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Crystal chemistry and features of the structure formation of mercury oxo- and chalcohalides

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Contents

I.	Introduction	101
II.	Mercury chalcohalides	102
III.	Mercuric oxohalides	113
IV.	Stable atomic groups (building blocks) in mercury compounds	116
V.	The modular principle in the structure formation of mercury oxo- and chalcohalides	124
VI.	Crystal chemical features of the MHgYX compounds (M = Cu or Ag; Y = S or Se; X = Cl, Br or I)	127
VII.	Conclusion	129

Abstract. Characteristic features of the crystal structures of mercury oxohalides, chalcohalides and related compounds are surveyed. The structures of these compounds are described using both the traditional way and a modern approach based on the identification of stable building blocks coupled with the analysis of their packing. The crystallographic and crystal chemical data for the title compounds are given. The bibliography includes 123 references.

I. Introduction

Crystal chemistry of mercury compounds is unique being principally different from that of lighter neighbours of mercury in Group 12 of the Periodic system, *viz*., Zn and Cd. In contrast to zinc and cadmium, the Hg^{2+} ions are capable of forming two linear shortened strong bonds that are prone to further association, in addition to ordinary tetrahedral bonds. The complexity and multiplicity of crystal chemistry of mercury compounds is also manifested in the co-existence of various combinations of ionic and covalent bonds in a mercury compound with various anions Y (N, O, S, Se or Te) and X (F, Cl, Br or I). Yet another characteristic feature consists of the frequently occurring short covalent bonds between mercury atoms giving rise to cluster-like polyatomic fragments, such as $[Hg_2]^{2+}$ dumbbells or $[Hg_3]^{4+}$ triangles (with the Hg – Hg bond lengths of 2.5 – 2.7 Å). There are a number of structures where mercury atoms form covalent bonds with other crystal chemically similar cations (*e.g*., Ag, Pb and Cu) to generate, for instance, $[Ag_3Hg]^{3+}$ or $[Ag_2Hg_2]^{4+}$ tetrahedra, *etc*. The mercury atoms in these cluster fragments occur in an oxidation state lower than +2. It is interesting to note that the $[Hg_2]^{2+}$ dumbbells tend to linear coordination to Y atoms to yield covalently bound $Y-[Hg_2]^{2+}-Y$ moieties, which can further be involved as building blocks in diverse assemblies (including extended ones), in addition to the $Y-Hg^{2+}-Y$ group. A similar behaviour is also typical of the $[Hg_3]^{4+}$ triangular clusters.

The results of structural investigations into inorganic compounds containing mercury atoms either in the bivalent (Hg^{2+}) or a 'low-valence' (*i.e*., $[Hg_2]^{2+}$, *etc*.) states gathered to date reveal a variety of covalently bound chains, layers and frameworks as building blocks to form the general structural motifs. These compounds also contain additional isolated or extended atomic groups, which compensate for the charges and fill in the voids of the structure presumably favouring the formation of specific motifs in some cases (owing to the so-called 'template' synthesis mechanism).

A special interest in the crystal chemistry of mercury compounds is partially explained by the fact that this environmentally important element is highly mobile in the earth's crust, waters and atmosphere. Presently, about 100 mercury-based and mercury-containing minerals are known. Among them, mercury amalgams, sulfo salts, oxo compounds (predominantly oxohalides) and sulfohalides can be distinguished as the most representative groups. Furthermore, about 30 minerals (mainly halides, oxohalides and oxochromates) contain low-valence mercury as $[Hg_2]^{2+}$ or $[Hg_3]^{4+}$ cluster fragments.

Several aspects of the crystal chemistry of mercuric inorganic compounds with Y and X anions have been elucidated for the first time by Karin Aurivillius.[1] The linear Y – Hg – Y fragment [with a YHgY bond angle of ~180° and short Hg – Y bond lengths: $(Hg-O)_{av}$ of 2.04 Å and $(Hg-S)_{av}$ of 2.34 Å] was recognised as the main building block in the crystal structures known at that time. It was also noted that two major types of assemblies based on these fragments are possible: the fragments can occur as isolated ions or molecules (such as linear X – Hg – X molecules in the crystal structures of mercuric halides or complex cation $[OHg_3Cl_3]^+$ in the structure of Hg_3OCl_4); or they can join into infinite chains characterised by a certain sequence of the HgYHg angles between the neighbouring Y – Hg – Y fragments. Aurivillius introduced [1] a classification of such chains including three distinct types: helical chains that can be either right-handed (+) or left-handed (–) (in particular, they occur in the hexagonal modification of HgO), zigzag chains '+ –' (occur in the orthorhombic modification of HgO) and crankshaft chains '+ + – –' (occur in $Hg_5O_4Br_2$). The exact geometry of a chain is determined by the HgYHg angle, which in turn depends on the nature of the Y

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anion (for instance, different forms of crankshaft chains '+ + − −' are realised in oxo- and sulfoxo compounds, such as $Hg_5O_4Br_2$ and $Hg_3S_2Cl_2$). These chains can assemble into various planar or puckered ribbons, layers or frameworks.

Bivalent, low-valence and mixed-valence mercury compounds (nitrates, molybdates, tungstates, vanadates, arsenates and so on containing the Hg^{2+}, $[Hg_2]^{2+}$ or $[Hg_3]^{4+}$ cations) have been the subject of investigations by many research groups, including the ones headed by Brodersen, Jeitschko, Beck, Keller, Mayer, *etc*. The group leaded by Voroshilov has contributed a lot into the structural studies of mercuric ternary chalcohalides. Over the recent years, about fifty mercury inorganic compounds in different oxidation states have been synthesised and characterised by Weil and co-workers. Over the recent years in Russia, the crystal chemical analysis of factors affecting the structure formation for these compounds has been in the focus of research interest of a group headed by Borisov.

Various aspects of crystal chemistry of naturally occurring and synthetic compounds containing low-oxidation-state mercury [including mixed-valence compounds, compounds with polyatomic groups $[Hg_n]^{x+}$ ($n > 2$), low-valence mercury compounds with organic ligands and mercury-containing transition metal clusters] have been surveyed in two reviews [2,3] and a monograph.[4]

The structures of inorganic mercury compounds are of significant interest from the viewpoint of the crystal formation process encompassing all changes in the interactions between atoms upon their incorporation into a crystalline phase imposed by the regular packing, symmetry and long-range ordering requirements. A number of characteristic representatives of those compounds have been analysed using an original software package KAP-PLATS [7] within a concept considering the crystalline state to be a result of ordering of atoms or rigid atomic fragments produced by families of parallel equi-distant (crystallographic) planes.[5,6] Such an approach has been extended to a wider range of mercury compounds in a recent review by Borisov *et al*.[8]

The present review is concerned with specific features of the crystal structure of mercury oxo- and chalcohalides and closely related compounds, which are determined to a large extent by crystal chemical preferences of the mercury atoms, in particular, their tendency to form strong covalent bonds yielding stable atomic fragments, the so-called 'rigid' atomic groups. The structures of compounds are described both in the traditional way and using a modern approach based on the recognition of such stable 'building blocks' coupled with the analysis of their packings.

II. Mercury chalcohalides

1. Preparation, properties and occurrence in nature

Within the Hg – S binary system, there are at least three sulfides corresponding to the composition HgS.[9] Two stoichiometric modifications, *viz*., low-temperature α modification, cinnabarite, and high-temperature β modification, metacinnabarite, are widely known. The third phase that becomes stable at even higher temperature mentioned for the first time in the mid 1960s [10] as non-stoichiometric γ-HgS has been later referred to as hypercinnabarite.

Mercuric sulfide occurs in nature predominantly as crimson cinnabarite (cinnabar, vermilion), whereas velvet black metacinnabarite is very scarce.[9] There has been some evidence [10] of natural occurrence of non-stoichiometric hypecinnabarite with iron impurities as well. Mercury selenide and telluride occur as rare minerals,[11] *viz*., purple black tiemannite HgSe and dark grey coloradoite HgTe.

Ternary mercury chalcohalides (with a 3 : 2 : 2 composition) $Hg_3Y_2X_2$ (Y = S, Se, Te; X = Cl, Br, I) have been known for a long time. Recently, they start to attract a great interest from reseachers due to their potential application in advanced technologies. These compounds manifest photoconductivity, large refraction indices and large specific angle-of-polarisation rotation in the visible light range. In particular, cubic mercury chalcohalides simultaneously demonstrate the optical activity and linear electrooptic effect, which makes them promising optical and gyrotropic materials in optoelectronics.

Comprehensive investigations into the crystal structures of ternary mercury chalcohalides started in the early 1960s. For instance, the crystal structures of $Hg_3S_2Cl_2$, $Hg_3Se_2Cl_2$, $Hg_3Te_2Cl_2$ and $Hg_3Te_2Br_2$ belonging to one of 9 rare cubic space symmetry groups, $I2_13$, which contain non-intersecting three-fold symmetry axes, were reported.[12,13] Polymorphism is very typical of these compounds. Puff *et al*.[14] elucidated polymorphism in a number of mercury sulfochlorides and sulfobromides. According to their results, the low-temperature cubic α-$Hg_3S_2Cl_2$ modification can be crystallised from a stoichiometric mixture of HgS and $HgCl_2$ at 300 °C. The high-temperature cubic β-$Hg_3S_2Cl_2$ modification is formed at 400 °C. The low-temperature α-$Hg_3S_2Cl_2$ modification can reversibly transform into β-$Hg_3S_2Cl_2$ under hydrothermal conditions at 300 ± 0.5 °C. The orthorhombic γ-$Hg_3S_2Cl_2$ phase can be produced at ~750 °C and is probably metastable over the entire temperature range studied.

The orthorhombic low-temperature modification of mercury sulfobromide, α-$Hg_3S_2Br_2$, can be synthesised from HgS and $HgBr_2$ at 200 °C, the high-temperature (also orthorhombic) phase β-$Hg_3S_2Br_2$ is formed from the same reactants at ~420 °C. The metastable γ-$Hg_3S_2Br_2$ phase was prepared *via* the interaction of a $HgBr_2$ solution with an excess of KBr and sodium thiosulfate at 80 °C. No single crystal of this modification has been grown, but the authors claimed that it was isomorphous to the tetragonal phase of mixed mercury sulfobromoiodide $Hg_3S_2Br_{0.5}I_{0.5}$.[14]

Single crystals of mercury sulfofluoride $Hg_3S_2F_2$ were grown by heating of a mixture of HgS and dipyridinium tetrafluoromercurate up to 260 °C in vacuum according to the reaction

$$2\,HgS + (C_5H_5NH)_2HgF_4 \longrightarrow Hg_3S_2F_2 + 2\,C_5H_5N + 2\,HF\uparrow.$$

This compound was isomorphous to cubic α-$Hg_3S_2Cl_2$; isomorphous mercury selenofluoride $Hg_3Se_2F_2$ can be prepared in a similar way.[15]

Earlier, an oxidative method for the synthesis of these compounds has been suggested,[16] which implied heating of the respective reaction mixtures in sealed evacuated ampoules at a temperature of the onest of exothermic effects:

$$3\,Hg_2X_2 + 4\,Y \longrightarrow 2\,Hg_3Y_2X_2 + X_2\uparrow.$$

Among all possible combinations, only $Hg_3Te_2F_2$ could not be prepared in pure form by this method, owing to the fact that heating of mixtures of Hg_2F_2 and Te in a temperature range of 180 – 350 °C always yielded liquid mercury. The oxidative synthesis of mercury seleno- and tellurohalides was successfully realised. The preparation of cubic mercury $Hg_3S_2I_2$ sulfoiodide was also reported.[17]

Systematic investigations into the ternary mercury chalcohalides are performed by a group of Ukranian researchers starting from the early 1980s.[18–23] The preparation, physical and crystallographic characterisation of cubic α-$Hg_3S_2Cl_2$, $Hg_3Se_2Cl_2$, $Hg_3Te_2Cl_2$, $Hg_3Te_2Br_2$ and $Hg_3S_2I_2$ were reported.[19] The phase equilibria in the HgS – HgTe – $HgCl_2$ ternary system were elucidated.[22] The existence of a single ternary compound, $Hg_3S_2Cl_2$, in the HgS – $HgCl_2$ system was confirmed, which occurs as three polymorph modifications, *viz*., low-temperature α modification with a cubic structure, high-temperature cubic β modification with the double lattice parameter and metastable γ modification. It turned out that the structure of the γ phase belonged to the so-called order – disorder type. In addition to the ternary compound $Hg_3Te_2Cl_2$, another compound with a composition Hg_3TeCl_4 was found in the HgTe – $HgCl_2$ system.

A study of the HgS – $HgBr_2$ system revealed [23] two modifications of mercury sulfobromide $Hg_3S_2Br_2$, *viz*., low- (α) and high-temperature (β) ones. According to single-crystal X-ray diffraction data, both compounds belong to the monoclinic system. No confirmation of the existence of a metastable phase γ-$Hg_3S_2Br_2$

was found. Two ternary mercury tellurobromides, *viz*., cubic $Hg_3Te_2Br_2$ and Hg_3TeBr_4 isomorphous to their chloro analogue, Hg_3TeCl_4, were found in the $HgTe-HgBr_2$ system. Within the $HgTe-HgI_2$ system, only one ternary compound $Hg_3Te_2I_2$ was identified.

Voroshilov and Slivka [18] have observed for the first time the formation of ternary compounds $Hg_3S_2I_2$ (at 658 K) with an orthorhombic lattice and $Hg_3Se_2I_2$ (at 693 K), in the $HgS-HgI_2$ and $HgSe-HgI_2$ systems, respectively. Syntheses of $Hg_3S_2I_2$ and $Hg_3Se_2I_2$ by heating stoichiometric mixtures of the respective mercury chalcogenides and iodide in sealed evacuated ampoules at 260 °C for 2–3 days were reported.[24]

Based on the analysis of equilibrium diagrams for the $HgY-HgX_2$ system, Voroshilov and Slivka [18] concluded that the reactivity of mercuric chalcogenides towards mercuric halides increases on going from sulfur to tellurium (an increase in the ionic character of bonding) and from iodine to chlorine (an increase in the covalency of bonding).

In nature, mercuric sulfohalides occur as typical but rare exogenous minerals within the oxidation zone of mercury deposits, which are often characterised by a variable composition, depending on the number and type of halogen atoms incorporated into the crystal structure. These include the following minerals: corderoite α-$Hg_3S_2Cl_2$,[25] lavrentievite $Hg_3S_2(Cl,Br)_2$ and arzakite $Hg_3S_2(Br,Cl)_2$,[26,27] grechishchevite $Hg_3S_2(Br,Cl,I)_2$,[28] radtkeite Hg_3S_2ClI [29] and kenshuaite γ-$Hg_3S_2Cl_2$.[30]

The data given above indicate that both naturally occurring and synthetic mercury chalcohalides are of interest in terms of their polymorphism and possible isomorphous replacements of the halogen atoms in the crystal structures.

2. The crystal structures of ternary mercury chalcohalides

The rare mineral metacinnabarite (β-HgS) crystallises in the sphalerite structural type (the Hg–S bond length is 2.54 Å).[31]

The more common trigonal modification, α-HgS (cinnabar),[31] possesses a unique structure with no close analogues among monosulfides, since it involves chains combined into helices with the mercury atoms surrounded by two closest S atoms at 2.368 Å, two more S atoms at 3.10 Å and two even more distant S atoms at 3.30 Å. The S–Hg–S and Hg–S–Hg bond angles are 173° and 105°, respectively (Fig. 1). Similar to β-HgS, HgSe (tiemannite) and HgTe (coloradoite) crystallise in the sphalerite structural type (Hg–Se 2.615, 2.634 Å, Hg–Te 2.797 Å, the YHgY angle of 109.47°). Upon compression to 1.5–2 GPa, the crystal structures of HgSe and HgTe are transformed into that of α-HgS.[32]

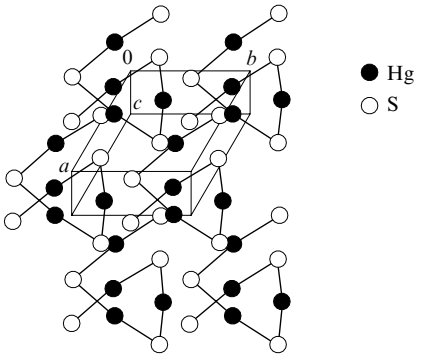


Figure 1. The crystal structure of α-HgS (cinnabarite).

a. 3:2:2 Mercury chalcohalides

The crystal structure of synthetic α-$Hg_3S_2Cl_2$ (natural mineral corderoite [25]) was determined by means of single-crystal X-ray diffraction.[33,34] An analysis of the interatomic distances and angles taking into account the tendency of mercury atoms towards

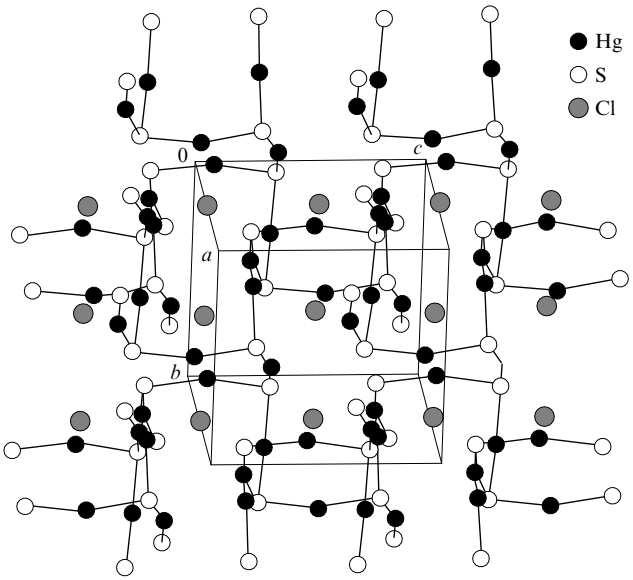


Figure 2. The crystal structure of α-$Hg_3S_2Cl_2$ (corderoite).

the formation of infinite chains [1] $(-S-Hg-S-)_\infty$ identified a $[Hg_3S_2]_n^{2n+}$ framework in the structure, which can be described in two ways. From the one side, the infinite nearly planar $(-S-Hg-S-)_\infty$ chains of the '++−−' type (Table 1, Fig. 2) can be considered as major building block of the structure. The chains go through the unit cell near the $z = \pm 1/4$ planes and include 8 out of 12 mercury atoms and all 8 sulfur atoms of a unit cell. The remaining mercury atoms combine the chains *via* the S–Hg–S bridges into a $[Hg_3Y_2]_n^{2n+}$ spatial framework with the halogen atoms localised in its cavities.[33] The cubic symmetry (space group $I2_13$) provides the equivalency of all three chain orientations.

The same authors [33] suggested an alternative method for the description of the α-$Hg_3S_2Cl_2$ structure based on the identification of the trigonal pyramidal SHg_3 groups. The sulfur atoms located on the spatial diagonal of the cubic cell, *i.e*., on the three-fold axis, coordinate three mercury atoms with Hg–S bond lengths of 2.42 Å. These three mercury atoms compose regular triangles with an edge of 3.543 Å. The distance from the centre of such a triangle to the sulfur atoms in the pyramid apex is 1.30 Å. The SHg_3 groups are combined into a common framework by sharing mercury vertices. Large cavities present in the framework are occupied by the chlorine atoms. Very long Hg–Cl bond lengths (2.87 Å) are indicative of the ionic character of bonding.

Frueh and Gray [34] described this structure in a more traditional way: each Hg atom is octahedrally coordinated by two S and four Cl atoms. Strongly distorted $[HgY_2X_4]$ octahedra are interlinked by face sharing.

Structural data on the isostructural compounds of the α-$Hg_3Y_2X_2$ family (Y = S, Se and Te; X = F, Cl, Br and I) [12] that crystallise in the enantiomorphous space group $I2_13$ with four formula units per unit cells are given in Table 1.

In order to rationalise the interatomic interactions in $Hg_3S_2Cl_2$, $Hg_3S_2F_2$, $Hg_3Se_2Cl_2$, $Hg_3Te_2Cl_2$ and $Hg_3Te_2Br_2$, a crystal chemical analysis of their structures has been accomplished.[18] The authors note that the interactions between the mercury and chalcogen atoms are predominantly covalent. The Hg–Y–Hg bond angles imply a significant contribution of the chalcogen p electrons to the chemical bond (the coordination is trigonal prismatic). Meanwhile, the Y–Hg–Y angles close to 180° are characteristic of six-coordinated mercury atoms in distorted $[HgY_2X_4]$ octahedra. The packing density of the structure calculated based on mean specific volumes of the atoms involved estimated from their effective radii is 65%–71%, which

Table 1. Crystallographic and crystal chemical parameters of ternary mercury chalcohalides.

Compound	Space group (R_f)	Unit cell parameters		Z	d_{exp}, d_{calc} /g cm^{-3}	Bond lengths [a] /Å		Bond angles [a] /deg.		Ref.
		translations /Å	β angle /deg.			Hg–Y	Hg–X	YHgY	HgYHg	
3 : 2 : 2 Chalcohalides										
α-$Hg_3S_2Cl_2$	$I2_13$ (0.065)	a = 8.940		4	6.74 6.90	2.42	2.86, 3.39	165.1	94.1	33
	$I2_13$ (0.08)	a = 8.949		4	6.895 6.827	2.45	2.87, 3.38	166	92	34
β-$Hg_3S_2Cl_2$	$Pm\bar{3}n$ (0.035)	a = 17.925		32	– 6.798	2.36 – 2.40	2.70 – 3.64	166.9 – 176.5	94.8 – 98.0	22
γ-$Hg_3S_2Cl_2$ (polytype 1)	$Pbmn$ (0.135)	a = 9.328 b = 8.410 c = 4.541		2	6.83 6.814	2.37 – 2.44	2.67 – 3.55	157.8 – 176.0	94.0 – 96.0	35
γ-$Hg_3S_2Cl_2$ (polytype 2)	$A2mm$ (0.213)	a = 4.664 b = 16.820 c = 9.081		4	6.83 6.814	2.37 – 2.44	2.67 – 3.55	157.8 – 176.0	94.0 – 96.0	35
γ-$Hg_3S_2Cl_2$ (kenshuaite)	see [b] –	a = 9.332 b = 16.820 c = 9.108		8	6.83 6.87	–	–	–	–	30
α-$Hg_3S_2Br_2$	$C2/m$ (0.0535)	a = 17.996 b = 9.281 c = 10.289	116.4	8	– 7.110	2.384 – 2.416	2.848 – 3.706	162.4 – 176.5	95.8 – 98.5	23
β-$Hg_3S_2Br_2$	$C2/m$ (0.086)	a = 17.273 b = 9.374 c = 9.473	89.78	8	– 7.13	2.24 – 2.69	2.64 – 3.39	137.8 – 180.0	84.4 – 109.3	23
$Hg_3S_2I_2$	$Imma$ (0.0449)	a = 9.799 b = 18.703 c = 9.462		8	– 7.045	2.399 – 2.423	–	160.8 – 169.9	99.11 – 99.50	24
$Hg_3Se_2Cl_2$	$I2_13$ –	a = 9.06		4	–	2.51	2.90	167	92	12
$Hg_3Se_2Br_2$	$C2/m$ (0.0517)	a = 17.529 b = 9.408 c = 9.775	89.51	8	– 7.577	2.496 – 2.536	2.815 – 3.305	159.2 – 180.0	92.9 – 94.6	36
$Hg_3Se_2I_2$	$C2/m$ (0.0749)	a = 19.392 b = 9.652 c = 10.918	116.54	8	– 7.37	2.36 – 2.66	2.79 – 4.09	150.7 – 166.4	85.7 – 108.4	36
	$Imma$ (0.0518)	a = 9.766 b = 19.381 c = 9.633		8	– 7.384	2.501 – 2.522	3.034 – 3.304	161.58 – 171.80	96.53 – 97.39	24
$Hg_3Te_2Cl_2$	$I2_13$ –	a = 9.336		4	–	2.65	2.99	167	91	12
$Hg_3Te_2Br_2$	$I2_13$ –	a = 9.54		4	–	2.64	3.08	167	91	12
$Hg_3Te_2I_2$	$C2/c$ (0.076)	a = 14.22 b = 9.70 c = 14.34	79.9	8	–	2.648 – 2.702	2.981 – 3.499	155.23 – 180.0	89.75 – 97.60	37
	Cc (0.0483)	a = 14.276 b = 9.722 c = 14.382	100.11	8	– 7.508	2.57 – 2.77	2.99 – 3.97	180.0	88.3 – 100.0	38
Hg_3Te_2BrI	$C2$ (0.1045)	a = 18.376 b = 9.587 c = 10.575	90.12	8	– 7.585	2.526 – 2.761	2.850 – 3.711 (Br) 3.270 – 3.838 (I)	–	88.7 – 100.2	39
$Hg_3S_2F_2$	$I2_13$ –	a = 8.14		4	8.64 8.68	–	–	–	–	15
$Hg_3Se_2F_2$	$I2_13$ –	a = 8.387		4	–	–	–	–	–	15

Table 1 (continued).

