The Crystal Structure of Potassium Tungstate, K_2WO_4

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K_2WO_4 crystallizes in space group $C2/m$ with the axes $a=12\cdot39$, $b=6\cdot105$, $c=7\cdot560$ Å and $\beta=115\cdot96°$. The four formula units per unit cell form layers parallel to the (001), in which each WO_4 tetrahedron is surrounded by an almost regular hexagon of potassium ions. The W–O bond length is $1\cdot79$ Å, the K–O and O–O distances are in general agreement with the accepted values. This structure type occurs also in other A_2BX_4 compounds, among which are K_2MoO_4, Rb_2WO_4, Rb_2MoO_4, $(NH_4)_2MoO_4$, $(NH_4)_2SeO_4$ and $(NH_4)_2CrO_4$.

Introduction

In recent years, whilst much work has been expended on the structures of the tungstates and molybdates of alkaline earth and other di- and trivalent metals, less attention has been given to those of the alkali metals. During investigations in this laboratory on compounds of the A_2BX_4 type, it was found that in the group of alkali tungstates and molybdates the crystal structures of the potassium, rubidium and caesium salts were still unknown. Lithium tungstate has the hexagonal phenacite structure (Zachariasen & Plettinger, 1961), and sodium tungstate the spinel structure (Sadikov & Shishakov, 1965). The corresponding molybdates are isomorphous with the tungstates (Zachariasen, 1926; Lindqvist, 1950). As it is interesting to note the conversion of one structure type into another when a larger but chemically similar cation is substituted in a compound, it seemed appropriate to determine the still unknown structures of K, Rb and Cs molybdates and tungstates. Together with this determination, work was carried out, and is still in progress, on the polymorphism which many of these alkali salts exhibit and extensive results of these investigations will be published later. They have proved useful in ascertaining that only one unknown type of structure was involved, namely the monoclinic structure in which potassium and rubidium tungstate and molybdate crystallize. The caesium compounds proved to be isomorphous with orthorhombic β-potassium sulphate.

The potassium tungstate structure has been found to occur in a number of other substances, among which are ammonium selenate, chromate and molybdate. Some evidence for this had already been given by Groth (1908), since the morphological constants resemble each other. Of all these compounds, Wyckoff (1965) in his description of the A_2BX_4 crystal structures only mentions ammonium chromate, the data for which were taken from Bujor (1944). The proposed structure was rather unlikely, however, and a new model was suggested by Hasegawa, Fujishige & Ogawa (1963).

Experimental

Potassium tungstate has some properties which make preparation of a suitable single crystal rather difficult. It is highly hygroscopic, reacts with carbon dioxide, reacts with hot water to form a paratungstate and gives a hydrate when crystallized at room temperature (Pascal, 1959). Single crystals cannot be prepared from the melt since there exists a transition point at about 370°C (Schmidt-Dumont & Weeg, 1951), at which the product decrepitates vigorously into very small fragments. The only way of obtaining crystals with the formula K_2WO_4 has already been described by de Marignac (1863), but the crystals are practically always twinned (Groth, 1908). The same difficulties arise to a certain extent when preparing the other molybdates and tungstates of previously unknown structure.

The procedure adopted was the following. Equivalent amounts of tungstic oxide, WO_3, and potassium carbonate were thoroughly mixed and heated at 1000°C in a covered platinum crucible for half an hour. On cooling the product in a desiccator it becomes a very fine white powder, sometimes with a tinge of violet, its melting point being 912°C (913°C found by Gelsing, Stein & Stevels, 1965). Good diffractometer diagrams, obtained from this powder, showed only peaks due to potassium tungstate and these were also used for estimating a few reflexions in the structure determination. A solution of 60 g in 100 ml of water was very slowly evaporated at 50°C; after three days, the first crystals were seen, and a few hours after that, about 10 g of the solid had crystallized; this was separated from the liquid by rapid suction through a coarse glass frit in a dry, warm air current, free from carbon dioxide. The precipitate was examined in a glove box (to exclude water and carbon dioxide); it consisted mostly of a poorly crystallized powder. However, a number of thin platelets could be observed, which were examined in polarized light. The crystals were so fragile and so thin that it was impossible to grind them to cylinders or spheres. Most of the crystals were heavily twinned, as was shown by their

shape and by X-ray photographs, but one rectangular platelet measuring $0.50 \times 0.19 \times 0.07$ mm was satisfactory, although it, too, was contaminated with a fragment of a twin. It was sealed in a Lindemann capillary. The extinction direction was parallel to the 0·50 mm edge of the crystal, corresponding to the monoclinic b axis, as was shown by X-rays.

