

## Synthesis and Structural Characterization of $K(\text{MoO}_2)(\text{PO}_4) \cdot \text{H}_2\text{O}$ , and Its Topotatic Reaction to Form $\text{KMoO}_2\text{PO}_4$

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$K(\text{MoO}_2)(\text{PO}_4) \cdot \text{H}_2\text{O}$  crystallized in the monoclinic space group  $P2_1/n$  with lattice parameters  $a = 5.846(1) \text{ \AA}$ ,  $b = 8.626(1) \text{ \AA}$ ,  $c = 12.364(1) \text{ \AA}$ ,  $\beta = 102.80(1)^\circ$ , and  $z = 4$ . It was synthesized under hydrothermal conditions from a mixture of  $\text{MoO}_3$ ,  $\text{MoO}_2$ , and  $\text{K}_2\text{HPO}_4$ . The structure was refined to  $R = 0.037$  with 1223 reflections for which  $I > 3\sigma$ . Its structure consists of alternating molybdenum–oxygen octahedra and phosphate tetrahedra forming four- and eight-membered rings. The rings are connected through alternating polyhedra to form sheets. Potassium ions are located between the layers above and below the eight-membered ring. Upon heating to  $500^\circ\text{C}$  water splits out and the layers collapse to form the three-dimensional molybdenum phosphate  $\text{KMoO}_2\text{PO}_4$ . This compound crystallizes in the orthorhombic space group  $Fddd$  with the cell parameters:  $a = 12.209(4) \text{ \AA}$ ,  $b = 15.535(2) \text{ \AA}$ ,  $c = 11.149(4) \text{ \AA}$ . The structure was determined and refined to  $R = 0.046$  using 464 reflections with  $I > 3\sigma$ . The coalescence of layers results in a three-dimensional framework structure containing tunnels in which the  $\text{K}^+$  ions reside. © 1991 Academic Press, Inc.

### Introduction

A number of molybdenum phosphorus oxides have been reported in the recent literature. These oxides consist of molybdenum–oxygen octahedra and phosphate tetrahedra. The rigid polyhedra do not easily form close-packed structures but instead tend to form microporous framework structures with cations located in tunnels or between layers. The oxidation state of molybdenum in these compounds varies from +3 to +6. These molybdenum framework structures with various oxidation states may be of interest as catalysts or as ion exchangers.

Recent examples of molybdenum phosphorus oxides with tunnel structures include  $\text{AMo}^{(\text{III})}\text{P}_2\text{O}_7$  ( $A = \text{K}, \text{Cs}, \text{and Rb}$ ) (1, 2a, 2b) (isostructural with  $\text{KFeP}_2\text{O}_7$ ) (3),  $\text{K}_{0.17}\text{Mo}^{(\text{III}, \text{IV})}\text{P}_2\text{O}_7$  (1),  $\text{AMo}^{(\text{IV})}\text{P}_2\text{O}_{12}$  ( $A = \text{K}, \text{Rb}, \text{and Tl}$ ) (4),  $\text{A}_4\text{Mo}^{(\text{V})}_8\text{P}_{12}\text{O}_{52}$  ( $A = \text{K}, \text{Cs}, \text{Rb}, \text{and Tl}$ ) (5, 6), and  $\text{AMo}^{(\text{V})}_5\text{P}_8\text{O}_{33}$  ( $A = \text{Ag}, \text{Li}, \text{Na}, \text{Ca}, \text{Sr}, \text{Ba}, \text{and Pb}$ ) (7).  $\text{Cs}_2\text{Mo}^{(\text{V})}_4\text{P}_6\text{O}_{26}$  (6) is an example of a layered structure. All these compounds were synthesized using solid state reactions where appropriate amounts of starting materials are ground together and then reacted at high temperatures in sealed tubes. These compounds are made up of molybdenum–oxygen octahedra, phosphate tetrahedra, and pyrophosphate groups. Recently, Hausalter and Lai (8), using a hydrothermal

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technique, synthesized  $(\text{Et}_4\text{N})_6[\text{Na}_{14}\text{Mo}^{(\text{V})}_{24}\text{P}_{17}\text{O}_{97}(\text{OH})_{31}] \cdot x\text{H}_2\text{O}$ . In this compound water and  $\text{Et}_4\text{N}$  are located within tunnels formed from the sharing arrangement of octahedra and tetrahedra.

We have also been applying hydrothermal techniques for the synthesis of molybdates (9, 10, 11) and more recently have examined the phosphomolybdate system. At this time we are reporting on the new compound  $\text{K}(\text{MoO}_2)(\text{PO}_4) \cdot \text{H}_2\text{O}$  which has been synthesized this way and its topotatic reaction to form  $\text{KMoO}_2\text{PO}_4$ .  $\text{K}(\text{MoO}_2)(\text{PO}_4) \cdot \text{H}_2\text{O}$  consists of alternating molybdenum-oxygen octahedra and phosphate tetrahedra arranged to form rings of four or eight polyhedra. The ring designation here is similar to that used in the description of zeolites (12) where an Si-O-Al or Si-O-Si bridge is considered as a single side of the ring. In the present case each Mo-O-P linkage represents a ring side. The rings connect through shared oxygen atoms to form sheets. The potassium ions are located between the sheets above and below the larger ring. The compound has both layered and tunnel structural features. Upon heating at 500°C for 2 days, water splits out from between the layers forming Mo-O-P crosslinks. The original layers are still intact but offset to form the crosslinks.  $\text{KMoO}_2\text{PO}_4$  is therefore a three-dimensional molybdenum phosphate with interconnecting tunnels.

