

NEW DATA ON THE MERCURY OXIDE-CHLORIDE MINERAL POYARKOVITE: THE SECOND FIND, AND CRYSTAL-STRUCTURE DETERMINATION

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ABSTRACT

Poyarkovite was first found in the Khaydarkan (Kyrgyzstan) antimony-mercury deposit in 1981. A second find is recorded in the oxidized cinnabar ores of the Arzak mercury deposit, situated about 12 km northeast of the well-known Terlig-Khaya mercury mine, Pii-Khem district, Tuva Republic, Russia. Here, poyarkovite is closely associated with supergene eglestonite, calomel, terlinguaite, montroydite, and native mercury. All these minerals occur in cavities with partly leached primary cinnabar. Poyarkovite is a rare constituent in ores. It forms small, mostly irregular, grains as inclusions in eglestonite and calomel aggregates, and sporadically as minute crystals growing on surfaces of altered cinnabar. The Arzak poyarkovite has the same physical properties as the Khaydarkan specimen, *i.e.*, vitreous to adamantine luster, purple or red-purple color, red or red-crimson streak, translucent (thin fragments and edges of grains), brittle, uneven or subconchoidal fracture, no cleavage, and hardness 2–2½. The measured density (9.56 g/cm³) is in good agreement with the calculated value (9.64 g/cm³), refined according to an X-ray structural study. The strongest seven lines in the X-ray powder-diffraction pattern [d in Å(I)(hkl)] are: 3.09(4–5)(514), 2.96(4)(600), 2.83(10)(132), 2.74(8)(512), 2.61(6)(712), 1.884(4)(1002), et 1.799(6)(640). The electron-microprobe analyses gave, on average, Hg = 91.70, Cl = 5.38, O = 2.45 (inferred value), total = 99.53 wt.%, corresponding to Hg_{3.000}O_{1.005}Cl_{0.995}, based on a total of five atoms. In the X-ray structural study, we have used poyarkovite from Khaydarkan. The structure of poyarkovite [Hg₃ClO, a 19.009(3), b 9.018(4), c 16.848(9) Å, β 110.82(3)°, V 2700(2) Å³, space group C2/c, Z = 24] was solved by direct methods, and refined to R = 6.0% on the basis of 1614 unique reflections measured with MoK α radiation on a CAD-4 automated diffractometer. The unit cell contains nine independent mercury atoms forming the six (Hg–Hg)²⁺ dimers, with the Hg–Hg distances equal to 2.502(2)–2.565(3) Å. Of six Hg₂ pairs, three are formed by the 1 or 2 symmetry-related atoms. The mercury dimers are located in three mutually orthogonal directions. Each O atom forms four Hg–O bonds in a tetrahedral arrangement [1.95(2)–2.60(2) Å, Hg–O–Hg 88.1(6)–121.4(9)°]. The shortest Hg–Cl distances are 2.816(10) Å. In terms of only the Hg–Hg and Hg–O bonds, the poyarkovite structure can be represented as two frameworks enclosed one inside the other. The frameworks are bound by the translation of the C unit cell (0.5, 0.5, 0). These interpenetrating frameworks of Hg and O atoms bind the Cl atoms together; the latter complement the Hg coordination.

Keywords: poyarkovite, mercury oxychloride, physical properties, composition, X-ray data, crystal structure, second find, Arzak mercury deposit, Tuva, Russia.

SOMMAIRE

La poyarkovite a d'abord été découverte au gisement d'antimoine et de mercure de Khaydarkan (au Kirghizstan) en 1981. Nous en signalons un deuxième indice dans la zone de minerai de cinabre oxydé du gisement de mercure d'Arzak, situé environ 12 km au nord-est du gisement de mercure bien connu de Terlig-Khaya, dans le district de Pii-Khem, République de Tuva, en Russie. Là, la poyarkovite est étroitement associée aux minéraux supergènes eglestonite, calomel, terlinguaite, montroydite, et mercure natif. Tous ces minéraux occupent des cavités avec le cinabre partiellement lessivé. La poyarkovite est un rare composant du minerai. Les grains sont petits, généralement irréguliers, et inclus dans les agrégats d'eglestonite et de calomel, et de façon sporadique, sous forme de cristaux de très petite taille sur les surfaces du cinabre altéré. La poyarkovite d'Arzak possède les mêmes propriétés physiques que l'échantillon de Khaydarkan, c'est-à-dire, éclat vitreux à adamantin, couleur violette à rouge-

