



Review Article

Host–guest Complementarity and Crystal Packing of Intercalated Layered Structures

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Abstract

Intercalated layered structures are analyzed in order to estimate the rules governing their crystal packing. An overview is given on structural types of layered intercalates based on various types of host structures and guest species. The factors describing the host–guest complementarity in intercalated layered structures like: the character of active sites, the host–guest and guest–guest interactions, the size of guests and topology of layers are investigated and their effect on crystal packing is illustrated on examples. Special attention will be paid to the conditions for the regular ordering of guests in the interlayer space, as the requirement of structure ordering is of great importance in design of intercalates for special applications, where one has to control the interlayer porosity or electronic properties of guest molecules etc. A method of structure analysis based on a combination of molecular modeling and experiments has been worked out for intercalates. Molecular modeling (force field calculations) in conjunction with experiments (diffraction methods and vibration spectroscopy) enables us to analyze the disordered intercalated structures, where the conventional diffraction analysis fails.

Introduction

Intercalation means an insertion of a guest molecule or ion into a suitable crystal structure without major rearrangement of the solid host structure (Jacobson [1]). Intercalation requires that the host structure has a strong covalent network of atoms, which remains unchanged on the intercalation reaction and that there are vacant sites in the structure. These vacant sites should be interconnected and of suitable size to permit the diffusion of the guest species into the host structure. Layered crystal structures satisfy these requirements very well being able to accommodate very large guest molecules in the interlayer space by the free adjustment of the interlayer separations. A strong intralayer and weak interlayer bonding characterize layered structures. A survey of different types of layered host structures and a discussion of intercalation reactions for neutral and charged layers is given in [1–4].

Intercalation provides new routes for the synthesis of materials with controlled changes in the chemical and physical properties. These properties can be tuned by the proper choice of the host–guest combination, by the guest concentration and by co-intercalation of further guest species. This allows creating a large variety of structures for a wide scale of practical use. Intercalates can be used as adsorbents, catalysts, pharmaceutical products, chemical sensors,

ionic conductors and various kinds of electrochemical and opto-electronical devices [1–9]. Clearfield [6] formulated the conditions, necessary for the intercalation of layered structures:

- The interaction of the guest molecules with the host layers must be stronger than the mutual interactions of the molecules themselves,
- the surface of the layers should possess active sites with which the guest molecules can interact,
- the host layers must spread apart to accommodate the guest molecules and must not exhibit the steric hindrance to the free diffusion of the guests.

Intercalates obey the rules of host–guest complementarity like all other supramolecular systems [10–12]. This complementarity in case of intercalated layered structures can be characterized by a series of chemical and geometrical factors describing the character and arrangement of the active sites in the host layers, guest species and geometry of guest molecules and host layers. In the present paper we discuss the effect of factors describing the host–guest complementarity on the crystal packing of intercalates using a series of intercalates based on various types of host structures (zirconium and vanadium phosphates, clay minerals, graphite, tantalum sulfide).

An interplay of chemical and geometrical factors results in a crystal packing of intercalated structures, which may exhibit a certain degree of disorder, due to a departure

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from the perfect host–guest complementarity. The structural disorder, which is very often present in intercalates, can obstruct the structure analysis based only on diffraction methods. Therefore, in the present work we pay attention to the method and strategy of structure analysis of intercalates using a combination of molecular modeling (force field calculations) with experimentation (diffraction methods and vibration spectroscopy).

Structure analysis of layered intercalates

As the intercalation is an insertion of a known molecule into a known layered crystal structure, the structure analysis of layered intercalates has to solve specific problems:

- To determine the positions, orientations and arrangement of the guest molecules in the interlayer space of the host structure;
- To determine the possible changes in conformation of guest molecules due to the crystal field in the interlayer space of the host structure;
- To determine the way of layer stacking in the intercalated structure;
- To characterize a possible disorder in an intercalated structure;

Thanks to the disorder, which is very often present in intercalated structures, single crystals are not available for these materials and powder diffraction pattern affected by the disorder is in addition influenced by the strong preferred orientation of crystallites and by surface absorption due to the surface roughness effect [15]. Intercalation of organic guests into an inorganic host structure introduces an additional specific problem into the diffraction analysis of intercalates. Scattering amplitudes of guest atoms, i.e., carbon, oxygen and hydrogen, are small in comparison with the atoms building the inorganic host structures and consequently, the contribution of guest molecules to the total intensity diffracted from the crystal is too small. This fact complicates the precious localization of guests in the intercalated compounds. For disordered guest molecules, which in addition contribute very little to the diffracted intensities, the diffraction analysis fails. In such a case, the molecular modeling represents a very powerful tool in structure analysis of intercalates, providing that the modeling is combined with an experiment. As a convenient complementary experiment to molecular modeling one can use X-ray, synchrotron and electron diffraction, vibration spectroscopy (IR and Raman), NMR spectroscopy, STM and AFM microscopy etc. An experiment plays an important role in creating the modeling strategy and in confirmation of modeling results. The complex structure analysis using a combination of modeling and an experiment, can provide us with the detailed structure model, including the characterization of the disorder. In addition to the diffraction analysis, we get the total crystal energy, the sublimation energy and the host–guest and guest–guest interaction energy.

Modeling of intercalates

Molecular modeling (molecular mechanics) is a method of optimization of the structure and bonding geometry using minimization of the total potential energy of the crystal or molecular system. The energy of the system in molecular mechanics is described by an empirical force field [16]. Classical molecular dynamics calculates the dynamic trajectory of the system, solving the classical equations of motion for a system of interacting atoms [13, 16, 20]. The temperature and distribution of atomic velocities in the system are related through the Maxwell–Boltzmann equation. Molecular modeling of intercalates presented in this paper was carried out using empirical force field calculations in a *Cerius²/Materials Studio* modeling environment (MSI/Accelrys) [13] and program *SUPRAMOL* [14] for structure analysis of intercalates. In a *Cerius²* modeling environment the atomic charges are calculated using a Qeq (Charge equilibration) method [17] and the Ewald summation method [18, 19] is used to calculate the Coulomb energy.

All the computational methods searching for the global energy minimum have to generate the large number of initial models using three different ways [14, 16]:

1. Deterministic method for generation of starting models, performing the systematic grid search that covers all areas of the potential energy surface [14, 21, 22].
2. Molecular dynamics generating the starting geometry [13, 20].
3. Stochastic methods (Monte Carlo [20] Genetic Algorithm [23] ...)

In the modeling of intercalated structures we used the first two methods: the grid search using program *SUPRAMOL* [14] with the final energy minimization in *Cerius²* and molecular dynamics in *Cerius^s* [24, 25]. The first method, performing the systematic grid search can be used easily to generate starting models in the case of small organic guest molecules or almost rigid large guests and rigid host layers. On the other hand, molecular dynamics is a very convenient method for the generation of starting models in case of the large flexible organic guest molecules. The strategy of modeling (i.e., the building of the initial models, the set up of energy expression, the choice and test of the force field, the definition of rigid fragments, the set up of fixed and variable structure parameters etc.) should be based on the available experimental data.

