Intercalation of Alkanediols into Layered Vanadyl Phenyl- and Ethylphosphonate

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Alkanediols $OH(CH_2)_nOH$ ($n = 2-5$) were intercalated into layered vanadyl phenylphosphonate $VOC_6H_5PO_3\cdot 2H_2O$ and ethylphosphonate $VOC_2H_5PO_3\cdot 1.5H_2O$. Considering alkanediols with $n = 2-3$, 1 mol of alkanediol was intercalated, forming layered compounds of composition $VOC_6H_5PO_3\cdot OH(CH_2)_nOH$ or $VOC_2H_5PO_3\cdot OH(CH_2)_nOH$ as characterized by powder X-ray diffraction, thermogravimetry, and infrared spectroscopy. These alkanediols coordinate to the vanadium atom at the two sites initially occupied by the water molecules. Alkanediols with $n = 4-5$ coordinate only to the interlayer site with replacement of a weakly bound water molecule. A comparison of the intercalation reactions with alcohol is included and evidences the strong hydrophobic sorbent character of these vanadyl organophosphonates.

Introduction

Since the late 1970s there has been a great deal of research activity aimed at the synthesis, structural chemistry and intercalation behavior of metal organophosphonates. Special interest is given to layered phosphonates with alternating organic and inorganic layers which can show further interlamellar reactivity and exhibit interesting properties as sorbents, catalysts, catalyst supports, chemical sensors, etc. Several tetravalent,[1−5] trivalent,[6−9] and divalent[7,8,10−13] systems have already been studied in detail, and it appears that the composition and structure of a specific metal phosphonate are controlled by the charge of the metal, the size of the organic groups and the synthetic method chosen. Moreover the water molecules in the metal coordination sphere play an important role on the layer connectivity, the interlamellar organic packing, and the intercalation behavior of these materials. For example, as first demonstrated by Johnson et al., alcohol-intercalated vanadyl organophosphonates can be prepared in alcoholic media [14−15] by reaction of vanadium pentoxide with the appropriate phosphonic acid. Thermal removal of the alcohol leaves a vacant site on the V^{IV} atoms of the layer and allows a variety of primary alcohols or a water molecule to bind at this site, with selectivity governed by the steric constraints imposed by the organic groups. On the other hand, we have shown elsewhere[16] that reactions of layered vanadyl phosphonates with alkylamines result in the hydrolysis of the phosphonate groups (P−C bond cleavage) and oxidation of vanadium atoms.

This paper reports the first systematic study of $VORPO_3\cdot xH_2O$ ($R = C_6H_5$, C_2H_5) intercalation with alkanediols $OH(CH_2)_nOH$ as a new route to novel intercalated vanadyl(IV) phosphonate phases.

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Experimental Section

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

Synthesis of Vanadyl Organophosphonates. The two 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 is refluxed and stirred at least for 2 days, then precipitates are recovered by filtration and washed with acetone. Subsequent thermal removal of the intercalated alcohol leads to vanadyl phenyl- ($VOC_6H_5PO_3{\cdot}2H_2O$) or ethylphosphonate ($VOC_2H_5PO_3{\cdot}1.5H_2O$) with interlayer distances of 9.82 and 9.71 Å, respectively.

Intercalation Reactions. Two experiments were carried out to prepare intercalation compounds:

Method A: Intercalated phases were obtained by heating at reflux 0.2 g of a phosphonate immersed in an excess (80 mL) of liquid alkanediol for 5 days.

Method B: Intercalation compounds were also directly prepared, following the Johnson procedure, the only change required was the replacement of the R′OH alcohol with the proper $OH(CH_2)_nOH$ alkanediol. The mixture was refluxed and stirred at least for 4 days.

In both methods, the intercalates were recovered by filtration and washed with acetone. The resulting blue solids were air-dried prior to characterization.

Chemical Analysis. $VOC_6H_5PO_3{\cdot}OH(CH_2)_2OH$: Calcd: V, 17.89; P, 10.87; C, 33.68; H, 3.86. Found: V, 17.74; P, 10.78; C, 33.42; H, 3.74. $VOC_6H_5PO_3{\cdot}OH(CH_2)_3OH$: Calcd: V, 17.05; P, 10.37; C, 36.12; H, 4.34. Found: V, 16.96; P, 10.21; C, 35.99; H, 4.27. $VOC_6H_5PO_3{\cdot}H_2O.OH(CH_2)_4OH$: Calcd: V, 15.40; P, 9.36; C, 36.25; H, 5.14. Found: V, 15.33; P, 9.30; C, 36.01; H, 5.00. $VOC_6H_5PO_3{\cdot}H_2O{\cdot}OH(CH_2)_5OH$: Calcd: V, 14.78; P, 8.98; C, 38.26; H, 5.51. Found: V, 14.75; P, 8.93; C, 38.15; H, 5.36.

