Tetranuclear Cobalt(III) Complex Having the Cubane Co_4O_4 Core: Synthesis and Structural Analysis of the Complex Containing (2-Pyridylmethyl)glycine

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(Received August 18, 1997; CL-970644)

A tetranuclear cobalt(III) complex with the cubane Co_4O_4 core, $[Co_4(pg)_4(\mu_3\text{-}O)_4]$ (Hpg: *N*-(2-pyridylmethyl)glycine), was prepared and the structure was determined by the X-ray diffraction method. This complex has the four N—H···O intramolecular hydrogen-bonds between the amino group on one of the four cobalt atoms and the carboxyl group on another cobalt atom. Its neutral aqueous solution showed no spectral change for at least 3 days.

The structures of Mn complexes with Mn_4O_4 core are of interest in connection with the photosynthetic water oxidation center (WOC) in green plants.[1] It is expected that the extension of the WOC modeling studies to cobalt(III) complexes with cubane gives important information for understanding the mechanism of the oxidation in WOC.[2 - 7] However, there are few reports concerning the preparation of the complexes with cubane Co_4O_4 core;[2 - 4] at the present stage, a reliable method to prepare more complexes is required.

In the present letter, we report that a tetranuclear cobalt(III) complex with the cubane Co_4O_4 core can be easily prepared in an aqueous solution. The complex has the attractive intramolecular N—H···O hydrogen-bonds as observed in $[Co_3(edma)_3(\mu\text{-}OH)_3(\mu_3\text{-}O)]^+$ (Hedma: ethylenediamine-*N*-acetic acid)[5, 7] and does not have the repulsive intramolecular N—H ↔ H—N interactions as observed in $[Co_3(dpa)_3(\mu\text{-}OH)_3(\mu_3\text{-}O)]^{4+}$ (dpa: bis(2-pyridyl-methyl)amine).[6]

The Co_4O_4 complex with pg (Hpg: *N*-(2-pyridylmethyl)-glycine) was prepared by the method described below. To a solution containing $CoCl_2\cdot 6H_2O$ (2.4 g) and Hpg (2.1 g) in 10 cm^3 of water, 0.2 M (M: mol dm^{-3}) KOH aqueous solution was added till the precipitate of $Co(OH)_2$ appeared. After air was bubbled through the solution for 1 h, PbO_2 (10 g) was added to the solution in order to oxidize the remaining Co(II) to Co(III) and stirred for 1 h. After the precipitate was filtered off, the pH of the filtrate was adjusted to 9 with 0.2 M KOH solution. The solution was allowed to stand at room temperature for 24 h and then charged on an SP-Sephadex column (K^+ form, ϕ 4.7 cm × 5 cm) to remove the cationic complexes. The eluted solution with water was again charged on a QAE-Sephadex column (Cl^- form, ϕ 4.7 cm × 90 cm). The adsorbed band was separated into one major (brown) and seven minor bands by the development with water. The eluate from the major brown band was evaporated to small volume. The brown complex (complex **1**) was obtained by adding acetone to the concentrated solution.[8] A single crystal for the X-ray diffraction method[9] was recrystallized from water by adding acetone.

A perspective view of complex **1** is illustrated in Figure 1. It is clear from the figure that the complex contains the cubane Co_4O_4 core; the Co—μ_3-O distances (μ_3-O: O1 ~ O4) are in the range 1.866 ~ 1.903 Å. The four-membered rings, Co—μ_3-O—Co'—μ_3-O', are approximately planar. The Co—μ_3-O—Co' angles (93.8 ~ 97.3°) and the μ_3-O—Co—μ_3-O' angles (82.5 ~ 85.1°) are larger and smaller than the right angle, respectively.

