

FULL PAPER

## Molecular Mechanics Simulations in Structure Analysis of Intercalate $\text{VOPO}_4 \cdot 2\text{CH}_3\text{CH}_2\text{OH}$

Pavla Čapková<sup>1,2</sup>, Daniel Janeba<sup>1,2</sup>, Ludvík Beneš<sup>3</sup>, Klára Melánová<sup>3</sup>, and Henk Schenk<sup>2</sup>

<sup>1</sup>Department of Chemical Physics and Optics, Faculty of Mathematics and Physics Charles University Prague, Ke Karlovu 5, CZ-12116 Prague, Czech Republic. E-mail: {Capkova,Janeba}@karlov.mff.cuni.cz

<sup>2</sup>Laboratory of Crystallography, AIMS, University of Amsterdam, Nieuwe Achtergracht 166, NL-1018 WV Amsterdam, The Netherlands. E-mail: hs@crys.chem.uva.nl; paulac@stamp.chem.uva.nl

<sup>3</sup>Joint Laboratory of Solid State Chemistry, Academy of Sciences and University Pardubice, Studentská 84, CZ-53009 Pardubice, Czech Republic. E-mail: Benes@pol.upce.cz

Received: 26 January 1998 / Accepted: 15 April 1998 / Published: 30 April 1998

**Abstract** Molecular mechanics simulations using Cerius<sup>2</sup> combined with X-ray diffraction and supported with vibrational spectroscopy have been used to investigate the layered structure of vanadyl phosphate  $\text{VOPO}_4$  intercalated with ethanol. This intercalated structure exhibits certain degree of disorder, which affects the diffraction diagram and obstructs the conventional structure analysis based on diffraction methods only. Present structure analysis is focused to the crystal packing in the interlayer space and layer stacking in the intercalate. The bilayer arrangement of ethanol molecules in the interlayer has been found, giving the basal spacing  $d = 13.21 \text{ \AA}$ , experimental  $d$ -value obtained from X-ray diffraction is  $13.17 \text{ \AA}$ . One half from the total number of  $\text{CH}_3\text{CH}_2\text{OH}$  molecules is anchored with their oxygens to  $\text{VOPO}_4$  layers to complete vanadium octahedra and their orientation is not very strictly defined. The second half of ethanoles is linked with hydrogen bridges to the anchored ethanoles and sometimes also to the layer oxygens. Positions and orientations of these unanchored ethanoles with respect to  $\text{VOPO}_4$  layers exhibit certain degree of disorder, resulting in the disorder in layer stacking. Molecular mechanics simulations revealed the character of this displacement disorder in layer stacking and enabled to determine the components of the displacement vector.

**Keywords** Molecular mechanics, Structure of intercalates, Vanadyl phosphate

### Introduction

Intercalated phosphates of transition metals have been widely investigated from the viewpoint of their remarkable physico-

chemical properties. These compounds may find applications in many fields that range from the catalysis to ionic conductivity [1-3]. To understand the structure-properties relationship in these intercalated layered structures we have to focus the structure analysis to the crystal packing in the interlayer space, that means to the position and orientation of guest molecules, including the host-guest and guest-guest interactions.

Correspondence to: P. Čapková

*Why to use molecular simulations to investigate the structure of intercalated vanadyl phosphate?*

X-ray diffraction structure analysis is usually difficult in case of intercalated layered structures. The diffraction diagrams are very often affected by many effects like disorder in arrangement of guest molecules in the interlayer space and disorder in stacking of layers. As a result of this disorder, it is almost impossible to prepare the single crystal of reasonable size for the diffraction analysis. Powder diffraction pattern affected by the disorder is in addition influenced by the strong preferred orientation, as it is usual in powder samples of layered structures. In such a case the X-ray powder diffraction alone can not provide all the necessary structure parameters and molecular simulations represent very powerful tools in structure analysis.

In the present work we use the Crystal Packer module in the Cerius<sup>2</sup> modelling environment to investigate the structure of intercalate: VOPO<sub>4</sub>·2CH<sub>3</sub>CH<sub>2</sub>OH. The X-ray powder diffraction measurements, supported by infrared and Raman spectroscopy have been used to create the strategy of modelling and to check the results. The structure of the host compound VOPO<sub>4</sub>·2H<sub>2</sub>O has been determined by Tietze [4] from single crystal X-ray diffraction data as a tetragonal, space group P4/nmm with a=6.202 Å, c=7.41 Å and z=2. Tachez et al. [5] presented the structure refinement of the deuterated compound VOPO<sub>4</sub>·2D<sub>2</sub>O based on neutron powder diffraction data: space group P4/n, a=6.2154(2) Å and c=7.4029(7) Å. The host structure of vanadyl phosphate consists of infinite sheets of distorted VO<sub>6</sub> octahedra and PO<sub>4</sub> tetrahedra linked by shared oxygen atoms. Shared water molecules link

