# inorganic compounds

# Thallium(III) selenite, $Tl_2(SeO_3)_3$

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The structure of $Tl_2(SeO_3)_3$ [dithallium(III) triselenium(IV) nonaoxide] is monoclinic ($P2_1/n$ symmetry), with all atoms in general positions. It is built up from $TlO_6$ octahedra, distorted $TlO_7$ pentagonal bipyramids and $(SeO_3)^{2-}$ pyramids sharing vertices and edges to form corrugated (001) layers. The Se lone pairs of electrons are accommodated in the interlayer regions.

## Comment

Inorganic selenites containing the pyramidal $(SeO_3)^{2-}$ ion are of ongoing crystallochemical interest because of the way the inherently asymmetric selenite ion packs into extended structures and the space requirements of the $Se^{IV}$ lone pair of electrons (Wontcheu & Schleid, 2005). Metal selenites have also been studied for their potentially useful physical properties, such as second-harmonic generation (Ok & Halasyamani, 2002). As part of our ongoing studies of metal selenites (Johnston & Harrison, 2004a,b), we report here the structure of the title compound, $Tl_2(SeO_3)_3$, (I).

A compound of the same stoichiometry as (I) was first reported almost 100 years ago (Marino, 1909). Much later, Gospodinov (1984) reported a lemon-yellow compound of stoichiometry $Tl_2(SeO_3)_3$, although its crystal structure was not determined. The simulated X-ray powder pattern of (I) (colourless compound) does not match the powder data reported by Gospodinov. Thus, the yellow phase could represent a second polymorph of $Tl_2(SeO_3)_3$. We could find no other detailed structural studies of thallium(III) selenites, although the structures of thallium(I) 'trihydroselenite', $TlH_3(SeO_3)_2$ (Shuvalov et al., 1983), and thallium(I) selenate, $Tl_2SeO_4$ (Fábry & Breczewski, 1993), have been determined from single-crystal data.

There are two Tl, three Se and nine O atoms in the asymmetric unit of (I), all of which occupy general positions in the unit cell. The three selenite groups show their expected (Verma, 1999) pyramidal coordination (Table 1), with the unobserved lone pair of electrons assumed to occupy the fourth tetrahedral vertex about each Se atom. The mean Se—

O bond lengths are 1.716 (2), 1.709 (2) and 1.706 (2) Å for Se1, Se2 and Se3, respectively. The bond-valence sums (BVS) for the Se atoms, calculated using the Brown (1996) formalism, are 3.88, 3.98 and 3.99 for Se1, Se2 and Se3, respectively. These are in satisfactory agreement with the expected value of 4.00. The Se atoms are displaced from the plane formed by their three attached O atoms by 0.794 (6) (Se1), 0.807 (6) (Se2) and 0.794 (6) Å (Se3). The O—Se—O bond angles in (I) show more variation than is typical for selenite groups (Johnston & Harrison, 2004a) [for Se1, $\theta$ = 95.4 (5)–102.7 (5)°, range = 7.3°; for Se2, $\theta$ = 89.7 (5)–107.3 (5)°, range = 17.6°; for Se3, $\theta$ = 93.4 (5)–103.9 (5)°, range = 10.5°]. These distortions in the O—Se—O bond angles correlate well with their edge-sharing connectivity to adjacent thallium polyhedra (see below).

Atom Tl1 is approximately octahedrally coordinated by six O atoms. The mean Tl—O bond length of 2.24 (2) Å is in excellent agreement with the value of 2.25 Å expected on the basis of the ionic radius sum for $Tl^{III}$ and $O^{-II}$ (Shannon, 1976). The BVS for Tl1 is 3.28, compared with an expected value of 3.00 for $Tl^{III}$. This discrepancy perhaps suggests a degree of 'overbonding' for this species, assuming that the BVS parameters for this species are reliable. The next-nearest O atom is 3.45 Å away from Tl1.

