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Article

Hydrothermal Single-Crystal Growth in the Systems Ag/Hg/X/O (X = $\mathrm{V^V}$, $\mathrm{As^V}$): Crystal Structures of $(\mathrm{Ag_3Hg})\mathrm{VO_4}$, $(\mathrm{Ag_2Hg_2})_3(\mathrm{VO_4})_4$, and $(\mathrm{Ag_2Hg_2})_2(\mathrm{HgO_2})(\mathrm{AsO_4})_2$ with the Unusual Tetrahedral Cluster Cations $(\mathrm{Ag_3Hg})^{3+}$ and $(\mathrm{Ag_2Hg_2})^{4+}$ and Crystal Structure of $\mathrm{AgHgVO_4}$

Matthias Weil,*,[†] Ekkehart Tillmanns,[‡] and Dmitry Yu. Pushcharovsky[§]

Institute for Chemical Technologies and Analytics, Vienna University of Technology,
Getreidemarkt 9/164-SC, A-1060 Vienna, Austria, Institute for Mineralogy and Crystallography,
University of Vienna, Althanstrasse 14, A-1090 Vienna, Austria, and Geology Department,
Moscow State University, 119899 Moscow, Russia

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Single crystals of $(\mathrm{Ag_3Hg})\mathrm{VO_4}$ (I), $(\mathrm{Ag_2Hg_2})_3(\mathrm{VO_4})_4$ (II), $\mathrm{AgHgVO_4}$ (III), and $(\mathrm{Ag_2Hg_2})_2(\mathrm{HgO_2})(\mathrm{AsO_4})_2$ (IV) were grown under hydrothermal conditions (250 °C, 5 d) from starting mixtures of elementary mercury, silver nitrate, ammonium vanadate, and disodium hydrogenarsenate, respectively. All crystal structures were determined from X-ray diffraction data, and their chemical compositions were confirmed by electron microprobe analysis. I crystallizes in the tillmannsite structure, whereas II–IV adopt new structure types: (I) $I\bar{4}$, $Z = 2$, $a = 7.7095(2)$ Å, $c = 4.6714(2)$ Å, 730 structure factors, 24 parameters, $R[F^2 > 2\sigma(F^2)] = 0.0365$; (II) $I\bar{4}2d$, $Z = 4$, $a = 12.6295(13)$ Å, $c = 12.566(3)$ Å, 1524 structure factors, 55 parameters, $R[F^2 > 2\sigma(F^2)] = 0.0508$; (III) $C2$, $Z = 4$, $a = 9.9407(18)$ Å, $b = 5.5730(8)$ Å, $c = 7.1210(19)$ Å, $\beta = 94.561(10)°$, 1129 structure factors, 48 parameters, $R[F^2 > 2\sigma(F^2)] = 0.0358$; (IV) $P31c$, $Z = 2$, $a = 6.0261(9)$ Å, $c = 21.577(4)$ Å, 1362 structure factors, 52 parameters, $R[F^2 > 2\sigma(F^2)] = 0.0477$. The most striking structural features of I, II, and IV are the formation of tetrahedral cluster cations $(\mathrm{Ag_3Hg})^{3+}$ and $(\mathrm{Ag_2Hg_2})^{4+}$, respectively, built of statistically distributed Ag and Hg atoms with a metal–metal distance of about 2.72 Å. The electronic structure of these clusters can formally be considered as two-electron–four-center bonding. The crystal structure of III differs from the protrusive structure types insofar as silver and mercury are located on distinct crystallographic sites without a notable metal–metal interaction >3.55 Å. All crystal structures are completed by tetrahedral oxo anions $\mathrm{XO_4}^{3-}$ (X = $\mathrm{V^V}$, $\mathrm{As^V}$) and for IV additionally by a mercurate group, $\mathrm{HgO_2}^{2-}$.

Introduction

The crystal chemistry of mercury with its various oxidation states is rather complex[1] and might roughly be classified into amalgams, the well-known mercurous and mercuric compounds with $\mathrm{Hg^{2+}}$ cations or $\mathrm{Hg_2}^{2+}$ dumbbells, respectively, mixed-valent mercury(I, II) compounds with both of the aforementioned structural motifs, and compounds with mercury in lower oxidation states which form polyatomic cluster cations. A comparative crystal chemical analysis of the latter structural family has been published lately[2] and, besides mercury chain and layer compounds,[3] includes structures with the triangular mercury cluster cation $\mathrm{Hg_3}^{4+}$.[4,5] This mercury cluster is of particular interest because of its unusual electronic structure which, in a simplified model, can be described as two-electron−three-center bonding. A calculation of the electronic structure of the $\mathrm{Hg_3}^{4+}$ cluster is in progress.[6] For a more detailed crystal chemical evaluation

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* Author to whom correspondence should be addressed. E-mail: mweil@mail.zserv.tuwien.ac.at. Tel: ++43-1-58801-17122. Fax: ++43-1-58801-17199.

[†] Vienna University of Technology.

[‡] University of Vienna.

[§] Moscow State University.

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of this structural unit, a recent project intended on the preparation and characterization of Hg_3^{4+}-containing compounds was started and some new compounds were synthesized and their structures determined. Representatives with this structural unit include the rare minerals terlinguaite, $(Hg_3)HgO_2Cl_2$,[7] and kuznetsovite, $(Hg_3)AsO_4Cl$,[8,9] the synthetic P and Br analogues of kuznetsovite, $(Hg_3)PO_4Cl$ and $(Hg_3)AsO_4Br$,[9] the isotypic arsenate and phosphate, $(Hg_3)_3(AsO_4)_4$[10] and $(Hg_3)_3(PO_4)_4$,[11] the basic phosphate $(Hg_3)_2(HgO_2)(PO_4)_2$,[11] and, most recently, the mixed-valent mercury selenium oxo compounds $Hg_7Se_3O_{13}H_2$ and $Hg_8Se_4O_{17}H_2$.[12] Besides these inorganic representatives, some metalorganic compounds comprising the Hg_3^{4+} cluster, mostly with chelating phosphinomethane derivatives as ligands, have been prepared by Peringer and co-workers in the past few years.[13−18] Closely related to the latter type of compounds is the silver mercury triflate $[(AgHg_2)(\mu\text{-dppm})_3](O_3SCF_3)_3$[19] the crystal structure of which is made up of a similar triangular metal cluster $(AgHg_2)^{3+}$ where one mercury atom is formally replaced by a silver atom. This structural unit was also observed very lately in the inorganic nitrates $(AgHg_2)(NO_3)_3$ and $(AgHg_2)Hg(NO_3)_5$.[20] The recent discovery and characterization of the very rare secondary alteration mineral tillmannsite with its empirical formula $(Ag_3Hg)(As,V)O_4$[21] extend the crystal chemistry of these silver mercury clusters. The crystal structure of the latter comprises a so far unknown tetrahedral $(Ag_3Hg)^{3+}$ cluster unit with metal−metal distances of about 2.75 Å.

