JOURNAL OF SOLID STATE CHEMISTRY **95**, 289–299 (1991)

Hydrothermal Synthesis of $Na_2(MoOPO_4)_2(HPO_4) \cdot 2H_2O$: A Layered Molybdenum (V) Phosphate Structure and Its Relationship to $2VOSO_4 \cdot H_2SO_4$

R. PEASCOE AND A. CLEARFIELD*

Department of Chemistry, Texas A&M University,
College Station, Texas, 77804

Received February 18, 1991

The hydrothermal synthesis and structure of the molybdenum (V) phosphate, $Na_2(MoOPO_4)_2(HPO_4) \cdot 2H_2O$, was determined and compared to the closely related $2VOSO_4 \cdot H_2SO_4$ (B. JORDAN AND C. CALVO, *Can. J. Chem.* **51,** 2621 (1973)). $Na_2(MoOPO_4)_2(HPO_4) \cdot 2H_2O$ crystallizes with lattice parameters $a = 6.452(2)$Å, $c = 15.999(1)$Å, and $z = 2$ in the tetragonal space group *I4/mmm* and was refined to $R_f = 0.041$ and $R_{wf} = 0.044$ with 426 reflections for which $I > 2\sigma$. The structure is made up of layers of $MoOPO_4$ composed of alternating molybdenum oxygen octahedra and phosphate tetrahedra. The layers are linked by disordered phosphorus tetrahedra forming tunnels. Thermogravimetric analysis, infrared, solid state, NMR, and ESR spectra indicate the presence of water in the tunnels and molybdenum with an oxidation state of (V).

Introduction

Compounds with the formula $MOAO_4$, where M = V, Nb, or Mo and A = P, As, Mo, or S, form an isostructural series with a layered tetragonal structure, space group *P4/n* (*1–8*). Cell parameters and metal oxygen contacts for these compounds are listed in Table I. The metal phosphate sheets are built up by the four equatorial oxygen atoms on the metal octahedra corner sharing with four phosphate tetrahedra. This arrangement forms a puckered layer of alternating octahedra and tetrahedra. Layers are connected through apical oxygen atoms on the metal octahedra. A short M=O bond has a long contact to the adjacent layer to fill in the open octahedral coordination site on the metal atom. The metal coordination can be thought of either as a distorted octahedron or as a square pyramid with the vacant site being filled by an oxygen atom in the M=O from the adjacent layer. A similar layer structure is seen in $2VOSO_4 \cdot H_2SO_4$, where the $VOSO_4$ layers are linked by bridging H_2SO_4 tetrahedra (*9*). This compound crystallizes in the tetragonal space group $P4_2/mnm$ with cell parameters $a = 8.971(3)$ Å and $c = 15.594(2)$ Å. In this paper we report on the synthesis and characterization of the closely related structure $Na_2(MoOPO_4)_2(HPO_4) \cdot 2H_2O$.

Experimental Section

$Na_2(MoOPO_4)_2(HPO_4) \cdot 2H_2O$ crystals were synthesized under a variety of hydro-

---

* To whom correspondence should be addressed.

0022-4596/91 $3.00

thermal conditions. In one case 500 mg of MoO_3, MoO_2, and Na_2HPO_4 or NaH_2PO_4 in a 2 : 1 : 1 ratio was placed in an 8-mm outer diameter sodium borosilicate glass tube along with enough 85% H_3PO_4 to fill a 15 to 20 cm long tube approximately $\frac{1}{3}$ full of solid and solution. The sealed tube was placed in a tube furnace kept at 180°C ± 5°C from two to four days. Light green crystals of $Na_2(MoOPO_4)_2(HPO_4) \cdot 2H_2O$ formed throughout the tube and the originally clear solution turned pale green. When the crystals were washed with water, the filtrate solution turned a dark blue. The amount of unreacted MoO_2 appears to be dependent on the ratio of MoO_3 to MoO_2 and the time the tube remained in the furnace.

A second synthetic method was to react 500 mg of 1 : 1 mix of MoO_2 and CuO with 85% H_3PO_4. In this case, green crystals were seen on the side of the reaction tubes after two days in the furnace. When these tubes were replaced in the furnace and allowed to react three more days, clear crystals of H_3MoPO_7 had replaced the green crystals at the top of the tube, while in the bottom of the tube was unreacted MoO_2 and copper metal.

Crystals of $Na_2(MoOPO_4)_2(HPO_4) \cdot 2H_2O$ also formed in tubes where only MoO_3 and MoO_2 were reacted with 85% H_3PO_4. It is assumed that the sodium incorporated into the structure was extracted from the sodium borosilicate glass tubes. Formation of *M*oO $PO_4 \cdot 2.5H_2O$ was observed in another tube when Na was not leached out of the glass. This hydrated compound is reported on in another paper. The leaching of boron from the glass tube was also observed when MoO_3, MoO_2, and Li_3PO_4 in 2 : 1 : 1 ratio was reacted in 5.3 *M* H_3PO_4 solution. In this case, clear crystals found at the top of the reaction tube were indexed on a Rigaku AFC5 rotating anode single crystal diffractometer with the BPO_4 cell.

