

# 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 $\text{Ag}_3\text{AsO}_4$ , $\text{AgHg}^{\text{I}}_2\text{AsO}_4$ , $\text{AgHg}^{\text{II}}\text{AsO}_4$ , $\text{Ag}_2\text{SeO}_4$ and the Crystal Structure of $\text{Ag}_2\text{Hg}^{\text{II}}(\text{SeO}_3)_2$

Matthias Weil

Institute of Chemical Technologies and Analytics, Division of Structural Chemistry,  
Vienna University of Technology, Getreidemarkt 9/164-SC, A-1060 Vienna, Austria

Reprint requests to Dr. M. Weil. E-mail: mweil@mail.zserv.tuwien.ac.at

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Single crystals of the already known phases  $\text{Ag}_3\text{AsO}_4$ ,  $\text{AgHg}^{\text{I}}_2\text{AsO}_4$ ,  $\text{AgHg}^{\text{II}}\text{AsO}_4$ ,  $\text{Ag}_2\text{SeO}_4$  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  $\text{Ag}_3\text{AsO}_4$  and  $\text{AgHg}^{\text{I}}_2\text{AsO}_4$  are isotopic with the corresponding phosphates,  $\text{Ag}_3\text{PO}_4$  and  $\text{AgHg}^{\text{I}}_2\text{PO}_4$ , whereas  $\text{AgHg}^{\text{II}}\text{AsO}_4$  and  $\text{Ag}_2\text{SeO}_4$  crystallize in the *thenardite* ( $\text{Na}_2\text{SO}_4$  (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 ( $\bar{d}(\text{Se}-\text{O}) = 1.709$  Å,  $\angle(\text{O}-\text{S}-\text{O}) = 100.1^\circ$ ) 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)

## Introduction

The crystal chemistry of mercury oxo compounds with different stable oxidation states for the mercury atom is multifarious and – compared to other metal atoms with similar ionic radii – more or less unique [1, 2]. Numerous Hg(II) and Hg(I) compounds, with the characteristic  $\text{Hg}_2^{2+}$  dumbbell for the latter structural family, have been known for a very long time whereas most of the compounds with mercury in the unusual oxidation state (4/3) and an  $\text{Hg}_3^{4+}$  triangle as the corresponding coordination figure were only recently structurally characterized [3 – 5]. Frequently, for most of these structures a pronounced linear coordination of the Hg atom is observed which, using a very simple approach, is caused by the *sp*-hybridisation of the metal atom. Very recently, the crystal structure of the rare mineral *tillmannsite* with its empirical formula  $(\text{Ag}_3\text{Hg})(\text{V}/\text{AsO}_4)$  was described [6] which contains a tetrahedral  $[\text{Ag}_3\text{Hg}]^{3+}$  cluster with the Ag and Hg

atoms statistically distributed on one crystallographic site. This cluster is of particular interest owing to the special electronic configuration with its two-electron four-centre bonding [7]. In search of other representatives which contain this peculiar structural element, systematic investigations were undertaken for the hydrothermal syntheses of compounds for the systems Ag-Hg-P-O, Ag-Hg-As-O, Ag-Hg-S-O, Ag-Hg-Se-O and Ag-Hg-V-O.

During these experiments, single crystals of the already known phases  $\text{Ag}_3\text{AsO}_4$  [8],  $\text{AgHg}^{\text{I}}_2\text{AsO}_4$  [9],  $\text{AgHg}^{\text{II}}\text{AsO}_4$  and  $\text{Ag}_2\text{SeO}_4$  [10] were grown\*. Since no structural details are published for these compounds, refinements of their structures by means of

\*Results of crystal growth experiments and structure analyses for the system Ag-Hg-V-O will be published elsewhere. For the systems Ag-Hg-P-O and Ag-Hg-S-O, single crystals of  $\text{Hg}_3(\text{PO}_4)_2$  [11] and  $\text{HgSO}_4 \cdot 2\text{HgO}$  [12], respectively, were obtained which both are crystallographically well-characterized. No Ag-containing solid phases were observed during the experiments in both systems.

Table 1. Details of data collection and structure refinement.

