

Structural Systematics in the Binary System Ta₂O₅–WO₃. I. The Structure of Ta₂₂W₄O₆₇

BY N. C. STEPHENSON* AND R. S. ROTH

National Bureau Standards, Washington, D. C. 20234, U.S.A.

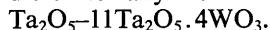
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The orthorhombic unit cell of the compound Ta₂₂W₄O₆₇ has dimensions $a=6.136$, $b=47.40$, $c=3.84$ Å and, on the average, contains one formula unit. The structure was solved in projection from the Patterson function and refined to a conventional R value of 0.089 using full-matrix least-squares methods. The metal atoms lie in sheets which are separated by $c=3.84$ Å. Within each sheet these atoms have a close-packed hexagonal arrangement. Oxygen atoms complete a coordination polyhedron around each metal atom in the form of either a distorted pentagonal bipyramid or octahedron. These polyhedra are joined by edge-sharing within the (001) planes. Extension of the structure along [001] occurs by corner-sharing. The structure differs from one having C -centered orthorhombic symmetry only in certain areas where metal atoms have reduced coordination numbers. These metal atoms lie in sheets parallel to (010) and the 'distortion planes' minimize the anionic packing distortions that would otherwise arise. In this structure there is, on the average, one distortion plane per unit cell.

Introduction

The X-ray diffraction patterns of each specimen from pure Ta₂O₅ to 26 $\frac{2}{3}$ mole per cent WO₃ all exhibit a slight but steady change in subcell dimensions and large changes in the positions of the superstructure peaks. Also, the positions of the superstructure peaks of a given composition change continuously with heat treatment, gradually approaching equilibrium values with increasing time and/or temperature.

To determine the structural mechanism responsible for these changes, crystal-structure determinations for the simplest members of the series were made and are reported in this and the following papers. Based on these structure determinations a building-block scheme has been developed (Roth & Stephenson, 1969) which enables the ideal or undistorted structure to be predicted for any member of the series



The compound Ta₂₂W₄O₆₇ is an end member of the above series and its crystal-structure determination is reported below. Crystals of this compound can be prepared by heating a 30 mole per cent WO₃ mixture at 1583°C for 64 hours in a sealed platinum tube and then quench cooling. At this temperature the mixture melts to the 11Ta₂O₅·4WO₃ compound and liquid containing a higher concentrations of WO₃. Crystals are therefore formed under solid-liquid equilibrium conditions and are large enough for X-ray work.

Experimental

Crystals of Ta₂₂W₄O₆₇ are very small, colorless and near-spherical in shape. X-ray data were collected from one of the larger crystals, a prolate spheroid with a

maximum dimension of 0.074 mm. The crystal data are: Ta₂₂W₄O₆₇, $M=5787$; $a=6.136$, $b=47.40$, $c=3.84$ Å, $V_0=1117$ Å³, $Z=1$, $D_c=8.602$ g.cm⁻³; space group $C2mm$ (C_{2v}^{14} , no. 38). Unit-cell dimensions were obtained using a Philips powder diffractometer with Cu $K\alpha$ radiation, and are considered accurate to ± 1 in the last decimal place.

Integrated intensities, $hk0$ were obtained on a Siemens A.E.D. single-crystal diffractometer with Ni-filtered Cu $K\alpha$ radiation. The five-values θ - 2θ scan method was used. (Hoppe, 1965). Attenuation filters and scanning times were adjusted automatically to give an approximately equal number of counts for each measurable reflection. Those reflections for which the integrated intensity was less than, or equal to, three standard deviations based only on counting statistics were regarded as unobserved and were assigned a value of half the minimum observed intensity. All reflections with a 2θ value below 140° were measured and Lorentz, polarization and absorption corrections ($\mu R=4.4$ for a spherical crystal) were applied. The atomic scattering factors for O²⁻ and Ta⁵⁺ were taken from Suzuki (1960) and Cromer & Waber (1965) respectively, and the real part of the anomalous dispersion correction was applied to the scattering curve for tantalum (Dauben & Templeton, 1955). Since the Ta⁵⁺ and W⁶⁺ atomic scattering curves are practically identical, the atomic scattering factor of Ta⁵⁺ was used for W atoms.

Determination of the structure

The principal structural features were determined by projection along the short c axis. The intensity distributions on zero and upper-level Weissenberg photographs taken about the c axis were visually identical so that atoms are predominantly located in the (001) planes. The Laue symmetry and systematic absences in spectra indicated an orthorhombic C -centered space

* Permanent address: School of Chemistry, University of New South Wales, Sydney, Australia.

group, probably $C2mm$, in which case most atoms would be found in position 4(*d*) with *z* coordinates equal to zero. In this and other structures in the $Ta_2O_5-WO_3$ system, the heavy metal atoms tend to lie close to ideal subcell positions and contribute to only a fraction of

the data, thereby adding confusion as to what are really systematic absences and what constitutes the correct space group. The observed $hk0$ data each have $h+k=2n$ and therefore the simplest of the centered rectangular plane groups, Cm , was assumed. Even this

Table 1. Positional and thermal parameters for $Ta_{22}W_4O_{67}$

Other atoms in the unit cell are related to those listed below by the symmetry elements of the plane group Cm . Atoms O(11) to O(16) and also O(19) have *z* parameters of $\frac{1}{2}$; the remaining atoms have *z* parameters of zero.

