Single-crystal to single-crystal phase transition of cucurbit[5]uril hydrochloride hydrates: large water-filled channels transforming to layers of unusual stability†

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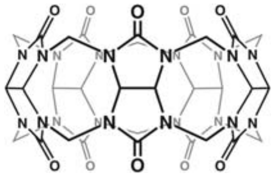
Cucurbit[5]uril hydrochloride hydrate crystals with large water-filled channels transform to a highly stable layer structure *via* a single-crystal to single-crystal mechanism; ^{129}Xe NMR showed that porosity in CB[5] samples depends critically on the method of preparation.

Water-filled channels are present in a variety of biologically important molecules where this one-dimensional organization is necessary for achieving their functionality.[1] Synthetic organic crystals with one-dimensional channels have become of increasing interest because of potential applications as organic zeolites,[2] for instance, for gas storage.[3] In rare cases, macrocyclic molecules are known to dispose themselves in the solid state such that channels are formed. Indeed, organic crystals that have water-filled channels[4] have been reported for calixarenes,[2c,5] pyrogallolarenes[6] and cyclic oligopeptides.[7]

Cucurbit[*n*]urils (CB[*n*]s) are versatile glycoluril-based macrocycles with a constricted toroidal cavity that displays interesting properties.[8] However, channels in solid-state structures based on these host materials are quite rare. Examples include (i) metal organic frameworks using cucurbiturils as ligands that display narrow to wide water-filled channels,[9] (ii) a CB[8]@tripeptide complex,[10] (iii) a CB[6]@rubidium complex[11] and (iv) a CB[6] 2D polyrotaxane[12] that display comparatively large channels. However, for the few instances reported, in only two cases are the channels large enough to reach the nanometer scale.[10,11] Moreover, some crystals are reported to be unstable once out of the mother-liquor.[11] In that instance, a metal cation is necessary to generate the tube-like structure. Recently we reported metal-free solid-state channels based on CB[6] and CB[8], delineated by the inner space of perfectly stacked macrocycles in one dimension.[13] Most recently Kim and co-workers[14] reported a form of CB[6] which shows permanent porosity once water is removed from its channel structure. Here we describe cucurbit[5]uril (Scheme 1) hydrate crystals presenting aqueous channels of diameter ∼0.7–0.9 nm which transform to a layer structure *via* a single-crystal to single-crystal mechanism. Such phase transitions in the field of organic crystals are not common[15] and, to the best of our knowledge, are reported here for the first time in the case of cucurbiturils.


Scheme 1 Molecular structure of cucurbit[5]uril.

For the previously reported CB[6] and CB[8] hydrate crystals,[13] heating to remove water in the hope of producing a porous material failed due to the collapse of the original framework. Conversely, the CB[5] crystals described here appear to be much more stable and are observed to retain crystallinity under harsher conditions (100 °C for 24 h).

Large CB[5] crystals were obtained from an aqueous hydrochloric acid solution containing glycerol as a side-product from the purification steps. We then recrystallized some of these, diffusing a THF–acetone mixture slowly into a formic–hydrochloric acid solution of CB[5]. Colourless plate crystals were then obtained that belong to the monoclinic system (space group *C*2/*m*, composition: CB[5]·$8H_2O$·2.75HCl).‡ The crystals (form **I**) are quite stable in air for hours at 295 K (elemental analysis (%) calculated for the same composition: calc (found): C 33.51 (33.57), H 4.57 (4.39), N 26.05 (26.03)). The CB[5] molecular structure is slightly distorted from the ideal D_{5h} symmetry (Fig. S1, ESI†) presumably due to crystal packing, but the most striking feature of the crystal structure is the presence of large water-filled channels (Fig. 1(a)). The structure contains four symmetry independent molecules of CB[5] arranged in a partial helix with disordered chloride anions and water. Symmetry expansion revealed a distorted honeycomb structure delineated by the CB[5] organization with water inside hydrophobic channels (Fig. 1(b)). Each macrocycle presents its mean plane tilted with respect to normal planes perpendicular to the channel axis. The CB[5] nanotubes share their edges, each CB[5] participating in three nanotubes. The water-filled channels are 14.2 to 15.8 Å apart (see Fig. 1(a) and ESI†). Six cucurbituril molecules constitute the basic circular unit (Fig. 1(b)) whose

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† Electronic supplementary information (ESI) available: Macrocycle preparation, purification, crystal growth, additional description of the crystal structures, PXRD and ^{129}Xe NMR data. CCDC 687155 and 687156. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b807033d

