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Flexible Pores

In situ X-ray Structural Studies of a Flexible Host Responding to Incremental Gas Loading**

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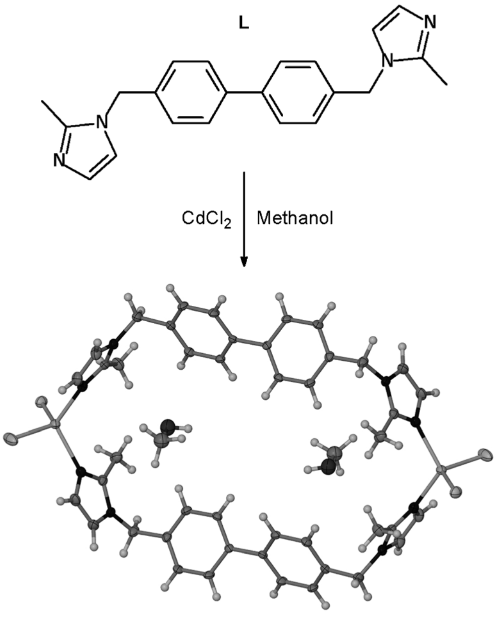
Synthetic materials with sub-nanometer scale pores and cavities are of considerable interest for catalysis, as well as the separation, storage and sensing of gases.[1] Much effort is therefore being devoted to thwarting close-packing tendencies with a view to engineering and even tuning empty space in crystals.[2] One of our approaches to the formation of porous materials is to utilize metallocyclic host molecules that exhibit poor self-complementarity thus precluding the assembly of close-packed structures.[3]

Porous materials with large voids and/or internal surface areas are highly desirable for applications where guest storage capacity is of primary importance.[4] However, materials that possess more restricted guest-accessible spaces are also of interest[5]—despite their often low storage capacities they have potential for discriminating between different guests[6] based on criteria such as size or electrostatics, and such selectivity may be useful for applications involving sensing and separation. Indeed, we are particularly interested in carrying out in situ structural studies to explore host–guest, as well as guest–guest interactions within constrained environments with a view to gaining a better molecular-level understanding of important processes.

We have now extended our previous work on metallocyclic hosts to engineer larger discrete cavities that are each capable of accepting exactly two volatile guest molecules. This incremental increase in complexity offers an excellent opportunity to study gas–solid interactions involving tightly confined guest-accessible spaces, as well as to construct a statistical mechanics model that appears to qualitatively explain subtle features in the experimental sorption isotherms that arise due to host flexibility.

The ligand 4,4′-bis(2-methylimidazol-1-ylmethyl)biphenyl (**L**) was combined with $CdCl_2{\cdot}2.5\,H_2O$ to afford crystals suitable for X-ray diffraction studies (SCD) (see Supporting Information). Structure elucidation reveals a $[Cd_2Cl_4\mathbf{L}_2]{\cdot}2\,CH_3OH$ metallomacrocycle (**1**·2MeOH, Scheme 1) that stacks to form columns in the solid state as shown in Figure 1a, with each complex encircling two methanol molecules. Analysis of the solvent-accessible volume[7] reveals that paired methanol guests are situated in discrete voids of 123 Å^3. Although permanent channels linking the guest pockets are not apparent, thermogravimetric analysis (Supporting Information) indicated spontaneous loss of the solvent molecules from the crystals, even under ambient conditions. This was confirmed by subsequent SCD as guest desolvation occurs in a single-crystal to single-crystal fashion (Figure 1b, Supporting Information).



Scheme 1. Formation of the solvated metallocycle $[Cd_2Cl_4L_2]{\cdot}2\,CH_3OH$ (**1**·2MeOH).

