X-Ray Structures of $(-)_{589}$-Bis(isothiocyanato)bis(1,3-propanediamine)-chromium(III) Bis[μ-(+)-tartrato(4−)]bis[antimonate(III)] Dihydrate and Its Cobalt(III) Analogue

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The crystal structures of $(-)_{589}$-[Cr(NCS)$_2$(tn)$_2$]1/2[Sb$_2$(+)-tart$_2$]·2H$_2$O (**1**) and $(-)_{589}$-[Co(NCS)$_2$(tn)$_2$]1/2-[Sb$_2$(+)-tart$_2$]·2H$_2$O (**2**) have been determined from the X-ray diffraction data. The structures were solved by the Patterson-Fourier method and refined by the least-squares method to R=0.043 (**1**) and 0.070 (**2**) for 2659 and 1826 reflections respectively. The two crystals are isomorphous with each other. The complex cations in **1** and **2** have a similar geometry. Their absolute configuration is Λ, and agrees with that assigned from the CD spectra in comparison with those in the first d-d band region of bis(ethylenediamine)cobalt(III) complexes. The six-membered chelate rings are of chair conformation. The chairs are flattened more than expected from the conformational analysis.

As a part of studies of circular dichroism(CD)-structure correlation of metal complexes involving 1,3-propanediamine,[1,2] we describe here X-ray structure analyses of $(-)_{589}$-bis(isothiocyanato)bis(1,3-propanediamine)chromium(III) bis[μ-(+)-tartrato(4−)]-bis-[antimonate(III)] dihydrate $(-)_{589}$-[Cr(NCS)$_2$(tn)$_2$]-1/2[Sb$_2$(+)-tart$_2$]·2H$_2$O (tn=1,3-propanediamine, [Sb$_2$(+)-tart$_2$]$^{2-}$=bis[μ-(+)-tartrato(4−)]-bis[antimonate(III)] anion) and its cobalt(III) analogue $(-)_{589}$-[Co(NCS)$_2$(tn)$_2$]1/2[Sb$_2$(+)-tart$_2$]·2H$_2$O. Preliminary communication on the cobalt(III) complex has already been reported.[3]

Experimental

X-Ray Data Collection. The crystal of $(-)_{589}$-[Cr(NCS)$_2$(tn)$_2$]1/2[Sb$_2$(+)-tart$_2$]·2H$_2$O (**1**) is red and hexagonal tablet. The $(-)_{589}$-[Co(NCS)$_2$(tn)$_2$]1/2[Sb$_2$(+)-tart$_2$]·2H$_2$O complex (**2**) crystallizes in dark red prisms. The compounds **1** and **2** were prepared and resolved by Kawaguchi and his co-workers.[4,5] Preliminary oscillation and Weissenberg photographs showed the space group and approximate unit-cell dimensions for each crystal. The unit-cell dimensions were refined by least-squares analyses of the θ values of 32 reflections for **1** and 23 for **2**. The crystal data for **1** and **2** are given in Table 1. Intensity data were collected at room temperature on a Philips PW1100 automated diffractometer, using graphite-monochromated Mo $K\alpha$ radiation. During the data collection, three standard reflections were monitored every 4 h to check the stability and orientation of each crystal. Both compounds remained quite stable. Each data set was corrected for Lorentz-polarization[6] and absorption effects.[7]

Structure Solution and Refinement. The structure of **2** was first solved by the Patterson-Fourier techniques. Since the two crystals **1** and **2** are isomorphous, the structure solution for **1** was straightforward. Refinement of the structures was carried out by using the block-diagonal least-squares method. The function minimized was $\sum w(F_o-|F_c|)^2$, where $w=1/\sigma^2(F_o)$ was used. In the final cycle of refinement, all the parameter shifts were less than 0.8σ for **1** and 0.4σ for **2**. Neutral-atom scattering factors for the Sb, Cr, Co, S, O, N, and C atoms were taken from Ref. 8, with anomalous dispersion corrections for Sb, Cr, and Co atoms. The final R values were 0.043 for **1** and 0.070 for **2**. No attempt was made to locate hydrogen atoms. No chemically significant peaks were observed on final difference Fourier maps for **1** and **2**. Maximum peaks were 1.0 e Å^{-3} for **1** and 1.5 e Å^{-3} for **2**.