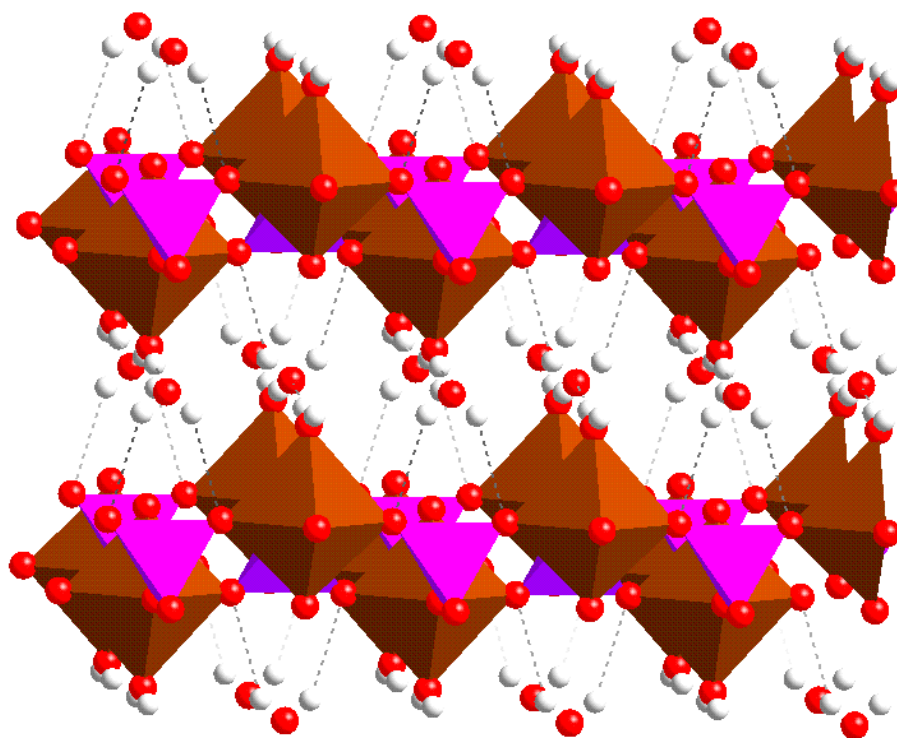
these sheets together. The host structure of vanadyl phosphate dihydrate according to Tachez et al. is illustrated in Figure 1.

### Experimental basis for the strategy of modelling

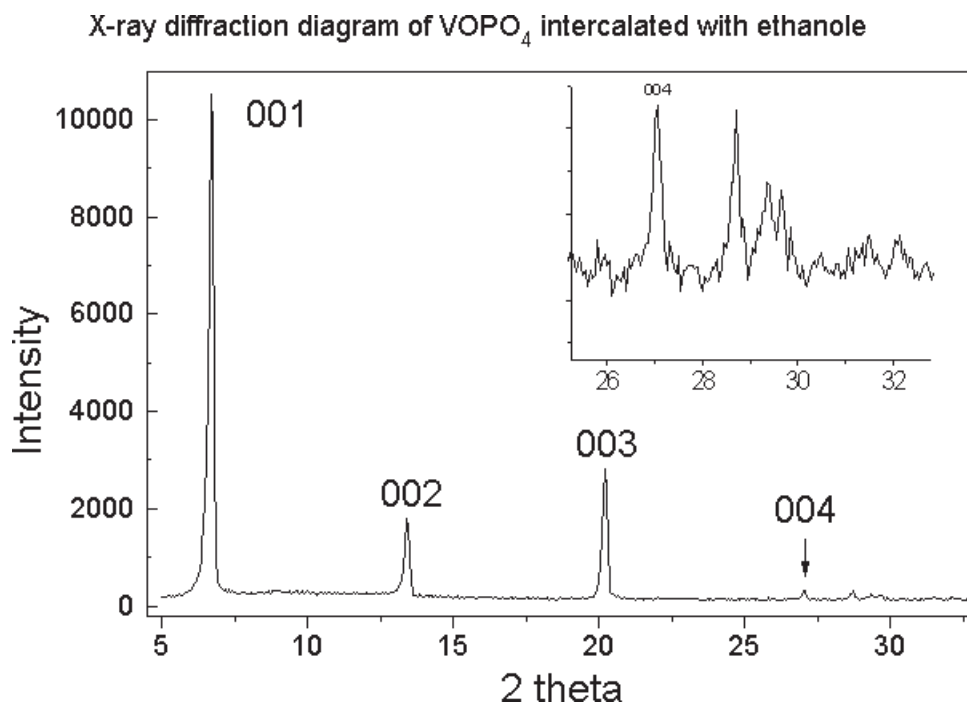
To create the strategy of modelling, i.e. the set up energy expression, the choice of the forcefield, the set up minimization conditions (assignment of constraints and rigid units), one has to consider the nature of host-guest and guest-guest interactions and consequently the possible changes of host resp. guest structures after intercalation. In the present study we based the strategy of modelling on the available experimental data. In spite of the low information content of powder diffraction pattern from intercalated layered structures, the limited number of parameters obtained from these data is very important for the strategy of modelling and also for the interpretation of the modelling results. In particular, if there is an evidence for a structure disorder in the diffraction diagram, the results of modelling can reveal the character and degree of this disorder. The character of host-guest interactions can be derived from IR resp. Raman spectroscopy, using comparison of spectra for host structure, intercalated structure and intercalating species.

