The Crystal Structure of $K_2W_3O_{10}$

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The crystal structure of $K_2W_3O_{10}$ has been determined from three-dimensional X-ray diffractometer data and refined to an R value of 0·074. $K_2W_3O_{10}$ crystallizes in the monoclinic space group $P2/c$ with $a = 10·947$ (5), $b = 3·864$ (1), $c = 31·955$ (8) Å, $V = 1282·1$ (8) Å^3, $Z = 6$ and $D_x = 6·14$ g cm^{-3}. The structure is built up of distorted WO_6 octahedra and KO_{13} and KO_9 coordination polyhedra. Four WO_6 octahedra are linked to form a W_4O_{18} group by sharing edges, and five WO_6 octahedra to form a W_5O_{24} group by sharing corners. These kinds of groups are further linked by sharing corners constructing a framework of the $[(W_3O_{10})^{2-}]_\infty$ anion. The W–O bond lengths vary from 1·68 (5) to 2·21 (3) Å having the mean value of 1·93 (3) Å. The potassium ions occupy large tunnel sites. The K(3) atom statistically occupies two positions, K(3a) and K(3b), separated by 0·65 (5) Å. The K–O bond lengths vary from 2·58 (4) to 3·55 (4) Å. The mean values are 3·07 for K(1)–O, 3·12 for K(2)–O, 3·07 for K(3a)–O and 3·04 Å for K(3b)–O.

Introduction

Alkali tungstates as well as molybdates form crystals with structures based on polymerized $M_nO_{3n+1}^{2-}$ anions ($n = 1, 2, 3, 4, 5$ or 6), when they are crystallized from the melts. In the case $n = 1$, the anion has the form of an isolated tetrahedron of WO_4^{2-} as found in Li_2WO_4 (Zachariasen & Plettinger, 1961), Na_2WO_4 (Okada, Morikawa, Marumo & Iwai, 1974), K_2WO_4 (Koster, Kools & Rieck, 1969), Rb_2WO_4 (Kools, Koster & Rieck, 1970) and Cs_2WO_4 (Kools *et al.*, 1970). Two types of $W_2O_7^{2-}$ anions are known for $n = 2$. The first type is that observed in $Li_2W_2O_7$ (Okada, Morikawa, Marumo & Iwai, 1975a), and an infinite chain of WO_6 octahedra sharing edges. The second is also an infinite chain, but built up of WO_4 tetrahedra and WO_6 octahedra by sharing corners as observed in $Na_2W_2O_7$ (Okada, Morikawa, Marumo & Iwai, 1975b). The $W_4O_{13}^{2-}$ anion in $K_2W_4O_{13}$ (Seleborg, 1967) is an example for $n = 4$. The structure is a three-dimensional framework of WO_6 octahedra sharing corners.

The structure of the trimolybdate anion $Mo_3O_{10}^{2-}$ in $K_2Mo_3O_{10}$ (Seleborg, 1966; Gatehouse & Leverett, 1968) was reported to be an infinite chain built up of MoO_6 octahedra and MoO_5 square pyramids by sharing edges. However, the structure of the $W_3O_{10}^{2-}$ anion ($n = 3$) has not been solved to date. It is interesting to compare the structure of the polymerized tritungstate anion, $W_3O_{10}^{2-}$, with that of the trimolybdate anion, $Mo_3O_{10}^{2-}$. The structure determination of $K_2W_3O_{10}$ was, therefore, undertaken by the X-ray single-crystal diffraction technique.

The existence of the phase $K_2W_3O_{10}$ was first pointed out by Hoermann (1928) and later confirmed by Gelsing, Stein & Stevels (1965). The crystallographic data were reported by Deschanvres, Desgardin, Raveau & Thomazeau (1967) and their results are compared with the present work in Table 1.