Compound	$\text{Ag}_3\text{AsO}_4$	$\text{AgHg}^{\text{I}}_2\text{AsO}_4$	$\text{AgHg}^{\text{II}}\text{AsO}_4$	$\text{Ag}_2\text{SeO}_4$	$\text{Ag}_2\text{Hg}^{\text{II}}(\text{SeO}_3)_2$
Diffractometer	CAD4 (Nonius)	CAD4 (Nonius)	SMART (Siemens)	CAD4 (Nonius)	SMART (Siemens)
Radiation; $\lambda$ [Å]			— Mo K $\alpha$ ; 0.71073 —		
Temperature [°C]			— 22(2) —		
Crystal dimensions [mm]	0.25 · 0.22 · 0.20	0.15 · 0.07 · 0.04	0.05 · 0.03 · 0.01	0.21 · 0.21 · 0.12	0.35 · 0.20 · 0.04
Crystal color; shape	dark-brown; spheroid	amber; rod	red; plate	light yellow, pinacoid	colourless; sword
Crystal system	cubic	orthorhombic	orthorhombic	orthorhombic	orthorhombic
Space group, no.	$P\bar{4}3n$ , 218	$Pbam$ , 55	$Fddd$ , 70	$Fddd$ , 70	$Pbca$ , 61
Formula units $Z$	2	4	8	8	8
$a$ [Å]	6.1391(3)	8.7251(6)	6.2185(8)	6.0531(9)	6.8206(11)
$b$ [Å]		9.6207(5)	10.5633(13)	10.3898(11)	11.237(3)
$c$ [Å]		6.2432(5)	12.1729(16)	13.0001(11)	16.876(2)
$V$ [Å <sup>3</sup> ]	231.37(2)	524.06(6)	799.61(18)	817.58(16)	1293.4(4)
Formula weight [g·mol <sup>-1</sup> ]	462.53	647.97	447.38	358.70	670.25
$\mu$ [mm <sup>-1</sup> ]	19.561	68.320	51.335	18.357	40.905
X-ray density [g·cm <sup>-3</sup> ]	6.639	8.213	7.433	5.828	6.884
Range $\theta_{\min} - \theta_{\max}$ [°]	4.70 – 39.74	3.15 – 32.43	5.11 – 29.96	4.20 – 32.49	2.41 – 30.51
Range					
$h$	–11 → 11	–13 → 13	–8 → 8	–9 → 9	–7 → 7
$k$	–11 → 11	–14 → 14	–14 → 14	–15 → 15	–15 → 15
$l$	–11 → 11	–9 → 9	–16 → 16	–19 → 19	–23 → 20
Absorption correction			— HABITUS [16] —		
Structure refinement			— SHELXL97 [17] —		
Measured reflections	4985	7121	2004	2708	11850
Independent reflections	245	1018	293	371	1677
Obs. reflections [ $I > 2\sigma(I)$ ]	236	821	226	315	1556
$R_i$	0.0900	0.0547	0.0551	0.0871	0.0570
Trans. Coef. $T_{\min}$ ; $T_{\max}$	0.0463; 0.1354	0.0515; 0.3760	0.2166; 0.6396	0.0808; 0.2148	0.0500; 0.3917
Number of parameters	12	44	19	19	101
Ext. coef. (SHELXL97)	0.304(15)	0.00314(13)	0.00064(5)	0.0026(3)	0.00787(14)
Diff. Elec. Dens. max.;	1.08 (2.09, Ag1);	1.92 (0.70, Hg)	1.40 (0.77, Hg);	2.63 (0.63, Ag)	1.83 (0.65, Hg)
min [ $e^- \cdot \text{Å}^{-3}$ ] (d [Å], atom)	–0.76 (0.60, Ag1)	–2.59 (0.68, Hg)	–1.66 (1.97, Hg)	–2.16 (0.59, Ag)	–1.77 (0.86, Hg)
$R[F^2 > 2\sigma(F^2)]$	0.0215	0.0211	0.0195	0.0291	0.0193
$wR2(F^2 \text{ all})$	0.0462	0.0430	0.0350	0.0840	0.0394
Goof	1.412	1.050	0.956	1.152	1.156
Flack parameter [26]	0.07(3)				
CSD number	413086	413087	413088	413089	413090
Structure type	$\text{Ag}_3\text{PO}_4$ [8, 18]	$\text{AgHg}_2\text{PO}_4$ [9]	<i>thenardite</i> [10]	<i>thenardite</i> [10]	this article

single crystal X-ray data were undertaken. Additionally, the so far unknown compound  $\text{Ag}_2\text{Hg}(\text{SeO}_3)_2$  was obtained whose preparation and crystal structure is the main subject of this article.

