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Novel Inclusion Compounds of Urea with Tetraalkylammonium Pentaborates

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New crystalline inclusion compounds $(n\text{-}C_3H_7)_4N^+[B_5O_6(OH)_4]^-\cdot 4(NH_2)_2CO\cdot H_2O$ (**1**) and $(n\text{-}C_4H_9)_4N^+[B_5O_6(OH)_4]^-\cdot 2(NH_2)_2CO\cdot B(OH)_3$ (**2**) have been prepared and characterized by X-ray crystallography. Crystal data, MoKα radiation: **1**, space group $P2_1$, $Z = 2$, $a = 8.343(2)$, $b = 16.037(3)$, $c = 13.343(3)$ Å, $\beta = 104.75(3)°$, $R_F = 0.079$ for 1820 observed data; **2**, space group $P2_1/n$, $Z = 4$, $a = 11.582(3)$, $b = 17.270(4)$, $c = 17.819(5)$ Å, $\beta = 96.85(3)°$, and $R_F = 0.056$ for 2291 observed data. Compound **1** has a channel-like host lattice built of urea molecules, pentaborate ions and water molecules, and the $(n\text{-}C_3H_7)_4N^+$ cations are arranged in a zigzag column within each channel. In compound **2** the host lattice comprises a stack of two-dimensional infinite layers of inter-connected urea molecules, pentaborate ions, and neutral $B(OH)_3$ molecules. The $(n\text{-}C_4H_9)_4N^+$ cations are sandwiched between adjacent layers, while another most unusual guest component, namely a hydrogen-bonded planar ribbon formed by $B_3O_3(OH)_2$ fragments belonging to different pentaborate ions, threads the central holes of macrocycles within the stacked layers.

INTRODUCTION

Urea forms non-stoichiometric crystalline inclusion compounds (space group $P6_122$ or $P6_522$) comprising an extensively hydrogen-bonded honeycomb-like host lattice that contains linear, parallel, non-intersecting, cylindrical channels within which a wide variety of straight-chain aliphatic guest molecules are accommodated.[1–3] Previous structural characterization of urea inclusion compounds, generally by X-ray diffraction[4] and solid-state NMR techniques,[5] has confirmed that they are incommensurate, that is, there exist no small integers m and n that satisfy $mc_h = nc_g$, where c_h and c_g are the host and guest repeat distances along the channel axis. Inter-channel ordering of n-alkane guest molecules have been experimentally and theoretically studied.[6] Very interesting stress-induced domain reorientation has been observed in commensurate ($3c_h = 2c_g$) 2,10-undecanedione/urea (1:9), whose lattice symmetry is lowered to $C222_1$ by hydrogen-bonding interaction between the guest molecule and every third urea molecule along a channel wall.[7] A recent review summarizes the current level of understanding of the structural and dynamic properties of urea and thiourea inclusion compounds as derived from the modern arsenal of physical methods, computer simulation and modelling.[8]

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Urea also forms hydrogen-bonded host lattices with other molecular species as the building blocks such as water molecules and halide ions. For example, in two series of isomorphous urea-tetraalkylammonium salt hydrate complexes, $(C_2H_5)_4N^+X^-\cdot(NH_2)_2CO\cdot 2H_2O$ (X = Cl, Br, CN)[9] and $(n\text{-}C_3H_7)_4N^+X^-\cdot 3(NH_2)_2CO\cdot H_2O$ (X = F, Cl, Br, I),[10,11] the host lattices are constructed from the cross-linkage of planar zigzag ribbons of hydrogen-bonded urea molecules by the water molecules and halide/pseudohalide anions. Urea is also known to form inclusion compounds with some simple trigonal planar oxo-anions such as HCO_3^-[12] and the novel planar allophanate ion $(NH_2CONHCO_2^-)$,[13] in which box-like cages, open parallel channel systems, or sandwich-like layer-type host lattices are built by urea molecules, anions, and water molecules *via* intermolecular hydrogen bonding.

A very interesting recent development in the field of host-guest chemistry is the construction of new three-dimensional hydrogen-bonded diamond-related ('diamondoid') networks formed by some molecules possessing tetrahedrally directed functional groups, such as tetracarboxylic acids[14,15] and rigid tetrapyridones.[16] Mixed diamondoid networks are also constructed with tetrafunctional cubane-like clusters $[M(CO)_3(\mu\text{-}OH)]_4$ (M = Mn, Re), which form donor hydrogen bonds to the complementary difunctional proton-acceptor molecule 1,2-diaminoethane.[17] It has been shown that the spirocyclic pentaborate ion, $[B_5O_6(OH)_4]^-$, is capable of self-assembly into open hydrogen-bonded host frameworks, thus forming structurally related channel-type clathrates, $A[B_5O_6(OH)_4]$, with a number of differently-sized quaternary ammonium cations as guest species (e.g., A = Me_4N^+, Et_4N^+, $PhMe_3N^+$, piperidinium).[18] Isotypic three-dimensional channel host systems can be generated by trapping the even larger quaternary ammonium ions, $(n\text{-}Pr)_4N^+$ and $(n\text{-}Bu)_4N^+$, in an assembly of hydrogen-bonded pentaborate ions and neutral boric acid molecules, and the resulting host network bears a close relationship to the diamond net.[19]

