

# A Molybdenotungsten Monophosphate with an Opened Structure $K_{6.6}Mo_{2.36}W_{3.64}O_{15}(PO_4)_4$

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Received February 5, 1996; in revised form April 29, 1996; accepted June 10, 1996

A new "MoW" monophosphate  $K_{6.6}Mo_{2.36}W_{3.64}O_{15}(PO_4)_4$  has been synthesized. This complex opened structure crystallizes in the  $R\bar{3}$  group with  $a = 17.545(2)$  Å and  $c = 15.714(2)$  Å. The  $[M_6P_4O_{31}]_\infty$  framework can be described from  $M_3P_3O_{19}$  and  $M_6P_6O_{48}$  units. The first unit consists of one  $PO_4$  tetrahedron sharing its apices with three  $MO_6$  octahedra, whereas the second one forms hexagonal rings in which one  $MO_6$  octahedron alternates with one  $PO_4$  tetrahedron. Another interesting feature of this framework deals with the existence of spiral-like octahedral  $[MO_5]_\infty$  chains running along  $\vec{c}$ , so that the structure can also be described as an assemblage of these chains through  $PO_4$  tetrahedra. This framework offers large cages that communicate with each other, so that five different sites are available for potassium. © 1996 Academic Press, Inc.

## INTRODUCTION

The exploration of the phosphate tungsten bronzes (for a review see Ref. (1, 2)) and of the molybdenum phosphates (for a review see Ref. (3, 4)) performed these last two decades has shown that molybdenum and tungsten exhibit a very different structural behavior in these materials. This suggests that it should be possible to generate new phosphates by associating these two transition elements in the same framework. This viewpoint is supported by the recent synthesis of two new mixed "MoW" monophosphates with an original structure,  $Na_x(MoW)_2O_3(PO_4)_2$  (5), which exhibits a tunnel structure, and  $Na_{1+x}(MoW)_2O_5PO_4$  (6), which is closely related to the phosphate tungsten bronzes. Thus it appears clearly that new mixed "MoW" phosphates with an original structure involving big interpolated cations such as potassium, rubidium, and thallium should be generated in the next years. For this reason we have investigated the system  $K-Mo-W-P-O$ , for which only one phase has been synthesized to date by a hydrothermal technique, the hydrated Keggin polyoxometallate  $K_6Mo_3W_9PO_{40} \cdot 13H_2O$  (7).

We report herein on the synthesis and crystal structure of a new monophosphate  $K_{6.6}Mo_{2.36}W_{3.64}O_{15}(PO_4)_4$  that exhibits a complex opened framework.

## SYNTHESIS AND CRYSTAL GROWTH

Single crystals of the title compound were grown from a mixture of nominal composition  $K_2MoWPO_9$ . The growth was carried out in two steps: first,  $H(NH_4)_2PO_4$ ,  $K_2CO_3$ ,  $WO_3$ , and  $MoO_3$  were mixed in an agate mortar in adequate ratios according to the composition  $K_2Mo_{0.83}WPO_9$  and heated at 700 K in a platinum crucible to decompose the ammonium phosphate and carbonate. In a second step the resulting mixture was then added to the required amount of molybdenum (0.17 mole), sealed in an evacuated silica ampoule, heated for eighteen hours at 853 K, cooled at 12 K per hour to 730 K, and then the sample was quenched to room temperature.

Two sorts of crystals were extracted from the resulting product, blue crystals identified as  $KMo_2P_3O_{13}$  (8) and rose plates. The latter were studied by X-ray diffraction and their microprobe analysis confirmed the composition  $K_{6.6}Mo_{2.36}W_{3.64}P_4O_{31}$  deduced from the structure determination.

The synthesis of the pure phase in the form of powder was carried out in the similar experimental conditions described above, except that it was heated at 873 K for 13 hours and cooled at 12 K per hour down to 773 K, starting with the ideal compositions  $K_{6.5}Mo_{2.35}W_{3.65}P_4O_{31}$  and  $K_7Mo_{2.35}W_{3.65}P_4O_{31}$ .

## STRUCTURE DETERMINATION

A rose, almost isometric crystal with dimensions  $0.05 \times 0.05 \times 0.04$  mm<sup>3</sup> was selected for the structure determination. The cell parameters reported in Table 2 were determined and refined by diffractometric technique at 294 K with a least-squares refinement based upon 25 reflexions with  $18 \leq \theta \leq 22^\circ$ . The diffraction pattern has the  $\bar{3}$  Laue symmetry and the systematic absences are consistent with the space groups  $R3$  and  $R\bar{3}$ . The structure was successfully refined in the  $R\bar{3}$  space group.

The data were collected with an Enraf Nonius CAD4 diffractometer with the parameters reported in Table 1.

**TABLE 1**  
**Summary of Crystal Data, Intensity Measurements and**  
**Structure Refinement Parameters for  $K_{6.6}Mo_{2.36}W_{3.64}O_{15}(PO_4)_4$**

Crystal data		
Space group	$R\bar{3}$	
Cell dimensions	$a = 17.545(2) \text{ \AA}$	$c = 15.714(2) \text{ \AA}$
Volume	$4188.3(8) \text{ \AA}^3$	
Z	6	
$\rho_{\text{calc}}$ ( $\text{gcm}^{-3}$ )	4.36	
Intensity measurements		
$\lambda$ (MoK $\alpha$ )	$0.71073 \text{ \AA}$	
Scan mode	$\omega$ -4/3 $\theta$	
Scan width ( $^\circ$ )	$1.2 + 0.35 \tan \theta$	
Slit aperture (mm)	$1.2 + \tan \theta$	
Max $\theta$ ( $^\circ$ )	45	
Standard reflections	3 every hour	
Reflections measured	8090	
Reflections with $I > 3\sigma$	1074	
$\mu$ ( $\text{mm}^{-1}$ )	17.4	
Structure solution and refinement		
Parameters refined	99	
Agreement factors	$R = 0.051$	$Rw = 0.052$
Weighting scheme	1/s	
$\Delta/\sigma$ max	0.001	

The reflections were corrected for Lorentz and polarization effects and for absorption.

