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Incorporation of Fluoride into a Tetranuclear Mn/O/RCO$_2$ Aggregate: Potential Relevance to Inhibition by Fluoride of Photosynthetic Water Oxidation

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Considerable effort is being concentrated on elucidating the structure of the predominantly carboxylate ligated, oxide-bridged Mn aggregate at the water oxidation center (WOC) of photosystem II in plants, and the determination of the mechanism by which it oxidatively couples two H_2O molecules to produce O_2. The WOC is oxidized through five so-called S_n states (S_0−S_4) until the transient S_4 state is reached, O_2 is evolved, and the system relaxes back to the S_0 state.[1,2] It has been proposed[3] that the water molecules are incorporated into the Mn aggregate as oxide (or hydroxide) bridges during the aggregate's advance to the higher S_n states and are thereby activated to oxidation. Therefore, we have been interested in developing and studying processes that involve coupled oxidation/oxide incorporation of tetranuclear Mn/O/RCO$_2^-$ complexes.[4] A number of other intriguing properties of the WOC are known, including the fact that it absolutely requires Cl$^-$ for activity[1,5] (Br$^-$ can substitute for Cl$^-$ *in vitro*) whereas F$^-$ is an inhibitor;[1,6] the presence of F$^-$ also affects the electronic properties of the WOC as judged by EPR studies of the S_2 state which show that the normal "multiline" signal at $g \approx 2$ is replaced by a $g \approx 4.1$ signal.[7] Thus, O_2 evolution activity by the WOC is critically dependent on and affected by the presence of halides and their precise identity. Unfortunately for our understanding of inhibition by F$^-$, there are no examples currently known of higher oxidation state (≥III) Mn$_x$ aggregates containing F$^-$.[8] This report describes two developments: preparation of a remarkable [Mn$_4$O$_3$(η^1-O$_2$CMe)] cubane possessing a *monoatomic*, triply-bridging MeCO$_2^-$ group, and the first incorporation of F$^-$ into a Mn carboxylate aggregate providing a potential model for F$^-$ inhibition of the WOC.

Investigation of the cyclic voltammetric properties of Mn$_4$O$_2$(O$_2$CMe)$_6$(py)$_2$(dbm)$_2$ (**1**; dbmH = dibenzoylmethane) in MeCN reveals a one-electron oxidation at 0.61 V *vs* Cp$_2$Fe/Cp$_2$Fe$^+$.[9] Controlled potential electrolysis at 0.84 V of **1** in MeCN/CH$_2$Cl$_2$ (3:1) containing 0.2 M NBu$^n_4$ClO$_4$ was performed under a dry Ar atmosphere; during the electrolysis, a solution of dbmH (1 equiv) in MeCN/0.2 M NBu$^n_4$ClO$_4$ was added dropwise. On completion of the experiment, the brown precipitate of Mn$_4$O$_3$(O$_2$CMe)$_4$(dbm)$_3$ (**2**) was collected by filtration; yield 54%.

On the basis of earlier precedence,[4] the conversion of **1** to **2** is concluded to be a result of reaction of adventitious H_2O (or other potential oxide sources) with oxidized **1** (eq 1). Single

$$\mathrm{Mn_4O_2(O_2CMe)_6(py)_2(dbm)_2 + dbmH + H_2O \xrightarrow{-e^-} Mn_4O_3(O_2CMe)_4(dbm)_3 + 2HO_2CMe + pyH^+ + py} \quad (1)$$

