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A Mo(V) Monophosphate with an Intersecting Tunnel Structure: $K_2Mo_2P_2O_{11}$

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A new molybdenum (V) monophosphate $K_2Mo_2P_2O_{11}$ has been isolated. The single crystal X-ray diffraction study of this phase has shown that it is isotypic with $K_2Nb_2As_2O_{11}$. It crystallizes in the $P21/c$ space group with $a = 9.867$ (2), $b = 10.122$ (1), $c = 9.903$ (2) Å, $\beta = 97.95$ (1)°. A new description of the structure is given, based on the existence of $Mo_2P_2O_{15}$ units formed of one Mo_2O_{11} group sharing four of its corners with two PO_4 tetrahedra and leading to $[Mo_2P_2O_{13}]_x$ chains running along **c**. The $[Mo_2P_2O_{11}]_x$ framework forms two different intersecting tunnels running along **c** and ⟨110⟩, respectively, where the K^+ cations are located. The existence of one free apex for each MoO_6 octahedron, which characterizes Mo(V), allows a great flexibility of the structure.

Introduction

Until recently, the pentavalent molybdenum oxides were regarded as forming a very small family. The study of the Mo(V)–P–O system has shown the possibility of stabilization of Mo(V) in phosphate with the compound $MoPO_5$ (*1*). Since 1983, more than twenty Mo(V) phosphates have been synthesized at high temperature (*2–11*) with various original structures. All these phosphates exhibit a common structural feature, which derives from the fact that the MoO_6 octahedra are isolated, i.e., are connected only to PO_4 tetrahedra. The particular geometry of such MoO_6 octahedra in which one oxygen atom, forming the molybdenyl ion, is unshared suggests a great flexibility in accommodating various tetrahedral frameworks. For this reason a systematic investigation of Mo(V) phosphates has been carried out in this laboratory. The present paper reports the crystal structure of new monophosphate $K_2Mo_2P_2O_{11}$, which is to our knowledge the first Mo(V) phosphate having two corner-sharing MoO_6 octahedra and an intersecting tunnel structure.

Experimental

The crystal growth of the phosphate $K_2Mo_2P_2O_{11}$ was performed in two steps from a mixture of composition "$K_3Mo_4P_4O_{22}$."

First an adequate mixture of K_2CO_3, $H(NH_4)_2PO_4$, and MoO_3 was heated to 673 K in order to eliminate CO_2, H_2O, and NH_3. In the second step the resulting finely ground product was mixed with an appropriate amount of molybdenum and sealed in an evacuated silica ampoule. This sample was then heated up to 1123 K for 1 day and cooled at 2 K per hr down to 923 K. The sample was finally quenched to room temperature. When the ampoule was opened, we obtained a mixture in which some brown needles were isolated. The composition deduced from the structural determination $K_2Mo_2P_2O_{11}$ was confirmed by microprobe analysis. Subsequently, a reaction to prepare pure $K_2Mo_2P_2O_{11}$ was performed. The powder X-ray diffraction pattern of the phase was indexed in a monoclinic cell (Table I), in agreement with the parameters obtained from the single crystal study (Table II).

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TABLE I

INTERRETICULAR DISTANCES

h	k	l	d_{cal} Å	d_{obs} Å	I	h	k	l	d_{cal} Å	d_{obs} Å	I
1	0	0	9.772	9.712	14	0	2	3	2.746	2.742	11
1	1	0	7.030	7.022	89	2	3	−1	2.728	2.726	27
1	1	−1	6.004	6.049	21	1	2	−3	2.727		
1	1	1	5.462	5.461	38	3	2	−1	2.721		
0	0	2	4.904	4.913	22	1	3	2	2.620	2.618	17
1	0	−2	4.648	4.651	18	2	3	1	2.618		
1	2	0	4.494	4.488	18	1	2	3	2.567	2.564	11
0	1	2	4.413	4.411	18	3	2	1	2.562		
1	1	−2	4.224	4.222	23	0	4	0	2.530	2.529	27
1	2	−1	4.187	4.190	19	2	2	−3	2.522		
1	0	2	4.158	4.161	18	2	3	−2	2.502	2.506	11
2	0	−2	3.729	3.722	8	2	1	3	2.480	2.482	9
2	2	0	3.515	3.513	12	3	1	2	2.478	2.470	9
2	1	2	3.499	3.499	8	1	4	0	2.450	2.448	18
2	0	2	3.244	3.248	29	4	0	0	2.443		
2	2	1	3.209	3.206	63	4	1	0	2.375	2.376	9
0	3	1	3.190	3.197	59	0	3	3	2.348	2.348	9
2	1	2	3.089	3.086	92	3	3	0	2.343		
1	1	−3	3.084			2	0	−4	2.324	2.322	12
3	1	−1	3.075	3.079	100	1	3	3	2.233	2.233	11
1	3	−1	3.074			3	2	−3	2.231		
2	2	−2	3.002	3.007	14	1	2	−4	2.212	2.216	20
3	0	−2	2.905	2.900	7	3	1	3	2.115	2.114	14
3	1	−2	2.792	2.792	18	2	2	−4	2.112		

