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Communications

Isolation of a Mixed-Valence Trinuclear Manganese Complex Potentially Relevant to the Photosynthetic Oxygen-Evolving Complex[1]

Sir:

The photosynthetic oxygen-evolving complex (OEC)[2,3] requires four manganese ions to convert water into dioxygen:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \qquad (1)$$

Speculation on the nuclearity of the active-site structure is often based on the EPR spectral features and magnetic properties of the two-electron-oxidized form (S_2) of the OEC and has ranged[4-10] from binuclear to tetranuclear with model complexes[11-16] being synthesized to address these alternatives. Recently, a proposal that a mononuclear manganese center which is in an electron-transfer equilibrium with a mixed-valence dimer has appeared.[17] Equally consistent with available data is a model that incorporates a trinuclear cluster in an electron-transfer equilibrium with a mononuclear center. While mononuclear Mn(IV) compounds are available for study,[1,18-20] trinuclear manganese complexes with biomimetic ligands that might evaluate this proposal are almost nonexistent. In this contribution, we report the synthesis and characterization of $Mn^{II}Mn^{III}_2(SALADHP)_2(O_2CCH_3)_4(CH_3OH)_2$, a mixed-valence complex that exhibits an $S = {}^3/_2$ ground state and provides the first example of a $g \cong 4$ signal in a homonuclear manganese cluster.

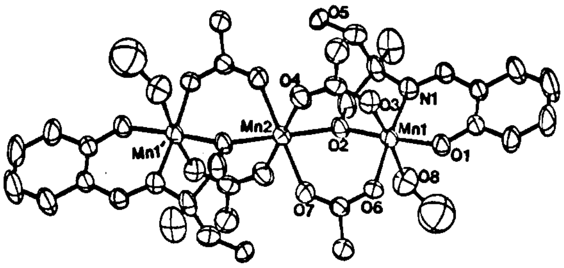

Figure 1. ORTEP drawing of $Mn_3(SALADHP)_2(OAc)_4(CH_3OH)_2$ with thermal ellipsoids at 50% probability.

The complex $Mn^{II}Mn^{III}_2(SALADHP)_2(O_2CCH_3)_4(CH_3OH)_2$ (**1**) was synthesized by refluxing a 100-mL methanolic solution containing 20 mmol of SALADHP[21] and 30 mmol of $Mn(OAc)_2 \cdot 4H_2O$ under nitrogen for 2 h, followed by air oxidation at room temperature for 12 h. A red-brown microcrystalline solid was isolated in 80% yield. Well-formed green crystals of **1** were isolated by slow evaporation of a methanolic solution. Infrared and UV–vis spectra, elemental analyses, and magnetic susceptibilities of the red-brown powder and pale green crystals were identical.

The structure[22-24] of **1** is illustrated as Figure 1. The central

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(21) Abbreviations used: H_2SALADHP = 2-(salicylideneamino)-1,3-dihydroxy-2-methylpropane; H_2SALAHP = 3-(salicylideneamino)-1-hydroxypropane; sal = salicylaldehyde; py = pyridine; H_2SALPS = bis[(2-salicylideneamino)phenyl]disulfide; OAc = acetate.

(22) Crystallographic data for **1**: monoclinic, $P2_1/a$: $a = 12.450$ (3) Å; $b = 13.502$ (4) Å; $c = 13.428$ (5) Å; $\beta = 102.53$ (2)°; $V = 22\,203$ (1) Å^3; $Z = 2$; $d_{calcd} = 1.422$ g/cm^3; $d_{measd} = 1.42$ g/cm^3; (flotation in hexane–CCl_4); crystal dimensions 0.395 × 0.464 × 0.297 mm; $\mu = 8.84$ cm^{-1}; $M_r = 939.6$; $0 < 2\theta < 45°$; 3420 data collected; 2111 data $>3\sigma(I)$; $R = 0.057$; $R_w = 0.055$; largest residual 0.67 e/Å^3. The methyl and uncoordinated hydroxymethyl groups of the SALADHP ligands were disordered with the best model giving occupancies of 0.70 and 0.30 for O5 and O5″, respectively.

