Neutron Powder Diffraction Study of Tantalum Tungstate, Ta$_2$WO$_8$

By A. Santoro, R. S. Roth and D. Minor

National Measurement Laboratory, National Bureau of Standards, Washington DC 20234, USA

Abstract. Ta$_2$WO$_8$, orthorhombic, *Pbcm*, a = 3·8762 (2), b = 17·716 (1), c = 16·684 (1) Å. The structure was studied by profile analysis. Contrary to previous conclusions based on X-ray diffraction data, it was found that the compound crystallizes with the symmetry of space group *Pbcm* and is isostructural with Nb$_2$WO$_8$.

Introduction. The existence of Ta$_2$WO$_8$ has been reported by Roth, Waring & Parker (1970) in a study of the system Ta$_2$O$_5$–Ta$_2$WO$_8$. The compound has been considered to be structurally related to Nb$_2$WO$_8$ (Stephenson, 1968), which is orthorhombic, with space group *Pbcm* (Lundberg, 1972). In a subsequent investigation (Holcombe, 1976) it was noted that the X-ray powder pattern of Ta$_2$WO$_8$ can be fully indexed on a unit cell similar to that found by Lundberg (1965) for LiNb$_6$O$_{15}$F, which is also orthorhombic, but with space group *Pmma*. It was therefore concluded that the two compounds must be isostructural, in agreement with an earlier suggestion by Roth *et al.* (1970).

The two proposed structures, shown in projection in Fig. 1, although closely related, differ in important respects. The mirror plane perpendicular to [010] in space group *Pmma*, is replaced by a glide plane (the *b*

Fig. 1. Projections of the structures of Nb$_2$WO$_8$ and LiNb$_6$O$_{15}$F. The unit cell in space group *Pbcm* is outlined on the left, and the unit cell in *Pmma* on the right. The symbols of the symmetry elements are those used in *International Tables for X-ray Crystallography* (1969).

glide) in space group *Pbcm*. As a consequence, the metal and O atoms, constrained by the mirror in the first case, are free to move along the direction perpendicular to the projection plane in the second case. This change in the point symmetries of the atomic positions causes, in turn, the doubling of the unit cell indicated in Fig. 1.

As mentioned previously, the selection of the model isostructural with LiNb$_6$O$_{15}$F is based on the absence, in the powder pattern, of diffraction lines consistent with the larger unit cell of the Nb$_2$WO$_8$ structure. Superlattice peaks are clearly discernible in the X-ray pattern of Nb$_2$WO$_8$. However, their absence in the pattern of Ta$_2$WO$_8$ cannot be considered a sufficient condition for selecting one model rather than the other for two reasons. First, the lattice translations defining the unit cells for the two structures are related by the transformation

$$\mathbf{a}(Pbcm) = (010/002/100)\,\mathbf{a}(Pmma), \qquad (1)$$

and, consequently, the angular positions of the non-extinct reflections are identical for most reflections, especially in the important low-angle region of 2θ. Secondly, the superlattice reflections that would require the space group to be *Pbcm* may be very weak and difficult to detect, especially with X-rays, even in the regions of the pattern free from interferences.

As an accurate knowledge of the structure of Ta$_2$WO$_8$ may be important in understanding the thermal expansion properties of the compound (Holcombe & Smith, 1978), an attempt was made to resolve the uncertainty previously mentioned by examining the neutron powder pattern with the method of profile analysis (Rietveld, 1969).

The single-phase composition was prepared by heating the appropriate mixture of Ta$_2$O$_5$ and WO$_3$ at 1623 K for 31·5 h and was found to occur at 52·4Ta$_2$O$_5$:47·6WO$_3$ rather than 50Ta$_2$O$_5$:50WO$_3$. [Note that the compound Nb$_2$WO$_8$ also could not be prepared as a single phase at the 50:50 composition (Roth & Waring, 1966).] Assuming the existence of a single phase, this composition may be interpreted either as oxygen deficient (M_3O$_{7·968}$; M = Ta, W) or as containing excess metal ($M_{3·012}$O$_8$).

