

Incorporation of Fluoride into a Tetranuclear Mn/O/RCO₂ Aggregate: Potential Relevance to Inhibition by Fluoride of Photosynthetic Water Oxidation

Michael W. Wemple,[†] David M. Adams,[‡] Kirsten Foltling,[†] David N. Hendrickson,^{*‡} and George Christou^{*‡}

Department of Chemistry and Molecular Structure Center
Indiana University, Bloomington, Indiana 47405-4001
Department of Chemistry—0358
University of California at San Diego
La Jolla, California 92093-0358

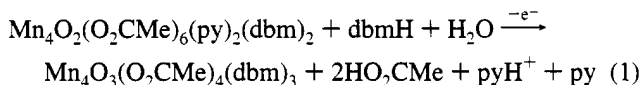
Received March 27, 1995

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 oxidized through five so-called S_n states (S₀–S₄) until the transient S₄ state is reached, O₂ is evolved, and the system relaxes back to the S₀ state.^{1,2} It has been proposed³ 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/RCO₂⁻ 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 S₂ state which show that the normal "multiline" signal at *g* ≈ 2 is replaced by a *g* ≈ 4.1 signal.⁷ 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_n aggregates containing F⁻.⁸ This report describes two developments: preparation of a remarkable [Mn₄O₃(η¹-O₂CMe)] cubane possessing a *monoatomic*, triply-bridging MeCO₂⁻ 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 Mn₄O₂(O₂CMe)₆(py)₂(dbm)₂ (**1**; dbmH = dibenzoylmethane) in MeCN reveals a one-electron oxidation at 0.61 V vs Cp₂Fe/

Cp₂Fe⁺.⁹ Controlled potential electrolysis at 0.84 V of **1** in MeCN/CH₂Cl₂ (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 Mn₄O₃(O₂CMe)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 H₂O (or other potential oxide sources) with oxidized **1** (eq 1). Single



crystals of **2** can be grown from CH₂Cl₂/MeCN.¹⁰ The structure of **2** (Figure 1, top) consists of a [Mn₄O₃]⁷⁺ (3Mn^{III}, Mn^{IV}) partial cubane whose vacant vertex is occupied by a η¹-μ₃-MeCO₂⁻ group to give a [Mn₄(μ₃-O)₃(μ₃-O₂CMe)]⁶⁺ "distorted-cubane" or face-capped trigonal pyramid core.¹¹ This is an extremely unusual and rare bridging mode for a RCO₂⁻ 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 Mn₄O₃Cl(O₂CMe)₃(dbm)₃ (**3**) reported previously¹³ which contains a [Mn₄(μ₃-O)₃(μ₃-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 μ₃-MeCO₂⁻ 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 CH₂Cl₂ with Et₂-NSF₃, a convenient source of F⁻ ions, followed by addition of hexanes (5 volumes) gives a brown precipitate of Mn₄O₃F(O₂-CMe)₃(dbm)₃ (**4**) in 93% yield. Single crystals of **4**^{5/2}CH₂Cl₂ can be grown from CH₂Cl₂/hexanes.¹⁴ The structure of **4**^{5/2}CH₂Cl₂ (Figure 1, bottom) confirms that a F⁻-for-MeCO₂⁻ substitution has occurred with little structural perturbation of the rest of the molecule. The F⁻ ion F(8) is in a μ₃ mode at a vertex of the resultant [Mn₄O₃F]⁶⁺ distorted-cubane core.¹¹ The

(9) Wang, S.; Wemple, M. W.; Tsai, H.-L.; Huffman, J. C.; Foltling, K.; Hagen, K. S.; Hendrickson, D. N.; Christou, G. Manuscript in preparation.

(10) Anal. Calcd (found) for C₅₃H₄₅O₁₇Mn₄: 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, and *c* = 16.618(2) Å; β = 103.74(1)°; Z = 4; V = 4885.49 Å³; *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* > 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 (*T_d*) symmetry; the [Mn₄O₃X] 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 η¹-RCO₂⁻ group occupying the vertex of a cubane structure: Hughes, D. L.; Wingfield, J. N. *J. Chem. Soc., Chem. Commun.* **1984**, 408.

(13) (a) Wang, S.; Foltling, K.; Streib, W. E.; Schmitt, E. A.; McCusker, J. K.; Hendrickson, D. N.; Christou, G. *Angew. Chem., Int. Ed. Engl.* **1991**, 30, 305. (b) Wang, S.; Tsai, H.-L.; Foltling, K.; Streib, W. E.; Hendrickson, D. N.; Christou, G. Manuscript in preparation.

