

THE CRYSTAL STRUCTURE OF A POLYMORPH OF $\text{Hg}^{2+}_3\text{S}_2\text{Br}_{1.0}\text{Cl}_{0.5}\text{I}_{0.5}$

NATALIE V. PERVUKHINA[§]

*Nikolaev Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences,
Lavrentiev Av. 3, RU-630090 Novosibirsk, Russia*

VLADIMIR I. VASIL'EV

*United Institute of Geology, Geophysics and Mineralogy, Siberian Branch of the Russian Academy of Sciences,
Koptuyug Av. 3, RU-630090 Novosibirsk, Russia*

STANISLAV V. BORISOV[§], SVETLANA A. MAGARILL[§] AND DMITRII YU. NAUMOV[§]

*Nikolaev Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences,
Lavrentiev Av. 3, RU-630090 Novosibirsk, Russia*

ABSTRACT

Grechishchevite, $\text{Hg}_3\text{S}_2(\text{Br},\text{Cl},\text{I})_2$, is the only known mercury sulfohalide whose anionic part involves three halogens Cl, Br, and I, in addition to sulfur. The crystal structure of the mineral was not solved. The structure of a synthetic polymorph of $\text{Hg}^{2+}_3\text{S}_2\text{Br}_{1.0}\text{Cl}_{0.5}\text{I}_{0.5}$, $Z = 8$, orthorhombic, a 13.249(3), b 13.259(3), c 8.710(2) Å, V 1530.1(5) Å³, space group $Pbnm$, has been solved by direct methods, and refined to an R of 0.0363 based on 1438 unique reflections ($R_{\text{int}} = 0.049$) measured with $\text{MoK}\alpha$ radiation on a CAD-4 automated diffractometer. The structure contains four independent mercury atoms; each Hg^{2+} ion is covalently bonded to two sulfur atoms at a distance of 2.358(4)–2.459(4) Å; the angles $\text{S}(2)\text{--Hg}(2)\text{--S}(1)$ and $\text{S}(1)\text{--Hg}(4)\text{--S}(2)$ are equal to 172.81(15)° and 172.90(15)°, respectively. It should be noted that the angles $\text{S}(2)\text{--Hg}(1)\text{--S}(2)$ [141.8(2)°] and $\text{S}(1)\text{--Hg}(3)\text{--S}(1)$ [140.9(2)°] greatly deviate from linearity. Each S^{2-} ion is covalently bonded to three mercury atoms at a distance 2.358(4)–2.459(4) Å; the $\text{Hg}\text{--S}\text{--Hg}$ angle ranges from 95.95(14) to 104.91(17)°. These units form the structural motif of the eight-member $[\text{Hg}_4\text{S}_4]$ rings, which are combined into infinite crankshaft-type bands running along [001]. The halogen atoms are located inside and between the crankshaft-type bands, with the $\text{Hg}\text{--Cl}$, $\text{Hg}\text{--Br}$ and $\text{Hg}\text{--I}$ distances equal to 2.768(6)–2.804(6), 3.040(2)–3.078(2) and 3.259(1)–3.304(1) Å, respectively. Taking into account the halogen atoms, the $\text{Hg}(1)\text{--Hg}(4)$ atoms have a distorted octahedral coordination. We describe the crystal-chemical peculiarities of the mercury chalcogenide halides, $\text{Hg}_3\text{X}_2\text{Hal}_2$ ($X = \text{S}, \text{Se}, \text{Te}$; $\text{Hal} = \text{F}, \text{Cl}, \text{Br}, \text{I}$).

Keywords: mercury minerals, mercury sulfohalide, polymorph of $\text{Hg}^{2+}_3\text{S}_2\text{Br}_{1.0}\text{Cl}_{0.5}\text{I}_{0.5}$, X-ray data, crystal structure, polymorphism.

SOMMAIRE

La structure de grechishchevite, $\text{Hg}_3\text{S}_2(\text{Br},\text{Cl},\text{I})_2$, le seul sulfohalogénure de mercure connu dont la partie anionique implique les trois halogènes Cl, Br, et I en plus du soufre, demeure méconnue. Ici, nous décrivons la structure d'un polymorphe synthétique de $\text{Hg}^{2+}_3\text{S}_2\text{Br}_{1.0}\text{Cl}_{0.5}\text{I}_{0.5}$, $Z = 8$, de symétrie orthorhombique, a 13.249(3), b 13.259(3), c 8.710(2) Å, V 1530.1(5) Å³, groupe spatial $Pbnm$, résolue par méthodes directes et affinée jusqu'à un résidu R de 0.0363 en utilisant 1438 réflexions uniques ($R_{\text{int}} = 0.049$) mesurées avec rayonnement $\text{MoK}\alpha$ et un diffractomètre automatisé CAD-4. La structure contient quatre atomes indépendants de mercure; chaque ion Hg^{2+} forme des liaisons covalentes avec deux atomes de soufre à une distance variant de 2.358(4) à 2.459(4) Å; les angles $\text{S}(2)\text{--Hg}(2)\text{--S}(1)$ et $\text{S}(1)\text{--Hg}(4)\text{--S}(2)$ sont 172.81(15)° et 172.90(15)°, respectivement. Il est à noter que les angles $\text{S}(2)\text{--Hg}(1)\text{--S}(2)$ [141.8(2)°] et $\text{S}(1)\text{--Hg}(3)\text{--S}(1)$ [140.9(2)°] dévient largement de la linéarité. Chaque ion S^{2-} est en liaison covalente avec trois atomes de mercure à une distance variant de 2.358(4) à 2.459(4) Å; l'angle $\text{Hg}\text{--S}\text{--Hg}$ varie de 95.95(14) à 104.91(17)°. Ces unités forment le motif structural des anneaux $[\text{Hg}_4\text{S}_4]$ à huit membres, qui sont agencés en rubans infinies en vilebroquin le long de [001]. Les atomes de halogènes sont situés soit à l'intérieur, soit à l'extérieur, de ces rubans, les distances $\text{Hg}\text{--Cl}$, $\text{Hg}\text{--Br}$ et $\text{Hg}\text{--I}$ étant égales à 2.768(6)–2.804(6), 3.040(2)–3.078(2) et 3.259(1)–3.304(1) Å, respectivement. Compte tenu des atomes de halogènes, les atomes $\text{Hg}(1)\text{--Hg}(4)$ font preuve d'une coordinence octaédrique