$VOC_2H_5PO_3{\cdot}OH(CH_2)_2OH$: Calcd: V, 21.52; P, 13.08; C, 20.25; H, 4.64. Found: V, 21.47; P, 13.00; C, 20.03; H, 4.50. $VOC_2H_5PO_3{\cdot}OH(CH_2)_3OH$: Calcd: V, 20.32; P, 12.35; C, 23.90; H, 5.18. Found: V, 20.28; P, 12.31; C, 23.78; H, 5.02. $VOC_2H_5PO_3{\cdot}H_2O{\cdot}{}^1/_2[OH(CH_2)_4OH]$: Calcd: V, 21.43; P, 13.03; C, 20.17; H, 5.04. Found: V, 21.48; P, 13.08; C, 19.84; H, 4.89. $VOC_2H_5PO_3{\cdot}H_2O{\cdot}{}^1/_2[OH(CH_2)_5OH]$: Calcd: V, 20.82; P, 12.65; C, 22.04; H, 5.31. Found: V, 20.79; P, 12.58; C, 21.91; H, 5.27.

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 monochromator. XRD experiments were also carried out by passing the samples through a 80 μm sieve before the filling of the sample holder in order to avoid preferred orientation. During data collection, the sample holder was also rotating at the speed of 30 rpm. Unfortunately preferred orientation effects cannot be reduced by changing the XRD conditions. Fourier transform infrared (FTIR) spectra were performed on a Perkin-Elmer 16PC spectrophotometer using the KBr disk method. The DTA and TGA diagrams 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 vanadium K-edge were obtained at the French Laboratoire pour l′Utilisation du Rayonnement Electromagnétique (L.U.R.E.) synchrotron radiation facility (line EXAFS IV). The EXAFS analyses were carried out using programs written by Dr. A. Michalowicz (L.U.R.E., Université Paris-Sud).[17] Magnetic susceptibility measurements were made using a Quantum Design Model MPMS SQUID magnetometer at the Institut des Matériaux de Nantes (IMN). Vanadium, phosphorus, carbon and hydrogen microanalyses (I.C.P. method) were made by the CNRS Analysis Laboratory, Vernaison.

Results and Discussion

Interlayer distances of the intercalates are summarized in Table 1 compared with those of the starting phosphonates (given in parentheses). Regardless of the synthetic method used, the intercalation compounds obtained are identical. From these values it clearly appears that strong interactions between alkanediols molecules and host structures exist, resulting in shorter interlayer spacings than intercalation compounds with alcohol's.[14d] This phenomenon is especially observed in the case of $OH(CH_2)_2OH$ (named C_2) and $OH(CH_2)_3OH$ (named C_3) intercalates. Intercalation of these alkanediols into vanadyl ethylphosphonate $VOC_2H_5PO_3{\cdot}1.5H_2O$ even leads to compounds with shorter interlayer distances than that recorded for the host structure. It seems to indicate that structural changes occur during the intercalation process.

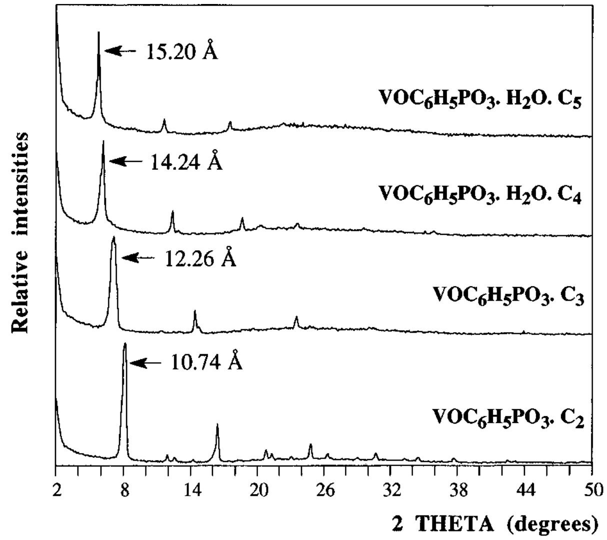

Figure 1. PXRD patterns of alkanediols intercalated vanadyl phenylphosphonate.

Table 1. Interlayer Distances (Å) of Alkanediols Intercalated $VOC_6H_5PO_3{\cdot}2H_2O$ and $VOC_2H_5PO_3{\cdot}1.5H_2O$

	R	
	C_6H_5 (d = 9.82 Å)	C_2H_5 (d = 9.71 Å)
intercalated alkanediol		
$OH(CH_2)_2OH = C_2$	10.74(1)	8.80(1)
$OH(CH_2)_3OH = C_3$	12.26(1)	9.50(1)
$OH(CH_2)_4OH = C_4$	14.24(1)	11.27(2)
$OH(CH_2)_5OH = C_5$	15.20(3)	11.68(3)

X-ray diffractograms of the intercalates are given in Figure 1 for $VOC_6H_5PO_3{\cdot}2H_2O$ and in Figure 2 for $VOC_2H_5PO_3{\cdot}1.5H_2O$. Although the powder XRD patterns show well-defined peaks, indicative of a well-ordered structure, they have generally not been indexed due to their featureless above 40° (2θ). The layered nature of the intercalation compounds clearly appears and is evidenced by the first-, second-, and third-order reflections of the interlayer distance which are enhanced owing to preferred orientation.

Results of the chemical analysis (see Experimental Section) undoubtedly indicate 1 mol of alkanediol is intercalated in $VOC_6H_5PO_3{\cdot}2H_2O$. However a water molecule is present in intercalation compounds with C_4 and C_5 whereas C_2 and C_3 intercalates contain no water molecule. It is very important to note that no dehydration is required to make the intercalation possible, showing $VOC_6H_5PO_3{\cdot}2H_2O$ and $VOC_2H_5PO_3{\cdot}1.5H_2O$ are very reactive with alkanediols.