In order to develop new urea/thiourea-anion host lattices, we consider some simple trigonal planar oxo-anions such as CO_3^{2-}, NO_3^-, HCO_3^- and $BO(OH)_2^-$, and also some nonplanar anions such as HSO_4^-, $H_2PO_4^-$ and the aforementioned pentaborate ion, which have functional O atoms or hydroxyl groups that can act as proton donors or acceptors in hydrogen bonding. In the present work, we report the preparation and structural characterization of the following urea-pentaborate complexes:

$$(n\text{-}C_3H_7)_4N^+[B_5O_6(OH)_4]^-\cdot 4(NH_2)_2CO\cdot H_2O \quad (1)$$

$$(n\text{-}C_4H_9)_4N^+[B_5O_6(OH)_4]^-\cdot 2(NH_2)_2CO\cdot B(OH)_3 \quad (2)$$

RESULTS AND DISCUSSION

Pentaborate Group

Boric acid exists almost exclusively as undissociated $B(OH)_3$ molecules and $B(OH)_4^-$ ions in dilute aqueous solution, whereas at concentrations above 0.1 M, secondary equilibria involving condensation reactions of the two dominant monomeric species give rise to oligomers such as the triborate monoanion $[B_3O_3(OH)_4]^-$, the triborate dianion $[B_3O_3(OH)_5]^{2-}$, the tetraborate $[B_4O_5(OH)_4]^{2-}$, and the pentaborate $[B_5O_6(OH)_4]^-$.[20] In the preparation of inclusion compounds **1** and **2**, the pentaborate ion is generated *in situ* and incorporated into the host lattice through hydrogen-bonding interactions with its nearest neighbors.

The pentaborate ion, characterized by its double-ring spiro structure assembled from one BO_4 tetrahedron and three BO_3 triangles through corner-sharing, was first discovered nearly sixty years ago in its hydrated potassium salt

TABLE I Data collection and processing parameters of urea-pentaborate complexes

Complex	1	2
Molecular formula	$(n\text{-}C_3H_7)_4N^+[B_5O_6(OH)_4]^-$ $\cdot 4CO(NH_2)_2\cdot H_2O$	$(n\text{-}C_4H_9)_4N^+[B_5O_6(OH)_4]^-$ $\cdot 2CO(NH_2)_2\cdot B(OH)_3$
Molecular weight	662.7	624.5
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1$ (No. 4)	$P2_1/n$ (No. 14)
Unit cell parameters		
a, Å	8.343(2)	11.582(3)
b, Å	16.037(3)	17.270(4)
c, Å	13.343(3)	17.819(5)
α, °	90	90
β, °	104.75(3)	96.85(2)
γ, °	90	90
V, ^{3}	1726.4(9)	3544.6(15)
Z	2	4
$F(000)$	708	1376
Density (calcd.), g cm^{-3}	1.275	1.204
Absorption coefficient, cm^{-1}	0.106	0.097
Crystal size, mm	0.32 × 0.34 × 0.38	0.30 × 0.32 × 0.42
Mean μr	0.06	0.06
Transmission factors	0.844 to 0.862	0.944 to 0.972
Scan speed (deg min^{-1})	3.9 to 29.3	3.0 to 29.3
Scan range (below $K\alpha_1$ to above $K\alpha_2$)	0.60 to 0.60	0.60 to 0.60
Background counting	stationary counts for one-half of scan time at each end of scan	
$2\theta_{max}$, °	45	46
Unique data measured	2823	4924
Observed data	$\lvert F_o\rvert > 4\sigma(\lvert F_o\rvert)$, 1820	$\lvert F_o\rvert > 4\sigma(\lvert F_o\rvert)$, 2291
Number of variables, p	406	398
$R_F = \Sigma\lVert F_o\rvert - \lvert F_c\rVert/\Sigma\lvert F_o\rvert$	0.079	0.056
Constant g in weighting scheme $\omega = [\sigma^2(F_o) + g\lvert F_o\rvert^2]^{-1}$	0.0005	0.0008
$R_G = [\Sigma\omega(\lvert F_o\rvert - \lvert F_c\rvert)^2/\lvert F_o\rvert^2]^{1/2}$	0.087	0.065
$S = [\Sigma\omega(\lvert F_o\rvert - \lvert F_c\rvert)^2/(n - p)]^{1/2}$	1.27	1.40
Residual extrema in final difference map, eÅ^{-3}	+0.78 to −0.54	+0.24 to −0.34
Largest and mean Δ/σ	0.003, 0.000	0.001, 0.000

$K[B_5O_6(OH)_4]\cdot 2H_2O$,[21,22] and is also present in the ammonium analogue $\beta\text{-}NH_4[B_5O_6(OH)_4]\cdot 2H_2O$ (commonly named larderellite)[23] and in sborgite, $Na[B_5O_6(OH)_4]\cdot 3H_2O$.[24] A more recent study confirmed that the basic structural unit in anhydrous $Na[B_5O_6(OH)_4]$ is the insular pentaborate ion.[25] A complex system of hydrogen bonds connect the discrete pseudo-tetrahedral oxo-anions and the cations in most of these compounds except larderellite, the principal component of which is the infinite polyanionic chain $[B_5O_7(OH)_2]_n^{n-}$, the condensation product of $[B_5O_6(OH)_4]^-$ formed by sharing an oxygen atom between two ions. The common feature of the host structures of inclusion compounds **1** and **2** is the three-dimensional assembly of hydrogen-bonded $[B_5O_6(OH)_4]^-$ ions and urea molecules, with the additional participation of either water or $B(OH)_3$ molecules.

