

Ag₂Hg₂(TeO₄)₃

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Red single crystals of disilver(I) dimercury(II) tris[tetraoxotellurate(VI)], Ag₂Hg₂(TeO₄)₃, were obtained under hydrothermal conditions at 523 K. The structure is built up of $\infty^1[(\text{TeO}_{2/1}\text{O}_{4/2})(\text{TeO}_{2/1}\text{O}_{2/2})_2\text{O}_{4/2}]$ chains, with an overall composition $[\text{TeO}_4]^{2-}$, that run parallel to the crystallographic *a* axis. Distorted AgO₆ and HgO₆ polyhedra (the latter with two short and nearly collinear Hg—O bonds) link the tellurate chains into a three-dimensional network. Except for one Te atom situated on an inversion center, all atoms occupy general positions.

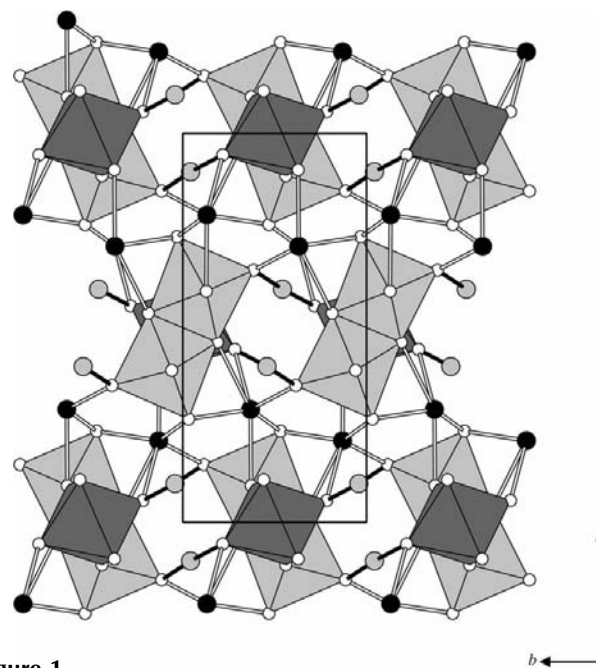
Comment

The recent interest in compounds that contain silver and mercury in the crystal structure arose from the discovery of the rare secondary alteration mineral tillmannsite with the empirical formula (Ag₃Hg)(As,V)O₄ (Sarp *et al.*, 2003). Its crystal structure contains the heretofore unknown tetrahedral silver–mercury cluster cation [Ag₃Hg]³⁺, with Ag and Hg atoms statistically distributed over one crystallographic site and a metal–metal distance of about 2.75 Å. This cluster is of particular interest because of its peculiar electronic situation, which might be described as two-electron–four-center (2e4c) bonding. Other compounds with tetrahedral cluster cations formed by statistically distributed Ag and Hg atoms include the vanadates (Ag₃Hg)(VO₄), which is isotypic with tillmannsite, and (Ag₂Hg₂)₃(VO₄)₄, as well as the mercurate arsenate (Ag₂Hg₂)₂(HgO₂)(AsO₄)₂ (Weil *et al.*, 2005). The last two compounds comprise cluster cations with composition [Ag₂Hg₂]⁴⁺ but with similar metal–metal distances of about 2.75 Å and 2e4c bonding. Other notable interactions between the Ag and Hg metal centers are realized in the isotypic compounds AgHg₂(PO₄) (Masse *et al.*, 1978) and AgHg₂(AsO₄) (Weil, 2003). In these structures, double tetrahedra with composition [Ag₂Hg₄]⁶⁺, and Ag··Hg, Ag··Ag and Hg··Hg separations of about 2.85, 2.90 and 2.64 Å, respectively, are observed. Besides all these compounds with tetrahedral metal cluster cations, structures comprising triangular [AgHg₂]³⁺ cluster cations are also known to exist. They are realized in the silver mercury nitrates (AgHg₂)(NO₃)₃ and (AgHg₂)Hg(NO₃)₅ (Nockemann *et al.*, 2004), as well as in the

