Canadian Mineralogist
Vol. 22, pp. 681-688 (1984)

THE CRYSTAL STRUCTURE OF TUNGSTITE, $WO_3 \cdot H_2O$

JAN T. SZYMAŃSKI
Mineral Sciences Laboratories, CANMET, Department of Energy, Mines & Resources,
555 Booth Street, Ottawa, Ontario K1A 0G1

ANDREW C. ROBERTS
Geological Survey of Canada, 601 Booth Street, Ottawa, Ontario K1A 0E8

ABSTRACT

The crystal structure of tungstite, $WO_3 \cdot H_2O$, has been solved from single-crystal X-ray-diffractometer data collected with Mo$K\alpha$ radiation (748 unique reflections, 405 observed), and has been refined to an R index of 4.3%. Tungstite is orthorhombic, *Pmnb* (*Pnma* with $ba\bar{c}$), with a 5.249, b 10.711, c 5.133 Å, $Z = 4$. The structure is characterized by distorted octahedral units of tungsten atoms coordinated by five oxygen atoms and a water molecule; the octahedra share four corners in the equatorial plane to form sheets. The structure is very similar to that found in $MoO_3 \cdot 2H_2O$ (Krebs 1972). The sheets are held together by hydrogen-bonding between the water molecule and the oxygen atom in the axial position in the adjacent layer. The W–O bond lengths are 1.69(2) [axial], 2 × 1.83(3), 2 × 1.93(3) [equatorial] and 2.34(2) Å [axial, water]. The published powder-pattern for tungstite is corrected and indexed.

Keywords: tungstite, aquatungsten(VI) oxide, crystal-structure determination, corrected powder-pattern.

SOMMAIRE

On établit la structure cristalline de la tungstite, $WO_3 \cdot H_2O$, à partir de données de diffraction X obtenues sur monocristal en rayonnement Mo$K\alpha$ (748 réflexions uniques, 405 observées) affinement jusqu'au résidu R de 4.3%. La tungstite est orthorhombique *Pmnb* (*Pnma* avec $ba\bar{c}$), avec a 5.249, b 10.711, c 5.133 Å et $Z = 4$. La structure contient des octaèdres déformés d'atomes de tungstène coordonnés par cinq atomes d'oxygène et une molécule d'eau; chaque octaèdre partage quatres sommets dans le plan équatorial pour former des feuillets. La structure ressemble beaucoup à celle du $MoO_3 \cdot 2H_2O$ (Krebs 1972). Les feuillets sont reliés par des liaisons hydrogène entre la molécule d'eau et l'atome d'oxygène en position axiale dans le feuillet adjacent. Les longueurs des liaisons W–O sont 1.69(2)[position axiale], 2 × 1.83(3), 2 × 1.93(3) [plan équatorial] et 2.34(2) Å [position axiale, eau]. Le cliché de poudre de la tungstite est corrigé et indexé.

Mots-clés: tungstite, oxyde de tungstène(VI) hydraté, détermination de la structure cristalline, correction du cliché de poudre.

INTRODUCTION

Tungstite, $WO_3 \cdot H_2O$, is a secondary mineral, formed as an oxidation product of wolframite, scheelite and other primary minerals of tungsten. It has been found in small amounts at various localities throughout the world, but apparently not in sufficient quantity nor as crystals large enough for comprehensive mineralogical study. Literature references to this mineral date back over 160 years (Palache *et al.* 1944), including studies by Walker (1908) and Kerr & Young (1944), but only recently have crystallographic unit-cell parameters, possible space-group and a fully indexed X-ray powder-diffraction pattern been reported (Roberts 1981). Sahama (1981), in his review of secondary tungsten minerals, concluded: "As a mineral species tungstite is still inadequately described and needs to be studied with modern laboratory techniques." Since crystalline masses of tungstite from the Kootenay Belle mine, Salmo, B.C. are available (National Mineral Collection of Canada, Systematic Reference Series, Geological Survey of Canada, specimen number 16549), the crystal-structure analysis of this somewhat enigmatic mineral was undertaken as part of a study of the minerals of that region. Prior to this study, the only crystallographic information available was that tungstite probably is orthorhombic on the basis of its optical properties (Sahama 1981), but even the published powder-pattern (PDF 18–1418) was unindexed.

COMPOSITION

The mineral specimen from which the crystals for structure analysis were extracted consists of a fine-grained intergrowth of tungstite and ferritungstite. It is not possible to isolate from it enough pure material for a microprobe analysis, or for a bulk analysis for H_2O. However, our powder-diffraction data fit synthetic $WO_3 \cdot H_2O$ (PDF 18–1418), and the synthetic material has been extensively analyzed (Freedman 1959, Freedman & Leber 1964). Natural material from various sources, identifed as tungstite by the powder pattern (Kerr & Young 1944), has also been analyzed and found to agree with the formula $WO_3 \cdot H_2O$. In the latter paper, the poorest agreement was found for tungstite from the Salmo mine (analysis of Walker 1908), the major impurity being formulated as Fe_2O_3 and FeO. This is consistent