Neutron diffraction measurements were made at room temperature on a powder diffractometer of intermediate resolution at the National Bureau of Standards
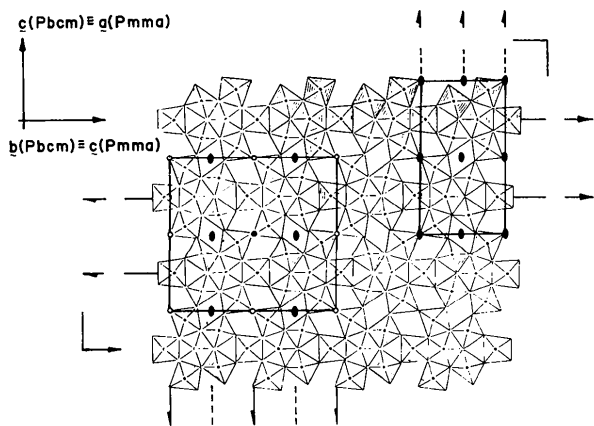
Reactor. The experimental conditions used for data collection are indicated in Table 1. The contribution to the profile from the background could be determined only up to $2\theta \simeq 37°$ because of severe overlapping of the diffracted peaks at higher Bragg angles. For $2\theta > 37°$ the shape of the curve background *versus* 2θ was assumed to be the same as that found for similar compounds (specifically CeTaO$_4$ and NdTaO$_4$, results to be published) analyzed with the same experimental conditions. Intensities were measured at 2θ intervals of $0.05°$.

No clear evidence of lines with $k = 2n + 1$, indicating the doubling of the unit cell, could be found in the powder pattern. The angular ranges over which the profile refinements were carried out were $7.0° \leq 2\theta \leq 84.5°$ with 262 independent Bragg reflections for *Pmma*, and $7.0° \leq 2\theta \leq 74.0°$ with 298 reflections for *Pbcm*.

Table 1. *Experimental conditions used to collect the powder intensity data for* Ta$_2$WO$_8$

Monochromatic beam: reflection 220 of a Cu monochromator (transmission geometry)
Mean neutron wavelength: 1·5416 (3) Å
Horizontal divergences:
    (i) In-pile collimator: 10 min arc
    (ii) Monochromatic beam collimator: 20 min arc
    (iii) Diffracted beam collimator: 10 min arc
Monochromator mosaic spread: ~15 min arc
Sample container: vanadium can of ~10 mm diameter

The structures were refined using the coordinates of the Nb and O atoms in LiNb$_6$O$_{15}$F as initial atomic parameters for space group *Pmma* and the coordinates of the Nb + W and O atoms in Nb$_2$WO$_8$ for space group *Pbcm*. The initial values of the lattice parameters were those determined by X-rays (Roth, Waring & Parker, 1970). The initial profile parameters U, V and W were calculated theoretically with the expressions derived by Caglioti, Paoletti & Ricci (1958). The neutron scattering amplitudes were b(Ta) = 0·70, b(W) = 0·48 and b(O) = 0·58 × 10^{-11} mm (Bacon, 1972). In view of the uncertainty in the determination of the background contribution to the observed intensities, only an overall temperature factor was refined. This does not seem to be too poor an approximation, considering that in these types of compounds the isotropic temperature factors of the individual atoms generally vary between 0·4 and 0·7 Å^2. Since departures from the ideal composition are 0·1 atoms per unit cell, at the most, all refinements were carried out assuming perfect stoichiometry. The structural, profile and lattice parameters were refined simultaneously until all shifts were less than 0·3 times the standard deviations. The results of these calculations are shown in Table 2.

As mentioned previously, there is no clear evidence of the presence in the powder pattern of diffraction peaks with $k = 2n + 1$. This is not surprising considering that (i) the structures based on *Pmma* and *Pbcm* are closely related and, consequently, the superlattice reflections are very weak (the highest calculated

Table 2. *Results of the structural refinements of* Ta$_2$WO$_8$ *in the space groups Pmma and Pbcm*

These results differ from those reported previously (Santoro, Roth & Minor, 1978) for a powder pattern measured with different experimental conditions. However, the conclusions in the two cases are identical.

