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Cobalt(III) complexes containing incomplete C_3O_4 or complete Co_4O_4 cubane core

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Abstract

The modeling study of the photosynthetic water oxidation center has been extended to the cobalt(III) complexes with incomplete or complete cubane core. In the preparation of the

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$[Co_3(N–N–O)_3(\mu\text{-}OH)_3(\mu_3\text{-}O)]^+$ complexes from $[Co(N–N–O)(H_2O)_3]^{2+}$, some isomers of the trinuclear complexes with three N–H···O hydrogen bonds are stereoselectively formed, as shown in the following: in the 38 possible geometrical isomers of $[Co_3(edma)_3(\mu\text{-}OH)_3(\mu_3\text{-}O)]^+$ (edma: ethylenediamine-*N*-acetato(1-)), each of the isolated four isomers has the three N–H···O hydrogen bonds, which was isolated. The tetranuclear cobalt(III) complex with Co_4O_4 core was not isolated when using edma as ligand, but isolated when using pg (pg = 2-pyridylmethylglycinato(1-)); the X-ray data shows that the Co_4O_4 structure of $[Co_4(pg)_4(\mu_3\text{-}O)_4]$ was stabilized by four N–H···O hydrogen bonds and two pairs of pyridyl–pyridyl attractive interactions. In the trinuclear L-histidinato complex, only one isomer has three hydrogen bonds, which was isolated. However, using D,L-histidine instead of L-histidine, the major products isolated were dinuclear cobalt(III) complexes.

Keywords: Cobalt complex; Incomplete cubane core; Complete cubane core

1. Introduction

The oxygen evolution photosystem has long been of great interest for its biological functions. The oxidation of water to O_2 is a characteristic reaction associated with photosynthesis in green plants. The oxo-bridged di-, tri-, and tetranuclear manganese complexes are of considerable current interest as they are thought to serve as a good synthetic models for the active site of the oxygen-evolving complex (OEC) of photosystem II (PS II) [1–7]. However, the arrangement of metal ions of the photosynthetic water oxidation center (WOC) is still obscure.

Recently, the modeling study of the WOC has been extended to cobalt(III) complexes with cubane and incomplete cubane cores [8–15]. The cobalt(III) complexes are suitable to study the structure in the solution and have some favorable characters as model complexes of WOC; these are described below. (1) Almost all complexes of cobalt(III) are inert: the structure of the inert complex in the crystalline form is retained for a long time after it is dissolved in solution, while it is frequently observed in labile complexes that the structure of the main isomer in solution is different from that in the crystal. (2) Almost all cobalt(III) complexes are diamagnetic: the structures of the diamagnetic complexes can be determined in solution by NMR in the same way as is used for organic compounds. (3) Co(III) complexes are easily reduced to Co(II) in a manner similar to the reduction of Mn(IV) to Mn(III) or Mn(II). (4) Both cobalt(III) and Mn(IV) complexes favor octahedral geometry and have similar ionic radii. (5) Many Co(II) complexes display the uptake of O_2, i.e., the inverse reaction of the O_2 evolution which remind us of the OEC.

Springborg has already published an excellent review concerning hydroxo-bridged complexes of Cr(III), Co(III), Rh(III), and Ir(III) [16]; however, the description of complexes containing incomplete cubane $Co^{III}_3O_4$ cores and complete $Co^{III}_4O_4$ cores is very brief. Accordingly, in this review, we describe cobalt(III) complexes containing cubane and incomplete cubane cores, especially from the view

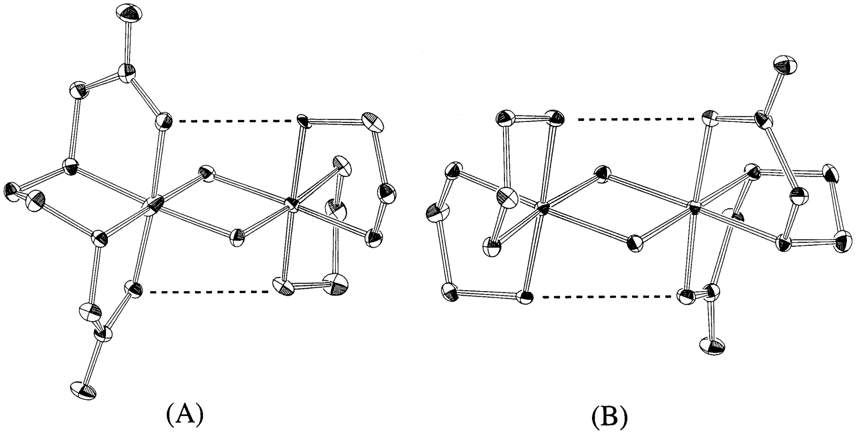

Fig. 1. Perspective views of the two isomers isolated for the $[Co(en)_2Co(edda)(\mu\text{-}OH)_2]^{2+}$ ions.

point of structure of the complexes and the ligand–ligand interactions assisting the formation of the cubane and incomplete cubane cores.

