

Hydrogen-Bonded Urea-Anion Host Lattices. Part 4. Comparative Study of Inclusion Compounds of Urea with Tetraethylammonium and Tetraethylphosphonium Chlorides

QI LI and THOMAS C. W. MAK*

Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong

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Abstract. New inclusion complexes $(\text{C}_2\text{H}_5)_4\text{E}^+\text{Cl}^- \cdot 2(\text{NH}_2)_2\text{CO}$ (**1**, E = N; **2**, E = P) have been prepared and characterized by X-ray crystallography. Crystal data, $\text{MoK}\alpha$ radiation: **1**, space group $P2_1/c$, $Z = 4$, $a = 10.492(6)$, $b = 14.954(8)$, $c = 10.335(6)$ Å, $\beta = 91.02(5)^\circ$, $R_F = 0.050$ for 1527 observed data; **2**, space group $Pmn2_1$, $Z = 2$, $a = 7.446(1)$, $b = 9.200(2)$, $c = 12.753(3)$ Å, $R_F = 0.079$ for 519 observed data. In compound **1** the tetraethylammonium ions are sandwiched between puckered layers, which are constructed from the linkage of chloride ions and wide urea ribbons each composed of a broadside arrangement of centrosymmetric hydrogen-bonded urea dimers. In the crystal structure of **2**, hydrogen-bonded urea ribbons running parallel to [100] are connected by chloride ions to generate a sawtooth wave layer, and stacked columns of tetraethylphosphonium cations are sandwiched between adjacent layers.

Key words: Urea, tetraethylammonium, tetraethylphosphonium, hydrogen bonding, inclusion compound.

Supplementary Data relating to this article have been deposited with the British Library as Supplementary Publication No. SUP 82216 (11 pages).

1. Introduction

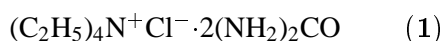
The chemistry of urea and thiourea inclusion compounds has received much attention and is still a subject of continuing interest since their discovery about fifty years ago [1, 2]. Urea is a good host molecule because it has a well-defined trigonal planar geometry and can form at least six hydrogen bonds [3]. The guest molecules in the classical channel-type urea inclusion compounds comprise straight-chain hydrocarbons such as paraffins, olefins, carboxylic acids, ketones and esters, and the host lattice contains linear, parallel, non-intersecting channels within which the guest molecules are accommodated [4–12].

Several years ago we reported the crystal structures of a series of isomorphous urea–tetraethylammonium salt hydrate complexes, namely $(\text{C}_2\text{H}_5)_4\text{N}^+\text{X}^- \cdot$

* Author for correspondence.

$(\text{NH}_2)_2\text{CO}\cdot 2\text{H}_2\text{O}$, ($X = \text{Cl}, \text{Br}, \text{CN}$), in which the cations are sandwiched between puckered layers constructed from the cross-linkage of planar zigzag chains of hydrogen-bonded urea molecules by the water molecules and halide/pseudohalide anions [13]. The planar zigzag urea chain in these structures contrasts with the relatively open framework in tetragonal urea [14] and the helical spirals in both the urea channel adducts [1, 2] and the isomorphous series $(n\text{-C}_3\text{H}_7)_4\text{N}^+\text{X}^- \cdot 3(\text{NH}_2)_2\text{CO}\cdot \text{H}_2\text{O}$, ($X = \text{F}, \text{Cl}, \text{Br}, \text{I}$) [15, 16]. We carried out subsequent studies on the generation of new host lattices by the combined use of urea or thiourea and other molecular species as the building blocks. In our design of new thiourea–anion host lattices, some simple trigonal planar oxo-anions that can easily form $\text{O} \cdots \text{H}—\text{N}$ acceptor hydrogen bonds such as CO_3^{2-} , NO_3^- , HCO_3^- , and H_2BO_3^- have been used, and the crystal structures of thiourea–bicarbonate [17] and thiourea–nitrate [18] complexes have been reported by us recently. Some monocarboxylic acid radicals such as HCO_2^- [19] and CH_3CO_2^- [20], as well as dicarboxylic acid radicals such as oxalate C_2O_4^- , hydrogen oxalate HC_2O_4^- and hydrogen fumarate $\text{HC}_4\text{H}_2\text{O}_4^-$ have also been used in our investigation.