(14) Solvent molecules are lost *in vacuo*. Anal. Calcd (found) for C_{51.5}H₄₃O_{15.5}FClMn₄: 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}CH₂Cl₂: triclinic, P1, *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 Å³; *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* > 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 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.

[†] Indiana University.

[‡] University of California at San Diego.

(1) For recent reviews, see: (a) Debus, R. J. *Biochim. Biophys. Acta* **1992**, 1102, 269. (b) *Manganese Redox Enzymes*; Pecoraro, V. L., Ed.; VCH Publishers: New York, 1992.

(2) (a) Kok, B.; Forbush, B.; McGloin, M. *Photochem. Photobiol.* **1970**, 11, 457. (b) Joliot, P.; Barbieri, G.; Chaband, R. *Ibid.* **1969**, 10, 309.

(3) (a) Brudvig, G. W.; Crabtree, R. H. *Proc. Natl. Acad. Sci. U.S.A.* **1986**, 83, 4586. (b) Christou, G.; Vincent, J. B. *Biochim. Biophys. Acta* **1987**, 895, 259.

(4) Wang, S.; Tsai, H.-L.; Hagen, K. S.; Hendrickson, D. N.; Christou, G. *J. Am. Chem. Soc.* **1994**, 116, 8376.

(5) Coleman, W. J. *Photosynth. Res.* **1990**, 23, 1 and references therein.

(6) (a) Sandusky, P. O.; Yocum, C. F. *Biochim. Biophys. Acta* **1986**, 849, 85. (b) Preston, C.; Pace, R. J.; Critchley, C. *Ibid.* **1987**, 894, 477.

(7) (a) Casey, J. L.; Sauer, K. *Biochim. Biophys. Acta* **1984**, 767, 21. (b) Ono, T.-A.; Nakayama, H.; Gleiter, H.; Inoue, Y.; Kawamori, A. *Arch. Biochem. Biophys.* **1987**, 256, 618. (c) Beck, W. F.; Brudvig, G. W. *Chem. Scr.* **1988**, 28A, 93. (d) Baumgarten, M.; Philo, J. S.; Dismukes, G. C. *Biochemistry* **1990**, 29, 10814.

(8) Mn^I and Mn^{II} species are, however, known: (a) Horn, E.; Snow, M. R.; Zeleny, P. C. *Aust. J. Chem.* **1980**, 33, 1659. (b) Abel, E. W.; Towle, I. D. H.; Cameron, T. S.; Cordes, R. E. *J. Chem. Soc., Dalton Trans.* **1979**, 1943. (c) Smit, J. J.; Nap, G. M.; De Jongh, L. J.; Van Ooijen, J. A. C.; Reedijk, J. *Physica* **1979**, 97B, 365.