2. Inter-ligands hydrogen bonds in di-μ-hydroxodicobalt(III) complexes

The isomers of di-μ-hydroxodicobalt(III) complexes, $[Co_2(N4)(edda)(\mu\text{-}OH)_2]^{2+}$ ($N4 = (en)_2$ or $(NH_3)_4$) were prepared in basic aqueous solutions by the dehydro-condensation between $[Co(N4)(H_2O)_2]^{3+}$ and $[Co(edda)(H_2O)_2]^{+}$ [17–20]. Although some isomers are possible in these complexes, all of the isomers isolated have two intramolecular N–H···O hydrogen bonds (Figs. 1 and 2). These results suggest that the isomers which have the two intramolecular hydrogen bonds are more preferably formed under the basic aqueous condition than the isomers which

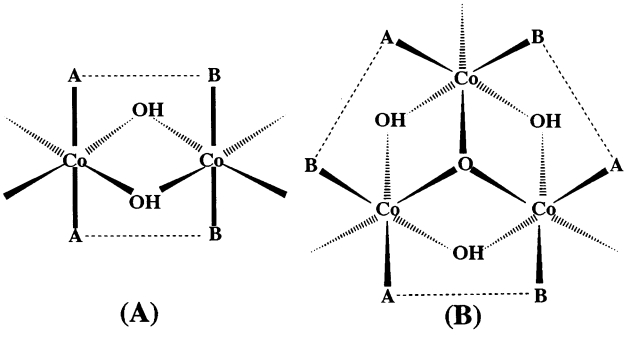

Fig. 2. The coordination sites, A and B, which have interactions with each other. (A) For the complex having the $Co_2(\mu\text{-}OH)_2$ moiety; and (B) for the complex having the $Co_3(\mu\text{-}OH)_3(\mu_3\text{-}O)$ moiety (the Co_3O_4 imcomplete cubane core). (See Tables 1 and 2.)

have one and no hydrogen bonds and that the isomers having the two hydrogen bonds are more stable than the other isomers. Similar results were reported for $[Co(en)_2Co(nta)(\mu\text{-}OH)_2]^+$ [18], $[Co(NH_3)_4Co(nta)(\mu\text{-}OH)_2]^+$ [16], $[Co(en)(gly)Co(en)(gly)(\mu\text{-}OH)_2]^+$ [21,22], $[Co(edda)Co(en)(gly)(\mu\text{-}OH)_2]^+$ [23], $[Co(\beta\text{-}ad)Co(en)(gly)(\mu\text{-}OH)_2]$ [24], $[Co_2(car)_2(\mu\text{-}OH)_2]$ [24], and $[Co_2(dtma)_2(\mu\text{-}OH)_2]^{2+}$ [25] (nta: nitrilotriacetato(3-); gly: glycinato(1-); β-ad: β-alanyl-L-aspartato(3-); car: β-alanyl-L-histidinato(2-); and dtma: diethylenetriamine-*N′*-acetato(1-)). However, it is not impossible to prepare the di-μ-hydroxodicobalt(III) complexes without two hydrogen bonds; for example, we can easily prepare $[Co_2(en)_4(\mu\text{-}OH)_2]^{4+}$ [26,27] and $[Co_2(NH_3)_8(\mu\text{-}OH)_2]^{4+}$ [28,29] which are very famous classical complexes. These results are interrelated for the following reasons. In such a case when the formation of the isomer stabilized by hydrogen bonds is not anticipated, the isomer without hydrogen bond may be formed. On the other hand, in the case when the formation of the isomer with two hydrogen bonds is anticipated, isomers with two hydrogen bonds are preferably formed.

The above mentioned difference was confirmed structurally in the X-ray crystallographic data of di-μ-hydroxodicobalt(III) complexes. The Co–Co distances of the complexes with the two hydrogen bonds are shorter than those with N–H···H–N interactions. In addition, the A–B distance (Fig. 2) of $\underline{N}$–H···$\underline{O}$ is much shorter than that of $\underline{N}$–H···H–$\underline{N}$ (Table 1).

The ionic radius of Co(III) is smaller than those of Co(II) and Cr(III). Accordingly, the energy difference between stabilization by the N–H···O hydrogen bonds and destabilization by the N–H···H–N repulsive interactions is less serious in Co(II) and Cr(III) than in Co(III). However, we can find results in di-μ-hydroxodichromium(III) complexes similar to those observed in di-μ-hydroxodicobalt(III) [29–31].

3. Cobalt(III) complexes with an incomplete cubane core

3.1. *Edma–cobalt(III) complexes with an incomplete cubane core. Importance of the inter-ligand hydrogen bonds*

The $[Co_3(edma)_3(\mu\text{-}OH)_3(\mu_3\text{-}O)]^+$ complex (edma: ethylenediamine-*N*-acetato-(1-)) was prepared in the following way. After a solution containing $[Co(edma)(H_2O)_3]^{2+}$ was obtained by the acid-hydrolysis of $[Co(edma)(CO_3)(HCO_3)]^-$ by $HClO_4$, the solution was basified to pH 8.5 in order to condense the three mononuclear edma complex ions into a partial cubane ion with edma. This solution was then chromatographed on an SP-Sephadex column; four isomers of $[Co_3(edma)_3(\mu\text{-}OH)_3(\mu_3\text{-}O)]^+$ were confirmed on the chromatogram [11,14,33].

The geometrical structures of these four isomers of $[Co_3(edma)_3(\mu\text{-}OH)_3(\mu_3\text{-}O)]^+$ have been revealed by X-ray crystallography (Fig. 3). In these isomers, the $\underline{N}$–H···$\underline{O}$ distances are observed in the range of 2.88–2.94 Å; these values are nearly equal to the $\underline{N}$–H···$\underline{O}$ distances and shorter than the $\underline{N}$–H···H–$\underline{N}$ distance observed in the di-μ-hydroxodicobalt(III) complexes (Table 2). The Co–Co distances of $[Co_3(edma)_3(\mu\text{-}OH)_3(\mu_3\text{-}O)]^+$ isomers with the three hydrogen bonds are also nearly

Table 1
Selected bond angles, atomic distances, and dihedral angles for di-μ-hydroxo complexes[a]

