Synthesis, X-ray Powder Structure, and Intercalation Behavior of Molybdenyl Phenylphosphonate, MoO2(O3PC6H5)·H2O

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The crystal and molecular structure of molybdenyl phenylphosphonate has been determined from X-ray powder diffraction data and refined by Rietveld methods. The compound crystallizes in the orthorhombic space group $P222$ with $a = 6.3610(3)$, $b = 16.0889(9)$, $c = 9.3573(7)$ Å, $Z = 4$. The final agreement factors are $R_p = 0.119$, $R_{wp} = 0.175$, $R_F = 0.056$. The structure consists of bent MoO_2 groups coordinated by three phosphonate oxygens and a water molecule. The bridging of the phosphonate group leads to the formation of double chains which are held together by hydrogen bonds involving water oxygens and phosphonate oxygens. The structure is similar to that of $MoO_2HPO_4·H_2O$ and the phosphonate also exhibits intercalation behavior toward amines.

Introduction

There has been a great deal of research activity aimed at the synthesis and structural chemistry of metal organophosphonates because of their interesting coordination chemistry and potential applications. Layered metal phosphonates, in particular, can act as hosts in intercalation reactions and thus may serve as sorbents, catalysts and ion exchangers.[1-7] We have been involved in the synthesis and structural characterization of a variety of metal phosphonates consisting of different metal ions and organic groups.[4,7,8] In this paper we describe the synthesis, structure and preliminary results of intercalation on a Mo(VI) compound containing the phenylphosphonate group. The structure is characterized by double molybdenyl phosphate type chains similar to those in $MoO_2HPO_4·H_2O$.[9a,b]

Molybdenyl hydrogen phosphate, $MoO_2HPO_4·H_2O$, a one-dimensional compound, has been shown to undergo reversible intercalation reactions with a variety of organic groups.[10] In these reactions the basic double chain structure is unaltered in the cases where alcohols and water molecules are intercalated. This molybdenyl phosphate is structurally similar to that of VOH-$PO_4·4H_2O$[11] and is also closely related to the structures

of $UO_2HPO_4·H_2O$,[12] β-$VOHPO_4·2H_2O$,[13] and α-Zr-$(HPO_4)_2·H_2O$[14] although the latter three compounds have a two-dimensional layered structure. All these materials have shown interesting intercalation or exchange properties.[15-18] Recently we have shown that the substitution of a phenylphosphonate group for phosphate in the Zr compound has little effect on the arrangement of the layers in the crystal structure.[19] This work was taken up to see whether such an isostructural derivatization is possible in the molybdenyl phosphate system. A knowledge of the structures of such phosphonates would greatly aid the development of model structures for related intercalation derivatives.

Experimental Section

Materials and Methods. Chemicals used were of reagent-grade quality and were obtained from commercial sources without further purification. Thermogravimetric analyses (TGA) were carried out with a DuPont Model No. 951 unit, at a rate of 10 °C/min. Infrared spectra were recorded on a Digilab Model FTS-40 FTIR unit by the KBr disk method. ^{31}P NMR spectra were obtained on a Bruker MSL-300 solid-state NMR spectrometer where proton and phosphorus nuclei resonate at 300.1 and 121.5 MHz, respectively. The ^{31}P chemical shifts were referenced to 85% H_3PO_4 (aqueous solution). X-ray powder patterns were taken with Cu Kα radiation on a Rigaku RU-200 automated powder diffractometer (rotating anode). The step width was 0.04° in 2θ and the time constant was 2.4 s/step.

Preparation of the Compound. The title compound was prepared as follows: 0.78 g of MoO_3 (Mallinckrodt), 1.04 g of $H_2O_3PC_6H_5$ (Aldrich), and 40 mL of deionized water were

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placed in a 90-mL Teflon-lined digestion bomb. The bomb was then kept at 150 °C for 5 days. The solution was nearly dry when it was opened. A slightly gray solid (1.37 g; 84% yield) was obtained after washing with water and air-drying.

