Intercalation of cyclic ketones into vanadyl phosphate

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Abstract

Intercalation compounds of vanadyl phosphate with cyclic ketones (cyclopentanone, cyclohexanone, 4-methylcyclohexanone, and 1,4-cyclohexanedione) were prepared from corresponding propanol or ethanol intercalates by a molecular exchange. The intercalates prepared were characterized using powder X-ray diffraction and thermogravimetric analysis. The intercalates are stable in dry environment and decompose slowly in humid air. Infrared and Raman spectra indicate that carbonyl oxygens of the guest molecules are coordinated to the vanadium atoms of the host layers. The local structure and interactions in the cyclopentanone intercalate have been suggested on the basis of quantum chemical calculations.
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Keywords: Intercalation; Vanadyl phosphate; Powder X-ray diffraction; Vibrational spectroscopy; Ab initio calculation

1. 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], aliphatic nitriles [8] belong to the compounds, which can be intercalated in such a way. Great attention was devoted to the intercalation of heterocyclic N- and S-donors [9–13]. Recently, intercalation of ketones [14,15], aldehydes [16], poly(ethylene glycol)s [17,18], heterocycles with O-donor [18–20], and γ-butyrolactone [21] into vanadyl phosphate has been described. These guests are anchored to the host layers by donor–acceptor bonds of their carbonyl or etheric oxygen 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 tetrahydrofuran intercalate

decomposes at about 160 °C [19]). It indicates that the host–guest interaction is very strong. Some of these intercalates are well crystalline solids and their diffractograms show, besides a series of sharp (00*l*) reflections, a number of (*hkl*) diffraction lines giving evidence of a regular structure.

The present paper reports the results of the intercalation of cyclopentanone, cyclohexanone, 4-methylcyclohexanone, and 1,4-cyclohexanedione into vanadyl phosphate.

2. Experimental

The propanol or ethanol intercalates were prepared by suspending microcrystalline $VOPO_4 \cdot 2H_2O$ in dry propanol or ethanol and subsequent short exposure to a microwave field. The intercalation compounds were obtained by displacing propanol or ethanol in $VOPO_4 \cdot 2ROH$ with the corresponding guest. The cyclopentanone intercalate was prepared by stirring the propanol intercalate (0.5 g) with cyclopentanone (20 mL) at room temperature overnight. The cyclohexanone and

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4-methylcyclohexanone intercalates were prepared by stirring the ethanol intercalate (0.5 g) with 20 mL of the guest at room temperature overnight. The intercalates prepared were filtered off, washed with diisopropylether, and dried in vacuo. The 1,4-cyclohexanedione intercalate was prepared by refluxing the ethanol intercalate in an acetonitrile solution of the guest for 15 min. The intercalate was filtered off, washed with acetonitrile and dried in nitrogen.

Powder data were obtained with a D8-Advance diffractometer (Bruker AXE, Germany) using $CuK\alpha$ radiation with secondary graphite monochromator. Diffraction angles were measured from 5° to 37° (2θ). The samples were covered with protection foil during the measurement.

TG analyses were performed using a Netzsch STA 449C. The measurements were carried out in air between 30 and 700 °C at a heating rate of 5 °C min^{-1}.

Infrared measurements in the range from 400 to 4000 cm^{-1} were made with a fully computerized Bruker IFS 55 EQUINOX FTIR Spectrometer with a DLATGS detector (256 scans per spectrum at 4 cm^{-1} resolution). Measurements of the intercalates were performed ex situ by an ATR technique using a Golden Gate^{TM} Heated Diamond ATR Top-Plate (Specac Ltd.) at ambient temperature. The spectrum of the corresponding liquid cyclopentanone was measured by an ATR technique on a ZnSe crystal. The spectra were corrected for the content of H_2O and CO_2 in the optical path.

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

Quantum chemical calculations were carried out at the ab initio and semiempirical levels of the theory employing Gaussian 98 [22] and MOPAC 2002 [23] program packages, respectively. Local interactions and structures in the intercalates of vanadyl phosphate with cyclopentanone were studied at a DFT level using a functional B3LYP with a basis set 6-31G(d). Geometrical optimizations of larger structures including two vanadyl phosphate layers were performed at a semiempirical level using the PM5 and AM1 methods.

