

Hg₃Se₃O₁₀, a mercury(II) compound with mixed-valence oxoselenium(IV/VI) anions

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Received 23 January 2002

Accepted 29 January 2002

Online 29 March 2002

The title compound, trimercury(II) bis[selenite(IV)] selenate(VI), contains three crystallographically inequivalent Hg^{II} cations with coordination numbers of eight (denoted Hg1 and Hg2) and five (denoted Hg3). The corresponding coordination polyhedra around the metal atoms might be described as intermediates between a square antiprism and a triangulated dodecahedron for both Hg1 and Hg2, and a strongly distorted truncated octahedron for Hg3. ∞^2 [HgO_{8/2}] layers of edge-sharing [HgO₈] polyhedra propagate parallel to the *bc* plane, and are connected *via* Se^{VI}O₄ tetrahedra and [Hg₃O₅] polyhedra along the *a* axis, forming an arrangement with channels propagating parallel to the *b* axis. The two independent Se^{IV}O₃ pyramids bridge the Hg atoms, and the non-bonding orbitals of the Se^{IV} ions protrude into the channels from opposite sides.

Comment

Although the preparation and some physical properties of numerous compounds within the Hg–Se–O system have been published (Gmelin, 1969), only a few representatives of the series have been crystallographically characterized. Complete structure analyses have been performed on the mercuric selenites(IV) HgSeO₃ (Koskenlinna, 1995), Hg₃(HSeO₃)₂(SeO₃)₂ (Koskenlinna & Valkonen, 1996*a*) and Hg₂(SeO₃)₂·H₂O (Koskenlinna & Valkonen, 1996*b*), the hydrated mercuric selenate(VI) HgSeO₄·H₂O (Stålhandske, 1978), and the mercurous selenate(VI) Hg₂SeO₄ (Dorm, 1969). Isotypism with the corresponding sulfates(VI) is reported for anhydrous HgSeO₄ and the basic salt Hg₃(SeO₄)O₂ (Aurivillius & Malmros, 1961), the selenium analogue of the mineral schuetteite, Hg₃(SO₄)O₂ (Nagorsen *et al.*, 1962; Weil, 2001).

For a more detailed knowledge of the crystal chemistry of this structural family, the title compound was investigated as part of a project to prepare oxoselenites(IV) and oxoselen-

ates(VI) with mercury cations in different oxidation states and to analyse their crystal structures.

The title compound is composed of three independent Hg^{II} cations, two Se^{IV}O₃ pyramids and an Se^{VI}O₄ tetrahedron, corresponding to the formula Hg₃(SeO₃)₂(SeO₄). It is one of the few crystallographically well characterized phases containing both selenium(IV) and selenium(VI) in the crystal structure. Other compounds with mixed-valent oxoselenium(IV/VI) anions, as listed in the latest version of the Inorganic Crystal Structure Database (ICSD; FIZ-Karlsruhe, 2001), are the mineral schmiederite, Pb₂Cu₂(OH)₄(SeO₃)₂(SeO₄) (Effenberger, 1987), and the synthetic phases Li₂Cu₃(SeO₃)₂(SeO₄)₂ (Giester, 1989), (Na₂SeO₄)(H₂SeO₃)·H₂O (Baran *et al.*, 1991), Fe(HSeO₃)(SeO₄)·H₂O (Giester, 1992), Er(SeO₃)(SeO₄)_{0.5}·H₂O (Morris *et al.*, 1992) and La(HSeO₃)(SeO₄)·2H₂O (Harrison & Zhang, 1997). These structures comprise isolated Se^{IV}O₃²⁻ or Se^{IV}O₃H⁻ anions, and Se^{VI}O₄²⁻ anions, with a characteristic pyramidal geometry for the Se^{IV} anions and tetrahedral geometry for the Se^{VI} anions, whereas the mixed-valent selenium(IV/VI) oxide Se₂O₅ (Zak, 1980) is composed of corner-sharing Se^{IV}O₃ and Se^{VI}O₄ building units.

In Hg₃Se₃O₁₀, the polyhedra are linked *via* common O atoms to form a three-dimensional network. Edge-sharing [HgO₈] polyhedra build ∞^2 [HgO_{8/2}] layers parallel to the *bc* plane, which are bridged by the Se^{IV}O₃ groups. Two adjacent layers are connected *via* Se^{VI}O₄ tetrahedra and [Hg₃O₅] polyhedra along the *a* axis, forming channels extending parallel to the *b* axis, as depicted in Fig. 1.

