqueous layer was extracted with methylene chloride (2 × 50 mL). The combined organic fractions were washed with 100 mL of water and were then dried over Na_2SO_4. Filtration followed by rotary evaporation gave a light orange oil that was purified by distillation (bp 79−81 °C, ∼0.1 Torr) to yield a colorless oil (23.75 g, 93%). ^{1}H NMR ($CDCl_3$): δ 3.36 (s, 6 H), 3.49 (s, 3 H), 5.23 (s, 2 H), 5.70 (s, 1 H), 7.03 (t, *J* = 7.5 Hz, 1 H), 7.10 (d, *J* = 8.2 Hz, 1 H), 7.28 (t, *J* = 7.5 Hz, 1H), 7.54 (d, *J* = 7.6 Hz, 1 H). ^{13}C NMR ($CDCl_3$): δ 53.39, 56.04, 94.36, 94.01, 114.28, 121.46, 126.85, 127.42, 129.64, 154.60. Anal. Calcd for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60; O, 30.15. Found: C, 62.38; H, 7.34; O, 30.27.

(3-Dimethoxymethyl-2-methoxymethoxyphenyl)dipyridin-2-ylmethanol (8) was prepared following a modified literature procedure.[12] *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (44 mmol, 6.2 mL) was added to a stirred solution of *n*-butyllithium (44 mmol, 27.5 mL of 1.6 M in hexane) in 20 mL of dry THF at 25 °C under N_2. After the mixture was cooled and stirred at 0 °C for 10 min, 1-dimethoxymethyl-2-methoxymethoxybenzene (40 mmol, 8.49 g) was added dropwise to the light orange solution over 30 min. The color changed from light orange to red-orange and a fine red precipitate formed. After being stirred for 1 h at 0 °C, the mixture was transferred dropwise via a wide-bore cannula to a solution of di-2-pyridyl ketone (44 mmol, 8.10 g) in 40 mL of dry THF at 0 °C with vigorous stirring over 30 min. After 4 h of vigorous stirring, a green suspension was obtained. The reaction was quenched by addition of aqueous NH_4Cl (7.5 g in 40 mL) to give an orange suspension. The reaction mixture was extracted with methylene chloride (3 × 50 mL). The combined organic layers were dried over Na_2SO_4, filtered, and rotary evaporated to dryness to give an orange-brown oil. The oil was dissolved in 50 mL of ether and passed through a short silica gel column (50 g). The eluant was reduced to a volume of ∼50 mL at 40 °C, and ∼150 mL of pentane was added slowly until the solution became turbid. After the solution was cooled slowly to room temperature, the flask was allowed to stand in a refrigerator for 5 h and yielded white crystalline plates. The crystals were collected and washed with 20 mL of ethanol followed by pentane (2 × 50 mL). Yield: 12.61 g (80%). Mp: 89−91 °C. ^{1}H NMR ($CDCl_3$): δ 3.23 (s, 3 H), 3.32 (s, 6 H), 4.76 (s, 2 H), 5.60 (s, 1 H), 6.63 (d, *J* = 7.9 Hz, 1 H), 6.93 (s, 1 H), 7.00 (t, *J* = 7.7 Hz, 1 H), 7.17 (m, 2 H), 7.54 (d, *J* = 7.6 Hz, 1 H), 7.67 (t, *J* = 7.9 Hz, 2 H), 7.80 (d, *J* = 8.0 Hz, 2 H), 8.51 (d, *J* = 4.8 Hz, 2 H). ^{13}C NMR ($CDCl_3$): δ 53.65, 56.95, 80.02, 99.70, 100.97, 121.97, 122.33, 123.39, 127.86, 130.12, 132.67, 136.33, 140.10, 147.32, 154.51, 163.23. Anal. Calcd for $C_{22}H_{24}N_2O_5$: C, 66.65; H, 6.10; N, 7.07. Found: C, 66.92; H, 6.37; N, 7.15.

1-Dimethoxymethyl-2-methoxymethoxy-3-(bis(2-pyridyl)methoxymethyl)benzene (9) was synthesized following a reported procedure.[13] In a 250-mL round-bottom flask was dissolved **8** (0.032 mol, 12.61 g) in 60 mL of DMSO with warming. After the light orange solution was cooled to 25 °C, powdered KOH (0.16 mol, 86%, 10.4 g) was added with stirring. The suspension was stirred for 5 min followed by addition of methyl iodide (0.064 mol, 4.0 mL). The mixture was stirred continuously at 25 °C for 30 min before it was poured into 200 mL of water. The product was extracted with methylene chloride (4 × 100 mL). After rotary evaporation, an orange oil was obtained. It was dissolved in 1:5 mixture of methylene chloride/hexane (200 mL) and washed with water (3 × 100 mL). The organic layer was dried over Na_2SO_4, filtered, and evaporated to yield an orange oil, 13.2 g (∼100%). The product was sufficiently pure for the next step. ^{1}H NMR ($CDCl_3$): δ 3.14 (s, 3 H), 3.21 (s, 3 H), 3.35 (s, 6 H), 4.67 (s, 2 H), 5.57 (s, 1 H), 7.06 (m, 2 H), 7.08 (t, *J* = 7.7 Hz, 1 H), 7.38 (d, *J* = 7.7 Hz, 1 H), 7.60 (m, 3 H), 7.75 (d, *J* = 8.0 Hz, 2 H), 8.55 (d, *J* = 4.8 Hz, 2 H).

2-Hydroxy-3-(methoxydipyridin-2-ylmethyl)benzaldehyde (10). In a 500-mL round-bottom flask was dissolved **9** (0.032 mol, 13.2 g) in 90 mL of THF followed by addition of 90 mL of aqueous 2 M HCl to afford an orange solution. After being stirred for 8 h, the solution was neutralized by addition of aqueous 1 M NaOH (180 mL) followed by extraction with methylene chloride (3 × 100 mL). The combined organic fractions were dried over Na_2SO_4 and were concentrated under reduced pressure to give an orange oil. The oil was partially purified by passing it in a chloroform solution through a short alumina column (basic, 40 g). The eluant was rotary evaporated to give an orange oil. The crude product was recrystallized from a mixture of chloroform (5 mL)−ether (20 mL)−pentane (20 mL) by slow addition of pentane (100 mL) to yield white crystals. The crystals were collected and washed with ether (2 × 20 mL) and pentane (2 × 20 mL) and dried under vacuum, 8.47 g (83%). Mp: 139−141 °C. ^{1}H NMR ($CDCl_3$): δ 3.13 (s, 3 H), 7.02 (t, *J* = 7.5 Hz, 1 H), 7.23 (m, 2 H), 7.62 (d, *J* = 8.0 Hz, 2 H), 7.74 (m, 3 H), 7.94 (d, *J* = 7.5, 1 H). 8.49 (d, *J* = 4.0 Hz, 2 H), 10.41 (s, 1H), 12.65 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 52.93, 86.27, 119.39, 122.65, 122.80, 125.82, 129.01, 130.71, 134.06, 137.14, 147.74, 160.04, 161.20, 192.09. Anal. Calcd for $C_{19}H_{16}N_2O_3$: C, 71.24; H, 5.03; N, 8.74. Found: C, 71.37; H, 5.20; N, 8.67. The compound decomposes on silica gel columns.