Compound	Space group (R_f)	Unit cell parameters		Z	d_{exp}, d_{calc} /g cm^{-3}	Bond lengths [a] /Å		Bond angles [a] /deg.		Ref.
		translations /Å	β angle /deg.			Hg–Y	Hg–X	YHgY	HgYHg	
3 : 2 : 2 Chalcohalides										
$Hg_3S_2Br_{1.0}Cl_{0.5}I_{0.5}$	*Pbnm* (0.0363)	a = 13.249 b = 13.259 c = 8.710		8	– 7.396	2.358 – 2.459	2.768 – 2.804 (Cl) 3.040 – 3.078 (Br) 3.259 – 3.304 (I)	140.9 – 172.9	95.95 – 104.91	40
$Hg_3S_2Cl_{1.0}I_{1.0}$	*C*2/*m* (0.0527)	a = 16.827 b = 9.117 c = 13.165	130.17	8	– 7.130	2.240 – 2.474	2.783 – 2.961 (Cl) 3.083 – 3.216 (I)	146.1 – 180.0	94.7 – 102.9	41
$Hg_3S_2Cl_{1.5}Br_{0.5}$ (I)	*C*2/*m* (0.0528)	a = 16.841 b = 9.128 c = 9.435	90.08	8	– 6.952	2.372 – 2.484	2.703 – 2.801 (Cl) 3.070 – 3.099 (Cl, Br) [c]	158.42 – 180.0	93.06 – 96.21	42
$Hg_3S_2Cl_{1.54}Br_{0.46}$ (II)	$Pm\bar{3}n$ (0.0282)	a = 18.0409		32	– 6.851	2.387 – 2.410	2.715 – 3.294 (Cl) 3.576 (Br) 2.884 – 3.448 (Cl, Br) [c]	166.0 – 176.1	95.4 – 96.6	42
$Hg_3S_2Br_{1.5}Cl_{0.5}$ (III)	*C*2/*m* (0.0513)	a = 17.824 b = 9.238 c = 10.269	115.69	8	– 7.005	2.366 – 2.430	2.826 – 2.854 (Cl) 2.923 – 3.697 (Br)	163.0 – 176.3	96.3 – 97.6	43
$Hg_3S_2Br_{1.5}Cl_{0.5}$ (IV)	$Pm\bar{3}n$ (0.0380)	a = 18.248		32	– 7.026	2.385 – 2.414	2.773 – 3.537 (Cl, Br) [c] 3.318 – 3.591 (Br)	165.2 – 175.0	95.7 – 96.5	43
3 : 1 : 4 Chalcohalides										
Hg_3TeCl_4	*Pbca* (0.0388)	a = 11.522 b = 12.140 c = 12.683		8	– 6.523	2.631 – 2.637	2.357 – 3.691	–	89.89 – 97.61	22
Hg_3TeBr_4	*Pbca* (0.1181)	a = 12.360 b = 12.523 c = 12.868		8	– 7.00	2.62 – 2.71	2.64 – 3.49	–	81.85 – 99.07	23
Hg_3TeI_4	$F\bar{4}3m$ (0.1181)	a = 6.244		–	7.03 –	–	2.704	–	–	44

[a] Y = S, Se, Te; X = Cl, Br, I; [b] the crystals are orthorhombic, the possible space groups are *Ammm*, *A*2*mm*, *Am*2*m*, *Amm*2 and *A*222; [c] the position is statistically occupied by Cl and Br.

indicates that the structure is organised similar to a dense packing typical of many chalcogenides and halides.

In the crystal structure of β-$Hg_3S_2Cl_2$, virtually linear –S–Hg–S– groups forming closed isolated [$Hg_{12}S_8$] cubes with the S atoms in their vertices (Table 1, Fig. 3) can be identified.[22] The Cl atoms are located both in the centres of the cubes and between them. According to an analysis of the interatomic distances and bond angles, the sulfur atoms are coordinated (similar to those in α-$Hg_3S_2Cl_2$) by three mercury atoms to form strong covalently bound trigonal pyramidal SHg_3 groups, which can be considered as basic building blocks of the structure. Closed isolated [$Hg_{12}S_8$] cubes are composed of eight SHg_3 groups. It is interesting to note that in both of these cubic structures (*i.e.*, α- and β-$Hg_3S_2Cl_2$), each sulfur atom is located on the spatial diagonal of the cubic lattice, *i.e.*, on the three-fold axis, in the intersection point of three virtually perpendicular linear –S–Hg–S– groups. Such isolated cubes occur also in other classes of compounds, in particular, they are similar to the [Si_8O_{12}] cubes found [45] in octasilsesquioxanes (and can be actually regarded as their antitypes).

The crystal structure of the γ modification of $Hg_3S_2Cl_2$ was solved [35] as belonging to the order–disorder type. It is composed of different polytypes with the prevalence of blocks with the *A*2/*m* or *F*2/*m* symmetries. The crystal structure includes layers built up of the SHg_3 groups interlinked by sharing mercury vertices to

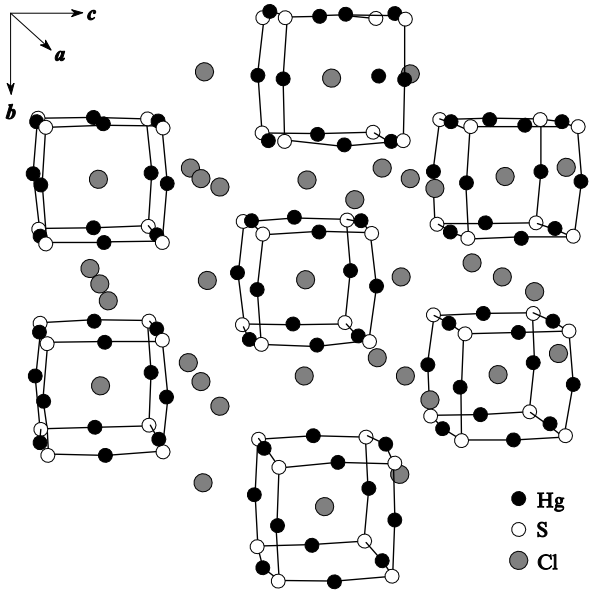


Figure 3. A fragment of the crystal structure of β-$Hg_3S_2Cl_2$.

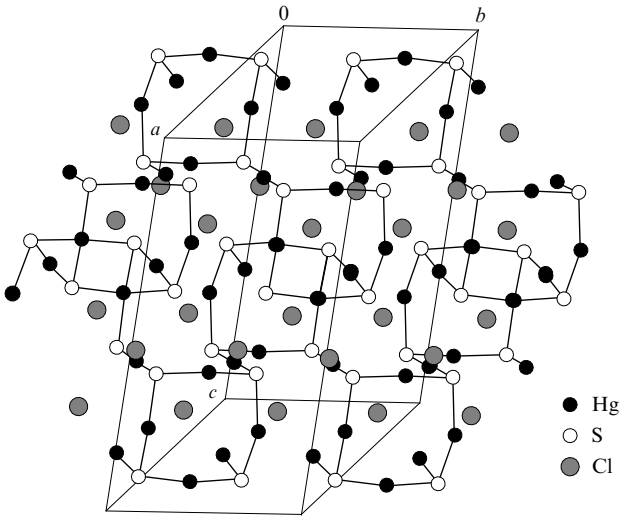


Figure 4. $[Hg_3S_2]^{2+}_{\infty\infty}$ puckered layers with closed $[S_4Hg_4]$ rings in the crystal structure of γ-$Hg_3S_2Cl_2$.

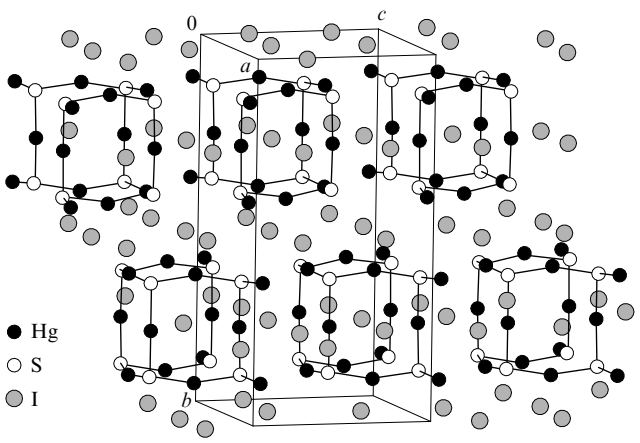


Figure 5. $[Hg_3Y_2]^{2+}_{\infty}$ step-like polycationic ribbons composed of the closed $[S_4Hg_4]$ rings going along the [100] direction in the crystal structure of $Hg_3S_2I_2$.

form $[Hg_3S_2^{2+}]_{\infty\infty}$ polycations. Within the layers, the Hg–S and Hg–Cl bonds are covalent and ionic, respectively (Table 1, Fig. 4). A comparison of the polycationic motifs in α-$Hg_3S_2Cl_2$ and γ-$Hg_3S_2Cl_2$ reveals that in the case of α-$Hg_3S_2Cl_2$, these groups are characterised by the 3*m* symmetry and the covalent Hg–S bonds form a spatial framework. In the γ modification, the SHg_3 groups appear distorted and the network of the covalent Hg–S bonds extends only in two dimensions. Each pair of neighbouring layers is bridged by a system of the Hg–S bonds. However, the whole structure is joined only by significantly weaker Hg···Cl contacts. This explains the perfect cleavage of the γ-$Hg_3S_2Cl_2$ crystals parallel to the (100) plane.

Two polymorph modifications of $Hg_3S_2Br_2$, *viz*., α and β, were prepared and characterised.[23] In the case of the α phase, nearly undistorted SHg_3 groups act as the basic structural unit. Similar to the situation observed in β-$Hg_3S_2Cl_2$, eight such groups linked by the mercury atoms compose isolated closed $[Hg_{12}S_8]$ cubes with the S atoms in their vertices, which can be regarded as main building blocks of the structure. The Br atoms are located both in the centres of the cubes and between them.

The monoclinic modification β-$Hg_3S_2Br_2$ (Ref. 23) is isostructural to $Hg_3Se_2Br_2$.[36] X-Ray diffraction patterns of $Hg_3Se_2Br_2$, γ-$Hg_3S_2Cl_2$ and β-$Hg_3S_2Br_2$ are very similar.[23] The crystal structure of γ-$Hg_3S_2Br_2$ remains unknown.

The crystal structures of isomorphous $Hg_3S_2I_2$ and $Hg_3Se_2I_2$ have been reported.[24] The mercury atoms therein are covalently bound to two chalcogen atoms with the mean Hg–Y bond lengths of 2.411 Å and 2.512 Å for Y = S and Se, respectively. The Y–Hg–Y bond angles lie in the range of 160.8–163.9° and 161.48–171.78° for $Hg_3S_2I_2$ and $Hg_3Se_2I_2$, respectively. The mercury and chalcogen atoms form Hg–Y chains with the mean Hg–Y–Hg angles of 99.3° and 96.9° for $Hg_3S_2I_2$ and $Hg_3Se_2I_2$, respectively. The Hg–Y chains go along the *a* axis parallel to each other and are interlinked by the mercury atoms to form step-like ribbons (Fig. 5). Since the tricoordinated chalcogen atoms in the YHg_3 groups are characterised by the oxidation state –2, these one-dimensional polycations can be formulated as $[Hg_3Y_2]^{2+}_{\infty}$. The Hg–I interatomic distances exceeding 3 Å clearly indicate the ionic character of bonding. The iodide ions are located both inside the covalently bound ribbons and between them. Therefore, the structures of $Hg_3S_2I_2$ and $Hg_3Se_2I_2$ reveal a new type of the mutual disposition of the trigonal YHg_3 groups for compounds of the $Hg_3Y_2X_2$ family (Y = S, Se or Te; X = Cl, Br or I).

Minets *et al*.[36] reported on the synthesis and structural studies of selenohalides $Hg_3Se_2Br_2$ and $Hg_3Se_2I_2$. The former compound is isostructural to β-$Hg_3S_2Br_2$. Each mercury atom is covalently bound to two selenium atoms, whereas each selenium atom is connected with three mercury atoms to form the $SeHg_3$ groups (see Table 1). These groups are linked by sharing Hg vertices into $[Hg_{12}Se_8]_{\infty\infty}$ puckered layers. The majority of the Hg–Se bonds (5/6) are involved into closed $[Hg_4Se_4]$ rings oriented in two different ways and the remaining bonds combine the rings into layers *via* the Hg–Se–Hg bridges. The Br atoms are localised inside the $[Hg_{12}Se_8]_{\infty\infty}$ layers and between them. Similar puckered layers are observed in the crystal structure of γ-$Hg_3S_2Cl_2$.[35]

The authors[36] assign the structure of $Hg_3Se_2I_2$ to the same type as α-$Hg_3S_2Br_2$, *i.e*., the structure containing isolated closed $[Hg_{12}Se_8]$ cubes with the Se atoms in their vertices. The I atoms are located both in the centres of the cubes and between them. It is of note that this conclusion contradicts the results reported by Beck and Hedderick.[24]

The crystal structure of $Hg_3Te_2I_2$ has been studied by several authors.[36, 37] Its unit cell contains three types of Hg atoms in the sites with point symmetries 1, $\bar{1}$ and 2. The coordination polyhedron of the Hg atoms in the inversion centres can be described as a distorted octahedron with four relatively long Hg–I bonds (3.425–3.499 Å) and two short Hg–Te bonds (2.648 Å, the TeHgTe angle is 180°). Meanwhile, the Hg atoms residing on the 2-fold axes are surrounded by two Te atoms with the Hg–Te bond lengths of 2.678 Å and two I atoms at longer distances [$(Hg–I)_{av}$ of 3.093 Å, the TeHgTe and IHgI angles are 157.80° and 100.99°, respectively]. Therefore, this type of crystallographically independent mercury atoms is characterised by the tetrahedrally distorted 'butterfly' coordination. The shortest Hg···Hg distance is 3.782 Å. According to a crystal chemical analysis, a complex framework of the Hg–Te bonds is realised in the $Hg_3Te_2I_2$ structure. It is built up of the $[Te_8Hg_{12}]$ fragments, which are in turn a combination of two $[Te_4Hg_4]$ rings related to each other by the two-fold symmetry axis parallel to the ring plane linked by a Te–Hg–Te bond. These fragments are assembled into a crankshaft ribbon, which differs from the $[Y_4Hg_6]_{\infty}$ ribbon in that only a half of the rings therein are closed and open rings form bonds with the neighbouring translationally equivalent chains. This gives rise to a framework with non-uniformly distributed bonds: 2/3 of the Hg–Te bonds form identically oriented closed $[Te_4Hg_4]$ rings, whereas 1/3 of the bonds link these rings by the Hg–Te–Hg bridges (Fig. 6). The eight-membered $[Te_4Hg_4]$ rings in the crystal structure of $Hg_3Te_2I_2$ have no shared edges with neighbouring rings, which is typical of other ribbon and layered Hg–Y motifs; this constitutes the principal distinction of this structural type from the structures of other known chalcohalides. All four Te–Hg–Te bonds formed by a ring are bridging, they link the ring with four neighbouring ones at different levels.

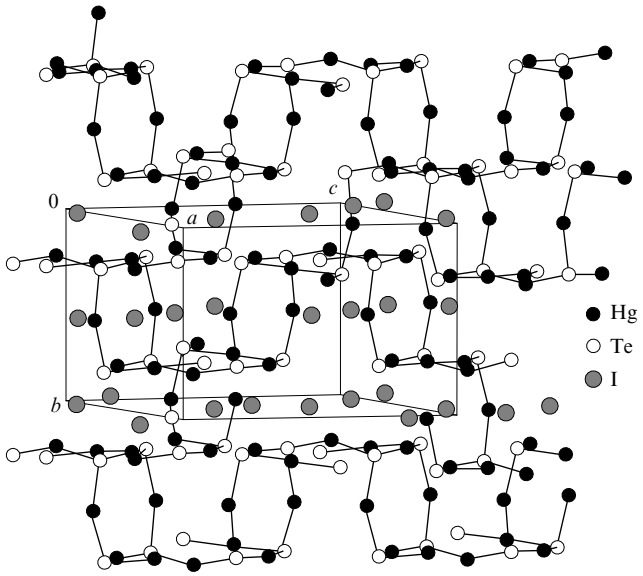


Figure 6. A complicated framework of the Hg – Te bonds in the crystal structure of $Hg_3Te_2I_2$.

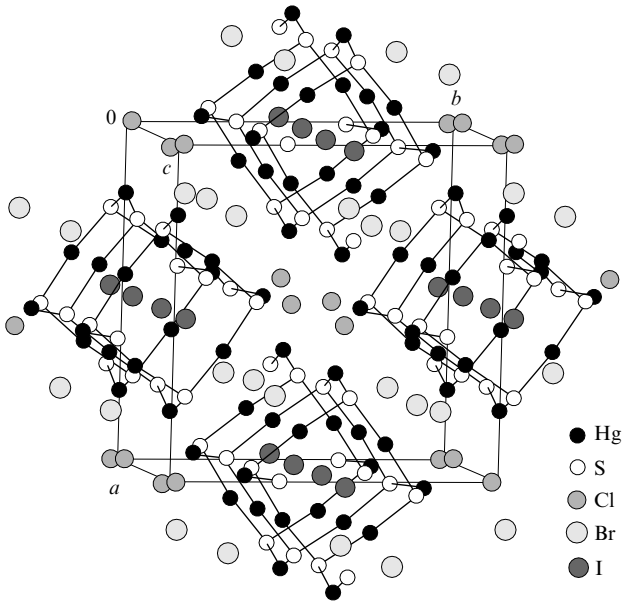


Figure 7. Crankshaft ribbons composed of closed $[S_4Hg_4]$ rings going along the [001] direction in the crystal structure of the synthetic analogue of grechishchevite $Hg_3S_2Br_{1.0}Cl_{0.5}I_{0.5}$.

Voroshilov and Minets [39] described the crystal structure of Hg_3Te_2BrI, which belongs to the structural type of β-$Hg_3S_2Br_2$ ($Hg_3Se_2Br_2$). Due to the presence of two different halogens, the morphotropic transition $Hg_3Se_2Br_2 \rightarrow Hg_3Te_2BrI$ is accompanied by lowering of the structure symmetry (space group $C2/m \rightarrow C2$) with the approximate retention of the unit cell parameters due to the regular iodide substitution for a half of the bromide ions.

Mercury sulfohalides rarely occur in nature. Only a few minerals within the ternary $Hg_3S_2Cl_2 - Hg_3S_2Br_2 - Hg_3S_2I_2$ system are known, all of them have structures closely related to each other. One of them (corderoite) has been discussed above in the beginning of Section II.2.a.

Crystals of a synthetic mercury chalcohalide that represents the analogue of naturally occurring mineral grechishchevite [28] have been structurally elucidated by means of X-ray diffraction.[40] In agreement with the refined stoichiometry $Hg_3S_2Br_{1.0}Cl_{0.5}I_{0.5}$, each mercury atom is connected with two sulfur atoms. As in other structures of mercury chalcohalides with a common formula $Hg_3Y_2X_2$, covalently bound S – Hg – S and SHg_3 groups assembled into a general motif can be readily identified in the crystal structure. A significant deviation of some of the SHgS angles (141.8° and 140.9°) from the linearity typical of bivalent mercury compounds [1] is of note. The halogen atoms are located between the zigzag chains. The eight-membered $[Hg_4S_4]$ rings composed of the SHg_3 groups are assembled into infinite crankshaft ribbons going along the [001] direction. As has been mentioned above, similar polycationic motifs were found [24] in $Hg_3S_2I_2$ and $Hg_3Se_2I_2$. In these structures, all ribbons are translationally equivalent, whereas they are related to each other by the inversion centre and 2_1-axis in $Hg_3S_2Br_{1.0}Cl_{0.5}I_{0.5}$. This difference is sufficient to classify the structure of the grechishchevite analogue as a new structural type (Fig. 7).

Naturally occurring mercury sulfohalide Hg_3S_2ClI was characterised as a new mineral radtkeite in 1991.[29] A few years later, its synthetic analogue $Hg_3S_2Cl_{1.00}I_{1.00}$ was prepared and its crystal structure was determined.[41] As in the case of $Hg_3S_2Br_{1.0}Cl_{0.5}I_{0.5}$,[40] the SHgS groups deviate significantly from the linearity (see Table 1). The SHg_3 groups form $[Hg_{12}S_8]_{\infty\infty}$ puckered layers similar to those found in the crystal structures of γ-$Hg_3S_2Cl_2$,[35] β-$Hg_3S_2Br_2$ [23] and $Hg_3Se_2Br_2$.[36] The orientation of the layers strictly corresponds to the planes of perfect cleavage of the crystals.

A series of isostructural minerals $Hg_3S_2Cl_mBr_n$ ($m+n=2$; $m > n$, lavrentievite and $m < n$, arzakite) [26, 27] have not been studied by means of X-ray crystallography due to the lack of suitable single crystals. Attempted syntheses of these minerals afforded new mercury chalcohalides corresponding to compositions $Hg_3S_2Cl_{1.5}Br_{0.5}$ (I), $Hg_3S_2Cl_{1.54}Br_{0.46}$ (II) [42] and $Hg_3S_2Br_{1.5}Cl_{0.5}$ (III, IV),[43] which have been successfully characterised by single-crystal X-ray diffraction (see Table 1).

Compound I is isostructural to synthetic γ-$Hg_3S_2Cl_2$, β-$Hg_3S_2Br_2$, $Hg_3Se_2Br_2$ and Hg_3S_2ClI (a synthetic analogue of radtkeite). A part of the halogen sites in the structure are statistically occupied by Cl and Br.

