

A Mo(V) Monophosphate with a Tunnel Structure: $K_3(MoO)_4(PO_4)_5$

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A Mo(V) monophosphate has been synthesized for the first time. It crystallizes in the space group *Pbca* with $a = 9.676(2)$ Å, $b = 14.366(2)$ Å, and $c = 28.391(5)$ Å. The host lattice of this phosphate consists of corner-sharing MoO_6 octahedra and PO_4 tetrahedra forming two kinds of six-sided tunnels running along c where the K^+ ions are located. Each PO_4 tetrahedron shares its four apices with the Mo(V) octahedra, whereas each Mo(V) octahedron shares five apices with the tetrahedra, its sixth apex being free. Six-sided tunnels running along b that intersect the large tunnels running along a are also observed. The distribution of K^+ in the different types of tunnels is studied. © 1995 Academic Press, Inc.

INTRODUCTION

The ability of pentavalent molybdenum to participate to the formation of mixed frameworks involving phosphate groups and MoO_6 octahedra was demonstrated these past years with the synthesis of about 30 new compounds. The variety of structures (for a review, see Refs. (1, 2)) is due to the particular electronic configuration of Mo(V) which forms a molybdenyl group and makes each octahedron always exhibit one free apex. Classification of these phosphates on the basis of their structural relationships (2) allows three families to be distinguished, according to whether the MoO_6 octahedra are isolated, or form bi- or triocathedral units (Mo_2O_{10} or Mo_3O_{14}) or infinite octahedral chains $[MoO_3]_z$. Curiously, in the first family involving isolated MoO_6 octahedra, no monophosphate has been synthesized up to now. For this reason, the system K–Mo–P–O, which already has several original Mo(V) phosphates (3–6), was reinvestigated. Taking into consideration the eventual metastable character of such Mo(V) monophosphates, the diagram K–Mo(V)–Mo(VI)–P–O was explored (7). We report here on a new Mo(V) monophosphate $K_3(MoO)_4(PO_4)_5$ with a tunnel structure.

SYNTHESIS

Single crystals of the title compound were grown from a mixture of nominal composition $K_3Mo_4P_4O_{22}$. First, $H(NH_4)_2PO_4$, K_2CO_3 , and MoO_3 were mixed in an agate

mortar in adequate ratios according to the composition “ $K_3Mo_{3.5}P_4O_{22}$ ” and heated at 600 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 (0.5 mole), placed in an alumina tube, and sealed in an evacuated silica ampoule, then heated for 1 day at 963 K and cooled at 9 K per hour to 823 K. The sample was finally quenched to room temperature.

Yellow crystals were extracted from the resulting product. The microprobe analysis of these crystals confirmed the composition $K_3(MoO)_4(PO_4)_5$ deduced from the structure determination.

Many attempts to prepare large amounts of this phase in the form of powder always led to a mixture of crystals: the $K_3(MoO)_4(PO_4)_5$ yellow crystals and the green crystals identified as the β - $K(MoO)_2(P_2O_7)PO_4$ (4) phase. The yellow crystals were picked out with tweezers, using a binocular in order to perform further characterizations. The crystals were then crushed, leading to a yellow powder which was studied by X-ray powder diffraction. The powder X-ray diffraction pattern was indexed in an orthorhombic cell, in agreement with the parameters obtained from the single-crystal X-ray study (Table 1).

STRUCTURE DETERMINATION

A yellow plate with dimensions $0.116 \times 0.077 \times 0.051$ mm was selected for the structure determination. The cell parameters reported in Table 2 were determined and refined by diffractometric techniques at 294 K with a least-squares refinement based upon 25 reflections with $18^\circ < \theta < 22^\circ$. The systematic absences $k = 2n + 1$ for $0kl$, $l = 2n + 1$ for $h0l$, and $h = 2n + 1$ for $hk0$ are consistent with the space group *Pbca* (No. 61). The data were collected on a CAD4 Enraf–Nonius diffractometer with the data collection parameters of Table 2. The reflections were corrected for Lorentz and polarization effects. No absorption corrections were performed.

The structure was solved with the heavy atom method. The refinement of the atomic coordinates and the anisotropic thermal factors led to $R = 0.027$ and $R_w = 0.030$, and to the atomic parameters of Table 3.