Bond lengths and angles in the present two structures are listed in Table II. The average B-O distance in the BO_3 triangles is 1.364 (for **1**), 1.363 (for **2**) and in the BO_4 tetrahedron 1.461 (for **1**), 1.470 (for **2**) Å, in good agreement with the results obtained for the corresponding tetra-n-propyl- and tetra-n-butylammonium clathrates, $(n\text{-}Pr)_4N^+[B_5O_6(OH)_4]^-\cdot 2B(OH)_3$ and $(n\text{-}Bu)_4N^+[B_5O_6(OH)_4]^-\cdot 2B(OH)_3$: 1.359, 1.365 and

Table II Selected bond distances (Å), bond angles (°) and torsion angles (°) in the urea-anionic systems*.

$(n\text{-}C_3H_7)_4N^+[B_5O_6(OH)_4]^- \cdot 4CO(NH_2)_2 \cdot H_2O$ (1)			
Hydrogen bonding			
O(7)...O(1W)	2.585	O(8)...O(12h)	2.750
O(9)...O(11)	2.769	O(10)...O(13e)	2.724
N(1)...O(3)	2.944	N(1)...O(141)	2.963
N(3)...O(13)	2.933	N(3)...O(6d)	3.133
N(4)...O(11)	2.910	N(4)...O(10d)	3.137
N(6)...O(4i)	2.925	N(6)...O(14a)	2.856
N(7)...O(7a)	3.080	N(8)...O(11)	3.095
O(1W)...O(1)	2.976	O(1W)...O(8j)	2.556
O(1W)...O(1)-B(1)	148.9	N(1)...O(3)-B(1)	119.9
N(1)...O(3)-B(4)	108.8	N(2)...O(5)-B(2)	120.6
N(2)...O(5)-B(3)	102.4	N(3b)...O(6)-B(4)	104.1
N(3b)...O(6)-B(5)	133.6	N(7g)...O(7)-B(2)	125.0
N(7g)...O(7)...O(1W)	104.5	B(3)-O(8)...O(12h)	121.0
O(1W)...O(8)-B(3)	108.5	O(1W)...O(8)...O(12h)	123.9
B(4)-O(9)...O(11)	95.3	B(5)-O(10)...O(13e)	113.2
N(4b)...O(10)-B(5)	106.1	N(4b)...O(10)...O(13e)	137.7
O(7)...O(1W)...O(8j)	88.2	O(8j)...O(1W)...O(1)	135.4
O(7)...O(1W)...O(1)	50.5	C(2)-N(4)...O(11)-C(1)	48.9
C(2)-N(3)...O(13)-C(3)	25.8	C(3)-N(6)...O(14a)-C(4a)	107.0
C(3)-N(6)...O(4)-B(4)	24.9	C(4g)-N(7g)...O(7)-B(2)	−12.2
C(2b)-N(3b)...O(6)-B(5)	−18.4	C(2b)-N(4b)...O(10)-B(5)	6.9
B(3)-O(8)...O(12h)-C(2h)	161.8	B(4)-O(9)...O(11)-C(1)	−67.1
B(5)-O(10)...O(13e)-C(3e)	−27.0		
$(n\text{-}C_4H_9)_4N^+[B_5O_6(OH)_4]^- \cdot 2CO(NH_2)_2 \cdot B(OH)_3$ (2)			
Hydrogen bonding			
N(3)...O(1)	3.023	O(14)...O(2)	2.733
O(9h)...O(3)	2.778	O(10b)...O(4)	2.807
N(1e)...O(5)	2.981	N(4)...O(7)	2.997
O(7d)...O(11)	2.679	O(13)...O(11)	2.676
N(1)...O(12a)	2.834	O(15c)...O(12a)	2.636
O(8)...O(13)	2.813	N(3c)...O(14)	2.951
N(2)...O(15)	2.998		
N(3)...O(1)-B(1)	111.5	N(3)...O(1)-B(2)	118.9
O(14)...O(2)-B(1)	114.6	O(14)...O(2)-B(3)	120.2
O(9h)...O(3)-B(1)	110.7	O(9h)...O(3)-B(4)	124.9
O(10b)...O(4)-B(1)	109.4	O(10b)...O(4)-B(5)	127.4
N(1e)...O(5)-B(2)	117.2	N(1e)...O(5)-B(3)	124.5
N(4)...O(7)-B(2)	121.9	B(2)-O(7)...O(11e)	107.3
N(4)...O(7)...O(11e)	129.6	B(3)-O(8)...O(13)	108.7

1.465, 1.470 Å, respectively.[19] Data for the best least-squares planes each passing through an almost planar six-membered B_3O_3 ring and two oxygen atoms of the attached hydroxyl groups (hereafter referred to as a $B_3O_3(OH)_2$ fragment) are listed in Table III. It is shown that all the atoms of the pentaborate group lie approximately in two planes making a dihedral angle of 81.8 and 88.0° for **1** and **2**, respectively. Thus the spirocyclic anion extends its four hydroxyl groups in an approximately tetrahedral fashion that deviates significantly from its idealized point group symmetry $\bar{4}2m$ (D_{2d}).