Experimental

The crystals of $K_2W_3O_{10}$ were synthesized by heating an intimate mixture of K_2CO_3 and $2WO_3$ in a platinum crucible at 750°C for 5 h and then cooling at the rate 20–30° C h^{-1}. They were colourless, transparent, thin needles adhering tightly to each other.

A preliminary X-ray study with Weissenberg photographs confirmed the monoclinic symmetry, and gave the cell dimensions in agreement with those given by Deschanvres *et al.* (1967) except that the c axis is doubled. As the systematic absences were $h0l$ for l odd and $00l$ for l odd, the space groups were restricted to $P2/c$ or Pc. The crystal data are given in Table 1.

Table 1. *Crystallographic data for* $K_2W_3O_{10}$, *monoclinic* $P2/c$

	This work	Deschanvres *et al.* (1967)
$a =$	10·947 (5) Å	$a =$ 10·87 Å
$b =$	3·864 (1)	$b =$ 3·86
$c =$	31·955 (8)	$c =$ 15·95
$\beta =$	108·44 (3)°	$\beta =$ 109°
$V =$	1282·1 (8) Å^3	$V =$ 632·8 Å^3
$M =$	789·75	$M =$ 789·75
$Z =$	6	$Z =$ 3
$D_x =$	6·14 g cm^{-3}	$D_x =$ 6·22 g cm^{-3}
$D_m =$	6·13	

A crystal with dimensions $0·16 \times 0·05 \times 0·03$ mm was used for intensity collection. Intensities were measured on a Philips automated four-circle diffractometer with Mo $K\alpha$ radiation, monochromated with graphite, up to $2\theta = 60°$ by the ω scan technique. Because of the large c dimension, the ω–2θ scan technique could not be applied. The scan speed was 8° min^{-1} and the scan width was determined according to the formula $1·1° + 0·3°$ tan θ. The intensities were corrected for Lorentz and polarization factors. Corrections for isotropic

secondary extinction and absorption factors were carried out in the course of the structure refinement assuming a sphere of 0·08 mm in diameter for the crystal shape. In all, 2400 independent intensity data, satisfying the condition $|F| > 3\sigma(|F|)$, were collected and used for the structure determination. Here, the $\sigma(|F|)$'s are standard deviations of structure amplitudes due to the counting statistics.

Structure determination

The structure was solved by the heavy-atom method. The arrangement of tungsten atoms was derived from the three-dimensional Patterson function assuming the space group $P2/c$. This model was refined with a full-matrix least-squares program *LINUS* (Coppens & Hamilton, 1970), and the R value became 0·138. Then

the plausible positions of potassium and oxygen atoms were found on the Fourier and difference Fourier maps synthesized with phases derived from the tungsten atoms. The structure was refined with the least-squares program with anisotropic temperature factors assigned to the W and K atoms and isotropic ones to the oxygen atoms. At this stage, the K(3) atom was found to be statistically distributed over two positions, K(3a) and K(3b), from the difference Fourier maps. Further refinements were carried out by putting the K(3) atom at these two positions with equal probability, and the R value was finally reduced to 0·074 for all the observed reflexions. The atomic scattering factors and the dispersion correction factors were taken from *International Tables for X-ray Crystallography* (1974). Unit weights were given for all the terms. The final positional and thermal parameters are listed in Table 2.*

Discussion

The interatomic distances are shown in Table 3 with their estimated standard deviations in parentheses. The structure viewed along the b axis is shown in Fig. 1. There are five crystallographically independent W atoms, each octahedrally coordinated to six oxygen atoms. The WO_6 octahedra are largely distorted, giving W–O bond lengths from 1·68 (5) to 2·21 (3) Å. The mean W(1)–O, W(2)–O, W(3)–O, W(4)–O and W(5)–O bond lengths are 1·93 (3), 1·95 (3), 1·91 (3), 1·93 (3) and 1·90 (4) Å, respectively. These W–O bond lengths seem to be a little shorter than those in $Li_2W_2O_7$ (Okada *et al.*, 1975a) and in $Na_2W_2O_7$ (Okada *et al.*, 1975b). The K(1) and K(2) atoms are surrounded by 13 oxygen atoms. The K(3) atom statistically occupies two positions, K(3a) and K(3b) (separated by 0·65(5) Å along the a axis) with equal probability. Both K(3a) and K(3b) sites are surrounded by 9 oxygen atoms in a similar manner. The mean K(1)–O, K(2)–O, K(3a)–O and K(3b)–O bond lengths are 3·07 (3), 3·12 (3), 3·07 (4) and 3·04 (5) Å, respectively.

