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Structural Study of Optical Resolution. IX. The Crystal Structure of $(-)_{589}$-Tris(biguanide)cobalt(III) Chloride *d*-Tartrate Pentahydrate

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The crystal structure of the less-soluble diastereomeric salt, $(-)_{589}$-[Co(Hbg)$_3$]Cl(*d*-tart)·5H$_2$O, has been determined by X-ray analysis (R=0.056, 1277 reflections). The crystals are orthorhombic, with the space group of C222, Z=4, a=24.846(5), b=12.970(2), and c=8.645(2) Å. The main features of the crystal structure are as follows: (1) The complex cation and Cl$^-$ anion are arranged alternately along the b-axis to form an infinite spiral chain. The distances between N(Hbg) and Cl are 3.452 and 3.376 Å. (2) The tartrate ions exist as a dimeric unit whose structure closely resembles that of [Sb$_2$(d-tart)$_2$]$^{2-}$. Through the center of this dimeric unit pass three mutually orthogonal twofold axes. (3) There are short contacts between the Hbg ligands and the tartrate ions along the twofold axis of the complex; N(A2)···OT3 2.862, N(B2)···OT2 3.116, N(B3)···OT2 2.754, and N(B4)···OT1 2.963 Å. On the basis of these features, the chiral discrimination mechanism is discussed.

In the previous papers of this series,[1–3] the crystal structures of the diastereomeric salts composed of Λ-[M(en)$_3$]$^{3+}$ and *d*-tartrate ions (*d*-$C_4H_4O_6^{2-}$, abbreviated as *d*-tart), $(+)_{589}$-[Co(en)$_3$]Br(*d*-tart)·5H$_2$O,[1] Li{$(+)_{589}$-[Cr(en)$_3$]}(*d*-tart)$_2$·3H$_2$O,[2] and H{$(+)_{589}$-[Co(en)$_3$]}(*d*-tart)$_2$·3H$_2$O,[3] were determined. In all these crystals there exists a unique face-to-face ion-pair between the complex and *d*-tart; four carbon atoms of *d*-tart make a plane which is perpendicular to the threefold axis of the complex, and four oxygen atoms of *d*-tart are projecting toward the complex and facing the triangular face formed by three NH$_2$ groups of the complex. From these observations, we assumed that such a one-to-one ion-pair formation plays a dominant role in the chiral discrimination.[3] Our presumption was strongly supported by chromatographic separation of enantiomers using the *d*-tart solution as the eluent. The complete separation of the enantiomers was accomplished not only for [Co(en)$_3$]$^{3+}$,[4] but also for many octahedral complexes with three NH$_2$ groups in their triangular face,[5,6] including electrically neutral fac-[Co(β-alaninato)$_3$].[7] Consistently with the chromatographic results, the ion-association constant of *d*-tart proved to be greater for the Λ complex than for the Δ complex.[8–12]

On the other hand, it was reported that tris(biguanide)cobalt(III), [Co(Hbg)$_3$]$^{3+}$ ($C_2H_7N_5$, abbr. Hbg) could be separated into enantiomers *via* a diastereomeric salt containing both chloride and *d*-tart anions.[13] Here, it is interesting to note that the less-soluble diastereomeric salt has the [Co(Hbg)$_3$]Cl(*d*-tart)·5H$_2$O composition, which is quite analogous to that of [Co(en)$_3$]Br(*d*-tart)·5H$_2$O. Moreover, in both cases, the Λ complex forms the less-soluble diastereomeric salt with *d*-tart. The crystal structure of the optically active chloride salt, $(+)_{589}$-[Co(Hbg)$_3$]Cl$_3$·H$_2$O, has been determined by Snow;[14] in it biguanide ligands form almost planar chelate rings. The N–H bonds in the Hbg ligand are presumed to be different in nature from those in the ethylenediamine ligand. Thus, the chiral discrimination by *d*-tart in the [Co(Hbg)$_3$]$^{3+}$ complex is expected to be different from that in the [Co(en)$_3$]$^{3+}$ complex. We also attempted to determine the crystal structure of the less-soluble diastereomeric salt, $(-)_{589}$-[Co(Hbg)$_3$]Cl(*d*-tart)·5H$_2$O, in order to obtain the mode of chiral discrimination effected by the *d*-tart.

Experimental

Preparation of Compound. Biguanide sulfate and [Co(Hbg)$_3$]Cl$_3$ were prepared by the method given in the literature.[15,16] The less-soluble diastereomeric salt, $(-)_{589}$-[Co(Hbg)$_3$]Cl(*d*-tart)·5H$_2$O, was prepared by the procedure of Ray and Dutt.[13] The crystals thus obtained are thin, brownish orange plates. The optical purity of the crystals was checked by the CD measurement ($\Delta\varepsilon_{510}=-3.52$ and $\Delta\varepsilon_{452}=+4.76$).[17] Found: C, 19.15; H, 4.94; N, 33.33%. Calcd for $(-)_{589}$-[Co(Hbg)$_3$]Cl(*d*-tart)·5H$_2$O (4H$_2$O): C, 18.89 (19.44); H, 5.55 (5.38); N, 33.04 (34.01)%.

