

The two anions which are not shared by Ge octahedra are identified as OH<sup>-</sup>, because the bond-valence sum is 1.0 for these two. The fact that the distances *M*—O for these two are considerably smaller than those for the others supports this identification. The contribution of the hydrogen atoms to the structure factors, however, was neglected in the structure refinement.

From the fact that the Ge(1) octahedron shares four edges and the Ge(2) and Ge(3) octahedra three, the Ge(1) octahedron is expected to be most distorted. As shown in Table 2, for the Ge(1) octahedron, the spreads of O—O distances and O—*M*—O angles are in fact larger than those in the Ge(2) and Ge(3) octahedra. Similarly to anatase (Horn, Schwerdtfeger & Meagher, 1972), the lengths of the shared edges are prominently shorter than those of the unshared edges. However, in the case of BaGe<sub>2</sub>O<sub>5</sub> II (Ozima, 1985), such a tendency was not so distinctive. Three- or four-edge sharing in an octahedron in germanate is unusual but it is often seen in titanate, e.g. brookite, TiO<sub>2</sub> (Baur, 1961) and anatase, TiO<sub>2</sub> (Horn *et al.*, 1972). In this respect, the present crystal could be compared to 'BaTi<sub>3</sub>O<sub>6</sub>(OH)<sub>2</sub>', but such a compound has not been reported. Furthermore, three- or four-edge sharing in octahedra in this crystal implies an intensive character for the covalent bonding. The structure was solved on the basis of an ionic model, which resulted in a comparatively large  $\Delta\rho$  in the final difference Fourier map.

In Table 3, the structure of Ba<sub>3</sub>Ge<sub>9</sub>O<sub>20</sub>(OH)<sub>2</sub> by Malinovskii *et al.* (1976) is compared with that of BaGe<sub>3</sub>O<sub>6</sub>(OH)<sub>2</sub> by the present author. The former is a low-pressure (probably including atmospheric pressure) phase and the latter is a high-pressure phase. This is consistent with the differences in the density and the structure in these two phases, *i.e.* in Ba<sub>3</sub>Ge<sub>9</sub>O<sub>20</sub>(OH)<sub>2</sub>,

Table 3. Comparison of BaGe<sub>3</sub>O<sub>6</sub>(OH)<sub>2</sub> (present study) with Ba<sub>3</sub>Ge<sub>9</sub>O<sub>20</sub>(OH)<sub>2</sub> (Malinovskii *et al.*, 1976)

	Density (g cm <sup>-3</sup> )	Ge tetrahedron	Ge tetragonal pyramid	Ge octahedron	Coordination number of Ba
Ba <sub>3</sub> Ge <sub>9</sub> O <sub>20</sub> (OH) <sub>2</sub>	5.70	0	0	9	12, 12, 12
Ba <sub>3</sub> Ge <sub>9</sub> O <sub>20</sub> (OH) <sub>2</sub>	4.98	6	1	2	8, 8, 9

only two of the nine Ge atoms are octahedrally coordinated and the mean coordination number of Ba is 8.3. In BaGe<sub>3</sub>O<sub>6</sub>(OH)<sub>2</sub>, on the other hand, all Ge atoms are octahedrally coordinated and the coordination number of Ba is 12.

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## Structure of Lead(II) Dimercury(II) Diiodide Disulfide

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**Abstract.** Hg<sub>2</sub>PbI<sub>2</sub>S<sub>2</sub>, *M<sub>r</sub>* = 926.31, tetragonal, *P4/mbm*, *a* = 13.501 (1), *c* = 4.593 (1) Å, *V* = 837.20 Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 7.349 g cm<sup>-3</sup>, λ(Mo Kα) = 0.71069 Å,

*μ* = 644.9 cm<sup>-1</sup>, *F*(000) = 1520, *T* = 293 K. Final *R* = 0.039 for 489 unique observed reflections. Crystals of Hg<sub>2</sub>PbI<sub>2</sub>S<sub>2</sub> were grown by annealing the proper

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amounts of HgS and PbI<sub>2</sub>. The Hg and S atoms form planar Hg<sub>4</sub>S<sub>4</sub> rings, packed into columns running along the [001] direction. The columns are connected by Pb atoms. The I atoms occupy three different types of holes. Hg<sub>2</sub>SnI<sub>2</sub>S<sub>2</sub> is related to Hg<sub>3</sub>I<sub>2</sub>S<sub>2</sub> and has space group *Imma*, *a* = 9.282 (3), *b* = 9.565 (2) and *c* = 13.460 (5) Å.

