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Mercury(II) Selenite Hemihydrate

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Abstract

The title compound, dimercury bis[trioxoselenate(2−)] monohydrate, $Hg_2(SeO_3)_2.H_2O$, contains two inequivalent Hg^{II} ions with coordination numbers of five and seven. The coordination polyhedra of these ions are a tetragonal pyramid and a monocapped trigonal prism, respectively. One of the two inequivalent selenite groups bridges three Hg^{II} ions and the other bridges four Hg^{II} ions, thus forming a structure extending in three dimensions.

Comment

The coordination number of divalent mercury usually varies between five and seven, and the coordination polyhedron is often a tetragonally flattened or elongated octahedron (Dubler, Beck, Linowsky & Jameson, 1981). We have described the structures of two mercury(II) selenites, $HgSeO_3$ and $Hg_3(HSeO_3)_2(SeO_3)_2$, previously (Koskenlinna & Valkonen, 1995*a*,*b*). The first compound is isostructural with the perovskite-like compounds MSeO$_3$ (M = Mg, Mn, Co, Ni, Cu, Zn and Cd; Kohn, Inoue, Horie & Akimoto, 1976; Valkonen, 1994*a*) and has a coordination polyhedron in the form of a flattened octahedron, while the latter is isostructural with the corresponding cadmium compound (Valkonen, 1994*b*) and contains coordination polyhedra of six and seven O atoms; the octahedron is tetragonally flattened and the other polyhedron has the form of a monocapped trigonal prism. In both compounds, the polyhedra of O atoms around the Hg^{II} ions are distorted compared with those of other metals in the respective isostructural series. We report here the structure of a novel mercury(II) selenite.

The title compound contains two inequivalent Hg^{II} ions, two selenite ions and a water molecule, corresponding either to the formula $Hg_2(SeO_3)_2.H_2O$ [mercury(II) selenite–water (2/1), $Z = 4$] or $HgSeO_3.0.5H_2O$ [mercury(II) selenite hemihydrate, $Z = 8$]. The structure is continuous in three dimensions, but contains a cavity. The cavity is in the middle of the unit cell and extends

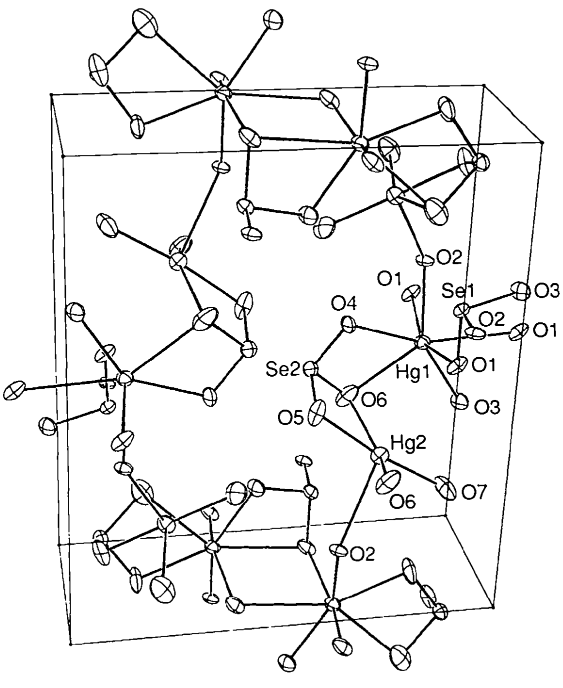

Fig. 1. An *ORTEP*II (Johnson, 1976) drawing of the unit cell with displacement ellipsoids shown at the 50% level. The *c* axis is horizontal and the *b* axis is vertical.

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parallel to the a axis, as depicted in Fig. 1. It is lined by the water molecules O7 on opposite sides of the cavity, and the Se2 ions. The cavity provides space for the non-bonding orbitals of the Se2 ions, which protrude into the cavity from opposite sides in accordance with the symmetry.

The Hg^{II} ions are five- and seven-coordinate. The coordination polyhedron around the heptacoordinate Hg1 ion is a slightly distorted monocapped trigonal prism. The bond distances from Hg1 to the O atoms range from 2.199 (15) to 2.751 (15) Å. In Hg$_3$(HSeO$_3$)$_2$(SeO$_3$)$_2$, the bond distances in the similar monocapped trigonal prism range from 2.213 (8) to 2.818 (7) Å. Four selenite groups, three formed by Se1 and one by Se2, act as ligands to each Hg1 ion, with three selenite groups acting as bidentate ligands.

