Intercalation of Aliphatic Amines into the Layered Structure of Vanadyl(IV) Hydrogen Phosphate Hemihydrate ($VOHPO_4 \cdot 0.5H_2O$)

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The vanadyl(IV) hydrogen phosphate hemihydrate, $VOHPO_4 \cdot 0.5H_2O$, is a pyrolytic precursor of the vanadyl(IV) pyrophosphate phase, $(VO)_2P_2O_7$, generally believed to be the active phase in the selective oxidation of *n*-butane into maleic anhydride.[1] Pyrolytic transformation into the pyrophosphate phase occurs with conservation of a morphology of the material.[1] $VOHPO_4 \cdot 0.5H_2O$ is a layered hydrogen phosphate, where –POH groups form interlayer hydrogen bonds with the water molecules shared by two face-linked vanadyl octahedra.[1] The structure of the hemihydrate is similar to that of α-zirconium hydrogen phosphate (α-ZrP), where hydrogen bonds are within the same layer and –POH groups are also pointed into the interlayer space.[2]

In contrast to α-ZrP, where extensive data exist,[3] intercalation chemistry of the layered vanadyl(IV) hydrogen phosphate hemihydrate at present is a terra incognita.

This paper reports the results of the first systematic study of $VOHPO_4 \cdot 0.5H_2O$ intercalation with aliphatic amines as a new route to novel vanadyl(IV) phosphate phases. *N*-Alkylamines have been commonly known as excellent intercalation agents for testing the intracrystalline reactivity of layered oxides.[4] Intercalated alkylamines may also facilitate introduction of thermostable guest molecules, or "pillars", by ion exchange producing microporous materials which can modify catalytic and sorptive properties.[5]

Preparation of Vanadyl(IV) Hydrogen Phosphate Hemihydrate. The vanadyl(IV) hydrogen phosphate hemihydrate (VHP) was prepared in an alcohol medium according to the standard patent procedure.[6] V_2O_5 (16 g, Aldrich) was added to stirred isobutyl alcohol (140 mL, Mallinckrodt). After the mixture was heated at reflux for 16 h, 20 g of 100% H_3PO_4 (Aldrich) dissolved in isobutyl alcohol were added, and the mixture was heated at reflux for another 8 h. The resultant slurry was filtered; the light blue solid was washed with acetone and air-dried at 150 °C for 2 h. The solid thus obtained was confirmed to be $VOHPO_4 \cdot 0.5H_2O$ by powder XRD and FTIR spectroscopy.[1]

Intercalation Procedure. The pure intercalated $VOHPO_4 \cdot 0.5H_2O$ phases were prepared by heating at reflux 1 g of VHP in either a large excess of liquid neat C_3–C_6 primary *n*-alkylamine (Aldrich) or 2 M solutions of the amines in *N,N*-dimethylacetamide. After 7–10 days of equilibration, the intercalates were collected on the filter, washed with hot ethanol, and dried in He at 373 K for 2 h.

Longer chain *n*-alkylamines did not intercalate VHP to a significant level by this procedure. However, *n*-amyl- or *n*-hexylamine intercalated in VHP could be exchanged for C_7–C_{12} primary *n*-alkylamines (Aldrich) when heated at reflux in a large excess of the neat amine for 3 days.

The ammonium salt of VHP was obtained by passing dry gaseous ammonia over powdered VHP for 24 h at room temperature.

Characterization. X-ray diffraction patterns were recorded with Scintag/USA DMS 2000 diffractometer using a Cu Kα radiation. SEM analysis was carried out on JEOL JSM-840 electron microscope at 5 kV. Infrared spectra were recorded on a Nicolet 730 FTIR spectrometer using the KBr disk technique. Thermogravimetric analysis of the intercalated phases was performed in air on a Perkin-Elmer TGS-2 thermal analyzer. Elemental C, H, N microanalysis of the solids was performed by Robertson Microlit Laboratories, Madison, NJ.

Intercalation of *n*-propylamine and *n*-butylamine was first attempted by titrating 1 g of VHP suspended in 20 cm^3 of deionized water at 60 °C with aqueous 0.1 M standard solution of amines at the equilibrium point in nitrogen atmosphere. As more amine solution was added, the solid gradually turned into an intractable gel,[7] and the blue color of the supernatant liquid indicated that vanadyl(IV) was partially released into the solution. Finally, all VHP dissolved after 5.8 mmol/g of the amine solution was added, corresponding to 1 mol of VHP dissolved per mole of amine. This behavior may be understood in terms of a "moving boundary model" of intercalation.[4] According to that model, amine molecules first diffuse into the interlayer space and expand the layers. This allows water molecules to penetrate the space between the layers and substantially disorder the hydrogen bond network and form VHP gels. The solvolysis was also observed in neat ethanolamine; complete solvolysis occurred at reflux temperature within a few minutes. Primary *n*-alkylamines did not noticeably intercalate VHP from 0.2 M ethanolic solutions, even at reflux. Only when much stronger ethanolic solutions (at least 2 M) of C_3–C_6 primary *n*-alkylamines were employed was the partial intercalation observed.