Diffraction data and vibration spectroscopy in the modeling strategy

Although the powder diffraction data may be affected by a structural disorder, sample effects like the preferred orientation of crystallites and eventual surface roughness, it can always provide us with some information, which is useful for the strategy of modeling. At least we can get the basal spacing (interlayer distance) and the type of the disorder. In a more favorable case, we can even get the lattice parameters

of the intercalated structure. These experimental data are valuable in the building of the initial model for the energy minimization. Comparing the diffraction pattern for the intercalated and host structures, one can deduce the changes of structure after intercalation and consequently set up the most suitable modeling strategy (variable and fixed structure parameters, rigidity of the host layers etc.). The diffraction line profiles indicate a possible lattice strain and disorder in guest arrangement and in layer stacking due to the intercalation.

Comparing the three vibration (IR/Raman) spectra of: (1) the intercalate, (2) the pristine guest compound and (3) the host compound we can see a possible changes in the bonding geometry and conformation of guest molecules and host layers, which may occur during the intercalation [26, 27]. If the spectral bands corresponding to the host layers exhibit the same positions and profiles in host structure and intercalate, one can conclude, that there are no changes in bonding geometry of host layers during intercalation. This is very important conclusion for the modeling strategy, as in such a case the host layers can be treated as rigid units during energy minimization. The same conclusion can be derived for the guest molecules. In case of rigid host layers and rigid guests we obtain the IR spectrum for this intercalate as a superposition of the host structure and guest compound spectra [26]. The rigidity of host layers is the crucial assumption in the modeling of intercalates, as in case of inorganic, covalently bonded host layers we could hardly use the force field calculations to reveal possible changes in their bonding geometry.

Factors affecting the crystal packing of intercalated layered crystal structures

The host–guest complementarity governing the crystal structure of intercalates can be described by a series of factors, characterizing the mutual host–guest interactions and geometry of the host and guest structures in the pristine state:

- The nature of the active sites on the host layer and guest species, i.e., the charge distribution on the host layers and guest species, the type of functional groups, etc.
- The ratio between the host–guest and guest–guest interaction energy.
- The topology of host layers, i.e., the distances and ordering of functional groups, the presence of steric barriers for the diffusion of the guest molecules etc.
- The size and shape of the guest molecules, especially the ratio between the size of guests and distances of the active sites on the host layer.

Interplay of these factors leads to a large variety of intercalated structures with various degree of disorder depending on the host–guest complementarity. The effect of these factors on the crystal packing of layered intercalates will be analyzed in details in the following paragraphs.

Ordering in intercalated structures: The role of active sites

The requirement of structure ordering is of great importance in the design of new intercalates for special applications, where one has to control the interlayer porosity (selective adsorbents, molecular sieves) or to control photofunctions of guest molecules in the interlayer space, etc. It is evident that the regular arrangement of guests in the interlayer space is the necessary condition for the order in layer stacking. However, there is another factor affecting the structural order in intercalates. It is the rigidity of guest molecules and the host layers. Intercalation of organic molecules containing long aliphatic chains may lead to chain distortions, depending on the chain length and on the guest concentration in the interlayer space. This can be illustrated in the example of montmorillonite, intercalated with cetylpyridinium (CP) [24] and octadecylamine (ODAM) [25], see Figure 1a,b. Intercalation of cetylpyridinium into Na-montmorillonite is the ion exchange reaction, where the interlayer Na^+ -cations are replaced by the cetylpyridinium cations. The guest concentration in this case is given by the layer charge of montmorillonite. The structure of CP-montmorillonite is in Figure 1a [24], where one can see the liquid like arrangement of guests in the interlayer space. On the other hand, the intercalation of octadecylamine is based on the ion-dipole interaction, that means the polar organic molecules intercalate into the interlayer space of montmorillonite interacting with the negatively charged layers and interlayer cations Na^+ . In this case, the guest concentration is not limited with the layer charge. That means for sufficiently high concentration of guests, the aliphatic chains can be more ordered than in a liquid state, see Figure 1b [25]. Anyway the ordering of chains in this case does not mean the regular anchoring of the polar head groups to the host layers.

The intercalation of rigid organic molecules into a host structure with rigid layers can lead to the ordered intercalated structure, if all other chemical and geometrical factors act in concert. Structure of tantalum sulfide intercalated with methylene blue (MB) is the example of 3D ordered structure [28, 29], where the predominant electrostatic host–guest interaction results in the equilibrium position of the guest molecule shown in Figure 2. (Figure 2 shows the phase-I of MB-TaS₂ with the lowest guest concentration, for more details see [29]).

The presence and character of the strong active sites on the host layers and guest species, determine the way of anchoring guest molecules on the host layers. It is evident that the regular arrangement of strong pronounced active sites on the host layers creates favorable conditions for the ordering of guest molecules. However, it will be shown that the ordering of active sites is not sufficient and not even a necessary condition for the ordering of guests in the interlayer space of the host structure.

Vanadyl phosphate dihydrate $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ (Figure 3) represents very convenient host structure for the intercalation of organic molecules [31–36] with the regular network of strong active sites. The structure of vanadyl phosphate di-

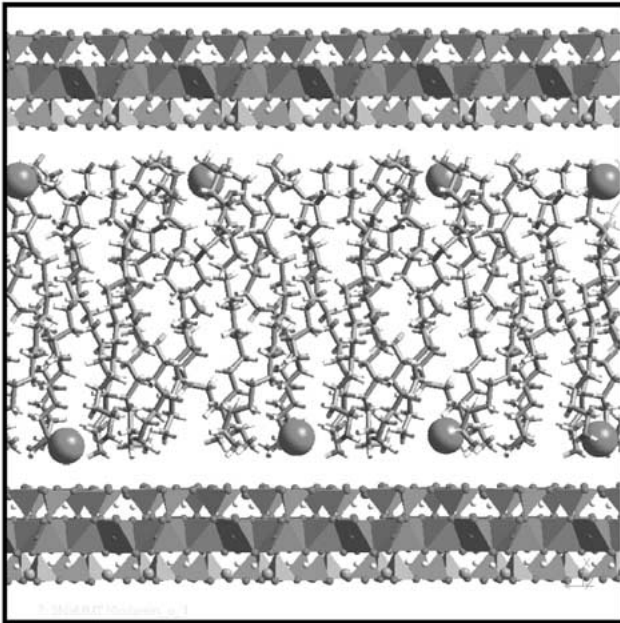
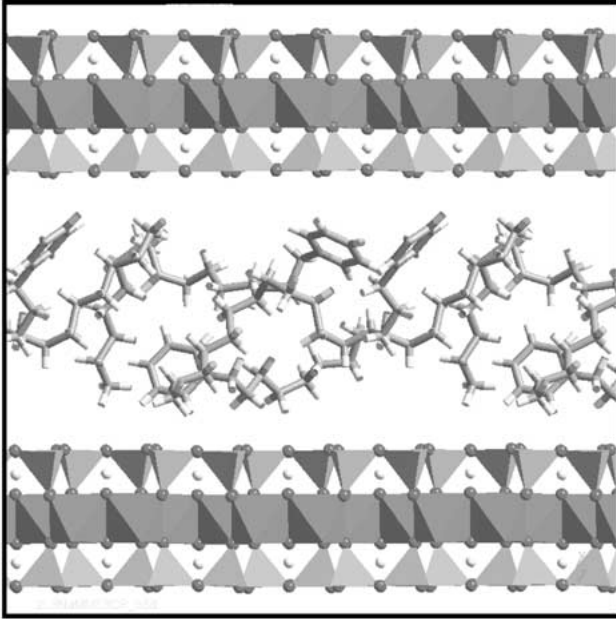


