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A Mixed-Valent Molybdenum Monophosphate with a Layer Structure: $KMo_3P_2O_{14}$

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A new mixed-valent molybdenum monophosphate with a layer structure $KMo_3P_2O_{14}$ has been isolated. It crystallizes in the space group $P2_1/m$ with $a = 8.599$ (2) Å, $b = 6.392$ (2) Å, $c = 10.602$ (1) Å, and $\beta = 111.65$ (2)°. The layers $[Mo_3P_2O_{14}]_\infty$ are parallel to (100) and consist of $[MoPO_8]_\infty$ chains running along $\vec{b}$, in which one MoO_6 octahedron alternates with one PO_4 tetrahedron. In fact, four $[MoPO_8]_\infty$ chains share the corners of their polyhedra and the edges of their octahedra, forming $[Mo_4P_4O_{24}]_\infty$ columns which are linked through MoO_5 bipyramids along $\vec{c}$. The K^+ ions interleaved between these layers are surrounded by eight oxygens, forming bicapped trigonal prisms KO_8. Besides the unusual trigonal bipyramids MoO_5, this structure is also characterized by a tendency to the localization of the electrons, since one octahedral site is occupied by Mo(V), whereas the other octahedral site and the trigonal bipyramid are occupied by Mo(VI). The similarity of this structure with pure octahedral layer structures suggests the possibility of generating various derivatives, and of ion exchange properties.

INTRODUCTION

A large series of molybdenum phosphates has been isolated over the past ten years, with a molybdenum valence ranging from III to VI. In most of these phosphates, molybdenum exhibits an octahedral coordination. Very few mixed-valent molybdenum phosphates involving Mo(V) have been synthesized. Only two kinds of frameworks, corresponding to the phosphates $AMo_2P_2O_{10}$ (1–3) and $AMo_3P_3O_{16}$ (4–5), characterized by the mixed valence Mo(IV)/Mo(V) and Mo(V)/Mo(VI), respectively, are known. This rarity of the Mo mixed valence may be related to the particular configuration of Mo(V), which tends to form molybdenyl ions and would prevent a delocalization of the electrons in the structure. Indeed, in the $AMo_2P_2O_{10}$ compounds, the $Mo^{IV}O_6$ and $Mo^{V}O_6$ octahedra are isolated on independent sites. On the other hand, in the $AMo_3P_3O_{16}$ phases the situation is more curious, since Mo(VI) exhibits a very unusual trigonal bipyramidal coordination, whereas Mo(V) is characterized by the usual octahedral coordination involving a very short Mo–O bond. Moreover, both species, the $Mo^{VI}O_5$ bipyramid and the $Mo^{V}O_6$ octahedron, share one apex forming isolated "Mo_2O_{10}" units. In order to understand this particular behavior of the Mo(V)–Mo(VI) phosphates, and especially this tendency to the localization of electrons, the system K–Mo–P–O has been investigated, varying the Mo(V):Mo(VI) molar ratio. The present paper deals with a new mixed-valent molybdenum phosphate, $KMo^{V}Mo_2^{VI}P_2O_{14}$, with a layer structure.

SYNTHESIS

Single crystals of this new phosphate were grown from a mixture of nominal $KMo_3P_2O_{14}$.

The synthesis was performed in two steps, starting from a mixture in stoichiometric ratios to obtain the above formula. First, a mixture of K_2CO_3, $H(NH_4)_2PO_4$, and MoO_3 was ground and heated to 673 K in air to eliminate CO_2, H_2O, and NH_3. Second, the appropriate amount of molybdenum was added and the finely ground mixture was placed in an alumina tube sealed in an evacuated silica ampoule, then heated for one day to 1123 K and cooled at 2 K per hr to 1023 K. The sample was finally quenched to room temperature.

Two kinds of crystals were obtained: green crystals corresponding to the $\beta KMo_2P_3O_{13}$ phase and black plate crystals. The microprobe analysis of the black crystals confirms the composition $KMo_3P_2O_{14}$, in agreement with the structure determination.

