

## THE NEW $[\text{Ag}_2\text{Hg}_2]^{4+}$ CLUSTER CATION IN RUDABÁNYAITE, $[\text{Ag}_2\text{Hg}_2][\text{AsO}_4]\text{Cl}$ (RUDABÁNYA ORE DEPOSIT, HUNGARY)

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Recently the new mineral rudabányaite,  $[\text{Ag}_2\text{Hg}_2][\text{AsO}_4]\text{Cl}$ , was found in cavities of siliceous sphaerosiderite and limonite rocks at the Rudabánya ore deposit (North-East Hungary). Rudabányaite forms small, mostly xenomorphic crystals up to a diameter of 0.8 mm, crystalline aggregates are usually a few mm across. Cubic symmetry is indicated by optical isotropy, the faces {110} and {100} are rarely observed. The colour is bright yellowish-orange to brownish yellow; however, in natural light it turns slowly to dark brown or dark olive green. EFFENBERGER *et al.* (2019) gave a detailed description of rudabányaite.

Chemical composition: A qualitative energy-dispersive analysis showed that the mineral is rich in Ag, Hg, As, and Cl, minor amounts of S were detected (JEOL JXA-8600 electron microprobe, Institute of Mineralogy and Geology, University of Miskolc, Hungary). No other elements with an atomic number > 10 were detected. Quantitative point analyses gave the experimental formula  $[(\text{Ag}_{2.06}\text{Hg}_{2.05})_{\Sigma=4.11}][(\text{As}_{0.97}\text{S}_{0.02})_{\Sigma=0.99}\text{O}_4]\text{Cl}_{1.06}$  based on 4 O atoms per formula unit (CAMECA SX 100 electron microprobe, State Geological Institute of Dionýz Štúr, Bratislava, Slovakia). Considering an Ag:Hg ratio of ~1:1, the idealized formula is  $[\text{Ag}_2\text{Hg}_2][\text{AsO}_4]\text{Cl}$ .

Raman spectroscopy: Micro-Raman spectra were taken on polished samples (HORIBA LabRAM HR UV-vis-NIR confocal microspectrometer). Spectra from areas exhibiting a slight reflectivity contrast observable on optical microscopy images (lighter and darker zones) show a minor but significant variability. Most probably it arises from the different photosensitivities in zones resulting from minor variations of the atomic arrangement (a local disorder of the Ag and Hg atoms is evident). The splitting of all internal modes is consistent with the presence of two symmetrically non-equivalent  $[\text{AsO}_4]$  tetrahedra in the crystal structure with slightly different As–O bond lengths; from the crystal structure analyses the average bond distances amount 1.718 and 1.694 Å, respectively. The difference correlates with the distinct coordination of the individual O atoms.

X-ray investigation: The crystal-structure investigation was performed using single-crystal X-ray data (four-circle Nonius Kappa diffractometer, CCD detector, 300 μm capillary optics collimator, conventional X-ray tube, monochromated  $\text{MoK}_\alpha$  radiation). The space group is  $F\bar{4}3c$ ,  $a = 17.360(3)$  Å,  $V = 5231.8$  Å<sup>3</sup>,  $Z = 32$ . In a first step of the structure