The absolute configurations of $(-)_{589}$-[Cr(NCS)$_2$(tn)$_2$]$^+$ and $(-)_{589}$-[Co(NCS)$_2$(tn)$_2$]$^+$ were determined on the basis of the known configuration of the (+)-tartric acid. The $F_o-|F_c|$ Tables for **1** and **2** and the anisotropic temperature factors are preserved by the Chemical Society of Japan (Document No. 8223). The final atomic coordinates are given in Table 2. Figures 1 and 2 were drawn by the use of ORTEP.[9] All the computations were performed by a FACOM 230-60 computer at Osaka City University using programs in the UNICS.[10]

Results and Discussion

The perspective views of $(-)_{589}$-[Cr(NCS)$_2$(tn)$_2$]$^+$ and $(-)_{589}$-[Co(NCS)$_2$(tn)$_2$]$^+$ are given in Fig. 1. They have a similar structure and their absolute configuration is Λ, which is consistent with the assignment from the CD data obtained by Kawaguchi and his co-workers.[4,5] Each complex cation has an approximate two-fold axis of rotation passing through the central metal and bisecting the N(NCS)–M–N(NCS) (M=Cr, Co) angle. The six-membered chelate rings are of chair conformation. The chairs in each complex have the Λpa[11](BB)[12] conformation and fold apart from one another (Fig. 1). Geue and Snow[12] calculated that the Λpa(BB) conformer is energetically more stable than the Λap(AA)

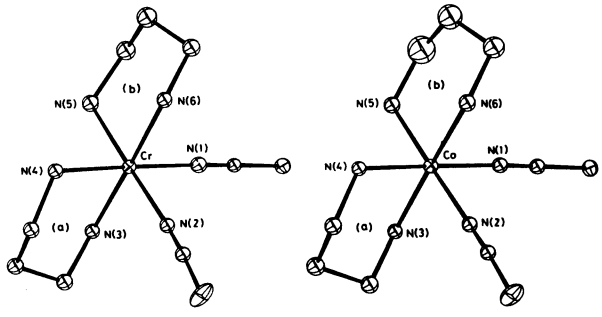

Fig. 1. The absolute configurations of the complex cations: $(-)_{589}$-[Cr(NCS)$_2$(tn)$_2$]$^+$ (left) and $(-)_{589}$-[Co(NCS)$_2$(tn)$_2$]$^+$ (right). The "a" ring is the "p" conformer and the "b" ring has the "a" form.

Table 1. Summary of crystal data and experimental details

Compound	**1** $(-)_{589}$-$[Cr(NCS)_2(tn)_2]$ 1/2$[Sb_2(+)$-tart$_2]\cdot 2H_2O$	**2** $(-)_{589}$-$[Co(NCS)_2(tn)_2]$ 1/2$[Sb_2(+)$-tart$_2]\cdot 2H_2O$
Crystal system	Orthorhombic	Orthorhombic
Space group	$P2_12_12$	$P2_12_12$
a/Å	12.121(5)	12.161(7)
b/Å	19.996(9)	19.502(24)
c/Å	9.240(6)	9.165(7)
$F(000)$	1140	1152
F.W.	594.05	600.98
U/Å^3	2239.5(16)	2173.5(33)
Z	4	4
D_m/g cm^{-3}	1.74	1.81
D_c/g cm^{-3}	1.76	1.84
μ(Mo $K\alpha$)/cm^{-1}	19.6	22.9
Crystal size/mm^3	0.57×0.39×0.15	0.35×0.11×0.08
Scan type	ω	ω
Scan speed/° s^{-1}	0.017	0.008
Scan range/°	1.4+0.2tan θ	1.0+0.2tan θ
$2\theta_{max}$/°	55	55
Background measurement/s	40	20
Maximum and minimum transmission factors	1.82, 1.31	1.20, 1.12
Number of unique reflections with $F_o^2 \geq 3\sigma(F_o^2)$	2659	1826
$R(R_w)$	0.043(0.055)	0.070(0.064)

Table 2. Positional and thermal parameters with their estimated standard deviations in parentheses

