

# Structure analysis of hydrotalcite intercalated with pyrenetetrakisulfonate; experiments and molecular modelling

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**Abstract** The structure of pyrenetetrakisulfonate intercalated with hydrotalcite, having the formula  $[\text{Zn}_{0.68}\text{Al}_{0.32}(\text{OH})_2] [(\text{C}_{16}\text{H}_6\text{O}_{12}\text{S}_4)_{0.08} \cdot x \text{H}_2\text{O}]$ , was proposed based on molecular simulations combined with experimental data (X-ray powder diffraction, thermogravimetry). Calculations were done for samples kept at various relative humidities (0%, 84%, 98%). The appropriate models were selected from comparison of calculated and measured diffraction patterns. Modelling revealed the arrangement of pyrenetetrakisulfonate anions, and the positions and the amount of water molecules in the interlayer space of the host structure. The results confirmed a large variability in the arrangement of the guest species. In the sample without water molecules (0% RH), pyrenetetrakisulfonate anions formed a layer at the centre of the interlayer distance. For the sample kept at 84% RH, the anions formed two layers at the thirds of the interlayer. For the sample kept at 98% RH, the anions became tilted with respect to the layered double hydroxides (LDH) layers and are less organised. Water molecules were arranged in three distinct planes: one in the middle and two at the quarters of interlayer distance. The number of water molecules obtained by the modelling basically agrees with the water content as measured by thermogravimetry.

**Keywords** Hydrotalcite · Pyrenetetrakisulfonate · Intercalation · Structure analysis · Molecular simulations

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## Introduction

Hydrotalcite-like compounds [also known as layered double hydroxides (LDH) or anionic clays] [1] are used in many industrial applications, e.g. as catalysts for oxidation or reduction and other types of reactions, selective absorbents for gas and electrolyte ions, antioxidants, polymer or acid stabilisers, or selective nanoporous membranes for various separation processes [2, 3].

Many of these applications stem from the structure of hydrotalcites. Hydrotalcites are layered compounds whose structure is based on that of brucite (magnesium hydroxide), in which some of the divalent cations are replaced by trivalent cations giving positively charged host layers. The layers are built from flattened octahedra with hydroxyl groups in their apexes and typically a metal cation in their centres. Each octahedron shares six edges with six other octahedra and thus they build up nearly endless layers. Charge compensating anions reside between the layers and—in the case of hydrated compounds—interlayer water molecules are also placed here. The interlayer distance depends on many factors: the density of the positive charge on the host layers (consequently on the number of charge compensating anions), the size of these anions, their arrangement, the number of water molecules, etc.

Atoms in the hydrotalcite layers are bonded strongly via covalent bonds, while the interlayer atoms are anchored to the layers only by weak non-bond interactions [Coulomb and van der Waals (vdW) interactions, hydrogen bonds]. The charge compensating anions can be replaced by other anionic species. The structure of the hydrotalcite layers remains unchanged after such replacement (or is reconstructed when the replacement takes place through the so-called “memory effect” [3]). The interlayer distance usually changes during such replacement due to the different size, arrangement and amount of the new charge compensating

anion. Also, the amount and type of other species (mostly water molecules) present between the layers influences the nature of the interlayer space.

The structure of solids is usually determined from X-ray diffraction data. Unfortunately, such intercalates of hydroxaltes are powders with disordered structures. The degree of disorder allows the distance between layers to be determined, but does not allow the complete structure of the intercalate to be solved [4]. The arrangement of host molecules must be then determined by other methods. One possible way to solve this problem is by using an appropriate computing method. Depending on the amount of atoms in the calculated structures, molecular simulations based on empirical force fields (i.e. molecular mechanics and classical molecular dynamics) are a relatively good choice for solving these structures.

Hydroxaltes hosting optically important anionic compounds in their interlayer space belong to a group of materials with possible commercial applications. Among others, guest anions interesting from the point of view of their optical properties, for instance pyrene derivatives, could make compounds with luminescence activity. The optical activity of such compounds depends on the amount and the arrangement of the anion in the interlayer space, i.e. on the structure of the intercalation complex as a whole. Using the molecular simulation described in this paper, we will be able to estimate the arrangement of the hosted species and thus enlarge our knowledge of the structure–property relationships of the materials studied. In this paper we report an arrangement of pyrenetetrasulfonate anions in the interlayer space of zinc-aluminum layered double hydroxide, as determined using molecular modelling.

## Materials and methods

### Sample preparation

Layered double hydroxide with the formula  $[Zn_{0.68}Al_{0.32}(OH)_2][(CO_3)_{0.16} \cdot 0.5 H_2O]$  (further denoted as Zn-Al- $CO_3$ ), was prepared by the urea method [5]. A solution obtained by mixing 100 mL 0.5 M  $AlCl_3$ , 200 mL 0.5 M  $ZnCl_2$  and 30 g urea was refluxed for 2 days. The precipitate obtained was filtered, washed with distilled water and equilibrated with 100 mL 0.1 M  $Na_2CO_3$  for 1 day. The solid was then recovered by filtration, washed with distilled water and air dried.

The tetrasodium salt of 1,3,6,8-pyrenetetrasulfonic acid (0.6 g) was converted into the acid by stirring its aqueous solution with an Amberlite IR 120 ion-exchange resin (2.5 g). The intercalate was prepared by reaction of 0.6 g Zn-Al- $CO_3$  with the solution of the acid. The reaction mixture was heated at 90°C while being stirred in an open vessel for 48 h.