### Synthesis and Structure Determination

As stated,  $\text{K}(\text{MoO}_2)(\text{PO}_4) \cdot \text{H}_2\text{O}$  crystals form under hydrothermal conditions. A mixture of 500 mg of  $\text{MoO}_3$ ,  $\text{MoO}_2$ , and  $\text{K}_2\text{HPO}_4$  in a 2 : 1 : 1 ratio was placed in an 8-mm outer diameter sodium borosilicate glass tube along with enough 5.3 M  $\text{H}_3\text{PO}_4$  to fill the 17.5-cm-long tube  $\frac{1}{3}$  full of solid and solution. The tube was placed in a tube furnace at  $180 \pm 5^\circ\text{C}$  for 4 days. Clear crystals of  $\text{K}(\text{MoO}_2)(\text{PO}_4) \cdot \text{H}_2\text{O}$  formed at the cooler end of the tube as well as yellow-

green crystals of  $\text{Na}_2(\text{MoOPO}_4)_2\text{H}_2\text{PO}_4 \cdot \text{H}_2\text{O}$  which formed on the side of the tube.  $\text{Na}_2(\text{MoOPO}_4)_2\text{H}_2\text{PO}_4 \cdot \text{H}_2\text{O}$  will be reported on in a subsequent paper. The original clear solution turned dark blue during the heating process. Crystals of  $\text{K}(\text{MoO}_2)(\text{PO}_4) \cdot \text{H}_2\text{O}$  were heated in a ceramic crucible for 2 days at 500°C to form  $\text{KMoO}_2\text{PO}_4$  crystals by a condensation reaction to remove  $\text{H}_2\text{O}$ .

A single clear crystal of  $\text{K}(\text{MoO}_2)(\text{PO}_4) \cdot \text{H}_2\text{O}$  or  $\text{KMoO}_2\text{PO}_4$  ( $0.2 \times 0.1 \times 0.1 \text{ mm}^3$  and  $0.2 \times 0.1 \times 0.05 \text{ mm}^3$ , respectively) was mounted on a glass fiber. Data were collected on a Rigaku AFC5 rotating anode automated single crystal diffractometer using graphite-monochromatized  $\text{MoK}\alpha$  radiation. All crystal data collection, data processing, and structure solution were performed on a Digital Equipment Corp. Micro VAX II computer using the TEXSAN (13) structure solving program library. The unit cell was determined and refined using 25 high angle reflections ( $20^\circ < 2\theta (\text{MoK}\alpha) < 40^\circ$ ). All crystal data, data collection parameters, and results of analysis are listed in Table I. Three reflections were monitored at 150 reflection intervals and no significant decay was detected over the course of data collection. An empirical absorption correction for  $\text{K}(\text{MoO}_2)(\text{PO}_4) \cdot \text{H}_2\text{O}$  or  $\text{KMoO}_2\text{PO}_4$  with transmission factors of 0.94–1.00 or 0.85–1.00, respectively was applied. In both structures the molybdenum atom was located using standard Patterson techniques with the remaining atoms being located in subsequent difference Fourier syntheses. Final refinement was performed on those data having  $I > 3\sigma(I)$ . All atoms were refined anisotropically with a full matrix least squares refinement to a final  $R_F = 0.036$  and  $R_{wF} = 0.043$  for  $\text{K}(\text{MoO}_2)(\text{PO}_4) \cdot \text{H}_2\text{O}$  and  $R_F = 0.046$  and  $R_{wF} = 0.054$  for  $\text{KMoO}_2\text{PO}_4$ . Hydrogen atoms could not be located in  $\text{K}(\text{MoO}_2)(\text{PO}_4) \cdot \text{H}_2\text{O}$  even when  $2\sigma$  data were used. Atomic coordinates and estimated standard deviations are listed in Table II. The largest peak in the final difference

TABLE I  
SUMMARY OF CRYSTAL DATA, INTENSITY MEASUREMENTS, AND STRUCTURE REFINEMENT PARAMETERS FOR  
 $\text{K}(\text{MoO}_2)(\text{PO}_4) \cdot \text{H}_2\text{O}$  AND  $\text{KMoO}_2\text{PO}_4$

Crystal data	$\text{K}(\text{MoO}_2)(\text{PO}_4) \cdot \text{H}_2\text{O}$	$\text{KMoO}_2\text{PO}_4$
Formula weight	280.02	262.01
Crystal system	Monoclinic	Orthorhombic
Lattice parameters	$a = 5.846(1) \text{ \AA}$ $b = 8.626(1) \text{ \AA}$ $c = 12.364(1) \text{ \AA}$ $\beta = 102.80(1)^\circ$ $V = 608.0(2) \text{ \AA}^3$	$a = 12.209(4) \text{ \AA}$ $b = 15.535(2) \text{ \AA}$ $c = 11.149(4) \text{ \AA}$ $V = 2114.6(9) \text{ \AA}^3$
Space group	$P2_1/n$ (No. 14)	$Fddd$ (No. 70)
Z value	4	16
$D_{\text{calc}}$	3.06 g/cm <sup>3</sup>	3.29 g/cm <sup>3</sup>
$\mu(\text{MoK}\alpha)$	30.32 cm <sup>-1</sup>	34.63 cm <sup>-1</sup>
Radiation	MoK $\alpha$ ( $\lambda = 0.71069$ ) Graphite-monochromated	
Temperature	23 $\pm$ 1°C	23 $\pm$ 1°C
Maximum $2\theta$	60.0°	60.0°
No. of reflections	2055 total 1892 unique	869 total 869 unique
Corrections	Lorentz-polarization	Lorentz-polarization
Empirical absorption	0.94–1.00	0.85–1.00
Secondary extinction	0.18337 $\times 10^{-5}$	Not applied
Reflections included	1223 with $I > 3.00 \sigma(I)$	464 with $I > 3.00 \sigma(I)$
Parameters refined	92	43
Residuals: $R$ ; $R_w$	0.037; 0.048	0.046; 0.054
Goodness of fit indicator	1.10	1.20
Maximum shift in final cycle	0.28	0.01
Largest peak in final diff. map	0.93 e/ $\text{\AA}^3$	1.02 e/ $\text{\AA}^3$