Intercalation of butylamine was carried out as follows: A 0.8 g sample of the title compound was kept in contact with an excess of liquid butylamine in a closed container. Portions of the sample were recovered after reactions for 3, 7, and 15 h, and their X-ray powder patterns recorded. The sample that had been contacted with the amine was then allowed to stand out of contact with the amine for up to 1 month and then recontacted with the amine for up to 200 h.

X-ray Data Collection. Step-scanned X-ray powder data for the sample (side-loaded into a flat aluminum sample holder) were collected on the finely ground sample by means of a Rigaku computer-automated diffractometer. The X-ray source was a rotating anode operating at 50 kV and 180 mA with a copper target and graphite monochromated radiation. Data were collected between 3 and 75° in 2θ with a step size of 0.02° and a count time of 15 s/step. Data were mathematically stripped of the $K\alpha_2$ contribution and peak picking was conducted by a modification of the double-derivative method.[20] The powder pattern was indexed by Ito methods[21] on the basis of the first 20 observed lines. The best solution which indexed all the lines (figure of merit = 31) indicated an orthorhombic unit cell with lattice vectors $a = 6.36$ Å, $b = 16.07$ Å, $c = 9.35$ Å. There were no systematic absences in the data although the intensities of the reflections with odd indexes along the a and c axes as well as those in the $h0l$ zone with $h + l =$ odd were very weak.

Structure Solution and Refinement. Integrated intensities were extracted from the profile over the range $5° < 2\theta < 61.6°$ by decomposition (MLE) methods as described earlier.[22] This procedure produced 62 single indexed reflections. The intensities of these reflections were used as a minimal data set for structure analysis in the TEXSAN[23] series of single-crystal programs. The positions of the Mo atom and that of the P atom were derived from a Patterson map. Constrained refinements and subsequent difference Fourier maps allowed the positioning of all the oxygen atoms in the structure. These atoms were used for Rietveld refinement in GSAS.[24]

Using the utility program GRAPH,[25] the raw data were transferred to the GSAS program package for full-pattern refinement. After the initial refinement of scale, background and unit cell constants, the atomic positions were refined with soft constraints consisting of both Mo—O and P—O bond distances and O—O nonbonded distances. Difference Fourier maps computed at this stage revealed the positions of the carbon atoms of the phenyl group. All the atoms were refined isotropically. In the final cycles of refinement the shifts in all the parameters were less than their estimated standard deviations. Neutral atomic scattering factors were used for all atoms. No corrections were made for anomalous dispersion, absorption, or preferred orientation.

Results and Discussion

Characterization of the Molybdenyl Phenylphosphonate. Thermogravimetric analysis showed that the sample lost 5.9% of its weight below 250 °C and underwent a 20% weight loss beginning at 400 °C. The first weight change is due to the loss of water (calculated for $MoO_2(O_3PC_6H_5)\cdot H_2O$, 5.96%) while the second is due to the decomposition of the organic group. The ^{31}P NMR

