Incorporation of Fluoride into a Tetraneurial Mn(II)/RCO₃⁻ Aggregate: Potential Relevance to Inhibition of Fluorosoluble 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 H₂O molecules to produce O₂. The WOC is composed through flux along S₀-S₄ states (S₀-S₄) until the transient S₄ state is reached. O₂ is evolved, and the system relaxes back to the S₀ state. It has been proposed that the water molecules are incorporated into the Mn aggregate as oxide (or hydroxide) bridges during the aggregate's advance to the higher S₄ states and are thereby activated to oxidation. Therefore, we have been interested in developing and studying processes that involve coupled oxidation/oxide incorporation of tetraneurial Mn(II)/RCO₃⁻ complexes. A number of other intriguing properties of the WOC are known, including the fact that it absolutely requires Cl⁻ for activity 1-2 (Br⁻ can substitute for Cl⁻ in vitro) whereas F⁻ is an inhibitor; 1,2 the presence of F⁻ also affects the electronic properties of the WOC as judged by EPR studies of the S₂ state which show that the normal “ multiline” signal at g ≈ 2 is replaced by a g ≈ 4.1 signal. 3 Thus, O₂ 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 aggregates containing F⁻. 4 This report describes two developments: preparation of a remarkable [Mn₄O₅(η^1-O-CMe₃)] cube possessing a mononuclear, triply-bridging MeCO₃⁻ 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 Mn₄O₅(C₆Me₃COOH)(η^1-O)(dbm)₃ (1; dbmH = dibenzoylmethane) in MeCN reveals a one-electron oxidation at 0.61 V vs CpFe/CpFe⁺. Controlled potential electrolysis at 0.84 V vs 1 in MeCN/CH₃Cl₃ (3:1) containing 0.2 M NBU₄ClO₄ was performed under a dry Ar atmosphere; during the electrolysis, a solution of dbmH (1 equiv) in MeCN/0.2 M NBU₄ClO₄ was added dropwise. On completion of the experiment, the brown precipitate of Mn₄O₅(C₆Me₃COOH)(dbm)₂ (2) was collected by filtration; yield 54%

On the basis of earlier precedents, 3 the conversion of 1 to 2 is concluded to be a result of reaction of adventitious H₂O (or other potential oxide sources) with oxidized 1 (Eq. 1).

Mn₄O₅(C₆Me₃COOH)(η^1-O)(dbm)₃ + dbmH + H₂O → Mn₄O₅(C₆Me₃COOH)(dbm)₂ + 2H₂O + CO₂ + pyH⁺ + py (1)

Crystals of 2 can be grown from CH₃CN/MeCN, 10. The structure of 2 (Figure 1, top) consists of a [Mn₄O₅]³⁺ (3Mn⁶⁺, Mn⁵⁺) partial cubane whose vacant vertex is occupied by a η^1-MeCO₃⁻ group to give a [Mn₄(µ₃-O)(µ₅-O-CMe₃)]⁻ "distorted-cubane" or face-capped trigonal pyramidal core. 11 This is an extremely unusual and rare bridging mode for a RCO₃⁻ group. 12,13 Metric parameters and the absence of a Jahn–Teller (JT) distortion on Mn(1) indicate this to be the Mn⁵⁺ ion, and the other metals are elongated Mn(II) acetate on the (O8) lies on the JT axes of Mn(1), Mn(3), and Mn(4). The structure is statistically based on a Mn₄O₅Cl(C₆Me₃COOH)(dbm)₂ (3) reported previously 13 which contains a [Mn₄(µ₃-O)(µ₁-OCl)]⁻ core, except that the Mn⁵⁺–O(8) distances in 2 (average 2.299 Å) are considerably shorter than the Mn⁵⁺–Cl bonds in 3 (average 2.650 Å).

Reactivity studies in progress on 2 indicate the µ₁-MeCO₃⁻ 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 CH₃CN with Et₂NSF₅, a convenient source of F⁻ ions, followed by addition of hexanes (5 volumes) gives a brown precipitate of Mn₄(O₇Me₃COOH)(dbm)₄ (4) in 93% yield. Single crystals of 4/2/CH₃Cl₃ can be grown from CH₃CN/hexanes. 14 The structure of 4/2/CH₃Cl₃ (Figure 1, bottom) confirms that a F⁻-for-MeCO₃⁻ substitution has occurred with little structural perturbation of the RCO₃⁻ ion. The F⁻ ion F(8) is in a µ₁ mode at a vertex of the resultant [Mn₄O₅F]⁻ distorted-cubane core. 15

