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Trinuclear Complexes Containing Incomplete Cubane $Co^{III}{}_3O_4$ Cores. Structures of the Isomers of the *N*-(2-Pyridylmethyl)glycinato Complex

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Two isomers of *N*-(2-pyridylmethyl)glycinatocobalt(III) complexes containing incomplete cubane Co_3O_4 cores, $[Co_3(pg)_3(\mu_3\text{-}O)(\mu\text{-}OH)_3]^+$, were isolated and their structures were determined by the X-ray diffraction method. While the trinuclear structure of one of the two isomers was stabilized by three inter-ligand N–H···O hydrogen bonds, that of the other was stabilized by two N–H···O hydrogen bonds and one inter-ligand pyridyl–pyridyl stacking interaction.

In the previous works, we have reported that some $[Co_3(L)_3(\mu_3\text{-}O)(\mu\text{-}OH)_3]$-type complexes that have incomplete cubane Co_3O_4 cores could be prepared by the dehydro-condensation of $[Co(L)(H_2O)_3]$-type complexes in basic aqueous solutions.[1–5] In the $[Co_3(edma)_3(\mu_3\text{-}O)(\mu\text{-}OH)_3]^+$ (Hedma: *N*-(aminoethyl)glycine) complex ion, thirty-eight geometrical isomers are anticipated; however, only four isomers were isolated by the condensation of $[Co(edma)(OH_2)_3]^{2+}$. As each of the four-isolated isomers has three N–H···O inter-ligand (intramolecular) hydrogen bonds, it was pointed out that the three attractive inter-ligand interactions such as the three inter-ligand hydrogen bonds are one of the important factors in stabilizing the incomplete cubane structures.[4]

N-(2-Pyridylmethyl)glycine (Hpg) is the same type of N–N–O tridentate as edma. However, pg is distinct from edma in the following two points: (1) A pyridyl-N in pg cannot form hydrogen bonds with carboxyl-O, while amino-N in edma can; (2) a pyridyl-ring in a $[Co_3(pg)_3(\mu_3\text{-}O)(\mu\text{-}OH)_3]^+$ ion contributes to stabilize the incomplete cubane structure by the attractive interaction caused by the stacking with the neighboring pyridyl-ring in the complex ion (pyridyl–pyridyl stacking), while the N–H↔H–N repulsive interaction destabilizes the incomplete cubane structure in the corresponding isomer of $[Co_3(edma)_3(\mu_3\text{-}O)(\mu\text{-}OH)_3]^+$. Accordingly, it is expected that some isomers that were not isolated in $[Co_3(edma)_3(\mu_3\text{-}O)(\mu\text{-}OH)_3]^+$ may be obtained in $[Co_3(pg)_3(\mu_3\text{-}O)(\mu\text{-}OH)_3]^+$, even though some isomers isolated in the former may not be isolated in the latter.

As described in the experimental section, we have succeeded in isolating two of the thirty-eight geometrical isomers of $[Co_3(pg)_3(\mu_3\text{-}O)(\mu\text{-}OH)_3]^+$ and determining their structures by the single-crystal X-ray diffraction method. In the following, the characteristics and the structures of the isolated isomers will be described.

The ORTEP drawing of the $[Co_3(pg)_3(\mu_3\text{-}O)(\mu\text{-}OH)_3]^+$ ion in the isomer **2** is illustrated in Fig. 1. The complex ion contains an incomplete cubane Co_3O_4 core and each cobalt atom in the cation is octahedrally surrounded by the amino-N, pyridyl-N, carboxyl-O in the coordinated pg, two μ-O, and one μ_3-O. In the isomer **2**, the three pyridyl-N occupy a position *trans* to μ_3-O, and there is a C_3-axis on the central μ_3-O perpendicular to the Co–Co–Co plane. The Co–μ_3-O and Co–μ-O distances are 1.89 and 1.91 Å (av.), respectively; these values agree well with the corresponding ones in the $[Co_3(edma)_3(\mu_3\text{-}O)(\mu\text{-}OH)_3]^+$ ion. The four-membered ring, μ_3-O–Co–μ-O–Co′, is approximately planar. However, the three four-membered rings are not regular squares; the Co–O–Co angles are 96.4–97.5° and O–Co–O ones are 82.9–83.1°. These values also agree with the corresponding ones in the $[Co_3(edma)_3(\mu_3\text{-}O)(\mu\text{-}OH)_3]^+$ isomers. The bond distances and angles in the coordinated pg ligands are similar to those of $[Co_4(pg)_4(\mu_3\text{-}O)_4]$.[6]