crystals of **2** can be grown from CH$_2$Cl$_2$/MeCN.[10] The structure of **2** (Figure 1, top) consists of a [Mn$_4$O$_3$]$^{7+}$ (3Mn^{III},Mn^{IV}) partial cubane whose vacant vertex is occupied by a η^1,μ_3-MeCO$_2^-$ group to give a [Mn$_4$(μ_3-O)$_3$(μ_3-O$_2$CMe)]$^{6+}$ "distorted-cubane" or face-capped trigonal pyramid core.[11] This is an extremely unusual and rare bridging mode for a RCO$_2^-$ group.[12] Metric parameters and the absence of a Jahn−Teller (JT) distortion at Mn(1) indicate this to be the Mn^{IV} ion, and the other metals are JT-elongated Mn^{III}. Acetate atom O(8) lies on the JT axes of Mn(2), Mn(3), and Mn(4). The structure is thus similar to Mn$_4$O$_3$Cl(O$_2$CMe)$_3$(dbm)$_3$ (**3**) reported previously[13] which contains a [Mn$_4$(μ_3-O)$_3$(μ_3-Cl)]$^{6+}$ core, except that the Mn^{III}−O(8) distances in **2** (average 2.299 Å) are considerably shorter than the Mn^{III}−Cl bonds in **3** (average 2.650 Å).

Reactivity studies in progress on **2** indicate the μ_3-MeCO$_2^-$ group to be *selectively* displaceable by a number of groups, opening up a whole area of site-specific ligand substitution chemistry. In particular, treatment of **2** in CH$_2$Cl$_2$ with Et$_2$NSF$_3$, a convenient source of F$^-$ ions, followed by addition of hexanes (5 volumes) gives a brown precipitate of Mn$_4$O$_3$F(O$_2$CMe)$_3$(dbm)$_3$ (**4**) in 93% yield. Single crystals of **4**·$^5/_2$CH$_2$Cl$_2$ can be grown from CH$_2$Cl$_2$/hexanes.[14] The structure of **4**·$^5/_2$CH$_2$Cl$_2$ (Figure 1, bottom) confirms that a F$^-$-for-MeCO$_2^-$ substitution has occurred with little structural perturbation of the rest of the molecule. The F$^-$ ion F(8) is in a μ_3 mode at a vertex of the resultant [Mn$_4$O$_3$F]$^{6+}$ distorted-cubane core.[11] The

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(10) Anal. Calcd (found) for C$_{53}$H$_{45}$O$_{17}$Mn$_4$: C, 54.24 (53.84); H, 3.86 (3.88). Crystal data for **2**: monoclinic, $P2_1/n$, a = 13.549(2) Å, b = 22.338(4) Å, and c = 16.618(2) Å; β = 103.74(1)°; Z = 4; V = 4885.49 Å^3; d_{calc} = 1.596 g·cm^{-3}; T = −171 °C. The structure was solved using MULTAN-78. R (R_w) = 4.63% (4.45%) with 4838 unique reflections with $F > 3\sigma(F)$. All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were placed at idealized positions.

(11) We use the phrase "distorted-cubane" for convenience, but wish to emphasize the *severe* distortions from true cubane (T_d) symmetry; the [Mn$_4$O$_3$X] core is best described as a "face-capped trigonal pyramid" of C_{3v} ideal symmetry.

(12) We are aware of only one other example of a η^1-RCO$_2^-$ group occupying the vertex of a cubane structure: Hughes, D. L.; Wingfield, J. N. *J. Chem. Soc., Chem. Commun.* **1984**, 408.

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(14) Solvent molecules are lost *in vacuo*. Anal. Calcd (found) for C$_{51.5}$H$_{43}$O$_{15}$FClMn$_4$: C, 52.59 (53.02); H, 3.69 (3.83); F, 1.62 (1.79); Mn, 18.68 (18.42). Crystal data for **4**·$^5/_2$CH$_2$Cl$_2$: triclinic, $P\bar{1}$, a = 21.077(4) Å, b = 22.853(4) Å, c = 11.687(2) Å; α = 95.45(1)°, β = 92.75(1)°, γ = 88.14(1)°; Z = 4 (with two independent molecules of **4** in the asymmetric unit); V = 5595.59 Å^3; d_{calc} = 1.598 g·cm^{-3}; T = −174 °C. The structure was solved using MULTAN-78. R (R_w) = 4.27% (4.63%) with 12 837 unique reflections with $F > 3\sigma(F)$. All non-hydrogen atoms were refined anisotropically, two of the five solvent molecules in the asymmetric unit exhibited some disorder in the position of a chlorine atom, and hydrogen atoms were placed at idealized locations on all carbon atoms except those of the solvent molecules. The two molecules of **4** in the asymmetric unit are statistically identical, and only one of them has been arbitrarily chosen here for presentation.

