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Key indicators

Single-crystal X-ray study
 $T = 293$ K
 Mean $\sigma(S-P) = 0.005$ Å
 R factor = 0.046
 wR factor = 0.125
 Data-to-parameter ratio = 22.5

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

TlPbPS₄

The quaternary thallium thiophosphate TlPbPS₄ (thallium lead phosphorus tetrasulfide) was obtained by reacting elemental Pb with a melt, formed *in situ*, of Tl₂S, P₂S₅ and S. The crystal structure is composed of parallel zigzag layers, which consist of condensed S₆ distorted trigonal prisms alternately centred by Tl and Pb atoms. The layers are stacked perpendicular to the crystallographic *a* axis and are joined by [PS₄] tetrahedra. TlPbPS₄ is isostructural with TlEuPS₄ and TlSnPS₄.

Comment

In the course of our work on chalcophosphates (Belkyal *et al.*, 2005, 2006), we have prepared the quaternary thallium lead tetrathiophosphate TlPbPS₄. The title compound has a layered structure and is structurally related to TlEuPS₄ (Carrillo-Cabrera *et al.*, 1995) and TlSnPS₄ (Becker *et al.*, 1987). The structure is characterized by layers of condensed S₆ distorted trigonal prisms alternately centred by Tl and Pb atoms and joined by [PS₄] tetrahedra (Fig. 1). Adjacent [TlS₆] and [PbS₆] prisms share common triangular faces to form one-dimensional chains parallel to [001]. These chains are connected along [010] by sharing edges of rectangular faces in such a way that apical edges of the prisms point alternately up and down, forming parallel zigzag layers (Fig. 2). These layers are then joined by [PS₄]³⁻ tetrahedra along [100] by sharing edges with the rectangles of the trigonal prisms. There are two *n*-glide-related layers per unit cell along *a*. In this way each [PbS₆] prism is connected to four [PS₄] tetrahedra. With two of the tetrahedra it shares a common edge; with the other two it

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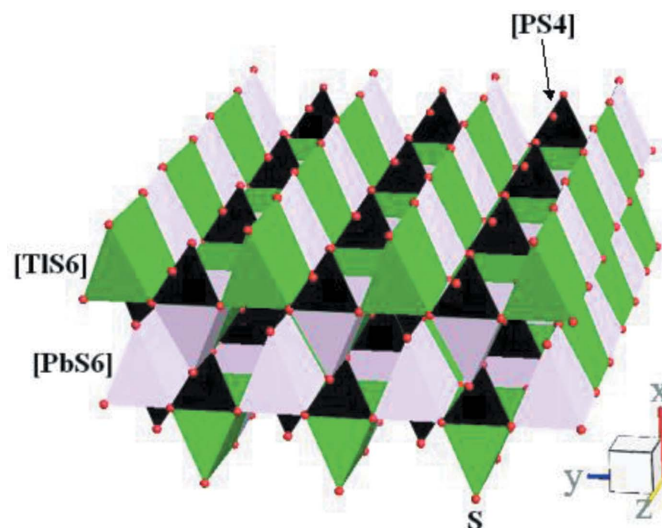


Figure 1
 Extended structure of TlPbPS₄, projected approximately along [001].

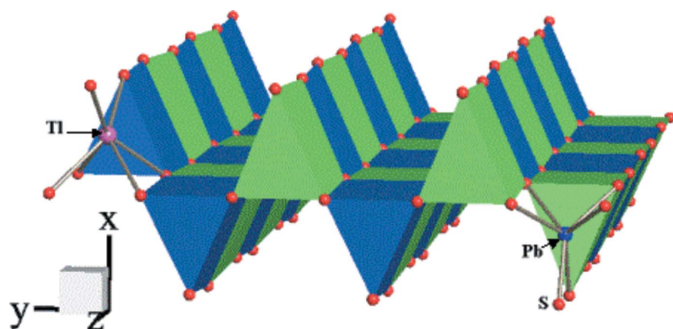


Figure 2
Projection approximately along the [001] direction, showing the pucker layer of condensed chains of adjacent [TlS₆] and [PbS₆] prisms.

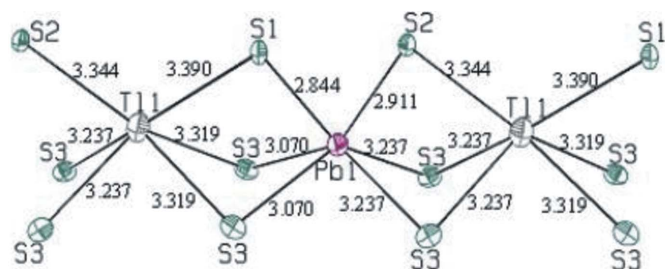


Figure 3
ORTEP plot of lead and thallium coordination in TIPbPS₄. The Pb—S and Tl—S distances are given in Å (anisotropic displacement parameters drawn at the 50% probability level).