Vanadyl phosphate dihydrate was obtained by long term boiling of vanadium pentoxide suspension in aqueous phosphoric acid, according to Ladwig [6]. Vanadyl phosphate intercalated with ethanol VOPO<sub>4</sub>·2CH<sub>3</sub>CH<sub>2</sub>OH was prepared by suspending microcrystalline VOPO<sub>4</sub>·2H<sub>2</sub>O in dry ethanol

**Figure 1** The layered host structure of VOPO<sub>4</sub>·2H<sub>2</sub>O



**Figure 2** X-ray powder diffraction pattern of intercalate  $\text{VOPO}_4 \cdot 2\text{CH}_3\text{CH}_2\text{OH}$ . The enlarged angle region  $2\theta = 25\text{--}33^\circ$  shows the presence of very weak and broaden  $hkl$  reflections



and subsequent short exposure (0.5-1 min) to a microwave field (2450 MHz). For more details see Beneš et al. [7,8]. X-ray diffraction data were obtained with the HZG4 diffractometer, using Ni-filtered radiation  $\text{CuK}\alpha$ . The samples for X-ray diffraction were left wet with a small residue of the ethanole and covered with Mylar foil to prevent powder particles from the exposure to the open air.

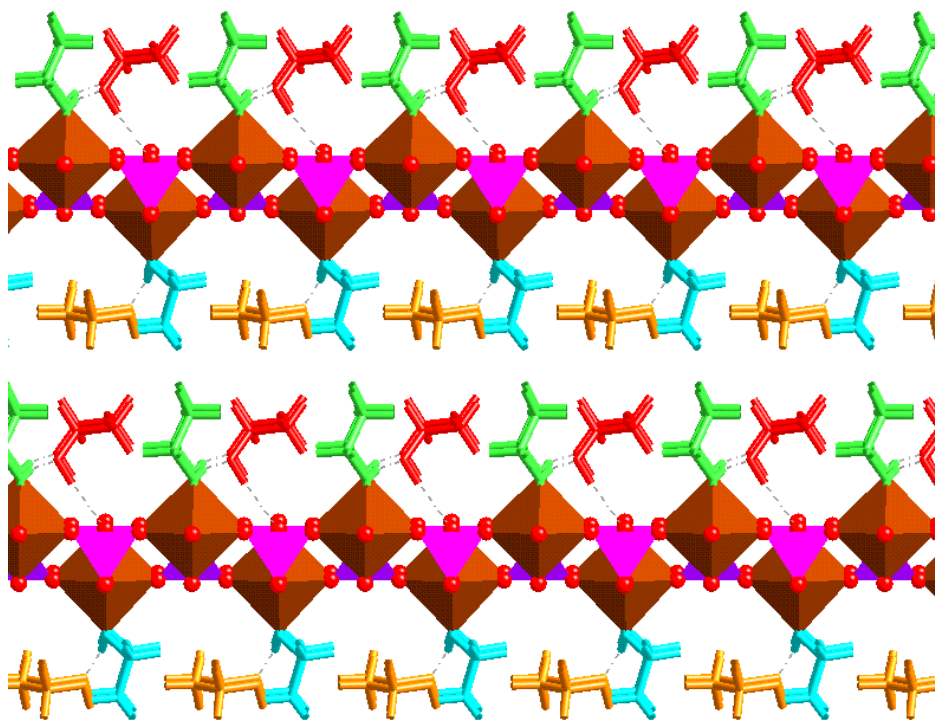
The diffraction diagram for the intercalate  $\text{VOPO}_4 \cdot 2\text{CH}_3\text{CH}_2\text{OH}$  is shown in the Figure 2. The strong basal reflections  $00l$  up to the 9th order have been observed, giving the basal spacing  $d=13.17 \text{ \AA}$ . This value suggests the bilayer arrangement of the ethanole molecules in the interlayer space. In spite of the strong preferred orientation of disk-shaped particles, there are still some very weak  $hkl$  reflections present in the diffraction diagram, (see Figure 2 - upper corner), showing a certain degree of ordering in the layer stacking. However the broadening of  $hkl$  reflections indicate the displacement disorder in layer stacking. This disorder resulting in line broadening and shift of certain reflections obstructs the indexing of powder pattern and assigning the space group. In such a case molecular simulations enable us to estimate the direction and length of layer displacement vector.

Comparison of the infrared and Raman spectra for the host structure  $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ , the intercalating species  $2\text{CH}_3\text{CH}_2\text{OH}$  and the intercalate  $\text{VOPO}_4 \cdot 2\text{CH}_3\text{CH}_2\text{OH}$  led us to the conclusion, that there are no significant distortions neither in  $\text{VOPO}_4$  layers nor in ethanole molecules. Consequently these both fragments in the intercalated structure can be treated as rigid units during energy minimization with nonbond mutual interactions, that means the Crystal Packer module in the Cerius<sup>2</sup> modeling environment can be used for structure analysis of  $\text{VOPO}_4 \cdot 2\text{CH}_3\text{CH}_2\text{OH}$ .