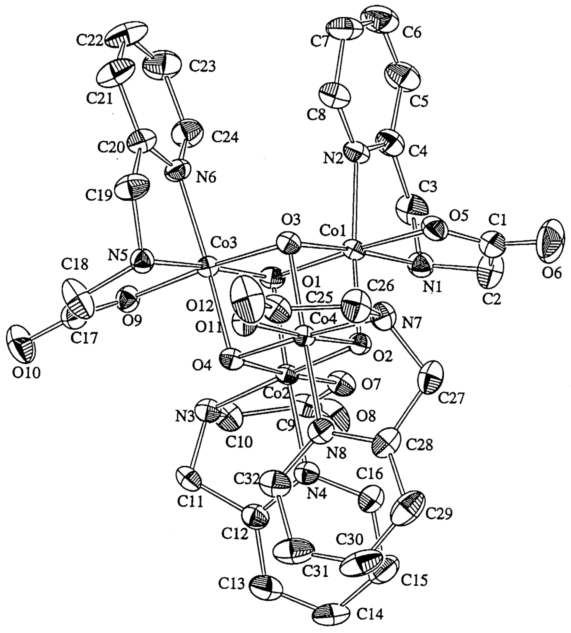

Figure 1. ORTEP drawing of the $[Co_4(pg)_4(\mu_3\text{-}O)_4]$ in complex **1**; selected bond distances(Å) and bond angles(°): Co1—O1 1.898(3), Co1—O2 1.866(3), Co1—O3 1.902(3), Co2—O1 1.902(3), Co2—O2 1.882(3), Co2—O4 1.876(3), Co3—O1 1.890(3), Co3—O3 1.890(3), Co3—O4 1.875(3), Co4—O2 1.887(3), Co4—O3 1.903(3), Co4—O4 1.868(3), Co1—O5 1.939(3), Co1—N1 1.973(4), Co1—N2 1.974(4), Co2—O7 1.957(3), Co2—N3 1.963(4), Co2—N4 1.934(4), Co3—O9 1.943(3), Co3—N5 1.967(4), Co3—N6 1.959(4), Co4—O11 1.941(3), Co4—N7 1.970(4), Co4—N8 1.938(4), O1—Co1—O2 85.1(1), O1—Co1—O3 82.5(1), O2—Co1—O3 84.3(1), O1—Co2—O2 84.6(1), O1—Co2—O4 84.2(1), O2—Co2—O4 83.0(1), O1—Co3—O3 83.0(1), O1—Co3—O4 84.6(1), O3—Co3—O4 84.4(1), O2—Co4—O3 83.7(1), O2—Co4—O4 83.0(1), O3—Co4—O4 84.3(1), Co1—O1—Co2 93.8(1), Co1—O1—Co3 97.3(1), Co2—O1—Co3 94.5(1), Co1—O2—Co2 95.5(1), Co1—O2—Co4 96.5(1), Co2—O2—Co4 96.4(1), Co1—O3—Co3 97.1(1), Co1—O3—Co4 94.8(1), Co3—O3—Co4 94.3(1), Co4—O4—Co3 95.9(1), Co2—O4—Co4 97.2(1), Co3—O4—Oo4 95.9(1).

The Co—Co distances (non-bonding) are in the range 2.77 ~ 2.87 Å. These values are similar to those observed in the

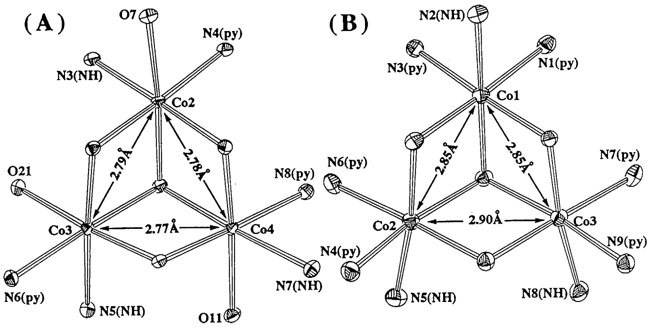

Figure 2. Core structures of the complexes; **A**: complex **1** (Co1 moiety is ommited), and **B**: $[Co_3(dpa)_3(\mu\text{-}OH)_3(\mu_3\text{-}O)]^{4+}$.[6]

$[Co_3(edma)_3(\mu\text{-}OH)_3(\mu_3\text{-}O)]^+$ ions[5 - 7] and the dinuclear $[Co(edda)Co(en)_2(\mu\text{-}OH)_2]^{2+}$ ion[10] which have intramolecular N—H···O hydrogen bonds, but shorter than those observed in $[Co_3(dpa)_3(\mu\text{-}OH)_3(\mu_3\text{-}O)]^{4+}$ (Figure 2),[6] and $[Co_2(en)_4(\mu\text{-}OH)_2]^{4+}$ [11] where the Co—Co distances are elongated by the intramolecular N—H ↔ H—N repulsive interactions. The N1—O7, N3—O9, N5—O11, and N7—O5 distances are in the range 2.78 ~ 2.93 Å; there are four intramolecular N—H···O hydrogen-bonds (the each 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 $[Co_3(edma)_3(\mu\text{-}OH)_3(\mu_3\text{-}O)]^+$ isomers.[5, 7] The N2—N6 and N4—N8 distances (3.09 ~ 3.54 Å) are larger than these N—O distances, but shorter than the N5—N8 distance (N—H ↔ H—N repulsive interaction) in $[Co_3(dpa)_3(\mu\text{-}OH)_3(\mu_3\text{-}O)]^{4+}$ (Figure 2).[6] These results suggest that the interaction between the two coordinating pyridyl-rings is not repulsive.

The ^{13}C NMR spectrum of complex **1** shows only 8 signals in D_2O,[8] suggesting that the ion has a S_4 symmetry axis in the D_2O solution (the four pg ligands are equivalent in D_2O solution). The visible and UV absorption spectrum of complex **1** is shown in Figure 3. The first and second *d-d* absorption bands of complex **1** appeared as vague shoulders overlapped with the strong band at ca. 30000 cm^{-1} arising from the Co—μ_3-O moiety. The complex **1** has higher intensity band at ca. 30000 cm^{-1} than $[Co_3(edma)_3(\mu\text{-}OH)_3(\mu_3\text{-}O)]^+$ and $[Co_3(dpa)_3(\mu\text{-}OH)_3(\mu_3\text{-}O)]^+$ [6, 7] have. The neutral aqueous solution of this complex did not show any spectral change for at least 3 days; i. e., complex **1** was not hydrolyzed so easily in the neutral aqueous solution.

