Intercalation of Poly(oxyethylene) Compounds into the $MOXO_4$ (M = V, Nb; X = P, As) Host Lattice

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Diethylene glycol (DEG), triethylene glycol (TEG), poly(ethylene glycol)s (PEG 200, PEG 400, and PEG 1000), and tripropylene glycol (TPG) were intercalated into vanadyl phosphate and isostructural niobyl phosphate and arsenate. X-ray powder diffraction patterns as a function of temperature were also measured. Depending on the temperature of the reaction, two phases were formed. Two types of $VOPO_4$ intercalates were formed depending on the temperature of the reaction (40 and 80 °C). The high-temperature phase was also formed by heating the low-temperature product. All of the intercalates are stable in dry environment but decompose slowly in humid air. It is presumed that the chains of the guest are deposited parallel to the host layer with every other oxygen atom of the guest coordinated to the vanadium or niobium atoms of the host layer. The chains are arranged in a bimolecular or monomolecular way in the interlayer space.

Introduction

Recently, there has been considerable interest in the synthesis of polymer/inorganic nanocomposites. The combination of organic and inorganic materials can lead to unusual electrical, optical, and mechanical properties which might not be achieved with each component separately. This type of material can be prepared either by intercalation of the organic monomers followed by polymerization in the interlayer space or by direct polymer intercalation. For example, a Nylon 6−clay hybrid was prepared by intercalation of ϵ-caprolactam into montmorillonite and its subsequent polymerization.[1] A composite consisting of poly(ϵ-caprolactone) intercalated silicate particles embedded in the same polymer matrix was synthesized by heating Cr^{3+}−fluorohectorite in the presence of an excess of ϵ-caprolactone.[2] Intercalative polymerization of aniline, pyrrole, and its derivatives was observed during intercalation into $VOPO_4 \cdot 2H_2O$[3−5] or vanadium oxide xerogel.[6]

On the other hand, intercalates of polyaniline into MoS_2,[7] poly(vinylpyrrolidone), polypropylene glycol, and methylcellulose into V_2O_5 xerogel,[8] and poly(ethylene imine) into α-$Zr(HPO_4)_2 \cdot H_2O$[9] were prepared by direct intercalation of polymers. The most common guest, poly(ethylene oxide) (PEO) or its analogue poly(ethylene glycol) (PEG) with smaller molecular weight was intercalated into α-$Zr(HPO_4)_2 \cdot H_2O$,[9] V_2O_5,[10,11] MoS_2,[12] MPS_3 (M = Mn, Cd),[13] and smectite clays.[14−16] The conformations that PEO adopts in the interlayer space of these inorganic hosts are quite variable. In some smectite clays, the PEO was proposed to form helixes, in which the interlayer cation was found within the helix.[14] In this case, the increase of interlayer distance is near 8 Å. Two different types of the arrangement of the PEO chains in V_2O_5 were described.[11] In the first type, PEO chains in planar zigzag conformation form monolayers with the increase of basal spacing corresponding to 4.5 Å. The presence of a double layer of polymer chains was presumed for the second type with the increase of basal spacing 8−9 Å. In MPS_3[13] and MoS_2[12] the PEO chains are thought to adopt a bilayer arrangement too.

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The intercalation of PEO and its analogues with smaller molecular weight into the structure of vanadyl phosphate has never been reported in the literature. Layers of $VOPO_4 \cdot 2H_2O$ are formed from corner sharing vanadium octahedra and phosphate tetrahedra. Vanadium octahedra are composed of four equatorial oxygens which are shared by phosphorus. One of the axial oxygens is a vanadyl oxygen, and the second axial oxygen belongs to a water molecule coordinated to vanadium. The second water molecule is bonded by a weak H-bridge to the oxygen atoms of the phosphate groups. The structure is tetragonal with parameters $a = 6.215$ and $c = 7.403$ Å, and the space group is $P4/n$.[17] Some other molecules can be incorporated between the layers; for example, aliphatic alcohols and diols,[18] amines,[19,20] carboxylic acids,[21] and amides.[22]

The present paper reports the results of intercalation of diethylene glycol (DEG), triethylene glycol (TEG), PEG 200, PEG 400, PEG 1000, PEG 20 000, and tripropylene glycol (TPG) into vanadyl phosphate and isostructural niobyl phosphate and arsenate.

