Acta Cryst. (1972). B**28**, 3128

Crystal Structure and Crystal Chemistry of Bismuth Indium Sulphide, $Bi_2In_4S_9$

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(*Received* 1 *July* 1972)

The compound $Bi_2In_4S_9$ was synthesized by transport reactions with iodine in the gas phase. The stoichiometric composition was confirmed by chemical and electron microprobe analysis. The space group is $P2_1/m$ with lattice parameters $a=16·167$ (12), $b=3·917$ (2), $c=11·111$ (6) Å and $\beta=94·044$ (3)°. The measured density is $D_{meas}=5·53$ g.cm^{-3} ($D_{calc}=5·52$) and $Z=2$. The structure of $Bi_2In_4S_9$ consists of a sulphur framework forming closest packing only in a prismatic domain parallel to the b axis. Three indium atoms are octahedrally surrounded by sulphur atoms, one of them with distortions; the coordination polyhedron of the fourth indium is a distorted tetrahedron. The 6 and 7 coordination of the two bismuth atoms by sulfur atoms is related only in a broader sense to the bismuth coordinations in the structure of Bi_2S_3.

Introduction

The compound $Bi_2In_4S_9$ has been synthesized by transport reactions in a temperature gradient of 680–600 °C and with iodine in the gas phase (Krämer & Nitsche, 1971). The stoichiometric composition has been confirmed by chemical and electron microprobe analysis. As $Bi_2In_4S_9$ is the first known compound in the pseudobinary system In_2S_3–Bi_2S_3, a structure investigation seemed worth while.

Experimental

Crystal data

$Bi_2In_4S_9$; Formula weight: 1165·81;
Habit: prismatic b (pinacoids);
Colour: metallic grey;
$a=16·167$ (12), $b=3·917$ (2), $c=11·111$ (6) Å,
$\beta=94·044$ (31)°; $V=701·9$ (1·2) Å^3, $Z=2$;
$D_{meas}=5·53$, $D_{calc}=5·52$ g.cm^{-3};
λ Mo $K\alpha_1=0·70926$ Å;
Systematic absences ($0k0$) $k\neq 2n$;
Space group $P2_1/m$; $\mu_{Mo}=313$ cm^{-1};
Crystal size: 0·070 × 0,120 × 0·070 mm

The intensities of $Bi_2In_4S_9$ have been measured on a four-circle computer-controlled X-ray diffractometer (Picker FACS I) by the θ–2θ scan method for half the sphere of reflexion between $2\theta=2·5°$ and $2\theta=60°$. The scan speed was 1°.min^{-1} with a base width of $1·2°+0·692\tan\theta$; the background was measured on both sides of the peak for 20 sec. The Mo $K\alpha$ radiation (graphite monochromator) was detected by a scintillation counter.

Data reduction

The programs of the X-ray 67 system (Stewart, Kundell & Baldwin, 1967) were used for data reduction, structure solution and refinement. The Lorentz–polarization and absorption corrections were applied on the 4329 measured intensities, which correspond to 2348 independent reflexions, 2052 of which had an intensity $\geq 3\sigma(I)$, where $\sigma^2(I)$ is the variance of the observation (Poisson). The internal R value $[R=\sum(I-\bar{I})/\bar{I}]$ was equal to 0·08.

Structure solution and refinement

The overall scale and temperature factors were calculated by a Wilson plot of the normalized structure factors which indicated centrosymmetry. From a three-dimensional Patterson map we found four metal positions (2 Bi, 2 In) by the superposition method. After calculation of three consecutive Fourier maps, we could locate all the In and S positions. A least-squares refinement with the overall scale and temperature factors has been applied by minimizing the function $\sum w||F_o|-|F_c||^2$ where $w=1/\sigma^2(F)$. A block least-squares approximation with three blocks, containing 2 metals and 3 nearest S atoms each, was made during refinement. The atomic scattering factors (Cromer & Mann, 1967) for neutral Bi, In and S were used in the structure factor calculation.

Further refinement cycles with isotropic temperature factors for S atoms and anisotropic temperature factors for Bi and In atoms were calculated until the shifts of all the parameters were less than 30% of their corresponding standard deviation. The least-squares re-

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finement yielded a final $R=\sum||F_o|-|F_c||/\sum|F_o|=0{\cdot}051$ and $R'=\sum|F_o|-|F_c|/\sum w|F_o|=0{\cdot}046$.*