3. Results and discussions

None of the cyclic ketones used can be intercalated directly in anhydrous vanadyl phosphate or VO-PO$_4 \cdot$2H$_2$O. All the intercalates can be prepared by replacing either propanol or ethanol in the corresponding VOPO$_4$ intercalate with the desired guest. The intercalates prepared were yellow crystalline solids, only the 4-methylcyclohexanone intercalate was greenish-yellow. This indicates that only a small part (less than 1 at % as follow from the vis spectra) of vanadium (v) was reduced during the intercalation of 4-methylcyclo-hexanone probably due to impurities present in the guest. The composition of the intercalates was determined by thermogravimetric analysis. During heating, the guest molecules are released in two steps. The product of the thermal decomposition is anhydrous vanadyl phosphate. Total weight losses correspond to the stoichiometric ratio x given in Table 1 together with the results of elemental analysis. The cyclopentanone, cyclohexanone, and 4-methylcyclohexanone intercalates contain one molecule of the guest per formula unit, the cyclohexanedione intercalate contains half of the guest molecule per formula unit.

The diffractograms (see Fig. 1) of the intercalates show a series of sharp (00l) reflections. Only weak (200) and/or (201) and (110) reflections can be seen in the diffractograms of the cyclopentanone, 4-methylcyclo-hexanone, and 1,4-cyclohexanedione intercalates. 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 mutually shifted in the directions of the x and/or y axes. The diffractogram of the cyclohexanone intercalate contain a number of the (hkl) diffraction lines (see Fig. 1b) giving evidence of a regular structure. These lines can be indexed using the c parameter as a double of the basal spacing. This is most likely caused by a mutual shift of the host layers by $a/2$. The lattice parameters of all the intercalates prepared are given in Table 1.

Table 1
Tetragonal lattice parameters and the guest content x in the intercalates prepared

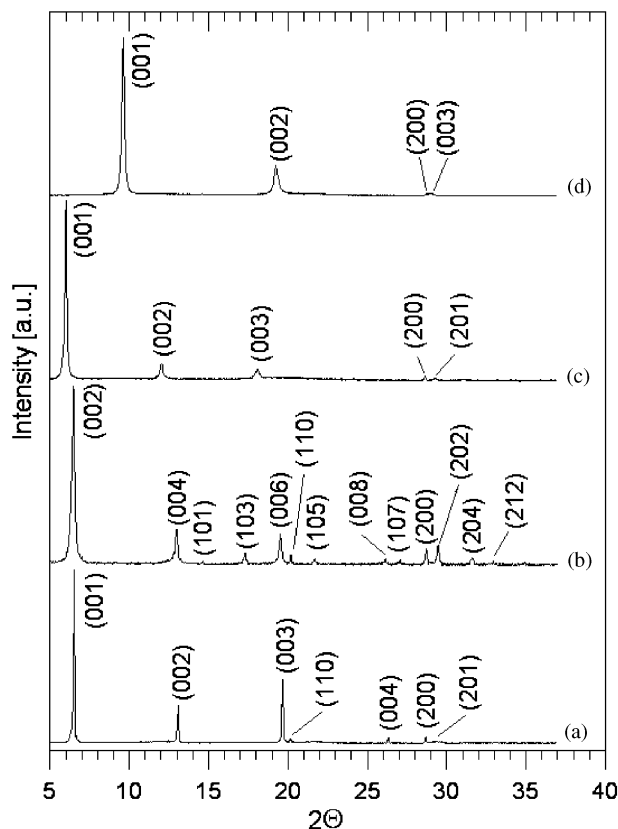| Guest	x	a (Å)	c (Å)	C%		H%	
				Found	Calculated	Found	Calculated
Cyclopentanone	1.05	6.221(2)	13.53(2)	24.50	24.21	4.30	4.06
Cyclohexanone	0.93	6.212(1)	27.258(7)	27.15	27.50	4.45	4.62
4-Methylcyclohexanone	1.00	6.234(3)	14.71(1)	30.10	30.45	5.22	5.11
1,4-Cyclohexanedione	0.55	6.218	9.24(1)	16.61	16.53	1.90	1.85

