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Hydrogen-bonded chains of α,ω-diaminoalkane and α,ω-dihydroxyalkane guest molecules lead to disrupted tunnel structures in urea inclusion compounds†

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Structural features of the urea inclusion compounds containing 1 : 1 mixtures of α,ω-diaminoalkane and α,ω-dihydroxyalkane guest molecules, reported in this paper, provide interesting contrasts to those of conventional urea inclusion compounds. All the α,ω-diaminoalkane/α,ω-dihydroxyalkane/urea inclusion compounds reported have a hydrogen-bonded chain of alternating α,ω-diaminoalkane and α,ω-dihydroxyalkane guest molecules, which is surrounded by urea molecules in a manner that bears some resemblance to the conventional urea tunnel structure, but with the urea–urea hydrogen bonding scheme disrupted by the formation of N–H···O hydrogen bonds between NH_2 groups of the urea molecules and OH groups of the α,ω-dihydroxyalkane molecules. As a consequence, the guest and host components have the same periodicity, and these inclusion compounds are commensurate, in contrast to conventional urea inclusion compounds. So far, attempts to prepare α,ω-diaminoalkane/α,ω-dihydroxyalkane/urea inclusion compounds for α,ω-dihydroxyalkanes longer than 1,3-dihydroxypropane have been unsuccessful, suggesting that there may be an upper limit to the length of the α,ω-dihydroxyalkane component in this family of structures.

1. Introduction

Over the past 50 years or so, hundreds of inclusion compounds containing urea tunnel host structures[1–7] have been prepared for different types of guest molecules (mainly based on *n*-alkane chains, with limited substitution). Most urea inclusion compounds have a hexagonal host structure[1,8] that comprises continuous, parallel tunnels constructed from a hydrogen-bonded arrangement of urea molecules. These conventional urea inclusion compounds are characterized by the following features at ambient temperature: (i) a hexagonal host tunnel structure ($P6_122$ or $P6_522$), (ii) an incommensurate relationship[9] between the periodicities of the host and guest substructures[8,10–14] along the tunnel axis, and (iii) substantial dynamic disorder (reorientation about the tunnel axis) of the guest molecules. For a few guest molecules,[15–19] distorted tunnel structures are formed at ambient temperature, usually when the length of the guest molecule corresponds to a simple multiple of the periodic repeat distance of the urea tunnel, allowing a commensurate structure to be formed. Different types of urea host structure are also formed with some polymeric guests.[20–23]

Recently, a fundamentally different type of urea host structure in an inclusion compound containing alkane-based guest molecules was reported.[24] In particular, for 1,7-diaminoheptane ($H_2N(CH_2)_7NH_2$) guest molecules, a layered host–guest structure is formed. Each layer comprises local segments of urea tunnel that are structurally and topologically very similar to the conventional urea tunnel structure, and the thickness of each layer corresponds to the length of a single guest molecule. Adjacent layers are displaced relative to each other (parallel to the plane of the layers), such that the local segments of tunnel in adjacent layers do not form a continuous tunnel. Adjacent layers are held together through hydrogen bonds to methanol molecules (the solvent normally employed for the crystal growth of urea inclusion compounds) that are incorporated into the crystal in the inter-layer region. The methanol molecules form hydrogen bonds both to urea molecules and to the NH_2 end-groups of the 1,7-diaminoheptane guest molecules, but there is no hydrogen bonding between 1,7-diaminoheptane guest molecules and urea molecules. Although some urea–urea hydrogen bonding exists between adjacent layers, the urea–urea hydrogen bonding network is significantly altered in the region between adjacent layers, in comparison to that in conventional urea inclusion compounds, as the presence of the methanol molecules effectively introduces gaps in the urea–urea hydrogen bonding network. Subsequently, other α,ω-diaminoalkane guest molecules ($H_2N(CH_2)_nNH_2$; n = 7, 8, 9, 10, 12) have been shown[25] to form urea inclusion compounds with similar layered structures. In each case, the thickness of the layer corresponds to the length of a single guest molecule, and methanol molecules are again present in the inter-layer region. Within the layer, the α,ω-diaminoalkane guest molecule is located within a segment of tunnel that is structurally similar to that in conventional urea inclusion compounds.

This new structure type for urea inclusion compounds was subsequently exploited[26] as a design component in the formation of bilayer structures, in which the α,ω-diaminoalkane ($H_2N(CH_2)_nNH_2$) guest molecule is replaced by two 1-aminoalkane ($H_2N(CH_2)_nCH_3$) guest molecules. In this case, a layered structure analogous to the α,ω-diaminoalkane/urea/methanol systems is formed, but in which the guest component within each layer comprises the "dimer" unit $H_2N(CH_2)_nCH_3\cdots H_3C(CH_2)_nNH_2$, representing a bilayer structure in which the thickness of the layer is approximately double that of the corresponding α,ω-diaminoalkane/urea/methanol material.

