Intercalates of Vanadyl Phosphate with Unsaturated Alcohols

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Keywords: Vanadium / Phosphorus / Alcohols / Intercalations / Vibrational spectroscopy / X-ray scattering

Intercalates of $VOPO_4$ with several linear unsaturated alcohols (2-propen-1-ol, 2-buten-1-ol, 2-propyn-1-ol, 2-butyn-1-ol, 3-butyn-1-ol 2-pentyn-1-ol, 3-pentyn-1-ol, 4-pentyn-1-ol, 5-hexyn-1-ol, 2-octyn-1-ol, and 10-undecyn-1-ol) have been prepared and characterized by powder X-ray diffractometry, IR and Raman spectrometry, and thermogravimetry. The arrangement of the alcohol molecules with respect to the type and position of the multiple bonds in the carbon chain is proposed. Alcohols with terminal triple bonds form very stable intercalates. It is presumed that these alcohols are anchored to the host layers by donor-acceptor bonds between their oxygen atoms and the vanadium atoms of the host, and by H-bonding between the acetylenic hydrogen of the terminal carbon and the oxygen atoms of the host.

Introduction

The tetragonal layer structure of $VOPO_4$ is made up of distorted VO_6 octahedra and PO_4 tetrahedra which are linked by corner-sharing oxygen atoms (O_{host}).[1−3] Each octahedron is joined to four tetrahedra and the layers are connected along the *c* axis by the sharing of the remaining two trans vertices of the octahedron. One of these two vanadium−oxygen bonds is short indicating the presence of a V=O bond, while the other is much longer and can be ascribed to the coordination of the oxygen atom from the V=O group of an adjacent $(VOPO_4)_\infty$ layer. Interlayer interactions are therefore established through V=O···V bonds in anhydrous $VOPO_4$. In $VOPO_4{\cdot}2H_2O$, the sixth position in the VO_6 octahedron is complemented by the oxygen atom of one water molecule which is then *trans* to the oxygen atom of the V=O bond. The second water molecule is located in the interlayer space and is H-bonded to O_{host} atoms and to the water molecules of the first type. The formation reaction of $VOPO_4{\cdot}2H_2O$ from $VOPO_4$ can be considered as a kind of intercalation reaction, in which the coordination of the guest species to the metal center provides the driving force.[3] Similar reactions have been described for other donor ligands containing oxygen or nitrogen containing functional groups, leading to new materials with interesting properties and structures.[4] Vanadyl phosphate forms a number of intercalation compounds with molecular guests having a Lewis base character.[5] Intercalations of aliphatic and aromatic amines,[6−10] heterocycles,[10−14] carboxylic acids[15] and their derivatives,[16] amino acids,[17] metallocenes,[18,19] alcohols,[20,21] diols,[20,22,23] and poly(oxyethylene) compounds[24] have been studied.

The reaction of solid $VOPO_4{\cdot}2H_2O$ with liquid or melted solid 1-alkanols in a microwave field leads to intercalation compounds with the composition $VOPO_4{\cdot}2C_nH_{2n+1}OH$ (n = 2−18). All the polycrystalline layer complexes retain the structure of the original $(VOPO_4)_\infty$ layers. The alcohol molecules are placed between the host layers in a bimolecular arrangement, that is, in two layers. The guest molecules are anchored to the host layers by donor−acceptor bonds between the oxygen atom of the OH group of the guest (O_{guest}) and the vanadium atom (V_{host}), and also by hydrogen bonds between the OH group and O_{host}. The aliphatic chains of the intercalated alcohol molecules possess an all-*trans* configuration and their axes are perpendicular to the plane of the host layers.[20] In the intercalates of $VOPO_4$ with 1,ω-diols and 1,2-diols, the guest molecules are bonded to the host layers in a similar way as in the alkanol intercalates.[20,22]

Intercalates of vanadyl phosphate with *cis*-2-butene-1,4-diol and 2-butyne-1,4-diol have been prepared. It was presumed from the values found for the basal spacing that the molecules of *cis*-2-butene-1,4-diol and 2-butyne-1,4-diol are arranged in a similar manner to those of 1,4-butanediol in the interlayer space. The observed differences in the basal spacings confirm this proposal because the distances between the terminal oxygen atoms calculated from the bond lengths and bond angles decrease in the order 1,4-butanediol (6.20 Å) > 2-butyne-1,4-diol (5.75 Å) > *cis*-2-butene-1,4-diol (5.62 Å).[23]

The influence of the multiple bond and its position in the alcohol chain on the arrangement of the guest molecules in the interlayer space of the host, and on the properties of the intercalate formed is reported.

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Results and Discussion

In contrast to ethanol, propanol and butyl alcohol,[25] no unsaturated alcohol can be intercalated into anhydrous vanadyl phosphate. Only 2-propen-1-ol, 2-buten-1-ol and 2-propyn-1-ol can replace the water molecules in $VOPO_4 \cdot 2H_2O$. The intercalates with longer unsaturated alcohols had to be prepared by reintercalation of propanol-intercalated vanadyl phosphate. The intercalates prepared were yellow, crystalline solids, indicating that the vanadium(V) had not been significantly reduced.

