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The Crystal Structure of $W_2O_3(AsO_4)_2$

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The crystal structure of $W_2O_3(AsO_4)_2$ has been determined and refined from three-dimensional X-ray diffractometer data. The structure is orthorhombic, space group *Pnma*. The elementary cell contains four formula units and has the dimensions $a = 16.0109 \pm 14$ Å, $b = 6.4341 \pm 7$ Å, $c = 8.0430 \pm 13$ Å.

The crystals are built up of AsO_4 tetrahedra sharing corners with four WO_6 octahedra, each of which is coupled with four different AsO_4 tetrahedra. Thus, four of the six oxygen atoms in each octahedron are shared with tetrahedra. Of the remaining two oxygen atoms, one is common with another WO_6 octahedron, while the sixth one is unshared. In the pair of octahedra thus obtained, the two wolfram atoms and those three oxygen atoms, which are not shared with arsenic, form a planar W_2O_3 group, parallel to the *xz* plane. Each AsO_4 tetrahedron links together four W_2O_3 groups, giving a three-dimensional arrangement.

In connection with an X-ray investigation of phosphorus-oxygen compounds of wolfram [1–2] undertaken at this Institute, an investigation of the system $WO_3 - As_2O_5$ was started. Only one crystalline phase, with the composition $2WO_3 \cdot As_2O_5$, was found in the system.

EXPERIMENTAL

Preparation of the crystals. A mixture of WO_3 and As_2O_5 in the ratio 2:1 was heated in sealed, evacuated platina capsules for about a month at 600°C. The product obtained was a mixture of the reactants with the intermediate phase, $2WO_3 \cdot As_2O_5$. The tentative formula $2WO_3 \cdot As_2O_5$, suggested by the preparative conditions, has been confirmed by the result of the structure determination (*vide infra*). Colourless crystals, in the shape of needles with a length to width ratio of approximately 10:1, suitable for X-ray work, could be picked out from the preparation.

X-Ray diffraction data and computing methods. The powder pattern of $2WO_3 \cdot As_2O_5$ was completely indexed on the basis of an orthorhombic unit cell. The cell parameters were calculated from a photograph taken with strictly monochromatized Cu$K\alpha_1$ radiation ($\lambda = 1.54050$ Å) in a focusing camera of Guinier-Hägg type. Potassium chloride

Table 1. X-Ray powder data for $W_2O_3(AsO_4)_2$. Cu$K\alpha_1$-radiation. $\lambda(CuK\alpha_1) = 1.54050$ Å. Reflections systematically absent in space group *Pnma* have been omitted.

hkl	$10^5\sin^2\theta$ obs	$10^5\sin^2\theta$ calc	I_{obs}	*hkl*	$10^5\sin^2\theta$ obs	$10^5\sin^2\theta$ calc	I_{obs}
200	935	925	w	503		14039	
201	1847	1842	m	131	14053	14046	v w
011		2350		620		14064	
210	2364	2358	st	800	14792	14812	w
111	2589	2581	m	323	16072	16069	w
301	3008	3000	m	603		16585	
211	3286	3276	st	430	16599	16601	v w
102	3898	3899	m	304	16763	16756	v w
311	4446	4433	v st	132		16798	
202	4597	4594	m	802	18465	18480	v w
401	4628	4620	m	523	19779	19772	m
020	5734	5732	st	414		19809	
302		5751		722	20730	20741	w
501	6716	6703	w	911		21096	
312	7187	7184	w	033	21127	21152	m
221	7583	7575	v v w	623	22319	22318	v w
600	8335	8331	m diff	532		22352	
103	8502	8485	w	040	22927	22930	v w
412	8805	8804	m	813	24519	24499	w
203	9192	9179	v v w	1011	25517	25494	v w
122	9634	9632	w diff	922	28123	28147	w
013	9682	9687	w	342	28681	28681	v w
610	9782	9764	v w	505		28713	
113	9905	9918	v w	605	31244	31259	v v w
222		10326		640		31261	
303	10343	10336	m	434		31275	
421		10352		1022		32544	
512	10903	10887	w	931	32569	32561	w
521	12445	12435	v w	106		33247	
612	13450	13433	v v w	343	33287	33267	v w
711	13703	13690	w	1004	37796	37817	v w
031		13815		144		37835	
230	13836	13823	w				

($a = 6.29228$ Å)[3] was used as an internal standard. Least squares refinement gave the following unit-cell dimensions (see Table 1) at 25°C: $a = 16.0109 \pm 14$ Å, $b = 6.4341 \pm 7$ Å, $c = 8.0430 \pm 13$ Å.

The value of 5.77 g/cm³ for the density of $2WO_3 \cdot As_2O_5$, found from the apparent loss of weight in benzene, indicates that there are four formula units in the unit cell. The calculated density = 5.52 g/cm³. The higher value of the density found is very likely due to contamination of the sample by unreacted WO_3 ($\varrho_{WO_3} = 7.16$ g/cm³).

From preliminary rotation and Weissenberg photographs – taken with Cu$K\alpha$ radiation – it was found that the reflections systematically absent are $0kl$ with $k + l = 2n + 1$, and $hk0$ with $h = 2n + 1$, which is characteristic for the two space groups *Pnma* (No. 62) and $Pn2_1a$ (No. 33).

Three-dimensional intensity data were collected with a manual General Electric X-Ray Diffractometer, equipped with a single-crystal orienter (Goniostat), and a scintillation counter with pulse height discrimination. Ni-filtered CuK radiation was used, and the $\theta - 2\theta$ scan technique [4] was applied, with a scan interval of 2° and a rate of 2° per min. The background intensity was calculated as the average of the background intensities at each end of the scan interval.