Single yellow-green crystals of $Na_2(MoOPO_4)_2(HPO_4) \cdot 2H_2O$ from different reactions indexed with the same unit cell parameters. The best crystal was a plate with dimensions $0.15 \times 0.15 \times 0.01$ mm^3 which had been removed from the side of a tube, containing a 2 : 1 ratio of MoO_3 to MoO_2 in 85% H_3PO_4. It was mounted on a glass fiber with silicon cement. Data were collected on a Rigaku AFC5 rotating anode automated single crystal diffractometer using graphite-monochromatized Mo*Kα* radiation (λ = 0.71069 Å). All crystal data collection, data processing, and structure solution were performed on a Digital Equipment Corp. MicroVAX II computer using the TEXSAN (*10*) structure solving program library. Indexing was based on the setting angles of 25 low angle reflections found in a random search of reciprocal space. Accurate unit cell parameters were determined at room temperature from a least-squares analysis of the setting angles of 25 high angle reflections ($20° < 2\theta$ (Mo*Kα*) $< 40°$) based on an idealized tetragonal cell. 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 was applied based on a psi scan which varied from 80.2 to 100.0% of *I*. Molybdenum was located by Direct Methods using the program MITHRIL with the remaining atoms being located in subsequent difference Fourier syntheses.

The structure was originally refined in the space group *I*422, but when the oxygen atoms associated with the disordered phosphorus atom were placed on the special position (.2300, .2300, .5) it was noted that the shortest P–O bond lengths, 1.58 and 1.63 Å, and O–P–O bond angle, 135.4°, was evidence that this phosphate group was quite strained. If extra symmetry was imposed on the system by allowing x and y to vary independently while z was held at .5, the bond lengths were 1.57 and 1.61 Å, with a bond angle of 100.2°. For equivalent iso-

TABLE I

CELL PARAMETERS[a] AND METAL OXYGEN CONTACTS FOR $MOAO_4$

Compound	a(Å)	c(Å)	M—O(Å)	M═O(Å)	M···O(Å)	Ref.
α-$VOPO_4$	6.014(7)	4.434(2)	1.858(7)	1.580(11)	2.853(11)	(*2*)
$VOAsO_4$[b]	6.33	4.18				(*3*)
α-$VOSO_4$[b]	6.261(3)	4.101(3)	2.04(3)	1.63(3)	2.47(3)	(*4*)
$VOMoO_4$[b]	6.6078(2)	4.2646(3)	1.972(13)	1.677(16)	2.588(16)	(*5*)
$NbOPO_4$	6.3873(10)	4.1037(8)	1.969(9)	1.783(12)	2.321(12)	(*6*)
$TaOPO_4$	6.425(3)	4.001(3)	1.970	1.786	2.215	(*7*)
$MoOPO_4$	6.1768(3)	4.2932(3)	1.979(3)	1.652(5)	2.641(5)	(*8, 9*)

[a] E.S.D.'s as reported in parenthesis.

[b] Structures determined using X-ray powder data.

tropic refinements using 2σ data in $I422$ space group, $R = 0.074$ and $R_w = 0.0894$ with 14 reflections where delF/sig$R > 5.0$ in the first case, while in the second case $R = 0.0689$ and $R_w = 0.0832$ with 11 reflections where delF/sig$F > 5.0$. This was the first indication that $I422$ might be an incorrect space group assignment. When fully refined anisotropically in the space group $I422$ the O–P–O bond distances and angles did not improve nor could the sodium atom be located within the structure. However, when the space group $I4/mmm$ was used, the shortest P–O bond lengths were 1.56 Å and the bond angle was 101°. Data was averaged with an R factor for the averaged reflections of 10.7%. At this point the sodium atom could be placed and refined anisotropically on a general position at an occupancy of $\frac{1}{8}$. Neither the water in the cell nor the hydrogen atoms could be located on the final difference map. Final refinement was performed on those data having $I > 2\sigma(I)$. All atoms were refined anisotropically with a full-matrix least-squares refinement to a final $R_F = 0.041$ and $Rw_F = 0.044$ with one reflection (8,2,18) where delF/sig$R > 5.0$. Atomic coordinates and estimated standard deviations are listed in Table II. The largest peak in the final difference map was 2.93 e/Å^3 and was located near the molybdenum atom.

TABLE II

SUMMARY OF CRYSTAL DATA, INTENSITY MEASUREMENTS, AND STRUCTURE REFINEMENT PARAMETERS FOR $Na_2(MoOPO_4)_2HPO_4 \cdot 2H_2O$

Formula	$Mo_2P_3O_{16}H_5Na_2$
Formula weight	591.81 g
Crystal system	Tetragonal
Lattice parameters	a = 6.452(2) Å c = 15.999(4) Å V = 666.0(3) Å^3
Space group	$I4/mmm$ (#139)
Z	2
D_{calc}	2.861 g/cm^3
mu (Mo$K\alpha$)	23.34 cm^{-1}
Radiation	Mo$K\alpha$ (λ = 0.71069) Graphite-monochromated
Temperature	23 ± 1°C
Maximum 2θ	74.9°
No. of reflections	1990 total, 558 unique
Lorentz-polarization correction	Applied
Empirical absorption correction	(*Trans*. factors: 80–100% of I)
Reflections included	426 with $I > 2.00\ \sigma(I)$
Parameters refined	37
Residuals: R; R_w	0.041; 0.044
Goodness of fit indicator	1.07
Maximum shift in final cycle	0.04
Largest peak in final diff. map	2.93 e/Å^3

