

Tetranuclear Manganese Carboxylate Complexes with a Trigonal Pyramidal Metal Topology via Controlled Potential Electrolysis

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Controlled potential electrolysis (CPE) procedures are described that provide access to complexes with a $[\text{Mn}_4(\mu_3\text{-O})_3(\mu_3\text{-O}_2\text{CR})]^{6+}$ core ($3\text{Mn}^{\text{III}}, \text{Mn}^{\text{IV}}$) and a trigonal pyramidal metal topology, starting from species containing the $[\text{Mn}_4(\mu_3\text{-O})_2]^{8+}$ core (4Mn^{III}). $[\text{Mn}_4\text{O}_2(\text{O}_2\text{CMe})_6(\text{py})_2(\text{dbm})_2]$ (**6**): triclinic, $P1$, $a = 10.868(3)$ Å, $b = 13.864(3)$ Å, $c = 10.625(3)$ Å, $\alpha = 108.62(1)^\circ$, $\beta = 118.98(1)^\circ$, $\gamma = 89.34(2)^\circ$, $V = 1307$ Å³, $Z = 1$, $T = -131$ °C, $R (R_w) = 3.24 (3.70)\%$. $[\text{Mn}_4\text{O}_2(\text{O}_2\text{CPh})_6(\text{py})(\text{dbm})_2]$ (**8**): monoclinic, $P2_1/c$, $a = 14.743(6)$ Å, $b = 15.536(8)$ Å, $c = 30.006(13)$ Å, $\beta = 102.79(1)^\circ$, $V = 6702$ Å³, $Z = 4$, $T = -155$ °C, $R (R_w) = 4.32 (4.44)\%$. Both **6** and **8** contain a $[\text{Mn}_4\text{O}_2]^{8+}$ core; **8** only has one py group, the fourth Mn^{III} site being five-coordinate. $(\text{NBu}^n)_4[\text{Mn}_4\text{O}_2(\text{O}_2\text{CPh})_7(\text{dbm})_2]$ (**10**) is available from two related procedures. CPE of **10** at 0.65 V vs ferrocene in MeCN leads to precipitation of $[\text{Mn}_4\text{O}_3(\text{O}_2\text{CPh})_4(\text{dbm})_3]$ (**11**); similarly, CPE of **6** at 0.84 V in MeCN/CH₂Cl₂ (3:1 v/v) gives $[\text{Mn}_4\text{O}_3(\text{O}_2\text{CMe})_4(\text{dbm})_3]$ (**12**). Complex **11**: monoclinic, $P2_1/n$, $a = 15.161(3)$ Å, $b = 21.577(4)$ Å, $c = 22.683(5)$ Å, $\beta = 108.04(3)^\circ$, $V = 7056$ Å³, $Z = 4$, $T = -100$ °C, $R (wR2) = 8.63 (21.80)\%$. Complex **12**: monoclinic, $P2_1/n$, $a = 13.549(2)$ Å, $b = 22.338(4)$ Å, $c = 16.618(2)$ Å, $\beta = 103.74(1)^\circ$, $V = 4885$ Å³, $Z = 4$, $T = -171$ °C, $R (R_w) = 4.63 (4.45)\%$. Both **11** and **12** contain a $[\text{Mn}_4(\mu_3\text{-O})_3(\mu\text{-O}_2\text{CR})]$ core with a Mn_4 trigonal pyramid (Mn^{IV} at the apex) and the RCO_2^- bridging the Mn^{III} base. However, in **11**, the carboxylate is η^2, μ_3 with one O atom terminal to one Mn^{III} and the other O atom bridging the other two Mn^{III} ions, whereas in **12** the carboxylate is η^1, μ_3 , a single O atom bridging three Mn^{III} ions. Variable-temperature, solid-state magnetic susceptibility studies on **11** and **12** show that, for both complexes, there are antiferromagnetic exchange interactions between $\text{Mn}^{\text{III}}/\text{Mn}^{\text{IV}}$ pairs, and ferromagnetic interactions between $\text{Mn}^{\text{III}}/\text{Mn}^{\text{III}}$ pairs. In both cases, the resultant ground state of the complex is $S = 9/2$, confirmed by magnetization vs field studies in the 2.00–30.0 K and 0.50–50 kG temperature and field ranges, respectively.

Introduction

Manganese carboxylate cluster chemistry is of interest from a variety of viewpoints, including magnetic materials and bioinorganic chemistry. In the former area, it has been found that such clusters often possess large numbers of unpaired electrons,² making them attractive as potential precursors to molecule-based magnetic materials or as discrete, nanoscale magnetic particles in their own right.^{2–5} In the bioinorganic arena, a tetranuclear Mn cluster is an integral component in the

photosystem II reaction center of green plants, which is responsible for the light-driven oxidation of water to O₂ gas.^{6–9} This Mn₄-containing water oxidation complex (WOC) is the site of water binding, deprotonation, and oxidative coupling to O₂, but the precise mechanism remains unestablished. EXAFS studies have shown that a minimal structural fragment of the WOC is a $[\text{Mn}_2(\mu\text{-O})_2]$ unit with a $\text{Mn}\cdots\text{Mn}$ separation of ca. 2.7 Å, and it has been suggested that the WOC contains two such units in close proximity, although several structural possibilities for the complete Mn₄ unit still remain.⁷ During function, the WOC cycles through five oxidation levels labeled S₀–S₄, the highest spontaneously reductively eliminating O₂ and returning to S₀.⁶

In the last 15 years or so, a variety of tetranuclear clusters have been synthesized as inorganic models of the WOC.^{10–12} Most of these have some structural/spectroscopic/physical properties similar to those of the WOC, but no synthetic species

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currently seems to reproduce the properties of the WOC in all ways, and a satisfactory synthetic model of the WOC has thus yet to be obtained.

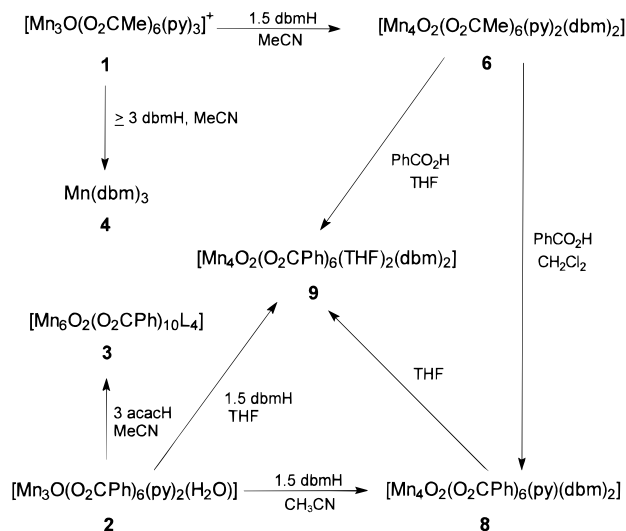
Although the mechanism of action of the WOC is uncertain, it is clear that the binding, deprotonation, and oxidation of substrate H₂O molecules are coupled to and driven by the sequentially increasing oxidation level of the WOC. For this reason, we have recently been exploring the oxidation reactions of certain synthetic Mn₄ complexes in our possession, seeking to identify the structural and reactivity consequences of oxidation, particularly in the presence of H₂O groups. Specifically, we have found that electrochemical oxidation of [Mn₄O₂]¹⁸⁺-containing species such as [Mn₄O₂(O₂CMe)₆(py)₂(dbm)₂] (4Mn^{III}; dbm⁻ is the anion of dibenzoylmethane) leads to a core transformation and a resultant increase in the O²⁻:Mn ratio from 2:4 to 3:4, suggesting incorporation and deprotonation of a H₂O molecule.

In this paper are described the preparation and solid-state structural and magnetochemical properties of the products of two such oxidation products, both of formula [Mn₄O₃(O₂CR)₄(dbm)₃]. In subsequent papers will be reported their solution properties and site-specific ligand substitution reactions.¹³

Experimental Section

Syntheses. All manipulations were performed under aerobic conditions, using materials as received, except where noted otherwise. Where dried solvents were required, they were distilled from CaH₂ (MeCN) or Na/benzophenone (Et₂O, THF). The complexes [Mn₃O(O₂CMe)₆(py)₃](ClO₄) (**1**),¹⁴ [Mn₃O(O₂CET)₆(py)₃](ClO₄),¹⁵ [Mn₃O(O₂CPh)₆(py)₂(H₂O)] (**2**),¹⁴ (NBuⁿ)₄[Mn₄O₂(O₂CPh)₆(H₂O)],¹⁶ and (NBuⁿ)₄[Mn₄O₂(O₂

Scheme 1



CPh)₆(dbm)]¹⁶ were prepared as described previously. The syntheses below are summarized in Scheme 1: acacH = acetylacetonate (pentane-2,4-dione); dbmH = dibenzoylmethane; picH = picolinic acid.

Na(dbm). A slurry of NaOH (1.06 g, 26.5 mmol) and dbmH (6.00 g, 26.8 mmol) in EtOH (45 mL) was stirred overnight to give a fine yellow precipitate. The solvent was removed in vacuo and the yellow solid washed with pentane (3 × 15 mL) to remove unreacted dbmH and dried in air. The yield was essentially quantitative. Anal. Calcd (found) for C₁₅H₁₁O₂Na: C, 73.16 (72.89); H, 4.50 (4.51); Na, 9.34 (9.38).

[Mn₆O₂(O₂CPh)₁₀L₄] (3). To a stirred yellow-brown solution of [Mn₃O(O₂CPh)₆(py)₃](ClO₄) (1.24 g, 1.00 mmol) in MeCN (30 mL) was added acacH (0.31 mL, 3.0 mmol) dropwise to give a deep brown solution. No immediate precipitate was observed, but slow formation of a fine orange-brown solid began soon after. When precipitation was judged complete (3 days), the orange-brown powder was collected by filtration, washed with MeCN, and dried in air. The complex was identified as [Mn₆O₂(O₂CPh)₁₀(py)₂(MeCN)₂] (**3a**) by IR spectral comparison with authentic material. The yield was 45–60%. Use of complex **2** also gives **3a** in comparable yield.

Recrystallization of complex **3a** from a DMF solution that was carefully layered with a 1:1 (v/v) solution of Et₂O/hexanes slowly gave large brown crystals that were collected by filtration, washed with Et₂O, and dried in air. The complex was identified as [Mn₆O₂(O₂CPh)₁₀(DMF)₄·C₆H₁₄] (**3b**) by IR, elemental analysis, and crystallography. Anal. Calcd (found) for C₈₈H₉₂N₄O₂₆Mn₆: C, 54.16 (54.15); H, 4.75 (4.5); N, 2.87 (3.15); Mn, 16.89 (16.6).

[Mn(dbm)₃] (4). To a stirred solution of complex **1**, [Mn₃O(O₂CMe)₆(py)₃](ClO₄) (0.87 g, 1.0 mmol), in MeCN (25 mL) was added solid dbmH (0.70 g, 3.1 mmol) in small portions. A brown precipitate was rapidly formed. After several hours, the solid was collected by filtration, washed with MeCN, and dried in air. Recrystallization from CH₂Cl₂/hexanes, CHCl₃/hexanes, or THF/Et₂O gave well-formed black crystals. The yield varies depending on the ratio of complex **1**:dbmH used. For example, when the ratio was 1:3, the yield was 20%; with the ratio changed to 1:5, the yield was 53%. Anal. Calcd (found) for C₄₅H₃₃O₆Mn: C, 74.58 (74.8); H, 4.60 (4.6); Mn, 7.58 (7.6). Electronic spectrum: λ_{max}, nm (ε_M, L mol⁻¹ cm⁻¹) in CH₂Cl₂: 368 (36 000), 284 (50 000).