### Strategy of modelling

Crystal Packer is a computational module in Cerius<sup>2</sup> modeling environment that assists in the estimation of the total sublimation energy and packing of molecular crystals. Crystal Packer (version3.5) has its own force field library for VDW parameters containing: (1) Dreiding force field [9], (2) Universal force field and (3) Tripos force field. The preliminary tests showed, that the use of Dreiding force field gives the best agreement of calculated basal spacing with the experimental value, obtained from x-ray diffraction. The problem is, that there are no parameters for vanadium in the Dreiding force field. This problem has been solved by editing the force field and including VDW parameters for vanadium, taken from the Universal force field into the Dreiding force field. As the comparison of the calculated and measured basal spacing showed that, there is good agreement, this parametrization has been accepted as a reasonable approximation. Energy calculations in Crystal Packer take into account the nonbond terms only, i.e. van der Waals interactions (VDW), Coulombic interactions (COUL), hydrogen bonding (HB), internal rotations and hydrostatic pressure. The asymmetric unit of the crystal is divided into fragment-based rigid units. Nonbond (VDW, COUL, H-B) energies are calculated between the rigid units. During energy minimization, the rigid units can be translated and rotated and the unit cell parameters varied. Energy term consisting of VDW, COUL and HB interactions was set up using the following parameters: Non-bond cut-off distance for the VDW interactions was  $7.0 \text{ \AA}$ , that means VDW interactions between atoms further apart than this distance are ignored. Ewald sum constant was  $0.5 \text{ \AA}^{-1}$ . Minimum charge taken into Ewald sum was

**Figure 3** The bilayer arrangement of ethanol molecules in the interlayer space of vanadyl phosphate



0.00001e. All atom pairs with separation less than 10.0 Å are included in the real-space part of the Ewald sum. All reciprocal-lattice vectors with lengths less than  $0.5 \text{ \AA}^{-1}$  are included in the reciprocal part of the Ewald summation. Hydrogen bonds with maximum hydrogen - acceptor distance 2.5 Å and minimum donor - hydrogen - acceptor angle  $90^\circ$  have been included into energy calculations.

The initial model of intercalated structure has been built using the known structure of the host compound and intercalated species, that means 2 formula units  $\text{VOPO}_4 \cdot 2\text{CH}_3\text{CH}_2\text{OH}$  and consequently 5 rigid units per one unit cell. The initial cell parameters were  $a=b=6.21 \text{ \AA}$ . The c-parameter in the initial model  $c=14 \text{ \AA}$  should be larger than that estimated from diffraction data, in order to allow the manipulation with intercalating species in the interlayer. In minimizing a very low density cell, the intermolecular distances may be larger than the nonbond cutoff distance and no attractive inter-unit forces are calculated. However, by applying an external pressure at the start of minimization one can bring the rigid units into closer contact. The external pressure 50 kbar has been applied for the first minimization and then the external pressure was removed and new minimization started. Supposing the rigid  $\text{VOPO}_4$  layers, the cell parameters  $a$ ,  $b$  and  $\gamma$  were fixed during energy minimization and variable parameters were:  $c$ ,  $\alpha$  and  $\beta$ .

The Charge Equilibration Method (QEq), available in Cerius<sup>2</sup>, has been used to calculate the atomic charges [10]. Preparing the initial model for Crystal Packer, one has to set up the intercalating species very close to their real positions on the host structure layers and this is in fact the crucial con-

dition for a successful structure analysis. That means, the careful charge mapping of host layers and guest molecules is strongly recommended for the building of the correct initial model.

## Results and discussion

### Crystal packing in the interlayer space

The results of energy minimization for the series of initial models led to the bilayer arrangement of the ethanol molecules in the interlayer space, illustrated in Figure 3. As one can see from this figure, one half from the total number of ethanol molecules, is anchored with their oxygens to the vanadium, to complete the vanadium octahedra instead of  $\text{H}_2\text{O}$  oxygens in the host structure. (Compare Figures 1 and 3.) The values of basal spacings obtained as a result of energy minimization for a series of initial models are within the range  $d = 13.18 - 13.24 \text{ \AA}$ , giving the average value 13.21 Å. The corresponding values of the total sublimation energy  $E_s$  per one unit cell range from 161.34 to 162.18 kcal. The complete sets of parameters for two examples of minimized models: Model-I and Model-II are summarized in Table 1. As one can see from Table 1, the main contribution to the total sublimation energy comes from the Coulombic interactions and the energy and  $d$ -values are nearly the same for two models with different cell angles  $\alpha$  and  $\beta$ . This is the clear evi-

**Table 1** Results of energy minimization for two models of  $\text{VOPO}_4 \cdot 2\text{CH}_3\text{CH}_2\text{OH}$ . The contributions of VDW, COUL and HB energy to the total sublimation energy  $E_s$ , basal spacing  $d$  and the cell parameters :  $c$ ,  $\alpha$ ,  $\beta$  are presented for Model-I and Model-II. (Cell parameters  $a=b=6.21\text{\AA}$  and  $\gamma=90^\circ$  were fixed during energy minimization). The components of the displacement vector  $\sigma$  in  $\mathbf{a}$  and  $\mathbf{b}$  directions  $\sigma_a$  and  $\sigma_b$  are given in the last two lines

MODEL	Model-I	Model-II
VDW (kcal/mol)	15.83	14.41
COUL (kcal/mol)	140.82	139.02
HB (kcal/mol)	4.69	8.75
$E_c$ (kcal/mol)	161.34	162.18
$d$ ( $\text{\AA}$ )	13.18	13.24
$c$ ( $\text{\AA}$ )	13.52	15.40
$\alpha$ ( $^\circ$ )	77.95	91.94
$\beta$ ( $^\circ$ )	85.16	59.39
$\sigma_a$ ( $\text{\AA}$ )	2.04	1.63
$\sigma_b$ ( $\text{\AA}$ )	0.29	0.52

dence for the disorder in layer stacking, which will be analysed in the next chapter.

