Migration of Heavy Metals in Natural and Technogenic Media: the Function of Atomic Fragmentation as Illustrated by the Structures of Mercury Minerals and Their Crystallochemical Analogues

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Abstract

With the use of literary data, the things on sources of mercury pollution in Siberian region have been considered. With allowance made for present-day data about chemical interactions and with the results of original chemical analysis of crystals, steady atomic groups have been distinguished: $[Hg_4O]$ and $[(Hg, M)_4S]$ tetrahedra (M = Cu, Ag), $[Hg_6O_2]$ r-octahedra, and $[Hg_3S_2]_n$ − the covalent bonded formations of different topology that can be preserved in natural processes, solid-phase and other transformations. This fact should be taken into consideration when discussing the forms of transport for mercury, lead, and alternative toxic elements in the environment.

INTRODUCTION

Mercury is a dispersed and mobile element, with easily variable behaviour in various environments; the element shows diversified types of chemical bonds and it is extremely important for the ecological background on the planet. The study of natural and technogenic ways for mercury migration is of much interest in an assessment of environmental situation. Siberia, which is the site where so large mercury deposits as Aktashskoye, Chaganuzunskoye, Sukhon'koye, Krasnogorskoye (Mountain Altai); Terligkhayskoye, Chazadyrskoye, Arzakskoye (Tuva); Barunshiveinskoye, Kelyanskoye (Transbaikalia); Zvezdochka, Northern (Yakutia) are concentrated, belongs to regions where the problem becomes particularly urgent since the rivers flowing to the north cause the pollution to extend beyond the limits of these regions.

The work [1] contains an in-depth description of natural sources of mercury in the territory of Siberia. The natural objects that concentrate mercury and that supply it into the environment represent, first, purely mercury deposits; second, mercury-containing deposits and the breeds that are infected with mercury as a result of the imposed envelope developed in them; and third, technogenic sources that are described in detail in [2].

It has been also demonstrated in [1] that the scientific and technological advance involves a gain in the mercury content of the atmosphere. Accordingly, it was found that a multiple increase of mercury concentration in dated layers of the sheet glacier of Greenland for the last decades of the past century is directly related to sharply increased extraction of mercury over the same period. These and alternative data bear witness to an increasing danger of mercury infection on a global scale. In this situation, one needs a clear concept on the natural and technogenic sources of mercury ingress in the environment and on its migration

ways in a variety of media. It should be noted that by virtue of its high migratory properties, mercury is actively involved in various natural processes and it enriches to some extent ore deposits of a widely variable composition together with deposits of hydrocarbon raw material.

Accordingly, appreciable concentrations of mercury have been detected in ore deposits of a non-mercury composition, namely, in those of pyrite, copper, and other nature, and in gas and gas-oil deposits. When compared to purely mercury deposits, they represent a less dangerous source of direct pollution of the environment by mercury, but they become a threat to the ecological well-being since they are present in significant amounts within the wastes from metallurgical refining of non-ferrous metal ores. Huge resources of gas that is being annually extracted and manufactured make us also consider this natural source of mercury entry in the environment. It has been known that the formation of mercury and mercury-bearing ore deposits is accompanied by the development of various (those lithochemical, hydrochemical, and gas) envelopes of mercury [1]. Their transformation occurs with mercury passing into soil, water, and atmosphere. Labile equilibrium of mercury and its compounds in these media define the part played by the given source of mercury in the environment.

Mercury and particularly its soluble compounds is a priority contaminant of the aqueous medium. Sea areas with volcanic and gas and hydrothermal activity deliver a great amount of mercury. In regions where the present-day volcanism is manifested, mercury anomalies are formed near to egresses of volcanic hydroterms. In areas of paleovolcanic activity, contrast mercury anomalies are formed in discharge zones of methanoic, nitro-alkaline, and carbonate sources. During the periods of regional seismic tectonic activization, combined anomalies of mercury and methane in ocean water appear within the limits of tectonic disruptions of both gas-oil, and coal deposits.

In 2003, the problem of the environment pollution by mercury became the main issue in the agenda of the annual session of the Executive Council of the UN Environment Programme (UNEP) [3]. According to the UNEP report, monitoring the activity of power sta-

tions could considerably reduce the pollution level of the planet by mercury. According to statistical data, power stations that burn a great deal of coal, and waste incinerators annually vent to the atmosphere 1500 t of mercury, mainly as a result of coal combustion. Asian countries vent to the atmosphere the greatest quantity of mercury − 860 t/year. For Africa, this index comprises 197 t/year, for Europe 186, for North America 105, for Australia and Oceania 100, and for South America 27 t/year. Since consumption of mineral combustible grows both in less developed and in industrially developed states, the degree of the environment pollution by mercury will continue growing, especially under conditions that there is no monitoring technology and alternative energy sources.

According to the data of UNEP experts, extraction of gold and silver that is in wide practise in less developed states constitutes an additional significant source of the environment pollution by mercury, the share of which accounts for 400 to 500 t of mercury that is annually discharged to the atmosphere, soil, and water. Mercury is in general use during extraction of these precious metals from ore, which damages health of people from miner's towns and harms the environment. Upon entering the atmosphere, this dangerous heavy metal may overcome hundreds and thousands kilometres, polluting territories.

Research has demonstrated that upon its ingress in small lakes, mercury inflicts a much greater loss to fish and to water resources as compared with large water bodies. This fact derives from the circumstance that the water temperature of small water bodies is higher and, consequently, the process of mercury methylation (transformation of mercury to its more toxic form) develops more actively. This interrelation takes on a new significance in the context of long-term climate changes and global warming.

For human beings, the greatest hazard to be poisoned with mercury is when using fish for food. Evidence of the performed research suggests that mercury is present in fish with the concentrations that reflect adversely on people health.

