Synthesis of Ester-Functionalized Vanadyl Phosphonates

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New layered vanadyl organophosphonates $VOHOOC(CH_2)_2PO_3{\cdot}2H_2O$ and $VO(O_3PR)_{1-x}(O_3PR')_x{\cdot}yH_2O$ with R being the ester function $(CH_2)_2COO(CH_2)_{n-1}CH_3$ and R′ the ethylcarboxylic function $(CH_2)_2COOH$ were prepared. Two different synthesis routes were used; the first compound is obtained in a water−acetone mixture with vanadyl acetylacetonate and 2-carboxyethylphosphonic acid $[HOOC(CH_2)_2PO(OH)_2]$, while the latter are prepared from the same phosphonic acid by reaction of vanadium pentoxide in an alcohol medium. These compounds were characterized by X-ray diffraction, IR spectrosopy, and thermal analysis. EXAFS experiments and magnetic measurements were also performed. The interlayer distance of esterified compounds increases as the alkyl chain length *n* increases. For the same value of *n*, the compounds esterified with alkanediols display shorter interlayer distances than those prepared from alkanols. This results from a pillaring process: both alcohol functions of the alkanediols react with the carboxylic functions of two adjacent layers. On the other hand, while the esterification reaction is observed with $HOOC(CH_2)_2PO(OH)_2$, nothing happens with $HOOCCH_2PO(OH)_2$ (Sabbar, E.; de Roy, M. E.; Besse, J. P. *Ann. Chim. Sci. Mater.* **1998**, *23*, 341). As already observed elsewhere, the accessibility of the carboxylic function depends on the alkyl chain length of the vanadyl carboxy *n*-alkylphosphonate.

Introduction

Since the late 1970s, there has been a growing interest in layered metal organophosphonates owing to their potential as sorbents and catalysts.

Several tetravalent,[1−5] trivalent,[6−9] and divalent[7,8,10−13] systems have already been studied in detail. Many structural information exist for metallic phosphonates with divalent cations (Mg, Mn, Zn, Co, Ni, Cd...), trivalent cations (Fe, La, Ce), and especially for zirconium phosphonates.[1,6,8,13] However little structural information is available for vanadyl organo phosphonates.[14] Generally the structure consists of layers of corner-sharing MO_n polyhedra and PO_3C tetrahedra. The organic groups fixed to these layers through a P−C covalent bond extend out from the both sides, forming either a monolayer or a bilayer, depending on the phosphorus atom layout; water molecules are usually present in the interlamellar space and act on the organic molecules packing. Vanadyl organophosphonates have been shown to intercalate alcohols[14,15] in place of these water molecules.

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In this paper we report the synthesis and the structural analysis of $VOHOOC(CH_2)_2PO_3{\cdot}2H_2O$ and $VO(O_3PR)_{1-x}(O_3PR')_x{\cdot}yH_2O$ with R being the ester function $(CH_2)_2COO(CH_2)_{n-1}CH_3$ and R′ the ethylcarboxylic function $(CH_2)_2COOH$. They were prepared in a water−acetone mixture with vanadyl acetylacetonate and 2-carboxyethylphosphonic acid for the first compound and by reaction of vanadium pentoxide with the same phosphonic acid in alcohol for the second.

With 2-carboxyethylphosphonic acid, we never obtain alcohol intercalated compounds, as we did with carboxymethylphosphonic acid,[15c] but only partially esterified compounds. Such a behavior has already been observed with zirconium phosphonates.[16]

Experimental Section

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

Synthesis. *Synthesis of* $VOHOOC(CH_2)_2PO_3{\cdot}2H_2O$. The attempts to synthesize vanadyl organophosphonates in a pure aqueous medium have been unsuccessful so far. The compound $VOHOOC(CH_2)_2PO_3{\cdot}2H_2O$ was prepared according to the procedure described by Drumel for functionalized zinc and copper phosphonates.[12c] A 1 mmol portion of 2-carboxyethyl phosphonic acid and 1 mmol of vanadyl acetylacetonate was added to 25 mL of a mixture of 5% water in acetone and stirred at 60 °C for 3 days. The light blue solid obtained was collected by filtration and washed with acetone.

Synthesis of $VO(O_3PR)_{1-x}(O_3PR')_x{\cdot}yH_2O$. The vanadyl organophosphonates can be prepared in alcohol, following the Johnson procedure.[14] Finely ground V_2O_5 is added to a solution of 2-carboxyethyl phosphonic acid in a molar ratio $V/P = 1$. This suspension is then heated for 3 days or more in refluxing alcohol. The reaction is catalyzed with a small amount of HCl. We have observed that the shorter the alcohol chain, the longer the reaction time.