[Mn(dbm)₂(py)₂](ClO₄) (5). Mn(ClO₄)₂·6H₂O (3.61 g, 10.0 mmol) and dbmH (5.94 g, 27.0 mmol) were dissolved in a solvent mixture comprising pyridine (15 mL) and EtOH (25 mL) to give an orange solution. To this solution was added solid NBuⁿ₄MnO₄ (1.26 g, 3.50 mmol) in small portions to give a green-brown solution and a brown crystalline precipitate. After several hours, the crystalline solid was

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collected by filtration, washed with EtOH and then Et₂O, and dried in air. The crude material was recrystallized from CH₂Cl₂/Et₂O. The overall yield was 25–30%. Anal. Calcd (found) for C₄₀H₃₂N₂O₈ClMn: C, 63.3 (63.2); H, 4.3 (4.4); N, 3.7 (3.5). Electronic spectrum in MeCN: 310 (38 800), 476 (2280), 510 (1810).

[Mn₄O₂(O₂CMe)₆(py)₂(dbm)] (6). To a stirred brown solution of complex **1** (0.87 g, 1.0 mmol) in MeCN (25 mL) was added solid dbmH (0.34 g, 1.5 mmol) in small portions to give a deep brown solution. After several minutes, a red-brown microcrystalline precipitate began to form. Approximately 24 h later, the precipitate was collected by filtration, washed with MeCN, and dried in vacuo; yield 75–80%. Recrystallization from hot MeCN yielded dark red-brown crystals in an overall yield of 60–70%. The crystallographic studies confirmed the title formulation, but dried samples analyzed for [Mn₄O₂(O₂CMe)₆(py)₂(dbm)]·H₂O, suggesting absorption of H₂O molecules from the atmosphere. Anal. Calcd (found) for C₅₂H₅₂N₂O₁₀Mn₄: C, 50.8 (50.5); H, 4.3 (4.1); N, 2.3 (2.1); Mn, 17.9 (17.7). Electronic spectrum in CH₂-Cl₂: 336 (35 660), 368 (29 630), 394 (18 360), 454 (2640), 488 (2100), 528 (1010). Selected IR data (cm⁻¹): 1610 (s), 1597 (s), 1587 (s), 1568 (s), 1533 (s), 1522 (s), 1487 (s), 1475 (s), 1441 (s), 1400 (s), 1350 (s), 1334 (s), 1321 (s), 1307 (m, sh), 1226 (m), 1070 (m), 1026 (m), 758 (m), 721 (s), 702 (m), 686 (m), 669 (s), 655 (s), 630 (s), 613 (s), 572 (m). When [Mn₃O(O₂CMe)₆(py)₃](py) was employed in place of complex **1**, the same product **6** was obtained in comparable yield, atmospheric O₂ presumably compensating for the lower oxidation state starting material.

[Mn₄O₂(O₂CET)₆(py)₂(dbm)] (7). To a stirred brown solution of [Mn₃O(O₂CET)₆(py)₃](ClO₄) (0.48 g, 0.50 mmol) in MeCN (20 mL) was added solid dbmH (0.19 g, 0.75 mmol) in small portions to give a deep brown solution. A red-brown microcrystalline solid began to precipitate within minutes. The next day, the solid was collected by filtration, washed with MeCN, and dried; yield 73–88%. The solid analyzed as 7·H₂O. Anal. Calcd (found) for C₅₈H₅₂N₂O₁₈Mn₄: C, 53.06 (53.2); H, 4.91 (4.8); N, 2.13 (2.1); Mn, 16.74 (16.5).

[Mn₄O₂(O₂CPh)₆(py)(dbm)] (8). **Method A.** A solution of complex **2** (1.10 g, 1.0 mmol) in MeCN (60 mL) was filtered, and to the stirred filtrate was added solid dbmH (0.34 g, 1.5 mmol) in small portions to give a homogeneous greenish-brown solution. This was allowed to stand undisturbed for 3 days. The resulting well-formed, essentially black crystals were collected by filtration, washed with MeCN, and dried in vacuo. The yield was 60–65%. No recrystallization was needed. Anal. Calcd (found) for C₇₇H₅₇NO₁₈Mn₄: C, 61.49 (61.65); H, 3.82 (3.85); N, 0.93 (0.90); Mn, 14.6 (14.4). Electronic spectrum in CH₂Cl₂: 338 (39 950), 368 (30 770), 390 (17 530), 458 (2180), 484 (1770), 506 (1165). Selected IR data (cm⁻¹): 1608 (s), 1589 (s), 1568 (s), 1522 (s), 1346 (s), 1321 (s), 1305 (s), 1223 (m), 1176 (s), 1070 (m), 1026 (m), 719 (s), 686 (s), 657 (s), 642 (s), 626 (m), 617 (m), 572 (m). When [Mn₃O(O₂CPh)₆(py)₃](ClO₄) was used in place of **2**, the same product was obtained in a comparable yield.

Method B. Solid benzoic acid (1.22 g, 10.0 mmol) was added to a stirred solution of complex **6** (0.60 g, 0.50 mmol) in CH₂Cl₂ (30 mL). The solution was stirred for a further 10 min to dissolve the acid, and the solution was then layered carefully with Et₂O (45 mL). After several days, the resulting black/brown crystals were collected by filtration, washed with Et₂O, and dried in air. The yield was 65–75%. IR spectral examination confirmed that the product was identical with that from method A.

[Mn₄O₂(O₂CPh)₆(THF)₂(dbm)] (9). **Method A.** To a brown solution of complex **2** (0.55 g, 0.50 mmol) in THF (25 mL) was added solid dbmH (0.19 g, 0.75 mmol) in small portions to give a homogeneous brown solution. The solution was filtered and the filtrate layered with Et₂O (40 mL) to give well-formed crystals of 9·2THF after several days. These were collected by filtration, washed with Et₂O, and dried in air. The yield was 35%. Anal. Calcd (found) for C₈₈H₈₄O₂₂-Mn₄: C, 61.7 (61.1); H, 4.9 (5.1); Mn, 12.8 (12.5). Electronic spectrum in CH₂Cl₂: 378 (31 730), 460 (3080), 488 (2620). Selected IR data (Nujol): 1610 (s), 1599 (s), 1589 (s), 1572 (s), 1523 (s), 1479 (s), 1348 (s), 1305 (s), 1223 (m), 1176 (m), 1157 (m), 1068 (m), 1045 (m), 1026 (m), 758 (m), 719 (s), 684 (s), 655 (s), 638 (s), 621 (s), 571 (m), 468 (m).

Method B. A red-brown solution of complex **8** in THF was layered with 1.5 volumes of Et₂O to give red-brown crystals after several days in 40–45% yield. The dried sample analyzed as 9·THF. Anal. Calcd (found) for C₈₄H₇₆O₂₁Mn₄: C, 61.5 (62.1); H, 4.7 (4.6); Mn, 13.4 (13.5).

Method C. A slurry of complex **6** (0.30 g, 0.20 mmol) and PhCO₂H (0.61 g, 5.0 mmol) in THF (25 mL) was stirred until all complex **6** had slowly dissolved to give a red-brown solution. The latter was then filtered and the filtrate layered with equivolume Et₂O/hexanes (1:1 v/v). The resulting red-brown crystals were collected by filtration, washed with hexanes, and dried in air. The yield was ~80%. IR spectral examination confirmed the identity of the product as complex **9**.

(NBu₄)[Mn₄O₂(O₂CPh)₇(dbm)] (10). **Method A.** To a stirred red-brown solution of (Buⁿ₄N)[Mn₄O₂(O₂CPh)₉(H₂O)] (0.40 g, 0.25 mmol) in CH₂Cl₂ (15 mL) was added solid Na(dbm) (0.125 g, 0.50 mmol). The solution color changed slowly from red-brown to brown over the course of 4 h. A precipitate (NaO₂CPh) was removed by filtration, and the filtrate was treated with Et₂O (15 mL) and hexanes (15 mL). After 2 days, a black crystalline product was isolated by filtration, washed with Et₂O, and dried in air; the yield was 60–70% of 10·1/4CH₂Cl₂. Anal. Calcd (found) for C_{95.25}H_{93.5}NO₂₀Cl_{0.5}Mn₄: C, 63.22 (63.26); H, 5.21 (5.23); N, 0.77 (0.75); Mn, 12.14 (12.23). Electronic spectrum in CH₂Cl₂: 452 (2390), 514 (1240). Selected IR data (Nujol): 1622 (s, sh), 1612 (s), 1589 (s), 1572 (s), 1533 (s), 1520 (s), 1321 (s), 1304 (s), 1224 (m), 1174 (m), 1157 (w, sh), 1068 (m), 1026 (m), 688 (m), 679 (s), 659 (s), 640 (s), 613 (m), 569 (w), 532 (w), 466 (w).

Method B. A slurry of (NBu₄)[Mn₄O₂(O₂CPh)₈(dbm)] (0.35 g, 0.20 mmol) and Na(dbm) (0.050 g, 0.20 mmol) in CH₂Cl₂ (15 mL) was stirred for 4 h. A precipitate (NaO₂CPh) was removed by filtration, and the brown filtrate was treated with Et₂O (15 mL) and hexanes (15 mL) to give a brown precipitate, which was collected by filtration, washed with Et₂O, and dried in air; the yield was 50%. The IR spectrum was identical to that of material prepared by method A.

Conversion of 10 to (NBu₄)[Mn₄O₂(O₂CPh)₇(pic)] (10). Complex 10·1/4CH₂Cl₂ (0.18 g, 0.10 mmol) and picolinic acid (0.028 g, 0.22 mmol) were dissolved in CH₂Cl₂ (10 mL) to give a red-brown solution. After 30 min, Et₂O (10 mL) and hexanes (20 mL) were added, causing the precipitation of a red-brown microcrystalline product, which was collected by filtration, washed with Et₂O, and dried in air. The yield of (NBu₄)[Mn₄O₂(O₂CPh)₇(pic)]₂, identified by IR spectral comparison with authentic material, was 85%. The same reaction but with Na(pic)⁻³/4H₂O in place of picH gave the same product in ~65% isolated yield.

[Mn₄O₃(O₂CPh)₄(dbm)] (11). **Method A.** (NBu₄)[Mn₄O₂(O₂CPh)₇(dbm)] (0.18 g, 0.10 mmol) and NBu₄ClO₄ (1.00 g, 2.92 mmol) were dissolved in MeCN (10 mL) to give a red-brown solution. The solution was electrolyzed at a potential of 0.65 V versus the ferrocene/ferrocenium (Fc/Fc⁺) couple (1.10 V vs SCE); a brown precipitate was slowly produced during the course of the electrolysis. After the electrolysis was complete (60–75 min), the solid was collected by filtration, washed with MeCN, and dried under vacuum; the yield was 30–45% (28–43 mg) based on dbm⁻ available. Recrystallization from CH₂Cl₂/hexanes gave dark red crystals susceptible to solvent loss. The crystallographic studies confirmed the formulation of the product as 11·3/2CH₂Cl₂; however, the dried solid analyzed as solvent-free. Anal. Calcd (found) for C₇₃H₅₃O₁₇Mn₄: C, 61.7 (61.4); H, 3.8 (3.8); Mn, 15.5 (15.3). Selected IR data (Nujol): 1599 (s), 1589 (s), 1558 (s), 1523 (vs), 1346 (s), 1323 (s), 1228 (m), 1174 (s), 1070 (m), 1026 (m), 943 (w), 844 (w), 760 (w), 719 (s), 686 (m), 648 (m), 621 (m), 603 (m), 578 (s), 540 (m), 509 (m), 470 (w).

Method B. The yield can be improved by adding dbmH to the electrolysis solution. Thus, dbmH (26.2 mg, 0.117 mmol) in MeCN (5 mL, 0.2 M NBu₄ClO₄) was added dropwise over 60 min to a solution of complex **10** (0.213 g, 0.117 mmol) in MeCN (20 mL, 0.2 M TBAClO₄) that was being electrolyzed at 0.65 V. The rate of addition of the dbmH solution was controlled to roughly parallel the rate of the oxidation of complex **10**. After the electrolysis was complete, the precipitate was collected by filtration, washed with MeCN, and dried under vacuum; the yield was 70–80%. The IR spectrum is identical to that of material prepared by method A.

