REGULAR STRUCTURAL PAPERS

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Thallium(I) Selenate

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Abstract

Tl_2SeO_4 belongs to the β-K_2SO_4 family; the asymmetric unit consists of a tetrahedral selenate anion and two Tl cations. Tl(1) and Tl(2) are surrounded by eleven and nine O atoms respectively. The six O atoms closest to Tl(2) form an irregular octahedron with Tl(2)—O distances of 2.83 (2)–3.04 (2) Å. The Tl(1) cation makes short contacts with two pairs of symmetrically equivalent O atoms at distances of 3.08 (2) and 3.082 (3) Å, respectively, and an even shorter contact [2.66 (2) Å] with a fifth O atom. These five O atoms are on one side of the Tl(1) atom. This irregular coordination may indicate stereochemical activity of the Tl(1) lone pair. The environments of the Tl atoms in the present compound are very similar to those in Tl_2CrO_4.

Comment

Thallium(I) compounds often resemble their alkali-metal analogues, particularly those of K and Rb, the ionic radii of which are not so different from that of Tl^+ [crystal radii of these cations for coordination number 8 are: $r(K^+) = 1.65$, $r(Rb^+) = 1.75$, $r(Tl^+) = 1.73$ Å (Shannon, 1976)]. The stereochemistry of Tl^I compounds is affected by the thallium lone-pair stereoactivity. This is manifested in compounds where Tl has a low coordination number ($n \leq 5$) by the formation of short bonds to bases with strengths of > 0.22 valence units (Brown & Faggiani, 1980).

Between 72 and 428 K it has been shown (Grunwald, Hoffmann & Seidel, 1984*b*; Gaultier & Pannetier, 1972) that Tl_2SeO_4 is isostructural with K_2SeO_4 (Kálmán, Stephens & Cruickshank, 1970), Rb_2SeO_4 (Takahashi, Onodera & Shizoaki, 1987) and Cs_2SeO_4 (Zuniga, Breczewski & Arnaiz, 1991), all of which belong to the β-K_2SO_4 family (space group *Pnma*). At 428 and 523 K it undergoes second-order phase transitions (Gaultier & Pannetier, 1972) and at 661 K a further phase transition takes place into a structure in space group $P\bar{3}m1$ (Gaultier & Pannetier, 1972; Gattow, 1962).

The low-temperature phase transition of Tl_2SeO_4 differs considerably from the phase transition sequence typical of many β-K_2SO_4 structures (*e.g.* K_2SeO_4) which first undergo transition into an incommensurately modulated phase, followed by a lock-in transition into a commensurately modulated structure. Tl_2SeO_4, however, undergoes at 72 K a first-order transition into a phase which belongs to space group $P2_12_12_1$ and which is stable down to 10 K (Grunwald, Hoffmann & Seidel, 1984*a*,*b*). This phase transition is accompanied by a discontinuous increase of the *b* lattice parameter by 0.2 Å and simultaneous decrease of *a* and *c* lattice parameters by 0.05 and 0.3 Å, respectively. Below this phase transition, domains parallel to the *b* axis develop (Grunwald, Hoffmann & Seidel, 1984*b*).

The phase transition of Tl_2SeO_4 has also been investigated by birefringence, dielectric measurements and Raman spectra (Unruh, 1980). Raman spectra suggest that no serious deformation of the selenate anion takes place during the phase transition.

The aim of the present work is to compare the structure of Tl_2SeO_4 with related compounds.

