

Structural Systematics in the Binary System $Ta_2O_5-WO_3$. II. The Structure of $Ta_{30}W_2O_{81}$

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The structure of the compound $Ta_{30}W_2O_{81}$ has been determined in projection using single-crystal diffractometer X-ray data. The orthogonal unit cell has dimensions $a=6.172$, $b=29.226$, $c=3.850$ Å and contains, on the average, one half of a formula unit. The structure of this unit cell represents the superposition of two structural blocks $M_{16}O_{40}$ and $M_{16}O_{42}$ (where M is a metal atom), which occur in the ratio 3:1. In both structural blocks the metal atoms are arranged in sheets and are surrounded by oxygen atoms forming either distorted octahedral or pentagonal bipyramidal coordination polyhedra. The difference in structure between the two blocks is that in $M_{16}O_{40}$ some metal atoms reduce their coordination numbers to minimize packing distortions. The resultant distortion planes are distributed so that three occur every two unit cell. The asymmetric structural unit was refined in two plane groups, pm and pg , using full-matrix least-squares methods. The final R value is 0.077 and pm was chosen as the correct plane group on the basis of noncrystallographic considerations.

Introduction

The compound $Ta_{30}W_2O_{81}$ melts congruently at 1815°C. Good single crystals can be prepared by heating a 13 mole per cent WO_3 mixture at 1760°C in a sealed platinum tube for one hour and quench cooling. Under these conditions the mixture melts to the 15:2 composition and crystals grow under solid-liquid equilibrium conditions.

Preliminary X-ray powder diffraction work shows that the structure of $Ta_{30}W_2O_{81}$ is based upon 8 UO_3 -type subcells. This unit cell is the smallest encountered in the series $Ta_2O_5-11Ta_2O_5.4WO_3$.

Experimental

Crystals of $Ta_{30}W_2O_{81}$ are generally larger than those of $Ta_{22}W_4O_{67}$, and are colorless and near-spherical in shape. X-ray data were collected with Cu $K\alpha$ radiation from a crystal of average radius 0.052 mm ($\mu R=5.9$). The crystal data are: $Ta_{30}W_2O_{81}$, $M=7090$; $a=6.172 \pm 0.001$, $b=29.226 \pm 0.001$, $c=3.850 \pm 0.001$ Å; $V_o=694.5$ Å³, $Z=\frac{1}{2}$, $D_o=8.48$ g.cm⁻³. Unit-cell dimensions were obtained using a Philips powder diffractometer with Cu $K\alpha$ radiation. Integrated intensities, $hk0$, were obtained on a Siemens A.E.D. single-crystal diffractometer, as described in the previous paper, and data were processed to give the set of observed structure amplitudes listed in Table 2. Atomic scattering curves and computer programs used in this analysis were the same as those referred to in the previous paper (Stephenson & Roth, 1971).

Determination of the structure

The intensity distributions on zero and upper-level Weissenberg photographs taken about c were visually

identical, indicating that atoms are predominantly located in the (001) planes. The Laue symmetry and systematic absences in spectra, *i.e.* $h0l$ data absent when $h \neq 2n$ and $0kl$ data absent when $k \neq 2n$, indicated a primitive, orthorhombic space group, probably $Pbam$ with atoms in position 4(*g*), or $Pba2$ with atoms in position 4(*c*). However, it was not possible to interpret the Patterson synthesis using either of these space groups. It became clear that the apparent 'systematic' absences due to glide planes were probably accidentally absent and too weak to be observed. This situation may arise owing to the very small size of the crystal or, more likely, to a special arrangement of the heavy metal atoms such that they make only contributions to certain intensity data.

In view of the large number of alternative space groups the most plausible procedure was to solve the structure in projection, since there are but five rectangular primitive plane groups. The small length of the c axis and the (001) planar arrangement of atoms in this structure presented ideal conditions for this type of refinement. The plane groups pgg and pmm were disregarded since the ($hk0$) Patterson function could not be interpreted using either of them, and an initial trial structure was conceived in the plane group pgm . This trial structure, derived from the Patterson function, was based on 8 UO_3 -type subcells (Zachariasen, 1948) extending along the [010] direction, each C -centered subcell containing two metal atoms. Deviations of the metal atoms from their ideal subcell positions were determined from superposition maps using the minimum function approach (Buerger, 1959). Least-squares refinement cycles, involving the positional and isotropic thermal parameters of the five metal atoms in the asymmetric unit, converged to a structure with a conventional R value of 0.24. This rather high value for R indicated that the symmetry requirements of either the mirror plane or the glide plane in the plane group pgm had to be relaxed. In keeping with the apparent orthorhombic nature of the unit cell, the plane group for the (001) projection is either pm or pg .