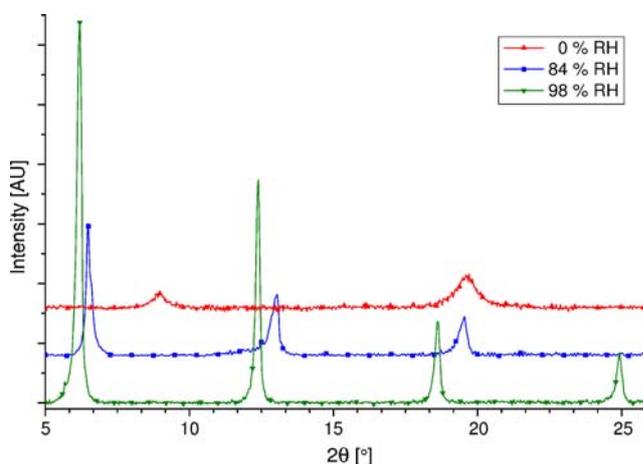
The volume of the reaction mixture (400 mL) was kept constant by automatic addition of distilled water. The intercalate prepared was filtered, washed with  $CO_2$ -free distilled water and dried. The samples were kept in a desiccator containing a KCl-saturated solution (84% RH). The contents of zinc, aluminum and sulfur were determined by energy-dispersive X-ray spectrometry (EDX) microanalysis. The content of pyrenetetrasulfonate anions was determined by elemental analysis (C, H, S) and water content was calculated from thermogravimetry. For measurements at various RH, the samples were stored over saturated solutions of  $K_2Cr_2O_7$  (98% RH) and over  $P_2O_5$  (0% RH).

Powder X-ray diffraction data were obtained with a D8-Advance diffractometer (Bruker AXS, Karlsruhe, Germany) using  $CuK\alpha$  radiation with secondary graphite monochromator. Diffraction angles were measured from 2° to 70° (2 $\theta$ ). Samples measured at 0% and 84% RH were covered with protection foil during measurements, with the signal of the foil being compensated in the diffractograms. A small aluminum signal came from the sample holder.

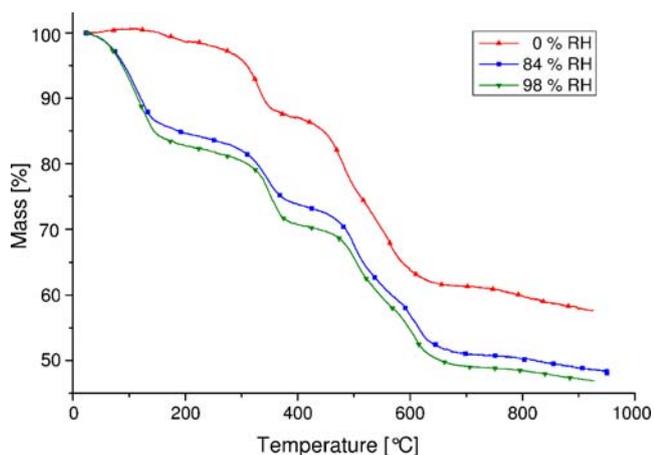
Thermogravimetric analysis (TGA) was performed using a homemade apparatus consisting of a computer-controlled oven and a Sartorius BP210 S balance. The measurements were carried out in air between 30°C and 900°C at a heating rate of 5°C min<sup>-1</sup>.

### Molecular modelling methods

Molecular simulations are based on calculations of potential energy for a given configuration of atoms according to the empirical force fields [6]. The force fields describe the interactions among the atoms by a simplified mechanical approach with parameters received from already known structures. The molecular mechanics principle is based on searching for a minimum on the potential energy surface of



