Hydrogen-Bonded Urea–Anion Host Lattices. 6. New Inclusion Compounds of Urea with Tetra-*n*-propylammonium Halides

Qi Li and Thomas C. W. Mak*

Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong. E-mail: tcwmak@cuhk.hk

Dedicated to Dr Richard K. McMullan on the occasion of his 67th birthday.

Abstract

New inclusion complexes tetra-*n*-propylammonium fluoride–urea–water (2/7/3), $2(n\text{-}C_3H_7)_4N^+F^-.7(NH_2)_2\text{-}CO.3H_2O$ (1), tetra-*n*-propylammonium chloride–urea (1/2), $(n\text{-}C_3H_7)_4N^+Cl^-.2(NH_2)_2CO$ (2), tetra-*n*-propylammonium chloride–urea (1/3), $(n\text{-}C_3H_7)_4N^+Cl^-.\allowbreak3(NH_2)_2CO$ (3), tetra-*n*-propylammonium bromide–urea–water (1/3/1), $(n\text{-}C_3H_7)_4N^+Br^-.3(NH_2)_2CO.H_2O$ (4), and tetra-*n*-propylammonium iodide–urea–water (1/3/1), $(n\text{-}C_3H_7)_4N^+I^-.3(NH_2)_2CO.H_2O$ (5), have been prepared and characterized by X-ray crystallography. Crystal data, Mo $K\alpha$ radiation: (1), space group $P2_1/c$, $Z = 4$, $a = 8.560$ (2), $b = 16.301$ (3), $c = 37.004$ (7) Å, $\beta = 92.31$ (3)°, $R_F = 0.075$ for 3945 observed data; (2), space group $P2_1/n$, $Z = 4$, $a = 9.839$ (2), $b = 15.160$ (3), $c = 14.583$ (3) Å, $\beta = 108.82$ (3)°, $R_F = 0.058$ for 1770 observed data; (3), space group $P2_1/c$, $Z = 4$, $a = 9.866$ (2), $b = 16.274$ (3), $c = 15.277$ (3) Å, $\beta = 103.36$ (3)°, $R_F = 0.060$ for 2272 observed data; (4), space group $P\bar{1}$, $Z = 2$, $a = 8.857$ (2), $b = 10.639$ (2), $c = 15.115$ (3) Å, $\alpha = 88.01$ (3), $\beta = 75.02$ (3), $\gamma = 66.72$ (3)°, $R_F = 0.064$ for 2694 observed data; (5), space group $P\bar{1}$, $Z = 2$, $a = 9.045$ (2), $b = 10.781$ (2), $c = 15.169$ (3) Å, $\alpha = 87.98$ (3), $\beta = 76.00$ (3), $\gamma = 65.73$ (3)°, $R_F = 0.052$ for 4973 observed data. In the crystal structure of (1) an alternate crisscross arrangement of urea ribbons, which are cross-bridged by other urea molecules, water molecules and fluoride ions, generates a three-dimensional host lattice containing an open-channel system running parallel to the *b* axis, with the $(n\text{-}C_3H_7)_4N^+$ cations accommodated in a zigzag column within each channel. In the crystal structure of (2) the cations are sandwiched between puckered layers resulting from parallel urea ribbons that are cross-bridged by chloride anions. In (3) the $(n\text{-}C_3H_7)_4N^+$ cations are accommodated in a channel-type host lattice built of planar arrays of twisted ribbons constructed from three independent urea molecules, which are cross-linked by bridging chloride ions. Complexes (4) and (5) are isomorphous with the same channel host framework built of parallel corrugated urea layers that are interlinked by cyclic $(H_2O.X^-)_2$ tetramers.

1. Introduction

In the classical urea inclusion compounds (Smith, 1952; Harris & Thomas, 1990, and references therein; Hollingsworth & Harris, 1996) the host structure comprises an extensively hydrogen-bonded arrangement of urea molecules, giving rise to linear parallel channels within which the guest molecules are densely packed. The minimum diameter of a typical urea channel ranges between 5.5 and 5.8 Å (George & Harris, 1995). Previous structural characterization of urea inclusion compounds, generally by X-ray diffraction (Harris & Thomas, 1990, and references therein) and solid-state NMR techniques (Imashiro, 1993), has confirmed that they are incommensurate, that is, no small integers *m* and *n* exist 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 (Harris *et al.*, 1991; Shannon *et al.*, 1993). 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 interactions between the guest molecule and every third urea molecule along a channel wall (Brown & Hollingsworth, 1995). 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 molecular modeling (Harris, 1996).

Urea also forms many inclusion compounds with the incorporation of other molecular species as additional building blocks of their hydrogen-bonded host lattices, for example, halides and pseudohalides (Mak & McMullan, 1988), simple trigonal planar oxo anions such as bicarbonate HCO_3^- (Li *et al.*, 1995) and the elusive dihydrogen orthoborate $BO(OH)_2^-$ (Li & Mak, 1998a), the novel planar allophanate ion $NH_2CONHCO_2^-$ (Mak *et al.*, 1995; Li & Mak, 1996a), as well as the spirocyclic pentaborate anion $[B_5O_6(OH)_4]^-$ (Li & Mak, 1997). A variety of box-like

cages, open-parallel-channel systems or sandwich-like layer-type structures have been shown to exist in these inclusion compounds. In the present work we report the preparation and structural characterization of the following complexes that contain tetra-n-propylammonium ions embedded within urea-halide host lattices: $2(n\text{-}C_3H_7)_4N^+F^-.7(NH_2)_2CO.3H_2O$ (1), $(n\text{-}C_3H_7)_4N^+Cl^-.2(NH_2)_2CO$ (2), $(n\text{-}C_3H_7)_4N^+Cl^-.3(NH_2)_2CO$ (3), $(n\text{-}C_3H_7)_4N^+Br^-.3(NH_2)_2CO.H_2O$ (4) and $(n\text{-}C_3H_7)_4N^+I^-.3(NH_2)_2CO.H_2O$ (5).

2. Experimental

Tetra-n-propylammonium hydroxide (1 M solution in water) and crystalline tetra-n-propylammonium salts (chloride 98%, iodide 98%) were obtained from Aldrich and Eastman Kodak, respectively.

Tetra-n-propylammonium hydroxide and urea were mixed in molar ratios of 1:4 and 1:3 for (1) and (4), respectively. A minimum quantity of water was used to dissolve the solid in each case, and hydrofluoric acid was added to the solution of (1) and hydrobromic acid was added to the solution of (4) in a 1:1 molar ratio for hydroxide:acid. Tetra-n-propylammonium chloride or iodide and urea were mixed in a molar ratio of 1:2, 1:3 and 1:3 for (2), (3) and (5), respectively. A minimum quantity of water was used 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 crystals appeared in the form of small blocks for (1), (2), (3) and (5), and small prisms for (4).

Information concerning crystallographic data and structure refinement of the five compounds is summarized in Table 1. Intensities were collected in the variable ω-scan mode (Sparks, 1976) on Siemens $R3m/V$ and AFC-7R diffractometers using Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) at 291 K. The raw data were processed with a learnt-profile procedure (Kopfmann & Huber, 1968) and an empirical absorption correction based on ψ-scan data was also applied.

All calculations were performed on a PC 486 computer with the *SHELXTL-Plus* program package

(Sheldrick, 1982). Direct methods yielded the positions of all non-H atoms. The thioamido, methylene and methyl H atoms were generated geometrically (C—H fixed at 0.96 Å, N—H at 0.90 Å) and allowed to ride on their respective parent atoms. Most methylene C atoms of the propyl groups belonging to the tetra-n-propylammonium ion in (4) exhibit twofold disorder and their X-ray scattering power was represented by two sets of partially occupied C atoms, $C(n)$ and $C(n')$; the H atoms of this disordered cation were not included in the structural model. Chemically reasonable positions for the H atoms of the water molecules in (1), (4) and (5) were located from difference maps. All H atoms were assigned appropriate isotropic temperature factors and included in the structure-factor calculations. Analytical expressions of atomic scattering factors were employed and anomalous dispersion corrections were incorporated (*International Tables for X-ray Crystallography*, 1974, Vol. IV). The refinement of the coordinates and anisotropic thermal parameters of the non-H atoms was carried out by the full-matrix least-squares method, and the final R indices and other parameters are listed in Table 1.

3. Results and discussion

The final positional and equivalent isotropic thermal parameters of (1), (2) plus (3), and (4) plus (5) are listed in Tables 2, 3 and 4, respectively.†

3.1. Crystal Structure of $2(n\text{-}C_3H_7)_4N^+F^-.7(NH_2)_2CO.3H_2O$ (1)

In (1) the urea molecules, water molecules and fluoride ions constitute a three-dimensional host lattice containing an open-channel system running in the [010] direction, as shown in Fig. 1. This urea–water–anion lattice is built from twisted urea ribbons running parallel to the [110] and [$\bar{1}$10] directions and cross-

† Atomic coordinates, anisotropic displacement parameters and structure factors have been deposited with the IUCr (Reference: SE0206). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
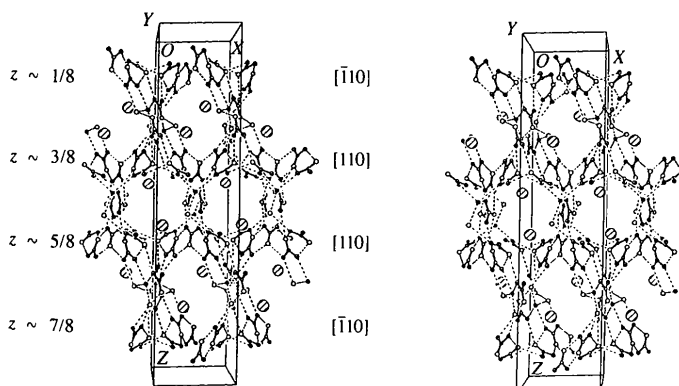
Fig. 1. Stereodrawing showing the channel structure of $2(n\text{-}C_3H_7)_4$-N⁺F⁻.7(NH₂)₂CO.3H₂O (1). The origin of the unit cell lies at the upper left corner, with a pointing from left to right, b towards the reader and c downwards. The directions of the urea ribbons at different levels along the c axis are indicated. Broken lines represent hydrogen bonds. For clarity the enclosed $(n\text{-}C_3H_7)_4N^+$ ions are represented by large shaded circles.

