

Tetranuclear Manganese(III)-Oxo-Carboxylate Complexes Possessing Terminal Phenoxide or Alkoxide Ligands

Elisabeth Bouwman,[†] Milissa A. Bolcar, Eduardo Libby, John C. Huffman, Kirsten Folting, and George Christou*

Department of Chemistry and Molecular Structure Center, Indiana University, Bloomington, Indiana 47405

Received April 6, 1992

The synthesis of tetranuclear manganese carboxylate complexes with the ligands 8-hydroxyquinoline (hqnH), 5-chloro-8-hydroxyquinoline (Cl-hqnH), and 2-(hydroxymethyl)pyridine (hmpH) is described. Reaction mixtures containing $Mn(O_2CR)_2$, HO_2CR ($R = Me, Ph$), NR'_4MnO_4 ($R' = Me, Et, Bu^n$), and L-L ($L-L = hqn, Cl-hqn, hmp$) in MeCN give red-brown solutions from which the products $(NR'_4)[Mn_4O_2(O_2CMe)_7(hqn)_2]$ ($R' = Bu^n, 1; R' = Et, 2; R' = Me, 3$), $(NMe_4)[Mn_4O_2(O_2CPh)_7(hqn)_2]$ (4), $(NMe_4)[Mn_4O_2(O_2CMe)_7(Cl-hqn)_2]$ (5), and $(NR'_4)[Mn_4O_2(O_2-CPh)_7(hmp)_2]$ ($R' = Me, 6; R' = Et, 7; R' = Bu^n, 8$) were isolated and characterized. Single crystals were obtained from a CH_2Cl_2 solution of 1, orthorhombic, space group $P2_12_12_1$, $a = 17.549$ (3) Å, $b = 23.801$ (6) Å, $c = 14.707$ (3) Å, $V = 6142.91$ Å³, and $Z = 4$, and from a MeCN solution of 6, triclinic, space group $P\bar{1}$, $a = 15.934$ (3) Å, $b = 16.896$ (4) Å, $c = 13.155$ (3) Å, $\alpha = 106.00$ (1)°, $\beta = 99.51$ (1)°, $\gamma = 85.71$ (1)°, $V = 3356.10$ Å³, and $Z = 2$. The structures were solved by direct methods (MULTAN) and refined by least-squares methods to residual R (R_w) values of 7.6 (7.0) and 9.1 (8.9), respectively. The structures of the anions in the two compounds are very similar. In the Mn_4O_2 core, the two O^{2-} ions each bridge to three Mn ions and the two Mn_3O units are edge-sharing, thus forming a "butterfly" Mn_4 arrangement. The seven carboxylate ligands each bridge between two manganese ions. The hqn and hmp ligands are deprotonated and are chelating to the "wingtip" manganese ions. The coordination number of each manganese ion is 6, and the coordination environment is elongated octahedral, which is indicative of Jahn-Teller-distorted high-spin Mn^{III} ions. Conductivity measurements show that all the described compounds are 1:1 electrolytes in MeCN and Me_2CO . In CH_2Cl_2 considerable ion-pairing is observed. The cyclic voltammograms of the compounds show a quasi-reversible, one-electron oxidation in the range 0.35–0.41 V (hqn) or 0.25 V (hmp) vs the ferrocene/ferrocenium couple, which is assigned to oxidation to a $3 Mn^{III}, Mn^{IV}$ compound. All compounds show an additional irreversible oxidation at ca. +1.0 V and an irreversible reduction at ca. -1.5 V. The proton NMR spectra of complexes 1–5 have been recorded in $CDCl_3$, CD_3CN , and $(CD_3)_2SO$. The resonances are broadened and shifted from their diamagnetic positions due to the large magnetic moments of the manganese complexes (ca. 8 μ_B). The spectra are very similar in the three solvents and support retention of the solid-state structure of the complex in solution.

Introduction

Manganese chemistry has been receiving a great deal of attention recently. This has been due to a variety of reasons, but the main ones are (i) the identification of Mn-containing enzymes¹ and (ii) the propensity of higher nuclearity Mn aggregates to display large spin ground states.² The former reason has stimulated a desire to understand the structural chemistry of Mn in the intermediate oxidation-state range (II–IV) and nuclearity 2–4 with oxide bridges and O- and/or N-based biologically-relevant ligands, followed by assessment of spectroscopic and physicochemical properties with a view to gaining insights into the nature and mode of action of the biological Mn sites. The

latter reason has given birth to a search for synthetic methodology to higher nuclearity (≥ 6) Mn species and a desire to understand the factors that lead to large ground-state spin values in these and, indeed, lower nuclearity species.

Recently, we introduced successful synthetic procedures to a new class of tetranuclear Mn carboxylate aggregates possessing the $[Mn_4(\mu_3-O)_2]$ core and the formulation $[Mn_4O_2(O_2-CR)_x(bpy)_z]^z$ ($x = 6, 7; z = 0, +; bpy = 2,2'$ -bipyridine)^{3a} encompassing metal oxidation states $2 Mn^{II}, 2 Mn^{III}$ through $4 Mn^{III}$. We proposed these as initial models for the photosynthetic water oxidation center (WOC), which contains 4 Mn and a predominantly O-based metal ligation environment.^{1,4,5} Additional examples of $[Mn_4O_2]$ -containing complexes have since been

* Author to whom correspondence should be addressed.

[†] Present address: Gorlaeus Laboratories, Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands.

- (1) (a) Wiegardt, K. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1153. (b) Vincent, J. B.; Christou, G. *Adv. Inorg. Chem.* **1989**, *33*, 197. (c) Govindjee; Kambara, T.; Coleman, W. *Photochem. Photobiol.* **1985**, *42*, 187. (d) Dismukes, G. C. *Ibid.* **1986**, *43*, 99. (e) Renger, G. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 643. (f) Brudvig, G. W. *J. Bioenerg. Biomembr.* **1987**, *19*, 91. (g) Babcock, G. T. In *New Comprehensive Biochemistry*; Ames, J., Ed.; Elsevier: Dordrecht, The Netherlands, 1987; Vol. 15, pp 125–158. (h) Pecoraro, V. L. *Photochem. Photobiol.* **1988**, *48*, 249. (i) Ghanotakis, D.; Yocum, C. F. *Annu. Rev. Plant Physiol. Mol. Biol.* **1990**, *41*, 255.
- (2) (a) Caneschi, A.; Gatteschi, D.; Laugier, J.; Rey, P.; Sessoli, R.; Zanchini, C. *J. Am. Chem. Soc.* **1988**, *110*, 2795. (b) Boyd, P. D. W.; Li, Q.; Vincent, J. B.; Folting, K.; Chang, H.-R.; Streib, W. E.; Huffman, J. C.; Christou, G.; Hendrickson, D. N. *Ibid.* **1988**, *110*, 8537. (c) Caneschi, A.; Gatteschi, D.; Sessoli, R.; Barra, A. L.; Brunel, L. C.; Guillot, M. *Ibid.* **1991**, *113*, 5873.

- (3) (a) Vincent, J. B.; Christmas, C.; Chang, H.-R.; Li, Q.; Boyd, P. D. W.; Huffman, J. C.; Hendrickson, D. N.; Christou, G. *J. Am. Chem. Soc.* **1989**, *111*, 2086. (b) Libby, E.; McCusker, J. K.; Schmitt, E. A.; Folting, K.; Hendrickson, D. N.; Christou, G. *Inorg. Chem.* **1991**, *30*, 3486. (c) Wang, S.; Huffman, J. C.; Folting, K.; Streib, W. E.; Lobkovsky, E. B.; Christou, G. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1672. (d) Thorp, H. H.; Sarneski, J. E.; Kulawiec, R. J.; Brudvig, G. W.; Crabtree, R. H.; Papaefthymiou, G. C. *Inorg. Chem.* **1991**, *30*, 1153. (e) Chandra, S. K.; Chakravorty, A. *Ibid.* **1991**, *30*, 3795. (f) Mikuriya, M.; Yamato, Y.; Tokii, T. *Chem. Lett.* **1991**, 1429.
- (4) (a) Guiles, R. D.; Yachandra, V. K.; McDermott, A. E.; Cole, J. L.; Dexheimer, S. L.; Britt, R. D.; Sauer, L.; Klein, M. P. *Biochemistry* **1990**, *29*, 486 and references therein. (b) Guiles, R. D.; McDermott, A.; Yachandra, V. K.; Cole, J. L.; Dexheimer, S. L.; Britt, R. D.; Wiegardt, K.; Bossek, U.; Sauer, K.; Klein, M. P. *Ibid.* **1990**, *29*, 471. (c) George, G. N.; Prince, R. C.; Cramer, S. P. *Science* **1989**, *243*, 789. (d) Penner-Hahn, J. E.; Fronko, R. M.; Pecoraro, V. L.; Yocum, C. F.; Betts, S. D.; Bowlby, N. R. *J. Am. Chem. Soc.* **1990**, *112*, 2549.

reported,^{3b-f} and it is clear that this structural unit represents a thermodynamically stable and preferred arrangement at this oxidation level (III). An alternative Mn₄ structural type possessing the [Mn₄(μ₃-O)₃(μ₃-Cl)]⁶⁺ core has been found at the 3 Mn^{III}, Mn^{IV} level.⁶ Further, the [Mn₂O₂]₂⁶⁺ "dimer of dimers" core⁷ and the adamantane-like [Mn₄O₆]⁴⁺ core⁸ currently characterize Mn₄ chemistry at the 2 Mn^{III}, 2 Mn^{IV} and 4 Mn^{IV} levels, respectively.