R factors*

	R	*R$_p$*	*R$_w$*	*N − P + C*	Σ wy^2(obs.) × 10^{-2}	*P*	*R$_E$*	(*R$_w$/R$_E$*)^2
Pmma	8·29	11·32	12·95	1319	2454	30	7·33	3·13
Pbcm	4·67	8·45	10·08	1134	2062	44	7·42	1·85

Lattice and thermal parameters†

		a (Å)	*b* (Å)	*c* (Å)	*Q*$_{overall}$ (Å^2)
Pmma	Neutrons	16·685 (1)	3·8762 (2)	8·8571 (4)	0·63 (4)
	X-rays	16·70 (1)	3·877 (1)	8·864 (2)	
Pbcm		3·8762 (2)	17·716 (1)	16·684 (1)	0·46 (4)

Profile parameters

	U	*V*	*W* (deg.^{2})
Pmma	0·55 (3)	−0·56 (3)	0·228 (6)
Pbcm	0·59 (3)	−0·60 (2)	0·236 (5)
Calculated	0·21	−0·23	0·11

* $R = 100 \times [\Sigma |I(\text{obs.}) - I(\text{cal.})|/\Sigma I(\text{obs.})]$; $R_p = 100 \times [\Sigma |y(\text{obs.}) - y(\text{cal.})|/\Sigma y(\text{obs.})]$; $R_w = 100 \times \{\Sigma w[y(\text{obs.}) - y(\text{cal.})]^2/ \Sigma w[y(\text{obs.})]^2\}^{1/2}$; $R_E = 100 \times \{(N - P + C)/\Sigma w[y(\text{obs.})]^2\}^{1/2}$. In these formulae I is the integrated intensity, y the profile intensity of weight $w = 1/[y(\text{obs.}) + y(\text{background})]$, N the number of observations above background, P the number of refined parameters and C the number of constraints.
† The cell-dimension errors obtained in the neutron refinements do not include the error in the neutron wavelength.

superlattice intensity is only 1·7% of the highest calculated intensity in the pattern), and (ii) severe overlapping further complicates the direct observation of the doubling of the unit cell. Therefore, a decision about the most appropriate structural model for Ta_2WO_8 can only be made on the basis of the results obtained from the refinements.

It has been pointed out recently (Cheetham & Taylor, 1977) that errors in background estimation and breakdowns in the assumption of Gaussian peak shape may make it difficult to distinguish between alternative models and may render unreliable the application of statistical tests [e.g. Hamilton's (1965) test] to the results of profile analyses. In our case, however, the variations of the R factors and $(R_W/R_E)^2$ ratios for the two structures are very large and strongly indicate that the space group of Ta_2WO_8 is Pbcm, and that this compound is isostructural with Nb_2WO_8, not with $LiNb_6O_{15}F$

The possibility of variable occupancies at the metal sites for this and for related compounds has been reported (Holcombe, 1976) and, in fact, Nb/W ratios different from those corresponding to random distribution of the cations have been found in Nb_2WO_8 (Lundberg, 1972). In the present study no attempts have been made to refine the Ta/W ratios at the four metal sites because tests on the validity of the Gaussian approximation, made on a sample of Al_2O_3 analyzed with the experimental conditions of Table 1, gave a 'goodness of fit' χ^2 ranging between 1·0 and 1·7; i.e. close to the value of 1·8 obtained for the ratio $(R_W/R_E)^2$ in Pbcm. This indicates that the refinement procedure is essentially complete, and that it would not be meaningful to try to refine more detailed structural models.

It has been suggested (Greaves, Jacobsen, Tofield & Fender, 1975) that, in general, correct structural models give $R_p \leq 2R_E$, a condition that, in our case, is satisfied for both space groups. The obvious conclusion is that this rule is not sufficient for all cases, and should be used with caution.

The profile parameters U, V and W obtained in the two refinements agree with one another and with those obtained for other compounds studied with the same experimental conditions. However, they differ significantly from the calculated values. Discrepancies of the same order between theoretical predictions and experimental results have been observed previously (Caglioti & Ricci, 1962) and they are probably caused by approximations made in deriving the original theory rather than by crystallite size effects or structural distortions.

