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Optically Active Cobalt(III) Complexes Containing Partial Cubane Co_3O_4 Core: Syntheses and Structures of the Isomers of $[Co_3(L)_3(\mu\text{-}OH)_3(\mu_3\text{-}O)]Cl$ (L = Ethylenediamine-*N*-acetate)

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Four isomers (**T0**, **T1**, **T2**, and **T3**) of $[Co_3(edma)_3(\mu\text{-}OH)_3(\mu_3\text{-}O)]Cl$ (edma: ethylenediamine-*N*-acetate) containing a partial cubane Co_3O_4 core were isolated and optically resolved. The geometrical structures and absolute configurations of optically active $(+)^{\mathrm{CD}}_{590}$-**T2** chloride–water (1/7) and $(+)^{\mathrm{CD}}_{604}$-**T3** chloride–water (1/7) were determined by the X-ray diffraction method. The absolute configurations of optically active **T0** and **T1** were assigned on the basis of the NMR, UV, and CD spectral data. Each isomer was stable for at least 5 d in its neutral aqueous solution. Reversible protonation accompanying a color change was observed for each isomer in the pH range 2—7; this protonation did not accompany the cleavage of its partial cubane core. However, slow decomposition of each isomer was observed in its 60% $HClO_4$ solution.

The Mn complexes with Mn_4O_4 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 are currently unclear.[1)] Recently, an extension of the WOC modeling studies to cobalt(III) complexes with cubane and partial cubane cores has provided important information for understanding the oxidation. However, there are only a few reports about the preparation of these types of cobalt(III) complexes[2—5)] and no report about the optical resolution of the partial cubane Co_3O_4 type complexes; at the present stage, a reliable method to prepare many complexes containing the partial cubane Co_3O_4 is required.

After our brief report on an X-ray crystallographic study of the **T1** isomer of $[Co_3(edma)_3(\mu\text{-}OH)_3(\mu_3\text{-}O)]^+$, which has a Co_3O_4 partial cubane core, was published,[2)] we optically resolved four isomers (**T0**, **T1**, **T2**, and **T3**) of this complex. We have succeeded to determine the geometrical structures and absolute configurations of $(+)^{\mathrm{CD}}_{590}$-**T2** and $(+)^{\mathrm{CD}}_{604}$-**T3** by the X-ray diffraction method. In the present paper we report on the determined structures and resolution method of the isomers, together with other detailed characteristics of the four isomers.

Experimental

Preparation of the Complexes: A previously reported method[2)] was modified for preparing the complexes. To a solution containing 2.9 g of $Co(NO_3)_2\cdot6H_2O$ in 5 cm^3 of water, 4 cm^3 of a 30% H_2O_2 aqueous solution was added. The mixed solution was added dropwise to a suspension containing 7 g of $KHCO_3$ in 7 cm^3 of water, while keeping the temperature of the reacted solution below 5 °C. To this solution, 2.3 g of $edma\cdot2HCl\cdot2H_2O$ was added and stirred for 24 h at room temperature. The pH of the solution was adjusted to ca. 1 with 60% $HClO_4$ (stirred for 10 min at room temperature) and then to 8.5 with 2 $mol\,dm^{-3}$ KOH (stirred for 60 min at 50 °C). A white precipitate ($KClO_4$) was removed by filtration, and the filtrate was charged on an SP-Sephadex column (K^+ form, ϕ 10 cm×20 cm). After the charged column was swept with 500 cm^3 of water, the adsorbed band was developed with 0.1 $mol\,dm^{-3}$ K_2SO_4. The major brown band was transferred to another SP-Sephadex column (K^+ form, ϕ 4.7 cm×90 cm) and chromatographed recyclically with 0.1 M K_2SO_4. The band was separated into four brown bands (**T0**, **T1**, **T2**, and **T3**; in the order of elution; formation ratio of these isomers was 1 : 20 : 52 : 26 (on the chromatograph)). The eluate from each band was evaporated under reduced pressure, and methanol was added to the concentrated solution. Deposited potassium sulfate 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 crude complexes obtained (sulfate) were converted to the chloride using a QAE-Sephadex column. That is, each crude complex was dissolved in a small amount of water, loaded on a short column (ϕ 4.7 cm×8 cm) of QAE-Sephadex (Cl^- form) and then eluted with water. The eluted brown solution was concentrated to a small volume. A crude complex was obtained upon the addition of methanol and acetone to the concentrated solution, which was recrystallized from water by adding methanol and acetone. Found for **T1** chloride: C, 20.10; H, 5.72; N, 12.02%. Calcd for $[Co_3(edma)_3(\mu\text{-}OH)_3(\mu_3\text{-}O)]Cl\cdot5H_2O = C_{12}H_{40}N_6O_{15}Co_3Cl$: C, 20.00; H, 5.59; N, 11.66%. Found for **T2** chloride: C, 20.31; H, 5.46; N, 11.73%. Calcd for $[Co_3(edma)_3(\mu\text{-}OH)_3(\mu_3\text{-}O)]Cl\cdot4.5H_2O = C_{12}H_{39}N_6O_{14.5}Co_3Cl$: C, 20.51; H, 5.45; N, 11.96%. Found for **T3** chloride: C, 20.72;

H, 5.33; N, 12.02%. Calcd for $[Co_3(edma)_3(\mu\text{-}OH)_3(\mu_3\text{-}O)]Cl\cdot3.5H_2O = C_{12}H_{37}N_6O_{13.5}Co_3Cl$: C, 20.78; H, 5.38; N, 12.11%.

The yields of the **T0**, **T1**, **T2**, and **T3** chloride were about 0.005, 0.3, 0.1, and 0.1 g, respectively.

Optical Resolution of the Complexes: The racemates of **T0**—**T3** were resolved into optically active isomers by a column chromatographic method. About 200 mg of the each isomer (**T0**, **T1**, **T2**, or **T3**) was dissolved in about 50 cm^3 of water and the pH of the solution was adjusted to 4 with 1 $mol\,dm^{-3}$ HCl. The solution was poured onto an SP-Sephadex column (ϕ 4.7 cm×90 cm) and developed with 0.1 $mol\,dm^{-3}$ $K_2Sb_2(d\text{-tart})_2$. This development was repeated on the column using a micro-pump until the adsorbed band completely separated into two brown bands. (The CD signs of the early and late eluted isomers were $(+)^{CD}_{567}$ and $(-)^{CD}_{567}$ for **T0**, $(+)^{CD}_{538}$ and $(-)^{CD}_{538}$ for **T1**, $(+)^{CD}_{590}$ and $(-)^{CD}_{590}$ for **T2**, and $(-)^{CD}_{604}$ and $(+)^{CD}_{604}$ for **T3**.) Each band was eluted out with 0.1 $mol\,dm^{-3}$ $K_2Sb_2(d\text{-tart})_2$ and concentrated to a small volume under reduced pressure. To the concentrated solution, methanol was added to deposit $K_2Sb_2(d\text{-tart})_2$. After the $K_2Sb_2(d\text{-tart})_2$ was filtered off, the filtrate was evaporated to dryness to exclude methanol and diluted with a little water. The solution was reloaded on a short column (ϕ 6.5 cm×6 cm) of QAE-Sephadex (Cl^- form) and eluted with water. The eluted solution was concentrated to a small volume. A crude complex of the optically active isomer was obtained by adding methanol and acetone to the concentrated solution, which was recrystallized from water by adding methanol and acetone. Found for $(+)^{CD}_{590}$-**T2** chloride: C, 19.40; H, 5.52; N, 11.16%. Calcd for $[Co_3(edma)_3(\mu\text{-}OH)_3(\mu_3\text{-}O)]Cl\cdot7H_2O=C_{12}H_{44}N_6O_{17}Co_3Cl$: C, 19.05; H, 5.86; N, 11.11%. Found for $(+)^{CD}_{604}$-**T3** chloride: C, 18.12; H, 5.12; N, 10.47%. Calcd for $[Co_3(edma)_3(\mu\text{-}OH)_3(\mu_3\text{-}O)]Cl\cdot7H_2O = C_{12}H_{44}N_6O_{17}Co_3Cl$: C, 19.05; H, 5.86; N, 11.11%.