## Experimental Section

### Syntheses

For single crystal growth of the title compounds, stoichiometric amounts of silver and mercury(I) or mercury(II) nitrates in the molar ratio  $\text{Ag}:\text{Hg} = 3:1$  were charged in a Teflon inlay with 10 ml capacity which was two-thirds filled with a slight excess of aqueous solutions of the respective acids  $\text{H}_2\text{SeO}_4$ ,  $\text{H}_2\text{SeO}_3$  or  $\text{H}_3\text{AsO}_4$ . All reagents used were of *p. A.* quality. The inlays were sealed in a steel autoclave, and this device was then heated to 250 °C within 3 h, left at that temperature for 5 d and cooled to room temperature in the course of 5 h. After filtering and washing with

Table 2.  $\text{Ag}_2\text{Hg}(\text{SeO}_3)_2$ . Atomic coordinates and isotropic displacement parameters [Å<sup>2</sup>]. All atoms are in Wyckhoff position 8c.

Atom	$x$	$y$	$z$	$U_{\text{eq}}$
Hg	0.13529(3)	0.158439(12)	0.148041(9)	0.02078(7)
Ag1	0.11182(5)	0.40723(3)	0.252918(18)	0.02565(9)
Ag2	0.35332(5)	0.38367(2)	0.453163(19)	0.02478(9)
Se1	0.16761(6)	0.13559(3)	0.35537(2)	0.01716(9)
Se2	0.34093(6)	0.37914(3)	0.06625(2)	0.01557(9)
O1	0.1311(4)	0.0676(3)	0.26516(17)	0.0259(7)
O2	0.1755(4)	0.2782(2)	0.02971(17)	0.0240(6)
O3	0.3061(5)	0.00014(19)	0.07975(16)	0.0228(6)
O4	0.3137(5)	0.2536(2)	0.33286(16)	0.0235(6)
O5	0.3410(4)	0.0428(2)	0.39312(17)	0.0244(6)
O6	0.3513(5)	0.3229(2)	0.16044(17)	0.0220(6)

mother liquor, water and ethanol, single crystals could be isolated from the reaction mixtures. It is noteworthy that during these experiments no single phase products were obtained.

Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
Hg	0.02129(13)	0.01807(8)	0.02299(10)	0.00375(5)	0.00095(6)	-0.00246(5)
Ag1	0.0263(2)	0.02222(13)	0.02845(18)	0.00005(11)	0.00593(12)	0.00353(11)
Ag2	0.0256(2)	0.02091(14)	0.02779(18)	-0.00039(12)	0.00230(13)	0.00263(10)
Se1	0.0166(3)	0.01717(15)	0.01774(19)	0.00141(12)	-0.00068(14)	0.00154(13)
Se2	0.0157(2)	0.01339(14)	0.01764(18)	0.00042(12)	0.00165(13)	-0.00020(12)
O1	0.034(2)	0.0241(13)	0.0197(14)	0.0017(11)	-0.0056(11)	-0.0075(10)
O2	0.0239(18)	0.0207(11)	0.0274(16)	-0.0056(11)	-0.0014(12)	-0.0066(10)
O3	0.0239(18)	0.0163(10)	0.0282(16)	-0.0026(10)	0.0008(12)	-0.0033(10)
O4	0.0259(19)	0.0206(11)	0.0239(15)	0.0016(10)	0.0003(12)	-0.0041(11)
O5	0.0216(18)	0.0240(12)	0.0275(16)	0.0074(11)	-0.0057(12)	0.0047(10)
O6	0.0251(19)	0.0220(12)	0.0189(14)	0.0041(10)	-0.0011(11)	0.0008(10)

Table 3.  $\text{Ag}_2\text{Hg}(\text{SeO}_3)_2$ . Anisotropic displacement parameters [ $\text{\AA}^2$ ].