A crystal with the dimensions $0.007(a) \times 0.090(b) \times 0.008(c)$ mm³ was mounted along the b-axis. The intensities of 544 observable reflections within the range $0 < \sin^2\theta_{hkl} \leq 0.75$ in one octant of the reciprocal lattice were measured twice.

The net intensities were corrected for Lorentz polarization and absorption effects. In the calculation of absorption factors, a linear absorption coefficient [5] with the value μ-622.9 cm^{-1} was used. The transmission factors for different reflections varied from 0.51 to 0.66.

In the first stages of this structural study, the computational work was performed on the electronic computer IBM 1800. The final calculations were performed on the electronic computer IBM 360/75. The programs used in the calculations are listed in Table 2.

Table 2. Computer programs used for the crystallographic calculations. All the programs are written in FORTRAN IV.

Program name and function. Computer	Authors
PIRUM. Indexing of powder photographs and least squares refinement of unit cell parameters. IBM 1800.	P.-E. Werner, Stockholm, Sweden.
VIP. Angle settings for three-circle diffractometers. IBM 1800.	R. Norrestam, Stockholm, Sweden.
ABS. Absorption, extinction and Lp-factors. IBM 1800.	P.-E. Werner and M. Leijonmarck, Stockholm, Sweden.
DRF. Fourier summations and structure factor calculations. IBM 360/75.	A. Zalkin, Berkeley, USA. Modified by R. Liminga and J.-O. Lundgren, Uppsala, Sweden. Further modified by O. Lindgren, Göteborg, and by A. G. Nord and B. G. Brandt, Stockholm, Sweden.
LALS. Full matrix least-squares refinement of positional and thermal parameters and of scale factors. IBM 360/75.	P. K. Gantzel, R. A. Sparks and K. N. Trueblood, Los Angeles, USA. Modified by A. Zalkin, Berkeley, USA, and by J.-O. Lundgren, R. Liminga and C.-I. Brändén, Uppsala, Sweden. Further modified by O. Lindgren, Göteborg, and by B. G. Brandt and A. G. Nord, Stockholm, Sweden.
DATAP2. Lp and absorption corrections. Preparative calculations for extinction correction according to Zachariassen's 1963-formula. IBM 360/75.	P. Coppens, L. Leiserowits and D. Rabinovich, Rehovoth, Israel. Modified by O. Olofsson and M. Elfström, Uppsala, Sweden. Inclusion of calculations for extinction correction by B. G. Brandt and S. Åsbrink, Stockholm, Sweden. Further modifications by B. G. Brandt and A. G. Nord, Stockholm, Sweden.
EXTDATA. Calculation of the factor c in Zachariasen's 1963-formula for extinction correction. Application of the correction. IBM 360/75.	B. G. Brandt, Stockholm, Sweden.
DISTAN. Calculation of interatomic distances and bond angles with estimated standard deviations. IBM 360/75.	A. Zalkin, Berkeley, USA. Modified by A. G. Nord and B. G. Brandt, Stockholm, Sweden.

STRUCTURE DETERMINATION

The higher possible symmetry, *Pnma*, was assumed at the beginning of the structure investigation. The result thus obtained was found to be throughout consistent.

In the space group *Pnma* the following point positions are possible:

4(*a*): 0,0,0; 0,½,0; ½,0,½; ½,½,½
4(*b*): 0,0,½; 0,½,½; ½,0,0; ½,½,0
4(*c*) ±(*x*,1/4,*z*); ±(½+*x*,1/4,½-*z*)
8(*d*): ±(*x*,*y*,*z*); ±(½+*x*,½−*y*,½−*z*); ±(*x*,½−*y*,*z*); ±(½+*x*,*y*,½−*z*)

From calculations of Patterson projections and sections, approximate parameter values were derived for the eight wolfram atoms occupying two sets of point position 4(*c*). Three-dimensional electron density calculations were performed, using signs of the observed structure factors derived from the wolfram contribution only. From these and subsequent calculations were derived the positions of the eight arsenic atoms, situated in two sets of point position 4(*c*), and forty-four oxygen atoms occupying seven sets of point position 4(*c*) and two sets of point position 8(*d*). In the calculations, atomic scattering curves for un-ionized atoms were used; the scattering curves for W and As taken from Cromer and Waber,[6] and for O from Hanson *et al.*[7] The real part of the anomalous dispersion correction [8] for W and As was applied to the scattering curves.

A refinement of the coordinates thus obtained was then performed by means of the full matrix least-squares method. Anisotropic temperature factors were used for the wolfram and arsenic atoms. A discrepancy factor, $R=\sum||F_o|-|F_c||/\sum|F_o|$, of 0.049 was obtained when all the observed 544 reflections were included.

In space group $Pn2_1a$, the type of special position represented above by 4(*c*): *x*, 1/4, *z* becomes a general position *x*, *y*, *z*. All attempts to lower the symmetry of the structure, by assigning values $\neq 1/4$ to the *y* coordinates of the atoms in these positions, failed, inasmuch as the values concerned refined towards $y=0.2500$, whereupon the refinements diverged.

At this stage, an investigation of the structure factors showed that for most of the strongest reflections, the observed structure factors was numerically less than the corresponding calculated one. For this reason, a correction for secondary extinction was made according to the expression derived by Zacha-

Table 3. Weight analysis. w=weighting factor. $\Delta=|F_o|-|F_c|$.