Numbers in parentheses are e.s.d.'s in the least significant digits.

The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + 2\beta_{12}hk)]$.

	<i>x/a</i>	<i>y/b</i>	$\beta_{11} \times 10^4$ or <i>B</i>	$\beta_{22} \times 10^5$	$\beta_{12} \times 10^5$
M(1)	0.0000	0.0000	-100 (27)	-13 (3)	
M(2)	0.0709 (42)	0.07223 (32)	132 (37)	15 (4)	-99 (45)
M(3)	0.0712 (50)	0.15270 (29)	19 (25)	10 (4)	-9 (21)
M(4)	0.0822 (19)	0.23368 (24)	-18 (26)	2 (3)	6 (32)
M(5)	0.1524 (27)	0.30921 (30)	31 (30)	13 (5)	-6 (21)
M(6)	0.0296 (33)	0.38227 (21)	-24 (30)	3 (3)	-9 (21)
M(7)	0.0317 (31)	0.46021 (18)	-9 (29)	-5 (3)	-1 (22)
O(1)	0.959 (30)	0.1969 (39)	1 (3)		
O(2)	0.194 (14)	0.1139 (18)	-2 (1)		
O(3)	0.368 (51)	0.2179 (63)	4 (6)		
O(4)	0.392 (13)	0.1580 (21)	-2 (1)		
O(5)	0.389 (36)	0.0736 (51)	3 (5)		
O(6)	0.642 (17)	-0.0030 (65)	-2 (2)		
O(7)	0.876 (18)	0.0461 (27)	1 (2)		
O(8)	0.736 (41)	0.2374 (54)	3 (5)		
O(9)	0.797 (16)	0.1499 (26)	-1 (2)		
O(10)	0.808 (46)	0.0959 (58)	2 (4)		
O(11)	0.980	0.000	0.1		
O(12)	0.080	0.077	0.1		
O(13)	0.082	0.153	0.1		
O(14)	0.082	0.234	0.1		
O(15)	0.156	0.309	0.1		
O(16)	0.032	0.382	0.1		
O(17)	0.240	0.015	0.1		
O(18)	0.210	0.034	0.1		
O(19)	0.500	0.038	0.1		

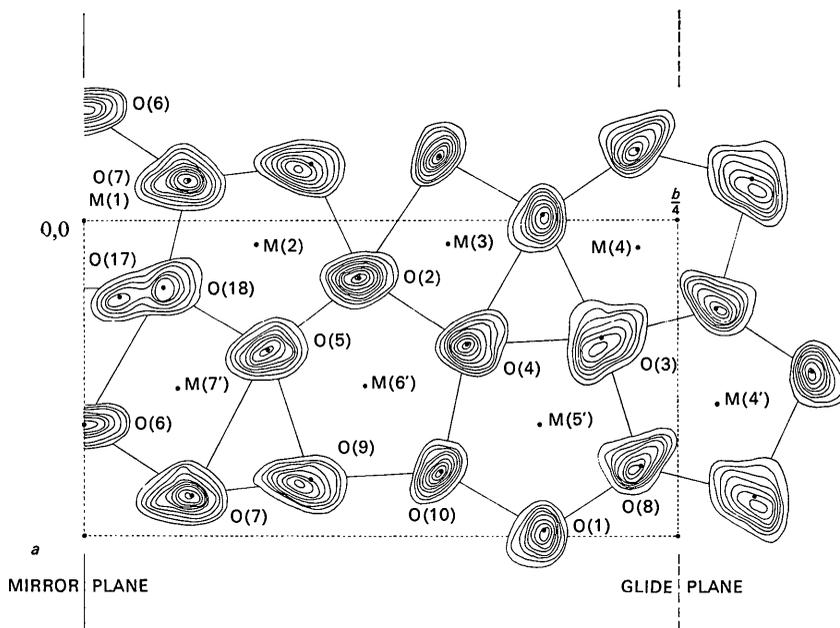


Fig. 1. A (001) difference Fourier synthesis showing resolved oxygen atoms in the (001) plane. One quarter of the unit cell is shown.

Table 2. Observed and calculated structure factors

Unobserved data are marked with an L.

