

Modelling of Intercalated Clay Minerals*

^{a,b}P. ČAPKOVÁ, ^aR. A. J. DRIESSEN, ^aM. NUMAN, ^aH. SCHENK, ^cZ. WEISS, and ^cZ. KLIKA

^aLaboratory of Crystallography, AIMS, University of Amsterdam,
1018 WV Amsterdam, The Netherlands

^bDepartment of Chemical Physics and Optics, Faculty of Mathematics and Physics,
Charles University, CZ-121 16 Prague

^cCentral Analytical Laboratory, Technical University Ostrava, CZ-708 33 Ostrava

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Molecular mechanics simulations in Cerius² modelling environment have been used to investigate the structure of montmorillonites, intercalated with aluminium complex cations. Two different intercalating species have been investigated: 1. Keggin cation (ideal and hydrolyzed) and 2. gibbsite-like polymers, arranged in two layers in the interlayer of montmorillonites. The results of molecular simulations showed that the position, orientation, and concentration of Keggin cations in the interlayer space depends on the degree of hydrolysis. The average values of basal spacings for different degree of hydrolysis are within the range of 19.51–20.05 10⁻¹⁰ m. In the case of gibbsite-like polymers, arranged in two layers in the interlayer of montmorillonites, basal spacing depends on the mutual position of Al—OH polymers. Average basal spacings for different arrangements of Al(OH)₃ fragments are in the range of 19.58–20.06 10⁻¹⁰ m. Molecular simulations also showed that for both intercalating species no two-dimensional ordering of complex cations can occur in the interlayer of montmorillonites.

Computer-aided design accelerates significantly the discovery and development of new materials and molecular modelling begins to play an increasingly important role in material research. Additional reason for the use of molecular simulations may also be the lack of experimental data of investigated structures.

Intercalated layered structures exhibit certain characteristic features, which may obstruct the structure analysis, based on the diffraction data (stacking faults, inhomogeneity in basal spacings and small particle size). In such case the molecular simulations represent a very powerful tool to study the structure—property relationship.

Smectites, intercalated with aluminium complex cations have been intensively studied during the last few years, as potential sorbents, suitable for the decontamination of water resources, that means, for the removal of pollutants that resist biological degradation, such as chlorinated phenols, polychlorinated biphenyls or polyaromatic hydrocarbons. Smectites are phyllosilicates of the type 2:1 (*i.e.* their structure is lamellar, two tetrahedral sheets enclosing an octahedral sheet). Dioctahedral smectite – montmorillonite has been used in the present study as the host structure for the intercalation. Each 2:1 layer of montmorillonite consists of two sheets of distorted

SiO₄ tetrahedra connected by a sheet of Al(M)O₆ octahedra (M having one positive charge less than Al). The composition of the unit cell of the montmorillonite without interlayer water is given by the formula (Al_{4-x}M_x)Si₈O₂₀(OH)₄Mi_{x/n}ⁿ⁺. The loss of positive charge by replacement of Al by M can be compensated by intercalation with Miⁿ⁺ ions. The so-called Keggin cation [Al₁₃O₄(OH)₂₄(H₂O)₁₂]⁷⁺ (structure according to *Johansson*, 1960 [1], see Fig. 1) has been widely accepted as the pillaring species (see *Pinnavaia et al.*, 1984 [2], *Plee et al.*, 1985 [3], *Schoonheydt et al.*, 1994 [4]). However, *Figueras et al.* (1990) [5] showed that the amount of Al sorbed during ion-exchange reaction usually exceeds that necessary for charge neutralization with Keggin cation. This may lead to the two possible conclusions:

1. The Keggin cations are partially hydrolyzed and consequently carrying a lower charge according to the formula [Al₁₃O₄(OH)_{24+x}(H₂O)_{12-x}]^{(7-x)+} (denoted as Al₁₃^{(7-x)+}).