Figure 1. (a) Structure of montmorillonite intercalated with cetylpyridinium with liquid-like arrangement of the guest molecules in the interlayer space. The pyridinium headgroups are positioned at the silicate layer surface. (b) Structure of montmorillonite intercalated with neutral molecules of octadecylamine in partially ordered monolayer arrangement. Polar headgroups and Na-cations (small balls) are positioned at the silicate layer surface.

hydrate has been determined by X-ray single crystal diffraction [37] and refined using neutron powder diffraction data of deuterated compound $\text{VOPO}_4 \cdot 2\text{D}_2\text{O}$ [38]. Host layer consists of distorted VO_6 octahedra and PO_4 tetrahedra linked by shared oxygen atoms. Shared water molecules link the VOPO_4 layers together, creating the regular network of hydrogen bridges in the interlayer space (see Figure 3). When water molecules are removed from the interlayer space, vanadium atoms act as strong active sites for the molecules,

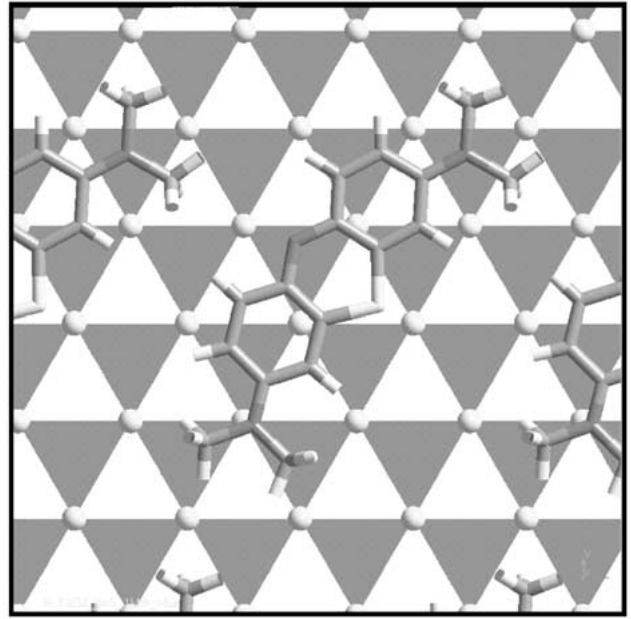


Figure 2. Top view of the arrangement of methylene blue (MB) cations on the tantalum sulfide layer for the phase I of MB-TaS_2 intercalate with the lowest MB concentration.

which can deliver their oxygen atom to complete vanadium octahedral coordination. Vanadium atoms on the lower and upper VOPO_4 layer create the regular network of active sites.

Almost perfect 3D ordering can be observed in the structure of vanadyl phosphate VOPO_4 intercalated with tetrahydrofuran (THF) and diethyleneglycol (DEG) [30], see Figures 4a–c. Both guest molecules, THF and DEG, are anchored with their oxygen to the vanadium atom in the host layer. Vanadium atoms represent the active sites on the host layer for the anchoring of the organic guest molecules via oxygen. Due to the tetragonal symmetry of the host layer VOPO_4 (4-fold axis in the V–O bond), the guest molecules can be positioned in two equivalent orientations with respect to the host layer, see Figures 4a–c. These two possible orientations of guest molecules introduce a certain degree of orientation disorder into these structures. Anyway, intercalated structures $\text{VOPO}_4 \cdot \text{THF}$ and $\text{VOPO}_4 \cdot \text{DEG}$, clearly illustrates the effect of guest size on the interlayer crystal packing. In both structures, the guest concentration is the same (one guest molecule per vanadium atom). The THF molecule is small enough to fit the distances between active sites (vanadium atoms) in the host layer and this favorable size factor, together with the character of the guest–guest interaction results in the mono-layer arrangement of THF molecules in the interlayer space of vanadyl phosphate (see Figure 4b). On the other hand, the DEG molecule is too large with respect to the distances of active sites and consequently the arrangement of guests in the interlayer space is bi-layer, see Figure 4c.

Intercalates $\text{VOPO}_4 \cdot \text{THF}$ and $\text{VOPO}_4 \cdot \text{DEG}$, show that 3D-ordered intercalated structure can exist, if the guest molecules fit the regular network of active sites and the cooperation of host–guest and guest–guest interaction keeps the guest molecule in well-defined positions and orienta-

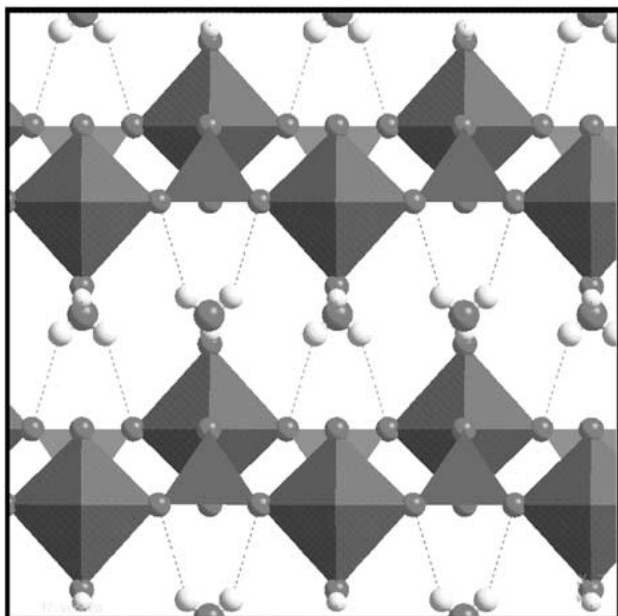


Figure 3. The side view of the host structure $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$. The network of hydrogen bonds is marked by dotted lines.

tions. On the other hand, the vanadyl phosphate intercalated with ethanol $\text{VOPO}_4 \cdot 2\text{CH}_3\text{CH}_2\text{OH}$ represents intercalate with the regular network of strong active sites on the host layers, but with disordered guests [39, 40]. Two ethanol molecules per one formula unit in $\text{VOPO}_4 \cdot 2\text{CH}_3\text{CH}_2\text{OH}$ are anchored by two different ways to the host layer. First, an ethanol molecule is anchored with the oxygen to the vanadium atom to complete its octahedron and the second one is hydrogen bonded to the oxygen atoms in the VOPO_4 layer. In this case the arrangement of guests is bi-layer, due to the double guest concentration compared with $\text{VOPO}_4 \cdot \text{THF}$ and $\text{VOPO}_4 \cdot \text{DEG}$. Figure 5 shows the host layer VOPO_4 with the adjacent lower guest layer. The upper guest layer was deleted for clarity. One can also see from Figure 5 that guest molecules possess a high degree of freedom, thanks to their size, especially those which are not attached to vanadium with their oxygen. This leads to the disorder in interlayer structure and in the layer stacking, which was observed by X-ray powder diffraction and explained by molecular modeling. (For more details, see [39, 40].)

