



## Intercalates of Vanadyl Phosphate with Aliphatic Nitriles

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### Abstract

Intercalates of vanadyl phosphate with aliphatic nitriles (acetonitrile, propionitrile, butyronitrile, valeronitrile and hexanenitrile) were prepared and characterized by X-ray powder diffraction, thermogravimetric analysis, IR and Raman spectroscopies. The basal spacings of all the intercalates prepared are practically identical. The nitrile intercalates (except acetonitrile) contain one nitrile molecule per formula unit. The nitrile molecules are anchored to the host layers by an N–V donor-acceptor bond and their aliphatic chains are parallel to the host layers. The acetonitrile intercalate contains two guest molecules per formula unit. Only half of them can be bonded to the vanadium atom, the second half is probably anchored by van der Waals interaction. The intercalates prepared are moisture-sensitive and the guest molecules are easily replaced by water molecules.

### Introduction

Vanadyl phosphate forms a number of intercalation compounds with molecular guests having Lewis base character [1]. Intercalations of aliphatic and aromatic amines [2–6], metallocenes [7, 8], alcohols [9–12], diols [9, 13, 14], ketones [15, 16], aldehydes [17], poly(ethylene) glycols [18] and heterocycles [19–24] have been studied. On the other hand, less attention has been paid to the intercalation of carboxylic acids and their derivatives. Intercalates with formic, acetic, propionic and butyric acids were prepared by exchange reactions of  $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$  with the acids in the presence of dehydrating agents [25]. Guest molecules are arranged in a monomolecular way and are anchored to the host layers by their functional groups. The presence of carboxylate anions in these intercalates was not observed. As regards amides, only formamide, *N,N*-dimethylformamide and *N,N*-dimethylacetamide form intercalates with  $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$  [26]. Glycine molecules are present as zwitterionic species in the  $\text{VOPO}_4 \cdot \text{NH}_2\text{CH}_2\text{COOH}$  intercalate [27].

Recently, values of the differential molar enthalpy accompanying the adsorption of organic molecules on the layered vanadyl phosphate modified with iron (FeVOP), a compound with the structure of layers similar to that of  $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ , have been reported [28]. It is suggested that the compounds anchored to the adsorbent surface by bonds substantially stronger than the van der Waals forces have a

considerable chance to be intercalated into FeVOP. This is the case with compounds possessing donor O or N atoms (alcohols, ketones, amines etc.). Besides methanol and acetone, acetonitrile also has a high value of the differential molar enthalpy. Nevertheless, to the best of our knowledge, an intercalation of nitriles into vanadyl phosphate has not been described as yet.

In this paper we report on the intercalation of acetonitrile, propionitrile, butyronitrile, valeronitrile and hexanenitrile into vanadyl phosphate.

### Experimental

**Preparation.** The intercalation compounds were obtained by a displacement reaction. A solid 2-propanol intercalate [12] was prepared in advance and used as a starting material for the reaction with the corresponding nitrile. The 2-propanol intercalate (1 g) was suspended in 50 mL of the nitrile and refluxed for 30 min. Samples used for the XRD measurements contained small amounts of the free nitrile. Dry samples for the TG and spectroscopic measurements were prepared by evaporation of the nitrile at 25 °C in an evacuated ampoule.

**XRD.** Powder data were obtained with a HZG-4 X-ray diffractometer (Freiberger Präzisionsmechanik, Germany) using  $\text{CuK}\alpha$  radiation with discrimination of the  $\text{CuK}\beta$  radiation by a Ni filter. Diffraction angles were measured from 5 to 37° ( $2\theta$ ). The samples were kept under protection foil

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during the measurements and the signal of this foil in the diffractograms was compensated.

**Thermogravimetry.** The TG analyses were performed using a Derivatograph C (MOM Budapest, Hungary). The measurements were carried out in air between 20 and 500 °C at a heating rate of 5 K min<sup>-1</sup>.

**Gas chromatography.** GC was used to check whether or not the intercalates contained starting 2-propanol. The samples were washed with an excess of the corresponding nitrile to remove 2-propanol released during the intercalation. The intercalates were then hydrolyzed in a small amount of water and the hydrolyzate was analyzed by GC with a Chrom 4 chromatograph (Czech Republic).

**IR spectral measurements.** Infrared spectra were recorded in a Nujol suspension in the range 2000–2500 cm<sup>-1</sup> using a Bio-Rad FTS spectrometer.

**Raman spectral measurements.** FT Raman spectra were collected using a Equinox 55/S Fourier transform near-infrared (FT-NIR) spectrometer equipped with FT Raman module FRA 106/S (Bruker) (128 interferograms were co-added per spectrum in the range 4000 – 1000) cm<sup>-1</sup> at 4 cm<sup>-1</sup> resolution).

