Novel Tetranulear Cobalt(II)-Cobalt(III) Mixed-Valence Complexes with a Significant Difference in Magnetism

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Tetranuclear cobalt(II)-cobalt(III) mixed-valence complexes with bis(benzoylacetone)-1,3-diiminopropan-2-ol (H_3L), $[Co_4L_2(C_2H_5O)_4]\cdot CH_3CN$ and $[Co_4L_2(CH_3O)_4]\cdot 2CH_2Cl_2$, have been synthesized and characterized by X-ray crystallography and magnetic susceptibility measurement.

Tetranuclear metal complexes have been the focus of active research because of their potential utility as model compounds for understanding the oxygen evolving center of the photosystem II of green plants.[1] While a number of tetranuclear manganese complexes were reported, only a few cobalt complexes have been documented as tetranuclear metal cores.[2-4] Such tetranuclear cobalt complexes also could provide important insights into the modeling studies. In this communication, we wish to report an interesting mixed-valent tetranuclear cobalt complex which has a twisted trapezoid core together with an analogous complex with a stepped cubane-like core.

Bis(benzoylacetone)-1,3-diiminopropan-2-ol (H_3L) is a pentadentate Schiff-base ligand and previous work using H_3L has established the formation of a trinuclear manganese(III) complex.[5] When H_3L was treated with cobalt(II) nitrate hexahydrate in C_2H_5OH:CH_3CN, a tetranuclear compound of $[Co_4L_2(C_2H_5O)_4]\cdot CH_3CN$ (**1**) was isolated instead of the trinuclear species.[6] The X-ray crystallography of **1** reveals a new type of tetranuclear structure as shown in Figure 1.[7] Each of the two Schiff-base ligands is coordinated to three cobalt atoms by the central alkoxo-oxygen atom (O1 for Co1, Co2, and Co4; O4 for Co1, Co2, and Co3) and an ethoxo-oxygen atom is further bonded to each pair of cobalt atoms (O7 for Co2 and Co3; O8 for Co3 and Co4; O9 for Co1 and Co4; O10 for Co1 and Co2), resulting a unique core with a di-μ-alkoxo(L)-μ-ethoxo bridge, two μ-alkoxo(L)-μ-ethoxo bridges, and a μ-ethoxo bridge. The Co1 and Co2 atoms take a distorted octahedral six-coordination with a keto-oxygen (O2 or O5), an imino-nitrogen (N1 or N3) and two alkoxo-oxygen (O1 and O4) atoms of L and two ethoxo-oxygen atoms (O10 and O9 or O7). On the other hand, the coordination geometry of the Co3 and Co4 atoms is five-coordinate trigonal bipyramid with an imino-nitrogen atom (N4 or N2) of L and two ethoxo-oxygen atoms (O8 and O7 or O9) in the equatorial plane, and a keto-oxygen (O6 or O3) and an alkoxo-oxygen (O4 or O1) atoms of L at the axial positions. The bond distances around the six-coordinate cobalt atoms [Co-O 1.861(10)—2.027(10) Å, Co-N 1.856(12), 1.861(14) Å] are significantly shorter than those of the five-coordinate cobalt atoms [Co-O 1.926(12)—2.399(10) Å, Co-N 2.017(13), 2.006(12) Å], suggesting that the oxidation states of these cobalt atoms are different. Charge considerations require a formal $Co^{II}{}_2Co^{III}{}_2$ description of **1**, and thus we can assign the Co1 and Co2 atoms to low-spin Co^{III} and the Co3 and Co4 atoms to high-spin Co^{II}, respectively, based on the coordination geometries and bonding parameters.[8] For tri(μ-hydroxo)dicobalt(III) complexes, Co-Co distances of 2.55—2.58 Å and Co-O-Co angles of 81—86° which may be diagnostic of $Co^{III}(\mu\text{-}O)_3Co^{III}$ core were reported.[9] The Co1-Co2 distance [2.595(3) Å] and Co1-O-Co2 angles [O1 83.3(3), O4 82.4(3), O10 85.9(4)°] are very close to these values. The Co1-Co4 and Co2-Co3 distances of 3.094(1) and 3.117(3) Å, respectively, are close to the Co^{II}-Co^{III} distances [3.034(2) and 3.042(2) Å] found in the $Co^{II}{}_2Co^{III}{}_4$ complex.[8] The Co3-Co4 distance [3.414(3) Å] is a little shorter than the Co^{II}-Co^{II} distance of 3.727(1) Å reported for the μ-hydroxodicobalt(II) complex.[10] To our knowledge, this is the first example of tetranuclear cobalt(II)-cobalt(III) mixed-valence complexes with a twisted trapezoid core which is a dimer-of-dimers arrangement accounting for the combination of ~2.7 and ~3.3 Å Mn-Mn vectors found in the photosystem II.[1]