One important objective is the assessment of the magnitude by which the peripheral ligands can influence the properties (structural, redox, magnetochemical, spectroscopic) of a *polynuclear* oxide-bridged Mn aggregate. Since the WOC, for example, is a multiredox enzyme whose precise structure and ligation are unknown and whose study is heavily dependent on the interpretation of spectroscopic and physicochemical data, information and resulting trends made available from studies on model complexes would be invaluable. Such data have not been available at the important Mn₄ nuclearity, and we have therefore been investigating the variation of properties vs peripheral ligation for both [Mn₄O₂]⁸⁺ and [Mn₄O₃Cl]⁶⁺ complexes. For the former, we have already reported the effects of replacing bpy with pic⁻ (picH = picolinic acid),^{3b} and we herein extend our study by reporting the characterization of the complexes obtained by employing the ligands 8-hydroxyquinoline (hqNH) and 2-(hydroxymethyl)pyridine (hmpH). These introduce phenoxide and alkoxide functionalities, respectively, into the ligand sphere as *terminal* ligands.

Experimental Section

Syntheses. All manipulations were performed under aerobic conditions using materials as received; water was distilled in-house. NBu₄MnO₄ was prepared as described elsewhere.⁹ NMe₄MnO₄ and NEt₄MnO₄ were prepared in a similar manner.¹⁰ Mn(O₂CPh)₂·2H₂O and Mn(O₂-CCD₃)₂·4H₂O were prepared according to the literature.^{3b} *Warning! Appropriate care should be taken in the use of MnO₄⁻ salts, and readers are referred to the detailed warning given elsewhere.⁹*

8-Hydroxyquinoline-d₅. The material was prepared using the procedure and scale described elsewhere;¹¹ NEt₃ (0.50 mL, 3.6 mmol) was employed as the base. The gray powder obtained by saturating the cooled reaction solution with CO₂ was collected by filtration, washed with H₂O (2 × 5 mL) and dried in vacuo for 5 h. The yield was 0.88 g (88%).

(NBu₄)[Mn₄O₂(O₂CMe)₇(hqNH)₂·H₂O (1·H₂O). To a slurry of Mn(O₂-CMe)₂·4H₂O (1.01 g, 4.1 mmol), NBu₄Cl (2.5 g, 9.0 mmol), and HO₂-CMe (1.0 mL) in MeCN (100 mL) was slowly added NBu₄MnO₄ (0.36 g, 1.0 mmol) in small portions. To the resulting brown solution was added a slurry of Na(hqN), prepared by adding 8-hydroxyquinoline (0.36 g, 2.5 mmol) to a solution of NaOH (0.10 g, 2.5 mmol) in H₂O (0.5 mL) and diluting with MeCN (5 mL). The brown solution was stirred for 25 min and filtered to remove a gray precipitate, and the filtrate was evaporated in vacuo to dryness. The brown solid was redissolved in MeCN (25 mL), and 5:1 ether/hexanes (150 mL) was slowly added. Storage at -10 °C for several weeks resulted in dark brown crystals, which were collected by filtration, washed with 3:1 ether/MeCN (40 mL) and ether (10 mL), and dried in air. The yield was 1.03 g (68% based on Mn).

Crystals suitable for X-ray crystallography were grown by dissolving 0.16 g of the complex in CH₂Cl₂ (10 mL), slowly adding ether (5 mL) to the solution, filtering the solution, and layering the filtrate with 2:1 hexanes/ether (30 mL). The crystals were crystallographically characterized to be the bis-CH₂Cl₂ solvates; to avoid rapid solvent-loss problems on drying, the crystallographic sample was kept in contact with the mother liquor and refrigerated until a suitable crystal was selected and rapidly transferred to the diffractometer cold stream for investigation. Anal. Calcd for C₄₈H₇₁N₃O₁₉Mn₄: C, 47.50; H, 5.90; N, 3.46. Found: C, 47.30; H, 5.95; N, 3.50. IR spectrum (Nujol mull): 3400 (br, w), 2250 (w), 1614 (s), 1576 (s), 1559 (s), 1499 (s), 1400 (s), 1337 (s), 1321 (s), 1273 (s), 1242 (m), 1231 (m), 1175 (m), 1154 (m), 1113 (s), 1044 (m), 1020 (m), 932 (w), 879 (w), 830 (m), 811 (w), 789 (w), 764 (m), 750 (s), 675 (s), 654 (s), 612 (m), 530 (m), 419 cm⁻¹ (w). Magnetic moment (solid at 23 °C): 8.1 μ_B.

(NEt₄)[Mn₄O₂(O₂CMe)₇(hqN)₂·H₂O (2). This complex was prepared as for 1 using NEt₄Cl·H₂O and NEt₄MnO₄. The oily solid obtained after vacuum removal of solvent from the filtered reaction solution was purified by two cycles of dissolution in MeCN (15 mL), filtration, and precipitation with ether (60 mL). The final solid was washed with ether and dried in air. The yield was 67%. Anal. Calcd for C₄₀H₅₅N₃O₁₉Mn₄: C, 43.61; H, 5.03; N, 3.81. Found: C, 43.3; H, 5.3; N, 4.1. Magnetic moment (solid at 23 °C): 8.3 μ_B. The deuterioacetate version of complex 2, (NEt₄)[Mn₄O₂(O₂CCD₃)₇(hqN)₂], was prepared in 78% yield in an analogous manner employing Mn(O₂CCD₃)₂·4H₂O and HO₂-CCD₃. The hqn-d_{5,7} version of 2, (NEt₄)[Mn₄O₂(O₂CMe)₇(hqN-d_{5,7})₂], was prepared analogously in 29% yield.

(NMe₄)[Mn₄O₂(O₂CMe)₇(hqN)₂·4H₂O·MeCN (3). This complex was prepared as for 1 using NMe₄Cl and NMe₄MnO₄. The product was purified by two cycles of MeCN/ether reprecipitation. The final solid was washed with ether and dried in air. The yield was 76%. Anal. Calcd for C₃₈H₅₆N₄O₂₂Mn₄: C, 40.01; H, 4.95; N, 4.91. Found: C, 39.60; H, 5.25; N, 4.59. Magnetic moment (solid at 23 °C): 7.6 μ_B. The PPh₄⁺ and PPN⁺ salts were also prepared by procedures similar to those for 1-3; they were required solely for NMR studies and were therefore not analyzed or studied additionally.

(NMe₄)[Mn₄O₂(O₂CPh)₇(hqN)₂·H₂O·MeCN (4). To a slurry of Mn(O₂CPh)₂·2H₂O (1.34 g, 4.0 mmol), NMe₄Cl (0.58 g, 5.3 mmol), and HO₂CPh (0.89 g, 7.3 mmol) in MeCN (100 mL) was slowly added NMe₄MnO₄ (0.21 g, 1.1 mmol) in small portions. To the resulting brown solution was added a slurry of Na(hqN) (2.5 mmol) in H₂O (0.5 mL) and MeCN (5 mL). The brown solution was stirred for 25 min and filtered to remove a gray precipitate, and the filtrate was evaporated in vacuo to an oil. The oil was redissolved in CH₂Cl₂ (20 mL) and filtered to remove a white precipitate, and the filtrate was layered with 2:1 ether/hexanes (30 mL) to produce a brown powder that was collected by filtration. The solid was redissolved in CH₂Cl₂ (20 mL), the solution was filtered to remove a white precipitate, and the filtrate was layered with 3:1 ether/hexanes (40 mL). The light brown product was collected by filtration, washed with ether (3 × 10 mL), and dried in air. The yield was 1.79 g (94%). Anal. Calcd for C₇₃H₆₄N₄O₁₉Mn₄: C, 57.64; H, 4.24; N, 3.68. Found: C, 57.72; H, 4.94; N, 3.48. Magnetic moment (solid at 23 °C): 7.4 μ_B.

(NMe₄)[Mn₄O₂(O₂CMe)₇(Cl-hqN)₂·H₂O (5). This complex was prepared as for 1 using NMe₄Cl, NMe₄MnO₄, and 5-chloro-8-hydroxyquinoline. The product was purified by three cycles of dissolution in CH₂Cl₂, filtration, and precipitation by either ether or hexanes. The yield was 59%. Anal. Calcd for C₃₆H₄₅N₃O₁₉Cl₂Mn₄: C, 38.80; H, 4.07; N, 3.77. Found: C, 39.01; H, 4.73; N, 4.07. Magnetic moment (solid at 23 °C): 7.8 μ_B.