[Mn₄O₃(O₂CMe)₄(dbm)] (12). A slurry of complex **6** (0.24 g, 0.20 mmol) in a solution of 0.2 M NBu₄ClO₄ or NBu₄PF₆ in dried MeCN/

Table 1. Crystallographic Data for Complexes **6**, **8**, **11**, and **12**

	6	8	11	12
formula	C ₅₂ H ₅₀ N ₂ O ₁₈ Mn ₄	C ₇₇ H ₅₇ NO ₁₈ Mn ₄	C _{74.5} H ₅₆ O ₁₇ Cl ₃ Mn ₄ ^a	C ₅₃ H ₄₅ O ₁₇ Mn ₄
fw, g/mol	1210.72	1504.05	1549.38 ^a	1173.68
space group	<i>P</i> 1	<i>P</i> ₂ / <i>c</i>	<i>P</i> ₂ / <i>n</i>	<i>P</i> ₂ / <i>n</i>
<i>a</i> , Å	10.868(3)	14.743(6)	15.161(3)	13.549(2)
<i>b</i> , Å	13.864(3)	15.536(8)	21.577(4)	22.338(4)
<i>c</i> , Å	10.625(3)	30.006(13)	22.683(5)	16.618(2)
α, deg	108.62(1)	90	90	90
β, deg	118.98(1)	102.79(1)	108.04(3)	103.74(1)
γ, deg	89.34(2)	90	90	90
<i>V</i> , Å ³	1307	6702	7056	4885
<i>Z</i>	1	4	4	4
<i>T</i> , °C	−131	−155	−100	−171
radiation, Å ^b	0.71069	0.71069	0.71069	0.71069
ρ _{calc} , g/cm ³	1.538	1.491	1.458	1.596
μ, cm ^{−1}	9.790	7.789	7.315	10.429
<i>R</i> (<i>R</i> _w or w <i>R</i> ₂)	3.24 (3.70) ^{c,d}	4.32 (4.44) ^{c,d}	8.63 (21.80) ^{c,e}	4.63 (4.45) ^{c,d}

^a Including 3/2 CH₂Cl₂ solvate molecules. ^b Graphite monochromator. ^c $R = 100 \sum ||F_o| - |F_c|| / \sum |F_o|$. ^d $R_w = 100 [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$ where $w = 1/\sigma^2(|F_o|)$. ^e $wR_2 = 100 [\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^4]^{1/2}$.

CH₂Cl₂ (3:1) (16 mL) was electrolyzed at 0.84 V (vs Fc/Fc⁺) under an argon atmosphere. During the electrolysis, a solution of dbmH (0.045 g, 0.20 mmol) in 0.2 M (NBu₄)(ClO₄) or (NBu₄)(PF₆) in dried MeCN (5 mL) was slowly added dropwise. When the electrolysis was complete (60–90 min), the precipitated solid was collected by filtration under anaerobic conditions, washed with MeCN, and dried in vacuo. The yield was typically 45–55%. Anal. Calcd (found) for C₅₃H₄₅O₁₇Mn₄: C, 54.24 (53.84); H, 3.86 (3.88). Selected IR data (Nujol): 1680 (m), 1597 (m), 1588 (m), 1568 (m), 1534 (s), 1522 (s), 1353 (s), 1339 (s), 1325 (s), 1254 (m), 1233 (m), 1076 (m), 1047 (w), 1024 (m), 945 (m), 785 (w), 772 (m), 731 (m), 704 (w), 693 (m), 648 (m), 612 (m), 590 (m), 573 (m), 544 (m), 523 (m), 473 (w). A CH₂Cl₂ solution of this solid was layered with MeCN and stored at 5 °C to give X-ray quality crystals. [Mn₄O₃(O₂CCD₃)₄(dbm)₃] can be prepared in an analogous manner using [Mn₄O₂(O₂CCD₃)₆(py)₂(dbm)₂].

X-ray Crystallography and Solution of Structures. Data were collected on complexes **6**, **8**, and **12** at the IUMSC, and on complex **11**·3/2CH₂Cl₂ at Emory University. Details of the diffractometry, low-temperature facilities, and computational procedures employed by the Molecular Structure Center are available elsewhere.¹⁷ Data collection parameters and structure solution details are listed in Table 1. The structures were solved by standard methods (MULTAN78 or SHELXL-92) and Fourier techniques and refined on *F* or *F*² by a full-matrix least-squares approach.

For complex **6**, a suitable crystal (0.25 × 0.30 × 0.35 mm) was affixed to a glass fiber using silicone grease and transferred to a goniostat, where it was cooled to −131 °C for characterization and data collection (+*h*, ±*k*, ±*l*; 6° ≤ 2θ ≤ 45°). A systematic search of a limited hemisphere of reciprocal space revealed no Laue symmetry or systematic absences. An initial choice of space group *P*1̄ was subsequently confirmed by the successful solution of the structure. Following intensity data collection, data processing gave a residual of 0.020 for 657 unique intensities which had been measured more than once. Four standards measured every 300 data showed no significant trends. No correction was made for absorption. After the non-hydrogen atoms had been located and partially refined, a difference Fourier map phased on the non-hydrogen atoms revealed most of the hydrogen atom positions. In the final cycles of least-squares refinement, the non-hydrogen atoms were varied with anisotropic thermal parameters and the hydrogen atoms were varied with isotropic thermal parameters. The final difference map was essentially featureless, the largest peak being 0.66 e/Å³.

For complex **8**, a suitable crystal (0.25 × 0.25 × 0.25 mm) was located and transferred to the goniostat as above for characterization and data collection (+*h*, +*k*, ±*l*; 6° ≤ 2θ ≤ 45°) at −155 °C. A systematic search of a limited hemisphere of reciprocal space located a set of diffraction maxima with Laue symmetry and systematic

absences corresponding to the unique monoclinic space group *P*₂/*c*. Subsequent solution and refinement of the structure confirmed this choice. The *R* for averaging of equivalent reflections measured more than once was 0.053. All non-hydrogen atoms were readily located and refined with anisotropic thermal parameters. A difference Fourier map phased on the non-hydrogen atoms revealed the location of some, but not all, hydrogen atoms. All hydrogen atom positions were therefore calculated using idealized geometries and *d*(C–H) = 0.95 Å. The hydrogen atoms were included as fixed atom contributors at these calculated positions for the final cycles of refinement. No absorption correction was performed. The final difference Fourier map was essentially featureless, with the largest peak being 0.53 e/Å³.

For complex **11**·3/2CH₂Cl₂, a suitable crystal (0.10 × 0.33 × 0.70 mm) was located while the sample was in mineral oil to prevent solvent loss and transferred to the goniostat as above for characterization and data collection (+*h*, +*k*, ±*l*; 1° ≤ 2θ ≤ 45°) at −100 °C. A systematic search of a limited hemisphere of reciprocal space located a set of diffraction maxima with Laue symmetry and systematic absences corresponding to monoclinic space group *P*₂/*n*, which was confirmed by the subsequent successful solution of the structure. The *R* for averaging equivalent reflections measured more than once was 0.0623. All non-hydrogen atoms were readily located and refined with anisotropic thermal parameters; the phenyl rings were included as rigid bodies with C–C bond lengths of 1.39 Å and C–C– angles of 120°. In the final cycles of least-squares refinement on *F*², the hydrogen atoms were included with isotropic thermal parameters. The final difference Fourier map was essentially featureless, the largest peak being 0.90 e/Å³.

For complex **12**, a suitable crystal (0.10 × 0.24 × 0.30 mm) was located and transferred to the goniostat as above for characterization and data collection (+*h*, +*k*, ±*l*; 6° ≤ 2θ ≤ 45°) at −171 °C. A systematic search of a limited hemisphere of reciprocal space yielded a set of reflections which exhibited monoclinic diffraction symmetry (2/*m*). The systematic extinction of *h*01 for *h* + 1 = 2*n* + 1 and of 0*k*0 for *k* = 2*n* + 1 identified the space group as *P*₂/*n*, confirmed by the subsequent solution and refinement of the structure. The *R* was 0.042 for the averaging of 5320 equivalent reflections measured more than once. Plots of the four standard reflections measured every 300 reflections showed no significant trends. No absorption correction was performed. All non-hydrogen atoms were readily located. Many of the hydrogen atoms were evident in a difference Fourier map phased on the non-hydrogen atoms. Hydrogen atoms were introduced in fixed, idealized positions, with a C–H distance of 0.95 Å and individual isotropic thermal parameters equal to 1.0 plus the isotropic equivalent of the parent atom; it should be noted that all of the methyl groups had at least one hydrogen atom located. The final difference map was essentially featureless, the largest peak being 0.42 e/Å³.

For all complexes, the values of discrepancy indices *R* and *R*_w, or *R* and w*R*₂, are included in Table 1.

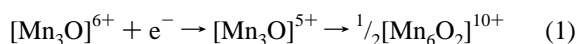
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Other Studies. Infrared and electronic spectra were recorded on Nujol mulls between KBr plates or in solution, respectively, using Nicolet 510P FTIR and Hewlett Packard 8452A spectrophotometers. Cyclic voltammograms (CV) and differential pulse voltammograms (DPV) were recorded on a BAS CV50W voltammetric analyzer: measurements were performed at room temperature using a glassy carbon working electrode, a Pt wire auxiliary electrode, and an SCE reference electrode. Potentials are quoted vs the ferrocene/ferrocenium couple under the same conditions. No IR compensation was employed. Controlled potential electrolyses were performed with a similar three-electrode system using a high surface area Pt basket electrode. The supporting electrolytes were $\text{NBu}^n_4\text{ClO}_4$ or $\text{NBu}^n_4\text{PF}_6$. ^1H NMR spectroscopy was performed using a Varian XL-300 instrument; chemical shifts are quoted using the δ scale (shifts downfield are positive). Variable-temperature magnetic susceptibility data were obtained with a Quantum Design MPMS5 SQUID susceptometer equipped with a 5.5 T magnet. Pascal's constants were used to estimate the diamagnetic correction for each complex, which was subtracted from the experimental susceptibility to give the molar magnetic susceptibility (χ_M).

Results

Syntheses. The transformations involving complexes **1**–**9** summarized below and the complex numbering scheme are presented for convenience in Scheme 1.

The reactions of the trinuclear complexes **1** and **2** with β -diketones represent an excellent entry point into tetranuclear Mn/O complexes with a predominantly or completely O-based ligation environment. AcacH itself is of little use, however, because it is too susceptible to oxidation by good oxidizing agents such as Mn^{III} ; the oxidation of acacH by metal ions has been well documented.¹⁸ Thus, treatment of **2** ($\text{Mn}^{\text{II}}, 2\text{Mn}^{\text{III}}$) with acacH leads to 45–60% isolated yields of the $4\text{Mn}^{\text{II}}, 2\text{Mn}^{\text{III}}$ complex $[\text{Mn}_6\text{O}_2(\text{O}_2\text{CPh})_{10}\text{L}_4]$ (**3**), where $4\text{L} = (\text{MeCN})_2(\text{H}_2\text{O})_2$ (**3a**) or $(\text{DMF})_4$ (**3b**) after recrystallization from DMF/ Et_2O /hexanes. As discussed previously,¹⁹ this conversion is rationalized as due to initial reduction of the $[\text{Mn}_3\text{O}]^{6+}$ core followed by dimerization (eq 1). Much more resistant to oxidation are



dbmH and dbm^- . Thus, reactions of **1** and **2** with dbmH lead to Mn^{III} products. In mapping out such reactions, it was found that $\text{dbmH}:[\text{Mn}_3\text{O}]$ ratios of 3:1 or greater give, as the main product, the mononuclear complex $\text{Mn}(\text{dbm})_3$ (**4**), or $[\text{Mn}(\text{dbm})_2(\text{py})_2](\text{ClO}_4)$ (**5**) if an excess of pyridine is present. With a $\text{dbmH}:[\text{Mn}_3\text{O}]$ ratio of 3:2 employing complex **1**, however, the product is $[\text{Mn}_4\text{O}_2(\text{O}_2\text{CMe})_6(\text{py})_2(\text{dbm})_2]$ (**6**), analogous to the earlier reactions with bpy^{10} or picH ,²⁰ which gave $[\text{Mn}_4\text{O}_2(\text{O}_2\text{CMe})_7(\text{bpy})_2]^+$ and $[\text{Mn}_4\text{O}_2(\text{O}_2\text{CMe})_7(\text{pic})_2]^-$ products, respectively. Similarly, the reaction of $[\text{Mn}_3\text{O}(\text{O}_2\text{CET})_6(\text{py})_3](\text{ClO}_4)$ with dbmH gives $[\text{Mn}_4\text{O}_2(\text{O}_2\text{CET})_6(\text{py})_2(\text{dbm})_2]$ (**7**). The analogous reaction with complex **2** gave essentially the same type of product, although the complex $[\text{Mn}_4\text{O}_2(\text{O}_2\text{CPh})_6(\text{py})(\text{dbm})_2]$ (**8**) contains only one py group, suggesting one Mn^{III} ion to be five-coordinate, a relatively unusual coordination number for Mn^{III} with such ligation; this was subsequently confirmed by a crystallographic study (vide infra). The cause may be steric congestion between the many Ph rings of hypothetical $[\text{Mn}_4\text{O}_2(\text{O}_2\text{CPh})_6(\text{py})_2(\text{dbm})_2]$. Recrystallization of **8** from THF, reaction

