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Trapping an Elusive Intermediate in Manganese–Oxo Cubane Chemistry

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A new member of the Mn–oxo cubane core complex family $[Mn^{2III,2IV}{}_4O_4L_6]$ (**1**), where L = $(p\text{-MeOPh})_2PO_2^-$, has been synthesized and characterized. Compound **1** possesses structurally inequivalent Mn^{III} and Mn^{IV} with clear valence electron localization in the crystal phase, quite unlike the structurally equivalent sites, tetrahedral core symmetry, and delocalized valence of its analogue where L = $Ph_2PO_2^-$. Compound **1** exhibits appreciable positive shifts (0.1–0.3 V) of both the oxidation and reduction electrochemical potentials, attributable to the remote electron donating *p*-MeO groups. Reduction of **1** by methanol yields a novel core complex $[Mn^{III}{}_4O_2(OMe)_2(MeOH)\{(p\text{-MeOPh})_2PO_2\}_6]$ (**2**). Each Mn^{III} of **2** is tetragonally distorted due to the Jahn–Teller effect with elongated Mn–O bonds that are directed at the two μ_3-MeO bridges and neither of the two μ_3-oxos. These electronically driven distortions provide a structural rationale for the greater basicity of the former sites and explain why 2 of the 4 corner oxos are preferentially reduced to water molecules.

The water-oxidizing complex (WOC) within the photosystem II (PSII) of oxygen-evolving phototrophs serves as nature's blueprint for a water splitting catalyst. The core structure has been debated on the basis of various spectroscopic and X-ray diffraction (XRD) methods.[1] The most recent XRD model of the resting state of a cyanobacterial PSII enzyme (at 3.5 Å, *R* factor 0.3) reveals a cubane-like Mn_3CaO_4 cluster bridged to a fourth Mn through one of the corner oxos.[1g] Spectroscopy reveals that the core changes in both oxidation state and geometry during the catalytic cycle of O_2 evolution. Thus, the availability of structurally characterized chemical models continues to be indispensable in providing real examples of Mn−oxo core types[2] and their redox interconversions.

Among the various postulated PSII−WOC mechanisms for O_2 formation, the Mn_4O_4-cubane ↔ Mn_4O_2-butterfly core rearrangement[3] has been experimentally validated to produce O_2 in the complex $[Mn_4O_4(Ph_2PO_2)_6]$, containing the $[Mn_4O_4]^{6+}$ cubane core.[4,5] Two of the core oxos are released as molecular O_2, following dissociation of a phosphinate ligand by UV illumination. They are also reduced in a four-electron/four-proton process using amines and phenols to form 2 equivalent H_2O species.[4,6] In both reactions, Mn_4O_2-butterfly core types are produced, but none were structurally characterized, nor were any of the partially reduced intermediates.

A highly unusual feature of $[Mn_4O_4(Ph_2PO_2)_6]$ is the tetrahedral symmetry of its core which lacks Jahn−Teller distortions, indicating delocalized valence electrons, in both the solid state and solution phases.[7] Delocalization has been confirmed in the same material produced by a different synthetic approach.[8] Here, we report a new phosphinate derivative of this family in two oxidation states: one which illustrates the transition to a localized electronic valence in the $[Mn_4O_4]^{6+}$ core, and a second that provides the first molecular structure of the $[Mn^{III}{}_4O_2(OR)_2]^{6+}$ core in the cubane family.

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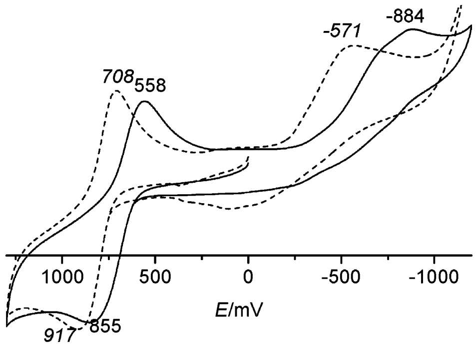

Figure 1. Cyclic voltammogram of **1** (—) and $[Mn_4O_4(Ph_2PO_2)_6]$ (- - -) in CH_2Cl_2 (0.4 mM) versus Ag/$AgNO_3$ (0.1 M in CH_3CN).

