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New Structural Type in Manganese Carboxylate Chemistry via Coupled Oxidation/Oxide Incorporation: Potential Insights into Photosynthetic Water Oxidation

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There continues to be great interest in the mechanism by which the tetranuclear Mn aggregate at the photosynthetic water oxidation center (WOC) of green plants and cyanobacteria binds H_2O molecules and oxidatively couples them to O_2.[1] The WOC cycles through a number of oxidation levels (S_n states; n = 0–4), with the highest (S_4) relaxing spontaneously to the lowest (S_0) with O_2 evolution.[1,2] Although a variety of spectroscopic and physicochemical studies have been performed, the precise structure of the WOC Mn_4 aggregate at any S_n state remains unclear.[1] In any event, the more important questions are (i) what is the mechanism by which two H_2O molecules are brought together, deprotonated, and activated to oxidative coupling to O_2 (together with the precise order in which these occur) and (ii) what is the nature of concomitant structural changes to the Mn_4 aggregate during this process?

In this regard, several speculative mechanistic schemes based on Mn_4 structures have been put forward.[3,4] Brudvig and Crabtree proposed[3a,b] a transformation involving hypothetical $[Mn_4O_4]$ cubane and known $[Mn_4O_6]$ adamantane core units at the lower and higher S_n states, respectively. In contrast, Vincent and Christou proposed[4] a stepwise incorporation of oxides, converting a known $[Mn_4(\mu_3\text{-}O)_2]$ complex into a known $[Mn_4O_3Cl]$ and hypothetical $[Mn_4O_4]$ at high S_n states (eq 1).[5,6] The common

$$[Mn_4O_2] \underset{\substack{-2H^+\\ +Cl^-}}{\overset{+H_2O}{\rightarrow}} [Mn_4O_3Cl] \underset{\substack{-2H^+\\ -Cl}}{\overset{+H_2O}{\rightarrow}} [Mn_4O_4] \rightarrow [Mn_4O_2] + O_2 \qquad (1)$$

theme in these two schemes is incorporation of substrate H_2O molecules *into* the Mn_4 aggregate, increasing the O^{2-}:Mn ratio and yielding the substrate deprotonation and activation required for water oxidation. A tetranuclear complex with an $[Mn_4O_4]$ cubane core is currently unknown in Mn/O^{2-} chemistry, so its postulated conversion to Mn_4O_6 or its reductive elimination of O_2 (eq 1) cannot be tested. However, the conversion of $[Mn_4O_2]$ ($4Mn^{III}$) to $[Mn_4O_3Cl]$ ($3Mn^{III}$, Mn^{IV}) complexes has been demonstrated, but only by Cl^--induced disproportionation (eq 2) rather than a true oxidation.[6] Thus, there has been no precedence

$$3[Mn_4O_2]^{8+} + 2Cl^- \rightarrow 2[Mn_4O_3Cl]^{6+} + 2Mn^{2+} + 2Mn^{3+} \qquad (2)$$

available for the suggestion that oxidation of a Mn_4 aggregate is followed by H_2O incorporation to increase the O^{2-}:Mn ratio. We herein describe the first such demonstrated transformation which establishes the feasibility of and provides a precedent for such a coupled oxidation/oxide-incorporation step during the water oxidation cycle.

The complex $(NBu^n_4)[Mn_4O_2(O_2CPh)_7(dbm)_2]$ (**1**; dmbH = dibenzoylmethane) may be readily prepared in ~70% yield by treatment of $(NBu^n_4)[Mn_4O_2(O_2CPh)_9(H_2O)]$[7] with 2 equiv of Na(dbm) in CH_2Cl_2. Complex **1** in MeCN displays two quasi-reversible oxidations at 0.48 and 1.17 V *vs* ferrocene and an irreversible reduction at –0.66 V. Further investigation of the first oxidation couple confirmed it as a one-electron process ($n \approx 1$ by coulometry at 0.65 V). Generation and isolation of an oxidized product was therefore sought by controlled potential electrolysis.

