β-Tl$_2$SO$_4$

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The ambient-temperature form of dithallium sulfate, β-Tl$_2$SO$_4$, is similar to β-K$_2$SO$_4$ and is characterized by isolated sulfate tetrahedra and two different thallium sites with coordination numbers 9 and 11. All the atoms, except one O atom, lie on mirror planes. In spite of there being a high concentration of Tl$^+$ cations, the stereochemical activity of the $6s^2$ pairs is low, similar to that of isotypic Tl$_2$XO$_4$ compounds (X = Cr and Se). This behaviour is the consequence of both weak Tl—O bonds and strong X—O bonds, because in a Tl—O—X linkage the electronic cloud of the O^{2-} anion is strongly distorted and displaced towards X, resulting in a low negative charge in the face of the Tl atom. Consequently, the Coulombic repulsions between the lone pair and the O^{2-} anions are weak. All of the Tl$_2$XO$_4$ compounds exhibit the same open packing of A^+ cations and [XO$_4$]$^{2-}$ anions as their isotypic alkali counterparts.

Comment

Heavy M^{m+} p-block cations with the electron configuration ns^2 np^0 may show stereochemical activity of the ns^2 pair that results in a very asymmetric anionic environment. It is commonly believed that this activity is stronger when the concentration of M^{m+} cations is high (Marchand *et al.*, 1975; Verbaere *et al.*, 1978; Jouini, 1986), especially for compounds of the Tl/X/O system with a Tl/X ratio greater than or equal to 2 (Jouanneaux *et al.*, 1991). An ideal example can be found in Tl$_2$SO$_4$, with a Tl/S ratio of 2 and a high specific volume per oxygen anion (V_{Ox} = 30.83 Å^3; Pannetier & Gaultier, 1966a); Tl$_2$SO$_4$ is similar to other compounds of thallium with tetrahedral oxyanions, *e.g.* Tl$_3$Li(MoO$_4$)$_2$ and Tl$_3$Li(WO$_4$)$_2$, which muster strong activity of the Tl$^+$ $6s^2$ lone pair (Colbeau-Justin *et al.*, 1997). However, the crystal structure of β-Tl$_2$SO$_4$ (low-temperature form) contains nearly regular TlO$_n$ polyhedra, accounting for the low stereochemical activity of the Tl$^+$ cations (Pannetier & Gaultier, 1966b). Furthermore, a comparative study of isotypic Tl$_2$XO$_4$ compounds (X = Cr, S and Se) showed the oxygen framework of β-Tl$_2$SO$_4$ to be different from those of the analogous compounds (Fábry & Breczewski, 1993). It should be noted, however, that the

structure of β-Tl$_2$SO$_4$ is the least reliably determined among this family. More recently, the structural instability of the Tl$_2$XO$_4$ compounds (X = Cr, Mo, W, S and Se) was studied (Friese *et al.*, 2004), relying on the only structural model published to date for β-Tl$_2$SO$_4$ (Pannetier & Gaultier, 1966b). As the accuracy of the paper cited does not meet today's standards, we decided to redetermine the crystal structure of β-Tl$_2$SO$_4$ to gain a better basis for stereochemical discussion. Previous crystallographic studies of Tl$_2$XO$_4$ compounds have established that they are isotypic with their potassium counterparts (Fischmeister, 1962; McGinnety, 1972; Carter & Margulis, 1972; Fábry & Breczewski, 1993). The present study confirms the isostructural relationship between β-Tl$_2$SO$_4$ and β-K$_2$SO$_4$ (orthorhombic, space group *Pnma*, Z = 4). The refinement of the atomic coordinates was performed from previously published data (Pannetier & Gaultier, 1966b). The final values show (i) an accuracy gain of a magnitude compared with previous work, (ii) a better reliability factor (R = 0.025 instead of 0.117), (iii) noticeable differences in some coordinates of the O atoms, and (iv) lower and more realistic displacement parameters.

