

**"Dimerization" of the [Co<sup>III</sup><sub>2</sub>(OH)<sub>2</sub>] Core to the First Example of a [Co<sup>III</sup><sub>4</sub>O<sub>4</sub>] Cubane: Potential Insights into Photosynthetic Water Oxidation**

Katerina Dimitrou, Kirsten Folting, William E. Streib, and George Christou\*

Department of Chemistry and the Molecular Structure Center, Indiana University Bloomington, Indiana 47405

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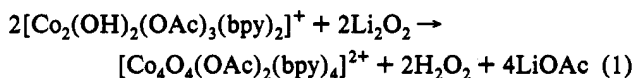
Intense effort is currently directed toward elucidating the structure and mode of action of the Mn<sub>4</sub> aggregate responsible for photosynthetic water oxidation in green plants and cyanobacteria.<sup>1</sup> The arrangement of the metal ions at any of the oxidation levels (S<sub>n</sub> states; n = -1 to 4) of this water oxidation center (WOC) is currently unclear. A number of structural proposals for S<sub>1</sub> have been put forward.<sup>2</sup> Which of these is correct is unknown, and the more important question is how this unit changes structure at the higher S<sub>n</sub> states, since these directly precede the O<sub>2</sub> evolution step.<sup>1,2</sup>

We have extended our WOC modeling studies to encompass Co. The reasoning is that we may obtain Co<sup>III</sup> systems that are structurally analogous to, but more stable than, the Mn<sup>III</sup>Mn<sup>IV</sup> species present at the highest S<sub>n</sub> states or that are intermediates in the O<sub>2</sub> evolution process. For example, Co<sup>III</sup> and Mn<sup>IV</sup> both favor octahedral geometry and have similar effective ionic radii.<sup>3</sup> Thus, it is a possibility that stable Co<sup>III</sup><sub>4</sub> complexes could be structurally analogous to unstable Mn<sup>IV</sup><sub>4</sub> complexes at higher S<sub>n</sub> states and could thus provide insights into the latter. Similarly, Co<sup>III</sup> is known to form stable peroxide complexes,<sup>4</sup> whereas Mn<sub>4</sub>/O<sub>2</sub><sup>2-</sup> species<sup>5</sup> thought to be formed on oxidation of S<sub>3</sub> are not observed, and only O<sub>2</sub> and regenerated S<sub>0</sub> are found.<sup>1</sup> We herein describe our initial successes in this area, the preparation of Co<sub>2</sub>, Co<sub>3</sub>, and Co<sub>4</sub> complexes. The Co<sub>3</sub> and Co<sub>4</sub> species possess the first examples of [Co<sub>3</sub>(μ<sub>3</sub>-O)(μ-OH)<sub>3</sub>]<sup>4+</sup> partial cubane and [Co<sub>4</sub>(μ<sub>3</sub>-O)<sub>4</sub>]<sup>4+</sup> cubane cores and represent interesting developments in the otherwise well-explored chemistry of Co<sup>III</sup>. The Co<sub>4</sub> species is also the first M<sub>4</sub>O<sub>4</sub> cubane complex with biologically-relevant ligands.

As a convenient route into Co<sup>III</sup>/O<sub>2</sub><sup>2-</sup> chemistry, we have explored the oxidation of Co<sup>II</sup> acetate/bpy mixtures with aqueous H<sub>2</sub>O<sub>2</sub>; this also provides the possibility of peroxide-containing products. Equimolar Co(OAc)<sub>2</sub>·4H<sub>2</sub>O and bpy in MeOH:H<sub>2</sub>O (3:1) were treated dropwise with H<sub>2</sub>O<sub>2</sub> (30%, ~3 equiv) and heated to 50 °C for 30 min, and then an approximately equal volume of THF was added, followed by 1 equiv of LiClO<sub>4</sub> in a minimum of water. Red crystals began to appear almost immediately. After 48 h at 50 °C, the cooled solution was filtered and the red crystals of [Co<sub>2</sub>(OH)<sub>2</sub>(OAc)<sub>3</sub>(bpy)<sub>2</sub>](ClO<sub>4</sub>)·H<sub>2</sub>O (1) were washed with warm H<sub>2</sub>O/THF; yield, 69%. A Co(OAc)<sub>2</sub>·4H<sub>2</sub>O/bpy (1.5:1) solution in EtOH:H<sub>2</sub>O (6:1) was treated with H<sub>2</sub>O<sub>2</sub> (30%, ~10 equiv), and LiClO<sub>4</sub> was added. After 3 h at room temperature, greenish-black crystals of [Co<sub>3</sub>O(OH)<sub>3</sub>(OAc)<sub>2</sub>