map was 0.93 e/ $\text{\AA}^3$  and was located near the molybdenum atom. To confirm the presence of hydrogen atoms an infrared spectrum (KBr disk, Bio-Rad FTS-40) and a thermogravimetric curve (Dupont Thermal Analyst 2000, heating rate of 4°C/min under N<sub>2</sub>) were obtained.

## Results

$\text{K}(\text{MoO}_2)(\text{PO}_4) \cdot \text{H}_2\text{O}$  is made up of distorted molybdenum–oxygen octahedra and phosphate tetrahedra. Selected bond distances and angles are listed in Table III. The four-membered ring structure is shown in Fig. 1A. This ring is formed by the phosphate group bridging Mo atoms through O4

and O5. An eight-membered ring of alternating molybdenum and phosphorus polyhedra is formed by connecting four, four-membered rings through O6 (Fig. 1B). Together the four- and eight-membered rings form a molybdenum phosphorus oxide sheet (Fig. 2). The sheets are held together by potassium ions positioned between the layers (Fig. 3). Two potassium ions which align the rings so that tunnel-like structures are formed running perpendicular to the layers are located above as well as below each eight-membered ring. The potassium is bonded to nine oxygen atoms with distances ranging from 2.71 to 3.22 Å. Similar eight-membered rings of alternating polyhedra are found in  $\text{K}_{0.17}\text{MoP}_2\text{O}_7$  (1) and  $\text{AgMo}_5\text{P}_8\text{O}_{33}$

TABLE II  
 POSITIONAL PARAMETERS AND  $B_{eq}$ 

Atoms	x	y	z	$B_{eq}(\text{\AA}^2)^a$
A. $\text{K}(\text{MoO}_2)(\text{PO}_4) \cdot \text{H}_2\text{O}$				
Mo	0.2004(1)	0.23945(5)	0.11571(4)	0.86(2)
K	0.3240(3)	0.1135(2)	-0.1747(1)	1.78(5)
P1	-0.1303(3)	0.3663(2)	-0.1257(1)	0.81(5)
O1	-0.0466(8)	0.1595(6)	0.1403(4)	1.8(2)
O2	0.3397(9)	0.0868(5)	0.0721(4)	1.9(2)
O3	0.5274(7)	0.3796(5)	0.1080(3)	1.3(1)
O4	0.1048(8)	0.4648(5)	0.1582(4)	1.2(1)
O5	0.0902(8)	0.3173(6)	-0.0386(3)	1.4(2)
O6	0.3780(8)	0.2364(5)	0.2729(3)	1.4(1)
O7	-0.3543(8)	0.3375(5)	-0.0865(4)	1.4(2)
B. $\text{KMoO}_2\text{PO}_4$				
Mo	0.40217(9)	0.125	0.125	0.68(4)
K	0.125	0.125	0.3453(3)	2.2(1)
P	0.375	0.0099(2)	-0.125	0.7(1)
O1	0.5374(5)	0.0432(4)	0.1858(6)	1.1(3)
O2	0.4314(5)	0.0714(4)	-0.0328(6)	0.8(2)
O3	0.3137(7)	0.0486(5)	0.1730(7)	1.9(3)

<sup>a</sup> The isotropic equivalent thermal parameter is defined as  $B_{eq} = \frac{1}{3}(a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + 2ab(\cos \gamma)\beta_{12} + 2ac(\cos \beta)\beta_{13} + 2bc(\cos \alpha)\beta_{23})$ .

(7) but in these compounds the phosphorus tetrahedra are fused to a second tetrahedron forming pyrophosphate groups. The  $\text{P}_2\text{O}_7$  groups connect the rings to form tunnels. In these two cases the cation is located in the center of a circular ring formed by alternating molybdenum and phosphorus polyhedra, while in  $\text{K}(\text{MoO}_2)(\text{PO}_4) \cdot \text{H}_2\text{O}$  the ring

 TABLE III  
 SELECTED INTERATOMIC DISTANCES ( $\text{\AA}$ ) IN  $\text{K}(\text{MoO}_2)(\text{PO}_4) \cdot \text{H}_2\text{O}$ 

Atom(1)	Atom(2)	Distance	ADC <sup>a</sup>	Atom(1)	Atom(2)	Distance	ADC <sup>a</sup>
Mo	O1	1.688(5)	1	K	O1	2.943(5)	3
Mo	O2	1.698(5)	1	K	O1	3.226(5)	4
Mo	O3	2.281(4)	1	K	O2	2.712(5)	3
Mo	O4	2.121(4)	1	K	O2	3.041(5)	1
Mo	O5	1.991(4)	1	K	O3	2.858(4)	4
Mo	O6	1.994(4)	1	K	O4	2.988(4)	4
Mo	O4	1.527(4)	3	K	O5	2.968(5)	1
P	O5	1.544(4)	1	K	O6	2.844(5)	4
P	O6	1.547(4)	4	K	O7	2.748(5)	1
P	O7	1.514(5)	1				
P							

<sup>a</sup> The ADC (atom designator code) specifies the position of atom(2) in the crystal relative to the position of atom(1) as given above. The symmetry operators relevant to this structure are (1)  $+x, +y, +z$ ; (2)  $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$ ; (3)  $-x, -y, -z$ ; (4)  $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$ .

