

symmetry space group *Pbna* (alternative setting for *Pbcn*) with a twofold rotation axis at $x, 0, \frac{1}{4}$. Inspection of the packing diagram in Fig. 2 shows that this is indeed the case and all atom positions in picrate ion (1) are closely approximated to atom positions of ion (2) by the pseudo-operator $(x, -y, \frac{1}{2}-z)$. The position and orientation of the dimethylammonium ions break the pseudosymmetry. N(3) and N(4) of the dimethylammonium ions are well defined ($U_{eq} 0.04 \text{ \AA}^2$) and lie 0.2 and 0.8 Å respectively off the pseudo twofold axis.

The structure is clearly laminar with sheets of anions hydrogen-bonded to sheets of cations. Picrate ions are only related to each other by symmetry within the sheets; adjacent sheets are only related by the pseudo twofold axis. The strongest interactions are hydrogen bonds between the deprotonated O on the picrate ions and the ammonium H atoms. Each O acts as a hydrogen-bond acceptor for two H atoms providing four crystallographically unrelated hydrogen bonds as given in Table 3 and Fig. 2. H(42) and H(31) may also form bifurcated hydrogen bonds to O(162) and O(122) respectively.

All other non-bonded contacts (Table 3) are within expected ranges for van der Waals interactions, though the short contacts involving the picrate aromatic H atoms to O(*n*21) and O(*n*61) ranging between 2.4 and 2.7 Å suggest a genuine electrostatic interaction.

Table 3. Intermolecular interactions

(i) Hydrogen bonding			
N(3)...O(21)	2.767 Å	H(32)...O(21)	2.013 Å
N(4)...O(21)	2.777	H(41)...O(21)	2.019
N(3)...O(11)	2.861	H(31)...O(11)	1.876
N(4)...O(11)	2.887	H(42)...O(11)	2.064
N(4)...O(162)	2.832	H(42)...O(162)	2.231
N(4)...O(262)	3.096	H(41)...O(262)	2.551
N(3)...O(122)	2.900	H(31)...O(122)	2.163
N(3)...O(222)	2.985	H(32)...O(222)	2.445
(ii) van der Waals contacts			
C(11)...H(31)	2.829 Å	H(25)...O(221)	2.422 Å
C(21)...H(32)	2.971	H(15)...O(121)	2.595
C(13)...O(161)	2.955	H(23)...O(261)	2.731
C(23)...O(261)	2.965	H(13)...O(161)	2.623

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Lead Indium Bismuth Chalcogenides. II. Structure of $\text{Pb}_4\text{In}_3\text{Bi}_7\text{S}_{18}$

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Abstract. $M_r = 3213.23$, monoclinic, $P2_1/m$, $a = 21.021$ (5), $b = 4.014$ (2), $c = 18.898$ (5) Å, $\beta = 97.07$ (2)°, $V = 1582.46$ Å³, $Z = 2$, $D_x = 6.744$ g cm⁻³, $\lambda(\text{Ag } K\alpha) = 0.56083$ Å, $\mu = 341.8$ cm⁻¹, $F(000) = 2688$, room temperature, final $R = 0.042$ for 3972 independent observed reflections. The structure consists of In–S octahedra [In–S 2.583 (12)–2.853 (8) Å], in which In³⁺ is partially substituted by Bi³⁺ as indicated

by the corresponding site-occupancy factor, mono- and bicapped trigonal Pb–S prisms [Pb–S 2.811 (8)–3.464 (13) Å], and Bi–S octahedra [Bi–S 2.625 (10)–3.287 (13) Å] as well as Bi–S₅ pyramids [Bi–S 2.735 (7)–3.018 (8) Å] with two additional S [Bi–S 2.817 (10), 3.398 (12) and 2.840 (9), 3.509 (12) Å] below the basal plane; all polyhedra are distorted and form chains along y . The In–S chains are mutually