Incineration factories also make a big contribution to mercury pollution. In addition,

they constitute a source of a significant amount of other heavy metals (lead, cadmium, arsenic, and chrome).

This work considers structural features of some mercury minerals and their analogues, these features being essential to study the mechanisms of mercury migration during solid-phase and other transformations.

MERCURY AND MERCURY-CONTAINING MINERALS OF SIBERIA

Zinnabar is the basic commercially significant mining mineral of mercury deposits. Native mercury, metacinnabar, livingstonite, and mercury-containing grey copper ores, together with amalgams of metals, are of a sharply subordinated significance and are mined as a by-product with zinnabar. Primary minerals of mercury in a hypergenesis zone undergo dissolving with the subsequent sorption of mercury by natural sorbents and with the formation of secondary mercury minerals; in so doing, mercury partially passes to water solutions and to the gas phase. Haloid, oxyhalogen, oxidic, and sulphate mercury compounds are recorded rather seldom among the secondary minerals. Many of these minerals can be referred to with the notion "seasonal", *i.e.* they periodically appear and disappear depending on the change of climatic and atmospheric conditions [1]. Under certain conditions, in spite of scarce amounts of these compounds, they can comprise rather significant suppliers of mercury from primary mining concentrates to underground and superficial waters, soil, and the atmosphere. Change in crystal chemical parameters of mercury compounds under the variation in composition of the environment and other external conditions is a rather important factor that has an influence on mercury migration within mineral associations. The main information on the issue is available through investigations and comparative analysis of crystal structures of primary and secondary mercury minerals.

Up to the middle 40s of the past century only about 20 mercury minerals have been reported; now their quantity is over 100 (for the most part due to findings of new minerals that are frequently unstable under surface

conditions). Table 1 contains the information on all mercury minerals reported for today's that have been found in the ores of deposits of Siberia [1].

Among distinctive features of coordination of Hg atoms by other atoms, mention should be made of the following: 1) a tendency to form covalent bonds with the same atoms and to form pairs $[Hg_2]^{2+}$ and, in rare cases, triangles $[Hg_3]^{4+}$; 2) the formation of covalent bonds with one or two anions to make up linear fragments, chemical bonds inside of which being stronger than with other atoms; 3) the formation of strong clusters with other crystal chemical close, heavy metals (to take an illustration, the tillmannsite mineral [4]).

We have studied the structures of some rare minerals of hypergenic origin, wherein mercury executes different crystal chemical functions [5, 6]. With a deficiency of oxygen, under high temperature and pressure, the minerals that contain mercury with the states of oxidation <2 (+1, +4/3) may form. While they get onto a surface or in an aqueous medium, these minerals undergo essential transformations owing to changes in the chemical state of mercury. There is about 20 compounds among them that include cluster groups $[Hg_2]^{2+}$ (calomel $[Hg_2]Cl_2$, shakhovite $[Hg_2]_2Sb(OH_3)_3$, poyarkovite $[Hg_2]_3O_2Cl_2$, chursinite $[Hg_2]_3(AsO_4)_2$, *etc.*); there are $[Hg_3]^{4+}$ groups (kuznetsovite $[Hg_3]AsO_4Cl$, terlinguaite $[Hg_3]HgO_2Cl_2$). They are present in certain compounds along with Hg^{2+} cations: terlinguaite $[Hg_3]HgO_2Cl_2$ contains in the structure both $[Hg_3]^{4+}$, and Hg^{2+}; wattersite $[Hg_2]HgCrO_6$, hanawaltite $[Hg_2]_3HgO_3Cl_2$, deanesmithite $[Hg_2]Hg_3CrO_9S_2$ contain $[Hg_2]^{2+}$ and Hg^{2+}.

RIGID STRUCTURAL BLOCKS AND THEIR PART IN THE FORMATION OF OXO- AND CHALCOHALIDE COMPOUNDS OF MERCURY AND HEAVY METALS

Chemistry of compounds with metal-metal bonds and other interactions that are unusual to classical crystal chemistry develops especially quickly during the last decades. The present-day crystal structure analysis and quantum chemical methods make it possible to determine and interpret complex atomic configurations

TABLE 1

Mercury and mercury-containing minerals that have been found in the ores of Siberian deposits [1]

