Synthesis of Layered $MoOPO_4 \cdot 2H_2O$ and Investigation of Its Intercalation Chemistry[†]

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We describe in this paper the synthesis and characterization of a new layered phosphate, $MoOPO_4 \cdot 2H_2O$ (**I**), and its intercalation chemistry. The phosphate **I**, crystallizing in a tetragonal structure ($a = 6.375(7)$, $c = 7.80(1)$ Å, and $Z = 2$) similar to that of $VOPO_4 \cdot 2H_2O$, has been synthesized by the reduction of $MoO_2(HPO_4) \cdot H_2O$ (**II**) using ethylene glycol in an CH_3CN medium at ∼60 °C. Interestingly, **I** could be readily oxidized back to **II** using Br_2 in CH_3CN at room temperature. Considering the close structural relationship existing between **I** and **II**, it is likely that the reduction and oxidation of the phosphates proceed by a topotactic mechanism. **I** is a novel layered host intercalating a variety of organic bases such as *n*-alkylamines, pyridine, and aniline, mainly through an acid−base interaction. Unlike $VOPO_4 \cdot 2H_2O$, **I** does not exhibit reductive intercalation reactivity.

Introduction

Two different structural modifications are known for transition metal phosphates of the general formula $MOPO_4$. The tetragonal (space group $P4/n$) α-form, which is stabilized at low temperatures or high pressures, is known[1−5] for M = V, Nb, Ta, Mo, and W, while the monoclinic (space group $P2_1/c$) β-form, which is usually obtained at high temperatures or low pressures, has been reported[5,6] for M = Nb, Ta, and W. The tetragonal structure of the α-form consists of chains of corner-shared MO_6 octahedra running parallel to the *c*-axis which are cross-linked by PO_4 tetrahedra to form the three-dimensional structure.[7] The structure can also be viewed as consisting of charge-neutral $[MOPO_4]_\infty$ sheets which are stacked one over the other in the *c*-direction. Interestingly, only the M = V and Nb members of the α-series form two-dimensional hydrates, $MOPO_4 \cdot xH_2O$ (x = 1, 2, or 3).[8,9] Because of the layered structure, the hydrates exhibit a rich interlayer chemistry.[9,10] The layered structure of the hydrates may be thought of as being formed by cleaving the three-dimensional α-$MOPO_4$ network perpendicular to the *c*-direction and inserting water molecules in between; one water molecule is coordinated to the M atom in the axial position and the remaining are held in between the layers through hydrogen bonds.[8]

It has been suggested[11] that formation of the hydrated phases of α-$MOPO_4$ is related to an off-center displacement of the M atoms in the MO_6 octahedra along the *c*-direction. This displacement gives rise to both short and long axial M−O bonds along the *c*-direction. For the $MOPO_4$ (M = V, Nb) compounds that form hydrates, the short and long M−O bond distances are 1.58 and 2.85 Å (α-$VOPO_4$) and 1.78 and 2.32 Å (α-$NbOPO_4$). Presumably, the longer the long axial bond, the easier it is to cleave the structure into layers forming the $MOPO_4$ hydrates. Among the other $MOPO_4$ compounds, $MoOPO_4$, which is known only in the α-modification, possesses short (1.65 Å) and long (2.64 Å) Mo−O axial bonds[4b] that are comparable to those of α-$VOPO_4$ and α-$NbOPO_4$. Accordingly, we expected that it should be possible to prepare hydrated $MoOPO_4$[12] that would exhibit interesting interlayer chemistry similar to $VOPO_4 \cdot 2H_2O$ and $NbOPO_4 \cdot 3H_2O$. We have been able to prepare hydrated $MoOPO_4 \cdot 2H_2O$ (**I**) by a novel method involving topotactic reduction of molybdenum(VI) phosphate, $MoO_2(HPO_4) \cdot H_2O$ (**II**), using ethylene glycol as the reducing agent. Here we report the synthesis and characterization of **I** as well as its intercalation behavior toward a variety of organic donors. We also propose a possible mechanism for the topotactic reduction of **II** to **I**.