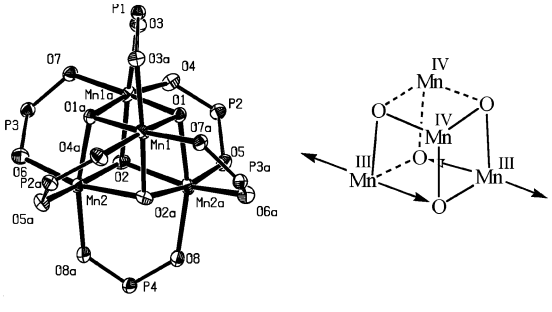

Figure 2. Left: ORTEP drawing (50% probability) of **1** with anisole rings omitted for clarity. Right: The cubane core with Mn(III) Jahn−Teller bond elongations depicted by arrows (average difference in Mn(III)−O bond length is 0.227 Å axial−equatorial).

$[Mn_4O_4\{(p\text{-}MeOPh)_2PO_2\}_6]$ (**1**) was synthesized by the "fusion" route[7] using bis(*p*-methoxyphenyl)phosphinic acid and $Mn_2O_2(bpy)_4(ClO_4)_3$. A solution of **1** in CH_2Cl_2/MePh (1/1) is EPR silent (4−300 K), using both perpendicular and parallel B_1 modes. The ^1H NMR signals of **1** in CD_2Cl_2 fall into the diamagnetic range with no appreciable contact shifts but are broadened due to thermal population of low-lying paramagnetic state(s). A singlet at 3.82 ppm originates from the 12 terminal methyl groups. A broader peak at 7.24 ppm is ascribed to 48 unresolved ortho and meta protons in the phenyl rings. Thus, **1** has tetrahedral symmetry in solution with all 12 anisole rings magnetically equivalent. Figure 1 compares the cyclic voltammogram of **1** to that of $[Mn_4O_4(Ph_2PO_2)_6]$.[7] A quasireversible oxidation at $E_{1/2} = 704$ mV and an irreversible reduction at −884 mV versus Ag/$AgNO_3$ (in MeCN) are displaced to negative potentials compared to the same processes in $[Mn_4O_4(Ph_2PO_2)_6]$ (813 and −570 mV, respectively). These appreciable shifts reflect the influence of electron donation from the *para*-OMe group on the phenyl rings.

Crystals of **1** can be obtained from CH_2Cl_2 mixed with either toluene or acetone. The former crystal diffracts sharply and exhibits minimal anisole ring disorder. The core (Figure 2) exihibits C_2 point symmetry. The O···O distances within the core ranging between 2.484(2) and 2.727(2) Å are beyond the van der Waals radii of O atoms, indicating no appreciable bond formation. The 6-fold coordination spheres of Mn(2) and Mn(2a) exhibit tetragonal bond distortion with two longer axes, O(2a)−Mn(2)−O(6) and O(2)−Mn(2a)−O(6a). Notably, the average axial and equatorial bond lengths of Mn(2) and Mn(2a) are 2.1517(16) and 1.9243(16) Å, respectively, indicative of typical Jahn−Teller distorted Mn(III) ions. By contrast, Mn(1) and Mn(1a) exhibit shorter average Mn−O bond lengths (1.9078(15) Å) and lack Jahn−Teller axes, consistent with Mn(IV) ions. The long bonds Mn(2)−O(2a) and Mn(2a)−O(2), 2.2268(16) Å, are comparable to those found for elongated Mn(III)−O in incomplete cubane-like Mn complexes having inequivalent ligands,[9] and analogous to the "diamond" core of $Fe_2(IV)(\mu\text{-}O)_2$ compounds.[10] By contrast, a tetrahedral core with no Jahn−Teller distortion was found for $[Mn_4O_4(Ph_2PO_2)_6]$, which differs only by *p*-OCH_3 replacing H.[7,8] This transition from delocalized to localized valence electrons is directly attributed to the stronger electron donation from the *p*-MeO group of the 12 phenyls, resulting in stronger interelectron core repulsions and increased probability of vibronic distortions.

