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CRYSTAL CHEMISTRY OF MERCURY SULFOHALIDES OF COMPOSITION $Hg_3S_2\textit{Hal}_2$ (*Hal*: Cl, Br). I. CRYSTAL STRUCTURES OF TWO POLYMORPHIC MODIFICATIONS OF $Hg_3S_2Cl_{2-x}Br_x$ ($x \approx 0.5$)

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Abstract

Two polymorphic modifications of $Hg_3S_2Cl_{2-x}Br_x$ ($x \approx 0.5$), have been prepared in attempts to synthesize lavrentievite, $Hg_3S_2(Cl,Br)_2$ ($Cl \geq Br$), a rare supergene sulfohalide of mercury. The growth of single crystals from a gaseous phase was carried out at 540°C in an evacuated silica ampoule filled with a mixture of HgS (cinnabar), $HgCl_2$ and $HgBr_2$. We obtained bright yellow crystals of two phases, monoclinic (I) and cubic (II). The crystal structures of the two polymorphs, $Hg^{2+}{}_3S_2Cl_{1.5}Br_{0.5}$ (I) and $Hg^{2+}{}_3S_2Cl_{1.54}Br_{0.46}$ (II), have been determined by single-crystal X-ray-diffraction analysis. The structures were solved by direct methods and refined to an R of 0.0528 and 0.0282 using 1361 and 1026 unique observed reflections ($|F_o| > 4\sigma_F$) for compounds I and II, respectively. Compound I is monoclinic, $C2/m$, a 16.841(2), b 9.128(2), c 9.435(4) Å, β 90.08(1)°, V 1450.3(7) Å^3, $Z = 8$. Compound II is cubic, $Pm\bar{3}n$, a 18.0409(2) Å, V 5871.84(11) Å^3, $Z = 32$. The Hg atoms are covalently bonded to two S atoms at 2.372(2)–2.484(2) Å [$\angle$S–Hg–S 158.42(7)–180.0(0)°] and 2.386(3)–2.410(3) Å [$\angle$S–Hg–S 166.0(2)–176.1(2)°] for compounds I and II, respectively. Each S atom is bonded to three Hg atoms to form the SHg_3 trigonal pyramids with the Hg–S–Hg angles of 93.06(8)–96.21(7)° and 95.4(1)–96.6(2)° for I and II, respectively. In compound I, the SHg_3 fragments share the Hg vertices to form corrugated $[Hg_6S_4]_{\infty\infty}$ layers. Within the layer, five of the six short Hg–S bonds form closed $[Hg_4S_4]$ rings of two orientations, whereas the sixth Hg–S bond joins these rings together *via* the Hg–S–Hg bridges into a two-dimensional system. The halogen atoms are located within and in between the $[Hg_6X_4]_{\infty\infty}$ layers. In compound II, the SHg_3 fragments share the Hg vertices to form isolated sulfur cubes with edges centered by the Hg atoms. The halogen ions are located both within and in between the $[Hg_{12}S_8]$ cubes. Taking into account the halogen ions, the Hg atoms are in distorted octahedral coordination to anions.

Keywords: mercury sulfohalide, chlorine dominance, crystal structure, polymorphism, lavrentievite, Arzak mercury deposit, Tuva, Kadyrel mercury deposit, Russia.

Sommaire

Nous avons synthétisé deux polymorphes de la composition $Hg_3S_2Cl_{2-x}Br_x$ ($x \approx 0.5$), dans le contexte de nos essais de synthèse de la lavrentièvite, $Hg_3S_2(Cl,Br)_2$ ($Cl \geq Br$), rare sulfohalogénure de mercure supergène. La croissance de monocristaux à partir de la phase gazeuse a été effectuée par transfert dans une phase gazeuse à 540°C dans une ampoule de silice évacuée contenant un mélange de HgS (cinnabre), $HgCl_2$ et $HgBr_2$. Nous avons obtenu des cristaux jaune brillant de deux phases, l'une monoclinique (I), l'autre cubique (II). Nous avons déterminé la structure cristalline de ces deux polymorphes, de composition $Hg^{2+}{}_3S_2Cl_{1.5}Br_{0.5}$ (I) et $Hg^{2+}{}_3S_2Cl_{1.54}Br_{0.46}$ (II), par diffraction X sur monocristaux. Les structures ont été résolues par méthodes directes et affinées jusqu'à un résidu R de 0.0528 et 0.0282 en utilisant 1361 et 1026 réflexions uniques observées ($|F_o| > 4\sigma_F$) pour les composés I et II, respectivement. Le composé I est monoclinique, $C2/m$, a 16.841(2), b 9.128(2), c 9.435(4) Å, β 90.08(1)°, V 1450.3(7) Å^3, $Z = 8$. Le composé II est cubique, $Pm\bar{3}n$, a 18.0409(2) Å, V 5871.84(11) Å^3, $Z = 32$. Les atomes de

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Hg sont liés de façon covalente à deux atomes de S [2.372(2)–2.484(2) Å, ∠S–Hg–S 158.42(7)–180.0(0)°, et 2.386(3)–2.410(3) Å, ∠S–Hg–S 166.0(2)–176.1(2)°] dans les composés I et II, respectivement. Chaque atome de S est lié à trois atomes de Hg pour former des pyramides trigonales SHg_3, les angles Hg–S–Hg étant 93.06(8)–96.21(7)° et 95.4(1)–96.6(2)° pour I et II, respectivement. Dans le composé I, les fragments SHg_3 partagent leurs coins Hg pour former des couches ondulantes $[Hg_6S_4]_{\infty\infty}$. Dans cette couche, cinq des six liaisons courtes Hg–S définissent des anneaux fermés $[Hg_4S_4]$ en deux orientations, tandis que la sixième liaison Hg–S raccorde ces anneaux l'un à l'autre *via* les ponts Hg–S–Hg dans un système en deux dimensions. Les atomes halogènes sont situés à l'intérieur et entre les couches $[Hg_6X_4]_{\infty\infty}$. Dans le composé II, les fragments SHg_3 partagent les coins Hg pour former des cubes isolés de soufre ayant des atomes de Hg au centre de chaque arête. Les ions halogènes sont situés à l'intérieur et entre les cubes $[Hg_{12}S_8]$. Compte tenu des ions halogènes, les atomes Hg sont en coordinence octaédrique difforme avec les anions.