Thermogravimetric analyses confirm the $VOC_6H_5PO_3{\cdot}C_2$ and $VOC_6H_5PO_3{\cdot}C_3$ stoichiometry as can be seen

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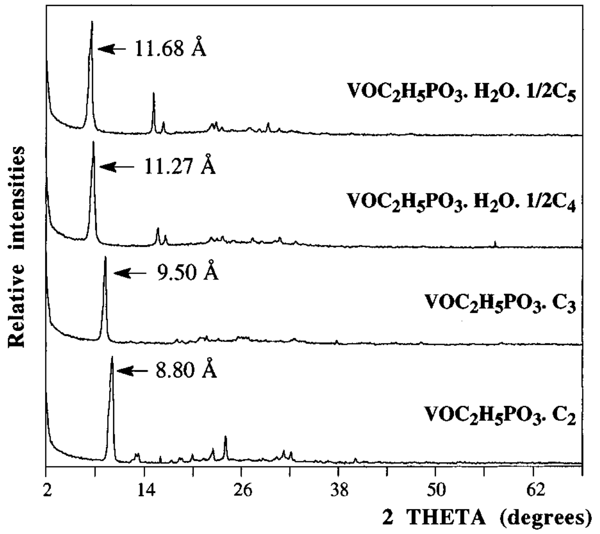


Figure 2. PXRD patterns of alkanediols intercalated vanadyl ethylphosphonate.

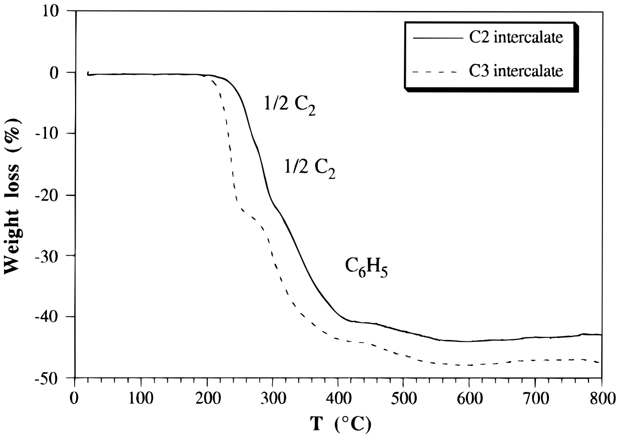


Figure 3. TG curves of $VOC_6H_5PO_3{\cdot}C_2$ and $VOC_6H_5PO_3{\cdot}C_3$.

Table 2. TG Results of $VOC_6H_5PO_3{\cdot}C_2$ and $VOC_6H_5PO_3{\cdot}C_3$

intercalated alkanediol	temp (°C)		
	200–271	271–308	308–600
$OH(CH_2)_2OH$	exp 10.9% cal 11.0% $^1/_2OH(CH_2)_2OH$	exp 11.1% cal 11.0% $^1/_2OH(CH_2)_2OH$	C_6H_5
	190–229	229–275	280–600
$OH(CH_2)_3OH$	exp 11.5% cal 12.5% $^1/_2OH(CH_2)_3OH$	exp 11.6% cal 12.5% $^1/_2OH(CH_2)_3OH$	C_6H_5

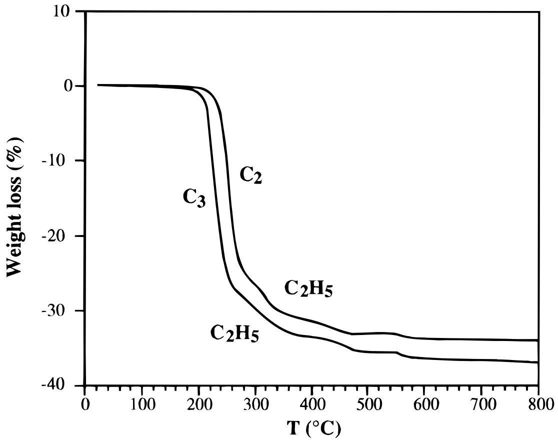


Figure 4. TG curves of $VOC_2H_5PO_3{\cdot}C_2$ and $VOC_2H_5PO_3{\cdot}C_3$.

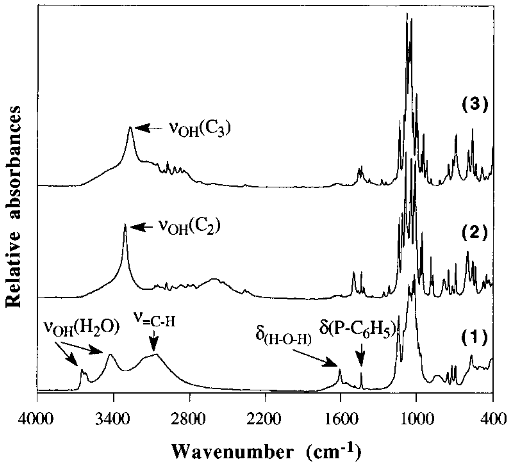


Figure 5. IR spectra of (1) $VOC_6H_5PO_3{\cdot}2H_2O$, (2) $VOC_6H_5PO_3{\cdot}C_2$, and (3) $VOC_6H_5PO_3{\cdot}C_3$.