Although we have not yet succeeded to isolate cubane type complexes (having Co_4O_4 cores) using edma, we can easily isolate the Co_4O_4 type complex using pg as mentioned above. These results can be interpreted as below. In the isolated $[Co_3(edma)_3(\mu\text{-}OH)_3(\mu_3\text{-}O)]^+$ isomers, the partial cubane structures are stabilized by the three N—H···O intramolecular hydrogen bonds without the intramolecular N—H ↔ H—N repulsive interactions.[7] In the imaginary $[Co_4(edma)_4(\mu_3\text{-}O)_4]$ isomers, it is impossible to constitute the full cubane structures without the intramolecular N—H ↔ H—N repulsive interactions; at least two N—H ↔ H—N repulsive interactions will appear. Accordingly, on condensing the $[Co(edma)(OH_2)_3]^{2+}$ to polynuclear, the formation ratio of the less stable $[Co_4(edma)_4(\mu_3\text{-}O)_4]^+$ isomers is much less than those of the more stable $[Co_3(edma)_3(\mu\text{-}OH)_3(\mu_3\text{-}O)]^+$ isomers. On the other hand, in the present isomer of $[Co_4(pg)_4(\mu_3\text{-}O)_4]$, the full cubane structure is stabilized by the four N—H···O intramolecular hydrogen bonds and two pyridyl-pyridyl interactions, which are not repulsive, instead of the N—H ↔ H—N interaction in the edma complexes, therefore, the formation ratio of the $[Co_4(pg)_4(\mu_3\text{-}O)_4]$ is high enough to be isolated.

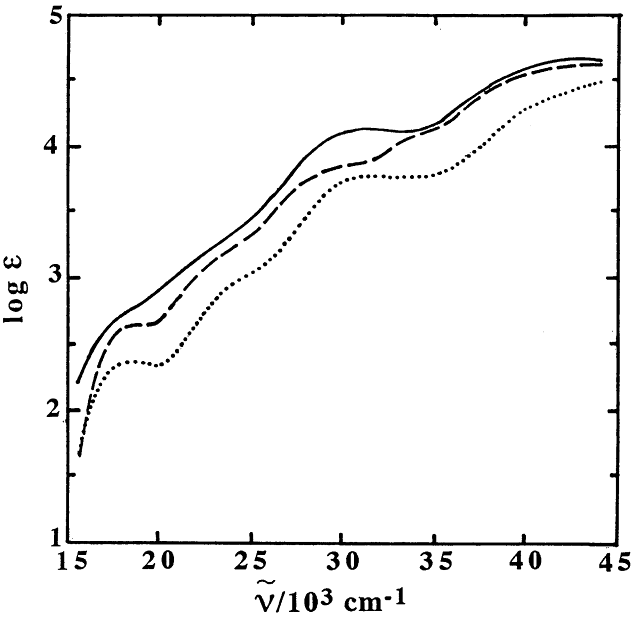

Figure 3. Visible and UV absorption spectra of complex **1** (———), $[Co_3(edma)_3(\mu\text{-}OH)_3(\mu_3\text{-}O)]^+$ (··············), and $[Co_3(dpa)_3(\mu\text{-}OH)_3(\mu_3\text{-}O)]^{4+}$ (— — — —). (The ε values are given in $mol^{-1}\ dm^3\ cm^{-1}$.

References and Notes

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8 Anal. Found: C, 34.25; H, 4.53; N, 9.94%. Calcd for $[Co_4(pg)_4(\mu_3\text{-}O)_4]\cdot 7.5H_2O$ ($C_{32}H_{51}N_8O_{19.5}Co_4$): C, 34.96; H, 4.69; N, 10.23%. ^{13}C NMR in D_2O: δ 55.92, 59.58, 123.86, 124.96, 139.99, 150.64, 162.79, 185.03.

9 Crystallographic data of complex **1**: formula $C_{32}H_{51}N_8O_{19.5}Co_4$, F.W. = 1095.53, triclinic, P $\bar{1}$ (No. 2), a = 14.189(2), b = 15.967(2), c = 11.014(1)Å, α = 103.038(10)°, β = 112.158(10)°, γ = 93.85(1)°, V = 2219.2(1)$Å^3$, Z = 2, D_{calc} = 1.64 g cm^{-3}, Mo K_α (graphite monochromated), l = 0.71069Å, crystal size 0.20 × 0.25 × 0.35mm, diffractometer Rigaku AFC7S, measured reflections 10223 (unique), diffraction measurement method ω - 2θ (2θ $_{max}$ = 55.0°), observed reflections 7824 (I > 1.5s(I)), refined parameters 585 (All non-hydrogen atoms are refined anisotropically, and hydrogen atoms are located at calculated positions.), R = 0.057, R_w = 0.079.

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