Trinuclear Cobalt(III) Complex Having Partial Cubane Co3O4 Core: Synthesis and Structural Analysis of the Complex Containing Bis(2-pyridylmethyl)amine

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The trinuclear cobalt(III) complex with the partial cubane Co_3O_4 core, $[Co_3(dpa)_3(\mu-OH)_3(\mu_3-O)]^{4+}$ (dpa: bis-(2-pyridylmethyl)amine), was prepared and the structure was determined by the X-ray diffraction method. Though the partial cubane structure was slightly distorted by the N—H ↔ H—N repulsive interaction, this complex is stable at least 5 days in its neutral aqueous solution.

The Mn complexes with Mn_4O_4 core are of interest in connection with the photosynthetic water oxidation center (WOC) in green plants, though the arrangements of the metal ions in the water oxidation centers are currently unclear.[1] Recently, the extension of the WOC modeling studies to the cobalt complexes with cubane and partial cubane cores gives important information for understanding of the mechanism of the oxidation. However, there are only few reports about preparations of these types of cobalt complexes.[2-5] In the previous letter, we reported the preparation and the structure of one of the isomers of $[Co_3(edma)_3(\mu-OH)_3(\mu_3-O)]^+$ (edma: ethylenediamine-N-acetate) which have Co_3O_4 partial cubane cores.[5] In the $[Co_3(edma)_3(\mu-OH)_3(\mu_3-O)]^+$ isomers, the partial cubane structures were stabilized by the intramolecular hydrogen bonds between the amino group on one of the three cobalt atoms and the carboxyl group on another cobalt atom. It is expected that the attractive interactions arising from the stacking of pyridyl rings also stabilize the polynuclear structure as the hydrogen bonds do: it may be possible to isolate the $[Co_3(dpa)_3(\mu-OH)_3(\mu_3-O)]^+$ (complex 1) (dpa: bis(2-pyridylmethyl)amine), if the stabilization arising from the stacking of pyridyl rings is effectively strong to overcome the repulsive interaction arising from the two neighboring N—H's in the trinuclear structure. From these expectations, we have attempted to prepare the $[Co_3(dpa)_3(\mu-OH)_3(\mu_3-O)]^+$. We report here on the results of the attempts, that is, isolation and determination of the crystal structure of $[Co_3(dpa)_3(\mu-OH)_3(\mu_3-O)](S_2O_6)_2 \cdot 7H_2O$.

The complex was prepared by the method described below. To a solution containing 2.4 g of $CoCl_2 \cdot 6H_2O$ and 2.0 g of dpa in 5 cm³ of water, 0.2 M (M: mol dm⁻³) KOH aqueous solution was added till the precipitation of $Co(OH)_2$ began to appear. Air was bubbled through the solution for 12 h, the precipitate which appeared was filtered off, and the filtrate was charged on an SP-Sephadex column (K⁺ form, ϕ 4.7 cm × 5 cm). After the charged column was swept with 0.2 M KCl in order to elute out the pink and orange bands containing undesirable mononuclear complexes, the adsorbed band was developed with 0.5 M KCl. The major brown band was transferred to another SP-Sephadex column (K⁺ form, ϕ 4.7 cm × 90 cm) and chromatographed recyclically with 0.5 M KCl. The band was separated into one major brown and three minor bands. The eluate from the major band was evaporated to dryness under reduced pressure. The desired brown complex was extracted with methanol, and a crude
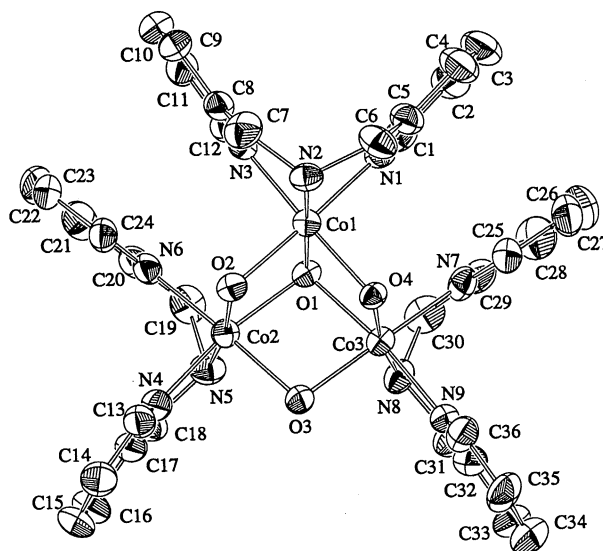