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violette, rayure rouge ou rouge écarlate, translucide (fragments minces et bordures des grains), cassante, fracture inégale ou sub-conchoïdale, absence de clivages, et dureté de 2 à 2½. La densité mesurée, 9.56 g/cm³, concorde bien avec la valeur calculée, 9.64 g/cm³, affinée dans le contexte d'une étude structurale par diffraction X. Les sept raies les plus intenses du spectre de diffraction, méthode des poudres [*d* en Å(I)(*hkl*)], sont: 3.09(4–5)(514), 2.96(4)(600), 2.83(10)(132), 2.74(8)(512), 2.61(6)(712), 1.884(4)(1002), et 1.799(6)(640). Les analyses à la microsonde électronique ont donné, en moyenne, Hg = 91.70, Cl = 5.38, O = 2.45 (valeur théorique), pour un total de 99.53% (poids), ce qui correspond à Hg_{3,000}O_{1,005}Cl_{0,995}, sur une base de cinq atomes. Dans l'étude structurale, nous avons utilisé un échantillon de Khaydarkan. La structure de la poyarkovite [Hg₃ClO, *a* 19.009(3), *b* 9.018(4), *c* 16.848(9) Å, β 110.82(3)°, *V* 2700(2) Å³, groupe spatial *C2/c*, *Z* = 24] a été résolue par méthodes directes, et affinée jusqu'à un résidu *R* de 6.0% en utilisant 1614 réflexions uniques mesurées avec rayonnement MoKα et un diffractomètre automatisé CAD-4. La maille élémentaire contient neuf atomes indépendants de mercure qui forment six dimères (Hg–Hg)²⁺, avec des distances Hg–Hg dans l'intervalle 2.502(2)–2.565(3) Å. Des six paires Hg₂, trois impliquent les atomes à liaisons régies par la symétrie $\bar{1}$ ou 2. Les dimères de mercure sont orientés dans trois directions mutuellement orthogonales. Chaque atome d'oxygène forme quatre liaisons Hg–O dans un agencement tétraédrique [1.95(2)–2.60(2) Å, Hg–O–Hg 88.1(6)–121.4(9)°]. Les distances Hg–Cl les plus courtes sont égales à 2.816(10) Å. Seulement en termes des liaisons Hg–Hg et Hg–O, on peut représenter la structure comme deux trames enchevêtrées, liées par la translation de la maille *C* (0.5, 0.5, 0). Ces trames enchevêtrées d'atomes de Hg et de O lient les atomes de Cl, qui viennent compléter la coordinence des atomes Hg.

(Traduit par la Rédaction)

Mots-clés: poyarkovite, oxychlorure de mercure, propriétés physiques, composition, données de diffraction X, structure cristalline, deuxième indice, gisement de mercure d'Arzak, Tuva, Russie.

INTRODUCTION

Information on the supergene mercury oxide–chloride mineral poyarkovite from the Khaydarkan antimony–mercury deposit in Kyrgyzstan was published by Vasil'ev *et al.* (1981). Optical, electron-microprobe, powder diffraction and single-crystal X-ray studies had been carried out on the type specimen, but the structure of this mineral was not solved. A monoclinic cell with *a* 18.82, *b* 9.02, *c* 16.79 Å, β 112°24', *V* 2635.2 Å³, a composition close to Hg₃OCl, and a measured density in the range 9.50–9.80 g/cm³, close to a *D*_{calc} of 9.88 g/cm³, were established. A new find of poyarkovite was recently made by the first author when reviewing ore samples collected at the Arzak mercury deposit (Tuva, Russia) in 1977. In the present paper, we characterize this new material and provide structural data.

OCCURRENCE AND PARAGENESIS

As reported by Grechishchev *et al.* (1978), the Arzak mercury deposit belongs to the structural type of mineralized shear-zones. Mercury mineralization is situated in hydrothermally altered (silicified) breccias of rhyolite–dacite porphyry, tuff-conglomerates, agglomerates and other rocks of a tuffaceous facies, and is disposed along the shear zone. The distribution of mercury and mercury-bearing sulfides is very irregular in the orebodies. The main primary mercury mineral is cinnabar; there also are local occurrences of Cd-rich metacinnabar (Hg,Cd,Zn)S and (Cd–Hg)-rich sphalerite (Zn,Cd,Hg)S. Cinnabar is mostly present as disseminations (up to 5 mm in diameter) or thin veinlets, and only locally as massive cinnabar ores with a granoblastic texture. Some lens-like orebodies are known. They are exposed in active open-cut mine workings.

Poyarkovite is found within the brecciated rhyolite–dacite porphyry (orebody 3), in small cavities lined with primary cinnabar. Here and near the cavities, cinnabar is slightly leached, and has a rough texture. Poyarkovite is closely associated with the following supergene minerals: (1) crystalline aggregates, individual rhombododecahedral or needle-shaped crystals of eglestonite (Fig. 1), (2) crystalline grains of calomel and terlinguaite, and (3) montroydite and native mercury. Except for native mercury, which fills the central parts of the

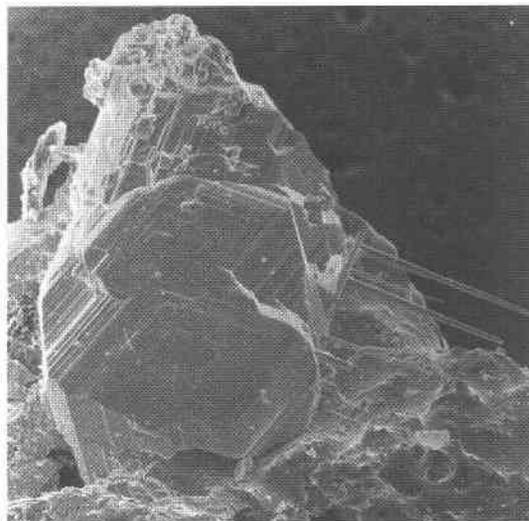


FIG. 1. The accretion of rhombododecahedral crystals and needle-shaped incrustations of eglestonite on the surface of facies. Arzak deposit. 70×.