Compound II is isostructural to β-$Hg_3S_2Cl_2$ except for some increase in the lattice parameter a due to the incorporation of larger bromine atoms. The monoclinic modification III is isostructural to the synthetic compound α-$Hg_3S_2Br_2$, and the cubic modification IV is isostructural to β-$Hg_3S_2Cl_2$. In the latter structure, 64 Br atoms are located in the nodes of a sublattice with a sublattice constant $a/4$, and eight $[Hg_{12}S_8]$ groups are arranged in a way similar to that found in β-W: they are located in the nodes and in the centre of the unit cell; additionally, each face of the unit cell accomodates these two groups.

b. 3 : 1 : 4 Mercury chalcohalides

Two isomorphous compounds Hg_3TeCl_4 and Hg_3TeBr_4 were found in the $HgTe - HgCl_2$ (see Ref. 22) and $HgTe - HgBr_2$ (Ref. 23) systems (see Table 1). Both Hg_3TeX_4 compounds (X = Cl or Br) have layered structures with puckered layers stacked nearly parallel to the crystallographic xz plane, which agrees with the fact that the crystals manifest perfect cleavage along the (010) plane. Double layers oriented perpendicular to the y axis contain the halogen, tellurium and mercury atoms along with the $TeHg_3$ pseudotrigonal pyramids analogous to the SHg_3 groups observed in the $Hg_3Y_2X_2$ chalcohalides described above. The isolated $TeHg_3$ groups are arranged in such a way that two mercury atoms are located in the same layer as the tellurium atom, whereas the third Hg atom is located in the neighbouring layer (Fig. 8) thus making a covalent contribution into the predominantly ionic bonding between the atoms within a double layer. Owing to the stoichiometry change, the $TeHg_3$ groups are slightly more distorted than the YHg_3 groups in $Hg_3Y_2X_2$ (Y = S, Se or

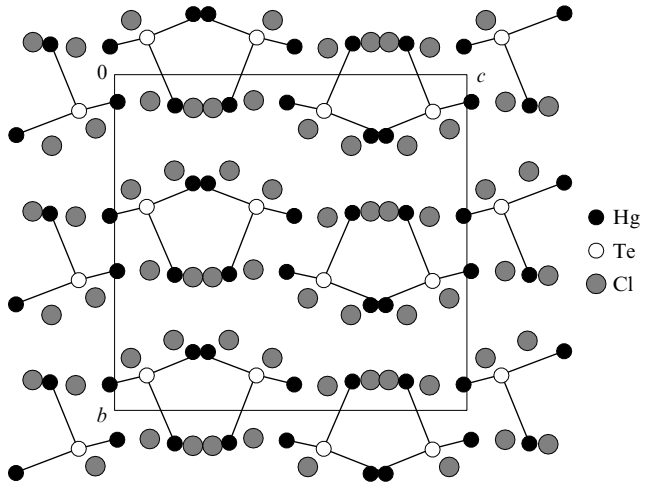


Figure 8. A projection of the crystal structure of Hg_3TeCl_4 onto the (100) plane.

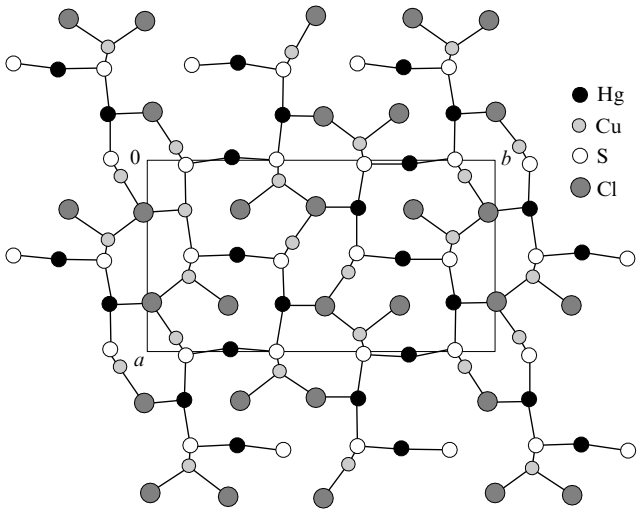


Figure 9. A projection of the crystal structure of CuHgSCl onto the (001) plane.

Te; X = Cl, Br or I); the spread in the HgYHg bond angles increases from 3° (in $Hg_3S_2Cl_2$) to 7° (in Hg_3TeCl_4).

In a study of the $HgTe-HgI_2$ system, a new compound Hg_3TeI_4 has been found and an attempt at determining its structure from powder X-ray diffraction data has been undertaken.[44] According to the results obtained, the compound possesses a structure similar to that of sphalerite (ZnS) with a statistical distribution of atoms over the available sites, which can be described as a cubic close packing of the anions with the mercury cations statistically occupying its tetrahedral cavities (see Table 1). The authors also suggested that Hg_3TeI_4 in the ordered form can contain fragments of the red modification of HgI_2 bridged by chains composed of the HgX_4 tetrahedra (X = Te or I) in a way similar to that observed in the crystal structure of SiS_2.

3. Preparation and crystal structures of quaternary mercury chalcohalides

a. Synthesis and crystal structures of MHgYX compounds (M = Cu or Ag; Y = S or Se; X = Cl, Br or I)

Silver and copper halides are well known cationic conductors. With this regard, the crystal structures of compounds of the MHgYX family (M = Cu or Ag; Y = S or Se; X = Cl, Br or I) have been in the focus of intense investigations. Main methods for their preparation can be classified into two types: (a) solid-state reactions of appropriate stoichiometric amounts of the binary precursors MX and HgY in sealed evacuated ampoules upon heating to a specific temperature for a certain time; (b) hydrothermal reactions of the starting binary components MX and HgY in concentrated or dilute solutions with HCl, HBr or HI as solvents in sealed evacuated ampoules at a certain temperature.

The major crystallographic and crystal chemical parameters of the MHgYX compounds are summarised in Table 2.

The quaternary sulfohalides CuHgSCl and CuHgSBr are isostructural. According to the X-ray diffraction study of their orthorhombic single crystals,[46] both crystal structures include planar crankshaft $-S-Hg-S-$ chains assembled into a spatial framework with pairs of strongly distorted $[CuS_2X_2]$ tetrahedra sharing an X–X edge (Fig. 9). The coordination polyhedron of the mercury atoms is supplemented to a distorted octahedron with the halogen atoms. The coordination polyhedron of the copper atoms can be regarded as a strongly distorted $[CuS_2X_2]$ tetrahedron, where the copper atom occupies a position shifted from the centre of the tetrahedron (see Table 2). The sulfobromide CuHgSBr undergoes a phase transition at 323 K transforming into another orthorhombic phase with the halved parameter *b*. The crystal structures of CuHgSBr (at 358 K) and β-AgHgSI (Ref. 50) become virtually identical after the *y* and *z* axes in the former crystal structure are interchanged.

The crystal structure of CuHgSI has been determined independently by two research groups using the Rietveld refinement of a powder X-ray diffraction pattern[48] and single-crystal X-ray diffraction.[47] As major structural units therein, the $-I-Cu-I-$ and $-S-Hg-S-$ zigzag chains going along the *c* axis can be identified (Fig. 10). The copper atoms are tetrahedrally coordinated by the S and I atoms, whereas the Hg atoms are linearly coordinated (see Table 2). The structure of CuHgSI is similar to those of CuHgSCl and CuHgSBr, except for the fact that the shape of the $-S-Hg-S-$ chains is distorted in the two latter structures.

As a part of an investigation into the CuCl–HgSe system, a new compound CuHgSeCl has been synthesised and character-

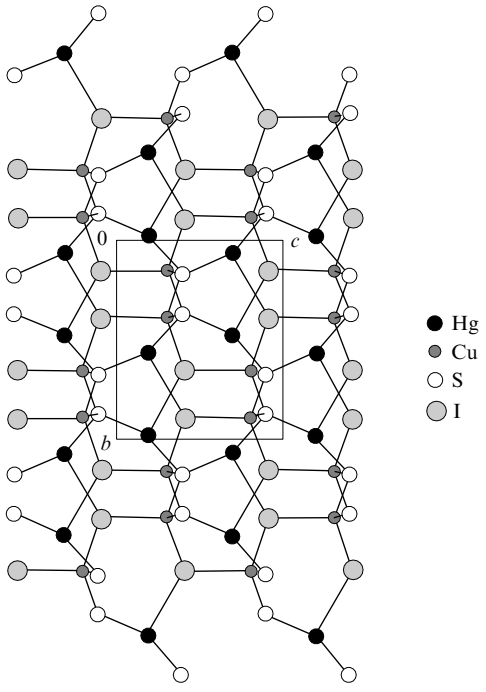


Figure 10. A projection of the crystal structure of CuHgSI onto the (100) plane.

Table 2. Crystallographic and crystal chemical parameters of quaternary mercury chalcohalides.

Compound	Space group (R_f)	Unit cell parameters /Å	Z	d_{calc} /g cm^{-3}	Bond lengths [a] /Å				Bond angles [a] /deg.						Ref.
					Hg–Y	M–Y	Hg–X	M–X	YHgY	HgYHg	YMY	XHgX	XMX	XMY	
Chalcohalides with a 1 : 1 cation-to-anion ratio															
CuHgSCl	*Pbam* (0.049)	a = 9.84 b = 17.75 c = 4.09	8	6.16	2.362 – 2.369	2.258 – 2.281	2.955 – 3.091	2.273 – 2.559	172.4 – 172.5	96.0 – 96.6	–	87.75	–	101.79 – 114.78	46
CuHgSBr (295 K)	*Pbam* (0.032)	a = 10.03 b = 18.33 c = 4.124	8	6.58	2.369 – 2.371	2.266 – 2.282	3.051 – 3.192	2.412 – 2.787	171.6 – 175.2	97.4 – 97.9	–	85.06	–	98.54 – 114.16	46
CuHgSBr (358 K)	*Pmam* (0.068)	a = 10.092 b = 9.184 c = 4.138	4	6.57	2.361 – 2.367	2.284	3.061 – 3.265	2.430 – 2.931	171.4 – 180.0	97.9	–	85.07	97.6	–	46
CuHgSI	$Pna2_1$ –	a = 7.183 b = 8.343 c = 6.989	4	–	2.359 – 2.369	2.311 – 2.322	3.212 – 3.999	2.633 – 2.743	153.8	98.8	–	–	106.5	103.8 – 116.0	47
	$Pna2_1$ (0.0416)	a = 7.1748 b = 8.3356 c = 6.9855	4	–	2.373	2.324	3.213	2.649	153.45	–	114.70	78.78	108.70	–	48
$CuHg_2S_2I$	$Cmc2_1$ –	a = 12.618 b = 7.224 c = 6.937	4	–	2.374	2.368 – 2.417 [b]	3.214 – 4.034	3.089 [b]	–	–	113.4 – 125.8 [b]	–	–	92.8 – 106.6 [b]	47
CuHgSeCl (see [c])	*Pbam* (0.071)	a = 6.9444 b = 12.7561 c = 4.2526	4	–	2.477 – 2.486	2.379	3.105 – 3.270	2.268 – 2.882	171.31	89.14	126.74	–	–	98.05 – 114.82	49
CuHgSeBr	*Pmma* (0.0591)	a = 10.201 b = 4.312 c = 9.256	4	–	2.462 – 2.475	2.392	3.073 – 3.358	2.434 – 2.787	173.02 – 180.0	–	128.7	–	–	109.52	50
AgHgSBr	*Pmma* (0.0547)	a = 9.648 b = 4.661 c = 9.426	4	–	2.354 – 2.363	2.498	3.092 – 3.357	2.679 – 3.109	171.4 – 180.0	–	137.80	–	–	109.23	50
α-AgHgSI	$P2_12_12_1$ –	a = 7.075 b = 7.732 c = 8.475	4	–	2.351	2.561 – 2.635	3.482 – 3.745	2.748 – 2.982	172.5	98.1	–	–	115.24	94.7 – 130.4	51
β-AgHgSI	*Pmma* –	a = 10.159 b = 4.648 c = 9.849	4	–	2.376	2.535	3.268 – 3.453	2.802 – 3.209	171.4 – 180.0	–	132.9	–	–	112.4	50
Ag_2HgSI_2	$Cmc2_1$ (0.0567)	a = 13.834 b = 7.470 c = 7.103	4	6.35	2.38 – 2.52	2.52	3.375 – 3.590	2.778 – 2.950	175.5	93.1	–	–	103.1 – 110.5	100.0 – 130.7	52

Table 2 (continued).

Compound	Space group (R_f)	Unit cell parameters /Å	Z	d_{calc} /g cm^{-3}	Bond lengths [a] /Å				Bond angles [a] /deg.						Ref.
					Hg–Y	M–Y	Hg–X	M–X	YHgY	HgYHg	YMY	XHgX	XMX	XMY	
Chalcohalides with a 3 : 4 cation-to-anion ratio															
$Hg_2SnS_2Br_2$ (see [d])	$P2_1/n$ (0.0543)	$a = 9.356$ $b = 8.028$ $c = 10.630$	4	6.352	2.345 – 2.369	2.909 – 2.921	–	2.840 – 2.966	171.5 – 173.5	86.8 – 105.0	–	–	–	–	53
$Hg_2PbS_2I_2$	$P4/mbm$ (0.039)	$a = 13.501$ $c = 4.593$	4	7.349	2.382 – 2.386	2.989	3.301 – 3.441	3.427 – 4.385	171.06	98.84	73.71 – 100.4	–	–	–	54
Naturally occurring chalcohalides															
$Hg_{4.6}Ag_{4.4}S_{4.6}\cdot$ $\cdot(Cl_2Br_{0.8}I_{1.6})$ (perroudite)	$P2_12_12_1$ (0.100)	$a = 17.430$ $b = 12.240$ $c = 4.350$	2	6.60	2.29 – 2.43	2.46 – 2.78	3.13 – 3.47	2.74 – 3.03	173.0 – 176.0	96.0 – 102.0	92.0 140.0	–	–	–	55
HgAgS(Cl,Br,I) (capgaronnite)	$P2_12_12_1$ (0.170)	$a = 6.803$ $b = 12.870$ $c = 4.528$	4	6.43	2.40 – 2.49	2.44 – 2.61	2.90 – 3.34	2.71 – 3.05	–	–	–	–	–	–	56
HgAgS(Cl,Br) (iltisite)	$P6_2$ –	$a = 8.234$ $c = 19.381$	12	6.59	–	–	–	–	–	–	–	–	–	–	57

[a] M = Cu, Ag, Sn, Pb; Y = S, Se; X = Cl, Br, I; [b] the position is occupied by the Cu and Hg atoms in a 0.53 : 0.47 ratio; [c] the Cl–Cl distance is 3.738 Å; [d] $\beta = 102.68°$; the HgSSn angles are 95.7 – 113.9°.

ised.[49] Its structure represents a framework assembled from the $-Se-Hg-Se-$ chains running along the [100] direction. Two chains related to each other by a translation along *c* are bridged by distorted $[CuSe_2Cl_2]$ tetrahedra involving two Se atoms from different chains and two Cl atoms. The copper atoms in these tetrahedra are strongly shifted from the centres. Pairs of these tetrahedra combined by sharing a Cl–Cl edge assemble the $-Se-Hg-Se-$ chains lying in the *xy* plane into a framework. The geometry of the $-Se-Hg-Se-$ chains in CuHgSeCl differs from that of the $-S-Hg-S-$ chains in MHgSX (M = Cu or Ag; X = Cl, Br or I).[58] The $-Se-Hg-Se-$ chains are similar to the chains present in the structures of HgO, $Hg(OHg)_4Br$ and Hg_2O_2NaI described as zigzag chains (the '+ – + –' type) by Aurivillius,[1] whereas the chains in CuHgSCl are of the '+ + – –' type (*i.e.*, crankshaft chains) according to the same classification.

The preparation methods and crystal structures of isostructural chalcohalides CuHgSeBr, AgHgSBr and β-AgHgSI have been reported by Beck *et al.*[50] The structures are built up of puckered layers composed of crankshaft chains with the covalent Hg–Y bonds. These chains are assembled into a framework by pairs of strongly distorted $M[Y_2X_2]$ tetrahedra with shared X–X edges (Table 2, Fig. 11).

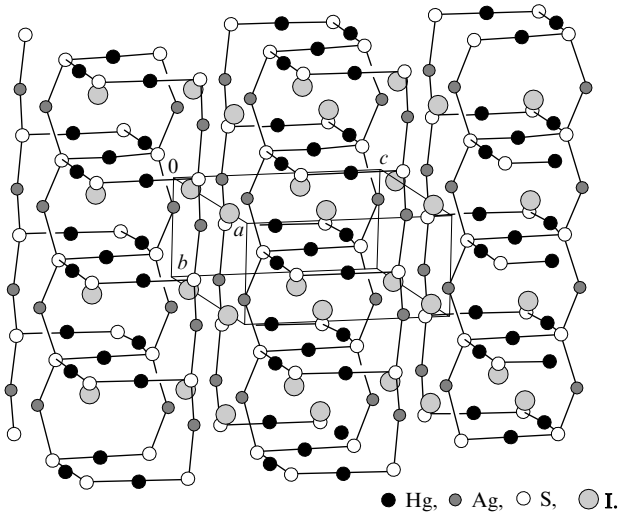


Figure 11. Puckered layers constituted by the Hg–S and Ag–S bonds in the crystal structure of β-AgHgSI.

A new phase, α-AgHgSI, has been synthesised recently.[51] Its structure is based on a distorted hexagonal close packing of the sulfur and iodine atoms. One fourth of the tetrahedral cavities of the packing is occupied by the silver atoms, whereas a half of the octahedral sites is occupied by the mercury atoms. The mercury atoms, like those in other mercuric compounds, are connected to two sulfur atoms. The $-S-Hg-S-$ chains (of the '+ – + –' type) oriented along the [100] direction are assembled into a framework by pairs of distorted $[AgS_2I_2]$ tetrahedra with shared I–I edges (Fig. 12). Each tetrahedron includes two S atoms from different chains and two I atoms. The low-temperature modification β-AgHgSI is transformed into high-temperature α-AgHgSI at 273 °C.

We conclude this section by considering two compounds that do not formally fall into the MHgYX family, although they also correspond to a 1 : 1 cation-to-anion ratio. The crystal structures of $CuHg_2S_2I$ (Ref. 47) and Ag_2HgSI_2 (Ref. 52) are similar. Each mercury atom is linearly coordinated to two sulfur atoms (see Table 2). In these structures, the planar (in the *yz* plane) zigzag $-S-Hg-S-$ chains go along the *c* axis (Fig. 13). The coordination polyhedron of the Hg atoms is supplemented by the I atoms to a distorted octahedron. In the crystal structure of

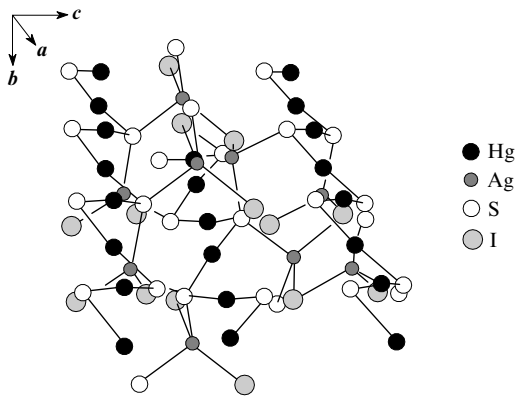


Figure 12. A fragment of the crystal structure of α-AgHgSI.

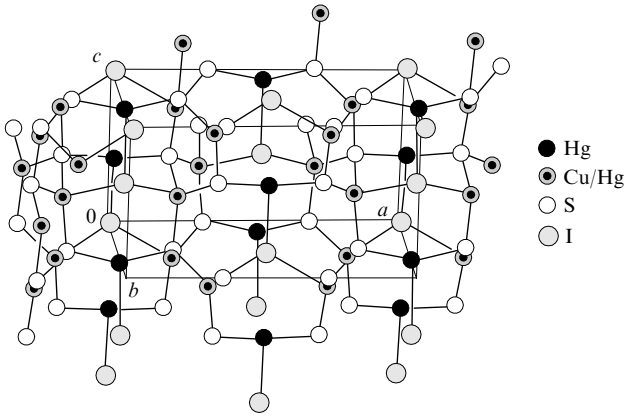


Figure 13. The crystal structure of $CuHg_2S_2I$.

$CuHg_2S_2I$, one of the cationic sites is statistically occupied by mercury and copper in a 0.47 : 0.53 ratio. The Hg/Cu cation is characterised by a distorted tetrahedral coordination environment composed of three S and one I atoms. The $[(Hg,Cu)S_3I]$ tetrahedra assemble the $-S-Hg-S-$ chains into a framework by vertex-sharing. In the crystal structure of $AgHg_2S_2I$, the silver atoms are surrounded by three I and one S atoms forming distorted tetrahedra. These tetrahedra assemble the $-S-Hg-S-$ chains into a framework by sharing their S vertices.

b. Quaternary mercury chalcohalides with a cation-to-anion ratio of 3 : 4

Blachnik *et al.*[53] reported on the synthesis of $Hg_2SnS_2Br_2$ by a solid-state reaction of HgS and $SnBr_2$. In the crystal structure of this compound, helical $-S-Hg-S-$ chains, which are nearly square in the cross-section, oriented parallel to [010] are packed into a tetragonal structure giving rise to voids accomodating the Sn_2Br_4 fragments (Fig. 14). The Hg atoms are characterised by a distorted octahedral coordination (two S plus four Br atoms, see Table 2).

In a study of quaternary compounds within the $HgS-PbI_2$ system involving elements of Groups 12, 14, 16 and 17,[54] a new sulfoiodide $Hg_2PbS_2I_2$ has been synthesised (see Table 2). In its crystal structure, the Hg atoms form two covalent bonds with the S atoms, and four longer Hg–I bonds supplement its coordination environment to distorted octahedral one. The coordination polyhedron of the Pb atoms can be described as a monocapped trigonal prism composed of four S and three I atoms. The sulfur atoms are tetrahedrally coordinated by two Hg and two Pd atoms. The 3D structure is built up of planar $[Hg_4S_4]$ rings stacked in columns along the [001] direction. The columns are linked by the

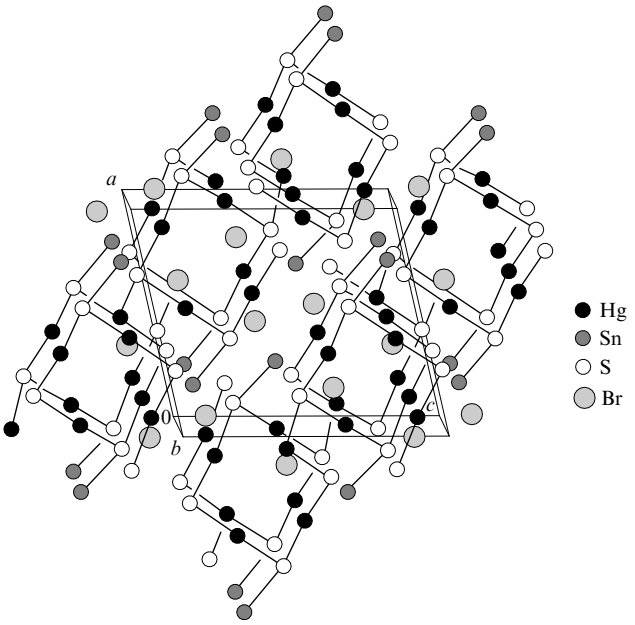


Figure 14. Helical axes $-S-Hg-S-$ going along the [010] direction in the crystal structure of $Hg_2SnS_2Br_2$.

Pb atoms coordinated to four S atoms from four $[Hg_4S_4]$ rings of two neighbouring columns into a spatial framework; the iodine atoms occupy its cavities (Fig. 15).

As has been noted by Blachnik *et al.*,[54] $Hg_2PbS_2I_2$ can be considered as a cinnabarite (α-HgS) (see Fig. 1) derivative built up of helical $-S-Hg-S-$ chains.[1] The replacement of an S^{2-} ion in cinnabarite with two I^- ions gives rise to the $Hg_3S_2I_2$ structure,[24] where the chains are joined by the Hg bridges. The coordination number of the sulfur atoms increases to three. The sulfoiodide $Hg_2PbS_2I_2$ can be regarded as a $Hg_3S_2I_2$ derivative that is obtained by the Pb^{2+} substitution for one third of the Hg^{2+} ions, this modification is accompanied by a change of the sulfur coordination to the tetrahedral one (2 Pb plus 2 Hg).