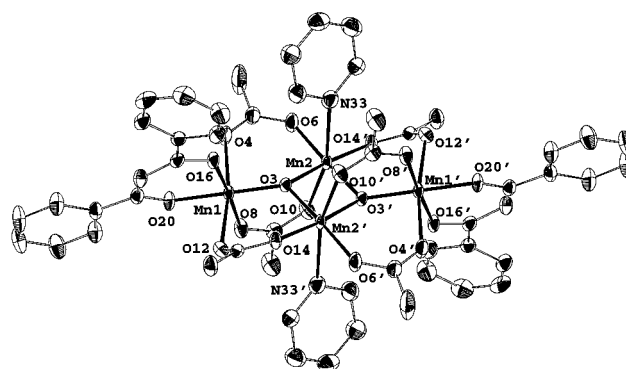
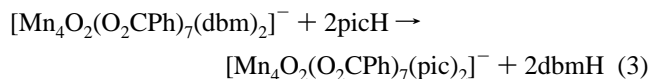
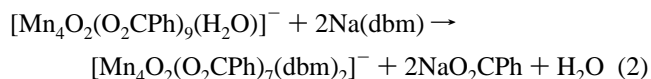


Figure 1. ORTEP representation at the 50% probability level of $[\text{Mn}_4\text{O}_2(\text{O}_2\text{CMe})_6(\text{py})_2(\text{dbm})_2]$ (**6**). Primed and unprimed atoms are related by an inversion center.

of **2** with dbmH in THF, or reaction of **6** with an excess of PhCO_2H in THF all gave $[\text{Mn}_4\text{O}_2(\text{O}_2\text{CPh})_6(\text{THF})_2(\text{dbm})_2]$ (**9**), containing two THF groups presumably due to the greater flexibility of THF vs rigid py groups. In contrast, reaction of **6** with PhCO_2H in CH_2Cl_2 gives **8**, again with a single py ligand. The reaction of **8** with an excess of py (25 equiv) caused core degradation, and the isolated product in 79% yield was the known $[\text{Mn}_6\text{O}_2(\text{O}_2\text{CPh})_{10}(\text{py})_4]$.¹⁹

The complex $(\text{NBu}^n_4)[\text{Mn}_4\text{O}_2(\text{O}_2\text{CPh})_7(\text{dbm})_2]$ (**10**) is not available from the reactions between dbmH and $[\text{Mn}_3\text{O}]$ species explored to date, but it can be conveniently prepared in high yield (60–70%) from the reaction of $\text{Na}(\text{dbm})$ with $(\text{NBu}^n_4)-[\text{Mn}_4\text{O}_2(\text{O}_2\text{CPh})_9(\text{H}_2\text{O})]$ or $(\text{NBu}^n_4)[\text{Mn}_4\text{O}_2(\text{O}_2\text{CPh})_8(\text{dbm})]$, the latter itself being obtained from the former as described elsewhere.¹⁶ This can be summarized in eq 2. Complex **10** will undergo chelate substitution with picolinic acid to give $[\text{Mn}_4\text{O}_2(\text{O}_2\text{CPh})_7(\text{pic})_2]^-$ in high yield (85%) (eq 3). It was of



interest to find the exchange to be so clean rather than the picolinate substituting at a benzoate position to give products containing both dbm^- and pic^- . The observed exchange is presumably facilitated by the protonation of dbm^- ($\text{p}K_a$ of $\text{dbmH} = 8.95$) by picH ($\text{p}K_a = 5.39$).²¹

Structures of Complexes 6 and 8. ORTEP representations of **6** and **8** are shown in Figures 1 and 2, respectively. Selected interatomic distances and angles are listed in Tables 2 and 3, respectively.

Complex **6** crystallizes in triclinic space group $P\bar{1}$ with the molecule lying on an inversion center. The $[\text{Mn}_4(\mu_3\text{-O})_2]^{8+}$ core thus contains an exactly planar Mn_4 parallelogram with $\text{Mn1}\cdots\text{Mn2}$ (3.308(1) Å) slightly shorter than $\text{Mn1}\cdots\text{Mn2}'$ (3.398(1) Å), consistent with two vs one MeCO_2^- bridges across these Mn_2 pairs. The $\mu_3\text{-O}^{2-}$ ions $\text{O3}'$ and O3 are 0.325 Å above and below their Mn_3 planes and give a central $[\text{Mn}_2\text{O}_2]$ rhomb with a short $\text{Mn2}\cdots\text{Mn2}'$ distance (2.875(1) Å). In addition to a total of six bridging MeCO_2^- groups, there are two chelating dbm^- groups at the two ends and two terminal py groups on the central Mn atoms, completing six-coordinate, near-octahedral

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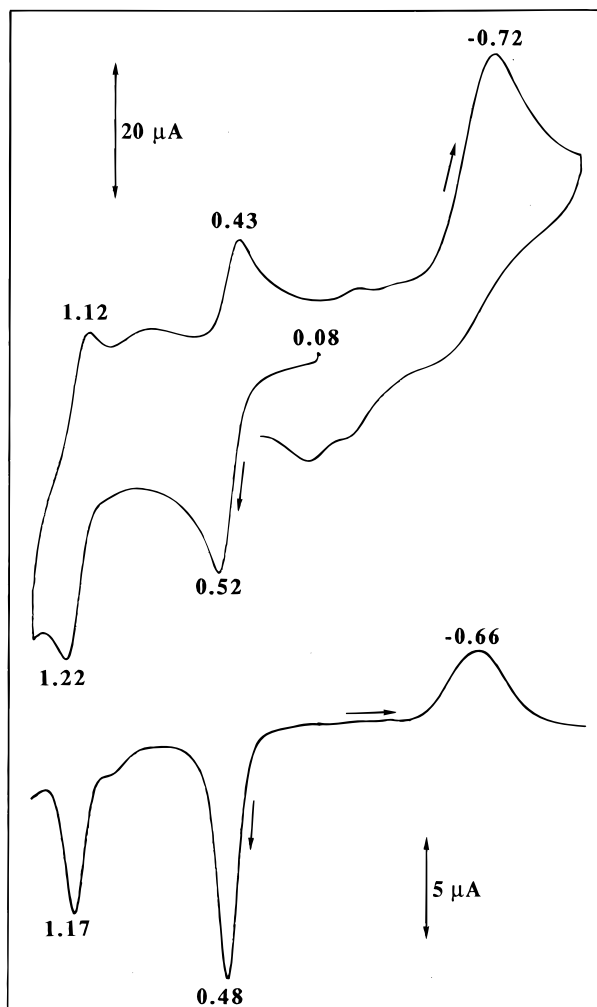
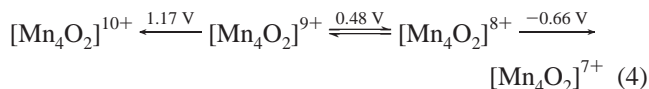


Figure 3. CV (top) and DPV (bottom) scans of $(\text{NBu}^n_4)[\text{Mn}_4\text{O}_2(\text{O}_2\text{-CPh})_7(\text{dbm})_2]$ (**10**) in MeCN; the scan rates were 100 and 5 mV/s, respectively. The potentials are given vs ferrocene under identical conditions.

to be a consequence of the competing J_{wb} and J_{bb} exchange parameters.

Electrochemical Studies. Complexes **6** and **8–10** were investigated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). Complex **10** displayed the most reversible behavior; its CV and DPV traces in MeCN are shown in Figure 3 and consist of an irreversible reduction at ~ -0.7 V and two oxidation processes at 0.48 and 1.17 V vs ferrocene, the first of which appears quasi-reversible in the DPV trace but not so in the CV scan. However, if the CV switching potential is set at a value less positive than for the second oxidation, the resulting CV scan (Figure 4) looks much more like that expected for a reversible process, with i_f/i_r approaching unity (i_f and i_r are the forward and reverse currents), and plots of peak current vs the square root of scan rate being linear in the 20–500 mV/s range, suggesting a diffusion-controlled process. The observed CV/DPV behavior suggests the electron-transfer series of eq 4,



with only the first oxidation appearing reversible on the electrochemical time scale. In contrast, the neutral complexes **6**, **8**, and **9** do not display behavior that approaches reversibility

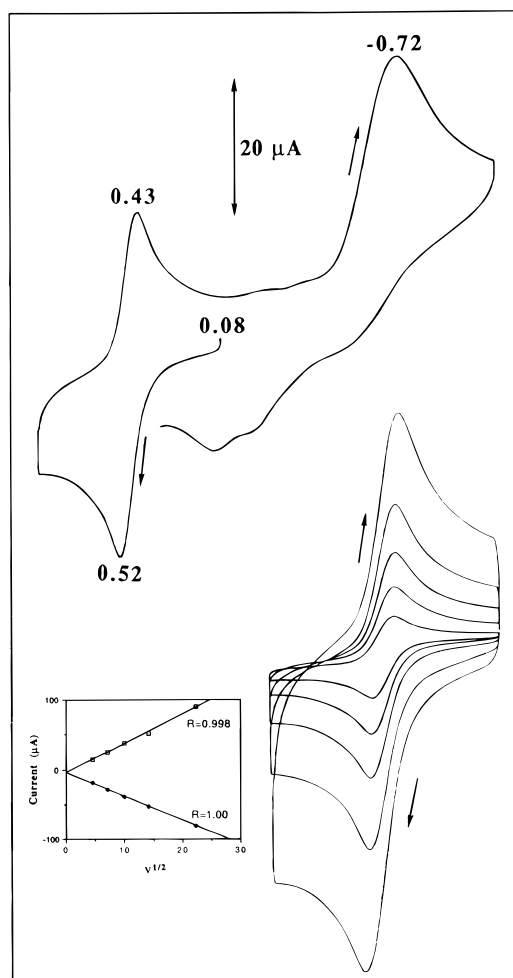
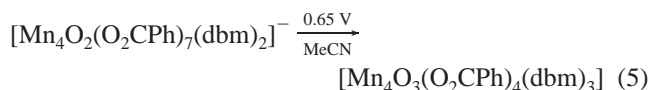


Figure 4. CV scan of complex **10** in MeCN showing only the first, reversible oxidation, and a scan rate (ν) dependence in the 20–500 mV/s range; the inset is a plot of the peak current vs $\nu^{1/2}$ for the forward and reverse scans.

on the electrochemical time scale. Figure 5 shows the results for **6**: an oxidation at 0.61 V is well observed (albeit broad) in the DPV but not the CV scan where the reverse wave is not particularly well formed. The reductions are again irreversible. In addition, there are several small features reproducibly seen in analytically pure material suggesting more than one species in solution, probably those formed by py dissociation and/or py/MeCN exchange. Additional, very irreversible oxidation processes are evident at more positive potentials than those shown in Figure 5. The main conclusion from the electrochemical studies is thus that the $[\text{Mn}_4\text{O}_2]^{8+}$ complexes display oxidation processes in MeCN but that only for **10** is reversibility by electrochemical criteria approached.