Fig. 1. The diffractograms of vanadyl phosphate intercalated with cyclopentanone (a), cyclohexanone (b), 4-methylcyclohexanone (c), and cyclohexanedione (d).
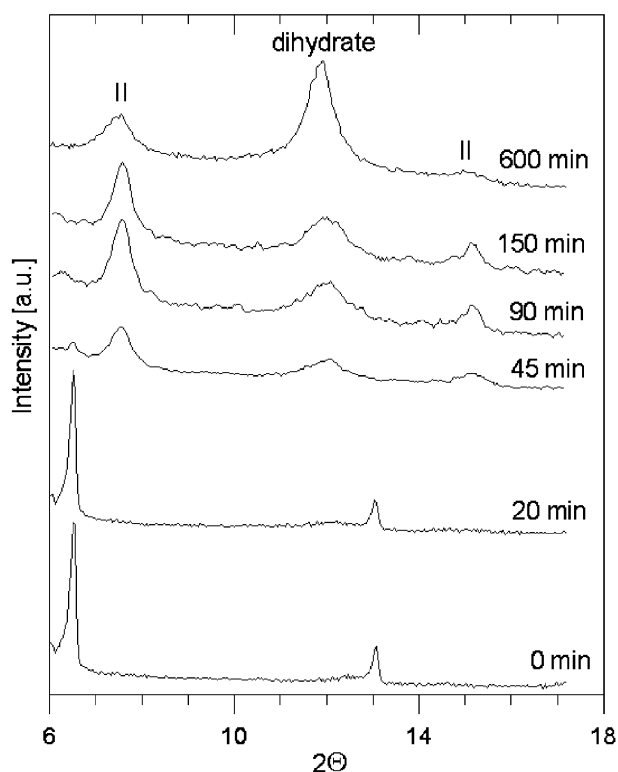

Fig. 2. Changes of the diffractograms of the cyclopentanone intercalate exposed to air (43% RH).

Fig. 3. FTIR spectra of vanadyl phosphate dihydrate, of pure cyclopentanone and of vanadyl phosphate intercalated with cyclopentanone after 5 min and 22 h in the purged spectrometer (5% RH), and after 22 h, 4 and 11 days at ambient conditions (60% RH) in the region from 2000 to 700 cm^{-1}.

The intercalates are not stable in air (at relative humidity (RH) higher than 40%). The guest molecules are gradually replaced by water molecules. At 30% RH, the intercalates are stable for several hours. The cyclohexanedione intercalate is the most stable one, the 4-methylcyclohexanone intercalate is the least stable one. The stability of the cyclopentanone intercalate was studied in detail. It is stable for several days at 33% RH and lower. The diffractograms measured during its hydration at 43% RH are given in Fig. 2. The (001) and (002) reflections of a new phase with basal spacing of 11.9 Å (marked II) appear very quickly together with a small amount of vanadyl phosphate dihydrate. Dihydrate become the prevailing phase after 600 min.

For the infrared measurements, the sample of vanadyl phosphate intercalated with cyclopentanone was placed in a purged sample compartment of the spectrometer (5% RH) for 5 min and for 22 h without removing the sample from the crystal between the subsequent spectral measurements. Another sample was exposed to ambient conditions (60% RH) for 22 h and for 4 and 11 days. Such conditions allow a progressive replacement of the cyclopentanone molecules in the vanadyl phosphate intercalate with atmospheric water. The infrared spectra of the intercalate in various stages of the deintercalation

process at ambient conditions were compared with the spectrum of vanadyl phosphate dihydrate and with the spectrum of pure cyclopentanone as seen in Fig. 3 (for the region from 2000 to 700 cm^{-1}) and in Fig. 4 (for the region from 4000 to 2500 cm^{-1}).

