J. Am. Chem. Soc. **1990**, *112*, 6248–6254

Design, Synthesis, and Characterization of Bis(μ-oxo)dimanganese(III,III) Complexes. Steric and Electronic Control of Redox Potentials

Patricia A. Goodson,[1a] Aderemi R. Oki,[1a] Jørgen Glerup,[1b] and Derek J. Hodgson*,[1a]

Contribution from the Department of Chemistry, University of Wyoming, Laramie, Wyoming 82071-3838, and Chemistry Laboratory I, H. C. Ørsted Institute, Universitetsparken 5, DK-2100, Copenhagen Ø, Denmark. *Received January 25, 1990*

Abstract: The syntheses of three bis(μ-oxo)dimanganese(III,III) complexes and one bis(μ-oxo)dimanganese(III,IV) complex are described. The Mn(III/III) complexes are all of the general formulation $[(L)MnO]_2^{2+}$, where the ligands L are related to *N*,*N*′-bis(2-pyridylmethyl)-1,2-ethanediamine (bispicen, **1a**) and tris(2-pyridylmethyl)amine (tmpa, **2a**). The complex bis(μ-oxo)bis[*N*,*N*′-bis((6-methylpyrid-2-yl)methyl)ethane-1,2-diamine]dimanganese(III) perchlorate monohydrate, $[(\mathbf{1b})MnO]_2(ClO_4)_2\cdot H_2O$, $Mn_2C_{32}H_{46}Cl_2N_8O_{11}$ (**4**), crystallizes in the triclinic space group $P\bar{1}$ with two binuclear complexes in a cell of dimensions a = 8.487 (3) Å, b = 10.868 (2) Å, c = 20.816 (5) Å, α = 77.34 (2)°, β = 88.28 (2)°, and γ = 84.02 (2)°. The structure has been refined to a value of the conventional R factor of 0.0759 based on 2787 independent observations. The complex bis(μ-oxo)bis[*N*,*N*-bis((6-methylpyrid-2-yl)methyl)-*N*-2-pyridylmethylamine]dimanganese(III) nitrate hexahydrate, $[(\mathbf{2c})MnO]_2(NO_3)_2\cdot 6H_2O$, $Mn_2C_{40}H_{56}N_{10}O_{14}$ (**5**), crystallizes in the monoclinic space group $C2/c$ with four binuclear complexes in a cell of dimensions a = 22.122 (7) Å, b = 16.419 (6) Å, c = 14.461 (4) Å, β = 117.15 (2)°. The structure has been refined to an R factor of 0.0683 based on 1396 independent observations. The complex bis(μ-oxo)bis[*N*,*N*′-bis(2-methylpyrazyl)-ethane-1,2-diamine]dimanganese(III) perchlorate heptahydrate, $[(\mathbf{1d})MnO]_2(ClO_4)_2\cdot 7H_2O$, $Mn_2C_{24}H_{46}Cl_2N_{12}O_{17}$ (**7**), crystallizes in the monoclinic space group $C2$ with four binuclear complexes in a cell of dimensions a = 21.371 (5) Å, b = 9.301 (3) Å, c = 21.180 (7) Å, β = 108.54 (2)°. The structure has been refined to an R value of 0.0515 based on 3766 independent observations. The complexes are all found to contain the isomer in which the substituted pyridine (or the pyrazine) groups are trans axially disposed around the metal relative to the bridging oxo groups. Complexes **4** and **5** display very long axial Mn–N bonds which can be attributed to the presence of the 6-methyl groups on the pyridine rings, and this steric constraint has been demonstrated to be the cause of the stabilization of the Mn(III,III) form in these complexes. In complex **7**, the stabilization of the III/III form is an electronic consequence of the change from pyridine (pK_a = 5.20) to pyrazine (pK_a = 0.65). Cyclic voltammograms of **4** and **5** show that the two redox waves are shifted by approximately 0.4 V in the positive direction in each case relative to the "parent" bispicen and tmpa complexes. The fully oxidized form of complex **5** has been shown to act as a two-electron electrocatalytic oxidant, selectively oxidizing benzyl alcohol to benzaldehyde.

Interest in binuclear and polynuclear complexes of manganese in relatively high oxidation states stems largely from the involvement of such species in a wide variety of biological oxidative processes; the example most relevant to the present work is the water oxidizing enzyme in photosystem II (PSII).[2] The S_2 state in PSII exhibits a complex EPR spectrum,[3] and its X-ray absorption spectrum[4] is indicative of a short Mn···Mn separation of approximately 2.70 Å. These same physical properties are exhibited by the mixed-valent binuclear species $[(L)MnO_2Mn(L)]^{3+}$, several of which have recently been structurally characterized by single-crystal X-ray diffraction techniques.[5-13]

Our own interest in complexes of this general type stems from their potential use as redox catalysts. Since most organic oxidations involve the cleavage of either a C–H or O–H bond, it is important that any catalytic oxidation system provide a site for proton transfer. Naturally, metal complexes containing either terminal or bridging oxo groups can serve this function. Mononuclear oxo complexes of transition metals, such as RuO_4, are often used in organic chemistry as general purpose oxidants, but these complexes are relatively unselective.[14] Moreover, there is very little opportunity to use them catalytically, since the primary oxidants that must be used to recycle them to their oxidized forms are so strong that they frequently influence the reaction themselves.[15] Consequently, many workers have recently investigated the electrocatalytic activity of mononuclear[16] and binuclear[17] transition-metal species, particularly involving the chemistry of ruthenium and osmium in which the systems make use of the abundant array of oxidation states available to these metals in aqueous medium. Thus, polypyridyl oxo complexes of ruthenium have been shown to electrocatalytically oxidize alcohols, phenols, aldehydes, cyclic ketones, and even certain C–H bonds, and oxo

---

(1) (a) Univeristy of Wyoming. (b) H. C. Ørsted Institute.

(2) (a) For a review, see: Babcock, G. T. *New Comprehensive Biochemistry: Photosynthesis*; Amesz, J., Ed.; Elsevier: New York, 1987; pp 125–158. (b) Brudvig, G. W.; Crabtree, R. H. *Proc. Natl. Acad. Sci. U.S.A.* **1986**, *83*, 4586–4588. (c) Beck, W. F.; Brudvig, G. W. *J. Am. Chem. Soc.* **1988**, *110*, 1517–1523, and references therein. (d) Dismukes, G. C. *Photochem. Photobiol.* **1986**, *43*, 99–115.

(3) Dismukes, G. C.; Siderer, Y. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 274–278.

(4) Kirby, J. A.; Robertson, A. S.; Smith, J. P.; Thompson, A. C.; Cooper, S. R.; Klein, M. P. *J. Am. Chem. Soc.* **1981**, *103*, 5529–5537.

(5) Plaskin, P. M.; Stoufer, R. C.; Mathew, M.; Palenik, G. J. *J. Am. Chem. Soc.* **1972**, *94*, 2121–2122.

(6) Stebler, M.; Ludi, A.; Bürgi, H. B. *Inorg. Chem.* **1986**, *25*, 4743–4750.

(7) Collins, M. A.; Hodgson, D. J.; Michelsen, K.; Pedersen, E. *J. Chem. Soc., Chem. Commun.* **1987**, 1659–1660.

(8) Towle, D. K.; Botsford, C. A.; Hodgson, D. J. *Inorg. Chim. Acta* **1988**, *141*, 167–168.

(9) Hagen, K. S.; Armstrong, W. H.; Hope, H. *Inorg. Chem.* **1988**, *141*, 167–168.

(10) Brewer, K. J.; Liegeois, A.; Otvos, J. W.; Calvin, M.; Spreer, L. O. *J. Chem. Soc., Chem. Commun.* **1988**, 1219–1220.

(11) Suzuki, M.; Senda, H.; Kobayashi, Y.; Oshio, H.; Uehara, A. *Chem. Lett.* **1988**, 1763–1766.

(12) (a) Goodson, P. A.; Hodgson, D. J.; Michelsen, K. *Inorg. Chim. Acta.* In press. (b) Goodson, P. A.; Oki, A. R.; Lynn, M. H.; Hodgson, D. J.; Michelsen, K.; Pedersen, E. Presented at the 197th National Meeting of the American Chemical Society, Dallas, Tx, April 1989; Paper INOR-415.

