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CRYSTAL CHEMISTRY OF MERCURY SULFOHALIDES OF COMPOSITION $Hg_3S_2Hal_2$ (Hal: Cl, Br). II. CRYSTAL STRUCTURES OF TWO POLYMORPHIC MODIFICATIONS OF $Hg_3S_2Br_{2-x}Cl_x$ ($x \approx 0.5$)

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ABSTRACT

Two polymorphic modifications of $Hg^{2+}{}_3S_2Br_{1.5}Cl_{0.5}$ (I, II) have been prepared in attempts to obtain a synthetic analogue of arzakite, $Hg_3S_2(Br,Cl)_2$ (Br ≥ Cl), a rare supergene sulfohalide mineral of mercury. The structures of the two phases were solved by direct methods and refined to an R of 0.0513 and 0.0380 using 1539 and 1006 unique observed reflections ($|F_o| > 4\sigma_F$) for compounds I and II, respectively. Compound I is monoclinic, space group $C2/m$, a 17.824(4), b 9.238(2), c 10.269(2) Å, β 115.69(1)°, V 1523.8(5) $Å^3$, Z = 8. Compound II is cubic, space group $Pm\bar{3}n$, a 18.248(2) Å, V 6076.4(1) $Å^3$, Z = 32. In both structures, the Hg atoms are covalently bonded to two S atoms each at 2.366(6)–2.430(5) Å [∠S–Hg–S 163.03(19)–176.3(2)°]. Each S atom is bonded to three mercury atoms to form SHg_3 trigonal pyramids with the Hg–S–Hg angles in the range 95.66(19)–97.60(20)°. In compounds I and II, the SHg_3 fragments share the Hg vertices to form isolated cubes with S atoms at the corner and Hg atoms in the middle of the edges. Halogen atoms are located both within and in between the $[Hg_{12}S_8]$ cubes. As in other mercury chalcohalide structures, the halogen atoms determine the structural architecture of the compounds, as they form the cubic sublattices that accommodate the Hg–S units. Taking into account the halogen atoms, the Hg atoms are in distorted octahedral coordination.

Keywords: mercury sulfohalide, bromine dominance, crystal structure, polymorphism, arzakite, Arzak mercury deposit, Tuva, Kadyrel mercury deposit, Russia.

SOMMAIRE

Nous avons préparé deux modifications polymorphiques de $Hg^{2+}{}_3S_2Br_{1.5}Cl_{0.5}$ (I, II) dans un travail visant la synthèse de l'arzakite, $Hg_3S_2(Br,Cl)_2$ (Br ≥ Cl), un sulfohalogénure rare supergène de mercure. Les structures de ces deux phases ont été résolues par méthodes directes, et affinées jusqu'à un résidu R de 0.0513 et 0.0380 en utilisant 1539 and 1006 réflexions uniques observées ($|F_o| > 4\sigma_F$) pour les composés I et II, respectivement. Le composé I est monoclinique, groupe d'espace $C2/m$, a 17.824(4), b 9.238(2), c 10.269(2) Å, β 115.69(1)°, V 1523.8(5) $Å^3$, Z = 8. Le composé II est cubique, groupe d'espace $Pm\bar{3}n$, a 18.248(2) Å, V 6076.4(1) $Å^3$, Z = 32. Dans les deux structures, les atomes de Hg sont liés de façon covalente à deux atomes de soufre chacun à 2.366(6)–2.430(5) Å [∠S–Hg–S 163.03(19)–176.3(2)°]. Chaque atome de soufre est lié à trois atomes de mercure pour former des pyramides trigonales SHg_3, avec les angles Hg–S–Hg entre 95.66(19) et 97.60(20)°. Dans les composés I et II, les fragments SHg_3 partagent leur coin Hg pour former des cubes isolés ayant les atomes de soufre aux coins et les atomes de Hg au centre des arêtes. Les atomes de halogènes sont situés à la fois à l'intérieur et entre les cubes $[Hg_{12}S_8]$. Tout comme c'est le cas dans la structure d'autres chalcohalogénures de mercure, les halogènes déterminent l'architecture structurale des composés, parce qu'ils forment la sous-maille cubique qui accommode les modules Hg–S. Compte tenu des atomes de halogènes, les atomes de Hg font preuve d'une coordinence octaédrique difforme.

(Traduit par la Rédaction)

Mots-clés: sulfohalogénure de mercure, dominance de brome, structure cristalline, polymorphisme, arzakite, gisement de mercure d'Arzak, Tuva, gisement de mercure de Kadyrel, Russie.

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INTRODUCTION

Arzakite, $Hg_3S_2(Br,Cl)_2$, is one of several known mercury sulfohalide minerals in the system $Hg_3S_2Cl_2 – Hg_3S_2Br_2 – Hg_3S_2I_2$. Other minerals are: lavrentievite, $Hg_3S_2(Cl,Br)_2$ (Vasil'ev *et al.* 1984, 1986), kenhsuite, γ-$Hg_3S_2Cl_2$ (McCormack & Dickson 1998), corderoite, α-$Hg_3S_2Cl_2$ (Puff & Küster 1962, Aurivillius 1967, Frueh & Gray 1968), radtkeite, $Hg_3S_2Cl_{1.0}I_{1.0}$ (McCormack *et al.* 1991, Pervukhina *et al.* 2004), and grechishchevite, $Hg_3S_2(Br,Cl,I)_2$ (Vasil'ev *et al.* 1989). From a mineralogical viewpoint, within the $Hg_3S_2Cl_2 – Hg_3S_2Br_2$ solid-solution series, all Br-dominant members are referred as arzakite, whereas Cl-dominant members are considered as lavrentievite.