## Results and discussion

None of the nitriles studied can be intercalated into anhydrous vanadyl phosphate. Similarly, attempts to replace water molecules in VOPO<sub>4</sub>·2H<sub>2</sub>O or 1-propanol molecules in VOPO<sub>4</sub>·2C<sub>3</sub>H<sub>7</sub>OH with nitriles do not lead to an intercalation. Considering that 2-alkanol molecules are anchored to the host layers more weakly than 1-alkanols [10] the nitrile intercalates can be prepared by replacing 2-propanol molecules in the corresponding VOPO<sub>4</sub> intercalate. Longer nitriles enter the layers very unwillingly. We did not succeed in a preparation of the pure hexanenitrile intercalate. Its existence in a mixture with the starting 2-propanol intercalate is only inferred from the X-ray measurement. The intercalates prepared were yellow crystalline solids indicating that the vanadium(V) had not been significantly reduced.

The diffractograms of all intercalates show sharp (001) and (002) and weak (200) reflections (see Figure 1). The absence of (*hkl*) lines in the intercalates is characteristic of a turbostratic structure where the original tetragonal layers of the host are retained but shifted in the directions of the *x* and/or *y* axes. The lattice parameters of the tetragonal structures are given in Table 1.

The composition of the nitrile intercalates was determined by thermogravimetric analysis (see Figure 2). Propionitrile, butyronitrile and valeronitrile are released in three exothermic steps. Acetonitrile starts to escape at about 30 °C and then a three-step decomposition similar to that for longer nitriles follows. A small weight increase above 560 °C is probably caused by the oxidation of vanadium(IV). The product of the thermal decomposition of the intercalates is

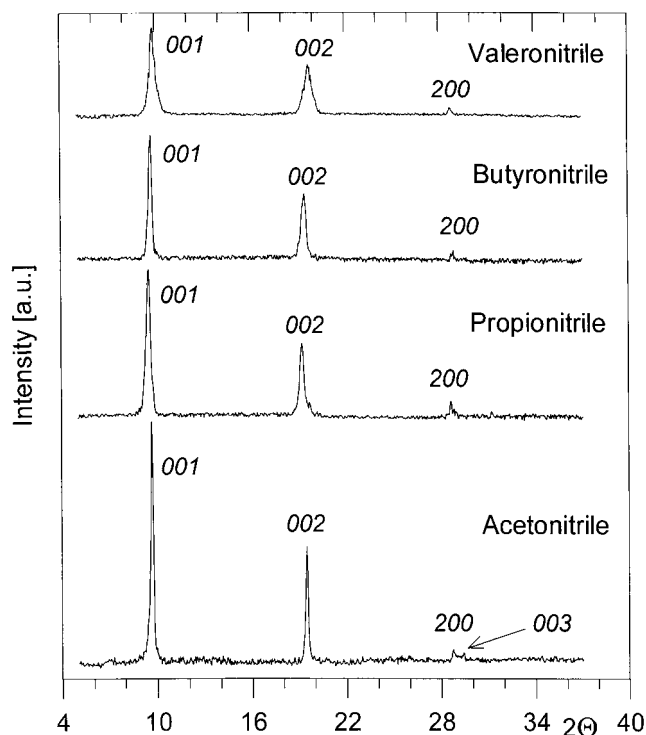


Figure 1. The diffractograms of vanadyl phosphate intercalated with nitriles.

Table 1. Lattice parameters and the guest content in the intercalates prepared

Guest	<i>a</i> [Å]	<i>c</i> [Å]	<i>x</i>
Acetonitrile	6.20	9.09	1.98
Propionitrile	6.20	9.18	1.00
Butyronitrile	6.20	9.16	1.05
Valeronitrile	6.22	9.02	0.95
Hexanenitrile	6.20	9.38	–

anhydrous vanadyl phosphate. The total weight losses correspond to the stoichiometric ratio *x* given in Table 1. The thermal decomposition of the acetonitrile intercalate was also observed by thermal XRD measurements. The basal spacing of this intercalate does not change up to 140 °C indicating that the first weight loss is not accompanied by a change of the basal spacing. Gas chromatography of the hydrolyzates of the solid intercalates showed that no mixed intercalates containing starting 2-propanol were formed.