The structure was solved with the heavy atom method and refined with a full matrix least-squares method. All

the calculations were performed with the XTAL chain programs (8). The W and Mo atoms are distributed over two sites M(1) and M(2). The refinement of the occupancy factors of the latter allows a preferential occupancy to be evidenced: the M(1) site is preferentially occupied by tungsten [0.75(2)W/0.25(2)Mo] whereas the M(2) site is equally occupied by molybdenum and tungsten [0.48(2)W/0.52(2)Mo].

The potassium ions are distributed over five sites. The first one, K(1), contains only 19(6)% potassium, the second, K(2), and third, K(3), are fully occupied, and the two last ones, K(4), are, respectively, filled at 44(2)% (K(41)) and 56(2)% (K(42)).

The refinement of the atomic coordinates, of the isotropic thermal factor of the oxygen atoms and the K(4), and the anisotropic thermal factors of all the other atoms leads to  $R = 0.051$  and  $Rw = 0.052$ . The resulting coordinates are listed in Table 2.

## DESCRIPTION OF THE STRUCTURE AND DISCUSSION

The projection of the structure along the  $c$  direction of the corresponding hexagonal cell (Fig. 1) shows its very great complexity. One observes that the  $[(MoW)_6P_4O_{31}]_\infty$  framework consists of corner-sharing  $PO_4$  tetrahedra and  $MO_6$  octahedra ( $M = Mo, W$ ), forming cages where the  $K^+$  ions are located.

One can distinguish two kinds of phosphorus sites and

**TABLE 2**  
**Positional Parameters and Their Estimated Standard Deviations for  $K_{6.6}Mo_{2.36}W_{3.64}O_{15}(PO_4)_4$**

Atom	$x$	$y$	$z$	Site	Occupancy	$B$ ( $\text{\AA}^2$ )
M(1)	0.46896(9)	0.17281(9)	0.00563(9)	18f	W0.74(2)/Mo0.26(2)	0.42(6)*
M(2)	0.2270(1)	0.2765(1)	0.1310(1)	18f	W0.48(2)/Mo0.52(2)	0.69(8)*
P(1)	0.1504(5)	0.4154(5)	0.1559(4)	18f	1	0.64(4)*
P(2)	2/3	1/3	0.0522(9)	6c	1	0.88(3)*
K(1)	0	0	0	3a	0.19(6)	5.6(7)*
K(2)	0	0	1/2	3b	1	2.6(5)*
K(3)	0.4633(5)	0.3873(5)	0.0230(4)	18f	1	1.4(3)*
K(41)	0.166(2)	0.032(1)	0.098(1)	18f	0.44(2)	2.5(3)
K(42)	0.214(1)	0.048(1)	0.095(1)	18f	0.56(2)	2.5(3)
O(1)	0.452(1)	0.239(1)	0.077(1)	18f	1	1.2(5)
O(2)	0.600(1)	0.247(1)	0.013(1)	18f	1	0.64(4)
O(3)	0.470(1)	0.092(1)	0.082(1)	18f	1	0.32(4)
O(4)	0.354(1)	0.094(1)	-0.029(1)	18f	1	0.48(4)
O(5)	0.479(1)	0.256(1)	-0.094(1)	18f	1	0.64(4)
O(6)	0.513(1)	0.112(1)	-0.083(1)	18f	1	1.04(5)
O(7)	0.143(1)	0.183(1)	0.083(1)	18f	1	1.28(5)
O(8)	0.310(1)	0.256(1)	0.126(1)	18f	1	0.88(5)
O(9)	0.314(1)	0.397(1)	0.198(1)	18f	1	0.80(4)
O(10)	0.134(1)	0.320(1)	0.147(1)	18f	1	0.56(4)
O(11)	2/3	1/3	0.147(3)	6c	1	2.4(1)

*Note.* The starred anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as  $B = 4/3 \sum_i \sum_j \vec{a}_i \cdot \vec{a}_j \beta_{ij}$ .