2. The Keggin cations are not the only pillaring species. *Hsu* (1992) [6] suggested the gibbsite-like polymers as possible Al-intercalating complex cations.

The crystal packing with Keggin cations and gibbsite-like polymers in the interlayer of montmorillonites has been investigated using molecular me-

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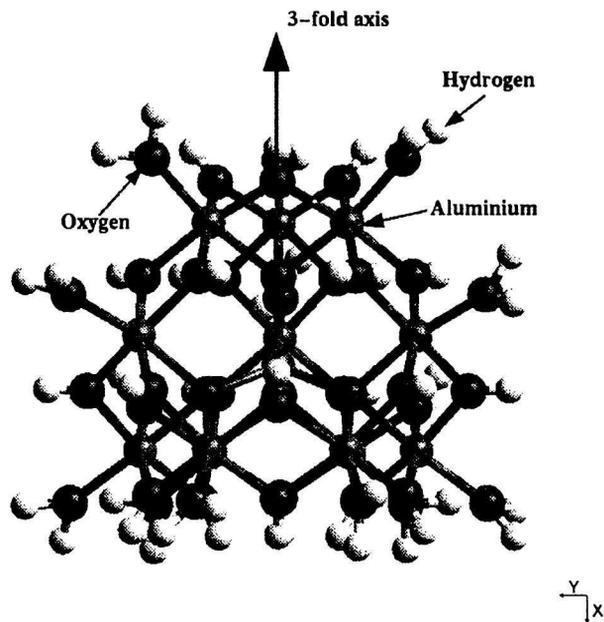


Fig. 1. Structure of Keggin cation according to Johansson [1].

chanics simulations. As the interactions between the aluminium complex cations and silicate layers are supposed to be noncovalent (Figueras, 1990 [5]), the Crystal Packer module in Cerius² modelling environment has been used for the present study.

Modelling with Cerius²

Crystal Packer is a computational module in Cerius² that assists in the estimation of the total sublimation energy E_s and packing of molecular crystals. Crystal Packer is based on DreidingII force field developed by Mayo *et al.* (1990) [7]. The primary advantage of the Dreiding force field is its robustness, *i.e.* it is a good, all-purpose force field, that can be used for structure predictions for large number of organic and inorganic structures. Its parametrization is based on both *ab initio* and experimental data. Energy calculations in Crystal Packer take into account the nonbonding terms only, *i.e.* van der Waals interactions (VDW), Coulombic interactions (COUL), hydrogen bonding (H-B), internal rotations, and hydrostatic pressure. The asymmetric unit of the crystal structure 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. The rigid units in this case were: 1. the silicate layer and 2. the complex cation.

The assumption of rigid silicate layers takes into account the generally accepted opinion, based on the results of infrared spectroscopy, that the basic structure of the clay sheet is not altered by ion exchange (see for example Ref. [8]). Furthermore, the assump-

tion of rigid silicate layers is supported by the X-ray powder diffraction experiment. The comparison of diffraction pattern of Al-intercalated montmorillonite and the host structure showed the same position of hk -bands, indicating the same lattice parameters a , b for both structures.

Intercalation with Keggin-Like Cations

Generating a structural model is the first step in molecular simulations. In our case the initial model of montmorillonite (MMT) was built using structural data [9, 10]. Supposing the composition of 2:1 layer (see [11, 12]), $(\text{Al}_{3.125}\text{Mg}_{0.875})\text{Si}_8\text{O}_{20}(\text{OH})_4$, and taking into account the size and charge of the guest cation Al_{13}^{7+} we created the supercell, containing 8 montmorillonite unit cells – 8MMT supercell – with the following supercell parameters A , B , C , α , β , γ in the initial model: $A = 4a = 20.83 \cdot 10^{-10}$ m, $B = 2b = 18.04 \cdot 10^{-10}$ m ($a = 5.208 \cdot 10^{-10}$ m and $b = 9.02 \cdot 10^{-10}$ m are the lattice parameters of the original MMT). Parameters A , B , $\gamma = 90^\circ$ were fixed during energy minimization. Parameters C (C -axis perpendicular to sheets), α , and β were variables. In this supercell, consisting of 8 montmorillonite unit cells, only 7 unit cells can contain the octahedral $\text{Al} \rightarrow \text{Mg}$ substitution. The layer composition supposed in the present work corresponds to the composition of montmorillonite samples presented in literature [11, 12]. The negative layer charge (-7) in this supercell is compensated by one cation Al_{13}^{7+} .