(13) (a) Spreer, L. O. Private communication. Brewer, K. J.; Calvin, M.; Lumpkin, R. S.; Otvos, J. W.; Spreer, L. O. *Inorg. Chem.* **1989**, *28*, 4446–4451. (b) Brewer, K. J.; Spreer, L. O.; Liegeois, A.; Otvos, J. W.; Calvin, M. Presented at the 196th National Meeting of the American Chemical Society, Los Angeles, CA, September 1988; Paper INOR-449.

(14) Lee, G.; van der Engh, M. *Oxidation in Organic Chemistry*; Trahanovsky, W., Ed.; Academic Press: London, 1973; Vol. 5B.

(15) Moyer, B. A.; Thompson, M. S.; Meyer, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 2310–2312.

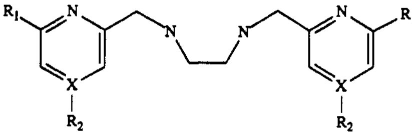
(16) Seok. W. K.; Meyer, T. J. *J. Am. Chem. Soc.* **1988**, *110*, 7358–7367, and references therein.

(17) (a) Gilbert, J. A.; Eggleston, D. S.; Murphy, W. R., Jr.; Geselowitz, D. A.; Gersten, S. W.; Hodgson, D. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 3855–3864. (b) Rotzinger, F. P.; Munavalli, S.; Conte, P.; Hurst, J. K.; Gratzel, M.; Pern, F. J.; Frank, A. J. *J. Am. Chem. Soc.* **1987**, *109*, 6619–6626. (c) Dobson, J. C.; Sullivan, B. P.; Doppelt, P.; Meyer, T. J. *Inorg. Chem.* **1988**, *27*, 3863–3866.

0002-7863/90/1512-6248$02.50/0

complexes of ruthenium(VI) and -(VII) have been shown to act as selective oxidants.[18] Evidence for the possible application of bis(μ-oxo)dimanganese complexes as redox catalysts derives from the preliminary observations of Gref et al.[19] who have electrochemically oxidized alcohols and ethers in the presence of both the bpy and phen complexes and by those of Ramaraj et al.[20] who have shown that the bpy complex oxidizes water in the presence of a chemical oxidant such as cerium(IV) ion.

In view of this apparent utility we are pursuing a comprehensive program designed to synthesize bis(μ-oxo)dimanganese complexes, in the expectation of producing useful catalytic complexes. One goal of our research is to obtain a variety of complexes with a diverse range of redox potentials, so that we can "fine-tune" the potentials for any particular application; our approach here is to chemically modify the ligands so as to bring about desired stereochemical and/or electronic changes at the metal centers. In order to prevent ligand substitution reactions during the presumed catalytic cycles, we have focused our attention on complexes formed with tetradentate ligands. We have provided accounts of the synthesis of the mixed-valent manganese(III,IV) species formed from the ligands *N*,*N'*-bis(2-pyridylmethyl)-1,2-ethanediamine (bispicen, **1a**)[7] and tris(2-pyridylmethyl)amine (tmpa, **2a**),[8] and Suzuki et al. have subsequently described the oxidized manganese(IV,IV) form of the latter complex.[21] As was noted above, other workers have structurally characterized the mixed-valent forms of the bpy[5] and phen[6] complexes, and following our work the tris(2-aminoethyl)amine (tren),[9] 1,4,7,10-tetraazacyclododecane (cyclen),[10] and *N*,*N*-bis(2-pyridylmethyl)glycinato[11] complexes were reported. Very recently, both we[12] and Calvin and co-workers[13] have characterized salts of the 1,4,8,11-tetraazacyclotetradecane (cyclam) complex. In addition, five Mn(IV,IV) forms have been structurally characterized; these are the phen,[6] 1,4,7-triazacyclononane,[22] and picolinate[23] complexes reported by other workers and our own reports of the complexes of bispicen (**1a**)[24] and the tmpa analogue (**2b**).[25]

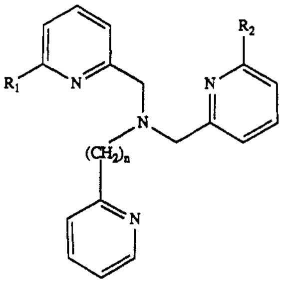


1a: $R_1 = R_2 = H$; X = C [bispicen]

1b: $R_1 = CH_3$; $R_2 = H$; X = C

1c: $R_1 = H$; $R_2 = CH_3$; X = C

1d: $R_1 = H$; X = N



2a: $R_1 = R_2 = H$; n = 1 [tmpa]

2b: $R_1 = CH_3$; $R_2 = H$; n = 2

2c: $R_1 = R_2 = CH_3$; n = 1

We have now turned our focus on the synthesis of complexes which are stable as the Mn(III,III) form. The value of these stabilized III/III complexes lies in their ability to be transformed into IV/IV complexes with very high IV/IV ↔ III/IV reduction potentials. Complexes with higher potentials for the Mn(III/IV) ↔ Mn(IV,IV) redox couple would be of greater use as oxidation catalysts.[26,27] Here we provide full details of the synthesis and characterization of three bis(μ-oxo)dimanganese(III,III) complexes, with ligands related to **1** and **2**, and propose a general methodology for the design of such complexes by the steric and/or electronic modification of the ligands. A brief preliminary description of one of these complexes has previously been reported.[28]

Experimental Section

Ligand Syntheses. *N*,*N'*-Bis((6-methylpyrid-2-yl)methyl)ethane-1,2-diamine (1b). The ligand was prepared as described previously.[28]

***N*,*N*-Bis((6-methylpyrid-2-yl)methyl)-*N*-2-pyridylmethylamine (2c).** A solution of 11.28 g (0.08 mol) of 2-(chloromethyl)-6-methylpyridine[29] in 10 mL of ethanol was added to 0.04 mol of 2-(2-aminomethyl)pyridine in 10 mL water and stirred at 50 °C for 24 h; during that time drops of a concentrated aqueous solution of Na_2CO_3 were added at intervals to maintain the pH between 8 and 9. The resulting solution was extracted with $CHCl_3$ and dried over Na_2SO_4. The solvent was evaporated under reduced pressure to give 8.1 g (63%) of a red-brown solid: ^1H NMR (270 MHz, $CDCl_3$) δ 8.52–6.9 (Ar multiplet, 10 H), 3.88 (s, 2 H), 3.85 (s, 4 H), 2.52 (s, 6 H).

CAUTION! Trimethylsilyl cyanide reacts with water to yield HCN. All reactions involving trimethylsilyl cyanide should be performed in an adequate hood.

2-Cyano-4-methylpyridine. The compound was prepared by the general methodology of Fife[30] for the synthesis of 2-cyanopyridines. To a solution of 2.00 g (18.0 mmol) of 4-picoline-*N*-oxide in 36 mL of dichloromethane under N_2 was added 2.65 mL (19.8 mmol) of trimethylsilyl cyanide. After stirring for 5 min, 1.66 mL (18.0 mmol) of dimethylcarbamyl chloride was slowly added. After stirring for 24 h at ambient temperature, a solution of 4.0 g of Na_2CO_3 in 40 mL of H_2O was slowly added, and the mixture was stirred for 15 min. The organic layer was separated and combined with CH_2Cl_2 extracts of the aqueous layer. The CH_2Cl_2 solution was dried over Na_2SO_4 and concentrated under reduced pressure to a solid. Recrystallization from hexane gave 1.6 g (75%) of 2-cyano-4-methylpyridine as a white solid: ^1H NMR (270 MHz, $CDCl_3$) δ 8.58 (d, *J* = 5.13 Hz, 1 H), 7.53 (s, 1 H), 7.34 (d, *J* = 5.13 Hz, 1 H), 2.44 (s, 3 H).

