

# Urea-Water-Anion Lattices. Part 1. Crystal Structures of $(C_2H_5)_4N^+X^-\cdot(NH_2)_2CO\cdot 2H_2O$ ( $X = Cl, Br, CN$ ), an Isomorphous Series of Layer-Type Inclusion Complexes

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**Abstract.** The title ternary complexes (**1**,  $X = Cl$ ; **2**,  $X = Br$ ; **3**,  $X = CN$ ) have been prepared and characterized by X-ray crystallography. Crystal data: space group  $P2_1/n$ ,  $Z = 4$ ; **1**,  $a = 7.505(2)$ ,  $b = 14.556(4)$ ,  $c = 14.453(3)$  Å,  $\beta = 98.13(2)^\circ$ , and  $R_F = 0.088$  for 1831 observed  $MoK_\alpha$  data; **2**,  $a = 7.483(1)$ ,  $b = 14.643(6)$ ,  $c = 14.443$  Å,  $\beta = 98.25(2)^\circ$ , and  $R_F = 0.113$  for 923 data; **3**,  $a = 7.490(2)$ ,  $b = 14.646(5)$ ,  $c = 14.594(5)$  Å,  $\beta = 98.85(5)^\circ$ , and  $R_F = 0.082$  for 915 data. In the isomorphous crystal structure of **1** and **2**, ordered  $(C_2H_5)_4N^+$  cations are sandwiched between puckered layers matching the (020) family of planes, each being constructed from the cross-linking of planar zigzag chains of hydrogen-bonded urea molecules by the water molecules and halide ions. Compound **3** has the same structure except that its cyanide group is disordered.

**Key words.** Inclusion complex, layer structure, hydrogen bonding, urea, tetraethylammonium salt.

**Supplementary Data** relating to this article are deposited with the British Library as Supplementary Publication No. SUP 82066 (30 pages).

## 1. Introduction

It is well known that urea forms non-stoichiometric, channel-type inclusion compounds with straight-chain hydrocarbons which include paraffins, olefins, carboxylic acids, ketones and ethers [1, 2]. These adducts usually dissociate when exposed to water. Crystalline complexes derived from the interaction of urea in aqueous solution with quaternary ammonium salts, both symmetrical [3] and unsymmetrical [4, 5], have been investigated in regard to their preparation, composition and phase diagrams. However, there has been no systematic study on the nature of this class of ternary complexes other than a preliminary report on the crystal structure of  $(n-C_3H_7)_4N^+Br^-\cdot 3(NH_2)_2CO\cdot H_2O$  [6].

Our interest in the title complexes also stems from another line of consideration. Crystalline hydrates of tetraalkylammonium salts with bulky alkyl groups and high hydration

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numbers, as typified by  $(i\text{-C}_5\text{H}_{11})_4\text{N}^+\text{F}^- \cdot 38 \text{H}_2\text{O}$  [7] and  $(n\text{-C}_4\text{H}_9)_4\text{N}^+\text{F}^- \cdot n \text{H}_2\text{O}$  ( $n = 32.8$ ) [8], are clathrates featuring hydrogen-bonded cageworks constructed from the packing of various polyhedra [9–11]. The fluoride ions in these anionic host lattices are located at the polyhedral vertices, generally with statistical distribution over two or more sites. A reduction in size of the alkyl substituents, and concomitantly the hydration number, results in less organized water-anion host structures. These range from the three-dimensional framework in  $4(\text{C}_2\text{H}_5)_4\text{N}^+\text{F}^- \cdot 11 \text{H}_2\text{O}$  [12], through the two-dimensional open channel systems in  $(\text{CH}_3)_4\text{N}^+\text{F}^- \cdot 4 \text{H}_2\text{O}$  [13] and  $(\text{C}_2\text{H}_5)_4\text{N}^+\text{Cl}^- \cdot 4 \text{H}_2\text{O}$  [14], the puckered layer in  $(\text{C}_2\text{H}_5)_4\text{N}^+\text{CH}_3\text{COO}^- \cdot 4 \text{H}_2\text{O}$  [15], the one-dimensional channel in  $[(\text{CH}_3)_4\text{N}^+]_2\text{SO}_4^{2-} \cdot 4 \text{H}_2\text{O}$  [16], to the discrete cyclic  $(\text{H}_2\text{O} \cdot \text{X}^-)_2$  moiety [17] in  $(\text{C}_2\text{H}_5)_4\text{N}^+\text{Cl}^- \cdot \text{H}_2\text{O}$  [18]. In the case of lower hydrates of unsymmetrical quaternary ammonium salts, the monohydrate [19] and hemihydrate [20] of dodecyldimethylpropylammonium bromide have been found to contain the  $(\text{H}_2\text{O} \cdot \text{Br}^-)_2$  and bent  $(\text{H}_2\text{O} \cdot \text{Br}^- \cdot \text{H}_2\text{O})$  systems, respectively. The introduction of urea as an additional ingredient for the construction of new anionic host lattices has been of interest to us, and we now report our structural study of the title series of isomorphous complexes (**1**, X = Cl; **2**, X = Br; **3**, X = CN).

