

The Mixed-valent Mercury(I/II) Compounds $\text{Hg}_3(\text{HAsO}_4)_2$ and $\text{Hg}_6\text{As}_2\text{O}_{10}$

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The mixed-valent mercury compounds $\text{Hg}_3(\text{HAsO}_4)_2$ ($= \text{Hg}^{\text{II}}\text{Hg}^{\text{I}}_2(\text{HAsO}_4)_2$) and $\text{Hg}_6\text{As}_2\text{O}_{10}$ ($= \text{Hg}^{\text{I}}_2\text{Hg}^{\text{II}}_2(\text{AsO}_4)_2 \cdot 2\text{Hg}^{\text{II}}\text{O}$) were obtained from the reaction of $(\text{Hg}_3)_3(\text{AsO}_4)_4$ with arsenic acid (60 wt-%) carried out at 65 °C and as a by-product under hydrothermal conditions, respectively. The crystal structure of $\text{Hg}_3(\text{HAsO}_4)_2$ ($Z = 2$, $C2/c$, $a = 13.010(3)$, $b = 8.149(2)$, $c = 9.496(3)$ Å, $\beta = 126.864(4)^\circ$, 1427 structure factors, 64 parameters, $R[F^2 > 2\sigma(F^2)] = 0.0272$; wR (all F^2) = 0.0490) contains a centrosymmetric O–Hg–Hg–O unit ($d(\text{Hg}–\text{Hg}) = 2.5226(8)$ Å, $d(\text{Hg}–\text{O}) = 2.141(5)$ Å), $\angle(\text{Hg}–\text{Hg}–\text{O}) = 167.68(13)^\circ$ and an Hg^{2+} cation that is located on a twofold rotation axis showing an almost linear coordination to two O atoms ($d(\text{Hg}–\text{O}) = 2.059(5)$ Å; $\angle(\text{O}–\text{Hg}–\text{O}) = 177.3(2)^\circ$). The O–Hg–Hg–O and O–Hg–O units are linked by AsO_3OH tetrahedra resulting in the formation of chains extending parallel to [102]. Strong hydrogen bonding ($d(\text{O}\cdots\text{O}) = 2.523(6)$ Å) between AsO_3OH tetrahedra of neighbouring chains is observed. The crystal structure of $\text{Hg}_6\text{As}_2\text{O}_{10}$ ($Z = 2$, $P2_1/n$, $a = 6.94750(10)$, $b = 8.9837(2)$, $c = 8.9966(2)$ Å, $\beta = 98.1630(10)^\circ$, 4842 structure factors, 83 parameters, $R[F^2 > 2\sigma(F^2)] = 0.0269$, wR (all F^2) = 0.0577) contains an O–Hg–Hg–O unit ($d(\text{Hg}–\text{Hg}) = 2.5337(3)$ Å, $d(\text{Hg}–\text{O}) = 2.181(3)$ Å, $\angle(\text{Hg}–\text{Hg}–\text{O}) = 168.05(10)^\circ$) and two O–Hg–O units ($d(\text{Hg}–\text{O}) = 2.048(3)$, $2.072(3)$ Å, $\angle(\text{O}–\text{Hg}–\text{O}) = 168.78(15)^\circ$; $2.149(4)$, $2.150(3)$ Å, $166.65(12)^\circ$) that are linked into a three-dimensional framework structure with As atoms of the AsO_4 tetrahedra in the voids. An alternative structural description of $\text{Hg}_6\text{As}_2\text{O}_{10}$ is presented under consideration of oxygen-centred $[\text{OHg}_4]$ tetrahedra.

Key words: Mercury, Mixed Valence, Arsenate, Crystal Structure

Introduction

Stable cationic species of mercury in (aqueous) solutions are Hg^{2+} (the mercuric ion, oxidation state +II), the dumbbell-shaped Hg_2^{2+} (the mercurous ion, oxidation state +I) and the triangular Hg_3^{4+} cluster cation (formal oxidation state of +4/3 for each of the mercury atoms)¹. These species also exist in the solid state as evidenced by numerous structure determinations of synthetic and naturally occurring compounds, making the crystal chemistry of mercury peculiar [1].

¹Besides Hg^{2+} , Hg_2^{2+} and Hg_3^{4+} , the linear clusters Hg_3^{2+} and Hg_4^{2+} , infinite chains of mercury atoms in ‘alchemists’ gold ($\text{Hg}_{2.86}(\text{AsF}_6)$) and mercury layers in Hg_3MF_6 ($M = \text{Nb}$, Ta) are additional cationic species of mercury but are known to exist only in the solid state.