Table 2. *Final atomic parameters for* $K_2W_3O_{10}$

The positional and isotropic thermal parameters

	x	y	z	B_o
W(1)	−0·0059 (1)	0·0584 (5)	0·05203 (4)	0·50 (3)*
W(2)	0·2945 (1)	−0·0531 (5)	0·05420 (4)	0·51 (3)*
W(3)	0·3995 (1)	0·0593 (5)	0·34947 (4)	0·53 (3)*
W(4)	0·1529 (1)	0·0598 (5)	0·23550 (4)	0·63 (3)*
W(5)	0·5	−0·0744 (7)	0·25	0·61 (4)*
K(1)	0·2845 (9)	0·493 (2)	0·1525 (3)	1·7 (2)*
K(2)	0·1119 (10)	0·537 (3)	0·3451 (4)	2·6 (2)*
K(3a)	0·3696 (33)	0·505 (6)	0·4509 (9)	4·1 (5)*
K(3b)	0·3143 (32)	0·523 (10)	0·4545 (9)	4·6 (7)*
O(1)	0·1172 (22)	0·018 (7)	0·0090 (8)	0·8 (4)
O(2)	0·3857 (28)	−0·041 (10)	0·0187 (10)	2·0 (5)
O(3)	0·1570 (24)	0·012 (7)	0·0900 (8)	1·1 (4)
O(4)	0·4163 (22)	0·010 (7)	0·1109 (8)	0·6 (4)
O(5)	0·4994 (28)	0·024 (9)	0·3074 (9)	2·0 (5)
O(6)	0·3192 (29)	0·021 (9)	0·2300 (10)	2·1 (5)
O(7)	0·2491 (28)	−0·028 (9)	0·3045 (10)	1·8 (5)
O(8)	0	0·027 (13)	0·25	1·8 (5)
O(9)	0·0757 (26)	0·000 (8)	0·1788 (9)	1·8 (5)
O(10)	0·1084 (25)	0·027 (8)	0·4170 (9)	1·7 (5)
O(11)	0·3338 (30)	0·027 (10)	0·3918 (10)	2·0 (6)
O(12)	−0·0016 (25)	0·527 (9)	0·0470 (9)	1·9 (5)
O(13)	0·2820 (25)	0·482 (8)	0·0562 (9)	1·8 (5)
O(14)	0·4167 (35)	0·512 (12)	0·3462 (12)	1·8 (6)
O(15)	0·1349 (30)	0·521 (10)	0·2419 (10)	1·9 (6)
O(16)	0·5	0·490 (13)	0·25	1·9 (6)

* Calculated from anisotropic thermal parameters according to the expression: $B = 4(B_{11}a^2 + B_{22}b^2 + B_{33}c^2 + B_{13}ac \cos \beta)/3$.