† Dedicated to Professor Dong-Han Kim on the occasion of his 70th birthday.

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Table 1 Structural data and parameters relating to the crystal structure refinements for **1–4**

	1	**2**	**3**	**4**
Formula	$(CH_4N_2O)_7 \cdot C_7H_{18}N_2 \cdot C_2H_6O_2$	$(CH_4N_2O)_7 \cdot C_8H_{20}N_2 \cdot C_2H_6O_2$	$(CH_4N_2O)_8 \cdot C_8H_{20}N_2 \cdot C_3H_8O_2$	$(CH_4N_2O)_2 \cdot C_4H_{10}O_2$
Molar mass/g mol^{-1}	612.74	626.76	700.85	210.24
T/K	296(2)	296(2)	296(2)	298(2)
λ/Å	1.54178	1.54178	1.54178	1.54178
Crystal system	Orthorhombic	Orthorhombic	Trigonal	Monoclinic
Space group	$Pna2_1$	$Pna2_1$	$P3_121$	$P2_1/c$
a/Å	14.7028(12)	14.5312(12)	8.2121(2)	5.2046(3)
b/Å	7.9159(7)	8.0457(7)	8.2121(2)	7.3638(4)
c/Å	28.661(2)	28.962(2)	48.6159(14)	14.6064(8)
β/°	—	—	—	98.604(3)
V/Å^3	3335.8(5)	3386.1(5)	2839.34(13)	553.50(5)
Z	4	4	3	2
ρ(calc)/Mg m^{-3}	1.220	1.229	1.230	1.261
Absorption coefficient/mm^{-1}	0.837	0.835	0.835	0.889
Crystal size/mm^3	0.40 × 0.40 × 0.08	0.40 × 0.30 × 0.12	0.50 × 0.40 × 0.08	0.40 × 0.14 × 0.06
Total reflections	20168	20612	18182	3392
Unique data	5684	5622	3552	1005
R(int)	0.042	0.037	0.078	0.033
R_1 [$2\sigma(I)$]	0.060	0.054	0.069	0.032
wR_2	0.170	0.148	0.206	0.093
Flack parameter	0.4(3)	0.0(3)	0.4(5)	—

To further extend our exploration of urea inclusion compounds containing α,ω-diaminoalkane guest molecules, we set out to explore systems analogous to the α,ω-diaminoalkane/urea/methanol structures discussed above, but in which the alcohol (methanol) is replaced by a short α,ω-dihydroxyalkane ($HO(CH_2)_nOH$), which has the capacity to interact by hydrogen bonding with the amino groups of two different α,ω-diaminoalkane molecules. The following urea/α,ω-diaminoalkane/α,ω-dihydroxyalkane materials were prepared in this work: urea/1,7-diaminoheptane/1,2-dihydroxyethane (**1**), urea/1,8-diaminooctane/1,2-dihydroxyethane (**2**) and urea/1,8-diaminooctane/1,3-dihydroxypropane (**3**). Clearly, comparison between **1** and **2** allows an assessment of the role of the α,ω-diaminoalkane component, and comparison between **2** and **3** allows an assessment of the role of the α,ω-dihydroxyalkane component. We also report the structural properties of a co-crystal (**4**) between urea and 1,4-dihydroxybutane that has been found in the course of this work.

2. Experimental

Crystals of α,ω-diaminoalkane/α,ω-dihydroxyalkane/urea inclusion compounds were grown by slow cooling from solutions containing the α,ω-diaminoalkane and urea dissolved in liquid α,ω-dihydroxyalkane. Single crystal X-ray diffraction data‡ were recorded at ambient temperature using $CuK_{\alpha 1}$ radiation on a Bruker Smart 6000 diffractometer equipped with a CCD detector system. The crystal structures were solved and refined using SHELX-97.[27] Refinement of non-hydrogen atoms was carried out anisotropically. A riding model with default bond distances was used for hydrogen atoms (except for the hydrogen atoms of the NH_2 groups of the α,ω-diaminoalkane molecules, which were found in the difference Fourier map and were restrained during refinement). In **1** and **3**, the α,ω-diaminoalkane molecules were found to be disordered (see discussion below), and thus fractional occupancies were refined and appropriate restraints were imposed on the molecular geometry. Relevant data for the crystal structure refinement calculations are given in Table 1, and details of hydrogen bonding geometries are given in Table 2.