H	K	F ₀	F _C	H	K	F ₀	F _C	H	K	F ₀	F _C	H	K	F ₀	F _C				
0	2	L	21	3	1	47	162	190	3	35	159	135	5	35	220	210			
0	4	L	29	6	1	49	402	395	3	37	512	494	5	37	471	444			
0	6	L	34	5	1	51	L	42	95	3	39	701	604	5	39	368	333		
0	8	L	40	20	1	53	L	102	89	3	41	551	230	5	41	200	187		
0	10	L	266	187	1	55	L	310	308	3	43	L	46	52	5	43	L	26	39
0	12	L	46	13	1	57	L	66	63	3	45	L	78	47	6	0	L	405	366
0	14	L	48	6	2	0	L	1022	1285	3	47	L	236	233	6	2	L	354	321
0	16	L	269	204	2	2	L	424	399	3	49	L	427	421	6	4	L	201	154
0	18	L	51	36	2	4	L	50	7	3	51	L	98	105	6	6	L	295	289
0	20	L	52	94	2	6	L	51	69	4	0	L	774	672	6	8	L	155	130
0	22	L	53	31	2	8	L	335	268	4	2	L	486	446	6	10	L	511	496
0	24	L	87	30	2	10	L	326	262	4	4	L	152	113	6	12	L	324	315
0	26	L	1284	1372	2	12	L	152	68	4	6	L	276	250	6	14	L	268	251
0	28	L	55	65	2	14	L	53	56	4	8	L	412	387	6	16	L	364	338
0	30	L	56	71	2	16	L	190	182	4	10	L	503	477	6	18	L	155	146
0	32	L	119	125	2	18	L	369	293	4	12	L	212	203	6	20	L	207	196
0	34	L	57	93	2	20	L	55	65	4	14	L	111	160	6	22	L	229	222
0	36	L	389	402	2	22	L	152	68	4	16	L	302	287	6	24	L	433	393
0	38	L	57	70	2	24	L	537	445	4	18	L	302	287	6	26	L	315	321
0	40	L	56	58	2	26	L	1071	1012	4	20	L	148	137	6	28	L	230	215
0	42	L	407	390	2	28	L	296	230	4	22	L	181	190	6	30	L	129	143
0	44	L	53	70	2	30	L	57	92	4	24	L	510	490	6	32	L	266	273
0	46	L	206	176	2	32	L	57	11	4	26	L	563	509	6	34	L	73	64
0	48	L	68	48	2	34	L	255	222	4	28	L	302	292	7	1	L	340	333
0	50	L	44	67	2	36	L	442	399	4	30	L	54	20	7	3	L	405	388
0	52	L	737	671	2	38	L	56	101	4	32	L	202	162	7	5	L	36	20
0	54	L	36	70	2	40	L	55	121	4	34	L	322	294	7	7	L	201	183
0	56	L	58	70	2	42	L	270	239	4	36	L	508	527	7	9	L	146	139
1	1	L	40	25	2	44	L	211	202	4	38	L	190	200	7	11	L	276	239
1	3	L	41	63	2	46	L	47	98	4	40	L	69	76	7	13	L	241	229
1	5	L	283	222	2	48	L	64	58	4	42	L	40	15	7	15	L	208	203
1	7	L	45	43	2	50	L	351	342	4	44	L	183	171	7	17	L	118	140
1	9	L	47	28	2	52	L	605	528	4	46	L	32	17					
1	11	L	360	264	2	54	L	116	107	4	48	L	144	126					
1	13	L	1316	1457	3	1	L	109	134	5	1	L	182	190					
1	15	L	238	195	3	3	L	356	289	5	3	L	351	342					
1	17	L	52	34	3	5	L	515	468	5	5	L	280	257					
1	19	L	53	37	3	7	L	248	176	5	7	L	258	260					
1	21	L	426	317	3	9	L	158	128	5	9	L	217	178					
1	23	L	466	371	3	11	L	575	558	5	11	L	501	457					
1	25	L	56	62	3	13	L	1089	1056	5	13	L	511	442					
1	27	L	56	27	3	15	L	502	443	5	15	L	368	311					
1	29	L	348	302	3	17	L	56	18	5	17	L	110	94					
1	31	L	166	132	3	19	L	188	149	5	19	L	316	295					
1	33	L	57	53	3	21	L	411	350	5	21	L	246	245					
1	35	L	57	46	3	23	L	514	490	5	23	L	491	463					
1	37	L	155	175	3	25	L	139	126	5	25	L	232	216					
1	39	L	887	853	3	27	L	56	47	5	27	L	78	75					
1	41	L	183	164	3	29	L	57	63	5	29	L	138	165					
1	43	L	54	84	3	31	L	340	328	5	31	L	136	195					
1	45	L	121	128	3	33	L	56	8	5	33	L	136	116					

is an oversimplification since the 67 oxygen atoms cannot be accommodated by this plane group.

A (001) Patterson projection indicated that the structure of Ta₂₂W₄O₆₇ is based upon 13 UO₃-type subcells (Zachariasen, 1948), each C-centered subcell containing two metal atoms (M) with the superstructure extending along the [010] direction. The origin of the unit cell was fixed on the mirror plane at M(1), and the displacements of the remaining metal atoms from their ideal positions at (0, n/13) and (½, n + ½/13), where n is an integer, were determined from superposition maps using the minimum function approach (Buerger, 1959). The positional and isotropic thermal parameters of each metal atom in the asymmetric unit were refined by least-squares methods to a conventional R of 0.164. A (001) difference Fourier synthesis, shown in Fig. 1, clearly resolved the oxygen atoms in the (001) plane. Oxygen atoms lying in the plane z = ½ projected close to the metal atom positions, and the coordinates obtained for these oxygen atoms were not varied during subsequent refinement cycles. These atoms have been omitted from Fig. 1 for clarity.

The difference Fourier synthesis indicated metal atom thermal anisotropy. Therefore, in the least-squares refinement cycles carried out on F, the isotropic and anisotropic thermal parameters for oxygen and metal atoms, respectively, were varied as well as the positional parameters. Statistical tests (Hamilton, 1965) also validated the use of anisotropic thermal parameters for the metal atoms during least-squares refinement cycles.

Standard deviations, σ(F₀), were assigned to F₀ data on the basis of counting statistics. The weighting scheme used followed the method suggested by Hughes (1941).