Crystallographic-data Collection. The unit-cell dimensions and crystal symmetry were initially checked from Weissenberg photographs taken with Ni $K\alpha$ radiation (λ=1.6591 Å). The results indicated an orthorhombic mmm Laue Symmetry. The systematic absence of *hkl* reflections when $h+k=2n+1$ suggested the following possible space groups: C222, Cmm2 (Cm2m), and Cmmm. Since the sample is optically active, the space group C222 was chosen; the later success of the structure determination confirmed the wisdom of this selection.

The intensities and cell dimensions were measured on a Rigaku AFC-5 automated four-circle diffractometer with Mo $K\alpha_1$ radiation (λ=0.70926 Å) monochromated by a graphite plate. The crystal size used was 0.39×0.19×0.08 mm. The unit-cell dimensions were refined by a least-squares treatment of the setting of 22 reflections. The crystal data were as follows: orthorhombic, space group C222, a=24.846(5), b=12.970(2), c=8.645(2) Å, D_m=1.51 g cm^{-3} (by flotation in a chloroform–bromoform mixture), Z=4, and D_c=1.52 g cm^{-3}. The intensity data were collected in the ω-2θ scan mode up to 2θ=55° with the scan rate of 16°/min (50 kV, 170 mA). The ω scan range was (1.0+0.45tanθ)°. Of the 1443 unique observed reflections, 1277 reflections with $|F_o|\geq 3\sigma(F_o)$ were used for the structure determination. Corrections for the absorption effect were neglected (μ(Mo $K\alpha$)=7.83 cm^{-1}).

Determination and Refinement of Crystal Structure

Since the number of formula units per unit-cell is four and the space group is C222, the central cobalt atom, one nitrogen atom of the $[Co(Hbg)_3]^{3+}$ cation, and the Cl^- anion should lie on a twofold axis. The position of the Co atom was determined from a three-dimensional Patterson map. Subsequent electron density maps calculated with the phase of the Co atom revealed the positions of the remaining non-hydrogen atoms. Several cycles of the block-diagonal least-squares refinement reduced the R value (defined as $\Sigma||F_o|-|F_c||/\Sigma|F_o|$) to 0.070. At this stage, all the hydrogen atoms were located from a difference Fourier map. The final refinement including these H atoms with isotropic temperature factors converged the R value to 0.056. The final difference map showed no peaks higher than 0.4 electron/Å^3, and the highest peak (*ca.* 0.4 electron/Å^3) remained around the OW2 water molecule.

In the refinement, the quantity minimized was $w(|F_o|-k|F_c|)^2$. The weighting scheme used was $w=(\sigma_{cs}{}^2+a|F_o|+b|F_o|^2)^{-1}$, where σ_{cs} is the standard deviation obtained from the counting statistics for each reflection; the values of a and b were 0.2 and 0.0009 respectively. All the atomic scattering factors, with corrections for the anomalous dispersion of Co and Cl, were taken from the International Tables for X-Ray Crystallography, Vol. IV.18)

All the computations were carried out by a HITAC 8700 computer at the Hiroshima University Information Processing Center. The computer programs used were FOUR-MMM19) and HBLS-IV, with a slight modification.20) An ORTEP drawing was carried out by the use of a computer system, XTL, in a Syntex R3 automated four-circle diffractometer.21) The final atomic parameters are listed in Table 1. The anisotropic thermal parameters and complete lists of the $|F_o|$ and $|F_c|$ values have been preserved by the Chemical Society of Japan (Document No. 8121).

Results and Discussion

The projections of the crystal structure along the c- and b-axes are shown in Figs. 1 and 2 respectively. The thermal ellipsoids in these figures are illustrated with a 50% probability. The crystallographic twofold axes of the space group C222 pass through the complex, *d*-tart, Cl^-, and three kinds of water molecules (OW1, OW2, and OW3).

Cation Geometry. The bond distances and angles for the complex cation are listed in Table 2. These values are in good agreement with those reported in previous works.14,22) However, there is a small but siginificant difference in geometry between the present results and those for $(+)_{589}$-$[Co(Hbg)_3]Cl_3\cdot H_2O$.14) In both crystals, the planarity of biguanide itself is nearly kept, but that of the chelate ring as a whole (including the metal atom) is lost. The dihedral angles between the plane of the biguanide ligand and the plane of Co and two donor nitrogen atoms are 6.9, 6.0, and 12.8° for the $(+)_{589}$-$[Co(Hbg)_3]Cl_3\cdot H_2O$. The mean value is 8.6°.