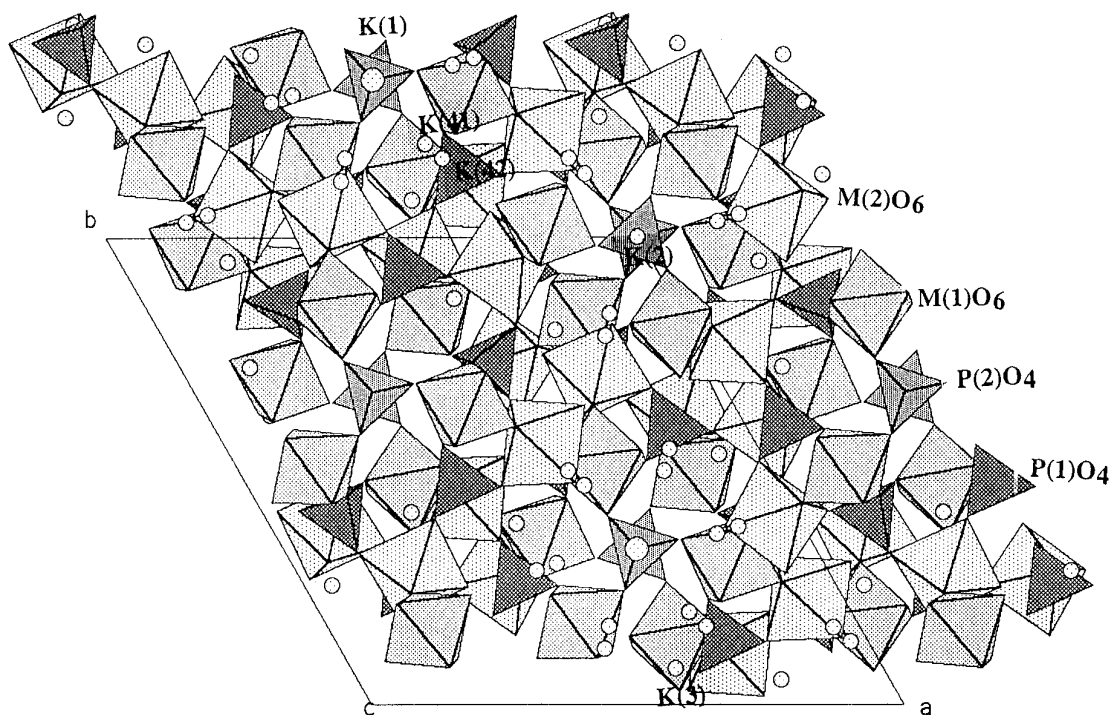


FIG. 1. Projection of the structure of  $K_{6.6}Mo_{2.36}W_{3.64}O_{15}(PO_4)_4$  along  $\vec{c}$ .

two kinds of transition metal sites, labeled P(1), P(2), and M(1), M(2), respectively. Each P(1) tetrahedron shares its four apices with four  $MO_6$  octahedra (two M(1) octahedra and two M(2) octahedra) and exhibits homogeneous P–O distances ranging from 1.55 to 1.57 Å (Table 3). Each P(2) tetrahedron is linked to three  $M(1)O_6$  octahedra and exhibits one free apex, its P–O distances remaining homogeneous (1.50 to 1.51 Å). As the oxygen atoms of the  $P(1)O_4$  phosphate are more strongly bonded to the potassium cations than those of  $P(2)O_4$ , the P(1) exhibits longer P–O bonds than P(2).

Each M(1) octahedron shares three apices with three  $PO_4$  tetrahedra (two P(1) tetrahedra and one P(2) tetrahedron) leading to the three longer M(1)–O distances corresponding to O(2), O(5), and O(6) ranging from 2.01 to 2.12 Å (Table 3); this octahedron is also linked to two M(2) octahedra so that the corresponding M(1)–O distances to O(3) and O(4) are intermediate of 1.87 Å. Its sixth apex (O(1)) is free, leading to the shortest M(1)–O distance of 1.74 Å (Table 3). This particular configuration of the M(1) octahedra, is in agreement with their preferential occupation by molybdenum, suggesting that in the latter, Mo(V) species are mainly involved.

Each M(2) octahedron shares two apices (O(9) and O(10)) with two P(1) tetrahedra leading to the two longer M(2)–O distances (2.14–2.16 Å), whereas two other apices (O(3) and O(4)) share with two M(1) octahedra, so that

the corresponding M(2)–O distances, ranging from 1.97 to 1.99 Å (Table 3), are intermediate. The remaining apices (O(7) and O(8)) are free, so that they correspond to the shortest M(2)–O distances (1.67–1.74 Å). This distorted octahedral geometry of the M(2) octahedra, which tends to be intermediate between an octahedron and a tetrahedron, suggests that the M(2) site is occupied by W(VI) and Mo(VI).

Though it is very complex, the  $[(MoW)_6P_4O_{31}]_\infty$  framework can be described in a rather simple manner by considering the stacking along  $\vec{c}$  of 001 identical  $[M_6P_4O_{34}]_\infty$  layers (Fig. 2). Each  $[M_6P_4O_{34}]_\infty$  layer can be described by the assemblage of two sublayers formed of disconnected units. The first sublayer consists of six-sided rings of 12 polyhedra  $M_6P_6O_{48}$  (Fig. 3a) in which one P(1) tetrahedron alternates with one M(2) octahedron. The second sublayer is built up from disconnected  $M_3PO_{19}$  units (Fig. 3b) in which one P(2) tetrahedron shares its apices with three M(1) octahedra. Along  $\vec{c}$  two P(1) tetrahedra and one M(2) octahedron of the first sublayer share their apices with the same M(1) octahedron of the second sublayer, forming the  $[M_6P_4O_{34}]_\infty$  layer (Fig. 3c). Note that in each  $[M_6P_4O_{34}]_\infty$  layer, one recognizes  $M_2P_2O_{15}$  units built up from corner-sharing octahedra and tetrahedra, already observed in the  $A_2Mo_2O_3(PO_4)_2$  monophosphate with  $A = K, Rb, Tl$  (9–11). Three such units are connected through a single  $PO_4$  tetrahedron (P2), forming  $M_{18}P_{13}O_{46}$  units. As a result, the

TABLE 3  
Distances (Å) and Angles (°) in Polyhedra in  $K_{6.6}Mo_{2.36}W_{3.64}O_{15}(PO_4)_4$