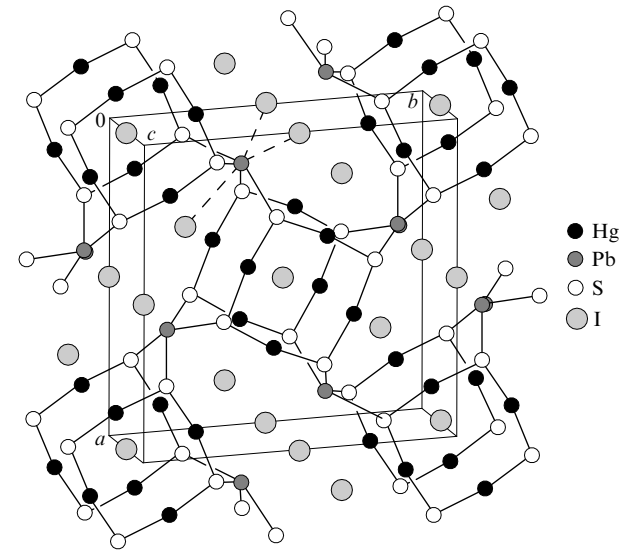


Figure 15. Columns of the $[Hg_4S_4]$ rings linked by the Pb atoms in the crystal structure of $HgPbS_2I_2$. The Pb—I bonds supplementing the coordination environment of the lead atoms to a monocapped trigonal prism are shown as dashed lines.

c. Naturally occurring quaternary mercury chalcohalides

Presently, there are only three known rare minerals falling into the class of quaternary mercury chalcohalides, *viz*., perroudite, capgaronnite and iltisite. Perroudite and capgaronnite contain three halogens (Cl, Br and I) at once; among naturally occurring ternary mercury suflohalides, all three halogens are present simultaneously only in grechishchevite.[28]

In the structure of perroudite $Hg_5Ag_4S_5(Cl,Br,I)_4$, the mercury atoms are covalently bound to two sulfur atoms to form specific crankshaft chains parallel to *b*.[55] The coordination environment of the mercury atoms is supplemented by the halogen X atoms to the distorted octahedral one; the halogen sites are occupied by the Cl, Br and I ions statistically. The silver atoms of the first type are tetrahedrally coordinated by three S and one X atoms (Ag—S 2.46–2.78 Å, Ag—X 2.99 Å), whereas those of the second type are tetrahedrally coordinated by three X and one S atoms (Ag—S 2.66 Å, Ag—X 2.59–3.03 Å). The $S-Hg-S-$ chains are assembled into a framework by the $[Ag(S,X)_4]$ tetrahedra (Fig. 16). An accurate refinement of the crystal structure indicated the complete mutual isomorphous substitution of the halogen atoms, Cl substitution for a part of the sulfur atoms and Ag substitution for a part of the mercury atoms. The mineral was finally formulated as $Hg_{4.6}Ag_{4.4}S_{4.6}Cl_{2.0}Br_{0.8}I_{1.6}$.

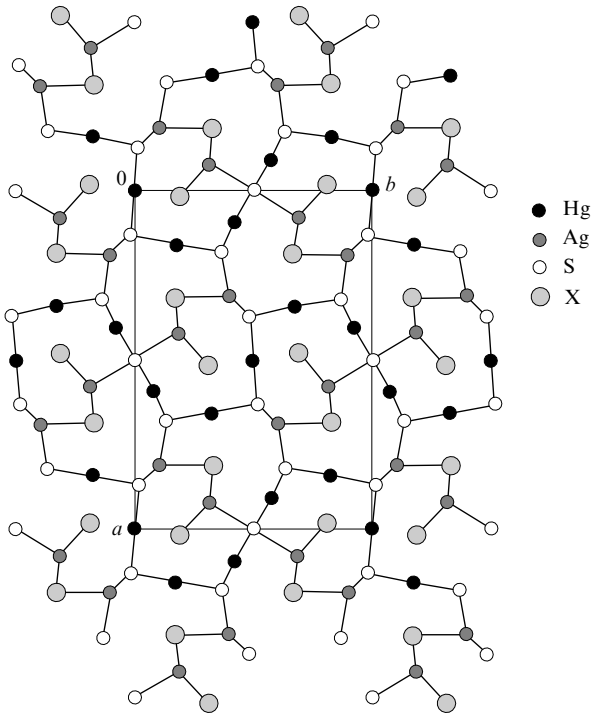


Figure 16. A projection of the crystal structure of perroudite $Hg_5Ag_4S_5X_4$ (X = Cl, Br or I) onto the (001) plane.

The mineral capgaronnite corresponds to the stoichiometry HgAgS(Cl,Br,I). In contrast to the framework structure of perroudite considered above, in the crystal structure of capgaronnite, the zigzag $-S-Hg-S-$ chains (of the '$+--+-$' type) are assembled into layers parallel to the (010) plane by pairs of edge-sharing $[AgS_2X_2]$ tetrahedra (Fig. 17).[56] The mercury atoms inside the chains are linearly coordinated by two S atoms, and four X atoms supplement their coordination to the octahedral one. The Ag atoms are tetrahedrally coordinated by two S and two X atoms.

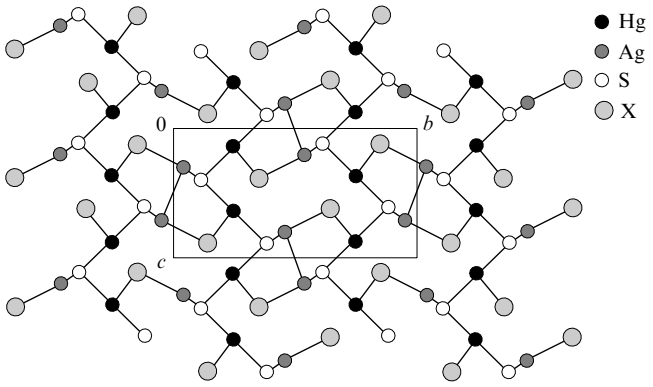


Figure 17. A projection of the crystal structure of capgaronnite HgAgSX (X = Cl, Br or I) onto the (100) plane.

A hexagonal polymorph of the orthorhombic capgaronnite, *viz*., iltisite HgAgS(Cl,Br), has been reported by Sarp *et al*.,[57] although its crystal structure has not been determined so far.

The major crystallographic and crystal chemical parameters of quaternary mercury chalcohalides are summarised in Table 2.

III. Mercuric oxohalides

Two binary mercury oxides are well known, *viz*., yellow orthorhombic (natural mineral montroidite) and red hexagonal phases.

According to investigations into the pressure-induced polymorphism in HgO,[59] a black polycrystalline powder with the tetragonal symmetry (the Laue class is 4/*mmm*) is formed at 35 GPa. The authors assume that the $-Hg-O-Hg-O-$ chains are preserved in the new structure, *i.e*., no dramatic structural rearrangement occurs.

A new triclinic phase of mercuric oxide has been reported by Benjamin.[60] It is spontaneously formed as a thin film on the surface of pure mercury under the action of oxygen under humidity. Meanwhile, stirring of mercury in ozonated oxygen affords a mixture of the orthorhombic and triclinic HgO modifications. According to X-ray diffraction data, the film represents the triclinic HgO modification with the double parameters of the orthorhombic unit cell. The structure contains zigzag $-Hg-O-Hg-O-$ chains with the bond lengths and angles typical of the HgO structures. Nevertheless, the Hg—Hg distance between the neighbouring chains is ~2.64 Å, which is rather typical of compounds of monovalent mercury. Therefore, Benjamin suggested this compound to be a mixed-valence one.

Mercury forms various oxo salts. In particular, a series of mercuric oxochlorides $n\,HgO \cdot HgCl_2$ (n = 0.5, 2, 3, 4) and an oxobromide $Hg(OHg)_4Br_2$ are known.

There are only a few quaternary mercury oxohalides. The heating of a mixture of PbO, $PbBr_2$, $HgBr_2$ and H_2O in a 3 : 1 : 2 : 1 ratio in a sealed evacuated ampoule at 280 °C yields[61] $HgPb_2O(OH)Br_3$. Within the $PbO-HgCl_2$ system, single crystal of $HgPb_2O_2Cl_2$ has been synthesised by heating a mixture of PbO and $HgCl_2$ (in a 2 : 1 ratio) in a sealed evacuated ampoule at 275–300 °C.[62] As a part of investigations into Hg-containing high-temperature superconductors, the first barium mercury oxochloride $BaHg_2O_2Cl_2$ has been synthesised by heating a mixture of BaO_2 and Hg_2Cl_2 in a sealed ampoule at 360 °C for three days.[63] The first strontium mercury oxochloride $SrHg_2O_2Cl_2$ has been prepared as reddish brown powder by the solid-state reaction of strontium peroxide SrO_2 with calomel Hg_2Cl_2.[64]

The crystal structure of the orthorhombic HgO modification reveals infinite planar zigzag $-O-Hg-O-Hg-$ chains (of the $+-+-$ type)[1] lying in the *ac* plane parallel to *a* (Hg—O 2.039–2.067 Å, the OHgO and HgOHg angles are 179.5° and 107.3°, respectively). A comparison of the crystal structures of HgO and the hexagonal modification of mercury sulfide (cinnabarite) reveals similar principles of their structural organisation. The planar zigzag $-O-Hg-O-Hg-$ chains in oxide correspond to the infinite helical $-S-Hg-S-Hg-$ chains oriented parallel to *c* in sulfide. In both cases, the X—Hg—X bond angles do not deviate substantially from 180°. A decrease in the Hg—X—Hg bond angle on going from oxygen (109°) to sulfur (105°) fully reproduces the respective trend observed in other structures.

The crystal structure of hexagonal red mercury oxide is built up of infinite helical $(-O-Hg-O-)_\infty$ chains going parallel to the *c* axis. The Hg—O bond lengths (2.03 Å) and Hg—O—Hg (108°) and O—Hg—O (176°) bond angles inside the chains are nearly the same as in the planar zizag chains of the orthorhombic modification.[59] Four O atoms at 2.79–2.90 Å supplement the coordination polyhedron of the Hg ions to a strongly distorted octahedron. Inside the chains, the Hg—O bond in the hexagonal modification is of the same type as in the orthorhombic modification but the interchain bonds are significantly weaker (the Hg···O distances are 2.79 and 2.90 Å, the Hg···Hg distances are 3.30, 3.58 and 3.72 Å, the O···O distances are 3.41–4.06 Å).

1. The crystal structures of ternary mercuric oxohalides

The basic crystallographic and crystal chemical parameters of mercury oxohalides are listed in Table 3.

The structure of Hg_3OCl_4 (n = 0.5) includes the Cl^- anions and pyramidal $[OHg_3Cl_3]^+$ cations (Ref. 65). The O atoms are located on the body diagonals of the cubic unit cell (that is on the three-fold axes) coordinating three mercury atoms. The oxygen atoms are shifted by 0.30 Å from the centres of regular triangles composed of the mercury atoms. Furthermore, each mercury atom is connected to a chlorine atom (2.302 Å) in a way that three linear Cl—Hg—O groups intersect at the central oxygen atom. Therefore, the triangle composed of mercury atoms is located inside the regular triangle of the chlorine atoms; their edges are virtually parallel. The remaining chlorine atoms are situated at significantly larger distances from the mercury atoms. Each $[OHg_3Cl_3]^+$ pyramidal cation is surrounded by three Cl^- anions and *vice versa* each Cl^- anion is surrounded by three $[OHg_3Cl_3]^+$ cations. The bonds inside the pyramidal cation are covalent, as evidenced by the respective Hg—O and Hg—Cl bond lengths (see Table 3). The Hg—O—Hg bond angle (118°) is also indicative of the covalent bonding between the oxygen and mercury atoms.

A similar nearly planar $[O(HgI)_2(HgOH)]^+$ cation occurs[71] in two isostructural compounds $[O(HgI)_2(HgOH)]ClO_4$ and $[O(HgI)_2(HgOH)]BF_4$ (Hg—O 1.99–2.12 Å, HgOHg 115.4–128.1°; Hg—OH 1.98 Å, Hg—I 2.57 Å, OHgI 175.0–177.2°, OHgOH 175.9°).

In the structure of α-$Hg_3O_2Cl_2$ (n = 2), two crystallographically independent mercury atoms are characterised by different coordination environments: the first type Hg atoms are linearly coordinated by two O atoms (Hg—O 2.07 Å), whereas the second type Hg atoms are coordinated by three O atoms (Hg—O 2.17, 2.32 and 2.33 Å).[66] Nearly planar HgO_3 triangles are combined by edge- and vertex-sharing into puckered layers lying in the *ac* plane. The layers are further assembled into a framework by the linearly coordinated Hg atoms. The chlorine atoms occupy cavities of the framework (Fig. 18). Examples of non-linear coordination types involving a third O atom (T-shaped, *etc*.), which are less typical of Hg^{2+} cations, can be found elsewhere.[3]

There is another modification of this compound, β-$Hg_3O_2Cl_2$, which can be alternatively formulated as $Hg_6O_4Cl_4$.[67] Its structure is more complex than that of the α phase, which is evidenced by a four times larger unit cell volume. A unit cell of the β-phase

Table 3. Crystallographic and crystal chemical parameters of mercury oxohalides.

Compound	Space group (R_f)	Unit cell parameters		Z	d_{exp}, d_{calc} /g cm^{-3}	Bond lengths[a] /Å				Bond angles[a] /deg.					Ref.
		translations /Å	β angle /deg.			Hg–O	Hg–X	M–O	M–X	OHgO	HgOHg	OHgX	MOM	HgOM	
Ternary oxohalides															
Hg_3OCl_4	$P2_13$ (0.108)	$a = 9.236$		4	6.43 6.45	2.062	2.302, 2.987–3.085			–	118.0	175.7			65
α-$Hg_3O_2Cl_2$	$P2_1/c$ (0.059)	$a = 6.3100$ $b = 6.8657$ $c = 6.8579$	114.36	2	8.53 8.59	2.07–2.23	2.706–3.259			82, 123, 149, 180	98.3–114.3	–			66
β-$Hg_3O_2Cl_2 \equiv Hg_6O_4Cl_4$	$P2_1/c$ (0.059)	$a = 10.838$ $b = 9.317$ $c = 11.564$	108.90	4	8.44 8.47	2.028–2.184, 2.436–2.781	2.364, 2.753–2.934			154.9–175.1	104.9–120.7	158.9			67
β-$Hg_3O_2Cl_2$	$P2_1/c$ (0.04)	$a = 10.826$ $b = 9.310$ $c = 11.515$	71.04	8	8.53 8.53	2.035–2.778	2.362–3.368			154.46–174.04	85.5–121.9	156.91			68
$Hg_5O_4Br_2$	*Ibam* (0.105)	$a = 11.888$ $b = 6.185$ $c = 11.746$		4	9.23 9.43	2.05–2.09	2.958			86–133, 163, 175	113	–			69
$Hg_5O_4Cl_2$ (pinchite)	*Ibam* (0.030)	$a = 11.619$ $b = 6.105$ $c = 11.710$		4	– 9.29	2.04–2.71	2.916–3.142			67.0–134.2	113.2	–			70
Quaternary oxohalides															
$HgPb_2O(OH)Br_3$	*Aba*2 (0.0653)	$a = 14.652$ $b = 14.6491$ $c = 7.782$		8	–	2.07	2.422–3.347	2.29–2.42	–	–	–	–	103.27–108.32	114.61–116.48	61
$HgPb_2O_2Cl_2$	$C2/m$ (0.047)	$a = 11.788$ $b = 3.910$ $c = 7.749$	122.64	2	–	2.054	2.981	2.340–2.388	3.291–3.402	–	–	–	105.99–109.87	108.26–113.10	62
$BaHg_2O_2Cl_2$	$P4/mbm$ (0.0621)	$a = 11.8442$ $c = 4.2865$		4	–	2.03–2.09, 2.382	3.030–3.107	2.72	3.119–3.220	169	101	–	–	–	63
$SrHg_2O_2Cl_2$	$P2_1/n$ (0.0598)	$a = 9.943$ $b = 7.023$ $c = 8.288$	102.4	4	–	2.046–2.491	–	2.542–2.684	–	–	108.42–108.56	–	107.24–113.16	103.88–119.13	64

[a] M = Ba, Pb, Sr; X = Cl, Br.

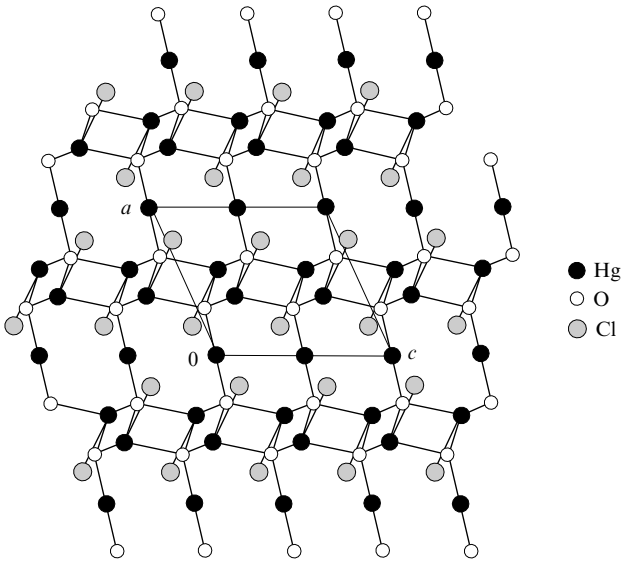


Figure 18. A projection of the crystal structure of α-$Hg_3O_2Cl_2$ onto the (010) plane.

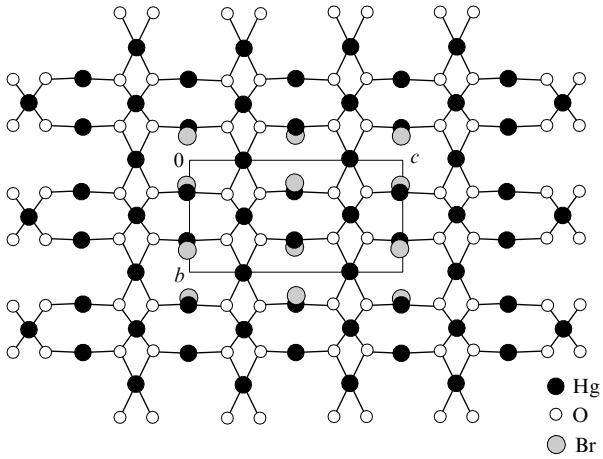


Figure 19. A projection of the crystal structure of $Hg(OHg)_4Br_2$ onto the (100) plane.

contains six crystallographically independent mercury atoms. One of them is linearly coordinated by two oxygen atoms (Hg–O 2.068 and 2.099 Å, the OHgO angle is 175.1°), four types of the Hg atoms are coordinated (similarly to the structure of α-$Hg_3O_2Cl_2$) by three O atoms in the 2+1 manner (Hg–O 2.028–2.184 and 2.436–2.781 Å, the OHgO angles are 154.9–171.4°). The last type of the Hg atoms forms close contacts with two O atoms (Hg–O 2.100 and 2.586 Å) and binds covalently a Cl atom (Hg–Cl 2.364 Å, the OHgCl angle is 158.9°). The structure is built up of infinite Hg–O chains (of the '+ + – –' type).[1] Four these symmetry-related chains cross a unit cell nearly parallel to the [001] direction, a repeating unit of a chain forms two O–Hg–O bonds with the nearest chain, *i.e.*, individual chains are assembled into pairs forming 12-membered $(Hg-O)_6$ rings. Taking into account slighlty longer contacts, these double chains are joined by pairs into extended ribbons. The sixth type of the Hg atoms is connected to a chain oxygen atom and a Cl atom to form a finite –Hg–Cl side chain. As a result, extended double ribbons with the general formula $[Hg_2(OHg)_4Cl^{3+}]_n$ act as the primary building blocks of the structure. The ribbons are further assembled by the Hg atoms into a complicated framework with the remaining Cl atoms occupying its cavities. The Hg–Cl bonds with these Cl atoms are essentially ionic, according to their lengths. The authors of this study proposed to write the crystal chemical formula of this compound as $[Hg_2(OHg)_4Cl]Cl_3$. It is of note that the structure of this phase was determined independently by another research group[68] and they described its structure as a motif of condensed cationic oxo-centred tetrahedra (see Section IV.1).

The presence of extended virtually planar –O–Hg–O– chains containing two of three crystallographically independent types of the Hg atoms and all O atoms constitutes the main structural feature of mercury oxobromide $Hg(OHg)_4Br_2$ ($n = 4$).[69] They can be classified as crankshaft chains of the '+ + – –' type (Hg–O 2.05 and 2.09 Å, the OHgO angles are 175° and 163°, whereas the HgOHg angles are 113°). The remaining Hg atoms bridging the chains into a framework are located between the planes of the chains; these Hg atoms are tetrahedrally coordinated by the oxygen atoms (Hg–O 2.24 Å, the OHgO angles are 86–133°). Cavities of the framework accomodate the Br atoms (Fig. 19). The crystal structure of naturally occurring mercury oxochloride $Hg_5O_4Cl_2$, or $Hg(OHg)_4Cl_2$ (pinchite), as determined by Hawthorne *et al.*,[70] appeared fully analogous to that of $Hg(OHg)_4Br_2$.

The Cl atoms play different roles in the structures of the mercury oxochlorides. Above, in α-$Hg_3O_2Cl_2$ and $Hg_5O_4Cl_2$, all bonds between the Cl atoms and the respective frameworks ($[Hg_3O_2^{2+}]_n$ and $[Hg_5O_4^{2+}]_n$, respectively) are ionic. In β-$Hg_3O_2Cl_2$ and Hg_3OCl_4, a fraction of the Cl atoms (25% and 75%, respectively) form covalent bonds with the mercury atoms giving rise to the $[Hg_6O_4Cl^{3+}]_n$ ribbons in the former case and isolated $[OHg_3Cl_3]^+$ cations in the latter one. The –O–Hg–O– fragments with terminal covalently bound Cl atoms present in the structure of β-$Hg_3O_2Cl_2$ loose them upon heating and the compound converts into $Hg_5O_4Cl_2$ with the liberation of $HgCl_2$. The similarity between the crystal structures of β-$Hg_3O_2Cl_2$ and α-$Hg_3O_2Cl_2$ is not obvious. The presence of planar HgO_3 groups is their common structural feature. The β-$Hg_3O_2Cl_2$ phase is more stable at 25 °C. Upon heating in air at 200 °C for 70 h, both modifications convert into $Hg_5O_4Cl_2$; its structure is similar to that of β-$Hg_3O_2Cl_2$. The α-$Hg_3O_2Cl_2$ phase can be transformed into the β-modification by annealing in vacuum at 200 °C for a week. A subsequent heating at 230 °C for three days affords a mixture of $Hg_5O_4Cl_2$ and $HgCl_2$, as evidenced by powder X-ray diffraction data. Therefore, β-$Hg_3O_2Cl_2$ remains stable at about 200 °C, whereas $Hg_5O_4Cl_2$ becomes more stable at 230 °C. In overall, solid oxohalides undergo the following reactions upon heating in vaccum in the above temperature range:[67]

$$2\,Hg_3O_2Cl_2 \longrightarrow Hg_6O_4Cl_4 \longrightarrow Hg_5O_4Cl_2 + HgCl_2,$$

$$Hg_5O_4Cl_2 \longrightarrow 4\,HgO + HgCl_2.$$

2. The crystal structures of quaternary mercuric oxohalides

In the crystal structure of $HgPb_2O(OH)Br_3$, it is a complex fragment $[Hg_2Pb_4O_2(OH)_2]^{6+}$ with the so-called heterocubane skeleton that acts as the principal building block.[61] The central empty tetrahedron therein is constituted by the lead cations; four exterior tetrahedra sharing faces with the central one contain interstitial oxygen atoms in their centres, whereas their exterior vertices are occupied by two mercury and two hydrogen atoms. The mercury atoms in the structure are linearly coordinated by O and Br at 2.07 Å and 2.42 Å, respectively (the OHgBr angle is 166.7°). The coordination polyhedron of the mercury atoms is supplemented to a distorted trigonal bipyramid with three Br atoms at larger distances. The $[Hg_2Pb_4O_2(OH)_2]^{6+}$ moieties are assembled into a framework by sharing Br vertices of the mercury polyhedra (Fig. 20).

