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Structural Study of Optical Resolution. XII. The Crystal and Molecular Structure of $(-)_{589}$-*trans-SS*-Bis(isothiocyanato)(triethylenetetramine)cobalt(III) μ-(+)-Tartrato(4−)-μ-(+)-hydrogentartrato(3−)-diantimonate(III) Tetrahydrate

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The crystal and molecular structure of the diastereoisomeric salt, $(-)_{589}$-*trans*-[Co(NCS)$_2$(trien)][Sb$_2$((+)-tart)((+)-tartH)]·4H$_2$O, has been determined by the X-ray diffraction method. The red crystals were monoclinic, with the space group P2$_1$, $a=8.987(1)$, $b=15.949(2)$, $c=10.726(1)$ Å, $\beta=102.57(2)°$, and $Z=2$. The structure was solved by the heavy-atom method and refined by the block-diagonal least-squares method, using 2976 independent reflections, to the final R-value of 0.033. In the complex cation, the conformations of the three five-membered chelate rings are ($\delta\lambda\delta$), while the absolute configurations of the two asymmetric nitrogen atoms are both S. The mononegative anion has a dimeric structure of $[Sb_2((+)\text{-}C_4H_2O_6)((+)\text{-}C_4H_3O_6)]^-$, in which (+)-$C_4H_2O_6^{4-}$ and (+)-$C_4H_3O_6^{3-}$ coordinate to two Sb^{III} atoms. The extra hydrogen atom in (+)-$C_4H_3O_6^{3-}$ bonds to the free oxygen atom(OTB5) of the carboxylato group, and a short contact is formed between this oxygen atom and a water molecule(OW2); OTB5···OW2 2.43(1) Å. Though six N–H hydrogen atoms are present in the complex cation, three of them form N–H···O hydrogen bonds to the oxygen atoms of the dimeric anion; NTR3···OTA1 2.86(1), NTR4···OTA6 2.86(1), and NTR1···OTB4 3.19(1) Å.

Potassium bis(μ-(+)-tartrato(4−))diantimonate(III), tartar emetic, is a familiar resolving reagent for metal complexes.[1] From the X-ray structure analyses, the presence of a unique dinegative dimeric structure in which two tetranegative (R,R)-tartrate anions, $(C_4H_2O_6)^{4-}$ abbreviated (+)-tart, coordinate to two Sb^{III} atoms was proved.[2] Recently, *trans*-[Co(NCS)$_2$(trien)]$^+$ complexes were newly prepared and resolved by using this anion.[3] Under acidic conditions, red crystals of the optically active diastereoisomeric salt with the chemical formula of [Co(NCS)$_2$(trien)][Sb$_2$((+)-tart)((+)-tartH)]·4H$_2$O were precipitated.[4] Since the ratio of cation *vs.* anion in this crystal is 1:1, the presence of a mononegative bis(μ-(+)-tartrato)diantimonate(III) anion is strongly suggested.

As a part of our structural studies of optical resolution, we recently determined several diastereoisomeric salts including the mononegative hydrogen (+)-tartrate anion, *d*-$C_4H_5O_6^-$, as the resolving reagent,[5] and compared their structures with those found in the diastereoisomeric salts with the dinegative (+)-tartrate anion, *d*-$C_4H_4O_6^{2-}$.[6] Thus, in order to determine the molecular structure of the mononegative bis(μ-(+)-tartrato)diantimonate(III) anion and the absolute configuration of $(-)_{589}$-*trans*-[Co(NCS)$_2$(trien)]$^+$ and in order to compare the crystal-packing mode with those found in diastereoisomeric salts including the [Sb$_2$((+)-tart)$_2$]$^{2-}$ anion, we have undertaken the single-crystal X-ray structure analysis of the title compound.

Experimental

Preparation of Compound. Racemic *trans-RR,SS*-[Co(NCS)$_2$(trien)]ClO$_4$ was prepared by the method given in the literature.[3] The less-soluble diastereoisomeric salt, $(-)_{589}$-*trans*-[Co(NCS)$_2$(trien)][Sb$_2$((+)-tart)((+)-tartH)]·4H$_2$O, was prepared by the following procedure.[4] A solution of racemic *trans-RR,SS*-[Co(NCS)$_2$(trien)]ClO$_4$(3×10^{-3} mol) was adsorbed on a column of SP-Sephadex C-25 (the total exchange capacity: 2.7 mequiv) and then eluted with an aqeous solution of Ca[Sb$_2$((+)-tart)$_2$] (1.3×10^{-3} mol). The eluent was concentrated to about 10 ml, and the diastereoisomeric salt was precipitated by the addition of 1.3 ml of 1 M HCl (1 M = 1 mol dm^{-3}). When the red precipitate thus obtained was recrystallized from a hot aqueous solution, red rectangular crystals were deposited. Found: C, 20.82; H, 3.42; N, 9.05%. Calcd for $C_{16}H_{31}O_{16}N_6S_2CoSb_2$: C, 20.66; H, 3.36; N, 9.04%.