4-Methylpyridine-2-carboxaldehyde. To a solution of 3.29 g (27.6 mmol) of 2-cyano-4-methylpyridine in 164 mL of dry CH_2Cl_2 cooled to −78 °C under N_2 was added dropwise 27.6 mL (27.6 mmol) of a 1 M solution of DIBAL in CH_2Cl_2 at such a rate that the temperature remained below −65 °C. The resulting solution was stirred for 2 h at −78 °C, and then the reaction was quenched by the dropwise addition of a solution of 13 mL of concentrated HCl in 52 mL of water. After warming to ambient temperature, the CH_2Cl_2 fraction was separated. Solid $NaHCO_3$ was added with stirring to the aqueous phase until an emulsion had formed. The emulsion was extracted several times with Et_2O. The Et_2O extracts were dried over Na_2SO_4 and concentrated under reduced pressure to 1.39 g (41%) of a yellow oil: ^1H NMR (270 MHz, $CDCl_3$) δ 10.07 (s, 1 H), 8.65 (d, *J* = 4.95 Hz, 1 H), 7.79 (s, 1 H), 7.35 (d, *J* = 4.95 Hz, 1 H), 2.46 (s, 3 H).

***N*,*N'*-Bis((4-methylpyrid-2-yl)methyl)ethane-1,2-diamine (1c).** To a solution of 1.73 g (14.0 mmol) of 4-methylpyridine-2-carboxaldehyde in 10 mL of EtOH was added 0.425 g (7.06 mmol) of ethylenediamine. The solution was heated to reflux for 10 min and then stirred at ambient temperature for 16 h. The solution was dried over Na_2SO_4 and then diluted with 10 mL of EtOH. To this solution was added 0.64 g (16.8 mmol) of $NaBH_4$, and the resulting mixture was stirred for 16 h at ambient temperature. The reaction was quenched by the dropwise addition of concentrated HCl (with ice bath cooling) until the pH reached 4.5. The mixture was filtered, and the filtrate was acidified further with

---

[18] Green, G.; Griffith, W. P.; Hollinshead, D. M.; Levy, S. V.; Schröder, M. *J. Chem. Soc., Perkin Trans. I* **1984**, 681–686.

[19] Gref, A.; Balavoine, G.; Riviere, H.; Andrieux, C. P. *Nouv. J. Chim.* **1984**, *8*, 615–618.

[20] Ramaraj, R.; Kira, A.; Kaneko, M. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 825–827.

[21] Suzuki, M.; Tokura, S.; Suhara, M.; Uehara, A. *Chem. Lett.* **1988**, 477–480.

[22] Wieghardt, K.; Bossek, U.; Nuber, B.; Weiss, J.; Bonvoisin, J.; Corbella, M.; Vitols, S. E.; Girerd, J. J. *J. Am. Chem. Soc.* **1988**, *110*, 7398–7411.

[23] Libby, E.; Webb, R. J.; Streib, W. E.; Folting, K.; Huffman, J. C.; Hendrickson, D. N.; Christou, G. *Inorg. Chem.* **1989**, *28*, 4037–4040.

[24] Goodson, P. A.; Glerup, J.; Hodgson, D. J.; Michelsen, K.; Pedersen, E. *Inorg. Chem.* **1990**, *29*, 503–508.

[25] Oki, A. R.; Glerup, J.; Hodgson, D. J. *Inorg. Chem.* In press.

[26] Chan, M. K.; Armstrong, W. H. *Inorg. Chem.* **1989**, *28*, 3777–3779.

[27] Chan, M. K.; Armstrong, W. H. *J. Am. Chem. Soc.* **1989**, *111*, 9121–9122.

[28] Goodson, P. A.; Hodgson, D. J. *Inorg. Chem.* **1989**, *28*, 3606–3608.

[29] Matsumura, F. *J. Chem. Soc. Jpn.* **1953**, *74*, 363–365.

[30] Fife, W. K. *J. Org. Chem.* **1983**, *48*, 1375–1377.

HCl until the pH reached 1.0. The white precipitate was collected by filtration and then dissolved in water. The aqueous solution was made very basic by the addition of 30% NaOH and extracted with toluene. The toluene extracts were dried over Na_2SO_4 and concentrated to 0.31 g of a pale yellow oil. Additional product was obtained by concentrating the acidic EtOH filtrate under reduced pressure, dissolving the residue in water, and treating the aqueous solution as described above to give a combined yield of 0.61 g (31%): ^1H NMR (270 MHz, $CDCl_3$) δ 8.39 (d, J = 4.76 Hz, 1 H), 7.14 (s, 1 H), 6.97 (d, J = 4.76 Hz, 1 H), 3.87 (s, 2 H), 2.82 (s, 2 H), 2.33 (s, 2 H), 1.95 (s, 1 H).

Methyl Pyrazinoate. To a mixture of 100 g (0.806 mol) of 2-pyrazinecarboxylic acid in 800 mL of anhydrous MeOH was added 1 drop of concentrated H_2SO_4. The mixture was heated to reflux for 48 h. After cooling to ambient temperature, solid $NaHCO_3$ was added, and the mixture was stirred for 16 h. After drying over Na_2SO_4, the mixture was filtered, and the filtrate was concentrated under reduced pressure. The residue was sublimed (100 °C, 12 mm) to give 105.5 g (95%) of methyl pyrazinoate as a white solid: ^1H NMR (270 MHz, $CDCl_3$) δ 9.34 (s, 1 H), 8.79 (d, J = 2.20 Hz, 1 H), 8.74 (d, J = 2.20 Hz, 1 H), 4.06 (s, 3 H).

Pyrazine-2-carboxaldehyde. This compound was prepared by a modification of the procedure of Rutner and Spoerri,[31] by using as reductant a solution of DIBAL in CH_2Cl_2 rather than LAH in THF as used by those workers: yield, 26% of a light yellow oil after distillation; ^1H NMR (270 MHz, $CDCl_3$) δ 10.17 (s, 1 H), 9.19 (s, 1 H), 8.83 (d, J = 2.02 Hz, 1 H), 8.78 (d, J = 2.02 Hz, 1 H).

***N*,*N'*-Bis(2-methylpyrazyl)ethane-1,2-diamine (1d).** To a solution of 2.06 g (19.5 mmol) of pyrazine-2-carboxaldehyde in 8 mL of EtOH was added 0.573 g (9.53 mmol) of ethylenediamine. A white solid formed within 2 min. After stirring for 16 h at ambient temperature, the mixture was diluted with 18 mL of EtOH before the addition of 0.89 g (23.4 mmol) of $NaBH_4$. The thick mixture was stirred at ambient temperature for 16 h. The reaction was quenched by the dropwise addition of concentrated HCl (with ice bath cooling) until the pH reached 5.0. The white precipitate was collected by filtration and dissolved in water. The resulting aqueous solution was made basic by the addition of 30% KOH and extracted several times with CH_2Cl_2. The CH_2Cl_2 extracts were dried over Na_2SO_4 and concentrated under reduced pressure to 1.09 g (47%) of a yellow oil: ^1H NMR (270 MHz, $CDCl_3$) δ 8.63 (s, 1 H), 8.53 (d, J = 2.19 Hz, 1 H), 8.47 (d, J = 2.19 Hz, 1 H), 3.98 (s, 2 H), 2.84 (s, 2 H), 2.03 (s, 1 H).

Complex Syntheses. Bis(μ-oxo)bis[*N*,*N'*-bis((6-methylpyrid-2-yl)methyl)ethane-1,2-diamine]dimanganese(III) Perchlorate Monohydrate, $[(\mathbf{1b})MnO]_2(ClO_4)_2\cdot H_2O$ (4). The complex was prepared as described previously.[28]

Bis(μ-oxo)bis[*N*,*N*-bis((6-methylpyrid-2-yl)methyl)-*N*-2-pyridylmethylamine]dimanganese(III) Nitrate Hexahydrate, $[(\mathbf{2c})MnO]_2(NO_3)_2\cdot 6H_2O$ (5). A solution of 0.4 g (1.3 mmol) of **2c** in 10 mL of acetonitrile was added to a solution of 0.37 g (1.3 mmol) of manganese(II) nitrate hexahydrate in 10 mL of water, and the resulting mixture was stirred for 10 min. Addition of a few drops of 30% H_2O_2 turned the red solution to a dark green color. The solution was allowed to stand at ambient temperature for several days, whereupon 0.48 g (76%) of brown crystals of **5** suitable for X-ray diffraction crystallized from the solution. Anal. Calcd for $Mn_2C_{40}H_{56}N_{10}O_{14}$: C, 47.53; H, 5.58; N, 13.86. Found:[32] C, 46.96; H, 4.97; N, 14.60.