Alcohols used are linear monoalcohols, $CH_3(CH_2)_{n-1}OH$ for $n = 1-5$, benzyl alcohol, butoxyethoxyethanol, and the dialcohols $HO(CH_2)_nOH$ for $n = 3, 4, 5, 6, 8, 10, 12$.

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. Experiments were carried out by passing the samples through a 80 mm sieve before filling of the sample holder in order to avoid preferred orientation. During the data collection, the sample holder was also rotating at the speed of 30 rpm. The samples were scanned from 2° to 70° (2θ) in step of 0.08° with a count time of 4 s at each point. Infrared transmission spectra were recorded on a Perkin-Elmer 2000 FT spectrophotometer using the KBr pellet technique. Thermogravimetric analyses TGA/DTA were performed on a Setaram TGA-DTA/DSC 92 analyzer. The samples were heated in air at a heating rate of 5 °C/min. Magnetic measurements were carried out at the IMN. The data were recorded on a Squid magnetometer at $H = 5000$ G in the temperature range 5−300 K. Magnetizations were corrected for diamagnetism as well as for sample holder contribution. X-ray absorption spectra at the vanadium K-edge were obtained at the French “Laboratoire pour l′Utilization du Rayonnement Electronique” (LURE) synchrotron radiation facility. The EXAFS analyses were carried out using programs written by Dr. A. Michalowicz (LURE, Université Paris-Sud).[23] Vanadium, carbon, phosphorus, and hydrogen microanalysis was done by the CNRS Analysis Laboratory, Vernaison, France.

Results and Discussion

The vanadyl 2-carboxyethyl phosphonate and the partially esterified compounds (with monoalcohols and dialcohols) will be abbreviated hereafter as VPC_2, $VPC_2/C_nOH/H_2O$ and $VPC_2/C_n2OH/H_2O$, where n is the number of carbon atoms of the alkyl chain of the alcohols.

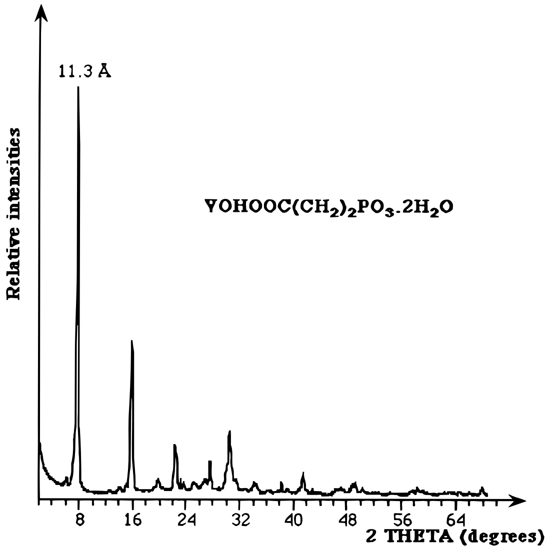

Figure 1. PXRD pattern of $VOHOOC(CH_2)_2PO_3{\cdot}2H_2O$.

Table 1. TG Results of $VOHOOC(CH_2)_2PO_3{\cdot}2H_2O$ at Varying Temperatures

60−100 °C	120−220 °C	300−390 °C
expt 6.5% calcd 7.1% H_2O	expt 6.4% calcd 7.1% H_2O	expt 19.8% calcd 19.2% combustion of organic group and transformation to vanadyl pyrophosphate

Vanadyl 2-Carboxyethyl Phosphonate: $VOHOOC(CH_2)_2PO_3{\cdot}2H_2O$. The elemental analysis of the phosphonate obtained in acetone gives a V/P/C ratio which is consistent with the above composition. The thermogravimetric analysis confirms this stoechiometry: two equal weight losses, each corresponding to one water molecule, are observed and provide strong evidence that two types of water molecule exist in the structure (Table 1).

Figure 1 shows the X-ray diffraction pattern of this compound. It is indexed in the same space group *Pmmn* (No. 59) as the vanadyl hydrogen phosphate hemihydrate $VO(HPO_4){\cdot}0.5H_2O$. The structural analogy with this compound is confirmed by both the magnetic and EXAFS studies, which are described below. The refinement of the lattice parameters leads to the following values: $a = 4.69(5)$ Å, $b = 11.14(8)$ Å, $c = 7.48(2)$ Å, in which the b value corresponds to the interlayer distance. The IR spectrum is presented in Figure 2 and the main absorption bands are listed in Table 2.