Interval sin θ	Number of reflections	$\overline{w\Delta^2}$	Interval F_o	Number of reflections	$\overline{w\Delta^2}$
0.0 −0.40	72	1.04	0− 36	54	1.26
0.40−0.51	65	1.09	36− 48	54	1.28
0.51−0.58	54	0.80	48− 59	55	0.90
0.58−0.64	63	1.06	59− 73	54	0.94
0.64−0.69	49	0.76	73− 88	55	0.78
0.69−0.73	49	1.36	88−109	54	1.40
0.73−0.77	59	1.49	109−132	54	0.56
0.77−0.80	47	0.72	132−173	55	0.69
0.80−0.84	50	0.76	173−255	54	0.62
0.84−0.87	36	0.66	255−701	55	1.59

riasen.[9] The value obtained for c was $3.43 \pm 0.37 \times 10^{-4}$. A refinement including all the reflections then gave a final R-value of 0.038.

Hughes' weighting function:[10] $w = 1/h^2|F_{o,\,min}|^2$ for $|F_o| \leq h|F_{o,\,min}|$ and $w = 1/|F_o|^2$ for $|F_o| > h|F_{o,\,min}|$ with $h = 4.0$ and $|F_{o,\,min}| = 21.0$ was used in the refinement. A weight analysis obtained in the last cycle is given in Table 3. The positional parameters and the temperature factors of all the atoms and their standard deviations are given in Table 4.

A list of observed and calculated structure factors is presented in Table 5.

Table 4. The structure of $W_2O_3(AsO_4)_2$.

Space group: *Pnma*
Unit cell dimensions: $a = 16.0109 \pm 14$ Å, $b = 6.4341 \pm 7$ Å, $c = 8.0430 \pm 13$ Å, $V = 828.6$ Å^3.
Cell content: 4 $W_2O_3(AsO_4)_2$
8 W(1), (2), 8 As(1), (2), 28 O(1) – (7) in 4(*c*): $\pm(x,1/4,z;\ 1/2+x,1/4,1/2-z)$
16 O(8), (9) in 8(*d*): $\pm(x,y,z;\ 1/2+x,1/2-y,1/2-z;\ x,1/2-y,z;\ 1/2+x,y,1/2-z)$
Atomic parameters and temperature factors (Å^2) with their standard deviations ($\pm\sigma$):

Atom	x	y	z	B
W(1)	0.19289 ± 5	1/4	0.60332 ± 11	
W(2)	0.05851 ± 5	1/4	0.24244 ± 10	
As(1)	0.74748 ± 12	1/4	0.48731 ± 23	
As(2)	0.41147 ± 13	1/4	0.59586 ± 24	
O(1)	0.3176 ± 7	1/4	0.5039 ± 15	0.64 ± 21
O(2)	0.2671 ± 7	1/4	0.8076 ± 15	0.69 ± 21
O(3)	0.1020 ± 8	1/4	0.7066 ± 18	1.30 ± 23
O(4)	0.1552 ± 9	1/4	0.3858 ± 17	1.34 ± 25
O(5)	0.4875 ± 8	1/4	0.1035 ± 15	1.17 ± 24
O(6)	0.4840 ± 8	1/4	0.4479 ± 16	1·20 ± 23
O(7)	0.1469 ± 9	1/4	0.0453 ± 18	1.46 ± 25
O(8)	0.2021 ± 5	0.5482 ± 17	0.6003 ± 12	1.48 ± 19
O(9)	0.0682 ± 5	0.5462 ± 16	0.2191 ± 11	1.34 ± 16

Anisotropic thermal parameters (Å^2) with their standard deviations ($\pm\sigma$)
$[T = \exp(-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl))]$

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
W(1)	0.00065 ± 4	0.00093 ± 28	0.00243 ± 17	0	−0.00020 ± 10	0
W(2)	0.00073 ± 4	0.00114 ± 27	0.00218 ± 17	0	0.00036 ± 10	0
As(1)	0.00082 ± 8	0.00139 ± 48	0.00156 ± 31	0	−0.00035 ± 25	0
As(2)	0.00063 ± 8	0.00118 ± 53	0.00358 ± 32	0	0.00030 ± 25	0

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The structure of $2WO_3 \cdot As_2O_5$ may be described as built up of distorted WO_6 octahedra and AsO_4 tetrahedra. Every wolfram atom is in contact with four AsO_4 groups, and every AsO_4 group is in contact with four wolfram atoms. Every wolfram atom is also in contact with one oxygen atom (O(3); O(5)) which is bound only to this wolfram atom, and with one oxygen atom (O(4)) that is shared by two wolfram atoms. In this way, the crystals are built up of planar W_2O_3 groups, parallel to the xz-plane and joined by AsO_4 tetrahedra so that every tetrahedron links together four W_2O_3 groups. This arrangement yields a three-dimensional network, which, in the y-direction, contains chains consist-

Table 5. Observed and calculated structure factors of $W_2O_3(AsO_4)_2$.

