SHORT STRUCTURAL PAPERS

Thallium(I) Thiosulphate

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Abstract. $Tl_2S_2O_3$, orthorhombic, *Pnma*; $a = 8.433$ (7), $b = 6.184$ (3), $c = 10.911$ (3) Å, $V = 569.01$ (8) Å^3 ($T = 295$ K); $Z = 4$, $D_x = 6.10$, $D_m = 6.21$ g cm^{-3}; μ(Mo $K\alpha$) = 578 cm^{-1}. By least-squares calculations for 394 independent counter intensities $R = 0.042$. The structure is built up of Tl^+ and $S_2O_3^{2-}$ ions, the latter being partly disordered.

Introduction. Thin crystal plates of $Tl_2S_2O_3$ were precipitated during cooling of a hot concentrated water solution of $TlNO_3$ and $Na_2S_2O_3$ in the molar ratio 1:1. A crystal of thickness 0·0084 mm with **c** perpendicular to the plate was used for the diffractometer measurements.

Weissenberg photographs showed the systematic absences $0kl$ with $k + l = 2n + 1$ and $hk0$ with $h = 2n + 1$ which indicate the space groups *Pnma* (No. 62) or $Pn2_1a$ (No. 33). The cell dimensions were obtained from a least-squares analysis of the settings of 30 reflexions measured on a single-crystal diffractometer with Mo $K\alpha_1$ radiation ($\lambda = 0.70926$ Å). D_m was determined by the displacement method with benzene. The diffractometer was an Enraf–Nonius computer-operated four-circle instrument (CAD 4) with equatorial geometry, equipped with a graphite monochro-

mator giving Mo $K\alpha$ ($\lambda = 0.71069$ Å) radiation. The reflexions were scanned in the $\omega/2\theta$ mode with the scan interval $\Delta\omega° = 0.80° + 0.50°$ tanθ. Intensities were recorded for 713 reflexions of which 319 were weaker than $2\sigma(I)$, where $\sigma(I)$ is the standard deviation based on counting statistics. The intensities of two control reflexions, measured at regular intervals, showed no decay. Corrections for Lorentz, polarization and absorption effects were applied; the transmission factors were in the range 0·10–0·62.

Preliminary positions of the atoms, taken from the isostructural K_2SO_4 (McGinnety, 1972), were consistent with the observed Patterson function. S(2) and O(2) [Table 1(*a*)] could not definitely be distinguished from each other in the subsequent least-squares refinements in *Pnma* because of disordering. Different occupancy factors for these atoms were tried. Because of the disordering, calculations were also made in $Pn2_1a$. The positions of the Tl atoms were first refined and this refinement was followed by difference syntheses. No improvement resulted. In the final least-squares refinement (*Pnma*) anisotropic temperature factors were used for Tl and isotropic for the others. An extinction parameter was also refined.

The weight function was $w_i^{-1} = \sigma^2(F_o^2)/4F_o^2 +$

Table 1(*a*). *Final positional parameters and isotropic temperature factors*

Standard deviations are given in parentheses.

	Point position in *Pnma*	Occupancy	x	y	z	B (Å^2)
Tl(1)	4(*c*)		0·6682 (2)	$\frac{1}{4}$	0·6055 (2)	–
Tl(2)	4(*c*)		−0·0224 (2)	$\frac{1}{4}$	0·3047 (2)	–
S(1)	4(*c*)		0·241 (2)	$\frac{1}{4}$	0·564 (2)	5·2 (3)
O(1)	4(*c*)		0·281 (3)	$\frac{1}{4}$	0·431 (3)	4·5 (5)
S(2)	4(*c*)	($\approx 50\%$ S; $\approx 50\%$ O)	0·038 (2)	$\frac{1}{4}$	0·594 (2)	4·7 (3)
O(2)	8(*d*)	($\approx 75\%$ O; $\approx 25\%$ S)	0·323 (2)	0·032 (3)	0·627 (2)	5·8 (3)

Table 1(*b*). *Final anisotropic temperature factors and r.m.s. components for the thallium atoms*

The form of the anisotropic temperature factor is: $\exp\left[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)\right]$. By symmetry $\beta_{12} = \beta_{23} = 0$. Standard deviations are given in parentheses. The β_{ij} values are multiplied by 10^4 and the r.m.s. components by 10^3.