The coordination about atom Tl2 is unusual (Fig. 1). There are seven near-neighbour O atoms, with the $Tl2—O1^{iv}$ bond of 2.496 (10) Å being significantly longer than the other six [mean = 2.28 (2) Å] (see Table 1 for symmetry codes). However, we feel that it is appropriate to consider it to be a bond because it contributes a significant 0.27 valence units to the Tl2 BVS of 3.20. The next-nearest neighbouring O atom is 3.78 Å distant from Tl2. There are no fewer than three edge-sharing selenite groups bonded to Tl2, involving the six shorter Tl2—O bonds. The three acute O—Se—O bond angles noted above are involved in these three edge-sharing inter-
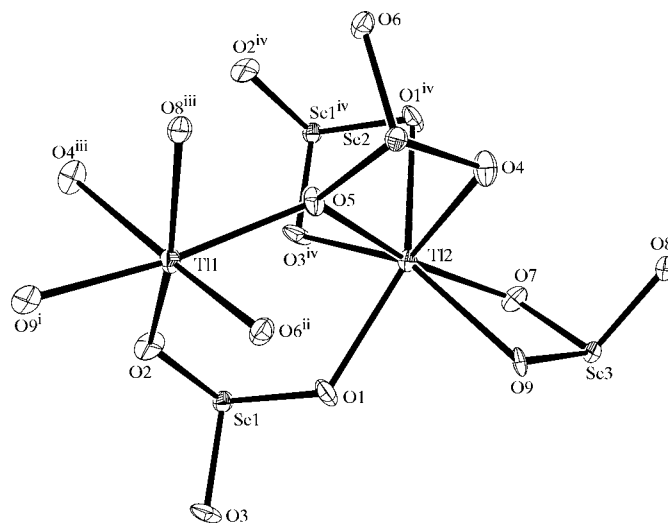


**Figure 1**
A view of a fragment of (I), showing 50% probability displacement ellipsoids. Symmetry codes are as given in Table 1.

actions and the corresponding O—Tl2—O edge-sharing bond angles are grouped in the narrow range of 64.7 (3)–66.0 (4)°. The $Tl2O_7$ polyhedron could be described as a very distorted pentagonal bipyramid, with atoms O5 and O7 in the axial positions [$\theta$(O5—Tl2—O7) = 166.0 (4)°]. The equatorial atoms Tl2, O1, $O1^{iv}$ and O3 are approximately coplanar (r.m.s. deviation from the best plane is 0.008 Å). However, atom O9, and especially atom O4, are substantially displaced from their nominal equatorial positions by 0.632 (15) and −1.179 (16) Å, respectively.

Of the nine O atoms in the structure of (I), four, namely O1 [bond angle sum = 359.6 (5)°], O4 [359.6 (6)°], O5 [354.2 (6)°] and O9 [358.9 (5)°], are tricoordinate to two Tl plus one Se neighbours. There is a wide variation in these angles, e.g. the Tl—O1—Tl angle is the most obtuse around O1, whereas a Tl—O4—Se angle is the largest around O4 (Table 1). The remaining five O atoms form bicoordinate Tl—O—Se bridges [mean $\theta$(Tl—O—Se) = 120.3°]. The bicoordinate bond-angle distribution is sharply bimodal, with two angles of around 104° and three angles of around 131° (Table 1).

The polyhedral connectivity in (I) results in corner-sharing (involving the long Tl2—O1 bond) chains of the $Tl2O_7$ groups propagating in the [100] direction. These are crosslinked by the $Tl1O_6$ groups to form (001) sheets (Fig. 2). The $Tl1O_6$ groups do not bond to other Tl1-centred polyhedra, but make four bonds to Tl2-centred moieties. Finally, the thallium/oxygen layers are decorated on both sides of the sheet by Se atoms (as parts of selenite groups).