Since the molecular volumes of CO_2 and C_2H_2 are approximately the same as that of methanol (Supporting Information), we surmised that **1** might absorb either of these two gases to achieve a maximum capacity of two guest molecules per void. A comparison of the gas sorption isotherms (Figure 2 and Supporting Information) indicates that **1** has marginally greater affinity for C_2H_2 than for CO_2, and both isotherms display Type I behavior with a noticeable inflection occurring at ca 2 bar for the sorption of C_2H_2. Since CO_2 and C_2H_2 have similar dimensions and boiling points, but inverse electrostatic profiles, it is reasonable to presume that subtle dissimilarities in the shapes of the isotherms may be due to differences in how the two gases interact with the host framework. We therefore consider this system to be an ideal test case for structural studies involving incremental gas

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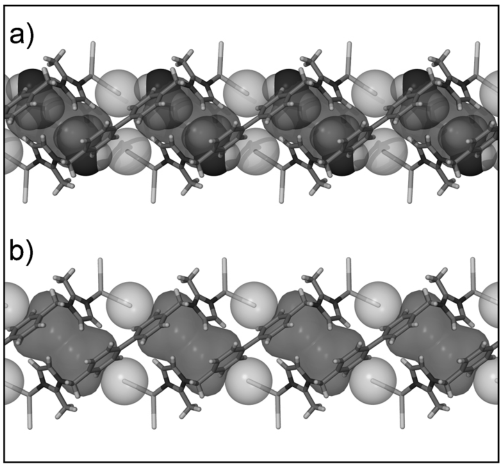

Figure 1. Columnar stacking of **1** along [001] (horizontal direction) as viewed down [010]. Each guest-accessible cavity (semi-transparent surface) is defined by four metallocycles and has an approximately rectangular cross-section terminated by a chloride ion (semi-transparent sphere) at each of the short ends. a) Each cavity (123 Å^3) in the structure of **1**·2 MeOH is occupied by a pair of methanol molecules. b) Upon desolvation at room temperature the crystals remain intact and the cavities maintain their shape (117 Å^3).

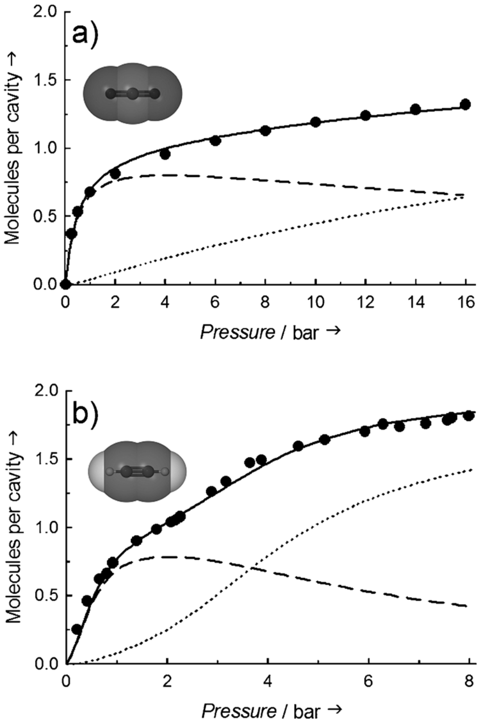

Figure 2. Sorption isotherms (solid circles) measured at 22 °C for a) CO_2 and b) C_2H_2. Both gases exhibit Type I sorption behavior. Superimposed lines are the result of the statistical physical model with elastic interactions (using structural data, reasonable energy estimates and two fitting parameters as described in the Supporting Information). Solid lines represent the total occupancy expression, which can be decomposed into the sum due to the singly (dashed lines) and doubly (dotted lines) occupied cavities.

loading,[8] and a series of single-crystal X-ray data collections was carried out using an environmental gas cell (Supporting Information).[9]

We first determined the crystal structure of desolvated **1** under vacuum at room temperature (RT = 22 °C) (hereafter designated as $\mathbf{1}_x$, where x = gas pressure in bar). X-ray data measured at RT for **1** under CO_2 pressures of 0.5, 1, 2, 4, 6, 8, 10, 12, and 14 bar ($\mathbf{2}_{0.5}$ to $\mathbf{2}_{14}$) did not yield reliable atomic coordinates for the CO_2 molecules. Nevertheless, it was still possible to determine the CO_2 occupancies by summing electron densities within the guest-accessible volume.[10] An X-ray diffraction measurement under 10 bar of CO_2 pressure and at −40 °C (${}^{\mathbf{LT}}\mathbf{2}_{10}$) yielded a fully occupied and ordered structure in which each CO_2 molecule (Supporting Information) is positioned approximately perpendicular to the Cl···Cl vector across the long axis of the cavity (Figure 3). The position and orientation of the CO_2 molecule are consistent with the existence of a weak electrostatic interaction (10.48 kJ mol^{-1} from DFT calculations; Supporting Information) between its electropositive carbon atom and the negatively charged chloride ion of the host.