Primary *n*-alkylamines, either neat or concentrated solutions in *N,N*-dimethylacetamide (>2 M), were found to readily intercalate VHP producing single phase materials with d_{001} spacings linearly increasing with the size of the alkyl group (Table 1 and Figure 1). The reflections corresponding to d_{002}, and in some cases d_{003} were observed. This linear relationship of d_{001} spacings with the number

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[1] Johnson, J. W.; Johnston, D. C.; Jacobson, A. J.; Brody, J. F. *J. Am. Chem. Soc.* **1984**, *106*, 8123.

[2] Clearfield, A.; Blessing, R. H.; Stynes, J. A. *J. Inorg. Nucl. Chem.* **1968**, *30*, 2249.

[3] For example, see: *Pillared Layered Structures: Current Trends and Applications*; Mitchell, I. V., Ed.; Elsevier Applied Science: London, 1990.

[4] Lagaly, G. *Solid State Ionics* **1986**, *22*, 43.

[5] For example, see: (a) Clearfield, A.; Roberts, B. D. *Inorg. Chem.* **1988**, *27*, 3237. (b) Lerf, A.; Lalik, E.; Kolodziejski, W.; Klinowski, J. *J. Phys. Chem.* **1992**, *96*, 7389.

[6] Milberger, E. C.; Bremer, N. J.; Dria, D. E. U.S. Patent 4,333,853, 1982.

[7] Gel formation was also observed in some cases of solution-phase intercalation of other transition metal hydrogen phosphates; e.g., see: (a) MacLachlan, D. J.; Morgan, K. R. *J. Phys. Chem.* **1990**, *94*, 7656. (b) Menéndez, F.; Espina, A.; Trobajo, C.; Rodríguez, J. *Mater. Res. Bull.* **1990**, *25*, 1531.

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Table 1. d_{001} Spacings of Some $VOHPO_4{\cdot}0.5H_2O{\cdot}xRNH_2$ Phases

base	d_{001}, Å	x (C, H, N analysis)[a]	x (TGA in air)
ammonia	7.38		2.17
n-propylamine	14.70	1.63	1.60
n-butylamine	16.11	1.64	1.53
n-amylamine	18.96	1.54	1.56
n-hexylamine	20.38	1.57	1.65
n-octylamine	25.09	1.81	1.73

[a] Ammonia: 2.47% C, 2.53% H, 6.56% N. Propylamine: 21.88% C, 6.08% H, 7.85% N. Butylamine: 26.54% C, 6.85% H, 7.60% N. Amylamine: 30.19% C, 7.05% H, 6.58% N. Hexylamine: 33.76% C, 7.61% H, 6.66% N. Octylamine: 42.60% C, 8.77% H, 6.21% N.

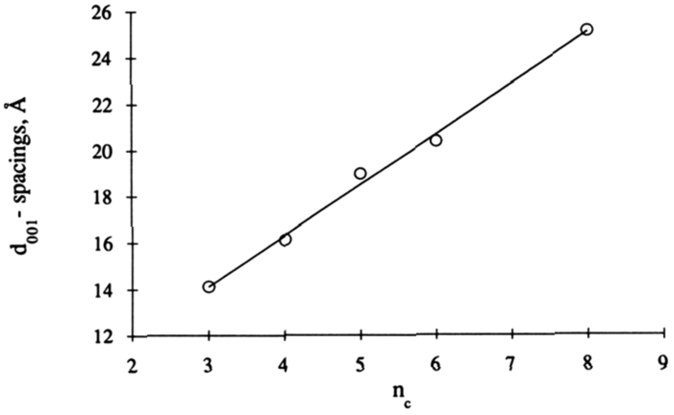

Figure 1. Interlayer d_{001} spacings of $VOHPO_4{\cdot}0.5H_2O$ intercalated with some primary *n*-alkylamines vs the number of amine carbon atoms n_c.

