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Mercury(II) tungstate from neutron powder data

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Mercury(II) tungstate powder, $HgWO_4$, was prepared by boiling a mixture of HgO and H_2WO_4 in water. Rietveld refinements on neutron powder data showed that the monoclinic structure ($C2/c$) consists of zigzag chains of edge-sharing HgO_6 and WO_6 octahedra. The Hg atom lies on an inversion centre and the W atom lies on a twofold axis. The Hg atom forms two characteristic short collinear Hg—O bonds.

Comment

The structure determination of the title compound is part of a study of divalent metal ion tungstates (MWO_4; Åsberg Dahlborg & Svensson, 1999). These materials are of interest for their luminescent properties and find their applications as detector materials for high-energy radiation and particles (Blasse & Grabmaier, 1994). The high density (9.2 Mg m^{-3}) and strong absorption of high-energy radiation makes $HgWO_4$ interesting for electromagnetic calorimetry applications.

$HgWO_4$ has not been as thoroughly examined as the other tungstates, but Swindells (1951) has previously reported the synthesis and emission spectra for $HgWO_4$. Later, Blasse & van den Heuvel (1974) investigated the luminescence properties further and compared them with other tungstates, but no structure refinements have been carried out on $HgWO_4$.

Most divalent metal ion tungstates (AWO_4) belong to either the scheelite structure (Sillén & Nylander, 1943), if the radius of A is greater than 1 Å, or the wolframite structure (Keeling, 1957), if the radius of A is smaller than 1 Å. The radius of the Hg^{2+} ion is close to 1 Å and $HgWO_4$ does not belong to either the wolframite or the scheelite structure. The structure of $HgMoO_4$ was published in 1973 (Jeitschko & Sleight, 1973) and is closely related to the wolframite structure. It was also shown that $HgWO_4$ belongs to the same structure type but no structural data were published. Difficulties in growing single crystals and the combination of light and heavy atoms together with strong X-ray absorption prompted us to use neutron powder diffraction and Rietveld refinements to get accurate structural parameters.

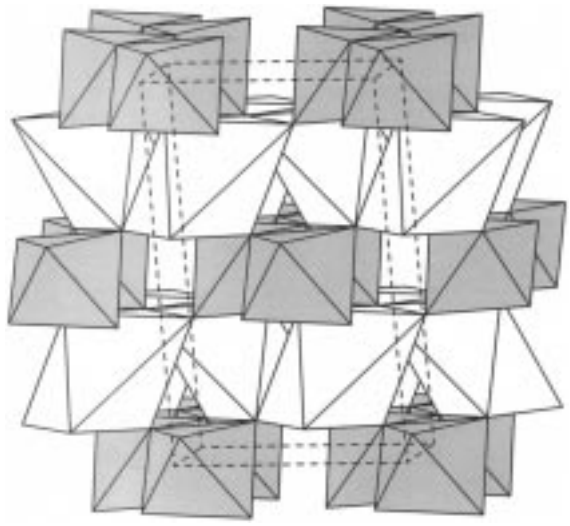

Figure 1
Polyhedral representation of $HgWO_4$ viewed along the c axis with b horizontal. The WO_6 octahedra are grey and the HgO_6 octahedra are white.

The structure of $HgWO_4$ consists of zigzag chains of edge-sharing WO_6 octahedra extending parallel to the c axis (Fig. 1). The O atoms form close-packed layers parallel to the yz plane. The stacking is close to cubic close-packing but adjacent ABC layers are slightly displaced relative to each other so that the fifth layer, B', corresponds to the A layer. Thus, the octahedral voids accommodating the Hg atoms are very distorted. As expected, mercury forms two short collinear Hg—O bonds with an Hg—O distance of 2.039 (4) Å. The other two pairs of Hg—O bonds are 2.627 (3) and 2.731 (3) Å, forming a very distorted octahedron. By edge-sharing, the HgO_6 octahedra also form zigzag chains running along the c axis.

The structure of $HgWO_4$ is closely related to the wolframite structure of the other d^{10} elements, $ZnWO_4$ and $CdWO_4$

