Intercalates of Vanadyl Phosphate with Dinitriles

LUDVÍK BENEŠ[1],*, VÍTĚZSLAV ZIMA[1], KLÁRA MELÁNOVÁ[1], MIROSLAVA TRCHOVÁ[2] and
PAVEL MATĚJKA[3]

[1]*Joint Laboratory of Solid State Chemistry of Academy of Sciencies of the Czech Republic and University of Pardubice, Studentská 84, 532 10 Pardubice, Czech Republic;* [2]*Faculty of Mathematics and Physics, Charles University, V Holešovičkách 2, 180 00 Prague 2, Czech Republic;* [3] *Department of Analytical Chemistry, Institute of Chemical Technology, Technická 5, 166 28 Prague, Czech Republic*

Abstract

Intercalates of vanadyl phosphate with aliphatic dinitriles (malononitrile, succinonitrile, glutaronitrile, adiponitrile, pimelonitrile and suberonitrile) 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 dinitrile content in the intercalates decreases with increasing chain length. The dinitrile 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 dinitrile intercalates are generally more stable in air (at relative humidity 40–50%) than nitrile intercalates and the guest molecules are slowly replaced by the water molecules.

Introduction

Vanadyl phosphate and other isostructural layered compounds are able to accommodate some types of organic compounds having a 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 intercalations of carboxylic acids and their derivatives. Intercalates with formic, acetic, propionic and butyric acids were prepared by reaction of $VOPO_4 \cdot 2H_2O$ with an acid in the presence of a dehydrating agent [25]. Among amides, only formamide, *N,N*-dimethylformamide and *N,N*-dimethylacetamide form intercalates with $VOPO_4 \cdot 2H_2O$ [26]. Glycine molecules are present as zwitterionic species in the intercalate $VOPO_4 \cdot NH_2CH_2COOH$ [27]. Intercalates of vanadyl phosphate with acetonitrile, propionitrile, butyronitrile, valeronitrile and hexanenitrile were prepared [28], and the basal spacings of all the intercalates prepared were found to be practically the same. 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 coordinated to the vanadium atom, the second half is probably anchored by van der Waals interaction.

In this paper we report on the intercalation of dinitriles ($NC(CH_2)_nCN$; $n = 1–6$) into vanadyl phosphate.

Experimental

Preparation. The intercalation compounds were obtained by a displacement reaction. The solid 2-propanol intercalate [12] was prepared in advance and used as a starting material for the reaction with corresponding dinitrile. The 2-propanol intercalate (0.5 g) was suspended in 10 mL of the liquid or melted dinitrile and heated in a microwave field for 10 min. The samples used for the XRD measurements contained small amounts of the free dinitrile. The samples for the TG and spectroscopic measurements were washed with toluene and dried in vacuum.

XRD. Powder data were obtained with an X-ray diffractometer HZG-4 (Freiberger Präzisionsmechanik, Germany) using $CuK\alpha$ radiation with discrimination of the $CuK\beta$ radiation by a Ni filter. Diffraction angles were measured from 5 to 37° (2θ). The samples were kept under protection foil 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 600 °C at a heating rate of 5 K.min^{-1}.

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* Author for correspondence.

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

n	Guest	a (Å)	c (Å)	x
3	Malononitrile	6.20	9.06	1.05
4	Succinonitrile	6.22	8.84	0.87
5	Glutaronitrile	6.21	8.76	0.65
6	Adiponitrile	6.21	8.76	0.66
7	Pimelonitrile	6.21	9.04	0.50
8	Suberonitrile	6.20	9.12	0.36

Gas chromatography. This method was used to check
whether or not the intercalates contained starting 2-propanol.
The samples were washed with an excess of corresponding
dinitrile or toluene 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 in the range
400–4000 cm^{-1} were measured with a fully computerized
Nicolet IMPACT 400 FTIR spectrometer (300 scans per
spectrum at 2 cm^{-1} resolution). Measurements were per-
formed *ex situ* in the transmission mode in Nujol suspension
and by the ATR technique on a ZnSe crystal. The spectra
were corrected for the H_2O and CO_2 content in the optical
path.

