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Crystal Structure and Absolute Configuration of *d*-Tartaric Acid-$(+)^{\rm CD}_{500}$-Tris(2-aminoethanesulfenato)cobalt(III)-Water (1/1/1)

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The crystal structure and absolute configuration of diastereomeric molecular compound, *d*-$C_4H_6O_6\cdot(+)^{\rm CD}_{500}$-$[Co\{S(O)CH_2CH_2NH_2\}_3]\cdot H_2O$, were determined by the X-ray diffraction method. The crystals are orthorhombic with space group $P2_12_12_1$, $Z=4$, and $a=13.034(4)$, $b=13.559(6)$, and $c=11.048(8)$ Å. The rifinement of 1724 reflections (Mo $K\alpha$ radiation) led to $R=0.068$. The complex molecule has the configuration *fac*(*S*)-Λ-(δ,δ,δ)-(*R*, *R*, *R*). All amino groups and the sulfenato oxygen atoms form hydrogen bonds with *d*-tartaric acid and/or water molecules three-dimensionally, which is responsible for the formation of the novel diastereomeric molecular compound.

Free sulfenic acids are recognized as important intermediates in reactions of many sulfur-containing organic compounds,[1,2] but a few ones have ever been isolated[1-3] because of the instability.[2,4,5] Some sulfenic acids which are S-coordinated to a cobalt(III) ion are stabler than their corresponding free acids,[6-11] their complexes providing a means for investigating the chemistry of sulfenic acids. Furthermore, sulfenato complexes are important for an understanding of redox reactions associated with metal-sulfur enzymes.[12]

The previous letter[11] reported the preparation and optical resolution for *fac*(*S*)-$[Co\{S(O)CH_2CH_2NH_2\}_n\{S(O)_2CH_2CH_2NH_2\}_{3-n}]$ type (n=3, 2, 1, and 0). In particular, one of the isomers of $[Co\{S(O)CH_2CH_2NH_2\}_3]$ was resolved by means of preferential crystallization of a diastereomeric molecular compound with *d*-tartaric acid, which is the first example of optical resolution by molecular compound formation in the field of metal complex chemistry. The crystal structure determination of this molecular compound, *d*-tartaric acid-$(+)^{\rm CD}_{500}$-tris(2-aminoethanesulfenato)cobalt(III)-water (1/1/1), is especially of interest in connection with (1) the absolute stereochemistry of this complex (*i.e.*, the absolute configuration about the cobalt center (Δ or Λ) and those of the three asymmetric sulfur donor atoms (*R* or *S*)), (2) the intramolecular bond distances in comparison with those of monosulfenato complex $[Co\{S(O)CH_2CH_2NH_2\}(en)_2](SCN)_2$,[10] and (3) intermolecular interactions among the complex, *d*-tartaric acid, and water in the packing (en=ethylenediamine).

Experimental

Preparation of Compound. The diastereomeric molecular compound was prepared by the reported procedure.[11] Recrystallization of the compound from an ethanol-water (2 : 1) solution gave orange-red crystals in the form of rectangular prism. Found: C, 23.72; H, 5.22; N, 8.35%. Calcd for *d*-$C_4H_6O_6\cdot(+)^{\rm CD}_{500}$-$[Co\{S(O)CH_2CH_2NH_2\}_3]\cdot H_2O=C_{10}H_{26}N_3O_{10}S_3Co$: C, 23.86; H, 5.21; N, 8.35%.

Data Collection. Precession photographs exhibited systematic absences h=odd for $h00$, k=odd for $0k0$, and l=odd for $00l$, indicating the unique space group $P2_12_12_1$. An orange-red crystal, of approximate dimensions 0.18 mm × 0.20 mm × 0.30 mm, was mounted with its long dimension along the axis of a glass fiber to protect it from moisture. The diffraction intensities were measured using a Rigaku four-circle diffractometer, with a graphite monochromatized Mo $K\alpha$ radiation (λ=0.71069 Å). Accurate lattice parameters were obtained by least-squares refinement of ten high angle reflections. The crystal data are summarized in Table 1. Three standard reflections fluctuated within 4% in intensity over the time of data collection. Within the sphere $2\theta<50°$, 1968 unique reflections were obtained. Among them 1724 reflections were $|F_o|>3\sigma_{cs}$ (σ_{cs} is the standard deviation of F in counting statistics). Only these reflections were used for the structure determination and refinement. No absorption correction was applied.

