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## The Crystal Structure of Bismuth Thiophosphate BiPS<sub>4</sub>

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Crystals of BiPS<sub>4</sub> have been grown from the vapour phase by iodine transport. They are orthorhombic, space group *Ibca*,  $a = 10.601$  (2),  $b = 11.112$  (3),  $c = 19.661$  (4) Å;  $Z = 16$ . The intensities were measured on a Nonius CAD-4 diffractometer. A Patterson synthesis revealed the basic structure. A least-squares refinement with anisotropic temperature factors for Bi and P led to a final  $R$  of 0.047. The structure consists of a network of S tetrahedra, every second of which is occupied by a P atom. Alternating chains of edge-shared tetrahedra, running parallel to **a** and **b** are stacked along **c**. Six- and eightfold coordination of S around Bi occurs.

### Introduction

Synthesis and crystal growth (by vapour transport with iodine between 590 and 560°C) of BiPS<sub>4</sub> has been reported (Nitsche & Wild, 1970). The structures of BPS<sub>4</sub> and AIPS<sub>4</sub> have been solved by Weiss & Schaefer (1963, 1960). The structure of InPS<sub>4</sub> has been determined by Carpentier, Diehl & Nitsche (1970), that of GaPS<sub>4</sub> by Buck & Carpentier (1973). Since all these structures are different, a structure determination of BiPS<sub>4</sub> seemed appropriate to gain further insight into the crystal chemistry of thiophosphates.

### Experimental

#### Crystal data

Vapour-grown BiPS<sub>4</sub> crystals are rhombic prisms, elongated along [110]. They have a metallic, gray lustre; the powder is dark red. Observations on very thin platelets in polarized light showed the crystals to be twinned along (110). The formula was confirmed by chemical analysis.  $F_w = 368.24$ . Lattice parameters (20°C):  $a = 10.601$  (2),  $b = 11.112$  (3),  $c = 19.661$  (4) Å,

$V = 2309.1$  (1) Å<sup>3</sup>,  $Z = 16$ ,  $D_m = 4.18$ ,  $D_c = 4.22$  g cm<sup>-3</sup>. Reflexion conditions:  $hkl: h + k + l = 2n$ ,  $0kl: k = 2n$ ,  $h0l: l = 2n$ ,  $hk0: h = 2n$ . Space group: *Ibca*. Mo  $K\alpha$ ,  $\lambda = 0.7109$  Å;  $\mu$  (Mo  $K\alpha$ ) = 306 cm<sup>-1</sup>. Crystal size: 0.04 × 0.05 × 0.07 mm.

The cell parameters were obtained by a least-squares refinement of Guinier powder data (Cu  $K\alpha_1$ ,  $\lambda = 1.54051$  Å) with the X-RAY 70 System (PARAM; Stewart, Kundell & Baldwin, 1970).

#### Data collection

Numerous crystals were checked on a precession camera but no untwinned specimens could be found or prepared. Finally a crystal with dimensions 0.04 × 0.05 × 0.07 mm containing 70% and 30% of the twins was selected. The two lattices transform into each other by reflexion across (110). The crystal was set with **c** parallel to the axis of the goniometer. The intensities were collected on a computer-controlled four-circle diffractometer (Nonius CAD-4) with Mo  $K\alpha$  radiation from a graphite monochromator. The intensities were measured with a scintillation counter.

The  $\omega$ - $2\theta$  scan method was used for a quarter of the

sphere of reflexion between  $2\theta=4.14$  and  $60.25^\circ$ . The scanning speed was adjusted to obtain 5000 counts per reflexion at a maximal scanning time of 300 s. A scanning width of  $(0.8+0.5 \tan \theta)^\circ$  was chosen to resolve the reflexions of the two twin lattices. The background was measured for one-quarter of the actual scanning time on both sides of the peak.

1672 reflexions were measured, of which 881 were independent. Of these, 412 had intensities  $\geq 3\sigma(I)$ , where  $\sigma(I)$  is the variance of the observations (Poisson). The internal  $R = \sum(I - I_m) / \sum I_m$  was 0.021 ( $I_m$  = mean intensity).

#### Data reduction

The X-RAY 70 System was used for data reduction, structure solution and refinement. Lorentz-polarization and absorption corrections were applied. The latter, based on the measured crystal dimensions, were determined numerically by the Gaussian integration method. The absorption corrections varied between 4.3 and 3.0. Since reflexions of the type  $hhl$  coincided in both reciprocal lattices, their intensities were corrected after the relative average intensities of each reciprocal lattice were determined.