TABLE 1
Interreticular Distances for $K_3(MoO)_4(PO_4)_5$

<i>h</i>	<i>k</i>	<i>l</i>	<i>d</i> _{calc} (Å)	<i>d</i> _{obs} (Å)	<i>I</i>	<i>h</i>	<i>k</i>	<i>l</i>	<i>d</i> _{calc} (Å)	<i>d</i> _{obs} (Å)	<i>I</i>
1	0	2	7.995	8.034	1.3	1	3	8	2.735	2.733	5.7
0	2	0	7.183	7.188	81.0	1	5	2	2.704	2.708	3.6
0	0	4	7.097	7.091	100.0	0	4	7	2.687	2.689	4.5
1	0	4	5.723	5.719	4.6	3	2	5	2.612	2.615	2.0
0	2	3	5.721			3	3	3	2.574	2.575	1.2
1	2	2	5.343	5.344	1.7	0	4	8	2.524	2.529	6.0
0	2	4	5.048	5.047	24.3	3	3	4	2.503	2.508	1.7
1	2	3	4.925	4.917	5.1	1	5	5	2.470	2.477	2.3
2	0	0	4.838	4.837	3.8	2	5	1	2.456	2.455	1.4
0	0	6	4.732	4.731	12.7	0	2	11	2.429	2.428	3.6
2	0	2	4.579	4.572	5.2	3	4	1	2.391	2.392	6.1
1	2	4	4.476	4.473	6.1	2	5	3	2.390		
1	3	1	4.243	4.242	10.2	4	1	0	2.385	2.385	6.0
1	3	2	4.108	4.105	12.9	4	0	2	2.384		
1	1	6	4.076	4.073	13.6	0	6	2	2.361	2.361	2.0
2	1	4	3.851	3.849	2.4	0	6	3	2.321	2.320	4.3
1	3	4	3.672	3.670	25.4	1	1	12	2.269	2.268	4.4
0	4	2	3.482	3.481	11.3	0	6	4	2.268		
1	3	5	3.424	3.424	20.1	0	2	12	2.247	2.245	4.4
1	4	1	3.344	3.344	37.7	0	4	10	2.227	2.225	3.5
1	2	7	3.317	3.317	17.0	3	4	5	2.210	2.210	6.0
1	1	8	3.246	3.246	13.1	1	5	8	2.176	2.174	5.3
0	4	4	3.205	3.205	37.0	4	3	1	2.153	2.152	2.0
2	3	3	3.203			3	2	9	2.152		
0	2	8	3.181	3.180	42.6	3	3	8	2.136	2.135	5.8
1	3	6	3.179			4	3	2	2.135		
1	4	4	3.042	3.040	9.8	3	5	2	2.121	2.120	3.6
2	1	7	3.038			1	6	6	2.089	2.088	1.4
1	2	8	3.022	3.020	9.3	0	6	7	2.062	2.060	7.8
2	3	5	2.919	2.917	7.7	2	3	11	2.056	2.055	4.7
3	1	4	2.877	2.874	11.4	4	1	7	2.056		
3	2	3	2.809	2.809	11.7	3	3	9	2.040	2.039	1.9
2	1	8	2.806			2	4	10	2.023	2.024	4.2
1	2	9	2.767	2.766	4.7	4	3	5	2.018	2.018	2.8
2	3	6	2.763			3	5	5	2.007	2.007	1.0

DESCRIPTION OF THE STRUCTURE AND DISCUSSION

The projection of the structure onto the (100) plane (Fig. 1) shows that the $[Mo_4P_5O_{24}]_\infty$ host lattice consists of monophosphate groups sharing their four apices with the MoO_6 octahedra, so that each octahedron is linked to five PO_4 tetrahedra and exhibits one free apex. This framework delimits large tunnels running along *a* where the potassium ions are located.

