Intercalation of γ-Butyrolactone into Vanadyl Phosphate and Niobyl Arsenate

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Intercalation compounds of vanadyl phosphate and isostructural niobyl arsenate with γ-butyrolactone, $VOPO_4{\cdot}C_4H_6O_2$ and $NbOAsO_4{\cdot}C_4H_6O_2$, respectively, were prepared from corresponding propanol intercalates by molecular exchange in a microwave field. The prepared intercalates were characterized using powder X-ray diffraction, density measurements, and thermogravimetric analysis. Infrared and Raman spectra indicate a coordination of the carbonyl oxygen atom of the γ-butyrolactone molecule to the vanadium or niobium atom of the host structure. Quantum mechanical calculations at the ab initio level confirm the proposed structure in which the γ-butyrolactone guest molecules are arranged with the plane of the ring perpendicular to the host layers and are anchored to the layers through the carbonyl oxygen atom coordinated to the transition metal atom of the host.

Introduction

Vanadyl phosphate dihydrate $VOPO_4{\cdot}2H_2O$ and other isostructural layered compounds are able to accommodate some types of organic molecules in the interlayer space.[1] Aliphatic alcohols and diols,[2−4] amines,[5] carboxylic acids,[6] carboxamides[7] and aliphatic nitriles[8] belong to the compounds which can be intercalated in such a way. Great attention has been devoted to the intercalation of heterocyclic N- and S-donors.[9−13] Recently, the intercalation of ketones,[14,15] aldehydes,[16] poly(ethylene glycol)s,[17,18] and heterocycles with O-donors[18−20] into vanadyl phosphates has been described. These guests are anchored to the host layers by donor−acceptor bonds of their carbonyl or ether oxygen atoms to the vanadium atoms. These intercalates, except aliphatic aldehyde intercalates, are generally very stable in air and the guest molecules are released at relatively high temperatures (for example, the tetrahydrofuran intercalate decomposes at about 160 °C[19]). It indicates that the host−guest interaction is very strong. The aliphatic aldehyde intercalates are unstable and the guests undergo aldol condensation and oxidation. On the other hand, aromatic aldehyde intercalates do not decompose in this way.[16] Some of these intercalates are crystalline solids and their diffractograms show, besides a series of sharp (00*l*) reflections, a number of (*hkl*) diffraction lines giving evidence for a regular structure.

This paper reports the results of the intercalation of γ-butyrolactone into vanadyl phosphate and isostructural niobyl arsenate.

Results and Discussion

γ-Butyrolactone cannot be intercalated directly in anhydrous vanadyl phosphate and replacement of water molecules in $VOPO_4{\cdot}2H_2O$ does not lead to an intercalation. The intercalate had to be prepared by replacing 1-propanol or 2-propanol in the corresponding $VOPO_4$ intercalate with the desired guest. The prepared intercalate was a yellow crystalline solid indicating that vanadium(V) had not been significantly reduced. Similarly, white niobyl arsenate intercalated with γ-butyrolactone was prepared from $NbOAsO_4{\cdot}2C_3H_7OH$. As follows from the results of elemental analyses, both intercalates contain one molecule of the guest per formula unit.

The diffractograms (see Figure 1) of both intercalates show a series of sharp (00*l*) reflections and also contain a number of (*hkl*) diffraction lines (Tables 1 and 2) giving evidence of a regular structure. The lattice parameters of the tetragonal structure are a = 6.2163(8) Å and c = 9.6681(9) Å for the $VOPO_4$ intercalate and a = 6.6557(8) Å and c = 9.805(3) Å for the $NbOAsO_4$ intercalate. The calculated density of 2.205 g/cm^3 for $VOPO_4{\cdot}C_4H_6O_2$ is in a good agreement with the experimental value of 2.21 g/cm^3. A new diffraction line with d = 11.100 Å was observed in the diffractogram of the $VOPO_4$ intercalate, measured using synchrotron radiation. This diffractogram can be in-