Bis(μ-oxo)bis[*N*,*N*-bis((6-methylpyrid-2-yl)methyl)-*N*-2-pyridylmethylamine]dimanganese(III) Perchlorate, $[(\mathbf{2c})MnO]_2(ClO_4)_2$ (5a). The complex was synthesized as above, starting with manganese(II) perchlorate hexahydrate in place of the nitrate salt. The yield was 0.51 g (81%) of a brown powder of **5a**. Anal. Calcd for $Mn_2C_{40}H_{44}N_8Cl_2O_{10}$: C, 49.18; H, 4.51; N, 11.47; Cl, 7.17. Found:[32] C, 49.12; H, 4.53; N, 11.46; Cl, 7.19.

Bis(μ-oxo)bis[*N*,*N'*-bis((4-methylpyrid-2-yl)methyl)ethane-1,2-diamine]dimanganese(III,IV) Perchlorate $[(\mathbf{1c})MnO]_2(ClO_4)_3$ (6). To a solution of 0.147 g (0.544 mmol) of **1c** in 7.5 mL of water was added 0.104 g (0.528 mmol) of manganese(II) chloride tetrahydrate. After 5 min, a few drops of 30% H_2O_2 were added, turning the solution dark olive green. The solution was filtered after 5 min, and a solution of 0.53 g of sodium perchlorate in 1 mL of water was added to the filtrate. The solution was decanted from the sticky tar that formed and was cooled to 0 °C for 45 min. The olive green solid which formed was collected by filtration and washed with cold water yielding 0.057 g (22%) of **6**. Anal. Calcd for $Mn_2C_{32}H_{44}N_8Cl_3O_{14}$: C, 39.18; H, 4.52; N, 11.42; Cl, 10.84. Found:[32] C, 39.91; H, 4.68; N, 11.30; Cl, 10.65.

Bis(μ-oxo)bis[*N*,*N'*-bis(2-methylpyrazyl)ethane-1,2-diamine]dimanganese(III) Perchlorate Heptahydrate, $[(\mathbf{1d})MnO]_2(ClO_4)_2\cdot 7H_2O$ (7). To a solution of 0.277 g (1.14 mmol) of **1d** in 3 mL of water was added 0.411 g (1.14 mmol) of manganese(II) perchlorate hexahydrate. After 5 min, four drops (about 100 mg) of 30% H_2O_2 were added. The solution turned dark and was cooled to 0 °C to precipitate 0.233 g of dark and light olive green solids. A portion of this mixture was recrystallized by dissolving it in warm water, removing the insolubles by filtration, and cooling the filtrate overnight in the refrigerator (5 °C). The major product from this recrystallization is a pale yellow complex which we have identified by X-ray diffraction techniques as the monomeric complex $[(\mathbf{1d})Mn(OH_2)_2](ClO_4)_2$. In addition to this complex, however, a small quantity of dark orange crystals of **7** crystallized out of the pale green solution. The yield (less than 5%) was not calculated because in the absence of the mother liquor the complex readily decomposes. This also prevented chemical analysis, but the identity of the complex was determined by X-ray diffraction techniques (vide infra).

Electrochemistry. Cyclic voltammograms were recorded in acetonitrile on a BAS 100A electrochemical analyzer by using a glassy carbon or platinum working electrode, a platinum wire auxiliary electrode, and a silver/silver chloride reference electrode. Solutions were approximately 1–2 mM, with 0.1 M tetraethylammonium perchlorate as supporting electrolyte. Bulk electrolyses were performed on a PAR Model 273 potentiostat/galvanostat at a fixed potential of 1.7 V vs Ag/AgCl. Preliminary electrocatalytic studies were carried out by using benzyl alcohol as the organic substrate and 2,6-lutidine as the base. Typical working conditions were 0.024 g of catalyst, 0.1 mL of substrate, 0.1 mL of base, and 0.44 g of tetraethylammonium perchlorate in 20 mL of acetonitrile in a compartment containing a working platinum electrode and a Ag/AgCl reference electrode and a separate compartment containing a platinum wire auxiliary electrode and 0.22 g of tetraethylammonium perchlorate in 10 mL of acetonitrile. The two compartments were separated by a glass frit. Samples (1 mL) were taken at intervals for electronic spectroscopy and GC analysis, with chlorobenzene employed as internal standard for the GC analyses. Completion of the bulk electrolysis was assumed when the final current was less than 5% of the initial current, at which point the solution had changed color from brown to dark green.

Magnetic Susceptibility. Magnetic susceptibility measurements were performed by the Faraday technique as described previously.[24] The molar susceptibilities were corrected for ligand diamagnetism by using Pascal's constants.

X-ray Structure Determination. The structures of the Mn(III/III) complexes **4** and **7** were determined at −100 °C [173 K], and the structure of the Mn(III/III) complex **5** was determined at room temperature [22 °C] on a Nicolet R3m/V diffractometer equipped with a molybdenum tube ($\lambda K\alpha_1$ = 0.70926 Å; $\lambda K\alpha_2$ = 0.71354 Å) and a graphite monochromator. Crystal data and experimental parameters are tabulated in Table I. The data were corrected for Lorentz-polarization effects. The structures were solved by Patterson and difference Fourier methods and refined by least-squares techniques; the programs used were from the SHELXTL system.

Bis(μ-oxo)bis[*N*,*N'*-bis((6-methylpyrid-2-yl)methyl)ethane-1,2-diamine]dimanganese(III) Perchlorate Monohydrate, $[(\mathbf{1b})MnO]_2(ClO_4)_2\cdot H_2O$ (4). The complex crystallizes in the centrosymmetric triclinic space group $P\bar{1}$ with two binuclear cations in the unit cell. All hydrogen atoms were placed in fixed calculated positions (C–H = 0.96 Å), while other atoms were refined anisotropically. The final values of the conventional R factors were R = 0.0759, wR = 0.0907, based on 2787 independent data with $I > 3\sigma(I)$. The atomic positional parameters, hydrogen atom parameters, anisotropic thermal motion parameters, and observed and calculated structure amplitudes for all three structures are available as supplementary material.

Bis(μ-oxo)bis[*N*,*N*-bis((6-methylpyrid-2-yl)methyl)-*N*-2-pyridylmethylamine]dimanganese(III) Nitrate Hexahydrate, $[(\mathbf{2c})MnO]_2(NO_3)_2\cdot 6H_2O$ (5). The complex crystallizes in the centrosymmetric monoclinic space group $C2/c$ with four binuclear cations in the unit cell. All hydrogen atoms were placed in fixed calculated positions (C–H = 0.96 Å), while other atoms were refined anisotropically. The final values of the conventional R factors were R = 0.0683, wR = 0.0901, based on 2906 independent data with $I > 3\sigma(I)$.

Bis(μ-oxo)bis[*N*,*N'*-bis(2-methylpyrazyl)ethane-1,2-diamine]dimanganese(III) Perchlorate Heptahydrate, $[(\mathbf{1d})MnO]_2(ClO_4)_2\cdot 7H_2O$ (7). The complex crystallizes in the noncentrosymmetric monoclinic space group $C2$ with four binuclear cations in the unit cell. The crystals are unstable out of an aqueous solution, presumably because of a tendency to lose some of the lattice water molecules. Consequently, the crystals were frozen immediately upon removal from solution and maintained at −100 °C at all times. All hydrogen atoms were placed in fixed calculated positions (C–H = 0.96 Å), while other atoms were refined anisotropically. The final values of the conventional R factors were R = 0.0515, wR = 0.0728, based on 3766 independent data with $I > 3\sigma(I)$.

---

[31] Rutner, H.; Spoerri, P. E. *J. Org. Chem.* **1963**, *28*, 1898–1899.

[32] Analyses were performed by Atlantic Microlab, Norcross, GA.