(NMe₄)[Mn₄O₂(O₂CPh)₇(hmp)₂ (6). To a stirred solution of Mn(O₂CPh)₂·2H₂O (1.33 g, 4.0 mmol) and HO₂CPh (0.12 g, 1.0 mmol) in MeCN (50 mL) was slowly added solid NMe₄MnO₄ (0.19 g, 1.0 mmol) in small portions to give a deep brown solution. To this was added 2-(hydroxymethyl)pyridine (0.33 g, 3.0 mmol) and NEt₃ (1.0 mL) to give a deep red solution. The reaction mixture was evaporated to dryness, and the resulting oily solid was dissolved in CH₂Cl₂ (30 mL). Ether (15 mL) and hexanes (10 mL) were added, and the solution was stored in the freezer overnight. The microcrystalline material was filtered out, washed with ether (2 × 10 mL), and dried in air. The yield was ca. 0.7 g (40% based on Mn). Dark brown crystals suitable for crystallography were grown by vapor diffusion of a 1:1 ether/hexanes mixture into a solution of the complex in MeCN. Anal. Calcd for C₆₅H₅₉N₃O₁₈Mn₄: C, 56.17; H, 4.28; N, 3.02. Found: C, 56.1; H, 4.5; N, 2.9. IR spectrum (KBr pellet): 3065 (w), 1611 (s), 1570 (s), 1487 (m), 1449 (m), 1393 (vs), 1285 (w), 1175 (m), 1144 (w), 1069 (m), 1051 (m), 1026 (m), 949

- (5) (a) Tsumura, N.; Ikeuchi, M.; Inoue, Y. *Biochim. Biophys. Acta* **1989**, *973*, 281. (b) Andreasson, L.-E. *Ibid.* **1989**, *973*, 465.
- (6) (a) Wang, S.; Folting, K.; Streib, W. E.; Schmitt, E. A.; McCusker, J. K.; Hendrickson, D. N.; Christou, G. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 305. (b) Li, Q.; Vincent, J. B.; Libby, E.; Chang, H.-R.; Huffman, J. C.; Boyd, P. D. W.; Christou, G.; Hendrickson, D. N. *Ibid.* **1988**, *27*, 1731. (c) Bashkin, J. S.; Chang, H.-R.; Streib, W. E.; Huffman, J. C.; Hendrickson, D. N.; Christou, G. *J. Am. Chem. Soc.* **1987**, *109*, 6502.
- (7) (a) Chan, M. K.; Armstrong, W. H. *J. Am. Chem. Soc.* **1991**, *113*, 5055. (b) Suzuki, M.; Hayashi, Y.; Munezawa, K.; Suenaga, M.; Senda, H.; Uehara, A. *Chem. Lett.* **1991**, 1929.
- (8) (a) Wiegardt, K.; Bossek, U.; Gebert, W. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 328. (b) Wiegardt, K.; Bossek, U.; Nuber, B.; Weiss, J.; Bonvoisin, J.; Corbella, M.; Vitols, S. E.; Girerd, J.-J. *J. Am. Chem. Soc.* **1988**, *110*, 7398. (c) Hagen, K. S.; Westmoreland, T. D.; Scott, M. J.; Armstrong, W. H. *Ibid.* **1989**, *111*, 1907.
- (9) Vincent, J. B.; Folting, K.; Huffman, J. C.; Christou, G. *Inorg. Chem.* **1986**, *25*, 996.
- (10) Libby, E. Ph.D. Thesis, Indiana University, 1990.
- (11) Addy, P.; Evans, D. F.; De Souza, Q. *Polyhedron* **1987**, *6*, 2003.

Table I. Crystallographic Data for Complexes 1-2CH₂Cl₂ and 6

parameter	1-2CH ₂ Cl ₂	6
formula	C ₅₀ H ₇₃ Cl ₄ Mn ₄ N ₃ O ₁₈	C ₆₁ H ₅₉ Mn ₄ N ₂ O ₂₄
<i>M_r</i>	1365.70	1423.89
space group	<i>P</i> 2 ₁ 2 ₁	<i>P</i> 1̄
temp, °C	-169	-172
<i>a</i> , Å	17.549 (3)	15.934 (3)
<i>b</i> , Å	23.801 (6)	16.896 (4)
<i>c</i> , Å	14.707 (3)	13.155 (3)
α, deg	90	106.00 (1)
β, deg	90	99.51 (1)
γ, deg	90	85.71 (1)
<i>V</i> , Å ³	6142.9 (12)	3356.1 (11)
<i>Z</i>	4	2
ρ _{calc} , g cm ⁻³	1.477	1.409
λ, Å	0.71069	0.71069
μ, cm ⁻¹	10.125	7.796
data coll'd	6° ≤ 2θ ≤ 45°	6° ≤ 2θ ≤ 45°
octants	+ <i>h</i> , + <i>k</i> , + <i>l</i>	+ <i>h</i> , ± <i>k</i> , ± <i>l</i>
tot. data	9004	9987
unique data	8039	8731
<i>R</i> _{merge}	0.046	0.127
obsd data	6691 ^a	3687 ^b
<i>R</i> (<i>R</i> _w), %	7.63 (6.95)	9.08 (8.87)

^a $F > 3.00\sigma(F)$. ^b $F > 2.33\sigma(F)$. ^c $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$, where $w = 1/\sigma^2(|F_o|)$.

(w), 839 (w), 720 (s), 677 (m), 650 (m), 615 (w), 465 cm⁻¹ (m). Magnetic moment (solid at 23 °C): 7.8 μ_B.

(NEt₄)[Mn₄O₂(O₂CPh)₇(hmp)₂] (7). This complex was prepared as for 6 using NEt₄MnO₄. The yield was ca. 60%. Anal. Calcd for C₆₉H₆₇N₃O₁₈Mn₄: C, 57.31; H, 4.67; N, 2.91. Found: C, 58.4; H, 4.0; N, 3.0. Magnetic moment (solid at 23 °C): 8.4 μ_B.

(NBu₄)[Mn₄O₂(O₂CPh)₇(hmp)₂] (8). This complex was prepared as for 6 using NBu₄MnO₄. The compound contains solvent of crystallization, and the initially shiny crystals decompose to a powder immediately after filtration. The yield was ca. 60%. Anal. Calcd for C₇₇H₈₃N₃O₁₈Mn₄: C, 59.35; H, 5.37; N, 2.70. Found: C, 58.6; H, 5.5; N, 2.5. Magnetic moment (solid at 23 °C): 8.1 μ_B.

Elemental Analysis and Spectroscopic Measurements. C, H, and N analyses were performed at the Microanalytical Laboratory, Department of Chemistry, University of Manchester (Manchester, U.K.), or Atlantic Microlab, Inc., Norcross, GA. Infrared (KBr or Nujol mull) spectra were recorded on a Nicolet 510P spectrophotometer. Cyclic voltammetry was performed using an IBM Model EC 225 voltammetric analyzer, a PAR Model 175 Universal Programmer, and a standard three-electrode assembly (glassy-carbon working, Pt-wire auxiliary, SCE reference electrode) with NBu₄PF₆ as the supporting electrolyte. No IR compensation was employed. Quoted *E*_{1/2} values are vs the ferrocene/ferrocenium couple under the same conditions. Conductivity measurements were performed with a YSI Model 31A conductance bridge and a YSI Model 3403 conductivity cell with a cell constant of 1.0 cm⁻¹. ¹H NMR spectra were recorded on a Varian XL-300 spectrometer. Chemical shifts are quoted on the δ scale (shifts downfield are positive). *T*₁ times were measured by the inversion recovery method. Magnetic susceptibilities were obtained using a JME magnetic susceptibility balance.

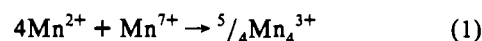
X-ray Crystallography. Data were collected on a Picker four-circle diffractometer at -169 °C (1-2CH₂Cl₂) and -172 °C (6); details of the diffractometry, low-temperature facilities, and computational procedures employed by the Molecular Structure Center are available elsewhere.¹² Data collection parameters are collected in Table I.

The structures were solved using direct methods phasing (MULTAN) and Fourier techniques and were refined by full-matrix least-squares. For both complexes, the non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were included in fixed idealized positions. The terminal C-atom in one of the *n*-butyl groups of 1-2CH₂Cl₂ is disordered. An initial examination of the structure of 6 revealed no sign of the NMe₄⁺ cation; besides the anion molecule, however, there is a void centered at [0.9865, 0.4688, 0.4941], with an effective diameter of 10.2 Å. Six additional peaks lie in this sphere; these peaks were assigned oxygen scattering factors and were included in the refinement with occupancies of 0.5 for the final cycles. It is considered possible that the NMe₄⁺ cation might be highly disordered and located in this void,

especially since elemental analysis and spectroscopic data confirm the formulation of 6 as the NMe₄⁺ salt in the bulk form. In fact, data were collected on the NEt₄⁺ salt (7) as well and the structure solved; to our surprise, this structure solution initially also failed to reveal the cation. After further investigation, however, one NEt₄⁺ molecule was located on an inversion center (i.e., disordered), and it is thought possible that the other required NEt₄⁺ might be on another inversion center or even delocalized between two inversion centers. Thus, we feel that the NMe₄⁺ cation in 6 is likely severely disordered. However, we cannot rule out the possible presence of a H₃O⁺ cation in the crystal chosen. Given that the problem is with the cation and not with the anion, and that this does not therefore affect the chemical conclusions of this work, we did not address this problem further. A final difference Fourier map for 6 phased on the non-hydrogen atoms revealed several peaks of intensity of 0.7 to 1.2 e/Å³, most of them in the general vicinity of the void. The final difference Fourier map for 1-2CH₂Cl₂ was essentially featureless, the largest peak being 1.0 e/Å³, in the vicinity of a Cl atom of a solvent molecule.

Results

Syntheses. In earlier reports, we have described two distinct procedures for the preparation of [Mn^{III}₄O₂(O₂CR)₇(L-L)₂]²⁻ (L-L = bpy, pic⁻) complexes that employ simple starting reagents.^{3a,b} One procedure involves the treatment of [Mn₃O(O₂CR)₆(py)₃]⁺ salts with bpy or Na(pic), the chelating ligand causing a structural and nuclearity change. The second procedure involves a comproportionation reaction between Mn^{II} and NBu₄MnO₄ in the presence of HO₂CR and L-L. Both procedures give high yields and are amenable to variations in the R group. For the present study, only the comproportionation reaction has been employed, and it has been found to successfully produce the desired materials. Thus, a MeCN reaction mixture containing Mn(O₂CMe)₂·4H₂O, NBu₄MnO₄, NBu₄Cl, HO₂CMe, and Na(hqn) gave a brown solution from which (NBu₄)[Mn₄O₂(O₂CMe)₇(hqn)₂] (1) was obtained with minimal workup and in good yield (68%) after recrystallization. The 4 Mn^{III} oxidation level of the product corresponds to that expected from the ca. 4:1 Mn^{II}:Mn^{VII} ratio employed in the comproportionation (eq 1). The corresponding



NEt₄⁺ (2) and NMe₄⁺ (3) salts can be obtained in a similar fashion using NEt₄MnO₄ and NMe₄MnO₄, respectively. The procedure has also been successfully employed for preparing the benzoate version, complex 4, the 5-chloro-8-hydroxyquinoline (Cl-hqnH) version, complex 5, the deuterioacetate version of complex 2, and the hqn-*d*_{5,7} version of complex 2.