‡ CCDC 264610–264613. See http://dx.doi.org/10.1039/b502004m for crystallographic data in CIF or other electronic format.

3. Results and discussion

3.1. Variation of the α,ω-diaminoalkane chain length

The crystal structure of **1** (Fig. 1) contains urea, 1,7-diaminoheptane and 1,2-dihydroxyethane in the stoichiometry (urea)$_7$(1,7-diaminoheptane)$_1$(1,2-dihydroxyethane)$_1$. One end of the 1,7-diaminoheptane molecule is found to be disordered between two positions. Our initial discussion is focused on the component of higher occupancy, while the nature of the disorder is discussed later.

Table 2 Selected D–H···A hydrogen bond distances (d) and angles (<) in crystal structures **1–4**

	D–H	A	$d_{D\cdots A}$/Å	$<_{D-H\cdots A}$/°
1	N(2)–H(2B)	O(9)	2.874(5)	168.9(2)
	N(5)–H(5B)	O(8)	3.083(5)	163.6(2)
	N(9)–H(9A)	O(8)	2.940(5)	161.4(4)
	N(14)–H(14A)	O(9)	3.052(5)	163.3(3)
	O(8)–H(8)	N(16)	2.739(10)	157.5(3)
	O(8)–H(8)[a]	N(16A)[a]	2.820(12)[a]	160.9(6)[a]
	O(9)–H(9)	N(15)	2.718(8)	170.8(6)
2	N(4)–H(4B)	O(9)	2.877(5)	170.0(2)
	N(8)–H(8A)	O(8)	2.937(4)	164.5(2)
	N(11)–H(11A)	O(9)	3.096(5)	163.1(2)
	N(14)–H(14B)	O(8)	3.047(5)	163.0(2)
	O(8)–H(8)	N(16)	2.744(6)	167.5(2)
	O(9)–H(9)	N(15)	2.735(9)	179.6(2)
3	N(6)–H(6B)	O(5)	2.999(4)	160.3(2)
	N(8)–H(8A)	O(5)	2.995(4)	155.0(1)
	O(5)–H(5)	N(9)	2.834(7)	161.4(2)
	O(5)–H(5)[a]	N(9A)[a]	2.704(6)[a]	144.7(2)[a]
4	N(1)–H(1A)	O(2)	3.002(4)	175.04(8)
	N(1)–H(1B)	O(2)	3.008(4)	168.22(8)
	N(2)–H(2C)	O(1)	2.983(2)	170.87(7)
	N(2)–H(2D)	O(1)	2.958(1)	140.96(8)
	O(2)–H(2)	O(1)	2.791(1)	163.37(7)

[a] Minor component of the disordered structure.