Table 1. *Experimental details*

	(1)	(2)	(3)	(4)	(5)
Crystal data					
Chemical formula	$2(C_3H_7)_4N^+.F^-.$ $7(NH_2)_2CO.3H_2O$	$(C_3H_7)_4N^+.Cl^-.$ $2(NH_2)_2CO$	$(C_3H_7)_4N^+.Cl^-.$ $3(NH_2)_2CO$	$(C_3H_7)_4N^+.Br^-.$ $3(NH_2)_2CO.H_2O$	$(C_3H_7)_4N^+.I^-.$ $3(NH_2)_2CO.H_2O$
Chemical formula weight	885.2	341.9	402.0	464.5	511.50
Cell setting	Monoclinic	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a (Å)	8.560 (2)	9.839 (2)	9.866 (2)	8.857 (2)	9.045 (2)
b (Å)	16.301 (3)	15.160 (3)	16.274 (3)	10.639 (2)	10.781 (2)
c (Å)	37.004 (7)	14.583 (3)	15.277 (3)	15.115 (3)	15.169 (3)
α (°)				88.01 (3)	87.98 (3)
β (°)	92.31 (3)	108.82 (3)	103.36 (3)	75.02 (3)	76.00 (3)
γ (°)				66.72 (3)	65.73 (3)
V (Å^3)	5159 (3)	2059 (1)	2386.5 (8)	1260.2 (4)	1304.5 (7)
Z	4	4	4	2	2
$F(000)$	1944	752	880	496	532
D_x (Mg m^{-3})	1.140	1.103	1.119	1.224	1.302
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
No. of reflections for cell parameters	25	25	25	25	25
θ range (°)	6–14	6–14	6–14	6–14	6–14
μ (mm^{-1})	0.089	0.199	0.186	1.661	1.257
Temperature (K)	291	291	291	291	291
Crystal form	Block	Block	Block	Prism	Block
Crystal size (mm)	0.54 × 0.54 × 0.48	0.54 × 0.45 × 0.32	0.62 × 0.44 × 0.36	0.65 × 0.60 × 0.58	0.52 × 0.46 × 0.42
Crystal color	Colorless	Colorless	Colorless	Colorless	Colorless
Data collection					
Diffractometer	Siemens $R3m/V$	Rigaku AFC-7R	Rigaku AFC-7R	Rigaku AFC-7R	Rigaku AFC-7R
Data collection method	ω scans (Sparks, 1976)	ω scans (Sparks, 1976)	ω scans (Sparks, 1976)	ω scans (Sparks, 1976)	ω scans (Sparks, 1976)
Scan speed (° min^{-1})	2–60	2–30	2–30	2–30	2–32
Scan range (below $K\alpha_1$ to above $K\alpha_2$)	0.6–0.6	0.6–0.6	0.6–0.6	0.6–0.6	0.6–0.6
Absorption correction	ψ scan (Kopfmann & Huber, 1968)	ψ scan (Kopfmann & Huber, 1968)	ψ scan (Kopfmann & Huber, 1968)	ψ scan (Kopfmann & Huber, 1968)	ψ scan (Kopfmann & Huber, 1968)
T_{min}	0.850	0.772	0.841	0.760	0.845
T_{max}	0.867	0.834	0.905	0.866	0.889
No. of measured reflections	8753	4987	4475	6089	6301
No. of independent reflections	8141	4722	4216	5775	5981
No. of observed reflections	3945	1770	2272	2694	4973
Criterion for observed reflections	$F_o > 4\sigma(F_o)$	$F_o > 4\sigma(F_o)$	$F_o > 4\sigma(F_o)$	$F_o > 4\sigma(F_o)$	$F_o > 4\sigma(F_o)$
R_{int}	0.021	0.026	0.022	0.040	0.023
Mean μr	0.05	0.06	0.06	0.8	0.8
θ_{max} (°)	23	25	25	27.5	27.5
Range of h, k, l	$0 \rightarrow h \rightarrow 9$ $0 \rightarrow k \rightarrow 18$ $-42 \rightarrow l \rightarrow 42$	$0 \rightarrow h \rightarrow 12$ $0 \rightarrow k \rightarrow 19$ $-18 \rightarrow l \rightarrow 17$	$0 \rightarrow h \rightarrow 11$ $0 \rightarrow k \rightarrow 19$ $-18 \rightarrow l \rightarrow 17$	$-11 \rightarrow h \rightarrow 10$ $-13 \rightarrow k \rightarrow 0$ $-19 \rightarrow l \rightarrow 19$	$-11 \rightarrow h \rightarrow 10$ $-13 \rightarrow k \rightarrow 0$ $-19 \rightarrow l \rightarrow 19$
No. of standard reflections	2	3	3	3	3
Frequency of standard reflections	Every 97 reflections	Every 97 reflections	Every 97 reflections	Every 97 reflections	Every 97 reflections
Refinement					
Refinement on	F	F	F	F	F
R	0.075	0.058	0.060	0.064	0.052
wR	0.075	0.069	0.065	0.075	0.067
S	2.05	1.47	1.68	1.71	1.67
No. of reflections used in refinement	3945	1770	2272	2694	4973

Table 1 (cont.)

	(1)	(2)	(3)	(4)	(5)
No. of parameters used	533	200	236	298	245
H-atom treatment	H atoms: see text	H atoms: see text	H atoms: see text	H atoms: see text	H atoms: see text
Weighting scheme	$w = 1/[\sigma^2(F_o) +0.0003F_o^2]$	$w = 1/[\sigma^2(F_o) +0.0005F_o^2]$	$w = 1/[\sigma^2(F_o) +0.0001F_o^2]$	$w = 1/[\sigma^2(F_o) +0.0001F_o^2]$	$w = 1/[\sigma^2(F_o) +0.0002F_o^2]$
$(\Delta/\sigma)_{max}$	0.001	0.000	0.000	0.005	0.001
$\Delta\rho_{max}$ (e Å^{-3})	1.11	0.19	0.43	0.39	0.87
$\Delta\rho_{min}$ (e Å^{-3})	−0.27	−0.18	−0.20	−0.57	−1.09
Extinction method	$F_{corr} = F_c(1+ 0.002\chi F_c^2/sin2\theta)^{-1/4}$	$F_{corr} = F_c(1+ 0.002\chi F_c^2/sin2\theta)^{-1/4}$	$F_{corr} = F_c(1+ 0.002\chi F_c^2/sin2\theta)^{-1/4}$	$F_{corr} = F_c(1+ 0.002\chi F_c^2/sin2\theta)^{-1/4}$	$F_{corr} = F_c(1+ 0.002\chi F_c^2/sin2\theta)^{-1/4}$
Extinction coefficient	0.00033 (8)	0.00065 (1)	0.00057 (9)	0.0081 (2)	0.0218 (1)
Source of atomic scattering factors	International Tables for X-ray Crystallography (1974, Vol. IV)	International Tables for X-ray Crystallography (1974, Vol. IV)	International Tables for X-ray Crystallography (1974, Vol. IV)	International Tables for X-ray Crystallography (1974, Vol. IV)	International Tables for X-ray Crystallography (1974, Vol. IV)

bridged by water molecules and fluoride anions *via* hydrogen bonds. Features of and relations between these ribbons and the bridging species may be conveniently described with reference to the hydrogen-bonding scheme shown in Fig. 2 and Table 5.

Five independent urea molecules C(1) [for simplicity the urea molecule composed of atoms C1, O1, N1 and N2 is designated as C(1)], C(2), C(3), C(4) and C(5) are

arranged sequentially and connected by pairs of N—H···O hydrogen bonds in the usual shoulder-to-shoulder manner to form a pentamer, which serves as a repeating structural unit in generating an infinite urea ribbon. The torsion angles in the range 12.8–72.4° between adjacent urea molecules indicate that this ribbon has a highly twisted configuration. Two urea ribbons related by inversion symmetry are extended
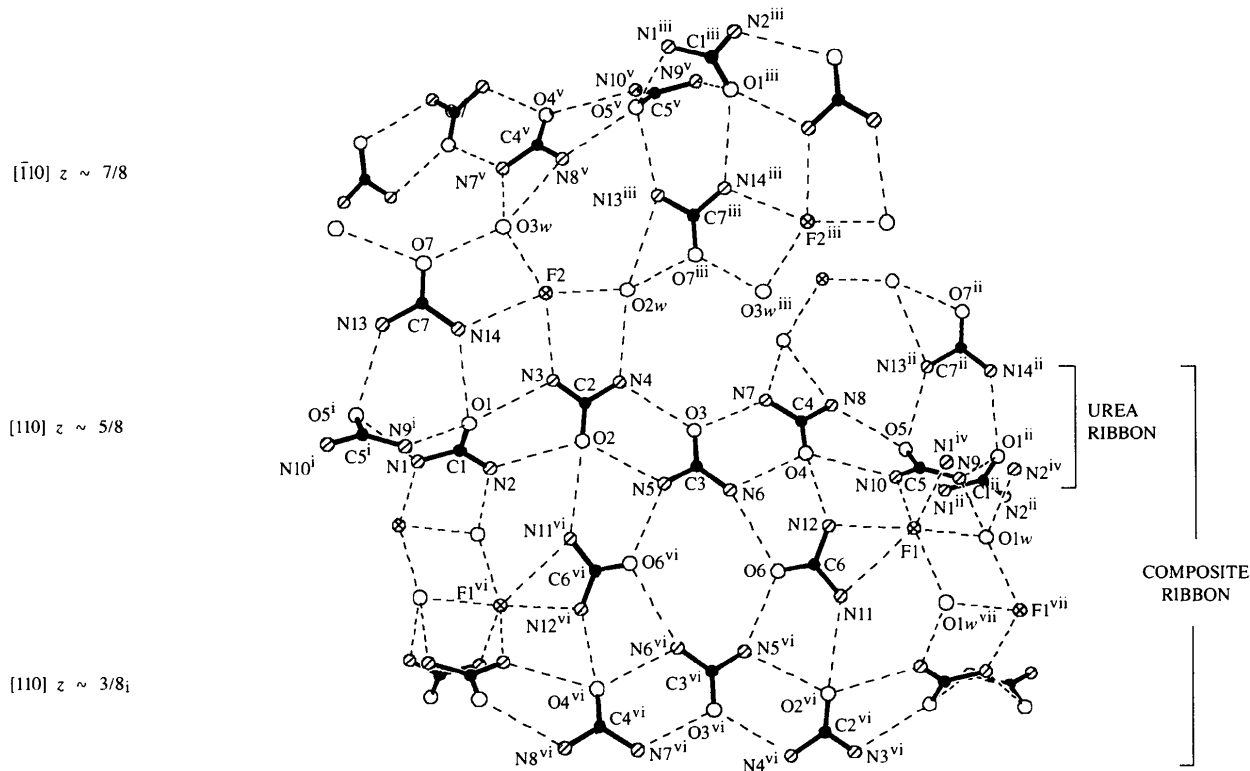