In contrast, in the present crystal, a crystallographic twofold axis passes through the chelate ring A along the direction Co···N(A3), and the dihedral angle is only 3.0°. The chelate ring A is approximately planar, as is shown in Table 3. On the other hand, the planarity of the chelate ring B is definitely broken (Table 3). The corresponding dihedral angle is 16.4°. This fairly large difference between their dihedral angles suggests that the *d*-tart interacts more strongly

TABLE 1. POSITIONAL AND THERMAL PARAMETERS FOR $(-)_{589}$-$[Co(Hbg)_3]Cl(d\text{-tart})\cdot 5H_2O$

Atom	x	y	z	B_{eq}/Å^2	Atom	x	y	z	B_{eq}/Å^2
Co	0.29836(5)	0.5	0.5	1.92	OW3	0.3715(6)	0.5	0.0	9.92
Cl	0.25	0.25	0.0924(4)	3.79	OW4	0.4438(3)	0.3392(6)	0.0269(9)	5.06
N(A1)	0.2435(2)	0.4281(5)	0.3886(8)	2.39	H(NA1)	0.255(5)	0.381(10)	0.331(14)	4.29
N(A2)	0.1591(3)	0.3666(7)	0.3240(11)	3.87	H(NA21)	0.132(3)	0.380(6)	0.344(10)	1.04
N(A3)	0.1671(3)	0.5	0.5	3.26	H(NA22)	0.178(4)	0.322(8)	0.250(12)	1.88
N(B1)	0.3526(2)	0.4265(5)	0.3884(7)	2.11	H(NA3)	0.133(6)	0.5	0.5	4.14
N(B2)	0.4322(3)	0.3323(6)	0.3687(9)	3.29	H(NB1)	0.354(4)	0.442(8)	0.296(14)	2.76
N(B3)	0.3823(3)	0.3231(5)	0.5891(8)	2.57	H(NB21)	0.452(4)	0.279(9)	0.415(14)	3.71
N(B4)	0.3356(3)	0.2580(7)	0.7950(9)	3.87	H(NB22)	0.428(4)	0.326(9)	0.288(14)	3.11
N(B5)	0.2997(3)	0.3933(5)	0.6551(8)	2.35	H(NB3)	0.408(4)	0.275(9)	0.632(13)	3.09
C(A1)	0.1922(3)	0.4315(6)	0.4020(10)	2.58	H(NB41)	0.310(4)	0.264(8)	0.872(12)	2.60
C(B1)	0.3870(3)	0.3639(6)	0.4436(10)	2.44	H(NB42)	0.358(4)	0.249(10)	0.827(14)	3.37
C(B2)	0.3370(3)	0.3285(6)	0.6819(9)	2.30	H(NB5)	0.270(4)	0.390(10)	0.714(15)	4.22
CT1	0.0338(3)	0.6337(6)	0.2373(10)	2.45	H(CT2)	−0.033(4)	0.568(8)	0.119(14)	2.85
CT2	−0.0125(3)	0.5550(6)	0.2241(9)	2.13	H(OT3)	−0.032(4)	0.612(8)	0.391(13)	2.35
OT1	0.0652(2)	0.6422(5)	0.1273(7)	3.16	H(OW1)	0.109(6)	0.573(11)	0.002(32)	9.01
OT2	0.0352(3)	0.6848(5)	0.3626(7)	3.51	H(OW2)	0.249(6)	0.430(10)	0.033(18)	6.02
OT3	−0.0500(2)	0.5645(4)	0.3473(7)	2.47	H(OW3)	0.382(3)	0.524(7)	0.069(11)	1.93
OW1	0.1440(5)	0.5	0.0	7.66	H(OW41)	0.453(3)	0.380(9)	−0.045(15)	3.92
OW2	0.2606(6)	0.5	0.0	9.60	H(OW42)	0.451(4)	0.276(9)	0.002(24)	5.03

$B_{eq}=(8/3)\pi^2(U_{11}+U_{22}+U_{33})$. The anisotropic thermal parameters bave been preserved by the Chemical Society of Japan.

with the Hbg B ligand than with the Hbg A ligand. Indeed, the atoms in the chelate ring B and the α-hydroxy carboxylate moiety of *d*-tart lie on nearly the same plane, as is shown in Fig. 3.

Anion Geometry. A crystallographic twofold axis passes through the middle point of *d*-tart. The bond distances and angles for *d*-tart are listed in Table 2. These values coincide with those reported in previous works.[23] The five non-hydrogen atoms of each α-hydroxy carboxylate moiety lie approximately on a plane, as is shown in Fig. 3. The dihedral agnle between the planes of two moieties is 50.8°. This value is within the range of hitherto reported values, which show a wide variation in many crystals: *ca.* 50—75° (av. 66°) for $[\mathrm{Sb}_2(d\text{-tart})_n(l\text{-tart})_{2-n}]^{2-}$ ($n=1$ or 2) and analogous compounds, and *ca.* 44—89° (av. 54°) for *d*- and *l*-tartrates.[24]

In addition, a unique dimeric structure of two *d*-tart anions is formed in the present crystal. The structure of this dimeric unit and that of $[\mathrm{Sb}_2(d\text{-tart})_2]^{2-}$ [25] are compared in Fig. 4. Three mutually orthogonal crystallographic twofold axes pass through the center of this dimeric unit ($x=0$, $y=1/2$, $z=1/2$). The structure of this dimeric unit closely resembles that of $[\mathrm{Sb}_2(d\text{-tart})_2]^{2-}$ if two Sb atoms are left out of consideration. However, the distances between the two hydroxyl oxygen atoms, 3.13 and 3.63 Å, in the dimeric unit differ from the corresponding distances, 3.69 and 3.08 Å, in $[\mathrm{Sb}_2(d\text{-tart})_2]^{2-}$, as is shown by

