

## Trinuclear Cobalt(III) Complexes Containing Partial Cubane Co<sub>3</sub>O<sub>4</sub> Core. Synthesis and Structure of [Co<sub>3</sub>(L)<sub>3</sub>(μ-OH)<sub>3</sub>(μ<sub>3</sub>-O)]Cl (L=ethylenediamine-*N*-acetate)

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Three isomers of [Co<sub>3</sub>(edma)<sub>3</sub>(μ-OH)<sub>3</sub>(μ<sub>3</sub>-O)]<sup>+</sup> (edma: ethylenediamine-*N*-acetate) containing a partial cubane Co<sub>3</sub>O<sub>4</sub> core were prepared and the structure of one of the isomers was determined by the X-ray diffraction method. These isomers are stable at least for 5 days in their neutral aqueous solutions.

The structures and action modes of Mn complexes with Mn<sub>4</sub>O<sub>4</sub> core are of interest in connection with the photosynthetic water oxidation center (WOC) in green plants, though the arrangements of the metal ions of the water oxidation centers (S<sub>n</sub> states; *n* = -1 to 4) are currently unclear.<sup>1</sup> Recently, it has been emphasized that the extension of the WOC modeling studies to the cobalt(III) complexes with cubane and partial cubane cores gives important information for understanding of the mechanism of the oxidation.<sup>2</sup> However, there are only two reports about preparation of these type cobalt(III) complexes.<sup>2</sup>

In the previous papers,<sup>3,4</sup> we reported on the preparation and characterization of some dinuclear cobalt(III) complexes. It has been clarified in the [Co(gly)(en)Co(gly)(en)-(μ-OH)<sub>2</sub>]<sup>2+</sup> complex ion that the N—H···O hydrogen bonds (each hydrogen bond is formed between the amino group on one of the two cobalt atoms and the carboxyl group on the other cobalt atom) stabilize the dinuclear structure. According to this suggestion, we thought that trinuclear cobalt(III) complexes with a partial cubane core which is stabilized by the N—H···O hydrogen bonds can be prepared and so we attempted to prepare trinuclear cobalt(III) complexes containing edma (ethylenediamine-*N*-acetate). We report here on the isolation of some isomers of [Co<sub>3</sub>(edma)<sub>3</sub>(μ-OH)<sub>3</sub>(μ<sub>3</sub>-O)]<sup>+</sup> and on the crystal structure of one of them determined by the X-ray diffraction methods.<sup>5</sup> The previously reported trinuclear complex with the partial cubane Co<sub>3</sub>O<sub>4</sub> core is significantly distorted by an extra μ<sub>2</sub>-acetate ligand,<sup>2</sup> whereas the present complex is not distorted so much because of absence of the extra bridging ligand.

The complex was prepared by the method described below. To a solution containing 2.9 g of Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O in 5 cm<sup>3</sup> of water, 4 cm<sup>3</sup> of 30% H<sub>2</sub>O<sub>2</sub> aqueous solution was added. The mixed solution was added dropwise to a suspension containing 7 g of KHCO<sub>3</sub> in 7 cm<sup>3</sup> of water, keeping the temperature of the reacted solution below 5 °C. To this solution, 2.3 g of edma·2HCl·2H<sub>2</sub>O was added and stirred for 24 h at room temperature. The pH of the solution was adjusted to ca. 1 with 60% HClO<sub>4</sub> (stirred for 10 min at room temperature) and then to 9 with 2 mol·dm<sup>-3</sup> KOH (stirred for 60 min at 50 °C). White precipitate (KClO<sub>4</sub>) was removed by filtration, and the filtrate was charged on an SP-

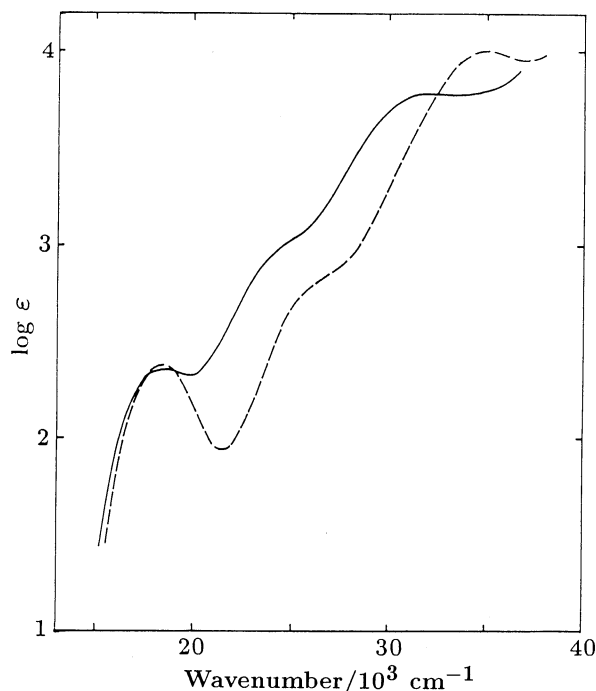
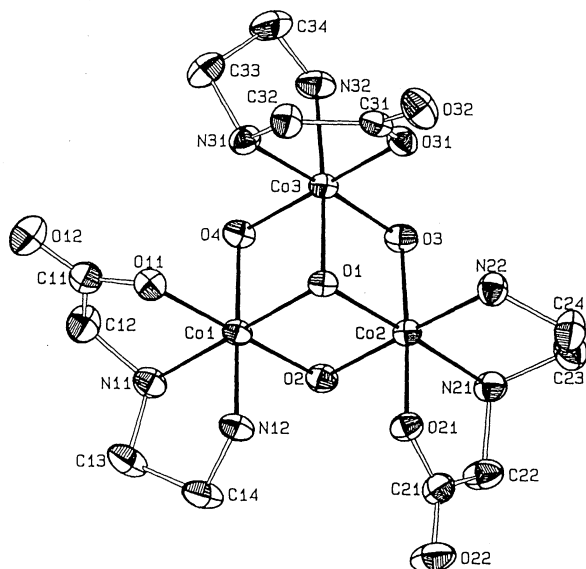