On the basis of X-ray analysis, pure $M_2Mo_2P_2O_{11}$ (M = Rb, Tl) compounds were obtained by heating stoichiometric mixtures of the starting materials at 1103 K in sealed silica tubes for several days. The powder diffractograms of these phases were indexed in a monoclinic cell similar to that of $K_2Mo_2P_2O_{11}$. The cell parameters of these compounds (Table II) are in agreement with the ionic radius size of the inserted cation.

A crystal with dimensions 0.077 × 0.051 × 0.051 mm was selected for the structure determination of $K_2Mo_2P_2O_{11}$.

The cell parameters reported in Table II 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 III. The reflections were corrected for Lorentz, polarization, and ab-

TABLE II

CELL PARAMETERS OF $M_2Mo_2P_2O_{11}$

	a (Å)	b (Å)	c (Å)	β (°)	V (Å^3)
$K_2Mo_2P_2O_{11}$	9.867(2)	10.122(1)	9.903(2)	97.95(2)	979
$Rb_2Mo_2P_2O_{11}$	9.88 (3)	10.15 (3)	9.93 (2)	98.1 (2)	987
$Tl_2Mo_2P_2O_{11}$	9.88 (3)	10.16 (3)	9.93 (2)	97.6 (2)	988

TABLE III

SUMMARY OF CRYSTAL DATA, INTENSITY MEASUREMENTS, AND STRUCTURE REFINEMENT PARAMETERS FOR $K_2Mo_2P_2O_{11}$

Crystal data	
Space group	$P\,2_1/c$
Cell dimensions	$a = 9.867(2)$ Å
	$b = 10.122(1)$
	$c = 9.903(2)$
	$\beta = 97.95°$
Volume	979(2) Å^3
Z	4
ρ_{calc} (g cm^{-3})	3.42
ρ_{exp} (g cm^{-3})	3.445
Intensity measurements	
λ (Mo$K\alpha$)	0.71073 Å
Scan mode	$\omega - \theta$
Scan width (°)	$1 + 0.35 \tan\theta$
Slit aperture (mm)	$1.05 + 1.0 \tan\theta$
Max θ (°)	45
Standard reflections	3 measured every 3000 sec
Reflections with $I > 3\sigma$	2720
μ (mm^{-1})	3.726
Structure solution and refinement	
Parameters refined	73
Agreement factors	$R = 0.041$, $R_w = 0.045$
Weighting scheme	$w = f(\sin\theta/\lambda)$
Δ/σ max	<0.005

sorption effects. The atoms were located by the heavy atom method. The positional and thermal parameters were refined by a full-matrix least-squares method leading to $R = 0.041$, $R_w = 0.045$, and the parameters of Table IV.

Description of the Structure and Discussion

The structure of $K_2Mo_2P_2O_{11}$ is isotypic with that of $K_2Nb_2As_2O_{11}$ (*12*); i.e., it consists of monophosphate groups sharing their four corners with MoO_6 octahedra. In this $[Mo_2P_2O_{11}]_\infty$ framework the MoO_6 octahedra share four of their corners with PO_4 tetrahedra and one with an other MoO_6 octahedron, the sixth apex being free.