The diffractograms of all intercalates show a series of relatively sharp (00*l*) reflections (see Figure 1 and 2). The *a* parameters of their tetragonal lattices were determined from the (200) and (*h*0*l*) lines, provided they were observed. The values found for the lattice parameters *a* and *c* are presented in Table 1. The number of alcohol molecules per formula unit in $VOPO_4 \cdot x$ROH is hereafter referred to as the stoichiometric quotient *x*. The experimental stoichiometric quotients x_{exp} obtained by the thermogravimetric analyses, and by the elemental analyses for the carbon and hydrogen content are given in Table 1. For comparison, the values of x_{calc}, calculated as a ratio of the volume of the alcohol intercalated and the molar volume of the free alcohol, which was calculated from its density, are also given in this table. The volume of the alcohol intercalated was calculated as the difference between the unit cell volume of the intercalate and anhydrous $VOPO_4$. It is obvious from Table 1 that the packing of the guest molecules is closer in the intercalate than in the free alcohol.

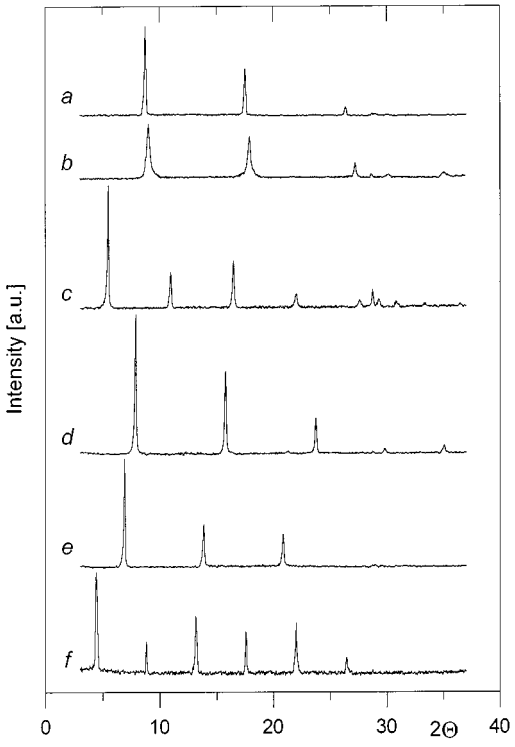

Figure 1. The diffractograms of the vanadyl phosphate intercalates with alcohols with a terminal triple bond: (a) 2-propyn-1-ol; (b) 3-butyn-1-ol (phase formed at laboratory temperature); (c) 3-butyn-1-ol (phase formed at higher temperature); (d) 4-pentyn-1-ol; (e) 5-hexyn-1-ol; (f) 10-undecyn-1-ol

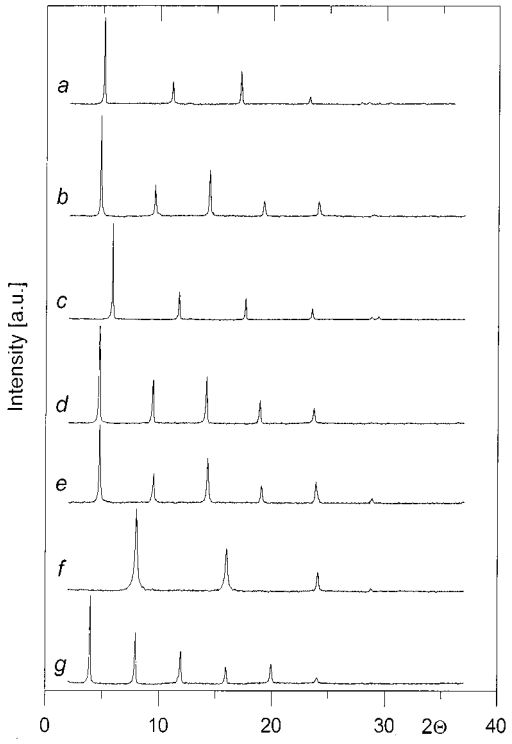

Figure 2. The diffractograms of the vanadyl phosphate intercalates with other unsaturated alcohols: (a) 2-propen-1-ol; (b) 2-buten-1-ol; (c) 2-butyn-1-ol; (d) 2-pentyn-1-ol; (e) 3-pentyn-1-ol (phase formed at laboratory temperature); (f) 3-pentyn-1-ol (phase formed at higher temperature); (g) 2-octyn-1-ol

Table 1. Lattice parameters and the guest contents in $VOPO_4$ intercalated with unsaturated alcohols

Alcohol	*a* [Å]	*c* [Å]	x_{exp}	x_{calc}
2-propen-1-ol	6.22	14.76	1.90	1.82
2-buten-1-ol	6.20	18.51	2.05	1.96
2-propyn-1-ol	6.22	10.15	1.60	1.20
2-butyn-1-ol	6.22	15.07	1.93	1.71
3-butyn-1-ol	6.21	16.15	1.95	1.84
	6.20	9.83	0.91	0.87
2-pentyn-1-ol	6.21	18.80	–	1.84
3-pentyn-1-ol	6.20	18.64	1.92	1.83
	6.21	11.10	1.11	0.89
4-pentyn-1-ol	6.22	11.23	1.08	0.89
5-hexyn-1-ol	6.16	12.76	1.10	0.90
2-octyn-1-ol	6.20	22.26	–	1.47
10-undecyn-1-ol	6.21	19.90	1.05	0.96