As a logical extension of the urea/thiourea–peralkylated ammonium salt family, some unsymmetrical quaternary ammonium ions have been used as guest moieties in our study. Following this idea of altering the quaternary organic cation, we have recently prepared analogous inclusion compounds in which the central nitrogen atom is replaced by phosphorus, a higher member of the pnictogen group. In the X-ray structures of $(\text{C}_4\text{H}_9)_4\text{P}^+\text{BF}_4^-$ [21] and $(\text{C}_2\text{H}_5)_4\text{P}^+[(\text{V}_2\text{O}_3)_2(\text{O}_3\text{PPh})_4\text{F}]^-$ [22], the $(\text{C}_4\text{H}_9)_4\text{P}^+$ cation exhibits crystallographic $23(T)$ symmetry with $\text{P}—\text{C} = 1.924$ and $\text{C}—\text{C} = 1.531$ Å but the carbon atoms of the $(\text{C}_2\text{H}_5)_4\text{P}^+$ cation suffer from unusually large ‘thermal motion’. A shorter average $\text{P}—\text{C}$ bond length (1.775 Å) for the tetramethylphosphonium cation was reported in its dicopper pentachloride complex [23]. In order to investigate the effect of employing larger cations in the construction of urea–anion host lattices, the following pair of anhydrous urea–chloride complexes were prepared and characterized:



2. Experimental

Tetraethylammonium hydroxide (25 wt.-% aqueous solution) and crystalline tetraethylphosphonium chloride (98%) were obtained from Eastman Kodak and Aldrich, respectively. Tetraethylammonium hydroxide (or tetraethylphosphonium chloride) and urea were mixed in a molar ratio of 1 : 2. A minimum quantity of water was added to dissolve the solid, and hydrochloric acid was added to the solution in a 1 : 1 molar ratio for hydroxide: acid in the first 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**, but complex **2** initially deposited from solution as very thin needles, and was recrystallized from 50% alcohol to yield larger plates that could be used for X-ray analysis.

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 [24] on a Siemens R3m/V diffractometer using $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at 291 K. The raw data were processed with a learnt-profile procedure [25], and 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 [26]. All non-hydrogen atoms were located by direct methods and refined using anisotropic thermal parameters. The amido, methylene, and methyl H atoms were generated geometrically (C—H distance fixed at 0.96 \AA) and allowed to ride on their respective parent atoms. 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 [27]. Two ethyl groups belonging to the tetraethylphosphonium ion in **2** exhibit two-fold disorder, and their scattering power was represented by fractional carbon atoms $\text{C}(n)$ and $\text{C}(n')$ (Table II); the H atoms of the disordered ethyl groups were not included in the structural model. Structure refinement was carried out by the full-matrix least-squares method, and the final R indices and other parameters are listed in Table I.

3. Results and Discussion

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

3.1. CRYSTAL STRUCTURE OF $(\text{C}_2\text{H}_5)_4\text{N}^+\text{Cl}^- \cdot 2(\text{NH}_2)_2\text{CO}$ (**1**)

In compound **1** the tetraethylammonium cations are separated by urea–chloride puckered layers to generate a sandwich-like packing mode, and its layer structure may be conveniently described with reference to the hydrogen bonding scheme shown in Figure 1 and Table III. Two independent urea molecules **C(1)** [for simplicity the urea molecule composed of atoms C(1), O(1), N(1) and N(2) is designated as **C(1)**] and **C(2)** are connected by a pair of N—H \cdots O hydrogen bonds to form a dimer. These dimers are arranged in a broadside manner and interlinked by pairs of N—H \cdots O hydrogen bonds to generate an approximately planar wide ribbon running parallel to the c axis; the deviation of its molecular moieties from coplanarity is shown by the torsion angles C(2)—N(4) \cdots O(1)—C(1) = -7.1 , C(1)—N(1) \cdots O(2)—C(2) = 5.2 , C(1)—N(1) \cdots O(1e)—C(1e) = -74.0 , and

Table I. Data collection and processing parameters of urea-tetraethylammonium and tetraethylphosphonium chloride complexes.