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The structure was refined in both plane groups. Oxygen atoms were located from difference Fourier syntheses and the positional and thermal atomic parameters were refined using the full-matrix least-squares program of Busing, Martin & Levy (1962). The weighting scheme used has been described previously (Stephenson

& Roth, 1971). The final agreement factors R_1 for the observed $hk0$ data for the plane groups pm and pg are 0.077 and 0.087 respectively.

The positional and thermal parameters for $Ta_{30}W_2O_{81}$, as well as corresponding standard deviations estimated from the inverse matrix, are given in Table 1. Table 2

Table 1. *Positional and thermal parameters for the compound $Ta_{30}W_2O_{81}$ refined in the plane groups pm and pg*

Standard deviations are given in brackets and the form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + 2\beta_{12}hk)]$. Atoms O(13) to O(20) and also O(23) have z parameters of $\frac{1}{2}$; the remaining atoms have z parameters of zero.

	x/a	y/b	$\beta_{11} \times 10_4$ or B	$\beta_{22} \times 10_5$	$\beta_{12} \times 10_5$
M(1)	0.0538 (57)	0.0000	123 (57)	39 (15)	59 (43)
M(2)	Related to M(1) by $(\bar{x}, \frac{1}{2} + y)$				
M(3)	0.9566 (59)	0.11837 (62)	148 (56)	65 (17)	51 (56)
M(4)	0.9749 (23)	0.24269 (47)	20 (26)	41 (11)	-94 (59)
M(5)	0.9772 (28)	0.37282 (74)	74 (35)	77 (14)	23 (81)
M(6)	0.4980 (45)	0.05699 (80)	73 (17)	49 (9)	-54 (30)
M(7)	0.5047 (38)	0.18899 (69)	58 (36)	66 (18)	114 (46)
M(8)	0.4213 (12)	0.31102 (69)	43 (16)	32 (7)	-27 (61)
M(9)	0.4971 (47)	0.42788 (67)	138 (45)	47 (2)	-104 (49)
O(1)	0.422 (41)	0.0015 (95)	3.75 (5.18)		
O(2)	0.219 (18)	0.0687 (52)	0.37 (2.49)		
O(3)	0.317 (13)	0.2450 (38)	-0.97 (1.32)		
O(4)	0.074 (12)	0.3149 (46)	-0.63 (1.72)		
O(5)	0.290 (30)	0.1503 (71)	3.44 (3.87)		
O(6)	0.219 (21)	0.4581 (54)	1.13 (2.60)		
O(7)	0.823 (21)	0.0536 (55)	-0.04 (1.96)		
O(8)	0.614 (20)	0.1239 (61)	-0.10 (2.12)		
O(9)	0.856 (15)	0.1835 (44)	-0.37 (2.09)		
O(10)	0.683 (19)	0.2667 (54)	-0.05 (2.30)		
O(11)	0.662 (25)	0.3556 (59)	0.89 (3.02) *		
O(12)	0.812	0.4312	1.0		
O(13)	0.060	0.0000	1.0		
O(14)	0.962	0.1160	1.0		
O(15)	0.978	0.2426	1.0		
O(16)	0.974	0.3729	1.0		
O(17)	0.502	0.0564	1.0		
O(18)	0.509	0.1892	1.0		
O(19)	0.420	0.3114	1.0		
O(20)	0.491	0.4279	1.0		
O(21)	0.310	0.3740	1.0†		
O(22)	Related to O(1) by $(\bar{x}, \frac{1}{2} + y)$				
O(23)	Related to O(13) by $(\bar{x}, \frac{1}{2} + y)$				
Plane group pm					
	x/a	y/b	$\beta_{11} \times 10_4$ or B	$\beta_{22} \times 10_5$	$\beta_{12} \times 10_5$
M(1)	0.0784	0.0000	54 (34)	32 (15)	00
M(2)	0.9241 (18)	0.5000	10 (28)	47 (13)	00
M(3)	0.9907 (39)	0.11934 (60)	45 (25)	70 (13)	22 (34)
M(4)	0.0061 (54)	0.24951 (62)	65 (18)	45 (7)	-17 (17)
M(5)	0.9911 (36)	0.37961 (48)	162 (35)	18 (8)	51 (38)
M(6)	0.5198 (48)	0.06571 (66)	95 (41)	73 (15)	-69 (36)
M(7)	0.5519 (55)	0.19105 (64)	235 (52)	43 (11)	23 (68)
M(8)	0.4543 (46)	0.30919 (53)	61 (25)	52 (10)	22 (48)
M(9)	0.4697 (51)	0.43500 (49)	20 (43)	38 (10)	-50 (42)
O(1)	0.438 (32)	0.0000	-0.99 (2.99)		
O(2)	0.179 (15)	0.0661 (52)	-1.48 (1.91)		
O(3)	0.298 (30)	0.2430 (111)	0.93 (5.5)		
O(4)	0.125 (22)	0.3126 (44)	0.31 (2.14)		
O(5)	0.256 (39)	0.1535 (125)	2.69 (4.31)		
O(6)	0.164 (47)	0.4585 (121)	2.30 (3.61)		
O(7)	0.822 (19)	0.0460 (56)	0.01 (2.05)		
O(8)	0.639 (21)	0.1278 (43)	0.41 (2.41)		
O(9)	0.889 (19)	0.1860 (47)	2.00 (2.09)		
O(10)	0.695 (23)	0.2610 (77)	1.12 (3.48)		
O(11)	0.708 (29)	0.3467 (87)	1.24 (3.50) *		
O(12)	0.789 (26)	0.4401 (64)	0.99 (3.79)		
O(13)	0.078	0.0000	1.0		

