significantly to those previously measured in other P_6O_{18} anions. These angles are: 108·5° for $(NH_4)_6P_6O_{18}.H_2O$; 112·2° for $Ag_6P_6O_{18}.H_2O$; 116·4 and 115·8° for $Cd_3P_6O_{18}.6H_2O$.

Here the values of the three P—P—P angles vary from 96·3 to 139·9° (Table 2) with an average of 116·8°.

In spite of this large angular distortion the calculation of the least-squares plane of the P and bonding O atoms (Table 2) shows this group of atoms to be almost planar.

The copper coordination. Two independent distorted copper octahedra are observed in the atomic arrangement. The first is located around the origin and is built up of four O atoms and two water molecules. This octahedron, whose main geometrical features are reported in Table 2, shares four of its O atoms with the P_6O_{18} ring anions, thus building chains: P_6O_{18}—$CuO_4(H_2O)_2$—P_6O_{18}..., spreading along the *c* axis. These chains are themselves interconnected by the centrosymmetric cluster $Cu_2(H_2O)_8O_2$ built up of two edge-sharing $CuO(H_2O)_5$ octahedra. This second kind of copper coordination polyhedron shares only one O atom with the phosphoric ring anion.

In addition it must be noted that two of the water molecules [O(*W*5) and O(*W*6)] are not involved in the copper coordination.

The three-dimensional network of hydrogen bonds is described in Table 2.

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$KMoWP_3O_{12}$, a Tunnel Structure of the $KMo_2P_3O_{12}$-Type

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Abstract. Potassium molybdotungstotriphosphate(V), $KMoWP_3O_{12}$, $M_r = 603{\cdot}80$, orthorhombic, *Pbcm*, $a = 8{\cdot}8180\,(6)$, $b = 9{\cdot}1574\,(8)$, $c = 12{\cdot}3836\,(8)$ Å, $V = 1000{\cdot}0\,(2)$ Å^3, $Z = 4$, $D_x = 4{\cdot}01$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71073$ Å, $\mu = 13{\cdot}9$ mm^{-1}, $T = 294$ K, $F(000) = 276$, $R = 0{\cdot}035$ and $wR = 0{\cdot}042$ for 2291 observed reflections. The framework is built up from MoO_6 octahedra and PO_4 tetrahedra which delimit tunnels running along **b**, where the K ions are located. The structure leads to the formula $KMoWO(PO_4)(P_2O_7)$.

Introduction. Molybdenum and tungsten exhibit very different behavior in spite of their similar electronic structure. Recent studies of the phosphates of these elements support this point of view, as shown for instance by the existence of phosphate tungsten bronzes (see Raveau, 1986, for review), and the synthesis of original frameworks of phosphates of Mo^{III} (Leclaire, Borel, Grandin & Raveau, 1988, 1989*a*; Riou, Leclaire, Grandin & Raveau, 1989; Lii & Haushalter, 1987*a*) and Mo^V (Leclaire, Monier & Raveau, 1983; Leclaire, Borel, Grandin & Raveau, 1989*b*; Lii & Haushalter, 1987*b*; Chen, Lii & Wang, 1988). On the other hand tetravalent molybdenum and tungsten have features in common: if one considers the MoO_2 and WO_2 oxides which are isostructural with the TiO_2 rutile form.

Since the synthesis of the tungsten phosphate isotypic with $AMo_2P_3O_{12}$ (A = K, Rb, Tl) (Leclaire, Monier & Raveau, 1985; Leclaire & Raveau, 1988) has so far been unsuccessful, the substitution of tungsten for molybdenum in $KMo_2P_3O_{12}$ has thus been investigated. We report here on the crystal structure of $KMoWP_3O_{12}$.

Experimental. The synthesis was performed in two steps. First, $(NH_4)_2HPO_4$, MoO_3, WO_3 and K_2CO_3

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were mixed in an agate mortar in the molecular ratio required for stoichiometric $KMo_{0.33}WP_3O_{12}$, and heated at 600 K to decompose the potassium carbonate and the ammonium phosphate. The resulting mixture was then added to the required amount of molybdenum and placed in an evacuated silica ampoule. This mixture was heated for 5 days at 1373 K and this allowed $KMoWP_3O_{12}$ to be isolated. Black crystals were obtained. The composition was confirmed by microprobe analysis.