The alcohols with a terminal triple bond (4-pentyn-1-ol, 5-hexyn-1-ol and 10-undecyn-1-ol) form intercalates containing one molecule of alcohol per formula unit; they are stable in air at ambient conditions (relative humidity 40–60%). 3-Butyn-1-ol forms an intercalate containing two alcohol molecules per formula unit at room temperature. This intercalate is unstable and slowly loses one molecule of alcohol to form a phase with a lower basal spacing. This transformation is irreversible. The same phase, which is stable at room temperature, is formed when $VOPO_4 \cdot 2C_3H_8OH$ is heated with 3-butyn-1-ol. The transformation is also observed at 38 °C during temperature XRD measurements of the $VOPO_4 \cdot 2$(3-butyn-1-ol) intercal-

ate. 2-Propyn-1-ol forms an intercalate, containing about 1.6 molecules of alcohol per formula unit, which is stable in air.

Alcohols with a triple bond at the second carbon atom (2-butyn-1-ol, 2-pentyn-1-ol and 2-octyn-1-ol) form unstable intercalates which rapidly decompose to $VOPO_4{\cdot}2H_2O$ in air at ambient conditions (relative humidity 40−60%). Therefore, it was not possible to determine the composition for 2-pentyn-1-ol- and 2-octyn-1-ol-intercalated vanadyl phosphate. Phases with lower basal spacing ($d = 10.56$ Å at 74−111 °C for 2-butyn-1-ol, and $d = 15.9$ Å at around 77 °C and 11.6 Å at 87−115 °C for 2-pentyn-1-ol) were found by XRD measurements in situ at the given temperatures. These phases cannot be synthesized by the method described in the Experimental Section at the given temperatures. The number of guest molecules probably increases during the cooling of the reaction mixture after the synthesis; compounds containing two guest molecules are then formed.

3-Pentyn-1-ol forms an intercalate with two alcohol molecules at room temperature. This intercalate slowly loses one molecule of alcohol and transforms to a phase with a lower basal spacing in air (relative humidity ≈ 40−60%). This then slowly decomposes to $VOPO_4{\cdot}2H_2O$. The intercalate with a basal spacing of 11.10 Å can be prepared by heating $VOPO_4{\cdot}2C_3H_7OH$ with 3-pentyn-1-ol at 80 °C. The phase with a higher alcohol content and a higher basal spacing is not formed, which indicates that the high-temperature phase is very stable. The same transformation was observed at about 50 °C during temperature XRD measurements of the $VOPO_4{\cdot}2$(3-pentyn-1-ol) intercalate.

Both alcohols with a double bond (2-propen-1-ol and 2-buten-1-ol) form intercalates with a similar composition and stability as the corresponding saturated alcohols.[20]

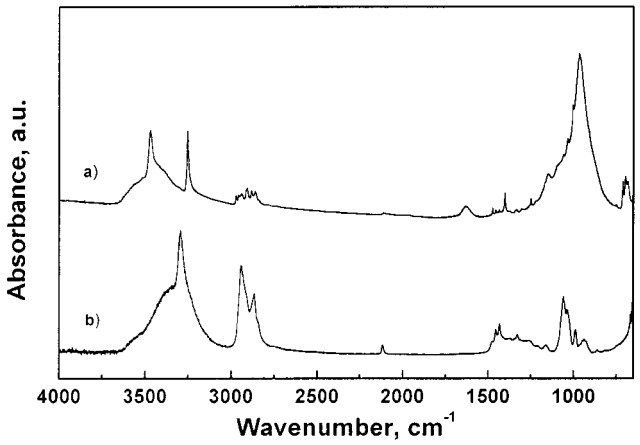

Figure 3. FTIR spectra: (a) 5-hexyn-1-ol-intercalated vanadyl phosphate (in KBr pellet); (b) liquid 5-hexyn-1-ol (ATR on ZnSe crystal)

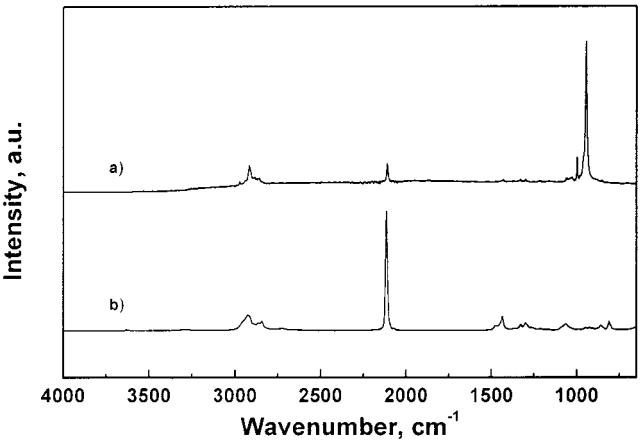

Figure 4. Raman spectra: (a) 5-hexyn-1-ol-intercalated vanadyl phosphate; (b) liquid 5-hexyn-1-ol

Infrared and Raman Spectra

The infrared spectra of 2-propen-1-ol, 2-propyn-1-ol, 4-pentyn-1-ol, 5-hexyn-1-ol and their $VOPO_4$ intercalates were measured in KBr pellets in the transmission mode. The spectra of the corresponding alkynols in the liquid state were measured by the ATR technique on ZnSe crystal.