In the first paper of the series (Pervukhina *et al.* 2006), we reported structures of two Cl-dominant compounds with the composition $Hg_3S_2Cl_{2–x}Br_x$ ($x \approx 0.5$), *i.e.*, compounds that are probably closely related (though not identical) to lavrentievite. The aim of this work is to report crystal structures of two novel polymorphic Br-dominant modifications, $Hg_3S_2Br_{2–x}Cl_x$ ($x \approx 0.5$), obtained in attemps to prepare a synthetic analogue of arzakite (Br > Cl).

EXPERIMENTAL

Powder-diffraction study

X-ray powder-diffraction (XRPD) patterns of arzakite can be indexed using two possible sets of unit-cell parameters: (i) monoclinic, *a* 8.99(4), *b* 5.24(1), *c* 18.45(8) Å, β 92.28(15)°, *V* 868.1 $Å^3$, possible space-groups *P*2/*m*, *P*2, or *Pm*; and (ii) triclinic, *a* 8.95(4), *b* 5.25(2), *c* 18.49(9) Å, α 89.57(24)°, β 88.74(24)°, γ 92.16(32)°, *V* 868.6 $Å^3$, possible space-groups *P*1 or $P\bar{1}$ (Vasil'ev *et al.* 1984, 1986). The calculated formulas of the both phases, based on results of the electron-microprobe analyses, are nearly identical: $Hg_{3.02}S_{2.04}Br_{1.49}Cl_{0.45}$ for I and $Hg_{3.00}S_{2.04}Br_{1.47}Cl_{0.48}$ for II.

TABLE 1. CRYSTAL DATA FOR COMPOUNDS I AND II

	I	II		I	II
a (Å)	17.824(4)	18.248(2)	D_{calc} (g/cm^3)	7.005	7.026
b (Å)	9.238(2)		μ (mm^{-1})	68.778	68.990
c (Å)	10.269(2)		Unique reflections	1538	1006
β (°)	115.69(1)				
V (Å^3)	1523.8(5)	6076.4(1)	Unique $F_o > 4\sigma_F$	1114	478
Space group	*C*2/*m*	$Pm\bar{3}n$			
Z	8	32	Final *R* ($F_o > 4\sigma_F$)	0.0513	0.0380

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

Synthesis

The synthesis of arzakite was performed by crystal growth from a gaseous phase (pyrosynthesis) in an evacuated silica ampoule. A mixture of HgS, $HgBr_2$, and $HgCl_2$ corresponding to the $Hg_3S_2Br_{1.5}Cl_{0.5}$ stoichiometry was used. This composition is close to the average composition of arzakite from the Arzak mineral deposit (Vasil'ev *et al.* 1984, 1986). The synthesis resulted in sparkling dark yellow single crystals of two polymorphs, monoclinic (I) and cubic (II), which were studied by single-crystal diffraction.

Single-crystal analysis of the structures

The unit-cell parameters were refined and X-ray-diffraction data were obtained for monoclinic (crystal size 0.10 × 0.08 × 0.07 mm) (I) and cubic (crystal size 0.20 × 0.20 × 0.20 mm) (II) phases using single-crystal Bruker Nonius X8 APEX diffractometer equipped with a 4K CCD detector. Diffraction data were collected by a standard technique at 293 K (Mo*K*α radiation, graphite monochromator). Absorption corrections were applied using XPREP (Bruker 2004) (analytical method) according to the real shape of the crystals of phases I and II. The structures were solved using the SIR97 program package (Altomare *et al.* 1999). The atom coordinates were refined anisotropically by the full-matrix least-squares procedure in SHELX97 (Sheldrick 1998). In compound II, the best *R* value was obtained for the structure model with some of the halogen positions statistically occupied by Br and Cl anions in a ratio of Br : Cl = 3 : 1. Experimental data for compounds I and II are given in Table 1, final atomic coordinates and thermal parameters U_{eq} are in Table 2, and selected bond-lengths and angles are in Table 3. Calculated and observed structure-factors and anisotropic displacement factors are available from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2, Canada.

RESULTS

The structure of phase I contains four crystallographically independent Hg atoms, each covalently bonded to two S atoms at 2.366(6)–2.430(5) Å [∠S–Hg–S 163.03(19)–176.3(2)°]. As in the structures of other mercury sulfohalides (Pervukhina *et al.* 2003), the S–Hg–S angles essentially deviate from 180°, which is typical of 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 in the range of 96.3(2)–97.6(2)°. The Hg–Cl and Hg–Br distances are 2.826(10)–2.854(7) and 2.923(5)–3.697(2) Å, respectively.

The structure of phase II contains four crystallographically independent Hg atoms bonded to two S atoms at the distances of 2.385(7)–2.414(5) Å

[∠S–Hg–S 165.2(3)–175.0(3)°]. As in the structure of phase I, each S atom is bonded to three Hg atoms forming the SHg_3 trigonal pyramids, with the S–Hg–S angles of 95.7(2)–96.5(4)°.