H	K	L	KFOB	FCAL	H	K	L	KFOB	FCAL	H	K	L	KFOB	FCAL	H	K	L	KFOB	FCAL
0	2	0	700.53	789.40	2	2	4	62.03	61.46	4	0	5	173.71	165.75	6	2	0	64.04	67.98
0	4	0	584.12	690.88	2	4	4	134.48	133.40	4	1	5	65.26	64.64	7	0	1	54.26	54.35
0	6	0	410.02	502.45	2	6	4	52.24	49.12	4	2	5	141.10	133.97	7	1	1	184.69	190.40
0	1	1	40.53	36.16	2	6	4	114.65	110.25	4	3	5	65.28	55.69	7	3	1	172.29	176.17
0	3	1	92.87	47.75	2	0	5	163.65	158.35	4	4	5	132.55	131.34	7	4	1	33.76	30.38
0	0	2	27.65	23.38	2	1	5	91.41	86.92	4	5	5	45.72	47.68	7	5	1	130.75	129.23
0	2	2	30.73	24.73	2	2	5	136.57	129.62	4	0	6	60.57	59.19	7	0	2	109.25	114.64
0	1	3	357.67	380.93	2	3	5	93.24	86.29	4	2	6	72.10	64.14	7	1	2	79.87	80.94
0	3	3	421.17	409.44	2	4	5	123.01	123.07	4	4	6	53.38	51.54	7	2	2	77.21	77.25
0	5	3	278.05	284.33	2	5	5	62.76	63.00	4	0	7	342.64	340.71	7	3	2	108.27	104.00
0	0	4	52.25	53.24	2	0	6	137.05	135.04	4	2	7	300.26	296.54	7	4	2	85.56	83.76
0	2	4	45.56	54.27	2	1	6	135.12	136.33	4	4	7	280.98	281.96	7	5	2	45.65	46.78
0	4	4	46.61	43.10	2	2	6	143.27	141.52	4	0	8	48.27	54.47	7	6	2	75.22	69.82
0	6	4	30.21	32.73	2	3	6	142.30	138.53	4	1	8	59.35	56.06	7	1	3	74.24	70.62
0	1	5	240.43	234.25	2	4	6	112.30	113.51	4	2	8	48.60	49.93	7	3	3	54.32	57.77
0	3	5	230.05	222.39	2	5	6	96.34	101.98	4	4	8	53.38	51.54	7	5	3	48.15	46.72
0	5	5	167.35	169.50	2	0	7	41.62	38.31	5	0	1	265.31	279.61	7	1	4	24.76	29.95
0	0	6	204.60	203.65	2	1	7	211.65	210.98	5	1	1	126.30	131.88	7	3	4	32.54	27.95
0	2	6	256.46	244.91	2	2	7	44.20	47.35	5	3	1	189.30	189.24	7	0	5	97.93	94.78
0	4	6	243.58	240.01	2	3	7	207.34	205.71	5	4	1	113.04	115.30	7	1	5	26.49	28.80
0	1	7	72.87	71.32	2	4	7	32.85	35.62	5	5	1	153.40	152.82	7	2	5	37.06	30.80
0	3	7	78.01	77.88	2	1	8	109.47	111.68	5	6	1	86.54	87.65	7	3	5	41.75	40.17
0	0	8	208.79	236.51	3	0	1	185.51	183.58	5	0	2	155.71	153.32	7	4	5	68.40	64.04
0	2	8	207.64	219.95	3	1	1	117.22	113.73	5	1	2	37.28	34.98	7	5	5	15.69	23.48
1	0	1	36.25	35.19	3	2	1	105.28	108.99	5	3	2	258.12	259.54	7	0	6	75.22	76.93
1	1	1	134.22	126.62	3	3	1	63.24	61.97	5	5	2	251.18	254.70	7	1	6	29.90	23.32
1	2	1	32.47	33.30	3	4	1	121.86	120.89	5	0	3	174.04	184.87	7	2	6	72.17	68.46
1	3	1	141.34	135.48	3	5	1	75.51	74.48	5	1	3	156.88	158.35	7	4	6	62.79	63.08
1	5	1	76.28	77.75	3	6	1	91.55	96.58	5	2	3	25.70	19.73	7	0	7	26.81	30.39
1	0	2	271.50	241.94	3	1	2	174.60	174.16	5	3	3	110.65	109.05	7	1	7	64.55	64.89
1	2	2	227.52	221.93	3	2	2	26.08	22.65	5	4	3	108.56	107.50	7	3	7	78.13	77.18
1	3	2	36.87	31.77	3	3	2	177.86	174.12	5	5	3	85.00	82.98	7	0	8	107.48	115.96
1	4	2	224.78	226.38	3	4	2	114.30	116.73	5	0	4	32.41	28.44	8	1	0	71.21	73.72
1	6	2	175.24	178.14	3	0	3	147.45	142.91	5	1	4	162.38	154.70	8	0	0	335.60	357.28
1	0	3	22.69	24.10	3	1	3	90.14	87.59	5	3	4	163.50	161.68	8	1	0	68.30	72.79
1	1	3	165.25	161.23	3	2	3	106.52	102.37	5	5	4	102.72	106.72	8	2	0	234.76	238.62
1	2	3	50.58	46.13	3	3	3	108.40	105.22	5	0	5	284.04	275.88	8	3	0	31.26	36.08
1	3	3	146.14	142.71	3	4	3	54.74	54.04	5	1	5	98.12	92.64	8	4	0	254.93	261.94
1	5	3	116.37	113.72	3	5	3	62.84	65.67	5	2	5	247.62	238.19	8	5	0	62.52	56.05
1	0	4	180.51	174.10	3	6	3	66.50	71.30	5	3	5	100.88	99.41	8	6	0	214.35	214.79
1	1	4	48.52	43.92	3	0	4	119.63	119.04	5	4	5	213.28	215.69	8	0	1	37.84	35.90
1	2	4	152.48	146.36	3	1	4	90.72	86.92	5	5	5	58.67	63.94	8	1	1	54.18	55.62
1	3	4	48.69	51.65	3	2	4	53.70	51.76	5	0	6	65.78	68.04	8	2	1	25.53	26.66
1	4	4	136.41	129.30	3	3	4	101.20	97.06	5	1	6	122.65	123.96	8	3	1	66.05	63.32
1	6	4	100.90	103.07	3	4	4	76.11	69.83	5	2	6	46.12	41.93	8	4	1	20.04	24.66
1	0	5	83.46	86.64	3	5	4	64.68	62.43	5	3	6	141.43	133.51	8	5	1	40.39	36.81
1	1	5	208.16	203.41	3	6	4	52.06	51.41	5	4	6	54.40	54.69	8	0	2	212.17	224.84
1	2	5	32.11	31.52	3	0	5	162.10	155.83	5	5	6	57.41	52.06	8	1	2	30.11	33.60