**Fig. 1** Diffraction pattern of the studied intercalates at different relative humidity (RH)

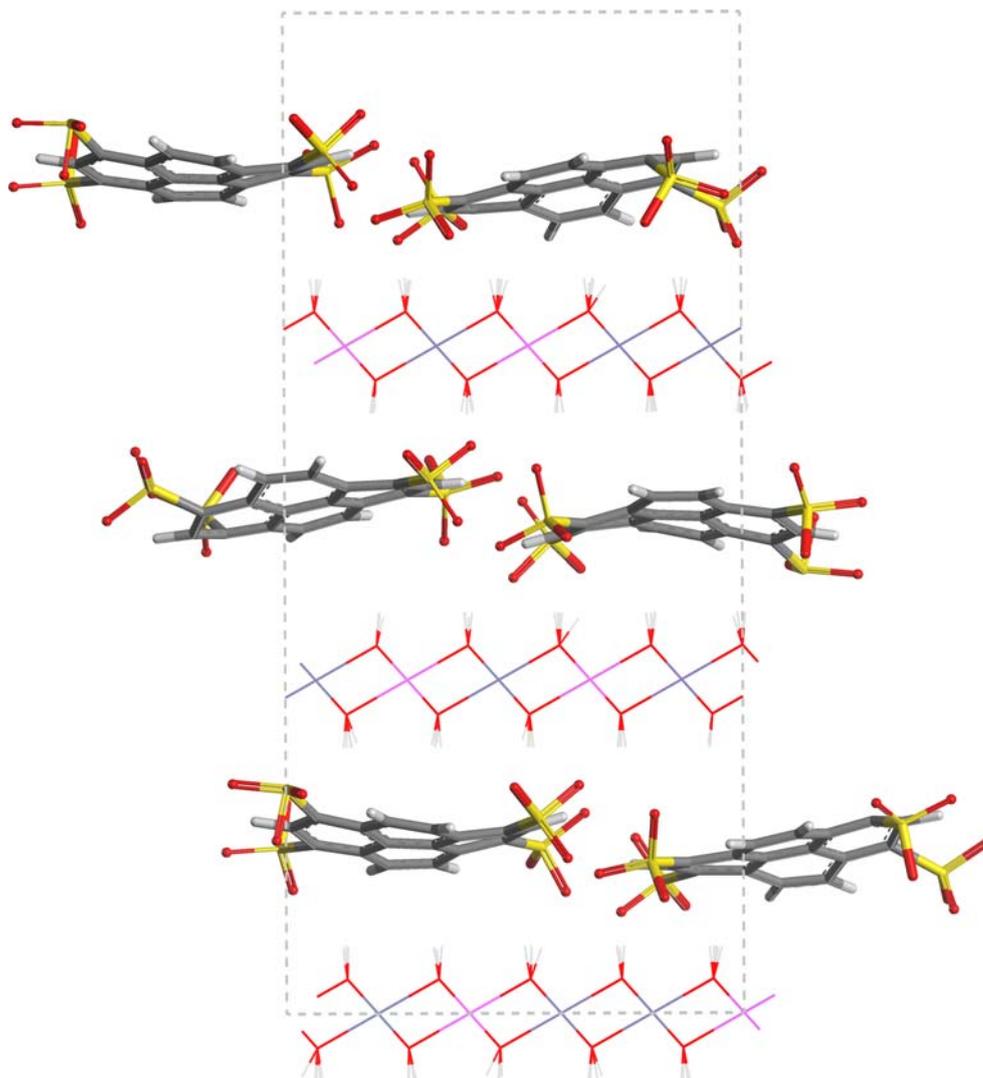


**Fig. 2** Thermogravimetric data of the studied intercalates at various RH

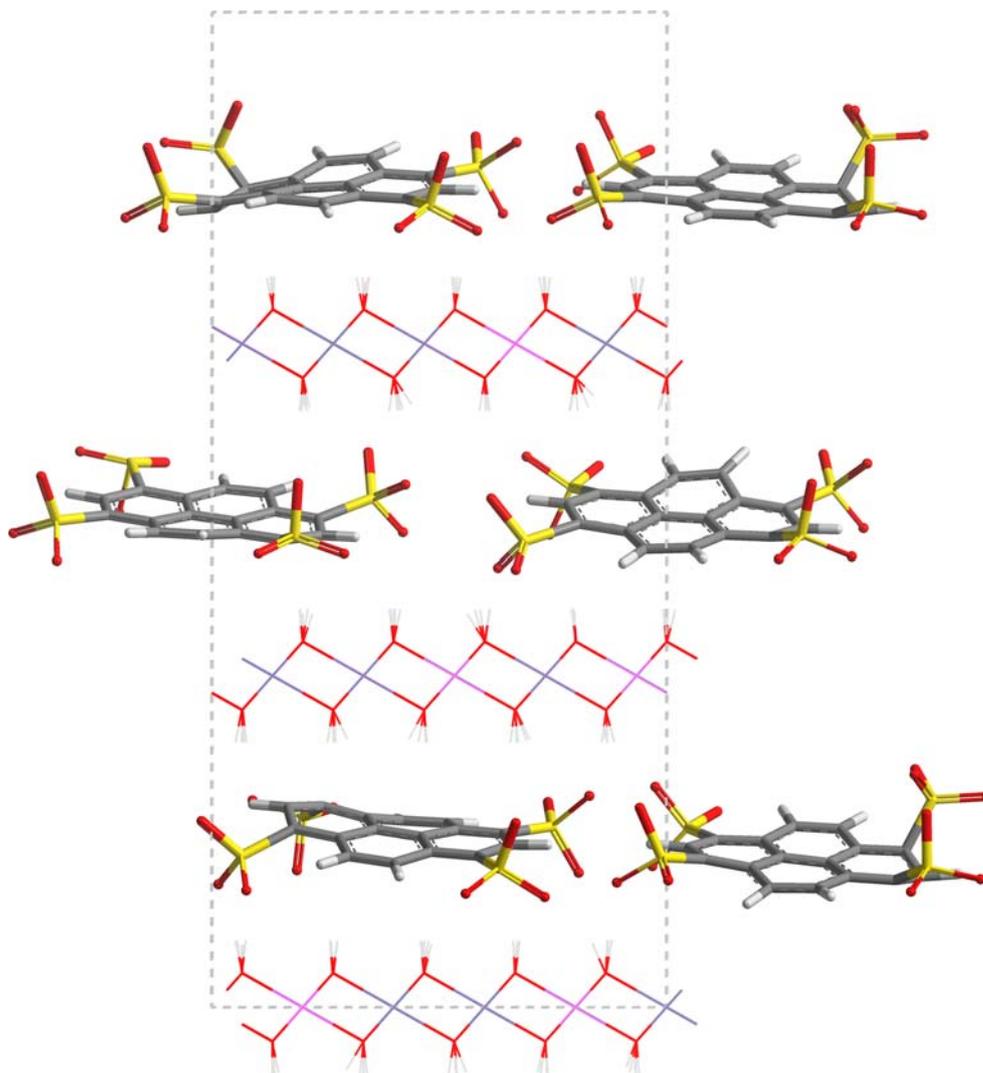
a given initial model. Molecular dynamics allows us to move with the atoms of the minimised models according to the forces applied to them. Molecular dynamics was used for more sophisticated structure refinement of the models obtained by molecular mechanics, because dynamics could take the model over a potential barrier to some better nearby minimum that is inaccessible for minimisation. The molecular simulations were performed in the Cerius<sup>2</sup> modelling environment [7]. However, neither method can reach a global minimum from the arbitrary initial model with certainty. Due to this fact, a systematic scanning of the entire potential energy surface was used to generate a set of desirable rough initial models for subsequent calculations. This was performed in the Supramol program [8].

The final results after the calculations were compared with regard to energy because models with the lowest energy are usually the most probable. As the calculations

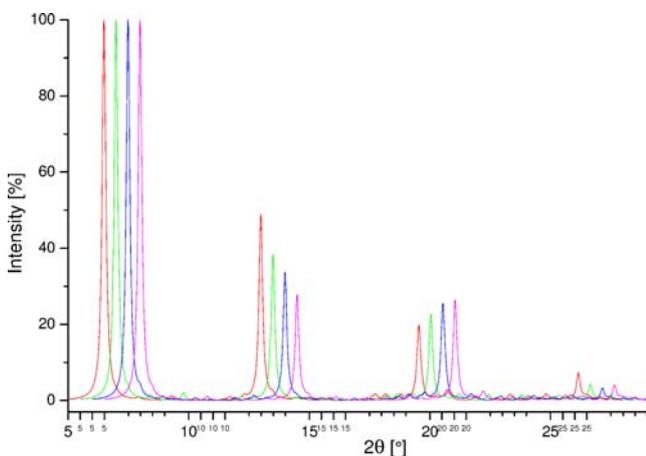
**Fig. 3** First resulting model for the 9.83-Å sample



**Fig. 4** Second resulting model for the 9.83-Å sample



were based on empirical force fields, it was necessary to compare the results with the experimental data—this simply means that the diffractions calculated from the model should be in agreement with the measured values.