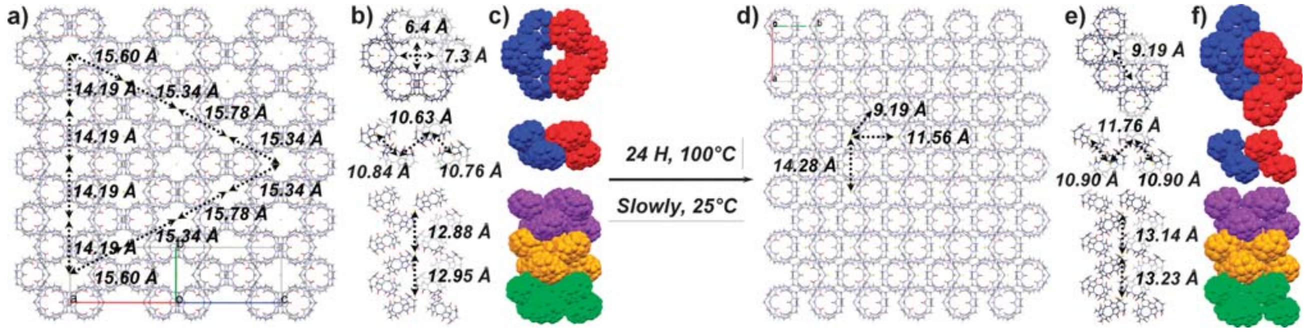

Fig. 1 Crystal packing (a) of structure **I** and highlight of the channel structure (b, top and side views). Space filling representation of the channels (c) showing the tubular arrangement of the cucurbiturils. Crystal packing (d) of structure **II** after transformation from structure **I** exhibiting a layer structure and highlight of the shifted disposition of the CB[5] molecules (e) within a six-unit structure as compared to (b). Space filling representation (f) of the analogous six-unit structure as compared to (c) (water and chlorine are omitted for clarity).

stacking gives rise to the channels and are arranged irregularly in this unit (*i.e.* imperfectly stacked into one preferred dimension). The centres of the CB[5] molecules constituting the building unit are disposed at the vertices of a distorted hexagon adopting a chair conformation and adjacent molecules are within 10.74 ± 0.12 Å of each other. The channel's corrugated walls show a zigzag succession of larger and smaller volumes delineated by the hydrophobic exterior surface of the cucurbiturils. Indeed, spheres of diameter ~9.4 and 7.4 Å could be accommodated inside the channels, defining constricted zones and larger pockets (Fig. S4, ESI†). The channel's cross section shows a six-branched star whose longest distance (from one vertex to the opposite) is around 10 Å. The channels are filled with water molecules, presumably with hydronium ions, which form a disordered hydrogen-bonded column with hydrogen bond linkages to the CB[5]s. There are also linkages between the columns *via* water molecules. Chloride ions reside both inside and between the CB[5], but not in the channels.

Upon exposure of the crystals to air at room temperature, cracks began to appear over a period of hours, suggesting the occurrence of a phase change, possibly with water released from the structure. Nevertheless, the crystals retained their shape over several days in air. Similarly, crystals heated to 100 °C for 24 h retained their shape, and despite severe cracking, still diffracted well and were found to have a different crystal structure.‡ Therefore the crystals transform from form **I** CB[5] (Fig. 1(a)–(c)) to another phase, form **II** CB[5] (Fig. 1(d)–(f)) *via* a single-crystal-to-single-crystal mechanism. Likewise, the slow transformation at room temperature produces form **II** CB[5] crystals. The bulk material also transforms to the new phase as evidenced by the good agreement between the experimental powder X-ray diffractogram and that calculated from the form **II** single crystal structure (Fig. S5, ESI†). In this structure the macrocycles are arranged in layers and the crystals belong to the orthorhombic space group $Pmn2_1$. The CB[5] molecular structure in form **II** is also slightly deformed from the C_5 symmetry (Fig. S2, ESI†). Surprisingly, the single-crystal (**I**) to single-crystal (**II**) transformation is accompanied by only a very slight change in guest content, with the loss of just 0.75 of a molecule of HCl per CB[5] and no water loss. In form **II**, however, a major rearrangement of the water/HCl/CB[5] network has occurred. There are no longer any chloride ions inside CB[5] cavities, and the water-filled channels of form **I** have been replaced by clusters of hydrogen-bonded water plus hydronium and chloride ions, linked *via* water molecules in one dimension parallel to the layers.

One possible transition mechanism is a cooperative sliding of adjacent double rows of CB[5] along the crystallographic *b* axis of form **I**, thus transforming to the layer structure and closing the channels (Fig. 1(c) and (f)).

Perhaps the most striking and unusual aspect of these materials is the thermal stability of the hydration network. Almost certainly the origin of this stability is in the hydrogen-bonding networks among the water and hydronium cations, and also with CB[5] surface atoms. Hydrated proton species generally have shorter hydrogen bonds than pure water and thus will help to strengthen the network.[16] The high hetero-atom content of CB[5] might give rise to unusual partial charge distributions along the macrocycle. Indeed, we found several weak hydrogen bonding contacts between the methine carbons and water, chlorine and neighbouring CB[5] oxygens; CH···O and CH···Cl. The effect of such interactions on CB[7] materials have been discussed previously regarding hydrogelation[17] for which they are thought to act as a glue in maintaining a special CB[7] arrangement, forming fibers responsible for gelation. Such interactions have also been reported to play a special role in thermally stable resorcinarene nanotubes.[18]

Another remarkable aspect of CB[5] is that this material appears to form a plethora of different structures depending on small variations in composition of the solutions and the conditions of crystallization. In addition to forms **I** and **II**, we have also found a different $C2/m$ structure with *small* channels, and a $Pbca$ structure with *large* channels (to be reported elsewhere).