## 2. Experimental

The tetraethylammonium salts were obtained from Eastman Kodak (chloride and bromide) and Fluka (cyanide). Each salt and urea were mixed in a ratio of 1 : 2, and a minimum quantity of water was added to dissolve the solid mixture. When the solution was subjected to slow evaporation at room temperature in a desiccator charged with drierite, colorless crystals appeared in the form of flat needles.\* A selected crystal was taken out of the mother liquor, quickly covered with petroleum jelly, cut to a suitable size, and sealed inside a 0.5 mm Lindemann glass capillary. Measurement of the crystal data and reflection intensities (which decreased rapidly with increasing Bragg angle) on a Nicolet R3m diffractometer using  $\text{MoK}_\alpha$  radiation ( $\lambda = 0.71069 \text{ \AA}$ ) followed the procedures described previously [21], and the relevant parameters are summarized in Table I.

Absorption corrections were applied by fitting a pseudo ellipsoid to the azimuthal scan data of twenty strong reflections spread over a range of  $2\theta$ -values [22, 23]. The structure of the chloride complex **1** was solved by direct phase determination guided by negative quartets [24]. The cyanide group in **3** was found to be disordered, and its scattering power was represented by N(4) and half-carbon atoms C(10) and C(11).

All non-hydrogen atoms except these two half-carbon atoms were assigned anisotropic thermal parameters. The amido, methylene and methyl H atoms were generated geometrically; those of the first two types were allowed to ride on their respective parent N and C atoms, and the methyl groups were treated as rigid groups. The water protons in **1** and **2** appeared in subsequent difference Fourier maps and their parameters were not varied in least-squares cycles. Isotropic temperature factors (about 20% larger than those of the corresponding parent atoms) were assigned to the H atoms.

Computations were performed on a Data General Nova 3 minicomputer using the SHELXTL program package [25]. Analytic expressions of neutral-atom scattering factors

\* A small quantity of another crystalline phase of polyhedral morphology and as yet unidentified composition was obtained after prolonged standing.

Table I. Data collection and processing parameters for inclusion complexes of general formula  $(C_2H_5)_4N^+X^-(NH_2)_2CO \cdot 2 H_2O$ .

