

$K_4Mo_8^V P_{12}O_{52}$, A Tunnel Structure Characterized by an Unusual Valence of Molybdenum

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A new phosphate of molybdenum (V) $K_4Mo_8^V P_{12}O_{52}$ has been isolated and its structure solved from a single crystal X-ray diffraction study. It crystallizes in a monoclinic cell, space group $C2/c$, with the parameters $a = 10.7433(16)$ Å, $b = 14.0839(9)$ Å, $c = 8.8519(7)$ Å, and $\beta = 126.42(1)^\circ$. After refinement of the different parameters, the reliability factors were lowered to $R = 0.026$ and $R_w = 0.029$. The framework " $Mo_8P_{12}O_{52}$ " can be described as corner-sharing PO_4 tetrahedra, P_2O_7 groups, and MoO_6 octahedra. Although the " O_6 " octahedron surrounding the molybdenum ion is almost regular, the metal ion is strongly off center so that its coordination is better described as a MoO_5 pyramid. This particular coordination, which characterizes Mo(V), is discussed.

Introduction

The catalytic properties of several molybdenum oxides suggest that the chemistry of these compounds, and particularly the relative stability of the different valences of Mo in oxides, is worth studying. In this respect, Mo(V) can be considered an unusual valence of molybdenum in oxides. Several mixed valence molybdenum oxides with a Mo valence intermediate between five and six have been isolated even in the binary system Mo-O (1-5), whereas the oxides characterized by the presence of Mo(V) only seem to be limited to the phosphates $(MoO)PO_4$ (6) and $(MoO)_2P_4O_{13}$ (7). Moreover, the coordination of Mo(V) in these latter phosphates is very particular since the molybdenum ion is so off center inside its octahedron that a description in terms of

a square pyramidal arrangement can be proposed. This behavior is very different from that of Mo(VI) in phosphates such as $(MoO_2)_2P_2O_7$, $(MoO_2)(PO_3)_2$, and $NaMoO_2PO_4$ (8-10), whose frameworks are built up from MoO_6 octahedra and PO_4 tetrahedra. This ability of PO_4 tetrahedra and MoO_6 octahedra to form a mixed framework is to be compared to the chemistry of tungsten (VI) phosphates such as $W_2O_3(PO_4)_2$, WOP_2O_7 , and $NaWO_2PO_4$ (10-13) whose frameworks are built up from WO_6 octahedra and PO_4 tetrahedra. The chemistry of molybdenum phosphates seems, however, not as developed as that of tungsten, as shown from the recent investigations of new structural series in the systems P-W-O and A-P-W-O ($A = K, Rb$) which are known as phosphate tungsten bronzes (14-19). We have thus investi-

gated the system K–P–Mo–O, and the present paper deals with the structure of a new phosphate of Mo(V), $K_4Mo_8P_{12}O_{52}$.

Determination of the Structure

Mixtures of P_2O_5 , MoO_3 , Mo, and K_2O in appropriate ratios were heated at $800^\circ C$ in an evacuated silica ampule. A green crystal with dimensions $0.48 \times 0.14 \times 0.07$ mm was selected for the structure determination.

The Laue patterns showed monoclinic symmetry ($2/m$). The cell parameters, initially measured on precession films and later refined by diffractometric techniques at $21^\circ C$ with a least squares refinement based on 25 reflections, are

$$\begin{aligned} a &= 10.7433(16) \text{ \AA} & b &= 14.0839(9) \text{ \AA} \\ c &= 8.8519(7) \text{ \AA} & \beta &= 126.42(1)^\circ. \end{aligned}$$

The systematic absences led to Cc or $C2/c$ space groups. Harker planes and Harker lines in the Patterson function led to the $C2/c$ space group. The data were collected on a CAD 4 Enraf–Nonius diffractometer with $MoK\alpha$ radiation filtered with a graphite monochromator ($\lambda MoK\alpha = 0.71069 \text{ \AA}$). The intensities were measured up to $\theta = 45^\circ$ with a $\omega - \frac{1}{2}\theta$ scan of $(1.00 + 0.35 \tan \theta)^\circ$ and a counter slit aperture of $(1.00 + \tan \theta)$ mm, all determined after a study of some reflections in the $\omega\theta$ plane. The background intensity was measured on both sides of each reflection. A periodic control reflection verified the stability of the sample. The 3777 reflections which had $\sigma(I)/I \leq 0.333$ were corrected for Lorentz and polarization effect; absorption corrections were not applied ($\mu R \approx 0.46$).

