Intercalation Reactions of Layered Vanadyl Organophosphonates with Alkylamines

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Layered vanadyl organophosphonates $VORPO_3 \cdot xH_2O$ were brought into contact with primary alkylamines $C_nH_{2n+1}NH_2$ ($n = 3-6$). Intercalation compounds have been characterized by their basal spacings, thermogravimetric analysis (TGA), XANES, and IR spectra. Regardless of the starting vanadyl phosphonate, a plot of the interlayer distances of the intercalates *vs* the number of carbon atoms (n_c) in the alkyl chain of the amine indicates that amine molecules were packed in the interlamellar space either as bilayer or as an interdigitated monolayer, depending on n_c. Hydrolysis of the phosphonate groups, oxidation of vanadium atoms, and the nature of the final products are described.

Introduction

The metal organophosphonates which form a group of layered compounds consisting of alternating inorganic and organic layers have received increasing interest since the late 1970s. Several tetravalent,[1−5] trivalent,[6−9] and divalent[7,8,10−13] systems have already been studied in detail because of their attractive structural chemistry, intercalation behavior, sorption, and cata-lytic properties. For example, vanadyl organophosphonates have been shown to intercalate alcohols by coordination of the intercalating molecule to the vanadium atom in the inorganic phosphonate layer.[14] Syntheses in alcoholic[14,15] or in aqueous media under refluxing conditions lead to polycrystalline vanadyl phosphonates, while hydrothermal syntheses have already produced single crystals of several phases.[16]

As *n*-alkylamines have been commonly known as excellent agents for testing the intracrystalline reactivity of layered oxides,[17] we report here the results of the first study of intercalation reactions of aliphatic amines with $VOC_6H_5PO_3 \cdot 2H_2O$, $VOC_2H_5PO_3 \cdot 1.5H_2O$, and $VOCH_3PO_3 \cdot 1.5H_2O$. The objective is to understand the mechanism of and changes occurring on intercalation, *i.e.*, to see whether these are similar to the behavior of alcohol intercalation or are different. It is also interesting to investigate the reactivity of the phosphonates with alkylamines (K_b essentially constant $\approx 10^{-3}$) of higher basic strength than the alcohols.

Experimental Section

All reagents were from commercial sources and were used without further purification.

Synthesis of Vanadyl Organophosphonates. The three title vanadyl organophosphonates can be prepared in alcoholic media, following the Johnson procedure:[14a] finely ground V_2O_5 (1.5 mmol) is added to a solution of an appropriate phosphonic acid RPO_3H_2 (3.5 mmol) in 50 mL of an alcohol plus 1 mL of 1 M HCl. The mixture

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is refluxed and stirred for at least 2 days, and then precipitates are recovered by filtration and washed with acetone. Subsequent thermal removal of the intercalated alcohol leads to vanadyl phenyl-, methyl-, or ethylphosphonate.

In the case of R = C$_6$H$_5$ or CH$_3$ another synthetic method consists of direct preparation of the vanadyl organophosphonates in refluxing aqueous media using VOSO$_4$·5H$_2$O as the vanadium source.

VOC$_6$H$_5$PO$_3$·2H$_2$O, VOCH$_3$PO$_3$·1.5H$_2$O, and VOC$_2$H$_5$PO$_3$·1.5H$_2$O appear to be layered with interlayer spacings of 9.82, 8.30, and 9.71 Å, respectively.