Black crystal: $0{\cdot}120 \times 0{\cdot}216 \times 0{\cdot}120$ mm. Symmetry *mmm* with systematic absences $0kl$ for k odd and $h0l$ for l odd. Space group *Pbcm*. Enraf–Nonius CAD-4 diffractometer. Unit cell: least squares on 25 reflections $\pm 2\theta$, $36 \leq 2\theta \leq 44°$; intensity measurement by ω–$2/3\theta$, scan of $(1{\cdot}0 + 0{\cdot}35\tan\theta)°$ and $(1 + \tan\theta)$ mm counter slit determined by a study of some reflections in the ω–θ plane. Scanning speed adjusted to obtain $\sigma(I)/I \leq 0{\cdot}018$ or to approach it in a time limited to 60 s. Three standards for count every 2000 s and orientation every 600 reflections: no appreciable trends, 2291 reflections ($h_{\max} = 17$, $k_{\max} = 18$, $l_{\max} = 24$), $2 \leq \theta \leq 45°$, with $I/\sigma_I \geq 3$ used to solve (heavy-atom method) and refine (on F) the structure. No correction made for extinction or absorption. all subsequent calculations on a MicroVAX II computer with the *SDP* system (B. A. Frenz & Associates Inc., 1982). $(\Delta/\sigma)_{\max} = 0{\cdot}005$, $\Delta\rho \leq 4{\cdot}0$ e Å^{-3}, $R = 0{\cdot}035$, $wR = 0{\cdot}042$, $w = f[(\sin\theta)/\lambda]$, $S = 1{\cdot}5$. Atomic parameters in Table 1.* Scattering factors and f', f'' values taken from *International Tables for X-ray Crystallography* (1974).

Discussion. The structure of $KMoWP_3O_{12}$ is very similar to those described for the pure molybdenum phosphates $AMo_2P_3O_{12}$ (A = K, Rb, Tl) (Leclaire *et al.*, 1985; Leclaire *et al.*, 1988). The host lattice $[MoWP_3O_{12}]$ (Fig. 1) is indeed built up from MoO_6 and WO_6 octahedra and PO_4 tetrahedra which form tunnels running along **b**, where the K ions are located. The simultaneous presence of PO_4 and P_2O_7 groups allows the formula $KMoWO(PO_4)(P_2O_7)$ to be proposed.

Unlike $KMo_2P_3O_{12}$ (Leclaire *et al.*, 1988), this phase does not exhibit a superstructure along **a**. In this respect it is more closely related to the rubidium and thallium monophosphates $AMo_2P_3O_{12}$ (Leclaire *et al.*, 1985; Leclaire *et al.*, 1988).

Table 1. *Positional parameters with estimated standard deviations in parentheses*

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $\frac{4}{3}[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

	x	y	z	B(Å^2)
Mo+W	0·24595 (3)	0·02674 (3)	0·10083 (2)	0·468 (3)
K	−0·1788 (7)	0·1620 (5)	0·250	5·1 (1)
P(1)	−0·0299 (2)	0·250	0·000	0·50 (2)
P(2)	0·4042 (2)	0·3660 (2)	0·1310 (1)	0·58 (2)
O(1)	0·2071 (8)	0·0184 (8)	0·250	1·12 (9)
O(2)	0·1279 (8)	−0·1586 (6)	0·0744 (5)	2·0 (1)
O(3)	0·30128 (6)	0·0411 (5)	−0·0620 (4)	1·25 (7)
O(4)	0·3804 (6)	0·2040 (5)	0·1204 (4)	1·20 (7)
O(5)	0·4309 (6)	−0·1031 (6)	0·1204 (4)	1·40 (8)
O(6)	0·0621 (6)	0·1536 (7)	0·0749 (5)	1·80 (9)
O(7)	0·3526 (9)	0·4138 (8)	0·250	1·2 (1)

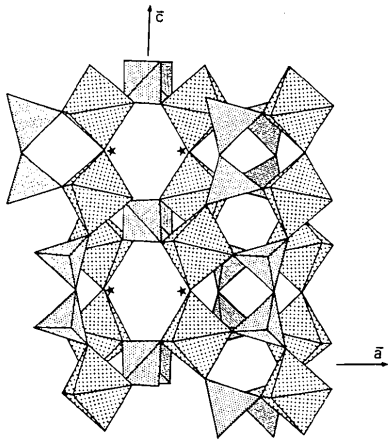

Fig. 1. Projection of $KMoWP_3O_{12}$ along **b**.

The P(1) tetrahedra which are only linked to MoO_6 and WO_6 octahedra are very regular, with P—O distances ranging from 1·515 to 1·516 Å (Table 2). On the other hand, the $P(2)O_4$ tetrahedra which belong to the P_2O_7 groups have one long P—O bond of 1·603 Å corresponding to the bridging oxygen of the diphosphate, and three other P—O distances ranging from 1·488 to 1·507 Å (Table 2). These bonds lengths are similar to those observed for $KMo_2P_3O_{12}$ at the 3σ level.

The geometry of the MoO_6 and WO_6 octahedra is very similar to that observed for $KMo_2P_3O_{12}$: one observes one shorter Mo—O distance of 1·88 Å (Table 2) which corresponds to the Mo—O—Mo bonds, and five longer Mo—O distances ranging from 2·018 to 2·079 Å corresponding to the Mo—O—P bonds.

The K ions are surrounded by eight O atoms at distances less than 3·35 Å. As in the other $AMo_2P_3O_{12}$ structures one observes three short K—O bonds ranging from 2·712 to 2·762 Å (Table 2) and six longer ones ranging from 3·037 to 3·273 Å.