Atomic coordinates of the molybdenum ion were fixed by the Patterson function and the other atoms were then located by the heavy atom method. The atomic parameters were refined by full matrix least squares and a linear weighting scheme $w =$

$f(\sin \theta/\lambda)$ was adjusted using the program Nanova of W. C. Hamilton (unpublished). Scattering factors for Mo, O, P, and K were taken from "International Tables for X-ray Crystallography" (20) corrected for anomalous dispersion.

The final reliability factors were $R = 0.026$ and $R_w = 0.029$.¹ Final atomic parameters are given in Table I. The potassium ion exhibits a high strongly anisotropic thermal motion. A distribution of this ion in the general positions $8(f)$ with an occupancy factor of 50% has thus been tried; a convergence of the refinement was obtained but the factors R and R_w were not lowered in spite of the increase in the number of parameters. The Hamilton test (21) allows us to rule out this hypothesis, and to locate K^+ on the $4(d)$ sites.

Description of the Structure and Discussion

The projection of the structure along the c axis onto the (001) plane (Fig. 1), shows that it can be described as a three-dimensional $Mo_8P_{12}O_{52}$ framework forming cavities where the potassium ions are located. The $Mo_8P_{12}O_{52}$ array is built up from PO_4 tetrahedra and MoO_6 octahedra. Two sorts of tetrahedral units are observed: PO_4 tetrahedra, corresponding to P(2), which share their corners with four MoO_6 octahedra, and pyrophosphate groups P_2O_7 , corresponding to P(1), which share their corners with four MoO_6 octahedra. Each MoO_6 oc-

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TABLE I

POSITIONAL PARAMETERS				
Atom	x	y	z	B_{eq}^a
MO	0.24451(1)	0.08184(1)	0.17016(2)	0.51(0.00)
K	0.25000(0)	0.25000(0)	0.50000(0)	4.93(0.06)
P(1)	0.44330(4)	0.20465(3)	0.06075(5)	0.51(0.01)
P(2)	0.00000(0)	0.01061(4)	0.25000(0)	0.46(0.01)
O(1)	0.13420(13)	0.07401(9)	0.29269(16)	0.86(0.03)
O(2)	0.41202(12)	0.15738(10)	0.40193(16)	0.89(0.03)
O(3)	0.32876(15)	0.13034(10)	0.03349(18)	1.04(0.03)
O(4)	0.12483(16)	0.22548(9)	0.09672(17)	1.00(0.03)
O(5)	0.05233(13)	0.05186(8)	-0.08101(15)	0.76(0.03)
O(6)	0.32703(21)	-0.02462(12)	0.22922(25)	1.57(0.04)
O(7)	0.50000(0)	0.26041(12)	0.25000(0)	0.80(0.04)

THERMAL PARAMETERS ^b						
Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
MO	0.00145(1)	0.00084(1)	0.00229(1)	-0.00018(1)	0.00115(1)	-0.00008(1)
K	0.01067(13)	0.00878(12)	0.02753(37)	-0.00280(10)	0.01268(20)	-0.01151(20)
P(1)	0.00140(3)	0.00083(1)	0.00232(4)	0.00013(1)	0.00108(3)	0.00023(2)
P(2)	0.00133(4)	0.00079(2)	0.00203(5)	0.00000(0)	0.00108(4)	0.00000(0)
O(1)	0.00288(9)	0.00140(4)	0.00411(13)	-0.00095(5)	0.00254(9)	-0.00068(6)
O(2)	0.00182(8)	0.00183(4)	0.00332(13)	-0.00070(5)	0.00150(9)	-0.00045(6)
O(3)	0.00376(11)	0.00178(5)	0.00486(15)	-0.00131(6)	0.00341(11)	-0.00095(7)
O(4)	0.00448(11)	0.00106(4)	0.00330(13)	0.00070(5)	0.00207(11)	0.00063(6)
O(5)	0.00255(9)	0.00119(4)	0.00276(12)	-0.00035(4)	0.00158(9)	-0.00065(5)
O(6)	0.00616(15)	0.00150(5)	0.00850(22)	0.00121(7)	0.00438(16)	0.00101(8)
O(7)	0.00332(13)	0.00107(5)	0.00239(16)	0.00000(0)	0.00162(13)	0.00000(0)

$$^a B_{eq} = \frac{1}{3} \sum \beta_{ij} \bar{a}_i \bar{a}_j.$$

$$^b F_j = F_{j0} \exp [-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)].$$

tahedron shares five corners either with PO_4 tetrahedra or P_2O_7 groups, the sixth being free.