refinement, two crystallographically distinct arsenate tetrahedra and one Cl atom was found. For two further positions a mixed occupation by Hg and Ag atoms is required to balance the scattering power:  $M1 = (\text{Ag,Hg})1$  and  $M2 = (\text{Ag,Hg})2$ . Furthermore, the final difference Fourier summation exhibited large residual densities between  $-2.31$  to  $+3.75$  eÅ<sup>-3</sup>, the largest maxima are in the surrounding of the  $M$  atoms. Three peaks ( $X1a$ ,  $X2a$  and  $X2b$ ) seen in the electron-density map were considered during structure refinements; the reliability factors were reduced significantly. The centres are < 0.5 Å apart from the sites  $M1$  ( $X1a$ ) and  $M2$  ( $X2a$ ,  $X2b$ ), respectively; consequently, vacancies at these  $M$  sites are required (12 atom% at the  $M1$  and 5 atom% at the  $M2$  position). For further refinement cycles, the occupation for the sites  $M1 + X1a$  and  $M2 + X2a + X2b$  was restricted to 1.0. In addition, isotropic displacement parameters for the  $X$  sites and anisotropic ones for the other sites as well as the variation of the scattering power Ag:Hg at the  $M$  sites were considered. As both  $M$  sites show a slight surplus of Ag as compared to Hg atoms, it is expected that the  $X$  sites compensate the mismatch to obtain a 1:1 ratio for the total composition expected from the chemical analyses. As conventional X-ray sources do not allow in such cases a refinement of the element ratio at one site, the occupation of the three  $X$  sites was arbitrarily set to each 50 atom% Ag and Hg. However, it cannot be proved experimentally by the structure determination due to the minor site-occupation factors of the  $X$  sites. The final refinement on  $F^2$  converged at  $wR2(F^2) = 0.068$ ,  $R1(F) = 0.031$  for all 972 unique data and 53 variable parameters.

The most striking feature of the crystal structure of rudabányaite are two crystallographically different tetravalent 4-center 2-electron bonded cluster cations  $[\text{M}_4]^{4+}$ ;  $M = (\text{Ag, Hg})$ , Ag:Hg ~ 1:1,  $M-M = 2.62$  to  $2.75$  Å (for a theoretical approach see PYYKKÖ & RUNEBERG, 1993). The point symmetry of the two tetrahedra is  $\bar{2}3$  and  $\bar{4}$ , respectively. Numerous attempts were performed to verify an order between Ag and Hg atoms but none of them was successful; any symmetry reduction could not be verified, *superstructure* reflections were not detectable. Most probable natural light triggers the displacement of small amounts of the  $M$  atoms (~0.5 Å) and cause slow changes of the colour. Raman spectra taken in distinctly coloured areas showed some differences mainly for the band at ~119 cm<sup>-1</sup>.

$[M_4]$  ( $M = \text{Ag}, \text{Hg}$ ) tetrahedra respectively  $[M_3]$  ( $M = \text{Ag}, \text{Hg}$ ) triangles are extremely rare (see Tab. 1). So far,  $[\text{Ag}_2\text{Hg}_2]^{4+}$  tetrahedra are known from the two synthetic compounds  $[\text{Ag}_2\text{Hg}_2]_3[\text{VO}_4]_4$  and  $[\text{Ag}_2\text{Hg}_2]_2[\text{HgO}_2][\text{AsO}_4]_2$  only (WEIL *et al.*, 2005). The change of the ratio Ag:Hg to 3:1 in the mineral tillmannsite,  $[\text{Ag}_3\text{Hg}][(\text{V},\text{As})\text{O}_4]$  (SARP *et al.*, 2003) and in its synthetic vanadate end-member (WEIL *et al.*, 2005) results in a trivalent cation complex. In these tetrahedral cluster cations  $[\text{Ag}_3\text{Hg}]^{3+}$  and  $[\text{Ag}_2\text{Hg}_2]^{4+}$  the atom ratio Ag:Hg is stoichiometric. The atoms Ag and Hg are statistically distributed with a metal—metal bond length of about 2.72 Å. This distance indicates a predominantly covalent bond. For a metallic bond character, the sum of the metal radii of the atoms under consideration would suggest a longer distance than that found in the  $[M_4]$  tetrahedra.