The two P(1) and P(2) tetrahedra exhibit P–O distances (Table V) characteristic of almost regular PO_4 monophosphate groups. The geometry of the Mo(1) and Mo(2) octahedra is characteristic of that observed for pentavalent molybdenum oxides and particularly in phosphates (*2–11*). The "O_6" octahedron containing Mo is almost regular, but molybdenum is off-centered toward the unshared oxygen, labeled O(1) and O(7) for Mo(1) and Mo(2), respectively; as a result the corresponding Mo–O distances are very short, of 1.683 and 1.615 Å, respectively (Table V), i.e., characteristic of the molybdenyl ion encountered for Mo(V) phosphates (*2–11*). Three of the four equatorial Mo–O distances are very similar to those observed in Mo(V) monophosphates, ranging from 2.031 to 2.096 Å (Table V) whereas the fourth one is abnormally short (1.868 Å) due to the fact that it corresponds to a Mo–O–Mo bond. The sixth Mo–O bond, opposite to the short molybdenyl type bond, is significantly longer, of 2.19 Å for Mo(1) and 2.144 Å for Mo(2), as usually observed for Mo(V) octahedra.

In spite of its great similarity to $K_2Nb_2As_2O_{11}$ (*12*), the framework $[Mo_2P_2O_{11}]_\infty$ deserves to be described, since no analysis of the latter was performed. The views of the structure along [001] (Fig. 1) and [110] or [1$\bar{1}$0] (Fig. 2) directions, respectively, show that the host lattice $[Mo_2P_2O_{11}]_\infty$ delimits large tunnels running along these directions.

One indeed observes eight-sided tunnels formed of rings of four PO_4 tetrahedra and four MoO_6 octahedra running along **c** (Fig. 1), whereas the ⟨110⟩ tunnels are also built up from rings of four PO_4 tetrahedra and four MoO_6 octahedra but with a different geometry (Fig. 2) leading to a smaller size of the bottleneck. Note that the unshared apexes of the MoO_6 octahedra are directed toward the centers of these two sorts of tunnels. Thus this compound represents the first Mo(V) phosphate with an intersecting tunnel structure which has been isolated up to now.

The second important characteristic of this structure results from the fact that two MoO_6 octahedra share their corners (Figs. 1 and 2), forming Mo_2O_{11} units. This is, to

TABLE IV

Positional Parameters and Their Estimated Standard Deviations

Atom	x	y	z	B(A2)
Mo(1)	0.34571(4)	0.08548(5)	0.13802(5)	0.585(5)
Mo(2)	0.07300(5)	0.31979(5)	0.14807(5)	0.576(5)
P(1)	0.3938(1)	0.3789(1)	0.3156(1)	0.66(2)
P(2)	0.1276(1)	0.0753(1)	0.3567(1)	0.63(2)
K(1)	0.000	0.000	0.000	1.51(3)
K(2)	0.7635(2)	0.1755(2)	0.3033(4)	4.13(5)
K(3)	0.5092(4)	0.0823(5)	0.5112(4)	2.42(6)
O(1)	0.2822(5)	−0.0602(4)	0.0766(5)	1.30(7)
O(2)	0.4282(4)	0.1449(5)	−0.0288(4)	0.92(6)
O(3)	0.2761(4)	0.0607(5)	0.3259(4)	1.01(6)
O(4)	0.5308(4)	0.0043(5)	0.2248(5)	1.04(6)
O(5)	0.1916(4)	0.1912(4)	0.0963(4)	0.77(5)
O(6)	0.4430(4)	0.2596(5)	0.2409(5)	0.98(6)
O(7)	−0.0758(5)	0.2569(5)	0.0677(5)	1.28(7)
O(8)	−0.0338(5)	0.4740(5)	0.2275(5)	1.13(6)
O(9)	0.1309(4)	0.4492(5)	0.0107(4)	0.89(6)
O(10)	0.0638(5)	0.2132(4)	0.3232(5)	1.07(6)
O(11)	0.2419(4)	0.4076(5)	0.2763(5)	1.02(6)