Experimental Section

Preparation of Hosts. Vanadyl phosphate dihydrate was prepared by boiling a mixture of V_2O_5 in diluted H_3PO_4 under a reflux for 14 h.[23] The product was filtered and washed with distilled water several times. Niobyl phosphate was obtained by the method of Chernorukov[24] modified by Bruque.[25] Ten grams of Nb_2O_5 was added to 70 mL of HF (40%w/w) and refluxed for 2 days using a Teflon-coated condenser. Then H_3PO_4 (41 mL 85%w/w) was added and the mixture was heated to evaporate HF. The resultant precipitate was filtered and washed several times with 5 M HNO_3 and distilled water. The solid was dried at ambient temperature and kept over a saturated aqueous solution of K_2CO_3 to maintain a constant relative humidity. Niobyl arsenate was prepared in a similar manner.

Preparation of Intercalates. The propanol intercalates were prepared by suspending microcrystalline host in dry propanol and subsequent short exposure (1−10 min) to a microwave field.[18,26] The intercalation compounds were obtained by reintercalation reaction of the propanol intercalate with the corresponding host. The propanol intercalate (1 g) was suspended in ca. 50 mL of the guests and stirred for 4 days at 40 or 80 °C. Solid PEGs (PEG 1000, PEG 20 000) were used either as a saturated acetonitrile solution (at 40 °C) or as a melt (80 °C). The solid products were filtered, washed with acetonitrile, and stored over P_2O_5.

Measurements. The powder data of the intercalates were obtained with an X-ray diffractometer (HZG-4, Germany) using CuKα1 radiation ($\lambda = 1.54051$ Å) with discrimination of the CuKβ by a Ni-filter. The CuKα2 intensities were removed from the original data. Silicium ($a = 5.43055$ Å) was used as internal standard. Diffraction angles were measured from 3 to 50° (2Θ). The obtained data were refined by the least squares program minimizing $(2\Theta_{exp} - 2\Theta_{calc})^2$. Temperature measurements (from 22 to 310 °C) were carried out on the heated corundum plate with a thermocouple.[27] Each diffractogram was measured at constant temperature and a cycle of heating and measuring lasted about 20 min.

The thermogravimetric analyses (TGAs) of the intercalates were performed with a Derivatograph MOM (Hungary), the measurements being carried out in the temperature interval 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, particularly for complexes of niobyl arsenate, the composition was determined by elemental analysis (C, H).

Infrared spectra were recorded on a Bio-Rad FTS spectrometer with a spectral range 4000−500 cm^{-1} using a dry KBr powder containing 10% of the intercalate. The resultant reflectance spectra were converted into Kubelka−Munk format.

Pellets for ac conductivity measurements were prepared by pressing 0.15 g of the $VOPO_4$−DEG intercalate in a rectangular matrix. Two opposite sides of the pellets were coated with graphite paste serving as electrodes. An impedance meter (Tesla BM 653) was used for ac conductivity measurements in frequency region from 20 Hz to 500 kHz. The data obtained showed an arc-shaped curve in a complex impedance plot (imaginary versus real parts of impedance) from which conductivities were calculated using complex nonlinear least-squares fitting.

Results and Discussion

As expected, the direct intercalations of the oligomers and polymers studied into anhydrous and hydrated hosts did not proceed. Therefore, the well-tried method of the reintercalation of the propanol intercalates was used. The intercalation of PEG 20 000 into the hosts studied was not successful.

The intercalates prepared were crystalline compounds and their diffractograms showed a series of relatively sharp (00*l*) reflections. The *a* parameter of the tetragonal lattice was usually determined from the (200) line of the vanadyl phosphate intercalates. For the niobyl compounds, the other (*hk*0) diffraction lines were observed. The presence of (*hk*0) and the absence of (*hkl*) reflections confirm a turbostratic structure of the intercalates in which the layers of the host are retained but shifted in the directions of the *x* and/or *y* axes. The exception is that all three hosts intercalated with diethylene glycol. These intercalates showed significant number of (*hkl*) diffraction lines (see Figure 1) giving evidence of a regular stacking of the host layers from which a regular arrangement of the DEG molecules in the interlayer space can be presumed. The distinctly smaller value of basal spacing of this intercalate also confirms the regular arrangement of the host molecules. The difference between the DEG intercalate and the other intercalates can be explained by a size distribution of the guest molecules. DEG as a guest is formed by molecules with a uniform size, whereas PEGs are formed by a mixture of molecules with more or less distributed length of the chain.