Table I. Crystallographic and Data Collection Parameters

	4	**5**	**7**
formula	$Mn_2C_{32}H_{46}Cl_2N_8O_{11}$	$Mn_2C_{40}H_{56}N_{10}O_{14}$	$Mn_2C_{24}H_{46}Cl_2N_{12}O_{17}$
a (Å)	8.487 (3)	22.122 (7)	21.371 (5)
b (Å)	10.868 (2)	16.419 (6)	9.301 (3)
c (Å)	20.816 (5)	14.461 (4)	21.180 (7)
α (deg)	77.34 (2)	90	90
β (deg)	88.28 (2)	117.15 (2)	108.54 (2)
γ (deg)	84.02 (2)	90	90
V (Å^3)	1863.1 (8)	4674 (3)	3991 (2)
no.	4656	3202	4059
no. (obs)	2787 [$I > 3\sigma(I)$]	1396	3766
no. variables	533	297	392
data collected	$+h,\pm k,\pm l$	$\pm h,+k,+l$	$+h,+k,\pm l$
index ranges	$0 \le h \le 10$	$-26 \le h \le 23$	$0 \le h \le 24$
	$-12 \le k \le 12$	$0 \le k \le 19$	$0 \le k \le 11$
	$-23 \le l \le 23$	$0 \le l \le 9$	$-23 \le l \le 23$
radiation	Mo Kα	Mo Kα	Mo Kα
space group	$P\bar{1}$	$C2/c$	$C2$
Z	2	4	4
R	0.0759	0.0683	0.0515
wR	0.0907	0.0901	0.0728
T (°C)	−100	22	−100

Table II. Selected Bond Lengths (Å) for **4**

atoms	distance	atoms	distance
Mn(1)–Mn(2)	2.676 (3)	Mn(1)–O(1)	1.814 (8)
Mn(1)–O(2)	1.853 (9)	Mn(1)–N(1A)	2.424 (11)
Mn(1)–N(2A)	2.117 (11)	Mn(1)–N(1B)	2.468 (10)
Mn(1)–N(2B)	2.115 (9)	Mn(2)–O(1)	1.830 (9)
Mn(2)–O(2)	1.863 (8)	Mn(2)–N(1C)	2.410 (11)
Mn(2)–N(2C)	2.121 (12)	Mn(2)–N(1D)	2.406 (11)
Mn(2)–N(2D)	2.099 (10)		

Table III. Selected Bond Angles (deg) for **4**

atoms	angle	atoms	angle
O(1)–Mn(1)–N(1A)	97.1 (4)	O(1)–Mn(1)–O(2)	87.1 (4)
O(1)–Mn(1)–N(2A)	94.3 (4)	O(2)–Mn(1)–N(1A)	100.7 (4)
N(1A)–Mn(1)–N(2A)	71.7 (4)	O(2)–Mn(1)–N(2A)	172.4 (4)
O(2)–Mn(1)–N(1B)	98.8 (4)	O(1)–Mn(1)–N(1B)	98.3 (4)
N(2A)–Mn(1)–N(1B)	88.4 (4)	N(1A)–Mn(1)–N(1B)	155.7 (4)
O(2)–Mn(1)–N(2B)	98.5 (4)	O(1)–Mn(1)–N(2B)	168.3 (4)
N(2A)–Mn(1)–N(2B)	81.5 (4)	N(1A)–Mn(1)–N(2B)	92.0 (4)
O(1)–Mn(2)–O(2)	86.3 (4)	N(1B)–Mn(1)–N(2B)	70.9 (4)
O(2)–Mn(2)–N(1C)	96.5 (4)	O(1)–Mn(2)–N(1C)	100.7 (4)
O(2)–Mn(2)–N(2C)	100.0 (4)	O(1)–Mn(2)–N(2C)	170.2 (4)
O(1)–Mn(2)–N(1D)	98.9 (4)	N(1C)–Mn(2)–N(2C)	71.4 (4)
N(1C)–Mn(2)–N(1D)	156.6 (4)	O(2)–Mn(2)–N(1D)	97.4 (4)
O(1)–Mn(2)–N(2D)	91.9 (4)	N(2C)–Mn(2)–N(1D)	87.7 (4)
N(1C)–Mn(2)–N(2D)	94.3 (4)	O(2)–Mn(2)–N(2D)	169.2 (4)
N(1D)–Mn(2)–N(2D)	72.3 (4)	N(2C)–Mn(2)–N(2D)	83.2 (4)
Mn(1)–O(2)–Mn(2)	92.1 (4)	Mn(1)–O(1)–Mn(2)	94.5 (4)

Table IV. Selected Bond Lengths (Å) for **5**

atoms	distance	atoms	distance
Mn–O(1)	1.818 (9)	Mn–N(1B)	2.079 (12)
Mn–N(1C)	2.386 (8)	Mn–N(1D)	2.117 (8)
Mn–N(1A)	2.353 (8)	Mn–Mn(A)	2.674 (4)
Mn–O(1A)	1.841 (6)		

Table V. Selected Bond Angles (deg) for **5**

atoms	angle	atoms	angle
O(1)–Mn–N(1B)	174.8 (3)	O(1)–Mn–N(1C)	97.4 (3)
N(1B)–Mn–N(1C)	80.7 (3)	O(1)–Mn–N(1D)	93.9 (4)
N(1B)–Mn–N(1D)	81.0 (4)	N(1C)–Mn–N(1D)	74.2 (3)
O(1)–Mn–N(1A)	94.8 (4)	N(1B)–Mn–N(1A)	84.4 (4)
N(1C)–Mn–N(1A)	147.3 (3)	N(1D)–Mn–N(1A)	74.8 (3)
O(1)–Mn–O(1A)	86.1 (3)	N(1B)–Mn–O(1A)	99.1 (4)
N(1C)–Mn–O(1A)	105.0 (3)	N(1D)–Mn–O(1A)	179.1 (3)
N(1A)–Mn–O(1A)	106.1 (3)	Mn–O(1)–Mn(A)	93.9 (3)

Results and Discussion

Description of the Structures. Bis(μ-oxo)bis[*N*,*N*′-bis((6-methylpyrid-2-yl)methyl)ethane-1,2-diamine]dimanganese(III) Perchlorate Monohydrate, [(1b)MnO]$_2$(ClO$_4$)$_2$·H$_2$O (4). The structure of this III/III complex consists of [(**1b**)MnO]$_2^{2+}$ cations, perchlorate anions, and water molecules. A view of the cation is given in Figure 1. Principal distances and angles are listed in Tables II and III, respectively.

The geometry about each manganese center is roughly octahedral, with axial ligation provided by the pyridyl groups and equatorial ligation by the diaminoethane nitrogen atoms and the bridging oxo groups. The separation between the two independent manganese(III) centers in each dimer is 2.676 (3) Å, which is only slightly different from the value of 2.659 (2) Å in the bispicen Mn(III,IV) complex[7] and is within the ranges of 2.639 (1)–2.741 (1) and 2.625 (2)–2.748 (2) Å observed for the analogous Mn(III,IV) and Mn(IV,IV) species, respectively.[5-13,22-25] The Mn(1)–O(1)–Mn(2) and Mn(1)–O(2)–Mn(2) bridging angles are 94.5 (4) and 92.1 (4)°, respectively, and again are not substantially different from those of the bispicen III/IV complex. The Mn–O bond lengths range from 1.814 (8) to 1.863 (8) Å, values consistent with the range of Mn–O bond lengths [1.833–1.856 Å] found for the Mn(III) centers in localized Mn(III/IV) structures. Jahn–Teller axial distortion of the octahedral geometry about each Mn(III) center, resulting in longer axial bond lengths than equatorial bond lengths, is clearly evident as expected for a high-spin d^4 ion. The Mn–N bond lengths to the axial nitrogen atoms of the substituted pyridine groups range from 2.406 (11) to 2.468 (10) Å, while the equatorial Mn–N bond lengths vary from 2.099 (10) to 2.117 (11) Å. For comparison, we note that the axial Mn–N bond length at the Mn(III) center in the bispicen Mn(III/IV) complex is 2.169 Å, while the equatorial distance is 2.083 Å. Thus, while the equatorial Mn–N bond lengths of **4** are similar to that seen in the parent III/IV complex, the values for the axial bond lengths are more than 0.2 Å longer.

An examination of Figure 1 demonstrates that the 6-methyl groups in **1b** impose severe steric constraints on the metal centers and make it energetically favorable for the complex to exhibit long axial Mn–N bonds; the structural results show that these axial bonds are the longest yet observed in a system of this type, and their average value of 2.427 Å is 0.31 Å longer than that of 2.113 Å for the equatorial Mn–N bonds. This geometrical pattern is readily accommodated by the high-spin d^4 Mn(III) centers, which are expected to exhibit axial elongation as a result of a Jahn–Teller distortion. The Mn(IV) centers in the oxidized forms, however, are d^3 ions and are expected to be spherically symmetric, which requires a significant shortening of the axial bonds. This arrangement brings the 6-methyl groups into close proximity with the metal centers; consequently, the Mn(IV) form is destabilized relative to the Mn(III) form, and the redox couples are shifted to more positive potentials.

