

the $[\text{PS}_4]$ tetrahedra is 3.32 Å, the P–S distances ranging between 2.03 and 2.04 Å. Such $[\text{PS}_4]$ tetrahedra occur in various thiophosphates, e.g. in GaPS_4 , $d_{\text{S-S}} = 3.34$, $d_{\text{P-S}} = 2.05$ (Buck & Carpentier, 1973); InPS_4 , $d_{\text{S-S}} = 3.36$, $d_{\text{P-S}} = 2.04$ (Diehl & Carpentier, 1978); $\text{Cd}_{13}\text{P}_4\text{S}_{22}\text{I}_2$, $d_{\text{S-S}} = 3.35$, $d_{\text{P-S}} = 2.05$ Å (Bubenzer, Nitsche & Grieshaber, 1976).

From a formal, electrochemical point of view, the compound therefore can be envisaged as containing two cations Ta^{5+} and P^{5+} (1:1) and two anions, namely $[\text{S-S}]^{2-}$ and S^{2-} (1:4), resulting in the formula $\text{Ta}[\text{PS}_4]_2\text{S}_2$.

Fig. 2 is a projection along $[00\bar{1}]$, Fig. 3 a stereoscopic drawing of the unit-cell contents. The $[\text{Ta}_2\text{S}_{12}]$ units, linked by the $[\text{PS}_4]$ tetrahedra, form endless chains, spiralling around the 4_1 and 4_3 axes. Spiral chains around adjacent screw axes of opposite sense do not interfere with each other and have no common units. Spiral chains around adjacent screw axes of the same sense are interconnected by common $[\text{Ta}_2\text{S}_{12}]$ units.

Similar metal chalcogen units, $[\text{Nb}_2\text{Se}_{12}]$, are found in Nb_2Se_9 (Meerschaut, Guémas, Berger & Rouxel, 1979). However, in this compound they are crosslinked by common Se atoms into parallel chains. In ZrSe_3 , on the other hand (Krönert & Plieth, 1965) and in NbSe_3 (Meerschaut & Rouxel, 1975) the bicapped triangular-prismatic arrangement of eight Se around each metal is still present, but these prisms have no common rectangular prism faces. Instead they are connected *via* common triangular endfaces into infinite chains.

A similar arrangement of metal–metal and (perpendicular) $[\text{S-S}]^{2-}$ pairs as in $\text{Ta}[\text{PS}_4]_2\text{S}_2$ is present in $\text{Nb}_2\text{S}_2\text{Cl}_2$ (von Schnering & Beckmann, 1966) and in VS_4 (Allmann, Baumann, Kutoglu & Rösch, 1964).

Another interesting feature of the $\text{Ta}[\text{PS}_4]_2\text{S}_2$ structure is the existence of rather large channels

extending along the fourfold screw axes (Fig. 3). It appears probable that foreign atoms or small molecules can be inserted into and move in these channels, the free diameter of which is about 4–6.5 Å.

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References

- ALLMANN, R., BAUMANN, I., KUTOGLU, A. & RÖSCH, H. (1964). *Naturwissenschaften*, **51**, 263–264.
- BECKER, P. J. & COPPENS, P. (1975). *Acta Cryst.* **A31**, 417–425.
- BUBENZER, J., NITSCHKE, R. & GRIESHABER, E. (1976). *Acta Cryst.* **B32**, 2825–2829.
- BUCK, P. & CARPENTIER, C. D. (1973). *Acta Cryst.* **B29**, 1864–1868.
- CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.
- DIEHL, R. & CARPENTIER, C. D. (1978). *Acta Cryst.* **B34**, 1097–1105.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.
- KRÖNERT, W. & PLIETH, K. (1965). *Z. Anorg. Allg. Chem.* **336**, 207–218.
- MEERSCHAUT, A., GUÉMAS, L., BERGER, R. & ROUXEL, J. (1979). *Acta Cryst.* **B35**, 1747–1750.
- MEERSCHAUT, A. & ROUXEL, J. (1975). *J. Less Common Met.* **39**, 197–203.
- SCHNERING, H. G. VON & BECKMANN, W. (1966). *Z. Anorg. Allg. Chem.* **347**, 231–239.
- STEWART, J. M. (1976). The XRAY system – version of 1976. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland.
- WYCKOFF, R. W. G. (1968). *Crystal Structures*. Vol. I, 2nd ed. New York: John Wiley.