This structure can be described in a simple way by the stacking along *a* of identical $[Mo_4P_5O_{30}]_\infty$ layers (Fig. 2), two successive layers being enantiomorphous and shifted by *b*/2 with respect to each other. In each layer the MoO_6 octahedra and the PO_4 tetrahedra form three kinds of eight-sided windows built up from four octahedra and four tetrahedra. In the first kind (labeled A in Fig. 2) all the polyhedra have their apices directed outside of the window. These most regular windows are the largest in the

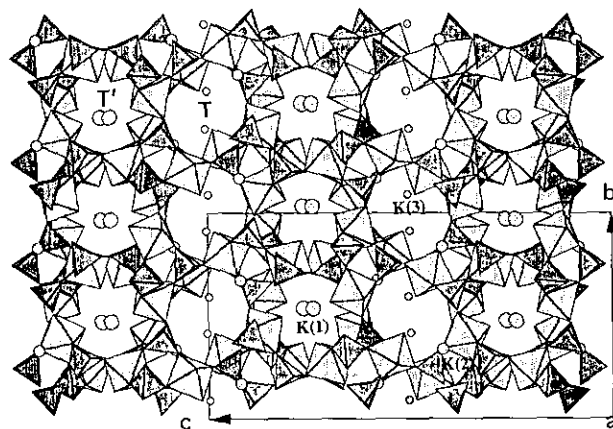


FIG. 1. Projection of the structure of $K_3(MoO)_4(PO_4)_5$ onto (100).

TABLE 2
Summary of Crystal Data Intensity, Measurements, and Structure Refinement Parameters for K₃(MoO)₄(PO₄)₅

Crystal data	
Space group	<i>Pbca</i>
Cell dimensions	<i>a</i> = 9.676(2) Å <i>b</i> = 14.366(2) Å <i>c</i> = 28.391(5) Å
Volume	3946(2) Å ³
Z	8
Intensity measurements	
λ(MoKα)	0.71073 Å
Scan mode	ω - θ
Scan width (°)	1.0 + 0.35 tan θ
Slit aperture (mm)	1.0 + tan θ
Max θ (°)	35
Standard reflections	3 every hr
No. of measured reflection	9512
Reflections with <i>I</i> > 3σ	3688
μ (mm ⁻¹)	3.58
Structure solution and refinement	
Parameters refined	325
Agreement factors	<i>R</i> = 0.027 <i>R_w</i> = 0.030
Weighting scheme	<i>w</i> = <i>f</i> (sin θ/λ)
Δ/σ max	0.004
Δρ (eÅ ⁻³)	0.9

structure. The second kind of windows (labeled B in Fig. 2) are less opened due to the fact that two Mo(V) octahedra have their free apices pointing toward the center of the window. The third window (labeled C in Fig. 2) is much smaller, since three Mo(V) octahedra have their free apices pointing inside the window. In these layers (Fig. 2), two A and B windows share their polyhedra along **b**, whereas two C windows are adjacent along that direction so that the sequences along **b** are [ABA. . .] and [CCC], respectively. In the same way, one observes that one C window is adjacent to one A and one B window along **c** so that the sequence is [ACBCA. . .] along that direction. The eight-sided rings are stacked along **a** in two

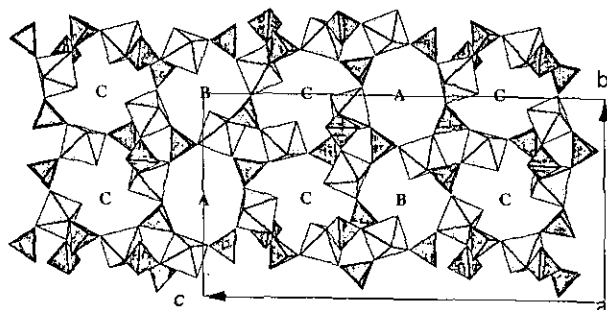


FIG. 2. Projection of a layer [Mo₄P₅O₃₀]_x⁻.