Atom	**1** $(-)_{589}$-$[Cr(NCS)_2(tn)_2]$1/2$[Sb_2(+)$-tart$_2]\cdot 2H_2O$ $10^4\times x$	$10^4\times y$	$10^4\times z$	$10\times B$/Å^2
Cr	2834.1(9)	1967.4(5)	8553.0(12)	21.5(3)[a]
S(1)	283(2)	1517(1)	12328(1)	29.8(5)[a]
S(2)	2460(3)	4310(1)	7967(4)	61.9(9)[a]
N(1)	1828(5)	1846(3)	10244(7)	33(1)
N(2)	2466(5)	2943(3)	8450(6)	27(1)
N(3)	1542(5)	1715(3)	7161(7)	27(1)
N(4)	3840(5)	2087(3)	6739(7)	29(1)
N(5)	3264(6)	956(3)	8701(8)	33(1)
N(6)	4153(5)	2190(3)	9940(7)	29(1)
C(1)	1174(6)	1705(3)	11124(8)	24(1)
C(2)	2461(6)	3515(4)	8276(8)	30(1)
C(3)	1370(7)	2128(4)	5824(9)	33(2)
C(4)	2347(7)	2132(4)	4828(9)	35(2)
C(5)	3391(7)	2452(4)	5432(9)	32(2)
C(6)	3586(8)	698(5)	10162(11)	46(2)
C(7)	4530(9)	1043(5)	10834(11)	50(2)
C(8)	4344(8)	1769(4)	11257(10)	39(2)
Sb(1)	5000.0	5000.0	485.3(6)	26.0(2)[a]
Sb(2)	5000.0	5000.0	5874.9(6)	21.6(2)[a]
C(9)	3847(6)	3853(3)	1778(8)	27(1)
C(10)	3240(6)	4488(3)	2339(8)	24(1)
C(11)	3288(6)	4439(3)	4002(8)	25(1)
C(12)	2794(6)	5116(3)	4567(7)	26(1)
O(1)	3718(4)	5076(2)	1834(5)	26(1)
O(2)	4755(4)	3975(3)	1121(6)	30(1)
O(3)	3456(5)	3292(3)	2007(6)	36(1)
O(4)	4360(4)	4350(2)	4479(5)	25(1)
O(5)	3436(4)	5482(2)	5283(6)	28(1)
O(6)	1831(5)	5251(3)	4255(7)	43(1)
O(7)	5122(14)	975(9)	5124(18)	156(5)
O(8)	1062(7)	3328(4)	2153(9)	62(2)

Table 2. (continued)

Atom	$10^4\times x$	$10^4\times y$	$10^4\times z$	$10\times B/Å^2$
	2 $(-)_{589}$-$[Co(NCS)_2(tn)_2]1/2[Sb_2(+)\text{-tart}_2]\cdot 2H_2O$			
Co	2870.0(17)	1943.6(10)	8507.9(23)	21.8(6)[a]
S(1)	354(4)	1557(4)	12296(5)	30.6(12)[a]
S(2)	2458(5)	4303(3)	8136(8)	57.6(18)[a]
N(1)	1899(10)	1833(7)	10143(14)	27(3)
N(2)	2505(10)	2900(6)	8442(15)	27(3)
N(3)	1609(10)	1715(6)	7166(14)	25(3)
N(4)	3853(10)	2061(6)	6790(15)	25(2)
N(5)	3250(10)	957(7)	8607(15)	29(3)
N(6)	4105(11)	2191(7)	9833(15)	32(3)
C(1)	1263(13)	1722(8)	11032(18)	27(3)
C(2)	2506(12)	3479(8)	8341(19)	27(3)
C(3)	1380(15)	2138(9)	5887(20)	35(4)
C(4)	2398(15)	2120(9)	4835(21)	39(4)
C(5)	3482(15)	2441(9)	5497(18)	34(4)
C(6)	3693(26)	701(16)	9906(32)	92(8)
C(7)	4469(20)	1003(13)	10742(27)	70(6)
C(8)	4334(17)	1752(11)	11144(23)	54(5)
Sb(1)	5000.0	5000.0	515.7(14)	30.1(4)[a]
Sb(2)	5000.0	5000.0	5961.0(14)	22.3(4)[a]
C(9)	3883(14)	3829(9)	1818(22)	37(14)
C(10)	3234(12)	4474(8)	2377(18)	25(3)
C(11)	3313(13)	4411(8)	4047(18)	24(3)
C(12)	2784(12)	5109(8)	4623(13)	26(3)
O(1)	3725(7)	5086(5)	1908(10)	24(2)
O(2)	4779(9)	3959(5)	1156(11)	32(2)
O(3)	3495(9)	3247(6)	2061(14)	41(3)
O(4)	4374(9)	4323(5)	4541(12)	26(2)
O(5)	3447(9)	5488(5)	5330(13)	31(2)
O(6)	1822(11)	5243(6)	4309(14)	48(3)
O(7)	5130(21)	949(12)	5188(23)	135(7)
O(8)	1068(16)	3360(10)	2157(22)	105(6)

a) Equivalent isotropic temperature factor (W. C. Hamilton, *Acta Crystallogr.*, **12**, 609 (1959)).

