Mixed-valence Hexanuclear Cobalt(II, III) Complex Made Up of Two Defective Cubane Cores

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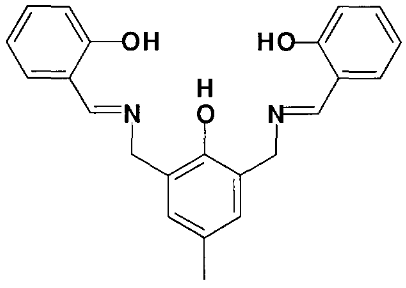
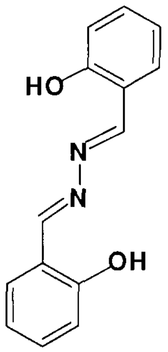
A mixed-valence cobalt(II, III) complex, $[Co_6L_2(CH_3COO)_2(CH_3O)_6L']\cdot 2CH_3OH$ (H_3L = 2,6-bis(saliclylideneaminomethyl)-4-methylphenol and H_2L' = salicylazine), has been isolated and characterized by X-ray crystallography, which reveals a unique hexanuclear structure consisting of two defective cubane-cores.

Oligonuclear metal complexes have much attention recently, since these compounds have specific complexation behavior, interesting structures, and unique magnetic properties.[1] We recently described synthesis of dinuclear,[2] tetranuclear,[3] and pentanuclear,[4] and infinite polynuclear[5] complexes which are formed by the use of a pentadentate Schiff-base ligand, 2,6-bis(saliclylideneaminomethyl)-4-methylphenol (H_3L). In the course of this activity, we have isolated an unprecedented hexanuclear cobalt(II, III) complex in the presence of a potential bridging group, salicylazine (H_2L'), $[Co_6L_2(CH_3COO)_2(CH_3O)_6L']\cdot 2CH_3OH$ (**1**). Herein we report the preparation and structural characterization of the novel hexanuclear cobalt complex.



H3L



H2L'

The cobalt complex **1** was isolated as follows.[6] To a methanol/acetonitrile solution containing H_3L and H_2L', cobalt(II) acetate tetrahydrate and triethylamine were successively added with stirring. The resulting solution was filtered and the filtrate was left to stand for several days. Dark brown crystals of **1** were deposited. The X-ray crystallography of **1** reveals a novel hexanuclear structure which consists of two defective cubane cores, $Co_3L(CH_3COO)(CH_3O)_3$, and a bridging group L' (Figure 1).[7,8] The molecule has a crystallographically inversion center at the midpoint of the N3-N3' of L'. In the asymmetric unit, the dinucleating ligand L binds two cobalt atoms, Co1 and Co2, with a *syn-syn* bridging acetate ion.[9] The Co1-Co2 distance is 2.897(2) Å. These cobalt atoms are further connected to the third cobalt atom Co3 by three methoxo-oxygen atoms, O6, O7, and O8, to form a defective cubane Co_3O_4 core. The Co1-Co3 and Co2-Co3 distances are 3.042(2) and 3.034(2) Å, respectively The core structure is shown in Figure 2. The Co1 and Co2 atoms take a distorted octahedral six-coordination and the geometry of the Co3 atom is five-coordinate trigonal bipyramid. The bond distances around the six-coordinate cobalt atoms [Co-O 1.855(6)—1.953(5), Co1-N1 1.894(6), Co2-N2 1.877(7) Å] are siginificantly shorter than those of the five-coordinate cobalt atom [Co3-O 1.904(6)—2.219(5), Co3-N3 2.055(6) Å]. This fact means that the oxidation states of these Co atoms are different. Considering with the charge balance and bonding parameters, we assign the Co1 and Co2 atoms to low-spin Co^{III} and the Co3 atom to high-spin Co^{II}, respectively.[10] Such defective cubane core has been found in other cobalt species recently.[11,12] However, these are all Co^{III}_3 species. To our knowledge, the present Co_3O_4 core is the first example of a defective cubane structure having the