The extension of the comproportionation procedure to hmpH was, however, not as straightforward. In fact, attempts to obtain pure salts of the anion [Mn₄O₂(O₂CMe)₇(hmp)₂]⁻ have failed, the reaction solution being dark brown and yielding a solid whose identity has yet to be established but which, on the basis of IR data, is clearly not the desired compound. Attempts to characterize this material are continuing. Better success was achieved with PhCO₂⁻, however; reaction mixtures consisting of Mn(O₂CPh)₂·2H₂O, PhCO₂H, NMe₄MnO₄, hmpH, and NEt₃ in MeCN produced deep red-brown solutions from which pure, crystalline complex 6 was obtained in 40% yield after recrystallization. Similar procedures were employed for the NEt₄⁺ (7) and NBu₄⁺ (8) salts. Although isolable, complexes 6-8 are not thermally very stable, as evidenced by the color change, upon gentle heating of MeCN solutions, from deep red-brown to dark brown, similar to the MeCO₂⁻ reaction mixture. IR and analytical data of obtained solid confirm the formation of a different and as yet uncharacterized product. We wondered whether the greater instability of 6-8 might be indicative of a product not structurally analogous to 1-5 or the previous bpy and pic⁻ complexes that are all thermally stable. Such a difference might result, for example, from the presence of the hmp⁻ alkoxide group; given the propensity of the latter to bridge, it was considered possible that a species with a bridging hmp⁻ unit might have resulted, either with

(12) Chisholm, M. H.; Folting, K.; Huffman, J. C.; Kirkpatrick, C. C. *Inorg. Chem.* 1984, 23, 1021.

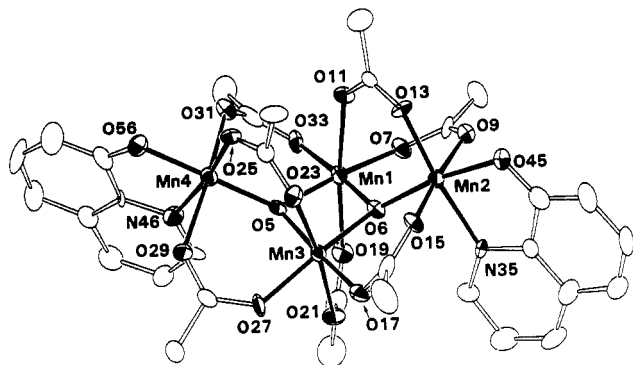


Figure 1. ORTEP representation of the tetranuclear anion in complex **1**·2CH₂Cl₂ at the 50% probability level, with the labeling scheme for the coordinating atoms only. Hydrogen atoms are omitted for clarity.

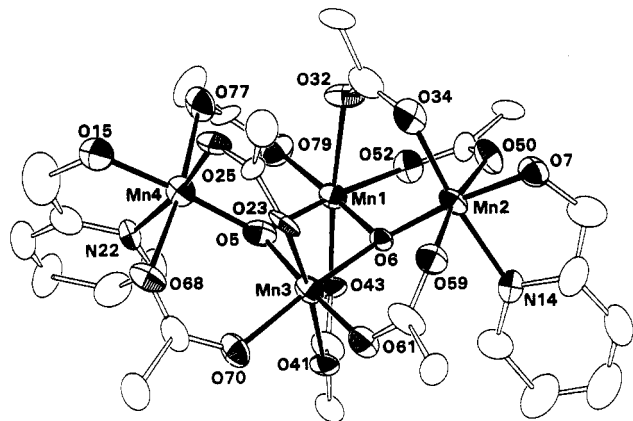


Figure 2. ORTEP representation of the tetranuclear anion in complex **6** at the 50% probability level, with labeling for the coordinating atoms only. To avoid congestion of the projection, hydrogen atoms are omitted and only one carbon atom of the benzoate ring is shown.

retention of a [Mn₄O₂] core (as seen by others with an alkoxide^{3f} or phenoxide^{3e} ligand and by us with salicylate^{13a}) or with the formation of a completely different core, as found when 2,2'-biphenoxide was employed and the products contained no oxide bridges.^{13b} Crystallography was thus considered essential, and subsequent structural characterization showed the hmp⁻ complexes to be analogous to **1**–**5** and the bpy and pic⁻ species;^{3a,b} i.e., a terminal alkoxide group was indeed present (vide infra). Thus, the confirmation of the structure of **6** extends to 4 the number of members of the family of [Mn₄O₂(O₂CR)₇(L-L)₂]²⁻ (L-L = chelate) complexes; the L-L chelate varies from N/N (bpy), N/O (carboxylate), and N/O (phenoxide) to N/O (alkoxide) and encompasses the O- and N-based amino-acid side-chain functionalities of Asp/Glu (carboxylate), Tyr (phenoxide), and His (imidazole; i.e., aromatic amine). This represents still a small, but now sufficient, number of related complexes on which to form some conclusions about the influence of the peripheral ligation.

Description of the Structures. ORTEP representations of the tetranuclear anions in complexes **1** and **6** are given in Figures 1 and 2, respectively. Crystallographic data for both structures are given in Table I, atomic coordinates of selected atoms are given in Tables II and III, and selected bond distances and angles for both structures are compared in Tables IV and V.

The anion in both complexes possesses a Mn₄O₂ core in which each oxygen atom is bridging to three manganese ions; the Mn₃O triangles are edge-sharing through Mn(1) and Mn(3), thus forming the familiar "butterfly" arrangement.³ The dihedral

Table II. Fractional Coordinates (×10⁴) and Isotropic Thermal Parameters (Å² × 10) for Selected Atoms of Complex **1**·2CH₂Cl₂

atom	x	y	z	B _{iso}
Mn(1)	5703 (1)	8316 (1)	8079 (1)	14
Mn(2)	4329 (1)	8955 (1)	9273 (1)	16
Mn(3)	4289 (1)	8360 (1)	7173 (1)	14
Mn(4)	5747 (1)	8689 (1)	5838 (1)	15
O(5)	5396 (4)	8342 (3)	6860 (4)	15
O(6)	4681 (4)	8476 (2)	8347 (4)	14
O(7)	6068 (4)	8206 (3)	9319 (5)	19
C(8)	5897 (6)	8472 (4)	10057 (6)	17
O(9)	5308 (4)	8757 (3)	10165 (4)	20
C(10)	6464 (6)	8415 (5)	10805 (8)	29
O(11)	5947 (4)	9232 (3)	8282 (5)	17
C(12)	5580 (6)	9633 (4)	8591 (6)	16
O(13)	4904 (4)	9617 (2)	8898 (5)	17
C(14)	5965 (7)	10199 (5)	8581 (8)	28
O(15)	3308 (4)	9181 (3)	8496 (4)	16
C(16)	2972 (6)	8906 (5)	7887 (7)	21
O(17)	3242 (4)	8456 (3)	7510 (4)	19
C(18)	2209 (8)	9091 (6)	7560 (9)	40
O(19)	5476 (4)	7411 (3)	8038 (5)	18
C(20)	4901 (7)	7183 (5)	7705 (8)	25
O(21)	4310 (5)	7443 (3)	7438 (4)	24
C(22)	4882 (8)	6552 (5)	7602 (9)	38
O(23)	4252 (4)	9245 (3)	6739 (4)	18
C(24)	4743 (6)	9580 (4)	6448 (7)	16
O(25)	5379 (4)	9449 (3)	6095 (5)	16
C(26)	4600 (6)	10195 (4)	6551 (8)	28
O(27)	3901 (4)	8141 (3)	5987 (4)	19
D(28)	4160 (6)	8214 (4)	5196 (7)	18
O(29)	4758 (4)	8471 (3)	4997 (5)	19
C(30)	3718 (7)	7925 (6)	4452 (8)	34
O(31)	6840 (4)	8767 (3)	6556 (4)	19
C(32)	7102 (6)	8393 (5)	7076 (8)	25
O(33)	6753 (4)	8150 (3)	7713 (4)	17
C(34)	7918 (7)	8226 (5)	6929 (8)	31
N(35)	3717 (4)	8306 (4)	9819 (5)	15
O(45)	3857 (4)	9354 (3)	10256 (5)	20
N(46)	6188 (5)	7941 (3)	5366 (6)	20
O(56)	6266 (4)	8976 (3)	4791 (5)	20

angle of the two edge-sharing triangular units is 135.5° (**1**) and 132.8° (**6**). The seven carboxylate ligands each bridge between two manganese ions. Unlike the central core in the triangular compounds [Mn₃O(O₂CR)₆(py)₃]⁺,⁹ the Mn₃O units are not perfectly planar. The oxygen atom is displaced 0.29–0.35 Å below the plane of the Mn₃ triangle. The "body"-Mn to μ₃-O distances are in the range of 1.875–1.907 Å (average 1.892 Å), whereas the "wingtip"-Mn to μ₃-O distances are very slightly shorter (1.857–1.882 Å) (average 1.868 Å). A much more pronounced reflection of the asymmetry is to be found in the bond angles at the triply bridging oxygen atoms: the Mn(1)–O(5)–Mn(3) and Mn(1)–O(6)–Mn(3) angles (95.7(3)–97.3(3)°) are notably smaller than the other Mn–O–Mn angles (122.6(6)–130.0(4)°), in contrast with the angles around the central oxygen atom in the triangular compounds [Mn₃O(O₂CR)₆(py)₃]⁺, which have approximately equal values of 120°.⁹ The central Mn(1)–Mn(3) distance is the shortest, ca. 2.82 Å, whereas the outer Mn–Mn distances are in the range 3.3–3.4 Å. The coordination number of each manganese ion is 6, and the 6 donor atoms are arranged in an axially elongated octahedral geometry, indicative of Jahn–Teller distorted high-spin Mn^{III} ions. The equatorial planes of Mn(2) and Mn(4) are nearly perpendicular to those of Mn(3) and Mn(1) (dihedral angles 75–80°). The chelate ligand oxygen atoms are coordinated trans to the O²⁻ ions at a distance of 1.9 Å; this bond distance indicates that the hydroxy groups are deprotonated. For alcohols, the mean bonding distance is 2.0 Å,^{14a} while, for alkoxides, an average of 1.9 Å is generally found.^{14b} Overall, the metal-containing ions of complexes **1** and **6** are