1,6-Bis(2-hydroxy-3-(bis(2-pyridyl)methoxymethyl)benzene)-2,5-diene-2,5-diazahexane, enpyimH$_2$ (11). In a 200-mL round-bottom flask **10** (20 mmol, 6.41 g) was dissolved in 100 mL of benzene followed by addition of ethylenediamine (10 mmol, 0.67 mL) to give an orange solution. After being heated on a steam bath for 1 h, the solution was concentrated to dryness on a rotary evaporator to give a yellow solid. The solid was dissolved in 100 mL of benzene and evaporated to dryness twice to remove water. The crude product was recrystallized from a mixture of benzene (40 mL)−ether (80 mL)−pentane (10 mL) at −10 °C. The yellow crystalline solid was collected and washed with ether (2 × 30 mL) and pentane (2 × 30 mL) and was dried under vacuum, 6.51 g (98%). ^{1}H NMR ($CDCl_3$): δ 3.24 (s, 6 H), 3.71 (s, 4 H), 6.86 (t, *J* = 7.5 Hz, 2 H), 7.09 (m, 4 H), 7.15 (d, *J* = 7.5, 2 H), 7.60 (m, 6 H), 7.71 (d, *J* = 8.0, 4 H), 8.21 (s, 2 H), 8.55 (d, *J* = 6.0 Hz, 4 H), 13.50 (s, 2 H, D_2O exchangeable). ^{13}C NMR ($CDCl_3$): δ 52.90, 59.27, 86.57, 117.69, 119.15, 121.58, 122.83, 128.98, 131.57, 133.65, 135.92, 148.24, 159.64, 161.75, 166.16. Anal. Calcd for $C_{40}H_{36}N_6O_4$: C, 72.27; H, 5.46; N, 12.64. Found: C, 72.51; H, 5.51; N, 12.33.

1,7-Bis(2-hydroxy-3-(bis(2-pyridyl)methoxymethyl)benzene)-2,6-diene-2,6-diazaheptane, tnpyimH$_2$ (12). To an orange solution of **10** (10 mmol, 3.20 g) in 50 mL of benzene was added 1,3-diaminopropane (5 mmol, 0.42 mL) with stirring. After the solution was stirred for 5 min, a cloudy yellow solution was obtained. The mixture was heated on a steam bath for 1 h. Upon evaporation of the solvent, a yellow solid formed. The solid was dissolved in benzene (30 mL), and the solvent was removed under reduced pressure (twice). The final product was recrystallized from benzene (50 mL)−ether (150 mL) at −10 °C, 3.26 g (96%). ^{1}H NMR ($CDCl_3$): δ 1.90 (m, 2 H), 3.27 (s, 6 H), 3.48 (t, *J* = 4.0, 4 H), 6.88 (t, *J* = 7.6 Hz, 2 H), 7.10 (m, 4 H), 7.22 (d, *J* = 7.2, 2 H), 7.57 (d, *J* = 7.6, 2 H), 7.66 (t, *J* = 7.6, 4 H), 7.76 (d, *J* = 8.0 Hz, 4 H), 8.25 (s, 2 H), 8.57 (t, *J* = 4 Hz, 4 H), 13.69 (s, 2 H). ^{13}C NMR ($CDCl_3$): δ 31.17, 52.86, 56.43, 86.55, 117.58, 119.15, 121.56, 122.77, 128.97, 131.39, 133.60, 135.92, 148.18, 159.84, 161.74, 165.03. Anal. Calcd for $C_{41}H_{38}N_6O_4$: C, 72.55; H, 5.64; N, 12.38. Found: C, 72.66; H, 5.85; N, 12.09.

1,6-Bis(2-hydroxy-3-(bis(2-pyridyl)methoxymethyl)benzene)-2,5-diazahexane, enpyamH$_2$ (13). In a 200-mL round-bottom flask was dissolved enpyimH$_2$ (1.87 mmol, 1.24 g) in 100 mL of hot absolute ethanol. After the mixture was cooled to room temperature, sodium borohydride (15 mmol, 0.57 g) was added in one portion with stirring. After 60 h of stirring, a very pale orange solution formed. Acetic acid (60 mmol, 3.5 mL) was then cautiously added dropwise over 10 min. The solution was taken down to dryness by rotary evaporation to yield a white solid, which was dissolved in 13 mL of aqueous 1 M HCl. After being stirred for 1 h, the solution was neutralized by the addition of 13 mL of 1 M NaOH to give a turbid white solution with pH ∼8. The product was extracted with methylene chloride (3 × 20 mL), and the combined methylene chloride extracts were concentrated on a rotary evaporator to give a white foam, sufficiently pure for the preparation of the complexes, 1.25 g (100%). ^{1}H NMR ($CDCl_3$): δ 3.03 (s, 6 H), 3.16 (s, 4 H), 3.94 (s, 4 H), 6.86 (t, *J* = 7.7 Hz, 2 H), 7.12 (m, 4 H), 7.30 (d, *J* = 7.3, 2 H), 7.56 (d, *J* = 8.0, 4 H), 7.60 (m, 6 H), 8.38 (d,

---

(12) Christensen, H. *Synth. Commun.* **1975**, *5*, 65.

(13) Johnstone, R. A. W.; Rose, M. E. *Tetrahedron* **1979**, *35*, 2169.

$J = 4.8$ Hz, 4 H). ^{13}C NMR (CDCl$_3$): δ 43.58, 47.17, 52.89, 86.34, 119.58, 122.46, 122.71, 122.81, 128.07, 129.17, 131.56, 137.28, 147.72, 154.59, 161.45.

1,7-Bis(2-hydroxy-3-(bis(2-pyridyl)methoxymethyl)benzene)-2,6-diazaheptane, tnpyamH$_2$ (14). To a stirred suspension of tnpyimH$_2$ in absolute ethanol (100 mL) was added sodium borohydride (12 mmol, 0.45 g) in one portion. The mixture was stirred at 25 °C for 20 h, when a clear and colorless solution was obtained. The reaction was quenched by slow addition of acetic acid (48 mmol, 2.7 mL) over 10 min. The solvent was removed, and the remaining white solid was dissolved in 30 mL of water and saturated aqueous NaHCO$_3$ was added until no more product precipitated (pH ~8). The product was extracted with methylene chloride (3 × 30 mL). The combined organic layers were dried over MgSO$_4$, filtered, and evaporated to give a white foam, which was sufficiently pure for the preparation of the complexes, 1.36 g (99%). ^{1}H NMR (CDCl$_3$): δ 1.63 (m, 2 H), 2.59 (t, $J = 7.0$, 4 H), 3.08 (s, 6 H), 3.75 (s, 4 H), 6.86 (t, $J = 7.5$ Hz, 2 H), 7.12 (m, 6 H), 7.53 (d, $J = 7.5$, 2 H), 7.59 (d, $J = 8.0$, 4 H), 7.66 (m, 4 H), 8.41 (d, $J = 4.5$ Hz, 4 H). ^{13}C NMR (CDCl$_3$): δ 29.00, 47.17, 49.86, 52.61, 86.32, 118.77, 122.17, 122.48, 126.52, 128.06, 128.13, 129.54, 136.50, 147.40, 154.27, 161.65.

Synthesis of the Complexes. [Ni(enpyim)Ni](PF$_6$)$_2$ (15). To an enpyimH$_2$ (0.6 mmol, 0.40 g) suspension in 12 mL of methanol was added Et$_3$N (1.2 mmol, 167 μL). The mixture was heated on a steam bath for 10 min, and then Ni(OAc)$_2$·4H$_2$O (0.6 mmol, 0.15 g) was added with stirring followed by the addition of NiCl$_2$·6H$_2$O (0.6 mmol, 0.14 g). An orange-brown solution formed. The solution was stirred and heated at ~70 °C for 1 h. A solution of NH$_4$PF$_6$ (2.4 mmol, 0.39 g) in methanol (2 mL) was then added into the solution. The solvent was removed to give a brown solid, which was slurried in 10 mL of ethanol. The pale orange solid was collected by filtration and washed with ethanol (2 × 2 mL). The analytically pure sample was obtained by recrystallization of the crude solid from acetonitrile by addition of ethanol. This yielded brown blocks that were collected and dried under vacuum, 0.48 g (68%). μ_{298} (solution) = 4.06 μ_B. Anal. Calcd for C$_{40}$H$_{34}$N$_6$O$_4$P$_2$F$_{12}$Ni$_2$: C, 44.90; H, 3.20; N, 7.85. Found: C, 44.99; H, 3.37; N, 8.18.

