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Preparation, Characterization, and Structure of Two Layered Molybdenum(VI) Phosphates: $KMo(H_2O)O_2PO_4$ and $NH_4Mo(H_2O)O_2PO_4$

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New layered Mo(VI) compounds, $KMo(H_2O)O_2PO_4$ (I) and $NH_4Mo(H_2O)O_2PO_4$ (II), were synthesized hydrothermally and their structures were determined from single-crystal X-ray analysis. Compounds (I) and (II) are isostructural and crystallize in the monoclinic $P2_1/n$ space group with a = 12.353(3), b = 8.623(2), c = 5.841(1) Å, β = 102.78(1)°, V = 606.8(2) Å^3, Z = 4, and R = 0.027 (Rw = 0.030) for compound (I) and a = 12.435(3), b = 8.761(2), c = 6.015(1) , β = 103.45(1)°, V = 637.3(2) Å^3, Z = 4, and R = 0.040 (Rw = 0.041) for compound (II). The structure consists of layers built up of eight- and four-membered rings resulting from the alternation of corner-sharing $[MoO_6]$ octahedra and $[PO_4]$ tetrahedra. The layers stack along the $(\bar{1}01)$ direction by intercalating K and NH_4 ions. © 1995 Academic Press, Inc.

1. INTRODUCTION

Several compounds with a framework based on $[MoO_6]$ octahedra and $[PO_4]$ tetrahedra were synthesized in the A–Mo–P–O system (A = alkali metal ion), characterized by different Mo oxidation states and Mo/P ratios.

Some of the A–Mo–P–O compounds display structural features (open three-dimensional networks with cages, tunnels, and micropores, or two-dimensional polymers forming layered materials) which make these materials potentially useful as heterogeneous catalysts, ion exchangers, ion conductors, and molecular sieves.

Examples of open three-dimensional networks include $AMo_2P_3O_{13}$ (A = Na (1), K (2–4), Rb (5), Cs (6, 7)), $AMo_5P_8O_{33}$ (A = Li, Na, Ag) (8), $AMoP_2O_7$ (A = Na (9), K (10), Rb (11) Cs (12)), $Cs_4Mo_{10}P_{18}O_{66}$ (13), and Na $Mo_3P_3O_{16}$ (14). Among these, $Cs_2Mo_4P_6O_{26}$ is the only one with a layer-type structure (6); this fact is reasonably explained when taking into account that these compounds are obtained by high-temperature (T > 750°C) solid state reactions.

Hydrothermal synthesis (generally performed at T < 200°C) seems to be more adequate for obtaining layered materials. In spite of that, only the layered structure of $Na_3Mo_2P_2O_{11}(OH) \cdot 2H_2O$ has been synthesized (15).

During our investigation on the A–Mo–P–O system, new $AMo(H_2O)O_2PO_4$ (A = K, NH_4) compounds were obtained by hydrothermal synthesis, displaying a hitherto unknown layered structure. This paper deals with the synthesis and structural characterization of these compounds.

2. EXPERIMENTAL

Preparation

$KMo(H_2O)O_2PO_4$ (I) was prepared by a reaction mixture containing MoO_3, H_3PO_4, KNO_3, and H_2O (6 : 21 : 10 : 170 molar ratio) at 170°C under autogeneous pressure between 15 hr and 7 days. The pale yellow solid product was separated from the mother liquor by filtration, washed with distilled water, and dried at 120°C for 5 hr.

$NH_4Mo(H_2O)O_2PO_4$ (II) was prepared by the same procedure, using NH_4NO_3 instead of KNO_3.

Characterization

Elemental analysis was performed by the ICP-AES technique with a Jobin Yvon II Plus spectrophotometer.

Thermogravimetric analyses (TGA) were obtained with a Mettler TG50 thermobalance controlled by a Mettler TC3000 microprocessor. Experiments were performed in the range 25–1000°C, at a 10°C · min^{-1} heating rate in an air flow of 300 ml · min^{-1}.

X-Ray powder diffraction (XRD) patterns were collected with a computer-controlled Philips vertical diffractometer equipped with a pulse height analyzer. The radiation was Cu$K\alpha$ (λ = 1.54178 Å).