During systematic experiments intended for the preparation of compounds with the triangular $(AgHg_2)^{3+}$ or the tetrahedral $(Ag_3Hg)^{3+}$ cluster in the systems Ag/Hg/X/O (X = As, V), the new compounds with the formulas $(Ag_3Hg)VO_4$ (I), $(Ag_2Hg_2)_3(VO_4)_4$ (II), $AgHgVO_4$ (III), and $(Ag_2Hg_2)_2(HgO_2)(AsO_4)_2$ (IV) were obtained and characterized by single-crystal X-ray diffraction and electron microprobe analysis.

Experimental Section

Preparation. Crystals of the title compounds were grown under hydrothermal conditions in Teflon-lined steel autoclaves [filling degree with demineralized water ca. 70%, 6 mL of H_2O; temperature program, RT (room temperature) → 250 °C (2 h) → 250 °C (5 d) → RT (2 d)]. For all batches commercially purchased chemicals with analytical grade (Merck) were applied and used without further purification. For typical batches in the system Ag/Hg/V/O, reagents in the stoichiometric ratio $Hg:AgNO_3:NH_4VO_3 = 1:3:1$ [e.g. 0.086 g of Hg (0.43 mmol), 0.221 g of $AgNO_3$ (1.3 mmol), and 0.051 g of NH_4VO_3 (0.43 mmol)] were used; for batches in the system Ag/Hg/As/O, reagents in the stoichiometric ratios $Hg:AgNO_3:Na_2HAsO_4 = 1:3:1$ and 2:2:1 were employed [e.g. 0.075 g of Hg (0.37 mmol), 0.191 g of $AgNO_3$ (1.1 mmol), and 0.070 g of Na_2HAsO_4 (0.37 mmol) and 0.105 g of Hg (0.52 mmol), 0.088 g of $AgNO_3$ (0.52 mmol), and 0.050 g of Na_2HAsO_4 (0.26 mmol), respectively].

After the reaction time, the crystals were filtered off the mother liquor, washed with demineralized water, ethanol, and acetone, and dried in a desiccator for several hours. Many crystals different in color and habit had formed during the syntheses. For batches in the Ag/Hg/V/O system, honey-colored rods of Hg_2VO_4,[22] amber-colored spheroids of $(Ag_2Hg_2)_3(VO_4)_4$ (II), yellow parallelepipeds of $AgHgVO_4$ (III), and red, mostly triangular plates of synthetic tillmannsite $(Ag_3Hg)VO_4$ (I) were obtained. Hg_2VO_4 was the main phase, whereas $(Ag_2Hg_2)_3(VO_4)_4$, $AgHgVO_4$, and $(Ag_3Hg)VO_4$ formed in minor yield.

For batches with the 1:3:1 reactant ratio in the Ag/Hg/As/O system, almost all crystals consisted of $AgHg_2AsO_4$ (amber rods or plates). Minor amounts of $AgHgAsO_4$ (red parallel plates) and Ag_3AsO_4 (dark-brown octahedra) were also present.[23] In some batches with a 2:2:1 reactant ratio, a few crystals of $AgHgAsO_4$ and a few light-yellow plates of the hitherto unknown mixed-valent nitrate $Hg_2(OH)(NO_3)\cdot HgO$ were found.[24] Only in one batch, very few and tiny red triangular platelike crystals of $(Ag_2Hg_2)_2(HgO_2)(AsO_4)_2$ (IV) could be isolated. The hypothetic arsenate end member of synthetic tillmannsite with its empirical formula $(Ag_3Hg)AsO_4$ was not observed during these experiments.

Microprobe Analyses. The chemical composition of the three (I−III) synthesized phases was analyzed using electron microprobe (Geology Department, Moscow State University; Camebax SX 50; operation conditions, 15 kV, 30 nA, electron beam 1.5 × 2.0 μm). The final results of these analyses for $(Ag_3Hg)VO_4$ (red plates, 11 points), $(Ag_2Hg_2)_3(VO_4)_4$ (amber-colored spheroids, 6 points), and $AgHgVO_4$ (yellow parallelepipeds, 6 points) are summarized in Table 1. The following phases were used as standards: $AgAsS_2$ for Ag and As; HgS for Hg; vanadinite, $Pb_5(VO_4)_3Cl$, for V. Calculations of the empirical formulas (Table 1) were based on the sum (V + As) = 1, taking into account the structural data for tillmannsite.[21] The chemical formula of IV was obtained in the result of its structural study.

Single-Crystal X-ray Diffraction. The crystal quality of all crystals was checked under a polarizing microscope before the diffraction experiments. Diffraction intensities for I were then collected at room temperature with $\omega/2\theta$ scans on a CAD4 diffractometer (Nonius) or for II−IV in the ω-scan technique with 0.3° rotation width and 35 s exposure time/frame using a SMART three-

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Table 1. Formula Coefficients Based on the Sum (V + As) = 1 for $(Ag_3Hg)VO_4$, $(Ag_2Hg_2)_3(VO_4)_4$, and $AgHgVO_4$