The geometry of the different polyhedra has been studied (Table II). The PO_4 tetrahedra which correspond to P(2) are quite regular, O–O distances ranging from 2.492 to 2.517 Å; the P–O distances ranging from 1.526 to 1.540 Å and O–P–O angles ranging from 108.7 to 110.3° show that P(2) is located at the center of gravity of its tetrahedron (Table II). The $P(1)O_4$ tetrahedra forming the P_2O_7 groups exhibit a “semi-eclipsed” configuration (Fig. 2); the O–O distances, ranging from 2.495 to 2.527 Å,

show that the O_4 tetrahedra are almost regular. However, the P(1) atom was displaced from its tetrahedron center by 0.076(3) Å, as shown by the P(1)–O distances which range from 1.495 to 1.607 Å and O–P–O angles ranging from 105.76 to 113.75°. Moreover, the P–O–P angle (121.5°) is rather far from 180°. These results are very similar to those observed for the “phosphate tungsten bronzes” previously studied. The $P_4W_{4n}O_{12n+8}$ bronzes exhibit “isolated” tetrahedra which are also almost regular (16–17), while the P_2O_7 groups belonging to the $A_xP_4O_8(WO_3)_m$ bronzes (14–15) and $P_8W_{12}O_{52}$ (19) also have their phos-

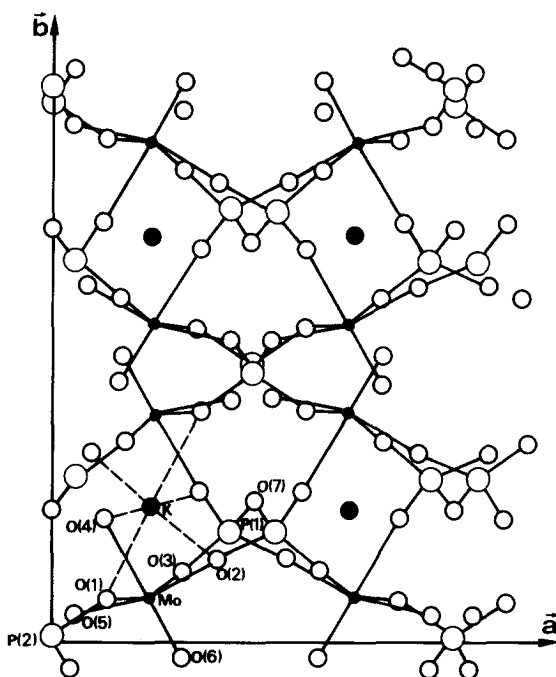


FIG. 1. Projection of the structure along c axis.

phorus atom off center in their tetrahedra by about the same distances, ranging from 0.06(3) to 0.09(2) Å. However, the configuration of the P_2O_7 groups is rather different in all these structures: the configuration is almost perfectly eclipsed in the phosphates bronzes $AP_3O_8(WO_3)_m$ and semieclipsed in $Mo_8P_{12}O_{52}$, whereas it is really staggered for $P_8W_{12}O_{52}$. These different configurations of the P_2O_7 group result from their way of connecting to the MoO_6 or WO_6 octahedra. In this respect, $K_4Mo_8P_{12}O_{52}$ is different, since each P_2O_7 group shares two oxygen atoms with the same MoO_6 octahedron. This has been previously observed in $NaFeP_2O_7$ (22), in which one FeO_6 octahedron shares one edge with a P_2O_7 group; however, the constraints on the P_2O_7 group seem more important here since two MoO_6 octahedra share one edge with the same P_2O_7 group (Fig. 1). This confirms the great adaptability of the P_2O_7 groups to the octahedra without disturbing the geometry of the PO_4 tetrahedra.