For the intercalation with hydrolyzed Keggin cations $\text{Al}_{13}^{(7-x)+}$, the layer composition of one MMT unit cell was supposed to be $(\text{Al}_3\text{Mg}_1)\text{Si}_8\text{O}_{20}(\text{OH})_4$. Two different supercells have been built for two different degrees of hydrolysis: $x = 2$ and $x = 4$. For slightly hydrolyzed Keggin cations $x = 2$, the supercell consisting of 10 montmorillonite unit cells (10MMT supercell) with 10 $\text{Al} \rightarrow \text{Mg}$ substitutions contained 2 hydrolyzed Al_{13}^{5+} cations. In case of strongly hydrolyzed cations $x = 4$, the supercell consisting of 6 montmorillonite unit cells (6MMT supercell) with 6 $\text{Al} \rightarrow \text{Mg}$ substitutions contained 2 Al_{13}^{3+} . In models with two hydrolyzed cations in one supercell, 3 independent rigid units have been defined: 2 cations and silicate layer. In order to compare the stability of models with different size of supercells, the presented values of energy are related to one MMT unit cell characterized with the formula $(\text{Al}_{4-x}\text{M}_x)\text{Si}_8\text{O}_{20}(\text{OH})_4$.

The results of energy minimization showed that the structure of the interlayer depends on the degree of hydrolysis x . The most stable crystal packing with the ideal Keggin cation Al_{13}^{7+} is shown in Fig. 2. The aluminium and oxygen planes perpendicular to the 3-fold axis in Keggin cation are parallel with the silicate 2:1 layers. The oxygen atoms in Keggin cation, adjacent to silicate layers are bonded *via* hydrogen bridges to the oxygens in tetrahedral sheets. The average basal spac-

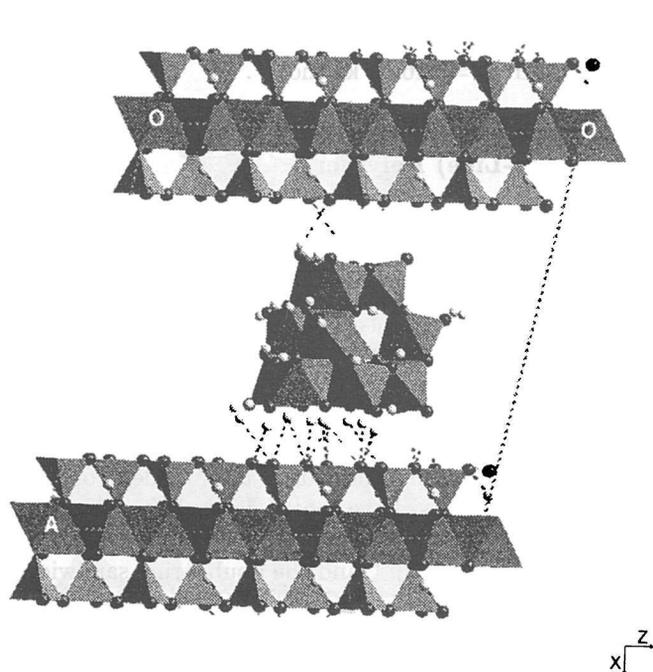


Fig. 2. The most stable crystal packing with the ideal Keggin cation Al_{13}^{7+} in 8MMT supercell. The aluminium and oxygen planes in Keggin cations are parallel with the sheets. Hydrogen bonds are marked with dotted lines.