**Introduction.** Recently an investigation of quaternary systems, prepared from elements of the Groups IIb, IVb, VIb and VIIb, was started in order to obtain information about the influence of the *s*<sup>2</sup>-electron pair on the structure. The formation of Hg<sub>2</sub>PbI<sub>2</sub>S<sub>2</sub> was observed in the section HgS–PbI<sub>2</sub>.

**Experimental.** Crystal in form of rectangular prism, 0.1 × 0.1 × 0.2 mm, selected for data collection. Enraf–Nonius CAD-4 four-circle diffractometer, graphite-monochromated Mo Kα, ω–2θ scan method. Accurate cell dimensions obtained by least-squares fitting of 27 Guinier powder reflections. 1469 symmetry-independent reflections measured up to θ = 40°, ranges of *hkl*: 0 ≤ *h* ≤ 24, 0 ≤ *k* ≤ 24, 0 ≤ *l* ≤ 8, 980 with *I* ≤ 2σ(*I*) [σ(*I*) from counter statistics] considered unobserved, 489 reflections with *I* > 2σ(*I*) used to solve structure. Lorentz–polarization and absorption corrections (North, Phillips & Mathews, 1968) applied (range of transmission factors 1.0 to 0.726). Measuring of three standard reflections (722, 311, 601) gave no significant variation. Atomic coordinates of Hg and Pb determined by direct methods; those of I and S revealed by Fourier difference maps and least-squares refinements in space group *P4/mbm* (No. 127). In this way Hg located at position 8(*i*) *m*.. (*x*, *y*, 0), Pb at position 4(*h*) *m*.2*m* (*x*, *x* + ½, ½). In difference maps four independent peaks found: at position 2(*b*) 4/*m*.. (0, 0, 0); at position 2(*d*) *m*.*mm* (0, ½, 0); at position 4(*h*) *m*.2*m* (*x*, *x* + ½, ½) and at position 8(*i*) *m*.. (*x*, *y*, 0). The first three positions were assigned to I atoms. Full-matrix weighted [*w* = 1/σ(*I*)] least-squares refinement using *F* magnitudes of 489 reflections with *I* > 2σ(*I*) carried out with anisotropic temperature factors for all atoms. Isotropic extinction [extinction coefficient 1.94 (2) × 10<sup>-7</sup>] introduced as an additional parameter. Refinements converged to *R* = 0.039, *wR* = 0.048 and *S* = 7.2 for 27 parameters. Maximum least-squares Δ/σ 0.15 in last cycle. Max. and min. heights in final difference map 2.5 (1.1) and -2.5 (1.1) e Å<sup>-3</sup>. Scattering factors for Hg, Pb, S and I from *International Tables for X-ray Crystallography* (1968). All computations carried out with *SDP* (Frenz & Associates, 1982) and *MULTAN82* (Main *et al.*, 1982).

The pure compound Hg<sub>2</sub>PbI<sub>2</sub>S<sub>2</sub> was prepared from PbI<sub>2</sub> (Ventron, 99.8%) and HgS (Merck, z.A.) by mixing the proper amounts. The mixture, enclosed in an evacuated quartz ampoule, was heated to 1000 K, kept

at this temperature for several hours, slowly cooled to 550 K, and held at this temperature for one month. The sample was then finely ground and treated with a pressure of 0.735 GPa. The specimen was again annealed at 600 K for six months. Orange crystals in the form of rectangular prisms were obtained after this period. The phase melts congruently at 668 ± 3 K. Precession photographs of a small single crystal showed the Laue symmetry 4/*mmm* with the extinction condition *Ok**l* with *k* = 2*n*, which agrees with the space groups *P4/mbm*, *P4bm* or *P4̄b2*. The structure analysis yielded the space group *P4/mbm*.

Table 1. Atomic coordinates and isotropic thermal parameters of Hg<sub>2</sub>PbI<sub>2</sub>S<sub>2</sub>

$B_{eq}$  defined as  $B_{eq} = \frac{4}{3} \sum_i \sum_j \beta_{ij} a_i \cdot a_j$ .