Table 1 (cont.)

	x/a	y/b	$\beta_{11} \times 10^4$ or β
O(14)	0.981	0.1130	1.0
O(15)	0.996	0.2480	1.0
O(16)	0.020	0.3860	1.0
O(17)	0.518	0.0660	1.0
O(18)	0.547	0.1910	1.0
O(19)	0.428	0.3080	1.0
O(20)	0.480	0.4300	1.0
O(21)	0.312	0.3750	1.0†
O(22)	0.579 (28)	0.5000	-1.05 (3.35)
O(23)	0.922	0.500	1.0

* Unresolved doublet.

† Population parameter is 0.25.

Table 2. Observed and calculated structure factors

Unobserved data are marked with L.

H	K	F _O	F _C	H	K	F _O	F _C	H	K	F _O	F _C	H	K	F _O	F _C					
0	34	L	7	9	1	1	L	14	3	17	20	18	5	19	89	84				
0	32		345	305	2	34		11	12	3	14	L	14	8	5	18	40	42		
0	30	L	11	1	2	33		49	46	3	15		53	61	5	17	32	32		
0	28		53	47	2	32		255	226	3	14		217	240	5	16	L	12	27	
0	26		204	203	2	31		137	132	3	13		181	194	5	15		103	102	
0	24	L	13	2	2	30		23	25	3	12		74	69	5	14		251	231	
0	22		172	184	2	29	L	10	22	3	11	L	14	13	5	13		121	113	
0	20		61	73	2	28		27	35	3	10		24	34	5	12		139	141	
0	18	L	14	19	2	27		65	56	3	9		236	222	5	11		28	25	
0	16		653	777	2	26		119	127	3	8		599	638	5	10		51	44	
0	14	L	14	18	2	25		26	24	3	7		300	282	5	9		157	154	
0	12		32	23	2	24	L	13	2	3	2		180	162	5	8		241	237	
0	10		131	100	2	23		29	40	3	1		43	59	5	7		234	227	
0	8	L	15	14	2	22		179	196	4	30		69	69	5	6		89	86	
0	6		107	92	2	21		82	90	4	29		17	15	5	5	L	14	5	
0	4		33	24	2	20	L	14	18	4	28	L	8	13	5	4		127	115	
0	2	L	10	4	2	19	L	14	9	4	27		65	68	5	3		140	134	
1	35		30	31	2	18		14	24	4	26	L	9	24	5	2		189	168	
1	34		146	131	2	17		118	112	4	25		34	33	5	1		88	86	
1	33		41	43	2	16		492	563	4	24		17	22	6	21		36	35	
1	32		16	9	2	15		212	231	4	23		76	74	6	20		115	113	
1	31		18	10	2	14		39	40	4	22		225	239	6	19		39	40	
1	30		147	175	2	13	L	14	20	4	21		133	136	6	18		33	29	
1	29		76	75	2	12	L	14	26	4	20		76	81	6	17		89	82	
1	28		60	56	2	11		168	199	4	19	L	13	14	6	16		135	127	
1	27	L	12	5	2	10		117	115	4	18	L	13	23	6	15		175	164	
1	26	L	13	10	2	9	L	14	15	4	17		109	119	6	14		96	95	
1	25		33	49	2	8	L	14	11	4	16		290	287	6	13	L	10	15	
1	24		404	435	2	7		26	39	4	15		216	213	6	12		88	85	
1	23		59	66	2	6		170	142	4	14		77	78	6	11		70	68	
1	22	L	14	21	2	5		183	152	4	13	L	14	9	6	10		164	160	
1	21	L	14	18	2	4		48	47	4	12		55	56	6	9		109	112	
1	20	L	14	23	2	3	L	14	10	4	11		119	140	6	8		23	43	
1	19		61	83	2	2	L	14	20	4	10		110	111	6	7		138	145	
1	18		161	171	2	1		245	199	4	9		36	46	6	6		243	239	
1	17		30	29	2	0		708	803	4	8	L	14	29	6	5		82	76	
1	16	L	14	4	3	32	L	6	11	4	7		91	91	6	4		140	131	
1	15		25	25	3	31		41	18	4	6		253	246	6	3		25	26	
1	14		216	211	3	30		177	180	4	5		201	203	6	2		62	56	
1	13		180	177	3	29		97	100	4	4		136	129	6	1		150	144	
1	12	L	14	29	3	28		29	32	4	3	L	14	14	6	0		186	182	
1	11	L	15	8	3	27	L	10	11	4	2		50	57	7	13		20	17	
1	10	L	15	8	3	26	L	11	18	4	1		234	231	7	12		98	100	
1	9		97	94	3	25		92	94	4	0		436	426	7	11		32	37	
1	8		807	878	3	24		290	302	5	26		25	25	7	10		22	27	
1	7		167	139	3	23		206	223	5	25		77	80	7	9		66	72	
1	6	L	14	23	3	22		68	68	5	24		133	126	7	8		99	105	
1	5	L	14	5	3	21		22	19	5	23		192	187	7	7		96	94	
1	4	L	14	26	3	20	L	14	28	5	22		86	87	7	6		52	58	
1	3		138	121	3	19		133	141	5	21		19	18	7	5	L	8	22	
1	2	L	14	13	3	18		30	30	5	20		45	39	7	4		71	81	
																			14	15
																			157	167
																			128	136