TABLE 1. CRYSTAL DATA

Tungstite: $WO_3.H_2O$
Source: Kootenay Belle mine, Salmo, British Columbia. (National Mineral Collection of Canada, Systematic Reference Series, Geological Survey of Canada, Specimen No. 16549).
Formula Weight: 249.86
Crystal System: Orthorhombic, $Z = 4$.
Systematic absences: hkl, generally present,
$0kl$, generally present,
$h0l$, $h + l = 2n+1$
$hk0$, $k = 2n+1$
Space group: *Pmnb* (#62, *Pnma* with $ba\bar{c}$).
Cell dimensions: $a = 5.249(2)$, $b = 10.711(5)$, $c = 5.133(2)$Å.
Density: D_{calc}=5.75 Mg m^{-3}, D_{obs} not measured, but Walker (1908) gives 5.517 for tungstite from the same locality, the low value probably caused by intergrowth with ferritungstite, (D_{obs}= 5.02 Mg m^{-3}).
Absorption: μ(Mo*K*α) = 406.9 cm^{-1}
Intensity Data: One octant of data collected with Mo*K*α radiation to 2θ=72°, measured three times and averaged: 748 unique reflections, 405 with $I > 1.65 \times \sigma(I)$.

with the above description of the mineralogy, and with our premise about the impossibility of doing precise analysis on material from the Salmo mine because of the intergrowth with ferritungstite. Thus it seemed necessary and justifiable, initially, to assume a formula $WO_3•H_2O$ for the single crystals of the natural material, and to check the final difference-synthesis for evidence of compositional differences. No significant peaks were found at the end of the refinement; though this does not preclude possible minor substitution for tungsten, no such substitution has been reported in the literature.

EXPERIMENTAL

Numerous crystalline fragments of tungstite were extracted from mineral specimen 16549. Of these, only two very small crystals showed no gross evidence of twinning, and both were used for extensive preliminary precession-photography. Exposures of up to 200 hours were used in order to try to observe the weak reflections from these very small crystals, and hence to differentiate weak reflections from systematically absent reflections, so as to determine the possible space-group.

It was apparent from the preliminary work that crystals of tungstite belong to the orthorhombic system, with the dimensions quoted in Table 1. The larger of the two crystals is a flat hexagonal tablet, whose faces were indexed from the precession work. The crystal is 53 μm between (100) and ($\bar{1}00$), 61 μm between (101) and ($\bar{1}0\bar{1}$), 66 μm between ($10\bar{1}$) and ($\bar{1}01$) and about 9 μm between (010) and ($0\bar{1}0$). The spots obtained on the precession photographs from this crystal show minor splitting in certain regions of reciprocal space and some displaced "tails", but as the other crystal is no better in terms of shape and singularity of diffraction spots, and in addition is less than half the size of this crystal, structural work proceeded with this less-than-satisfactory specimen.

The crystal was mounted on a Picker four-circle X-ray diffractometer, and precise cell-dimensions and orientation matrix were determined from the least-squares refinement of the observed 2θ, χ, ϕ and ω values of 59 reflections in the range $20° < 2\theta < 34°$ using Mo*K*α radiation ($\lambda = 0.71073$ Å) (Busing 1970). At this stage, although it was apparent that the crystals are orthorhombic, the space group was still uncertain.

A positive octant of reciprocal space was defined where the shape of the diffraction spots was best, and one octant of data was collected three times to a maximum of $2\theta = 72°$ using monochromated Mo*K*α radiation. All reflections within this 2θ limit were measured without reference to systematic absences. A scan rate of 1°/min was used with a base peak-width of 2.1°, increasing with dispersion (0.69 tanθ). Background counts were measured for 80 seconds on either side of the peak. Three standard reflections were monitored in order to check crystal alignment and instrument stability. No systematic variation was observed, and the minor variations were ignored. Absorption corrections were applied using a Gaussian integration procedure (Gabe & O'Byrne 1970) and a grid of 10 × 10 × 10 points. The correction factors varied between 1.85 and 7.05. The three segments of data were averaged and reduced to structure amplitudes with the application of Lorentz and polarization corrections. Reflections were considered as "observed" on the criterion that $I_{obs} > 1.65 \times \sigma(I)$, where $\sigma(I)$ is obtained from counting statistics.

SYSTEMATIC ABSENCES AND SPACE GROUP

The lattice is primitive, with reflections *hkl* generally present; reflections 0*kl* are generally present, although reflections not obeying the *A*-centring condition (*hkl*, $k + l = 2n$) are very weak. Reflections *h*0*l* were observed only for $h = 2n$ and $l = 2n$, with the exception of the (102) reflection, which appeared to be present but weak, and reflections (104) and (106), which were at the extreme limit of observability on the 1.65 $\sigma(I)$ criterion. Reflections *hk*0 are present for $k = 2n$. The above absences indicate space group *Pmcb* or *P2cb*. However, the Patterson function and the vector map (E^2–1) could not be interpreted on the basis of these space groups.