of carbon atoms n_c in amine molecule (Figure 1) could be described by the following expression:

$$d_{001} = 7.55 \times 2.19 n_c \text{ (Å)} \qquad (1)$$

As seen from ref 1, the d_{001} spacings increase by 2.19 Å per carbon atom in the amine molecule. In the case of straight (*trans–trans*) alkyl chain, an increase of alkyl chain length is estimated to be 1.27 Å per carbon atom; the 2.19 Å increase indicates amine bilayers tilted at arcsin{2.19/(2·1.27)} = 59.6° relative to the *ab* plane of vanadium atoms. This agrees well with the reported values of tilt angles in other layered hydrogen phosphates: 58.7° (α-TiP), 54.2° (α-ZrP), and 66.0° (α-SnP).[7b] The value of the tilt angle indicates that the N–C bond is nearly perpendicular to the *ab* plane (53.8° for perpendicular arrangement).

The change in morphology of the starting material was followed with scanning electron microscopy. The change from the typical rosette morphology of the precursor phase ($VOHPO_4{\cdot}0.5H_2O$) to a sheetlike morphology of the amylamine-intercalated phase shown in Figure 2 is characteristic of the layered material.

The infrared spectrum of the hexylamine-intercalated phase (Figure 3) taken as representative, shows bands in 1625–1380-cm^{-1} region due to the asymmetric and symmetric RNH_3^+ bending modes. The amine appears to be only partially ionized as suggested by the presence of the characteristic bicuspid peak of the free amine at ca. 3250 cm^{-1}. The same feature in neat *n*-hexylamine is found at ca. 3309 cm^{-1}, which indicates that the intercalated amine participates in hydrogen bonding broadening the spectrum in the 3800–2200-cm^{-1} range. The IR spectrum of ammonium salt is characteristic of fully protonated NH_4^+ species (NH bending modes ca. 1636 and 1401 cm^{-1}); no free NH_3 stretches were observed due to strong and broad features of hydrogen bonding ca. 3600–3000 cm^{-1} resulting from the ammonia and structural water. The IR spectrum of vanadyl(IV) hydrogen phosphate hemihydrate is shown for comparison in Figure 3 as well.

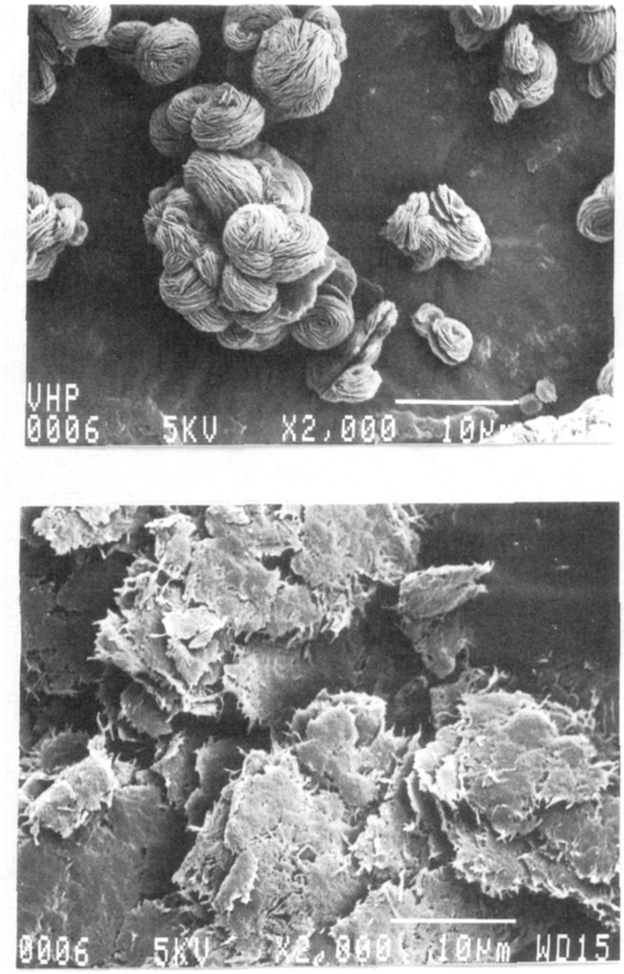

Figure 2. SEM micrographs of (A) $VOHPO_4{\cdot}0.5H_2O$ and (B) its intercalation compound with *n*-amylamine (×2000).

