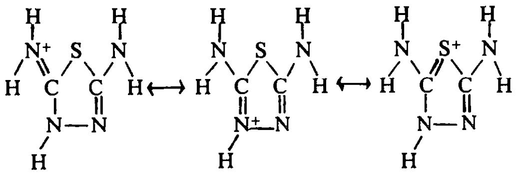
The five-membered heterocyclic ring is planar: the sum of internal bond angles is 539·98° and maximum deviation from the least-squares plane is 0·008 Å for C(1). The deviation from the plane of the H atom attached to the ring N is 0·03 Å, and for the exocyclic N(3) and N(4) atoms the deviations are −0·011 and −0·023 Å. All N—H distances lie in the range 0·80–0·88 Å, and O—H distances are 0·82 and 0·72 Å. The bonding parameters of the ring are comparable with those reported by Flippen (1972) for a mesoionic thiadiazole derivative. Consideration of the bond lengths shows that in the crystalline state the cation exists mainly in the resonance structures indicated below, with partly double S—C(1), C(1)—N(1) and C(1)—N(3) bonds and a C(2)=N(2) bond.



The cation, the chloride ion and the water molecule are held together with four types of H bonds as seen from Fig. 1. A pair of N(4)—H···N(2) H bonds across the center of symmetry results in an H-bonded dimer of the cation. Such dimerization has also been observed in some other 1,3,4-thiadiazole derivatives (Mathew & Palenik, 1974; Kornis, Marks & Chidester, 1980). The H-bond parameters are listed in Table 2. The remaining shortest contacts are Cl···N(4^{iv}) 3·345 (1) [(iv) $1-x$, $1-y$, $1-z$] and Cl···O^{v} 3·347 (1) Å [(v) x, y, $-1+z$].

The authors thank Professor Yukiteru Katsube and Dr Nobuo Tanaka of the Crystallographic Research Center, Institute for Protein Research, Osaka University for permission to use the X-ray diffractometer and also Dr Ken-ichi Sakaguchi of the Center for his technical assistance.

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SHORT-FORMAT PAPERS

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Acta Cryst. (1986). C**42**, 1089–1091

Lead Indium Bismuth Chalcogenides. III. Structure of $Pb_4In_2Bi_4S_{13}$

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Abstract. $M_r = 2311{\cdot}15$, orthorhombic, $Pcma$ (conventional setting $Pbam$ by transforming b into $-c$ and c into b), $a = 21{\cdot}344\ (4)$, $b = 4{\cdot}002\ (1)$, $c = 26{\cdot}494\ (5)$ Å, $V = 2263{\cdot}08$ Å^3, $Z = 4$, $D_x = 6{\cdot}783$ g cm^{-3}, $\lambda(\mathrm{Mo}\ K\alpha) = 0{\cdot}71069$ Å, $\mu = 614{\cdot}0$ cm^{-1}, $F(000) = 3864$, room temperature, final $R = 0{\cdot}054$ for 1373 independent observed reflections. The structure consists of In—S tetrahedra and octahedra, mono- and bicapped trigonal prisms of Pb—S, and Bi—S octahedra; all polyhedra are distorted and

0108-2701/86/081089-03$01.50

form chains parallel to [010]. The site-occupancy factors >1 of the octahedrally coordinated In atoms indicate a partial substitution of In^{3+} by Bi^{3+}.

Experimental. Needle-shaped crystals with maximum length of 10 mm were grown by chemical-vapour transport with iodine in a two-zone furnace adjusted at 823/773 K; black crystals with high metallic lustre, elongated along y, pinacoids $\{20\bar{3}\}$, $\{010\}$, and $\{101\}$; D_m not measured; crystal size 30 × 400 × 30 µm; Enraf–Nonius CAD-4 diffractometer, graphite-monochromatized Mo $K\alpha$ radiation; lattice parameters from refinement of 24 reflections in the range $7 < \theta < 21°$; reflection conditions $0kl$: $l = 2n$, $hk0$: $h = 2n$; scan width 1·2°, ω–2θ scan mode, max. $\sin\theta/\lambda = 0\cdot594$ Å^{-1}, h: −11 to 25, k: −2 to 4, l: −31 to 31. *SHELX76* (Sheldrick, 1976) and *XRAY76* systems (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976); two standard reflections: no significant variation; 5350 total reflections, 2305 independent, 1373 with $I > 3\sigma(I)$; $R_{\text{int}} = 0\cdot071$ (on F, 1215 contributors); corrections for Lorentz–polarization, absorption (numerical integration with subprogram *ABSORB*: A^* 4·57 to 6·79), and extinction effects [Lorentz distribution, $g = 1\cdot95\,(8) \times 10^{-4}$]. A starting set of heavy atoms was selected from an E map calculated with direct methods (*SHELX76*); remaining atoms from successive Fourier syntheses, $\sum w(\Delta F^2)$ minimized, unit weights. Refinement of positional and anisotropic thermal parameters as well as of the site-occupancy factors of In(1,3) resulted in a final $R = 0\cdot054$,† unit weights, least squares based on F; $S = 2\cdot8$; 143 parameters refined; max. $\Delta/\sigma =$

