cis- and *trans*-Li[$\mathrm{Co^{III}}${L-tart(2−)-$\mathrm{O^1}$}$_2$(en)$_2$] Hydrate Separated from the Reaction Products of [$\mathrm{Co^{III}(CO_3)(en)_2]^+}$ with L-Tartaric Acid

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The title compounds, trans(**1**) and cis(**2**) isomers, were isolated by means of QAE-Sephadex A-25 column chromatography from a reaction mixture of $\mathrm{[Co(CO_3)(en)_2]Cl}$ with L-tartaric acid. The crystal structure of **1** was determined by the X-ray diffraction study. The crystal is orthorhombic, space group $C222_1$ with a=12.008(1), b=9.496(2), c=18.524(4) Å, U=2112.2(7) Å^3, Z=4, and final R=0.0291. The two tartrate(2−) anions coordinate to the cobalt atom as a unidentate ligand in trans position each other. The two ethylenediamine rings are in the $\delta\delta$ gauche conformation. The lithium ion is tetrahedrally surrounded by two carboxylate oxygens of the tartrato(2−) ligands and two oxygens of the crystal waters. The compounds **1** and **2** were also characterized by UV-vis, NMR, and CD spectra.

It has been known that the reaction of $\mathrm{[Co(CO_3)(en)_2]^+}$ with L-tartaric acid in aqueous media yields a mixture of various cationic and neutral species of Co(III) complexes containing L-tartrato having different coordination modes and ethylenediamine ligands. Gillard and Price isolated Δ-,Δ-$\mathrm{[(en)_2Co(tart)(4-)Co(en)_2](ClO_4)_2\cdot 5H_2O}$ (tart=L-tartrate ion) from the mixture by the column chromatography on Sephadex G-10 resin.[1] Haines et al. isolated [Co{tart(2−)-$\mathrm{O^1,O^2}$}$\mathrm{(en)_2}$]Cl and [Co{tart(3−)-$\mathrm{O^1,O^2}$}$\mathrm{(en)_2]\cdot H_2O}$ by using the thin layer chromatography technique.[2] By means of SP-Sephadex column chromatography, the present authors isolated Δ-*cis*(O,O), *trans*(O,O)-[(en)$_2$Co{tart(3−)-$\mathrm{O^1,O^2,O^4}$}Co{tart(1−)-$\mathrm{O^1}$}(en)$_2$]$\mathrm{\cdot Na(ClO_4)_3\cdot 5H_2O}$ in which two cobalt atoms are bridged through a terdentate L-tartrate ion.[3] However, there has been no report on the isolation of anionic species formed by the reaction of $\mathrm{[Co(CO_3)(en)_2]^+}$ with L-tartaric acid. The authors have now isolated two anionic species, *cis*- and *trans*-Li[Co{tart(2−)-$\mathrm{O^1}$}$_2$(en)$_2$]$\cdot n\mathrm{H_2O}$ having unidentate tartrato ligands, **1** (n=3) and **2** (n=4),[#] by the use of QAE-Sephadex A-25 column, and determine the structure of **1**.

Experimental

Visible and ultraviolet absorption spectra were measured with a Hitachi 340 spectrophotometer. CD curves were recorded on a JASCO J-500A spectropolarimeter. ^{1}H and ^{13}C NMR spectra of the complexes in deuterium oxide were obtained with a JEOL JNM-GX-270 spectrophotometer and were referred to internal sodium 2, 2-dimethyl-2-silapentane-5-sulfonate (DSS).