The results of elemental and thermogravimetric analyses (Figure 4 and Table 1) correspond to the general formula $VOHPO_4{\cdot}0.5H_2O{\cdot}xRNH_2$ (Table 1), where more than one amine molecule is associated with each surface –POH group. According to the hydrogen bonding scheme proposed by Leonowicz et al.[8] for VHP (Figure 5), the interlayer hydrogen bonding runs in the *b* direction connecting the water molecule protons H1 with –POH oxygen and the hydroxyl proton H2 with one of the vanadyl oxygens, i.e., both –POH groups and structural water are involved in hydrogen bonding. A possible explanation for $x \cong 1.5$ (Table 1) is that if the structural water molecules form hydrogen bonds with amino groups, then a 2:1 ratio of the number of –POH to H_2O in $VOHPO_4{\cdot}0.5H_2O$ would lead to $x = 1.5$ products, as shown in Figure 6. The IR spectra also suggest hydrogen bonding between the intercalated amine and the structural water.

Our model agrees with the "space-filling" model employed by Menéndez et al.[7b] According to that model, the most probable arrangements of amines are those in which the interlayer space is most economically used. We consider directly only the "space-filling" effect of alkyl chains in an intercalated amine, since the contribution of

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[8] Leonowicz, M. E.; Johnson, J. W.; Brody, J. F.; Shannon, H. F., Jr.; Newsam, J. M. *J. Solid State Chem.* **1985**, *56*, 370.

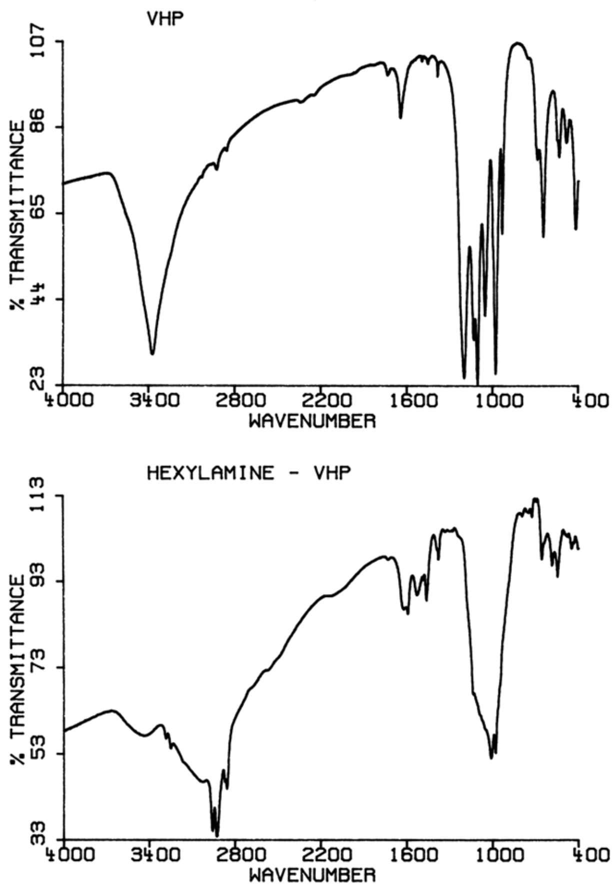

Figure 3. FTIR spectra of (a, top) vanadyl(IV) hydrogen phosphate hemihydrate and (b, bottom) its *n*-hexylamine-intercalated phase.

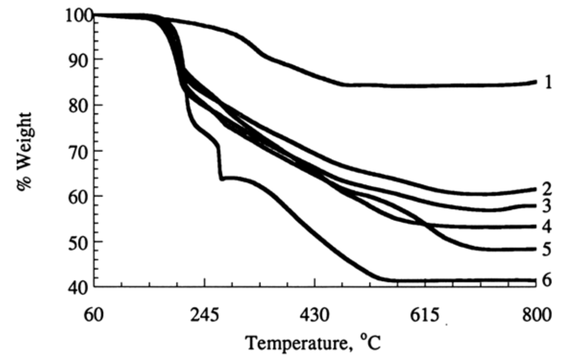

Figure 4. TGA curves of $VOHPO_4 \cdot 0.5H_2O$ in air intercalated with (1) ammonia, (2) *n*-propylamine, (3) *n*-butylamine, (4) *n*-amylamine, (5) *n*-hexylamine, and (6) *n*-octylamine. Scan rate 10 °C/min.