	V	As	Hg	Ag
$(Ag_3Hg)VO_4$				
1	1.00	0.00	1.05	3.25
2	1.00	0.00	1.13	3.32
3	1.00	0.00	0.84	3.04
4	1.00	0.00	0.90	3.12
5	0.96	0.04	1.01	3.10
6	1.00	0.00	1.09	3.27
7	0.98	0.02	0.92	3.41
8	1.00	0.00	0.95	3.45
9	1.00	0.00	1.11	3.55
10	0.99	0.01	0.92	2.87
11	0.98	0.02	1.00	3.15
$(Ag_2Hg_2)_3(VO_4)_4$				
1	1.00	0.00	1.66	1.49
2	1.00	0.00	1.56	1.41
3	0.94	0.06	1.40	1.37
4	0.98	0.02	1.48	1.47
5	1.00	0.00	1.57	1.43
6	0.95	0.05	1.41	1.44
$AgHgVO_4$				
1	1.00	0.00	1.06	0.87
2	1.00	0.00	1.18	0.89
3	1.00	0.00	1.11	0.98
4	1.00	0.00	1.16	0.96
5	1.00	0.00	1.15	1.00
6	1.00	0.00	1.08	0.98

circle diffractometer (Siemens) equipped with a CCD camera. For all crystals, the full reciprocal sphere was measured. The recorded intensities were corrected for Lorentz and polarization effects, and numerical absorption corrections were applied to all data sets using the program HABITUS.[25] The crystal structure of I was refined with the atomic coordinates of natural tillmannsite[21] as starting parameters. All other structures were solved by direct methods and refined using the SHELX97 programs.[26] Further details of data collections and structure refinements are listed in Table 2. For compounds I, II, and IV, the silver and mercury atoms are statistically distributed on the respective sites. Population analyses with freely refined site occupation factors (sof) for the silver and mercury positions led to a reasonable agreement between the resultant formula and the chemical analyses obtained from microprobe analysis which are presented in Table 1. After charge-balance calculations the sofs were constrained during the last refinement cycles to the idealized values which are given in Table 3. For I all atoms were refined with anisotropic displacement parameters. For II−IV the heavy atoms were refined with anisotropic displacement parameters and the O atoms with isotropic displacement parameters.

All structures crystallize in noncentrosymmetric space groups (Table 2). For I, the refined Flack parameter[27] gives a clear indication of the absence of an inversion center. Structures II−IV were refined as enantiomeric twins with a resultant twin ratio of 0.90(3):0.10(3) for II, 0.57(4):0.43(4) for III, and 0.53(15): 0.47(15) for IV. Although the PLATON program[28] suggested a higher symmetry for II, space group $I\bar{4}3d$ (No. 220), and for IV, space group $P6_3mc$ (No. 186), the present space groups were retained. For compound II, a close check of the internal symmetry clearly revealed a tetragonal lattice. Moreover, the deviation of the lattice parameter *c* from the cubic metric is significant. Nevertheless, this compound is regarded as pseudocubic. It should also be noted that the finally chosen space group $I\bar{4}2d$ (No. 122) has the same reflection conditions as space group $I4_1md$ (No. 109). However, for the latter space group no structure solution was possible. Likewise all attempts to solve or to refine the structure of IV in a higher symmetric space group failed. For compound III a bond valence analysis[29] using the parameters by Brese and O'Keeffe[30] was performed and the bond valence sums (BVS) are summarized in Table 3. Due to the existence of metal cluster cations with a mixed occupancy of the silver and mercury atoms, a reasonable calculation of the bond valences for compounds I, II, and IV was not possible.

Final atomic coordinates and equivalent isotropic displacement parameters, as well as selected interatomic distances and angles, for all structures are given in Tables 3 and 4, respectively. Drawings of structural details were produced using the program ATOMS.[31]

Results and Comments

For a preparative working chemist the technique of the hydrothermal synthesis[32,33] is a great tool for the construction and single-crystal growth of new materials under relatively mild conditions in comparison with conventional solid-state techniques which often require aggravated reaction conditions, primarily high temperatures. The application of the hydro- or solvothermal route has therefore led to numerous new materials with fascinating properties. Despite the broad practicability of these syntheses, one of the biggest disadvantages of this technique is the unsatisfactory prediction and control of the product formation. Very frequently, the reproducibility of syntheses is poor, and sometimes unexpected or even unwanted products form during these experiments. Unfortunately, the reasons for this behavior are difficult to elucidate since a large number of different parameters (applied temperature, container material, filling degree, pH value, Eh value, heating−cooling rates, auxiliary materials, etc.) have to be adjusted and to be coordinated with each other. In case of the silver mercury oxo compounds presented in this article and of other mercury oxo compounds prepared recently, very complex interplays of different redox, protolysis, and precipitation equilibria take place during the hydrothermal syntheses. This results frequently in the formation of several crystalline products in one batch and even in the formation of phases with atoms of one element in different oxidation states in one crystal structure. The mercury selenium oxo compounds $Hg_7Se_3O_{13}H_2$ and $Hg_8Se_4O_{17}H_2$[12] are probably the most striking examples of this behavior. In these crystal structures different oxidation states for mercury of +II, +IV/3, and +I and of selenium of +VI and +IV with corresponding crystal chemical functions as Hg^{2+} cations, Hg_3^{4+} triangles, Hg_2^{2+} dumbbells, HgO_2^{2-} mercurate groups, SeO_4^{2-} tetrahedra, and SeO_3^{2-} trigonal pyramids are present.

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Table 2. Details of Data Collection and Structure Refinement