Crystallographic Data Collection. The intensities and cell dimensions were measured on a SYNTEX-R3 diffractometer with Mo $K\alpha$ radiation ($\lambda=0.7107$ Å), monochromated by a graphite plate. The size of the crystal used for the X-ray measurement was $0.22\times0.20\times0.18$ mm^3. The systematic absences for $0k0$ ($k=2n+1$) suggested P2$_1$ or P2$_1$/m as the possible space groups, but the latter was eliminated because of the optical activity of the compound. The unit cell dimensions were refined by a least-squares treatment of the setting angles of 25 reflections. The crystal data were as follows: monoclinic, space group P2$_1$, $a=8.987(1)$, $b=15.949(2)$, $c=10.726(1)$ Å, $\beta=102.57(2)°$, $D_m=2.04$ g cm^{-3} (by flotation in a chloroform-bromoform mixture), $Z=2$, and $D_c=2.06$ g cm^{-3}. The intensity data were collected in the ω-scan mode up to $2\theta=55°$. Of the 3128 unique observed reflections, 2976 reflections with $|F_o|>3\sigma(F_o)$ were used for the structure determination. Corrections for absorption effect were neglected (μ(Mo $K\alpha$) = 25.9 cm^{-1}).

Determination and Refinement of Crystal Structure. The coordinates of the Sb and Co atoms could be deduced from a Patterson map. The positions of the other lighter atoms, except for the hydrogen atoms, were revealed by the Fourier synthesis. Several cycles of the block-diagonal least-squares refinement with anisotropic temperature factors reduced the R-value ($R=\{\sum(|F_o|-|F_c|)/\sum|F_o|\}$) to 0.050. At this stage, a difference map was examined for the hydrogen-atom positions with reference to the calculated ones (1.0 Å for N–H and C–H bond distances and tetrahedral angle). There were clear indications for most of the hydrogen atoms. The final refinement including these H atoms with isotropic temperature factors caused the R-

value to converge to 0.033. 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 a and b values were 0.2 and 0.0009 respectively.

All the atomic scattering factors, with corrections for the anomalous dispersion of Sb, Co, and S atoms, were taken from the International Tables for X-ray Crystallography, Vol. IV.[7] All the computations were carried out by a HITAC M-180 computer at the Hiroshima University Information Processing Center. The computer programs used were FOURP21[8] and HBLS-IV, with a slight modification.[9] An ORTEP drawing was carried out by the use of a computer system, XTL, in a SYNTEX-R3 diffractometer.[10] 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. 8337).

Results and Discussion

The projections of the crystal structure along the a- and b-axes are shown in Figs. 1 and 2 respectively. The thermal ellipsoids in these figures are illustrated with a 50% probability.

Cation Geometry. Figure 3 shows a perspective drawing of the complex cation, which has an approximate two-fold axis through the midpoint of the CTR3-CTR4 bond and the central Co atom. The absolute structure of the crystal could be deduced, since the absolute configuration of (R,R)-tartrate was known.[11] Figure. 3 represents the absolute configuration of the complex cation correctly. The conformations of the three chelate rings of the triethylenetetramine ligand are of a $\delta\lambda\delta$ form, and the absolute configurations of the two asymmetric nitrogen atoms, NTR2 and NTR3, are both S.[12] Thus, the absolute configuration of the present $(-)_{589}$-*trans*-[Co(NCS)$_2$(trien)]$^+$ can be denoted as *trans*-SS-$\delta\lambda\delta$.