[§] E-mail addresses: pervukh@che.nsk.su, borisov@che.nsk.su, svetlana@che.nsk.su, d.y.naumov@ngs.ru

difforme. Nous décrivons les particularités cristallographiques des chalcogénures à halogènes de mercure, $\text{Hg}_3\text{X}_2\text{Hal}_2$ ($\text{X} = \text{S}, \text{Se}, \text{Te}; \text{Hal} = \text{F}, \text{Cl}, \text{Br}, \text{I}$).

(Traduit par la Rédaction)

Mots-clés: minéraux de mercure, sulfohalogénure de mercure, polymorphe de $\text{Hg}_3^{2+}\text{S}_2\text{Br}_{1.0}\text{Cl}_{0.5}\text{I}_{0.5}$, données de diffraction X, structure cristalline, polymorphisme.

INTRODUCTION

Grechishchevite, $\text{Hg}_3\text{S}_2(\text{Br}, \text{Cl}, \text{I})_2$, was first described by Vasil'ev *et al.* (1989) as a rare supergene mercury sulfohalide mineral. It was discovered in cinnabar-bearing ores of the Arzak deposit and the Kadyrel occurrence, unique localities of secondary minerals of mercury in the Tuva region of Russia. The supergene mineral occurs in thin cracks and small cavities in grains of cinnabar and metacinnabar: 1) in silicified breccias of rhyolite-dacite porphyry and other rocks of a tuffaceous facies (Arzak), and 2) in calcite veins cross-cutting medium- and coarse-grained feldspathic arenites (Kadyrel). At the both localities, grechishchevite is closely associated with corderoite, bromian corderoite, lavrentievite, and arzakite. There are other secondary mercury-bearing minerals in the ores at these localities: calomel, bromian calomel, kuzminite, eglestonite, bromian eglestonite, kadyrelite, poyarkovite, terlinguaite, montroydite, native mercury, kuznetsovite, and schuetteite.

Optical, electron-microprobe and powder-diffraction studies were carried out on a typical specimen and its artificial analogue by Vasil'ev *et al.* (1989), but the structure of the mineral was not solved. A tetragonal cell of the synthetic single crystal with a 13.225(5), c 8.685(5) Å, space group $P4_2m$, $P4m2$ or $P4mm$, $P4/\mu$, a composition close to $\text{Hg}_3\text{S}_2(\text{Br}_{1.0}\text{Cl}_{0.5}\text{I}_{0.5})_{\Sigma 2}$, and a measured density equal to 7.16 g/cm³ close to a D_{calc} of 7.23 g/cm³, were established (Vasil'ev *et al.* 1989).

The present paper is a part of the general study of the crystal chemistry of sulfohalide mercury minerals. We report new information on the crystal structure of a synthetic polymorph of $\text{Hg}_3\text{S}_2(\text{Br}_{1.0}\text{Cl}_{0.5}\text{I}_{0.5})_{\Sigma 2}$; preliminary details were reported by Borisov *et al.* (1999).

EXPERIMENTAL

As specimens of natural grechishchevite suitable for X-ray structure analysis have not yet found, repeated experiments were performed to synthesize a compound with a ratio of components that fits the composition of the grechishchevite. As starting materials, we used the artificial red mercury sulfide, HgS, and the mercury halides, HgCl_2 , HgBr_2 , and HgI_2 , prepared previously and mixed in a stoichiometric ratio. The synthesis was carried out by growing the compound from a gaseous phase in equilibrium with a molten mixture of the above components in evacuated quartz ampoules at 225°C.

Orange prismatic crystals measuring $0.01 \times 0.02 \times 0.05$ mm were obtained, and found to be suitable for a study of the crystal structure.

The unit-cell parameters were refined and a three-dimensional set of intensities was obtained for a single crystal by a standard procedure (an Enraf Nonius CAD-4 automated diffractometer, graphite monochromator, $\text{MoK}\alpha$ radiation, $\theta/2\theta$ scan with a variable rate). All measured intensities were corrected for Lorentz and polarization effects. Absorption corrections were applied using X-RED program package (X-RED 1998) according to the real shape of the crystal. The possibility of tetragonal symmetry was checked. We found that this symmetry is retained for the Hg and S atoms, but not for the halogen atoms. Our analysis of the intensity data show that an orthorhombic symmetry is more likely than a tetragonal one (R_{int} for orthorhombic symmetry equals to 4.90, whereas R_{int} for tetragonal symmetry, it is about 15%).

The structure was solved by direct methods using SIR97 (Altomare *et al.* 1999) and refined anisotropically by the full-matrix least-squares technique using the SHELX97 package of programs (Sheldrick 1998). Selected experimental data are given in Table 1, final coordinates and thermal parameters of the atoms in Table 2, and selected bond-lengths and angles in Table 3. A table of structure factors is available from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

A comparison of theoretical X-ray powder-diffraction pattern of the compound prepared and studied by us and the XRD pattern of natural grechishchevite (Vasil'ev *et al.* 1989) shows good agreement and allows the compound to be considered as a polymorph of $\text{Hg}_3\text{S}_2(\text{Br}_{1.0}\text{Cl}_{0.5}\text{I}_{0.5})_{\Sigma 2}$.