Complexes	Bond angle (°)			Atomic distance (Å)			Dihedral angle (°)	Reference
	M–μ-O–M	μ-O–M–μ-O	M–μ-O	M–M	μ-O–μ-O[b]	A–B[b,c]	Co–μ-O-μ-O-Co[b]	
$[Cr_2(NH_3)_8(\mu\text{-}OH)_2]^{4+}$	99.9	80.1	1.97	3.02	2.54	3.25[d]	180.0	[30]
$[Cr_2(en)_4(\mu\text{-}OH)_2]^{4+}$	103.4	76.6	1.95	3.06	2.41	3.56[d]	180.0	[31]
$[Cr_2(\text{L-pro})_4(\mu\text{-}OH)_2]$	100.0	80.0	1.95	2.98	2.50	3.17[e]	178.7	[32]
$[Co_2(NH_3)_8(\mu\text{-}OH)_2]^{4+}$	100.1	79.9	1.91	2.93	2.49	3.14[d]	180.0	[28]
$[Co_2(en)_4(\mu\text{-}OH)_2]^{4+}$	100.1	79.8	1.93	2.95	2.47	3.30[d]	180.0	[26]
$[Co(en)_2Co(edda)(\mu\text{-}OH)_2]^{2+}$								
$((+)580^{CD}, \Lambda_{en},\Lambda_{edda})$	96.8	83.2	1.91	2.86	2.54	2.98[e]	179.3	[19]
$((+)565^{CD}, \Delta_{en},\Lambda_{edda})$	97.5	82.5	1.92	2.88	2.52	3.00[e]	178.2	[20]
$[Co(en)(gly)Co(en)(gly)(\mu\text{-}OH)_2]^{2+}$ (*meso*)	97.4	82.6	1.91	2.87	2.52	2.97[e]	180.0	[21]

[a] The corresponding values in the reference were averaged.

[b] The values were calculated from the atomic coordinations and the cell parameters in the references.

[c] See Fig. 2.

[d] Values for the $\underline{\mathrm{N}}$–H···H–$\underline{\mathrm{N}}$ distances.

[e] Values for the $\underline{\mathrm{N}}$–H···$\underline{\mathrm{O}}$ distances.

Table 2
Selected bond angles, atomic distances, and dihedral angles of the cobalt(III) complexes with an incomplete cubane core[a]

Complex	Bond angle (°)		Atomic distance (Å)				Dihedral angle (°)	Reference
	$M–\mu_3$-O–M M–μ-O–M	μ_3-O–M-μ–O	$M–\mu_3$-O M-μ-O	M–M	μ_3-O–μ–O[b]	A–B[b,c]	Co–μ_3-O-μ-O-Co[b]	
$[Co_3(\mu\text{-}OH)_3(\mu_3\text{-}O)(edma)_3]^+$								
T0	96.7	82.3	1.93	2.89	2.52	2.94[d]	177.5	[33]
	98.7		1.90					
T1	96.4	84.0	1.90	2.84	2.54	2.88[d]	176.2	[11]
	95.4		1.91					
T2	95.6	83.5	1.91	2.84	2.54	2.92[d]	176.9	[14]
	96.6		1.90					
T3	95.8	84.3	1.90	2.82	2.56	2.93[d]	174.5	[14]
	95.3		1.91					
$[Co_3(\mu\text{-}OH)_3(\mu_3\text{-}O)(\text{L-}his)_3]^+$								
	97.1	83.6	1.89	2.83	2.53	2.88[d]	174.7	[35]
	98.7		1.90					
$[Co_3(\mu\text{-}OH)_3(\mu_3\text{-}O)(dpa)_3]^{4+}$								
	96.1	83.1	1.93	2.85[g]	2.54	3.09[e]	175.4	[12]
	97.4		1.91	2.90[h]		3.58[f]		

[a] The corresponding values in the reference were averaged.

[b] The values were calculated from the atomic coordinations and the cell parameters in the references.

[c] See Fig. 2.

[d] Distances for N–H···O.

[e] Distances for $N_{py}\cdots N_{py}$.

[f] Distances for N–H···H–N.

[g] Average value for Co1–Co2 and Co1–Co3 distances (see Fig. 5).

[h] Value for Co2–Co3 distance (see Fig. 5).

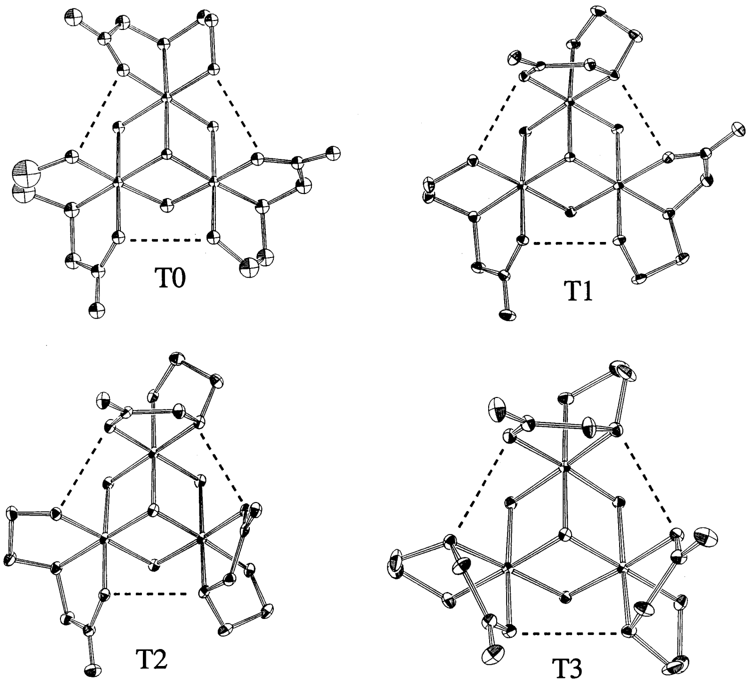

Fig. 3. Perspective views of the four isomers isolated for the $[Co_3(edma)_3(\mu\text{-}OH)_3(\mu_3\text{-}O)]^+$ ions.

equal to those of the di-μ-hydroxodicobalt(III) complexes with N–H···O hydrogen bonds. The Co–μ_3-O distances are in the range 1.90–1.93 Å; these values are slightly shorter than those of Co–μ-OH. The dihedral angles of Co–μ–OH-μ_3-O–Co in these isomers are about 180°; that is, the Co–μ–O-μ_3-O–Co is almost coplanar.