Reflexions were collected on an integrating Weissenberg camera; the axis of rotation was **b**. Six layers were recorded by the multiple-film equi-inclination tech-

Table 1. *Calculated and observed structure amplitudes*

Reflexions omitted from the least-squares calculation are denoted by an asterisk.

H	K	L	F(C)	F(O)

nique; for the layers 0–3, Ni-filtered Cu $K\alpha$ radiation was used; for the layers 4 and 5, Zr-filtered Mo $K\alpha$ radiation. The intensities (767 in number) were measured photometrically, except the very weak ones which were estimated visually. They were corrected for the Lorentz and polarization factors and for absorption. The latter correction was a rather important one, and it may be supposed that it constituted a major cause of the discrepancies between calculated and observed structure amplitudes. The layers were scaled by a Wilson plot and as the analysis progressed, more exact scale factors were obtained by comparison between observed amplitudes and calculated absolute values. A few intensities (like 020 and 040) were estimated from powder data.

The cell constants were determined by least-squares calculations on high-order $h0l$ reflexions and a rotating crystal photograph [010], both calibrated with aluminum powder lines (Cu $K\alpha_1 = 1\cdot5405$ Å), and checked with powder data from a carefully adjusted diffractometer.

Crystal data and space group

K_2WO_4. $M = 326\cdot14$. Monoclinic, $a = 12\cdot39 \pm 0\cdot01$, $b = 6\cdot105 \pm 0\cdot005$, $c = 7\cdot560 \pm 0\cdot005$ Å, $\beta = 115\cdot96° \pm 0\cdot03°$. $V = 513\cdot9$ Å^3, $Z = 4$, $D_c = 4\cdot21$ g.cm^{-3}, $D_o = 4\cdot18$ g.cm^{-3}. μ for Cu $K\alpha$, 599 cm^{-1}; μ for Mo $K\alpha$, 272 cm^{-1}.

Reflexions with $h + k = 2n + 1$ are systematically absent, thus the space group is $C2$, Cm or $C2/m$. Space group Cm was excluded, since the occurrence of a mirror plane perpendicular to the small b axis would place the potassium ions too near to each other. By the same argument, the positions $(e), (f), (g)$ and (h) of space group $C2/m$ (*International Tables for X-ray Crystallography*, 1952) can be ruled out. A choice is left between $C2$ (c) and $C2/m$ (i), the latter being taken as the most probable, since physical tests for non-centrosymmetry proved negative and the structure analysis supported centrosymmetry.

Determination of structure

It was expected that the W–W vector would show up very strongly in a Patterson projection (uw). The highest peak, at $u = 0\cdot35$, $w = 0\cdot45$, however, was not outstandingly stronger than another one at $u = \frac{1}{6}$, $w = 0$. Furthermore, there was a peak at $u = \frac{1}{2}$, $w = \frac{1}{2}$ and a smaller one at $u = 0\cdot03$, $w = 0\cdot15$. The marked localization of peaks around $w = 0$ and $w = \frac{1}{2}$ seemed to point to a layer structure parallel to (001), which was corroborated by the fact that the compound crystallizes in {001} platelets. In such a layer, the W and K atoms would lie at a distance $x = \frac{1}{6}$ apart, and much overlapping of interatomic vectors would occur. The highest peak was assumed to represent the W–W vector and from the two possible positions of W the one was selected which placed the WO_4 groups as far away as possible from the twofold axis. Signs of structure factors based on the W atom were computed and an electron density map (xz) was produced. The K atoms appeared, and also a number of peaks around the W atom, which could also arise, however, from the series termination ripple of the heavy atom. Upon reversal of the sign of the reflexion $\overline{4}02$, whose intensity was calculated as extremely small, an oxygen tetrahedron around W could be seen more clearly in what later appeared to be the correct position.

In the three-dimensional Patterson synthesis the W–W and W–K maxima were all found in the planes $(u, 0, w)$ and $(u, \frac{1}{2}, w)$. In the space group $C2$, the W and K atoms need not lie exactly $\frac{1}{2}b$ apart, so this was further evidence that $C2/m$ is the correct space group. The W–W vector was by far the largest. If the W atom is placed at $(x, 0, z)$, then the two K atoms must lie in the plane $(x, \frac{1}{2}, z)$. A three-dimensional Fourier synthesis

Table 2. *Parameters and standard deviations*

	x	y	z	B (Å^2)
W	0·1755 (3)	0	0·2275 (5)	
K(1)	0·010 (1)	0·5	0·235 (2)	2·5 (3)
K(2)	0·346 (1)	0·5	0·259 (2)	2·5 (3)
O(1)	0·084 (2)	0	0·351 (4)	4·0 (1·0)
O(2)	0·336 (2)	0	0·377 (4)	4·0 (1·0)
O(3)	0·141 (2)	0·239 (3)	0·074 (4)	4·0 (1·0)

