INORGANIC COMPOUNDS

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Mercury(II) Hydrogenselenite Selenite

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Abstract

The structure of trimercury bis[hydrogentrioxoselenate(1−)] bis[trioxoselenate(2−)], $Hg_3(HSeO_3)_2(SeO_3)_2$, is formed from layers parallel to the *bc* plane with hydrogen bonds between the layers. The two inequivalent Hg^{2+} ions are six- and seven-coordinate. The Hg polyhedra are substantially more distorted in terms of bond lengths compared with the polyhedra in the isomorphous compound $Cd_3(HSeO_3)_2(SeO_3)_2$, but the bond lengths of the hydrogenselenite and the selenite groups in the two compounds are the same within the margin of error.

Comment

Gospodinov & Barkov (1991) reported two different selenites of divalent mercury in the system HgO–SeO_2–H_2O, namely $HgSeO_3$ and $3HgSeO_3.H_2SeO_3$. We reported the crystal structure of $HgSeO_3$ previously; it was found to be isomorphous with the series of compounds $M\text{SeO}_3$, where M = Mg, Mn, Co, Ni, Cu and Zn (Koskenlinna & Valkonen, 1995; Kohn, Inoue, Horie & Akimoto, 1976). $CdSeO_3$ is also isomorphous with this series of selenites (Valkonen, 1994*a*). Cadmium has, in fact, been shown to form a variety of selenium(IV) oxo compounds (Valkonen, 1994*a*,*b*). We have sought to clarify further the structural features of mercury–selenium(IV) oxo compounds.

The title compound contains two Hg^{2+} ions in the asymmetric unit, one in a general and the other in a special position, a selenite ion and a hydrogenselenite ion, making the formula $Hg_3(HSeO_3)_2(SeO_3)_2$. The compound is isomorphous with $Cd_3(HSeO_3)_2(SeO_3)_2$ (Valkonen, 1994*b*). It can be depicted as a layered structure, with layers parallel to the *bc* plane. The coordination polyhedra of the Hg^{2+} ions form edge-sharing pairs which are connected by an edge and a vertex to two other pairs, forming zig-zag double chains; these are connected by selenium ions to form the layers.

The layers are probably held together by hydrogen bonds between atoms O1 and O3 of adjacent layers. The H atom was not detected in difference Fourier maps, but scrutiny of the O···O distances between the protonated O atom O3 and other O atoms reveals only one O···O distance under 3.0 Å between two different selenite groups, making it a plausible choice for a hydrogen-bond donor–acceptor pair. This distance is 2.742 (11) Å, slightly longer than that in $Cu(SeO_2OH)_2$ [2.690 (4) Å; Effenberger, 1985].

One of the Hg^{2+} ions is six-coordinate and the other seven-coordinate. The octahedron of O atoms around the six-coordinate Hg^{2+} ion is tetragonally flattened, with three different pairs of Hg2—O distances [2.163 (8), 2.399 (8) and 2.560 (7) Å]. The distortion is almost as substantial as that in $HgSeO_3$, where the corresponding three pairs of Hg—O distances are 2.103 (11), 2.593 (10) and 2.641 (11) Å (Koskenlinna & Valkonen, 1995). The distortion is notably larger than in the isomorphous compound $Cd_3(HSeO_3)_2(SeO_3)_2$, where the distances are 2.224 (5), 2.282 (4) and 2.425 (5) Å. Two hydrogenselenite and four selenite ions are attached to the six-coordinated Hg^{2+} ion, Hg2, as monodentate ligands.

The heptacoordinate Hg^{2+} ion, Hg1, has a coordination polyhedron which is also more distorted in terms of bond lengths compared with the corresponding CdO_7 polyhedron in $Cd_3(HSeO_3)_2(SeO_3)_2$: the coordination distances in the title compound range between 2.215 (8) and 2.820 (6) Å, while in $Cd_3(HSeO_3)_2(SeO_3)_2$ they range from 2.247 (4) to 2.647 (5) Å (Valkonen, 1994*b*). The coordination polyhedron of Hg1 can be best described as a monocapped trigonal prism. There are two

