A New Quaternary Chalcogenide Halide: Synthesis and Structure of $Hg_2SnS_2Br_2$

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DEDICATED TO PROF. DR. H. G. V. SCHNERING ON THE OCCASION OF HIS 65TH BIRTHDAY.

The new quaternary compound $Hg_2SnS_2Br_2$ was prepared by the reaction of HgS with $SnBr_2$. It crystallizes in the space group C_{2h}^5-$P2_1/n$ of the monoclinic system with four formula units in the cell and lattice parameters of $a = 935.6(1)$, $b = 802.8(1)$, $c = 1063.0(2)$ pm and $\beta = 103.06(1)°$. The structure consists of [Hg–S–] helices arranged in a tetragonal rod packing which are separated by Sn_2Br_4-units. Both structural features appear in the structures of the pure components, too. The intercalation of $SnBr_2$ in HgS (cinnabar-type) may be compared with that of Br_2 in CsF. © 1996 Academic Press, Inc.

INTRODUCTION

Recently many ternary compounds have been synthesized which contain halogen and chalcogen anions with a common cation (1–4). Structural units of the pure binary halide resp. chalcogenide are preserved in some of these materials, which indicates a tendency for ''immiscibility'' in the solid state. This phenomenon may even lead to peritectic or syntectic melting of such a compound (5, 6). The quaternary compound $Hg_2SnS_2Br_2$, which is reported on in this paper, clearly reveals this unusual building principle.

EXPERIMENTAL

A. Synthesis

The compound $Hg_2SnS_2Br_2$ was prepared by solid state reaction of HgS and $SnBr_2$. Both components, HgS (p.a., Merck) and $SnCl_2$ (p.a., Merck), were dried at 400 K and 1 Pa. The compounds were mixed in stoichiometric amounts and loaded into a dry silica glass tube which was evacuated and then sealed under vacuum. The ampoules were placed in a furnace and annealed for four weeks at 490 K. By this

procedure transparent trapezoid single crystals of yellow color were obtained; larger crystals with a diameter of more than 2 mm were red.

B. Thermal Measurements

The thermal analyses were carried out with a DuPont 990 differential scanning calorimeter and Si as reference substance. The heating/cooling rate was 10 K min^{-1}.

C. Structure Determination

The structure was determined by single-crystal X-ray diffraction methods. A summary of the crystallographic data is given in Table 1. Intensity data were collected on an Enraf-Nonius CAD4 automatic four-circle diffractometer with graphite monochromated Mo$K\alpha$ radiation in the ω-2θ scan technique. Three standard reflections were monitored every 60 min and showed no significant deviation during the period of data collection. The structure was solved by direct methods (SHELXS-86) (7) and refined by the least-squares method for F^2 (SHELXL-93) (8). An analytical absorption correction was applied to the data. After complete anisotropic refinement the R and wR were 5.43% and 12.26%, respectively.

Table 2 contains atomic positional and displacements parameters. Bond length and angles are listed in Table 3. Details of the structure determination are available from the authors on request.

RESULTS AND DISCUSSION

The system HgS–$SnBr_2$ is not quasibinary. In samples which were annealed at 493 K with compositions of less than 33.3 mol% $SnBr_2$ the compounds HgS and $Hg_2SnS_2Br_2$ were observed. At 33.3 mol% only $Hg_2SnS_2Br_2$, which decomposes peritectically at 565($\pm$3) K, was detected. Above 33.3 mol% $Hg_2SnS_2Br_2$ and Sn_2Br_2S were found. In addition the reflections of $SnBr_2$

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TABLE 1
Crystal Data of $Hg_2SnS_2Br_2$