parameter	$(Ag_3Hg)VO_4$ (I)	$(Ag_2Hg_2)_3(VO_4)_4$ (II)	$AgHgVO_4$ (III)	$(Ag_2Hg_2)_2(HgO_2)(AsO_4)_2$ (IV)
temperature (°C)	22(2)			
radiation; λ (Å)	Mo K$\bar{\alpha}$ graphite monochromator; 0.710 73			
crystal dimensions (mm)	0.030 × 0.068 × 0.068	0.050 × 0.060 × 0.060	0.050 × 0.080 × 0.110	0.015 × 0.070 × 0.070
crystal color; shape	dark-red; triangular	amber; spheroid	canary; parallelepiped	red, hexagonal plate
crystal system	tetragonal	tetragonal	monoclinic	trigonal
space group, No.	$I\bar{4}$, No. 82	$I\bar{4}2d$, No. 122	$C2$, No. 5	$P31c$, No. 159
formula units Z	2	4	4	2
a (Å)	7.7095(2)	12.6295(13)	9.9407(18)	6.0261(9)
b (Å)			5.5730(8)	
c (Å)	4.6714(2)	12.566(3)	7.1210(19)	21.577(4)
β (deg)			94.561(10)	
V (Å^3)	277.651(16)	2004.3(5)	393.25(14)	678.56(19)
V/Z (Å^3) (based on one XO_4)	138.81	125.27	98.31	169.65
fw	639.14	2310.52	423.40	1744.27
μ (mm^{-1})	39.481	53.301	46.067	66.849
X-ray density (g cm^{-3})	7.645	7.657	7.151	8.537
range $\theta_{min}-\theta_{max}$ (deg)	3.74−37.39	2.29−30.54	2.87−30.53	1.89−30.50
hkl range				
h	$-13 \rightarrow 13$	$-18 \rightarrow 17$	$-13 \rightarrow 13$	$-8 \rightarrow 8$
k	$-13 \rightarrow 13$	$-17 \rightarrow 17$	$-7 \rightarrow 7$	$-8 \rightarrow 7$
l	$-7 \rightarrow 7$	$-17 \rightarrow 17$	$-9 \rightarrow 9$	$-29 \rightarrow 29$
measured reflections	2897	14721	2202	7466
independent reflections	730	1524	1129	1362
observed reflections [$I > 2\sigma(I)$]	639	1199	959	1292
R_i	0.0529	0.0995	0.0824	0.0550
transmission coefficients T_{min}, T_{max}	0.1634; 0.3777	0.0904; 0.1226	0.0355; 0.2051	0.0272; 0.4526
no. of parameters	24	55	48	50
extinction coefficients (SHELXL97)	0.001 50(14)	0.000 57(6)	0.010 3(6)	0.000 30(15)
diff elec dens max, min (e$^-$ Å^{-3}) (dist (Å), atom)	1.89 (0.53, Hg/Ag) −1.98 (1.56, Hg/Ag)	3.01 (0.69, Ag/Hg3) −2.03 (0.59, Ag/Hg1)	4.40 (1.74, Hg2) −2.64 (0.92, Hg1)	7.96 (1.40, Ag/Hg1) −4.58 (0.25, Ag/Hg3)
$R[F^2 > 2\sigma(F^2)]$	0.0365	0.0508	0.0358	0.0480
$wR2(F^2$ all)	0.0846	0.1271	0.0888	0.1368
Flack parameter[27]	0.01(6)	0.10(3)	0.57(4)	0.47(15)
goof	1.193	1.062	1.019	1.132
ICSD no.	414428	414427	414429	414426

Similar observations with multiphase formation and different oxidation states for mercury were made for the present systems Ag/Hg/X/O with X = As and V. Besides the silver(I) compound Ag_3AsO_4, the mercury(II) compounds $AgHgVO_4$ and $AgHgAsO_4$, the mercury(I) compound $AgHg_2AsO_4$, the mixed-valent mercury phases Hg_2VO_4 and $Hg_2(OH)(NO_3)\cdot HgO$, and the cluster compounds $(Ag_3Hg)VO_4$ (I), $(Ag_2Hg_2)_3(VO_4)_4$ (II), and $(Ag_2Hg_2)_2HgO_2(AsO_4)_2$ (IV) formed under the given hydrothermal conditions. However, it was not possible to reproduce the synthesis of compound IV. A few tiny crystals of this phase were obtained in only one batch; one crystal was then used for the structure determination. Apparently, all manually isolated crystals of IV were too small for a subsequent microprobe analysis. During attempts to prepare the crystals for this kind of experiment, they broke and, thus, could not be used for a reasonable measurement. Nevertheless, as a result of employed educts, preparation conditions, and crystal chemical considerations, the structure and composition of IV are regarded as essentially correct.

Inorganic oxo compounds containing silver and mercury in the crystal structure are relatively rare. Until recently, only the isotypic arsenate $AgHg_2AsO_4$[34] and phosphate $AgHg_2PO_4$,[23] the arsenate $AgHgAsO_4$,[23] the oxide nitrate $AgHg_2NO_5$,[35] the selenite(IV) $Ag_2Hg(SeO_3)_2$,[23] the double oxide Ag_2HgO_2,[36] and the mercurate $BaAg_2Hg_2O_4$,[37] as well as the clathrates $HgAg_6O_8ClO_4$, $HgAg_6O_8NO_3$, and $Hg_2Ag_{18}O_{33}H_{22}(ClO_4)_4$[38] have been structurally characterized. Except for the $AgHg_2XO_4$ (X = As, P) phases which show considerable metal−metal interactions between the Hg_2^{2+} dumbbells and the silver atoms, all other compounds contain mercury in oxidation state +II and exhibit no notable metal−metal interactions.[39] The recent discovery of the synthetic nitrates $(AgHg_2)Hg(NO_3)_5$ and $(AgHg_2)(NO_3)_3$[20] as well as of the mineral tillmannsite[21] augment our knowledge about these silver mercury oxo compounds. In all these structures metal cluster cations are present. For both silver mercury nitrates distorted $(AgHg_2)^{3+}$ triangles are found with bond lengths of d(Hg1−Hg2) = 2.567 Å, d(Hg1−Ag) = 2.737 Å, and d(Hg2−Ag) = 2.761 Å for $(AgHg_2)(NO_3)_3$ and d(Hg1−Hg3) = 2.536 Å, d(Hg1−Ag) = 2.883 Å, and d(Hg3−Ag) = 2.814 Å for $(AgHg_2)Hg(NO_3)_5$. In tillmannsite an $(Ag_3Hg)^{3+}$ tetrahedron with metal−metal separations of 2.738 and 2.752 Å is observed. The distances within all these (Ag/Hg) clusters are considerably shorter than the sum of the metal radii (1.44 Å (Ag) + 1.50 Å (Hg)),[40] thus indicating a strong bonding metal−metal interaction.

The structure of I is made up of isolated tetrahedral $(Ag_3Hg)^{3+}$ cluster cations and VO_4^{3-} tetrahedra which form a