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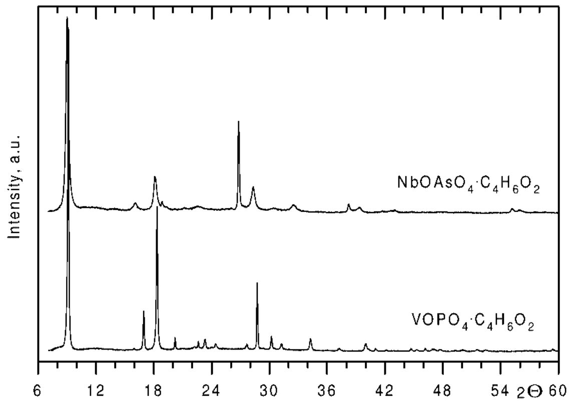

Figure 1. Diffractograms of the prepared intercalates

Table 1. Powder data for $VOPO_4$ intercalated with γ-butyrolactone [a = 6.2163(8) Å, c = 9.6681(9) Å]

2θ [°]	d [Å]	Intensity	h	k	l	$2\theta_{exp} - 2\theta_{calcd.}$ [°]
9.139	9.6680	96	0	0	1	0.000
16.943	5.2285	10	1	0	1	0.001
18.334	4.8349	100	0	0	2	−0.003
20.193	4.3937	2	1	1	0	0.009
22.185	4.0036	1	1	1	1	−0.012
23.287	3.8166	5	1	0	2	−0.004
27.652	3.2232	5	0	0	3	−0.005
28.699	3.1080	21	2	0	0	0.002
30.182	2.9586	6	2	0	1	0.005
31.238	2.8608	6	1	0	3	0.003
34.276	2.6139	8	2	0	2	0.007
37.191	2.4154	3	0	0	4	0.025
39.990	2.2526	12	1	0	4	0.002
41.033	2.1977	1	2	2	0	0.001
42.131	2.1430	1	2	2	1	0.003
42.652	2.1180	1	1	1	4	−0.001
44.691	2.0260	1	3	0	1	0.002
45.297	2.0003	1	2	2	2	0.011
46.122	1.9664	1	3	1	0	−0.016
46.958	1.9333	4	0	0	5	0.008
47.690	1.9053	1	3	0	2	−0.022
49.299	1.8469	2	1	0	5	−0.014
49.994	1.8228	1	2	1	4	0.036
			3	1	2	−0.053
51.591	1.7701	4	1	1	5	−0.004
52.445	1.7432	1	3	0	3	−0.010
57.112	1.6114	1	0	0	6	0.000
61.170	1.5138	1	1	1	6	−0.042
67.958	1.3782	2	3	1	5	0.017

dexed in the triclinic space group $P1$ using a fourfold cell with shifted layers. Butyrolactone molecules form a superstructure in the interlayer space.[21]

Table 2. Powder data for $NbOAsO_4$ intercalated with γ-butyrolactone [a = 6.6557(8) Å, c = 9.805(3) Å]

2θ [°]	d [Å]	Intensity	h	k	l	$2\theta_{exp} - 2\theta_{calcd.}$ [°]
9.010	9.8069	100	0	0	1	−0.002
16.080	5.5074	7	1	0	1	−0.002
18.112	4.8939	20	0	0	2	0.033
18.846	4.7049	8	1	1	0	0.006
22.515	3.9458	5	1	0	2	0.009
26.768	3.3278	56	2	0	0	0.000
28.283	3.1529	15	2	0	1	−0.015
30.441	2.9341	3	1	0	3	−0.003
32.497	2.7530	6	2	0	2	0.005
38.215	2.3532	7	2	2	0	−0.001
39.317	2.2897	4	2	2	1	−0.028
42.574	2.1218	1	2	2	2	−0.008
55.146	1.6641	2	4	0	0	−0.008
55.844	1.6450	1	3	0	4	−0.003
62.361	1.4878	1	4	2	0	0.020
63.135	1.4714	1	4	2	1	−0.001