ing corresponding to this arrangement is $19.51 \cdot 10^{-10}$ m and the total sublimation energy per 1 MMT unit cell for Al_{13}^{7+} $E_s = 1554.6 \text{ kJ mol}^{-1}$ consist of van der Waals 72.1 kJ mol^{-1} , Coulombic $1474.1 \text{ kJ mol}^{-1}$, and hydrogen bond contribution 8.4 kJ mol^{-1}

During the translations of Keggin cations along the silicate layer in any direction, the basal spacing varies within the range $19.41\text{--}19.61 \cdot 10^{-10}$ m and the corresponding fluctuations of the Coulombic and total sublimation energy are lower than 1.5%. That means the system does not exhibit a deep global energy minimum and can be characterized by a huge number of very flat local minima with the differences in the total sublimation energy lower than 1.5%. Consequently, one can hardly expect the two-dimensional ordering of cations in the interlayer.

In case of slightly hydrolyzed Keggin cations Al_{13}^{5+} , the concentration of cations with lower charge must be higher to compensate the layer charge, which results in lower distances between them and lower porosity in the interlayer. The orientation of Al_{13}^{5+} cations in the interlayer is nearly the same as for ideal Keggin cations, illustrated in Fig. 2. The corresponding basal spacing $d = 19.60 \cdot 10^{-10}$ m is slightly higher than for ideal Keggin cation. This is in agreement with the lower Coulombic E_c and total sublimation energy E_s in this case, due to the mutual repulsions between Al_{13}^{5+} cations with lower mutual distances, than in case of Al_{13}^{7+} . For Al_{13}^{5+} energy values per 1 MMT unit cell

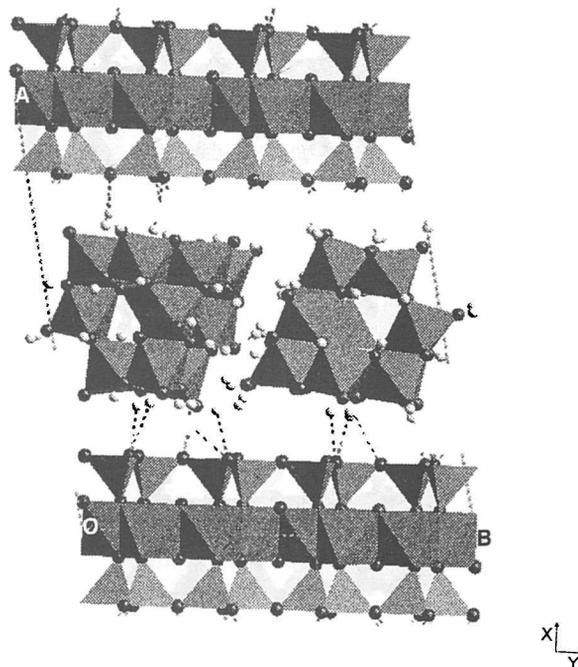


Fig. 3. The most stable crystal packing with two hydrolyzed Keggin cations; Al_{13}^{3+} cations in antiparallel arrangement in 6MMT ($3a \times 2b$) supercell.

are $E_c = 971.7 \text{ kJ mol}^{-1}$ and $E_s = 1078.5 \text{ kJ mol}^{-1}$

With increasing degree of hydrolysis and decreasing charge of $\text{Al}_{13}^{(7-x)+}$, the concentration of cations increases and consequently mutual interactions between cations become more important. This effect is more pronounced in case of strongly hydrolyzed cations Al_{13}^{3+} . In this case the Coulombic and total sublimation energy depends strongly on the arrangement of cations in 6MMT supercell.