Figure 1. ORTEP drawing of the $[Co_3(dpa)_3(\mu-OH)_3(\mu_3-O)]^+$ cation in complex 1; selected bond distances(Å) and bond angles(°): Co1—O1 1.898(5), Co2—O1 1.947(5), Co3—O1 1.932(5), Co1—O2 1.912(5), Co1—O4 1.906(5), Co2—O2 1.910(5), Co2—O3 1.903(5), Co3—O3 1.907(5), Co3—O4 1.902(5), Co1—N1 1.929(6), Co1—N2 1.955(6), Co1—N3 1.928(6), Co2—N4 1.941(7), Co2—N5 1.956(6), Co2—N6 1.940(6), Co3—N7 1.926(7), Co3—N8 1.967(6), Co3—N9 1.947(6), Co1—O1—Co2 95.5(2), Co2—O1—Co3 96.9(2), Co3—O1—Co1 96.0(2), Co1—O2—Co2 96.3(2), Co2—O3—Co3 99.3(2), Co3—O4—Co1 96.7(2), O1—Co1—O2 84.6(2), O1—Co1—O4 83.9(2), O1—Co2—O2 83.3(2), O1—Co2—O3 81.8(2), O1—Co3—O3 82.1(2), O1—Co3—O4 83.0(2).

complex was obtained from the concentrated methanolic solution by adding ether, which was recrystallized from water by adding acetone.[6] The complex obtained as chloride salt was fine needle crystals and was not suitable for the X-ray crystal analysis. Therefore, we converted the chloride salt to dithionate one in the following way. To the saturated aqueous solution of the chloride, excess of sodium dithionate was added in solid. The deposited crystals of the dithionate complex appeared were filtered and washed with cold water. Recrystallization was carried out from hot water (complex 1);[7] this recrystallized dithionate was analyzed by the X-ray diffraction method.[8]

A perspective view of the $[Co_3(dpa)_3(\mu-OH)_3(\mu_3-O)]^+$ cation in complex 1 is illustrated in Fig. 1. The coordinations around cobalt(III) atoms are roughly octahedral. It is clear from the figure that the complex ion contains the partial cubane Co_3O_4 core. That is, the Co—O2, Co—O3, and Co—O4 distances are in the range 1.903 ~ 1.912 Å; the O2, O3, and O4 atoms (μ-OH) span two independent Co atoms. The O1 atom (μ_3-O) bridges three Co atoms, however, the Co2—O1 and Co3—O1 distances (1.947 and 1.932 Å) are longer than the Co1—O1 (1.898 Å) and
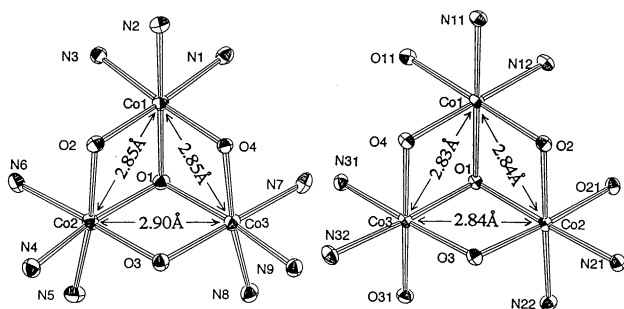
Figure 2. Structures of the partial cubane Co₃O₄ cores; **A**: complex **1**, and **B**: [Co₃(edma)₃(μ-OH)₃(μ₃-O)]⁺ (**T1** isomer).[5]

the Co—μ₃-O distances reported in the previous letter (1.899 ~ 1.923 Å).[5]