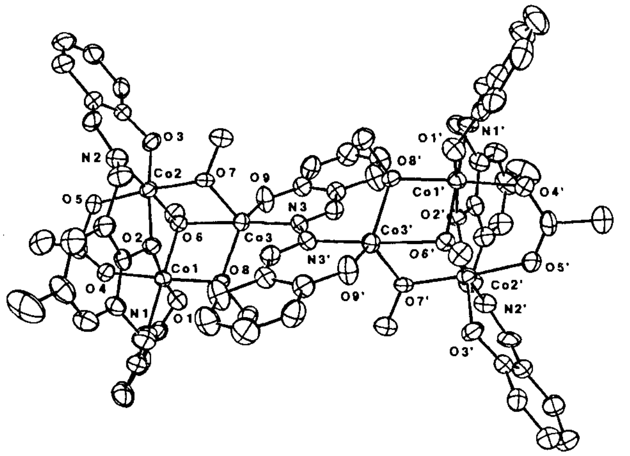


Figure 1. Perspective view of **1**, showing the atom-labeling scheme.

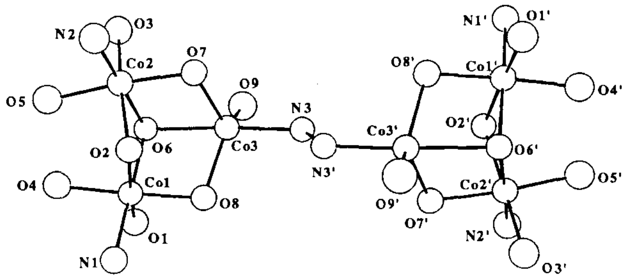


Figure 2. Perspective view of coordination spheres of **1**. Selected bond distances (l/Å) and angles (ϕ/°): Co1-Co2 2.897(2), Co1-Co3 3.042(2), Co2-Co3 3.034(2), Co3-Co3' 5.069(1), Co1-O1 1.855(6), Co1-O2 1.953(5), Co1-O4 1.904(5), Co1-O6 1.923(5), Co1-O8 1.889(5), Co1-N1 1.894(6), Co2-O2 1.949(5), Co2-O3 1.859(6), Co2-O5 1.913(6), Co2-O6 1.915(5), Co2-O7 1.892(5), Co2-N2 1.877(7), Co3-O6 2.219(5), Co3-O7 1.986(5), Co3-O8 1.980(5), Co3-O9 1.904(6), Co3-N3 2.055(6); Co1-O2-Co2 95.9(2), Co1-O6-Co2 98.0(2), Co1-O6-Co3 94.2(2), Co1-O8-Co3 103.6(3), Co2-O6-Co3 94.1(2), Co2-O7-Co3 102.9(3).

$Co^{III}_2Co^{II}$-mixed-valence state. This type of defective cubane core is interesting in relation to the unknown Mn_4 structure of the OEC of the photosystem II.[11,12] The bridging group L' takes a *trans* conformation such as to avoid a steric crowding of the two Co_3 units, forming a unique hexanuclear structure. The Co3-Co3' separation is 5.069(1) Å. Thus far such a bridging property of salicylazine has not been found in the literatures.

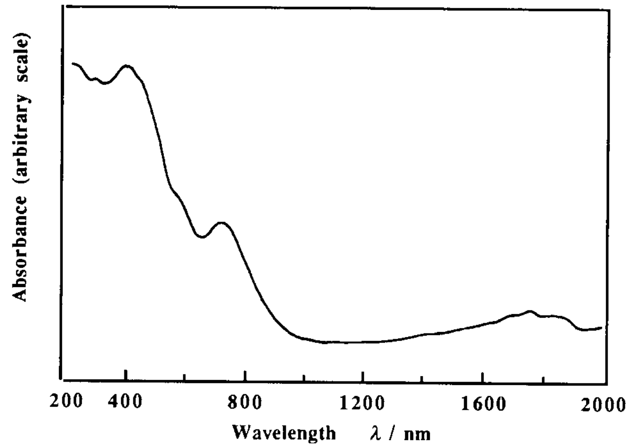


Figure 3. Diffuse reflectance spectrum of **1**.