Table 1. Fractional atomic coordinates ($\times 10^4$) ($y = 2500$) and equivalent isotropic thermal parameters ($\times 10^2$) with *e.s.d.*'s in parentheses

	x	z	$U_{eq}(\text{\AA}^2)$	S.o.f.
Pb(1)	358 (1)	8080 (1)	4.2 (1)	
Pb(2)	1796 (1)	5176 (1)	3.4 (1)	
Pb(3)	3582 (1)	6297 (1)	3.6 (1)	
Pb(4)	7400 (1)	8499 (1)	3.2 (1)	
In(1)	1359 (1)	2813 (1)	2.0 (1)	1.26 (1)
In(2)	4341 (1)	4474 (1)	2.3 (1)	1.20 (2)
In(3)	7194 (1)	6268 (1)	1.8 (1)	1.33 (1)
Bi(1)	32 (1)	5963 (1)	2.7 (1)	
Bi(2)	2349 (1)	9329 (1)	2.1 (1)	
Bi(3)	4199 (1)	439 (1)	2.2 (1)	
Bi(4)	5373 (1)	7691 (1)	2.4 (1)	
Bi(5)	6111 (1)	1561 (1)	2.1 (1)	
Bi(6)	7946 (1)	2675 (1)	2.1 (1)	
Bi(7)	9150 (1)	9596 (1)	2.6 (1)	
S(1)	89 (5)	812 (5)	2.1 (4)	
S(2)	122 (6)	2883 (6)	2.6 (5)	
S(3)	1246 (5)	6939 (6)	2.5 (4)	
S(4)	1928 (4)	580 (5)	1.9 (4)	
S(5)	2591 (5)	2743 (6)	2.8 (5)	
S(6)	3053 (5)	7869 (6)	2.7 (5)	
S(7)	3056 (5)	4671 (5)	2.3 (4)	
S(8)	3783 (4)	1698 (5)	2.3 (4)	
S(9)	4826 (5)	9038 (6)	2.3 (4)	
S(10)	5576 (5)	4550 (5)	2.8 (5)	
S(11)	5583 (5)	2757 (5)	2.5 (4)	
S(12)	5934 (6)	6437 (6)	3.5 (6)	
S(13)	6667 (5)	44 (7)	3.0 (5)	
S(14)	7444 (5)	3896 (5)	2.2 (4)	
S(15)	8437 (5)	6110 (7)	3.4 (6)	
S(16)	8461 (5)	1195 (6)	2.7 (5)	
S(17)	8757 (5)	8104 (6)	2.6 (5)	
S(18)	9297 (5)	4613 (5)	2.4 (4)	

Table 2. Bond distances (\AA)

Standard deviations are in parentheses.

Pb(1)–S(3)	3.021 (12)	Bi(1)–S(3)	2.958 (10)
Pb(1)–S(17)	3.370 (11)	Bi(1)–S(5)	3.398 (12)
Pb(1)–S(16)	3.352 (9) 2x	Bi(1)–S(18)	2.817–(10)
Pb(1)–S(1)	3.127 (8) 2x	Bi(1)–S(18)	2.753 (7) 2x
Pb(1)–S(2)	2.811 (8) 2x	Bi(1)–S(2)	3.011 (9) 2x
Pb(2)–S(7)	2.926 (10)	Bi(2)–S(6)	3.287 (13)
Pb(2)–S(14)	2.995 (7) 2x	Bi(2)–S(4)	2.625 (10)
Pb(2)–S(15)	3.143 (10) 2x	Bi(2)–S(13)	3.018 (8) 2x
Pb(2)–S(18)	3.112 (8) 2x	Bi(2)–S(16)	2.737 (7) 2x
Pb(3)–S(6)	3.297 (13)	Bi(3)–S(8)	2.633 (10)
Pb(3)–S(7)	3.136 (10)	Bi(3)–S(9)	3.099 (12)
Pb(3)–S(10)	3.228 (9) 2x	Bi(3)–S(9)	2.951 (8) 2x
Pb(3)–S(11)	3.087 (8) 2x	Bi(3)–S(13)	2.786 (8) 2x
Pb(3)–S(14)	2.936 (10) 2x		
Pb(4)–S(17)	3.036 (11)	Bi(4)–S(9)	2.919 (12)
Pb(4)–S(13)	3.464 (13)	Bi(4)–S(12)	2.774 (13)
Pb(4)–S(4)	2.906 (7) 2x	Bi(4)–S(8)	2.829 (6) 2x
Pb(4)–S(5)	3.090 (8) 2x	Bi(4)–S(11)	2.892 (7) 2x
Pb(4)–S(8)	3.183 (7) 2x		
In(1)–S(2)	2.620 (12)	Bi(5)–S(11)	2.638 (11)
In(1)–S(5)	2.609 (11)	Bi(5)–S(13)	3.227 (13)
In(1)–S(15)	2.853 (8) 2x	Bi(5)–S(6)	2.795 (7) 2x
In(1)–S(17)	2.643 (9) 2x	Bi(5)–S(9)	2.940 (7) 2x
In(2)–S(7)	2.771 (10)	Bi(6)–S(14)	2.654 (11)
In(2)–S(10)	2.583 (12)	Bi(6)–S(16)	3.121 (12)
In(2)–S(10)	2.718 (7) 2x	Bi(6)–S(3)	2.672 (7) 2x
In(2)–S(12)	2.661 (8) 2x	Bi(6)–S(6)	2.994 (8) 2x
In(3)–S(12)	2.707 (13)	Bi(7)–S(17)	2.838 (11)
In(3)–S(15)	2.668 (12)	Bi(7)–S(1)	2.840 (9)
In(3)–S(5)	2.743 (7) 2x	Bi(7)–S(16)	3.509 (12)
In(3)–S(7)	2.687 (7) 2x	Bi(7)–S(1)	2.735 (7) 2x
		Bi(7)–S(4)	3.015 (7) 2x