(23) Intensity data were obtained by using Mo Kα radiation monochromatized from a graphite crystal whose diffraction vector was parallel to the diffraction vector of the sample. Three standard reflections were measured every 50 reflections. Crystal faces were measured. A numerical absorption correction was applied, and the structure was solved by using MULTAN78 by Peter Main. Additional computer programs were from the SHELX program package by George Sheldrick, Institute for Anorganische Chemie der Universitat Gottingen, Federal Republic of Germany, and ORTEP, a thermal ellipsoidal drawing program by C. K. Johnson. Atomic scattering factors were from: *International Tables for X-ray Crystallography*; Ibers, J. A., Hamilton, W. C., Eds.; Kynoch: Birmingham, England, 1974; Vol. IV, Tables 2.2 and 2.3.1.

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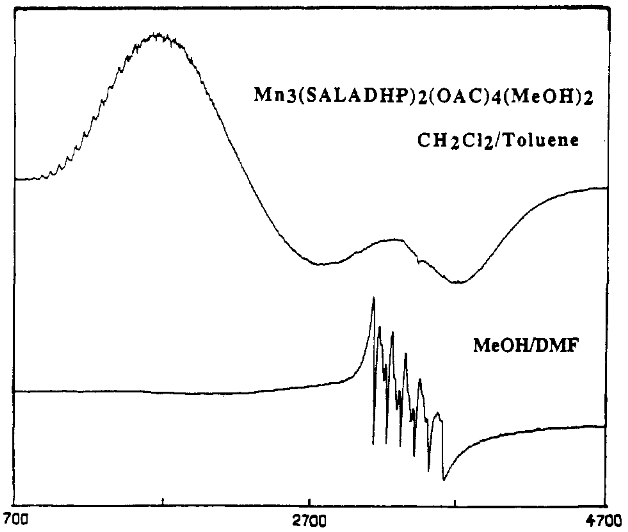

Figure 2. X-Band EPR spectrum of $Mn_3(SALADHP)_2(OAc)_4(CH_3OH)_2$ at 4.2 K in a CH_2Cl_2–toluene glass and in methanol–DMF (ν = 9.4696 GHz; frequency modulation 100 kHz).

Mn(II) ion [Mn2] is located on a crystallographic inversion center. Two Mn(III) ions [Mn1, Mn1′) are located 3.551 Å[24] from Mn2. The octahedral coordination sphere for M2 is composed entirely of bridging ligands using oxygen atoms [O4, O4′ and O7, O7′] from four acetate molecules and alkoxide oxygen atoms [O2, O2′] of two SALADHP ligands. Each Mn(III) ion is six-coordinate with acetate oxygen atoms O3 and O6, SALADHP atoms O2 (alkoxide), O1 (phenoxide), and N1 (imine), and a methanolic oxygen atom, O8. The Mn(III) polyhedron is tetragonally distorted as demonstrated by the short Mn(III)–N or –O distances for the atoms comprising the plane O1, O2, O6, and N1 (2.001 Å or less) relative to the axial bonds by Mn1–O8 (2.207 Å) and Mn1–O3 (2.155 Å). With the exception of the axial ligands, the heteroatom to Mn(III) bond lengths are significantly shorter than those to Mn(II) (e.g., Mn1–O2 = 1.885 Å, Mn2–O2 = 2.144 Å[26]). The SALADHP ligand acts as a meridional, tridentate chelating agent as reported for $Mn^{IV}(SALADHP)_2$[1,18] and the related $[Mn^{III}(SALAHP)(OAc)]_2$.[21,25] Both μ-alkoxo and μ-phenolato Mn(II) or Mn(III) dimers exhibit Mn–O–Mn angles in the range 95–105° (e.g., $[Mn^{II}SALPS]_2$,[21,26] 101.3° (Mn–Mn = 3.300 Å); $[Mn^{III}(SALAHP)(OAc)]_2$[25] 96.34° (Mn–Mn = 2.869 Å); $[Mn^{III}(sal)_2(py)]_2$,[21,27] 99.78° (Mn–Mn = 3.247 Å)). It is not surprising that the Mn1–O2–Mn2 angle for **1** (121.1°) is much larger than these, given the long Mn1–Mn2 distance.

