

# Molecular modeling of layered double hydroxide intercalated with benzoate, modeling and experiment

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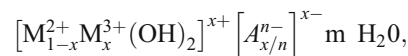
**Abstract** The structure of  $Zn_4Al_2$  Layered Double Hydroxide intercalated with benzenecarboxylate ( $C_6H_5COO^-$ ) was solved using molecular modeling combined with experiment (X-ray powder diffraction, IR spectroscopy, TG measurements). Molecular modeling revealed the arrangement of guest molecules, layer stacking, water content and water location in the interlayer space of the host structure. Molecular modeling using empirical force field was carried out in Cerius<sup>2</sup> modeling environment. Results of modeling were confronted with experiment that means comparing the calculated and measured diffraction pattern and comparing the calculated water content with the thermogravimetric value. Good agreement has been achieved between calculated and measured basal spacing:  $d_{calc}=15.3 \text{ \AA}$  and  $d_{exp}=15.5 \text{ \AA}$ . The number of water

molecules per formula unit ( $6H_2O$  per  $Zn_4Al_2(OH)_{12}$ ) obtained by modeling (i.e., corresponding to the energy minimum) agrees with the water content estimated by thermogravimetry. The long axis of guest molecules are almost perpendicular to the LDH layers, anchored to the host layers via  $COO^-$  groups. Mutual orientation of benzoate ring planes in the interlayer space keeps the parquet arrangement. Water molecules are roughly arranged in planes adjacent to host layers together with  $COO^-$  groups.

**Keywords** Benzoate · Layered double hydroxide · Molecular modeling · X-ray diffraction

## Introduction

Layered double hydroxides (LDHs), sometimes called hydrotalcites, belong to a wide family of lamellar compounds called anionic clays. They are characterized by regular stacking of layers that bear a positive charge. The layers are formed of octahedral units  $M(OH)_2$  where  $M$  is mostly a divalent or a trivalent cation. The interlayer space contains water molecules and anions that compensate the positive charge of the layers. Hydrotalcites can be represented by a general formula:



where  $M^{2+}$  and  $M^{3+}$  are bi- and trivalent metal cations.  $A$  is the interlayer anion with the charge of  $n^-$  [1].

The charge balancing anions can be exchanged by a wide amount of anions of inorganic or organic molecules [1–4]. The anion exchange is a widely used intercalation method [5, 6].

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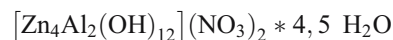
LDH offer a wide scale of practical application like catalysts (e.g., precursors for preparation of other catalysts [7], synthesis of organic molecules [8], chemical reactions [9]), polymer stabilizers [10, 11], drug carriers [12] and drug improvers [13], sorbents [14, 15], etc. Intercalation of guest species possessing chromophoric groups into LDH gives rise to hybrid organo - inorganic nanostructure materials for various photofunction [16, 17].

In the present work we investigated the structure of LDH intercalated with benzoate anions. Many papers dealing with LDH intercalated with benzoic acid and its derivatives such as salts of benzoic acid, terephthalate have been published [18–25] mostly with only on a rough assessment of structure model based on the measured basal spacing. In this paper we investigated the structure and guest arrangement in benzoate - LDH intercalate using combination of molecular modeling with experiment (X-ray powder diffraction, IR spectroscopy and thermogravimetry).

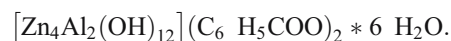
## Experiment

### Samples preparation and chemical analysis

Well crystallized hydrotalcite - like compound (HTlc) of formula  $[Zn_4Al_2(OH)_{12}](CO_3)_2 \cdot 4H_2O$ , was obtained with a procedure accomplished by the thermal hydrolysis of urea [26]. The corresponding chloride form was obtained by titrating the carbonate form, dispersed in a  $0.1 \text{ mol/dm}^3$  NaCl solution, with a  $0.1 \text{ mol/dm}^3$  HCl by means of Radiometer automatic titrator operating at pH stat mode, and pH value of 5. Finally, the hydrotalcite in nitrate form was obtained by equilibrating the chloride form with an aqueous solution of  $NaNO_3$   $0.5 \text{ mol/dm}^3$  (molar ratio  $NO_3^-/Cl^- = 10$ ). The composition of host structure was the following:



The intercalation of benzoate anions was achieved by equilibrating the nitrate form of hydrotalcite with an aqueous solution of  $C_6H_5COONa$   $0.5 \text{ mol/dm}^3$  (molar ratio  $C_6H_5COO^-_{(solution)}/NO_3^-_{(solid)} = 10$ ) for 24 hours. The recovered solid was three times washed with  $CO_2$ -free deionized water and dried over  $P_4O_{10}$ . The composition of the intercalated structure was:



The Zn and Al content of the HTlc, was obtained with standard EDTA titration after having dissolved a weighed amount of the sample (~100 mg) in a few drops of concentrated HCl and diluted with water to 50 ml. The

$Cl^-$ ,  $NO_3^-$  and  $C_6H_5COO^-$  counterions in solution, before and after equilibration, were determined by ion chromatography. Water and  $C_6H_5COO^-$  content of the solids were obtained by thermogravimetry.

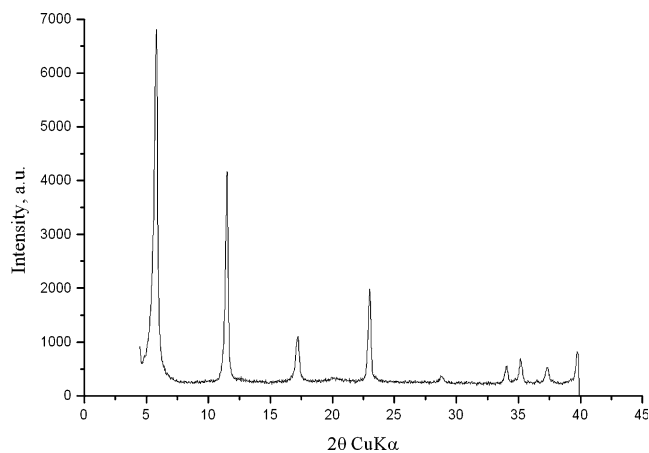
TG/DTA analysis were performed in air by a Stanton 781 Thermoanalyser at the heating rate of  $5 \text{ }^\circ\text{C}/\text{min}$ .

The thermogravimetric analysis (TGA) and differential thermal analysis (DTA) showed two endothermic peaks related to loss of co-intercalated water and to dehydroxylation of the inorganic layers between  $80^\circ$  and  $300 \text{ }^\circ\text{C}$ . Furthermore, the main weight loss between  $300 \text{ }^\circ\text{C}$  and  $600 \text{ }^\circ\text{C}$  may be ascribed to decomposition of organic parts. ZnO and  $ZnAl_2O_4$ , starts to be formed at temperatures higher than  $600 \text{ }^\circ\text{C}$  as confirmed by the XRPD patterns of the sample heated at  $900 \text{ }^\circ\text{C}$ .

### X-ray diffraction

The measurement conditions: X-ray powder diffraction (XRPD) patterns were taken with a computer-controlled PW 1710 Philips diffractometer operating at 40 kV, 30 mA, using a PW 1820 goniometer, supplied with a bent graphite monochromator in the diffracted beam, and Cu-K $\alpha$  radiation. XRPD patterns were taken with the step-scanning technique. The samples were prepared using the side-loading procedure in order to minimize preferred orientations. Diffractograms were collected from  $2\theta = 2$  to  $120^\circ$  using steps of  $0.01^\circ$  and a counting time of 20 s per step.

The diffraction pattern of the intercalated structure measured at temperature of  $30 \text{ }^\circ\text{C}$  is shown in Fig. 1. It exhibits characteristic features of a layered structure, that means very strong basal reflections due to the strong preferred orientation and weak broaden non-basal reflections indicating a slight stacking disorder. Nevertheless the crystal structure of the intercalate exhibits a high degree of three-dimensional ordering (non-basal reflections quite pronounced). Anyway due to the slight structural disorder



**Fig. 1** Powder diffraction pattern of the intercalated structure

the structure of the intercalate cannot be solved by diffraction method only and it is suitable to use molecular modeling.