Fig. 2. Projection drawing of the hydrogen-bonded urea ribbons in (1). The atom labels correspond to those given in Tables 2 and 5. Portions of a urea ribbon and a composite ribbon are indicated. Broken lines represent hydrogen bonds and atom types are distinguished by size and shading.

Table 2. *Fractional atomic coordinates and equivalent displacement parameters ($\mathring{A}^2$) for (1)*

$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq}
(n-C$_3$H$_7$)$_4$N$^+$F$^-$.7(NH$_2$)$_2$CO.3H$_2$O (1)				
Urea–fluoride–water host lattice				
O1	0.1370 (4)	0.0714 (2)	0.3856 (1)	0.060 (1)
C1	0.2436 (7)	0.0422 (3)	0.4055 (2)	0.053 (1)
N1	0.2451 (5)	−0.0372 (3)	0.4150 (1)	0.064 (1)
N2	0.3638 (5)	0.0884 (3)	0.4178 (1)	0.063 (1)
O2	0.3772 (4)	0.2667 (2)	0.3934 (1)	0.058 (1)
C2	0.3385 (6)	0.2729 (3)	0.3609 (2)	0.050 (1)
N3	0.2488 (5)	0.2174 (3)	0.3440 (1)	0.068 (1)
N4	0.3873 (5)	0.3363 (3)	0.3405 (1)	0.060 (1)
O3	0.5595 (4)	0.4738 (2)	0.3783 (1)	0.063 (1)
C3	0.5372 (6)	0.4803 (3)	0.4109 (2)	0.053 (1)
N5	0.4550 (5)	0.4238 (3)	0.4286 (1)	0.063 (1)
N6	0.5960 (5)	0.5427 (3)	0.4306 (1)	0.074 (1)
O4	0.7192 (4)	0.6855 (2)	0.3943 (1)	0.066 (1)
C4	0.7661 (6)	0.6746 (3)	0.3637 (2)	0.049 (1)
N7	0.7393 (5)	0.6045 (4)	0.3452 (1)	0.063 (1)
N8	0.8447 (5)	0.7323 (3)	0.3462 (1)	0.068 (1)
O5	0.9454 (4)	0.8826 (2)	0.3846 (1)	0.063 (1)
C5	0.8428 (7)	0.9112 (4)	0.4041 (2)	0.055 (1)
N9	0.8447 (5)	0.9903 (3)	0.4138 (1)	0.065 (1)
N10	0.7275 (5)	0.8647 (3)	0.4156 (1)	0.072 (1)
O6	0.6149 (5)	0.6360 (3)	0.5012 (1)	0.080 (1)
C6	0.5669 (6)	0.7069 (4)	0.4956 (2)	0.056 (1)
N11	0.5467 (5)	0.7592 (3)	0.5231 (1)	0.067 (1)
N12	0.5255 (6)	0.7361 (3)	0.4629 (1)	0.081 (1)
O7	−0.0679 (4)	−0.0007 (2)	0.2560 (1)	0.072 (1)
C7	−0.0401 (6)	−0.0040 (4)	0.2887 (2)	0.060 (1)
N13	−0.0697 (13)	−0.0731 (3)	0.3077 (1)	0.075 (1)
N14	0.0275 (5)	0.0570 (3)	0.3077 (1)	0.083 (1)
F1	0.4700 (4)	0.9013 (2)	0.4660 (1)	0.078 (1)
F2	0.1100 (5)	0.2119 (3)	0.2740 (1)	0.132 (1)
O1w	0.6272 (4)	1.0390 (2)	0.4702 (1)	0.079 (1)
O2w	0.2525 (5)	0.3580 (3)	0.2646 (1)	0.093 (1)
O3w	0.0606 (5)	0.1310 (3)	0.2183 (1)	0 090 (1)
Tetra-n-propylammonium ion				
N15	1.0808 (4)	0.8026 (3)	0.0620 (1)	0.051 (1)
C8	0.9809 (6)	0.7357 (3)	0.0443 (2)	0.060 (1)
C9	1.0632 (7)	0.6737 (4)	0.0219 (2)	0.083 (1)
C10	0.9515 (8)	0.6153 (4)	0.0038 (2)	0.115 (1)
C11	1.1686 (6)	0.8486 (4)	0.0339 (2)	0.064 (1)
C12	1.0742 (7)	0.8826 (4)	0.0019 (2)	0.086 (1)
C13	1.1815 (8)	0.9288 (4)	−0.0230 (2)	0.106 (1)
C14	0.9695 (6)	0.8589 (3)	0.0808 (2)	0.060 (1)
C15	1.0443 (6)	0.9309 (4)	0.1015 (2)	0.073 (1)
C16	0.9262 (7)	0.9716 (4)	0.1247 (2)	0.093 (1)
C17	1.2033 (6)	0.7659 (3)	0.0879 (2)	0.059 (1)
C18	1.1423 (6)	0.7218 (4)	0.1202 (2)	0.067 (1)
C19	1.2742 (7)	0.6814 (4)	0.1424 (2)	0.084 (1)
N16	0.3580 (5)	0.7150 (3)	−0.2056 (1)	0.054 (1)
C20	0.4695 (6)	0.6473 (3)	−0.1932 (2)	0.060 (1)
C21	0.3929 (6)	0.5689 (3)	−0.1817 (2)	0.072 (1)
C22	0.5147 (7)	0.5109 (4)	−0.1657 (2)	0.092 (1)
C23	0.2464 (6)	0.6852 (4)	−0.2362 (1)	0.060 (1)
C24	0.3247 (7)	0.6576 (4)	−0.2703 (2)	0.082 (1)
C25	0.2032 (7)	0.6213 (4)	−0.2966 (2)	0.099 (1)
C26	0.4594 (6)	0.7859 (4)	−0.2181 (2)	0.074 (1)
C27	0.3732 (7)	0.8611 (4)	−0.2317 (2)	0.100 (1)
C28	0.4816 (9)	0.9284 (5)	−0.2399 (3)	0.159 (1)
C29	0.2573 (6)	0.7416 (4)	−0.1753 (2)	0.065 (1)
C30	0.3433 (8)	0.7724 (5)	−0.1420 (2)	0.103 (1)
C31	0.2340 (8)	0.7963 (5)	−0.1134 (2)	0.129 (1)

Table 3. *Fractional atomic coordinates and equivalent displacement parameters ($\mathring{A}^2$) for (2) and (3)*