After preliminary investigation, the following optimized procedure was developed. Complex **1** in MeCN (*not* dried) containing $NBu^n_4ClO_4$ (~14 equiv) was electrolyzed under air at 0.65 V. During the electrolysis (60–75 min), dbmH (1 equiv) in MeCN/$NBu^n_4ClO_4$ was added dropwise. On completion of the experiment, the precipitated brown solid of $[Mn_4O_3(O_2CPh)_4(dbm)_3]$ (**2**) was collected by filtration; the yield was 70–80% based on eq 3. In optimizing this preparation, the following

$$[Mn_4O_2(O_2CR)_7(dbm)_2]^- + dbmH + H_2O \xrightarrow{-e^-} [Mn_4O_3(O_2CR)_4(dbm)_3] + 3RCO_2H \qquad (3)$$

observations were made: (i) omission of dbmH and use of distilled MeCN and an Ar atmosphere gave only a 10% yield of **2**; (ii) use of undistilled MeCN under air in (i) leads to an increased yield of 25%; (iii) addition of dbmH to the filtrate of (ii) leads to precipitation of more **2** and a total yield of 41%; and (iv) addition of the dbmH to the initial solution prior to electrolysis leads to a yield of **2** of ~25%. These observations are consistent with eq 3, involving incorporation of exogenous dbmH and H_2O into the generated, oxidized form of **1**, leading to a product with an increased O^{2-}:Mn ratio.

Single crystals of $\mathbf{2}\cdot{}^3/_2CH_2Cl_2$ can be grown from CH_2Cl_2/hexanes.[8] The structure of **2** (Figure 1) consists of a $[Mn_4O_3]^{7+}$ partial cubane core. Metric parameters and the absence of a Jahn–Teller distortion at Mn(1) indicate this to be the Mn^{IV} ion, and the other metal ions are JT-elongated Mn^{III}. Each of the latter possesses a chelating dbm group, and three $PhCO_2^-$ groups bridge each $Mn^{III}\cdots Mn^{IV}$ pair. The latter distances are 2.787(2)–2.802(3) Å, consistent with the $[Mn_2(\mu\text{-}O)_2]$ unit. The structure of **2** is thus similar to previously-reported Mn_4O_3Cl-

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(8) Anal. Calcd (found) for $C_{73}H_{53}O_{17}Mn_4$: C, 61.66 (61.4); H, 3.76 (3.75); Mn, 15.45 (15.3). Crystal data for $\mathbf{2}\cdot{}^3/_2CH_2Cl_2$: monoclinic, $P2_1/n$, a = 15.161(3), b = 21.577(4), and c = 22.683(5) Å; β = 108.04(3)°; Z = 4; V = 7056(3) Å^3; d_{calc} = 1.458 g·cm^{-3}; T = 173(2) K. The structure was solved using SHELXL-92. A total of 7418 independent reflections were refined using full-matrix least-squares on F^2 to final R indices ($I > 2\sigma(I)$) of $R1$ = 0.0863 and $wR2$ = 0.2180. The phenyl rings were included as rigid bodies. In the final refinement cycles, non-hydrogen and hydrogen atoms were refined with anisotropic and isotropic thermal parameters, respectively. One CH_2Cl_2 solvate molecule had 100% occupancy, and the other only 50%.

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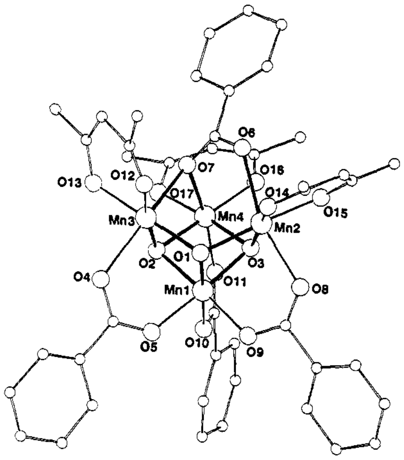

