HgWO$_4$ synthesized at high pressure and temperature

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Crystals of mercury(II) tungstate(VI), HgWO$_4$, were grown in sealed gold tubes under an Ar atmosphere at 300 MPa and 973 K. The monoclinic crystal structure ($C2/c$) of HgWO$_4$ consists of zigzag chains of edge-sharing WO$_6$ octahedra running along the c axis and layers of very distorted corner-sharing HgO$_6$ octahedra in the bc plane. The Hg atom lies on an inversion centre and the W atom is on a twofold axis. No structural effects which can be ascribed to the high pressure used in the synthesis were found.

Comment

Tungstates are of interest for their luminescent properties, for use as detectors and calorimeters in high-energy experiments and in X-ray imaging. Strong absorption of high-energy radiation, in combination with a high density (9.2 Mg m^{-3}), are some of the attractive properties of the title compound.

The crystal structure of HgWO$_4$ has recently been determined from neutron powder diffraction data by Rietveld refinements (Åsberg Dahlborg & Svensson, 2000). The two main differences between the previous powder study and the present single-crystal study are, first, that isotropic displacement parameters were used in the powder study, and secondly, the high pressure which was used for the growth of single crystals. In order to correlate structure with luminescent properties, precise structural information is needed, preferably from single-crystal data. This prompted us to perform the study which is presented herein.

HgWO$_4$ has a structure related to that of wolframite (Keeling, 1957) and is isostructural with HgMoO$_4$ (Jeitschko & Sleight, 1973). The structure consists of zigzag chains of edge-sharing WO$_6$ octahedra extending parallel to the c axis. There are two short W—O bonds [1.733 (5) Å], two medium [1.953 (4) Å] and two long bonds [2.197 (5) Å]. The O1—O1($-x$, $-y$, $-z$) edge distance shared between connected WO$_6$ octahedra is only 2.372 (8) Å, while the other O—O distances are in the range 2.753 (8)–2.916 (8) Å. The W atom is displaced 0.337 Å from the centre of the WO$_6$ octahedron, calculated as the centre of gravity for the six O atoms.

In the bc plane, layers of corner-sharing HgO$_6$ octahedra are formed. The HgO$_6$ octahedra are very distorted, with two short collinear Hg—O bonds [2.044 (4) Å] and two pairs of long Hg—O distances [2.633 (5) and 2.743 (5) Å]. If the next O atoms, at a distance of 3.131 (5) Å from Hg, are included in the coordination, Hg is eight-coordinate. These HgO$_8$ polyhedra can be described as distorted cubes. The layer in the bc plane is then formed by edge-sharing HgO$_8$ cubes.

The only significant difference in bond distances in this study, compared with the neutron powder diffraction study, is the shorter W—W distance of 3.4143 (4) Å, compared with a distance of 3.425 (4) Å in the powder study. All the W—O distances are slightly shorter and all the Hg—O distances are
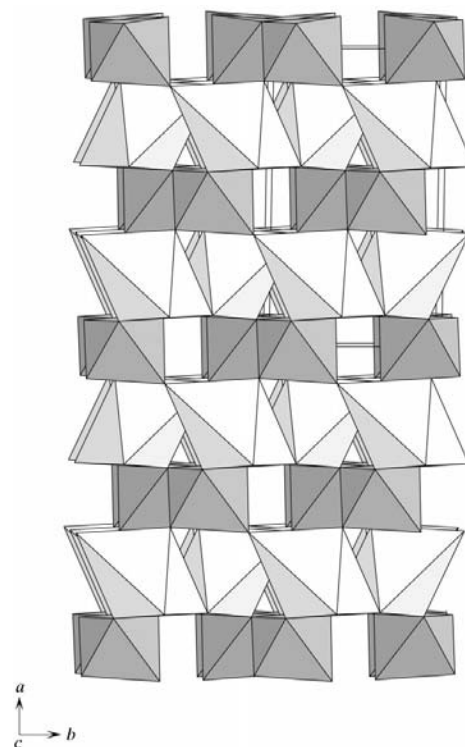
Figure 1
A polyhedral representation of HgWO$_4$ viewed along the c axis, with the b axis horizontal. The WO$_6$ octahedra are dark grey and the HgO$_6$ octahedra are light grey.
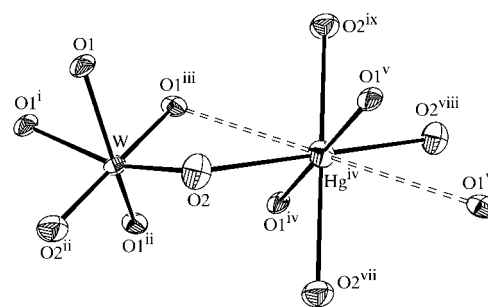
Figure 2
An *ORTEP*-3 plot (Farrugia, 1997) of the Hg and W coordination to O atoms in HgWO$_4$. Displacement ellipsoids are drawn at the 80% probability level [symmetry codes: (i) $-x$, $-y$, $-z$; (ii) $-x$, y, $\frac{1}{2} - z$; (iii) x, $-y$, $\frac{1}{2} + z$; (iv) x, y, $1 + z$; (v) $\frac{1}{2} - x$, $\frac{1}{2} - y$, $1 - z$; (vi) $\frac{1}{2} - x$, $\frac{1}{2} + y$, $\frac{3}{2} - z$; (vii) x, $1 - y$, $\frac{1}{2} + z$; (viii) $\frac{1}{2} - x$, $\frac{1}{2} - y$, $2 - z$; (ix) $\frac{1}{2} - x$, $y - \frac{1}{2}$, $\frac{3}{2} - z$].

