New insights into the formation of extended supramolecular architectures from simple building blocks

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Reaction of uranyl acetate with HCl and 15-crown-5 in toluene results in the formation of a liquid clathrate phase from which crystals of $(H_5O_2)[UO_2Cl_3(H_2O)_2]\cdot(15\text{-crown-}5)_2$ 1 are deposited; on standing, loss of HCl results in the isolation of a second product $[UO_2Cl_2(H_2O)_3]_{16}\cdot(15\text{-crown-}5)_{16}$ 2 which displays an extremely complex hydrogen bonded chain structure in the solid state.

In crystal growth the task presented to Nature is one of three dimensional tesselation. Often irregular molecular shapes must be fitted together in such a way as to minimise the amount of wasted space (vacuum) within the crystal.[1] In some cases, particularly those in which the molecule to be crystallised possesses a molecular cavity or cleft, the occurrence of vacant space is difficult to avoid and adventitious molecules of solvent, other species present in the reaction mixture or even gases[2,3] are incorporated within the crystalline lattice. The study of this phenomenon has given birth to the rich field of inclusion chemistry.[4,5]

A significant amount of work within the field of crystal engineering has been devoted in attempts to predict how Nature will solve the crystal 'tesselation' problem for a wide range of solid compounds.[6,7] Many synthetic chemists are, however, familiar with compounds which 'just will not crystallise'. The amorphous nature of such solids, which are often found to form oils in which a well defined ratio of solvent and solute comprises a separate phase from the bulk solvent, may often be rationalised in terms of molecular size and shape and its consequences on the lattice energy of the crystalline solid.[1] An excellent, and well studied example of this phenomenon is the formation of liquid clathrates in which an aromatic solvent serves to separate anions and cations of widely differing shape and size.[8–10] Under certain circumstances however, liquid clathrates may be decomposed by, for example, loss of HCl from the reaction medium and a consequent gradual decrease in polarity. In this way, studies of crown ether/metal salt mixtures in liquid clathrate media[8] have resulted in the isolation of a wide range of crystalline arrays of type '$H(H_2O)_n^+$(crown ether)(anion)' in which the oxonium ion acts as a hydrogen bond donor and the crown ether as a hydrogen bond acceptor, thus giving insight into the precursor solution species.[11–14] In the case of the larger crown ethers such as 18-crown-6 and 21-crown-7 the oxonium cation is encapsulated by the macrocycle.[11,12,15] For 15-crown-5 and 12-crown-4, extended hydrogen bonded arrays are formed involving alternating hydrogen bond donors and acceptors, as a result of the inability of the small crown ether to surround the oxonium cation.[16]

The key to the production of materials with predictable crystal structures lies in the engineering of complementary crystal building blocks either by consideration of molecular shape,[17,18] electronic properties,[19] or hydrogen bond donor/acceptor ability.[20] We report herein the preliminary results of crystal engineering studies carried out in liquid clathrate media between hydrogen bond donor–acceptor pairs, which are not sterically complementary, and exhibit a symmetry mismatch.

The reaction of uranyl acetate with HCl and 15-crown-5 in toluene was carried out as shown in Scheme 1. This resulted in the formation of a large, yellow liquid clathrate layer over a period of *ca.* 12 h. Upon standing for a further 12 h gradual loss of HCl resulted in the deposition of crystals of formula $(H_5O_2)[UO_2Cl_3(H_2O)_2]\cdot(15\text{-crown-}5)_2$ **1**. The X-ray crystal structure† of this complex is shown in Fig. 1 and consists of an infinite chain comprising alternating $H_5O_2^+$ and $[UO_2Cl_3(H_2O)_2]^-$ anions linked by hydrogen bonding *via* 15-crown-5 molecules. Within the $H_5O_2^+$ cation the O···O distance is extremely short at 2.371(8) Å (*cf.* typical values of O···O separations 2.40–2.45 Å[11,15,21–23]) although distances as low as 2.336(14) Å have been noted.[24] Oxonium–crown contacts are in the range 2.70–3.20 Å, while the opposite face of each crown ether is hydrogen bonded to coordinated water molecules at distances of 2.92–3.04 Å. The $[UO_2Cl_3(H_2O)_2]^-$ anion itself exhibits normal bond lengths and angles with U=O 1.743(6), U–OH$_2$ 2.37(3), 2.45(5) [O(2) and O(3) are disordered] and U–Cl 2.708(3), 2.709(3). This may be compared to typical distances of 1.763, 2.455 and 2.653 respectively.[25] The $[UO_2Cl_3(H_2O)_2]^-$ anion adopts a pentagonal bipyramidal geometry resulting in the hydrogen bond donating H_2O ligands both residing in the equatorial plane with a O–U–O angle of 146.4(9)°. This, in turn, enforces a zigzag structure to the $[UO_2Cl_3(H_2O)_2]^-\cdots$15-crown-5 chain.

$$\begin{tikzcd}
UO_2(O_2CMe)_2 + 15\text{-crown-}5 + HCl_{(g)} + H_2O \arrow[d, "\text{toluene}"', "\text{warm, 12 h}"] \\
\text{two-phase liquid clathrate / toluene mixture} \arrow[d, "\text{crystallisation}"', "\text{12 h}"] \\
{[H_5O_2][UO_2Cl_3(H_2O)_2]\bullet(15\text{-crown-}5)_2} \arrow[d, "-HCl"', "\text{6 weeks}"] \\
{[UO_2Cl_2(H_2O)_3]_{16}\bullet(15\text{-crown-}5)_{16}}
\end{tikzcd}$$