The Raman spectra of vanadyl phosphate dihydrate, vanadyl phosphate intercalated with cyclopentanone
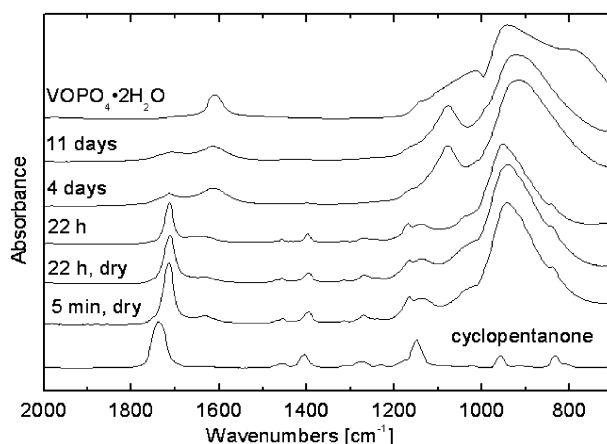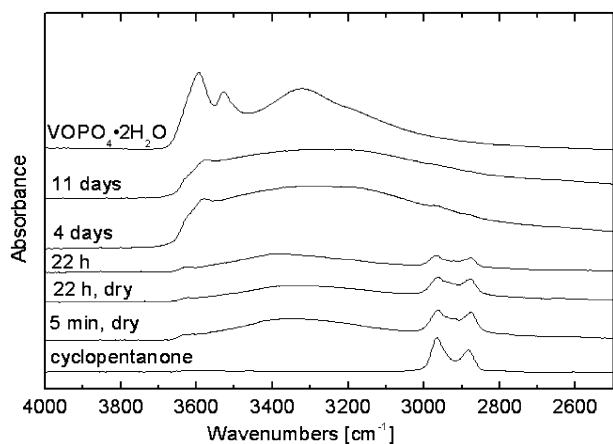
Fig. 4. FTIR spectra of vanadyl phosphate dihydrate, of pure cyclopentanone and of vanadyl phosphate intercalated with cyclopentanone after 5 min and 22 h in the purged spectrometer (5% RH), and after 22 h, 4 and 11 days at ambient conditions (60% RH) in the region from 4000 to 2500 cm^{-1}.
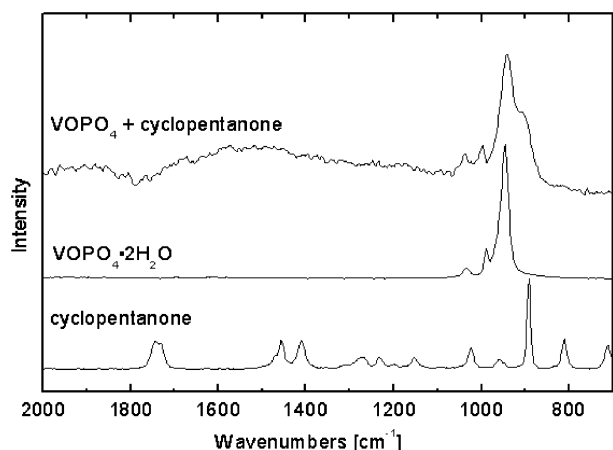

Fig. 5. Raman spectra of vanadyl phosphate dihydrate, of vanadyl phosphate intercalated with cyclopentanone and of pure cyclopentanone.

and pure cyclopentanone in the region from 2000 to 700 cm^{-1} are shown in Fig. 5. Unfortunately, it was not possible to measure the kinetics of the replacement of cyclopentanone by Raman spectroscopy, because a partial escape of the cyclopentanone molecules due to the laser beam occurs during the measurements. Besides, the Raman spectrum is influenced by a thermal emission of the sample, which is due to the excitation in the NIR range (1064 nm).

The bands of vibrations of the PO$_4$ tetrahedron, of the vanadyl group V = O, and the P–O–V group can be identified in all spectra. The intense band at 945 cm^{-1} in the Raman spectrum of vanadyl phosphate dihydrate (see Fig. 5) corresponds to the symmetric v(PO$_4$) stretching vibration of the phosphate tetrahedron in (VOPO$_4$)$_\infty$. This band is shifted to 940 cm^{-1} in vanadyl