(bpy)<sub>3</sub>](ClO<sub>4</sub>)<sub>2</sub> (2) were collected by filtration; yield, 51%.

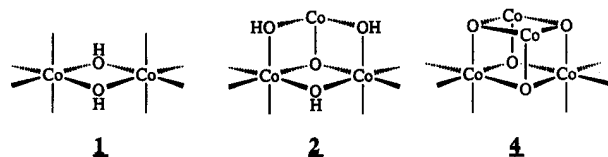
In an attempt to replace the bridging AcO<sup>-</sup> with O<sub>2</sub><sup>2-</sup>, complex 1 in DMSO was treated with Li<sub>2</sub>O<sub>2</sub> (~5 equiv), and the mixture heated to 70 °C. After 3 days, the cooled solution was filtered, CH<sub>2</sub>Cl<sub>2</sub> added to the filtrate, and the flask stored at -5 °C overnight. Brown crystals of [Co<sub>4</sub>O<sub>4</sub>(OAc)<sub>2</sub>(bpy)<sub>4</sub>](ClO<sub>4</sub>)<sub>2</sub> (3) were collected by filtration; yield, 64%.<sup>6</sup> The conversion of 1 to 3 is believed to be triggered by deprotonation of the bridging OH<sup>-</sup> groups (eq 1). Complex 3 was a weak diffractor of X-rays,



and it was therefore converted to [Co<sub>4</sub>O<sub>4</sub>(O<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>-p-Me)<sub>2</sub>(bpy)<sub>4</sub>](ClO<sub>4</sub>)<sub>2</sub>·2MeCN (4·2MeCN) with an excess of p-toluic acid in refluxing MeCN for 3 days; yield, 97%.

The cation of 1 (Figure 1, top)<sup>a</sup> consists of two edge-sharing Co<sup>III</sup> distorted octahedra with peripheral bpy and AcO<sup>-</sup> groups. The idealized symmetry is C<sub>2v</sub>. The [Co<sub>2</sub>(μ-OH)<sub>2</sub>(μ-RCO<sub>2</sub>)<sub>3</sub>]<sup>3+</sup> core is a known unit in Co<sup>III</sup> chemistry.<sup>8</sup> The cation of 2 (Figure 1, bottom)<sup>b</sup> has a [Co<sub>3</sub>(μ<sub>3</sub>-O)(μ-OH)<sub>3</sub>]<sup>4+</sup> partial cubane core. The idealized symmetry is C<sub>s</sub>, and Co1...Co2 (2.717(4) Å) is slightly shorter than the other Co...Co separations. The cation of 4 (Figure 2)<sup>9</sup> possesses a [Co<sub>4</sub>(μ<sub>3</sub>-O)<sub>4</sub>]<sup>4+</sup> core, a bpy on each Co<sup>III</sup>, and two bridging carboxylate groups. The cation has idealized D<sub>2d</sub> symmetry with the S<sub>4</sub> axis passing through the carboxylate C atoms. The Co...Co distances separate into two types, 2.665 vs 2.852 Å (av), the former value applying to cube faces bridged by the RCO<sub>2</sub><sup>-</sup> groups.

The cores of 1, 2, and 4 (below) can be seen to represent the progressive buildup of a cubane by addition of 1 and 2 Co<sup>III</sup> ions



(and O<sub>2</sub><sup>2-</sup>/OH<sup>-</sup> ions) to the [Co<sub>2</sub>(OH)<sub>2</sub>]<sup>4+</sup> core of 1. The chemical conversion of 1 to 4 cements this relationship, which we believe to be the first synthesis of an M<sub>4</sub>O<sub>4</sub> cubane by dimerization of an M<sub>2</sub>O<sub>2</sub> or M<sub>2</sub>(OH)<sub>2</sub> unit.