The bond distances from Hg2 to the five closest O atoms range between 2.064 (15) and 2.757 (13) Å, with two short bonds, 2.064 (15) and 2.072 (16) Å, and three longer bonds, ranging from 2.447 (16) to 2.757 (13) Å. The O atom O7 is part of a water molecule, and shows a short Hg2—O bond. The H atoms of the water molecule could not be located in the difference Fourier map. The nearest O-atom neighbours of O7 (within 3.1 Å) are, in order of distance, O4 at 2.84 (2), O3 at 2.96 (2), O5 at 3.03 (2) and O3 at 3.04 (2) Å. The two closest O atoms to O7 may act as acceptor atoms in hydrogen-bond formation, but this cannot be confirmed with the present crystallographic data. The two short Hg2—O bonds form an angle of 170.5 (6)°. There is a sixth O atom, O1, at a distance of 3.219 (15) Å from Hg2; this O atom can be pictured as being situated at the apex of a grossly distorted octahedron. As the sum of the van der Waals radii of Hg^{2+} and O^{2-} is 2.9 Å, this is not considered to be a bonding distance (Grdenic, 1965). The bonding scheme resembles the system of two short bonds and four long bonds found in the six-coordinate polyhedra in HgSeO$_3$ and Hg$_3$(HSeO$_3$)$_2$(SeO$_3$)$_2$. In these compounds, the bond distances vary between 2.103 (11) and 2.641 (11) Å, and 2.167 (9) and 2.561 (7) Å, respectively. The coordination polyhedron of Hg2 is a tetragonal pyramid. The four O atoms of the tetragonal base and Hg2 are situated approximately within the same plane. Three selenite groups, one containing Se1 and two containing Se2, act as ligands to each Hg2 ion; one selenite group acts as a bidentate ligand.

The selenite group formed by Se1 has slightly longer than normal Se—O bond lengths; these range between 1.675 (14) and 1.704 (15) Å. Considering the error limits, the bond lengths are statistically close but not the same. O1 is bonded to three Hg1 ions, O2 is bonded to an Hg1 ion and an Hg2 ion, and O3 is bonded to one Hg1 ion. The selenite group bridges four Hg ions, as O1 and O2 are bonded to the same Hg1 ion, O1 and O3 are both bonded to a further Hg1 ion, O1 is bonded to a third Hg1 ion and O3 is bonded to an Hg2 ion. In HgSeO$_3$, in which each selenite O atom is bonded to two Hg ions, the Se—O bond lengths vary between 1.660 (17) and 1.734 (12) Å.

The selenite group containing Se2 has two Se—O bonds which are the same length as those as in the Se1-containing selenite group, namely Se2—O5 [1.705 (14) Å] and Se2—O6 [1.699 (17) Å]. The bond Se2—O4 [1.663 (16) Å] is shorter than the other two and is of normal length. O4 is bonded to one Hg1 ion while O6 lies within bonding distance of one Hg1 and two Hg2 ions. O5 is bonded to one Hg2 ion. The selenite group bridges three Hg ions, as O4 and O6 are bonded to the same Hg1 ion, and, similarly, O5 and O6 are bonded to the same Hg2 ion.

Experimental

The title compound was crystallized from an aqueous suspension of mercury(II) oxide and selenious acid, which was allowed to evaporate very slowly at 330 K. After a few weeks, the resulting suspension formed large flat prisms of the title compound, together with unreacted mercury(II) oxide.

Crystal data

Hg$_2$(SeO$_3$)$_2$.H$_2$O
M_r = 673.11
Monoclinic
$P2_1/c$
a = 5.034 (2) Å
b = 13.281 (2) Å
c = 11.507 (3) Å
β = 92.04 (3)°
V = 768.8 (4) Å^3
Z = 4
D_x = 5.81 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 12–18°
μ = 49.259 mm^{-1}
T = 294 K
Prism
0.10 × 0.05 × 0.05 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North, Phillips & Mathews, 1968) and spherical
$T_{\min}$ = 0.030, $T_{\max}$ = 0.069
4449 measured reflections
2323 independent reflections

1079 observed reflections [$I > 3\sigma(I)$]
$R_{\rm int}$ = 0.081
$\theta_{\max}$ = 29.96°
$h = 0 \rightarrow 7$
$k = -18 \rightarrow 18$
$l = -16 \rightarrow 16$
2 standard reflections
frequency: 60 min
intensity decay: 16.3%

Refinement

Refinement on F
R = 0.036
wR = 0.040
S = 0.855
1079 reflections
101 parameters
H atoms not located