In $3a \times 2b$ supercell (*i.e.* $15.62 \times 18.04 \cdot 10^{-20} \text{ m}^2$) two Al_{13}^{3+} cations were placed in the diagonal 110 direction in antiparallel arrangement (see Fig. 3). After energy minimization the cations were oriented still nearly by the same way as for ideal Keggin cations. The 3-fold axis is only slightly tilted (about $3\text{--}4^\circ$) from the direction perpendicular to the silicate layers. The corresponding values of Coulombic E_c and the total sublimation energy E_s related to 1 MMT unit cell in this case are: $E_c = 1441.5 \text{ kJ mol}^{-1}$ and $E_s = 1595.3 \text{ kJ mol}^{-1}$ and the basal spacing $d = 19.65 \cdot 10^{-10}$ m.

In $2a \times 3b$ supercell (*i.e.* $10.42 \times 27.06 \cdot 10^{-20} \text{ m}^2$) two Al_{13}^{3+} cations were placed in the b direction in antiparallel arrangement. That means, the distances $10.42 \cdot 10^{-10}$ m between the central aluminium atoms of Al_{13}^{3+} cations in neighbouring supercells were fixed, due to periodicity. After energy minimization the cations were strongly tilted with respect to the silicate layers, as can be seen in Fig. 4. This strong tilting of

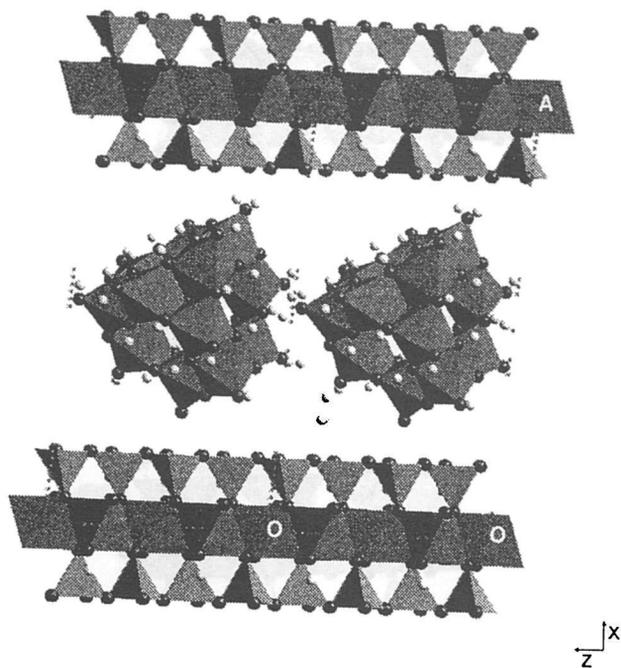


Fig. 4. Crystal packing with strongly tilted Al_{13}^{3+} cations in 6MMT ($2a \times 3b$) supercell. Two neighbouring supercells are illustrated along A direction. For the transparency only one cation in each supercell is shown.

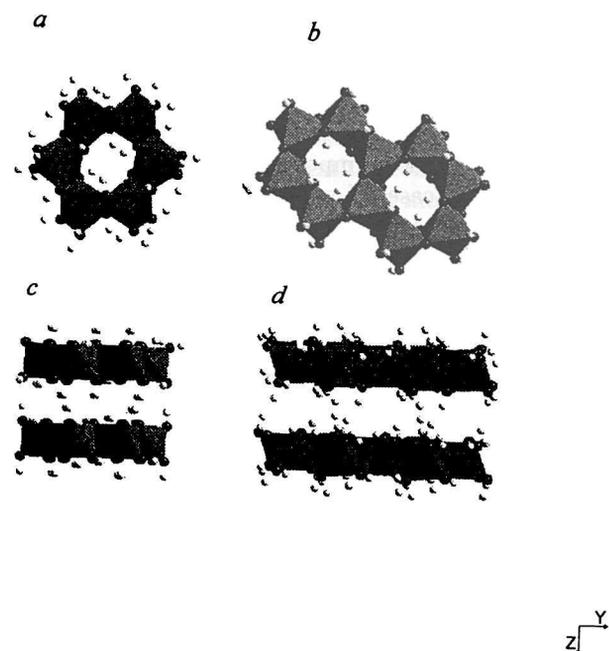


Fig. 5. Fragments of Al—OH polymers: a) single and b) double ring, arranged in c) single and d) double ring sandwich.

