TlBiS$_2$

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The ternary compound thallium bismuth disulfide crystallizes in the space group $R\bar{3}m$ and is isotypic with the structures of most of the ABQ_2 chalcogenides (A = monovalent atom, B = trivalent atom and Q = chalcogen), which are members of the α-NaFeO$_2$ structure type. In the title compound, the Tl and Bi atoms are situated on positions with $\bar{3}m$ symmetry, whereas the S atom sites exhibit $3m$ symmetry. The metal atoms occupy octahedral voids in distinct planes perpendicular to the c axis. The environment around Tl is more distorted than the polyhedron around Bi.

Comment

The d values for TlBiS$_2$ were determined from a study of the pseudo-binary system PbS–TlBiS$_2$ by Malevskii (1966). Later, the Tl$_2$S–Bi$_2$S$_3$ system was investigated using different methods (Dembovskii *et al.* 1968) and vacuum-annealed films deposited on NaCl surfaces were investigated (Palatnik *et al.*, 1972). The authors report most (actually ten) of 'the stronger lines of the X-ray and electron diffraction pattern as indicative of a cubic face-centred lattice'. The remaining weak lines were indexed on the basis of a hexagonal lattice. The connection between the dimensions of the cubic and the hexagonal cell can be explained by application of the usual equations. In our opinion, it is therefore not very likely to be a question of polymorphism. Further structural investigations were made (Julien-Pouzol & Guittard, 1975) and the cell parameters of TlBiS$_2$ were redetermined (Özer *et al.*, 1996, 1998). The particular interest in TlBiS$_2$ is due to the fact that it is a narrow-gap semiconductor, isoelectronic with PbS (Özer *et al.*, 1996).

The structure of TlBiS$_2$ and the closely related ABQ_2-type compounds (A = monovalent atom, B = trivalent atom and Q = chalcogen) can be derived from a simple NaCl-type lattice by a rhombohedral distortion along the cubic [111] direction, corresponding to the c axis of the primitive hexagonal arrangement. The important question is not answered as to whether Tl and Bi occupy the layers perpendicular to [111] in an ordered or a statistical fashion, because Tl and Bi cannot easily be distinguished from each other by X-ray diffraction. This problem was discussed in detail for the structural investigation of the isotypic TlBiSe$_2$ (Toubektsis & Polychroniadis, 1987). Electron microscopic studies of this compound confirmed the rhombohedral lattice and revealed a superstructure due to the ordering of individual layers in the sequence –Se–Tl–Se–Bi–Se– (Toubektsis & Polychroniadis, 1987). However, the superstructure reflections were not observed by complementary X-ray diffraction studies of TlBiSe$_2$. In the present case, we prefer an ordered model based on crystal chemical considerations.
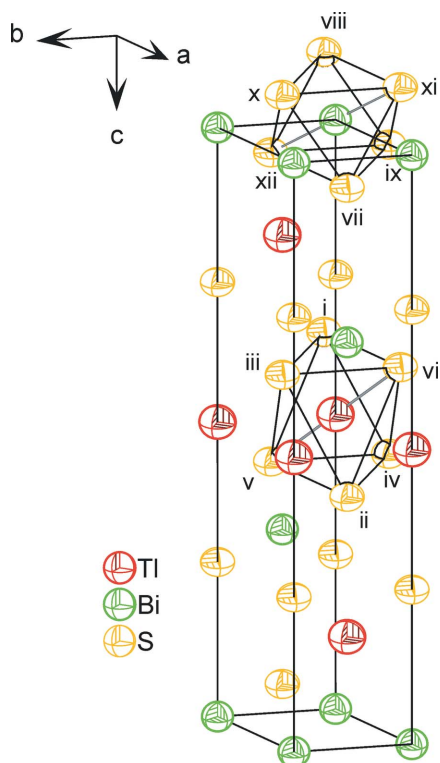
Figure 1
The arrangement of the atoms in the structure of TlBiS$_2$. The unit cell and the coordination polyhedra around Bi and Tl are outlined. Displacement ellipsoids are drawn at the 90% probability level. [Symmetry codes are as in Table 1.]

The close packing of the S atoms comprises small and larger octahedral voids for the metal positions, with interatomic distances of 2.832 (5) Å for Bi—S (6×) and 3.162 (6) Å for Tl—S (6×) for the chosen arrangement. The Tl and Bi atoms are located at positions with $\bar{3}m$ symmetry, whereas the S atom sites exhibit $3m$ symmetry. The sum of the ionic radii for a coordination number (CN) of 6 is 2.87 Å for Bi^{3+}/S^{2-} and 3.34 Å for Tl$^+$/S^{2-} [r(Bi^{3+}) = 1.03 Å, r(Tl$^+$) = 1.50 Å and r(S^{2-}) = 1.84 Å (Shannon, 1976)]. The experimentally determined bond length matches well for Bi—S, but for the Tl—S distance the value is about 5.3% smaller.