Many attempts to prepare this new phase in the form of a powder always led to a mixture. Thus black crystals were picked out with tweezers using a binocular microscope, and the powder X-ray pattern (Table 1) of this phase was indexed in a monoclinic cell in agreement with the parameters obtained from the single crystal study (Table 2).

STRUCTURE DETERMINATION

A black crystal with dimensions $0.193 \times 0.058 \times 0.013$ mm^3 was selected for the structure determination. The

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TABLE 1
Interplanar Distances

h	k	l	d_{calc}(Å)	d_{obs}(Å)	I	h	k	l	d_{calc}(Å)	d_{obs}(Å)	I
1	0	0	7.992	7.987	39.3	3	0	$\bar{4}$	2.275	2.277	2.9
0	1	$\bar{1}$	5.363	5.376	1.4	2	2	$\bar{3}$	2.253	2.255	0.6
0	1	1	5.363			4	0	$\bar{2}$	2.148	2.146	1.2
1	0	1	5.321	5.332	2.9	4	0	$\bar{1}$	2.116	2.118	2.8
1	1	0	4.992	5.008	1.3	0	3	$\bar{1}$	2.083	2.084	1.9
2	0	$\bar{1}$	4.296	4.295	2.0	4	0	$\bar{3}$	2.082		
1	1	$\bar{1}$	4.089	4.104	3.4	3	0	2	2.049	2.050	1.1
1	1	$\bar{2}$	3.997	3.998	100	2	2	$\bar{2}$	2.045	2.044	0.7
2	1	$\bar{1}$	3.566	3.572	5.2	2	2	$\bar{4}$	1.999	2.001	16.2
2	1	0	3.388	3.393	3.6	2	3	$\bar{1}$	1.909	1.910	1.4
0	2	0	3.196	3.200	4.2	0	1	$\bar{5}$	1.883	1.883	0.7
2	0	$\bar{3}$	3.178	3.181	8.7	3	1	$\bar{5}$	1.882		
1	1	2	3.161	3.157	2.3	2	3	0	1.880		
1	2	0	2.967	2.964	0.7	2	3	$\bar{2}$	1.868	1.867	0.5
2	1	1	2.934	2.941	1.8	4	1	$\bar{4}$	1.858	1.860	1.3
0	1	$\bar{3}$	2.922	2.925	1.0	1	3	$\bar{3}$	1.824	1.825	0.9
3	0	$\bar{1}$	2.850	2.855	0.5	2	3	$\bar{3}$	1.770	1.769	2.1
1	2	$\bar{2}$	2.712	2.713	1.5	3	1	$\bar{3}$	1.709	1.711	6.5
3	0	0	2.664	2.667	27.0	1	1	$\bar{6}$	1.679	1.681	7.0
3	0	$\bar{3}$	2.588	2.591	1.7	3	1	$\bar{6}$	1.650	1.650	3.8
2	2	$\bar{1}$	2.564	2.564	0.4	4	1	2	1.599	1.600	3.0
2	2	0	2.496	2.498	1.0	5	0	0	1.598		
0	0	4	2.464	2.464	4.3						

TABLE 2
Summary of Crystal Data Intensity, Measurements, and Structure Refinement Parameters for $KMo_3O_2O_{14}$

1. Crystal data	
Space group	$P2_1/m$
Cell dimensions	a = 8.599 (2) Å
	b = 6.392 (1) Å, β = 111.65 (2)°
	c = 10.602 (2) Å
Volume	542 (3) Å^3
Z	2
d_{calc}	3.76
2. Intensity measurements	
λ(Mo$K\alpha$) (Å)	0.71073
Scan mode	ω
Scan width (°)	2 + 0.35 tan θ
Slit aperture (mm)	1.5 + tan θ
Max θ(°)	45
Standard reflections	3 (every 3000 sec)
Reflections with $I > 3\sigma$	1643
μ (mm^{-1})	4.1
3. Structure solution and refinement	
Parameters refined	113
Agreement factors	R = 0.042 R_w = 0.047
Weighting scheme	$w = f(\sin\theta/\lambda)$ (Hamilton scheme)
Δ/σ max	<0.04
$\Delta\rho$ (eÅ^{-3})max	1.6