Structure Determination and Refinement

Crystals of (I) (dimensions 0.1 × 0.1 × 0.2 mm) and of (II) (dimensions 0.2 × 0.3 × 0.5 mm) were mounted in a Lindemann glass capillary for data collection on a Siemens AED diffractometer; Zr-filtered Mo$K\alpha$ radiation

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TABLE 1
Crystallographic Data

	(I)	(II)
Formula	H_2KMoO_7P	H_6MoNO_7P
MW	280.02	258.96
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
a (Å)	12.353(3)	12.435(2)
b (Å)	8.623(1)	8.761(1)
c (Å)	5.841(1)	6.015(1)
β (°)	102.78(1)	103.45(1)
V (Å^3)	606.8(2)	637.3(2)
Z	4	4
D_{calc} (mg/m^3)	3.065	2.699
$F(000)$	536	504
μ (Mo$K\alpha$) (mm^{-1})	3.038	2.245
λ(Mo$K\alpha$) (Å)	0.71069	
Diffractometer	Siemens AED	
Scan type	$\theta/2\theta$	
$\theta_{\max}$ (°)	30	35
Standard reflection	(400)	(400)
Decay	None	None
No. of reflections		
Total	2654	3180
Unique	2294	2824
R_{int}	0.0139	0.0285
Observed ($I > 2\sigma(I)$)	1895	2160
Weighting scheme	$w = 1/(\sigma^2(F) + 0.001581F^2)$	$w = 1/(\sigma^2(F) + 0.008359F^2)$
R	0.027	0.040
Rw	0.030	0.041
S (goodness of fit)	1.33	1.49

(λ = 0.71069 Å) was used. Refined unit cell parameters were obtained from the angular setting of 30 intense reflections, collected in the range 13° $< \theta <$ 22°. The data were collected to $\theta_{\max}$ = 35°, using a θ–2θ scan, with an index range ± h, k, l. A periodic check of the (400) reflection, monitored every 50 measurements, verified the stability of the crystals. Systematic extinctions indicated the monoclinic $P2_1/n$ (No. 14) space group for both crystals. The intensities were corrected for Lorentz and polarization effects; no absorption corrections were applied. Both structures were solved by direct methods (program SIR92 (16)) and refined by full-matrix least-squares methods (program SHELX-76 (17)). Refinement converged at R = 0.027 and Rw = 0.030 for (I), and R = 0.040 and Rw = 0.041 for (II).

TABLE 2
Atomic Coordinates and Equivalent Isotropic Thermal Parameters for Compound (I) (e.s.d.'s in Parentheses)

	x	y	z	U_{eq} (Å^2 × 10^4)
Mo	0.38420(2)	0.26039(3)	0.29954(5)	103(1)
P	0.12561(6)	0.36616(9)	0.1307(1)	97(2)
K	0.17450(7)	0.11335(9)	0.6757(1)	216(2)
O(1)	0.3594(2)	0.3412(3)	0.5466(5)	215(7)
O(2)	0.4281(2)	0.4126(3)	0.1594(5)	235(8)
O(3)	0.0384(2)	0.3172(3)	−0.0910(4)	173(6)
O(4)	0.2270(2)	0.2640(3)	0.1191(4)	165(6)
O(5)	0.1582(2)	0.5348(3)	0.1041(4)	150(6)
O(6)	0.0862(2)	0.3370(3)	0.3535(4)	171(7)
Ow(7)	0.3914(2)	0.1211(3)	−0.0279(4)	162(6)

Scattering factors and anomalous dispersion corrections for the different atoms were taken from Ref. (18).

More details concerning the data collection and structure determinations are given in Table 1. Positional and thermal parameters are reported in Tables 2 and 3; the main geometrical features are given in Tables 4 and 5.

3. RESULTS AND DISCUSSION

The title compounds can be prepared hydrothermally in nearly quantitative yield. The solid products consisted of pale yellow powders formed by spherical aggregates of crystals with diameter increasing with crystallization time. After 7 days, aggregates with diameter on the order of millimeters were obtained together with a small

TABLE 3

Atomic Coordinates and Equivalent Isotropic Thermal Parameters for Compound (II) (e.s.d.'s in Parentheses)

	x	y	z	U_{eq} (Å^2 × 10^4)
Mo	0.38910(2)	0.26300(3)	0.31241(5)	129(1)
P	0.12803(6)	0.37022(9)	0.1366(1)	117(2)
N	0.1790(3)	0.1134(4)	0.6708(6)	221(8)
O(1)	0.3661(3)	0.3358(3)	0.5591(5)	239(8)
O(2)	0.4335(2)	0.4160(3)	0.1833(5)	270(8)
O(3)	0.0414(2)	0.3185(3)	−0.0781(5)	198(7)
O(4)	0.2317(2)	0.2713(3)	0.1319(5)	183(6)
O(5)	0.1577(2)	0.5375(3)	0.1057(5)	175(7)
O(6)	0.0889(2)	0.3452(3)	0.3556(5)	190(7)
Ow(7)	0.3974(2)	0.1298(3)	−0.0106(5)	188(7)