Experimental Section

$MoO_2(HPO_4) \cdot H_2O$ (**II**) was prepared, as reported in the literature,[13] by dissolving 15 g of MoO_3 in 45 mL of 85% phosphoric acid. The green solution that formed was cooled, and 400 mL of 16 M HNO_3 was added and then evaporated, during which a white solid separated out. The solid was filtered, washed with cold water, and dried in air. Reduction of **II** was investigated using 2-propanol, 2-butanol, and ethylene glycol in an CH_3CN medium. It was found that reduction with ethylene glycol under the following conditions yielded reproducible results. Two grams (8.3 mmol) of **II** in 20 mL of CH_3CN was treated with 5 mL (90 mmol) of ethylene glycol at ∼60 °C for 4 days. A blue solid (**I**) separated out which was washed with acetone and dried under vacuum. The oxidation state of the molybdenum in the product was determined by a potentiometric titration using Ce^{IV} as the oxidant. The product, **I**, could be oxidized back to **II** by treating it (0.5 g) with 1 mL of bromine in 10 mL of CH_3CN at room temperature with intermittent stirring.

Intercalation of *n*-alkylamines into **I** was carried out by treating 0.5 g of the solid with 10 mL of a 1% amine solution in *n*-heptane for 24

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h. The intercalation products were filtered, washed with *n*-heptane, and dried in vacuum. Intercalation of pyridine into **I** was carried out by reacting 0.5 g of the solid with 20 mL of a 10% pyridine solution in *n*-heptane for 1 week at 50 °C. The resulting green solid was separated by vacuum filtration. The product was treated again with a fresh aliquot of a 10% pyridine solution in *n*-heptane for 4 more days to complete the intercalation reaction. This final product was filtered under vacuum, washed with acetone, and dried in air. Aniline was intercalated into **I** by treating the solid (1 g) with 20 mL of a 10% aniline solution in *n*-heptane at ~60 °C for 1 day. The monomer that aniline intercalated into **I** was polymerized by heating the intercalate in an air-oven at 130 °C for 1 week with intermittent grinding.

A JEOL JDX-8P X-ray powder diffractometer operating with Cu Kα radiation was used to record X-ray diffraction patterns. Unit cell parameters were derived by least-squares refinement of powder X-ray diffraction (XRD) data. The water of hydration of **I** and the amine contents of its intercalates were determined from the weight losses in thermogravimetric (TG) curves. The TG curves were recorded using a Cahn TG-131 system (heating rate 2 °C/min) in a flowing nitrogen atmosphere. In selected cases, the composition of the amine intercalates of **I** were determined by C, H, and N analysis. Infrared (IR) spectra of the samples were recorded with a Bruker IFS 66v FTIR spectrometer using KBr disks.

Results and Discussion

We investigated the formation of a molybdenum(V) phosphate by reduction of $MoO_2(HPO_4) \cdot H_2O$ (**II**) with 2-propanol, 2-butanol, and ethylene glycol. While it is known that 2-propanol and 2-butanol reduce $VOPO_4 \cdot 2H_2O$ to vanadium(IV) phosphate,[14] common alcohols such as methanol, ethanol, and 2-propanol form intercalation compounds[15] with **II**. We found that the phosphate **II** dissolves in 2-propanol and 2-butanol under reflux giving a blue solution. On the other hand, **II** is smoothly reduced to a blue solid by ethylene glycol in an CH_3CN medium under the conditions employed by us (*cf.* Experimental Section). The oxidation state of molybdenum in the blue product, determined by a potentiometric titration using Ce^{IV} as oxidant, was 4.98 ± 0.02. The powder XRD pattern of the product (Figure 1a) was similar to that of α-$VOPO_4 \cdot 2H_2O$ and could be indexed on a tetragonal unit cell with $a = 6.375(7)$ and $c = 7.80(1)$ Å (Table 1). The corresponding cell parameters of α-$VOPO_4 \cdot 2H_2O$ are $a = 6.215$ and $c = 7.403$ Å.[8] The TG analysis (Figure 2) carried out under N_2 flow shows weight loss in two steps. These weight losses correspond to the loss of two water molecules, the total weight loss (15%) being consistent with the reaction:

$$MoOPO_4 \cdot 2H_2O \xrightarrow{125\ °C} MoOPO_4 \cdot H_2O \xrightarrow{350-450\ °C} MoOPO_4 \xrightarrow[\text{at 600 °C}]{\text{anneal in } N_2} \alpha\text{-}MoOPO_4 \quad (1)$$

Accordingly, the combined results of chemical analysis (oxidation state of molybdenum), TG analysis, and powder XRD reveal that the ethylene glycol reduction product of $MoO_2(HPO_4) \cdot H_2O$ (**II**) is $MoOPO_4 \cdot 2H_2O$ (**I**). The reduction reaction could be written as follows:

$$4MoO_2(HPO_4) \cdot H_2O + (CH_2OH)_2 \rightarrow 4MoOPO_4 \cdot 2H_2O + (CHO)_2 \quad (2)$$