The bond lengths and angles within the complex cation are listed in Table 2. The Co–N(NCS) distances are 1.901(7) and 1.884(7) Å, while the Co–N–C angles are 162.0(7) and 161.4(7)°. The bond distances of the Co–N(trien) are 1.964(8) and 1.961(7) Å for the

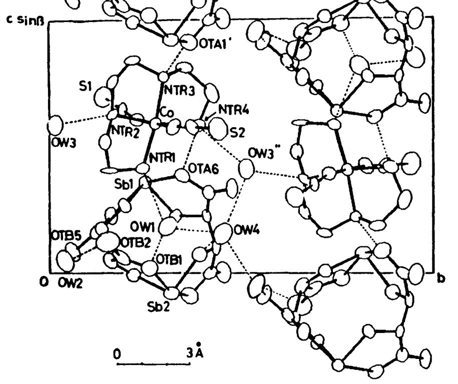

Fig. 1. A perspective drawing of the contents of the unit cell viewed down the a-axis. Possible hydrogen bonds are indicated by bloken lines. Hydrogen atoms are omitted for clarity.

Table 1. Positional parameters ($\times 10^4$) and thermal parameters

Atom	x	y	z	B_{eq} or B/Å^2
Sb(1)	257(1)	2500(1)	3613(1)	2.15(2)
Sb(2)	1102(1)	3183(1)	-803(1)	2.88(2)
C(TA1)	-1283(10)	4173(5)	-22(7)	2.57(31)
C(TA2)	194(9)	4339(5)	978(7)	2.34(30)
C(TA3)	-98(9)	4094(4)	2300(7)	2.21(28)
C(TA4)	1441(10)	4143(5)	3219(7)	2.62(32)
C(TB1)	3068(9)	1875(6)	649(7)	2.86(34)
C(TB2)	1444(9)	1568(5)	495(7)	2.49(31)
C(TB3)	1166(9)	1337(5)	1787(7)	2.39(31)
C(TB4)	-523(9)	1161(5)	1667(7)	2.47(31)
O(TA1)	-1128(7)	3633(4)	-893(5)	3.08(25)
O(TA2)	-2451(8)	4529(4)	23(7)	4.05(31)
O(TA3)	1434(7)	3905(4)	733(5)	2.66(23)
O(TA4)	-747(6)	3291(3)	2281(5)	2.28(20)
O(TA5)	2234(8)	4761(4)	3342(6)	3.69(30)
O(TA6)	1879(6)	3454(4)	3869(5)	2.46(22)
O(TB1)	3227(7)	2620(5)	198(6)	3.58(28)
O(TB2)	4145(8)	1454(6)	1164(7)	4.46(35)
O(TB3)	367(6)	2176(4)	-79(5)	2.64(23)
O(TB4)	1693(6)	1950(3)	2710(5)	2.43(22)
O(TB5)	-1139(7)	603(4)	885(6)	3.63(29)
O(TB6)	-1246(6)	1594(3)	2298(5)	2.64(23)
Co	5433(1)	2768(1)	5938(1)	1.84(3)
S(1)	1331(3)	1413(2)	6977(3)	4.55(12)
S(2)	9563(4)	4413(2)	5710(3)	5.68(15)
N(1)	3534(8)	2300(4)	6087(6)	2.52(28)
N(2)	7293(7)	3262(4)	5794(6)	2.46(26)
N(TR1)	5074(7)	2436(5)	4134(5)	2.27(24)
N(TR2)	6301(7)	1670(4)	6307(5)	1.95(23)
N(TR3)	6017(8)	2981(4)	7747(5)	2.27(25)
N(TR4)	4494(8)	3884(4)	5807(6)	2.56(27)
C(1)	2616(8)	1934(5)	6471(7)	2.16(28)
C(2)	8235(11)	3760(6)	5776(8)	3.11(36)
C(TR1)	5741(11)	1600(5)	4048(7)	3.06(35)
C(TR2)	6993(10)	1426(5)	5219(8)	2.88(34)
C(TR3)	7244(10)	1662(5)	7615(7)	2.69(32)
C(TR4)	6356(10)	2165(5)	8407(7)	2.79(32)
C(TR5)	4879(10)	3550(6)	8095(7)	2.88(33)
C(TR6)	4706(11)	4257(6)	7128(8)	3.22(37)
O(W1)	6153(7)	3113(5)	1902(6)	3.74(28)
O(W2)	6130(8)	385(5)	533(7)	4.21(33)
O(W3)	4274(8)	147(4)	5900(7)	4.20(33)
O(W4)	4454(9)	4523(5)	1566(8)	4.97(38)
H(CB2)	129(14)	107(8)	-9(12)	3.2(27)
H(CB3)	177(14)	82(8)	207(12)	3.5(29)
H(CA2)	-24(18)	491(11)	87(14)	5.5(38)
H(CA3)	-84(14)	450(8)	258(12)	3.5(29)
H(N2)	553(13)	124(8)	633(11)	3.2(27)
H(N3)	699(14)	329(9)	800(12)	3.7(28)
H(N1A)	554(14)	285(9)	364(11)	4.0(31)
H(N1B)	396(14)	240(9)	375(12)	3.9(29)
H(N4A)	341(15)	382(9)	542(13)	3.7(29)
H(N4B)	495(15)	424(8)	526(12)	3.3(27)
H(C1A)	614(13)	156(8)	325(11)	2.6(25)
H(C1B)	492(15)	117(10)	400(13)	4.5(33)
H(C2A)	795(14)	180(8)	522(11)	3.3(28)
H(C2B)	734(15)	82(9)	529(13)	4.5(34)
H(C3A)	827(12)	192(7)	763(10)	2.5(24)
H(C3B)	743(15)	107(9)	795(13)	4.3(32)
H(C4A)	697(13)	225(8)	930(11)	2.7(25)
H(C4B)	539(14)	187(8)	845(12)	3.6(29)
H(C5A)	390(12)	324(7)	804(9)	1.9(21)
H(C5B)	526(13)	377(8)	897(11)	3.1(27)
H(C6A)	563(17)	463(10)	730(15)	5.7(39)
H(C6B)	379(14)	460(8)	719(11)	3.0(26)
H(OB5)	-228(19)	53(11)	75(16)	6.6(43)
H(W2A)	589(15)	6(9)	-28(12)	3.9(30)
H(W2B)	540(16)	77(10)	77(13)	4.8(35)
H(W4A)	339(17)	431(10)	128(14)	5.4(37)
H(W4B)	509(17)	399(10)	169(13)	5.2(37)
H(W1A)	729(17)	319(11)	209(14)	5.8(37)
H(W1B)	555(15)	279(9)	125(13)	4.4(31)
H(W3A)	471(16)	-7(10)	678(14)	5.1(36)
H(W3B)	320(16)	24(9)	558(14)	5.0(36)