TABLE 3
Positional Parameters and Their Estimated Standard Deviations

Atom	x	y	z	B(Å2)
Mo(1)	0.23363(8)	0.25	0.00971(8)	0.91(1)
Mo(2)	0.24876(8)	0.25	0.32984(8)	0.894(9)
Mo(3)	0.84014(8)	0.25	0.38009(8)	1.06(1)
P(1)	0.8530(2)	0.25	0.0650(2)	0.92(3)
P(2)	0.1120(3)	0.75	0.2998(2)	0.95(3)
K	0.4841(3)	0.75	0.2485(2)	1.75(3)
O(1)	0.3904(9)	0.25	−0.0467(9)	1.9(1)
O(2)	0.0373(8)	0.25	−0.1656(8)	1.5(1)
O(3)	0.2170(6)	0.5597(8)	0.0265(5)	1.45(8)
O(4)	0.3539(7)	0.25	0.2049(7)	0.99(9)
O(5)	0.0438(8)	0.25	0.1169(7)	1.3(1)
O(6)	0.4165(8)	0.25	0.4731(7)	1.3(1)
O(7)	0.0710(7)	0.25	0.3876(7)	1.2(1)
O(8)	0.2252(5)	0.5619(7)	0.3096(5)	1.37(7)
O(9)	0.7219(7)	0.037(1)	0.3719(6)	2.3(1)
O(10)	0.7896(9)	0.25	0.1801(8)	1.8(1)
O(11)	0.9544(9)	0.25	0.5843(7)	1.4(1)

Note. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $B = 4/3\,[\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2 + \beta_{12}ab\cos\gamma + \beta_{13}ac\cos\beta + \beta_{23}bc\cos\alpha]$.

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 $18° < \theta < 22°$. The data were collected on a CAD 4 Enraf–Nonius diffractometer with the data collection parameters reported in Table 2. The reflections were corrected for Lorentz, polarization, secondary extinction, and absorption effects.

Atomic coordinates of the molybdenum were deduced from the Patterson function, and the other atoms were located by subsequent Fourier series. Refinement of the atomic coordinates and their anisotropic thermal parameters led to R = 0.042 and R_w = 0.047, and to the atomic parameters of Table 3.

DESCRIPTION OF THE STRUCTURE AND DISCUSSION

The projection of the structure of this phase along $\vec{b}$ (Fig. 1) shows its lamellar character. It is built from $[Mo_3P_2O_{14}]_\infty$ layers parallel to (100), interleaved with potassium ions.

Each (100) layer (Fig. 2) consists of $[MoPO_8]_\infty$ chains running along $\vec{b}$, similar to those frequently observed in molybdenum phosphates (6), i.e., in which one PO_4 tetrahedron alternates with one MoO_6 octahedron. These chains share the corners of their polyhedra and the edges of their MoO_6 octahedra, forming $[Mo_4P_4O_{24}]_\infty$ (Fig. 3) columns parallel to $\vec{b}$. In fact, each column is built from four $[MoPO_8]_\infty$ chains in the following way:

(i) Each $[MoPO_8]_\infty$ chain shares the edges of its MoO_6 octahedra with an identical chain forming dimeric Mo_2O_{10} units with two free corners and leading to brownmillerite-like windows (Fig. 4a).

(ii) Two adjacent $[MoPO_8]_\infty$ chains are also linked to each other in such a way that a PO_4 tetrahedron of one chain is connected to a MoO_6 octahedron of the other chain (Fig. 4b). This results in $[Mo_2P_2O_{14}]_\infty$ double chains being frequently observed in molybdenum monophosphates.

(iii) The columns $[Mo_4P_4O_{24}]_\infty$ (Fig. 3) result from the association of two $[Mo_2P_2O_{14}]_\infty$ double chains (Fig. 4b) through the edges of their octahedra according to the scheme described in Fig. 4a. This kind of association of the $[MoPO_8]_\infty$ chains means that one oxygen atom O(5) is shared between three polyhedra, i.e., one PO_4 tetrahedron and one Mo_2O_{10} unit.