(Traduit par la Rédaction)

Mots-clés: sulfohalogénure de mercure, dominance de chlore, structure cristalline, polymorphisme, lavrentièvite, gisement de mercure de Arzak, Tuva, gisement de mercure de Kadyrel, Russie.

INTRODUCTION

Arzakite, $Hg_3S_2(Br,Cl)_2$, and lavrentievite, $Hg_3S_2(Cl,Br)_2$, are rare mercury sulfohalides with closely related chemical compositions, discovered as a result of mineralogical studies of oxidized cinnabar-bearing ores of the Arzak and Kadyrel mineral deposits, Russia (Vasil'ev *et al.* 1984, 1986). These minerals belong to zones of supergene oxidation of Hg deposits and thus have a secondary origin. As for other natural mercury sulfohalides, the Hg:S:*Hal* proportion (*Hal*: Cl, Br, I) is 3:2:2, and the ratio of Cl and Br is variable. Lavrentievite and arzakite have similar physical and optical properties, and differ in the Cl:Br ratio only. Vasil'ev *et al.* (1984, 1986) assumed that these minerals are members of the $Hg_3S_2Cl_2$ – $Hg_3S_2Br_2$ solid-solution series and are separated by a hypothetical mineral Hg_3S_2ClBr. According to the IMA convention, all Br-dominant members of the $Hg_3S_2Cl_2$ – $Hg_3S_2Br_2$ solid solution are referred as arzakite, whereas Cl-dominant members are considered as lavrentievite.

It should be noted that mercury sulfohalides are rare in nature. Usually, the occurrence of the relevant mineral species is controlled by a dominant halogen in the composition, *e.g.*, corderoite, α-$Hg_3S_2Cl_2$ (Foord *et al.* 1974), kenhsuite, γ-$Hg_3S_2Cl_2$ (McCormack & Dickson 1998), lavrentievite, $Hg_3S_2(Cl,Br)_2$ and arzakite, $Hg_3S_2(Br,Cl)_2$ (Vasil'ev *et al.* 1984, 1986), radtkeite, Hg_3S_2ClI (McCormack *et al.* 1991), and grechishchevite, $Hg_3S_2(Br,Cl,I)_2$ (Vasil'ev *et al.* 1989). As a rule, these minerals are associated with other mercury compounds of similar origin.

The precise determination of the crystal structure of Hg minerals is usually very difficult because of the poor quality of natural samples. However, in some cases, the structure model can be obtained from a study of synthetic single crystals. This work is the first of two papers that report results of X-ray single-crystal structure studies of mercury sulfohalides with the general composition $Hg_3S_2Hal_2$ (*Hal*: Cl, Br). Here, we present structures of two synthetic sulfohalides prepared in attempts to obtain single crystals of lavrentievite, $Hg_3S_2(Cl,Br)_2$.

BACKGROUND INFORMATION

The structures of cubic corderoite, α-$Hg_3S_2Cl_2$ (Puff & Küster 1962a, Aurivillius 1967, Frueh & Gray 1968), and radtkeite, $Hg_3S_2Cl_{1.0}I_{1.0}$ (Pervukhina *et al.* 2004), were determined on synthetic crystals. In attempts to synthesize tetragonal grechishchevite, $Hg_3S_2Br_{1.0}Cl_{0.5}I_{0.5}$, single crystals of its polymorph were obtained, and the structure was determined (Pervukhina *et al.* 2003). Judging from the unit-cell parameters, the structure of kenhsuite, γ-$Hg_3S_2Cl_2$ (McCormack & Dickson 1998), seems to be identical to that of the synthetic metastable phase γ-$Hg_3S_2Cl_2$ (Ďurovič 1968).

Lavrentievite, $Hg_3S_2(Cl,Br)_2$, and arzakite, $Hg_3S_2(Br,Cl)_2$, occur in contact with disintegrated primary cinnabar, corderoite (slightly admixed with Br), and grechishchevite. Calomel with a large amount of bromine, eglestonite, kuzminite, and kadyrelite were found in association with lavrentievite and arzakite. In nature, the end members, $Hg_3S_2Cl_2$ and $Hg_3S_2Br_2$, have not been found, although their synthetic polymorphs are known (Voroshilov *et al.* 1996a, b).

Vasil'ev *et al.* (1984) proposed two possible unit-cell parameters for lavrentievite on the basis of its X-ray powder-diffraction patterns (XPRD): (i) monoclinic, *a* 8.94(2), *b* 5.194(7), *c* 18.33(4) Å, β 92.44(8)°, *V* 850.3 Å^3, possible space groups *P*2/*m*, *P*2 and *Pm*, and (ii) triclinic, *a* 8.90(1), *b* 5.207(6), *c* 18.34(3) Å, α 89.67(7)°, β 88.88(7)°, γ 92.28(9)°, *V* 849.2 Å^3, possible space groups *P*1 or $P\bar{1}$. No symmetry, space group or unit-cell parameters were determined, since single crystals suitable for X-ray analysis were unavailable.