Partially Esterified Compounds: $VO[PO_3R]_{1-x}[PO_3R']_x{\cdot}yH_2O$ with Alcohols. The IR spectra of the esterified vanadyl phosphonates $VPC_2/C_1OH/H_2O$ and $VPC_2/C_82OH/H_2O$ are displayed Figure 3. Except for the compounds prepared in ethylenediol and pentanediol, all the others exhibit vibration bands characteristic of the ester function. However, the ν(O−C−O) (570 cm^{-1}) and the ν(C═O) (1708−1740 cm^{-1}) bands show a shoulder or are split, which indicates the presence of unreacted carboxylic functions. For all the compounds, the region characteristic of the host structure looks the same, with three strong vibration bands ν(P−O) at 1070, 1060, and 1040 cm^{-1} and the ν(V═O)

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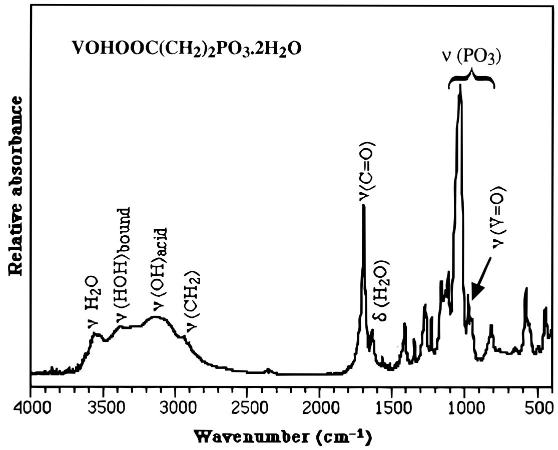

Figure 2. IR spectra of $VOHOOC(CH_2)_2PO_3{\cdot}2H_2O$.

Table 2. Observed Infrared Frequencies of $VOHOOC(CH_2)_2PO_3{\cdot}H_2O$

frequencies (cm^{-1})	band assignment
3570	$\nu_3(H_2O)$
3528	$\nu_1(H_2O)$
3387	$\nu(HO)$
3106	ν(HO)acid
2940−2899	$\nu a(CH_2)$
1700	$\nu s(C{=}O)$
1633	$\delta(H_2O)$, $\nu_2(H_2O)$
1401−1335	$\delta(CH_2)$ + C−C
1268	$\delta(P-CH_2)$
1227	w, t(CH_2), ν(C−C)
1161−1111, 1111−1037	$\nu a(PO_3)$
971	$\nu(V{=}O)$
954	$\nu s(PO_3)$
813	$\rho_r(H_2O)$
656	$\nu(P-CH_2)$
582	δ(O−P−O), δ(O−V−O)
449	$\delta s(PO_3)$

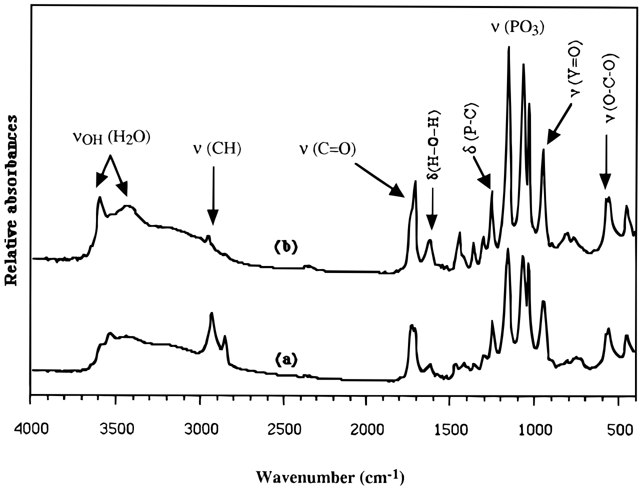

Figure 3. IR spectra of (a) $VPC_2/C_82OH/H_2O$ and (b) $VPC_2/C_1OH/H_2O$.

