

The channel structure of the mercury(II) selenite(IV) oxide hydrate $\text{HgSeO}_3 \cdot \text{HgO} \cdot \frac{1}{6} \text{H}_2\text{O}$

Matthias Weil

Institute for Chemical Technologies and Analytics, Division of Structural Chemistry, Vienna University of Technology, Getreidemarkt 9/164-SC, A-1060 Vienna, Austria
Correspondence e-mail: mweil@mail.zserv.tuwien.ac.at

Received 1 October 2002

Accepted 2 October 2002

Online 8 November 2002

The main building units of the title compound, dimercury(II) selenite(IV) oxide hydrate, are strongly distorted $[\text{Hg1O}_6]$ and $[\text{Hg2O}_7]$ polyhedra, and a pyramidal $\text{Se}^{\text{IV}}\text{O}_3$ group. Slightly corrugated hexagonal rings made up of six $[\text{Hg1O}_6]$ octahedra spread parallel to the *ab* plane and are connected *via* $[\text{Hg2O}_7]$ polyhedra parallel and perpendicular to this direction, which results in a three-dimensional arrangement with channels propagating parallel to the *c* axis. The $\text{Se}^{\text{IV}}\text{O}_3$ groups are situated below and above the rings and bridge both types of Hg atoms. The non-bonding orbitals are stereochemically active and protrude into the channels of the three-dimensional network. Additional water molecules are located at the centres of the channels and show weak interactions with the Se^{IV} lone pairs and the O atoms of the $\text{Se}^{\text{IV}}\text{O}_3$ groups.

Comment

Numerous compounds within the Hg–Se–O(–H) system, with different oxidation states of both Hg and Se, are compiled in standard textbooks on mercury (Gmelin, 1969), of which only a few have been crystallographically characterized, including α - HgSeO_3 (Koskenlinna & Valkonen, 1995), $\text{Hg}_3(\text{HSeO}_3)_2 \cdot (\text{SeO}_3)_2$ (Koskenlinna & Valkonen, 1996a), $\text{Hg}_2(\text{SeO}_3)_2 \cdot \text{H}_2\text{O}$ (Koskenlinna & Valkonen, 1996b), $\text{HgSeO}_4 \cdot \text{H}_2\text{O}$ (Stålhandske, 1978) and Hg_2SeO_4 (Dorm, 1969).

In a recent project intended to provide a more detailed knowledge of the crystal chemistry of this structure family, various compounds, some already described in the Gmelin textbook and some new, were prepared and structurally analyzed. These compounds were three polymorphs of mercury(I) selenite(IV), *viz.* α -, β - and γ - Hg_2SeO_3 (Weil, 2002a), two new modifications of mercury(II) selenite(IV), *viz.* β - and γ - HgSeO_3 (Weil, 2002b), the mixed-valent selenium^{IV/VI} compound $\text{Hg}_3\text{Se}_3\text{O}_{10}$ (Weil & Kolitsch, 2002), and the selenium^{IV/–II} compound $\text{Hg}_4\text{Se}_4\text{O}_9$ (Weil, 2002b), as well as the mercury(II) selenites(VI) HgSeO_4 , Hg_2SeO_5 and

Hg_3SeO_6 (Weil, 2002c). The title compound is the first basic mercury(II) selenite(IV) obtained so far and is composed of two crystallographically inequivalent Hg^{II} cations, one $[\text{Se}^{\text{IV}}\text{O}_3]^{2-}$ pyramid, one oxide O atom and a water molecule, corresponding to the formula $\text{HgSeO}_3 \cdot \text{HgO} \cdot \frac{1}{6} \text{H}_2\text{O}$.

The two Hg atoms are surrounded by six and seven O atoms to form a strongly distorted $[\text{Hg1O}_6]$ octahedron and a $[\text{Hg2O}_7]$ polyhedron, the intrapolyhedral geometry of which might be described as intermediate between a monocapped trigonal prism and a pentagonal bipyramid (Fig. 1). Although both polyhedra exhibit comparable mean Hg–O distances (2.490 Å for Hg1–O and 2.453 Å for Hg2–O), the crystal chemical situation is quite different. $[\text{Hg1O}_6]$ shows an explicit linear coordination, with two short axial distances (mean axial Hg1–O = 2.074 Å) and four considerably longer equatorial distances (mean equatorial Hg1–O = 2.698 Å). Such a tetragonal flattened octahedron is a frequently observed coordination figure within the unique crystal chemistry of Hg^{II} oxo-compounds. In $[\text{Hg2O}_7]$, the Hg atom is also virtually linearly coordinated by the two closest bonded O atoms, O1 and O4, with a mean distance of 2.264 Å, and augmented by the remaining O atoms at longer distances, with a mean of 2.528 Å. Compared with $[\text{Hg1O}_6]$, these mean distances are significantly longer and shorter, respectively.

