

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

Sheyi Wang,[†] Hui-Lien Tsai,[‡] Karl S. Hagen,[‡] David N. Hendrickson,^{*,‡} and George Christou^{*,‡}

Department of Chemistry, Indiana University
Bloomington, Indiana 47405-4001

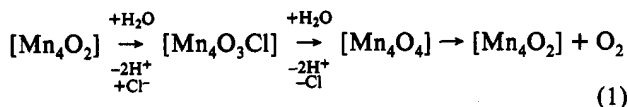
Department of Chemistry, Emory University
Atlanta, Georgia 30322

Department of Chemistry-0358
University of California at San Diego
La Jolla, California 92093-0358

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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 H₂O molecules and oxidatively couples them to O₂.¹ The WOC cycles through a number of oxidation levels (S_n states; n = 0–4), with the highest (S₄) relaxing spontaneously to the lowest (S₀) with O₂ evolution.^{1,2} Although a variety of spectroscopic and physicochemical studies have been performed, the precise structure of the WOC Mn₄ 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 H₂O molecules are brought together, deprotonated, and activated to oxidative coupling to O₂ (together with the precise order in which these occur) and (ii) what is the nature of concomitant structural changes to the Mn₄ aggregate during this process?

In this regard, several speculative mechanistic schemes based on Mn₄ structures have been put forward.^{3,4} Brudvig and Crabtree proposed^{3a,b} a transformation involving hypothetical [Mn₄O₄] cubane and known [Mn₄O₆] adamantane core units at the lower and higher S_n states, respectively. In contrast, Vincent and Christou proposed⁴ a stepwise incorporation of oxides, converting a known [Mn₄(μ₃-O)₂] complex into a known [Mn₄O₃Cl] and hypothetical [Mn₄O₄] at high S_n states (eq 1).^{5,6} The common



theme in these two schemes is incorporation of substrate H₂O molecules into the Mn₄ aggregate, increasing the O²⁻:Mn ratio and yielding the substrate deprotonation and activation required

[†] Indiana University.

[‡] Emory University.

^{*} University of California at San Diego.

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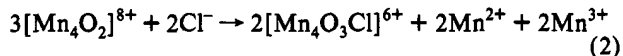
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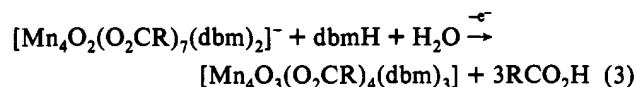
for water oxidation. A tetranuclear complex with an [Mn₄O₄] cubane core is currently unknown in Mn/O²⁻ chemistry, so its postulated conversion to Mn₄O₆ or its reductive elimination of O₂ (eq 1) cannot be tested. However, the conversion of [Mn₄O₂] (4Mn^{III}) to [Mn₄O₃Cl] (3Mn^{III}, Mn^{IV}) complexes has been demonstrated, but only by Cl⁻-induced disproportionation (eq 2) rather than a true oxidation.⁶ Thus, there has been no precedence



available for the suggestion that oxidation of a Mn₄ aggregate is followed by H₂O incorporation to increase the O²⁻: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 (NBuⁿ)₄[Mn₄O₂(O₂CPh)₇(dbm)₂] (**1**; dbmH = dibenzoylmethane) may be readily prepared in ~70% yield by treatment of (NBuⁿ)₄[Mn₄O₂(O₂CPh)₅(H₂O)]⁷ with 2 equiv of Na(dbm) in CH₂Cl₂. 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 ≈ 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 NBuⁿClO₄ (~14 equiv) was electrolyzed under air at 0.65 V. During the electrolysis (60–75 min), dbmH (1 equiv) in MeCN/NBuⁿClO₄ was added dropwise. On completion of the experiment, the precipitated brown solid of [Mn₄O₃(O₂CPh)₄(dbm)₃] (**2**) was collected by filtration; the yield was 70–80% based on eq 3. In optimizing this preparation, the following



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 H₂O into the generated, oxidized form of **1**, leading to a product with an increased O²⁻:Mn ratio.

Single crystals of **2**·³/₂CH₂Cl₂ can be grown from CH₂Cl₂/hexanes.⁸ The structure of **2** (Figure 1) consists of a [Mn₄O₃]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 PhCO₂- groups bridge each Mn^{III}...Mn^{IV} pair. The latter distances are 2.787(2)–2.802(3) Å, consistent with the [Mn₂(μ-O)₂] unit. The structure of **2** is thus similar to previously-reported Mn₄O₃Cl-

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(8) Anal. Calcd (found) for C₇₃H₅₃O₁₇Mn₄: C, 61.66 (61.4); H, 3.76 (3.75); Mn, 15.45 (15.3). Crystal data for **2**·³/₂CH₂Cl₂: monoclinic, P2₁/n, a = 15.161(3), b = 21.577(4), and c = 22.683(5) Å; β = 108.04(3)°; Z = 4; V = 7056(3) Å³; 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 F² to final R indices (I > 2σ(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 CH₂Cl₂ solvate molecule had 100% occupancy, and the other only 50%.