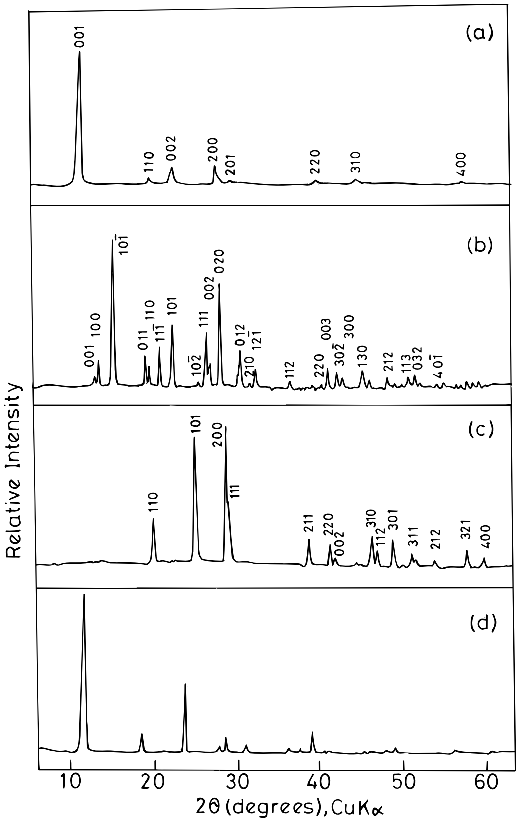

Figure 1. X-ray powder diffraction patterns of (a) $MoOPO_4 \cdot 2H_2O$ (**I**) and (b) $MoO_2(HPO_4) \cdot H_2O$ (**II**) obtained by Br_2 oxidation of **I**, (c) anhydrous $MoOPO_4$ obtained by dehydration of **I**, and (d) $VOPO_4 \cdot 2H_2O$.

Table 1. X-ray Powder Diffraction Data for $MoOPO_4 \cdot 2H_2O$ (**I**)[a]

hkl	d_{obs} (Å)	d_{cal} (Å)	I_{obs}
001	7.762	7.800	100
110	4.506	4.508	6
002	3.900	3.900	11
200	3.192	3.187	16
201	2.959	2.950	2
220	2.254	2.254	6
310	2.022	2.016	8
400	1.600	1.594	4
420	1.427	1.425	3

[a] $a = 6.375(7)$; $c = 7.80(1)$ Å.

Significantly, we could oxidize **I** back to the parent **II** by reaction with bromine in acetonitrile. The oxidation occurs at room temperature in about 3 days. The XRD pattern of the oxidation product (Figure 1b) matches exactly with the pattern of the parent **II**. The reoxidation of **I** back to **II** could be written as follows:

$$MoOPO_4 \cdot 2H_2O + {}^1/_2Br_2 \xrightarrow{CH_3CN} MoO_2(HPO_4) \cdot H_2O + HBr \quad (3)$$

Considering that both the reduction and reoxidation occur around room temperature without a visual dissolution of the solid, we believe that both reactions are topotactic in nature. A possible structural model for the reduction reaction could be visualized on the basis of the structures of **I** and **II**. The structure of the latter[16] consists of double chains of alternating MoO_6 octahedra and PO_4 tetrahedra, oriented parallel to the *b*-axis (Figure 3). Three corners of each MoO_6 octahedron and PO_4 tetrahedron are shared in the chain. Among the three unshared corners of the octahedron, one is occupied by a water molecule and the remaining two oxygens constitute the molybdenyl (MoO_2) group. A proton is attached to the unshared corner of the PO_4 tetrahedron. The double chains are linked