TABLE 3
Positional Parameters and Their Estimated Standard Deviations

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²)
Mo(1)	0.08166(5)	0.07282(3)	0.13996(2)	0.387(6)
Mo(2)	0.42492(5)	0.39753(3)	0.35521(2)	0.440(6)
Mo(3)	0.15227(5)	0.18304(3)	0.45592(2)	0.388(6)
Mo(4)	0.49008(5)	0.22201(3)	0.20472(2)	0.416(6)
P(1)	0.0978(1)	0.38266(9)	0.38551(5)	0.40(2)
P(2)	0.4091(1)	0.09741(9)	0.10587(4)	0.40(2)
P(3)	0.6632(1)	0.28253(9)	0.30368(4)	0.46(2)
P(4)	0.4813(1)	0.24566(9)	0.44649(4)	0.43(2)
P(5)	0.2861(1)	0.17366(9)	0.34431(5)	0.41(2)
K(1)	0.1457(2)	0.46816(9)	0.26185(5)	1.73(2)
K(2)	0.2861(2)	0.3334(1)	0.08124(6)	2.22(3)
K(3)	0.2373(2)	0.4115(1)	0.49747(6)	2.02(3)
O(1)	0.1371(5)	0.0098(3)	0.1856(2)	1.41(8)
O(2)	0.0077(4)	-0.0384(3)	0.1032(1)	0.75(6)
O(3)	0.2570(4)	0.0661(3)	0.0997(1)	0.79(6)
O(4)	-0.1102(4)	0.0943(3)	0.1645(1)	0.68(6)
O(5)	0.1438(5)	0.1921(3)	0.1701(2)	1.22(7)
O(6)	0.0109(5)	0.1590(3)	0.0821(1)	0.80(6)
O(7)	0.3879(5)	0.4412(3)	0.3022(2)	1.38(8)
O(8)	0.2443(4)	0.4250(3)	0.3874(2)	0.87(6)
O(9)	0.6232(4)	0.3650(3)	0.3358(2)	0.89(7)
O(10)	0.5019(5)	0.5137(3)	0.3826(2)	1.29(7)
O(11)	0.3590(5)	0.2673(3)	0.3433(2)	1.00(7)
O(12)	0.4968(5)	0.3374(3)	0.4198(1)	1.00(7)
O(13)	0.1932(5)	0.0852(3)	0.4847(2)	1.38(8)
O(14)	0.3371(4)	0.2434(3)	0.4697(2)	1.02(7)
O(15)	0.2136(4)	0.1566(3)	0.3916(1)	0.87(6)
O(16)	-0.0450(4)	0.1391(3)	0.4418(1)	0.75(6)
O(17)	0.0909(4)	0.2533(3)	0.5136(1)	0.69(6)
O(18)	0.0822(5)	0.3135(3)	0.4260(1)	0.89(6)
O(19)	0.4338(5)	0.1308(3)	0.2347(2)	1.46(8)
O(20)	0.4192(5)	0.1758(3)	0.1419(2)	0.98(6)
O(21)	0.6789(4)	0.1668(3)	0.1948(1)	0.82(6)
O(22)	0.3143(4)	0.2975(3)	0.2099(1)	0.79(6)
O(23)	0.5726(5)	0.2910(3)	0.2597(1)	0.77(6)
O(24)	0.5665(5)	0.3403(3)	0.1624(1)	0.82(6)

Note. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as

$$B = 4/3[\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2 + \beta_{12}ab \cos \gamma + \beta_{13}ac \cos \beta + \beta_{23}bc \cos \alpha].$$

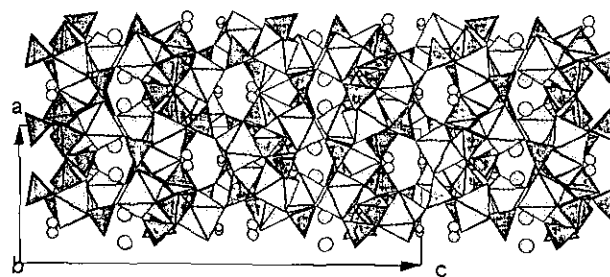


FIG. 3. Projection of the structure of K₃(MoO)₄(PO₄)₅ onto (010).