A formation of two products was observed during preparation of the $VOPO_4$−PEG 1000 and $VOPO_4$−DEG intercalates. At lower temperature (40 °C) the intercalate with higher basal spacing and higher content of the guest is formed; at higher temperature (more than 80 °C) the product with basal spacing of about 7.9 Å and

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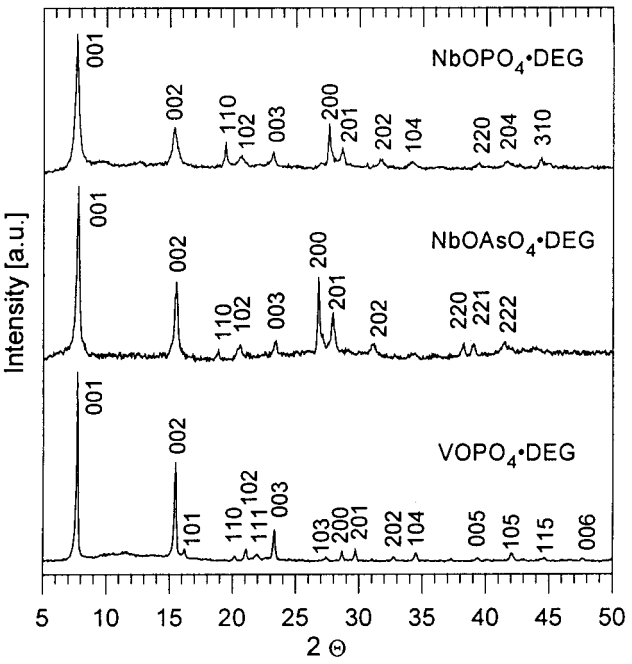

Figure 1. X-ray powder diffraction patterns of DEG-intercalated $MOXO_4$.

Table 1. Lattice Parameters and Content of the Guest in the Intercalates Prepared

	$VOPO_4$			$NbOPO_4$			$NbOAsO_4$		
guest	*a* [Å]	*c* [Å]	*x*	*a* [Å]	*c* [Å]	*x*	*a* [Å]	*c* [Å]	*x*
DEG	6.23	11.45	2.0	6.46	11.49	1.8	6.67	11.45	1.8
	6.22	7.90	1.1						
TEG	6.23	12.36	2.1	6.47	12.04	2.1	6.67	12.03	2.2
PEG 200	6.21	12.16	1.9	6.45	11.98	1.9	6.64	12.06	2.0
PEG 400	6.22	12.10	2.0	6.46	12.16	2.1	6.66	12.19	2.0
	6.22	7.83	1.2						
PEG 1000	6.22	12.04	2.1	6.45	12.36	2.0	6.64	12.47	1.9
	6.22	7.85	1.2						
TPG	6.22	13.94	1.8	6.45	14.04	1.8	6.66	13.95	1.9

with lower content of the guest is generated (composition and lattice parameters are given in Table 1). The diffractograms of both PEG-intercalated $VOPO_4$ phases are shown in Figure 2. The presence of the phases with lower content of the guest was not observed during preparation of $NbOPO_4$ and $NbOAsO_4$ intercalates because the temperature of their formation, as found by thermal measurements, was higher than 80 °C.

The composition of the intercalates of $VOPO_4$ and $NbOPO_4$ was determined using TGA and checked by the elemental analysis. Thermogravimetry could not be used for the $NbOAsO_4$ intercalates, because the host is decomposed at about 500 °C.[26] The lattice parameters of all intercalates prepared and the content of the guests, given by a number of oxyethylene units *x* per formula unit of the host, are given in Table 1.

All of the intercalates prepared are stable in dry air but slowly decompose in contact with air humidity. The hydration of the $VOPO_4$−DEG, $NbOPO_4$−DEG, and $NbOPO_4$−PEG 1000 in an atmosphere with the relative humidity of 58% was studied by X-ray powder diffraction. The diffractograms obtained are given in Figure 3. Both intercalates with DEG show relatively high stability at the beginning of the hydration and are not practically changed during the first 10 days of the contact. For the $VOPO_4$ intercalate, the dihydrate is