Crystal description	Orange yellow, trapezoid
Crystal system	Monoclinic
Space group	$P2_1/n$ (No. 14)
Lattice parameters:	
a [pm]	935.6(1)
b [pm]	802.8(1)
c [pm]	1063.0(2)
β [°]	103.06(1)
Cell volume [nm³]	777.8(2) × 10⁶
Z	4
F (000)	1248
D_{calc} [g cm⁻³]	6.352
Absorption coefficient μ(Mo$K\alpha$) [mm⁻¹]	53.267
Temperature [K]	293(2)
Measuring range	$2.62° \geq \theta \leq 28°$
	$-14 < h < 14$
	$0 < k < 12$
	$0 < l < 17$
Absorption correction	Analytical, T_{min} = 0.0368, T_{max} = 0.1051
No. of measured reflections	1618
No. of unique reflections with $I > 2\sigma(I)$	1266
Data/parameter/restrain	1618/0/65
$R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$	5.43%
$wR = \Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2$	12.26%
Extinction coefficient	0.0021(3)
Goodness of fit	1.0403
Maximum/minimum rest electron density [e/Å³]	3.231/−3.401

TABLE 2
Positional and Displacement Parameters Equivalent Isotropic and Anisotropic Parameters [pm² × 10⁻¹] of Atoms in the Asymmetric Unit of $Hg_2SnS_2Br_2$ with esd's in Parentheses

	x	y	z	U_{eq}
Hg(1)	0.3718(1)	0.0530(1)	0.6139(1)	24(1)
Hg(2)	0.4626(1)	0.3189(1)	0.8762(1)	26(1)
Sn(1)	0.7782(2)	0.0896(2)	0.9185(1)	24(1)
Br(1)	0.6763(3)	0.1056(3)	1.1185(2)	27(1)
Br(2)	1.0204(2)	0.1787(3)	1.1208(2)	26(1)
S(1)	0.5842(6)	0.1830(5)	0.7331(5)	19(1)
S(2)	0.1751(5)	0.0838(6)	0.4770(4)	16(1)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Hg(1)	21(1)	30(1)	22(1)	−7(1)	6(1)	−3(1)
Hg(2)	30(1)	32(1)	22(1)	−7(1)	13(1)	−1(1)
Sn(1)	28(1)	26(1)	19(1)	0(1)	7(1)	−3(1)
Br(1)	33(1)	34(1)	18(1)	0(1)	12(1)	−4(1)
Br(2)	26(1)	28(1)	21(1)	8(1)	−1(1)	−11(1)
S(1)	20(2)	26(3)	15(2)	2(2)	8(2)	−2(2)
S(2)	15(2)	17(2)	17(2)	7(2)	3(2)	2(2)

Note. The equivalent isotropic parameter U_{eq} was calculated as one third of trace of the orthogonal tensor U_{ij}; the anisotropic displacement exponent takes the form $-2\pi^2(U_{11}h^2a^{*2} + \cdots + 2U_{23}klb^*c^*)$.

TABLE 3
Bond Lengths [pm] and Angles [°] of $Hg_2SnS_2Br_2$ (esd's Are Given in Parentheses)

Hg(1)–S(2)	234.5(5)
Hg(1)–S(1)	234.6(5)
Hg(2)–S(1)	236.2(5)
Hg(2)–S(2)¹	236.9(5)
Sn(1)–Br(2)	284.0(3)
Sn(1)–Br(2)²	295.4(3)
Sn(1)–Br(1)	296.6(3)
S(1)–Sn(1)³	292.1(5)
S(2)–Hg(2)⁴	236.9(5)
S(2)–Sn(1)⁵	290.9(5)
S(2)–Hg(2)⁶	294.3(5)
Hg(1)–Hg(2)	346.2(1)
S(2)–Hg(1)–S(1)	173.5(2)
S(1)–Hg(2)–S(2)¹	171.5(2)
S(1)–Hg(2)–S(2)⁷	100.6(2)
S(2) 1–Hg(2)–S(2)⁷	86.8(2)
Sn(1)–Br(2)–Sn(1)²	97.74(8)
Br(2)–Sn(1)–Br(1)	85.49(8)
Br(2)–Sn(1)–Br(2)²	82.26(8)
Br(2) 2–Sn(1)–Br(1)	91.99(8)
Hg(1)–S(1)–Hg(2)	94.6(2)
Hg(1)–S(1)–Sn(1)³	113.9(2)
Hg(2)–S(1)–Sn(1)³	113.8(2)
Hg(1)–S(2)–Hg(2)⁴	102.3(2)
Hg(1)–S(2)–Sn(1)⁵	107.6(2)
Hg(2) 4–S(2)–Sn(1)⁵	95.7(2)
Hg(1)–S(2)–Hg(2)⁶	105.0(2)
Hg(2) 4–S(2)–Hg(2)⁶	93.2(2)
Sn(1) 5–S(2)–Hg(2)⁶	143.4(2)