The  $M$  atoms in all these  $[M_4]$  clusters are [6] coordinated by each three  $M$  atoms and by three anions; new is the coordination by two O and one Cl atoms in the title mineral whereas in the three other compounds under discussion only O atoms occur in the first coordination sphere of the  $M$  atoms. The  $M$ —O bond lengths vary on a larger scale obviously because of the distinct coordinations of the O atoms. A clear trend is not observed: The shortest average  $M$ —O bond lengths are observed in rudabányaite ( $M1$ —O = 2.415 Å) and in tillmannsite (natural and synthetic sample 2.417 Å and 2.398 Å, respectively) despite the different tetrahedral cation clusters  $[\text{Ag}_2\text{Hg}_2]^{4+}$  and  $[\text{Ag}_3\text{Hg}]^{3+}$ . In  $[\text{Ag}_2\text{Hg}_2]_3[\text{VO}_4]_4$  (WEIL, 2005) they are slightly longer: 2.52 to 2.59 Å for the three distinct  $M$  atoms. In  $[\text{Ag}_2\text{Hg}_2]_2[\text{HgO}_2][\text{AsO}_4]_2$  they scatter on a large scale (WEIL 2005).  $[\text{Ag}_2\text{Hg}_2]$  tetrahedra occur also in  $[\text{Ag}_2\text{Hg}_4][\text{XO}_4]_2$  ( $X = \text{P}, \text{As}$ ) (MASSE *et al.*, 1978; WEIL, 2003). However, the Ag and Hg atoms are ordered; each two  $[\text{Ag}_2\text{Hg}_2]$  tetrahedra share a common Ag—Ag edge forming an  $[\text{Ag}_2\text{Hg}_4]^{6+}$ -cluster cation. The shared edge (2.824(4) / 2.8531(11) Å in the phosphate / arsenate compound) is slightly shorter than in native silver but larger than the  $M$ — $M$  distance in rudabányaite. The length of the Hg—Hg edges (2.608(2)

/ 2.6214(5) Å) is comparable to the  $M$ — $M$  bond length in rudabányaite, but the Ag—Hg edges again are significantly longer (2.840(3) and 2.941(3) / 2.8388(5) and 2.9404(6) Å). Remarkable is the one-sided coordination of the  $\text{Cl}^{1-}$  ions in rudabányaite.

Rudabányaite exhibits strong crystal chemical, structural, and topological similarities to tillmannsite,  $[\text{Ag}_3\text{Hg}][(\text{V},\text{As})\text{O}_4]$  (space group  $\bar{4}$ ; SARP *et al.*, 2003, WEIL *et al.*, 2005). Even in both minerals Ag and Hg atoms are disordered, Ag:Hg is stoichiometric. In kuznetsovite ( $[\text{Hg}_3][\text{AsO}_4]\text{Cl}$ , space group  $P2_13$ ,  $a = 8.3983(6)$  Å; SOLOVEVA *et al.*, 1991, WEIL, 2001), trigonal  $[\text{Hg}_3]^{4+}$  clusters substitute the larger  $[(\text{Hg},\text{Ag})_4]^{4+}$  metal clusters of rudabányaite. The two synthetic compounds exhibiting tetrahedral cationic clusters, *i.e.*,  $[\text{Ag}_2\text{Hg}_2]_3[\text{VO}_4]_4$  and  $[\text{Ag}_2\text{Hg}_2]_2[\text{HgO}_2][\text{AsO}_4]$  (WEIL, 2005), display stoichiometry but disorder of the  $M$  atoms. However, in the double-tetrahedron  $[\text{Ag}_2\text{Hg}_4]$  in  $[\text{Ag}_2\text{Hg}_4][\text{XO}_4]_2$  ( $X = \text{P}, \text{As}$ ) the Ag and Hg atoms are ordered (MASSE *et al.*, 1978; WEIL *et al.*, 2005). New in rudabányaite is the partial displacement of the  $M$  atoms.

In rudabányaite the ratio of the  $[M_4]^{4+}$ : $[M_2_4]^{4+}$  clusters and  $[\text{As}_1\text{O}_4]^{3-}$ : $[\text{As}_2\text{O}_4]^{3-}$  tetrahedra is consistently 1:3.  $M$ —O bonds running approximately parallel to  $\langle 100 \rangle$  link these tetrahedra among each other. Considering the distinct kinds of tetrahedra, they are linked to two different 2D arrangements with the compositions  $[\text{M}_2_4]_2[\text{As}_1\text{O}_4][\text{As}_2\text{O}_4]$  and  $[\text{M}_1_4][\text{M}_2_4][\text{As}_2\text{O}_4]_2$ ; they are aligned parallel to  $\{100\}$  (Fig. 1). These layer-like arrangements penetrate each other according to the cubic symmetry. All the  $[\text{AsO}_4]^{3-}$  tetrahedra are arranged parallel to each other, the As—O bonds point towards  $\langle 111 \rangle$ ; the  $[M_1_4]^{4+}$  tetrahedra point into the opposite direction  $\{\bar{1}\bar{1}\bar{1}\}$ . Thus, polarity of the crystal structure is verified; merohedral twinning was not observed.