Mineral	Formula	Maximum content of mercury, mass %
Native elements and intermetallic compounds		
Mercury	Hg	100
Mercurous silver (arquerite, kongsbergite, bordosite)	α-$Ag_{1-x}Hg_x$	51.8
Silver:		
Golden	Ag	up to 14.5
Antimonous	Ag	up to 1.0
Mercurous gold	α-$Au_{1-x}Hg_x$	up to 15.8
Mercurous palladium	$Pd_{1-x}Hg$	up to 22.7
Mochellandsbergite	γ_1-$Ag_{1-x}Hg_{1+x}$	up to 73.4
Schachnerite	β-$Ag_{1.1}Hg_{0.9}$	61.8
Gold and silver amalgamide	β-$(Au,Ag)_3Hg$	34.1
Gold amalgamide	Au_2Hg	35.3
Kolymite	γ_2-Cu_7Hg_6	74.0
Zvyagintsevite	$(Pd,Pt,Au)_3(Pb,Sn)$	0.87
Arsenides and antimonides		
Tennantite-Hg	$(Cu,Hg)_2Cu_{10}As_4S_{13}$	up to 21.0
Aktashite	$Cu_6Hg_3As_4S_{12}$	36.0
Gruzdevite	$Cu_6Hg_3Sb_4S_{12}$	33.2
Galkhaite	$(Cs,Tl)(Hg,Cu,Zn)_6(As,Sb)_4S_{12}$	52.2
Tvalchrelidzeite	$Hg_{12}(Sb,As)_8S_{15}$	65.5
Hackite	$(Cu,Hg,Ag)_{12}Sb_4(Se,S)_{13}$	15.3
Halides		
Calomel	Hg_2Cl_2	86.2
Kuzminite	$Hg_2(Br,Cl)_2$ до Hg_2Br_2	77.7
Eglestonite	$Hg_6O_2Cl_3H$	90.8
Kadyrelite	$Hg_6O_2(Br,Cl)_3H$	84.7
Terlinguaite	$Hg_4O_2Cl_2$	88.6
Poyarkovite	Hg_3OCl	91.3
Sulphides, selenides, thio salts and selenosalts		
Zinnabar	α-HgS	≈86
Metacinnabar	β-HgS	≈86
Timanite	HgSe	75.1
Sphalerite-Hg	$(Zn,Hg,Cd)S$	up to 35.0
Tetrahedrite-Hg	$(Cu,Hg)_2Cu_{10}Sb_4S_{13}$	up to 22.0
Kelyanite	$Hg_{36}Sb_3O_{28}(Cl,Br)_9$	85.6
Corderoite	α-$Hg_3S_2Cl_2$	82.8
Lavrentievite	$Hg_3S_2(Cl,Br)_2$	80.6
Arzakite	$Hg_3S_2(Br,Cl)_2$	78.4
Grechishchevite	$Hg_3S_2(Cl,\ Br,\ I)_2$	74.5
Montroydite	HgO	92.9
Shakhovite	Hg_4SbO_6	78.4
Oxides, sulphates, arsenates		
Schuetteite	$Hg_3O_2(SO_4)$	87.7
Kuznetsovite	$Hg_3Cl(AsO_4)$	77.8
Chursinite	$(Hg_2)_3(AsO_4)_2$	81.3

that are peculiar especially to heavy metals. This can be exemplified by giving an indication of a structure with a tetrahedral group of gold atoms that are centred by oxygen atom [7]. With Au−Au distance being approximately equal to 3.36 Å and with Au−O being equal to 2.06 Å, this group is assumed to feature "six valence electrons of oxygen atom that fill three degenerated binding orbitals that have formed within the point group T_d (or T) that are vacant in a metal cluster Au_4^{2+}".

Another work reveals an "unusual", in opinion of the authors, $[Ag_4Rh_2O_2]$ atomic group that consists in two cationic tetrahedra with a common edge that are centred by oxygen atoms [8]. External vertexes are occupied by four Au atoms, the common edge is by 2Rh. Distances Au−Au, Rh−Au, and Rh−Rh comprise 2.98−3.58 Å; Au−O and Rh−O comprise approximately 2.05 and 2.10 Å, respectively. Previously, when interpreting several structures of fluorides, a similar group has received the name "r-octahedron" [9]; likewise, it has been demonstrated that many structures can be split to such groups, especially those with close-packed cationic matrices.

Several compounds of mercury are also typified by cationic complexes available around "free" oxygen anion (oxocentred tetrahedra), *i.e.* the anion that is not included into acid radicals (SiO_4, PO_4, AsO_4, *etc.*). The strength of oxygen-metal bonds that are created by a "free" anion of oxygen in certain cases exceeds the strength of the remaining bonds that have been formed by atoms of metal. In symbolical terms, these oxygen atoms pull cations onto themselves thus forming oxocentered tetrahedra with comparatively high strength of the chemical bond.

Since 1997, papers of S. K. Filatov and S. V. Krivovichev [10−12] on oxocentred tetrahedral groups, wherein copper atoms play typically the part of cations, started to be published. In 2001, the monograph of these authors was published that summarized the information on complexes of anion-centred tetrahedra [13]. We recognized tetrahedral groups $[Hg_4O]$ (Fig. 1, *a*) in studies of crystal structures of natural and synthetic mercury oxo salts. Once the nearest anions are added to this oxocentred tetrahedron, it will combine well a tendency of mercury to form linear *sp* hybridisation of bonds Hg−O and sp^3
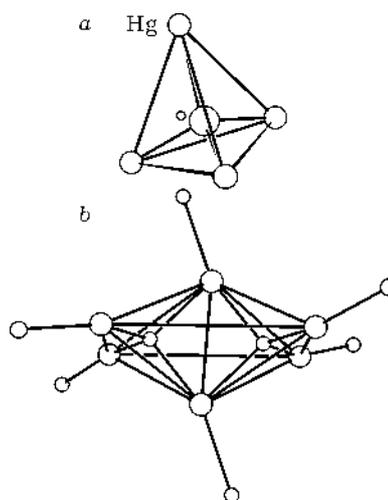
Fig. 1. Crystal structure of atomic groups $[Hg_4O]$ (*a*) and $[Hg_6O_2]$ (*b*): *a* − oxocentred tetrahedron, *b* − *r*-octahedron.

hybridisation of the central oxygen atom. Oxo complexes $[Hg_4O]$ make up isolated groups, chains, belts, layers, and three-dimensional skeletons. By analogy with a classification of anion centred complexes that has been offered in [13], we performed their classification regarding the bond types between the groups [14] (Table 2). Nevertheless, these facts were considered to be exotic in chemical scientific community, and in 2002, French authors publish a paper about an "unprecedented" oxo cluster $[Hg_4O_5]$ that constitutes an oxocentred tetrahedron $[Hg_4O]$ with four oxygen atoms adjacent to it that supplement the linear covalent coordination of mercury atoms [15]. Quantum chemical calculation of the fragment has demonstrated that with Hg−Hg distances being equal to 3.2−3.5 Å (the edges of $[Hg_4O]$ tetrahedron), the chemical bond between Hg atoms, together with Hg−O covalent bonds (2.05−2.10 Å), accounts for the stability of the given group.