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The Structure of Pentaindium Tetrasulfide

BY TOMMY WADSTEN, LARS ARNBERG AND JAN-ÉRIC BERG

Departments of Inorganic and Structural Chemistry, Arrhenius Laboratory, University of Stockholm, S-106 91 Stockholm, Sweden

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Abstract

The structure of the new compound In_3S_4 has been determined by direct methods using single-crystal

X-ray diffractometer data and refined to $R = 0.046$. The symmetry is $Pa\bar{3}$ and the cell edge is 12.340 (10) Å. There are eight formula units in the cell. The structure consists of a three-dimensional network of corner-

sharing In_2S_3 tetrahedra with one of the In atoms at the center of the tetrahedron. The other In atom is the common corner of four tetrahedra; these aggregates form major building units of the structure. The coordination around In is thus either four In atoms or one In (at 2.77 Å) and three S (at 2.54 Å). Each S coordinates three In atoms. There are no S—S bonds.

Introduction

In the binary system In—S the existence of several phases has been proposed. During extensive work in recent years only a few have been proved to be real. They are InS, reported by Schubert, Dörre & Günzel (1954), In_6S_7 , investigated by Hogg & Duffin (1967), and three polymorphic forms of In_2S_3 . The α type was studied by Hahn & Klingler (1949), the β type by Steigmann, Sutherland & Goodyear (1965) and the γ type by Diehl, Carpentier & Nitsche (1976).

These compounds can be prepared by direct combination of the elements at elevated temperatures. The successful application of molten tin as a solvent in the synthesis of silicon monophosphide (Wadsten, 1975) and of gallium chalcogenides (Wadsten, 1977) suggested its use also in this binary system.

By heating mixtures of In and S with excess Sn in evacuated silica tubes the new compound In_5S_4 was obtained in high yield. The crystals are red and transparent and sometimes up to a few mm in length. The preparation procedure will be described in a separate paper by Wadsten (1980).

The S content of the purified material was determined by gas chromatographic techniques according to Kirsten (1961). The value observed was $18.5 \pm 2\%$ by weight and the calculated value is 18.3%. No tin impurity could be observed by X-ray fluorescence. The detection limit with this technique is of the order of 100 p.p.m.

Experimental

The lattice constant was obtained from powder data (Guinier—Hägg camera) using Cu $K\alpha$ radiation ($\lambda = 1.5418$ Å) and KCl ($a = 6.2930$ Å) as an internal standard.

A preliminary investigation was performed with Weissenberg methods, and a suitable crystal was selected with the approximate volume 0.0007 mm³.

Crystal data are: space group $Pa\bar{3}$ (No. 205), $a = 12.340$ (10) Å, $V = 1884$ Å³, $Z = 8$, $D_m = 4.87$, $D_x = 4.95$ Mg m⁻³, $\mu(\text{Cu } K) = 91.29$ mm⁻¹.

The reflexion intensities were measured on a Philips PW 1100 diffractometer using graphite monochromatized Cu $K\alpha$ radiation. Diffraction intensities within the $+h$ hemisphere of reciprocal space were

collected out to $2\theta = 134^\circ$ with the θ - 2θ scan technique. Of the 1937 reflexions measured, 560 were unique. All unique reflexions were used in the subsequent refinements. Lorentz, polarization and spherical absorption corrections were applied.

Structure determination and refinement

An E map computed from 107 reflexions with $|E| \geq 1.2$ displayed all In atoms as prominent peaks. The remaining atoms were placed from a difference F map. The structural parameters, assuming first isotropic and then anisotropic thermal vibrations, were refined by the full-matrix least-squares method, using unit weights, to a final R value of 0.046.* Direct-method, Fourier and least-squares programs were those included in the *SHELX* system (Sheldrick, 1976). The complex atomic scattering factors for In and S were those listed in *International Tables for X-ray Crystallography* (1974) for neutral atoms. Table 1 comprises the atomic positional parameters.