Whereas a plethora of inorganic mercuric *or* mercurous oxo-compounds exist, compounds with the presence of discrete Hg^{2+} and Hg_2^{2+} cations are less prevalent. Up to now, such mixed-valent mercury compounds are restricted to $\text{Hg}^{\text{I}}_2\text{Hg}^{\text{II}}_2\text{-Re}_2\text{O}_{10}$ [2], $\text{Hg}^{\text{I}}_4\text{Hg}^{\text{II}}\text{Re}_2\text{O}_{10}$ [3, 4], $\text{Hg}^{\text{I}}_2\text{Hg}^{\text{II}}_2\text{-O}_2\text{I}_2$ [5], $\text{Hg}^{\text{I}}_2(\text{NO}_3)_2 \cdot 2\text{Hg}^{\text{II}}\text{O}$ [6, 7], $\text{Hg}^{\text{I}}_2(\text{NO}_3)_2 \cdot \text{Hg}^{\text{II}}(\text{OH})(\text{NO}_3) \cdot \text{Hg}^{\text{II}}(\text{NO}_3)_2 \cdot 4(\text{Hg}^{\text{II}}\text{O})$ [8], $\text{Hg}^{\text{I}}_2(\text{OH})(\text{NO}_3) \cdot \text{Hg}^{\text{II}}\text{O}$ [9], $\text{Hg}^{\text{I}}_5\text{Hg}^{\text{II}}_3\text{O}_4\text{Br}_3$ [10], $\text{Hg}^{\text{I}}_2\text{Hg}^{\text{II}}_2\text{-V}_2\text{O}_8$ [11], $\text{Hg}^{\text{I}}_2\text{Hg}^{\text{II}}(\text{OH})_2(\text{ClO}_4)_2$ [12], the minerals wattersite $\text{Hg}^{\text{I}}_4\text{Hg}^{\text{II}}\text{CrO}_6$ [13], hanawaltite $\text{Hg}^{\text{I}}_6\text{Hg}^{\text{II}}\text{-Cl}_2\text{O}_3$ [14, 15], deansmithite $\text{Hg}^{\text{I}}_2\text{Hg}^{\text{II}}_3\text{CrO}_5\text{S}_2$ [16], and tedhadleyite $\text{Hg}^{\text{I}}_{10}\text{Hg}^{\text{II}}\text{O}_4\text{I}_2(\text{Cl},\text{Br})_2$ [17].

Inorganic compounds with discrete Hg_3^{4+} cations in an oxidic surrounding once more are much less frequent, and only about ten representatives have been

structurally characterised so far, including the very rare minerals terlinguaite (Hg₃)HgO₂Cl₂ [18–20] and kuznetsovite (Hg₃)(AsO₄)Cl [21, 22], the synthetic and isotypic Br and P analogues of kuznetsovite, (Hg₃)(AsO₄)Br and (Hg₃)(PO₄)Cl [22], the mercurate phosphate (Hg₃)₂(HgO₂)(PO₄)₂ [23], the isotypic phases (Hg₃)₃(PO₄)₄ [23] and (Hg₃)₃(AsO₄)₄ [24], and the selenite/selenates Hg₇Se₃O₁₃H₂ and Hg₈Se₄O₁₇H₂ [25].

In the course of experiments intended for single crystal growth of the desclozite-type phase CoHg(AsO₄)(OH) (isotypic with ZnHg(AsO₄)(OH) [26]), single crystals of a new mixed-valent mercury(II) arsenate with composition Hg₆As₂O₁₀ were obtained by serendipity. In the system Hg–As^V–O–(H) the following phases have been structurally characterised up to now: Mercuric orthoarsenate Hg₃(AsO₄)₂ with a graphonite-type structure [27], mercuric metaarsenate HgAs₂O₆ [28, 29] crystallising in the PbSb₂O₆ structure type, two polymorphs of mercurous orthoarsenate (Hg₂)₃(AsO₄)₂, viz. the mineral chursinite [30, 31] (α -form) and the synthetic β -form [31], mercurous dihydrogenarsenate Hg₂(H₂AsO₄)₂ [29], mercurous diarsenate (Hg₂)₂As₂O₇ [32], mercurous metaarsenate Hg₂As₂O₆ [29], and the orthoarsenate (Hg₃)₃(AsO₄)₄ with discrete Hg₃⁴⁺ triangles [24]. In addition, the crystal structure of the mixed-valent hydrogenarsenate Hg₃(HAsO₄)₂ has been presented at the 15th congress of the IUCr, Bordeaux, France, in 1990. The only details regarding this phase available in the literature are space group and lattice parameters, accompanied by a very general structure description in the book of abstracts [33]. Because the preparation conditions, atomic coordinates and a more detailed description of the crystal structure have not been published afterwards, renewed crystal growth and structure analysis of Hg₃(HAsO₄)₂ seemed appropriate.

In this article, the preparation conditions and the crystal structures of the two mercury(I/II) arsenates Hg₃(HAsO₄)₂ and Hg₆As₂O₁₀ are reported and compared.