According to Puff & Küster (1962a), Puff *et al.* (1966), and Voroshilov *et al.* (1996a), in the system Hg – S – Cl, there is one ternary compound, $Hg_3S_2Cl_2$, possessing three polymorphs: low-temperature α, high-temperature β, and γ modifications. The latter results from chemical transport reactions and is metastable. The low-temperature α modification has a cubic symmetry and is known in nature as corderoite (Aurivillius 1967, Frueh & Gray, 1968). The high-temperature β phase is not known as a mineral. It crystallizes in the cubic system with the doubled lattice-parameter compared to the α modification. Its crystal structure was first determined for a synthetic specimen (Voroshilov *et al.* 1996a). The γ phase belongs to the class of the order–disorder type structures (Ďurovič 1968) and has as its natural analogue, the mineral kenhsuite (McCormack & Dickson 1998).

According to Puff *et al.* (1966), the system Hg – S – Br contains one ternary compound, $Hg_3S_2Br_2$, also having three polymorphic modifications, α, β and γ, whose structures have not been studied. Voroshilov *et al.* (1996b) have investigated two monoclinic polymorphs of $Hg_3S_2Br_2$, low-temperature and high-temperature phases. An X-ray-diffraction study of these compounds demonstrated that the crystal structure of α-$Hg_3S_2Br_2$ is a distorted version of the β-$Hg_3S_2Cl_2$ structure (Voroshilov *et al.* 1996a), whereas the β-$Hg_3S_2Br_2$ structure, determined by X-ray powder diffraction, is the same as that of $Hg_3Se_2Br_2$ (Puff & Küster 1962b, Minets *et al.* 2004) (the structure model agrees well with that determined by Ďurovič (1968) for γ-$Hg_3S_2Cl_2$).

EXPERIMENTAL

Synthesis

In order to prepare a synthetic analogue of lavrentievite, the pyrosynthesis method (a two-region electric furnace, with a temperature gradient of 1–3°C/cm) was used. The growth of single crystals from a gaseous phase was carried out in an evacuated silica ampoule filled with a mixture of HgS (cinnabar), $HgCl_2$ and $HgBr_2$. The reagents were taken in amounts to provide a stoichiometry of the suggested compound, $Hg_3S_2Cl_{1.5}Br_{0.5}$, which is close to the average composition of lavrentievite from the Arzak deposit (Vasil'ev *et al.* 1984). The ampoule with the mixture was heated to 540°C and was held for 96 h to sublimate the substance in the lower-temperature section of the furnace. At the end of the experiment, the temperature of the furnace was lowered to room temperature in the cut-off regime. Bright, light yellow single crystals of two phases, monoclinic (I) and cubic (II), were obtained. The crystals of the first phase are elongate pseudohexagonal plates with a perfect cleavage parallel to {001}. The second phase forms a well-shaped, almost isometric crystals with no cleavage. The calculated formulas of the two phases, based on results of the electron-microprobe analyses, are nearly identical: $Hg_{2.99}S_{2.06}Cl_{1.41}Br_{0.50}$ for phase I and $Hg_3S_{1.96}Cl_{1.55}Br_{0.46}$ for phase II.

TABLE 1. CRYSTAL DATA FOR COMPOUNDS I AND II

	I	II		I	II
a (Å)	16.841(2)	18.0409(2)	D_{calc} (g/cm^3)	6.952	6.851
b (Å)	9.128(2)		μ (mm^{-1})	67.12	66.084
c (Å)	9.435(4)		Unique reflections	2717	1026
β (°)	90.08(1)				
V (Å^3)	1450.3(7)	5871.84(11)	Unique $F_o > 4\sigma_F$	1008	667
Space group	$C2/m$	$Pm\bar{3}n$			
Z	8	32	Final R ($F_o > 4\sigma_F$)	0.0528	0.0282

$R = \Sigma (|F_o| - |F_c|) / \Sigma|F_o|$

Single-crystal analysis of the structure

Unit-cell parameters were refined and X-ray crystal data were obtained for both phases by a standard procedure [an Enraf–Nonius CAD–4 automated diffractometer, graphite monochromator, λ Mo*K*α, θ–2θ scan with a variable rate, crystal size 0.11 × 0.07 × 0.06 mm (I), and on a single- crystal Bruker Nonius X8 Apex diffractometer equipped with a 4K CCD detector, crystal size 0.06 × 0.02 × 0.02 mm (II)]. All measured intensities were corrected for Lorentz and polarization effects. The structures were solved using the SIR97 package of programs (Altomare *et al.* 1999). The atom coordinates were refined by the full-matrix least-squares method in an anisotropic approximation using the SHELX97 program (Sheldrick 1998). Absorption corrections were applied using X-RED program package (X-RED 1999) and XPREP (Bruker 2004) (analytical method) according to the real shape of the crystal for I and II, respectively. Selected experimental data for compounds I and II are given in Table 1, the final coordinates and thermal parameters U_{eq} of the atoms are in Table 2, and selected bond-distances and angles are in Table 3. Tables of structure factors and anisotropic displacement factors are available from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2.

