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Molecular Mechanics Study on Organometallic Complexes in Crystalline Silica Matrixes Using the ESFF (Extensible Systematic Force Field)

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Structure refinement from powder diffraction data is nowadays a routine and powerful tool if based on high-quality data. The application of this method, however, becomes difficult when only data of lower quality are available and when severe disorder is present in the solid material investigated. On the other hand, it is possible to confirm and even predict crystal structures using molecular modeling techniques. The latter method will fail if the employed force field is not designed for the actual problem. In the following paper we show how experimental data of low quality can be supplemented by the results of an accompanying modeling study, employing a force field which is validated before on a well-characterized similar compound.

The inclusion of molecular species into the crystallographically defined voids of molecular sieves is a valuable method to generate supralattices of these species.[1,2] Especially metal complexes are of interest with respect to potential applications as immobilized metal-complex catalysts[3,4] and in the fields of linear or nonlinear optics.[4−6] Recently, it was shown that metal complexes are able to act as structure-directing agents in hydrothermal syntheses of zeolite-type compounds (zeotypes).[5−11] This direct synthesis method, where the metal complexes become occluded by the crystallizing framework, leads to stoichiometric and homogeneous compounds with an optimum loading of the metal complex, quite in contrast to the products of postsynthesis modifications (as ion-exchange, vapor-phase insertion, or ship-in-the-bottle synthesis).[3] Although the crystallinity of the products of the direct synthesis tends to be higher, too, it is not always possible to perform a structural analysis on a single crystal or by a Rietveld refinement of powder diffraction data to reveal structural details. Molecular mechanics methods allow us to predict these details and to support the experimental methods. The quality of these predictions depends on the quality of the forcefield employed. Therefore, it is necessary to test available force fields with regard to known experimental findings.

Recently, a new force field (ESFF, extensible systematic forcefield) was introduced by BIOSYM Technologies. It was tested on poly(ferrocenylsilanes).[12] Due to the universality and the transferability of the ESFF it seemed to be suited for the more complex organometallic/silica host−guest systems, too. Here, we present

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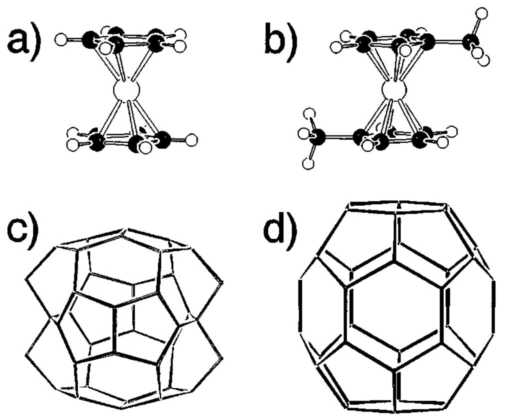

Figure 1. Organometallic complex cations $[Co(C_5H_5)_2]^+$ (a) and $[Co(C_5H_4(CH_3))_2]^+$ (b) and the large cages of the three-dimensional framework structures of nonasil (NON, $[5^86^{12}]$ cage) (c) and dodecasil 1H (DOH, $[5^{12}6^8]$ cage) (d). Detailed descriptions of the clathrasil structures are given in refs 16 and 15, respectively.

(1) minimization studies on the well-characterized compound cobalticinium fluoride nonasil ($[Co(C_5H_5)_2]F-NON$) and (2) the structure of [bis(methylcyclopentadienyl)cobalt] fluoride dodecasil 1H ($[Co(C_5H_4CH_3)_2]F-DOH$) as determined from a combination of minimization techniques and Rietveld refinement of X-ray powder diffraction data of this compound. The organometallic structure-directing agents and relevant parts of the three-dimensional structure of the porosils are shown in Figure 1. All force-field calculations were performed using BIOSYM's molecular modeling software package.[13] The Rietveld refinement was carried out using the XRS82 structure refinement package.[14]

The study on the NON compound was undertaken in order to test the force field with respect to its application to this type of host−guest compounds. The crystal structure of $[Co(C_5H_5)_2]F-NON$ at 220 K is discussed in detail in refs 6 and 7. The most striking feature of the structure (Figure 2a) are two symmetrically equivalent short $C-H_{guest}\cdots O_{host}-Si$ distances (2.31 Å) between the occluded organometallic complex and the silica framework. These hydrogen bonds are probably responsible for the absence of rotational or positional disorder of the $[Co(C_5H_5)_2]^+$ cation.[7] The remaining $d(H_{guest}-O_{host})$ distances are found in the expected range (2.60−2.88 Å).