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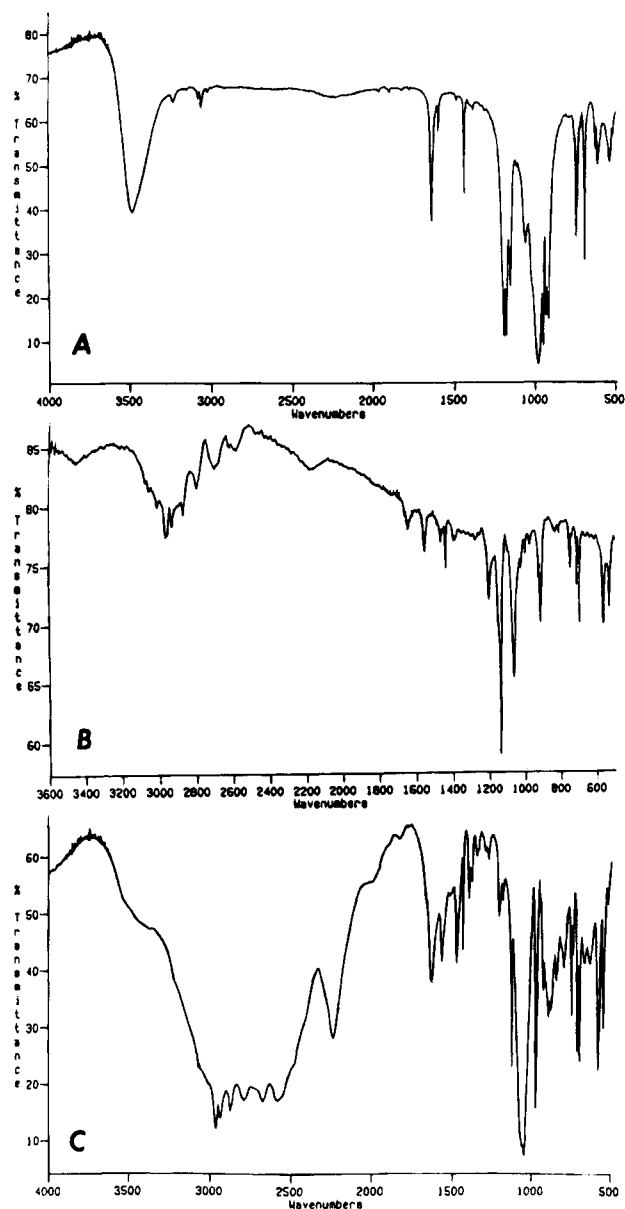
Figure 1. FTIR spectra of (A) molybdenyl phenylphosphonate, (B) the butylamine intercalate after 15 h contact with the amine, and (C) after 80 h.

indicated a single phosphorus site (chemical shift, 18.27 ppm) in the structure. The EDAX analysis of the sample showed the average P:Mo ratio of 47:53; the difference from a 1:1 stoichiometry is due to the presence of a small amount of free MoO_3 in the sample. The IR spectrum (Figure 1A) contains a large band at 3482 cm^{-1} for the water −OH stretch and a sharp band at 1640 cm^{-1} representing the water scissors motion. The phenyl ring C−H stretch bands are at 3023, 3057, and 3092 cm^{-1} and the aromatic C=C stretch band is at 1438 cm^{-1}. The bands at 689 and 742 cm^{-1} represent the out-of-plane bending of the monosubstituted phenyl ring and the −PO₃ stretching bands occur in the region of 1000 cm^{-1}. The band at 950 cm^{-1} is characteristic of M=O stretching. On the basis of weight loss and IR data we assumed that the composition of the compound is $MoO_2(O_3PC_6H_5)\cdot H_2O$, and this was confirmed by the structure solution.

Crystal Structure. Crystallographic and experimental parameters are given in Table 1, and final positional and thermal parameters in Table 2. Bond

Table 1. Crystallographic Data for MoO₂ (O₃PC₆H₅)·H₂O^a

empirical formula	MoO₆PC₆H₇
fw	302.03
pattern range (2θ), deg	15.5–75
step scan increment (2θ), deg	0.02
step scan time, s	15
radiation source	Rotating Anode
λ (Cu Kα_1, Kα_2), Å	1.5406, 1.5444
a, Å	6.3610(3)
b, Å	16.0889(9)
c, Å	9.3573(6)
V, Å³	957.64
Z	4
space group	P222(No. 16)
D_c, g/cm³	2.094
no. of contributing reflections	634
no. of geometric observations	37
P–O distances and tolerance (Å)	1.53(1)
MoO₆ distances and tolerance (Å)	1.70(1); 2.03(1)
O–O distances for PO₄ (Å)	2.55(1)
O–O distances for MoO₆ (Å)	2.73(2)
no. of structural parameters	46
no. of profile parameters	11
statistically expected R_{wp}	0.02
R_{wp}	0.175
R_p	0.119
R_F	0.056

^{a} $R_{wp} = (\Sigma w (I_0 - I_c)^2 / \Sigma [w I o^2])^{1/2}$; $R_p - (\Sigma |I_o - I_c| / \Sigma I_c)$; $R_F = \langle |F_\Sigma| - |F_c| \rangle / \langle |F_o| \rangle$; expected $R_{wp} = R_{wp}/(\chi^2)^{1/2}$; $\chi^2 = \Sigma w (I - I_c)^2 / (N_{obs} - N_{var})$.