linked by edge-sharing octahedra forming a sixfold band parallel to $(\bar{2}03)$; between parallel bands four wavy Pb/Bi–S layers are inserted.

Experimental. Needle-shaped crystals with maximum length 15 mm grown by chemical vapour transport with iodine in a two-zone furnace adjusted to 913/843 K; black crystals with high metallic lustre, elongated along y , pinacoids $\{100\}$, $\{\bar{2}03\}$, and $\{010\}$; density not measured; crystal size $24 \times 750 \times 16 \mu\text{m}$, Enraf–Nonius CAD-4 diffractometer, graphite-monochromatized Ag $K\alpha$ radiation, lattice parameters from refinement of 24 reflections, reflection condition $0k0: k = 2n$, scan width 1.2° , $\omega-2\theta$ scan mode, $2\theta < 46^\circ$, $h: 0$ to 28, $k: 0$ to 5, $l: -26$ to +26. *SHELXS84* (Sheldrick, 1984) and *XRAY76* (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) systems; two standard reflections: no significant variation; 8964 total reflections, 5081 independent, 3972 with $I > 3\sigma(I)$; $R_{int} = 0.023$ (on F , 1922 contributors); corrections for Lorentz–polarization, absorption ($A^* 1.600$ to 2.608), and extinction [$g = 3.2 (1) \times 10^{-4}$] effects. A starting set of heavy atoms was selected from an E map calculated with direct methods (*SHELXS84*); remaining atoms from successive Fourier syntheses. Refinement of positional and anisotropic thermal parameters as well as of the site occupancy of In(1–3) resulted in a final $R = 0.042$,* unit weights; least squares based on F ; $S = 1.9$; 196 parameters refined; max. $\Delta/\sigma = 7.2 \times 10^{-5}$; max.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42551 (34 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

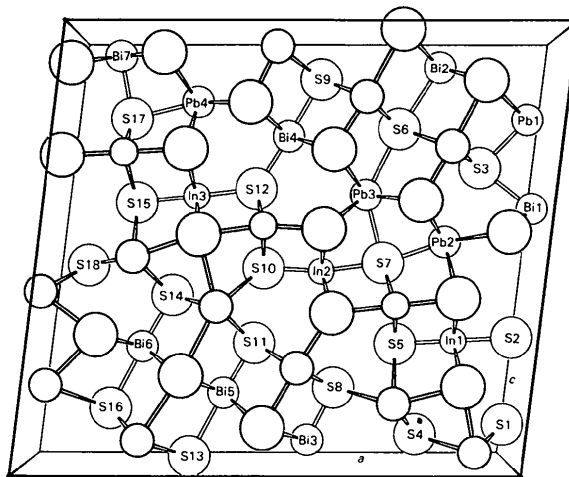


Fig. 1. Perspective view of the structure of $\text{Pb}_4\text{In}_3\text{Bi}_7\text{S}_{18}$ in the $[010]$ direction; labelled atoms at $y = \frac{1}{4}$, all others at $y = \frac{3}{4}$ [drawn with *SCHAKAL* (Keller, 1984)].