In both structures, the SHg_3 fragments share the Hg vertices to form isolated cubes with S at the corners and Hg at the center of the edges. The halogen atoms are located both within and in between the $[Hg_{12}S_8]$ cubes (Figs. 1, 2). In the structure of II, the Br(3), Br(4), Br(5), Br(6), and Br(7) sites are statistically occupied by halogen atoms (Br > Cl), with the Hg – (Br,Cl) distances in the range of 2.773(1)–3.537(2) Å. The Hg(2)–Br(1) and Hg(3)–Br(2) distances are 3.591(1) and 3.318(2) Å respectively. Taking into account the halogen ions, the Hg atoms in structures I and II are in distorted octahedral coordination, similar to those in other Hg sulfohalides (Pervukhina *et al.* 2003) (Figs. 3, 4).

In the cubic modification, 64 Br atoms are located in the sublattice nodes with the *a*/4 parameter, and eight $[Hg_{12}S_8]$ groups reproduce the β-W structure-type. They are located at the vertices, center and centers of faces of the cubic unit-cell (Fig. 5).

We note that monoclinic modification (I) is isostructural with synthetic α-$Hg_3S_2Br_2$ (Voroshilov *et al.* 1996a), whereas the cubic modification (II) is isostructural with synthetic β-$Hg_3S_2Cl_2$ (Voroshilov *et al.* 1996b).

Discussion

The structures of the $Hg_3\mathit{X}_2\mathit{Hal}_2$ compounds (X = S, Se*;* Hal = Cl, Br, I) can be understood in terms of the "modular" principle. According to Borisov *et al.* (2001), in these structures, the *Hal* anion sublattice is close to the primitive cubic arrangement. This sublattice is body-centered by the *X* anions and face-centered by the Hg cations. If we estimate the reflection intensities of the sublattice, the {1'1'1'}, {2'0'0'}, and {2'2'0'} reflections (the braces denote that all equivalent planes of the cubic symmetry are considered) would be the most intense, as the Hg and *Hal* atoms form a distorted face-centered sublattice. Taking a' = 4.5 Å as an average sublattice parameter, the {1'1'1'}, {2'0'0'} and {2'2'0'} intense reflections should be observed at

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

Atom	*x*	*y*	*z*	U_{eq}*	Site-occupancy factor
			Compound I		
Hg(1)	0.1325(1)	0.2378(1)	0.5016(1)	0.030(1)	1
Hg(2)	0.2166(1)	0.50	0.7847(2)	0.050(1)	1
Hg(3)	0.0768(1)	0.50	0.2259(2)	0.049(1)	1
Hg(4)	-0.0733(1)	0.2327(1)	0.2057(1)	0.028(1)	1
S(1)	0.0714(3)	0.2453(6)	0.2461(6)	0.024(1)	1
S(2)	0.1992(3)	0.2443(6)	0.7614(6)	0.022(1)	1
Cl(1)	0.3820(6)	0.50	0.0031(11)	0.045(3)	1
Br(1)	0.2496(2)	0	0.4954(4)	0.025(1)	1
Br(2)	0	0	0.50	0.029(1)	1
Br(3)	0	0.50	0.50	0.028(1)	1
Br(4)	0.1241(3)	0.50	-0.0134(5)	0.051(1)	1
			Compound II		
Hg(1)	0.25	0.3575(1)	0.1425(1)	0.024(1)	1
Hg(2)	0	0.1438(1)	0.1344(1)	0.020(1)	1
Hg(3)	0.1160(1)	0.50	0.1401(1)	0.021(1)	1
Hg(4)	0.1172(1)	0.3643(1)	0	0.021(1)	1
S(1)	0.1188(2)	0.3697(4)	0.1306(3)	0.016(1)	1
S(2)	0.1315(4)	0.1315(4)	0.1315(4)	0.017(4)	1
Br(1)	0	0	0	0.024(4)	1
Br(2)	0	0.50	0	0.029(2)	1
Br(3)	0	0.2465(5)	0	0.014(1)	0.671(4)
Cl(3)	0	0.2465(5)	0	0.014(1)	0.329(4)
Br(4)	0.25	0.50	0	0.013(3)	0.71(5)
Cl(4)	0.25	0.50	0	0.013(3)	0.29(5)
Br(5)	0	0.2489(3)	0.2550(2)	0.019(2)	0.83(3)
Cl(5)	0	0.2489(3)	0.2550(2)	0.019(2)	0.17(3)
Br(6)	0	0.50	0.25	0.011(3)	0.54(4)
Cl(6)	0	0.50	0.25	0.011(3)	0.46(4)
Br(7)	0.25	0.25	0.25	0.019(2)	0.57(3)
Cl(7)	0.25	0.25	0.25	0.019(2)	0.43(3)