X-Ray Crystallographic Study. **$(+)^{CD}_{590}$-T2 Chloride–Water (1/7):** A brown prismatic crystal having approximate dimensions of 0.40×0.15×0.10 mm^3, recrystallized from water by adding acetone, was used. Intensity data were collected on a Rigaku RAXIS IV imaging-plate area detector with graphite-monochromated Mo $K\alpha$ radiation (λ = 0.71069 Å) at 25 °C.

Crystal data: $C_{12}H_{44}N_6O_{17}ClCo_3$, $M = 756.76$, orthorhombic, space group $P2_12_12_1$ (# 19), $a = 15.911(1)$, $b = 22.397(1)$, $c = 7.757(1)$ Å, $V = 2764.1(1)$ $Å^3$, $Z = 4$, $D_c = 1.82$ $g\,cm^{-3}$, $F_{000} = 1568$, $\mu(\text{Mo}\,K\alpha) = 19.60$ cm^{-1}.

The structure was solved by direct methods[7,8] and refined by least-squares techniques to $R = 0.043$ and $R_w = 0.060$ for 2487 reflections ($I > 3.00\ \sigma(I)$) of 2687 measured in the range of $2\theta < 50.3°$. The non-hydrogen atoms were refined anisotropically and the hydrogen atoms, excluding those of 7 water molecules, were included for calculations of the structure factors, but not refined.

The absolute configuration was determined based on the Bijvoet's inequality relationship between the intensities of Bijvoet pairs measured on a Rigaku AFC7 diffractometer in the range of $2\theta < 50.0°$ using Cu $K\alpha$ radiation (λ = 1.54178 Å) (Table 1). Atomic positional parameters representing the absolute configuration are given in Table 2.

$(+)^{CD}_{604}$-T3 Chloride–Water(1/7): A brown prismatic crystal having approximate dimensions of 0.35×0.20×0.10 mm^3, obtained from water by adding acetone, was used. Intensity measurements were made on a Rigaku AFC7R diffractometer using graphite monochromated Mo $K\alpha$ radiation at 23 °C.

Crystal data: $C_{12}H_{44}N_6O_{17}ClCo_3$, $M = 756.76$, trigonal hexagonal, space group $R3$ (# 146), $a = 11.022(6)$, $c = 21.03(1)$ Å, $V = 2212(2)$ $Å^3$, $Z = 3$, $D_c = 1.70$ $g\,cm^{-3}$, $F_{000} = 1176$, $\mu(\text{Mo}\,K\alpha) = 18.37$ cm^{-1}.

The structure was also solved by direct methods[7,8] and refined by least-squares techniques to $R = 0.039$ and $R_w = 0.053$ for 1140 reflections ($I > 3.00\ \sigma(I)$) of 1258 collected in the range of $2\theta < 55°$. The atom of O(4), μ_3-O, lies on a 3-fold axis in the crystal so that the complex ion has C_3 symmetry. Cl(1) and O(6) lie on the same 3-fold axis. The non-hydrogen atoms were refined anisotropically and hydrogen atoms, excluding those of O(5) and O(6) water molecules, were included but not refined.

The absolute configuration was determined based on the Bijvoet method using the intensity data ($2\theta_{max} = 120°$) measured with Cu $K\alpha$ radiation (Table 1). The positional parameters are presented in Table 3.

Selected bond distances and angles within the cation are summarized in Tables 4 and 5. The absolute configurations with the atom-numbering systems are shown in Fig. 1. All calculations were performed using the teXsan crystallographic software package.[9] Lists of the structure factors, anisotropic thermal parameters for non-hydrogen atoms, and positional parameters for the hydrogen atoms have been deposited as Document No. 70171 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Spectral Measurements. The absorption and CD spectra were measured by a JASCO UVIDEC-670 spectrometer and a JASCO J-720 spectropolarimeter, respectively. The ^1H and ^{13}C NMR spectra were recorded on a Hitachi R-90H spectrometer relative to internal references of sodium (trimethylsilyl)propionate-2,2,3,3-d_4 ($\delta = 0.0$) and dioxane ($\delta = 67.4$), respectively.

Results and Discussion

Preparation of the Trinuclear Complexes. The partial cubane cobalt(III) complexes reported in this paper were prepared by a convenient method described in the experimental section. The reaction path which we have considered is as follows. A violet solution, obtained by the reaction of edma with the green solution of $[Co(CO_3)_3]^{3-}$, contains the

Table 1. Determination of the Absolute Configurations of the Complexes (The Bijvoet Inequality Relationships by the Cu $K\alpha$ Radiation)

Significant difference[a)]	$(+)^{CD}_{590}$-**T2** chloride–water (1/7)		$(+)^{CD}_{604}$-**T3** chloride–water (1/7)	
	Correct trend	Incorrect trend	Correct trend	Incorrect trend
>4.0	16	1	180	3
3.0—4.0	13	1	80	9
2.0—3.0	22	2	98	16
1.0—2.0	29	6	102	34
<1.0	31	25	98	66

a) Significant difference = $||F_c(+)| - |F_c(-)||/\text{sqrt}(\sigma[F_o(+)]^2+\sigma[F_o(-)]^2)$.