trifluoromethanesulfonate [(AgHg₂)(μ-dppm)₃](O₃SCF₃)₃ (dppm is diphenylphosphinomethane; Knoepfler *et al.*, 1995). The structural unit of the [AgHg₂]³⁺ clusters observed in these compounds is roughly characterized by Hg··Hg distances between 2.54 and 2.66 Å, and two Ag··Hg distances between 2.74 and 2.90 Å. In a search for other representatives that contain silver–mercury cluster cations, systematic investigations of crystal growth under hydrothermal conditions were undertaken in the systems Ag–Hg–X–O(–H) with X = P, As, Se and V (Weil, 2003; Weil *et al.*, 2005). The crystal structure of the compound Ag₂Hg₂(TeO₄)₃, obtained during these experiments when X = Te, is reported in this article.

The structure of Ag₂Hg₂(TeO₄)₃ contains one Ag, one Hg, two Te and six O atoms in the asymmetric unit. Except for atom Te1, which shows $\bar{1}$ symmetry (Wyckoff notation 2c), all atoms occupy general positions. The main building blocks of the structure are TeO₆ octahedra and considerably distorted AgO₆ and HgO₆ polyhedra. The TeO₆ octahedra are condensed to build chains, with an overall composition of $[\text{TeO}_4]^{2-}$, that extend parallel to the *a* axis. Adjacent tellurate chains are linked by $\infty^1[\text{AgO}_{4/1}\text{O}_{2/2}]$ chains that extend parallel to the *b* axis. Hg atoms situated between the two types of chains complete the three-dimensional structure (Fig. 1).

Both Te atoms display a distorted octahedral coordination by O atoms. Two TeO₆ octahedra share a common edge to form Te₂O₁₀ dimers. One dimer is connected to two neighboring Te1O₆ octahedra by sharing corner atoms, as displayed in Fig. 2. The scatter within the Te—O distances, ranging from 1.840 (5) to 1.981 (4) Å (Table 1), mirrors the different types of O atoms present in the anionic entity. While

**Figure 1**

The crystal structure of Ag₂Hg₂(TeO₄)₃ projected down the *a* axis, with the unit cell outlined. For clarity, only short Hg—O bonds are shown. Ag atoms are shown as dark-gray, Hg atoms as light-gray and O atoms as white spheres; Te1O₆ octahedra are dark gray and Te2O₆ octahedra are light gray. Hg—O bonds are plotted with filled lines; all other bonds are plotted with open lines.

the terminal atoms O4 (Te1), O1 and O6 (Te2) have the shortest Te—O contacts (mean Te—O_{terminal} = 1.885 Å), the bridging atoms O2 (Te1 and Te2), O5 (Te1 and Te2) and O3 (Te2 and Te2) show considerably longer Te—O bonds (mean Te—O_{bridging} = 1.958 Å). The overall mean Te—O distances for both Te atoms (Te1—O = 1.936 Å and Te2—O = 1.932 Å) are nearly the same and are in very good agreement with the values observed for other structures containing [TeO₆] units. For reviews of the crystal chemistry of oxotellurate(VI) compounds, see, for example, Kratochvíl & Jenšovský (1986) and Levason (1997). The resulting $\infty[(\text{Te1O}_{2/1}\text{O}_{4/2})-(\text{Te2O}_{2/1}\text{O}_{2/2})_2\text{O}_{4/2}]$ chain has an arrangement identical to that of the tellurate chain recently observed in the structure of disilver(I) oxotellurate(VI), Ag₂TeO₄ (Klein *et al.*, 2005). These authors have also discussed in detail the relationship between the $\infty[(\text{TeO}_{2/1}\text{O}_{4/2})-(\text{TeO}_{2/1}\text{O}_{2/2})_2\text{O}_{4/2}]$ chain and sections of the rutile structure type.

The metal atoms of the title compound are situated between the polyanionic chains and interconnect the tellurate units into a three-dimensional framework. Unlike the aforementioned silver–mercury compounds comprising metal cluster cations, the Ag and Hg atoms in the title compound show no bonding interactions and are well separated [shortest distances: Ag···Ag = 3.3882 (5) Å, Hg···Ag = 3.5391 (7) Å and Hg···Hg = 3.7876 (5) Å].