TABLE 1. CRYSTAL DATA

$C_{10}H_{26}N_3O_{10}S_3Co$	$F.W.=503.44$
Orthorhombic	Space group $P2_12_12_1$
$a=13.034(4)$ Å	
$b=13.559(6)$ Å	
$c=11.048(8)$ Å	
$U=1952.49$ Å^3	
$D_m=1.70(5)$ g cm^{-3} (by flotation)	
$D_c=1.72$ g cm^{-3}	$Z=4$
μ(Mo $K\alpha$)=13.44 cm^{-1}	

Structure Solution and Refinement. The structure was solved by the usual heavy-atom method; the positions of cobalt and sulfur atoms were picked up by means of the Patterson synthesis, and all the nonhydrogen atoms were located by the subsequent Fourier synthesis. Absolute configurations of the two asymmetric carbon atoms of *d*-tartaric acid were fitted to those reported previously.[13] Therefore, the absolute configuration of the metal complex molecule, $[Co\{S(O)CH_2CH_2NH_2\}_3]$, was determined definitely. The structure was refined by the block-diagonal least-squares method with the positional and isotropic thermal parameters for all nonhydrogen atoms. Further subsequent refinement was carried out using anisotropic thermal parameters for all nonhydrogen atoms. In the last cycles of least-squares refinement, 245 parameters were varied including an overall thermal parameter, a scale factor, positional and anisotropic thermal parameters for all nonhydrogen atoms. Convergence was achieved with $R=0.075$ ($R=\sum||F_o|-|F_c||/\sum|F_o|$). Although no hydrogen position was detected from the difference electron density map, hydrogen positions except those of carboxyl and hydroxyl groups of *d*-tartaric acid and those of water were tentatively calculated based on the following conditions; N-H=0.87 Å, C-H=0.97 Å, and tetrahedral geometry. Postulating B=4.0 Å^3 for each H atom, these twenty H atoms were added to the least-squares refinement, which gave the final R value of 0.068.

Atomic scattering factors from International Tables for

X-Ray Crystallography[14] were used for Co, S, O, N, C, and H atoms. Anomalous dispersion correction was made for Co and S atoms.[14] All computations were performed on an ACOS-S700 at Crystallographic Research Center, Institute for Protein Research, Osaka University. The computer programs used were RSSFR-5,[15] HBLS V,[16] DAPH,[17] and ORTEP.[18]

Final positional parameters, the corresponding isotropic thermal parameters which were calculated from respective anisotropic ones by Hamilton's method,[19] and their estimated standard deviations for nonhydrogen atoms are given in Table 2. The calculated positional parameters of hydrogen atoms, the anisotropic thermal parameters for all nonhydrogen atoms, and the complete list of the $|F_o|$ and $|F_c|$ values have been preserved by the Chemical Society of Japan (Document No. 8143).

TABLE 2. FRACTIONAL ATOMIC POSITIONAL AND ISOTROPIC THERMAL PARAMETERS FOR NONHYDROGEN ATOMS[a,b)]