Table 3. Comparison of the torsion angles, bond angles, and dihedral angles

Six-membered chelate ring	Torsion angle about N–C	(τ/°)	Bond angle (ϕ/°) N–M–N	M–N–C		Dihedral angle(ϕ/°) D_1[a]	D_2[a]
Ring A in Λ ap (AA)[b]	54.4	61.6	92.6	119.0			
Ring B in Λ pa (BB)[b]	67.2	68.6	87.7	113.3			
Ring (a) (**1**)	59.7	57.9	88.4	119.1	118.6	37.8	56.1
Ring (b) (**1**)	58.3	59.0	88.6	117.2	119.7	37.2	58.2
Ring (a) (**2**)	57.5	61.4	90.0	120.8	120.7	38.1	56.8
Ring (b) (**2**)	53.2	42.8	91.8	118.5	119.3	32.1	41.9

a) D_1 is the dihedral angle between the N–M–N and N–C–C–N planes and D_2 is that between the N–C–C–N and C–C–C planes. b) Ring A or Ring B in *cis*-$[Co(CO_3)(tn)_2]^+$ in Ref. 12.

and Λpp(AB) conformations. They also indicated that no flattening should occur for two rings in Λpa(BB) conformation. However, we observed the flattening of the chairs in the crystals. Table 3 compares the tortion angles and bond angles calculated by Geue and Snow with those of the present work. The chairs of (a) and (b) in **1** and (a) in **2** have a similar geometry and are flattened more than expected from the calculation. The chair (b) in **2** shows a much pronounced flattening in comparison with the former three, and consequently the geometries of two rings in **2** are significantly different from each other. Since these flattenings are not predicted by the conformational analysis, the chair conformation in the present complexes presumably results from the

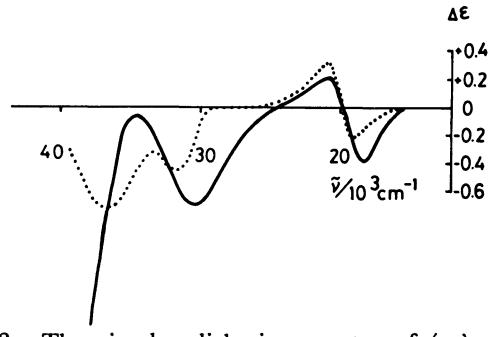

Fig. 2. The circular dichroism spectra of $(-)_{589}$-$[Cr(NCS)_2(tn)_2](NCS)$ (·····) in methanol and $(-)_{589}$-$[Co(NCS)_2(tn)_2](ClO_4)$ (——) in water.