The ^{13}C-NMR data summarized in Table 3 show that the three edma ligands in the T0 or T3 are equivalent; the T0 and T3 isomers have C_3-symmetry in the D_2O

Table 3
^{13}C-NMR chemical shifts of the isomers of $[Co_3(\mu\text{-}OH)_3(\mu_3\text{-}O)(edma)_3]^+$

Isomers	Chemical shifts			
	$\underline{C}OO^-$ (δ ppm^{-1})		$-\underline{C}H_2-$ (δ ppm^{-1})	
T0	185.67	43.34	54.50	56.09
T1	185.24	41.51	54.72	55.78[a]
	185.76	42.37	55.08	–
	185.85	43.19	55.20	56.19
T2	185.61	41.24	54.69	55.75[a]
	185.91	41.61	55.60[a]	–
	186.34	42.73	–	56.72
T3	185.85	42.15	55.57	56.79

[a] Two signals overlap.

solutions. On the other hand, the three edma in the T1 or T2 isomer are non-equivalent.

The four geometrical isomers of $[Co_3(edma)_3(\mu\text{-}OH)_3(\mu_3\text{-}O)]^+$ are optically active. Each of the four isomers was optically resolved by chromatography using an SP-Sephadex (K^+ form) column with 0.1 mol dm^{-3} aqueous solution of $[Sb_2(d\text{-}tart)_2]^{2+}$ as eluent. The CD spectra are shown in Ref. [14].

In complexes with a incomplete cubane core, the N–H···O hydrogen bonds are one of the important factors to determine the stability of the geometrical isomers. In the $[Co_3(edma)_3(\mu\text{-}OH)_3(\mu_3\text{-}O)]^+$, 38 isomers are possible, however, only four isomers which have three N–H···O hydrogen bonds were confirmed as mentioned above. These results suggest that the principal incomplete cubane species in the reacted solution are the four isomers; the amounts of the other isomers are so little that we cannot confirm them on the column chromatogram. If many isomers were formed in the reacted solution, it might be impossible to separate and isolate them by column chromatography. Accordingly, it is very lucky for our structural investigation that only four isomers are stabilized by the hydrogen bonds and are easily isolated.

The edma ligand is suitable for the formation of the incomplete cubane complexes as described above. Using the edma ligand, complexes with the Mo_3S_4 incomplete cubane core were also prepared and two of the four isomers have been determined by the X-ray diffraction method [34]. In each of the two isomers, the three inter-ligand N–H···O moieties, which contribute to stabilize the incomplete cubane structure in the four $[Co_3(edma)_3(\mu\text{-}OH)_3(\mu_3\text{-}O)]^+$ isomers, were found. The $\underline{N}$–H···$\underline{O}$ distances in the $[Mo_3(edma)_3(\mu\text{-}S)_3(\mu_3\text{-}S)]^+$ isomers are in the range 3.37–3.47Å. The importance of the synthesis of complexes with the Mo_3S_4 incomplete cubane core has been described by Shibahara in the Ref. [35].

3.2. L-His-cobalt(III) complexes with an incomplete cubane core

The L-histidine (L-his) is a N–N–O type tridentate similar to the edma ligand described above. However, the L-his is different from the edma in the following points. (1) The absolute configuration of L-his is fixed to *S* (on the asymmetric carbon): it is impossible to form an enantiomeric pair on the coordination of L-his, while with edma it is possible to coordinate to cobalt(III) in both *R* and *S* configurations (on the asymmetric nitrogen). (2) It is impossible to form an N–H···O hydrogen bond with the coordinated imidazole N in the tridentate L-his, while the hydrogen bond can be formed in edma complexes with either the NH or NH_2 group. According to these reasons, the number of isomers stabilized by the three N–H···O hydrogen bonds is reduced to only one. The X-ray diffraction study revealed that the isolated isomer, $[Co_3(L\text{-}his)_3(\mu\text{-}OH)_3(\mu_3\text{-}O)]^+$, really has three N–H···O hydrogen bonds (Fig. 4).

In the incomplete cubane cobalt(III) complexes with L-his, the $\underline{N}$–H···$\underline{O}$ average distances are 2.88 Å; these values are nearly equal to the $\underline{N}$–H···$\underline{O}$ distances in $[Co_3(edma)_3(\mu\text{-}OH)_3(\mu_3\text{-}O)]^+$. The Co–Co, Co–$\mu_3$-O, and Co–$\mu$-OH distances in the L-his complex are also nearly equal to the corresponding distances in the

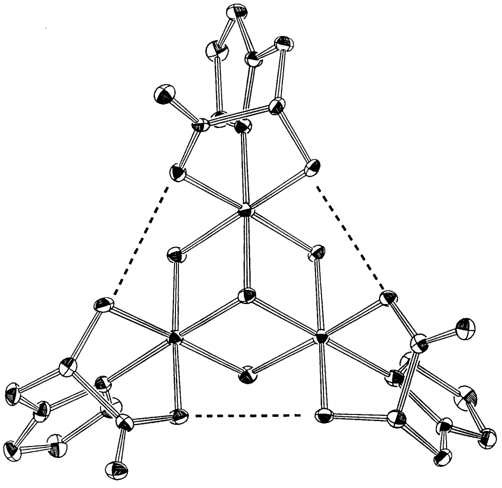

Fig. 4. Perspective view of the isolated $[Co_3(\text{L-his})_3(\mu\text{-}OH)_3(\mu_3\text{-}O)]^+$ ion.