Intercalation Reactions. Intercalations of alkylamines were carried out as follows:

A 0.2 g sample of the phosphonate was kept in contact with an excess of liquid alkylamine (C$_3$–C$_6$) in a closed container at room temperature for 2 months (*method A*) or heated at reflux for 10 days (*method B*). In *method C* a 0.2 g sample of the phosphonate was exposed to alkylamine vapor at room temperature using an apparatus already described.[18] The gas phase reaction continued for 2 months. It is important to note that liquid amine often formed on the vanadyl phosphonates so that filtration and washing were required to remove the absorbed excess of amine.
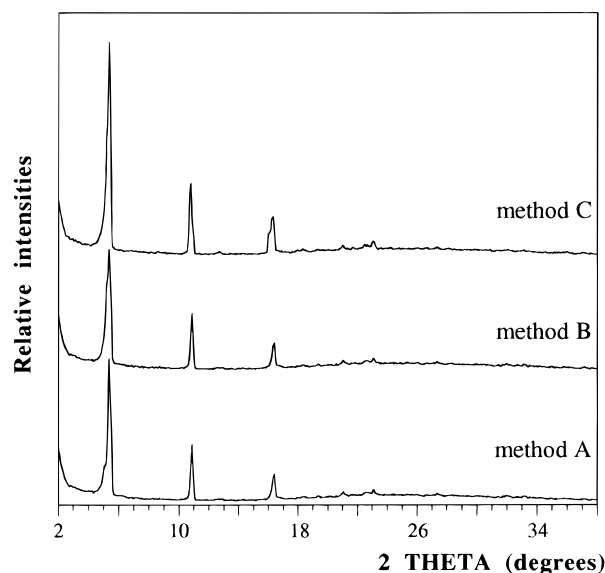
In each of the three methods, the intercalates were recovered by filtration and washed with acetone. The resulting colorless solids were air-dried prior to characterization.

Physical Methods. Powder X-ray diffraction (PXRD) patterns were recorded on a Siemens D501 diffractometer using Cu Kα radiation and fitted with a graphite back-end monochromator. XRD experiments were also carried out by passing the samples through an 80 μm sieve before the sample holder was filled in order to avoid preferred orientation. During data collection, the sample holder was also rotating at the speed of 30 revolutions per minute. Unfortunately preferred orientation effects cannot be reduced by changing the XRD conditions. Fourier transformed infrared (FTIR) spectra were obtained on a Perkin-Elmer 16PC spectrophotometer using the KBr disk method. The differential thermal analysis (DTA) and thermogravimetric analysis (TGA) studies were performed with a Setaram TG-DTA92 analysis unit, at a heating rate of 5 °C/min under air atmosphere. X-ray absorption spectra at the K-edge of vanadium were obtained at the French Laboratoire pour l'Utilisation du Rayonnement Electromagnétique (LURE.) synchrotron radiation facility (line EXAFS IV). Vanadium, phosphorus, carbon, nitrogen, and hydrogen microanalyses were made by the CNRS Analysis Laboratory, Vernaison, France.

Results and Discussion

An interesting feature of the solid–liquid or solid–gas amine intercalation reactions of vanadyl organophosphonates is that they are accompanied by a color change of the compounds. First, the apparent volume of the blue solids increases noticeably when amines are absorbed, and then a deep brown solution appears after 5 h. The presence of this coloration has already been noted, but as vanadium(IV) complexes are known to be labile and have often been found to exhibit different structures in solution than in the solid state, two different explanations are given in the literature: (i) for Iannuzi and Rieger it is the consequence of vanadium(IV) species in basic solution;[19] (ii) for Riley *et al.* the brown color is indicative of vanadium(V) released in the solution.[20] As the reaction proceeds, this coloration gradually disappears until a clear colorless supernatant remains. The isolation of the intercalates is difficult because the amine is liberated by washing and drying, resulting sometimes in the formation of an intractable gel, especially with methods A and B. However pure phases can be isolated, and the synthetic method used seems to have almost no effect, as can be seen in Figure 1.