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

Results and discussion

The dinitriles used as guests cannot be intercalated directly
into anhydrous vanadyl phosphate and also a replacement of
water molecules in $VOPO_4 \cdot 2H_2O$ or 1-propanol molecules
in $VOPO_4 \cdot 2C_3H_7OH$ does not lead to an intercalation. The
dinitrile intercalates can be prepared by replacing 2-propanol
molecules in the corresponding $VOPO_4$ intercalate. The in-
tercalates prepared were greenish-yellow crystalline solids
indicating that the vanadium(V) was slightly reduced to
vanadium(IV). The diffractograms of all intercalates show
sharp (001) and (002) and weak (200) reflections (see Fig-
ure 1). The absence of (*hkl*) lines in the intercalates is a
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 compositions of the dinitrile intercalates were de-
termined by thermogravimetric analysis. During heating,
dinitriles are slowly released in one step in the temperature
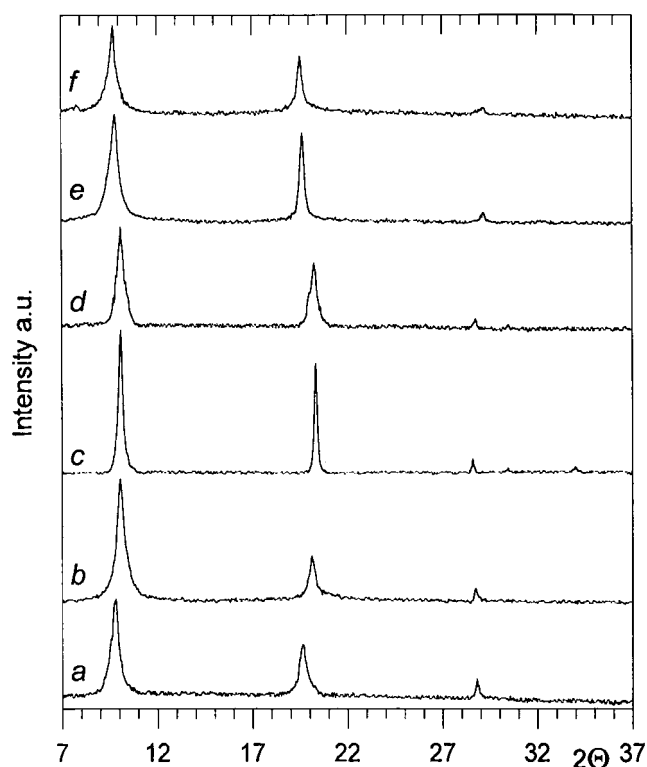range 250–550 °C. The product of the thermal decompos-

Figure 1. The diffractograms of vanadyl phosphate intercalated with
malononitrile (a); succinonitrile (b); glutaronitrile (c); adiponitrile (d);
pimelonitrile (e); suberonitrile (f).

ition of the intercalates is anhydrous vanadyl phosphate.
Total weight losses correspond to the stoichiometric ratio
x given in Table 1. Gas chromatography of hydrolyzates
of the solid intercalates showed that no mixed intercalates
containing starting 2-propanol were formed. Compared to
the mononitrile intercalates, which have almost stoichiomet-
ric compositions [28] with the host/guest ratio 1/1 for the
propionitrile, butyronitrile, and valeronitrile intercalates, the
composition of the dinitrile intercalates change with the
number of the carbon atoms in the chain as given in Table
1.

The dinitrile intercalates are generally more stable in air
(at relative humidity 40-50%) than the nitrile intercalates
[28]. There is no correlation between the chain length of
dinitriles and the stability of the intercalates. The suber-
onitrile intercalate seems to be the most stable one. The
diffractograms measured during its hydration are given in
Figure 2. After one hour, no formation of vanadyl phosphate
dihydrate was observed. A small amount of dihydrate ap-
peared after twenty hours and became the prevailing phase
after 7 days. The course of the hydration of the least stable
intercalate of glutaronitrile is given in Figure 3. A small
amount of dihydrate appeared after twenty minutes and the
intercalate was completely decomposed after 40 hours.