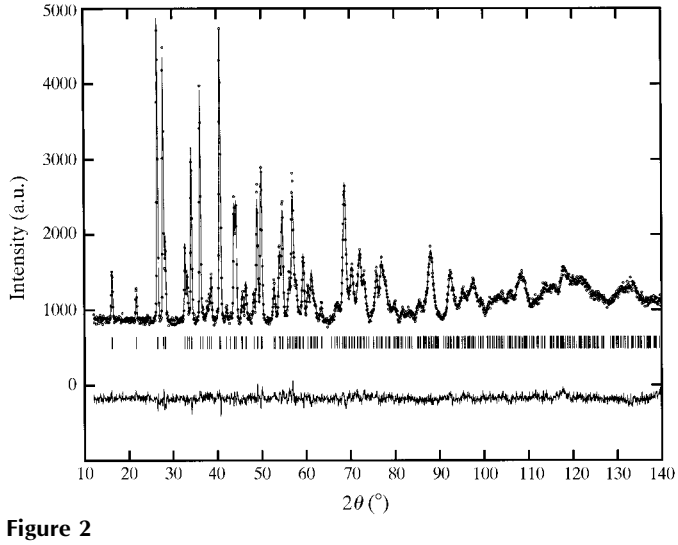

Figure 2
Comparison of observed (dots) and calculated (solid line) intensities for $HgWO_4$. Tick marks below the diffractogram represent the allowed Bragg reflections. The difference intensities are located at the bottom of the figure.

(Åsberg Dahlborg & Svensson, 1999), since the polyhedra are interconnected in the same way. However, the coordination polyhedron around the Hg atom makes the $HgWO_4$ structure different from $ZnWO_4$ and $CdWO_4$. The O—Hg—O angles are all 180°, whereas the O—Zn—O and O—Cd—O angles are about 160° in $ZnWO_4$ and $CdWO_4$. The WO_6 octahedra in the three structures are very similar. The WO_6 octahedron in $HgWO_4$, however, is more tetrahedral than in $ZnWO_4$ and $CdWO_4$.

Experimental

The title compound was prepared by mixing equal amounts of HgO and H_2WO_4 in water. The mixture was boiled for a few minutes until the orange colour of HgO disappeared. The product was filtered and dried at room temperature. The resulting powder was pale yellow.

Crystal data

$HgWO_4$
M_r = 448.44
Monoclinic, $C2/c$
a = 11.3606 (8) Å
b = 6.0125 (4) Å
c = 5.1482 (4) Å
β = 113.159 (4)°
V = 323.32 (4) Å^3
Z = 4
D_x = 9.212 Mg m^{-3}
Neutron radiation
λ = 1.470 Å
T = 295 K
Specimen shape: cylinder
Specimen colour: pale yellow
10 × 10 × 10 mm
Specimen prepared at 373 K

Data collection

Neutron powder diffractometer
Neutron Powder Diffractometer at NFL, Studsvik, Sweden
Specimen mounting: vanadium can
Specimen mounted in transmission mode
T = 295 K
$2\theta_{min}$ = 4, $2\theta_{max}$ = 139.92°
Increment in 2θ = 0.08°

Table 1
Selected geometric parameters (Å, °).

Hg—O1	2.039 (4)	Hg—W	3.5690 (5)
Hg—O2^{i}	2.627 (3)	Hg—W^{iii}	3.712 (3)
Hg—O2^{ii}	2.731 (3)	Hg—W^{i}	3.8064 (5)
W—O2	1.745 (4)	Hg—Hg^{iv}	3.9577 (2)
W—O1	1.958 (4)	W—W^{iii}	3.425 (4)
W—O1^{iii}	2.201 (5)		
O1—Hg—O1^{v}	180		

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

Refinement

Refinement on I_{net}
R_p = 0.0282
R_{wp} = 0.0354
R_{exp} = 0.0288
R_B = 0.0466
$2\theta_{min}$ = 12.0, $2\theta_{max}$ = 139.92°
Increment in 2θ = 0.08°
Wavelength of incident radiation: 1.470 Å
Excluded region(s): 4–12°, no Bragg peaks
Profile function: pseudo-Voigt
27 parameters
Weighting scheme based on measured s.u.'s
$(\Delta/\sigma)_{max}$ < 0.01
Preferred orientation correction: none
Scattering factors from *FULLPROF* (Rodriguez-Carvajal, 1997)

As $HgWO_4$ is isostructural with $HgMoO_4$ and the ionic radius of W is very close to that of Mo, the structural parameters of $HgMoO_4$ were taken as starting parameters for the structural refinement of $HgWO_4$. The program *FULLPROF* (Rodriguez-Carvajal, 1997) was used for refining the cell and structure. The profile shape was represented by a pseudo-Voigt function. Profile, lattice, structure parameters, zero-point shift, six background parameters and the scale factor were refined without correction for preferred orientation. Atomic displacements were assumed to be isotropic. *WINPLOTR* (Roisnel & Rodriguez-Carvajal, 1999) was used for plotting the powder diffractogram and *ATOMS* (Dowty, 1998) was used for the polyhedral representation. The weight function used in the refinements was $1/u^2$, where u is the s.u. for the observed intensities of each data point.

Program(s) used to refine structure: *FULLPROF*; software used to prepare material for publication: *WINPLOTR*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1261). Services for accessing these data are described at the back of the journal.

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