To confirm the presence of hydrogen an infrared spectrum (KBr disk, Bio-Rad FTS-40) and a thermogravimetric curve (Dupont Thermal Analyst 2000, heating rate of 4°/min under N_2) were obtained. To further characterize the compound solid state NMR results were obtained for ^{31}P and ^1H on a Bruker MSL-300 Spectrometer. The spectra were collected by using magic angle spin-

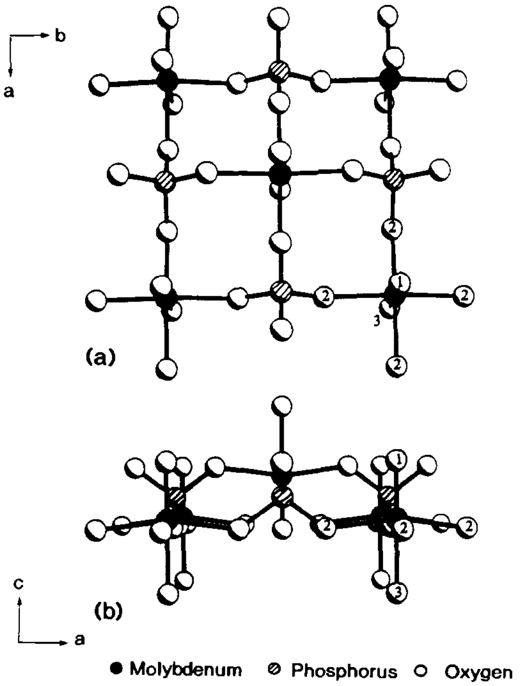

FIG. 1. Molybdenum phosphate layer as seen in $Na_2(MoOPO_4)_2(HPO_4) \cdot 2H_2O$. The layer is composed of molybdenum atoms connected through four equivalent O2 oxygen atoms to P1. O1 and O3 are bonded to Mo to complete the octahedral coordination. View (a) is approximately down the *c*-axis while view (b) is perpendicular to the *c*-axis and shows how O3 extends out of the plane of the molybdenum phosphate layer.

ning (MAS) at 2 kHz. Both proton-coupled and proton-decoupled spectra were collected. The time between pulses was 20 sec. Chemical shifts are reported relative to 85% H_3PO_4 with negative shifts reflecting greater shielding (i.e., higher external field). The estimated error in the reported chemical shifts is ±0.3 ppm. To confirm the presence of Mo(V) an ESR spectrum was obtained on a Varian E-6S EPR spectrometer.

Results

The single crystal structure indicated that the hydrothermal reaction of MoO_3, MoO_2, and Na_2HPO_4 in 85% H_3PO_4 crystallizes a new molybdenum phosphate with a layered structure based on that of $MoOPO_4$. The layer is composed of phosphorus–oxygen tetrahedra and molybdenum–oxygen octahedra as shown in Fig. 1. Selected bond distances and bond angles are listed in Tables III and IV, respectively. Molybdenum atoms are located on a 4-fold rotation axis on the edges of the unit cell at $z = \pm 0.29049(8)$ and in the center of the cell at $x = \frac{1}{2}$, $y = \frac{1}{2}$, and $z = \frac{1}{2} \pm 0.29046(5)$. Two oxygen atoms, O1 and O3, occupy the axial positions of the molybdenum octahedron and are located on the same 4-fold axis 1.657(8) Å and 2.123(7) Å from the molybdenum center, respectively. A 4-fold rotation axis places O2 in four equivalent equatorial sites on the molybdenum octahedron at a distance of 2.029(3) Å. The O1–Mo–O2 and O2–Mo–O3 angles are 97.8(1)° and 82.2(1)°, respectively. The molybdenum octahedron is distorted with Mo located closest to O1

TABLE III

POSITIONAL PARAMETERS AND B_{eq} FOR $Na_2(MoOPO_4)_2HPO_4 \cdot 2H_2O$

Atoms	*x*	*y*	*z*	$B_{eq}{}^{a}$(Å)
Mo	0.0	0.0	0.29046(5)	0.58(2)
P(1)	−0.5	0.0	0.25	0.74(5)
P(2)	−0.134(1)	0.0	0.5	1.0(2)
O(1)	0.0	0.0	0.1869(5)	1.9(2)
O(2)	−0.3116(5)	0.0	0.3078(2)	1.5(1)
O(3)	0.0	0.0	0.4231(4)	1.4(2)
O(4)	−0.288(2)	−0.186(2)	0.5	1.8(5)
Na(1)	−0.427(3)	0.200(3)	0.464(1)	4.3(8)

[a] The isotropic equivalent thermal parameter is defined as $B_{eq} = (\frac{4}{3})[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + 2ab(\cos\gamma)\beta_{12} + 2ac(\cos\beta)\beta_{13} + 2bc(\cos\alpha)\beta_{23}]$.