### IR spectroscopy

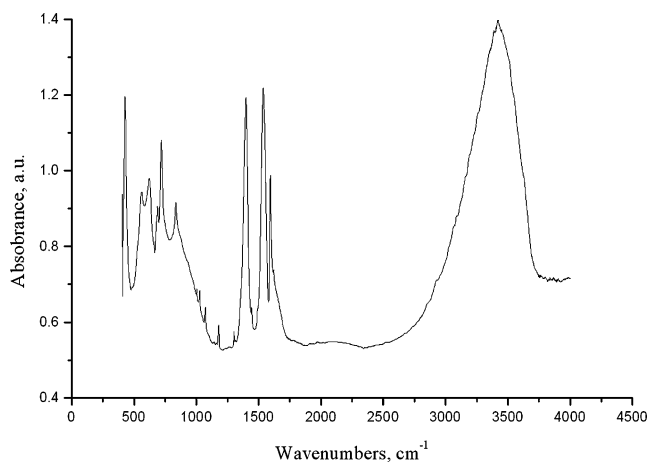
FT-IR spectra of the solid samples were recorded under vacuum with a Bruker IFS 113V spectrometer by the KBr pellet technique.

The FT-IR spectrum (see Fig. 2) shows a strong broad band in the 3000–3750  $\text{cm}^{-1}$  range due to the lamellae OH stretching which are involved in H-bonds. The sharp and intense bands at 1537  $\text{cm}^{-1}$  and 1397  $\text{cm}^{-1}$  are ascribable to the asymmetric and symmetric stretching vibrations of the equivalent carbon-oxygen bonds of  $\text{COO}^-$  group. Moreover, are visible the typical signals of monosubstituted aromatic ring: the in-plane skeletal vibration at 1595  $\text{cm}^{-1}$  and the two adsorption bands at 719  $\text{cm}^{-1}$  and 689  $\text{cm}^{-1}$  due to the bending of the five adjacent hydrogen atoms of the ring.

### Molecular modeling

Molecular modeling using an empirical force field was carried out in *Cerius<sup>2</sup>* modeling environment [27]. Initial model of the host structure was built according the crystallographic structure data obtained from refinement by means of Rietveld procedure. Unit cell of the host structure is trilayer, the space group is *R-3m* with triclinic cell and lattice parameters  $a=3.07598 \text{ \AA}$ ,  $c=23.2048 \text{ \AA}$ ,  $\alpha = 90^\circ$ ,  $\beta = 90^\circ$ ,  $\gamma = 120^\circ$ .

The Al and Zn atoms in the host layers were randomly distributed so that the composition of the host structure corresponded to the experimental one. The measured value of basal spacing, was  $d_{\text{exp}}=15.5 \text{ \AA}$ , thus the interlayer



**Fig. 2** IR spectra of the intercalated structure

distance in the initial model was set to this value. To investigate the arrangement of guest molecules in the interlayer space we built the supercell  $4a \times 6a \times 1c$  with the lattice parameters:  $4a=12.3039 \text{ \AA}$ ,  $6a=18.4559 \text{ \AA}$ , where the  $c=3d_{\text{exp}}=46.5 \text{ \AA}$ . The charge of this trilayer supercell is + 24 *el.*, that means 24 benzoate anions were placed into the interlayer space of the supercell, consisting of 3 host layers and 3 guest layers (i.e., 8 benzoates per one guest layer in the supercell).

A series of initial models have been built with various positions and orientations of guests and with variable water content:

- (1) Benzoate ring planes parallel to the host layers in bilayer or trilayer guest arrangement in the interlayer space.
- (2) Benzoate ring planes tilted to the host layers in bilayer guest arrangement in the interlayer space.
- (3) Benzoate ring planes perpendicular to the host layers and with various mutual orientations and various positions of  $\text{COO}^-$  groups with respect to OH groups on the host structure.