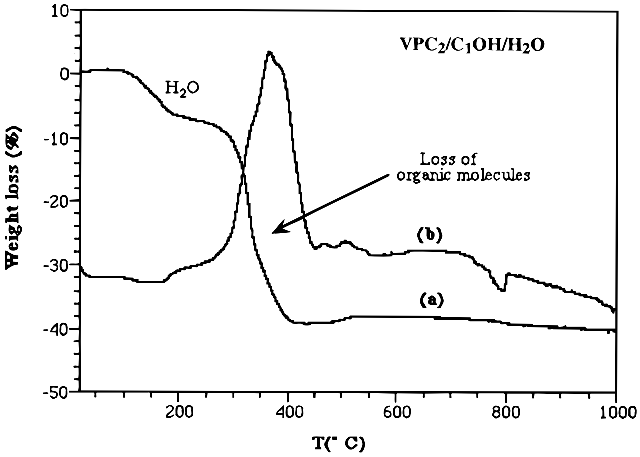

Figure 4. TG (a) and DTA (b) curves of $VPC_2/C_1OH/H_2O$.

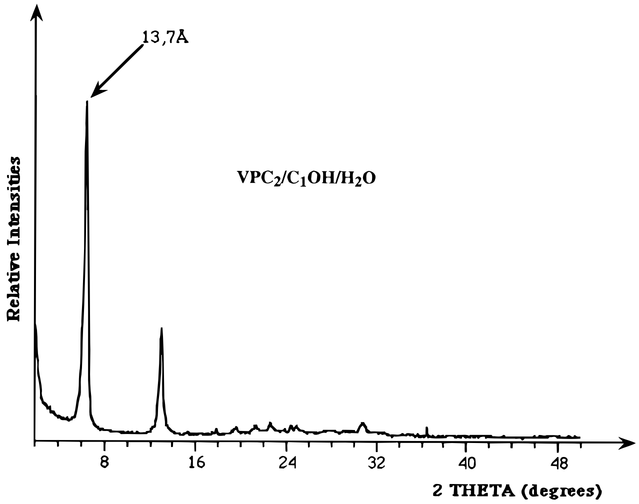

Figure 5. PXRD pattern of $VPC_2/C_1OH/H_2O$.

stretch at 955 cm^{-1}. Water molecules generate the OH stretching bands (3485, 3440, and 3595 cm^{-1}) and the δ(H−O−H) bending vibration at 1624 cm^{-1}. These values are slightly lower than the usual values observed for free molecules. Thus, the water molecules must be located in the environment of the vanadium atoms. Working with monoalcohols or dialcohols only modifies the intensity of a few IR absorption bands. No change appears in the OH region, where we would expect additional bands due to the second alcohol function of the dialcohol.

Figure 4 shows the TG and DTA curves for the compound synthesized in methanol, $VPC_2/C_1OH/H_2O$, as a representative example. For all the compounds prepared with monoalcohols, the loss of water molecules occurs below 200 °C. The decomposition of the organic groups is then observed between 260 and 430 °C. The comparison of the experimental organic weight loss with the theoretical one confirms that the esterification reaction between the carboxylic and the alcohol functions is not complete. No alcohol molecules are intercalated in the layered structure, as was observed for other vanadyl phosphonates.[15] The esterification and the hydration ratios calculated from the chemical analysis are respectively 0.7 and 1.0, leading to the following formula: $VO[PO_3R]_{0.7}[PO_3R']_{0.3}{\cdot}H_2O$.

Structural Considerations. Esterified Compounds Obtained in Alkanols. The powder X-ray diffraction pattern of $VPC_2/C_1OH/H_2O$ is shown in Figure 5. The general aspect indicates a lamellar structure with a strong series of reflections characteristic of the interlayer separation (*b* or *d*). The mixed reflections are often too weak to determine the unit cells parameters (*a* and *c*) except for the compound esterified in methanol. Calculations were made by analogy with the vanadyl hydrogen phosphate hemihydrate VO-

Table 3. Lattice Parameters Calculated for Some Vanadyl 2-Carboxyethyl Phosphonates Esterified with Methanol and Alcanediols

reacting alcohol	compound	*a* (Å)	*b* (Å)	*c* (Å)
CH_3OH	$VPC_2/C_1OH/H_2O$	7.48(7)	13.45(9)	5.67(7)
$OH(CH_2)_3OH$	$VPC_2/C_32OH/H_2O$	7.45(4)	14.62(6)	5.70(2)
$OH(CH_2)_4OH$	$VPC_2/C_42OH/H_2O$	7.48(1)	15.06(9)	5.70(2)
$OH(CH_2)_6OH$	$VPC_2/C_62COH/H_2O$	7.42(8)	17.99(2)	5.66(1)
$OH(CH_2)_8OH$	$VPC_2/C_82OH/H_2O$	7.44(4)	19.83(7)	5.70(1)
$OH(CH_2)_{10}OH$	$VPC_2/C_{10}2OH/H_2O$	7.50(1)	22.20(2)	5.69(6)