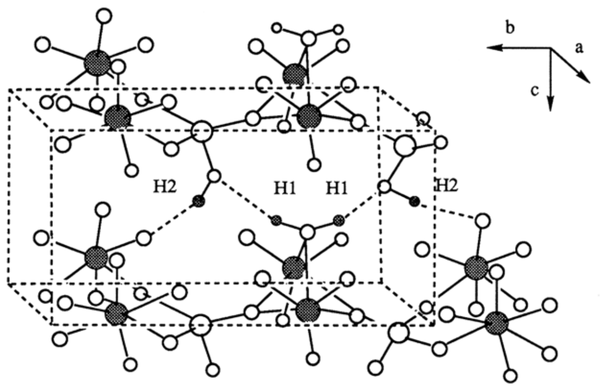

Figure 5. Hydrogen bond network in $VOHPO_4 \cdot 0.5H_2O$. H1 and H2 belong to the water molecule and –POH hydroxyl, respectively.

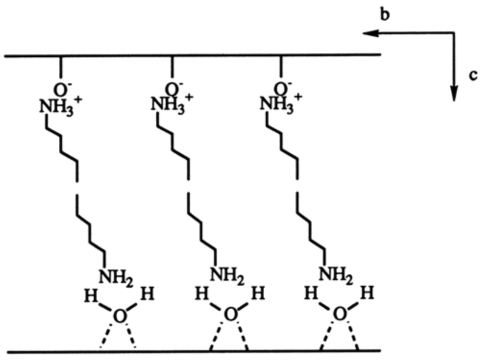

Figure 6. Proposed arrangement of *n*-amylamine bilayer in $VOHPO_4 \cdot 0.5H_2O$ along the (200) direction.

Table 2. Packing Parameters V_p of *n*-Alkylamines Intercalated into Layered Structures of Some Hydrogen Phosphates

amine	VHP	α-ZrP	α-TiP	α-SnP
propylamine	0.99	0.92	0.96	
butylamine	1.02	1.02	1.01	0.99
amylamine	0.90	0.96	0.99	0.97
hexylamine	0.97	0.95	1.01	1.00
octylamine	1.09	0.92	0.99	0.98

the amino groups should be the same for all amines. The packing density of the alkyl chains in the interlayer space V_p is the ratio of the alkyl chain volume V_c to the interlayer space volume V_t per unit area of layer surface, e.g., 1 cm²:

$$V_p = V_c/V_t \qquad (2)$$

$$V_c = xNV_a = xNn_c\Delta l\sigma \ (\mathrm{cm}^3) \qquad (3)$$

where x is the average number of amine molecules per acid site on the layer (Table 1), $N = 5.61 \times 10^{14}$, the surface density of –POH groups/cm² of VHP layer, V_a is the volume of individual amine molecule, $n_c\Delta l$, the length of the hydrocarbon chain and $\sigma = 18.6 \times 10^{-16}$ cm², the cross-section area of a *trans–trans* alkyl chain (found from the *a* and *b* unit cell parameters of crystalline $C_{29}H_{60}$[9]). All interlayer space apart from the region occupied by the phosphate layer with protonated amino groups is available to alkyl chains. The available volume V_l per 1 cm² of layer surface is

$$V_t = d_{001} - d° \ (\mathrm{cm}^3) \qquad (4)$$

where d°, the combined height of the phosphate layer and $-NH_3^+$ groups, is assumed to be independent of n_c and equal to the extrapolated value of d_{001} for $n_c = 0$.

Calculated V_p values for VHP along with the previously reported results for other layered metal hydrogen phosphates are shown in Table 2. These values indicate that the packing density in the alkylamine-intercalated VHP is essentially the same as in the crystalline *n*-paraffin.

An unusually high value for packing of ammonia ($x = 2$) can be the result of a small area of the NH_4^+ (ca. 7.9 Å²) and hydrogen bonding between ammonium cations coordinated to the POH groups and free ammonia (e.g., NH_4^+–NH_3 hydrogen bonding). Alternatively, it is possible that due to their smaller size, two ammonia molecules

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(9) Kitaigorodsky, A. I. *Molecular Crystals and Molecules*; Academic Press: New York, 1973.

may form hydrogen bonds with the structural water protons H1 (Figure 5), leading to the observed 1:2 stoichiometry.

We believe that the parallel arrangement of the alkyl chains, $x = 1.5$ shown in Figure 6 is representative of the close-packing situation in alkylamine-intercalated $VOHPO_4 \cdot 0.5H_2O$. The slight excess of amine stoichiometry may result from adsorption along the edges of the phosphate sheets.

In conclusion, we have shown for the first time that the *n*-alkylamine-intercalated vanadyl(IV) hydrogen phosphate hemihydrate phases can be routinely obtained, that exhibit consistent increase of interlayer spacing with the length of amine molecules. The intercalated amines close-pack on VHP layer ($V_p = 1$), consistent with a model of the hydrogen bonding in alkylamine-intercalated VHP involving both –POH and structural water.

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