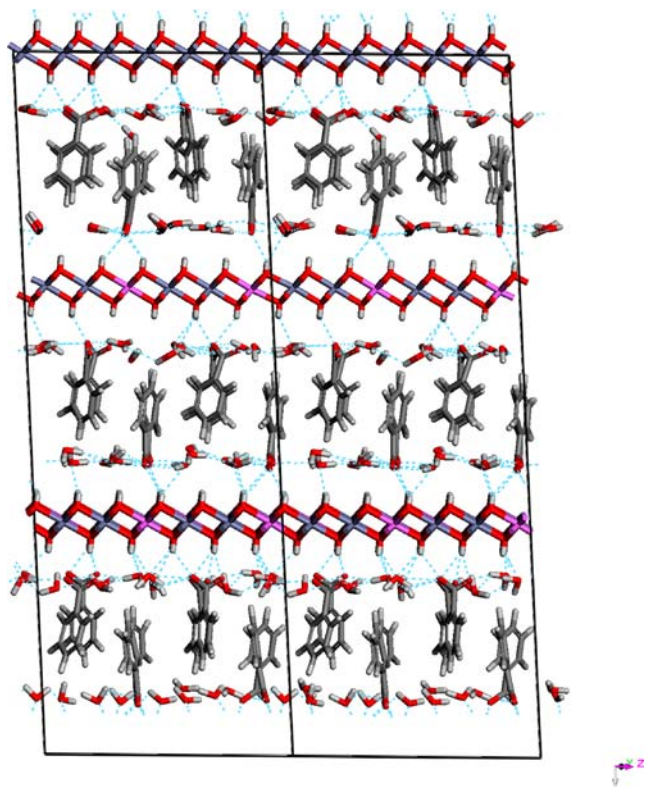
Energy minimization was carried out in *Universal force field* [28]. The electrostatic energy was calculated by Ewald summation method [29], van der Waals energy was expressed by Lennard-Jones potential [30]. The minimization of the total crystal energy was carried out in the *Minimizer* module according to the following strategy:

All the host layers in the supercell were kept as rigid units during energy minimization. Variable parameters were:  $c$ ,  $\alpha$ ,  $\beta$  (this enables to optimize the mutual positions of the layers) and all atomic positions in guest layers. The minimization was carried out by modified Newton procedure.

The calculated structure models obtained from various starting geometries were sorted using two criteria:

- The value of crystal energy minimum.
- The similarity of calculated and measured diffraction pattern.

After reaching the optimum positions and orientation of guest molecules we tried to find the optimum water content and water location. As the water content has the significant influence on the total energy we could find the optimum water content. The following strategy was used: We compared the total nonbonded energy (i.e., sum of electrostatic and van der Waals interactions) of the optimized structure models containing various water content in the interlayer space. By using this procedure we can find out the affinity rate of water molecules to the interlayer space. On the other hand position of water molecules in the interlayer space affects strongly the intensity profiles in the diffraction pattern. This effect enables us to refine the water location.



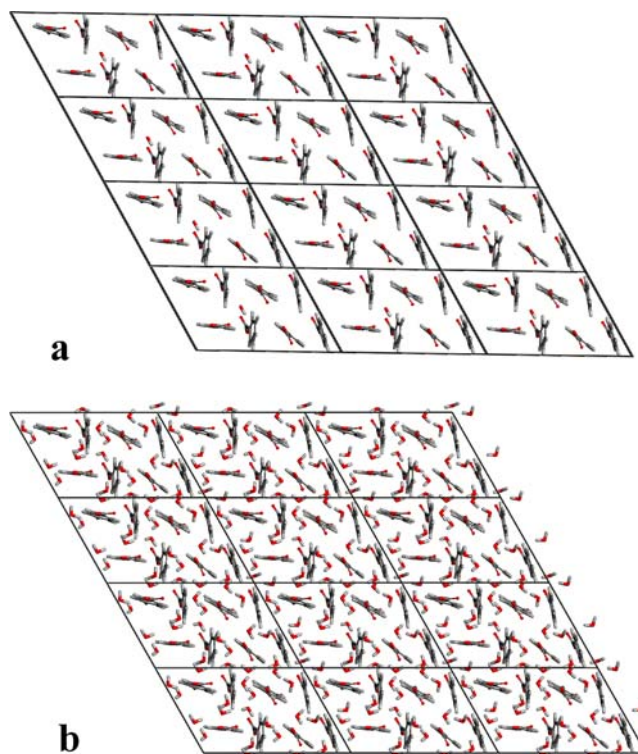
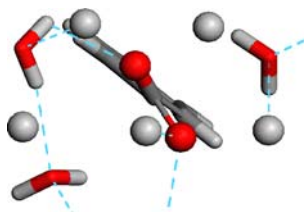
**Fig. 3** Side view of the optimized structure with the hydrogen-bond interactions (broken line)