The nitrile intercalates are very unstable in air (at 40–50% relative humidity), the nitrile molecules are very easily replaced by water molecules. The diffraction line (001) of vanadium phosphate dihydrate was observed after several minutes as in the case of 2-alkanols [10] and most of the branched alcohols [12]. The valeronitrile intercalate seems to be more stable than other nitrile intercalates. The course of its hydration is given in Figure 3. After twenty minutes, about one half of the intercalate had decomposed and a broad diffraction line of vanadyl phosphate dihydrate appeared.

The character of the bonding between the guest and the host layer in the nitrile intercalates was studied by infrared

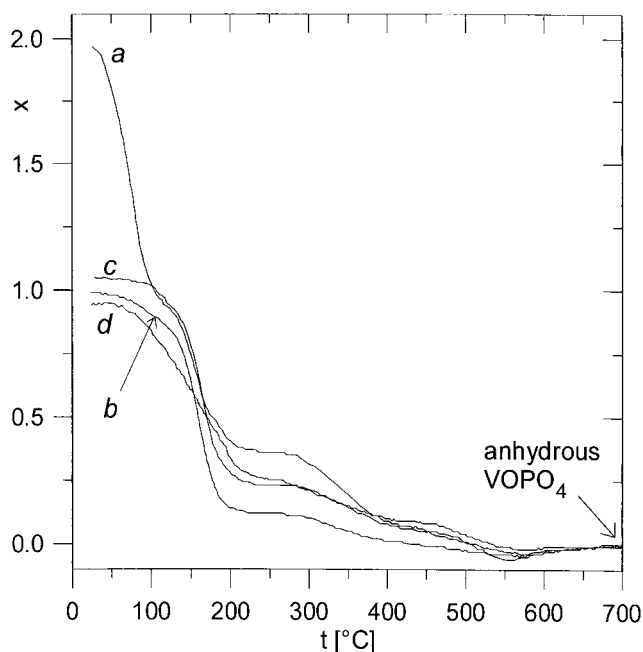


Figure 2. TG curves of vanadyl phosphate intercalated with acetonitrile (a), propionitrile (b), butyronitrile (c), and valeronitrile (d). The weight loss is recalculated to the stoichiometric quotient  $x$ .

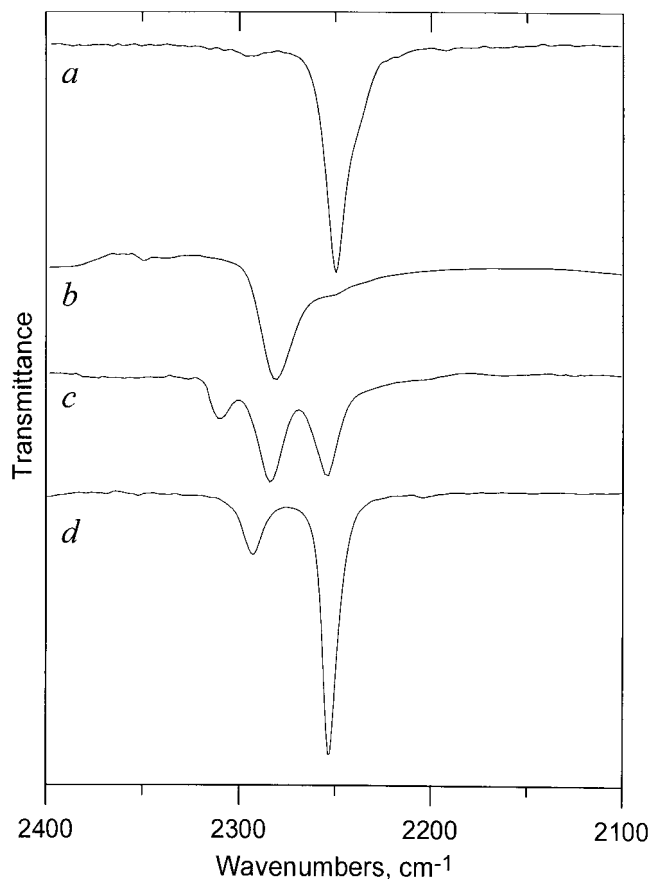


Figure 4. FTIR spectra of butyronitrile (a), butyronitrile intercalate (b), acetonitrile intercalate (c), and acetonitrile (d).