lists observed and calculated structure amplitudes. Bond distances and angles, together with their estimated standard deviations (e.s.d.'s), are given in Table 3.

Table 3. Bond distances (Å) and angles (°) for the coordination polyhedra

Plane group *pm*. Prime indicates atoms related by x, \bar{y}, z . Second number in parentheses denotes frequency of occurrence.

M(1) Pentagonal bipyramid

M(1)—O(1)	2.22 (19) (1)
—O(2)	2.03 (15) (2)
—O(7)	2.08 (14) (2)
—O(13)	1.93 (20) (2)

M(2) Pentagonal bipyramid

M(2)—O(12)	1.94 (18) (2)
—O(22)	2.14 (17) (1)
—O(6)	1.91 (32) (2)

Table 3 (cont.)

O(1)—O(2)	2.51 (18) (2)
O(2)—O(7)	2.28 (16) (2)
O(7)—O(7')	2.69 (23) (1)
O(13)—O(1)	2.94 (24) (2)
—O(2)	2.80 (24) (4)
—O(7)	2.83 (22) (4)
O(1)—O(2)—O(7)	115 (8) (2)
O(2)—O(7)—O(7')	105 (8) (2)
O(2)—O(1)—O(2')	101 (8) (1)

Table 3 (cont.)

M(2)—O(23)	1.93 (30) (2)
O(6)—O(12)	2.38 (34) (2)
O(12)—O(22)	2.30 (20) (2)
O(6)—O(6')	2.43 (50) (1)
O(23)—O(22)	2.87 (22) (2)
—O(12)	2.73 (15) (4)
—O(6)	2.72 (26) (4)
O(12)—O(22)—O(12')	107 (10) (1)
O(22)—O(12)—O(6)	111 (12) (2)
M(3) Pentagonal bipyramid	
M(3)—O(2)	1.94 (14) (1)
—O(5)	1.92 (28) (1)
—O(9)	2.05 (14) (1)
—O(8)	2.18 (13) (1)
—O(7)	2.38 (16) (1)
—O(14)	1.94 (20) (2)
O(2)—O(5)	2.60 (39) (1)
O(5)—O(9)	2.46 (29) (1)
O(9)—O(8)	2.30 (18) (1)
O(8)—O(7)	2.64 (20) (1)
O(7)—O(2)	2.28 (16) (1)
O(14)—O(2)	2.66 (21) (2)
O(14)—O(5)	2.83 (29) (2)
—O(9)	2.93 (24) (2)
—O(8)	2.89 (21) (2)
—O(7)	2.92 (24) (2)
O(2)—O(5)—O(9)	102 (10) (1)
O(5)—O(9)—O(8)	109 (10) (1)
O(9)—O(8)—O(7)	113 (7) (1)
O(8)—O(7)—O(2)	100 (7) (1)
O(7)—O(2)—O(5)	115 (8) (1)
M(4) Octahedra	
M(4)—O(3)	1.89 (19) (1)
—O(4)	1.99 (13) (1)
—O(9)	1.99 (14) (1)
—O(10)	1.95 (15) (1)
O(3)—O(4)	2.30 (33) (1)
O(4)—O(10)	3.05 (21) (1)
O(10)—O(9)	2.50 (25) (1)
O(9)—O(3)	3.02 (27) (1)
O(15)—O(3)	2.68 (22) (2)
—O(4)	2.81 (23) (2)
—O(9)	2.73 (22) (2)
—O(10)	2.70 (20) (2)
O(3)—O(4)—O(10)	88 (9)
O(4)—O(10)—O(9)	91 (6)
O(10)—O(9)—O(3)	85 (7)
O(9)—O(3)—O(4)	96 (7)
M(5) Pentagonal bipyramid	
M(5)—O(4)	2.13 (13) (1)
—O(11)	2.00 (20) (1)
—O(12)	2.16 (18) (1)
—O(6)	2.54 (34) (1)
—O(21)	1.99 (25) (1)
—O(16)	1.94 (20) (2)
O(4)—O(11)	2.76 (23) (1)
O(11)—O(12)	2.78 (31) (1)
O(12)—O(6)	2.38 (33) (1)
O(6)—O(21)	2.61 (45) (1)
O(21)—O(4)	2.16 (31) (1)
O(16)—O(4)	2.95 (24) (2)
—O(11)	2.96 (25) (2)
—O(12)	2.87 (24) (2)
—O(6)	3.00 (34) (2)
—O(21)	2.66 (24) (2)
O(4)—O(11)—O(12)	108 (8)
O(11)—O(12)—O(6)	113 (11)
O(12)—O(6)—O(21)	97 (14)