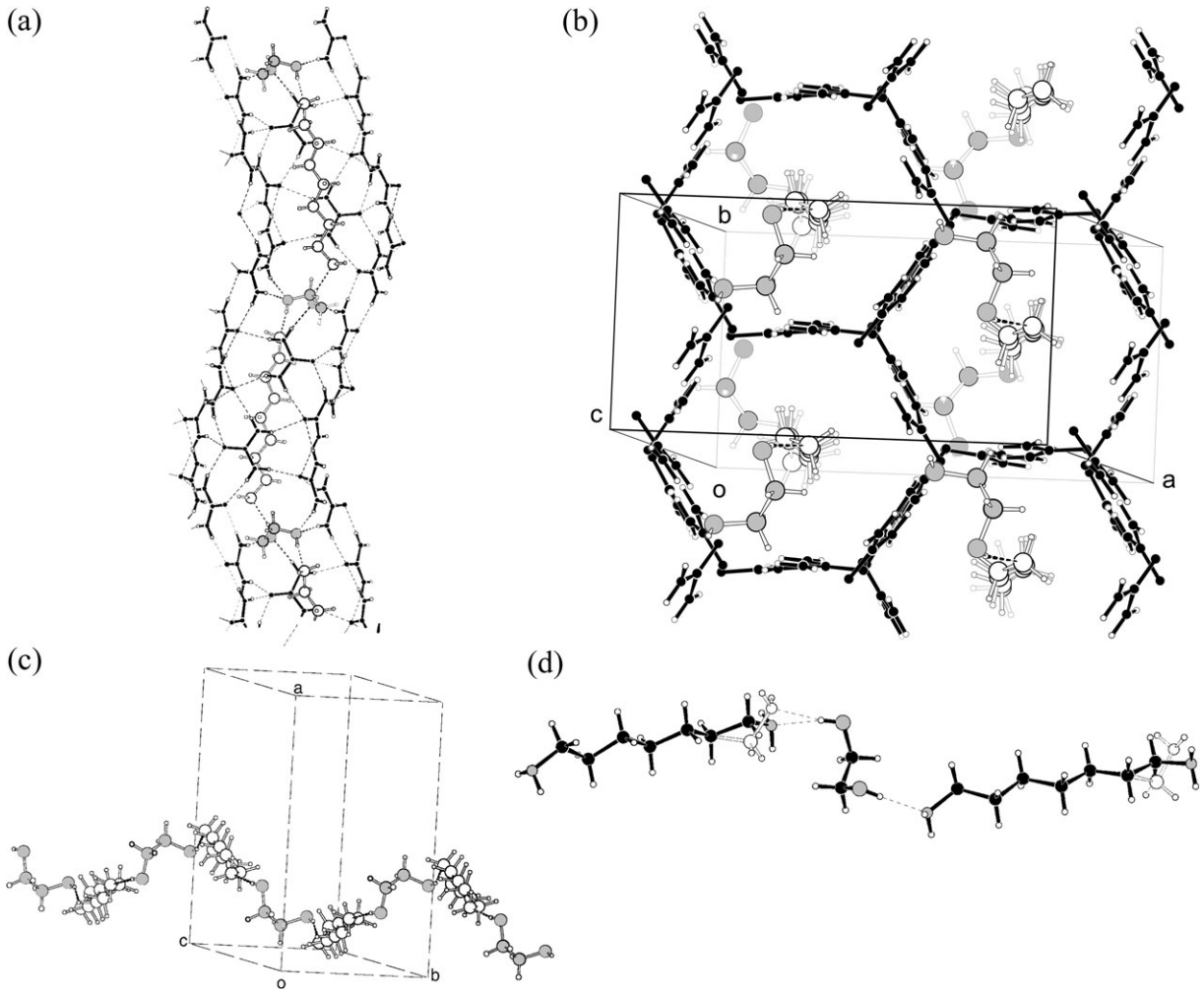

Fig. 1 (a) The hydrogen-bonded chain of alternating 1,7-diaminoheptane and 1,2-dihydroxyethane molecules in the crystal structure of **1**, and the urea molecules that form the local tunnel segments around the 1,7-diaminoheptane molecules. Dashed linkages indicate hydrogen bonds. The urea tunnel segments around the different 1,7-diaminoheptane molecules shown do not join up to form a continuous tunnel (as clear from Fig. 1(b)). Only the major component of the disordered 1,7-diaminoheptane is shown. (b) Crystal structure of **1**, viewed along the direction of each local urea tunnel segment, showing two hydrogen-bonded chains. A given hydrogen-bonded chain propagates upwards and into the plane of the page. Clearly the direction of propagation of the hydrogen-bonded chain is different from the direction of the local tunnel segments, such that a given hydrogen-bonded chain effectively weaves different tunnel segments together. Only the major component of the disordered 1,7-diaminoheptane is shown. (c) The hydrogen-bonded chain in the crystal structure of **1**, illustrating the irregular spiral architecture. Only the major component of the disordered 1,7-diaminoheptane is shown. (d) The disorder involving one end of the 1,7-diaminoheptane molecule in **1**. Filled circles represent the major component of the disorder and open circles represent the minor component.

The first feature to note is that the structure contains hydrogen-bonded chains of alternating 1,7-diaminoheptane and 1,2-dihydroxyethane molecules linked by O–H···N hydrogen bonds (Fig. 1(a)–(c)). These chains propagate along the [0 1 −1] direction. The conformation of the 1,7-diaminoheptane molecule is close to all-*trans* (Table 3). The relative orientations of the 1,2-dihydroxyethane and 1,7-diaminoheptane molecules are such that the hydrogen-bonded chain is not straight, but is instead best described as an irregular spiral. There are two 1,2-dihydroxyethane and two 1,7-diaminoheptane molecules in the periodic repeat unit of this spiral. The long-axis of each 1,7-diaminoheptane molecule points approximately along the c-axis. The hydrogen-bonded chains of 1,2-dihydroxyethane and 1,7-diaminoheptane molecules are surrounded by a hydrogen-bonded network of urea molecules in a manner that is, in some respects, reminiscent of the urea host tunnels found in the conventional urea inclusion compounds, although with some notable differences. Firstly, it is important to emphasize that the urea molecules surrounding a given hydrogen-bonded chain do not constitute a single continuous tunnel. Rather, each 1,7-diaminoheptane molecule within the hydrogen-bonded chain is surrounded by a local tunnel segment that is similar in structure and hydrogen bonding connectivity to the urea host structure in conventional urea inclusion compounds. These tunnel segments are oriented approximately along the [0 0 1] direction. As the hydrogen-bonded chains propagate along the [0 1 1] and [0 1 −1] directions, it is clear that the local tunnel segments around the 1,7-diaminoheptane molecules in a given hydrogen-bonded chain do not join up to form a continuous tunnel. In the region of each 1,2-dihydroxyethane molecule, the urea structure is disrupted, in comparison to the conventional urea inclusion compounds, by the formation of N–H···O hydrogen bonds between urea molecules (N–H-donor) and 1,2-dihydroxyethane molecules (O-acceptor). Each OH group of the 1,2-dihydroxyethane molecule is engaged in such hydrogen bonds with two different urea molecules. Clearly, the participation of the 1,2-dihydroxyethane molecules in direct hydrogen bonding with urea molecules significantly disrupts the urea–urea hydrogen bonding scheme in the region between the local tunnel segments. In conventional urea inclusion compounds, on the other hand, urea molecules are hydrogen-bonded only to other urea molecules, and there is no urea–guest hydrogen bonding. In spite of this disruption to the urea–urea hydrogen bonding scheme, there is still some hydrogen bonding between urea molecules in different local tunnel segments, and the structure