Table 2. Positional and Isotropic Thermal Parameters for MoO₂9O₃PC₆H₅)·H₂O

	x	y	z	U_{iso}, Å²
Mo	0.270(1)	0.1404(3)	0.260(1)	0.009(2)
P	0.748(3)	0.1739(7)	0.351(1)	0.025(2)
O1	0.560(3)	0.132(1)	0.274(3)	0.042(2)
O2	0.726(6)	0.173(1)	0.513(1)	0.042^a
O3	0.956(3)	0.132(1)	0.299(3)	0.042^a
O4	0.246(6)	0.096(1)	0.108(2)	0.042^a
O5	0.256(6)	0.246(1)	0.259	0.042^a
O(w)	0.268(6)	0.025(1)	0.383(2)	0.042^a
C1	0.758(6)	0.282(1)	0.294(2)	0.053(2)
C2	0.788(16)	0.344(1)	0.394(3)	0.053^b
C3	0.744(16)	0.425(1)	0.352(4)	0.053^b
C4	0.762(11)	0.444(1)	0.205(4)	0.053^b
C5	0.753(20)	0.380(1)	0.106(3)	0.053^b
C6	0.726(16)	0.301(1)	0.151(2)	0.053^b

$U_{iso} = B_{iso}/8\pi^2$

^{a} Constrained to be equal to U_{iso} of O1. ^{b} Constrained to be equal to U_{iso} of C1.

lengths and angles are shown in Table 3 and the final Rietveld refinement difference plot is shown in Figure 2. Figure 3 represents the structure as viewed down the c axis and Figure 4 shows the distorted octahedral coordination about the molybdenum atom and the connectivity of the double chains.

The structure is one dimensional consisting of double-stranded chains running parallel to the a axis. In the unit cell all the atoms except O1 and O3 are positioned nearly on a plane situated at $x \sim 0.25$ (Table 2) and the symmetry related plane at $x \sim 0.75$ (Figure 3). The double-stranded chains lie roughly parallel to the ac plane with one strand at $z = \frac{1}{4}$ and the other at $z = \frac{3}{4}$. Molybdenum atoms in a single chain are bridged by oxygen atoms O1 and O3 of the phosphonate group while the third phosphonate oxygen atom, O2, binds to the Mo atoms in the adjacent strand of the double linear chain. The octahedral coordination of Mo atoms is completed by the two molybdenum oxygens and a coordinating water molecule.

Table 3. Bond Lengths (angstroms) and Bond Angles (degrees) for MoO₂(O₃PC₆H₅)·H₂O

|			
Mo–O1	1.85(2)	P–O1	1.55(1)
Mo–O2	2.19(1)	P–O2	1.52(1)
Mo–O3	2.03(2)	P–O3	1.56(1)
Mo–O4	1.60(2)	P–C1	1.81(1)
Mo–O5	1.71(2)	C1–C2	1.39(2)
Mo–O(W)	2.18(2)	C2–C3	1.39(2)
		C3–C4	1.42(1)
		C4–C5	1.39(1)
		C5–C6	1.35(2)
		C6–C1	1.39(1)
O1–Mo–O2	86(1)	O1–P–O2	113(1)
O1–Mo–O3	164(1)	O1–P–O3	109(1)
O1–Mo–O4	97(1)	O1–P1–C1	108(1)
O1–Mo–O5	97(1)	O2–P–O3	112(1)
O1–Mo–O(W)	85(1)	O2–P–C1	108(1)
O2–Mo–O3	82(1)	O3–P–C1	107(1)
O2–Mo–O4	166(1)	C1–C2–C3	118(2)
O2–Mo–O5	77(1)	C2–C3–C4	117(1)
O2–Mo–O(W)	72(1)	C3–C4–C5	119(1)
O3–Mo–O4	92(1)	C4–C5–C6	120(1)
O3–Mo–O5	91(1)	C5–C6–C1	120(1)
O3–Mo–O(W)	81(1)	C6–C1–C2	120(1)
O4–Mo–O5	116(1)	P–C1–C2	120(1)
O4–Mo–O(W)	95(1)	P–C1–C6	112(1)
O5–Mo–O(W)	148(1)		
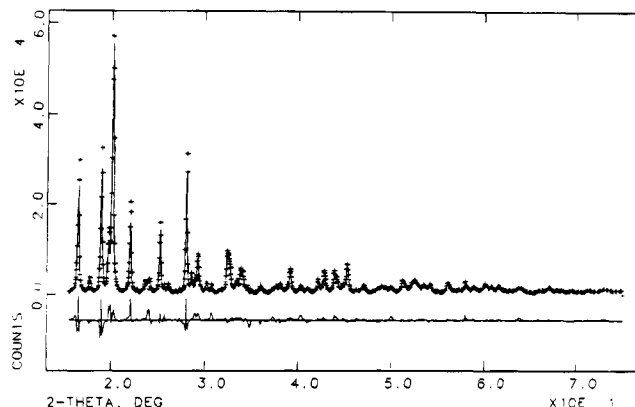
Figure 2. Observed (+) and calculated (−) profiles (X-ray intensity versus 2θ) for the Rietveld refinement of MoO₂(O₃-PC₆H₅)·H₂O. The bottom curve is the difference plot on the same intensity scale. The small differences between the observed and calculated profiles is mainly due to problems with preferred orientation and hkl-dependent line-broadening effects. For the same reason the first two reflections along $0k0$ are not used for Rietveld refinement. Their integrated intensities, however, match with those calculated from the final refined model.