M(1)	O(1)	O(2)	O(93)	O(4)	O(5)	O(6)
O(1)	<b>1.74(3)</b>	2.73(3)	2.75(3)	2.79(3)	2.72(3)	3.85(3)
O(2)	93.3(9)	<b>2.01(2)</b>	2.75(2)	3.84(2)	2.78(3)	3.57(3)
O(3)	99.4(9)	90.5(8)	<b>1.87(2)</b>	2.70(3)	3.93(3)	2.69(3)
O(4)	101.3(9)	164.6(8)	92.4(8)	<b>1.87(2)</b>	2.77(2)	2.79(3)
O(5)	90.1(9)	85.6(8)	170.0(9)	89.0(8)	<b>2.08(2)</b>	2.86(4)
O(6)	169.5(7)	76.9(8)	84.4(9)	88.4(8)	85.7(9)	<b>2.12(2)</b>
M(2)	O(3 <sup>i</sup> )	O(4 <sup>ii</sup> )	O(7)	O(8)	O(9)	O(10)
O(3 <sup>i</sup> )	<b>1.97(2)</b>	3.89(2)	2.82(2)	2.71(3)	2.60(2)	2.71(3)
O(4 <sup>ii</sup> )	157.6(8)	<b>1.99(2)</b>	2.78(3)	2.75(3)	2.80(3)	2.71(4)
O(7)	98.8(8)	96.3(9)	<b>1.74(2)</b>	2.63(3)	3.89(2)	2.69(3)
O(8)	96.1(9)	97(1)	101(1)	<b>1.67(2)</b>	2.69(3)	3.79(4)
O(9)	77.7(6)	84.7(7)	170(1)	88.2(9)	<b>2.16(2)</b>	2.86(3)
O(10)	82.3(8)	82(1)	87(1)	171.7(7)	83.5(8)	<b>2.14(2)</b>
P(1)	O(5 <sup>ii</sup> )	O(6 <sup>iii</sup> )	O(9 <sup>iv</sup> )	O(10)		
O(5 <sup>ii</sup> )	<b>1.55(2)</b>	2.54(3)	2.54(5)	2.57(3)		
O(6 <sup>iii</sup> )	109(1)	<b>1.57(2)</b>	2.57(3)	2.52(3)		
O(9 <sup>iv</sup> )	109(1)	110(1)	<b>1.57(3)</b>	2.55(4)		
O(10)	111(1)	107(1)	109(1)	<b>1.56(2)</b>		
P(2)	O(2)	O(2 <sup>v</sup> )	O(2 <sup>vi</sup> )	O(11)		
O(2)	<b>1.51(2)</b>	2.38(3)	2.38(3)	2.52(4)		
O(2 <sup>v</sup> )	104(1)	<b>1.51(2)</b>	2.38(3)	2.52(4)		
O(2 <sup>vi</sup> )	104(1)	104(1)	<b>1.51(2)</b>	2.52(2)		
O(11)	114(1)	114(1)	114(1)	<b>1.50(3)</b>		
	K(1)–O(7 <sup>vii</sup> )	3.20(3)	K(2)–O(2 <sup>xii</sup> )	3.14(3)	K(3)–O(1)	2.64(3)
	K(1)–O(7)	3.20(3)	K(2)–O(2 <sup>i</sup> )	3.14(3)	K(3)–O(2 <sup>vi</sup> )	3.11(3)
	K(1)–O(7 <sup>viii</sup> )	3.20(3)	K(2)–O(2 <sup>iv</sup> )	3.14(3)	K(3)–O(3 <sup>ii</sup> )	3.04(3)
	K(1)–O(7 <sup>ix</sup> )	3.20(3)	K(2)–O(2 <sup>xiii</sup> )	3.14(3)	K(3)–O(3 <sup>vi</sup> )	2.82(3)
	K(1)–O(7 <sup>ii</sup> )	3.20(3)	K(2)–O(2 <sup>xiv</sup> )	3.14(3)	K(3)–O(4 <sup>ii</sup> )	3.32(3)
	K(1)–O(7 <sup>x</sup> )	3.20(3)	K(2)–O(2 <sup>xv</sup> )	3.14(3)	K(3)–O(5)	3.08(3)
	K(1)–O(11 <sup>i</sup> )	2.92(3)	K(2)–O(5 <sup>xii</sup> )	3.08(3)	K(3)–O(6 <sup>ii</sup> )	2.72(3)
	K(1)–O(11 <sup>xi</sup> )	2.92(3)	K(2)–O(5 <sup>i</sup> )	3.08(3)	K(3)–O(6 <sup>vi</sup> )	3.06(3)
			K(2)–O(5 <sup>iv</sup> )	3.08(3)	K(3)–O(8)	2.99(3)
			K(2)–O(5 <sup>xiii</sup> )	3.08(3)	K(3)–O(9 <sup>xvi</sup> )	2.60(3)
			K(2)–O(5 <sup>xv</sup> )	3.08(3)	K(3)–O(10 <sup>xvii</sup> )	2.87(3)
			K(2)–O(5 <sup>xiv</sup> )	3.08(3)		
	K(41)–O(1 <sup>i</sup> )	2.69(3)	K(42)–O(1 <sup>i</sup> )	2.66(3)		
	K(41)–O(7)	2.89(3)	K(42)–O(4)	2.91(3)		
	K(41)–O(7 <sup>ix</sup> )	2.85(3)	K(42)–O(7)	3.19(3)		
	K(41)–O(7 <sup>x</sup> )	2.76(3)	K(42)–O(7 <sup>ix</sup> )	2.84(3)		
	K(41)–O(10 <sup>x</sup> )	3.18(3)	K(42)–O(7 <sup>x</sup> )	3.22(3)		
	K(41)–O(11 <sup>i</sup> )	3.02(3)	K(42)–O(8)	2.89(3)		
			K(42)–O(10 <sup>x</sup> )	3.08(3)		