Scattering factors for  $\text{Bi}^{3+}$ ,  $\text{S}^{2-}$  and  $\text{P}^{5+}$  were taken from *International Tables for X-ray Crystallography* (1968).

#### Structure determination and refinement

The overall scale and temperature factors were taken from a Wilson plot of the normalized structure factors. Intensity statistics indicated centrosymmetry. A Patterson map revealed two sets of Bi atoms in the special, eightfold position ( $e$ ) with  $z=0.141$  and  $0.399$ .

Structure-factor calculations with isotropic Debye-Waller factors yielded an  $R$  of 0.23. From further interpretation of the Patterson and consecutive Fourier maps, the P and S atoms could be located. Then a least-squares refinement was carried out with isotropic temperature factors for the S and anisotropic temperature factors for the P and Bi atoms. The function minimized was:  $\sum w ||F_{\text{meas}}| - |F_{\text{calc}}||^2$ , where  $w = 1/\sigma^2(F)$ . Refinement was stopped when the shifts of all parameters were less than one-third of the corresponding standard deviations. The resulting  $R = \sum ||F_{\text{meas}}| - |F_{\text{calc}}|| / \sum F_{\text{meas}}$  was 0.052. Introduction of isotropic extinction as an additional parameter (Larson, 1967) yielded a final  $R$  of 0.047.\*

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30955 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. Fractional coordinates and thermal parameters

All values  $\times 10^5$ . Estimated standard deviations in parentheses. The Debye-Waller terms are defined as

$$T = \exp \left[ -2\pi^2 \sum_i \sum_j a_i^* a_j^* h_i h_j U^{ij} \right] \text{ for Bi and P and } T = \exp \left[ -2\pi^2 U^{11} (2 \sin \theta / \lambda)^2 \right] \text{ for S.}$$

	$x$	$y$	$z$	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Bi(1)	0 (0)	2500 (0)	3986 (1)	125 (11)	280 (16)	159 (9)	-16 (22)	0 (0)	0 (0)
Bi(2)	0 (0)	2500 (0)	1414 (1)	326 (16)	276 (17)	146 (9)	63 (28)	0 (0)	0 (0)
P(1)	2500 (0)	2210 (11)	0 (0)	78 (46)	172 (96)	97 (44)	0 (0)	14 (45)	0 (0)
P(2)	347 (13)	0 (0)	2500 (0)	117 (61)	157 (61)	92 (46)	0 (0)	0 (0)	17 (50)
S(1)	979 (10)	1094 (9)	30 (11)	162 (18)					
S(2)	2603 (10)	3274 (10)	860 (10)	196 (20)					
S(3)	709 (11)	5032 (9)	1657 (10)	201 (20)					
S(4)	1395 (10)	1583 (10)	2429 (10)	247 (23)					

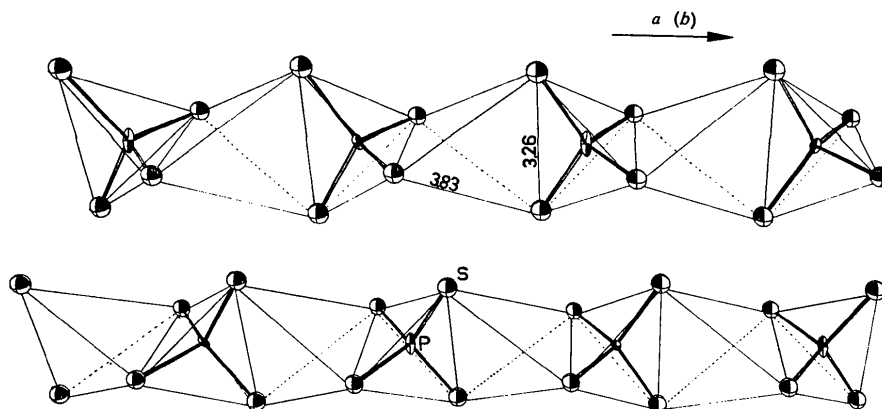


Fig. 1. Two adjacent chains of sulphur tetrahedra running parallel to  $[100]$  and  $[010]$ .