From the point of view of the host-guest interactions,
the position of the C≡N stretching vibration is the most
important. The C≡N group can act either as a σ-donor by
donating nitrogen electrons to a metal or a π-donor by donat-
ing electrons of a nitrile π-bond. The wavenumber of the
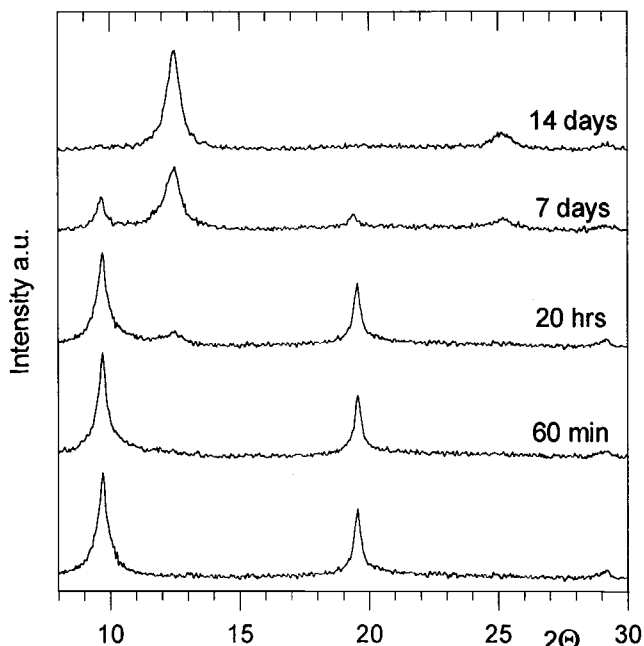C≡N stretching vibration is shifted to higher values in the

Figure 2. Changes of the diffractograms of the suberonitrile intercalate exposed to air (relative humidity 40–50%).
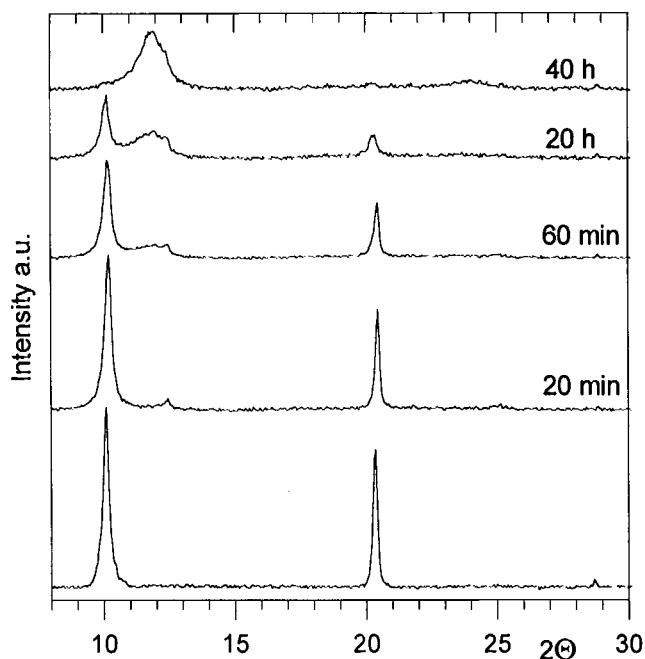

Figure 3. Changes of the diffractograms of the glutaronitrile intercalate exposed to air (relative humidity 40–50%).

case of σ-donation and to lower values in the case of the π donation [29].