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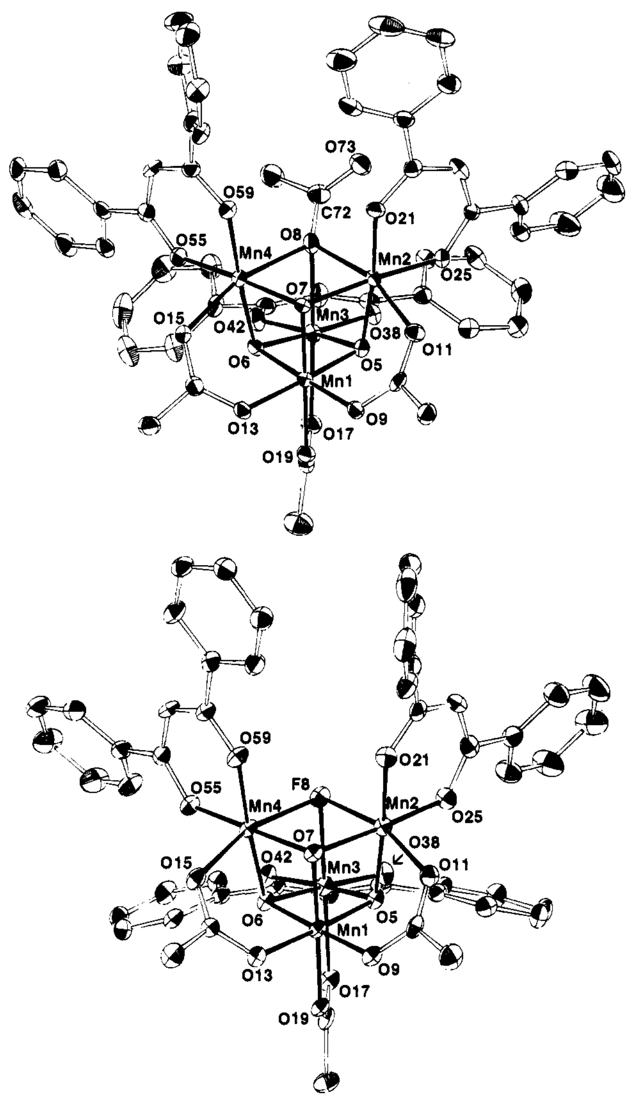

Figure 1. ORTEP representations of complexes **2** (top) and **4** (bottom) at the 50% probability level. For **2**: Mn(1)···Mn(2), 2.811(1); Mn(1)···Mn(3), 2.791(1); Mn(1)···Mn(4), 2.794(1); Mn(2)···Mn(3), 3.195(1); Mn(2)···Mn(4), 3.196(1); Mn(3)···Mn(4), 3.213(1); Mn(2)–O(8), 2.281(3); Mn(3)–O(8), 2.297(4); Mn(4)–O(8), 2.320(3) Å. For **4**: Mn(1)···Mn(2), 2.7774(5); Mn(1)···Mn(3), 2.7802(5); Mn(1)···Mn(4), 2.8000(7); Mn(2)···Mn(3), 3.1636(7); Mn(2)···Mn(4), 3.1348(8); Mn(3)···Mn(4), 3.1357(9); Mn(2)–F(8), 2.258(2); Mn(3)–F(8), 2.224(2); Mn(4)–F(8), 2.237(2) Å.

Mn^{III}–F(8) bonds (average 2.239 Å) are slightly shorter than the Mn^{III}–O(8) bonds in **2**. Structural comparison of the $[Mn_4(\mu_3\text{-}O)_3]$ units in **2** and **4** show them to be essentially identical. Thus, we conclude that the F^- ion can be accommodated into this Mn/O core with no accompanying structural strain. Both complexes **2** and **4** are stable in CH_2Cl_2 solution, as evidenced by ^1H and ^2H NMR spectroscopy.