in Figure 3 but also provide strong evidence that two types of intercalated alkanediol molecule exist in the structures (Table 2). Two equal weight losses, each corresponding to one-half alkanediol molecule, were observed and seem to demonstrate that two different sites are available for intercalation in $VOC_6H_5PO_3{\cdot}2H_2O$. Furthermore as no water molecule remains in the intercalation compounds, we can put forward that the two kinds of intercalated molecules are taken up at the sites initially occupied by the water molecules. It is now well-known that the two $VOC_6H_5PO_3{\cdot}2H_2O$ water molecules are differently bonded. In the structure VO_6 octahedra share corners with the three oxygen atoms of the phosphonate group. One water molecule is coordinated in the fourth planar equatorial position of the vanadium atoms within the layer. It is worth noting that this water molecule cannot be thermally removed without a collapse of the structure and remains unchanged upon alcohol intercalation. In contrast the second water molecule complete the octahedral coordination of vanadium (with the vanadyl oxygen atom) in the axial position directed toward the interlayer space. This water molecule is replaced by one alcohol molecule upon intercalation.[14d] With alkanediols C_2 or C_3 the mechanism seems to be quite different because on one hand the two water molecules are replaced and on the other hand two half alkanediol molecules are intercalated differently.

In the case of $VOC_2H_5PO_3{\cdot}1.5H_2O$ intercalates, even if alkanediol weight loss appears as a clean one-step process (Figure 4), the compositions are nearly identical with one intercalated alkanediol molecule and no remaining water molecule. This suggests some similarities between C_2 and C_3 intercalation compounds obtained either from $VOC_6H_5PO_3{\cdot}2H_2O$ or $VOC_2H_5PO_3{\cdot}1.5H_2O$.

Moreover IR spectra of the intercalates also provide strong evidence that alkanediols occupy the water coordination sites. The O–H stretching bands (3640–3417 cm^{-1}) of coordinated water in $VOC_6H_5PO_3{\cdot}2H_2O$ (Figure 5) are replaced by three sharper bands between 2990 and 2700 cm^{-1}, attributed to the C–H stretch of the alkanediol chain, and by a strong band at 3320 cm^{-1} ($VOC_6H_5PO_3{\cdot}C_2$) and 3286 cm^{-1} ($VOC_6H_5PO_3{\cdot}C_3$), which is due to O–H stretching of the diol coordinated to vanadium atom. IR spectra of the intercalates show a

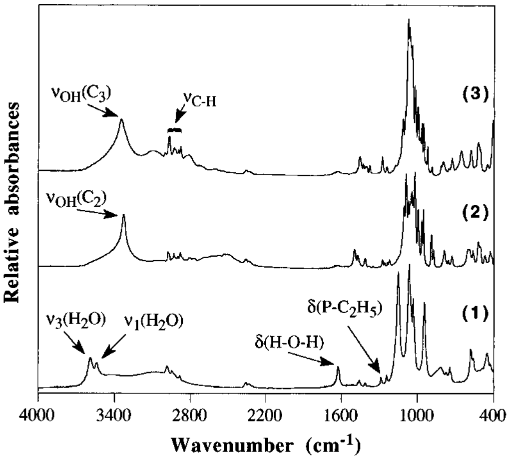


Figure 6. IR spectra of (1) $VOC_2H_5PO_3{\cdot}1.5H_2O$, (2) $VOC_2H_5PO_3$. C_2, and (3) $VOC_2H_5PO_3{\cdot}C_3$.

broad O−H stretching region which extends to lower frequency (3150−2500 cm^{-1}) indicating of a strong hydrogen bonding network. We can also note the H−O−H bending vibration (1616 cm^{-1}) is missing. However the phenyl ring C−H stretch band (3066 cm^{-1}), the $P-C_6H_5$ bending mode (1446 cm^{-1}), which remain virtually unchanged, may indicate that the basic structure is retained after intercalation. A few additional bands appear in the PO_3 and the V=O stretching vibration domain (1200−900 cm^{-1}) which are certainly due to hydrogen-bonded OH moieties.

All these remarks can be made in the case of $VOC_2H_5PO_3{\cdot}1.5H_2O$ intercalation compounds (Figure 6) and we can observe some similarities between IR spectra of the series $VOC_6H_5PO_3{\cdot}C_n$ and $VOC_2H_5PO_3{\cdot}C_n$ ($n = 2, 3$), whereas the two original phosphonate structures are quite different. According to the shortening of the interlayer distance of $VOC_2H_5PO_3{\cdot}1.5H_2O$ upon C_2 and C_3 intercalation a structural rearrangement must occur in the case of vanadyl ethylphosphonate.

To determine what are the main differences between the two types of intercalated alkanediol we attempt to remove the less thermally stable intercalated alkanediol by heating the solids in vacuo at 150 °C overnight. Then compounds were subsequently exposed to ambient moisture. Although there is no evidence of two types of intercalated alkanediol in $VOC_2H_5PO_3{\cdot}C_n$ ($n = 2, 3$) we have also used this procedure to treat the ethylphosphonate intercalates.

