

# Synthesis and Crystal Structure of $\text{Hg}_3\text{S}_2\text{I}_2$ and $\text{Hg}_3\text{Se}_2\text{I}_2$ , New Members of the $\text{Hg}_3\text{E}_2\text{X}_2$ Family

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The reactions of HgS and HgSe with  $\text{HgI}_2$  yield  $\text{Hg}_3\text{S}_2\text{I}_2$  and  $\text{Hg}_3\text{Se}_2\text{I}_2$ , respectively. Orange crystals of  $\text{Hg}_3\text{S}_2\text{I}_2$  and light red crystals of  $\text{Hg}_3\text{Se}_2\text{I}_2$  are formed in evacuated glass ampoules at 260°C in yields of 50% as the only crystalline compounds. The crystal structures have been solved and refined to  $R = 0.0449$ ,  $wR(F^2) = 0.0751$  for  $\text{Hg}_3\text{S}_2\text{I}_2$  and  $R = 0.0518$ ,  $wR(F^2) = 0.0993$  for  $\text{Hg}_3\text{Se}_2\text{I}_2$  on the basis of single-crystal X-ray diffraction data. Both compounds are isotypic and crystallize in the orthorhombic space group *Imma* with  $Z = 8$ . The lattice constants are  $a = 979.92(8)$  pm,  $b = 1870.3(3)$  pm,  $c = 946.22(7)$  pm for  $\text{Hg}_3\text{S}_2\text{I}_2$  and  $a = 976.60(9)$  pm,  $b = 1938.1(3)$  pm,  $c = 963.32(9)$  pm for  $\text{Hg}_3\text{Se}_2\text{I}_2$ . The structures contain one-dimensional polycationic folded bands  $(\text{Hg}_3\text{E}_2)^{2+}$  ( $E = \text{S}, \text{Se}$ ) with intercalated  $\text{I}^-$  ions. Alternatively, the polycationic part can be described as trigonal  $\text{Hg}_3\text{E}$  pyramids which are interconnected in the way that they form one-dimensional channels. Discrete iodide ions separate these cationic channels. © 2000 Academic Press

**Key Words:** mercury sulfide iodide; mercury selenide iodide; crystal structure; one-dimensional polycationic bands.

## INTRODUCTION

In the late 1960s and 1970s the ternary systems mercury/chalcogen/halogen were the subjects of extensive investigations and many compounds of the composition  $\text{Hg}_3\text{E}_2\text{X}_2$  ( $E = \text{O}, \text{S}, \text{Se}, \text{Te}; X = \text{Cl}, \text{Br}, \text{I}$ ) were found. Puff and Küster synthesized and characterized  $\text{Hg}_3\text{E}_2\text{X}_2$  compounds with  $E = \text{S}, \text{Se}, \text{Te}$  and  $X = \text{Cl}, \text{Br}, \text{I}$  and solved the structures of the cubic compounds  $\alpha\text{-Hg}_3\text{S}_2\text{Cl}_2$ ,  $\text{Hg}_3\text{Se}_2\text{Cl}_2$ ,  $\text{Hg}_3\text{Te}_2\text{Cl}_2$ , and  $\text{Hg}_3\text{Te}_2\text{Br}_2$  (1). Durovic succeeded in determining the structure of  $\gamma\text{-Hg}_3\text{S}_2\text{Cl}_2$  (2), which is orthorhombic. Recently crystal structures of  $\alpha\text{-Hg}_3\text{S}_2\text{Br}_2$ ,  $\beta\text{-Hg}_3\text{S}_2\text{Br}_2$ , (3) and  $\beta\text{-Hg}_3\text{S}_2\text{Cl}_2$  (4) were published. The characteristic structure motif of these compounds is interconnected trigonal  $\text{Hg}_3\text{E}$  pyramids in different arrangements.  $\alpha\text{-Hg}_3\text{S}_2\text{Br}_2$  and  $\beta\text{-Hg}_3\text{S}_2\text{Cl}_2$  contain isolated  $\text{Hg}_{12}\text{E}_8$  cubes made up of eight  $\text{Hg}_3\text{E}$  pyramids, while  $\gamma\text{-Hg}_3\text{S}_2\text{Cl}_2$  is built from two-