Preparation of 1 and 2. $\mathrm{[Co(CO_3)(en)_2]Cl}$ was prepared as described by Pfeiffer and Angern.[4] A mixture of 5 g of $\mathrm{[Co(CO_3)(en)_2]Cl}$ and 2.7 g of L-tartaric acid in 50 cm^3 of water was refluxed for 5 h. The mixture was transferred to an evaporating dish and evaporated to dryness fully on a steam bath. The complete dryness was very important for increasing yields of the anionic species, **1** and **2**, and for reproducing cationic and neutral species in definite yields. An aqueous solution (50 cm^3) of the dry products was further refluxed for 5 h. The solution was added on a cation-exchange column (ϕ4×40 cm) of SP-Sephadex C-25 (Na form). In the first fraction, two anionic species were eluted together with water. Two anionic species were separated by the use of a QAE-Sephadex A-25 (Cl form) column (ϕ4×70 cm) and 0.1 mol dm^{-3} LiCl as the eluent. **1** was eluted from the first fraction and **2** from the second fraction. These were separately collected, concentrated under reduced pressure at about 30 °C for the prevention of decomposition, and precipitated by adding ethanol. The products were recrystallized several times from a mixture of water and ethanol. Yields 0.084 g, 1.7% for **1** and 0.005 g, 0.1% for **2** based on $\mathrm{[Co(CO_3)(en)_2]Cl}$. Found for **1**: Co, 10.7; C, 26.7; H, 5.3; N, 10.3%. Calcd for $\mathrm{C_{12}H_{30}N_4O_{15}CoLi}$: Co, 11.0; C, 26.9; H, 5.6; N, 10.5%. Found for **2**: Co, 10.9; C,25.7; H, 5.3; N, 10.1%. Calcd for $\mathrm{C_{12}H_{32}N_4O_{16}CoLi}$: Co, 10.6; C, 26.0; H, 5.8; N, 10.1%.

Preparation of the Single Crystal of 1. Complex **1** (0.1 g) was dissolved in water (3 cm^3) and then CsCl (0.1 g) was added to the solution. Ethanol was added slowly on the solution at room temperature until faint turbidity appeared and diffused into the solution. Several days after, red prismatic crystals were obtained. Crystals were formed in much better crystallinity in the presense of LiCl, NaCl, KCl, or CsCl than in the absence. No difference in crystallinity was found among the uses of these chlorides.

Crystal Structure Analysis of 1. The crystal used for the structural analysis was of approximately square cross section (0.3 mm in thickness) and 0.5 mm in length. Preliminary Weissenberg photographs taken with Cu $K\alpha$ radiation (λ=1.54184 Å) was assumed the crystal to be orthorhombic. The crystal was transferred to a Rigaku AFC-5 automated four-circle diffractometer at Rikkyo University and intensity data were collected using graphite-monochromated Mo $K\alpha$ radiation (λ=0.71073 Å). The lattice parameters were obtained by the least-squares refinement using 20 reflections ($20° \leqq 2\theta \leqq 25°$).

[#] The formal name of **1** is lithium (OC-6-12)-bis(ethylenediamine)bis{L-tartrato(2−)-$\mathrm{O^1}$}cobaltate(1−)trihydrate, that of **2** being lithium (OC-6-22)-bis(ethylenediamine)bis{L-tartrato-(2−)-$\mathrm{O^1}$}cobaltate(1−) tetrahydrate.

Crystal Data. $C_{12}H_{30}N_4O_{15}CoLi$, $M_r=536.26$, orthorhombic, space group $C222_1$, $a=12.008(1)$, $b=9.496(2)$, $c=18.524(4)$ Å, $U=2112.2(7)$ Å^3, $D_m=1.68$ g cm^{-3}, $D_c=1.69$ g cm^{-3}, $Z=4$, $\mu(\text{Mo } K\alpha)=9.37$ cm^{-1}, $F(000)=1120$.

Intensity data were to be collected by ω–2θ scan technique ($2° \leqq 2\theta \leqq 65°$) at a scan rate of 4° min^{-1} in ω. For weak reflections, measurements were repeated up to four times. Crystal stability was monitored by recording three standard reflections (200, $\bar{1}\bar{1}5$, 068) every 100 reflections, and no significant variation was observed. Intensities were corrected for Lorentz and polarization effects, but the absorption correction was not applied. For the structure determination and refinement, 1657 unique reflections with $|F_o| \geqq 3\sigma(|F_o|)$ were used. All calculations were made on a FACOM M-360 computer by using UNICS III Program System[5)] at the Computer Center of Rikkyo University. The structure was solved by the heavy-atom method and refined by the block-diagonal least-squares method. All hydrogen atoms, except for an OH group of the tartrate ions, were observed in difference Fourier syntheses. The hydrogen atom was introduced to calculated position assuming hydroxyl group. In the final stage, the structure was refined by the full-matrix least-squares method. The final R value is 0.0291 ($R=\sum||F_o|-|F_c||/\sum|F_o|$), and the R_w value is 0.0426 ($R_w=(\sum w\times(||F_o|-|F_c||)^2/\sum w|F_o|^2)^{1/2}$, where $w=1.0$) with equivalent isotropic temperature factors except hydrogen atoms, and with isotropic for hydrogen atoms. The atomic scattrering factors were taken from Ref. 6 for non-hydrogen atoms and from Ref. 7 for hydrogen atoms. The positional and thermal parameters are given in Table 1.