Solid-state magnetic susceptibility studies were performed on **2** and **4** in the range 2–320 K. The data are presented in Figure 2 as μ_{eff} *vs* T plots, also showing the fits (solid lines) of the data to the theoretical expression derived previously for a Mn^{III}_3-Mn^{IV} pyramid of C_{3v} symmetry.[15] The obtained fitting parameters are, in the format **2**/**4**, $J_{34} = J(Mn^{III}\cdots Mn^{IV}) = -33.9/-20.8$ cm^{-1}, $J_{33} = J(Mn^{III}\cdots Mn^{III}) = +5.4/+7.4$ cm^{-1}, and g = 1.94/1.94, using the $\hat{H} = -2JS_i{\cdot}S_j$ convention. Complex **3** has corresponding values of $J_{34} = -28.4$ cm^{-1} and $J_{33} = +8.3$ cm^{-1}.[13b] The dominance of the antiferromagnetic J_{34} exchange interaction leads to these complexes all having $S = {}^9/_2$ ground states, but the weakening of J_{34} by the F^- in **4** leads to closer-lying excited states compared with the other complexes; the lower-lying excited states in **4** *vs* **2** are the origin of the significant deviations in the μ_{eff} *vs* T plots in Figure 2 at higher temperatures. Thus, even though its influence on the structure is minimal, incorporation of F^- does have a noticeable influence on the electronic structure of the host $[Mn_4O_3]$ core, especially on the $[Mn^{III}(\mu_3\text{-}O)_2Mn^{IV}]$ units that mediate the stronger J_{34} exchange interaction.

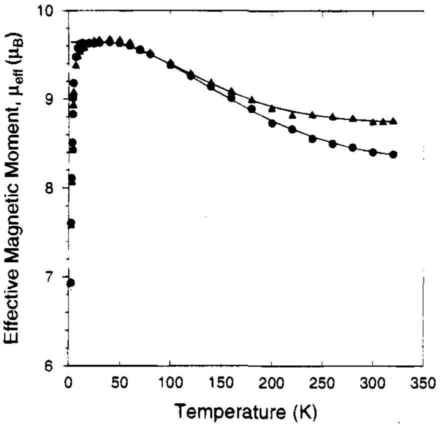

Figure 2. Plots of effective magnetic moment (μ_{eff}) per Mn_4 *vs* temperature for complexes **2** (●) and **4** (▲). The solid lines are fits to the theoretical data; see text for fitting parameters.

In summary, electrochemical oxidation of **1** leads to spontaneous incorporation of a third oxide to yield **2** with an unusual $[Mn_4O_3(\eta^1\text{-}MeCO_2)]$ core. Treatment with a F^- source yields **4**, the initial example of a F^--containing Mn/O/RCO_2 aggregate and one that can be considered a potential model of F^--inhibited WOC. Its ready formation and the minimal structural perturbation by the F^- of the host Mn/O core are of interest *vis-à-vis* the similarly ready F^- incorporation into the WOC Mn/O/RCO_2 cluster, whose precise structure has yet to be defined; note, however, that the $[Mn_4O_3]$ partial cubane is one of the structural units consistent with EXAFS data on the WOC.[16] The present work suggests that F^- in the WOC could enter a μ_x mode by displacing a μ_x-RCO_2^- group and/or occupying a site that would normally be occupied by a μ_x-O^{2-} or -OH^- group derived from substrate H_2O. Work in progress is directed toward more fully characterizing the influence of F^- on the properties of the Mn_4O_3 host, including the redox potentials of further oxidations, and incorporating other groups into the vacancy of the partial cubane unit.

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Supporting Information Available: Data collection and refinement details and listings of atomic coordinates and thermal parameters for complexes **2** and **4** (20 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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