(6) Anal. Calcd for Co<sub>4</sub>O<sub>17</sub>C<sub>44</sub>H<sub>40</sub>N<sub>8</sub>Cl<sub>2</sub> (3·H<sub>2</sub>O): C, 41.96; H, 3.20; N, 8.90; Cl, 5.63. Found: C, 42.16; H, 3.23; N, 8.76; Cl, 5.62. NMR spectroscopy and FAB/MS confirm the structural similarity between 3 and 4.

(7) (a) Crystallographic data for 1 at -175 °C: triclinic space group P $\bar{1}$ ; a = 14.285(1) Å, b = 15.048(1) Å, c = 9.031(1) Å, α = 95.17(0)°, β = 107.18(0)°, γ = 109.65(0)°, Z = 2; R (R<sub>w</sub>) = 8.04 (7.66)% with 3409 unique reflections with F > 3.00σ(F). The non-hydrogen atoms of the cation, the Cl atom of the perchlorate anion, and the O atom of the solvent water molecule were refined anisotropically; the remainder of the non-hydrogen atoms were refined using isotropic thermal parameters. Hydrogen atoms in fixed, idealized positions were included in the final cycles. Anal. Calcd for Co<sub>2</sub>O<sub>13</sub>·C<sub>26</sub>H<sub>29</sub>N<sub>4</sub>Cl: C, 41.15; H, 3.85; N, 7.38; Cl, 4.67. Found: C, 41.23; H, 3.84; N, 7.40; Cl, 4.67. (b) Crystallographic data for 2 at -170 °C: monoclinic, space group P2<sub>1</sub>/C; a = 10.501(2) Å, b = 17.087(4) Å, c = 22.596(6) Å, β = 93.51(1)°, Z = 4; R (R<sub>w</sub>) = 11.56 (10.77)% with 3039 unique reflections with F > 3.00σ(F). All non-hydrogen atoms were refined anisotropically; hydrogen atoms in fixed positions were included in the final cycles. The dried solid is hygroscopic. Anal. Calcd for Co<sub>3</sub>O<sub>18</sub>C<sub>34</sub>H<sub>37</sub>N<sub>6</sub>Cl<sub>2</sub> (2·2H<sub>2</sub>O): C, 38.33; H, 3.50; N, 7.89; Cl, 6.66. Found: C, 38.12; H, 3.65; N, 7.93; Cl, 6.71.

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(9) Crystallographic data for 4·2MeCN at -156 °C: triclinic, space group P $\bar{1}$ ; a = 12.590(2) Å, b = 23.233(5) Å, c = 11.734(2) Å, α = 98.69(1)°, β = 105.83(1)°, γ = 104.30(1)°, Z = 2; R (R<sub>w</sub>) = 7.13 (7.03)% with 6383 unique reflections with F > 3.00σ(F). All non-hydrogen atoms were refined anisotropically except for the solvent atoms which were refined using isotropic thermal parameters. Hydrogen atoms in fixed, idealized positions were included in the final refinement cycles. Dried solid loses solvent and is hygroscopic. Anal. Calcd for Co<sub>4</sub>O<sub>17</sub>C<sub>56</sub>H<sub>48</sub>N<sub>8</sub>Cl<sub>2</sub> (4·H<sub>2</sub>O): C, 47.65; H, 3.43; N, 7.94; Cl, 5.02. Found: C, 47.35; H, 3.45; N, 8.02; Cl, 5.12.