Figure 4 shows the positions of ethanole molecules adjacent to  $\text{VOPO}_4$  layers from the direction perpendicular to the layers. One can see from Figure 4 that the anchored ethanoles (green) have their oxygens (green balls) placed just in the apex of vanadium octahedra. The rest of ethanole molecules (red) - not anchored directly to  $\text{VOPO}_4$  layers, (further denoted as free ethanoles) - are placed in the middle of the cavities, created by anchored ethanoles. It is also evident from Figures 3 and 4 that the anchored ethanoles are almost in

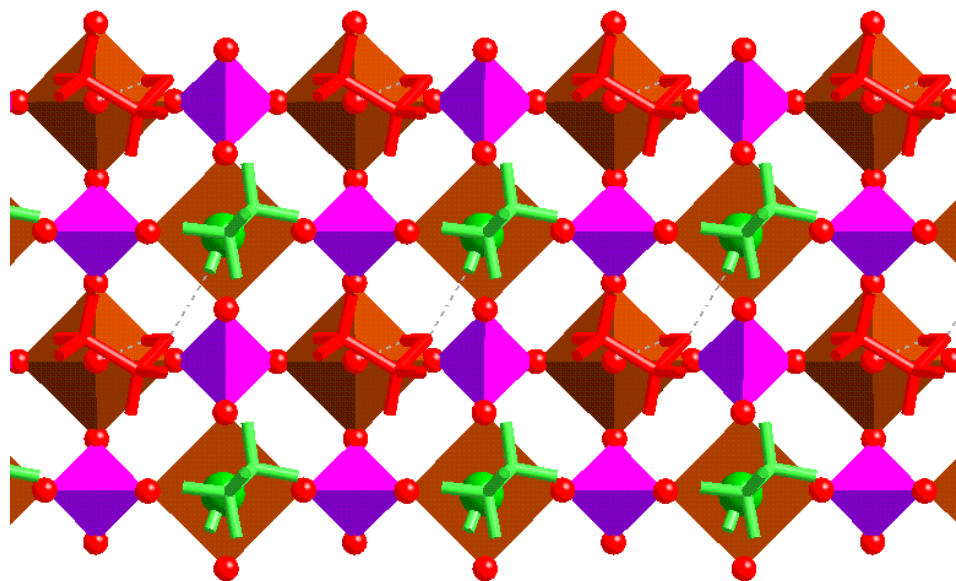
stand-up positions with respect to layers, while the free ethanoles (yellow and red) are lying with their C-C bonds nearly parallel to the layers. Free ethanoles are linked with hydrogen bridges to that anchored ones and in some cases also to the layer oxygens.

It is obvious from the way of arrangement and bonding of  $\text{CH}_3\text{CH}_2\text{OH}$  molecules to the layers that there will be a certain degree of disorder in their positions and orientations. One can also conclude from Figures 3 and 4 that in case of free ethanole, their positions are not strictly defined. One can also notice, that there are no strict rules for the orientation of both ethanole molecules (anchored and free). There is in fact only one strict rule for the ethanole position on the  $\text{VOPO}_4$  layer: the anchoring of ethanole oxygens in the apex of vanadium octahedra.

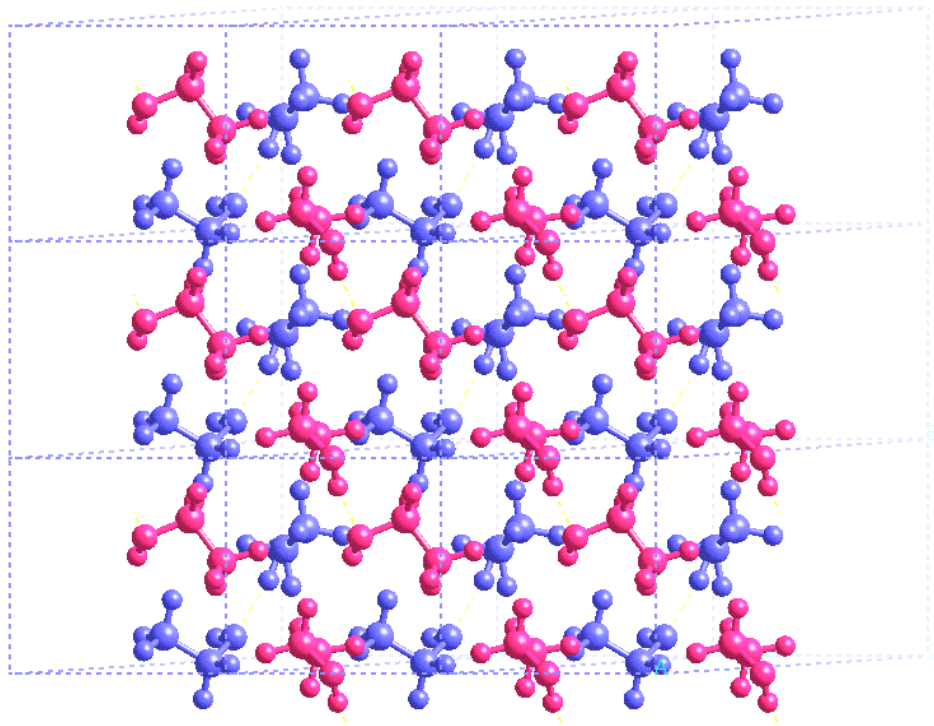
Taking into account only the non-bond host - guest interactions, we are neglecting the  $\text{V-O}_e$  bonding forces between the vanadium and ethanole oxygen  $\text{O}_e$ . The possible error caused by this approximation should be noticeable in the  $\text{V-O}_e$  distance. The  $\text{V-O}$  distance  $d(\text{V-O}) = 2.233(5)\text{\AA}$  has been determined for the host structure  $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$  by Tietze (1981) from X-ray single crystal diffraction. The average  $d(\text{V-O})$  value  $2.38\text{\AA}$  obtained from present modelling is slightly higher than that in the host structure, what can be also explained with the lower oxygen charge ( $-0.62e$ ) in ethanole than in water molecule ( $-0.81e$ ). Anyway the comparison of experimental ( $13.17\text{\AA}$ ) and calculated ( $13.21\text{\AA}$ ) basal spacings shows, that the possible error arising from the omitting of  $\text{V-O}_e$  bond interaction is not significant.