The final atomic parameters obtained from the refinement in space group Pbcm are given in Table 3.*

Discussion. In Ta_2WO_8, $\frac{5}{6}$ of the metal cations are octahedrally coordinated and they are located in three crystallographically independent positions, two general and one special. The remaining cations are surrounded by seven O atoms in a pentagonal-bipyramidal configuration. Octahedra and pentagonal bipyramids share edges as indicated in Fig. 2 to form the same structural unit as that found in Nb_2WO_8, $LiNb_6O_{15}F$, and numerous other compounds (Stephenson, 1968). Selec-

---

* A table of observed and calculated profile intensities has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34234 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Atomic parameters for* Ta_2WO_8 *in space group Pbcm*

Figures in parentheses are standard deviations in the last decimal place.

	x	y	z
$M(1)^*$	0·016 (5)	0·3426 (5)	$\frac{1}{4}$
$M(2)$	0·019 (4)	0·1982 (3)	0·1296 (4)
$M(3)$	0·980 (3)	0·4061 (4)	0·0612 (4)
$M(4)$	0·083 (3)	0·0277 (5)	$\frac{1}{4}$
$O(1)$	0·006 (7)	0·2288 (4)	$\frac{1}{4}$
$O(2)$	0·997 (3)	0·3108 (3)	0·1307 (4)
$O(3)$	0·995 (4)	0·4402 (3)	0·1767 (4)
$O(4)$	0·491 (6)	0·3456 (5)	$\frac{1}{4}$
$O(5)$	0·971 (3)	0·0972 (4)	0·1668 (3)
$O(6)$	0·988 (5)	0·1668 (3)	0·0224 (4)
$O(7)$	0·484 (3)	0·2008 (3)	0·1317 (4)
$O(8)$	0	0	0
$O(9)$	0·519 (4)	0·4077 (4)	0·0629 (5)
$O(10)$	0·530 (5)	0·0229 (5)	$\frac{1}{4}$

* M indicates 0·687 Ta + 0·313 W.

Table 4. *Interatomic distances* (Å) *in the structure of* Ta_2WO_8

Numbers in parentheses are standard deviations in the last decimal place. Atoms are labeled as in Fig. 2.

$M(1)-M(2)$	3·254 (9)		$O(1)-O(2)$	2·467 (8)
$M(1)-M(3)$	3·351 (8)		$O(2)-O(3)$	2·420 (8)
$M(1)-M(4)$	3·30 (1)		$O(3)-O(3')$	2·45 (1)
$M(2)-O(7)$	1·81 (2)		$M(3)-O(9)$	1·79 (2)
$M(2)-O(7)^*$	2·07 (2)		$M(3)-O(9)^*$	2·09 (2)
$M(2)-O(1)$	2·083 (7)		$M(3)-O(2)$	2·050 (9)
$M(2)-O(2)$	1·998 (8)		$M(3)-O(3)$	2·024 (9)
$M(2)-O(5)$	1·905 (9)		$M(3)-O(6'')$	1·902 (9)
$M(2)-O(6)$	1·878 (9)		$M(3)-O(8')$	1·955 (7)
$M(1)-O(4)$	1·84 (3)		$M(4)-O(10)$	1·74 (2)
$M(1)-O(4)^*$	2·04 (3)		$M(4)-O(10)^*$	2·14 (2)
$M(1)-O(1)$	2·02 (1)		$M(4)-O(3)$	1·998 (9)
$M(1)-O(2)$	2·072 (7)		$M(4)-O(5'')$	2·908 (9)
$M(1)-O(3)$	2·122 (9)			

* Oxygen atom belonging to the structural unit below the plane of Fig. 2.

ted interatomic distances are shown in Table 4. The pentagonal bipyramid is quite regular: the O—O distances corresponding to the edges shared with the octahedra vary from 2·420 (8) to 2·467 (8) Å and the remaining distances from 2·80 (3) to 2·88 (3) Å. On the other hand, the MO_6 octahedra are highly distorted with O—O distances between 2·420 (8) and 3·129 (8) Å. The average M—O distances of the three octahedrally coordinated cations are 1·957 (5), 1·969 (6) and 1·950 (5) Å, while that for the seven-coordinated cation is 2·041 (7) Å. These values agree closely with those found for Nb₂WO₈ (Lundberg, 1972).