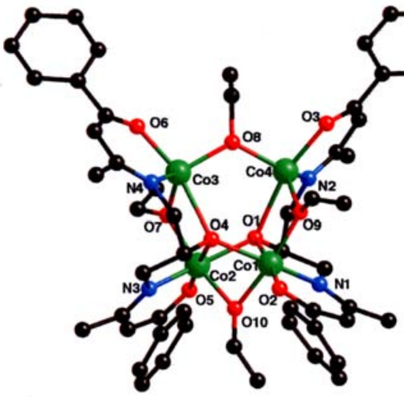

Figure 1. Perspective view of **1**.

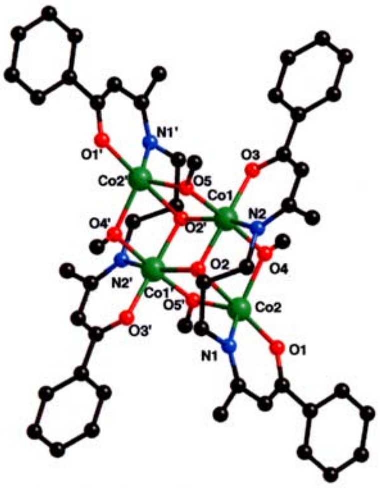

Figure 2. Perspective view of **2**.

In contrast, treatment of H_3L with cobalt(II) chloride hexahydrate in $CH_3OH:CH_3CN$ led to brown microcrystals and subsequent recrystallization from $CH_3OH:CH_2Cl_2$ gave a tetranuclear complex $[Co_4(L)_2(CH_3O)_4]\cdot 2CH_2Cl_2$ (**2**) as dark brown crystals.[11] The X-ray crystal structure of **2** shows a mixed-valent tetranuclear complex with a stepped cubane-like core (Figure 2).[7] The molecule has a crystallographic inversion center at the midpoint between the Co1 and Co1' atoms. In the asymmetric unit, the Co1 and Co2 atoms are bridged by the alkoxo-oxygen atom (O2) of L and methoxo-oxygen atom (O4), and further bound to the Co2' and Co1' atoms of the other asymmetric unit by the methoxo-oxygen atom (O5 and O5'), respectively. The Co1 atom adopts a distorted octahedral geometry with a keto-oxygen (O3), an imino-nitrogen (N2), and an alkoxo-oxygen (O2) atoms of L, an alkoxo-oxygen atom (O2') of another L, and two methoxo-oxygen atoms (O4 and O5), while the Co2 atoms has a trigonal bipyramidal arrangement with an imino-nitrogen (N1) of L and two methoxo-oxygen atoms (O4 and O5') in the equatorial plane and a keto-oxygen (O1) and an alkoxo-oxygen (O2) of L at the axial positions. The Co1-O/N bonds [Co1-O 1.870(6)—2.009(6) Å, Co1-N2 1.861(8) Å] are shorter compared with the Co2-O/N bond lengths [Co2-O 1.932(7)—2.193(6) Å, Co2-N1 1.993(8) Å]. These coordination features and the charge balance of **2** show that the Co1 and Co2 atoms are low-spin Co^{III} and high-spin Co^{II} ions, respectively. We are unaware of such an example of $Co^{II}{}_2Co^{III}{}_2$ tertranuclear mixed-valence complexes except for only one known complex $[Co^{II}{}_2Co^{III}{}_2R_2(OH)_2(CH_3COO)_2]$ (H_3R=a dinucleating ligand).[2]

The diffuse reflectance spectra of **1** and **2** show several absorptions in the visible and near-infrared region, which can be assigned to d-d transitions due to the high-spin Co^{II} and low-spin Co^{III} in accordance with the mixed-valence state of these complexes.[12] The magnetic moments of **1** and **2** are 6.00 and 6.73 B.M. at 300 K, respectively. These values are greater than the spin-only value 5.48 B.M. for the two local S=3/2 and two diamagnetic S=0 spins, suggesting an orbital contribution of the high-spin Co^{II} to the magnetic moments. As shown in Figure 3, the magnetic moment of **1** exhibits continuous decrease upon cooling to 1.12 B.M. at 2 K. This behavior implies antiferromagnetic interaction is operating between the two Co^{II} atoms, although the orbital contribution must be involved. Fitting of the data ($20<T\leq 300$ K) for **1** gives a value of $-8.5\ cm^{-1}$ for J.[13] The deviation from the calculated curve at low temperature may come from a phase change around 20 K which is suggested from the variation of the inverse of the susceptibility of **1** with temperature. The observed magnetic interaction should operate through the ethoxo-bridge and the large Co3-O8-Co4 angle of 123.6(6)° may be favorable for the antiferromagnetism. On the other hand, the magnetic moment of **2** slowly increases to 7.47 B.M. at 12 K and then decreases to 6.72 B.M. at 2 K. The increase in the magnetic moment with lowering of temperature is consistent with ferromagnetic interaction between the two Co^{II} atoms mediated by the $Co^{III}{}_2O_2$ moiety. Fitting process yields the value $J=2.2\ cm^{-1}$.[13] Reports of ferromagnetic interaction in cobalt complexes are few.[14] The small bond angles [Co2-O2-Co1' 94.0(2)°, Co2-O2-Co1 96.7(2)°] may be a major origin of the observed ferromagnetism, because the unpaired electron lies in the d-orbital along the Co2-O2 bond. The present results show that a structural rearrangement of tetranuclear core causes a significant difference in the magnetism. Such a large change in magnetic property was observed in the Mn cluster of the photosystem II.[15]