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

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

Compound I		Compound II	
Hg(1) – S(1)	2.366(6)	Hg(1) – S(1)	2.414(5)
Hg(1) – S(2)	2.405(6)	Hg(1) – S(1) #1	2.414(5)
Hg(2) – S(2)	2.381(6)	Hg(2) – S(2)	2.410(6)
Hg(2) – S(2) #1	2.381(6)	Hg(2) – S(2) #2	2.410(6)
Hg(3) – S(1)	2.367(6)	Hg(3) – S(1)	2.385(7)
Hg(3) – S(1) #1	2.367(6)	Hg(3) – S(1) #3	2.385(7)
Hg(4) – S(1)	2.430(5)	Hg(4) – S(1)	2.386(5)
Hg(4) – S(2) #3	2.413(5)	Hg(4) – S(1) #5	2.386(5)
Hg(1) – Br(1)	3.050(3)	Hg(1) – Cl(5) #4	3.204(3)
Hg(1) – Br(1) #1	3.199(3)	Hg(1) – Cl(5) #6	3.204(3)
Hg(1) – Br(2)	3.220(1)	Hg(1) – Cl(7)	2.773(1)
Hg(1) – Br(3)	3.378(1)	Hg(1) – Br(4)	3.678(1)
Hg(2) – Cl(1) #3	2.826(10)	Hg(2) – Br(1)	3.591(1)
Hg(2) – Br(1) #1	3.185(4)	Hg(2) – Cl(3)	3.087(5)
Hg(2) – Br(3)	3.697(2)	Hg(2) – Cl(3) #7	3.326(5)
Hg(2) – Br(4) #3	3.159(5)	Hg(2) – Br(5)	2.919(6)
Hg(3) – Br(1) #1	3.176(4)	Hg(3) – Br(2)	3.318(2)
Hg(3) – Br(3)	3.625(3)	Hg(3) – Br(4)	3.537(2)
Hg(3) – Br(4)	2.923(5)	Hg(3) - Br(5) #4	3.122(6)
Hg(3) – Br(4) #4	3.288(5)	Hg(3) – Br(6)	2.916(2)
Hg(4) – Cl(1) #4	2.854(7)	Hg(4) – Br(2)	3.272(1)
Hg(4) – Br(2)	3.469(1)	Hg(4) – Br(3)	3.031(6)
Hg(4) – Br(3)	3.677(1)	Hg(4) – Br(4)	3.466(1)
Hg(4) – Br(4) #5	3.044(3)	Hg(4) – Br(5) #6	3.123(3)
S(1) – Hg(1) – S(2)	176.3(2)	S(1)#1 – Hg(1) – S(1)	165.2(3)
S(2) – Hg(2) – S(2)#1	165.6(3)	S(2)#2 – Hg(2) – S(2)	169.0(5)
S(1) – Hg(3) – S(1)#1	167.2(3)	S(1) – Hg(3) – S(1)#3	171.4(3)
S(2)#3 – Hg(4) – S(1)	163.03(19)	S(1) – Hg(4) – S(1)#5	175.0(3)
Hg(1) – S(1) – Hg(3)	96.3(2)	Hg(3) – S(1) – Hg(4)	96.5(2)
Hg(1) – S(1) – Hg(4)	97.6(2)	Hg(3) – S(1) – Hg(1)	96.1(2)
Hg(3) – S(1) – Hg(4)	96.5(2)	Hg(4) – S(1) – Hg(1)	95.66(19)
Hg(2) – S(2) – Hg(1)	96.7(2)	Hg(2)#6 - S(2) – Hg(2)	96.5(4)
Hg(2) – S(2) – Hg(4)#3	96.8(2)	Hg(2)#6 – S(2) – Hg(2)#7	96.5(4)
Hg(1) – S(2) – Hg(4)#3	96.41(19)	Hg(2) – S(2) – Hg(2)#7	96.5(4)

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

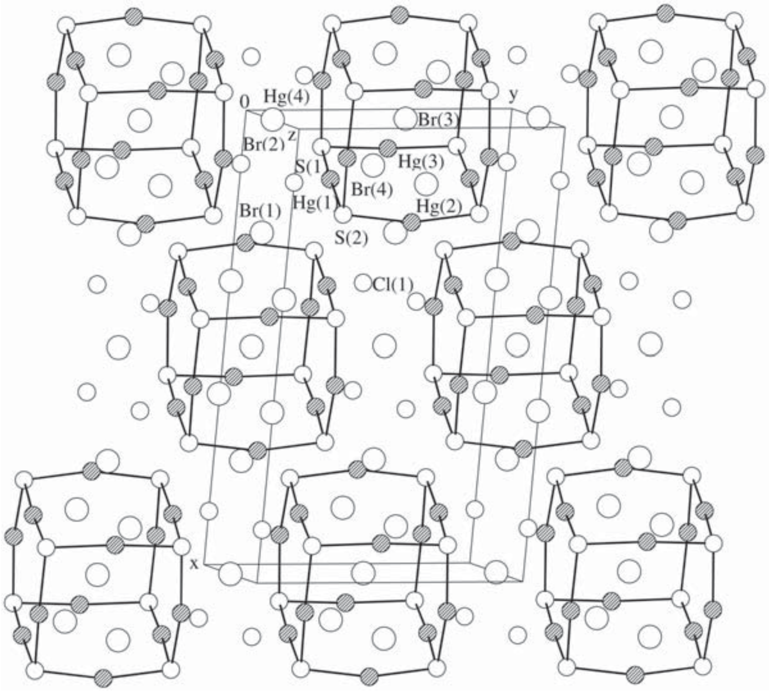

FIG. 1. The crystal structure of monoclinic modification of $Hg_3S_2Br_{1.5}Cl_{0.5}$ (phase I).