Crystal Structure of $(n\text{-}C_3H_7)_4N^+[B_5O_6(OH)_4]^- \cdot 4(NH_2)_2CO \cdot H_2O$ (1)

A stereoview of the crystal structure of **1** along the *b* axis is presented in Fig. 1. In the host lattice

Table II (Continued)

$(n\text{-}C_4H_9)_4N^+[B_5O_6(OH)_4]^-\cdot 2CO(NH_2)_2\cdot B(OH)_3$ (2)

Hydrogen bonding

O(13)...O(11)-C(1)	133.2	O(13)...O(11)...O(7d)	93.3
N(1)...O(12a)-C(2)	115.1	O(15c)...O(12a)-C(2a)	131.0
O(15c)...O(12a)...N(1)	111.8	O(8)...O(13)-B(6)	119.6
B(6)-O(13)...O(11)	115.3	O(8)...O(13)...O(11)	118.5
N(3b)...O(14)-B(6)	119.9	B(6)-O(14)...O(2)	112.7
N(3b)...O(14)...O(2)	126.7	N(2)...O(15)-B(6)	121.0
B(6)-O(15)...O(12c)	116.8	N(2)...O(15)...O(12c)	121.3
B(3)-O(8)...O(13)-B(6)	−38.7	B(6)-O(13)...O(11)-C(1)	−0.1
C(1)-N(1)...O(12)-C(2)	157.2	C(2)-N(3)...O(1)-B(2)	54.5
C(2)-N(4)...O(7)-B(2)	34.2	C(1)-N(2)...O(15)-B(6)	10.9
B(6)-O(14)...O(2)-B(3)	39.4	C(2b)-N(3b)...O(14)-B(6)	12.0
B(6)-O(15)...O(12b)-C(2b)	−4.5	C(1e)-N(1e)...O(5)-B(2)	3.2
B(2)-O(7)...O(11e)-C(1e)	23.5	B(5b)-O(10b)...O(4)-B(1)	176.1
B(1)-O(3)...O(9h)-B(4h)	177.6		

***Symmetry transformations**:
1, a (1 − x, −0.5 + y, −z); b (1 − x, 0.5 + y, 1 − z); c (−x, 0.5 + y, −z);
d (1 − x, −0.5 + y, 1 − z); e (x, 1 + y, z); f (1 − x, 0.5 + y, −z);
g (1 − x, 1 − y, −z); h (x, −1 + y, z); i (1 + x, y, z);
j (−x, −0.5 + y, −z) k (−1 + x, y, z)
2, a (x, −1 + y, z); b (1 − x, −y, −z); c(−x, 1 − y, −z);
d (0.5 − x, 0.5 + y, 0.5 − z); e (0.5 − x, −0.5 + y, 0.5 − z);f (0.5 − x, 1 − y, 0.5 − z);
g(x, 1 + y, z); h (−x, −y, −z)

Standard deviations in hydrogen bond lengths and bond angles:
1, σ (*l*) ≈ 0.005 Å, σ (θ) ≈ 0.3°;
2, σ (*l*) ≈ 0.006 Å, σ (θ) ≈ 0.4°;

built of urea, water molecules and pentaborate ions, a series of parallel elliptic channels extend along the [010] direction, and the tetra-*n*-propylammonium cations are arranged in a zigzag column within each channel.

As shown in Fig. 1, the channel walls are partly made up of highly undulate layers parallel to (101) family of planes. The complicated layer structure may be conveniently described with reference to the hydrogen bonding scheme shown in Fig. 2 and Table II. Three independent urea molecules and a $B_3O_3(OH)_2$ fragment of the pentaborate ion are linked by hydrogen bonds to form an infinite twisted ribbon running through the structure in the [010] direction. It can be seen from the values of torsion angles between these molecules (Table II) that they are roughly coplanar, except for the urea molecule composed of atoms C(1), O(11), N(1) and N(2) [hereafter conveniently referred to as **C(1)**]. The torsion angles between **C(1)** and its adjacent molecules are: B(4)-O(9)...O(11)-C(1) = −67.1, C(1)-N(1)...O(3)-B(4) = −62.0, C(2)-N(4)...O(11)-C(1) = 48.9°, while the average

Table III Least-squares planes of **1** and **2** equations in the form Ax + By + Cz = D, where x, y, and z are fractional coordinates of the monoclinic cell.