Table 3 (cont.)

O(6)—O(21)—O(4)	127 (13)
O(21)—O(4)—O(11)	101 (10)
M(5) Distorted octahedron	
M(5)—O(4)	2.13 (13) (1)
—O(11)	2.00 (20) (1)
—O(12)	2.16 (18) (1)
—O(6)	2.54 (34) (1)
—O(16)	1.94 (20) (2)
O(4)—O(11)	2.76 (23) (1)
O(11)—O(12)	2.78 (31) (1)
O(12)—O(6)	2.38 (33) (1)
O(6)—O(4)	4.27 (38) (1)
O(16)—O(4)	2.95 (24) (2)
—O(11)	2.96 (25) (2)
—O(12)	2.87 (24) (2)
—O(6)	3.00 (34) (2)
O(4)—O(11)—O(12)	101 (8)
O(11)—O(12)—O(6)	113 (11)
O(12)—O(6)—O(4)	77 (8)
M(6) Octahedron	
M(6)—O(1)	1.99 (05) (1)
—O(2)	2.10 (10) (1)
—O(7)	1.95 (13) (1)
—O(8)	1.96 (13) (1)
—O(17)	1.93 (20) (2)
O(1)—O(2)	2.51 (18) (1)
O(2)—O(8)	3.36 (17) (1)
O(8)—O(7)	2.64 (20) (1)
O(7)—O(1)	2.73 (22) (1)
O(17)—O(1)	2.77 (21) (2)
—O(2)	2.84 (19) (2)
—O(8)	2.74 (22) (2)
—O(7)	2.75 (20) (2)
O(1)—O(2)—O(8)	83 (5)
O(2)—O(8)—O(7)	83 (5)
O(8)—O(7)—O(1)	94 (5)
O(7)—O(1)—O(2)	100 (4)
M(7) Pentagonal bipyramid	
M(7)—O(3)	2.18 (26) (1)
—O(5)	2.13 (28) (1)
—O(8)	1.93 (13) (1)
—O(9)	2.09 (12) (1)
—O(10)	2.23 (22) (1)
—O(18)	1.93 (20) (2)
O(3)—O(5)	2.63 (49) (1)
O(5)—O(8)	2.48 (29) (1)
O(8)—O(9)	2.30 (18) (1)
O(9)—O(10)	2.50 (25) (1)
O(10)—O(3)	2.51 (24) (1)
O(18)—O(3)	2.90 (28) (2)
—O(5)	2.86 (28) (2)
—O(8)	2.72 (22) (2)
—O(9)	2.85 (20) (2)
—O(10)	2.95 (27) (2)
O(3)—O(5)—O(8)	102 (11)
O(5)—O(8)—O(9)	114 (10)
O(8)—O(9)—O(10)	109 (7)
O(9)—O(10)—O(3)	107 (11)
O(10)—O(3)—O(5)	108 (12)
M(8) Pentagonal bipyramid	
M(8)—O(3)	2.16 (30) (1)
—O(4)	2.04 (14) (1)
—O(21)	2.11 (29) (1)
—O(11)	1.91 (21) (1)
—O(10)	2.05 (19) (1)
—O(19)	1.93 (20) (2)
O(3)—O(4)	2.30 (33) (1)

Table 3 (cont.)