Note. ¹ $-x + 1/2, y + 1/2, -z + 3/2$; ² $-x + 2, -y, -z + 2$; ³ $-x + 3/2, y + 1/2, -z + 3/2$; ⁴ $-x + 1/2, y - 1/2, -z + 3/2$; ⁵ $x + 1/2, -y - 1/2, z - 1/2$; ⁶ $x - 1/2, -y + 1/2, z - 1/2$; ⁷ $x + 1/2, -y + 1/2, z + 1/2$.

appeared in the X-ray powder data of samples with more than 66 mol% $SnBr_2$.

A DSC trace of an unreacted $HgS + SnBr_2$ mixture showed three thermal effects, two endothermic effects at 485 and 565 K (Fig. 1a; 1 + 3) and a weak exothermic peak at ~500 K (Fig. 1a; 2). The effect at 565 K is caused by the peritectic decompostion of $Hg_2SnS_2Br_2$. The observation reveals that the quaternary compound is formed within minutes during the DSC run. The first effect at 475 K is due to a metastable eutectic between HgS and $SnBr_2$. This eutectic melt reacts exothermically with solid HgS to $Hg_2SnS_2Br_2$ at 500 K. The reaction is nearly complete as shown by a repeated DSC run with the same sample (Fig. 1b), in which only the peritectic effect was found at 565 K.

A. Description of the Structure

$Hg_2SnS_2Br_2$ crystallizes with monoclinic symmetry in the space group C_{2h}^5-$P2_1/n$ with lattice parameters of $a = 935.6(1)$, $b = 802.8(1)$, $c = 1063.0(2)$ pm, and $\beta = 103.06(1)°$ and four formula units in the unit cell.
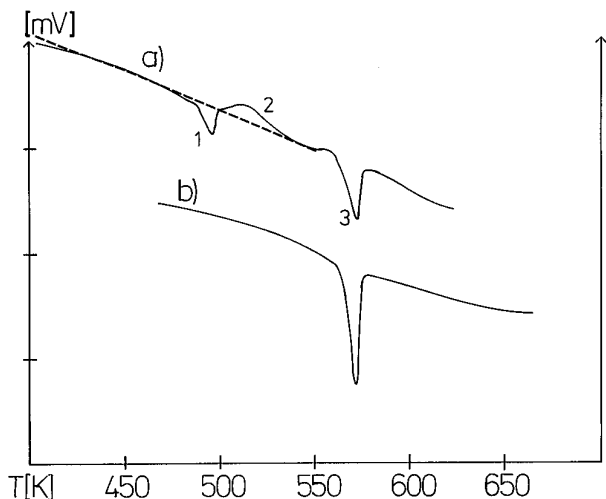
FIG. 1. (a) DSC trace of a HgS–$SnBr_2$ mixture on heating (1,3 endothermic, 2 exothermic effect). (b) Repeated heating run with the same sample

FIG. 2. Schematic detail of the crystal structure of $Hg_2SnS_2Br_2$ showing the cavity between two HgS-helices in which the dimeric $SnBr_2$-units are located; the thermal vibration ellipsoids represent 50% of the probability of finding the corresponding atoms. The ellipsoidal cavity has a length of about 1190 pm and a height of about 800 pm.