Mercury lead oxochloride $HgPb_2O_2Cl_2$ is characterised by a significantly different structure.[62] In this case, the $[OHgPb_3]$ tetrahedra and the linear –O–Hg–O– groups can be considered as basic structural units. The $[OHgPb_3]$ tetrahedra are

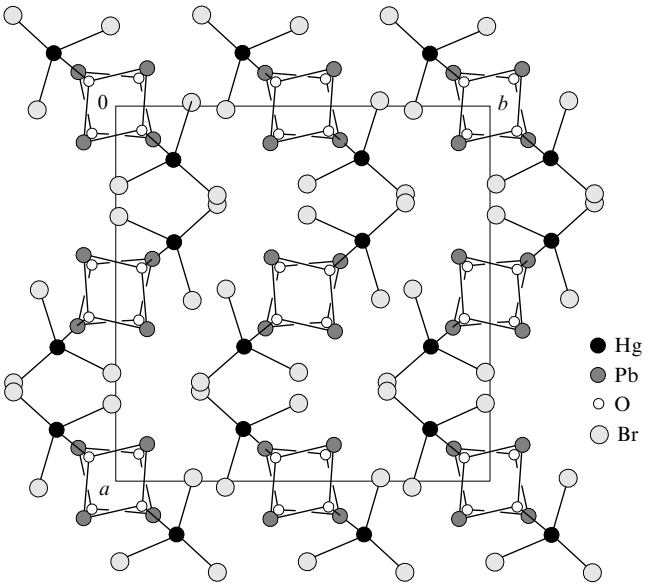


Figure 20. A projection of the crystal structure of $HgPb_2O(OH)Br_3$ onto the (001) plane. The $[Hg_2Pb_4O_2(OH)_2]^{6+}$ groups are localised in the nodes of the unit cell and in the centres of its faces (the H atoms are omitted for clarity).

assembled into puckered $[HgPb_2O_2^{2+}]_{\infty\infty}$ layers in the *ab* plane by sharing vertices and edges. The Cl^- anions are located between the layers (Fig. 21).

The crystal structure of $BaHg_2O_2Cl_2$ has been solved from powder X-ray diffraction data.[63] The Hg atoms in the structure form two covalent bonds with the O atoms with bond lengths of 2.03 – 2.09 and 2.382 Å. The coordination environment of the Hg atoms is supplemented to a distorted octahedron by four Cl atoms (see Table 3). The coordination polyhedron of the Ba atoms can be described as a monocapped trigonal prism composed of four O (Ba – O 2.72 Å) and three Cl atoms. The structure is built up of planar Hg_4O_4 rings stacked into columns along the [001] direction.

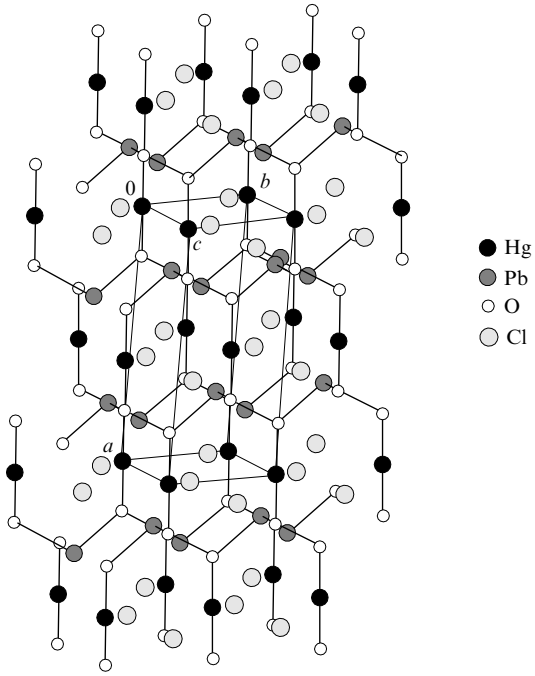


Figure 21. The crystal structure of $HgPb_2O_2Cl_2$.

These columns are assembled into a framework *via* the Ba atoms coordinated by four O atoms from four Hg_4O_4 rings belonging to two neighbouring columns; cavities of the framework accomodate the Cl atoms. Oxochloride $BaHg_2O_2Cl_2$ is isostructural to sulfoiodide $Hg_2PbS_2I_2$ (see Fig. 15), its structure contains columns of isolated Hg_4S_4 squares.

The crystal structure of $SrHg_2O_2Cl_2$ has been determined using powder X-ray diffraction owing to the lack of suitable single crystals.[64] Two crystallographically independent types of mercury atoms present in the structure are characterised by different coordination environments. The first type Hg atoms are linearly coordinated by two O atoms (Hg – O_{av} 2.07 Å), whereas the second type Hg atoms have the so-called T-shaped HgO_3 coordination.[3,4] Two HgO_3 groups form four-membered rings, which are further assembled into extended $[Hg_2O_2]_\infty$ puckered layers oriented perpendicular to the $[\bar{1}01]$ direction with the linear –O–Hg–O– bridges. The $[Hg_2O_2]_\infty$ layers are joined together into a framework (Fig. 22) by the Sr^{2+} cations, which are characterised by irregular coordination polyhedra composed of three oxygen and five chlorine atoms. Thus the structure of $SrHg_2O_2Cl_2$ can be classified as a new structural type. The crystallographic and crystal chemical parameters of quaternary mercuric oxohalides are summarised in Table 3.

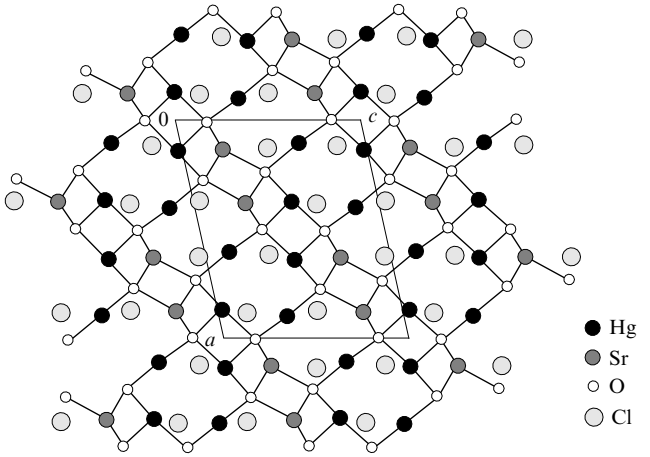


Figure 22. A projection of the crystal structure of $SrHg_2O_2Cl_2$ onto the (010) plane.

IV. Stable atomic groups (building blocks) in mercury compounds

1. Oxo-centred complexes in mercury compounds

In addition to the traditional crystal chemical approach to the structure description based on the coordination polyhedra of cations, an alternative method relying on the identification of anion-centred $[M_4Y]$ tetrahedra (M = Hg, Cu, Pb or Ln; Y = O or N) in the structures came in use starting from 1968.[72] More details on this concept can be found elsewhere.[73–77]

The $[Hg_4O]$ tetrahedra that are stable in terms of their shape and size are capable of forming finite groups, chains, ribbons, layers and spatial frameworks in the crystal structures of mercury oxo compounds.[78] The Hg – O bond lengths in the oxo-centred tetrahedra lie in the range of 1.90 – 2.78 Å. The upper limit significantly exceeds the sum of the ionic radii of Hg and O, which implies that no chemical bonding is realised in such cases. It is worth noting that the spread in the Hg – O bond lengths in mercury oxo compounds is much larger than that in the M – O bond lengths for the $[M_4O]$ tetrahedra (M = Cu, Pb or Ln).[75] This is explained by the ability of Hg atoms to form strong covalent bonds with only one or two oxygen atoms, which gives rise to a

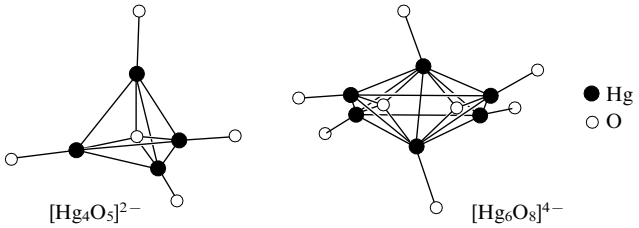
shift of the O^{2-} anion from the centre of the Hg-tetrahedron to one or two of its vertices.

As has been demonstrated by theoretical calculations, not only Hg–O covalent bonds are of importance in the $[Hg_4O]$ tetrahedra, but the interactions between the mercury atoms as well, despite relatively large Hg–Hg interatomic distances (~3.5 Å).[79] This fact additionally justifies the consideration of these groups in crystal structures. The relative spread in the Hg···Hg distances in the oxo-centred tetrahedra is smaller than that in the Hg–O bond lengths. Therefore, the interatomic interactions in the $[Hg_4O]$ groups (or in the $[Hg_4O_5]$ groups formed by the addition of external covalent Hg–O bonds to the oxo-centred tetrahedron) cannot be represented as a mere sum of the pairwise Hg–O contacts. It is a more complex system of many-body interactions also involving the Hg···Hg bonding.[79]

The oxo-centred $[Hg_4O]$ tetrahedra can form topologically complicated assemblies by sharing vertices and edges. Their examples can be found elsewhere.[78] The Hg : O* ratio (where O* is the so-called free oxygen, *i.e.*, oxygen atoms not involved into stable groups, such as AsO_4 or CrO_4 acid anions, *etc.*) is the main parameter governing the type of the structures. Below, a series of such crystal structures are considered, where all oxygen atoms are 'free' and the remaining anions are represented by halogens.[80] These compounds contain mercury in different oxidation states. The crystallographic and crystal chemical parameters of some of these compounds are given in Tables 3 and 4.

The structure of the mineral poyarkovite[81] Hg_3OCl, or $[Hg_2]_3O_2Cl_2$, is determined both by the covalent Hg–Hg bonds in the binuclear Hg_2 fragments and the Hg–O bonds giving rise to the bond angles of 87.9–121.6° at the central oxygen atom.[78] Taking into account the geometry of the covalent bonds, a $[Hg_6O_2]$ moiety composed of two edge-sharing oxo-centred mercury tetrahedra can be identified in the structure. The convex polyhedron, which is a joint coordination polyhedron of two central oxygen atoms of the two tetrahedra, has been considered earlier for the structures of rare-earth metal fluorides and denoted as *r*-octahedron, *i.e.*, rhombically distorted octahedron.[90] It can be considered as a fragment of a cubic close packing, which means that its long edge and diagonal have lengths of $a_r\sqrt{2}$ and $a_r\sqrt{3}$, respectively (where a_r is the length of its short edge).

In order to confirm the reasonability of the consideration of this moiety, quantum chemical calculations on $[Hg_4O_5]^{2-}$ and $[Hg_6O_8]^{4-}$ have been accomplished using the ZORA method[92] as implemented in the software code ADF-2002.02.[91] In addition to the internal oxygen atoms in the moiety, the covalent bonds formed by the Hg atoms with the 'external' O atoms were taken into account. According to the results obtained,[93] the $[Hg_6O_8]^{4-}$ fragment is substantially more preferable in terms of energy as compared to the isolated oxo-centred tetrahedron $[Hg_4O_5]^{2-}$.



This implies that these energetically favourable fragments would spontaneously form during the crystallisation provided that appropriate conditions are realised (the required Hg/O stoichiometry, the availability of suitable charge-compensating components, *etc.*). The crystal structure formation is completed by the packing of such hingedly joint moieties and remaining componens in an ordered way. Indeed, many structures of mercury oxohalides support this concept.

Table 4. Crystallographic and crystal chemical parameters of low-valence and mixed-valence mercury oxohalides.

Compound	Space group (R_f)	Unit cell parameters		Z	d_{calc} /g cm^{-3}	Bond lengths[a] /Å			Bond angles[a] /deg.		Ref.
		translations /Å	β angle /deg.			Hg–Hg	Hg–O	Hg–X	OHgO	OHgHg	
Hg_3OCl (poyarkovite)	$C2/c$ (0.0607)	$a = 19.009$ $b = 9.018$ $c = 16.848$	$\beta = 110.84$	24	9.643	2.502–2.565	1.95–2.60	2.816–3.043	77.5–82.1	116.9–173.2	81
$Hg_6O_2HCl_3$ (eglestonite)	$Ia\bar{3}d$ (0.044)	$a = 16.036$		16	–	2.516	2.165	3.010–3.095	114.6	162.6	82
Hg_2OI (aurivilliusite)	$C2/c$ (0.036)	$a = 17.603$ $b = 6.981$ $c = 6.701$	$\beta = 101.61$	8	8.96	2.534	2.128–2.471	3.466–3.761	–	174.6	83, 84
$Hg_7O_3Cl_2$ (hanawaltite)	$Pmba$ (0.049)	$a = 11.796$ $b = 13.890$ $c = 6.471$		4	9.51	2.536–2.544	2.10–2.65	2.992–3.340	–	175.4–177.0	85
$Hg_8O_4Br_3$	$P2_1/n$ 0.068	$a = 6.8554$ $b = 6.3033$ $c = 31.093$	$\beta = 96.09$	4	9.49	2.517–2.557	2.10–2.57	$\geqslant$3.02	79.6–176.7	102.0–172.4	86
$Hg_4O_2Cl_2$ (terlinguaite)[b]	$C2/c$ –	$a = 11.953$ $b = 5.904$ $c = 9.466$	$\beta = 105.5$	4	9.35[c]	2.703	2.234–2.462	2.587	–	–	87
Hg_3AsO_4Cl (kuznetsovite)[b]	$P2_13$ –	$a = 8.3790$		4	8.763	2.675	–	2.17–2.28	–	–	88
Vasilyevite[d]	$P\bar{1}$ –	$a = 9.344$ $b = 10.653$ $c = 18.265$	$\alpha = 93.262$ $\beta = 90.548$ $\gamma = 115.422$	2	9.57	2.533–2.595	2.00–2.32	–	–	157.1–176.0	89

[a] X = Cl, Br, I; [b] the HgHgHg angles are 60°; [c] $d_{meas} = 9.40$ g cm^{-3}; [d] $Hg_{20}O_6I_3Br_2Cl(CO_3)$, *i.e.*, $[(Hg_2^{2+})_{10}O_6]I_3Br_2Cl(CO_3)$.

Table 5. Building blocks in the structures of mercury oxohalides with tetrahedral anions.[a]

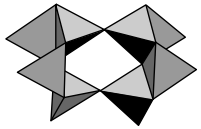
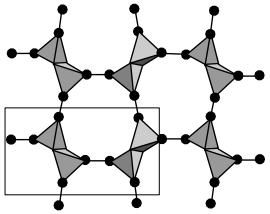
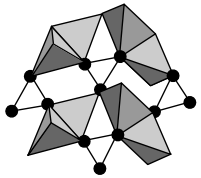
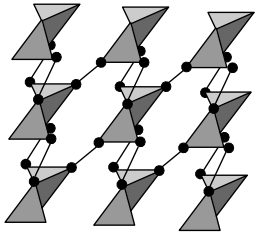
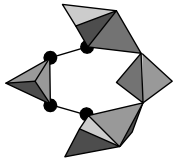
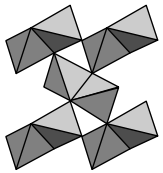
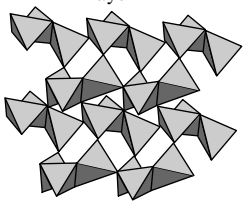
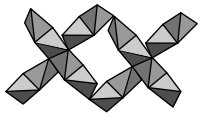
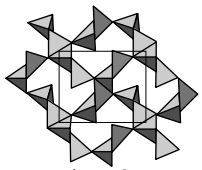
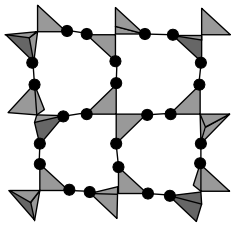
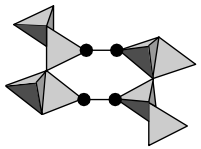
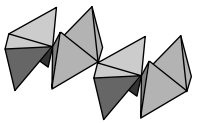
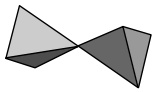
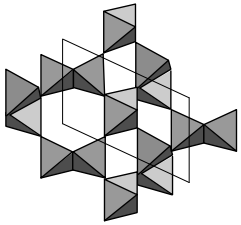
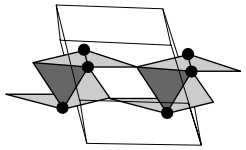
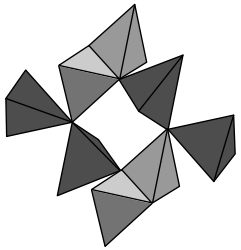
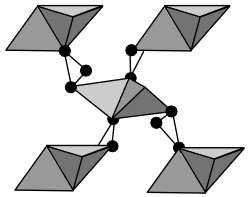
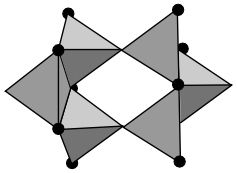
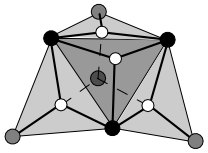
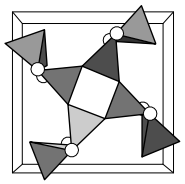
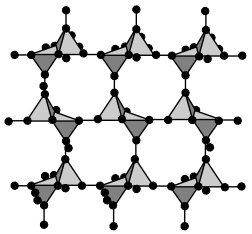
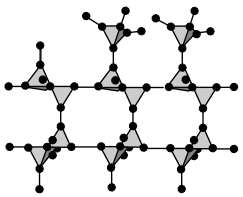
Compound, Hg : O* ratio	Geometry parameters of the [OM_4] tetrahedron (M is a metal)		Structure-forming fragment	Ref.	Compound, Hg : O* ratio	Geometry parameters of the [OM_4] tetrahedron (M is a metal)		Structure-forming fragment	Ref.
$Hg_5O_4Cl_2$ (pinchite) 5 : 4	Hg – O Hg···Hg HgOHg	2.045 – 2.707 Å 3.416 – 3.945 Å 100.4 – 113.5°		70	Hg_3OCl (poyarkovite) 3 : 1	Hg – O Hg···Hg HgOHg	1.949 – 2.601 Å 3.109 – 3.943 Å 87.9 – 121.6°		81
$Hg_4O_2Cl_2$ (terlinguaite) 4 : 2	Hg – O Hg···Hg HgOHg	2.016 – 2.486 Å 3.408 – 3.963 Å 91.6 – 123.3°		87					
					$Hg_8O_4Br_3$ 2 : 1	Hg – O Hg···Hg HgOHg	2.041 – 2.571 Å 3.225 – 3.948 Å 88.1 – 118.3°		86
$Hg_7O_3Cl_2$ (hanawaltite) 7 : 3	Hg – O Hg···Hg HgOHg	2.095 – 2.642 Å 3.311 – 3.937 Å 81.52 – 124.8°		85					
α-$Hg_3O_2Cl_2$ 3 : 2	Hg – O Hg···Hg HgOHg	2.063 – 2.319 Å 3.511 – 3.766 Å 98.3 – 112.5°		66				layer 1  layer 2	
β-$Hg_3O_2Cl_2$ 3 : 2	Hg – O Hg···Hg HgOHg	1.891 – 2.588 Å 3.338 – 3.989 Å 104.9 – 120.7°	 layer 1  layer 2	67, 68					
					$Hg_6O_2Cl_3H$ (eglestonite) 3 : 1	Hg – O[b] Hg···Hg HgOHg	1.23 – 2.179 Å 3.654 – 3.994 Å 105.0 – 113.6°		82
Hg_2OI 2 : 1	Hg – O Hg···Hg HgOHg	2.128 – 2.471 Å 3.590 – 3.775 Å 101.3 – 111.0°		83, 84	$Hg_5O_2CrO_4$ (wattersite) 5 : 2	Hg – O Hg···Hg HgOHg	2.064 – 2.705 Å 3.217 – 3.814 Å 86.6 – 121.9°		94

Table 5 (continued).

Compound, Hg : O* ratio	Geometry parameters of the [OM_4] tetrahedron (M is a metal)		Structure-forming fragment	Ref.
$Hg_5OS_2CrO_4$ (deanesmithite) 5 : 1	Hg – O Hg···Hg HgOHg	2.014 – 2.585 Å 3.404 – 3.987 Å 87.3 – 125.5°		95
$Hg_3O_2CrO_4$ 3 : 2	Hg – O Hg···Hg HgOHg	2.161 – 2.583 Å 3.552 – 3.843 Å 100.65 – 112.69°		96
$HgPb_2O_2CrO_4$ 3 : 2	Hg – O Pb – O Pb···Pb Hg···Pb PbOPb HgOPb	2.019 Å 2.375 – 2.395 Å 3.579 – 4.044 Å 3.665 – 3.940 Å 97.25 – 111.76° 110.28 – 116.20°		97
$SrHg_2O_2Cl_2$ 3 : 2	Hg – O Hg···Hg HgOHg	2.046 – 2.491 Å 3.194 – 3.689 Å 108.42 – 108.56°		64
$[Hg_3]_2HgO_2(PO_4)_2$ 7 : 2	Hg – O Hg···Hg HgOHg	2.031 – 2.526 Å 3.563 – 3.607 Å 101.61 – 119.83°		98

Compound, Hg : O* ratio	Geometry parameters of the [OM_4] tetrahedron (M is a metal)		Structure-forming fragment	Ref.
$HgPb_2O_2Cl_2$ 3 : 2	Hg – O Pb – O Pb···Pb Hg···Pb PbOPb HgOPb	2.048 Å 2.341 – 2.388 Å 3.777 – 3.980 Å 3.560 – 3.706 Å 105.99 – 109.87° 108.26 – 113.10°		62
$HgPb_2O(OH)Br_3$ 3 : 2	Hg – O Pb – O Pb···Pb Hg···Pb PbOPb HgOPb	2.117 Å 2.240 – 2.456 Å 3.699 – 3.781 Å 3.611 – 3.763 Å 100.27 – 107.32° 114.61 – 116.48°		61
$BaHg_2O_2Cl_2$ 3 : 2	(see Table 3)			63
$Hg_{20}O_6I_3Br_2Cl.$ $.(CO_3) \equiv [(Hg_2^{2+})_{10}O_6].$ $.I_3Br_2Cl(CO_3)$ (vasilyevite) 5 : 3	Hg – O Hg···Hg HgOHg	2.00 – 2.735 Å 3.041 – 3.497 Å 92.9 – 121.1°	 layer 1	89
			 layer 2	

[a] Some discrepancies in the listed geometry parameters as compared to those reported in Tables 3, 4 and 6 are due to the use of different software codes for their calculation (based on the same structural data); [b] 1.23 Å is the O – H distance in the [OM_3H] tetrahedron.