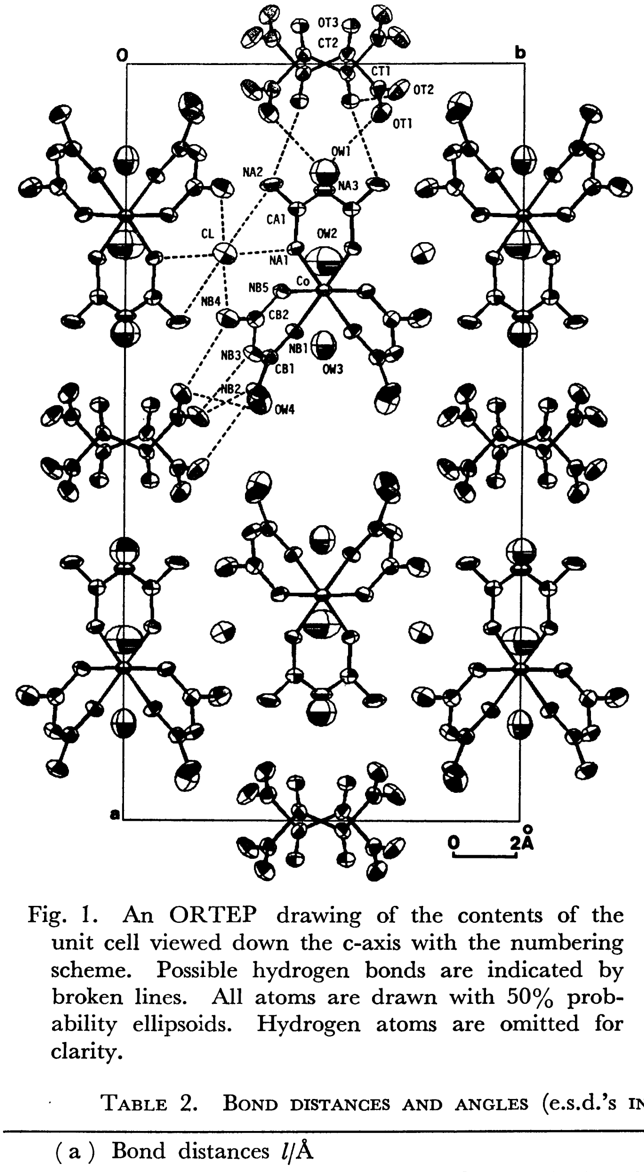

Fig. 1. An ORTEP drawing of the contents of the unit cell viewed down the c-axis with the numbering scheme. Possible hydrogen bonds are indicated by broken lines. All atoms are drawn with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.

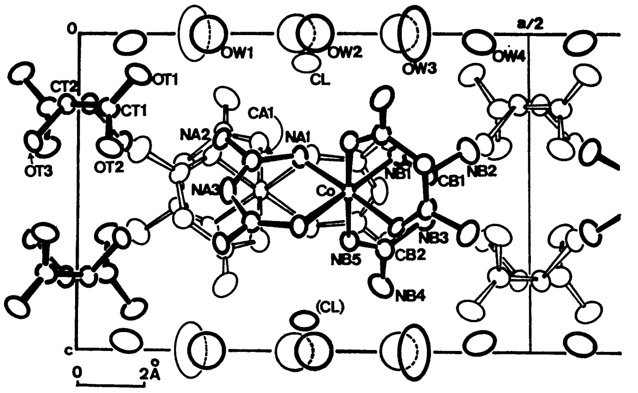

Fig. 2. A perspective drawing of the contents of the unit cell viewed down the b-axis with the numbering scheme.

TABLE 2. BOND DISTANCES AND ANGLES (e.s.d.'s IN PARENTHESES) FOR $(-)_{589}$-[Co(Hbg)$_3$]Cl(d-tart)·5H$_2$O

(a) Bond distances l/Å

Co-N(A1)	1.911(7)	N(B5)-C(B2)	1.273(10)	C(A1)-N(A2)	1.355(13)	CT1-OT1	1.235(11)
Co-N(B1)	1.913(7)	C(A1)-N(A3)	1.378(12)	C(B1)-N(B2)	1.358(11)	CT1-OT2	1.271(11)
Co-N(B5)	1.927(7)	C(B1)-N(B3)	1.369(11)	C(B2)-N(B4)	1.339(12)	CT2-OT3	1.420(10)
N(A1)-C(A1)	1.282(11)	C(B2)-N(B3)	1.384(11)	CT1-CT2	1.542(12)	CT2-CT2$^{\text{i}}$	1.555(16)
N(B1)-C(B1)	1.272(10)						