Although the powder XRD patterns of compounds show well-defined peaks, indicative of a well-ordered structure, they have generally not been indexed due to the lack of information above

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Figure 1. PXRD patterns of hexylamine intercalated compounds obtained by methods A–C starting from VOC$_6$H$_5$PO$_3$·2H$_2$O.
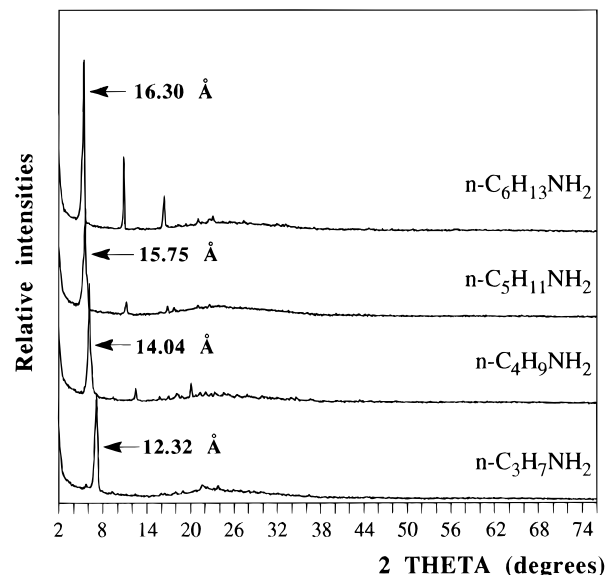
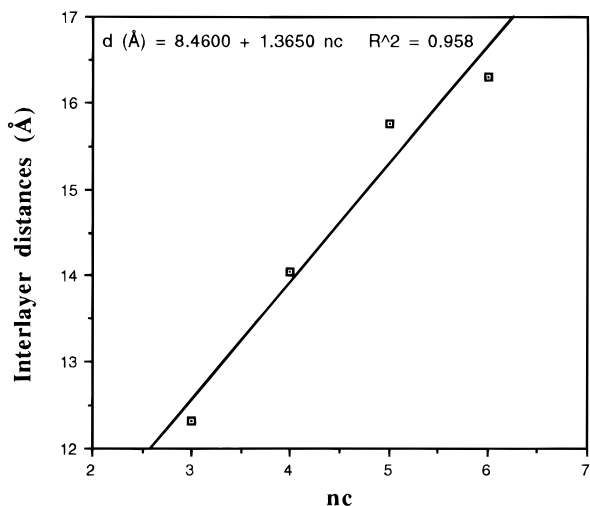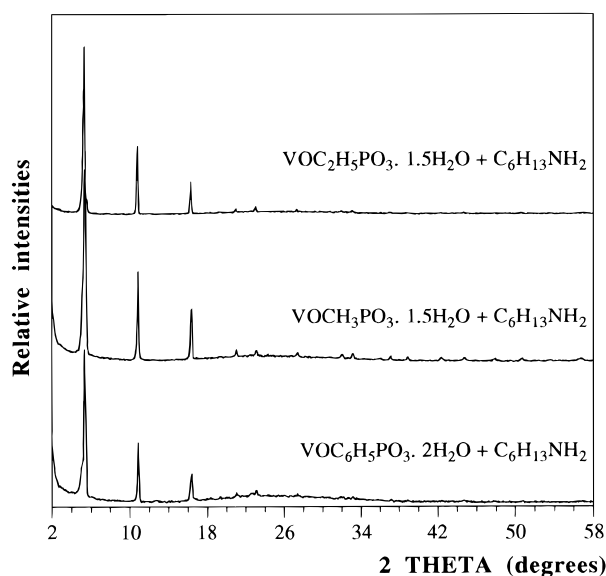**Figure 2.** PXRD patterns of intercalation compounds prepared by contacting VOC$_6$H$_5$PO$_3$·2H$_2$O with different alkylamines.