The three four-membered rings, Co1—O1—Co2—O2, Co1—O1—Co3—O4, Co2—O1—Co3—O3, are approximately planar, however, the planes are deviated from the regular square. The Co—O—Co angles are larger than 90°; the deviation from 90° is larger in Co2—O3—Co3 (99.3°) than in the other Co—O—Co (95.5 ~ 96.9°). The O—Co—O angles in the approximate planes are smaller than the 90° and in the range 81.8 ~ 84.86°. These values are also in agreement with those of the corresponding angles in the trinuclear [Co₃(edma)₃(μ-OH)₃(μ₃-O)]⁺ ion (**T1** isomer)[5] and dinuclear [Co(edda)Co(en)₂(μ-OH)₂]²⁺ ion.[9] The Co2—Co3 distance (non-bonding) is 2.90 Å and larger than the Co1—Co2 and Co1—Co3 distances (ca. 2.85 Å) and also larger than the Co—Co distances observed in the [Co₃(edma)₃(μ-OH)₃(μ₃-O)]⁺ ion which has a partial cubane core (2.83 ~ 2.84 Å; Fig. 2). The N5—N8 distance is 3.58Å and much larger than the N1—N7 (3.09 Å) and N3—N6 (3.11 Å). These results suggest that the N5—H and N8—H repulsively interact to each other.

The core Co₃O₄ structure of the complex **1** is slightly distorted from the regular cubane structure as mentioned above. However, the distortion is not so significant because of the absence of the extra ligands as observed in [Co₃O₃(OH)₃(OAc)₂(bpy)₃]²⁺ [2] where the extra μ₂-acetato ligands distorted the regular structure so much.

The ¹³C NMR spectrum in D₂O[7] showed that complex **1** has three kinds of pyridylmethyl groups, which suggests that the partial cubane structure with a mirror plane including N2, Co1 O1, and O3 atoms restored in the D₂O solution (in the crystal cell, the complex molecule defects from the mirror plane by the requirement of crystal packing) and that this complex was not hydrolyzed to mononuclear complexes during the ¹³C NMR measurement.

The UV and visible absorption spectrum of this complex

showed the clear first *d-d* absorption band at ca. 18500 cm⁻¹, while the second *d-d* band appeared as a vague shoulder at ca. 23000 cm⁻¹ beside the characteristic strong band arising from Co(μ-OH)Co moiety (29000 ~ 37000 cm⁻¹) in a similar manner to the [Co₃(edma)₃(μ-OH)₃(μ₃-O)]⁺ isomer which has the Co₃O₄ core.[5] The neutral aqueous solution did not show the spectral change for several days. This observation also suggests that this complex was not hydrolyzed so easily in the neutral aqueous solution. Accordingly, it is reasonable to suppose that the trinuclear structure of complex **1** is stabilized by the stacking of the pyridyl rings, of which stabilization overcome the unstability caused by the N5—H ↔ H—N8 repulsion. The spectrum of complex **1** also did not exhibits a obvious time-course change in the pH 11 solution. However, in the pH 1 solution, it exhibited a obvious and faster spectral change than the [Co₃(edma)₃(μ-OH)₃(μ₃-O)]⁺,[5] whose Co₃O₄ structure is fully stabilized by the three N—H···O intramolecular hydrogen-bonds; accordingly, complex **1** is less stable than the [Co₃(edma)₃(μ-OH)₃(μ₃-O)]⁺ and suitable for the study on the reaction mechanism of the complex having the Co₃O₄ core.

References and Notes

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6   Anal. Found: C, 37.51; H, 5.19; N, 10.78%. Calcd for [Co₃(dpa)₃(OH)₃(O)]Cl₄·9.5H₂O (C₃₆H₆₁N₉O₁₃.₅Cl₄Co₃): C, 37.45; H, 5.32; N, 10.92%.

7   Anal. Found: C, 33.00; H, 4.41; N, 9.68%. Calcd for [Co₃(dpa)₃(OH)₃(O)](S₂O₆)₂·7H₂O (C₃₆H₅₆N₉O₂₃S₄Co₃): C, 33.57; H, 4.38; N, 9.79%. ¹³C NMR in D₂O: δ 59.87, 60.42, 61.79, 121.85, 123.01, 124.51, 125.18, 125.70, 126.06, 140.09, 140.76, 141.624, 148.47, 148.83, 150.55, 161.95, 163.77, 163.78.

8   Crystallographic data of **1**: formula C₃₆H₅₆N₉O₂₃S₄Co₃, F.W. = 1287.92, monoclinic, P 2₁/n (No. 14), a = 13.021(3), b = 19.972(4), c = 19.691(3) Å, β = 96.15(2)°, V = 5091(1) Å³, Z = 4, D_calc = 1.680 g cm⁻³, unique reflections = 7761 (I > 3σ(I)), R = 0.069 (R_w = 0.075).

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