The metal atoms are located in the 'centroid' (Balić Žunić & Makovicky, 1996) of the octahedron, although their environments are slightly distorted. The planes defined by the S atoms generated by symmetry operators (x), (viii), (ix) and (ii) for the polyhedron around Bi, and (iv), (iii), (v) and (i) for that around Tl (Fig. 1), are not perpendicular to the straight line between the S atoms defined by symmetry operators (xii) and (xi), and (vi) and (vii) [inclination 4.162 (3)° for Bi and 11.973 (6)° for Tl]. For more detailed information and symmetry codes, see Table 1. As expected, the rhombohedral distortion has the strongest effect on the environment of the Tl position.

Experimental

Crystal data

TlBiS$_2$	D_x = 7.455 Mg m^{-3}
M_r = 477.47	Mo $K\alpha$ radiation
Trigonal, $R\bar{3}m$	μ = 79.89 mm^{-1}
a = 4.1041 (5) Å	T = 295 (2) K
c = 21.872 (4) Å	Irregular fragment, black
V = 319.05 (8) Å^3	0.12 × 0.10 × 0.08 mm
Z = 3	

Data collection

Stoe IPDS diffractometer	706 measured reflections
ω scans	127 independent reflections
Absorption correction: numerical [*X-SHAPE* (Stoe & Cie, 1998) and *X-RED* (Stoe & Cie, 1998)] T_{min} = 0.003, T_{max} = 0.019	108 reflections with $I > 2\sigma(I)$ R_{int} = 0.097 θ_{max} = 28.0°

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} < 0.001$
$R[F^2 > 2\sigma(F^2)]$ = 0.049	$\Delta\rho_{max}$ = 3.15 e Å^{-3}
$wR(F^2)$ = 0.130	$\Delta\rho_{min}$ = −5.55 e Å^{-3}
S = 1.09	Extinction correction: *SHELXL97* (Sheldrick, 1997)
127 reflections	Extinction coefficient: 0.008 (2)
9 parameters	
$w = 1/[\sigma^2(F_o^2) + (0.0911P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$	

Table 1
Selected geometric parameters (Å, °).

Tl—S1^i	3.162 (6)	Bi—S1^{ii}	2.832 (5)
S1^{iii}—Tl—S1^i	180.000 (1)	S1^{ii}—Bi—S1^{viii}	180.0 (3)
S1^{iii}—Tl—S1^{iv}	80.92 (18)	S1^{ii}—Bi—S1^{ix}	92.9 (2)
S1^i—Tl—S1^{iv}	99.08 (18)	S1^{viii}—Bi—S1^{ix}	87.1 (2)
S1^{iii}—Tl—S1^v	99.08 (18)	S1^{ii}—Bi—S1^x	87.1 (2)
S1^i—Tl—S1^v	80.92 (18)	S1^{viii}—Bi—S1^x	92.9 (2)
S1^{iv}—Tl—S1^v	180.0	S1^{ix}—Bi—S1^x	180.0 (3)
S1^{iii}—Tl—S1^{vi}	99.08 (18)	S1^{ii}—Bi—S1^{xi}	87.1 (2)
S1^i—Tl—S1^{vi}	80.92 (18)	S1^{viii}—Bi—S1^{xi}	92.9 (2)
S1^{iv}—Tl—S1^{vi}	99.08 (18)	S1^{ix}—Bi—S1^{xi}	87.1 (2)
S1^v—Tl—S1^{vi}	80.92 (18)	S1^x—Bi—S1^{xi}	92.9 (2)
S1^{iii}—Tl—S1^{vii}	80.92 (18)	S1^{ii}—Bi—S1^{xii}	92.9 (2)
S1^i—Tl—S1^{vii}	99.08 (18)	S1^{viii}—Bi—S1^{xii}	87.1 (2)
S1^{iv}—Tl—S1^{vii}	80.92 (18)	S1^{ix}—Bi—S1^{xii}	92.9 (2)
S1^v—Tl—S1^{vii}	99.08 (18)	S1^x—Bi—S1^{xii}	87.1 (2)
S1^{vi}—Tl—S1^{vii}	180.0 (2)	S1^{xi}—Bi—S1^{xii}	180.0 (3)

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

Superstructure reflections were not observed. The atomic coordinates of the isotypic structure RbBiS$_2$ (Voroshilov *et al.*, 1972) were used as a starting model. The highest peak is located 0.55 Å from Bi and the deepest hole 0.66 Å from the same atom.

Data collection: *IPDS* (Stoe & Cie, 1998); cell refinement: *IPDS*; data reduction: *IPDS*; method used to solve structure: coordinates taken from an isotypic compound (Voroshilov *et al.*, 1972); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *SHELXL97*.

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