The infrared spectra of liquid 5-hexyn-1-ol and its $VOPO_4$ intercalate are given in Figure 3. The Raman spectra of these compounds are given in Figure 4. The results for 4-pentyn-1-ol are very similar to that obtained for 5-hexyn-1-ol, and they are not presented here. The positions of the main spectral bands of the host structure in the spectrum of $VOPO_4$ intercalated with 5-hexyn-1-ol differ only slightly from those of anhydrous vanadyl phosphate or its hydrated form.[26] This confirms that the structure of the original $VOPO_4$ layers remains unchanged after the intercalation reaction. The intense band at 948 cm^{-1} in the Raman spectrum corresponds to the symmetric $\nu(PO_4)$ stretching vibration of the phosphate tetrahedron in the $(VOPO_4)_\infty$ layers, and is observed at 966 cm^{-1} in the infrared spectrum. The position of the vanadyl stretching vibration V=O at 1004 cm^{-1} in the Raman spectrum indicates coordination of O_{guest} to V_{host}. This band is observed at 1007 cm^{-1} in the infrared spectrum, allowing us to distinguish this band from other bands belonging to the intercalated alcohol molecules.

The infrared and Raman spectra of pure and intercalated 5-hexyn-1-ol differ in the position, shape and intensity of the corresponding bands as a consequence of the intercalation reaction in the interlayer space. The O−H stretching vibration must be sensitive to a phase change as in the case of 2-propyn-1-ol.[27] The infrared spectrum of liquid 5-hexyn-1-ol shows that the alcohol is completely associated. The ν(O−H) frequencies occur at about 3575 and 3392 cm^{-1}. The higher frequency band results from ν(O−H) of the terminal OH group, where the oxygen atom is hydrogen-bonded to the hydrogen atom of the O−H group of the adjacent guest molecule in the intermolecularly hydrogen-bonded chain. The lower frequency of the ν(O−H) band results from the intermolecularly hydrogen-bonded OH groups within the chain.[27] Remarkable changes are observed in this region upon intercalation into $VOPO_4$. A new sharp band at 3474 cm^{-1} occurs in the intercalated compound. Such bands are usually observed for unassociated hydroxyl groups, absorbing strongly in the region 3670−3580 cm^{-1}.[28] The presence of this new band is likely

to be related to the steric hindrance resulting from the hydrogen bonds. We suggest that it arises as a result of the anchoring of the oxygen atom from the OH group to the vanadium atom by donor−acceptor bonds. The shoulder on the higher frequency side of this band probably results from an association with other alcohol molecules, or from the formation of hydrogen bonds to the oxygen atoms from the layers. A sharp band at about 1404 cm^{-1} corresponds to the O−H bending vibration and strongly supports the assignment of the hindered hydroxyl stretching vibration. The band observed at about 1630 cm^{-1} is probably due to the association of the hydroxyl groups and the water molecules in KBr pellet.

The acetylenic C−H stretching vibration is observed at 3295 cm^{-1} for liquid 5-hexyn-1-ol. This vibration is remarkably constant with respect to the variation of the chemical structure of the rest of the molecule, but is sensitive to its physical state.[29] The acetylenic hydrogen is able to associate freely with proton-accepting groups, which leads to the shift of the vibration up to 120 cm^{-1} in extreme cases.[30] The position of this vibration is shifted to 3254 cm^{-1} after intercalation in $VOPO_4$, reflecting the association with the hydroxyl group of the second alcohol molecule or the formation of hydrogen bonds to the oxygen atoms from the layers. The ≡C−H bending vibration results in one or two strong absorption bands in the 610−680 cm^{-1} region.[29]

The remarkable change in the C−H vibrations is observed when going from liquid 5-hexyn-1-ol to its intercalated form. During the fixation of the intercalated molecules in the interlayer space some new bands arise in the region of the stretching vibrations, where only two bands at 2945 and 2867 cm^{-1} are observed in the infrared spectrum of the liquid alcohol. The interaction of the alcohol molecules with the host in the intercalate leads to the splitting of the bands in the 1150−1490 cm^{-1} region. The four fundamental bands expected to occur in this region are: CH_2 bending δ(C−H), CH_2 wagging ω(C−H), O−H bending δ(O−H) and CH_2 twisting γ(C−H).[27] The C≡C stretching absorption band has appreciable intensity only in hydrocarbons with terminal triple bonds.[30] This band occurs at 2121 cm^{-1} both in the infrared and Raman spectra of the liquid alcohol, and is very intense in the latter. It is shifted to 2114 cm^{-1} in the intercalate.