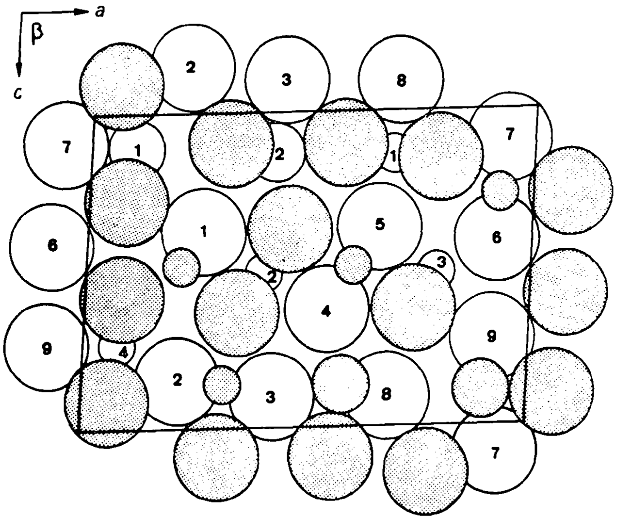

Fig. 1. Projection of $Bi_2In_4S_9$ along the *b* axis. Large circles represent S, medium, Bi, and small, In. Unshaded atoms are at $y=\frac{1}{4}$, shaded at $y=\frac{3}{4}$.

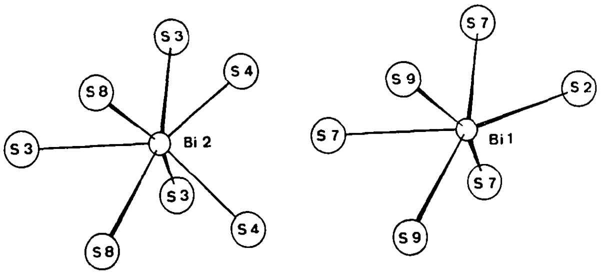

Fig. 2. Coordination polyhedron of (*a*) Bi(1) and (*b*) Bi(2).

Results and discussion

The fractional coordinates and thermal parameters are shown in Table 1. All atoms occupy special equipoints (*e*) $(x,\frac{1}{4},z;\ -x,\frac{3}{4},\ -z)$ on the mirror plane. The origin of the cell has been placed on the symmetry center. The anisotropies of the thermal parameters are weak for all metals with the exception of In(3), the only indium with non-octahedral coordination.

This new type of structure is shown in Fig. 1. Considering the partial structure of sulphur atoms only we find two domains, one of which forms a closest packing [S(1), S(4), S(5) and symmetry related]. This domain containing one indium atom [In(2)] in an octahedral void may be described as a prism parallel to the *b* axis. The second domain is not regularly packed.

The surroundings of the two Bi atoms are rather unusual (Fig. 2). Table 2 shows the interatomic distances Bi–S. There are five nearest S atoms around Bi(1) forming an orthorhombic pyramid with S(7), S(9), S(9) and S(7) delimiting the base, and another S(7) on the top [Fig. 2(*a*)]. The Bi(1) atom is located in the base centre with a displacement opposite to the top of the pyramid. The angle between Bi(1) and the two sulphur atoms on the base diagonal is equal to 158·6°. This angle is a measure of the displacement. A sixth sulphur contributing to the coordination polyhedron is very weakly bonded $d_{\mathrm{Bi(1)-S(2)}}=3{\cdot}533$ Å.

The five nearest neighbours of Bi(2) also form an orthorhombic pyramid [Fig. 2(*b*)]. Like Bi(1), Bi(2) is slightly outside the base with a corresponding 'displacement angle' of 161·5°. Two supplementary S(4) atoms with a distance of 3·304 Å contribute to the coordination, forming with S(3) and S(8) a trigonal prism parallel to **b**. Note that these two coordination polyhedra have no quantitative relation to the seven-coordination of Bi atoms in the Bi_2S_3 compound (Kupčik and Veselà-Novàkovà, 1970), but only a similarity in the form of the polyhedra.

Table 1. *Fractional coordinates and thermal parameters*

Estimated standard deviations are in parentheses. Values are $\times 10^4$. The Debye–Waller term is defined as

$$T=\exp\,[-2\pi^2\sum_{i=1}^{3}\sum_{j=1}^{3}a_i^*a_j^*h_ih_jU^{ij}]\text{ for Bi and In and}$$

$$T=\exp\,[-2\pi^2U^{11}(2\sin\theta/\lambda)^2]\text{ for S.}$$

	$x\ (y=\frac{1}{4})$	z	U^{11}	U^{22}	U^{33}	U^{13}
Bi(1)	1015 (1)	1082 (1)	127 (2)	151 (2)	207 (2)	32 (2)
Bi(2)	4207 (1)	1339 (1)	184 (2)	145 (2)	132 (2)	−13 (2)
In(1)	6837 (1)	1418 (1)	128 (4)	113 (4)	113 (4)	−2 (3)
In(2)	4050 (1)	5068 (1)	87 (4)	103 (4)	140 (4)	8 (3)
In(3)	7886 (1)	5142 (1)	155 (4)	106 (4)	286 (5)	94 (4)
In(4)	798 (1)	7326 (1)	103 (4)	135 (4)	157 (4)	12 (4)
S(1)	2590 (3)	3755 (5)	111 (6)			
S(2)	2167 (3)	8495 (5)	128 (6)			
S(3)	4329 (3)	9002 (4)	102 (5)			
S(4)	5452 (3)	6279 (4)	110 (6)			
S(5)	6581 (3)	3679 (5)	117 (6)			
S(6)	9180 (3)	4141 (4)	116 (5)			
S(7)	9424 (3)	902 (4)	96 (5)			
S(8)	6892 (3)	9044 (4)	120 (5)			
S(9)	9191 (3)	7301 (4)	110 (5)			

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* The list of the structure factors F_o and F_c is available on request.

