

Références

- ABRAHAMS, S. C. & BERNSTEIN, J. L. (1974). *J. Chem. Phys.* **61**, 1140–1146.
- DELOUME, J. P. & ROUBIN, M. (1976). *C. R. Acad. Sci. Sér. C*, **283**, 747–749.
- EULENBERGER, G. (1977). *Monatsh. Chem.* **108**, 901–913.
- GOROCHOV, O. (1968). *C. R. Acad. Sci. Sér. C*, **266**, 1054–1062.
- HAHN, H., FRANK, G., KLINGLER, W., MEYER, A. D. & STÖRGER, G. (1953). *Z. Anorg. Chem.* **271**, 153–170.
- HAHN, H., SCHULZE, H. & SECHSER, L. (1965). *Naturwissenschaften*, **52**, 451.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.
- MIKKELSEN, J. C. (1977). *Mater. Res. Bull.* **12**, 497–502.
- RYSANEK, N., LARUELLE, P. & KATTY, A. (1976). *Acta Cryst.* **B32**, 692–696.
- WIEGERS, G. A. (1971). *Am. Mineral.* **56**, 1882–1888.

Acta Cryst. (1978). **B34**, 3193–3195

The Crystal Structure of $K_2W_4O_{13}$

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The crystal structure of $K_2W_4O_{13}$ has been determined from three-dimensional X-ray diffractometer data collected with a twinned crystal and refined to an R value of 0.081 for 2569 observed reflexions. $K_2W_4O_{13}$ crystallizes in the trigonal space group $P\bar{3}$ with $a = 15.566$ (1), $c = 3.846$ (1) Å, $Z = 3$ and $D_x = 6.31$ g cm⁻³. The structure is built up of distorted WO_6 octahedra, and KO_{14} and KO_{18} coordination polyhedra. Six $W(1)O_6$ octahedra are linked to form a six-membered ring by sharing corners. Such rings are stacked along the c axis, sharing corners of the octahedra. Strings of $W(2)O_6$ octahedra connect the hexagonal tube of $W(1)O_6$ octahedra by sharing corners to form the framework of the $(W_4O_{13}^{2-})_\infty$ anion. The $W-O$ bond lengths vary from 1.75 (3) to 2.12 (4) Å (mean value 1.92 Å). $K(1)$ is located in the pentagonal tunnel of the framework running along the c axis and $K(2)$ is in the hexagonal tunnel. The $K-O$ bond lengths range from 2.72 (3) to 3.75 (4) Å, with mean values of 3.13 Å for $K(1)-O$ and 3.41 Å for $K(2)-O$.

Introduction

A model of the crystal structure of $K_2W_4O_{13}$ was proposed by Seleborg (1967) on the basis of the space group $P6$. However, no description has been given to date based on the atomic parameters. The structural investigation of $K_2W_4O_{13}$ was, therefore, undertaken to elucidate the details of this structure and its relationship to the structures of other alkali-metal tungstates.

and the crystals are always finely twinned to give diffraction patterns with higher symmetry than the real one. The crystallographic data are given in Table 1 together with the results of Seleborg (1967).

A crystal with dimensions 0.13 × 0.13 × 0.07 mm was used for intensity collection. Intensities were measured up to $2\theta = 80^\circ$ on an automated four-circle diffractometer (Philips PW 1100), with $Mo K\alpha$ radiation reflected from a graphite monochromator,

Experimental

Crystals of $K_2W_4O_{13}$ were synthesized by heating an intimate mixture of K_2CO_3 and WO_3 in a molar ratio of 1:4 in a Pt crucible at 750°C for 2 weeks. They are pale-green transparent needles.

From Weissenberg and precession photographs, the crystals were found to show hexagonal Laue symmetry $6/m$. Since systematic absences were not observed, the Laue symmetry restricts the possible space groups to $P6$, $P\bar{6}$ and $P6/m$. However (as is explained under *Structure determination*), the true space group is $P\bar{3}$