$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq}
(i) (n-C$_3$H$_7$)$_4$N$^+$Cl$^-$.2(NH$_2$)$_2$CO (2)				
Urea–chloride host lattice				
O1	0.1588 (3)	0.2728 (2)	0.5338 (2)	0.066 (1)
C1	0.0626 (5)	0.2420 (3)	0.5627 (3)	0.052 (2)
N1	−0.0748 (4)	0.2412 (3)	0.5069 (3)	0.069 (2)
N2	0.0896 (4)	0.2096 (3)	0.6518 (3)	0.062 (2)
O2	−0.1317 (3)	0.2403 (2)	0.2961 (2)	0.063 (1)
C2	−0.0297 (5)	0.2555 (3)	0.2642 (3)	0.053 (2)
N3	−0.0501 (4)	0.2555 (3)	0.1688 (3)	0.069 (2)
N4	0.1013 (4)	0.2752 (3)	0.3225 (3)	0.066 (2)
Cl1	0.2604 (1)	0.3320 (1)	0.1585 (1)	0.067 (1)
Tetra-n-propylammonium ion				
N5	0.5442 (4)	0.0587 (2)	0.2978 (3)	0.058 (2)
C3	0.6271 (6)	0.0590 (3)	0.2257 (4)	0.076 (3)
C4	0.6396 (7)	−0.0293 (4)	0.1815 (4)	0.094 (3)
C5	0.7318 (8)	−0.0205 (5)	0.1166 (5)	0.152 (5)
C6	0.6148 (5)	−0.0007 (3)	0.3832 (4)	0.067 (2)
C7	0.7726 (6)	0.0138 (4)	0.4353 (4)	0.086 (3)
C8	0.8225 (6)	−0.0417 (4)	0.5255 (4)	0.088 (3)
C9	0.5440 (5)	0.1545 (3)	0.3300 (3)	0.061 (2)
C10	0.4701 (5)	0.1740 (3)	0.4040 (3)	0.068 (2)
C11	0.4849 (6)	0.2720 (3)	0.4279 (3)	0.074 (2)
C12	0.3914 (5)	0.0246 (3)	0.2525 (4)	0.067 (2)
C13	0.2978 (6)	0.0750 (4)	0.1664 (4)	0.086 (3)
C14	0.1531 (7)	0.0336 (5)	0.1305 (5)	0.129 (4)
(ii) (n-C$_3$H$_7$)$_4$Cl$^-$.3(NH$_2$)$_2$CO (3)				
Urea–chloride host lattice				
O1	0.0594 (3)	0.2650 (2)	0.4078 (2)	0.075 (1)
C1	0.1028 (4)	0.3187 (2)	0.3647 (3)	0.060 (1)
N1	0.2236 (4)	0.3582 (2)	0.3974 (2)	0.077 (1)
N2	0.0323 (4)	0.3417 (2)	0.2827 (2)	0.077 (1)
O2	0.3992 (3)	0.2884 (2)	0.5661 (2)	0.067 (1)
C2	0.3654 (4)	0.2217 (3)	0.5941 (3)	0.058 (1)
N3	0.4532 (4)	0.1771 (2)	0.6553 (2)	0.087 (1)
N4	0.2384 (4)	0.1893 (2)	0.5644 (2)	0.074 (1)
O3	0.7469 (3)	0.2283 (2)	0.7201 (2)	0.068 (1)
C3	0.7470 (4)	0.3032 (4)	0.7364 (3)	0.055 (1)
N5	0.8407 (3)	0.3373 (2)	0.8042 (2)	0.065 (1)
N6	0.6535 (3)	0.3543 (2)	0.6860 (2)	0.064 (1)
Cl1	0.2539 (1)	0.4675 (1)	0.2114 (1)	0.072 (1)
Tetra-n-propylammonium ion				
N7	0.7437 (3)	0.5501 (2)	0.2409 (2)	0.055 (1)
C4	0.6513 (5)	0.5198 (3)	0.3015 (3)	0.079 (1)
C5	0.6977 (5)	0.4507 (3)	0.3614 (3)	0.098 (2)
C6	0.6037 (5)	0.4325 (3)	0.4225 (3)	0.106 (2)
C7	0.8879 (5)	0.5669 (3)	0.2946 (3)	0.086 (2)
C8	0.9053 (6)	0.6213 (3)	0.3713 (4)	0.113 (2)
C9	1.0513 (5)	0.6312 (4)	0.4238 (3)	0.128 (2)
C10	0.6791 (5)	0.6285 (3)	0.1947 (3)	0.086 (2)
C11	0.5466 (5)	0.6228 (3)	0.1287 (4)	0.098 (2)
C12	0.4794 (5)	0.7060 (3)	0.1050 (3)	0.098 (2)
C13	0.7489 (5)	0.4840 (3)	0.1715 (3)	0.083 (2)
C14	0.8315 (6)	0.4998 (3)	0.1054 (3)	0.101 (2)
C15	0.8298 (7)	0.4322 (3)	0.0408 (3)	0.121 (2)

along the [110] direction and at a location which is one-half translation away along the *c* axis, there are two similar ribbons which extend in the [$\bar{1}$10] direction (Fig. 1). Fluoride ion F(1) and water molecule O1*w* plus their centrosymmetrically related partners form a cyclic (H$_2$O.F$^-$)$_2$ tetramer consolidated by two pairs of O—

Table 4. *Fractional atomic coordinates and equivalent displacement parameters ($\mathring{A}^2$) for (4) and (5)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
(i) $(n\text{-}C_3H_7)_4N^+Br^-.3(NH_2)_2CO.H_2O$ (4)				
Urea–bromide–water host lattice				
O1	0.1064 (2)	1.1502 (2)	0.4108 (2)	0.053 (1)
C1	0.1760 (2)	1.2010 (2)	0.4532 (2)	0.047 (1)
N1	0.3340 (2)	1.1272 (2)	0.4629 (2)	0.054 (1)
N2	0.0940 (2)	1.3289 (2)	0.4929 (2)	0.061 (1)
O2	0.4833 (2)	0.8281 (2)	0.4146 (2)	0.049 (1)
C2	0.3722 (2)	0.7887 (2)	0.4564 (2)	0.045 (1)
N3	0.4137 (2)	0.6728 (2)	0.5004 (2)	0.062 (1)
N4	0.2065 (2)	0.8611 (2)	0.4614 (2)	0.060 (1)
O3	0.7862 (2)	0.4908 (2)	0.4260 (2)	0.050 (1)
C3	0.8242 (2)	0.4791 (2)	0.3393 (2)	0.052 (1)
N5	0.9310 (2)	0.3590 (2)	0.2930 (2)	0.065 (1)
N6	0.7594 (2)	0.5860 (2)	0.2917 (2)	0.071 (1)
Br1	1.1415 (1)	0.2386 (1)	0.0640 (1)	0.088 (1)
O1w	0.8058 (3)	0.5426 (2)	0.0976 (2)	0.133 (1)
Tetra-n-propylammonium ion				
N7	0.6010 (2)	0.1669 (2)	0.1783 (2)	0.058 (1)
C4	0.7065 (3)	0.2132 (3)	0.0965 (2)	0.068 (1)
C4'	0.6278 (3)	0.1870 (3)	0.0790 (2)	0.068 (1)
C5	0.6115 (3)	0.2838 (3)	0.0267 (2)	0.101 (1)
C5'	0.7105 (3)	0.2857 (3)	0.0469 (2)	0.125 (1)
C6	0.7309 (5)	0.3126 (3)	−0.0544 (2)	0.102 (1)
C7	0.4378 (3)	0.2911 (2)	0.2233 (2)	0.064 (1)
C7'	0.5232 (3)	0.2909 (3)	0.2453 (2)	0.061 (1)
C8	0.4593 (3)	0.4165 (3)	0.2519 (2)	0.084 (1)
C8'	0.3562 (3)	0.3973 (3)	0.2351 (2)	0.085 (1)
C9	0.2838 (3)	0.5269 (3)	0.2974 (2)	0.103 (1)
C10	0.5555 (3)	0.0590 (3)	0.1408 (2)	0.061 (1)
C10'	0.4813 (3)	0.0929 (3)	0.2043 (3)	0.063 (1)
C11	0.4737 (3)	−0.0075 (3)	0.2181 (2)	0.088 (1)
C11'	0.5542 (3)	−0.0536 (3)	0.1652 (3)	0.100 (1)
C12	0.4226 (3)	−0.1131 (2)	0.1821 (2)	0.101 (1)
C13	0.7066 (3)	0.1228 (2)	0.2455 (2)	0.064 (1)
C13'	0.7719 (3)	0.0791 (3)	0.1892 (2)	0.073 (1)
C14	0.8637 (3)	−0.0079 (3)	0.2146 (2)	0.091 (1)
C14'	0.7808 (3)	−0.0204 (3)	0.2614 (2)	0.253 (1)
C15	0.9446 (3)	−0.0648 (3)	0.2932 (2)	0.113 (1)
(ii) $(n\text{-}C_3H_7)_4N^+I^-.3(NH_2)_2CO.H_2$ (5)				
Urea–bromide–water host lattice				
O1	0.1005 (3)	1.1524 (2)	0.4176 (2)	0.050 (1)
C1	0.1704 (3)	1.2019 (3)	0.4583 (2)	0.043 (1)
N1	0.3275 (3)	1.1287 (3)	0.4662 (2)	0.054 (1)
N2	0.0935 (4)	1.3297 (3)	0.4941 (3)	0.062 (1)
O2	0.4769 (3)	0.8294 (2)	0.4207 (2)	0.049 (1)
C2	0.3678 (3)	0.7892 (3)	0.4606 (2)	0.043 (1)
N3	0.4110 (4)	0.6719 (3)	0.5017 (3)	0.062 (1)
N4	0.2058 (3)	0.8616 (3)	0.4642 (3)	0.058 (1)
O3	0.7817 (3)	0.4928 (2)	0.4302 (2)	0.049 (1)
C3	0.8172 (4)	0.4811 (3)	0.3442 (2)	0.049 (1)
N5	0.9213 (5)	0.3611 (3)	0.2988 (2)	0.067 (1)
N6	0.7474 (5)	0.5871 (3)	0.2967 (2)	0.069 (1)
I1	1.1324 (1)	0.2183 (1)	0.0591 (1)	0.075 (1)
O1w	0.7815 (7)	0.5423 (5)	0.1014 (3)	0.118 (2)
Tetra-n-propylammonium ion				
N7	0.5914 (4)	0.1649 (3)	0.1826 (2)	0.054 (1)
C4	0.6880 (6)	0.2069 (6)	0.0965 (3)	0.074 (2)
C5	0.5874 (8)	0.2735 (7)	0.0276 (4)	0.090 (3)
C6	0.6964 (10)	0.3071 (8)	−0.0511 (4)	0.097 (3)
C7	0.4363 (6)	0.2866 (4)	0.2290 (3)	0.072 (2)
C8	0.4552 (9)	0.4129 (6)	0.2551 (4)	0.097 (3)
C9	0.2903 (10)	0.5236 (6)	0.2991 (5)	0.109 (3)
C10	0.5455 (5)	0.0562 (4)	0.1535 (3)	0.066 (2)

Table 4 *(cont.)*

	x	y	z	U_{eq}
C11	0.4694 (9)	−0.0090 (6)	0.2294 (4)	0.089 (3)
C12	0.4291 (8)	−0.1166 (6)	0.1941 (4)	0.085 (2)
C13	0.7061 (6)	0.1154 (5)	0.2464 (3)	0.076 (2)
C14	0.8613 (7)	−0.0140 (7)	0.2154 (4)	0.094 (3)
C15	0.9522 (8)	−0.0608 (9)	0.2905 (5)	0.111 (3)

For (4), atoms C4, C5, C7, C8, C10, C11, C13, C14 and C4', C5', C7', C8', C10', C11', C13', C14' belong to a disordered tetra-n-propylammonium ion with s.o.f. = 0.687 for the above unprimed C atoms and 0.313 for the primed C atoms.