The final agreement factors for the observed data, R₁ = Σ||F₀| - |F_c||/Σ|F₀| and R₂ (as weighted R factor) = [Σw(|F₀| - |F_c||)²/ΣwF₀²]¹/², were 0.089 and 0.114, respectively. The programs of Stewart (1967) were used on the NBS UNIVAC 1108 computer.

Positional and thermal parameters for Ta₂₂W₄O₆₇ as well as corresponding standard deviations estimated from the inverse matrix, are given in Table 1. Table 2 lists observed and calculated structure amplitudes. Bond distances and angles, and their estimated standard deviations (e.s.d.'s), are given in Table 3.

Table 3. Bond distances (Å) and angles (°)

Superscripts refer to symmetry-related atoms

No superscript	x	y	z
'	x + ½	½ - y	z
''	x + ½	½ + y	z
'''	x	½	z

The second number in parentheses refers to the relative occurrences of that bond distance or angle. Superscripts have been omitted from the oxygen atoms.

M(1) Pentagonal bipyramid

M(1)—O(6)	2.18 (22) (1)
—O(7)	2.34 (32) (2)
—O(18)	2.05 (29) (2)
—O(11)	1.92 (01) (2)
O(6)—O(7)	2.60 (33) (2)

Table 3 (cont.)

O(7)—O(18)	2.18 (38) (2)
O(18)—O(18)	3.18 (45) (1)
O(11)—O(6)	2.82 (23) (2)
—O(7)	3.00 (38) (4)
—O(18)	2.86 (30) (4)
O(6)—O(7)—O(18)	106 (15)
O(7)—O(18)—O(18)	106 (13) (2)
O(7)—O(6)—O(7)	116 (12) (2)
M(1') Distorted octahedron	
M(1)—O(6)	2.18 (22) (1)
—O(7)	2.34 (32) (2)
—O(11)	1.92 (01) (2)
—O(17)	1.64 (25) (1)
O(6)—O(7)	2.60 (33) (2)
O(7)—O(17)	3.69 (42) (1)
O(17)—O(7)	2.72 (40) (1)
O(11)—O(6)	2.82 (23) (2)
—O(7)	3.00 (38) (4)
—O(17)	2.60 (23) (2)
O(7)—O(6)—O(7)	116 (13)
O(6)—O(7)—O(17)	70 (9)
O(7)—O(17)—O(7)	85 (10)
O(17)—O(7)—O(6)	89 (12)
M(2) Pentagonal bipyramid	
M(2)—O(2)	2.08 (31) (1)
—O(5)	1.95 (24) (1)
—O(10)	1.98 (31) (1)
—O(12)	1.94 (04) (2)
—O(18)	2.02 (31) (1)
—O(7)	1.74 (31) (1)
O(7)—O(10)	2.37 (46) (1)
O(10)—O(2)	2.52 (40) (1)
O(2)—O(5)	2.20 (41) (1)
O(5)—O(18)	2.23 (41) (1)
O(18)—O(7)	2.18 (38) (1)
O(12)—O(7)	2.73 (30) (2)
—O(10)	2.71 (28) (2)
—O(2)	2.67 (30) (2)
—O(5)	2.70 (23) (2)
—O(18)	2.93 (33) (2)
O(7)—O(10)—O(2)	99 (14)
O(10)—O(2)—O(5)	104 (16)
O(2)—O(5)—O(18)	117 (14)
O(5)—O(18)—O(7)	103 (16)
O(18)—O(7)—O(10)	116 (17)
M(3) Octahedron	
M(3)—O(1)	2.05 (29) (1)
—O(2)	2.03 (31) (1)
—O(4)	1.97 (23) (1)
—O(9)	1.68 (23) (1)
—O(13)	1.92 (01) (2)
O(1)—O(4)	3.08 (34) (1)
O(4)—O(2)	2.44 (42) (1)
O(2)—O(9)	3.01 (38) (1)
O(9)—O(1)	2.35 (41) (1)
O(13)—O(1)	2.83 (31) (2)
—O(2)	2.78 (32) (2)
—O(4)	2.69 (23) (2)
—O(9)	2.62 (22) (2)
O(1)—O(4)—O(2)	94 (11)
O(4)—O(2)—O(9)	84 (12)
O(2)—O(9)—O(1)	98 (11)
O(9)—O(1)—O(4)	84 (11)
M(4) Pentagonal bipyramid	
M(4)—O(1)	2.00 (29) (1)
—O(8)	1.92 (30) (1)
—O(3)	2.58 (25) (1)
—O(8)	1.80 (30) (1)

Table 3 (cont.)