### Structural results and discussion

Table 1 gives the atomic coordinates and thermal parameters. One half of the Bi atoms [Bi(1)] occupy the eightfold equipoints (*e*) ( $0, \frac{1}{4}, z; 0, \frac{3}{4}, z; \frac{1}{2}, \frac{3}{4}, z; \frac{1}{2}, \frac{1}{4}, z$ ) with  $z=0.1414$  and the other half [Bi(2)] those with  $z=0.3986$ . The P atoms are located on the eightfold equipoints (*c*) ( $x, 0, \frac{1}{4}; \bar{x}, 0, \frac{3}{4}; x, \frac{1}{2}, \frac{3}{4}; \bar{x}, \frac{1}{2}, \frac{1}{4}$ ) and (*d*) ( $\frac{1}{4}, y, 0; \frac{3}{4}, y, 0; \frac{3}{4}, \bar{y}, \frac{1}{2}; \frac{1}{4}, \bar{y}, \frac{1}{2}$ ) with  $x=0.035$  and  $y=0.221$ .

The S atoms [located in the general positions (*f*)] form chains of edge-shared tetrahedra, every other tetrahedron being occupied by a P atom. Two such chains are shown in Fig. 1. The  $PS_4$  tetrahedra are fairly regular with angles ranging from  $104.9^\circ$  to  $115.6^\circ$  and edge lengths between 3.26 and 3.39 Å. The unoccupied S tetrahedra are more distorted with angles between  $92.7^\circ$  and  $121.3^\circ$  and edge lengths between 3.26 and 3.83 Å. The S framework can be envisaged as consisting of four types of slabs (*a, b, a', b'*) extending parallel to (001) and stacked along *c*. In slabs of type *a* and *a'* the chains of edge-sharing S tetrahedra run in the [010] direction; in slabs of type *b* and *b'* they run in the [100] direction. Slabs of type *a, a'* and *b, b'* are transformed into each other by the diad screw axes parallel to [001]. The chains of S tetrahedra are interconnected by strings of equidistant Bi atoms running parallel to [001] (Fig. 2). The Bi atoms are located roughly midway between neighbouring S

chains. Adjacent chains of Bi atoms are shifted relative to each other by 0.8 Å in the *c* direction. The distance between two Bi atoms on a string equals  $\frac{1}{4}c$ , *i.e.* 4.9 Å. This results in two types of Bi sites, Bi(1) and Bi(2), alternating on each string. These two Bi sites are surrounded by different S coordination polyhedra, depicted in Fig. 3. Bi(1) is coordinated by six S atoms. It can be envisaged as occupying the centre of a nearly planar, square assembly of four S atoms [S(2), S'(2), S(3), S'(3)] with a dovetail-like arrangement of two further S atoms [S(1), S'(1)] extending downward. The coordination of Bi(1) thus resembles a distorted octahedron, opposite pairs of vertices being S(1)–S'(3), S(2)–S'(2) and S'(1)–S(3). The Bi(1)–S distances vary between 2.7 and 3.1 Å.

Bi(2) on the other hand is coordinated by eight S atoms. It is also surrounded by a nearly planar, now rectangular assembly of four S atoms [S''(2), S'''(2), S''(4), S'''(4)] at distances varying between 2.7 and 3.3 Å. In addition, two further pairs of S atoms [S''(1), S'''(1) and S''(3), S'''(3)], also in dovetail-like arrangement, are located below and above this plane. This coordination polyhedron could be described as a distorted trigonal prism of sulphur [S''(2), S'''(2), S''(3), S'''(3), S''(4), S'''(4)] with the Bi(2) atom at the centre of one base [S''(2), S'''(2), S''(4), S'''(4)] and two additional S atoms [S''(1), S'''(1)] pointing downward with Bi–S distances of 3.304 Å.