Although **1** is neutral, the oxidation state of the terminal manganese ions cannot be assigned solely from the crystallographic data because the structure cannot distinguish an Mn(III)–methanol from Mn(IV)–methoxide unit. To resolve the protonation-state ambiguity of the coordinated solvent, we prepared the isostructural THF analogue of **1**. This material has magnetic properties and UV–vis, IR, and EPR spectral behavior identical with those of **1**. Since THF has no dissociable protons, the THF moiety must be coordinated as a neutral ligand in this neutral complex. By analogy, we conclude that the solvate in **1** must be methanol not methoxide, and this establishes the terminal manganese atoms as +3 ions.

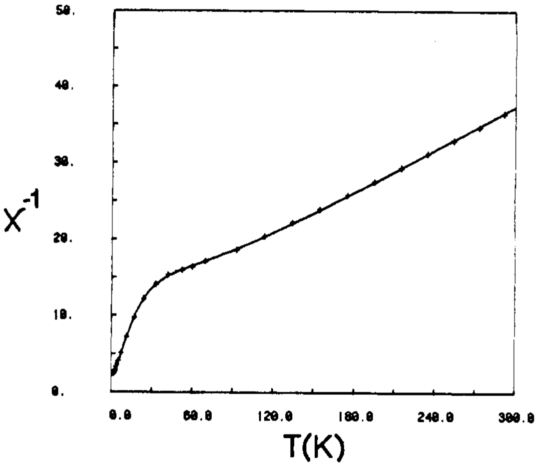

Figure 3. $1/\chi$ vs T for $Mn_3(SALADHP)_2(OAc)_4(CH_3OH)_2$. The solid line is a fit to the data.

Further support for this oxidation-state assignment comes from magnetic data and the EPR spectra of the associated and dissociated forms of the complex. In donor solvents, **1** dissociates into ions. The conductance of DMF–MeOH (3:2) solution indicates that a 2:1 electrolyte forms. The EPR spectrum of **1** dissolved in DMF–MeOH shows a six-line signal centered at $g = 2$. This signal, shown in Figure 2, is diagnostic of mononuclear Mn(II). The room-temperature moment for a DMF–MeOH solution of **1** is 9.1 μ_B, which is fully consistent with one Mn(II) ion and two Mn(III) ions, which have dissociated from the complex.

In contrast, **1** has μ = 8.1 μ_B at 300 K in the solid state and in a 1:1 toluene–CH_2Cl_2 solution, indicating that the manganese atoms are weakly coupled. Variable-temperature solid-state magnetic data for **1** were collected between 4 and 300 K. The data shown in Figure 3 were fitted[28] to a model that accounted for Mn(III)/Mn(II) coupling (J_{12}) as well as Mn(III)/Mn(III) coupling ($J_{11'}$). The best fit parameters are $J_{12} = -7.09$ cm^{-1}, $J_{11'} = 0$ cm^{-1} (fixed), $g_1 = 2.04$ and $g_3 = 2.0$ (fixed). These data also indicate that **1** has an $S = {}^3/_2$ ground state. A low-field feature is observed in the EPR spectrum shown as Figure 2. This signal, which arises from the $S = {}^3/_2$ spin manifold, grows in below 30 K.