Wyckoff position	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>eq</sub> (Å <sup>2</sup> )	
Hg	8( <i>i</i> )	0.16896 (8)	0.08649 (8)	0	2.19 (2)
Pb	4( <i>h</i> )	0.6332 (2)	0.1332	0.5	2.91 (3)
I(1)	2( <i>b</i> )	0	0	0.5	1.66 (4)
I(2)	2( <i>d</i> )	0	0.5	0	2.14 (5)
I(3)	4( <i>h</i> )	0.8130 (3)	0.3139	0.5	1.81 (3)
S	8( <i>i</i> )	0.0763 (4)	0.2370 (4)	0	1.4 (1)

Table 2. Relevant bond distances (Å) and angles (°)

Hg–S	2.382 (2)	Pb–S (4×)	2.989 (1)
	2.386 (2)	Pb–I(2) (2×)	3.427 (1)
Hg–I(1) (2×)	3.441	Pb–I(3) (2×)	3.431 (1)
Hg–I(3) (2×)	3.301 (1)	Pb–I(3) (2×)	4.385 (2)
Hg–Hg	3.624 (1)		
S–Hg–S	171.06 (8)	S <sub>s</sub> –Pb–Sb <sub>s</sub> *	73.71 (7)
Hg–S–Hg	98.94 (8)	S <sub>s</sub> –Pb–Sb <sub>a</sub>	100.40 (7)

\* Subscript *s*: atom in the same column; subscript *a*: atom in an adjacent column.

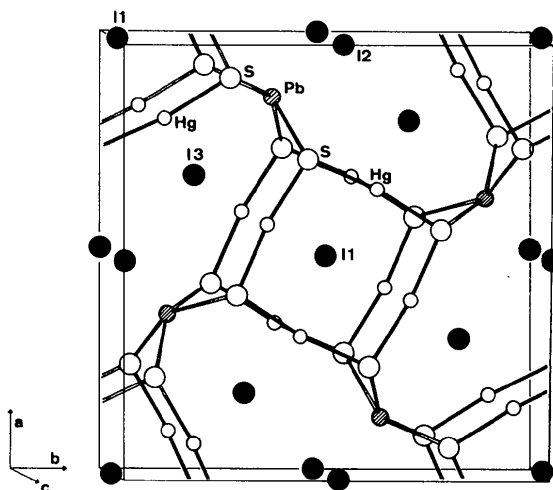


Fig. 1. Perspective view of the elementary cell of Hg<sub>2</sub>PbI<sub>2</sub>S<sub>2</sub> (small open circles: Hg, large open circles: S, cross hatched circles: Pb, filled circles: I).

**Discussion.** Table 1 lists the refined positional and thermal parameters, Table 2 the relevant bond distances and angles.\* A perspective view with atom labeling is shown in Fig. 1. The Hg atom forms two approximately collinear bonds to one S atom at 2.386 (2) Å and one at 2.382 (2) Å. Four I atoms, two at 3.301 (1) Å and two at 3.441 (1) Å, complete the distorted octahedral coordination. The Pb atom is surrounded by four S atoms at 2.989 (1) Å, two I(2) atoms at 3.427 (1) Å and one I(3) atom at 3.431 (1) Å. An appreciable degree of ionic bond character might be responsible for the formation of these monocapped trigonal prismatic groups. The S atoms are nearly tetrahedrally coordinated by two Hg atoms and two Pb atoms. The I atoms are positioned in three different crystallographic sites: I(1) is surrounded by a cube of eight Hg atoms at 3.441 Å, I(2) centers a square of four Pb atoms at 3.427 Å and I(3) is coordinated by four equatorial Hg atoms at 3.301 Å and one axial Pb atom at 3.431 Å at the vertices of a square pyramid and is situated slightly below the base of the pyramid.

The structure is built from planar  $\text{Hg}_4\text{S}_4$  rings with an S—Hg—S bond angle of  $171.06^\circ$ . These rings are packed in columns running in the [001] direction. The columns are connected by the Pb atoms which have four S neighbors belonging to four rings in two adjacent columns. Thus a three-dimensional network is formed in which three different types of holes are filled by the I atoms.

