

## Synthesis and Characterization of $Mn_4O_4L_6$ Complexes with Cubane-like Core Structure: A New Class of Models of the Active Site of the Photosynthetic Water Oxidase

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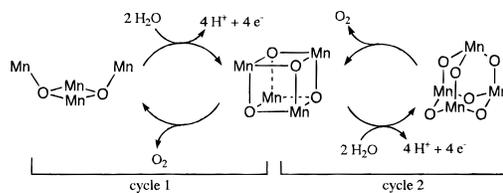
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The oxo-manganese cubane core structure,  $[Mn_4O_4]^{X+}$ , is particularly interesting because it has not been previously isolated as a discrete complex and because it was proposed to be part of the catalytic cycle for dioxygen production by the photosynthetic water oxidizing complex (WOC) in two independent hypotheses, depicted in Scheme 1.<sup>2</sup> In one of these proposals, oxide ions from water are incorporated into a butterfly-type core,  $Mn_4O_2$ , resulting in the formation of an "activated" cubane core which releases dioxygen with regeneration of the butterfly core. This proposal was based on the established structure of several butterfly core complexes.<sup>3b</sup> In the second proposal, oxide ions from water were proposed to add to a cubane core, forming an "activated"  $Mn_4O_6$ -adamantane core which in turn eliminates dioxygen and reverts to the cubane. This proposal was based on the established adamantane structure of the  $Mn_4O_6$  core.<sup>3a</sup> Neither of these proposed reactions has been experimentally demonstrated, nor do the adamantane or butterfly-type complexes characterized so far exhibit spectral properties like those of the WOC of PSII.<sup>3</sup>

Herein we report the synthesis of the first example of the  $Mn_4O_4$  cubane core. Several tetranuclear Mn complexes with distorted cubane-like cores have been synthesized before, including several  $Mn_4X_4$  alkoxo complexes in low oxidation states<sup>4</sup> or having incomplete core structures,  $Mn_4O_3X$ ,<sup>5</sup> or being part of a larger Mn cluster.<sup>6</sup>

Synthesis<sup>7</sup> of  $Mn_4O_4(O_2P(Ph)_2)_6$  **1**, was done by fusing together two pre-formed  $Mn_2O_2^{3+}$  units. A dimerization ap-

**Scheme 1.** Proposed Mechanisms for Water Oxidation by the WOC of PSII (ref 2)



proach was previously successful for the synthesis of a  $Co_4O_4$  cubane complex starting from a complex with a dimeric  $Co^{III}_2(OH)_2$  core and using bidentate ligands with shorter bridging atom separation.<sup>8</sup> This method was suggested as a possible route to the  $Mn_4O_4$  cubane core but was not realized until now. **1** forms after addition of diphenylphosphinate salts to a solution of  $[Mn_2O_2(bpy)_4](ClO_4)_3$  in acetonitrile.<sup>9</sup> The IR spectrum of **1** shows mainly vibrations due to the phosphinate group<sup>10</sup> and confirms the absence of perchlorate counterions or bpy ligands. MALDI-TOF mass spectral data<sup>11</sup> indicate a parent molecular mass of 1583–1584 D, corresponding to the formulation  $Mn_4O_4L_6$  (1586.7 D), which is also supported by elemental analysis.<sup>12</sup>