Thus the structure of the $[Mo_3P_2O_{14}]_\infty$ layers can be described by the association of the $[Mo_4P_4O_{24}]_\infty$ columns through MoO_5 trigonal bipyramids. In these layers, each MoO_5 bipyramid has two free corners, and shares one corner with one PO_4 tetrahedron of one column, and the two other corners with one PO_4 tetrahedron and one MoO_6 octahedron of the other column.

In this structure each PO_4 tetrahedron is isolated, i.e., shares its four corners with MoO_6 octahedra and MoO_5 bipyramids so that this phase corresponds to a monophosphate. The geometry of the PO_4 tetrahedra is almost regular as usually observed in molybdenum monophosphates. Indeed, the P(1) and P(2) tetrahedra, which are both linked to the same Mo(3) bipyramid and share their three other apices with four and three MoO_6 octahedra, respectively, do not exhibit significantly different P–O distances.

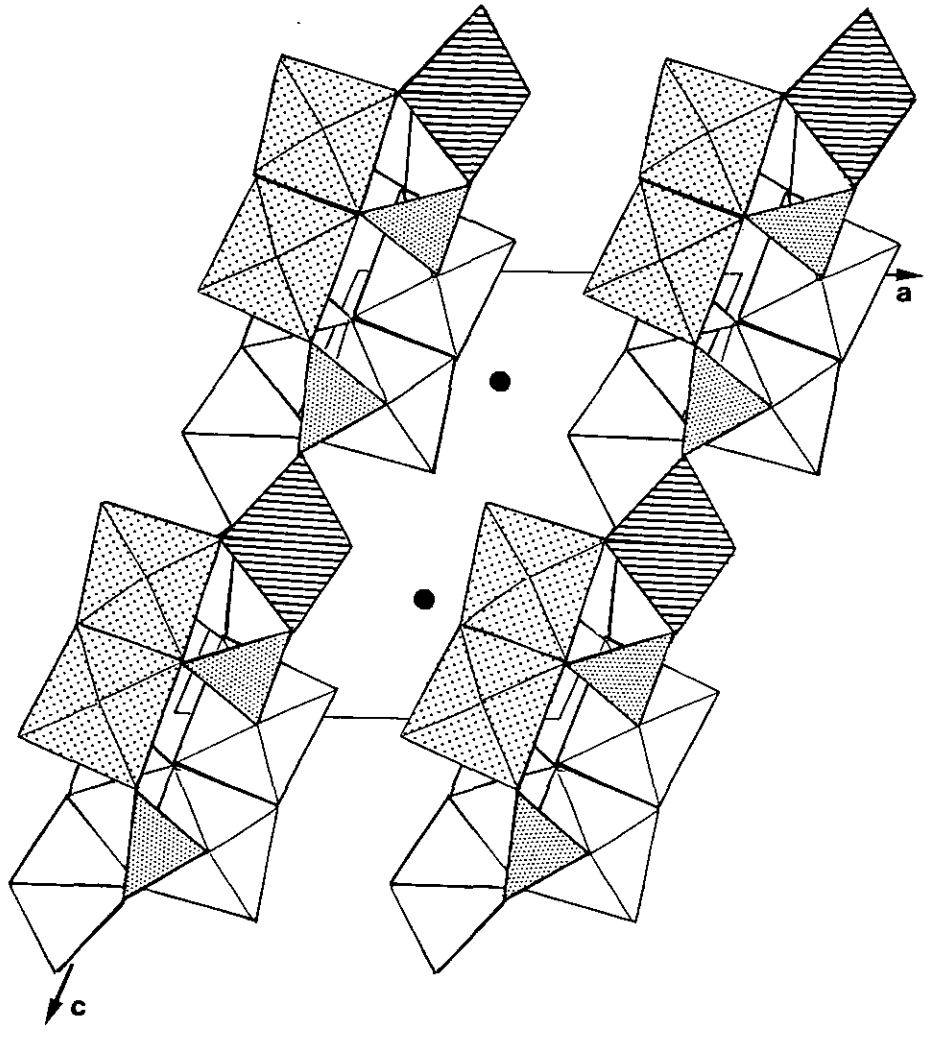

FIG. 1. Projection of the structure of $KMo_3P_2O_{14}$ along $\vec{b}$.