TABLE 1. CRYSTAL DATA FOR $\text{Hg}_3\text{S}_2(\text{Br}_{1.0}\text{Cl}_{0.5}\text{I}_{0.5})_{\Sigma 2}$

a (Å)	13.249(3)	D_{calc} (g/cm ³)	7.180
b (Å)	13.259(3)	μ (mm ⁻¹)	67.90
c (Å)	8.710(2)	Unique reflections	5231
V (Å ³)	1530.1(5)	Unique $F_o > 4\sigma_F$	1438
Space group	$Pbnm$	Final R $F_o > 4\sigma_F$	0.0363
Z	8		

$$R = \sum (|F_o| - |F_c|) / \sum |F_o|.$$

TABLE 2. ATOMIC COORDINATES AND DISPLACEMENT PARAMETERS (\AA^2) FOR $\text{Hg}_3\text{S}_2(\text{Br}_{1.0}\text{Cl}_{0.5}\text{I}_{0.5})_{\Sigma 2}$

Atom	x	y	z	U_{eq}^*	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Hg(1)	0.3083(1)	0.4653(1)	0.2500	0.045(1)	0.045(1)	0.046(1)	0.044(1)	0	0	0.001(1)
Hg(2)	0.1124(1)	0.3473(1)	-0.0087(1)	0.021(1)	0.021(1)	0.021(1)	0.022(1)	0.000(1)	0.000(1)	0.001(1)
Hg(3)	-0.0360(1)	0.1876(1)	0.2500	0.049(1)	0.050(1)	0.048(1)	0.049(1)	0	0	0.000(1)
Hg(4)	0.1513(1)	0.6119(1)	-0.0064(1)	0.027(1)	0.027(2)	0.027(1)	0.027(1)	0.000(1)	0.000(1)	0.000(1)
S(1)	-0.0389(3)	0.2495(3)	-0.0160(5)	0.025(1)	0.027(2)	0.023(2)	0.024(2)	0.003(2)	-0.003(2)	0.002(2)
S(2)	0.2491(3)	0.4612(3)	-0.0109(5)	0.039(1)	0.038(3)	0.041(3)	0.038(3)	0	0	-0.002(2)
Br(1)	0.2108(2)	0.2129(2)	0.2500	0.042(1)	0.041(2)	0.047(2)	0.037(2)	0	0	0.002(2)
Br(2)	0.2280(2)	0.2232(2)	-0.2500	0.035(1)	0.035(2)	0.035(1)	0.036(1)	0	0	0.002(1)
Cl(1)	-0.0194(4)	-0.0205(4)	0.2500	0.027(2)	0.025(4)	0.016(4)	0.040(4)	0	0	-0.005(3)
I(1)	-0.0004(1)	0.5030(1)	-0.2500	0.032(1)	0.033(1)	0.031(1)	0.031(1)	0	0	0.000(1)

* $U_{\text{eq}} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$.

TABLE 3. INTERATOMIC DISTANCES (\AA) AND ANGLES ($^\circ$) FOR $\text{Hg}_3\text{S}_2(\text{Br}_{1.0}\text{Cl}_{0.5}\text{I}_{0.5})_{\Sigma 2}$

Hg(1)-S(2)	2.405(5)	Hg(1) - Cl(1)#2	2.804(6)
Hg(1) - S(2)#1	2.405(5)	Hg(2) - Br(2)	3.078(2)
Hg(2) - S(2)	2.358(4)	Hg(2) - I(1)	3.304(2)
Hg(2) - S(1)	2.389(4)	Hg(3) - Cl(1)	2.768(6)
Hg(3) - S(1)#1	2.459(4)	Hg(4) - Br(2)#2	3.040(2)
Hg(3) - S(1)	2.459(4)	Hg(4) - I(1)	3.259(2)
Hg(4) - S(1)#3	2.373(4)		
Hg(4) - S(2)	2.382(5)		
S(2)#1 - Hg(1) - S(2)	141.8(2)	Hg(4)#3 - S(1) - Hg(2)	95.95(14)
S(2) - Hg(2) - S(1)	172.8(2)	Hg(4)#3 - S(1) - Hg(3)	101.01(16)
S(1)#1 - Hg(3) - S(1)	140.9(2)	Hg(2) - S(1) - Hg(3)	98.19(16)
S(1)#3 - Hg(4) - S(2)	172.9(2)	Hg(2) - S(2) - Hg(4)	96.82(16)
		Hg(2) - S(2) - Hg(1)	104.91(17)
		Hg(4) - S(2) - Hg(1)	98.21(17)

#1	$x, y, -z + \frac{1}{2}$	#2	$-x + \frac{1}{2}, y + \frac{1}{2}, z$	#3	$-x, -y + 1, -z$
#4	$-x + \frac{1}{2}, y - \frac{1}{2}, z$	#5	$-x + \frac{1}{2}, y - \frac{1}{2}, -z - \frac{1}{2}$	#6	$x, y, -z - \frac{1}{2}$

DESCRIPTION OF THE STRUCTURE

The structure of the synthetic phase $\text{Hg}_3\text{S}_2(\text{Br}_{1.0}\text{Cl}_{0.5}\text{I}_{0.5})_{\Sigma 2}$ involves four crystallographically independent Hg^{2+} cations. Each Hg^{2+} ion is covalently bonded to two sulfur atoms at 2.358(4)–2.459(4) \AA distances; the angles S(2)–Hg(2)–S(1) and S(1)–Hg(4)–S(2) are equal to 172.81(15) $^\circ$ and 172.90(15) $^\circ$, respectively. It should be noted that the S(2)–Hg(1)–S(2) [141.8(2) $^\circ$] and S(1)–Hg(3)–S(1) [140.9(2) $^\circ$] angles greatly deviate from the linearity that is typical of Hg^{2+} compounds (Aurivillius 1965). Each S^{2-} ion is covalently bonded to three mercury atoms at distances in the range 2.358(4)–2.459(4) \AA , and the Hg–S–Hg angle ranges from 95.95(14) to 104.91(17) $^\circ$. As a result, in the structure, there are linear covalently bonded S–Hg–S' groups and SHg3 "umbrellas" similar to those in the structure of certain mercury chalcogenide halides of composition $\text{Hg}_3\text{X}_2\text{Hal}_2$ (X = S, Se, Te; Hal = Cl, Br, I). These units

