First example of an ice-like water hexamer boat tape structure in a supramolecular organic host†

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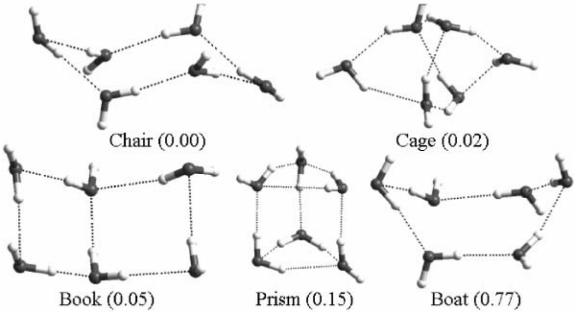
A T6(2) tape of hydrogen bonded water molecules in boat cyclohexane conformation resides in the channel structure of a dibromophloroglucinol (DBPG) host; water escapes at 40–90 °C but is readily re-absorbed by the sponge-like apohost.

A proper theoretical, structural, spectroscopic and thermodynamic understanding of finite and infinite water clusters is a central research problem in chemistry.[1] It comes as no surprise that studies on water were ranked in the top ten breakthroughs of 2004 by *Science*.[2] The primary aim of structural studies on water clusters is to accurately characterize finite ring motifs (*e.g.* tetramers, pentamers, hexamers, dodecamers, *etc.*), 1D chains, helices and tapes, and 2D sheet-like water motifs by X-ray crystallography[3] for a detailed insight into related patterns in Nature and/or that control biological processes. The dominant category of hexamer water clusters occur in different six-membered ring conformations (Scheme 1) within an energy of 0.8 kcal mol^{-1}: chair $\approx$ cage $\approx$ book $<$ prism $<$ boat.[4] There is no example of an ice-like four-coordinated water hexamer tape structure in the boat conformation to our knowledge. Intercalated water sheet structures in chair–boat and boat conformations have been published.[5] We report the first example of a cyclohexane boat conformation water tape in dibromophloroglucinol tetrahydrate, DBPG·4H_2O. Interestingly, and in contrast to several previously published hydrate structures wherein the authors did not simultaneously report the anhydrous form,[6] we disclose the X-ray crystal structure of anhydrous DBPG and reversible loss/uptake of water from its sponge-like channel framework.

Crystals of the composition DBPG·4H_2O were obtained by the slow evaporation of a solution of dibromophloroglucinol in aqueous methanol.‡ The asymmetric unit (space group *C*2/*c*) contains 0.5 molecule of DBPG (with O1 phenol and C4 atoms residing on the 2-fold rotation axis) and two water molecules (O3 and O4). Four DBPG molecules are hydrogen bonded *via* water molecules (O2–H···O3 2.67 Å, O3–H···O2 2.81 Å) and Br···Br contacts (3.45 Å) to form a rectangular grid of 8.0 × 4.5 Å voids in the *ab*-plane (Fig. 1a). Aromatic rings of adjacent layers stack with excellent π···π overlap at a 3.42 Å inter-planar distance to make channels along the *c*-axis. Hydrogen bonded water molecules reside in the tubular framework of the DBPG host connected *via* water···phenol H bonding. The H atom of phenol O1 is disordered over two locations by crystallographic 2-fold symmetry and one of the H atoms of water O4 has 0.5 occupancy (H4B, H4C). The intricate H bond network of water molecules along [001] is shown in Fig. 1b. Three structural features of the water cluster deserve discussion. (1) O3 and O4 water molecules are H bonded in a hexamer of boat cyclohexane conformation. The four O atoms that constitute the bottom of the boat are nearly coplanar, deviating by only 0.25 Å from the mean plane of O3–O4–O3–O4 atoms. (2) Such hexamers are connected at the O4–O4 bond to form a linear tape of tetra-coordinated boat water clusters for the first time (Fig. 1c), similar to the H bond network along the *c*-axis in hexagonal ice (I_h) (see Fig. 1d). (3) The edge O atoms pointing towards each other in the high-energy boat hexamer of water molecules are stabilized by cooperative H bonds with the phenol host (O1–H···O4 2.77 Å).



Scheme 1 Computed energies (MP2/aVTZ level) of the five lowest energy (relative to chair, in kcal mol^{-1}) water hexamer structures (ref. 4).