H$\cdots$F hydrogen bonds, which together with the sixth urea molecule C(6) lie between a pair of ribbons running in the same direction, *i.e.* parallel to [110] or [$\bar{1}$10]. The last urea molecule C(7) in the asymmetric unit, fluoride ion F2 and water molecule O3w are linked by O(water)—H$\cdots$O, O(water)—H$\cdots$F and N—H$\cdots$F hydrogen bonds to form a cyclic trimer, which together with water molecule O2w are situated between two urea ribbons extending in different directions. The alternate crisscross arrangement of these urea ribbons, which are cross-bridged by urea and water molecules, and fluoride ions lying in layers corresponding to the (004) family of planes, generates a three-dimensional host lattice containing an open-channel system running parallel to the *b* axis, as illustrated in Fig. 1.

The basic component of the host lattice of (1) may also be described as a composite ribbon constructed from urea molecules C(1)–C(6) and $(H_2O.F^-)_2$ units (Fig. 2). These composite ribbons point alternately in the [110] and [$\bar{1}$10] directions and their cross-linkage by C(7), F2, O2w and O3w generates the channel-type host network.

The tetra-n-propylammonium cations are well ordered and almost attain idealized $\bar{4}2m$ molecular symmetry. When the crystal structure of (1) is viewed parallel to the *b* axis (Fig. 1), the $(n\text{-}C_3H_7)_4N(15)^+$ cations are accommodated within the channels at $z = 0$ and $\frac{1}{2}$, and the $(n\text{-}C_3H_7)_4N(16)^+$ cations are accommodated within the channels at $z = \frac{1}{4}$ and $\frac{3}{4}$.

3.2. Anhydrous chloride complexes $(n\text{-}C_3H_7)_4$-$N^+Cl^-.2(NH_2)_2CO$ (2) and $(n\text{-}C_3H_7)_4N^+Cl^-.3(NH_2)_2$-$CO$ (3)

Fig. 3 shows a portion of a urea–chloride layer consolidated by hydrogen bonding in the host structure of (2). Both independent urea molecules C(1) and C(2) are alternately linked by pairs of N—H$\cdots$O hydrogen bonds to form a slightly buckled ribbon running parallel to the [101] direction; the ribbon is close to being planar, as indicated by the small mean deviation (0.199 $\mathring{A}$) of atoms from the least-squares plane involving urea molecules C(1), C(2), C(1*b*) and C(2*c*). Adjacent ribbons are related by an *n*-glide plane and aligned in such a way that each has a urea molecule

forming donor hydrogen bonds to the same chloride ion in a bidentate chelating mode. The resulting puckered layer which corresponds to the (040) plane is thus generated by hydrogen-bonded urea ribbons and bridging chloride ions. As shown in Fig. 3, an open octagon (neglecting H atoms) lies between a pair of chloride ions in each layer. This urea–halide lattice can be contrasted with that of the related inclusion compound $(n\text{-}C_4H_9)_4N^+Cl^-.2(NH_2)CS$ (Li & Mak, 1996b), in which each independent thiourea molecule gives rise to a thiourea ribbon, and the compound $(n\text{-}C_4H_9)_3(CH_3)N^+Cl^-.2(NH_2)CS$ (Mak, 1990), in which each thiourea ribbon is constructed from two independent thiourea molecules and the ribbons are arranged in a crisscross fashion.

A stereoview of the crystal structure of (2) is illustrated in Fig. 4. It is seen that the ordered $(n\text{-}C_3H_7)_4N^+$ cations are sandwiched between hydrophilic layers with one alkyl leg pointing toward a neighboring octagonal void. The interlayer spacing is 7.58 Å ($= b/2$), which is smaller than the corresponding value for a similar layer structure with tetra-n-butylammonium cations accommodated in the urea–bicarbonate host lattice, $1/a^* = 8.32$ Å in triclinic $(n\text{-}C_4H_9)_4N^+HCO_3^-.3(NH_2)_2CO$ (Li

et al., 1995), as may be expected in view of the relative sizes of the cations.

The atom-labeling scheme and hydrogen-bonding interactions among the components of the host framework of (3) are shown in Fig. 5. The three independent urea molecules in the asymmetrical unit are linked into spiral ribbons, as found in the crystal structures of urea and thiourea. These three-molecule ribbons run parallel to the [201] direction. Urea molecules C(1) and C(2) are essentially coplanar, as the $C—N\cdots O—C$ torsion angles between them are 7.5 and 8.6°. However, the third urea molecule C(3) is inclined with respect to the main plane of the ribbon, the relevant torsion angles being $C2—N3\cdots O3—C3 = 45.7$, $C3—N6\cdots O2—C2 = 26.8$, $C3—N5\cdots O1^{ii}—C1^{ii} = 35.2$ and $C1^{ii}—N2^{ii}\cdots O3—C3 = 45.0°$, respectively. Ribbons related by the c-glide operation and lying side by side are concentrated about the plane $z = \frac{1}{2}$; the 2_1 glide operation generates an equivalent, but staggered, planar arrangement of urea ribbons located at $z = \frac{3}{4}$ (Fig. 6). The chloride ions are sandwiched between these planar arrays and each forms six $N—H\cdots Cl$ accepted hydrogen bonds in the bidentate chelating mode with two urea molecules on one side and one urea molecule on the other (Fig. 5). As
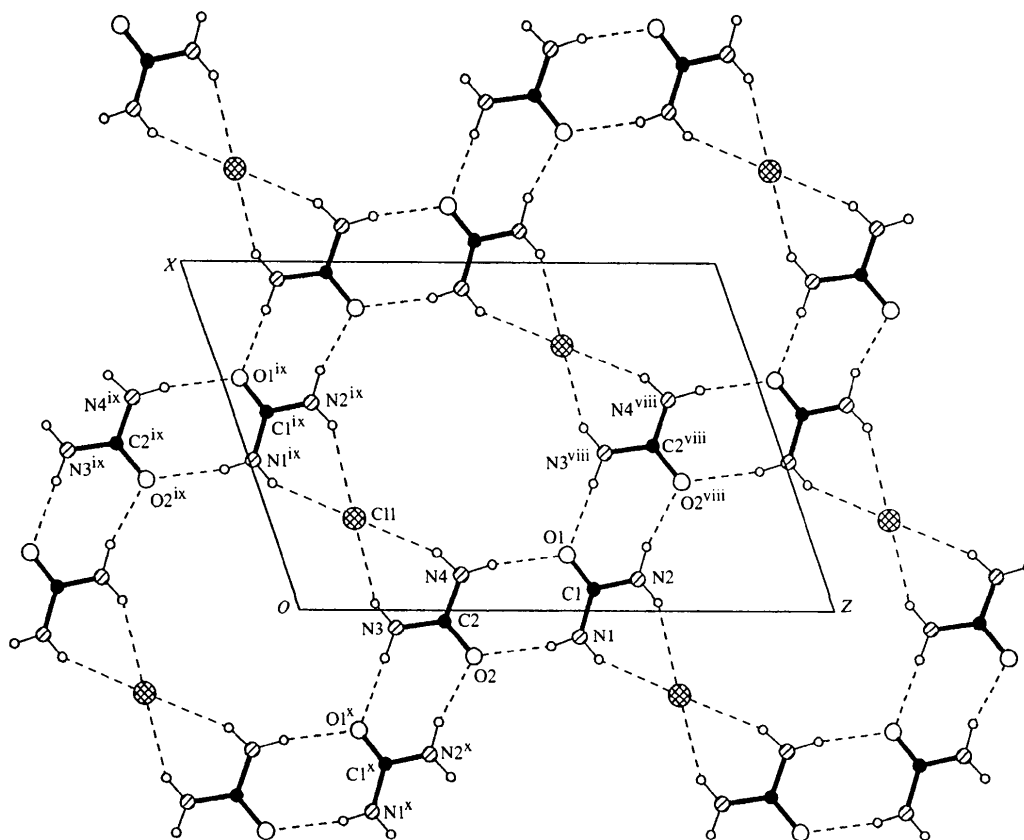

Fig. 3. The hydrogen-bonding scheme in a urea–anion layer in the crystal structure of $(n\text{-}C_3H_7)_4N^+Cl^-.2(NH_2)_2CO$ (2). The atom labels correspond to those given in Tables 3 and 5. Broken lines represent hydrogen bonds.

shown in a stereoview of the crystal structure, the resulting three-dimensional framework contains open channels that run parallel to the $[10\bar{1}]$ direction (Fig. 6). The well ordered tetrahedral $(n\text{-}C_3H_7)_4N^+$ cations are stacked in a single column within each channel.

3.3. Isomorphous channel-type structure of $(n\text{-}C_3H_7)_4\text{-}N^+Br^-.3(NH_2)_2CO.H_2O$ (4) and $(n\text{-}C_3H_7)_4N^+I^-.3(NH_2)_2CO.H_2O$ (5)

Complexes (4) and (5) are isomorphous with the same basic host skeleton and differ only in the halide anions; a preliminary account of the crystal structure of
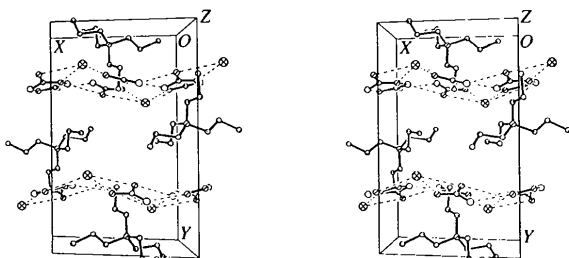

Fig. 4. Stereodrawing of the layer structure of (2). The origin of the unit cell lies at the upper right corner, with a pointing from right to left, b downwards and c towards the reader. Broken lines represent hydrogen bonds and atom types are distinguished by size and shading.

(4) was reported in 1973 (Rosenstein et al., 1973). As shown in Fig. 7, the dominant feature is a channel system extending parallel to the $[1\bar{1}0]$ direction. This channel framework is built of corrugated urea layers that are interlinked by cyclic $(H_2O-X)_2$ tetramers via $N-H\cdots X$ and $N-H\cdots O(\text{water})$ hydrogen bonds. Structural characteristics of an individual urea layer may be conveniently described with reference to the hydrogen-bonding scheme shown in Fig. 8 and Table 5.

