Novel inclusion compounds with urea/thiourea/selenourea-anion host lattices

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The chemistry of inclusion compounds has a long history and is nowadays a subject of wide-ranging and intense study. With the awarding of the 1987 Nobel Prize in Chemistry to Donald J. Cram, Jean-Marie Lehn and Charles J. Pedersen for their fundamental work on “host-guest” or “supramolecular” systems, inclusion chemistry has come to the fore front in contemporary researches. Increasing varieties of novel inclusion compounds and new host molecules have been synthesized recently. The term “crystal engineering” was coined by Schmidt to describe the rational design and control of molecular packing arrangements in the solid state, and the structural study of clathrates has contributed substantially to our understanding of the problem. Generalizations concerning the preferred structural motifs generated by hydrogen bonding and weaker non-covalent interactions between specific functional groups or molecular fragments have led to the realization of some impressive predictions about the construction of supramolecular networks.

Urea, thiourea and selenourea are good host molecules because they have a well-defined trigonal planar geometry and can form at least six hydrogen bonds. The co-crystallization behavior of urea and thiourea with straight- and branched-chain aliphatic compounds, respectively, was first reported over half a century ago. New concepts about various structural aspects of urea inclusion compounds, such as temperature-dependent structural properties, phase transition and structure change, disordered crystal structure, and migration of molecules into the channel structure, as well as unusual conformational behavior in thiourea inclusion compounds, have been reported. More and more research work about them has shown that the inclusion phenomenon is much more complex, varied, and interesting than that had been realized all along.

The strategy for the generation of inclusion compounds by use of various organic host materials with appropriate guest molecules as templates has been shown to be an important approach in the structural design or modification of the host lattice, and has the potential of yielding fruitful results in crystal engineering. Our interest in urea[1−10]/thiourea[11−20]/selenourea[21] adducts stems from an attempt to generate different inclusion topologies by incorporating additional components into the construction of the hydrogen-bonded host lattice[22]. In our research program more than 70 novel inclusion compounds have been prepared. The versatility of urea or thiourea as a key component in the construction of novel anionic host lattices is clearly demonstrated by the occurrence of many new types of linkage modes. The results show that co-molecular aggregates of urea or thiourea with other neutral molecules or anionic moieties can be considered as fundamental building blocks for the constructions of various types of novel host lattices.

1 General structural features and relationships of urea/thiourea/selenourea-anion inclusion compounds

The results of our studies on urea/thiourea/selenourea-anion inclusion compounds have demonstrated that the classical urea or thiourea hydrogen-bonded host lattice can be modified in interesting ways by the incorporation of various anionic moieties, with or without co-crystallized water or other uncharged molecules, and that novel host frameworks bearing different urea, thiourea or selenourea/guest molar ratios are generated by variation in size of the hydrophobic, pseudo-spherical R_4N^+ guest species. As envisaged, the urea/thiourea/selenourea-anion host lattices exhibit a rich variety of inclusion topologies besides the typical uni-directional channel structure, such s a channel with widened cross-section accommodating two parallel columns of guest species, corrugated-layer or double-layer sandwich structure, and a three-dimensional network containing isolated cages, intersecting tunnels, or dual channel systems. It is noted that the types of host lattices formed are dependent on the stoichiometric ratio of urea derivatives to anions and co-crystallized solvent molecules (water in most cases) or neutral molecules as additional host components.

Only van der Waals contacts are made between the included guest molecules and the molecules or anions of the host lattices in almost all inclusion compounds. The fundamental role of hydrogen bonding in stabilizing the host lattices is so outstandingly important that regiospecific hydrogen bonds control the way in which small molecular units, such as the present urea derivatives and various anions, form aggregate host lattices. It can be seen that the requirement for strong host-host hydrogen bonding in the maintenance of a host lattice need not be restrictive on the shape or dimensions of the lattice. Hydrogen bonding dimensions, particularly angles, are variable, and host-host hydrogen bonding networks can possess a substantial flexibility.

We now present our results demonstrating that the N—H···O and N—H···S hydrogen bonds play an instrumental role in the structures of a novel class of urea/thiourea inclusion compounds. There have been the average lengths of 103 measured N—H···O hydrogen bonds in 23 urea-anion inclusion complexes and 148 measured N—H···S hydrogen bonds in 28 thiourea-anion host lattices. Although these bond lengths vary over a wide range of values, the average values of N—H···O and N—H···S are in good agreement with those found for several types of hydrogen bonds, N···O = 2.93±0.11 and N···S = 3.40±0.20 Å[23]. Generally, the hydrogen bond length is related to the environment and configuration of both donor and acceptor atoms, following the order of head-to-tail mode < shoulder-to-shoulder fashion < singly H-bond.

The C—H···O hydrogen bond exists in only one case, in which the formyl atom forms a C—H···O hydrogen bond with the carboxy O atom belonging to the adjacent molecule, with H···O = 2.303(6), C···O = 3.213(6) Å and C—H···O = 157.9(4)°. The H···O distance is shorter than the sum of the relevant van der Waals radii ($W_H + W_O = 2.4$ Å) and lies closer to the lower end of the H···O range of 1.5—3.0 Å for C—H···O hydrogen bonding established by accurate X-ray and neutron diffraction analyses, indicating that the formyl CH group has a relatively strong donor capability.