1	3	5	201.86	204.56	3	1	5	72.67	67.47	5	0	7	78.48	75.94	8	2	2	179.88	176.32
1	4	5	56.05	52.09	3	2	5	128.93	123.23	5	1	7	59.45	57.81	8	3	2	25.70	29.52
1	5	5	213.05	211.62	3	3	5	56.77	55.01	5	2	7	32.30	28.75	8	4	2	176.77	170.91
1	6	5	40.76	39.93	3	4	5	125.11	119.46	5	1	8	124.24	126.42	8	6	2	141.07	136.67
1	0	6	63.55	62.29	3	5	5	50.56	49.14	6	0	0	169.34	176.04	8	0	3	40.68	39.99
1	1	6	68.77	65.47	3	0	6	77.67	76.73	6	1	0	273.45	288.05	8	1	3	367.92	399.59
1	2	6	60.18	54.17	3	1	6	109.35	103.24	6	2	0	115.34	121.74	8	2	3	80.15	78.75
1	3	6	68.30	67.70	3	3	6	111.48	109.21	6	3	0	315.65	317.56	8	3	3	354.35	352.25
1	4	6	56.12	53.58	3	4	6	45.24	47.17	6	4	0	131.41	131.18	8	4	3	50.28	46.90
1	5	6	36.64	37.15	3	5	6	35.42	39.01	6	5	0	211.89	217.53	8	5	3	283.07	286.46
1	0	7	70.40	71.22	3	0	7	61.70	64.44	6	6	0	108.03	105.16	8	6	3	33.25	39.09
1	1	7	56.33	62.29	3	1	7	62.88	60.06	6	0	1	54.45	60.84	8	0	4	43.67	44.55
1	2	7	39.69	43.87	3	2	7	53.50	46.71	6	1	1	74.53	80.29	8	2	4	51.50	46.88
1	3	7	55.44	55.80	3	3	7	67.25	73.28	6	2	1	57.75	58.52	8	4	4	46.20	39.00
1	4	7	52.69	52.71	3	0	8	64.65	64.89	6	3	1	119.83	113.55	8	1	5	125.65	122.35
1	0	8	103.17	130.57	3	1	8	70.55	74.59	6	4	1	51.00	48.04	8	3	5	128.00	123.66
1	2	8	95.00	94.98	3	2	8	69.50	71.49	6	5	1	65.57	69.05	8	5	5	99.38	96.92
1	3	8	41.06	43.50	3	3	8	73.51	75.22	6	6	1	42.53	37.53	8	0	6	269.28	267.75
2	0	0	75.16	82.58	4	0	0	114.01	120.13	6	0	2	141.51	140.77	8	1	6	54.88	45.47
2	1	0	257.01	260.23	4	1	0	87.00	91.09	6	1	2	116.77	117.49	8	2	6	271.44	268.18
2	2	0	55.32	56.65	4	2	0	86.15	89.78	6	2	2	68.74	70.87	8	3	6	40.48	41.15
2	3	0	263.54	269.13	4	3	0	76.88	73.88	6	3	2	109.84	107.77	8	4	6	263.08	255.79
2	4	0	53.78	50.90	4	4	0	75.73	80.70	6	4	2	76.65	77.73	8	0	8	133.99	140.10
2	5	0	151.48	152.05	4	5	0	65.40	60.72	6	5	2	78.26	80.42	9	1	1	287.85	310.16
2	6	0	42.67	40.85	4	6	0	58.42	63.04	6	6	2	53.05	54.49	9	2	1	24.12	30.19
2	0	1	160.16	155.27	4	0	1	455.58	466.00	6	0	3	405.40	420.32	9	3	1	280.56	290.54
2	1	1	291.05	278.52	4	1	1	56.82	57.07	6	1	3	104.17	102.35	9	5	1	218.12	222.28
2	2	1	99.88	100.17	4	2	1	299.04	304.71	6	2	3	311.15	314.76	9	0	2	260.08	281.93
2	3	1	273.88	277.55	4	3	1	36.50	33.66	6	3	3	95.25	98.98	9	1	2	35.08	36.29
2	4	1	95.33	98.41	4	4	1	315.07	319.13	6	4	3	261.05	302.52	9	2	2	234.56	212.82
2	5	1	162.24	170.76	4	5	1	37.93	39.98	6	5	3	65.65	62.02	9	3	2	35.32	32.06
2	6	1	75.24	74.04	4	6	1	246.13	253.32	6	6	3	240.55	240.00	9	4	2	212.49	210.44
2	0	2	366.35	349.53	4	0	2	74.68	77.56	6	0	4	244.50	247.66	9	5	2	35.14	32.15
2	1	2	163.88	156.88	4	1	2	318.45	318.29	6	2	4	201.04	195.99	9	6	2	171.61	170.13
2	2	2	252.44	248.31	4	2	2	48.92	52.04	6	4	4	151.24	188.18	9	0	3	46.05	47.11
2	3	2	187.55	191.05	4	3	2	311.67	315.47	6	6	4	155.18	151.95	9	2	3	26.67	20.36
2	4	2	240.76	239.98	4	4	2	53.84	50.32	6	0	5	142.81	142.64	9	4	3	26.52	29.13
2	5	2	100.36	98.85	4	5	2	200.60	209.94	6	1	5	95.20	92.84	9	6	4	92.34	92.74
2	6	2	184.54	188.20	4	6	2	39.60	37.62	6	2	5	130.66	124.35	9	2	4	87.82	87.32
2	0	3	222.13	211.33	4	0	3	39.89	37.63	6	3	5	98.56	95.18	9	4	4	87.52	79.31
2	1	3	57.52	54.01	4	1	3	35.81	36.85	6	4	5	125.52	117.75	9	0	5	91.88	85.80
2	2	3	119.69	119.05	4	2	3	28.69	33.76	6	5	5	73.66	71.11	9	1	5	128.80	126.86
2	3	3	35.87	41.22	4	3	3	31.44	32.22	6	1	6	216.19	212.07	9	2	5	77.67	73.99
2	4	3	151.71	148.26	4	0	4	97.01	93.22	6	3	6	215.58	212.02	9	3	5	152.42	142.67
2	5	3	41.41	44.32	4	1	4	418.32	414.66	6	0	7	35.52	36.97	9	4	5	68.30	67.79
2	6	3	119.75	121.72	4	2	4	114.62	108.99	6	1	7	74.80	74.46	9	0	6	128.76	134.07
2	0	4	155.55	187.25	4	3	4	411.64	406.14	6	3	7	75.88	75.64	9	2	6	135.65	131.21
2	1	4	65.87	65.75	4	4	4	80.05	83.62	6	0	8	66.90	68.98	9	4	6	120.16	116.14
2	2	4	118.52	112.63	4	5	4	285.11	293.08	6	1	8	145.45	146.61	9	0	7	62.63	56.80