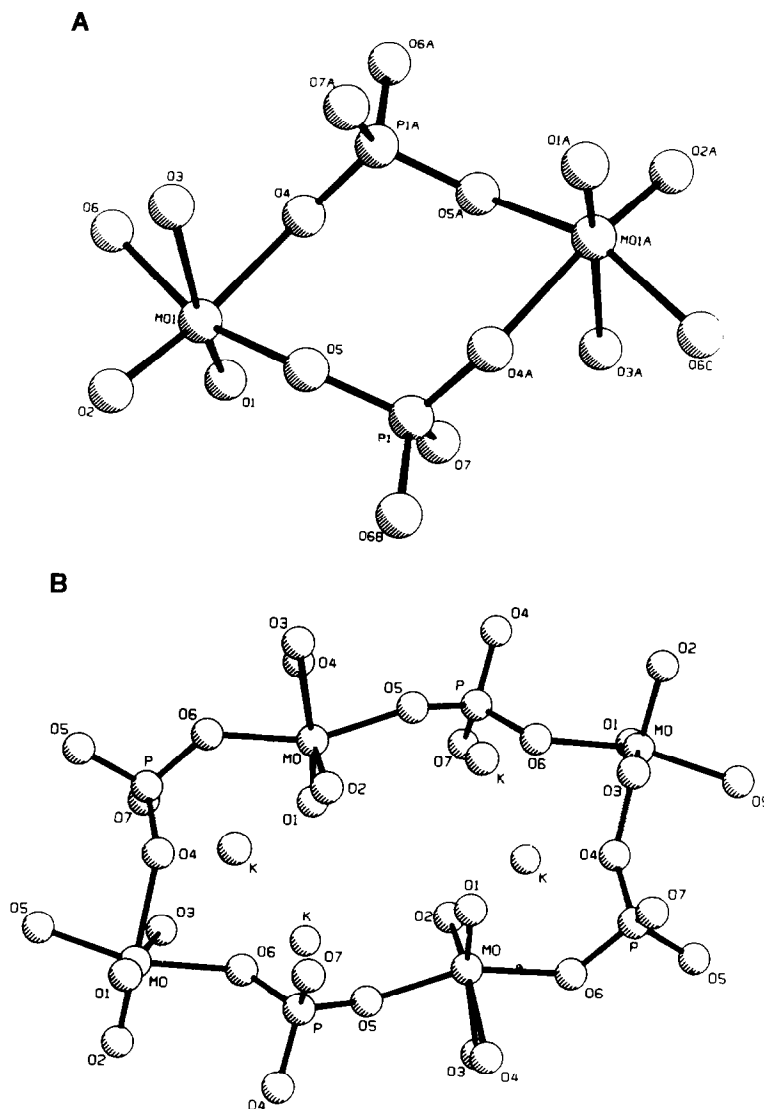


FIG. 1. (A) A PLUTO representation of the four-membered ring of molybdenum-oxygen octahedra and phosphate tetrahedra found in  $K(\text{MoO}_2)(\text{PO}_4) \cdot \text{H}_2\text{O}$ , and (B) a PLUTO representation of the eight-membered ring found in  $K(\text{MoO}_2)(\text{PO}_4) \cdot \text{H}_2\text{O}$ . Each Mo-O-P unit is counted as a single side of the ring.

is compressed and appears elongated into a more elliptical shape.  $K(\text{MoO}_2)(\text{PO}_4) \cdot \text{H}_2\text{O}$  and  $(\text{Et}_4\text{N})_6[\text{Na}_{14}\text{Mo}^{(V)}_{24}\text{P}_{17}\text{O}_{97}(\text{OH})_{31}] \cdot x\text{H}_2\text{O}$  (8) differ from the solid state reaction products in that hydrogen atoms are present and pyrophosphate groups are absent.

Since the hydrogen atoms could not be located in the X-ray structure determination, other methods were explored. The hydrogen atoms are present in the structure as either coordinated  $\text{H}_2\text{O}$  or two OH groups. An infrared spectrum of the compound ex-