The infrared spectra of crystalline malononitrile (measured in a Nujol suspension), liquid glutaronitrile and suberonitrile (measured by the ATR technique) and their intercalates with VOPO$_4$ (measured in a Nujol suspension) in the region from 2100 to 2400 cm^{-1} are given in Figures 4, 5, and 6. A strong C≡N stretching absorption band of pure crystalline malononitrile is observed at 2267 cm^{-1} (with a shoulder at 2272 cm^{-1} corresponding to a Fermi resonance), a weaker band at 2289 cm^{-1} (with a shoulder at 2296 cm^{-1})
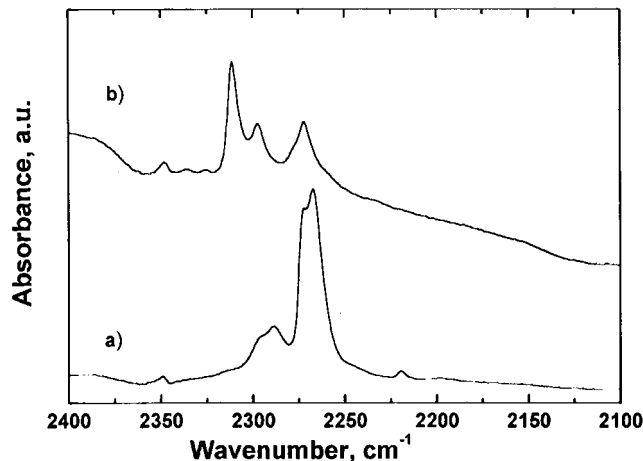

Figure 4. FTIR spectra of crystalline malononitrile (a) and of the malononitrile intercalate (b).

is also observed in the crystalline state of malononitrile. A strong C≡N band at 2311 cm^{-1} with two weaker bands at 2298 and 2273 cm^{-1} is observed in the malononitrile intercalate. The shift of the C≡N stretching vibration to higher wavenumbers indicates formation of a C≡N → V bond in the intercalate. The existence of three different positions of the C≡N band in the spectrum of the intercalate indicates some additional guest–guest and guest–host interactions. It is in agreement with the stoichiometry of this intercalate, where one half of the C≡N groups cannot be coordinated to the vanadium atoms. The strong C≡N stretching absorption band of pure liquid glutaronitrile and suberonitrile is observed at 2250 cm^{-1} and 2244 cm^{-1}. This band is observed at 2274 cm^{-1} with a weak shoulder at 2250 cm^{-1} in the glutaronitrile intercalate and at 2285 cm^{-1} in the suberonitrile intercalate. As for the malononitrile intercalate, the shift of the C≡N stretching vibration to higher wavenumbers in both intercalates indicates formation of a C≡N → V bond in the intercalate. One can deduce from the values of the shifts that a stronger C≡N → V bond is formed in the intercalate with suberonitrile than that with glutaronitrile. This is in agreement with the observed stability of these two intercalates in air. The weak shoulder in the spectrum of the glutaronitrile intercalate is probably caused by non-coordinated C≡N groups (about 0.3 group per formula unit). Such a band of the non-coordinated guest was not observed in the spectrum of the suberonitrile intercalate which agrees well with the small amount of the intercalated nitrile in the intercalate. A similar shift of the C≡N stretching vibrations was observed also in the mononitrile intercalates [28]. In addition, a C≡N stretching vibration band corresponding to presence of the non-bonded guest in the interlayer space was observed for the acetonitrile intercalate with the host/guest ratio 1/2.

The Raman spectra of all intercalates are strongly influenced by a baseline radiation. It is connected most probably with the excitation of the radiation of partially escaped guest molecules due to the laser beam during the measurement. A band corresponding to the C≡N stretching vibration is completely overlapped by the strong baseline radiation. Only in the spectrum of the glutaronitrile intercalate one can observe
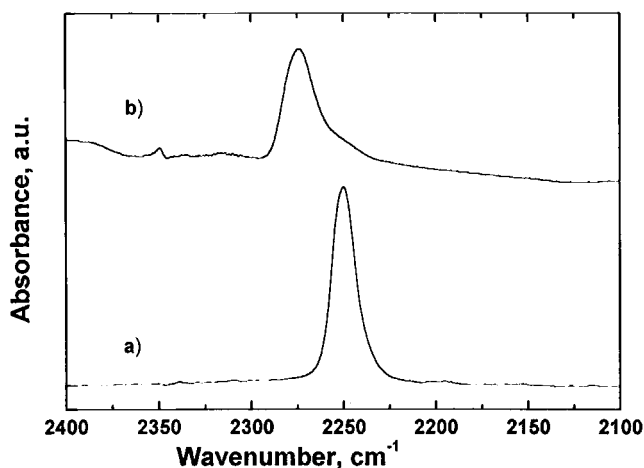
Figure 5. FTIR spectra of liquid glutaronitrile (a) and of the glutaronitrile intercalate (b).
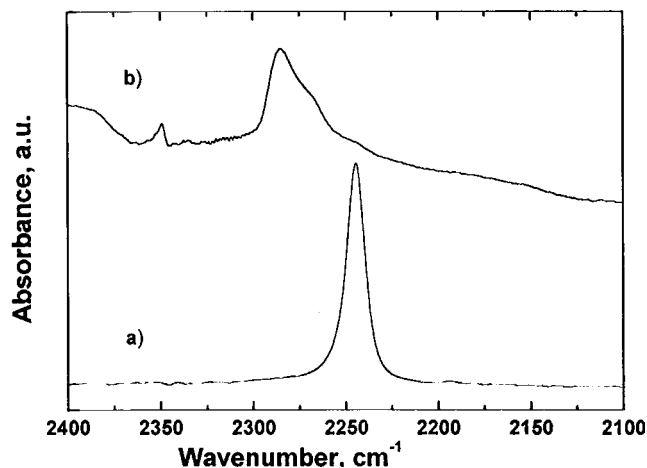