The selenite(IV) group displays the well known pyramidal geometry, with a mean Se–O distance of 1.692 Å and a mean O–Se–O angle of 100.2°. This is similar to the bond-length distribution observed for other mercury selenites(IV) and various metal selenites(IV) compiled in the most recent review of this structural family (Verma, 1999).

A characteristic feature of the present structure is the corrugated hexagonal rings built of six corner-sharing $[\text{Hg1O}_6]$ octahedra, with short Hg–O distances to the bridging O atoms and longer distances to the equatorial O atoms (Fig. 1). The Hg–O–Hg angle of 115.0 (2)° indicates a slight deviation from ideal hexagonal geometry. Similar rings are found in the compounds Hg_3XO_6 , with X = S (Weil, 2001), Se (Weil,

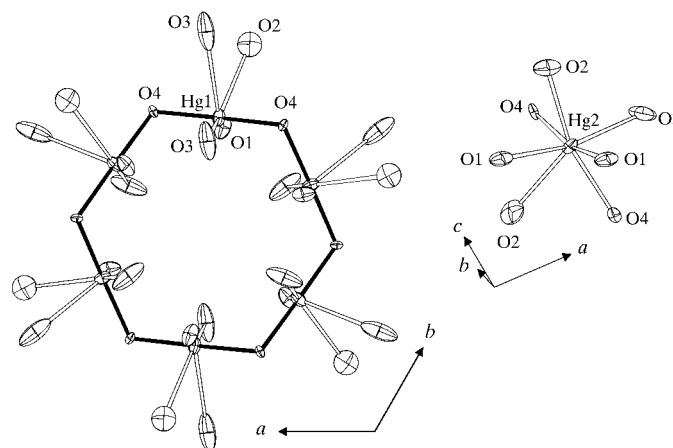


Figure 1

The hexagonal six-membered ring in $\text{HgSeO}_3 \cdot \text{HgO} \cdot \frac{1}{6} \text{H}_2\text{O}$, made up of six $[\text{Hg1O}_6]$ polyhedra, and the $[\text{Hg2O}_7]$ polyhedron, both with displacement ellipsoids drawn at the 74% probability level. Short Hg–O bonds of less than 2.2 Å are drawn as solid lines.

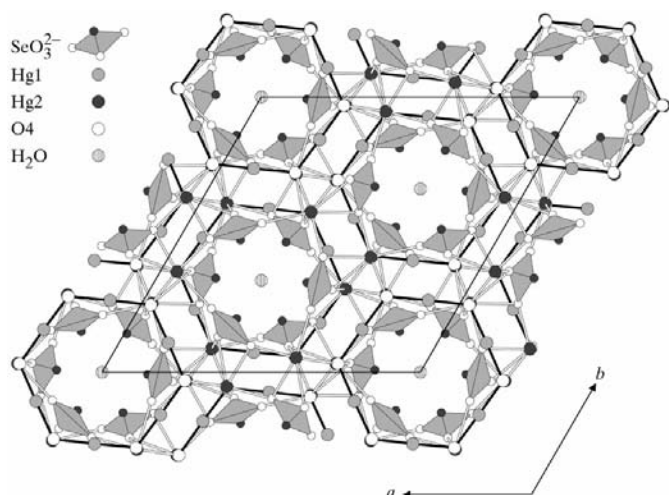


Figure 2

A projection of the crystal structure of $\text{HgSeO}_3 \cdot \text{HgO} \cdot \frac{1}{6}\text{H}_2\text{O}$ along [001]. For atoms Hg1, only short Hg—O bonds of less than 2.2 Å are shown, and are drawn as solid lines.