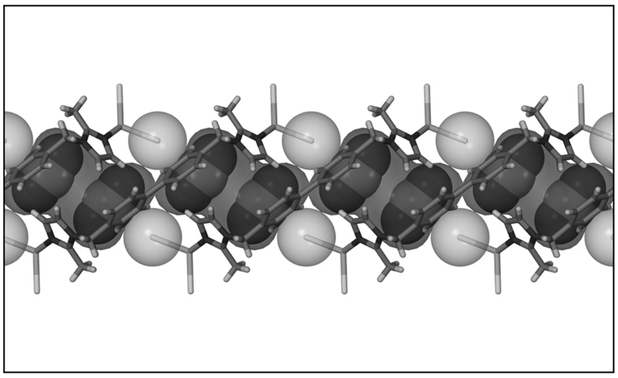

Figure 3. Crystal structure of **2** determined at −40 °C under a pressure of 10 bar of CO_2. The CO_2 molecules are positioned at approximately right angles relative to the Cl···Cl vector across the cavity (137 Å^3), and form a weak $C(\delta^+)\cdots Cl^-$ interaction with the host complex.

Successive X-ray intensity data sets were collected at RT with **1** exposed to C_2H_2 pressures of 0.5, 1, 2, 4, 6, 8, and 16 bar ($\mathbf{3}_{0.5}$ to $\mathbf{3}_{16}$). The C_2H_2 molecules were located in difference electron density maps and their positions and orientations contrast sharply with those of CO_2 in ${}^{\mathbf{LT}}\mathbf{2}_{10}$. At 2 bar the linear C_2H_2 molecule is aligned approximately along the Cl···Cl axis across the cavity (Figure 4 a) and does not allow room for a second molecule within the confined space of the void. At 16 bar the cavities are almost all doubly occupied (i.e. the host is 95 % occupied according to sorption analysis) by C_2H_2 molecules (Figure 4 b). By comparing $\mathbf{3}_2$ and $\mathbf{3}_{16}$, it is possible to rationalize the structural consequences of inserting a second molecule into the cavity—the first molecule to occupy the cavity is required to change its orientation in order to accommodate the second within the confined space. The CH···Cl hydrogen bond is maintained (decreasing in strength from 16.1 to 9.2 kJ mol^{-1}, according to DFT calculations; Supporting Information), but the two molecules align themselves across the cavity such that the CH···Cl angle changes by approximately 25° relative to that in $\mathbf{3}_2$.

Tracking the pressure-dependent changes in the lattice parameters as well as in the host conformation and packing (Table 1 and Supporting Information) proves very useful with

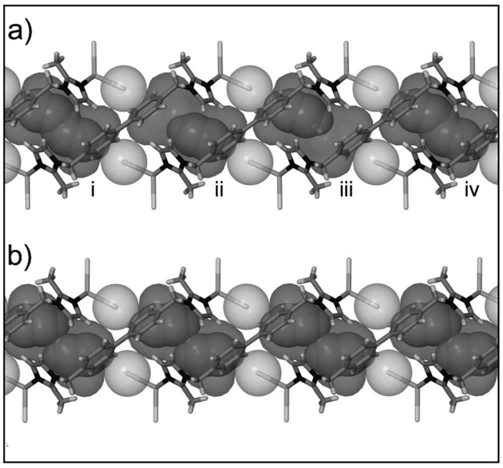

Figure 4. Crystal structures of **3** determined at pressures of 2 and 16 bar of C_2H_2. a) In $\mathbf{3}_2$ each void is, on average, occupied by approximately one molecule of C_2H_2. The molecule is situated at either end of the void and is partially stabilized in that position by the formation of a CH⋯ Cl hydrogen bond (C⋯Cl 3.54(3) Å, ∡C–H⋯Cl 169.4°). The C_2H_2 molecule is disordered over two equivalent positions (ii and iii) and the model therefore shows overlapping molecules (i and iv) indicating that either, but not both, of the positions can be occupied at any given moment. b) In $\mathbf{3}_{16}$ each cavity accommodates two molecules of C_2H_2. The CH⋯Cl hydrogen bonds are maintained (C⋯Cl 3.41(3) Å, ∡C–H⋯Cl 142.1°).