Note. Symmetry codes: i,  $2/3 - x, 1/3 - y, 1/3 - z$ ; ii,  $x - y, x, -z$ ; iii,  $x - 1/3, 1/3 + y, 1/3 + z$ ; iv,  $y - 1/3, 1/3 - x + y, 1/3 - z$ ; v,  $1 - y, x - y, z$ ; vi,  $1 - x + y, 1 - x, z$ ; vii,  $-x, -y, -z$ ; viii,  $-y, x - y, z$ ; ix,  $y, -x + y, -z$ ; x,  $y - x, -x, z$ ; xi,  $2/3 - x, 1/3 - y, 1/3 - z$ ; xii,  $x - 2/3, y - 1/3, 2/3 - z$ ; xiii,  $1/3 - y, x - y - 1/3, 2/3 + z$ ; xiv,  $1/3 - x + y, 2/3 - x, 2/3 + z$ ; xv,  $x - y - 1/3, x - 2/3, 1/3 - z$ ; xvi,  $1/3 - x + y, 2/3 - x, z - 1/3$ ; xvii,  $2/3 + x - y, 1/3 + x, 1/3 + z$ .

$[M_6P_4O_{34}]_\infty$  layer can also be described as built up from  $M_{18}P_{13}O_{46}$  and  $M_3PO_{19}$  units sharing the corners of their octahedra. The opened character of the  $[M_6P_4O_{34}]_\infty$  layers is remarkable: one indeed observes that they exhibit very

large three-lobbed windows. Finally the  $[M_6P_4O_{31}]_\infty$  framework results from the stacking along  $\vec{c}$  of the  $[M_6P_4O_{34}]_\infty$  layers translated of  $2/3; 1/3; 1/3$  according to the  $R\bar{3}$  symmetry. As a consequence of this translation, the three-

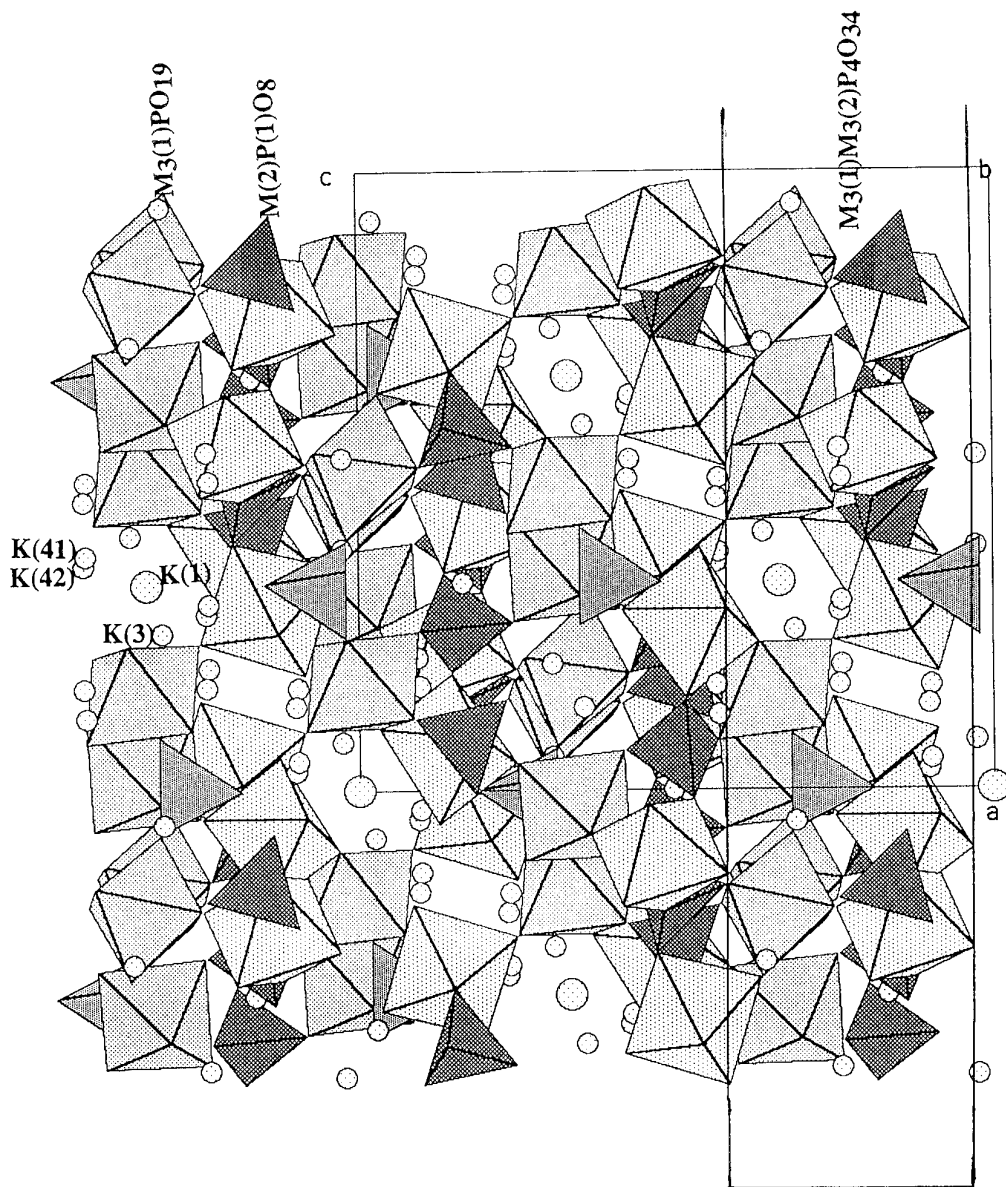


FIG. 2. Projection of the structure of  $K_{6.6}Mo_{2.36}W_{3.64}O_{15}(PO_4)_4$  along  $\vec{a}$ .