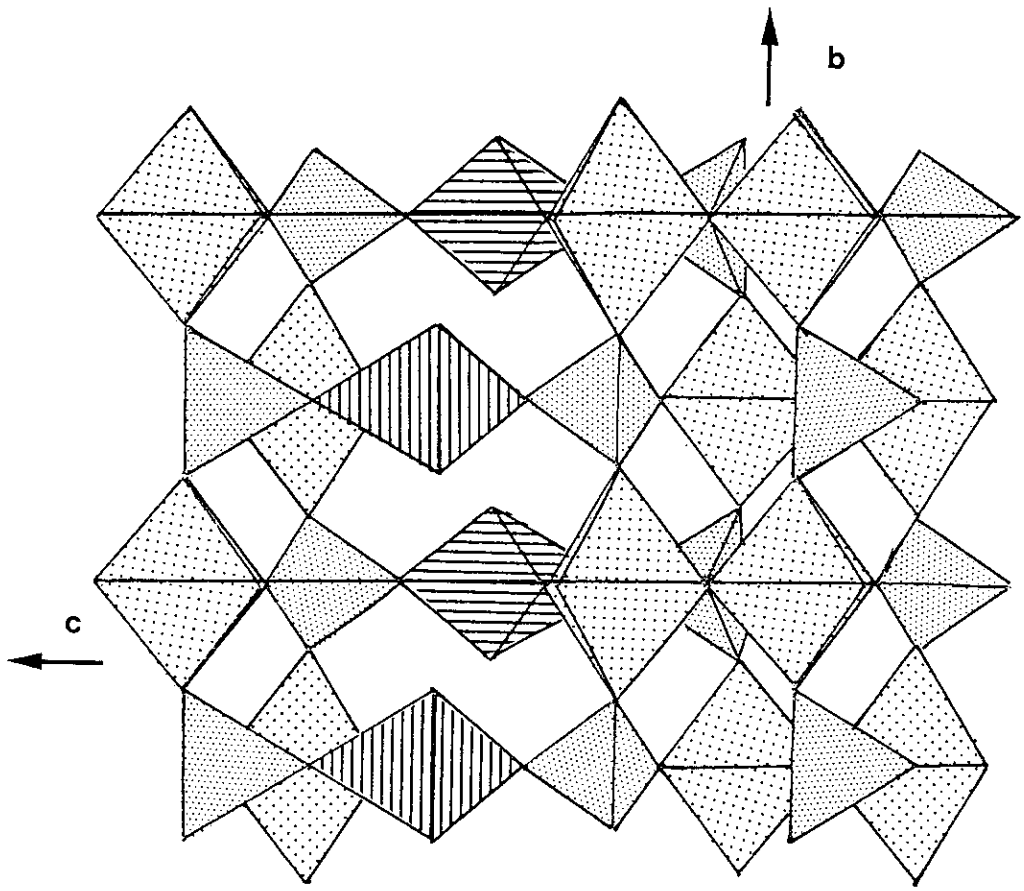

FIG. 2. The (100) layer : $[Mo_3P_2O_{14}]_\infty$.