(13) Christmas, C.; Vincent, J. B.; Chang, H.-R.; Huffman, J. C.; Christou, G.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1988**, *110*, 823. (b) Schake, A. R.; Schmitt, E. A.; Conti, A. J.; Streib, W. E.; Huffman, J. C.; Hendrickson, D. N.; Christou, G. *Inorg. Chem.* **1991**, *30*, 3192.

(14) (a) Schake, A. R. Ph.D. Thesis, Indiana University, 1990. (b) Bouwman, E.; Lobkovsky, E. B.; Christou, G. *Inorg. Chem.*, in press.

Table III. Fractional Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($\text{\AA}^2 \times 10$) for Selected Atoms of Complex 6

atom	x	y	z	B_{iso}
Mn(1)	6979 (2)	2501 (2)	7325 (2)	21
Mn(2)	7515 (2)	537 (2)	7177 (2)	23
Mn(3)	6571 (2)	1962 (2)	9035 (2)	23
Mn(4)	7539 (2)	3738 (2)	9837 (2)	27
O(5)	6881 (7)	2944 (8)	8789 (9)	25
O(6)	6873 (7)	1493 (7)	7645 (8)	20
O(7)	8038 (8)	-504 (8)	6594 (10)	31
N(14)	6403 (9)	-130 (9)	6529 (11)	24
O(15)	8084 (8)	4632 (9)	10869 (10)	37
N(22)	6618 (9)	4651 (9)	9703 (11)	21
O(23)	7815 (8)	1895 (8)	10015 (9)	28
C(24)	8471 (11)	2313 (11)	10263 (14)	19
O(25)	8512 (7)	3022 (8)	10157 (10)	29
C(26)	9274 (13)	1935 (13)	10718 (16)	35
O(32)	8371 (8)	2272 (9)	7434 (10)	32
C(33)	8849 (12)	1735 (13)	7773 (14)	34
O(34)	8642 (8)	1010 (8)	7725 (11)	32
C(35)	9751 (11)	2003 (14)	8231 (15)	32
O(41)	5256 (7)	2103 (7)	8211 (9)	23
C(42)	5097 (12)	2451 (14)	7457 (15)	35
O(43)	5602 (7)	2673 (8)	6981 (9)	27
C(44)	4130 (11)	2594 (13)	7091 (14)	28
O(50)	7448 (8)	765 (8)	5631 (9)	27
C(51)	7236 (11)	1369 (11)	5267 (15)	23
O(52)	6934 (8)	2051 (8)	5762 (9)	27
C(53)	7318 (10)	1248 (13)	4096 (14)	25
O(59)	7421 (8)	141 (8)	8590 (10)	30
C(60)	6785 (12)	271 (13)	9110 (15)	30
O(61)	6333 (8)	912 (8)	9248 (10)	31
C(62)	6523 (12)	-413 (12)	9501 (15)	27
O(68)	6950 (8)	3575 (9)	11145 (10)	34
C(69)	6385 (13)	3101 (13)	11137 (14)	29
O(70)	6102 (8)	2483 (8)	10371 (9)	31
C(71)	5966 (13)	3226 (13)	12130 (13)	35
O(77)	8063 (8)	4100 (8)	8570 (10)	33
C(78)	7599 (11)	4118 (12)	7708 (15)	25
O(79)	7118 (8)	3572 (8)	7100 (10)	32
C(80)	7592 (16)	4893 (16)	7397 (19)	55

extremely similar to each other and to those of the bpy and pic complexes.^{3a,b} Except for the identity of the chelate ligand, the four ions are essentially superimposable.

Conductivity. Conductivity measurements were performed to see whether they support the composition of the obtained complexes as 1:1 salts. The complexes are adequately soluble in acetone, acetonitrile, and dichloromethane, and the measurements were carried out in each of these solvents. The obtained molar conductivity data are given in Table VI. It is difficult to list a range of conductivity values that 1:1 electrolytes should give for a particular solvent; in the literature, values are reported for various solvents that cover a wide range.¹⁵ A bulky cation or anion will considerably lower the conductivity of the electrolyte solution. For simple coordination compounds, a range of 80–200 $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ for 1:1 electrolytes in acetone is found.¹⁵ In MeCN, dissociation of the complexes or coordination of MeCN is often observed, and it is difficult to give a reliable range of conductivity data in this solvent. The conductivity data for complexes 1–3 and 6–8 are all in the same range (60–130 $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$), in agreement with their formulation as mono- NR_4^+ salts. All compounds are also readily soluble in CH_2Cl_2 ; however, the conductivity values are very low (2–40 $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$), indicating strong ion-pairing in this solvent. The conductivity of these complexes in MeCN or Me_2CO solution cannot be caused by ligand dissociation, as NMR studies have shown that the compounds maintain their structure in solution (vide infra).

Electrochemistry. The cyclic voltammograms (CV) of complexes 1–8 have been recorded in CH_2Cl_2 solution. The ferrocene/ferrocenium couple was used as a standard: $E_{1/2}$ for the ferrocene/ferrocenium couple under similar conditions (no IR compensation

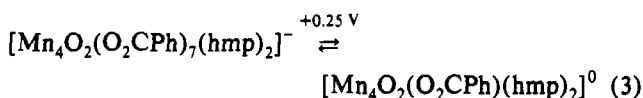
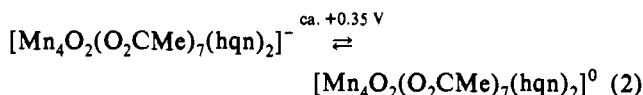
Table IV. Selected Bond Distances (\AA) for Complexes 1-2 CH_2Cl_2 and 6^a

1-2 CH_2Cl_2		6	
Mn(1)–O(5)	1.907 (6)	Mn(1)–O(5)	1.892 (12)
Mn(1)–O(6)	1.875 (7)	Mn(1)–O(6)	1.889 (12)
Mn(1)–O(7)	1.951 (7)	Mn(1)–O(52)	1.977 (12)
Mn(1)–O(11)	2.242 (7)	Mn(1)–O(32)	2.211 (13)
Mn(1)–O(19)	2.191 (7)	Mn(1)–O(43)	2.180 (12)
Mn(1)–O(33)	1.959 (7)	Mn(1)–O(79)	1.945 (12)
Mn(2)–O(6)	1.882 (6)	Mn(2)–O(6)	1.847 (12)
Mn(2)–O(9)	2.213 (7)	Mn(2)–O(50)	2.156 (11)
Mn(2)–O(13)	1.949 (6)	Mn(2)–O(34)	1.963 (14)
Mn(2)–O(15)	2.192 (6)	Mn(2)–O(59)	2.173 (11)
Mn(2)–O(45)	1.917 (7)	Mn(2)–O(7)	1.904 (13)
Mn(2)–N(35)	2.047 (8)	Mn(2)–N(14)	2.099 (15)
Mn(3)–O(5)	1.894 (7)	Mn(3)–O(5)	1.891 (12)
Mn(3)–O(6)	1.879 (6)	Mn(3)–O(6)	1.907 (11)
Mn(3)–O(17)	1.917 (7)	Mn(3)–O(61)	1.945 (13)
Mn(3)–O(21)	2.218 (6)	Mn(3)–O(41)	2.223 (12)
Mn(3)–O(23)	2.203 (7)	Mn(3)–O(23)	2.192 (12)
Mn(3)–O(27)	1.944 (6)	Mn(3)–O(70)	1.977 (12)
Mn(4)–O(5)	1.861 (6)	Mn(4)–O(5)	1.874 (13)
Mn(4)–O(25)	1.957 (6)	Mn(4)–O(25)	1.957 (12)
Mn(4)–O(29)	2.194 (7)	Mn(4)–O(68)	2.179 (13)
Mn(4)–O(31)	2.197 (7)	Mn(4)–O(77)	2.225 (13)
Mn(4)–O(56)	1.915 (7)	Mn(4)–O(15)	1.886 (13)
Mn(4)–N(46)	2.061 (8)	Mn(4)–N(22)	2.070 (14)
Mn(1)–Mn(2)	3.349 (4)	Mn(1)–Mn(2)	3.325 (7)
Mn(1)–Mn(3)	2.818 (4)	Mn(1)–Mn(3)	2.829 (7)
Mn(1)–Mn(4)	3.414 (4)	Mn(1)–Mn(4)	3.404 (7)
Mn(2)–Mn(3)	3.399 (4)	Mn(2)–Mn(3)	3.386 (7)
Mn(2)–Mn(4)	5.667 (4)	Mn(2)–Mn(4)	5.573 (7)
Mn(3)–Mn(4)	3.319 (4)	Mn(3)–Mn(4)	3.301 (7)

^a Although the labeling schemes differ, corresponding bonds for the two anions have been placed adjacently.

employed) occurred at 0.45 V vs SCE, and the peak separation was 180 mV. Complexes 1–8 all give similar results; Table VII contains pertinent data, and the CVs of 1 and 6 are shown in Figures 3 and 4, respectively. Both complexes display a quasi-reversible one-electron oxidation, at $E_{1/2}$ values of 0.35 V (1) and 0.25 V (6) vs ferrocene. The peak separations for both 1 and 6 are 170 mV. Additionally, complexes 1–8 display a second irreversible oxidation, at 0.81 V (1) and 0.95 V (6), which affects the first quasi-reversible oxidation. The reverse current for the first oxidation process is very sensitive to the switching potential, increasing markedly if the scan is reversed before the second oxidation. All complexes also display a broad, irreversible reduction at peak potentials between -1.1 and -1.6 V. Plots of i_p vs $v^{1/2}$ for the first oxidation were linear in the scan rate (v) range of 20–500 mV/s, indicating a diffusion-controlled process.