Both intercalates are stable in air (at a relative humidity of ca. 50%) as are tetrahydrofuran or tetrahydropyran intercalates.[19]

The thermal stability of the $VOPO_4$ intercalate was monitored by X-ray diffraction and thermogravimetry. The position and the intensity of the diffraction lines did not change up to 160 °C. Above this temperature, the intensity of the diffraction lines decreases and the sample becomes green which means that vanadium(v) is reduced and butyrolactone starts to decompose as follows from the thermogravimetry. The total weight loss (34.8%) corresponds to the formula $VOPO_4 \cdot C_4H_6O_2$. The $NbOAsO_4 \cdot C_4H_6O_2$ intercalate was not monitored by thermogravimetry, because the host is decomposed at ca. 500 °C.

The character of the bonding between the guest and the host layers in the butyrolactone intercalates was studied by IR and Raman spectroscopy. The IR spectrum of liquid butyrolactone, its intercalates in $VOPO_4$ and $NbOAsO_4$ and the spectra of corresponding hosts in the region from 4000 to 650 cm^{-1} are given in Figures 2 and 3. The Raman spectra of these compounds are given in Figures 4 and 5. The observed bands of the host compounds can be assigned properly, based on the previous studies of the $MOXO_4$ compounds.[22] The spectra have been interpreted in terms of the vibrations of the PO_4^{3-} and AsO_4^{3-} tetrahedrons. Positions of all of the arsenate bands are shifted to lower wavenumbers due to the mass effect of the As atom compared to the P atom.

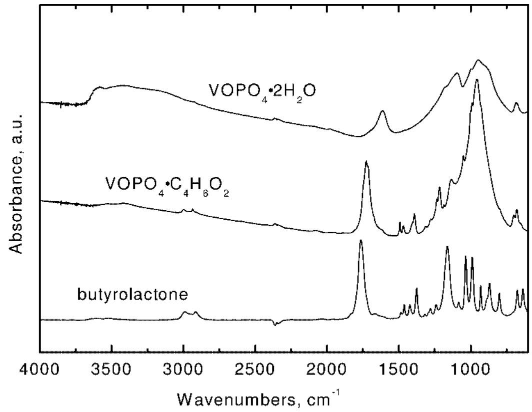

Figure 2. FT IR spectra of liquid butyrolactone (ATR on ZnSe crystal), vanadyl phosphate intercalated with butyrolactone and vanadyl phosphate dihydrate (in KBr pellets)

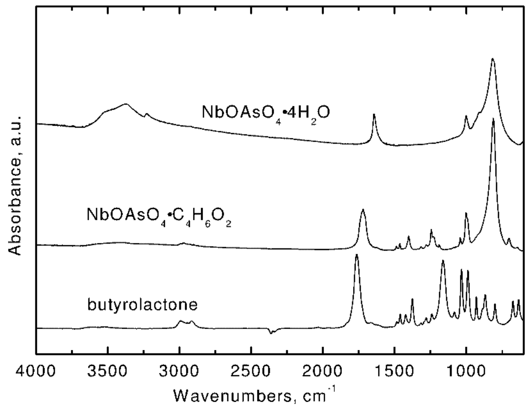

Figure 3. FT IR spectra of liquid butyrolactone (ATR on ZnSe crystal), niobyl arsenate intercalated with butyrolactone and niobyl arsenate tetrahydrate (in KBr pellets)