Complex	<b>1</b>	<b>2</b>	<b>3</b>
Anion X <sup>-</sup>	Cl <sup>-</sup>	Br <sup>-</sup>	CN <sup>-</sup>
Molecular weight	261.79	306.25	252.35
Cell parameters in space group $P2_1/n$			
<i>a</i> , Å	7.505(2)	7.483(1)	7.490(2)
<i>b</i> , Å	14.556(4)	14.643(6)	14.646(5)
<i>c</i> , Å	14.453(3)	14.443(5)	14.594(5)
$\beta$ , deg	98.13(2)	98.25(2)	98.85(5)
<i>V</i> , Å <sup>3</sup>	1563.0(6)	1566.2(8)	1581.9(8)
Density (floatation in <i>n</i> -hexane/CCl <sub>4</sub> ), g cm <sup>-3</sup>	1.133	1.300	1.083
Density (calcd. with <i>Z</i> = 4), g cm <sup>-3</sup>	1.113	1.299	1.060
Absorption coefficient, cm <sup>-1</sup>	2.42	25.97	0.73
Crystal size, mm	0.54 × 0.50 × 0.36	0.44 × 0.36 × 0.30	0.20 × 0.16 × 0.16
Scan type and speed		$\omega$ -2 $\theta$ ; 2.03–8.37 deg min <sup>-1</sup>	
Scan range		1° below <i>K</i> $\alpha_1$ to 1° above <i>K</i> $\alpha_2$	
Background counting	stationary counts for one-half of scan time at each end of scan		
$2\theta_{max}$ for collection			
range ( <i>h</i> , <i>k</i> , $\pm l$ ), deg	50°	42°	40°
Mean $\mu_r$	0.055	0.47	0.006
Transmission factors	0.839 to 0.940	0.304 to 0.346	0.952 to 0.968
Unique data measured	2314	1502	1199
Observed data with $ F_o  > 3\sigma( F_o )$ , <i>n</i>	1831	923	915
Number of variables, <i>p</i>	157	157	165
$(\Delta/\sigma)_{max}$	0.098	0.098	0.065
$R_F = \sum   F_o  -  F_c   / \sum  F_o $	0.088	0.113	0.082
Constant <i>g</i> in weighting scheme $w = [\sigma^2(F_o) + g F_o ^2]^{-1}$	0.0015	0.0020	0.0015
$R_G = [\sum w( F_o  -  F_c )^2 / \sum w F_o ^2]^{1/2}$	0.128	0.155	0.120
$S = [\sum w( F_o  -  F_c )^2 / (n - p)]^{1/2}$	2.403	2.553	2.361
Residual extrema in final difference map, <i>e</i> Å <sup>-3</sup>	1.12 to -0.26	1.59 to -0.87	0.35 to -0.17

were employed, and anomalous dispersion corrections were incorporated [26]. Blocked-cascade least-squares refinement [27] converged to the *R* indices and other parameters listed in Table I.

### 3. Results and Discussion

The final positional and thermal parameters of **1** and **2** are listed in Table II, and those of **3** in Table III. Anisotropic temperature factors, hydrogen coordinates, and structure factors have been deposited as Supplementary Data.

#### 3.1. THE UREA-WATER-ANION LATTICE IN **1** AND **2**

The location of the water protons in stereochemically plausible positions is consistent with an ordered layer structure, which may be conveniently described with reference to the hydrogen bonding scheme shown in Figure 1 and Table IV. The urea molecules are linked

Table II. Atomic coordinates ( $\times 10^4$ ) and thermal parameters<sup>a</sup> ( $\text{\AA}^2 \times 10^3$ ) for  $(\text{C}_2\text{H}_5)_4\text{N}^+\text{Cl}^-\cdot(\text{NH}_2)_2\text{CO}\cdot 2\text{H}_2\text{O}$  (1) and  $(\text{C}_2\text{H}_5)_4\text{N}^+\text{Br}^-\cdot(\text{NH}_2)_2\text{CO}\cdot 2\text{H}_2\text{O}$  (2).