RESULTS

The structure of phase I contains five crystallographically independent Hg atoms, each being covalently bonded to two S atoms at 2.372(2)–2.484(2) Å [∠S–Hg–S 158.42(7)–180.0(0)°]. As in the structure of the synthetic analogue of radtkeite (Pervukhina *et al.* 2004), the S(2)–Hg(2)–S(2) and S(1') angles, 158.42(7), 168.47(11) and 166.7(1)°, respectively, considerably deviate from 180°, which is typical for Hg^{2+} compounds (Aurivillius 1965). Each S atom is bonded to three Hg atoms to form SHg_3 trigonal pyramids, with the Hg–S–Hg angles 93.06(8)–96.21(7)°. The SHg_3 fragments share Hg vertices to form corrugated $[Hg_6S_4]_{\infty\infty}$ layers (Fig. 1). Within the layer, five of the six short Hg–S bonds form closed $[Hg_4S_4]$ rings of two orientations, whereas the sixth Hg–S bond joins these rings together *via* the Hg–S–Hg bridges into a two-dimensional system. The corrugated $[Hg_6S_4]_{\infty\infty}$ layers in compound I are similar to those found in the structures of synthetic γ-$Hg_3S_2Cl_2$ (Ďurovič 1968), β-

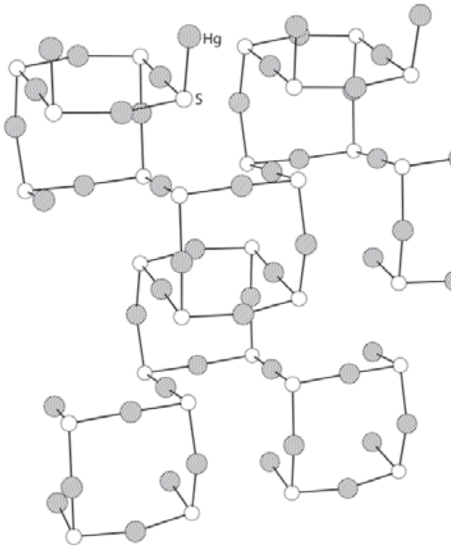

FIG. 1. The Hg–S two-dimensional layer in the unit cell of $Hg_3S_2Cl_{1.5}Br_{0.5}$ (phase I).

TABLE 2. ATOMIC PARAMETERS AND EQUIVALENT ISOTROPIC DISPLACEMENT PARAMETERS (Å²) FOR COMPOUNDS I AND II

Atom	*x*	*y*	*z*	U_{eq}*	Site-occupancy factor
			Compound I		
Hg(1)	0.5	-0.2412(1)	0.5	0.028(1)	1
Hg(2)	0.3749(1)	-0.2252(1)	0.7993(1)	0.023(1)	1
Hg(3)	0.2225(1)	-0.5	0.7699(1)	0.035(1)	1
Hg(4)	0.25	-0.25	0.5	0.029(1)	1
Hg(5)	0.5265(1)	-0.5	0.7774(1)	0.034(1)	1
S(1)	0.5147(1)	-0.2361(2)	0.7564(2)	0.026(1)	1
S(2)	0.2303(1)	-0.2403(2)	0.7487(2)	0.033(1)	1
Cl(1)	0.1315(2)	-0.5	1.0150(3)	0.032(1)	1
Cl(2)	0.6255(2)	-0.5	1.0161(3)	0.034(1)	1
Br(1)	0.3734(1)	0	0.5175(2)	0.042(1)	0.625(3)
Cl(3)	0.3734(1)	0	0.5175(2)	0.042(1)	0.375(3)
Br(2)	0.3736(1)	-0.5	0.5274(2)	0.035(1)	0.623(3)
Cl(4)	0.3736(1)	-0.5	0.5274(2)	0.035(1)	0.377(3)
			Compound II		
Hg(1)	0.25	0.3564(1)	0.1436(1)	0.038(1)	1
Hg(2)	0	0.1447(1)	0.1355(1)	0.034(1)	1
Hg(3)	0.1153(1)	0.5	0.1415(1)	0.035(1)	1
Hg(4)	0.1160(1)	0.3638(1)	0	0.035(1)	1
S(1)	0.1174(2)	0.3680(2)	0.1322(2)	0.027(1)	1
S(2)	0.1323(2)	0.1323(2)	0.1323(2)	0.029(2)	1
Br(1)	0	0	0	0.075(4)	1
Cl(1)	0	0.5	0	0.012(2)	1
Cl(2)	0	0.2450(3)	0	0.037(2)	0.72(2)
Br(2)	0	0.2450(3)	0	0.037(2)	0.28(2)
Cl(3)	0.25	0.5	0	0.032(2)	0.67(3)
Br(3)	0.25	0.5	0	0.032(2)	0.33(3)
Cl(4)	0	0.2486(2)	0.2570(2)	0.034(1)	0.70(1)
Br(4)	0	0.2486(2)	0.2570(2)	0.034(1)	0.30(1)
Cl(5)	0	0.5	0.25	0.019(2)	1
Cl(6)	0.25	0.25	0.25	0.023(1)	1

* $U_{eq} = ⅓ (U_{11} + U_{22} + U_{33})$.

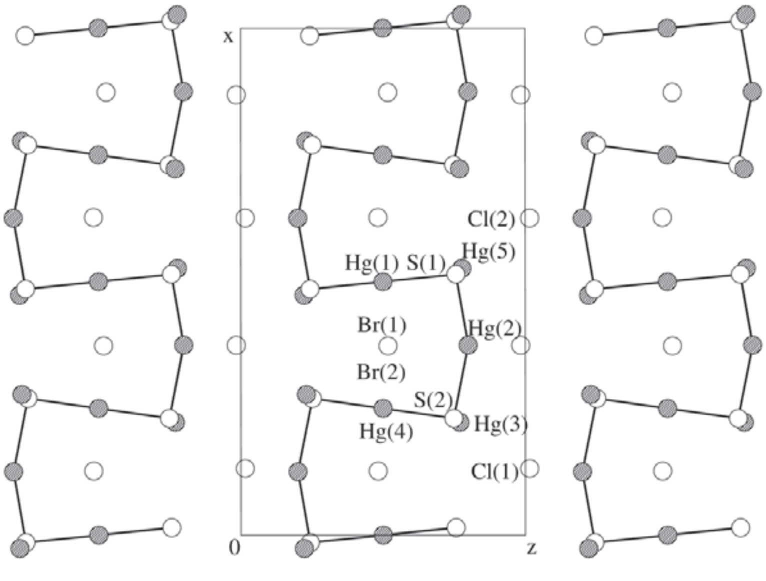

FIG. 2. Projection of the structure of $Hg_3S_2Cl_{1.5}Br_{0.5}$ (phase I) on the (010) plane.