α -zirconium phosphate intercalated with ethanol $\text{Zr}(\text{HPO}_4)_2 \cdot 2\text{CH}_3\text{CH}_2\text{OH}$ is another example illustrating that the perfect ordering of active sites does not guarantee the perfect ordering of guest molecules. α -zirconium phosphate $\alpha\text{-Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ is a widely used host structure with the regular network of strong active sites [6–8]. The layers in $\alpha\text{-Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ consist of infinite sheets of ZrO_6 octahedra, where the Zr atoms lie almost in a plane and are bridged by the phosphate groups, creating the six-sided cavities on the layer surface [41]. The OH groups in the vertex of each PO_4 tetrahedron are active sites on the host layer. The ethanol molecules reside in the cavities on the host layer, hydrogen bonded to OH groups (Figure 6) [42]. Looking at the structure of the host layer and orientation of the OH groups in Figure 6, one can see that there are two types

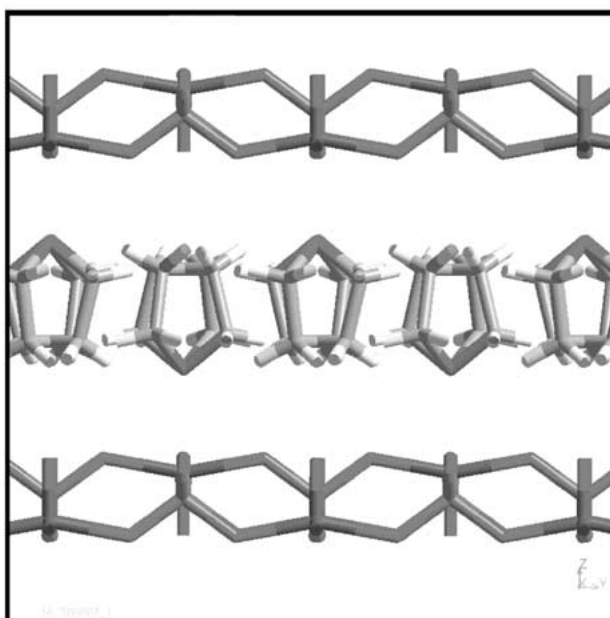
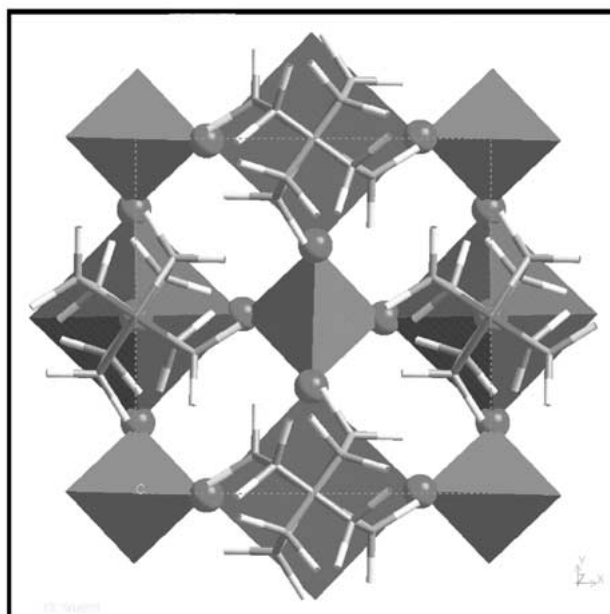


Figure 4. (a) Vanadyl phosphate intercalated with tetrahydrofuran (THF); two possible orientations of THF molecules attached with their oxygen to vanadium atoms. The THF molecules over the oxygen atom (left and right octahedron) are attached to the upper VOPO_4 layer, THF molecules over the vanadium atom complete its octahedron (i.e., upper and lower octahedron in the figure) are attached to the lower VOPO_4 layer. (b) The side view of the structure $\text{VOPO}_4 \cdot \text{THF}$ with monolayer arrangement of guests.

of cavities on the host layers differing in the orientation of the PO_4 tetrahedra and OH-groups. Consequently the anchoring of ethanol molecules is different in both types of cavities. In the first cavity the ethanol molecule is fixed by three hydrogen bonds to the surrounding OH groups in a well-defined position. The ethanol molecule in the second – more open – cavity is bonded to one OH group only (see Figure 6) and possesses a certain degree of freedom in its position inside the cavity. Thanks to this bonding and the

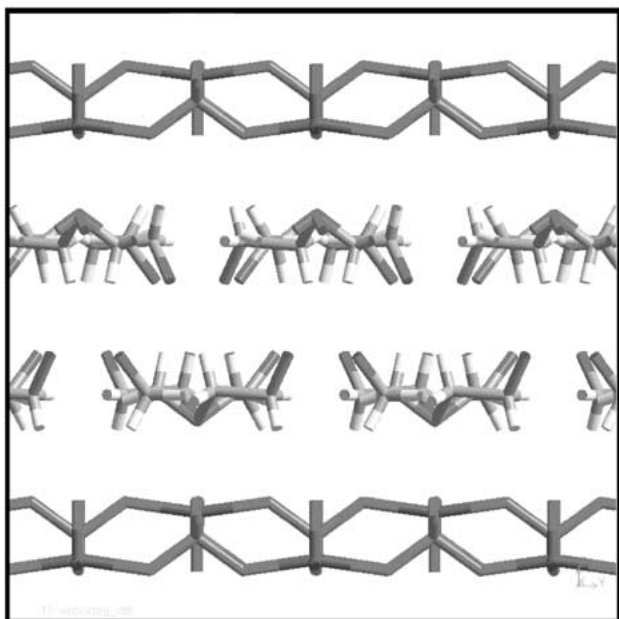


Figure 4c. (c) Vanadyl phosphate intercalated with diethylene glycol (DEG); bilayer arrangement of guests with two possible orientations of DEG molecules attached with their oxygen to vanadium atoms.

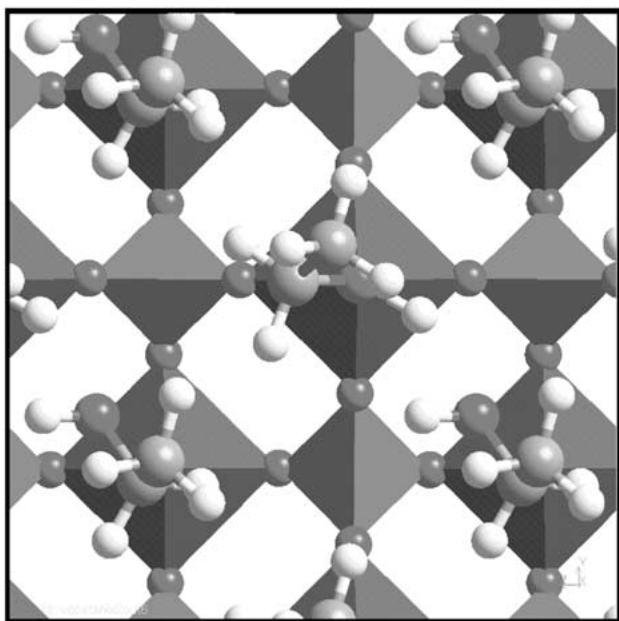


Figure 5. Structure fragment of vanadyl phosphate intercalated with ethanol. The host layer of VOPO₄ with one attached guest layer of ethanol molecules. The upper guest layer in the bilayer guest arrangement in the interlayer space was removed for clarity. One can see in the figure, that one half of the ethanol molecules is attached to vanadium with their oxygen. The second half of the ethanol molecules positioned above the vanadium has their OH group positioned out of vanadium octahedron.