Plane	Atoms defining the plane	A	B	C	D	d_{mean}	Crystal
I	B(2), B(3), O(1), O(2), O(5), O(7), O(8)	0.376	15.979	0.780	9.1568	0.030	**1**
		11.334	0.053	1.561	3.2398	0.022	**2**
II	B(4), B(5), O(3), O(4), O(6), O(9), O(10)	8.115	−2.522	−5.513	−0.6678	0.033	**1**
		0.705	17.073	−2.567	0.3476	0.035	**2**

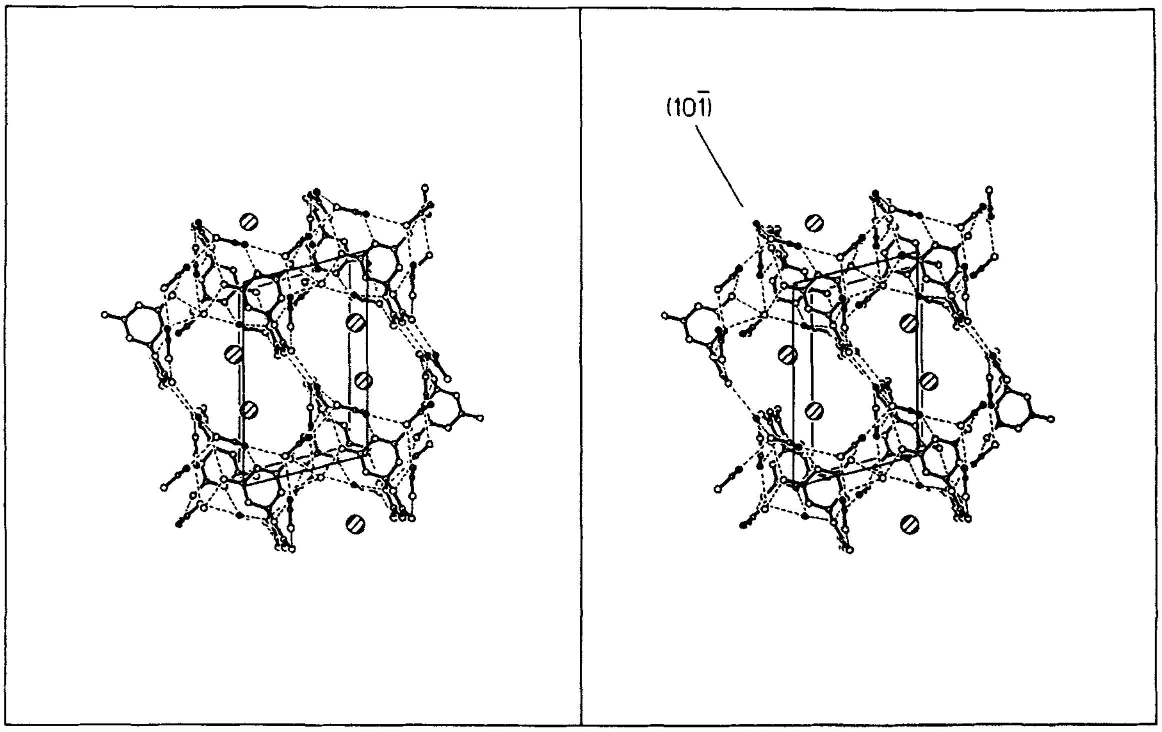

FIGURE 1 Stereodrawing of the crystal structure of $(n\text{-}C_3H_7)_4N^+[B_5O_6(OH)_4]^-\cdot 4(NH_2)_2CO\cdot H_2O$ (**1**). The origin of the unit cell lies at the upper left corner, with *a* pointing from left to right, *b* towards the reader, and *c* downwards. For clarity the enclosed $(n\text{-}C_3H_7)_4N^+$ ions are represented by large shaded circles.

value for the other molecules and the $B_3O_3(OH)_2$ fragment is about 25.9°. A pair of twisted ribbons arranged about a 2_1 screw axis are linked by lateral N-H...O hydrogen bonds to form a puckered double ribbon. A puckered layer is then constructed by means of hydrogen bonds [N(1j)...O(14), N(6f)...O(14), N(2)...O(5j), and O(8)...O(12h)] formed by the oxygen atom of the fourth urea molecule **C(4)**, the other "vertical" $B_3O_3(OH)_2$ fragment of the pentaborate ion (which is almost orthogonal to the double ribbon), and the nitrogen atoms of the urea molecules inside the double ribbon. Finally, the hydrogen bonds [O(1W)...O(1), O(1W)...O(8j), O(7)...O(1W), N(7)...O(7a), and N(8)...O(11)] generated between water molecules, urea **C(4)**, and pentaborate ions belonging to different adjacent layers link them together to built a three-dimensional channel framework. The channel wall is lined with hollows, each of which is surrounded by a pair of "vertical" $B_3O_3(OH)_2$ fragments.

The tetrahedral $(C_3H_7)_4N^+$ cation is well ordered and nearly attains its idealized 222 molecular symmetry. Individual bond distances and angles are given in the Supplementary Data. From the stereoview of the crystal structure illustrated in Fig. 1, it is seen that the cations are arranged in a zigzag column within each channel, so that some of the *n*-propyl groups fit within the concave hollows of the channel wall.