O(4)—O(21)	2·16 (31) (1)
O(21)—O(11)	2·58 (31) (1)
O(11)—O(10)	2·51 (34) (1)
O(10)—O(3)	2·51 (24) (1)
O(19)—O(3)	2·82 (31) (2)
—O(4)	2·69 (20) (2)
—O(21)	2·84 (30) (2)
—O(11)	2·82 (24) (2)
—O(10)	2·88 (24) (2)
O(3)—O(4)—O(21)	120 (11)
O(4)—O(21)—O(11)	104 (13)
O(21)—O(11)—O(10)	107 (10)
O(11)—O(10)—O(3)	104 (11)
O(10)—O(3)—O(4)	106 (13)
M(8) Distorted octahedron	
M(8)—O(3)	2·16 (30) (1)
—O(4)	2·04 (14) (1)
—O(10)	2·05 (19) (1)
—O(11)	1·91 (21) (1)
—O(19)	1·93 (20) (2)
O(3)—O(4)	2·30 (33) (1)
O(4)—O(11)	2·76 (33) (1)
O(11)—O(10)	2·51 (34) (1)
O(10)—O(3)	2·51 (24) (1)
O(19)—O(3)	2·82 (31) (2)
—O(4)	2·69 (20) (2)
—O(11)	2·82 (24) (2)
—O(10)	2·88 (24) (2)
O(3)—O(4)—O(11)	78 (8)
O(4)—O(11)—O(10)	73 (6)
O(11)—O(10)—O(3)	104 (11)
O(10)—O(3)—O(4)	106 (13)
M(9) Pentagonal bipyramid	
M(9)—O(6)	2·01 (30) (1)
—O(22)	2·15 (06) (1)
—O(12)	1·98 (16) (1)
—O(11)	2·97 (24) (1)
—O(21)	2·01 (28) (1)
—O(20)	1·93 (20) (2)
O(6)—O(22)	2·78 (34) (1)
O(22)—O(12)	2·10 (21) (1)
O(12)—O(11)	2·78 (31) (1)
O(11)—O(21)	2·58 (31) (1)
O(21)—O(6)	2·61 (45) (1)
O(20)—O(11)	3·40 (30) (2)
—O(12)	2·73 (21) (2)
—O(21)	2·71 (28) (2)
—O(6)	2·86 (29) (2)
—O(22)	2·98 (22) (2)
O(6)—O(22)—O(12)	96 (8)
O(22)—O(12)—O(11)	135 (9)
O(12)—O(11)—O(21)	82 (10)
O(11)—O(21)—O(6)	129 (4)
O(21)—O(6)—O(22)	92 (11)
M(9) Distorted octahedron	
M(9)—O(6)	2·01 (30) (1)
—O(22)	2·15 (06) (1)
—O(12)	1·98 (16) (1)
—O(11)	2·97 (24) (1)
—O(20)	1·93 (20) (2)
O(6)—O(22)	2·78 (34) (1)
O(22)—O(12)	2·10 (21) (1)
O(12)—O(11)	2·78 (31) (1)
O(11)—O(6)	4·68 (39) (1)
O(20)—O(11)	3·40 (30) (2)
—O(6)	2·86 (29) (2)
—O(22)	2·98 (22) (2)
—O(12)	2·73 (21) (2)

Table 3 (cont.)

O(12)—O(11)—O(6)	56 (6)
O(11)—O(6)—O(22)	72 (7)
O(8)—O(22)—O(12)	96 (8)
O(22)—O(12)—O(11)	135 (9)

Description of the structure

The structure of the asymmetric unit is essentially the same for both refinements; the overall structure depends on the way in which the asymmetric unit propagates itself and is therefore different for each of the plane groups *pm* and *pg*. The structure of the asymmetric unit is described first.

Metal atoms have a close-packed hexagonal arrangement within sheets separated by 3·85 Å. 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.

There are 16 metal atoms and 40½ oxygen atoms in the unit cell derived from the X-ray data. The ideal structure has 42 oxygen atoms in the unit cell and can be generated from a chain of 6 edge-sharing pentagons which is regularly folded as shown in Fig. 1. Each folded chain is fused to an identical one by corner-sharing. The folding process introduces anionic packing distortions at the folding planes (Roth & Stephenson, 1969), and the real structure differs from the ideal structure by the manner in which the pentagonal bipyramids lying on, or near, the folding planes accommodate the distortions imposed upon them by the folding process.

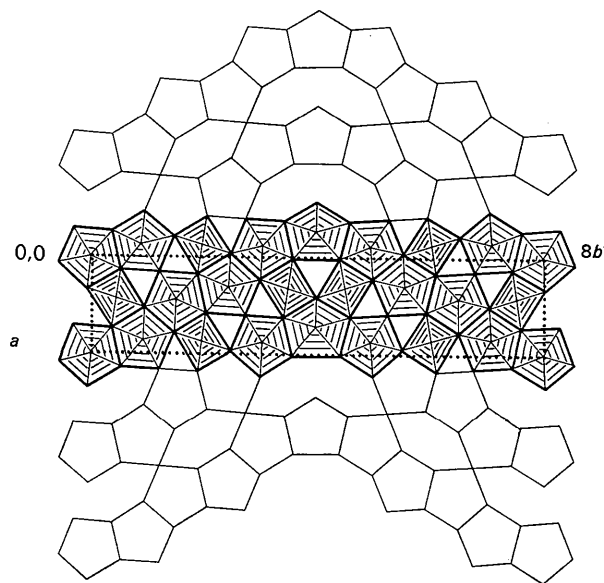


Fig. 1. The ideal structure of the compound Ta₃₀W₂O₈₁ derived from fused chains of regular pentagons. Each straight portion of the chain is six pentagons long and the (010) and (020) planes are the folding planes. *b'* is the subcell parameter.