2002c) and Cr (Hansen *et al.*, 1995). However, in this latter structure type, the rings are condensed to form infinite two-dimensional cationic nets with a composition of $[\text{Hg}_3\text{O}_2]^{2+}$, and with disordered XO_4 tetrahedra situated in the interstices of the nets. In the title compound, the isolated rings spread parallel to the *ab* plane and are connected *via* the $[\text{Hg}_2\text{O}_7]$ polyhedra parallel and perpendicular to this direction (Figs. 2 and 3). This arrangement leads to a three-dimensional framework with channels running parallel to the *c* axis, as depicted in Fig. 2.

The SeO_3 pyramids are situated above and below the rings and bridge both Hg atoms. The lone-pair electrons of the Se^{IV} groups are stereochemically active and protrude into the channels of the three-dimensional network. At the centres of the channels are located water molecules which show only very weak interactions with the remaining O atoms

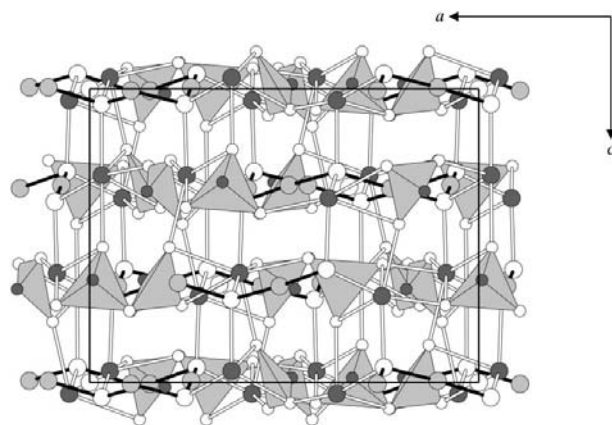


Figure 3

A projection of the crystal structure of $\text{HgSeO}_3 \cdot \text{HgO} \cdot \frac{1}{6}\text{H}_2\text{O}$ along [010]. For atoms Hg1, only short Hg—O bonds of less than 2.2 Å are shown, and are drawn as solid lines. Water molecules have been omitted for clarity.

($\text{H}_2\text{O} \cdots \text{O} > 3.7$ Å) and the non-bonding orbitals of the Se^{IV} atoms. The presence of water molecules is confirmed by complementary IR spectroscopic measurements of the yellow crystals obtained from the precipitation reaction.

Atoms O1–O4 are four-coordinate. Atom O4 is surrounded by four Hg atoms forming a slightly distorted $[\text{OHg}_4]$ tetrahedron, whereas all other O atoms have one Se and three Hg atoms as coordination partners. The corresponding $[\text{OSeHg}_3]$ tetrahedra are strongly distorted from the ideal geometry.

The results of the bond-valence-sum (BVS) calculations, using the parameters provided by Brese & O'Keeffe (1991), are in accordance with expected values, with Hg1 2.094, Hg2 2.034, Se 4.144, O1 2.131, O2 1.943, O3 1.919 and O4 2.280.

Experimental

Precipitation of a slightly acidified $\text{Hg}_2(\text{NO}_3)_2$ solution with an excess of selenic acid solution (both Merck, p.A.) produced a dark-brown polycrystalline material, the X-ray powder diffraction pattern of which revealed Hg_2SeO_4 (Dorm, 1969) as the main phase. Some weak additional reflections could not be assigned to any known phase within this system. Hydrothermal treatment of this material in demineralized water at 453 K for 7 d in a 10 ml-capacity Teflon-lined steel autoclave resulted in a few amber-coloured hexagonal crystals of $\text{HgSeO}_3 \cdot \text{HgO} \cdot \frac{1}{6}\text{H}_2\text{O}$, in addition to other crystalline phases that are being investigated further. In an alternative procedure, single crystals of $\text{HgSeO}_3 \cdot \text{HgO} \cdot \frac{1}{6}\text{H}_2\text{O}$ were obtained during a precipitation experiment. A small beaker was filled with an $\text{Hg}(\text{Ac})_2$ solution (Sigma–Aldrich, >99%; Ac is acetate), which was acidified with an excess of acetic acid. This beaker was then placed in a larger container which was carefully filled with demineralized water. After adding a selenous acid solution (Merck, p.A.) to the large container, this apparatus was set aside in a dark room. After several days, colourless single crystals of α - and β - HgSeO_3 (Weil, 2002b) were observed at the bottom of the large container. Besides a few crystals of these two polymorphs, yellow needle-shaped crystals of $\text{HgSeO}_3 \cdot \text{HgO} \cdot \frac{1}{6}\text{H}_2\text{O}$, with an edge length of up to 2 mm, had formed in the small beaker containing the $\text{Hg}(\text{Ac})_2$ solution. For the present structure analysis, a hydrothermally grown crystal was used. The yellow crystals obtained from the precipitation experiment exhibited no significant differences in their lattice constants or structural parameters after refinement compared with the hydrothermally grown crystals.