[Ni(enpyam)Ni](PF$_6$)$_2$ (16). [Ni(enpyam)Ni](PF$_6$)$_2$ was prepared by a method similar to that described for [Ni(enpyim)Ni](PF$_6$)$_2$. After the solvent was removed from the reaction mixture, the residue was dissolved in acetonitrile (3 mL) and was filtered. The filtrate was evaporated to give red-brown oil. The oil was dissolved in methanol (2 mL) and was heated on a steambath. Water (15 mL) was added until turbidity appeared. After being heated for 2 h, the solution was allowed to cool slowly to 25 °C. A brick red solid was obtained. The solid was collected and washed with water, and ether and was dried under vacuum. Yield: 0.18 g (84%). μ_{298} (solution) = 3.74 μ_B. Anal. Calcd for C$_{40}$H$_{38}$N$_6$O$_4$P$_2$F$_{12}$Ni$_2$: C, 44.73; H, 3.57; N, 7.82. Found: C, 44.42; H, 3.59; N, 7.50.

[Cu(enpyim)Cu](PF$_6$)$_2$·1.5CH$_3$CN (17). To enpyimH$_2$ (0.60 mmol, 0.40 g) suspended in MeOH (12 mL) was added Et$_3$N (1.20 mmol, 167 μL) in one portion. The mixture was refluxed for 10 min, and then solid Cu(OAc)$_2$·H$_2$O (1.20 mmol, 0.24 g) was added to the ligand solution. A deep green solution formed, and the solution was heated on a steambath. After the solution was stirred for 1 h, a solution of NH$_4$PF$_6$ (2.40 mmol, 0.39 g) in methanol (2 mL) was added to precipitate the green product. After addition of water (5 mL), the mixture was allowed to cool to 25 °C and then the mixture was cooled to −10 °C for 3 h. The dark green solid was collected and was recrystallized from acetonitrile−ethanol. Large dark green crystals suitable for X-ray structure determination were collected. The crystals turned opaque within minutes, and they were dried to constant weight under high vacuum at 25 °C for 5 h prior to characterization. Yield: 0.42 g (61%). IR (Nujol): 2250 (C≡N). Anal. Calcd for C$_{40}$H$_{34}$N$_6$O$_4$P$_2$F$_{12}$Cu$_2$·1.5CH$_3$CN: C, 45.78; H, 3.40; N, 9.20. Found: C, 45.16; H, 3.56; N, 9.55.

[Cu(enpyam)Cu](PF$_6$)$_2$ (18). The ligand enpyamH$_2$ (1.0 mmol, 0.67 g) was dissolved in 20 mL of ethanol followed by addition of solid Cu(OAc)$_2$·H$_2$O (2.0 mmol, 0.41 g) to give a green solution. The solution turned turbid after stirring at 25 °C for 30 min. The mixture was heated for 10 min at ~70 °C followed by addition of Et$_3$N (2 mmol, 0.28 mL). After the mixture was refluxed and stirred for 30 min, NH$_4$PF$_6$ (8.0 mmol, 1.30 g) was added in one portion and the turbid solution was heated for 1 h. The mixture was cooled to 25 °C slowly and then to −10 °C. After 3 h, the solid was collected and washed with ethanol followed by ether. The product was obtained as a green crystalline solid after recrystallization from acetonitrile−ethanol. The solid was washed with ethanol, ether, and pentane. Yield: 0.59 g (52%). Anal. Calcd for C$_{40}$H$_{38}$N$_6$O$_4$P$_2$F$_{12}$Cu$_2$: C, 44.33; H, 3.53; N, 7.75. Found: C, 44.42; H, 3.53; N, 7.69.

[Cu(tnpyim)Cu](PF$_6$)$_2$ (19). [Cu(tnpyim)Cu](PF$_6$)$_2$ was prepared by a method similar to the one used for the preparation of [Cu(enpyam)-Cu](PF$_6$)$_2$. The crude salt was recrystallized from acetonitrile (5 mL)−ethanol (10 mL) to give green platelike crystals that were suitable for X-ray structure analysis. Yield: 1.03 g (94%). The crystals were dried to constant weight under high vacuum at 25 °C for 5 h prior to characterization. Anal. Calcd for C$_{41}$H$_{36}$N$_6$O$_4$P$_2$F$_{12}$Cu$_2$: C, 45.02; H, 3.32; N, 7.68. Found: C, 45.09; H, 3.33; N, 7.71.

[Cu(tnpyam)Cu](PF$_6$)$_2$·CH$_3$CN (20). The complex was prepared by the same method used for the preparation of [Cu(enpyam)Cu](PF$_6$)$_2$. The tnpyamH$_2$ (0.8 mmol, 0.55 g) was used. This yields a green copper complex, 0.36 g (41%). IR (Nujol): 2262 (C≡N). Anal. Calcd for C$_{41}$H$_{36}$N$_6$O$_4$P$_2$F$_{12}$Cu$_2$·CH$_3$CN: C, 45.11; H, 3.74; N, 8.14. Found: C, 45.27; H, 3.45; N, 7.71.

[(H$^+$)$_2$(enpyam)Mn](PF$_6$)$_2$·CH$_3$CN (21). The ligand enpyamH$_2$ (1.2 mmol, 0.80 g) and Mn(OAc)$_2$·H$_2$O (2.5 mmol, 0.61 g) were dissolved in deaerated EtOH (30 mL) under Ar to afford a yellow solution. The clear solution was stirred at 25 °C. After 30 min, the now cloudy solution was treated with deaerated Et$_3$N (4.8 mmol, 0.67 mL). After the mixture was heated at 70 °C for 30 min, NH$_4$PF$_6$ (14.4 mmol, 2.35 g) solution in deaerated water (100 mL) was added slowly under argon over 30 min to give a cloudy solution. After being heated for an additional 30 min on a water bath, the mixture was cooled slowly to 25 °C and then was cooled in an ice-bath. The pale yellow crystals were collected after 2 h and were washed with a mixture of 1:5 acetonitrile/diethyl ether solution (2 × 2 mL) followed by diethyl ether (2 × 5 mL) and were dried under vacuum. Yield: 1.01 g (84%). The crystals are somewhat stable in air in the solid state but an acetonitrile solution in air slowly turns red. IR (Nujol): 2266 (C≡N). Anal. Calcd for C$_{40}$H$_{40}$N$_6$O$_4$P$_2$F$_{12}$Mn·CH$_3$CN: C, 47.92; H, 4.12; N, 8.30; Mn, 5.22. Found: C, 47.14; H, 4.28; N, 8.30; Mn, 5.04.

[Mn^{IV}Cl$_2$(enpyam)]·2H$_2$O (22). To a yellow solution of [(H$^+$)$_2$-(enpyam)Mn^{II}](PF$_6$)$_2$ (0.37 mmol, 0.40 g) in dry acetonitrile was added LiCl (1.48 mmol, 63 mg) solution in methanol (1 mL). When exposed to air, the color changed to red-brown in seconds. A crystalline solid formed within hours. After the solution was stirred overnight in air, the solid was collected by filtration, washed with acetonitrile (2 mL), acetone (2 mL) and hexane (2 × 2 mL), and dried under vacuum. Yield: 0. 18 g (48%). The solid was recrystallized from DMF (10 mL) and MeOH (3 mL) mixture by vapor diffusion with diethyl ether. Long orange-brown needles were collected and washed with diethyl ether and dried under vacuum to give brown powder. Yield: 0. 13 g (35%). Crystals for X-ray structure analysis were kept in the mother liquor to prevent the loss of solvent of crystallization. $\Lambda_M = 136$ cm^2 Ω^{1-} mol^{-1} (1.0×10^{-3} M in MeOH). Anal. Calcd for C$_{40}$H$_{40}$N$_6$O$_4$MnCl$_2$·2H$_2$O: C, 58.12; H, 4.88; N, 10.17; Cl, 8.58. Found: C, 57.50; H, 4.77; N, 9.79; Cl, 8.78.