Table 2 (*cont.*)

The anisotropic thermal parameters ($\times 10^5$) for W and K atoms expressed in the form:

$$\exp\left[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)\right]$$

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
W(1)	147 (9)	911 (74)	7 (1)	4 (27)	−22 (2)	−15 (9)
W(2)	141 (9)	692 (73)	9 (1)	−26 (26)	−20 (2)	2 (9)
W(3)	126 (9)	864 (72)	10 (1)	22 (26)	−16 (3)	−9 (9)
W(4)	145 (9)	1009 (79)	12 (1)	−21 (27)	−19 (3)	−4 (9)
W(5)	173 (13)	836 (107)	12 (2)	0	−8 (4)	0
K(1)	601 (75)	1622 (684)	27 (7)	−64 (154)	−10 (19)	16 (46)
K(2)	548 (78)	2160 (592)	91 (11)	240 (189)	2 (24)	−26 (73)
K(3a)	1626 (357)	1942 (1503)	114 (29)	−9 (510)	287 (92)	31 (144)
K(3b)	1243 (329)	7258 (2730)	90 (30)	426 (807)	83 (83)	219 (229)

The $W(1)O_6$ octahedron shares edges with one $W(1)O_6$ octahedron and one $W(2)O_6$ octahedron and shares corners with two $W(1)O_6$ octahedra. The

Table 3. *Interatomic distances* (Å) *for* $K_2W_3O_{10}$

Symmetry code

0	$x,$	$y,$	z	v	$1-x, 1+y, \frac{1}{2}-z$
i	$1-x,$	$1-y,$	$1-z$	vi	$-x, \quad y, \frac{1}{2}-z$
ii	$x,$	$1-y,$	z	vii	$-x, 1+y, \frac{1}{2}-z$
iii	$1-x,$	$y, \frac{1}{2}-z$		viii	$x, \quad -y, \frac{1}{2}+z$
iv	$x,$	$1+y,$	z	ix	$x, 1-y, \frac{1}{2}+z$

$W(1)-O(1^0)$	1·97 (2)	$W(1)-O(1^i)$	2·21 (3)
$W(1)-O(3^0)$	1·82 (2)	$W(1)-O(10^i)$	1·72 (3)
$W(1)-O(12^0)$	1·82 (3)	$W(1)-O(12^{ii})$	2·06 (3)
$W(2)-O(1^0)$	2·04 (2)	$W(2)-O(2^0)$	1·73 (4)
$W(2)-O(3^0)$	2·17 (3)	$W(2)-O(4^0)$	1·90 (2)
$W(2)-O(13^0)$	2·07 (2)	$W(2)-O(13^{ii})$	1·81 (3)
$W(3)-O(4^{iii})$	2·02 (2)	$W(3)-O(5^0)$	1·99 (3)
$W(3)-O(7^0)$	1·84 (3)	$W(3)-O(10)$	1·73 (4)
$W(3)-O(14^0)$	2·13 (4)	$W(3)-O(14^{ii})$	1·77 (4)
$W(4)-O(6^0)$	1·89 (3)	$W(4)-O(7^0)$	2·15 (3)
$W(4)-O(8^0)$	1·877 (4)	$W(4)-O(9^0)$	1·76 (3)
$W(4)-O(15^0)$	2·11 (4)	$W(4)-O(15^{ii})$	1·81 (4)
$W(5)-O(5^{0,iii})$ (×2) 1·87 (3)		$W(5)-O(6^{0,iii})$ (×2) 1·91 (3)
$W(5)-O(16^0)$	2·18 (5)	$W(5)-O(16^{ii})$	1·68 (5)
$K(1)-O(3^0)$	2·76 (3)	$K(2)-O(7^0)$	3·15 (4)
$K(1)-O(3^{iv})$	2·86 (3)	$K(2)-O(7^{iv})$	2·83 (4)
$K(1)-O(4^0)$	2·92 (3)	$K(2)-O(8^0)$	3·50 (3)
$K(1)-O(4^{iv})$	3·01 (3)	$K(2)-O(8^{iv})$	3·46 (3)
$K(1)-O(5^{iii})$	2·93 (3)	$K(2)-O(9^{vi})$	2·85 (3)
$K(1)-O(5^v)$	3·09 (3)	$K(2)-O(9^{vii})$	2·65 (3)
$K(1)-O(6^0)$	3·00 (3)	$K(2)-O(10^0)$	3·04 (3)
$K(1)-O(6^{iv})$	3·14 (3)	$K(2)-O(10^{iv})$	2·99 (3)
$K(1)-O(9^0)$	3·28 (3)	$K(2)-O(11^0)$	3·12 (3)
$K(1)-O(9^{iv})$	3·31 (3)	$K(2)-O(11^{iv})$	3·07 (3)
$K(1)-O(13^0)$	3·07 (3)	$K(2)-O(14^0)$	3·33 (4)
$K(1)-O(14^{iii})$	3·26 (4)	$K(2)-O(15^0)$	3·39 (4)
$K(1)-O(16^0)$	3·26 (7)	$K(2)-O(15^{vi})$	3·21 (3)
$K(3a)-O(2^{viii})$	2·77 (4)	$K(3b)-O(2^{viii})$	2·70 (5)
$K(3a)-O(2^{ix})$	2·96 (4)	$K(3b)-O(2^{ix})$	2·79 (5)
$K(3a)-O(2^{iii})$	3·30 (4)	$K(3b)-O(2^v)$	3·55 (4)
$K(3a)-O(2^v)$	3·09 (4)	$K(3b)-O(10^0)$	2·91 (4)
$K(3a)-O(10^0)$	3·29 (4)	$K(3b)-O(10^{iv})$	2·93 (4)
$K(3a)-O(10^{iv})$	3·38 (4)	$K(3b)-O(11^0)$	2·83 (5)
$K(3a)-O(11^0)$	2·58 (4)	$K(3b)-O(11^{iv})$	2·85 (5)
$K(3a)-O(11^{iv})$	2·71 (4)	$K(3b)-O(12^{vi})$	3·44 (5)
$K(3a)-O(14^0)$	3·54 (5)	$K(3b)-O(13^{viii})$	3·38 (4)