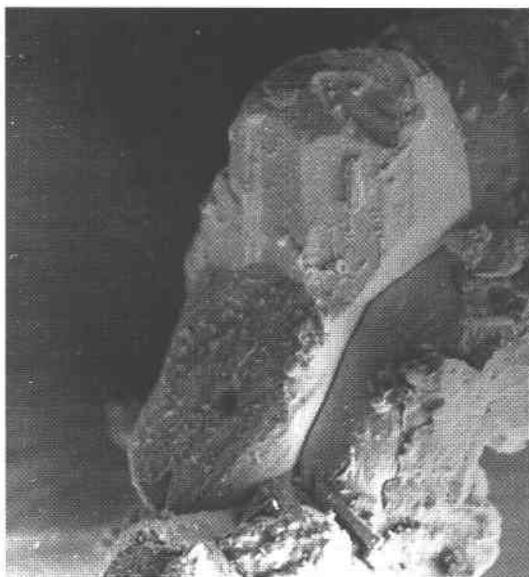


FIG. 2. The accretion of two poyarkovite crystals on cinnabar. Arzak deposit. 300 \times .

cavities, these minerals are sporadically present on masses of cinnabar as thin crusts. The presence of these crusts indicates the incipient oxidation of this mercury sulfide. Eglestonite and calomel are the predominant mercury chlorides. Poyarkovite is very rare. It forms small irregular grains up to 0.3 mm in diameter in eglestonite or calomel aggregates and as sporadic minute, free-growing crystals on the surface of cinnabar grains, but these smaller crystals are too small for a morphological study (Fig. 2). The mutual relations among poyarkovite, terlinguaite and montroydite are still obscure.

Other secondary minerals of mercury were discovered in the Arzak oxidized ores, including Br-rich corderoite, $\text{Hg}_3\text{S}_2(\text{Cl},\text{Br})_2$ (cubic), lavrentievite, $\text{Hg}_3\text{S}_2(\text{Cl},\text{Br})_2$ (monoclinic), arzakite, $\text{Hg}_3\text{S}_2(\text{Br},\text{Cl})_2$ (monoclinic), grechishchevite, $\text{Hg}_3\text{S}_2(\text{Br},\text{Cl},\text{I})_2$ (tetragonal), kuznetsovite, $\text{Hg}_3(\text{AsO}_4)\text{Cl}$ (cubic), and schuetteite, $\text{Hg}_3\text{O}_2(\text{SO}_4)$ (hexagonal). All these minerals are present in various associations without poyarkovite. These species, together with poyarkovite, terlinguaite and montroydite, should be added to the list of minerals reported by Grechishchev *et al.* (1978). There also are two unknown Hg-halides present that are currently under investigation.

PHYSICAL AND OPTICAL PROPERTIES

The poyarkovite from Arzak is characterized by the same properties as those found in the Khaydarkan deposit specimens (Vasil'ev *et al.* 1981); therefore, only some features are outlined here. Poyarkovite is opaque,

but under a binocular microscope, the small grains and fragments are translucent purple or crimson. Among other physical characteristics of the mineral are high brittleness, a vitreous (to adamantine) luster on a fresh uneven or conchoidal fracture, and no cleavage. Its hardness may attain 2–2½ (the mineral is easily scratched by a copper needle in polished sections), but crystals and grains are too small for an accurate determination of hardness. The measured density (D_m) is 9.56 g/cm³ (sample weight: 8 mg, glass-capillary volumetric method). In plane-polarized reflected light, the mineral is white with a weak bluish gray tint, and shows a weak pleochroism. It is strongly anisotropic with color varying from sky-blue to brown-red or from violet to gray. Thick purple, purple-red or crimson-red internal reflections are common in air, especially in a thin powder produced by a needle. Because we have identified the mineral as poyarkovite by the X-ray method, no further studies of quantitative optical properties and microhardness were carried out.

Poyarkovite is unstable when extracted from a primary place of "conservation", and it eventually transforms completely to an X-ray-amorphous substance.

X-RAY-DIFFRACTION DATA AND CHEMICAL COMPOSITION

Crystals and grains of the Arzak mineral proved to be useless for single-crystal structural study, but they gave X-ray powder-diffraction patterns identical with those of the Khaydarkan poyarkovite (Table 1). However, the patterns of the material from Arzak are qualitatively worse, and contain fewer reflections. Some reflections are very weak, most likely by virtue of the partial decomposition of samples, collected 20 years ago.

The quantitative analyses were performed with a CAMEBAX-MICRO electron microprobe at the United Institute of Geology, Geophysics and Mineralogy of the Siberian Branch of Russian Academy of Sciences, and operated at an accelerating voltage of 20 kV and a beam current of 6 nA, with a 5- μm beam spot. A 10-second count time and a scanning method were used, as the mineral was found to be unstable under the electron beam. The X-ray lines and standards used were $\text{HgM}\alpha$, $\text{ClK}\alpha$ (natural calomel), Hg_2Cl_2 , with an admixture of Br (≤ 0.01 wt.%) and synthetic cinnabar, HgS , for $\text{HgM}\alpha$ -line control). The oxygen content as an essential constituent has not been tested. The compositions of poyarkovite from the Arzak and Khaydarkan deposits are given for comparison (Table 2).