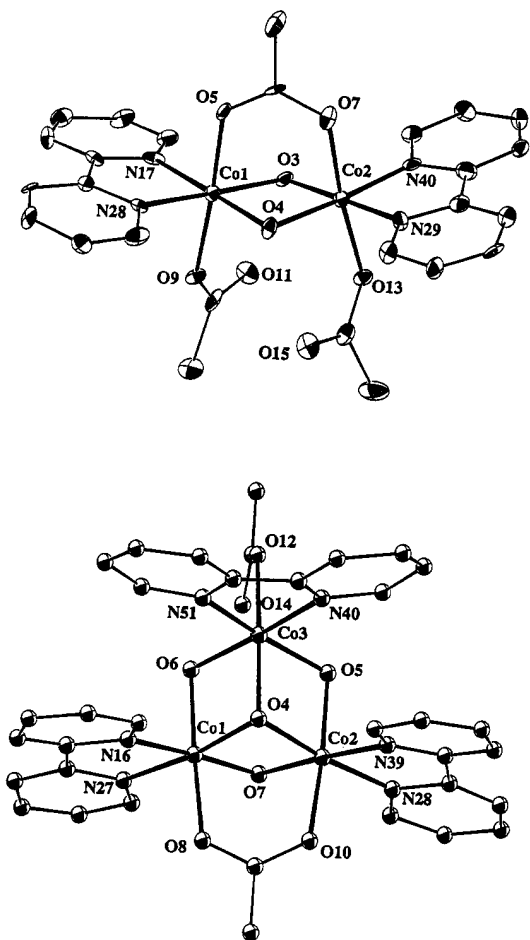
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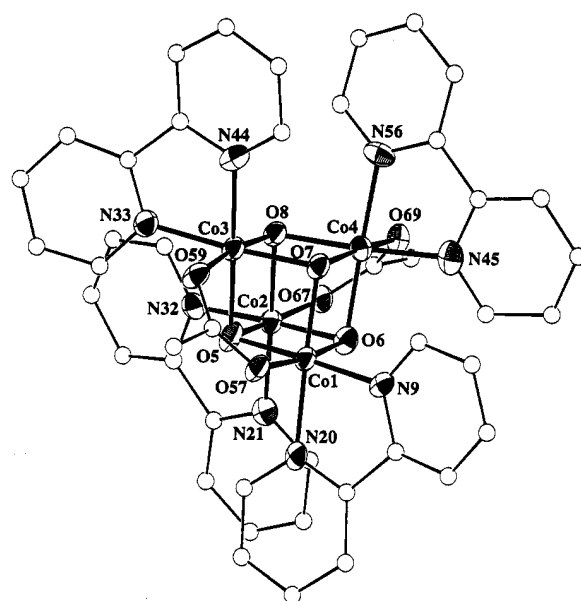
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(5) No Mn<sub>4</sub>/O<sub>2</sub><sup>2-</sup> complexes are known, although one Mn<sub>2</sub>/O<sub>2</sub><sup>2-</sup> and one Mn<sub>3</sub>/O<sub>2</sub><sup>2-</sup> species have been reported: (a) Bossek, U.; Weyhermüller, T.; Wieghardt, K.; Nuber, B.; Weiss, J. *J. Am. Chem. Soc.* 1990, 112, 6387. (b) Bhula, R.; Gainsford, G. J.; Weatherburn, D. C. *J. Am. Chem. Soc.* 1988, 110, 7550.



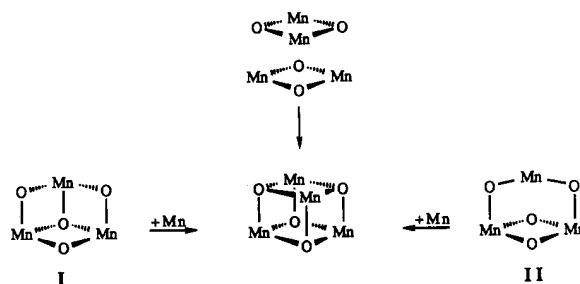
**Figure 1.** Structures of the cations of complexes 1 (top) and 2 (bottom). Selected distances (Å) and angles (deg) are listed as follows. Complex 1: Co1...Co2, 2.793(2); Co1-O3, 1.894(6); Co1-O4, 1.899(6); Co1-O5, 1.926(6); Co1-O9, 1.891(6); Co1-N17, 1.924(8); Co1-N28, 1.921(7); Co2-O3, 1.883(6); Co2-O4, 1.901(6); Co2-O7, 1.906(6); Co2-O13, 1.908(6); Co2-N29, 1.926(8); Co2-N40, 1.900(7); Co1-O3-Co2, 95.42(26); Co1-O4-Co2, 94.61(26). Complex 2: Co1...Co2, 2.717(4); Co1...Co3, 2.853(3); Co2...Co3, 2.874(4); Co1-O4, 1.900(11); Co2-O4, 1.880(13); Co3-O4, 1.907(10); Co1-O6, 1.889(11); Co1-O7, 1.902(14); Co1-O8, 1.919(10); Co1-N16, 1.934(20); Co1-N27, 1.970(14); Co2-O5, 1.907(10); Co2-O7, 1.899(11); Co2-O10, 1.896(10); Co2-N28, 1.916(18); Co2-N39, 1.937(13); Co3-O5, 1.933(13); Co3-O6, 1.885(11); Co3-O12, 1.953(11); Co3-N40, 1.926(13); Co3-N51, 1.937(17); Co1-O6-Co3, 98.2(5); Co1-O7-Co2, 91.3(5); Co2-O5-Co3, 96.9(5); Co1-O4-Co2, 91.9(5); Co1-O4-Co3, 97.1(5); Co2-O4-Co3, 98.7(5).