form the structural motif of the eight-member $[\text{Hg}_4\text{S}_4]$ rings with the Hg–S–Hg angle of 95.95(14)–104.91(17) $^\circ$. The rings are combined into infinite crankshaft-type bands running along [001] (Fig. 1). The halogen atoms are located inside and between the crankshaft-type bands, with the Hg–Cl, Hg–Br and Hg–I distances equal to 2.768(6)–2.804(6), 3.040(2)–3.078 and 3.259(1)–3.304(1) \AA , respectively (Fig. 2). Taking into account the halogen atoms, the Hg(1)–Hg(4) atoms have a distorted octahedral coordination (Fig. 3).

RELATED SPECIES

The structure of natural and synthetic mercury chalcogenide halides is of interest because of the formation of numerous polymorphs as well as the presence of isomorphous substitutions in the anion (halogen) sublattice.

Natural sulfosalides of mercury with the formula $\text{Hg}_3\text{S}_2\text{Hal}_2$ (Hal = Cl, Br, I) are few. Those are the minerals such as corderoite, α - $\text{Hg}_3\text{S}_2\text{Cl}_2$ (Foord *et al.* 1974), lavrentievite, $\text{Hg}_3\text{S}_2(\text{Cl}, \text{Br})_2$, arzakite, $\text{Hg}_3\text{S}_2(\text{Br}, \text{Cl})_2$ (Vasil'ev *et al.* 1984), radteite, $\text{Hg}_3\text{S}_2\text{ClI}$ (McCormack *et al.* 1991), and the recently discovered kenh suite, γ - $\text{Hg}_3\text{S}_2\text{Cl}_2$ (McCormack & Dickson 1998). All have a variable composition depending on the proportion and nature of the halogens in the crystal structure. Grechishchevite, $\text{Hg}_3\text{S}_2(\text{Br}, \text{Cl}, \text{I})_2$, is the only known mercury sulfosalide whose anionic part involves all three halogens Cl, Br, and I, in addition to sulfur.

In the late 1960s and 1970s, ternary chalcogen – halogen – mercury systems were the subjects of extensive investigations. Puff & Küster (1962a, b) and Puff *et al.* (1966, 1968) synthesized and characterized the cubic mercury chalcogenide halides $\text{Hg}_3\text{X}_2\text{Hal}_2$ (X = S, Se, Te; Hal = F, Cl, Br, I), studied polymorphism typical of these compounds, and solved the crystal structures of α - $\text{Hg}_3\text{S}_2\text{Cl}_2$, $\text{Hg}_3\text{Se}_2\text{Cl}_2$, $\text{Hg}_3\text{Te}_2\text{Cl}_2$, $\text{Hg}_3\text{Te}_2\text{Br}_2$, $\text{Hg}_3\text{S}_2\text{F}_2$, and $\text{Hg}_3\text{Se}_2\text{F}_2$, which are isostructural with

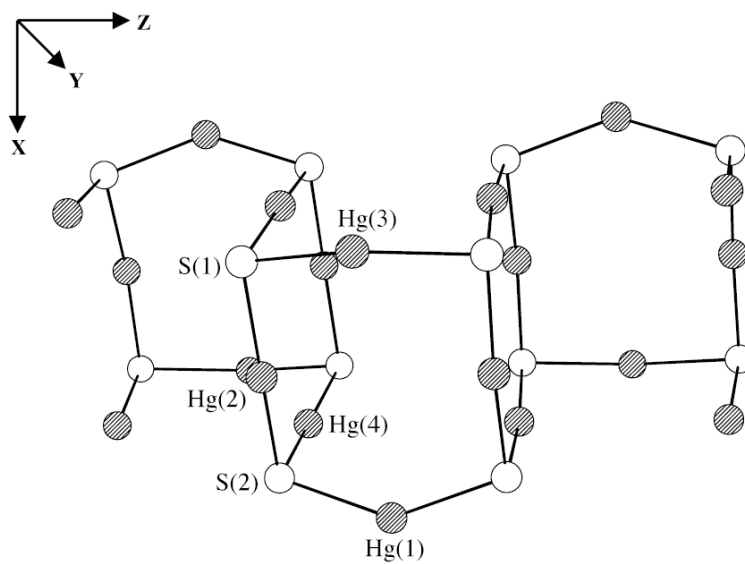


FIG. 1. The crankshaft-type $[\text{Hg}_3\text{S}_2]^{2+}_\Sigma$ band in the structure of $\text{Hg}_3\text{S}_2\text{Br}_{1.0}\text{Cl}_{0.5}\text{I}_{0.5}$.