Finally, a CAD4 diffractometer was used to collect a new data-set (Mo*K*α radiation, hemisphere of data with *k* positive, all reflections collected to $2\theta = 60°$). It was found that none of the four reflections of the {102}, {104}, {106} forms were observed in this second data-set. In the latter, the "FLAT" option in the CAD4 data-collection routine was used. The crystal was automatically rotated about the scattering vector (ψ) to the position of minimum absorption for each reflection. Consequently, the diffraction geometry was totally different from that on the

TABLE 2. ATOMIC POSITIONAL AND THERMAL PARAMETERS

Atom	Position	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
W	4*c*	1/4	0.22090(8)	-0.0037(3)	0.72(3)	1.54(3)	0.83(3)	0.0	0.0	-0.28(9)
O(1)	4*c*	1/4	0.436(2)	0.075(4)	3.4(1.2)	2.4(1.0)	1.5(0.8)	0.0	0.0	-0.2(8)
O(2)	4*c*	1/4	0.066(2)	-0.064(4)	1.7(0.8)	2.0(0.8)	1.5(0.8)	0.0	0.0	0.2(6)
O(3)	8*d*	0.495(8)	0.227(2)	0.249(5)	6.1(1.2)	2.0(0.9)	7.4(1.3)	-0.6(1.6)	-6.0(1.1)	-0.6(1.3)
H(1)	4*c*	1/4	0.479	0.200	3.3	3.3	3.3	–	–	–
H(2)	4*c*	1/4	0.478	-0.055	3.3	3.3	3.3	–	–	–

The anisotropic temperature-factors are expressed in the form:
$T = \exp[-2\pi^2(U_{11}a^{*2}h^2..+ 2U_{12}a^*b^*hk..)]$, and the values quoted are x100.

Picker diffractometer. Re-examination of the (102) reflection with rotation about the scattering vector produced a minor peak in certain orientations, indicating it to be a Renninger reflection.

The structure was treated as triclinic, and the structure determination proceeded in space group $P1$, then $P\bar{1}$ until the symmetry became apparent, and the space group was identified as *Pmnb (#62, Pnma* with *ba$\bar{c}$*). This requires that reflections $h0l$ be observed for $h + l = 2n$, whereas all $h0l$ reflections with odd indices ($h = 2n + 1$, $l = 2n + 1$) were too weak to be observed. Furthermore, the (102), (104) and (106) are systematically absent in this space group, and indeed they were not observed in the CAD4 data-set. Evidently, the differences between the two geometries of diffraction were sufficient to eliminate these Renninger reflections. However, as the Picker data-set had been corrected for absorption, the above three offending reflections were removed, and the Picker data-set was used in the structure determination and refinement.

SOLUTION OF THE STRUCTURE

As explained above, the structure was solved by Fourier and Patterson methods in the triclinic space-group $P1$, and, later, $P\bar{1}$. In the latter space-group, the spatial relationship between the four atoms of tungsten was identified*, and the mirror planes at $x = ¼, ¾$ became evident. Finally, the spatial symmetry of the elements not on the mirror planes was identified, and the space group was fixed. The tungsten atom was found to be octahedrally co-ordinated by five oxygen atoms and one water molecule [identified by the long axial bond, 2.34 Å, as opposed to the short axial bond, W–O(2) = 1.69 Å, by analogy to the structure of $MoO_3{\cdot}2H_2O$ (Krebs 1972)].

Examination of the environment of the water molecule showed it to be within 3 Å of two neighboring O(2) oxygen atoms, and the geometry of this trio was such that a hydrogen-bonding scheme could be proposed. Using an idealized water molecule with an O–H distance of 0.8 Å and an H–O–H angle of 110°, the proposed positions of hydrogen atoms were examined in a difference synthesis. Two peaks were found clearly corresponding to these positions, but refinement of these was not found possible in the least-squares process. The hydrogen atoms were included in the latter stages of refinement, with their calculated positions and isotropic temperature-factors averaged from O(2) and O(1). The Residual Index improved marginally, though significant positional shifts were observed in the water oxygen O(1). The idealized positions of the hydrogen atoms were then re-calculated, and the final cycle of anisotropic refinement yielded an overall Residual of 4.3%.

No attempt was made at the end to release the constraints of the mirror plane in space group *Pmnb*, *i.e.*, to decrease the symmetry to space group $P2_1nb$. During an earlier stage of the refinement in space group $P\bar{1}$, atoms W, O(1) and O(2) had all refined to within one standard deviation of $x = ¼$, and O(3) and its subsequently mirror-related O(3′) had refined to corresponding co-ordinates $x \pm ¼$, again to within one standard deviation.

In the structure-factor and least-squares calculations, the atomic scattering factors used were those of the neutral species W, O, and were calculated from the coefficients given by Cromer & Mann (1968). The scattering factor for hydrogen was taken from Stewart *et al.* (1965). The anomalous scattering contributions for W and O were taken from Cromer & Liberman (1970). All the crystallographic calculations were carried out using the XRAY-76 system of programs (Stewart *et al.* 1976).

The final fractional co-ordinates and thermal parameters are listed in Table 2. The observed and calculated structure-factors are given in Table 3, available at a nominal charge from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2.

---

*The relationship between an equivalent position, x, y, z for $x = ¼$ and an equivalent position with $x = ¾$ is not unambiguous. The result can be achieved *via* $½ + x$ or $1-x$, and these are not equivalent. Similarly, with $z \simeq 0$, confusion occurs between z and $-z$, and between $½ + z$ and $½ - z$.