25° (2θ), suggesting that the layers of the intercalation compounds have become turbostratic. The layered nature of the intercalates clearly appears on the diffractograms and is shown by the first, second, and third order reflections of the interlayer distance which are enhanced due to preferred orientation. Interlayer distances evolve with the alkyl chain length of the amine molecule (Figure 2) indicating that alkylamines have been intercalated. A plot of the interlayer distance of the intercalates *vs* the number of carbon atoms n_c in the alkyl chain of the amines (Figure 3) gives a straight line with a slope of 1.36 Å/CH$_2$. In the case of straight *trans–trans* alkyl chains, the increase with alkyl chain length is estimated to be 1.27 Å per carbon atom;[21] the 1.36 Å increase indicates amine bilayers tilted at arcsin{1.36/(2 × 1.27)} = 32.4°. However, interlayer distances for n_c = 3–5, which show a perfect straight line fitting $R^2 = 1$, may indicate that the interlayer distance for n_c = 6 corresponds to one phase with less contents in amine, suggesting the reaction rate decreases as the C chain length increases.

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Figure 3. Layer spacings of intercalation compounds as a function of alkyl chain length of the amine molecule.

Figure 4. PXRD patterns of hexylamine intercalated compounds of different vanadyl phosphonates.

Table 1. Interlayer Distances of Intercalation Compounds of VOP Systems with Alkylamines or Alkylammonium Ions

| intercalated amine $C_nH_{2n+1}NH_2$	d (Å)			
	$VORPO_3 \cdot xH_2O + C_nH_{2n+1}NH_2$[a]	$VOPO_4 \cdot 2H_2O + C_nH_{2n+1}NH_3I$[25]	$VOHPO_4 \cdot 1/2H_2O + C_nH_{2n+1}NH_2$[26]	$VOPO_4 + C_nH_{2n+1}NH_2$[27]
C_3H_7	14.6	14.6	14.7	14.6
C_4H_9	15.9		16.1	18.3
C_5H_{11}	18.4	17.0	18.9	19.8
C_6H_{13}	20.0	18.8	20.4	22.9

[a] This work (interlayer distances of the 1 month intercalates).

Furthermore, considering $n_c = 3-5$ the linear relationship of the interlayer spacings with the number of carbon atoms in the amine molecule is given by the following expression:

$$d \text{ (Å)} = 7.18 + 1.71n_c$$

Then the estimation for the amine bilayers tilt angle becomes 42.5°, which compares with the usual value (about 50°) found in these kinds of compounds. Anyway, the value of the tilt angle indicates that the N—C bond is not strictly perpendicular to the layers (53.8° for perpendicular arrangement).
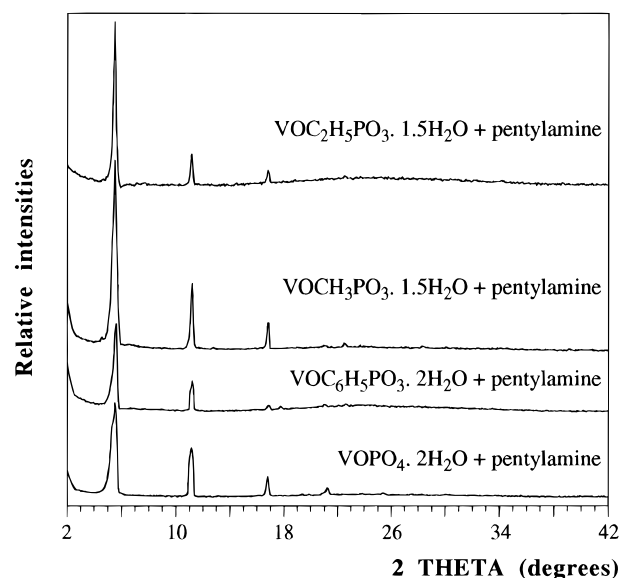
On the other hand, we can also note the change in interlayer spacing when going from an n_c to $n_c + 1$ compound, which
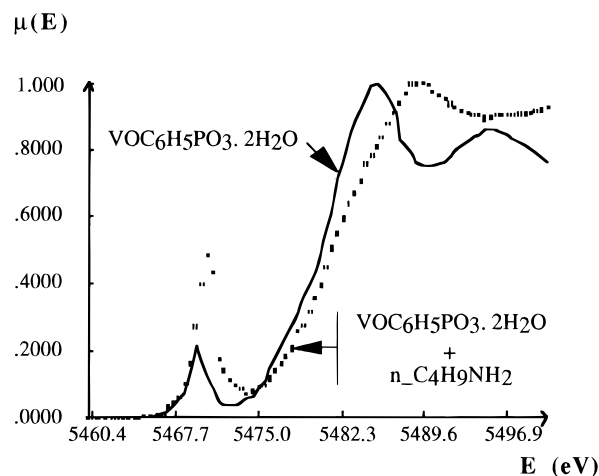
Figure 5. XANES spectrum of an intercalation compound compared with the one obtained for the original $VOC_6H_5PO_3 \cdot 2H_2O$.
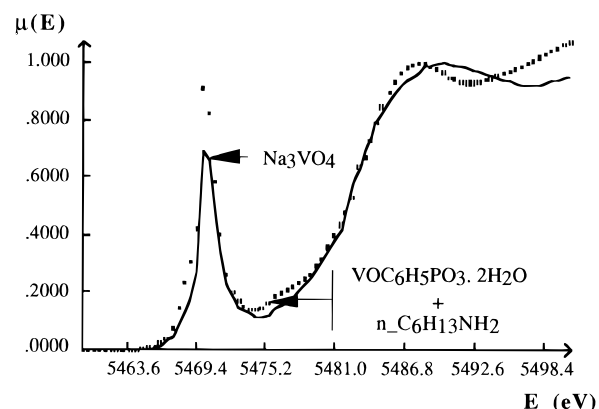