Table 5 lists possible types of building blocks based on the $[OHg_4]$ tetrahedra and $[Hg_6O_2]$ *r*-octahedra realised in the crystal structures of some natural and synthetic mercury oxohalides.

The dimensions of the *r*-octahedra determine the unit cell parameters and, to a some extent, its symmetry. Most frequently, they are packed in a herringbone manner. Herringbone layers of the *r*-octahedra represent stable structural units, which occur in various structures.

Two independent *r*-octahedra can be identified in the structure of poyarkovite $[Hg_2]_3O_2Cl_2$. A crystallographic inversion centre resides in the centre of one of them. The second *r*-octahedron has no symmetry elements, although its geometry is close to that of the first one. All cation vertices of an *r*-octahedron covalently link them with the neighbouring *r*-octahedra *via* the Hg—Hg bonds. If the $[Hg_2]^{2+}$ dumbbell is taken as the cation, the ideal poyarkovite stoichiometry 3 : 2 : 2 is resulted. It is important to note that the unit cell parameters of the poyarkovite structure are determined by the size and orientation of the cationic *r*-octahedra coupled with the lengths of the Hg—Hg bonds that join the *r*-octahedra together (these are the so-called contact links). The poyarkovite structure is composed of two types of layers made up of the *r*-octahedra oriented parallel to the *yz* plane.

The structure of α-$Hg_3O_2Cl_2$ analysed earlier in Section III.1 can be regarded as a result of the Hg^{2+} 'isomorphous' substitution for the $[Hg_2]^{2+}$ dumbbells in the poyarkovite structure; this is accompanied by a reduction in the length of the contact link between the *r*-octahedra to zero, *i.e.*, the octahedra are directly linked by sharing Hg vertices. In a unit cell of α-$Hg_3O_2Cl_2$, there are two symmetry-related *r*-octahedra. Furthermore, there are two types of the mutual orientations of the neighbouring *r*-octahedra: the neighbouring *r*-octahedra are translationally equivalent along the *x* axis, which means that the translation *a* is equal to their long diagonal. In other directions, translationally equivalent *r*-octahedra alternate with the *r*-octahedra tranformed by a 2_1 screw axis or a *c* gliding reflection plane. As a result, the unit cell parameters *b* and *c* are nearly identical being equal to the vector sum of two short edges of the *r*-octahedra.

The structure of mixed-valence Hg_2OI takes[83,84] a position intermediate between those of poyarkovite and α-$Hg_3O_2Cl_2$. In these structures, only two Hg-vertices of the *r*-octahedra are replaced with the $[Hg_2]^{2+}$ dumbbells. The layer of vertex-sharing *r*-octahedra analogous to that in the structure of α-$Hg_3O_2Cl_2$ is located in the *yz* plane, which gives rise to nearly identical *b* and *c* in these two structures. Two vertices of an *r*-octahedron (at the ends of the long diagonal) are occupied by the $[Hg_2]^{2+}$ dumbbells extended along the *a* axis. The vector sum of the parameter *a* with the long diagonal of the *r*-octahedron is $a/2 = 8.8$ Å, which is close to the parameter *b* of the poyarkovite structure. The residual free volume is filled with bulky I^- anions.

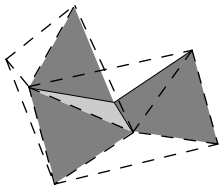
In the structure of α-$Hg_3O_2Cl_2$, the translation parameters of the orthogonal two-dimensional lattice of the herringbone layer are 6.8657 and 6.8759 Å, whereas its thickness is $\sim$6 Å. The structure of Hg_2OI can be represented as two herringbone layers parallel to *x*, which are linked by the Hg—Hg dumbbells ($\sim$2.5 Å) also oriented along the *x* axis, rather than by shared Hg vertices. Thus the *a* parameter of the Hg_2OI structure corresponds to the doubled *a* of the α-$Hg_3O_2Cl_2$ structure (6.310 Å) plus two Hg—Hg bond lengths: 17.603 Å $\approx 2 \times 6.310 + 2 \times 2.50$ Å.

The symmetry centre of an *r*-octahedron often coincides with the crystallographic inversion centre of the structure, which implies that the 'rigid' moiety partially determines the structure symmetry in addition to the unit cell dimensions. In particular, a single $[Hg_4O]$ tetrahedron with no inversion centre can posess a dipole moment. Meanwhile, a pair of the inversion-related tetrahedra mutually compensate for their dipole moments in the minimum volume, which gives rise to the stabilisation of such a structural fragment.

In contrast to the α-$Hg_3O_2Cl_2$ structure, a $[Hg_{10}O_4]$ moiety with an inversion centre localised in the middle of an edge shared by two *r*-octahedra acts as the basic building block in the β-modification of $Hg_3O_2Cl_2$ due to the condensation of a part of the *r*-octahedra. Dimensions of this moiety determine the unit cell parameters *b* and *c*: the double *r*-octahedra centred at $^1/_2\,^1/_2\,^1/_2$ form a layer in the *yz* plane, the packing of the moieties in the layer is determined by the symmetry (a *c* plane and a 2_1 axis). This layer is stacked along *a* on another layer constituted by two types of the *r*-octahedra formed around oxygen atoms of two other types with the invesion centres at $00^1/_2$ and $0^1/_2\,^1/_2$. The condensation of the two *r*-octahedra changes the Hg : O stoichiometry, a ratio of Hg : O = 5 : 4 is expected provided that each vertex of the double *r*-octahedron is shared with the neighbouring ones. In order to compensate for the stoichiometry violation, two Hg atoms from the $[Hg_{10}O_4]$ fragment become terminal; this is accompanied by the introduction of a Cl^- anion at a distance of 2.36 Å (the sum of ionic radii of Hg and Cl is 2.50 Å!) into their coordination environments in place of oxygen. Taking into account that all other vertices of the *r*-octahedra in the structure are bridging, this configuration restores the 3 : 2 Hg : O stoichiometry.

The ratio of mercury cations to oxygen anions (taking into account dumbbell groups) in the structure of mixed-valence hanawaltite $[Hg_2]_3HgO_3Cl_2$ is 4 : 3, *i.e.*, it includes a larger amount of cations than $Hg_3O_2Cl_2$. As a result, isolated $[Hg_4O]$ tetrahedra are present in the structure in addition to the *r*-octahedra. The *r*-octahedra are grouped nearby the inversion centres $^1/_2\,^1/_2\,^1/_2$ filling the space between the mirror planes that accomodate the isolated $[Hg_4O]$ tetrahedra. The unit cell parameter *c* is determined by the length of the long diagonal of the *r*-octahedron. The only Hg^{2+} atom resides in an inversion centre and is characterised by the strictly linear O—Hg—O coordination.

Despite a relatively small number of cations in the structure of pinchite $Hg_5O_4Cl_2$, all oxygen atoms therein are tetrahedrally surrounded by the cations. There are two types of the *r*-octahedra with partially overlapping volumes; their centres are located at an inversion centre $^1/_4\,^1/_4\,^1/_4$ (the packing of this type of polyhedra determines the structure in the *ab* plane) and at a two-fold axis parallel to *x*, respectively.



In overall, the pinchite structure can be represented as an assembly of four symmetry-related columns composed of the *r*-octahedra extended along the *b* axis. The bonding between the columns is realised by sharing Hg vertices. Within the columns, the bonding is stronger: each *r*-octahedron shares a common $[Hg_4O]$ tetrahedron with a neighbouring one. Therefore, this represents a new pattern of bonding between structural units, *viz.*, partial volume-sharing in addition to known types, such as vertex-, edge- and face-sharing.

The structure of mixed-valence oxobromide $Hg_8O_4Br_3$ reveals a complex combination of structural elements observed in pinchite and poyarkovite. All four basic oxygen atoms are involved in *r*-octahedra but only one of the *r*-octahedra (composed of the mercury atoms forming dimeric $[Hg_2]$ groups) is located at an inversion centre ($^1/_200$). This type of the *r*-octahedra form a layer in the *xy* plane (layer 1), which is similar in terms of its structure to layers present in poyarkovite. Two other types of the *r*-octahedra with partly overlapping volumes (similar to those found in the pinchite structure) occupy larger volume filling the space between the layers composed of the first type *r*-octahedra separated by *c*/2 (layer 2). Pairs of overlapping *r*-octahedra are linked by sharing Hg^{2+} vertices in such a way that one of the typical coordination types is realised for all mercury atoms. The unit cell parameter *b* is equal to the long diagonal of the *r*-octahedron (like *b* parameter of pinchite, *c* parameter of hanawaltite and *b* parameter of α-$Hg_3O_2Cl_2$).

In the mineral terlinguaite $[Hg_3]HgO_2Cl_2$, the $[Hg_3]^{4+}$ triangular clusters and $[Hg_6O_2]$ *r*-octahedra (taking into account the covalent Hg—O interactions) act as basic structure-forming units. The structure is built up by their packing together with the Cl^- anions. A unit cell includes one type of the *r*-octahedra centred at the inversion centre in the origin (000). In agreement with the space group $C2/c$, they are arranged in a way that all equatorial Hg-vertices are bridging and all axial vertices are terminal, which provides the requred stoichiometry Hg : O = 4 : 2. The first type of the mercury atoms are characterised by the linear O—Hg—O coordination; the second type of the Hg atoms reside in the plane composed of two oxygen atoms and two mercury atoms of the third type; the latter are characterised by a non-typical 2 O + 2 Hg + Cl coordination. These structural peculiarities are due to the presence of the $[Hg_3]^{4+}$ cluster fragment, which includes two mercury atoms of different types.

In Hg-deficient structures, a part of vertices of the *r*-octahedra can be occupied by other cations (Sr, Pb), which results in only insignificant geometry changes ($SrHg_2O_2Cl_2$, $HgPb_2O_2Cl_2$, see Table 5). The approach based on the identification of 'rigid' atomic groups in crystal structures becomes increasingly more popular.[99–102] In particular, very similar atomic arrangements were found in gold $[Au_6O_2]$ (Ref. 103) and mixed gold–rhodium $[Rh_2Au_4O_2]$ (Ref. 104) clusters. These fragments manifest a high stability due to the formation of Au—Au (3.008 Å) and Au—Rh (3.00 Å) bonds.

In the structure of $SrHg_2O_2Cl_2$, a cationic *r*-octahedron with an inversion centre and two strontium atoms occupying two its vertices can be identified. The $[Sr_2Hg_4O_2]$ *r*-octahedra are assembled by isolated $[Sr_2Hg_2O]$ tetrahedra into a three-dimensional motif, like that in the hanawaltite structure. The formation of stable atomic groups explains many structural features of these compounds, in particular, irregular coordination polyhedra of some atoms, as noted by Harrison *et al.*[64]

In the above compounds, the charge-compensating halogen atoms play an insignificant structure-forming role, since rigid polyatomic moieties ($[Hg_4O]$ tetrahedra and $[Hg_6O_2]$ *r*-octahedra) by far exceed them in terms of both mass and size. In this class of compounds, they play a secondary role merely filling available space.

In the majority of structures analysed above, *r*-octahedra possess only inversion centres, their short edges, long edges and long diagonals are 3.40–4.00 Å, 5.30–5.40 Å and 6.10–6.30 Å, respectively. Each Hg vertex of the polyhedra is involved into covalent bonding with external oxygen atoms belonging to neighbouring *r*-octahedra in addition to one or two internal oxygen atoms. Therefore, these groups can be regarded as isolated ones only formally similar to, for instance, SiO_4 tetrahedra in framework silicates. It is the mutual packing of these polyhedra that governs the crystal structure. Although Hg vertices of *r*-octahedra are also involved into external covalent bonding, in particular, with neighbouring *r*-octahedra, the spread in the respective bonding angle is significantly larger than for the internal bonds. It is worth noting that up-to-date methods for the quantitative simulation of chemical bonding fully support the emergence of intuitively apparent cation–cation bonds in these groups.[79, 105]

2. Stable structural units in mercury compounds with the AO_4 tetrahedral anions (A = Cr, P, As or V)

A number of crystal structures of naturally occurring and synthetic mercury sulfo- and oxochromates reveal even more complex fragmentation patterns. The crystal structures of mercury compounds with the AO_4 tetrahedral anions (A = Cr, P, As or V) include, in addition to the Hg—S and Hg—O covalent bonds formed by the mercury atoms, covalent A—O bonds within the $[AO_4]$ tetrahedral complexes, which are also incorporated into the structure as 'rigid' moieties.[106] The crystallographic and crystal chemical parameters of these compounds are summarised in Table 6, whereas the types of cationic and anionic 'rigid' atomic fragments are listed in Table 7.

With an increase in the effective size of the anionic fragments, their role in the structure formation becomes more important. The $[AO_4]$ tetrahedra can combine into inversion centre-related pairs in such a way that two triangular faces looking toward each other form an octahedral cavity of oxygen atoms. For example, such pairs are present in the structures of edoylerite and deanesmithite (see Table 7); the distances between the centres of the tetrahedra in these structures are 4.10 and 4.30 Å, respectively. The cationic part of the edoylerite structure is represented by zigzag chains composed of the $[Hg_4S_4]$ rings that separate the anionic fragments from each other. The centres of gravity of these rings coincide with the crystallographic inversion centres. In the deanesmithite structure, a three-dimensional framework of Hg—Hg and Hg—S covalent bonds constitutes the cationic part.

The crystal structures of mercury chromates ($HgCrO_4$, $Hg_3O_2CrO_4$ and $HgPb_2O_2CrO_4$) contain various configurations of the $[CrO_4]$ tetrahedra retaining the same type of contacts *via* the octahedral cavity of oxygen atoms. Edge-sharing oxo-centred tetrahedra, which can be identified as $[Hg_6O_2]$ and $[Hg_2Pb_4O_2]$ *r*-octahedra and $[HgPb_2O]$ triangles (in $HgPb_2O_2CrO_4$), act as the cationic parts of these structures. Similar structural units occur in the crystal structure of $[Hg_3]HgO_2(PO_4)_2$ (see Table 5), where centrosymmetrical $[Hg_6O_2]$ *r*-octahedra are assembled into a framework by shared vertices and the $[Hg_3]^{4+}$ cluster cation; the $[PO_4]^{3-}$ tetrahedra together with the centrosymmetric empty oxygen octahedra separating them from each other form zigzag columns, which run through the cationic framework parallel to the *z* axis.

In the crystal structure of mineral wattersite $[Hg_2^{2+}]_2Hg^{2+}O_2CrO_4$, a more complex moiety acts as the basic unit, which in the ideal shape is known as stella quadrangula.[111] The central core of this unit comprises an empty $[Hg_4]$ tetrahedron (Hg···Hg 3.30–3.72 Å) capped with two $[Hg_4O]$ and two $[CrHg_3O]$ tetrahedra at each face; the rotation axis 2 of this group coincides with the crystallographic two-fold axis. Along the *z* axis, the groups are sharing Hg vertices (these Hg atoms reside in the inversion centres so that the Hg—Hg distance is $c/2$ = 3.30 Å); in other directions, these groups are bridged by the $[Hg_2]^{2+}$ dumbbells. Zigzag columns formed by the $[CrO_4]$ tetrahedra alternating with the centrosymmetrical empty oxygen octahedra are strongly elongated (the Cr—Cr distance is 5.407 Å), which implies that they play only a secondary role in the structure formation as compared to the cationic moiety. In the wattersite structure, the $[Hg_6O_2]$ cationic group can be represented in terms of both composition and geometry as a distorted *r*-octahedron in which one of the long Hg—Hg edges is shortened to ~3.5 Å. Taking into account two additional relatively close oxygen atoms of the $[CrO_4]$ tetrahedra along with the chromium atoms themselves, this group can be considered as an intermediate case between an *r*-octahedron and a more symmetric stella quadrangula.

The crystal structure of $HgPb_2O(OH)Br_3$ reveals a similar fragment referred to as 'heterocubane skeleton' (see Table 5), which is similar to the aforementioned group in terms of both symmetry and dimensions.[61] The central empty tetrahedron is formed by four Pb cations, four adjacent (face-sharing) tetrahedra contain interstitial oxygen anions, two mercury and two hydrogen atoms act as external vertices. This example as well as the structure of $HgPb_2O_2CrO_4$ described above demonstrate similar crystal chemistry of Pb^{2+} and Hg^{2+} cations in compounds of the approximate compositions.[112] Notwithstanding, there are substantial differences between them: the mercury atoms preferably form linear O—Hg—O fragments and thus tend to occupy equatorial positions of the *r*-octahedra, whereas the lead atoms tend to form three covalent bonds with the oxygen atoms and can occupy both equatorial and apical positions.

Quite different atomic groups occur in the $HgCrO_4$ structure (see Tables 6, 7): these include two $[CrHg_2O]$ triangles sharing a

Table 6. Crystallographic and crystal chemical parameters of mercury compounds with AO_4 tetrahedral anions (A = Cr, P, As or V).

Compound	Space group (R_f)	Unit cell parameters		Z	d_{calc} /g cm^{-3}	Interatomic distances /Å		Bond angles /deg.		Ref.
		tranlsations /Å	angles /deg.							
$Hg_3S_2CrO_4$ (edoylerite)	$P2_1/c$ (0.079)	$a = 7.528$ $b = 14.832$ $c = 7.463$	$\beta = 118.8$	4	7.11	Hg – O Hg – S	2.441 – 2.580 2.365 – 2.415	SHgS HgSHg	163.70 – 173.93 93.52 – 125.42	107
$Hg_5S_2OCrO_4 \equiv [Hg_2^{2+}](Hg^{2+})_3S_2OCrO_4$ (deanesmithite)	$P\bar{1}$ (0.0292)	$a = 8.129$ $b = 9.492$ $c = 6.894$	$\alpha = 100.4$ $\beta = 110.2$ $\gamma = 83.0$	2	8.14	Hg – Hg Hg – O Hg – S	2.536 2.11 2.352 – 2.442	HgHgS	167.6 – 171.3	95
$HgCrO_4$	$P2_1/n$ (0.049)	$a = 7.342$ $b = 8.522$ $c = 5.202$	$\beta = 94.0$	4	6.47	Hg – O	2.000 – 2.047	–		108
$Hg_3O_2CrO_4$	$P3_221$ (0.0768)	$a = 7.137$ $c = 10.017$		3	8.45	Hg – O	2.161 – 2.170	OHgO HgOHg	166.27 102.83 – 122.47	96
$HgPb_2O_2CrO_4$	$P\bar{1}$ (0.049)	$a = 6.505$ $b = 7.201$ $c = 7.605$	$\alpha = 91.82$ $\beta = 92.17$ $\gamma = 111.33$	2	7.65	Hg – O Pb – O	1.993 – 2.019 2.236 – 2.448	OHgO HgOHg	174.45 112.65	97
$[Hg_3]_2HgO_2(PO_4)_2$	$P2_1/c$ (0.028)	$a = 6.2506$ $b = 9.9366$ $c = 9.6663$	$\beta = 95.783$	2	7.65	Hg – Hg Hg – O	2.652 – 2.705 2.031 – 2.600	OHgO HgHgHg	180 58.927 – 60.880	98
$Hg_5O_2CrO_4 \equiv [Hg_2^{2+}]_2Hg^{2+}O_2CrO_4$ (wattersite)	$C2/c$ (0.055)	$a = 11.274$ $b = 11.669$ $c = 6.603$	$\beta = 98.19$	4	8.891	Hg – Hg Hg – O	2.526 2.06 – 2.16	HgHgO	153.3 – 169.5	94
$AgHg_2PO_4$	$Pbam$ –	$a = 9.256$ $b = 8.614$ $c = 6.152$		4	8.18	Hg – Hg Ag – Ag Hg – Ag Hg – O	2.608 2.824 2.840, 2.941 2.224 – 2.348	HgHgO	101.2	109
$[Ag_3Hg][(V,As)O_4]$ (tillmannsite)	$I\bar{4}$ (0.037)	$a = 7.727$ $c = 4.648$		2	7.733	Hg/Ag – Hg/Ag Hg/Ag – O	2.752, 2.738 (see [a]) 2.395 – 2.449	–		110
$[Ag_3Hg]VO_4$	$I\bar{4}$ (0.0365)	$a = 7.7095$ $c = 4.6714$		2	7.645	Hg/Ag – Hg/Ag Hg/Ag – O	2.723, 2.739 2.373 – 2.444	Hg/Ag – Hg/Ag – Hg/Ag	59.60 – 60.198	100
$[Ag_2Hg_2]_3(VO_4)_4$	$I\bar{4}2d$ (0.0508)	$a = 12.6295$ $c = 12.566$		4	7.657	Hg/Ag – Hg/Ag	2.684 – 2.739	Hg/Ag – Hg/Ag – Hg/Ag	59.31 – 60.77	100
$AgHgVO_4$	$C2$ (0.0358)	$a = 9.9407$ $b = 5.5730$ $c = 7.1210$	$\beta = 94.56$	4	7.151	Hg – O Ag – O	2.084 – 2.699 2.282 – 3.133	–		100
$[Ag_2Hg_2]_2(HgO_2)(AsO_4)_2$	$P3_1c$ (0.0480)	$a = 6.0261$ $c = 21.577$		2	8.537	Hg/Ag – Hg/Ag Hg/Ag – O Hg – O	2.710 – 2.774 2.214 – 2.597 2.00 – 2.24	Hg/Ag – Hg/Ag – Hg/Ag	59.56 – 62.38	100

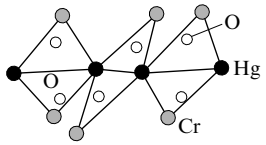
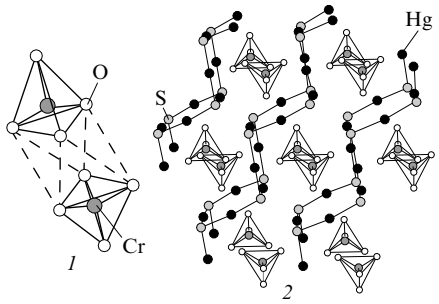
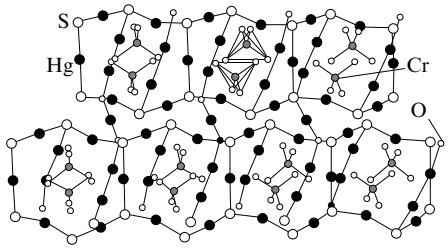
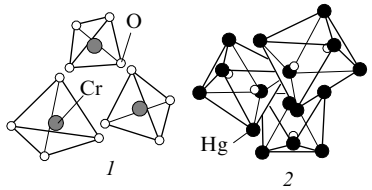
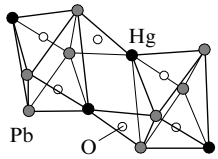
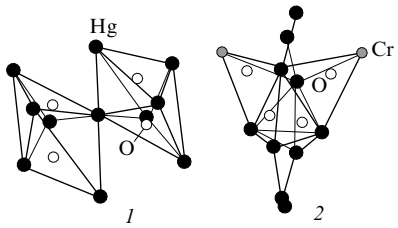
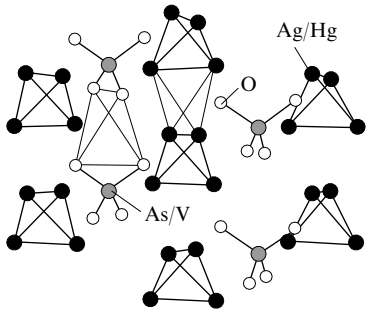
[a] Hg/Ag means that the respective sites are occupied statistically.

common Hg – Hg edge (~3.5 Å) (an inversion centre is located in the middle of this bond) forming a nearly planar rhombus.