$[Co_3(edma)_3(\mu\text{-}OH)_3(\mu_3\text{-}O)]^+$ isomers. In addition, the planarity in the Co–μ-OH–μ_3-O–Co four-membered ring is the same as observed for the $[Co_3(edma)_3(\mu\text{-}OH)_3(\mu_3\text{-}O)]^+$ isomers [36].

In the trinuclear L-histidinato complex, only one isomer was isolated with three hydrogen bonds. However, using D,L-histidine instead of L-histidine, dinuclear cobalt(III) complexes with $Co(\mu\text{-}OH)_2(\mu\text{-}CO_3)Co$ cores were isolated in the following way. After D,L-his was reacted with $[Co(CO_3)_3]^{3-}$, the solution was acidified (pH 0) in order to hydrolyze some of the coordinated CO_3^{2-} and then basified to pH 8 to lead to dehydro-condensation. The major products in the solution were five isomers of $[Co_2(\mu\text{-}OH)_2(\mu\text{-}CO_3)(his)_2]$, which were confirmed on the QAE-Sephadex column chromatogram with eluent H_2O [36]. When we used L-his instesd of D,L-his, we obtained the $Co(\mu\text{-}OH)_2(\mu\text{-}CO_3)Co$ type isomers in very low yields, but obtained the $[Co_3(\text{L-his})_3(\mu\text{-}OH)_3(\mu_3\text{-}O)]^+$ isomers in good yields. The structures of the two $[Co_2(\mu\text{-}OH)_2(\mu\text{-}CO_3)(his)_2]$ isomers were determined by the X-ray method. The Co–μ-O–μ-O–Co dihedral angles are about 160° and the nonbonding Co–Co distances are about 2.79 Å which are smaller than observed in the incomplete cubane L-his complex ($[Co_3(\text{L-his})_3(\mu\text{-}OH)_3(\mu_3\text{-}O)]^+$). The core structures of these isomers are similar to the $[Co_2(\mu\text{-}OH)_2(\mu\text{-}O_2CCH_3)(bpy)_2]^+$ [8].

3.3. dpa-Cobalt(III) complexes with an incomplete cubane core. Stacking of the pyridine rings stabilizing the core structure

Using dpa (di(2-pyridylmethyl)amine) as a tridentate N–N–N ligand, we also isolated the incomplete cubane type complex $[Co_3(dpa)_3(\mu\text{-}OH)_3(\mu_3\text{-}O)]^{4+}$ [12]. The structure analyzed by the X-ray diffraction method is shown in Fig. 5. In the $[Co_3(dpa)_3(\mu\text{-}OH)_3(\mu_3\text{-}O)]^{4+}$ cation, we find two pairs of pyridyl–pyridyl stacks, which make it possible to avoid the steric hindrance caused by the two pyridyl rings. The Co–Co distances with the stacking rings are 2.85 Å; these values are nearly equal to the Co–Co distances of $[Co_3(edma)_3(\mu\text{-}OH)_3(\mu_3\text{-}O)]^+$. The $\underline{N}_{py}$–$\underline{N}_{py}$ nonbonding distances (3.07 and 3.11 Å) are slightly longer than the N–H···O distances (hydrogen bonded) in the $[Co_3(edma)_3(\mu\text{-}OH)_3(\mu_3\text{-}O)]^+$ isomers but much shorter than the $\underline{N}$–H···H–$\underline{N}$ distance in the $[Co(en)_2Co(en)_2(\mu\text{-}OH)_2]^{4+}$ ion. Accordingly, it is reasonable to consider an attractive interaction between the two stacking pyridyl rings. However, in the $[Co_3(dpa)_3(\mu\text{-}OH)_3(\mu_3\text{-}O)]^{4+}$ ion, we also find an N–H···H–N repulsive interaction. The $\underline{N}$–H···H–$\underline{N}$ distance is 3.58 Å and the Co2–Co3 distance is 2.90 Å; these values are much longer than the corresponding ones accompanying the pyridyl–pyridyl stacks. In spite of these interactions, the planarity of the three Co–μ-OH–μ_3-O–Co four-membered rings is retained (the dihedral angles are observed in the range 173.3–178.7°).

The importance of the pyridyl–pyridyl stacks has been suggested in the *racemic*-$[Cr_2(\mu\text{-}OH)_2(bpy)_4]^{4+}$ to remove the steric hindrance which may appear in the *meso* form [16]. Moreover, we suggest that the stacks are important to stabilize the complete cubane core in $[Co_4O_4(O_2CC_6H_4\text{-}p\text{-}CH_3)_2(bpy)_4]^{2+}$ type complexes [8], as described below.

3.4. Another cobalt(III) complex with an incomplete cubane core

Dimitrou et al. reported the structure of another incomplete cubane cobalt(III) complex ion $[Co_3(bpy)_3(O_2CCH_3)(\mu\text{-}OH)_3(\mu\text{-}O_2CCH_3)(\mu_3\text{-}O)]^{2+}$ [8]. In this ion, the Co1 and Co2 are bridged and the distance shortened by μ-OAc; the Co1–Co2 distance (2.717(4) Å) is shorter than those of Co2–Co3 (2.853(3) Å) and Co1–Co3