shares only corners. Each [TlS₆] prism is connected to five [PS₄] units. With one of the tetrahedra it shares a common edge; with the other it shares corners. The Pb—S distances found in TIPbPS₄ range from 2.844 (4) to 3.120 (3) Å and compare very well with those reported for KPbPS₄ (Belkhal et al., 2006) and CsPbPS₄ (Belkhal et al., 2005). Likewise, the Tl—S distances range from 3.237 to 3.399 Å and are comparable with those of TlEuPS₄ (Carrillo-Cabrera et al., 1995). The mean Pb—S and Tl—S distances are close to the sum of the ionic radii (Shannon, 1976). The average P—S distance within the [PS₄] unit [2.040 (5) Å] is in good agreement with the P—S distances found in related phases. The [PbS₆] and [TlS₆] polyhedra are very irregular, as shown in Fig. 3. Responsible for this distorted coordination are stereoactive lone electron pairs (LEPs) of Pb and Tl atoms that point in the direction of the longer M—S (M = Tl, Pb) distances. These lone pairs are, presumably, stereochemically expressed by the S—M—S angles. For the [TlS₆] prism, the S1—Tl—S2 angle of 108.21° suggests that the LEP of the Tl atom is pointing between atoms S1 and S2 along [100]. In the [PbS₆] prism, the Pb atom's LEP is directed at the rectangular face formed by S3 atoms along [100]. In this way, the electrostatic repulsion between the LEPs is minimized.

Experimental

TIPbPS₄ was prepared from a stoichiometric mixture of Pb (99.9%, Aldrich), P₂S₅ (99.99%, Alfa), S (99.99%, Heraeus) and Tl₂S. The latter was prepared by thermal decomposition of Tl₂CS₃ (Horn &

Sterzel, 1973; Johri et al., 1970) in an argon atmosphere under reduced pressure at $T_{\max} = 523$ K. The reaction mixture was thoroughly mixed in an N₂-filled glove box and loaded into a quartz ampoule. After evacuation to 10⁻³ mbar the ampoule was flame-sealed and placed in a computer-controlled furnace. The sample was heated to 1143 K, kept at this temperature for 3 d and then cooled to 408 K at a rate of 4.5 K h⁻¹; the furnace was then turned off. After washing with diethyl ether, transparent orange crystals were obtained. The compound is slightly air- and moisture-sensitive. An EDX analysis indicated the presence of all four elements (Tl, Pb, P, S) in an approximate atomic ratio of 1:1:1:4. The EDX analysis was performed using a Philips ESEM XL 30 scanning electron microscope equipped with an EDAX analyser.

Crystal data

TIPbPS₄
 $M_r = 570.77$
Orthorhombic, $Pnma$
 $a = 12.0976$ (9) Å
 $b = 6.5816$ (5) Å
 $c = 8.8093$ (6) Å
 $V = 701.41$ (9) Å³

$Z = 4$
 $D_x = 5.405$ Mg m⁻³
Mo $K\alpha$ radiation
 $\mu = 48.21$ mm⁻¹
 $T = 293$ (2) K
Platelet, orange
0.08 × 0.06 × 0.05 mm

Data collection

Stoe IPDS diffractometer
 ω scans
Absorption correction: numerical
(*X-SHAPE*; Stoe & Cie, 1998)
 $T_{\min} = 0.005$, $T_{\max} = 0.046$

4828 measured reflections
921 independent reflections
743 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.114$
 $\theta_{\max} = 28.0^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.046$
 $wR(F^2) = 0.125$
 $S = 1.00$
921 reflections
41 parameters

$w = 1/[\sigma^2(F_o^2) + (0.0775P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 2.57$ e Å⁻³
 $\Delta\rho_{\min} = -3.30$ e Å⁻³
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0021 (3)

Table 1

Selected geometric parameters (Å, °).

| | | | |
|---|-------------|--|-------------|
| Pb1—S1 | 2.844 (4) | Pb1—S3 ⁱⁱⁱ | 3.120 (3) |
| Pb1—S2 | 2.911 (4) | P1—S1 | 2.035 (6) |
| Pb1—S3 ⁱ | 3.070 (3) | P1—S3 | 2.038 (4) |
| S1—Pb1—S2 | 71.53 (12) | S1—P1—S3 | 109.45 (16) |
| S1—Pb1—S3 ⁱ | 143.95 (6) | S3—P1—S3 ^{iv} | 107.1 (3) |
| S2—Pb1—S3 ⁱ | 91.71 (9) | S1—P1—S2 | 110.9 (3) |
| S3 ⁱ —Pb1—S3 ⁱⁱⁱ | 65.09 (11) | S3—P1—S2 | 109.94 (15) |
| S1—Pb1—S3 ⁱⁱⁱ | 83.26 (9) | P1—S1—Pb1 | 89.85 (17) |
| S2—Pb1—S3 ⁱⁱⁱ | 139.66 (7) | P1—S2—Pb1 | 87.73 (17) |
| S3 ⁱ —Pb1—S3 ⁱⁱⁱ | 125.35 (2) | P1—S3—Pb1 ⁱⁱ | 96.62 (14) |
| S3 ⁱⁱ —Pb1—S3 ⁱⁱⁱ | 90.764 (13) | P1—S3—Pb1 ^v | 82.37 (13) |
| S3 ⁱⁱⁱ —Pb1—S3 ^{vi} | 63.37 (11) | Pb1 ⁱⁱ —S3—Pb1 ^v | 176.20 (12) |

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

The highest peak in the difference electron-density map is located 0.76 Å from Pb1 and the deepest hole 0.77 Å from Tl1.

Data collection: *IPDS Program Package* (Stoe & Cie, 1998); cell refinement: *IPDS Program Package*; data reduction: *IPDS Program Package*; 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 *BS* (Ozawa

& Kang, 2004); software used to prepare material for publication: *SHELXL97*.

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