$B_{eq}=8\pi^2\ (U_{11}+U_{22}+U_{33})/3$. The anisotropic thermal parameters have been preserved by the Chemical Society of Japan. The positional parameters of the hydrogen atoms are represented on the scale of $\times 10^3$.

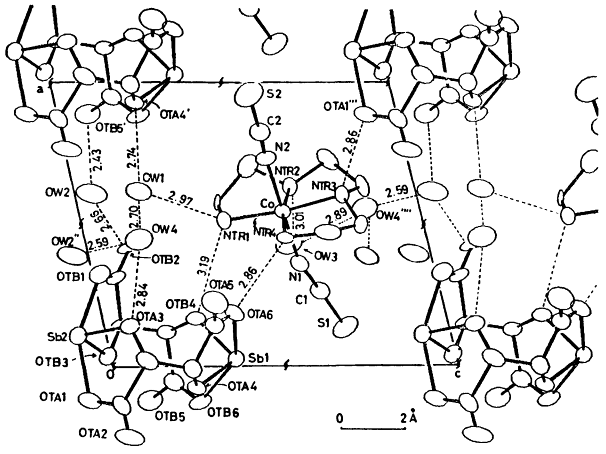

Fig. 2. A boundary projection of the contents of the unit cell viewed down the b-axis (from $y=0.54$ to $y=-0.06$) with the numbering scheme.

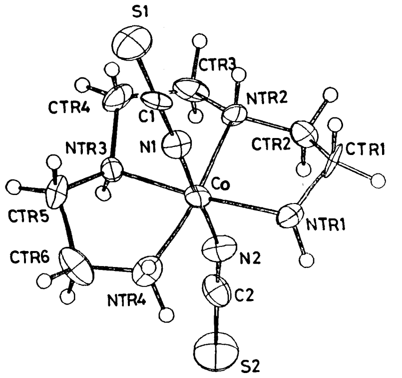

Fig. 3. An ORTEP drawing of the complex cation. All atoms are drawn with the 50% probability ellipsoids.

terminal nitrogen atoms and 1.923(7) and 1.927(6) Å for the middle nitrogen atoms respectively. The N–Co–N angles of the outer chelate rings are 86.0(3) and 86.0(3)°, while that of the central one is 86.8(3)°. These values are in good agreement with the values obtained for *trans-meso*-$[Co(CN)_2(trien)]ClO_4$.[13]

