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The Incomplete Cubane Complexes Having Co_3O_4 or Mo_3S_4 Core with the N–N–O Type Tridentates; L-histidinato and Ethylenediamine-*N*-acetato

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A trinuclear cobalt(III) complex, $[Co_3(\text{L-his})_3(\mu\text{-OH})_3(\mu_3\text{-O})]ClO_4\cdot H_2O$ (L-Hhis: L-histidine), containing an incomplete cubane Co_3O_4 core was isolated and the structure was compared with $[Co_3(\text{edma})_3(\mu\text{-OH})_3(\mu_3\text{-O})]^+$ (Hedma: $NH_2CH_2CH_2NHCH_2COOH$) isomers. Using the edma and L-his as N–N–O type ligands, $[Mo_3(L)_3(\mu\text{-S})_3(\mu_3\text{-S})]^+$ complexes with a Mo_3S_4 incomplete cubane core were also prepared, and their structures were determined by the X-ray diffraction method. A structural similarity between $[Mo_3(L)_3(\mu\text{-S})_3(\mu_3\text{-S})]^+$ and $[Co_3(L)_3(\mu\text{-OH})_3(\mu_3\text{-O})]^+$ is discussed; it is suggested that three N–H···O inter-ligand (intra-molecular) attractive interaction has an important role in stabilizing the incomplete cubane structure.

In the $[Co_3(\text{edma})_3(\mu\text{-OH})_3(\mu_3\text{-O})]^+$ (Hedma: $NH_2CH_2CH_2NHCH_2COOH$) complex ion, thirty-eight geometrical isomers are possible; however, four isomers were isolated based on a condensation of the basic aqueous solution of $[Co(\text{edma})(H_2O)_3]^{2+}$.[1,2] Because each of the isolated four isomers has three N–H···O inter-ligand (intra-molecular) hydrogen bonds, it is also pointed out that the "three hydrogen bonds" are one of the important factors to stabilize the incomplete cubane structures.[3] The L-histidine (L-Hhis) is a N–N–O type tridentate, just like the edma ligand. However, the L-his is different from edma: because the absolute configuration of L-his is fixed to *S* on the α-carbon, it is impossible to form an enantiometric pair in the L-his complexes, while it is possible in edma. In other words, it is expected in the many isomers of $[Co_3(\text{L-his})_3(\mu\text{-OH})_3(\mu_3\text{-O})]^+$ that only one isomer is stabilized by the three N–H···O inter-ligand hydrogen bonds. Based on the above-mentioned recognition, we tried to prepare incomplete cubane-type complexes containing L-his, and obtained the desired complexes.

According to these results, it is expected in the molybdenum incomplete cubane complexes, such as $[Mo_3(\text{edma})_3(\mu\text{-S})_3(\mu_3\text{-S})]^+$ and $[Mo_3(\text{L-his})_3(\mu\text{-S})_3(\mu_3\text{-S})]^+$, that the isomers having the three N–H···O inter-ligand interaction are also more stable than the other isomers. In this paper, we describe about the results to prepare molybdenum–edma and molybdenum–L-his complexes with an incomplete cubane Mo_3S_4 core, and want to estimate the important role of the three N–H···O inter-ligand interactions.

Experimental

Preparation of the Complexes. **$[Co_3(\text{edma})_3(\mu\text{-OH})_3(\mu_3\text{-O})]^+$ (T0, T1, T2, and T3):** The preparation and separation of these isomers have been described in previous papers.[1,2]

$[Co_3(\text{L-his})_3(\mu\text{-OH})(\mu_3\text{-O})]^+$ (CH): To a solution containing 2.5 g of $CoCl_2\cdot 6H_2O$ and 2.01 g of L-Hhis·HCl in 50 cm^3 of water, 2 mol dm^{-3} of a KOH aqueous solution was slowly added until the precipitation of $Co(OH)_2$ appeared. Air was bubbled through the solution for about 35 h while adjusting the pH to about 8. The solution was heated for one additional hour in a water bath at 60 °C, and then filtered. The filtrate was poured onto an SP-Sephadex C-25 column (K^+ form, ϕ 4.7 cm × 90 cm), and the column was swept with water in order to discard any anionic or neutral complexes. Being developed with a 0.1 mol dm^{-3} KCl aqueous solution, the band separated into three individual bands (pink, orange-red, and brown). A brown eluate was evaporated under reduced pressure, and then methanol was added to the concentrated solution. Potassium chloride deposited was removed by filtration, and the filtrate was again evaporated. A crude complex was obtained from the concentrated solution upon the addition of acetone. The obtained crude complexes (chloride) was converted to the perchlorate by using a Dowex 1 × 8 column. That is, the crude complex was dissolved in a small amount of water, loaded on a short column (ϕ 4.7 cm × 5 cm) of Dowex 1 × 8 (ClO_4^- form) and then eluted with water. The crude **CH** perchlorate was crystallized from its concentrated aqueous solution upon standing at room temperature for several days. Yield: 150 mg. The crude complex was recrystallized from warm water. Found for **CH** perchlorate: C, 23.96; H, 4.10; N, 13.93%. Calcd for $[Co_3(\text{L-his})_3(\mu\text{-OH})_3(\mu_3\text{-O})]ClO_4\cdot 5H_2O$ ($C_{18}H_{37}N_9O_{19}ClCo_3$): C, 24.13; H, 4.16; N, 14.07%.

$[Mo_3(\text{L-his})_3(\mu\text{-S})_3(\mu_3\text{-S})]^+$ (MH): This complex was prepared from $[Mo_3S_4(H_2O)_9]^{4+}$, which was obtained from $Na_2[Mo_2O_2S_2(\text{L-cys})_2]\cdot H_2O$ by the method described in Refs. 4 and 5.