Table 1. Crystallographic data for $K_2W_4O_{13}$

	This work	Seleborg (1967)
Crystal system	Trigonal	Hexagonal
Space group	$P\bar{3}$	$P6$
a (Å)	15.566 (1)	15.530
c (Å)	3.846 (1)	3.8502
V (Å ³)	807.0 (1)	804.2
Z	3	3
M_r	1021.6	1021.6
D_x (g cm ⁻³)	6.31	6.33
μ (Mo $K\alpha$)	459.8 cm ⁻¹	

and the ω - 2θ scan technique. The scan speed was 4° min^{-1} in ω and the scan width was determined as $(1.2 + 0.1 \tan \theta)^\circ$. The intensities were corrected for the Lorentz-polarization factor. Absorption corrections were also applied by a local version of the program *ACACA* (Wuensch & Prewitt, 1965), the maximum and minimum transmission factors being 0.1508 and 0.0394 respectively. Corrections for isotropic secondary extinction were carried out in the course of the structure refinement. (The crystal was assumed to be a sphere 0.10 mm in diameter.) 2569 independent intensity data satisfying the condition $|F| > 3\sigma(|F|)$ were collected and used for the structure determination, where $\sigma(|F|)$ is the standard deviation due to counting statistics.

Structure determination

First, the atomic coordinates estimated from Seleborg (1967) were refined with the least-squares program *LINUS* (Coppens & Hamilton, 1970) on the basis of the space group $P6$. The refinement resulted in $R = 0.30$ for all the observed reflexions. A detailed examination revealed that the c -axis projection of the model is correct in principle, giving an R value of 0.12 for $hk0$ reflexions. An attempt was made to construct a structure model which gives the same c -axis projection as in Seleborg's structure. However, the attempt was unsuccessful if the hexagonal symmetries $P\bar{6}$ or $P6/m$ were assumed; this is because the c dimension (3.846 Å) is too short to locate two W atoms at different z levels.

Therefore, the crystal used for the structure determination was assumed to be a merohedral twin formed from crystals in space groups $P3$ or $P\bar{3}$ in two orientations. Crystals in one orientation were related to those in the other by a rotation of 60° around the c axis. In this case, the hkl reflexions of one component crystal coincide with the $\bar{k}, h+k, l$ reflexions of the other in reciprocal space. The volume ratio between the crystals in the two orientations was assumed to be 1:1; this was because all the specimens examined always gave diffraction patterns with hexagonal Laue symmetry $6/m$. A reasonable model was derived based on the space group $P\bar{3}$. The parameters were refined with the least-squares procedure, using the $hk0$ and $00l$ data which were not influenced by the twinning, and used for the calculation of the structure factors of all the observed reflexions. Each of the observed intensities was then separated into the contributions from the crystals in the respective orientations according to:

$$|F_o(hkl)|^2 = \frac{[|F_o(hkl)|^2 + |F_o(\bar{k}, h+k, l)|^2] |F_c(hkl)|^2}{[|F_c(hkl)|^2 + |F_c(\bar{k}, h+k, l)|^2]},$$

$$|F_o(\bar{k}, h+k, l)|^2 = [|F_o(hkl)|^2 + |F_o(\bar{k}, h+k, l)|^2] - |F_o(hkl)|^2.$$

Thus, the structure was refined with all the reflexion data by means of the least-squares procedure, anisotropic thermal parameters being assumed for all the atoms. The populations of K(1) and K(2) were determined to be $\frac{2}{3}$ and $\frac{1}{3}$, respectively, from the results of the difference Fourier synthesis and the least-squares refinement. After correction for secondary extinction, the calculation converged to give an R value of 0.081 for the 2569 observed reflexions; the extinction parameter (G) was $0.05(8) \times 10^{-4}$. The weighting scheme of Hughes (1941) was adopted: $w = 1.0$ if $F_o < 200.0$, and $w = (200.0/F_o)^2$ if $200.0 \leq F_o$. The atomic scattering factors for neutral atoms and the dispersion correction factors were taken from *International Tables for X-ray Crystallography* (1974). The final positional and thermal parameters are listed in Table 2.*