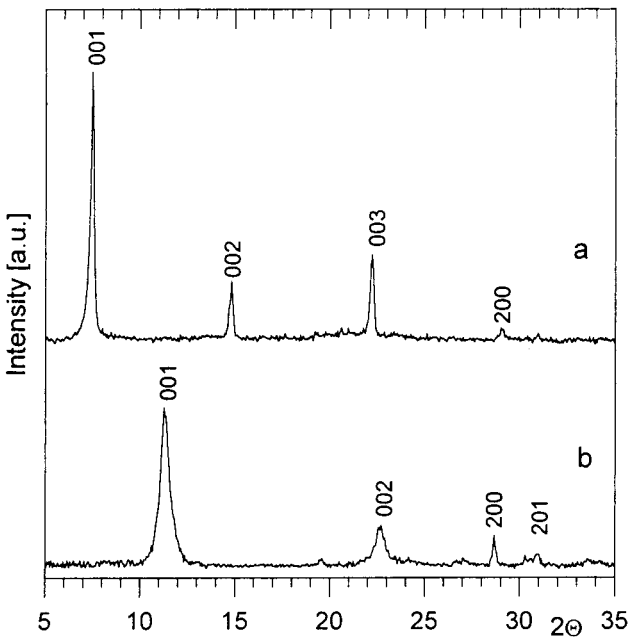

Figure 2. XRPD patterns of the PEG-intercalated $VOPO_4$ phases prepared at 40 °C (a) and 80 °C (b).

formed in addition to the original intercalate, as shown by a broad diffraction line at about 7.4 Å. After 75 days, the lines of the intercalate disappear, the diffraction lines of $VOPO_4 \cdot 2H_2O$ become sharp, and a transition phase with basal spacing 7.9 Å appears. For the niobyl phosphate intercalate, the lines of two transition phases (10.8 and 8.7 Å) are present after 75 days; the formation of any defined hydrate was not observed. The decomposition of $NbOPO_4$−PEG 1000 is significantly more rapid. Distinct broadening and shift of the (00*l*) line was observed after 4 days. After 16 days, a transition phase with basal spacing 10.7 Å is present and the diffractogram remains the same even after 75 days.

Basal spacing as a function of temperature for all DEG-intercalated hosts is shown in Figure 4. All three intercalates give a phase with basal spacing 7.9 Å when heated. For $VOPO_4$ intercalate, this phase is formed at 80 °C, whereas for $NbOPO_4$ and $NbOAsO_4$ intercalates it was observed above 110 and 130 °C, respectively. These phases are stable up to 300 °C. The temperature at which the phase with smaller basal spacing is formed increases with increasing formula weight of the guest. During heating, broad and ill-defined diffraction lines occur in a large temperature region as a consequence of the disorder of layered structure. For instance, the diffraction line corresponding to the interlayer distance of 12.36 Å observed for this phase in PEG 1000-intercalated $NbOPO_4$ disappears at 143 °C and the diffraction line of the pure phase at 7.98 Å appears at 218 °C. This thermal behavior explains why two products are formed during the intercalation.

The thermal decomposition of TPG intercalates is slightly different. The $VOPO_4$ intercalate decomposes at temperature above 100 °C and an amorphous product is formed; the $NbOPO_4$ intercalate decomposes at substantially higher temperature (above 200 °C). A phase with smaller basal spacing and lower TPG content is not formed.

Infrared spectra were measured to elucidate interactions between the guest molecules and the host lattice.