Table 4. Interlayer Distances of Vanadyl 2-Carboxyethyl Phosphonates Esterified with Monoalcohols

reacting alcohol	compound	*d* (Å)
CH_3OH	$VPC_2/C_1OH/H_2O$	13.46
CH_3CH_2OH	$VPC_2/C_2OH/H_2O$	14.50
$CH_3(CH_2)_2OH$	$VPC_2/C_3OH/H_2O$	16.00
$CH_3(CH_2)_3OH$	$VPC_2/C_4OH/H_2O$	17.50
$CH_3(CH_2)_4OH$	$VPC_2/C_5OH/H_2O$	19.00
$C_6H_5CH_2OH$	$VPC_2/C_6COH/H_2O$	20.20
$C_4H_9OC_2H_4OC_2H_4OH$	$VPC_2/C_4C_2C_2OH/H_2O$	23.00

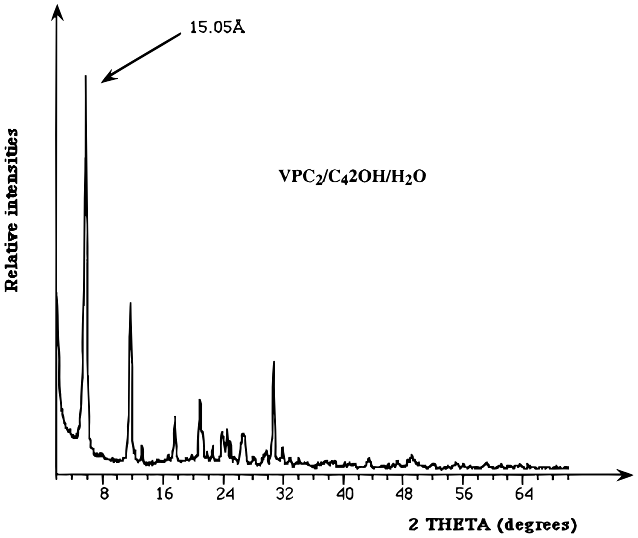

Figure 6. PXRD pattern of $VPC_2/C_42OH/H_2O$.

$(HPO_4)\cdot 0.5H_2O$. A reasonable fit was obtained with the space group *Pmmn*, leading to the lattice parameters listed in Table 3. The interlayer separations (*d*) and the alcohol chain length *n* are listed in Table 4. The relationship between *d* and *n* is given by the following formula: d (Å) $= 12.50 + 1.20n$ (Figure 7). In the *all-trans*-polyethylene chain, the calculated increase of the length is 1.27 Å per CH_2 group.[24] Therefore, if the organic chain $CH_2CH_2COOC_nH_{2n+1}$ was attached to the phosphorus atom perpendicular to the layer to form a bilayer, we would expect the slope to be 2.54. Since the experimental slope is less than half this value, the chains are not perpendicular to the layer and must be slanted at an angle equal to arcsin(1.20/1.27) = 71°.

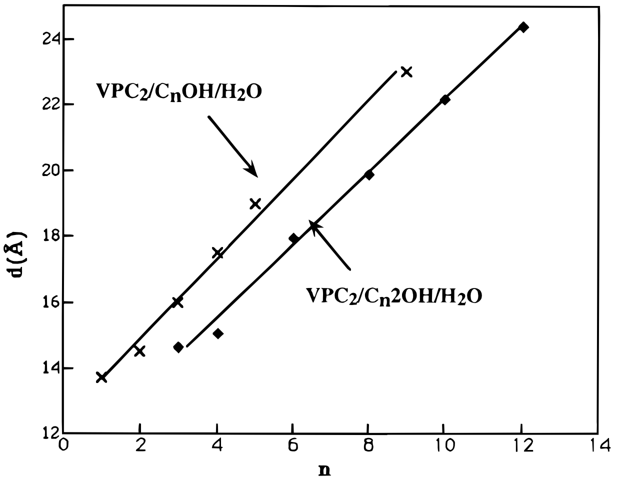

Figure 7. Layer spacing of partially esterified compounds as a function of alkyl chain length of the organic component.