lobbed windows of each layer are obstructed by the  $M_3PO_{19}$  units of the adjacent layer. It results in spacious cages that communicate with each other where the  $K^+$  ions are located.

Another remarkable feature of this structure deals with the fact that the  $MO_6$  octahedra form spiral-like  $[MO_5]_{\infty}$  chains running along  $\vec{c}$  (Fig. 4). In these chains one M(1) octahedron shares one apex with one M(2) octahedron alternately. Thus, the  $[M_6P_4O_{31}]_{\infty}$  framework can also be described by the assemblage of spiral-like octahedral  $[MO_5]_{\infty}$  chains, connected through single  $PO_4$  tetrahedra.

Such an opened framework offers large cavities, so that

the  $K^+$  ions exhibit generally abnormally long K–O distances and consequently high thermal factors. This is the case for the K(1) site which is only 19% occupied and is surrounded by eight oxygen atoms forming a bicapped octahedron (Fig. 5a); the minimum K(1)–O distance of 2.92 Å observed for this site explains the abnormally high thermal factor of 5.6 Å<sup>2</sup>. In fact, the elongated shape of the thermal ellipsoid of this cation indicates the K(1) sites close to the ternary axis of the rhombohedral cell but is delocalized around this direction. In the same way, the K(2) atom that is surrounded by 12 oxygen atoms, six being at 3.08 Å and six at 3.14, also exhibits a rather high thermal

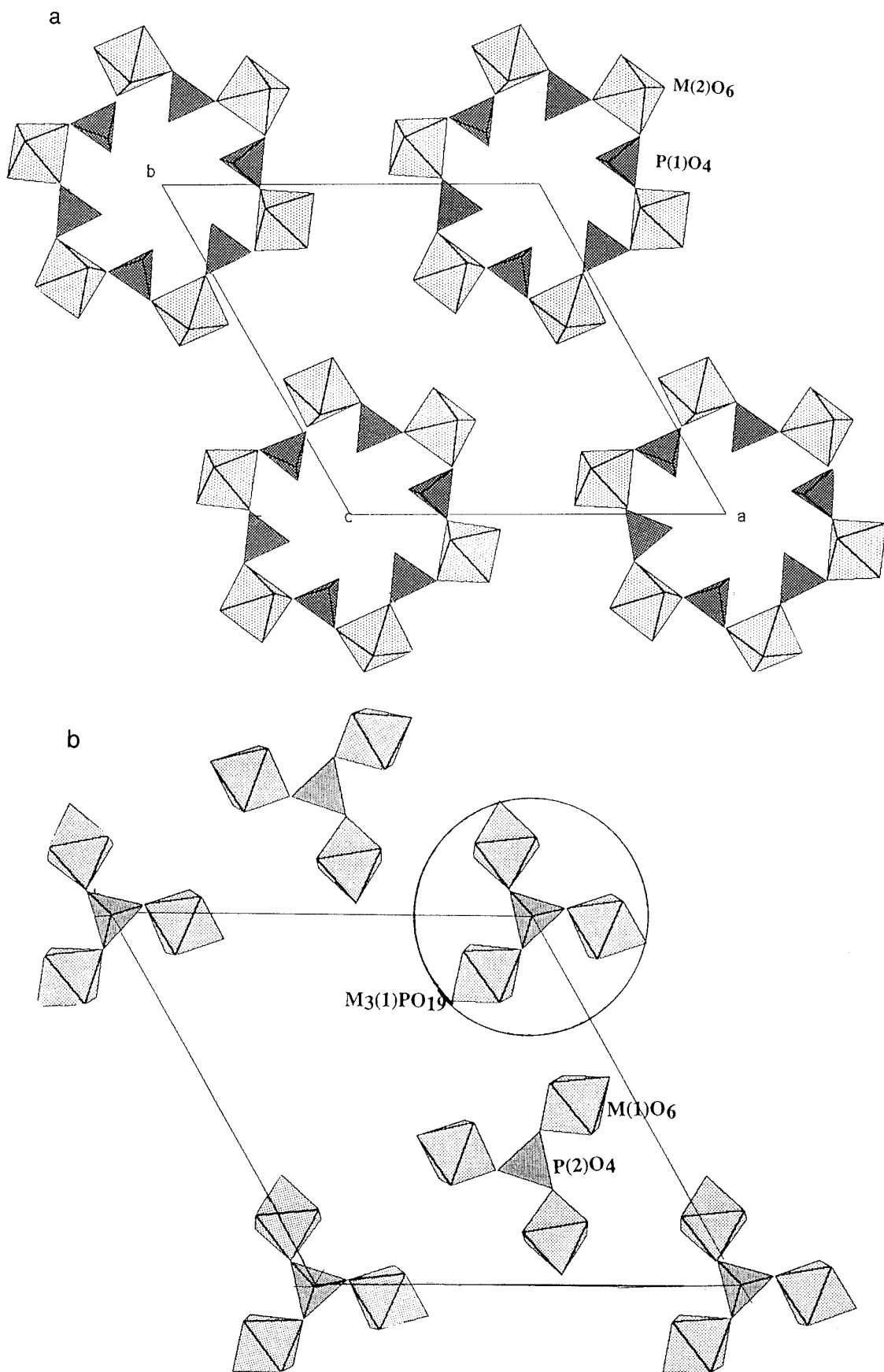


FIG. 3. (a) Sublayer  $M_6P_6O_{48}$ . (b) Sublayer  $M_3PO_{19}$ . (c) The  $[M_6P_4O_{34}]^{2-}$  layer.