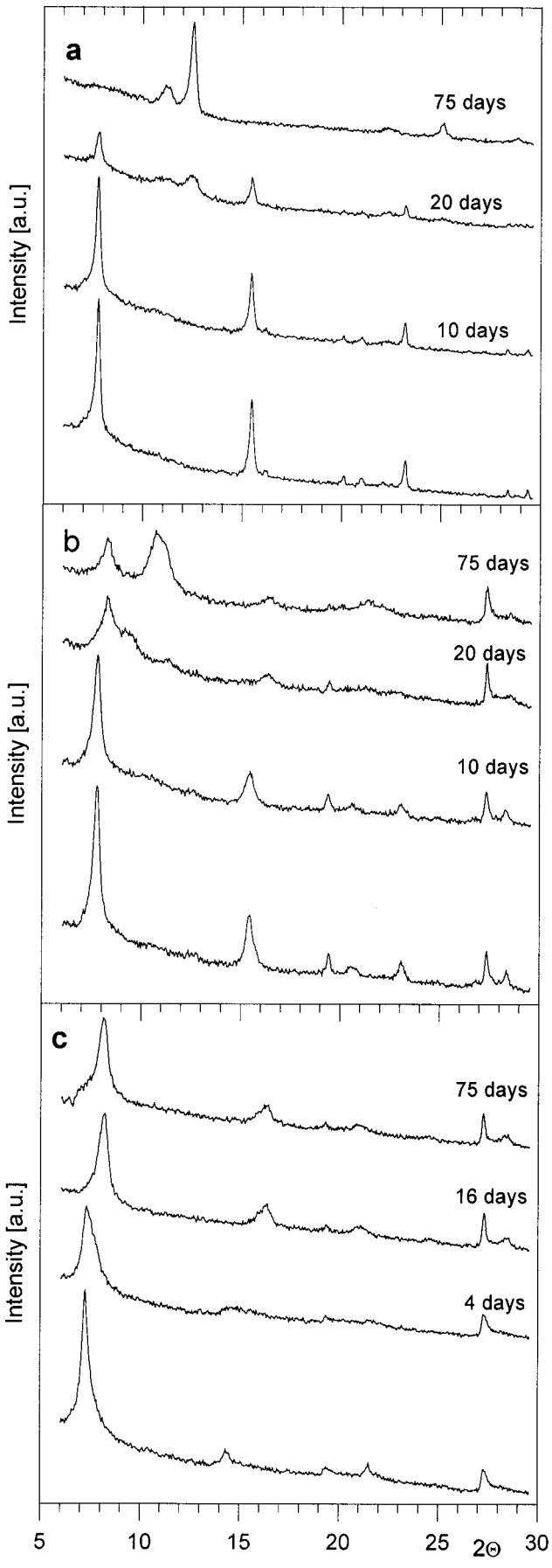

Figure 3. XRPD patterns as a function of time taken during hydration of DEG-intercalated $VOPO_4$ (a) and $NbOPO_4$ (b), and PEG 1000-intercalated $NbOPO_4$ (c).

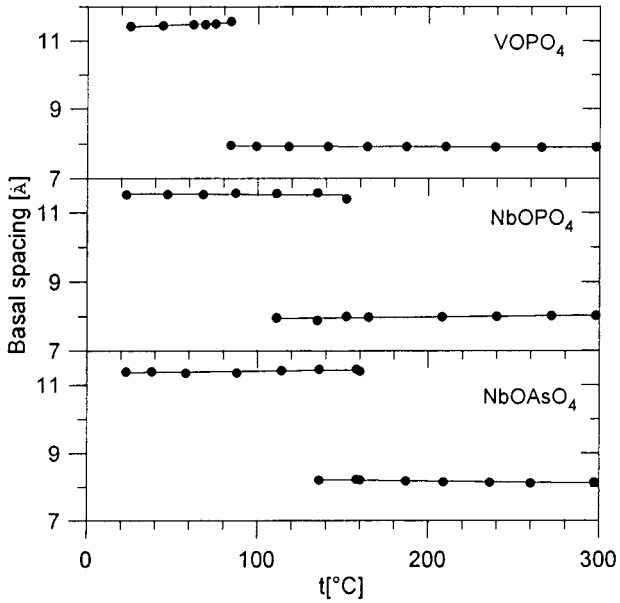

Figure 4. Basal spacing as a function of temperature during thermal decomposition of DEG-intercalated $MOXO_4$.

The valence vibration band of the M═O group in this type of compound is sensitive to the donor ability of the ligand which coordinates the metal atoms at the position opposite to the oxygen atom. For $VOPO_4$ and $NbOPO_4$, the region of the ν(M═O) vibration is overlapped by the intense bands of the PO_4 tetrahedron. Therefore, the intercalation compounds of $NbOAsO_4$ were studied in more detail. The ν(Nb═O) vibration was found at 1020 and 998 cm^{-1} for anhydrous niobyl arsenate and tetrahydrate, respectively.[28] The intercalation of basic molecules causes this band to shift to lower wavenumbers.[29,30] IR spectra of neat PEG 1000 and $NbOAsO_4$ intercalated with PEG 1000 are shown in Figure 5.

In all of the intercalates studied, the broad and intense O−H stretching band is shifted significantly to lower wavenumbers. This is caused by weakening of the O−H bond owing to the coordination of the oxygen atom to the niobium atom of the host lattice. The system of the hydrogen bonds, either between the guest molecules or between the guest and host, is retained in the intercalate.