Esterified Compounds Obtained in Alkanediols: $OH(CH_2)_nOH$. Figure 6 shows the XRD powder pattern of $VPC_2/C_42OH/H_2O$, as a representative example. The lattice parameters calculated in the space group *Pmmn* are listed in Table 3. The interlayer distances for n = 3, 4, 6, 8, 10, 12 increase almost linearly with the number of carbon atoms *n*. The *d* value is related to *n* by the equation d (Å) $= 10.93 + 1.12n$ (Figure 7). It follows that the alkyl chains, assumed to be in a trans−trans conformation, have the longitudinal axis inclined with respect to the layer plane at arcsin(1.12/1.27) = 62°.

We observe that the interlayer distance is shorter for compounds esterified with dialcohol than for compounds esterified with the monoalcohol having the same value of *n*. Because of the small difference between the chain slope for mono- or dialcohols, we can attribute this phenomenon to a pillaring process. Experimental interlayer distances and organic chain slants are consistent with the calculated values obtained with a fully extended chain in a trans configuration in the interlamellar region; both alcohol functions of the alkanediol react with a carboxylic function belonging to two adjacent layers. Then the general formula for these compounds can be written as $VO[HOOC(CH_2)_2PO_3]_x[(CH_2)_nOOC(CH_2)_2PO_3]_{(1-x)/2}\cdot nH_2O$.

Magnetic Study of $VO(CH_3COO(CH_2)_2PO_3)_{0.7}(HOOC(CH_2)_2PO_3)_{0.3}\cdot H_2O$. Figure 8 displays the temperature dependence of the magnetic susceptibility for the compound $VPC_2/C_1OH/H_2O$. The compound seems to retain its paramagnetic behavior until ca. 140 K. Below this temperature, the behavior is similar to that of $VO(HPO_4)$, $0.5H_2O$,[10b] indicating the presence of exchange-coupled vanadyl dimers. The data were analyzed using the Bleaney−Bowers expression for an isolated dimer model containing two $S = {}^1/_2$ cations with isotropic *g* tensor[17]

$$\chi = \chi_0 + C_i/(T - \theta) + 4C_d/\{T[3 + \exp(-2J/KT)]\}$$

where χ_0 is the temperature independent contribution, C_d is the Curie constant associated with the vanadyl dimers, C_i and θ are the constants associated with the

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Table 5

compounds	μ_{eff} (μ_B)	$\chi_0 \cdot 10^5$ (emu/mol)	C_i (emu K/mol)	θ (K)	C_d (emu K/mol)	$2J/K$ (K)
$VOHPO_4 \cdot 0.5H_2O$	1.72	−5.16	$6.9 \cdot 10^{-3}$	−25.3	0.36	−22
$VOHPO_3 \cdot 1.5H_2O$	1.73	17	$4.2 \cdot 10^{-2}$	−37.6	0.33	−21
$VOC_4H_9PO_3 \cdot H_2O$	1.69	−11.3	$3.7 \cdot 10^{-2}$	−1.4	0.30	−78.2
mixed phosphonate[a]	1.73	−14.6	0.12	−21.3	0.34	−43.7
$VPC_2/C_1OH/H_2O$[b]	1.73	1.58	$3.2 \cdot 10^{-2}$	1.7	0.34	−103

[a] $VO(C_6H_5PO_3)_{0.5}(CH_3PO_3)_{0.5} \cdot 1.5H_2O$. [b] $VO(CH_3COO(CH_2)_2PO_3)_{0.7}(HOOC(CH_2)_2PO_3)0.3 \cdot H_2O$.

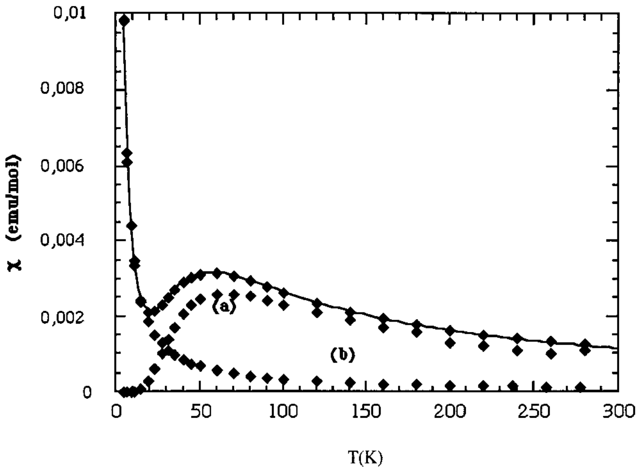

Figure 8. Thermal evolution of the magnetic susceptibility per mole of V for the compound $VPC_2/C_1OH/H_2O$. Dotted lines represent the contribution of (a) vanadyl dimers and (b) isolated paramagnetic centers.