Table 3 Geometric information relating to the α,ω-diaminoalkane molecules in the crystal structures **1–3**. For **1** and **3** the values in square parentheses refer to the minor component of the disordered structure

	1		**2**	**3**	
Intramolecular N···N distance/Å	9.93(1)	[9.60(3)]	10.07(1)	11.00(1)	[11.00(1)]
C–C–C–C and N–C–C–C torsion angles/°	−179.1(12)	[–90.2(17)]	−77.6(11)	−160.2(10)	[177.9(14)]
	−175.0(8)	[–145.4(10)]	171.0(10)	−156.9(11)	[176.5(12)]
	−171.2(9)		112.4(11)	−136.6(8)	[148.7(9)]
	−170.7(9)		163.5(10)	−130.0(8)	[134.6(8)]
	−175.7(9)		160.4(11)	−136.6(8)	[148.6(9)]
	−162.4(12)		−174.5(10)	−156.9(10)	[176.5(11)]
			−95.0(12)	−160.2(10)	[177.9(14)]

as a whole still comprises a contiguous hydrogen-bonded network of urea molecules, although not in the form of continuous tunnels that extend throughout the crystal. Importantly, the NH_2 groups of the 1,7-diaminoheptane molecules are not involved in any hydrogen bonding with urea molecules. The only hydrogen bonding involving these NH_2 groups is the O–H···N interaction within the hydrogen-bonded chain, and the N–H bonds are not involved as donors in any hydrogen bonding interactions. It is noteworthy that the atomic displacement parameters for the 1,7-diaminoheptane molecule are larger (typically by a factor of about 3) than those for the urea and 1,2-dihydroxyethane molecules. This suggests that, in addition to the specific aspect of disorder discussed below, there may be some degree of conformational variation (dynamic or static) of the 1,7-diaminoheptane molecules within the structure.

As discussed above, there is disorder at one end of the 1,7-diaminoheptane guest molecule (Fig. 1(d)), involving the positions of the NH_2 group and the adjacent CH_2 group, with refined occupancies of 0.644(11) and 0.356(11) for the two components. For both positions of this end-group, the NH_2 group acts as the hydrogen bond acceptor in an O–H···N hydrogen bond with the OH group of the adjacent 1,2-dihydroxyethane molecule. The disorder involves a shift of the N atom position by 1.41(2) Å, whereas the position of the O atom is the same in both disorder components. For both disorder components, the positions of the NH_2 and OH groups[28] correspond to reasonable hydrogen bonding geometries (Table 2), and the description of the guest as a hydrogen-bonded chain of 1,2-dihydroxyethane and 1,7-diaminoheptane molecules is not affected by the existence of this disorder.