All the atoms, except atom O3, lie on mirror planes. Consequently, all the anionic polyhedra have crystallographically imposed *m* symmetry. The structure is made up of independent SO$_4$ tetrahedra, with one pseudo-threefold axis aligned almost parallel or antiparallel to the *a* axis (Fig. 1). The two distinct thallium cations provide the electrostatic cohesion between the anionic entities. Using bond-valence parameters (Brese & O'Keeffe, 1991), the coordination numbers for atoms Tl1 and Tl2 are, respectively, 11 and 9. Around each Tl atom there are one very close and four close O-atom neighbours (Table 1), in an arrangement similar to that of the isotypic Tl$_2$SeO$_4$ (Fábry & Breczewski, 1993) and Tl$_2$CrO$_4$ (Carter & Margulis, 1972) compounds. For each Tl atom, the strongest Tl—O bond (nearly 2.8 Å) is far shorter than the sum of the ionic radii (3.05 Å; Shannon, 1976). Furthermore, the sum of the bond strengths around atom Tl1 appears much lower than 1 valence unit (Table 2). Therefore, in order to estimate the stereochemical effect of the Tl$^+$ cations, we used a simple method based on an electrostatic approach (Verbaere *et al.*, 1978). The Tl$^+$ cation is treated as a Tl^{3+}—E^{2-} dipole (where E^{2-} denotes the lone pair) inter-
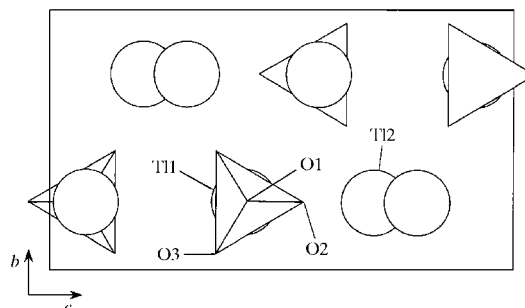
Figure 1
A cell projection along the *a* axis, showing the Tl atoms (circles) and SO$_4$ tetrahedra pointing up or down.

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inorganic compounds

acting with the local electrostatic field ε, dominated by the coordinating anions. Assuming that the high polarizability of thallium(I) ($\alpha = 7.28$ Å^3; Shannon, 1993) arises mainly from the ability of the s^2 orbital to hybridize, we used the following relation: $2e$ Tl$-E = \alpha\varepsilon$. The ions were treated as point charges, with values derived from the ionicities of the bonds according to a recent model (Guo *et al.*, 1999), *viz.* +0.72 for atom Tl, +1.75 for the S atom and −0.78 for the O atoms. The program *HYBRIDE* (Wallez, 1999), based on Ewald's method, was run iteratively until reaching the self-consistent position of the lone pair E. The two Tl$-E$ distances obtained for β-Tl$_2$SO$_4$ are short and account for the low stereochemical activity, although the activity is higher for the Tl1 atom, at variance with previous results (Table 2). For symmetry reasons, each lone pair E is constrained to the same mirror plane as the corresponding Tl atom. The dipole vectors are aligned roughly parallel to [100], and for atom Tl1 the activity is enough to push away the five shortest Tl$-$O bonds (Fig. 2). A comparison can be made with other oxygen compounds of thallium(I), for which active lone pairs are generally found to be 0.4–0.7 Å distant from the bearer, with correlatively shorter Tl$-$O bonds (2.38–2.69 Å; El Abiad *et al.*, 2000; Lafjij *et al.*, 2003), close to the sum of the ionic radii of the Tl^{3+} and O^{2-} ions (2.4 Å; Shannon, 1976). Our results show that β-Tl$_2$SO$_4$ is structurally comparable to isotypic Tl$_2$CrO$_4$ (Carter & Margulis, 1972) and Tl$_2$SeO$_4$ (Fábry & Breczewski, 1993). It is, however, surprising to observe such a low stereochemical activity of the lone pair, considering that the following two conditions are fulfilled.

(i) A Tl/S ratio of 2. In Tl/X/O systems (X = B, C, Si, Ti, Sn, P and Sb), the $6s^2$ lone pair exhibits a stereochemical activity that ensures structural cohesion when the ratio is greater than or equal to 2 (Jouanneaux *et al.*, 1991).

