

# MOLECULAR MODELLING OF LAYERED DOUBLE HYDROXIDE INTERCALATED WITH BENZOATE

Petr Kovář and Pavla Čapková

Faculty of Mathematics and Physics, Charles University Prague, Ke Karlovu 3, 12116 Prague 2, Czech Republic

kovar@karlov.mff.cuni.cz

## Keywords:

molecular modelling, structure analysis, Layered Double Hydroxide, benzoate

## Abstract

The structure of  $Zn_4Al_2$  Layered Double Hydroxide (LDH) intercalated with benzenecarboxylate ( $C_6H_5COO^-$ ) was solved by methods of molecular modelling. Molecular modelling using empirical force field was carried out in Cerius<sup>2</sup> modelling environment. According to the comparison of total crystal energy of optimized structure models with different geometry it was found out that benzoate anions are almost perpendicular to LDH layers, anchored to OH groups of the host layers via hydrogen bonds. Mutual orientation of benzoate ring planes in the interlayer space keeps parquet arrangement. Water molecules are arranged in planes adjacent to host layers together with  $COO^-$  groups.

## Introduction

The object of molecular modelling is the generation, manipulation and representation of realistic three-dimensional molecular structures, or description of a system of interacting molecules with the purpose of understanding the physicochemical properties and macroscopic phenomena at the molecular level. In the past *ab-initio* calculations have been extensively used to characterize the structure and properties of a large variety of molecules [1]. Since the requirements on the size of the investigated system are growing all the time the *ab-initio* calculations remain slow to be used in realistic modelling of important systems such as catalysts, biomolecules, polymers, etc. Nevertheless the *ab-initio* calculations remain extremely useful in the determination of force field parameters being used in molecular modelling [1] and for systems containing tens or hundreds of atoms. Molecular modelling plays an important role in everyday research in medical, natural and engineering sciences [2]. In some cases force fields calculations can provide answers that are as accurate as even the highest-level quantum mechanical calculations, in a fraction of the computer time.

The important role by using molecular modelling is combination with experimental data such as IR spectroscopy, X-ray powder diffraction or statistical thermodynamic quantities in case of molecular dynamics simulations to verify the models obtained from calculations. A ten year - old history of molecular modelling at the Faculty of Mathematics and Physics of Charles University has carried

many important results concerning the structure analysis and connection of the structure and physical and chemical properties of intercalated clays by organic molecules. Since these structures mostly exhibit a certain degree of disorder the classical structure analysis based on X - ray diffraction fails and molecular modelling is an appropriate tool how to reveal the character of this disorder and so wholly clear up the structure. In this paper we report structure analysis of  $Zn_4Al_2$  Layered Double Hydroxide intercalated with benzoate by methods of molecular modelling related to diffraction.

## Molecular modelling

Molecular modelling using empirical force field was carried out in Cerius<sup>2</sup> modelling environment. The first stage was a construction of  $Zn_4Al_2$  host framework. Unit cell of the host structure is trilayer, the space group is  $R\bar{3}m$  with trigonal cell in hexagonal axes. Lattice parameters are:  $a = 3.076 \text{ \AA}$ ,  $c = 23.20 \text{ \AA}$ . 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  $d_{exp} = 15.3 \text{ \AA}$  (measured from the mid-width of the peak of the first basal reflection), thus the interlayer distance in the initial model was set to this value. To investigate the arrangement of guest molecules in the interlayer space a  $P1$  superlattice was created with the dimensions  $4a \ 6a \ 1c$  where the  $c = 3d_{exp} = 45.9 \text{ \AA}$ . The charge of this trilayer supercell was + 24 el. That means 24 benzoate anions that were created in *3-D Sketcher* module were placed into the interlayer space to compensate the charge of the layer, i.e. the supercell consisted of 3 host layers and 3 guest layers. The composition of the structure model was  $[Zn_{16}Al_8(OH)_{12}][C_6H_5COO^-]_8 \cdot 24 H_2O$ . The amount of water was obtained from thermogravimetric measurements.