Infantes *et al.*[7] classified water clusters as ring (R), chain (C), tape (T), layer (L) motifs, *etc*. The infinite tape motif in the present hydrate structure has the notation T6(2), namely a tape of 6-membered rings with 2 shared water molecules. The seven examples of T6(2) water topology[7a] reported in the 2002 version of the Cambridge Structural Database (CSD)[8] have chair cyclohexane conformation. However, a very recent (2005) critical evaluation of water oligomers by Mascal *et al.*[9] shows that out of 31 examples of T6(2) clusters, 7 structures have water molecules in the boat conformation (CSD refcodes ODIMAP, BELFED, WUXLOQ, PIZPET, PIZPIX/01 and PIZPOD). Six of these hits are metal–organics and one is an organic host structure. However, water H atoms are located in only 2 crystal structures, ODIMAP and PIZPIX01, but both these were determined at room temperature.[10] We have collected reflections on a DBPG·4H_2O crystal at 298 K and 100 K to confirm that there is no phase transition and water H atom positions are assigned from the difference electron density map at 100 K. The T6(2) boat water tape in the DBPG host is unique among the 7 CSD refcodes. (1) Our structure has tetra-coordinated water molecules, as in ices I_h and I_c, in contrast to a mixture of 4-coordinated and

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† Electronic supplementary information (ESI) available: Synthesis of DBPG, crystallographic data, and H bond parameters. See DOI: 10.1039/b600348f

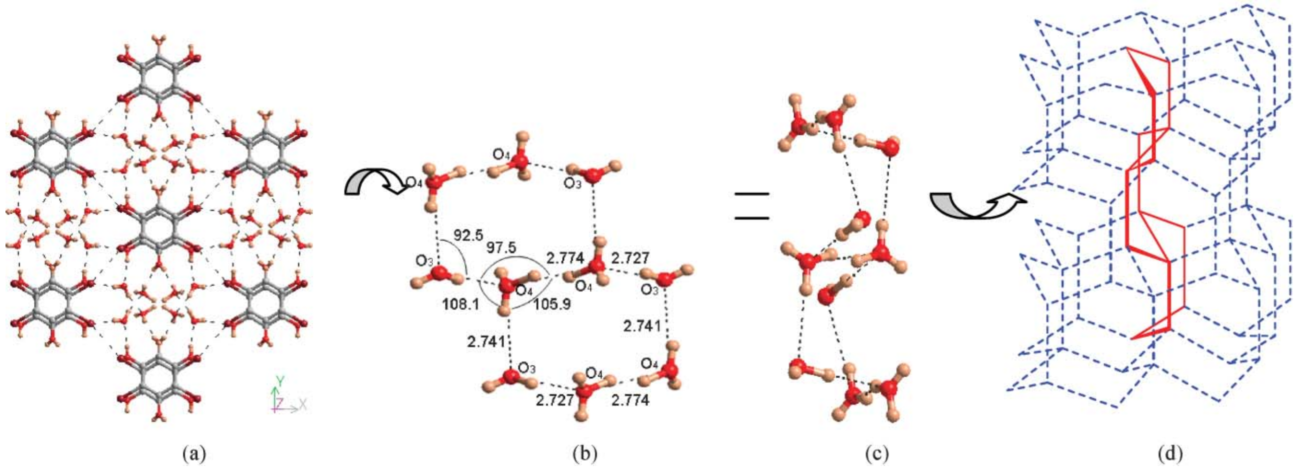

Fig. 1 (a) Rectangular voids between DBPG molecules in the *ab*-plane and stacking of aromatic rings with little offset generate channels down the *c*-axis. (b) Hydrogen bonding between O3 and O4 water molecules in the water hexamer tape structure bonded to phenol O1 and O2 atoms along the tubular host framework. (c) The boat cyclohexane conformation of T6(2) water tape in $DBPG\cdot 4H_2O$. (d) The T6(2) tape (red) highlighted in the structure of hexagonal ice I_h (blue). Water O atoms are located at the nodes and H bonds are represented as lines in the 3D network.