Two independent urea molecules $C(1)$ and $C(2)$ in the asymmetric unit are connected by a pair of $N-H\cdots O$ hydrogen bonds to form a dimer. The dimers are arranged in a broadside manner and interlinked by pairs of lateral $N-H\cdots O$ hydrogen bonds to generate a puckered wide ribbon running parallel to the a axis; the deviation of its molecular moieties from co-planarity is shown by the torsion angles $C1-N1\cdots O2-C2 = -50.4$ and $C2-N4\cdots O1-C1 = -47.6°$ in (4) and the corresponding values in (5) are -47.1 and $-45.2°$, respectively. These wide ribbons are arranged side-by-side and cross-linked by other urea molecules derived from $C(3)$, each forming two $N-H\cdots O$ donor and four $O\cdots H-N$ acceptor hydrogen bonds to four urea molecules in adjacent ribbons to generate a corrugated layer (Fig. 8). The mean plane of this urea layer corresponds to (002) and the inter-layer separation is $1/c^* = 14.561$ (3) Å for (4) and 14.674 (3) Å for (5).
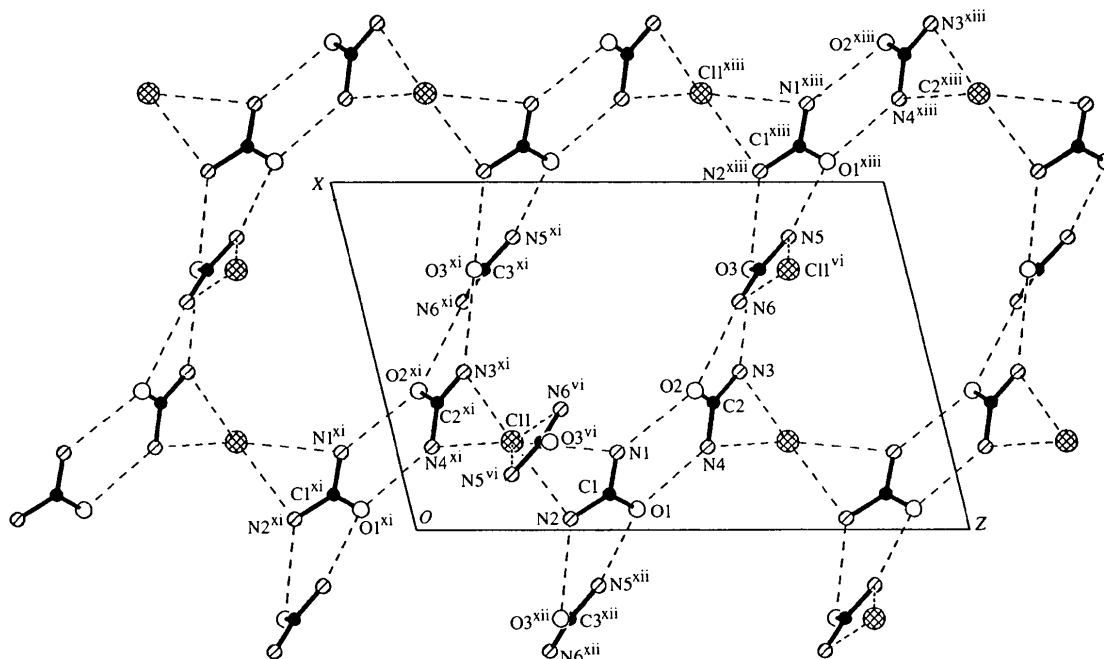

Fig. 5. Hydrogen-bonding scheme showing a layer of spiral urea ribbons cross-linked by $N-H\cdots Cl$ hydrogen bonds in $(n\text{-}C_3H_7)_4N^+Cl^-.3(NH_2)_2CO$ (3). The linkage of Cl(1) to a urea molecule belonging to an adjacent layer is also illustrated; this type of linkage generates the channel-type host lattice as shown in Fig. 6. The atom labels correspond to those given in Tables 3 and 5. Broken lines represent hydrogen bonds.
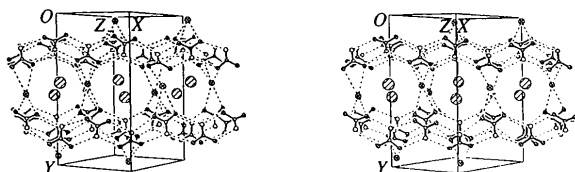
Fig. 6. Stereodrawing of the crystal structure of (3), showing the layers of urea ribbons at $y \simeq \frac{1}{4}$ and $\frac{3}{4}$ and the channels running parallel to [10$\bar{1}$]. Broken lines represent hydrogen bonds and atom types are distinguished by size and shading. For clarity the enclosed (*n*-C₃H₇)₄N⁺ ions are represented by large shaded circles.

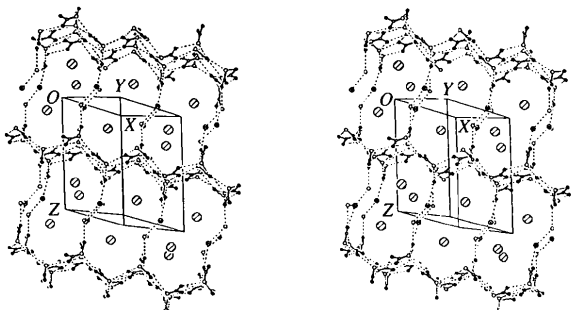Fig. 7. Stereodrawing of the crystal structure of (*n*-C₃H₇)₄N⁺X⁻.3(NH₂)₂CO.H₂O [*X* = Br for (4), *X* = I for (5)], showing the accommodation of a zigzag column of (*n*-C₃H₇)₄N⁺ ions in each channel running parallel to the [1$\bar{1}$0] direction. The host structure is built from corrugated urea layers and bridging cyclic (H₂O—*X*⁻)₂ tetramers. Note the peanut shape of the cross-section of each channel. Broken lines represent hydrogen bonds and atom types are distinguished by size and shading.

Pairs of centrosymmetrically related water molecules and halide ions are linked together by O—H···*X* hydrogen bonds to form a cyclic tetramer, the dimensions of which are shown in Table 6. Functioning as bridging units, these (H₂O—*X*⁻)₂ quadrilaterals are located between the corrugated urea layers and cross-link them to generate a channel host lattice, as illustrated in Fig. 7. Note that the urea molecules of type C(3) protrude from both sides of each urea layer, thus facilitating their linkage to the water–halide tetrameric units (Fig. 8).

The cross-section of a channel in the host lattice of (4) and (5) has the shape of a peanut and the diameter of each semicircular bulge is ∼ 7.56 Å for (4) and 7.59 Å for (5). The tetrahedral (*n*-C₃H₃)₄N⁺ cations are well ordered and arranged in a zigzag double column within each channel (Fig. 7).

3.4. Structural features and relationships

The present series of inclusion compounds exhibit urea–halide host lattices that are distinctly different from one another, depending on the stoichiometric ratio of urea-to-halide ion and the presence of co-crystallized water molecules. The anhydrous chloride complexes (2) (2/1/0) and (3) (3/1/0) feature layer and channel-type host lattices, respectively, constructed from urea ribbons that are bridged by chloride ions in different modes, while complex (1) (7/2/3) contains a novel channel framework built from urea ribbons that
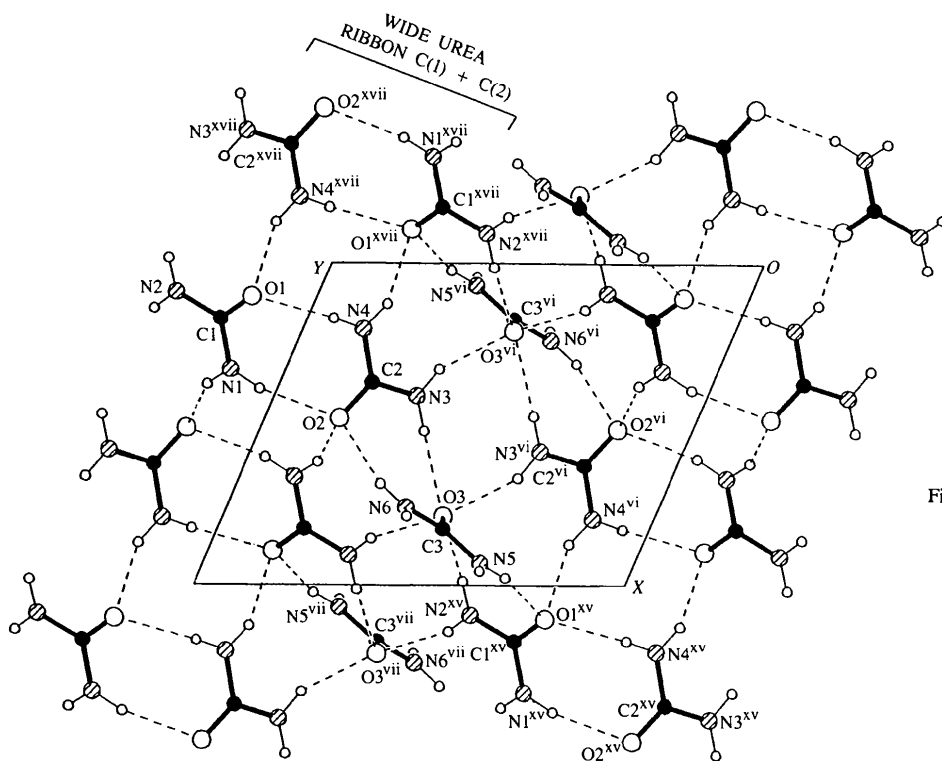

Fig. 8. Projection drawing of a hydrogen-bonded corrugated urea layer in (4) [or (5)] at $z = \frac{1}{2}$ comprising wide urea ribbons derived from C(1) + C(2) and bridging urea molecules derived from C(3), which point alternately up and down along the ribbon direction. The atom labels correspond to those given in Tables 4 and 5. Broken lines represent hydrogen bonds.