Bis(μ-oxo)bis[*N*,*N*-bis((6-methylpyrid-2-yl)methyl)-*N*-2-pyridylmethylamine]dimanganese(III) Nitrate Hexahydrate,

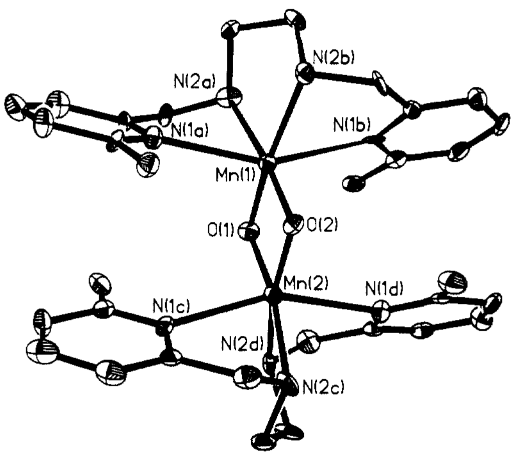


Figure 1. View of the binuclear cation in **4**. Carbon atoms are unlabeled, and hydrogen atoms are omitted for clarity.

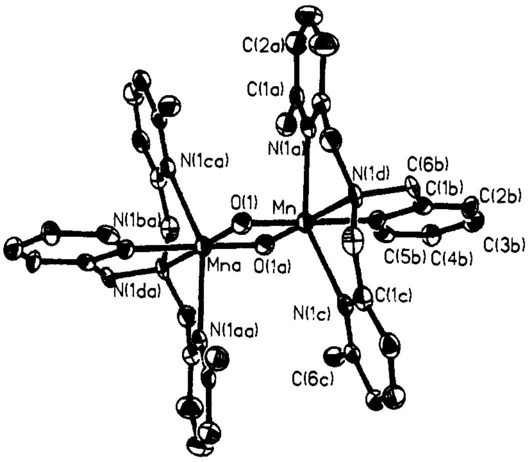


Figure 2. View of the binuclear cation in **5**. Some carbon atoms are unlabeled, and hydrogen atoms are omitted for clarity.

[(2c)MnO]$_2$(NO$_3$)$_2$·6H$_2$O (5). The structure of this III/III complex consists of [(**2c**)MnO]$_2^{2+}$ cations, nitrate anions, and water molecules. A view of the cation is given in Figure 2. Principal distances and angles are listed in Tables IV and V, respectively.

Here also, the geometry about each manganese center is roughly octahedral, with axial ligation provided by the 6-methylpyridyl groups, while the equatorial sites are occupied by the pyridyl and amine nitrogen atoms and the cis bridging oxo groups. The Mn–Mn separation in the dimer is 2.674 (4) Å, which is insignificantly different from the value of 2.676 (3) Å reported above for **4**. The Mn–O(1)–Mn bridging angle is 93.9 (3)°, again not substantially different from the average value of 93.3° in **4**. The Mn–O bond lengths range from 1.818 (9) to 1.841 (6) Å, which are again consistent with the range of Mn–O bond lengths in **4**. The anticipated Jahn–Teller axial distortion of the octahedral geometry is again observed, the axial bond lengths of 2.353 (8)–2.386 (8) Å [average, 2.370 Å] being approximately 0.27 Å longer than the equatorial Mn–N bond of 2.079 (12)–2.117 (8) Å [average 2.098 Å]. It is again apparent from an examination of Figure 2 that the steric constraints imposed by the axially disposed 6-methyl groups in **2c** are responsible for this elongation and are the cause of the stabilization of **5** relative to its III/IV and IV/IV forms. It is noteworthy that in the structure of the monomeric manganese(II) complex *cis*-[Mn(**2c**)Cl$_2$] the axial bonds are again very long [2.431 (2)–2.456 (3) Å], while the equatorial distances are 2.286 (3)–2.329 (3) Å.[33] Hence, even in the absence of a Jahn–Teller distortion, this ligand forces an axial elongation in the d^5 Mn(II) complex.

Bis(μ-oxo)bis[*N*,*N*'-bis[2-methylpyrazyl)ethane-1,2-diamine]dimanganese(III) Perchlorate Heptahydrate, [(1d)MnO]$_2$(ClO$_4$)$_2$·7H$_2$O (7). The structure of this III/III complex consists of [(**1d**)MnO]$_2^{2+}$ cations, perchlorate anions, and water molecules.

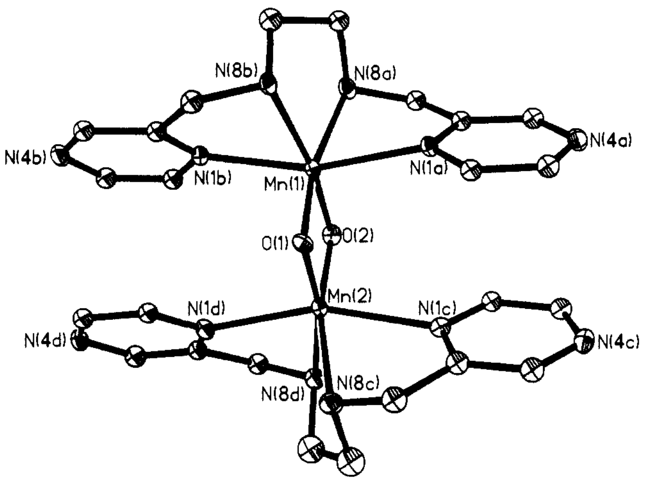


Figure 3. View of the binuclear cation in **7**. Carbon atoms are unlabeled, and hydrogen atoms are omitted for clarity.

Table VI. Selected Bond Lengths (Å) for **7**

atoms	distance	atoms	distance
Mn(1)–Mn(2)	2.686 (1)	Mn(1)–O(1)	1.855 (4)
Mn(1)–O(2)	1.851 (4)	Mn(1)–N(1A)	2.312 (6)
Mn(1)–N(8A)	2.119 (5)	Mn(1)–N(1B)	2.320 (6)
Mn(1)–N(8B)	2.107 (5)	Mn(2)–O(1)	1.839 (4)
Mn(2)–O(2)	1.824 (4)	Mn(2)–N(1C)	2.354 (7)
Mn(2)–N(8C)	2.135 (5)	Mn(2)–N(1D)	2.304 (7)
Mn(2)–N(8D)	2.130 (5)		

Table VII. Selected Bond Angles (deg) for **7**

atoms	angle	atoms	angle
O(1)–Mn(1)–O(2)	85.7 (2)	O(1)–Mn(1)–N(1A)	92.7 (2)
O(2)–Mn(1)–N(1A)	96.7 (2)	O(1)–Mn(1)–N(8A)	165.5 (2)
O(2)–Mn(1)–N(8A)	96.2 (2)	N(1A)–Mn(1)–N(8A)	72.8 (2)
O(1)–Mn(1)–N(1B)	99.7 (2)	O(2)–Mn(1)–N(1B)	95.3 (2)
N(1A)–Mn(1)–N(1B)	163.4 (2)	N(8A)–Mn(1)–N(1B)	94.5 (2)
O(1)–Mn(1)–N(8B)	98.0 (2)	O(2)–Mn(1)–N(8B)	168.1 (2)
N(1A)–Mn(1)–N(8B)	94.5 (2)	N(8A)–Mn(1)–N(8B)	83.1 (2)
N(1B)–Mn(1)–N(8B)	73.0 (2)	O(1)–Mn(2)–O(2)	87.0 (2)
O(1)–Mn(2)–N(1C)	98.9 (2)	O(2)–Mn(2)–N(1C)	94.3 (2)
O(1)–Mn(2)–N(8C)	96.8 (2)	O(2)–Mn(2)–N(8C)	166.3 (3)
N(1C)–Mn(2)–N(8C)	72.1 (2)	O(1)–Mn(2)–N(1D)	93.7 (2)
O(2)–Mn(2)–N(1D)	101.7 (2)	N(1C)–Mn(2)–N(1D)	160.1 (2)
N(8C)–Mn(2)–N(1D)	91.2 (2)	O(1)–Mn(2)–N(8D)	167.5 (2)
O(2)–Mn(2)–N(8D)	96.7 (2)	N(1C)–Mn(2)–N(8D)	92.7 (2)
N(8C)–Mn(2)–N(8D)	82.4 (2)	N(1D)–Mn(2)–N(8D)	73.9 (2)
Mn(1)–O(1)–Mn(2)	93.3 (2)	Mn(1)–O(2)–Mn(2)	93.9 (2)

A view of the cation is given in Figure 3. Principal distances and angles are listed in Tables VI and VII, respectively.