Mercury(II)–oxo compounds and their unique crystal chemistry have been discussed in detail in the past (Grdenić, 1965; Aurivillius, 1965; Müller-Buschbaum, 1995). The most peculiar structural unit of many of these compounds is the pronounced linear coordination of Hg^{II}, with two short Hg—

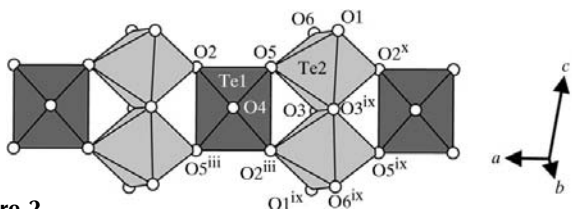


Figure 2
Part of a $\infty[(\text{Te1O}_{2/1}\text{O}_{4/2})-(\text{Te2O}_{2/1}\text{O}_{2/2})_2\text{O}_{4/2}]$ chain. Te1O₆ octahedra are dark gray and Te2O₆ octahedra are light gray. [Symmetry codes: (iii) $-x + 1, -y + 2, -z + 1$; (ix) $-x, -y + 2, -z + 1$; (x) $x - 1, y, z$]

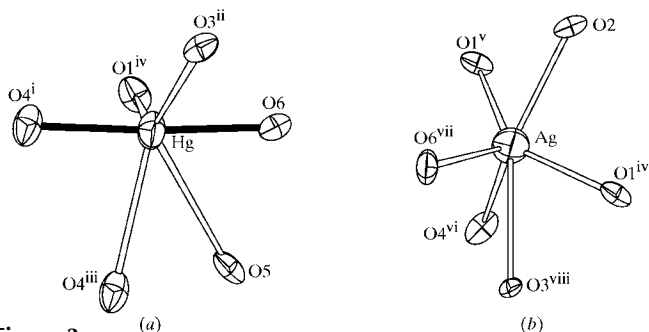


Figure 3
O-atom coordination around (a) Hg and (b) Ag, including distances less than 3.0 Å, with displacement ellipsoids at the 90% probability level. The two short Hg—O bonds are plotted with closed lines; all other bonds are plotted with open lines. [Symmetry codes: (i) $x, y - 1, z$; (ii) $-x, -y + 1, -z + 1$; (iii) $-x + 1, -y + 2, -z + 1$; (iv) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$; (v) $x + 1, y, z$; (vi) $-x + \frac{3}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$; (vii) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$; (viii) $x + \frac{1}{2}, -y + \frac{3}{2}, z + \frac{1}{2}$]

O distances ranging from *ca* 2.02 to 2.20 Å. If all Hg—O distances less than 3.0 Å are considered as bonding interactions, the more remote O atoms are located at significantly longer distances and augment the coordination sphere under formation of distorted (2 + *x*)-coordination polyhedra (*x* can range from 2 to 8), with *x* = 4 being the most frequently observed polyhedron (tetragonal flattened or elongated octahedron). A similar situation is observed for the Hg atom in Ag₂Hg₂(TeO₄)₃. The two closely bonded O atoms O6 and O4 have a mean Hg—O_{short} distance of 2.064 Å and a nearly linear O6—Hg—O4 angle of 176.2 (2)°. The next nearest O atom is located at a distance of 2.464 (4) Å, whereas three more distant O atoms have contacts greater than 2.7 Å (Fig. 3a). The overall mean Hg—O distance under consideration of coordination number 6 for the Hg atom is 2.511 Å, which is in good agreement with other oxo compounds containing (2 + 4)-coordinated Hg atoms.

A recent review on the peculiarities of the crystal chemistry of oxoargentates and silver oxometallates has been given by Müller-Buschbaum (2004). In various oxo compounds, the Ag^I cation shows no preference for any particular coordination number. Therefore, very different AgO_{*x*} coordination polyhedra with coordination numbers (CNs) ranging from 2, for linearly coordinated Ag, up to 12 are realized. The Ag atom in Ag₂Hg₂(TeO₄)₃ is surrounded by six O atoms (Fig. 3b) at distances ranging from 2.330 (5) to 2.824 (5) Å. The resulting AgO₆ polyhedron is considerably distorted and difficult to derive from the geometry of an octahedron. However, the mean Ag—O distance of 2.530 Å is comparable to that of other silver compounds that contain Ag in a distorted octahedral environment (Weil, 2003; Klein & Jansen, 2005) and is in excellent agreement with the value of 2.53 Å calculated from the sum of the radii for six-coordinated Ag⁺ and O²⁻ given by Shannon (1976).