Crystal Structure of $(n\text{-}C_4H_9)_4N^+[B_5O_6(OH)_4]\cdot 2(NH_2)_2CO\cdot B(OH)_3$ (2)

As shown in Fig. 3, the host lattice of **2** comprises a set of two-dimensional infinite layers

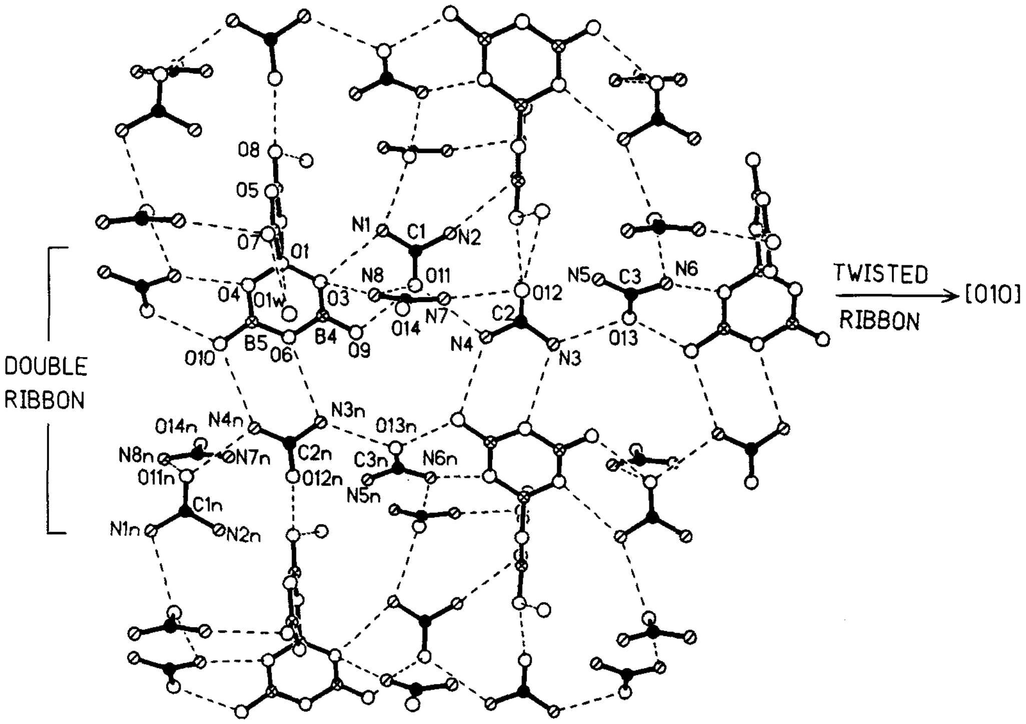

FIGURE 2 Hydrogen-bonded layer in **1** formed by the linkage of urea molecules and pentaborate anions. Note the double ribbon that runs parallel to [010]. The atom labels correspond to those given in Tables 2. Broken lines represent hydrogen bonds. Symmetry transformation: n: 1 − *x*, 0.5 + *y*, 1 − *z*.

extending parallel to the (202) family of planes. One type of guest species, the tetra-*n*-butylammonium cations (represented by large shaded circles in Fig. 3), are sandwiched between adjacent layers, while another most unusual guest component, namely a hydrogen-bonded ribbon formed by $B_3O_3(OH)_2$ fragments belonging to different pentaborate ions, threads a row of central holes of the macrocycles in a stacking of the host layers. The host architecture may be conveniently described with reference to the hydrogen bonding scheme shown in Fig. 4. The average B-O distance in the BO_3 triangles (1.363 Å) and in the BO_4 tetrahedron (1.470 Å) are in good agreement with those in the corresponding tetra-*n*-butylammonium clathrates, 1.365 and 1.470 Å, respectively.[16] All the atoms of the pentaborate group lie approximately in two planes: the mean deviation from the best least-squares planes each passing through an almost planar six-membered B_3O_3 ring and two oxygen atoms of the attached hydroxyl groups are 0.022 and 0.035 Å. The two planar fragments of the pentaborate group makes a dihedral angle of 88.0°. One $B_3O_3(OH)_2$ fragment [composed of atoms B(1), B(2), B(3), O(1), O(2), O(5), O(7) and O(8); B(1) is also shared by the other fragment] lies in the main plane of the host layer and interacts with its nearest neighbours, forming a pair of N-H...O acceptor hydrogen bonds with urea molecule **C(2)** [composed of atoms C(2), O(12), N(3) and N(4), and hereafter conveniently referred to as **C(2)**] on one side, and both O...H-O acceptor and O-H...O donor hydrogen bonds with a boric acid molecule [composed of atoms B(6), O(13), O(14) and O(15), and hereafter abbreviated as **B(6)**] on the other side, to yield a trimeric aggregate. This trimer unit together with its centrosymmetrically-related companion are linked by two pairs of hydrogen bonds involving boric