X-RAY CRYSTALLOGRAPHY

Methods

For the structure study, we have used poyarkovite from the Khaydarkan (Kyrgyzstan) antimony-mercury

TABLE 1. X-RAY POWDER-DIFFRACTION DATA FOR POYARKOVITE

ARZAK ¹⁾		KHAYDARKAN ²⁾		CALCULATED		
<i>I</i> _{obs}	<i>d</i> _{meas} , Å	<i>I</i> _{obs}	<i>d</i> _{meas} , Å	<i>I</i>	<i>d</i> , Å	hkl
		2	7.73	26	7.6786	-111
		2	5.18	19	5.1835	-311
1	4.35	0.5-1	4.36	12	4.3657	311
3	4.20	3-4	4.20	59	4.1924	-204
0.25	3.49	0.25	3.48	4	3.4876	-512
2	3.34	3	3.34	29	3.3299	114
3	3.26	3	3.27	20	3.2660	-421
4-5	3.09	5	3.09	41	3.0829	-514
4	2.96	4	2.96	22	2.9613	600
10	2.83	10	2.83	100	2.8294	-132
8	2.74	8	2.74	76	2.7416	512
		0.25	2.67	21	2.6696	-316
			2.63	22	2.6239	006
6	2.61	6	2.60	54	2.5987	-712
2	2.481	2	2.479	19	2.4751	620
		0.5	2.385	2	2.4024	-334
		3b*	2.324	17	2.3241	-317
2b*	2.330	1	2.254	1	2.2543	040
0.25	2.256	1	2.254	1	2.2543	040
1	2.215	2	2.212	7	2.2161	-534
				9	2.2081	424
		0.25	2.151	3	2.1467	-626
		1	2.099	5	2.0969	135
				3	2.0962	-408
		1	2.058	3	2.0595	242
2	1.994	3	1.992	<5	1.9955	-825
				>5	1.9937	425
		1	1.929	7	1.9285	910
4	1.884	4	1.883	5	1.8829	-10.0.2
				10	1.8784	-718
				7	1.8780	-337
+++		1b*	1.850	9	1.8510	317
6	1.799	6-7	1.799	38	1.7937	640
0.5	1.773	1	1.765	10	1.7631	-152
				>2	1.7403	336
		0.25	1.734	<2	1.7374	-10.2.2
				5	1.7272	-479
		1	1.714	11	1.7099	046
1	1.697	2	1.691	6	1.6960	351
				6	1.6884	606
		1	1.658	14	1.6562	-646
		0.5	1.618	4	1.6164	-844
		0.25	1.602	5	1.6007	337
		1	1.582	7	1.5779	734
		2b*	1.544	8	1.5460	-12.0.6
		1	1.501	2	1.5002	1.1.10
				8	1.4962	-11.3.4
				>2	1.4904	-12.2.3
0.5	1.488	2	1.485	<2	1.4846	446

1) RKD powder camera, diameter 57.3 mm, Ni filtered CuK α radiation.
 2) X-ray powder-diffraction data are given in abbreviated form, from Vasil'ev *et al.* (1981).
*I*_{obs}: intensities visually observed; calculated intensities *I* from crystal-structure determination, indexed relative to a cell having dimensions *a* 19.009, *b* 9.018, *c* 16.848 Å, β 110.82°.
 *: broad line; **: very weak line.

deposit mentioned above, since the Arzak mineral seems to be unfit for this purpose. A grain 0.80 × 0.06 × 0.04 mm was protected against atmospheric conditions with a coat of BF-2 glue immediately after its extraction from

TABLE 2. COMPOSITION DATA OF POYARKOVITE

sample	Hg	Cl	O	total	formula
Arzak ¹	91.70	5.38	2.45*	99.53	Hg _{3.000} O _{1.005} Cl _{0.995}
Khaydarkan ²	91.30	5.30	2.36**	98.96	Hg _{3.02} O _{1.00} Cl _{0.98}
Theoretical	92.12	5.43	2.45	100.00	Hg ₃ OCl

¹ The average result of measurements in six grains. Compositions quoted in wt.%.
² Compiled data from Vasil'ev *et al.* (1981); the average result of measurements in ten grains.
 * Assumed value. ** Direct measurement.

TABLE 3. CRYSTAL DATA FOR POYARKOVITE

<i>a</i> (Å)	19.009(3)	Z	24
<i>b</i>	9.018(4)	μ (MoK α , mm ⁻¹)	102.51
<i>c</i>	16.848(9)	Total <i>F</i> _o	1726
β	110.82(3)°	[$\geq 2\sigma$ (<i>I</i>)]	1614
<i>V</i> (Å ³)	2700(2)	<i>R</i> (observed)	0.0607
Space group	C2/c	<i>R</i> _w (observed)	0.1275
<i>d</i> _{calc} (g/cm ³)	9.643		

$$R = \frac{\sum(|F_o| - |F_c|)}{\sum |F_o|}$$

$$R_w = \frac{[\sum w(|F_o| - |F_c|)^2]^{0.5}}{[\sum w|F_o|^2]^{0.5}}, w = [\sigma^2(F_o)]^{-1}$$

a specimen of oxidized ore. X-ray-diffraction data were collected for this specimen using an Enraf Nonius CAD-4 automated four-circle diffractometer with graphite-monochromated MoK α radiation. The cell dimensions (Table 3) were obtained from the least-squares fit of 24 reflections in the range 10 ≤ θ ≤ 15°.

Data were collected in the $\theta:2\theta$ scan mode for the whole sphere of reflections to a 2 θ limit of 50° at a speed of 1°(2 θ)/minute. Three standard reflections were measured every 100 reflections to check for stability and constancy of the crystal alignment.