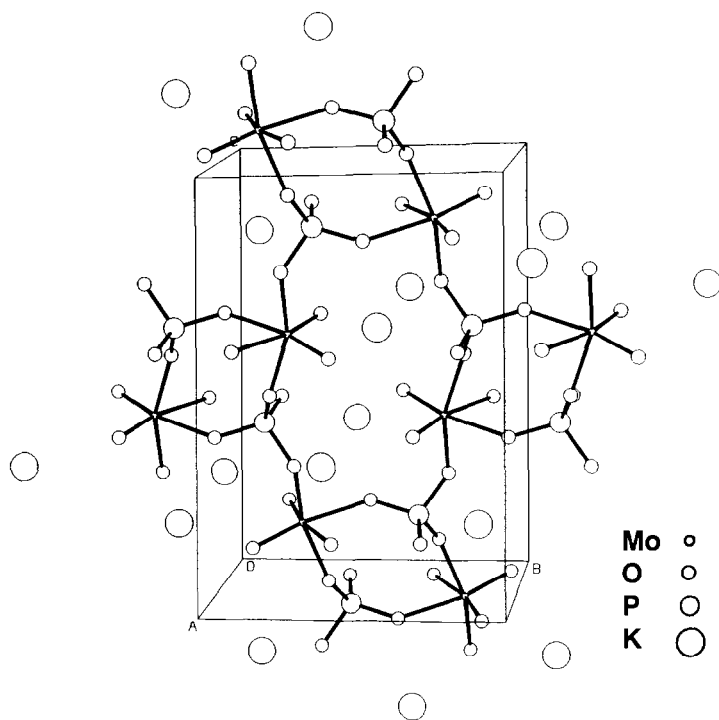


FIG. 2. A portion of a molybdenum phosphate sheet found in  $\text{K}(\text{MoO}_2)(\text{PO}_4) \cdot \text{H}_2\text{O}$  built up by alternation of eight- and four-membered rings.

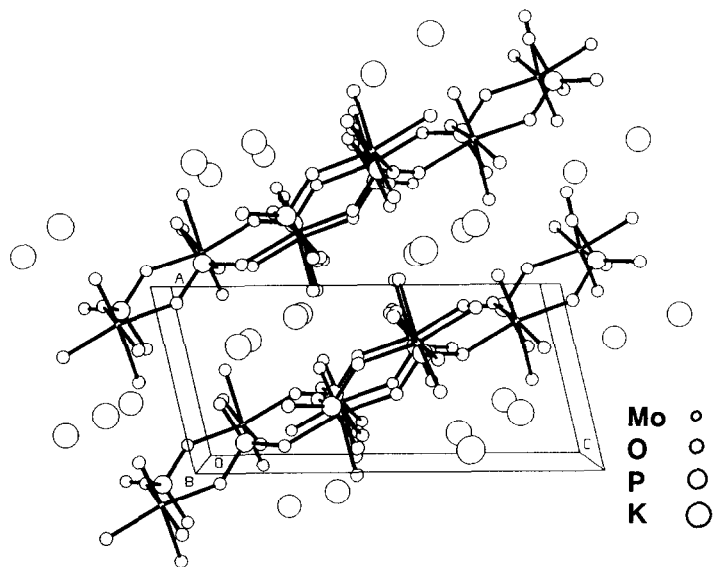


FIG. 3. Unit cell of  $\text{K}(\text{MoO}_2)(\text{PO}_4) \cdot \text{H}_2\text{O}$  showing the molybdenum phosphate layers and potassium atoms between the layers.

TABLE IV  
 SELECTED INTERATOMIC DISTANCES (Å) IN  $\text{KMoO}_2\text{PO}_4$ 

Atom(1)	Atom(2)	Distance	ADC <sup>a</sup>	Atom(1)	Atom(2)	Distance	ADC <sup>a</sup>
Mo	O1	2.191(7)	1	K	O1	2.952(8)	18
Mo	O1	2.191(7)	2	K	O1	2.952(8)	19
Mo	O2	1.979(6)	1	K	O1	3.298(7)	21
Mo	O2	1.979(6)	2	K	O1	3.298(7)	24
Mo	O3	1.692(7)	1	K	O2	2.851(7)	17
Mo	O3	1.692(7)	2	K	O2	2.851(7)	20
Mo	O1	1.512(7)	5	K	O3	2.806(8)	21
P	O1	1.512(7)	23	K	O3	2.806(8)	24
P	O2	1.563(6)	1	K	O3	3.226(9)	1
P	O2	1.563(6)	19	K	O3	3.226(9)	4

<sup>a</sup> The ADC (atom designator code) specifies the position of atom(2) in the crystal relative to the position of atom(1) as given above. The symmetry operators relevant to this structure are (1)  $+x, +y, +z$ ; (2)  $+x, \frac{1}{4} - y, \frac{1}{4} - z$ ; (4)  $\frac{1}{4} - x, \frac{1}{4} - y, +z$ ; (5)  $-x, -y, -z$ ; (17)  $\frac{1}{2} + x, +y, \frac{1}{2} + z$ ; (18)  $\frac{1}{2} + x, \frac{1}{4} - y, \frac{3}{4} - z$ ; (19)  $\frac{3}{4} - x, +y, \frac{3}{4} - z$ ; (20)  $\frac{3}{4} - x, \frac{1}{4} - y, \frac{1}{2} + z$ ; (21)  $\frac{1}{2} - x, -y, \frac{1}{2} - z$ ; (23)  $\frac{3}{4} - x, -y, \frac{3}{4} + z$ ; (24)  $\frac{3}{4} + x, \frac{1}{4} + y, \frac{1}{2} - z$ .

hibited a broad band centered at  $3100\text{ cm}^{-1}$  and another at  $1545\text{ cm}^{-1}$ , which can be assigned to OH and water, respectively (Fig. 4). A thermogravimetric analysis (TGA) showed a single weight loss of 6.2% between 294 and  $455^\circ\text{C}$  (Fig. 5). This decrease in weight is roughly equivalent to the loss of a mole of water (6.43% theoretical). However, the temperature at which the water splits out is the usual temperature range for OH condensation, but higher than expected for coordinated  $\text{H}_2\text{O}$  loss. The weight

gain of less than 1% observed after the water split out and before decomposition of the sample at  $875^\circ\text{C}$  may be due to the reaction of the sample with a slight amount of  $\text{O}_2$  in the  $\text{N}_2$  stream. These experiments indicate that the two hydrogen atoms are most likely present as water but tightly held within the structure. To determine where the water is located the bonding of oxygen with molybdenum, phosphorus, and potassium was examined in more detail.