Discussion

The W—O and K—O bond lengths in the WO_6 , KO_{14} and KO_{18} coordination polyhedra and their mean values are given in Table 3 with their estimated standard deviations in parentheses. The structure viewed along the c axis is shown in Fig. 1. There are two crystallographically independent W atoms in the unit cell, each being octahedrally surrounded by six O atoms. The WO_6 octahedra are highly distorted. The W—O bond lengths range from 1.75 (3) to 2.12 (4) Å with a mean value of 1.92 Å. The O—W—O angles between neighbouring W—O bonds range from $80.9(11)$ to $101.8(14)^\circ$ and those between W—O bonds on the opposite sides of a W atom range from $161.2(9)$ to $174.3(13)^\circ$. There are two crystallographically independent K atoms in the unit cell. K(1) is surrounded by 14 O atoms, and K(2) by 18 O atoms.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33754 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Final atomic parameters for $K_2W_4O_{13}$

	x	y	z	B (Å ²)*
W(1)	0.26688 (5)	0.08818 (5)	-0.0591 (2)	0.37
W(2)	0.45214 (5)	0.36222 (5)	-0.0559 (2)	0.40
K(1)	0.4977 (5)	0.1821 (6)	0.474 (2)	1.72
K(2)	0.0	0.0	0.5	4.73
O(1)	0.350 (2)	0.039 (2)	0.016 (6)	2.17
O(2)	0.374 (2)	0.225 (1)	-0.008 (7)	2.31
O(3)	0.5	0.0	0.0	2.66
O(4)	0.028 (1)	0.179 (2)	0.002 (9)	2.94
O(5)	0.567 (2)	0.368 (2)	-0.012 (6)	1.91
O(6)	0.275 (3)	0.098 (2)	0.479 (5)	4.22
O(7)	0.445 (3)	0.358 (3)	0.470 (7)	4.95

* Calculated from the anisotropic thermal parameters according to: $B = 4(B_{11}a^2 + B_{22}b^2 + B_{33}c^2 + B_{12}ab \cos \gamma)/3$.

The K—O bond lengths in the K(1)O₁₄ polyhedron range from 2.72 (3) to 3.64 (5) Å (mean value 3.13 Å). Those in the K(2)O₁₈ polyhedron are classified into

three kinds, their respective lengths being 3.23 (3), 3.24 (3) and 3.75 (4) Å (mean value 3.41 Å).

The WO₆ octahedra form strings parallel to the *c* axis by sharing corners. Six such strings of W(1)O₆ octahedra construct a hexagonal tube by a further sharing of corners. The symmetry of the tube is not 6/*m* but $\bar{3}$. Strings of the W(2)O₆ octahedra connect the groups of W(1)O₆ octahedra laterally by sharing corners to form the framework of a (W₄O₁₃)_∞ anion group. K(1) is located in the pentagonal tunnels running in the framework along the *c* axis, and K(2) in the hexagonal tunnels.

Seleborg (1967) reported the structure of K₂W₄O₁₃ based on the space group *P6*. He may have used only *hk0* and *hk1* reflexions [and missed a slight puckering (about 0.4 Å) of W atoms around the *c* axis] because the structure can be refined to an *R* value of 0.13 with the space group *P6* if only these reflexions of the present investigation are used. A similar puckering of W atoms was also reported in the structure of K₂W₃O₁₀ (Okada, Morikawa, Marumo & Iwai, 1976).

It is interesting to compare the present structure with that of Na₂W₄O₁₃ (Viswanathan, 1974) to examine the effect of alkali-metal atoms on the structure of isopolytungstates. The structure of Na₂W₄O₁₃ is formed by layers of the (W₄O₁₃)_∞ anion group constructed from WO₆ octahedra by sharing corners and edges. Na atoms are located between these layers, and have a pentagonal-pyramidal environment of O atoms. The structures of both isopolytungstates are seemingly quite different. However, Na₂W₄O₁₃ has the period *b* = 3.894 Å (Viswanathan, 1974), which corresponds to the diagonal of the WO₆ octahedron. Thus, both structures consist of strings of WO₆ octahedra parallel to directions with periods of about 3.9 Å.

We are very grateful to Professor Y. Iitaka for allowing us to use an automated four-circle diffractometer. Computations were carried out on an M-180 computer at the Computer Centre of the Tokyo Institute of Technology.