3/5-coordinated waters in the reported structures. The 1D water tape in ODIMAP is highly distorted compared to the tetrahedral geometry in I_h. Gillon *et al.*[11] surveyed the CSD for hydration motifs in molecular crystals: 3-coordinated water is the most common (38.40%) followed by 4-coordinated water (27.45%), or the so-called Walrafen pentamer.[1a] (2) Whereas the T6(2) tapes are coordinated to other water molecules in CSD structures, only water molecules that are part of the boat cyclohexane cluster propagate the tape motif in DBPG tetrahydrate. The water cluster boat geometry shows the expected variation with temperature.† The mean O···O distance of 2.75 Å at 100 K (2.77 Å at 298 K) is closer to the distance in hexagonal ice (2.75 Å) than liquid water (2.85 Å), whereas O–O–O angles vary from 92 to 108° compared to the mean value of 109.5° in the tetrahedral arrangement of water neighbors in ice.

The evolution of water from the channel structure of DBPG was analyzed by thermal gravimetric analysis and differential scanning calorimetry (TGA, DSC plots in Fig. 2). There is a 19.5% weight loss between 40 and 90 °C in $DBPG\cdot 4H_2O$ (calc. = 20.2%) consistent with the broad endothermic peak at 81.6 °C. The enthalpy for water release is 29.7 kJ mol^{-1}, which means 10.8 kJ mol^{-1} per hydrogen bond. This value is lower than the H bond energy in water helices[3i] and a $(H_2O)_{17}$ cluster[12] but about half that in crystalline ice polymorphs (~22 kJ mol^{-1}).[13] The second endotherm at 97.7 °C is a phase transition of the channel structure to the anhydrous form since this thermal event in the DSC trace is not concomitant with a weight loss in the TGA data. DBPG melts at 170–171 °C. Whereas there are several examples of water clusters trapped in organic and metal–organic host lattices, the structure of the apohost is seldom reported at the same time because of their high tendency to include water molecules and not crystallize in a guest-free form.[6] A rare example of a water sheet structure and clathrate hydrate was recently reported.[14]

Crystallization of DBPG from $CHCl_3$–EtOAc afforded an anhydrous crystalline form (space group *Pbcn*) exhibiting a pseudo-hexagonal arrangement of molecules (Fig. 3a) *via* phenol O–H···O H bonds (2.92, 3.12 Å) and Br···Br interactions (3.49 Å); however, there is no significant π–π stacking. Here too, the

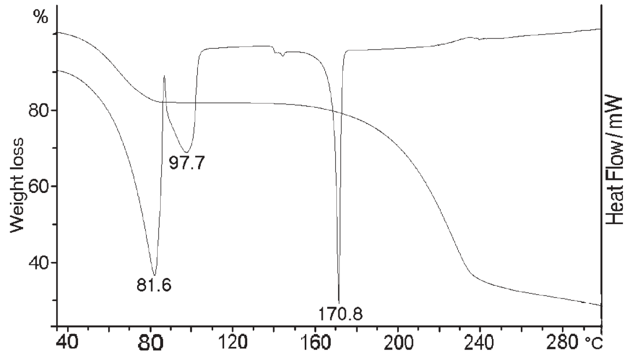

Fig. 2 DSC and TGA thermograms of $DBPG\cdot 4H_2O$. The major endothermic peak at 81.6 °C is due to water loss consistent with TGA data. The endotherm at 97.7 °C is a phase transition of the water-filled channel structure to the anhydrous apohost, which starts melting at ~140 °C (small endotherm) and then DBPG completely melts at 170.8 °C. DSC/TGA data were recorded at a temperature ramp of 10 °C min^{-1} under dry N_2 purge of 150/50 mL min^{-1}.

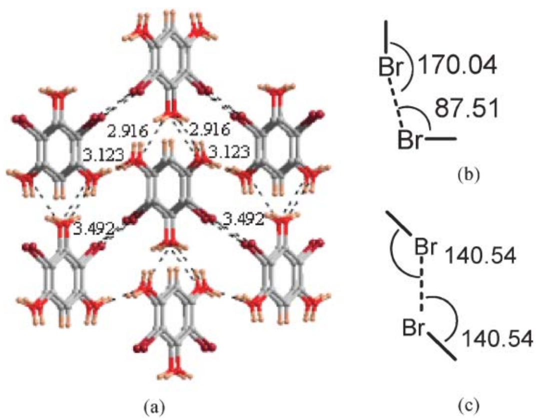

Fig. 3 (a) Crystal structure of anhydrous DBPG. (b) The type II interhalogen interaction in the anhydrous form and (c) the type I contact in the hydrate.

