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Communications

Synthesis and Characterization of Complexes Containing the (μ-Oxo)(μ-acetato)dimanganese(III/III) Core

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The photosystem II oxygen-evolving complex (PSII OEC) found in the chloroplast thylakoid membranes of higher plants and algae catalyzes the splitting of water. The process is generally believed to occur on four or two manganese aggregates.[2] Recently, on the basis of EXAFS data,[3] at least three different Mn–Mn distances (ca. 2.7, 3.3, and 4.3 Å) in the photosystem are suggested; the longest distance (4.3 Å) is also interpretable as a Mn–Ca separation.[3]

Owing to their relevance to the catalytic center of the photosystem, binuclear and tetranuclear manganese complexes have become the subjects of intensive research.[4-9] Binuclear bis(μ-oxo)dimanganese,[4] bis(μ-oxo)(μ-acetato)dimanganese,[5] and (μ-oxo)bis(μ-acetato)dimanganese[6] complexes are known, and very recently an example of a (μ-oxo)(μ-acetato)dimanganese complex was reported.[9] Recently, we and others reported[10] the synthesis of (μ-oxo)(μ-acetato)diiron(III) complexes of tetradentate ligands as models for diiron(III) centers in ribonucleotide reductase.[11] It is reasonable to postulate that an analogous dimanganese core could be present in PSII OEC, since it could account for the Mn–Mn separation of ~3.3 Å. Hence, we have synthesized and studied two such complexes, namely, $\{[(\text{bispicen})\text{Mn}]_2(\mu\text{-O})(\mu\text{-OAc})\}(\text{ClO}_4)_3$ (**1**), where bispicen is *N,N'*-bis(2-pyridylmethyl)ethane-1,2-diamine,[12] and $\{[(\text{bispicMe}_2\text{en})\text{Mn}]_2(\mu\text{-O})(\mu\text{-OAc})\}(\text{ClO}_4)_3$ (**2**), where bispicMe$_2$en is *N,N'*-bis(2-pyridylmethyl)-*N,N'*-dimethylethane-1,2-diamine.[13]

Complex **1** was synthesized as follows. To an aqueous solution (20 mL) of bispicen[12] (0.484 g, 2 mmol) were added manganese(II) perchlorate hexahydrate (0.724 g, 2 mmol) and sodium acetate trihydrate (0.136 g, 1 mmol) with stirring. The pH was adjusted to 5 by the addition of drops of 70% perchloric acid and the solution stirred for 2 days at room temperature. The red-brown solid that formed was recrystallized from acetonitrile (0.198 g, 20% yield).[14] In the absence of perchloric acid, the reaction yields the bis(μ-oxo)dimanganese(III/IV) complex $\{[(\text{bispicen})\text{Mn}]_2(\mu\text{-O})_2\}(\text{ClO}_4)_3$.[4a] Complex **2** was prepared by the reaction of basic manganese acetate (0.597 g, 0.91 mmol) and bispicMe$_2$en·2HClO$_4$ (0.641 g, 1.36 mmol)[13] in dry acetonitrile (15 mL). The solution was warmed for a few minutes and filtered; the filtrate was then carefully layered with *n*-hexane (10 mL). Red-brown needles of **2** were deposited after several days of standing (0.288 g, 20%).[14] A similar procedure, using methanol solvent and the free ligand, was recently shown to produce the corresponding bis(μ-acetato)dimanganese(II/II) complex.[15]

The crystal structure[16] of **1** consists of $\{[(\text{bispicen})\text{Mn}]_2(\mu\text{-O})(\mu\text{-OAc})\}^{3+}$ cations (Figure 1) and perchlorate anions. The geometry about each manganese(III) center is roughly octahedral; the isomer isolated is the *cis*-α species. A 2-fold symmetry axis

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(16) X-ray analysis: orthorhombic space group *Pbcn*, $a = 18.909(8)$ Å, $b = 13.753(4)$ Å, $c = 15.238(7)$ Å, $V = 3963(3)$ Å^3, $\rho_{\text{calcd}} = 1.622$ g cm^{-3}, $Z = 4$. Data collection at 295 K in the 2θ range 4–55° using Mo Kα ($\lambda = 0.710\,73$ Å) radiation provided 1714 reflections with $F > 6\sigma(F)$. The structure was solved by direct methods (SHELXTL program) and refined by least-squares techniques to final R (R_w) of 5.55% (6.80%).