A non-typical combination of cationic and anionic fragments occurs in the crystal structure of $AgHg_2PO_4$ (see Table 6).[109] Its cationic part is represented by an $[Ag_2Hg_4]$ *r*-octahedron composed of two $[Ag_2Hg_2]$ tetrahedra sharing an Ag – Ag edge with the crystallographic inversion centre in the middle. In contrast to the structures described above, the tetrahedra are substantially smaller since they contain no interstitial oxygen atoms. A pair of the $[PO_4]$ tetrahedra separated by an empty oxygen octahedron constitutes the anionic fragment of the structure. The centres of the complex cations and anions are packed into a pseudocubic *I*-centred cell with the following parameters: $\boldsymbol{a}' = {}^1/_2\boldsymbol{a} + {}^1/_2\boldsymbol{b}$ (6.32 Å); $\boldsymbol{b}' = -{}^1/_2\boldsymbol{a} + {}^1/_2\boldsymbol{b}$ (6.32 Å); $\boldsymbol{c}' = \boldsymbol{c}$ (6.152 Å); $\alpha' = \beta' = \gamma' = 94.12°$.

The recently solved tetragonal crystal structure of tillmannsite $[Ag_3Hg][(V,As)O_4]$ (see Tables 6, 7) [110] also includes an 'empty' $[Ag_3Hg]$ cationic tetrahedron with three Ag and one Hg atoms statistically distributed over four vertices. The $[(V,As)O_4]^{3-}$ tetrahedra alternating with empty oxygen tetrahedra and combined with them by shared edges form a ribbon going along the *z* axis, and the centres of both tetrahedra types have the $\bar{4}$ point symmetry. Two other sites with the $\bar{4}$ symmetry are located in the centres of the aforementioned cationic tetrahedron and another adjacent, also 'empty', $[Ag_3Hg]$ tetrahedron sharing cation – cation edges with the former one. The latter tetrahedron is

Table 7. Anionic and cationic 'rigid' atomic moieties in mercury compounds with AO_4 tetrahedral anions (A = Cr, P, As or V).

Compound	Types of anionic and cationic fragments	Anionic and cationic fragments	Ref.
$HgCrO_4$	isolated chains of the $[Cr_2Hg_2O_2]$ rhombs incorporating the $[CrO_4]$ tetrahedra		108
$Hg_3S_2CrO_4$ (edoylerite)	(*1*) isolated pairs of the $[CrO_4]_2$ tetrahedra; (*2*) zigzag ribbons of the $[Hg_4S_4]$ rings		107
$Hg_5S_2OCrO_4 \equiv [Hg_2^{2+}](Hg^{2+})_3S_2OCrO_4$ (deanesmithite)	isolated pairs of the $[CrO_4]_2$ tetrahedra inside a spatial framework of the S – Hg – Hg – O, S – Hg – S and O – Hg – O bonds		95
$Hg_3O_2CrO_4$	(*1*) isolated helical chains of tetrahedra $[CrO_4]_\infty$; (*2*) a spatial framework of the $[Hg_6O_2]$ *r*-octahedra linked by vertex-sharing		96
$HgPb_2O_2CrO_4$	ribbons of the $[Hg_2Pb_4O_2]$ *r*-octahedra linked by the $[HgPb_2O]$ triangles		97
$Hg_5O_2CrO_4 \equiv [Hg_2]_2^{2+}Hg^{2+}O_2CrO_4$ (wattersite)	(*1*) a fragment of a chain composed of distorted $[Hg_6O_2]$ *r*-octahedra; (*2*) $[Cr_2Hg_6O_4]$ stella quadrangula, a fragment of the cationic framework		94
$[Ag_3Hg][(V,As)O_4]$ (tillmannsite)	alternating pairs of *r*-octahedra composed of $[Ag_3Hg]$ 'empty' cationic tetrahedra and ribbons of the $[(V,As)O_4]$ anions sharing edges with empty O-tetrahedra		110

tetragonally distorted along the z axis [the Ag(Hg)–Ag(Hg) side edges are 3.316 Å]. As in the $AgHg_2PO_4$ structure, the two adjacent edge-sharing cationic tetrahedra can be considered as a deformed 'empty' r-octahedron. The overall crystal structure is built up of ribbons of such r-octahedra packed in the xy projection together with the ribbons of anionic tetrahedra in a herringbone manner. The positions of (Ag,Hg) and (V,As) cations themselves form a pseudocubic F-centred sublattice with a volume constituting 2/5 of the unit cell volume with the following parameters: $\boldsymbol{a}' = 3/5\boldsymbol{a} + 1/5\boldsymbol{b} = 4.90$ Å; $\boldsymbol{b}' = -1/5\boldsymbol{a} + 3/5\boldsymbol{b} = 4.90$ Å; $\boldsymbol{c}' = \boldsymbol{c} = 4.648$ Å; $\alpha' = \beta' = \gamma' = 90°$.

A series of compounds with the $[Ag,Hg]_4$ clusters have been synthesised within the Ag–Hg–E–O system ($E = V^{5+}$, As^{5+}) (see Table 6). In the tetragonal structure of $[Ag_3Hg]VO_4$, the tetrahedral cluster is formed by the statistical distribution of the Ag and Hg atoms in a 3 : 1 ratio over the available positions. Meanwhile, the tetragonal clusters corresponding to the $[Ag_2Hg_2]$ stoichiometry also with the statistical distribution of Ag and Hg with a mean metal–metal distance of 2.72 Å are present in tetragonal $[Ag_2Hg_2]_3(VO_4)_4$ and trigonal $[Ag_2Hg_2]_2HgO_2 \cdot (AsO_4)_2$. Assuming the $[Ag,Hg]_4$ moieties and the VO_4 or AsO_4 tetrahedra to be pseudospherical 'building blocks', the structures of $[Ag_3Hg]VO_4$ and $[Ag_2Hg_2]_2HgO_2(AsO_4)_2$ can be described as a cubic close packing with the (ABC) stacking sequence and a mixed-layer packing with the ABACACAB stacking sequence, respectively, where A is the layer formed by VO_4 or AsO_4, B and C are the layers formed by the $[Ag_2Hg_2]$ clusters. The crystal structure of $[Ag_2Hg_2]_3(VO_4)_4$ cannot be described in a similar way. It is interesting that another compound synthesised in this system, $AgHgVO_4$, which has a monoclinic structure, contains no cluster groups; the cations therein are characterised by usual coordination types: Ag and V are tetrahedrally coordinated by oxygen, the Hg coordination is a distorted octahedron.[100]

Therefore, it might be concluded that the crystal structures considered above represent the net result of two major structure-forming factors: the 'chemical' one, which induces the formation of stable atomic fragments that can undergo only minor changes after their formation and the crystallographic one, which promotes their dense packing into highly symmetric extended assemblies by fixing centres of these groups or single atoms at specific families of crystallographic planes.

V. The modular principle in the structure formation of mercury oxo- and chalcohalides

The presence of linear Y–Hg–Y groups (Y = O, S, Se or Te) is commonly accepted as a specific structural feature of mercury oxo- and chalcohalides. Additionally, trigonal pyramidal $[YHg_3]$ groups, in which the Y atom is connected to three mercury atoms forming variable Hg–Y–Hg bond angles in a range from 110° to 90° frequently occur in the crystal structures of ternary chalcohalides with the 3 : 2 : 2 stoichiometry, *i.e.*, $Hg_3Y_2X_2$ (Y = S or Se, Te; X = Cl, Br or I). These groups can be assembled into various one-, two- or three-dimensional motifs.[1] Typically, large monovalent halogens (X = Cl, Br or I) in these structures merely fill the space between chains, ribbons or frameworks formed by these stereochemically active structural elements and compensate for their positive charge. A more thorough analysis shows [113] that the halogen atoms tend to form a pseudocubic primitive sublattice with a periodicity constant of 4.4–5.4 Å, depending on the nature of X.

The original software package KAP-PLATS [7] can be efficiently applied to objectively evaluate the role played by all types of atoms in the crystal structure formation and indentify common structural features of these compounds. As a starting postulate, this approach assumes that the atoms most important for the structure formation are characterised by most densely occupied atomic planes within the range of interplane distances d_{hkl} of the order of shortest interatomic distances. Furthermore, an analysis of the distribution of special positions, *i.e.*, of the location of different types of atoms with respect to space group symmetry elements, is of importance. This is due to the fact that any special position represents a locus of intersection of both symmetry elements and closely packed atomic layers and thus they serve as natural boundaries in dividing a structure into fragments.

1. The role of halogen atoms in the structures of ternary mercury chalcohalides $Hg_3Y_2X_2$ (Y = S, Se or Te; X = Cl, Br or I)

In the crystal structure of α-$Hg_3S_2Cl_2$ (corderoite) (see Table 1), a single basis Cl atom occupies a special position 8(a) on a three-fold axis. These atoms form a primitive cubic sublattice with a translation vector $a' = a/2 = 4.47$ Å. Deviations of the Cl atoms from expected ideal positions of the sublattice nodes do not exceed 0.15 Å. The sulfur atoms are located in the centres of cubes of the Cl sublattice, their deviations from the geometric centres being ~0.3 Å. The mercury atoms centre three of six faces intersecting in a vertex deviating from the centres by ~0.5 Å. Therefore, the chlorine atoms (as well as other atoms) can shift along the three-fold axis and appear most rigidly ordered in the lattice since they are located in the intersection of the (200), (020) and (002) planes and planes derived from them, such as (222).

A similar situation is observed in the structure of β-$Hg_3S_2Cl_2$ (see Table 1); its unit cell comprises 64 cubic Cl sublattices ($a' = a/4 = 4.48$ Å). The Cl atoms are dominantly localised in special positions and are most rigidly ordered by systems of the {004}, {044} and {444} planes, which intersect in nodes of the sublattice. The sulfur atoms localised in the centres of the Cl sublattices are ordered nearly as rigidly, whereas the mercury atoms deviate substantially from the centres of faces of the Cl sublattice.

In the monoclinic structure of β-$Hg_3S_2Br_2$ (see Table 1), all Br atoms are located on the mirror reflection planes, which determine one of the lattice parameters of the Br sublattice as $b/2$. Two other lattice parameters are $a/4$ and $c/2$, since the intersection points of the (400), (020) and (002) crystallographic planes most densely occupied by the Br ions form a pseudocubic primitive sublattice with exactly these translation vectors: $a' = 4.42$, $b' = 4.69$ and $c' = 4.72$ Å. The S atoms localised in the centres of cubes of the Br sublattice are ordered by the same systems of crystallographic planes but are phase-shifted by 180°. The ordering of the S atoms is again less rigid than that of the Br atoms due to the fact that the sulfur atoms occupy general positions in the structure. The disposition of the Hg atoms is even less ordered.

In the crystal structure of the α-modification of this compound (α-$Hg_3S_2Br_2$) (see Table 1), a unit cell is constructed from the Br sublattices in a different manner as compared to the β-phase, thus the sublattice of nodes occupied by Br is formed by the intersection locus of the $(\bar{4}01)$, (020) and (002) crystallographic planes, which cut a pseudocubic sublattice with $a' = a/4 = d_{\bar{4}01} = 4.50$, $b' = b/2 = 4.64$ and $c' = d_{002} = 4.62$ Å (Fig. 23 *a*). The sulfur atoms are arranged nearly as regularly as the bromine atoms, whereas the mercury atoms are distinctly shifted from the centres of faces of the Br cubes.

The unit cell of $Hg_3Te_2I_2$ (see Table 1) is constructed of the iodine sublattices in an even more complicated manner. It is formed by the intersection of families of the (202), (020) and $(\bar{2}02)$ crystallographic planes. They cut a parallelepiped with edges of 5.47, 4.85 and 5.45 Å and angles close to 90° (Fig. 23 *b*).

Therefore, the structures of $Hg_3Y_2X_2$ compounds (Y = S, Se, Te) despite their formal diversity are constructed, to the first approximation, from 'cubic' modules with the halogen atoms in the vertices, chalcogen atoms in the centres and the mercury atoms in the centres of three faces intersecting in a common vertex. Such a cubic module is further attached to a common motif by bonds going out from the centres of three faces towards the centres of neighbouring modules. Each of them can be connected by sharing a face in four possible orientations differing from each other by the rotation around the Y–Hg–Y bond by 90°. Using this algorithm, various puckered ribbon, layered and spatial frameworks can be assembled from them (Table 8). The dimensions of a

Table 8. The Hg – Y motifs in the structures of 3 : 2 : 2 ternary mercury chalcohalides.

Compound	Hg – Y motif type	Examples of isomorphous compounds	Ref.
α-$Hg_3S_2Cl_2$ (corderoite)	a uniform framework of the –Hg–S–Hg– bonds devoid of closed rings (see Fig. 2)	α-$Hg_3Se_2Cl_2$, $Hg_3Te_2Cl_2$, $Hg_3Te_2Br_2$, $Hg_3S_2F_2$, $Hg_3Se_2F_2$	12, 15, 33, 34
β-$Hg_3S_2Cl_2$	isolated $[Hg_{12}S_8]$ groups (see Fig. 3)	$Hg_3S_2Cl_{1.54}Br_{0.46}$, α-$Hg_3S_2Br_2$, $Hg_3Se_2I_2$ (monoclinic), $Hg_3S_2Br_{1.5}Cl_{0.5}$ (monoclinic), $Hg_3S_2Br_{1.5}Cl_{0.5}$ (cubic)	22, 23, 36, 42, 43
β-$Hg_3S_2Br_2$	the $[Hg_3S_2]^{2+}$ layers incorporating the $[Hg_4S_4]$ rings in two different orientations (see Fig. 4)	γ-$Hg_3S_2Cl_2$, $Hg_3Se_2Br_2$, $Hg_3S_2Cl_{1.5}Br_{0.5}$ (monoclinic), Hg_3S_2ClI (radtkeite), Hg_3Te_2BrI	23, 35, 36, 39, 41, 42
$Hg_3S_2I_2$	$[Hg_3S_2]^{2+}$ double crankshaft ribbons (see Fig. 5)	$Hg_6S_4Br_2ClI$ (grechishchevite), $Hg_3Se_2I_2$ (orthorhombic)	24, 40
$Hg_3Te_2I_2$	a spatial framework with identically oriented closed $[Hg_4Te_4]$ rings (see Fig. 6)	–	37, 38

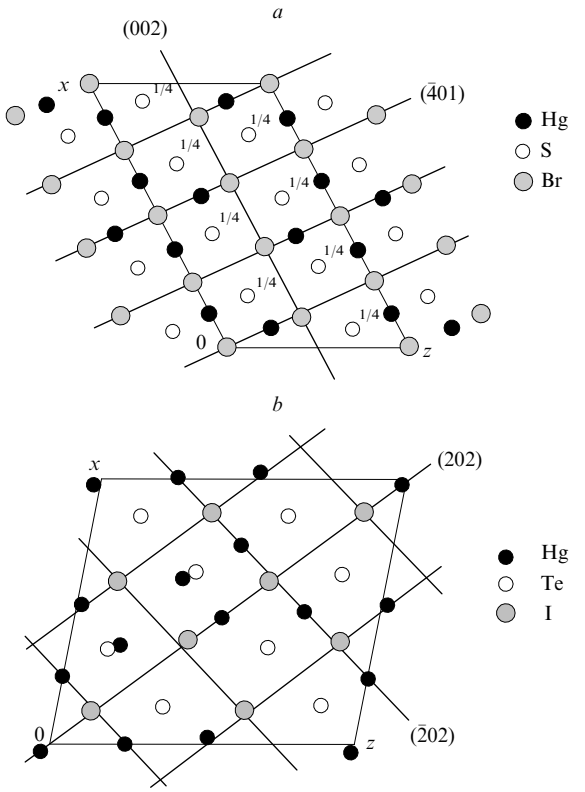


Figure 23. Projections of the crystal structures of $Hg_3Y_2X_2$.
(*a*) A partial projection $0 \leqslant y \leqslant 1/2$ of the crystal structure of α-$Hg_3S_2Br_2$ onto the *xz* plane; the Br sublattice is formed by the ($\bar{4}$01), (020) and (002) planes;
(*b*) a projection of the crystal structure of $Hg_3Te_2I_2$ onto the *xz* plane; the I sublattice is formed by the (202), ($\bar{2}$02) and (020) planes.

module determine the unit cell dimensions and partially the general symmetry of the structure, although the prevailing contribution is made by the specific pattern of the covalent bonding distribution.[113]

Signatures of the modular structure preserved to a greater or lesser extent can be observed in the crystal structures of a number of mercury oxohalides and more complex compounds.

2. The role of halogen atoms in the structures of mercury oxohalides

In the crystal structure of the orthorhombic mineral pinchite $Hg_5O_4Cl_2$ (see Table 3), the halogen atoms form a planar network with the translation periods of the Cl sublattices of 4.13 and 4.34 Å. This network is centred by the mercury atoms. In addition to these eight centring mercury atoms, a unit cell contains 12 mercury atoms, which constitute together with the oxygen atoms a second layer, where two distorted tetragonal networks of oxygen atoms sandwich a hexagonal network composed of the mercury atoms. The commensurability of the (Hg_4Cl_4) and (Hg_6O_8) networks is provided by a change in the geometry of the latter, which gives rise to a non-typical flattened tetrahedral oxygen coordination of the mercury atoms within the hexagonal network. Meanwhile, the Hg atoms of the tetragonal network are characterised by the linear O–Hg–O coordination supplemented to an octahedral one by a square of the Cl atoms.

The halogen atoms play a key role in the structure formation of some low-valence mercury halides. In particular, in the crystal structure of the cubic mineral kuznetsovite $[Hg_3]AsO_4Cl$ (see Table 4), the Cl atoms occupy special positions on a three-fold axis (*xxx*, $x \approx 0.23$). A point on the three-fold axis with a coordinate $x = 0.25$ corresponds to the intersection of families of the (200), (020) and (002) crystallographic planes (with phases of 180° for all planes), which cut a unit cell into eigth cubes with an edge $a' = a/2 = 4.19$ Å. A half of nodes of this sublattice are occupied by the Cl atoms according to the chessboard pattern; the centres of the sublattices are alternately filled with the $[Hg_3]^{4+}$ triangles and $[AsO_4]^{3-}$ tetrahedra. In the crystal structure of cubic eglestonite $[Hg_2]_3O_2HCl_3$ (see Table 4), which is characterised by a lattice parameter nearly doubled as compared to that of kuznetsovite, the cubic sublattice ($a' = a/4 = 4.01$ Å) is formed by the intersection of families of the (400), (040) and (004) crystallographic planes, which gives rise to 64 sublattice nodes per unit cell. Among them, 48 nodes are occupied by the Cl atoms and 16 nodes remain vacant. The centres of the sublattices virtually coincide with the centres of the $[Hg_2]^{2+}$ dumbbells (again 48 centres out of 64 sublattices are occupied). Two latter examples demonstrate that in the absence of large S^{2-} anions, space-filling structural units larger than the oxygen atoms, such as $[Hg_3]^{4+}$, $[AsO_4]^{3-}$ or $[Hg_2]^{2+}$ moieties are required to preserve the cubic sublattice of halogen atoms. In both cases, the sublattice has vacant nodes, which gives rise to its slight contraction with respect to the sublattice with no vacancies.[113]

3. General trends in the structure formation and an analysis of the structure-forming factors in the crystal structures of mercury oxo- and chalcohalides

The crystal structures of mercury oxo- and chalcohalides fully confirm general regulation of the structure formation formulated by Borisov *et al.*[5, 6, 114] Rigid multiatomic fragments, *e.g.*, $[M_4O]$, $[M_6O_2]$, $[M_{10}O_4]$, $[AO_4]$, *etc.*, are most probably generated in a reaction medium even prior to the initiation of crystallisation. The forces driving the transition of a substance into the crystalline state are substantially weaker than the interatomic interactions within these fragments, thus they remain nearly unchanged upon the the nucleation and crystal growth. The dimensions and shape of the rigid multiatomic fragments determine the unit cell parameters and partially the space symmetry group, since the sym-

metry element intrinsic to these groups often convert into the symmetry elements of the whole crystal structure.

In some complicated cases, the software package KAPPLATS [7] helps a lot in the analysis of structure-forming factors. Among the crystallographic planes it seperates those are closely populated by atoms or gravity centres of rigid multiatomic moieties.[115, 116] The crystal structure is then interpreted as a result of the spatial ordering of these atoms and centres of moieties by a set of basis crystallographic planes.[6] The stability of the crystal structure is increased if these planes are related to each other by symmetry operations (even provided that these operations are slightly violated [6, 114]).

As has been shown by Borisov *et al.*,[116] the relative space-filling density for isolated Hg atoms is significantly lower than that for centres of rigid fragments, which implies that the effect of the ordering of isolated mercury atoms is weakly pronounced and the overall structure is predominantly determined by the ordering of centres of rigid atomic fragments.

The spatial segregation of Hg cations with different oxidation states over different layers [116] facilitates solid-state mercury disproportionation reactions, since the pre-existing layers with bivalent mercury are retained thus stabilising the structure-forming motif, whereas the low-valence mercury (*i.e.*, Hg in the $[Hg_3]^{4+}$ and $[Hg_2]^{2+}$ clusters) partly leave the structure. It has to be noted that naturally occurring compounds with 'cluster' mercury, *e.g.*, $[Hg_2]^{2+}$ or $[Hg_3]^{4+}$ moieties, are characterised by a cation-to-anion ratio distinctly different from that of more common rock-forming minerals. In particular, in known mercury minerals, this ratio is close to unity, whereas it is about 1.5 in poyarkovite. The minerals growing in an anion-deficient medium are obliged to saturate the valence bonds by forming Hg···Hg contacts, which gives rise to cluster fragments. Due to the deficit, anions can act as a core for the formation of polyatomic groups, which probably exist in a mother liquor even prior to the initiation of crystallisation.

Since the total sequence of solid-state transformations happening to a mercury mineral upon its transition into an oxygen-rich medium and giving rise to the complete mercury oxidation, which is actually realised in nature, cannot be elucidated, the relevant information can be retrieved from an analysis of methods for the synthesis of compounds containing the $[Hg_3]^{4+}$ and $[Hg_2]^{2+}$ clusters and their stepwise oxidation as realised under laboratory conditions. Typically, the synthesis is accomplished starting from Hg^{2+} oxides and other components in sealed evacuated ampoules at a temperature >400 °C or under hydrothermal conditions at a sufficiently high temperature. It would be reasonable to assume that minerals with the $[Hg_3]^{4+}$ and $[Hg_2]^{2+}$ clusters are formed in nature under similar conditions. When the minerals are transferred to the earth's surface, the mercury disproportionation processes are initiated:

$$[Hg_2]^{2+}, [Hg_3]^{4+} \longrightarrow Hg^{2+} + Hg^0.$$

In a laboratory, the disproportionation of 'cluster' mercury to Hg^{2+} and Hg^0 is typically carried out in an open system, since mercury vapour is liberated. The process proceeds at a high rate at 200–450 °C, however presumably, this process proceeds at a lower temperature and thus at a lower rate under natural conditions. A pair of closely related compounds, $[Hg_2]As_2O_6$ and $HgAs_2O_6$, offer a very illustrative example of this process.[117] These compounds include identical layers of interlinked AsO_6 octahedra; layers formed by the Hg cations are also similar provided that the centres of the $[Hg_2]^{2+}$ dumbbells are taken as cations in the former case. Therefore, the reaction

$$[Hg_2]As_2O_6 \longrightarrow HgAs_2O_6 + Hg$$

can be interpreted as a progressive withdrawal of a half of the mercury atoms from the cationic layers of the $[Hg_2]As_2O_6$ structure, which gives rise to the replacement of the $[Hg_2]^{2+}$ dumbbells with single Hg^{2+} cations. This transformation is accompanied only by a decrease in the *c* parameter of the hexagonal lattice (Fig. 24).