To a green solution containing ca. 0.003 mol of $[Mo_3S_4(H_2O)_9]^{4+}$ in 20 cm^3 of 2 mol dm^{-3} HCl, 1.81 g of L-histidine hydrochloride hydrate (L-Hhis·HCl·H_2O) was dissolved. The pH of the solution was raised to ca. 1 with 2 mol dm^{-3} KOH, and then gradually raised to ca. 7 with 1 mol dm^{-3} KOH. After removing the precipitate by filtration, the filtrate was concentrated to ca. 10 mL under reduced pressure. Methanol was added to a concentrated solution to deposit KCl. After the KCl was removed by filtration, the filtrate was evaporated to a few milliliters, and then ca. 2 ml of methanol was added. Green hair-like crystals containing $[Mo_3S_4(\text{L-his})_3]^+$ (**MH**) were obtained from the concentrated solution by keeping it for a few days at room temperature. Yield: 200 mg. Another column of crystals was obtained by recrystallizing the hair like crystals from a hot saturated KCl aqueous solution, which was used for an X-ray structural analysis. Found for the column crystals: C, 19.65; H, 3.26; N, 11.60%. Calcd for $[Mo_3S_4(\text{L-his})_3]Cl\cdot KCl\cdot 6H_2O$ ($C_{18}H_{36}N_9O_{12}Mo_3S_4Cl_2K$): C, 19.72; H, 3.31; N, 11.50%. Found for the hair-like crystals: C, 20.90; H, 3.79; N, 11.67%. Calcd for $[Mo_3S_4(\text{L-his})_3]Cl\cdot 0.5KCl\cdot MeOH\cdot 6H_2O$ ($C_{19}H_{46}N_9O_{13}Mo_3S_4Cl_{1.5}K_{0.5}$): C, 20.90; H, 3.69; N, 11.59%.

$[Mo(edma)_3(\mu\text{-}S)_3(\mu_3\text{-}S)]^+$ (ME1, ME2, ME3, and ME4): These isomers were also prepared from the green solution containing $[Mo_3S_4(H_2O)_9]^{4+}$ mentioned above. That is, to the green solution, 2.15 g of ethylenediamine-*N*-acetate dihydrochloride dihydrate ($Hedma\cdot 2HCl\cdot 2H_2O$) was dissolved. The pH of the solution was raised to ca. 1 with 2 mol dm^{-3} KOH, and then gradually raised to ca. 9 with 1 mol dm^{-3} KOH. The solution was concentrated under reduced pressure, and methanol was added to the concentrated solution to eliminate KCl. After removing KCl, the solution was poured onto an SP-Sephadex column (ϕ 3.5 cm × 80 cm, K$^+$ form). Elution with 0.2 mol dm^{-3} KCl gave four green bands (el. 1–4 contains **ME1**–**ME4** isomers respectively; the formation-ratio on the chromatography is **ME1**:**ME2**:**ME3**:**ME4** = 20:45:34:1) of $[Mo_3S_4(edma)_3]^+$ isomers. After each eluate from the band was concentrated under reduced pressure, methanol was added. The deposited KCl was removed by filtration and the filtrate was again evaporated. Green plate crystals of $[Mo_3S_4(edma)_3]PF_6\cdot 2.5H_2O$ (**ME1**) were deposited by the addition of saturated NH_4PF_6 to a concentrated el. 1 solution. Yield of **ME1**PF_6: 50 mg. Keeping the concentrated solution of el. 2 in a refrigerator for a few days, green crystals, $[Mo_3S_4(edma)_3]Cl\cdot 7H_2O$ (**ME2**), were deposited. From the concentrated solution of el. 3, the chloride, $[Mo_3S_4(edma)_3]Cl\cdot 5H_2O$ (**ME3**), was obtained by keeping the solution in a refregirator for 7 days. However, we did not succeed to isolate a single crystal of **ME3** suitable for an X-ray analysis. Anal. Found for **ME1**$PF_6\cdot 2.5H_2O$: C, 14.83; H, 3.40; N, 8.58%. Calcd for $C_{12}H_{33}N_6O_{8.5}Mo_3S_4PF_6$: C, 15.03; H, 3.36; N, 8.77%. Found for **ME2**$Cl\cdot 7H_2O$: C, 15.49; H, 4.43; N, 8.95%. Calcd for $C_{12}H_{41}N_6O_{13}Mo_3S_4Cl$: C, 15.50; H, 4.41; N, 9.04%. Found for **ME3**$Cl\cdot 5H_2O$: C, 16.16; H, 4.23; N, 9.16%. Calcd for $C_{12}H_{37}N_6O_{11}Mo_3S_4Cl$: C, 16.14; H, 4.18; N, 9.41%.

X-ray Crystallographic Study. Crystallographic data are given in Table 1. All of the measurements were made on a Rigaku AFC7S diffractometer with graphite-monochromated Mo $K\alpha$ radiation (λ = 0.71069 Å). The single crystals selected for X-ray measurements were loaded onto glass fibers. The data were collected at 25 °C using ω-2θ (for **ME1**, **ME2**, and **MH**) or ω (for **CH**) scan made. The intensity data were corrected for Lorentz and polarization effect.

The calculations were performed using the TEXSAN crystallographic software package of Molecular Structure Corporation.[6] The positions of the non-hydrogen atoms were refined together with their anisotropic thermal parameters. Hydrogen atoms bonding C or N were fixed at the calculated positions. Selected bond distances are listed in Tables 2–5. Tables of the anisotropic thermal parameters, coordinates of the atoms, and the observed and calculated structure factors have been deposited as Document No. 74061 at the Office of the Editor of Bull. Chem. Soc. Japan. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition numbers 170483–170486.

Measurements. The absorption and CD spectra were measured by a JASCO V-550 spectrophotometer and a JASCO J-720 spectrophotometer, respectively. The ^{1}H and ^{13}C NMR spectra were recorded on a JEOL spectrophotometer relative to an internal reference of sodium (trimethylsilyl)propionate-2,2,3,3-d_4 (δ = 0.0) and dioxane (δ = 67.4), respectively.