Experimental

Crystal data

Tl_2SeO_4
$M_r = 551.72$
Orthorhombic
Pnma
$a = 7.927$ (2) Å
$b = 6.086$ (2) Å
$c = 10.934$ (3) Å
$V = 527.5$ (3) Å^3
$Z = 4$
$D_x = 6.945$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 5.62$–$18.03°$
$\mu = 68.4$ mm^{-1}
$T = 291$ K
Ellipsoidal, strongly refracting, many natural faces
0.156 × 0.117 mm
0.0667 mm (radius)
Colourless

Data collection

CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical (Flack, 1974)
$T_{min} = 0.00523$, $T_{max} = 0.02877$
3894 measured reflections
$\theta_{max} = 26°$
$h = -9 \rightarrow 9$
$k = -7 \rightarrow 7$
$l = -13 \rightarrow 13$
3 standard reflections
frequency: 120 min
intensity variation: 5%

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Table 1. *Atomic positional parameters and anisotropic thermal parameters* (Å^2 × 10^4)

The anisotropic temperature factors are of the form: $U = \exp\{-2\pi^2[U_{11}h^2(a^*)^2 + U_{22}k^2(b^*)^2 + U_{33}h^2(c^*)^2 + 2U_{12}hk(a^*b^*) + 2U_{13}hl(a^*c^*) + 2U_{23}kl(b^*c^*)]\}$.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Tl(1)	0.1718 (1)	0.2500	0.08348 (9)	313 (5)	346 (5)	401 (6)	—	44 (4)	—
Tl(2)	−0.0016 (1)	0.2500	0.71609 (8)	302 (5)	424 (6)	312 (5)	—	−3 (4)	—
Se	0.2091 (2)	0.2500	0.4217 (2)	227 (10)	222 (10)	212 (10)	—	−4 (8)	—
O(1)	0.0072 (23)	0.2500	0.4228 (23)	373 (110)	721 (151)	846 (160)	—	146 (115)	—
O(2)	0.2796 (26)	0.2500	0.5560 (19)	538 (112)	632 (132)	476 (113)	—	−137 (91)	—
O(3)	0.2802 (19)	0.0341 (22)	0.3535 (15)	813 (93)	365 (79)	744 (101)	122 (67)	211 (81)	−291 (73)

568 independent reflections
403 observed reflections
[$I > 3\sigma(I)$]

$R_{\rm int} = 0.063$

Refinement

Refinement on F
Final $R = 0.0472$
$wR = 0.0392$
$S = 0.896$
568 reflections
41 parameters
$w = 1/\sigma^2(|F_o|)$
$(\Delta/\sigma)_{\max} = 0.01$
$\Delta\rho_{\max} = 2.50$ e Å^{-3}
$\Delta\rho_{\min} = -1.95$ e Å^{-3}

Extinction correction: Becker & Coppens (1974), type I crystal, Lorentzian
Extinction coefficient: 0.41 (2) × 10^{-4}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV) and Cromer & Mann (1968)

Table 2. *Relevant interatomic distances* (Å) *and angles* (°) *within the selenate anion*

Symmetry code is given in Table 3.

Se—O(1)	1.60 (2)	O(1)—Se—O(2)	110.4 (1.0)
Se—O(2)	1.57 (2)	O(1)—Se—O(3)	110.7 (7)
Se—O(3)	1.61 (1)	O(1)—Se—O(3$^{\rm vii}$)	110.7 (7)
Se—O(3$^{\rm vii}$)	1.61 (1)	O(2)—Se—O(3)	107.9 (7)
O(3)—Se—O(3$^{\rm vii}$)	109.2 (8)	O(2)—Se—O(3$^{\rm vii}$)	107.9 (7)

The crystal was prepared by the reaction of H_2SeO_4 with Tl_2CO_3 and subsequent crystallization. Data collection and cell refinement: CAD-4 software (Enraf-Nonius, 1988). Data reduction and absorption correction: *INTER* (Langer, 1977) with locally adapted *CAMEL JOCKEY* program (Flack, 1974). Program for structure solution and refinement: *SDS* system (Petricek & Maly, 1988). Molecular graphics: *SCHAKAL*88 (Keller, 1988).