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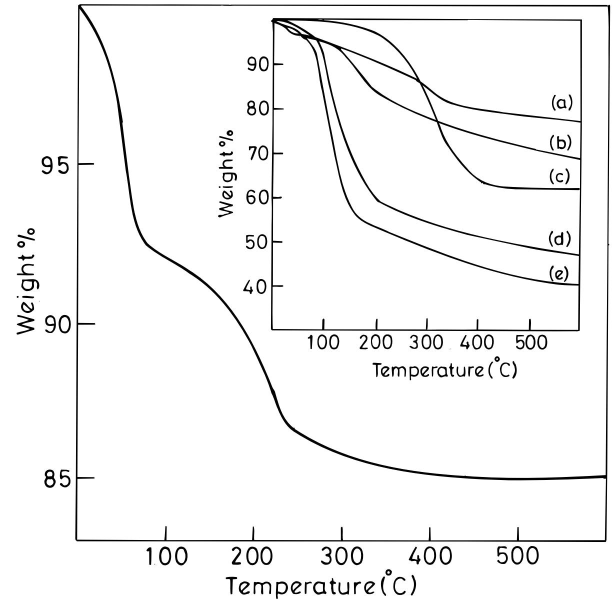


Figure 2. TG curve of $MoOPO_4 \cdot 2H_2O$ (**I**). Inset shows TG curves of intercalation compounds of **I** with (a) pyridine, (b) *n*-butylamine, (c) polyaniline, (d) *n*-hexylamine, and (e) aniline.

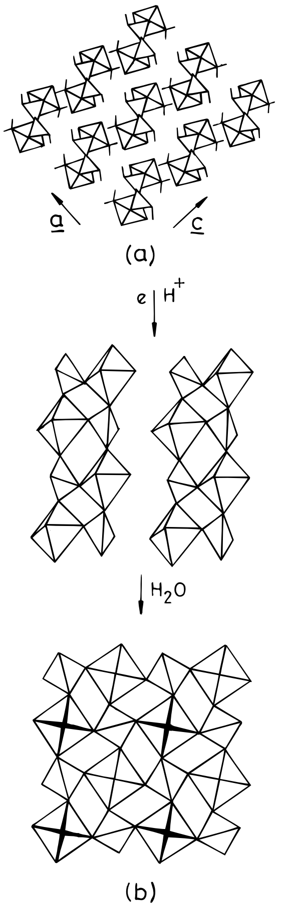


Figure 3. (a) Structure of $MoO_2(HPO_4) \cdot H_2O$ (**II**) viewed down the *b*-axis. (b) Schematic representation of the reductive condensation of the double chains of **II** to form (001) sheets of $MoOPO_4 \cdot 2H_2O$ (**I**) structure.

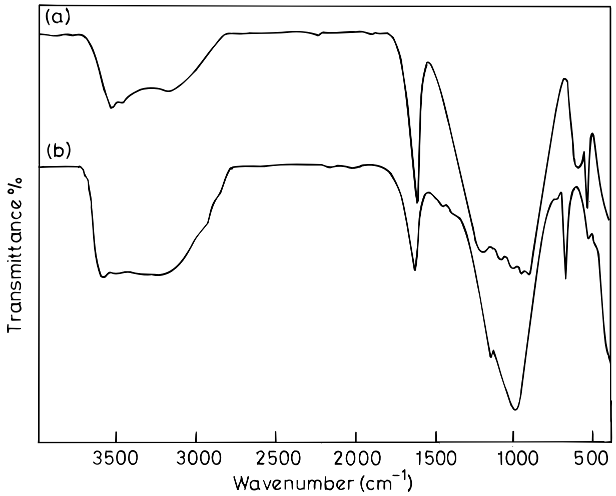
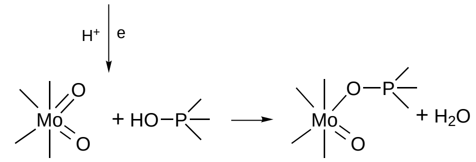


Figure 4. FTIR spectra of (a) $MoO_2(HPO_4) \cdot H_2O$ (**II**) and (b) $MoOPO_4 \cdot 2H_2O$ (**I**).

Scheme 1



together by hydrogen bonds formed between the protons attached to the PO_4 groups and the water molecules coordinated to the molybdenums. Formation of **I** from **II** could be visualized as occurring *via* a reductive condensation of one of the unshared oxygens of the MoO_6 octahedron with the P–OH group of the neighboring chain through the addition of a proton and an electron resulting in elimination of a water molecule.

