Hydrogen-bonding geometry

D—H$\cdots A$	H$\cdots A$	D—H$\cdots A$
O(1^{iv})—H(12^{iv})$\cdots$O	1.79 (2)	178 (2)
O(2)—H(21)$\cdots$O	1.80 (2)	177 (2)
O(3^v)—H(31^v)$\cdots$O	1.63 (2)	177 (2)
O(3^{vi})—H(32^{vi})$\cdots$O	2.26 (2)	164 (2)
O(4^{vii})—H(41^{vii})$\cdots$O	2.12 (2)	164 (2)
O(4^{viii})—H(42^{viii})$\cdots$O	1.88 (2)	173 (2)

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

All H atoms were found in difference Fourier maps and refined isotropically. All calculations were performed on a PC486 with the program SHELXL93 (Sheldrick, 1993). Graphics were produced using the program SCHAKAL92 (Keller, 1993).

Lists of structure factors and anisotropic displacement parameters have been deposited with the IUCr (Reference: OH1071). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Mercury(II) Selenite

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Abstract

The title structure, HgSeO$_3$, is isomorphous with those of a series of perovskite-like MSeO$_3$ compounds and contains corner-sharing HgO$_6$ octahedra, connecting to form a three-dimensional network, and Se^{4+} ions in the cavities of the structure. The octahedron is substantially distorted with Hg—O bond distances between 2.103 (11) and 2.641 (11) Å. The geometry of the selenite group

deviates significantly from those of the selenites of the isomorphous series.

Comment

Crystal structures of selenite compounds of mercury(II) have not been reported previously. In a study of the solubility of the system HgO–SeO$_2$–H$_2$O, two phases with compositions HgSeO$_3$ and 3HgSeO$_3$.H$_2$SeO$_3$ were reported to exist (Gospodinov & Barkov, 1991). The study further confirmed previous findings that HgSeO$_3$ crystallizes in two polymorphic forms of which one is stable at 298 K and the other at 373 K. The two forms are reported to be isomorphous with corresponding polymorphs of ZnSeO$_3$ and CdSeO$_3$ (Markovskii & Sapozhnikov, 1961; Gospodinov & Bogdanov, 1983; Micka, Uchytilova & Ebert, 1984).

Selenite forms an isomorphous series of distorted perovskite-like MSeO$_3$ structures in space group $Pnma$, where M is Mg^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+}, as reported by Kohn, Inoue, Horie & Akimoto (1976). The metal in compounds of this series is octahedrally coordinated. Recently, Cd^{2+} was also found to form two polymorphous forms of selenite, one of which is isomorphous with the perovskite-like structures, while the other was found to be a monoclinic CdSeO$_3$ structure (Valkonen, 1994). In addition, the crystal structure of another polymorph of ZnSeO$_3$, in space group $Pbca$, has been reported, in which the Zn atom is five-coordinate (Bensch & Gunter, 1986). It seemed interesting to explore the crystallization of HgSeO$_3$ and compare the structure to the above different crystal forms.

HgSeO$_3$ (prepared in this study) crystallizes in space group $Pnma$, isomorphous with the series of perovskite-like MSeO$_3$ structures. The structure can be depicted as composed of HgO$_6$ octahedra linked together at corners to form a three-dimensional network, with Se^{4+} ions in the cavities of this network. Alternatively, it can be considered as a structure in which the selenite group bridges six Hg^{2+} ions, with all selenite O atoms within bonding distance of two Hg^{2+} ions.

Within the Hg^{2+} coordination octahedron, three unequal pairs of metal–oxygen distances were found [2.103 (11), 2.593 (10) and 2.641 (11) Å] representing a substantial tetragonal flattening of the octahedron. Tetragonal flattening, although notably less marked, was also found in isomorphous ZnSeO$_3$, where the corresponding distances were 2.089, 2.177 and 2.223 Å, whereas in isomorphous CdSeO$_3$, the octahedron about the metal ion was rather regular with corresponding distances of 2.271, 2.348 and 2.357 Å. In isomorphous CuSeO$_3$, the difference between the smallest and largest metal–oxygen distance was even larger than that in the present compound (0.602 Å), but the octahedron was elongated, as is typical of six-coordinate copper (Kohn, Inoue, Horie & Akimoto, 1976; Valkonen, 1994).

The metal–oxygen distances in the present compound are rather typical of six-coordinate Hg^{2+}, as is the 2 + 4 coordination scheme. In $HgHPO_4$, the bond range for the 2 + 4 distorted HgO_6 octahedron is 2.060(9)–2.924(10) Å and the sites of nine other distorted 2 + 4 octahedra (with either tetragonal elongation or flattening) were reported, having a short-bond range of 2.0–2.1 and a long-bond range of 2.6–2.8 Å (Dubler, Beck, Linowsky & Jameson, 1981).