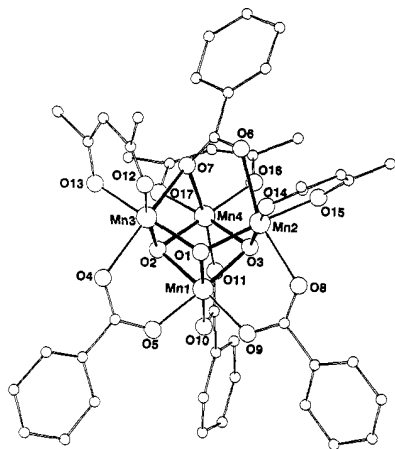


Figure 1. ORTEP representation of **2** at the 50% probability level. Selected distances (Å) and angles (deg): Mn(1)···Mn(2), 2.802(3); Mn(1)···Mn(3), 2.780(2); Mn(1)···Mn(4), 2.787(3); Mn(2)···Mn(3), 3.277(2); Mn(2)···Mn(4), 3.432(2); Mn(3)···Mn(4), 3.197(2); Mn(1)–O(1), 1.856(8); Mn(1)–O(2), 1.835(7); 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).

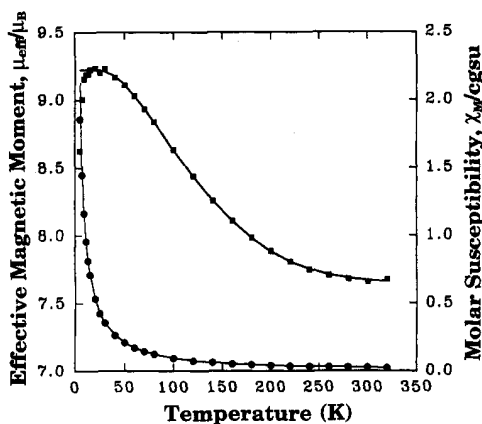


Figure 2. Plots of effective magnetic moment (μ_{eff}) per Mn_4 (■) and molar magnetic susceptibility (●) vs temperature for $\text{Mn}_4\text{O}_3(\text{O}_2\text{CPh})_4(\text{dbm})_3$ (**2**). The solid lines are fits to the experimental data; see text for fitting parameters.

$(\text{O}_2\text{CMe})_3(\text{dbm})_3$ (**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 $\text{Mn}^{\text{III}}\cdots\text{Mn}^{\text{III}}$ 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 $\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}$ interactions are equivalent. An excellent fit (Figure 2) was obtained with (using the $\hat{H} = -2JS_rS_j$ convention): $J_1 = J(\text{Mn}^{\text{III}}\cdots\text{Mn}^{\text{IV}}) = -28.5 \text{ cm}^{-1}$, $J_2 = J(\text{Mn}^{\text{III}}\cdots\text{Mn}^{\text{III}}) = +2.8 \text{ cm}^{-1}$, $J_3 = J(\text{Mn}^{\text{III}}\cdots\text{Mn}^{\text{III}}) = +2.1 \text{ cm}^{-1}$, and $g = 1.85$, where J_3 refers to the unique Mn(3)/Mn(4) pair. These values are similar to those for **3** ($J(\text{Mn}^{\text{III}}\cdots\text{Mn}^{\text{IV}}) = -28.4 \text{ cm}^{-1}$, $J(\text{Mn}^{\text{III}}\cdots\text{Mn}^{\text{III}}) = +8.3 \text{ cm}^{-1}$).⁶ As for **3**, complex **2** has an $S = 9/2$ ground state.

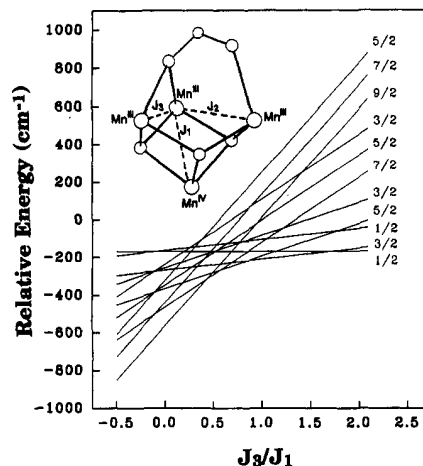


Figure 3. Change in the ground state spin value as a function of the J_3/J_1 ratio; J_1 and J_2 have been held constant at -28.5 and $+2.8 \text{ cm}^{-1}$, respectively.

In the past, we have offered the $[\text{Mn}_4\text{O}_3\text{Cl}]^{6+}$ -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 $J_3 \approx 0.7J_1 = -20 \text{ cm}^{-1}$ is sufficient to yield an $S = 5/2$ state, as seen in the $g \approx 4 S_2$ state, whereas $J_3 \approx 2J_1 \approx -55 \text{ cm}^{-1}$ 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 $[\text{Mn}_4\text{O}_2]^{8+}$ complex leads to spontaneous incorporation of a third O^{2-} to give a novel $[\text{Mn}_4\text{O}_3]^{7+}$ 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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