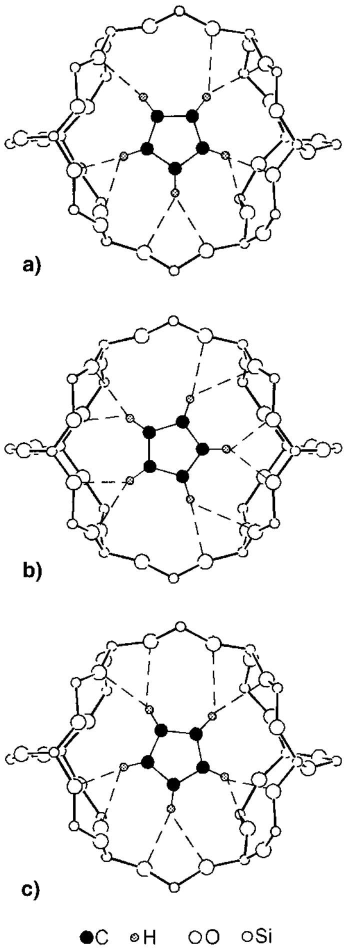

Figure 2. $[Co(C_5H_5)_2]F-NON$: Orientational relationship between one of the two (symmetrically equivalent) cyclopentadienyl rings of the cobaltocenium cation and the relevant part of the silica host structure. Comparison between (a) the crystal structure from the single-crystal refinement, (b) the global minimum from the minimization in the $[5^86^{12}]$ cage of symmetry *mmm*, and (c) the global minimum from the minimization in the $[5^86^{12}]$ cage of symmetry $\bar{1}$.

For the minimization study, single $[5^86^{12}]$-cages of NON were cut out of the structure. Dangling bonds were saturated with OH groups while retaining the symmetry. We started the minimization study using a NON cage of topological symmetry (*mmm*) as described by Marler et al.[15] To ensure that the global minimum in the system was found, an appropriate set of 1000 different starting geometries of the $[Co(C_5H_5)_2]^+$ cation inside the cage was generated by docking the guest molecule randomly to the cage employing Monte Carlo methods. The energy of that assembly was minimized by relaxing the positional parameters of the guest cation, while the positions of the host atoms were fixed. In the global minimum, the $[Co(C_5H_5)_2]^+$ cation was found in a staggered conformation in accordance with the experiment. However, the orientation of the cation with respect to the cage is different by a rotation of about 20° around the 5-fold axis of the complex (Figure 2b). This leads to different interactions between the silica framework and the occluded molecule (Figure 2a,b). The offsets (the distances between the atomic positions determined by the experiment and by the minimization) of the carbon atoms range from 0.34 to 0.41 Å, those of the hydrogen atoms from 0.67 to 0.74 Å. Under these starting conditions, the minimization is obviously not able to reproduce all details of the experimental result; it would, however, provide a reasonable starting model for structure refinement. In the second minimum, the cation was found in an eclipsed conformation, which is not found in the experiment. The difference in energy between the global and the second minimum is negligibly small ($\Delta E = 0.001$ kcal/mol) compared to the total interaction energy ($E = -116$ kcal/mol). This difference can be attributed to the energy difference found between the staggered and the ecliptic

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conformation of the free $[Co(C_5H_5)_2]^+$ cation. Due to the high symmetry of the NON cage used, both conformations show essentially the same interactions between host and guest. Therefore, we switched to a system that is closer to the structure as determined by the experiment. The symmetry of the host structure was reduced (loss of mirror planes and 2-fold axes) and the experimentally derived positions of the host atoms[6] were used to generate a $[5^86^{12}]$ cage of symmetry $\bar{1}$. In this case, the agreement between modeling and experiment is excellent (Figure 2a,c). Now, the offsets of the carbon atoms range from 0.09 to 0.18 Å, and those of the hydrogen atoms from 0.24 to 0.28 Å. Even the remarkable $C-H_{guest}\cdots O_{host}$-Si hydrogen bonds are reproduced fairly well with a distance $d(H_{guest}-O_{host}) = 2.45$ Å.