Table 1. Crystallographic Data of the Complexes

	CH$(ClO_4)\cdot 5H_2O$	**MH**$Cl\cdot KCl\cdot 6H_2O$	**ME1**$(PF_6)\cdot 2.5H_2O$	**ME2**$Cl\cdot 7H_2O$
Formula	$C_{18}H_{37}N_9O_{19}Co_3Cl$	$C_{18}H_{36}N_9O_{12}Mo_3S_4Cl_2K$	$C_{12}H_{32}N_6O_{8.5}Mo_3S_4PF_6$	$C_{12}H_{41}N_6O_{13}Mo_3S_4Cl$
Crystal system	orthorhombic	orthorhombic	triclinic	monoclinic
Space group	$P2_12_12$ (#18)	$P2_12_12_1$ (#19)	$P\bar{1}$	$P2_1/n$
a/Å	14.893(5)	15.393(3)	13.567(5)	17.973(2)
β/Å	26.965(4)	15.882(3)	14.853(3)	10.125(2)
c/Å	7.943(4)	14.937(3)	7.182(1)	18.740(2)
α/deg	90	90	91.40(2)	90
β/deg	90	90	92.49(2)	112.696(9)
γ/deg	90	90	82.62(2)	90
Z	4	4	2	4
D_{calc}/g cm^{-3}	1.865	1.994	2.239	1.953
Crystal size/mm	0.2 × 0.4 × 0.1	0.4 × 0.3 × 0.2	0.5 × 0.2 × 0.1	0.5 × 0.2 × 0.1
μ(Mo $K\alpha$)/cm^{-1}	17.22	15.68	17.30	15.88
No. of observations	5516	3968	4939	4377
No. of valiables	454	444	368	353
$R^{a)}$	0.054	0.061	0.042	0.045
$R_w^{b)}$	0.057	0.067	0.047	0.040

a) $R = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$ b) $R_w = \sqrt{\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2}$

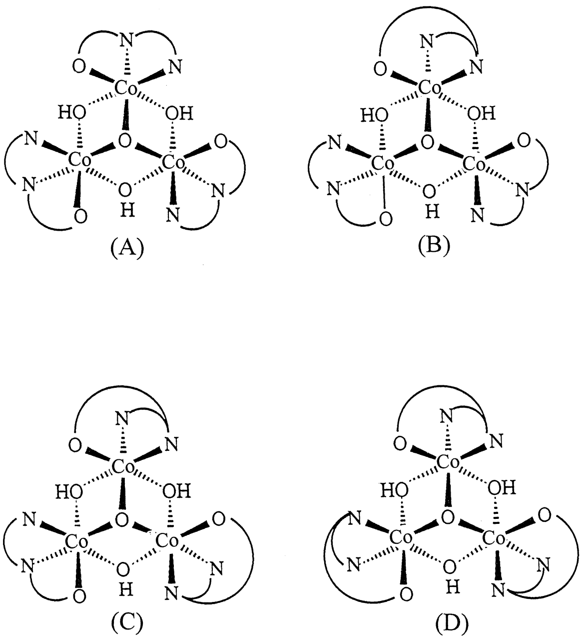

Fig. 1. Isolated geometrical isomers of [Co$_3$(edma)$_3$(μ-OH)$_3$(μ_3-O)]$^+$: (A) **T0**, (B) **T1**, (C) **T2**, and (D) **T3**.

Results and Discussion

Geometrical Structures of the [Co$_3$(edma)$_3$(μ-OH)$_3$(μ_3-O)]$^+$ Isomers. The four isomers of [Co$_3$(edma)$_3$(μ-OH)$_3$(μ_3-O)]$^+$ were isolated and their structures were clarified in previous studies (Fig. 1).[1] The isolated complex cations contain incomplete cubane Co$_3$O$_4$ cores. Each cobalt atom in the cations is octahedrally surrounded by two amino N (in the coordinated edma), one coordinated carboxyl O (in the edma), two μ-O, and one μ_3-O. The structures of three (T1, T2, and T3) of the four isolated isomers were analyzed by the X-ray diffraction method; the results show that the each isomer contains three $\underline{\mathrm{N}}$–H···$\underline{\mathrm{O}}$ inter-ligand hydrogen-bonds, which stabilize the trinuclear (incomplete cubane) structure.

Geometrical Structure and the Visible and CD Spectra of [Co$_3$(L-his)$_3$(μ-OH)$_3$(μ_3-O)]$^+$ (CH). As described in the Experimental Section, we newly prepared one isomer (**CH**) of [Co$_3$(L-his)$_3$(μ-OH)$_3$(μ_3-O)]$^+$, and succeeded to determine its structure by the X-ray diffraction method (Fig. 2). The complex ion contains incomplete cubane Co$_3$O$_4$ cores and each cobalt atom in the cation is octahedrally surrounded by one amino N$_{\mathrm{am}}$ (amino-N in the coordinated L-his), one N$_{\mathrm{im}}$ (imidazole-N), one carboxyl O, two μ-O, and one μ_3-O. The three N$_{\mathrm{im}}$ occupy *trans* positions to μ_3-O, and the complex cation has a pseudo-C_3 axis on the central μ_3-O perpendicular to the Co–Co–Co plane. Only five signals arising from the coordinated L-his (δ27.33, 56.41, 117.62, 133.34, 137.58, 186.78) were observed in the ^{13}C{^{1}H}-NMR spectrum of this complex, showing that the complex cation has C_3 symmetry in a D$_2$O solution, and that the three coordinated L-his in the cation are equivalent.

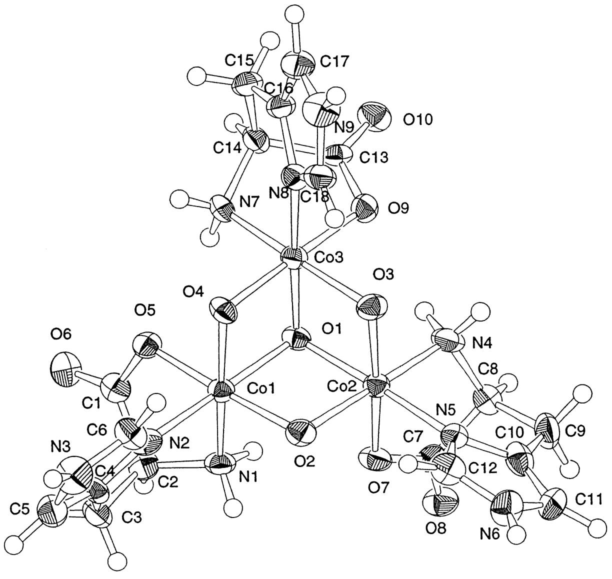

Fig. 2. Perspective view of [Co$_3$(L-his)$_3$(μ-OH)$_3$(μ_3-O)]$^+$ ion (**CH**) in [Co$_3$(L-his)$_3$(μ-OH)$_3$(μ_3-O)]ClO$_4$·5H$_2$O.