We and others have proposed  $[\text{Mn}_4\text{O}_4]$  cubanes to be involved in the WOC cycle, either at the higher<sup>2a,10</sup> or lower  $S_n$  states.<sup>2a,b,11</sup> Unfortunately, no complex with a discrete  $[\text{Mn}_4\text{O}_4]$  core at the  $\text{Mn}^{\text{III}}$  and/or  $\text{Mn}^{\text{IV}}$  oxidation level has yet been prepared. In our proposal, we suggested that a  $[\text{Mn}_4\text{O}_4]$  cubane at  $S_2$  or higher might form from an open  $[\text{Mn}_4\text{O}_2]$  unit present at a lower  $S_n$  state.<sup>2a,10</sup> But a cubane structure at  $S_2$  or higher could also be achieved by alternate methods such as fusion of dinuclear units. Such a possibility warrants consideration given (i) the precedence provided by the Co results above, (ii) recent EXAFS data suggesting that two closely-spaced  $[\text{Mn}_2\text{O}_2]$  units might be present at the lower  $S_n$  states,<sup>12,13</sup> (iii) theoretical studies that conclude that  $\text{O}_2$  evolution from an  $\text{Mn}_4\text{O}_4$  cubane is as energetically feasible as from the other candidates considered,<sup>14</sup> and (iv) magne-



**Figure 2.** Structure of the cation of complex 4. Selected distances (Å) are given as follows: Co1...Co2, 2.850(2); Co1...Co3, 2.666(2); Co1...Co4, 2.849(2); Co2...Co3, 2.865(2); Co2...Co4, 2.663(2); Co3...Co4, 2.845(2); Co1-O5, 1.877(6); Co1-O6, 1.891(6); Co1-O7, 1.874(6); Co1-N9, 1.930(7); Co1-N20, 1.943(7); Co1-O57, 1.951(6); Co2-O5, 1.895(6); Co2-O6, 1.873(6); Co2-O8, 1.877(6); Co2-N21, 1.949(7); Co2-N32, 1.947(7); Co2-O67, 1.969(5); Co3-O5, 1.878(6); Co3-O7, 1.863(5); Co3-O8, 1.890(6); Co3-N33, 1.929(7); Co3-N44, 1.936(7); Co3-O59, 1.956(6); Co4-O6, 1.874(6); Co4-O7, 1.893(5); Co4-O8, 1.880(6); Co4-N45, 1.940(7); Co4-N56, 1.941(7); Co4-O69, 1.943(6).

tochemical arguments against closely-spaced  $[\text{Mn}_2\text{O}_2]$  units being present at the higher  $S_n$  states but supporting a condensed structure such as a cubane.<sup>15</sup> Closely-spaced trinuclear and mononuclear units at the lower  $S_n$  states could also yield an  $\text{Mn}_4\text{O}_4$  cubane at  $S_2$  or higher (see below). Core I is unknown, but some precedence is now provided by complex 2; core II is known for  $\text{Mn}^{\text{IV}}$ .<sup>16</sup>



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**Supplementary Material Available:** Crystal structure analyses, including listings of atomic coordinates, thermal parameters, and bond distances and angles for complexes 1, 2, and 4 (49 pages); listing of calculated and observed structure factors (42 pages). Ordering information is given on any current masthead page.

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