Vibration parameters of the W atom

b_{11}	b_{12}	b_{13}	b_{22}	b_{23}	b_{33}
0·0016 (1)	0	0·0047 (4)	0·0046 (6)	0	0·0111 (5)

Table 3. *Bond lengths* (Å)

W–O(1)	1·76	K(1)–O(1)	3·20	K(2)–O(2)	3·20
W–O(2)	1·80	K(1)–O(2′)	2·80	K(2)–O(1′)	2·72
W–O(3)	1·79	K(1)–O(2″)	2·71	K(2)–O(1″)	2·70
		K(1)–O(3)	2·90	K(2)–O(3)	2·97
		K(1)–O(3′)	2·77	K(2)–O(3′)	2·80

based on the W positions indicated all the atoms involved. Also, a shell of electron density around the W atom with a radius of about 1·2 Å could be observed, as a result of the series termination effect. The same effect gave rise to an at first inexplicable peak in the three-dimensional Patterson map at $v=0·2$, with the u and w coordinates of the W–W vector. To remove this error, an $[F_o - F_c(\mathrm{W})]$ synthesis was computed, which showed the oxygen atoms more clearly and, furthermore, indicated an anisotropic thermal vibration of the W atom, by the presence of positive and negative areas around its position (Lipson & Cochran, 1953).

The final refinement was carried out by a least-squares program minimizing $\Sigma\, w(I_o - I_c)^2$. As this function is non-linear in its parameters, a relaxation factor <1 was applied to speed up its convergence. The coefficients for computing the scattering factors of K^+, W^{6+} and O^{2-} were derived from Cromer & Waber (1964), the anomalous dispersion terms $\Delta f'$ and $\Delta f''$ having been taken into account. The oxygen positions determined from the difference synthesis were kept fixed during the refinement. The tungsten atom was given an isotropic temperature factor of 1·1 Å², which was anisotropically refined, while preserving the mirror plane perpendicular to **b** through its centre. Because of the somewhat limited accuracy of the intensities, as a result of absorption, all reflexions were given unitary weighting factors. A few were omitted from the refinement because of extra high absorption or possible extinction. The observed and calculated structure factors are compared in Table 1. The variables converged in 5 cycles to the values shown in Table 2. The final residual $R = 100\,\Sigma\,|\Delta|/\Sigma\,|F_o|$ is 14·7% taking into account all observed reflexions.

Description of the structure

The projection of the structure on the (010) plane is shown in Fig. 1. The structure is seen to consist of layers parallel to (001), in which discrete tungsten–oxygen tetrahedra are linked together by almost regular hexagons of potassium ions. The bonding between layers is brought about by the attraction betw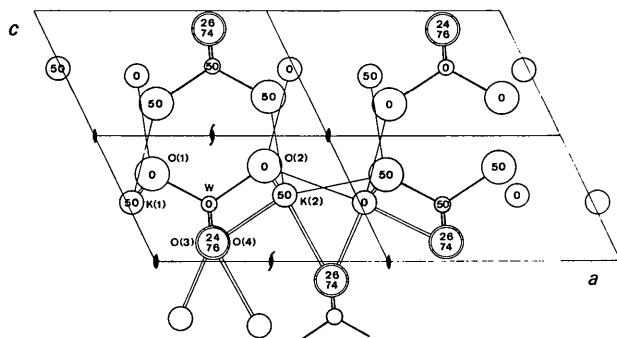een the oxygen atoms protruding from the layer and the K ions in the next layer; a tungstate tetrahedron is surrounded by 11 K ions. The vibration of the W atom is greatest in the direction perpendicular to the layer. The WO_4 tetrahedron is almost regular; the O(1)–W–O(2) angle, however, is 117°(estimated standard deviation $1\frac{1}{2}°$) and is thus somewhat greater than the expected value of 109½°. Bond lengths are given in Table 3; the estimated standard deviation is 0·02 Å.

The W–O average bond length of 1·79 Å agrees well with the value of 1·79 Å found by Zachariasen & Plettinger (1961) in Li_2WO_4, where tetrahedra are also present. Sadikov & Shishakov (1965) found W–O = 1·88 Å in Na_2WO_4; in an idealized spinel structure (O parameter = 0·375) this value would have been 1·98 Å. Abrahams (1966) gives the value $1·76 \pm 0·04$ Å for the average tetrahedral W–O distance. In K_2WO_4, each potassium ion is surrounded by eight oxygen atoms, two at a distance of 3·2 Å and six at an average distance of 2·8 Å. The W and K positions do not lie exactly in a plane; the angle between the K(1)–K(2) vector and **a** is about 3°, and the WO_4 tetrahedron is also tilted by about 3°. The distances between oxygen atoms of neighbouring anions are 3·2 Å or more.