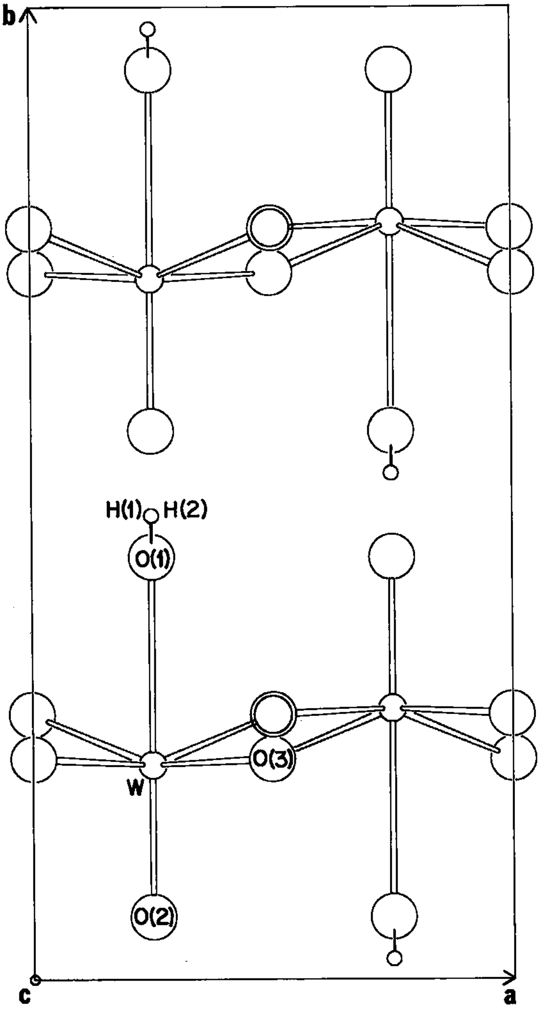

FIG. 1. The unit cell of tungstite. The atoms of the asymmetric unit are labeled. The doubled circles for the O(3) atoms near $x = \frac{1}{2}$ indicate that the bonding from adjacent atoms of tungsten is directed to two O(3) atoms separated by $z = 1$.

DESCRIPTION OF THE STRUCTURE

The unit cell of tungstite is illustrated in Figure 1, which clearly shows the two distinct sheets of W and O(3) atoms near $y = \frac{1}{4}, \frac{3}{4}$. Figure 2 shows the distorted octahedron of oxygen atoms that surrounds the W atom. The octahedra are distorted as follows: one axial bond, to O(2), is significantly shorter [1.69(2) Å] than the other axial bond [2.34(2) Å], which is to the water oxygen O(1). The equatorial bonds to O(3) are 2 × 1.83(3) and 2 × 1.93(3) Å, and these four are displaced away from O(2), such that the O(2)-W-O(3) angles are all close to 100°.

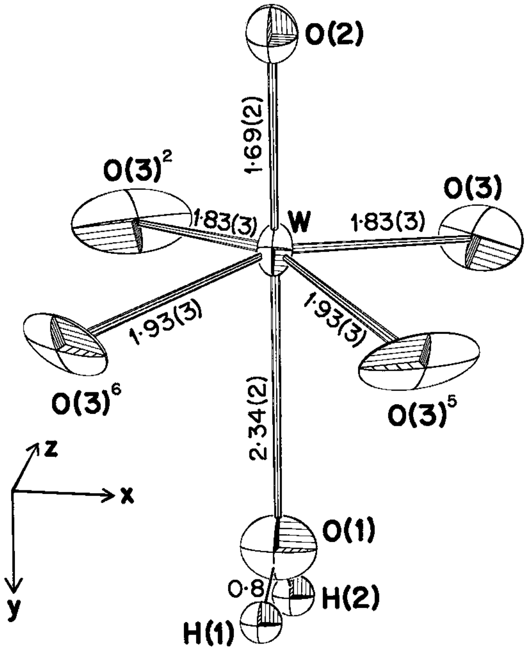

FIG. 2. The co-ordination octahedron of oxygen atoms around tungsten. Atoms W, O(1), O(2), H(1) and H(2) lie on the mirror planes at $x = \frac{1}{4}, \frac{3}{4}$. The thermal ellipsoids are drawn at 50% probability (Johnson 1965).

TABLE 4. BOND LENGTHS AND ANGLES WITH STANDARD DEVIATIONS

1. Coordination of W:

Atom	d(Å)	O(2)	O(3)	O(3)^1	O(3)^5	O(3)^6
O(1)	2.34(2)	179.3(9)	80.9(7)	80.9(7)	80.1(7)	80.1(7)°
O(2)	1.69(2)	—	99.6(7)	99.6(7)	99.4(7)	99.4(7)
O(3)	1.83(3)	—	—	98.4(1.5)	88.2(1.5)	161.0(8)
O(3)^1	1.83(3)	—	—	—	161.0(8)	88.2(1.5)
O(3)^5	1.93(3)	—	—	—	—	88.1(1.5)
O(3)^6	1.93(3)	—	—	—	—	—

2. Coordination of O(1), (Water):

O(1) – W	2.335(23)Å	W – O(1)...O(2)	129.0(1.0)°
O(1)...O(2)	2.87(3)	W – O(1)...O(2)	108.1(9)
O(1)...O(2)	2.97(3)	O(2) ...O(1)...(2)	122.9(1.0)