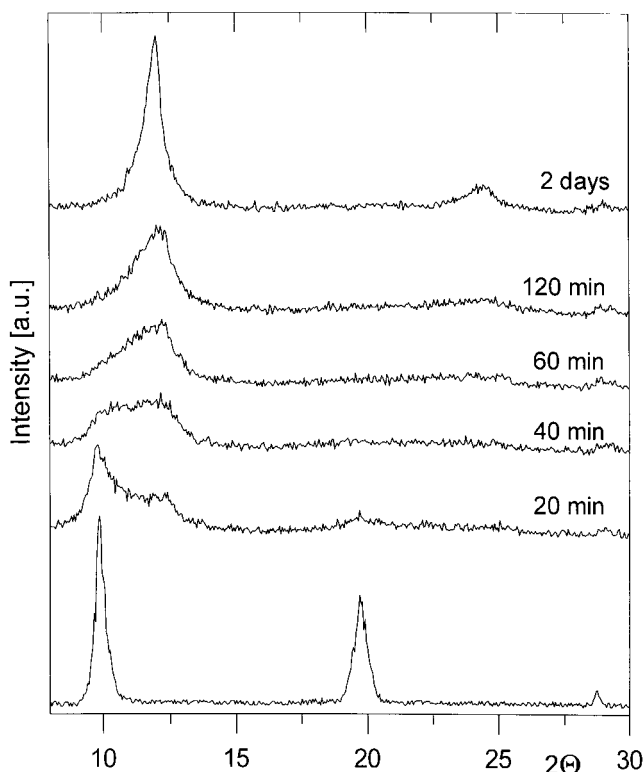


Figure 3. The changes of the diffractograms of the valeronitrile intercalate exposed to air (40–50% relative humidity).

and Raman spectroscopies. From the point of view of the host-guest interactions, the position of the  $\text{C}\equiv\text{N}$  stretching vibration is the most important. The  $\text{C}\equiv\text{N}$  group can act either as a  $\sigma$ -donor by donating nitrogen electrons to the metal or as a  $\pi$ -donor by donating electrons of a nitrile  $\pi$ -bond. The wavenumber of the  $\text{C}\equiv\text{N}$  stretching vibration is shifted to higher values in the case of  $\sigma$ -donation, and to lower values in the case of  $\pi$ -donation [29].

The infrared spectra of butyronitrile and its intercalate in  $\text{VOPO}_4$  in the region from 2100 to 2400  $\text{cm}^{-1}$  are given in Figure 4. The strong  $\text{C}\equiv\text{N}$  stretching absorption band of pure butyronitrile is observed at 2250  $\text{cm}^{-1}$ . This band was shifted to 2281  $\text{cm}^{-1}$  in the butyronitrile intercalate which indicated formation of a  $\text{C}\equiv\text{N} \rightarrow \text{V}$  bond in the intercalate. The same shift of the  $\text{C}\equiv\text{N}$  stretching band was observed for the propionitrile intercalate. A similar shift of the  $\text{C}\equiv\text{N}$  stretching vibration to higher wavenumber (2285  $\text{cm}^{-1}$ ) was observed for  $\text{PtCl}_2(\text{PhCN})_2$  and  $\text{PdCl}_2(\text{PhCN})_2$  (2231  $\text{cm}^{-1}$  for free benzonitrile) and was ascribed to the formation of  $\text{C}\equiv\text{N} \rightarrow \text{Pt}$  and  $\text{C}\equiv\text{N} \rightarrow \text{Pd}$  bonds, respectively [30, 31].

The strong  $\text{C}\equiv\text{N}$  stretching absorption band of pure acetonitrile is observed at 2252  $\text{cm}^{-1}$  (the weak band at 2293  $\text{cm}^{-1}$  is due to Fermi resonance). There are three absorption bands at 2254, 2284 and 2310  $\text{cm}^{-1}$  in the IR spectrum of the acetonitrile intercalate. In contrast to the other intercalates, the acetonitrile intercalate contains two acetonitrile molecules per formula unit. Only one of them can be co-

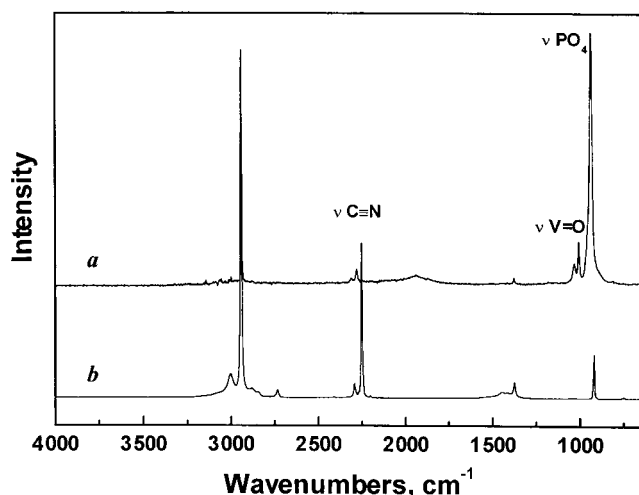


Figure 5. Raman spectra of  $\text{VOPO}_4 \cdot \text{CH}_3\text{CN}$  (a) and liquid acetonitrile (b).

ordinated to the vanadium atom, the second one is probably anchored only by van der Waals forces. The first band, with the same wavenumber as for free acetonitrile, probably corresponds to a non-coordinated acetonitrile molecule. Two bands at  $2284$  and  $2310 \text{ cm}^{-1}$  correspond to coordinated acetonitrile (analogously to the butyronitrile intercalate).