Of 1726 unique reflections measured, 1614 are classified as observed (*I*_{hkl} > 2 σ ₁). Lp corrections and absorption corrections were applied using the empirical

TABLE 4. ATOMIC PARAMETERS FOR POYARKOVITE

Atom	x	y	z	*U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂	U _{eq}
Hg(1)	0.6637(1)	0.1301(1)	0.8657(1)	15(1)	8(1)	21(1)	-1(1)	3(1)	1(1)	16(1)
Hg(2)	0.6635(1)	-0.1476(1)	0.8439(1)	33(1)	10(1)	22(1)	-1(1)	10(1)	-1(1)	22(1)
Hg(3)	0.8349(1)	0.1199(1)	0.9722(1)	16(1)	21(1)	7(1)	2(1)	7(1)	-5(1)	14(1)
Hg(4)	0.8275(1)	0.1254(1)	0.8198(1)	24(1)	22(1)	8(1)	-2(1)	9(1)	0(1)	17(1)
Hg(5)	0.9038(1)	0.4620(1)	0.9640(1)	8(1)	21(1)	24(1)	-5(1)	1(1)	-7(1)	19(1)
Hg(6)	0.7667(1)	0.5162(2)	0.8913(1)	13(1)	51(1)	25(1)	-11(1)	-5(1)	22(1)	33(1)
Hg(7)	0.0152(1)	0.1381(1)	0.0116(1)	22(1)	9(1)	41(1)	-2(1)	8(1)	1(1)	25(1)
Hg(8)	0.9320(1)	0.0144(2)	0.2021(1)	5(1)	57(1)	32(1)	-14(1)	4(1)	-8(1)	32(1)
Hg(9)	0.0111(1)	0.3740(1)	0.1792(1)	15(1)	24(1)	8(1)	-2(1)	5(1)	-4(1)	15(1)
Cl(1)	0.8501(5)	0.8127(10)	0.0185(5)	40(5)	39(4)	36(5)	2(4)	24(4)	-1(4)	36(3)
Cl(2)	0.9693(4)	0.3066(6)	0.8472(4)	21(3)	5(2)	11(3)	-4(3)	6(3)	-8(3)	13(2)
Cl(3)	0.6673(4)	0.2863(7)	0.7133(5)	35(4)	6(3)	29(4)	1(3)	12(4)	-8(3)	23(2)
O(1)	0.0098(8)	0.3625(22)	0.0550(10)	9(8)	21(9)	7(8)	-4(10)	1(7)	-5(9)	13(6)
O(2)	0.6664(11)	0.3333(21)	0.9064(12)	33(11)	33(12)	19(11)	-4(11)	3(9)	-4(11)	30(7)
O(3)	0.6677(10)	0.6060(18)	0.8105(11)	13(8)	15(8)	27(11)	-5(10)	10(8)	-9(10)	18(6)

* U_{ij} and U_{eq} values are listed ×10³. Temperature factors = -2 π^2 (U₁₁h²(a*)² + ... + 2U₁₂hka*b*)

TABLE 5. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) FOR POYARKOVITE

Hg(1)-Hg(2)	2.531(2)	O(2)-Hg(1)-Hg(2)	168.3(6)
Hg(3)-Hg(4)	2.523(2)	O(2)-Hg(1)-Cl(3)	81.5(6)
Hg(5)-Hg(6)	2.502(2)	Hg(2)-Hg(1)-Cl(3)	110.2(1)
Hg(7)-Hg(7) ¹²	2.555(3)	O(3) ³ -Hg(2)-Hg(1)	173.2(5)
Hg(8)-Hg(8) ¹⁵	2.516(2)	O(3) ³ -Hg(2)-Cl(1) ⁴	73.4(5)
Hg(9)-Hg(9) ¹⁶	2.565(3)	Hg(1) ⁶ -Hg(2)-Cl(1) ⁴	113.3(2)
Hg(1)-O(2)	1.95(2)	O(1) ⁶ -Hg(3)-Hg(4)	166.8(5)
Hg(1)-Cl(3)	2.950(8)	O(2) ⁶ -Hg(3)-Cl(1) ⁷	88.0(6)
Hg(2)-O(3) ³	2.30(2)	Hg(4)-Hg(3)-Cl(1) ⁷	105.0(2)
Hg(2)-Cl(1) ⁴	2.844(10)	O(3) ⁵ -Hg(4)-Hg(3)	172.4(4)
Hg(3)-O(2) ⁶	2.10(2)	O(1) ⁸ -Hg(5)-O(1) ¹⁰	82.1(7)
Hg(3)-Cl(1) ⁷	2.865(9)	O(1) ⁸ -Hg(5)-Hg(6)	160.1(5)
Hg(4)-O(3) ⁵	2.24(2)	O(1) ¹⁰ -Hg(5)-Hg(6)	116.9(4)
Hg(4)-Cl(2) ⁷	3.043(6)	O(3)-Hg(6)-Hg(5)	161.8(6)
Hg(5)-O(1) ⁸	2.24(2)	O(3)-Hg(6)-O(2)	77.5(7)
Hg(5)-O(1) ¹⁰	2.38(2)	Hg(5)-Hg(6)-O(2)	120.0(4)
Hg(6)-O(3)	2.06(2)	O(1)-Hg(7)-Hg(7) ¹²	157.9(5)
Hg(6)-O(2)	2.60(2)	O(1)-Hg(7)-Cl(1) ¹³	94.0(5)
Hg(7)-O(1)	2.17(2)	Hg(7) ¹² -Hg(7)-Cl(1) ¹³	107.3(2)
Hg(7)-Cl(1) ¹³	2.816(10)	O(3) ⁴ -Hg(8)-O(2) ⁴	78.5(6)
Hg(8)-O(3) ⁴	2.13(2)	O(3) ⁴ -Hg(8)-Hg(8) ¹⁵	137.8(4)
Hg(8)-O(2) ⁴	2.51(2)	O(2) ⁴ -Hg(8)-Hg(8) ¹⁵	142.9(5)
Hg(9)-O(1)	2.09(2)	O(1)-Hg(9)-Hg(9) ¹⁶	170.1(4)
Hg(9)-Cl(2) ¹⁰	2.959(6)	O(1)-Hg(9)-Cl(2) ¹⁰	81.7(6)
		Hg(9) ¹⁶ -Hg(9)-Cl(2) ¹⁰	102.2(2)