The Se—O distances in $HgSeO_3$ are not similar to those in isomorphous $ZnSeO_3$ and $CdSeO_3$. While in the latter compounds the bond lengths are 1.717 and 1.723 Å (2×), and 1.706 and 1.713 Å (2×), respectively, in the present compound they are 1.660(17) and 1.734(11) Å (2×). Also, the pyramidal shape of the selenite group in the present compound is flatter than usual, with the O—Se—O bond angles between 102.9(6) and 103.2(5)°, as compared to 95.4 and 104.1° for $ZnSeO_3$, and 100.5 and 103.0° for $CdSeO_3$ (Kohn, Inoue, Horie & Akimoto, 1976; Valkonen, 1994).
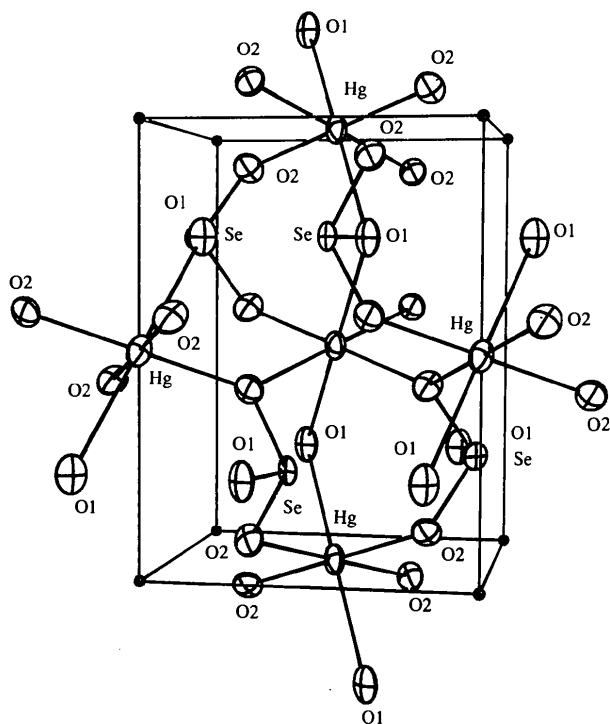

Fig. 1. An *ORTEPII* (Johnson, 1976) drawing of the unit cell with 75% probability ellipsoids. The a axis is horizontal and the b axis vertical.

Experimental

The title compound was crystallized from an aqueous solution of SeO_2 with solid $HgSO_4$ by allowing the suspension to stand at temperatures between 330 and 370 K for one to two weeks.

Crystal data

HgSeO₃
$M_r = 327.55$

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å

Orthorhombic
Pnma
$a = 6.110(1)$ Å
$b = 8.205(1)$ Å
$c = 5.868(1)$ Å
$V = 294.16(7)$ Å³
$Z = 4$
$D_x = 7.40$ Mg m⁻³

Cell parameters from 25 reflections
$\theta = 15$–26°
$\mu = 64.349$ mm⁻¹
$T = 294$ K
Prism
$0.07 \times 0.04 \times 0.04$ mm
White

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical via ψ scan (North, Phillips & Mathews, 1968)
$T_{min} = 0.510$, $T_{max} = 0.998$
2584 measured reflections
791 independent reflections

296 observed reflections $[I > 3.0\sigma(I)]$
$R_{int} = 0.049$
$\theta_{max} = 34.95°$
$h = 0 \rightarrow 9$
$k = -13 \rightarrow 13$
$l = -9 \rightarrow 9$
2 standard reflections frequency: 60 min intensity decay: 0.1%

Refinement

Refinement on F
$R = 0.026$
$wR = 0.032$
$S = 0.363$
296 reflections
29 parameters
H atoms were not included in the refinement
$w = 1/[\sigma^2(F) + (0.02F)^2 + 1]$ (Killean & Lawrence, 1969)
$(\Delta/\sigma)_{max} = 0.001$

$\Delta\rho_{max} = 2.542$ e Å⁻³
$\Delta\rho_{min} = -2.598$ e Å⁻³
Extinction correction: isotropic (Zachariasen, 1963)
Extinction coefficient: $0.80(1) \times 10^{-6}$
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* (Å²)

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

	x	y	z	U_{eq}
Hg	0	0	0	0.0129 (2)
Se	0.0558 (2)	1/4	0.5021 (9)	0.0112 (5)
O1	0.134 (3)	1/4	0.231 (3)	0.014 (6)
O2	0.195 (2)	0.085 (1)	0.616 (2)	0.017 (5)

Table 2. *Selected geometric parameters* (Å)