When analysing the structures of mercury minerals and synthetic compounds (pinchite, hanawaltite, poyarkovite, terlinguaite, Hg_2OI, α-$Hg_3O_2Cl_2$, and β-$Hg_3O_2Cl_2$ compounds, *etc.*), we also distinguished a frequent $[Hg_6O_2]$ atomic group [16, 17]. It consists in two oxocentred tetrahedra $[Hg_4O]$ that are bonded by the common edge Hg−Hg with a centre of symmetry in the edge middle. The convex polyhedron that represents a coordination polyhedron of two central oxygen atoms, is identified as *r*-octahedron, *i.e.* a rhombically distorted octahedron (see Fig. 1, *b*).

TABLE 2

Structural blocks from [OHg$_4$] tetrahedra in certain structures of natural and synthetic oxo halides of mercury

Formula Hg : O Space group Z	Parameters of the unit cell (Å, deg) V (Å^3)	[OHg$_4$] tetrahedron: d(O−Hg), Å ∠HgOHg, deg, d(Hg−Hg), Å	Cross-linking fragment from [OHg$_4$] tetrahedra
Hg$_5$O$_4$Cl$_2$ (pinchite) 5 : 4 *Ibam* 4	11.619 6.105 11.710 830.6	2.045−2.707 100.4−113.5 3.416−3.945	
Hg$_4$O$_2$Cl$_2$ (terlinguaite) 2 : 1 *C2/c* 4	11.953 5.904 9.466 105.59 (β) 643.0	2.016−2.486 91.6−123.3 3.408−3.963	
α-Hg$_3$O$_2$Cl$_2$ 3 : 2 *P2$_1$/c* 2	6.3100 6.8657 6.8579 114.36 (β) 270.6	2.063−2.319 98.3−112.5 3.511−3.766	
β-Hg$_3$O$_2$Cl$_2$ 3 : 2 *P2$_1$/c* 4	10.838 9.317 11.564 108.90 (β) 1104.7	1.891−2.588 84.7−117.8 3.338−3.989	
Hg$_3$OCl (poyarkovite) 3 : 1 *C2/c* 24	19.009 9.018 16.848 110.81 (β) 2700.0	1.949−2.601 87.9−121.6 3.109−3.943	
Hg$_6$O$_2$Cl$_3$H (eglestonite) 3 : 1 *Ia3d* 16	16.036 16.036 16.036 4123.7	1.23(H)−2.179 105.0−113.6 3.654−3.994	
Hg$_3$O$_2$SO$_4$ 3 : 2 *P3$_2$2$_1$* 3	7.137 7.137 10.017 120 (γ) 441.9	2.161−2.583 100.65−112.69 3.552−3.843	

To provide support to the advisability for this atomic group to distinguish, quantum chemical calculations have been made for [Hg$_4$O$_5$]$^{2-}$ and [Hg$_6$O$_8$]$^{4-}$ systems (an oxocentred tetrahedron and oxocentred *r*-octahedron with the nearest anions added). The calculation has suggested that [Hg$_6$O$_8$]$^{4-}$ group shows essential advantages over [Hg$_4$O$_5$]$^{2-}$ [18]. Consequently, the formation of these energetically favourable groups under favourable conditions will be the first stage, prior to crystallisation. On the contrary, these groups must be preserved in

Description of the oxocentred motive; the classification type according to [13]	Fragment of packing for the cross-linking fragments
Zigzag columns from pairs of edge-linked tetrahedra [OHg$_4$] (r-octahedra) that are combined to form a skeleton by tetrahedron vertices. **F23**	
Zigzag arched chains from pairs of vertex-linked tetrahedra [OHg$_4$] (r-octahedra). The chains are combined by Hg−Hg bonds of triangular [Hg]$_3$ clusters to form layers and by vertices of tetrahedra, to form a skeleton. **F24**	
Layers from vertex-linked tetrahedra [OHg$_4$] (r-octahedra). The layers are combined by vertices of tetrahedra to form a skeleton. **F6**	
Layers from edge-linked and vertex-linked tetrahedra [OHg$_4$] (r-octahedra). The layers are combined by vertices of tetrahedra to form a skeleton. **F27**	
Pairs of edge-linked tetrahedra [OHg$_4$] (r-octahedra) that are combined by dumbbell Hg−Hg bonds to form a skeleton. **I4**	
Pairs of tetrahedra [OHg$_3$H] that are linked by a common vertex (H atom) and that are combined by dumbbell Hg−Hg bonds to form a skeleton.	
A three-dimensional skeleton from r-octahedra that are combined by their common vertices. **F6**	
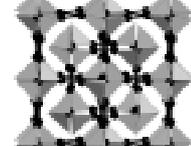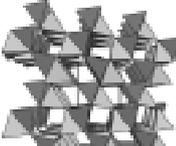
the course of dissolving or alternative processes of the destruction of the crystals.