The crystal structure of **2** contains 1,2-dihydroxyethane, urea and 1,8-diaminooctane molecules in the stoichiometry $(urea)_7(1,8\text{-diaminooctane})_1(1,2\text{-dihydroxyethane})_1$. Although the 1,8-diaminooctane molecule in **2** has one more methylene group than the 1,7-diaminoheptane molecule in **1**, the crystal structures of **1** and **2** are very similar. For example, they have the same stoichiometry, very similar unit cell parameters and the same space group symmetry. Furthermore, the hydrogen bonding scheme in **2** is essentially identical to that described above for **1**. The fact that the NH_2 end-groups of the α,ω-diaminoalkanes in **1** and **2** can participate in almost identical intermolecular contacts, in spite of having different chain lengths, is possible because the α,ω-diaminoalkane adopts a different conformation in the two structures (Table 3). Thus, the 1,7-diaminoheptane molecule in **1** is close to an all-*trans* conformation, whereas the 1,8-diaminooctane molecule in **2** adopts a range of torsion angles that give rise to a "twisted" conformation. As a consequence, the effective lengths of the α,ω-diaminoalkane molecules (as reflected by the intramolecular N···N distances) and the relative positioning of the NH_2 end-groups are similar in **1** and **2** (9.93 and 10.07 Å respectively). Our structure refinement calculations provide no evidence to suggest that there is any disorder in the structure of **2**, unlike the situation discussed above for **1**. In line with observations for **1**, the atomic displacement parameters for the 1,8-diaminooctane molecule in **2** are larger than those of the urea and 1,2-dihydroxyethane molecules.

At present, the reasons for the fact that there is disorder involving the 1,7-diaminoheptane molecule in **1**, but no disorder involving the 1,8-diaminooctane molecule in **2**, are unclear. Equally, we make no attempt to explain why only one end-group of the 1,7-diaminoheptane molecule in **1** exhibits disorder. Given the structural similarity of **1** and **2**, and the structural similarity of the two ends of the 1,7-diaminoheptane molecule in **1**, it may be assumed that plausible alternative orientations of the NH_2 end-groups (giving O–H···N hydrogen bonds) might also exist for all the end-groups that are ordered, but presumably in the case of the ordered end-groups, the energetic differences are sufficiently large that the alternative orientations are not occupied to any appreciable extent. Clearly, the relative energies of the alternative end-group orientations could depend significantly on small differences in the hydrogen bond geometries.

3.2. Variation of the α,ω-dihydroxyalkane chain length

The crystal structure of **3** (Fig. 2) contains urea, 1,8-diaminooctane and 1,3-dihydroxypropane in the stoichiometry $(urea)_8(1,8\text{-diaminooctane})_1(1,3\text{-dihydroxypropane})_1$. The 1,8-diaminooctane molecule is found to be disordered over two positions. Our initial discussion is focused on the component of higher occupancy, and the nature of the disorder is discussed later. In this structure, the 1,3-dihydroxypropane molecule is located on a 2-fold symmetry axis.

Comparison of the structures of **2** and **3** provides a basis for assessing the role of the α,ω-dihydroxyalkane in controlling the structural properties of the inclusion compound. There are indeed several similarities between the structures of **2** and **3**. For example, the structure of **3** contains hydrogen-bonded chains of alternating 1,8-diaminooctane and 1,3-dihydroxypropane molecules (Fig. 2(a) and 2(b)), linked by O–H···N hydrogen bonds, with these hydrogen-bonded chains surrounded by a hydrogen-bonded network of urea molecules. Each 1,8-diaminooctane molecule is surrounded by a local segment of urea tunnel structure that is structurally similar to that in conventional urea inclusion compounds. There are also similarities between the local interactions in **3** and those in **1** and **2**. Thus, the 1,3-dihydroxypropane molecule in **3** is engaged in N–H···O hydrogen bonds with urea molecules; each 1,3-dihydroxypropane OH group is engaged in two N–H···O hydrogen bonds with two different urea molecules. Thus, as in **1** and **2**, the fact that the 1,2-dihydroxyethane molecules in **3** participate in direct hydrogen bonding with urea molecules causes a significant disruption to the urea–urea hydrogen bonding scheme in the region between the local tunnel segments. Also, as in **2**, the 1,8-diaminooctane molecule in **3** adopts a "twisted" conformation (Table 3), although the intramolecular N···N distance is almost 1 Å longer in **3**.

In spite of these structural similarities, other details of the crystal structures of **2** and **3** differ significantly. For example, **3** has one more urea molecule per 1,8-diaminooctane molecule