The Raman spectra of acetonitrile and its intercalate are given in Figure 5. The intense band at  $939 \text{ cm}^{-1}$  in the Raman spectrum of the intercalate corresponds most probably to the symmetric  $\nu(\text{PO}_4)$  stretching vibration of tetrahedral phosphorus in  $(\text{VOPO}_4)_\infty$ . The sharp band at  $1006 \text{ cm}^{-1}$  originates from the  $\text{V}=\text{O}$  vanadyl stretching vibration. The vanadyl stretching band appears to be especially sensitive to the atoms coordinated to vanadium within an octahedral arrangement in the host lattice structure. The vanadyl stretching vibration is seen at  $1035 \text{ cm}^{-1}$  in anhydrous  $\text{VOPO}_4$  and at  $995 \text{ cm}^{-1}$  in vanadyl phosphate dihydrate. The presence of the band at  $1032 \text{ cm}^{-1}$  can be caused by a partial escape of the guest molecules due to laser-beam heating during the measurements. A similar situation was observed during the Raman spectral measurement of  $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$  and  $\text{VOPO}_4 \cdot 2\text{D}_2\text{O}$  where we observed simultaneously a band at  $1032 \text{ cm}^{-1}$  in the Raman spectrum corresponding to the anhydrous form of vanadyl phosphate [32]. The position of the main spectral bands of the host structure only slightly differs from those of anhydrous vanadyl phosphate or its hydrated form [32, 33, 34]. It confirms that the structure of the original  $\text{VOPO}_4$  layers remains unchanged after the intercalation reaction.

The strong  $\text{C}\equiv\text{N}$  stretching absorption band of pure acetonitrile observed at  $2253 \text{ cm}^{-1}$  (the second band at  $2293 \text{ cm}^{-1}$  is due to Fermi resonance) is shifted to  $2280 \text{ cm}^{-1}$  (the second band at  $2313 \text{ cm}^{-1}$ ) in the Raman spectra of the intercalate. In contrast to the IR spectrum, the band at about  $2254 \text{ cm}^{-1}$  corresponding to non-coordinated acetonitrile was not observed in the Raman spectrum. This is caused by the escape of non-coordinated acetonitrile due to laser-beam heating during the measurements. This is in agreement with the very low thermal stability of the non-coordinated acetonitrile molecules observed by TGA. Other

bands of acetonitrile in the intercalate are very weak and their position is not significantly changed compared to that observed for free acetonitrile.

The Raman spectra of both propionitrile and butyronitrile intercalates are strongly influenced by a baseline radiation. The band (doublet in the host spectra) corresponding to the nitrile stretching vibration is completely overlapped by the strong baseline radiation in the Raman spectra. It is connected most probably with the excitation of radiation of partially escaped guests molecules due to the laser beam during the measurements. It corresponds to the fact that the nitrile intercalates are very unstable in air. For this reason the infrared spectra of the nitrile intercalates could not be measured by dispersing the samples in KBr pellets. During their preparation the samples decomposed to the corresponding nitrile and vanadyl phosphate hydrate. No shifts of the nitrile bands were observed for these samples.

For most of the  $\text{VOPO}_4$  intercalates with guest molecules with aliphatic chains the basal spacing increases with increasing chain length [3, 9–13, 17, 25]. On the other hand, the basal spacings of all nitrile intercalates prepared are practically identical (see Table 1). This indicates that nitrile molecules are parallel with the host layers. From this point of view, it is surprising that the IR spectra suggest that the nitrile molecules are anchored to the vanadium atoms by the  $\text{C}\equiv\text{N} \rightarrow \text{V}$  donor-acceptor bonds, for which a perpendicular arrangement of the guest molecules with respect to the host layers should be expected. The nitrile intercalates have a stoichiometric quotient  $x = 1$  except for the acetonitrile intercalate which contains two guest molecules per formula unit. Only half of them can be bonded to the vanadium atom, the second half fills empty space among coordinated molecules and is anchored probably by van der Waals interaction. It is in agreement with the thermal behavior of the acetonitrile intercalate, where one half of acetonitrile is released between  $30$  and  $100 \text{ }^\circ\text{C}$  without a change of the basal spacing.

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