Atom	*x*	*y*	*z*	$\frac{B^{c)}}{\text{Å}^2}$
Co	0.1894(1)	−0.1105(1)	0.0817(1)	2.57(3)
S(1)	0.1471(2)	0.0473(2)	0.0988(3)	3.20(7)
S(2)	0.1071(2)	−0.1389(3)	0.2548(3)	3.79(8)
S(3)	0.3335(2)	−0.0819(2)	0.1843(3)	2.91(7)
O(1)	0.1998(7)	0.1060(7)	−0.0065(8)	3.9(3)
O(2)	−0.0072(7)	−0.1513(10)	0.2271(12)	6.4(4)
O(3)	0.3880(6)	−0.1823(7)	0.2046(9)	3.9(2)
O(4)	−0.3463(8)	0.0408(7)	0.2003(10)	5.1(3)
O(5)	−0.2511(10)	−0.0139(9)	0.0455(11)	6.3(3)
O(6)	−0.1983(7)	−0.1802(7)	0.1693(10)	4.7(3)
O(7)	−0.4144(6)	−0.1807(7)	0.1517(8)	3.2(2)
O(8)	−0.2913(8)	−0.2437(7)	0.4274(9)	4.6(3)
O(9)	−0.3532(7)	−0.3373(6)	0.2781(8)	4.0(2)
O(10)	0.4111(9)	−0.3021(8)	0.4179(13)	6.8(4)
N(1)	0.0608(7)	−0.1299(8)	−0.0135(10)	3.1(3)
N(2)	0.2210(8)	−0.2538(7)	0.0746(11)	3.6(3)
N(3)	0.2676(7)	−0.0860(8)	−0.0713(9)	3.2(2)
C(1)	0.0198(10)	0.0366(11)	0.0431(13)	4.0(4)
C(2)	0.0130(10)	−0.0381(11)	−0.0589(12)	4.1(4)
C(3)	0.1508(11)	−0.2637(10)	0.2737(13)	4.1(4)
C(4)	0.1538(11)	−0.3147(11)	0.1542(15)	4.5(4)
C(5)	0.4044(9)	−0.0306(9)	0.0590(13)	3.5(3)
C(6)	0.3783(9)	−0.0887(9)	−0.0530(12)	3.4(3)
C(7)	−0.2842(11)	−0.0223(11)	0.1452(14)	4.6(4)
C(8)	−0.2613(10)	−0.1111(11)	0.2270(12)	3.8(3)
C(9)	−0.3619(9)	−0.1639(9)	0.2598(12)	3.4(3)
C(10)	−0.3358(10)	−0.2550(10)	0.3228(12)	3.6(3)

a) The estimated error in the last digit is shown in parentheses. This form is used throughout. b) O(10) is for the water of hydration; the rest of numberings are as shown in Fig. 1. c) *B* is evaluated from the corresponding anisotropic thermal parameters according to Ref. 17. Isotropic thermal parameters are of the form $\exp\{-B(\sin^2\theta/\lambda^2)\}$.

Results and Discussion

Figure 1 shows the notation of the complex, *d*-tartaric acid, and the oxygen atom of water. Nonhydrogen atom bond distances and angles are given in Tables 3 and 4, respectively. Table 5 lists several selected plane equations, sets of deviations of atoms from the plane, and dihedral angles between the pair of planes.

Structure of $(+)^{\mathrm{CD}}_{500}$-$[\mathrm{Co}\{\mathrm{S(O)CH_2CH_2NH_2}\}_3]$. The perspective view of the complex projected down its threefold axis is shown in Fig. 2. The cobalt(III) center is six-coordinate in approximately octahedral configuration (Table 5). The bidentate 2-aminoethanesulfenate coordinates to a cobalt(III) ion through sulfur and nitrogen atoms and the complex has *fac*(*S*) geometry. The average coordination angles of S–Co–S, N–Co–N, and S–Co–N (the S and N atoms are in trans) are 89.4°, 90.7°, and 177.7°, respectively (Table 4). The values indicate that the $\mathrm{CoS_3}$ parasol constituted of three facial S atoms and a Co atom at the top is less blown

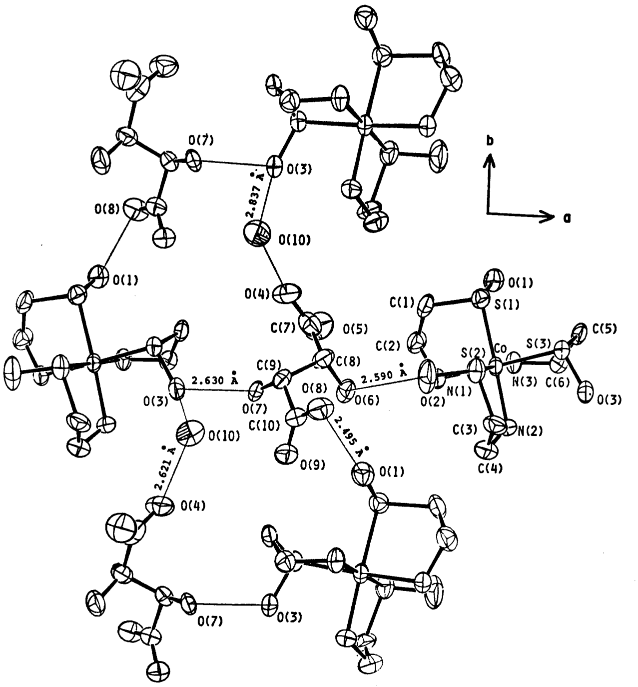


Fig. 1. A perspective view of a layer constituted by hydrogen bonds onto ab plane projected along c-axis, where line bonds denote hydrogen bonds within 3.10 Å. Thermal ellipsoids are drawn at the 50% probability level.