Tables of anisotropic thermal parameters, coordinates of hydrogen atoms and the complete F_o-F_c data are deposited as Document No. 9029 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Results and Discussion

Synthesis and Isolation. Several cationic and neutral Co(III) complexes containing L-tartrato and ethylenediamine ligands have been isolated as major product from a reaction mixture of $[Co(CO_3)(en)_2]^+$ with L-tartaric acid.[1-3)] Tartaric acid is potentially expected to coordinate to a metal in a variety of ways in response to degree of its deprotonation. The authors have attempted to isolate the anionic complexes by exploring the preparative conditions. Two anionic complexes were isolated by using QAE-Sephadex column chromatography although in low yields. Elemental analysis suggests that complexes **1** and **2** have the same composition, so **1** and **2** are geometrical isomers each other.

Table 1. Positional and Thermal Parameters for *trans*-Li[Co(tart)$_2$(en)$_2$]·3H$_2$O

Atom	x	y	z	B_{eq}/Å$^{2\,a)}$
Co	0.2267(1)	0.0000(0)	0.0000(0)	1.1(0)
O(1)	0.2257(6)	0.1411(5)	0.0728(3)	1.6(1)
O(2)	0.2265(6)	0.3377(6)	0.0061(3)	2.4(1)
O(3)	0.2393(6)	0.5021(8)	0.1223(3)	2.4(1)
O(4)	0.4038(6)	0.3032(9)	0.1659(4)	2.5(2)
O(5)	0.1806(6)	0.3887(8)	0.3881(3)	2.2(1)
O(6)	0.3644(6)	0.4347(8)	0.2911(4)	2.8(2)
O(7)	0.4360(7)	0.3565(8)	−0.1730(4)	3.0(2)
O(8)	0.5000(0)	0.073(1)	0.2500(0)	4.5(4)
N(1)	0.1090(7)	0.0936(9)	−0.0538(4)	1.7(2)
N(2)	0.3448(7)	0.0874(9)	−0.0569(4)	1.8(2)
C(1)	0.2249(7)	0.2734(7)	0.0646(4)	1.5(1)
C(2)	0.2159(7)	0.3572(8)	0.1345(4)	1.6(1)
C(3)	0.2931(7)	0.2990(8)	0.1926(4)	1.6(2)
C(4)	0.2794(8)	0.3823(8)	0.2632(4)	1.7(2)
C(5)	0.0031(8)	0.074(1)	−0.0145(5)	2.6(2)
C(6)	0.4507(8)	0.017(2)	−0.0405(6)	2.7(3)
Li	0.5000(0)	0.511(4)	0.2500(0)	2.7(5)
H(O4)$^{b)}$	0.061(9)	0.24(1)	−0.191(6)	2(2)

a) $B_{eq}=8/3\pi\sum_i\sum_j U_{ij}a^*_i a^*_j \boldsymbol{a}_i\cdot\boldsymbol{a}_j$. b) The hydrogen atom bound to the oxygen atom O(4) as hydroxyl group.

Molecular Structure of 1, *trans*-Li[Co{tart(2−)}$_2$(en)$_2$]·3H$_2$O. ORTEP drowing of the complex anion is shown in Fig. 1. Table 2 shows the selected intramolecular bond lengths and angles of the complex anion. The two tartrate(2−) anions coordinate as unidentate ligand to the cobalt atom through the oxygen atom of the carboxylato group, and the two tartrate anions are in trans position each other. The O(1)–Co–O(1′) bond angle is about 180°. The complex anion is of a slightly distorted octahedron. The C(1)–O(1) bond length of coordinated carboxylate ion is shorter than the C(4)–O(5) bond length of uncoordinated carboxylate ion. Other bond lengths and angles in the tartrato(2−) ligands agreed with those in the tartaric acid.