Figure 6. XANES spectra of an intercalated phase and Na_3VO_4 (V^{5+}).

Figure 7. PXRD patterns of pentylamine intercalated compounds prepared either from different phosphonates or from $VOPO_4 \cdot 2H_2O$.

depends on whether n_c is even or odd. The alternating small and large changes in the interlayer spacings suggest that the N—C bond is nearly perpendicular to the layer, so that the terminal C—C bond makes a smaller or larger angle relative to the layer, depending on n_c. Assuming the N—C bond perpendicular to the layer, tetrahedral bond angles and a C—C bond length of 1.54 Å, the $d(n_c + 1) - d(n_c)$ for amine bilayers is expected to be 1.01 Å (n_c is odd) and 3.08 Å (n_c is even) or
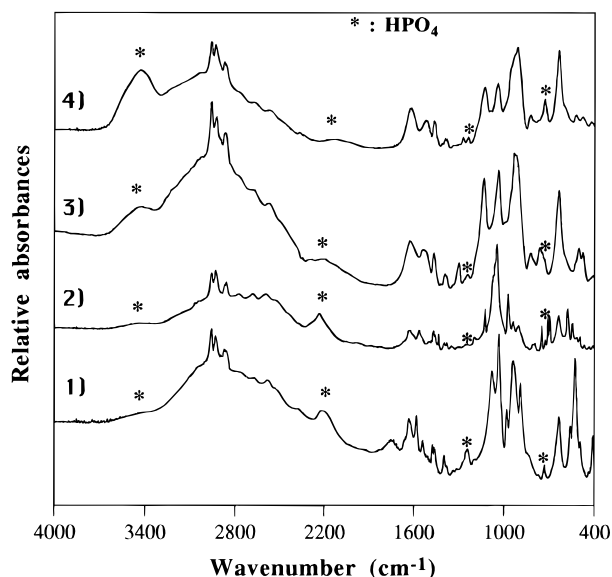
Figure 8. IR spectra of (1) VOPO$_4$·2H$_2$O + C$_5$H$_{11}$NH$_2$, (2) VOC$_6$H$_5$-PO$_3$·2H$_2$O + C$_5$H$_{11}$NH$_2$, (3) VOCH$_3$PO$_3$·1.5H$_2$O + C$_5$H$_{11}$NH$_2$, and (4) VOC$_2$H$_5$PO$_3$·1.5H$_2$O + C$_5$H$_{11}$NH$_2$.