Controlled Potential Electrolysis (CPE) Studies. In order to probe the stability and/or reactivity of oxidized **10** on a longer time scale, CPE studies were performed in distilled MeCN under argon at a potential of 0.65 V. A solid was found to precipitate during the course of the electrolysis (60–75 min), and this was subsequently identified to be not the one-electron-oxidized version of **10**, but instead $[\text{Mn}_4\text{O}_3(\text{O}_2\text{CPh})_4(\text{dbm})_3]$ (**11**) (eq 5) in a yield of 10%. Consideration of the formulas of **10** and **11**



indicates that a one-electron oxidation from a 4Mn^{III} to a 3Mn^{III} ,

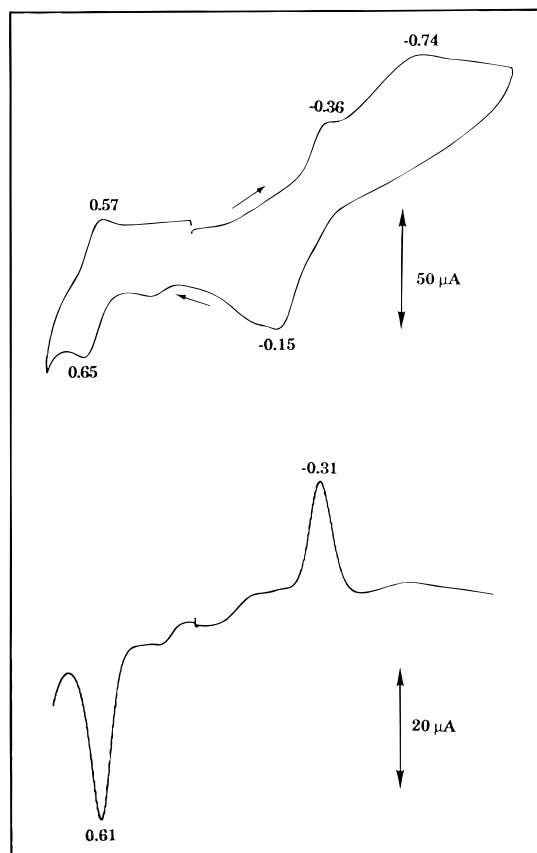


Figure 5. CV (top) and DPV (bottom) scans of $[\text{Mn}_4\text{O}_2(\text{O}_2\text{CMe})_6(\text{py})_2(\text{dbm})_2]$ (**6**) in MeCN at 100 and 5 mV/s, respectively. The potentials are vs ferrocene.

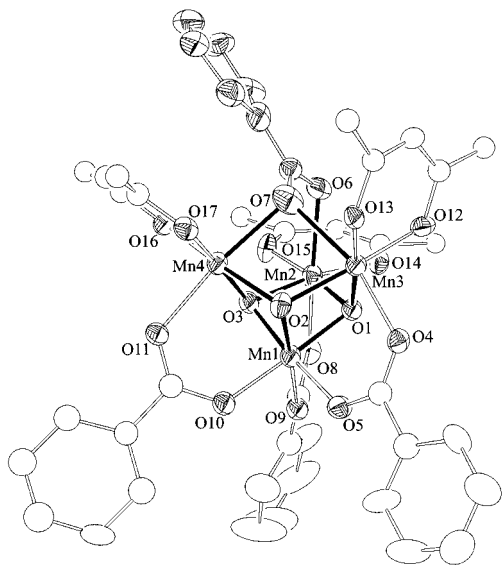


Figure 6. ORTEP representation at the 50% probability level of $[\text{Mn}_4\text{O}_3(\text{O}_2\text{CPh})_4(\text{dbm})_3]$ (**11**). For clarity, only the *ipso*-carbon atom of each dbm phenyl ring is shown.

Mn^{IV} product had indeed occurred, but that the product had increased $\text{O}^{2-}:\text{Mn}$ and $\text{dbm}:\text{Mn}$ ratios compared with **10**. Thus, the CPE was repeated under a variety of conditions and the following observations were made: (i) use of undistilled MeCN under air gave an increased yield of **11** of 20–30%; (ii) addition of dbmH to the filtrate from (i) resulted in precipitation of more **11** for a total yield of 40–45%, and (iii) addition of 1 equiv of dbmH to the solution *before* electrolysis gave a reduced yield of ~25%. These observations suggested that, upon oxidation

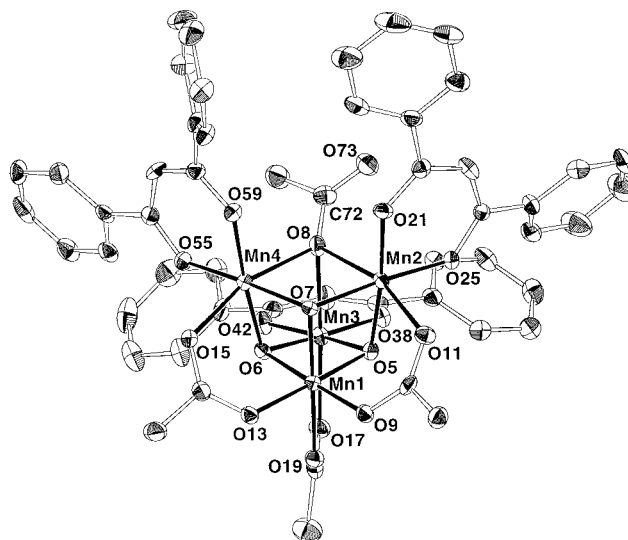
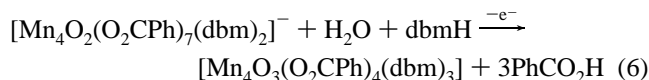
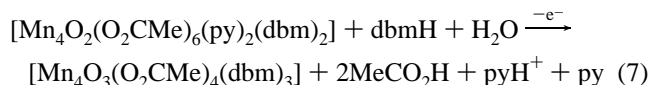


Figure 7. ORTEP representation at the 50% probability level of $[\text{Mn}_4\text{O}_3(\text{O}_2\text{CMe})_4(\text{dbm})_3]$ (**12**).

of **10**, the generated species reacts with H_2O and undergoes a rearrangement involving additional dbm incorporation to give **11**. This allowed the procedure described in the Experimental Section (method B) to be developed: the CPE was carried out in air in undistilled MeCN with 1 equiv of dbmH added dropwise over ~ 60 min; the yield under these conditions is reproducibly in the 70–80% range. The transformation may now be summarized as in eq 6.



Given these results for **10**, CPE was also performed on complex **6**. After preliminary experimentation, which showed that a mixed-solvent system ($\text{MeCN}:\text{CH}_2\text{Cl}_2 = 3:1$) was required to cause product precipitation and that this product was sensitive to subsequent reaction with air, the procedure under argon in the Experimental Section was developed that leads to isolation of $[\text{Mn}_4\text{O}_3(\text{O}_2\text{CMe})_4(\text{dbm})_3]$ (**12**) in 45–55% yield. This is summarized in eq 7. Thus, the CPE of **6** proceeds analogously to that of **10** with a similar (but *not* structurally identical) product (*vide infra*).



Structures of Complexes 11 and 12. ORTEP representations of **11** and **12** are shown in Figures 6 and 7, respectively, and selected interatomic distances and angles are listed in Tables 4 and 5.

Complex **11** crystallizes in monoclinic space group $P2_1/n$ with the Mn_4 molecule in a general position. The structure consists of a Mn_4 trigonal pyramid with the Mn^{IV} ion Mn(1) at the apex. The three vertical faces are capped by a $\mu_3\text{-PhCO}_2^-$ group ligated through both its O atoms, with O(6) terminal to Mn(2) and O(7) bridging Mn(3) and Mn(4). The latter O atom O(7) does not bridge symmetrically, however; Mn(3)–O(7) (2.267(10) Å) is noticeably longer than Mn(4)–O(7) (2.173(9) Å). This asymmetry is also seen in the resulting $\text{Mn}^{\text{III}}\cdots\text{Mn}^{\text{III}}$ separations: as expected, Mn(3) \cdots Mn(4) (3.197(2) Å) is the shortest, but the others are noticeably different, with Mn(2) \cdots Mn(3) (3.277(2) Å) much shorter than Mn(2) \cdots Mn(4) (3.432(2) Å).

Table 4. Selected Interatomic Distances (Å) and Angles (deg) for $[\text{Mn}_4\text{O}_3(\text{O}_2\text{CPh})_4(\text{dbm})_3]$ (**11**)

Mn(1)···Mn(2)	2.802(3)	Mn(2)···Mn(3)	3.277(2)
Mn(1)···Mn(3)	2.780(2)	Mn(2)···Mn(4)	3.432(2)
Mn(1)···Mn(4)	2.787(3)	Mn(3)···Mn(4)	3.197(2)
Mn(1)–O(2)	1.835(7)	Mn(3)–O(13)	1.900(7)
Mn(1)–O(1)	1.856(8)	Mn(3)–O(1)	1.912(7)
Mn(1)–O(3)	1.859(8)	Mn(3)–O(2)	1.942(7)
Mn(1)–O(5)	1.912(8)	Mn(3)–O(4)	2.169(7)
Mn(1)–O(10)	1.941(8)	Mn(3)–O(7)	2.267(10)
Mn(2)–O(15)	1.905(8)	Mn(4)–O(16)	1.894(7)
Mn(2)–O(1)	1.932(7)	Mn(4)–O(2)	1.920(7)
Mn(2)–O(14)	1.935(8)	Mn(4)–O(17)	1.924(7)
Mn(2)–O(13)	1.935(8)	Mn(4)–O(3)	1.947(7)
Mn(2)–O(6)	2.164(9)	Mn(4)–O(11)	2.134(8)
Mn(2)–O(8)	2.183(8)	Mn(4)–O(7)	2.173(9)
Mn(3)–O(12)	1.867(8)		
O(2)–Mn(1)–O(1)	86.2(3)	O(1)–Mn(3)–O(2)	81.7(3)
O(2)–Mn(1)–O(3)	84.7(3)	O(12)–Mn(3)–O(4)	99.5(3)
O(1)–Mn(1)–O(3)	83.0(3)	O(13)–Mn(3)–O(4)	93.9(3)
O(2)–Mn(1)–O(5)	92.5(3)	O(1)–Mn(3)–O(4)	88.8(3)
O(1)–Mn(1)–O(5)	92.7(3)	O(2)–Mn(3)–O(4)	86.3(3)
O(3)–Mn(1)–O(5)	175.0(3)	O(12)–Mn(3)–O(7)	99.2(3)
O(2)–Mn(1)–O(9)	177.3(4)	O(13)–Mn(3)–O(7)	80.3(3)
O(1)–Mn(1)–O(9)	96.5(3)	O(1)–Mn(3)–O(7)	96.1(3)
O(3)–Mn(1)–O(9)	95.9(3)	O(2)–Mn(3)–O(7)	75.8(3)
O(5)–Mn(1)–O(9)	87.1(3)	O(4)–Mn(3)–O(7)	160.5(3)
O(2)–Mn(1)–O(10)	93.6(3)	O(16)–Mn(4)–O(2)	171.3(3)
O(1)–Mn(1)–O(10)	178.2(3)	O(16)–Mn(4)–O(17)	92.4(3)
O(3)–Mn(1)–O(10)	95.2(3)	O(2)–Mn(4)–O(17)	95.6(3)
O(5)–Mn(1)–O(10)	89.0(3)	O(16)–Mn(4)–O(3)	92.0(3)
O(9)–Mn(1)–O(10)	83.7(3)	O(2)–Mn(4)–O(3)	80.1(3)
O(15)–Mn(2)–O(1)	172.7(4)	O(17)–Mn(4)–O(3)	174.7(3)
O(15)–Mn(2)–O(14)	93.2(4)	O(16)–Mn(4)–O(11)	90.2(3)
O(1)–Mn(2)–O(14)	94.0(3)	O(2)–Mn(4)–O(11)	93.4(3)
O(15)–Mn(2)–O(3)	93.7(3)	O(17)–Mn(4)–O(11)	88.5(3)
O(1)–Mn(2)–O(3)	79.0(3)	O(3)–Mn(4)–O(11)	88.6(3)
O(14)–Mn(2)–O(3)	170.6(3)	O(16)–Mn(4)–O(7)	97.8(3)
O(15)–Mn(2)–O(6)	81.5(4)	O(2)–Mn(4)–O(7)	78.5(3)
O(1)–Mn(2)–O(6)	100.1(4)	O(17)–Mn(4)–O(7)	91.9(3)
O(14)–Mn(2)–O(6)	83.9(4)	O(3)–Mn(4)–O(7)	90.4(3)
O(3)–Mn(2)–O(6)	103.3(3)	O(11)–Mn(4)–O(7)	171.9(3)
O(15)–Mn(2)–O(8)	85.6(4)	Mn(1)–O(1)–Mn(3)	95.1(3)
O(1)–Mn(2)–O(8)	94.2(3)	Mn(1)–O(1)–Mn(2)	95.4(3)
O(14)–Mn(2)–O(8)	84.8(3)	Mn(3)–O(1)–Mn(2)	116.9(4)
O(3)–Mn(2)–O(8)	89.5(3)	Mn(1)–O(2)–Mn(4)	95.8(3)
O(6)–Mn(2)–O(8)	162.3(4)	Mn(1)–O(2)–Mn(3)	94.7(3)
O(12)–Mn(3)–O(13)	90.8(3)	Mn(4)–O(2)–Mn(3)	111.7(4)
O(12)–Mn(3)–O(1)	92.0(3)	Mn(1)–O(3)–Mn(2)	95.2(3)
O(13)–Mn(3)–O(1)	175.7(3)	Mn(1)–O(3)–Mn(4)	94.1(3)
O(12)–Mn(3)–O(2)	171.4(3)	Mn(2)–O(3)–Mn(4)	124.2(4)
O(13)–Mn(3)–O(2)	95.1(3)	Mn(4)–O(7)–Mn(3)	92.1(4)