The two outer chelate rings have an unsymmetrical envelope conformation. The ring carbon atoms, CTR1 and CTR2, lie at -0.105 and -0.736 Å from the plane formed by NTR1, Co, and NTR2. The corresponding deviations of CTR5 and CTR6 from the plane of NTR3, Co, and NTR4 are 0.677 and 0.034 Å respectively. In the central chelate ring, CTR3 and CTR4 lie 0.347 below and 0.386 Å above the plane of NTR2, Co, and NTR3. These values are in good agreement with the values obtained for $(-)_{589}$-*trans*-$[Co(NO_2)_2$ (L-3,8-dimetrien)]ClO_4.[14]

Anion Geometry. Figure 4 shows a perspective drawing of the dimeric anion with the water molecule OW2. The geometry of the mononegative dimeric anion, whose interatomic distances and angles are listed in Table 2, resembles the structure found for a number of dinegative bis(μ-(+)-tartrato(4−))-diantimonate(III).[2] The coordination geometry is pseudotrigonal bipyramidal, with average axial and equatrial angles of 150.8(2) and 99.3(2)° respectively (compared with 150(2) and 100(4)° for $[Sb_2((+)\text{-tart})_2]^{2-}$).[15]

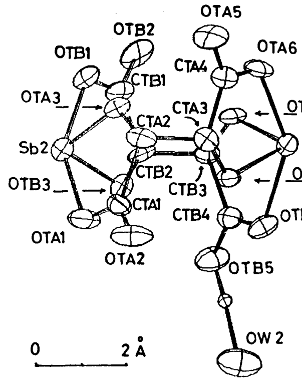

Fig. 4. Structure of the mononegative dimeric anion with including the water molecule OW2.

Of great interest are the bond distances and angles given in Table 2 for the (+)-$C_4H_3O_6$(TB-tart) group. Though four –COO groups are present in this anion, only one –COO group in TB-tart has a symmetrical structure; CTB4–OTB5 1.266(11) and CTB4–OTB6 1.245(10) Å and CTB3–CTB4–OTB5 118.1(7), CTB3–CTB4–OTB6 118.8(7), and OTB5–CTB4–OTB6 123.1 (8)°, respectively. The other –COO group in TB-tart and two –COO groups in TA-tart have the usual unsymmetrical form, as is summarized in Table 2; the averaged C–O distances are 1.207(12) Å for free oxygen atoms and 1.306(12) Å for oxygen atoms bonded to Sb^{III}. Additionally, the Sb1–OTB6 distance, 2.252(6) Å, is longer than the other Sb–O(–COO distance); 2.084(6), 2.111(6), and 2.171(6) Å. Moreover, a short contact is found between OTB5 and the water molecule OW2; OTB5···OW2 2.43(1) Å. Thus, we can safely conclude that the extra hydrogen atom (proton) of the (+)-$C_4H_3O_6$ group bonds to the OTB5 carboxyl oxygen atom. It is noteworthy that the present short O(–COOH)···$O(H_2O)$ contact, 2.43 Å, is nearly equal to the $O(H_2O)\cdots H\cdots O(H_2O)$ 2.431 Å in $(H_5O_2)^+$ included in *trans*-$[CoCl_2(en)_2]Cl\cdot(H_5O_2)\cdot Cl$[16] and to the O(–COOH)···O(OOC–) 2.44 Å observed in $(+)_{589}$-$[Co(ox)(en)_2]H$-*d*-tart·H_2O.[17]

Tapscott *et al.* recently determined the crystal structure of sodium hydrogen bis(μ-*meso*-tartrato)-bis(2,2′-bipyridyl) dichromate(III) heptahydrate.[18] They found that this mononegative Cr^{III} complex anion has a dimeric structure and that the extra hydrogen atom (proton) bridges the gap between the two hydroxyl oxygen atoms which belong to the *meso*-tartrate groups within the dimeric unit. This marked difference in the position of the extra hydrogen atom(proton) between the Sb^{III} and the Cr^{III} mononegative dimeric anions probably comes from the different structural features of these anions. The former, the present Sb^{III} complex anion, has two (+)-tartrate anions in the trigonal bipyramidal configuration, but the latter, the Cr^{III} complex, has two *meso*-tartrate anions in the distorted octahedral configuration. The O(hydroxyl)···O(hydroxyl) interatomic distances of the former, OTA3···OTB3 2.986(8) and OTA4···OTB4 3.026(8) Å, are considerably longer than that in the latter, O(hydroxyl)···

TABLE 2. BOND DISTANCES AND ANGLES (e.s.d.'s IN PARENTHESES)