Figure 1 shows the structure of **1** determined by X-ray diffraction<sup>13</sup> together with selected bond distances and angles. The molecule shown is one of four independent molecules in each unit cell with slightly different bond distances and angles. The molecules differ mainly in the orientation of the phenyl rings, probably due to packing effects. Diphenylphosphinate ligands bridge between Mn pairs across each of the six  $Mn_2O_2$  faces of the cube. This feature distinguishes **1** from the more compact  $Co_4O_4$  cubane, which has two  $\mu$ -bridging acetates on opposite faces,<sup>8</sup> and the pseudo-cubanes,  $Mn_4O_3X$ , which have three faces bridged by carboxylates ( $Mn^{IV}-Mn^{III}$ , 2.8 Å) and three open faces ( $Mn^{III}-Mn^{III}$ , 3.2–3.3 Å). Each independent cluster of **1** contains one unique and three symmetry-related Mn ions. No large (Jahn–Teller) distortions are observed in the Mn–O bond lengths, and this absence appears not to be due to a superposition of inequivalent Mn valences. Further support comes from the absence of appreciable differences in the anisotropic displacement factors for different O atoms, unlike the mixed valence complex  $Mn_2O_2(phen)_4^{3+}$ , where these are 5–8 times larger for the axial metal ligand bonds.<sup>14c</sup> These features suggest that the valence electrons may be delocalized, yielding a rare example of a class III (delocalized) mixed-valence  $Mn^{III}Mn^{IV}$  compound.<sup>14a</sup> This conclusion is supported

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(7) Diphenylphosphinic acid (Aldrich) (0.8 mmol) suspended in 5 mL of methanol is added under stirring to 0.8 mL of 1 M tetra-*N*-butylammonium hydroxide in methanol (Aldrich). After stripping solvent in vacuum, the residue is dissolved in 10 mL acetonitrile/acetone (2/1 v/v) and added to a solution of 0.2 mmol of  $[Mn_2O_2(bpy)_4](ClO_4)_3$  in 10 mL of acetonitrile and stirred overnight. The resulting red-brown precipitate is filtered and washed with acetonitrile and with methanol. Yield: 38%. Single crystals were isolated from methylene chloride solvent.

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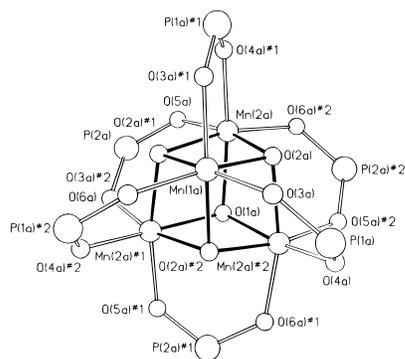
(10) IR (KBr disk): 1438, 1132, 1109, 1032, 1007, 985, 754, 732, 693, 551, 526  $cm^{-1}$ .

(11) Available as Supporting Information.

(12) Found (calcd for  $Mn_4O_{16}P_6C_{72}H_{60}$ ) (%): C, 53.19 (54.49); H, 3.78 (3.78); N, 0 (<0.5); P, 11.19 (11.72); Mn, 14.27 (13.87).

(13) The details of the structure determination can be found in Supporting Information. Crystal data for **1**: cubic,  $P2_13$ ,  $a = b = c = 30.223(2)$  Å,  $Z = 16$ ,  $V = 27606(3)$  Å<sup>3</sup>,  $d_{calc} = 1.527$  g  $cm^{-3}$ ,  $T = 298$  K. Data collection was done with a standard Siemens SMART CCD area detector system equipped with a normal focus molybdenum-target X-ray tube. A total of 146 293 reflections were measured, of which 13 249 were independent ( $R_{int} = 5.28\%$ ,  $R_{sig} = 5.12\%$ ) and 9700 were above  $4\sigma(F)$ . The solution and refinement of the structure was nontrivial, owing to twinning. Refinement of the structure in the space group  $P2_13$  converged at  $R_1 = 9.65\%$ , only after application of a general 4-fold twinning law with a twinning parameter of 0.50. All atoms were then refined anisotropically without restraints to yield the final  $R_1$  value of 8.65%. The absolute structure was established by refinement of the Flack parameter.