Atom	Complex 1, X = Cl				Complex 2, X = Br			
	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>
<i>(i)</i> Halide ion								
X	3447(2)	4804(1)	1468(1)	88(1)	3191(5)	5076(2)	1348(2)	138(1)
<i>(ii)</i> Water molecules								
O(1)	-130(7)	5790(4)	1946(3)	113(1)	-276(25)	5953(12)	1999(11)	150(4)
O(2)	-3169(6)	5701(4)	719(3)	108(1)	-3145(24)	5837(15)	794(13)	178(4)
<i>(iii)</i> Urea molecule								
O(3)	2563(4)	4937(2)	5174(2)	54(1)	2566(12)	4928(7)	5169(6)	57(3)
C(1)	2313(5)	4977(3)	4307(3)	43(1)	2304(16)	4994(9)	4316(10)	42(3)
N(1)	638(5)	4998(3)	3819(3)	56(1)	623(16)	5050(8)	3832(9)	61(3)
N(2)	3698(5)	5001(3)	3812(3)	57(1)	3673(17)	5061(8)	3812(8)	66(3)
<i>(iv)</i> Tetraethylammonium ion								
N(3)	3499(4)	2326(3)	6688(3)	48(1)	3516(15)	2224(8)	6508(8)	44(3)
C(2)	4307(7)	1869(4)	5891(4)	68(1)	4341(28)	1855(13)	5675(11)	94(4)
C(3)	5034(8)	2529(5)	5232(4)	100(1)	4971(24)	2556(14)	5061(13)	98(4)
C(4)	2820(6)	1559(4)	7256(3)	63(1)	2881(21)	1410(12)	7001(13)	76(4)
C(5)	2011(7)	1859(4)	8098(4)	80(1)	2079(23)	1623(14)	7867(12)	91(4)
C(6)	4872(6)	2905(4)	7291(4)	64(1)	4949(19)	2774(11)	7139(11)	56(4)
C(7)	6503(7)	2390(5)	7752(4)	89(1)	6571(21)	2224(15)	7540(14)	103(4)
C(8)	1977(6)	2977(3)	6317(4)	60(1)	2000(21)	2875(11)	6200(12)	62(4)
C(9)	464(7)	2556(5)	5664(4)	91(1)	457(27)	2451(15)	5538(15)	119(4)

<sup>a</sup> Equivalent isotropic temperature factor  $U_{\text{eq}}$  defined as  $1/3$  of the trace of the orthogonalised  $U$  matrix.

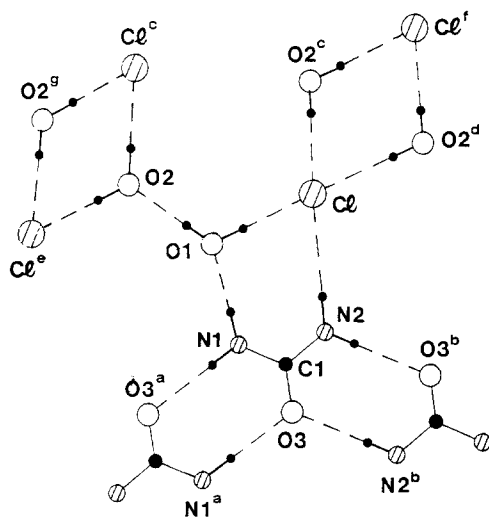


Fig. 1. Perspective view, along the  $b$  axis, of a portion of an urea-water-chloride layer consolidated by hydrogen bonding. The idealized positions of the ordered H atoms are represented by small black circles, and hydrogen bonds are represented by broken lines. The atom labels correspond to those given in Tables II and IV. Symmetry transformations: <sup>a</sup> $-x, 1-y, 1-z$ ; <sup>b</sup> $1-x, 1-y, 1-z$ ; <sup>c</sup> $-x, 1-y, -z$ ; <sup>d</sup> $1+x, y, z$ ; <sup>e</sup> $-1+x, y, z$ ; <sup>f</sup> $1-x, 1-y, -z$ ; <sup>g</sup> $-1-x, 1-y, -z$ .

Table III. Atomic coordinates ( $\times 10^4$ ) and thermal parameters<sup>a</sup> ( $\text{\AA}^2 \times 10^3$ ) for  $(\text{C}_2\text{H}_5)_4\text{N}^+\text{CN}^-(\text{NH}_2)_2\text{CO}\cdot 2\text{H}_2\text{O}$  (3).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}/U_{\text{iso}}$
<i>(i)</i> Water molecules				
O(1)	-327(12)	5892(5)	1972(5)	193(1)
O(2)	-3229(13)	5770(6)	838(6)	221(2)
<i>(ii)</i> Urea molecule				
O(3)	2565(5)	4920(3)	5173(3)	77(1)
C(1)	2301(8)	5009(4)	4323(4)	60(1)
N(1)	623(7)	5049(4)	3834(4)	74(1)
N(2)	3677(7)	5050(4)	3826(4)	78(1)
<i>(iii)</i> Tetraethylammonium ion				
N(3)	3430(7)	2253(3)	6504(3)	65(1)
C(2)	4221(10)	1835(5)	5695(5)	98(1)
C(3)	4892(11)	2542(6)	5066(5)	126(2)
C(4)	2813(10)	1430(5)	7034(6)	95(1)
C(5)	2038(10)	1683(6)	7913(6)	129(2)
C(6)	4847(9)	2795(5)	7131(5)	83(1)
C(7)	6524(10)	2280(6)	7569(6)	125(2)
C(8)	1896(10)	2913(5)	6181(5)	96(1)
C(9)	360(11)	2508(7)	5528(8)	147(2)
<i>(iv)</i> Atoms representing the scattering of the disordered cyanide ion				
N(4)	3254(13)	5016(8)	1444(10)	222(2)
C(10)	2121(22)	5214(15)	1528(15)	178(3)
C(11)	4019(25)	5088(20)	1131(20)	263(3)