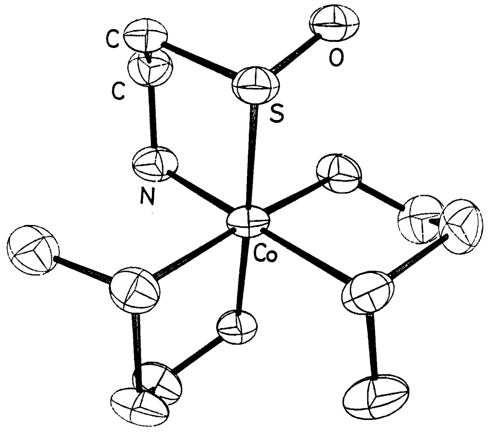


Fig. 2. A perspective drawing of the complex projected down the threefold axis of the complex (50% probability thermal ellipsoids).

Table 3. Intramolecular bond distances (l/Å)

For complex						Average
Co–S(1)	2.222(4)	Co–S(2)	2.228(4)	Co–S(3)	2.229(3)	2.226
Co–N(1)	2.015(11)	Co–N(2)	2.011(12)	Co–N(3)	2.012(11)	2.013
S(1)–O(1)	1.567(10)	S(2)–O(2)	1.531(13)	S(3)–O(3)	1.545(10)	1.548
S(1)–C(1)	1.793(15)	S(2)–C(3)	1.837(15)	S(3)–C(5)	1.823(14)	1.818
N(1)–C(2)	1.501(17)	N(2)–C(4)	1.479(20)	N(3)–C(6)	1.485(16)	1.488
C(1)–C(2)	1.535(20)	C(3)–C(4)	1.513(21)	C(5)–C(6)	1.516(19)	1.521
For *d*-tartaric acid						
O(4)–C(7)	1.333(19)	O(5)–C(7)	1.158(20)	O(6)–C(8)	1.390(17)	
O(8)–C(10)	1.303(17)	O(9)–C(10)	1.215(16)	O(7)–C(9)	1.394(16)	
C(7)–C(8)	1.569(21)	C(8)–C(9)	1.544(20)	C(9)–C(10)	1.494(19)	

Table 4. Intramolecular bond angles (ϕ/°)

For complex						
Metal coordination angles						Average
S(1)–Co–S(2)	88.4(1)	S(2)–Co–S(3)	89.9(1)	S(3)–Co–S(1)	89.9(1)	89.4
S(1)–Co–N(1)	88.4(3)	S(2)–Co–N(2)	88.5(4)	S(3)–Co–N(3)	88.8(3)	88.6
S(1)–Co–N(3)	91.9(3)	S(2)–Co–N(1)	91.5(3)	S(3)–Co–N(2)	90.8(4)	91.4
S(1)–Co–N(2)	176.8(4)	S(2)–Co–N(3)	178.6(3)	S(3)–Co–N(1)	177.8(3)	177.7
N(1)–Co–N(2)	91.0(5)	N(2)–Co–N(3)	91.2(5)	N(3)–Co–N(1)	89.8(4)	90.7
Intraligand angles						
Co–S(1)–O(1)	108.3(4)	Co–S(2)–O(2)	108.2(5)	Co–S(3)–O(3)	108.1(4)	108.2
Co–S(1)–C(1)	97.2(5)	Co–S(2)–C(3)	96.5(5)	Co–S(3)–C(5)	96.5(5)	96.7
O(1)–S(1)–C(1)	101.6(6)	O(2)–S(2)–C(3)	103.6(7)	O(3)–S(3)–C(5)	102.4(6)	102.5
S(1)–C(1)–C(2)	110.5(10)	S(2)–C(3)–C(4)	107.6(10)	S(3)–C(5)–C(6)	107.9(9)	108.7
C(1)–C(2)–N(1)	106.4(11)	C(3)–C(4)–N(2)	107.7(12)	C(5)–C(6)–N(3)	108.6(10)	107.6
Co–N(1)–C(2)	113.6(8)	Co–N(2)–C(4)	112.0(9)	Co–N(3)–C(6)	112.1(8)	112.5
For *d*-tartaric acid						
O(4)–C(7)–O(5)	126.5(15)	O(4)–C(7)–C(8)	110.6(12)	O(5)–C(7)–C(8)	122.9(14)	
O(6)–C(8)–C(7)	111.2(12)	O(6)–C(8)–C(9)	108.9(11)	C(7)–C(8)–C(9)	108.4(11)	
O(7)–C(9)–C(10)	112.1(11)	O(7)–C(9)–C(8)	107.5(11)	C(8)–C(9)–C(10)	106.1(11)	
O(8)–C(10)–O(9)	123.7(13)	O(8)–C(10)–C(9)	115.6(12)	O(9)–C(10)–C(9)	120.7(12)	