Crystallographic Structural Determination. Crystal data collection, and refinement parameters are given in Table 3. Suitable crystals for data collection were selected and mounted with epoxy cement on the tip of a fine glass fiber. All data were collected with a Siemens P4 diffractometer equipped with a SMART/CCD detector.

The systematic absences in the diffraction data of **19** are uniquely consistent with the reported space group. Space group assignments for **17** and **22** were based on *E*-statistics, which suggested centro-symmetric options, $P\bar{1}$ and $C2/c$ respectively, which yielded chemically reasonable and computationally stable results of refinement. All structures were solved using direct methods, completed by subsequent difference Fourier syntheses and refined by full-matrix least-squares procedures. Structure **17** cocrystallized with two molecules of acetonitrile. Structure **22** lies on a crystallographic 2-fold axis of rotation and cocrystallized with one molecule of diethyl ether which is disordered over two

Table 1. Physical Properties of Bimetallic Copper(II) and Nickel(II) Complexes

complex[a]	color	conductivity[b] ($cm^2\ \Omega^{-1}\ mol^{-1}$)	visible absorption[c] spectra $\lambda_{max,nm}$ (ϵ)	CV[d]			solid-state magnetic moment $\mu_{25°C}$ (BM)
				$E_{1/2}V$	ΔE (mV)	ip_c/ip_a	
$[Cu(enpyim)Cu]^{2+}$	green	264	580 (280)	−0.96	107	1.1	2.52
$[Cu(enpyam)Cu]^{2+}$	green	256	593 (220)	−0.36	195	2.4	2.44
$[Cu(CH_3CN)(tnpyim)Cu]^{2+}$	green	256	615 (200) 720 sh (∼108)	∼−0.2	irr		2.58
$[Cu(tnpyam)Cu]^{2+}$	green	277	607 (270)	−0.37	75	1.2	2.54
$[Ni(enpyim)Ni]^{2+}$	orange	223	560 (70)	−0.95	65	1.3	3.81
$[Ni(enpyam)Ni]^{2+}$	brick-red	257	494 (250)	−1.23	140	1.6	3.67

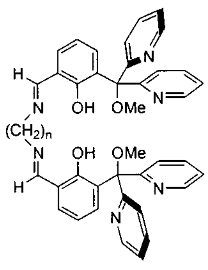
[a] All complexes were isolated as PF_6^- salts. The metal in the 4-coordinate site is written first. [b] All conductivities were measured in CH_3CN solutions at 10^{-3} M concentrations of the complex. [c] All absorption spectra were measured in CH_3CN solutions. ϵ in L $mol^{-1}cm^{-1}$. sh = shoulder. [d] Cyclic votammetry (CV) was conducted in CH_3CN solutions at 25 °C using a Pt electrode. Potentials are versus Ag/AgCl. Scan rate 100 mV/S. Supporting electrolyte $TBAPF_6$. irr = irreversible.

positions with an equal ratio. One molecule of water has also cocrystallized with **22** and resides within the outstretched arms of the enpyam ligand. The close proximity of this molecule of water to the oxygen atoms of the enpyam ligand (2.1−2.3A) suggests a strong hydrogen bonding network although no hydrogen atoms were located from the electron difference map. All non-hydrogen atoms were refined with anisotropic displacement coefficients. Hydrogen atoms were omitted from the cocrystallized solvent of **22** and the remaining hydrogen atoms were treated as idealized contributions.

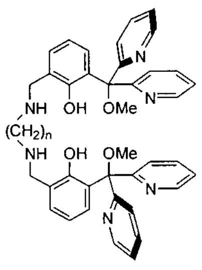
All software and sources of the scattering factors are contained in the SHELXTL (5.1) program library (Sheldrick, G. Siemens XRD, Madison, WI).

Results

1. Ligands and their Synthesis. The four ligands **11**, **12**, **13**, and **14** have 4- and 6-coordinate sites but, unlike **3** and **4**, are not macrocylic.



11: enpyimH_2 (n = 2)
12: tnpyimH_2 (n = 3)



13: enpyamH_2 (n = 2)
14: tnpyamH_2 (n = 3)

The ligands were expected to form bimetallic complexes bridged by two phenolate oxygen atoms. Although the ligands are rigid in some respects, they were not expected to exert the same conformational constraints as was observed for the macrocylic systems **3** and **4**. Molecular models suggested that the four ligands should accommodate two metals without obvious strain.

The ligand syntheses were accomplished with efficiency following conventional procedures (Scheme 1). Salicylaldehyde was acetylated in high yield to give **5**,[9] and the transformation **5** → **6** is a known procedure.[10] The phenol group of **6** was protected by phase-transfer catalysis to give **7**, which in turn was ortho-metalated using *n*-butyllithium in the presence of tetra-*N*,*N*′-methylethylenediamine. To obtain a high yield of the solid, **8**, inverse addition of the lithium salt to a solution of the bis(2-pyridyl) ketone was required. Methylation of the alcohol **8** gave **9**, which was deprotected to give the solid aldehyde **10**. Schiff base formation occurred readily to give the yellow crystalline solids **11** and **12**, and upon borohydride reduction, the white solids **13** and **14** were obtained.

2. Copper(II) and Nickel(II) Complexes. The dicopper(II) and dinickel(II) complexes were prepared by similar methods, where the metal acetate and/or the metal chloride in methanol solution were added to methanol solutions of the ligand in the presence of triethylamine. In most cases, the reaction solutions required heating to form the desired bimetallic complexes. It appears that sometimes not very soluble oligomers are formed. In most cases, the presumably thermodynamically stable bimetallic complexes are slow to form and require heating. All of the complexes were isolated as their PF_6^- salts, which are poorly soluble in protic solvents but are conveniently soluble in acetonitrile and dimethylformamide in which they are stable. Table 1 lists the physical properties of six of these complexes. All the complexes are 2:1 electrolytes[14] in CH_3CN solutions and their visible absorption spectra (400−700 nm) show weak d−d bands.

At energies above 400 nm, the spectra are dominated by intense ligand and metal−ligand charge-transfer bands. Cyclic votammetry gave quasi-reversible and irreversible waves for both the nickel and copper complexes. We list the quasi-reversible potentials in Table 1, although we include the irreversible wave for $[Cu(tnpyim)Cu]^{2+}$ to give an indication where the redox wave occurs. The other (irreversible) waves occur at more negative potentials compared to those listed. These data do not appear to provide a pattern which is readily explained. Table 2 lists redox couples of a series of analogous monometallic complexes. The potential of the Ni^{2+}/Ni^{+} couple of $[Ni(phen)_3]^{2+}$ (Table 2) is similar to that observed for $[Ni(enpyim)Ni]^{2+}$ and for $[Ni(enpyam)Ni]^{2+}$ (Table 1) and may suggest that the couples observed for these bimetallic complexes refer to reduction of the nickel (II) in the 6-coordinate site. Similarly, the redox couple observed for $[Cu(enpyim)Cu]^{2+}$ of −0.96 V is comparable to that observed for the [Cu(salen)] complex and may suggest that the couple observed for the bimetallic complex refers to the reduction of the copper(II) in the 4-coordinate site. The other three copper couples (Table 1) are similar in magnitude but are more positive. The fact that the [Cu(saltn)] complex shows a couple more positive than that of [Cu(salen)] is a pattern that obtains for the comparison between $[Cu(enpyim)Cu]^{2+}$ and $[Cu(tnpyim)Cu]^{2+}$. Whatever is the precise interpretation of the bimetallic redox couples, it is clear that their magnitude is subject to variation due to changes caused by the nature of the ligand and by the presence of the other metal. We noted in the Introduction that electrostatic, covalent, and conformational effects can perturb the redox couple of a metal in a particular site.