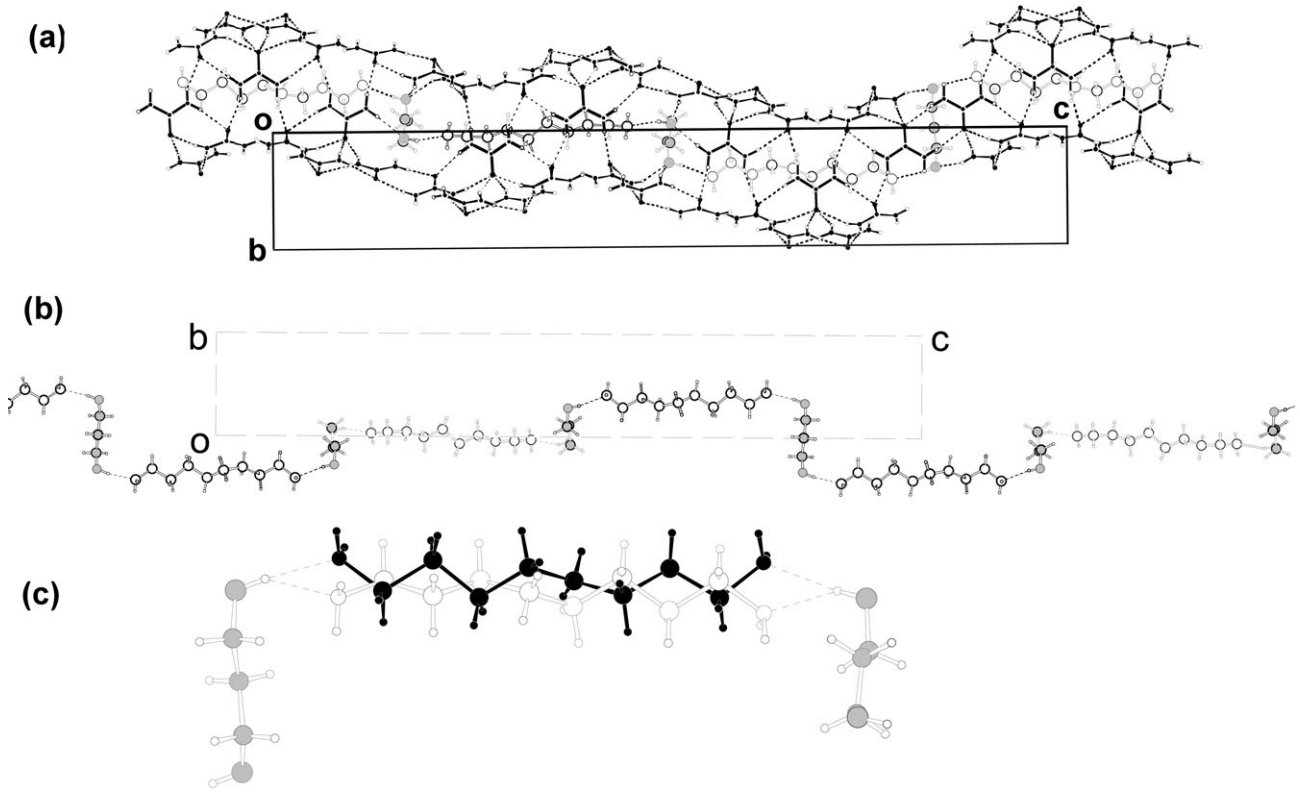

Fig. 2 (a) The hydrogen-bonded chain of alternating 1,8-diaminooctane and 1,3-dihydroxypropane molecules in the crystal structure of **3**, and the urea molecules that form the local tunnel segments around the 1,8-diaminooctane molecules. Dashed linkages indicate hydrogen bonds. The urea tunnel segments around the different 1,8-diaminooctane molecules shown do not join up to form a continuous tunnel, although the different local tunnel segments shown are parallel to each other. Only the major component of the disordered 1,8-diaminooctane is shown. (b) The hydrogen-bonded chain in **3**, illustrating the regular helical (3_1) architecture. Only the major component of the disordered 1,8-diaminooctane is shown. (c) The disorder involving the 1,8-diaminooctane molecule in **3**. Filled circles represent the major component of the disorder, and open circles represent the minor component.

than **2**, and the unit cells and space groups are different. This leads to substantial differences in terms of the long-range propagation of the hydrogen-bonded chains. Thus, the hydrogen-bonded chain in **3** has a regular helical architecture and is wrapped around the 3_1 screw axis (c-axis) of the space group. In contrast, the hydrogen-bonded chains in **1** and **2**, while loosely described as irregular spirals, are not propagated along any symmetry element. Furthermore, in the structure of **3**, the direction of propagation of the hydrogen-bonded chain (c-axis) is parallel to the direction of the local segments of the urea tunnel structure around each 1,8-diaminooctane molecule. In contrast, in **1** and **2**, the direction of propagation of the hydrogen-bonded chain and the directions of the local segments of urea tunnel structure are not parallel to each other, as discussed above.

