

**THE 4-CENTER 2-ELECTRON BONDED CLUSTER CATIONS
[Ag₃Hg]³⁺ AND [Ag₂Hg₂]⁴⁺**

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[Ag₃Hg]³⁺ and [Ag₂Hg₂]⁴⁺ are rare cation complexes. The first evidence was found in tillmannsite, [Ag₃Hg][(V,As)O₄], which was described from an old copper mine of Roua (Alpes-Maritimes, France): space group *I*4̄ (SARP et al., 2003). Later on, WEIL et al. (2005) synthesized the V-end member besides the compounds [Ag₂Hg₂]₃[VO₄]₄ and [Ag₂Hg₂]₂[HgO₂][AsO₄]₂ (*I*4̄2*d* and *P*31*c*). Just recently, rudabányaite - [Ag₂Hg₂][AsO₄]Cl was found in cavities of siliceous sphaerosiderite and limonite rocks at the Rudabánya ore deposit (Adolf mine area, NE Hungary; *F*4̄3*c*; EFFENBERGER et al., 2019).

The *M* = (Ag, Hg) atoms in all these [*M*₄] clusters are located at the corners of an empty tetrahedron; the complex is stoichiometric with Ag:Hg = 2:2 or 3:1, respectively. The *M* atoms are ~1.66 Å apart from their vacant centres; thus, the size of the [*M*₄] tetrahedra corresponds with the arsenate and vanadate tetrahedra. The *M*—*M* bond distances of ~2.60 to 2.72 Å suggest predominantly covalent bonding. Order between Ag and Hg atoms is not verified. The *M* atoms are [6] coordinated by each three *M* atoms and by three anions. In rudabányaite a partial displacement of the *M* atoms was observed (about 0.5 Å). Remarkable is the pronounced one-sided [3] coordination of the Cl⁻ ions in rudabányaite.

Only in [Ag₂Hg₄][XO₄]₂ (*X* = P, As) (MASSE et al., 1978; WEIL, 2003) the Ag and Hg atoms are ordered: each two [Ag₂Hg₂] tetrahedra share a common Ag—Ag edge forming an [Ag₂Hg₄]⁶⁺-cluster cation. The shared edge (~2.85 Å) is slightly shorter than in native silver but larger than the *M*—*M* distance in the [Ag₂Hg₂] complex. The other *M*—*M* bond distances are comparable to the [*M*₄] clusters.

On interest are some crystal chemical, structural, and topological similarities: In kuznetsovite ([Hg₃][AsO₄]Cl, space group *P*2₁3; WEIL, 2001) trigonal [Hg₃]⁴⁺ clusters substitute for the larger [Hg₂Ag₂]⁴⁺ metal clusters of rudabányaite; the Cl atom is planar [3] coordinated. – In tillmannsite, two distinct column-like arrangements built solely by [Ag₃Hg]³⁺ cation clusters respectively [(V,As)O₄]³⁻ tetrahedra are running parallel to [001]; alternatingly arranged [Ag₃Hg] clusters and [(V,As)O₄] tetrahedra are verified parallel to <100>. In rudabányaite [Ag₂Hg₂] clusters and [AsO₄] tetrahedra alternate due to the cubic symmetry in all <100> directions.

The dominance of acentric crystal structures in this group of compounds should be noted.

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