The OEC cycles through five distinct oxidation levels, S_0–S_4, during the water-splitting process.[29,30] The EPR spectral and magnetic properties of the S_2 state have been intensively studied. Depending on the choice of cryoprotectant or illumination temperature of the PSII particles, both $g = 2$ multiline and $g = 4.1$ features have been reported. Brudvig[8,10,31] has forwarded a single-center model to account for these observations. The $g = 2$ multiline pattern arises from a low-lying $S = {}^1/_2$ excited state of a cluster that has an $S = {}^3/_2$ ground state. The $g = 4.1$ signal arises from a perturbed conformation of the cluster in this model. In contrast, the EPR data of Vanngard[17] indicate that the multiline feature arises from an $S = {}^1/_2$ spin system that follows Curie law behavior. From these results, a dual-center model that incorporates a mononuclear center involved in an electron-transfer equilibrium with a binuclear cluster has been suggested.

The available data cannot eliminate a dual-center model that utilizes a trinuclear center. For example, a trinuclear cluster could be the origin of the magnetic behavior reported by Brudvig for the $g = 2$ signal. The $g = 4.1$ feature could then arise through

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(24) Important distances (Å) and angles (deg) for **1**: Mn1–Mn2, 3.551 (1); Mn1–O1, 1.876 (5); Mn1–O2, 1.885 (5); Mn1–O3, 2.155 (5); Mn1–O6, 1.962(5); Mn1–O8, 2.346 (6); Mn1–N1, 2.001 (5); Mn2–O2, 2.144 (4); Mn2–O4, 2.175 (5); Mn2–O7, 2.206 (5); Mn1–Mn2–Mn1′, 180; O1–Mn1–N1, 91.0 (2); O1–Mn1–O2, 172.6 (2); O1–Mn1–O3, 91.9 (2); N1–Mn1–O2, 83.0 (2); N1–Mn1–O3, 95.1 (2); O2–Mn1–O3, 93.0 (2); O1–Mn1–O6, 87.2 (2); N1–Mn1–O6, 173.5 (2); O2–Mn1–O6, 98.3 (2); O3–Mn1–O6, 91.2 (2); O1–Mn1–O8, 91.2 (2); O2–Mn1–O8, 84.5 (2); N1–Mn1–O8, 90.0 (2); O3–Mn1–O8, 174.0 (2); O6–Mn1–O8, 84.5 (2); O2–Mn2–O4, 91.3 (2); O2–Mn2–O7, 88.5 (2); O4–Mn2–O7, 92.5 (2); Mn1–O2–Mn2, 121.7 (2).

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either a conformational change mechanism (Brudvig) or an electron-transfer process (Vanngard). The dual center, conformational change mechanism incorporates a mononuclear manganese center that acts solely as an electron-transfer intermediate between P680$^+$ or Z$^+$ and the trinuclear cluster. Both the multiline and $g = 4$ features would result from conformationally distinct clusters. Alternatively, in the dual-center, electron-transfer mechanism, a mononuclear center would be involved in a redox equilibrium between a mononuclear center with an Mn(III)/Mn(IV) couple and a trinuclear center with an Mn(III)Mn(III)Mn(III)/Mn(III)Mn(III)Mn(IV) couple. The mononuclear Mn(IV) would result in the $g = 4$ signal while the multiline signature could be generated by the $S = {}^1/_2$ excited state of the Mn(III)Mn(III)Mn(IV) cluster. The Mn(III) and Mn(III)Mn(III)Mn(III) states would be EPR-silent.

In this context, the new structural class of trinuclear acetates described for this contribution provides an interesting model for a trinuclear formulation for the OEC. However, it must be noted that **1** does not fulfill many of the requirements for the spectroscopically observable S$_2$ state. There is no evidence for the multiline feature over the temperature range 4–30 K. The S$_2$ state probably consists of three Mn(III) ions and one Mn(IV) ion while **1** would best represent the S$_0$ level, which may be composed of three Mn(III) ions and one Mn(II) ion. Finally, recent EXAFS results[32] suggest that there is a short manganese-manganese vector at 2.7 Å, a longer distance at 3.3 Å, and a very short Mn–(C,N,O) distance of 1.79 Å ascribed to a μ-oxo or μ-hydroxo bridge. Clearly, **1** cannot mimic these distances.