Table 2. Positional Parameters, Equivalent Isotropic Temperature Factors (B_{eq}) for Non-H Atoms of $(+)^{CD}_{590}$-**T2** Chloride–Water (1/7)

Atom	x	y	z	B_{eq}
Co(1)	0.57949(6)	0.20280(4)	0.7998(1)	1.86(2)
Co(2)	0.73652(6)	0.15076(4)	0.7069(1)	1.90(2)
Co(3)	0.70164(6)	0.27232(4)	0.6285(1)	1.81(2)
Cl(1)	0.2563(2)	−0.0754(1)	0.4394(3)	4.30(5)
O(1)	0.6492(3)	0.1963(2)	0.6014(5)	2.00(9)
O(2)	0.6663(3)	0.1593(2)	0.9061(6)	2.13(10)
O(3)	0.7841(3)	0.2268(2)	0.7459(6)	2.30(10)
O(4)	0.6364(3)	0.2782(2)	0.8314(5)	2.20(9)
O(5)	0.4956(3)	0.2421(2)	0.6631(6)	2.41(10)
O(6)	0.4257(3)	0.2205(3)	0.4177(7)	3.0(1)
O(7)	0.6834(3)	0.0744(2)	0.6771(6)	2.4(1)
O(8)	0.6702(4)	−0.0128(2)	0.8185(9)	3.8(1)
O(9)	0.7572(3)	0.2641(2)	0.4108(6)	2.4(1)
O(10)	0.7315(4)	0.2635(3)	0.1294(6)	3.2(1)
O(11)	0.6222(4)	0.1514(3)	0.2837(7)	3.8(1)
O(12)	0.5300(5)	0.0429(3)	0.316(1)	5.3(2)
O(13)	0.3690(5)	0.0153(4)	0.208(1)	6.2(2)
O(14)	0.5271(5)	−0.0264(4)	0.619(1)	6.2(2)
O(15)	0.8632(7)	0.1833(4)	0.113(1)	9.2(3)
O(16)	0.1330(7)	−0.0032(5)	0.181(1)	8.5(3)
O(17)	0.5222(10)	0.3573(7)	0.978(2)	14.1(5)
N(1)	0.5129(4)	0.2053(3)	1.0129(8)	2.6(1)
N(2)	0.5194(4)	0.1293(3)	0.7479(8)	2.4(1)
N(3)	0.8007(4)	0.1388(3)	0.4975(8)	2.5(1)
N(4)	0.8234(4)	0.1046(3)	0.8214(8)	2.5(1)
N(5)	0.7585(4)	0.3486(3)	0.6691(8)	2.7(1)
N(6)	0.6171(4)	0.3173(3)	0.5025(8)	2.2(1)
C(1)	0.4460(6)	0.1590(4)	1.008(1)	3.3(2)
C(2)	0.4841(5)	0.1068(4)	0.911(1)	3.1(2)
C(3)	0.4560(5)	0.1414(4)	0.614(1)	2.9(2)
C(4)	0.4586(5)	0.2059(4)	0.5571(9)	2.3(1)
C(5)	0.8896(5)	0.1266(4)	0.549(1)	3.0(2)
C(6)	0.8864(5)	0.0835(4)	0.695(1)	3.2(2)
C(7)	0.7789(5)	0.0534(4)	0.9053(9)	3.1(2)
C(8)	0.7061(5)	0.0354(3)	0.7947(10)	2.6(1)
C(9)	0.7215(6)	0.3944(4)	0.549(1)	3.4(2)
C(10)	0.6278(5)	0.3812(4)	0.539(1)	3.0(2)
C(11)	0.6249(5)	0.3027(4)	0.319(1)	3.0(2)
C(12)	0.7104(5)	0.2750(3)	0.2813(9)	2.4(1)

Table 3. Positional Parameters, Equivalent Isotropic Temperature Factors (B_{eq}) and Occupancy for Non-H Atoms of $(+)^{CD}_{604}$-**T3** Chloride–Water (1/7)

Atom	x	y	z	B_{eq}	Occ
Co(1)	0.51448(5)	0.19018(5)	0.0000	1.60(1)	1.0000
Cl(1)	0.6667	0.3333	−0.16377(10)	2.95(2)	0.3333
O(1)	0.5092(5)	0.0486(5)	0.0554(2)	2.24(7)	1.0000
O(2)	0.4645(6)	−0.0244(7)	0.1544(2)	4.4(1)	1.0000
O(3)	0.6588(4)	0.1909(4)	−0.0510(3)	1.82(8)	1.0000
O(4)	0.6667	0.3333	0.0466(4)	1.81(7)	0.3333
O(5)	0.5645(4)	−0.1295(3)	−0.0676(2)	2.98(7)	1.0000
O(6)	0.6667	0.3333	−0.2973(6)	7.4(2)	0.3333
O(7)	0.664(1)	−0.111(1)	0.1270(5)	7.0(2)	1.0000
N(1)	0.3600(6)	0.0491(6)	−0.0510(3)	2.62(9)	1.0000
N(2)	0.3717(5)	0.1843(6)	0.0568(2)	2.31(8)	1.0000
C(1)	0.2292(7)	0.0613(9)	−0.0370(5)	4.9(2)	1.0000
C(2)	0.2314(6)	0.0795(9)	0.0311(4)	4.2(1)	1.0000
C(3)	0.3976(7)	0.1428(7)	0.1195(3)	3.3(1)	1.0000
C(4)	0.4598(5)	0.0470(6)	0.1107(2)	2.60(9)	1.0000

mononuclear cobalt(III) complex with carbonato and tridentate edma ligands ($[Co(edma)(CO_3)(HCO_3)]^-$). When the solution was acid-hydrolyzed by $HClO_4$ (evolution of CO_2 gas), the main product in the reacted solution changes into the mononuclear complex with edma and aqua ($[Co(edma)(OH_2)_3]^{2+}$). The pH of the solution being basified to pH 8.5, the three mononuclear complex ions, $[Co(edma)(OH_2)_3]^{2+}$, condense into a partial cubane complex ion (each isomer of $[Co_3(edma)_3(\mu\text{-}OH)_3(\mu_3\text{-}O)]^+$). It is often observed that the condensation of aqua or hydroxo mononuclear cobalt(III) complexes into polynuclear μ-hydroxo complexes takes place in the basic aqueous solution, e.g., the $[Co(L)(OH_2)_2]$ type complexes condense to $[Co_2(L)_2(\mu\text{-}OH)_2]$ type dinuclear complexes.[12—16]

Geometrical Structure of the T1 Isomer. The geometrical structure of *rac*-**T1** chloride–water (1/5) has been determined by the X-ray diffraction method and reported previously.[2] The complex cation in **T1** contains a partial cubane Co_3O_4 core. Each cobalt atom in the cation is octahedrally surrounded by two amino N (in the coordinated edma), one carboxyl O (in the edma), two μ-O, and one μ_3-