TABLE IV

SELECTED DISTANCES (Å) IN $Na_2(MoOPO_4)_2HPO_4 \cdot 2H_2O$

Atoms	Atoms	Distance (Å)	Atoms	Atoms	Distance (Å)
Mo	O(1)	1.657(8)	P(1)	O(2)	1.527(3) × 4
Mo	O(2)	2.029(3) × 4	P(2)	O(3)	1.502(7) × 2
Mo	O(3)	2.123(7)	P(2)	O(4)	1.56(2) × 2

TABLE V

SELECTED ANGLES (°) IN $Na_2(MoOPO_4)_2HPO_4 \cdot 2H_2O$

Atom	Atom	Atom	Angle	Atom	Atom	Atom	Angle
O1	Mo	O2	97.8(1) × 4	O2	P1	O2	105.5(3) × 2
O1	Mo	O3	180.00	O2	P1	O2	111.5(1) × 4
O2	Mo	O2	88.93(3) × 4	O3	P2	O3	109.9(5)
O2	Mo	O2	164.3(2) × 2	O3	P2	O4	111.5(3) × 4
O2	Mo	O3	82.2(1)	O4	P2	O4	101 (1)
P1	O2	Mo	134.9(2)	P2	O3	Mo	145.0(3)

above the equatorial oxygen atoms so that the molybdenum octahedron has three Mo–O bond lengths: one short, four equivalent of medium length, and one long. The phosphorus atoms in the layer are located on the faces of the unit cell on a bar-4 axis at $z = \frac{1}{4}$ and $\frac{3}{4}$. Four equivalent O2 atoms are tetrahedrally coordinated to P1 at a distance of 1.527(3) Å and O2–P1–O2 angles of 105.5(3)° and 111.5(1)°. The phosphorus atom is located in the center of the tetrahedron.

The perspective of the layer down the *c*-axis (Fig. 1(a)) shows that the molybdenum–oxygen octahedra and phosphorus–oxygen tetrahedra alternate to form a sheet. Each octahedron corner shares through the four equivalent equatorial oxygen atoms (O2) to four phosphate tetrahedra. The tetrahedra are located in the mean plane of the layer with molybdenum–oxygen octahedra alternating above and below the plane. Oxygen atoms O1 and O3 fill in the molybdenum coordination sites. The O3 atoms extend the furthest out of the layer both above and below (Fig. 1(b)).

The layer is similar to that seen in $MoOPO_4$ which crystallizes in the tetragonal space group *P*4/*n* with the lattice parameters $a = 6.17768(3)$ Å, and $c = 4.2932(3)$ Å (*7, 8*). Kierkegaard and Westerlund (*7*) prepared crystals of $MoOPO_4$ by heating 13.2 g of a mixture of 86.4% MoO_3, 9.4% NH_3 and 14.5 *M* phosphoric acid (6 ml) to about 1000°C for 20 min. After the mixture was cooled then washed with hot water, they obtained thin plate-like yellowish crystals. Their single crystal structure refined to $R = 0.045$. In $MoOPO_4$, the equatorial oxygen atoms connect the molybdenum octahedra to the phosphorus tetrahedra. The two axial Mo–O distances are 1.652(5) and 2.641(5) Å, with the shorter one representing the molybdenum–oxygen double bond. The distorted molybdenum–oxygen octahedron can be regarded as a square pyramid with the axial oxygen atom from the layer below filling in the open (sixth) coordination site at the long 2.641(5) Å distance (Fig. 2).

In $MoOPO_4$ indentical molybdenum phosphate layers are stacked perpendicular to the *c*-axis, while in $Na_2(MoOPO_4)_2(HPO_4) \cdot 2H_2O$ the $MoOPO_4$ layer is the mirror image of the layer above or below. The oxygen atom with the longest Mo–O distance, O3, sticks out of the layers and is bonded to the phosphorus atom, P2, between the layers (Fig. 3). This phosphate group consists of O3, P2, and O4. P2 and O4 are located on a mirror plane and are disordered around the 4-fold axis. The disordered PO_4 group can be thought of as rotating around the 4-fold axis, but usually being located in one of four positions required by the 4-fold symmetry, and the oxygen atoms are positioned to be offset from the oxygen atoms in the layers to reduce repulsion between the oxygen atoms as well as retain a reasonable O4–P2–O4 angle (Fig. 4). A disordered sodium atom is located above or below the

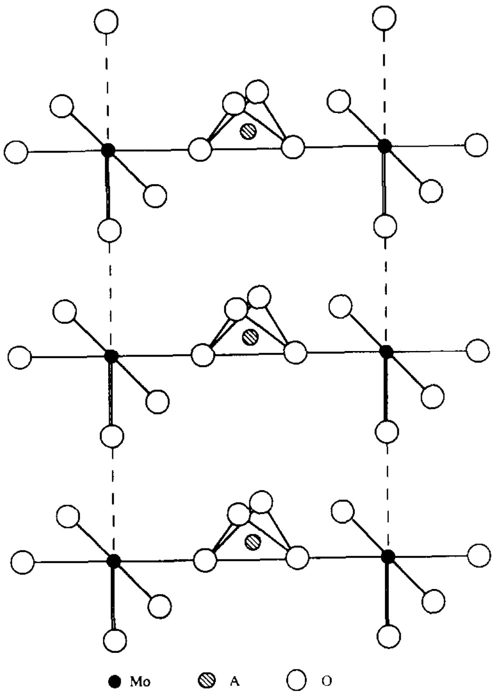

FIG. 2. An idealized representation of the bonding between $MOAO_4$ layers as seen perpendicular to the *c*-axis. These compounds crystallize in the tetragonal space group *P*4/*n*. Within the layers of $MOAO_4$, *M* appears to have a square pyramid coordination with a short *M*═O bond and where the open sixth coordination site has a long *M*···O contact with an oxygen from an identical layer below.