Complex	1	2
Molecular formula	(C ₂ H ₅) ₄ N ⁺ Cl ⁻ · 2(NH ₂) ₂ CO	(C ₂ H ₅) ₄ P ⁺ Cl ⁻ · 2(NH ₂) ₂ CO
Molecular weight	285.8	292.7
Crystal system	Monoclinic	Orthorhombic
Space group	<i>P</i> 2 ₁ / <i>c</i> (No. 14)	<i>Pmn</i> 2 ₁ (No. 31)
Unit cell parameters		
<i>a</i> , Å	10.492(6)	7.446(1)
<i>b</i> , Å	14.954(8)	9.200(2)
<i>c</i> , Å	10.335(6)	12.753(3)
α , °	90	90
β , °	91.02(5)	90
γ , °	90	90
<i>V</i> , Å ³	1621(2)	873.6(3)
<i>Z</i>	4	2
<i>F</i> (000)	624	308
Density (calcd.) g cm ⁻³	1.171	1.113
Absorption coefficient, mm ⁻¹	0.240	0.311
Crystal size, mm	0.30 × 0.40 × 0.42	0.28 × 0.30 × 0.36
Mean μ_r	0.048	0.060
Transmission factors	0.894 to 0.807	0.852 to 0.813
Scan speed (deg min ⁻¹)	3.97 to 19.53	2.0 to 29.3
Scan range (deg)		
(below <i>K</i> α_1 to above <i>K</i> α_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	
$2\theta_{\max}$, °	48	50
Unique data measured	2551	874
Observed data	$ F_0 > 4\sigma(F_0)$, 1527	$ F_0 > 3\sigma(F_0)$, 519
Number of variables, <i>p</i>	163	111
$R_F = \Sigma F_0 - F_c /\Sigma F_0 $	0.050	0.079
Constant <i>g</i> in weighting scheme		
$\omega = [\sigma^2(F_0) + g F_0 ^2]^{-1}$	0.0003	0.0002
$R_G = [\Sigma\omega(F_0 - F_c)^2/ F_0 ^2]^{1/2}$	0.055	0.081
$S = [\Sigma\omega(F_0 - F_c)^2/(n - p)]^{1/2}$	1.68	1.04
Residual extrema in final difference map, e Å ⁻³	+0.18 to -0.16	+0.44 to -0.30
Largest and mean Δ/σ	0.002, 0.000	0.081, 0.004

C(2e)—N(4e) ··· O(2)—C(2) = 28.1°. The distance between N(1) and O(1e) (3.271 Å) is too long to be considered as that of a hydrogen bond. The chloride ions lie in between the ribbons, and hydrogen bonds of the types N—H ··· Cl link them

Table II. Atomic coordinates ($\times 10^4$) and thermal parameters* ($\text{\AA}^2 \times 10^3$) of $(\text{C}_2\text{H}_5)_4\text{N}^+\text{Cl}^- \cdot 2\text{CO}(\text{NH}_2)_2$ (1) and $(\text{C}_2\text{H}_5)_4\text{P}^+\text{Cl}^- \cdot 2\text{CO}(\text{NH}_2)_2$ (2).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq} or U
(i) $(\text{C}_2\text{H}_5)_4\text{N}^+\text{Cl}^- \cdot 2\text{CO}(\text{NH}_2)_2$ (1)				
<i>Urea-chloride host lattice</i>				
O(1)	7046(2)	7956(2)	4614(2)	74(1)
C(1)	7648(4)	8018(2)	3597(3)	57(1)
N(1)	7037(3)	8039(2)	2432(3)	67(1)
N(2)	8923(3)	8076(2)	3596(3)	69(1)
O(2)	4299(2)	7525(2)	2486(2)	65(1)
C(2)	3752(3)	7371(2)	3520(3)	53(1)
N(3)	2523(3)	7116(2)	3535(3)	67(1)
N(4)	4368(3)	7441(2)	4658(3)	76(1)
Cl(1)	598(1)	7694(1)	1030(1)	81(1)
<i>Tetraethylammonium ion</i>				
N(5)	7517(3)	5148(2)	2533(3)	60(1)
C(3)	7302(4)	4693(3)	3814(3)	78(2)
C(4)	7086(5)	5292(3)	4951(4)	120(2)
C(5)	6346(4)	5703(2)	2149(4)	76(2)
C(6)	5114(4)	5202(3)	1990(5)	105(2)
C(7)	7748(4)	4416(2)	1567(3)	69(2)
C(8)	8025(4)	4715(3)	216(4)	95(2)
C(9)	8627(4)	5780(3)	2607(4)	79(2)
C(10)	9890(4)	5355(3)	2963(4)	97(2)
(ii) $(\text{C}_2\text{H}_5)_4\text{P}^+\text{Cl}^- \cdot 2\text{CO}(\text{NH}_2)_2$ (2)				
<i>Urea-chloride host lattice</i>				
O(1)	0	-232(3)	2672(3)	100(1)
C(1)	0	865(3)	2113(3)	103(1)
N(1)	1469(3)	1463(3)	1745(3)	88(1)
O(2)	5000	162(3)	2347(3)	82(1)
C(2)	5000	-858(4)	3002(3)	55(1)
N(2)	6584(3)	-1439(3)	3342(3)	85(1)
Cl(1)	0	3956(2)	21(3)	72(1)

together to form a puckered layer normal to the *b* axis (Figure 1). Urea-chloride layers of this type are located at $y = 1/4$ and $3/4$ (Figure 2).