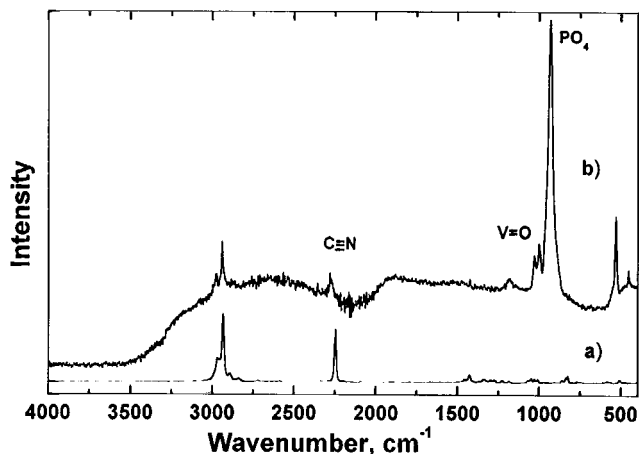*Figure 6.* FTIR spectra of liquid suberonitrile (a) and of the suberonitrile intercalate (b).

Figure 7. Raman spectra of liquid glutaronitrile (a) and of the glutaronitrile intercalate (b).

a shift of the C≡N band from 2251 to 2282 cm^{-1} (see Figure 7). The intense bands at 934 cm^{-1} in the Raman spectrum of the malononitrile intercalate and at 933 cm^{-1} in the spectrum of glutaronitrile and suberonitrile intercalates correspond most probably to a symmetric $\nu(PO_4)$ stretching vibration. The sharp band at 1012 cm^{-1} in the spectrum of the malononitrile intercalate (at 1000 cm^{-1} for the glutaronitrile and suberonitrile intercalates) came from a vanadyl (V = O) stretching vibration. The vanadyl stretching band appears to be especially sensitive to atoms coordinated to vanadium within an octahedral arrangement in the host lattice structure. The vanadyl stretching vibration is seen at 1035 cm^{-1} in anhydrous VOPO$_4$ and at 995 cm^{-1} in vanadyl phosphate dihydrate [30]. The presence of the band at 1031 cm^{-1} in all intercalates can be caused by a partial escape of the guest molecules due to the laser beam during the measurements. The position of the main spectral bands of the host structure only slightly differs from those of anhydrous vanadyl phosphate or its hydrated form [30]. It confirms that the structure of the original VOPO$_4$ layers remains unchanged after the intercalation reaction.

In contrast to most VOPO$_4$ intercalates with guest molecules with aliphatic chains where the basal spacing increases with increasing chain length [3, 9–13, 17, 25], the basal spacings of all the dinitrile intercalates prepared are practically the same (see Table 1) as in the case of the nitrile intercalates [28]. This indicates that the dinitrile 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 C≡N → V donor-acceptor bonds, for which a perpendicular arrangement of the guest molecules with respect to the host layers should be expected.

Acknowledgements

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