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

our knowledge, the first Mo(V) phosphate involving two corner-sharing octahedra, all other being built up from isolated MoO_6 octahedra (*2–11*) or $[MoO_3]_\infty$ chains (*1, 13*). In fact, the view of the structure of this phase along **c** (Fig. 1) shows that the structure consists of $Mo_2P_2O_{15}$ units (Fig. 3a1) built up from one Mo_2O_{11} group sharing four corners with two PO_4 tetrahedra. The $Mo_2P_2O_{15}$ structural units share their corners along **c** in such a way that two MoO_6 octahedra of one unit are connected with two PO_4 tetrahedra of the next one, forming $[Mo_2P_2O_{13}]_\infty$ columns running along **c** (Fig. 3b). Laterally in the (001) plane (Fig. 2) the $[Mo_2P_2O_{13}]_\infty$ columns share the corners of their polyhedra, leading to the tridimensional framework $[Mo_2P_2O_{11}]_\infty$.

Note that the $Mo_2P_2O_{15}$ units which form this structure differ from those of α-$KMo_2P_3O_{13}$ (*2*) (Fig. 3a2) in spite of their identical composition; the latter correspond indeed to the association of one P_2O_7 group with two MoO_6 octahedra in such a way that the latter are isolated from each other, sharing two corners with the same diphosphate group.

The structure of this host lattice can also be described by the assemblage of infinite chains $[MoPO_8]_\infty$ running along **c**. Similar chains in which one PO_4 tetrahedron alternates with one MoO_6 octahedron have previously been observed in many molybdenum (V) phosphates such as $MoPO_5$ (*1*), $MoAlP_2O_9$ (*13*), and $NaMo_2P_3O_{13}$ (*10*). Nevertheless the geometry obtained here (Fig. 3c) forms a zigzag configuration particular to this framework.

The distribution of the potassium cations in the tunnel is remarkable since the three kinds of independant potassium ions do not sit at the intersections of the two sorts of tunnels. The K(1) atoms are located on the symmetry center, i.e., on the axis of the tunnels parallel to ⟨110⟩ and at the bondary between two tunnels parallel to [001]. These cations exhibit an eightfold coordination forming an almost regular bipyramid (Fig. 4). The K–O distances obtained for these cations (Table V), ranging from 2.686 to

TABLE V

DISTANCES (Å) AND ANGLES (°) IN MoO$_6$ AND PO$_4$ POLYHEDRA AND MEAN K–O DISTANCES (Å)[a]

Mo(1)	O(1)	O(2)	O(3)	O(4)	O(5)	O(6)
O(1)	1.683(5)	2.810(7)	2.763(7)	2.757(7)	2.714(6)	3.864(9)
O(2)	97.9(2)	2.031(4)	4.095(9)	2.941(7)	2.821(6)	2.897(6)
O(3)	93.7(2)	168.4(2)	2.085(4)	2.887(6)	2.661(6)	2.803(6)
O(4)	93.7(2)	91.5(2)	87.8(2)	2.077(4)	3.901(8)	2.736(7)
O(5)	99.9(2)	93.3(2)	84.7(2)	164.8(2)	1.859(4)	2.776(6)
O(6)	172.2(2)	86.6(2)	81.9(2)	79.7(2)	86.1(2)	2.190(5)

Mo(2)	O(5)	O(1)	O(8)	O(9)	O(10)	O(11)
O(5)	1.868(4)	2.697(6)	3.952(8)	2.785(6)	2.732(6)	2.823(6)
O(7)	98.3(2)	1.695(5)	2.706(7)	2.930(7)	2.744(7)	3.825(9)
O(8)	171.1(2)	90.5(2)	2.096(5)	2.877(6)	2.922(6)	2.778(6)
O(9)	91.2(2)	103.5(2)	88.5(2)	2.027(5)	4.036(9)	2.738(6)
O(10)	88.2(2)	93.6(2)	89.5(2)	162.8(2)	2.055(5)	2.720(7)
O(11)	89.2(2)	170.5(2)	81.9(2)	82.0(2)	80.8(2)	2.143(4)

P(1)	O(2^{iv})	O(4^{viii})	O(6)	O(11)
O(2^{iv})	1.550(4)	2.536(6)	2.500(6)	2.533(6)
O(4^{viii})	109.7(3)	1.552(5)	2.509(7)	2.449(6)
O(6)	108.5(3)	109.0(3)	1.530(5)	2.550(6)
O(11)	110.9(3)	105.5(3)	113.2(3)	1.525(4)