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Table 3. Atomic Coordinates and Equivalent Isotropic Displacement Parameters

atom	Wyckoff position	x	y	z	U_{eq}^{a}	sof
$(Ag_3Hg)VO_4$						
Hg	8*g*	0.06963(7)	0.33773(6)	0.45854(12)	0.02386(17)	$^1/_4$
Ag	8*g*	0.06963(7)	0.33773(6)	0.45854(12)	0.02386(17)	$^3/_4$
V	2*a*	0	0	0	0.0108(6)	1
O	8*g*	0.1633(7)	0.0855(7)	0.2103(13)	0.0175(11)	1
$(Ag_2Hg_2)_3(VO_4)_4$						
Hg1	16*e*	0.44699(9)	0.18945(8)	0.21277(8)	0.0298(3)	$^3/_4$
Ag1	16*e*	0.44699(9)	0.18945(8)	0.21277(8)	0.0298(3)	$^1/_4$
Hg2	16*e*	0.29531(12)	0.33963(10)	0.18636(10)	0.0269(3)	$^1/_4$
Ag2	16*e*	0.29531(12)	0.33963(10)	0.18636(10)	0.0269(3)	$^3/_4$
Hg3	16*e*	0.05900(10)	0.41049(8)	0.32604(10)	0.0291(3)	$^1/_2$
Ag3	16*e*	0.05900(10)	0.41049(8)	0.32604(10)	0.0291(3)	$^1/_2$
V	16*e*	0.3967(2)	0.1451(3)	0.4781(3)	0.0159(6)	1
O1	16*e*	0.3453(11)	0.2671(12)	0.4629(11)	0.023(3)	1
O2	16*e*	0.3168(11)	0.0682(11)	0.5539(12)	0.025(3)	1
O3	16*e*	0.5205(13)	0.1556(12)	0.5306(13)	0.028(3)	1
O4	16*e*	0.4142(12)	0.0916(12)	0.3517(12)	0.027(3)	1
$AgHgVO_4$						
Hg1	2*b*	0	0.0005(3)	$^1/_2$	0.01537(19)	1
Hg2	2*a*	0	−0.0001(3)	0	0.01354(19)	1
Ag	4*c*	0.13903(10)	0.4996(8)	0.75522(12)	0.0259(3)	1
V	4*c*	0.18596(18)	0.4966(17)	0.2484(2)	0.0118(4)	1
O1	4*c*	0.1410(11)	0.200(2)	0.2315(14)	0.025(2)	1
O2	4*c*	0.3675(9)	0.5548(17)	0.2620(11)	0.018(2)	1
O3	4*c*	0.3755(12)	0.121(2)	0.5519(14)	0.032(2)	1
O4	4*c*	0.6198(10)	0.153(2)	0.0510(14)	0.023(2)	1
$(Ag_2Hg_2)_2(HgO_2)(AsO_4)_2$						
Hg1	6*c*	0.0563(3)	0.4201(4)	0.34974(7)	0.0153(3)	$^1/_2$
Ag1	6*c*	0.0563(3)	0.4201(4)	0.34974(7)	0.0153(3)	$^1/_2$
Hg2	2*b*	$^2/_3$	$^1/_3$	0.20624(10)	0.0160(5)	$^1/_2$
Ag2	2*b*	$^2/_3$	$^1/_3$	0.20624(10)	0.0160(5)	$^1/_2$
Hg3	2*b*	$^1/_3$	$^2/_3$	0.45162(16)	0.0326(7)	$^1/_2$
Ag3	2*b*	$^1/_3$	$^2/_3$	0.45162(16)	0.0326(7)	$^1/_2$
Hg4	6*c*	0.4104(5)	0.3514(4)	0.10676(7)	0.0210(5)	$^1/_2$
Ag4	6*c*	0.4104(5)	0.3514(4)	0.10676(7)	0.0210(5)	$^1/_2$
Hg5	2*b*	$^2/_3$	$^1/_3$	0.48266(9)	0.0139(3)	1
As1	2*a*	0	0	0.23840(18)	0.0038(6)	1
As2	2*a*	0	0	0.4803(2)	0.0074(7)	1
O1	6*c*	0.151(6)	0.295(4)	0.5081(10)	0.026(4)	1
O2	2*b*	$^2/_3$	$^1/_3$	0.3899(14)	0.006(5)	1
O3	2*b*	$^2/_3$	$^1/_3$	0.586(3)	0.043(12)	1
O4	2*a*	0	0	0.3979(14)	0.011(5)	1
O5	6*c*	−0.136(4)	0.166(5)	0.2677(8)	0.015(3)	1
O6	2*a*	0	0	0.1567(16)	0.019(6)	1

[a] $U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i\cdot\mathbf{a}_j$ (Å^2).

three-dimensional network by sharing common O atoms linked to both V and (Ag, Hg) atoms (Figure 1). Each metal atom is coordinated by 3 metallic neighbors with an average distance of 2.734 Å and by three O atoms with an average distance of 2.398 Å. Compared to natural occurring tillmannsite these distances are slightly smaller. In the mineral mean values of $\bar{d}(\mathrm{M{-}M}) = 2.747$ Å and $\bar{d}(\mathrm{M{-}O}) = 2.417$ Å are observed. On the other hand, the V−O distances in the synthetic compound are elongated when compared with tillmannsite with its mixed V and As occupancy for the anionic XO_4 tetrahedron (ratio V:As = 1:1). Whereas in the mineral a (V, As)−O distance of 1.678(8) Å is observed, the mean V−O bond length in I is 1.728(6) Å, which is in accordance with the slightly greater ionic radius[41] of $V^{5+} = 0.355$ Å compared to that of $As^{5+} = 0.335$ Å.

The structures of II and IV (Figures 2 and 3) are closely related with each other and also show similarities with the tillmannsite structure of I. All three structure types are made up of tetrahedral metal cluster cations built of statistically distributed Ag and Hg atoms and complex tetrahedral oxo anions XO_4^{3-}. Both building units share common oxygen atoms and create a three-dimensional network. In structure IV an additional oxomercurate group HgO_2^{2-} is present which formally belongs to the anionic part of the structure. The linear oxomercurate group HgO_2^{2-} reflects the typical coordination geometry as observed for various other oxomercurates compiled in the literature.[42] The corresponding mercury atom (Hg5) is tightly bonded to two oxygen atoms at short distances with a mean of $\bar{d}(\mathrm{Hg5{-}O}) = 2.12$ Å; the six more distant oxygen atoms located at distances of about 3.07 Å show only weak interactions and do not contribute to the first coordination sphere.