Often, Hg^{II}-oxo compounds show a linear coordination of Hg with two short axial distances and a [2 + *x*] coordination, or, rarely, an [*x* + 2] coordination with two long axial distances; *x* ranges from 2 to 8, with *x* = 4 being the most frequently observed coordination polyhedron (tetragonal flattened or

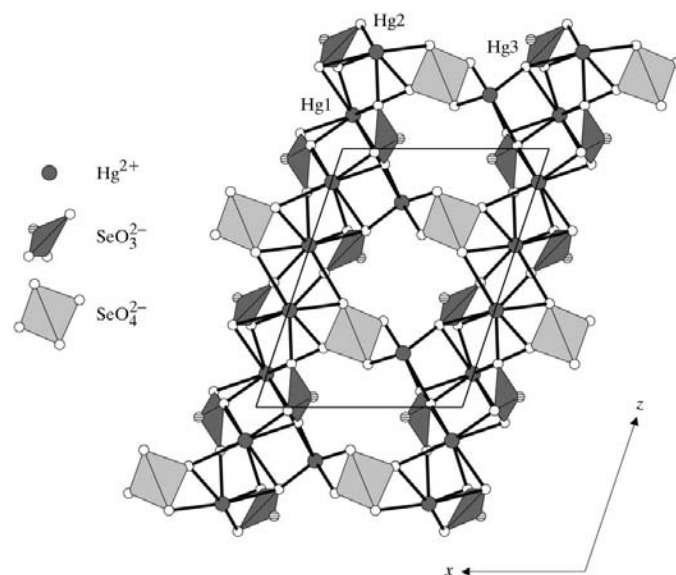


Figure 1
A projection of the crystal structure of Hg₃Se₃O₁₀ along [010].

elongated octahedron). The influence of relativistic effects for the preference of this linear coordination has been published in the past (Norrby, 1991), and many examples of this behaviour are given in surveys of the unique crystal chemistry of Hg^{II}, with its d^{10} electronic configuration (*e.g.* Aurivillius, 1965; Grdenić, 1965; Stålhandske, 1980; Müller-Buschbaum, 1995). However, none of the strongly distorted [HgO_x] polyhedra in Hg₃Se₃O₁₀ shows an explicit linear [2 + x] or [x + 2] arrangement.

The coordination numbers (CN) of the Hg^{II} cations are eight (Hg1 and Hg2) and five (Hg3), excluding a very long Hg3...O3 distance of ≈ 3 Å. The corresponding polyhedra around the Hg^{II} cations might be described as intermediates between a square antiprism and a triangulated dodecahedron for both Hg1 and Hg2, and a truncated octahedron for Hg3 (Fig. 2). The mean Hg—O distances for the eight-coordinate Hg^{II} cations are comparable (mean Hg—O 2.521 Å for Hg1 and 2.530 Å for Hg2), whereas the mean Hg—O distance for the five-coordinate Hg3, 2.349 Å, is considerably shorter.

The two inequivalent selenite(IV) groups are situated above and below the cavities of the ∞^2 [HgO_{8/2}] layers. Each selenite(IV) group acts as a bidentate ligand to two Hg^{II} cations, with the O—O edges of the [HgO₈] polyhedra as common atoms and, additionally, by corner-sharing to the neighbouring Hg^{II} cations as a monodentate ligand (Fig. 3). This construction provides space for the lone pairs of the two Se^{IV} ions, and both non-bonding orbitals protrude into the channels of the three-dimensional network. The arrangement of the selenite(IV) groups, with the apices adjusted to each other in the cavity of the structure, is a frequently observed structural unit in the crystal chemistry of Se^{IV} compounds. The mean Se—O distances of 1.710 Å for Se1 and 1.712 Å for Se2 are in the same range as the corresponding values within other mercuric selenites(IV): 1.709 (HgSeO₃; Koskenlinna, 1995), 1.692 and 1.689 [Hg₂(SeO₃)₂·H₂O; Koskenlinna & Valkonen, 1996*b*], 1.692 [[Hg(NH₃)]SeO₃; Koskenlinna *et al.*, 1996] and 1.705 Å [Hg₃(HSeO₃)₂(SeO₃)₂; Koskenlinna & Valkonen, 1996*a*]. Also, the intrapolyhedral geometry of the Se^{IV}O₃ pyramids (mean O—Se—O 97.1° for Se1 and 97.8° for Se2) are in good agreement with the data for other selenites(IV) listed in the most recent review of this structural family (Verma, 1999).

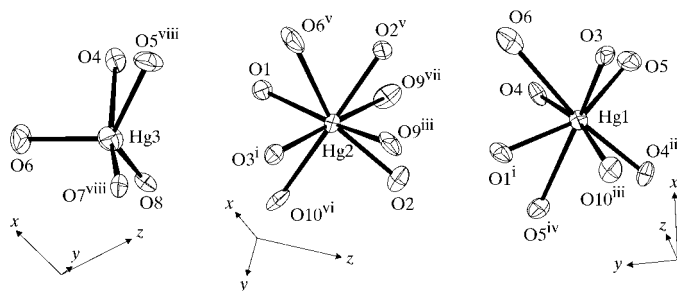


Figure 2
View of the [HgO_x] coordination polyhedra in Hg₃Se₃O₁₀, with displacement ellipsoids drawn at the 74% probability level (the symmetry codes are as in Table 1).