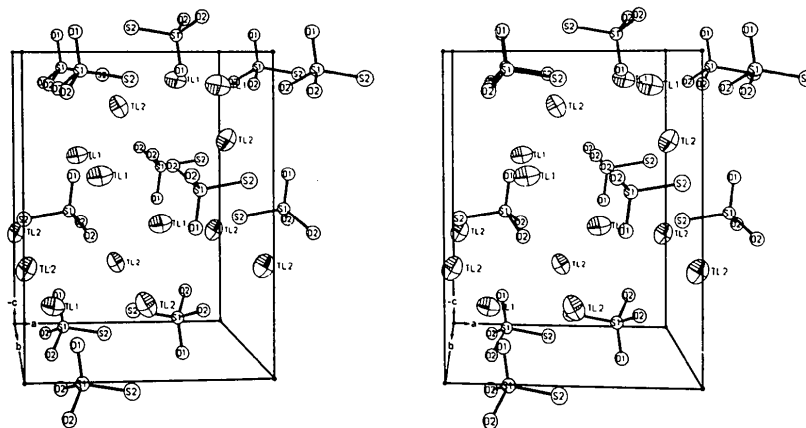|	β_{11}	β_{22}	β_{33}	β_{13}	R_1 (Å)	R_2 (Å)	R_3 (Å)
Tl(1)	244 (4)	277 (4)	89 (2)	−15 (2)	229 (2)	232 (2)	299 (3)
Tl(2)	159 (3)	356 (5)	127 (3)	−32 (2)	222 (3)	263 (2)	291 (3)

Fig. 1. A stereo view of the structure of $Tl_2S_2O_3$.

$0.0003F_o^2$ and the final $R=\sum|\Delta F|/\sum|F_o|=0.042$ and R_w $=(\sum w_i|\Delta F|^2/\sum w_i|F_o|^2)^{1/2}=0.051$. $S=[\sum w_i(|F_o|-|F_c|)^2/$ $(m-n)]^{1/2}$, where m and n are the number of observations and parameters varied, was 1·78. The value of the isotropic extinction parameter was 1.3×10^3. Scattering factors were taken from Doyle & Turner (1968). For Tl a correction for anomalous dispersion was applied (Cromer & Liberman, 1970). The fractional coordinates of the atoms and their thermal parameters are given in Table 1.*

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31719 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Discussion. A stereoscopic drawing of the structure is shown in Fig. 1 and a projection of six unit cells along [010] in Fig. 2. Selected interatomic distances and angles are presented in Table 2.

The structure is built up of $S_2O_3^{2-}$ and Tl^+ ions. The tetrahedral $S_2O_3^{2-}$ ion takes various positions around the O(1)–S(1) line in the tetrahedron (cf. Table 1). Due to this stepwise rotation S(2) and the two O(2) cannot clearly be distinguished. About 50% S and 50% O are situated in the position S(2) (Fig. 1) which causes an occupation of about 25% S and 75% O in the O(2) positions. A further refinement of the occupancy factors was not successful with the present intensities.
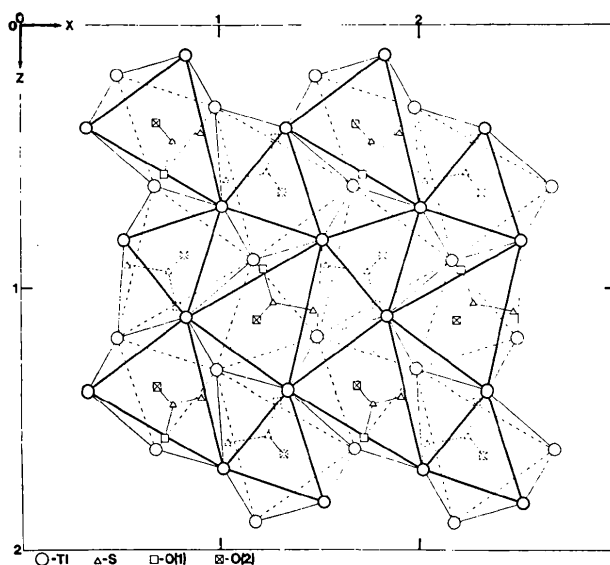
Table 2. *Selected distances* (Å) *and bond angles* (°) *for* $Tl_2S_2O_3$

Standard deviations are given in parentheses. Corresponding values for Rb_2SO_4 (Nord, 1974) are also given. For $Tl_2S_2O_3$, in the position denoted O(2) are situated about 75% oxygen and 25% sulphur and in S(2) about 50% sulphur and 50% oxygen.