phosphate intercalated with cyclopentanone. The sharp band at 995 cm^{-1} in the spectrum of vanadyl phosphate dihydrate came from a vanadyl V = O 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. During the intercalation of water molecules into VOPO$_4$, its position at 1035 cm^{-1} in the anhydrous form changes to 995 cm^{-1} typical for mono- and dihydrate [24]. This indicates a coordination of the oxygen atom of the water molecules to vanadium. In the Raman spectrum of the intercalate with cyclopentanone the band observed at 998 cm^{-1} corresponds most probably to the coordination of the oxygen atom of cyclopentanone to vanadium and the band observed at 1036 cm^{-1} to the anhydrous form of the host compound. With the help of the Raman spectrum, we can assign the band with the maximum at 942 cm^{-1} in the infrared spectrum (see Fig. 3) of vanadyl phosphate dihydrate to the symmetric v(PO$_4$) stretching vibration which is infrared active due to the distortion of the phosphate tetrahedron in the intercalate. The shoulder at 1015 cm^{-1} in the infrared spectrum is most probably the V = O stretching band of the vanadyl group. The band at 1142 cm^{-1} in the infrared spectrum of the host is the asymmetric v(PO$_4$) stretching vibration of phosphate tetrahedron. In agreement with the authors [25] the sharp bands near 3600 and 1620 cm^{-1} in the spectrum of VOPO$_4$·2H$_2$O are due to strongly bonded water molecules within the crystalline lattice associated with the water molecule bound to vanadium. The additional water molecules, which are bonded to the host layers by H-bonds, are indicated by a broadband near 3300 and 1620 cm^{-1} in the spectrum of the dihydrate. In the bending vibration at 1620 cm^{-1}, sharp and broadbands are superimposed. The positions of the main spectral bands of the host structure only slightly differ from those of anhydrous vanadyl phosphate or its hydrated form [24]. It confirms that the structure of the original VOPO$_4$ layers remains unchanged after the intercalation reaction.

Some of the bands observed in the spectrum of pure cyclopentanone are shifted in the spectrum of the intercalate (see Figs. 3 and 4). Especially, the band of the carbonyl stretching vibration observed at about 1739 cm^{-1} is shifted to 1714 cm^{-1} in the spectrum of the intercalate. The bands of the C–H stretching vibrations observed at 2965 and 2884 cm^{-1} are shifted to 2962 and 2876 cm^{-1}, the bands of the C–H deformation vibrations observed at 1407 and 1150 cm^{-1} are shifted to 1397 and 1166 cm^{-1} in the spectrum of the intercalate. Similar shifts of position of the C = O stretching vibration in infrared spectra were observed in the intercalates of vanadyl phosphate with other guests. Positions of this band for individual intercalates together with those of pure cyclic ketones are given in Table 2. On the basis of

Table 2
Wavenumbers of the $v(C=O)$ vibration in the IR spectra of the pure cyclic ketones and their intercalates

Guest	$v(C=O)$ (cm^{-1})	
	Pure guest	Intercalate
Cyclopentanone	1739	1714
Cyclohexanone	1713	1678
4-Methylcyclohexanone	1716	1676
1,4-Cyclohexanedione	1705	1681

the vibrational spectra, we suppose that the molecules of cyclic ketones are coordinated to the vanadium atoms of the host by their carbonyl oxygen atoms.

In the spectrum measured 5 min after taking out the sample from the ampoule and putting it in the purged sample compartment of the spectrometer (5% RH) we observe some sharp maximum at $3625\,cm^{-1}$, a broadband at $3350\,cm^{-1}$ and a band at $1629\,cm^{-1}$. These bands correspond to unbound water adsorbed on the surface during manipulation of the sample after its removal from the ampoule. These bands are more pronounced in the spectrum of the sample measured at ambient conditions (60% RH) after 22 h. The intensity of the bands of cyclopentanone is reduced during the exposition to ambient conditions for 4 and 8 days. At the same time, the sharp maximum at $3625\,cm^{-1}$ shifts to $3579\,cm^{-1}$ and the band observed at $1629\,cm^{-1}$ shifts to $1616\,cm^{-1}$. These new positions correspond to the spectrum of vanadyl phosphate dihydrate. The new maximum observed at $1080\,cm^{-1}$ in the spectrum of the intercalate after 4 and 8 days corresponds most probably to the asymmetric $v(PO_4)$ stretching vibration of the phosphate tetrahedron.