The tetraethylammonium cations, which are well ordered and nearly attain idealized $\bar{4}2m$ molecular symmetry, are arranged in a column running parallel to the [100] direction. Adjacent columns are arranged side by side, separated by a distance of $c/2$ but shifted by $a/2$ in the [100] direction, to generate a cationic layer parallel to the (010) family of planes. These layers are located at $y = 0$ and $\frac{1}{2}$ in

Table II. Continued.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} or <i>U</i>
(ii) (C₂H₅)₄P⁺Cl⁻·2CO(NH₂)₂ (2)				
<i>Tetraethylphosphonium ion</i>				
P(1)	0	3827(3)	5000	99(1)
C(3)	1941(4)	2838(3)	5463(3)	118(1)
C(4)	2438(4)	1643(3)	4738(3)	231(1)
C(5)	0	4485(3)	3649(4)	190(1)
C(6)	0	6107(3)	3557(4)	182(1)
C(7)	0	5439(4)	5876(3)	333(1)
C(8)	-661(4)	5258(4)	6978(3)	129(1)
C(5')	0	5596(4)	4292(3)	53(1)
C(6')	0	5351(4)	3130(3)	40(1)
C(7')	0	4254(3)	6414(4)	310(1)
C(8')	0	5800(3)	6783(4)	67(1)

* For non-hydrogen atoms, equivalent isotropic temperature factor U_{eq} defined as 1/3 of the trace of the orthogonalised **U** matrix.

The exponent of the isotropic temperature factor takes the form $-8\pi^2 U \sin^2 \theta / \lambda^2$, s.o.f. for C(5) to C(8) are 0.308; for C(5') to C(8') are 0.192.

the unit cell, each being sandwiched between two hydrogen-bonded urea–chloride layers (Figure 2).

3.2. CRYSTAL STRUCTURE OF (C₂H₅)₄P⁺Cl⁻·2(NH₂)₂CO (2)

Figure 3 shows a portion of a urea–chloride layer consolidated by hydrogen bonding. Both independent urea molecules are located in sites of symmetry *m*, and are alternately linked by pairs of N—H···O hydrogen bonds to form a slightly buckled ribbon running parallel to the *a* axis; the resulting ribbon is virtually planar as indicated by the torsion angles C(1)—N(1)···O(2)—C(2) = -5.3 and C(2)—N(2b)···O(1)—C(1) = -3.6°. Adjacent ribbons related by a 2₁ screw axis are aligned in such a way that matching pairs of urea molecules face each other to form donor hydrogen bonds to the same chloride ion in a bidentate chelating mode. The net result is that the urea ribbons are bridged periodically by chloride ions to generate a sawtooth-wave-like layer. This type of linkage is very similar to that in the host structure of the tetrabutylammonium chloride–thiourea inclusion compound [(*n*-C₄H₉)₄N⁺Cl⁻·2(NH₂)₂CS, space group *P*2₁, *a* = 8.754(2), *b* = 8.857(2), *c* = 16.748(3) Å, β = 92.00(3)°, *Z* = 2] [28], except that in that case the layer is nearly planar. Finally, the present sawtooth layers are alternately stacked parallel to the (010) family of planes, such that the ‘crests’ and ‘troughs’ of each layer are concentrated at *z* = 0 and $\frac{1}{2}$, respectively. The (C₂H₅)₄P⁺ cations are