cations ($\approx 14^\circ$) is the result of the stronger Coulombic interaction (attraction) between Al_{13}^{3+} cations, than in previous cases, resulting in stronger total sublimation energy. The average value of basal spacing in this case

is $20.05 \cdot 10^{-10}$ m, the Coulombic and total sublimation energy per 1 MMT unit cell are: $E_c = 2014.2$ kJ mol $^{-1}$ and $E_s = 2165.2$ kJ mol $^{-1}$.

Intercalation with $\text{Al}(\text{OH})_3$ Fragments (Gibbsite-Like) Polymers

Two different $\text{Al}(\text{OH})_3$ fragments have been used in our modelling of intercalated montmorillonites: single and double ring (Fig. 5a, b). The published experimental values of basal spacings for smectites intercalated with aluminium complex cations derived from the diffraction data are within the range $18.6\text{--}20 \cdot 10^{-10}$ m. That means, the gibbsite-like polymers are arranged in two layers in the interlayer of smectites. Therefore, two models of intercalating species have been derived from single and double ring: the single ring sandwich (Fig. 5c) $[\text{Al}_{12}(\text{OH})_{30}(\text{H}_2\text{O})_{18}]^{6+}$ and the double ring sandwich (Fig. 5d) $[\text{Al}_{20}(\text{OH})_{54}(\text{H}_2\text{O})_{22}]^{6+}$. Consequently, two initial models have been built: 1. single ring sandwich in 6MMT ($3a \times 2b$) supercell, 2. the double ring sandwich in 6MMT ($3a \times 2b$) supercell. The single and double rings in sandwich were independent rigid units during energy minimization.

The crystal packing with the single ring sandwich is shown in Fig. 6. The aluminium planes are parallel with the silicate layers. Hydrogen bridges occur between the rings and silicate layers and between both rings. The corresponding d -spacing is $19.94 \cdot 10^{-10}$ m and the total sublimation energy per 1 MMT unit cell $E_s = 1733.6$ kJ mol $^{-1}$ consists of dominating Coulombic contribution $E_c = 1609.1$ kJ mol $^{-1}$, van der Waals contribution $E_{\text{vdw}} = 98.3$ kJ mol $^{-1}$, and hydrogen bond energy $E_{\text{hb}} = 26.2$ kJ mol $^{-1}$.

In case of gibbsite-like polymers in the interlayer, the sublimation energy and d -spacings depend strongly on the mutual position of the rings. This effect will be illustrated on the example of double rings arranged in two layers. For the position with maximum overlap of double rings, as it is illustrated in Fig. 5d and Fig. 7, the total sublimation energy $E_s = 1638.2$ kJ mol $^{-1}$ is lower than for single ring sandwich, due to the significantly lower Coulombic energy $E_c = 1460.9$ kJ mol $^{-1}$, resulting in higher basal spacing $d = 20.06 \cdot 10^{-10}$ m in comparison with the single ring sandwich. The decrease of Coulombic energy due to the mutual repulsion between the double rings with maximum overlap (see Figs. 5d and 7), led us to build the initial model with the shifted double rings, with minimum overlap (see Fig. 8a, b).