O4–P2–O4 plane in 2 of 16 positions. To confirm the number of hydrogen atoms and the valence of molybdenum, it was necessary to interpret spectral data.

Solid state NMR spectra were obtained for both hydrogen and ^{31}P (Figs. 5 and 6). The proton NMR spectrum showed only one type of hydrogen to be present. This equivalence of chemical shifts indicates that hydrogen atoms are mobile within the crystal. The solid state ^{31}P NMR spectrum indicated the presence of two types of phosphorus with chemical shifts at 61.901 and 31.145 ppm, but in ratios quite different than the 2 : 1 expected. To check for incomplete relaxation the pulse delay was increased from 20 to 100 sec with no change in the ratio of peak intensities. A proton coupling experiment indicated that the phosphorus responsible for the major peak was coupled to hydrogen and thus that the peak must be assigned to the HPO_4 group between the layers. Since a paramagnetic atom can broaden out or totally obscure an NMR signal, the lack of a second intense phosphorus signal suggests that a paramagnetic species is in close proximity to the phosphorus (P1) in the layer. Mo(V) with its spin state of $\frac{1}{2}$ would supply such a paramagnetic species, and an EPR spectrum confirmed the presence of Mo(V).

A thermogravimetric analysis curve of the green crystals of $Na_2(MoOPO_4)_2HPO_4 \cdot$

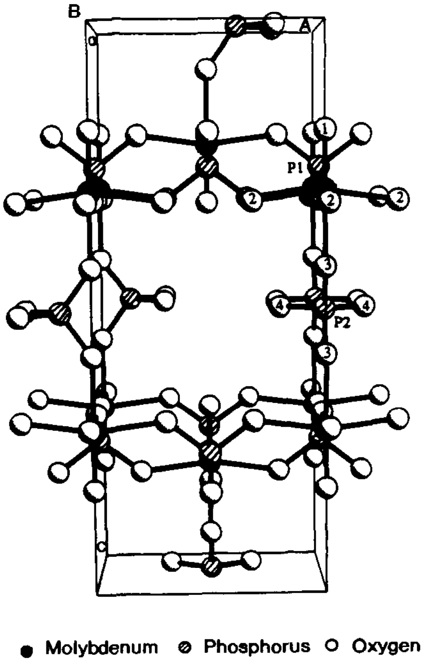

FIG. 3. Idealized unit cell of $Na_2(MoOPO_4)_2(HPO_4) \cdot 2H_2O$ where the disordered phosphate groups appear on only one of the four equivalent positions on the edge of the unit cell. The disordered phosphate groups bridge the molybdenum phosphate layers along the *c*-axis forming tunnels in the process.

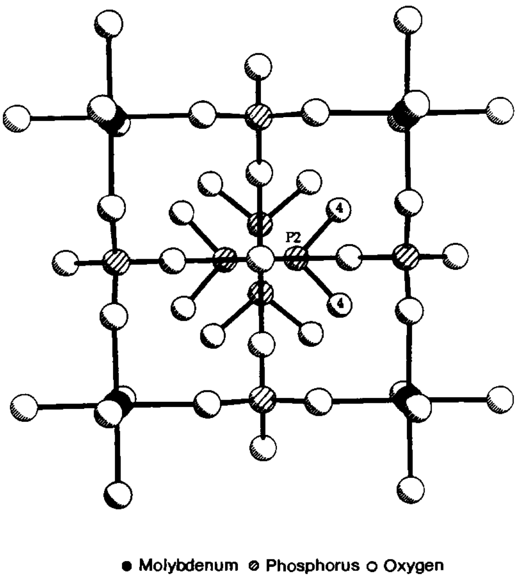

FIG. 4. The four equivalent positions of P2 and O4 seen directly down the *c*-axis of $Na_2(MoOPO_4)_2(HPO_4) \cdot 2H_2O$ showing the position of the O4 atoms in the phosphate group relative to the oxygen atoms (O2) in the molybdenum phosphate layer as seen in Fig. 1(a).

$2H_2O$ was obtained with the sample in a glass bucket under a N_2 flow to 600°C, held there 20 min, and allowed to cool to room temperature. Under these conditions there was an initial weight loss of 5.92% between 30 and 248°C, which is equivalent to the loss of two moles of water (6.09%, theoretical). This was followed by a weight gain of 0.07% and a second weight loss between 334 to 409°C of 1.77%, which is roughly equivalent to the loss of $\frac{1}{2}$ mole of water (1.52%, theoretical). After the two initial weight losses there was a steady weight gain up to 600°C amounting to 0.59%. The temperature was held at 600°C for 20 min, and then the sample was allowed to cool down to room temperature. As the sample cooled a steady weight loss was observed. A total weight loss of 10.30% was recorded, which is equivalent to the loss of two moles of water, $\frac{1}{2}$ mole of water, and a $\frac{1}{2}$ mole of O_2 (theoretical losses of 6.09, 1.52, and 2.64% for a total of 10.25%). The sample had changed colors from a lime green to a dark, almost black-green material. This indicates that the oxidation state of some of the molybdenum had reduced from Mo(V) to Mo(IV) with the loss of O_2.