Replacement of the three 2-pyridylmethyl groups of three pg's in the isomer **2** with three aminoethyl groups gives the compounds corresponding to the **T3** isomer[3,4] of $[Co_3(edma)_3(\mu_3\text{-}O)(\mu\text{-}OH)_3]^+$, which has already been reported. In the isomer **2**, there are three inter-ligand (intra-molecular) N–H···O hydrogen bonds (N1*–O3 etc.) such as are observed in the **T3** isomer. These three attractive interactions help to stabilize the incomplete cubane Co_3O_4 structure, as described in the references.[4]

The $^{13}C\{^1H\}$ NMR spectrum of the complex shows only 8 signals (57.57, 60.93, 123.69, 125.68, 141.44, 149.89, 163.30, and 185.64 ppm) in a D_2O solution, suggesting that the ion retains C_3 symmetry in the D_2O solution (the three pg ligands in the same $[Co_3(pg)_3(\mu_3\text{-}O)(\mu\text{-}OH)_3]^+$ ion are equivalent in the D_2O solution).

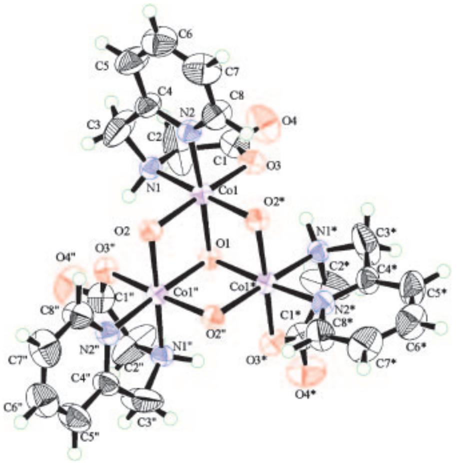

Fig. 1. ORTEP drawing of $[Co_3(pg)_3(\mu_3\text{-}O)(\mu\text{-}OH)_3]^+$ in isomer **2**. Selected bond distances (Å) and angles (°) are as follows: Co1–O1, 1.893(2); Co1–O2, 1.905(3); Co1–O2*, 1.912(3); Co1–O3, 1.900(3); Co1–N1, 1.944(4); Co1–N2, 1.922(4); O1–Co1–O2, 83.1(1); O1–Co1–O2*, 82.9(1); Co1–O1–Co1*, 97.5(2); Co1–O2–Co1″, 96.4(1).

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There are two crystallographically independent $[Co_3(pg)_3(\mu_3\text{-}O)(\mu\text{-}OH)_3]^+$ fragments whose geometrical structures resemble each other in the unit cell of the isomer **1**. We describe only the fragment containing Co1–Co3 atoms in the following (Fig. 2); however, similar discussion is possible for the other fragments containing Co4–Co6 atoms (see Supporting Information).

It is clear from Fig. 2 that the coordinations around cobalt(III) atoms are roughly octahedral and that this complex contains an incomplete cubane Co_3O_4 core. That is, the three Co–μ_3-O distances are in the range 1.88–1.89 Å, showing that the O1 atom bridges three Co atoms. The Co–μ-O distances are in the range 1.89–1.91 Å. These Co–O values agree well with the corresponding ones in the $[Co_3(edma)_3(\mu_3\text{-}O)(\mu\text{-}OH)_3]^+$ isomers. The three four-membered rings, O1–Co1–O2–Co2, O1–Co2–O3–Co3, and O1–Co3–O4–Co1, are approximately planar and the Co–O–Co and O–Co–O angles are greater than 90° and smaller than 90°, respectively. These values also agree with the corresponding ones in the **T1**–**T3** isomers[1,3] of $[Co_3(edma)_3(\mu_3\text{-}O)(\mu\text{-}OH)_3]^+$.