In pure solid PEG 1000 the symmetric and asymmetric C−H stretching modes are not resolved and only one broad deformed band centered at 2885 cm^{-1} was observed. Upon intercalation, one observes the splitting of this broad band into two distinct bands (2941 and 2887 cm^{-1}). A similar phenomenon was observed for various PEO/M^{n+} montmorilonite complexes,[14] polyether derivatives intercalated into zirconium phosphate,[31] and PEG-intercalated kaolinite.[16] In the region 1500−1200 cm^{-1}, a number of bands indicative of various C−H deformations originating from the oxyethylene species were found (1455 cm^{-1} CH_2 bending, 1353 cm^{-1} combination band of CH_2 wagging and C−C stretching, 1250

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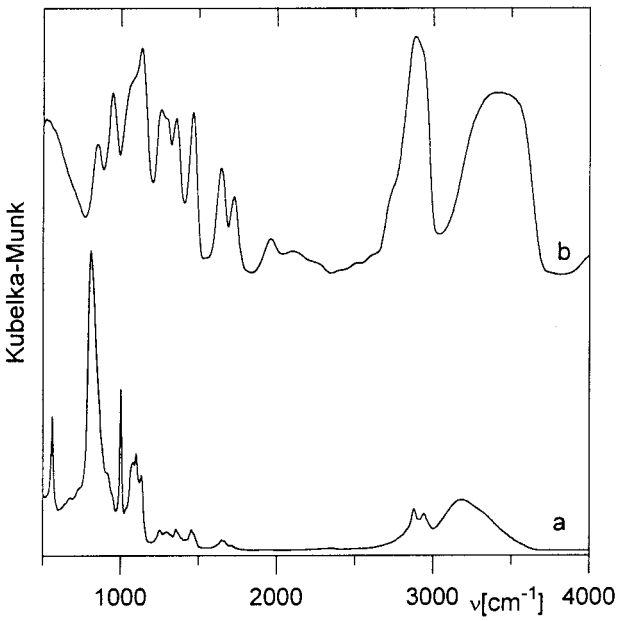

Figure 5. FT-IR reflectance spectra of $NbOAsO_4$ intercalated with PEG 1000 (a) and solid PEG 1000 (b).

cm^{-1} CH_2 twisting). Their positions are the same as in the neat PEG 1000. A weak band about 1320 cm^{-1} was not observed in the spectra of any intercalates prepared. This band is important because it is indicative of the conformation of the oxyethylene species.[14,32,33] The presence of this band has been proposed to be due to $-OCH_2CH_2O-$ groups in the trans conformation.[32] We presume, therefore, that the oxyethylene units are not in the trans conformation.

A splitting of the bands and a change of a ratio of their intensities in the intercalates, compared to pure guest, were observed in the region of C−O−C stretching vibrations. This can be caused by the presence of the donor−acceptor oxygen−niobium bonds.

A sharp intense band at 1000 cm^{-1} can be assigned to the ν(Nb═O) vibrations. This indicates the presence of the donor−acceptor bond between an oxygen atom of the guest molecule and the niobium atom of the host which is analogous to the bond of water or alcohol molecules.[26] Intense bands of the host at 559 and 805 cm^{-1} and a shoulder at 906 cm^{-1} are not affected by the intercalation of the oxyethylene compounds. It is obvious that the guest molecules are bonded to the host layers mainly by donor−acceptor oxygen−metal bonds. In addition, H-bridges via terminal OH groups of the guest molecules to the oxygen atoms of the host are present.

The increment of basal spacing for all intercalates containing two oxyethylene units per one formula unit of the host (7.2−8.2 Å) indicates either helical[14] or bilayer[11] arrangement of the PEG chains in the interlayer space. The lowest increment for the DEG intercalates can be connected with higher density of the OH groups and stronger bond interaction because of the H-bridges. Methylation of the oxyethylene unit in TPG leads to another increase of basal spacing of about 2 Å. This value is in good agreement with that calculated from the equation

$$\Delta l = l_{CC} + l_{CH} \sin \alpha = 1.88 \text{ Å} \qquad (1)$$

where $l_{CC} = 1.54$ Å is C−C bond length, $l_{CH} = 1.05$ Å is C−H bond length, and angle $\alpha = \angle CCH - 90° = 109.5 - 90 = 19.5°$. This increment of basal spacing supports the idea of the chain arrangement as a bilayer parallel to the host layers. The methyl groups of both parallel chains are arranged so that the resulting increment of basal spacing corresponds to one methyl group. This idea of the parallel arrangement is also supported by the fact that the similar monomolecular arrangement of the layers is indicated by the increment of basal spacing (3.6−3.7 Å) at the intercalates containing only one oxyethylene unit per formula unit.[11]

The monomolecular arrangement was not observed for the intercalates with TPG as inferred from the absence of the phase with basal spacing corresponding to that observed for the poly(oxyethylene) compounds (about 7.9 Å).