The relevant distances and bond angles are given in Tables 2 and 3. Table 3 also contains the corresponding cation-oxygen distances in related isostructural compounds. From Table 3 and Table 4, which lists cation bond valences (Brown & Altermatt, 1985; Brese & O'Keeffe, 1991), the following may be inferred. (1) The cation coordinated to nine O atoms (hereafter C-IX) is more firmly bound than that with 11 surrounding O atoms (C-XI). (2) The five O atoms which are closest to C-XI are distributed as 1 + 4, thus forming the first and second coordination spheres. Tl_2SO_4, which is the least reliably determined structure, seems to be an exception. (3) As the size of the anion increases (sulfate < chromate < selenate) the shortest C-XI—O distance becomes shorter. (4) Table 5 lists average C-XI—O distances for the first and second coordination spheres. In compounds with the same cation the latter values increase with the size of the anion (sulfate < chromate < selenate). This is in contrast to the C-XI—O distance. However, average distances for the second coordination sphere are similar for compounds with the same

Table 3. *Relevant* Tl—O *distances* (Å) *in* Tl_2SeO_4 *and corresponding distances in some isostructural compounds*

	Tl_2SeO_4	Tl_2CrO_4^{a}	Tl_2SO_4^{b}	Rb_2SeO_4^{c}	Rb_2SO_4^{d}	K_2SeO_4^{e}	K_2CrO_4^{f}	K_2SO_4^{g}
M	Tl	Tl	Tl	Rb	Rb	K	K	K
$R_{\rm val}$	0.027	0.070	0.117	0.039	0.015	0.048	0.0305	0.051
M(1)—O(1$^{\rm i}$)	2.66 (2)	2.70 (9)	2.97 (6)	2.810 (6)	2.921 (2)	2.62 (2)	2.681 (1)	2.723 (4)
M(1)—O(3$^{\rm ii}$)	3.08 (2)	2.98 (5)	3.17 (3)	3.094 (4)	3.055 (2)	3.001 (7)	2.967 (2)	2.925 (3)
M(1)—O(3$^{\rm vi}$)	3.08 (2)	2.98 (5)	3.17 (3)	3.094 (4)	3.055 (2)	3.001 (7)	2.967 (2)	2.925 (3)
M(1)—O(2$^{\rm ii}$)	3.082 (3)	2.98 (9)	2.95 (7)	3.0988 (6)	3.0223 (3)	3.016 (1)	2.9741 (2)	2.9072 (5)
M(1)—O(2$^{\rm iii}$)	3.082 (3)	2.98 (9)	2.95 (7)	3.0988 (6)	3.0223 (3)	3.016 (1)	2.9741 (2)	2.9072 (5)
M(1)—O(3)	3.34 (1)	3.31 (5)	3.10 (4)	3.307 (5)	3.159 (2)	3.200 (7)	3.210 (2)	3.059 (3)
M(1)—O(3$^{\rm vii}$)	3.34 (1)	3.31 (5)	3.10 (4)	3.307 (5)	3.159 (2)	3.200 (7)	3.210 (2)	3.059 (3)
M(1)—O(3$^{\rm iv}$)	3.44 (2)	3.36 (5)	3.26 (4)	3.324 (5)	3.208 (2)	3.266 (8)	3.166 (2)	3.093 (3)
M(1)—O(3$^{\rm v}$)	3.44 (2)	3.36 (5)	3.26 (4)	3.324 (5)	3.208 (2)	3.266 (8)	3.166 (2)	3.093 (3)
M(1)—O(2$^{\rm i}$)	3.46 (2)	3.52 (8)	3.06 (6)	3.387 (6)	3.323 (2)	3.22 (1)	3.225 (2)	3.189 (4)
M(1)—O(1)	3.93 (2)	3.80 (7)	3.65 (6)	3.759 (8)	3.520 (3)	3.77 (1)	3.660 (3)	3.448 (4)
Average	3.27	3.21	3.16	3.237	3.150	2.925	3.103	3.030
M(2)—O(2)	2.83 (2)	2.71 (8)	3.06 (6)	2.909 (6)	2.882 (2)	2.81 (1)	2.749 (2)	2.727 (4)
M(2)—O(3$^{\rm viii}$)	2.89 (2)	2.80 (5)	2.83 (4)	2.871 (5)	2.884 (2)	2.738 (7)	2.736 (2)	2.741 (3)
M(2)—O(3$^{\rm ix}$)	2.89 (2)	2.80 (5)	2.83 (4)	2.871 (5)	2.884 (2)	2.738 (7)	2.736 (2)	2.741 (3)
M(2)—O(3$^{\rm x}$)	2.91 (1)	2.82 (5)	2.91 (4)	2.963 (5)	2.955 (2)	2.822 (8)	2.801 (2)	2.799 (3)
M(2)—O(3$^{\rm xi}$)	2.91 (1)	2.82 (5)	2.91 (4)	2.963 (5)	2.955 (2)	2.822 (8)	2.801 (2)	2.799 (3)
M(2)—O(2$^{\rm xii}$)	3.04 (2)	2.85 (8)	3.01 (5)	2.905 (6)	2.953 (2)	2.79 (1)	2.784 (2)	2.794 (3)
M(2)—O(1)	3.21 (2)	3.08 (6)	2.97 (6)	3.135 (8)	3.051 (3)	2.98 (1)	2.915 (3)	2.918 (4)
M(2)—O(1$^{\rm xi}$)	3.40 (1)	3.24 (3)	3.22 (2)	3.366 (3)	3.243 (1)	3.316 (5)	3.211 (1)	3.134 (2)
M(2)—O(1$^{\rm xiii}$)	3.40 (1)	3.24 (3)	3.22 (2)	3.366 (3)	3.243 (1)	3.316 (5)	3.211 (1)	3.134 (2)
Average	3.05	2.93	3.00	3.039	3.006	2.925	2.883	2.865