	$Tl_2S_2O_3$	Rb_2SO_4
Tl(1)–O(2) × 2	3·07 (2)	3·05 (1)
–S(2)	3·12 (2)	2·91 (2)
–O(1) × 2	3·15 (1)	3·02 (2)
–O(2) × 2	3·22 (2)	3·16 (1)
–O(2) × 2	3·46 (2)	3·20 (2)
–S(2)	3·47 (1)	3·52 (2)
Tl(2)–O(1)	2·91 (3)	2·88 (2)
–O(1)	3·06 (3)	2·95 (2)
–O(2) × 2	3·11 (2)	2·89 (1)
–O(2) × 2	3·16 (2)	2·96 (2)
–S(2)	3·20 (2)	3·05 (2)
–S(2) × 2	3·29 (1)	3·24 (1)
S(1)–O(1)	1·49 (3)	
–O(2) × 2	1·66 (2)	
–S(2)	1·75 (2)	
S(2)–S(1)–O(2)	109 (1)	
S(2)–S(1)–O(1)	114 (2)	
O(2)–S(1)–O(2)	109 (2)	
O(2)–S(1)–O(1)	108 (1)	

Fig. 2. A projection of the structure of $Tl_2S_2O_3$ along [010] showing six unit cells. Heavy marked thallium atoms are situated in $y=\frac{3}{4}$, other thallium atoms in $y=\frac{1}{4}$. The atoms of the $S_2O_3^{2-}$ tetrahedron are situated in the planes $y=\pm\frac{1}{4}$, except the O(2) atoms which have their positions on both sides of the plane.

From a geometrical point of view the Tl$^+$ ions can be described as forming a deformed hexagonal close packing (Fig. 2). On account of the disorder of the S$_2$O$_3^{2-}$ tetrahedra the position O(2) outside the mirror planes at $y = \pm \frac{1}{4}$ contains both S and O.

In a S$_2$O$_3^{2-}$ group the S–S distance is 1·979 (3) Å and the S–O distances 1·484 (3), 1·472 (3) and 1·475 (3) Å (Manojlović-Muir, 1975). With respect to the occupancy factors for the S(2) and O(2) positions in the present thiosulphate tetrahedron a calculated distance S(1)–S(2) of 1·73 Å and S(1)–O(2) of 1·61 Å can be obtained from the reported distances of Manojlović-Muir (1975). These results are in good agreement with the observed distances S(1)–S(2) and S(1)–O(2) of 1·75 (2) and 1·66 (2) Å, respectively. The distance S(1) to O(1) between the atoms which are not disordered is 1·49 Å. The disorder explains the high temperature factors of S(2) and O(2) (cf. Manojlović-Muir, 1975). S(1) and O(1) also have high temperature factors, probably due to the fact that the axis S(1)–O(1) of the tetrahedron may have a minor oscillatory movement caused by the imperfection.

The fact that the structure is partly disordered makes it difficult to discuss the environments of Tl(1) and Tl(2) (Fig. 1). Tl(1) is coordinated to two O(1), not statistically distributed, at identical distances of 3·15 Å (Table 2). Tl(1) is also surrounded by five S or O atoms ranging from 3·07 to 3·22 Å. Further, three O or S atoms are situated at approximately 3·46 Å.

Tl(2) has two O(1) at 2·91 and 3·06 Å and seven S or O atoms ranging from 3·11 to 3·29 Å. These distances are in agreement with reported values for other Tl^I compounds (Table 3). A comparison with the isostructural Rb$_2$SO$_4$ (Nord, 1974) reveals no apparent differences in the environments of the corresponding cations (Table 2). This indicates that the Tl ions in Tl$_2$S$_2$O$_3$ may be stereochemically inactive, as in TlZnSO$_4$Cl (Bosson, 1976a), Tl$_3$[Hg(SO$_4$)$_2$][HgSO$_4$Cl] (Bosson, 1976b) and Tl$_2$[Cu(SO$_3$)$_2$] (Hjertén & Nyberg, 1973).

Table 3. Tl–O *distances in some compounds*

	Nearest Tl–O distances (Å)	Next distance (Å)	Reference
TlZnSO$_4$Cl	2·89–3·24	3·48	Bosson (1976a)
Tl$_3$[Hg(SO$_4$)$_2$] [HgSO$_4$Cl]	2·80–3·25	3·45	Bosson (1976b)
	2·60–3·21	3·40	
	2·68–3·20	3·44	
Tl$_2$[Cu(SO$_3$)$_2$]	2·82–3·04	3·28	Hjertén & Nyberg (1973)
Tl$_2$S$_2$O$_3$	3·07–3·22	3·46	This work
	2·91–3·29		

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Refinement of Neodymium Trihydroxide*

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Abstract. Nd(OH)$_3$, hexagonal, $P6_3/m$, $Z=2$, $a=6\cdot418$ (2), $c=3\cdot743$ (1) Å (single-crystal data), $a=6\cdot422$ (2), $c=3\cdot742$ (2) Å (high-angle powder data). The structure was refined independently from both powder and single-crystal X-ray intensity data. The powder sample was prepared by dissolving Nd$_2$O$_3$ in dilute HCl and precipitating with NH$_4$OH; the resulting amorphous gel was washed and aged in deionized water at 100 °C for six days. Single crystals were grown by aging in strong alkali at high temperature and pressure. The single-crystal data refinement ($R=$