$W(2)O_6$ octahedron shares edges with one $W(1)O_6$ octahedron and shares corners with one $W(3)O_6$ octahedron and two $W(2)O_6$ octahedra. The $W(3)O_6$ octahedron shares corners with one $W(2)O_6$ octahedron, one $W(4)O_6$ octahedron, one $W(5)O_6$ octahedron and two $W(3)O_6$ octahedra. The $W(4)O_6$ octahedron shares corners with one $W(3)O_6$ octahedron, one $W(5)O_6$ octahedron and three $W(4)O_6$ octahedra. The $W(5)O_6$ octahedron shares corners with two $W(3)O_6$, two $W(4)O_6$ and two $W(5)O_6$ octahedra. In this way, two $W(1)O_6$ and two $W(2)O_6$ octahedra link into a W_4O_{18} group by sharing edges. Two $W(3)O_6$, two $W(4)O_6$ octahedra and one $W(5)O_6$ octahedron link into a W_5O_{24} by sharing corners. These two kinds of groups are further joined by sharing corners of octahedra to form a framework of $[(W_9O_{30})^{6-}]_\infty$. The framework has large tunnels running along the **b** direction. The cross-section of the tunnel is shown in Fig. 2 in an idealized form. It is surrounded by 32 WO_6 octahedra, elongating in the [103] direction. The K atoms occupy these tunnel sites. The corner sharing and edge sharing linkage of WO_6 octahedra give long and short $W\cdots W$ distances between neighbouring octahedra, the distances ranging from 3·714 (2) to 3·790 (2) and from 3·167 (2) to 3·318 (2) Å, respectively.