Symmetry transformations used to generate equivalent atoms: ¹ $-x + 1/2, -y + 1/2, -z + 1$; ² $x + 1/2, -y + 1/2, z + 1/2$; ³ $x, y - 1, z$; ⁴ $-x + 3/2, -y + 1/2, -z + 1$; ⁵ $-x + 3/2, y - 1/2, -z + 3/2$; ⁶ $-x + 3/2, -y + 1/2, -z + 2$; ⁷ $x, y - 1, z + 1$; ⁸ $x + 1, y, z + 1$; ⁹ $-x + 3/2, y + 1/2, -z + 3/2$; ¹⁰ $-x + 1, -y + 1, -z + 1$; ¹¹ $-x + 2, -y + 1, -z + 2$; ¹² $-x, -y, -z$; ¹³ $-x + 1, -y + 1, -z$; ¹⁴ $x - 1, y, z - 1$; ¹⁵ $-x + 2, y, -z + 1/2$; ¹⁶ $-x, y, -z + 1/2$; ¹⁷ $x - 1/2, -y + 1/2, z - 1/2$; ¹⁸ $x, y + 1, z - 1$; ¹⁹ $x, y + 1, z$.

method of North *et al.* (1968). The structure was solved in the space group $C2/c$ with the program SIR92 (Altomare *et al.* 1994). Refinement of the structure was carried out with the SHELX93 program (Sheldrick 1993). Positional coordinates, anisotropic and equivalent isotropic-displacement factors are given in Table 4; selected interatomic distances and angles are listed in Table 5. Structure factors may be obtained from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Canada K1A 0S2.

Description of the structure

A projection of the structure of poyarkovite is shown in Figure 3. The unit cell contains nine independent mercury atoms forming six $(\text{Hg}-\text{Hg})^{2+}$ dimers, with the Hg-Hg distances in the range 2.502(2)–2.565(3) Å, in good agreement with the Hg-Hg bond lengths found in the structures of other known mercury minerals (Szymański *et al.* 1997). On this basis, the mineral formula should be written as $[\text{Hg}_2]_6\text{O}_4\text{Cl}_4$. Of six Hg pairs, three are formed by the 1 or 2 symmetry-related atoms (Fig. 4). Figure 4 shows the coordination environment of the metal atoms in these dimers. Note that the struc-

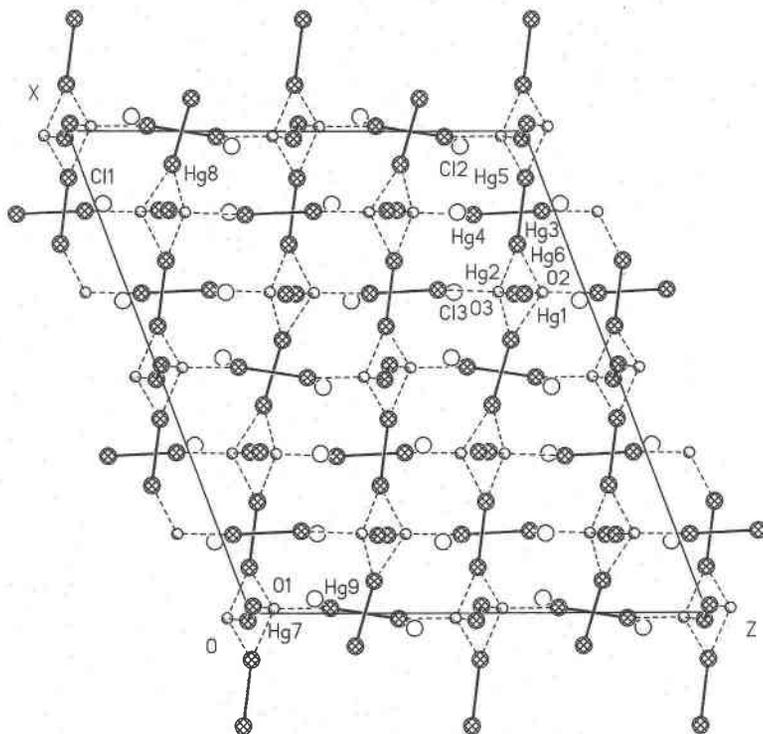


FIG. 3. The projection of the structure of poyarkovite on the x - z plane. Symbols: large open circle: Cl, circle with rectangular grid shading: Hg, small open circle with partial shading in bottom left quadrant: O.