$Hg_3S_2Br_2$ (Voroshilov *et al*. 1996b), $Hg_3Se_2Br_2$ (Minets *et al*. 2004), and the analogue of radtkeite, Hg_3S_2ClI (Pervukhina *et al*. 2004). The halogen atoms are located within and in between the $[Hg_6X_4]_{\infty\infty}$ layers (Fig. 2). The Hg(2)–Cl(1'), Hg(3)–Cl(1), Hg(5)–Cl(2) distances are 2.703(2), 2.777(3) and 2.801(3) Å, respectively. The remaining halogen positions in the structure are statistically occupied by Br and Cl atoms (Br > Cl), and the Hg – (Br, Cl) distances are equal to 3.070(1)–3.099(1) Å.

The structure of phase II contains four crystallographically independent Hg atoms bonded to two S atoms at 2.386(3)–2.410(3) Å [$\angle$SHgS 166.0(2)–176.1(2)°]. As in the structure of phase I, each S atom is bonded to three Hg atoms to form the SHg_3 trigonal pyramids with the HgSHg angles in the range of 95.4(1)–96.6(2)°. The SHg_3 fragments share the Hg vertices to form the isolated cubes of sulfur with edges shared by the Hg atoms (Fig. 3), and the halogen atoms are located both within and in between the $[Hg_{12}S_8]$ cubes (Fig. 4). The Cl(2), Cl(3), Cl(4) positions are statistically occupied by halogen atoms (Cl > Br); the Hg – (Cl, Br) distances are 2.884(4) – 3.448(9) Å. The remaining Hg–Cl and Hg–Br distances are 2.715(1)

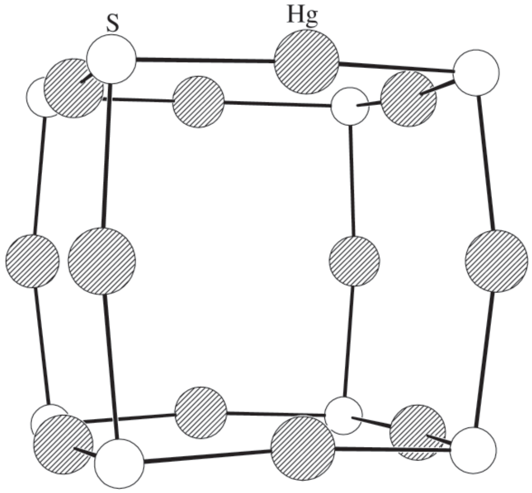

FIG. 3. The isolated $[X_8Hg_{12}]$ cube in $Hg_3S_2Cl_{1.5}Br_{0.5}$ (phase II).

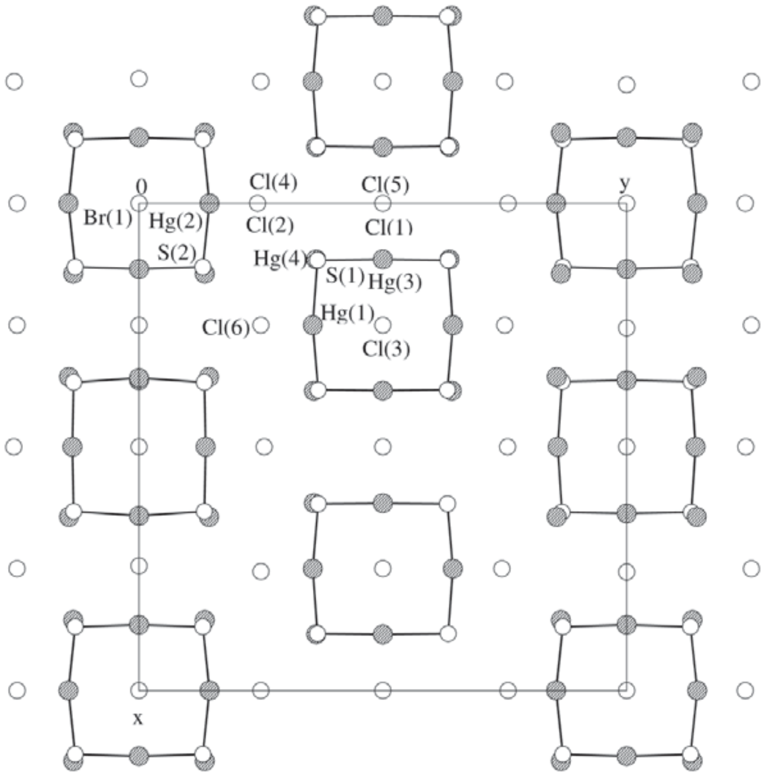

FIG. 4. Projection of the structure of $Hg_3S_2Cl_{1.5}Br_{0.5}$ (phase II) on the (001) plane.