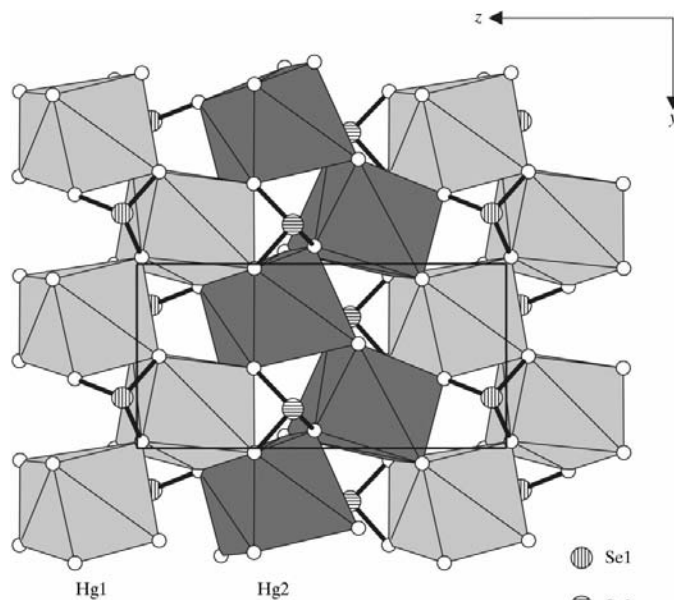


Figure 3
Part of a ∞^2 [HgO_{8/2}] layer in Hg₃Se₃O₁₀, with bridging selenite(IV) groups above and below the cavities. [Hg1O₈] polyhedra are light grey and [Hg2O₈] polyhedra are dark grey.

The selenate(VI) group is slightly distorted from the geometry of an ideal Se^{VI}O₄ tetrahedron, and the mean Se—O distance of 1.644 Å is similar to the observed bond-length distribution for other mercury selenates(VI): 1.641 (HgSeO₄·H₂O; Stålhandske, 1978) and 1.64 Å (Hg₂SeO₄; Dorm, 1969). The closest bonded O atom (O9) is also coordinated to two Hg atoms with long distances, whereas the long bonded O8 atom has only one Hg atom (Hg3) with a short Hg—O bond as an additional coordination partner. Another O atom with CN = 2 is O7, and both atoms bridge the SeO₄ tetrahedron and the [HgO₅] polyhedron. The coordination numbers of the other O atoms range from 3 to 4; CN = 3 for atoms O1, O2, O3, O9 and O10 (1 × Se, 2 × Hg), and CN = 4 for atoms O4, O5 and O6 (1 × Se, 3 × Hg).

Results from the bond-valence sum (BVS) calculations, using the parameters provided by Brese & O'Keefe (1991), are in accordance with the expected values: Hg1 2.10, Hg2 2.18, Hg3 2.06, Se1 3.93, Se2 3.93 and Se3 5.91. The BVS for the O atoms of the selenite(IV) groups range from 2.09 to 2.20, and those of the selenate(VI) group from 1.76 to 1.89.

Experimental

Single crystals of the title compound were synthesized under hydrothermal conditions, starting from microcrystalline HgSeO₄ in demineralized water (Teflon-lined steel autoclave, filling degree *ca* 70%, 493 K, 10 d). Besides yellow crystals of the hitherto unknown basic salt HgSeO₄·HgO [space group $P2_1/c$ (No. 14), $a = 9.6247$ (12) Å, $b = 7.1313$ (9) Å, $c = 14.8713$ (18) Å and $\beta = 109.811$ (2)°; Weil, 2002] and red-brown crystals of Hg₃(SeO₄)O₂ (Aurivillius & Malmros, 1961; Nagorsen *et al.*, 1962), colourless crystals of the title compound of up to 2 mm in length were also obtained.