P(2)	O(3)	O(8^{v})	O(9^{iv})	O(10)
O(3)	1.545(4)	2.534(6)	2.478(6)	2.599(7)
O(8^{v})	110.1(3)	1.546(5)	2.542(6)	2.482(1)
O(9^{iv})	106.8(3)	110.8(3)	1.541(4)	2.499(6)
O(10)	114.4(3)	106.7(3)	108.1(3)	1.548(5)

K(1)–O(1^{i})	2.849(5)
–O(1)	2.849(5)
–O(5^{i})	2.781(4)
–O(5)	2.781(4)
–O(7)	2.812(5)
–O(7^{i})	2.812(5)
–O(8^{vi})	2.686(5)
–O(8^{v})	2.686(5)

K(2)–O(1^{viii})	2.986(5)
–O(4)	2.896(5)
–O(6)	3.250(5)
–O(7^{ii})	3.109(6)
–O(7^{ix})	2.947(6)
–O(9^{vii})	3.033(6)
–O(10^{ii})	2.968(5)
–O(11^{vii})	2.822(6)

K(3)–O(2^{iv})	2.886(7)
–O(3^{iii})	2.871(6)
–O(3)	2.744(6)
–O(4i^{ii})	2.836(6)
–O(4)	2.979(6)
–O(6)	3.213(6)
–O(6^{iv})	2.928(6)

Symmetry code

i	$-x$	$-y$	$-z$
ii	$1 + x$	y	z
iii	$1 - x$	$-y$	$1 - z$
iv	x	$\frac{1}{2} - y$	$\frac{1}{2} + z$
v	$-x$	$-\frac{1}{2} + y$	$\frac{1}{2} - z$
vi	x	$\frac{1}{2} - y$	$-\frac{1}{2} + z$
vii	$1 - x$	$-\frac{1}{2} + y$	$\frac{1}{2} - z$
viii	$1 - x$	$\frac{1}{2} + y$	$\frac{1}{2} - z$
ix	$1 + x$	$\frac{1}{2} - y$	$\frac{1}{2} + z$

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[a] The Mo–O or P–O distances are on the diagonals of the respective matrices. Above are the O(i) · · · O(j) distances and below are the O(i)–Mo–O(j) or O(i)–P–O(j) angles.

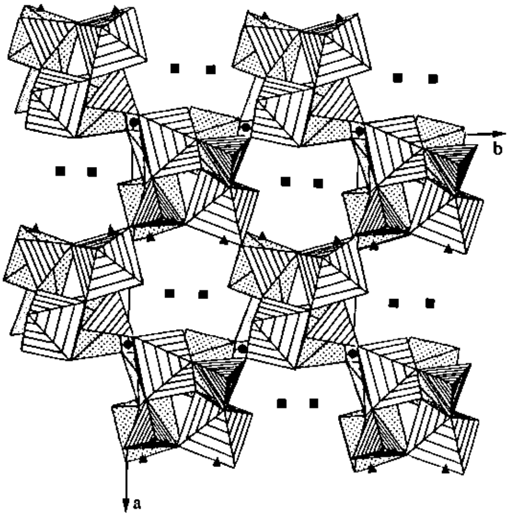

FIG. 1. Projection of $K_2Mo_2P_2O_{11}$ along [001]: (●) K_1, (■) K_2, (▲) K_3.

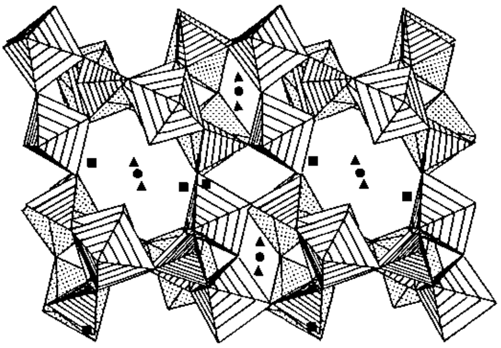

FIG. 2. Projection of $K_2Mo_2P_2O_{11}$ along [$\bar{1}$10]: (●) K_1, (■) K_2, (▲) K_3.