Scheme 1 Formation of the hydrogen bonded array $[UO_2Cl_2(H_2O)_3]_{16}\cdot(15\text{-crown-}5)_{16}$

Over a period of six weeks continued loss of HCl from the same reaction mixture results in the replacement of the yellow rectangular crystals of complex **1** by large, multifaceted crystals of a second product of empirical formula $[UO_2Cl_2(H_2O)_3]\cdot$15-crown-5. X-Ray crystallographic analysis† revealed a striking structure of trigonal symmetry, space group $P3_2$, consisting of sixteen unique uranium complexes and 15-crown-5 molecules, Fig. 2. The structure is arranged in sheets consisting of approximately linear, infinite hydrogen bonded strands, which

Fig. 1 Infinite chain structure of $H_5O_2^+$ and $[UO_2Cl_3(H_2O)_2]^-$ linked by 15-crown-5

Fig. 2 The asymmetric unit of $[UO_2Cl_2(H_2O)_3]_{16}\cdot(15\text{-crown-}5)_{16}$ **2** comprising four parallel, helical columns of alternating $[UO_2Cl_2(H_2O)_3]$ and 15-crown-5 (end and side views)

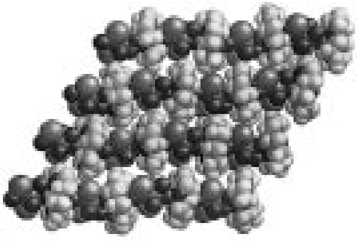

Fig. 3 Space filling plot of **2** showing the interlocking of the chains

repeat every four uranium centres. The strands are held together by interactions between the crown oxygen atoms and water molecules O(*n*3) and O(*n*4) (where *n* represents the number of the uranium centre to which the atom is attached) which form the most nearly linear H_2O–U–OH_2 angle of *ca*. 152° [the analogous O(*n*3)–U–O(*n*5) angle is *ca*. 140°]. Typically both O(*n*3) and O(*n*4) form two hydrogen bonds to an adjacent crown ether with a wide range of $O_{water}\cdots O_{crown}$ distances of between 2.60(2) and 2.92(2) Å highlighting the individual nature of each of the sixteen crown–metal complex pairs. In addition, O(*n*5) forms a single short hydrogen bond to a further crown oxygen on the same side as O(*n*4) with distances ranging from 2.49(2) to 2.71(2) Å. While some disorder was evident in the 15-crown-5 molecules of **1**, complex **2** is ordered at −100 °C with each of the sixteen 15-crown-5 units exhibiting a structure in which three oxygen atoms point towards O(*n*4) and O(*n*5) of one metal complex and two others interact with O(*n*3) on the next. It is the unsymmetrical nature of this conformation with three donor atoms one side and two on the other, which, in the absence of oxonium ions, leads to such a complicated structure. In forming the interactions to water ligands O(*n*4) and O(*n*5) with three of the crown oxygen atoms, two are left for forming the next interaction to an adjacent anion [*via* O(*n*3)]. This results in the docking of this anion in such a way as to maximise O(*n*3)···crown interactions, in the process fixing its orientation. Hydrogen bonding from O(*n*4) and O(*n*5) to the next crown ether must now necessarily occur in a different orientation to the previous member of the chain. This results in a rotation perpendicular to the chain direction of *ca*. 25–35° accompanied by a tilt along the chain axis of *ca*. 10°. The net result is that it is not until the fifth such donor–acceptor pair that the crown has rotated back to its starting point. Furthermore, the displacement of the uranium centres to one side of the chain axis as a consequence of the non-linear O(*n*3)–U–O(*n*4) axis results in the formation of grooves in the chain into which the crown ethers of adjacent stacks slot. Again, the steric requirements of one chain dictate the orientation of the next such that each chain is rotated with respect to its neighbour. This pattern also does not repeat itself until the fifth chain resulting in a unique 4 × 4 array of donor acceptor pairs, Fig. 3.

In summary, the rigid and uncomplementary nature of both uranyl species in **1** and **2** results in interesting crystal packing motifs. In the former case the presence of a linear oxonium ion serves to simplify the crystal packing. For **2** a highly complex crystalline array is required before the problem of three-dimensional tessellation of such mismatched building blocks can be solved.

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Footnotes and References

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† *Crystal data*: **1**: $C_{20}H_{29}Cl_3O_{16}U$, M = 869.81, orthorhombic, *Pmcn*, a = 12.1740(5), b = 14.7740(7), c = 18.4920(11) Å, U = 3325.9(3) Å^3, Z = 4, data 2434, parameters 204, $R_1 = [F^2 > 2\sigma(F^2)] = 0.042$, wR_2 (all data) = 0.111. **2**: $C_{10}H_{26}Cl_2O_{10}U$, M = 615.24, trigonal, $P3_2$, a = 35.3500(2), c = 21.3755(2) Å, U = 23 132.7(3) Å^3, Z = 48, data 51 913, parameters 3305, R_1 $[F^2 > 2\sigma(F^2)] = 0.072$, wR_2 (all data) = 0.158. CCDC 182/735.

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