(b) Bond angles ϕ/°

N(A1)-Co-N(A1)$^{\text{ii}}$	89.1(3)	N(A1)-C(A1)-N(A3)	121.9(8)	N(B3)-C(B2)-N(B4)	114.3(8)
N(B1)-Co-N(B5)	88.9(3)	N(B1)-C(B1)-N(B3)	122.2(8)	OT1-CT1-OT2	126.3(8)
Co-N(A1)-C(A1)	130.3(6)	N(B5)-C(B2)-N(B3)	121.3(7)	OT1-CT1-CT2	118.3(8)
Co-N(B1)-C(B1)	127.1(6)	C(A1)-N(A3)-C(A1)$^{\text{ii}}$	126.1(8)	OT2-CT1-CT2	115.4(7)
Co-N(B5)-C(B2)	127.9(6)	C(B1)-N(B3)-C(B2)	125.7(7)	CT1-CT2-OT3	112.1(6)
N(A1)-C(A1)-N(A2)	122.5(9)	N(A3)-C(A1)-N(A2)	115.6(8)	CT1-CT2-CT2$^{\text{i}}$	108.0(7)
N(B1)-C(B1)-N(B2)	124.7(8)	N(B3)-C(B1)-N(B2)	113.1(7)	OT3-CT2-CT2$^{\text{i}}$	110.0(6)
N(B5)-C(B2)-N(B4)	124.4(8)				

Roman numerals as superscripts refer to the following equivalent positions, relative to the reference atom at x, y, z: i $(-x, 1-y, z)$, ii $(x, 1-y, 1-z)$.

the asterisk in Fig. 4. The central C–C bonds of the two d-tart anions in the $[Sb_2(d\text{-tart})_2]^{2-}$ are nearly parallel, but those in the dimeric unit are not parallel.

Crystal-packing Mode. The crystal-packing modes viewed down along the c- and b-axes are shown in Figs. 1 and 2 respectively. The intermolecular distances and angles are summarized in Table 4.

The complex cation and Cl anion are arranged alternately along the b-axis, as is shown in Fig. 1. Short contacts are formed between the N atoms of the Hbg A ligand and the Cl^- anion. The arrangement of the complex cation, $(-)_{589}$-$[Co(Hbg)_3]^{3+}$, and Cl^- can be regarded as an infinite spiral chain along the twofold screw, which is parallel to the b-axis through the ($x=1/4$, $z=1/2$) position, as is clearly shown in Fig. 2. Figure 5 shows the schematic illustration of the present crystal structure. If the complex cation and the Cl^- anion are linked alternately, as is shown by arrows in Fig. 5, the spiral is left-handed. Here, it should be noted that such a spiral arrangement of the complex cation, $(+)_{589}$-$[Co(Hbg)_3]^{3+}$, and the Cl^- anion is also found in the crystal structure of $(+)_{589}$-$[Co(Hbg)_3]Cl_3 \cdot H_2O$,[14] but the spiral is the opposite, that is, right-handed.

There are short contacts between the Hbg ligands and the dimeric unit $(d\text{-tart})_2{}^{4-}$, as is shown in Table 4. It is worth noting that, while the hydroxyl oxygen atom of the d-tart forms a short contact with the Hbg

Table 3. Distances of atoms from least-squares planes in Ångstroms

(a) Complex Ring A		Ring B		(b) Tartrate	
Co	−0.013	Co	−0.140	CT1	0.015
N(A1)	−0.072	N(B1)	0.213	CT2	0.080
N(A2)	0.077	N(B2)	−0.017	OT1	−0.047
N(A3)	0.008	N(B3)	−0.206	OT2	0.016
N(A2)^{ii}	−0.059	N(B4)	0.098	OT3	−0.061
N(A1)^{ii}	0.064	N(B5)	0.066		
C(A1)	−0.009	C(B1)	0.019		
C(A1)^{ii}	0.017	C(B2)	−0.024		

Plane equations. Each plane is represented by $lx'+my'+nz'+p=0$ with respect to the orthogonal axes, where x', y', and z' are coordinates in Å.

l	−0.00628	−0.56310	0.54287
m	−0.68237	−0.65314	−0.72340
n	0.73098	−0.50629	0.42660
p	1.29976	10.45853	4.62939

Angles between planes (rings): A and B, 94.5°; A and B^{ii}, 95.1°; B and B^{ii}, 66.2°.

Roman numerals as superscripts refer to the following equivalent positions, relative to the reference atom at x, y, z: ii (x, $1-y$, $1-z$).

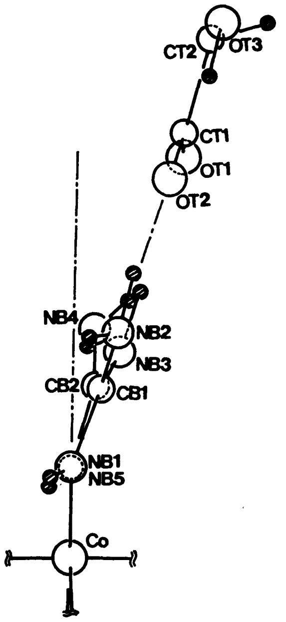

Fig. 3. Projecting of Hbg(B) ligand and α-hydroxycarboxylate moiety of d-tartrate viewed down the direction of N(B1)···N(B5).