TABLE 4

Selected Bond Lengths (Å) and Angles (°) for Compound (I) (e.s.d.'s in Parentheses)

		S_{Mo-O}		
Mo–O(1)	1.690(3)	1.798	K–O(1)	2.935(3)
Mo–O(2)	1.698(3)	1.759	K–O(1)	3.226(3)
Mo–O(3)	1.986(2)	0.808	K–O(2)	2.709(3)
Mo–O(4)	1.994(2)	0.791	K–O(2)	3.032(3)
Mo–O(5)	2.123(3)	0.558	K–O(3)	2.964(3)
Mo–Ow(7)	2.277(3)	0.368	K–O(4)	2.841(3)
Average	1.961 Å	V_{Mo} 6.082	K–O(5)	2.983(3)
			K–O(6)	2.747(3)
P–O(3)	1.549(2)		K–Ow(7)	2.851(2)
P–O(4)	1.545(3)			
P–O(5)	1.526(3)			
P–O(6)	1.508(3)			
Average	1.532 Å			
O(1)–Mo–O(2)	103.3(1)		O(1)–Mo–O(3)	101.9(1)
O(1)–Mo–O(4)	96.1(1)		O(1)–Mo–O(5)	92.8(1)
O(1)–Mo–Ow(7)	169.4(1)		O(2)–Mo–O(3)	91.7(1)
O(2)–Mo–O(4)	96.4(1)		O(2)–Mo–O(5)	163.8(1)
O(2)–Mo–Ow(7)	85.7(1)		O(3)–Mo–O(4)	158.1(1)
O(3)–Mo–O(5)	83.2(1)		O(3)–Mo–Ow(7)	83.2(1)
O(4)–Mo–O(5)	83.5(1)		O(4)–Mo–Ow(7)	77.2(1)
O(5)–Mo–Ow(7)	78.4(1)			
O(3)–P–O(4)	103.2(1)		O(3)–P–O(5)	109.0(1)
O(3)–P–O(6)	112.2(1)		O(4)–P–O(5)	107.7(1)
O(4)–P–O(6)	111.3(1)		O(5)–P–O(6)	112.9(1)
Mo–O(3)–P	143.2(1)		Mo–O(4)–P	133.6(1)
Mo–O(5)–P	139.5(1)			

amount of crystals suitable for single crystal X-ray analysis.

Compounds (I) and (II) are isostructural, being constituted by layers built up of [MoO_6] octahedra and [PO_4] tetrahedra forming eight and four-membered rings (Fig. 1) with the K and NH_4 ions lying between the layers (Fig. 2). Each [MoO_6] octahedron shares three corners with [PO_4] tetrahedra, with the other three corners being unshared. The [MoO_6] octahedra deviate from the ideal O_h symmetry, being characterized by two short, one long, and three intermediate bonds (Tables 4 and 5). The last involve the O atoms sharing three [PO_4] tetrahedra; the shortest values are indicative of two Mo=O double bonds, while the longest bond is associated with the H_2O molecule coordinated to the metal ion.

The geometry of the [PO_4] tetrahedron is also slightly distorted (Table 4 and 5). The P–O bond lengths of the three O atoms sharing three different [MoO_6] octahedra are slightly but significantly longer than the corresponding value observed for the unshared O(6) atom.

The oxidation state of Mo (V_{Mo}) in compounds (I) and (II) has been evaluated with the method proposed by