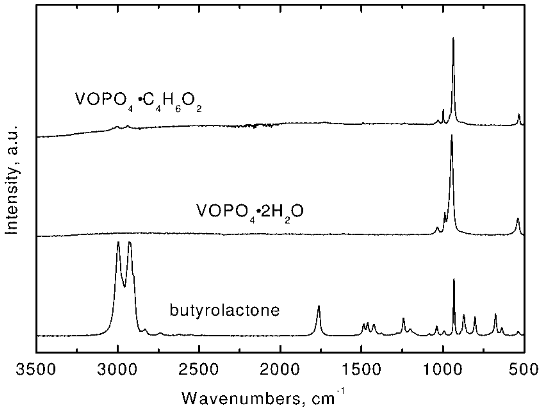

Figure 4. Raman spectra of liquid butyrolactone, vanadyl phosphate intercalated with butyrolactone and vanadyl phosphate dihydrate

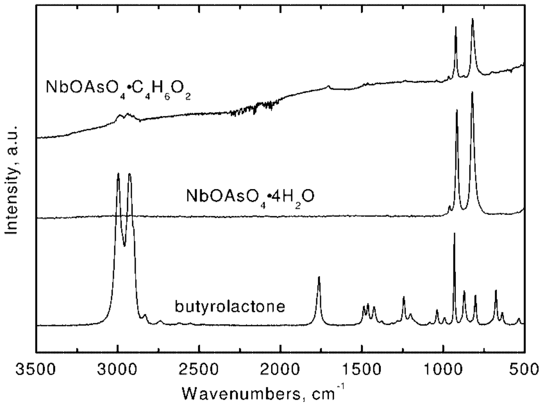

Figure 5. Raman spectra of liquid butyrolactone, niobyl arsenate intercalated with butyrolactone and niobyl arsenate tetrahydrate

The positions of the main spectral bands of the host structures in the vibration spectra of $VOPO_4$ and $NbOAsO_4$ intercalated with butyrolactone differ only slightly from those of vanadyl phosphate and niobyl arsenate hydrates. It confirms that the structures of the original $VOPO_4$ and $NbOAsO_4$ layers remain unchanged after the intercalation reaction. This conclusion is extremely important for the strategy of modeling.

The intense band at 937 cm^{-1} in the Raman spectrum of the $VOPO_4$ intercalate (see Figure 4) corresponds to the symmetric $\nu(PO_4)$ stretching vibration of the phosphate tetrahedron in the $(VOPO_4)_\infty$ layers and it is observed at 957 cm^{-1} in the IR spectrum of the intercalate (see Figure 2). Analogously the intense band at 820 cm^{-1} in the Raman spectrum of the $NbOAsO_4$ intercalate (see Figure 5) corresponds to the symmetric $\nu(AsO_4)$ stretching vibration of the arsenate tetrahedron in the $(NbOAsO_4)_\infty$ layers and it is observed at 817 cm^{-1} in the IR spectrum of the intercalate (see Figure 3). The positions of the V=O and Nb=O stretching vibrations appear to be especially sensitive to atoms coordinated to the vanadium atom within an octahedral arrangement in the host lattice structure. For instance, when water molecules are intercalated into $VOPO_4$, the position of this band at 1035 cm^{-1} in the IR spectrum of the anhydrous form of vanadyl phosphate changes to 995 cm^{-1} typical of mono- and dihydrates.[23] In the Raman spectrum of the vanadyl phosphate we can observe the V=O stretching vibration at 989 cm^{-1} corresponding to the hydrate form and also the vibration at 1035 cm^{-1} corresponding to the anhydrous form of vanadyl phosphate (see Figure 4). It is a result of the partial escape of the water molecules which occurs during the measurements due to the laser beam. In the Raman spectrum of niobyl arsenate, the Nb=O stretching vibration of the hydrate form is observed at 919 cm^{-1} and for the anhydrous form it is situated at 961 cm^{-1} (Figure 5). In the Raman spectrum of the vanadyl phosphate intercalate, the peak at 1000 cm^{-1} corresponds most probably to the V=O stretching vibration with an oxygen atom of butyrolactone coordinated to the vanadium atom (see Figure 4). Analogously, the peak at 924 cm^{-1} in the Raman spectrum of niobyl arsenate corresponds to the Nb=O stretching vibration with an oxygen atom of butyrolactone coordinated to the niobyl atom (see Figure 5). In the IR spectra of the intercalates these bands are overlapped by the spectrum of butyrolactone.