To visualize the packing of  $\text{CH}_3\text{CH}_2\text{OH}$  in the interlayer, we present in Figures 5a,b only the ethanole molecules in bilayer arrangement in the interlayer, with deleted  $\text{VOPO}_4$  layers, for two models presented in Table 1: Model-I (a), Model-II (b). In view perpendicular to the layers one can see the homogeneous distribution of intercalating species, in both

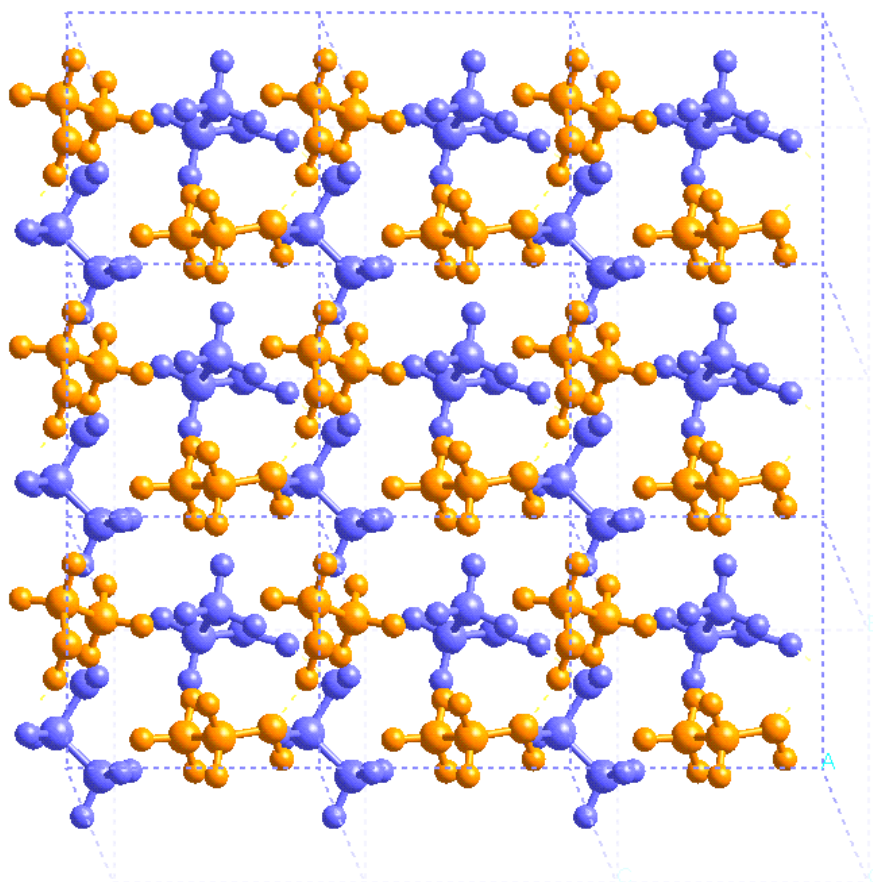
**Figure 4** Positions of ethanole molecules adjacent to  $\text{VOPO}_4$  layers. The green ethanoles are anchored to vanadium, with their oxygens (green balls) in the apex of vanadium octahedra. The vanadium octahedra below the red ethanoles, partially immersed in  $\text{VOPO}_4$  are oriented with their  $\text{V=O}$  bonds towards to the red ethanoles

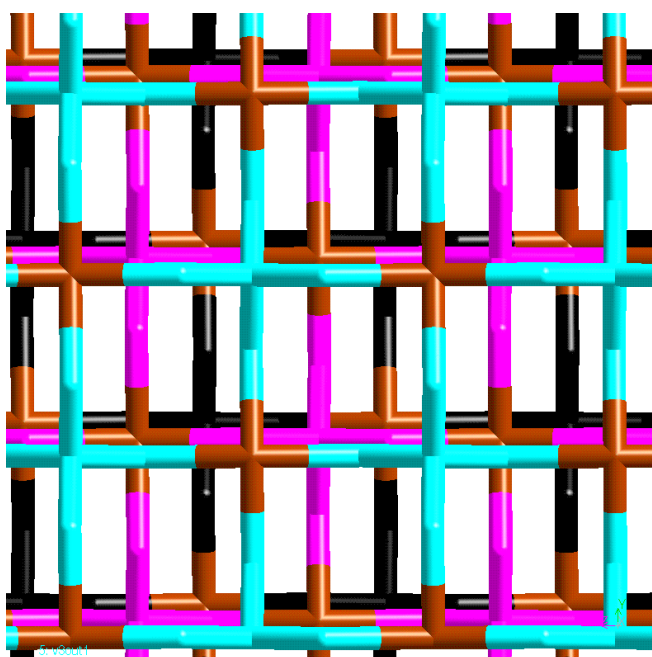


**Figure 5a** Two layers of ethanole molecules in the interlayer space for Model-I (a). Host layers were deleted for clarity. The lower layer of ethanols is drawn in blue color, upper layer is yellow