TABLE 4
Main Distances (Å) and Angles (°) in the Polyhedra

Mo(1)	O(1)	O(2)	O(3)	O(4)	O(5)	O(6)
O(1)	1.669(4)	2.742(6)	2.819(6)	2.749(6)	2.656(7)	3.836(7)
O(2)	94.9(2)	2.038(4)	2.843(6)	2.823(6)	4.038(7)	2.899(6)
O(3)	98.1(2)	88.1(2)	2.048(4)	4.022(7)	2.910(6)	2.774(6)
O(4)	96.4(2)	88.5(2)	165.3(2)	2.007(4)	2.835(6)	2.778(5)
O(5)	92.1(2)	172.9(2)	91.7(2)	89.9(2)	2.007(4)	2.849(6)
O(6)	178.0(2)	87.1(2)	82.2(2)	83.3(2)	85.9(2)	2.168(4)
Mo(2)	O(7)	O(8)	O(9)	O(10)	O(11)	O(12)
O(7)	1.669(4)	2.798(6)	2.701(6)	2.739(7)	2.771(6)	3.803(7)
O(8)	98.6(2)	2.011(4)	4.040(7)	2.803(6)	2.814(6)	2.898(6)
O(9)	92.6(2)	168.5(2)	2.050(4)	2.775(6)	2.924(6)	2.707(6)
O(10)	96.7(2)	89.1(2)	86.9(2)	1.986(4)	3.960(7)	2.744(6)
O(11)	97.5(2)	89.0(2)	92.3(2)	165.7(2)	2.005(4)	2.738(6)
O(12)	172.9(2)	88.5(2)	80.4(2)	83.3(2)	82.6(2)	2.142(4)
Mo(3)	O(13)	O(14)	O(15)	O(16)	O(17)	O(18)
O(13)	1.672(4)	2.699(7)	2.841(6)	2.718(6)	2.736(6)	3.831(7)
O(14)	93.3(2)	2.025(4)	2.809(6)	4.066(6)	2.693(6)	2.938(6)
O(15)	102.7(2)	89.7(2)	1.957(4)	2.892(6)	3.916(7)	2.767(6)
O(16)	93.3(2)	172.5(2)	92.4(2)	2.050(4)	2.927(6)	2.827(6)
O(17)	95.4(2)	83.6(2)	161.0(2)	92.2(2)	2.013(4)	2.633(6)
O(18)	172.8(2)	88.9(2)	84.1(2)	84.2(2)	78.0(2)	2.166(4)
Mo(4)	O(19)	O(20)	O(21)	O(22)	O(23)	O(24)
O(19)	1.654(5)	2.715(7)	2.679(7)	2.750(6)	2.758(6)	3.863(7)
O(20)	94.7(2)	2.022(4)	2.930(6)	2.795(6)	4.015(7)	2.819(6)
O(21)	93.4(2)	93.1(2)	2.012(4)	4.020(7)	2.765(6)	2.871(6)
O(22)	96.3(2)	87.4(2)	170.2(2)	2.023(4)	2.873(6)	2.856(6)
O(23)	96.9(2)	163.3(2)	86.7(2)	90.7(2)	2.014(4)	2.854(5)
O(24)	177.8(2)	83.4(2)	85.6(2)	84.8(2)	84.9(2)	2.209(4)
P(1)	O(2)	O(8)	O(18)	O(24 ⁱⁱ)		
O(2)	1.559(4)	2.508(6)	2.443(6)	2.525(6)		
O(8)	107.9(2)	1.543(5)	2.496(6)	2.536(6)		
O(18)	104.7(2)	108.7(3)	1.527(4)	2.544(6)		
O(24 ⁱⁱ)	110.2(2)	111.8(3)	113.2(2)	1.520(4)		
P(2)	O(3)	O(10 ⁱⁱⁱ)	O(16 ^v)	O(20)		
O(3)	1.549(5)	2.503(6)	2.482(6)	2.528(6)		
O(10 ⁱⁱⁱ)	109.5(3)	1.515(5)	2.501(6)	2.547(6)		
O(16 ^v)	106.6(2)	109.5(3)	1.547(4)	2.460(6)		
O(20)	110.6(2)	113.8(3)	106.5(2)	1.525(4)		
P(3)	O(5 ^{iv})	O(9)	O(22 ^{iv})	O(23)		
O(5 ^{iv})	1.510(5)	2.497(6)	2.508(6)	2.543(6)		
O(9)	109.7(3)	1.545(4)	2.459(6)	2.458(6)		
O(22 ^{iv})	111.4(3)	106.4(2)	1.527(4)	2.494(6)		
O(23)	115.5(3)	106.1(2)	109.4(2)	1.530(4)		
P(4)	O(6 ^v)	O(12)	O(14)	O(17 ^v)		
O(6 ^v)	1.513(4)	2.567(6)	2.542(6)	2.442(5)		
O(12)	115.1(3)	1.529(4)	2.494(6)	2.471(6)		
O(14)	112.5(3)	108.5(3)	1.544(4)	2.502(6)		
O(17 ^v)	105.7(2)	106.7(2)	107.9(2)	1.552(4)		