IR spectra of the parent and product phosphates (Figure 4) lend support to this condensation mechanism. A band at 1210 cm^{-1} in the spectrum of **II**, which is diagnostic[17] of $(HPO_4)^{2-}$, disappears in the product. In addition, the bands at 960 and 910 cm^{-1} in **II** which are due to the molybdenyl group are replaced by a strong band at 998 cm^{-1} in **I**. This band, which is due to ν(Mo=O), occurs at 990 cm^{-1} in the anhydrous $MoOPO_4$.[18]

The reduction of **II** to **I** is most likely topotactic, in view of the close structural relationship between the two phosphates (Figure 3). The structure of **II** in the $(10\bar{1})$ plane is topologically similar to that of **I** projected on the (001) plane except for the interconnection between the chains. The reductive condensation (Scheme 1) provides the interconnection between the double chains, transforming the $(10\bar{1})$ planes of the parent structure into (001) planes of the product structure. Accordingly, the topotactic relationship between the two structures could be written as:

$$b(MoO_2(HPO_4) \cdot H_2O) \parallel b(MoOPO_4 \cdot 2H_2O)$$

$$(10\bar{1})\ (MoO_2(HPO_4) \cdot H_2O) \parallel (001)(MoOPO_4 \cdot 2H_2O)$$

$$[101]\ (MoO_2(HPO_4) \cdot H_2O) \parallel [100]\ (MoOPO_4 \cdot 2H_2O)$$

Anhydrous $MoOPO_4$ is obtained by the topochemical dehydration of **I** at 600 °C for 4 h in a nitrogen atmosphere. The powder XRD pattern of the dehydrated product (Figure 1c) is similar to that of $MoOPO_4$ reported in the literature (JCPDS No. 18-845). The tetragonal lattice parameters ($a = 6.210(2)$ and $c = 4.321(2)$ Å) obtained from this pattern (Table 2) also

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Table 2. Composition, Color, and Lattice Parameters of $MoOPO_4 \cdot 2H_2O$ (**I**) and Its Derivatives

compound	color	lattice parameters (Å) *a*	*c*
$MoOPO_4 \cdot 2H_2O$	blue	6.375(7)	7.80(1)
$MoOPO_4 \cdot H_2O$	blue	6.30	6.80
$MoOPO_4$	yellowish green	6.210(2)	4.321(2)
$MoOPO_4 \cdot 0.4py \cdot H_2O$	green	6.37	9.58
$MoOPO_4 \cdot 1.7C_6H_5NH_2 \cdot H_2O$	brown	6.37	14.78
$MoOPO_4(PANI)_{1.1}$	black	6.33	12.89

compare favorably with the values ($a = 6.1768(3)$ and $c = 4.2932(3)$ Å) reported for anhydrous $MoOPO_4$ in the literature.[4]

The transformations, $Mo^{VI}O_2(HPO_4) \cdot H_2O \rightarrow Mo^{V}OPO_4 \cdot 2H_2O \rightarrow MoOPO_4$, are reminiscent of the transformations in the vanadium phosphate series, $V^{V}OPO_4 \cdot 2H_2O \rightarrow V^{IV}OHPO_4 \cdot 0.5H_2O \rightarrow (VO)_2P_2O_7$.[10,19] The latter is a well-known catalyst for the selective oxidation of *n*-butane to maleic anhydride.[20] Accordingly, it is tempting to speculate that $MoOPO_4 \cdot 2H_2O/MoOPO_4$ would be potential catalyst materials for the partial oxidation of hydrocarbons, if not specifically for the oxidation of *n*-butane to maleic anhydride.

Unlike α-$VOPO_4$, anhydrous $MoOPO_4$ does not undergo hydration directly to form a layered hydrate. $MoOPO_4$ also does not intercalate organic species or alkali metal cations. On the other hand, $VOPO_4 \cdot 2H_2O$ and $NbOPO_4 \cdot 3H_2O$ are known to intercalate a variety of organic molecules mainly because of their layered structure.[9,10] The intercalation occurs either through coordination (e.g., pyridine) or an acid−base interaction (e.g., *n*-alkylamines). In addition, $VOPO_4 \cdot 2H_2O$ also intercalates inorganic species such as alkali metals through a redox reaction.[21] Since **I** is isostructural with $VOPO_4 \cdot 2H_2O$, containing Mo(V), we expected that **I** would exhibit a rich intercalation chemistry. We found that *n*-alkylamines (C_3−C_{12}) react readily with **I** forming intercalation compounds. In Figure 5 we give powder XRD patterns and in Figure 2 we show the TG patterns of typical amine intercalates. The amine contents determined from weight losses in TG curves and from C, H, and N analyses in selected cases (Table 3) are around 1.0−1.6 mol of amine per mole of the host (except for *n*-dodecylamine). A plot of the interlayer distance (*c*-parameter) versus the number of carbon atoms in the *n*-alkylamines (Figure 6) shows a linear relationship which is described by the equation c (Å) $= 2.00n + 6.728$. Assuming that the alkyl chains are in the all-*trans* conformation, a slope of 2.00 Å indicates a bilayer arrangement of the alkyl chains. The amine bilayers are tilted at an angle, $\sin^{-1}(2.00/(2 \times 1.27)) \simeq 52°$, relative to the *ab* plane of the host. Similar arrangements of *n*-alkylamines are found in other related hosts, $NbOPO_4 \cdot 3H_2O$, $VOPO_4 \cdot 2H_2O$, and $V_{0.14}Nb_{0.86}OPO_4 \cdot 2.7H_2O$, where the *n*-alkyl chains are oriented at 55−60° to the inorganic layers.[9,22] Taking into account the average area around each active site (20.45 Å^2) in the host, the cross-sectional area of an alkyl chain (∼19.3 Å^2) together with the average tilting angle (52°), we calculated the number of *n*-alkylamine molecules per formula unit of the host to be 1.67. This value compares favorably with the maximum amine content (1.6) found for *n*-hexyl and *n*-heptylamine intercalates (Table 3).