$\Delta\rho = 4.7$, min. $\Delta\rho = -4.9 \text{ e } \text{Å}^{-3}$ close to the heavy atoms (Pb, Bi). Scattering factors of neutral atoms (Cromer & Mann, 1968) were used and corrected for anomalous dispersion (Cromer & Liberman, 1970).

The atomic coordinates are listed in Table 1, bond lengths in Table 2; the site-occupancy factors of $\text{In}(1-3) > 1.0$ indicate a partial substitution of In^{3+} by Bi^{3+} . Fig. 1 displays a perspective view of the unit-cell contents in the [010] direction.

Related literature. The present paper is the second part of a series (part I: Krämer, 1983) on the study of lead indium bismuth chalcogenides.

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SHELXS84 program system for testing purposes. Numerical computations were performed on the Sperry 1100/82 computer of the Rechenzentrum der Universität Freiburg.

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Structure of 1,1-Diphenylphosphorinium Bromide Monohydrate

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Abstract. $\text{C}_{17}\text{H}_{20}\text{P}^+\text{Br}^-\cdot\text{H}_2\text{O}$, $M_r = 353.24$, orthorhombic, $P2_12_12_1$, $a = 8.542$ (1), $b = 12.202$ (2), $c = 15.864$ (3) Å, $V = 1653.5 \text{ Å}^3$, $Z = 4$, $D_m = 1.42$, $D_x = 1.42 \text{ g cm}^{-3}$, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 27.2 \text{ cm}^{-1}$, $F(000) = 728$, $T = 295 \text{ K}$, $R = 0.062$, $wR = 0.067$, 1270 observed reflections. The phosphorus–carbon bond lengths are 1.794 (9), 1.806 (10), 1.796 (9) and 1.783 (10) Å. The phosphorus heterocyclic ring is in the chair form and the torsional angles indicate that it is highly symmetrical. The bond angles around the phosphorus atom are 103.7 (5), 111.7 (4), 110.5 (4), 109.8 (4), 111.0 (4) and 109.9 (4)°.

Experimental. Title compound prepared by previously described methods (Gray, Cremer & Marsi, 1976). D_m by flotation in ethanol and methyl iodide mixture.

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Colorless crystals suitable for X-ray analysis obtained by recrystallization from acetonitrile. Crystal size $0.2 \times 0.25 \times 0.43 \text{ mm}$, Nicolet *R3m* diffractometer, graphite monochromator, accurate unit-cell parameters (Campana, 1981) from least-squares refinement of 25 reflections (θ range $10\text{--}20^\circ$); three standard reflections (057, 434, 623) measured every 100 reflections, 4% variation. Range of hkl : $0 \leq h \leq 10$, $0 \leq k \leq 14$, $0 \leq l \leq 18$. Data taken as $\theta/2\theta$ scans, 1770 data measured ($3 \leq 2\theta \leq 55^\circ$) with 1270 observed $I \geq 2\sigma(I)$, corrections for Lorentz and polarization effects (decay correction ignored). Absorption corrections by numerical Gaussian integration method from crystal dimensions and indexed faces. Max. and min. transmission coefficients 0.63 and 0.59, respectively. Trial structure from Patterson map provided Br^- ion position, refined by full-matrix least-squares procedures, $\sum w(|F_o| - |F_c|)^2$ minimized, $w = 1/[\sigma^2(F) + G(F)^2]$ and $G = 0.001$; non-hydrogen atoms anisotropic, H atoms located in ΔF map, idealized coordinates calculated, not refined, isotropic thermal parameters