M(4)—O(3)	1.92 (22) (1)
—O(14)	1.92 (03) (2)
O(1)—O(8)	2.37 (41) (1)
O(8)—O(3)	2.16 (40) (1)
O(3)—O(8)	2.58 (37) (1)
O(8)—O(3)	2.16 (40) (1)
O(3)—O(1)	2.76 (32) (1)
O(14)—O(1)	2.79 (30) (2)
—O(8)	2.71 (27) (2)
—O(3)	3.20 (31) (2)
—O(8)	2.63 (28) (2)
—O(3)	2.72 (23) (2)
O(1)—O(8)—O(3)	133 (16)
O(8)—O(3)—O(8)	88 (13)
O(3)—O(8)—O(3)	126 (15)
O(8)—O(3)—O(1)	99 (13)
O(3)—O(1)—O(8)	95 (13)
M(5) Pentagonal bipyramid	
M(5)—O(1)	1.96 (21) (1)
—O(3)	2.17 (23) (1)
—O(4)	2.23 (27) (1)
—O(8)	2.33 (30) (1)
—O(9)	2.12 (30) (1)
—O(15)	1.92 (05) (2)
O(3)—O(4)	2.89 (40) (1)
O(4)—O(9)	2.53 (32) (1)
O(9)—O(1)	2.35 (41) (1)
O(1)—O(8)	2.37 (41) (1)
O(8)—O(3)	2.58 (37) (1)
O(15)—O(1)	2.71 (22) (2)
—O(8)	2.99 (33) (2)
—O(3)	2.91 (26) (2)
—O(4)	2.98 (29) (2)
—O(9)	2.86 (32) (2)
O(4)—O(3)—O(8)	108 (11)
O(3)—O(8)—O(1)	101 (13)
O(8)—O(1)—O(9)	122 (12)
O(1)—O(9)—O(4)	108 (14)
O(9)—O(4)—O(3)	100 (12)
M(6) Pentagonal bipyramid	
M(6)—O(2)	2.06 (26) (1)
—O(4)	2.10 (30) (1)
—O(5)	2.22 (29) (1)
—O(9)	2.24 (29) (1)
—O(10)	2.01 (30) (1)
—O(16)	1.92 (05) (2)
O(2)—O(4)	2.44 (42) (1)
O(4)—O(9)	2.53 (32) (1)
O(9)—O(10)	2.57 (46) (1)
O(10)—O(5)	2.74 (38) (1)
O(5)—O(2)	2.20 (41) (1)
O(16)—O(2)	2.84 (26) (2)
—O(4)	2.85 (31) (2)
—O(9)	2.92 (29) (2)
—O(10)	2.76 (29) (2)
—O(5)	2.95 (32) (2)
O(2)—O(4)—O(9)	110 (14)
O(4)—O(9)—O(10)	100 (13)
O(9)—O(10)—O(5)	110 (13)
O(10)—O(5)—O(2)	102 (14)
O(5)—O(2)—O(4)	117 (14)
M(7') Octahedron	
M(7')—O(18)	1.99 (23) (1)
—O(5)	1.87 (29) (1)
—O(7)	2.10 (29) (1)
—O(6)	2.00 (08) (1)
—O(19)	1.93 (03) (2)
O(18)—O(5)	2.23 (41) (1)
O(5)—O(7)	3.23 (38) (1)

Table 3 (cont.)

O(7)—O(6)	2.60 (33) (1)
O(6)—O(18)	3.10 (32) (1)
O(19)—O(18)	2.63 (22) (2)
—O(5)	2.69 (30) (2)
—O(7)	3.00 (29) (2)
—O(6)	2.76 (23) (2)
O(18)—O(5)—O(7)	96 (12)
O(5)—O(7)—O(6)	82 (10)
O(7)—O(6)—O(18)	91 (09)
O(6)—O(18)—O(5)	91 (09)

M(7) Octahedron

M(7)—O(5)	1.87 (28) (1)
—O(6)	2.00 (08) (1)
—O(7)	2.10 (29) (1)
—O(17)	2.13 (26) (1)
—O(19)	1.93 (03) (2)
O(6)—O(7)	2.60 (43) (1)
O(7)—O(5)	3.23 (38) (1)
O(5)—O(17)	2.97 (42) (1)
O(17)—O(6)	2.58 (32) (1)
O(19)—O(5)	2.69 (30) (2)
—O(6)	2.76 (23) (2)
—O(7)	3.00 (29) (2)
—O(17)	2.72 (26) (2)
O(6)—O(7)—O(5)	82 (11)
O(7)—O(5)—O(17)	84 (10)
O(5)—O(17)—O(6)	88 (11)
O(17)—O(6)—O(7)	106 (14)

M(7'') Distorted octahedron

M(7'')—O(5)	1.87 (28) (1)
—O(7)	2.10 (29) (1)
—O(6)	2.00 (08) (1)
—O(17)	3.14 (29) (1)
—O(19)	1.93 (03) (2)
O(5)—O(7)	3.23 (38) (1)
O(7)—O(6)	2.60 (43) (1)
O(6)—O(17)	2.58 (32) (1)
O(17)—O(5)	4.34 (43) (1)
O(19)—O(5)	2.69 (21) (2)
—O(7)	3.00 (29) (2)
—O(6)	2.76 (23) (2)

Table 3 (cont.)

O(19)—O(17)	3.53 (27) (2)
O(5)—O(7)—O(6)	82 (11)
O(7)—O(6)—O(17)	138 (15)
O(6)—O(17)—O(5)	62 (10)
O(17)—O(5)—O(7)	78 (09)

Description of the structure

The metal atoms lie in sheets separated by $c = 3.84 \text{ \AA}$. Within each sheet these atoms have a close-packed hexagonal arrangement. Oxygen atoms complete a coordination polyhedron around each metal atom in the form of either a distorted pentagonal bipyramid or octahedron. These polyhedra are joined by edge-sharing within the (001) planes. Extension of the structure along [001] occurs by corner-sharing. The structure, viewed along [001], is shown in Fig. 2.