Description of the structure

The structure analysis of this compound has revealed a new structure type which can be visualized as a three-dimensional network of corner-sharing In_2S_3 tetrahedra.

The In(1) and In(3) atoms are each surrounded by one In(2) and three S atoms. The coordination polyhedra around In(1) and In(3) are somewhat distorted tetrahedra since the In—In contacts are longer than the In—S. In Table 2 the interatomic distances within these tetrahedra are collected.

One In(1)- and three In(3)-centered tetrahedra have a common In(2) corner and thus form what might be called a tetra-tetrahedron, with composition In_5S_{12} . In this way all In atoms achieve tetrahedral coordination

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35441 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic positional parameters* ($\times 10^5$) with *e.s.d.'s in parentheses and isotropic temperature factors* ($\times 10^4$) with *e.s.d.'s*

		<i>x</i>	<i>y</i>	<i>z</i>	U_{iso} (Å ²)
In(1)	8(c)	27108 (8)	27108 (8)	27108 (8)	146 (5)
In(2)	8(c)	40018 (8)	40018 (8)	40018 (8)	102 (5)
In(3)	24(d)	26925 (8)	2646 (8)	6670 (8)	138 (4)
S(1)	24(d)	32323 (30)	7265 (30)	25849 (30)	135 (9)
S(2)	8(c)	7443 (30)	7443 (30)	7443 (30)	137 (13)

Table 2. Atomic distances (\AA) and angles ($^\circ$) with *e.s.d.'s* in parentheses in the In(1)- and In(3)-centered tetrahedra with composition In_2S_3 and corresponding values for the In(2)-centered indium tetrahedron

In(1)-centered			
In(1)—In(2)	2.762 (2)	3[In(2)—In(1)—S(1)]	116.50 (9)
In(1)—3S(1)	2.539 (4)	3[S(1)—In(1)—S(1)]	101.61 (13)
3[S(1)—S(1)]	3.935 (5)		
3[In(2)—S(1)]	4.509 (4)		
In(2)-centered			
In(1)—In(2)	2.762 (2)	In(3)—In(2)—In(3)	112.54 (8)
In(2)—In(3)	2.769 (1)	In(1)—In(2)—In(3)	106.32 (7)
In(3)-centered			
In(3)—In(2)	2.769 (1)	In(2)—In(3)—S(1A)	115.13 (9)
In(3)—S(1A)	2.534 (4)	In(2)—In(3)—S(1B)	117.94 (9)
In(3)—S(1B)	2.526 (4)	In(2)—In(3)—S(2)	121.14 (10)
In(3)—S(2)	2.480 (4)	S(1A)—In(3)—S(1B)	103.42 (12)
In(2)—S(1A)	4.477 (4)	S(1B)—In(3)—S(2)	99.56 (12)
In(2)—S(1B)	4.538 (4)	S(1A)—In(3)—S(2)	95.99 (12)
In(2)—S(2)	4.573 (4)		
S(1A)—S(1B)	3.972 (5)		
S(1A)—S(2)	3.726 (5)		
S(1B)—S(2)	3.822 (5)		

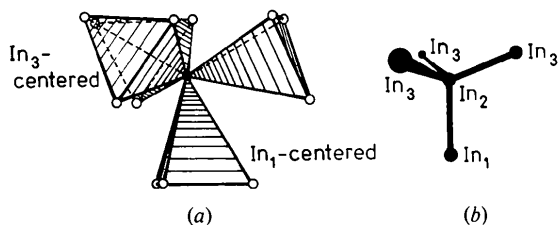


Fig. 1. The atomic arrangement in the tetra-tetrahedra. In (a) the In(1) and In(3) atoms are omitted, and in (b) the 12 S atoms are omitted.