The geometry about each manganese center is again roughly octahedral, with axial ligation provided by the pyrazyl groups and equatorial ligation by the diaminoethane nitrogen atoms and the bridging oxo groups. The separation between the two independent manganese(III) centers in each dimer is 2.686 (1) Å, which is again only slightly different from the values of 2.676 (3) and 2.674 (4) Å reported above for **4** and **5**, respectively. The Mn(1)–O(1)–Mn(2) and Mn(1)–O(2)–Mn(2) bridging angles are 93.3 (2) and 93.9 (2)°, again not substantially different from the average value of 93.3° in **4** and that of 93.9° in **5**. The Mn–O bond lengths range from 1.824 (4) to 1.855 (4) Å, which are again consistent with the range of Mn–O bond lengths in **4** and **5**. The complex again exhibits a Jahn–Teller axial distortion of the octahedral geometry, the axial bond lengths of 2.304 (7)–2.354 (7) Å [average, 2.323 Å] being approximately 0.20 Å longer than the equatorial Mn–N bonds of 2.107 (5)–2.135 (5) Å [average 2.123 Å].

In the absence of the steric crowding in **4** and **5**, the only reason for the observed stabilization of the Mn(III,III) form in **7** is electronic. This result can be understood in terms of the relative acidities of pyridine and pyrazine; the pK_a of pyridine is 5.20, while that of pyrazine is 0.65.[34] Obviously, therefore, **1d** would be

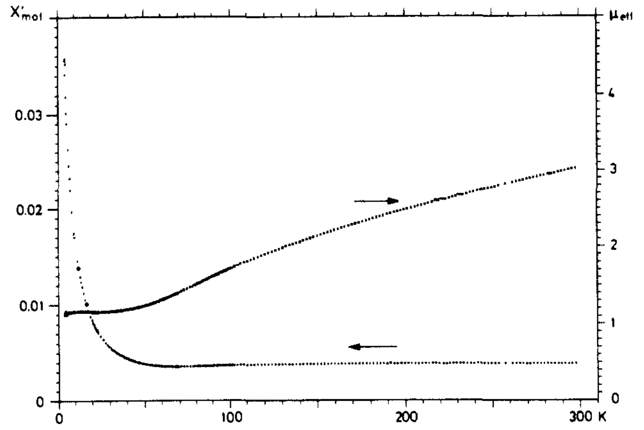


Figure 4. Magnetic susceptibility (left scale) and effective magnetic moment (right scale) of a powdered sample of the Mn(III,III) complex **4**.

expected to be a poorer electron donor than **1a** or **1b**, thereby stabilizing Mn(III) relative to Mn(IV).

Electronic Spectra. It is apparent that the spectra of these III/III complexes are far less complex than those of the analogous Mn(III,IV) complexes. For example, while the spectrum of the "parent" bispicen (III,IV) complex exhibits bands at 661, 554, 440 (sh), and 388 (sh) in acetonitrile [655, 553, 432, 386 in water],[24] the visible spectrum of **4** exhibits only a broad absorbance at 461 nm (ϵ = 141 cm^{-1} M^{-1}), which can be attributed to a d–d transition centered on the Mn(III) sites, and a very weak feature at 545 nm. Similarly, the spectrum of **5** contains bands at 443 nm (ϵ = 361 cm^{-1} M^{-1}) and a weaker band at 575 (ϵ = 249 cm^{-1} M^{-1}). The bands below 350 nm in the spectra can be attributed to the ligands; for example, the spectrum of **2c** contains bands at 335 and 240 nm which correspond to the high energy bands in the spectrum of **5**. While there are no other bis(μ-oxo)dimanganese(III,III) complexes whose spectra can be compared to those of **4** and **5**, it is noteworthy that these spectra are comparable to those of the binuclear μ-oxo-bis(μ-acetato)dimanganese(III) complexes of triazacyclononane, trimethyltriazacyclononane, and hydrotris(1-pyrazolyl)borate which have been described by other workers;[22,35] for example, the trimethyltriazanonane complex exhibits bands at 486 (ϵ = 667 cm^{-1} M^{-1}) and 521 (ϵ = 638 cm^{-1} M^{-1}),[22] while the hydrotris(1-pyrazolyl)borate complex shows a broad feature at 486 nm (ϵ = 210 cm^{-1} M^{-1}).[35] Absent from our spectra, however, are weak bands at 720 and 760 nm found in the trimethyltriazanonane and hydrotris(1-pyrazolyl)borate complexes, respectively.

Magnetic Properties. The temperature dependence of the magnetic susceptibility of a powdered sample of the Mn(III/III) complex **4** was measured in the range 4–296 K. As is shown in Figure 4, the effective magnetic moment at room temperature is approximately 3.05 μ_B, declining monotonically to a value of 1.17 μ_B at 30 K; the moment is essentially constant below 30 K.

The susceptibility data were analyzed by fitting them to the expression

$$\chi'_{\mathrm{mol}} = \frac{N}{H}\,\frac{\sum_i \frac{\delta E_i}{\delta H}\exp(-E_i/kT)}{\sum_i \exp(-E_i/kT)} + K + \frac{C}{T}$$

where the E_i are the energies of the twenty components of the ground-state manifold. The term C/T accounts for paramagnetic impurities, and K accounts for TIP (temperature independent paramagnetism) and minor deviations in the correction for the diamagnetic contribution of the atoms. The fitting was accomplished by using the isotropic spin Hamiltonian

$$\mathcal{H} = -2J\vec{S}_1\cdot\vec{S}_2 + g_1\beta\vec{S}_1\cdot\vec{H} + g_2\beta\vec{S}_2\cdot\vec{H}$$

where $S = S_1 + S_2$, and we have set $g_1 = g_2$. With two $S = 2$ centers, the Heisenberg term $-2JS_1{\cdot}S_2$ gives rise to singlet, triplet, quintet, septet, and nonet states with energies of 0, $-2J$, $-6J$, $-12J$, and $-20J$, respectively. The fitting leads to a value of $2J = -172.8 \pm 0.3$ cm^{-1}, or $J = -86.4 \pm 0.2$ cm^{-1}. C was found to be 1.6×10^{-1}, which implies approximately 1.6% of a monomeric Mn(II) impurity; the presence of this impurity explains the observation of the tail in the susceptibility at very low temperatures.

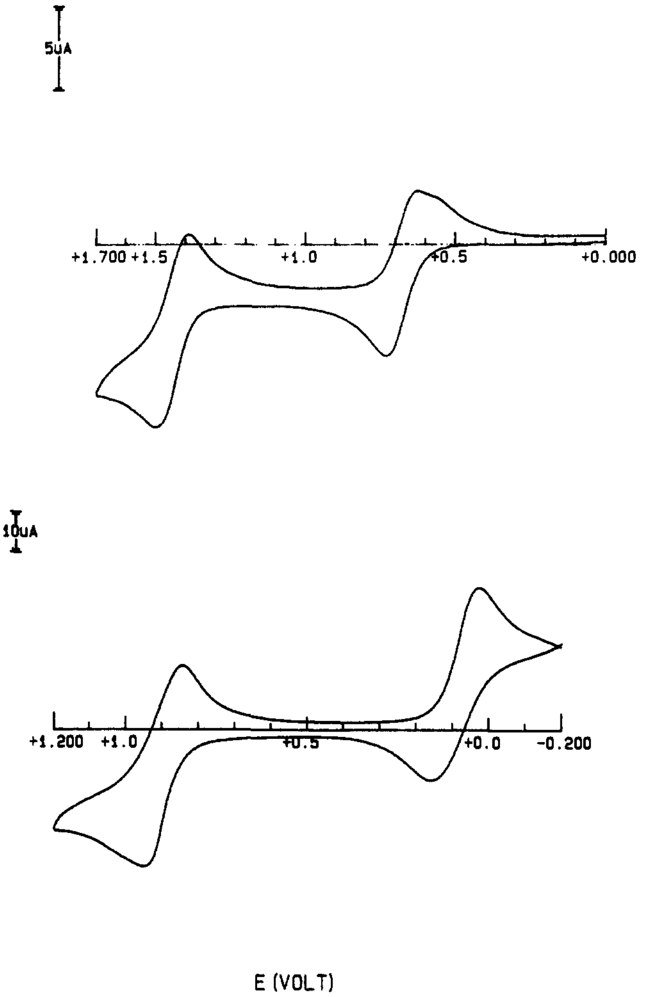


Figure 5. Cyclic voltammograms vs Ag/AgCl with Et_4NClO_4 as supporting electrolyte in acetonitrile solution: (a) top, complex **5** and (b) bottom, complex **6**.