3. Coordination of O(2):

O(2) – W	1.688(23)Å	W – O(2)...O(1)^7	108.5(1.0)°
		W – O(2)...O(1)^8	128.6(1.1)
		O(1)^7...O(2)...O(1)^8	122.9(9)

3. Coordination of O(3):

O(3) – W	1.829(35)Å	W^4 – O(3) – W	165.2(1.0)°
O(3) – W^4	1.926(34)		

4. Unrefined hydrogen-bond distances and angles,
(Based on idealized water molecule, O-H = 0.8Å, H-O-H = 110°):

Donor – H.....Acceptor	d(H..O)Å	Angle at H
O(1) – H(1).....O(2)	2.09	171°
O(1) – H(2).....O(2)	2.17	172

Superscripts used above, in the text and the diagrams refer to the following equivalent positions:-

1.	$\frac{1}{2}-x,\ y,\ z$	5.	$1-x,\ \frac{1}{2}-y,\ -\frac{1}{2}+z$
2.	$x,\ \frac{1}{2}+y,\ \frac{1}{2}-z$	6.	$-\frac{1}{2}+x,\ \frac{1}{2}-y,\ -\frac{1}{2}+z$
3.	$x,\ \frac{1}{2}+y,\ -\frac{1}{2}-z$	7.	$x,\ -\frac{1}{2}+y,\ \frac{1}{2}-z$
4.	$1-x,\ \frac{1}{2}-y,\ \frac{1}{2}+z$	8.	$x,\ -\frac{1}{2}+y,\ -\frac{1}{2}-z$

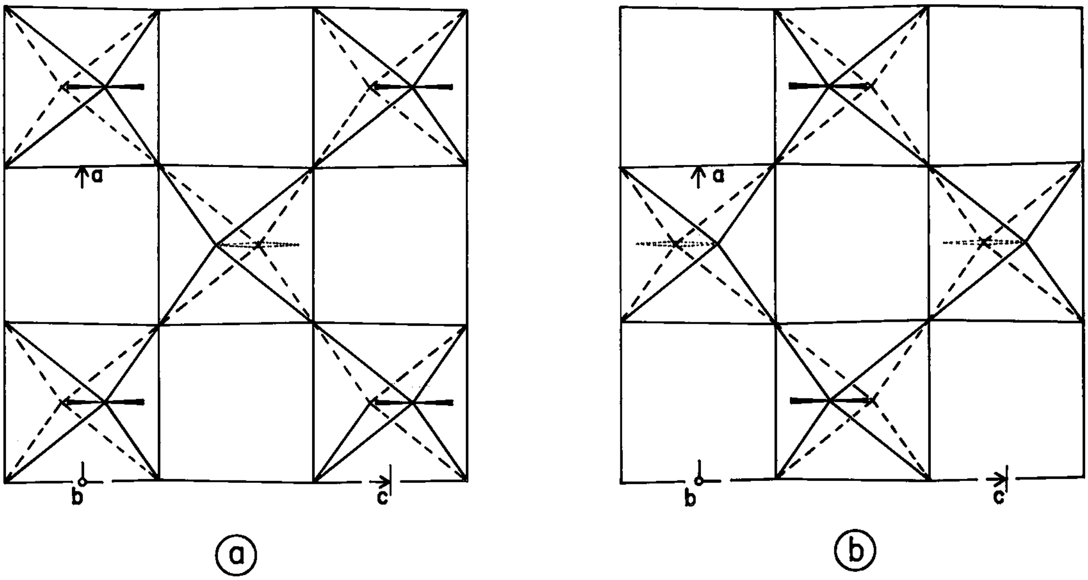

FIG. 3. (a), (b). The W-O corner-sharing octahedra stacked in the layers near $y = \frac{1}{4}, \frac{3}{4}$, respectively. The hydrogen atoms are located at the extremities of the tapered bonds at the axial vertex of each octahedron. In the structure, each sheet overlaps the other, so that a three-dimensional checkerboard network of octahedra and holes is formed.

Full details of bond lengths and angles are given in Table 4. The tungsten-oxygen octahedra, as indicated above, are stacked in sheets, and share all four corners in the equatorial plane, thus producing a checkerboard pattern of octahedra and holes in the *xz* plane (Fig. 3). The checkerboard layers above and below the first are displaced by $b/2$, so that the octahedra lie over holes. (Using the checkerboard analogy, black overlays white, and *vice versa,* in three dimensions).

The sheets are held together by a network of hydrogen bonds, such that the water molecule O(1), H(1), H(2), which is in an axial position in a given octahedron, bonds two axial O(2) atoms from octahedra in the adjacent layer. Each O(2) atom is hydrogen-bonded to two O(1) oxygen atoms, separated by $z = 1$. Thus, a *zig-zag* pattern of hydrogen bonds is formed, extending in the z direction, as illustrated in Figure 4.