Generally, the conformation of ethylenediamine rings of trans type of bis(ethylenediamine)cobalt(III) complexes is $\delta\lambda$, with a few exceptions.[3,8-11)] However, the

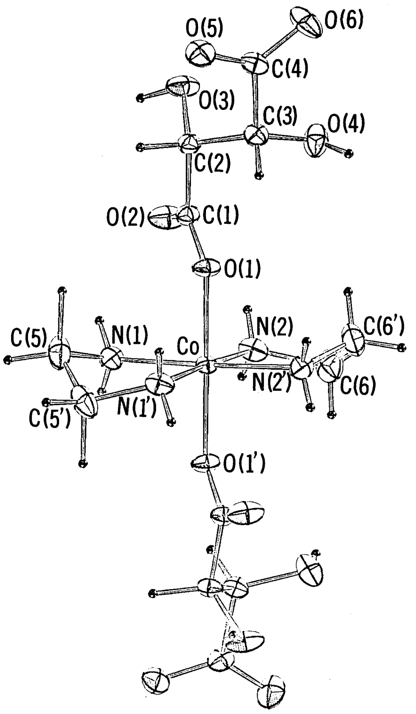

Fig. 1. ORTEP drawing and atomic numbering scheme of the *trans*-[Co(tart)$_2$(en)$_2$]$^-$ anion in *trans*-Li[Co(tart)$_2$(en)$_2$]·3H$_2$O.

Table 2. Selected Bond Lengths and Angles in *trans*-$[Co(tart)_2(en)_2]^-$ Anion

Bond length (l/Å)			
Co–O(1)	1.901(5)	Co–N(1)	1.945(8)
Co–N(2)	1.952(8)	C(1)–O(1)	1.266(9)
C(1)–O(2)	1.244(9)	C(4)–O(5)	1.27(1)
C(4)–O(6)	1.25(1)	C(1)–C(2)	1.52(1)
C(2)–C(3)	1.52(1)	C(3)–C(4)	1.54 (1)
N(1)–C(5)	1.48(1)	N(2)–C(6)	1.47(1)
C(5)–C(5′)[a]	1.50(1)	C(6)–C(6′)[a]	1.53(1)
Bond angle (ϕ/deg)			
O(1)–Co–N(1)	92.1(3)	O(1)–Co–N(2)	95.0(3)
O(1)–Co–N(1′)[a]	87.4(3)	O(1)–Co–N(2′)[a]	85.5(3)
O(1)–Co–O(1′)[a]	179.3(3)	N(1)–Co–N(2)	93.3(3)
N(1)–Co–N(1′)[a]	86.8(3)	N(2)–Co–N(2′)[a]	86.8(3)
N(1)–Co–N(2′)[a]	177.6(3)		
Co–O(1)–C(1)	128.0(5)	O(1)–C(1)–O(2)	126.2(7)
O(1)–C(1)–C(2)	114.7(6)	O(2)–C(1)–C(2)	119.1(6)
C(1)–C(2)–O(3)	110.9(6)	C(1)–C(2)–C(3)	111.6(6)
O(3)–C(2)–C(3)	110.1(6)	C(2)–C(3)–C(4)	110.4(6)
C(2)–C(3)–O(4)	108.6(7)	O(4)–C(3)–C(4)	112.5(7)
C(3)–C(4)–O(5)	115.7(7)	C(3)–C(4)–O(6)	118.1(8)
O(5)–C(4)–O(6)	126.2(7)		
Co–N(1)–C(5)	108.3(6)	Co–N(2)–C(6)	108.8(7)
N(1)–C(5)–C(5′)[a]	107.1(8)	N(2)–C(6)–C(6′)[a]	107.3(8)

a) Key to symmetry operation; x, $-y$, $-z$.