The character of the bonding between the guest molecules and the host layers in the cyclopentanone intercalate was investigated by the methods of quantum mechanical calculations and modeling. Fig. 6 shows a DFT optimized structure of the molecular segment representing local interactions of vanadyl phosphate with cyclopentanone, using a B3LYP functional and 6-31G(d) basis set. In order to keep the overall planar structure of the segment during full geometry optimizations and to make the electronic structure in the segment close to the conditions appearing in the intercalates, an oxygen atom was inserted between two neighboring PO_4 groups and terminal oxygen atoms were substituted by OH groups [21]. The total charge of the model compound was set to $+3$. It was found that all geometry optimizations with various starting orientations of cyclopentanone with respect to the vanadyl group lead to the structure displayed in Fig. 6 which indicates formation of the $C=O \rightarrow V$ bond in the intercalates.

The simulations of larger local intercalate structures including two $VOPO_4$ layers were performed using
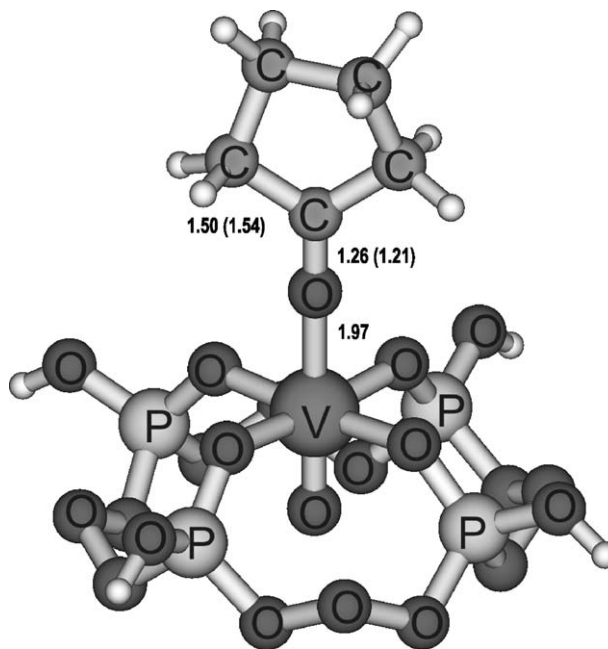

Fig. 6. Optimized B3LYP/6-31G (d) structure of the molecular segment modeling the vanadyl phosphate–cyclopentanone interaction with indicated bond lengths (in Å); the values in parentheses show the $C=O$ and C–C bond lengths in free cyclopentanone.