## Results

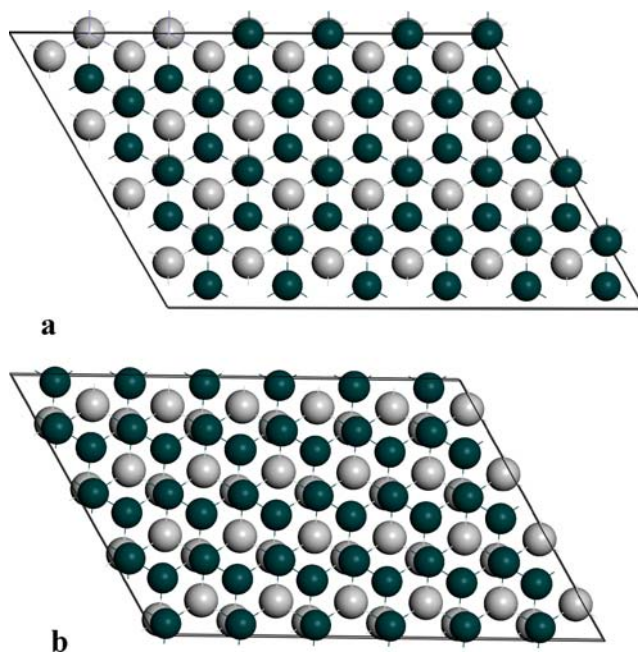
Results of modeling led to the conclusions concerning the orientation and position of the benzoate anions in the interlayer space. The optimized structure model is shown in Fig. 3. The long axis of benzoate is oriented perpendicular to the hydroxalcite layers with small departure within the range of  $\pm 10$  degrees.  $\text{COO}^-$  groups are anchored to OH groups of the LDH layer via the hydrogen bond. The detailed view of orientation of  $\text{COO}^-$  groups with respect to OH groups is shown in Fig. 4. Carboxyl group can rotate freely along the C-C bond in long benzoate axis that means while the ring planes exhibit ordering, the orientation of carboxyl groups is disordered. Mutual orientation of the ring planes keeps parquet arrangement with a small departure within the range of  $\pm 10$  degrees (see Fig. 5a,b).

Mutual positions of two successive host layers in the intercalated structure exhibit a slight shift from their starting