**Fig. 5** Calculated diffraction patterns of four 13.63-Å models

Models of the hydrotalcite layers were built according to a template having the formula  $[\text{Zn}_{0.65}\text{Al}_{0.35}(\text{OH})_2][\text{Cl}_{0.35} \cdot 0.5 \text{H}_2\text{O}]$ , which has the same crystallographic data as in reference [9].

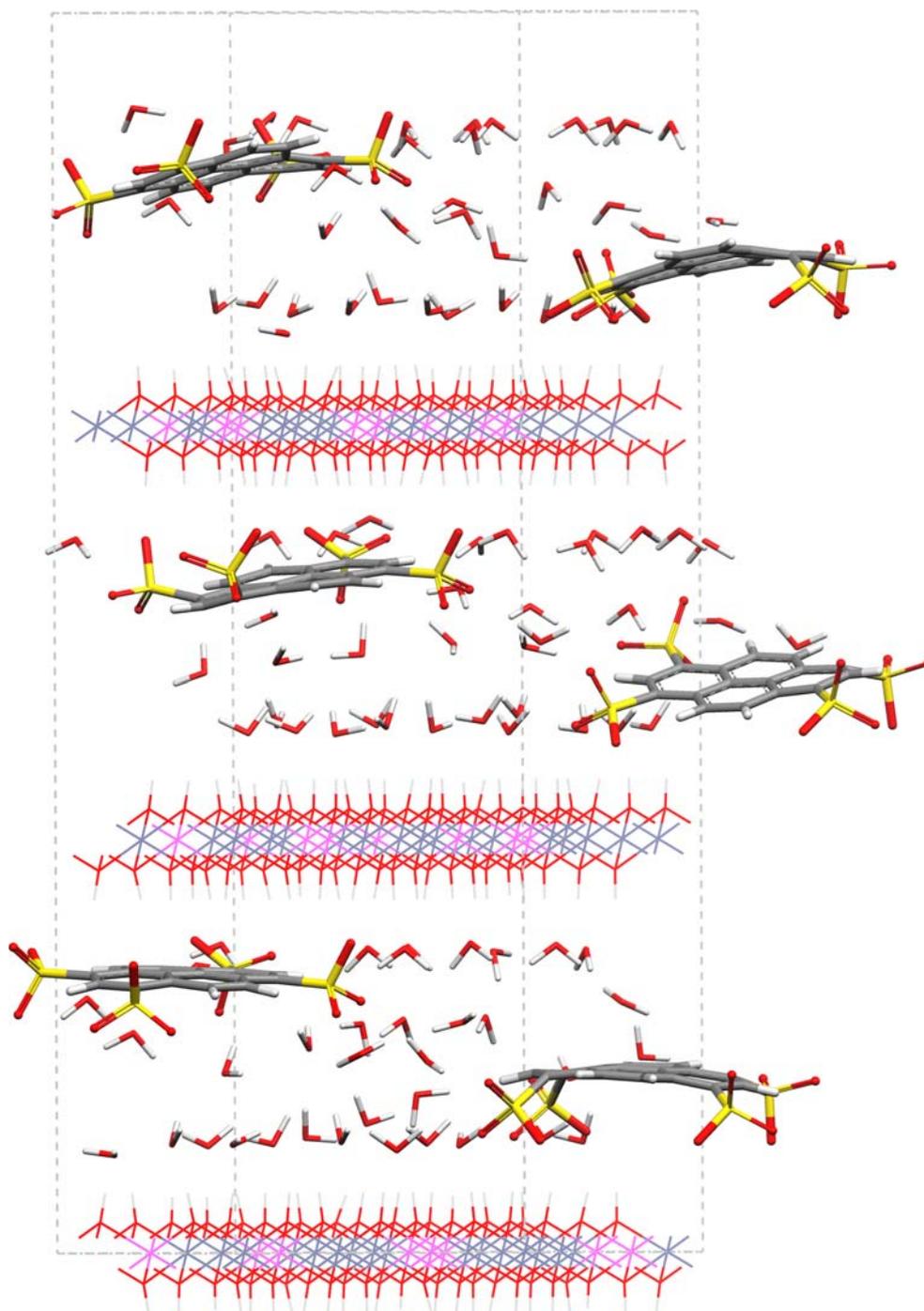
- Trigonal crystal system, space group  $R\bar{3}m$ ;
- Cell parameters:  $a=b=3.07598 \text{ \AA}$ ;  $c=23.2048 \text{ \AA}$ ;  $\alpha=\beta=90^\circ$ ;  $\gamma=120^\circ$ ;
- Atomic coordinates:

Element	$x/a$	$y/b$	$z/c$
Zn (Al)	0.0	0.0	0.0
O	0.0	0.0	0.37700

The composition of atoms in the models was based on the experimentally detected formula (see experimental results). Connecting 25 primitive cells to 1 supercell results in the formula  $[\text{Zn}_{17}\text{Al}_8(\text{OH})_{50}][(\text{C}_{16}\text{H}_6\text{O}_{12}\text{S}_4)_2 \cdot 25x \text{H}_2\text{O}]$ .

A state space for the Supramol program was defined by setting appropriate ranges and steps for independent