Table 4. Selected Bond Distances (Å) of the Complexes

$(+)^{CD}_{590}$-**T2** chloride–water (1/7)						$(+)^{CD}_{604}$-**T3** chloride–water (1/7)	
Co(1)–O(1)	1.903(4)	Co(2)–O(1)	1.908(5)	Co(3)–O(1)	1.907(5)	Co(1)–O(1)	1.925(4)
Co(1)–O(2)	1.881(5)	Co(2)–O(3)	1.887(5)	Co(3)–O(4)	1.890(5)	Co(1)–O(3)	1.914(4)
Co(1)–O(4)	1.931(5)	Co(2)–O(2)	1.917(5)	Co(3)–O(3)	1.895(5)	Co(1)–O(3*)	1.906(5)
Co(1)–O(5)	1.919(5)	Co(2)–O(7)	1.922(5)	Co(3)–O(9)	1.915(5)	Co(1)–O(4)	1.902(4)
Co(1)–N(1)	1.964(6)	Co(2)–N(3)	1.936(7)	Co(3)–N(5)	1.959(7)	Co(1)–N(1)	1.954(5)
Co(1)–N(2)	1.945(6)	Co(2)–N(4)	1.941(6)	Co(3)–N(6)	1.944(6)	Co(1)–N(2)	1.951(5)
O(5)–C(4)	1.297(9)	O(7)–C(8)	1.313(8)	O(9)–C(12)	1.274(9)	O(1)–C(4)	1.280(7)
O(6)–C(4)	1.245(9)	O(8)–C(8)	1.235(9)	O(10)–C(12)	1.252(9)	O(2)–C(4)	1.228(7)
N(1)–C(1)	1.49(1)	N(3)–C(5)	1.50(1)	N(5)–C(9)	1.50(1)	N(1)–C(1)	1.54(1)
N(2)–C(2)	1.473(9)	N(4)–C(6)	1.48(1)	N(6)–C(10)	1.470(10)	N(2)–C(2)	1.494(8)
N(2)–C(3)	1.47(1)	N(4)–C(7)	1.50(1)	N(6)–C(11)	1.462(10)	N(2)–C(3)	1.469(8)
C(1)–C(2)	1.52(1)	C(5)–C(6)	1.49(1)	C(9)–C(10)	1.52(1)	C(1)–C(2)	1.44(1)
C(3)–C(4)	1.51(1)	C(7)–C(8)	1.50(1)	C(11)–C(12)	1.52(1)	C(3)–C(4)	1.530(7)

Table 5. Selected Bond Angles (°) of the Complexes

$(+)^{CD}_{590}$-**T2** chloride–water (1/7)						$(+)^{CD}_{604}$-**T3** chloride–water (1/7)	
O(1)–Co(1)–O(2)	83.5(2)	O(1)–Co(2)–O(3)	83.0(2)	O(1)–Co(3)–O(4)	85.0(2)	O(4)–Co(1)–O(3)	84.2(1)
O(1)–Co(1)–O(4)	84.0(2)	O(1)–Co(2)–O(2)	82.4(2)	O(1)–Co(3)–O(3)	82.8(2)	O(4)–Co(1)–O(3*)	84.4(1)
O(2)–Co(1)–O(4)	93.1(2)	O(3)–Co(2)–O(2)	90.9(2)	O(4)–Co(3)–O(3)	91.0(2)	O(3)–Co(1)–O(3*)	87.7(3)
Co(1)–O(1)–Co(2)	96.8(2)	Co(2)–O(1)–Co(3)	96.4(2)	Co(3)–O(1)–Co(1)	95.6(2)	Co(1)–O(4)–Co(1*)	95.8(3)
Co(1)–O(2)–Co(2)	97.2(2)	Co(2)–O(3)–Co(3)	97.5(2)	Co(3)–O(4)–Co(1)	95.2(2)	Co(1)–O(3)–Co(1*)	95.3(2)
O(1)–Co(1)–O(5)	89.6(2)	O(1)–Co(2)–O(7)	96.0(2)	O(1)–Co(3)–O(9)	91.1(2)	O(4)–Co(1)–O(1)	91.0(2)
O(1)–Co(1)–N(1)	175.9(2)	O(1)–Co(2)–N(3)	95.6(2)	O(1)–Co(3)–N(5)	176.6(2)	O(4)–Co(1)–N(1)	177.5(3)
O(1)–Co(1)–N(2)	93.1(2)	O(1)–Co(2)–N(4)	178.1(2)	O(1)–Co(3)–N(6)	96.0(2)	O(4)–Co(1)–N(2)	94.2(3)
O(2)–Co(1)–O(5)	172.3(2)	O(3)–Co(2)–O(7)	176.7(2)	O(4)–Co(3)–O(9)	174.1(2)	O(3)–Co(1)–O(1)	91.8(2)
O(2)–Co(1)–N(1)	92.4(2)	O(3)–Co(2)–N(3)	92.7(2)	O(4)–Co(3)–N(5)	93.4(2)	O(3)–Co(1)–N(1)	95.0(2)
O(2)–Co(1)–N(2)	90.7(2)	O(3)–Co(2)–N(4)	97.0(2)	O(4)–Co(3)–N(6)	90.1(2)	O(3)–Co(1)–N(2)	176.0(3)
O(4)–Co(1)–O(5)	89.7(2)	O(2)–Co(2)–O(7)	85.9(2)	O(3)–Co(3)–O(9)	93.0(2)	O(3*)–Co(1)–O(1)	175.4(2)
O(4)–Co(1)–N(1)	97.0(2)	O(2)–Co(2)–N(3)	175.7(2)	O(3)–Co(3)–N(5)	94.1(2)	O(3*)–Co(1)–N(1)	93.1(2)
O(4)–Co(1)–N(2)	175.0(2)	O(2)–Co(2)–N(4)	95.7(2)	O(3)–Co(3)–N(6)	178.3(2)	O(3*)–Co(1)–N(2)	95.8(2)
O(5)–Co(1)–N(1)	94.4(2)	O(7)–Co(2)–N(3)	90.5(2)	O(9)–Co(3)–N(5)	90.7(2)	O(1)–Co(1)–N(1)	91.5(2)
O(5)–Co(1)–N(2)	86.1(2)	O(7)–Co(2)–N(4)	83.9(2)	O(9)–Co(3)–N(6)	85.8(2)	O(1)–Co(1)–N(2)	84.6(2)
N(1)–Co(1)–N(2)	86.2(2)	N(3)–Co(2)–N(4)	86.3(3)	N(5)–Co(3)–N(6)	87.1(3)	N(1)–Co(1)–N(2)	86.7(2)
Co(1)–O(5)–C(4)	112.2(5)	Co(2)–O(7)–C(8)	112.8(5)	Co(3)–O(9)–C(12)	114.0(5)	Co(1)–O(1)–C(4)	113.6(4)
Co(1)–N(1)–C(1)	110.1(5)	Co(2)–N(3)–C(5)	107.4(5)	Co(3)–N(5)–C(9)	108.3(5)	Co(1)–N(1)–C(1)	107.9(4)
Co(1)–N(2)–C(2)	107.4(5)	Co(2)–N(4)–C(6)	110.4(5)	Co(3)–N(6)–C(10)	109.1(5)	Co(1)–N(2)–C(2)	108.0(4)
Co(1)–N(2)–C(3)	109.1(5)	Co(2)–N(4)–C(7)	105.7(5)	Co(3)–N(6)–C(11)	108.2(5)	Co(1)–N(2)–C(3)	106.2(4)
O(5)–C(4)–C(3)	115.1(6)	O(7)–C(8)–C(7)	115.6(6)	O(9)–C(12)–C(11)	116.5(6)	O(1)–C(4)–C(3)	115.8(5)
O(5)–C(4)–O(6)	125.1(7)	O(7)–C(8)–O(8)	123.9(7)	O(9)–C(12)–O(10)	123.1(7)	O(1)–C(4)–O(2)	122.3(5)
N(1)–C(1)–C(2)	105.4(7)	N(3)–C(5)–C(6)	106.8(7)	N(5)–C(9)–C(10)	106.5(7)	N(1)–C(1)–C(2)	104.5(6)
N(2)–C(2)–C(1)	108.2(6)	N(4)–C(6)–C(5)	108.6(7)	N(6)–C(10)–C(9)	108.2(7)	N(2)–C(2)–C(1)	113.9(4)
N(2)–C(3)–C(4)	111.3(6)	N(4)–C(7)–C(8)	108.8(6)	N(6)–C(11)–C(12)	110.9(6)	N(2)–C(3)–C(4)	109.3(4)
O(6)–C(4)–C(3)	119.7(6)	O(8)–C(8)–C(7)	120.4(7)	O(10)–C(12)–C(11)	120.4(7)	O(2)–C(4)–C(3)	121.9(5)
C(2)–N(2)–C(3)	113.9(6)	C(6)–N(4)–C(7)	111.4(6)	C(10)–N(6)–C(11)	113.3(6)	C(2)–N(2)–C(3)	111.8(6)