In contrast, the $\text{Mn}^{\text{III}}\cdots\text{Mn}^{\text{IV}}$ separations are much shorter at 2.780(2)–2.802(3) Å. The Mn^{III} ions Mn(2–4) are Jahn–Teller (JT) distorted, as expected for a high-spin d^4 ion in near-octahedral geometry, and the $\mu_3\text{-PhCO}_2^-$ group occupies positions on all three JT elongation axes (which again avoid O^{2-} ions). Three $\mu\text{-PhCO}_2^-$ groups bridging each $\text{Mn}^{\text{III}}/\text{Mn}^{\text{IV}}$ pair and a chelating dbm[−] group on each Mn^{III} complete ligation to the metals. The molecule has virtual C_s symmetry with the mirror plane passing through Mn(1), Mn(2), and O(2).

Complex **12** also crystallizes in monoclinic space group $P2_1/n$ with no crystallographically imposed symmetry on the Mn_4 molecule. The structure is very similar to that of **11** except that a $\mu_3\text{-MeCO}_2^-$ group now bridges the three Mn^{III} ions with only O(8). This $\eta^1:\mu_3$ -bridging mode leaves O(73) uncoordinated. The molecule is consequently more symmetric, with virtual C_{3v} symmetry if free rotation about O(8)–C(72) is assumed. The $\text{Mn}^{\text{III}}\cdots\text{Mn}^{\text{III}}$ separations are now in a much narrower range of 3.195(1)–3.213(1) Å, although the three $\text{Mn}^{\text{III}}\text{–O}(8)$ bonds show some small asymmetry, with Mn(4)–O(8) (2.320(3) Å)

Table 5. Selected Interatomic Distances (Å) and Angles (deg) for $[\text{Mn}_4\text{O}_3(\text{O}_2\text{CMe})_4(\text{dbm})_3]$ (**12**)

Mn(1)···Mn(2)	2.8113(10)	Mn(2)–O(25)	1.914(3)
Mn(1)···Mn(3)	2.7910(11)	Mn(3)–O(5)	1.935(3)
Mn(1)···Mn(4)	2.7941(11)	Mn(3)–O(6)	1.924(3)
Mn(1)–O(5)	1.866(3)	Mn(3)–O(8)	2.297(4)
Mn(1)–O(6)	1.860(3)	Mn(3)–O(17)	2.141(3)
Mn(1)–O(7)	1.876(3)	Mn(3)–O(38)	1.926(3)
Mn(1)–O(9)	1.923(3)	Mn(3)–O(42)	1.912(3)
Mn(1)–O(13)	1.961(3)	Mn(4)–O(6)	1.936(3)
Mn(1)–O(19)	1.941(3)	Mn(4)–O(7)	1.914(3)
Mn(2)–O(5)	1.936(3)	Mn(4)–O(8)	2.320(3)
Mn(2)–O(7)	1.954(3)	Mn(4)–O(15)	2.154(3)
Mn(2)–O(8)	2.281(3)	Mn(4)–O(55)	1.913(3)
Mn(2)–O(11)	2.173(3)	Mn(4)–O(59)	1.932(3)
Mn(2)–O(21)	1.918(3)		
O(5)–Mn(1)–O(6)	85.45(14)	O(8)–Mn(3)–O(38)	96.10(14)
O(5)–Mn(1)–O(7)	85.76(14)	O(8)–Mn(3)–O(42)	98.99(14)
O(5)–Mn(1)–O(9)	94.29(14)	O(17)–Mn(3)–O(38)	95.08(14)
O(5)–Mn(1)–O(13)	177.36(14)	O(17)–Mn(3)–O(42)	89.48(14)
O(5)–Mn(1)–O(19)	93.41(15)	O(38)–Mn(3)–O(42)	92.11(14)
O(6)–Mn(1)–O(7)	85.11(14)	O(6)–Mn(4)–O(7)	82.02(13)
O(6)–Mn(1)–O(9)	178.46(14)	O(6)–Mn(4)–O(8)	79.13(13)
O(6)–Mn(1)–O(13)	91.93(14)	O(6)–Mn(4)–O(15)	86.38(13)
O(6)–Mn(1)–O(19)	92.51(15)	O(6)–Mn(4)–O(55)	92.08(14)
O(7)–Mn(1)–O(9)	93.35(14)	O(6)–Mn(4)–O(59)	175.76(14)
O(7)–Mn(1)–O(13)	94.34(14)	O(7)–Mn(4)–O(8)	80.14(13)
O(7)–Mn(1)–O(19)	177.54(15)	O(7)–Mn(4)–O(15)	91.14(13)
O(9)–Mn(1)–O(13)	88.34(14)	O(7)–Mn(4)–O(55)	173.67(15)
O(9)–Mn(1)–O(19)	89.02(14)	O(7)–Mn(4)–O(59)	94.36(14)
O(13)–Mn(1)–O(19)	86.39(14)	O(8)–Mn(4)–O(15)	163.95(13)
O(5)–Mn(2)–O(7)	81.74(13)	O(8)–Mn(4)–O(55)	96.54(13)
O(5)–Mn(2)–O(8)	80.26(13)	O(8)–Mn(4)–O(59)	98.13(13)
O(5)–Mn(2)–O(11)	87.83(13)	O(15)–Mn(4)–O(55)	90.78(14)
O(5)–Mn(2)–O(21)	173.91(14)	O(15)–Mn(4)–O(59)	95.93(14)
O(5)–Mn(2)–O(25)	92.89(14)	O(55)–Mn(4)–O(59)	91.45(14)
O(7)–Mn(2)–O(8)	80.32(13)	Mn(1)–O(5)–Mn(2)	95.35(15)
O(7)–Mn(2)–O(11)	86.48(13)	Mn(1)–O(5)–Mn(3)	94.49(14)
O(7)–Mn(2)–O(21)	92.81(14)	Mn(2)–O(5)–Mn(3)	111.23(16)
O(7)–Mn(2)–O(25)	174.63(14)	Mn(1)–O(6)–Mn(3)	95.02(15)
O(8)–Mn(2)–O(11)	163.32(12)	Mn(1)–O(6)–Mn(4)	94.76(14)
O(8)–Mn(2)–O(21)	96.21(14)	Mn(3)–O(6)–Mn(4)	112.64(15)
O(8)–Mn(2)–O(25)	98.82(13)	Mn(1)–O(7)–Mn(2)	94.43(15)
O(11)–Mn(2)–O(21)	94.57(14)	Mn(1)–O(7)–Mn(4)	95.00(14)
O(11)–Mn(2)–O(25)	93.36(14)	Mn(2)–O(7)–Mn(4)	11.41(16)
O(21)–Mn(2)–O(25)	92.56(14)	Mn(2)–O(8)–Mn(3)	88.49(12)
O(5)–Mn(3)–O(6)	81.84(14)	Mn(2)–O(8)–Mn(4)	87.98(12)
O(5)–Mn(3)–O(8)	79.88(13)	Mn(2)–O(8)–C(72)	122.3(3)
O(5)–Mn(3)–O(17)	90.35(14)	Mn(3)–O(8)–Mn(4)	88.18(11)
O(5)–Mn(3)–O(38)	94.63(14)	Mn(3)–O(8)–C(72)	124.2(3)
O(5)–Mn(3)–O(42)	173.24(15)	Mn(4)–O(8)–C(72)	132.8(3)
O(6)–Mn(3)–O(8)	79.94(13)	Mn(1)–O(9)–C(10)	125.7(3)
O(6)–Mn(3)–O(17)	88.39(13)	O(8)–C(72)–C(73)	122.8(5)
O(6)–Mn(3)–O(38)	175.08(14)	O(8)–C(72)–C(74)	116.1(4)
O(6)–Mn(3)–O(42)	91.40(14)	O(73)–C(72)–C(74)	121.1(5)
O(8)–Mn(3)–O(17)	165.69(13)		

being slightly longer than the others (2.281(3) and 2.297(4) Å). The $[\text{Mn}_4\text{O}_3(\mu_3\text{-O}_2\text{CR})]$ cores of **11** and **12** are conveniently compared in Figure 8, where it can be seen that the $[\text{Mn}_4\text{O}_3]$ positions are nearly superimposable.

Complexes **11** and **12** thus possess structures that represent new additions to the near-isostructural family of $[\text{Mn}_4\text{O}_3\text{X}(\text{O}_2\text{-CMe})_3(\text{dbm})_3]$ ($X = \text{Cl}, \text{Br}$) species,¹² the only difference between them being the identity of X. Complex **11** does differ in the bidentate nature of its $\mu_3\text{-PhCO}_2^-$, which begs the question why. It appears that the origin of the different bridging modes in **11** vs **12** is steric: in Figure 9 are shown space-filling stereoviews down the C_3 rotation axis of the $[\text{Mn}_4\text{O}_3]$ core (i.e., through the Mn^{IV} ion). The dbm groups form a concave cavity in which resides the $\mu_3\text{-RCO}_2^-$ group. For the latter to convert to a $\eta^1:\mu_3$ -mode, its Ph ring would have to tilt by $\sim 60^\circ$, but this would be unfavorable due to steric interactions with the dbm groups. In contrast, the smaller MeCO_2^- group can bind $\eta^1:\mu_3$ without steric problems. It could, of course, also bind like the PhCO_2^- group in **11**, and this suggests that, other things

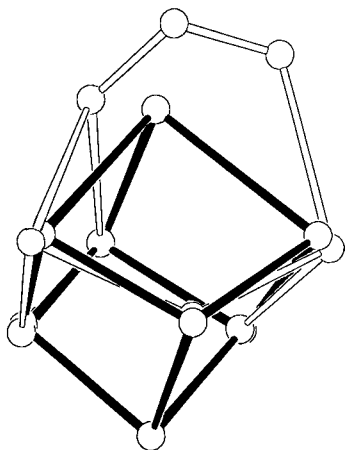


Figure 8. Comparison of the cores of **11** (open lines) and **12** (black lines) showing the near superimposability of the $[\text{Mn}_4(\mu_3\text{-O})_3]$ portions. For **11**, the PhCO_2^- phenyl group is omitted, while for **12** only the metal-bound MeCO_2^- O atom is shown.

being equal, the $\eta^1\text{:}\mu_3$ -binding mode for a RCO_2^- group is the favored one.