**Fig. 6** First resulting model for the 13.63-Å sample

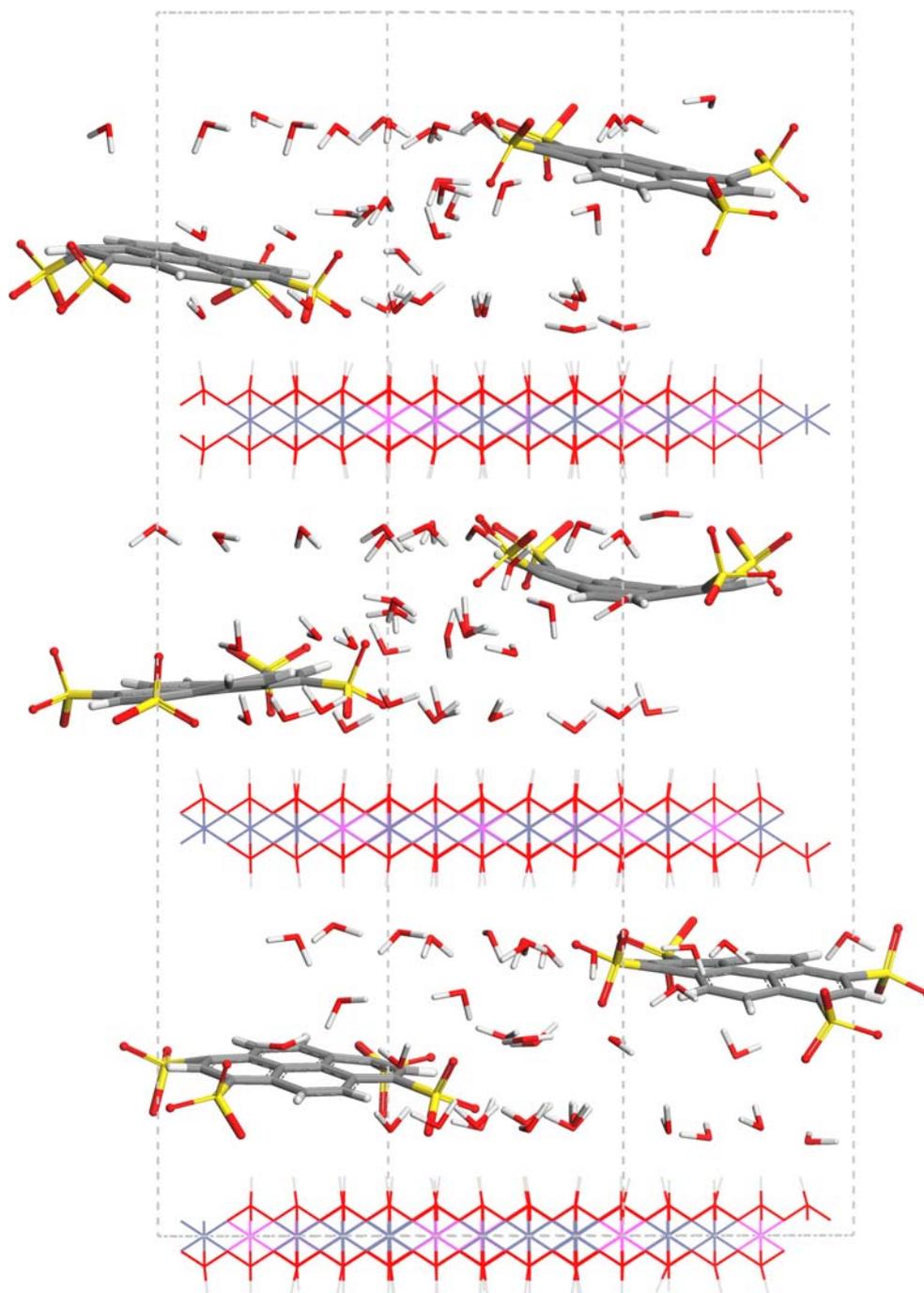


motion, and rotation of two pyrenetetrasulfonates treated as rigid units. The whole state space contained about 12 billion models for each sample (0%, 84% and 98% RH). Finally, about ten models for each sample were selected using the criterion of minimal vdW energy and a choice of markedly different models.

Water molecules were then randomly placed into appropriate models: the 9.83-Å sample (0% RH) has 0 water molecules, the 13.63-Å sample (84% RH) has 36 water molecules, and the 14.30-Å sample (98% RH or wet

sample) has 43 water molecules. The basal spacing and number of water molecules were determined experimentally (see experimental results; the number of water molecules for the 14.30-Å sample was estimated by extrapolation because no measurements could be carried out). In each model, the hydrocalcite layers were kept as rigid units (except the hydrogen atoms). As the diffraction patterns exhibited quite sharp basal reflections, and the interlayer distances were quite stable, the cell parameters and the positions of the layers could be fixed. The Universal force

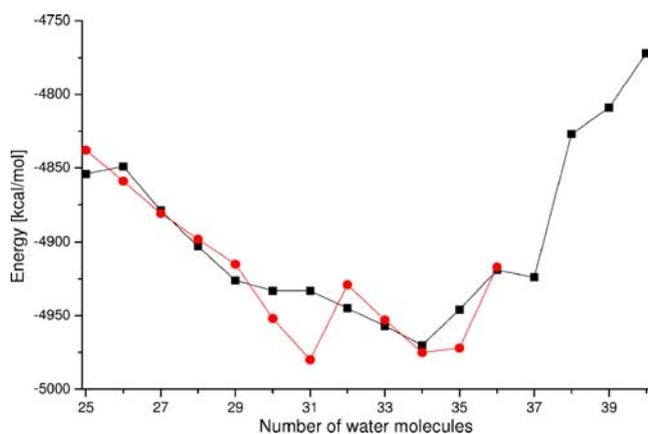
**Fig. 7** Second resulting model for the 13.63-Å sample



field [10] was used for these calculations because the parameters for all required atoms were included. The Ewald summation method [11] at a precision of  $10^{-4}$  kcal/mol was used to calculate non-bonded interactions. The charge equilibration (QEq) method [12] was used to calculate the charge distribution in the model. The minimisation procedure consisted of an iteration of (1) the charge recalculation for each molecule and each layer separately, and (2) minimisation until convergence was reached (for example, one of the criteria was maximal  $10^{-3}$  kcal/mol energy

difference per step). If necessary, up to hundreds of thousands of steps of molecular dynamics (in an NVT statistical ensemble at a temperature of 300 K and with a step duration of 0.001 ps) were carried out, in which at least half of the steps were already in an equilibrium state. The model with the lowest energy was subsequently properly minimised. Further details on the modelling and the parameters used can be found in our previous work [13].

It is not possible to directly compare the measured and calculated diffraction pattern, because the computer models



**Fig. 8** Energy vs water molecules for two models of the 13.63-Å sample

contain a simulated periodicity in themselves and, on the other hand, the measured diffraction pattern is incalculably influenced by the roughness of a sample surface, which leads mainly to a lower intensity of the first reflection. Thus, models were selected according to the agreement in the ratio of intensity from the second to the fourth reflection between the experimental and the calculated diffraction patterns.