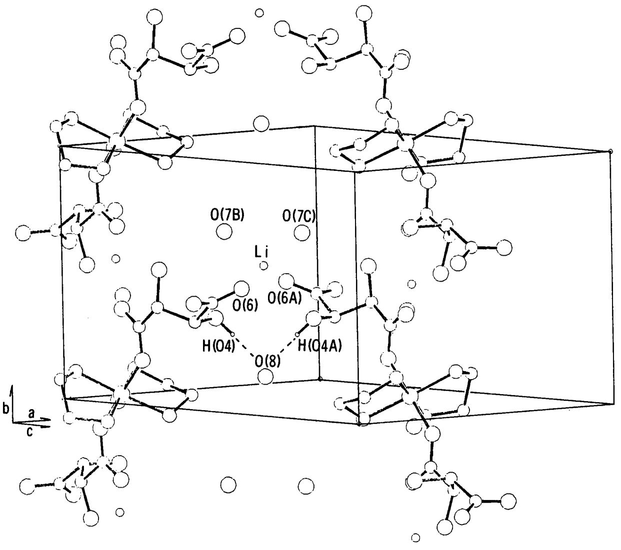

Fig. 2. View of packing around lithium ions. Hydrogen atoms are omitted except for H(O4) and H(O4A) binding O(8) by hydrogen bond. Key to the symmetry operation; A: $-x+1, y, -z+1/2$; B: $x, -y+1, -z$; C: $-x+1, -y+1, z+1/2$.

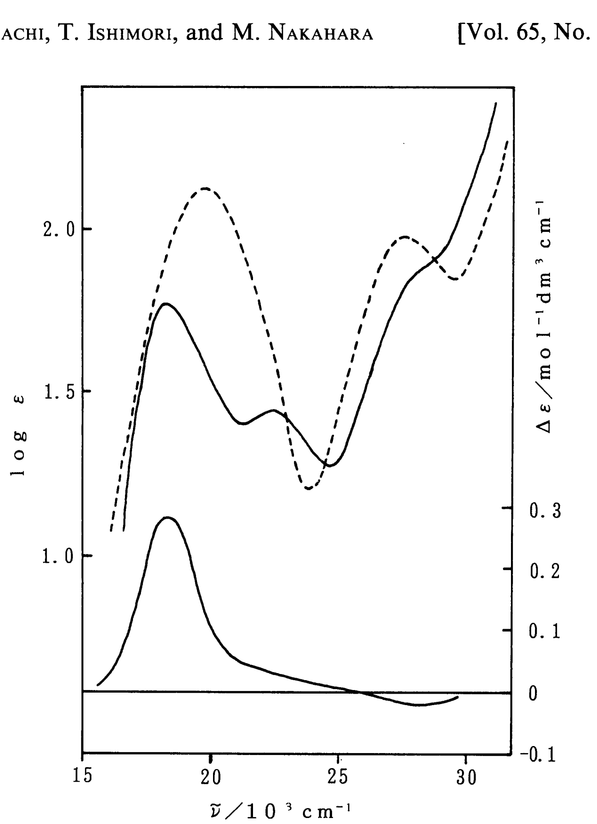

Fig. 3. UV-vis and CD spectra of $Li[Co(tart)_2(en)_2]$ in water: —— trans form, ---- cis form.

two ethylenediamine rings of this complex are in the $\delta\delta$ gauche conformation. Figure 2 shows a view of packing around lithium ion. A crystal water O(8) is bound with the hydroxyl group, H–O(4), of the tartrate anion through hydrogen bond, and the distance is 2.0(1) Å. The lithium ion is tetrahedrally surrounded by two carboxylate oxygens, O(6) and O(6A), of the tartrate ions and two oxygen atoms, O(7B) and O(7C), of the crystal waters. The interatomic lengths and angles are as follows; Li–O(6) and Li–O(7C) are 1.94(1) and 2.05(2) Å respectively, and O(6)–Li–O(6A), O(6)–Li–O(7B), O(6)–Li–O(7C), and O(7B)–Li–O(7C) are 136(2)°, 100.9(4)°, 105.7(4)°, and 104(1)° respectively. The lithium ion as the counter ion is considered to stabilize the crystal packing through the tetrahedral coordination around the lithium ion. This may be the reason for the fact that the complex was always crystallized as the lithium salt even from its solution containing a large excess of sodium, potassium, or cesium chloride.