This process can involve a reduction in the coordination number of some metal atoms and in the previous paper such a distortion plane was readily located by a splitting of one of the oxygen peaks. No such splitting occurs in the structure of $Ta_{30}W_2O_{81}$ but one oxygen peak, O(21), is very much lower in peak height than any of the remaining oxygen peaks. In either plane group pg or pm the general position is twofold and therefore the $40\frac{1}{2}$ oxygen atoms will completely fill 20 general positions together with one half an oxygen atom distributed over one twofold position. This latter situation corresponds to the observed lower oxygen peak height, which is equivalent to $\frac{1}{4}$ oxygen atom.

Each distortion plane in the structure of $Ta_{30}W_2O_{81}$ is therefore associated with O(21) and there are $1\frac{1}{2}$ distortion planes per unit cell, or three distortion planes in two unit cells *i.e.* distributed over a distance of

58.452 \AA along the [010] direction. This means that the O(21) position which occurs *four* times in two unit cells of the *ideal* structure is only occupied *once* in two unit cells of the real structure. Metal atoms M(8), M(9) and M(5) therefore have distorted, pentagonal bipyramidal coordination polyhedra in the absence of a distortion plane but in 75% of the structure these metal atoms have distorted octahedral coordination polyhedra. The atom O(21) was therefore given a population parameter of 0.25 in all crystallographic calculations.

One other consequence of the dual coordination features of atoms M(8), M(9) and M(5) is the shape of the oxygen peak O(11) which is noticeably elongated in the Fourier syntheses. Probably, O(11) occupies slightly different positions depending on whether it belongs to the pentagonal bipyramidal or octahedral coordination polyhedra.

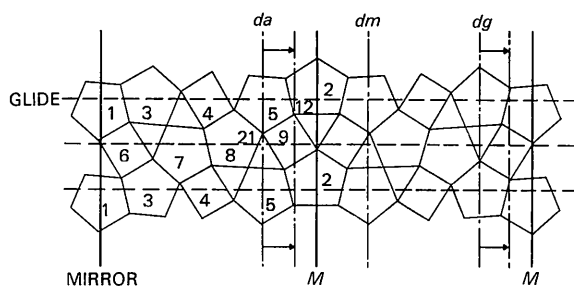


Fig. 2. The locations of the mirror (M) and glide planes of the ideal 8 subcell structure and the distortion planes (d) of the real structure. The distortion plane da can propagate to dm or dg by a mirror or glide plane respectively. The distortion plane through O(12), shown arrowed, cannot propagate by mirroring. Polyhedra are marked according to the number (Table 1) of the metal atom.

Discussion

The plane group symmetry of the 8 UO_3 -type subcell structure, shown in Fig. 1, is pgm . It has been shown that the structure of the compound $Ta_{30}W_2O_{81}$ differs slightly from this ideal structure because of the packing distortions occurring in the ideal model. The plane group symmetry of the structure of $Ta_{30}W_2O_{81}$ is either pm or pg and, although the structure of the asymmetric unit (*viz.* $a \times b/2 \times c$) is not greatly dependent on the plane group, the manner in which it repeats itself does lead to a different overall structure for each plane group. Particularly dependent on the choice of plane group is the distribution of distortion planes along the b axis. The distortion plane incorporating O(21) of the asymmetric unit is shown in Fig. 2 by da , and the distortion

Table 4. Correlation coefficients, Q_{ij} , for metal-metal positional parameter interactions using (a) plane group pm (b) plane group pg

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.

(a)	1	2	3	4	5	6	7	8	9
1	1.0	—	—	—	—	—	—	—	—
2	—	1.0	—	—	—	—	—	—	—
3	—	0.41	1.0	-0.28	0.80	0.08	0.11	0.14	0.14
4	—	0.55	0.77	1.0	-0.27	0.04	-0.22	-0.28	0.02
5	—	0.46	0.89	0.75	1.0	-0.07	-0.02	0.09	0.01
6	—	0.44	0.73	0.60	0.62	1.0	-0.35	-0.25	0.81
7	—	0.29	0.56	0.54	0.48	0.71	1.0	0.80	-0.43
8	—	0.35	0.62	0.59	0.56	0.81	0.89	1.0	-0.24
9	—	0.41	0.76	0.67	0.65	0.96	0.67	0.80	1.0

(b)	1	2	3	4	5	6	7	8	9
1	1.0	—	—	—	—	—	—	—	—
2	—	1.0	—	—	—	—	—	—	—
3	0.88	—	1.0	0.09	0.14	-0.04	0.26	0.15	0.13
4	0.07	—	0.10	1.0	0.41	-0.06	0.09	-0.30	-0.02
5	0.07	—	0.02	-0.83	1.0	0.08	-0.08	-0.22	0.01
6	0.40	—	0.32	0.15	0.03	1.0	-0.01	-0.56	-0.30
7	0.68	—	0.67	0.03	0.02	0.50	1.0	0.43	0.58
8	0.39	—	0.25	-0.02	0.06	0.17	0.30	1.0	0.42
9	-0.63	—	-0.56	0.11	-0.22	-0.52	-0.91	-0.22	1.0

The values omitted were not calculated.