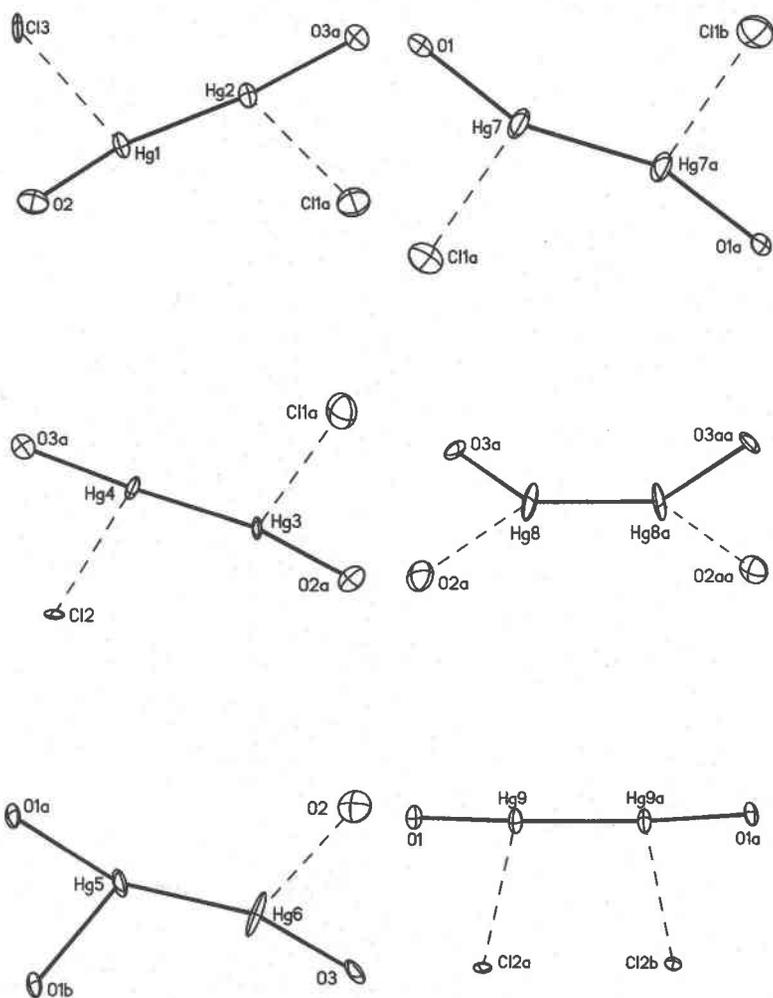


FIG. 4. The coordination environment of Hg atoms in poyarkovite.

ture description in terms of the ionic model is highly conventional owing to the presence of the strong metal Hg–Hg bond.

In poyarkovite, the mercury dimers are located in three mutually orthogonal directions. The Hg(1)–Hg(2) and Hg(3)–Hg(4) pairs have the oxygen and chlorine atoms as the nearest neighbors; the Hg–O and Hg–Cl distances are 1.95(2)–2.30(2) and 2.844(9)–2.950(8) Å, respectively. The remaining distances of the Hg(4) atom to the chlorine atoms exceed 3 Å [3.043(6) – 3.274(8) Å]. The Hg(7)–Hg(7') and Hg(9)–Hg(9') dimers have a similar coordination environment; the Hg–O and Hg–Cl distances are 2.17(2), 2.09(2) and 2.816(9), 2.959(6) Å, respectively. The Hg(5)–Hg(6) and symmetrically related Hg(8)–Hg(8') pairs are coordinated by four O

atoms with two short [2.06(2) – 2.24(2) Å] and two longer [2.38(2) – 2.60(2) Å] Hg–O bonds. In addition, the Hg(8)–Cl contacts of 3.244(8) – 3.447(9) Å are present. Deviations from the linearity in the O–Hg–Hg–O groups (selected with regard to the short Hg–O distances) are the most significant in the dimers formed by the Hg(5)–Hg(6), Hg(7)–Hg(7') and Hg(8)–Hg(8') atoms with the T-shaped coordination environment [Hg–Hg–O angles are 137.8(8) – 161.8(6)°]. In the Hg(1)–Hg(2), Hg(3)–Hg(4) and Hg(9)–Hg(9') pairs, the Hg–Hg–O angles vary within 166.8(5) – 173.2(5)° (Fig. 4). The chlorine atoms surrounding the Hg pair form Hg–Hg–Cl angles of 97.5(2) – 113.3(2)°.

Each O atom forms four Hg–O bonds [1.95(2) – 2.60(2) Å, \angle Hg–O–Hg 88.1(6) – 121.4(9)°]. The short