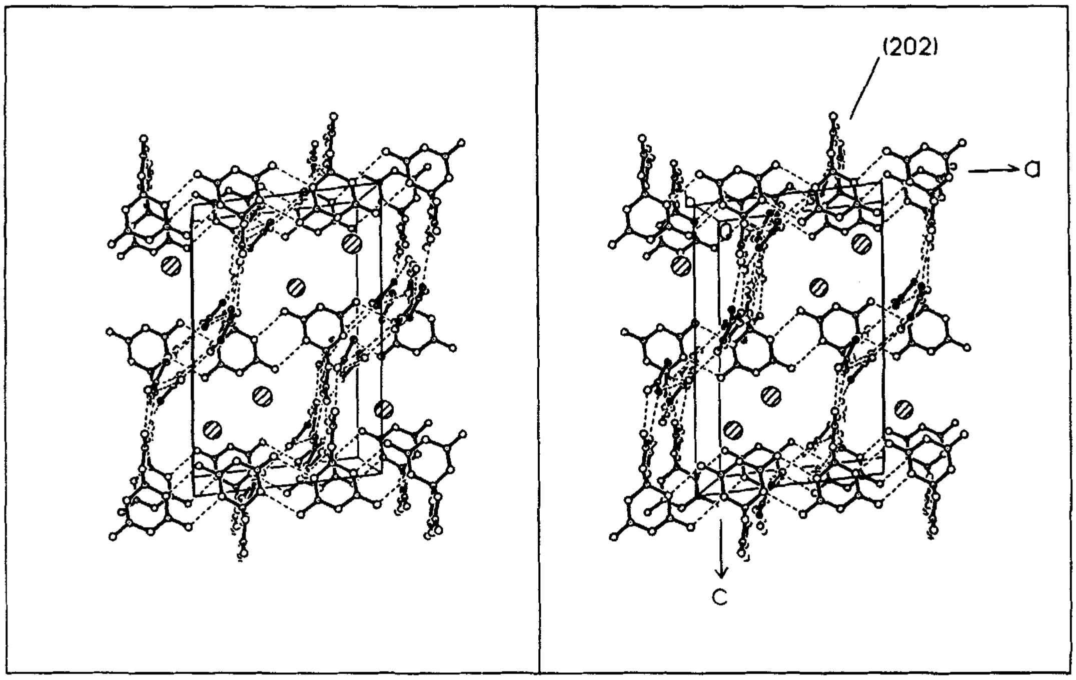

FIGURE 3 Stereodrawing of the crystal structure of $(n\text{-}C_4H_9)_4N^+[B_5O_6(OH)_4]^-\cdot 2(NH_2)_2CO\cdot B(OH)_3$ (**2**) showing the puckered layers parallel to (202) and planar $B_3O_3(OH)_2^-$ ribbons extending in the [010] direction. The origin of the unit cell lies at the upper left corner, with *a* pointing from left to right, *b* towards the reader and *c* downwards. Broken lines represent hydrogen bonds, and atom types are distinguished by size and shading. For clarity the enclosed $(n\text{-}C_4H_9)_4N^+$ ions are represented by large shaded circles.

acid **B(6)** and urea **C(2)** to generate a doughnut-like macrocyclic ring with a central hollow (Fig. 4). The relevant torsion angles, C(2b)-N(3b)...O(14)-B(6) = 12.0 and B(6)-O(15)...O(12b)-C(2b) = −4.5°, show that boric acid **B(6)** and urea **C(2)** are nearly co-planar, but the $B_3O_3(OH)_2$ fragment is inclined to them at C(2)-N(4)...O(7)-B(2) = 34.2 and B(3)-O(8)...O(13)-B(6) = −38.7°. The hydrogen-bonded macrocyclic rings constitute a pseudo-hexagonal array: the distances between the centers of adjacent macrocycles are AD = 13.694 and DC = 17.270 (= *b*) Å, and the angle ADC between these two repeat distances is 127.7° (Fig. 4). The urea molecule **C(1)** functions as a bridge in linking these macrocycles into a hydrogen-bonded puckered layer that is oriented parallel to the (202) family of planes (Fig. 3), and the well-ordered tetrahedral $(n\text{-}C_4H_9)_4N^+$ cations are sandwiched between adjacent anionic urea-pentaborate-boric acid layers.

The remaining $B_3O_3(OH)_2$ fragment of the pentaborate ion [composed of atoms B(1), B(4), B(5), O(3), O(4), O(6), O(9) and O(10)], together with identical units generated from a row of inversion centers, form an essentially planar hydrogen-bonded ribbon that is oriented parallel to (010). These ribbons extend parallel to the *a* axis and pass through the central holes of the macrocycles of stacked layers, so that the pentaborate ion plays a dual role as both host and guest.

The spacing between two adjacent urea-pentaborate-boric acid layers is 9.12 Å, which is considerably larger than the corresponding value (*a* = 8.40 Å) for tetra-*n*-butylammonium cations accommodated in the urea-bicarbonate layer structure.[12] These parameters are consistent with the difference in size between the bicarbonate and pentaborate ions and the particular modes of molecular packing.