than the corresponding CoN_3 parasol. The three sulfenato sulfur atoms are three-coordinate (to the cobalt atom, the carbon atom of chelate ring, and the oxygen atom) in an approximately tetrahedral configuration counting the sulfur lone pair of electrons as occupying the fourth site. The oxygen atoms of sulfenato groups occupy the least repulsive positions on the *fac*(*S*) plane to one another. Therefore, the oxygen atoms are on the plane perpendicular to the threefold axis of the complex.

Since the sulfur atom of sulfenato group becomes chiral on coordination, the stereochemical possibilities for this *fac*(*S*) complex are as follows: (1) the wrapping of the chelate rings about the cobalt center may be either *Δ* or *Λ*, (2) the conformations of the three chelate rings generate four sets of isomers (*δ*,*δ*,*δ*), (*δ*,*δ*,*λ*), (*δ*,*λ*,*λ*), and (*λ*,*λ*,*λ*), and (3) four configurations (*R*,*R*,*R*), (*R*,*R*,*S*), (*R*,*S*,*S*), and (*S*,*S*,*S*) are possible from the combination of three chiral sulfur atoms. Therefore, 32 configurations in all, *i.e.*, 16 enantiomeric pairs of diastereoisomers are expected. However, the crystal contains only the configuration *fac*(*S*)-*Λ*-(*δ*,*δ*,*δ*)-(*R*,*R*,*R*). The result is consistent with the previous assignment based on the absorption, CD, and ^{13}C NMR spectra.[11]

Table 6 shows the selected bond distances and angles of the complex in comparison with those of *Δ*-{*λ*′(*S*), *λ*,*δ*}$[Co\{S(O)CH_2CH_2NH_2\}(en)_2]^{2+}$.[10] There are no large differences between the two complexes in the bond distance and angle. In the monosulfenato complex ion, the Co–N distance (2.048 Å) *trans* to the sulfur donor atom is significantly larger than the average *cis* Co–N one (1.976 Å) which is consistent with the ordinary Co–N distance. Such a phenomenon is referred to as *structural trans effect* (*STE*).[10] The present *fac*(*S*) complex has exclusively the *trans* Co–N bond. The average Co–N distance is longer than the ordinary Co–N one but trivially shorter than the *trans* Co–N distance of the monosulfenato cobalt(III) complex ion. The Co–S bond distance (2.226 Å) is also somewhat shorter than that (2.253 Å) of the reference complex. The XPS data of both complexes show the existence of a significant amount of electron-transfer from the sulfenato sulfur donor atom to cobalt(III) ion in comparison with the tris(ethylenediamine)cobalt(III) complex.[20] The Co-$2p_{3/2}$, S-$2p_{3/2}$, and N-1s binding energies of the present complex (779.0, 163.8, and 398.9 eV, respectively) are lower than those of the monosulfenato complex (781.0, 164.9, and 400.1 eV, respectively). The results indicate that the saturation on the electron-transfer to cobalt(III) ion occurs

TABLE 5. DISPLACEMENTS OF ATOMS FROM LEAST-SQUARES PLANE AND DIHEDRAL ANGLES BETWEEN PLANES

For complex (coordination planes)

Planel. [Co, S(1), S(2), N(2), and N(3)]
$-0.8403X-0.1657Y-0.5162Z+2.2964=0$
Co 0.0049, S(1) 0.0165, S(2) −0.0188, N(2) 0.0179, N(3) −0.0199, O(1) −0.0990

Plane 2. [Co, S(1), S(3), N(1), and N(2)]
$-0.5004X-0.1708Y+0.849Z+0.2069=0$
Co −0.0064, S(1) 0.0656, S(3) −0.0486, N(1) −0.0170, N(2) 0.0394, O(3) 0.0138