0.51 and 1.54 Å for odd and even n_c, respectively, in the case of amine monolayers.

From these overall remarks, we suspect that two different interlamellar arrangements exist, depending on the n_c value. In fact, the abrupt slope decrease at $n_c = 6$ may be explained by the passage from a packing of alkyl chains as double layers $n_c = 3-5$, to an interdigitated monolayer of amine molecule with a larger tilt angle $\approx 63°$. Such a phenomenon may conceivably occur, assuming longer alkyl chain lengths force the amine molecule to adopt a more upright position, giving rise to a monolayer of alkyl chain.

The most surprising feature observed is that, for a given amine molecule, the resulting X-ray diffractograms are totally identical independent of the starting vanadyl phosphonate (as illustrated in Figure 4). Consequently as each vanadyl phosphonate possesses its own characteristics, it seems that reaction with the strong basic amine molecules results in decomposition of the phosphonate groups by P—C bond cleavage as described in other works.[22-24]

In order to isolate eventual intermediates between starting phosphonates and final reaction products, portions of the samples are recovered after reaction for 1 month via methods A and C, and their X-ray powder patterns are recorded. As can be seen in Table 1, the interlayer distances are quite similar to those obtained by intercalation of alkylamines into vanadyl hydrogenophosphate hemihydrate, VOHPO$_4$·0.5H$_2$O.

So, it clearly appears that the first reaction step consists of the hydrolysis of the phosphonate RPO$_3$ groups by P—C bond scission, into hydrogenophosphate HPO$_4$ groups. But, interlayer distances of the 1 month intercalates are different from those recorded for the final products. Moreover, the passage to HPO$_4$ groups implies the conservation of vanadium atoms in a +IV

oxidation state, which is why we believe that it is not the only process involved.

In fact, X-ray absorption spectra of the final intercalates (Figures 5 and 6), provide strong evidence that the vanadium oxidation state has increased. Compared with the XANES spectrum of the starting vanadyl phenylphosphonate, characteristic of a compound containing V^{4+}, it is important to note a shift which displaces both the prepeak and the threshold region of the intercalates XANES spectrum to higher energies. Also a more intense prepeak feature is observed. From these overall remarks, and given that spectra of the intercalate and Na$_3$VO$_4$ (choosen as reference standard for V^{5+}) are quite similar in energy position, we can put forward that vanadium atoms are oxidized to the +V oxidation state.

To our knowledge, it is the first time that such a phenomenon involving oxidation of vanadium in basic alkylamine solutions is described. Until now, partial reduction has often been observed,[28] caused either by the strong electron donor ability (nitrogen lone pair) of the amine molecule, or by host—guest electron transfer.

These two phenomena, P—C bond hydrolysis and vanadium atoms oxidized to the +V oxidation state, lead us to think that the final products could be intercalation compounds of a vanadyl phosphate. To verify this assumption, we have prepared amine intercalated phases of vanadyl phosphate dihydrate VOPO$_4$·2H$_2$O, choosen as a model compound, because of the presence of water molecules as in the vanadyl phosphonates. Indeed, these water molecules can play a role in the reaction process.

VOPO$_4$·2H$_2$O was prepared by refluxing V$_2$O$_5$ in 85% H$_3$PO$_4$ according to the method of Ladwig.[29] VOPO$_4$·2H$_2$O is a layered compound with an interlayer distance of 7.41 Å. The remarkable similarity in X-ray diffractograms (Figure 7) of the pentylamine intercalates obtained from VOPO$_4$·2H$_2$O and the vanadyl phosphonates confirms the obtaining of vanadyl phosphate intercalation compounds.

IR spectra of these pentylamine-intercalated phases (Figure 8) display a series of identical bands and with only small differences in some band intensities. However, the basic structure is undoubtedly the same. Intercalated amines participate in hydrogen bonding, broadening the spectra in the 2400—3200 cm^{-1} range, while weak bands from the C—H stretch of the alkyl chain are present at 2967, 2930, and 2877 cm^{-1}.