(ii) A high specific volume per O atom (V_{Ox} = volume of the unit cell/number of O atoms in the unit cell). The stereochemical activity of a lone pair often results in a supplementary bulk that can be compared with that of an O^{2-} anion (Galy *et al.*, 1975). In the present case, $V_{Ox} = 30.82$ Å^3, and if considering each lone pair as an additional O atom, $V_{Ox,E} = 20.55$ Å^3, which is a value commonly observed within compact oxygen frameworks (Galy *et al.*, 1975).

This result should not be seen as an anomaly but as an effect of the very nature of the Tl$^+$ ion (a large and low-charge cation) and of the S$-$O bond (strong and covalent). In a Tl$-$O$-$S linkage, the electronic cloud of the O^{2-} anion is strongly distorted and displaced toward the S atom, resulting in a low negative charge in the face of the Tl atom. Therefore, the Tl$^+$ cation is coordinated *via* weak bonds to a high number of low-charge anions that generate a low electrostatic field on the cation site, which is unlikely to stimulate the stereochemical activity of the $6s^2$ pair. All Tl$_2XO_4$ compounds of β-K$_2$SO$_4$ type, that is, hosting a small tetracoordinated X^{VI} cation (X = S, Se and Cr; Friese *et al.*, 2004), show a similar behaviour. In order to compare to the A_2XO_4 isotypes, we have plotted the volume of the crystal cell (from the JCPDS files) as a function of r^3_{A+} (Fig. 3). The corresponding V_{Ox} values, ranging from 21.7 (Na$_2$SO$_4$) to 38.1 Å^3 (Cs$_2$SeO$_4$), appear particularly high and indicate an open packing of the A^+ cations and $[XO_4]^{2-}$ oxyanions. Otherwise, the volume evolution appears almost linear with cation volume, and the Tl$^+$ ion does not seem to behave differently from an alkali cation. Therefore, in contrast to the predictive criteria (high Tl/X ratio and $V_{Ox} > 25$ Å^3), the stereochemical activity of the Tl$^+$ $6s^2$ pair cannot be anything but low, at variance with the behaviour of isoelectronic cations of higher oxidation states (Pb^{2+} and Bi^{3+}).

To summarize, the criteria Tl/$X \geq 2$ and high V_{Ox} are not really predictive of a strong activity of the $6s^2$ pair of the Tl$^+$ ion in oxygen compounds. The activity will be stronger if the anions of the coordination polyhedron exert a strong and directional Coulombic repulsion on the $6s^2$ pair. For this purpose, the anions must generate a strong field by being (i) in a reduced number around atom Tl in order to form a small and irregular coordination polyhedron, and (ii) strongly bound to Tl and bearing high real charges. Because none of these conditions is fulfilled in the Tl$_2XO_4$ compounds, the faint stereochemical activity of the $6s^2$ pair is quite understandable.
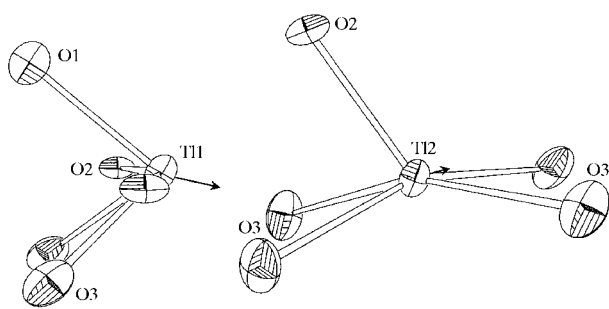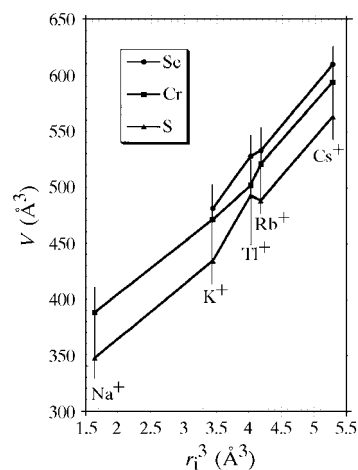

Figure 2
A view of the Tl-atom environments (only the five nearest O atoms are shown), with 50% probability displacement ellipsoids and localization of the lone pairs. The projection plane is nearly the mirror plane. For clarity, the Tl$-E$ distances (arrows) have been multiplied by a factor of 5.