<sup>a</sup> Equivalent isotropic temperature factor  $U_{\text{eq}}$  defined as 1/3 of the trace of the orthogonalised  $U$  matrix. For C(10) and C(11) of half site occupancy,  $U_{\text{iso}}$  takes the form  $-8\pi^2 U_{\text{iso}} \sin^2\theta/\lambda^2$ .

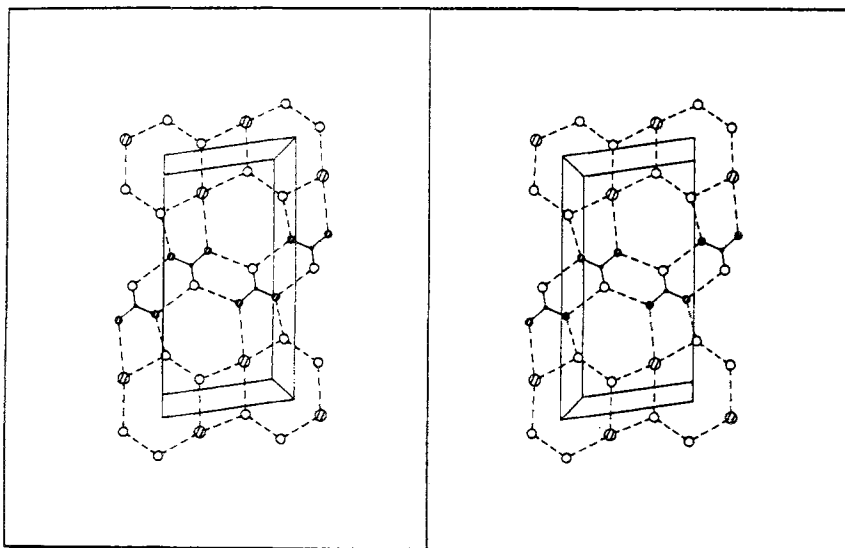


Fig. 2. Stereo drawing showing the extent of puckering in a urea-water-halide layer in the crystal structure of 1 and 2. The origin of the unit cell lies at the upper left corner, with  $a$  pointing from left to right,  $b$  towards the reader, and  $c$  downwards.

Table IV. Bond distances (Å) and angles (deg) in the urea-water-anion layer structure.\*