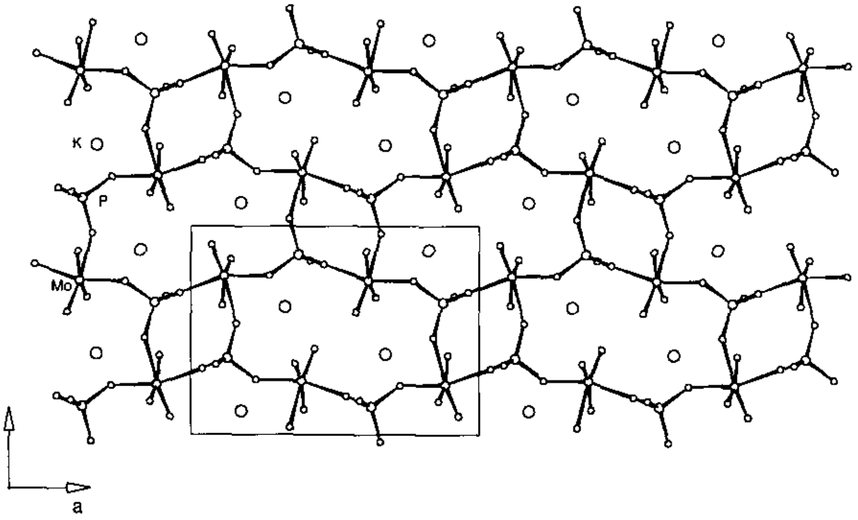

FIG. 1. Projection of the structure of compound (I) on the a–b plane.

TABLE 5
Selected Bond Lengths (Å) and Angles (°) for Compound (II) (e.s.d.'s in Parentheses)

		s_{Mo-O}		
Mo–O(1)	1.699(3)	1.754	N–O(1)	3.048(5)
Mo–O(2)	1.704(3)	1.731	N–O(1)	3.223(5)
Mo–O(3)	1.987(2)	0.806	N–O(2)	2.846(4)
Mo–O(4)	2.007(2)	0.763	N–O(2)	3.082(5)
Mo–O(5)	2.149(3)	0.521	N–O(3)	3.105(5)
Mo–Ow(7)	2.289(3)	0.356	N–O(4)	3.032(5)
Average	1.972 Å	V_{Mo} 5.931	N–O(5)	2.984(5)
			N–O(6)	2.826(4)
P–O(3)	1.545(2)		K–Ow(7)	2.941(4)
P–O(4)	1.559(3)			
P–O(5)	1.533(3)			
P–O(6)	1.523(3)			
Average	1.540 Å			
O(1)–Mo–O(2)	103.9(1)		O(1)–Mo–O(3)	100.8(1)
O(1)–Mo–O(4)	96.8(1)		O(1)–Mo–O(5)	92.0(1)
O(1)–Mo–Ow(7)	169.2(1)		O(2)–Mo–O(3)	92.8(1)
O(2)–Mo–O(4)	95.9(1)		O(2)–Mo–O(5)	164.0(1)
O(2)–Mo–Ow(7)	86.0(1)		O(3)–Mo–O(4)	157.9(1)
O(3)–Mo–O(5)	83.2(1)		O(3)–Mo–Ow(7)	82.6(1)
O(4)–Mo–O(5)	82.8(1)		O(4)–Mo–Ow(7)	77.9(1)
O(5)–Mo–Ow(7)	78.1(1)			
O(3)–P–O(4)	103.9(1)		O(3)–P–O(5)	108.7(1)
O(3)–P–O(6)	112.3(1)		O(4)–P–O(5)	107.8(1)
O(4)–P–O(6)	111.6(1)		O(5)–P–O(6)	112.1(1)
Mo–O(3)–P	143.9(1)		Mo–O(4)–P	135.8(1)
Mo–O(5)–P	139.9(1)			

Brown and Altermatt (19). In general, the oxidation state of a cation i, V_i, can be estimated by summing the valences of the bonds, s_{ij}, between the cation i and the surrounding anions j, according to the equation

$$V_i = \Sigma_j s_{ij} = \Sigma_j \exp[(r_0 - r_{ij})/B],$$

where r_0 is the length of a cation–anion bond with unit valence and $B = 0.37$ is a fitted constant. Using the values reported in Tables 4 and 5, and assuming for the Mo–O bond $r_0 = 1.907$ (19), oxidation states, V_{Mo}, of 6.082 and 5.931 are estimated for Mo in compounds (I) and (II), respectively, in agreement with what is expected on the basis of their stoichiometry.

TGA analysis showed that compounds are stable at temperatures up to 300°C. Above this temperature, compound (I) starts losing H_2O, which is completed at about 450°C (6.61% weight loss compared to 6.43% expected for the loss of one H_2O molecule). Above 300°C, a weight loss of 13.35% was observed for (II), corresponding to the simultaneous loss of H_2O and NH_3 (calculated weight loss, 13.52%). Elimination of water and/or ammonia results in a complete amorphization of the structure.

In an attempt to exchange interlayer cations, compound (I) was repeatedly treated with solutions containing CH_3COONH_4 or CH_3COONa at 60–80°C with stirring for 1 hr. The product, after being recovered, washed, and dried, was found, by XRD and elemental analysis, to be unchanged. This reflects the strong interaction between the K ions and the O atoms of the layers, indicated by the rather short K–O distance (Table 4).