$\text{Ag}_2\text{Hg}^{\text{II}}(\text{SeO}_3)_2$									
Hg	O1	2.225(3)	Se1	O5	1.701(3)	O5	Se1	O4	98.88(14)
Hg	O6	2.373(3)	Se1	O4	1.701(3)	O5	Se1	O1	99.19(14)
Hg	O3	2.419(3)	Se1	O1	1.722(3)	O4	Se1	O1	103.49(13)
Hg	O2	2.424(3)	$\bar{d}(\text{Se1-O})$		1.708				100.52
Hg	O4	2.462(3)	Se2	O3	1.705(3)	O3	Se2	O6	101.21(13)
Hg	O5	2.490(3)	Se2	O6	1.712(3)	O3	Se2	O2	100.87(14)
$\bar{d}(\text{Hg-O})$		2.399	Se2	O2	1.714(3)	O6	Se2	O2	96.72(14)
			$\bar{d}(\text{Se2-O})$		1.710				99.60
Ag1	O6	2.450(3)	Ag2	O5	2.446(3)				
Ag1	O1	2.467(3)	Ag2	O2	2.513(3)				
Ag1	O6	2.489(3)	Ag2	O4	2.516(3)				
Ag1	O1	2.523(3)	Ag2	O3	2.524(3)				
Ag1	O4	2.588(3)	Ag2	O2	2.539(3)				
Ag1	O5	2.832(3)	Ag2	O3	2.723(3)				
$\bar{d}(\text{Ag1-O})$		2.558	$\bar{d}(\text{Ag2-O})$		2.544				

Table 4. Selected distances [ $\text{\AA}$ ] and angles [ $^\circ$ ] for all structures as well as bond-valence sums (BVS) [v.u.] for  $\text{Ag}_2\text{Hg}^{\text{II}}(\text{SeO}_3)_2$ .

BVS: Hg 1.95, Ag1 0.91, Ag2 0.92, Se1 3.96, Se2 3.94, O1 2.12, O2 1.91, O3 1.90, O4 1.91, O5 1.86, O6 2.09

$\text{Ag}_3\text{AsO}_4$		$\text{AgHg}^{\text{I}}_2\text{AsO}_4$		$\text{AgHg}^{\text{II}}\text{AsO}_4$			
Ag	Ag	0.232(7)	Hg	O3	2.247(3)		
Ag	O	2.3499(12)	2 $\times$	Hg	O2	2.318(3)	
Ag	O	2.4040(15)	2 $\times$	Hg	O1	2.357(4)	
$\bar{d}(\text{Ag-O})$		2.377		Hg	Hg	2.6214(5)	
As	O	1.696(3)	4 $\times$	Hg	Ag	2.8388(5)	
				2 $\times$	Hg	Ag	2.9404(6)
				2 $\times$	Ag	Ag	2.8531(11)
				2 $\times$	Ag	O1	2.292(4)
				2 $\times$	As	O2	1.687(5)
				2 $\times$	As	O1	1.690(4)
				2 $\times$	As	O1	1.690(4)
				2 $\times$	As	O3	1.700(5)
				2 $\times$			1.692
				2 $\times$	$\text{Ag}_2\text{SeO}_4$		
				2 $\times$	Ag	O	2.400(3)
				2 $\times$	Ag	O	2.449(3)
				2 $\times$	Ag	O	2.710(3)
				2 $\times$	$\bar{d}(\text{Ag-O})$		2.520
				2 $\times$	Se	O	1.644(3)

Batches in the system Ag-Hg-As<sup>V</sup>-O yielded crystal mixtures of  $\text{Ag}_3\text{AsO}_4$ ,  $\text{AgHg}^{\text{I}}_2\text{AsO}_4$  and  $\text{AgHg}^{\text{II}}\text{AsO}_4$ , batches in the system Ag-Hg-Se<sup>IV</sup>-O gave  $\alpha$ - $\text{HgSeO}_3$  [13],  $\text{Ag}_2\text{SeO}_3$  [14] and  $\text{Ag}_2\text{Hg}^{\text{II}}(\text{SeO}_3)_2$ , and in batches in the system Ag-Hg-Se<sup>VI</sup>-O,  $\text{Ag}_2\text{SeO}_4$  and the mixed-valent Se<sup>IV</sup>/<sup>VI</sup> compound  $\text{Hg}_3\text{Se}_3\text{O}_{10}$  [15] were identified.