The diffuse reflectance spectrum of **1** does not show the expected intervalence-transfer bands but several d-d absorptions in the visible and near-infrared region [571, 720, 1380, 1690, 1750, and 1840 nm]. These absorptions can be assigned to d-d transitions of $^4A_2' \rightarrow {}^4E''$, $^4A_2' \rightarrow {}^4A_2'(P)$, $^4A_2' \rightarrow {}^4E''(P)$ for Co^{II} in D_{3h} symmetry and/or $^1A_{1g} \rightarrow {}^1T_{1g}$, $^1A_{1g} \rightarrow {}^1T_{2g}$ for Co^{III} in O_h symmetry and is in harmony with the coexistence of the low-spin Co^{III} and high-spin Co^{II} ions in the hexanuclear molecule.[13]

The magnetic data also support our assignment on the mixed-valence state.[14] The magnetic moment of **1** is 6.47 B.M. at 299 K. This value is indicative of an appreciable orbital contribution of the high-spin Co^{II} to the magnetic moment,[13] because the spin-only value is 5.48 B.M. for the two local S = 3/2 and four diamagnetic S = 0 spins. The magnetic moment decreases to 6.08 B.M. at 80 K with lowering of temperature and the susceptibility data (80—300 K) follow the Curie-Weiss law with $\theta = -18.1$ K. These facts suggest that there is an antiferromagnetic interaction between the two high-spin Co^{II} atoms mediated by the L' group, although the decrease in the magnetic moment with temperature is consistent with the spin-orbit coupling of high-spin Co^{II} in trigonal bipyramidal coordination.

The present results show that the combination of the L and L' Schiff-base ligands afford a unique $Co^{III}Co^{III}Co^{II}Co^{II}Co^{III}Co^{III}$ hexanuclear complex. In the formation of the hexanuclear unit, the bridging group L' plays an important role to connect the two $Co^{III}Co^{III}Co^{II}$ units and seems to control the oxidation state of the third Co producing a novel mixed-valence state.

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References and Notes

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6 Cobalt(II) acetate tetrahydrate (25 mg, 0.10 mmol) and three drops of triethylamine were added to a suspension of H_3L (37 mg, 0.10 mmol) and H_2L' (12 mg, 0.05 mmol) in methanol—acetonitrile (1:2) to give a dark reddish brown solution. The solution was filtered and allowed to stand for sevearl days at room temperature. Dark brown crystals deposited were collected by filtration.
7 Crystallographic data: for **1**; $C_{72}H_{80}Co_6N_6O_{20}$ F.W. = 1703.07, monoclinic, space group $P2_1/n$, $a = 10.053(7)$, $b = 19.180(7)$, $c = 20.856(14)$ Å, $\beta = 101.69(3)°$, $V = 3938(4)$ Å^3, $Z = 2$, $D_m = 1.43$, $D_c = 1.44$ gcm^{-3}, μ(Mo Kα) = 13.01 cm^{-1}, 6391 reflections measured ($2\theta_{max} = 48°$), 3002 [$I \geq 3\sigma(I)$] used in the refinement, $R = 0.046$, $R_w = 0.051$. 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.
8 Infrared spectrum of **1** exhibits two absorptions [1629, 1603 cm^{-1}] due to ν(C=N) stretching bands which confirm the presence of two kinds of Schiff-bases, L and L'.
9 Infrared spectrum of **1** shows absorptions indicative of the symmetric bidentate nature of the acetate group [$\nu_{as}(CH_3COO)$) 1535s, $\nu_s(CH_3COO)$ 1431s cm^{-1}].
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14 The magnetic susceptibilities were measured by the Faraday method over the 80—300 K temperature range. The apparatus was calibrated using $[Ni(H_2NCH_2CH_2NH_2)_3]S_2O_3$.