Most of the alkali isopolymolybdates and tungstates have structures based on infinite chains of $(M_nO_{3n+1}^{2-})_\infty$ as stated already. The only exception before the present work was $K_2W_4O_{13}$ (Seleborg, 1967). It is interesting that the structure of $K_2W_3O_{10}$ is quite different from the structure of $K_2Mo_3O_{10}$ and rather similar to that of $K_2W_4O_{13}$ in spite of the similarity in chemical properties of tungsten and molybdenum. These two isopolytungstate anions have framework structures of WO_6 octahedra with tunnels running along the directions which have the period of about 3·8 Å. The frameworks are considered to be composed of strings of WO_6 octahedra parallel to the tunnel direction. Each octahedron in a string is arranged to have a body-diagonal on a common straight line, sharing two op-
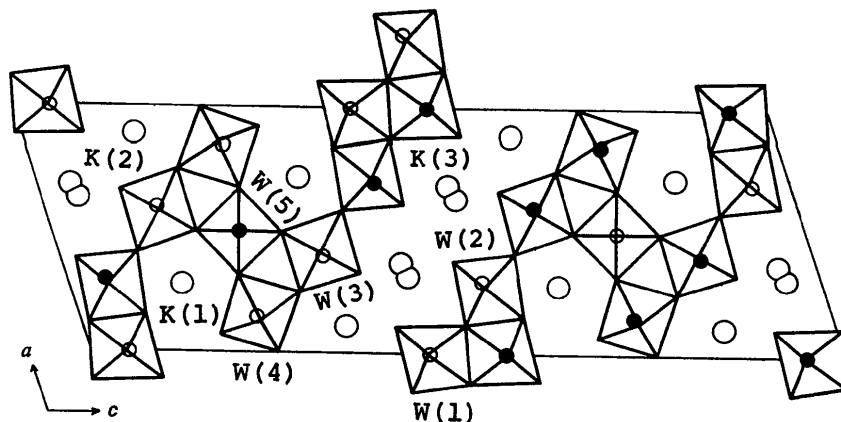

Fig. 1. The crystal structure of $K_2W_3O_{10}$ viewed along the b axis. Small open and filled circles represent W atoms a little above and below the plane $y=0$, respectively. Large open circles represent K atoms.
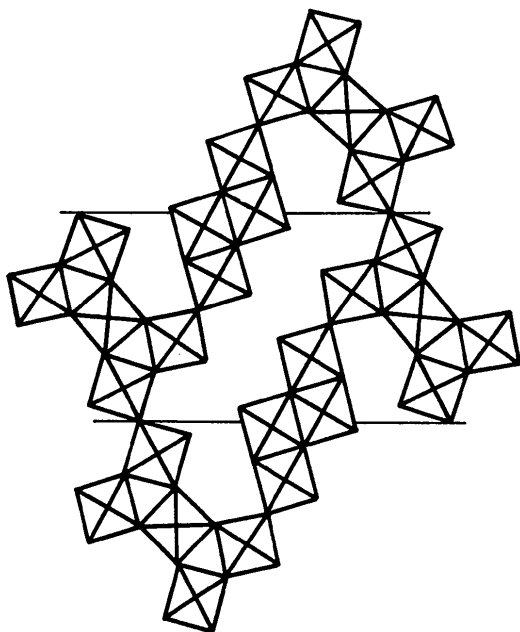
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Fig. 2. Part of the WO_6 arrangement spreading in the ac plane, shown in an idealized form.

posite corners with the neighbouring octahedra. Thus, the period of 3·8 Å corresponds to the length of the body-diagonal. The difference between the structures is in the lateral combinations of the strings. It may be noteworthy that the structure of WO_3 (Kehl, Hay & Wahl, 1952) is also composed of the same kind of strings of WO_6, having tunnels along the strings, while the structure of $K_2Mo_3O_{10}$ has a close relation to that of MoO_3 (Andersson & Magnéli, 1950) as mentioned by Gatehouse & Miskin (1975). The periods of about 3·8 Å have been observed also in crystals of $Na_2W_4O_{13}$ (Bouilland, 1968), $K_2W_4O_{13}$ (Seleborg, 1967), $K_2W_6O_{19}$ and $Rb_2W_6O_{19}$ (Okada, 1976). The facts suggest that the structures of these crystals are also composed of strings of WO_6 octahedra.

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