Similar results were obtained by treating (II) with CH_3COONa solutions, which may be accounted for by hydrogen bonds formed by the ammonium ions with the O atoms of $[MoO_6]$ and $[PO_4]$ polyhedra (Table 5).

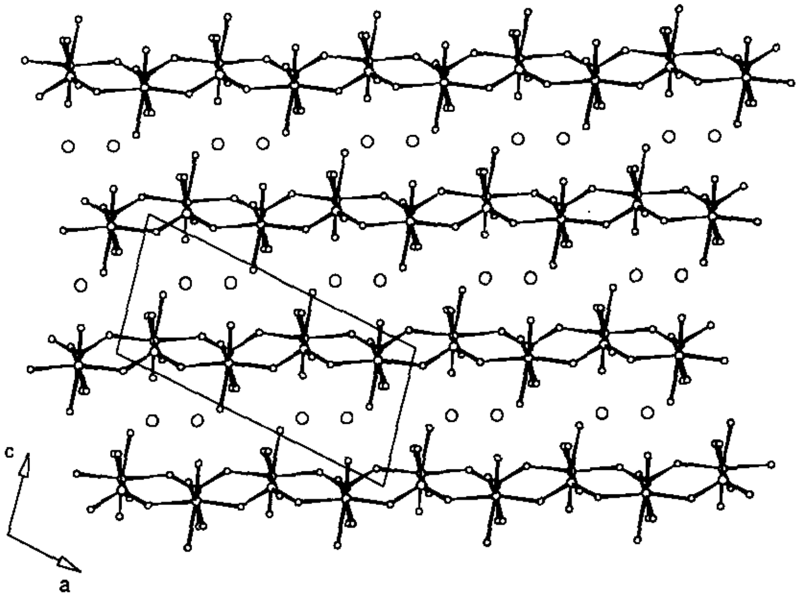

FIG. 2. Projection of the structure of compound (I) on the *a–c* plane.

REFERENCES

1. A. Leclaire, M. M. Borel, A. Grandin, and B. Raveau, *J. Solid State Chem.* **89,** 10 (1990).
2. A. Leclaire, J. C. Monier, and B. Raveau, *J. Solid State Chem.* **48,** 147 (1983).
3. A. Leclaire, M. M. Borel, A. Grandin, and B. Raveau, *Z. Kristallogr.* **188,** 77 (1989).
4. A. Leclaire, M. M. Borel, A. Grandin, and B. Raveau, *Acta Crystallogr. Sect. C* **46,** 2009 (1990).
5. D. Riou and N. Goreaud, *J. Solid State Chem.* **79,** 99 (1989).
6. K.-H. Lii and R. C. Haushalter, *J. Solid State Chem.* **69,** 320 (1987).
7. J. J. Chen, K.-H. Lii, and S. L. Wang, *J. Solid State Chem.* **76,** 204 (1988).
8. H.-K. Lii, D. C. Johnston, D. P. Goshorn, and R. C. Haushalter, *J. Solid State Chem.* **71,** 131 (1987).
9. A. Leclaire, M. M. Borel, A. Grandin, and B. Raveau, *J. Solid State Chem.* **76,** 131 (1988).
10. A. Leclaire, M. M. Borel, A. Grandin, and B. Raveau, *J. Solid State Chem.* **78,** 200 (1989).
11. D. Riou, A. Leclaire, A. Grandin, and B. Raveau, *Acta Crystallogr. Sect. C* **45,** 989 (1989).
12. K. H. Lii and R. C. Haushalter, *Acta Crystallogr. Sect. C* **43,** 2036 (1987).
13. R. C. Haushalter and F. W. Lai, *J. Solid State Chem.* **76,** 218 (1988).
14. G. Costentin, M. M. Borel, A. Grandin, A. Leclaire, and B. Raveau, *J. Solid State Chem.* **95,** 168 (1991).
15. L. A. Mundi and R. C. Haushalter, *Inorg. Chem.* **29,** 2879 (1990).
16. A. Altomare, G. Cascarano, C. Giacovazzo, and A. Guagliardi, *J. Appl. Crystallogr.* **26,** 343 (1993).
17. G. M. Sheldrick, "SHELX. A Program for Crystal Structure Determination." University of Cambridge, England, 1976.
18. "International Tables for X-Ray Crystallography," Vol. IV, Kynoch Press, Birmingham, UK, 1974.
19. I. D. Brown and D. Altermatt, *Acta Crystallogr. Sect. B* **41,** 244 (1985).