Table 2 lists the interatomic distances. The  $BiPS_4$

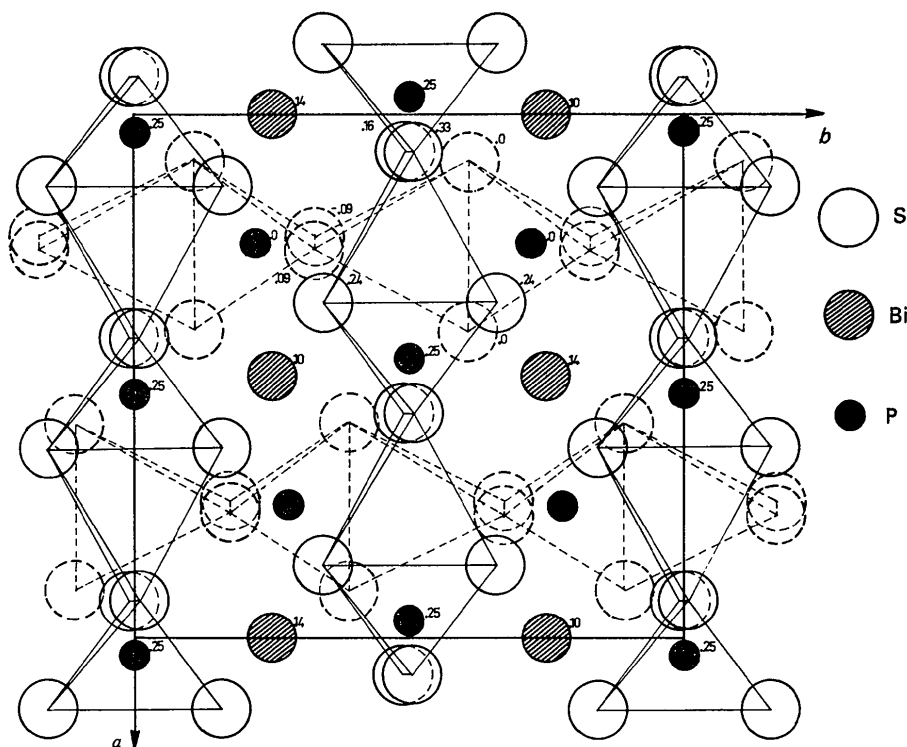


Fig. 2. Projection of one half of the cell onto the (001) plane. The figures indicate the *z* coordinates. The other half of the cell is obtained by the  $2_1$  operation of the space group.

lattice thus constitutes a new structure type which is not related to the structures of thiophosphates of type  $\text{MePS}_4$  ( $\text{Me}=\text{B}, \text{Al}, \text{Ga}, \text{In}$ ). In the latter, the S atoms form more or less distorted close packings with P and metal atoms in tetrahedral interstices. In  $\text{BiPS}_4$  on the other hand, the structure appears to be dominated by the large Bi atoms. Although the P atoms are still coordinated by rather regular S tetrahedra, a close-packed arrangement in the S sublattice can no longer be discerned. However, the coordination of Bi by S in  $\text{BiPS}_4$  resembles that in other Bi-S compounds. The coordination polyhedra in  $\text{Bi}_2\text{S}_3$  (Kupčik & Veselá-Novaková, 1970) also show a nearly planar, rectangular arrangement of four S atoms around Bi and additional S atoms in 'dovetail-like' arrangement having distances similar to those in  $\text{BiPS}_4$ . The recently published structure of  $\text{Bi}_2\text{In}_4\text{S}_9$  (Chapuis, Gnehm & Krämer, 1972) also contains two non-equivalent Bi atoms with coordination polyhedra bearing strong similarities to those in  $\text{BiPS}_4$ .

Table 2. *Bismuth-sulphur and phosphorus-sulphur interatomic distances in  $\text{BiPS}_4$*

(Distances are in Å; standard deviations are 0.01 Å.)

Bi(1)-S(1)	2.78 (2 ×)	P(1)-S(1)	2.03 (2 ×)
-S(2)	2.70 (2 ×)	-S(2)	2.07 (2 ×)
-S(3)	3.11 (2 ×)		
Bi(2)-S(1)	3.30 (2 ×)	P(2)-S(3)	2.00 (2 ×)
-S(2)	3.10 (2 ×)	-S(4)	2.08 (2 ×)
-S(3)	2.95 (2 ×)		
-S(4)	2.68 (2 ×)		

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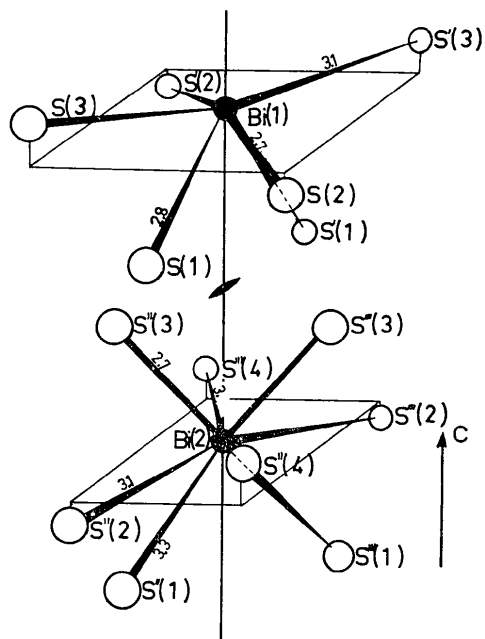


Fig. 3. The two different - six- and eightfold - sulphur coordination polyhedra around Bi(1) and Bi(2).

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