Bond distance	l/Å	Bond distance	l/Å	Bond distance	l/Å
Co - N1	1.901(7)	CTR4 - NTR3	1.481(11)	CTA1 - OTA1	1.301(11)
Co - N2	1.884(7)	NTR3 - CTR5	1.475(12)	CTA1 - OTA2	1.203(11)
Co - NTR1	1.964(8)	CTR5 - CTR6	1.517(13)	CTA2 - OTA3	1.384(10)
Co - NTR2	1.923(6)	CTR6 - NTR4	1.509(12)	CTA3 - OTA4	1.406(10)
Co - NTR3	1.927(7)	Sb1 - OTA4	1.971(5)	CTA4 - OTA5	1.208(11)
Co - NTR4	1.961(7)	Sb1 - OTB4	1.979(6)	CTA4 - OTA6	1.314(10)
N1 - C1	1.157(10)	Sb1 - OTA6	2.084(6)	CTB1 - CTB2	1.513(12)
C1 - S1	1.610(8)	Sb1 - OTB6	2.252(6)	CTB2 - CTB3	1.507(12)
N2 - C2	1.165(12)	Sb2 - OTA3	1.979(6)	CTB3 - CTB4	1.521(12)
C2 - S2	1.596(10)	Sb2 - OTB3	1.960(6)	CTB1 - OTB1	1.303(12)
NTR1 - CTR1	1.474(13)	Sb2 - OTA1	2.111(6)	CTB1 - OTB2	1.209(13)
CTR1 - CTR2	1.519(14)	Sb2 - OTB1	2.171(7)	CTB2 - OTB3	1.413(10)
CTR2 - NTR2	1.488(11)	CTA1 - CTA2	1.537(12)	CTB3 - OTB4	1.399(10)
NTR2 - CTR3	1.473(11)	CTA2 - CTA3	1.547(12)	CTB4 - OTB5	1.266(11)
CTR3 - CTR4	1.516(13)	CTA3 - CTA4	1.516(12)	CTB4 - OTB6	1.245(10)

Bond angle	ϕ/°	Bond angle	ϕ/°	Bond angle	ϕ/°
N1-Co-N2	178.5(3)	Co-NTR2-CTR2	107.3(5)	OTA3-Sb2-OTB3	98.6(2)
Co-N1-C1	162.0(7)	Co-NTR2-CTR3	109.1(5)	CTA2-CTA1-OTA1	113.8(7)
Co-N2-C2	161.4(7)	NTR2-CTR3-CTR4	105.4(7)	CTA2-CTA1-OTA2	121.3(8)
N1-C1-S1	178.8(7)	CTR3-CTR4-NTR3	106.0(7)	OTA1-CTA1-OTA2	124.9(8)
N2-C2-S2	177.2(9)	CTR4-NTR3-CTR5	120.0(7)	CTA1-CTA2-OTA3	113.0(7)
NTR1-Co-NTR2	86.0(3)	Co-NTR3-CTR4	108.0(5)	CTA1-CTA2-CTA3	107.6(7)
NTR2-Co-NTR3	86.8(3)	Co-NTR3-CTR5	108.2(5)	CTA3-CTA2-OTA3	110.6(7)
NTR3-Co-NTR4	86.0(3)	NTR3-CTR5-CTR6	104.9(7)	CTA2-CTA3-OTA4	111.7(7)
NTR4-Co-NTR1	101.5(3)	CTR5-CTR6-NTR4	108.8(7)	CTA2-CTA3-CTA4	105.7(7)
Co-NTR1-CTR1	108.9(6)	Co-NTR4-CTR6	109.0(5)	CTA4-CTA3-OTA4	111.9(7)
NTR1-CTR1-CTR2	110.6(8)	OTA4-Sb1-OTB4	100.0(2)	CTA3-CTA4-OTA5	123.1(8)
CTR1-CTR2-NYR2	103.9(7)	OTA6-Sb1-OTB6	149.1(2)	CTA3-CTA4-OTA6	115.3(7)
CTR2-NTR2-CTR3	119.5(7)	OTA1-Sb2-OTB1	152.6(3)	OTA5-CTA4-OTA6	121.5(8)
CTB2-CTB1-OTB1	115.8(8)	CTB1-CTB2-CTB3	109.1(7)	CTB4-CTB3-OTB4	111.5(7)
CTB2-CTB1-OTB2	121.9(9)	CTB3-CTB2-OTB3	109.4(7)	CTB3-CTB4-OTB5	118.1(7)
OTB1-CTB1-OTB2	122.3(9)	CTB2-CTB3-OTB4	112.4(7)	CTB3-CTB4-OTB6	118.8(7)
CTB1-CTB2-OTB3	112.2(7)	CTB2-CTB3-CTB4	109.3(7)	OTB5-CTB4-OTB6	123.0(8)