(Fig. 1). The In(1) and the three In(3) atoms in the tetra-tetrahedron form a fairly regular tetrahedron around In(2). Bond angles and distances are given in Table 2.

As can be seen from Fig. 1, six S atoms, every second S(1A) and S(1B), form a zig-zag, six-membered ring with a departure from a least-squares plane of ± 0.064 (1) \AA . The distance between each atom is the same, *viz.* 3.972 (5) \AA . This almost planar S_6 ring is common to two tetra-tetrahedra, and in this way a double tetra-tetrahedron is formed (Fig. 2). There are eight In_2S_3 tetrahedra in this arrangement, and the composition is $\text{In}_{10}\text{S}_{18}$. The sequence of In(1) and In(2) atoms, In(1)—In(2)—In(2)—In(1), is directed along the body diagonals of the cubic cell. The void formed between the two tetra-tetrahedra has two In(2) atoms at a distance of 2.14 \AA and six In(3) atoms at a distance of 2.98 \AA from its center. The double tetra-tetrahedra are centered at the sites of a close-packed cubic lattice (Fig. 3), whose stereoscopic equivalent is shown in Fig.

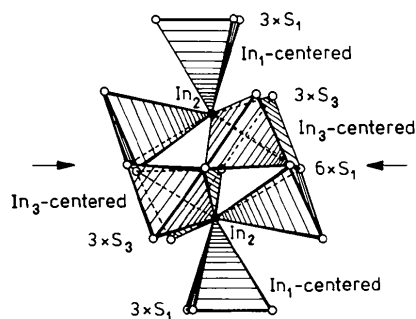


Fig. 2. The arrangement of eight In_2S_3 tetrahedra forming the double tetra-tetrahedron. The arrows indicate the hexagonal S_6 ring.

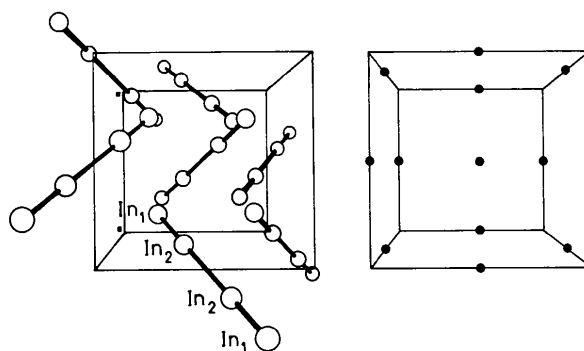


Fig. 3. Orientation and center of gravity of the double tetra-tetrahedra, here represented by the In(1)—In(2)—In(2)—In(1) sequence, in one elementary cell. One of these clusters is centrosymmetrical.

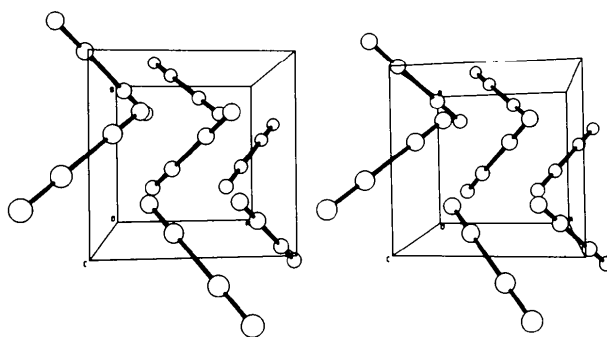


Fig. 4. Stereoscopic representation of the In(1)—In(2)—In(2)—In(1) arrangements in the cubic In_2S_3 structure.

4, and each double tetra-tetrahedron will thus be surrounded by twelve others. They are linked together by the S(1) atoms common to one In(1) and two In(2) tetrahedra. The S(2) atoms are shared by three different double tetra-tetrahedra.

In this way all S atoms achieve coordination to three In atoms as nearest neighbors.

The composition is now $\text{In}_{40}\text{S}_{32}$, which corresponds to the unit-cell content.

Structural relationships

The In atom at the center of the In_2S_3 tetrahedron has an environment of three S and one In atom.