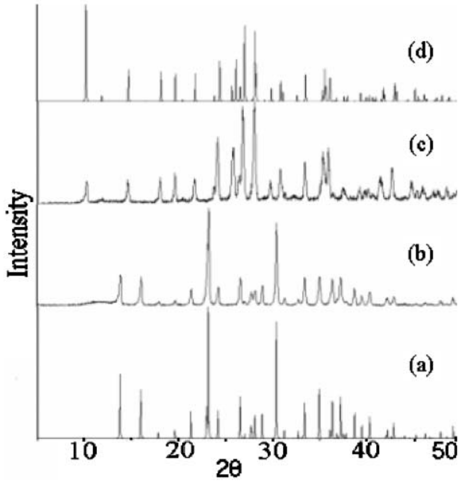

Fig. 4 Powder X-ray diffraction plots. (a) Anhydrous DBPG (simulated); (b) expulsion of water from the tetrahydrate (experimental); (c) rehydration of the anhydrous form with water vapor (experimental); (d) DBPG·4H_2O (simulated).

molecule resides on the 2-fold rotation axis and phenol protons are disordered over two sites with 0.5 occupancy. The packing fraction of DBPG·4H_2O is 68.3% with water occupying 35.8% of the crystal volume; the DBPG packing fraction is 73.7%. Stronger H bonding in the tetrahydrate structure (see ESI for distances at 298 K†) compared to the anhydrous form is the reason for water inclusion despite a lower packing fraction in the hydrate crystal. Whereas the inter-halogen geometry[15] is of type I in the hydrate structure, polarization-induced type II contacts are present in the anhydrous form (Fig. 3b, c). The greater significance of halogen bonding over hydrogen bonding in anhydrous DBPG compared to the tetrahydrate structure is consistent with ongoing experiments.§ The halogen atom plays a significant role in these strong H bonded structures because diiodophloroglucinol ($P\bar{1}$) has a different crystal packing.

Dehydration of the water-filled channels at 90 °C for 30 min at 0.2 Torr gave a microcrystalline solid whose powder XRD pattern matches with simulated peaks from the *Pbcn* X-ray crystal structure (Fig. 4). When the dehydrated material was left overnight in a chamber saturated with water vapour it completely converts to the tetrahydrate form (PXRD, TGA). Thus, the organic host DBPG functions like a supramolecular sponge:[16] it readily uptakes moisture and releases the guest under relatively mild conditions (<100 °C). The IR spectra (KBr) of anhydrous and hydrated DBPG show similar broad peaks for the OH stretch in the range 3000–3500 cm^{-1} due to H bonded phenol and water aggregates, making it difficult to identify the peaks from water clusters (compare with hexagonal ice at 3220 cm^{-1} and liquid water at 3280 cm^{-1}). Cyclic water hexamers are prototypical structural motifs in ice polymorphs I_c, I_h, proton-disordered ice II, and bulk water. Cubic ice is stable below −120 °C but undergoes a phase transition to normal hexagonal ice above −80 °C. The absence of a phase transition in DBPG·4H_2O between 100 and 298 K provides a 1D ice-like structural motif for variable-temperature diffraction and spectroscopy experiments.

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Notes and references

‡ **DBPG·4H_2O**: monoclinic, *C*2/*c*, a = 16.0309(12), b = 10.6848(8), c = 7.3246(5) Å, β = 111.4500(10)°, V = 1167.71(15) $Å^3$, Z = 4, $R1$ = 0.0198, $wR2$ = 0.0502, T = 100 K. **DBPG**: orthorhombic, *Pbcn*, a = 5.4011(5), b = 12.8974(13), c = 10.9478(11) Å, V = 762.63(13) $Å^3$, Z = 4, $R1$ = 0.0298, $wR2$ = 0.0794, T = 298 K. Structure solution and refinement were carried out with Bruker SHELXTL. See ESI for further crystallographic details and crystal data of DBPG·4H_2O at 298 K.† CCDC 294904–294906. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b600348f

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