There are three inter-ligand attractive interactions in the $[Co_3(pg)_3(\mu_3\text{-}O)(\mu\text{-}OH)_3]^+$ fragment appearing in Fig. 2; there are two inter-ligand (intra-molecular) N–H⋯O hydrogen bonds (N1–O9 and N3–O5) such as those observed in the isomer **2** of the $[Co_3(pg)_3(\mu_3\text{-}O)(\mu\text{-}OH)_3]^+$ ion, and one inter-ligand pyridyl–pyridyl stacking interaction. These three attractive interactions help to stabilize the incomplete cubane Co_3O_4 structure, as described in the references.[4] On the other hand, the corresponding isomer of $[Co_3(edma)_3(\mu_3\text{-}O)(\mu\text{-}OH)_3]^+$, which is given by replacing the three 2-pyridylmethyl groups on **2** with three aminoethyl groups, will have two inter-ligand N–H⋯O hydrogen bonds and one repulsive $NH_2 \leftrightarrow H_2N$ interaction (instead of one attractive pyridyl–pyridyl stacking interaction in $[Co_3(pg)_3(\mu_3\text{-}O)(\mu\text{-}OH)_3]^+$). Accordingly, the unstabilized isomer of $[Co_3(edma)_3(\mu_3\text{-}O)(\mu\text{-}OH)_3]$ corresponding to the isomers **1** of $[Co_3(pg)_3(\mu_3\text{-}O)(\mu\text{-}OH)_3]$ has not been isolated yet, while the isomer of $[Co_3(edma)_3(\mu_3\text{-}O)(\mu\text{-}OH)_3]^+$ (**T3**)[3,4] corresponding to the isomer **2** of $[Co_3(pg)_3(\mu_3\text{-}O)(\mu\text{-}OH)_3]$, which has three inter-ligand N–H⋯O hydrogen bonds, has been isolated.

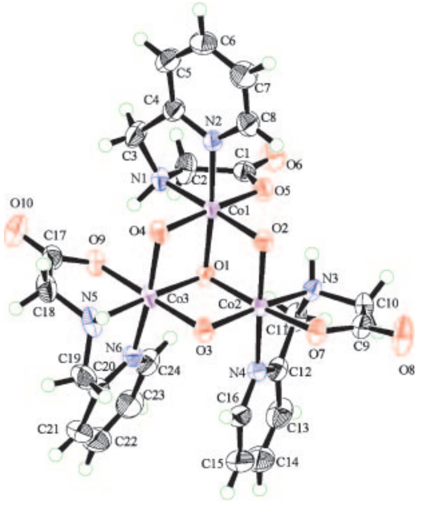

Fig. 2. ORTEP drawing of one of the two $[Co_3(pg)_3(\mu_3\text{-}O)(\mu\text{-}OH)_3]^+$ fragments in isomer **1**. Selected bond distances (Å) and angles (°) are as follows: Co1–O1, 1.890(3); Co2–O1, 1.881(3); Co3–O1, 1.884(3); Co1–O2, 1.912(3); Co1–O4, 1.905(3); Co2–O2, 1.911(3); Co2–O3, 1.915(3); Co3–O3, 1.913(3); Co3–O4, 1.899(3); Co1–O5, 1.902(3); Co1–N1, 1.938(4); Co1–N2, 1.942(4); Co2–O7, 1.936(3); Co2–N3, 1.946(4); Co2–N4, 1.928(4); Co3–O9, 1.913(3); Co3–N5, 1.977(4); Co3–N6, 1.925(4); O1–Co1–O2, 83.8(1); O1–Co1–O4, 84.2(1); O1–Co2–O2, 84.1(1); O1–Co2–O3, 82.7(1); O1–Co3–O3, 82.7(1); O1–Co3–O4, 84.6(1); Co1–O1–Co2, 96.8(1); Co1–O1–Co3, 95.9(1); Co2–O1–Co3, 98.3(1); Co1–O2–Co2, 95.0(1); Co2–O3–Co3, 96.2(1); Co1–O4–Co3, 94.9(2).