TABLE 3. DISTANCES OF ATOMS FROM LEAST-SQUARES PLANES IN Å

Least-squares planes

Plane(1)		Plane(2)		Plane(3)	
Co	−0.001	CTA1	0.054	CTB1	−0.058
NTR1	−0.048	CTA2	−0.055	CTB2	0.063
NTR2	0.064	CTA3	−0.049	CTB3	0.051
NTR3	−0.066	CTA4	0.052	CTB4	−0.051
NTR4	0.054				

Plane(4)		Plane(5)		Plane(6)		Plane(7)	
CTA1	0.006	CTB1	0.005	CTA3	−0.025	CTB3	−0.021
CTA2	0.023	CTB2	0.023	CTA4	−0.010	CTB4	0.014
OTA1	0.008	OTB1	0.006	OTA4	0.023	OTB4	0.016
OTA2	−0.017	OTB2	−0.015	OTA5	0.019	OTB5	0.018
OTA3	−0.020	OTB3	−0.019	OTA6	−0.008	OTB6	−0.020

Dihedral angles between the planes

Plane(2)—Plane(3)	0.9°	Plane(3)—Plane(5)	54.4
Plane(2)—Plane(4)	58.4	Plane(3)—Plane(7)	56.6
Plane(2)—Plane(6)	55.1	Plane(5)—Plane(7)	69.0
Plane(4)—Plane(6)	66.5		

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.

Plane	(1)	(2)	(3)	(4)	(5)	(6)	(7)
l	−0.920	0.273	0.262	−0.351	0.226	0.624	0.046
m	−0.383	−0.950	−0.952	−0.743	−0.399	−0.309	−0.689
n	0.084	−0.151	−0.161	0.570	−0.889	−0.717	0.723
p	4.383	6.688	2.217	4.565	1.215	4.111	0.067

O(hydroxyl) 2.418(6) Å.[18]

The relevant least-squares planes are listed in Table 3. The two planes of the C–C–C–C skeletons of TA-tart and TB-tart are quite parallel. The planes including five non-hydrogen atoms of each α-hydroxycarboxylate moiety are approximately coplanar. The angles between the two planes, 66.5° for TA-tart and 69.0° for TB-tart, are normal.[2]

Crystal-packing Mode and Waters of Crystallization. The packing features of the complex cations and dimeric anions are shown in Figs. 1 and 2. There are four waters of crystallization associated with the ionic species contained in the structural unit. The selected intermolecular distances, including the hydrogen-

Table 4. Intermolecular distances and angles

Hydrogen-bond distances and bonding modes

D–H···A	D···A l/Å	H···A l/Å	D–H···A ϕ/°
OTB5–HOB5···OW2$^{\mathrm{i}}$	2.43(1)	1.42(18)	177(18)
OW2–HW2A···OW4$^{\mathrm{ii}}$	2.59(1)	1.60(14)	178(13)
OW2–HW2B···OTB2	2.66(1)	1.69(15)	179(14)
OW4–HW4B···OW1	2.70(1)	1.69(16)	179(14)
OW4–HW4A···OTA3	2.84(1)	1.44(16)	179(14)
OW1–HW1A···OTA4$^{\mathrm{iii}}$	2.74(1)	1.74(17)	175(15)
OW1–HW1B···OTB1	2.96(1)	2.16(15)	143(12)
OW3–HW3A···OW4$^{\mathrm{iv}}$	2.89(1)	1.88(16)	179(14)
NTR1–HN1A···OW1	2.97(1)	2.10(14)	146(11)
NTR2–HN2···OW3	3.01(1)	2.08(13)	160(11)
NTR4–HN4B···OW3$^{\mathrm{v}}$	3.09(1)	2.12(13)	179(13)
NTR4–HN4A···OTA6	2.86(1)	2.00(14)	145(15)
NTR3–HN3···OTA1$^{\mathrm{vi}}$	2.86(1)	1.92(14)	159(15)
NTR1–HN1B···OTB4	3.19(1)	2.22(14)	175(15)

Selected intermolecular distances (l/Å)

Sb1···C1	3.446(8)	OTA6···N1	3.12(1)
Sb1···N1	3.524(7)	OTA6···NTR1	3.26(1)
Sb1···S1	3.930(3)	OTA5···OW4	3.07(1)
Sb1···S2$^{\mathrm{i}}$	3.920(4)	N2···OTA1$^{\mathrm{vi}}$	3.58(1)
Sb2···S1$^{\mathrm{vii}}$	3.727(3)	C2···OTA1$^{\mathrm{vi}}$	3.50(1)

Roman numerals as superscripts refer to the following equivalent positions, relative to the reference atom at (x, y, z): i ($-1+x$, y, z), ii ($1-x$, $-1/2+y$, $-z$), iii ($1+x$, y, z), iv ($1-x$, $-1/2+y$, $1-z$), v ($1-x$, $1/2+y$, $1-z$), vi ($1+x$, y, $1+z$), vii (x, y, $-1+z$).

