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A New Type of Layered Structure for Urea Inclusion Compounds Containing Local Segments of Tunnels

Sang-Ok Lee, Benson M. Kariuki, Angela L. Richardson, and Kenneth D. M. Harris*

School of Chemistry, University of Birmingham
Edgbaston, Birmingham B15 2TT, United Kingdom

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Among the broad range of solid inclusion compounds[1] that have been studied in recent years, the urea inclusion compounds[2−7] have received particular attention in view of the wide range of fundamental physicochemical phenomena that they exhibit, including incommensurate structural properties,[8−13] order−disorder phase transitions,[14−20] molecular motion,[21−26] properties relating to one-dimensional confinement,[27−29] and ferroelastic properties.[30] In the conventional urea inclusion compounds, the host structure[2,8] is constructed from a hydrogen-bonded arrangement of urea molecules and contains one-dimensional, continuous, parallel tunnels. These tunnels are filled with a dense packing of guest molecules. A wide range of different types of guest molecules have been shown to form these inclusion compounds with urea, and a remarkable fact is that, in virtually all cases, the same urea host structure is formed at ambient temperature. We refer to such cases as "conventional" urea inclusion compounds, characterized by: (i) a hexagonal host tunnel structure (space group $P6_122$ or $P6_522$), (ii) an incommensurate relationship[31] between the periodicities of the host and guest substructures along the tunnel axis, and (iii) substantial dynamic disorder (reorientation about the tunnel axis) of the guest molecules at ambient temperature. In most cases, order−disorder phase transitions occur at a sufficiently low temperature and are associated with a distortion of the host tunnel (to a lower symmetry than hexagonal) and a concomitant decrease in the reorientational motion of the guest molecules. In a few cases,[32−36] a distorted tunnel structure is formed at ambient temperature, usually when the length of the guest molecule is close to a simple multiple of the periodic repeat distance of the urea tunnel, allowing a commensurate structure to be formed, and different host structures are also known to be formed with some polymeric guests.[37−40] However, in all cases reported thus far, the urea host structure comprises continuous one-dimensional tunnels constructed from an essentially infinite three-dimensional hydrogen-bonded network of urea molecules. In general terms, we may speculate that other types of structural motif may be possible for inclusion compounds of urea, particularly when the guest molecules contain appropriate hydrogen-bonding functionalities, which may engage in direct hydrogen-bonding interactions with urea molecules and/or co-included solvent molecules.

In contrast to the continuous tunnel structures found in all other urea inclusion compounds, this paper reports a completely new type of host structure in urea inclusion compounds, based on a *layered* structure of urea and guest molecules. The layers are composed of local segments of urea tunnel structure, which have a hydrogen-bonding topology similar to that in the conventional urea tunnel structure, and a layer thickness that is close to the length of a single guest molecule. Adjacent layers are *displaced* relative to each other, such that the local segments of tunnel in adjacent layers do *not* form a continuous tunnel running through the crystal.

This new structure type has been found during attempts to prepare urea inclusion compounds containing 1,7-diaminoheptane [$H_2N(CH_2)_7NH_2$] as the guest component, by crystal growth under conventional conditions using methanol as the solvent. Powder X-ray diffraction analysis of these crystals indicated that no detectable amounts of conventional urea inclusion compounds were present in the sample.

The structure of the new material has been determined from single-crystal X-ray diffraction data, and is found to contain methanol in addition to urea and 1,7-diaminoheptane, with the stoichiometry: $(\text{urea})_7(\text{1,7-diaminoheptane})_1(\text{methanol})_2$. The structure is monoclinic (space group $C2/c$; $a = 8.32$ Å, $b = 13.95$ Å,

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* To whom correspondence should be addressed. E-mail: K.D.M.Harris@bham.ac.uk. Telephone: +44-121-414-7474. Fax:+44-121-414-7473.

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(31) The structural relationship between the periodicity (denoted c_h) of the host structure along the tunnel and the periodicity (denoted c_g) of the guest molecules along the tunnel is incommensurate if there are no sufficiently small integers m and n that satisfy the relationship: $mc_g = nc_h$. Thus, c_g/c_h is not equal to a rational number with sufficiently small denominator. The nature of incommensurate versus commensurate behaviour in tunnel inclusion compounds is discussed in refs 9 and 11.

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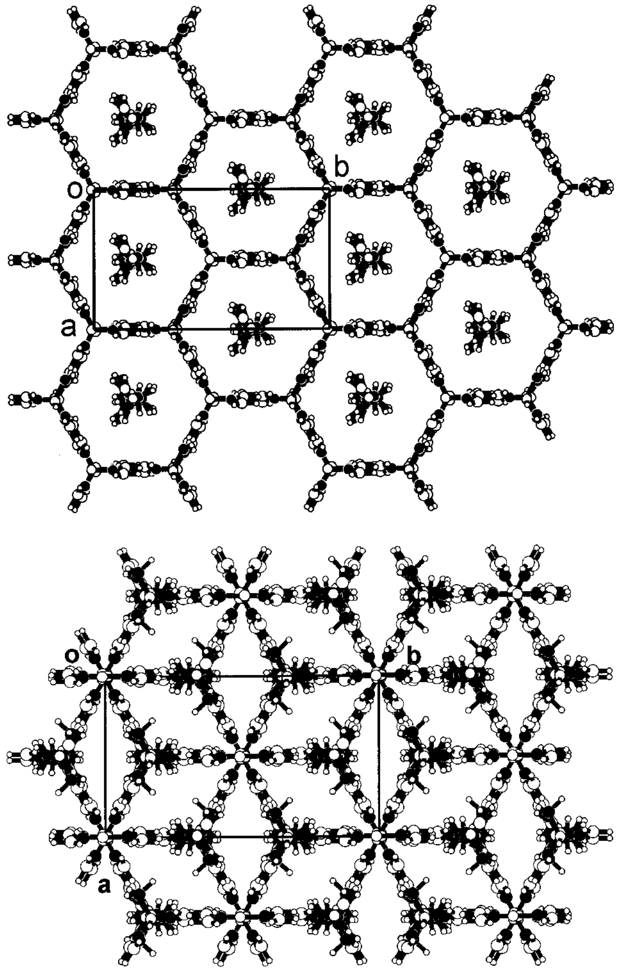