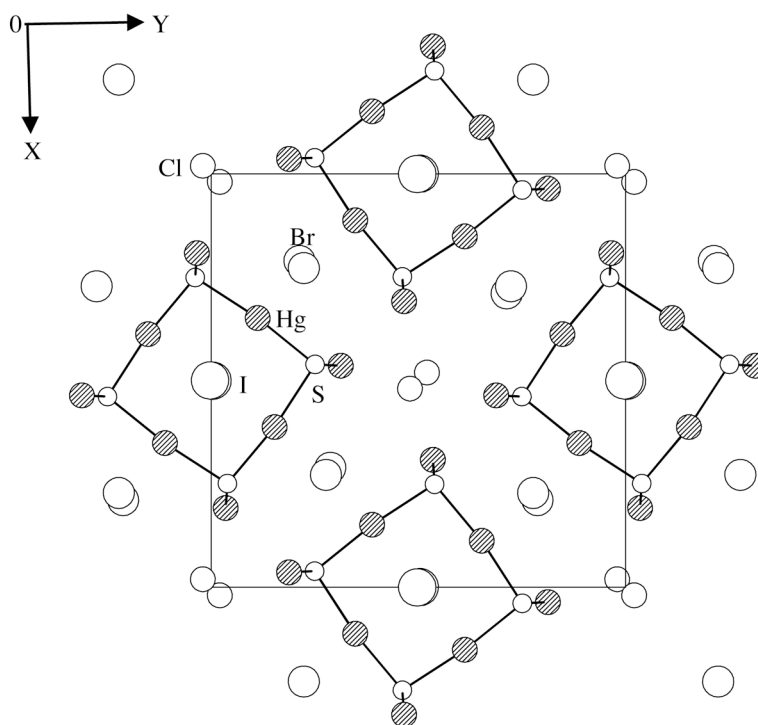


FIG. 2. The structure of $\text{Hg}_3\text{S}_2\text{Br}_{1.0}\text{Cl}_{0.5}\text{I}_{0.5}$ projected onto (001).

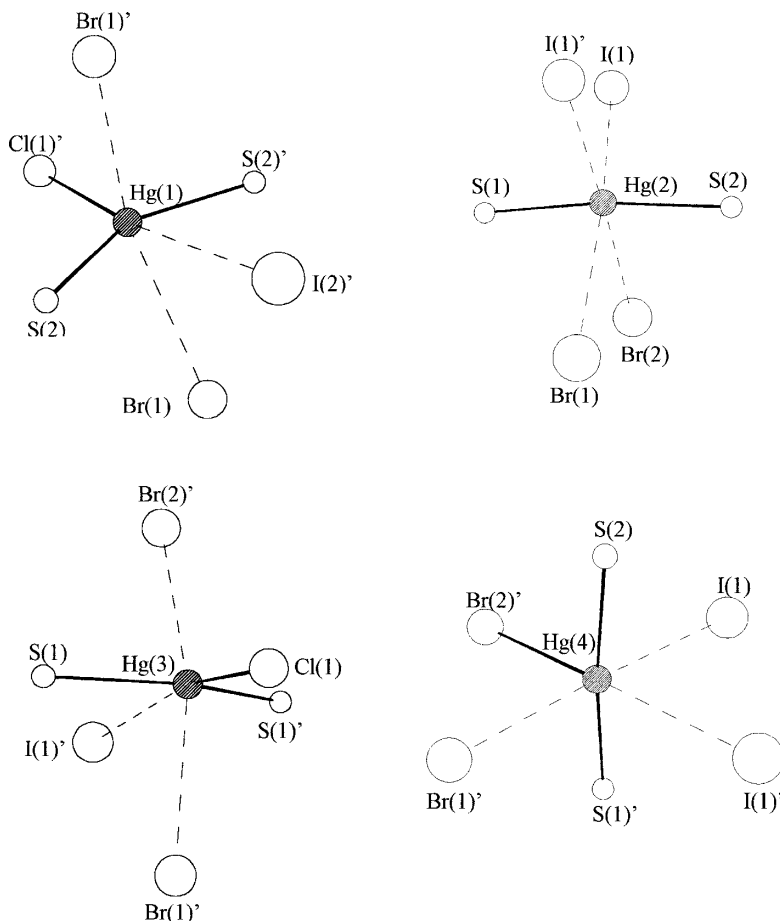


FIG. 3. The environments of the Hg^{2+} cations.

cubic corderoite, $\alpha\text{-Hg}_3\text{S}_2\text{Cl}_2$. The structure of the latter was determined and refined by Aurivillius (1967) and Frueh & Gray (1968). The structure of a metastable orthorhombic phase, $\gamma\text{-Hg}_3\text{S}_2\text{Cl}_2$ was determined by Đurovič (1968). Later, a systematic study of pseudobinary and pseudoternary systems of mercury chalcogenides and halides was carried out. The crystal structures of $\alpha\text{-Hg}_3\text{S}_2\text{Br}_2$ (Voroshilov *et al.* 1996a), $\beta\text{-Hg}_3\text{S}_2\text{Cl}_2$ (Voroshilov *et al.* 1996b), $\beta\text{-Hg}_3\text{S}_2\text{Br}_2$ (Voroshilov *et al.* 1996a), and $\text{Hg}_3\text{Se}_2\text{Br}_2$ (Voroshilov *et al.* 1995) were determined. The structure of synthetic $\text{Hg}_3\text{Te}_2\text{I}_2$ (Lyakhovitskaya *et al.* 1989) was solved. The compounds $\text{Hg}_3\text{S}_2\text{I}_2$ and $\text{Hg}_3\text{Se}_2\text{I}_2$ were synthesized and structurally studied by Beck & Hedderich (2000). In an attempt to prepare synthetic analogues of lavrentievite and arzakitite, we have obtained two phases with a mixed halogen composition: 1) $\text{Hg}_3\text{S}_2\text{Cl}_{1.5}\text{Br}_{0.5}$, isotypic with cubic $\alpha\text{-Hg}_3\text{S}_2\text{Br}_2$, and 2) monoclinic $\text{Hg}_3\text{S}_2\text{Cl}_{1.5}\text{Br}_{0.5}$ (Borisov *et al.* 1999).

DISCUSSION

As shown by Borisov *et al.* (2001), all structural varieties of minerals and synthetic compounds can be represented on the basis of the pseudocubic elementary lattice of the Hal atoms. The covalently bonded X and Hg atoms are located in the lattice voids to form the so-called Hg–X radicals. The crystallographic data of $\text{Hg}_3\text{X}_2\text{Hal}_2$ (X = S, Se, Te; Hal = Cl, Br, I) compounds and types of Hg–X radicals are given in Table 4. The radical has a closed form, the X_8Hg_{12} cube (Fig. 4a) in the structures of cubic $\alpha\text{-Hg}_3\text{S}_2\text{Br}_2$ (Voroshilov *et al.* 1996a), monoclinic $\beta\text{-Hg}_3\text{S}_2\text{Cl}_2$ (Voroshilov *et al.* 1996b), and the cubic compound $\text{Hg}_3\text{S}_2\text{Cl}_{1.5}\text{Br}_{0.5}$ studied by us (Borisov *et al.* 1999).