Single crystal diffraction intensities were collected either in the  $\omega$ -scan technique using a SMART three-circle diffractometer (Siemens) equipped with a CCD camera, or in the  $\omega/2\theta$  mode using a CAD-4 four-circle diffractometer (Non-

ius). All measured intensities were corrected for Lorentz and polarization effects. Absorption corrections were applied using the program HABITUS [16] by minimizing the internal  $R_i$  value and optimizing the crystal shape. The so derived habit was the basis of the numerical absorption correction. The crystal structure of  $\text{Ag}_2\text{Hg}^{\text{II}}(\text{SeO}_3)_2$  was solved by direct methods and refined with the SHELX97 program package [17]. The crystal structures of  $\text{Ag}_3\text{AsO}_4$ ,  $\text{AgHg}^{\text{I}}_2\text{AsO}_4$ ,  $\text{AgHg}^{\text{II}}\text{AsO}_4$  and  $\text{Ag}_2\text{SeO}_4$  were refined starting from the atomic coordinates of the isotopic compounds  $\text{Ag}_3\text{PO}_4$  [18],

$\text{AgHg}^{\text{I}}_2\text{PO}_4$  [5] and  $\text{Na}_2\text{SO}_4$  (V) [6] using the same program. The final difference Fourier maps did not indicate any additional atomic sites, and the highest difference peaks were located close to the metal positions. Further details of the data collections and structure refinements are summarized in Table 1. Final atomic coordinates and equivalent isotropic displacement parameters of  $\text{Ag}_2\text{Hg}^{\text{II}}(\text{SeO}_3)_2$  are listed in Table 2 and anisotropic displacement parameters in Table 3, respectively. Selected interatomic distances and angles for all structures are given in Table 4. Additional crystallographic information on  $\text{Ag}_2\text{Hg}^{\text{II}}(\text{SeO}_3)_2$  and on all other structures are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany, email: [crysdata@fiz-karlsruhe.de](mailto:crysdata@fiz-karlsruhe.de), by quoting the literature citation, the name of the author and the depository numbers listed at the end of Table 1. Drawing of structural details were produced using the program ATOMS [19].

## Results and Discussion

$\text{Ag}_3\text{AsO}_4$ ,  $\text{AgHg}^{\text{I}}_2\text{AsO}_4$ ,  $\text{AgHg}^{\text{II}}\text{AsO}_4$  and  $\text{Ag}_2\text{SeO}_4$  adopt known structure types that have already been substantially specified. Therefore the reader is referred to the original literature (see Table 1) for a more detailed description of the corresponding structures. Here only a brief outline of the main structural building units will be given.

$\text{Ag}_2\text{Hg}^{\text{II}}(\text{SeO}_3)_2$  is the first selenite(IV) containing both Ag and Hg in the cationic part of the structure. The refinement of the occupation factors of Ag and Hg did not indicate any statistical distribution of these atoms on the crystallographically different metal sites.

The structure of  $\text{Ag}_2\text{Hg}^{\text{II}}(\text{SeO}_3)_2$  is made up from  $[\text{AgO}_6]$  and  $[\text{HgO}_6]$  octahedra and trigonal pyramidal  $\text{SeO}_3^{2-}$  groups as the main building units. A complex framework structure is achieved by edge- and corner-sharing of the  $[\text{MO}_6]$  octahedra with the  $\text{Se}^{\text{IV}}\text{O}_3$  pyramids located in the vacancies of this arrangement (Fig. 1). Neither the structure derives from simple dense-packed structure types nor it reveals any relation to other structures with the general  $\text{ANX}$ -formula  $\text{AB}_2\text{C}_2\text{X}_6$  as listed in the ICSD database.

Mercury(II) oxo compounds and their crystal chemistry have been thoroughly investigated in the past [1, 2]. The most peculiar structural element of many of these compounds is the pronounced linear coordination of  $\text{Hg}^{\text{II}}$  with short Hg-O distances, ranging from  $ca. 2.02 \leq d(\text{Hg-O})_{\text{short}} \leq 2.20 \text{ \AA}$ . More remote oxygen atoms are located at significantly longer dis-