Table 5. Continued.

H	K	L	KFCB	FCAL	H	K	L	KFCB	FCAL	H	K	L	KFCB	FCAL	H	K	L	KFCB	FCAL
9	2	7	28.82	34.98	11	0	1	47.55	52.17	12	4	2	97.74	97.51	14	3	1	96.32	93.78
10	0	0	19.59	12.01	11	1	1	158.55	160.70	12	5	2	91.66	92.37	14	0	2	124.96	130.26
10	1	0	120.25	122.04	11	2	1	42.75	44.70	12	0	3	24.61	25.22	14	1	2	78.84	81.93
10	3	0	125.76	126.24	11	3	1	166.04	165.77	12	1	3	67.91	69.99	14	2	2	98.17	104.04
10	5	0	81.80	83.93	11	4	1	45.81	43.48	12	2	3	73.62	71.84	14	3	2	80.26	75.90
10	0	1	97.56	102.31	11	5	1	109.11	115.14	12	0	4	35.75	34.41	14	4	2	105.18	105.43
10	1	1	281.07	293.94	11	0	2	101.22	107.37	12	1	4	224.13	231.49	14	0	3	294.06	307.39
10	2	1	52.92	51.25	11	2	2	80.27	80.44	12	3	4	225.75	230.11	14	2	3	266.56	268.60
10	3	1	282.28	287.21	11	3	2	28.74	29.84	12	0	5	125.93	126.65	14	3	3	42.55	36.73
10	4	1	73.74	67.38	11	4	2	81.65	80.03	12	1	5	27.36	26.44	14	0	4	26.73	26.04
10	5	1	210.42	214.72	11	0	3	41.64	39.00	12	2	5	112.58	108.60	14	1	4	43.05	41.58
10	0	2	143.42	155.08	11	1	3	37.79	25.08	12	0	6	76.06	80.48	14	2	4	48.21	44.55
10	1	2	97.16	101.57	11	2	3	35.85	35.31	12	1	6	44.29	44.76	14	0	5	117.39	117.88
10	2	2	116.83	118.40	11	4	3	37.64	32.19	12	2	6	65.65	66.37	14	1	5	29.61	30.41
10	3	2	108.97	110.19	11	0	4	53.85	55.83	13	0	1	166.56	169.43	14	2	5	109.19	110.16
10	4	2	122.29	121.19	11	3	4	32.99	28.40	13	2	1	139.67	139.55	15	0	1	119.11	118.85
10	5	2	69.32	69.52	11	4	4	45.85	37.28	13	4	1	135.89	136.92	15	2	1	101.04	99.35
10	0	3	95.85	100.18	11	0	5	29.36	28.43	13	1	2	173.43	177.89	15	3	1	25.45	21.99
10	1	3	56.33	63.49	11	2	5	30.47	22.96	13	2	2	46.28	49.95	15	0	2	55.26	50.44
10	2	3	71.15	71.98	11	4	5	22.18	23.66	13	3	2	166.57	169.63	15	1	2	120.07	117.78
10	3	3	68.15	69.39	11	0	6	131.73	139.62	13	4	2	31.51	27.89	15	2	2	57.40	54.83
10	4	3	82.51	80.61	11	1	6	69.52	71.02	13	0	3	40.47	48.74	15	3	2	128.05	127.18
10	5	3	46.27	44.35	11	2	6	101.05	98.86	13	1	3	73.24	72.65	15	1	3	44.90	45.53
10	0	4	341.79	367.34	11	3	6	67.64	67.77	13	2	3	28.10	29.09	15	2	3	39.35	42.60
10	2	4	309.10	313.87	12	0	0	31.04	38.45	13	3	3	70.26	69.30	15	1	4	58.75	63.79
10	3	4	36.28	33.60	12	1	0	65.59	68.25	13	4	3	36.56	37.58	16	0	0	251.10	236.49
10	4	4	301.63	298.28	12	2	0	54.08	51.45	13	0	4	58.48	58.73	16	2	0	217.80	205.67
10	0	5	92.43	98.69	12	3	0	63.38	67.36	13	1	4	88.57	85.06	16	0	1	84.36	82.06
10	1	5	126.46	140.67	12	5	0	49.04	42.39	13	2	4	55.62	55.32	16	1	1	78.10	76.89
10	2	5	83.95	79.12	12	0	1	277.55	254.83	13	3	4	93.42	91.79	16	2	1	80.41	78.37
10	3	5	137.41	132.74	12	1	1	44.35	40.69	13	0	5	140.45	147.19	16	3	1	81.62	80.74
10	4	5	77.06	78.74	12	2	1	231.48	236.40	13	1	5	44.34	41.43	16	0	2	55.70	54.88
10	0	6	65.58	73.25	12	3	1	25.35	20.02	13	2	5	141.48	141.25	16	1	2	45.95	44.41
10	1	6	88.87	93.13	12	4	1	221.80	228.12	13	0	6	36.12	33.77	16	2	2	34.30	36.10
10	2	6	56.01	54.77	12	5	1	27.06	38.70	13	1	6	110.06	108.69	16	1	3	159.32	157.67
10	3	6	92.58	89.65	12	0	2	108.05	109.04	14	1	0	320.14	319.42	16	0	4	101.26	102.54
10	0	7	49.82	50.13	12	1	2	110.42	112.71	14	2	0	58.63	56.39	17	1	1	45.41	48.25
10	1	7	200.24	203.77	12	2	2	127.81	126.25	14	3	0	322.14	312.34	17	0	2	131.85	129.49
10	2	7	47.18	41.28	12	3	2	127.25	125.76	14	1	1	93.07	91.97	17	1	2	47.93	41.98