UV-vis, NMR, and CD Spectra of 1 and 2. Figure 3 shows absorption spectra of **1** and **2** in water. The first absorption band of **1** split into two components at 18500 (ε/mol^{-1} dm^3 cm^{-1}=60.3) and 22400 cm^{-1} (ε=28.8), while for **2**, an absorption band at 20000 cm^{-1} (ε=134.9) was observed. According to Yamatera's rule,[12)] the first absorption band of a N_4O_2 type of cobalt(III) complex is expected to split into two components and degree of the split is larger in trans form than in cis form. For *trans*- or *cis*-$[Co(RCOO)_2N_4]^+$ (R=H, CH_3, C_2H_5, C_3H_7, C_4H_9 or C_5H_{11}; N=NH_3 or 1/2en) having the same chromophore as for **1** and **2**, the first absorption band splits into two bands for the trans isomer but not for the corresponding cis isomer.[13,14)] Thus, the first absorption bands of **1** and **2** support that **1** is trans form and **2** is cis form. The result of absorption spectrum for **1** consists with that of the structural analysis for **1**.

Resonance signals of ^1H NMR spectra for **1** in deuterium oxide due to methylene protons and amine protons of the ethylenediamine ligands were observed at 2.83 and 5.86 ppm, respectively, while for **2**, each two signals were observed at 2.57 and 2.88, and 6.01 and 6.19 ppm, respectively. Also, a resonance signal in ^{13}C NMR spectra due to methylene carbon of ethylenediamine ligands was observed at 47.43 ppm for **1**, and two signals were observed at 46.36 and 47.62 ppm for **2**. These observations indicate that **1** is trans form and **2** is cis form. Two resonance signals resulted from carboxylate carbon of the tartrato ligands were observed at 180.36 and 185.85 ppm for **1**, and at 180.51 and 185.47 ppm for **2** respectively, indicating that the tartrato ligands coordinate to the cobalt atom as carboxylato unidentate ligand.

A CD spectrum of the trans isomer is shown in Fig. 3 with the absorption spectra of trans and cis isomers. The trans isomer showed a positive CD peak at 18300 cm^{-1} ($\Delta\varepsilon$/mol^{-1} dm^3 cm^{-1}=0.28) which reflects vicinal effect due to two unidentate L-tartrato ligands. The additivity can be applied to the vicinal effect of the unidentate L-tartrato ligand, then $\Delta\varepsilon$ (per L-tartrato ligand) is 0.14. This value was similar to that observed for [Co{L-tart(2−)}(NH$_3$)$_5$]$^+$ ($\Delta\varepsilon$=0.10 at 19700 cm^{-1}).[15] On the other hand, in the cis isomer, the CD signs of the first and last parts in the elution reversed each other: the former showed a positive CD peak ($\Delta\varepsilon$=0.1) at 17400 cm^{-1} and a negative peak ($\Delta\varepsilon$=−0.3) at 20400 cm^{-1}, and the latter showed a negative CD peak ($\Delta\varepsilon$=−0.1) at 17400 cm^{-1} and a positive peak ($\Delta\varepsilon$=1.1) at 20400 cm^{-1}. This suggests that a pair of diastereomer of the cis isomer is partially resolved by the QAE-Sephadex A-25 column. Generally, cis form of bis(ethylenediamine) complex has two CD bands in region of the first absorption band, and the main CD band is positive provided the complex has Λ conformation.[16] This empirical low indicates that the first eluate mainly contains a Δ form and the last eluate a Λ form. The complete optical resolution could not be performed under the present conditions because of a small yield. The whole eluate of the cis isomer showed two CD peaks, $\Delta\varepsilon$=−0.05 at 17400 cm^{-1} and $\Delta\varepsilon$=0.48 at 20400cm^{-1}. This suggests that the Λ form yields more than the corresponding Δ form even if the vicinal effect is considered. The same result has been reported on the cationic complexes separated from the reaction products of [Co(CO$_3$)(en)$_2$]$^+$ with tartaric acid [2,17]

X-Ray crystal structure analysis of the trans isomer supports the interpretations for UV-vis, NMR and CD spectra. The results of the cis isomer also explain reasonably its structure.

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