POWDER PATTERN OF TUNGSTITE

A revised powder-pattern for tungstite is given in Table 5. This shows the powder-diffraction intensities, calculated on the basis of the absorption-corrected single-crystal intensities, using the program POWGEN (Hall & Szymański 1975). For comparison, the observed X-ray powder-diffraction intensities and d values of Freedman & Leber (1964) (PDF 18-1418) are included. Two spurious lines and a third marked "(Beta?)" observed by Freedman & Leber are noted, and one line that should have been observed (d 1.747, I 5/100) has been included. Other than these discrepancies, the agreement between I_{obs} and I_{calc} and between d_{obs} and d_{calc} is excellent. The indexed powder-pattern previously given by Roberts (1981) shows significantly poorer agreement, espe-

TABLE 5. POWDER PATTERN (Cu$K\alpha$) FOR TUNGSTITE

hkl	d_{calc}	d_{obs}	I_o	I_c	hkl	d_{calc}	d_{obs}	I_o	I_c
020	5.355	5.39	75	59	113	1.608	1.611	8	9
011	4.629	4.66	2	2	251	1.579	1.583	2	5
120	3.749	3.77	4	5	033	1.543	—	–	1
111	3.472	3.49	100	100	242	1.514	1.515	4	5
031	2.931	2.95	6	6	331	1.502	1.504	4	5
040	2.678	2.687	10	9	133	1.480	1.482	4	5
200	2.625	2.626	12	11	260	1.476	—	–	1
002	2.566	2.570	25	8	071	1.466	1.470	2	2
131	2.559			18	062	1.465			1
140	2.385	2.387	4	5	340	1.465			1
220	2.357	2.360	8	6	162	1.411	1.414	2	4
022	2.314	2.322	6	6	322	1.396	—	–	1
211	2.283	—	–	1	053	1.337	1.338	2	1
112	2.254	2.260	2	1	233	1.330	—	–	1
122	2.118	2.122	2	3	400	1.312	1.312	2	2
051	1.977	1.979	4	5	351	1.310			2
231	1.955	1.959	2	5	180	1.297	1.298	2	2
240	1.874	1.875	4	2	153	1.295	—	–	1
042	1.853	1.854	10	2	004	1.283	1.282	2	1
151	1.850			7	271	1.280			3
202	1.835	1.837	14	11	262	1.280			1
060	1.785	1.788	2	1	420	1.275	1.276	2	2
142	1.747	—	–	5	342	1.272	—	–	2
222	1.736	1.739	10	12	360	1.250	1.250	2	1
160	1.690	1.693	2	3	024	1.248			2
320	1.663	—	–	1	313	1.215	1.211	2	4
311	1.637	1.637	8	13					

I_c and d_{calc} data from POWGEN (Hall & Szymański 1975), powder-pattern generating program based on single-crystal intensities. I_o and d_{obs} data from Freedman & Leber (1964), (PDF No. 18-1418). Reflections at d=3.86, 3.29, 3.17 in PDF 18-1418 are not genuine.

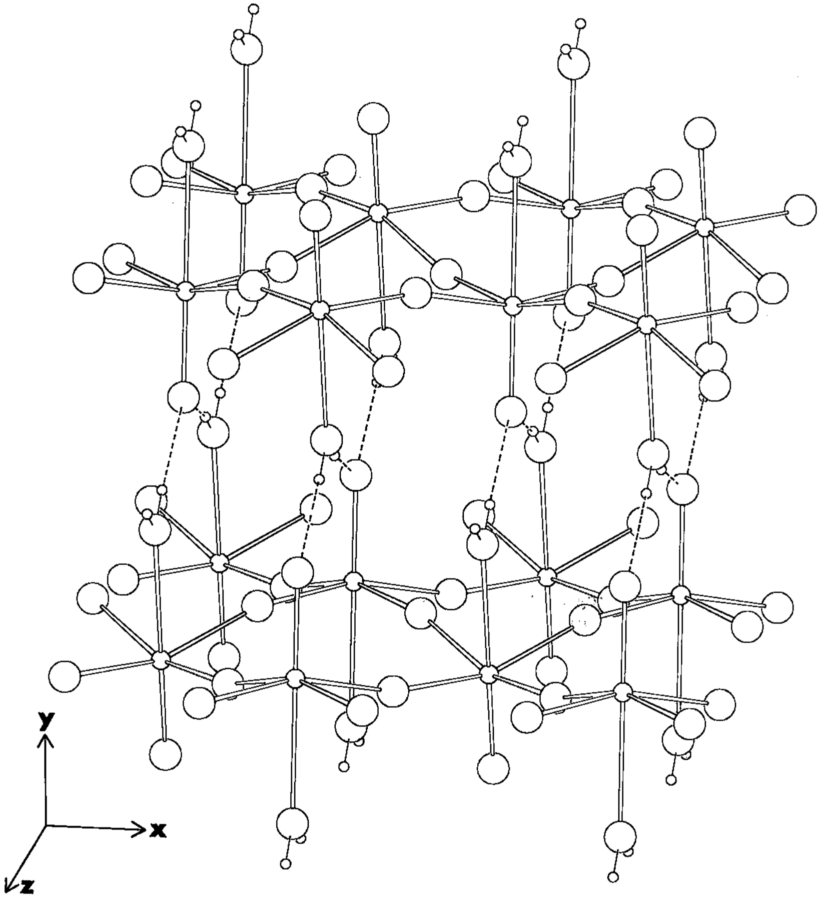

FIG. 4. The layer-like structure of tungstite, illustrating the interlayer hydrogen bonding. Each octahedrally co-ordinated tungsten is bonded to four O(3) oxygen atoms, forming W–O(3) sheets in the x–z plane. Two such sheets are illustrated, near $y = 1/4$ and $y = 3/4$. The W–O axial bonds are to O(2) and to the water molecule, O(1), H(1), H(2). Each water molecule is hydrogen-bonded to two O(2) atoms, and each O(2) bonds two water molecules separated by $z = 1$.

cially with regard to intensities. It must be presumed that the intensity values of Roberts (1981), visually estimated from Debye–Scherrer photographs made from very small quantities of specimen material, are not reliable. The indexed and corrected values of PDF 18–1418 should now be used as the standard powder-data for tungstite.