The infrared spectra of liquid 2-propyn-1-ol and its intercalate in $VOPO_4$ are given in Figure 5. The Raman spectra of these compounds are given in Figure 6. These spectra differ from those of 5-hexyn-1-ol and 4-pentyn-1-ol intercalated in $VOPO_4$. The Raman spectrum of the intercalate with 2-propyn-1-ol is strongly influenced by baseline radiation. The intense broad band centered at about 915 cm^{-1} in this spectrum probably corresponds to the symmetric ν(PO_4) stretching vibration of the phosphate tetrahedron,[26] overlapped by the strong band of 5-hexyn-1-ol. The sharp band at 996 cm^{-1} corresponds to the V=O stretching vibration. Interpretation of this region in the infrared spectrum is rather complicated. The ν(PO_4) stretching vibration, the V=O stretching vibration and the C−O_{guest}H stretching vibration overlap in this part of the spectrum. With the help

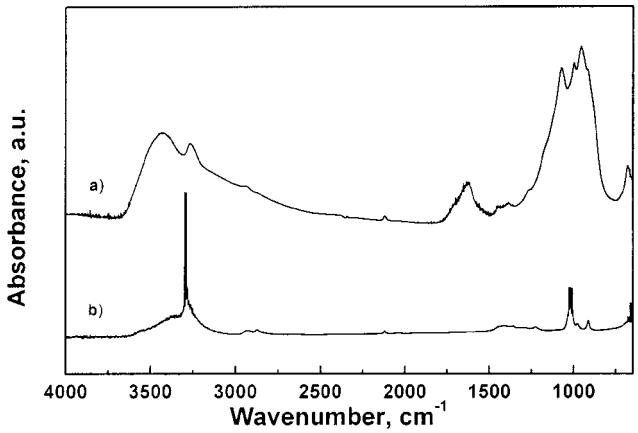

Figure 5. FTIR spectra: (a) 2-propyn-1-ol-intercalated vanadyl phosphate (in KBr pellet); (b) liquid 2-propyn-1-ol (ATR on ZnSe crystal)

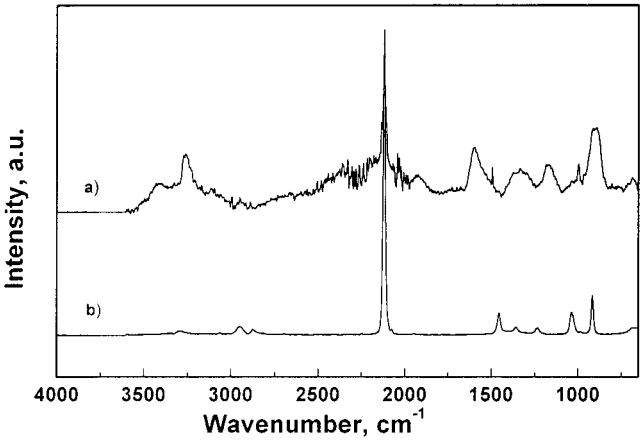

Figure 6. Raman spectra: (a) 2-propyn-1-ol-intercalated vanadyl phosphate; (b) liquid 2-propyn-1-ol

of the Raman spectrum, the band at 959 cm^{-1} in the infrared spectrum is assigned to the symmetric ν(PO_4) stretching vibration which is infrared active due to the distortion of the phosphate tetrahedron in the intercalate. The band at about 1004 cm^{-1} is probably due to the vanadyl V=O stretching vibration corresponding to the anchoring of the hydroxyl oxygen of 2-propyn-1-ol to V_{host}. The C−O_{guest}H stretching band of the alcohol is likely to be overlapped by other bands. The intense band at about 1074 cm^{-1} may be an asymmetric stretching vibration ν(PO_4) of the phosphate tetrahedron. This band is due to the strong interaction between the alcohol hydroxyl and acetylenic groups, and the phosphate oxygen through hydrogen-bonds.

Changes are also observed in the high frequency region of the spectrum of the intercalate relative to that of liquid 2-propyn-1-ol. The strong hydrogen bonding of the alcohol in the intercalate leads to a broad band for the OH stretching vibration centered at about 3434 cm^{-1}. The band at about 1630 cm^{-1} with a shoulder at about 1719 cm^{-1} corresponds to the bending vibrations of the hydrogen-bonded OH groups and of the water molecules in the KBr pellet. The sharp and intense band of the acetylenic CH vibration observed in the spectrum of the liquid alcohol at 3295 cm^{-1}

is shifted to 3270 cm^{-1} in the spectrum of the intercalate. In the Raman spectrum, this band is broadened and observed at 3265 cm^{-1}, which corresponds to the hydrogen bonding of the acetylenic CH group with O_{host}. The position of the C≡C stretching absorption band both in liquid 2-propyn-1-ol and in the intercalate occurs at 2121 cm^{-1} in the infrared spectrum and is very intense in the Raman spectrum at about 2125 cm^{-1}.