Symmetry code: (i) $x+\frac{1}{2}, y, -z+\frac{1}{2}$; (ii) $-x+\frac{1}{2}, -y, z-\frac{1}{2}$; (iii) $-x+\frac{1}{2}, 1-y, z-\frac{1}{2}$; (iv) $x-\frac{1}{2}, y, -z+\frac{1}{2}$; (v) $x-\frac{1}{2}, -y+\frac{1}{2}, -z+\frac{1}{2}$; (vi) $\frac{1}{2}-x, y+\frac{1}{2}, z-\frac{1}{2}$; (vii) $x, -y+\frac{1}{2}, z$; (viii) $-x+\frac{1}{2}, y+\frac{1}{2}, z+\frac{1}{2}$; (ix) $-x+\frac{1}{2}, -y, z+\frac{1}{2}$; (x) $-x, y+\frac{1}{2}, -z+1$; (xi) $-x, -y, -z+1$; (xii) $x-\frac{1}{2}, -y+\frac{1}{2}, -z+\frac{3}{2}$; (xiii) $-x, -y+1, -z+1$.

References: (*a*) Carter & Margulis (1972); (*b*) Pannetier & Gaultier (1966); (*c*) Takahashi, Onodera & Shizoaki (1987); (*d*) Weber, Schulz, Schmitz, Granzin & Siegert (1989); (*e*) Kálmán, Stephens & Cruickshank (1970); (*f*) Toriumi & Saito (1978); (*g*) McGinnety (1972).

anion but different cations. (5) The first coordination sphere of the C-IX cation is formed by the six nearest O atoms (Tl_2SO_4 is again an exception). These distances are similar for the compounds with the same cation irrespective of the anion (Table 6).

The five O atoms nearest to Tl(1) are at < 3.1 Å and lie on the same side of the Tl(1) atom, thus indicating the stereoactivity of the Tl(1) lone pair. The bond valence of the shortest Tl(1)—O bond (Table 7) exceeds 0.22 valence units which is also in accordance with the assumed stereoactivity of this lone pair (Brown & Faggiani, 1980). Thus O(1) in this bond acts as a strong base unlike other O atoms from the same selenate anion. However, similar stereochemistry to that of the cation coordinated by 11 O atoms is found in other isostructural compounds, K_2SeO_4 being the most pronounced example.

