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"Dimerization" of the $[Co^{III}_2(OH)_2]$ Core to the First Example of a $[Co^{III}_4O_4]$ Cubane: Potential Insights into Photosynthetic Water Oxidation

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Intense effort is currently directed toward elucidating the structure and mode of action of the Mn_4 aggregate responsible for photosynthetic water oxidation in green plants and cyanobacteria.[1] The arrangement of the metal ions at any of the oxidation levels (S_n states; $n = -1$ to 4) of this water oxidation center (WOC) is currently unclear. A number of structural proposals for S_1 have been put forward.[2] Which of these is correct is unknown, and the more important question is how this unit changes structure at the higher S_n states, since these directly precede the O_2 evolution step.[1,2]

We have extended our WOC modeling studies to encompass Co. The reasoning is that we may obtain Co^{III} systems that are structurally analogous to, but more stable than, the $Mn^{III}Mn^{IV}$ species present at the highest S_n states or that are intermediates in the O_2 evolution process. For example, Co^{III} and Mn^{IV} both favor octahedral geometry and have similar effective ionic radii.[3] Thus, it is a possibility that stable Co^{III}_4 complexes could be structurally analogous to unstable Mn^{IV}_4 complexes at higher S_n states and could thus provide insights into the latter. Similarly, Co^{III} is known to form stable peroxide complexes,[4] whereas Mn_4/O_2^{2-} species[5] thought to be formed on oxidation of S_3 are not observed, and only O_2 and regenerated S_0 are found.[1] We herein describe our initial successes in this area, the preparation of Co_2, Co_3, and Co_4 complexes. The Co_3 and Co_4 species possess the first examples of $[Co_3(\mu_3\text{-}O)(\mu\text{-}OH)_3]^{4+}$ partial cubane and $[Co_4(\mu_3\text{-}O)_4]^{4+}$ cubane cores and represent interesting developments in the otherwise well-explored chemistry of Co^{III}. The Co_4 species is also the first M_4O_4 cubane complex with biologically-relevant ligands.

As a convenient route into Co^{III}/O^{2-} chemistry, we have explored the oxidation of Co^{II} acetate/bpy mixtures with aqueous H_2O_2; this also provides the possibility of peroxide-containing products. Equimolar $Co(OAc)_2{\cdot}4H_2O$ and bpy in MeOH:H_2O (3:1) were treated dropwise with H_2O_2 (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 $LiClO_4$ 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 $[Co_2(OH)_2(OAc)_3(bpy)_2](ClO_4){\cdot}H_2O$ (**1**) were washed with warm H_2O/THF; yield, 69%. A $Co(OAc)_2{\cdot}4H_2O$/bpy (1.5:1) solution in EtOH:H_2O (6:1) was treated with H_2O_2 (30%, ~10 equiv), and $LiClO_4$ was added. After 3 h at room temperature, greenish-black crystals of $[Co_3O(OH)_3(OAc)_2(bpy)_3](ClO_4)_2$ (**2**) were collected by filtration; yield, 51%.

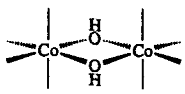
In an attempt to replace the bridging AcO^- with O_2^{2-}, complex **1** in DMSO was treated with Li_2O_2 (~5 equiv), and the mixture heated to 70 °C. After 3 days, the cooled solution was filtered, CH_2Cl_2 added to the filtrate, and the flask stored at -5 °C overnight. Brown crystals of $[Co_4O_4(OAc)_2(bpy)_4](ClO_4)_2$ (**3**) were collected by filtration; yield, 64%.[6] The conversion of **1** to **3** is believed to be triggered by deprotonation of the bridging OH^- groups (eq 1). Complex **3** was a weak diffractor of X-rays,

$$2[Co_2(OH)_2(OAc)_3(bpy)_2]^+ + 2Li_2O_2 \rightarrow [Co_4O_4(OAc)_2(bpy)_4]^{2+} + 2H_2O_2 + 4LiOAc \quad (1)$$

and it was therefore converted to $[Co_4O_4(O_2CC_6H_4\text{-}p\text{-}Me)_2(bpy)_4](ClO_4)_2{\cdot}2MeCN$ (**4**·2MeCN) with an excess of *p*-toluic acid in refluxing MeCN for 3 days; yield, 97%.