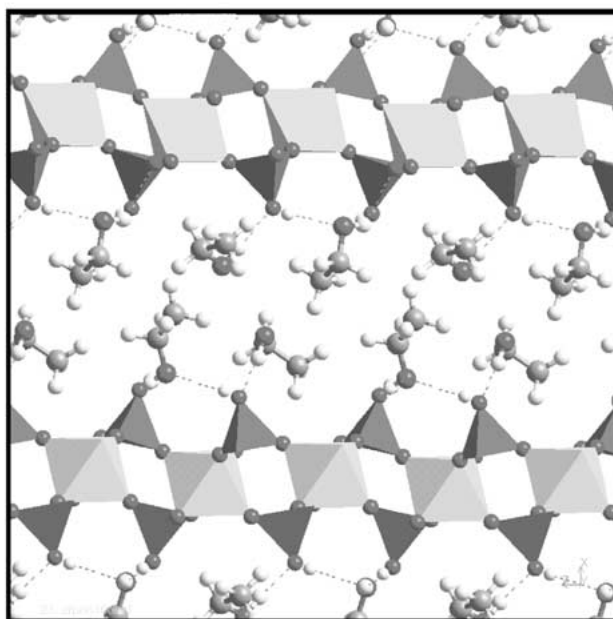


Figure 6. Structure of an α -zirconium phosphate intercalated with ethanol. Guest molecules in a bilayer arrangement are partially immersed in the host layer cavities. One can see two types of cavities with a different orientation of PO₄ tetrahedra and a different position of ethanol molecule. Hydrogen bonds are marked with dotted lines (some of them are hidden).

size of the guests, the ethanol positions and orientations in the second cavity are slightly disordered. This disorder of guests results in a slight disorder in the layer stacking, where the magnitude of the shift vector characterizing the positions of two successive host layers exhibits a maximum value of $\sim 0.8 \text{ \AA}$ [42].

In the example of graphite intercalated with tantalum chloride (TaCl₆-graphite) [43], we can show that the existence of a regular network of strong active sites is not a necessary condition for the ordering of guests in the interlayer space. In spite of the absence of strong active sites in the graphite layers, the intercalated structure of TaCl₆-GIC exhibits ordered guest structure in the interlayer space (see Figure 7) [43]. However, the ordered guest structure in the interlayer space does not lead to the ordered host layers and TaCl₆-graphite is an example of intercalate with ordered guests and disordered (turbostratic) stacking of the host layers. This structure will be discussed in more details in the next paragraph dealing with the host layers without strong active sites.

Host structures without strong pronounced active sites

The arrangement of guest molecules in the host structures with the strong active sites is mainly ruled by the strong host-guest interaction. However, in the case of the host layers without strong pronounced active sites, the role of the guest-guest interactions and geometrical host-guest complementarity become more important for the arrangement of guest molecules. This situation can be demonstrated using two examples: (1) graphite intercalation compounds (GIC) and (2) intercalated layer silicates, especially smectites

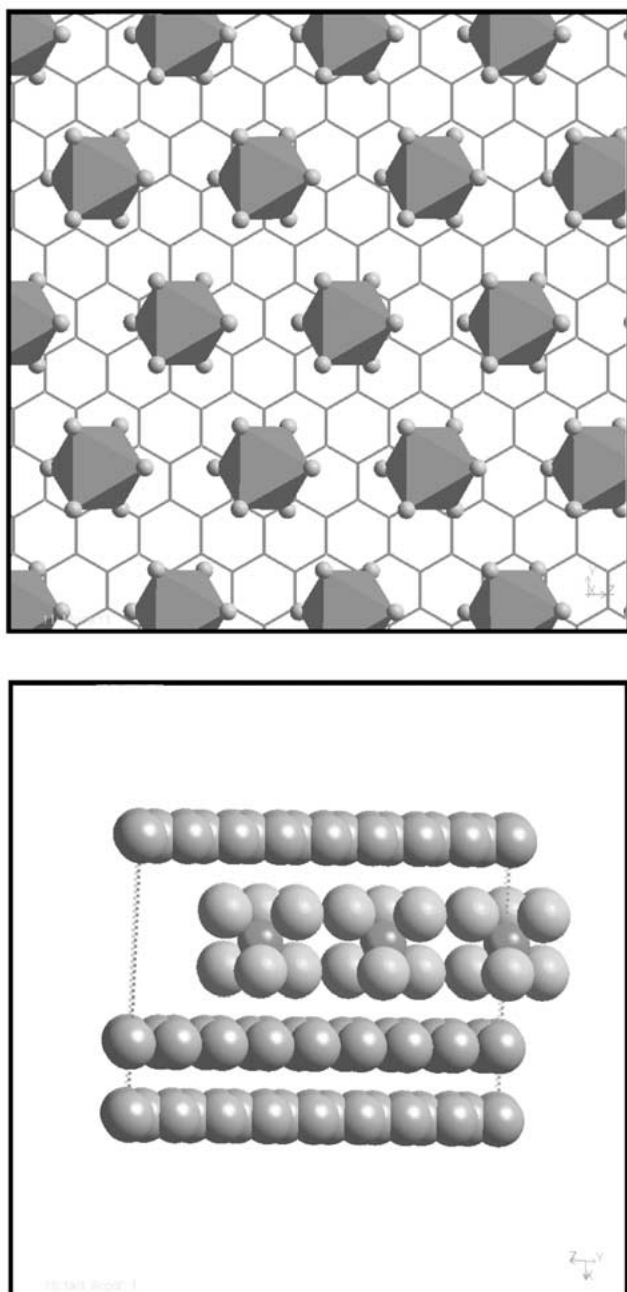


Figure 7. (a) The regular network of TaCl_6 octahedra in the interlayer space of graphite. (b) The side view of the TaCl_6 -graphite structure, second stage (i.e. every second interlayer space is intercalated).

with prevailing octahedral substitutions (montmorillonite and hectorite).

Graphite is the typical example of the host structure without strong active sites. In spite of the absence of strong active sites we can get the graphite intercalation compound with ordered guest species. Figure 7a,b shows the structure of graphite intercalated with tantalum chloride, where the TaCl_6 octahedra are ordered in a two-dimensional regular hexagonal network. The mutual positions and orientations of guests in this case are ruled by the strong guest-guest interaction. The strong repulsion between guests keeps the TaCl_6 octahedra in the hexagonal plane lattice, see Figure 7a. This figure also shows that the structures of host and

guest layers are incommensurate, anchoring of TaCl_6 octahedra to the graphite layer is not regular and consequently the ordering of guests does not lead to the order in the stacking of the host layers. The structure of TaCl_6 -graphite was analyzed by modeling and the results of modeling have been confirmed by X-ray and electron diffraction [43–46]. Graphite intercalation compounds with transition metal chlorides are analyzed in [47] and their experimental investigation is presented in [48–51]. For the general overview of graphite intercalation compounds, see for example [9, 52].

Smectites represent widely used host structures without strong pronounced active sites (functional groups) on the host layers. Smectites belong to the group of 2:1 layer silicates with the disordered – so-called “turbostratic” layer stacking, characterized by the random shift and random azimuth rotation of two successive silicate layers. The structure of 2:1 silicate layer (schematically shown in the Figure 8a,b) consists of one octahedral and two adjacent tetrahedral sheets [53]. Octahedra are linked to sharing octahedral edges. Tetrahedra in the tetrahedral sheets are linked to sharing three corners, to form the hexagonal mesh pattern (Figure 8a). The common plane of junction between the tetrahedral and octahedral sheets consists of the sheared apical oxygens plus unshared OH groups that lie at the center of each tetrahedral six-fold ring at the same z -level as the apical oxygens. The smallest structural unit contains three octahedra. If all three octahedra are occupied, i.e., have octahedral cations at their centers, the silicate layer is classified as trioctahedral. If only two octahedra are occupied and the third octahedron is vacant, the layer is classified as dioctahedral (see Figure 8a). The octahedral cations are usually Mg, Al, Fe^{2+} and Fe^{3+} . The tetrahedral Si cations may be substituted for Al or Fe^{3+} . Substitutions of octahedral and tetrahedral cations for the cations with lower charge, produce negative charge on the silicate layer, which is balanced by interlayer cations; these are commonly Na^+ , Ca^{2+} and Mg^{2+} , but a wide range of inorganic and organic cations can be introduced by exchange reactions.