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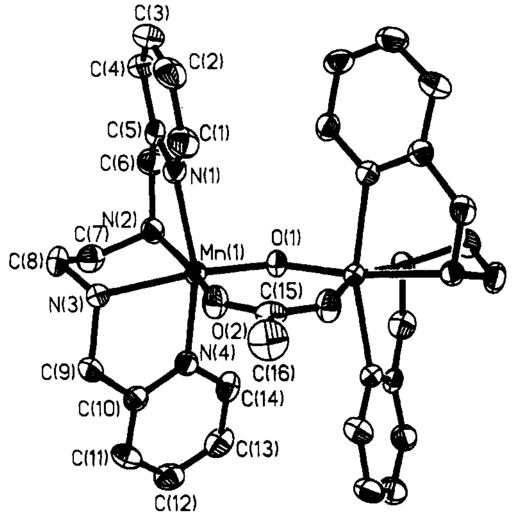

Figure 1. View of the $\{[(\text{bispicen})\text{Mn}]_2(\mu\text{-O})(\mu\text{-OAc})\}^{3+}$ cation in the crystals of the perchlorate salt. Hydrogen atoms are omitted for clarity. The two ends of the binuclear unit are related to each other by a crystallographic 2-fold axis passing through the bridging oxo group. Selected bond distances (Å) and angles (deg): Mn(1)–O(1), 1.801(3); Mn(1)–O(2), 2.031(5); Mn(1)–N(1), 2.213(6); Mn(1)–N(2), 2.228(6); Mn(1)–N(3), 2.091(6); Mn(1)–N(4), 2.112(6); Mn(1)···Mn(1A), 3.276(3); Mn(1)–O(1)–Mn(1A), 130.8(4).

passes through the bridging oxo group and the carbon atoms of the bridging acetato group. The Mn–Mn distance is 3.276(3) Å, and the Mn–O–Mn bridging angle is 130.8(4)°. The Mn–O_{oxo} and Mn–$O_{acetato}$ bond lengths of 1.801(3) and 2.031(5) Å, respectively, are comparable to the corresponding bond lengths in (μ-oxo)bis(μ-acetato)dimanganese(III/III) complexes.[6] As was observed in the related complex with tris((1-methylimidazol-2-yl)methyl)amine (TMIMA),[9] the Mn–N bond *trans* to the acetate group is longer than the other Mn–N bonds; in the present case, however, this distortion is much smaller than that in the TMIMA complex, the Mn–N(2) bond of 2.228(6) Å being only 3σ longer than the axial Mn–N(1) bond of 2.213(6) Å. This lengthening of Mn–N(2) has been attributed[17] to the *trans* effect of the acetate ligand, but since no lengthening is observed[10c] in the Fe(III) analogue of **1**, it is more probably the result of the Jahn–Teller distortion of the d^4 Mn(III) ion.

The crystals of **2**[18] diffracted very poorly and hence the structure determination is of low quality but suffices to show that the geometry of the cation is similar to that of **1**. The Mn–Mn separation is 3.292(14) Å, and the Mn–O–Mn bridging angle is 133(3)°. The Mn–O_{oxo} and Mn–$O_{acetato}$ bond distances are 1.79(2) and 1.90(3) Å, respectively; the axial Mn–N_{py} bond distances are 2.19(3) and 2.17(3) Å; and the equatorial Mn–N_{amine} distances are 2.01(4) and 2.24(5) Å, the latter being *trans* to the acetato group. Thus the expected Jahn–Teller distortion for a d^4 Mn(III) ion is also suppressed in the structure of **2**.

The electronic spectrum of **1** in acetonitrile exhibits two strong absorptions at 260 and 295 nm and a shoulder at 380 nm in the UV region and two absorptions of moderate intensity at 490 nm (ϵ = 225 M^{-1} cm^{-1}) and at 532 nm (ϵ = 242 M^{-1} cm^{-1}) in the visible region. The spectrum of **2** is very similar to that of **1**. The bands in the visible region are attributable to the d–d transitions,[19] and the spectrum is comparable to that of the manganese(III)-

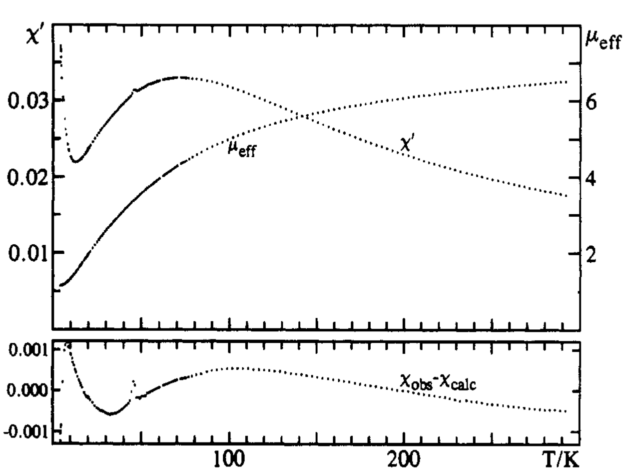

Figure 2. Magnetic susceptibility (left scale) and effective magnetic moment (right scale) of complex **1**.