Crystal data

$\text{HgSeO}_3 \cdot \text{HgO} \cdot \frac{1}{6}\text{H}_2\text{O}$
 $M_r = 547.14$
 Trigonal, $R\bar{3}$
 $a = 15.3965$ (6) Å
 $c = 10.0549$ (5) Å
 $V = 2064.20$ (15) Å³
 $Z = 18$
 $D_x = 7.923$ Mg m⁻³

Mo $K\alpha$ radiation
 Cell parameters from 4279 reflections
 $\theta = 2.5$ – 29.9°
 $\mu = 74.68$ mm⁻¹
 $T = 293$ (2) K
 Spheroid, amber
 $0.13 \times 0.10 \times 0.10$ mm

Data collection

Siemens SMART area-detector diffractometer
 ω scans
 Absorption correction: numerical (Herrendorf, 1993–1997)
 $T_{\min} = 0.011$, $T_{\max} = 0.051$
 9998 measured reflections

1355 independent reflections
 1147 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.065$
 $\theta_{\text{max}} = 30.2^\circ$
 $h = -21 \rightarrow 21$
 $k = -21 \rightarrow 21$
 $l = -14 \rightarrow 13$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0166P)^2 + 35.2262P]$
$R[F^2 > 2\sigma(F^2)] = 0.022$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.054$	$(\Delta/\sigma)_{\max} = 0.001$
$S = 1.09$	$\Delta\rho_{\max} = 2.32 \text{ e } \text{\AA}^{-3}$
1355 reflections	$\Delta\rho_{\min} = -1.43 \text{ e } \text{\AA}^{-3}$
67 parameters	Extinction correction: <i>SHELXL97</i>
H-atom parameters not refined	Extinction coefficient: $8.3(5) \times 10^{-5}$

Table 1

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

Hg1—O4	2.074 (5)	Hg2—O3 ^{iv}	2.494 (6)
Hg1—O1	2.613 (5)	Hg2—O1 ^v	2.550 (6)
Hg1—O3 ⁱ	2.634 (6)	Hg2—O2 ^v	2.556 (6)
Hg1—O2	2.718 (7)	Hg2—O2 ^{vi}	2.601 (7)
Hg1—O3 ⁱⁱ	2.828 (8)	Se—O2 ^{vii}	1.681 (6)
Hg2—O4 ⁱⁱⁱ	2.243 (5)	Se—O3	1.684 (6)
Hg2—O1 ^{iv}	2.284 (5)	Se—O1 ^{vi}	1.710 (5)
Hg2—O4 ^v	2.442 (5)		
O4—Hg1—O4 ⁱ	176.60 (11)	O2 ^{vii} —Se—O3	100.3 (4)
O4 ⁱⁱⁱ —Hg2—O1 ^{iv}	162.60 (17)	O2 ^{vii} —Se—O1 ^{vi}	98.7 (3)
Hg1—O4—Hg1 ⁱⁱⁱ	115.0 (2)	O3—Se—O1 ^{vi}	101.5 (3)

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

The crystal shape was optimized by minimizing the internal R_i value of selected reflections [$I > 20\sigma(I)$] using the program *HABITUS* (Herrendorf, 1993–1997). The habit so derived was used for the numerical absorption correction. After location and refinement of the framework structure, an obvious electron density of $ca\ 11 \text{ e } \text{\AA}^{-3}$ was found at the inversion centre (Wyckoff position $3a$), which was assigned to the O atom of a water molecule. The H atoms of this molecule were not located. The highest difference peak was then 0.84 \AA from Se and the deepest hole 1.09 \AA from Hg.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); 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, 2000); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1593). Services for accessing these data are described at the back of the journal.

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