Figure 3
Unit-cell volumes of isotypic A_2XO_4 compounds (A = Na, K, Tl, Rb and Cs, and X = S, Cr and Se) as a function of r^3_{A+} (r_{A+} is the ionic radius of the A^+ cations).

Experimental

Crystals of β-Tl$_2$SO$_4$ were grown from an aqueous solution of commercially obtained material (Aldrich, 99.99% purity) by slow evaporation at room temperature. The crystals appear as colourless acicular polyhedra.

Crystal data

Tl$_2$SO$_4$	Mo $K\alpha$ radiation
$M_r = 504.80$	Cell parameters from 21
Orthorhombic, $Pnma$	reflections
$a = 7.818\,(1)$ Å	$\theta = 8.7–12.1°$
$b = 5.931\,(1)$ Å	$\mu = 65.60$ mm^{-1}
$c = 10.634\,(2)$ Å	$T = 293\,(2)$ K
$V = 493.1\,(2)$ Å^3	Needle, colourless
$Z = 4$	$0.11 \times 0.04 \times 0.02$ mm
$D_x = 6.800$ Mg m^{-3}	
$D_m = 6.75\,(7)$ Mg m^{-3}	
D_m measured by picnometry	

Data collection

Syntex Nicolet P3F diffractometer	$\theta_{max} = 27.5°$
$\theta/2\theta$ scans	$h = 0 \rightarrow 10$
Absorption correction: analytical	$k = 0 \rightarrow 7$
(de Meulenaer & Tompa, 1965)	$l = 0 \rightarrow 13$
$T_{min} = 0.074$, $T_{max} = 0.356$	3 standard reflections
605 measured reflections	every 60 reflections
605 independent reflections	intensity decay: 1.1%
571 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.048P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.025$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.064$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.06$	$\Delta\rho_{max} = 1.60$ e Å^{-3}
605 reflections	$\Delta\rho_{min} = -1.58$ e Å^{-3}
41 parameters	Extinction correction: $SHELXL$97
	Extinction coefficient: 0.0136 (7)

Table 1
Selected interatomic distances (Å).

Tl1—O1^i	2.843 (11)	Tl2—O3^{iii}	2.910 (7)
Tl1—O2^{ii}	3.013 (2)	Tl2—O3^{vi}	2.942 (6)
Tl1—O3^{iv}	3.029 (9)	Tl2—O1^i	3.071 (12)
Tl1—O3^v	3.250 (9)	Tl2—O2^{vii}	3.082 (10)
Tl1—O3	3.260 (7)	Tl2—O1^{iii}	3.239 (5)
Tl1—O2	3.366 (8)	S—O2	1.461 (10)
Tl1—O1^v	3.651 (12)	S—O3	1.467 (6)
Tl2—O2^i	2.801 (8)	S—O1	1.480 (11)

Symmetry codes: (i) $1+x, y, z$; (ii) $1-x, 1-y, 1-z$; (iii) $1-x, -y, 1-z$; (iv) $1-x, \frac{1}{2}+y, 1-z$; (v) $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}-z$; (vi) $\frac{3}{2}-x, \frac{1}{2}+y, \frac{1}{2}+z$; (vii) $\frac{1}{2}+x, \frac{1}{2}-y, \frac{3}{2}-z$.

Data collection: *P3 Software* (Nicolet, 1987); cell refinement: *P3 Software*; data reduction: *XDISK* (Nicolet, 1987); program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics:

Table 2
Bond valence sums, Tl—E distances (Å) and E positions.

Atom	Coordination number	Bond valence sum		Tl—E distance		E coordinates		
		(a)	(b)	(a)	(b)	x	y	z
Tl1	[11]	0.840	0.840	0.077	0.152	0.655	1/4	0.404
Tl2	[9]	1.044	0.989	0.160	0.077	0.985	1/4	0.701
S	[4]	5.186	6.094	–	–	–	–	–

Notes: (a) Pannetier & Gaultier (1966b); (b) this work.

ORTEP-3 (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.

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