Figure 1. Visible and UV absorption spectra of **T1**: at pH 6 (—), and pH 3 (---). ( $\epsilon$  values are given in mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>.)

Sephadex column (K<sup>+</sup> form). After the charged column was swept with 500 cm<sup>3</sup> of water, the adsorbed band was developed with 0.1 mol·dm<sup>-3</sup> K<sub>2</sub>SO<sub>4</sub>. The desired trinuclear complexes were obtained from the faster eluted three brown bands (**T1**, **T2**, and **T3**; in the order of elution). Each of the **T1**—**T3** eluates was concentrated to a few milliliters by a rotary evaporator at 35–40 °C before adding about 100 cm<sup>3</sup> of methanol. After the deposited K<sub>2</sub>SO<sub>4</sub> was removed by filtration, the filtrate was again concentrated to a few milliliters. A crude complex obtained by adding acetone was recrystallized from water upon the addition of acetone. The obtained sulfate was converted to chloride by using a QAE-Sephadex column (Cl<sup>-</sup> form). The visible and UV absorption spectrum of **T1** is shown in Fig. 1. The absorption spectra of **T2** and **T3** are very similar to that of **T1**, suggesting that they are the stereoisomers having the same core structure. **T2** and **T3** were obtained as fine needle crystals and crystalline powder, respectively; we have not yet succeeded to clarify their crystal structures by the X-ray diffraction method. The crystal structure of **T1** chloride was clarified as described below.<sup>5</sup>



**Figure 2.** ORTEP drawing of the complex cation in **T1**; selected bond distances (Å) and bond angles (°):

Co1—O1 1.901(2), Co2—O1 1.898(2), Co3—O1 1.889(2), Co1—O2 1.899(3), Co1—O4 1.923(2), Co2—O2 1.915(3), Co2—O3 1.911(2), Co3—O3 1.914(3), Co3—O4 1.904(2), Co1—O11 1.936(3), Co1—N11 1.967(3), Co1—N12 1.936(3), Co2—O21 1.913(2), Co2—N21 1.959(3), Co2—N22 1.955(3), Co3—O31 1.906(3), Co3—N31 1.941(3), Co3—N32 1.983(3), Co1—O1—Co2 96.7(1), Co2—O1—Co3 96.3(1), Co3—O1—Co1 96.3(1), Co1—O2—Co2 96.2(1), Co2—O3—Co3 95.1(1), Co3—O4—Co1 95.0(1), O1—Co1—O2 83.7(1), O1—Co1—O4 83.9(1), O1—Co2—O2 83.3(1), O1—Co2—O3 84.0(1), O1—Co3—O3 84.2(1), O1—Co3—O4 84.8(1).

A perspective view of  $[\text{Co}_3(\text{edma})_3(\mu\text{-OH})_3(\mu_3\text{-O})]^+$  in **T1** is illustrated in Fig. 2. The coordinations around cobalt(III) atoms are roughly octahedral. It is clear from the figure that **T1** contains the partial cubane  $\text{Co}_3\text{O}_4$  core. That is, the three Co—O1 distances are in the range 1.889—1.901 Å, showing that the O1 atom bridges three Co atoms. The Co—O2, Co—O3, and Co—O4 distances are in the range 1.899—1.923 Å; the O2, O3, and O4 atoms span two independent Co atoms. These Co—O values agree well with those of the corresponding ones in the dinuclear  $[\text{Co}(\text{edda})\text{Co}(\text{en})_2(\mu\text{-OH})_2]^{2+}$  ion.<sup>4</sup> The three four-membered rings, O1—Co1—O2—Co2, O1—Co2—O3—Co3, and O1—Co3—O4—Co1, are approximately planar, (sums of the four angles are 359.5—360.1°). However, these approximated planes are not regular squares; the Co—O—Co angles are 95.0—96.7° and the O—Co—O ones are 83.7—84.8°. These values are also agree with those of the corresponding ones in the  $[\text{Co}(\text{edda})\text{Co}(\text{en})_2(\mu\text{-OH})_2]^{2+}$  ion.<sup>4</sup> The bond distances and angles in the coordinated edma ligands are similar to those of the  $(+)\text{C}_{519}\text{D}-[\text{Co}(\text{edma})(\text{en})(\text{NH}_3)]^{2+}$  ion (F-4)<sup>6</sup>. The Co—Co distances are in the range 2.83—2.84 Å, and  $\mu_3\text{-O}-\mu\text{-O}$  distances are in the range 2.51—2.56 Å.