Table 2. Selected Bond Lengths (Å) of [Co$_3$(L-his)$_3$(μ-OH)$_3$(μ_3-O)]$^+$ (**CH**)

Atom	Atom	Distance	Atom	Atom	Distance
Co1	O1	1.886(6)	Co1	O2	1.913(6)
Co1	O4	1.923(6)	Co1	O5	1.901(6)
Co1	N1	1.921(7)	Co1	N2	1.933(8)
Co2	O1	1.882(6)	Co2	O2	1.912(6)
Co2	O3	1.903(6)	Co2	O7	1.919(6)
Co2	N4	1.935(8)	Co2	N5	1.922(7)
Co3	O1	1.890(4)	Co3	O3	1.923(6)
Co3	O4	1.891(6)	Co3	O9	1.933(6)
Co3	N7	1.928(8)	Co3	N8	1.922(6)
O5	C1	1.310(9)	O6	C1	1.212(9)
O7	C7	1.267(9)	O8	C7	1.236(9)
O9	C13	1.277(8)	O10	C13	1.238(9)
N1	C2	1.49(1)	N2	C4	1.39(1)
N2	C6	1.33(1)	N3	C5	1.35(1)
N3	C6	1.338(10)	N4	C8	1.47(1)
N5	C10	1.36(1)	N5	C12	1.40(1)
N6	C11	1.39(1)	N6	C12	1.32(1)
N7	C14	1.489(9)	N8	C16	1.379(7)
N8	C18	1.351(9)	N9	C17	1.363(10)
N9	C18	1.336(9)	C1	C2	1.52(1)
C2	C3	1.55(1)	C3	C4	1.48(1)
C4	C5	1.36(1)	C7	C8	1.53(1)
C8	C9	1.52(1)	C9	C10	1.52(1)
C10	C11	1.34(1)	C13	C14	1.53(1)
C14	C15	1.56(1)	C15	C16	1.490(10)
C16	C17	1.357(9)			

The selected bond lengths of the [Co$_3$(L-his)$_3$(μ-OH)$_3$(μ_3-O)]$^+$ cation in **CH** are listed in Table 2. The three $\underline{\mathrm{N}}$–H···$\underline{\mathrm{O}}$ distances (Fig. 2; O(7)–N(1) (2.825 Å), O(9)–N(4) (2.919 Å), and O(5)–N(7) (2.906 Å)) are nearly equal to those observed in the **T0**, **T1**, **T2**, and **T3** isomers of [Co$_3$(edma)$_3$(μ-OH)$_3$(μ_3-O)]$^+$ (ca. 2.92 Å).[1] The N–H–O angles in these $\underline{\mathrm{N}}$–H···$\underline{\mathrm{O}}$ parts are ca. 110°. These results suggest intra-molecular hydrogen-bonds between the coordinating carboxyl and amino groups in a similar way as observed in the isomers of [Co$_3$(edma)$_3$(μ-

OH)$_3$(μ_3-O)]$^+$.

The Co–μ_3-O distances of **CH** are 1.884–1.889 Å; these values are nearly equal to the Co–μ_3-O distance observed in the [Co$_3$(edma)$_3$(μ-OH)$_3$(μ_3-O)]$^{2-}$ isomers (ca. 1.91 Å).[1] The Co–μ-OH distances are in the range 1.892 Å–1.923 Å; these values also agree well with those of the corresponding ones in the [Co$_3$(edma)$_3$(μ-OH)$_3$(μ_3-O)]$^{2-}$ isomers (ca. 1.91 Å). The three four-membered rings (μ_2-O–Co–μ_3-O–Co′) are approximately planar (dihedral angles: ca. 175°). However, these approximated planes are not regular squares; the Co–μ-O–Co (or Co–μ_3-O–Co angles) are 95.3–97.3° and the μ-O–Co–μ_3-O ones are 83.2–83.9°.

The Co–Co non-bonding distances are ca. 2.83 Å and μ_3-O–μ-O distances are ca. 2.53 Å These values also agree with those of the corresponding ones in the [Co$_3$(edma)$_3$(μ-OH)$_3$(μ_3-O)]$^+$. The Co–N$_{\rm im}$ distances are ca. 1.92 Å and are nearly equal to those observed for Co–N$_{\rm am}$ (ca. 1.93 Å). Each imidazole-ring in the coordinated L-his is almost planer. It is known that for each isolated isomer of [Co$_3$(edma)$_3$(μ-OH)$_3$(μ_3-O)]$^+$ (**T0–T3**) the three N–H···O inter-ligand hydrogen bonds have an important role to stabilize the trinuclear structure. Three hydrogen bonds were also found in the structure of **CH**, as shown in Fig. 2.

The L-his is a N–N–O type tridentate similar to the edma ligand. However, the L-his is different from the edma regarding the following points: (1) The absolute configuration of L-his is fixed to *S* (on the asymmetric carbon); it is impossible to form an enantiometric pair on the coordination of L-his because the configuration on the asymmetric carbon of L-his is fixed to *S*, while in edma it is possible to coordinate to cobalt(III) in both the enantiomeric *R* and *S* configurations (on the asymmetric nitrogen). (2) It is impossible to form an $\underline{\rm N}$–H···$\underline{\rm O}$ hydrogen bond with the coordinated N$_{\rm im}$ 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 $\underline{\rm N}$–H···$\underline{\rm O}$ hydrogen bonds is reduced to only one in the [Co$_3$(L-his)$_3$(μ-OH)$_3$-(μ_3-O)]$^+$ ion. In other words, the L-his is a more suitable ligand to form only one isomer in [Co$_3$(L)$_3$(μ-OH)$_3$(μ_3-O)]$^+$ (L = L-his) than edma to form four isomers; the separation of the isomers, which is troublesome in the [Co$_3$(L)$_3$(μ-OH)$_3$(μ_3-O)]$^+$ isomers,[1,2] is unnecessary in the [Co$_3$(L-his)$_3$(μ-OH)$_3$(μ_3-O)]$^+$ ion.