The octahedron consists of two short Mo=O bonds (1.60(2) Å, 1.71(2) Å), two medium [Mo–O1, 1.85(2) Å; Mo–O3, 2.03(2) Å] and two long molybdenum–oxygen bonds Mo–O(W) and Mo–O2 (2.18 and 2.19 Å, respectively). This distribution of long, medium, and short bonds is quite common in MoO₆ octahedra.[26] The molybdenyl group is bent with an O–Mo–O angle of 116°.

The water molecule is involved not only in coordinating the metal atom but also in holding the double chains intact through hydrogen bonding. There are three contacts involving the water molecules and the phosphonate oxygens (Figure 3). These are O(W)--O(WA) (2.34 Å), O(W)--O1 (2.95 Å) and O(W)--O3 (3.01 Å). It should be noted in Figure 3 that one of the double chains

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Behavior of Molybdenyl Phenylphosphonate
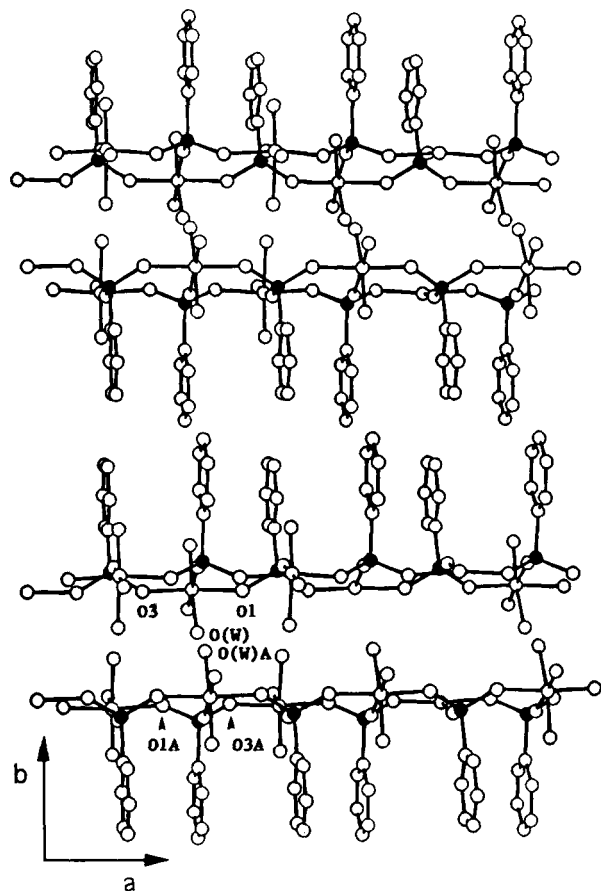
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Figure 3. Structure of molybdenyl phenylphosphonate as viewed down the c axis showing the arrangement of phenyl groups in the lattice. O(W) is hydrogen bonded to O(W)A, O1A, and O3A in the adjacent double chain.
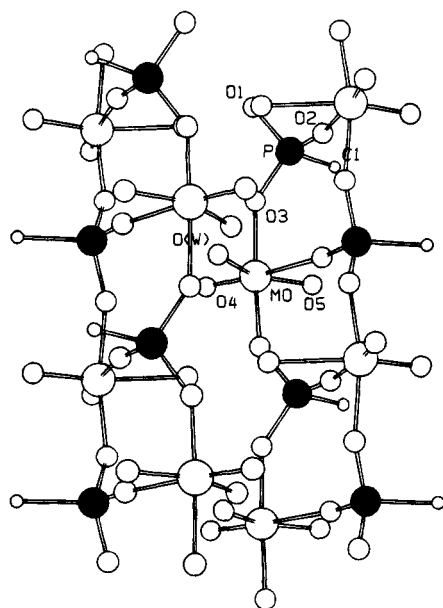