The room-temperature magnetic moments of the bimetallic copper(II) complexes are expected to have a spin-only value of

---

(14) Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81.

Scheme 1. Synthesis of the Ligands enpyimh$_2$, tnpyimh$_2$, enpyamh$_2$, and tnpyamh$_2$

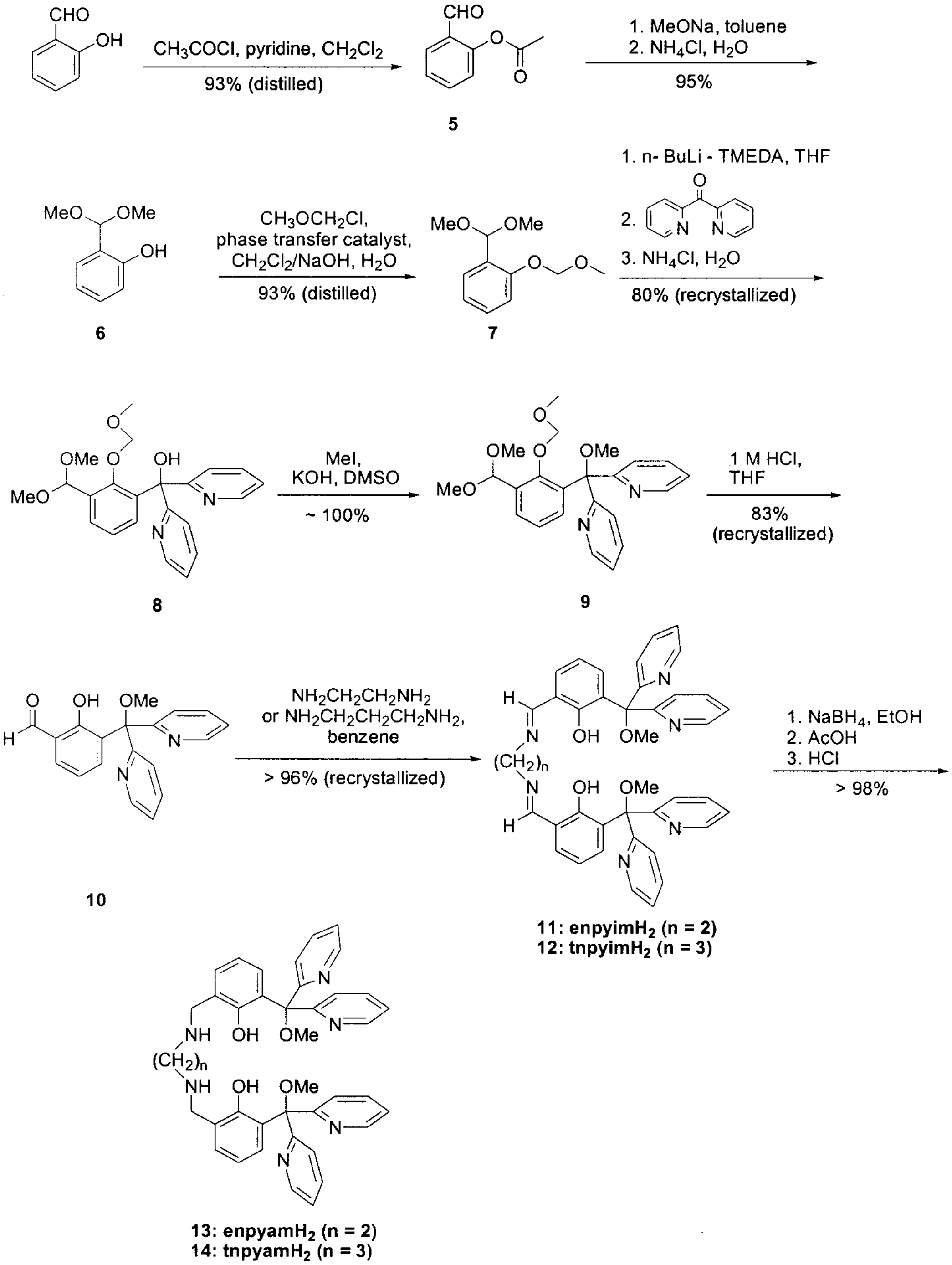


Table 2. Redox Couples for Monometallic Complexes Scaled to the Ag/AgCl Electrode

		redox potentials (solvent), V					
metal	couple	salen[a]	ref	saltn[a]	ref	tris-phen[a]	ref
Cu	Cu^{2+}/Cu^{+}	−1.14 (DMF) −1.13 (DMSO)	20 19	−0.97 (DMF)	20	0.00 (DMSO)	15
Ni	Ni^{3+}/Ni^{2+}	0.78 (DMSO)[b]	16	0.75 (DMSO)	16	+1.65 (CH_3CN)	17
	Ni^{2+}/Ni^{+}					−1.17 (DMSO)	15
Mn	Mn^{3+}/Mn^{2+}	−0.23 (DMSO)	18	−0.17 (DMSO)	22	1.34 (CH_3CN)	21

[a] salen = ethylenediamine-bis-salicylaldimine, saltn = trimethylenediamine-bis-salicylaldimine, and phen = *o*-phenanthroline. [b] Wave is irreversible; only the anodic half-wave was observed.

2.83μ_B. The values observed (Table 1) are less than this value, indicating weak antiferromagnetic coupling between the two centers. Were both of the nickel(II) ions in the two bimetallic complexes high spin, a spin-only value of 4.90μ_B ($S = 4/2$) would be expected. The values observed are intermediate between the $S = 2/2$ and $S = 4/2$ spin states. Given that the nickel(II) ions in the 6-coordinate site are expected to be paramagnetic ($S = 2/2$), the interpretation of the magnetic

Table 3. Crystallographic Data for $[Cu(CH_3CN)(tnpyim)Cu](PF_6)_2$ (**19**), $[Cu(enpyim)Cu](PF_6)_2{\cdot}2CH_3CN$ (**17**), and $[MnCl_2(enpyam)]{\cdot}H_2O{\cdot}Et_2O$ (**22**)

$[Cu(CH_3CN)(tnpyim)Cu](PF_6)_2$ (**19**)	
$C_{43}H_{39}Cu_2F_{12}N_7O_4P_2$	formula weight 1134.83
$a = 21.9346(3)$ Å	space group $P2_1/c$
$b = 8.85063(2)$ Å	$T = 173(2)$ K
$c = 24.7046(2)$ Å	$\lambda = 0.71073$ Å
$\alpha, \gamma -$	D(calc) = 1.572 g cm^{-3}
$\beta = 91.7382(4)°$	μ(Mo Kα) = 10.50 cm^{-1}
$V = 4793.83(8)$ Å^3	$R(F) = 6.13\%^a$
$Z = 4$, $Z\_ = 1$	$R(wF^2) = 11.37\%^a$
$[Cu(enpyim)Cu](PF_6)_2{\cdot}2CH_3CN$ (**17**)	
$C_{44}H_{40}Cu_2F_{12}N_8O_4P$	formula weight 1161.86
$a = 13.4631(3)$ Å	space group $P\bar{1}$
$b = 13.7955(2)$ Å	$T = 173(2)$ K
$c = 14.7086(4)$ Å	$\lambda = 0.71073$ Å
$\alpha = 97.3390(3)°$	D(calc) = 1.663 g cm^{-3}
$\beta = 106.5214(7)°$	μ(Mo Kα) = 10.88 cm^{-1}
$\gamma = 113.0535(8)°$	$R(F) = 4.76\%^a$
$V = 2319.66(11)$ Å^3	$R(wF^2) = 13.27\%^a$
$Z = 2$, $Z\_ = 1$	
$[MnCl_2(enpyam)]{\cdot}H_2O{\cdot}Et_2O$ (**22**)	
$C_{44}H_{52}Cl_2MnN_6O_6$	formula weight 886.76
$a = 17.7509(2)$ Å	space group $C2/c$
$b = 20.6898(4)$ Å	$T = 203(2)$ K
$c = 11.7860(2)$ Å	$\lambda = 0.71073$ Å
$\alpha, \gamma -$	D(calc) = 1.419 g cm^{-3}
$\beta = 106.5346(8)°$	μ(Mo Kα) = 5.04 cm^{-1}
$V = 4149.57(14)$ Å^3	$R(F) = 7.00\%^a$
$Z = 4$, $Z\_ = {}^1/_2$	$R(wF^2) = 19.86\%^a$