There are 26 metal atoms and 67 oxygen atoms in the unit cell (as determined from X-ray data). The problem of accommodating an odd number of atoms in a C-centered space group is related to the doublet which appears in the Fourier synthesis, *viz.* O(17) and O(18) (Fig. 1). Atom O(18), together with its mirror image counterpart and atoms O(6), O(7) and O(11), complete a slightly distorted pentagonal bipyramid about M(1). The polyhedra about atoms M(2) and M(7') (superscripts denote symmetry-related atoms as defined in Table 3) which also involve O(18) are a pentagonal bipyramid and an octahedron respectively. Atom sites O(18) and O(17) cannot, for steric reasons, be occupied simultaneously. Atom sites O(17) and that related to it by the (010) mirror plane, *cannot be occupied simultaneously*, since this O(17)---O(17) approach distance is only 1.41 \AA . Therefore the (010) plane is only statistically a mirror plane. The use of atom site

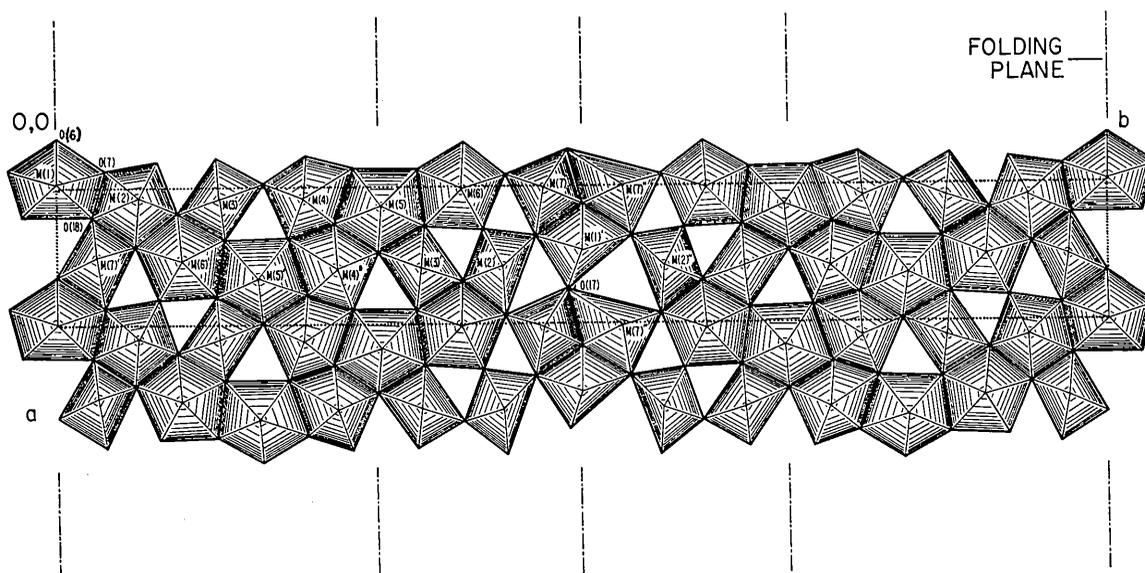


Fig. 2. A (001) projection of the structure of one unit cell of $Ta_{22}W_4O_{67}$. Folding planes are shown as dashed lines (see Fig. 3).

O(17) therefore involves the replacement of *two* atoms, namely O(18) and its mirror-image counterpart, by a *single* atom with a resulting change in the shape of the coordination polyhedra about metal atoms M(1'), M(2'), M(7) and M(7'') (See Fig. 2). These polyhedra become distorted octahedra and M(1') suffers a reduction in coordination number from 7 to 6. The reduction in the coordination number of metal atom M(1') occurs every 6.136 Å along [100] and every 3.84 Å along [001]; therefore, a plane of distortions is formed which is parallel to (010). The introduction of one such 'distortion plane' (Roth & Stephenson, 1969) in the structure reduces the number of oxygen atoms in the unit cell by one, and the composition of $Ta_{22}W_4O_{67}$ demands that, on the average, there is one distortion plane per unit cell, *i.e.* every 47.40 Å, in the structure of $Ta_{22}W_4O_{67}$. Atoms O(18) and O(17) were therefore given population parameters of 0.5 and 0.25, respectively, in all crystallographic calculations involving the plane group Cm .

Fig. 2 depicts the structure of a unit cell with contents $Ta_{22}W_4O_{67}$ and having one (020) distortion plane. It would represent the structure of the real unit cell if the distortion planes were ordered. However, restriction to the plane group Cm requires that the distortion plane be disordered over four positions which are related to the position shown in Fig. 2 by the 4(*b*) positions of the plane group Cm . If the distortion planes were ordered, as shown, the *C*-centering would be destroyed as well as the *mmm* Laue symmetry. The small changes in structure-factor amplitudes resulting from such an

ordering process (involving only one light atom) are not detectable using X-rays, and the unit cell depicted in Fig. 2 must therefore be regarded as an 'average' unit cell until proven otherwise by more sensitive techniques.

The unit cell contains 15 metal atoms with pentagonal bipyramidal coordination polyhedra and 11 metal atoms with distorted octahedral environments. The degree of distortion depends upon the location of the polyhedra and is greatest in the vicinity of a 'folding plane'. These planes, shown in Fig. 2 and Fig. 3, represent regions where extensive anion packing distortions occur (see discussion below). The most regular pentagonal bipyramid, located midway between two folding planes, is associated with M(6). Metal-oxygen and oxygen-oxygen approach distances average at 2.07 (9) and 2.73 (9) Å, respectively within this polyhedron. The most regular octahedron is associated with M(3), again located midway between two folding planes, and the average M-O and O-O approach distances are 1.93 (6) and 2.73 (9) Å respectively.