Figure 4. Portion of the structure showing the molybdenyl groups linked by phosphonate oxygens leading to double chains. Only the carbon atom bonded to the P atom is shown for clarity.

is about 2.25 Å above the basal ac plane ($y = 0$) and another is below this plane the same distance. The water molecules are at $y = \pm 0.025$ or 0.8 Å apart in the b direction. This proximity allows for the very short observed hydrogen bond. The consequences of the hydrogen bonding scheme is that it ties together two

adjacent double chains in the b direction in such a way that the oxygen atoms in the adjacent double chains face each other and the phenyl groups point in the opposite directions (Figure 3). As a result, a hydrophobic region of phenyl groups is created which alternates with a hydrophilic region in which essentially oxygen atoms and water molecules reside. The phenylphosphonate groups display regular tetrahedral geometry in the structure with normal P–O bond distances. This structure is closely related to that of the hydrated molybdenum hydrogen phosphate, $MoO_2HPO_4 \cdot H_2O$,[9a] although the parent phosphate compound crystallizes in the space group $P2_1/m$. The sole interaction between the double chains in this compound is through the molybdenum oxygen and the P–O–H groups.[9b] Accurate bond distances are available[9b] for $MoO_2(D-PO_4) \cdot D_2O$ for comparison with the phosphonate. The double-bonded oxygens in this phosphate have bond distances to Mo of 1.673(3) Å and 1.747(3) Å and an O–Mo–O angle of 104.1(9)° as compared to 116° in the phosphonate. The O–P–O bridging oxygens within a single strand of the double chain in the phosphate are related by symmetry, with Mo–O distances of 2.021(4) Å and the longest bonds are the Mo–O bond distance across the strands, 2.071(4) Å, and the Mo–O(W) distance 2.271(6) Å.

It is rather interesting to compare the structures of molybdenyl phosphate and that of molybdenyl phenylphosphonate to the analogous structures of zirconium. As described above, the double-chain structure is retained in both phosphate and phenylphosphonates of molybdenum. A similar relationship has been observed in the case of the layered zirconium structures.[14,19] In the case of zirconium, however, the structures are layered and the ratio of metal to phosphonate and/or phosphate is 1:2. The zirconium atoms lie in a plane and are bridged by phosphate oxygens. The phosphate groups alternate above and below the metal plane and the O–H group or the phenyl group points away from this plane. All six coordination sites are occupied by the phosphate oxygens. This type of bridging leads to a layer structure both in the case of phosphate and the phenylphosphonate. The only difference in these two structures is that in the latter compound the layers are separated to accommodate the bulky organic group. These results show that large organic groups like phenyl groups can be introduced into the metal phosphate structures without disturbing the basic structural units.