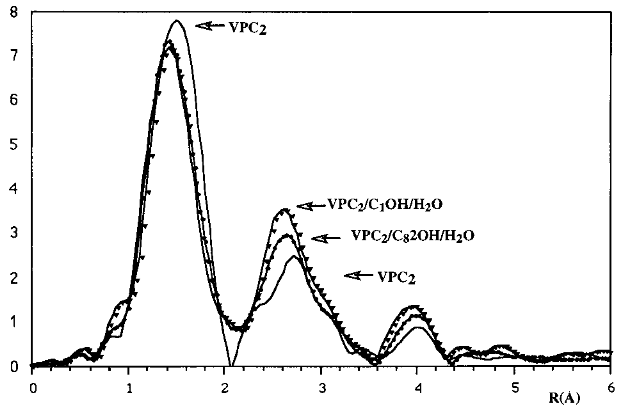

Figure 9. Fourier-transformed vanadium K-edge EXAFS spectra of VPC_2, $VPC_2/C_1OH/H_2O$, and $VPC_2/C_82OH/H_2O$.

magnetic impurity (i.e., the residual isolated paramagnetic vanadyl monomers), J is the coupling constant within the vanadyl pairs, K is Boltzmann's constant, and T is temperature. The results of the least-squares fit in the whole temperature range are reported in Table 5, along with the values obtained with other vanadyl phosphonates,[10b,18] a vanadyl phosphite,[19] and a vanadyl hydrogen phosphate hemihydrate.[20]

The contributions of vanadyl dimers and isolated paramagnetic centers are presented in Figure 8. If V(IV) defects are attributed to isolated paramagnetic centers, the ratio of isolated to paired V=O is then $C_i/C_d = 9.4\%$.

Above 140 K, the data follow a modified Curie−Weiss law

$$\chi = \chi_0 + C_g/(T - \theta)$$

with a Curie constant $C_g = 0.375$ emu K/mol, a temperature-independent paramagnetic $\chi_0 = 10^{-4}$ emu/mol, and a paramagnetic curie temperature $\theta_p = -45.6$ K.

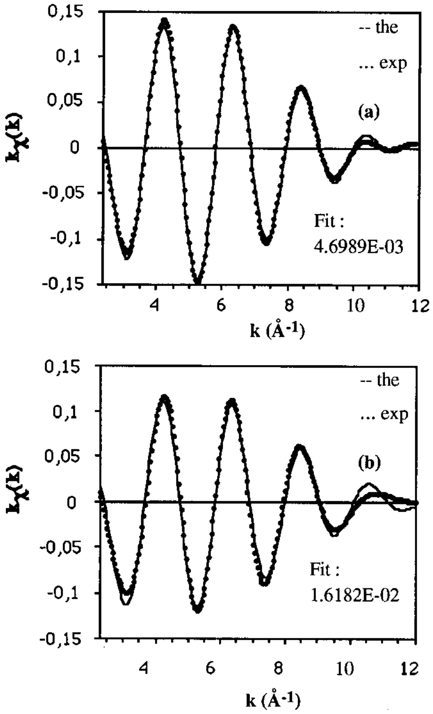

Figure 10. EXAFS analysis around the vanadium atom in the inorganic layer for VPC_2 (a) and $VPC_2/C_82OH/H_2O$ (b).

The C_g value is close to the sum $C_i + C_d = 0.372$ emu K/mol, leading to an effective moment of $\mu_{eff} = 1.732$ μ_B/formula unit and 1.725 μ_B, respectively, which is identical to the theoretical value for a spin $^1/_2$ ion with $g = 2$.