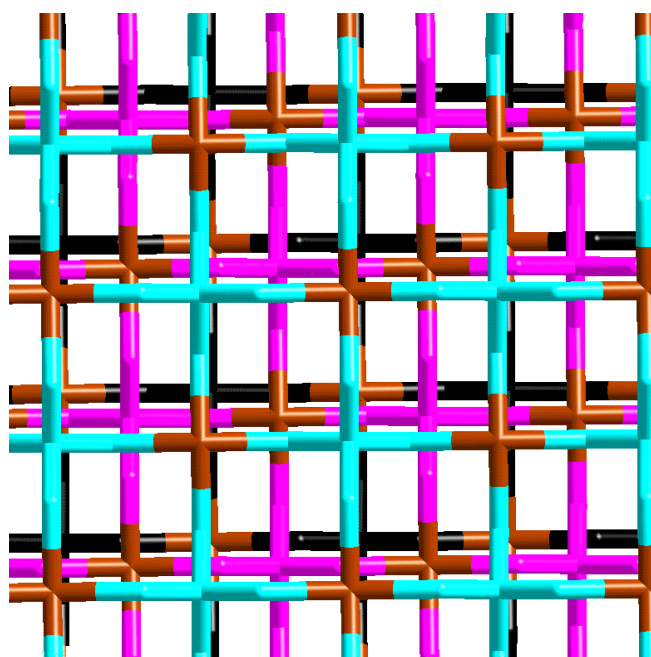


**Figure 5b** Two layers of ethanole molecules in the interlayer space for Model-II in the view perpendicular to the layers. Host layers were deleted for clarity. The lower layer of ethanols is drawn in blue color, upper layer is pink





**Figure 6a** Illustration of the layer stacking for Model-I. The ethanoles were deleted from the interlayer. View - perpendicular to layers. Vanadium atoms - brown,  $PO_4$  groups are black, magenta and blue in 3 successive  $VOPO_4$  layers



**Figure 6b** Illustration of the layer stacking for Model-II. The ethanoles were deleted from the interlayer. View - perpendicular to layers. Vanadium atoms - brown,  $PO_4$  groups are black, magenta and blue in 3 successive  $VOPO_4$  layers

minimized models, where the blue color marks the ethanoles in the lower layer. It is clear from the comparison of Figures 5a,b that the orientation of ethanole molecules may be different in different models, resulting in nearly the same d-values and total crystal energy (see Table 1).

#### Layer stacking in the intercalated structure

The stacking of layers in the intercalate  $VOPO_4 \cdot 2CH_3CH_2OH$  is ruled by two factors:

- the positions and orientations of ethanoles with respect to  $VOPO_4$  layers (see Figure 4)
- the alternation of upper and lower ethanoles in the two-dimensional arrangement in the interlayer (see Figures 5a, 5b) Two models presented in Table 1, with different cell angles and with nearly the same sublimation energy exhibit only slightly different layer stacking (see Figures 6a-b). This disorder is a natural consequence of the disorder in positions and orientations of ethanole molecules in the interlayer, which can be seen from Figures 3 and 4. Figures 6a and 6b illustrate schematically the stacking of layers in two models from Table 1: Model-I (6a) and Model-II (6b). For transparency, the ethanole molecules have been deleted in Figures 6a,b, and three successive layers with brown vanadium and black, magenta and blue  $PO_4$  groups are shown in view perpendicular to the layers. Comparing Figures 6a and 6b one can see that the different layer stacking in both models, exhibits certain common features. The displacement vector  $\sigma$  has in both cases