Recently two molybdenum(V) structures containing phenylphosphonate groups have been reported. These are $[N(C_2H_5)_4]_2Na_3(H_3O)_4\{Na[Mo_6O_{15}(O_3PC_6H_5)(HO_3-PC_6H_5)_3]_2\} \cdot 14H_2O$[26] and $(NH_4)_5Na_4\{Na[Mo_6O_{15}(HO_3-PC_6H_5)_3(O_3PC_6H_5]_2 \cdot 6H_2O$.[27] These structures are not layered nor do they form chains. Both these compounds contain isolated cations and hexanuclear molybdenum polyoxophosphonate anions. Phosphonate derivatives of other molybdenum and tungsten polyoxometallates have also been described.[28]

Intercalation Reactions. The molybdenum phenylphosphonate is capable of intercalating various spe-

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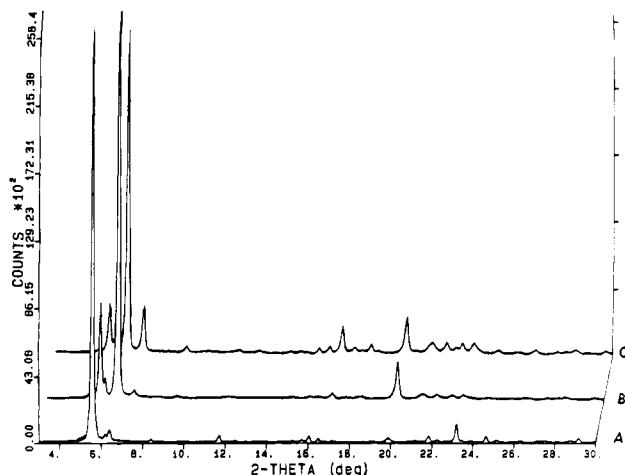(28) Pope, M. T. *Heteropoly and Isopoly Oxometallates*; Spring-Verlag: New York, 1983; pp 119–121.

Figure 5. X-ray powder patterns of molybdenyl phenylphosphonate after contacting with neat butylamine for (A), 3, (B) 7, and (C) 15 h. The X-ray patterns are offset from each other by the amount shown by the slanted line at the right.
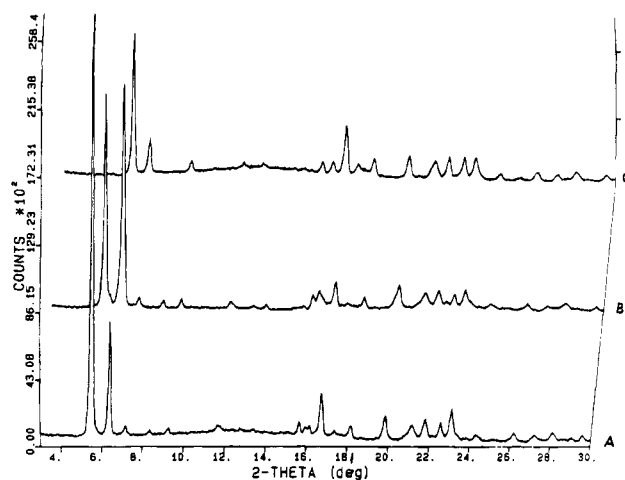

Figure 6. XRD patterns of molybdenyl phenylphosphonate intercalated with butylamine for 15 h and (A) left to stand in air for 30 days. The very intense reflection at the left is of unintercalated molybdenyl phenylphosphonate, (B) the sample shown in A recontacted with butylamine for 30 h, and (C) for 60 h for complete conversion to the butylamine intercalate. The patterns are offset as in Figure 5.

cies of organic molecules. Here we will describe only the results with amines. Intercalation occurs slowly as shown by the X-ray patterns of Figure 5. After 3 h contact with neat butylamine (Figure 5A) the diffractogram is essentially that of the host molybdenyl phenylphosphonate except for a small peak at $2\theta = 6.35°$ ($d = 13.9$ Å). This latter phase increases relative to that of the unreacted host phosphonate as shown by the changing nature of the X-ray patterns. The peak at $2\theta = 5.5$ ($d = 16.1$ Å) decreases in intensity while the 13.9 Å peak increases. The reaction is complete in about 20 h.

The 15 h intercalate was removed from contact with the amine and allowed to stand exposed to the atmosphere for 30 days. The X-ray pattern, Figure 6A revealed that most of the amine has been lost as the major component of the pattern was the starting host molybdenyl phenylphosphonate. Reimmersion of the sample in neat butylamine again resulted in uptake of amine. Complete conversion this time required 60 h of contact with the amine as shown by the X-ray diffractogram in Figure 6C. However, longer immersion in the

amine resulted in slow decomposition of the molybdenyl phosphonate (vide infra).