The infrared spectra of liquid 2-propen-1-ol and its $VOPO_4$ intercalate are given in Figure 7. The Raman spectra of these compounds are given in Figure 8. The Raman spectrum of the intercalate is only slightly influenced by baseline radiation. The intense band at about 944 cm^{-1} in the Raman spectrum probably corresponds most to the symmetric $\nu(PO_4)$ stretching vibration of the phosphate tetrahedron, and the sharp band at 1000 cm^{-1} to the V=O stretching vibration. The bands of 2-propen-1-ol in the Raman spectrum are at the same positions in the intercalate and in liquid 2-propen-1-ol. With the help of the Raman spectrum, the band at 948 cm^{-1} in the infrared spectrum was assigned to the symmetric $\nu(PO_4)$ stretching vibration. The band at about 996 cm^{-1} is probably the $C-O_{guest}H$ stretching band of the intercalated alcohol. Its position is also not changed in the intercalate as a consequence of the weak interaction between the alcohol and the host layers. The intense band at about 1104 cm^{-1} in the spectrum of the intercalate is assigned to the asymmetric stretching vibration $\nu(PO_4)$ of the phosphate tetrahedron. This band is due to the hydrogen bonds between the alcohol hydroxyl and the phosphate oxygen, analogous to the saturated 1-alkanols.[31] The strong hydrogen bonding of the alcohol in the intercalate leads to broad OH stretching vibration bands centered at about 3403 and 3582 cm^{-1}. The band at about 1630 cm^{-1} is assigned to the bending vibration of the hydrogen-bonded OH groups and the water molecules in the KBr pellet, and is overlapped by the C=C stretching vibration band in 2-propen-1-ol. This band is very strong in the Raman spectra.

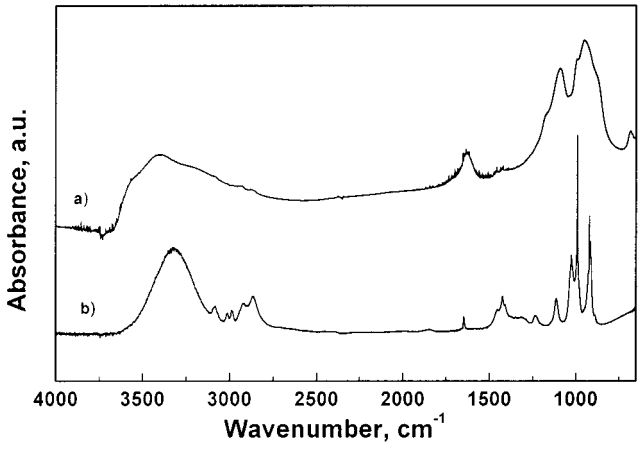

Figure 7. FTIR spectra: (a) 2-propen-1-ol-intercalated vanadyl phosphate (in KBr pellet); (b) 2-propen-1-ol (ATR on ZnSe crystal)

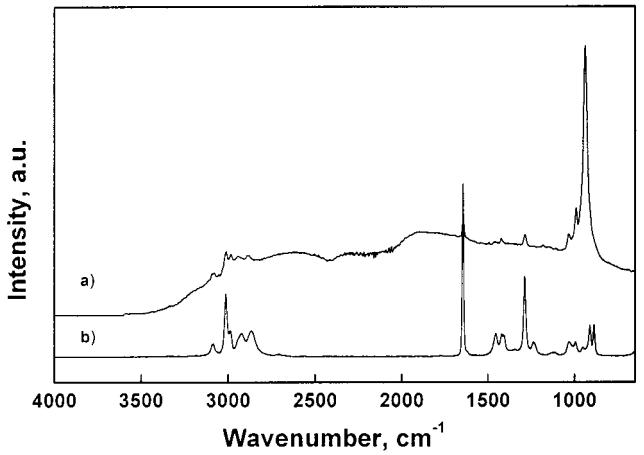

Figure 8. Raman spectra: (a) 2-propen-1-ol-intercalated vanadyl phosphate; (b) liquid 2-propen-1-ol

Suggested Structures

Alcohols with a double bond in their aliphatic chain are placed in the interlayer space of the host in a way similar to that of saturated alcohols with the same chain length (i.e. the distance from C_1 to C_n).[20,31] This means that they are arranged in two layers and the angle, α, at which they are tilted to the plane of the host sheets, increases with an increasing number of carbon atoms, as in the homologous series of ethanol, 1-propanol and 1-butanol intercalates.[31] Half of the guest molecules are anchored to V_{host} by donor−acceptor bonds with O_{guest}. The rest of the guest molecules forms hydrogen bonds between their OH groups and O_{host} or between these OH groups and the guest oxygen atoms coordinated to V_{host}.

The intercalates containing about two molecules of alcohols with a triple bond (2-butyn-1-ol, less stable phase of 3-butyn-1-ol with a higher basal spacing, 2-pentyn-1-ol, and 3-pentyn-1-ol) per formula unit have distinctly lower basal spacings than the intercalates with saturated alcohols with the same chain length.[20] The shortening of the chain length by the triple bond is insignificant irrespective of its position. This means that in the presumed bimolecular arrangement of the guest molecules, the carbon chain must be tilted towards the host layers more (it must have a smaller α value) than the intercalates with saturated alcohols, in which the chains are perpendicular to the host layers.[20,31] With respect to other aspects, it can be presumed that the guest molecules are bonded in a manner similar to that found for the alken-1-ol and 1-alkanol intercalates discussed previously.