Experimental Section

Preparation conditions to obtain Hg₆As₂O₁₀

200 mg of the amorphous product that was obtained by reaction of an aqueous suspension of CoCO₃ with half-

concentrated H₃AsO₄ (ca. 40 wt-%) were mixed with 180 mg HgO. The mixture was charged in a Teflon container that was filled up to two thirds of its volume (12 mL) with water, sealed in a steel autoclave and heated at 220 °C for one week. After filtering off the mother liquor, the obtained multi-phase product was washed with water and acetone. Phase analysis was performed on the basis of single-crystal X-ray diffraction of selected crystals and powder X-ray diffraction of the ground bulk material. Besides light-yellow single crystals of Hg₃(AsO₄)₂ [27], honey-coloured crystals of Hg₆As₂O₁₀, yellow to brownish crystals of α -(Hg₂)₃(AsO₄)₂ [31], red crystals of a yet unknown phase, pink tabular crystals of Co₂(AsO₄)(OH) [34], pink needles of Co_{0.75}(OH)₃(H_{0.166}AsO₄)₃(HAsO₄) [35], and brownish crystals of CoHg(AsO₄)(OH) [36] were identified. The bulk material consisted mainly of Hg₃(AsO₄)₂ and CoHg(AsO₄)(OH).

Preparation of Hg₃(HAsO₄)₂

Diluted aqueous solutions of mercurous and mercuric nitrate were slightly acidified (HNO₃, 10 wt-%) to avoid precipitation of basic nitrates. To the combined solutions (molar ratio 1:1) arsenic acid (ca. 15 wt-%) was added dropwise, resulting in immediate precipitation of light-yellow (Hg₃)₃(AsO₄)₄ [24]. The dried product was then reacted in a closed vessel with an excess of arsenic acid (ca. 60 wt-%) at 65 °C for three days. The unreacted solid was filtered off. From the remaining mother liquor few colourless crystals of Hg₃(HAsO₄)₂ with a lath-like form and up to 1 mm in length formed at room temperature in the course of one week.

Single-crystal diffraction and structure analysis

Crystals were separated manually under a microscope. Their quality was pre-checked optically under a polarising microscope prior to the diffraction experiments. The crystals were then fixed on thin silica glass fibres and embedded in perfluorinated polyether.

Intensity data of Hg₃(HAsO₄)₂ were recorded at –143 °C on a Siemens SMART CCD diffractometer using ω scans with 0.3° rotation width; intensity data of Hg₆As₂O₁₀ were recorded at room temperature on a Bruker-AXS APEXII CCD diffractometer using ω and ϕ scans with 1° rotation width. For both data collections MoK α radiation was used. The crystal structures were solved by using Direct Methods and were refined using the SHELXTL program package [37]. Both data sets were numerically corrected for absorption effects with the program HABITUS [38]. The difference Fourier maps of the final models showed no significant residual electron density attributable to additional atoms. The highest remaining electron densities (see Table 1) are situated close to the heavy Hg atoms.

	Hg ₃ (HAsO ₄) ₂	Hg ₆ As ₂ O ₁₀
Diffractionmeter	Siemens SMART CCD	Bruker APEXII CCD
Radiation; wavelength λ , Å		MoK α ; 0.71073
Temperature, °C	−143	25
Crystal dimensions, mm ³	0.063-0.020-0.018	0.190-0.080-0.060
Crystal description	colourless lath	amber fragment
Space group	<i>C2/c</i> (no. 15)	<i>P2₁/n</i> (no. 14)
Formula units <i>Z</i>	2	2
Lattice parameters		
<i>a</i> , Å	13.010(3)	6.94750(10)
<i>b</i> , Å	8.149(2)	8.9837(2)
<i>c</i> , Å	9.496(3)	8.9966(2)
β , deg	126.864(4)	98.1630(10)
Volume <i>V</i> , Å ³	805.4(4)	555.827(19)
Formula weight	881.63	1513.38
μ , mm ^{−1}	65.2	88.5
X-Ray density, g·cm ^{−3}	7.27	9.04
Range θ_{\min} – θ_{\max}	3.17–32.69	3.22–46.22
Range <i>h</i> ; <i>k</i> ; <i>l</i>	−19 → 19; −12 → 11; −14 → 13	−14 → 13; −18 → 18; −18 → 18
Structure solution and refinement		SHELXTL
Measured reflections	6561	81174
Independent reflections	1427	4842
<i>R</i> _{int}	0.0547	0.0869
Observed reflections [<i>I</i> > 2 σ (<i>I</i>)]	1298	3890
Absorption correction		numerical; HABITUS
Coeff. of transmission <i>T</i> _{min} / <i>T</i> _{max}	0.186 / 0.519	0.013 / 0.126
Number of ref. parameters	64	83
Extinction coefficient (SHELXL-97)	0.00029(4)	0.00320(9)
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)] / <i>wR</i> (<i>F</i> ² all)	0.0272 / 0.0490	0.0269 / 0.0577
Goof	1.059	1.092
Difference electron density, e·Å ^{−3}	$\Delta\rho_{\max} = 2.25$ [0.80; Hg2]	$\Delta\rho_{\max} = 4.77$ [0.55; Hg2]
[distance to atom, Å]	$\Delta\rho_{\min} = -2.40$ [1.74; Hg1]	$\Delta\rho_{\min} = -2.44$ [0.53; Hg2]

Table 1. Details of data collections, structure solutions and refinements.