Interlayer spacings slightly decrease upon this treatment (for example 10.64 Å for treated $VOC_6H_5PO_3$. C_2 and 8.74 Å for treated $VOC_2H_5PO_3{\cdot}C_2$) and the layered nature of the materials is retained. Two representative TGA curves are shown in Figure 7. All the observed results agree with the removal of one-half intercalated alkanediol molecule while a water molecule is absorbed from air. The more thermally stable alkanediol and the organic component losses remain unchanged on the thermograms. Attempts to remove the strongly bonded alkanediol results in the destruction of the layered structure consistent with the existence of two different intercalation sites.

IR spectra of these compounds of composition $VOC_6H_5PO_3{\cdot}H_2O^1/_2C_2$ and $VOC_2H_5PO_3{\cdot}H_2O{\cdot}{}^1/_2C_2$, respectively, are given in Figure 8 and confirm the presence of water molecule evidenced by ν_{OH} and δ_{H-O-H} vibration bands. From these overall remarks we can conclude the first site available for coordinative intercalation is directed toward the interlayer space (position *trans* to the vanadyl bond). This site can be reversibly occupy by a water molecule or a half alkanediol molecule according to Scheme 1. This indicates that the two OH functions of the alkanediol are involved in the binding. In contrast the second site, where the alkanediol is more strongly bonded, is a structural site within the layer (position *cis* to the vanadyl bond). In consequence this site is occupied by either a water molecule or a half alkanediol molecule but is not found to be reversible.

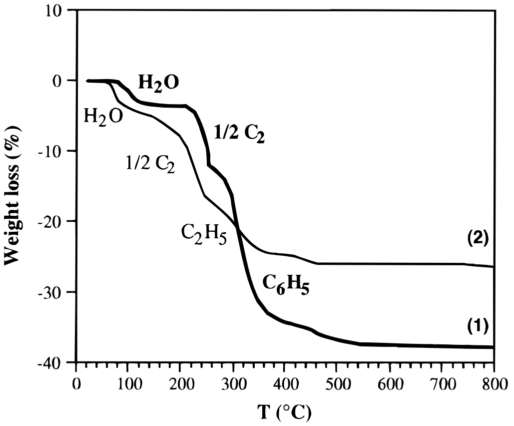


Figure 7. TG curves of (1) $VOC_6H_5PO_3{\cdot}H_2O{\cdot}{}^1/_2C_2$ and (2) $VOC_2H_5PO_3{\cdot}H_2O{\cdot}{}^1/_2C_2$.

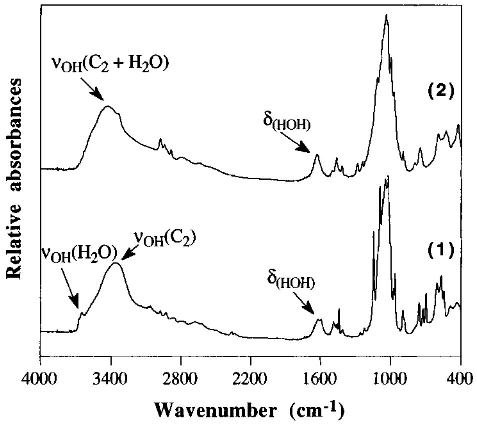
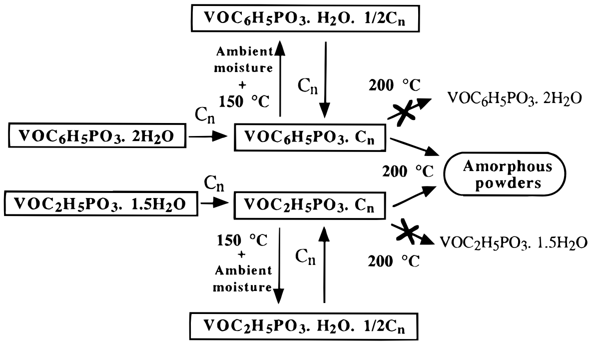


Figure 8. IR spectra of (1) $VOC_6H_5PO_3{\cdot}H_2O{\cdot}{}^1/_2C_2$ and (2) $VOC_2H_5PO_3{\cdot}H_2O{\cdot}{}^1/_2C_2$.

Scheme 1



The presence of this intralayer site allows to explain the interlayer distance shortening in the case of vanadyl ethylphosphonate. In fact the intercalated C_2 or C_3 bond at this site increases the layer area and consequently spaces the organic group distribution. Then sufficient free space remains in the interlayer region to

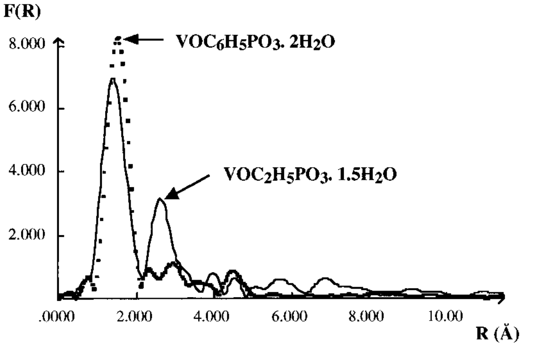


Figure 9. Radial distribution curves of $VOC_6H_5PO_3{\cdot}2H_2O$ and $VOC_2H_5PO_3{\cdot}1.5H_2O$.