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

(C₂H₅)₄N⁺Cl⁻·2CO(NH₂)₂ (1)			
<i>(i) Urea molecules</i>			
O(1)—C(1)	1.239(4)	C(1)—N(1)	1.354(5)
C(1)—N(2)	1.340(5)	O(2)—C(2)	1.243(4)
C(2)—N(3)	1.345(5)	C(2)—N(4)	1.336(4)
O(1)—C(1)—N(1)	121.0(3)	O(1)—C(1)—N(2)	122.0(3)
N(1)—C(1)—N(2)	117.0(3)	O(2)—C(2)—N(3)	121.3(3)
O(2)—C(2)—N(4)	121.3(3)	N(3)—C(2)—N(4)	117.4(3)
<i>(ii) Hydrogen bonding (donor atom listed first)</i>			
N(4)···O(1)	2.915	N(1)···O(2)	2.975
N(4e)···O(2)	2.925	N(1)···O(1e)	3.271
N(2a)···Cl(1)	3.258	N(3)···Cl(1)	3.368
N(3e)···Cl(1)	3.316	N(2f)···Cl(1)	3.254
N(4)···O(1)—C(1)	122.6	N(1)···O(2)—C(2)	121.6
N(1)···O(1e)···N(4e)	81.2	N(1)···O(2)···N(4e)	86.3
C(1)—N(1)···O(2)—C(2)	5.2	C(2)—N(4)···O(1)—C(1)	-7.1
C(2e)—N(4e)···O(2)—C(2)	28.1	C(1)—N(1)···O(1e)—C(1e)	-74.0
(C₂H₅)₄P⁺Cl⁻·2CO(NH₂)₂ (2)			
<i>(i) Urea molecules</i>			
O(1)—C(1)	1.235(5)	C(1)—N(1)	1.311(4)
O(2)—C(2)	1.257(5)	C(2)—N(2)	1.366(3)
O(1)—C(1)—N(1)	123.3(2)	N(1)—C(1)—N(1b)	113.0(4)
O(2)—C(2)—N(2)	120.2(2)	N(2)—C(2)—N(2b)	119.5(4)
<i>(ii) Hydrogen bonding (donor atom listed first)</i>			
N(2b)···O(1)	2.904	N(1)···O(2)	2.989
N(1)···Cl(1)	3.360	N(2c)···Cl(1)	3.367
N(2b)···O(1)—C(1)	118.8	N(1)···O(2)—C(2)	118.0
N(1)···Cl(1)···N(2c)	93.5	N(1)···Cl(1)···N(1e)	38.0
N(2c)···Cl(1)···N(2d)	41.0		
C(1)—N(1)···O(2)—C(2)	-5.3	C(2)—N(2b)···O(1)—C(1)	-3.6

* Symmetry transformations:

- $a(x, y, -1 + z);$ $b(x, y, 1 + z);$ $c(1 + x, y, z);$
 $d(-1 + x, y, z)$ $e(1 + x, y, 1 + z)$ $f(-1 + x, y, -1 + z)$
- $a(1 + x, y, z);$ $b(1 - x, y, z);$ $c(-0.5 + x, -y, -0.5 + z);$
 $d(0.5 - x, -y, -0.5 + z);$ $e(-x, y, z);$ $f(-1 + x, y, z)$

Standard deviations in hydrogen bond lengths and bond angles:

- $\sigma(l) \approx 0.009 \text{ \AA}, \sigma(\theta) \approx 0.5^\circ;$
- $\sigma(l) \approx 0.004 \text{ \AA}, \sigma(\theta) \approx 0.2^\circ.$