[a] Quantity minimized $= R(wF^2) = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[(wF_o^2)^2]^{1/2}$; $R = \Sigma\Delta/\Sigma(F_o)$, $\Delta = (F_o - F_c)$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [2F_c^2 + \max(F_o, 0)]/3$.

moments in Table 1 depends on whether the nickel(II) in the 4-coordinate site is in a S = 0 or S = 2/2 or some mixture of the two states. The [Ni(salen)] complex is diamagnetic[23] but, for example, bis-(*N*-methylsalicyladimine) nickel (II) shows partial paramagnetism because of complex association.[24] The [Ni(tetrahydrosalen)] complex is paramagnetic[25] because of complex association but an analogous complex bearing two *tert*-butyl groups is diamagnetic[26] ($\mu_{eff} = 0.35\ \mu_B$) because the *tert*-butyl groups prevent association. It could be argued that the magnetic moments observed for the $[Ni(enpyim)Ni]^{2+}$ are due to a contribution from a paramagnetically populated nickel(II) in the 4-coordinate site. Given that octahedral nickel(II) complexes can have μ_{eff} of up to 3.5 μ_B, presumably due to augmentation by temperature independent paramagnetism, and that, as just noted, diamagnetic 4-coordinate nickel(II) complexes can have temperature independent moments of 0.35 μ_B, the magnetic moments of the bimetallic complexes can be accounted for by assuming a 4-coordinate S = 0 site and a S = 2/2 6-coordinate site. The presence of a large contiguous 6-coordinate site is likely to prevent association of the 4-coordinate centers as has been observed previously.[26] These same magnetic moments are observed in CH_3CN solutions at the same temperature (25 °C).

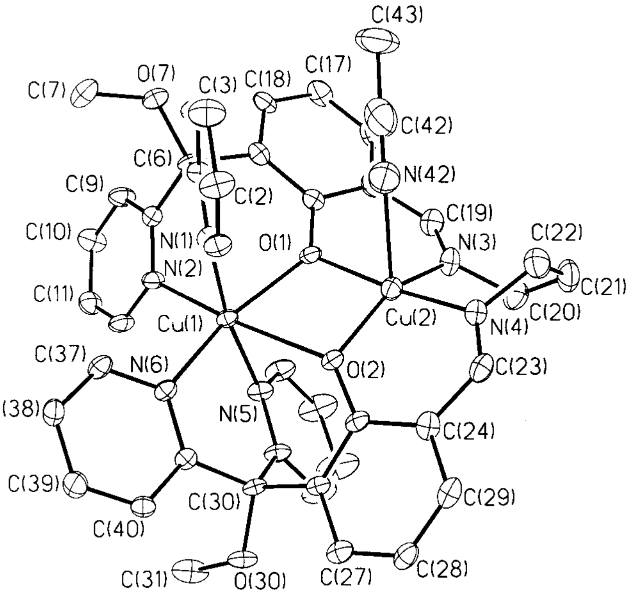


Figure 1. ORTEP diagram of $[Cu(CH_3CN)(tnpyim)Cu](PF_6)_2$ (**19**). Thermal ellipsoids at 30% probability and hydrogen atoms and counterions are omitted for clarity.

Table 4. Selected Bond Lengths and Angles for $[Cu(CH_3CN)(tnpyim)Cu](PF_6)_2$

Bond Lengths (Å)			
Cu(1)−N(1)	1.981(4)	Cu(1)−N(5)	1.987(5)
Cu(1)−N(6)	2.033(4)	Cu(1)−N(2)	2.120(4)
Cu(1)−O(1)	2.137(4)	Cu(1)−O(2)	2.418(4)
Cu(2)−O(2)	1.925(4)	Cu(2)−N(4)	1.951(5)
Cu(2)−N(3)	1.959(5)	Cu(2)−O(1)	1.970(3)
Cu(2)−N(42)	2.388(7)		
Angles (deg)			
N(1)−Cu(1)−N(5)	170.94(18)	N(1)−Cu(1)−N(6)	95.79(18)
N(5)−Cu(1)−N(6)	89.82(18)	N(1)−Cu(1)−N(2)	89.23(18)
N(5)−Cu(1)−N(2)	96.97(18)	N(6)−Cu(1)−N(2)	98.62(18)
N(1)−Cu(1)−O(1)	82.06(16)	N(5)−Cu(1)−O(1)	90.48(16)
N(6)−Cu(1)−O(1)	162.86(15)	N(2)−Cu(1)−O(1)	98.35(16)
N(1)−Cu(1)−O(2)	95.06(15)	N(5)−Cu(1)−O(2)	77.75(15)
N(6)−Cu(1)−O(2)	90.42(15)	N(2)−Cu(1)−O(2)	169.57(15)
O(1)−Cu(1)−O(2)	72.92(13)	O(2)−Cu(2)−N(4)	93.61(19)
O(2)−Cu(2)−N(3)	148.8(2)	N(4)−Cu(2)−N(3)	90.5(2)
O(2)−Cu(2)−O(1)	88.44(15)	N(4)−Cu(2)−O(1)	172.45(19)
N(3)−Cu(2)−O(1)	91.53(18)	O(2)−Cu(2)−N(42)	110.2(2)
N(4)−Cu(2)−N(42)	87.6(2)	N(3)−Cu(2)−N(42)	100.8(2)
O(1)−Cu(2)−N(42)	84.85(19)		

Copper(II) Crystal Structures. Crystallographic data is provided in Table 3 for $[Cu(CH_3CN)(tnpyim)Cu](PF_6)_2$ and $[Cu(enpyim)Cu](PF_6)_2{\cdot}2CH_3CN$. The structure of the complex $[Cu(CH_3CN)(tnpyim)Cu]^{2+}$ is shown in Figure 1, and selected bond lengths and angles are collected in Table 4. Overall, the structure is as expected. The copper ion in the ligand 4-coordinate site is in a distorted trigonal bipyramidal geometry with the acetonitrile ligand occupying the equatorial plane. Whereas the other copper(II) ion is 6-coordinate, the octahedral geometry is highly distorted as expected for a Jahn−Teller system. In particular, the Cu(1)−O(2) bond length of 2.418(4) Å is elongated compared to the other metal−ligand bond lengths of this copper site. The ligand−metal−ligand bond angles in the 6-coordinate site are generally larger than those normally