In all three structure types I, II, and IV, each metal atom is coordinated by 3 metallic neighbors and by three additional oxygen atoms. In both II and IV structures, two crystallo-

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Table 4. Selected Distances (Å) and Angles (deg) for All Structures and Bond Valence Sums (BVS) (vu)[a] for III

$(Ag_3Hg)VO_4$					
Ag/Hg−O	2.373(6)		Ag/Hg−Ag/Hg−Ag/Hg	60.198(11)	
Ag/Hg−O	2.376(5)		Ag/Hg−Ag/Hg−Ag/Hg	59.60(2)	
Ag/Hg−O	2.444(6)				
Ag/Hg−Ag/Hg	2.7226(10)	2×			
Ag/Hg−Ag/Hg	2.7390(10)	4×			
V−O	1.728(6)	4×			
$(Ag_2Hg_2)_3(VO_4)_4$					
Ag/Hg1−O4	2.179(15)		Ag/Hg3−O1	2.231(14)	
Ag/Hg1−O4	2.388(15)		Ag/Hg3−O3	2.344(16)	
Ag/Hg1−O2	2.498(15)		Ag/Hg3−O2	2.501(14)	
Ag/Hg1−Ag/Hg1	2.6843(19)		Ag/Hg3−Ag/Hg3	2.705(2)	4×
Ag/Hg1−Ag/Hg2	2.7048(18)	2×	Ag/Hg3−Ag/Hg3	2.708(2)	2×
Ag/Hg1−Ag/Hg2	2.7160(17)	2×	V−O1	1.683(15)	
Ag/Hg2−O3	2.215(16)		V−O2	1.694(15)	
Ag/Hg2−O1	2.366(14)		V−O3	1.702(16)	
Ag/Hg2−O2	2.476(14)		V−O4	1.739(16)	
Ag/Hg2−Ag/Hg2	2.739(2)				
Ag/Hg1−Ag/Hg1−Ag/Hg2	60.17(4)		Ag/Hg3−Ag/Hg3−Ag/Hg3	60.23(6)	
Ag/Hg1−Ag/Hg2−Ag/Hg1	60.52(5)		Ag/Hg3−Ag/Hg3−Ag/Hg3	59.89(3)	
Ag/Hg2−Ag/Hg1−Ag/Hg2	60.77(6)				
Ag/Hg1−Ag/Hg2−Ag/Hg1	59.31(6)				
Ag/Hg1−Ag/Hg2−Ag/Hg2	59.79(4)				
Ag/Hg1−Ag/Hg2−Ag/Hg2	59.44(5)				
$AgHgVO_4$					
Hg1−O2	2.084(9)	2×	Ag−O3	2.282(10)	
Hg1−O3	2.494(13)	2×	Ag−O4	2.295(10)	
Hg1−O1	2.699(10)	2×	Ag−O1	2.452(11)	
Hg2−O4	2.285(11)	2×	Ag−O2	2.482(10)	
Hg2−O1	2.358(11)	2×	Ag−O3	2.968(12)	
Hg2−O2	2.388(8)	2×	Ag−O2	3.097(10)	
V−O1	1.713(17)		Ag−O4	3.133(10)	
V−O3	1.736(12)				
V−O4	1.738(12)				
V−O2	1.828(9)				
$(Ag_2Hg_2)_2(HgO_2)(AsO_4)_2$					
Ag/Hg1−O5	2.25(2)		Ag/Hg4−O3	2.214(12)	
Ag/Hg1−O2	2.304(10)		Ag/Hg4−O1	2.37(2)	
Ag/Hg1−O4	2.597(12)		Ag/Hg4−O6	2.554(15)	
Ag/Hg1−Ag/Hg3	2.710(3)	3×	Ag/Hg4−Ag/Hg4	2.774(4)	3×
Ag/Hg1−Ag/Hg1	2.746(3)	3×	Hg5−O2	2.00(3)	
Ag/Hg2−O5	2.322(19)	3×	Hg5−O3	2.24(6)	
Ag/Hg2−Ag/Hg4	2.678(3)	3×	As1−O5	1.700(17)	3×
Ag/Hg3−O1	2.29(2)	3×	As1−O6	1.76(4)	
			As2−O1	1.65(2)	3×
Ag/Hg1−Ag/Hg1−Ag/Hg1	60.0		As2−O4	1.78(3)	
Ag/Hg1−Ag/Hg3−Ag/Hg1	60.88(9)				
Ag/Hg3−Ag/Hg1−Ag/Hg1	59.56(5)		Ag/Hg4−Ag/Hg2−Ag/Hg4	62.38(9)	
			Ag/Hg2−Ag/Hg4−Ag/Hg4	58.81(4)	

[a] BVS: Hg1 2.25, Hg2 2.22, Ag (CN = 4) 0.97, V 4.61, O1 1.96, O2 2.18, O3 1.80, O4 1.92.

graphically distinct metal clusters are present. The individual M−M and M−O distances are very similar and range from 2.677 to 2.775 Å for the metal clusters and from 2.18 to 2.60 Å for the M−O bond lengths. The average metal−metal distances of the individual clusters are 2.711 and 2.706 Å for structure II and 2.723 and 2.710 Å for structure IV, respectively. The overall average metal−metal distance of the four metal clusters is 2.725(27) Å, which is considerably longer than average Hg−Hg distances in Hg_2^{2+} dumbbells or Hg_3^{4+} triangles. Figure 4 shows a bar chart of various observed metal−metal distances in mercury oxo compounds with Hg_2^{2+} dumbbells and Hg_3^{4+} triangles as well as the Ag/Hg tetrahedra presented in this article.

The overall average M−O distance in II and IV is 2.350 Å. In reference to these distances, both values for the average metal−metal and M−O separations are virtually identical with the respective distances in synthetic tillmannsite. In contrast to the latter where the metal cluster has a composition of $(Ag_3Hg)^{3+}$, the metal cluster cations in II and IV have an Ag:Hg ratio of 1:1. Simple electron counting under consideration of charge balances with the counteranions VO_4^{3-} for I and II and AsO_4^{3-} and HgO_2^{2-} for IV leads to a formal charge of 3+ for the cluster with an overall composition of (Ag_3Hg) and of 4+ for the cluster with an overall composition of (Ag_2Hg_2). The latter kind of cluster has not yet been observed in any other inorganic or metalorganic compound, and in a very simplified closed-shell model, its electronic structure might been described as two-electron−four-center bonding, just as is the case for the aforementioned $(Ag_3Hg)^{3+}$ cluster. The realization of two-

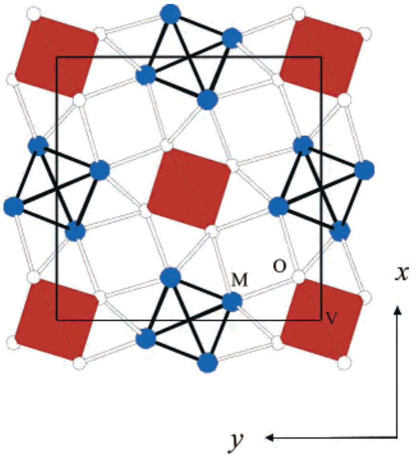

Figure 1. $(Ag_3Hg)VO_4$: projection of the structure along [001]. Metal atoms are given as blue spheres, and VO_4 tetrahedra are given in the polyhedral representation.