Figure 1. ORTEP representation of **2** at the 50% probability level. Selected distances (Å) and angles (deg): Mn(1)···Mn(2), 2.802(3); Mn(1)···Mn(3), 2.780(2); Mn(1)···Mn(4), 2.787(3); Mn(2)···Mn(3), 3.277(2); Mn(2)···Mn(4), 3.432(2); Mn(3)···Mn(4), 3.197(2); Mn(1)–O(1), 1.856(8); Mn(1)–O(2), 1.835(7); Mn(1)–O(3), 1.859(8); Mn(2)–O(1), 1.932(7); Mn(2)–O(3), 1.935(8); Mn(3)–O(1), 1.912(7); Mn(3)–O(2), 1.942(7); Mn(4)–O(2), 1.920(7); Mn(4)–O(3), 1.947(7); Mn(3)–O(7), 2.267(10); Mn(4)–O(7), 2.173(9); Mn(2)–O(6), 2.164(9); Mn(3)–O(7)–Mn(4), 92.1(4); Mn(3)–O(2)–Mn(4), 111.7(4); Mn(2)–O(1)–Mn(3), 116.9(4); Mn(2)–O(3)–Mn(4), 124.2(4).

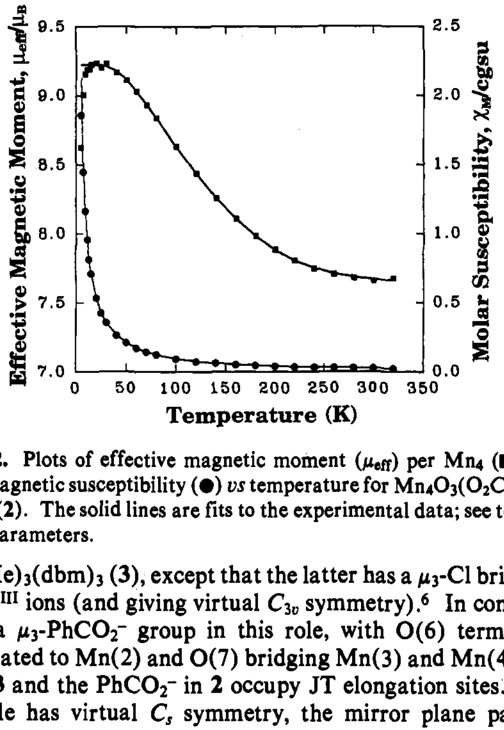

Figure 2. Plots of effective magnetic moment (μ_{eff}) per Mn_4 (■) and molar magnetic susceptibility (●) *vs* temperature for $Mn_4O_3(O_2CPh)_4$)-(dbm)$_3$ (**2**). The solid lines are fits to the experimental data; see text for fitting parameters.

$(O_2CMe)_3(dbm)_3$ (**3**), except that the latter has a μ_3-Cl bridging the Mn^{III} ions (and giving virtual C_{3v} symmetry).[6] In contrast, **2** has a μ_3-$PhCO_2^-$ group in this role, with O(6) terminally coordinated to Mn(2) and O(7) bridging Mn(3) and Mn(4); the Cl^- in **3** and the $PhCO_2^-$ in **2** occupy JT elongation sites. The molecule has virtual C_s symmetry, the mirror plane passing through Mn(1), Mn(2), and O(2). As a result, the $Mn^{III}\cdots Mn^{III}$ distances span a much greater range (3.197(2)–3.432(2) Å) than in **3** (3.237(5)–3.264(5) Å).

Complex **2** was investigated by solid-state magnetic susceptibility studies in the range 5–320 K. The effective magnetic moment (μ_{eff}) per Mn_4 gradually increases from 7.81 μ_B at 320.0 K to a maximum of 9.24 μ_B at 20.0 K and then drops slightly to 8.63 μ_B at 5.01 K. The data were fit to an equation derived employing the C_s symmetry of **2** but assuming (reasonably) that all $Mn^{III}Mn^{IV}$ interactions are equivalent. An excellent fit (Figure 2) was obtained with (using the $\hat{H} = -2JS_i{\cdot}S_j$ convention): $J_1 = J(Mn^{III}\cdots Mn^{IV}) = -28.5$ cm^{-1}, $J_2 = J(Mn^{III}\cdots Mn^{III}) = +2.8$ cm^{-1}, $J_3 = J(Mn^{III}\cdots Mn^{III}) = +2.1$ cm^{-1}, and $g = 1.85$, where J_3 refers to the unique Mn(3)/Mn(4) pair. These values are similar to those for **3** ($J(Mn^{III}\cdots Mn^{IV}) = -28.4$ cm^{-1}, $J(Mn^{III}\cdots Mn^{III}) = +8.3$ cm^{-1}).[6] As for **3**, complex **2** has an $S = {}^9/_2$ ground state.