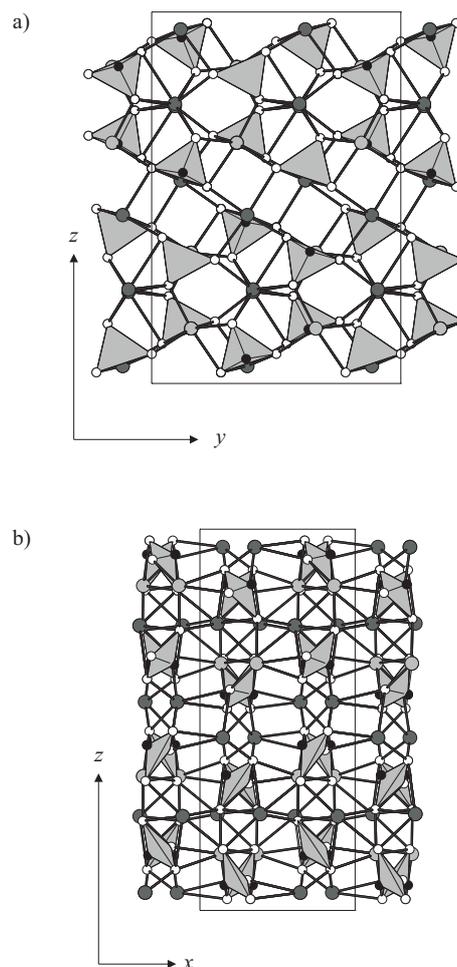


Fig. 1.  $\text{Ag}_2\text{Hg}^{\text{II}}(\text{SeO}_3)_2$ . Projection of the crystal structure along  $[100]$  (a) and along  $[010]$  (b). Ag atoms are given as dark-grey spheres, Hg atoms as light-grey spheres, Se atoms as black spheres and O atoms as white spheres; the trigonal  $\text{SeO}_3$  pyramids are plotted in the polyhedral representation.

tances and augment the distorted coordination figures. Considering that a notable interaction between Hg and O atoms is realized for Hg-O distances  $\leq 3.0 \text{ \AA}$ , the corresponding overall coordination numbers can range from 4 to 10. In  $\text{Ag}_2\text{Hg}^{\text{II}}(\text{SeO}_3)_2$  the  $\text{Hg}^{\text{II}}$  atom is surrounded by six O atoms forming a distorted octahedron; in this coordination figure no explicit linear coordination is found. The Hg-O distances range from 2.225(3) to 2.490(3)  $\text{ \AA}$ , with an average of 2.399  $\text{ \AA}$ . This distance is in good agreement with comparable  $[\text{HgO}_6]$  octahedra found for other Hg(II) oxo compounds but is significantly shorter than the average Ag-

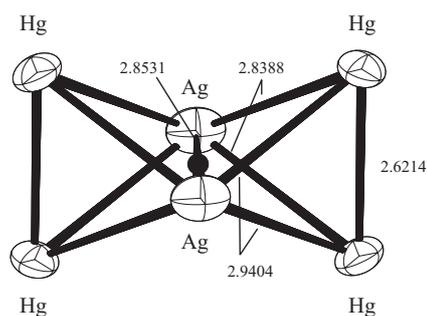


Fig. 2.  $\text{AgHg}^{\text{I}}_2\text{AsO}_4$ . The  $[\text{Ag}_2\text{Hg}_4]$  cluster with  $M$ - $M$  distances [ $\text{\AA}$ ] plotted with displacement parameters at the 90% probability level. The black point on the Ag-Ag axis denotes the inversion centre.

O distance of 2.551  $\text{\AA}$  observed for both  $[\text{AgO}_6]$  octahedra in  $\text{Ag}_2\text{Hg}^{\text{II}}(\text{SeO}_3)_2$ .

The scattering of the average Ag-O distances in the presented structures is caused by the different coordination numbers of the Ag atoms. In  $\text{Ag}_3\text{AsO}_4$ , the silver atom is tetrahedrally surrounded ( $(\text{Ag-O}) = 2.377 \text{\AA}$ ), whereas for both  $\text{Ag}_2\text{Hg}^{\text{II}}(\text{SeO}_3)_2$  (2.551  $\text{\AA}$ ) and  $\text{Ag}_2\text{SeO}_4$  (2.520  $\text{\AA}$ ) an octahedral coordination is observed. The similar average Ag-O distances of the latter are in excellent agreement with the value of 2.53  $\text{\AA}$  calculated from the radii for six-coordinate  $\text{Ag}^+$  and  $\text{O}^{2-}$  given by Shannon [20]. In  $\text{AgHg}^{\text{II}}\text{AsO}_4$  the metal atoms also show a coordination number of 6, but in this structure the crystallographically unique metal position is statistically occupied by both Ag and Hg which leads to a contraction of the average  $M$ -O distance (2.431  $\text{\AA}$ ) as compared to the above mentioned  $[\text{AgO}_6]$  octahedra. For a five-coordinate Ag atom, realized *e.g.* in the oxide nitrate  $\text{AgHg}^{\text{II}}\text{NO}_5$  [21], an average Ag-O distance of 2.472  $\text{\AA}$  is found which lies between that for the four- and six-coordinate Ag atoms in the presented structures. The geometry of the corresponding [4+1] coordination polyhedron in  $\text{AgHg}^{\text{II}}\text{NO}_5$  might be described as an intermediate between a tetrahedron and a square-pyramid with an additional capping O atom. In agreement with the tendency, that with decreasing coordination numbers shorter Ag-O bond lengths are real-