Table 2. *Interatomic distances in* Å

The standard deviations are given in parentheses.

	Bi(1)–			Bi(2)–	
–S(7)	2·562 (4)	1 ×	–S(3)	2·618 (4)	1 ×
–S(9)	2·697 (3)	2 ×	–S(8)	2·663 (3)	2 ×
–S(7)	2·996 (3)	2 ×	–S(3)	3·115 (3)	2 ×
–S(2)	3·533 (4)	1 ×	–S(4)	3·304 (3)	2 ×
	In(1)–			In(2)–	
–S(2)	2·532 (3)	2 ×	–S(4)	2·557 (4)	1 ×
–S(5)	2·573 (4)	1 ×	–S(4)	2·626 (3)	2 ×
–S(8)	2·641 (4)	1 ×	–S(5)	2·650 (3)	2 ×
–S(3)	2·736 (3)	2 ×	–S(1)	2·686 (4)	1 ×
	In(3)–			In(4)–	
–S(6)	2·440 (4)	1 ×	–S(2)	2·489 (4)	1 ×
–S(1)	2·460 (3)	2 ×	–S(6)	2·548 (3)	2 ×
–S(5)	2·574 (4)	1 ×	–S(9)	2·592 (4)	1 ×
–S(9)	3·078 (4)	1 ×	–S(7)	2·819 (3)	2 ×

Three indium atoms are octahedrally coordinated. The angle between In(4) and the two sulphur atoms on the top of the octahedron (on the same mirror plane as indium) is 149·3°. The corresponding angles are 172·8° for In(1) and 179° for In(2), respectively. On the other hand, the In(3) is tetrahedrally surrounded by S atoms, distorted due to the S(9) atom at a distance of 3·078 Å.

One of us (V.K.) is indebted to the 'Deutsche Forschungsgemeinschaft' for financial support.

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Acta Cryst. (1972). B**28**, 3130

Structure Cristalline et Moléculaire du Diphényl-2,2 Sila-2 Δ3 Bromo-3 Tetralone-1

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(*Reçu le* 15 *mai* 1972)

The crystal structure of 3-bromo-2,2-diphenyl-2-sila-Δ3-1-tetralone, $C_{21}H_{15}OSiBr$, has been determined from intensities obtained using a Nonius semi-automatic single-crystal diffractometer and Cu *Kα* radiation. The structure has been solved with the aid of the heavy-atom method and refined by full-matrix least-squares calculations including anisotropic thermal parameters. The final *R* value is 0·06 for 1824 observed reflexions.

La synthèse et l'étude chimique du diphényl-2,2 sila-2 Δ3 bromo-3 tétralone-1 ont été effectuées dans le laboratoire de M le Professeur Corriu.

La détermination de la structure de ce composé entre dans le cadre de l'étude d'un groupe d'organosilanes cycliques.

Partie expérimentale

Le diphényl-2,2, sila-2 Δ3 bromo-3 tétralone-1 est purifié par recristallisation lente dans un mélange benzène–hexane. Ces cristaux, de couleur orange, sont essentiellement prismatiques et allongés suivant **a**.

La mesure des paramètres et la détermination du groupe spatial ont été effectuées en utilisant les chambres de Weissenberg et de précession de Buerger.

La valeur des paramètres a été précisée sur le diffractomètre semi-automatique Enraf–Nonius qui a servi à mesurer les intensités de toutes les réflexions.

Les paramètres ont été affinés par la méthode des moindres carrés sur 143 réflexions.

Données cristallographiques

$a = 15{,}543 \pm 0{,}004$ Å $\quad \beta = 108{,}58 \pm 0{,}05°$

$b = 10{,}566 \pm 0{,}003$ $\quad V = 1787$ Å^3

$c = 11{,}486 \pm 0{,}003$ $\quad Z = 4$

Coefficient linéaire d'absorption $\mu_l = 41$ cm^{-1}.

Groupe spatial: $P2_1/c$ (d'après les extinctions systématiques).

Densité mesurée: 1,456 g.cm^{-3}.

Densité calculée: 1,453 g.cm^{-3}.

Le cristal était monté suivant **b** et avait un volume de 0,034 mm^3.

L'enregistrement des intensités diffractées a été fait en employant la méthode de balayage $\theta/2\theta$ et la radiation Cu *Kα*.

Sur les intensités furent effectuées les corrections d'absorption et de Lorentz–polarisation pour un cristal polyèdrique complètement noyé dans le faisceau des rayons X, cette dernière correction à l'aide d'un programme écrit en Fortran par Escande (1971) pour IBM 360-40 64 K.