Crystal packing with the shifted double rings (Fig. 8a, b) exhibits the higher sublimation energy and the lower basal spacing, than in case of double rings with maximum overlap, as the minimum overlap reduced the repulsion forces between the double rings in lower and upper layer. For shifted double rings the basal spacing is $19.58 \cdot 10^{-10}$ m. The total sublimation

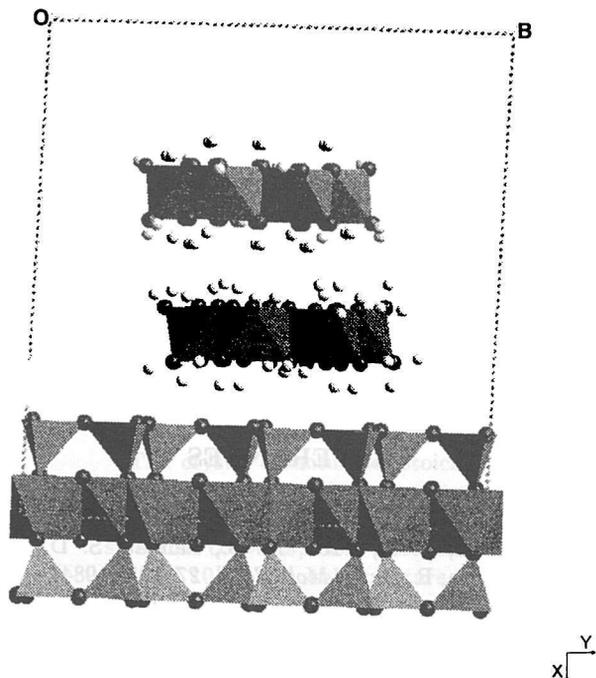


Fig. 6. Crystal packing with the single ring sandwich in 6MMT ($3a \times 2b$) supercell.

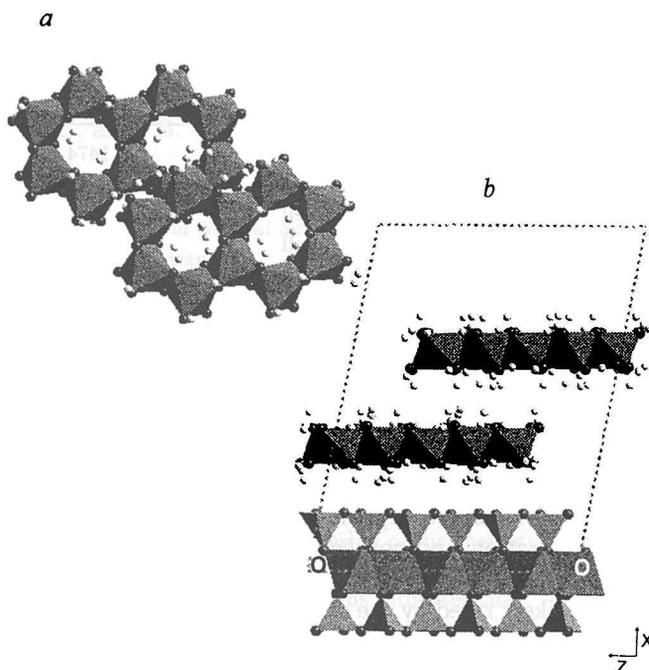


Fig. 8. a) Two shifted double rings in lower and upper layer with the minimum overlap. b) The schematic view of crystal packing with the shifted double rings in 6MMT ($3a \times 2b$) supercell.