A search for stable "structural blocks" in structures of mercury chalcogenides has resulted in that it is advisable to distinguish cationic tetrahedra (M,Hg)$_4$Y in structures of composition MHgYX (M = Cu, Ag; Y = S, Se; X = Cl, Br, I). Theses tetrahedra are linked by their common (M,Hg) vertices to form two-dimensional or three-dimensional formations [19] (Table 3). Sulphur atoms of cationic tetrahedra have shorter bonds with two

TABLE 3

Structural blocks from $(M,Hg)_4Y$ tetrahedra in certain structures MHgYX (M = Cu, Ag, Y = S, Se, X = Cl, Br, I)

Compound	Y–(Hg,M) (Å)	(Hg,M)–(Hg,M) (Å)
CuHgSI	Hg–S = 2.359, 2.369	Hg–Hg = 3.589
$Pna2_1$, $Z = 4$	Cu–S = 2.322, 2.311	Hg–Cu = 3.970–3.617
$a = 7.183$; $b = 8.343$;		Cu–Cu = 4.078
$c = 6.989$ Å		
$V = 418.8$ Å^3		
$CuHg_2S_2I$	Hg–S = 2.37	Hg–(Hg,Cu) = 3.775–4.152
$Cmc2_1$, $Z = 4$	(Cu,Hg)–S = 2.368, 2.391,	(Hg,Cu)–(Hg,Cu) = 3.696–3.832
$a = 12.618$; $b = 7.224$;	2.417	
$c = 6.937$ Å		
$V = 632.3$ Å^3		
Ag_2HgSI_2 $Cmc2_1$, $Z = 4$	Hg–S = 2.380, 2.24	Hg–Hg = 3.559
$a = 13.834$; $b = 7.470$;	Ag–S = 2.479(x2)	Hg–Ag = 3.629–4.112
$c = 7.103$ Å		Ag–Ag = 4.555
$V = 734.5$ Å^3		
CuHgSBr (295K)	Hg(1)–S(1) = 2.371	Hg–Hg = 3.568
$Pbam$, $Z = 8$	Hg(2)–S(1) = 2.380	Hg–Cu = 3.530–3.831
$a = 10.03$; $b = 18.33$;	Cu(1)–S(1) = 2.266(x2)	Cu–Cu = 4.124
$c = 4.124$ Å	Hg(1)–S(2) = 2.369	Hg–Hg = 3.576
$V = 759.0$ Å^3	Hg(2)–S(2) = 2.372	Hg–Cu = 3.481–3.881
	Cu(2)–S(2) = 2.282(x2)	Cu–Cu = 4.124
β-AgHgSI $Pmma$, $Z = 4$	Hg(1)–S = 2.376	Hg(1)–Hg(2) = 3.598
$a = 10.159$; $b = 4.648$;	Hg(2)–S = 2.376	Hg(1)–Ag = 3.999(x2)
$c = 9.849$ Å	Ag–S = 2.535(x2)	Hg(2)–Ag = 3.776(x2)
$V = 465$ Å^3		Ag-Ag = 4.648
CuHgSeCl	Hg–Se = 2.477, 2.486	Hg–Hg = 3.483
$Pbam$, $Z = 4$	Cu–Se = 2.379(x2)	Hg–Cu = 3.592, 4.121(x2)
$a = 6.9444$; $b = 12.561$;		Cu–Cu = 4.253
$c = 4.2526$ Å		
$V = 386.0$ Å^3		

Motive from [Hg$_4$S] tetrahedra	Description of the motive from [Hg$_4$S] tetrahedra
	Chains of [Cu$_2$Hg$_2$S] tetrahedra that are linked by their common Hg vertices. The parameter c of the cell (6.989 Å) is equal to the vector sum of the two edges Hg−Hg.
	A layer of [(Hg,Cu)$_4$S] tetrahedra in the structure of CuHg$_2$S$_2$I. The bond in the layer is through the vertices (Hg,Cu).
	The isolated chains of [Ag$_2$Hg$_2$S] tetrahedra in Ag$_2$HgSI$_2$.
	The xy projection of CuHgSBr structure (295 K). Hg and S atoms are on $z = 1/2$, Cu and Br are on $z = 0$. Hg−Hg edges of [Hg$_2$Cu$_2$S] tetrahedra form a zigzag with the angle ~90°. Anions of Br divide the corrugated layers of [Hg$_2$Cu$_2$S] tetrahedra.
	Structure β-AgHgSI with a single corrugated layer of [Ag$_2$Hg$_2$S] tetrahedra per a unit cell.
	A layer from [Hg$_2$Cu$_2$Se] tetrahedra that are linked along an axis x by Hg vertices in the xz plane; along an axis z, by Cu vertices. Parameter a (6.9444 Å) is equal to the vector sum of two Hg−Hg edges.
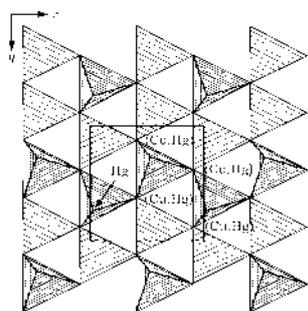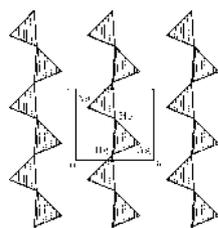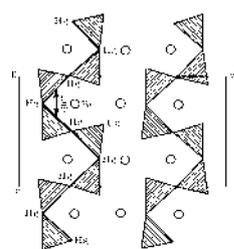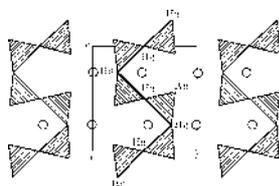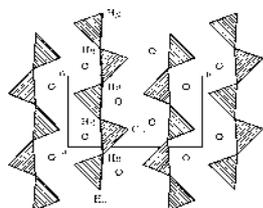
mercury atoms in these compounds, than do the bonds with Cu or Ag vertices, but the tetrahedral cationic group is possibly linked also by cation-cation interactions.