The molybdenum ion is surrounded by six oxygen atoms located at distances ranging from 1.66 to 2.275 Å with O–M–O angles very different from 90 and 180° (Table III). The O_6 octahedron surrounding Mo, characterized by O–O distances ranging from 2.714 to 2.891 Å, is almost regular. The molybdenum ion is off center in the octahedron by 0.32 Å, thus forming a very short Mo–O distance and a very long one. The coordination of the molybdenum ion

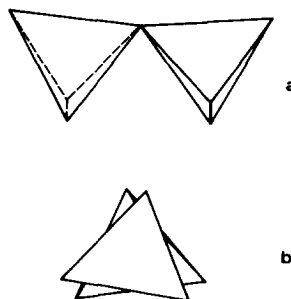


FIG. 2. P_2O_7 groups. (a) view across P . . . P line, (b) view along P . . . P line.

TABLE II
INTERATOMIC DISTANCES (Å) AND ANGLES (°) IN
THE PO_4 TETRAHEDRA

P_2O_7 group				
P(1)–O(2 ^{iv}) = 1.536(2) Å				
P(1)–O(3) = 1.522(2) Å				
P(1)–O(4 ^v) = 1.495(2) Å				
P(1)–O(7) = 1.607(1) Å				
iv = 1 - x; y; ½ - z				
v = ½ - x; ½ - y; -z				
P(1)–O				
	O(3)	O(4 ^v)	O(7)	
O				
O(2 ^{iv})	110.85(8)	111.01(10)	106.19(5) ^a	
	2.517(2)	2.498(2)	2.513(2) ^b	
O(3)		113.75(7)	105.76(8)	
		2.527(2)	2.495(2)	
O(4 ^v)			108.85(8)	
			2.524(1)	
PO_4 group				
P(2)–O(1) = 1.540(1) Å × 2				
P(2)–O(5 ⁱⁱ) = 1.526(1) Å × 2				
i = -x; y; ½ - z				
ii = -x; -y; -z				
iii = x; -y; ½ - z				
P(2)–O				
	O(1 ⁱ)	O(5 ⁱⁱ)	O(5 ⁱⁱⁱ)	
O				
O(1)	109.12(8)	108.73(8)	110.32(6) ^a	
	2.509(2)	2.492(2)	2.517(2) ^b	
O(1 ⁱ)		110.32(6)	108.73(8)	
		2.517(2)	2.492(2)	
O(5 ⁱⁱ)			109.60(7)	
			2.494(2)	

^a First line: O–P–O angle (°).

^b Second line: O . . . O length (Å).

could be described as a tetragonal pyramid (Fig. 3). The very short Mo–O distance, close to that observed for the phosphates $(MoO)PO_4$ and $(MoO)_2P_4O_{13}$, which have been characterized as molybdenyl phosphates (6–7), leads us to the formulation $K_4(MoO)_8P_{12}O_{44}$. It appears in agreement with the recent analysis by Pouchard (23) that this type of configuration is necessary for the stabilization of the d^1 state of Mo(V). The octahedron formed by the six oxygen atoms surrounding the molybde-

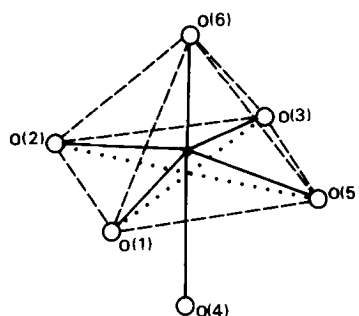


FIG. 3. Oxygen bulk around molybdenum.

num ion in $MoOPO_4$ (6) is also approximately regular with O–O distances ranging from 2.72 to 2.92 Å, whereas the Mo ion is displaced 0.48 Å from the center of gravity of its octahedron so that its coordination can be considered as pyramidal; in the latter compound, the difference between the shortest and the longest distance is even more pronounced, with 1.66 and 2.63 Å, respectively. Molybdenyl ions $(MoO)^{3+}$ belonging to distorted octahedra are also observed for the phosphate $(MoO)_2P_4O_{13}$ (7) but unfortunately the atomic distances and Mo–O distances corresponding to this compound are not available.

This behavior of molybdenum is very different from that of tungsten, for which a decrease in the mean oxidation number involves a more symmetrical coordination of W, tending towards a regular octahedron. This difference is easily explained by the fact that the electron in $K_4P_{12}Mo_8O_{52}$, as well as in $MoOPO_4$, is really located on molybdenum, while in the phosphate tungsten bronzes, a delocalization of the electron is observed.