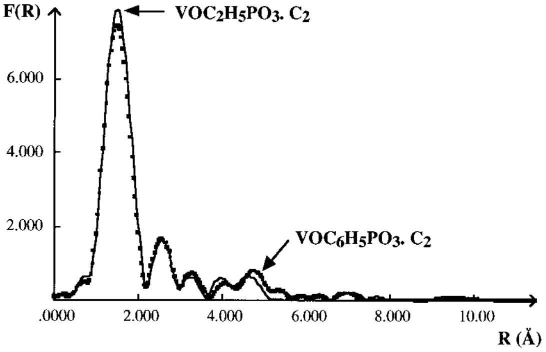


Figure 10. Radial distribution curves of $VOC_6H_5PO_3{\cdot}C_2$ and $VOC_2H_5PO_3{\cdot}C_2$.

permit organic groups from opposing layers to interpenetrate (instead of being packed as a bilayer in $VOC_2H_5PO_3{\cdot}1.5H_2O$). Finally the C_6H_5 and C_2H_5 packing in the interlayer domain is found to become the same upon C_2 and C_3 intercalation. This structural rearrangement leads to similar intercalated structures without any water molecule but with one intercalated alkanediol molecule evenly distributed in the interlayer region and in a structural site within the layer.

Moreover, the EXAFS study at the vanadium K-edge is consistent with this assumption. As can be seen in Figure 9, the Fourier transformed spectra of the starting phosphonates $VOC_6H_5PO_3{\cdot}2H_2O$ and $VOC_2H_5PO_3{\cdot}1.5H_2O$ are quite different. The first peak is much more intense in the case of $VOC_6H_5PO_3{\cdot}2H_2O$ while we notice a very important second peak corresponding to the nearest vanadium atom engaged in vanadyl dimers $V_2O_8(H_2O)$ expected in $VOC_2H_5PO_3{\cdot}1.5H_2O$. In contrast, the C_2 intercalates obtained either from vanadyl ethylphosphonate or phenylphosphonate display very similar spectra (Figure 10) where no vanadyl dimers are detected. For the first coordination shell of the two intercalation compounds, the best fit is obtained when V^{4+} is surrounded by 4 oxygen atoms: 3 at 2.02 Å (V−O bonds) and 1 at 1.62 Å (V=O bond). Even if it would be highly speculative to draw further structural conclusions, all the observed results clearly evidence the structural analogies between the two intercalated phases.

To further demonstrate the structural change of the ethylphosphonate host lattice upon C_2 diol intercalation, we have performed magnetic measurements on the intercalated compounds. The magnetic behavior of the starting materials was investigated and described elsewhere. The vanadyl phenylphosphonate dihydrate built up from isolated VO_6 octahedra is paramagnetic. On the other hand, $V_2O_8(H_2O)$ dimers in vanadyl ethylphosphonate are responsible for an antiferromagnetic order below 40 K.[18]

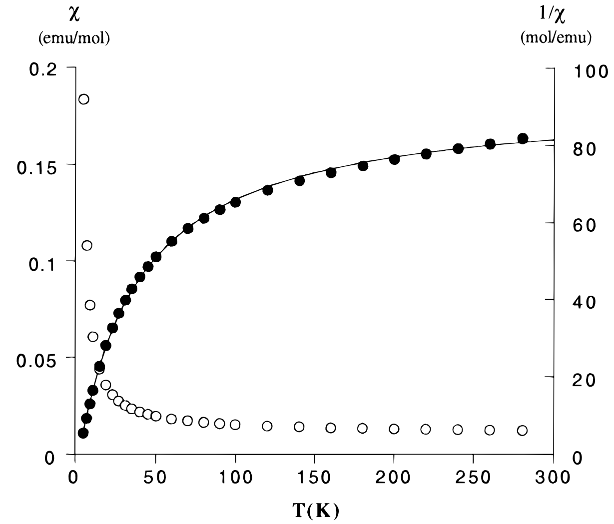


Figure 11. Magnetic susceptibility data for $VOC_6H_5PO_3{\cdot}C_2$.

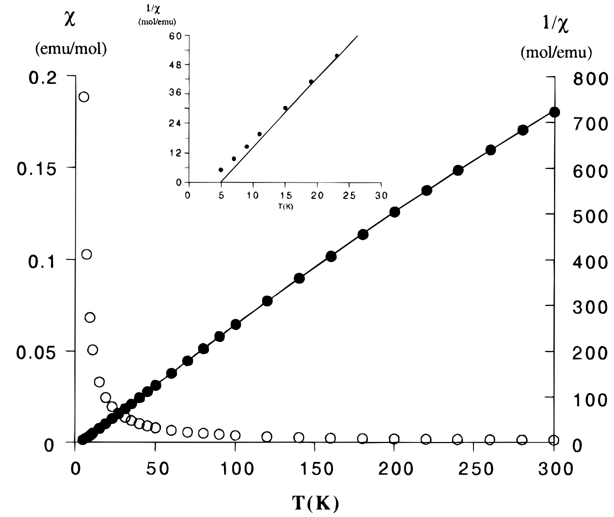


Figure 12. Magnetic susceptibility data for $VOC_2H_5PO_3{\cdot}C_2$.