Plane 3. [Co, S(2), S(3), N(1), and N(3)]
$-0.2243X+0.9723Y+0.0658Z+1.9432=0$
Co −0.0100, S(2) −0.0149, S(3) 0.0201, N(1) 0.0226, N(3) −0.0171, O(2) 0.1446

Dihedral angles (ϕ/°)

between the planes 1 and 2	89.4
between the planes 1 and 3	90.4
between the planes 2 and 3	89.9
average	89.9

For *d*-tartaric acid

Plane 4. [C(7), C(8), C(9),and C(10)]
$0.0796X-0.5405Y-0.8376Z+1.5215=0$
C(7) 0.0531, C(8) −0.0319, C(9) −0.0670, C(10) 0.0523

Plane 5. [O(4), O(5), C(7), and C(8)]
$0.7944X+0.4826Y+0.3688Z+2.5013=0$
O(4) −0.0028, O(5) −0.0035, C(7) 0.0085, C(8) −0.0022

Plane 6. [O(8), O(9), C(9), and C(10)]
$0.8942X+0.0107Y-0.4476Z+5.5402=0$
O(8) 0.0023, O(9) 0.0026, C(9) 0.0020, C(10) −0.0068

Dihedral angles (ϕ/°)

between the planes 4 and 5	120.4
between the planes 4 and 6	63.9
between the planes 5 and 6	56.6

The X, Y, and Z coordinates in Å refer to the crystallographic axes.

according to the increase in number of sulfenato groups which lowers the S-2p$_{3/2}$ binding energy of the present complex. However, there is an apparent conflict between the XPS data and the Co–S bond distances: the present tris(sulfenato) complex with the more negative sulfur donor atoms has the shorter Co–S bond distance than the monosulfenato complex. This conflict may be interpreted as that the electron-transfer from sulfur to cobalt in sulfenato complex contains an antibonding character.

Structure of d-*Tartaric Acid.* The *d*-tartaric acid molecule has reasonable bond distances, angles, and dihedral angles as compared with other structure analyses[13] (Tables 3, 4, and 5). The carbon skelton C(7)–C(8)–C(9)–C(10) is planar, and the dihedral

TABLE 6. SELECTED BOND DISTANCES (l/Å) AND ANGLES (ϕ/°)

Bond	Present complex[a)] Average l	Reference complex[b)] l
Co–S	2.226	2.253(1)
Co–N	2.013	2.048(3)[c)] 1.976[d)]
S–O	1.548	1.552(3)
S–C	1.818	1.815(4)
N–C[e)]	1.488	1.484(5)
C–C[e)]	1.521	1.513(5)
Angle	**Average ϕ**	**ϕ**
Co–S–O	108.2	107.7(1)
Co–S–C	96.7	96.5(1)
O–S–C	102.5	102.3(2)

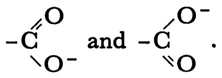
a) Data from Tables 2 and 3. b) Data from Ref. 10. c) *trans*-Position against S atom. d) Average for *cis*-positions against S atom. e) Associated with the sulfenato chelate ring.

TABLE 7. POSSIBLE HYDROGEN BONDING IN *d*-$C_4H_6O_6$·[Co{S(O)$CH_2CH_2NH_2$}$_3$]·H_2O[a)]

B···(H–)A	B···A(l/Å)	X–B···A(ϕ/°)	B···A–Y(ϕ/°)
O(1)···O(8)$^{\mathrm{I}}$	2.495(14)	111.3(5)	115.2(7)
O(2)···O(6)	2.590(17)	176.1(8)	110.5(8)
O(3)···O(7)$^{\mathrm{II}}$	2.630(11)	114.3(5)	106.5(5)
O(3)···O(10)	2.837(16)	131.2(6)	92.1(8)[b)]
O(10)···O(4)$^{\mathrm{I}}$	2.621(17)	92.1(8)[b)]	119.9(8)
A–H···B	**A···B(l/Å)**	**H···B(l/Å)**	**A–H···B(ϕ/°)**
N(1)–H(16)···O(7)$^{\mathrm{III}}$	2.982(13)	2.205	148.5
N(2)–H(18)···O(6)$^{\mathrm{III}}$	3.011(16)	2.262	144.2
N(3)–H(20)···O(9)$^{\mathrm{III}}$	2.955(14)	2.204	144.4

a) Includes H bonding where A···B <3.1 Å. b) O(3)···O(10)···O(4) angle. I: Transformed to $-x, y+1/2, -z+1/2$. II: Transformed to $x+1, y, z$. III: Transformed to $x+1/2, -y-1/2, -z$.