Discussion

The ideal structure of $Ta_{22}W_4O_{67}$ suggested by the building-block principle of Roth & Stephenson (1969) is shown in Fig. 3. The fundamental building chain is built up of edge-sharing regular pentagons. The chain has a regular 'herring-bone weave' and the folding occurs after six, then four, then four, then six pentagons *etc.* The places at which folding, or breaks in line-

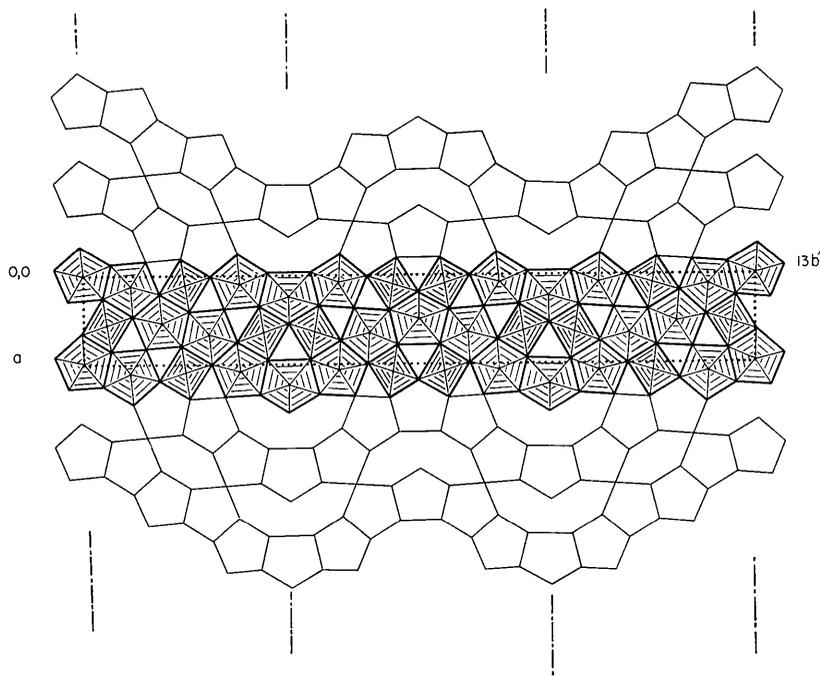


Fig. 3. The ideal structure of the compound $Ta_{22}W_4O_{67}$ derived from fused chains of regular pentagons. Each chain has a regular 'herring-bone weave' and the folding occurs after six, then four, then four, then six pentagons *etc.* The places at which folding occurs are the folding planes, marked as dashed lines.

arity, occur are the folding planes referred to above. Each chain can attach to other identical chains by corner-sharing and this process produces rectangular sites (octahedral in three dimensions) between adjacent chains.

There is a perfect fusion of regular pentagons provided the chain remains linear. When such linear chains are linked to other identical chains by corner-sharing the structure is that of U_3O_8 as described by Andresen (1958). It is necessary to fold the U_3O_8 structure in a repeating manner to decrease the oxygen: metal ratio (2.667:1 in U_3O_8 ; 2.577:1 in $Ta_{22}W_4O_{67}$). Folding in the manner illustrated in Fig. 3 causes some rectangles to share corners with each other as well as edges with adjacent pentagons, whereas in the U_3O_8 structure these rectangles share edges only. Folding in this manner also causes distortions to occur at the folding planes; in particular, pentagonal bipyramids lying on these folding planes cannot remain regular.

The structure of $Ta_{22}W_4O_{67}$ differs from the ideal structure shown in Fig. 3 by the manner in which those pentagonal bipyramids that lie on folding planes accommodate the distortions imposed upon them by the folding process. Thus $M(1')$, lying on the (020) folding plane, reduces its coordination number from 7 to 6. The two adjacent $M(2')$ and $M(2'')$ pentagonal bipyramids are therefore reduced to distorted octahedra while the $M(7)$ and $M(7'')$ octahedra, which lie either side of the (020) folding plane, become distorted. The penta-

gonal bipyramid centered on $M(5)$ also lies on a folding plane but in this case the distortions are accommodated by movements of the oxygen atoms from their ideal positions. As a result of these movements, adjacent metal atoms $M(4)$ and $M(4')$ each acquire a distorted pentagonal bipyramidal environment rather than the distinctly dissimilar 7 to 6 coordinated configurations they possess in the ideal or undistorted structure.

Intractability in the refinement of the structure

The conventional R value for this structure is acceptably low (0.089) but not as low as expected for diffractometer data. In addition, the e.s.d.'s for atomic coordinates, and therefore for bond distances and angles, are extremely high. These factors may arise because the structure for the unit cell, shown in Fig. 2 is really an average structure and is a superposition of four ideal unit cells, each of which has been modified by the presence of a distortion plane in one of the (4b) positions of plane group Cm . The composite atoms would therefore be blurred, have low curvatures and large standard deviations in positional parameters. Our studies on other members of the series $Ta_2O_5-WO_3$ indicate, however, that distortion planes tend to order to equidistant positions. The structure shown in Fig. 2 for the compound $Ta_{22}W_4O_{67}$, may therefore be the structure of the real unit cell with an ordering of distortion planes on $y = \frac{1}{2}$. This unit cell is primitive, although departures

Table 4. Correlation coefficients, q_{ij} , for metal-metal positional parameter interactions

x_i-x_j type interactions are shown below the q_{ii} diagonal while y_i-y_j type interactions are found above this diagonal.