The water stretching and bending bands of the original vanadyl phosphonates and δ(P—C) characteristic bands of the phosphonate groups are absent, confirming both displacement of the water molecules and hydrolysis of the phosphonate groups. Four IR bands, marked by an asterisk, correspond to HPO$_4$ groups:[30]

$$\nu(\text{PO}-\text{H}) = 3425 \text{ cm}^{-1}$$

$$\delta(\text{POH}) + \nu(\text{PO}_3) = 2250 \text{ cm}^{-1}$$

$$\delta(\text{POH, in plane}) = 1250 \text{ cm}^{-1}$$

$$\delta(\text{POH, out of plane}) = 720 \text{ cm}^{-1}$$

Moreover, it is important to note that both free alkylamine molecules RNH$_2$ and protonated alkylamines RNH$_3$$^+$ exist in

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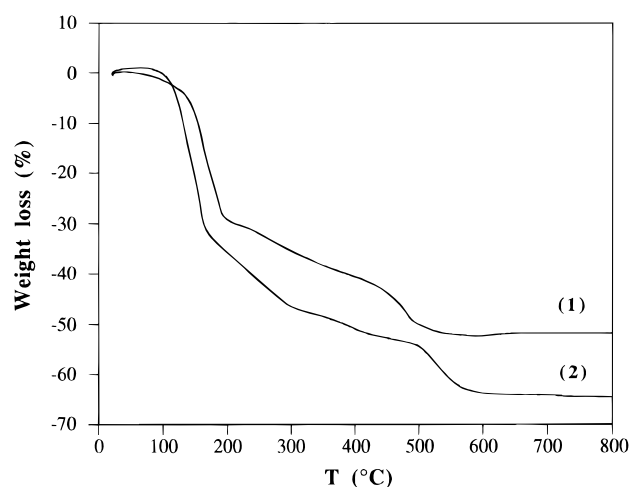
Table 2. IR Bands of Amine Intercalated Compounds (1350−1650 cm^{-1} Range)

| VOPO$_4$·2H$_2$O		VOC$_6$H$_5$PO$_3$·2H$_2$O		VOCH$_3$PO$_3$·1.5H$_2$O		VOC$_2$H$_5$PO$_3$·1.5H$_2$O	
IR peak (cm^{-1})	assignment	IR peak (cm^{-1})	assignment	IR peak (cm^{-1})	assignment	IR peak (cm^{-1})	assignment
1641	δ_s(NH$_2$)	1636	δ_s(NH$_2$)	1631	δ_s(NH$_2$)	1631	δ_s(NH$_2$)
1591	δ_s(NH$_2$)	1613	δ_s(NH$_2$)	1551	δ_{as}(NH$_3^+$)	1526	δ_{as}(NH$_3^+$)
1546	δ_{as}(NH$_3^+$)	1571	δ_{as}(NH$_3^+$)	1476	δ(CH)	1472	δ(CH)
1481	δ_s(NH$_3^+$) + δ(CH)	1475	δ_s(NH$_3^+$) + δ(CH)	1465	δ(CH)	1462	δ(CH)
1470	δ(CH)	1466	δ(CH)	1402	ν(CN)	1406	ν(CN)
1407	ν(CN)	1407	ν(CN)	1392	ν(CN)	1388	ν(CN)
1387	ν(CN)	1387	ν(CN)				

Table 3. Results of the Elemental Analysis for the Final Intercalation Compounds

| intercalated alkylamine	% N		% C		% H	
	calc^a	expt	calc^a	expt	calc^a	expt
C$_3$H$_7$NH$_2$	10.00	9.86	25.71	25.19	6.43	6.27
C$_4$H$_9$NH$_2$	9.09	8.73	31.17	30.93	7.14	7.05
C$_5$H$_{11}$NH$_2$	8.33	7.98	35.71	35.11	7.74	7.69
C$_6$H$_{13}$NH$_2$	7.69	7.48	39.56	38.71	8.24	8.18

^{a} Calculated for VOPO$_4$·2RNH$_2$.