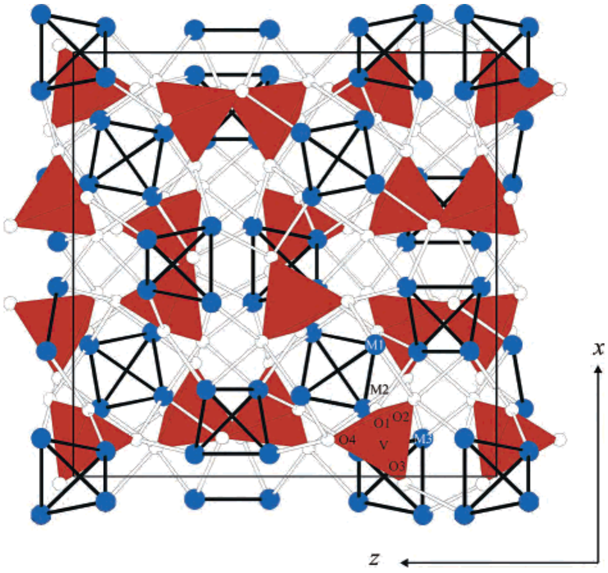

Figure 2. $(Ag_2Hg_2)_3(VO_4)_4$: projection of the structure along [010]. Metal atoms are given as blue spheres, and VO_4 tetrahedra are given in the polyhedral representation.

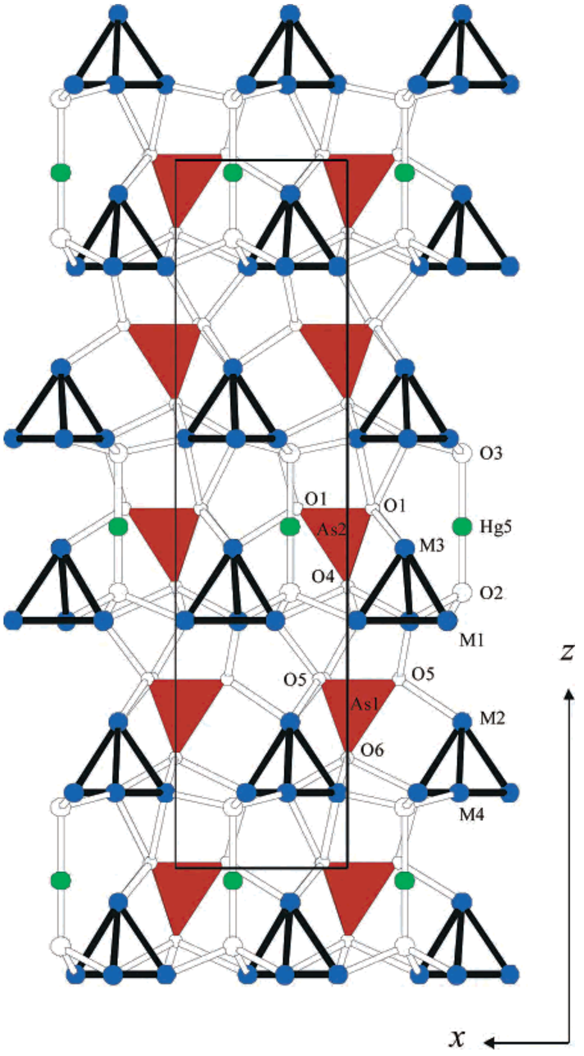

Figure 3. $(Ag_2Hg_2)_2(HgO_2)(AsO_4)_2$: projection of the structure along [010]. Metal atoms of the clusters are given as blue spheres, and Hg atoms of the mercurate groups are given as green spheres. AsO_4 tetrahedra are given in the polyhedral representation.

electron−four-center systems for the comparable metal clusters Ag_4^{2+} and Au_4^{2+} with T_d symmetry has been calculated by Pyykkö and Runeberg.[43]

For an alternative description of compounds with covalently bonded mercury in lower oxidation states it is a convenient method to consider the resultant groups as one large spherical atom which is located on the center of gravity.[4,44] Application of this approach leads to the following (partly) idealized centers of gravity for the metal clusters: $(0\ {}^{1}/_{2}\ {}^{1}/_{4})$ for I, (0 0 0) and $({}^{3}/_{8}\ {}^{1}/_{4}\ {}^{1}/_{8})$ for II, and $({}^{2}/_{3}\ {}^{1}/_{3}\ {}^{1}/_{8})$ and $({}^{1}/_{3}\ {}^{2}/_{3}\ {}^{3}/_{8})$ for IV. If the large XO_4 oxo anions are treated the same way, i.e., as one large spherical atom with the X atoms as the centers of gravity, then the structures of I and IV can be derived from simple sphere packings of the respective atoms. The structure of I with its 1:1 ratio of the tetrahedral units is then regarded as a distorted cubic closed packed structure, whereas the structure of IV is derived from a hexagonal close packing of the units with a stacking sequence of ABACACAB along [001] where the A layer is composed of closed-packed VO_4 tetrahedra and the B and C layers are composed of closed-packed metal complex cations. The atoms of the oxomercurate group (Hg5, O2, and O3) are located in the interstices of this arrangement. Although structure II crystallizes as pseudocubic with *c* close to *a* and *b*, a simple description in terms of a sphere packing as for structures I and IV was not possible.

In contrast to all other structures described in this article, the structure of III does not contain any metal clusters (Figure 5). Even though it has the same formula type as the arsenate analogue $AgHgAsO_4$,[23] it crystallizes in a unique structure type. Two crystallographically independent Hg atoms and one Ag atom are located on distinct sites with site symmetry 2 for both Hg atoms and the Ag atom located on a general position. The mercury atoms adopt a distorted octahedral coordination, whereas the silver atom is coordinated to four oxygen atoms resulting in a distorted tetrahedral environment.