dimensional layers of  $\text{Hg}_3\text{E}$  units, which are also present in the structure of  $\beta\text{-Hg}_3\text{S}_2\text{Br}_2$ . The cubic phases are characterized by a complicated three-dimensional network. Only in the structures of  $\text{Hg}_3\text{Te}_2\text{I}_2$  (5) and  $\text{Hg}_3\text{O}_2\text{Cl}_2$  (6, 7) is the characteristic motif of trigonal  $\text{Hg}_3\text{E}$  pyramids not present. In the structure of  $\text{Hg}_3\text{Te}_2\text{I}_2$  planar Hg–Te chains form the cationic part of the layered structure with alternating Hg–Te and iodide layers. In the monoclinic structures of  $\alpha$ - and  $\beta\text{-Hg}_3\text{O}_2\text{Cl}_2$  tetrahedral  $\text{OHg}_4$  units build three-dimensional networks.

The crystal structures of the other  $\text{Hg}_3\text{E}_2\text{X}_2$  phases are still unknown; only lattice constants have been determined for some compounds and probable space groups have been assigned. We succeeded in synthesizing two new representatives of this structure family,  $\text{Hg}_3\text{S}_2\text{I}_2$  and  $\text{Hg}_3\text{Se}_2\text{I}_2$ . Lattice constants of  $\text{Hg}_3\text{S}_2\text{I}_2$  were already published (8) but nothing was known about  $\text{Hg}_3\text{Se}_2\text{I}_2$ . In this article, we report on the syntheses and the crystal structures of these two compounds.

## EXPERIMENTAL

### Syntheses

Black mercury sulfide and mercury selenide respectively were used for the synthesis of  $\text{Hg}_3\text{S}_2\text{I}_2$  and  $\text{Hg}_3\text{Se}_2\text{I}_2$ . Black mercury sulfide was prepared from mercury(II) chloride and hydrogen sulfide (9). HgSe was obtained from yellow mercury(II) oxide and elemental selenium (10).

Single crystals of  $\text{Hg}_3\text{S}_2\text{I}_2$  and  $\text{Hg}_3\text{Se}_2\text{I}_2$  were grown by heating stoichiometric mixtures of the mercury chalcogenide and mercury(II) iodide in sealed glass ampoules at 260°C for 2–3 days.  $\text{Hg}_3\text{S}_2\text{I}_2$  and  $\text{Hg}_3\text{Se}_2\text{I}_2$  were the only crystalline products formed with yields of 40% to 60%. On exposure to daylight, crystals of both compounds slowly get covered by a black material, which implies a decomposition to elemental mercury.

### Structure Determinations

Suitable single crystals of  $\text{Hg}_3\text{S}_2\text{I}_2$  and  $\text{Hg}_3\text{Se}_2\text{I}_2$  were selected from the reaction product, filled in glass capillaries

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**TABLE 1**  
Crystallographic Data and Refinement Parameters for  $\text{Hg}_3E_2\text{I}_2$   
( $E = \text{S}, \text{Se}$ )

	$\text{Hg}_3\text{S}_2\text{I}_2$	$\text{Hg}_3\text{Se}_2\text{I}_2$
Lattice constants (pm)	$a = 979.92(8)$ $b = 1870.3(3)$ $c = 946.22(7)$	$a = 976.60(9)$ $b = 1938.1(3)$ $c = 963.32(9)$
Volume ( $10^6 \text{ pm}^3$ )	1734.2(3)	1823.3(3)
$Z$	8	
Calculated density ( $\text{g}/\text{cm}^3$ )	$\rho = 7.045$	$\rho = 7.384$
Color	Orange	Light red
Crystal size ( $\text{mm}^3$ )	$0.04 \times 0.01 \times 0.4$	$0.08 \times 0.09 \times 0.2$
Crystal system, space group	Orthorhombic, <i>Imma</i> (No. 74)	
Measuring range	$6^\circ < 2\theta < 56^\circ$	$4^\circ < 2\theta < 56^\circ$
No. of measured reflections	7848	8174
No. of unique reflections, $R_{\text{merge}}$	1115, 0.0437	1126, 0.0496
No. of refined parameters	42	
Final $R$ values		
$wR(F^2)$	0.0751	0.0993
$R( F )$ (all data)	0.0449	0.0518
$R( F )$ ( $F^2 > 4\sigma F^2$ )	0.0308 (860 data)	0.0373 (868 data)
Goodness of fit	0.985	1.123
Largest peak and deepest hole ( $\text{e}/10^6 \text{ pm}^3$ )	+1.98/−1.78	+2.71/−2.12