semiempirical PM5 and AM1 quantum-chemical methods. Adequacy of the semiempirical methods for the vanadyl phosphate intercalates was illustrated in previous studies of the intercalates in which the results of the modeling were in a very good agreement with experimental data obtained by X-ray, IR and Raman spectroscopy [21,26,27]. The model structure shown in Fig. 6 was also reoptimized with the PM5 and AM1 methods and only slight changes of parameters were found in comparison with the DFT method. The optimized geometries of the molecular segment representing two layers of $VOPO_4$ and five molecules of cyclopentanone intercalated between the two layers are shown in Fig. 7. Terminal oxygen atoms were substituted by OH groups and the total charge of the model compounds was set to -2. The coordinations of cyclopentanone molecules to the vanadium atoms in adjacent guest interlayer spaces were simulated by coordinations with 2-propanone molecules not shown in Fig. 7. The initial values of the bond lengths and angles for the $VOPO_4$ layers were taken from the previous study of the vanadyl phosphate intercalates with diethyl ether [27], the initial basal spacing was set to the above given value of the lattice parameter $c = 13.53\,Å$ determined by the X-ray diffraction and the structure and bonding of cyclopentanone were taken from the results of DFT calculations shown in Fig. 6. All the variables defining the positions of the atoms both in the host and guest layers were fully optimized with the exception of the constraints exposed by the symmetry
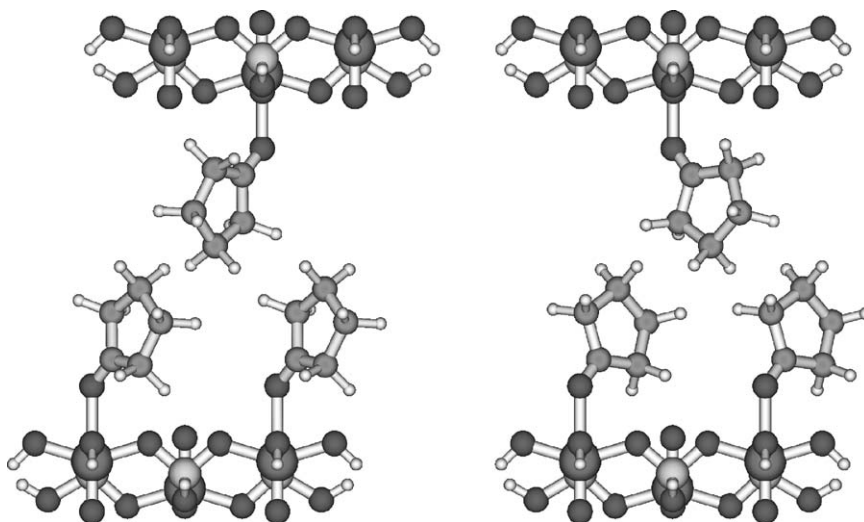
Fig. 7. Side views of the PM5 optimized geometry of the molecular segment modeling the arrangement of the cyclopentanone molecules between the VOPO$_4$ layers.
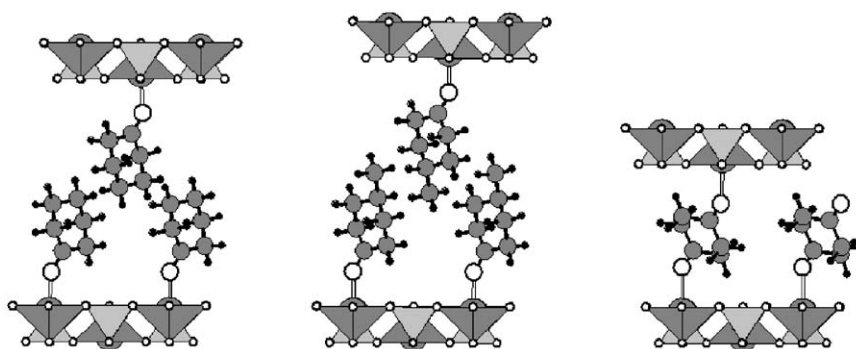

Fig. 8. Proposed arrangement of the guest molecules in the interlayer space of the cyclohexanone (a), 4-methylcyclohexanone (b), and 1,4-cyclohexanedione intercalates.

conditions defining polyhedra in the VOPO$_4$ layers and relative orientations of the guest molecules in the interlayer with respect to the VOPO$_4$ layer. The basal spacings calculated with the PM5 and AM1 methods are 13.28 and 13.21 Å, respectively, which is in a good agreement with the experimental value of 13.53 Å. The mutual positions of the successive tetragonal layers exhibit a shift characterized by a vector with calculated components of 0.02 and 2.44 Å obtained with the PM5 method and 0.08 and 2.35 Å with the AM1 method. This result complies with the absence of the (*hkl*) lines in the X-ray diffractograms of the intercalates, which is characteristic of a turbostratic structure.

Analogously to the arrangement of cyclopentanone, also arrangements of other cyclic ketones in the interlayer space of the host layers can be deduced. Taking into account the interlayer distance and assuming that the distance between the ketonic oxygen and the vanadium atom is the same as in the cyclopentanone intercalate, we proposed the structure of other inter-

calates as depicted in Fig. 8. For the cyclohexanone intercalate a slight interdigitation of the guest rings in the interlayer space can be presumed. This interdigitation is more pronounced in the case of the 4-methylcyclohexanone intercalate. For 1,4-cyclohexanedione the determined interlayer distance allows only a monomolecular arrangement of the host molecules, which due to the presence of two ketonic oxygens in the guest molecule, form pillars between the host layers.

Similarly as aliphatic ketones studied previously [14,15], the cyclic ketones studied are anchored to vanadium with their carbonyl oxygen. In contrast to the acetone and methylethylketone intercalates, no formation of an enol form was observed.

Acknowledgments

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