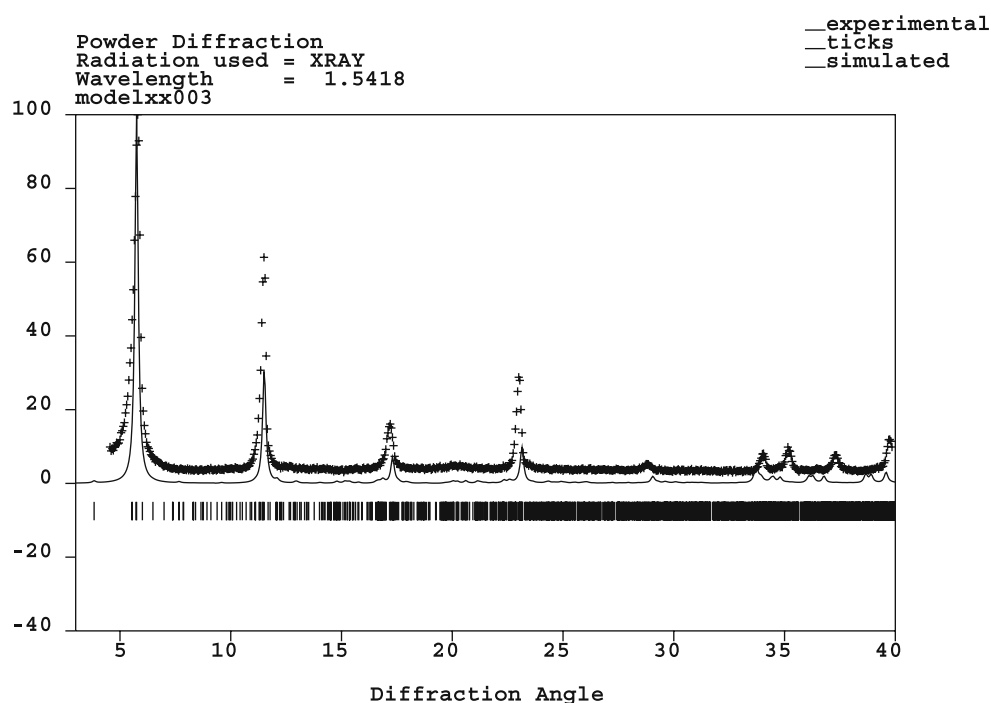
**Fig. 4** Detailed top view of the orientation of  $\text{COO}^-$  groups with respect to the OH groups (gray balls represent hydrogen atoms of OH groups of the layer)



**Fig. 5** a) Top view of parquet arrangement of the ring planes b) Top view of parquet arrangement of the ring planes and arrangement of water molecules



**Fig. 6** a) Top view of stacking of two successive layers in the starting model (metal atoms represented by bright balls, oxygen atoms represented by dark balls) b) Top view of stacking of two successive layers in the optimized model (metal atoms represented by bright balls, oxygen atoms represented by dark balls)

**Fig. 7** Calculated powder diffraction pattern

positions in the host structure. This shift in direction along metal - oxygen bonds is about 0.3 Å at maximum (see Fig. 6a,b).

The calculated diffraction pattern of the optimized structure is shown in Fig. 7. The higher intensity of basal reflection with respect to the others in comparison to the experimental diffraction pattern is due to the roughness of the surface of the experimental sample which is not taken into account in the calculating software. The roughness of the surface takes effect just at low values of diffraction angle and results in a decline of the intensity of basal reflection in the experimental diffraction pattern. Optimum water content found using energy minimization is 72 water molecules per unit cell, that means 24 H<sub>2</sub>O in one guest layer, see Table 1. This water content is in good agreement with that estimated by thermogravimetric measurement. The location of water molecules refined using comparison of calculated and measured intensity ratio in the diffraction pattern is illustrated in Figs. 3 and 5b. Water molecules are not regularly distributed in the interlayer space, but concentrated in the two planes adjacent to the host layers

coinciding with the COO<sup>-</sup> planes, as they are hydrogen bonded to the OH groups in host layers and to carboxyl groups.

### Discussion and conclusions

Molecular modeling enabled us to solve the crystal structure of benzenecarboxylate-LDH intercalate, where the conventional diffraction analysis failed due to the slight structural disorder, caused by the slight disorientation of guests.

Molecular modeling provides not only the detailed structure model but in addition revealed the character of this disorder. There is a slight disorder arising from mutual slight shift of two successive host layers. This disorder in the host layers is a consequence of slight disorder in the orientation of guests (rotation about long guest axis), disorder in orientation of carboxyl groups and in position of guests on the host layers. Results of the present work show that molecular modeling is useful not only in

**Table 1** Comparing the total nonbonded energy of models containing various number *n* of water molecules per one inter-layer space

<i>n</i>	<i>E</i> <sub>total</sub> /kcal	<i>E</i> <sub>elst</sub> /kcal	<i>E</i> <sub>vdw</sub> /kcal	<i>d</i> <sub>calc</sub> /Å
20	-15051	-14830	-221	15,2
22	-15165	-14977	-188	15,2
24	-15363	-15167	-196	15,3
26	-15200	-15110	-90	15,3
28	-15110	-15050	-60	15,4

structure analysis but also in estimation of water content and guest concentration. The close cooperation of modeling and experiment is a necessary requirement for successful structure solution.

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