A ribbon form of the radical, revealed as a crankshaft-type band of the square X_4Hg_4 rings [the + + – – type by analogy with the classification of Aurivillius (1965)] was established in the structures of $\text{Hg}_3\text{S}_2\text{I}_2$ and

TABLE 4. CRYSTALLOGRAPHIC DATA FOR NATURAL AND SYNTHETIC MERCURY CHALCOGENIDE HALIDES, $\text{Hg}_3\text{X}_2\text{Hal}_2$ ($\text{X} = \text{S}, \text{Se}, \text{Te}$; $\text{Hal} = \text{Cl}, \text{Br}, \text{I}$)

Compound Space group <i>R</i>	Unit-cell parameters (Å, °)	$V(\text{Å}^3)$; Z D_{meas} D_{calc} (g/cm^3)	$d(\text{X-Hg})$, (Å) $\angle \text{XHgX}$ $\angle \text{HgXHg}$ (°)	Mineral name Structure type Type of Hg-X radical	Reference
α - $\text{Hg}_3\text{S}_2\text{Cl}_2$ <i>I23</i> 0.065	8.940	714.5; 4 6.74 6.90	2.42 165.1 94.1	Synthetic corderoite α - $\text{Hg}_3\text{S}_2\text{Cl}_2$ Three-dimensional framework	Aurivillius (1967)
β - $\text{Hg}_3\text{S}_2\text{Cl}_2$ <i>Pm3n</i> 0.035	17.925	5759; 32 - 6.798	2.36-2.40 166.9-176.5 94.8-98.0	- β - $\text{Hg}_3\text{S}_2\text{Cl}_2$ Isolated cubes X_8Hg_{12}	Voroshilov <i>et al.</i> (1996b)
γ - $\text{Hg}_3\text{S}_2\text{Cl}_2$ <i>Pbmm</i> 0.135	9.328 8.410 4.541	356.2; 2 6.83 6.814	2.38-2.44 157.8-176 94-96	-(order-disorder structure, substructure I) γ - $\text{Hg}_3\text{S}_2\text{Cl}_2$ Two-dimensional layers	Đurovič (1968)
γ - $\text{Hg}_3\text{S}_2\text{Cl}_2$ <i>A2mm</i> 0.213	4.664 16.820 9.081	712.2; 4 6.83 6.814	2.38-2.44 157.8-176 94-96	-(substructure II) γ - $\text{Hg}_3\text{S}_2\text{Cl}_2$ Two-dimensional layers	Đurovič (1968)
α - $\text{Hg}_3\text{S}_2\text{Br}_2$ <i>C2/m</i> 0.0535	17.996 9.281 10.289 116.4 (β)	1542.7; 8 - 7.110	2.384-2.416 162.4-176.5 95.8-98.5	- Distorted β - $\text{Hg}_3\text{S}_2\text{Cl}_2$ Isolated cubes X_8Hg_{12}	Voroshilov <i>et al.</i> (1996a)
β - $\text{Hg}_3\text{S}_2\text{Br}_2$ <i>C2/m</i> 0.05	17.223 9.374 9.473 89.78 (β)	1533.8; 8 - 7.13	2.24-2.69 137.8-174.5 84.4-109.3	- β - $\text{Hg}_3\text{S}_2\text{Br}_2$ Two-dimensional layers	Voroshilov <i>et al.</i> (1996a)
$\text{Hg}_3\text{S}_2\text{I}_2$ <i>Imma</i> 0.0449	9.799 18.703 9.462	1734.2; 8 - 7.045	2.399-2.423 160.8-169.9 99.11-99.50	- $\text{Hg}_3\text{S}_2\text{I}_2$ Infinite crankshaft-type bands	Beck & Hedderich (2000)
$\text{Hg}_3\text{Se}_2\text{I}_2$ <i>Imma</i> 0.0518	9.766 19.381 9.633	1823.3; 8 - 7.384	2.501-2.522 161.58-171.8 96.53-97.39	- $\text{Hg}_3\text{S}_2\text{I}_2$ Infinite crankshaft-type bands	Beck & Hedderich (2000)
$\text{Hg}_3\text{Te}_2\text{I}_2$ <i>C2/c</i> 0.076	14.22 9.70 14.34	1947.3; 8 - -	2.648-2.702 155.23-180 89.8-97.6	- $\text{Hg}_3\text{Te}_2\text{I}_2$ Three-dimensional framework	Lyakhovitskaya <i>et al.</i> (1989)
$\text{Hg}_3\text{S}_2\text{Cl}_{1.5}\text{Br}_{0.5}$ <i>C2</i> 0.089	16.852 9.136 9.457 90.09 (β)	1456.0; 8 - 6.925	2.21-2.54 154.7-177.6 91.1-102.0	- β - $\text{Hg}_3\text{S}_2\text{Br}_2$ Two-dimensional layers	Borisov <i>et al.</i> (1999)
$\text{Hg}_3\text{S}_2\text{Cl}_{1.5}\text{Br}_{0.5}$ <i>Pm3n</i> 0.044	18.006	5837.8; 32 - 6.909	2.329-2.450 163.8-178.8 93.3-100.1	- β - $\text{Hg}_3\text{S}_2\text{Cl}_2$ Isolated cubes X_8Hg_{12}	Borisov <i>et al.</i> (1999)
$\text{Hg}_3\text{S}_2\text{ClI}$ <i>C2/m</i> 0.0527	16.827 9.117 13.165 130.17 (β)	1543.2; 8 - 7.130	2.240-2.474 146.1-180.0 95.4-102.9	Synthetic analogue of radtkeite - Two-dimensional layers	Pervukhina <i>et al.</i> (2004)
$\text{Hg}_3\text{S}_2\text{Br}_{1.0}\text{Cl}_{0.5}\text{I}_{0.5}$ <i>Pbmm</i> 0.0363	13.249 13.259 8.7102	1530.1; 8 - 7.180	2.358-2.459 140.9-172.9 95.9-104.9	A polymorph of $\text{Hg}_3\text{S}_2\text{Br}_{1.0}\text{Cl}_{0.5}\text{I}_{0.5}$ - Infinite crankshaft-type bands	this work