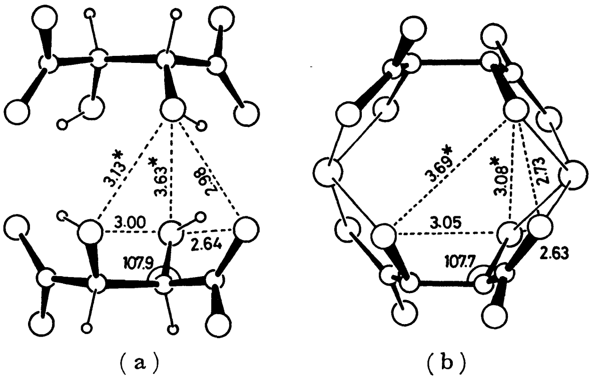

Fig. 4. (a) Structure of the $(d\text{-tart})_2{}^{4-}$ dimeric unit. (b) Structure of $[Sb_2(d\text{-tart})_2]^{2-}$. Short contacts are indicated by broken lines and their values are in Å.

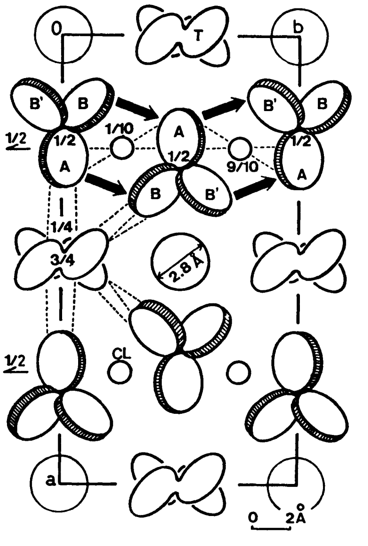

Fig. 5. A schematic drawing of the crystal structure viewed down the c-axis. A, B, and B′ are biguanide ligands. T and CL mean d-tartrate and chloride anions respectively. The numerals represent the fractional z-coordinates for the center of each molecule. Big open circles indicated empty channels. Water molecules are omitted for clarity.

TABLE 4. SELECTED INTERMOLECULAR DISTANCES AND ANGLES

D-H···A	D···A l/Å	H···A l/Å	D-H···A ϕ/°
N(A1)-H(NA1)···Cl	3.452(8)	2.68(13)	156(16)
N(A2)-H(NA22)···Cl	3.376(10)	2.44(10)	160(8)
N(A2)-H(NA21)···OT3$^{\mathrm{i}}$	2.862(12)	2.17(8)	166(9)
N(B2)-H(NB21)···OT2$^{\mathrm{iii}}$	3.116(11)	2.30(12)	145(10)
N(B2)-H(NB21)···OT2$^{\mathrm{iv}}$	3.197(11)	2.44(12)	137(10)
N(B3)-H(NB3)···OT2$^{\mathrm{iii}}$	2.754(10)	1.83(12)	159(11)
N(B4)-H(NB41)···Cl$^{\mathrm{v}}$	3.338(9)	2.41(11)	169(9)
N(B4)-H(NB42)···OT1$^{\mathrm{iii}}$	2.963(11)	2.38(13)	151(14)
OT1···OT3$^{\mathrm{i}}$	3.309(9)	—	—
OT2···OT2$^{\mathrm{vi}}$	2.951(14)	—	—
OT2···OT3$^{\mathrm{i}}$	3.258(9)	—	—
OT3$^{\mathrm{vii}}$-H(OT3)···OT2	2.977(9)	2.33(12)	133(10)
OT3···OT3$^{\mathrm{i}}$	2.996(12)	—	—
OT3···OT3$^{\mathrm{ii}}$	3.126(12)	—	—
OW1-H(OW1)···OT1	2.905(15)	1.78(28)	142(20)
OW1···OW2	2.898(19)	—	—
OW2-H(OW2)···Cl	3.350(14)	2.11(21)	151(19)
OW2···OW3	2.754(20)	—	—
OW3-H(OW3)$^{\mathrm{viii}}$···OW4	2.763(16)	2.48(10)	105(9)
OW4-H(OW42)···OT1$^{\mathrm{vii}}$	2.890(11)	2.11(21)	151(19)
OW4···OW4$^{\mathrm{ix}}$	2·833(16)	—	—

Roman numerals as superscripts refer to the following equivalent positions, relative to the reference atom at x, y, z:

i ($-x$, $1-y$, z), ii (x, $1-y$, $1-z$), iii ($1/2-x$, $-1/2+y$, $1-z$),
iv ($1/2+x$, $-1/2+y$, z), v (x, y, $1+z$), vi ($-x$, y, $1-z$),
vii ($1/2-x$, $-1/2+y$, $-z$), viii (x, $1-y$, $-z$), ix ($1-x$, y, $-z$).