We built a series of initial models with various positions and orientations of guests with respect to the layers:

- 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  $COO^-$  groups with respect to OH groups on the host structure.

Energy minimization was carried out in *Universal* force field [3]. The electrostatic energy was calculated by Ewald summation method, van der Waals energy was expressed by Lenard - Jones potential [4]. The minimization of the to-



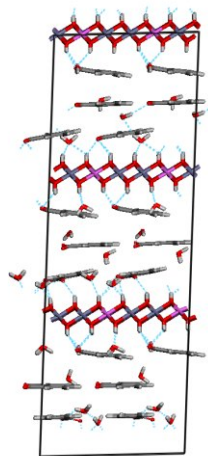
tal crystal energy was carried out in the *Minimizer* module according to the following strategy:

All the host layers in the supercell were kept as rigid units during energy minimization. Variable parameters were:  $c$ , (It enabled 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 were sorted according to the minimum of total crystal energy.

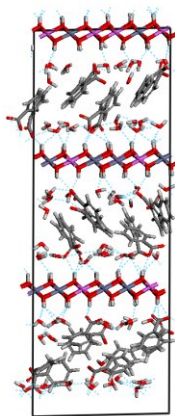
The work concerning the similarity of experimental and calculated diffraction patterns was recently published in *Journal of Molecular Modelling* [5]. A good agreement has been achieved between modelling and experiment.

## Results

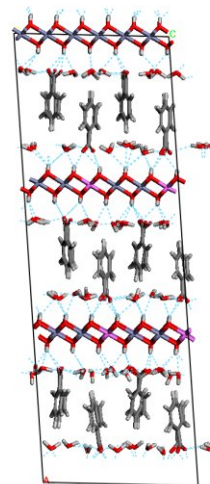
Results of modelling led to the conclusion concerning the orientation and position of the benzoate anions and water molecules in the interlayer space. Table 1 shows total energy and basal spacing  $d$  of selected optimized models with various arrangement of guest anions in the interlayer space (trilayer parallel, tilted, perpendicular with a slight disorder (perp.disordered) and perpendicular ordered arrangement (perp.ordered)). Some types of these structure models are



**Figure 1.** Structure model with parallel orientation of guest anions with respect to the host layers.



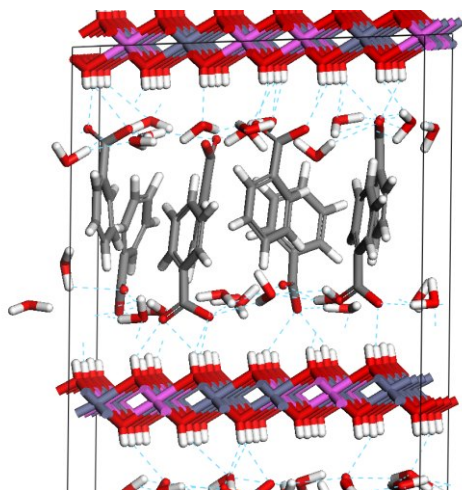
**Figure 2.** Structure model with tilted orientation of guest anions with respect to the host layers.



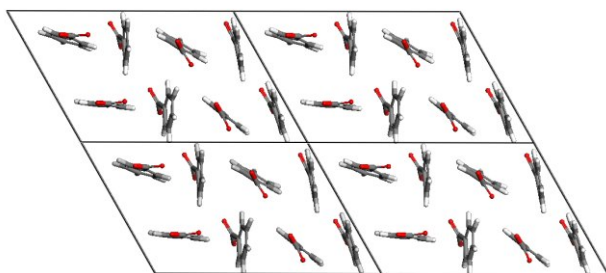
**Figure 3.** Structure model with perpendicular orientation of guest anions with respect to the host layers.