The cation of **1** (Figure 1, top)[7a] consists of two edge-sharing Co^{III} distorted octahedra with peripheral bpy and AcO^- groups. The idealized symmetry is C_{2v}. The $[Co_2(\mu\text{-}OH)_2(\mu\text{-}RCO_2)]^{3+}$ core is a known unit in Co^{III} chemistry.[8] The cation of **2** (Figure 1, bottom)[7b] has a $[Co_3(\mu_3\text{-}O)(\mu\text{-}OH)_3]^{4+}$ partial cubane core. The idealized symmetry is C_s, and Co1···Co2 (2.717(4) Å) is slightly shorter than the other Co···Co separations. The cation of **4** (Figure 2)[9] possesses a $[Co_4(\mu_3\text{-}O)_4]^{4+}$ core, a bpy on each Co^{III}, and two bridging carboxylate groups. The cation has idealized D_{2d} symmetry with the S_4 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_2^- 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^{III} ions (and O^{2-}/OH^- ions) to the $[Co_2(OH)_2]^{4+}$ core of **1**. The chemical conversion of **1** to **4** cements this relationship, which we believe to be the first synthesis of an M_4O_4 cubane by dimerization of an M_2O_2 or $M_2(OH)_2$ unit.



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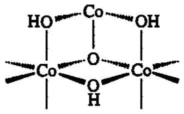

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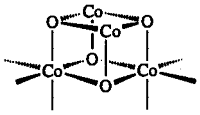

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(6) Anal. Calcd for $Co_4O_{17}C_{44}H_{40}N_8Cl_2$ (**3**·H_2O): C, 41.96; H, 3.20; N, 8.90; Cl, 5.63. Found: C, 42.16; H, 3.23; N, 8.76; Cl, 5.62. NMR spectroscopy and *FAB/MS* confirm the structural similarity between **3** and **4**.

(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, $\alpha = 95.17(0)°$, $\beta = 107.18(0)°$, $\gamma = 109.65(0)°$, $Z = 2$; R (R_w) = 8.04 (7.66)% with 3409 unique reflections with $F > 3.00\sigma(F)$. 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 $Co_2O_{13}C_{26}H_{29}N_4Cl$: 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 $P2_1/C$; $a = 10.501(2)$ Å, $b = 17.087(4)$ Å, $c = 22.596(6)$ Å, $\beta = 93.51(1)°$; $Z = 4$; R (R_w) = 11.56 (10.77)% with 3039 unique reflections with $F > 3.00\sigma(F)$. 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 $Co_3O_{18}C_{34}H_{37}N_6Cl_2$ (**2**·$2H_2O$): 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; $\alpha = 98.69(1)°$, $\beta = 105.83(1)°$, $\gamma = 104.30(1)°$, $Z = 2$; R (R_w) = 7.13 (7.03)% with 6383 unique reflections with $F > 3.00\sigma(F)$. 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 $Co_4O_{17}C_{56}H_{48}N_8Cl_2$ (**4**·H_2O): 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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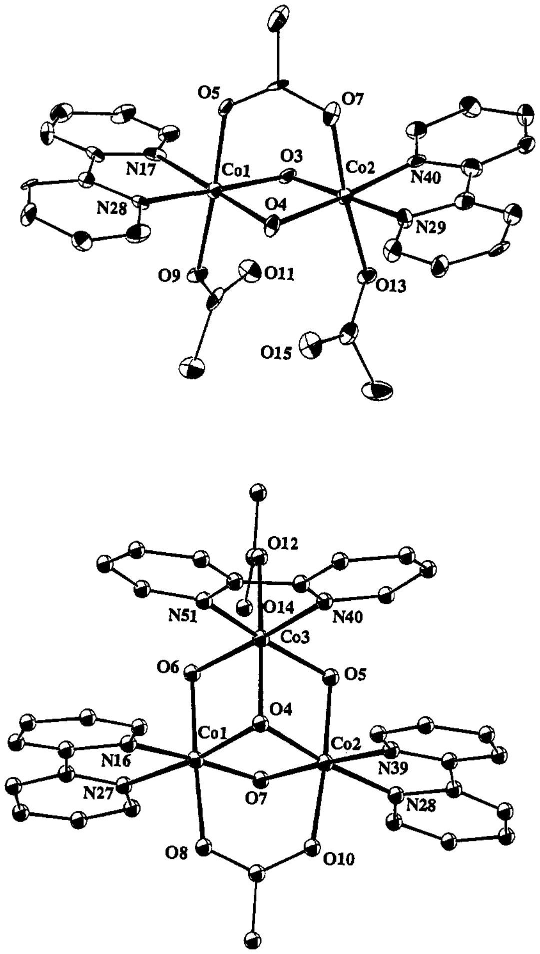