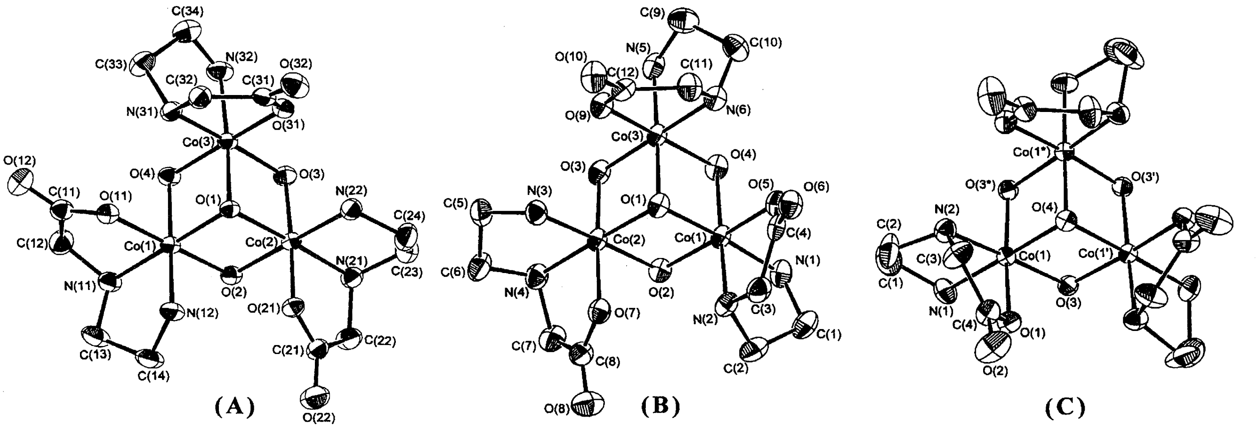

Fig. 1. Perspective views of the isomers of $[Co_3(edma)_3(\mu\text{-}OH)_3(\mu_3\text{-}O)]^+$ ions: (A) **T1** chloride–water (1/5), (B) $(+)^{CD}_{590}$-**T2** chloride–water (1/7), and (C) $(+)^{CD}_{604}$-**T3** chloride–water (1/7).

O. As shown in Fig. 1(A), the trinuclear cation contained two $\underline{N}H_2$–C and one C–$\underline{N}$H–C moieties forming three $\underline{N}$–H···O intra-molecular hydrogen-bonds, which stabilize the trinuclear structure.[2)]

Geometrical Structures of the T2 and T3 Isomers. As described in the Experimental Section, we have succeeded to determine the structures of the $(+)^{CD}_{590}$-**T2** and $(+)^{CD}_{604}$-**T3** isomers. In addition, the absolute configurations of the optically active complex ions have been determined based on the Bijvoet's inequality relationship using Cu *Kα* radiation. Perspective views of the $[Co_3(edma)_3(\mu\text{-}OH)_3(\mu_3\text{-}O)]^+$ ions in these isomers are given in Fig. 1(B) and (C). Though the former and latter complex ions have C_1- and C_3-symmetries respectively, the coordinations around cobalt(III) atoms in both the isomers are roughly octahedral. It is clear from the figures that the $(+)^{CD}_{590}$-**T2** and $(+)^{CD}_{604}$-**T3** complex ions contain the partial cubane Co_3O_4 cores. The Co–μ_3-O distances of the present isomers are ca. 1.905 Å: this value is nearly equal to the Co–μ_3-O distance observed in the **T1** isomer (1.901 Å).[2)] The Co–μ-O distances are in the range 1.88—1.93 Å; these values agree well with those of the corresponding ones in the trinuclear **T1** isomer[2)] and the binuclear

$[Co(edda)Co(en)_2(\mu\text{-}OH)_2]^{2+}$ ion.[10] The three four-membered rings (μ-O–Co–μ_3-O–Co′) are approximately planar (dihedral angles (absolute values) are less than 4°); however, these approximated planes are not regular squares; the Co–μ-O–Co (or Co–μ_3-O–Co) angles are 95.2—97.5° and the μ-O–Co–μ_3-O ones are 82.4—85.0°. These values are also agree with those of the corresponding ones in the $[Co(edda)Co(en)_2(\mu\text{-}OH)_2]^{2+}$ ion[10] and **T1** isomer ($[Co_3(edma)_3(\mu\text{-}OH)_3(\mu_3\text{-}O)]^+$.[2]) The Co–Co non-bonding distances are in the range 2.82—2.85 Å, and μ_3-O–μ-O distances are 2.52—2.57 Å.

Each of the edma ligands in the $(+)^{\mathrm{CD}}_{590}$-**T2** and $(+)^{\mathrm{CD}}_{604}$-**T3** complex ions coordinates to a cobalt(III) ion as a facial tridentate. The bond distances in the coordinated edma are similar to those of the **T1** isomer and $[Co(edma)(en)(NH_3)]^{2+}$ ion (F-4).[11] In the six edma's in the **T2** and **T3** complex ions, only one (N(4) in $(+)^{\mathrm{CD}}_{590}$-**T2**) of the six secondary amino N's has an *R* absolute configuration (N_R), while the other secondary amino N's (N(2) and N(6) in $(+)^{\mathrm{CD}}_{590}$-**T2** and three N(2)'s in $(+)^{\mathrm{CD}}_{604}$-**T3**) have $S(N_S)$.

In the $(+)^{\mathrm{CD}}_{590}$-**T2** complex ion, the O(7)–N(2), O(9)–N(3), and O(5)–N(6) distances are 2.935, 2.968, and 2.849 Å; there are three intramolecular hydrogen-bonds (N–H···O hydrogen-bond formed between the amino group on one of the cobalt atoms and the carboxyl group on another cobalt atom such as observed in the **T1** isomer of $[Co_3(edma)_3(\mu\text{-}OH)_3(\mu_3\text{-}O)]^+$ [2]). We also find the three hydrogen-bonds in the $(+)^{\mathrm{CD}}_{604}$-**T3** isomer; the O(1)–N(2*) distances are 2.930 Å.