(diameter 0.3 mm), and mounted on a STOE imaging plate diffraction system using graphite-monochromated  $\text{MoK}\alpha$  radiation ( $\lambda = 71.073 \text{ pm}$ ). The crystal dimensions, crystallographic data, and details of the data collection are given in Table 1. All measured intensities were corrected for Lorentz and polarization effects. Systematic absences ( $hkl$ ,  $h + k + l = 2n$ ;  $0kl$ ,  $k, l = 2n$ ;  $h0l$ ,  $h + l = 2n$ ,  $hk0$ ,  $h + k = 2n$ ,  $h00$ :  $h = 2n$ ,  $0k0$ ,  $k = 2n$ ,  $00l$ ,  $l = 2n$ ) lead to the space groups *Ibm2*, nonconventional setting of *Ima2* (No. 46), and *Ibmm*, nonconventional setting of *Imma* (No. 74). After the data sets were transformed into the conventional settings, only the refinement in *Imma* (No. 74) led to acceptable  $R$  values. The crystal structures were solved by direct methods (SHELXS-86 (11)), which revealed the positions of the mercury atoms. The positions of the chalcogen and halide ions were obtained from difference Fourier maps. The structures were refined by the full-matrix least-squares method (SHELXL-93 (12)) based on  $F^2$  with anisotropic displacement parameters for all atoms. Due to the high absorption coefficients ( $\mu = 604.9 \text{ cm}^{-1}$  for  $\text{Hg}_3\text{S}_2\text{I}_2$ ,  $\mu = 650.6 \text{ cm}^{-1}$  for  $\text{Hg}_3\text{Se}_2\text{I}_2$ ) a numerical absorption correction with the program HABITUS (13) was applied to both data sets. Final atomic coordinates and selected bond lengths and angles are given in Tables 2 and 3. The crystal drawings were produced with the program DIAMOND (14).

Further details of the crystal structure analyses are deposited at the Fachinformationszentrum Karlsruhe, D-77449 Eggenstein-Leopoldshafen, Germany, and can be obtained

**TABLE 2**  
Atomic Coordinates and Equivalent Isotropic Displacement  
Parameters ( $10^4 \text{ pm}^2$ ) for  $\text{Hg}_3E_2\text{I}_2$  ( $E = \text{S}, \text{Se}$ )

Atom	Position	$x$	$y$	$z$	$B_{\text{eq}}$
$\text{Hg}_3\text{S}_2\text{I}_2$					
Hg1	8h	0	0.61302(4)	0.04060(7)	3.36(2)
Hg2	8i	0.23568(7)	0.75	0.49755(6)	2.96(2)
Hg3	8g	0.25	0.39937(4)	0.25	4.03(2)
I1	4e	0	0.75	0.7358(1)	1.96(2)
I2	4e	0	0.75	0.2586(1)	1.96(2)
I3	8h	0	0.50189(5)	0.26952(8)	2.28(2)
S	16j	0.2427(3)	0.6222(2)	0.0024(3)	2.07(4)
$\text{Hg}_3\text{Se}_2\text{I}_2$					
Hg1	8h	0	0.61447(5)	0.0451(1)	4.07(3)
Hg2	8i	0.2293(2)	0.75	0.50032(9)	3.81(3)
Hg3	8g	0.25	0.39968(5)	0.25	4.81(3)
I1	4e	0	0.75	0.7447(2)	2.17(3)
I2	4e	0	0.75	0.2532(2)	2.22(3)
I3	8h	0	0.50089(5)	0.2619(2)	2.49(3)
Se	16j	0.2544(2)	0.62127(6)	0.0084(2)	2.28(3)

by quoting the literature citation, the names of the authors, and the depository numbers CSD-411154 for  $\text{Hg}_3\text{S}_2\text{I}_2$  and CSD-411153 for  $\text{Hg}_3\text{Se}_2\text{I}_2$  on request.