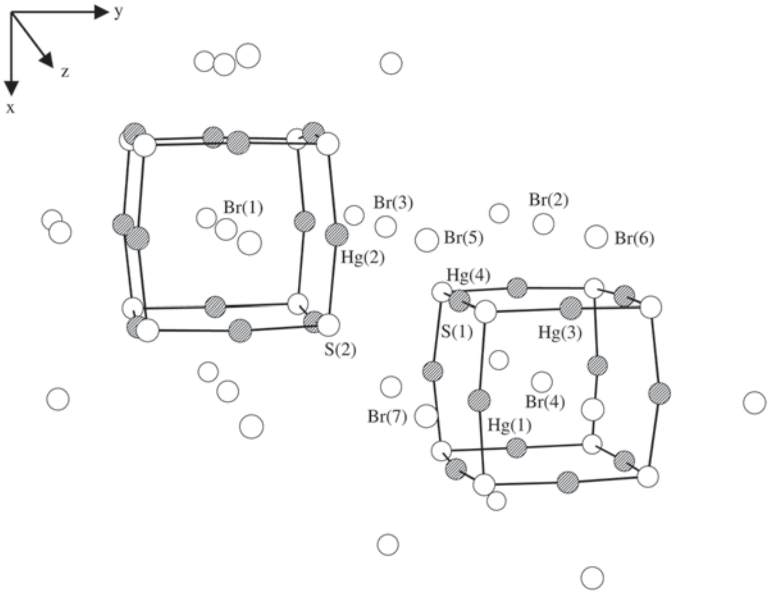

FIG. 2. The fragment of cubic structure of $Hg_3S_2Br_{1.5}Cl_{0.5}$ (phase II).

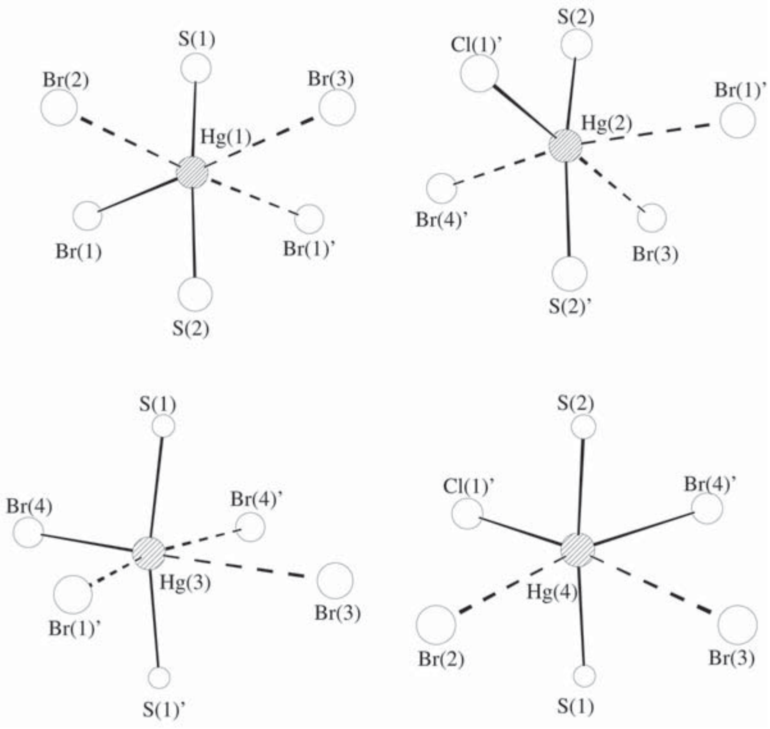

FIG. 3. The environments of the Hg^{2+} cations in $Hg_3S_2Br_{1.5}Cl_{0.5}$ (phase I).

d ~2.60, 2.25 and 1.60 Å, respectively. In the real structures, the sublattice parameters (*a*'≠ *b*'≠ *c*') may vary from 4 to 5 Å depending upon the size of the *Hal* anion and other factors. Thus, each characteristic reflection is split into two or three reflections that occupy a certain *d* interval in the XRPD pattern. Even if the structure is unknown, the size and orientation of the pseudocubic subcell can be determined using the unit-cell parameters obtained from the indexing of the XPRD pattern. This may be of help in the solution of the structure.

Table 4 lists parameters of the halogen sublattice, characteristic reflections, and the indices and intensities on the XPRD patterns for some mercury minerals and their analogues. No crystal structure is known for kenhsuite, γ-$Hg_3S_2Cl_2$ (McCormack & Dickson 1998), but the presence of the halogen sublattice and the importance of the "modular" principle in it are very likely. This is confirmed by the whole set of the intense sublattice reflections present in the XPRD pattern. The same is true for radtkeite, Hg_3S_2ClI (McCormack *et al.* 1991), for which we have determined the crystal structure of a lower-symmetry synthetic analogue (Pervukhina *et al.* 2004). There are strong grounds to believe that the structures of radtkeite and its analogue at least differ very slightly, since a similar sublattice of halogen anions should be present in both structures, and there is a good agreement between the intensities of reflections in the corresponding sublattices.