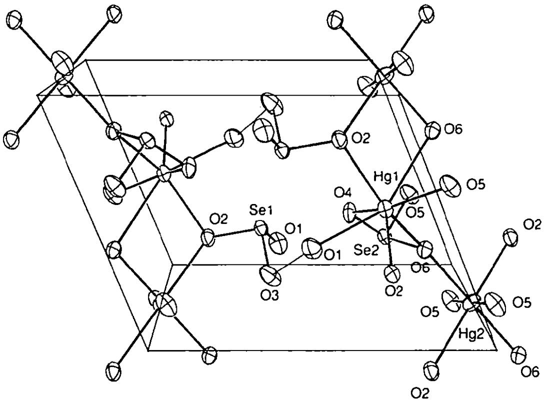

Fig. 1. An *ORTEP*II (Johnson, 1976) drawing of the structure with displacement ellipsoids shown at the 50% level. The *a* axis is horizontal and the *c* axis vertical. Thin lines indicate hydrogen bonding. For clarity, only half of the unit cell in the *b* direction is shown (0.25 < *b* < 0.75).

hydrogenselenite and two selenite ions arranged around Hg1 as one monodentate (a hydrogenselenite) and three bidentate ligands.

The hydrogenselenite ion exhibits an elongated Se—O bond length, 1.764 (9) Å, to the protonated O atom; this O atom is not within bonding distance of either of the Hg ions. A second O atom of the hydrogenselenite group forms an elongated bond, 1.707 (7) Å, probably because it is coordinated to three metals ions. The third bond length is normal, 1.654 (9) Å. In $Cu(SeO_2OH)_2$, the short Se—O bonds are 1.665 (2) and 1.688 (2) Å, while the elongated bond is 1.773 (2) Å (Effenberger, 1985). The hydrogenselenite ion links three Hg^{2+} ions.

The selenite group exhibits two bond lengths which are longer than normal, 1.705 (7) and 1.730 (8) Å, while the third lies within the normal range, 1.680 (9) Å. The shorter of the elongated bonds is to an O atom coordinated to two metal ions, while the longer one is to an O atom coordinated to three metal ions. The third bond is to an O atom coordinated to one metal ion. The selenite ion joins four metal ions.

The corresponding Se—O bond lengths of the selenite and hydrogenselenite groups are the same, within the margin of error, in the isomorphous Cd compound, where they range between 1.663 (6) and 1.750 (7) Å in the hydrogenselenite ion and between 1.683 (4) and 1.725 (4) Å in the selenite ion. Thus, the selenite ion seems to maintain its geometry in the two isomorphous compounds.

Experimental

The title compound was prepared by adding aqueous, concentrated selenious acid to solid Hg_2SO_4 in stoichiometric excess together with a few drops of HNO_3. When allowed a controlled partial evaporation at 370 K over one week, the oxidation of Hg_2^{2+} yielded Hg^{2+} ions, and bar-like colourless crystals of the title compound formed. Needle-like crystals of $HgSeO_3$ are formed at the same time.

Crystal data

$Hg_3(HSeO_3)_2(SeO_3)_2$
$M_r = 1111.62$
Monoclinic
$P2_1/c$
$a = 9.480 (3)$ Å
$b = 9.400 (3)$ Å
$c = 7.399 (2)$ Å
$\beta = 112.22 (3)^\circ$
$V = 610.4 (4)$ Å^3
$Z = 2$
$D_x = 6.05$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 2–10^\circ$
$\mu = 49.50$ mm^{-1}
$T = 294$ K
Prism
0.2 × 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)
$T_{\min} = 0.016$, $T_{\max} = 0.069$
1882 measured reflections
1882 independent reflections

1355 observed reflections [$I > 3\sigma(I)$]
$\theta_{\max} = 29.95^\circ$
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 13$
$l = -10 \rightarrow 9$
2 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F
$R = 0.029$
$wR = 0.036$
$S = 1.037$
1355 reflections
89 parameters
H atoms not included
$w = 1/[\sigma^2(F) + (0.02F)^2 + 1.00]$ (Killean & Lawrence, 1969)
$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 2.595$ e Å^{-3}
$\Delta\rho_{\min} = -1.797$ e Å^{-3}
Extinction correction: isotropic (Zachariasen, 1963)
Extinction coefficient: 0.19×10^{-6}
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)*

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

	x	y	z	U_{eq}
Hg1	0.83927 (4)	0.14044 (4)	0.95892 (6)	0.0233 (1)
Hg2	1	1/2	1	0.0270 (2)
Se1	0.5938 (1)	0.3759 (1)	0.7042 (1)	0.0213 (4)
Se2	0.1988 (1)	0.1564 (1)	0.2534 (1)	0.0209 (4)
O1	0.5706 (9)	0.2325 (9)	0.8194 (12)	0.036 (4)
O2	0.7838 (8)	0.3546 (8)	0.7545 (11)	0.028 (3)
O3	0.6134 (9)	0.5121 (9)	0.8759 (13)	0.039 (4)
O4	0.2797 (7)	0.0709 (9)	0.1179 (11)	0.030 (3)
O5	0.0592 (9)	0.2549 (8)	0.0860 (12)	0.030 (4)
O6	0.0846 (7)	0.0166 (8)	0.2672 (10)	0.027 (3)