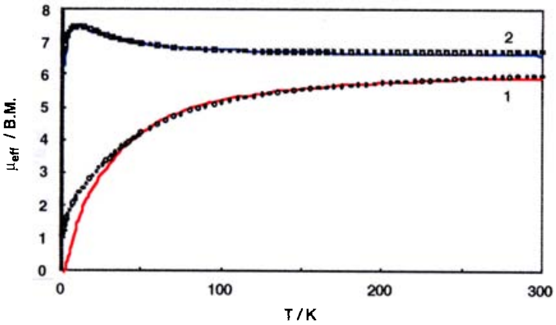

Figure 3. Temperature dependence of magnetic moments of **1** and **2**. Solid lines were calculated with parameters ($J = -8.5\ cm^{-1}$, $g = 2.3$, $\theta = -1.0$ K for **1**; $J = 2.2\ cm^{-1}$, $g = 2.4$, $\theta = -1.5$ K for **2**).[13]

References and Notes

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6 Cobalt(II) nitrate hexahydrate (43 mg, 0.15 mmol) was dissolved in 10 cm^3 of $C_2H_5OH:CH_3CN$. Then H_3L (28 mg, 0.075 mmol) and triethylamine (92 mg, 0.91 mmol) were successively added. The mixture was stirred and filtered; a slow evaporation gave dark brown plates.
7 Crystallographic data: for **1**; $C_{56}H_{69}Co_4N_5O_{10}$, *F.W.*=1208.02, monoclinic, space group $P2_1/n$, a=16.307(3), b=13.378(6), c=26.314(1), β=91.25(5)°, V=5745.6(4) $Å^3$, Z=4, D_m=1.39, D_c=1.40 gcm^{-3}, μ(Mo Kα)=11.91 cm^{-1}, crystal dimensions 0.25×0.32×0.41 mm^3, 10570 reflections mesured ($2\theta_{max}$=50°), 2929 [$I\geq 3\sigma(I)$] used in the refinement, R=0.061, R_w=0.071. For **2**; $C_{52}H_{62}Cl_4Co_4N_4O_{10}$, *F.W.*=1280.63, monoclinic, space group $P2_1/c$, a=8.466(4), b=15.614(5), c=21.074(13) Å, β=90.86(2)°, V=2785.5(2) $Å^3$, Z=2, D_m=1.52, D_c=1.53 gcm^{-3}, μ(Mo Kα)=14.20 cm^{-1}, crystal dimensions 0.15×0.15×0.52 mm^3, 4042 reflections measured ($2\theta_{max}$=46°), 2198 [$I\geq 3\sigma(I)$] used in the refinement, R=0.057, R_w=0.062. Intensity data were collected on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo-Kα radiation. All the structures were solved by the direct method and refined by the full-matrix least-squares method using a MolEN program package.
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11 Cobalt(II) chloride hexahydrate (562 mg, 2.36 mmol) was dissolved in 18 cm^3 of $CH_3OH:CH_3CN$. Then H_3L (892 mg, 2.36 mmol) and triethylamine (730 mg, 7.21 mmol) were successively added. The mixture was stirred and filtered; a slow evaporation gave brown microcrystals. Recrystallization of these from $CH_3OH:CH_2Cl_2$ gave dark brown plates.
12 Diffused reflecrtance spectra: λ_{max}/nm **1**: 523sh, 630sh, 827sh, 1387, 1692, 1856; **2**: 551sh, 674sh, 817, 1362, 1582, 1865sh.
13 The magnetic data were fitted with the van Vleck equation including a Weiss temperature θ based on the Heisenberg model ($\mathbf{H}=-2J\mathbf{S}_1\cdot\mathbf{S}_2$ ($S_1=S_2=3/2$).[14]
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