For lavrentievite and arzakite (Vasil'ev *et al.* 1984, 1986), Table 4 shows that the experimental XPRD patterns exhibit strong reflections that confirm the presence of the halogen sublattice centered by the S and Hg atoms discussed above. However, we were unable to find an agreement between the lattice parameters of these minerals determined by Vasil'ev *et al.* (1984, 1986) and their sublattice parameters. One can suggest that the indexing of the experimental XPRD patterns was poor owing to the problems associated with large unit-cell parameters and low symmetry. This can be justified by the unit-cell volume *V*', which is essentially smaller than the expected value for a Br-containing compound.

A check of the sublattice parameters indicates that even in more simple cases, the indexing of the XPRD pattern fails. For instance, the experimental XPRD pattern of orthorhombic radtkeite (McCormack *et al.* 1991) lacks the strongest (442) reflection, and the pattern of synthetic cubic α-$Hg_3S_2Cl_2$ [an analogue of corderoite (Puff & Küster 1962, Aurivillius 1967, Frueh & Gray 1968)] lacks the strong (044) reflection observed in its single-crystal-diffraction data. Data on grechishchevite, $Hg_3S_2(Br,Cl,I)_2$ (Vasil'ev *et*

TABLE 4. CRYSTALLOGRAPHIC DATA FOR $Hg_3S_2\mathit{Hal}_2$ AND *Hal* SUBLATTICES

Compound	Unit-cell parameters (Å, °)		Sublattice parameters (Å)	*hkl*	*h'k'l'*	d_{hkl} (Å)	I_{hkl}
Kensuite	*a*	9.332	$\mathbf{a}' = \mathbf{a}/2 = 4.67$	242	111	2.58	100
γ-$Hg_3S_2Cl_2$	*b*	16.82	$\mathbf{b}' = \mathbf{b}/4 = 4.21$	400	200	2.33	41
orthorhombic	*c*	9.108	$\mathbf{c}' = \mathbf{c}/2 = 4.55$	004	002	2.27	6
Ammm → *A*222	*V*	1429.63	$V' = V/16 = 89.5$	080	020	2.11	31
Z = 8					220	1.634	23
McCormack & Dickson (1998)					022	1.603	6
Radtkeite	*a*	16.92	$\mathbf{a}' = \mathbf{a}/4 = 4.23$	442	111	2.64	100
Hg_3S_2ClI*	*b*	20.25	$\mathbf{b}' = \mathbf{b}/4 = 5.06$	080	020	2.53	28
orthorhombic	*c*	9.110	$\mathbf{c}' = \mathbf{c}/2 = 4.56$	800	200	2.107	18
Fmmm, *F*222, *Fmm*2	*V*	3119.4	$V' = V/32 = 97.5$	084	022	1.695	21
Z = 16				880	220	1.622	11
McCormack (1991)							
Radtkeite, synthetic	*a*	16.827	$\mathbf{a}' = \mathbf{a}/4 = 4.21$	$\bar{4}24$	$\bar{1}11$	2.64	100
Hg_3S_2ClI	*b*	9.117	$\mathbf{b}' = \mathbf{b}/2 = 4.56$	420	111	2.63	99
monoclinic	*c*	13.105	$\mathbf{c}' = \mathbf{a}/4 + \mathbf{c}/2 = 4.97$	004	002	2.51	62
*C*2/*m*	β	130.17	$V' = V/16 = 96.7$	040	020	2.28	52
Z = 8	*V*	1543.2		$\bar{8}04$	200	2.10	32
Pervukhina *et al.* (2004)				044	022	1.69	25
				$\bar{8}08$	$\bar{2}02$	1.62	7
				800	202	1.61	7
Arzakite	*a*	8.99		007, 020		2.63	100
$Hg_3S_2(Br,Cl)_2$	*b*	5.24		123, 207		2.313	40
Br>Cl	*c*	18.45		008			
Monoclinic	β	92.28		$12\bar{4}$, 108		2.212	
*P*2/*m*, *P*2, *Pm*	*V*	868.5	$V' = V/10 = 86.8$	228, 232		1.595	30
Vasil'ev *et al.* (1984, 1986)				$12\bar{9}$			40
Lavrentievite	*a*	8.94		007, 020		2.61	100
$Hg_3S_2(Cl,Br)_2$	*b*	5.194		123, 207		2.292	40
Cl > Br	*c*	18.33		008			
Monoclinic	β	92.44		$12\bar{4}$, 108		2.199	
*P*2/*m*, *P*2, *Pm*	*V*	850.3	$V' = V/10 = 85.0$	228, 232		1.587	40
Vasil'ev *et al.* (1984)				$12\bar{9}$			4.5
Corderoite	*a*	≈ 8.96-8.92	$\mathbf{a}' = \mathbf{a}/2$	{222}	{111}	2.58	80-40
α-$Hg_3S_2Cl_2$	*V*	≈ 720	$\mathbf{b}' = \mathbf{b}/2$	{400}	{200}	2.24	30-25
cubic			$\mathbf{c}' = \mathbf{c}/2$	{440}	{220}	1.585	20-10
-			$V' = V/8 \approx 90$				
Z = 4							
Foord *et al.* (1974)							
Corderoite synthetic	*a*	8.94	$\mathbf{a}' = \mathbf{a}/2 = 4.47$	{222}	{111}	2.58	56
α-$Hg_3S_2Cl_2$**	*V*	716	$\mathbf{b}' = \mathbf{b}/2 = 4.47$	{040}	{020}	2.23	100
cubic			$\mathbf{c}' = \mathbf{c}/2 = 4.47$	{044}	{022}	1.58	21
$I2_13$			$V' = V/8 = 89.5$	{444}	{222}	1.29	10
Z = 4							
Aurivillius (1967)							
Grechishchevite	*a*	13.225	$\mathbf{a}' = \mathbf{a}/4 + \mathbf{b}/4 = 4.68$	042	111	(2.6374)	100
$Hg_3S_2(Br,Cl,I)_2$		(13.249)	$\mathbf{b}' = -\mathbf{a}/4 + \mathbf{b}/4 = 4.68$	402	$\bar{1}11$		
$P\bar{4}2m$, $P\bar{4}m2$ or	*b*	13.225	$\mathbf{c}' = \mathbf{c}/2 = 4.35$	440	200	(2.6369)	40
*P*4*mm*, *P*4/*mmm*		(13.259)	$V' = V/16 = 95.5$	004	002	2.341	
Vasil'ev *et al.* (1989)	*c*	8.685				(2.343)	
polymorph		(8.710)		444	202	2.180	
$Hg_3S_2(Br_{1.0}Cl_{0.5}I_{0.5})$	*V*	1519				(2.177)	
Pbnm		(1530)				1.599	
Z = 8						(1.595)	
Pervukhina *et al.* (2003)							