Atom	Wyckoff position	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} ^a
Hg₃(HAsO₄)₂					
Hg1	4 <i>e</i>	0	0.75375(4)	1/4	0.00821(9)
Hg2	8 <i>f</i>	0.06746(2)	0.34774(3)	0.41579(3)	0.00942(8)
As1	8 <i>f</i>	0.19957(6)	0.07649(7)	0.13689(8)	0.00587(13)
O1	8 <i>f</i>	0.1100(5)	0.0139(6)	0.2037(6)	0.0104(9)
O2	8 <i>f</i>	0.1313(5)	0.2522(5)	0.0200(6)	0.0093(9)
O3	8 <i>f</i>	0.2004(4)	0.0740(5)	0.5191(6)	0.0077(9)
O4	8 <i>f</i>	0.3511(5)	0.1213(6)	0.3120(6)	0.0101(9)
H1	8 <i>f</i>	0.111(10)	0.075(10)	0.284(10)	0.050
Hg₆As₂O₁₀					
Hg1	4 <i>e</i>	0.49400(3)	0.636934(18)	0.154187(17)	0.01384(3)
Hg2	4 <i>e</i>	0.74063(2)	0.504937(17)	0.515284(18)	0.01242(3)
Hg3	4 <i>e</i>	0.48846(3)	0.870118(17)	0.444602(19)	0.01522(4)
As1	4 <i>e</i>	0.48479(6)	0.74075(4)	0.78844(4)	0.00910(6)
O1	4 <i>e</i>	0.5214(5)	0.6374(3)	0.3838(3)	0.0109(5)
O2	4 <i>e</i>	0.3044(5)	0.7299(4)	0.6428(4)	0.0135(5)
O3	4 <i>e</i>	0.6962(5)	0.6789(4)	0.7415(4)	0.0180(6)
O4	4 <i>e</i>	0.4093(6)	0.6288(4)	0.9240(4)	0.0184(6)
O5	4 <i>e</i>	0.5003(5)	0.9187(4)	0.8543(4)	0.0173(6)

Table 2. Atomic coordinates and equivalent isotropic displacement parameters (Å²).^a $U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$.

Table 3. Anisotropic displacement parameters (Å²).

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Hg₃(HAsO₄)₂						
Hg1	0.00739(17)	0.00998(16)	0.00523(15)	0	0.00270(13)	0
Hg2	0.00920(13)	0.01156(13)	0.00411(11)	−0.00010(8)	0.00219(9)	0.00002(9)
As1	0.0054(3)	0.0070(3)	0.0036(3)	−0.0007(2)	0.0018(2)	−0.0004(2)
O1	0.010(2)	0.016(2)	0.006(2)	−0.0045(17)	0.0052(19)	−0.0024(18)
O2	0.013(2)	0.006(2)	0.005(2)	−0.0005(16)	0.0036(19)	−0.0003(17)
O3	0.009(2)	0.007(2)	0.005(2)	0.0007(16)	0.0026(18)	−0.0011(17)
O4	0.007(2)	0.017(2)	0.005(2)	0.0016(17)	0.0027(19)	−0.0019(18)
Hg₆As₂O₁₀						
Hg1	0.02011(8)	0.01376(6)	0.00756(5)	−0.00028(4)	0.00169(4)	−0.00103(5)
Hg2	0.01127(6)	0.01200(5)	0.01361(6)	0.00196(4)	0.00045(4)	0.00131(4)
Hg3	0.02374(8)	0.00862(5)	0.01350(6)	−0.00231(4)	0.00334(5)	−0.00101(5)
As1	0.01179(16)	0.00858(13)	0.00647(13)	−0.00150(11)	−0.00026(11)	0.00024(12)
O1	0.0160(13)	0.0102(10)	0.0059(9)	−0.0010(8)	−0.0004(9)	0.0018(9)
O2	0.0135(13)	0.0160(12)	0.0101(11)	−0.0042(9)	−0.0014(9)	0.0004(10)
O3	0.0120(14)	0.0222(15)	0.0193(15)	−0.0087(12)	0.0005(11)	0.0038(11)
O4	0.0290(19)	0.0166(13)	0.0088(11)	0.0025(10)	−0.0002(11)	−0.0033(13)
O5	0.0162(15)	0.0117(11)	0.0231(15)	−0.0097(11)	0.0000(12)	0.0012(10)