TABLE 4—Continued

P(5)	O(4 ^{iv})	O(11)	O(15)	O(21 ⁱⁱ)
O(4 ^{iv})	1.540(4)	2.513(6)	2.500(6)	2.446(6)
O(11)	110.5(2)	1.520(4)	2.527(6)	2.509(6)
O(15)	108.8(2)	111.7(3)	1.534(4)	2.480(6)
O(21 ⁱⁱ)	106.1(2)	111.1(3)	108.5(2)	1.522(4)
K(1)–O(1 ^{vi})	3.076(5)			
K(1)–O(1)	3.174(6)			
K(1)–O(4)	2.787(4)			
K(1)–O(7)	2.638(5)			
K(1)–O(7 ⁱⁱ)	3.111(5)			
K(1)–O(9 ⁱⁱ)	3.153(5)			
K(1)–O(19 ⁱⁱ)	2.578(5)			
K(1)–O(22)	3.293(4)			
K(1)–O(23 ⁱⁱ)	2.712(4)			
K(1)–O(24 ⁱⁱ)	2.931(4)			
K(2)–O(2 ^{vi})	2.786(5)			
K(2)–O(9 ⁱⁱ)	2.869(5)			
K(2)–O(12 ⁱⁱ)	2.800(5)			
K(2)–O(13 ⁱⁱ)	3.113(5)			
K(2)–O(16 ^{iv})	3.299(5)			
K(2)–O(17 ⁱⁱ)	2.968(5)			
K(2)–O(18 ^{iv})	2.887(5)			
K(2)–O(20)	3.123(5)			
K(3)–O(3 ^{viii})	2.925(4)			
K(3)–O(8)	3.133(5)			
K(3)–O(13 ⁱⁱ)	2.611(5)			
K(3)–O(14)	2.717(5)			
K(3)–O(16 ^v)	2.816(4)			
K(3)–O(17)	2.716(4)			
K(3)–O(18)	2.889(5)			
Symmetry code				
i	–x	1/2 + y	1/2 – z	
ii	–1/2 + x	y	1/2 – z	
iii	1 – x	–1/2 + y	1/2 – z	
iv	1/2 + x	y	1/2 – z	
v	1/2 + z	1/2 – y	1 – z	
vi	1/2 – x	1/2 + y	z	
vii	x	1/2 – y	–1/2 + z	
viii	x	1/2 – y	1/2 + z	

Note. The Mo–O or P–O distances are on the diagonal, above it are the O_i···O_j distances, and below it are the O_i···Mo···O_j or O_i···P···O_j angles.

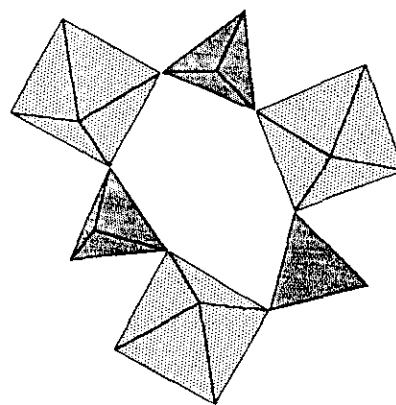


FIG. 4. The six-sided window built up from three octahedra and three tetrahedra.