The phase transition at 72 K is accompanied by an abrupt change in the lattice parameters; the least affected lattice parameter is the *a* axis. This may be explained by the fact the most stable bonding pattern [$Tl(1^{iv})$—O(1)—Se] between Tl atoms and selenate anions [2.66 (2) Å] is almost parallel to the *a* axis. Thus the supposed rotational movement of selenate groups during the phase transition would take place predominantly along the direction imposed by the most stable bonds in the structure.

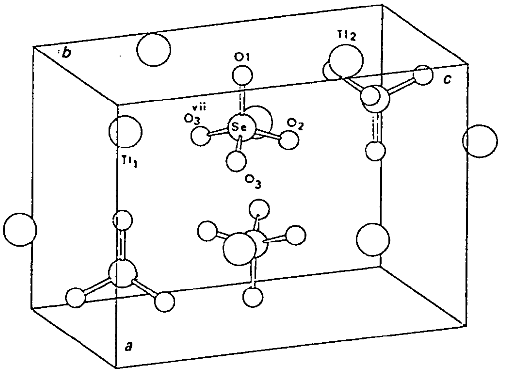

Fig. 1. View of the unit cell of Tl_2SeO_4.

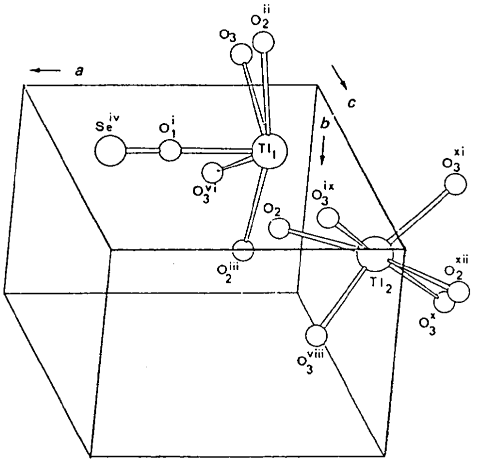

Fig. 2. O atoms closest to Tl(1) and Tl(2) in Tl_2SeO_4.

Table 4. *Cation bond-valence sums (valence units) for* Tl_2SeO_4 *and some isostructural compounds*

The first and second lines apply for eleven- and nine-oxygen-coordinated cations, respectively. The bond-valence parameters for K—O and Rb—O bonds were taken from Brown & Altermatt (1985), those for Tl—O bonds from Brese & O'Keeffe (1991).

	$[SO_4^{2-}]$	$[CrO_4^{2-}]$	$[SeO_4^{2-}]$
K^+	1.081	0.941	0.910
	1.336	1.308	1.214
Rb^+	1.085		0.947
	1.285		1.235
Tl^+	0.840	0.901	0.801
	1.041	1.309	0.962

Table 5. *The average cation–oxygen distances (Å) for the first and second coordination sphere of the eleven-oxygen-coordinated cation*

The first and second lines apply for the first and second coordination spheres, respectively. (Tl_2SO_4 is an exceptional compound, the first and second coordination spheres of which are not composed of one and four O atoms respectively – Table 3.)

	$[SO_4^{2-}]$	$[CrO_4^{2-}]$	$[SeO_4^{2-}]$
K^+	2.723	2.681	2.62
	2.916	2.971	3.096
Rb^+	2.921	—	2.810
	3.039	—	3.096
Tl^+	—	2.70	2.66
	—	2.98	3.08

Table 6. *The average cation–oxygen distances (Å) for the first coordination sphere of the nine-oxygen-coordinated cation*

Tl_2SO_4 is an exceptional compound – see Table 3.