Dioctahedral smectites with prevailing octahedral substitutions are called montmorillonites and analogically the trioctahedral smectites with prevailing octahedral substitutions are called hectorites. Dioctahedral smectites with prevailing tetrahedral substitutions are called beidellites and analogically the trioctahedral smectites with prevailing tetrahedral substitutions are called saponites. Both substitutions: in octahedral as well as in tetrahedral sheets, create the charge fluctuations in the surface oxygen layers and it is evident, that the charge fluctuations caused by octahedral substitutions are lower than those caused by tetrahedral substitution [54, 55]. Consequently no pronounced strong active sites on the host layer can exist in montmorillonites and hectorites. As a result of this character of silicate layers, the arrangement of the guests and the layer stacking in intercalated montmorillonites and hectorites is disordered [55–57]. The irregularity in the positions of tetrahedral substitutions leads to the irregularity in the charge distribution in the surface oxygen layer, which is crucial for the anchoring of guest cations on the silicate layer. This irregular charge distri-

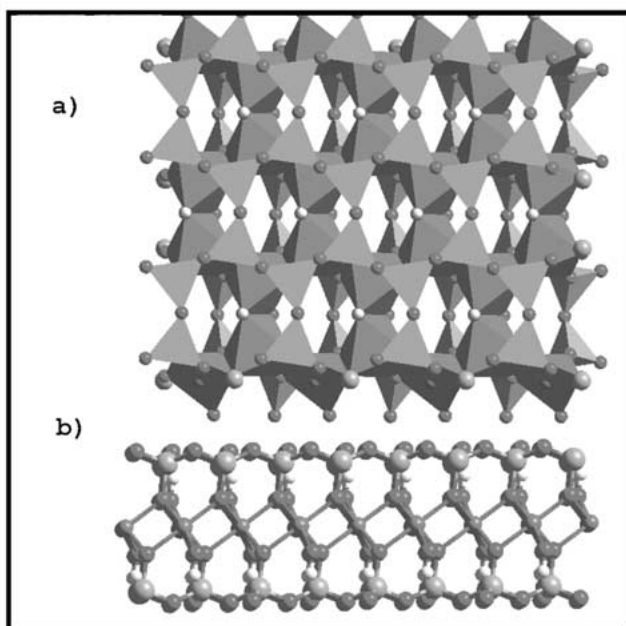


Figure 8. The top (a) and side (b) view of the silicate host layer.

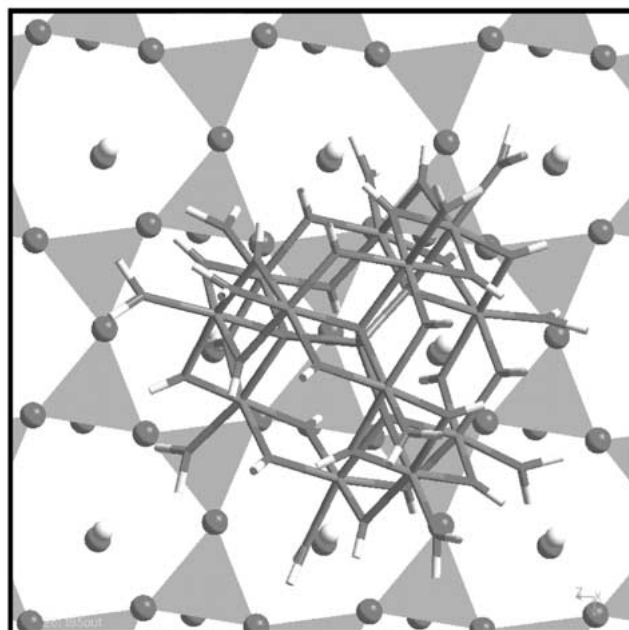
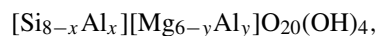


Figure 9. Top view of the Keggin cation $[\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$ attached to the silicate layer.

bution leads to the irregular anchoring and arrangement of guests even in the case of saponite and beidelite (smectites with tetrahedral substitutions), where the charge fluctuations in the surface oxygen layer are higher than in montmorillonite and hectorite [54]. Hence, the intercalation compounds of smectites display disordered guest structure and turbostratic disorder in layer stacking [57–60]. This disorder has unfavorable consequences for all practical applications, where the interlayer porosity should be under control and this is also the key enduring problem in the development of selective sorbents, based on clays intercalated with large complex cations (so called “pillared clays”). Figure 9 shows the Keggin cation $[\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$ attached to the montmorillonite layer. This cation was widely used as pillar in smectite host structures [57, 59–63] and as one can see in Figure 9, in addition to the absence of the strong active sites, there is no geometrical host–guest complementarity. Moving the cation along the host layer in any direction, one obtains only small changes in the host–guest interaction energy and consequently no preferential positions for anchoring of guests exist in this intercalate [56, 57]. Therefore, smectites can be used as a convenient host matrix for intercalates, where the ordering of guest structure is not important for the desired properties. For example, an intercalation of various organoammonium cations has to create precursors with hydrophobic interlayer [5, 64–66] for further intercalation of organic molecules or oligomers to prepare sorbents [67], catalysts [68, 69], polymer-clay nanocomposites [70] etc.

In contradiction to smectites, vermiculite intercalated with small rigid organoammonium cations creates the 3D ordered structures in spite of the absence of strong active sites on the host layer [71–74]. Vermiculite belongs to 2 : 1 trioctahedral phyllosilicates with prevailing tetrahedral substitutions, but in contradiction to smectites, the silicate layer in vermiculite has significantly higher layer charge. *A priori*, no qualitative

distinction can be seen between the structural formulas of silicate layer for vermiculite and saponite (saponite is trioctahedral smectite with prevailing tetrahedral substitutions) [75]:



where the value of x - y determines the layer charge per unit cell. According to [53, 75], the formal charge per formula unit in saponite is approximately 1 el. unit, in vermiculite 1.2–1.8 el. units. Thanks to the relatively high layer charge intercalated vermiculite exhibits two specific features in intercalation behaviour:

- the stronger host–guest interaction in vermiculite than in saponite,
- the higher guest concentration in the interlayer space of vermiculite, than in saponite and consequently the guest–guest interactions become more important for the arrangement of guests in the interlayer space of vermiculite.

These conditions lead to the ordering of guests and consequently to the ordering of layers in intercalated vermiculite. The 3D ordered structures of vermiculite intercalated with tetramethylammonium and anilinium cations were solved using single crystal diffraction data [71, 73] and modeling in *Cerius²* [74]. Figure 10 shows the ordered structure of TMA-vermiculite [74], where one can see the ordered guests in the interlayer space and the order in layer stacking. Two adjacent tetrahedral sheets belonging to the two successive host layers are visualized as polyhedra and cylinders.