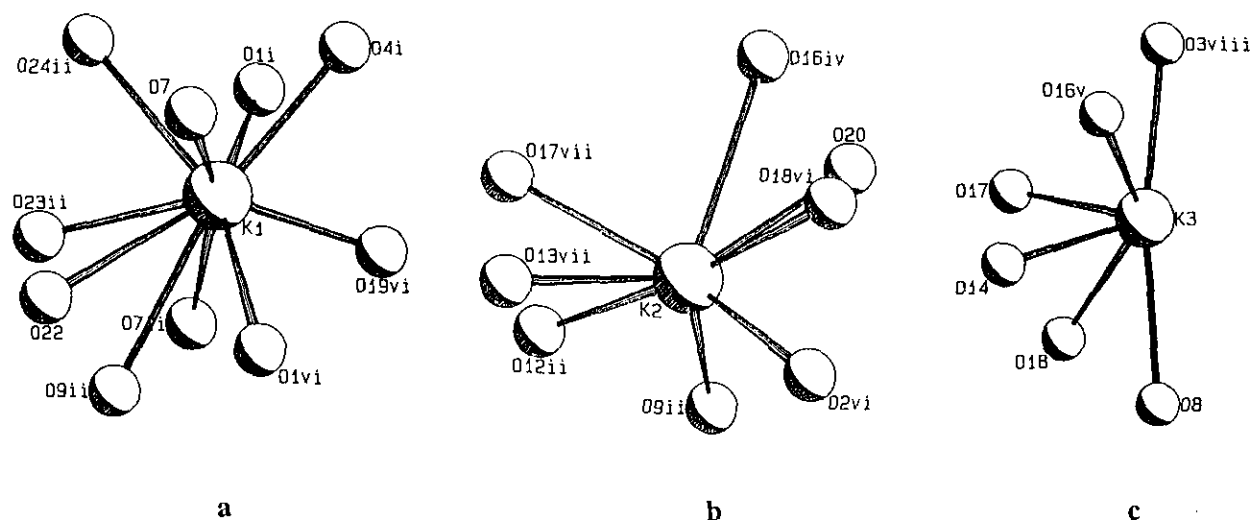


FIG. 5. The K⁺ environments: (a) K(1), (b) K(2), and K(3).

different ways. Two A and B rings alternate along **a**, forming the largest tunnels (labeled T in Fig. 1) running along **a**, where the K(2) and K(3) ions are located.

The second kind of tunnels running along **a** (labeled T' in Fig. 1) consists of the stacking of identical C rings along that direction. The latter tunnels that exhibit a smaller section contain the K(1) ions.

The stacking of the [Mo₄P₅O₃₀]_∞ layers along **a** delimit smaller tunnels running along **b**, as shown from the projection of the structure along that direction (Fig. 3). It must be pointed out that these tunnels exhibit, in fact, rather large six-sided windows built up from three octahedra and three octahedra (Fig. 4), which allow the migration of K⁺ ions along **b**. Note that the K(1) and the K(3) cations are located at the intersection of the T tunnels running along **a** and of the tunnels running along **b**.

The four independent molybdenum octahedra exhibit a geometry characteristic of Mo(V); they all have one free apex directed toward the centers of the tunnels, characterized by a very short Mo–O bond (1.654–1.677 Å). The opposite distances are abnormally long (2.142–2.209 Å), whereas the intermediate Mo–O distances are rather homogeneous (1.986–2.049 Å) (Table 4). The valence calculations (8) which lead to values ranging from 5.04 to 5.14 confirm the pentavalent character of molybdenum. The PO₄ tetrahedra, which share their corners with four octahedra, are significantly distorted with P–O distances ranging from 1.509 to 1.559 Å. One observes that the shorter P–O bond corresponds to the oxygen atoms that are linked to phosphorus and molybdenum only, i.e., that do not

have any potassium neighbors. The P–O bond length increases with the number of potassium ions surrounding the oxygen atom and with the strength of the K–O bonds (Table 4).

The K(1) atoms are surrounded by 10 oxygen atoms with distances ranging from 2.578 to 3.174 Å. The oxygen atoms delimit a bicapped distorted cube (Fig. 5a). The K(2) atoms are linked to eight oxygen atoms with K–O distances ranging from 2.786 to 3.299 Å and delimiting a very distorted cube (Fig. 5b). These K⁺ ions are located in cages near the walls of the T' tunnels at the intersection with the tunnels running along **b**.

The K(3) atoms are located near the walls of the T tunnels so that their six oxygen nearest neighbors sit on the same side (Fig. 5c) at distances ranging from 2.611 to 3.133 Å.

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