It would be interesting to compare the structures of two natural HgS modifications: trigonal zinnobers (cinnabar) α-HgS (Fedorov group $P3_12$, $a = 4.149$, $c = 9.495$ Å, $Z = 3$, $V = 141.5$ Å^3) and cubic metacinnabar β-HgS (Fedorov group $F\bar{4}3m$, $a = 5.85$ Å, $Z = 4$, $V \approx 200$ Å^3). Based on formal data, the structures of these phases are believed to be different, although the availability of phase transitions is recorded, predominantly from cubic into more stable trigonal phase. Our method of chemical analysis of crystals as regards revealing the tightly filled crystal planes (those of cationic and anionic nature, individually [20]) has made it possible to establish that the cationic matrix for both phases is the same, specifically, cubic three-layered closest packing (the ABC type). The cubic phase has both cations and anions packed under this law, and the structure can be seen as a three-dimensional ligature of both [S$_4$Hg] tetrahedra, and [Hg$_4$S] tetrahedra. Packing of anions changes cardinally in the trigonal phase. Anions S pass from the cationic tetrahedron to the next cationic octahedron through their common facet, as they preserve the bond with two Hg atoms, and in the octahedron, they are most strongly bonded to the same two mercury atoms alone. The ideal identity of F cubic and R rhombohedral cells is true when $c_R/a_R = 2.45$ [21]. This ratio is equal to 2.29 in zinnober, and thus the rhombohedron of Hg atoms somewhat differs from a cube:

$$a'_R = 5.74 \text{ Å}; \quad a'_R = 92.5° \text{ (Fig. 2, } a\text{)}.$$

Stability of the cationic skeleton of α- and β-HgS is supported by its preservation upon the replacement of one-fourth part of Hg cations with Al, as it has been revealed in the crystal structure of Hg$_3$AlF$_6$O$_2$H (Fedorov group $R3m$, $a = 7.262$; $c = 10.441$ Å, $Z = 3$, $V = 476.89$ Å^3 [22]). Contrary to the α-HgS skeleton, the deformation of the cubic F cell of cations here is of another sign, the cube is elongated along the triple axis: $a'_R = 5.449$ Å, $a'_R = 83.57°$ [22]. This pseudocubic cationic subcell corresponds to a hexagonal cationic
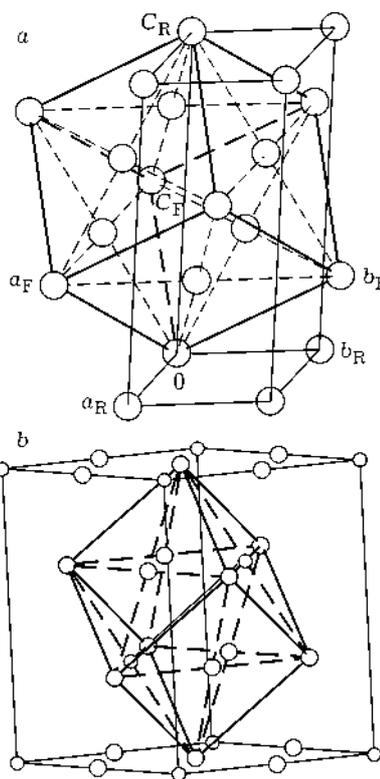
Fig. 2. Structures of zinnober HgS (*a*) and Hg$_3$AlF$_6$O$_2$H (*b*): *a* – only those Hg atoms are shown that form a subcell that is similar to F cubic ($a_F = b_F = c_F = 5.74$ Å; $\alpha_F = \beta_F = \gamma_F = 92.5°$); *b* – the cationic F cell ($a_F = b_F = c_F = 5.449$ Å; $\alpha_F = \beta_F = \gamma_F = 83.57°$) is highlighted; large circled are the Hg atoms, the smaller ones are the Al atoms.

subcell with $a_R = a/2 = 3.631$ and with $c_R = c = 10.441$ Å. The c_R/a_R ratio is equal to 2.88, which is significantly over the ideal magnitude of 2.45 (see Fig. 2, *b*). Let us note that F atoms in the structure occupy cationic tetrahedrons, and the coordination of O atoms that make up an O−Hg−O "line" is less regular. Even though the compound of the work [22] has been received from other than HgS, nevertheless an assumption makes sense that an interaction of HgS and AlF$_3$ may occur. The fact of a stronger bonding of S with only two Hg atoms may be a factor responsible for zinnober "solving" during natural processes with replacement of four remote Hg atoms in the coordination environment by 2Cu, 2Ag, or 2Pb, and the like These cations that are accompanied by Cl, Br, and I anions, give rise to the structures mentioned above of composition MHgXY, where the ratio HgS : MX = 1 : 1.

TABLE 4

Data of crystal structure for mercury chalcohalides of composition $Hg_3X_2Hal_2$ (X = S, Se, Te; Hal = Cl, Br, I)