Figures 11 and 12 display the temperature dependence of the reciprocal susceptibility of $VOC_6H_5PO_3{\cdot}C_2$ and $VOC_2H_5PO_3{\cdot}C_2$, respectively. The polycrystalline samples were first cooled in zero field and then measured upon heating in a field of 5 kG.

The C_2 intercalated phenylphosphonate seems to retain a paramagnetic behavior in the whole temperature range 2−300 K. The data are well described by a modified Curie−Weiss law, $\chi = C/(T - \theta_p) + \chi_0$, with a Curie constant $C = 0.414(6)$ uem K/mol, a paramagnetic Curie temperature $\theta_p = 2.5(2)$ K and a temperature independent parameter(TIP) $\chi_0 = 0.01093(5)$ uem/mol or $3.82(2) \times 10^{-5}$ cm^3/g. The C value leads to an effective moment of 1.82 μ_B/formula unit, close to the theoretical high spin and spin-only moment expected for V^{4+} cations in octahedral environment: 1.73 μ_B/formula unit. The quite large temperature-independent term χ_0 might be ascribed to a second-order Zeeman effect regarding to the highly distorted octahedron of oxygen (C_{4v} symmetry)[19] around the V^{4+} cation.

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[18] Huan, G.; Johnson, J. W.; Brody, J. F.; Goshorn, D. P.; Jacobson, A. J. *Mater. Chem. Phys.* **1993**, *35*, 199.

[19] Mabbs, F. E.; Machin, D. J. *Magnetism and Transition Metal Complexes*; Chapman and Hall: London, 1973.

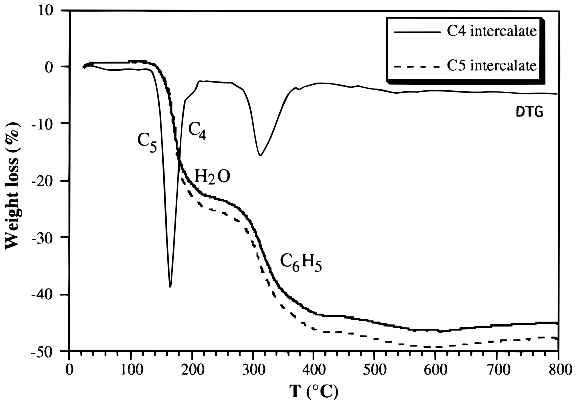

Figure 13. TG curves of C_4 and C_5 intercalated $VOC_6H_5PO_3\cdot 2H_2O$ and DTG trace of the C_5 intercalate.

The paramagnetic state of $VOC_2H_5PO_3\cdot C_2$ above 50 K is also fitted to a modified Curie–Weiss expression $\chi = C/(T - \theta_p) + \chi_0$. The best agreement is obtained with a Curie constant $C = 0.350(1)$ uem K/mol leading to an effective moment of 1.675(3) μ_B/formula unit, a paramagnetic Curie temperature $\theta_p = 4.9 \pm 0.2$ K and a temperature-independent term $\chi_0 = 192(5) \times 10^{-6}$ uem/mol or $8.1(2) \times 10^{-7}$ cm^3/g. Below 15 K, a deviation from the Curie–Weiss behavior occurs. This might be attributed to the presence of very weak antiferromagnetic interactions between V^{4+} cations. The minimum in the reciprocal susceptibility versus T observed for the starting material $VOC_2H_5PO_3\cdot 1.5H_2O$ and characteristic of antiferromagnetically exchange-coupled dimers has disappeared. This clearly evidences a structural change for the vanadyl ethylphosphonate host lattice upon C_2 diol intercalation.

In contrast, C_4 and C_5 intercalation in phenyl- and ethylphosphonate does not occur in the same way. Intercalation of C_4 and C_5 into $VOC_6H_5PO_3\cdot 2H_2O$ leads to intercalates of composition $VOC_6H_5PO_3\cdot H_2O\cdot C_n$. As can be seen in Figure 13 no weight loss appears at 100 °C, suggesting the *trans* water molecule has been replaced upon intercalation process. The first region involves loss of an intercalated alkanediol molecule which occurs between 130 and 200 °C. Then we observed a feature (evidenced by DTG trace) corresponding to the loss of the remaining *cis* water molecule which accounts for about 5% of the mass. Following dehydration, the compounds decompose with loss of the organic portion at temperatures between 300 and 600 °C.

IR spectra of the intercalates confirm these results (Figure 14), showing the O–H stretching bands of both the water molecule and the alkanediol, and the H–O–H scissors motion at 1645 cm^{-1}. We can also note that no broadening of the spectra in the O–H stretching region appears.

As the original vanadyl phenylphosphonate can be recovered by removing the intercalated alkanediol molecule, there is no doubt that only the *trans* water molecule is replaced during the intercalation process. The *cis* water molecule is retained and unaffected so that C_4 and C_5 intercalation reaction proceeds by a mechanism similar to that recorded for alcohol intercalation. This could be explained by the larger size of the alkyl chain of these alkanediols which cannot allow them to intercalate in a structural site within the layer, in such a way that intercalated structures are different from those obtained with C_2 and C_3.