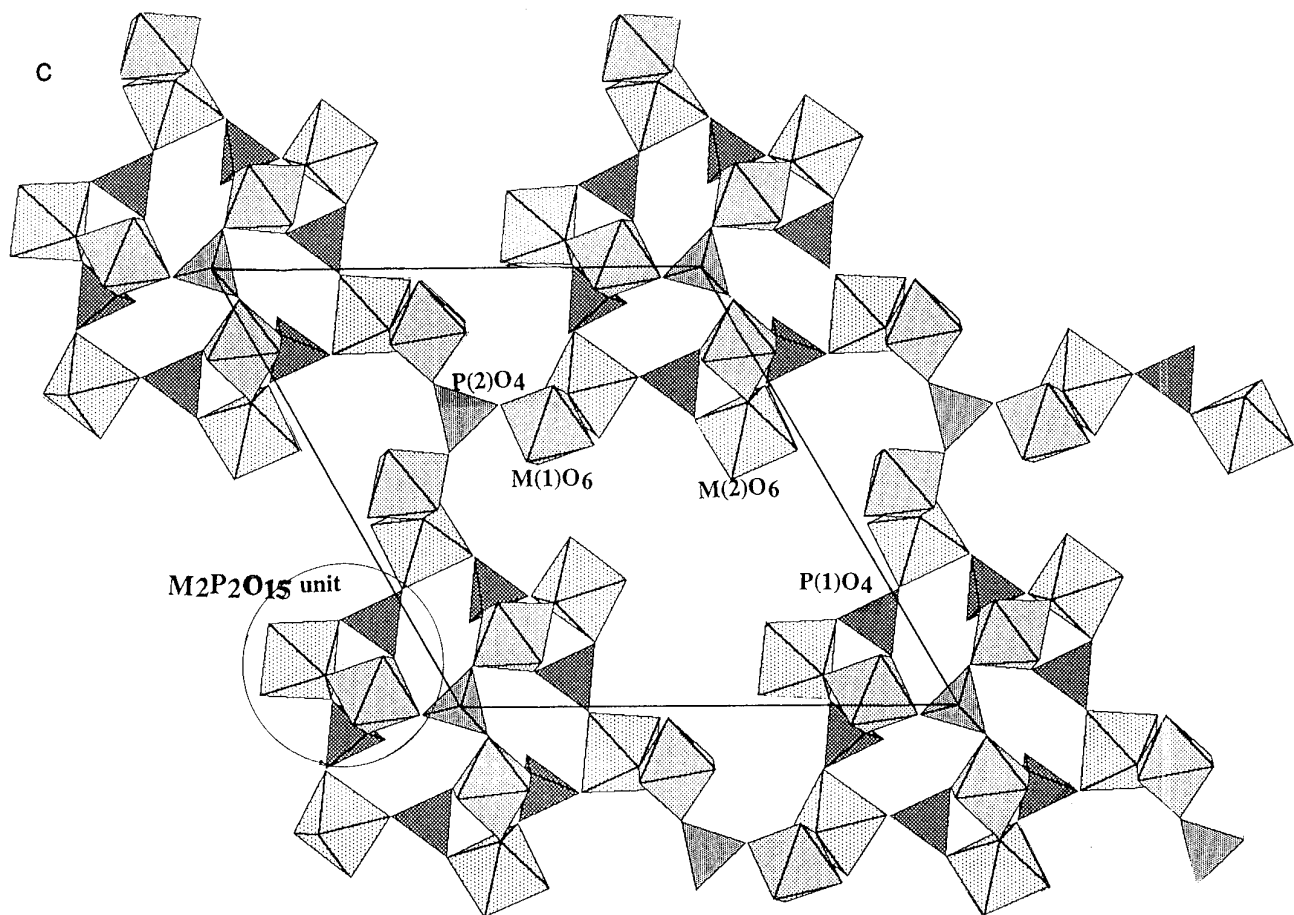
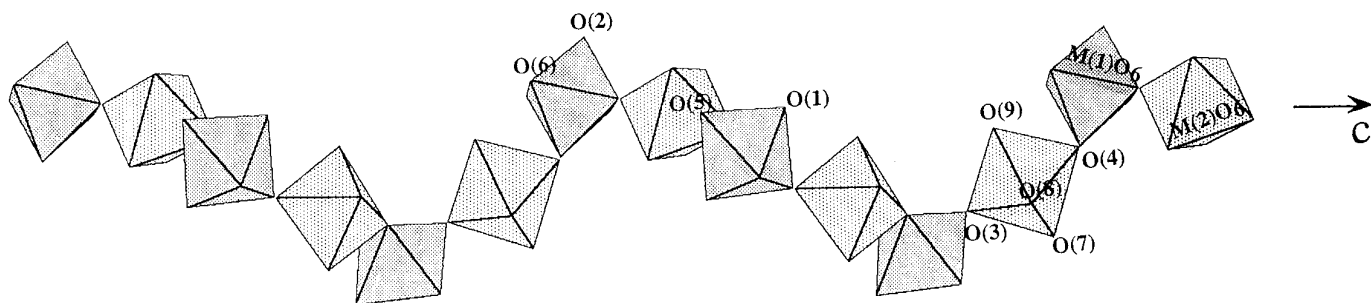