Comparing the positions of the stretching vibration bands of the C=O and C−O groups in the IR and Raman spectra of the pristine butyrolactone with these bands in the spectra of $VOPO_4$ and $NbOAsO_4$ intercalates we observed some shifts which indicate an interaction between the butyrolactone molecules and the host structure. The C=O stretching vibration observed at 1764 cm^{-1} in the IR spectrum of pure liquid butyrolactone is shifted to 1727 cm^{-1} in the IR spectrum of the $VOPO_4$ intercalate and to 1721 cm^{-1} in the IR spectrum of the $NbOAsO_4$ intercalate. In addition, a shoulder is clearly visible on the lower wavenumber side of the C=O stretch peak in the IR spectra. Its position changes from 1762 cm^{-1} in the Raman spectrum of pure butyrolactone to a small peak at 1726 cm^{-1} in the Raman spectrum of the $VOPO_4$ intercalate and at 1707 cm^{-1} of the $NbOAsO_4$ intercalate. The band due to the C−O stretching ring vibration of butyrolactone, observed at 1161 cm^{-1} in its IR spectrum is most probably shifted to the higher wavenumbers; to 1217 cm^{-1} in the IR spectrum of the vanadyl phosphate intercalate (see Figure 2) and to 1244 cm^{-1} in the IR spectrum of the niobyl arsenate intercalate (see Figure 3). In the Raman spectra, these peaks are very small.

When the carbonyl oxygen atom of an ester is the donor, a weakening of the C=O bond can be expected together with a strengthening of the adjacent C−O bond as a secondary effect. When forming adducts with Lewis acids in which the metal ion is hexacoordinated by the ester molecule, esters show a negative shift in their carbonyl stretching frequency and a positive shift in their C−O stretching frequency.[24] It was shown[25] that the lithium ions are bound through the oxygen atom of the carbonyl group of butyrolactone in $LiClO_4$/butyrolactone solution. Both the C−C and C=O stretch vibrations are sensitive to an interaction between the Li^+ ion and the butyrolactone molecule. The shifts observed in the spectra of the butyrolactone intercalates indicate a coordination of the O_{guest} of the C=O group of butyrolactone to the vanadium and niobium atoms of the hosts.

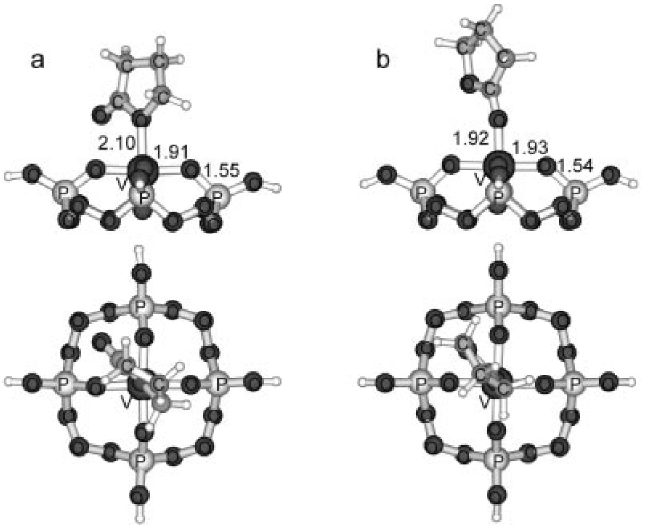

Figure 6. Two optimized HF/TZV structures of the molecular segment modeling the vanadyl phosphate−butyrolactone interaction with indicated bond lengths [Å]