When viewed down [100] (Fig. 3), the (001) layers are seen to be significantly corrugated, with the $Se^{IV}$ lone pairs of electrons appearing to point into the interlayer regions of the structure. This suggests that, at least in part, the Se lone pairs are responsible for the layered nature of (I).

## Experimental

$Tl_2O_3$ (0.761 g, 1.66 mmol) was added to a 0.5 M $H_2SeO_3$ (20 ml) aqueous solution (i.e. dissolved $SeO_2$) and heated to 353 K in a plastic bottle. Thin colourless plates and shards of (I) grew over a few days and were recovered by vacuum filtration; they were accompanied by a small amount of black residue of $Tl_2O_3$. [Caution! All thallium compounds are exceedingly toxic. All appropriate safety precautions must be taken during their handling, especially with respect to dust contamination.]
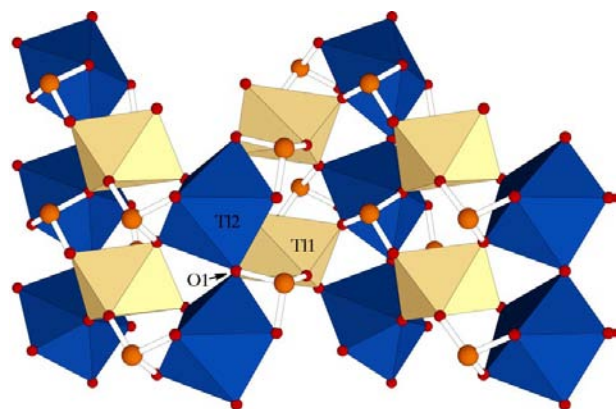


**Figure 2**
Part of an (001) layer in (I), showing the [100] chains of $Tl2O_7$ groups (dark shading) crosslinked by the $Tl1O_6$ octahedra (light shading). Se and O atoms are represented by large and small spheres, respectively.
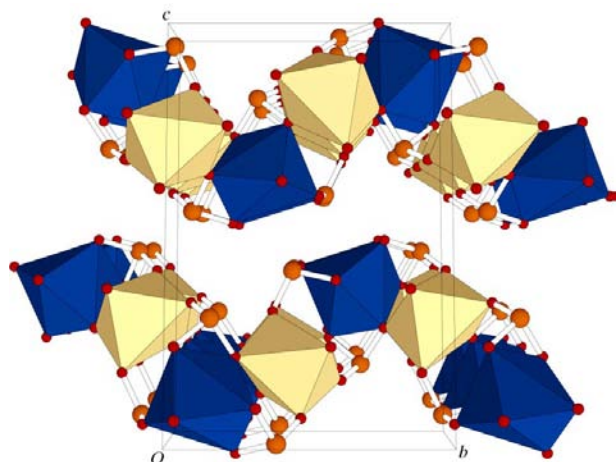


**Figure 3**
The unit-cell packing in (I), projected on to (100). Drawing conventions are as in Fig. 2.

### Crystal data

| | |
|---|---|
| $Tl_2(SeO_3)_3$ | $D_x$ = 6.148 Mg m$^{-3}$ |
| $M_r$ = 789.62 | Mo $K\alpha$ radiation |
| Monoclinic, $P2_1/n$ | Cell parameters from 1734 |
| $a$ = 4.5666 (3) Å | reflections |
| $b$ = 11.2194 (10) Å | $\theta$ = 2.9–27.5° |
| $c$ = 16.7595 (13) Å | $\mu$ = 50.56 mm$^{-1}$ |
| $\beta$ = 96.549 (6)° | $T$ = 120 (2) K |
| $V$ = 853.06 (12) Å$^3$ | Shard, colourless |
| $Z$ = 4 | 0.13 × 0.05 × 0.01 mm |