Formula, Fedorov group, Z; V_{cell}, Å³, a, b, c, Å α, β, γ°	$d(X-Hg)$, Å, ∠XHgX ∠HgXHg, deg	Type of Hg−X radical (X = S, Se, Te)	Compounds containing isotype radicals
$Hg_3S_2Cl_{1.5}Br_{0.5}$ $Pm3n$, 32; 5837.8 18.006	2.329−2.450 163.8−178.8 93.3−100.1	Isolated groups $[Hg_{12}S_8]$	β-$Hg_3S_2Cl_2$ α-$Hg_3S_2Br_2$ β-$Hg_3S_2Cl_2$ $Hg_3S_2Br_{0.5}Cl_{1.5}$ (arzakite)
β-$Hg_3S_2Br_2$ $C2/m$, 8; 1533.8 17.223 9.374 9.473 89.78(β)	2.24−2.69 137.8−174.5 84.4−109.3	A layer of $[Hg_4S_4]$ rings with two orientations	γ-$Hg_3S_2Cl_2$ (kenshuaite) Hg_3Te_2BrI $Hg_3S_2Cl_{1.5}Br_{0.5}$ (lavrentievite) Hg_3S_2ClI (radtkeite) $Hg_3Se_2Br_2$
$Hg_3S_2I_2$ $Imma$, 8; 1734 9.799 18.703 9.462	2.399−2.423 160.8−169.9 99.1−99.50	Double angular belts from $[Hg_4S_4]$ rings	$Hg_3Se_2I_2$ $Hg_3S_2(Cl,Br,I)_2$ (grechishchevite)
α-$Hg_3S_2Cl_2$ $I2_13$, 4; 800 8.94	2.42 165.1 94.1	Homogeneous skeleton without closed cycles of Hg−S−Hg−... bonds	α-$Hg_3Se_2Cl_2$, (corderoite) $Hg_3Te_2Cl_2$, $Hg_3Te_2Br_2$, $Hg_3S_2F_2$
$Hg_3Te_2I_2$ $C2/c$, 8; 1965 14.22, 9.70, 14.34 79.9 (β)	2.648−2.702 155.23−180 89.8−97.6	Three-dimensional skeleton with closed rings $[Hg_4Te_4]$ of the same orientation	−
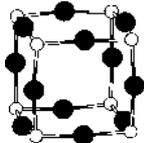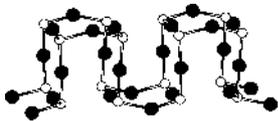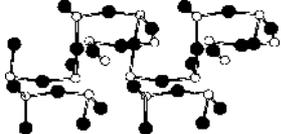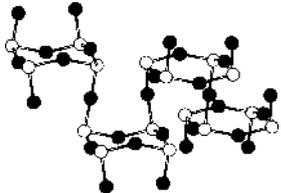
For compositions that are richer with mercury, for example, with the stoichiometry Hg : Y : X = 3 : 2 : 2 (as the most frequent in the studied compounds), the basis of crystal structures is made up of two factors: covalently bonded Hg and S atoms that form isolated, belt-shaped, layer-shaped, and three-dimensional combinations, as well as stacking of halogen atoms that is similar to that cubic primitive [17, 23] (Table 4). An idealised "structural" block module for such structures constitutes a cube of halogen atoms that is centred by volume with a chalcogen atom with Hg cations that centre three cube facets converging in a single vertex [24] (Fig. 3). Proportionality of geometrical parameters of these two components explains the stability of crystalline constructions even in the case of appreciable variations in the composition of halogens, and the possibility of a rotation of blocks when joining explains a wide variety of topologies of the $[HgS]_n$ component, which is responsible for the abundant polymorphism that is intrinsic to these compounds.

MERCURY DISPROPORTIONATION PROCESSES IN MERCURY MINERALS − SOURCES OF MERCURY INGRESS TO WATER AND ATMOSPHERE

A cardinal difference between the composition of compounds with "cluster"
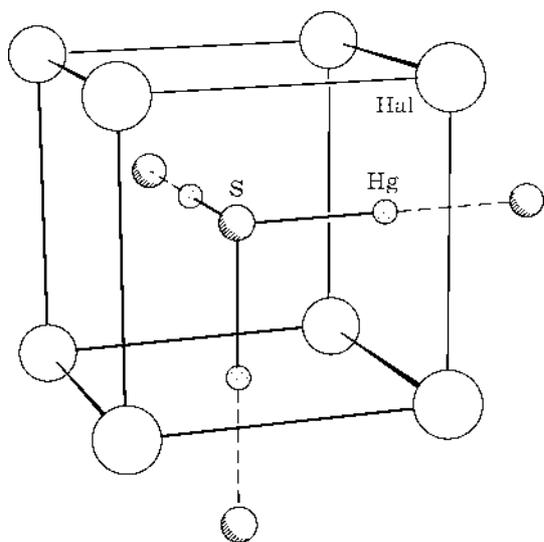
Fig. 3. Pseudocubic block module of a sublattice of halogen atoms in $Hg_3X_2Hal_2$ crystal structures, where X = S, Se, Te; Hal = F, Cl, Br, I (an idealised view).

mercury $[Hg_2]^{2+}$ and $[Hg_3]^{4+}$ and the composition of well studied rock-forming minerals lies in their relative content of cations and anions. Their quantities in the studied compounds are comparable, and, for example, poyarkovite contains 1.5 times more Hg cations than anions. Being in an anion deficit medium, they are under the necessity of creating cluster groups thus sating valence bonds in Hg−Hg contacts. Meanwhile, by virtue of the deficiency, anions become centres of the formation of peculiar polyatomic groups that possibly exist in liquids before the beginning of crystallisation. However, chemical analysis of crystals shows an apparent anisotropy of bonds in these compounds: linear groups, chains, and layers with stronger bonds can be clearly distinguished. The bonding between these structural fragments is much weaker and, consequently, variations in the composition of a certain part of such fragments are not blocked by building blocks that surround them [25].

As we have no opportunity to observe directly in nature entire sequence of the solid-phase transformations that lead to a complete oxidation of mercury upon its transition in a medium that is rich with oxygen, the information on them is possible through analysing the ways of synthesis for compounds with $[Hg_3]^{4+}$ and $[Hg_2]^{2+}$ clusters and stages of their "oxidation" under laboratory conditions. As a rule, the synthesis of the compounds is performed from Hg^{2+} oxides and alternative ingredients in evacuated ampoules at the temperatures of $>400\ ^{\circ}C$ as well as by a hydrothermal procedure at high temperatures. It is believed that minerals with $[Hg_3]^{4+}$ and $[Hg_2]^{2+}$ clusters originate naturally under similar conditions. It appears that the minerals, as they outcrop on the Earth surface, undergo processes that are related to the disproportionation of mercury: $[Hg_2]^{2+}, [Hg_3]^{4+} \rightarrow Hg^{2+} + Hg^0$.