## Results and discussion

### Characterisation of the prepared samples

Carbonate ions are strongly held in the interlayer region of Zn-Al-CO<sub>3</sub> and cannot be replaced by other anions in a neutral or basic medium. This means that pyrenetetrasulfonate anions cannot be intercalated into Zn-Al-CO<sub>3</sub> using sodium salt. Therefore, single-phase products were prepared by heating Zn-Al-CO<sub>3</sub> with a solution of pyrenetetrasulfonic acid in an open reaction vessel. Heating supports removal of the carbonate anions from solution and thus favours formation of the product.

The intercalate prepared was a light grey crystalline solid. On the basis of elemental analysis and TGA, the formula of the intercalate stored at 84% RH is [Zn<sub>0.68</sub>Al<sub>0.32</sub>(OH)<sub>2</sub>][(C<sub>16</sub>H<sub>6</sub>O<sub>12</sub>S<sub>4</sub>)<sub>0.08</sub> · 1.32 H<sub>2</sub>O] (calculated C 9.96%, H 3.35%, S 6.65%; found C 9.98%, H 3.40%, S 6.62%). This means that all the carbonate anions were replaced by pyrenetetrasulfonate. It was found that the basal spacing of the intercalate depended on the RH. Figure 1 shows X-ray diffractograms of the intercalate at various RH. The basal spacing of the intercalate decreases with decreasing RH and the diffraction lines becomes broader.

Thermogravimetric curves of the intercalate kept at various RH are given in Fig. 2. The intercalate kept at 84% RH decomposed in three steps. The interlayer water was released in the first step up to 200°C, and dehydroxylation occurred between 200°C and 430°C. Observed weight losses of

15.2% and 11.8% are in good agreement with the values (15.4% and 11.7%) calculated for the sample containing 1.32 molecules of interlayer water per formula unit. The decomposition of intercalated pyrenetetrasulfonate occurred in the third step above 450°C. The total weight loss (52%) is in good agreement with the calculated value (53.6%). The product of thermal decomposition of the intercalate was a mixture of ZnO and ZnAl<sub>2</sub>O<sub>4</sub>. The sample stored over P<sub>2</sub>O<sub>5</sub> did not contain interlayer water so it decomposed in only two steps. The sample stored at 98% RH had the same basal spacing as the wet sample and contained 1.6 molecules of water per formula unit; the thermogravimetry for this sample had a similar decomposition process as that of the sample stored at 84% RH.

### Modelling of the 9.83-Å sample

The diffraction pattern of the sample with a basal spacing of 9.83 Å shows only the first two reflections, with the second reflection being more intensive than the first. As the intensity of the first reflection is lowered by the roughness of the sample, we can presume that, in the absence of this effect, both reflections have comparable intensities. Consequently, the model in which the guest anions are situated in the middle of the interlayer distance is the most probable.

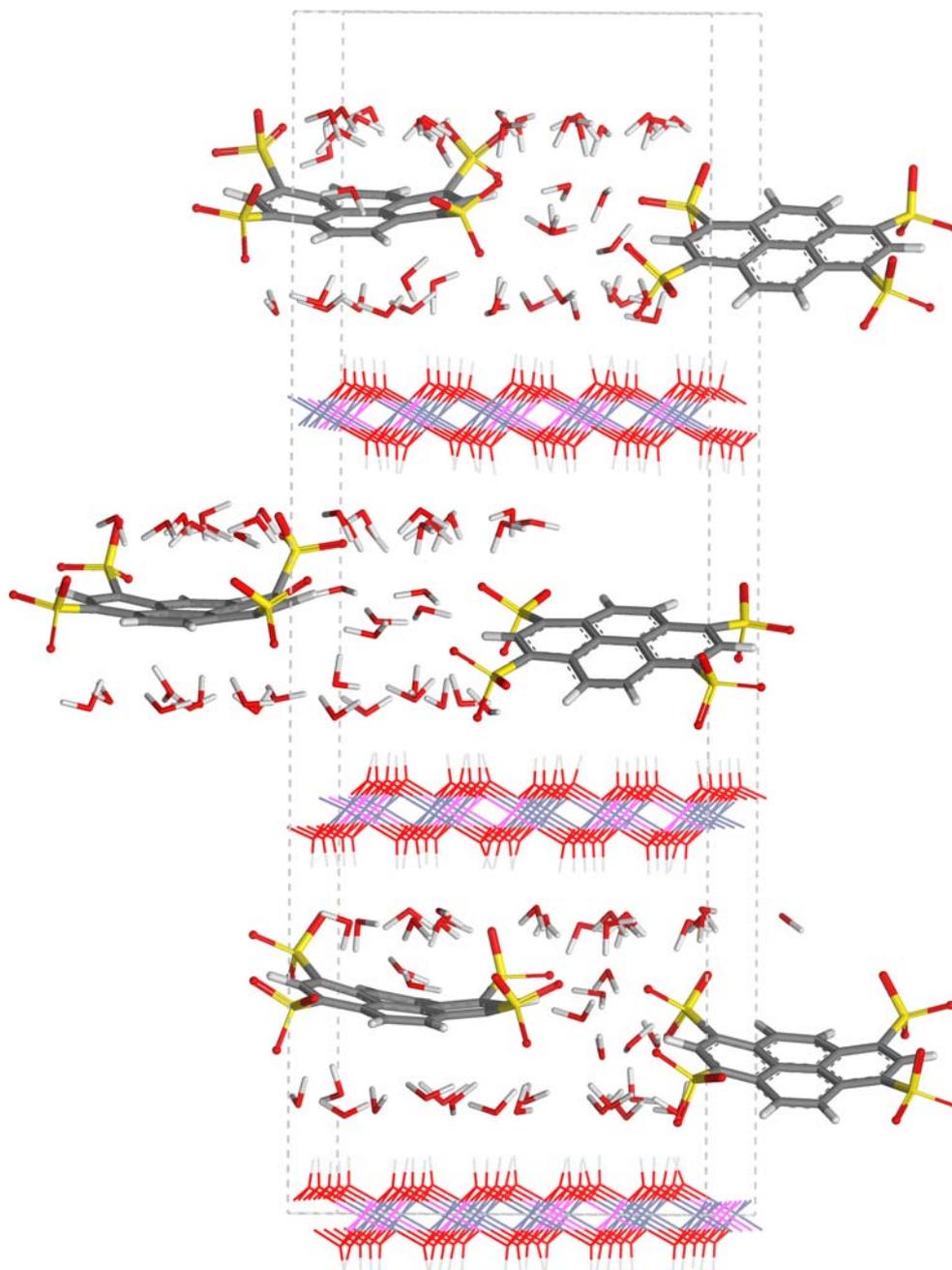
The models obtained using the Supramol program basically confirmed this idea. All the models have one of the following: (1) the pyrenetetrasulfonate anions are situated in one layer parallel to the hydroxalite layers, (2) the anions are only slightly tilted but still in one layer, (3) the anions are located in only a short distance from the middle of the interlayer, or (4) various combinations of these preceding arrangements. After minimisation, the energies differed at most by several percent units. The dynamics did not change the positions of the pyrenetetrasulfonates significantly. Thus, the dynamics, or an adjustment of sulfonates, did not help improve the energy by more than a couple of percent units. Thus all the minimised models have—with respect to the energy—a similar probability of occurrence in the real sample.