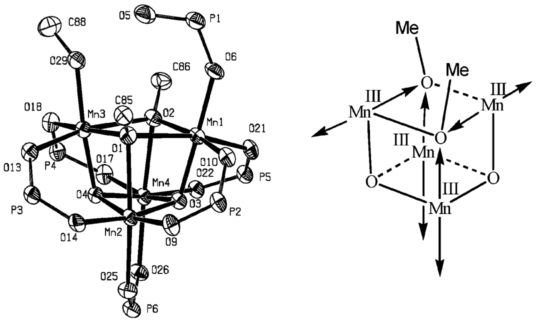

Figure 3. Left: ORTEP drawing (50% probability) of **2** with anisole rings omitted for clarity. Right: The cubane core with Mn(III) Jahn−Teller bond elongations shown by arrows.

Unlike the reduction chemistry of $[Mn_4O_4(Ph_2PO_2)_6]$,[4,6,7] crystallization of **1** in solvent mixtures containing MeOH leads to a reduced product that forms crystals composed of $[Mn_4O_2(OMe)_2(HOMe)\{(MeOPh)_2PO_2\}_6]$ (**2**). As shown in Figure 3, one of the bidentate phosphinate ligands becomes monodentate, and the released phosphinate-O is hydrogen-bonded to a methanol molecule terminally coordinated to the Mn at the vacated O-phosphinate position, O(29)···O(5) 2.456(5) Å. Two oxide bridges (μ_3-O^{2-}) are replaced by two methoxide bridges (μ_3-MeO^-), yielding the core $[Mn_4O_2(OMe)_2]^{6+}$. Electroneutrality requires that **1** is reduced to the all Mn(III) level. This valence assignment is confirmed by the typical Jahn−Teller distortions observed at all four Mn ions. The average axial and equatorial Mn−O lengths are 2.206(3) and 1.927(3) Å, respectively, for all 4 Mn atoms. Each methoxide O atom forms long bonds to two Mn ions on parallel faces of the cube, while the two μ_3-oxos have three short Mn−O bonds involving no Jahn−Teller elongations. To the best of our knowledge, this is the first example of this core type and Mn oxidation state isolated in a molecular system. A similar core type in a different Mn oxidation state and having a polydentate alkoxide bridge has been observed in the complex $[Mn^{2II,2III}{}_4O_2(OR)_2(CH_3CO_2)_2]$-

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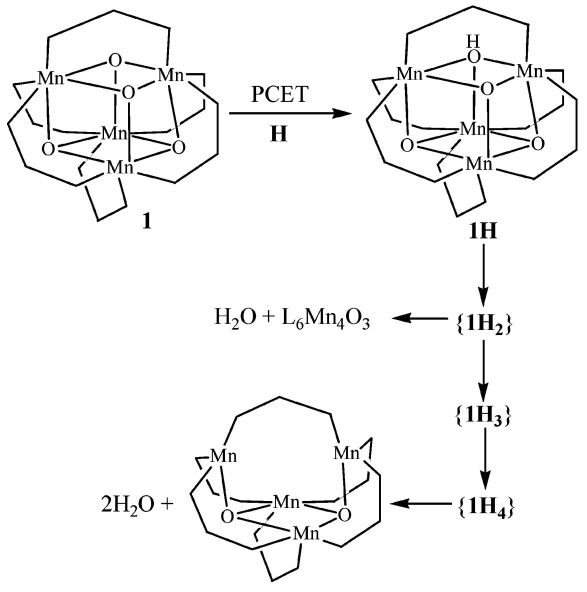
$(ClO_4)_2$ where HOR is 2,6-bis[*N*-(4-imidazolylethyl)iminomethyl]-4-methylphenol.[11]