The pyridyl-ring on Co1, which does not participate in the above-mentioned intra-molecular pyridyl–pyridyl stacking, forms another inter-molecular pyridyl–pyridyl stacking interaction with that on Co4, which belongs to the neighboring $[Co_3(pg)_3(\mu_3\text{-}O)(\mu\text{-}OH)_3]^+$ fragment (see Supporting Information).

The absorption spectrum of **1** in an aqueous solution is illustrated in Fig. 3, together with that in a 0.1 mol dm^{-3} HCl solution. The spectrum of **1** showed a characteristic absorption band (shoulder) arising from the Co(μ-OH)(μ_3-O)Co moiety at 320–380 nm in the aqueous solution.[3] The aqueous solution of **1** showed a reversible absorption spectral change with pH: when the spectrum was measured in 0.1 mol dm^{-3} HCl, the ε value decreased around the 350 nm region and increased around the 300 nm region (Fig. 3), which seems to result from the protonation on μ_3-O in the Co_3O_4 core.[3] The UV absorption spectra of the isomer **2** are very similar to those of the isomer **1** in both aqueous and 0.1 mol dm^{-3} HCl solutions.

In summary, two (isomers **1** and **2**) of the thirty-eight isomers of $[Co_3(pg)_3(\mu_3\text{-}O)(\mu\text{-}OH)_3]^+$ were isolated and their structures were determined. The isomer **1** has three attractive inter-ligand interactions (one pyridyl–pyridyl stacking and two N–H⋯O hydrogen bonds) and the isomer **2** has three inter-ligand N–H⋯O hydrogen bonds. In the isomer **2**, the corresponding isomer of $[Co_3(edma)_3(\mu_3\text{-}O)(\mu\text{-}OH)_3]^+$ (**T3**)[3,4] has been isolated. However, in the isomer **1**, the corresponding isomer of edma, which has one inter-ligand repulsive $NH_2 \leftrightarrow H_2N$ interaction, has not been isolated yet. The present

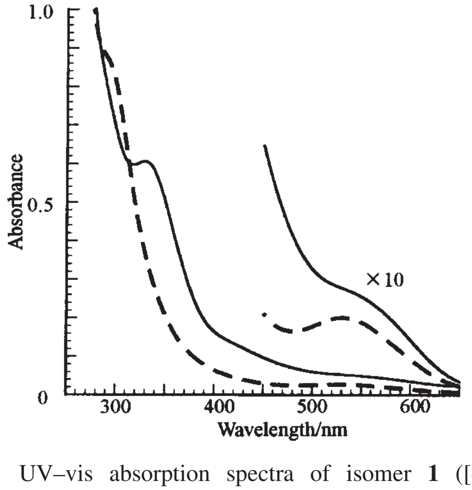

Fig. 3. UV–vis absorption spectra of isomer **1** ([complex] = 7.31 × 10^{-4} mol dm^{-3}; cell length: 1 cm); (—): in H_2O, and (- - -): in 0.1 mol dm^{-3} HCl solution.

results suggest that isomers that have three attractive interligand interactions are preferentially formed during the dehydro-condensation of $[Co(pg)(H_2O)_3]^+$ to $[Co_3(pg)_3(\mu_3\text{-}O)(\mu\text{-}OH)_3]^+$ in a basic aqueous solution.