Absorption Spectra of the T1, T2, and T3 Isomers. The visible and UV absorption spectra of $(+)^{\mathrm{CD}}_{590}$-**T2** and $(+)^{\mathrm{CD}}_{604}$-**T3** were very similar to those of the **T1**, whose structure and spectra were reported previously. That is, these complexes showed the characteristic absorption band arising from the Co–μ-OH–Co at ca. 30000 cm^{-1}, the first absorption band at ca. 19000 cm^{-1} as clear peak, and the second absorption band at ca. 25000 cm^{-1} as a vague shoulder. Accordingly, it is expected that $(+)^{\mathrm{CD}}_{590}$-**T2** and $(+)^{\mathrm{CD}}_{604}$-**T3** are the isomers of **T1** and have the partial cubane Co_3O_4 cores, which are confirmed by the X-ray crystallographic study as mentioned above.

The aqueous solutions of **T1**—**T3** showed reversible absorption spectral changes with pH (pH range 2 to 7), as described below, although these spectra did not show a time-course spectral change in this pH range. These isomers showed broad absorption bands at 27000—34000 cm^{-1} in the pH 7 solutions. When the spectra of the solutions were measured at pH 2, the ε values decreased in the 20000—32000 cm^{-1} region and increased in the 32000—37000 cm^{-1} region (Fig. 2), which seems to result from the protonations on the μ_3-O in the Co_3O_4 cores. The pK_a values estimated from the spectral changes are 4.20 (**T1**), 3.85 (**T2**), and 3.32 (**T3**), respectively. However, when each isomer of **T1**, **T2**, and **T3** dissolved in the 60% $HClO_4$, the absorption bands which appeared at 20000—37000 cm^{-1} (the characteristic absorption band arising from the Co–μ-OH–Co and the Co–μ-O–Co) decreased with time: it took more than 5 h for the band intensity of the each solution to decrease to the three fourths of the initial intensity. These results suggest that the trinuclear complexes decomposed to mononuclear complexes under the higher acidic condition.

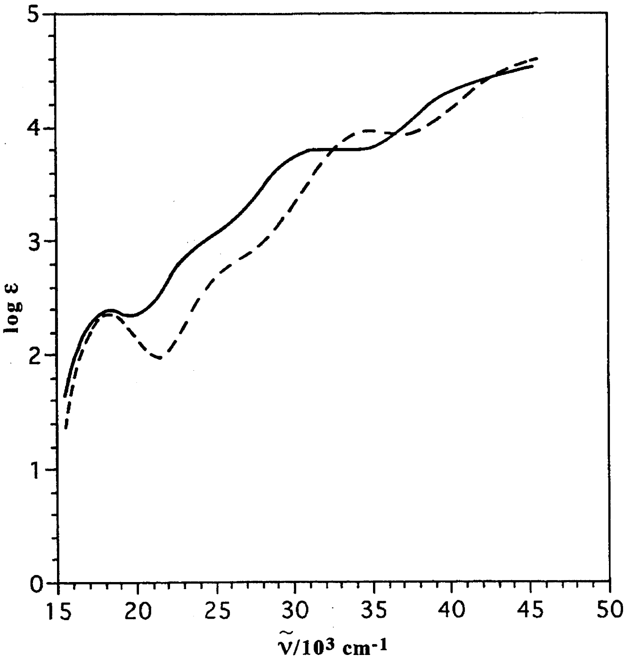

Fig. 2. Absorption Spectra of $(+)^{\mathrm{CD}}_{590}$-**T2**: (—) at pH 7; and (- - -) at pH 3. The ε values are given in $mol^{-1}\,dm^3\,cm^{-1}$.

Geometrical Structure of the T0 Isomer. We have not yet succeeded to prepare a single crystal of the **T0** isomer, which is suitable for X-ray analysis. However, the structure of **T0** is assignable from the UV and NMR spectral data, as described below.

The UV absorption spectra of **T0** (at pH 7) is very similar to those of the **T1**, **T2**, and **T3** isomers, whose structures are reported above; the characteristic absorption band arising from the Co–μ-OH–Co was found at ca. 30000 cm^{-1}, a clear peak of the first absorption band at 19000 cm^{-1}, and a vague shoulder of the second absorption band at ca. 25000 cm^{-1}. The aqueous solution of **T0** showed a reversible absorption spectral change with pH (pH range 3 to 7; the spectrum did not show the time-course spectral change in this pH range). In addition, the spectral pattern at pH 2 is also very similar to those of **T1**, **T2**, and **T3**. Since all of these behaviors resemble those of **T1**, **T2**, and **T3**, it is reasonable to conclude that the **T0** complex ion is one of the $[Co_3(edma)_3(\mu\text{-}OH)_3(\mu_3\text{-}O)]^+$ isomers.

It is known in the di-μ-hydroxo-dicobalt(III) complex ions that the isomers involving two intramolecular N–H···O hydrogen bonds (the 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) are preferentially formed.[10,12—18] According to this suggestion, it is expected for the possible isomers of $[Co_3(edma)_3(\mu\text{-}OH)_3(\mu_3\text{-}O)]^+$ that only the four isomers which can form the three intramolecular hydrogen bonds are preferentially prepared (Fig. 3). Therefore, it is considered that the four isomers that we have succeeded to isolate correspond to these four

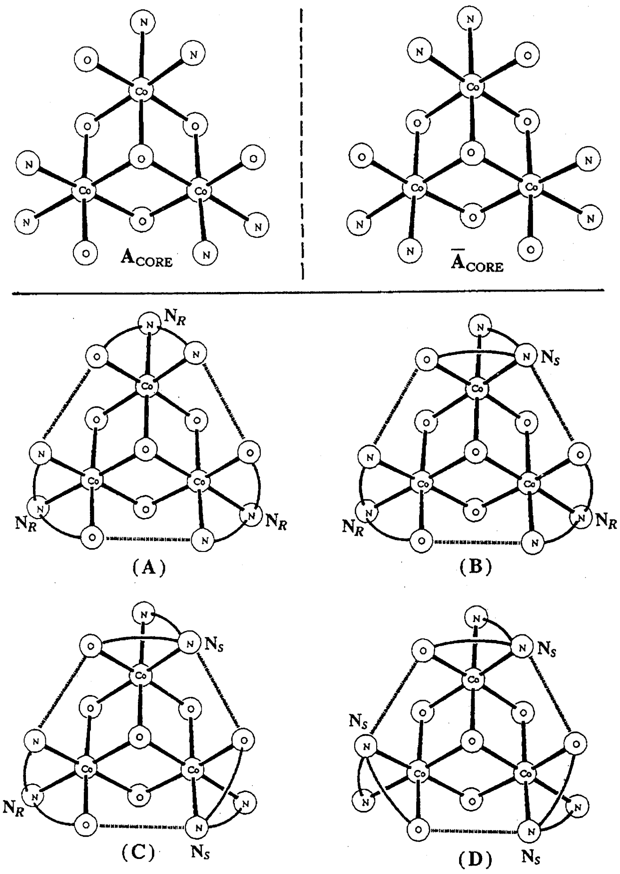

Fig. 3. (Top) Asymmetric core structures of the $[Co_3(edma)_3(\mu\text{-}OH)_3(\mu_3\text{-}O)]^+$: A_{core} and $\bar{A}_{core}$ (the antipode of A_{core}). (Bottom) Geometrical isomers of $[Co_3(edma)_3(\mu\text{-}OH)_3(\mu_3\text{-}O)]^+$ ions having three intramolecular hydrogen bonds and A_{core}: (A) **T0**, (B) **T1**, (C) **T2**, and (D) **T3**.