To see whether water can be readsorbed a thermogravimetric analyses curve was obtained where crystals of $Na_2(MoOPO_4)_2HPO_4 \cdot 2H_2O$ were heated to 300°C, held there for 20 min, and allowed to cool. In this case the curve indicated the loss of slightly more than two moles of water (6.61% observed, 6.09% theoretical), and then the sample increased in weight upon cooling, with a slight darkening of the green color. Infrared spectra of the original sample, after heating to 300°C as well as after heating to 600°C were obtained (Fig. 7). The spectrum of the original material had bands associated with water at 3574, 3471, and 1638 cm^{-1} as well as those associated with phosphate tetrahedra at 1000 cm^{-1} and at 680 cm^{-1}. For the PO_4^{3-} tetrahedral ion, the fundamental vibrational frequencies are:

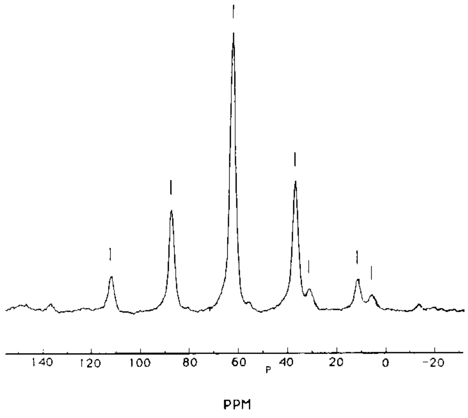

FIG. 5. Solid state NMR spectra for ^{31}P collected using magic angle spinning (MAS) at 2 kHz. The time between pulses was 20 sec and chemical shifts are reported relative to 85% H_3PO_4, with negative shifts reflecting greater shielding (i.e., higher external field).

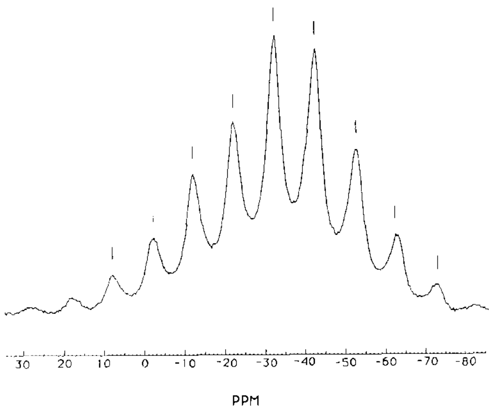

FIG. 6. Solid state NMR spectra was obtained for ^1H collected using magic angle spinning (MAS) at 2 kHz. The time between pulses was 20 sec.

970 cm^{-1} (ν_1, ν_{sym}), 358 cm^{-1} (ν_2, δ), 1080 cm^{-1} (ν_3, ν_{asym}), and 500 cm^{-1} (ν_4, δ) (*11*). When the green crystals are heated to 300°C they lose two moles of water of crystallization but reabsorb them upon cooling. The infrared spectrum in this case has stronger and better defined bands associated with the OH and H_2O vibrations. New bands observed at 1383 cm^{-1} and 533 cm^{-1} are most likely due to the (P)–O–H and P–O–(H) bending frequencies, which are in the range of 1200–1400 cm^{-1} and 450–550 cm^{-1}, respectively (*11*). Both of these changes suggest that the reabsorption of water takes place in an ordered fashion. After heating to 600°C the material is dark, almost black-green in color, and the infrared spectrum is devoid of bands associated with H_2O or OH vibrations. The P–O vibrations at 1000 cm^{-1} are quite wide and may include some P═O bands which would appear in the 1320–1200 cm^{-1} range. This broadening of the peak may also be due to the addition of Mo(IV)–O stretches.

The green crystals were allowed to sit in a 40% solution of $CH_3NH_3^+$ overnight and then placed in a desiccator for a day. An infrared spectrum indicates that the amine had been incorporated into the compound. A thermogravimetric curve of this material under a N_2 flow had a weight loss of 1.7% between 35 and 78°C, which is roughly equivalent to $\frac{1}{2}$ mole of water (1.6% theoretical) and a second weight loss of 7% between 320 and 478°C, which is roughly slightly more than one mole of methylamine (5.7% theoretical) but less than two moles. The weight loss in the range of 400°C confirms that the methylamine was incorporated within the compound. It is assumed that some of the methylamine ion exchanged with sodium ions located between the molybdenum phosphate layers.

Crystals of $Na_2(MoOPO_4)_2HPO_4 \cdot 2H_2O$ were placed in 1*N* NaOH and allowed to sit for a week. In this case there is the possibility of a sodium ion replacing the hydrogen ion. A possible reaction would be

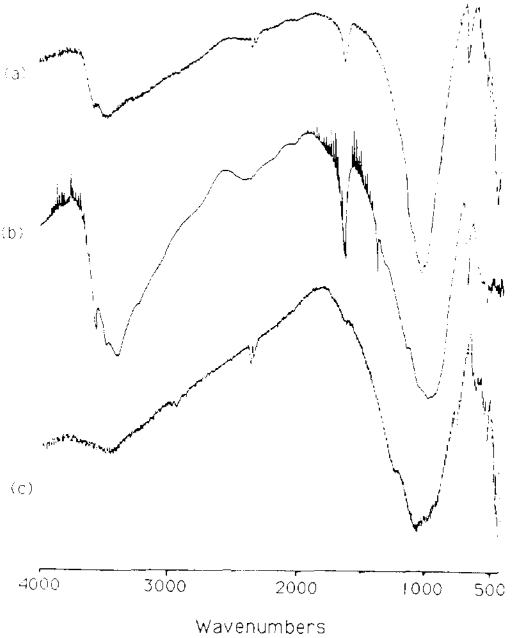

FIG. 7. Infrared absorbance spectra (KBr disk, Bio-Rad FTS-40) from 4000 to 400 cm^{-1} of (a) $Na_2(MoOPO_4)_2(HPO_4) \cdot 2H_2O$ (b) after heating to 300°C and the reabsorbtion of water upon cooling, and (c) after heating to 600°C and cooling to 23°C.