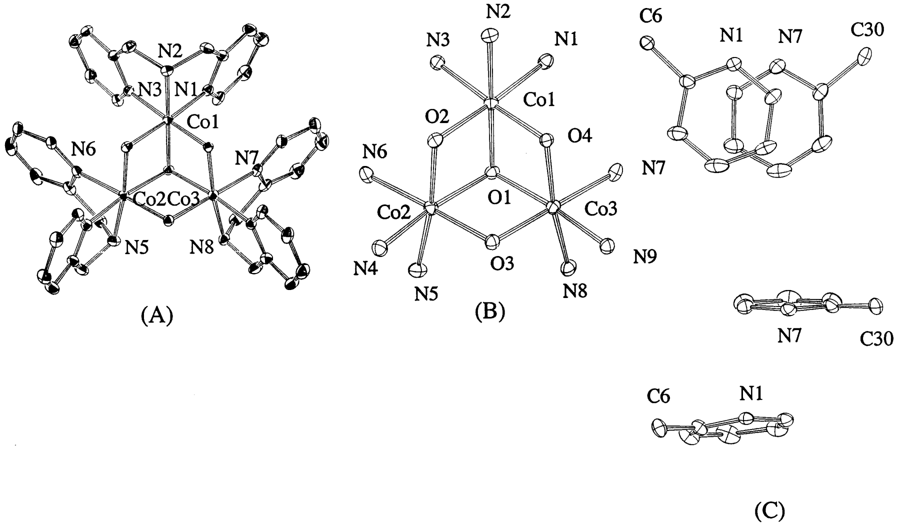

Fig. 5. Perspective view of the isolated $[Co_3(dpa)_3(\mu\text{-}OH)_3(\mu_3\text{-}O)]^+$ ion. (A) The structure of the trinuclear complex ion; (B) the incomplete cubane core of the ion; and (C) stacking of the pyridyl rings observed in the ion.

(2.847(4) Å) and also shorter than those observed in $[Co_3(edma)_3(\mu\text{-}OH)_3(\mu_3\text{-}O)]^+$ where the $\underline{N}$–H···$\underline{O}$ inter-ligand hydrogen bonds are formed. Although the description on the pyridyl–pyridyl stacking is not found in the report, the stacking may stabilize the incomplete cubane structure in a similar manner to that observed in the $[Co_3(dpa)_3(\mu\text{-}OH)_3(\mu_3\text{-}O)]^{4+}$.

The $[Co_3(bpy)_3(\mu\text{-}OH)_3(\mu\text{-}O_2CCH_3)_3(\mu_3\text{-}O)]^{2+}$ ion has a structure slightly different from that with the incomplete cubane Co_3O_4 core. That is, this complex ion has the structure in which one μ-hydroxo forming the incomplete Co_3O_4 core is replaced by a $\mu\text{-}O_2CCH_3$ ligand and the trinuclear structure is reinforced by two other $\mu\text{-}O_2CCH_3$ [7]. These complexes can be regarded to belong to the group of $[M_3(\mu_3\text{-}O)(\mu\text{-}O_2CR)_6L_3]$ [37–39].

The complex with the calixarene-related ligand $[L_rCo_3(\mu_3\text{-}OH)(\mu\text{-}O_2CCH_3)_3]^+$ [40], also has a core structure similar to the $[Co_3(bpy)_3(\mu\text{-}OH)_3(\mu\text{-}O_2CCH_3)_3(\mu_3\text{-}O)]^{2+}$ ion regarding the bridging phenolate-$\underline{O}$ as the μ-$\underline{O}$H in the bpy complex ion.

Some complexes of Co(II) with Co_3O_4 cores were reported [15,41–43]. As most of these complexes are not diamagnetic, structural study by the ordinary NMR chemical shifts is difficult. On the other hand, the study on the paramagnetic shielding and effective magnetic moment of the complexes give important information about the structure. We should denote much attention to the Co(II) complexes because the incomplete cubane Co(III) ones are possibly reduced to Co(II). However, important differences are known between Co(II) and Co(III) complexes; e.g. inter-ligand compression in these Co(II) complexes is not so serious as in Co(III), which is related to the larger ionic radius of the Co(II). However, we limit our description to Co(III) complexes in this review.

3.5. Absorption and CD spectra of the incomplete cubane type complexes

In neutral aqueous solutions, the isomers of $[Co_3(edma)_3(\mu\text{-}OH)_3(\mu_3\text{-}O)]$ showed the characteristic absorption band arising from the Co–μ-OH–Co at ca. 30 000 cm^{-1}, the first d–d transition band at ca. 19 000 cm^{-1} as a clear peak, and the second d–d transition band at ca. 25 000 cm^{-1} as a vague shoulder. The spectra of T0, T1, and T3 were very similar to those of T2 (Fig. 6).

The aqueous solution of the T2 isomer of $[Co_3(edma)_3(\mu\text{-}OH)_3(\mu_3\text{-}O)]^+$ showed a reversible absorption spectral change with pH (pH range 3 to 7), as described below, although these spectra did not show a time–course spectral change in this pH range (Fig. 6). The T2 isomer showed a broad band at 27 000–34 000 cm^{-1} in pH 7 solution. When the spectrum of the solution was measured at pH 3, the ε values decreased in the 20 000–32 000 cm^{-1} region and increased in the 32 000–37 000 cm^{-1} region, which seems to result from the protonation on the μ_3-O in the Co_3O_4 core. Reversible spectral changes with pH were also found with the T0, T1, T3 isomers. From these spectral changes, we calculate pK_a values of $[Co_3(edma)_3(\mu\text{-}OH)_3(\mu_3\text{-}OH)]^{2+}$; T1, 4.2; T2, 3.85; and T3, 3.32.

The visible and UV absorption spectra of the T0-T3 isomers are similar to each other. The circular dichroism spectra (CD) of their optically resolved isomers are, however, different from each other. The CD spectral changes with pH (in range of

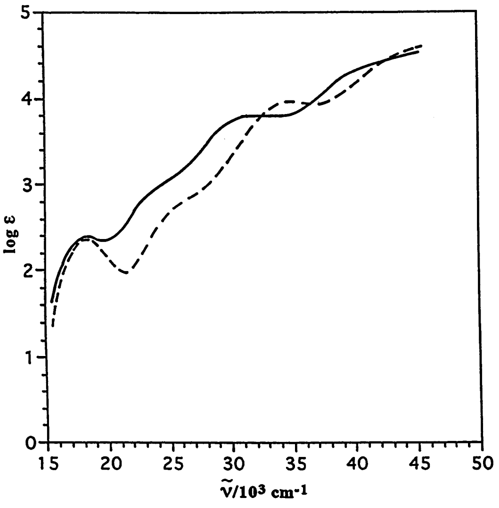

Fig. 6. Absorption spectra of the T2 isomer of $[Co_3(edma)_3(\mu\text{-}OH)_3(\mu_3\text{-}O)]^+$. Solid line: at pH 7; and broken line: at pH 3.