Figure 1. (a) A single host−guest layer in the structure of the 1,7-diaminoheptane/urea/methanol inclusion compound viewed along the *c*-axis (perpendicular to the layer). (b) The complete structure of the 1,7-diaminoheptane/urea/methanol inclusion compound (showing host, guest, and methanol molecules) viewed along the *c*-axis (perpendicular to the layers). This view shows that adjacent layers are offset with respect to each other, such that the local segments of tunnel in adjacent layers do not form a continuous tunnel.

$c = 29.03$ Å, $\beta = 95.03°$). The *a*-axis and *b*-axis are very close to those in the orthohexagonal description of the *ab* plane of the host structure in the conventional urea inclusion compounds. The host−guest layers in the 1,7-diaminoheptane/urea/methanol structure lie parallel to the *ab* plane and are stacked along the *c*-axis. Figure 1a shows the tunnel segments (directed along the *c*-axis) within each layer. The hydrogen-bonding topology of the urea molecules within these tunnel segments is essentially the same as that in the conventional urea tunnel structure, although the symmetry is different (only a two-fold axis perpendicular to the tunnel is “retained” from the $P6_122$ symmetry of the conventional urea tunnel structure). There are two layers within the repeat unit along the *c*-axis, and the thickness of an individual layer is close to the length (ca. 12.9 Å) of the 1,7-diaminoheptane molecule. Adjacent layers are related to each other by the *c*-glide operation. The tunnel segments of adjacent layers are displaced (parallel to the *ab* plane) with respect to each other (Figure 1b), such that continuous tunnels are *not* formed along the *c*-axis. Within a given layer, all helical tunnel segments have the same chirality, and the helical tunnel segments in adjacent layers have opposite chirality. The methanol molecules are located between adjacent layers (see Figure 2) and are engaged in hydrogen-bonding interactions with the NH_2 end groups of the 1,7-diaminoheptane guest molecules and with urea molecules at the surface of the layers. A given methanol molecule serves as a hydrogen-bond donor (O−H···N) to a 1,7-diaminoheptane molecule in one layer, and as a hydrogen-bond acceptor (N−H···O) from two different urea molecules in the other layer. Each end group of the 1,7-diaminoheptane molecule is associated with one methanol molecule in this way, corresponding to the 1:2 ratio of 1,7-diaminoheptane to methanol in the structure. There are no hydrogen-bonding interactions between the 1,7-diaminoheptane guest molecules and urea molecules. A two-fold axis passes through the central carbon atom of the 1,7-diaminoheptane guest molecule, and the conformation is close to all-trans (torsion angles 170.9°, 165.7° and 169.8°). On moving from one end group to the other, all torsion angles deviate from 180° in the same sense, leading to a helical conformation (N−C···C−N dihedral angle 61.5°). While this structure comprises a helical guest conformation within a helical tunnel segment, we note that the pitches of the host and guest helices are significantly different.

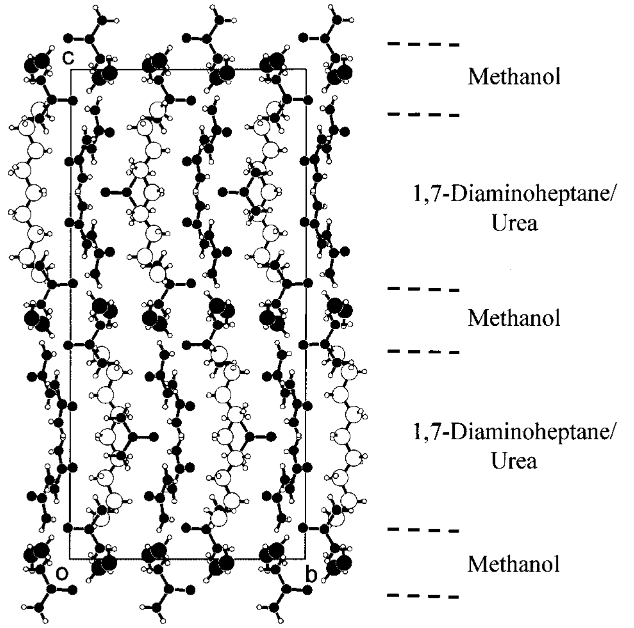

Figure 2. The structure of the 1,7-diaminoheptane/urea/methanol inclusion compound viewed along the *a*-axis, showing the layered structure with methanol molecules located in the interlayer region.

The discovery of this new type of host structure in urea inclusion compounds promises to provide a unique opportunity to compare the physicochemical properties of inclusion systems based on a continuous tunnel structure (the conventional urea inclusion compounds) with those based on noncontinuous local segments of a very similar tunnel structure (the new inclusion compound type). Furthermore, an understanding of the relation between the new structure type reported here and the conventional urea tunnel structure has wider relevance in connection with the concept of “architectural isomerism”, which has received much recent interest.[41−48]

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