The IR spectra of the butylamine intercalate taken after the molybdenyl phenylphosphonate had been immersed in butylamine for 15 h and 80 h are shown in Figure 1B,C. In the spectrum shown as Figure 1B the very prominent water band is much diminished but still present while weak bands for the CH stretch of the alkyl chain are present at 2871, 2933, and 2960 cm^{-1}. The aromatic CH stretching bands are observed at 3009, 3064, and 3091 cm^{-1} but there is no clear indication of an NH$_2$ stretch. However, new bands appear at 2575 and 2702 cm^{-1}. These bands are indicative of hydrogen bonded OH or NH$_2$ groups. The band at 1549 cm^{-1} is undoubtedly the NH$_2$ bending mode. Several of the bands in the P–O and O–H stretching region of the spectrum are diminished in intensity. The spectrum in Figure 1C will be considered after the following remarks on the intercalation reaction.

Our picture of the amine intercalation reaction involves initial displacement of the water molecule coordinated to Mo by the nitrogen lone pair. The alkyl chain however must be directed essentially along the *b* direction lying in between the phenyl rings. This concentration of alkyl and aromatic groups greatly increases the van der Waals forces between the chains pulling them closer together in the *b* direction. The butylamine chain is approximately 5.6 Å long from the nitrogen to the end of the methyl group. If the nitrogen atom has the same *y* parameter as the water molecule, ±0.025, then the end of the chains would be alternately about 6 Å above and below the basal *ac* plane at *y* = 0. In the original unintercalated structure the gap between phenyl rings from above and below is 1.8 Å. This value added to 12 Å allowed for the amine chains yields a distance of 13.8 Å which is very close to that observed for the 010 reflection. A similar shrinkage in interlayer spacing has been observed in the layered compound Zn(O$_3$PC$_6$H$_5$)·H$_2$O when the coordinated water molecule is replaced by propylamine.[29]

Hexylamine is 2.54 Å longer than butylamine in its trans conformation and if situated in a position similar to that of butylamine, should extend beyond the phenyl rings. In fact the initial hexylamine phase exhibits a strong first reflection at 17.6 Å. On continued contact with the amine a second reflection appeared at 20.5 Å and finally a phase with a strong reflection at 21.7 Å grew in. A similar change in the X-ray pattern of the butylamine intercalate occurred as it remained in contact with the liquid amine. The X-ray pattern contained strong reflections at 15.4, 14.8, and 13.0 Å, while the original reflection at 13.8 Å is no longer present. In the process additional amine was taken up as shown by increased weight losses by TG analysis. Figure 1C shows the IR spectrum after 80 h of contact with the amine. We note some profound differences in the spectrum including a large water band and a band at 2233 cm^{-1} which was just beginning to be evident in the spectrum of Figure 1B. These changes could indicate decomposition of the molybdenyl phenylphosphonate by hydrolysis of the phenylphosphonate group. This conjecture is bolstered by the fact that attempts to remove the amine by heating (200 °C) or treatment

(29) Zhang, Y.-P.; Scott, K. J.; Clearfield, A. *J. Mater. Chem.*, in press.

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with acid produced only amorphous powders. Evidently amine intercalation in this compound is an extremely complex process which does not end with formation of a single specific compound.

Ethanol did not intercalate into the molybdenyl phenylphosphonate as determined by X-ray and TG analysis. However, methanol was reportedly taken up by the molybdenyl phosphate.[10] The alcohol was inserted between the double stranded chain and is hydrogen bonded by the P—OH group and in turn is the donor to a phosphate oxygen. Our molybdenyl phenylphosphonate double-stranded chains are oriented such that the phenyl rings of one chain are directed toward phenyl rings of another chain creating an hydrophobic region. This separation of hydrophobic and hydrophilic regions is common in metal phosphonate structures and appears to be a dominating factor in determining their structures. This separation undoubtedly also determines the nature of the intercalation process. Additional structural and computer modelling studies now underway should help to clarify these questions.

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