D, Hydrogen donor; A, Hydrogen acceptor.

A ligand, the carboxylate oxygen atoms of the *d*-tart form short contacts with the Hbg B ligand. All short contacts are formed along the twofold axes of the complex.

The positions of the water molecules are also shown in Fig. 2. There are four kinds of crystallographically independent water molecules. Three of them, OW1, OW2, and OW3, lie on a twofold axis parallel to the a-axis at the ($y=1/2$, $z=0$) position. The fourth water molecule, OW4, occupies the general position, but its z-coordinate ($z=0.0269$) is nearly equal to zero. Therefore, all the water molecules form a sheet on the ab plane at $z=0$.

The most remarkable feature of the present crystal is that a large empty channel with a diameter of *ca.* 2.8 Å passes through the ($x=1/2$, $y=1/2$) position along the c-axis, as is shown in Fig. 5. The size of the diameter is estimated from the van der Waals radii of the N(B2) and OW4 atoms[26] which surround this channel. The overall crystal-packing mode is highly symmetrical in comparison with those of the diastereomeric salts of $[Co(en)_3]^{3+}$–*d*-tart systems.

Chiral Discrimination Mode. As has been descrived above, there is no one-to-one intimate ion-pair of the complex cation and *d*-tart anion in the present crystal. This is a remarkable difference as compared with the case of the corresponding $(+)_{589}$-$[Co(en)_3]Br(d\text{-tart})\cdot 5H_2O$ crystal,[1] in which a unique one-to-one ion-pair, called "face-to-face" close contact, has been found. It has been proposed, on the basis of the CD change on the addition of *d*-tart, that *d*-tart probably discriminates the Λ- and Δ-forms of $[Co(en)_3]^{3+}$ through the formation of such a unique face-to-face close contact.[27]

An attempt was then made to see if any change in the CD spectrum of the optically active $[Co(Hbg)_3]^{3+}$ in solution is observed upon the addition of *d*-tart. No appreciable change was detected.[28] Another attempt was also made to see if the CD spectrum was induced for the racemic complex salt by the addition of *d*-tart, but no CD spectrum was observed. We also tried to separate the racemic $[Co(Hbg)_3]^{3+}$ ions into enantiomers through an SP-Sephadex ion-exchange column, using the *d*-tart solution as the eluent, but no separation was achieved. These facts suggest that the individual *d*-tart ion can not discriminate the chirality of the individual $[Co(Hbg)_3]^{3+}$ complex ion.

Therefore, it should be considered that the crystal-packing mode as a whole is responsible for the chiral discrimination in the present $[Co(Hbg)_3]^{3+}$–*d*-tart system. Figure 5 shows the schematic illustration of the left-handed spiral chain $\{\Lambda\text{-}[Co(Hbg)_3]Cl\}_\infty$. A similar but right-handed spiral chain is also found in the crystal of $(+)_{589}$-$[Co(Hbg)_3]Cl_3\cdot H_2O$. Therefore, it is reasonable to presume that $[Co(Hbg)_3]^{3+}$ ions have a strong tendency toward the formation of an infinite spiral chain in the presence of Cl^- ions. The questions are why such spiral chains of the same chirality come together to form a crystal, and why the crystal is less-soluble in the present case. In relation to those points, it must be noted that a layer is formed on the ab plane, linked by hydrogen bonds between $\{\Lambda\text{-}[Co(Hbg)_3]Cl\}_\infty$ and $(d\text{-tart})_2^{4-}$, as is shown in Figs. 2 and 5. Between these layers, a sheet composed of water molecules is stacked along the c-axis; this prevents a strong interaction between these layers along the c-axis. Therefore, it can be considered that a strong interaction is present only in a layer structure of $\{\Lambda\text{-}[Co(Hbg)_3]Cl\}_\infty$ and $(d\text{-tart})_2^{4-}$ on the ab plane. The strong interaction in this layer is probably attributable to the hydrogen bonding. If the absolute configuration of the complex changes from Λ to Δ, the spiral chain would change from left-handed to right-handed, and a discrepancy would take place on the N–H···O hydrogen bonding between the right-handed spiral chains, $\{\Delta\text{-}[Co(Hbg)_3]Cl\}_\infty$, and the dimeric unit, $(d\text{-tart})_2^{4-}$, so that a reasonable crystal packing could not be formed in this layer. In other words, the *d*-tart is locked by the left-handed spiral chains, $\{\Lambda\text{-}[Co(Hbg)_3]Cl\}_\infty$, formed along the b-axis. Therefore, it seems that the discrimination of optical isomers in this crystal originates in the formation of such a "lock-in-column" structure through the strong hydrogen-bond network on the ab plane. The crystal structures of several less-soluble diastereomeric salts, $(+)_{589}$-$[Ni(bpy)_3]_2Cl_2(d\text{-tart})\cdot nH_2O$,[29] $(+)_{589}$-$[Ru(bpy)_3]_2Cl_2(d\text{-tart})\cdot nH_2O$,[30] $\Delta\text{-}[Co(bpy)_3]d\text{-tart}\cdot nH_2O$,[30] and $(+)_{589}$-$[Co(tame)_2]Cl(d\text{-tart})\cdot 5.4H_2O$,[31] have been determined. In these crystals, the dimeric unit of *d*-tart anions is not found. Thus, it is probable that, between the $\{\Lambda\text{-}[Co(Hbg)_3]Cl\}_\infty$ spiral chain and *d*-tart anions, there is a stereospecific interaction which stabilizes the dimeric unit of *d*-tart anions, and the formation of the dimeric unit, $(d\text{-tart})_2^{4-}$, plays a dominant part in the optical resolution of $[Co(Hbg)_3]^{3+}$, using *d*-tart as a resolving agent *via* the diastereomeric salt.