Hg₃(HAsO₄)₂				Hg₆As₂O₁₀			
Hg1–O2	2.059(5)	2×		Hg1–O1	2.048(3)		
–O4	2.576(5)	2×		–O4	2.072(3)		
–O1	2.737(5)	2×		–O2	2.481(3)		
Hg2–O4	2.141(5)			–O4	2.604(4)		
–Hg2	2.5226(8)			–O3	2.845(4)		
–O3	2.625(4)			Hg2–O5	2.149(4)		
–O3	2.770(5)			–O1	2.150(3)		
As1–O3	1.664(4)			–O1	2.499(3)		
–O4	1.688(5)			–O2	2.539(3)		
–O2	1.700(4)			–O5	2.562(4)		
–O1	1.705(5)			–O3	2.619(3)		
O2–Hg1–O2	177.3(2)			Hg3–O1	2.181(3)		
O4–Hg2–Hg2	167.68(13)			–Hg3	2.5337(3)		
O3–As1–O4	110.3(2)			–O3	2.569(4)		
O3–As1–O2	113.2(2)			–O2	2.655(4)		
O4–As1–O2	107.8(2)			–O4	2.956(4)		
O3–As1–O1	108.1(2)			As1–O3	1.679(4)		
O4–As1–O1	110.7(2)			–O2	1.682(3)		
O2–As1–O1	106.8(2)			–O5	1.703(3)		
				–O4	1.719(3)		
				O1–Hg1–O4	168.78(15)		
				O5–Hg2–O1	166.65(12)		
<i>D</i>	<i>H</i>	<i>A</i>	<i>D–H</i>	<i>H...A</i>	<i>D...A</i>	<i>D–H...A</i>	
O1	H1	O3	0.90	1.80(7)	2.523(6)	136(9)	
				Hg3–Hg3–O1	168.05(10)		
				O3–As1–O2	111.49(17)		
				O3–As1–O5	112.54(18)		
				O2–As1–O5	109.19(17)		
				O3–As1–O4	110.5(2)		
				O2–As1–O4	104.50(18)		
				O5–As1–O4	108.23(18)		
				Hg1–O1–Hg2	120.72(15)		
				Hg1–O1–Hg3	104.89(12)		
				Hg2–O1–Hg3	118.95(14)		
				Hg1–O1–Hg2	113.41(13)		
				Hg2–O1–Hg2	90.72(10)		
				Hg3–O1–Hg2	106.97(13)		
BVS: Hg1 1.84, Hg2 1.05, As 4.94, O1 1.36, O2 1.93, O3 1.64, O4 2.00.				BVS: Hg1 2.11, Hg2 2.07, Hg3 1.03, As1 4.86, O1 1.86, O2 1.86, O3 1.73, O4 2.04, O5 1.94.			

Table 4. Selected interatomic distances (in Å), angles (in deg) as well as bond valence sums (BVS; in valence units v. u.) for Hg₃(HAsO₄)₂ and Hg₆As₂O₁₀. Details of hydrogen bonding for Hg₃(HAsO₄)₂ are also given.

The H atom of the AsO₃(OH) tetrahedron in the Hg₃(HAsO₄)₂ structure was assigned by crystal-chemical considerations and in fact could be located from difference Fourier maps. Its position was refined with a distance restraint of $d(\text{O}-\text{H}) = 0.90 \text{ \AA}$ and a fixed U_{iso} parameter of 0.05 \AA^2 . In the previous structure determination of Hg₃(HAsO₄)₂, the crystal structure has been reported in space group $C2/c$, $Z = 4$, with lattice parameters $a = 13.068(6)$, $b = 8.194(2)$, $c = 10.570(5) \text{ \AA}$, $\beta = 133.99(1)^\circ$ [33]. The given cell is not reduced. By application of the matrix $(\bar{1}00, 0\bar{1}0, 101)$ the then reduced cell setting leads to the lattice parameters $a = 13.068(6) \text{ \AA}$, $b = 8.194(2) \text{ \AA}$, $c = 9.520(8) \text{ \AA}$, $\beta = 126.98(1)^\circ$, $V = 814.3(8)$. These values are reasonably close to those of the current measurement, neglecting apparent different measurement temperatures (note that the measuring temperature was not indicated in the book of abstracts [33]; however, it is assumed that the crystal was measured at room temperature).

Numerical details of the two data collections and structure refinements are listed in Table 1. Atomic coordinates and equivalent isotropic displacement parameters are listed in Table 2. Anisotropic displacement parameters are listed in Table 3, and selected bond lengths and angles together with details of the hydrogen bonding geometry and results of bond valence sum calculations are gathered in Table 4. Drawings of structural details were generated with the program ATOMS [39].

Further details of the crystal structure investigations may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-karlsruhe.de/request_for_deposited_data.html) on quoting the deposition numbers CSD-427417 for Hg₃(HAsO₄)₂ and CSD-427418 for Hg₆As₂O₁₀.