– 3.228(1) and 3.576(1) Å, respectively. Compound II is isostructural with β-$Hg_3S_2Cl_2$ (Voroshilov *et al*. 1996a), with an enlarged *a* parameter due to the presence of the bromine atoms. The similar Hg–S radicals were found as isolated [$Hg_{12}S_8$] cubes in the structure of the monoclinic α-$Hg_3S_2Br_2$ (Voroshilov *et al*. 1996b). Taking into account the halogen atoms, the Hg atoms are in distorted octahedral environments as in the other mercury sulfohalides (Pervukhina *et al*. 2003) (Figs. 5, 6).

CONCLUSIONS

As Pervukhina *et al*. (2003) pointed out, in the structures of mercury chalcohalides $Hg_3X_2Hal_2$ (X = S, Se, Te; *Hal* = Cl, Br, I), large *Hal* anions pack together to form a high-symmetry primitive cubic arrangement. The halogen sublattice parameters are close to each other ($a' = a/4$ = 4.210, $b' = b/2$ = 4.564, $c' = c/2$ = 4.717 Å), whereas all the angles are *ca*. 90° in phase I, and $a' = b' = c' = a/4$ = 4.501 Å, with the angles equal to 90° in phase II, respectively. The sublattice is stabilized by participation of the large Hg^{2+} cations in the packing of halogen ions through ionic interactions with four *Hal* anions and owing to two covalent apical Hg–X bonds. Such a geometrical configuration seems to be highly stable, allowing for a wide variation in the halogen atoms, which are weakly bonded to the basic Hg–S moieties. The fact that two different polymorphs with

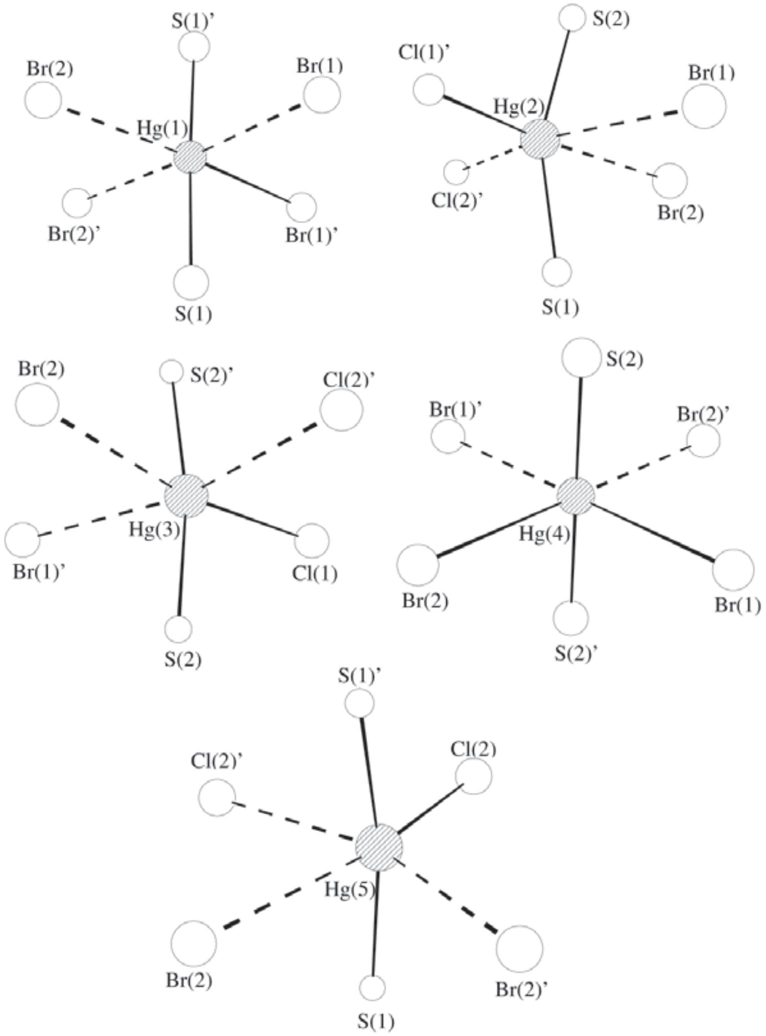

FIG. 5. The environments of the Hg^{2+} cations in $Hg_3S_2Cl_{1.5}Br_{0.5}$ (phase I).