The observation of a large antiferromagnetic interaction in the present complex is consistent with the reported interactions in analogous Mn(III,IV) and Mn(IV,IV) complexes. In all known cases, the exchange interaction is antiferromagnetic [$J < 0$]; in the Mn(III,IV) systems, J is in the range −140 to −151 cm^{-1}, while in the Mn(IV,IV) complexes it lies in the much larger range of −86.5 to −144 cm^{-1}.[23,24] It is, however, in marked contrast to the observations of Wieghardt and co-workers,[22] who found a relatively weak ferromagnetic interaction [J = +18 cm^{-1}] in their μ-oxo-bis(μ-acetato)dimanganese(III,III) complex with trimethyltriazacyclononane, and of those of Lippard and co-workers,[35] who observed a very weak [$-J < 1$ cm^{-1}] antiferromagnetic interaction in their analogous complex with hydrotris(1-pyrazolyl)borate.

Electrochemical Properties. The cyclic voltammogram of **4** has been described previously and consists of two redox couples at 0.568 and 1.337 V (vs Ag/AgCl in acetonitrile). The cyclic voltammogram of **5**, shown in Figure 5a, consists of two quasi-reversible waves at 0.678 and 1.446 V vs Ag/AgCl. The first of

---

(33) Goodson, P. A.; Oki, A. R.; Hodgson, D. J. *Inorg. Chim. Acta.* In press. Unpublished observations.

(34) *Comprehensive Heterocyclic Chemistry*; Boulton, A. J., McKillop, A., Eds.; Pergammon Press: New York, 1984. (a) Vol. 2, pp 170–171. (b) Vol. 3, p 162.

(35) Sheats, J. E.; Czernuszewicz, R. S.; Dismukes, G. C.; Rheingold, A. L.; Petrouleas, V.; Stubbe, J.; Armstrong, W. H.; Beer, R. H.; Lippard, S. J. *J. Am. Chem. Soc.* **1987**, *109*, 1435–1444.

these waves corresponds to the III/III ↔ III/IV couple, while the second corresponds to the III/IV ↔ IV/IV couple. These values in **5** are quite remarkable, being shifted by 390 and 360 mV from those reported by Suzuki et al. for the "parent" tmpa complex. Similarly, the values in **4** are shifted by 443 and 378 mV realtive to the values for the "parent" bispicen complex.[36] These values of 0.568 and 0.678 V are the highest values ever reported for the III/III ↔ III/IV couple and are (evidently) sufficiently high to cause the III/III form to be the stable form in aqueous medium; according to a recent tabulation,[24] the highest previously recorded value is 0.38 V (vs Ag/AgCl) in the phen complex. Similarly, the values of 1.337 and 1.446 V are higher than the value of 1.31 V reported for the phen complex, which is the highest value previously reported for that couple.

In order to demonstrate that the significant changes in the redox couples noted above are due to steric rather than electronic factors, we have examined the cyclic voltammetry of **6**. The pK_a of 4-methylpyridine (6.03) is essentially the same as that of 2-methylpyridine (5.97),[34a] and so the electronic consequences of changing from the pyridine ($pK_a = 5.20$) moiety of bispicen to the methylpyridines in **1b** and **1c** should be virtually identical. The 4-methyl groups in **6** are on the side of the ligand away from the metal, however, and would not be expected to introduce any steric strain involving the Mn–N axial bonds; consequently, if the electrochemical differences between **4** and the bispicen complex are entirely due to the steric factors suggested earlier, we anticipate that the electrochemical properties of **6** should be similar to those of the bispicen complex and different from those of **4**. The cyclic voltammogram of **6**, which is shown in Figure 5b, shows two quasi-reversible waves at 0.090 and 0.903 V vs Ag/AgCl, which can be compared to the values of 0.125 and 0.959 found for the bispicen complex in the same solvent.[36] Hence, it is apparent that the electrochemical differences between **4** and **5** and their unsubstituted parent complexes are attributable entirely to stereochemical factors.

As was noted earlier, however, the same effect can be achieved by electronic modification of the ligand. Thus, the electronic modification of pyridine to pyrazine in ligand **1d** leads to a complex (**7**) in which the III/III is again the stable form in aqueous solution. This complex, however, does not show any electrochemistry in the range −0.5 to +1.8 V (vs. Ag/AgCl), which may suggest that the Mn(IV) form is so destabilized by this ligand that it cannot be reached.

In order to demonstrate the utility of these new complexes, we have examined the ability of **5** to act as an electrochemical oxidant. Controlled potential electrolyses of benzyl alcohol in the presence of **5** were performed at 1.7 V vs Ag/AgCl, which is adequate to oxidize the complex to the IV/IV form (vide supra). For 2.45×10^{-5} mol of complex, in the absence of any substrate, a total charge of 6.02 C was passed; for a one-electron oxidation, this value should be only 2.36 C, while for a two-electron process it should be 4.73 C. Complex **5** selectively oxidized benzyl alcohol to benzaldehyde with yields as high as 100 ± 10% (based on total charge passed); the observed charge passed was 96 C, while that calculated for 4.5×10^{-4} mol of benzaldehyde produced is 87 C for a two-electron process. The product was pure benzaldehyde as analyzed by GC methods. The turnover number was as high as 20, based on the ratio of aldehyde concentration to complex concentration.

Our present results can be compared and contrasted with those of Gref et al.[19] for the phen complex. For the phen complex, these workers demonstrated that the oxidation involved a series of one-electron processes rather than a two-electron process. These workers also noted that they could not use 2,6-lutidine as base because they observed loss of electrochemical reversiblity in the presence of this base; this is unfortunate in terms of the potential applicability of the phen system, since bases like 2,6-lutidine are known to accelerate anodic oxidations.[19] In view of the higher potential of the IV/IV form of **5** relative to that of the phen complex, it is also probable that **5** can electrochemically oxidize substrates which are not oxidizable with the phen complex. Hence, it seems probable that the two-electron oxidant **5** may be a much more versatile mediator than the phen complex.

Acknowledgment. This work was supported by the donors of the Petroleum Research Fund, administered by the American Chemical Society, through Grant No. 19457-AC3 (to D.J.H.), by the National Science Foundation through Grant No. CHE-8912675 (to D.J.H.), and by the Scientific Affairs Division, North Atlantic Treaty Organization (N.A.T.O.) through Grant No. RG 0790/85 (to J.G. and D.J.H.). We are very grateful to our colleagues Dr. Ricardo Borjas and Professor Daniel Buttry for assistance with the electrochemical measurements.

Supplementary Material Available: Tables S1–S3 (hydrogen atom parameters for **4**, **5**, and **7**, respectively), S4–S6 (anisotropic thermal parameters for **4**, **5**, and **7**, respectively), and S10–S12 (atomic positional parameters for **4**, **5**, and **7**, respectively) (9 pages); Tables S7–S9 (observed and calculated structure amplitudes for **4**, **5**, and **7**, respectively) (43 pages). Ordering information is given on any current masthead page.

---

[36] The values for the parent bispicen complex used for this comparison differ from those published in ref 24, since those in ref 24 are in water rather than in acetonitrile. In acetonitrile, the parent bispicen complex exhibits waves at 0.125 and 0.959 V vs Ag/AgCl.