Table 5. *Selected bond distances (Å), bond angles (°) and torsion angles in the urea–halide anionic systems*

$2(n\text{-}C_3H_7)_4N^+F^-.7(NH_2)_2CO.3H_2O$ (1)

(i) Urea molecules

O1—C1	1.244 (7)	C1—N1	1.341 (7)
C1—N2	1.341 (7)	O2—C2	1.240 (7)
C2—N3	1.328 (7)	C2—N4	1.355 (7)
O3—C3	1.233 (7)	C3—N5	1.346 (7)
C3—N6	1.337 (7)	O4—C4	1.232 (7)
C4—N7	1.346 (7)	C4—N8	1.339 (7)
O5—C5	1.250 (7)	C5—N9	1.339 (7)
C5—N10	1.329 (7)	O6—C6	1.242 (7)
C6—N11	1.343 (8)	C6—N12	1.335 (8)
O7—C7	1.228 (8)	C7—N13	1.356 (8)
C7—N14	1.335 (8)		

O1—C1—N1	121.7 (5)	O1—C1—N2	121.3 (5)
N1—C1—N2	117.1 (5)	O2—C2—N3	122.0 (5)
O2—C2—N4	121.7 (5)	N3—C2—N4	116.3 (5)
O3—C3—N5	121.4 (5)	O3—C3—N6	121.9 (5)
N5—C3—N6	116.6 (5)	O4—C4—N7	122.4 (5)
O4—C4—N8	122.1 (5)	N7—C4—N8	115.5 (5)
O5—C5—N9	120.9 (5)	O5—C5—N10	121.4 (5)
N9—C5—N10	117.7 (5)	O6—C6—N11	121.1 (5)
O6—C6—N12	123.8 (5)	N11—C6—N12	115.0 (5)
O7—C7—N13	121.0 (5)	O7—C7—N14	123.3 (6)
N13—C7—N14	115.7 (6)		

(ii) Hydrogen bonding

N3···O1	3.010	N14···O1	3.004
N9^i···O1	3.052	N2···O2	3.046
N5···O2	2.936	N11^{vi}···O2	3.160
N4···O3	2.997	N7···O3	2.927
N6···O4	2.905	N10···O4	3.025
N12···O4	3.194	N8···O5	2.942
N13^{ii}···O5	2.933	N1^{ii}···O5	3.054
N6···O6	3.021	N5^{vi}···O6	2.861
O2w···O7^{iii}	2.879	O3w···O7	2.808
N1^{iv}···F1	2.823	N12···F1	2.737
N10···F1	3.003	N11···F1	3.187
O1w···F1	2.620	O1w···F1^{vii}	2.716
N3···F2	2.805	N14···F2	2.914
O2w···F2	2.705	O3w···F2	2.471
N2^{iv}···O1w	3.024	N9···O1w	2.961
N4···O2w	3.015	N13^{iii}···O2w	3.244
N7^v···O3w	2.993	N8^v···O3w	3.039

N12···F1···N10	69.3	N10···F1···N1^{iv}	98.9
N1^{iv}···F1···O1w	94.1	O1w^{vii}···F1···N12	116.6
N3···F2···O2w	85.1	O3w···F2···N14	81.9
O2w···F2···O3w	115.1	N14···F2···N3	74.6
F1···O1w···F1^{vii}	100.6	N2^{iv}···O1w···N9	95.3
F1···O1w···N9	93.6	F2···O2w···N4	86.2
N4···O2w···O7^{iii}	121.7	F2···O2w···O7^{iii}	119.6
O7···O3w···F2	92.9	F2···O3w···N8^v	108.9
O7···O3w···N7^v	121.8		

C1—N2···O2—C2	−40.9	C2—N4···O3—C3	−21.8
C3—N6···O4—C4	−25.3	C4—N8···O5—C5	−42.6
C5—N9···O1^{ii}—C1^{ii}	−72.1	C1^{ii}—N1^{ii}···O5—C5	−72.4
C5—N10···O4—C4	−35.3	C4—N7···O3—C3	−12.8
C3—N5···O2—C2	−40.9	C2—N3···O1—C1	−43.3

$(n\text{-}C_3H_7)_4N^+Cl^-.2(NH_2)_2CO$ (2)

(i) Urea molecules

O1—C1	1.244 (7)	C1—N1	1.334 (6)
C1—N2	1.333 (6)	O2—C2	1.257 (7)
C2—N3	1.340 (6)	C2—N4	1.329 (5)

Table 5 (cont.)

O1—C1—N1	122.0 (4)	O1—C1—N2	122.2 (4)
N1—C1—N2	115.8 (5)	O2—C2—N3	121.0 (4)
O2—C2—N4	122.0 (4)	N3—C2—N4	117.0 (5)

(ii) Hydrogen bonding

N3^{viii}···O1	2.937	N4···O1	2.949
N1···O2	2.941	N2^{x}···O2	2.967
N1^{ix}···Cl1	3.325	N2^{ix}···Cl1	3.332
N3···Cl1	3.317	N4···Cl1	3.366

N1^{ix}···Cl1···N2^{ix}	39.7	N2^{ix}···Cl1···N4	130.7
N1^{ix}···Cl1···N4	145.6	N3···Cl1···N4	39.8

C2—N4···O1—C1	9.1	C1—N2···O2^{viii}—C2^{viii}	−51.5
C2^{viii}—N3^{viii}···O1—C1	−33.3	C1—N1···O2—C2	−11.8

(n-C$_3$H$_7$)$_4$N$^+$Cl$^-$.3(NH$_2$)$_2$CO (3)
(i) Urea molecules

O1—C1	1.230 (6)	C1—N1	1.344 (5)
C1—N2	1.339 (5)	O2—C2	1.241 (5)
C2—N3	1.332 (5)	C2—N4	1.339 (5)
O3—C3	1.244 (5)	C3—N5	1.339 (5)
C3—N6	1.344 (5)		

O1—C1—N1	122.0 (4)	O1—C1—N2	122.0 (4)
N1—C1—N2	116.0 (4)	O2—C2—N3	122.4 (4)
O2—C2—N4	122.2 (4)	N3—C2—N4	115.5 (4)
O3—C3—N5	122.0 (4)	O3—C3—N6	121.4 (3)
N5—C3—N6	116.6 (4)		

(ii) Hydrogen bonding

N4···O1	2.899	N5^{xii}···O1	2.890
N1···O2	2.978	N6···O2	2.946
N3···O3	2.957	N2^{xiii}···O3	2.984
N1···Cl1	3.424	N2···Cl1	3.355
N3^{xi}···Cl1	3.304	N4^{xi}···Cl1	3.379
N5^{vi}···Cl1	3.303	N6^{vi}···Cl1	3.323

C1—N1···O2—C2	8.6	C2—N3···O3—C3	45.7
C3—N5···O1^{xiii}—C1^{xiii}	35.2	C1^{xiii}—N2^{xiii}···O3—C3	45.0
C3—N6···O2—C2	26.8	C2—N4···O1—C1	7.5

(n-C$_3$H$_7$)$_4$N$^+$Br$^-$.3(NH$_2$)$_2$CO.H$_2$O (4)
(i) Urea molecules

O1—C1	1.254 (4)	C1—N1	1.351 (3)
C1—N2	1.338 (3)	O2—C2	1.237 (3)
C2—N3	1.346 (4)	C2—N4	1.344 (3)
O3—C3	1.264 (4)	C3—N5	1.334 (3)
C3—N6	1.335 (4)		

O1—C1—N1	121.3 (2)	O1—C1—N2	121.0 (2)
N1—C1—N2	117.7 (3)	O2—C2—N3	120.6 (2)
O2—C2—N4	121.6 (2)	N3—C2—N4	117.8 (2)
O3—C3—N5	120.6 (3)	O3—C3—N6	121.1 (2)
N5—C3—N6	118.3 (3)		

(ii) Hydrogen bonding

N4···O1	2.977	N4^{xvii}···O1	2.984
N5^{xiv}···O1	2.992	N1···O2	2.956
N1^{vii}···O2	2.913	N6···O2	3.012
N3···O3	3.014	N3^{vi}···O3	2.947

Table 5 (cont.)

N2^{xv}···O3	3.001	N2^{vii}···O3	2.958
N5···Br1	3.490	O1w···Br1	3.360
O1w···Br1^{xvi}	3.389		

N5···Br1···O1w	64.4	Br1···O1w···Br1^{xvi}	113.1
N5···Br1···O1w^{xvi}	120.8		

C1−N1···O2−C2	−50.4	C2−N3···O3−C3	−48.6
C3−N5···O1^{xv}−C1^{xv}	−53.1	C1^{xv}−N2^{xv}···O3−C3	−48.6
C3−N6···O2−C2	−58.6	C2−N4···O1−C1	−47.6

(n-C$_3$H$_7$)$_4$N$^+$I$^-$.3(NH$_2$)$_2$CO.H$_2$O (5)

(i) Urea molecules

O1−C1	1.246 (5)	C1−N1	1.346 (4)
C1−N2	1.327 (4)	O2−C2	1.255 (4)
C2−N3	1.340 (4)	C2−N4	1.335 (4)
O3−C3	1.263 (4)	C3−N5	1.335 (4)
C3−N6	1.339 (5)		

O1−C1−N1	121.4 (3)	O1−C1−N2	121.2 (3)
N1−C1−N2	117.4 (4)	O2−C2−N3	120.6 (3)
O2−C2−N4	121.4 (3)	N3−C2−N4	118.0 (3)
O3−C3−N5	120.6 (3)	O3−C3−N6	121.0 (3)
N5−C3−N6	118.4 (3)		

(ii) Hydrogen bonding

N4···O1	2.991	N4^{xvii}···O1	2.972
N5^{xiv}···O1	3.012	N1···O2	2.972
N1^{vii}···O2	2.908	N6···O2	3.036
N3···O3	3.036	N3^{vi}···O3	2.967
N2^{xv}···O3	3.019	N2^{vii}···O3	2.968
N5···I1	3.722	O1w···I1	3.570
O1w···I1^{xvi}	3.672		