The coordination numbers of the O atoms are 3 (O2, O5 and O6) and 4 (O1, O3 and O4), with corresponding distorted trigonal and tetrahedral coordination polyhedra. Results from the bond-valence-sum calculations (Brown, 2002), using the parameters of Brese & O'Keeffe (1991), are in good agreement with the expected values for monovalent Ag, divalent Hg and hexavalent Te [Hg (including all distances < 3.0 Å) 2.14, Ag (including all distances < 3.0 Å) 1.02, Te1 5.72, Te2 5.82, O1 (CN = 4) 1.91, O2 (CN = 3) 1.93, O3 (CN = 4) 1.93, O4 (CN = 4) 2.04, O5 (CN = 3) 1.87 and O6 (CN = 3) 2.16].

Experimental

Stoichiometric amounts of AgNO₃ (Fluka, p.A.), Hg₂(NO₃)₂·2H₂O (Merck, p.A.) and H₆TeO₆ (Aldrich, 99%) were mixed in the molar ratio 6:2:1 and placed in a Teflon inlay with 10 ml capacity. The inlay was filled to two-thirds with demineralized water, sealed and placed in a steel autoclave, which was heated at 523 K for three weeks. After this time, a few red single crystals of Ag₂Hg₂(TeO₄)₃ (approximate yield 2%) with a needle-like habit were obtained. Besides the main phase consisting of dark-red crystals of Ag₂TeO₄ (Klein *et al.*, 2005), a small number (*ca* 5% yield) of colourless crystals of a yet unknown composition were also present in the reaction mixture. Multiphase formation of crystalline products has been observed for several

Ag–Hg–X–O systems ($X = \text{P, As, Se and V}$; Weil, 2003; Weil *et al.* 2005). This behavior is caused by complex interplays of different redox, protolysis and precipitation equilibria taking place under hydrothermal conditions.

Crystal data

$\text{Ag}_2\text{Hg}_2(\text{TeO}_4)_3$	$D_x = 7.614 \text{ Mg m}^{-3}$
$M_r = 1191.72$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 2690 reflections
$a = 6.4664 (6) \text{ \AA}$	$\theta = 3.1\text{--}30.5^\circ$
$b = 6.1623 (5) \text{ \AA}$	$\mu = 41.48 \text{ mm}^{-1}$
$c = 13.0851 (11) \text{ \AA}$	$T = 295 (2) \text{ K}$
$\beta = 94.548 (2)^\circ$	Needle, red
$V = 519.77 (8) \text{ \AA}^3$	$0.15 \times 0.03 \times 0.02 \text{ mm}$
$Z = 2$	

Data collection

Bruker SMART APEX CCD diffractometer	1573 independent reflections
ω scans	1366 reflections with $I > 2\sigma(I)$
Absorption correction: numerical (<i>HABITUS</i> ; Herrendorf, 1997)	$R_{\text{int}} = 0.044$
$T_{\text{min}} = 0.078$, $T_{\text{max}} = 0.683$	$\theta_{\text{max}} = 30.5^\circ$
5772 measured reflections	$h = -9 \rightarrow 9$
	$k = -8 \rightarrow 8$
	$l = -18 \rightarrow 18$

Table 1

Selected geometric parameters (\AA , $^\circ$).