Results and Discussion

Formation

The preparation of single-phase (Hg₃)₃(AsO₄)₄ is based on the redox equilibrium $\text{Hg}_2^{2+}(\text{aq}) + \text{Hg}^{2+}(\text{aq}) \rightleftharpoons \text{Hg}_3^{4+}(\text{aq})$, starting from stoichiometric aqueous solutions of Hg₂(NO₃)₂ and Hg(NO₃)₂ and precipitation with diluted arsenic acid at room temperature. This equilibrium is shifted to the left when treating (Hg₃)₃(AsO₄)₄ with half-concentrated arsenic acid at 60 °C, leading to the crystallisation of the mixed-valent title phase Hg₃(HAsO₄)₂. Such redox equilibria are easily influenced if additional redox partners are available, in particular under hydrothermal conditions. This makes the course of the reaction very difficult

to predict because of the high number of adjustable and interacting parameters (*e.g.* temperature, pH, concentration, ratio of reactants, filling degree, *etc.*), as has been shown for cases where the three different mercury species Hg²⁺, Hg₂²⁺ and Hg₃⁴⁺ exist in one compound [25], or are present in multi-component solid reaction products [40]. A similar complex interplay of different redox equilibria occurred in the present case. Reacting HgO and an amorphous cobalt(II) arsenate under hydrothermal conditions led to the formation of Hg²⁺ and Hg₂²⁺ and isolation of the mixed-valent Hg₆As₂O₁₀, mercuric Hg₃(AsO₄)₂, mercurous α -(Hg₂)₃(AsO₄)₂, mercuric CoHg(AsO₄)(OH), mercury-free Co₂(AsO₄)(OH), and a yet unidentified product.

Crystal structures

The unique crystal chemistry of mercury in oxidation states +I and +II shows a strong preference for linear coordination [1]. This behaviour is also realised in the structures of Hg₃(HAsO₄)₂ and Hg₆As₂O₁₀ where linear O–Hg–O and O–Hg–Hg–O units with Hg–O bond lengths less than 2.2 Å are present. In crystal-chemically more detailed formulae, the two compounds can be expressed as Hg^I₂Hg^{II}(HAsO₄)₂ and Hg^I₂Hg^{II}₂(AsO₄)₂·2Hg^{II}O, respectively.

In the structure of Hg₃(HAsO₄)₂, the Hg²⁺ cation (Hg1) is located on a twofold rotation axis and is bound to two O atoms in a distance of 2.059(5) Å with an almost linear O–Hg–O angle of 177.3(2)°. The centrosymmetric O–Hg–Hg–O unit (Hg2) exhibits a Hg–Hg distance of 2.5226(8) Å and two Hg–O distances of 2.141(5) Å, with slightly bent Hg–Hg–O angles of 167.68(13)°. Hg₆As₂O₁₀ contains two O–Hg–O units and one O–Hg–Hg–O unit. One of the O–Hg–O units (Hg1) is characterised by Hg–O distances of 2.048(3) and 2.072(3) Å and an O–Hg–O angle of 168.78(15)°, whereas the other O–Hg–O unit (Hg2) exhibits considerably longer Hg–O distances of 2.149(4) and 2.150(3) Å, however, with a very similar O–Hg–O angle of 166.65(12)°. The Hg–Hg and Hg–O bond lengths and the Hg–Hg–O angles in the centrosymmetric O–Hg–Hg–O unit (Hg3) are 2.5337(3), 2.181(3) Å and 168.05(10)°. The Hg–Hg distances in both title structures are in good agreement with the mean value of 2.51(2) Å that was calculated for more than 70 different Hg₂²⁺ dumbbells in various mercurous oxo-compounds [40]. In comparison with

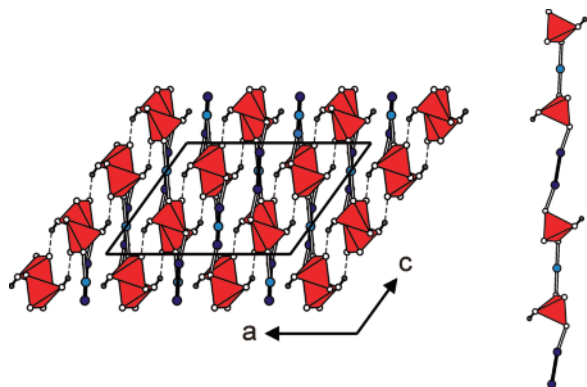


Fig. 1 (colour online). The crystal structure of $\text{Hg}_3(\text{HAsO}_4)_2$ in a projection along $[010]$. Mercurous Hg atoms are displayed as black spheres (online version dark blue), mercuric Hg atoms as dark-grey spheres (light-blue), H atoms as grey spheres; AsO_4 tetrahedra are given in red (light-grey). Only strong Hg–O bonds $< 2.2 \text{ \AA}$ are displayed; hydrogen bonding is indicated by dashed lines. A single $[\text{O}-\text{Hg}-\text{O}-\text{As}(\text{O},\text{OH})-\text{O}-\text{Hg}-\text{Hg}-\text{OAs}(\text{O},\text{OH})-\infty]$ chain is displayed on the right.

this mean bond length, the Hg–Hg bonds within an Hg_3^{4+} unit are considerably elongated with a mean of $2.67(3) \text{ \AA}$ that was calculated for seven independent Hg_3^{4+} triangles [40].