TABLE 4. INTERATOMIC DISTANCES AND BOND ANGLES WITH THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

1 $(-)_{589}$-$[Cr(NCS)_2(tn)_2]1/2[Sb_2(+)\text{-tart}_2]\cdot 2H_2O$

Bond lengths(l/Å)		Bond angles(ϕ/°)	
Cr–N(1)	1.996(7)	Cr–N(1)–C(1)	170.7(6)
Cr–N(2)	2.003(6)	Cr–N(2)–C(2)	166.4(6)
Cr–N(3)	2.089(6)	N(1)–C(1)–S(1)	179.6(7)
Cr–N(4)	2.086(7)	N(2)–C(2)–S(2)	177.9(7)
Cr–N(5)	2.094(7)	N(3)–Cr–N(4)	88.4(3)
Cr–N(6)	2.097(7)	N(5)–Cr–N(6)	88.6(3)
N(1)–C(1)	1.17(1)	Cr–N(3)–C(3)	118.6(5)
N(2)–C(2)	1.16(1)	Cr–N(4)–C(5)	119.1(5)
C(1)–S(1)	1.595(7)	Cr–N(5)–C(6)	117.2(5)
C(2)–S(2)	1.615(8)	Cr–N(6)–C(8)	119.7(5)
N(3)–C(3)	1.50(1)	N(3)–C(3)–C(4)	113.5(7)
N(4)–C(5)	1.51(1)	N(4)–C(5)–C(4)	112.8(7)
N(5)–C(6)	1.50(1)	N(5)–C(6)–C(7)	114.9(8)
N(6)–C(8)	1.50(1)	N(6)–C(8)–C(7)	110.5(8)
C(3)–C(4)	1.50(1)	C(3)–C(4)–C(5)	115.7(7)
C(4)–C(5)	1.52(1)	C(6)–C(7)–C(8)	116.1(9)
C(6)–C(7)	1.47(2)	N(1)–Cr–N(2)	91.1(3)
C(7)–C(8)	1.52(2)		

Short contacts (l/Å)[a)]

N(3)···O(2)^{V}	3.019(8)	N(5)···O(6)^{III}	3.076(10)
N(3)···O(5)^{III}	3.344(8)	N(6)···O(3)^{II}	3.037(9)
N(4)···S(1)^{IV}	3.407(7)	O(8)···O(7)^{V}	3.093(21)
N(4)···O(7)^{I}	3.095(20)		

2 $(-)_{589}$-$[Co(NCS)_2(tn)_2]1/2[Sb_2(+)\text{-tart}_2]\cdot 2H_2O$

Bond lengths(l/Å)		Bond angles(ϕ/°)	
Co–N(1)	1.920(15)	Co–N(1)–C(1)	173.1(13)
Co–N(2)	1.919(14)	Co–N(2)–C(2)	166.3(14)
Co–N(3)	2.015(13)	N(1)–C(1)–S(1)	179.6(16)
Co–N(4)	1.990(14)	N(2)–C(2)–S(2)	177.2(17)
Co–N(5)	1.980(14)	N(3)–Co–N(4)	90.0(6)
Co–N(6)	1.991(14)	N(5)–Co–N(6)	91.8(6)
N(1)–C(1)	1.15(2)	Co–N(3)–C(3)	120.7(2)
N(2)–C(2)	1.13(2)	Co–N(4)–C(5)	120.8(11)
C(1)–S(1)	1.633(17)	Co–N(5)–C(6)	118.5(11)
C(2)–S(2)	1.619(19)	Co–N(6)–C(8)	119.3(11)
N(3)–C(3)	1.46(2)	N(3)–C(3)–C(4)	109.3(14)
N(4)–C(5)	1.47(2)	N(4)–C(5)–C(4)	111.5(14)
N(5)–C(6)	1.40(3)	N(5)–C(6)–C(7)	126.5(26)
N(6)–C(8)	1.50(3)	N(6)–C(8)–C(7)	112.0(17)
C(3)–C(4)	1.57(3)	C(3)–C(4)–C(5)	114.4(15)
C(4)–C(5)	1.58(3)	C(6)–C(7)–C(8)	118.9(23)
C(6)–C(7)	1.35(4)	N(1)–Co–N(2)	89.5(6)
C(7)–C(8)	1.52(3)		

Short contacts (l/Å)[a)]

N(3)···O(2)^{V}	3.008(17)	N(5)···O(6)^{III}	3.015(19)
N(3)···O(5)^{III}	3.312(17)	N(6)···O(3)^{II}	2.994(19)
N(4)···S(1)^{IV}	3.361(15)	O(8)···O(7)^{V}	3.007(32)
N(4)···O(7)^{I}	3.044(29)		

a) Roman numeral Superscripts refer to the following equivalent positions: I x, y, z; II $x, y, 1+z$; III $1/2-x, -1/2+y, 1-z$; IV $1/2+x, 1/2-y, 2-z$; V $-1/2+x, 1/2-y, 1-z$.