In a further study, we examined the structure of $[Co(C_5H_4CH_3)2]F-DOH$.[8] It was not possible to obtain proper single crystals of this compound. An X-ray powder diffraction pattern was collected on a Guinier Huber G600 diffractometer employing Cr Kα radiation (Cu Kα would cause strong X-ray fluorescence from Co). The long wavelength of the X-ray radiation and the use of the Guinier geometry lead to a rather limited data set for the Rietveld refinement (143 contributing reflections for $2\theta = 4-100°$). As a starting model for the refinement, the $[5^{12}6^8]$ cage structure determined by Gerke et al.[16] was used. During the refinement we were able to locate the Co atom using difference Fourier maps, but the method failed for the carbon atoms of the guest complex. A minimization study was performed in the same way as described for NON, using a highly symmetric $[5^{12}6^8]$ cage (symmetry $6/mmm$). It was expected that the minimization would result in positions for the atoms of the guest molecule accurate enough for use in a subsequent Rietveld refinement. The most important result is that a relatively large energy gap of 2.8 kcal/mol occurs between the global and the following minimum. This allowed us to derive several disorder models for the occluded cation on the basis of the minimization results. In all models, four symmetrically distinct carbon atoms occur. Refinements of these models finish at similar R values ($R_e = 0.091$, $R_{wp} = 0.16$, $\chi^2 = 1.51$) and similar differences between the calculated and the measured diffractogram (Figure 3). A comparison of the structural arrangements as determined by modeling and by experiment is shown in Figure 4. The offsets are very small for the carbon atoms of the organic (C_5H_4) five-membered ring (0.09–0.19 Å) and somewhat larger for the carbon atoms of the methyl groups (0.63 Å). During the refinement, the framework structure of the host had to be modified by introducing disorder and split positions for some of the oxygen atoms (compare ref 17).

The agreement between modeling and Rietveld refinement is favorable, especially if one takes into account that the host structure as determined in the final Rietveld refinement exhibits considerable disorder of the oxygen atoms. Both methods complement each other, because the disorder of the host structure cannot be determined by modeling techniques in an easy and computationally cheap way; on the other hand, it was not possible to determine the positions of the carbon atoms during the course of the Rietveld refinement without support from the modeling study.

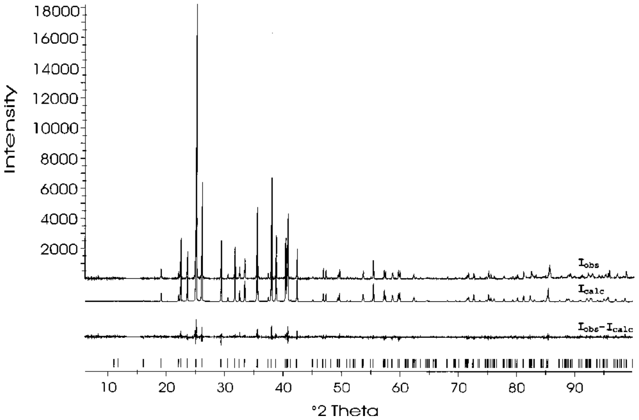

Figure 3. $[Co(C_5H_4(CH_3))_2]F-DOH$: Experimental ($I_{obs}$), calculated ($I_{calc}$), and difference ($I_{obs} - I_{calc}$) powder X-ray diffraction profiles. The positions of possible Bragg reflections are marked at the bottom.

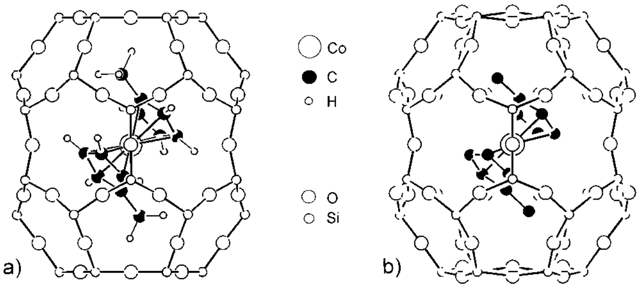

Figure 4. $[Co(C_5H_4(CH_3))_2]F-DOH$: The arrangement of the $[Co(C_5H_4(CH_3))_2]^+$ cation in the $[5^{12}6^8]$ cage as determined in (a) the minimization study and (b) the Rietveld refinement. The $[Co(C_5H_4(CH_3))_2]^+$ cation is shown in one of six symmetrically equivalent positions.

The ESFF has proved to give reliable results in the systems investigated. This study shows that the structural chemistry of host–guest compounds in the system zeotype–organometallic complex can be well understood using modeling methods employing the ESFF force field, especially as the quality of the force field has now been tested on a standard system. This favorable performance of the force field on this type of complex host–guest compounds was not to be expected since two very different subsystems—an organometallic complex and a silica structure—and their interactions have to be described correctly.

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Supporting Information Available: Details of the structure refinement and listings of atomic parameters as well as bond distances and angles of $[Co(C_5H_4CH_3)_2]F-DOH$ (7 pages). Ordering information is given on any current masthead page.

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