The structure of **2** is most probably retained in solution, as suggested by ^1H NMR, which indicates lower symmetry than C_{2v}. This symmetry is expected if the terminal methanol were lost and replaced by the terminal oxygen of the monodentate phosphinate. At 9.24 and 7.34 ppm are found shouldered broad peaks from the anisole rings, indicative of two or more different environments. The *para*-methoxyl groups exhibit two relatively sharp peaks around 3.90 and 3.70 ppm and flanking broad shoulders. A very broad peak at 1.74 ppm (line width ca. 360 Hz) can be assigned to the terminal methanol and methoxide bridges. Their closer distances to Mn(III) lead to the larger line width.[7] The absence of significant contact shifts indicates that the molecule is not appreciably paramagnetic at room temperature. A solution of **2** in CH_2Cl_2/MePh (1/1) is EPR-silent at 4−77 K in both perpendicular and parallel B_1 modes. We may tentatively conclude that the ground state has spin $S = 0$ and that excited paramagnetic states are thermally accessible at 300 K.

Although Mn(II)−alkoxide cubes such as $[Mn_4(OMe)_4(HOMe)_4X_4]$ (HX = dipivaloylmethane or dibenzoylmethane, Hdbm) have been reported,[12] no further reduction of **2** is observed with excess methanol. In fact, **2** is electroinactive in cyclic voltammetry using the same conditions as for **1**. Previous reactions of $[Mn_4O_4(Ph_2PO_2)_6]$ revealed four sequential H atom reduction steps to the $Mn^{2II,2III}{}_4$ level using stronger reductants such as phenanthiozine and phenols in the reaction sequence depicted in Scheme 1.[4,6] The anticipated intermediates, $\mathbf{1H_2}$ ($[Mn_4O_2(OH)_2]^{6+}$ core) and $\mathbf{1H_4}$ ($[Mn_4(OH)_4]^{6+}$ core), were not observed as they both dehydrate as shown. This indicates that only two of the four oxo bridges are active in proton-coupled reduction chemistry despite the equivalence of all four oxo sites in $[Mn_4O_4(Ph_2PO_2)_6]$. This is different from the $[Mn_4O_3(O_2CMe)_4(dbm)_3]$ type of incomplete cubane, which exhibits ligand exchange at one vertex (^-O_2CMe) with ^-OMe or ^-OH, and without oxidation state changes or significant core structural changes.[9c]

Scheme 1. Proton Coupled Electron Transfer (PCET) Reduction of $[Mn^{2III,2IV}{}_4O_4L_6]$



The reason for the selective reduction at two rather than all four oxos in the $[Mn_4O_4]^{6+}$ core complexes, including those with a tetrahedrally symmetric core, is proposed to be due to the Jahn−Teller distortions at Mn(III) in **2** and its redox analogue $\mathbf{1H_2}$. These electronically induced bond elongations create two long Mn−OMe bonds, one for each Mn(III) ion in **2**, while the μ_3-O species have no Jahn−Teller elongated bonds ($\Delta R = 0.279$ Å, Figure 3). The Jahn−Teller elongated bonds are much weaker, and the bond order is lower. Each Mn(III) contains an occupied antibonding e_g orbital (local d_{z^2} type electron) that is directed at a μ_3-OMe. Thus, the σ bond order is $^1/_2$ for each such bond, while it is 1 for each of the μ_3-O−Mn bonds which lack a σ antibonding electron. Consequently, the μ_3-OH bridges in $\mathbf{1H_2}$ and the μ_3-OMe bridges in **2** have greater electron density and could possibly be more basic than the μ_3-O. Accordingly, the μ_3-OH and μ_3-OMe bridges in $\mathbf{1H_2}$ and **2**, respectively, are the thermodynamically favored sites for proton-coupled reduction.[13] As a result, successive reduction occurs at the μ_3-OH sites, releasing water molecules rather than sequentially forming the $[Mn_4O_2(OH)_2]^{6+}$ and $[Mn_4(OH)_4]^{6+}$ cores (Scheme 1).

Methanol selectively sharpens the EPR hyperfine structure of the S_0 and S_2 states of the PSII−WOC, by interacting directly with the inorganic core.[14] The reaction of methanol with **1** to form **2** provides a possible clue pointing to the corner hydroxos as sites for methanol exchange in the S state(s) containing Mn(III).

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Supporting Information Available: CIF files, selected bond lengths for **1** and **2**, and NMR, IR, and UV−vis data. This material is available free of charge via the Internet at http://pubs.acs.org.

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