regard to correlating structural data with the sorption isotherms. It is apparent that deformation of the host structure with increasing pressure is far more significant for C_2H_2 than for CO_2. During C_2H_2 uptake, the size and shape of the cavity change with the void volume increasing smoothly from 113 Å^3 for $\mathbf{1}_0$ to 139 Å^3 for $\mathbf{3}_{16}$. As the pressure increases from vacuum to 16 bar, the void stretches and narrows: the Cl⋯Cl distance across the cavity expands by 11% overall (from 10.61 Å to 11.85 Å) while the Cd⋯Cd distance across the cavity contracts by 9% (from 9.44 to 8.59 Å). The analogous changes due to CO_2 loading are far less striking due to the electrostatically controlled orientation of the CO_2. In contrast, C_2H_2 molecules cannot be accommodated in the same manner because of repulsion between their electron-rich triple bonds and the host chloride anions. Instead the CH⋯Cl hydrogen bonds force the two C_2H_2 molecules into orientations that bring them into van der Waals contact with each other. In order to accommodate this crowded arrangement of the two guest molecules, it is necessary for the host cavity to deform.

Table 1: Selected parameters of the vacuum structure and the carbon dioxide (**2**) and acetylene (**3**) loaded structures.

Label	Void [Å^3]	*a* [Å]	*b* [Å]	*c* [Å]	Β [°]	*V* [Å^{-3}]	Cl⋯Cl [Å]
$\mathbf{1}_0$	113	18.208	15.527	9.353	114.9	2398	10.61
$\mathbf{2}_{0.5}$	122	18.046	15.525	9.394	114.5	2394	10.78
$\mathbf{3}_{0.5}$	126	18.046	15.525	9.394	114.5	2394	10.83
$\mathbf{2}_1$	121	18.033	15.535	9.398	114.5	2396	10.79
$\mathbf{3}_1$	125	17.901	15.618	9.447	114.3	2407	10.94
$\mathbf{2}_2$	123	18.030	15.535	9.400	114.5	2397	10.81
$\mathbf{3}_2$	131	17.788	15.640	9.506	114.1	2413	10.95
$\mathbf{2}_4$	119	18.009	15.546	9.403	114.4	2398	10.84
$\mathbf{3}_4$	131	17.501	15.637	9.693	113.8	2427	11.51
$\mathbf{2}_6$	122	18.028	15.537	9.409	114.4	2401	10.85
$\mathbf{3}_6$	133	17.313	15.610	9.832	113.6	2435	11.73
$\mathbf{2}_8$	127	18.025	15.544	9.410	114.3	2403	10.86
$\mathbf{3}_8$	132	17.269	15.608	9.855	113.5	2435	11.81

In rationalizing a sorption process involving essentially identical cavities that can each accommodate a maximum of two guest molecules, it is useful to consider that any individual cavity can only exist in one of three possible occupancy states at any given moment (Figure 5, top): the void can be a) empty or it can be occupied by either b) one or c) two gas molecules. For a representative cavity, these three states most likely interchange rapidly with one another as gas molecules travel through the material, and the probability of the existence of each state should be a constant value at equilibrium. Although the sorption isotherm provides information regarding the time-averaged occupancy of each cavity at equilibrium, it does not yield information about the absolute or even relative distributions of the three possible states. To this end we endeavored to combine the experimental observations with a statistical mechanical treatment in order to derive the individual isotherms of the three possible occupancy states.