Figure 1. Structures of the cations of complexes **1** (top) and **2** (bottom). Selected distances (Å) and angles (deg) are listed as follows. Complex **1**: Co1⋯Co2, 2.793(2); Co1–O3, 1.894(6); Co1–O4, 1.899(6); Co1–O5, 1.926(6); Co1–O9, 1.891(6); Co1–N17, 1.924(8); Co1–N28, 1.921(7); Co2–O3, 1.883(6); 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 [Mn_4O_4] cubanes to be involved in the WOC cycle, either at the higher[2e,10] or lower S_n states.[2a,b,11] Unfortunately, no complex with a discrete [Mn_4O_4] core at the Mn^{III} and/or Mn^{IV} oxidation level has yet been prepared. In our proposal, we suggested that a [Mn_4O_4] cubane at S_2 or higher might form from an open [Mn_4O_2] unit present at a lower S_n state.[2e,10] 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 [Mn_2O_2] units might be present at the lower S_n states,[12,13] (iii) theoretical studies that conclude that O_2 evolution from an Mn_4O_4 cubane is as energetically feasible as from the other candidates considered,[14] and (iv) magnetochemical arguments against closely-spaced [Mn_2O_2] units being present at the *higher* S_n states but supporting a condensed structure such as a cubane.[15] Closely-spaced trinuclear and mononuclear units at the lower S_n states could also yield an Mn_4O_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 Mn^{IV}.[16]

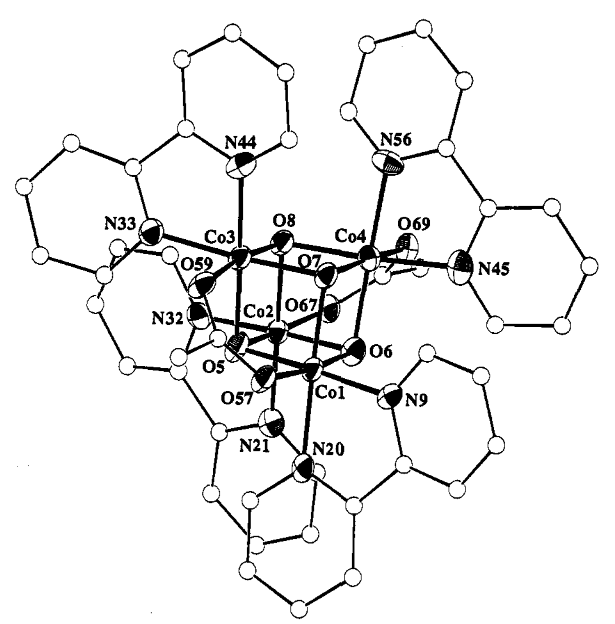
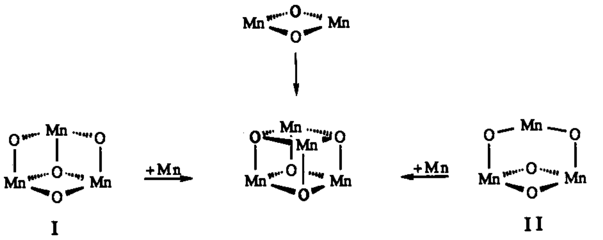


Figure 2. Structure of the cation of complex **4**. Selected distances (Å) are given as follows: Co1⋯Co2, 2.850(2); Co1⋯Co3, 2.666(2); Co1⋯Co4, 2.849(2); Co2⋯Co3, 2.865(2); Co2⋯Co4, 2.663(2); Co3⋯Co4, 2.845(2); Co1–O5, 1.877(6); Co1–O6, 1.891(6); Co1–O7, 1.874(6); Co1–N9, 1.930(7); Co1–N2O, 1.943(7); 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).



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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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