The other common structural feature in $\text{Hg}_3(\text{HAsO}_4)_2$ and $\text{Hg}_6\text{As}_2\text{O}_{10}$ is the appearance of tetrahedral AsO_4 units. Although angular distortions, As–O bond lengths distributions (Table 4) and the mean bond lengths of 1.689 \AA for $\text{Hg}_3(\text{HAsO}_4)_2$ and 1.694 \AA for $\text{Hg}_6\text{As}_2\text{O}_{10}$ do not point to significant differences in the two AsO_4 tetrahedra, they are in fact different, as manifested by the formation of HAsO_4^{2-} and AsO_4^{3-} units. The presence of HAsO_4^{2-} and AsO_4^{3-} anions is required for the electroneutrality in the two compounds and is clearly evidenced by bond valence calculations (Table 4) and the localisation of the corresponding H atom in $\text{Hg}_3(\text{HAsO}_4)_2$.

In the structure of $\text{Hg}_3(\text{HAsO}_4)_2$, the linear O–Hg–O and O–Hg–Hg–O units are arranged in rows and are linked by AsO_3OH tetrahedra *via* corner-sharing O2 and O4 atoms into chains extending parallel to $[102]$. The two remaining O atoms in the AsO_3OH tetrahedron are involved in strong hydrogen bonding ($\text{O1}\cdots\text{O3} = 2.523(6) \text{ \AA}$) between adjacent chains with O1 as the donor and O4 as the acceptor (Table 4), leading to the formation of layers parallel to (001) (Fig. 1). The cohesion of the structure into a three-dimensional

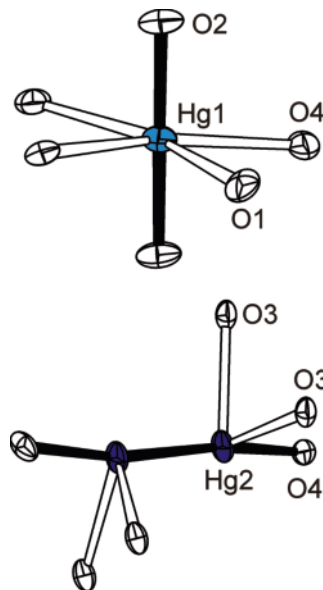


Fig. 2 (colour online). The oxygen surrounding of the Hg atoms in $\text{Hg}_3(\text{HAsO}_4)_2$, considering Hg–O distances $< 3 \text{ \AA}$. Strong Hg–O bonds are black, weaker Hg–O bonds are displayed with open lines. Displacement ellipsoids are given at the 97% probability level.

network is accomplished by more remote Hg–O interactions. If Hg–O distances less than 3 \AA are considered as relevant (the contribution of an O atom in a distance of 3 \AA to Hg accounts for about 0.05 valence units), then Hg1 has an overall coordination number of six, resulting in a considerably distorted $[2 + 4]$ octahedron with the tightly bonded O atoms in axial positions. Hg2, besides the other Hg atom in the dumbbell and the tightly bonded O atom, is additionally bonded to two other O atoms at longer distances (Table 4, Fig. 2).

The linkage of the O–Hg–O and O–Hg–Hg–O units within the structural set-up of $\text{Hg}_6\text{As}_2\text{O}_{10}$ leads to a three-dimensional framework structure (Fig. 3). The AsO_4 tetrahedra are located in the voids of this arrangement and share two O atoms (O4, O5) with the Hg–O framework. These O atoms show the longest As–O bonds. Again, Hg–O interactions to more remote O atoms (Table 4) further stabilise the structure. Hg1 is surrounded by three additional O atoms in the form of a $[2 + 3]$ trigonal bipyramid with the axially bound O atoms at shorter distances. The coordination polyhedron around Hg2 is a distorted $[2 + 4]$ octahedron,

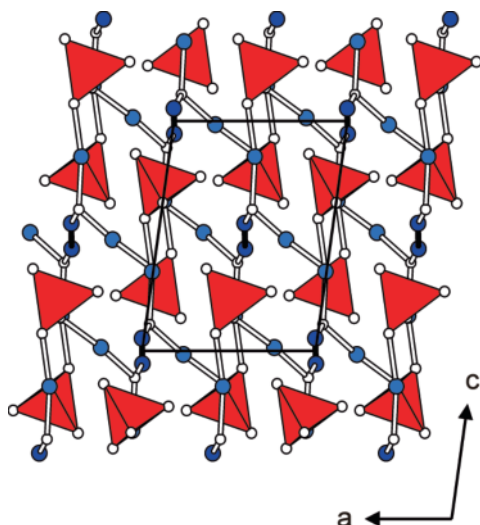


Fig. 3 (colour online). The crystal structure of Hg₆As₂O₁₀ in a projection along [010]. Colour code as in Fig. 1.