D; Hydrogen donor, A; Hydrogen acceptor.

bonding modes, are summarized in Table 4.

The hydrogen-bonding features in this crystal are as follows:

(1) Along the a-axis, there are strong hydrogen bondings, OTB5···OW2···OTB2$^{\mathrm{i}}$, and the dimeric anions are joined to each other by the water molecule OW2; OTB5···OW2 2.43(1) and OW2···OTB2$^{\mathrm{i}}$ 2.66 (1) Å. (2) Along the c-axis, there are bonds from the tartrate oxygens of (+)-$C_4H_2O_6$(TA-tart) to triethylenetetramine nitrogens, with distances of OTA6···NTR4 2.86(1) and NTR3···OTA1$^{\mathrm{vi}}$ 2.86(1) Å respectively. (3) Along the b-axis, near the $y=0$ and $y=1/2$ there are sheets of the waters of crystallization, as shown in Fig. 1. (4) The planes of C–C–C–C skeleton of the two (+)-tart groups(TA and TB-tart) are approximately perpendicular to the crystallographic b-axis(within 4°), and the cell length of the b-axis is probably determined by the size of the dimeric anion. (5) As a result, the *trans-SS* complex cation is surrounded by the four dimeric anions on the ac-plane, and they are piled up along the b-axis by the two-fold screw operations. The short contacts around the complex cation along the b-axis are NTR2···OW3 3.01(1) and NTR4···OW3$^{\mathrm{v}}$ 3.09(1) Å.

It is interesting to note that, though there are two tartrate groups in the present $[Sb_2((+)\text{-}C_4H_2O_6)((+)\text{-}C_4H_3O_6)]^-$ complex, only the (+)-$C_4H_2O_6$ group(TA-tart) has short contacts to the nitrogen atoms of the triethylenetetramine ligand. The other group, (+)-$C_4H_3O_6$ (TB-tart), has short contacts to the water molecules and forms the hydrogen-bonding chain mentioned above along the a-axis. If the absolute configurations of the two nitrogen atoms of the trien ligand (NTR2 and NTR3) change from *S* to *R*, the hydrogen-bonding modes around these nitrogen atoms change completely. Thus, the optical discrimination between the $(+)_{589}$-*RR*- and $(-)_{589}$-*SS*-*trans*-$[Co(NCS)_2(trien)]^+$ probably comes from the different contact modes between the (+)-$C_4H_2O_6$ (TA-tart) of the dimeric anion and the corresponding optically active complex cations.

In contrast, in diastereoisomeric salts containing $[Sb_2((+)\text{-tart})_2]^{2-}$ as the resolving reagent, for example *cis*-$[Co(NCS)_2(tn)_2]_2[Sb_2((+)\text{-tart})_2]\cdot 2H_2O$ and its Cr^{III} analogue, the dimeric anions lie exactly on a crystallographic two-fold axis and the two (+)-tart groups are equivalent.[19] In $[Fe(phen)_3][Sb_2((+)\text{-tart})_2]\cdot 8H_2O$, the dimeric anion has a crystallographic two-fold axis again, and only the halves of the two (+)-tart groups are crystallographically independent.[20] Thus, the crystal-packing modes in these salts are different from the present one.

Another interesting point in this crystal is in the averaged O···O distances around the water molecules: 2.80 Å for OW1, 2.56 Å for OW2, 2.89 Å for OW3, and 2.76 Å for OW4. The oxygen atom (OTB5) of the (+)-$C_4H_3O_6$(TB-tart) group is linked by hydrogen bonding to OW2 with the following sequence of the water molecules, as is shown in Fig. 2: OTB5···OW2···OW4···OW1 or ···OW3. The averaged distances around the water molecules reflect the positive charges which spread from the OTB5 to the water molecules through the hydrogen bodings: these results confirm the presence of an extra hydrogen atom(proton) between the OTB5 and water molecule OW2.

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