The absorption and CD spectra of **CH** are illustrated in Fig. 3, together with those of [Co$_3$(edma)$_3$(μ-OH)$_3$(μ_3-O)]$^+$ ($(-)^{\rm CD}_{590}$-**T2**). The absorption spectrum of **CH** is very similar to that of **T2**, and characteristic absorption bands (shoulder) arising from the Co(μ-OH)(μ_3-O)Co moieties were observed in both complexes at ca. 30000 cm^{-1}. The CD spectrum of **CH**, which has the $\mathbf{A}_{\rm core}$ core-structure, is not antisymmetrical to that of $(-)^{\rm CD}_{590}$-**T2**, which has the $\bar{\mathbf{A}}_{\rm core}$ core-structure.[1] These results suggest that the vicinal CD in **CH** arising from the L-his around the core (the effect of asymmetric carbons (three C_S)) is different from those in **T2** arising from edma (the effect of asymmetric nitrogens (two N$_R$ and one N$_S$)).

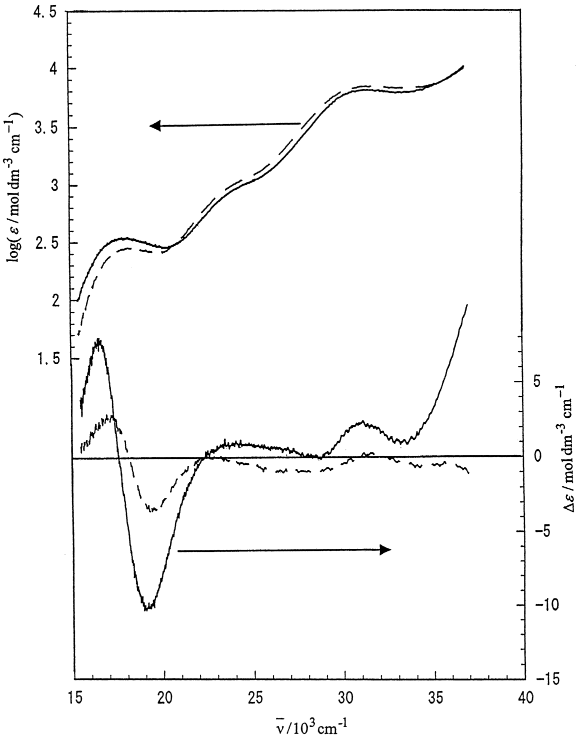

Fig. 3. Absorption and CD spectra of [Co$_3$(L-his)$_3$(μ-OH)$_3$(μ_3-O)]$^+$ (**CH**) (———) and [Co$_3$(edma)$_3$(μ-OH)$_3$(μ_3-O)]$^+$ ($(-)^{\rm CD}_{590}$-**T2**) (– – – –).

Geometrical Structure of [Mo$_3$(L-his)$_3$(μ-S)$_3$(μ_3-S)]$^+$ (MH). We obtained a column of crystals of [Mo$_3$(L-his)$_3$(μ-S)$_3$(μ_3-S)]Cl suitable for an X-ray analysis by crystallizing from a KCl-aqueous solution, while the recrystallization of this column of crystals from an aqueous-methanol solution gave hair-like crystals. Because the CD spectral pattern of an aqueous solution of hair-like crystals is identical to that of the column ones at 15000–35000 cm^{-1}, it is suggested that the amount of KCl in the crystal lattice in the hair-like is different from that in the column. These results are in agreement with those on their elemental analysis data (see Experimental section). The X-ray analysis results showed that the [Mo$_3$(L-his)$_3$(μ-S)$_3$(μ_3-S)]Cl and KCl ratio in the lattice is 1 : 1 in the column crystal.

It is clear from Fig. 4 that the complex ion in **MH** contains an incomplete cubane Mo$_3$S$_4$ core, and that each molybdenum atom in the cation is octahedrally surrounded by one N$_{\rm am}$ (amino-N in the coordinated L-his), one N$_{\rm im}$ (coordinated imidazole-N in the L-his), one carboxyl O$_{\rm coord}$ (coordinated carboxyl-O in the L-his), two μ-S, and one μ_3-S. The three N$_{\rm im}$ in the cation occupy a *trans* position to the μ_3-S, and the cation has a pseudo-C_3 axis on the central μ_3-S perpendicular to the Mo–Mo–Mo plane.

The selected bond lengths of [Mo$_3$(L-his)$_3$(μ-S)$_3$(μ_3-S)]$^+$ cation in **MH** are listed in Table 3. The observed Mo–Mo distances (av 2.76 Å) are smaller than the Co–Co distance (av 2.83 Å) in [Co$_3$(L-his)$_3$(μ-OH)$_3$(μ_3-O)]$^+$; these results suggest weak bonding in Mo–Mo in the incomplete cubane complexes.

The Mo–μ_3-S and Mo–μ-S distances of **MH** are ca.2.33 Å and ca. 2.30 Å respectively; these values are nearly equal to the Mo–μ_3-S distance observed in the [Mo$_3$(ida)$_3$(μ-S)$_3$(μ_3-S)]$^{2-}$ (ida: NH(CH$_2$COO$^-$)$_2$) isomers (ca. 2.29 Å).[4] The three four-membered rings (μ-S–Mo–μ_3-S–Mo′) are not a regular square; moreover, the rings are not planar, while the μ-O–Co–μ_3-O–