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**Figure 1.** (a) Thermal ellipsoid plot (50% probability) of one of four molecules in the unit cell of **1**. Phenyls omitted for clarity. (b) Selected bond distances (Å) and angles (deg): Mn(1a)–Mn(2a), 2.914(3); Mn(2a)–Mn(2a)#1, 2.949(3); Mn(1a)–O(2a), 1.917(7); Mn(1a)–O(3a)#1, 1.951(8); Mn(2a)–O(1a), 1.982(7); Mn(2a)–O(2a), 1.882; Mn(2a)–O(4a)#1, 1.955(9); O(2a)–Mn(1a)–O(2a)#1, 82.8(3); O(1a)–Mn(2a)–O(2a), 84.3(3); O(2a)–Mn(2a)–O(2a)#1, 80.8(3).

by variable-temperature <sup>1</sup>H NMR spectra of **1**, showing that even in solution only one set of three paramagnetically shifted resonances for all 12 phenyl rings is observable.<sup>15</sup>

The Mn–Mn distances in **1** vary between 2.904 and 2.954 Å in the four independent molecules (average for all Mn–Mn distances in all four independent molecules is 2.926 Å). The Mn–Mn distances are considerably longer than observed for both the di- $\mu_2$ -oxo-bridged dimers (2.6–2.7 Å),<sup>16</sup> as well as the tri- $\mu_2$ -oxo-bridged Mn(IV) dimer (2.296 Å),<sup>3a</sup> both of which contain  $\mu_2$ -bridging oxo ligands. The Mn–Mn distances are comparable to the Mn<sup>IV</sup><sub>4</sub> cubanes embedded within the larger clusters of Mn<sub>12</sub>O<sub>12</sub> and Mn<sub>8</sub>Fe<sub>4</sub>O<sub>12</sub> (2.82–2.99 Å) and to the central pair in the Mn<sub>4</sub>O<sub>2</sub> butterfly complexes (2.85 Å) (Scheme 1, left),<sup>17</sup> both of which contain exclusively triply-bridging  $\mu_3$ -oxos. The distorted cubane core in Mn<sub>4</sub>O<sub>3</sub>X also contains exclusively  $\mu_3$ -oxo bridges. Here the Mn–Mn separations are either slightly shorter (2.8 Å) across the faces of Mn<sub>2</sub>O<sub>2</sub> rhombohedra that are bridged by carboxylate or much longer (3.3 Å) across unbridged faces of Mn<sub>2</sub>OCl rhombohedra.<sup>5b,c</sup> From this comparison, we propose that the core expansion by 0.2–0.3 Å observed upon fusion of two Mn<sub>2</sub>( $\mu_2$ -O)<sub>2</sub> rhombohedra to form the Mn<sub>4</sub>( $\mu_3$ -O)<sub>4</sub> cubane **1** is promoted by coordination of the six  $\mu$ -bridging phosphinates, while carboxylates do not stabilize this expansion. (The O,O' distance in diphenylphosphinic acid is 2.58 Å, whereas the O,O' distance in acetic acid is only 2.22 Å. These distance change only slightly (<1%) upon coordination in  $\mu$ -bridging phosphinate or acetate complexes.<sup>18</sup>)

Complex **1** exhibits several electronic transitions at (nm;  $\epsilon$ , M<sup>-1</sup> cm<sup>-1</sup>) 498 (1.4 × 10<sup>3</sup>), and 697 (1.4 × 10<sup>2</sup>) and overlapping bands between 800 and 1100 (1.2 × 10<sup>2</sup>). The latter bands bleach upon partial reduction by two H atoms using phenothiazine, suggesting assignment as Mn intervalence electronic transitions.<sup>14a</sup> However, contributions from oxo-to-Mn charge transfer reactions are possible as well.<sup>14b</sup> **1** is EPR silent in CH<sub>2</sub>Cl<sub>2</sub> solution between 10 K and room temperature, indicating magnetic coupling within the tetramer.