The structure proposed for ammonium selenate by Hasegawa, Fujishige & Ogawa (1963) appears to bear a general resemblance to the K_2WO_4 structure. These authors, however, based their model to a large extent upon packing considerations. It follows that this structure type occurs in several compounds, which are sometimes quite chemically dissimilar, like the highly hygroscopic tungstates and the non-hygroscopic selenate or chromate. Packing conditions of cation and anion groups are of prime importance in creating this structure type, rather than the formation of hydrogen bonds, as is assumed by Hasegawa *et al.*

The structure has a marked pseudo-orthorhombic character, the axes of this orthorhombic cell being defined by **a**, **b** and [104]. In the [104] direction, the layers have a pseudo twofold axis through the tungsten atom, which accounts for the easy twinning along (001), since the next layer can be oriented at 180° with respect to the correct position.

Comparison with the other tungstates

The increase of the coordination number when substituting a larger cation in these compounds is very marked. In Li_2WO_4 with the phenacite arrangement, the lithium ion is fourfold coordinated and the oxygen atoms are approximately close-packed, but in order to create a tetrahedral environment of oxygen for both lithium and tungsten, there are holes in this packing. When the radius of the cation is increased full close-packing becomes possible, with sixfold coordination for the cation and fourfold for the tungsten so that the olivine or the spinel structure could arise. Na_2WO_4 has a spinel structure and obviously the olivine structure demands a smaller cation. This spinel structure, however, is not ideal, the W–O bond being somewhat short.

Fig. 1. Projection on (010) of the K_2WO_4 structure. The values within the circles denote the fractional y coordinate $\times 100$.

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There is a tendency to form definite WO_4 ions, removing the double oxide character of the pure spinel. In the other tungstates, fully discrete WO_4 tetrahedra are present; in the potassium and rubidium salt each alkali ion is surrounded by 8 oxygen atoms, while in the caesium salt with the β-K_2SO_4 structure, one caesium ion is surrounded by 10, and the other by 9 oxygen atoms.

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A Nuclear Magnetic Resonance Study of Magnesium Thiosulphate Hexahydrate*

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The angular dependence of the nuclear magnetic resonance spectrum of single crystals of MgS_2O_3. $6H_2O$ has been studied in four planes of rotation with a view to establishing the proton–proton vectors. The experimentally determined vectors were employed to (*a*) confirm the hydrogen-bonding scheme predicted by the X-ray authors, (*b*) resolve the conflict with a previous n.m.r. study of MgS_2O_3.$6H_2O$ and, (*c*) determine the coordinates of the hydrogen atoms.

1. Introduction

The X-ray studies of Nardelli, Fava & Giraldi (1962) give the space group of MgS_2O_3.$6H_2O$ as *Pnma* with unit-cell dimensions $a = 9.32$, $b = 14.36$, $c = 6.87$ Å, and with $Z = 4$. The structure consists of alternating layers of $Mg(OH_2)_6^{2+}$ octahedra and $S_2O_3^{2-}$ tetrahedra perpendicular to the *b* axis. Each octahedron is linked by OH---O hydrogen bonding to four neighboring octahedra in the same layer and to four tetrahedra in the two adjacent layers. The hydrogen-bonding scheme suggested by Nardelli *et al.* (1962) is as follows:

$$O_I\text{---}H\text{--}O_I^w\text{--}H\text{---}S_{II}$$
$$O_{II}\text{---}H\text{--}O_{II}^w\text{--}H\text{---}S_{II}$$
$$O_{II}\text{---}H\text{--}O_{III}^w\text{--}H\text{---}O_I$$

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* The experimental part of this work was carried out at the Department of Chemistry, Johns Hopkins University, Baltimore, Maryland, U.S.A.
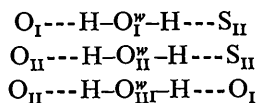
where the designations of Nardelli *et al.* are used, except for H_2O, which is replaced here by O^w.

A study of the angular dependence of the nuclear magnetic resonance spectrum of MgS_2O_3. $6H_2O$ in one plane of rotation has been made previously by Visweswaramurthy (1963). The p–p (proton–proton) vectors given by Visweswaramurthy were inconsistent with the hydrogen-bonding scheme above. The finding of this inconsistency (El Saffar, 1968) led to the present investigation.

2. Experimental

Large single crystals of commercial-grade MgS_2O_3. $6H_2O$ were grown from saturated aqueous solutions. The samples were cut in approximately cylindrical form and varied in volume from 1 to 4 cm³. They were mounted in Teflon holders which were in turn attached to a simple indexed head which allowed rotation about the axis of the cylinder. The measurements were made at room temperature. The resonance spectrum was re-