Unfortunately the form **I** → form **II** CB[5] transformation precludes the formation of a form **I** CB[5] porous framework similar to Kim's CB[6] structure.[14] However, Me_{10}CB[5] has been reported to bind gas molecules inside the molecular cavity,[19] and so we probed for microporosity in powdered samples of form **II** CB[5] using ^{129}Xe NMR (Fig. 2). The signal at 230 ppm represents Xe inside a small, tight cavity,[20] consistent with an endo complex, with the implication that a dynamic opening and closing must occur to allow exit of water and entry of the Xe atom. The signal at ~105 ppm in the hyperpolarized ^{129}Xe NMR spectra below 203 K likely comes

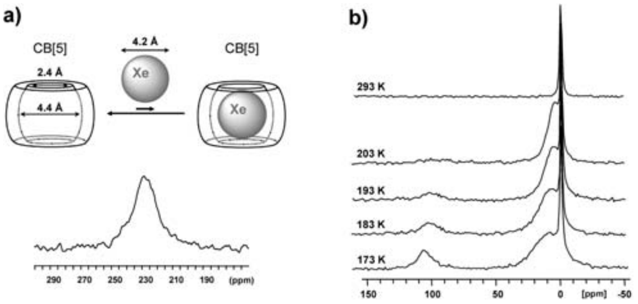

Fig. 2 (a) ^{129}Xe cross-polarization MAS NMR spectrum of thermally polarized and (b) one-pulse NMR spectra of hyperpolarized Xe of powdered samples of form **II** CB[5] crystals.

from Xe adsorbed in interstitial sites or cavities on the surface of the particles. The signal near that of the gas phase (~10 ppm) is from Xe adsorbed in interparticle pore spaces. In marked contrast, a sample of CB[5] prepared by rapid evaporation of a CB[5] solution and drying at 100 °C for 24 h, which was found to be amorphous by PXRD, showed no absorbed Xe. We speculate that this may be due to a self-closure of the cavity by neighbouring cucurbiturils. This shows that the way CB[5] is prepared is critical regarding gas binding.

In conclusion, CB[5] can be constructed in a water-filled crystalline channel structure (form **I**) which, once outside of its mother solution, transforms to a thermodynamically stable layered form (**II**) *via* a single-crystal to single-crystal mechanism. Our observations confirm the previously reported importance and strength of the H bonded network surrounding each CB. It has also become very clear that porosity in CB[5] materials depends critically upon the mode of preparation. Further investigations concerning gas uptake using CB[5] materials and higher homologues are now in progress.

Notes and references

‡ Single-crystal X-ray diffraction data were measured on a Bruker Apex 2 Kappa diffractometer at 100.0(1) K, using graphite-monochromatized Mo-Kα radiation (λ = 0.71073 Å). The unit cell was determined from randomly selected reflections obtained using the Bruker Apex2 automatic search, center, index and least-squares routines. Integration was carried out using the program SAINT, and an absorption correction was performed using SADABS.[21] The crystal structures were solved by direct methods and refined by full-matrix least-squares routines using the SHELXTL program suite.[22] All atoms were refined anisotropically. Hydrogen atoms on cucurbituril molecules were placed in calculated positions and allowed to ride on the parent atoms.

Structure **I**. Crystal size 0.55 × 0.25 × 0.08 mm, $C_{30}H_{48.75}Cl_{2.75}N_{20}O_{18}$, M = 1075.13, monoclinic, space group $C2/m$, a = 37.248(3), b = 14.191(1), c = 37.892(3), β = 92.00(1), V = 20016(2) Å^3, T = 100.0(1) K, Z = 16, D_c = 1.427 Mg m^{-3}, $2\theta_{max}$ = 49.42°, 1549 parameters, 143 restrains, residual electron density max. 1.62, min. −1.69 e Å^{-3}. Final R indices ($I > 2\sigma(I)$): R_1 = 0.127, wR_2 = 0.380 (149 575 reflections total, 17 755 unique, 12 658 ($I > 2\sigma(I)$)).

Structure **II**. Crystal size 0.50 × 0.30 × 0.08 mm, $C_{30}H_{45}Cl_2N_{20}O_{17.5}$, M = 1036.76, orthorhombic, space group $Pmn2_1$, a = 14.280(4), b = 11.560(3), c = 13.183(3), V = 2176.2(9) Å^3, T = 100.0(1) K, Z = 2, D_c = 1.582 Mg m^{-3}, $2\theta_{max}$ = 46.84°, 343 parameters, 172 restrains, residual electron density max. 1.39, min. −0.95 e Å^{-3}. Final R indices ($I > 2\sigma(I)$): R_1 = 0.110, wR_2 = 0.265 (15 278 reflections total, 3289 unique, 2378 ($I > 2\sigma(I)$)).

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