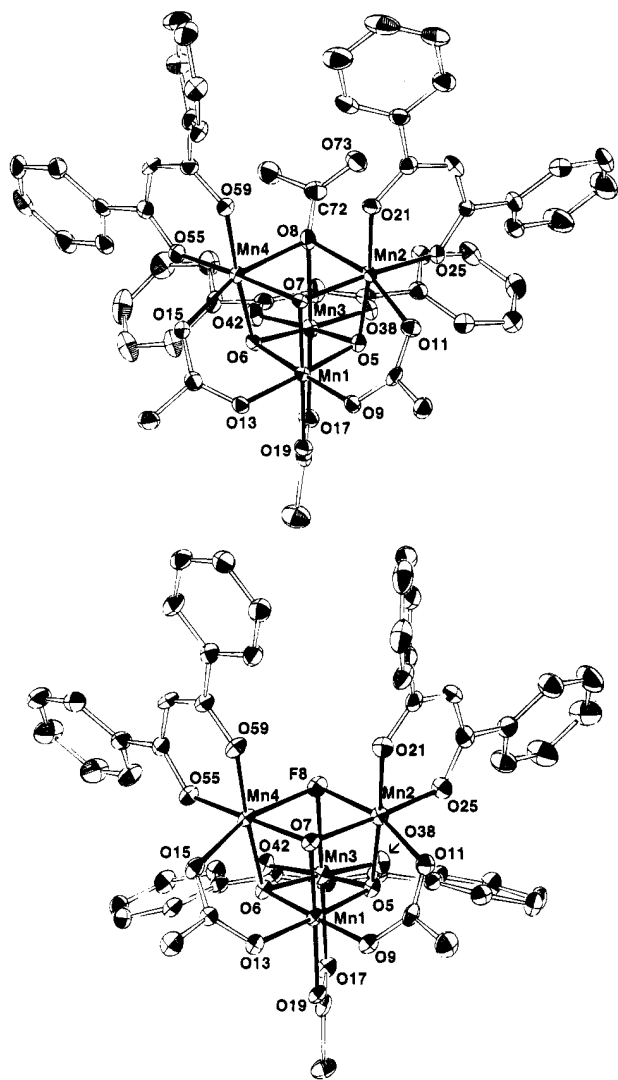


Figure 1. ORTEP representations of complexes **2** (top) and **4** (bottom) at the 50% probability level. For **2**: Mn(1)–Mn(2), 2.811(1); Mn(1)··Mn(3), 2.791(1); Mn(1)··Mn(4), 2.794(1); Mn(2)··Mn(3), 3.195(1); Mn(2)··Mn(4), 3.196(1); Mn(3)··Mn(4), 3.213(1); Mn(2)–O(8), 2.281(3); Mn(3)–O(8), 2.297(4); 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 [Mn₄(μ₃-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 CH₂Cl₂ 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, $J_{34} = J(\text{Mn}^{\text{III}} \cdots \text{Mn}^{\text{IV}}) = -33.9/-20.8 \text{ cm}^{-1}$, $J_{33} = J(\text{Mn}^{\text{III}} \cdots \text{Mn}^{\text{III}}) = +5.4/+7.4 \text{ cm}^{-1}$, and $g =$

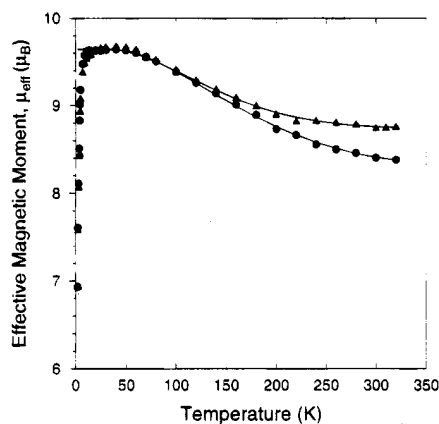


Figure 2. Plots of effective magnetic moment (μ_{eff}) per Mn₄ vs temperature for complexes **2** (●) and **4** (▲). The solid lines are fits to the theoretical data; see text for fitting parameters.

1.94/1.94, using the $\hat{H} = -2JS_T S_j$ convention. Complex **3** has corresponding values of $J_{34} = -28.4 \text{ cm}^{-1}$ and $J_{33} = +8.3 \text{ cm}^{-1}$.^{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 [Mn₄O₃] core, especially on the [Mn^{III}(μ₃-O)₂Mn^{IV}] units that mediate the stronger J_{34} exchange interaction.

In summary, electrochemical oxidation of **1** leads to spontaneous incorporation of a third oxide to yield **2** with an unusual [Mn₄O₃(η¹-MeCO₂)] core. Treatment with a F⁻ source yields **4**, the initial example of a F⁻-containing Mn/O/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 Mn/O core are of interest *vis-à-vis* the similarly ready F⁻ incorporation into the WOC Mn/O/RCO₂ cluster, whose precise structure has yet to be defined; note, however, that the [Mn₄O₃] 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-RCO₂⁻ group and/or occupying a site that would normally be occupied by a μ_x-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 Mn₄O₃ host, including the redox potentials of further oxidations, and incorporating other groups into the vacancy of the partial cubane unit.

Acknowledgment. This work was supported by NIH Grants GM 39083 and HL 13652.

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.

JA9509801

(15) Hendrickson, D. N.; Christou, G.; Schmitt, E. A.; Libby, E.; Bashkin, J. S.; Wang, S.; Tsai, H.-L.; Vincent, J. B.; Boyd, P. D. W.; Huffman, J. C.; Folting, K.; Li, Q.; Streib, W. E. *J. Am. Chem. Soc.* **1992**, *114*, 2455.

(16) DeRose, V. J.; Mukerji, I.; Latimer, M. J.; Yachandra, V. K.; Sauer, K.; Klein, M. P. *J. Am. Chem. Soc.* **1994**, *116*, 5239.