---

(15) Simpson, T. C.; Durand, R. R., Jr. *Electrochim. Acta* **1988**, *33*, 581.
(16) de Castro, B.; Freire, C.; Pereira, E. *J. Chem. Soc., Dalton Trans.* **1994**, 571.
(17) Brodovitch, J. C.; Haines, R. I.; McAuley, A. *Can. J. Chem.* **1981**, *59*, 1610.
(18) Coleman, W. M.; Boggess, R. K.; Hughes, J. W.; Taylor, L. T. *Inorg. Chem.* **1981**, *20*, 700.
(19) Nishida, Y.; Unoura, K.; Watanabe, I.; Yokomizo, T.; Kato, Y. *Inorg. Chim. Acta* **1991**, *181*, 141.
(20) Elder, R. C.; Blubaugh, E. A., Jr.; Heineman, W. R.; Burke, P. J.; McMillin, D. R. *Inorg. Chem.* **1983**, *22*, 2777.
(21) Richert, S. A.; Tsang, P. K. S.; Sawyer, D. T. *Inorg. Chem.* **1989**, *28*, 2471.
(22) Nishida, Y.; Takahashi, S.; Watanabe, I.; Yamazaki, A.; Itoh, H.; Sakamoto, M. *Polyhedron* **1994**, *13*, 1539.
(23) Singh, P. P.; Singh, N. B. *Polyhedron* **1990**, *9*, 557.
(24) Holm, R. H. *J. Am. Chem. Soc.* **1961**, *83*, 4683.
(25) O′Connor, M. J.; West, B. O. *Aust. J. Chem.* **1967**, *20*, 2077.
(26) Böttcher, A.; Elias, H.; Müller, L.; Paulus, H. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 623.

Table 5. Selected Bond Lengths and Angles for $[Cu(enpyim)Cu](PF_6)_2 \cdot 2CH_3CN$

Bond Lengths (Å)			
Cu(1)−N(5)	1.972(2)	Cu(1)−N(2)	1.970(2)
Cu(1)−N(1)	2.046(2)	Cu(1)−O(2)	2.1290(19)
Cu(1)−N(6)	2.296(3)	Cu(1)−O(1)	2.432(2)
Cu(2)−N(4)	1.941(2)	Cu(2)−O(1)	1.9457(19)
Cu(2)−N(3)	1.966(3)	Cu(2)−O(2)	2.013(2)
Angles (deg)			
N(5)−Cu(1)−N(2)	175.50(10)	N(5)−Cu(1)−N(1)	92.85(10)
N(2)−Cu(1)−N(1)	91.36(10)	N(5)−Cu(1)−O(2)	83.56(9)
N(2)−Cu(1)−O(2)	92.77(8)	N(1)−Cu(1)−O(2)	164.85(9)
N(5)−Cu(1)−N(6)	86.39(10)	N(2)−Cu(1)−N(6)	92.20(10)
N(1)−Cu(1)−N(6)	87.51(10)	O(2)−Cu(1)−N(6)	106.87(9)
N(5)−Cu(1)−O(1)	101.97(8)	N(2)−Cu(1)−O(1)	79.65(8)
N(1)−Cu(1)−O(1)	89.47(8)	O(2)−Cu(1)−O(1)	76.96(7)
N(6)−Cu(1)−O(1)	171.25(8)	N(4)−Cu(2)−O(1)	170.89(9)
N(4)−Cu(2)−N(3)	83.60(11)	O(1)−Cu(2)−N(3)	91.43(10)
N(4)−Cu(2)−O(2)	94.07(10)	O(1)−Cu(2)−O(2)	91.99(8)
N(3)−Cu(2)−O(2)	170.91(9)		

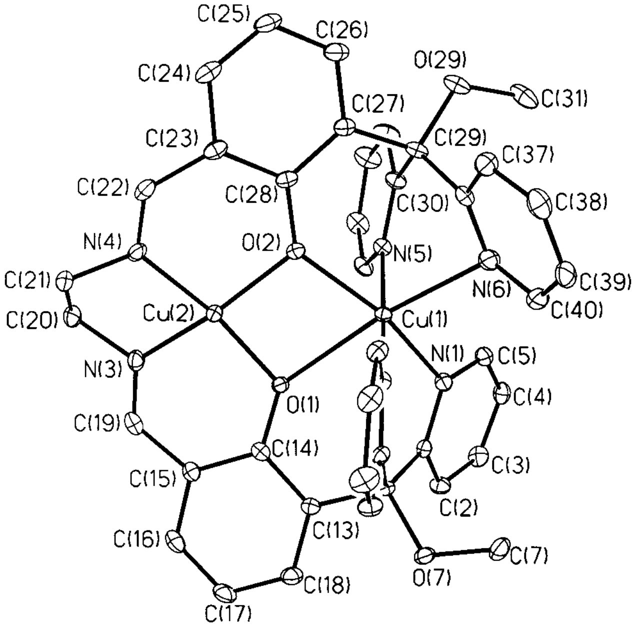


Figure 2. ORTEP diagram of $[Cu(enpyim)Cu][PF_6]_2$ (**17**)$\cdot 2CH_3CN$. Thermal ellipsoids at 30% probability and hydrogen atoms, counterions, and solvent molecules are omitted for clarity.

observed. Table 5 lists the selected corresponding parameters for the $[Cu(enpyim)Cu]^{2+}$ ion, the structure of which is shown in Figure 2. In this case, Cu(2) is four coordinate and the metal−ligand parameters for this site are unexceptional. The copper in the 6-coordinate site (Cu(1)) exerts a Jahn−Teller distortion where both the Cu(1)−O(1) and Cu(1)−N(6) bond lengths are elongated compared to the others. It is interesting that the bond elongation in both complexes should occur along the quasi-linear O−Cu−N bonds rather than along the quasi-linear N−Cu−N bonds which lie perpendicular to the mean molecular planes.

Manganese Complexes. It was found that bimetallic complexes of the four ligands were difficult to isolate in a pure form because the ligands tended to give oligomeric complexes. In attempting to prepare the dimanganese(II) complex of the enpyam ligand, a yellow monometallic complex of the formula, $[(H^+)_2(enpyam)Mn](PF_6)_2 \cdot CH_3CN$ was isolated. It has a solid-state magnetic moment of $\mu_{25°} = 5.80\ \mu_B$ (S = 5/2) and a conductivity of 286 $cm^2\ \Omega^{-1}\ mol^{-1}$ in CH_3CN solutions (2:1 electrolyte). A quasi-reversible cyclic voltammetry wave at +0.622 V (versus Ag/AgCl) in CH_3CN solutions is observed together with irreversible waves at −0.91 and −1.30 V. The site occupancy of the two protons has not been determined but our previous work on analogous monometallic-diproton manganese(II) complexes suggests that the protons are likely to be more stable in the 4-coordinate site[7b] with the metal in the 6-coordinate site. The monometallic complex is conveniently stable to aerial oxidation in the solid state but, when dissolved in CH_3CN solutions, and exposed to dioxygen, the solution slowly turns brown. If two equivalents of LiCl (in methanol) are added initially to such solutions, they are very rapidly oxidized by O_2 and deep red-brown needles of a complex having the formula, $[MnCl_2(enpyam)(H_2O)]$ are deposited. If, as we suggest, the Mn(II) ion is in the 6-coordinate site, it is likely that it is transferred to the 4-coordinate site prior to O_2 oxidation. In CH_3CN solutions this manganese(IV) compound is stable and the orange solution is a nonelectrolyte. It has an electronic absorption band in CH_3CN solution at 440 nm ($\epsilon = 2330$), which carries a shoulder at ~480 nm. There may be weak bands to lower energies but the poor solubility precluded their clear identification. In methanol the material dissolves to give a purple-blue solution and in dimethylformamide (DMF) a green solution is observed. In these solutions the compound is a 1:1 electrolyte, indicating the color changes are the result of Cl^- ion dissociation. Over time, both the methanol and DMF solutions slowly change color, suggesting that reduction of the metal may occur. In CH_3CN or CH_2Cl_2 solutions, the compound appears to be indefinitely stable. In CH_3CN solution cyclic voltammetry reveals a quasi-reversible wave at +0.07 V and an irreversible wave at +0.87 V versus Ag/AgCl.