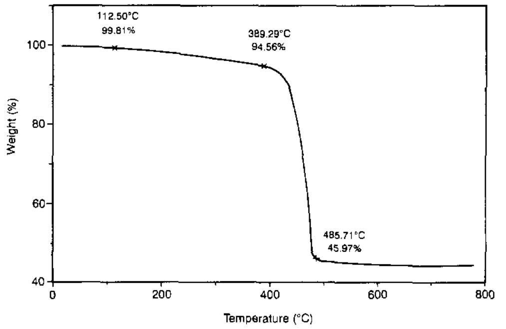

FIG. 8. Thermogravimetric curve of the NaOH treated crystals of $Na_2(MoOPO_4)_2(HPO_4) \cdot 2H_2O$, showing the two stage weight loss. Heating rate 4°/min.

$$NaOH + Na_2(MoOPO_4)_2HPO_4 \cdot 2H_2O \rightarrow Na_3(MoOPO_4)_2PO_4 \cdot 2H_2O + H_2O. \quad (1)$$

The infrared spectrum of the NaOH treated crystals was the same as that of $Na_2(MoOPO_4)_2HPO_4 \cdot 2H_2O$ with the addition of bands at 550 and 540 cm^{-1}. These bands may be due to (P)–O–Na vibrations. The thermogravimetric curve of the NaOH treated crystals under a N_2 flow in a platinum bucket indicated two stages of weight loss (Fig. 8). The first stage, has a weight loss of 5.29%. This is equivalent to the removal of two moles of water since a weight loss of 2.93% is required for each mole of water. The second weight loss, between 375 and 492°C, of 48.59% may be due to the loss of 1.5 moles of P_2O_5 + one mole of Na_2O_2 (34.68% and 12.70%, respectively, for a total of 47.38%, theoretical). The material remaining in the bottom of the bucket had turned from a light green associated with a Mo(V) oxidation state to a black glass, which indicates a reduction of molybdenum to the +4 state with the possible formula of $NaMo_2O_{4.5}$. The same sample heated under identical conditions in a glass bucket lost only water and never underwent the second weight loss, through it too changed to a black glassy material. The difference in weight loss curves indicates that platinum may act as a catalyzing agent at elevated temperatures for the redox reaction needed to form P_2O_5 + Na_2O_2 and reduced molybdenum.

To satisfy the requirements of TGA, NMR, ESR, and IR data the formula should be written as $Na_2(MoOPO_4)_2(HPO_4) \cdot 2H_2O$ with molybdenum in the oxidation state of +5 and two water molecules located within the tunnels.

Discussion

The molybdenum phosphate layers in the subject compound are similar to those seen in a number of compounds in the tetragonal isomorphous series with the formula of $MOAO_4$, where M = Mo, V, or Nb and A = P, As, Mo, or S (Table 1). These compounds crystallize out in the tetragonal space group $P4/n$ where the layers of $MOAO_4$ have a short, $M{=}O$, contact and the sixth coordination site on the $MOAO_4$ layer has a long contact, $M \cdots O$, with an oxygen in an identical layer below (Fig. 2).

In $Na_2(MoOPO_4)_2(HPO_4) \cdot 2H_2O$, the $MoOPO_4$ layer is the mirror image of the layer above or below. A hydrogen phosphate group bridges across the layers (Fig. 3). This hydrogen phosphate group is disordered around the 4-fold axis between the $MoOPO_4$ layers. The disordered hydrogen phosphate group links the layers together forming tunnels in which water molecules are located, but the exact position of the H_2O could not be determined from the X-ray data. This is consistent with the fluxional nature of the hydrogen atoms as seen in the ^1H NMR spectra. The synthesis under hydrothermal conditions may be responsible for the mobility of the water within the lattice. The dehydration and rehydration under a steady cooling rate may have allowed the water to be reabsorbed in a more orderly fashion.

The sodium ion has a rather high temperature factor. This comes about because the sodium ions are rather loosely coordinated to oxygens in the tunnels and therefore able to have a greater amplitude of vibration. The average of six Na–O interatomic distances is 2.87 Å. However, the water molecules which were not located may form shorter bonds to Na^+. It should be noted that O1 and O(4) have approximately equal temperature factors even though O(4) exhibits 4-fold disorder. O1 is the molybdenyl oxygen and therefore is not bonded to any other atoms than molybdenum. O2, on the other hand, is bonded to a proton as well as to phosphorus. The proton is also presumably hydrogen bonded to water molecules in the channels. Thus O4 is not disordered in a sense that it is loosely bonded to neighboring atoms, but rather the entire assembly of phosphate and water can occupy one of four positions about the 4-fold axis.