The crystal structure of rudabányaite is on high interest from a topological point of view. The barycentres of the  $[M_4]^{4+}$  cluster cations and the  $[\text{AsO}_4]^{3-}$  tetrahedra are arranged in an ideal rock-salt structure type with  $a' = \frac{1}{2}a = 8.680$  Å. Considering the grid

Rudabányaite,  $[\text{Ag}_2\text{Hg}_2][\text{AsO}_4]\text{Cl}$ , space group  $F\bar{4}3c$

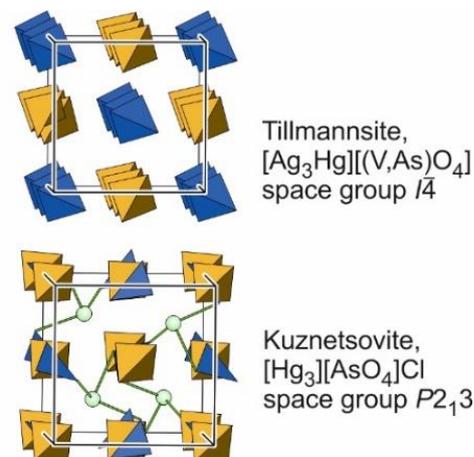
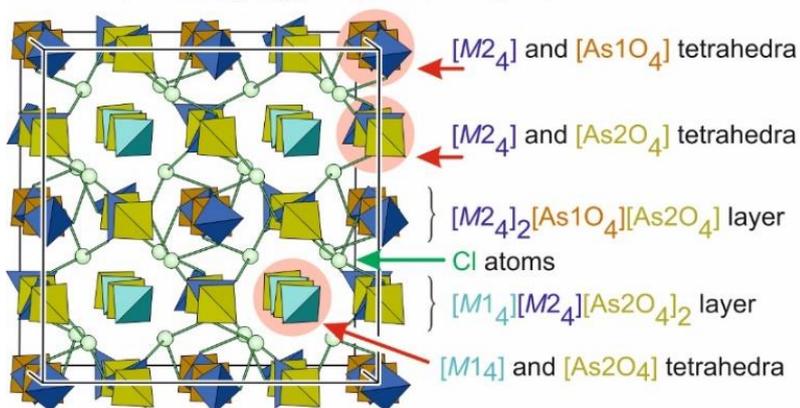


Fig. 1: Topological relations between rudabányaite, tillmannsite, and kuznetsovite.

formed by these two barycentres, *i.e.*, of all the tetrahedral structural units, a cubic primitive (cp) lattice is obtained. The filling of all voids of this lattice results in the well-known CsCl-structure type. Filling only half of the interstitial positions of a cp arrangement suggests a relation to one of the three distinct structure types fluorite (CaF<sub>2</sub>) respectively *anti*-fluorite,  $\alpha$ -FeSi<sub>2</sub>, and Hg<sub>2</sub>Pt. In rudabányaite the [M<sub>4</sub>]<sup>4+</sup> barycenters of the tetrahedral [(Ag,Hg)<sub>4</sub>] clusters and the As<sup>5+</sup> cations correspond to the position of the F<sup>-</sup> ions of the fluorite-structure type whereas the Cl<sup>-</sup> ions of the title compound to the positions of the Ca<sup>2+</sup> ions; consequently the crystal structure of rudabányaite can be derived from the anti-fluorite structure-type. Derivatives of this structure type are well known as the C1<sub>b</sub>-structure type respectively half-Heusler compounds.