Table 1. *Fractional atomic coordinates* (×10⁴) *and equivalent isotropic thermal parameters* (×10²) *with e.s.d.'s in parentheses*

$$U_{\text{eq}} = \tfrac{1}{3}\textstyle\sum_i \sum_j a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j U_{ij}.$$

	x	y	z	U_{eq}(Å^2)	S.o.f.
Pb(1)	359 (1)	5000	1586 (1)	3·2 (1)	
Pb(2)	1724 (1)	5000	2788 (1)	3·7 (1)	
Pb(3)	1830 (1)	5000	4324 (1)	3·2 (1)	
Pb(4)	3754 (1)	5000	2501 (1)	3·4 (1)	
In(1)	0	0	0	1·5 (2)	1·24 (3)
In(2)	2255 (2)	0	1624 (2)	2·1 (2)	
In(3)	5000	0	0	1·9 (3)	1·12 (3)
Bi(1)	232 (1)	0	3431 (1)	2·9 (1)	
Bi(2)	1547 (1)	5000	249 (1)	2·0 (1)	
Bi(3)	3573 (1)	0	3903 (1)	2·4 (1)	
Bi(4)	3834 (1)	5000	848 (1)	2·1 (1)	
S(1)	91 (7)	5000	4292 (6)	2·6 (8)	
S(2)	262 (6)	5000	2785 (5)	2·3 (7)	
S(3)	833 (7)	0	725 (6)	2·7 (8)	
S(4)	1211 (7)	0	2025 (6)	2·5 (7)	
S(5)	1467 (7)	0	3578 (5)	2·1 (7)	
S(6)	2452 (6)	5000	1100 (5)	1·6 (6)	
S(7)	2729 (6)	0	2452 (6)	2·1 (7)	
S(8)	2761 (7)	0	4740 (6)	2·9 (8)	
S(9)	2929 (7)	5000	3520 (6)	2·4 (7)	
S(10)	3819 (7)	0	87 (5)	2·6 (8)	
S(11)	3951 (8)	0	1574 (6)	3·5 (9)	
S(12)	4348 (8)	5000	4502 (6)	3·0 (8)	
S(13)	4381 (7)	0	3134 (6)	2·4 (8)	

Table 2. *Bond distances* (Å)

Standard deviations are in parentheses.

Pb(1)–S(3)	3·197 (12)	2×	Bi(1)–S(2)	2·634 (9)	2×
S(4)	2·944 (11)	2×	S(1)	3·050 (12)	2×
S(13)	2·985 (11)	2×	S(5)	2·666 (14)	
S(2)	3·184 (14)		S(11)	2·732 (16)	
Pb(2)–S(5)	2·947 (10)	2×	Bi(2)–S(3)	2·814 (11)	2×
S(4)	3·049 (12)	2×	S(8)	2·829 (11)	2×
S(7)	3·066 (10)	2×	S(12)	2·752 (16)	
S(2)	3·120 (14)		S(6)	2·967 (14)	
S(9)	3·235 (18)				
			Bi(3)–S(9)	2·631 (10)	2×
Pb(3)–S(5)	2·917 (10)	2×	S(12)	3·043 (12)	2×
S(8)	3·028 (12)	2×	S(13)	2·670 (15)	
S(10)	3·165 (11)	2×	S(8)	2·812 (16)	
S(9)	3·166 (15)				
			Bi(4)–S(11)	2·787 (11)	2×
Pb(4)–S(7)	2·968 (10)	2×	S(10)	2·841 (10)	2×
S(11)	3·196 (13)	2×	S(1)	2·707 (15)	
S(13)	2·934 (11)	2×	S(6)	3·025 (13)	
S(9)	3·225 (15)				
S(2)	3·306 (14)				
In(1)–S(3)	2·618 (15)	2×			
S(12)	2·771 (11)	4×			
In(2)–S(7)	2·417 (15)				
S(4)	2·469 (15)				
S(6)	2·472 (9)	2×			
In(3)–S(10)	2·531 (14)	2×			
S(1)	2·750 (11)	4×			