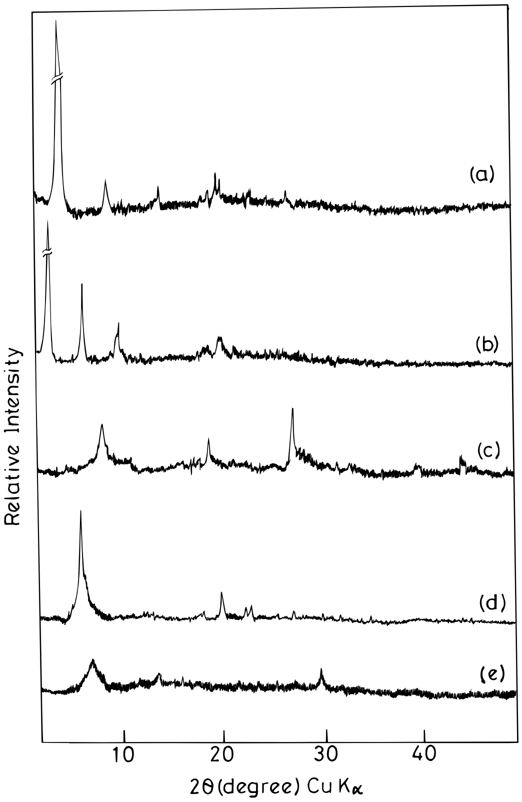

Figure 5. X-ray powder diffraction patterns of typical intercalation compounds of **I** with (a) *n*-hexylamine, (b) *n*-nonylamine, (c) pyridine, (d) aniline, and (e) polyaniline.

Table 3. Composition and Lattice Expansion of *n*-Alkylamine Intercalation Compounds of $MoOPO_4 \cdot 2H_2O$ (**I**)

amine	amine content	*c* (Å)[a]	Δ*c* (Å)[b]
n-propylamine	1.0	12.74	8.54
n-butylamine	1.0	15.35	11.06
n-pentylamine	1.0 (1.05)[c]	16.16	11.87
n-hexylamine	1.5 (1.55)[c]	18.45	14.16
n-heptylamine	1.5 (1.57)[c]	20.48	16.19
n-octylamine	1.3	22.94	18.65
n-nonylamine	1.3	24.35	20.06
n-decylamine	1.5	27.21	22.92
n-dodecylamine	0.6	30.66	26.37

[a] The *a* parameter of all the intercalates is ∼6.37 Å. [b] Lattice expansion is given with respect to the anhydrous $MoOPO_4$. [c] From C, H, and N analyses.

We could intercalate pyridine (pK_a) into $MoOPO_4 \cdot 2H_2O$ (**I**) by repeated reaction of the host solid with a 10% solution of pyridine in *n*-heptane for 4−5 days; the powder XRD of the product obtained at this stage showed near absence of reflections due to the host. TG analysis (Figure 2) showed the composition of the intercalate to be $MoOPO_4 \cdot 0.4py \cdot H_2O$ (py = pyridine). The powder XRD pattern of the pyridine intercalate (Figure 5c) could be indexed on a tetragonal unit cell with the lattice parameters $a = 6.37$ and $c = 9.58$ Å.