$\text{Hg}_3\text{Se}_2\text{I}_2$ (Beck & Hedderich 2000). In the structure of the synthetic phase $\text{Hg}_3\text{S}_2(\text{Br}_{1.0}\text{Cl}_{0.5}\text{I}_{0.5})_{\Sigma 2}$, there are the similar crankshaft-type bands, but they are packed differently. In $\text{Hg}_3\text{S}_2\text{I}_2$, the bands are translationally equivalent (Fig. 4b), whereas in $\text{Hg}_3\text{S}_2(\text{Br}_{1.0}\text{Cl}_{0.5}\text{I}_{0.5})_{\Sigma 2}$, they are connected *via* the 2₁ axis (Fig. 4c). Note that the radical revealed as the band of the square X_4Hg_4 rings of the other form [the + - + - type, by analogy with the classification of Aurivillius (1965)] was found

in the crystal structure of mercury chromate sulfide, the mineral edoyleite (Fig. 4d) (Burns 1999).

A layered form of the Hg-X radical, present as a corrugated $[\text{X}_4\text{Hg}_6]_{\Sigma\Sigma}$ layer, occurs in the structures of γ - $\text{Hg}_3\text{S}_2\text{Cl}_2$ (Đurovič 1968), β - $\text{Hg}_3\text{S}_2\text{Br}_2$ (Voroshilov *et al.* 1996a), $\text{Hg}_3\text{Se}_2\text{Br}_2$ (Voroshilov *et al.* 1995), possibly in the mineral kenhsuite (McCormack & Dickson 1998), and the synthetic monoclinic $\text{Hg}_3\text{S}_2\text{Cl}_{1.5}\text{Br}_{0.5}$ (Borisov *et al.* 1999) (Fig. 4e). In the layer, five-sixths of the Hg-S bonds form the closed $[\text{Hg}_4\text{S}_4]$ rings of two

