

Investigations in the Systems Ag-Hg-X-O ($X = \text{As}^{\text{V}}, \text{Se}^{\text{IV}}, \text{Se}^{\text{VI}}$): Hydrothermal Single Crystal Growth of Ag_3AsO_4 , $\text{AgHg}^{\text{I}}_2\text{AsO}_4$, $\text{AgHg}^{\text{II}}\text{AsO}_4$, Ag_2SeO_4 and the Crystal Structure of $\text{Ag}_2\text{Hg}^{\text{II}}(\text{SeO}_3)_2$

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Single crystals of the already known phases Ag_3AsO_4 , $\text{AgHg}^{\text{I}}_2\text{AsO}_4$, $\text{AgHg}^{\text{II}}\text{AsO}_4$, Ag_2SeO_4 and of the hitherto unknown compound $\text{Ag}_2\text{Hg}^{\text{II}}(\text{SeO}_3)_2$ were obtained under hydrothermal conditions (250 °C, 5 d) from starting mixtures of the metal nitrates and the respective acids. Both Ag_3AsO_4 and $\text{AgHg}^{\text{I}}_2\text{AsO}_4$ are isotypic with the corresponding phosphates, Ag_3PO_4 and $\text{AgHg}^{\text{I}}_2\text{PO}_4$, whereas $\text{AgHg}^{\text{II}}\text{AsO}_4$ and Ag_2SeO_4 crystallize in the *thenardite* (Na_2SO_4 (V)) structure. All crystal structures were refined by means of single crystal X-ray data. The crystal structure of $\text{Ag}_2\text{Hg}^{\text{II}}(\text{SeO}_3)_2$ [$Pbca$, $Z = 8$, $a = 6.8206(11)$, $b = 11.237(3)$, $c = 16.876(2)$ Å, 1677 structure factors, 101 parameters, $R[F^2 > 2\sigma(F^2)] = 0.0193$, $wR(F^2 \text{ all}) = 0.0394$] consists of considerably distorted $[\text{AgO}_6]$ and $[\text{HgO}_6]$ octahedra, and trigonal $\text{Se}^{\text{IV}}\text{O}_3$ pyramids as the main building units. The $[\text{MO}_6]$ octahedra build a complex framework by sharing common edges and corners, and the $\text{Se}^{\text{IV}}\text{O}_3$ pyramids are located in the vacancies of this arrangement. The average Hg-O distance of 2.399 Å is significantly shorter than the average Ag-O distance of 2.551 Å. The geometries of the two crystallographically independent $\text{Se}^{\text{IV}}\text{O}_3$ pyramids are very similar and the average distance and angle ($\bar{d}(\text{Se-O}) = 1.709$ Å, $\angle(\text{O-S-O}) = 100.1^\circ$) lie in the characteristic range for a selenite(IV) group. A short comparative structural discussion between the various compounds obtained during the hydrothermal experiments is given.

Key words: Silver, Mercury, Selenites(IV), Selenates(VI), Arsenates(V)