N5···I1···O1w	61.1	I1···O1w···I1^{xvi}	110.0
N5···I1···O1w^{xvi}	115.5		

C1−N1···O2−C2	−47.1	C2−N3···O3−C3	−51.6
C3−N5···O1^{xv}−C1^{xv}	−53.4	C1^{xv}−N2^{xv}···O3−C3	−51.8
C3−N6···O2−C2	−61.8	C2−N4···O1−C1	−45.2

Symmetry codes: (i) $x − 1, y − 1, z$; (ii) $1 + x, 1 + y, z$; (iii) $−x, \frac{1}{2} + y, \frac{1}{2} − z$; (iv) $x, 1 + y, z$; (v) $1 − x, y − \frac{1}{2}, \frac{1}{2} − z$; (vi) $1 − x, 1 − y, 1 − z$; (vii) $1 − x, 2 − y, 1 − z$; (viii) $\frac{1}{2} + x, \frac{1}{2} − y, \frac{1}{2} + z$; (ix) $\frac{1}{2} + x, \frac{1}{2} − y, z − \frac{1}{2}$; (x) $x − \frac{1}{2}, \frac{1}{2} − y, z − \frac{1}{2}$; (xi) $x, \frac{1}{2} − y, z − \frac{1}{2}$; (xii) $x − 1, \frac{1}{2} − y, z − \frac{1}{2}$; (xiii) $1 + x, \frac{1}{2} − y, \frac{1}{2} + z$; (xiv) $x − 1, 1 + y, z$; (xv) $1 + x, y − 1, z$; (xvi) $2 − x, 1 − y, −z$; (xvii) $−x, 2 − y, 1 − z$. Standard deviations in hydrogen-bond lengths and angles: (1), σ (l) $\simeq$ 0.008 Å, σ (θ) $\simeq$ 0.5°; (2), σ (l) $\simeq$ 0.007 Å, σ (θ) $\simeq$ 0.4°; (3), σ (l) $\simeq$ 0.007 Å, σ (θ) $\simeq$ 0.4°; (4), σ (l) $\simeq$ 0.003 Å, σ (θ) $\simeq$ 0.2°; (5), σ (l) $\simeq$ 0.008 Å, σ (θ) $\simeq$ 0.5°.

are bridged by fluoride ions, water molecules and other urea molecules. Isomorphous compounds (4) and (5) (3:1:1) exhibit a channel-type host lattice built of corrugated urea layers and centrosymmetric water–halide tetramers.

Notably the cyclic hydrogen-bonded water–halide dimers (H$_2$O−X^-)$_2$ (X = F, Br, I) make their presence in inclusion compounds (1), (4) and (5). As shown in Table 6, the dimensions of these centrosymmetric cyclic moieties can be compared with those reported in a variety of complexes, such as [Zn(en)$_3$]F$_2$.2H$_2$O (en = ethylenediamine) [(1a); Emsley et al., 1989], (C$_2$H$_5$)$_4$N$^+$Cl$^-$.(NH$_2$)$_2$CO.2H$_2$O (2a), (C$_2$H$_5$)$_4$N$^+$Cl$^-$.-H$_2$O (2b) (Loehlin & Kvick, 1978), 2[Mo(S$_2$C-NEt$_2$)$_4$]$^+$.(H$_2$O.Cl$^-$)$_2$.xCHCl$_3$ [$x \simeq$ 1.76, (2c); Mak et al.,

1985], (C$_2$H$_5$)$_4$N$^+$Br$^-$.(NH$_2$)$_2$CO.2H$_2$O [(4a); Mak & McMullan, 1988] and [(CH$_2$)$_6$N$_4$CH$_3$]Br.H$_2$O [(4b); Mak, 1984].

It is of interest to compare the modes of linkage of the urea molecules in the present series of complexes. In (1) twisted five-molecule urea ribbons are extended along different directions and cross-bridged by urea and water molecules, and fluoride ions to generate a channel-type host lattice. In the crystal structure of (2) the slightly buckled urea ribbon is composed of two independent urea molecules and a chloride bridge occurs at every other urea molecule along each ribbon to yield an anionic layer. In contrast to this, the urea ribbon in (3) is composed of three independent urea molecules, one of which is twisted out of plane, and the

Table 6. *Structural parameters for* $(H_2O - X^-)_2$ *systems in crystalline complexes*

Compound	$Ow \cdots X$ (Å)	$Ow \cdots X'$ (Å)	$X \cdots O \cdots X'$ (°)	Site symmetry	Reference
$(H_2O-F^-)_2$ in (1a)	2.586	2.679		None	Emsley *et al.* (1989)
$(H_2O-F^-)_2$ in (1)	2.620 (8)	2.716 (8)	100.6 (5)	$\bar{1}$	This work
$(H_2O-Cl^-)_2$ in (2a)	3.178 (5)	3.223 (5)	107.2 (4)	$\bar{1}$	Mak & McMullan (1988)
$(H_2O-Cl^-)_2$ in (2b)	3.204 (4)	3.247 (4)	103.8 (1)	$\bar{1}$	Loehlin & Kvick (1978)
$(H_2O-Cl^-)_2$ in (2c)	3.287 (8)	3.311 (8)	108.9 (4)	$\bar{1}$	Mak *et al.* (1985)
$(H_2O-Br^-)_2$ in (4a)	3.17 (2)	3.36 (2)	101 (1)	$\bar{1}$	Mak & McMullan (1988)
$(H_2O-Br^-)_2$ in (4b)	3.338 (5)	3.386 (5)	105.7 (4)	$\bar{1}$	Mak (1984)
$(H_2O-Br^-)_2$ in (4)	3.360 (3)	3.389 (3)	113.1 (2)	$\bar{1}$	This work
$(H_2O-I^-)_2$ in (5)	3.570 (8)	3.672 (8)	110.0 (5)	$\bar{1}$	This work

chloride bridge occurs at every third molecule along each ribbon, thereby enabling the connection between planar arrays to generate a uni-directional channel network. While the wide urea ribbons built from the broadside linkage of cyclic urea dimers in (4) and (5) are the same as those found in $(C_2H_5)_4N^+Cl^-.-2(NH_2)_2CO$ (Li & Mak, 1998b), they are further bridged by additional out-of-plane urea molecules to generate a corrugated urea layer.

References

Brown, M. E. & Hollingsworth, M. D. (1995). *Nature*, **376**, 323–327.

Emsley, J., Arif, M., Bates, P. A. & Hursthouse, M. B. (1989). *J. Chem. Soc. Chem. Commun.* pp. 738–739.

George, A. R. & Harris, K. D. M. (1995). *J. Mol. Graphics*, **13**, 138–141.

Harris, K. D. M. (1996). *J. Mol. Struct.* **374**, 241–250.

Harris, K. D. M., Smart, S. P. & Hollingsworth, M. D. (1991). *J. Chem. Soc. Faraday Trans.* **87**, 3423–3429.

Harris, K. D. M. & Thomas, J. M. (1990). *J. Chem. Soc. Faraday Trans.* **86**, 2985–2996.

Hollingsworth, D. D. & Harris, K. D. M. (1996). In *Comprehensive Supramolecular Chemistry. Vol. 6. Solid-State Supramolecular Chemistry: Crystal Engineering*, edited by D. D. MacNicol, F. Toda & R. Bishop, Ch. 7, pp. 177–237. Oxford: Pergamon Press.

Imashiro, F. (1993). *Reactivity in Molecular Crystals*, edited by Y. Ohashi, pp. 91–92. Tokyo: Kodansha.

Kopfmann, G. & Huber, R. (1968). *Acta Cryst.* A**24**, 348–351.

Li, Q. & Mak, T. C. W. (1996a). *Supramol. Chem.* **8**, 73–82.

Li, Q. & Mak, T. C. W. (1996b) *Acta Cryst.* C**52**, 2830–2832.

Li, Q. & Mak, T. C. W. (1997). *Supramol. Chem.* **8**, 147–156. Part 5 of this series.

Li, Q. & Mak, T. C. W. (1998a). In preparation.

Li, Q. & Mak, T. C. W. (1998b). *J. Incl. Phenom.* In the press. Part 4 of this series.

Li, Q., Yip, W. H. & Mak, T. C. W. (1995). *J. Incl. Phenom.* **23**, 233–244. Part 2 of this series.

Loehlin, J. H. & Kvick, Å. (1978). *Acta Cryst.* B**34**, 3488–3490.

Mak, T. C. W. (1984). *Inorg. Chem.* **23**, 620–622.

Mak, T. C. W. (1990). *J. Incl. Phenom.* **8**, 199–214.

Mak, T. C. W. & McMullan, R. K. (1988). *J. Incl. Phenom.* **6**, 473–481. Part 1 of this series.

Mak, T. C. W., So, S. P., Chieh, C. & Jasim, K. S. (1985). *J. Mol. Struct.* **127**, 375–377.

Mak, T. C. W., Yip, W. H. & Li, Q. (1995). *J. Am. Chem. Soc.* **117**, 11995–11996. Part 3 of this series.

Rosenstein, D., McMullan, R. K., Schwarzenbach, D. & Jeffrey, G. A. (1973). *Am. Cryst. Assoc. Abstr. Papers (Summer Meeting)*, p. 152.

Shannon, I. J., Harris, K. D. M., Rennie, A. J. O. & Webster, M. B. (1993). *J. Chem. Soc. Faraday Trans.* **89**, 2023–2029.

Sheldrick, G. M. (1982). *Computational Crystallography*, edited by D. Sayre, pp. 506–514. New York: Oxford University Press.

Smith, A. E. (1952). *Acta Cryst.* **5**, 224–235.

Sparks, R. A. (1976). *Crystallographic Computing Techniques*, edited by F. R. Ahmed, p. 452. Copenhagen: Munksgaard.