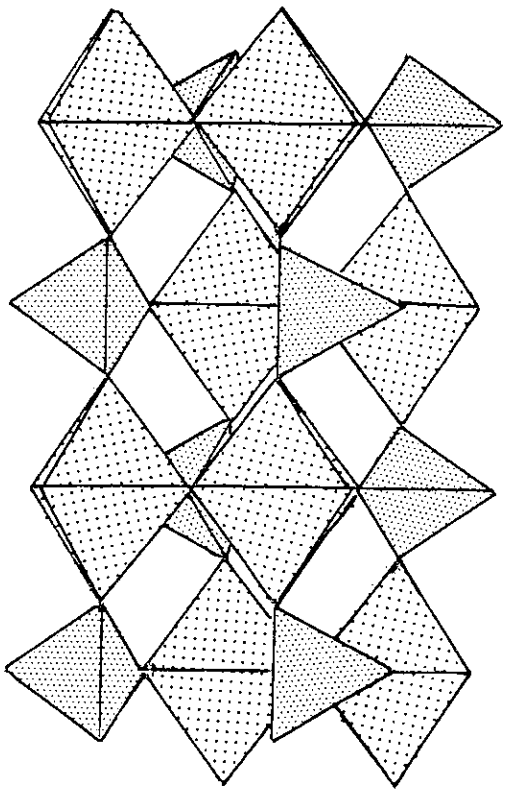

FIG. 3. $[Mo_4P_4O_{24}]_\infty$ columns parallel to $\vec{b}$.

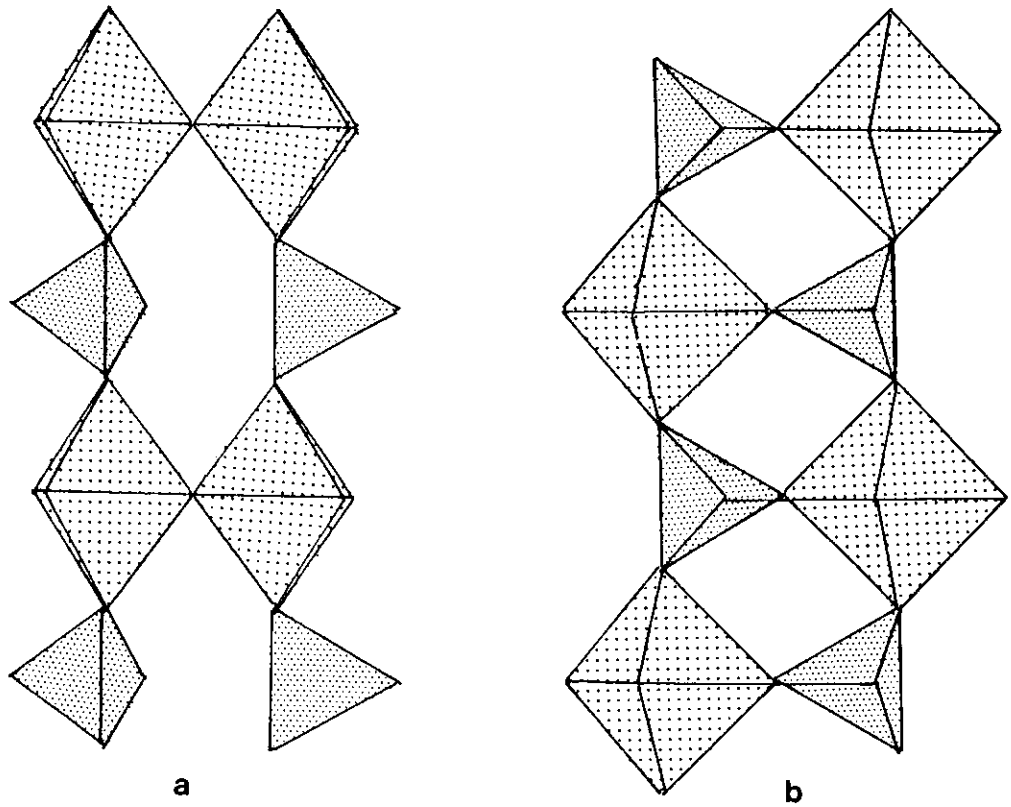

FIG. 4. (a) Two chains MoP_2O_8 forming Mo_2O_{10} units and brownmillerite-like windows; (b) two chains MoP_2O_8 forming $[Mo_2P_2O_{14}]_\infty$ double chains.