Magnetochemistry of Complexes 11 and 12. Variable-temperature magnetic susceptibility data (χ_M) were collected on powdered samples of **11** and **12** in the 2.00–320 K range.

For **11**, the effective magnetic moment (μ_{eff}) per Mn_4 gradually increases from $7.81 \mu_B$ at 320 K to a maximum of $9.24 \mu_B$ at 20.0 K and then decreases slightly to $8.63 \mu_B$ at 5.01 K (Figure 10). These correspond to $\chi_M T$ values of 7.62, 10.67, and $9.31 \text{ cm}^3 \text{ K mol}^{-1}$ at three temperatures. The data thus suggest a relatively high ground state spin value, and the maximum μ_{eff} value of $9.24 \mu_B$ at 20.0 K is comparable with the spin-only ($g = 2.00$) value of $9.95 \mu_B$ expected for a $S = 9/2$ state.

In order to fit the experimental data, an appropriate theoretical χ_M vs T and μ_{eff} vs T expression for **11** was sought. The C_s symmetry of the core requires four exchange parameters (J), as shown in Figure 11. The Heisenberg spin Hamiltonian describing the pairwise interactions is given in eq 8. A full-matrix

$$\hat{H} = -2J_{34}(\hat{S}_1\hat{S}_3 + \hat{S}_1\hat{S}_4) - 2J'_{34}\hat{S}_1\hat{S}_2 - 2J_{33}(\hat{S}_2\hat{S}_4 + \hat{S}_3\hat{S}_4) - 2J'_{33}\hat{S}_3\hat{S}_4 \quad (8)$$

diagonalization approach for obtaining the eigenvalues of this spin Hamiltonian would require diagonalization of a 500×500 matrix. Unfortunately, the more convenient equivalent operator approach, based on the Kambe vector coupling method,²³ is not possible for this C_s symmetry system. However, a very reasonable simplifying approximation is possible by taking $J_{34} = J_{34}'$: these interactions are likely very similar since both pathways involve very similar $[\text{Mn}_2(\mu\text{-O}^{2-})_2]^{3+}$ rhombs (vide supra). The spin Hamiltonian now becomes that given in eq 9, for which the Kambe method is applicable. Using the substitu-

$$\hat{H} = -2J_{34}(\hat{S}_1\hat{S}_2 + \hat{S}_1\hat{S}_3 + \hat{S}_1\hat{S}_4) - 2J_{33}(\hat{S}_2\hat{S}_4 + \hat{S}_3\hat{S}_4) - 2J'_{33}\hat{S}_3\hat{S}_4 \quad (9)$$

tions $\hat{S}_A = \hat{S}_3 + \hat{S}_4$, $\hat{S}_B = \hat{S}_A + \hat{S}_2$, and $\hat{S}_T = \hat{S}_B + \hat{S}_1$, where S_T is the spin of the complete Mn_4 unit, the spin Hamiltonian of eq 9 can be converted to the equivalent one in eq 10. The

$$\hat{H} = -J_{34}[\hat{S}_T^2 - \hat{S}_B^2 - \hat{S}_1^2] - J_{33}[\hat{S}_B^2 - \hat{S}_A^2 - \hat{S}_2^2] - J'_{33}[\hat{S}_A^2 - \hat{S}_3^2 - \hat{S}_4^2] \quad (10)$$

eigenvalues for this Hamiltonian are given in eq 11, where constant terms contributing to all states have been omitted. For

$$E(S_T) = -J[S_T(S_T + 1) - S_B(S_B + 1)] - J_{33}[S_B(S_B + 1) - S_A(S_A + 1)] - J'_{33}[S_A(S_A + 1)] \quad (11)$$

complex **11**, $S_1 = 3/2$, $S_2 = S_3 = S_4 = 2$, and the overall degeneracy of the spin system is 500, made up of 70 individual spin states ranging from $S_T = 1/2$ to $15/2$.

A theoretical χ_M vs T expression for complex **11** was derived using the Van Vleck equation²⁴ and eq 11, and this expression, in the form of μ_{eff} vs T , was used to fit the experimental data: only data at 20.0 K and above were employed since the decrease below 20.0 K is likely due to a combination of Zeeman effects, zero-field splitting (ZFS), and intermolecular exchange interactions, none of which is incorporated into the fitting model. An excellent fit was obtained (solid line in Figure 10) having fitting parameters $J_{34} = -28.5 \text{ cm}^{-1}$, $J_{33} = +2.8 \text{ cm}^{-1}$, $J'_{33} = +2.1 \text{ cm}^{-1}$, and $g = 1.85$, with temperature independent paramagnetism (TIP) held constant at $800 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$. These parameters indicate a $S_T = 9/2$ ground state for **11**, with a $S_T = 7/2$ first excited state.

For complex **12**, the μ_{eff} per Mn_4 gradually decreases from $8.37 \mu_B$ at 320 K to a plateau of $9.64 \mu_B$ at 20.0–40.0 K, and then decreases to $6.93 \mu_B$ at 2.00 K (Figure 12). These correspond to $\chi_M T$ values of 8.76, 11.62, and $6.00 \text{ cm}^3 \text{ K mol}^{-1}$ at these three temperatures. The experimental data at temperatures ≥ 20.0 K were fit to the theoretical expression derived previously^{12a} for a C_{3v} symmetry Mn_4 trigonal pyramid with exchange parameters J_{34} and J_{33} for the $\text{Mn}^{\text{III}}/\text{Mn}^{\text{IV}}$ and $\text{Mn}^{\text{III}}/\text{Mn}^{\text{III}}$ interactions, respectively. This is also that obtained from Figure 11 and eqs 8–11 by putting $J_{34} = J'_{34}$ and $J_{33} = J'_{33}$. The fit, shown as a solid line in Figure 12, has $J_{34} = -33.9 \text{ cm}^{-1}$, $J_{33} = +5.4 \text{ cm}^{-1}$, and $g = 1.94$, with TIP held constant at $800 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$. This fit again indicates a $S_T = 9/2$ ground state and a $S_T = 7/2$ first excited state.

In order to confirm the $S_T = 9/2$ ground states for **11** and **12**, magnetization (M) data were collected in the 2.00–30.0 K range in magnetic fields of 0.50–50 kG. These data, shown in Figures 13 and 14 as reduced magnetization ($M/N\mu_B$) vs h/T plots, were fit by diagonalization of the spin Hamiltonian matrix incorporating axial ZFS (DS_Z^2) and Zeeman interactions, and assuming only the ground state to be occupied at these temperatures. In both cases, good fits were obtained (shown as solid lines in Figures 13 and 14) with fitting parameters, in the format **11/12**, of $S_T = 9/2$ (for both), $g = 2.01/1.96$, and $D = -0.58/-0.47 \text{ cm}^{-1}$.

The S_T and J values obtained for **11** and **12** are compared in Table 6 with those obtained previously for $[\text{Mn}_4\text{O}_3\text{X}(\text{O}_2\text{CMe})_3\text{(dbm)}_3]$ complexes with the C_{3v} -symmetry $[\text{Mn}_4(\mu_3\text{-O})_3(\mu_3\text{-X})]^{6+}$ core.¹² As can be seen, the four complexes have similar properties: in all cases, the J_{34} and J_{33} parameters are antiferromagnetic and ferromagnetic, respectively, and although there is some variation in absolute magnitude, they are all in the $-30 \pm 3 \text{ cm}^{-1}$ and $5 \pm 3 \text{ cm}^{-1}$ ranges, respectively. This is as expected from their very similar structural parameters, and it appears that the additional structural perturbations present as a result of the η^2 -benzoate group in **11** have little consequence to the resultant magnetic properties. This is consistent with the conclusion that the dominant pathways for the exchange interactions between $\text{Mn}^{\text{III}}/\text{Mn}^{\text{IV}}$ pairs and between $\text{Mn}^{\text{III}}/\text{Mn}^{\text{III}}$

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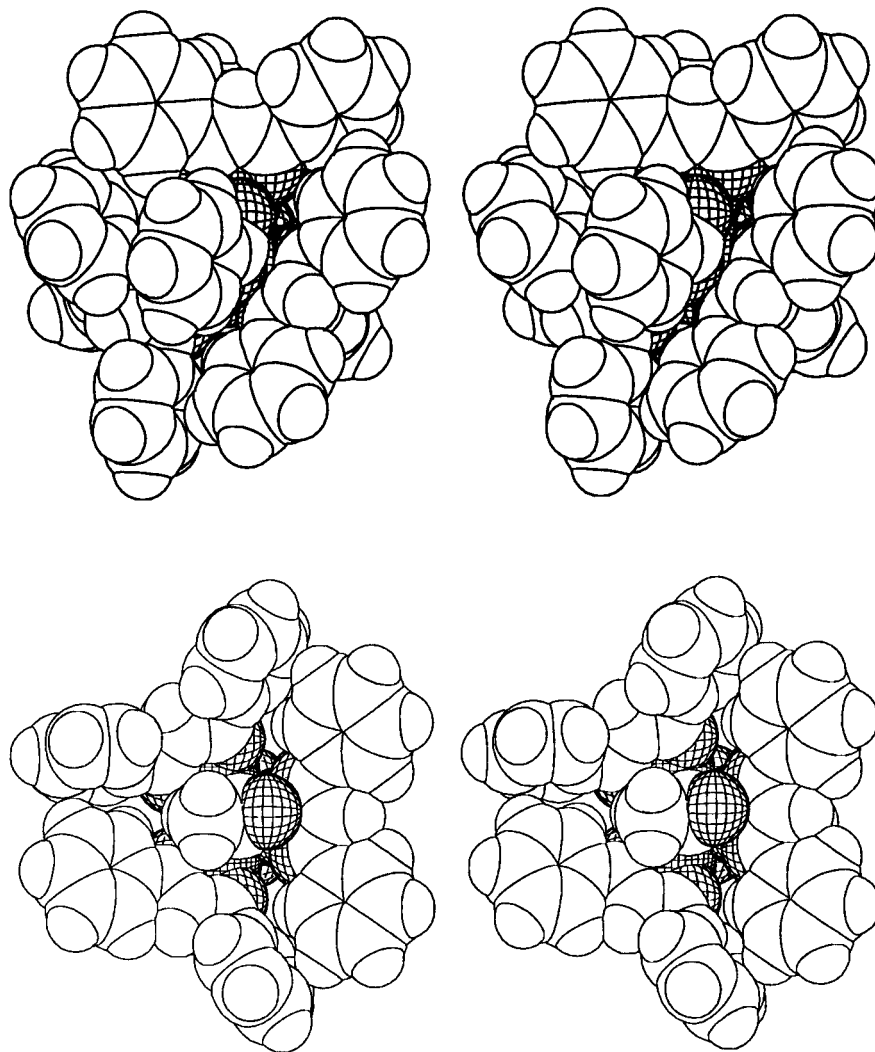


Figure 9. Space-filling stereoviews approximately along the C_3 virtual axes of **11** (top) and **12** (bottom) showing the μ_3 -O₂CR group in a concave cavity formed by the dbm groups.