The coordination of tin in the pyramidal $SnBr_3$ groups (d(Sn–Br) = 284.0, 295.4, and 296.6 pm) is complemented by three S atoms (290.9, 292.1, and 321.7 pm) to a distorted octahedron. Two of the Br atoms are shared between two neighboring groups, thus forming Sn_2Br_2 rings with Sn–Br distances of 295.4 and 296.6 pm in the ring and of 284.0 pm to the exo-Br atoms. The bond angles in the ring are Br–Sn–Br 82.26° and Sn–Br–Sn 97.74°; the exo-Br–Sn–Br angles are 85.49° and 91.99°.

Hg(1) is placed in an octahedron of four equatorial Br atoms at relatively long distances (324.0, 330.2, 330.4, and 360.8 pm) and two axial S atoms at distances of 234.5 and 234.6 pm. Hg(2) is surrounded by three Br atoms, two at 335.2 and one at 365.2 pm, one S atom at 294.3 pm, and two at the short distances of 236.2 and 236.9 pm. These distorted octahedra are well known in the structural chemistry of Hg^{2+} and are very similar to those of $Hg_3S_2Cl_2$ (9). The short Hg–S bonds lead to $[-Hg-S-]_\infty$ helices of nearly quadratic cross section, running parallel to the b axis. Interbond angles in these helices are Hg–S–Hg 94.6° and 102.3°, respectively, S–Hg–S 173.5° and 171.5°. These spiral chains are arranged in a tetragonal rod packing (10) to a one-dimensional solid state framework with cavities, grouped in strings along the b axis. The diameter and height of these cavities are 1190 pm, respectively, 800 pm. Neutral centrosymmetric Sn_2Br_4 units are located in these holes (Fig. 2). In the [101] plane the terminal Br atoms point into the Hg–S–Hg corners of two opposite neighboring helices, so that the Sn_2Br_4 units are also packed in columns along the b direction (Fig. 3).

B. Discussion

The bond distances and the partial structures of the Hg–S chains and Sn_2Br_4 units are comparable with those of
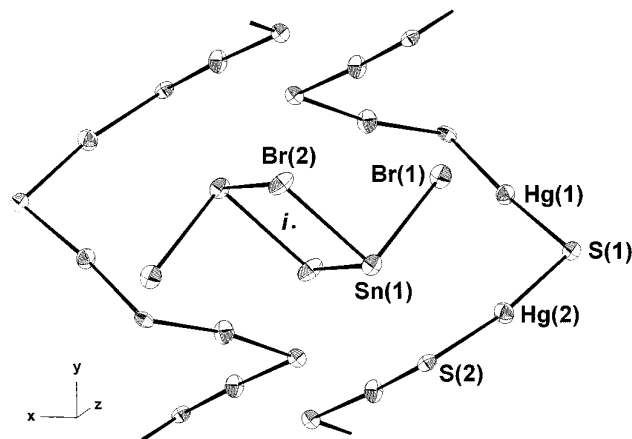
the pure components. HgS is dimorphic. Metacinnabarite crystallizes in the zinc–blende structure, in which Hg is surrounded by four S atoms at 253.0 pm (11). The structure of the other form, cinnabar, contains as a structural element trigonal helical chains in which Hg has two nearest neighbors at 235.8 pm and bond angles of 174.4° at Hg atoms and 105.3° at S atoms (12). These data compare well with distances and bond angles in the chains of $Hg_2SnS_2Br_2$. The Hg–S bond in cinnabar is marginally weaker than in the structure of the quaternary compound (mean Hg–S distance in $Hg_2SnS_2Br_2$ 235.1 pm)

The structure of $SnBr_2$ is related to the $PbCl_2$ type (13). It contains pyramidal $SnBr_3$ units with Sn–Br distances of
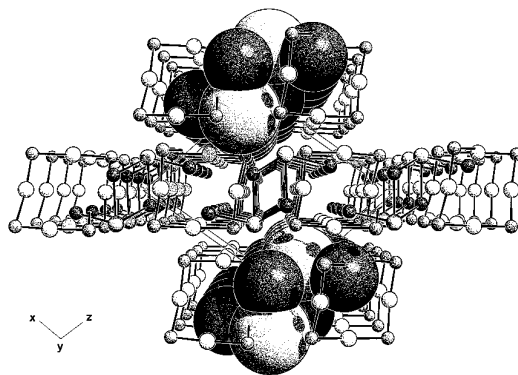

FIG. 3. Perspective view of the complete crystal structure of $Hg_2SnS_2Br_2$. To show the insertion of dimeric $SnBr_2$-units between HgS-helices, these molecules are shown as space-filling and ball-and-stick models, respectively (in ball-and-stick Hg, big, only slightly shadowed spheres; Sn, big, more shadowed spheres; S, small, moderately strong shadowed spheres; Br, small, most shadowed spheres).