containing enzymes of *Lactobacillus plantarum*[20] and the ribonucleotide reductase of *Brevibacterium ammoniagenes* especially in the 350–550-nm region.[21] Similar spectra have also been observed for (μ-oxo)bis(μ-acetato)dimanganese (III/III) complexes.[6]

The magnetic susceptibility of **1** (Figure 2) maximizes at approximately 72 K, suggesting that while the interaction is antiferromagnetic, the triplet energy is relatively small; the magnetic susceptibility of **2** maximizes at 50 K, implying an even lower energy for the triplet in **2**. While the susceptibility of strongly antiferromagnetically-coupled dimanganese(III/III) complexes can be fitted to a simple Heisenberg operator because only a few states are effectively populated, the interpretation of the antiferromagnetic coupling between two manganese(III) ions is not a trivial problem, because each Mn(III) in octahedral symmetry can be classified as a ^5E state. In lower symmetries, this state will be split into ^5A and ^5B states. Coupling of the ^5A and ^5B states on one center with the ^5A and ^5B states on the other center gives rise to a maximum of four *J* values and three parameters to describe the relative zero points among the four sets of levels. This is far too many parameters to be determined from susceptibility data.

Another model incorporates the zero-field splitting of the individual Mn(III) ions and treats the ^5E state as an orbitally nondegenerate state. We have, therefore, attempted to fit the susceptibility data to the operator

$$\hat{H} = J\hat{S}_1\cdot\hat{S}_2 + g\mu_B\sum\hat{S}_1\cdot B + D\sum[\hat{S}_{iz}^{\,2} - S_i(S_i + 1)]$$

where we have assumed that the two Mn(III) ions are equivalent; *i.e.*, we have set $g_1 = g_2$ and $D_1 = D_2$. We obtained the values $J = 19.5(1)$ cm^{-1}, $g = 1.86(1)$, and $D = -4.21(2)$ cm^{-1} with 3.4% monomeric Mn(II) impurity. This model is not really satisfying, but it is the most acceptable available at present.

A cyclic voltammogram of **1** in acetonitrile displays a quasi-reversible one-electron oxidation at +1.03 V vs a Ag/AgCl reference electrode and an irreversible reduction at +0.10 V. These features are similar to those reported for the (μ-oxo)bis(μ-acetato)dimanganese(III/III) complexes[6] and could be similarly interpreted to be due to a quasi-reversible oxidation process of (III/III) ↔ (III/IV) and an irreversible reduction process of (III/III) ↔ (II/III). Complex **2** exhibits only a single quasi-reversible one-electron reduction at +0.40 V, presumably due to the (III/III) ↔ (II/III) couple. No oxidation waves were observed up to a potential of +1.80 V, indicating that N-methylation of bispicen decreases the stability of both the (III/IV) and (IV/IV) forms of **2**.

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(18) X-ray analysis: monoclinic space group *I*2, a = 13.327(16) Å, b = 9.743(13) Å, c = 16.726(1) Å, β = 92.47(5)°, V = 2170(4) Å^3, ρ_{calcd} = 1.567 g cm^{-3}, Z = 2. Data collection at 294 K in the 2θ range 2–50° using Mo Kα (λ = 0.710 73 Å) radiation provided 740 reflections with $F > 3\sigma(F)$. The structure was solved by direct methods (SHELXTL86 program) and refined by least-squares techniques to final R (R_w) of 12.0% (13.5%). Mn and Cl atoms were refined anisotropically; hydrogen atoms were not included.

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In summary, examples of novel dinuclear manganese(III) complexes with Mn–Mn distances of 3.276(3) and 3.292(14) Å, close to one of the suggested Mn–Mn distances in PSII OEC, have been synthesized. Along with the recently reported TMIMA analogue,[9] these present complexes might be viewed as completing the "series" of complexes exhibiting the Mn–Mn separations found in PSII OEC. The approximately 2.7 Å distances, which are well established from EXAFS studies,[3] are found in the bis(μ-oxo)dimanganese(III/III), -(III/IV), and -(IV/IV) complexes.[4] The approximately 4.3 Å separation recently found in EXAFS studies and attributed to either a Mn–Mn or Mn–Ca separation in the enzyme[3] is observed in the bis(μ-acetato)dimanganese(II/II) complex,[15] and now the approximately 3.3 Å distance is found in the (μ-oxo)(μ-acetato)dimanganese(III/III) complexes **1** and **2** described here.

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Supplementary Material Available: Summary of X-ray analyses for **1** and **2** (Table S1), atomic coordinates for **1** and **2** (Tables S2 and S6), bond distances and angles for **1** and **2** (Tables S3 and S7), H atom coordinates for **1** (Table S4), and anisotropic thermal parameters for **1** (Table S5) (10 pages). Ordering information is given on any current masthead page. Listings of observed and calculated structures factors for **1** and **2** are available from the authors.