The geometries of the Mo(1) and Mo(2) octahedra which form the Mo_2O_{10} unit show significant differences (Table 4). The Mo(1) octahedron, which shares four corners with the PO_4 tetrahedra and one edge with the Mo(2) octahedron, has one free corner, O(1). This O_6 octahedron is distorted, with O–O distances ranging from 2.48 to 2.97 Å; the displacement of Mo(1) inside this octahedron toward the O(1) free atom leads to a very short distance of 1.66 Å, and an opposite long distance of 2.30 Å, whereas the other four equatorial distances are close to each other (1.942–1.997 Å). This geometry suggests strongly that Mo(1) is pentavalent. Indeed, in all other Mo(V) phosphates one observes a very similar behavior, characteristic of the molybdenyl ion (7). This viewpoint is not contradicted by the electrostatic valence calculations according to Brown and Altermatt (8), since a valence of 5.5 is obtained for Mo(1). The Mo(2) octahedron which shares three apices with PO_4 tetrahedra, one edge with Mo(1), and one apex with the Mo(3) bipyramid has also one free apex O(6). This octahedron is more symmetric, with O–O distances ranging from 2.48 to 2.87 Å, whereas the Mo(2)–O distances of the basal plane spread over a larger range (1.844–2.00 Å) with a mean value (1.928 Å) less than in Mo(1) (1.983 Å), the shorter (1.665 Å) and the longer (2.295 Å) bonds being similar to those observed for Mo(1). This dissymmetry is close to that observed for Mo(VI) in phosphomolybdates (9–10). The bond valence calculations, which led for this Mo(2) site to a valence of 6.12, support strongly this hypothesis.

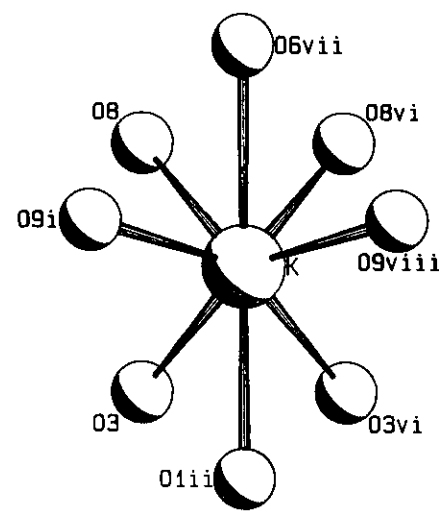

FIG. 5. The K^+ environment.

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

Mo(1)	O(1)	O(2)	O(3)	O(3^{i})	O(4)	O(5)
O(1)	1.665(9)	2.826(2)	2.756(1)	2.756(1)	2.798(1)	3.963(2)
O(2)	100.6(5)	1.997(8)	2.851(1)	2.851(1)	3.867(2)	2.974(2)
O(3)	97.3(2)	91.1(2)	1.997(6)	3.958(2)	2.690(1)	2.847(1)
O(3^{i})	97.3(2)	91.1(2)	164.7(4)	1.997(6)	2.690(1)	2.847(1)
O(4)	101.4(4)	157.9(3)	86.1(2)	86.2(2)	1.942(8)	2.480(1)
O(5)	172.3(4)	87.1(3)	82.5(2)	82.5(2)	70.8(3)	2.307(8)

MO(2)	O(4)	O(5)	O(6)	O(7)	O(8)	O(8^{i})
O(4)	1.859(8)	2.48(1)	2.69(1)	3.626(9)	2.709(8)	2.709(8)
O(5)	72.4(3)	2.295(8)	3.950(9)	2.79(1)	2.869(8)	2.869(8)
O(6)	99.4(3)	171.9(3)	1.665(8)	2.77(1)	2.753(8)	2.753(8)
O(7)	156.5(3)	84.1(3)	104.5(4)	1.844(8)	2.688(7)	2.688(7)
O(8)	88.9(2)	83.4(2)	96.7(2)	88.4(2)	2.004(5)	3.99(1)
O(8^{i})	88.9(2)	83.4(2)	96.7(2)	88.4(2)	166.6(3)	2.007(5)