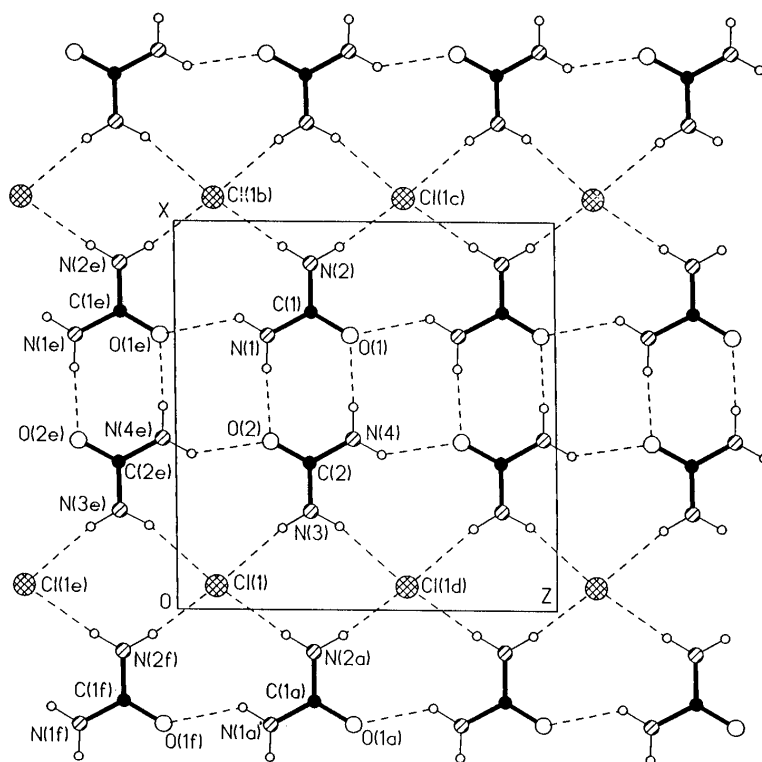


Figure 1. Hydrogen-bonded puckered layer in $(\text{C}_2\text{H}_5)_4\text{N}^+\text{Cl}^- \cdot 2(\text{NH}_2)_2\text{CO}$ (**1**) formed by wide urea ribbons bridged by chloride ions. The atom labels and symmetry transformations correspond to those given in Tables II and III. Broken lines represent hydrogen bonds.

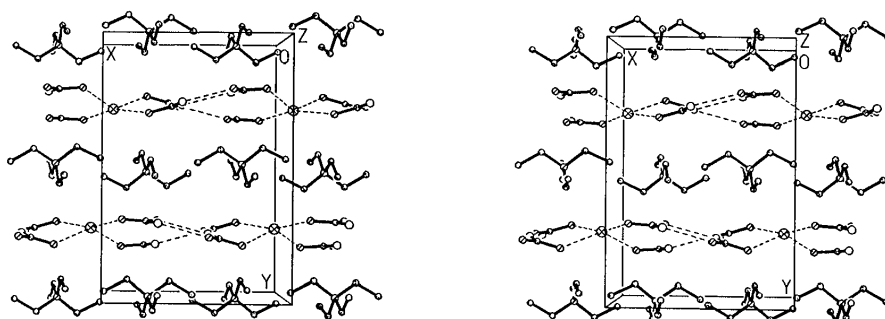


Figure 2. Stereodrawing of the crystal structure of **1**. The origin of the unit cell lies at the upper right corner, with a pointing from right to left, b downwards, and c towards the reader. Broken lines represent hydrogen bonds, and atom types are distinguished by size and shading.

sandwiched between these layers, as shown in a stereoview of the crystal structure in Figure 4.

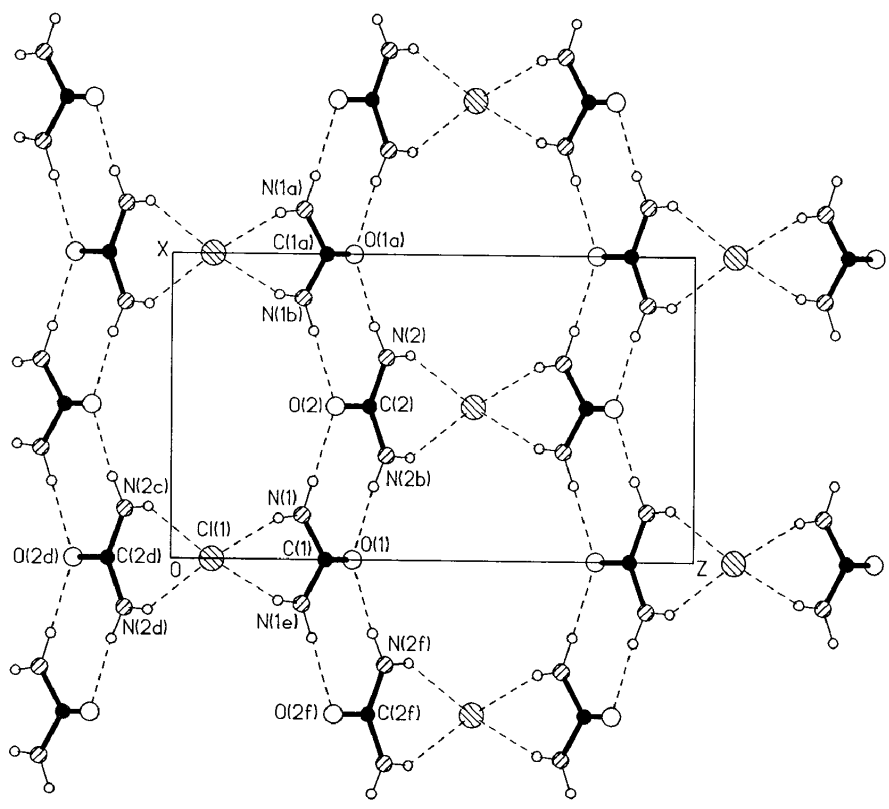


Figure 3. Hydrogen-bonded layer in $(C_2H_5)_4P^+ Cl^- \cdot 2(NH_2)_2CO$ (**2**) formed by urea ribbons bridged by chloride ions. The atom labels and symmetry transformations correspond to those given in Tables II and III. Broken lines represent hydrogen bonds.