The coordination of the Hg atoms is well known in the chemistry of  $\text{Hg}^{\text{II}}$  and very similar to that of Hg in  $\text{Hg}_3\text{I}_2\text{S}_2$  (Puff, 1985), in which Hg is placed in a distorted octahedron of four equatorial I at relatively long distances and two axial S atoms at short distances. The Hg—S distances (2.38 Å) are slightly shorter than those observed in the ternary compound (2.40 Å) and indicate a strong covalent bond character in the rings [sum of covalent radii: 2.32 Å (Wells, 1984)]. The Hg—I distances (3.30, 3.44 Å) are longer than the shortest Hg—I distance in the ternary compound (3.00 Å) and than those reported by Wells (1984) for the covalent mercury iodides (2.62–2.78 Å).

$\text{Pb}_5\text{I}_6\text{S}_2$  (Krebs, 1975) contains Pb atoms in a trigonal prismatic coordination. Additional atoms above the prism faces raise the coordination number to seven and eight respectively. In  $\text{Hg}_2\text{PbI}_2\text{S}_2$  Pb is coordinated similarly by four S and three I and two additional distant I atoms at 4.385 (2) Å. The coordination group around  $\text{Pb}^{2+}$  might be regarded as a tricapped trigonal prism which is also found in the  $\text{PbCl}_2$  structure. The Pb—I distances in the compounds are comparable [ $\text{Pb}_5\text{I}_6\text{S}_2$ : 3.232 to 3.782 Å (Krebs, 1975);  $\text{Hg}_2\text{PbI}_2\text{S}_2$ : 3.43 Å]. However, the Pb—S dis-

tance (2.99 Å) of the quaternary phase is larger than that in  $\text{Pb}_5\text{I}_6\text{S}_2$  (2.70 Å).

A comparison of the sum of the ionic radii (Shannon & Prewitt, 1970) and the observed bond length ( $r_{\text{Hg}^{2+}} + r_{\text{I}^-} = 3.16$  Å;  $d_{\text{Hg—I}} = 3.30$  Å;  $r_{\text{Pb}^{2+}} + r_{\text{I}^-} = 3.33$  Å;  $d_{\text{Pb—I}} = 3.43$  Å;  $r_{\text{Pb}^{2+}} + r_{\text{S}^{2-}} = 2.82$  Å;  $d_{\text{Pb—S}} = 2.99$  Å) indicates the ionic character of these bonds. The structure consists thus of  $\text{Hg}_4\text{S}_4$  rings with covalent bonds which are connected by  $\text{Pb}^{2+}$  bridges. The  $\text{I}^-$  ions fill the interstices of this array and seem to be rather weakly bonded.

The compound is chemically derived from cinnabar, which is built of helical chains. The S atoms have two Hg atoms as nearest neighbors (Aurivillius, 1950). By the substitution of  $\text{S}^{2-}$  by two  $\text{I}^-$  in cinnabar one obtains  $\text{Hg}_3\text{I}_2\text{S}_2$  (Puff, 1985), in which these chains are connected by Hg bridges. The coordination number of S increases to three. The new compound is derived from the latter phase by substitution of one third of the  $\text{Hg}^{2+}$  by  $\text{Pb}^{2+}$ . The S is now coordinated tetrahedrally by two Pb and two Hg atoms.

The structure of the ternary parent compound  $\text{Hg}_3\text{I}_2\text{S}_2$  is not yet published. It crystallizes in an orthorhombic lattice with the lattice parameters  $a = 9.791$ ,  $b = 18.666$  and  $c = 9.444$  Å (Puff, 1985) in the space group *Imma* and with  $Z = 8$ . The lattice parameters of the quaternary and the ternary compound are closely related:  $a_q^2 \approx a_t^2 + c_t^2$ ,  $c_q = b_t/4$ . The substitution of one  $\text{Hg}^{2+}$  atom by  $\text{Pb}^{2+}$  increases the symmetry of the phase, whereas by the introduction of  $\text{Sn}^{2+}$  the space group of  $\text{Hg}_3\text{I}_2\text{S}_2$  is not influenced. The phase  $\text{Hg}_2\text{SnI}_2\text{S}_2$  crystallizes with orthorhombic symmetry, space group *Imma* and lattice parameters  $a = 9.282$  (3),  $b = 9.565$  (2) and  $c = 13.460$  (5) Å.

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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 42695 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.