	1, X = Cl	2, X = Br	3, X = N(4)
(i) Urea molecule			
C(1)—O(3)	1.242	1.22	1.23
C(1)—N(1)	1.352	1.36	1.34
C(1)—N(2)	1.344	1.34	1.35
O(3)—C(1)—N(1)	121.6	122	122.1
O(3)—C(1)—N(2)	121.4	122	121.8
N(1)—C(1)—N(2)	117.0	116	116.0
(ii) Hydrogen bonding			
N(1)···O(3) <sup>a</sup>	2.981	2.97	2.98
N(1)···O(1)	2.923	2.95	2.97
N(2)···O(3) <sup>b</sup>	2.978	2.99	2.97
N(2)···X	3.379	3.53	3.44
O(1)···X	3.204	3.16	3.17
O(1)···O(2)	2.687	2.58	2.53
O(2)···X <sup>c</sup>	3.223	3.36	3.52
O(2)···X <sup>e</sup>	3.178	3.17	3.11
C(1)—O(3)···N(1) <sup>a</sup>	118.3	118	118.1
C(1)—O(3)···N(2) <sup>b</sup>	119.5	120	119.2
N(1) <sup>a</sup> ···O(3)···N(2) <sup>b</sup>	121.8	122	122.2
C(1)—N(1)···O(1)	122.7	125	125.4
C(1)—N(1)···O(3) <sup>a</sup>	120.0	120	119.6
O(1)···N(1)···O(3) <sup>a</sup>	111.9	110	109.8
C(1)—N(2)···X	126.5	125	125.6
C(1)—N(2)···O(3) <sup>b</sup>	119.0	118	118.8
O(3) <sup>b</sup> ···N(2)···X	114.3	117	115.5
N(1)···O(1)···O(2)	129.0	130	129.2
N(1)···O(1)···X	87.8	90	87.7
O(2)···O(1)···X	119.7	115	119.1
N(2)···X···O(1)	71.1	71	72.5
N(2)···X···O(2) <sup>c</sup>	171.7	156	161.1
N(2)···X···O(2) <sup>d</sup>	111.9	107	109.4
O(1)···X···O(2) <sup>c</sup>	111.9	122	118.7
O(1)···X···O(2) <sup>d</sup>	128.6	136	135.3
X <sup>c</sup> ···O(2)···X <sup>d</sup>	107.2	101	105.7
O(1)···O(2)···X <sup>c</sup>	126.1	122	121.4
O(1)···O(2)···X <sup>d</sup>	116.1	136	121.4

\* Symmetry transformations are given in Fig. 1. Estimated standard deviations of individual bond distances and angles are 0.005 Å and 0.04° for **1**, 0.02 Å and 1° for **2**, and 0.01 Å and 0.07° for **3**.

by pairs of N—H···O hydrogen bonds, each arranged about an inversion center, to form a nearly planar zigzag chain parallel to the *a* axis (Fig. 2). The water molecules and halide ions constitute a hydrogen-bonded ribbon of edge-sharing (H<sub>2</sub>O·X<sup>-</sup>)<sub>2</sub> parallelograms and six-membered (2 H<sub>2</sub>O·X<sup>-</sup>)<sub>2</sub> rings. The latter two moieties are each centered at an inversion center, such that the ribbon is aligned in the direction of the *a* axis in between two urea chains. Cross-linking between the two series of alternating urea chains and water-halide ribbons, by hydrogen bonds of the types N—H···O<sub>w</sub> and N—H···Cl, gives rise to a puckered layer normal to the *b* axis (Fig. 2).

The accuracy of the present structure analysis (especially for **2** and **3**) is severely limited by the unfavorable data-to-parameter ratio. Nevertheless, the measured dimensions of the

urea molecule (Table IV) are consistent with the best available data as determined in tetragonal urea at room temperature [ $C-O = 1.260(3)$ ,  $C-N = 1.352(2)$  Å,  $O-C-N = 121.7(1)$ ,  $N-C-N = 116.6(1)^\circ$ ] [28] and at 12 K [ $1.262(1)$ ,  $1.345(1)$  Å,  $121.4(1)$ ,  $117.2(1)^\circ$ ] [29]. In the centrosymmetric cyclic  $(H_2O \cdot X^-)_2$  moiety, the non-equivalence of the two  $O-H \cdots X$  hydrogen bonds follows the rule established previously from experimental data and theoretical calculation [17], but the observed  $Br \cdots O \cdots Br$  angle of  $101(1)^\circ$  is much smaller than typical values such as  $105.7(4)^\circ$  in  $[(CH_2)_6N_4CH_3]^+ Br^- \cdot H_2O$  [30] and  $108.0(1)^\circ$  in  $[(n-C_{12}H_{25})Me_2(n-Pr)N]^+ Br^- \cdot H_2O$  [19]. The coordination geometry about  $X^-$  is that of a highly flattened and distorted tetrahedron, with bond angles of  $71.1(4)$ – $171.7(4)^\circ$  subtended at the chloride ion in **1**, for example. The bonding configuration about N(2) is virtually planar (sum of valence angles  $\Sigma = 359.8^\circ$  in **1**), whereas those of N(1), O(2) and O(1) become increasingly pyramidal ( $\Sigma = 354.6$ ,  $349.4$  and  $336.5^\circ$ , respectively), the trend being clearly discernible from Fig. 2.