Experimental

Preparation of the Complexes. To a solution containing 2.4 g of $CoCl_2 \cdot 6H_2O$ in 50 cm^3 of water was added an aqueous solution containing 1.94 g of pgOEt (ethyl *N*-(2-pyridylmethyl)glycinate: purchased from Tokyo Kasei Kogyo Co., Ltd). To this mixture was added a 2 $mol\,dm^{-3}$ KOH aqueous solution until the precipitation of $Co(OH)_2$ appeared. Air was bubbled through the solution for approximately 8 h, while the pH was adjusted to about 8. The solution was heated for an additional 1 h in a water bath at 60 °C, and then filtered. The filtrate was poured into an SP-Sephadex C-25 column (K^+ form, ϕ 9.0 cm × 15 cm) and the column was swept with water in order to discard anionic and neutral complexes. Having been developed with a 0.1 $mol\,dm^{-3}$ KCl aqueous solution, the adsorbed brown band was transferred to another SP-Sephadex C-25 column (K^+ form, ϕ 4.7 cm × 90 cm). By further development with a 0.1 $mol\,dm^{-3}$ KCl solution, this band separated into four bands. Each eluate from the four bands was concentrated to a small volume with a rotary evaporator, followed by a large amount of methanol being added to the solution, and then the deposited KCl was filtered off. A crude complex was obtained by the addition of diethyl ether to the methanolic solution, which was recrystallized from warm water. From the second and forth elution, we obtained the isomers **1** and **2** as chloride crystals, which are both complexes with incomplete cubane Co_3O_4 cores. The complex isolated from the first elution was dinuclear cobalt(III) complex and that from the third was mononuclear cobalt(III) complex. Anal. Calcd for $C_{24}H_{40}N_6O_{15}Co_3Cl_1$ (**1**: $[Co_3(pg)_3(\mu_3\text{-}O)(\mu\text{-}OH)_3]Cl \cdot 5H_2O$): C, 33.33; H, 4.66; N, 9.72%. Found: C, 33.45; H, 4.74; N, 9.82%. Calcd for $C_{24}H_{39}N_6O_{14.5}Co_3Cl_1$ (**2**: $[Co_3(pg)_3(\mu_3\text{-}O)(\mu\text{-}OH)_3]Cl \cdot 4.5H_2O$): C, 33.68; H, 4.59; N, 9.82%. Found: C, 33.49; H, 4.72; N, 9.60%.

X-ray Crystallography. Crystals of **1** and **2** suitable for X-ray diffraction study were obtained by recrystallization from water/acetone. Each was mounted on a glass needle. All measurements were made on a Rigaku AFC7S diffractometer with graphite monochromated Mo Kα radiation. The structures of the isomers **1** and **2** were solved by direct methods and expanded using Fourier techniques.[7] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined.

Crystal data for **1**: $C_{24}H_{40}N_6O_{15}Co_3Cl$, fw 864.86, triclinic, space group $P\bar{1}$(#2), $a = 20.560(2)$, $b = 14.095(2)$, $c = 14.147(2)$ Å, $\alpha = 60.647(9)°$, $\beta = 109.836(9)°$, $\gamma = 102.14(1)°$, $V = 3356.7(7)$ Å^3, $Z = 4$, $D_{calcd} = 1.71\,g\,cm^{-3}$, crystal dimensions: $0.4 \times 0.4 \times 0.4\,mm^3$. Total reflections (Mo Kα radiation, ω scan technique, $2\theta_{max} = 55.0°$): 15407 unique diffrection with $I > 0\sigma(I)$: 13851. Final R and R_w values, based on F^2, were 0.092 and 0.152, respectively. Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition number CCDC-290356 for the isomer **1**. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Crystal data for **2**: $C_{24}H_{45}N_6O_{17.5}Co_3Cl$, fw 909.90, rhombohedral hexagonal, space group $R\bar{3}c$ (#167), $a = 19.39(1)$, $c = 32.38(2)$ Å, $V = 10538(13)$ Å^3, $Z = 12$, $D_{calcd} = 1.72\,g\,cm^{-3}$, crystal dimensions: $0.5 \times 0.4 \times 0.2\,mm^3$. Total reflections (Mo Kα radiation, ω–2θ scan technique, $2\theta_{max} = 55.0°$): 5352 unique diffrection with $I > 0\sigma(I)$: 4495. Final R and R_w values, based on F^2, were 0.106 and 0.151, respectively. Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition number CCDC-290357 for the isomer **2**.

Supporting Information

An ORTEP drawing including one of the $[Co_3(pg)_3(\mu_3\text{-}O)(\mu\text{-}OH)_3]^+$ fragments containing Co4–Co6 atoms in the isomer **1** and stacking of the pyridyl-ring (on Co4) on the fragment with the pyridyl-ring (on Co1) on the other $[Co_3(pg)_3(\mu_3\text{-}O)(\mu\text{-}OH)_3]^+$ fragment containing Co1–Co3 atoms. This material is available free of charge on the web at http://www.csj.jp/journals/bcsj/.

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