$\Delta\rho_{\max}$ = 2.50 e Å^{-3}
$\Delta\rho_{\min}$ = −2.13 e Å^{-3}
Extinction correction: isotropic (Zachariasen, 1963)
Extinction coefficient: 0.20 × 10^{-7}

$w = 1/[\sigma^2(F) + (0.02F)^2 + 1.00]$ (Killean & Lawrence, 1969)
$(\Delta/\sigma)_{\max} = 0.002$

Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Tables 2.2B and 2.3.1)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

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

	x	y	z	$U_{\rm eq}$
Hg1	0.2518 (2)	0.02260 (6)	0.36781 (7)	0.0248 (3)
Hg2	0.7070 (2)	0.18874 (7)	0.22898 (7)	0.0282 (3)
Se1	0.2260 (4)	0.1344 (2)	0.6136 (2)	0.0234 (9)
Se2	0.2659 (4)	0.0675 (2)	0.0934 (2)	0.0269 (9)
O1	0.268 (3)	0.007 (1)	0.606 (1)	0.033 (8)
O2	−0.105 (3)	0.141 (1)	0.623 (1)	0.024 (6)
O3	0.269 (3)	0.162 (1)	0.471 (1)	0.032 (8)
O4	0.292 (4)	−0.034 (1)	0.177 (1)	0.037 (9)
O5	0.586 (3)	0.108 (1)	0.083 (1)	0.029 (8)
O6	0.174 (3)	0.150 (1)	0.197 (1)	0.043 (9)
O7	0.772 (4)	0.261 (1)	0.387 (1)	0.045 (9)

Table 2. *Selected geometric parameters* (Å, °)

Hg1—O1	2.751 (15)	Hg2—O6	2.742 (16)
Hg1—O1$^{\rm i}$	2.671 (14)	Hg2—O6$^{\rm iv}$	2.447 (16)
Hg1—O1$^{\rm ii}$	2.459 (14)	Hg2—O7	2.072 (16)
Hg1—O2$^{\rm i}$	2.294 (13)	Se1—O1	1.704 (15)
Hg1—O3	2.199 (15)	Se1—O2	1.675 (14)
Hg1—O4	2.332 (15)	Se1—O3	1.696 (15)
Hg1—O6	2.617 (17)	Se2—O4	1.663 (16)
Hg2—O1$^{\rm ii}$	3.219 (15)	Se2—O5	1.705 (14)
Hg2—O2$^{\rm iii}$	2.757 (13)	Se2—O6	1.699 (17)
Hg2—O5	2.064 (15)		
O1—Se1—O2	100.1 (7)	O4—Se2—O5	103.8 (9)
O1—Se1—O3	98.3 (7)	O4—Se2—O6	97.9 (8)
O2—Se1—O3	102.4 (7)	O5—Se2—O6	97.1 (8)

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

The data were corrected for decay. As the absorption is high, both ψ-scan (North, Phillips & Mathews, 1968) and spherical absorption corrections were applied (*International Tables for X-ray Crystallography*, 1967, Vol. II, Table 5.3.6B) with $T_{\max} = 0.995$ and $T_{\min} = 0.705$ for the ψ-scan correction, and $T_{\max} = 0.069$ and $T_{\min} = 0.042$ for the spherical correction. The maximum and minimum electron densities in the final difference Fourier map are located within 1 Å of Hg atoms.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *MolEN PROCESS* (Fair, 1990). Program(s) used to solve structure: *MULTAN* (Main *et al.*, 1982). Program(s) used to refine structure: *MolEN LSFM*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *MolEN*.

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: BR1119). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Amminemercury(II) Selenite

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Abstract

The title compound {amminemercury(II) trioxoselenate(IV), $[Hg(NH_3)]SeO_3$} has a structure comprising corrugated edge-sharing chains of $HgNO_5$ octahedra and SeO_3 pyramids. The chains are apparently held in position by hydrogen bonds. The octahedra are 2 + 4 distorted. The selenite group exhibits one significantly differing Se—O bond length involving an O atom coordinated to three Hg^{II} ions.

Comment

We have reported the structures of three different mercury(II) selenites, $HgSeO_3$, $Hg_3(HSeO_3)_2(SeO_3)_2$ and $Hg_2(SeO_3)_2.H_2O$, previously (Koskenlinna & Valkonen, 1995*a*,*b*, 1996). These compounds contain Hg^{II} ions coordinated by six, six and seven, and five and seven O

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