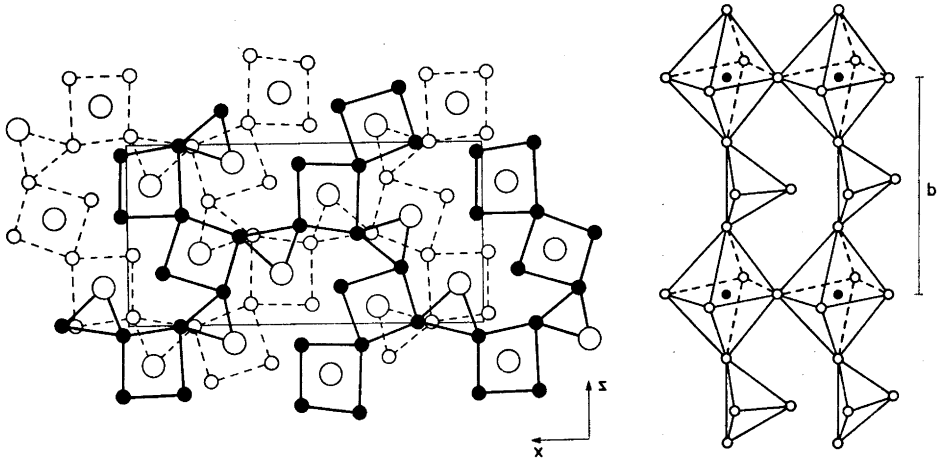

Fig. 1. Schematic drawings, showing the structure of $W_2O_3(AsO_4)_2$. (*a*) The structure viewed along [010] showing the pairs of WO_6 octahedra, and the links between these and the AsO_4 tetrahedra. Small open and full circles denote oxygen atoms situated in two separate planes, $b/2 = 3.22$ Å apart. Large open circles denote oxygen atoms shared between WO_6 octahedra and AsO_4 tetrahedra, as shown in *b*. The wolfram and arsenic atoms have not been indicated. (*b*) The links in the *y*-direction between the pairs of WO_6 octahedra and AsO_4 tetrahedra. Open circles denote oxygen atoms, and full ones wolfram atoms. The arsenic atoms in each AsO_4 tetrahedron have been omitted. The two remaining oxygens in each AsO_4 tetrahedron are linked – as shown in *a* – with two further octahedra which have not been indicated.

ing of pairs of octahedra linked together by corner-sharing alternating with mutually unconnected tetrahedra. Schematic drawings, showing the links between octahedra and tetrahedra, are given in Fig. 1. The building principle is most adequately expressed by the formula $W_2O_3(AsO_4)_2$, rather than by $2WO_3 \cdot As_2O_5$.

The interatomic distances and standard deviations (σ) in $W_2O_3(AsO_4)_2$ are given in Table 6. From the table we can see that all distances are within the normal ranges.

Table 6. Interatomic distances (Å) and some angles (°) with standard deviations ($\pm\sigma$) in $W_2O_3(AsO_4)_2$. The distances are uncorrected for thermal motion.