Two models that best satisfy the preceding considerations, and that have a ratio of second and first reflections up to 66% are shown in Figs. 3 and 4 (these models are also energetically slightly more probable). The basal reflections are greatly broadened and thus the interlayer distance of 9.83 Å is only a mean value. Also, the acid anions do not exhibit any significant ordering and the organisation is variable within the scope of one layer.

### Modelling of the 13.63-Å sample

Only one initial model from the Supramol program had the acid anions tilted; in all the other models, the anions were

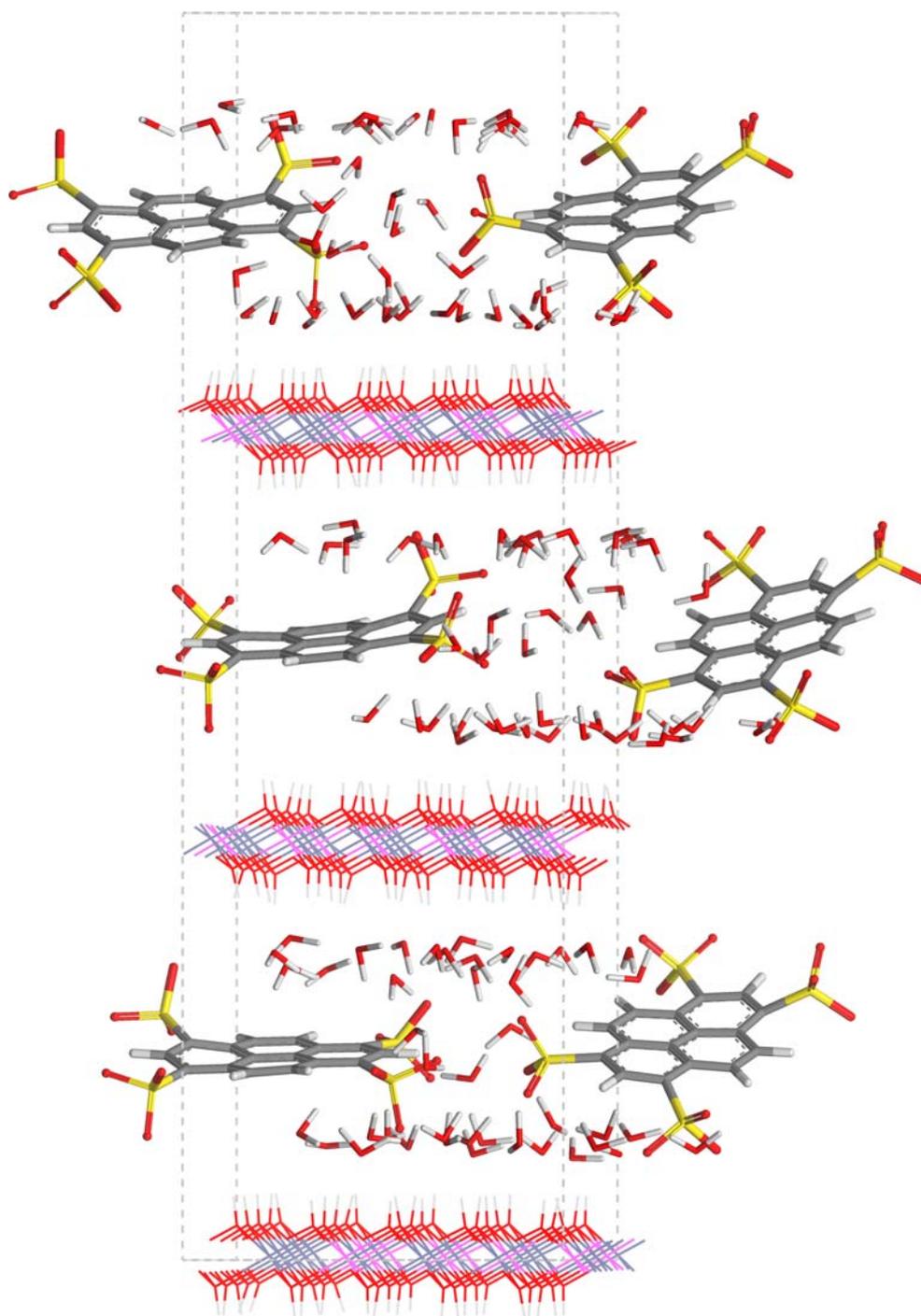
**Fig. 9** First resulting model for the 14.30-Å sample



contained in two layers in which anions were variously turned and shifted horizontally. The initial distribution of the water molecules did not have a significant influence because the optimisation, especially by molecular dynamics, sorted the water molecules to similar final positions. The resulting energies of the models after minimisation were also very similar. Molecular dynamics did not introduce any changes. In conclusion, with respect to energy we can say that the configuration of the acid anions within the frame of the tested models is highly variable.