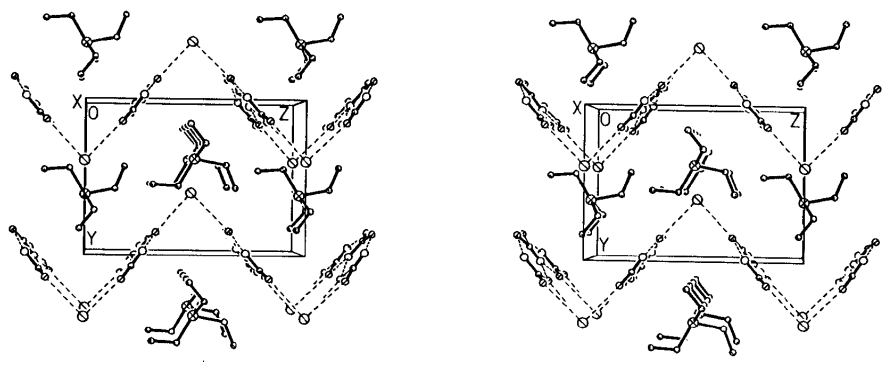


Figure 4. Stereodrawing of the crystal structure of **2**. The origin of the unit cell lies at the upper left corner, with a pointing towards the reader, b downwards, and c from left to right. Broken lines represent hydrogen bonds, and atom types are distinguished by size and shading.

3.3. STRUCTURAL FEATURES AND RELATIONSHIPS

The layer-type host structure of **1** can be compared to those found in our previous studies on urea–water–tetraethylammonium halide inclusion complexes [13] and adducts of urea and peralkylated ammonium bicarbonate salts [29]. The interlayer spacing of $b/2 = 7.48 \text{ \AA}$ in complex **1** is slightly larger than the corresponding values of the previous structures, namely the nearly planar urea–water–halide layer ($b/2 = 7.28 \text{ \AA}$) in monoclinic $(\text{C}_2\text{H}_5)_4\text{N}^+\text{Cl}^-\cdot(\text{NH}_2)_2\text{CO}\cdot 2\text{H}_2\text{O}$ [13], and the nearly planar urea–water–bicarbonate dimer layer ($b/4 = 7.29 \text{ \AA}$) in monoclinic $(\text{C}_2\text{H}_5)_4\text{N}^+\text{HCO}_3\cdot(\text{NH}_2)_2\text{CO}\cdot 2\text{H}_2\text{O}$ [29], and the variation is consistent with the different extent of deviation from planarity of the layers.

The crystal structure of **2** is similar to those found in the thiourea/tetra-*n*-propylammonium acetate complex [20], in which the $(n\text{-C}_3\text{H}_7)_4\text{N}^+$ cations are sandwiched between wave-like layers formed by thiourea dimers and acetate dimers. The interlayer spacing of 9.20 \AA ($= b$) in complex **2** is considerably larger than the corresponding values found in related urea complexes containing the tetraethylammonium cation, for example the three aforementioned compounds, and even exceeds that of the thiourea/tetra-*n*-propylammonium acetate complex, 8.61 \AA ($= b$). Since the host layer in **2** is really a pleated sheet, a more appropriate estimate of the size of the entrapped $(\text{C}_2\text{H}_5)_4\text{P}^+$ ion must take account of the ‘dead space’ around the folded region. The above interlayer spacing data for the urea adducts can be rationalized in terms of the difference in size between the individual quaternary ammonium and phosphonium ions. As expected, the average value of the P—C bond lengths of $(\text{C}_2\text{H}_5)_4\text{P}^+$ in **2** (1.839 \AA) is shorter than that of $(n\text{-C}_4\text{H}_9)_4\text{P}^+$ (1.924 \AA) [21], but longer than 1.775 \AA in the $(\text{CH}_3)_4\text{P}^+$ ion [23] and 1.76 \AA in $(\text{CH}_3)_3\text{PCH}_2\text{BH}_3$ [31]; the present value is in good agreement with the majority of P—C(*sp*³) bond lengths, for example 1.840 and 1.846 \AA in methyl(1-hydroxy-1-phenylethyl)phenylphosphinate [32] and 1.814 \AA in the 5-uracilylmethyltriphenylphosphonium cation [33].