### 3.2. THE TETRAETHYLAMMONIUM ION

The tetrahedral cation is well ordered and nearly attains its idealised 222 molecular symmetry (see Fig. 3). Its averaged dimensions in **1** are  $N-C = 1.519(6)$ ,  $C-C = 1.504(8)$  Å,  $C-N-C = 109.5(3)$ , and  $N-C-C = 115.2(4)^\circ$ . Individual bond distances and angles are given in the Supplementary Data.

### 3.3. CRYSTAL STRUCTURE

A stereo view of the crystal structure is illustrated in Fig. 3. It is seen that the cations are sandwiched between hydrophilic layers which correspond to the (020) family of planes.

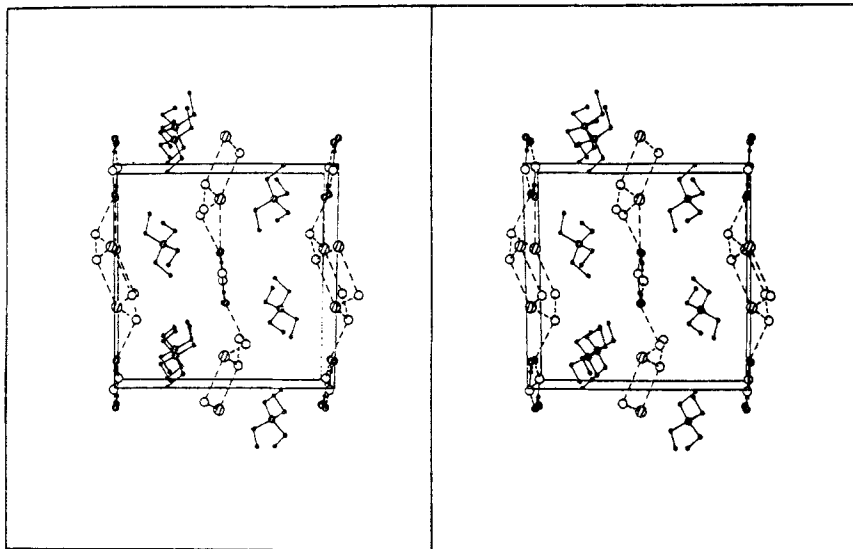


Fig. 3. Stereo drawing of the crystal structure of  $(C_2H_5)_4N^+X^-(NH_2)_2CO \cdot 2H_2O$ . The origin of the unit cell lies at the lower left corner, with  $a$  pointing towards the reader,  $b$  from left to right, and  $c$  upwards. Hydrogen atoms have been omitted for clarity, and atom types are distinguished by size and shading. Broken lines represent hydrogen bonds.

The interlayer spacing of  $b/2$  in the present series of complexes is comparable to the value  $1/b^* = 7.39 \text{ \AA}$  in triclinic  $(\text{C}_2\text{H}_5)_4\text{N}^+\text{CH}_3\text{COO}^- \cdot 4 \text{H}_2\text{O}$  [15].

The host lattice in **3** is similar to that of **1** and **2** except for the disorder of the cyanide group. In the model used for refinement, the latter was represented by N(4) and half-carbon atoms C(10) and C(11), and the water protons which failed to appear on the final difference map were excluded in the least-squares calculations.

#### 3.4. COMPARISON WITH RELATED STRUCTURES

Previous work on the ternary system  $(\text{C}_2\text{H}_5)_4\text{N}^+\text{X}^-$ -urea-water ( $\text{X} = \text{Cl}, \text{Br}$ ) indicated the existence of two complexes in the form of flat needles [3]. Their stoichiometric compositions, established analytically to have mole ratios of 1 : 1 : 0.8 and 1 : 2.5 : 0 (anhydrous), are entirely different from the present mole ratio of 1 : 1 : 2.

The planar zigzag urea chain in the present structure contrasts with the relatively open framework in tetragonal urea [28] and the helical spirals in both the urea channel adducts [1, 2] and the isomorphous series  $(n\text{-C}_3\text{H}_7)_4\text{N}^+\text{X}^- \cdot 3(\text{NH}_2)_2\text{CO} \cdot \text{H}_2\text{O}$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) [6, 31].

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