Nevertheless, when comparing the calculated diffraction pattern with the experimental pattern, considerable differences were revealed. The ratio between the measured intensities of the third and second reflections is 64%. But the same ratio in the calculated diffractions gave values from 40% to 94% (as an illustration, the diffraction patterns of the four most different models are shown in Fig. 5). Two models have ratios roughly equal to the value obtained from the experimental diffraction pattern. The structures of these models are shown in Figs. 6 and 7. About five to six

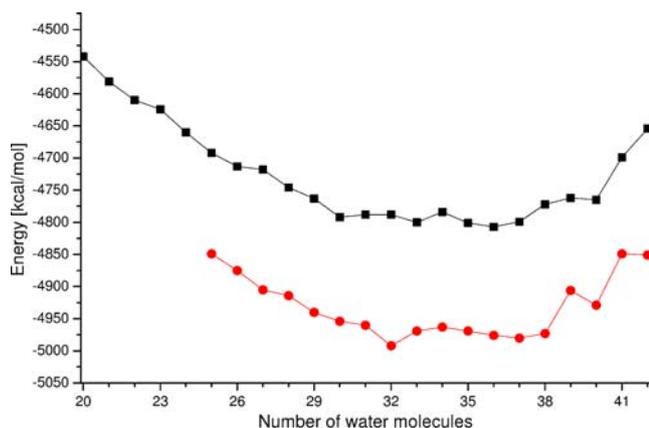
**Fig. 10** Second resulting model for the 14.30-Å sample



sulfonates of both acid anions are located exactly in the thirds of the interlayer distance; other models have either more or less of their acid anion sulfonates exactly in the thirds of the interlayer. Overall, the anions adopt a rather horizontal position near the thirds. However, as the measured ratio of the intensities is an approximate average value of all calculated values, it is probable that the measured diffraction pattern is also obtained as an average result of the sample, which was disordered and included

the whole spectrum of conformations to which the calculated models conform.

Water is organised in three distinct layers: the first in the middle, two others in the quarters of the interlayer distance (with vacant places close to aromatic nuclei). The ratio between measured intensities of the fourth and second reflections is 13%. Roughly this value was attained for all models when the water was finely organised and refined in the layers by the dynamics.



**Fig. 11** Energy vs water molecules for two models of the 14.30-Å sample

The energies of these two models were calculated with different amounts of water in the interlayer; the graph is shown in Fig. 8. The average number given by a minimum is around 33 molecules, which is in good agreement with the experimental results.

#### Modelling of the 14.30-Å sample

In contrast to the 13.63-Å sample, the models selected from Supramol results no longer preferred a unique configuration. Some models had the acid anions in bi-layer arrangement, and there were also models with anions variably tilted through the interlayer space. All these models had similar energy values after energy minimisation. Thus, there was greater variability in ion organisation compared to the 13.63-Å models. Nevertheless the water molecules were still located in three distinct layers.

However, the measured and the calculated diffractograms were quite different for the 14.30-Å sample with respect to the 13.63-Å sample. The ratio between the measured intensities of the third and the second reflections was 36%, but the ratio from calculated diffractograms was (with the exception of one model) consistently above the measured value (34–89%). Further testing revealed that the ratio of reflection intensities did approach the measured value when the water molecules were initially situated not uniformly but were placed rather closer to the host layers.

However, two models were found to agree very well with the measured diffractogram. Their proposed structures are shown in Figs. 9 and 10. Up to five of the eight sulfonates of the two anions in these structures were located in the thirds of the interlayer (in contrast to the 13.63-Å models). The rest of the sulfonates were close to the middle of the interlayer distance. Moreover, some anions are tilted and, overall, they fill more central space of the interlayer where there are fewer water molecules. Conversely, the

water molecules are positioned more in water sheets in the quarters of the interlayer distance.

This shows how the higher amount and different organisation of water molecules causes differences between the 14.30-Å and 13.63-Å samples. The water molecules close to the host layers isolate the sulfonate anions from the hydrotalcite layers. The anions are thus located further from the host layers. Consequently, electrostatic interaction between the positively charged host layers and negatively charged guest anions is weaker, resulting in the higher interlayer distance observed for this sample. The anions then have more freedom to adopt arbitrary positions at the halfway point of the interlayer distance, which leads to the displacement of some water molecules from their position in the middle of the interlayer distance to the edge water layers. This further weakens the interactions between the guest anions and the host layers. (This relatively strong influence of water can explain why we did not obtain the full set of models that could provide the measured diffractogram as the average. Supramol did not include water molecules in its calculations and so the acid anions could be relatively far from the optimal configuration.)

Concerning the ratio between the intensities of the fourth and the second reflection, the measured value is 22%, i.e. higher than all calculated values. However, again here, dynamics helped to refine the molecule positions more finely so that this ratio could reach the optimal value.

The calculated amount of water given by the average minimum of energy is about 35 molecules. The graphs for both selected models are shown in Fig. 11. This number differs somewhat from 43 molecules, which was the value extrapolated from previous thermogravimetry results. Although the calculations were carried out with 43 molecules, lowering the number to 35 did not affect the diffractograms or resulting configurations significantly. Hence the calculations could be taken as relevant.

#### Summary

Both molecular mechanics and classical dynamics calculations proved their suitability for proposing the structure of the studied samples. The studies revealed differences among the samples that would be hard to elucidate using other methods. Nevertheless, a large variability in configuration was found, in addition to notable changes in character together with interlayer distance that depended on relative humidity.

This behaviour is not typical. Generally, if the amount of water in hydrotalcite intercalated by some dye changes in response to the relative humidity of the surrounding air or temperature, then the samples usually exhibit only two different interlayer distances—the first for the hydrate and the second for the anhydrous compound. It is not common for

interlayer distances to change to such a large extent. Thus, although the modelling was useful and interesting from this point of view, it remains questionable if this is an interesting behaviour for an optically active material. Also, independence from environmental conditions would be rather desirable.

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