2.849 Å, show that they are strongly linked to the surrounding oxygen atoms, in agreement with the normal value of their thermal factor, close to 1.52 $Å^2$. The K(2) atoms, which are located in the [001] tunnels, are also close to the axes of these tunnels (Fig. 1) and sit in the ⟨110⟩ tunnels close to the wall (Fig. 2). These cations are characterized by an eightfold coordination and exhibit large K–O distances (Table V) ranging from 2.82 to 3.25 Å, showing that they are much less strongly bonded to oxygen in agreement with their high thermal factor of 4.2 $Å^2$. The K(3) atoms are located near the axes of the ⟨110⟩ tunnels (Fig. 2) and sit in the [001] tunnels close to the walls of the latter (Fig. 1); the K(3) sites are split over two positions related by the symmetry center, which are half occupied owing to their too short distance. This cation is characterized by a sevenfold coordination with K–O distances, ranging from 2.744 to 3.213 Å, significantly lower than those obtained for K(2), in agreement with its lower *B* factor of 2.42 $Å^2$.

Concluding Remarks

These results confirm the extraordinary potential of Mo(V) phosphate chemistry in

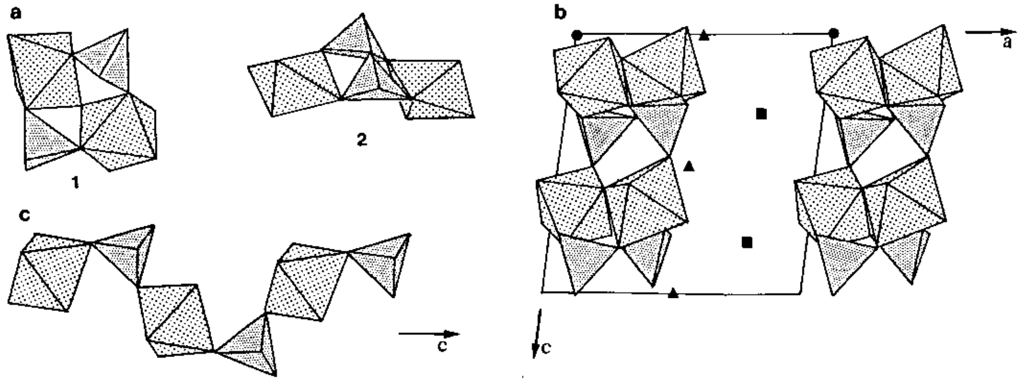

FIG. 3. (a) $Mo_2P_2O_{15}$ unis (1) in $K_2Mo_2P_2O_{11}$, (2) in α-$KMo_2P_3O_{13}$. (b) $[Mo_2P_2O_{13}]_\infty$ columns running along **c**: (●) K_1, (■) K_2, (▲) K_3. (c) The $MoPO_8$ chain in $K_2Mo_2P_2O_{11}$.

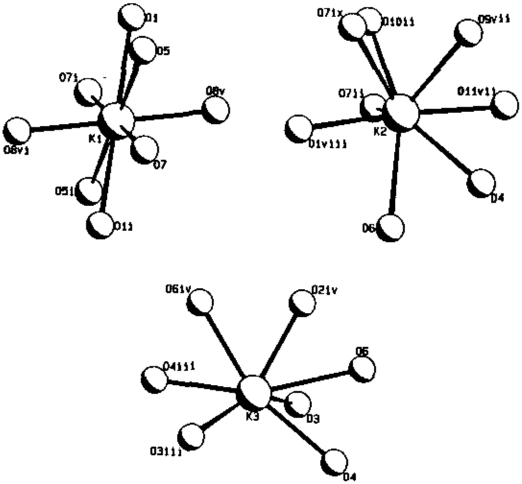

FIG. 4. The coordination of potassium in $K_2Mo_2P_2O_{11}$.

agreement with those recently obtained in this field. The ability to form mixed frameworks with various structures is due to the ability of Mo(V) to form octahedra with a free apex, which introduces a great flexibility in accommodating PO_4 tetrahedra. The large size of the tunnels allows cations larger than potassium, such as Rb^+ or Tl^+, to be inserted. The large B factors of some of the potassium ions suggest a possible mobility of the latter in this intersecting tunnel structure. The ion exchange properties of this new oxide will be investigated.

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