Crystal data

Hg ₃ Se ₃ O ₁₀	$D_x = 7.002 \text{ Mg m}^{-3}$
$M_r = 998.65$	Mo $K\alpha$ radiation
Monoclinic, $P2_1$	Cell parameters from 981 reflections
$a = 8.3979 (9) \text{ \AA}$	$\theta = 5.3\text{--}59.7^\circ$
$b = 5.3327 (6) \text{ \AA}$	$\mu = 60.07 \text{ mm}^{-1}$
$c = 11.1482 (12) \text{ \AA}$	$T = 293 (2) \text{ K}$
$\beta = 108.422 (2)^\circ$	Fragment, colourless
$V = 473.67 (9) \text{ \AA}^3$	$0.18 \times 0.07 \times 0.04 \text{ mm}$
$Z = 2$	

Data collection

Siemens SMART CCD area-detector diffractometer	1553 independent reflections (plus 1131 Friedel-related reflections)
ω scans	2435 reflections with $I > 2\sigma(I)$
Absorption correction: numerical (HABITUS; Herrendorf, 1993–1997)	$R_{\text{int}} = 0.060$
$T_{\text{min}} = 0.064$, $T_{\text{max}} = 0.446$	$\theta_{\text{max}} = 30.3^\circ$
6813 measured reflections	$h = -11 \rightarrow 11$
	$k = -7 \rightarrow 7$
	$l = -15 \rightarrow 15$

Refinement

Refinement on F^2	$(\Delta/\sigma)_{\text{max}} = 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.027$	$\Delta\rho_{\text{max}} = 1.98 \text{ e \AA}^{-3}$
$wR(F^2) = 0.060$	$\Delta\rho_{\text{min}} = -1.51 \text{ e \AA}^{-3}$
$S = 1.02$	Extinction correction: <i>SHELXL97</i> (Sheldrick, 1997)
2684 reflections	Extinction coefficient: 0.0090 (3)
146 parameters	Absolute structure: Flack (1983)
$w = 1/[\sigma^2(F_o^2) + (0.025P)^2]$	Flack parameter = $-0.015 (11)$
where $P = (F_o^2 + 2F_c^2)/3$	

Systematic absences $k = 2n + 1$ for the $(0k0)$ reflections indicated space groups $P2_1$ (No. 4) and $P2_1/m$ (No. 11). Initial attempts to solve the crystal structure in one of these two possible space groups using both direct methods and a Patterson synthesis with *SHELXS97*

Table 1

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

Hg1—O1 ⁱ	2.287 (6)	Hg3—O5 ^{viii}	2.197 (7)
Hg1—O3	2.293 (7)	Hg3—O6	2.201 (7)
Hg1—O4 ⁱⁱ	2.312 (7)	Hg3—O8	2.263 (7)
Hg1—O4	2.411 (7)	Hg3—O7 ^{viii}	2.304 (7)
Hg1—O5	2.612 (8)	Hg3—O4	2.782 (7)
Hg1—O10 ⁱⁱⁱ	2.677 (7)	Hg3—O3 ^{viii}	3.027 (6)
Hg1—O5 ^{iv}	2.738 (8)	Se1—O1	1.705 (6)
Hg1—O6	2.840 (9)	Se1—O5 ^{ix}	1.709 (7)
Hg2—O2	2.226 (6)	Se1—O4 ^{ix}	1.720 (6)
Hg2—O2 ^v	2.295 (7)	Se2—O6	1.702 (7)
Hg2—O1	2.301 (6)	Se2—O3	1.714 (6)
Hg2—O3 ⁱ	2.340 (6)	Se2—O2	1.719 (6)
Hg2—O10 ^{vi}	2.686 (7)	Se3—O9	1.613 (7)
Hg2—O6 ^v	2.686 (8)	Se3—O7	1.643 (6)
Hg2—O9 ^{vii}	2.796 (7)	Se3—O10	1.647 (6)
Hg2—O9 ⁱⁱⁱ	2.906 (8)	Se3—O8	1.674 (7)
O1—Se1—O5 ^{ix}	94.7 (3)	O9—Se3—O7	109.2 (3)
O1—Se1—O4 ^{ix}	100.8 (3)	O9—Se3—O10	113.6 (4)
O5 ^{ix} —Se1—O4 ^{ix}	95.8 (3)	O7—Se3—O10	109.4 (4)
O6—Se2—O3	97.7 (4)	O9—Se3—O8	109.3 (4)
O6—Se2—O2	93.5 (3)	O7—Se3—O8	108.4 (3)
O3—Se2—O2	102.3 (3)	O10—Se3—O8	106.9 (3)

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

(Sheldrick, 1997) and *SHELXL97* (Sheldrick, 1997) were unsuccessful. Therefore, attempts were made in space group $P1$ (No. 1). The Hg atoms were located by direct methods, and the Se and O atoms were found by subsequent Fourier syntheses. Analysis of the atomic coordinates thus obtained using *PLATON* (Spek, 2001) clearly indicated a higher symmetry in $P2_1$ (No. 4). After transformation of the appropriate parameters, the structure was refined in this monoclinic space group. No additional symmetry was then suggested by *PLATON*. Moreover, the Flack parameter (Flack, 1983) gives a clear indication of the absence of any centre of symmetry.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97*; program(s) used to refine structure: *SHELXL97*; molecular graphics: *ATOMS* (Dowty, 1998); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1358). Services for accessing these data are described at the back of the journal.

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