The quasi-reversible oxidation is assigned to oxidation to the 3 $\text{Mn}^{\text{III}}, \text{Mn}^{\text{IV}}$ level, as shown in eqs 2 and 3. The oxidation



potentials for complexes 1–8 can be compared to those found in CH_2Cl_2 for the corresponding couples in $[\text{Mn}_4\text{O}_2(\text{O}_2\text{CPh})_7(\text{bpy})_2]-(\text{ClO}_4)$ (9; 0.87 V)^{3a} and $(\text{NBu}^n_4)[\text{Mn}_4\text{O}_2(\text{O}_2\text{CPh})_7(\text{pic})_2]$ (10; 0.54 V)^{3b} as seen in Table VII. From the $E_{1/2}$ data, the following order of oxidation potentials is established: $\text{bpy} > \text{pic} > \text{hqn} > \text{hmp}$. The bpy complex is the hardest to oxidize, and the hmp complex, the easiest. As described earlier, the nature of the chelating ligand does not significantly affect the structures; however, the electrochemical results indicate a significant

Table V. Selected Bond Angles (deg) for Complexes 1-2CH₂Cl₂ and 6^a

1-2CH ₂ Cl ₂		6	
O(5)-Mn(1)-O(6)	82.39 (27)	O(5)-Mn(1)-O(6)	82.7 (5)
O(5)-Mn(1)-O(7)	174.2 (3)	O(5)-Mn(1)-O(52)	173.3 (5)
O(5)-Mn(1)-O(11)	99.11 (26)	Mn(1)-O(32)	100.4 (5)
O(5)-Mn(1)-O(19)	86.83 (26)	O(5)-Mn(1)-O(43)	87.4 (5)
O(5)-Mn(1)-O(33)	93.78 (27)	O(5)-Mn(1)-O(79)	93.6 (5)
O(6)-Mn(1)-O(7)	98.4 (3)	O(6)-Mn(1)-O(52)	97.2 (5)
O(6)-Mn(1)-O(11)	87.57 (25)	O(6)-Mn(1)-O(32)	89.6 (5)
O(6)-Mn(1)-O(19)	91.83 (26)	O(6)-Mn(1)-O(43)	92.0 (5)
O(6)-Mn(1)-O(33)	176.18 (28)	O(6)-Mn(1)-O(79)	176.0 (5)
O(7)-Mn(1)-O(11)	86.71 (26)	O(52)-Mn(1)-O(32)	86.3 (5)
O(7)-Mn(1)-O(19)	87.36 (26)	O(52)-Mn(1)-O(43)	85.9 (5)
O(7)-Mn(1)-O(33)	85.4 (3)	O(52)-Mn(1)-O(79)	86.6 (5)
O(11)-Mn(1)-O(19)	173.89 (25)	O(32)-Mn(1)-O(43)	172.2 (5)
O(11)-Mn(1)-O(33)	93.00 (26)	O(32)-Mn(1)-O(79)	89.4 (5)
O(19)-Mn(1)-O(33)	88.01 (26)	O(43)-Mn(1)-O(79)	89.5 (5)
O(6)-Mn(2)-O(9)	92.57 (27)	O(6)-Mn(2)-O(50)	90.8 (5)
O(6)-Mn(2)-O(13)	96.6 (3)	O(6)-Mn(2)-O(34)	97.3 (5)
O(6)-Mn(2)-O(15)	92.25 (26)	O(6)-Mn(2)-O(59)	91.9 (5)
O(6)-Mn(2)-O(45)	171.1 (3)	O(6)-Mn(2)-O(7)	172.5 (5)
O(6)-Mn(2)-N(35)	89.9 (3)	O(6)-Mn(2)-N(14)	90.8 (5)
O(9)-Mn(2)-O(13)	86.47 (28)	O(50)-Mn(2)-O(34)	94.3 (5)
O(9)-Mn(2)-O(15)	174.96 (26)	O(50)-Mn(2)-O(59)	169.9 (5)
O(9)-Mn(2)-O(45)	89.6 (3)	O(50)-Mn(2)-O(7)	87.3 (5)
O(9)-Mn(2)-N(35)	90.8 (3)	O(50)-Mn(2)-N(14)	86.3 (5)
O(13)-Mn(2)-O(15)	94.43 (27)	O(34)-Mn(2)-O(59)	95.0 (5)
O(13)-Mn(2)-O(45)	92.2 (3)	O(34)-Mn(2)-O(7)	90.0 (5)
O(13)-Mn(2)-N(35)	173.1 (3)	O(34)-Mn(2)-N(14)	171.9 (6)
O(15)-Mn(2)-O(45)	85.37 (28)	O(59)-Mn(2)-O(7)	88.7 (5)
O(15)-Mn(2)-N(35)	87.8 (3)	O(59)-Mn(2)-N(14)	84.0 (5)
O(45)-Mn(2)-N(35)	81.4 (3)	O(7)-Mn(2)-N(14)	81.9 (6)
O(5)-Mn(3)-O(6)	82.65 (28)	O(5)-Mn(3)-O(6)	82.3 (5)
O(5)-Mn(3)-O(17)	174.3 (3)	O(5)-Mn(3)-O(61)	175.5 (5)
O(5)-Mn(3)-O(21)	90.2 (3)	O(5)-Mn(3)-O(41)	90.7 (5)
O(5)-Mn(3)-O(23)	88.86 (28)	O(5)-Mn(3)-O(23)	89.8 (5)
O(5)-Mn(3)-O(27)	96.7 (3)	O(5)-Mn(3)-O(70)	96.9 (6)
O(6)-Mn(3)-O(17)	95.5 (3)	O(6)-Mn(3)-O(61)	94.6 (5)
O(6)-Mn(3)-O(21)	88.67 (26)	O(6)-Mn(3)-O(41)	86.6 (4)
O(6)-Mn(3)-O(23)	97.83 (25)	O(6)-Mn(3)-O(23)	99.9 (5)
O(6)-Mn(3)-O(27)	172.9 (3)	O(6)-Mn(3)-O(70)	172.0 (5)
O(17)-Mn(3)-O(21)	95.1 (3)	O(61)-Mn(3)-O(41)	92.4 (5)
O(17)-Mn(3)-O(23)	86.11 (27)	O(61)-Mn(3)-O(23)	87.6 (5)
O(17)-Mn(3)-O(27)	85.9 (3)	O(61)-Mn(3)-O(70)	86.6 (5)
O(21)-Mn(3)-O(23)	173.26 (25)	O(41)-Mn(3)-O(23)	173.5 (4)
O(21)-Mn(3)-O(27)	84.28 (26)	O(41)-Mn(3)-O(70)	85.5 (5)
O(23)-Mn(3)-O(27)	89.20 (26)	O(23)-Mn(3)-O(70)	88.0 (5)
O(5)-Mn(4)-O(25)	97.30 (28)	O(5)-Mn(4)-O(25)	98.2 (5)
O(5)-Mn(4)-O(29)	92.42 (27)	O(5)-Mn(4)-O(68)	94.1 (5)
O(5)-Mn(4)-O(31)	89.35 (27)	O(5)-Mn(4)-O(77)	90.1 (5)
O(5)-Mn(4)-O(56)	172.9 (3)	O(5)-Mn(4)-O(15)	172.7 (6)
O(5)-Mn(4)-N(46)	91.9 (3)	O(5)-Mn(4)-N(22)	91.6 (6)
O(25)-Mn(4)-O(29)	93.79 (27)	O(25)-Mn(4)-O(68)	91.5 (5)
O(25)-Mn(4)-O(31)	96.80 (27)	O(25)-Mn(4)-O(77)	95.4 (5)
O(25)-Mn(4)-O(56)	89.0 (3)	O(25)-Mn(4)-O(15)	89.1 (6)
O(25)-Mn(4)-N(46)	170.7 (3)	O(25)-Mn(4)-N(22)	170.2 (6)
O(29)-Mn(4)-O(31)	168.96 (26)	O(68)-Mn(4)-O(77)	171.3 (5)
O(29)-Mn(4)-O(56)	90.38 (28)	O(68)-Mn(4)-O(15)	85.4 (5)
O(29)-Mn(4)-N(46)	84.4 (3)	O(68)-Mn(4)-N(22)	87.3 (5)
O(31)-Mn(4)-O(56)	86.7 (3)	O(77)-Mn(4)-O(15)	89.5 (5)
O(31)-Mn(4)-N(46)	84.7 (3)	O(77)-Mn(4)-N(22)	85.0 (5)
O(56)-Mn(4)-N(46)	81.9 (3)	O(15)-Mn(4)-N(22)	81.1 (6)
Mn(1)-O(5)-Mn(3)	95.7 (3)	Mn(1)-O(5)-Mn(3)	96.9 (6)
Mn(1)-O(5)-Mn(4)	130.0 (4)	Mn(1)-O(5)-Mn(4)	129.3 (7)
Mn(3)-O(5)-Mn(4)	124.2 (4)	Mn(3)-O(5)-Mn(4)	122.6 (6)
Mn(1)-O(6)-Mn(2)	126.1 (3)	Mn(1)-O(6)-Mn(2)	125.1 (6)
Mn(1)-O(6)-Mn(3)	97.3 (3)	Mn(1)-O(6)-Mn(3)	96.4 (5)
Mn(2)-O(6)-Mn(3)	129.4 (3)	Mn(2)-O(6)-Mn(3)	128.2 (6)