DISCUSSION

The solution of the present structure fills an important gap in the field of tungsten and molybdenum oxide hydrates. The crystal structure of $MoO_3{\cdot}2H_2O$ has been examined (Lindqvist 1950, 1956) and redetermined (Krebs 1972). The powder patterns of $MoO_3{\cdot}2H_2O$ and $WO_3{\cdot}2H_2O$ show these compounds to be isostructural, yet the powder patterns of the monohydrates are different. This has not prevented the dissemination of some confusion, *e.g.*, "The yellow modification (of $MoO_3{\cdot}H_2O$) has been mentioned to be isotypic with $WO_3{\cdot}H_2O$ (Freedman 1959), the crystal structure of which is, however, unknown as well" (Günter 1972). The crystal structure described in this paper fills half this gap, and the definitive powder-data should supplant the unindexed powder-pattern for tungstite in the Powder Diffraction File (No. 18–1418).

The structure presented here is very closely related to that of $MoO_3{\cdot}2H_2O$ (Krebs 1972). The latter is monoclinic, $P2_1/n$, and characterized by

$MoO_3 \cdot H_2O$ octahedra, corner-sharing to form sheets, exactly analogous to the sheets found in the present structure. The additional molecule of water in $MoO_3 \cdot 2H_2O$ fills one of the holes, and is utilized in further hydrogen-bonding of the octahedra. The octahedra found in the two structures are very comparable. In $MoO_3 \cdot 2H_2O$, there are four different Mo atoms, all with very similar geometry. The mean bond-lengths are as follows, with the present W–O distances in square brackets for comparison: Mo–O (axial) = 1.694 [1.69]; Mo–O (water, axial) = 2.288 [2.34]; Mo–O (equatorial, shorter) = 1.766, 1.800 [1.83]; Mo–O (equatorial, longer) = 2.054, 2.156 [1.93] Å. As $MoO_3 \cdot 2H_2O$ appears to be isostructural with hydrotungstite $WO_3 \cdot 2H_2O$ from the very close correspondence of their powder patterns (Freedman & Leber 1964), it seems logical to presume that the same type of metal co-ordination is found in the latter structure.

The only tungsten oxide hydrate on which structural work has been done is $WO_3 \cdot \frac{1}{3}H_2O$ (Gerand *et al.* 1981). Its structure has been determined from the intensities obtained from powder diffraction. The rather rough geometry obtained from the refinement shows that the W–O corner-sharing octahedron is retained as the basic unit of the structure, but the arrangement of the octahedra is totally different; the voids in the sheets of this structure are either triangular (three octahedra) or hexagonal (six octahedra). The stacking of the individual layers upon each other cannot follow the simple checkerboard pattern found in tungstite.

The structure determination of tungstite accounts well for the physical and optical properties of the crystalline material. Walker (1933), later quoted in Palache *et al.* (1944), gives the indices of refraction as 2.09 perpendicular to the cleavage direction and 2.24 and 2.26 (all ± 0.02) in the other two directions. The perfect cleavage (Walker 1908) is the crystallographic {010}, and occurs where the layers of W–O octahedra, which are hydrogen-bonded in the *y* direction, are separated. Within these sheets, the structural packing is very comparable in the *x* and *z* directions, so that one can expect the indices of refraction to be about the same. Within experimental error, this is exactly what is found. The other cleavage given by Walker (1933) (reindexed on present axes) is {101} imperfect. This can be explained in terms of a shear across the plane of O(3) atoms at the corners of the octahedra. However, as the shear plane in a given layer is displaced by $a/4 + c/4$ from that in the adjacent layer (owing to the checkerboard stacking of octahedra), the cleavage will be imperfect. We have observed {101} to be one of the forms in the hexagonal-shaped crystal used, the other being {100}. Walker (1933) states that "many of the cleavage plates show edges at right angles to one another, with extinction directions bisecting the angle between these edges." Owing to the fact that the *a* and *c* dimensions are very similar, the angle between the faces of the {101} form is close to a right angle (88.72°). The bisectors of these angles are the axial directions.

Finally, a word about the role of the hydrate molecule is warranted. The earlier literature on tungsten and molybdenum oxide hydrates contains much discussion on the role of water in these compounds: are these compounds true hydrates containing crystalline water? Are they acids (*e.g.*, H_2WO_4, H_4WO_5)? At one stage, an H_4O^{2+} ion was proposed to exist in $MoO_3 \cdot 2H_2O$ (Lindqvist 1950), though this was later refuted (Lindqvist 1956). It is evident from the detailed structure-analysis of $MoO_3 \cdot 2H_2O$ (Krebs 1972) and from the present work, that these compounds contain water molecules, co-ordinated oxygen-to-metal in their crystal structures and should be considered as aquametal(VI) oxides. Furthermore, the molybdenum trioxide dihydrate contains both an aqua- water (bonded to metal) and a hydrate water (not bonded to metal). It is strictly aquamolybdenum(VI) oxide hydrate. This nomenclature applied to the tungsten compound [aquatungsten(VI) oxide] is in agreement with the proton magnetic resonance and infrared-absorption spectra (Maričić & Smith 1958, Schwarzmann & Glemser 1961). The earlier nomenclature applied to these compounds ("tungstic acids", "molybdic acids") is definitely incorrect, and should not be used in a chemical description.