Two conditions must necessarily be fulfilled for PEG molecules to be anchored to the host layers by the oxygen atoms: (i) the oxygen atoms which are coordinated to the layer (central metal atoms) must be arranged at one side of the chain; and (ii) the distance between these oxygen atoms must be roughly the same as the distance between the central metal atoms in the host layer. For $VOPO_4$, $NbOPO_4$, and $NbOAsO_4$, this distance is equal to 6.22, 6.46, and 6.65 Å in the direction of the *a* axis of the tetragonal lattice or 8.80, 9.14, and 9.40 Å in the direction of the diagonal, respectively. The distance of two nearest oxygen atoms in the PEG chain is 3.48 Å when the chain is in an all-trans configuration, considering that only every other oxygen atom is placed at the same side of the chain. The distance of such two oxygen atoms is distinctly larger than the metal−metal distance in the direction of the *a* axis and distinctly smaller than the metal−metal distance in the direction of the diagonal. If the conformation of the PEG chain is cis, then the distance of two nearest oxygen atoms is 2.33 Å. Note that such a conformation tends to form chains in a circular or helical shape.

The chain is formed by freely rotating C−C bonds and therefore is able to adopt any arbitrary configuration between cis and trans conformation. For the PEG−kaolinite intercalate, for instance,[16] a rather complicated arrangement of the chain has been proposed, which allows all oxygen atoms to lie at one side of the guest structure with the O···O distance of 2.94 Å. This value is very close to that found for the distance between OH groups of the kaolinite layers.

In our case, it is presumed that the all-trans conformation of the PEG chain, which is the most favorable conformation, is affected by the coordination of the oxygen atoms of the guest to the M atoms of the host. The energy demands caused by the distortion of this all-trans conformation are more than satisfactorily compensated by the generation of donor−acceptor oxygen−metal bonds. Only every other oxygen atom is coordinated to the layer and lies at one side of the chain. Such arrangement is energetically less demanding than that in the case of the PEG−kaolinite intercalates. In addi-

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tion, in all-trans conformation, the oxygen−metal bonds would be sterically hindered by hydrogen atoms of neighboring methylene groups of the guest chain. From the comparison of the metal−metal distance in the direction of the diagonal and the *a* axis, we can assume that the axis of the chains is parallel to the *x* or *y* axes of the lattice. This leads to shifts in the layer packing and consequently to the formation of the above-mentioned turbostratic structure.

The absence of the monomolecular arrangement of the guest in the TPG intercalates can be explained by the following considerations: When the chain is coordinated to one $(MOXO_4)_\infty$ layer, then the methyl groups are arranged at the opposite side of the chain so that they hinder sterically the coordination of the remaining noncoordinated oxygens of the guest to the metal atoms of the host layer. In addition, owing to the hydrophobic nature, the methyl groups prefer an interaction with other methyl groups in the bilayer than an interaction with rather hydrophilic host layer in the monolayer arrangement. Accordingly, a phase with monomolecular arrangement is not formed during either preparation or thermal treatment of the product with bilayer arrangement.

Vanadyl phosphate dihydrate is known to be a mixed protonic−electronic conductor with prevailing protonic conductivity at room temperature. Its total conductivity determined using impedance spectroscopy is around 10^{-6} S·cm^{-1}. In $VOPO_4 \cdot 2H_2O$, the protonic conductivity is accomplished by protons formed by dissociation of water molecules present in the interlayer space. It was found for the $VOPO_4$−DEG intercalate that the total conductivity measured by impedance spectroscopy is much lower, around 10^{-7} S·cm^{-1}, and corresponds roughly to the conductivity of anhydrous $VOPO_4$. It is presumed from these facts that the OH groups, contrary to the H_2O molecules in $VOPO_4 \cdot 2H_2O$, do not contribute to the electric conductivity in these types of intercalates. This can be illustrated by a larger distance between OH groups which prevents a transfer of protons from one OH group to another. Therefore, the conductivity in the $VOPO_4$−DEG intercalate is purely electronic.

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