Table 3. Bond lengths (Å) for K₂W₄O₁₃

Symmetry code

(0)	<i>x, y, z</i>	(viii)	<i>y, -x + y, 1 - z</i>
(i)	<i>y, -x + y, -z</i>	(ix)	<i>-y, x - y, z</i>
(ii)	<i>-x + y, -x, z</i>	(x)	<i>-x, -y, 1 - z</i>
(iii)	<i>x, y, -1 + z</i>	(xi)	<i>x - y, x, 1 - z</i>
(iv)	<i>x - y, x, -z</i>	(xii)	<i>-y, x - y, 1 + z</i>
(v)	<i>x, y, 1 + z</i>	(xiii)	<i>-x + y, -x, 1 + z</i>
(vi)	<i>1 - y, x - y, z</i>	(xiv)	<i>-x, -y, -z</i>
(vii)	<i>1 - y, x - y, 1 + z</i>		

W(1)O₆ octahedron

W(1)—O(1 ⁰)	1.82 (3)
W(1)—O(2 ⁰)	1.95 (2)
W(1)—O(4 ¹)	2.06 (4)
W(1)—O(4 ⁱⁱ)	1.82 (2)
W(1)—O(6 ⁰)	2.08 (2)
W(1)—O(6 ⁱⁱⁱ)	1.78 (2)
Mean	1.92

W(2)O₆ octahedron

W(2)—O(1 ^{iv})	2.12 (4)
W(2)—O(2 ⁰)	1.86 (2)
W(2)—O(3 ^{iv})	1.898 (1)
W(2)—O(5 ⁰)	1.75 (3)
W(2)—O(7 ⁰)	2.03 (3)
W(2)—O(7 ⁱⁱⁱ)	1.82 (3)
Mean	1.91

K(1)O₁₄ polyhedron

K(1)—O(1 ⁰)	2.86 (2)
K(1)—O(2 ⁰)	2.98 (3)
K(1)—O(3 ⁰)	3.38 (1)
K(1)—O(5 ⁰)	3.15 (2)
K(1)—O(5 ^v)	3.21 (2)
K(1)—O(6 ⁰)	3.04 (4)
K(1)—O(7 ^{vi})	3.25 (7)
Mean	3.13

K(1)—O(1 ^v)	3.07 (2)
K(1)—O(2 ^v)	3.06 (3)
K(1)—O(3 ^v)	3.50 (1)
K(1)—O(5 ^{vi})	2.72 (3)
K(1)—O(5 ^{vii})	2.80 (3)
K(1)—O(7 ⁰)	3.22 (6)
K(1)—O(7 ^{viii})	3.64 (5)

K(2)O₁₈ polyhedron

K(2)—O(4 ^{0,ii,viii,ix,x,xi})	3.23 (3) (×6)
K(2)—O(4 ^{i,iv,v,xii,xiii,xiv})	3.24 (3) (×6)
K(2)—O(6 ^{0,ii,viii,ix,x,xi})	3.75 (4) (×6)
Mean	3.41

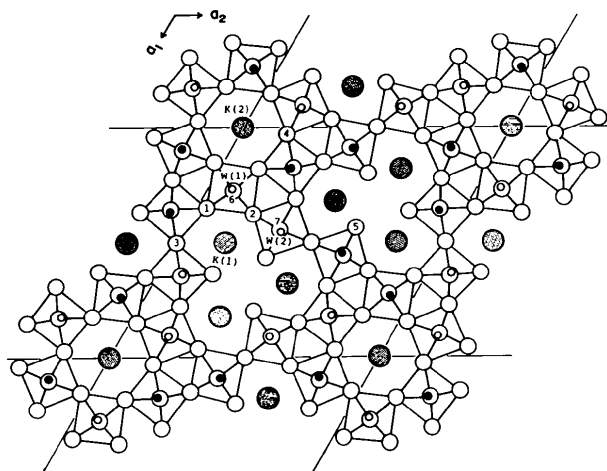


Fig. 1. The crystal structure of K₂W₄O₁₃ viewed along the *c* axis. Small filled and open circles represent W atoms just above and below the plane *y* = 0 respectively. Large open and shaded circles represent O and K atoms respectively.

References

- COPPENS, P. & HAMILTON, W. C. (1970). *Acta Cryst.* A26, 71–83.
- HUGHES, E. W. (1941). *J. Am. Chem. Soc.* 63, 1737–1752.
- International Tables for X-ray Crystallography* (1974). Vol. IV, pp. 71–151. Birmingham: Kynoch Press.
- OKADA, K., MORIKAWA, H., MARUMO, F. & IWAI, S. (1976). *Acta Cryst.* B32, 1522–1525.
- SELEBORG, M. (1967). *Chem. Commun.* pp. 1126–1127.
- VISWANATHAN, K. (1974). *J. Chem. Soc. Dalton Trans.* pp. 2170–2172.
- WUENSCH, B. J. & PREWITT, C. T. (1965). *Z. Kristallogr.* 122, 24–59.