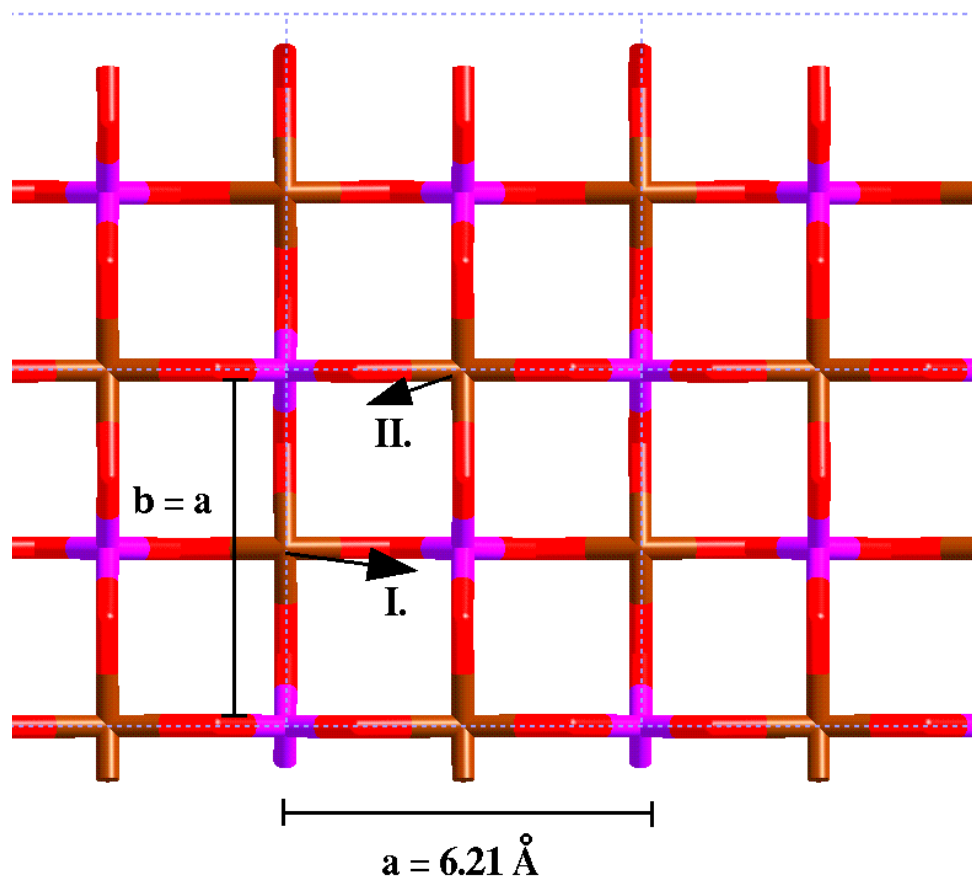
the predominant component in **a**, resp. **b** direction in the tetragonal lattice of the host structure, with the small component in perpendicular direction. Both models in figures 6a,b represent the limiting values, found for the components of the displacement vector  $\sigma$ :  $\sigma_a = 1.63 - 2.04 \text{ \AA}$  and  $\sigma_b = 0.29 - 0.52 \text{ \AA}$ . The displacement vectors for both models Model-I and Model-II are illustrated in Figure 7. As the displacement vector is determined by the two rules for layer stacking, mentioned above, the magnitude of the displacement vector is given by the van der Waals thickness of  $CH_3CH_2OH$  molecule in the  $\sigma$  direction. Due to the disorder in positions and orientations of ethanole molecules, described above, the directions and magnitudes of the displacement vectors  $\sigma$  may vary within the limits given in Figure 7.

#### Conclusions

Molecular mechanics simulations combined with X-ray powder diffraction and supported by vibrational spectroscopy has been found as a powerful tool in structure analysis of intercalated layered structures. There are two main advantages of this combined structure analysis:

- It provides the detailed insight into the structures exhibiting the disorder, which can obstruct the normal structure analysis based on diffraction method alone. As a result of combined structure analysis, we obtained the structure model including the qualitative and quantitative characterization of

**Figure 7** Displacements vectors  $\sigma$  (black arrows) showing the shift of two successive VOPO<sub>4</sub> layers in intercalate VOPO<sub>4</sub>·2CH<sub>3</sub>CH<sub>2</sub>OH for two models Model-I and Model-II



disorder, which would be hardly attainable from the diffraction diagram presented in Figure 2.

• Besides the detailed structure model, we are able to analyse the crystal energy, i.e. in our case the van der Waals, Coulombic and hydrogen bonds contributions to the total sublimation energy. Experimentally based strategy of modelling assuming the rigid layers of host structure and rigid intercalating species and nonbond host-guest and guest-guest interactions led to the results, which agree with the available (limited) parameters and informations obtained from the experiment. That means the approximations used in present work represent a reasonable compromise between the computational efficiency and the desired accuracy in structure analysis.

**Acknowledgement** We are grateful to professor J. Votinský from University Pardubice for the fruitful discussions. This work was supported by the grant agency GACR, grant no: 203/97/1010 and 203/96/0111 and grant agency GAUK, grant no: 37/97/B.

## References

1. Clearfield, A. (Ed.) *Inorganic Ion Exchange Materials* CRC-Press, Boca Raton, FL, **1982**, Chapters 1, 2, 3.
2. Clearfield, A. *Comments Inorg. Chem.* **1990**, 10, 89.
3. Alberti, G. in *Recent developments in Ion Exchange*; Williams, P. A. and Hudson, M. J. (Ed.), Elsevier Applied Science, London **1987**, pp 233-248.
4. Tietze, H. R. A. *J. Chem.* **1981**, 34, 2035.
5. Tachez, M.; Theobald, F.; Bernard, J.; Hewat, A. W. *Revue de Chemie Minerale* **1982**, 19, 291.
6. Ladwig, G. *Z. Anorg. Allg. Chem.* **1965**, 338, 266.
7. Beneš, L.; Melánová, K.; Zima, V.; Kalousová, J.; Votinský, J. *Inorg. Chem.* **1997**, 36, 2850.
8. Trchová, M.; Uhlířová, E.; Melánová, K.; Beneš, L.; Matějka P. *Inorganic Chemistry*, prepared for publication **1998**.
9. Mayo, L. S.; Olafson, B. D.; Goddard, W. A. *J. Phys. Chem.* **1990**, 94, 8897.
10. Rappé, A. K.; Goddard, W. A.; *J. Phys. Chem.* **1991**, 95, 3358.