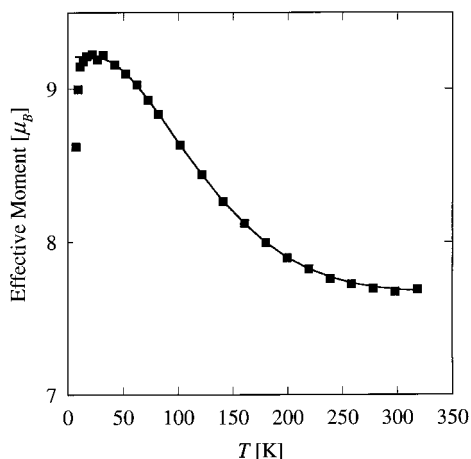


Figure 10. Plot of effective magnetic moment (μ_{eff}) vs temperature for [Mn₄O₃(O₂CPh)₄(dbm)₃] (**11**). The solid line is a fit of the data to the appropriate theoretical expression; see the text for the fitting parameters.

pairs are the oxide bridges. Also compared in Table 6 are the energy separations between the $S_T = 9/2$ ground states and the $S_T = 7/2$ first excited states, and the D values obtained from the $M/N\mu_B$ vs H/T fits. In all cases, the $S_T = 7/2$ first excited state is at relatively high energy, and the complexes thus possess well-isolated ground states. Note, however, that this separation

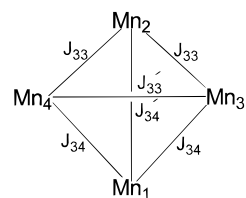


Figure 11. The exchange interactions in complex **11** with C_s symmetry. The Mn numbering corresponds to that in Figure 6: Mn₁ = Mn^{IV}, Mn₂ = Mn₃ = Mn₄ = Mn^{III}. J_{33} and J_{34} refer to Mn^{III}/Mn^{III} and Mn^{III}/Mn^{IV} interactions, respectively.

for **11** is the smallest among these compounds as a result of its weaker J_{33} and J_{33}' interactions compared with J_{33} for the μ_3, η^1 -X⁻ complexes. Similarly, the D values of the four complexes are of comparable magnitude, with complex **11** having the greatest absolute magnitude. Note that the absolute magnitudes of the D values are slightly larger than we reported previously;^{4c} for complex **12**, we previously reported that $D = -0.32 \text{ cm}^{-1}$. The present values in Table 6 are considered more reliable because they have been obtained with a matrix diagonalization theoretical approach that calculates a full powder average, whereas the earlier procedure did not involve a powder average. Also note that fitting of magnetization data generally yields two minima, one with $D > 0$ and one with $D < 0$, usually giving comparable fits of the data.^{4c} However, we consider only the D

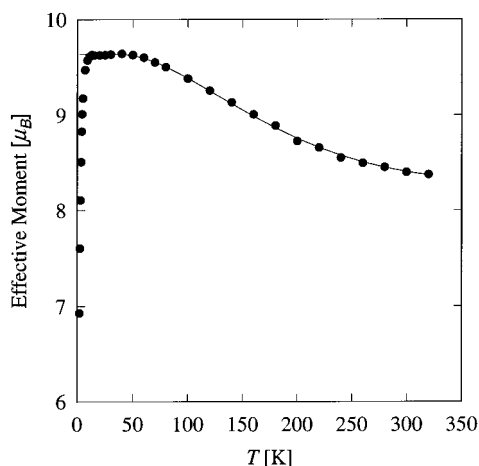


Figure 12. Plot of effective magnetic moment (μ_{eff}) vs temperature for $[\text{Mn}_4\text{O}_3(\text{O}_2\text{CMe})_4(\text{dbm})_3]$ (**12**). The solid line is a fit of the data to the appropriate theoretical expression; see the text for the fitting parameters.

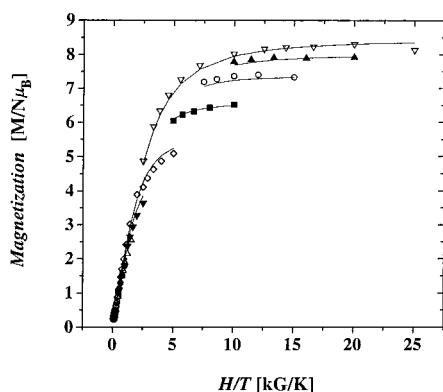


Figure 13. Plot of reduced magnetization ($M/N\mu_B$) vs H/T for complex **11** at 0.50 (\bullet), 1.00 (\square), 3.00 (\triangle), 5.00 (\blacktriangledown), 10.0 (\diamond), 20.0 (\blacksquare), 30.0 (\circ), 40.0 (\blacktriangle), and 50.0 kG (∇). The solid lines result from a least-squares fit of the data; see the text for the fitting procedure and the fitting parameters.

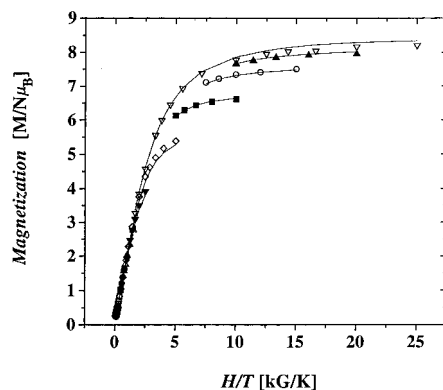


Figure 14. Plot of reduced magnetization ($M/N\mu_B$) vs H/T for complex **12** at 0.50 (\bullet), 1.00 (\square), 3.00 (\triangle), 5.00 (\blacktriangledown), 10.0 (\diamond), 20.0 (\blacksquare), 30.0 (\circ), 40.0 (\blacktriangle), and 50.0 kG (∇). The solid lines result from a least-squares fit of the data; see the text for the fitting procedure and the fitting parameters.

< 0 fits in the present work because previous studies of the temperature dependencies of high-field EPR signals have shown unequivocally that $D < 0$ for these $[\text{Mn}_4\text{O}_3\text{X}(\text{O}_2\text{CMe})_3(\text{dbm})_3]$ complexes.^{4b}

Discussion

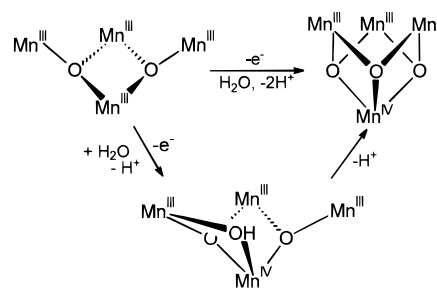
A variety of Mn carboxylate species has been obtained by a combination of synthetic methods. The dbm^- anion continues

Table 6. Comparison of Fitting Parameters for $[\text{Mn}_4\text{O}_3\text{X}(\text{O}_2\text{CR})_3(\text{dbm})_3]$ Complexes

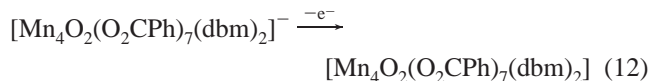
param ^a	X			
	O ₂ CPh (11)	O ₂ CMe (12)	Cl	Br
J_{34} , cm^{-1}	-28.5	-33.9	-28.4	-30.1
J_{33} , cm^{-1}	+2.8	+5.4	+8.3	+7.4
J'_{33} , cm^{-1}	+2.1			
ground S_T	$9/2$	$9/2$	$9/2$	$9/2$
$E(S_T = 7/2)$, ^b cm^{-1}	114	167	185	179
g	2.01	1.96	2.00	2.01
D , cm^{-1}	-0.58	-0.47	-0.35	-0.50
ref	<i>c</i>	<i>c</i>	<i>d</i>	<i>e</i>

^a $J_{34} = J(\text{Mn}^{\text{III}}/\text{Mn}^{\text{IV}})$; $J_{33} = J(\text{Mn}^{\text{III}}/\text{Mn}^{\text{III}})$. ^b Energy of the $S_T = 7/2$ first excited state above the ground state. ^c This work. ^d Ref 4c. ^e Redetermined with a negative D (see text).

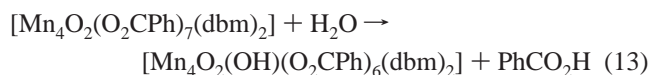
Scheme 2



to prove a valuable chelate in the stabilization of tetranuclear species, as well as other nuclearities, and this has allowed reactivity characteristics of certain species to be assessed. In the present work, dbm^- has been used to prepare new $[\text{Mn}_4\text{O}_2]^{8+}$ -containing complexes **6–10** whose electrochemical signatures suggest a quasi-reversible oxidation. The consequences of this oxidation have been explored, and the products of the CPE experiments, complexes **11** and **12**, have been found to have distinctly different cores from the starting materials, with an increased $\text{O}^{2-}:\text{Mn}$ ratio. This and the reaction conditions and yields of **11** and **12** suggest that these final products are forming by reaction of the electrochemically oxidized starting materials with H_2O molecules in the solvent. The overall transformations to give **11** and **12** are summarized in eqs 6 and 7, respectively. We envisage the sequence of events to, e.g., complex **11** to involve an initial oxidation of the $[\text{Mn}_4\text{O}_2(\text{O}_2\text{CPh})_7(\text{dbm})_2]^-$ anion of **10** to give $[\text{Mn}_4\text{O}_2(\text{O}_2\text{CPh})_7(\text{dbm})_2]$ (eq 12), which is then attacked by an H_2O molecule. Although



the identity of transient intermediates is not known, we suggest that it may involve species in which the water has bound, has been deprotonated, and is bridging a $\text{Mn}^{\text{III}}/\text{Mn}^{\text{IV}}$ pair as a OH^- , the displaced PhCO_2^- acting as the H^+ acceptor (eq 13); the core transformation is depicted in Scheme 2. The conversion



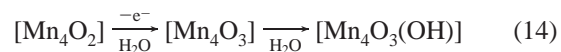
of this $[\text{Mn}_4\text{O}_2(\text{OH})]$ core to that of final product **11** now requires deprotonation of the OH^- and its conversion to a $\mu_3\text{-O}^{2-}$ (Scheme 2) concomitant with attachment of a third dbm^- group, with the displaced PhCO_2^- groups again acting as Brønsted bases for the OH^- and dbmH deprotonations (eqs 6 and 7). Note that Scheme 2 is consistent with the structural

relationship between the $[\text{Mn}_4\text{O}_2]$ and $[\text{Mn}_4\text{O}_3]$ cores, i.e., the latter is a “closed-up” version of the former caused by the presence of a third $\mu_3\text{-O}^{2-}$ ion. Also note that the spontaneous incorporation of an extra O^{2-} ion on oxidation of the $[\text{Mn}_4\text{O}_2]$ core is consistent with the general trend that increasing average oxidation state favors an increase in the proportion of hard O^{2-} ions.²⁵ The MnO_4^- ion lies at one extreme of this relationship. The spontaneous incorporation of a third O^{2-} ion in **11** and **12** is thus consistent with the average oxidation state increase from +3.00 to +3.25. Alternatively, one can describe this as the third O^{2-} ion helping to stabilize the higher oxidation state species.^{12a}

From a biological viewpoint, the results described in this paper offer some food for thought. The coupled oxidation/oxide incorporation seen in going from, for example, $[\text{Mn}_4\text{O}_2]$ complex **10** to $[\text{Mn}_4\text{O}_3]$ complex **11** could be considered a model system for the progressive oxidation/substrate activation processes in the native WOC, i.e., H_2O -derived O^{2-} ions are stabilizing the increasing WOC S_n oxidation level, and, inversely, of course, the increasing WOC S_n oxidation level is stabilizing activated/deprotonated forms of H_2O in preparation for their oxidative coupling to O_2 .

The above discussion can be extended one step further when our recently reported²⁶ observation is noted that complex **12**

will react with H_2O to give $[\text{Mn}_4\text{O}_3(\text{OH})(\text{O}_2\text{CMe})_3(\text{dbm})_3]$, a $\mu_3\text{-OH}^-$ replacing the $\mu_3\text{-O}_2\text{CMe}^-$. In effect, this and the conversion of **6** to **12** provide the demonstration of the sequence of eq 14 that represents the activation of two H_2O molecules



by binding to Lewis acidic Mn^{n+} centers and partial or complete deprotonation. Fuller details will be provided in a subsequent paper on the hydrolysis of **12**. The $[\text{Mn}_4\text{O}_2]$ and $[\text{Mn}_4\text{O}_3]$ complexes are not exact structural models of the WOC on the basis of, for example, EXAFS data²⁷ and ground state spin differences; however, the oxidation-driven chemistry they are exhibiting may nevertheless be providing important insights into the means by which H_2O molecules are bound and activated to oxidation to O_2 in photosynthesis, whatever the precise structure of the native WOC may be.

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Supporting Information Available: Tables of crystallographic data, structure refinement details, atomic coordinates, interatomic distances and angles, anisotropic thermal parameters, and calculated hydrogen parameters. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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