W(1)–O(1)	2.151 ± 12	O(1)–W(1)–O(2)	76.0 ± 5
W(1)–O(2)	2.028 ± 12	O(1)–W(1)–O(4)	87.2 ± 5
W(1)–O(3)	1.676 ± 13	O(1)–W(1)–O(8)	85.7 ± 3
W(1)–O(4)	1.851 ± 14	O(2)–W(1)–O(8)	88.0 ± 3
W(1)–2O(8)	1.924 ± 11	O(3)–W(1)–O(2)	96.2 ± 6
O–O	2.574 ± 17 – 2.776 ± 13	O(3)–W(1)–O(4)	100.7 ± 6
O–O	2.711	O(3)–W(1)–O(8)	94.2 ± 3
		O(4)–W(1)–O(8)	90.7 ± 3
W(2)–O(4)	1.931 ± 14	O(4)–W(2)–O(5)	95.9 ± 6
W(2)–O(5)	1.682 ± 13	O(4)–W(2)–O(7)	84.9 ± 6
W(2)–O(6)	1.941 ± 13	O(4)–W(2)–O(9)	89.6 ± 3
W(2)–O(7)	2.126 ± 14	O(5)–W(2)–O(6)	99.5 ± 6
W(2)–2O(9)	1.922 ± 10	O(5)–W(2)–O(9)	97.3 ± 3
O–O	2.610 ± 19 – 2.771 ± 18	O(6)–W(2)–O(7)	79.7 ± 6
O–O	2.700	O(6)–W(2)–O(9)	88.4 ± 3
		O(7)–W(2)–O(9)	82.7 ± 3
		W(1)–O(4)–W(2)	145.7 ± 8
As(1)–O(2)	1.679 ± 12	O(2)–As(1)–O(7)	110.1 ± 6
As(1)–O(7)	1.631 ± 14	O(2)–As(1)–O(8)	108.7 ± 4
As(1)–2O(8)	1.683 ± 10	O(7)–As(1)–O(8)	114.0 ± 4
O–O	2.597 ± 22 – 2.779 ± 15	O(8)–As(1)–O(8)	101.0 ± 7
O–O	2.722		
As(2)–O(1)	1.675 ± 12	O(1)–As(2)–O(6)	108.1 ± 6
As(2)–O(6)	1.662 ± 13	O(1)–As(2)–O(9)	115.8 ± 4
As(2)–2O(9)	1.675 ± 10	O(6)–As(2)–O(9)	106.7 ± 4
O–O	2.622 ± 20 – 2.839 ± 14	O(9)–As(2)–O(9)	103.0 ± 7
O–O	2.726		

The AsO_4 tetrahedra can be regarded as nearly regular; an average O – As – O angle = 109.4° is calculated. The average As – O distance, 1.67 Å, is comparable to the corresponding value, 1.69 Å, found in $LiMoO_2AsO_4$.[11] The average distance, is also consistent with that found in the tetrahedron in $As_2O_5 \cdot 5/2H_2O$,[12] 1.69 Å. The distances are, however, somewhat shorter than those given in the *Tables of Interatomic Distances* [13] and in the *International Tables*,[5] which both give the value 1.75 ± 5 Å.

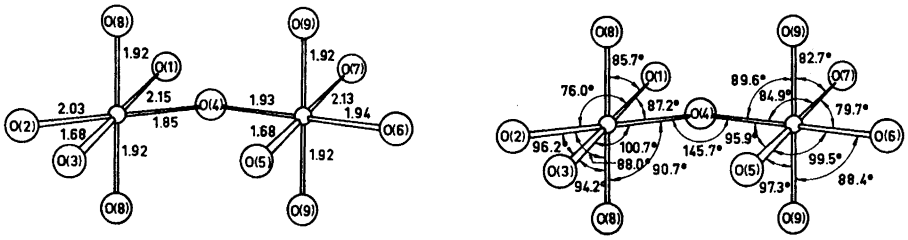

Fig. 2, a and b. The coordination of oxygen atoms around the pairs of wolfram atoms in $W_2O_3(AsO_4)_2$. Large circles denote oxygen atoms, and small ones wolfram atoms.

The coordination polyhedron around wolfram is a distorted octahedron of oxygen atoms (*cf.* Fig. 2). These oxygen atoms have three different surroundings, one oxygen atom (O(3); O(5)) is unshared, one (O(4)) is shared with another octahedron, and each of the remaining four is shared with one AsO_4 tetrahedron. The average values of the corresponding W – O distances are 1.68 Å, 1.89 Å, and 1.99 Å, respectively. These distances are consistent with those found in the refinement of $W_2O_3(PO_4)_2$,[14] where the corresponding W – O distances are 1.69 Å, 1.95 Å, and 2.03 Å. The W – O distances, 1.68 – 2.15 Å, are also comparable to those found in the refinement of monoclinic WO_3,[15] 1.757 – 2.162 Å. The structure of WO_3, however, consists of corner-sharing octahedra, which makes a straight-forward comparison difficult.

The structures of $W_2O_3(AsO_4)_2$ and $W_2O_3(PO_4)_2$ are not identical, but they do have similarities. They both consist of W_2O_3 groups linked together by tetrahedra in the *xz* plane, and they both contain chains consisting of pairs of WO_6 octahedra linked together by corner-sharing alternating, in the *y*-direction, with mutually unconnected tetrahedra (*cf.* Fig. 1).

The W_2O_3 groups in $W_2O_3(AsO_4)_2$ are linked together by corner-sharing with AsO_4 tetrahedra into a network parallel to the *xz* plane. Each one of the four AsO_4 tetrahedra, surrounding the W_2O_3 group, connects to one other, separate W_2O_3 group in the same plane.

In $W_2O_3(PO_4)_2$, there exists yet another type of linkage. Parallel to the *x*-direction, chains are formed, consisting of W_2O_3 groups mutually connected by two PO_4 tetrahedra.

The W – O – W angle in the W_2O_3 group of $W_2O_3(AsO_4)_2$ is 145.7°. In $W_2O_3(PO_4)_2$, the angle in the corresponding W_2O_3 group is 149.2°, and in the other W_2O_3 group 160.6°.

The difference between the two structures may be due to the fact that the phosphate group is smaller than the arsenate group, the average P – O distance being 1.51 Å, compared to the average As – O distance, 1.67 Å. A further discussion of this and related structures will be given later, in a separate article.

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