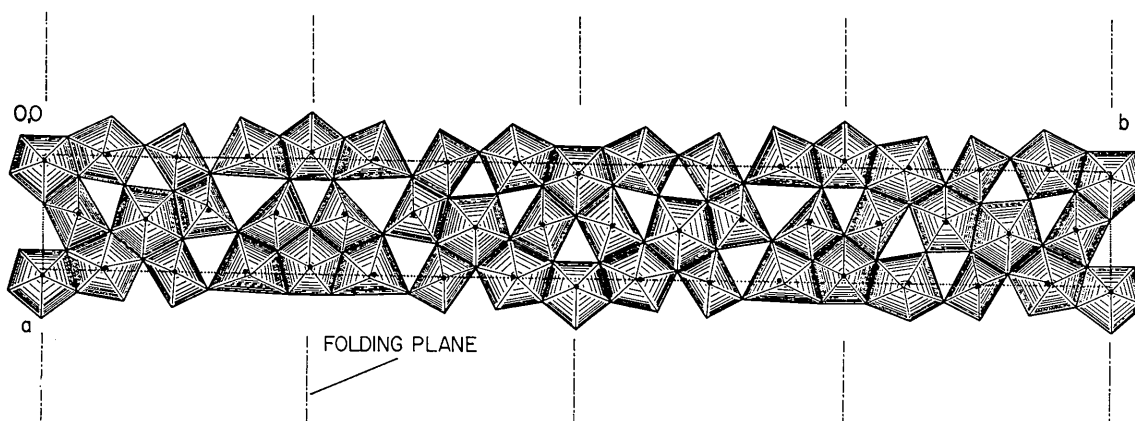


Fig. 3. A projection of the real structure of $\text{Ta}_{30}\text{W}_2\text{O}_{81}$ onto the (001) plane. Distortion planes have been propagated according to the plane group pm . Black dots represent metal atoms and shaded areas oxygen coordination polyhedra.

planes related to da by a mirror plane and by a glide plane are identified in Fig. 2 by dm and dg , respectively. Further repeat positions along [010] are determined by a b translation vector and the frequency of the distortion planes, which is determined by the molecular formula, is such that 3 distortion planes occur every $2b = 58.452$ Å. If the plane group of $\text{Ta}_{30}\text{W}_2\text{O}_{81}$ is pm the distortion planes occur in pairs (e.g. da and dm in Fig. 2), whereas if the plane group is pg the distortion planes are distributed regularly along [010] with an average separation distance of $b/2$, e.g. da and dg in Fig. 2.

It is not possible to choose between pm and pg based on the plausibility of bond lengths and angles for the structure refined in each plane group. Standard deviations are so large as to make quantitative comparisons impossible. The reason for the large standard deviations is again the extensive interdependence of positional parameters particularly x - x and y - y interactions. The correlation coefficients for these types of interactions were obtained from the inverse matrix calculated by Busing, Martin & Levy's (1962) *ORFLS* program and are listed in Table 4 for the metal atoms of the asymmetric unit. The values are high, a consequence of the small perturbation of the real structure from ideal pgm symmetry. However there are 13 values of q_{ij} greater than 0.70 for the pm refinement compared with 3 values of q_{ij} greater than 0.70 for the pg refinement and it would seem that a more satisfactory refinement, with lower standard deviations in atomic parameters, is to be obtained in the plane group pg .

To reach a decision on the correct space group of potassium hydrogen malonate, Parthasarathy, Sime & Speakman (1969) found it necessary to have recourse to noncrystallographic considerations. In the present in-

stance such considerations favor the plane group pm . Consider the situation where the distortion plane da (Fig. 2) is propagated along the [010] direction by a glide plane so that no association of distortion planes occurs. It would be reasonable to expect that the distortion plane would be located as close as possible to the region of maximum distortion, as was the case in the structure of $\text{Ta}_{22}\text{W}_4\text{O}_{67}$. This position is shown in Fig. 2 by arrows and involves the atom O(12). A distortion plane in this position could not be propagated along the [010] direction by mirroring since it is too close to the (020) mirror plane. A retraction from this mirror plane to the position that it does occupy, i.e. O(21), permits the possibility of propagation by mirroring and, although indirect, may be the evidence needed to decide between pm and pg .

Fig. 3 represents a projection of the structure of $\text{Ta}_{30}\text{W}_2\text{O}_{81}$ onto the (001) plane. The distortion planes have been propagated according to the plane group pm .

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