^a See footnote a of Table IV.

influence of the chelating ligand on the redox properties. The large difference in potential on going from bpy to pic⁻ is intuitively consistent with the change in overall charge on the molecule on replacement of a neutral bpy ligand with an anionic pic⁻ ligand. The effect of anionic hqn⁻ and hmp⁻ on the electrochemistry must be explained by the donor properties of the ligands.

Table VI. Conductivity Data (Ω⁻¹ cm² mol⁻¹, at 23 °C) for Tetranuclear Butterfly Complexes in Acetonitrile and Acetone

compd	acetonitrile	acetone	compd	acetonitrile	acetone
1	94	100	6	90	63
2	129	112	7	94	82
3	114	87	8	81	83

Table VII. Cyclic Voltammetry Data for Tetranuclear Manganese Complexes

compd	E _{1/2} (V) ^a	E _{pa} (V) ^b	E _{pc} (V) ^c
1	0.35	0.81	-1.6
2	0.35	0.75	-1.5
3	0.36	0.84	-1.3
4	0.39	0.94	-1.1
5	0.41	0.93	-1.4
6	0.25	0.95	-1.5
7	0.25	0.90	-1.5
8	0.25	1.0	-1.5
9 ^{3a}	0.87		-0.16
10 ^{3b}	0.54	1.0	-0.8

^a Oxidation to 3 Mn^{III}/Mn^{IV}. ^b Oxidation to 2 Mn^{III}/2 Mn^{IV}. ^c Reduction to Mn^{II}/3 Mn^{III}.

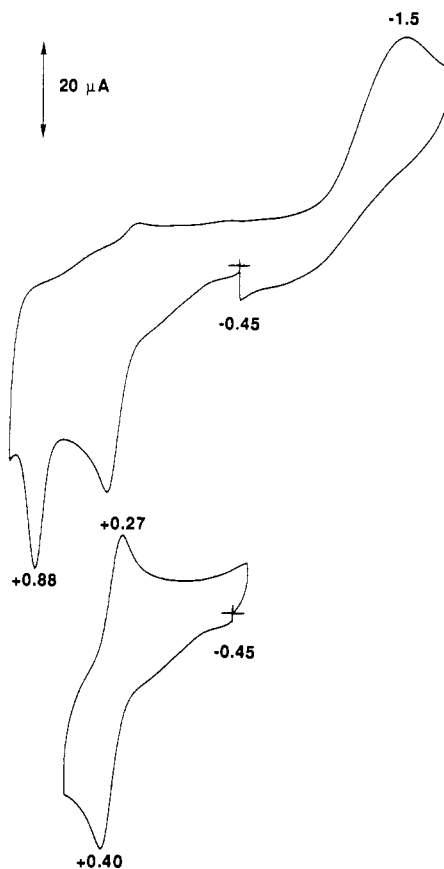


Figure 3. Cyclic voltammograms of complex 1 (ca. 0.5 mM) in the ranges +1.05 to -1.85 V (top) and +0.65 to -0.55 V (bottom). Potentials are quoted vs ferrocene (+0.45 V vs SCE under the same conditions).

Phenoxide and alkoxide coordination stabilizes the higher oxidation state(s) of complexes 1-8 with respect to carboxylate (pic⁻) coordination. The ordering for reduction potentials is the reverse of the oxidation ordering, as intuitively expected: hmp > hqn > pic > bpy. The hmp complex has the most negative potential; the bpy complex displays a quasi-reversible reduction to the neutral complex (3 Mn^{III}, Mn^{II}),^{3a} behavior not exhibited by the other complexes that display only irreversible features, and the reduced species Mn₄O₂(O₂CPh)₇(bpy)₂ (Mn^{II}, 3 Mn^{III}) has been isolated.

Proton NMR Spectroscopy. An NMR investigation of the [Mn₄O₂(O₂CMe)₇(hqn)₂]⁻ anion has been carried out to complement those previously reported for complexes 9 and 10^{3a,b} and

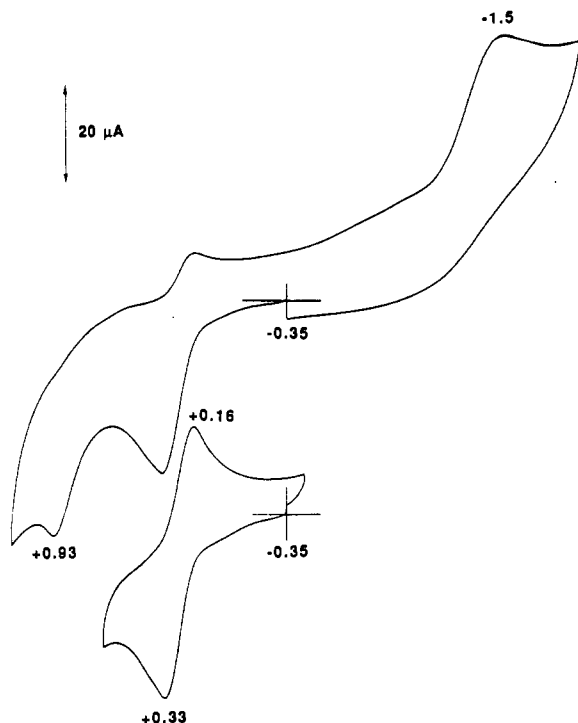


Figure 4. Cyclic voltammograms of complex **8** (ca. 1 mM) in the range +1.15 to -1.95 V (top) and +0.65 to -0.45 V (bottom). Potentials are quoted vs ferrocene (+0.45 V vs SCE under the same conditions).

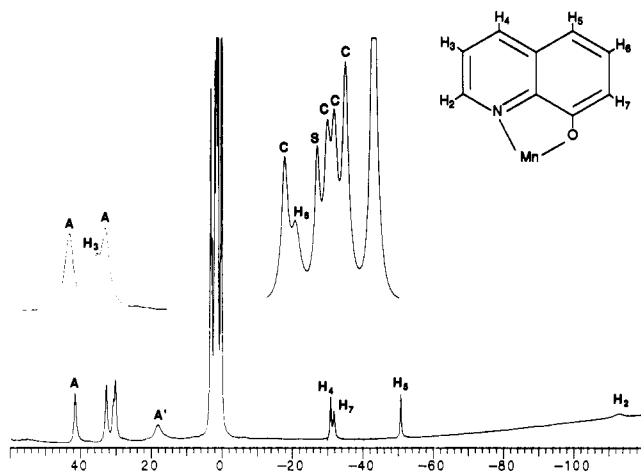


Figure 5. ^1H NMR spectrum of complex **1** in CD_3CN : A = acetate; H = hqn ring protons; C = NBu_4^+ protons; S = solvent protio impurities. The peak at 0 ppm is TMS. The spectrum inset at top left is an enlargement of the 36.0–25.6 ppm region; the inset at top right is of the 3.8 to -0.7 ppm region.

to probe the identity of species in solution. Complexes **1**–**3** all give essentially identical spectra, with differences only in the cation region. The NMR spectrum of complex **1** in CD_3CN is shown in Figure 5. As for **9** and **10**, the complex has a large magnetic moment at room temperature ($8.1 \mu_B$) and the proton resonances are thus very broadened and shifted from their diamagnetic positions. As can be seen in Figure 5, however, the resonances were clearly located and are well resolved except for the two partially resolved peaks at ca. 30 ppm. A total of 10 peaks are observed that can be assigned to anion groups. This number corresponds exactly to that expected for the idealized C_2 symmetry observed in the solid-state structure, four resonances from four inequivalent acetates and six resonances from the hqn protons. The spectrum thus supports retention of the solid-state structure in solution. The spectra were also recorded in CDCl_3 and $(\text{CD}_3)_2\text{SO}$ solution, and the data are included in Table VIII. As anticipated, the NMR spectrum in CDCl_3 solution was very

Table VIII. Proton NMR Data^a for $(\text{NBu}_4^+)[\text{Mn}_4\text{O}_2(\text{O}_2\text{CMe})_7(\text{hqn})_2]$ and Derivatives

resonance	CDCl_3	CD_3CN	$(\text{CD}_3)_2\text{SO}$	T_1 , ms	r , Å ^b
acetate (A) ^c	42.3	41.5	41.6	d	d
acetate (A) ^c	33.2	32.6	32.8	d	d
H ₃	30.1	30.7	30.1	4.9 ^e	5.1
acetate (A) ^c	29.2	30.1	29.3	d	d
acetate (A') ^{c,f}	17.2	18.0	18.2	d	d
H ₆	f	2.8	f	d	6.0
H ₄	-29.3 ^h	-31.1	-30.2	8.8	5.8
H ₇	-29.3 ^h	-32.1	-30.9	3.7	4.5
H ₅	-47.6	-51.0	-50.2	13.2	6.1
H ₂	ca. -108	ca. -113	ca. -111	i	3.2