In spite of the absence of a composition range which would correspond to the possibility of a potassium nonstoichiometry, this oxide can be considered to have a tunnel structure, as shown from Fig. 4: large tunnels running along [101] are indeed observed. In these tunnels the potassium ions are located at the center of gravity of a ring formed by the edges of four octahedra and

TABLE III
INTERATOMIC DISTANCES AND ANGLES IN THE MoO_6 OCTAHEDRON

Mo-O						
O	O(2)	O(3)	O(4)	O(5)	O(6)	
O(1)	86.41(6) 2.792(2)	162.45(6) —	77.92(6) 2.714(2)	92.19(6) 2.891(2)	98.89(10) ^a 2.814(3) ^b	
O(2)		89.12(6) 2.849(2)	80.54(4) 2.800(2)	160.77(5) —	99.57(6) 2.843(2)	
O(3)			84.61(7) 2.892(3)	86.48(6) 2.737(2)	98.58(10) 2.794(3)	
O(4)				80.41(4) 2.758(2)	176.81(11) —	
O(5)					99.59(16) 2.791(2)	

^a First line: O-Mo-O angle (°).

^b Second line: O . . . O length (Å).

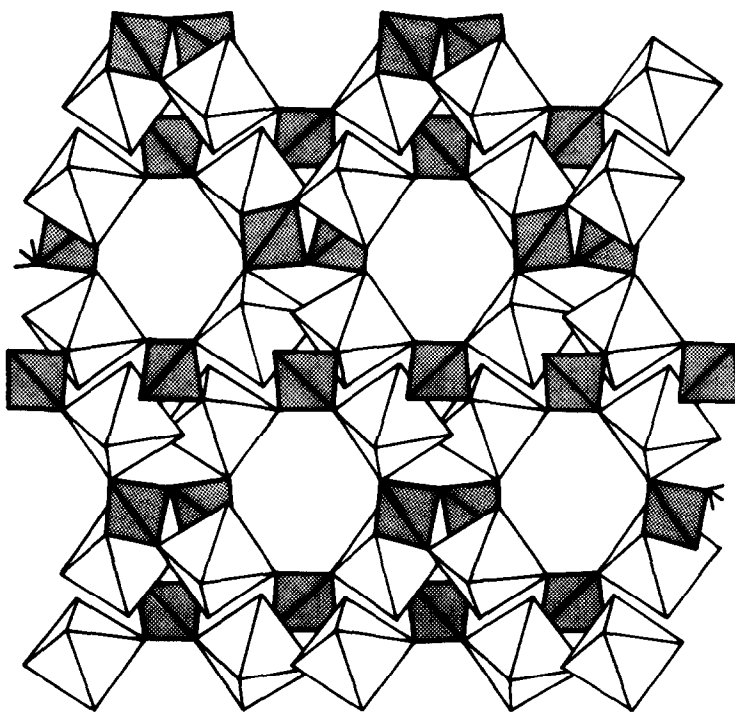


FIG. 4. Projection along [101] showing the tunnels.

four tetrahedra. The oxygen atoms forming this ring are not displaced more than 0.15 Å from the mean plane of this ring. The K^+ is surrounded by six oxygen atoms located at distances ranging from 2.698 to 2.995 Å and forming a triangular antiprism. The major axis of the thermal ellipsoid of K^+ is almost normal to the mean plane of the ring; the angle formed by this perpendicular and the major axis direction is 16.8°. This shows that the maximum displacement direction is not directed along the tunnel axis but towards the O(6) atoms of the MoO_6 octahedron which is only linked to one molybdenum ion.

Conclusion

This structural study of the oxide $K_4P_{12}Mo_8O_{52}$ confirms the great ability of PO_4 tetrahedra and P_2O_7 groups to form a mixed framework with the molybdenum polyhedra. It emphasizes the particular behavior of Mo(V), whose stabilization appears to be ensured by a pyramidal coordination involving a very short Mo–O distance; this corresponds, in fact, to an important displacement of the molybdenum ion inside an almost regular “ O_6 ” octahedron. The existence of large tunnels in this structure suggests the possibility of the existence of other tunnel structures for oxides containing phosphorus and molybdenum and large monovalent ions such as Rb^+ , Tl^+ , and Cs^+ . The possibility of formation of mixed valence molybdenum phosphate will also be investigated.

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