FIG. 3—Continued

factor of  $2.6 \text{ \AA}^2$ , but in that case the agitation is more isotropic due to the icosahedral geometry of the  $O_{12}$  polyhedron (Fig. 5b). Like the K(2) site, the K(3) site is fully occupied; this cation, located in a distorted tricapped cube (Fig. 5c) exhibits much smaller K(3)–O distances, five of them ranging from 2.60 to 2.87  $\text{\AA}$ , in agreement with its smaller thermal factor of  $1.4 \text{ \AA}^2$ . Like the K(1) site, the K(4) site is only partly occupied. In fact K(4) is split over

two sites, K(41) and K(42), that cannot be occupied simultaneously; more K(1) and K(41) cannot be filled simultaneously due to their small distance, whereas K(1) and K(42) may be. As a result both sites, K(41) and K(42), are about half occupied. In spite of the existence of four rather short K–O distances for K(41) (2.69 to 2.85  $\text{\AA}$ ) and for K(42) (2.66 to 2.91  $\text{\AA}$ ) these cations exhibit rather high  $B$  values of  $2.5 \text{ \AA}^2$ . In fact, one observes an anisotropic thermal

FIG. 4. The chain  $[\text{MO}_5]_n$  running along  $\vec{c}$ .

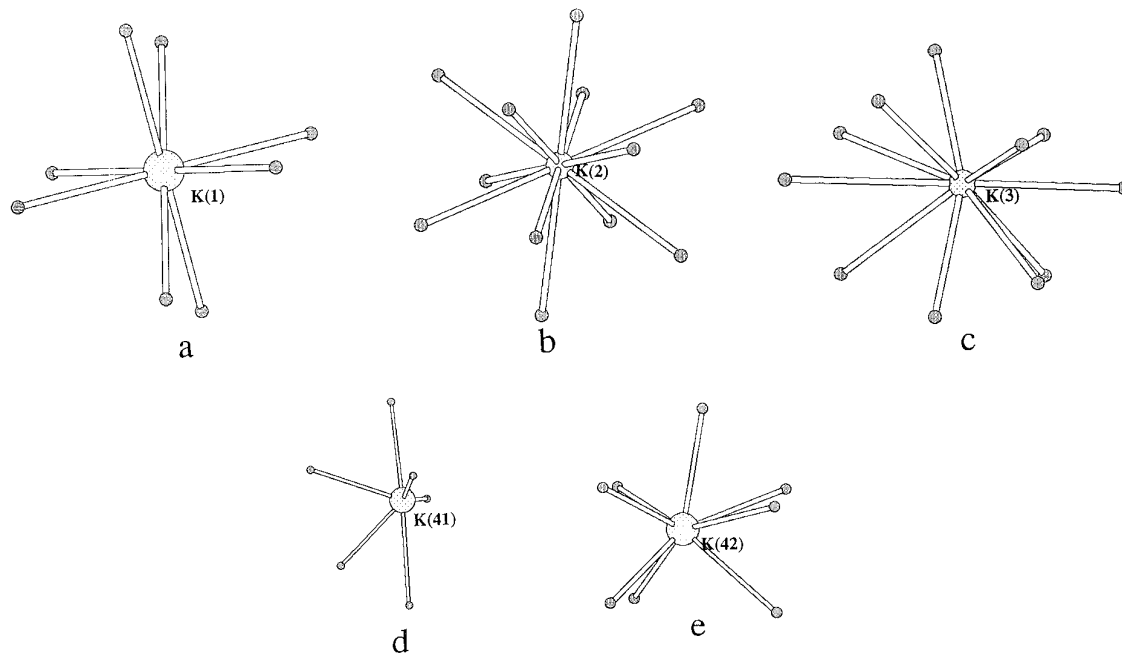


FIG. 5. The  $K^+$  surroundings.

motion due to the fact that most of the oxygen atoms that surround each cation are located on the same side with respect to the latter (Figs. 5d–5e). This distribution of the cations in the different cavities of the structure suggests the isolation of limiting composition  $K_7Mo_{6-x}W_xP_4O_{31}$ , which may correspond to a total occupancy of the K(1), K(2), K(3), and K(42) sites by potassium. The random occupation of the metal sites by either Mo or W also allows solid solutions with different Mo/W molar ratio. The compounds  $K_7Mo_{6-x}W_xP_4O_{31}$  exists within the range  $2 \leq x \leq 4$ .

### CONCLUDING REMARKS

A new monophosphate with an original but complex structure  $K_{6.6}Mo_{2.36}W_{3.64}O_{15}(PO_4)_4$  has been synthesized.

The opened character of this framework suggests that large cations such as rubidium, thallium, or cesium should enter into the matrix. The possible communication between the cages indicates the possibility of ion exchange properties as well as cationic conductivity.

The redox equilibria between tungsten and molybdenum in this complex structure are so far not understood.

These results open the route to the research of new mixed “MoW” frameworks that should be obtained by

varying not only the cationic molar ratios but also the mean oxidation states of tungsten and molybdenum in these materials.

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