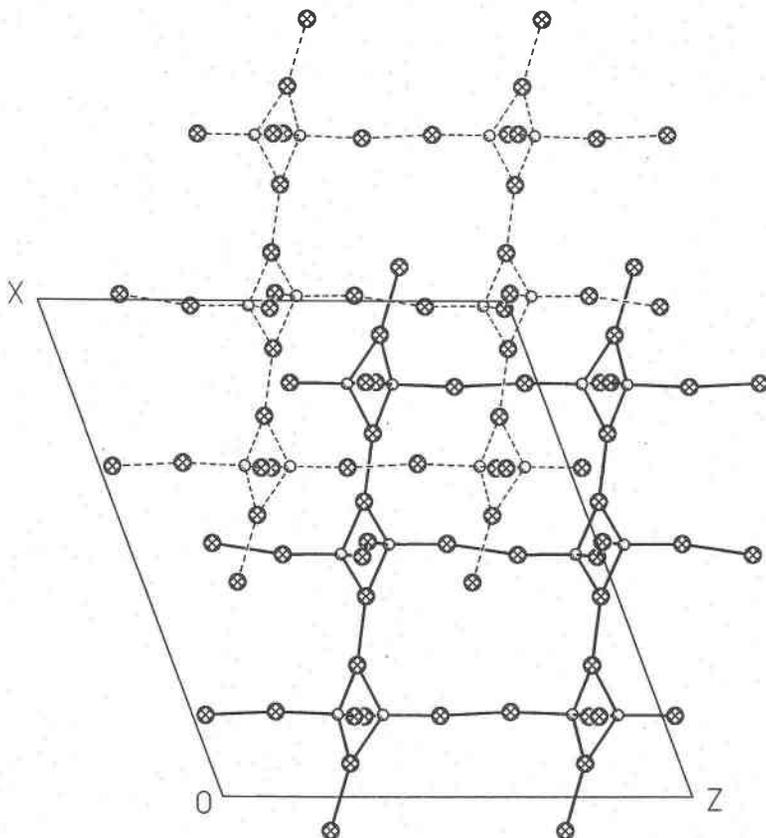


FIG. 5. The projection of the structure on the xz plane. Two frameworks in the structure of poyarkovite. The atoms in one framework are connected by straight lines and in other framework by broken lines. The ...O–Hg–Hg–O... bond chains along the b axis are identical with those shown in Figure 3 along the c axis and the $2a + c$ direction. No chlorine atoms are shown. The symbols for Hg and O are the same as in Figure 3.

Hg–O distances [2.06(2) – 2.30(2) Å] slightly exceed the sum of covalent radii (Hg¹⁺ 1.29 Å, O²⁻ 0.73 Å), but are less than the sum of ionic radii (Hg¹⁺ 0.97 Å, O²⁻ 1.40 Å) (Batsanov 1991). Such a lengthening of the Hg–O bonds was noted in additive calculations of the interatomic distances in the structure of fluorine- and oxygen-containing compounds of mercury as compared to other halogens and chalcogens (Batsanov 1991). In the poyarkovite structure, as also in hanawaltite (Roberts *et al.* 1996), an anomalously short Hg–O distance (1.95 Å) has been found. The shortest Hg–Cl distances [2.816(10) – 3.490(8) Å] are substantially greater than the sum of the ionic radii of Hg⁺ (0.97 Å) and Cl (1.81 Å). As in the structures of other mercury minerals containing the (Hg–Hg)²⁺ groups, the following correlation is observed between the Hg–X (X: O, Cl, S) bond lengths and the Hg–Hg–X angles: the greater the Hg–X distance, the closer to 90° is the Hg–Hg–X angle.

Considering the Hg–Hg and Hg–O bonds alone, the poyarkovite structure can be represented as two three-dimensional frameworks enclosed one inside the other (Fig. 5). The frameworks are bound by the translation of the C -unit cell (0.5 0.5 0). These interpenetrating frameworks of Hg and O atoms bind the Cl atoms together, the latter complementing the Hg coordination.

The coordination environment of the mercury atoms in poyarkovite is similar to that found in the structures of other minerals of monovalent mercury. If more distant O and Cl atoms (Hg–O > 2.5 Å and Hg–Cl > 3 Å, CN of Hg ≥ 3) are considered, the Hg polyhedron seems to be strongly distorted. It would be reasonable to consider the environment of the Hg₂ pair as a whole, taking into account the packing of polyhedra in the vicinity of the geometric center of the Hg_n group. In the synthetic analogue of chursinite, (Hg₂)₃(AsO₄)₂, for example, the environment of the Hg pair represents a trigonal

antiprism formed by the oxygen atoms of the AsO_4 tetrahedra (Kamenar *et al.* 1973). In poyarkovite, similarly, the coordination polyhedron about one of the Hg pairs can be described as a distorted square prism.

Pairs of Hg atoms oriented in three mutually orthogonal directions also have been found in the structure of eglestonite, $(\text{Hg}_2)_3\text{O}_2\text{Cl}_2\text{H}$, with the space group $Ia3d$ and an a of 16.036 Å (Mereiter *et al.* 1992). This structure contains three-dimensional $(\text{Hg}_2)_3\text{O}_2$ nets with the oxygen atoms forming Hg–O bonds with three Hg pairs. The nets are linked to one another by the symmetrical hydrogen bonds (2.48 Å) and the chlorine atoms (Hg–Cl 3.025–3.076 Å). This arrangement distinguishes the structures of eglestonite and poyarkovite in a topological sense. In addition, a ratio of the oxygen and chlorine anions other than that in poyarkovite causes a different geometry of the cation–anion bonds and essentially leads to the higher symmetry of eglestonite.

ACKNOWLEDGEMENTS

The authors thank Mrs. L.V. Usova for the study of poyarkovite from Arzak deposit under the electron-microprobe analyzer, and Dr. S.V. Letov (Analytical Center of United Institute of Geology, Geophysics and Mineralogy, Siberian Branch of the Russian Academy of Science), for the scanning electron photomicrographs. The authors are grateful to Dr. Jan T. Szymański for providing data and an interest to our work. We thank Drs. Robert F. Martin, Frank W. Dickson, Stephen Peters and K. Brock for editorial guidance and valuable comments. This work is financially supported by RFBR (Grant 98–05–65223).

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Received March 10, 1998, revised manuscript accepted December 10, 1998.