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References

1. L. C. Fetterly: in L. Mandelcorn (ed.), *Non-stoichiometric Compounds*, pp 491–567. Academic Press, New York (1964).
2. K. Takemota and N. Sonoda: in J. L. Atwood, J. E. D. Davies and D. D. MacNicol (eds.), *Inclusion Compounds*, Vol. 2, pp 47–67. Academic Press, London (1984).
3. T. W. Bell and J. Liu: *J. Am. Chem. Soc.* **110**, 3673 (1988).
4. W. Schlenk: *Liebigs Ann. Chem.* **565**, 204 (1949).
5. A. E. Smith: *J. Chem. Phys.* **18**, 150 (1950).
6. A. E. Smith: *Acta Crystallogr.* **5**, 224 (1952).
7. F. Laves, N. Nicolaides, and K. C. Peng: *Z. Kristallogr.* **121**, 258 (1965).

8. Y. Chatani, Y. Taki and H. Tadokoro: *Acta Crystallogr. Sect. B* **33**, 309 (1977).
9. Y. Chatani, H. Anraku, and Y. Taki: *Mol. Cryst. Liq. Cryst.* **48**, 219 (1978).
10. R. Forst, H. Jagodzinski, H. Boysen, and F. Frey; *Z. Kristallogr.* **174**, 56 (1986); **174**, 58 (1986).
11. R. Forst, H. Boysen, F. Frey, H. Jagodzinski, and C. Zeyen: *J. Phys. Chem. Solids* **47**, 1089 (1986).
12. R. Forst, H. Jagodzinski, H. Boysen, and F. Frey: *Acta Crystallogr., Sect. B* **43**, 187 (1987).
13. T. C. W. Mak and R. K. McMullan: *J. Incl. Phenom.* **6**, 473 (1988).
14. W. Pryor and P. L. Sanger: *Acta Crystallogr., Sect. A* **26**, 543 (1970).
15. D. Rosenstein, R. K. McMullan, D. Schwarzenbach, and G. A. Jeffrey: *Am. Crystallogr. Assoc. Abstr. Papers (Summer Meeting)*, p. 152 (1973).
16. T. C. W. Mak: unpublished data.
17. Q. Li and T. C. W. Mak: *J. Incl. Phenom.* **20**, 73 (1995).
18. Q. Li and T. C. W. Mak: *Acta Crystallogr., Sect. B* (CR 511).
19. Q. Li and T. C. W. Mak: *J. Incl. Phenom.* **27**, 319 (1997).
20. Q. Li and T. C. W. Mak: *J. Incl. Phenom.* accepted.
21. H. Schmidbaur, G. Blaschke, B. Zimmer-Gasser, and U. Schubert: *Chem. Ber.* **113**, 1612 (1980).
22. D. L. Thorn, R. L. Harlow, and N. Herron: *Inorg. Chem.* **34**, 2629 (1995).
23. W. G. Haije, J. A. L. Dobbelaar, and W. J. A. Maaskant: *Acta Crystallogr., Sect. C* **42**, 1485 (1986).
24. R. A. Sparks: in F. R. Ahmed (ed.), *Crystallographic Computing Techniques*, p. 452. Munksgaard, Copenhagen (1976).
25. G. Kopfmann and R. Huber: *Acta Crystallogr., Sect. A* **24**, 348 (1968).
26. G. M. Sheldrick: in D. Sayre (ed.), *Computational Crystallography*, Oxford University Press, New York (1982), pp 506–514.
27. *International Tables for X-ray Crystallography*, Vol. IV, Kynoch Press, Birmingham (1974) (Distrib.: Kluwer Academic Publishers, Dordrecht), pp. 55, 99, 149.
28. Q. Li and T. C. W. Mak: *Acta Crystallogr., Sect. C* in press (C960826-KH1101).
29. Q. Li and T. C. W. Mak: *J. Incl. Phenom.* **23**, 233 (1995).
30. M. R. Pressprich and R. D. Willet: *Acta Crystallogr., Sect. C* **47**, 1188 (1991).
31. H. Schmidbaur, G. Muller, B. Milewski-Mahrle, and U. Schubert: *Chem. Ber.* **113**, 2575 (1980).
32. M. L. Glówka and Z. Galdecki: *Acta Crystallogr., Sect. B* **36**, 2312 (1980).
33. T. Kovacs and L. Parkanyi: *Cryst. Struct. Commun.* **11**, 1565 (1982).