With these caveats in mind, **1** can still provide useful information toward structural proposals for the OEC. The complex **1** is the first reported multinuclear manganese species that has an $S = {}^3/_2$ ground state and a low-lying $S = {}^1/_2$ excited state and gives rise to a low-field EPR sigal. This illustrates that trinuclear formulations can generate the magnetic behavior reported by Brudvig for the OEC. Furthermore, Brudvig has suggested that the $g = 4.1$ signal originates from a cluster rather than a mononuclear Mn(IV) center. Clearly, **1** demonstrates that certain conformations of multinuclear manganese clusters can result in such a low-field EPR component.

Acknowledgment. We thank Dr. W. E. Hatfield for magnetic susceptibility data, Dr. G. T. Babcock for EPR measurements, and Dr. W. Butler for X-ray structure refinement. V.L.P. thanks the G. D. Searle Family/Chicago Communty Trust for a Biomedical Research Scholarship. This work was supported by the donors of the Petroleum Research Fund, administered by the American Chemical Society, the Horace H. Rackham Foundation (University of Michigan), and an NIH Biomedical Research Support Grant to the Vice-President for Research.

Supplementary Material Available: Fractional atomic coordinates (Table I), thermal parameters (Table II), fit of variable-temperature magnetic data (Table III), and numbering scheme (Figure 4) for **1** (9 pages). Ordering information is given on any current masthead page.

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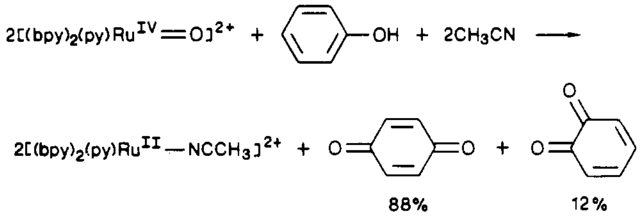
Mechanisms of Oxidation of Phenol and Cyclohexene by an Oxo Complex of Ruthenium(IV)

Sir:

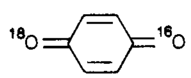
In the oxidation of olefins by epoxidation or allylic oxidation or in the oxidations of phenols to quinones or hydroquinones there is a net O atom demand. Discovering how such reactions occur is important in the design of models for biological oxidations or of catalytic reagents for the oxidative activation of hydrocarbons, but detailed mechanistic insight is often lacking.[1] The substitutionally inert polypyridyl and related oxo complexes of Ru(IV), e.g., $[(bpy)_2(py)Ru^{IV}(O)]^{2+}$ (bpy = 2,2′-bipyridine; py = pyridine), have an extensive stoichiometric and/or catalytic chemistry as oxidants.[2-10] Their reactions have proven to be especially amenable to mechanistic investigations based on a variety of techniques including kinetics, ^{18}O labeling, H/D kinetic isotope effects, and the appearance of reaction intermediates. We describe here in preliminary detail the results of a series of studies that illustrate the mechanistic versatility of the $Ru^{IV}{=}O^{2+}$ oxidant in the allylic oxidation of cyclohexene and the oxidation of phenol to quinone.

In acetonitrile or water the oxidation of phenol by $[(bpy)_2(py)Ru^{IV}(O)]^{2+}$ is rapid. By integration of appropriate resonances in the ^1H NMR spectrum of the final product solution at 25 °C, the reaction stoichiometry in CH_3CN is as shown in reaction 1.



(1)

Further, by use of ^{18}O-labeled $[(bpy)_2(py)Ru^{IV}(O)](ClO_4)_2$[11] (~85% as ^{18}O) and IR monitoring of the quinone product, $\nu(C{=}^{16}O) = 1660\ cm^{-1}$ [12,13] and $\nu(C{=}^{18}O) = 1646\ cm^{-1}$, it was seen that the transfer of one O atom from the $Ru^{IV}{=}O^{2+}$ oxidant to phenol is quantitative, as shown by the integration of relative peak areas in the product



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