Mo(3)	O(7)	O(9)	O(9^{i})	O(10)	O(11)
O(7)	1.958(7)	3.246(9)	3.246(9)	2.60(1)	2.63(1)
O(9)	125.9(3)	1.685(7)	2.73(1)	2.68(1)	2.76(1)
O(9^{i})	125.9(3)	108.2(5)	1.685(7)	2.68(1)	2.75(1)
O(10)	82.2(4)	93.1(3)	93.1(3)	2.000(9)	3.98(1)
O(11)	82.6(4)	95.8(3)	95.8(3)	164.8(3)	2.020(9)

P(1)	O(3^{ii})	O(3^{iii})	O(5^{iv})	O(10)
O(3^{ii})	1.533(6)	2.43(1)	2.511(9)	2.488(8)
O(3^{iii})	105.0(5)	1.533(6)	2.511(9)	2.488(8)
O(5^{iv})	110.3(3)	110.3(3)	1.526(8)	2.51(1)
O(10)	109.7(3)	109.7(3)	111.7(5)	1.510(9)

P(2)	O(2^{v})	O(8)	O(8^{vi})	O(11^{vii})
O(2^{v})	1.525(8)	2.516(9)	2.516(9)	2.48(1)
O(8)	111.1(3)	1.526(5)	2.40(1)	2.525(9)
O(8^{vi})	111.1(2)	103.9(4)	1.526(5)	2.525(9)
O(11^{vii})	108.2(5)	111.2(3)	111.2(3)	1.534(9)

K–O(1^{ii}) = 2.728(9)
K–O(3) = 2.882(6)
K–O(3^{vi}) = 2.882(6)
K–O(6^{vii}) = 2.753(8)
K–O(8) = 2.808(6)
K–O(8^{vi}) = 2.808(6)
K–O(9^{viii}) = 2.697(7)
K–O(9^{i}) = 2.697(7)

Symmetry Code

i	x	$1/2 - y$	z
ii	$1 - x$	$1 - y$	$-z$
iii	$1 - x$	$-1/2 + y$	$-z$
iv	$1 + x$	y	z
v	$-x$	$1 - y$	$-z$
vi	x	$3/2 - y$	z
vii	$1 - x$	$1 - y$	$1 - z$
viii	x	$1 + y$	z

The Mo(3) bipyramid exhibits three normal and almost equal Mo(3)–O distances (1.958–2.020 Å) corresponding to the oxygen atoms linked to two PO_4 tetrahedra and one MoO_6 octahedron, whereas the other two abnormally short Mo(3)–O distances (1.685 Å) correspond to the free O(9) apices. The electrostatic valence calculations, lead for Mo(3) to a valence of 6.03, in agreement with the hexavalent character previously observed for molybde-

num with a similar coordination in the phases $AMo_3P_3O_{16}$ with A = Na, Ag (4–5).

The K^+ ions, which ensure cohesion between the layers, are surrounded by eight oxygen atoms; this results in a bicapped trigonal prism (Fig. 5) usually observed for potassium, with K–O distances ranging from 2.697 to 2.882 Å (Table 4).

CONCLUDING REMARKS

This structural study shows once again the high tendency of electronic localization in phosphates with the mixed valence Mo(V)–Mo(VI) systems, leading to the formulation $KMo^{V}_{oct1}Mo^{VI}_{oct2}Mo^{VI}_{bipy}P_2O_{14}$. Despite the fact that the three polyhedra share their corners and edges, one does not detect any local electron delocalization inside the units formed by the Mo_2O_{10} unit and the MoO_5 bipyramid. An interesting characteristic of this structure is its similarity with pure octahedral layered structures such as the titanates $A_x(Ti_{2-y}M_x)O_4$ (11–12), in which potassium exhibits also a trigonal prismatic coordination. In this respect the substitution of other cations for potassium should allow other phases with a similar composition $A_xMo_3P_2O_{14}$ and identical layers to be synthesized; nevertheless the relative positions of the layers should vary according to the nature of the A cation. The ion exchange properties of this phase will be investigated, as well as the possible intercalation of amines.

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