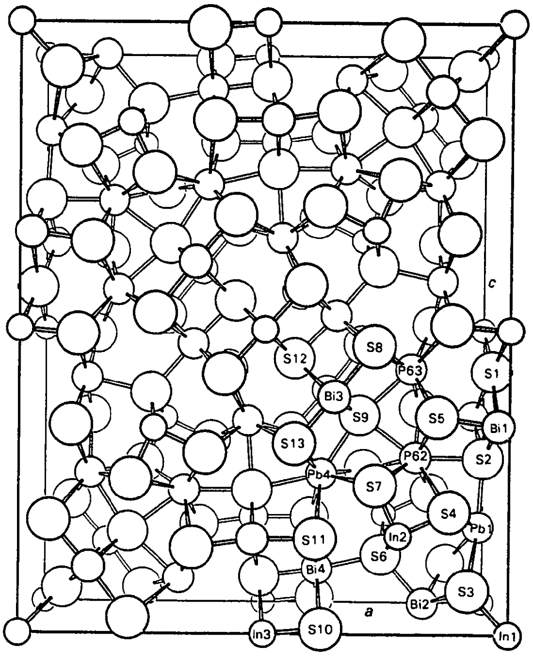

Fig. 1. Perspective view of the structure; projection direction [010]; atoms of the asymmetric unit are labelled [drawn with *SCHAKAL* (Keller, 1984)].

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† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42841 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

$2{\cdot}3 \times 10^{-4}$; max. $\Delta\rho = 4{\cdot}7$, min. $\Delta\rho = -4{\cdot}6$ e Å^{-3}. 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; Fig. 1 displays a perspective view of the unit-cell contents.

Related literature. The present paper is the third part of a series (part I: Krämer, 1983; part II: Krämer & Reis, 1986) on the study of lead indium bismuth chalcogenides.

The author thanks Dr E. Keller for the intensity collection and for the *SCHAKAL* plot. Numerical computations were performed on the Sperry 1100/82 computer of the Rechenzentrum der Universität Freiburg.

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Structure of Potassium Tetrabromoaurate(III) Dihydrate

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Abstract. $\mathrm{K[AuBr_4].2H_2O}$, $M_r = 591{\cdot}71$, monoclinic, $P2_1/n$, $a = 9{\cdot}579\,(1)$, $b = 12{\cdot}006\,(1)$, $c = 8{\cdot}480\,(1)$ Å, $\beta = 94{\cdot}31\,(5)^\circ$, $V = 972{\cdot}5$ Å^3, $Z = 4$, $D_x = 4042$ kg m^{-3}, $\lambda = \mathrm{Mo}\ K\alpha = 0{\cdot}7107$ Å, $\mu = 31{\cdot}069$ mm^{-1}, $F(000) = 1032$, $T = 291$ K, $R = 0{\cdot}0406$ for 1755 unique reflections with $F > \sigma(F)$. The structure is significantly different from that of $\mathrm{K[AuCl_4].2H_2O}$ [Théobald & Omrani (1980). *Acta Cryst.* B**36**, 2932–2935]. The $\mathrm{AuBr_4^-}$ ion is almost square planar and symmetry about the Au atoms is almost centrosymmetric, despite the fact that the Au atoms do not lie in the special positions, Au(1) 000 and Au(2) $\frac{1}{2}\frac{1}{2}0$, previously reported by Cox & Webster [*J. Chem. Soc.* (1936), pp. 1635–1637].

Experimental. Platelets crystallized from aqueous solution, $0{\cdot}20 \times 0{\cdot}06 \times 0{\cdot}03$ mm. Philips PW 1100 diffractometer. Bisecting geometry. Cell parameters from 25 reflections with $10 < \theta < 16^\circ$. Absorption correction according to *DIFABS* (Walker & Stuart, 1983), min. absolute correction 0·767, max. 1·367. $0 \le h \le 17$, $0 \le k \le 19$, $-12 \le l \le 12$, $3{\cdot}5 < \theta < 40^\circ$. Three intensity standards: $hkl = 422$, 060, 200; $\Delta I/I < 0{\cdot}03$. 1840 reflections measured, 1755 unique, $R_{\mathrm{int}} = 0{\cdot}020$. About 4500 weak reflections. Location of Au and Br by *MULTAN* (Main *et al.*, 1980); K and O located by Fourier difference mapping (*SHELX*; Sheldrick, 1976). Refinement of F. The planarity of the $\mathrm{AuBr_4^-}$ group helped eliminate erroneous peaks appearing in maps owing to the coordinates of Au that were almost in the special positions. H atoms not considered. Unit weights, $R = 0{\cdot}0406$. Max. shift/e.s.d. ratio $< 0{\cdot}01$, largest peaks in final difference Fourier synthesis 0·32 e Å^{-3}. Scattering factors f' and f'' from *International Tables for X-ray Crystallography* (1974).

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