isomers. For three of the four isomers, the geometrical structures were confirmed by the X-ray analysis (mentioned above): **T1** corresponds to Fig. 3(B), **T2** to Fig. 3(C), and **T3** to Fig. 3(D). Accordingly, we assigned the **T0** to the remaining structure (Fig. 3(A)). This assignment for **T0** can be also confirmed by the NMR spectral data, which is described below.

The ^{13}C NMR data summarized in Table 6 show that the three edma ligands in the **T0** isomer are equivalent, that is, the **T0** complex ion has C_3-symmetry in the D_2O solution. In the ^1H NMR spectrum of **T0**, one AB quartet arising from the facially coordinated glycinate-ring $-CH_2-$ was observed (δ_A and δ_B: 4.18 and 3.39 ppm; $J = 17$ Hz). In addition, it was found in the ^1H NMR measurements in D_2O that the H- -D exchange rate on the secondary amino groups (C–N$\underline{H}$–C) of the coordinated edma's in **T0** (δ = ca. 7.5 ppm (broad)) were significantly faster than those in **T3** (δ = 6.3 ppm (broad)). (In the three secondary amino groups on the **T1** isomer, number of the faster deuterated (δ = 7.0 ppm (broad)) was two and that of the slower (δ = 6.5 ppm (broad)) was one. In the **T2** isomer, the faster (δ = 7.1 ppm (broad)) is one and the slower (δ = 6.7 ppm (broad)) is two.) It has been clarified that the amino proton which takes part in the hydrogen bond between the amino group on one of the cobalt atoms and the carboxyl group on another cobalt atom (intramolecular hydrogen bond) shows a slower H- -D exchange than the amino proton which does not take part in the hydrogen bond.[15,16] Accordingly, the three secondary amino groups of the coordinated edma's in **T0** do not take part in the intramolecular hydrogen bonds. Based on these views, we assigned the **T0** isomer to structure (A) in Fig. 3.

Table 6. ^{13}C NMR Data of the Cobalt(III) Complexes Containing Ethylenediamine-*N*-acetate (edma)

Complexes	$-CH_2-$			$-COO-$
T0 $[Co_3(edma)_3(\mu\text{-}OH)_3(\mu_3\text{-}O)]^-$	43.34	54.50	56.09	185.67
T1 $[Co_3(edma)_3(\mu\text{-}OH)_3(\mu_3\text{-}O)]^-$	41.51	42.37	43.19	185.24
	54.72	55.08	55.20	185.76
	55.78	55.78	56.19	185.85
T2 $[Co_3(edma)_3(\mu\text{-}OH)_3(\mu_3\text{-}O)]^-$	41.24	41.61	42.73	185.61
	54.69	55.60	55.60	185.91
	55.75	55.75	56.72	186.34
T3 $[Co_3(edma)_3(\mu\text{-}OH)_3(\mu_3\text{-}O)]^-$	42.15	55.57	56.79	185.85
C_2-*trans*(*O*)-$[Co(edma)_2]^+$	41.76	55.36	56.28	185.61

CD Spectra of the Complexes. The CD spectra of the optically active complexes are illustrated in Fig. 4. The solution of each isomer showed a reversible CD spectral change with pH, in a similar manner as it showed a reversible absorption spectral change. In addition, a decrease in the CD intensity was not observed for 2 d in the pH range 2—10; that is, the **T0**—**T3** isomers racemize with difficulty in this pH range.

The CD pattern of $(+)^{\mathrm{CD}}_{590}$-**T2** differs from that of $(+)^{\mathrm{CD}}_{604}$-**T3**, while the core configuration of $(+)^{\mathrm{CD}}_{590}$-**T2** is the same as that of $(+)^{\mathrm{CD}}_{604}$-**T3** (A_{core} in Fig. 3). This difference in the CD pattern results from the difference in the chelation mode of edma around each cobalt(III) atom; that is, $(+)^{\mathrm{CD}}_{604}$-**T3** has three N_S mode edma's, but $(+)^{\mathrm{CD}}_{590}$-**T2** has two N_S and one N_R mode edma's (Fig. 3).

Assuming that the CD component arising from the core moiety and that arising from the each $Co(edma)(\mu\text{-}OH)(\mu_3\text{-}O)$ moiety are additive, we can calculate the CD patterns of both components by the following equations, where A_{core} and N_S mean the CD contributions arising from the core and $Co(edma)(\mu\text{-}OH)(\mu_3\text{-}O)$ moieties respectively.

$$\bar{A}_{core} = -A_{core} \qquad N_S = -N_R$$
$$(+)^{\mathrm{CD}}_{590}\text{-}\mathbf{T2} = A_{core}(N_SN_SN_R) = A_{core} + N_S$$
$$(+)^{\mathrm{CD}}_{604}\text{-}\mathbf{T3} = A_{core}(N_SN_SN_S) = A_{core} + 3\,N_S$$
$$N_S = 1/2\{(+)^{\mathrm{CD}}_{604}\text{-}\mathbf{T3} - (+)^{\mathrm{CD}}_{590}\text{-}\mathbf{T2}\}$$
$$A_{core} = (+)^{\mathrm{CD}}_{604}\text{-}\mathbf{T3} - 3\,N_S$$
$$= 3/2\{(+)^{\mathrm{CD}}_{590}\text{-}\mathbf{T2}\} - 1/2\{(+)^{\mathrm{CD}}_{604}\text{-}\mathbf{T3}\}$$

Based on the calculated A_{core} and N_S, we can predict the CD curves of optically active **T0** and **T1**. For example, the