In conclusion, it is worth pointing out that tungsten and molybdenum are distributed at random on only one equivalent site, contrary to what could have

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51899 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Distances* (Å) *and angles* (°) *in the* PO_4 *tetrahedron and* $(MoW)O_6$ *octahedra, and* K—O *distances* (Å) *in the* KO_8 *polyhedron*

P(1)	O(2^{i})	O(2^{ii})	O(6)	O(6^{iii})
O(2^{i})	1·515 (6)	2·490 (8)	2·495 (9)	2·402 (9)
O(2^{ii})	110·5 (4)	1·515 (6)	2·402 (9)	2·495 (9)
O(6)	110·8 (3)	104·8 (3)	1·516 (6)	2·561 (9)
O(6^{iii})	104·8 (3)	110·8 (3)	115·3 (2)	1·516 (6)

P(2)	O(3^{iii})	O(4)	O(5^{iv})	O(7)
O(3^{iii})	1·507 (5)	2·540 (7)	2·530 (7)	2·407 (5)
O(4)	115·1 (3)	1·504 (5)	2·427 (7)	2·515 (7)
O(5^{iv})	115·4 (3)	108·4 (3)	1·488 (5)	2·499 (8)
O(7)	101·4 (3)	108·1 (3)	107·9 (4)	1·603 (3)

MoW	O(1)	O(2)	O(3)	O(4)	O(5)	O(6)
O(1)	1·880 (1)	2·801 (7)	3·958 (8)	2·793 (7)	2·776 (8)	2·805 (7)
O(2)	91·8 (3)	2·018 (6)	2·923 (8)	4·038 (8)	2·779 (8)	2·917 (8)
O(3)	176·5 (3)	91·0 (2)	2·079 (5)	2·794 (7)	2·853 (7)	2·898 (8)
O(4)	91·2 (3)	174·8 (2)	85·8 (2)	2·024 (5)	2·847 (7)	2·899 (8)
O(5)	90·3 (3)	86·6 (2)	87·9 (2)	89·1 (2)	2·032 (5)	4·051 (8)
O(6)	91·9 (3)	92·5 (3)	90·0 (2)	91·6 (2)	177·6 (2)	2·020 (6)

K—O(7^{v})	2·742 (9)	K—O(6^{vii})	3·037 (7)
K—O(2^{ii})	2·762 (6)	K—O(3^{i})	3·172 (6)
K—O(2^{vi})	2·762 (6)	K—O(3^{viii})	3·172 (6)
K—O(6)	3·037 (7)	K—O(1^{ii})	3·273 (8)

Symmetry codes: (i) $-x, -y, -z$; (ii) $-x, 0·5+y, z$; (iii) $x, 0·5-y, -z$; (iv) $1-x, 0·5+y, z$; (v) $-x, y-0·5, z$; (vi) $-x, 0·5-y, 0·5-z$; (vii) $x, y, 0·5-z$; (viii) $-x, -y, 0·5+z$.

been expected from the structure of $KMo_2P_3O_{12}$ which is characterized by a double cell with two equivalent sites for molybdenum. The difficulty in obtaining $KW_2P_3O_{12}$, containing only tungsten, is probably due to the great tendency of tungsten to form oxides characterized by electron delocalization. This is indeed the case for the phosphate tungsten bronzes, which exhibit a large homogeneity range and may have greater stability than the molybdenum-type phosphates whose valence electrons are localized.

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Structure of Copper(II) Perchlorate Hexahydrate

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Abstract. $Cu(ClO_4)_2.6H_2O$, $M_r = 370·54$, monoclinic, $P2_1/c$, $a = 5·137$ (1), $b = 22·991$ (3), $c = 13·849$ (2) Å, $\beta = 90·66$ (1)°, $V = 1635·4$ (4) Å^3, $Z = 6$, $D_x = 2·26$ g cm^{-3}, λ(Mo $K\bar{\alpha}$) = 0·71069 Å, $\mu = 26·44$ cm^{-1}, $T = 296$ K, $F(000) = 1122$, 2911 unique reflections having $I > \sigma_I$, $R = 0·030$. Each of the two inequivalent copper ions is coordinated by six water-molecule O atoms in a significantly distorted octahedral arrangement. Each of the three inequivalent but geometrically quite similar perchlorate groups is slightly distorted from regular tetrahedral geometry. The overall observed mean Cl—O distance is 1·429 (5) Å while the overall observed mean perchlorate O—O distance is 2·333 (8) Å. Both the Cu–O complexes and the perchlorate ions were tested and found to behave as rigid bodies. The perchlorate-ion parameters corrected for rigid-body motion are: overall mean Cl—O distance, 1·453 (6) Å; overall mean perchlorate O—O distance, 2·372 (8) Å. Location and refinement of the 18 H atoms gave a detailed account of hydrogen bonding, which occurs between oxygen octahedra, between oxygen octahedra and perchlorate groups, and, more weakly, within oxygen octahedra.

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