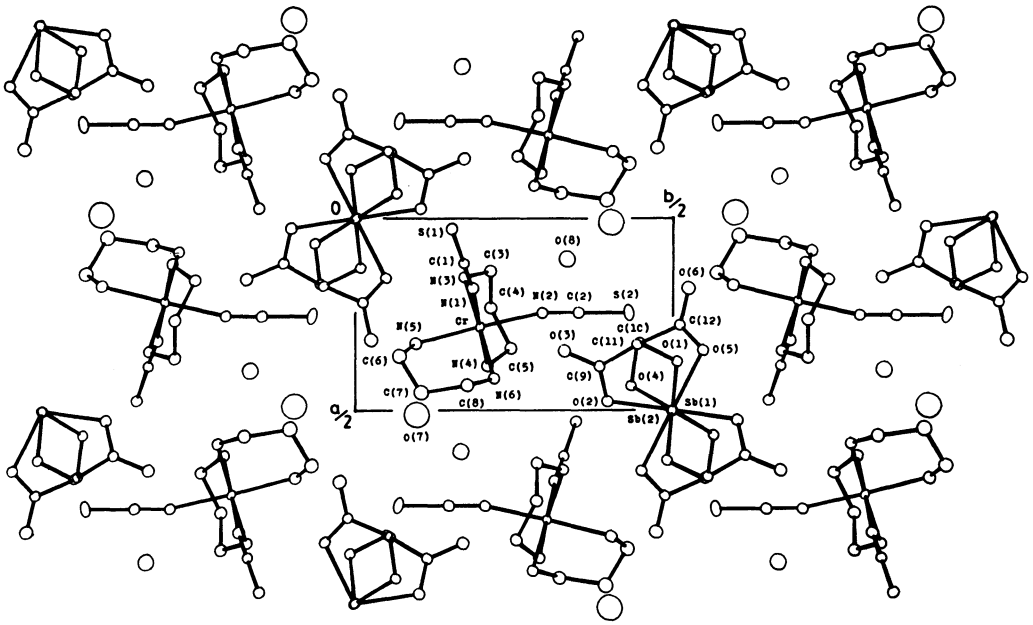

Fig. 3. The crystal structure of **1** viewed down the c axis, showing the atom numbering scheme.

crystal packing.

The bond distances between the metal ion and the ligator atoms are slightly larger in **1** than in **2**.[13] The average M–N bond distances are Cr–N(amine) 2.092 Å, Cr–N(NCS) 2.000 Å, Co–N(amine) 1.994 Å, and Co–N(NCS) 1.920 Å. These values are in agreement with those previously reported.[11-13] Deviations of the M–N(1)–C(1) bonds (Cr–N(1)–C(1)=170.7°, Co–N(1)–C(1)=173.1°) from 180° are less than the M–N(2)–C(2) bonds (Cr–N(2)–C(2)=166.4°, Co–N(2)–C(2)=166.3°). The isothiocyanato groups are approximately linear. The chelate bite angle (88.5°) in **1** is slightly less than 90°, but in **2** the value is 90.9° (Table 4).

The CD spectra of Λ-$(-)_{589}$-$[Cr(NCS)_2(tn)_2](NCS)$ and Λ-$(-)_{589}$-$[Co(NCS)_2(tn)_2](ClO_4)$ are given in Fig. 2. The CD pattern in the first d-d band region is

similar to each other and to the corresponding bis(ethylenediamine)cobalt(III) complexes.[14,15] Therefore, by analogy with bis(ethylenediamine)cobalt(III) complexes, each positive CD peak at higher wave-number could be assigned to the combined A and B components derived from the E_a component of the parent trigonal complex and each negative CD peak in the lower wave-number to the B component. Mason's criterion[16] that the absolute configuration of bis(ethylenediamine) cobalt(III) complex should be *Λ* if the CD of the combined A and B components are positive in sign, appears to hold in the present cases. It is noticed, however, that in *Λ*-$(-)_{589}$-$[Co(NCS)_2(tn)_2]^+$, the absolute configuration is related to the sign of the less dominant CD peak in the first absorption band region.

The $[Sb_2(+)\text{-tart}_2]^{2-}$ anion has a crystallographically imposed two-fold axis of rotation which passes through the two Sb atoms. The geometry of $[Sb_2(+)\text{-tart}_2]^{2-}$ anion is identical with those previously reported.[17]

Figure 3 gives the crystal structure of **1**. The crystals **1** and **2** are isomorphous. Each crystal consists of *Λ*-$(-)_{589}$-$[M(NCS)_2(tn)_2]^+$ cations, $[Sb_2(+)\text{-tart}_2]^{2-}$ anions, and water molecules, which are mainly bound by the N–H···O and N–H···S hydrogen bonds. Short contact distances are given in Table 4.

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