angle between the planes [O(4), O(5), C(7), and C(8)] and [O(8), O(9), C(9), and C(10)] is 56.6°.Furthermore, a proof of no dissociation of its two carboxyl groups can be given by two kinds of bond distances C–O(–H) (1.333 Å, 1.303 Å) and C=O (1.158 Å, 1.215 Å), that is, the *d*-tartaric acid being not in resonance structure between



$$-\mathrm{C}\begin{smallmatrix}{/\!\!/}\mathrm{O}\\ \backslash\mathrm{O}^-\end{smallmatrix} \quad \text{and} \quad -\mathrm{C}\begin{smallmatrix}/\mathrm{O}^-\\ \backslash\!\!\backslash\mathrm{O}\end{smallmatrix}\ .$$

Crystal Packing. As for the intermolecular bond, possible hydrogen bond distances and angles are listed in Table 7. The perspective view of a layer constituted of hydrogen bonds onto ab plane projected along the c-axis is given in Fig. 1, where line bonds denote hydrogen bonds within 3.10 Å. This layer further interacts with the upper and lower layers by hydrogen bonds between the hydrogen atoms of amino groups of the complex and oxygen atoms of *d*-tartaric acid onto bc plane (Fig. 3). Thus, seven hydrogen bonds are possible per one *d*-tartaric acid molecule. The hydrogen bond distances between oxygen atoms of sulfenato groups and hydrogen atoms of carboxyl groups, hydroxyl groups, or water are considerably short (2.495—2.837 Å), that is, the sulfenato oxygens have a significantly basic character. The S–O bond distance (1.548 Å) is rather longer than that of the sulfinato group of $[\mathrm{Co}\{\mathrm{S(O)_2CH_2CH_2NH_2}\}(\mathrm{en})_2]^{2+}$ (1.456 Å, 1.476 Å).[21] The facts indicate that the sulfur-oxygen bond of sulfenato complex has a large polarity (*right*) in analogy with that of sulfoxide (*left*).[22] Such a basic property of oxygen atoms in sulfenato groups is confirmed for the first time. The hydrogen bonding mode in Fig. 3 is similar to the so-call *face-to-face close contact* between a triangular face of the octahedral complex cation and the hydrogen *d*-tartrate or the *d*-tartrate anion.[23] The hydrogen bond interaction between the neutral complex and the *d*-tartaric acid molecule seems to be a key for the successful optical resolution of this molecular complex.

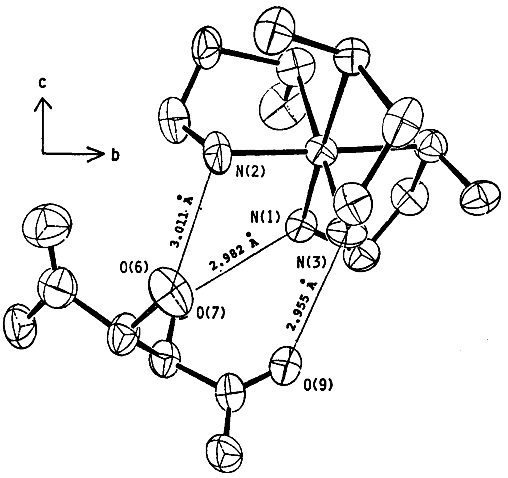
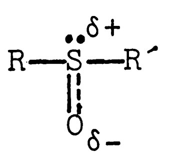
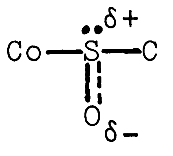


Fig. 3. The arrangement of the complex and *d*-tartaric acid molecule projected along a-axis (50% probability thermal ellipsoids). The line bonds represent possible hydrogen bonds (the distances within 3.10 Å).



$$\mathrm{R}-\underset{\substack{\| \\ \mathrm{O}_{\delta-}}}{\overset{\bullet\bullet\,\delta+}{\mathrm{S}}}-\mathrm{R}'$$



$$\mathrm{Co}-\underset{\substack{\| \\ \mathrm{O}_{\delta-}}}{\overset{\bullet\bullet\,\delta+}{\mathrm{S}}}-\mathrm{C}$$

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