Figure 9. TG curves of (1) pentylamine intercalated phase and (2) hexylamine intercalated phase.

the intercalates, as can be seen in Table 2. This may be explained by the following equilibrium:

$$RNH_2 + H_2O \leftrightarrow RNH_3^+ + OH^-$$
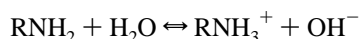
Indeed, intercalation reactions proceed with displacement of water molecules coordinated to V^{4+} of the host lattice. These water molecules react with excess alkylamine with subsequent formation of protonated alkylamine and OH$^-$ groups to assure neutrality of the system.

The 850−1200 cm^{-1} region is composed of ν(PO) and ν(V=O) stretching bands. The ν(V=O) stretching frequency occurs at *ca.* 980−985 cm^{-1}. This value is significantly lower than those found for VO^{3+} complexes (typically 1015−1030 cm^{-1}). Such a large shift to lower energy suggests a coordination between intercalated alkylamines and vanadium atoms through a strong V−N bond.[28c,31] Indeed, increasing the electron density at the vanadium through ligand coordination

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(31) Borovik, A. S.; Dewey, T. M.; Raymond, K. N. *Inorg. Chem.* **1993**, *32*, 413.

Scheme 1. Proposed Mechanism for Oxidation of Vanadium Atoms
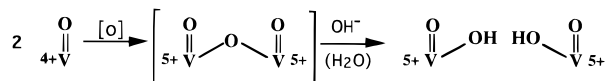
causes a reduction in the amount of p$_\pi$(oxo) → d$_\pi$(V) donation from the multiply bonded oxygen reflected in a lowering of ν(V=O).

Moreover, elemental (Table 3) and thermogravimetric analyses (Figure 9) indicate that approximately 2 mol of amine are taken up either from the gas or liquid phase. These amine molecules are bonded differently in the intercalates: first amine loss occurs at *ca.* 120 °C, while the second amine weight loss is a multistep process beginning at about 180 °C to afford β-VOPO$_4$.

Solid−liquid or solid−gas reactions were also performed under nitrogen atmosphere to prevent oxidation of vanadium atoms from air oxygen. By this way, the nature of the end products of the amine interaction reactions remains unchanged, suggesting oxidation of the vanadium atoms may arise from dissolved oxygen in the solution according to the following proposed mechanism of Scheme 1.

Conclusion

Although amine intercalation reactions are extremely complex (which have not resulted in the isolation of amine intercalated vanadyl(IV) organophosphonates), we have shown that, hydrolysis of the phosphonate groups (by P−C bond cleavage) leading to hydrogenophosphate groups occurs, followed by oxidation of vanadium atoms (by dissolved oxygen) with subsequent formation of alkylamine intercalated compounds of VOPO$_4$·2H$_2$O. This is the first time that such an oxidation phenomenon of vanadium atoms in strong basic media is reported. The final intercalation compounds exhibit an increase of interlayer spacing consistent with the length of amine molecules, but with two different arrangements of alkyl chains according to the n_c value. Two moles of alkylamines are present, both as free RNH$_2$ molecules and in a protonated form, RNH$_3^+$, with a direct coordination of N to the (V=O)$^{3+}$ group. Crystal structure determination of the intercalates would be helpful to elucidate the coordination site of the two amine molecules. Unfortunately, as is often the case for layered compounds, efforts to obtain single crystals of the intercalates have so far been unsuccessful. Anyway, further work should include studies of the reactivity of the starting vanadyl phosphonates with intercalation agents of different basicity since this work has evidenced the important fact was the basicity of the −NH$_2$ group more than the length of the alkyl chain.