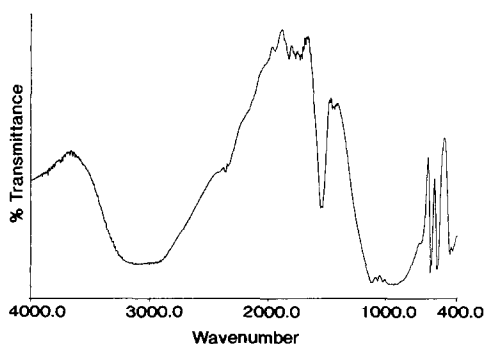


FIG. 4. Infrared transmission spectrum of  $\text{K}(\text{MoO}_2)(\text{PO}_4) \cdot \text{H}_2\text{O}$ .

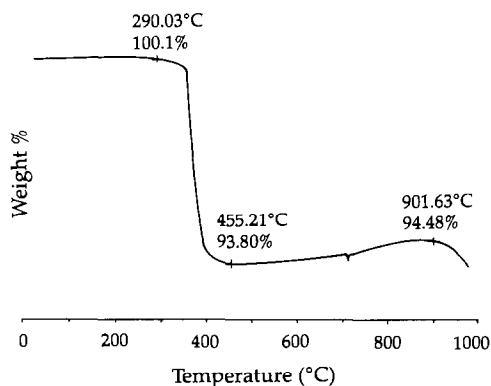


FIG. 5. A thermogravimetric analysis curve of  $\text{K}(\text{MoO}_2)(\text{PO}_4) \cdot \text{H}_2\text{O}$  taken under a constant  $\text{N}_2$  flow at a heating rate of  $4^\circ/\text{min}$ .

TABLE V  
 SELECTED ANGLES (°)

Atom	Atom	Atom	Angle	Atom	Atom	Atom	Angle
A. $K(MoO_2)(PO_4) \cdot H_2O$							
O1	Mo	O2	103.3(2)	O4	Mo	O5	83.2(2)
O1	Mo	O3	169.2(2)	O4	Mo	O6	83.2(2)
O1	Mo	O4	92.7(2)	O5	Mo	O6	158.0(2)
O1	Mo	O5	101.7(2)	O4	P	O5	109.2(3)
O1	Mo	O6	96.1(2)	O4	P	O6	108.0(3)
O2	Mo	O3	86.1(2)	O4	P	O7	112.5(3)
O2	Mo	O4	163.9(2)	O5	P	O6	103.4(3)
O2	Mo	O5	91.9(2)	O5	P	O7	112.3(3)
O2	Mo	O6	96.5(2)	O6	P	O7	111.0(3)
O3	Mo	O4	78.1(2)	Mo	O4	P	139.7(3)
O3	Mo	O5	83.0(2)	Mo	O5	P	143.5(3)
O3	Mo	O6	77.4(2)	Mo	O6	P	133.7(3)
B. $KMoO_2PO_4$							
O1	Mo	O1	82.2(4)	O2	Mo	O3	97.4(3) × 2
O1	Mo	O2	84.0(3) × 2	O3	Mo	O3	100.6(6)
O1	Mo	O2	80.4(3) × 2	O1	P	O1	113.8(6)
O1	Mo	O3	88.6(3) × 2	O1	P	O2	108.5(4) × 2
O1	Mo	O3	170.4(4) × 2	O1	P	O2	110.5(4) × 2
O2	Mo	O2	159.2(4)	O2	P	O2	104.7(5)
O2	Mo	O3	95.8(3) × 2				

The distorted molybdenum octahedra consist of two short, two medium, and two long Mo–O bond distances with three of the oxygens shared (with phosphorus) and three unshared oxygen atoms. The three shared oxygen atoms have two midlength bond distances both at 1.99 Å, and a long bond distance of 2.12 Å. The three unshared oxygen atoms have the two shortest Mo–O bonds, 1.69 and 1.70 Å, and the longest Mo–O bond distance of 2.28 Å. This longest distance is to O3, which has one contact to potassium at 2.86 Å while O1 and O2 each have two potassium contacts at 2.94, 3.23 Å and 2.75, 3.04 Å, respectively. Thus it appears that O3 is a coordinated water molecule. With this assignment the formula is  $K(MoO_2)(PO_4) \cdot H_2O$ .

The phosphorus tetrahedron is quite regular with P–O bond distances from 1.51 to

1.55 Å and O–P–O angles between 103° and 112° which indicate phosphorus is located at the center of the tetrahedron. The phosphorus tetrahedron has one unshared oxygen atom, O7, with the shortest phosphorus oxygen distance of 1.51 Å. While all the phosphorus oxygen atoms appear to have single bond characteristics and all have similar oxygen potassium distances ranging from 2.75 to 2.99 Å, only O7 is not bonded to molybdenum. O3 and O7 extend out of the plane of the molybdenum phosphate sheet (Fig. 6) and have the shortest contacts between oxygen atoms on different polyhedra at 2.634(7) and 2.670(6) Å. The second shortest oxygen–oxygen contact is between O3 and O7 atoms on adjacent sheets with equivalent O7 and O3 atoms on either of the sheets above and below (Fig. 6). These oxygen atoms alternate on adjacent sheets to form