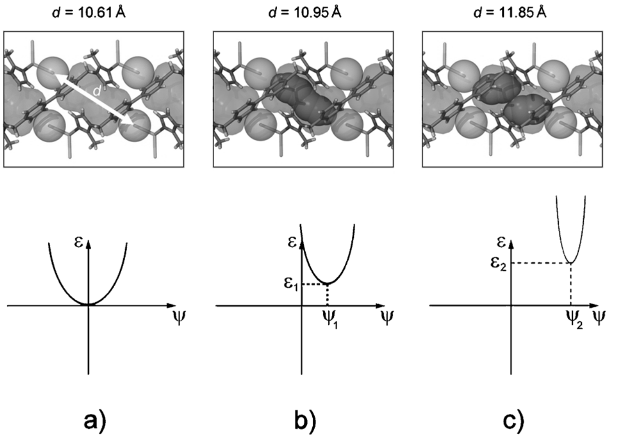

Figure 5. The three different occupancy states of the C_2H_2-loaded structures. Top: crystallographic models showing an individual cavity in its a) zero-, b) single-, and c) double-occupancy states. The length of the cavity is related to the Cl⋯Cl vector, *d*. Bottom: the statistical mechanical model presumes different elastic properties of the cavities depending on the state of occupancy, and is shown schematically for the three occupancy states. Different equilibrium deformations ($\psi = 0$, ψ_1, ψ_2) are associated with energetic minima ($\varepsilon = 0$, ε_1, ε_2) in each type of occupancy state. The presence of guest molecules changes the local elastic constant (given by the curvature of the potential at the minimum).

The energy of the system decreases when guest molecules are accommodated in the framework, but when deformation of the host is required there is also an energetic penalty (Figure 5, bottom). Owing to cooperative effects acting through the lattice, deformation of an individual cavity could also cause deformation of neighboring cavities, thus affecting the ability of those voids to accommodate guest molecules. In the context of three possible occupancy states as described above, we formulated a simple statistical mechanical approach (see Supporting Information). The model assumes host–guest and guest–guest interactions within a cavity and incorporates cavity deformation as well as elastic coupling between neighboring cavities in a one-dimensional crystal. A reduced version of this model, intended to represent the CO_2 sorbing system, assumes that host–guest and guest–guest interactions occur, but that host deformation is negligible (Supporting Information). The calculations for both systems are analogous to that of a standard lattice gas derivation of the adsorption isotherm,[11] with host deformation determining the interaction between nearest sites (much related work[12] has been applied in different contexts to elastic lattice gases). They yield the total occupancy as a function of pressure, as well as the contribution to total occupancy by singly and doubly filled voids (Figure 2). The full model represents the C_2H_2 sorbing system, but is also applicable to CO_2. Assuming reasonable elastic constants and using calculated interaction energies (Supporting Information), the inflection in the overall sorption isotherm (as observed experimentally for acetylene) becomes apparent (Figure 2b). The qualitative origin of this feature represents the excess energy required to add a second molecule to a singly occupied cavity as deformation of the surrounding voids is taken into account. As filling of the voids continues, further occupation is eased because much of the required deformation has already taken place through elastic coupling to already filled voids. The model also enables the derivation of expressions for the contributions due to singly and doubly occupied cavities to the total occupancy that can then be superimposed on the experimental data. Upon applying two fitting parameters, the model agrees almost exactly with the experimental data. We note, however, that steps have also been observed for open frameworks and host distortion is therefore not exclusively responsible for inflections[13] present in sorption isotherms.

We have developed a relatively simple procedure suitable for routine single-crystal structure analysis with the sample exposed to controlled gas pressures. As a proof of concept, a series of "pressure-lapse" crystal structure snapshots was recorded to smoothly track subtle changes resulting from gas loading by a porous host. These experiments are analogous to the measurement of a sorption isotherm, but provide detailed structural information regarding the underlying mechanism of the gas uptake process. We observed that carbon dioxide and acetylene are accommodated in different orientations within the available space and were able to rationalize this on the basis of intermolecular host–guest interactions and space filling considerations.[8h] Furthermore, we have utilized our observations both quantitatively and qualitatively to formulate a statistical mechanical model that accounts for the shapes of the experimental sorption isotherms. These models allow deconvolution of the total occupancy into components representing the statistical distributions of the three possible occupancy states for a representative cavity with a maximum possible occupancy of two guest molecules. Future routine application of our systematic method in conventional SCD laboratories promises to yield significant advances in the field of gas sorption studies by providing an improved understanding of the processes that occur at the molecular level.

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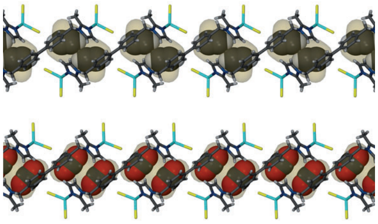
In situ X-ray Structural Studies of a Flexible Host Responding to Incremental Gas Loading



Crystallographic pressure-lapse snapshots of a porous material responding to gas loading were used to investigate the stepwise uptake of carbon dioxide and acetylene molecules into discrete confined spaces. Based on the data a qualitative statistical mechanical model was devised that reproduces even subtle features in the experimental gas sorption isotherms.