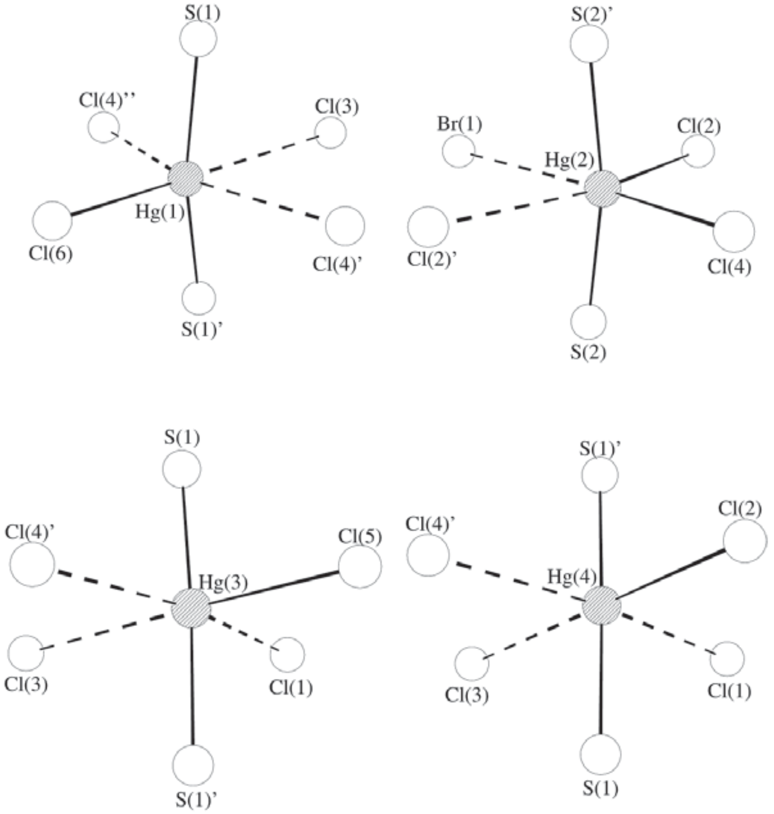

FIG. 6. The environments of the Hg^{2+} cations in $Hg_3S_2Cl_{1.54}Br_{0.46}$ (phase II).

different Hg–S units were obtained under identical conditions indicates that the role of the halide ions is to isolate Hg–S units one from the other. Thus both structures confirm the "modular" principle of formation suggested by Borisov *et al*. (2001).

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REFERENCES

ALTOMARE, A., BURLA, M. C., CAMALLI, M., CASCARANO, G.L., GIACOVAZZO, C., GUAGLIARDI, A., MOLITERNI, A.G.G., POLIDORI, G. & SPAGNA, R. (1999): SIR97: a new tool for crystal structure determination and refinement. *J. Appl. Crystallogr.* **32**, 115-119.

AURIVILLIUS, K. (1965): The structural chemistry of inorganic mercury(II) compounds. *Ark. Kemi* **24**, 151-187.

AURIVILLIUS, K. (1967): An X-ray single crystal study of $Hg_3S_2Cl_2$. *Ark. Kemi* **26**, 497-505.

BORISOV, S.V., MAGARILL, S.A. & PERVUKHINA, N.V. (2001): Module principle in structure formation studies of mercury oxo and halogen halides. *J. Struct. Chem.* **42**, 429-435.

ĎUROVIČ, S. (1968): The crystal structure of γ-$Hg_3S_2Cl_2$. *Acta Crystallogr.* **B24**, 1661-1670.

FOORD, E.E., BERENDSEN, P. & STOREY, L.O. (1974): Corderoite, first natural occurrence of α-$Hg_3S_2Cl_2$, from the Cordero mercury deposit, Humboldt County, Nevada. *Am. Mineral.* **59**, 652-655.

FRUEH, A.J. & GRAY, N. (1968): Confirmation and refinement of the structure of $Hg_3S_2Cl_2$. *Acta Crystallogr.* **B24**, 156-157.

MCCORMACK, J.K. & DICKSON, F.W. (1998): Kenhsuite, γ-$Hg_3S_2Cl_2$, a new mineral species from the McDermitt

TABLE 3. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) FOR COMPOUNDS I AND II

Compound I		Compound II	
Hg(1) – S(1)	2.431(2)	Hg(1) – S(1)	2.410(3)
Hg(1) – S(1) #1	2.431(2)	Hg(1) – S(1) #1	2.410(3)
Hg(2) – S(1)	2.391(2)	Hg(2) – S(2)	2.398(4)
Hg(2) – S(2)	2.484(2)	Hg(2) – S(2) #4	2.398(4)
Hg(3) – S(2)	2.383(2)	Hg(3) – S(1)	2.387(4)
Hg(3) – S(2) #4	2.383(2)	Hg(3) – S(1) #5	2.387(4)
Hg(4) – S(2)	2.372(2)	Hg(4) – S(1)	2.386(3)
Hg(4) – S(2) #5	2.372(2)	Hg(4) – S(1) #6	2.386(3)
Hg(5) – S(1)	2.425(2)	Hg(1) – Cl(6)	2.715(1)
Hg(5) – S(1) #4	2.425(2)	Hg(1) – Cl(4) #2	3.151(2)
Hg(1) – Br(1)	3.070(1)	Hg(1) – Cl(4) #3	3.151(2)
Hg(1) – Br(1) #2	3.070(1)	Hg(1) – Cl(3)	3.663(1)
Hg(1) – Br(2)	3.190(1)	Hg(2) – Cl(4)	2.884(4)
Hg(1) – Br(2) #1	3.190(1)	Hg(2) – Cl(2)	3.041(4)
Hg(2) – Cl(1) #3	2.703(2)	Hg(2) – Br(1)	3.576(1)
Hg(2) – Cl(2) #4	3.053(2)	Hg(2) – Cl(2) #7	3.274(4)
Hg(2) – Br(1)	3.361(2)	Hg(3) – Cl(1)	3.294(1)
Hg(2) – Br(2)	3.588(2)	Hg(3) – Cl(5)	2.856(1)
Hg(3) – Cl(1)	2.777(3)	Hg(3) – Cl(4) #2	3.063(4)
Hg(3) – Cl(2) #4	3.258(3)	Hg(3) – Cl(3)	3.525(1)
Hg(3) – Cl(3) #6	3.153(2)	Hg(4) – Cl(1)	3.228(1)
Hg(3) – Br(2)	3.425(2)	Hg(4) – Cl(2)	2.995(5)
Hg(4) – Br(1)	3.091(1)	Hg(4) – Cl(3)	3.448(1)
Hg(4) – Br(1) #5	3.091(1)	Hg(4) – Cl(4) #3	3.071(3)
Hg(4) – Br(2)	3.099(1)		
Hg(4) – Br(2) #5	3.099(1)		
Hg(5) – Cl(2)	2.801(3)		
Hg(5) – Cl(2) #4	3.218(3)		
Hg(5) – Br(2) #7	3.334(2)		
Hg(5) – Br(2)	3.489(2)		
S(1) – Hg(1) – S(1)#1	177.8(1)	S(1) – Hg(1) – S(1)#1	166.0(2)
S(1) – Hg(2) – S(2)	158.42(7)	S(2) – Hg(2) – S(2)#4	168.9(3)
S(2) – Hg(3) – S(2)#4	168.5(1)	S(1) – Hg(3) – S(1)#5	171.7(2)
S(2) – Hg(4) – S(2)#5	180.0(0)	S(1) – Hg(4) – S(1)#6	176.1(2)
S(1) – Hg(5) – S(1)#4	166.7(1)	Hg(1) – S(1) – Hg(4)	95.4(1)
Hg(2) – S(1) – Hg(5)	96.21(7)	Hg(4) – S(1) – Hg(3)	95.9(1)
Hg(1) – S(1) – Hg(2)	94.06(7)	Hg(1) – S(1) – Hg(3)	95.5(1)
Hg(1) – S(1) – Hg(5)	94.05(7)	Hg(2) – S(2) – Hg(2)#7	96.6(2)
Hg(3) – S(2) – Hg(4)	93.06(8)	Hg(2)#7 – S(2) – Hg(2)#3	96.6(2)
Hg(2) – S(2) – Hg(4)	93.09(7)	Hg(2) – S(2) – Hg(2)#3	96.6(2)
Hg(2) – S(2) – Hg(3)	95.36(8)		