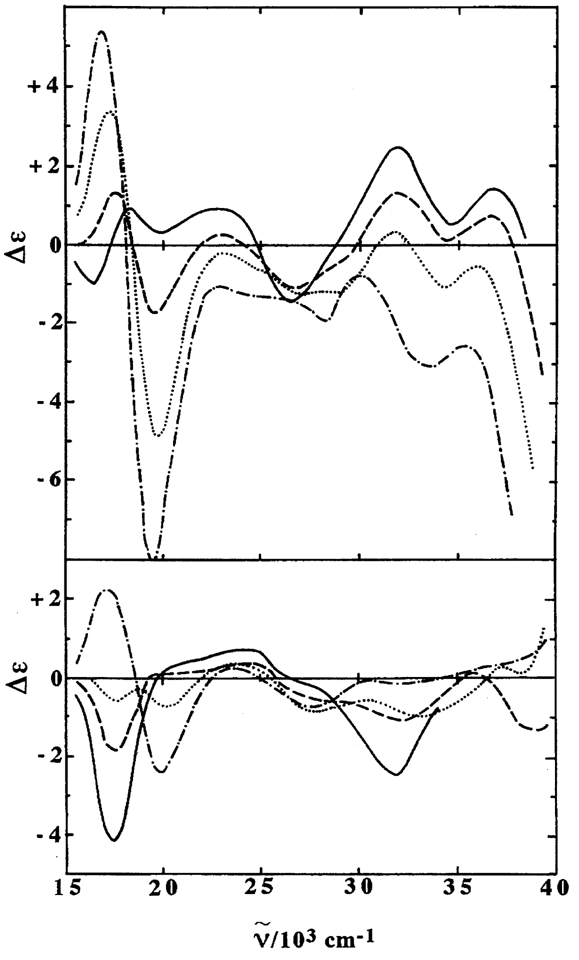

Fig. 4. CD spectra of the complexes at pH 7 (upper) and at pH 2 (lower): (——) $(-)^{\mathrm{CD}}_{567}$-**T0**; (- - -) $(+)^{\mathrm{CD}}_{538}$-**T1**; (····) $(+)^{\mathrm{CD}}_{590}$-**T2**; and (–·–) $(+)^{\mathrm{CD}}_{604}$-**T3**. The $\Delta\varepsilon$ values are given in $\mathrm{mol^{-1}\,dm^{3}\,cm^{-1}}$.

CD curve of $(\mathrm{A_{core}}(\mathrm{N}_R\mathrm{N}_R\mathrm{N}_R))$-**T0** and $(\mathrm{A_{core}}(\mathrm{N}_S\mathrm{N}_R\mathrm{N}_R))$-**T1** with $\mathrm{A_{core}}$ can be calculated by the following equations:

$$\begin{aligned}\mathbf{T0}\,(\mathrm{A_{core}}(\mathrm{N}_R\mathrm{N}_R\mathrm{N}_R)) &= \mathrm{A_{core}} - 3\,\mathrm{N}_S\\ &= 3\{(+)^{\mathrm{CD}}_{590}\text{-}\mathbf{T2}\} - 2\{(+)^{\mathrm{CD}}_{604}\text{-}\mathbf{T3}\}\\ \mathbf{T1}\,(\mathrm{A_{core}}(\mathrm{N}_S\mathrm{N}_R\mathrm{N}_R)) &= \mathrm{A_{core}} - \mathrm{N}_S\\ &= 2\{(+)^{\mathrm{CD}}_{590}\text{-}\mathbf{T2}\} - \{(+)^{\mathrm{CD}}_{604}\text{-}\mathbf{T3}\}\end{aligned}$$

The calculated curve $(\mathrm{A_{core}}(\mathrm{N}_R\mathrm{N}_R\mathrm{N}_R))$-**T0** (Fig. 5) coincides well with the observed $(-)^{\mathrm{CD}}_{567}$-**T0**, but not with the observed $(+)^{\mathrm{CD}}_{567}$-**T0** (the CD curve of $(+)^{\mathrm{CD}}_{567}$-**T0** resembles the calculated one of $(\overline{\mathrm{A}}_{\mathrm{core}}(\mathrm{N}_S\mathrm{N}_S\mathrm{N}_S))$-**T0**). Accordingly, it is reasonable to propose that the $(-)^{\mathrm{CD}}_{567}$-**T0** is assigned to $\mathrm{A_{core}}(\mathrm{N}_R\mathrm{N}_R\mathrm{N}_R)$. In the similar manner as above, the $(+)^{\mathrm{CD}}_{538}$-**T1** is assigned to $\mathrm{A_{core}}(\mathrm{N}_S\mathrm{N}_R\mathrm{N}_R)$.

Four isomers of $[\mathrm{Co_3(edma)_3(\mu\text{-}OH)_3(\mu_3\text{-}O)}]^+$ were isolated and the geometrical structures and absolute configurations were assigned. Each of the isolated isomers has three intramolecular hydrogen bonds between the amino group on one of the cobalt atoms and the carboxyl group on another cobalt atom; on the other hand, in the isomers of $[\mathrm{Co_3(edma)_3(\mu\text{-}OH)_3(\mu_3\text{-}O)}]^+$ except for **T0**, **T1**, **T2**, and **T3**, some of the three intramolecular hydrigen bonds which are attractive will be replaced by the corresponding number of N–H↔H–N interactions which are pepulsive. It seems reasonable to consider that the large stability difference between the former and the latter causes the present result that the only isomers having three intramolecular hydrogen bonds are isolated.

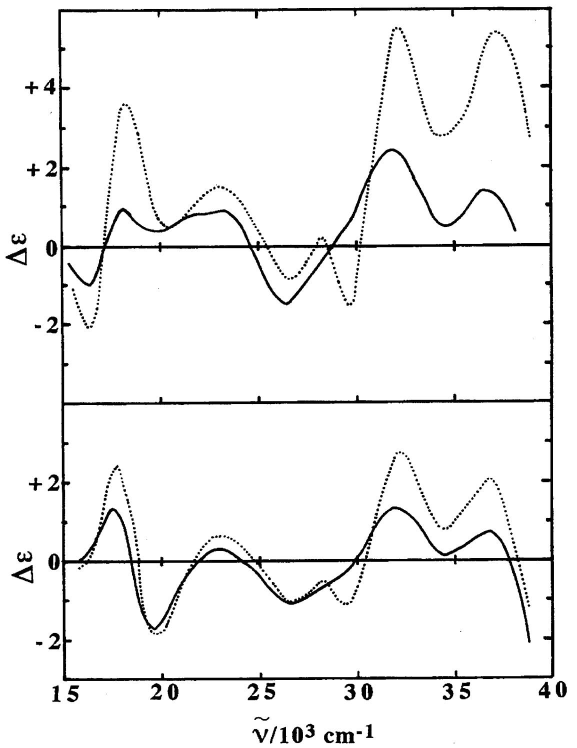

Fig. 5. Calculated and observed CD spectra of **T0** (upper) and **T1** (lower) isomers: (upper ····) Calcd $\mathrm{A_{core}}(\mathrm{N}_R\mathrm{N}_R\mathrm{N}_R)$-**T0**; (upper ——) Obsd $(-)^{\mathrm{CD}}_{567}$-**T0**; (lower ····) Calcd $\mathrm{A_{core}}(\mathrm{N}_S\mathrm{N}_R\mathrm{N}_R)$-**T1**; and (lower ——) Obsd $(+)^{\mathrm{CD}}_{538}$-**T1**. The $\Delta\varepsilon$ values are given in $\mathrm{mol^{-1}\,dm^{3}\,cm^{-1}}$.

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