Hg–O6	2.059 (5)	Te2–O5	1.958 (4)
Hg–O4 ⁱ	2.068 (5)	Te2–O3 ^{ix}	1.964 (5)
Hg–O1 ^{iv}	2.464 (4)	Te2–O2 ^x	1.970 (4)
Hg–O3 ⁱⁱ	2.717 (5)	Te2–O3	1.981 (4)
Hg–O4 ⁱⁱⁱ	2.782 (5)	Ag–O6 ^{vii}	2.330 (5)
Hg–O5	2.975 (5)	Ag–O1 ^{iv}	2.410 (5)
Te1–O4	1.910 (5)	Ag–O1 ^v	2.450 (5)
Te1–O2	1.945 (4)	Ag–O4 ^{vi}	2.576 (5)
Te1–O5	1.952 (5)	Ag–O2	2.589 (5)
Te2–O1	1.840 (5)	Ag–O3 ^{viii}	2.824 (5)
Te2–O6	1.880 (5)		
O6–Hg–O4 ⁱ	176.2 (2)	O5–Te2–O3	89.15 (19)
O4–Te1–O2 ⁱⁱⁱ	88.7 (2)	O3 ^{ix} –Te2–O3	79.4 (2)
O4–Te1–O2	91.3 (2)	O2 ^x –Te2–O3	86.52 (19)
O4–Te1–O5 ⁱⁱⁱ	89.8 (2)	O6 ^{vii} –Ag–O1 ^{iv}	106.04 (16)
O2–Te1–O5 ⁱⁱⁱ	95.90 (19)	O6 ^{vii} –Ag–O1 ^v	114.97 (17)
O4–Te1–O5	90.2 (2)	O1 ^{iv} –Ag–O1 ^v	137.17 (15)
O2–Te1–O5	84.10 (19)	O6 ^{vii} –Ag–O4 ^{vi}	105.34 (17)
O1–Te2–O6	99.2 (2)	O1 ^{iv} –Ag–O4 ^{vi}	102.20 (16)
O1–Te2–O5	94.2 (2)	O1 ^v –Ag–O4 ^{vi}	79.00 (15)
O6–Te2–O5	90.5 (2)	O6 ^{vii} –Ag–O2	116.14 (16)
O1–Te2–O3 ^{ix}	92.3 (2)	O1 ^{iv} –Ag–O2	87.14 (15)
O6–Te2–O3 ^{ix}	168.5 (2)	O1 ^v –Ag–O2	64.53 (14)
O5–Te2–O3 ^{ix}	88.3 (2)	O4 ^{vi} –Ag–O2	133.03 (15)
O1–Te2–O2 ^x	89.9 (2)	O6 ^{vii} –Ag–O3 ^{viii}	70.90 (16)
O6–Te2–O2 ^x	90.8 (2)	O1 ^{iv} –Ag–O3 ^{viii}	62.66 (14)
O5–Te2–O2 ^x	175.48 (19)	O1 ^v –Ag–O3 ^{viii}	142.52 (14)
O3 ^{ix} –Te2–O2 ^x	89.60 (19)	O4 ^{vi} –Ag–O3 ^{viii}	64.24 (14)
O1–Te2–O3	170.9 (2)	O2–Ag–O3 ^{viii}	149.31 (14)
O6–Te2–O3	89.2 (2)		

Symmetry codes: (i) $x, y - 1, z$; (ii) $-x, -y + 1, -z + 1$; (iii) $-x + 1, -y + 2, -z + 1$; (iv) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$; (v) $x + 1, y, z$; (vi) $-x + \frac{3}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$; (vii) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$; (viii) $x + \frac{1}{2}, -y + \frac{3}{2}, z + \frac{1}{2}$; (ix) $-x, -y + 2, -z + 1$; (x) $x - 1, y, z$.

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0208P)^2 + 0.7394P]$
$R[F^2 > 2\sigma(F^2)] = 0.024$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.052$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.03$	$\Delta\rho_{\text{max}} = 1.97 \text{ e \AA}^{-3}$
1573 reflections	$\Delta\rho_{\text{min}} = -1.44 \text{ e \AA}^{-3}$
88 parameters	

Refinement of the occupation factors for the individual metal atoms did not reveal any statistical disorder of Ag and Hg over the two metal sites. The highest peak in the final Fourier map is located 0.84 \AA from Hg and the deepest hole 0.55 \AA from Ag.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ATOMS* (Dowty, 2004); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ1228). Services for accessing these data are described at the back of the journal.

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