$Hg_3S_2Cl_{1.5}Br_{0.5}$	*a*	18.006	$\mathbf{a}' = \mathbf{a}/4 = 4.50$	444	111	2.599	100
Pm$\bar{3}$*n*	*V*	5837.8	$\mathbf{b}' = \mathbf{b}/4 = 4.50$	008	002	2.251	69
$Z = 32$			$\mathbf{c}' = c/4 = 4.50$	088	022	1.592	26
Pervukhina *et al.* (2005)			$V' = V/64 = 91.2$				
$Hg_3S_2Cl_{1.5}Br_{0.5}$	*a*	16.841	$\mathbf{a}' = \mathbf{a}/4 = 4.21$	$\bar{4}22$	$\bar{1}11$	2.599	100
*C*2/*m*	*b*	9.128	$\mathbf{b}' = \mathbf{b}/2 = 4.56$	422	111	2.586	97
$Z = 8$	*c*	9.435	$\mathbf{c}' = \mathbf{c}/2 = 4.72$	004	002	2.359	44
Pervukhina *et al.*	β	90.08	$V' = V/16 = 90.64$	040	020	2.282	62
(2005)	*V*	1450.3		800	200	2.105	31
				044	022	1.640	23
				$\bar{8}04$	$\bar{2}02$	1.572	6
				804	202	1.569	5
				840	220	1.547	17
$Hg_3S_2Br_{1.5}Cl_{0.5}$	*a*	18.248	$\mathbf{a}' = \mathbf{a}/4 = 4.56$	444	111	2.634	100
Pm$\bar{3}$*n*	*V*	6076.4	$\mathbf{b}' = \mathbf{b}/4 = 4.56$	008	002	2.281	70
$Z = 32$			$\mathbf{c}' = \mathbf{c}/4 = 4.56$	088	022	1.632	34
(this work)			$V' = V/64 = 94.94$				
$Hg_3S_2Br_{1.5}Cl_{0.5}$	*a*	17.824	$\mathbf{a}' = \mathbf{a}/4 = 4.456$	421	111	2.636	97
*C*2/*m*	*b*	9.238	$\mathbf{b}' = \mathbf{b}/2 = 4.619$	$\bar{4}23$	$\bar{1}11$	2.635	100
$Z = 8$	*c*	10.269	$\mathbf{c}' = \mathbf{a}/8 + \mathbf{c}/2 = 4.62$	004	002	2.314	39
(this work)	β	115.69	$V' = V/16 = 95.23$	040	020	2.309	58
	V	1523.8		$\bar{8}02$	200	2.228	41
				044	022	1.635	21
				802	202	1.605	7
				$\bar{8}06$	$\bar{2}02$	1.604	8
				$\bar{8}42$	$\bar{2}20$	1.603	22

* In McCormack (1991), Table 2 lacks the (442) reflection though it is the closest to the maximum value I/I_o for the mineral.

** The powder data in Aurivillius (1967) lack the (220) reflection for α-$Hg_3S_2Cl_2$, whereas those for a single crystal involve it. These data provide the intensities of all reflections normalized on a scale of 100.

al. 1989) and the synthetic orthorhombic polymorph $Hg_3S_2Br_{1.0}Cl_{0.5}I_{0.5}$ (Pervukhina *et al.* 2003) are similar and are combined in Table 4 (the orthorhombic version in parentheses). The lack of the crystal-structure determination surely hinders indexing of the tetragonal and orthorhombic variants with $a \approx b$, but this does not warrant the absence of the (042) ($d = 2.65$ Å) and (004) ($d = c/4 = 2.171$ Å) reflections in the tetragonal modification, which must be attributed to two intense lines of the XPRD pattern. The reason for the absence is perhaps that the programs of the automatic indexing of XPRD patterns first treat the reflections with small indices, *i.e.*, maximal d_{exp}, as basic, whereas the remaining part of the pattern is used to refine the parameters and to reject poor choices. Data on the suggested substructures allow the middle section of the experimental patterns to be used as well. In our case, this is the $2.5 > d_{hkl} > 1.5$ Å range and, as shown in Table 4, all sublattice reflections over this d_{hkl} interval are rather intense. As a rule, the $(h'k'l') \sim (111)$ reflection with $d \approx 2.65$ Å is the most intense in the XPRD patterns.