2–7, reversible) were observed in the same mannar as observed in their UV spectra, showing that no racemization occurs in these complexes under these conditions.

Similar absorption and CD spectral changes with pH were observed in $[Co_3(\text{L-his})_3(\mu\text{-}OH)_3(\mu_3\text{-}O)]^+$. It is expected that a similar absorption change is observed in the achiral $[Co_3(dpa)_3(\mu\text{-}OH)_3(\mu_3\text{-}O)]^{4+}$ ion. However, the strong absorption near the 27 000–34 000 cm^{-1} makes the spectral change unclear.

However, under very acidic conditions such as in 60% $HClO_4$, the characteristic band arising from the Co–μ-OH–Co core disappeared with time: these results suggest that the trinuclear structure decomposes to mononuclear under these conditions.

4. Cobalt(III) complexes with the complete cubane core

4.1. Incomplete cubanes versus complete cubanes in the cobalt(III) complexes

In both the $[Co_4(\mu_3\text{-}O)_4(edma)_4]$ and $[Co_3(edma)_3(\mu\text{-}OH)_3(\mu_3\text{-}O)]^+$ Co(III) complexes, the edma:Co ratio is 1:1. Forming the complete and incomplete cubane complexes in the solution reaction is competitive. However, the edma ligand is not suitable for formation of the complete cubane structure because each of the anticipated complete cubane isomers has at least two N–H···H–N repulsive interactions; i.e. even if the four N–H···O hydrogen bonds are formed in the $[Co_4(\mu_3\text{-}O)_4(edma)_4]$, the N–H···H–N interactions will remain in two sites, while the four isomers of $[Co_3(edma)_3(\mu\text{-}OH)_3(\mu_3\text{-}O)]^+$ have three N–H···O hydrogen bonds without N–H···H–N repulsive interactions. These considerations will be useful for the preparative study of the complete cubane Co(III) complexes as described below. If we make six attractive interactions such as the pyridyl–pyridyl stacks or the N–H···O hydrogen bonds on all six surfaces of the complete cubane core, complexes with the cubane core will be easily prepared. Another way to stabilize the cubane structure will be reinforcing with another extra ligand such as μ-CO_3^{2-} or μ-$CH_3CO_2^-$.

Though the repulsive interactions caused by the steric hindrance as observed in N–H···H–N interactions are serious on the polynuclear Co(III) complexes whose ionic radii are small, those in the Co(II) will be reduced by their larger ionic radii. Accordingly, even if some Co(II) complexes with complete cubane cores are isolated using a particular ligand, there may be some difficulties in the preparation of the complete cubane Co(III) complexes with the same ligand.

4.2. pg-Cobalt(III) complexes with a complete cubane core

The [Co_4(μ$_3$-O)$_4$(pg)$_4$] (pg = 2-pyridylmethylglycinato(1-)) was prepared by oxidizing an aqueous solution containing Co(II) and pg in a 1:1 ratio and condensing into a tetranuclear species by basifying the solution to pH 9 [13]. A perspective view of [Co_4(μ$_3$-O)$_4$(pg)$_4$] analyzed by the X-ray diffraction method is illustrated in Fig. 7. The average Co–μ$_3$-O distances are 1.89 Å. The four-membered rings, Co–μ$_3$-O–Co′–μ$_3$-O, are approximately planar. The Co–μ$_3$-O–Co′ angles (av. 95.8°) and the μ$_3$-O–Co–μ$_3$-O′ angles (av. 83.9°) are larger and smaller than a right angle, respectively. The average Co–Co distances (non-bonding) are 2.81 Å. These values are similar to those observed in the [Co_3(edma)$_3$(μ-OH)$_3$(μ$_3$-O)]$^+$ isomers. The average N1–O7, N3–O9, N5–O11, and N7–O5 distances are 2.86 Å; there are four inter-ligand N–H···O hydrogen bonds such as observed in the [Co_3(edma)$_3$(μ-OH)$_3$(μ$_3$-O)]$^+$ isomers. The N2(py)–N6(py) and N4(py)–N8(py) distances (av. 3.31 Å) are larger than these $\underline{\mathrm{N}}$–H···$\underline{\mathrm{O}}$ distances, but shorter than the N5–N8 distance

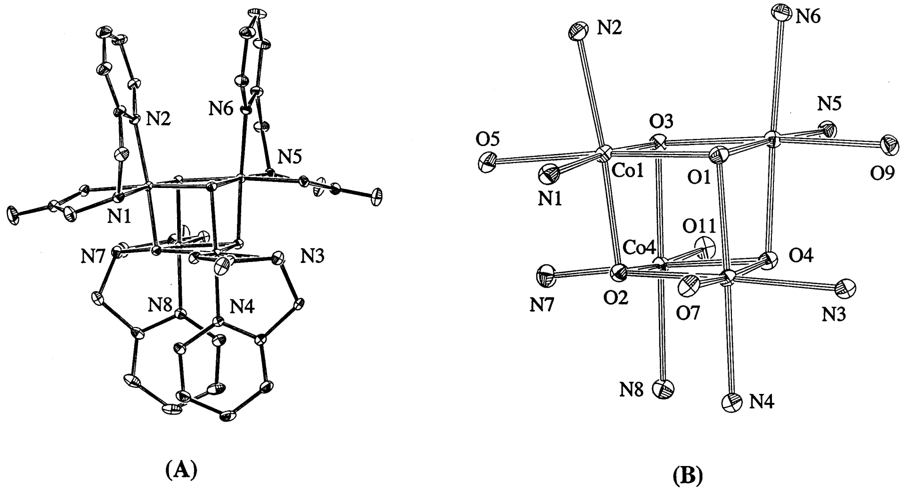

Fig. 7. Perspective view of the isolated [Co_4(pg)$_4$(μ$_3$-O)$_4$] isomer. (A) The structure of the tetranuclear complex and (B) the complete cubane core of the complex.