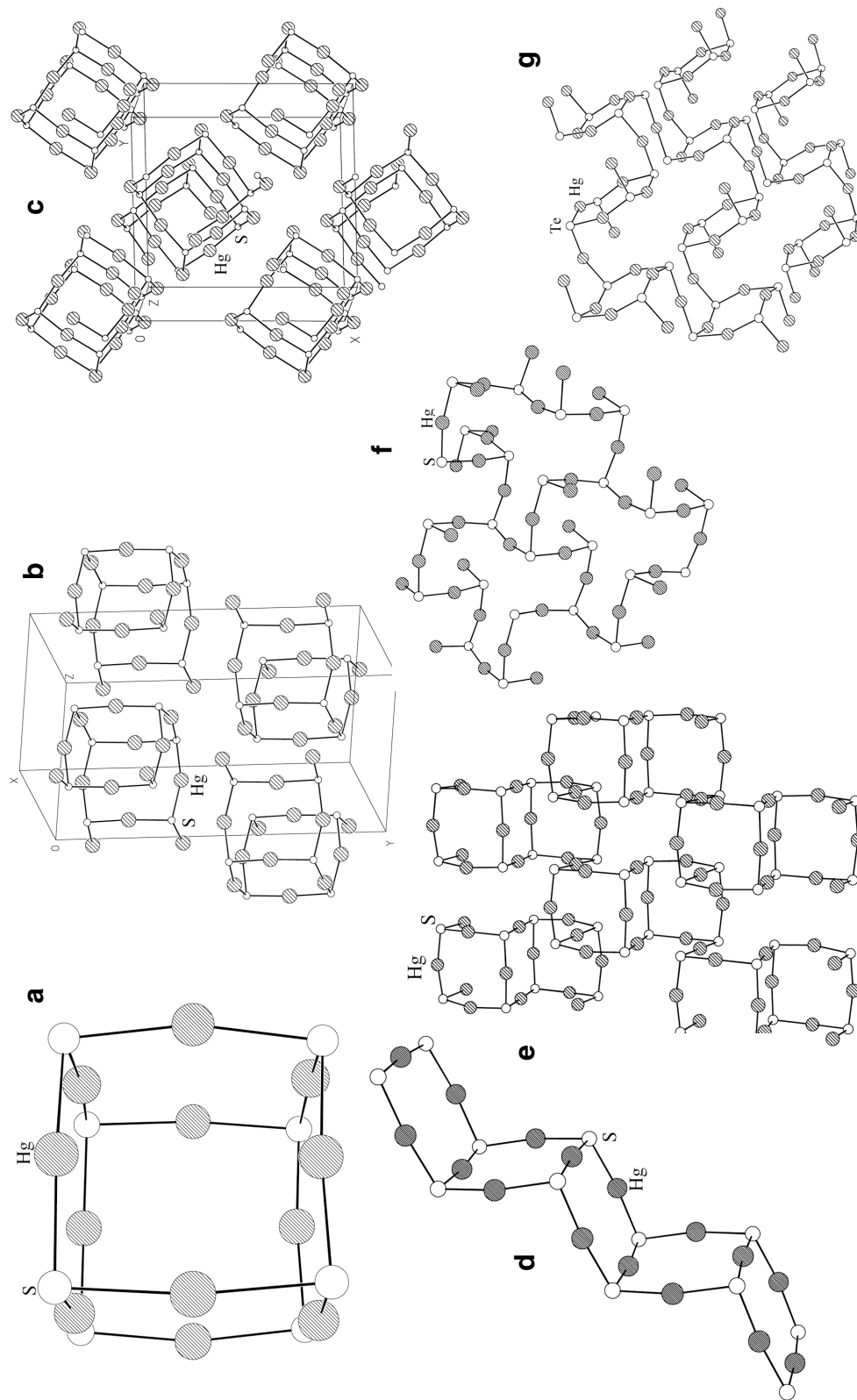


FIG. 4. The types of Hg-X radicals in the structures of $Hg_3X_2Hal_2$ (X = S, Se, Te; Hal = Cl, Br; D): a) the isolated $[X_8Hg_{12}]$ cube; b) the packing of the crankshaft-type $[Hg_3X_2]^{2+}$ bands in the structure of $Hg_3S_2L_2$; c) the packing of the crankshaft-type $[Hg_3X_2]^{2+}$ bands in the structure of $Hg_3S_2(Br_{10}Cl_{0.5}I_{0.5})_2$; d) the crankshaft-type Hg-S band in the structure of eddylerite; $Hg_3S_2CrO_4$; e) the layered form of the Hg-X radical in corderoite; f) the three-dimensional form of the Hg-X radical; g) the three-dimensional form of the Hg-Te radical in $Hg_3Te_2I_2$.

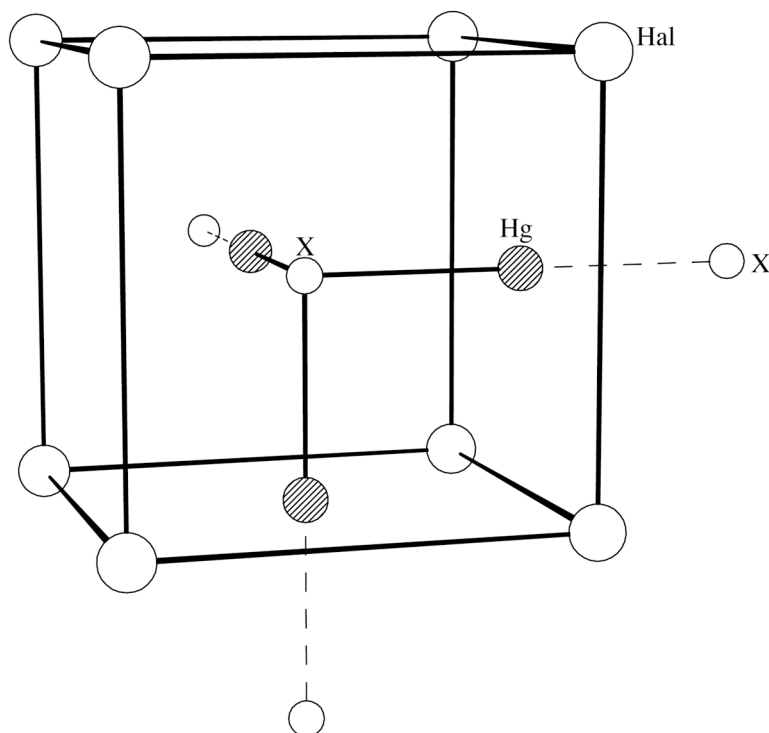


FIG. 5. The pseudocubic block module of the halogen sublattice of idealized form (Borisov *et al.* 2001).

orientations, and one-sixth combines the rings *via* the Hg–S–Hg bridges to form the layer.

A framework form of the mercury–sulfur radical is observed in corderoite (Aurivillius 1967, Frueh & Gray 1968). It is classed among the cubic structures, with the non-intersecting axes of threefold symmetry. In the three-dimensional complex construction $[X_2Hg_3]_{\Sigma\Sigma}$, the sulfur–mercury bonds are distributed in such a way that no closed rings form in the structure (Fig. 4f).

A crystal-chemical analysis of the $Hg_3Te_2I_2$ structure (Lyakhovitskaya *et al.* 1989) showed the presence of a rather complicated three-dimensional framework of Hg–Te bonds (Fig. 4g). The fundamental difference between the $Hg_3Te_2I_2$ structure and the others is that its eight-member $[Te_4Hg_4]$ rings have no shared “edges” with the neighboring rings, as in the band and layered radicals. Four Te–Hg–Te bonds bridge the ring to four other rings on different levels.

CONCLUSIONS

There are four halogen positions in the structure of synthetic $Hg^{2+}_3S_2Br_{1.0}Cl_{0.5}I_{0.5}$. Two of them are occu-

ried by Br, whereas two others are occupied by Cl and I. Thus, the halogen ions are perfectly ordered in the structure. However, experiments show that in synthetic compounds and most likely in minerals as well, the Cl : Br : I proportions may change, with statistical occupancies of halogen positions. It is apparent, that this does not change the integrity of the structure and unit-cell parameters in an essential way. The crystal-chemical role of these ions is to compensate the positive charge of relatively rigid Hg–S units.

As for structural peculiarities of the mercury chalcogenide halides, we can suppose that a large number of polymorphic variations results from the large variety of arrangements of the Hg–X radical forming the firmly bonded part of the structure. The structures of the $Hg_3X_2Hal_2$ are built of “cubic” module units (Borisov *et al.* 2001), with Hal atoms lying at the vertices, X atoms lying at the center, and Hg atoms centering three faces converging at a common vertex (Fig. 5). The cubic module has bonds issuing from the three faces and extending to the centers of the neighboring modules; the neighbors may have a common face in four possible orientations, differing in 90° rotation around the X–

Hg–X' bond. Further assemblage by this algorithm yields various corrugated ribbon, layered, and three-dimensional motifs.

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