ized, an average Ag-O distance of 2.292  $\text{\AA}$  is found for  $\text{AgHg}^{\text{I}}_2\text{AsO}_4$  with a two-coordination by the O atoms. However, this value is significantly longer than that of  $\bar{d}(\text{Ag-O}) = 2.119 \text{\AA}$  in the silver mercurate  $\text{Ag}_2\text{HgO}_2$  [22]. Here, a two-coordination with very strong and almost co-linear Ag-O bonds is observed, whereas in  $\text{AgHg}^{\text{I}}_2\text{AsO}_4$  the O-Ag-O angle is bent ( $94.0(2)^\circ$ ). In addition, in  $\text{AgHg}^{\text{I}}_2\text{AsO}_4$  the elongation of the Ag-O bond lengths is caused by notable interactions of the Ag atom with other metal centres forming an inversion-symmetric  $[\text{Ag}_2\text{Hg}_4]$  cluster which is built of two  $[\text{Ag}_2\text{Hg}_2]$  tetrahedra sharing a common Ag-Ag edge (Fig. 2). The metal-metal distances ( $d(\text{Ag-M}) \approx 2.88 \text{\AA}$ ,  $M = \text{Ag, Hg}$ ) in this cluster are about 0.15  $\text{\AA}$  longer than in the tetrahedral  $[\text{Ag}_3\text{Hg}]$  cluster ( $\bar{d}(M-M) = 2.747 \text{\AA}$ ) observed for *tillmannsite* [6].

The very similar intrapolyhedral geometries of the two crystallographically independent trigonal pyramidal  $\text{SeO}_3$  anions in  $\text{AgHg}^{\text{II}}(\text{SeO}_3)_2$ , with mean distances of  $\bar{d}(\text{Se1-O}) = 1.708 \text{\AA}$ ,  $\bar{d}(\text{Se2-O}) = 1.710 \text{\AA}$ , and  $\angle(\text{O-Se-O})$  angles of  $100.52^\circ$  (Se1) and  $99.60^\circ$  (Se2), respectively, show the typical features of a selenite(IV) group [23]. The arrangement of the  $\text{SeO}_3$  polyhedra with the non-bonding lone-pair electrons of the  $\text{Se}^{\text{IV}}$  atoms arranged opposite to each other in the cavities is also a structural characteristic frequently observed in the crystal chemistry of oxoselenites(IV).

The bond lengths and angles in the  $\text{SeO}_4$  ( $\text{Ag}_2\text{SeO}_4$ ) and the various  $\text{AsO}_4$  ( $\text{Ag}_3\text{AsO}_4$ ,  $\text{AgHg}^{\text{I}}_2\text{AsO}_4$  and  $\text{AgHg}^{\text{II}}\text{AsO}_4$ ) tetrahedra show the expected values [24] and are in very good agreement with the data for comparable selenates(VI) and arsenates(V), respectively.

In  $\text{Ag}_2\text{Hg}^{\text{II}}(\text{SeO}_3)_2$  all O atoms show CN = 4 and are coordinate by one Se atom, one Hg atom and two Ag atoms resulting in considerably distorted  $[\text{OSeHgAg}_2]$  tetrahedra.

For all atoms of the crystal structure of  $\text{Ag}_2\text{Hg}^{\text{II}}(\text{SeO}_3)_2$  the corresponding bond-valence sums (BVS) were calculated using the parameters given by Brese and O'Keeffe [25] and are within the scope of the expected values (Table 4).

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