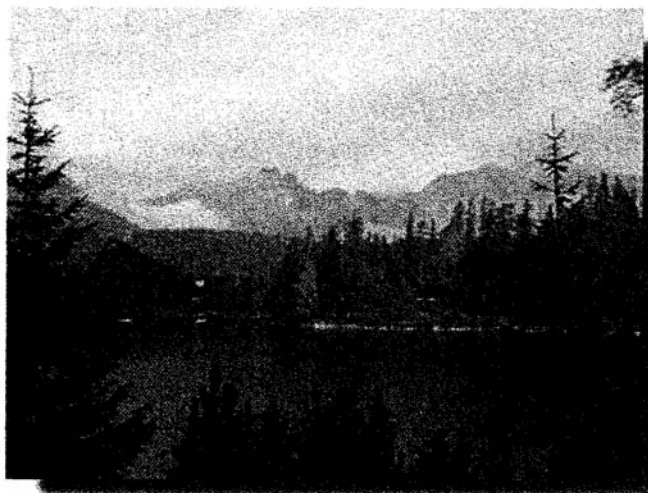


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# TOWARDS A MODEL OF THE $\text{Al}_{13}$ -PILLARED LAYER CLAY – A COMPUTATIONAL STUDY

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## Abstract

A step-by-step construction of an  $\text{Al}_{13}$ -Keggin ion pillared montmorillonite segment is shown with the use of the MM+ general force field. The starting structures for the montmorillonite as well as the  $\text{Al}_{13}$ -Keggin ion were obtained as pdb files. The two layers of the clay were dissected and segmented, then optimised with the MM+ force field. The Keggin ion was optimised with the PM3 semiempirical method. Then, the Keggin ion was attached to the layer through chemical bonds and was optimised with the MM+ force field once again. Finally, the structure was capped with the second layer and was optimised once again with the MM+ force field.

**Keywords:** pillared layer clay;  $\text{Al}_{13}$ -Keggin ion; construction of the layered structure; molecular modelling.

## Introduction

Pillared layer clays offer numerous application possibilities in many areas, among others, in the shape selective synthesis of larger organic molecules. The materials have well defined quasi two-dimensional porous structure with sizable pore openings of 10+ Å and at the same time variable concentrations of Brønsted and Lewis acid sites of different strengths [1]. The presence of acid sites and the controllable pore structure with wide channels provide many possibilities for acid-catalysed transformations of large organic molecules. At the same time the confined environment

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exerts significant effect on the selectivities of the reactions. The chemistry occurring in the pillared structures can be studied experimentally [2, 3]. The understanding of the chemical events may be deeper if experiments are complemented by molecular modelling. First, a suitable segment of the pillared layer clay should be constructed containing all important features of the material. Then, adsorption processes as well as chemical reactions may also be modelled. As the first step, the building of an  $Al_{13}$ -pillared layer montmorillonite segment was attempted. Details and results of this effort are communicated in the followings.

### **Methods of computations**

The pdb files of montmorillonite and the  $Al_{13}$ -Keggin ion [4] were obtained from databases and the clay was transformed manually to resemble the experimentally used sample the best. A portion of the montmorillonite structure was cut and the two layers were separated. The dangling oxygen bonds were closed with hydrogen atoms. For optimisation the MM+ force field (montmorillonite layers and the pillared structures) or the PM3 semiempirical ( $Al_{13}$ -Keggin ion) codes were used as implemented in the Hyperchem package [5]. The model pillared layer segment was so large that even semiempirical methods failed during optimisation, however, it was not possible to reduce the size further without the loss of characteristic features of the pillared layer clay. These two factors may explain why we have used the force field method, mentioned above.

### **Results and discussion**

First, the essential building blocks were constructed, then they were fit together to obtain an  $Al_{13}$ -pillared layer clay slab. To achieve this, one needs a montmorillonite segment and an  $Al_{13}$ -Keggin ion both with reliable, experimentally determined structures.

It was computationally efficient to fully optimise the  $Al_{13}$ -Keggin ion applying

the PM3 semiempirical quantum chemical method [6] as implemented in the Hyperchem package. The resulting structure is shown in Figure 1.