The symmetry of the structural units and the mechanism by which they are connected to form the structure are in general different from compound to compound. In Ta₂WO₈ and Nb₂WO₈ they are linked by corner sharing and form layers like that shown in Fig. 1. In the third direction the layers are stacked on top of one another and each polyhedron shares a vertex with the corresponding one of the next layer. The array of corner-sharing octahedra creates large tunnels extending in the direction of the a(Pbcm) axis. The tunnels are surrounded by three- or four-octahedron rings. Probably these are the sites in which the Li ions are located in the structures of LiNb₆O₁₅F and the high-temperature form of LiTa₃O₈ (Santoro, Roth & Minor, 1976).
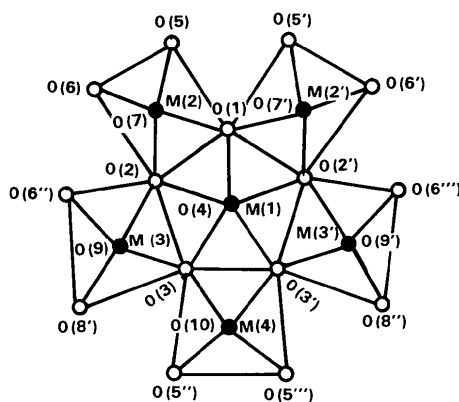

Fig. 2. Basic unit in the structure of Ta₂WO₈. A mirror perpendicular to the plane of the figure passes through the atoms O(1), M(1), O(4), M(4), and O(10).

References

BACON, G. E. (1972). *Acta Cryst.* **A28**, 357–358.
CAGLIOTI, G., PAOLETTI, A. & RICCI, F. P. (1958). *Nucl. Instrum.* **3**, 223–228.
CAGLIOTI, G. & RICCI, F. P. (1962). *Nucl. Instrum. Methods*, **15**, 155–163.
CHEETHAM, A. K. & TAYLOR, J. C. (1977). *J. Solid State Chem.* **21**, 253–275.
GREAVES, C., JACOBSEN, A. J., TOFIELD, B. C. & FENDER, B. E. F. (1975). *Acta Cryst.* **B31**, 641–646.
HAMILTON, W. C. (1965). *Acta Cryst.* **18**, 502–510.
HOLCOMBE, C. E. (1976). Report Y-2061. Oak Ridge National Laboratory, Tennessee.
HOLCOMBE, C. E. & SMITH, D. D. (1978). *J. Am. Ceram. Soc.* **61**, 163–169.
International Tables for X-ray Crystallography (1969). Vol. I, 3rd ed., pp. 49–50. Birmingham: Kynoch Press.
LUNDBERG, M. (1965). *Acta Chem. Scand.* **19**, 2274–2284.
LUNDBERG, M. (1972). *Acta Chem. Scand.* **26**, 2932–2940.
RIETVELD, H. M. (1969). *J. Appl. Cryst.* **2**, 65–71.
ROTH, R. S. & WARING, J. L. (1966). *J. Res. Natl Bur. Stand. Sect. A*, **70**, 281–303.
ROTH, R. S., WARING, J. L. & PARKER, H. S. (1970). *J. Solid State Chem.* **2**, 445–461.
SANTORO, A., ROTH, R. S. & MINOR, D. (1976). Proc. 3rd Eur. Crystallogr. Meet. Zurich, Switzerland, p. 105.
SANTORO, A., ROTH, R. S. & MINOR, D. (1978). *Acta Cryst.* **A34**, S159.
STEPHENSON, N. C. (1968). *Acta Cryst.* **B24**, 637–653.

Dodecacarbonyltetrakis-μ₃-[(pentacarbonylrhenio)indio]-*tetrahedro*-tetrarhenium, Re₄(CO)₁₂{μ₃-InRe(CO)₅}₄

BY HANS PREUT AND HANS-JÜRGEN HAUPT

Lehrstuhl für Anorganische Chemie II der Universität, D-4600 Dortmund 50, Federal Republic of Germany

Abstract. In₄Re₈(CO)₃₂, M_r = 2845·22, tetragonal, a = 15·042 (2), b = 15·040 (2), c = 12·075 (2) Å, U = 2731·7 Å³; Z = 2, D_c = 3·457 Mg m⁻³; F(000) = 2488; Mo Kα radiation, λ = 0·71069 Å, μ(Mo Kα) = 18·537 mm⁻¹. Space group P4̄2₁c. The structure was solved by the heavy-atom method with 1586 unique reflexions (I > 3σ) and refined to a final R of 0·0435. The core of the molecule is formed by eight Re atoms and four In atoms which are bonded to each other by a total of 16 In—Re bonds [r(In—Re): 2·796 (2), 2·820 (2), 2·848 (2); 2·720 (2) Å] and four Re—Re bonds [r(Re—Re): 2·997 (1), 3·034 (1) Å]. Four Re