Compound **2** is of interest as the pentaborate ion takes the unusual hybrid role of both host

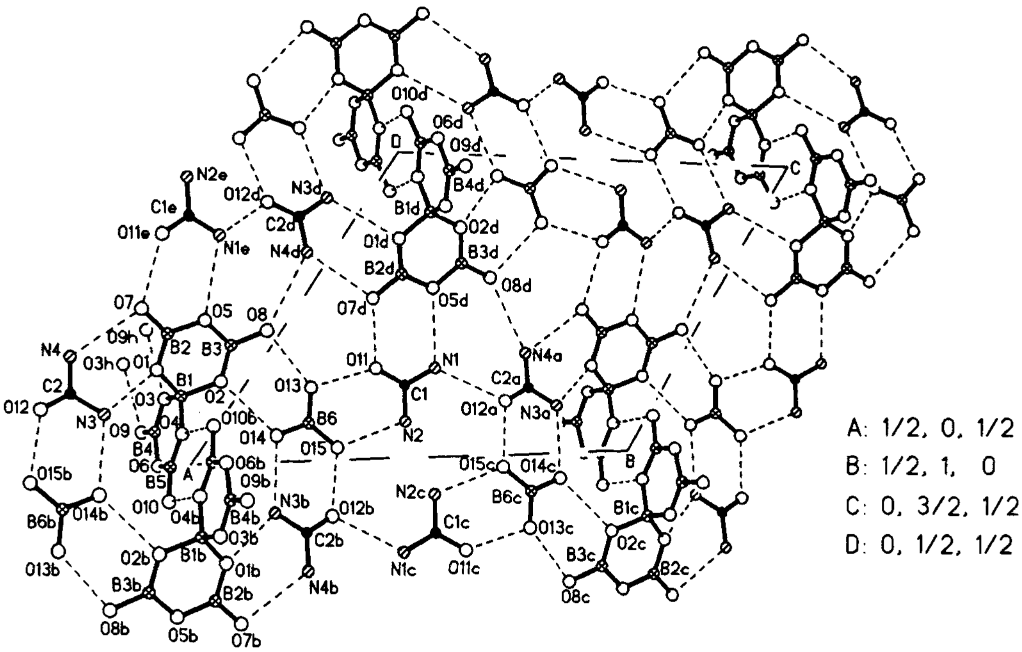

FIGURE 4 Hydrogen-bonded host layer in **2** showing an approximately planar array of macrocyclic rings formed by urea and boric acid molecules and pentaborate $B_3O_3(OH)_2$ fragments, plus the bridging urea molecules that weave them together. The corresponding pseudo-hexagonal "two-dimensional unit cell" is outlined and the coordinates of its corners listed; AD = 13.694 Å, DC = b = 17.270 Å, angle ADC = 127.7°. Note that a portion of a planar $B_3O_3(OH)_2$ ribbon passes obliquely through the central hole of each macrocyclic ring. Broken lines represent hydrogen bonds. Symmetry transformations: a: x, $1 + y$, z; b: $1 - x$, $-y$, $-z$; c: $1 - x$, $1 - y$, $-z$; d: $0.5 - x$, $0.5 + y$, $0.5 - z$; e: $0.5 - x$, $-0.5 + y$, $0.5 - z$; f: $-x$, $-y$, $-z$.

and guest. From an alternative point of view, the pentaborate ion may be considered to participate fully in the construction of the host framework. In that case the resulting architecture resembles a multi-storeyed building supported by leaning slab-like pillars.

EXPERIMENTAL

Tetra-*n*-propyl- and tetra-*n*-butyl-ammonium hydroxide were prepared from their corresponding chloride salts by reaction with moist silver(I) oxide.[26] Crystalline boric acid was obtained from Beijing Chemical Works.

Each hydroxide, boric acid and urea were mixed in molar ratios of 1:1:3 and 1:1:4 for **1** and **2**, respectively. A minimum quantity of deionized water was added to dissolve the solid in each case. After stirring for about half an hour, the solution was subjected to slow evaporation at room temperature in a desiccator charged with drierite. Colorless transparent crystals appeared in the form of larger blocks.

Information concerning crystallographic data and structure refinement of the two compounds is summarized in Table I. Intensities were collected in the variable ω-scan technique[27] on a Siemens R3m/V diffractometer using Mo*K*α radiation (λ = 0.71073Å) at 291 K. The raw data were processed with a learnt-profile procedure,[28] and empirical absorption correction based on ψ-scan data was also applied.

All calculations were performed on a PC 486 computer with the SHELXTL-PC program package.[29] Direct methods yielded the positions of all non-hydrogen atoms. The amido, methylene, and methyl H atoms were generated geometrically (C-H fixed at 0.96Å) and allowed to ride on their respective parent atoms. The hydrogen atoms of the water molecule plus the pentaborate ion $[B_5O_6(OH)_4]^-$ in **1**, and the H_3BO_3 molecule plus the pentaborate ion $[B_5O_6(OH)_4]^-$ in **2**, were generated in their idealized positions according to plausible hydrogen-bonding schemes (O-H fixed at 0.85 Å). All hydrogen atoms were assigned appropriate isotropic temperature factors and included in the structure-factor calculations. Analytic expressions of atomic scattering factors were employed, and anomalous dispersion corrections were incorporated.[30] The refinement of the coordinates and anisotropic thermal parameters of the non-hydrogen atoms was carried out by the full-matrix least-squares method, and the final *R* indices and other parameters are listed in Table I.

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