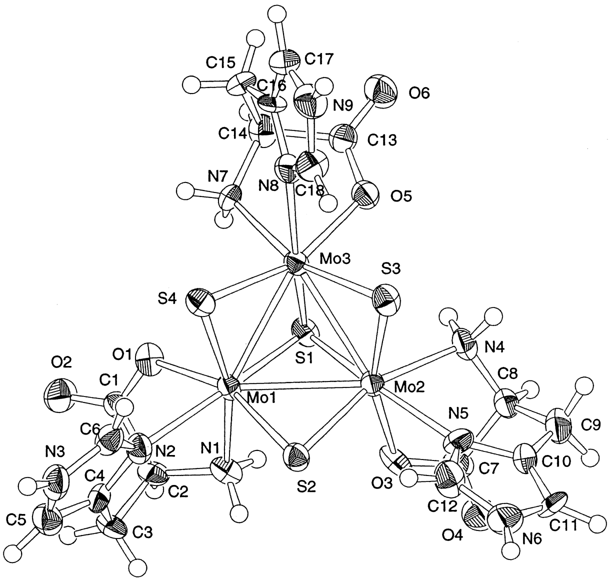

Fig. 4. Perspective view of $[Mo_3(\text{L-his})_3(\mu\text{-S})_3(\mu_3\text{-S})]^+$ ion (**MH**) in $[Mo_3(\text{L-his})_3(\mu\text{-S})_3(\mu_3\text{-S})]Cl\cdot KCl\cdot 6H_2O$.

Co′ are almost planar, as described above: the Mo–μ_2-S–μ_3-S–Mo′ dihedral angles in the $[Mo_3(\text{L-his})_3(\mu\text{-S})_3(\mu_3\text{-S})]^+$ are about 157° and the corresponding dihedral angles in $[Co_3(\text{L-his})_3(\mu\text{-OH})_3(\mu_3\text{-O})]^+$ (Co–μ_2-OH–μ_3-O–Co′) are ca.175°. The Mo–μ-S–Mo′ (or Mo–μ_3-S–Mo′) angles are 72.4–73.8° and less than a right angle (90°), while the corresponding angles in the $[Co_3(\text{L-his})_3(\mu\text{-OH})_3(\mu_3\text{-O})]^+$ (Co–μ-O–Co′ or Co–μ_3-O–Co′) are larger than a right angle. The μ-S–Mo–μ_3-S angles are 104.2–106.0°, and are larger than a right angle, while the corresponding angles in the $[Co_3(\text{L-his})_3(\mu\text{-OH})_3(\mu_3\text{-O})]^+$ are less than a right angle. The μ_3-S–μ-S and μ-S–μ-S non-bonding distances are ca. 3.67 and 3.54 Å, respectively. The Mo–N_{im} distances are ca. 2.26 Å, and are nearly equal to those observed for Mo–N_{am} (ca. 2.26 Å). Each imidazole-ring in the coordinated L-his is almost planar.

In the isomer of $[Co_3(\text{L-his})_3(\mu\text{-OH})_3(\mu_3\text{-O})]^+$, the three $\underline{\text{N}}$–H···$\underline{\text{O}}$ inter-ligand hydrogen bonds have an important role to stabilize the trinuclear structure, as described above. In the preparation of $[Mo_3(\text{L-his})_3(\mu\text{-S})_3(\mu_3\text{-S})]^+$, the number of isolated isomers from the main chromatographic band was only one; it was confirmed that the isomer has three $\underline{\text{N}}$–H···$\underline{\text{O}}$ moieties based on an X-ray study ($\underline{\text{N}}$–H···$\underline{\text{O}}$ distances: ca. 3.54 Å and N–H–O angles: ca. 110°). These results suggest that stabilization by the three $\underline{\text{N}}$–H···$\underline{\text{O}}$ interactions is sufficiently large, though the $\underline{\text{N}}$–H···$\underline{\text{O}}$ distances in $[Mo_3(\text{L-his})_3(\mu\text{-S})_3(\mu_3\text{-S})]^+$ (ca. 3.54 Å) are larger than those in $[Co_3(\text{L-his})_3(\mu\text{-OH})_3(\mu_3\text{-O})]^+$ (ca. 2.88 Å); in other words, the $\underline{\text{N}}$–H ↔ H–$\underline{\text{N}}$ moieties which are expected in those isomers other than the present isolated ones may destabilize the incomplete cubane structures.

Geometrical Structure and the Visible and CD Spectra of $[Mo_3(edma)_3(\mu\text{-S})_3(\mu_3\text{-S})]^+$ (ME1, ME2, ME3, and ME4). The four isomers of $[Mo_3(edma)_3(\mu\text{-S})_3(\mu_3\text{-S})]^+$ were confirmed based on the chromatography of the reacted solution of $[Mo_3S_4(H_2O)_9]^{4+}$ with edma, as described in the experimental section. As described below, the structures of two of the four isomers (**ME1** and **ME2**) were determined by the X-ray diffraction method.

Table 3. Selected Bond Lengths (Å) of $[Mo_3S_4(\text{L-his})_3]^+$ (**MH**)

Atom	Atom	Distance	Atom	Atom	Distance
Mo1	Mo2	2.751(2)	Mo1	Mo3	2.762(2)
Mo1	S1	2.326(4)	Mo1	S2	2.273(4)
Mo1	S4	2.325(4)	Mo1	O1	2.111(10)
Mo1	N1	2.27(1)	Mo1	N2	2.23(1)
Mo2	Mo3	2.759(2)	Mo2	S1	2.331(4)
Mo2	S2	2.307(4)	Mo2	S3	2.281(4)
Mo2	O3	2.14(1)	Mo2	N4	2.24(1)
Mo2	N5	2.25(1)	Mo3	S1	2.327(4)
Mo3	S3	2.317(4)	Mo3	S4	2.281(4)
Mo3	O5	2.144(10)	Mo3	N7	2.25(1)
Mo3	N8	2.28(1)	O1	C1	1.28(2)
O2	C1	1.24(2)	O3	C7	1.31(2)
O4	C7	1.23(2)	O5	C13	1.28(2)
O6	C13	1.22(2)	N1	C2	1.48(2)
N2	C4	1.39(2)	N2	C6	1.34(2)
N3	C5	1.36(2)	N3	C6	1.33(2)
N4	C8	1.50(2)	N5	C10	1.40(2)
N5	C12	1.32(2)	N6	C11	1.37(2)
N6	C12	1.34(2)	N7	C14	1.46(2)
N8	C16	1.36(2)	N8	C18	1.30(2)
N9	C17	1.36(2)	N9	C18	1.32(2)
C1	C2	1.49(2)	C2	C3	1.55(2)
C3	C4	1.51(2)	C4	C5	1.37(2)
C7	C8	1.53(2)	C8	C9	1.55(2)
C9	C10	1.50(2)	C10	C11	1.32(2)
C13	C14	1.53(2)	C14	C15	1.52(2)
C15	C16	1.53(2)	C16	C17	1.33(2)