Figure 6 shows ab initio (HF/TZV) optimized structures of the molecular segment representing local interactions of vanadyl phosphate with butyrolactone. In order to preserve the overall planar structure of the segment during full geometry optimizations and at the same time make the electronic structure in the segment close to the conditions appearing in the intercalates, an oxygen atom had to be inserted between two neighboring PO_4 groups. Free terminal oxygen atoms have been replaced by OH groups and the total charge of the model compound was set to +3. It was found that all geometry optimizations with various starting orientations of butyrolactone with respect to the vanadyl group lead to the structures displayed in Figure 6 (a and b), which indicates that both C=O→V and C−O(−C)→V bonds can be formed. However, the structure shown in Figure 6 (b) is energetically more favorable by 22.7 kcal/mol and thus only the structure with the C=O→V bond is expected to be formed in the intercalates. This is also confirmed by the results of calculations of vibrational frequencies. While the calculated frequency of the C=O stretching vibration in the structure at Figure 6 (a) is shifted to higher wavenumbers compared to free butyrolactone, the C=O stretching vibration of the structure with the C=O→V bond [Figure 6 (b)] is shifted to lower wavenumbers as observed in the IR and Raman spectra.

Experimental Section

Preparation: The propanol intercalates were prepared by suspending microcrystalline $VOPO_4{\cdot}2H_2O$ or $NbOAsO_4{\cdot}4H_2O$ in dry propanol and monitored by a short exposure to a microwave field. The intercalation compounds were obtained by displacing propanol in $VOPO_4{\cdot}2C_3H_7OH$ or $NbOAsO_4{\cdot}2C_3H_7OH$ by γ-butyrolactone. The propanol intercalate (0.5 g) was dispersed in 15 mL of γ-butyrolactone and exposed to a microwave field for 5 min. The intercalates were filtered off, washed with diethyl ether, and dried in nitrogen. The composition of the intercalate was determined by elemental analyses. $C_4H_6O_7PV$ (248.0): calcd. C 19.37, H 2.44; found C 19.61 H 2.39. $C_4H_6AsNbO_7$ (333.9): calcd. C 14.39, H 1.81; found C 14.25, H 1.87.

XRD: Powder data were obtained with a D8-Advance diffractometer (Bruker AXE, Germany) using Cu-K_α radiation with a secondary graphite monochromator. Diffraction angles were measured from 7 to 80° (2θ).

Density: Density of the $VOPO_4$ intercalate was measured with an automated helium pycnometer (AutoPycnometer 1320, Micromeritics, USA) to 0.01 g·cm^{-3} accuracy.

Thermogravimetry: The TG analyses were performed using a Netzsch STA 449C instrument. The measurements were carried out in air between 30 and 800 °C at a heating rate of 5 °C·min^{-1}.

IR Spectroscopy: IR measurements in the range 400−4000 cm^{-1} were made with a fully computerized Bruker IFS 55 EQUINOX FTIR spectrometer with DLATGS detector (256 scans per spectrum at 4 cm^{-1} resolution). Measurements of the intercalates were performed ex situ in the transmission mode using KBr pellets. The spectrum of the corresponding liquid butyrolactone was measured by the ATR technique on a ZnSe crystal. The spectra were corrected for the content of H_2O and CO_2 in the optical path.

Raman Spectroscopy: FT Raman spectra were collected using a Bruker IFS 55 EQUINOX FTIR spectrometer equipped with an FT Raman module FRA 106/S with diode-pumped, temperature-stabilized Nd YAG laser, and InGaAs detector (128 interferograms were co-added per spectrum in the range 4000 to −1000 cm^{-1} at 4 cm^{-1} resolution).

Calculations: Quantum chemical calculations were carried out at the ab initio level of theory employing the Gaussian 98[26] program package. Local interactions and structures in intercalates of vanadyl phosphate with the nitrile group were studied at the HF level using a TZV basis set.[27]

Acknowledgments

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