In laboratory conditions, the process of disproportionation of "cluster" mercury to form Hg^{2+} and Hg^0 is typically conducted in an open system; gaseous mercury is among the products. The process runs with a sufficiently high speed at the temperatures of $200−450\ ^{\circ}C$, but it can be inferred that in nature, this occurs at lower temperatures, even though the speed is low. A most vivid example is the structures

$[Hg_2]As_2O_6$ and $HgAs_2O_6$ whose basis is comprised with identical layers of AsO_6 octahedra bonded with one other, and the layers of Hg cations also coincide, once the centre of a "dumbbell" $[Hg_2]^{2+}$ is assumed to be a cation in the first structure. Thus, the reaction $[Hg_2]As_2O_6 \rightarrow HgAs_2O_6 + Hg$ might be treated as a gradual coming of a half of mercury atoms out of a cationic layer in the $[Hg_2]As_2O_6$ structure, so a single Hg^{2+} cation remains at the place of the "dumbbell" $[Hg_2]^{2+}$ and in so doing, only a single parameter c goes down in the hexagonal unit cell (Fig. 4) [26].

Since many crystal structures show significant hollows and channels (to take an illustration, the diameter of channels in the structure of shimanskiite mineral is approximately equal to 13.6 Å [5]), transition of a part of mercury atoms from cluster groups into a divalent state with the simultaneous release of free metallic mercury from the structure can occur, especially in near-surface layers of crystals. The process may be one of the sources that mercury appears in natural waters and in the atmosphere.

The intimated differentiation of various forms of mercury in the structures of minerals as regards their layers [25] is apparently a consequence of transformations that slowly proceed in the nature, wherein the most stable forms are fixed. It has been just layered structures, where most readily solid-phase transitions proceed with the variation in composition, but with the preserved significant fragments. A variant of a "layer-by-layer" transformation has been suggested in [27] when discussing the structures of monoclinic terlinguaite and rhombic pinchite that show a close interrelation in the nature.

CONCLUSIONS

The approach set forth above will be available in studies of structure of compounds of crystallochemical analogues of mercury, specifically, heavy toxic metals Cd, Pb, Bi, Tl, Ag, and Cu (M). For the last few years, minerals of a technogenic origin arouse particular interest in connection with studying speciation of toxic elements under conditions of the terrestrial surface. The majority of phases that are produced in the technogenic formations contain toxic elements as mineralogenetic ingredients. Study of crystal chemistry of these minerals is essential to obtain basic characteristics for the behaviour of toxic elements in natural processes. It has been pointed out in [13] that "processes of metal transfer by gases are in many respects similar to the processes of metal transfer in metallurgical processes. Accordingly, the basic source of lead in biosphere is metal smelting from ores of polymetallic deposits, while chloride and oxo chloride complexes and nanoparticles represent forms of lead transfer in connection with their higher than usual fugitiveness. It is also interesting that the formation of lead oxohalides on internal walls of the working cylinder, which proceeds with the direct involvement of gaseous products, is considered among the reasons for malfunctioning aviation engines".

To take an illustration, it is possible to consider exhalation processes that occur on volcanoes, upon a spontaneous warming up of waste heaps in coal industry. In all mentioned cases, groups of M atoms that have been shaped around "free" oxygen atoms appear to
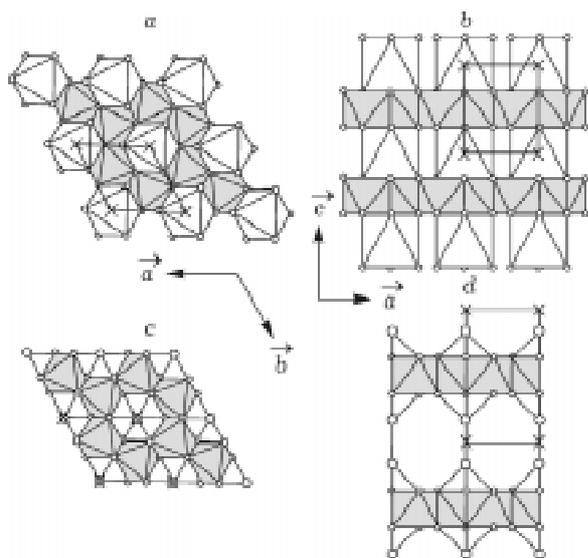
Fig. 4. Two projections of $HgAs_2O_6$ (above) and $[Hg_2]As_2O_6$ structures (below) on the same scale. The projections to the plane *ab* being identical, the projections to the plane *ac* differ for the length of the "dumbbell" Hg–Hg = 2.5 Å along an axis *c* (below, on the right). Dark octahedra stand for AsO_6, small circles do for O atoms, and large ones do for Hg atoms.

be among possible forms of metal transfer by gases. The availability of ready-to-work atomic groups in gases simplifies and accelerates the process of a subsequent grain formation. Consequently, investigation of oxidic and chloride phases of heavy elements that crystallize from gas is of interest not only from mineralogical point of view, but also in the context of ecology and technology. By virtue of the fact that chemical compounds with $[OM_4]$ groups are also synthesized from a liquid phase, it is believed that such tetrahedra and, conceivably, their larger assemblies are available in liquids as well. Fairly high strength of analogous atomic groups can ensure their preservation in various natural and technogenic media [13]. Thus, allowance should be made for this fact when discussing the transfer forms for mercury, lead, and other toxic elements under conditions of the terrestrial surface. Reliable information about the structure, about the major factors that influence upon the stability of these complexes, and about the possibility that the complexes are captured by secondary minerals are essential to solve the problem of immobilisation of toxic elements in the environment [13].

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