The O11—N31, O21—N12, and O31—N22 distances are less than 2.95 Å; there are three intramolecular hydrogen-bonds (the each N—H···O hydrogen-bond is formed between the amino group on one of the cobalt atoms and the carboxyl group on another cobalt atom such as observed in the  $[\text{Co}(\text{edda})\text{Co}(\text{en})_2(\mu\text{-OH})_2]^{2+}$  ion<sup>4</sup>) in the **T1** complex ion. In the <sup>1</sup>H NMR spectrum of freshly prepared  $\text{D}_2\text{O}$  solution of **T1**, we found one  $\text{NH}$  (ca. 6.5 ppm) and four  $\text{NH}_2$  (ca. 4.8 ppm) protons, while the other amino protons were disappeared. This result shows that the found protons are bonded more tightly to the trinuclear complex ion than the disappeared ones, which suggests the formation of the intramolecular hydrogen-bonds. It is reasonable to propose that the trinuclear structure of **T1** is stabilized by these hydrogen bonds and to expect that its aqueous solution does this not hydrolyzed to mononuclear complexes so easily (the neutral aqueous solution of **T1** showed no spectral change for 5 days).

The aqueous solution of **T1** showed the reversible absorption spectral change with pH (pH range 3 to 6) as described below, although these spectra did not show the time course spectral changes in this pH range. The present complex showed a broad absorption band at 27000—34000  $\text{cm}^{-1}$  in the pH 6 solution. When the spectrum of the solution was measured at pH 3, the  $\epsilon$  value decreased in the 20000—32000  $\text{cm}^{-1}$  region and increased in the 32000—37000  $\text{cm}^{-1}$  region (Fig. 1), which seems to result from the protonation on the  $\mu\text{-O}$  in the  $\text{Co}_3\text{O}_4$  core.

#### References and Notes

- D. F. Ghanotakis and C. F. Yocum, *Annu. Rev. Plant Physiol. Mol. Biol.*, **41**, 255 (1990).
- K. Dimitrou, K. Foltig, W. E. Streib, and G. Christou, *J. Am. Chem. Soc.*, **115**, 6432 (1993); K. Dimitrou, K. Foltig, W. E. Streib, and G. Christou, *J. Chem. Soc., Chem. Commun.*, **1994**, 1385.
- T. Ama, T. Yonemura, H. Kawaguchi, and T. Yasui, *Bull. Chem. Soc. Jpn.*, **67**, 410 (1994); T. Ama, H. Kawaguchi, and T. Yasui, *Bull. Chem. Soc. Jpn.*, **61**, 1141 (1988); T. Ama, H. Kawaguchi, and T. Yasui, *Bull. Chem. Soc. Jpn.*, **60**, 1183 (1987).
- K. Okamoto, H. Hidaka, T. Yasui, *Acta Crystallogr., Sec. C*, **C47**, 2099 (1991).
- Crystallographic data of **T1**: formula  $\text{C}_{12}\text{H}_{40}\text{ClCo}_3\text{N}_6\text{O}_{15}$  ( $[\text{Co}_3(\text{edma})_3(\mu\text{-OH})_3(\mu_3\text{-O})]\text{Cl}\cdot 5\text{H}_2\text{O}$ ), *F.W.* = 720.74, triclinic,  $P\bar{1}$ ,  $a = 9.716(1)$ ,  $b = 10.8146(5)$ ,  $c = 13.215(1)$  Å,  $\alpha = 96.768(5)$ ,  $\beta = 99.30(1)$ ,  $\gamma = 94.581(6)$ °,  $U = 1353.8(2)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_{\text{calcd}} = 1.77$  g  $\text{cm}^{-3}$ ,  $\mu(\text{Mo K}\alpha) = 19.9$   $\text{cm}^{-1}$ , crystal size 0.25 × 0.50 × 0.50 mm, diffractometer Enraf-Nonius CAD4, measured reflections 8286 ( $2^\circ \leq 2\theta \leq 60^\circ$ ), observed reflections 7325, refined parameters 334 (All non-hydrogen atoms are refined anisotropically, and hydrogen atoms are located at calculated positions.),  $R = 0.043$ ,  $R_w = 0.054$ .
- T. Yasui, T. Ama, H. Kawaguchi, K. Okamoto, and J. Hidaka, *Bull. Chem. Soc. Jpn.*, **65**, 1920 (1992).