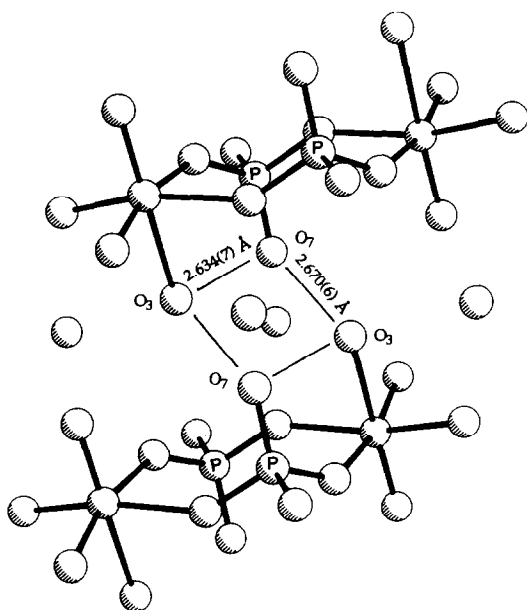


FIG. 6. Short oxygen-oxygen contacts between  $\text{O}_7$  and  $\text{O}_3$  on adjacent molybdenum phosphorus layers in  $\text{K}(\text{MoO}_2)(\text{PO}_4) \cdot \text{H}_2\text{O}$  illustrating the hydrogen bonding.

the corners of a parallelogram with edges of 2.634(7) Å and 2.670(6) Å and angles of 101.8° and 78.18°. The location of the water molecule on  $\text{O}_3$  indicates that not only the potassium ion but hydrogen bonding holds the molybdenum phosphate sheets together. This extensive hydrogen bonding accounts for the high temperature of water removal seen in the TGA curve. The location of the water molecule between the layers suggests that the layers could easily collapse to form a three-dimensional framework structure. This indeed happens when  $\text{K}(\text{MoO}_2)(\text{PO}_4) \cdot \text{H}_2\text{O}$  is heated at 500°C for 2 days.

In the new phase, the molybdenum octahedra and phosphorus tetrahedra have similar bond lengths and angles (Tables II and III) to their counterparts in the unheated phase. The original molybdenum phosphate sheet is quite similar though not identical in both structures. By looking down the diagonal of the unit cell the eight-membered ring

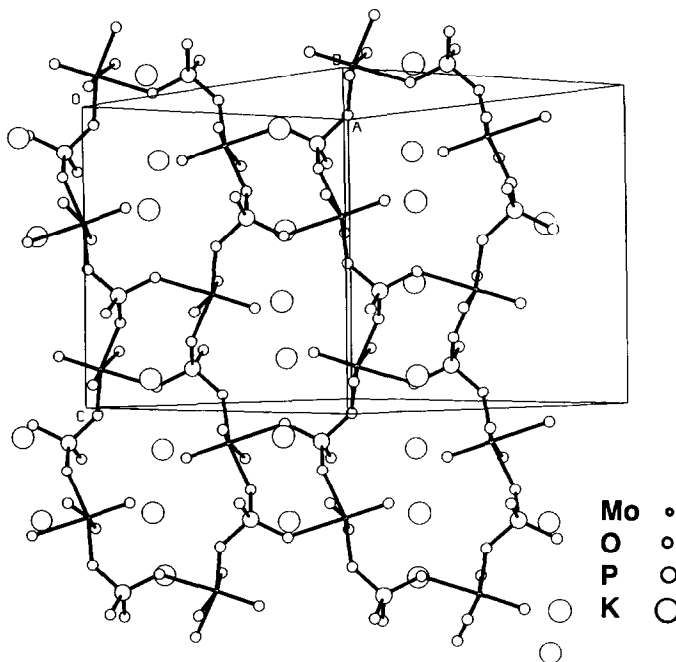


FIG. 7. The molybdenum phosphate sheet in  $\text{KMoO}_2\text{PO}_4$  as seen down the diagonal of the unit cell, showing the eight- and four-membered rings.

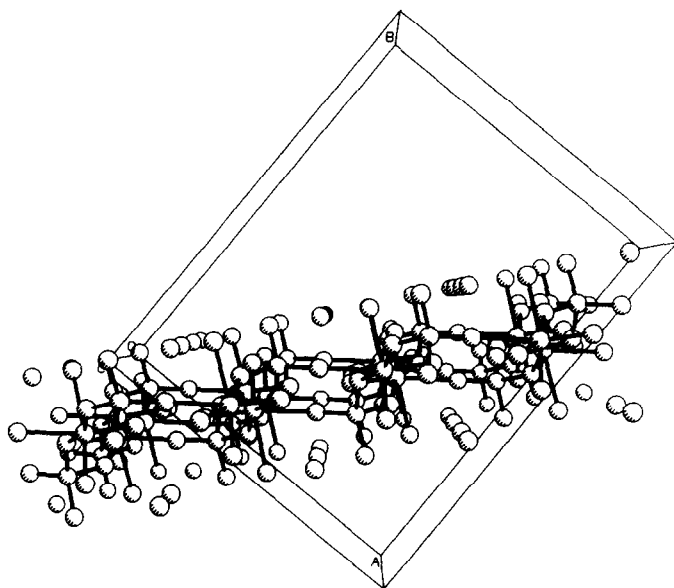


FIG. 8. The molybdenum phosphate sheet in  $\text{KMoO}_2\text{PO}_4$  as seen edge on.