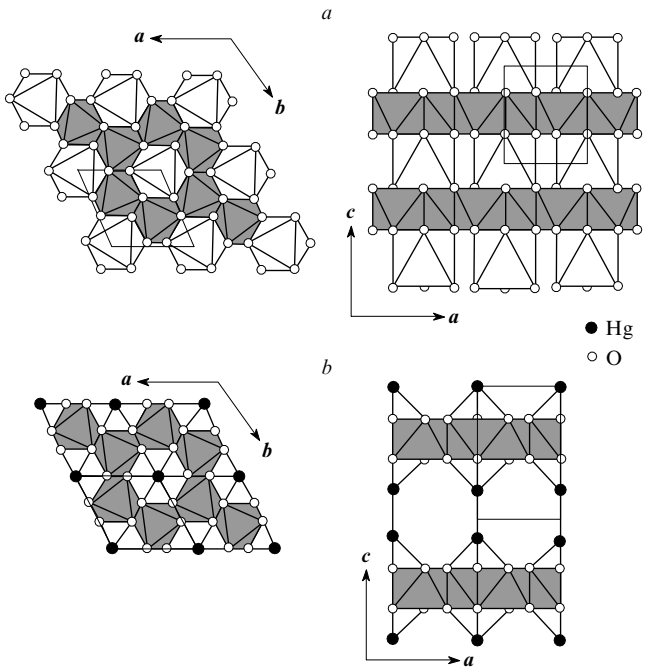


Figure 24. Projections of the crystal structures of $HgAs_2O_6$ (*a*) and $[Hg_2]As_2O_6$ (*b*) drawn to a common scale.
Plain octahedra denote HgO_6, grey octahedra denote AsO_6; the As atoms are not shown for clarity, the Hg atoms are shown only in Fig. *b*. Although the projections onto the *ab* plane are identical, those onto the *ac* plane differ by a length of the Hg–Hg dumbbell (2.5 Å) along the *c* axis.

The conversion of a part of mercury atoms from cluster moieties into the bivalent state with the simultaneous withdrawal of free mercury metal from the structure is well possible, especially in the surface regions of crystals owing to the fact that many crystal structures reveal large voids and channels (in particular, channels with a diameter as large as ~13.6 Å are present in the structure of the mineral szymanskiite [118]). This process can serve as a source of mercury in natural waters and atmosphere.[119]

The segregation of different types of mercury over different layers observed in the structures of some minerals [116] can be a consequence of processes directed towards most stable forms, which slowly proceed under natural conditions. Solid-state transformations changing the overall composition but retaining the structure of large fragments occur most easily exactly in layered compounds. The mechanism of the 'layer-by-layer' transformation was suggested by Hawthorne *et al.*[70] within a discussion of the crystal structures of monoclinic terlinguaite and orthorhombic pinchite, which are tightly associated in nature.

The important role in the crystal structure formation played by large anions (Cl, Br and I) has already been noted above as a part of discussion concerning mercury chalcohalides (see Tables 1 and 8). Mercury and chalcogen atoms are bound by strong covalent bonds and thus are incorporated into the structure as extended atomic groups with constrained variations in the bond lengths and angles. In contrast, quite bulky and large halide anions are not involved into strictly oriented chemical bonding and thus are free to form a more ordered sublattice.[113]

The phenomenon of ordering of various atomic groups by independent systems of crystallographic planes has earlier been observed for other classes of compounds, including rare-earth metal sulfides.[120] Normally, the subdivision into groups is performed according to the spectrum of shortest cation–cation, anion–anion and cation–anion interatomic distances. Within

this approach, the effective size of an atom or atomic group rather than only their chemical nature are of importance.[6]

Therefore, the crystal structure formation in mercury compounds can be formally subdivided into two steps.[6] As the first step, larger 'building blocks' are ordered by basis families of planes (which are the coordinate planes constituting the translation sublattice of these large blocks). As the second step, which proceeds simultaneously, smaller building blocks and single atoms are ordered by basis planes of independent sublattices within a range of shorter interplane distances d_{hkl}. Some atoms of large building blocks are also involved in the second step. The crystal formation means that an initial set of independent sublattices possible for all combinations of atoms and 'rigid' atomic groups converts into a common lattice (least common multiple) with a unit cell composed of an integer number of sublattices and the ordering families of planes become crystallographic planes, which requires the respective indices to be integers.

VI. Crystal chemical features of the MHgYX compounds (M = Cu or Ag; Y = S or Se; X = Cl, Br or I)

1. An analysis of the anion packing

According to several groups of authors,[46–52] the two-layer hexagonal close packing is realised in the crystal structures of MHgYX (M = Cu or Ag; Y = S or Se; X = Cl, Br or I). On the other hand, the anion packing therein is rather close to body-centred cubic packing, at least for some representatives of this class of compounds, according to our results.[113]

A comprehensive analysis of all closely packed anionic planes for typical structures of MHgYX[46–52] as well as of Ag_2HgSI_2 (Ref. 52) and $CuHg_2S_2I$,[47] which are characterised by similar stoichiometries, was performed using the software package KAP-PLATS[7] to establish the character of their anionic packings. It was demonstrated that idealised hexagonal close packing (hcp) and body-centred cubic packing (bcc) differ from each other only in the stacking sequence of dense hexagonal layers 3^6 and some distortions of the layers themselves, which complicates the straightforward assignment of real structures to one of the two packing types.[58]

For all the structures, the degree of anion ordering significantly (by 15%–20%) exceeds that of cation ordering for the same range of interplane distances d_{hkl} essential for the crystal packing formation. This is surprising taking into account the respective results for the structures of heavy metal fluorides, oxides and sulfides,[114, 120] where cations are more ordered.

In the series of the compounds considered, the anion packing varies from ideal hcp (*e.g.*, in CuHgSI)[47,48] to ideal bcc (*e.g.*, in Ag_2HgSI_2).[52] This result requires additional elucidation for the cases of large differences in the sizes of the Y^{2-} and X^- anions (r = 1.84 Å and 2.20 Å for S^{2-} and I^-, respectively). According to an analysis of the arrangement of all atoms in these structures,[58] the relatively small radii of an S^{2-} anion is compensated for by the fact that all direct S–S contacts, which could have distorted the packing (due to a large difference as compared to typical lengths of the I–I or I–S contacts) involve cations, which results in either linear S–Hg–S or bent S–M–S fragments, and the S···S contact appears comparable in length with the S–I and I–I distances (in the former case, S···S ~4.7 Å). Therefore, the mercury atoms, due to the covalent Hg–S and, to a lesser extent, M–S interactions, actually occupy positions with a coordination number of 2, which are non-typical from the classical viewpoint, thus acting as an auxiliary spacer to the S–S contact, which apparently increases its length to that of the I–I contact of the anion packing. The resultant commensurability of the strongest covalent S–Hg–S bond and the van der Waals contact between the large I^- anions enables the regularity of a stable collective packing involving anions with different sizes.

Within this concept, the reason for a less ordered arrangement of cations becomes evident: it is controlled by the covalent interactions between cations and anions and between cations, which is a more powerful factor than mere ordering. As has been mentioned in Section IV.4, weak attractive Hg···Hg interactions in the oxo-centred $[Hg_4O]$ tetrahedra exist at a Hg–Hg distance of ~3.5 Å.[79] Thus it would be reasonable to consider the crystal structures in more detail taking into account both well known Hg–Y interactions and possible Hg···Hg and Hg···M interactions.

2. The structure-forming role of the $[(Hg,M)_4Y]$ tetrahedra

According to structural studies on quaternary chalcohalides MHgYX (M = Ag or Cu; Y = S or Se; X = Cl, Br or I) and closely related Ag_2HgSI_2 and $CuHg_2S_2I$, the S^{2-} anions in these compounds are characterised by the stable tetrahedral surrounding by cations (in contrast to the umbrella-like environment typical of mercury chalcohalides). A similar environment of the sulfur anions is observed in the structures of $Hg_2PbS_2I_2$ (Ref. 54), perroudite $Hg_{4.6}Ag_{4.4}S_{4.6}(Cl,Br,I)_{4.8}$ (Ref. 55) and capgaronnite HgAgS(Cl,Br,I),[56] where the $[M_2Hg_2S]$ tetrahedra similar to the oxo-centred $[Hg_4O]$ tetrahedra present in mercury oxosalts can be identified. These tetrahedra can be considered as Y-centred; it would be reasonable to assume that it is the sp^3-hybridised orbitals of the chalcogen atoms that are involved into the bonding with the cations, since sulfur and selenium are similar to oxygen in terms of the valence electron structures.[58]

Experimental data summarised in Table 9 indicate that the cationic tetrahedra surrounding the S^{2-} anions (only one example is available for Se^{2-}) are sufficiently stable in terms of the geometry parameters.

Tetrahedron edge	Length /Å
Hg–Hg	3.56–3.60
Cu–Cu	4.08–4.14
Hg–Cu	3.48–3.90
Hg–Ag	3.63–4.08
Ag–Ag	4.56–4.83

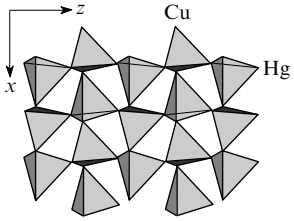
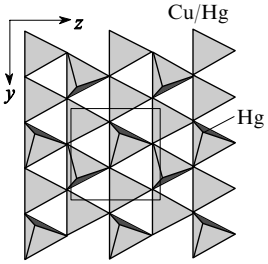
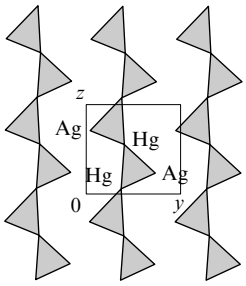
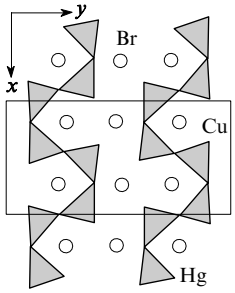
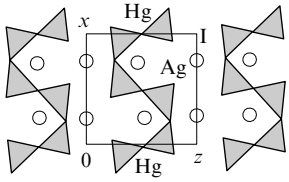
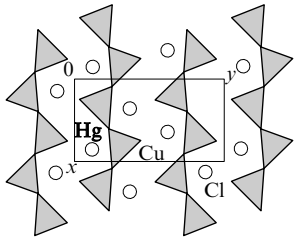
Noting the small variations in the cation–anion distances (see Table 2), the $[(M,Hg)_4Y]$ tetrahedra can be considered as 'rigid' atomic moieties (building blocks), which are incorporated into a crystal structure as a whole. This is due to both well known Hg–S and Hg–Hg covalent interactions and less elucidated M–S, M–Hg and M–M bonding.

In the crystal structure of CuHgSI, a chain of the $[Cu_2Hg_2S]$ tetrahedra going along the 2_1 axis parallel to the z axis acts as the 'load-bearing' structural unit, which includes the strongest interatomic interactions, *i.e.*, Hg–S and Hg···Hg. A unit cell includes two such chains, *viz.*, in the origin and in the centre of the xy projection. The chains are assembled into a common framework by sharing Cu vertices, the I atoms coordinated (like the S atoms) by four cations (2 Hg + 2 Cu) fill the interchain cavities.

In the structure of $CuHg_2S_2I$, the $[(Cu,Hg)_4S]$ tetrahedra are assembled into a layer in the yz plane by sharing (Hg,Cu) vertices. The layers are further assembled into a framework by sharing Hg vertices. As outlined in Table 9, some edges of the $[(Cu,Hg)_4S]$ tetrahedra are shorter than 3.8 Å, which assumes attractive interactions.

In both $CuHg_2S_2I$ and Ag_2HgSI_2, mercury and sulfur are present in a 1 : 1 ratio. Although the anion packings in the two structures are similar (positions of the S and I ions are interchanged), the covalent skeleton in Ag_2HgSI_2 involves only isolated chains composed of the $[Ag_2Hg_2S]$ tetrahedra going along the z axis together with a virtually linear rows of the Hg atoms with Hg–Hg ≈ $c/2$ = 3.55 Å. In a projection onto the xy plane, the chains of the $[Ag_2Hg_2S]$ tetrahedra go through the origin and the centre of the unit cell composing an approximate hexagonal packing of these isolated one-dimensional fragments in this cross-section.

Table 9. Frameworks of the $[(M,Hg)_4Y]$ tetrahedra in the structures of some quaternary mercury chalcohalides.

Compound	Metal–metal distance [a] /Å	Motif of the $[(M,Hg)_4Y]$ tetrahedra	Ref.
CuHgSI	3.589 (Hg–Hg) 3.617–3.970 (Hg–Cu) 4.078 (Cu–Cu)		47
$CuHg_2S_2I$	3.775–4.152 (Hg–Hg/Cu) [b] 3.696–3.832 (Hg/Cu–Hg/Cu)		47
Ag_2HgSI_2	3.559 (Hg–Hg) 3.629–4.112 (Hg–Ag) 4.555 (Ag–Ag)		52
CuHgSBr (295 K) (see [c])	3.568 (Hg–Hg) 3.530–3.831 (Hg–Cu) 4.124 (Cu–Cu) 3.576 (Hg–Hg) 3.481–3.881 (Hg–Cu) 4.124 (Cu–Cu)		46
β-AgHgSI	3.598 (Hg–Hg) 3.999 (Hg–Ag) 3.776 (Hg–Ag) 4.648 (Ag–Ag)		50
CuHgSeCl	3.483 (Hg–Hg) 3.592, 4.121 (Hg–Cu) 4.253 (Cu–Cu)		49

[a] For the Hg–Y, Cu–Y and Ag–Y distances, see Table 2; [b] Hg/Cu means that the respective site is statistically occupied by Hg and Cu (see Fig. 13); [c] data for crystallographically independent $[(M,Hg)_4]$ tetrahedra are given.

In the crystal structures of CuHgSCl and CuHgSBr (295 K),[46] the vertex-sharing $[Cu_2Hg_2S]$ tetrahedra form puckered layers lying in the *xz* plane. The mercury atoms in these structures are arranged into zigzag rows [in contrast to the linear Hg–Hg columns that determine the respective unit cell parameters in the above structures (the double Hg–Hg distance is ~7 Å)]. Two Hg–Hg–Hg fragments intersect at an angle close to 90° and thus $a \approx 7\sqrt{2} = 9.84$ Å. A unit cell accomodates two layers related to each other by a glide-reflection plane associated with a shift by $b/2 = 9.17$ Å. Meanwhile, unit cells of similarly organised β-AgHgSI and CuHgSBr (358 K) accomodate only one such layer. These structures feature a short translation (~4 Å) normal to the mirror reflection plane.

In the structure of CuHgSeCl, the Se^{2-} anions are also characterised by the tetrahedral environment (2 Cu and 2 Hg, see Table 9). The structure is based on chains of the $[Cu_2Hg_2Se]$ tetrahedra formed around linear rows of the Hg^{2+} cations with the doubled Hg–Hg distance of $a = 6.94$ Å. The chains are assembled into a layer in the *xz* plane by sharing Cu vertices. Due to the short translation *c* (4.25 Å), the Cl atoms lie in the same plane as the Cu atoms, thus the layers formed by the $[Cu_2Hg_2Se]$ tetrahedra are separated from each other by layers of the Cl^- anions In the structure of α-AgHgSI,[51] symmetry factors do not prevent the formation of a framework of vertex-sharing $[Ag_2Hg_2S]$ tetrahedra; cavities of the framework are occupied by the large iodine atoms.

3. Crystal structure-forming factors for the MHgYX structures

Summarising structural data outlined above, we conclude that it is the Hg–Y covalent interactions and Hg···Hg bonding contacts that act as the prevailing structure-forming factors in the crystals of quaternary mercury chalcohalides.[58] Linear or zigzag ···Hg···Hg···Hg··· chains (with Hg–Hg distances of ~3.5 Å) determine one of the unit cell dimensions. Other unit cell dimensions are dictated by the necessity to combine the $[(M,Hg)_4Y]$ tetrahedra by vertex-sharing. The commensurability of the Hg···Hg, X···X and X···Y contacts enables the close packing of anions and a rather high symmetry of the resultant crystal structure. The stability of a structure towards isomorphous substitution of components can be regarded as an additional argument in favour of its robustness. In particular, the isomorphous substitution HgS ⇄ AgX over a wide concentration range with the preservation of the crystal structure type (minerals perroudite [55] and capgaronnite [56]) has been reported. Structural investigations into the synthetic analogues of minerals grechishchevite, lavrentievite, arzakite, radtkeite (corresponding to the $Hg_3Y_2X_2$ stoichiometry) confirm the ability of the anion packings to remain unchanged over significant variations in the halogen composition within the $Hg_3S_2Cl_2$–$Hg_3S_2Br_2$–$Hg_3S_2I_2$ system.[40–43] The halogen atoms always occupy positions in the nodes of a primitive cubic sublattice centred by the S^{2-} anions. The introduction of monovalent atoms, *i.e.*, Cu and Ag, relieves this limitation making the X and Y anions more equivalent.

Within the approach adopted (based on the identification of stable 'building blocks') it would be interesting to compare the structures of two natural HgS modifications, *viz*., trigonal α-HgS (cinnabar or cinnabarite) and cubic β-HgS (metacinnabarite). These structures are traditionally considered as distinctly different. Our approach to the crystal chemical analysis aimed at the identification of densely packed crystallographic planes [7] (separately for cations and anions) established that the cationic matrices are identical in both phases. It can be represented as the three-layer cubic close packing (with the stacking sequence ABC).[121] In the cubic phase, both anions and cations are packed according to this pattern and thus the overall structure can be considered as a three-dimensional motif of $[S_4Hg]$ or, alternatively, $[Hg_4S]$ tetrahedra. Meanwhile, the anion packing is significantly different in the trigonal phase. The S^{2-} anions are shifted from the initial cationic tetrahedron through a common face to a neighbouring cationic octahedron while the bonds with two Hg atoms are preserved and remain the strongest in the new location. *F*-centred cubic and rhombohedral cells are equivalent provided that $c_R/a_R = 2.45$.[122] For the cinnabar structure, this ratio is 2.29, which means that the rhombohedron of Hg atoms somewhat deviates from cube: $a'_R = 5.74$ Å; $\alpha'_R = 92.5^\circ$ (Fig. 25).

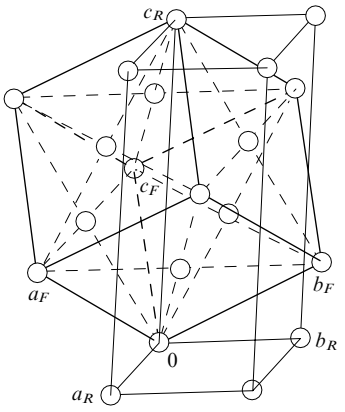


Figure 25. A relation between the rhombohedral and *F*-centred cubic cells in the cinnabarite (α-HgS) structure. Only mercury atoms involved into a lattice close to the *F*-centred cubic one are shown.

The stability of the cationic framework both in α- and β-HgS is confirmed by its preservation upon the Al substitution for 1/4 of the Hg cations, as evidenced by the crystal structure of $Hg_3AlF_6O_2H$ (space group $R\bar{3}m$, $a = 7.262$ Å, $c = 10.441$ Å, $Z = 3$).[123] In contrast to the framework realised in α-HgS, the *F*-centred cubic sublattice of cations is deformed in the opposite direction, *i.e*., the cube is elongated along the three-fold axis: $a'_R = 5.449$ Å, $\alpha'_R = 83.57^\circ$. This pseudocubic cationic sublattice corresponds to a hexagonal one with $a_R = a/2 = 3.631$ and $c_R = c = 10.441$ Å. In this case, the $c_R/a_R = 2.88$, which by far exceeds the ideal value of 2.45 (Fig. 26). We note that the F atoms in this structure occupy cationic tetrahedra, whereas the O atoms composing the linear O—Hg—O fragments are characterised by a less regular coordination environment.

The fact that the coordination of an S atom to only two Hg atoms is preferred can be a reason for the 'dissolution' of cinnabar in specific natural processes, which gives rise to the replacement of two remote Hg atoms in the coordination environment of the sulfur atoms with two Cu, Ag, Pb, *etc*. atoms. The incorporation of these cations is accompanied by the introduction of charge-compensating anions, *viz*., Cl, Br or I, which results in the formation of structures considered above corresponding to the MHgXY stoichiometry with HgS : MX = 1 : 1.

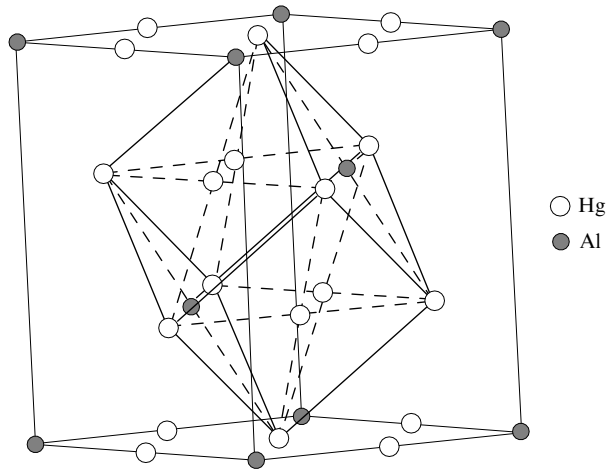


Figure 26. The cationic *F*-centred sublattice in the crystal structure of $Hg_3AlF_6O_2H$.

In the case of more mercury-excessive compounds (here, we focus on the Hg : Y : X = 3 : 2 : 2 stoichiometry, since it is best represented by structurally studied compounds), the crystal structures emerge under the action of two factors: covalent bonding between the Hg and S atoms giving rise to isolated, ribbon, layer or framework assemblies and arrangement of the halogen atoms into a packing close to a primitive cubic one.[8, 113] As has already been stated above, the 'cubic' unit in these structures provides the commensurability of the geometric parameters of this two components resulting in the stability of the packing motifs even against substantial variations in the halogen composition. The freedom in the rotation of the blocks upon their assembling produces $[HgS]_n$ moieties with diverse topologies, which explains rich polymorphism intrinsic to these class of compounds.

VII. Conclusion

The crystal chemical analysis of natural and synthetic inorganic mercury compounds with anions abundant in nature (O, S, Se, Te, F, Cl, Br, I, CrO_4, PO_4 and AsO_4) also containing auxiliary cations similar to mercury in terms of structural preferences (*i.e*., Cu, Ag and Pb) demonstrate a huge diversity of their crystal structures. As has been established, some atomic groups with strong covalent Hg—O, Hg—Y (Y = S, Se or Te) and A—O (A = Cr, P or As) bonds are not substantially deformed in the course of the crystallisation. These include oxo-centred $[Hg_4O]$ tetrahedra (which also involve weaker attractive Hg···Hg interactions), S- and Se-centred $[(M,Hg)_4Y]$ tetrahedra, $[Hg_6O_2]$ *r*-octahedra, *etc*. The centres of these 'rigid' groups upon their incorporation into a crystal structure undergo ordering by systems of parallel (crystallographic) planes to form sublattices and the true translation lattice.

In the crystal structures of compounds with the 3 : 2 : 2 stoichiometry, the monovalent anions are more strictly ordered than the cations. This is explained by the fact that large weakly bound anions adapt much easier to the sublattice requirements than the covalently bound Hg—Y component of the structure.

Specific features of the assembly of these covalently bound groups and their ability to change the configuration without substantial redistribution of the bonding topology facilitate polymorph transitions and other structural transformations therein. This observation can shed light upon complex associations between naturally occurring mercury-containing minerals. A deep understanding of the mechanisms underlying structural transitions in associations of these minerals is of great environmental significance.

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