Let’s compare the structure of vermiculite and montmorillonite intercalated with tetramethylammonium (Figures 10 and 11). Figure 11 shows the disordered structure of TMA-montmorillonite [54], where one can see, in contrast to

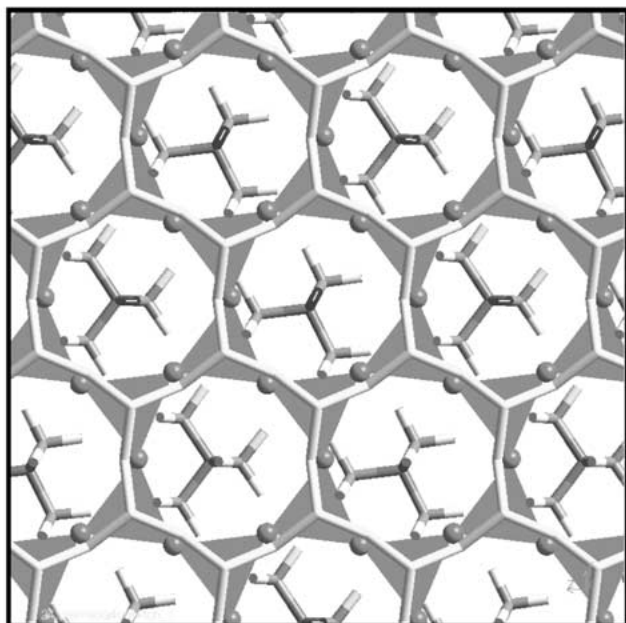


Figure 10. Structure of vermiculite intercalated with tetramethylammonium, top view showing the position of guests and the mutual positions of two successive host layers. For clarity only, two adjacent tetrahedral sheets are visualized as tetrahedral and cylinders.

Figure 10, the irregular attachment of TMA cations to the silicate layer and disorder in positions and orientations of guest. The same disorder can be observed in all TMA-smectites [54]. In montmorillonite, the layer charge and consequently the guest cation concentration is very low, that means, the main interaction ruling the crystal packing is the host–guest interaction. On the other hand, in vermiculite, the high layer charge and consequently the high guest concentration leads to the increased significance of the guest–guest interactions. Consequently the ordered structure of TMA-vermiculite is the result of competition between the strong host–guest and guest–guest interactions.

Conclusions

Intercalation is a very promising route to synthesis of new materials with desired properties, which can be tuned by the proper choice of host–guest combination, by the guest concentration and by co-intercalation of further guest species. The scale of practical applications is very wide, based on sorption and catalytic properties, photofunctions, biological activity etc. The understanding of a structure-properties relationship is crucial for the design of new intercalates and their applications and this field is the challenge for molecular modeling. Molecular mechanics (using empirical force field) is a very helpful tool in design and analysis of new intercalates. It can provide us with the quick analysis of the host–guest complementarity and hence with the search for the most suitable host–guest combination for a given purpose.

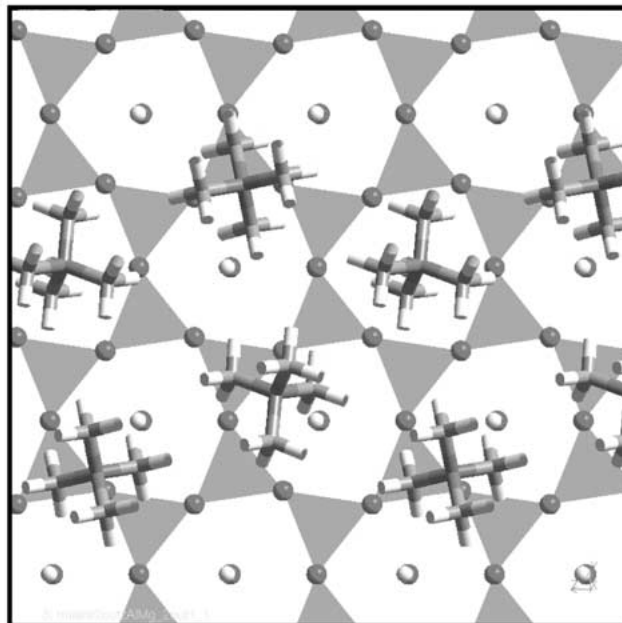


Figure 11. Structure of montmorillonite intercalated with tetramethylammonium cations, with low concentration of disordered guests.

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References

1. A.J. Jacobson: Intercalation reaction of layered compounds, in A.K. Cheetham and P. Day (eds.), *Solid State Chemistry Compounds*, Clarendon Press, Oxford (1992), p. 182.
2. R. Schöllhorn: in J.L. Atwood, J.E.D. Davies, and D.D. MacNicol (eds.), *Inclusion Compounds*, Academic Press, New York (1984), p. 249.
3. A. Lurf: Intercalation compounds in layered host lattices: Supramolecular chemistry in nanodimensions, in H.S. Nalwa (ed.), *Handbook of Nanostructured Materials and Nanotechnology*, Vol. 5, Academic Press, New York (2000), p. 5.
4. M. Ogawa and K. Kuroda: *Chem. Rev.* **95**, 399 (1995).
5. G. Lagaly: *Solid State Ionics* **22**, 43 (1986).
6. A. Clearfield: *Inorganic Ion Exchange Material*, CRC Press Inc., Boca Raton, FL (1982), p. 1.
7. G. Alberti: in P.A. Williams and M.J. Hudson (eds.), *Recent Developments in Ion Exchange*, Elsevier Applied Science, London (1987), p. 233.
8. U. Costantino: *Chem. Soc. Dalton Trans.*, 402 (1979).
9. S.A. Solin: in I. Prigogine and Stuart A. Rice (eds.), *Advances in Chemical Physics*, John Wiley & Sons, New York (1982) p. 455.
10. J.M. Lehn: *Angew. Chem. Int. Ed. Engl.* **29**, 1304 (1990).
11. A. Nangia and G.R. Desiraju: *Acta Cryst.* **A54**, 934 (1998).
12. A. Gavezzotti: *J. Am. Chem. Soc.* **113**, 4622 (1991).
13. *Cerius² documentation*, June 2000, Molecular Simulations Inc., San Diego (2000).
14. B. Koudelka and P. Čapková: *J. Mol. Model* **8**, 184 (2002).
15. P. Suortti: *J. Appl. Cryst.* **5**, 325 (1972).
16. P. Comba and T.W. Hambley: *Molecular Modeling of Inorganic Compounds*, VCH, Weinheim, New York, Basel, Cambridge, Tokyo (1995), p. 4.
17. A.K. Rappé and W.A. Goddard III: *J. Phys. Chem.* **95**, 3358 (1991).
18. P.P. Ewald: *Ann Phys (Leipzig)* **64**, 253 (1921).
19. N. Karasawa and W.A. Goddard III: *J. Phys. Chem.* **93**, 7320 (1989).