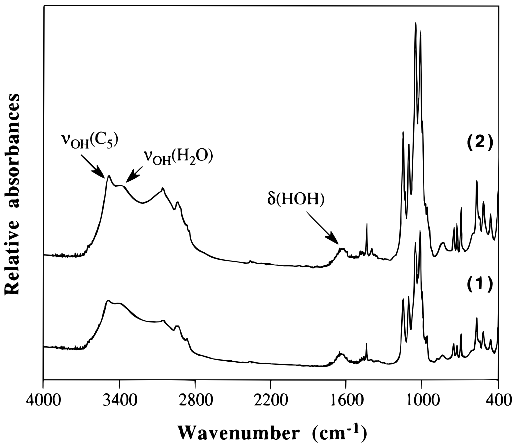

Figure 14. IR spectra of (1) $VOC_6H_5PO_3\cdot H_2O\cdot C_4$ and (2) $VOC_6H_5PO_3\cdot H_2O\cdot C_5$.

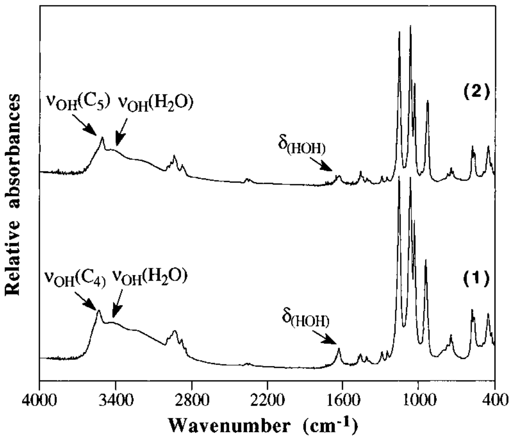

Figure 15. IR spectra of (1) $VOC_2H_5PO_3\cdot H_2O\cdot {}^1/_2C_4$ and (2) $VOC_2H_5PO_3\cdot H_2O\cdot {}^1/_2C_5$.

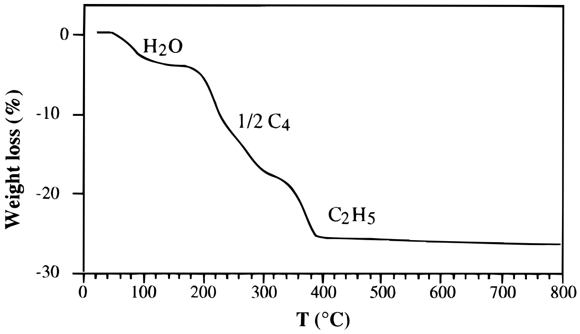

Figure 16. TG curve of $VOC_2H_5PO_3\cdot H_2O\cdot {}^1/_2C_4$.

We now turn to the C_4 and C_5 intercalated ethylphosphonate phases. IR spectra of the intercalates (Figure 15) also indicate the presence of both water and alkanediol. However chemical analyses and TGA curves (an example is given in Figure 16) clearly demonstrate only just one half alkanediol molecule is intercalated. From these results and according to interlayer distance values, C_2H_5 groups undoubtedly remain unchanged (arranged as a bilayer in the interlamellar space of the intercalates) but the content of intercalated alkanediol may indicate some pillaring of the layers has occurred upon intercalation.

Conclusion

This work has evidenced alkanediols can be intercalated into vanadyl phenylphosphonate $VOC_6H_5PO_3{\cdot}2H_2O$ and ethylphosphonate $VOC_2H_5PO_3{\cdot}1.5H_2O$. As expected, water molecules included in the metal coordination sphere were involved in the intercalation process. For the first time we have demonstrated that even water molecules within the layer can be substituted by an alkanediol molecule. In the case of C_2 and C_3, two different sites are available for coordinative intercalation into $VOC_6H_5PO_3{\cdot}2H_2O$ and $VOC_2H_5PO_3{\cdot}1.5H_2O$. The resulting intercalates of general formula $VOC_6H_5PO_3{\cdot}C_n$ and $VOC_2H_5PO_3{\cdot}C_n$ are very similar in terms of their IR spectra, thermal behavior, and organic packing, whereas the starting phosphonates are quite different.

The first coordination site is situated in the interlayer domain and can be reversibly occupied by one-half alkanediol molecule or a water molecule. The second is located within the layer where also one-half alkanediol molecule can bind. The presence of this site is sufficient to allow the organic groups to interpenetrate in the interlayer space. It is very important to note that no dehydration step is required to create vacant sites and to obtain intercalated phosphonate phases. Anyway attempts to remove the more strongly bonded water molecule result in the obtaining of amorphous powders so that it would not have been possible to prepare fully converted phases. This reveals the strong reactivity of both phosphonates with alkanediols and shows the great hydrophobic sorbent character of these materials.

In the case of C_4 and C_5 intercalation reactions, owing to their larger alkyl chain length, these alkanediols cannot bind at the intralayer site and a water molecule remains unchanged. Only the water molecule weakly tied to vanadium atom is replaced upon intercalation according to a process similar to that found for alcohol intercalation.

Evidently alkanediol intercalation into vanadyl phosphonates is a complex process and additional structural studies would be helpful to elucidate the exact layer connectivity and both the interlamellar alkyl chain and organic group packing.

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