CONCLUSIONS

A special feature of the natural and synthetic $Hg_3S_2Hal_2$ (*Hal* = Cl, Br, I) compounds studied is a stronger ordering of the anions, as compared to the cations, owing to the strong covalent Hg–*X* (*X* = S, Se) bonds. These bonds form various configurations (Borisov *et al.* 2001) with virtually the same fixed bond-lengths. The less "fixed" halogen anions form regular sublattices in which the isomorphous Cl–Br–I substitutions are plausible over a wide range of compositions. At the same time, the presence of the "hinge-joint" bonds in the covalent –S–Hg–S–Hg–S– radical results in the appearance of many polymorphic modifications.

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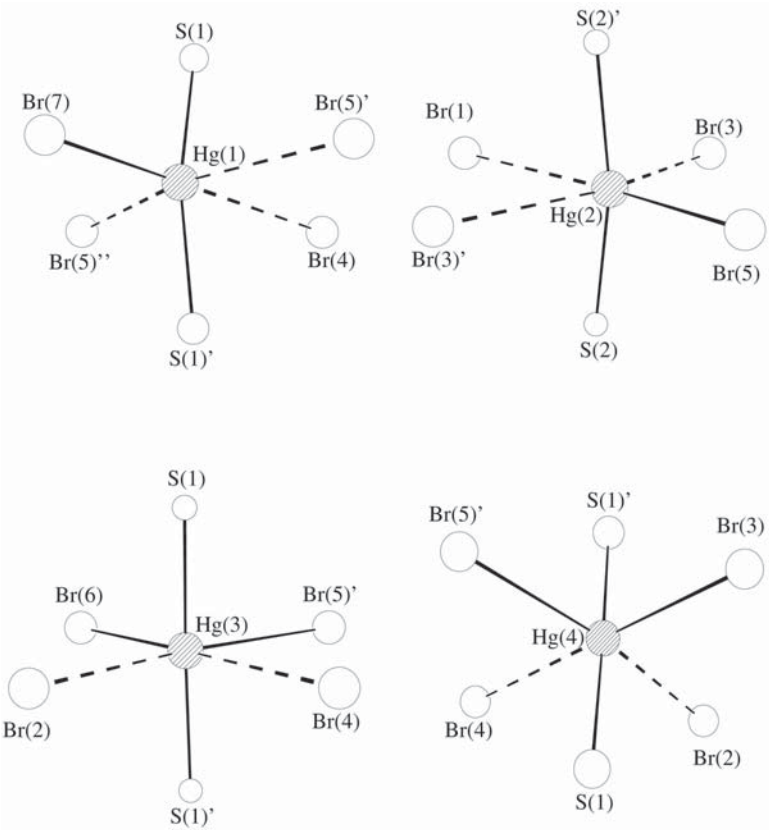

FIG. 4. The environments of the Hg^{2+} cations in $Hg_3S_2Br_{1.5}Cl_{0.5}$ (phase II).

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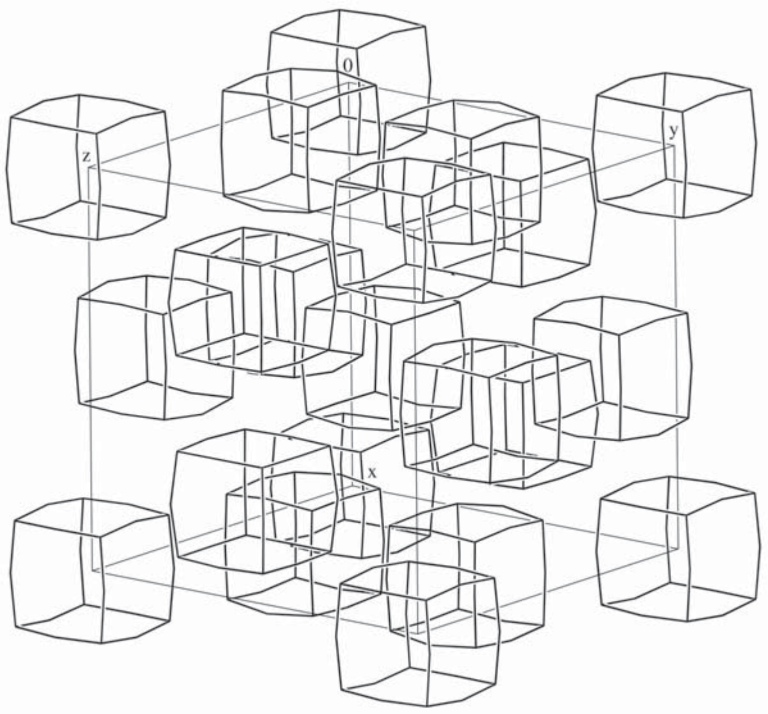

FIG. 5. The arrangement of $[Hg_{12}S_8]$ blocks in the cubic modification of $Hg_3S_2Br_{1.5}Cl_{0.5}$ (phase II).

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