$(CH_3)_3N^+(CH_2)_2OH \cdot NH_2CONHCO_2^- \cdot (NH_2)_2CO$ (fig. 1) is an inclusion compound consolidated by host-host and host-guest hydrogen bonding, in which the allophanate O atoms of the resulting hydrogen-bonded hydrophilic host lattice form acceptor hydrogen bonds with the hydroxyl groups of choline guests. This may be contrasted with the classical urea or thiourea inclusion compounds formed by self-assembly, as well as inclusion compounds built of urea or thiourea together with various anions, in which the hydrophobic guest species are retained by steric barriers formed by the hydrogen-bonded host lattices.

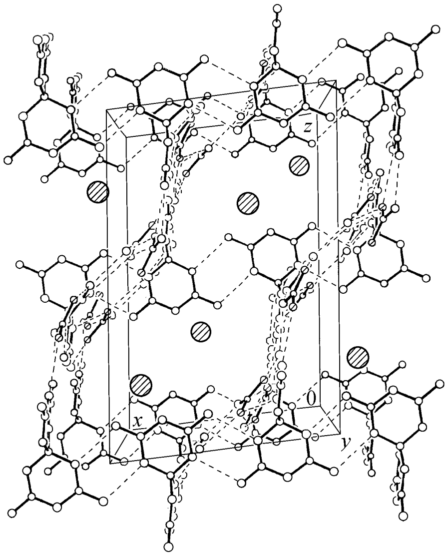

Fig. 1. Packing diagram of crystal of $(n\text{-}C_4H_9)_4N^+[B_5O_6(OH)_4]^- \cdot 2(NH_2)_2CO \cdot B(OH)_3$ viewed down the *b* axis, showing the puckered layers parallel to (202) and planar $B_3O_3(OH)_2^-$ ribbons extending in the [010] direction. Broken lines represent hydrogen bonds, and atom types are distinguished by size and shading; ○, oxygen; ○, boron; ○, carbon; ∅, nitrogen. For clarity the enclosed $(n\text{-}C_4H_9)_4N^+$ ions are represented by large shaded circles and hydrogen atoms are omitted.

2 Linkage modes of urea and thiourea molecules

In an idealized scheme of host design, the well-knit hexagonal ($P6_122$ or $P6_522$) urea or pseudo-hexagonal ($R\overline{3}$) thiourea channel framework is first divided into hydrogen-bonded chains or ribbons, and hydrogen bonding between these units with suitable anionic and neutral species would then lead to new varieties of host systems. The versatility of urea, thiourea or selenourea as a key component in the construction of novel host lattices is clearly demonstrated by the occurrence of many new types of linkage modes, which include various discrete units, chains or ribbons and composite ribbons with corresponding anions. The hydrogen-bonded layers can be generated by replication of the isostructural and independent discrete units or by other bridging moieties. The hydrogen-bonded layers can also be built from a parallel arrangement of ribbons or composite ribbons, ribbons bridged by some anions, or an alternate arrangement of two different types of ribbons. The three dimensional channel-type network may be formed by cross-linkage of two types of layers or by two crisscross series of ribbons (fig. 1).

3 Co-molecular aggregates of urea/thiourea and other host components

As mentioned above, in urea/thiourea-anion inclusion compounds both urea and thiourea molecules adopt various linkage modes not only of self-assembled hydrogen-bonded chains or ribbons but also of composite ribbons with the corresponding anions. The results show that co-molecular aggregates of urea or thiourea with other neutral molecules or anionic moieties can be considered as fundamental building blocks for the constructions of various types of novel host lattices. As compared with urea, the thiourea molecule has a lesser tendency to combine with other host components to form a dimer or composited ribbon. In most thiourea-anion inclusion compounds the host lattices are built from connections of thiourea ribbons and the anionic dimers or just the ribbons only.

It is of interest to note that the allophanate ion, which is known in the form of its derivatives, and the dihydrogen borate anion $BO(OH)_2^-$, the fugitive conjugate base of boric acid, can be generated *in situ* and stabilized in the crystalline state through hydrogen-bonding interactions with its nearest neighbors. Notably the bulky and hydrophobic tetraalkylammonium ion plays a dual and complementary role, i.e. it serves as a template for the self-assembly of the anionic host lattice and, abetted by the presence of urea, provides a suitably alkaline aqueous medium that induces boric acid to function as a Brønsted acid.

In summary, we have shown that novel anionic host lattices can be constructed from urea, thiourea or selenourea molecules and various anions as building blocks, which readily adopt different topologies for the accommodation of tetraalkylammonium ions of various sizes. By employing organic cations as templates and suitable counter anions as an ancillary host material, the 'lattice engineering' of new urea, thiourea and selenourea inclusion compounds by self-assembly may be further explored.

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