Metal	1	2	3	4	5	6	7
1	1.0	—	—	—	—	—	—
2	—	1.0	0.09	0.16	-0.05	-0.24	-0.03
3	—	-0.08	1.0	0.19	-0.15	-0.14	0.09
4	—	0.57	0.03	1.0	0.01	-0.01	0.18
5	—	0.04	0.56	0.17	1.0	0.23	0.05
6	—	0.47	0.53	0.45	0.41	1.0	0.03
7	—	0.43	0.57	0.58	0.21	0.60	1.0

The values omitted were not calculated.

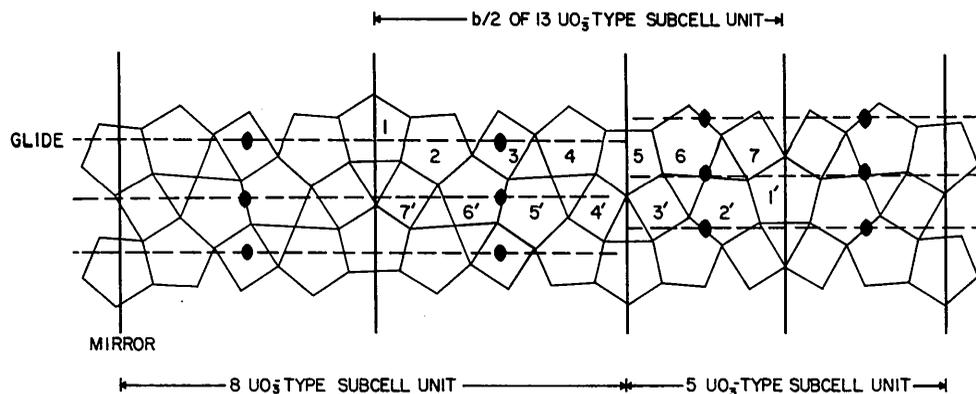


Fig. 4. The symmetry elements (glide and mirror planes, and twofold axes) of the 5 and 8 UO_3 -type subcell building blocks. Polyhedra are marked according to the number (Table 1) of the metal atom and superscripts represent symmetry transformations of the plane group Cm (Table 3).

from *C*-centering are small. The extremely small size of the crystals results in a minimum F_{obs} value of 50–100 electrons and reflections of the type hkl with $h+k \neq 2n$, which should appear if long-range ordering of distortion planes does occur, may not be recorded owing to the small diffracting power of the crystal. As a result of this enforced *C*-centered symmetry, a restriction is placed on the number of parameters which can be refined using standard methods, and a relatively high *R* value could result.

Although these factors reflect a degree of intractability in the solution of the crystal structure of $\text{Ta}_{22}\text{W}_4\text{O}_{67}$, the main reason for the unusually large standard deviations in bond lengths and angles is the high degree of parameter interaction in this structure. The correlation matrix obtained by the Busing, Martin & Levy *ORFLS* program showed interdependence particularly between the *x* parameters of the metal atoms in the asymmetric unit; some values of the correlation coefficients, ρ_{ij} , calculated during the last refinement cycle, are given in Table 4. The correlation coefficients are independent of the sum of the residuals and are directly related to the structure model. It is interesting to note that high correlations occur between metal atoms which, although not related to each other by the symmetry elements of the plane group *Cm* (describing the overall structure of the 13 UO_3 -type subcell), are related by the symmetry elements of the ideal 5 and 8 UO_3 -type subcells that combine to form the total structure. Both ideal 5 and 8 UO_3 -type subcells have plane group symmetry *pgm*, and the location of the glide planes, mirror planes and twofold axes are shown in Fig. 4. Apart from the (010) and (020) mirror planes these symmetry elements are not implemented by the plane group *Cm*, and the relaxation of these symmetry conditions are accompanied by small shifts in atomic positions (~ 0.15 Å). Atoms which are no longer strictly related by, for example, the

twofold axes of the 8 UO_3 -type subcell unit *i.e.* M(2) and M(4), nevertheless are still interdependent as evidenced by the correlation coefficient $\rho_{4,2}$ with value 0.57.

The magnitudes of the parameter interactions listed in Table 4 are much less than those found in tetragonal BaTiO_3 (Evans, 1961), LiMnPO_4 and grossularite (Geller, 1961). The structure of $\text{Ta}_{22}\text{W}_4\text{O}_{67}$ should therefore be regarded not as indeterminate but as inherently inaccurate. Complete convergence to the precise structure has not occurred; some temperature factors are (not significantly) negative and standard deviations are so large as to prevent significant comparisons of bond lengths and distortions. However the X-ray data provide an acceptable description of $\text{Ta}_{22}\text{W}_4\text{O}_{67}$ with structural features consistent with those found in other members of the Ta_2O_5 - WO_3 system. Such structures are described in the following papers.

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