

NEW CRYSTAL STRUCTURES WITH TETRAHEDRAL SILVER-MERCURY CLUSTER CATIONS: $(\text{Ag}_3\text{Hg})\text{VO}_4$, $(\text{Ag}_2\text{Hg}_2)_3(\text{VO}_4)_4$, AND $(\text{Ag}_2\text{Hg}_2)_2(\text{HgO}_2)(\text{AsO}_4)_2$

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The first experimental evidence of a tetrahedral silver-mercury cluster with composition $(\text{Ag}_3\text{Hg})^{3+}$ was supplied from the crystal structure of the rare secondary alteration mineral *tillmannsite*, $(\text{Ag}_3\text{Hg})(\text{V,As})\text{O}_4$ (SARP et al., 2003). The $(\text{Ag}_3\text{Hg})^{3+}$ cluster cation in this structure is composed of statistically distributed Ag and Hg atoms with a metal-metal distance of about 2.75 Å.

During systematic phase formation experiments in the systems Ag–Hg–V–O and Ag–Hg–As–O, the new compounds $(\text{Ag}_3\text{Hg})\text{VO}_4$ (I), $(\text{Ag}_2\text{Hg}_2)_3(\text{VO}_4)_4$ (II), and $(\text{Ag}_2\text{Hg}_2)_2(\text{HgO}_2)(\text{AsO}_4)_2$ (III) were obtained under hydrothermal conditions (250 °C, 5d) from starting mixtures of AgNO_3 , elementary Hg, NH_4VO_3 and Na_2HAsO_4 , respectively. All crystal structures were determined from single crystal X-ray data sets. The chemical composition of the compounds was confirmed by microprobe analyses (WEIL et al., 2005).

(I) crystallizes in the *tillmannsite* structure type and is composed of tetrahedral $(\text{Ag}_3\text{Hg})^{3+}$ and VO_4^{3-} units. (II) and (III) adopt new structure types and contain a so far unknown tetrahedral $(\text{Ag}_2\text{Hg}_2)^{4+}$ cluster cation and tetrahedral XO_4^{3-} anions ($X = \text{V, As}$). In (III) an additional mercurate unit, HgO_2^{2-} , completes the structural set-up. Both cluster cations $(\text{Ag}_3\text{Hg})^{3+}$ and $(\text{Ag}_2\text{Hg}_2)^{4+}$ deviate marginally from T_d symmetry and are formed by statistically distributed Ag and Hg atoms with a metal-metal distance of about 2.72 Å. This distance is considerably shorter than the sum of the metal radii, 1.44 Å {Ag} + 1.50 Å {Hg} (PAULING, 1962), but longer than the average Hg–Hg distances in Hg_2^{2+} -dumbbells (2.518 Å) or Hg_3^{4+} -triangles (2.677 Å). The electronic structure of the tetrahedral clusters can formally be considered as two-electron-four-centre bonding (PYYKKÖ & RONEBERG, 1983).

References

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