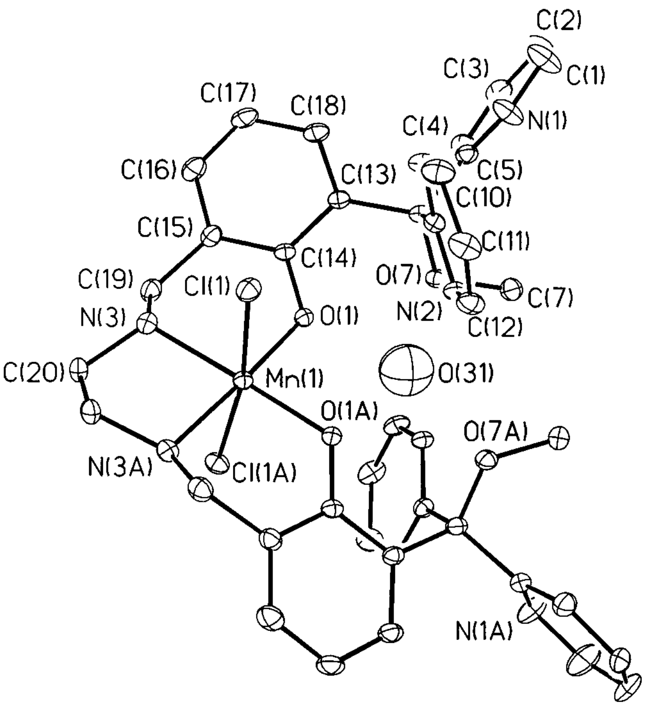


Figure 3. ORTEP diagram of $[MnCl_2(enpyam)]$ (**22**)$\cdot H_2O$, Et_2O. Thermal ellipsoids at 30% probability and hydrogen atoms and solvent ether are omitted for clarity.

Crystallographic data for the $[MnCl_2(enpyam)(H_2O)] \cdot OEt_2$ complex is given in Table 3. Figure 3 shows the crystal structure of the complex, and Table 6 lists selected bond-lengths and angles. The manganese(IV) is octahedrally coordinated in the 4-coordinate site of the ligand. The 6-coordinate site supports a water molecule, O(31). The O(31) atom is closest to N(2) and N(2A) at about 2.052 Å suggesting that hydrogen bonding occurs between the hydrogen atoms of the water molecule and

Table 6. Selected Bond Lengths and Angles for $[MnCl_2(enpyam)]\cdot H_2O\cdot Et_2O$[a]

Bond Lengths (Å)			
Mn(1)−O(1)	1.904(2)	Mn(1)−O(1)#1	1.904(2)
Mn(1)−N(3)	2.028(3)	Mn(1)−N(3)#1	2.028(3)
Mn(1)−Cl(1)	2.5924(9)	Mn(1)−Cl(1)#1	2.5924(9)

Angles (deg)			
O(1)−Mn(1)−O(1)#1	90.31(15)	O(1)−Mn(1)−N(3)	93.35(12)
O(1)#1−Mn(1)−N(3)	175.17(11)	O(1)−Mn(1)−N(3)#1	175.17(11)
O(1)#1−Mn(1)−N(3)#1	93.35(12)	N(3)−Mn(1)−N(3)#1	83.17(18)
O(1)−Mn(1)−Cl(1)	91.81(8)	O(1)#1−Mn(1)−Cl(1)	94.20(8)
N(3)−Mn(1)−Cl(1)	82.54(9)	N(3)#1−Mn(1)−Cl(1)	91.06(9)
O(1)−Mn(1)−Cl(1)#1	94.20(8)	O(1)#1−Mn(1)−Cl(1)#1	91.81(8)
N(3)−Mn(1)−Cl(1)#1	91.06(9)	N(3)#1−Mn(1)−Cl(1)#1	82.54(9)
Cl(1)−Mn(1)−Cl(1)#1	171.47(6)		

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x, y, -z + {}^1/_2$.

the two pyridine nitrogen atoms, N(2) and N(2A). The distance between O(31) and O(1), O(1A) is 2.118 Å and between O(31) and O(7), O(7A) is 2.317 Å.

Dioxygen oxidation of manganese(II) complexes to manganese(IV) is unusual but not unknown. Schiff base ligands formed from salicylaldehyde when coordinated to manganese(II) lead to O_2 oxidation to the manganese(IV) state.[27−30] Other dimeric Mn(IV)-Mn(IV) complexes have been prepared by H_2O_2 oxidation of the manganese(III) species.[31] Unlike these imine systems, the present amine system is expected to stabilize better the manganese(IV) state. Even so, as we have noted, the present complex is not stable in polar solvents where Cl^- ion dissociation occurs. In DMF/water, for example, the initial pale green solution fades over 20h to a colorless solution, suggesting reduction to manganese(II). The stability of the complex in CH_3CN or CH_2Cl_2 solutions indicates that the coordination of the two Cl^- ligands is necessary for prolonged stability.

Discussion

The four binucleating ligands **11−14**, were found to form bimetallic complexes of copper(II) and nickel(II). It was found that in all of these preparations presumably oligomeric complexes were formed first and only after an unusual time of heating did the complexes assemble to the desired products. Fortunately, the bimetallic complexes crystallized from the solvent mixtures used. In the cases of the manganese(II), iron(II) and -(III) and cobalt(II) only oligomeric complexes were isolated. Consequently, we were unable to investigate the one-site addition two-metal oxidation reactions with bimetallic complexes of these ligands. The tendency to form oligomers is perhaps surprising because it might be expected that a metal in the 4-coordinate site would predispose the ligand to accept a metal in the 6-coordinate site. It appears that in the cases where oligomers are formed, the metal is coordinated to the phenolic oxygen and the two neighboring pyridine ligands, allowing the system to oligomerize in a chain of bis-tridentate chelate complexes. Presumably the stability of the metal in quadridentate 4-coordinate site is not sufficient to force the formation of binucleating complexes in these cases. In the cases of copper(II) and nickel(II), it appears that the stability of the 4-coordinate site is sufficient to drive binuclear formation. Seven-membered chelate rings with little flexibility are formed in the 6-coordinate site and it may be that, in binuclear complexes, these factors may lead to instability at this site.

Acknowledgment. This work was supported by grants from PRF, the National Science Foundation, and the National Institutes of Health.

Supporting Information Available: X-ray crystallographic files in CIF format for the structure determinations of complexes **19**, **17**, and **22**. This material is available free of charge via the Internet at http://pubs.acs.org

IC0012625

---

(27) Tiraut, M.; Smith, T. O. *Inorg. Chim. Acta* **1986**, *121*, 5.

(28) Horwitz, C. P.; Ciringh, Y.; Liu, C.; Park, S. *Inorg. Chem.* **1993**, *32*, 5951.

(29) Rocha, C.; Nascimento, O. R.; Da Costa Ferreira, A. M. *J. Coord. Chem.* **1999**, *47* (3), 479.

(30) Coleman, W. M.; Taylor, L. T. *Coord. Chem. Rev.* **1980**, *32*, 1.

(31) (a) Baldwin, M. J.; Stemmler, T. L.; Riggs-Gelasco, P. J.; Kirk, M. L.; Penner-Hahn, J. E.; Pecoraro, V. L. *J. Am. Chem. Soc.* **1994**, *116*, 11349. (b) Baldwin, M. J.; Law, N. A.; Stemmler, T. L.; Kampf, T. W.; Penner-Hahn, J. E.; Pecoraro, V. L. *Inorg. Chem.* **1999**, *38*, 4801.