20. D. Frenkel and B. Smit: *Understanding Molecular Simulation*, Academic Press, San Diego, New York, London (1996) p. 19.
21. P. Erk: *Crystal Engineering: From Molecules and Crystals to Materials*, Kluwer Academic Publishers, Netherlands (1999), p. 143.
22. P. Verwer and F.J.J. Leusen: Computer simulation to predict possible crystal polymorphs, in K.B. Lipkowitz and D.B. Boyd (eds.), *Reviews in Computational Chemistry*, Vol. 12, Wiley-VCH, New York, p. 327.
23. K.D.M. Harris, B.M. Kariuki, and R.L. Johnston: Advances in structure analysis, in R. Kužel and J. Hašek (eds.), Czech and Slovak Crystallographic Association, Prague (2001) p. 190.
24. M. Pospíšil, P. Čapková, D. Měřínská, Z. Maláč, and J. Šimoník: *Journal of Colloid and Interface Science* **236**, 127 (2001).
25. M. Pospíšil, P. Čapková, Z. Weiss, Z. Maláč, and J. Šimoník: *Journal of Colloid and Interface Science* **245**, 126 (2002).
26. P. Čapková, M. Trchová, P. Matějka, J. Votinský, and H. Schenk: *J. Mol. Model* **4**, 284 (1998).
27. L. Beneš, K. Melánová, V. Zima, M. Trchová, E. Uhlířová, and P. Matějka: *Eur. J. Inorg. Chem.* **3**, 713 (2001).
28. A. Hauptmann, A. Lerf, and W. Biberacher: *Z. Naturforsch.* **51b**, 1571 (1996).
29. P. Čapková, M. Pospíšil, and A. Lerf: *Solid State Sciences* **4**, 671 (2002).
30. K. Goubitz, P. Čapková, K. Melánová, W. Molleman, and H. Schenk: *Acta Crystallographica B, Structural Science* **B57**, 178 (2001).
31. L. Beneš, J. Votinský, J. Kalousová, and K. Handlír: *Inorg. Chim. Acta* **176**(2), 255 (1990).
32. L. Beneš, J. Kalousová, J. Votinský, and R. Hyklová: *Inorg. Chim. Acta* **177**(1), 71 (1990).
33. L. Beneš, V. Zima, J. Kalousová, and J. Votinský: *Collect. Czech. Chem. Commun.* **59**, 1616 (1994).
34. L. Beneš, K. Melánová, V. Zima, J. Kalousová, and J. Votinský: *Inorg. Chem.* **36**, 2850 (1997).
35. V. Zima, L. Beneš, and K. Melánová, *Solid State Ionics* **106**, 285 (1998).
36. J. Kalousová, J. Votinský, L. Beneš, K. Melánová, and V. Zima: *Collect. Czech. Chem. Commun.* **63**, 1 (1998).
37. H.R. Tietze: *A. J. Chem.* **34**, 2035 (1981).
38. M. Tachez, F. Theobald, J. Bernard, and A.W. Hewat: *Revue de Chemie Minerale* **19**, 291 (1982).
39. P. Čapková, D. Janeba, L. Beneš, K. Melánová, and H. Schenk: *J. Mol. Model.* **4**, 150 (1998).
40. P. Čapková, M. Trchová, P. Matějka, L. Beneš, K. Melánová, D. Janeba, and H. Schenk: in R. Kužel and J. Hašek (eds.), *Advances in Structure Analysis*, Czech and Slovak Crystallographic Association, CSPA, Prague (2001), p. 285.
41. J.M. Troup and A. Clearfield: *Inorganic Chemistry* **16**, 3311 (1977).
42. P. Čapková, L. Beneš, K. Melánová, and H. Schenk: *J. Appl. Cryst.* **31**, 845 (1998).
43. P. Čapková and J. Walter: *J. Solid State Chem.* **149**, 68 (2000).
44. J. Walter, H. Shioyama, Y. Sawada, and S. Hara: *Carbon* **36**, 1277 (1998).
45. J. Walter: *Solid State Ionics*, **101–103**, 833 (1997).
46. J. Walter and H.P. Boehm: *Carbon* **33**, 1121 (1995).
47. P. Behrens and W. Metz: *Synth. Met.* **34**, 223 (1989).
48. J. Walter and H. Shioyama: *J. Phys.: Condens. Matter* **11**, L21 (1999).
49. J. Walter: *Synth. Met.* **89**, 39 (1997).
50. J. Walter and M. Metz: *Mikrochim. Acta* **127**, 183 (1997).
51. P. Behrens, J. Ehrlich, W. Metz, and W. Niemann: *Synth. Met.* **34**, 199 (1989).
52. G.R. Hennig, in F.A. Cotton (ed.), *Progress in Inorganic Chemistry*, Vol. 1, Interscience, New York (1959), p. 125.
53. G.W. Brindley: in G.W. Brindley and G. Brown (eds.), *Crystal Structures of Clay Minerals and their X-Ray Identification*, Mineralogical Society, Monograph No. 5, London (1980), p. 125.
54. P. Čapková, M. Pospíšil, J. Miehé-Brendlé, M. Trchová, Z. Weiss, and R. Le Dred: *J. Mol. Model.* **6**, 600 (2000).
55. D.J. Pruijsen, P. Čapková, R.A.J. Driessen, and H. Schenk: *Applied Catalysis A General* **193**, 103 (2000).
56. P. Čapková, R.A.J. Driessen, H. Schenk, and Z. Weiss: *J. Mol. Model.* **3**, 467 (1997).
57. P. Čapková, R.A.J. Driessen, M. Numan, H. Schenk, Z. Weiss, and Z. Klika: *Clays Clay Miner.* **46**, 232 (1998).
58. J. Breu, A. Stoll, K.G. Lange, and T. Probst: *Phys. Chem. Chem. Phys.* **3**, 1232 (2001).
59. T.J. Pinnavaia, M.S. Tzou, S.D. Landau, and R.H. Raythatha: *J. Mol. Catal.* **27**, 195 (1984).
60. R.A. Schoonheydt, H. Leeman, A. Scorpion, I. Lenotte, and P. Grobet: *Clays Clay Miner.* **42**, 518 (1994).
61. F. Figueras, Z. Klapyta, P. Massiani, Z. Mountassir, D. Tichit, and F. Fajula: *Clays Clay Miner.* **38**, 257 (1990).
62. P.B. Malla and S. Komarneni: *Clays Clay Miner.* **41**, 472 (1993).
63. D. Zhao, G. Wang, Y. Yang, X. Guo, Q. Wang, and J. Ren: *Clays Clay Miner.* **41**, 317 (1993).
64. G. Chen, B. Han, and H. Yan: *J. Colloid Interf. Sci.* **201**, 158 (1998).
65. A. Tahani, M. Karroua, H. Van Damme, P. Levitz, and F. Bergaya: *J. Colloid Interf. Sci.* **216**, 242 (1999).
66. M. Ogawa, T. Aono, K. Kuroda, and C. Kato: *Langmuir* **9**, 1529 (1993).
67. J.F. Lee, M.M. Mortland, CT. Chiou, D.E. Kile, and S.A. Boyd: *Clays Clay Miner.* **38**, 113 (1990).
68. A.G. Galarneau, A. Barodawalla, and T.J. Pinnavaia: *Chem. Commun.*, 1661 (1997).
69. M. Polverejan, Y. Liu, and T.J. Pinnavaia: in A. Sayari (ed.), *Studies in Surface Science and Catalysts*, Vol. 129, Elsevier Science B (2000), p. 401.
70. A. Okada and A. Usuki: *Materials Science and Engineering* **C3**, 109 (1995).
71. A. Vahedi-Faridi and S. Guggenheim: *Clays Clay Miner.* **45**, 859 (1997).
72. A. Vahedi-Faridi and S. Guggenheim: *Clays Clay Miner.* **47**, 338 (1999).
73. P.G. Slade and P.A. Stone: *Clays Clay Miner.* **32**, 223 (1984).
74. P. Čapková, J.V. Burda, Z. Weiss, and H. Schenk: *J. Mol. Model.* **5**, 8 (1999).
75. J. Mering: in J.E. Gieseking (ed.), *Soil Components, Vol. 2, Inorganic Components*, Springer-Verlag, New York (1975), p. 97.