Hg—O1	2.593 (10)	Hg—O2^v	2.103 (11)
Hg—O1^i	2.593 (10)	Se—O1	1.660 (17)
Hg—O2^{ii}	2.641 (11)	Se—O2	1.734 (12)
Hg—O2^{iii}	2.641 (11)	Se—O2^{vi}	1.734 (12)
Hg—O2^{iv}	2.103 (11)		

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

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: *MULTAN*11/82 (Main *et al.*, 1982). Program(s) used to refine structure: *MolEN LSFM*. Molecular graphics: *ORTEPII* (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: HU1145). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Polytypism of CuFe$_2$(OH)$_2$(AsO$_4$)$_2$: the Triclinic Modification

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Abstract

The triclinic modification of dimorphic CuFe$_2$(OH)$_2$-(AsO$_4$)$_2$ is presented. The O atoms are cubic close packed; between succeeding layers only alternate octahedral or tetrahedral positions are occupied. Within the 'octahedral sheets', Cu$^{[4+2]}$(O$_h$)$_2$O$_4$ and Fe$^{[6]}$(O$_h$)$_2$O$_4$ (O$_h$ = hydroxyl O atom) polyhedra are edge-connected

to form bands; 2/5 of the positions are vacant. These □O$_6$ octahedra each share one face with an AsO$_4$ anion of the 'tetrahedral sheet'; bifurcated hydrogen bonds link neighbouring octahedral sheets.

Comment

A number of structure types for compounds with the general formula $M^{2+}M_2^{3+}$(OH)$_2$(XO$_4$)$_2$ (X = P, As) have been described. The most prominent is the monoclinic lazulite-type known from several minerals: lazulite, MgAl$_2$(OH)$_2$(PO$_4$)$_2$ (Giuseppetti & Tadini, 1983), scorzalite, (Fe,Mg)Al$_2$(OH)$_2$(PO$_4$)$_2$ (Lindberg & Christ, 1959), barbosalite, Fe$_3$(OH)$_2$(PO$_4$)$_2$ (Lindberg & Christ, 1959), and hentschelite, CuFe$_2$(OH)$_2$(PO$_4$)$_2$ (Sieber, Tillmanns & Hofmeister, 1987). Even the substitution of M^{3+} by M^{2+} combined with the incorporation of a protonated XO_3OH group has been described: Co$_3$(OH)$_2$(PO$_3$OH)$_2$ (Effenberger, 1992). Lazulite-type arsenates are unknown.

With cations of larger atomic radii and, therefore, higher coordination numbers, the structure type changes, *e.g.* jagowerite, BaAl$_2$(OH)$_2$(PO$_4$)$_2$ (Meagher, Gibbons & Trotter, 1974), and carminite, PbFe$_2$(OH)$_2$(AsO$_4$)$_2$ (Finney, 1963). Moreover, Fe$_3$(OH)$_2$(PO$_4$)$_2$ forms a tetragonal polytype (lipscombit; Vencato, Mattievich & Mascarenhas, 1989).

The orthorhombic modification of CuFe$_2$(OH)$_2$-(AsO$_4$)$_2$ (Effenberger, 1988) is closely related to the lazulite structure type: one M^{2+}(O$_h$)$_2$O$_4$ and two M^{3+}(O$_h$)$_2$O$_4$ octahedra share faces to form $M^{2+}M_2^{3+}$-(O$_h$)$_4$O$_8$ trimers. The M^{3+}(O$_h$)$_2$O$_4$ octahedra are linked *via* O$_h$ atoms into chains. As a result, corrugated sheets are formed with the undulations in the two phases being different. The layers are interconnected by XO_4 tetrahedra and by hydrogen bonds.

In triclinic CuFe$_2$(OH)$_2$(AsO$_4$)$_2$ (Fig. 1), the modes of coordination are as usual. The Cu^{II} atom has site symmetry $\bar{1}$ and is [4 + 2] coordinated to form an elongated octahedron, showing characteristic Jahn–Teller distortions due to the d^9 electronic configuration (Norrestam, 1994). The two Cu—O$_h$ bonds are the shortest bonds within this polyhedron; the average bond length within the square formed by the four nearest neighbours is 1.957 Å. The additional bonds are almost 2.50 Å in length, indicating only weak interactions. The Fe(O$_h$)$_2$O$_4$ octahedron is less distorted. The longest bonds are to the O$_h$ atoms. Contrary to the orthorhombic polytype the O$_h$ atoms are in a *cis* arrangement. The average Fe—L bond length of 2.017 Å is in accordance with expectations for the trivalent oxidation state (L is an unspecified ligand belonging either to the arsenate group or to the hydroxyl group). The arsenate tetrahedron has an average As—O bond length of 1.687 Å. As a result of face-to-face connection, orthorhombic CuFe$_2$(OH)$_2$(AsO$_4$)$_2$ shows stronger distortion of the coordination polyhedra.