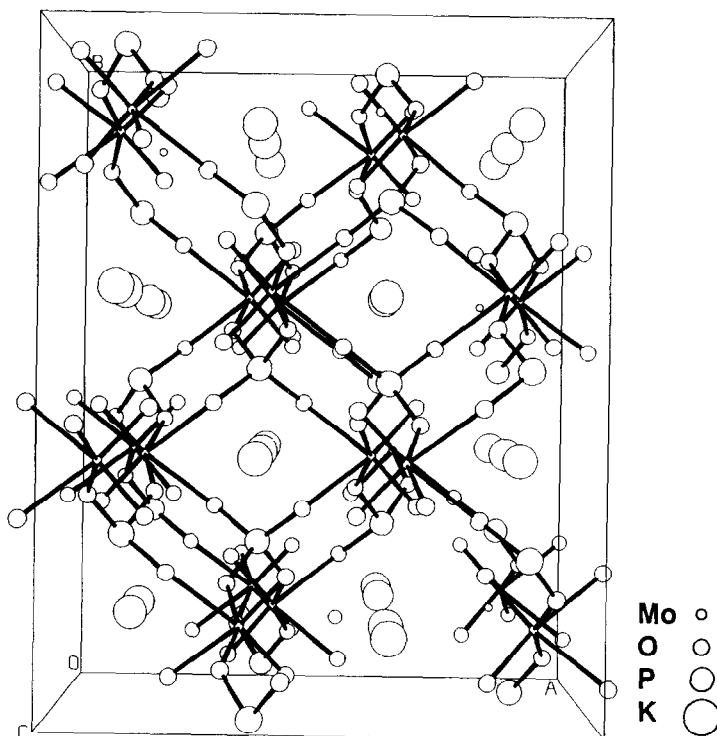


FIG. 9. The unit cell of  $\text{KMoO}_2\text{PO}_4$  showing the location of the potassium atoms within the tunnels formed by the Mo-O-P bonding between the molybdenum phosphate sheets.

in  $\text{KMoO}_2\text{PO}_4$  (Fig. 7) is seen to be slightly more circular than that of  $\text{K}(\text{MoO}_2)(\text{PO}_4) \cdot \text{H}_2\text{O}$  (Fig. 2). Looking at the layers edge on (Figs. 8 and 3) the sheets appear to be identical. The mechanism by which the layers collapse to form  $\text{KMoO}_2\text{PO}_4$  can be visualized by looking at the unit cell along the  $c$ -axis (Fig. 9) and noting how the single sheets (Fig. 8) are shifted relative to each other to form Mo–O–P crosslinks. These Mo–O–P bonds form tunnels in which the potassium atoms are located. The potassium ions are 10-coordinated by oxygen with K–O bonds ranging from 2.58 to 3.29 Å. The longer K–O contacts and higher temperature factor for potassium in  $\text{KMoO}_2\text{PO}_4$  compared to  $\text{K}(\text{MoO}_2)(\text{PO}_4) \cdot \text{H}_2\text{O}$  suggest that  $\text{KMoO}_2\text{PO}_4$  might have some ion-exchange potential.

It appears that the hydrothermal synthesis allows for the incorporation of  $\text{H}_3\text{PO}_4$ , OH, and  $\text{H}_2\text{O}$  into molybdenum phosphorus oxide structures. The inclusion of reduced molybdenum, in this case  $\text{MoO}_2$ , may be responsible for the ease of the hydrothermal reaction. Under elevated temperature and pressure all the  $\text{MoO}_3$  is dissolved into the 5.3 M phosphoric acid solution. By reducing this solution with  $\text{MoO}_2$  the formation of heteropolyanions is limited. The molybdenum solution with the mean oxidation state of Mo between +5 and +6 may facilitate the formation of  $\text{K}(\text{MoO}_2)(\text{PO}_4) \cdot \text{H}_2\text{O}$ .

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## References

1. A. LECLAIRE, M. M. BOREL, A. GRANDIN, AND B. RAVEAU, *J. Solid State Chem.* **78**, 220 (1989).
2. (a) J. J. CHEN, C. C. WANG AND K. H. LIU, *Acta Crystallogr. Sect. C* **45**, 673 (1989); (b) K. H. LIU AND R. C. HAUSHALTER, *Acta Crystallogr. Sect. C* **43**, 2036–2038 (1987).
3. B. RAVEAU, *Proc. Indian Natl. Sci. Acad.* **52**, 67 (1986).
4. A. LECLAIRE AND B. RAVEAU, *Acta Crystallogr. Sect. C* **44**, 226 (1988).
5. A. LECLAIRE, J.-C. MONIER, AND B. RAVEAU, *J. Solid State Chem.* **48**, 147 (1983).
6. K.-H. LIU AND R. C. HAUSHALTER, *J. Solid State Chem.* **69**, 320 (1987).
7. K. LIU, D. C. JOHNSTON, D. P. GOSHORN, AND R. C. HAUSHALTER, *J. Solid State Chem.* **71**, 131 (1987).
8. R. C. HAUSHALTER AND F. W. LAI, *Angew. Chem. Int. Ed. Engl.* **28**, 743 (1989).
9. A. CLEARFIELD, A. MOINI AND P. R. RUDOLF, *Inorg. Chem.* **24**, 4606 (1985).
10. A. MOINI, R. PEASCOE, P. R. RUDOLF AND A. CLEARFIELD, *Inorg. Chem.* **25**, 3782 (1986).
11. A. MOINI, R. PEASCOE, P. R. RUDOLF, AND A. CLEARFIELD, *Inorg. Chem.* **27**, 2200 (1988).
12. D. W. BRECK, "Zeolite Molecular Sieves: Structure, Chemistry, and Use," Wiley, New York (1974).
13. TEXSAN, "Texray Structural Analysis Package," Molecular Structure Corp., The Woodlands, TX. (1987, revised).