	$[SO_4^{2-}]$	$[CrO_4^{2-}]$	$[SeO_4^{2-}]$
K^+	2.767	2.768	2.787
Rb^+	2.919	—	2.914
Tl^+	—	2.80	2.91

Table 7. *Oxygen–thallium distances (Å), corresponding bond valences and oxygen bond-valence sums (valence units)*

Distance/bond valence		Distance/bond valence		Bond-valence sum
Tl(1)···O(1)	2.66 (2)/0.268	Tl(2)···O(1)	3.21 (2)/0.061	0.41
Tl(1)···O(1)	3.93 (2)/0.009	Tl(2)···O(1)	3.40 (1)/0.036	
		Tl(2)···O(1)	3.40 (1)/0.036	
Tl(1)···O(2)	3.082 (3)/0.086	Tl(2)···O(2)	2.83 (2)/0.167	0.43
Tl(1)···O(2)	3.082 (3)/0.086	Tl(2)···O(2)	3.04 (2)/0.097	
Tl(1)···O(3)	3.08 (2)/0.087	Tl(2)···O(3)	2.89 (2)/0.145	0.44
Tl(1)···O(3)	3.34 (2)/0.042	Tl(2)···O(3)	2.91 (1)/0.138	
Tl(1)···O(3)	3.44 (2)/0.032			
Tl(1)···O(3)	3.46 (2)/0.031			

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Lists of structure factors and anisotropic thermal parameters, have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71230 (37 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: MU1031]

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Structure of a Citrate Double Salt: Potassium Dihydrogen Citrate–Lithium Potassium Hydrogen Citrate Monohydrate

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Abstract

The crystal structure of a double salt of potassium dihydrogen citrate and lithium potassium hydrogen citrate monohydrate has been determined. One potassium ion is coordinated with eight O atoms and the other with nine O atoms at *M*—O distances in the range 2.660 (1) to 3.139 (1) Å. Two of these O atoms are shared by both potassium ions. The lithium ion is tetrahedrally surrounded by four O atoms at distances in the range 1.870 (3) to 1.988 (3) Å. This crystal structure contains nine hydrogen bonds in the asymmetric unit. The water molecule connects different citrate ions along the **c** direction by hydrogen bonding.

Comment

The crystal structure of a double salt of citric acid, potassium dihydrogen citrate–lithium potassium hydrogen citrate monohydrate, was determined in order to compare the metal chelation with that found in other potassium and lithium citrates.

The asymmetric unit of this crystal structure contains one dihydrogen citrate ion (*B*) (Fig. 1) and one hydrogen citrate ion, two potassium ions, a lithium ion and a water molecule. Table 2 gives the dimensions of the citrate ions which are in the fully-extended conformation, along with selected torsion angles. Data on the metal coordination and hydrogen bonding in the crystal are given in Table 3. The potassium ion K(1) is surrounded by eight O atoms and K(2) by nine O atoms. The distances between the potassium ion and the O atoms are, in general, larger when the coordination number is higher. The minimum values are 2.660 (1) Å for a coordination number of eight and 2.729 (1) Å for a coordination number of nine. In both cases the potassium ion spans the α-hydroxycarboxylate group, and forms a tridentate chelate O(6*A*), O(7*A*), O(1*A*) and O(6*B*), O(7*B*), O(4*B*). Such chelation has been found in potassium deoxyfluorocitrate (Carrell, Glusker, Piercy, Stallings, Zacharias, Davis, Astbury & Kennard, 1987) but not in other potassium citrates to date. The location of the citrate H(O5*A*) atom, between O(5*A*) and O(2*A*) of another citrate ion, was checked by calculation of a difference electron-density map. The peak corresponding to this H atom in the map was elongated. Since the e.s.d. values for H atoms are somewhat high, particularly in view of the presence of potassium ions in the structure, it is assumed that either this H(O5*A*) atom is disordered between two positions or that its location is questionable. Therefore, the question as to which O atom [O(5*A*) or O(2*A*)] is involved in the ionization of this citrate ion (*A*) is uncertain in this crystal structure determination, although the C—O distances suggest that the carboxyl group containing O(5*A*) is not ionized (Table 2).

The lithium ion is surrounded by four O atoms from different citrate ions, as found in certain other crystal structures of other lithium citrates (Gabe, Glusker, Minkin & Patterson, 1967; Rossi, Rickles &

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