Thus, the magnetic susceptibility data of this compound are consistent with the layered structure of $VO(HPO_4) \cdot 0.5H_2O$, in which weakly exchange-coupled vanadyl dimers ($J = -60.8$ cm^{-1} from ref 21 and $J = -72.4$ cm^{-1} for our compound) are effectively isolated from each other.[22]

EXAFS Study. Figure 9 sums up the EXAFS study for compounds VPC_2, $VPC_2/C_1OH/H_2O$, and $VPC_2/C_82OH/H_2O$. As can be seen, the Fourier-transformed spectra of the two latter compounds are very similar, while the spectrum of the phosphonate without the ester function shows a little longer distances between the vanadium atom and its first and second neighbors. However it seems that the structure of the inorganic layer (V−O−P) remains the same for the three compounds, which is in agreement with the X-ray diffraction study. We notice an important second peak corresponding to the nearest vanadium atom engaged in vanadyl dimers $V_2O_8(H_2O)$, the existence of which appears clearly in the magnetic study. For the first coordination shell of the V^{4+} cation in VPC_2, the best fit is obtained

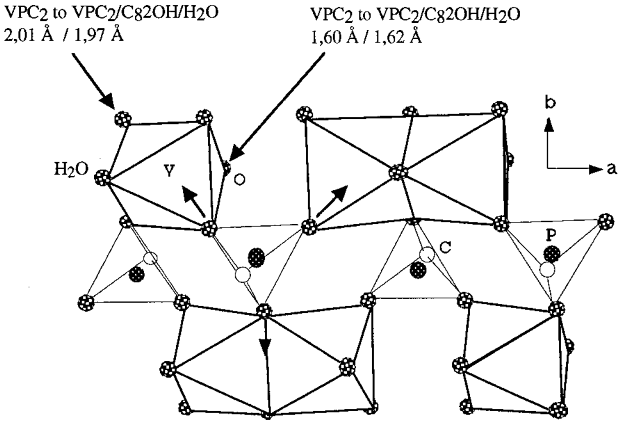

Figure 11. View of the structure of the inorganic layer proposed for our phosphonates based on the well-known disposition of $VOHPO_4 \cdot 0.5H_2O$.

when this ion is surrounded by five oxygen atoms: four at 2.01 Å (V−O bonds) and one at 1.60 Å (V=O bond). For $VPC_2/C_82OH/H_2O$, the distances are 4 × 1.98 Å (V−O bonds) and 1 × 1.62 Å (V=O bond) (Figure 10). It was not possible to complete the oxygen atom octahedra around the vanadium atom with a water molecule, which is probably too far away.

This study confirms the structural analogy of our compounds with the vanadyl hydrogen phosphate hemihydrate $VO(HPO_4) \cdot 0.5H_2O$ (Figure 11) and evidences that the structure is maintained when the carboxylic acid function is partially esterified. However the esterification induces some minor modifications: the three P−O bonds of the tetrahedral environment of the phosphorus atom increase in length while the four V−O bonds of the V^{4+} octahedra decrease, as shown in Figure 11 with arrows.

Conclusion

Several tries have been undertaken in order to hydrolyze the partially esterified compounds, but all attempts have failed. It is noteworthy that we have obtained the vanadyl carboxymethylphosphonate $VO(O_3PCH_2COOH) \cdot xH_2O$ in alcoholic media with the same synthesis method.[15c] In this case, no esterification of the carboxylic function in the interlayer domain is observed. In a previous work,[16] Thompson explains that, in metal phosphonates, the carboxylic group at the end of the $P(CH_2)_nCOOH$ chain has a lower reactivity for n = odd relative to n = even. For the n = odd compounds, the steric constraints of the surface of the metal phosphonate lamellae act to retard the reaction of the carboxylic groups in this materials relative to n = even compounds, where unfavorable steric interactions do not exist. These observations are confirmed by the utilization of the phosphonic acid $HOOC(CH_2)_3PO(OH)_2$, for which no esterification occurs. So it seems that, during the synthesis in refluxing alcohol, the mechanism of esterification occurs after the formation of the vanadyl phosphonate $VO(O_3P(CH_2)_nCOOH)$, otherwise we would obtain esterified compounds even with $n = 1$ or 3.

Synthetically, the ability to make single phase mixed derivatives of general formula $VO[PO_3R]_{1-x}[PO_3R']_x \cdot yH_2O$, relied heavily on being able to control the creation of microporous material in which the presence of both $R' = (CH_2)_2COOH$ functions and $R = (CH_2)_2COO(CH_2)_{n-1}CH_3$ organic chains can leave a place for pores in the interlayer region. Actually we are not able to propose a distribution for the two different organic functions because there is no evidence in the PXRD patterns of the structural organization of the staged disposition. Finally, pillared derivatives can be prepared by reaction with alkanediols. A next step is to obtain enough product to determine the surface areas and porosity of mixed derivatives obtained with alkanediols where $n \gg 2$, so that we can check if pores may be built into the interlayer region.

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