As mentioned earlier, there is disorder of the 1,8-diaminooctane guest molecule in the structure of **3**, involving two components with refined occupancies of 0.559(7) and 0.441(7). The two components differ in the orientation of the complete 1,8-diaminooctane molecule, although the two different orientations occupy approximately the same region of space within the crystal (Fig. 2(c)). There are also slight differences in the conformation of the 1,8-diaminooctane molecule in the two orientations (Table 3). For both disorder components, the NH_2 groups of the 1,8-diaminooctane molecule are engaged in O–H···N hydrogen bonds with the OH groups of the adjacent 1,2-dihydroxyethane molecules. The disorder involves a shift in the position of the N atom of each end-group by 1.30(3) Å (recall that the two ends of the 1,8-diaminooctane molecule are symmetry equivalent), whereas the positions of the O atoms of the OH groups are not disordered. For both disorder components, the positions of the NH_2 and OH groups correspond to reasonable hydrogen bonding geometries (Table 2), and the description of the guest as a hydrogen-bonded chain of alternating 1,3-dihydroxypropane and 1,8-diaminooctane molecules is not affected by the existence of this disorder. As noted above for **1**, the refined atomic displacement parameters are significantly higher for the 1,8-diaminooctane molecule than for the urea and 1,3-dihydroxypropane molecules, typically by a factor of about 3.

Attempts to further explore the role of the α,ω-dihydroxyalkane component in these structures by growing crystals containing urea, α,ω-diaminoalkanes (1,7-diaminoheptane and 1,8-diaminooctane) and 1,4-dihydroxybutane proved unsuccessful. Such experiments led only to the co-crystallization of urea and 1,4-dihydroxybutane as the binary co-crystal, **4**. This observation may suggest that the urea/α,ω-diaminoalkane/α,ω-dihydroxyalkane inclusion compounds are formed only for sufficiently short α,ω-dihydroxyalkanes, and that 1,3-dihydroxypropane may represent an upper limit for the length of the α,ω-dihydroxyalkane component in this family of structures. However, a wider range of experiments would be required to substantiate this assertion. Although not directly related to the structures described above, we now briefly describe the structure of the urea/1,4-dihydroxybutane co-crystal, **4**, which has not been reported previously.

3.3. Structural properties of the 1,4-dihydroxybutane/urea co-crystal

The crystal structure of **4** contains urea and 1,4-dihydroxybutane in a 2 : 1 ratio. In this structure, urea molecules are hydrogen-bonded to each other to form double-stranded ribbons that run parallel to the a-axis (Fig. 3). The two strands of the ribbon are linked by a network of N–H···O hydrogen bonds between urea molecules, involving the C=O group and

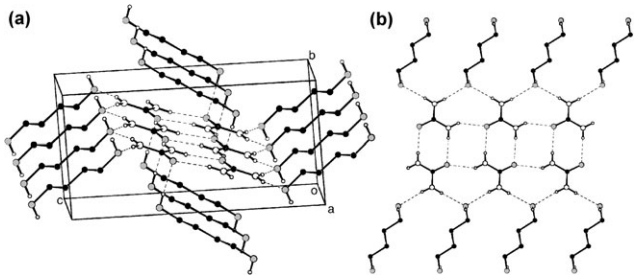

Fig. 3 Crystal structure of **4** viewed (a) approximately along the direction of propagation of the ribbons (a-axis), and (b) perpendicular to the average plane of a corrugated sheet (ac-plane) with the ribbons running in the horizontal direction.

one NH_2 group of each urea molecule, and contain two different types of cyclic hydrogen-bonded array ($R_2^2(8)$ and $R_4^2(8)$ in graph set notation[29–31]), alternating along the centre of the ribbon. The other NH_2 group of each urea molecule protrudes from the edge of the ribbon (with a periodic spacing of 5.20 Å). For these pendant NH_2 groups, each N–H bond is engaged in a N–H···O hydrogen bond with the OH group of a 1,4-dihydroxybutane molecule, and each OH group is involved in two N–H···O hydrogen bonds with two different urea molecules. The 1,4-dihydroxybutane molecules that form hydrogen bonds with the NH_2 groups along a given edge of a urea ribbon are themselves arranged in a planar, ribbon-like manner, with OH groups running along each edge of the ribbon. Each edge of the urea ribbon is linked to the edge of a 1,4-dihydroxybutane ribbon and *vice versa* by means of the N–H···O hydrogen bonding discussed above. The planes of the urea ribbons and 1,4-dihydroxybutane ribbons linked in this way are not parallel to each other, and, as shown in Fig. 3(a), the arrangement of urea and 1,4-dihydroxybutane ribbons propagates as a corrugated sheet. The average plane of the sheet is parallel to the ac-plane, and the individual ribbons run along the a-axis. The O–H bonds of the 1,4-dihydroxybutane molecules protrude outwards from the sheet and participate in O–H···O hydrogen bonds with the oxygen atoms of urea molecules in an adjacent sheet. Each urea oxygen atom is involved in one hydrogen bond of this type.

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