The cyclic voltammogram of **1** in dichloromethane exhibits a quasi-reversible oxidation at  $E_{1/2} = +680$  mV vs ferrocene (Fc) estimated +1.38 V vs NHE).<sup>19</sup> The ratio of peak currents for Fc<sup>+</sup>/Fc and **1**<sup>+</sup>/**1** equals 1.2 ± 0.05 at scan rates between 5 and 50 mV/s. The peak-to-peak separations are slightly larger

for **1** compared to Fc, but the ratio of the values remains constant at 0.7 ± 0.06. The deviation from the ideal values of 1.0 for the ratio of peak currents and the peak-to-peak separation might reflect the difference in the diffusion coefficients for the two compounds and cannot be accounted for by a two-electron process for **1**. The oxidation product is EPR active.<sup>20</sup> Accordingly, the oxidative process at +680 mV is assigned to a quasireversible one-electron oxidation (2III, 2IV) ↔ (III, 3IV). **1**<sup>+</sup> exhibits a considerably more positive reduction potential by 0.7–1.7 V than found for dimanganese (III,IV)/(III,III) couples and greater than the majority of known (IV,IV)/(III,IV) couples of dimeric Mn<sub>2</sub>O<sub>2</sub> complexes.<sup>17</sup>

**1** also exhibits an irreversible reduction process at an anodic peak potential of –730 mV vs Fc in dichloromethane (at a scan rate of 50 mV/s; peak-to-peak separation of 700–800 mV). Titration of **1** with phenothiazine, monitored by the electronic absorption band of the phenothiazine neutral radical at 380 nm and its EPR spectrum, reveals that a total of four to five H atoms are taken up upon reduction of **1** without decomposition to monomeric Mn(II). The stoichiometry suggests formation of the tetrakis( $\mu$ -hydroxo) cubane core, Mn<sub>4</sub>(OH)<sub>4</sub>L<sub>6</sub>.

**1** exhibits X-ray K-edge absorption that is 0.25 eV above the K-edge for the S<sub>1</sub> state of the WOC and has a more symmetrical core structure based on Mn EXAFS.<sup>21,22</sup> **1** is not a complete or good structural model for the S<sub>1</sub> or S<sub>2</sub> states of the WOC based upon comparison of the amplitudes and distances of the EXAFS scattering vectors. This is not surprising when one compares the symmetrical structure of **1** with the postulated structures that simulate the Mn EXAFS<sup>22</sup> and EPR<sup>23</sup> of the WOC.

Comparing the functional aspects, **1** undergoes a reduction process with uptake of four to five H atoms, as well as one-electron oxidation to form **1**<sup>+</sup>. Both reactions lead eventually to rearrangement of the cluster with, to date, unidentified reaction products and no multiline EPR signal as would be expected for an intact cluster. Mn EXAFS of **1** indicates that it is not a close structural model of the S<sub>0</sub>–S<sub>3</sub> oxidation states of the WOC.<sup>22</sup> We are also examining EPR of transiently produced **1**<sup>+</sup> or **1**<sup>-</sup> as additional comparisons. The six bridging phosphinate ligands are critical for stabilizing the [Mn<sub>4</sub>O<sub>6</sub>]<sup>6+</sup> core. Removal of the phosphinate ligands leads to new chemistry which is being explored, including tests for water binding and oxygen evolution.

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**Supporting Information Available:** Describing of the method of structure solution and refinement, tables giving atomic coordinates, bond lengths and angles, and (nonhydrogenic) anisotropic displacement parameters, and figures showing a MALDI-TOF mass spectrum of **1**, variable-temperature <sup>1</sup>H-NMR spectra and analysis, and Mn XANES and EXAFS spectra of **1** (32 pages). See any current masthead page for ordering and Internet access instructions.

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(19) The Fc/Fc<sup>+</sup> couple  $E_{1/2} = 0.68$ –0.74 V vs NHE in various solvents: *Electrochemistry for Chemists*, 2nd ed.; Sawyer, D. T., Sobkowiak, A., Roberts, J. L., Jr., Eds.; J. Wiley & Sons: New York, 1995; p 203.

(20) A broad, uninterpretable 10 K EPR spectrum was seen after controlled potential electrolysis at room temperature. The only interpretable part of the spectrum consisted of monomeric Mn(II) which is assumed to be a decomposition product of **1**<sup>+</sup>.

(21) The Mn XANES and EXAFS spectra of **1** are given in the Supporting Information (courtesy of Dr. V. Yachandra).

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(15) Analysis of the <sup>1</sup>H-NMR spectrum of **1** is provided as Supporting Information.

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