^a Ca. 24 °C, referred to TMS in ppm with shifts downfield taken as positive. ^b Distance to the nearest Mn atom, calculated from the crystallographic data. ^c Not present in $(\text{NEt}_4)[\text{Mn}_4\text{O}_2(\text{O}_2\text{CCD}_3)_7(\text{hqn})_2]$. ^d Not determined. ^e Unique acetate bridging Mn(1) and Mn(3). ^f Not resolved from NBu_4^+ resonances. ^g CD_3CO_2^- complex. ^h Not resolved from each other. ⁱ Too small for accurate determination: estimated <1 ms.

similar to that in CD_3CN , but it was not clear whether the solid-state structure would be retained in the good donor solvent $(\text{CD}_3)_2\text{SO}$. Table VIII shows clearly, however, that the spectrum in this solvent is essentially identical to the others. We conclude that the tetranuclear anion maintains its structural integrity in solution, as previously found for the bpy and pic⁻ complexes **9** and **10**.^{3a,b}

The assignments in Table VIII were accomplished by a combination of selective substitutions and consideration of relative T_1 times and previous studies. The spectrum of the deuterioacetate version of **2** clearly identified the four acetate resonances as those that were absent; this also showed the unobscured hqn H₃ resonance, in contrast to Figure 5 where it is only just resolved from the acetate signals. The relative integrals establish the ca. 18 ppm resonance as due to the unique acetate bridging the central body-Mn atoms. For the hqn ring, the resonance at ca. -110 ppm is assigned to the H₂ proton, the most relaxation-broadened signal due to the fact that it is the closest to the paramagnetic centers. The H₅ proton was assigned to the ca. -50 ppm signal on the basis of its absence from the 5-Cl-hqn complex **5**. Both this peak and the one at ca. -32 ppm in Figure 5 were absent in the spectrum of the hqn-*d*_{5,7} derivative of **2**, establishing the latter as due to H₇. The remaining assignments (H₃, H₄, H₆) were made by comparison of T_1 times and distances (r) to the paramagnetic Mn centers and by reference to the complete assignments of $\text{Mn}(\text{hqn})_3$ protons available elsewhere.¹¹ Thus, we assign the ca. 30 ppm peak to H₃, the signal in the diamagnetic region (ca. 3 ppm) to H₆, and the ca. -31 ppm signal to H₄. This pattern is consistent with the spectrum of *mer*- $\text{Mn}(\text{hqn})_3$, where H₃ resonances were downfield, H₄, H₇, and H₅ were upfield, and H₆ was in the diamagnetic region; the very broad H₂ signals were in the 114–142 ppm range.¹¹ The assignments of the H₃, H₄, and H₆ proton resonances are less firm than for the other hqn protons but are in accord with observed T_1 times, r values, and previous studies that have concluded that the major contribution to the line widths in Mn^{III} complexes is dipolar broadening (proportional to r^{-6}).^{11,16}

The NMR spectra of the benzoate complex **4** and the benzoate/hmp complexes **6**–**8** are more complicated and more difficult to interpret than those of complexes **1**–**3** and **5**, due to the greater number of inequivalent proton types present and overlap of several resonances. As a result, we have limited our efforts at assignments of the hqn/acetate complexes.

(16) (a) Eaton, D. R. *J. Am. Chem. Soc.* **1965**, *87*, 3097. (b) LaMar, G. N.; Walker, F. A. *Ibid.* **1973**, *95*, 6950. (c) *NMR of Paramagnetic Molecules*; LaMar, G. N., Horrocks, W. DeW., Holm, R. H., Eds.; Academic Press: New York, 1973.

Discussion

It has been demonstrated in this work that the tetranuclear Mn carboxylates with the $[\text{Mn}_4\text{O}_2]^{8+}$ core are amenable to peripheral ligand variation, both in the identity of the carboxylate (alkyl vs aryl) and the chelate ligand. The structural parameters show insignificant variation. Interestingly, the alkoxide group in **6** remains terminal instead of becoming bridging with possible perturbation of the $[\text{Mn}_4\text{O}_2]$ core. Further, on the basis of room-temperature magnetic moments and, where available, similar data for liquid-helium temperatures,^{3a,b} the magnetic exchange interactions within the $[\text{Mn}_4\text{O}_2]^{8+}$ core are little affected by the peripheral ligation. This is also reflected in the NMR spectra, where the four acetate resonance positions are essentially unaffected by the chelate identity. In contrast, however, it is clear that the redox properties are particularly sensitive to the chelate. The systematic variation of chelate from N/N through N/O(alkoxide) has resulted in a change to the potential of the 4 $\text{Mn}^{\text{III}}/3 \text{Mn}^{\text{III}}, \text{Mn}^{\text{IV}}$ couple of more than 0.6 V. This is a surprisingly large figure given that ligation is changing at only two of the eighteen peripheral coordination sites. Variation of the seven carboxylates from acetate to benzoate causes, in contrast, only small (0.02–0.04 V) changes to this potential. It is clear that the donor properties of the chelate are responsible, with alkoxide being the strongest donor in accord with its greatest basicity.

At various Mn nuclearities, it has long been known that alkoxides will favor higher oxidation states and allow access to Mn^{IV} -containing products. In a series of papers, Pecoraro and co-workers have shown that higher oxidation state products and Mn^{IV} , in particular, are remarkably stabilized by alkoxide-containing ligands.^{17a–d} Thus, Mn^{IV} monomers and Mn^{IV}_2 dimers are readily formed by alkoxide (and/or phenoxide) functionalities, and α -hydroxy acid complexes of Mn^{IV} have been reported.^{17c} Alkoxides have also been involved in stabilizing Mn^{IV} in the "dimer-of-dimers" complexes ($2 \text{Mn}^{\text{III}}, 2 \text{Mn}^{\text{IV}}$) and also in linking the dimers together.⁷ Thus, we were not surprised by the direction of the changes in the oxidation potential. Further, Chakravorty recently studied the variation of reduction potential in a Mn^{IV} monomer as a function of carboxylate, phenoxide, or alkoxide ligation at two sites, the other four sites remaining constant.¹⁸

The total change on going from two carboxylates to two alkoxides was 620 mV, compared with 290 mV for **10** vs **6**, but note that the latter are tetranuclear (only two sites per 4 Mn altered). Since the chelate ligands are attached to the wingtip Mn atoms, it could be argued that the former affect the oxidation potential significantly primarily because the oxidation is centered at one of these Mn atoms (almost invariably, mixed $\text{Mn}^{\text{III}}/\text{Mn}^{\text{IV}}$ complexes are trapped valence). However, we resist this conclusion, because precedence with Mn would suggest that the higher oxidation states would be the sites bound to the greater number of oxide bridges, viz. the central or body Mn(1) and Mn(3). Isolation and structural characterization of an oxidized $[\text{Mn}_4\text{O}_2]$ complex will be required before this point may be addressed further.

From a biological viewpoint, the $[\text{Mn}_4\text{O}_2]^{8+}$ data suggest that redox potentials of a particular cluster type can be *significantly* altered by even low levels of peripheral ligand variation. This provides a ready means for fine-tuning redox properties of the WOC Mn_4 aggregate.

The Mn_4O_2 complexes were first-generation WOC models, and recent data on the biological system suggest that they are structurally noncongruent with the biological site.⁴ However, being readily prepared and amenable to ligand variation, they have proven useful starting points to increase our knowledge of Mn carboxylate chemistry. More recent work has extended $[\text{Mn}_4\text{O}_2]$ chemistry to completely O-based chelates;^{3c} these have proven very reactive and excellent springboards into new $[\text{Mn}_4\text{O}_3\text{Cl}]^{6+}$ chemistry.^{6a} This will be the subject of a future report.

Acknowledgment. We are indebted to Mr. F. B. Hulsbergen (Leiden University, Leiden, The Netherlands) for measuring some of the conductivity data. We thank Mr. E. B. Lobkovsky for crystallographic assistance. E.B. is grateful to NATO for a postdoctoral fellowship. This work was supported by the National Institutes of Health (Grant GM 39083).

Supplementary Material Available: Text giving crystallographic details, complete listings of atomic coordinates, isotropic and anisotropic thermal parameters, and bond lengths and angles, and figures showing atom labeling (40 pages). Ordering information is given on any current masthead page. Complete MSC structure reports (Nos. 91064 and 90329 for **1-2CH₂Cl₂** and **6**, respectively) are available on request from the Indiana University Chemistry Library.

(17) (a) Kessissoglou, D. P.; Butler, W. M.; Pecoraro, V. L. *J. Chem. Soc., Chem. Commun.* **1986**, 1253. (b) Kessissoglou, D. P.; Li, X.; Butler, W. M.; Pecoraro, V. L. *Inorg. Chem.* **1987**, *26*, 2487. (c) Li, X.; Lah, M. S.; Pecoraro, V. L. *Acta Crystallogr.* **1989**, *C45*, 1517. (d) Larson, E. J.; Pecoraro, V. L. *J. Am. Chem. Soc.* **1991**, *113*, 3810. (e) Saadeh, S. M.; Lah, M. S.; Pecoraro, V. L. *Inorg. Chem.* **1991**, *30*, 8.

(18) Dutta, S.; Basu, P.; Chakravorty, A. *Inorg. Chem.* **1991**, *30*, 4031.