The increase in *c*-parameter (5.3 Å) as compared to $MoOPO_4$ is similar to the values observed for $V_{0.14}Nb_{0.86}OPO_4 \cdot 0.5py \cdot H_2O$ (5.8 Å).[23] Accordingly, pyridine is most likely oriented horizontally in the interlayer space of the host. Pyridine could be bound to the host through a Bronsted acid−base interaction forming the pyridinium ion or as a Lewis base coordinating directly to the metal atom. IR spectroscopy is useful to

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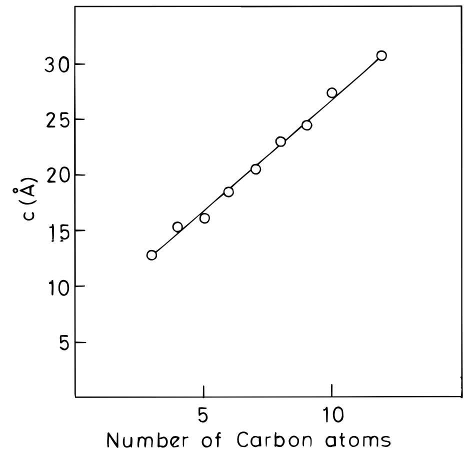

Figure 6. Plot of *c*-parameter of *n*-alkylamine intercalation compounds of $MoOPO_4 \cdot 2H_2O$ (**I**) versus the number of carbon atoms in the *n*-alkyl chain.

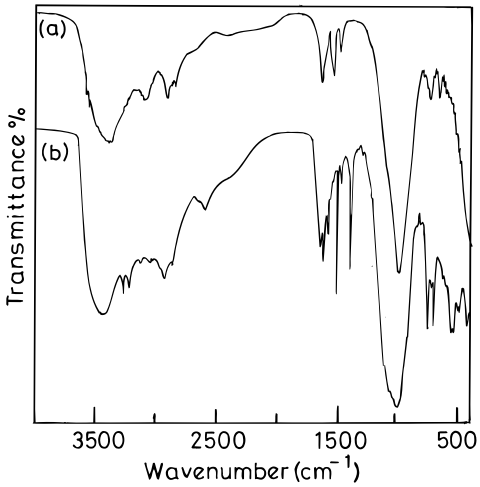

Figure 7. FTIR spectra of intercalation compounds of $MoOPO_4 \cdot 2H_2O$ (**I**) with (a) pyridine and (b) aniline.

distinguish between the two modes of pyridine intercalation.[24] Lewis-bound (coordinated) pyridine shows characteristic absorption bands at ~1450 and 1620 cm^{-1}, and Bronsted-bound pyridine shows characteristic bands at ~1490 and 1540 cm^{-1}.[24] The FTIR spectrum of $MoOPO_4 \cdot 0.4py \cdot H_2O$ shows absorption bands at 1485 and 1530 cm^{-1} (Figure 7a) indicating the presence of pyridinium ions. A band at 1630 cm^{-1} shows the presence of coordinated water. Accordingly, it appears that Bronsted-bound pyridine replaces the hydrogen-bonded water in **I** upon intercalation of pyridine.

It is interesting to compare the intercalation behavior of pyridine in $VOPO_4 \cdot 2H_2O$ and $MoOPO_4 \cdot 2H_2O$ (**I**). Firstly, the compositions of the pyridine intercalates are different: $VOPO_4 \cdot py$ and $MoOPO_4 \cdot 0.4py \cdot H_2O$. Secondly, it has been established[10] that the pyridine is coordinated to vanadium in $VOPO_4 \cdot py$ (Lewis-bound pyridine) whereas in the molybdenum intercalate,pyridine appears to be Bronsted-bound existing as pyridinium ion. Moreover, the coordinated H_2O in **I** is retained in the pyridine intercalate.

Aniline readily intercalates into **I**. The composition of the intercalate, determined from the TG curve (Figure 2), is $MoOPO_4 \cdot 1.7C_6H_5NH_2 \cdot H_2O$. Presumably, the intercalate retains the coordinated H_2O of the host, the hydrogen bonded H_2O in the interlayer space being replaced by the intercalated aniline molecules. We should therefore express the lattice expansion of the aniline intercalate relative to the *c*-parameter of $MoOPO_4 \cdot H_2O$. We have obtained a sample of the monohydrate by careful dehydration of $MoOPO_4 \cdot 2H_2O$ (**I**) up to 125 °C and immediately recorded its XRD pattern. The lattice parameters of this monohydrate are $a \simeq 6.30$ and $c \simeq 6.8$ Å. Accordingly, the host lattice expands by ~8.0 Å (relative to $MoOPO_4 \cdot H_2O$) upon aniline intercalation. The composition and lattice parameters of the aniline intercalate of **I** are comparable to those of $VOPO_4 \cdot 2H_2O$ obtained by using neat aniline, which shows a basal spacing of 14.8 Å, where a bilayer arrangement of the aniline molecules in the interlayer space is proposed.