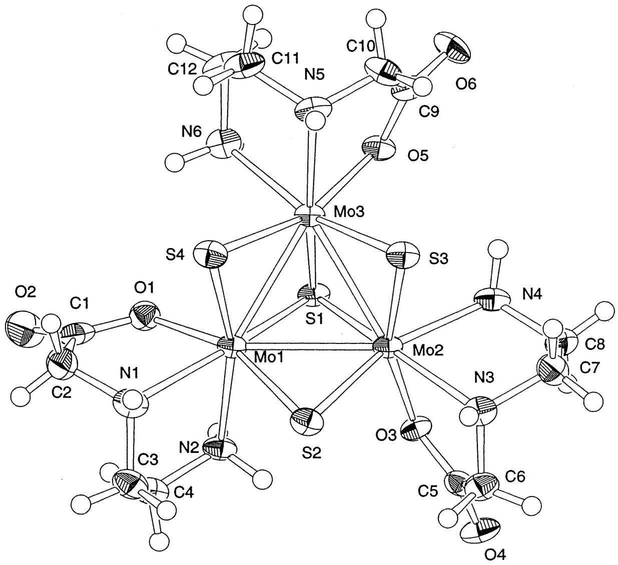

Fig. 5. Perspective view of $[Mo_3(edma)_3(\mu\text{-S})_3(\mu_3\text{-S})]^+$ ion (**ME1**) in $[Mo_3(\text{L-his})_3(\mu\text{-S})_3(\mu_3\text{-S})]PF_6\cdot 2.5H_2O$.

It is obvious from Fig. 5 that each of the Mo atoms in **ME1** are surrounded octahedrally by two μ-S, one μ_3-S, and one carboxyl-O and two amino-N in edma ligand; the coordination modes of edma in **ME1** are the same as those in **T0** ($[Co_3(edma)_3(\mu\text{-OH})_3(\mu_3\text{-O})]^+$);[1,3] the three N_{am} in the cation occupy a

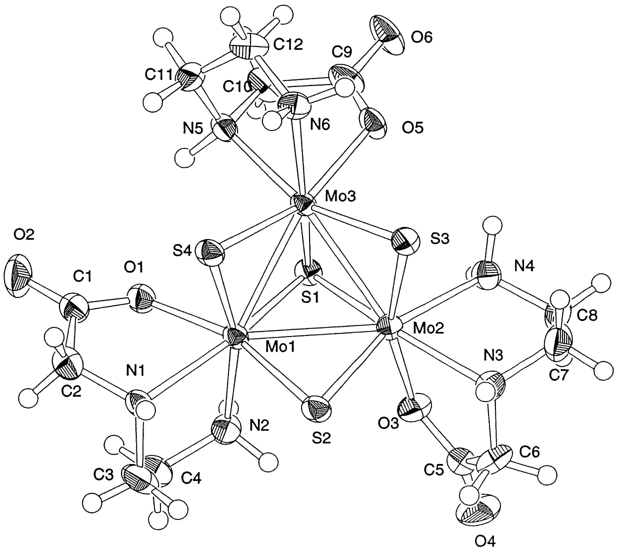

Fig. 6. Perspective view of $[Mo_3(edma)_3(\mu\text{-}S)_3(\mu_3\text{-}S)]^+$ ion (**ME2**) in $[Mo_3(\text{L-his})_3(\mu\text{-}S)_3(\mu_3\text{-}S)]Cl\cdot7H_2O$.

trans position to the μ_3-X (X: O or S), and the cation has a pseudo-C_3 axis on the central μ_3-S perpendicular to the M–M–M plane (M: Mo or Co). In **ME2**, each Mo was also coordinated by one edma as a tridentate with one carboxyl-O and two amino-N (Fig. 6). However, the coordination modes of three edma in **ME2**, similar to those of **T1** (**ME2** and **T1** do not have a pseudo-C_3 axis).

Selected bond lengths of **ME1** and **ME2** are listed in Tables 4 and 5. The observed Mo–Mo distances in **ME1** and **ME2** (ca. 2.76 Å) are nearly equal to those observed in **MH**; these results suggest weak bonding present in these Mo–Mo. The Mo–μ_3-S and Mo–μ-S distances are ca.2.34 Å and ca. 2.30 Å, respectively. The three four-membered rings (μ-S–Mo–μ_3-S–Mo′) are not a regular square and not planar; the dihedral angles (Mo–μ_2-S–μ_3-S–Mo′) are about 158°. The Mo–μ-S–Mo

Table 4. Selected Bond Lengths (Å) of $[Mo_3S_4(edma)_3]^+$ (**ME1**)

Atom	Atom	Distance	Atom	Atom	Distance
Mo1	Mo2	2.762(1)	Mo1	Mo3	2.7417(9)
Mo1	S1	2.342(2)	Mo1	S2	2.301(2)
Mo1	S4	2.304(2)	Mo1	O1	2.080(5)
Mo1	N1	2.233(7)	Mo1	N2	2.258(6)
Mo2	Mo3	2.737(1)	Mo2	S1	2.348(2)
Mo2	S2	2.296(2)	Mo2	S3	2.290(2)
Mo2	O3	2.103(5)	Mo2	N3	2.240(6)
Mo2	N4	2.251(7)	Mo3	S1	2.336(2)
Mo3	S3	2.301(2)	Mo3	S4	2.303(2)
Mo3	O5	2.101(5)	Mo3	N5	2.229(6)
Mo3	N6	2.270(7)	O1	C1	1.266(10)
O2	C1	1.210(9)	O3	C5	1.291(9)
O4	C5	1.220(9)	O5	C9	1.312(9)
O6	C9	1.213(9)	N1	C2	1.48(1)
N1	C3	1.491(10)	N2	C4	1.473(10)
N3	C6	1.485(10)	N3	C7	1.489(10)
N4	C8	1.499(10)	N5	C10	1.472(10)
N5	C11	1.482(10)	N6	C12	1.474(10)
C1	C2	1.54(1)	C3	C4	1.51(1)
C5	C6	1.53(1)	C7	C8	1.52(1)
C9	C10	1.53(1)	C11	C12	1.50(1)