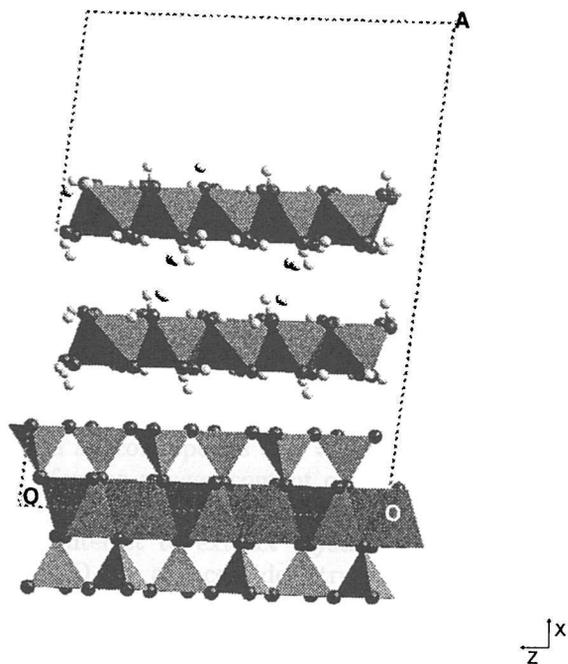


Fig. 7. Crystal packing with the double ring sandwich in 6MMT ($3a \times 2b$) supercell.

energy per 1 MMT unit cell $E_s = 2316.3 \text{ kJ mol}^{-1}$ consists of $E_c = 2132.3 \text{ kJ mol}^{-1}$, $E_{vdw} = 139.3 \text{ kJ mol}^{-1}$, $E_{hb} = 44.7 \text{ kJ mol}^{-1}$. Comparison of results for different intercalating species is presented in Table 1.

DISCUSSION AND CONCLUSION

Results of modelling (Table 1) showed that for both intercalating species (Keggin cations and gibbsite-like polymers) the crystal packing shows certain common features, which can be summarized as follows:

1. The dominating contribution to the total sublimation energy comes from Coulombic interactions.

2. For both intercalating species, no deep global minimum of energy has been found in dependence on complex cation positions during translations along the silicate layers. Consequently, no ordering of complex cations can be expected in the interlayer of montmorillonites.

3. The values of average basal spacings are within the range $19.51\text{--}20.05 \cdot 10^{-10} \text{ m}$ for Keggin cations with different degree of hydrolysis and within the range $19.58\text{--}20.06 \cdot 10^{-10} \text{ m}$ for different arrangements of gibbsite-like polymers. As the values of basal spacings for Keggin cations are nearly the same as for gibbsite-like polymers, we cannot distinguish them using diffraction measurements.

It is evident that the absence of cations ordering in the interlayer makes the porosity control very problematic. In pillaring clays, the main aim is to achieve as large basal spacing as possible, according to widely accepted opinion that the large basal spacing gives rise to large volume of pores. Present results, however, showed that the relation between the basal spacing and porosity can be more complicated. The d -values

Table 1. Comparison of Coulombic E_c and Total Sublimation Energy per 1 MMT Unit Cell and Average Values of Basal Spacings d_{av} for Models with Different Intercalating Species in the Interlayer of Montmorillonite

Intercalating species	$E_c/(\text{kJ mol}^{-1})$	$E_s/(\text{kJ mol}^{-1})$	$d_{av}/10^{-10}$ m
Al_{13}^{7+} ideal Keggin cation	1474.1	1554.6	19.51
Al_{13}^{5+} hydrolyzed Keggin cation	971.7	1078.5	19.60
Al_{13}^{3+} hydrol. $3a \times 2b$ supercell	1441.5	1595.3	19.65
Al_{13}^{3+} hydrol. $2a \times 3b$ supercell	2014.2	2165.2	20.05
Single ring sandwich	1609.1	1733.6	19.94
Double ring sandwich	1460.9	1638.2	20.06
Double rings shifted	2132.3	2316.3	19.58

for Keggin cations in the interlayer increase with increasing degree of hydrolysis and decreasing charge of cation. This is accompanied with the increase of cation concentration and consequently decrease of porosity volume in the interlayer. That means, the porosity is more likely ruled by the charge of Keggin cations. The value of basal spacing may be misleading in characterization of porosity in montmorillonites, intercalated with Keggin cations.

Present conclusions are in agreement with the experimental data in two following points: 1. the values of basal spacings reported in Refs. [5, 6] $19\text{--}20 \cdot 10^{-10}$ m agree with the present results, 2. inhomogeneity in cations distribution and resulting irregularity in stacking of silicate layers is evident in all diffraction patterns for intercalated smectites.

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