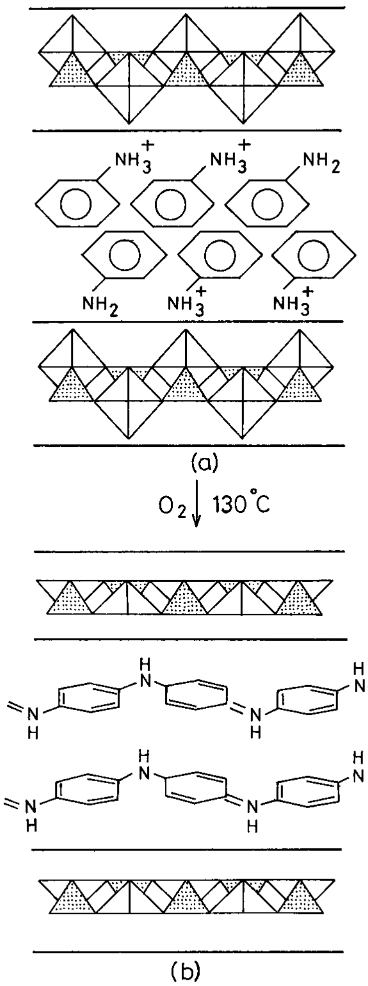

Figure 8. Possible arrangement of (a) aniline and (b) polyaniline between $MoOPO_4$ sheets. Negative charges localized in the inorganic sheets are not shown.

The FTIR spectrum of the aniline intercalate shows absorption bands due to both the anilinium ion[25] (2915 and 1490 cm^{-1}) as well as neutral aniline[26] (3379, 741, and 689 cm^{-1}). Taking into account the composition lattice parameters and the IR spectral data, we propose a bilayer model for the aniline intercalate as shown in Figure 8a. It is most likely that 1 mol of aniline is protonated in the interlayer region as

$$\equiv Mo-OH_2 + H_2NC_6H_5 \rightarrow \equiv Mo-OH^- \, ^+H_3NC_6H_5 \qquad (4)$$

and the remaining aniline is inserted between the protonated species.

We investigated the polymerization of the intercalated aniline in $MoOPO_4 \cdot 1.7C_6H_5NH_2 \cdot H_2O$ by heating the solid in air at 130

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°C. The color of the solid gradually changed from brown to black. The composition of the black product, as determined by TG analysis (Figure 2), is approximately $MoOPO_4(PANI)_{1.1}$ (PANI = polyaniline). The powder XRD pattern (Figure 5e) shows that the material is poorly crystalline. It is likely that part of the aniline migrates out and polymerizes on the surface, destroying the crystallinity of the solid to a great extent. From the prominent 001 and 002 reflections, we could however estimate the lattice expansion of the polymerized product to be ~8.5 Å relative to anhydrous $MoOPO_4$. This value is comparable to the lattice expansion (8.8 Å) found in $VOPO_4 \cdot PANI$.[27] We show in Figure 8 a possible model for the intercalated monomer and polymer aniline within the galleries of the host.

Since $VOPO_4 \cdot 2H_2O$ is known to exhibit a rich reductive intercalation chemistry[21] by reaction with alkali metal iodides and borohydrides, we investigated the possibility of a similar reductive intercalation with **I**. While the alkali metal iodides did not react at all with **I**, reaction with $NaBH_4$ gave a brown product where the oxidation state of Mo was close to V. We did not characterize the brown product further.

In summary, we have synthesized layered $MoOPO_4 \cdot 2H_2O$ (**I**), which is similar to $VOPO_4 \cdot 2H_2O$, by reduction of $MoO_2(HPO_4) \cdot H_2O$ (**II**) using ethylene glycol in CH_3CN. We have shown that **I** is oxidized back to the parent compound with bromine in CH_3CN. We have suggested that both the reduction and reoxidation of the phosphates are likely to involve a topotactic mechanism. We have also shown that **I** is a new host for intercalation of a wide variety of guest species including *n*-alkylamines, pyridine, and aniline.

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