(N–H···H–N repulsive interaction) in $[Co_3(dpa)_3(\mu\text{-}OH)_3(\mu_3\text{-}O)]^{4+}$ (Figs. 6 and 7). Thus the isolated $[Co_4(\mu_3\text{-}O)_4(pg)_4]$ has the complete cubane structure stabilized by four N–H···O hydrogen bonds and two pyridyl–pyridyl stacks.

The ^{13}C-NMR of $[Co_4(\mu_3\text{-}O)_4(pg)_4]$ shows only eight signals in D_2O, suggesting that the complex has S_4 symmetry in the D_2O solution (the four pg ligands are equivalent).

4.3. Another cobalt(III) complex with a complete cubane core

The structure of another cobalt(III) complex containing a complete cubane unit, $[Co_4O_3(OH)(O_2CC_6H_4Me\text{-}p)_2(bpy)_4]^{2+}$, was reported. In the complex ion, the R–COO$^-$ group bridging two Co(III) strengthens the cubane structure. The average nonbonding Co–Co distances between the two Co(III) atoms bridged by the R–COO$^-$ are 2.69 Å and shorter than the other nonbonding Co–Co distances (av. 2.88 Å) [8,9]. However, the Co–μ_3-O distances (av. 1.88 Å), except for Co–O(8) (av. 1.93 Å) where O(8) has a hydrogen bond interaction, are nearly equal to those observed in $[Co_4(\mu_3\text{-}O)_4(pg)_4]$.

It was also reported by Dimitrou et al. that the $Co_4^{III}O_4$ cubane unit is present in each of the mixed valence octanuclear complexes $[Co_8O_4(O_2CPh)_{12}(solv)_4]$ (solv = DMF, MeCN, H_2O). One of the complexes, $[Co_8O_4(O_2CPh)_{12}(MeCN)_3(H_2O)]$, has already been analyzed by X-ray diffraction. Each of the four Co^{II} is coordinated by five atoms; the μ_4-O^{2-} of the $[Co_4^{III}O_4]^{4+}$ core, three $PhCO_2^-$ which bridge this Co^{II} and Co^{III} in the cubane core, and a unidentate ligand (CH_3CN/H_2O) [10]. The average Co^{III}–Co^{III} nonbonding and Co^{III}–μ_4-O distances are 2.83 and 1.88 Å, respectively. These values are nearly equal to the corresponding distances in $[Co_4(\mu_3\text{-}O)_4(pg)_4]$. The average Co^{II}–$\mu_4$-O distances are 2.01 Å larger than the Co^{III}–μ_4-O distances.

Another mixed valence cobalt complex with a triple cubane core $[Co_8(OH)_4(O_2CCH_3)_6L_2]^{2+}$ (L = 1,2-bis(2,2′-bipyridyl-6-yl)ethane), was reported by Grillo et al. [44]. The six CH_3COO^- found in the complex ion reinforce the triple cubane. The average nonbonding distances between the two Co^{III} bridged by the μ-CH_3COO^- are 2.70 Å, shorter than the other Co^{III}–Co^{III} distances (av. 2.83 Å). Each of the four μ-O^{2-} ions forming the central cubane also coordinate to Co^{II}. The distances between this μ-O^{2-} and Co^{III} are observed in the range 1.85–1.95 Å, much smaller than those between μ-O^{2-} and Co^{II} (2.70–2.88 Å).

Another octanuclear cobalt complex, $[Co_8(O)_4(O_2CCH_3)_6(OCH_3)_4Cl_4(OH_n)_4]$ (n = 1, 2), whose structure was determined by X-ray diffraction was reported [45]. This complex also has the triple cubane structure and six μ-CH_3COO^- reinforcing the triple cubane; the core structure of this complex resembles that of the $[Co_8(OH)_4(O_2CCH_3)_6L_2]^{2+}$ complex mentioned above.

The structure of $[Co_{12}(chp)_{18}(OH)_4(\mu_2\text{-}Cl)_2(Hchp)_2(MeOH)_2]$ (Hchp: 6-chloro-2-pyridone) was determined by X-ray. This complex contains two $[Co_4O_3Cl]$ cubes linked by a central eight membered ring involving four Co atoms and four μ-O atoms derived from chp ligands [46]. As this is a Co(II) complex, we may leave the details to another review. However, it is clear that by using well-designed ligands we have the possibility to isolate complexes with multi-cubane cores.

5. Summary

In summary, we propose the following three points concerning the structural aspects of the incomplete and complete cubane Co(III) complexes. (1) Ligand–ligand interactions such as the N–H···O hydrogen bond and pyridyl–pyridyl stacks are important factors to stabilize the polynuclear structure as demonstrated in $[Co_4(edma)_4(\mu\text{-}OH)_3(\mu_3\text{-}O)_4]$ [14] and $[Co_4(pg)_4(\mu_3\text{-}O)_4]$ [13]. (2) Each complex which has an incomplete cubane Co_3O_4 or complete Co_4O_4 core has the possibility to develop to polynuclear complexes coordination with μ-O or μ-OH as Beattie et al. showed in $[Co_8(O)_4(O_2CCH_3)_6(OCH_3)_4Cl_4(OH_n)_4]$ [45]. (3) With a well-designed ligand, we can prepare interesting multi-cubane complexes linking small polynuclear compounds into larger units.

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