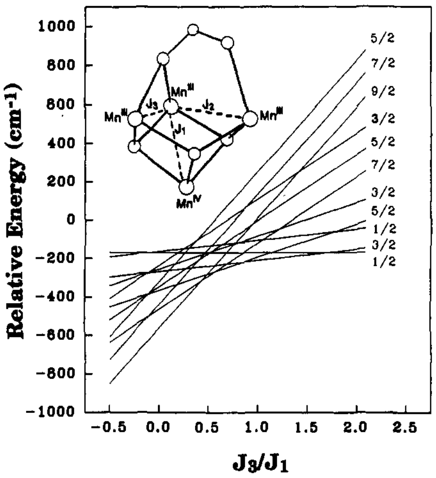

Figure 3. Change in the ground state spin value as a function of the J_3/J_1 ratio; J_1 and J_2 have been held constant at –28.5 and +2.8 cm^{-1}, respectively.

In the past, we have offered the $[Mn_4O_3Cl]^{6+}$-containing complexes such as **3** as potential models of an S_n state of the WOC.[5,6] However, a major drawback has been their $S = {}^9/_2$ ground states; S_2, for example, has been generated in forms possessing $S = {}^1/_2$ or ${}^5/_2$ states,[9] but no evidence for a $S = {}^9/_2$ state is available. Although the $S = {}^1/_2$ and $S = {}^5/_2$ forms are reasonably assumed to differ slightly in overall structure/conformation, no detailed proposal for a type of structure and an associated coupling scheme that can readily give both a $S = {}^1/_2$ and a $S = {}^5/_2$ state has been put forward. The C_s symmetry of **2**, however, allows such a scheme to be presented (Figure 3). J_1 and J_2 are difficult to vary significantly, but J_3 should be particularly sensitive to the nature of oxygen atom O(7) (i.e., carboxylate as in **2**, OR^-, OH^- or O^{2-}). Figure 3 summarizes the change in ground state S as a function of the J_3/J_1 ratio, J_1 and J_2 being kept constant. It can be clearly seen that S can change dramatically, from $S = {}^9/_2, {}^7/_2, {}^5/_2, {}^3/_2$, and ${}^1/_2$. A value of $J_3 \approx 0.7J_1 = -20$ cm^{-1} is sufficient to yield an $S = {}^5/_2$ state, as seen in the $g \approx 4$ S_2 state, whereas $J_3 \approx 2J_1 \approx -55$ cm^{-1} is sufficient to yield an $S = {}^1/_2$ state, as seen in the normal ("multiline") S_2 state. These values of J_3 might reasonably be expected if O(7) were an OH^- and O^{2-} atom, respectively. Thus, it is clear that a precedent is provided by **2** and Figure 3 for how the ground state S value of a Mn_4 aggregate could vary significantly *with little structural change.* Attempts to prepare analogues of **2** with O(7) replaced by other oxygen-based groups are currently in progress to probe this matter further, as are additional studies of the conversion of **1** to **2**.

In summary, one-electron oxidation of a $[Mn_4O_2]^{8+}$ complex leads to spontaneous incorporation of a third O^{2-} to give a novel $[Mn_4O_3]^{7+}$ core, a type of process speculatively suggested in the past as possibly involved in the WOC catalytic cycle. Its demonstration now provides precedence for this possibility.

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Supplementary Material Available: Data collection and refinement details and listings of atomic coordinates and thermal parameters for complex **2** (7 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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