Similarities with the crystal structures of the mineral tillmannsite, [Ag<sub>3</sub>Hg][(V,As)O<sub>4</sub>], are evident (Fig. 1). Tillmannsite crystallises in the rarely verified tetragonal space group  $\bar{I}4$ . Two distinct column-like arrangements built solely by [Ag<sub>3</sub>Hg]<sup>3+</sup> cation clusters and [(V,As)O<sub>4</sub>]<sup>3-</sup> tetrahedra are running parallel to [001]; alternately arranged [Ag<sub>3</sub>Hg] clusters and [(V,As)O<sub>4</sub>] tetrahedra are verified only parallel to <100>.

The chemical formula [Hg<sub>3</sub>][AsO<sub>4</sub>]Cl of kuznetsovite suggests a structural relation to rudabányaite; in fact, the atomic arrangements are identical from a topological point of view. Kuznetsovite crystallizes cubic, space group *P*2<sub>1</sub>3, the cell parameter *a*(kuznetsovite) is 8.3983(6) Å which is roughly 1/2 *a* (rudabányaite) = 8.680 Å. The difference is caused by the substitution of the trigonal planar [Hg<sub>3</sub>]<sup>4+</sup> clusters by the larger tetrahedral [(Hg,Ag)<sub>4</sub>]<sup>4+</sup> metal clusters. The

substitution cause slight rotations respectively shifts of the [AsO<sub>4</sub>]<sup>3-</sup> tetrahedra and Cl<sup>-</sup> ions. The atomic arrangement in monoclinic terlinguaite is different: The coplanar [Hg<sub>3</sub>]<sup>4+</sup> triangles are linked by the O atoms to layers running parallel to (100); they are connected by insular Hg<sup>2+</sup> cations and Cl<sup>-</sup> anions to a three-dimensional network. The dominance of acentric crystal structures in this group of compounds should be noted.

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Table 1: Minerals and synthetic compounds with polyatomic [(Ag,Hg)<sub>n</sub>] metal clusters related to rudabányaite.

Mineral name	Chemical composition	Space group symmetry	Reference
rudabányaite	[Ag <sub>2</sub> Hg <sub>2</sub> ][AsO <sub>4</sub> ]Cl	<i>F</i> $\bar{4}3c$	EFFENBERGER <i>et al.</i> (2019)
tillmannsite	[Ag <sub>3</sub> Hg][(V,As)O <sub>4</sub> ]	$\bar{I}4$	SARP <i>et al.</i> (2003), WEIL <i>et al.</i> (2005)
	[Ag <sub>3</sub> Hg][VO <sub>4</sub> ]	$\bar{I}4$	WEIL <i>et al.</i> (2005)
	[Ag <sub>2</sub> Hg <sub>2</sub> ] <sub>3</sub> [VO <sub>4</sub> ] <sub>4</sub>	<i>I</i> $\bar{4}2d$	WEIL <i>et al.</i> (2005)
	[Ag <sub>2</sub> Hg <sub>2</sub> ] <sub>2</sub> [HgO <sub>2</sub> ][AsO <sub>4</sub> ] <sub>2</sub>	<i>P</i> 31 <i>c</i>	WEIL <i>et al.</i> (2005)
	[Ag <sub>2</sub> Hg <sub>4</sub> ][AsO <sub>4</sub> ] <sub>2</sub>	<i>P</i> bam	WEIL (2003)
terlinguaite	[Ag <sub>2</sub> Hg <sub>4</sub> ][PO <sub>4</sub> ] <sub>2</sub>	<i>P</i> bam	MASSE <i>et al.</i> (1978)
kuznetsovite	[Hg <sub>3</sub> ][AsO <sub>4</sub> ]Cl	<i>P</i> 2 <sub>1</sub> 3	SOLOV'eva <i>et al.</i> (1991), WEIL (2001)
	[Hg <sub>3</sub> ][PO <sub>4</sub> ]Cl	<i>P</i> 2 <sub>1</sub> 3	WEIL (2001)
	[Hg <sub>3</sub> ]HgO <sub>2</sub> Cl <sub>2</sub>	<i>C</i> 2/ <i>c</i>	BRODERSEN <i>et al.</i> (1989)