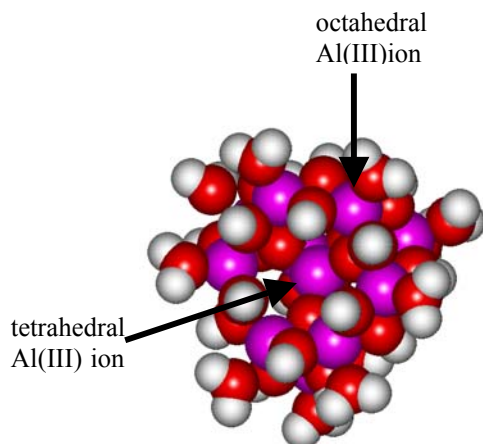


Fig. 1. The PM3-optimised structural model of the  $\text{Al}_{13}$ -Keggin ion.

The two layers of montmorillonite obtained as a pdb file were separated and we worked with one of the layers further. The layer taken was manipulated as follows: the dangling bonds were closed with hydrogen atoms and the Mg(II) ions in the tetrahedral silicon layer were changed to Al(III) ions. The negative charges were compensated as is usual in zeolite chemistry, i.e. hydrogens were bonded onto the oxygen bridge of the Al–O–Si structural moieties. Then, the structural unit was optimised with the MM+ method. The result is seen in Figure 2.

The next step was fitting together these basic units. After doing this, the structure was optimised again, but now, due to the size of this structural moiety, only the MM+ method could be used. The result is displayed in Figure 3.

The final step was capping the montmorillonite layer– $\text{Al}_{13}$ -Keggin ion with another montmorillonite layer to regain the layered structure. It could be done successfully and the final pillared layer clay slab could be optimised once again with the MM+ method only.

The last two structures are shown in one figure (Figure 3).

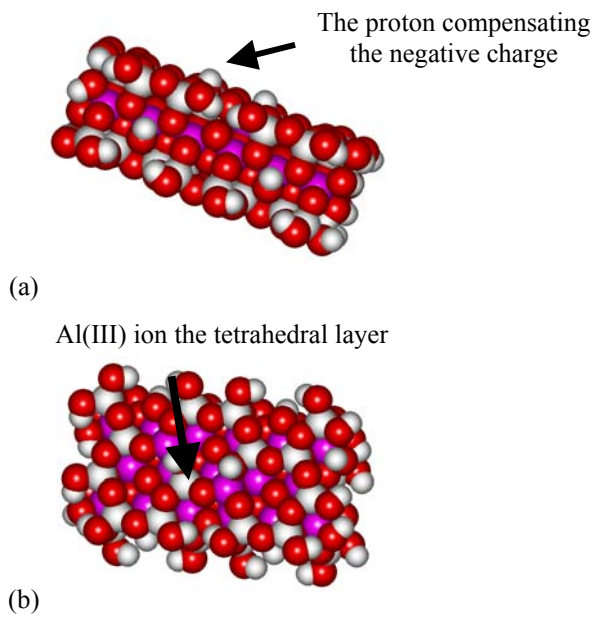


Fig. 2. The MM+-optimised montmorillonite layer, (a) side view (at the top), (b) top view (underneath).

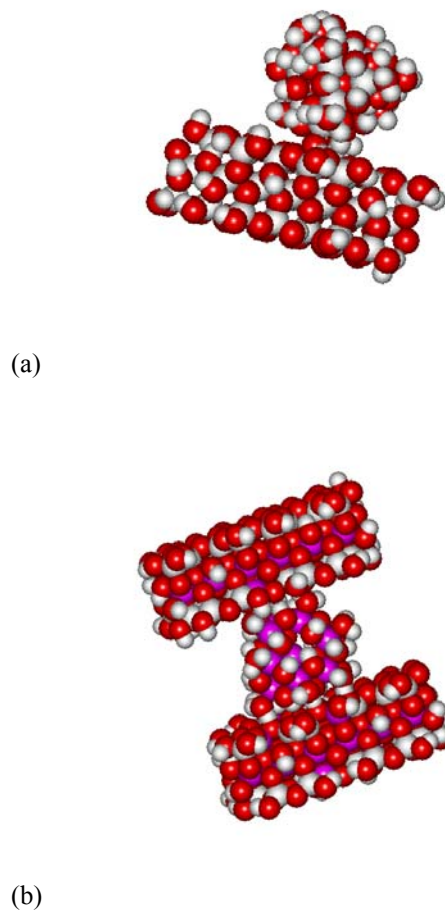


Fig. 3. The MM+-optimised (a)  $Al_{13}$ -Keggin ion-clay monolayer and (b) the  $Al_{13}$ -Keggin ion pillared clay bilayer

## Conclusions

In this work we built an Al<sub>13</sub>-Keggin ion pillared layer clay segment having all the characteristic features of the experimentally used material. The model will allow the computational study of reactions performed experimentally.

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