Compound I: #1 –x + 1, y, –z + 1; #2 –x + 1, –y, –z + 1; #3 –x + ½, –y – ½, –z + 2; #4 x, –y – 1, z; #5 –x + ½, –y – ½, –z + 1.
Compound II: #1 –x + ½, –z + ½, –y + ½; #2 –y + ½, x + ½, –z + ½; #3 y, z, x; #4 –x, y, z; #5 x, –y + 1, z; #6 x, y, –z; #7 z, x, y.

mercury deposit, Humboldt County, Nevada. *Can. Mineral.* **36**, 201-206.

McCormack, J.K., Dickson, F.W. & Leshendok, M.P. (1991): Radkeite, Hg_3S_2ClI, a new mineral from the McDermitt mercury deposit, Humboldt County, Nevada. *Am. Mineral.* **76**, 1715-1721.

Minets, Yu.V., Voroshilov, Yu.V., Pan'ko, V.V. & Khudolii, V.A. (2004): Phase equilibria in the HgSe–$HgBr_2$–HgI_2 system and crystal structure of $Hg_3Se_2Br_2$ and $Hg_3Se_2I_2$. *J. Alloys Compounds* **365**, 121-125.

Pervukhina, N.V., Vasil'ev, V.I., Borisov, S.V., Magarill, S.A. & Naumov, D.Yu. (2003): The crystal structure of a polymorph of $Hg^{2+}{}_3S_2Br_{1.0}Cl_{0.5}I_{0.5}$. *Can. Mineral.* **41**, 1445-1453.

Pervukhina, N.V., Vasil'ev, V.I., Naumov, D.Yu., Borisov, S.V. & Magarill, S.A. (2004): The crystal structure of synthetic radtkeite, Hg_3S_2ClI. *Can. Mineral.* **42**, 87-94.

Puff, H., Harpain, A. & Hoop, K.-P. (1966): Polymorphie bei Quecksilberschwefel-halogeniden. *Naturwiss.* **53**(11), 274.

Puff, H. & Küster, J. (1962a): Die Kristallstruktur von $Hg_3S_2Cl_2$. *Naturwiss.* **49**, 299-300.

Puff, H. & Küster, J. (1962b): Die Kristallstruktur der kubischen Triquecksilber-dichalkonium-dihalogenide. *Naturwiss.* **49**, 464-465.

Sheldrick, G.M. (1998): SHELX97, Release 97–2. Program for the Refinement of Crystal Structures. Univ. of Göttingen, Göttingen, Germany.

Vasil'ev, V.I., Lavrent'ev, Yu.G. & Pal'chik, N.A. (1986): The new data about arzakite and lavrentievite. *Dokl. Akad. Nauk USSR* **290**, 948-951.

Vasil'ev, V.I., Pal'chik, N.A. & Grechishchev, O.K. (1984): Lavrentievite and arzakite, new natural mercury sulfohalides. *Sov. Geol. Geophys.* **25**(7), 49-56.

Vasil'ev, V.I., Usova, L.V. & Pal'chik, N.A. (1989): Grechischevite – $Hg_3S_2(Br,Cl,I)_2$. A new supergene sulfohalides of mercury. *Sov. Geol. Geophys.* **7**, 61-68.

Voroshilov, Yu.V., Hudoliy, V.O. & Panyko, V.V. (1996a): Phase equilibria in the HgS–HgTe–$HgCl_2$ and crystal structure of β-$Hg_3S_2Cl_2$ and Hg_3TeCl_4. *Zh. Neorg. Khimii* **41**(2), 287-293.

Voroshilov, Yu.V., Hudoliy, V.O., Panyko, V.V. & Minets, Yu.V. (1996b): Phase equilibria in the HgS–HgTe–$HgBr_2$ and crystal structure of $Hg_3S_2Br_2$ and Hg_3TeBr. *Izv. Akad. Nauk, Neorg. Mater.* **32**, 1466-1472.

XPREP, Version 6.14 (2004): Bruker AXS Inc., Madison, Wisconsin, USA.

X-RED, Data Reduction Program (1999): STOE & Cie GmbH, Darmstadt, Germany.

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