A similar coordination is found among other combinations of elements from the same groups, for instance GaS (Hahn & Frank, 1955). However, the building units in the layer structure of GaS are S_6 prisms with two Ga atoms inside.

Mixed tetrahedral coordination is also exhibited by 1:1 combinations of elements from the Groups IV and V such as SiAs (Wadsten, 1965) and SiP (Wadsten, 1975). The building units of these layer compounds are As_6 or P_6 octahedra surrounding two Si atoms.

The compound InS (Schubert *et al.*, 1954) can also be included as an example of mixed tetrahedral environment for the In atoms, but the structure can be visualized as being built up of corner-sharing In_2S_6 octahedra.

References

- DIEHL, R., CARPENTIER, C.-D. & NITSCHKE, R. (1976). *Acta Cryst.* **B32**, 1257–1260.
 HAHN, H. & FRANK, G. (1955). *Z. Anorg. Chem.* **278**, 340–348.
 HAHN, H. & KLINGLER, W. (1949). *Z. Anorg. Chem.* **260**, 97–109.
 HOGG, J. H. C. & DUFFIN, W. J. (1967). *Acta Cryst.* **23**, 111–118.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.
 KIRSTEN, W. J. (1961). *Z. Anal. Chem.* **181**, 1–22.
 SCHUBERT, K., DÖRRE, E. & GÜNZEL, E. (1954). *Naturwissenschaften*, **41**, 448–449.
 SHELDRIK, G. M. (1976). Private communication.
 STEIGMANN, G. A., SUTHERLAND, H. H. & GOODYEAR, J. (1965). *Acta Cryst.* **19**, 967–971.
 WADSTEN, T. (1965). *Acta Chem. Scand.* **19**, 1232–1238.
 WADSTEN, T. (1975). *Chem. Scr.* **8**, 63–69.
 WADSTEN, T. (1977). *Chem. Commun. Univ. Stockholm*, No. 10.
 WADSTEN, T. (1980). *J. Cryst. Growth*. In the press.

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Sulphides with the GdFeO_3 Structure

BY R. LELIEVELD AND D. J. W. IJDO

Gorlaeus Laboratories, Section of Solid State Chemistry, University of Leiden, PO Box 9502, 2300 RA Leiden, The Netherlands

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Abstract

CaZrS_3 , SrZrS_3 , BaZrS_3 , BaUS_3 , CaHfS_3 , BaHfS_3 , EuZrS_3 and EuHfS_3 have been found to have the GdFeO_3 (CaTiO_3) structure, *Pnma*, with $Z = 4$. For the first four compounds, atomic positional parameters have been determined by neutron diffraction powder methods. [R_w values were 8.00, 7.51, 8.14 and 8.49 respectively.]

Introduction

We have investigated the crystal structures of ABS_3 type compounds with $A = \text{Ca, Sr, Ba and Eu}$, and $B = \text{Zr, Hf and U}$. This is part of a research programme on the structural relations of compounds ABX_3 , where A represents an alkaline or an alkaline-earth metal, B a transition metal and X a halogen or S (van Loon &

Verschoor, 1973; van Loon, 1974; Crama, Maaskant & Verschoor, 1978; Lelieveld & IJdo, 1978).

Single crystals of the ABS_3 compounds were not available, so we decided to use the neutron powder-profile-refinement technique (Rietveld, 1969) in order to obtain precise structural information for the Zr and U compounds. The ionic radii for Zr and Hf for six-coordination are 0.72 and 0.71 Å respectively; hence, the same structures for AZrS_3 and AHfS_3 can be expected. Moreover, for routine neutron powder-diffraction experiments samples of about 30 g are needed, so we limited ourselves to the Zr and U compounds. Neutron diffraction for Eu compounds is not useful because of the high absorption of Eu.

Hahn & Mutschke (1956) prepared BaZrS_3 and produced an X-ray powder diagram, which they indexed as a tetragonal deformed perovskite; they were unable to prepare SrZrS_3 and CaZrS_3 . Clearfield (1963) published the X-ray powder diagrams of