Vasil'ev V.I.[1], Nenashev B.G.[1], Pervukhina N.V.[2], Magarill S.A.[2], Borisov S.V.[2] Synthetic analogies of rare hypergenic mercury-bearing minerals of the cordieroite type: synthesis and structure

[1] The United Institute of Geology, Geophysics and Mineralogy, Siberian Branch of RAS, Novosibirsk
[2]Institute of Inorganic Chemistry, Novosibirsk, borisov@che.nsk.su

key words: [mercury sulfohalogenides, mercury-bearing minerals, corderoite, module structural principle]

Natural compounds of bivalent mercury (corderoite, arzakite, laurentievite, radkeite, kenshuaite, grecheshchevite) with general formula of the cordieroite type $Hg_3S_2Hal_2$ (Hal = Cl, Br, I) are the typical rare exogenic minerals of newly formed oxidation zones of mercury deposits. These minerals are of inconstant composition, depending on the number and type of halogenides in their crystalline structure. Another peculiarity of these compounds is the presence of numerous polymorphic modifications, identified by investigation of their synthetic analogies.

Orange crystals of the composition $Hg_3S_2Cl_{0.56}Br_{0.88}I_{0.56}$ ($P2_12_12_1$ a = 13.225(3), b = 13.230(3), c = 8.718(2) Å, V = 1525.4(5) Å^3, Z = 8, d = 7.201 g/cm^3) were synthesized by means of pyrosynthesis from the stoicheometrical mixture of HgS, $HgCl_2$, $HgBr_2$, HgI_2 in the experiment on the synthesis of grecheshchevite $Hg_3S_2Cl_{0.5}Br_{1.00}I_{0.5}$ (*P42m, P4mm, P4/mmm* a = 13.225, c = 8.685 Å). All crystals are twinned. Analysis of reflections showed the tetragonal symmetry at $a=b=a$(т) and $c=c$(т) with space group $P4_22_12$. Accounting for the twinning, R-factor is 0.097. Distances: Hg-S 2.405-2.526 Å, Hg-Br 2.955-3.410 Å, Hg-I 2.727-2.759 Å; angles: SHgS 170.7-176.8^O and 139.9-144.6^O, HgSHg 94.5-103.1^O.

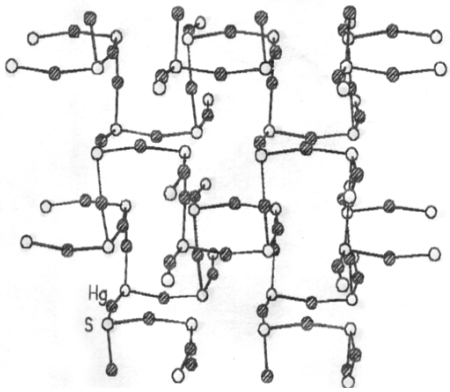

Fig.1.

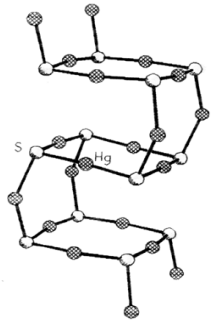

Fig.2.

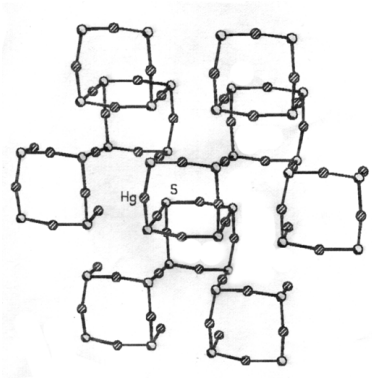

Fig.3.

The synthesis of compounds $Hg_3S_2(Br_{1-x}Cl_x)$, where x = 0.25 and 0.75, which are analogies of rare minerals arzakite $Hg_3S_2(Br, Cl)_2$ and laurentievite $Hg_3S_2(Cl, Br)_2$, was conducted in evacuated quartz ampoules by the method of growth from gas at stoichiometric ratio of the starting components (previously synthesized mercury sulfide and halogenides). As a result, new mercury sulfohalogenides were obtained and studied by x-ray: $Hg_3S_2Cl_{0.60}Br_{1.40}$ (I) (a = 16.852(3), b = 9.136(2), c = 9.457(2) Å, β = 90.09(3)^O, V = 1456.0(5) Å^3, Z = 8, $C2$, d = 6.966 g/cm^3, R = 0.0964) and $Hg_3S_2Cl_{0.61}Br_{1.39}$ (II) (a = 18.006(2), V = 5837.8(11) Å^3, Z = 32, $Pm3n$, d = 6.952 g/cm^3, R = 0.0369). The compound (I) is isostructural to β- $Hg_3S_2Br_2$ [1], but is of lower symmetry. Distances: Hg-S 2.21-2.54 Å, Hg-Hal 2.70-3.60 Å; angles: SHgS 154.7-177.6^O, HgSHg 91.1-102.1^O. The compound (II) is isostructural to β- $Hg_3S_2Cl_2$ [2] with larger parameter a, that is related to bromine. Distances: Hg-S 2.329-2.450 Å, Hg-Hal 2.709-3.557 Å; angles: SHgS 163.8-178.8^O, HgSHg 93.3-100.1^O.