## RESULTS AND DISCUSSION

$\text{Hg}_3\text{S}_2\text{I}_2$  and  $\text{Hg}_3\text{Se}_2\text{I}_2$  crystallize isotypically and represent a new structure type among the  $\text{Hg}_3E_2X_2$  family. The three crystallographically different mercury atoms are each bound to two chalcogen atoms. The mean Hg– $E$  ( $E = \text{S}, \text{Se}$ ) distances of 241.1 pm for  $\text{Hg}_3\text{S}_2\text{I}_2$  and 251.2 pm for  $\text{Hg}_3\text{Se}_2\text{I}_2$  indicate the covalent character of the bonds. The  $E$ –Hg– $E$  angles are between  $160.8^\circ$  and  $163.9^\circ$  for  $\text{Hg}_3\text{S}_2\text{I}_2$  and  $161.48^\circ$  and  $171.78^\circ$  for  $\text{Hg}_3\text{Se}_2\text{I}_2$ . These values are

**TABLE 3**  
Selected Bond Lengths (pm) and Angles ( $^\circ$ ) for  $\text{Hg}_3E_2\text{I}_2$   
( $E = \text{S}, \text{Se}$ )

Atoms	Distance		Atoms	Angles	
	$\text{Hg}_3\text{S}_2\text{I}_2$	$\text{Hg}_3\text{Se}_2\text{I}_2$		$\text{Hg}_3\text{S}_2\text{I}_2$	$\text{Hg}_3\text{Se}_2\text{I}_2$
Hg1– $E$	241.1(2)	251.3(1)	$E$ –Hg1– $E$	160.9(1)	162.71(7)
Hg1–I3	300.2(1)	303.4(1)	I2–Hg1–I3	94.98(3)	99.16(4)
Hg1–I2	328.9(1)	330.4(1)	$E$ –Hg2– $E$	169.9(2)	171.78(7)
Hg2– $E$	239.9(2)	250.1(1)	I1–Hg2–I2	88.70(2)	93.17(3)
Hg2–I1	322.7(1)	324.9(1)	$E$ –Hg3– $E$	160.8(2)	161.48(7)
Hg2–I2	323.2(1)	326.8(1)	I3–Hg3–I3	104.06(3)	102.50(4)
Hg3– $E$	242.3(2)	252.2(1)	Hg1– $E$ –Hg2	99.11(9)	96.87(5)
Hg3–I3	311.6(1)	313.4(1)	Hg1– $E$ –Hg3	99.50(9)	96.53(5)
			Hg2– $E$ –Hg3	99.42(8)	97.39(5)

characteristic for twofold coordinated mercury atoms in the oxidation state  $2+$ . The mercury and the chalcogen atoms form  $\text{Hg}-E$  chains ( $E = \text{S}, \text{Se}$ ) with  $\text{Hg}-E-\text{Hg}$  angles of on average  $99.3^\circ$  for  $\text{Hg}_3\text{S}_2\text{I}_2$  and  $96.9^\circ$  for  $\text{Hg}_3\text{Se}_2\text{I}_2$ . The  $\text{Hg}-E$  chains run pairwise parallel to the crystallographic  $a$ -axis. They are interconnected by  $\text{Hg}(2)$  atoms to form folded bands, which are reminiscent of stacks of cubes with two open edges in each cubelike unit (see Fig. 1). The oxidation state of the three-coordinated chalcogen atoms can be set to  $2-$ . So, the one-dimensional polycationic bands can be described with the formula  $\frac{1}{3}[\text{Hg}_3E_2]^{2+}$ . The ionic character of the structures is underlined by  $\text{Hg}-\text{I}$  distances longer than 300 pm. The iodide ions are located within (I(1)) and between (I(2), I(3)) the cationic bands. I(2) atoms separate the bands in the direction of the crystallographic  $c$ -axis and I(3) atoms build halide layers in the  $(a,c)$  plane. Figure 2 shows a view of the structure viewed along the  $[100]$  direction. The folded bands are arranged in the motif of a hexagonal rod packing. A second description of the crystal structure emphasizes the threefold coordination sphere of the chalcogen atoms: these are surrounded by three independent mercury atoms forming an irregular trigonal pyramid with S/Se in the apical position. These pyramids, which are well-known from other  $\text{Hg}_3E_2X_2$  compounds, are connected in a corner-sharing manner, thereby forming channels running along  $[100]$ .