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References

1) Y. Kushi, M. Kuramoto, and H. Yoneda, *Chem. Lett.*, **1976**, 135.
2) Y. Kushi, M. Kuramoto, and H. Yoneda, *Chem. Lett.*, **1976**, 339.
3) T. Tada, Y. Kushi, and H. Yoneda, *Chem. Lett.*, **1977**, 379.
4) Y. Yoshikawa and K. Yamasaki, *Inorg. Nucl. Chem. Lett.*, **6**, 523 (1970).
5) M. Kojima, H. Takayanagi, and J. Fujita, *Bull. Chem. Soc. Jpn.*, **50**, 1891 (1977).
6) H. Yoneda, *J. Liquid Chromatogr.*, **2**, 1157 (1979).
7) H. Yoneda and T. Yoshizawa, *Chem. Lett.*, **1976**, 707.
8) K. Ogino and U. Saito, *Bull. Chem. Soc. Jpn.*, **40**, 826 (1967).
9) B. Norden, *Acta Chem. Scand.*, **26**, 111 (1972).
10) H. Yoneda, K. Miyoshi, S. Suzuki, and T. Taura, *Bull. Chem. Soc. Jpn.*, **47**, 1661 (1974).
11) H. Yoneda and T. Taura, *Chem. Lett.*, **1977**, 63.
12) T. Taura, H. Tamada, and H. Yoneda, *Inorg. Chem.*, **17**, 3127 (1978).
13) P. Ray and N. K. Dutt, *J. Indian Chem. Soc.*, **18**, 289 (1941).
14) M. R. Snow, *Acta Crystallogr., Sect. B*, **30**, 1850 (1974).
15) D. Karipides and W. C. Fernelius, *Inorg. Synth.*, Vol. VII, 56 (1963).
16) P. Ray and N. K. Dutt, *J. Indian Chem. Soc.*, **16**, 621 (1939).
17) K. Igi, T. Yasui, J. Hidaka, and Y. Shimura, *Bull. Chem. Soc. Jpn.*, **44**, 426 (1971).
18) "International Tables for X-Ray Crystallography," Kynoch Press, Birmingham (1974), Vol. IV, pp. 72—79, 149.
19) Y. Kushi, unpublished work.
20) T. Ashida, "The Universal Crystallographic Computation Program System," ed by T. Sakurai, The Crystallographic Society of Japan (1967).
21) C. K. Johnson, ORTEP, Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee, U. S. A., 1965.
22) W. C. Moucharafieh, P. G. Eller, J. A. Bertrand, and D. J. Royer, *Inorg. Chem.*, **17**, 1220 (1978).
23) For example, J. M. Bijvoet, A. F. Peerdeman, and A. J. van Bommel, *Nature*, **168**, 271 (1951); R. Sadanaga, *Acta Crystallogr.*, **3**, 416 (1950); S. Perez, *ibid., Sect. B*, **33**, 1083 (1977).
24) R. E. Tapscott, *Coordin. Chem. Rev.*, **4**, 323 (1969).
25) A. Miyanaga, Y. Kushi, and H. Yoneda, Presented at the 41st National Meeting of the Chemical Society of Japan, Osaka, March 1980, Abstr. I, 3L02.
26) L. Pauling, "The Nature of The Chemical Bond," 3rd ed, Cornell University Press, Ithaca (1960), p. 260.
27) M. Fujita and H. Yamatera, *Bull. Chem. Soc. Jpn.*, **49**, 1301 (1976).
28) The CD change of $[Co(Hbg)_3]^{3+}$ reported by G. R. Brubaker and L. E. Webb (*J. Am. Chem. Soc.*, **91**, 7199 (1969)) upon the addition of PO_4^{3-} is attributed to the deprotonation of the complex in a basic solution, leading to neutral $[Co(bg)_3]$[17] rather than to the stereoselective association of the complex with PO_4^{3-} along its C_3 axis.
29) A. Wada, C. Katayama, and J. Tanaka, *Acta Crystallogr., Sect. B*, **32**, 3194 (1976).
30) T. Tada, Y. Kushi, and H. Yoneda, Presented at the 30th Annual Meeting on Coordination Chemistry of Japan, Tokyo, October 1980, Abstr. No. 2C03.
31) R. J. Geue and M. R. Snow, *Inorg. Chem.*, **16**, 231 (1977).