Alcohols with terminal triple bonds (except 2-propyn-1-ol) form intercalates which are very stable in air and which contain one guest molecule per formula unit ($x = 1$). Elongating their carbon chain by one atom increases the basal spacing of the intercalate by 1.4 Å, which is more than the value corresponding to adding one carbon atom to a chain perpendicular to the host layer (1.279 Å).[20] On the other hand, the basal spacing of the 3-butyn-1-ol intercalate (9.83 Å) excludes a bimolecular arrangement with slanted alcohol chains, as two alkyl chains placed parallel with $(VOPO_4)_\infty$ sheets in the interlayer space require a basal spacing of 12 Å.[24] An alcohol with a terminal triple bond

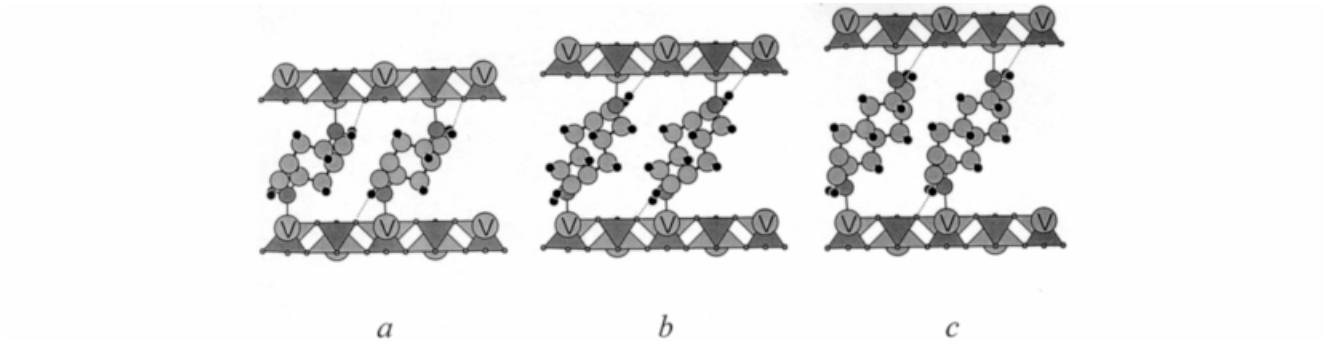

Figure 9. Proposed arrangement of 3-butyn-1-ol (a), 4-pentyn-1-ol (b) and 5-hexyn-1-ol (c) molecules between the host layers; the hydrogen bonds between the acetylenic hydrogen of the guest and O_{host} are depicted as dotted lines

must therefore be arranged in the monomolecular manner depicted in Figure 9. The alcohols with terminal triple bonds are anchored to the $(VOPO_4)_\infty$ layers in two ways. Firstly, by coordination of their O_{guest} from the OH group to V_{host}, and secondly by forming a hydrogen bond between the acidic hydrogen of the guest H−C≡C− group and O_{host} in such a way that the guest molecules generate a pillared structure similar to that found in the 1,ω-diol intercalates,[17] thus increasing the stability of the intercalate. As can be seen in Figure 9 for the 3-butyn-1-ol, 4-pentyn-1-ol and 5-hexyn-1-ol series, α increases with increasing length of the alkyl chain. This increase can be attributed to the increase of guest−guest hydrophobic interactions between the carbon chains. In the case of the 10-undecyn-1-ol intercalate, the alkyl chains are almost perpendicular ($\alpha \approx 90°$) to the host layers (see Figure 10), and the basal spacing of the intercalate is accordingly about 1 Å more than that of the 1,10-decandiol intercalate with a chain that is one carbon atom shorter. In the arrangement described above, the O_{guest} atoms are placed so that they cause a mutual shift of the neighboring host layers. This shift leads to the formation of a turbostratic structure in the intercalate, which explains the absence of (*hkl*) reflections in the diffractograms.

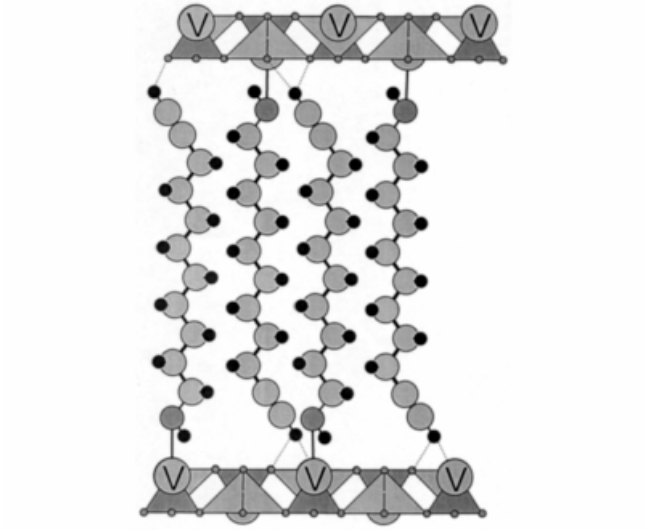

Figure 10. Proposed arrangement of 10-undecyn-1-ol molecules between the $VOPO_4$ layers; the hydrogen bonds between the acetylenic hydrogen of the guest and O_{host} are depicted as dotted lines