### Data collection

| | |
|---|---|
| Nonius KappaCCD area-detector diffractometer | 1948 independent reflections |
| | 1690 reflections with $I > 2\sigma(I)$ |
| $\omega$ and $\varphi$ scans | $R_{int}$ = 0.059 |
| Absorption correction: multi-scan (SADABS; Bruker, 2003) | $\theta_{max}$ = 27.5° |
| | $h$ = −5 → 5 |
| $T_{min}$ = 0.053, $T_{max}$ = 0.632 | $k$ = −14 → 14 |
| 10219 measured reflections | $l$ = −21 → 21 |

### Refinement

| | |
|---|---|
| Refinement on $F^2$ | $w = 1/[\sigma^2(F_o^2) + (0.0696P)^2$ |
| $R[F^2 > 2\sigma(F^2)]$ = 0.044 | $+ 26.3163P]$ |
| $wR(F^2)$ = 0.121 | where $P = (F_o^2 + 2F_c^2)/3$ |
| $S$ = 1.08 | $(\Delta/\sigma)_{max}$ = 0.002 |
| 1948 reflections | $\Delta\rho_{max}$ = 2.53 e Å$^{-3}$ |
| 127 parameters | $\Delta\rho_{min}$ = −3.22 e Å$^{-3}$ |

The highest difference peak is 0.94 Å from O2 and 1.40 Å from Tl1; the deepest hole is 0.92 Å from O5 and 1.38 Å from Tl2.

Data collection: COLLECT (Nonius, 1998); cell refinement: SCALEPACK (Otwinowski & Minor, 1997); data reduction: DENZO (Otwinowski & Minor, 1997) and SCALEPACK; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP-3 (Farrugia, 1997) and ATOMS (Dowty, 2000); software used to prepare material for publication: SHELXL97.

# inorganic compounds

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| Tl1—O2 | 2.131 (10) | Tl2—O9 | 2.382 (10) |
| Tl1—O9$^i$ | 2.229 (10) | Tl2—O1$^{iv}$ | 2.496 (10) |
| Tl1—O5 | 2.231 (10) | Se1—O3 | 1.706 (10) |
| Tl1—O6$^{ii}$ | 2.251 (10) | Se1—O1 | 1.718 (10) |
| Tl1—O8$^{iii}$ | 2.269 (10) | Se1—O2 | 1.724 (11) |
| Tl1—O4$^{iii}$ | 2.298 (10) | Se2—O6 | 1.650 (10) |
| Tl2—O3$^{iv}$ | 2.198 (10) | Se2—O5 | 1.734 (10) |
| Tl2—O7 | 2.207 (11) | Se2—O4 | 1.743 (10) |
| Tl2—O4 | 2.280 (11) | Se3—O8 | 1.681 (10) |
| Tl2—O1 | 2.293 (10) | Se3—O7 | 1.713 (10) |
| Tl2—O5 | 2.299 (10) | Se3—O9 | 1.725 (10) |
| | | | |
| Se1—O1—Tl2 | 121.2 (5) | Se2—O5—Tl2 | 102.4 (4) |
| Se1—O1—Tl2$^{ii}$ | 93.5 (4) | Tl1—O5—Tl2 | 127.0 (5) |
| Tl2—O1—Tl2$^{ii}$ | 144.9 (5) | Se2—O6—Tl1$^{iv}$ | 130.6 (6) |
| Se1—O2—Tl1 | 132.3 (6) | Se3—O7—Tl2 | 102.8 (5) |
| Se1—O3—Tl2$^{ii}$ | 105.1 (5) | Se3—O8—Tl1$^v$ | 130.8 (5) |
| Se2—O4—Tl2 | 102.8 (5) | Se3—O9—Tl1$^{vi}$ | 122.3 (5) |
| Se2—O4—Tl1$^v$ | 132.4 (6) | Se3—O9—Tl2 | 95.8 (4) |
| Tl2—O4—Tl1$^v$ | 124.4 (5) | Tl1$^{vi}$—O9—Tl2 | 140.8 (5) |
| Se2—O5—Tl1 | 124.8 (5) | | |

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

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BC1073). Services for accessing these data are described at the back of the journal.

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