(10) Anal. Calcd (found) for C₅₆H₅₄O₇Mn: C, 54.24 (53.84); H, 3.86 (3.88). Crystal data for 2: monoclinic: P2₁/n, a = 13.549(2) Å, b = 22.338 (4) Å, c = 16.618(2) Å, β = 93.744(11)°, V = 4; V = 4859.46 Å³; dcalc = 1.596 g/cm³; T = -171 °C. The structure was solved using MULTAN-78. R = 0.059 (4.45%) with 4838 unique reflections with F > 3σ(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 (Tₐ) symmetry; the [Mn₄O₅]⁻ core is best described as a “face-capped trigonal pyramidal” of C₃ symmetry.
(12) We are aware of only one other example of a η^1-RCO₃⁻ group occupying the vertex of a cubane structure: Hughes, D. L.; Winkfield, J. N. J. Chem. Soc. Chem. Commun. 1984, 408.
(14) Solvent molecules are lost in vacuo. Anal. Calcd (found) for C₅₆H₅₄O₇FClMn: C, 52.59 (53.02); H, 3.69 (3.83); F, 1.62 (1.79); Mn, 16.68 (18.42). Crystal data for 4/2/CH₃Cl₃: triclinic: P₁, a = 21.077(4) Å, b = 21.873(4) Å, c = 11.243(2) Å, α = 118.3(2)°, β = 87.8(2)°, γ = 88.14(1)°, V = 4 (with two independent molecules of 4 in the asymmetric unit); μ = 5559.39 Å⁻¹; dcalc = 1.598 g/cm³; T = -174 °C. The structure was solved using MULTAN-78. R = 0.055 (4.63%) with 1287 unique reflections with F > 3σ(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 chloride atom, and hydrogen atom positions were placed at idealized locations, 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.
Figure 1. ORTEP representations of complexes 2 (top) and 4 (bottom) at the 50% probability level. For 2: Mn(I)···Mn(2), 2.811(1); Mn(I)···Mn(3), 2.791(1); Mn(I)···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(I)···Mn(2), 2.7774(5); Mn(I)···Mn(3), 2.7802(5); Mn(I)···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), 2.259(2); Mn(3)···F(8), 2.224(2); Mn(4)···F(8), 2.237(2) Å.

Mn(II)···F(8) bonds (average 2.239 Å) are slightly shorter than the Mn(II)···O(8) bonds in 2. Structural comparison of the [Mn(II)·(μ-O)] units in 2 and 4 show them to be essentially identical. Thus, we conclude that the F⁻ ion can be accommodated into this MnO core with no accompanying structural strain. Both complexes 2 and 4 are stable in CH₂Cl₂ solution, as evidenced by H and D 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 μeff vs T plots, also showing the fits (solid lines) of the data to the theoretical expression derived previously for a Mn(II)···Mn(II) pyramid of C₃ᵥ symmetry. The obtained fitting parameters are, in the format 2/4, J₁₂ = J(Mn(II)···Mn(IV)) = −33.9/−20.8 cm⁻¹, J₁₃ = J(Mn(III)···Mn(IV)) = −5.4/+7.4 cm⁻¹, and γ = 1.94/1.94, using the H = −2S₁S₂ convention. Complex 3 has corresponding values of J₃₄ = −28.4 cm⁻¹ and J₃₅ = +8.3 cm⁻¹. The dominance of the antiferromagnetic J₃₅ exchange interaction leads to these complexes all having S = 3/2 ground states, but the weakening of J₃₄ 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 η₁eff 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 [MnO₃] core, especially on the [Mn(II)·(μ-O)] units that mediate the stronger J₃₄ exchange interaction.

In summary, electrochemical oxidation of 1 leads to spontaneous incorporation of a third oxide to yield 2 with an unusual [MnO₃(η₁-MeCO₂)] core. Treatment with a F⁻ source yields 4, the example of a F⁻-containing MnO/RCO₂ 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 MnO core are of interest vis-à-vis the similarly ready F⁻ incorporation into the WOC MnO/RCO₂ cluster, whose precise structure has yet to be defined; note, however, that the [MnO₃] partial cubane is one of the structural units consistent with EXAFS data on the WOC. The present work suggests that F⁻ in the WOC could enter a μ₂ mode by displacing a μ₂-RCO₂⁻ group and/or occupying a site that would normally be occupied by a μ₂-O₂⁻ or OH⁻ group derived from substrate H₂O. Work in progress is directed toward more fully characterizing the influence of F⁻ on the properties of the MnO₃ 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 the current masthead page for ordering information and Internet access instructions.

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