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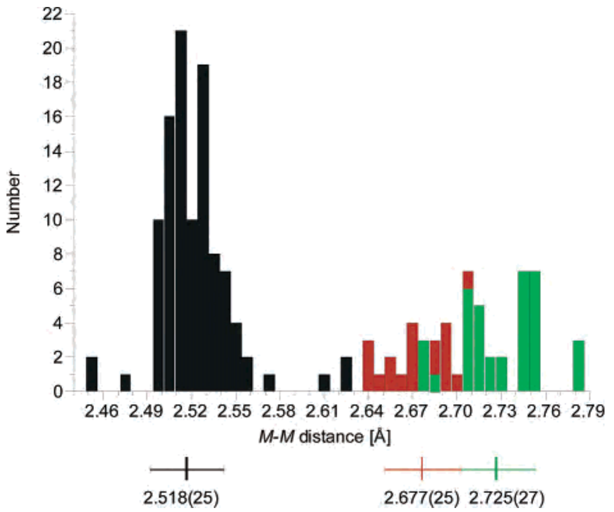

Figure 4. Bar chart of the frequency of metal−metal separations in inorganic mercury oxo compounds with mercury in oxidation state <+II, which also includes the present Ag−Hg clusters. The width of one column is 0.075 Å. The arithmetic means with standard deviations are 2.518(25) Å for 105 different Hg_2^{2+} dumbbells (black), 2.677(25) Å for 27 distances in Hg_3^{4+} triangles (red), and 2.725(27) Å for 36 distances in Ag/Hg tetrahedra (green). The graphic includes all entries of the inorganic structure database (ICSD) up to version 2004/1 with *R* values <10% and in addition a small number of our own unpublished data. Due to clarity, M−M distances observed in inorganic compounds with $(AgHg_2)^{3+}$ triangles[20] are not included.

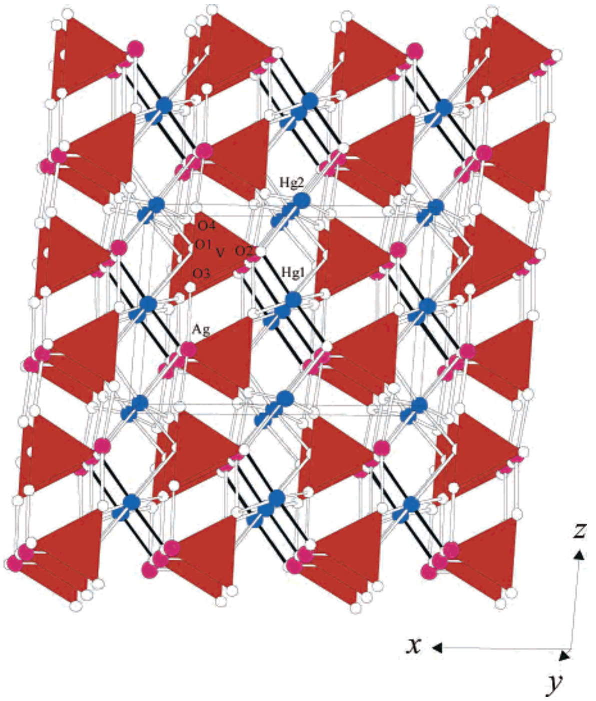

Figure 5. $AgHgVO_4$: projection of the structure approximately along [010]. Hg atoms are given as blue spheres and Ag atoms given as purple spheres. VO_4 tetrahedra are given in the polyhedral representation. Short Hg−O distances <2.10 Å are indicated with closed lines.

These polyhedra share corners and vertices to form a two-dimensional layer parallel to (100). The layers are linked perpendicularly by interstitial V atoms and an Ag−O1 bond of 2.452(11) Å. Although the mean Hg−O distances of 2.426 Å for Hg1 and 2.344 Å for Hg2 are in the same range, the coordination geometries around both Hg atoms are quite different. Hg1 is linearly coordinated to two tightly bonded O atoms <2.10 Å and to four remote O atoms at distances >2.5 Å. The resulting [2 + 4] octahedron reflects the typical behavior for Hg^{2+} with its d^{10} electronic configuration when surrounding oxygen or halogen atoms are present.[1] The most frequently observed coordination figures around Hg in these structural families are distorted [2 + *x*] polyhedra (*x* can range from 2 to 8) with two short Hg−Y distances and a linear (or roughly linear) (Y−Hg−Y) angle where Y's are oxygen or halogen atoms. The bond lengths distribution within the likewise distorted $[Hg2O_6]$ polyhedron is less scattered. Here the Hg2−O distances range from 2.29 to 2.39 Å. In III a distorted tetrahedral environment around the Ag atom with a mean of $\bar{d}(Ag-O) = 2.378$ Å is realized which is in good agreement with other oxo compounds where silver(I) is tetrahedrally surrounded.[23,45] Three remote O atoms augment this coordination figure at distances >2.95 Å but show negligible interactions. The V−O distances of the tetrahedral VO_4^{3-} anion range from 1.713 to 1.828 Å and have a mean of 1.754 Å. The considerably long distance $d(V-O2) = 1.828$ Å is caused by the other coordination partners of O2 since this atom is also bonded to Hg1 at a very short distance. A contraction of the V−O2 bond would cause an increase of its bond strength resulting in a higher bond valence sum. However, O2 already shows a BVS of 2.18 and thus avoids a shorter V−O bond.

Summary

The geometries of the tetrahedral metal cluster cations $(Ag_3Hg)^{3+}$ and $(Ag_2Hg_2)^{4+}$ deviate only slightly from that of an ideal tetrahedron with T_d symmetry. Their electronic structure might be described as two-electron−four-center bonding. The interatomic metal−metal distances of these clusters are very similar and show an overall mean of 2.723 Å with individual values ranging from 2.677(3) to 2.775(4) Å. The average M−M distance of the tetrahedral silver−mercury cluster cations is significantly longer than those of a single Hg−Hg dumbbell (2.518 Å) or a Hg_3^{4+} triangle (2.677 Å), but it is comparable to the Ag−Ag separations of 2.73−2.76 Å which are observed in the trigonal Ag_3[46] or quadratic Ag_4[47] cluster units stabilized by bridging chelate ligands.

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Supporting Information Available: A crystallographic information file (CIF) for the structure reported herein. This material is available free of charge via the Internet at http://pubs.acs.org. Furthermore, the data have been deposited with the Fachinformationzentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (crysdata@FIZ-Karlsruhe.de), and are available on quoting this article and the deposition numbers listed at the end of Table 2.

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