The intercalate with 2-propyn-1-ol has a different arrangement of the guest molecules. The number of guest molecules in the intercalate is about 1.6 molecules per vanadium atom. Accordingly, we can propose that one molecule of alcohol is anchored to the host layer by a $V_{host}-O_{guest}$ donor-acceptor bond. The guest molecules are bonded to the adjacent host layer by the hydrogen bond between the H−C≡C− group and O_{host}, as in other alcohols with terminal triple bonds.. The diffractograms of the intercalate correspond to a turbostratic structure, this means that the host layers are mutually shifted. Such an arrangement forms cavities in the interlayer space, in which other alcohol molecules can be placed (Figure 11). These molecules are bonded by hydrogen bonds both to the host layers and to neighboring coordinated alcohol molecules.

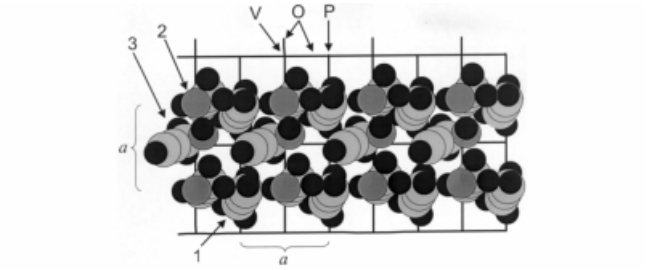

Figure 11. Arrangement of 2-propyne-1-ol molecules between the $VOPO_4$ layers viewed down the *c* axis; the upper $VOPO_4$ layer is not depicted; 1 = guest molecules coordinated to the lower host layer; 2 = guest molecules coordinated to the upper host layer; 3 = H-bonded guest molecules

Experimental Section

Preparation: Intercalates of 2-propen-1-ol, 2-propyn-1-ol and 2-buten-1-ol were prepared by suspending $VOPO_4 \cdot 2H_2O$ (0.3 g) in dry alcohol (7 mL), and subsequent short exposure (0.5−2 min) to a microwave field. Intercalates of the other unsaturated 1-alcohols were obtained by the following reintercalation reaction. The solid propanol-intercalated host ($VOPO_4 \cdot 2C_3H_7OH$) was prepared first and used as the starting material.[20] The reintercalation reactions were carried out by shaking $VOPO_4 \cdot 2C_3H_7OH$ (0.4 g) in the corresponding alcohol (5 mL) for two days. The solid product formed was filtered off. All samples for the X-ray diffraction analyses were left with a small residue of the respective alcohol. The samples for the TG-DTA and elemental analyses were washed with dry ether and dried under dry nitrogen at room temperature.

Analyses: The TGAs of the intercalates were performed with a Derivatograph MOM (Hungary), the measurements were carried out in the temperature range of 30−600 °C in air, at a heating rate of 5 °C/min. The weight of the samples was 100 mg. In some cases the composition was checked by elemental analysis (C, H).

Diffraction Measurements: The powder data of the intercalates with a minor surplus of the guest alcohol were obtained with an X-ray diffractometer (HZG-4, Freiberger Präzisionsmechanik, Germany) using Cu-$K_{\alpha 1}$ radiation (λ = 1.54051 Å) with discrimination of the Cu-K_{β} by a Ni filter. The Cu-$K_{\alpha 2}$ intensities were removed from the original data. Silicon (a = 5.43055 Å) was used as an internal standard. Diffraction angles were measured from 1.5° to 37° (2Θ). The polycrystalline sample containing an excess of the liquid guest was placed in a flat sample holder and protected against moisture by a polyethylene foil. The stability of the intercalate in air was tested by exposing it to air with ambient humidity, on a glass plate. Temperature measurements (from 22 to 240 °C) were carried out on a heated corundum plate with a thermocouple.[32] Each diffractogram was measured at constant temperature and a cycle of heating and measuring lasted about 20 min.

IR Spectra Measurements: Infrared measurements in the range 400−4000 cm^{-1} were made with a fully computerized Nicolet IMPACT 400 FTIR spectrometer (300 scans per spectrum at 2 cm^{-1} resolution). Measurements were performed in the transmission mode as KBr pellets and by the ATR technique on ZnSe crystal.[33] The spectra were corrected for the H_2O and CO_2 content in the optical path.

Raman Spectra Measurements: FT Raman spectra were collected using a Fourier transform near-infrared (FT-NIR) spectrometer Equinox 55/S (Bruker) equipped with an FT Raman module FRA 106/S (Bruker) (128 interferograms were co-added per spectrum in the range 4000−(−1000) cm^{-1} at 4 cm^{-1} resolution).

Acknowledgments

This work was supported by the Grant Agency of the Czech Republic, grant no. 203/97/1010 and the Academy of Sciences of the Czech Republic (Key Project 12).

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Received July 31, 2000
[I00301]