TABLE 4
Bond Valence Sums of Cations and Anions in $Hg_2SnS_2Br_2$

1st coordination shell, $r_{max} = 300$ pm		2nd coordination shell, $r_{max} = 500$ pm	
Atom	v_i	Contribution	v_i
Hg(1)	1.805	Hg–S	2.129
Hg(2)	1.897	Hg–S	2.182
S(1)	1.776	S–Hg	2.186
S(2)	1.926	S–Hg	2.222
Sn(1)	1.119	Sn–Br	1.849
Br(1)	0.794	Br–Sn	0.943
Br(2)	0.325	Br–Sn	0.700

280.1(one) and 289.8(two) pm which are shorter than the comparable distances in the Sn_2Br_4 units. The next nearest Br neighbors are at 341.6(one) and 365.5(two) pm (14). The structure of Hg_2SnS_2Br resembles that of $Hg_2PbS_2I_2$. In this compound the quadratic $[-Hg-S-]_\infty$ helices are split into Hg_2S_4 squares which are placed in columns in the c axis. Pb atoms connect four squares in two adjacent columns by bonds to an S atom in each of these squares, thus channels which are occupied by I atoms are formed in the c-direction (15).

The bond valence concept (16, 17) can be used to describe quantitatively the cation anion interactions. The bond valence sum is given by the expression

$$\nu_i = \Sigma_i \exp(r_0 - D)/0.37.$$

The bond valence sums of Hg and Sn atoms in $Hg_2SnS_2Br_2$ are given in Table 4. Atomic valences calculated with this equation generally deviate no more than 0.2 unit from the integer oxidation numbers, as in the case of Hg atoms, which have a bond valence sum of 2.

The bond valence sum of Sn is much lower than expected, 1.12 instead of 2. Wang and Liebau (18) have shown from a statistical analysis of $[Sb(III)S_3]$ polyhedra that r_0 is also correlated with α, the average of the S–Sb–S angles, caused by a progressive retraction of the s electron pair from the Sb(III) nucleus. Such an effect has to be regarded in the case of Sn(II) too.

$Hg_2SnS_2Br_2$ may be seen as a one-dimensional intercalation compound in which the guest molecules Sn_2Br_4 are inserted into the host HgS. However, it deviates from usual intercalation compounds because guests are neither placed in channels in three-dimensional structures nor occupy the van der Waals gap in layer structures. It can be compared with the intercalation of Br_2 in CsF, in which the structure of the host is changed and its bond strength increased (19). In $Hg_2SnS_2Br_2$ the host removes preformed Sn_2Br_4 molecules from solid $SnBr_2$, thereby the diameter of the helical Hg–S chains in HgS is increased and the pitch is reduced. The bond valence sums reveal that the guest takes the part of the second coordination sphere in HgS and the host that of the second coordination sphere in $SnBr_2$.

For this material to relate to intercalation compounds the Sn_2Br_4 units must be removable or exchangeable. Soft chemical methods, based on the solubility of $SnBr_2$ were attempted. Ground powders were leached in pyridine at 70°C for 3 h. The material changes its color immediately to black. These samples were washed, dried, and subjected to powder XRD. The material showed broad reflections of cinnabar, which indicated that $SnBr_2$ was removed from the structure and HgS in a highly disordered state was formed. Experiments to exchange Br by I were performed by refluxing SnI_2 and $Hg_2SnS_2Br_2$ in butylether; the recovered material consisted of HgI_2 and amorphous products.

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