$Na_2(MoOPO_4)_2(HPO_4) \cdot 2H_2O$ is closely related to the $2VOSO_4 \cdot H_2SO_4$ structure which crystallizes in the space group $P4_2/mnm$ with cell parameters $a = 8.971(3)$ Å and $c = 15.594(2)$ Å (*9*). $VOSO_4$ layers are joined together by sulfuric acid molecules with V in the +5 oxidation state. The 8.971(3) Å unit cell dimension is the diagonal distance of the $a = b = 6.261(3)$ Å observed in α-$VOSO_4$ (*3*) and arises from the presence of two distinct sulfur atoms, S1 and S2, residing in the $VOSO_4$ layer. S1 has four S–O bonds at 1.44(2) Å, while S2 has two sets of S–O bonds at 1.48(3) and 1.57(3) Å. The ordering within the $VOSO_4$ layers in turn orders the position of the sulfate tetrahedron that bridges the layers. In the case of $Na_2(MoOPO_4)_2(HPO_4) \cdot 2H_2O$ the phosphate groups within the layers are identical. Thus, the layer arrangement does not order the bridging phosphate tetrahedra between the layers.

Hydrated compounds of α-vanadium sulfate have been shown to intercalate ethanol (*12*), while those of vanadium phosphates, arsenates, and niobium phosphates have been found to intercalate a number of alcohols and amines (*13–15*). The hydrates of the niobium and vanadium phosphates have been found by Beneke and Lagaly (*13*) to intercalate a number of different amines as well as long-chain alkylamines ($C_nH_{2n+1}NH_2$). The long-chain alkylamines form bilayers with a chain orientation of 60° ($n \leq 10$) or 90° ($n \geq 10$). The intercalation process is easier for the vanadium phosphates than for the niobium phosphates.

$VOPO_4 \cdot 2H_2O$ and $VOAsO_4 \cdot 2H_2O$ can also undergo redox intercalation reactions such as

$$VOPO_4 \cdot 2H_2O + {}^x\!/_n M^{n+}I_n + y\,H_2O \rightarrow M_{x/n}VOPO_4(2 + y)H_2O + {}^x\!/_2 I_2, \quad (2)$$

where aqueous iodide ions are used to reduce vanadium from +5 to +4 and incorporate mono- or divalent cations between the layers (*16, 17*). Other reducing agents such as SO_3^{2-}, NO_2^-, Sn^{2+}, Fe^{2+}, and $NH_2OH \cdot HCl$ are also effective.

The ease with which ethanol was intercalated in the structure, the mobility of the water within the cavities, as well as the similarity of $Na_2(MoOPO_4)_2(HPO_4) \cdot 2H_2O$ to the $MOPO_4$ hydrates all suggest that other small molecules and amines might intercalate into the tunnels. But because of the bridging phosphate group present, large molecules or amines will probably not be incorporated into the structure since no swelling of the layers can occur. There also exists the possibility of redox intercalation reactions occurring where the molybdenum can either be reduced or oxidized.

Acknowledgments

We thank Dr. Po Jen Chu and Roberto Frausto for help in obtaining and interpreting the NMR spectra. This work was supported by the Materials, Science and Engineering Program as part of the Regents "Commitment to Texas" initiative.

References

1. B. Jordan and C. Calvo, *Can J. Chem.* **51,** 2621 (1973).

2. N. G. Chernorukov, N. P. Egorov, and I. A. Korshunov, *Russ. J. Inorg. Chem. Engl. Transl.* **23,** 1479 (1978).
3. J. M. Longo and R. J. Arnott, *J. Solid State Chem.* **1,** 394 (1970).
4. H. A. Eick and L. Kihlborg, *Acta Chem. Scand.* **20,** 722 (1966).
5. J. M. Longo and P. Kierkegaard, *Acta Chem. Scand.* **20,** 72 (1966).
6. J. M. Longo, J. W. Pierce, and J. A. Kafalas, *Mater. Res. Bull.* **6,** 1157 (1971).
7. P. Kierkegaard and M. Westerlund, *Acta Chem. Scand.* **18,** 2217 (1964).
8. P. Kierkegaard and J. M. Longo, *Acta Chem. Scand.* **24,** 427 (1970).
9. P. M. Tachez and F. Theobald, *Acta. Crystallogr., Sect. B* **37,** 1978 (1981).
10. TEXSAN, "Texray Structural Analysis Package," Molecular Structure Corp., The Woodlands, TX. (1987 (revised)).
11. D. E. C. Corbridge, "Phosphorus: An Outline of its Chemistry, Biochemistry and Technology," 3rd ed., Elsevier New York (1985).
12. G. Ladwig, *Z. Chem.* **20,** 70 (1980).
13. K. Beneke and G. Lagaly, *Inorg. Chem.* **22,** 1503 (1982).
14. J. W. Johnson, A. J. Jacobson, J. F. Brody, and S. M. Rich, *Inorg. Chem.* **21,** 3820 (1982).
15. M. M. Lara, L. M. Real, A. J. Lopez, S. B. Gamez, and A. R. Garcia, *Mater. Res. Bull.* **21,** 13 (1986).
16. J. W. Johnson and A. J. Jacobson, *Angew. Chem. Int. Ed. Engl.* **22,** 412 (1983).
17. M. M. Lara, A. J. Lopez, L. M. Real, S. Bruque, B. Casal, and E. Ruiz-Hitzky, *Mater. Res. Bull.* **20,** 549 (1985).