Table 5. Selected Bond Lengths (Å) of $[Mo_3S_4(edma)_3]^+$ (**ME2**)

Atom	Atom	Distance	Atom	Atom	Distance
Mo1	Mo2	2.739(1)	Mo1	Mo3	2.742(1)
Mo1	S1	2.334(2)	Mo1	S2	2.285(2)
Mo1	S4	2.324(3)	Mo1	O1	2.097(6)
Mo1	N1	2.220(7)	Mo1	N2	2.271(8)
Mo2	Mo3	2.749(1)	Mo2	S1	2.339(2)
Mo2	S2	2.303(2)	Mo2	S3	2.295(3)
Mo2	O3	2.119(7)	Mo2	N3	2.212(7)
Mo2	N4	2.254(7)	Mo3	S1	2.358(3)
Mo3	S3	2.290(2)	Mo3	S4	2.282(2)
Mo3	O5	2.128(6)	Mo3	N5	2.230(7)
Mo3	N6	2.228(8)	O1	C1	1.28(1)
O2	C1	1.22(1)	O3	C5	1.30(1)
O4	C5	1.20(1)	O5	C9	1.283(10)
O6	C9	1.24(1)	N1	C2	1.49(1)
N1	C3	1.50(1)	N2	C4	1.48(1)
N3	C6	1.45(1)	N3	C7	1.46(1)
N4	C8	1.48(1)	N5	C10	1.51(1)
N5	C11	1.46(1)	N6	C12	1.46(1)
C1	C2	1.52(1)	C3	C4	1.49(1)
C5	C6	1.54(1)	C7	C8	1.51(1)
C9	C10	1.48(1)	C11	C12	1.47(1)

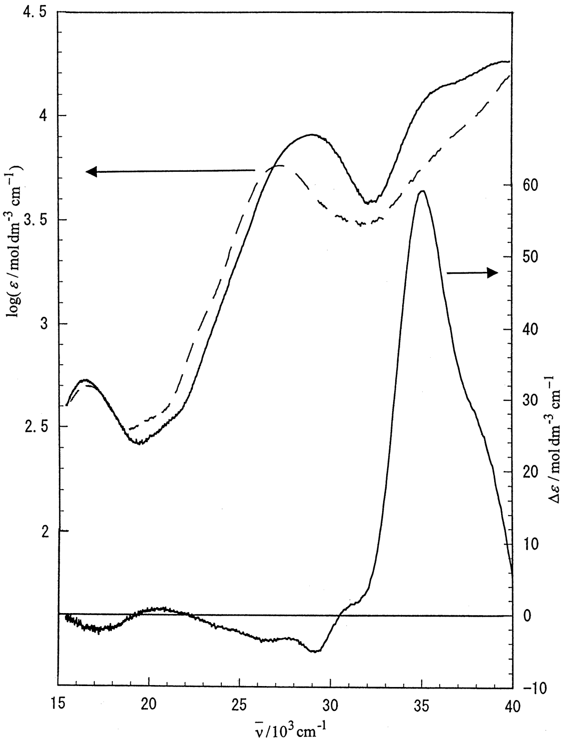

Fig. 7. Absorption and CD spectra of $[Mo_3(\text{L-his})_3(\mu\text{-}S)_3(\mu_3\text{-}S)]^+$ (**MH**) (———) and $[Mo_3(edma)_3(\mu\text{-}S)_3(\mu_3\text{-}S)]^+$ (**ME2**) (– – – –).

(or Mo–μ_3-S–Mo) angles (71.5–73.9°) are less than a right angle (90°) and the μ-S–Mo–μ_3-S angles (105.1–106.6°) are larger than a right angle. The μ_3-S–μ-S and μ-S–μ-S nonbonding distances are ca. 3.71 and 3.45 Å, respectively. These values are nearly equal to those of the corresponding bond or angles in $[\mathrm{Mo_3(L\text{-}his)_3(\mu\text{-}S)_3(\mu_3\text{-}S)}]^+$. However, the μ-S–μ-S non-bonding distances (ca. 3.45 Å) of **ME1** (or **ME2**) are about 0.1 Å longer than those observed in **MH**. The Mo–$\mathrm{N_{am}}$ distances have an average value of 2.24 Å.

We can find the three N–H···O moiety in these two isomers (the $\underline{\mathrm{N}}$–H···$\underline{\mathrm{O}}$ distances: ca. 3.54 Å and N–H–O angles: ca. 120°). These results suggest that the three $\underline{\mathrm{N}}$–H···$\underline{\mathrm{O}}$ interactions also have important roles in stabilizing the incomplete cubane structures in the $[\mathrm{Mo_3(edma)_3(\mu\text{-}S)_3(\mu_3\text{-}S)}]^+$ isomers.

The visible and UV absorption spectra of **ME2** resemble those of the **MH** in the range 15000–32000 $\mathrm{cm^{-1}}$ (Fig. 7). Those of **ME1**–**ME4** chlorides are similar to each other over the whole examined range. Accordingly, it is reasonable to estimate that the structures of **ME3** and **ME4** are similar to those of **ME1** and **ME2**. Taking into the consideration that the stabilization of the incomplete cubane-type structures by the three $\underline{\mathrm{N}}$–H···$\underline{\mathrm{O}}$ interactions is important, as observed in the $[\mathrm{Co_3(edma)_3(\mu\text{-}OH)_3(\mu_3\text{-}O)}]^+$ isomers, we propose that the structures of **ME3** and **ME4** can be assigned to the isomers of $[\mathrm{Mo_3(edma)_3(\mu\text{-}S)_3(\mu_3\text{-}S)}]^+$ with three $\underline{\mathrm{N}}$–H···$\underline{\mathrm{O}}$ moieties, though we have not yet succeeded to prepare single crystals of **ME3** and **ME4** suitable for an X-ray analysis.

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