illustrated in the figures 1 - 3. Hydrogen bonds are represented by broken lines. The figures represent a superlattice containing 8 guest anions and its dimensions are the same as mentioned above. The Figure 1 represents a model where benzoate rings adopt a three – layer arrangement nearly parallel to the hydrotalcite layers with a free distribution of water molecules in the interlayer space.  $\text{COO}^-$  groups are anchored to the OH groups of the host layers. Since the phenyl rings are hydrophobic and the host layers itself is hydrophilic benzoate rings of guest anions that are near to the host layer do not adopt exactly parallel orientation with respect to the host layers but they exhibit a slight tilted orientation. In Figure 2 one can see a model with tilted orientation of guest anions in the interlayer space and water molecules located by the host layers. The tilted angle is about 45 degrees. The benzoate planes are not regularly organized with respect to each other, the mutual departure of the ring planes is mostly about  $20^\circ$  but in some cases it can exhibit a higher value. One can see from the Table 1, that the most convenient model according to the minimum of total energy is the one with ordered perpendicular arrangement of the guest anions with respect to the host layers. One can see in the Figure 3 that benzoate exhibit a slight departure of its long axis from the perpendicular orientation in the range of 10 degrees.  $\text{COO}^-$  groups are anchored to OH groups of the LDH layer via hydrogen bonds. The detailed view of orientation of  $\text{COO}^-$  groups with respect to the OH groups and possible hydrogen bonding is shown in the figure 4.

The structure exhibits a high degree of order of the guest anions in the interlayer space. The benzoate planes keep parquet arrangement as it is shown in the figure 5. Molecular modelling revealed two types of structure models with two different orientations of benzoate anions that keep parquet arrangement. The first type is shown in figure 3 where two neighbouring benzoates exhibit the same orientation of  $\text{COO}^-$  groups. The second one shown in the Figure 4 exhibits opposite orientations of  $\text{COO}^-$  groups with respect to each other. It is seen in the Figure 5 that  $\text{COO}^-$  groups can freely rotate around the long axis of the guest



**Figure 4.** Detailed view of orientation of COO<sup>-</sup> groups with respect to OH groups.



**Figure 5.** Parquet arrangement of benzoate ring planes.

anions. The energy minimization procedure showed that water molecules are not randomly distributed in the interlayer space but they are aggregated in planes adjacent to host layers coinciding with COO<sup>-</sup> planes in case of perpendicular arrangement of guests with respect to the layers.

**Table 1.** Comparing the total energy of optimized models with various arrangement of guests (parallel orientation, tilted, perpendicular with a slight disorder (perp.disordered) and perpendicular ordered arrangement).

Model	E <sub>total</sub> / kcal	d / Å	fig.No.
parallel	-11471	15.57	1
tilted	-10000	15.10	2
perp. disordered	-10717	15.20	-
perp. ordered	-13227	15.20	3

## Conclusion

This work shows that molecular modelling using empirical force field is a powerful instrument in structure analysis in case of hydrotalcite - like compounds. The energy minimization revealed that the most probable structure model, i.e. model corresponding to the energy minimum, exhibits a high degree of order of guest anions in the interlayer space that are oriented perpendicular to the host layers. The basal spacing  $d = 15.2$  Å of this structure model is in good agreement with experimental basal spacing  $d_{exp} = 15.3$  Å. This shows that *Universal* forcefield used in these calculations is able to well describe these structures. One can see that in this case molecular modelling is a sufficient instrument for structure solving based on the comparing of the total energy of optimized models obtained from a series of models with various starting geometry. Resulting model was also in good agreement with experimental data.

## References

1. M. A. C. Nascimento, *Molecular Modeling*. Singapore: World Scientific Publishing Co. Pte. Ltd. 1994.
2. T. F. Kumosinski, M. N. Liebman, *Molecular Modeling*. Washington, DC: American Chemical Society. 1993.
3. *Cerius<sup>2</sup> User guide, Forcefield - Based Simulations*. San Diego: Molecular simulations Inc. 1997.
4. J. E. Lennard-Jones, *Proc. Of the Royal Society of London*, series A, **109** No. 752 (1925) 584.
5. P. Kovář, M. Pospíšil, M. Nohcetti, P. Čapková, K. Melánová, *Journal of Molecular Modeling*, No. 8, Vol. **13** (2007) pp 937-942.

## Acknowledgements

*This work was supported by grant MSM 0021620835.*