Table 2. *Selected geometric parameters (Å)*

Hg1—O1	2.513 (8)	Hg2—O5^{v}	2.399 (8)
Hg1—O2	2.453 (8)	Hg2—O6^{vi}	2.163 (8)
Hg1—O2^{i}	2.435 (9)	Hg2—O6^{vii}	2.163 (8)
Hg1—O4^{ii}	2.249 (8)	Se1—O1	1.654 (9)
Hg1—O5^{iii}	2.215 (8)	Se1—O2	1.707 (7)
Hg1—O6^{iii}	2.820 (6)	Se1—O3	1.764 (9)
Hg1—O6^{ii}	2.532 (8)	Se2—O4	1.680 (9)
Hg2—O2	2.560 (7)	Se2—O5	1.705 (7)
Hg2—O2^{iv}	2.560 (7)	Se2—O6	1.730 (8)
Hg2—O5^{iii}	2.399 (8)		

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

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: direct methods (*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 BTABLE PTABLE* and *CIF IN*.

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: BR1108). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Hydrazinium(1+) Hexafluorogallate(III) and Hydrazinium(2+) Aquapentafluorogallate(III)

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Abstract

$(N_2H_5)_3[GaF_6]$ contains GaF_6^{3-} octahedra arranged in a distorted cubic close-packed manner and linked to hydrazinium(1+) ions *via* N—H···F hydrogen bonds. $(N_2H_6)[GaF_5(H_2O)]$ contains $[GaF_5(H_2O)]^{2-}$ octahedra arranged in a similar distorted cubic close-packed manner; in addition to N—H···F hydrogen bonds to hydrazinium(2+) ions, these octahedra are also linked directly *via* O—H···F hydrogen bonds.

Comment

The structures studied here are those of two members of the family of hydrazinium(1+) [hydrazinium(1+) hexafluorogallate, (I)] or -(2+) [hydrazinium(2+) aquapentafluorogallate, (II)] fluorometallates of main Group III metals. Compounds in this family for which the structures are known are $N_2H_5[BF_4]$ (Conant & Roof, 1970), $N_2H_6[BF_4]_2$ (Frlec, Gantar, Golič & Leban, 1984) and $(N_2H_{5.5})_2[GaF_6].2H_2O$ (Meden, Golič & Šiftar, 1992), which contain isolated fluorometallate ions, and $N_2H_5[InF_4(H_2O)]$ (Bukovec & Golič, 1976), which contains chains of complex ions. Extensive hydrogen bonding of the type N—H···F is present in all of the above. The structures of both (I) and (II) contain quite regular octahedra, which are isolated from each other and are arranged in a distorted f.c.c. fashion (see Figs. 1 and 2).

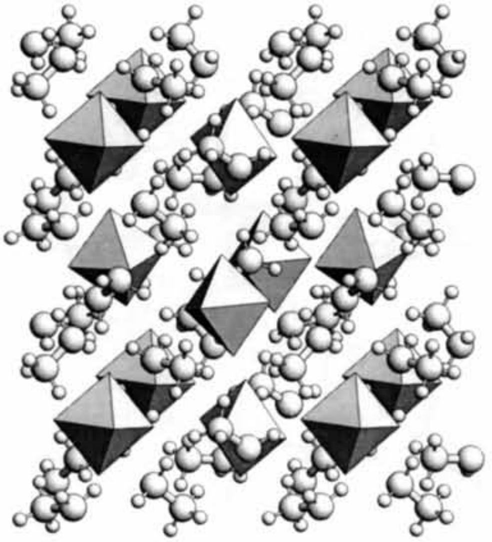

Fig. 1. *ATOMS* (Dowty, 1991) plot of the structure of $(N_2H_5)_3[GaF_6]$ showing the packing of the octahedra and positions of hydrazinium(1+) ions (more than one unit cell is shown).

Fig. 2. *ATOMS* (Dowty, 1991) plot of the structure of $(N_2H_6)[GaF_5(H_2O)]$ showing the packing of the octahedra and positions of hydrazinium(2+) ions (more than one unit cell is shown).