The displacement parameters of the atoms (see Table 2) reflect the respective coordination spheres. The linearly coordinated Hg atoms exhibit high displacement parameters while S/Se and I atoms with their higher coordination numbers have smaller thermal displacements.

In the structures of  $\text{Hg}_3\text{S}_2\text{I}_2$  and  $\text{Hg}_3\text{Se}_2\text{I}_2$  a novel arrangement of trigonal  $\text{Hg}_3E$  pyramids within the structural

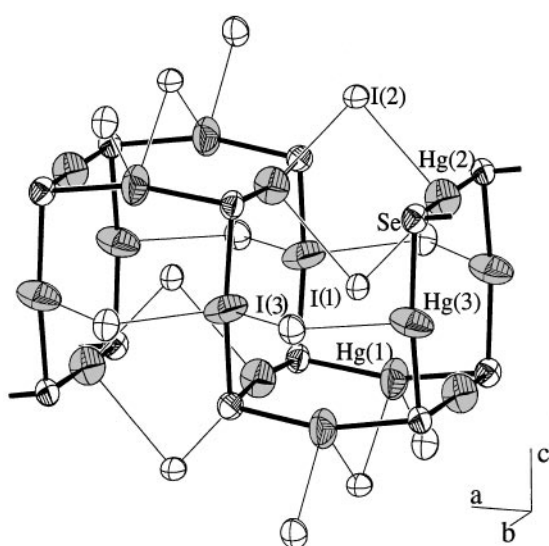


FIG. 1. Polycationic  $\frac{1}{3}[\text{Hg}_3E_2]^{2+}$  strand in the structure of  $\text{Hg}_3\text{Se}_2\text{I}_2$ . The thermal ellipsoids are scaled to enclose a probability of 70%.

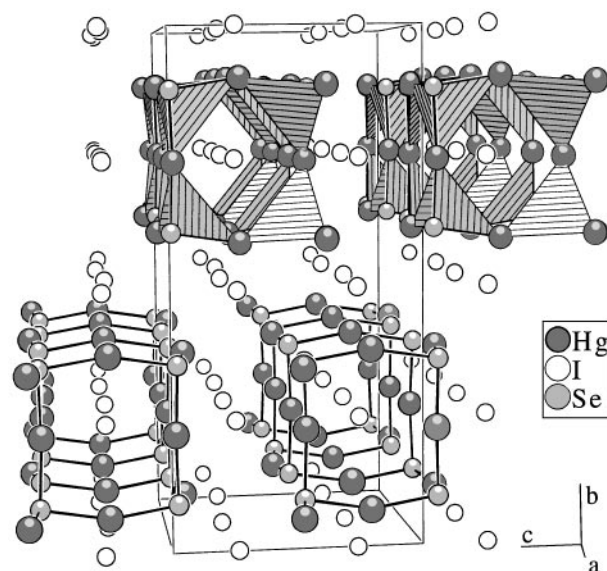


FIG. 2. Unit cell of  $\text{Hg}_3E_2\text{I}_2$  ( $E = \text{S}, \text{Se}$ ) in a perspective view along the  $a$ -axis. The cationic  $[\text{Hg}_3E_2]^{2+}$  strands are shown in a ball-and-stick model and are simultaneously represented as interconnected  $\text{Hg}_3E$  ( $E = \text{S}, \text{Se}$ ) pyramids with intercalated iodide ions.

chemistry of the  $\text{Hg}_3E_2X_2$  ( $E = \text{O}, \text{S}, \text{Se}, \text{Te}; X = \text{Cl}, \text{Br}, \text{I}$ ) compounds is present. Earlier structure work on compounds of the  $\text{Hg}_3E_2X_2$  formula type revealed  $\text{Hg}_{12}E_8$  groups and  $\text{Hg}_3E$  units connected to layers and three-dimensional networks. Now,  $\text{Hg}_3\text{S}_2\text{I}_2$  and  $\text{Hg}_3\text{Se}_2\text{I}_2$  are the first representatives exhibiting  $\text{Hg}_3E$  groups connected to form chains.

Temperature-dependent Guinier powder diagrams recorded from powder samples of  $\text{Hg}_3\text{S}_2\text{I}_2$  and  $\text{Hg}_3\text{Se}_2\text{I}_2$  in the temperature range  $-160^\circ\text{C}$  to  $300^\circ\text{C}$  show no sign of phase transitions.

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