The covalent bonded linear groups X-Hg-X' and "umbrellas" XHg_3 (X = S, Se, Te) forming diverse individual and branched structural motives are characteristic for the "corderoite" structures. In the corderoite structure [3], each sulfur atom is a point of transaction of three perpendicular infinite zigzag-like chains –S-Hg-S-Hg-. The pattern of distribution of the S-Hg bonds prevents from the formation of the reserved cycles in the structure (Fig. 1). In the structures of grecheshchevite ($Hg_3S_2I_2$ and $Hg_3Se_2I_2$) [4], these chains, which are parallel to each other and bonded by Hg atoms, form the infinite ribbons. The basic structural element of the ribbons are 8-memebered rings of $[Hg_4S_4]$ (Fig. 2). The structures of natural kenshuaite and synthetic compounds γ- $Hg_3S_2Cl_2$, β- $Hg_3S_2Br_2$ and (I) are built of similar rings connected by the third S-Hg bond to the goffered layers (Fig. 3). The synthetic compounds (II) and β- $Hg_3S_2Cl_2$ contain isolated cubes built of sulfur atoms, whose edges are centered by Hg atoms (Fig. 4), while halogen atoms are distributed

both inside and between the $[Hg_{12}S_8]$-cubes. In all these structures, each S atom is surrounded by three Hg atoms, forming the umbrella-like groups SHg_3 with distances Hg-S 2.21-2.54 Å and angles HgSHg 91.1-102.0^O. The topology of the bonds is defined both by the linear groups of S-Hg-S and the tetrahedral sp^3-hybridization of sulfur atoms.

The structural role of another structural component, i.e. univalent large anions Cl^-, Br^-, and I^- was not considered so far. We have recognized the high degree of ordering of halogen atoms in the unit cells of these compounds. An analysis of the close-packed crystallographic planes showed quadratic nets of halogen ions in three perpendicular directions. That shows the features of the primitive cubic sub-cell. The structures can be characterized as a combination of similar sub-cells, connected by edges, but in different orientation. The sub-cell is a cube of Hal atoms with the edge ~4.5 Å, centered by X atom. Three cube planes meeting at one cube apex are centered by Hg atoms. Through these planes, the neighbor motives are connected by the linear bond X-Hg-X'. The common plane of adjusted modules allows for four possible orientations differing by rotation through 90^{O}C around this X-Hg-X' bond (Fig. 5). Following to this algorithm, diverse structural motives can be produced.

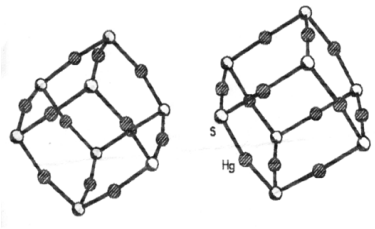

Fig.4.

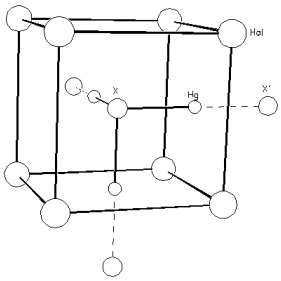

Fig.5.

References:

1. Yu.V. Voroshilov, V.A. Khudolii, V.V. Pan'ko, Yu.V. Minets. *Neorganicheskie Materialy*, 32, 12 (1996), 1466.
2. Yu.V. Voroshilov, V.A. Khudolii, V.V. Pan'ko. *Zhurnal Neorganicheskoi Khimii*, 41, 2 (1996), 287.
3. K. Aurivillius. Arkiv. Kemi., 26, 42 (1966), 497.
4. J. Beck, S. Hedderich. J. Solid State Chemistry, 151 (2000), 73.

The study is supported by the Russian Foundation for Basic Research (project no. 01-05-65104).