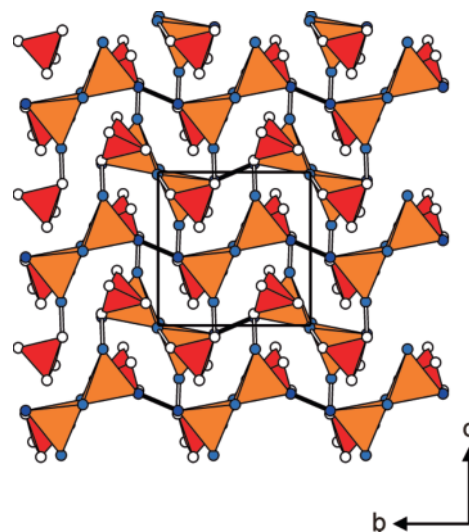


Fig. 5 (colour online). The crystal structure of Hg₆As₂O₁₀ in a projection along [100] considering [OHg₄] tetrahedra. Colour code as in Fig. 1 ([OHg₄] tetrahedra are dark-grey; online version orange).

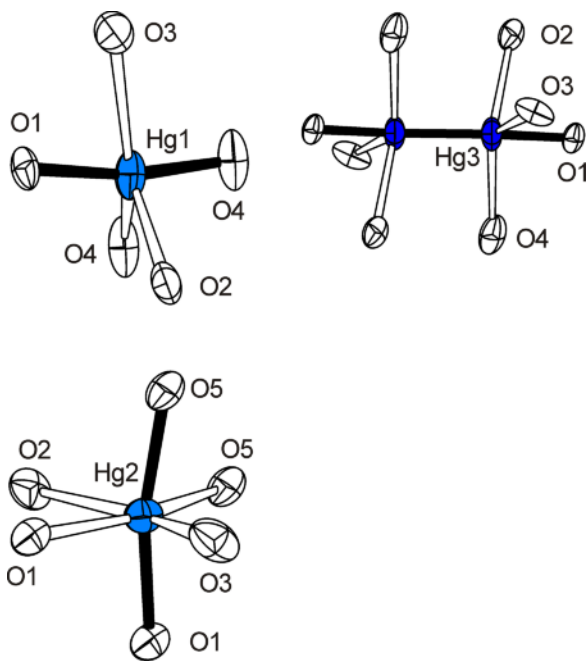


Fig. 4 (colour online). The oxygen atoms surrounding the Hg atoms in Hg₆As₂O₁₀, considering Hg–O distances < 3 Å. Strong Hg–O bonds are black, weaker Hg–O bonds are displayed with open lines. Displacement ellipsoids are given at the 97% probability level.

also with the axial O atoms at the shortest distances. Mercurous Hg3 shows an overall coordination number of five, resulting from the neighbouring Hg atom, the tightly bonded O atom and three additional O atoms (Fig. 4).

A different approach for the structural description of Hg₆As₂O₁₀ can be based on the consideration of oxygen-centred [OHg₄] tetrahedra. The concept of oxygen-centred [OM₄] tetrahedra has been resumed by Krivovichev and co-workers for a rational structure description and classification of mineral and synthetic lead(II) oxo-compounds [41]. In these structures, O atoms are present that do not participate in the formation of oxo-anions (*e.g.* carbonates, nitrates, phosphates, arsenates, *etc.*) but are solely surrounded by lead atoms, thus defining the ‘basic’ part (in an acid/base sense) of the structure. A review of such anion-centred [OM₄] tetrahedra in inorganic compounds has been published recently, including [OHg₄] tetrahedra [42]. Such an oxygen-centred tetrahedron is also present in the structure of one of the title compounds (Hg₆As₂O₁₀). This [O1Hg₄] tetrahedron is considerably distorted (Table 4), with O–Hg distances in the range 2.048(3)–2.499(3) Å and Hg–O–Hg angles between 90.72(10) and 120.72(15)°. Two [OHg₄] tetrahedra share an edge, each with a long

and a short distance to the central Hg atom. The [O₂Hg₆] double tetrahedra are linked by an additional Hg–Hg contact (representing the Hg₂ dumbbell) into chains propagating in [010], a structural motif unprecedented in the crystal chemistry of oxygen-centred mercury compounds [42]. These chains are then linked by AsO₄ tetrahedra and the longer Hg–O interactions into the three-dimensional framework structure (Fig. 5).

Bond valence sums (BVS) [43], using the bond valence parameters of Brese and O’Keeffe [44], were calculated for both structures without contribution of H atoms (Table 4). The results are reasonably close to

the expected values (in valence sums) of 1 for mercurous Hg, 2 for mercuric Hg, 5 for As and 2 for O (Table 4). The O atoms in the structure of Hg₃(HAsO₄)₂ involved in hydrogen bonding are readily identifiable. The donor atom O1 has the lowest BVS, followed by the acceptor atom O3, in agreement with the rather strong hydrogen bond between these two O atoms.

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