REFERENCES

BUSING, W.R. (1970): Least-squares refinement of lattice and orientation parameters for use in automatic diffractometry. *In* Crystallographic Computing (F.R. Ahmed, ed.). Munksgaard, Copenhagen.

CROMER, D.T. & LIBERMAN, D. (1970): Relativistic calculation of anomalous scattering factors for X rays. *J. Chem. Phys.* **53**, 1891-1898.

______ & MANN, J.B. (1968): X-ray scattering factors computed from numerical Hartree–Fock wave functions. *Acta Cryst.* **A24**, 321-325.

FREEDMAN, M.L. (1959): The tungstic acids. *J. Amer. Chem. Soc.* **81**, 3834-3839.

______ & LEBER, S. (1964): Identification of tungstic and molybdic "acids" by X-ray powder diffraction. *J. Less-Common Metals* **7**, 427-432.

GABE, E.J. & O'BYRNE, T. (1970): An absorption correction program for the PDP-8. *Amer. Cryst. Assoc. Summer Meet. Abstr.* **A4.** (translated into FORTRAN and adapted to CDC computers by Gabe & Szymański).

GERAND, B., NOWOGROCKI, G. & FIGLARZ, M. (1981): A new tungsten trioxide hydrate, $WO_3 \cdot \frac{1}{3}H_2O$: preparation, characterization, and crystallographic study. *J. Solid State Chem.* **38**, 312-320.

GÜNTER, J.R. (1972): Topotactic dehydration of molybdenum trioxide-hydrates. *J. Solid State Chem.* **5**, 354-359.

HALL, S.R. & SZYMAŃSKI, J.T. (1975): Powder pattern generation from single-crystal data. *Amer. Cryst. Assoc. Winter Meet. Abstr.* **F13.** Now incorporated into the XRAY-76 system of programs (Stewart *et al.* 1976).

JOHNSON, C.K. (1965): ORTEP: A FORTRAN thermal-ellipsoid plot program for crystal structure illustrations. Rep. ORNL-3794, 2nd Revision ORTEP-II addition 1971, *Oak Ridge Nat. Lab.*, Oak Ridge, Tennessee. The Johnson program has been modified for use in the Stewart XRAY-76 System by J.F. Guédon, S.R. Hall, P. Richard and S. Whitlow, 1974.

KERR, P.F. & YOUNG, F. (1944): Hydrotungstite, a new mineral from Oruro, Bolivia. *Amer. Mineral.* **29**, 192-210.

KREBS, B. (1972): Die Kristallstruktur von $MoO_3 \cdot 2H_2O$. *Acta Cryst.* **B28**, 2222-2231.

LINDQVIST, I. (1950): The crystal structure of the yellow molybdic acid, $MoO_3 \cdot 2H_2O$. On the existence of an H_4O^{2+} ion. *Acta Chem. Scand.* **4**, 650-657.

______ (1956): A correction of the crystal structure of $MoO_3 \cdot 2H_2O$. *Acta Chem. Scand.* **10**, 1362-1364.

MARIČIĆ, S. & SMITH, J.A.S. (1958): A nuclear magnetic resonance study of the hydrates of molybdenum trioxide. *J. Chem. Soc.*, 886-891.

PALACHE, C., BERMAN, H. & FRONDEL, C. (1944): *The System of Mineralogy. I. Elements, Sulfides, Sulfosalts, Oxides.* John Wiley & Sons, New York.

ROBERTS, A.C. (1981): The X-ray crystallography of tungstite. *Geol. Surv. Can. Paper* **81-1C,** 82.

SAHAMA, T.G. (1981): The secondary tungsten minerals, a review. *Mineral. Rec.* **12,** 81-87.

SCHWARZMANN, E. & GLEMSER, O. (1961): Zur Bindung des Wassers in den Hydraten des Wolframtrioxids. *Z. Anorg. allgem. Chem.* **312,** 45-49.

STEWART, J.M., MACHIN, P.A., DICKINSON, C.W., AMMON, H.L., HECK, H. & FLACK, H. (1976): The X-RAY System of Crystallographic Programs. *Univ. Maryland Comp. Sci. Ctr. Tech. Rep.* **TR-446.**

STEWART, R.F., DAVIDSON, E.R. & SIMPSON, W.T. (1965): Coherent X-ray scattering for the hydrogen atom in the hydrogen molecule. *J. Chem. Phys.* **42,** 3175-3187.

WALKER, T.L. (1908): A review of the minerals tungstite and meymacite. *Amer. J. Sci.* **175,** 305-308.

______ (1933): Notes on tungstite. *Univ. Toronto Stud., Geol. Ser.* **35,** 13-14.

Received November 23, 1983, revised manuscript accepted January 20, 1984.