DOI: 10.1107/S0108270102000379   **i35**

slightly longer in the present single-crystal structure determination.

Displacement ellipsoids show that Hg has the largest displacements in the plane of the four long Hg—O bonds of the HgO$_6$ octahedron, as expected. U_{eq} is smaller for O1 than for Hg, which is in agreement with the neutron powder refinement. The displacement parameters for W are small and only slightly anisotropic.

Despite the differences in pressure, sample preparation and experimental data collection, there are very small differences between the results from the present single-crystal determination and the older structure determined from powder data. No effects which can be ascribed to the high pressure used for single-crystal synthesis have been found.

Experimental

Colourless prismatic crystals of HgWO$_4$ were synthesized under high gas pressure in collapsible gold tubes. The reaction mixture was composed of Na$_2$WO$_4$·2H$_2$O (Johnson Matthey, 95%) and HgCl$_2$ (Merck, 99.5%) in a 1:1 ratio. The reactants were loaded into a gold tube, which was then welded shut and placed inside a three-zone kanthal furnace, which was part of a high-pressure system (Lada *et al.*, 1998). The pressure was increased to 300 MPa using Ar as the pressure medium and the temperature was adjusted to 973 K. After 10 h, the temperature was decreased to room temperature over a period of a few hours, after which the pressure was decreased to 1 atm (1 atm = 101 325 Pa). The resulting prismatic crystals of HgWO$_4$ were washed with water. The largest crystals were about 1 mm in the longest direction.

Crystal data

HgWO$_4$	$D_x = 9.212$ Mg m^{-3}
$M_r = 448.44$	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 25
$a = 11.3791$ (4) Å	reflections
$b = 6.00794$ (15) Å	$\theta = 23.4$–46.5°
$c = 5.1456$ (3) Å	$\mu = 82.80$ mm^{-1}
$\beta = 113.202$ (3)°	$T = 293$ (2) K
$V = 323.33$ (2) Å^3	Prism, colourless
$Z = 4$	$0.06 \times 0.03 \times 0.03$ mm

Data collection

Enraf–Nonius TurboCAD-4 diffractometer	620 reflections with $I > 2\sigma(I)$
$\omega/2\theta$ scans	$R_{int} = 0.053$
Absorption correction: Gaussian; a grid of $12 \times 20 \times 48$ was used (Spek, 1990)	$\theta_{max} = 34.9°$
	$h = -18 \rightarrow 0$
	$k = -9 \rightarrow 9$
	$l = -7 \rightarrow 8$
$T_{min} = 0.078$, $T_{max} = 0.172$	3 standard reflections
1750 measured reflections	frequency: 60 min
713 independent reflections	intensity decay: none

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} < 0.001$
$R(F) = 0.027$	$\Delta\rho_{max} = 3.10$ e Å^{-3}
$wR(F^2) = 0.070$	$\Delta\rho_{min} = -3.13$ e Å^{-3}
$S = 1.10$	Extinction correction: *SHELXL*97
713 reflections	(Sheldrick, 1997)
31 parameters	Extinction coefficient: 0.0031 (3)
$w = 1/[\sigma^2(F_o^2) + (0.0453P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$	

Table 1
Selected geometric parameters (Å, °).

W—O2	1.733 (5)	Hg—O2^{iv}	2.743 (5)
W—O1	1.953 (4)	Hg—O1^{v}	3.131 (5)
W—O1^{i}	2.197 (5)	W—W^{i}	3.4143 (4)
Hg—O1^{ii}	2.044 (4)	W—Hg	3.57426 (12)
Hg—O2^{iii}	2.633 (5)	W—Hg^{vi}	3.7082 (2)
O1—W—O1^{i}	69.42 (19)	O1^{ii}—Hg—O2^{iv}	85.33 (18)
O1^{i}—W—O1^{vii}	80.8 (2)	O1—Hg—O2^{iii}	88.22 (17)
O1—W—O1^{vii}	84.61 (13)	O1^{ii}—Hg—O2^{iii}	91.78 (17)
O2^{viii}—W—O1^{i}	89.3 (2)	O1—Hg—O2^{iv}	94.67 (18)
O2—W—O1	96.5 (2)	O2^{ix}—Hg—O2^{iv}	111.29 (14)
O2—W—O2^{viii}	103.2 (4)	O1^{ii}—Hg—O1	180.0 (2)
O2^{viii}—W—O1	104.5 (2)	O2^{iii}—Hg—O2^{ix}	180.0 (2)
O1—W—O1^{viii}	146.0 (3)	O2^{iv}—Hg—O2^{x}	180.00 (19)
O2—W—O1^{i}	163.4 (2)	W—O2—Hg^{xi}	119.9 (3)
O2^{iii}—Hg—O2^{iv}	68.71 (14)		

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

The maximum extinction correction (*SHELXL*97; Sheldrick, 1997) was $y = 0.84$ for the 111 reflection (the observed structure factor is $F_{obs} = yF_{kin}$, where F_{kin} is the kinematic value of the structure factor). The highest residual electron-density peak was located 0.95 Å from O2 and 0.97 Å from W. There were also peaks between Hg and O1.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *LATCON* (Schwarzenbach & King, 1999); data reduction: *XCAD*4 (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97; molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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