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A Novel Inclusion Compound Consolidated by Host-host and Host-guest Hydrogen Bonding: (2-hydroxyethyl)trimethylammonium Ions Included in a Channel Host Lattice Built of Urea Molecules and Allophanate Ions

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A new inclusion compound, $(CH_3)_3N^+(CH_2)_2OH \cdot NH_2CONHCO_2^- \cdot (NH_2)_2CO$ (**1**), has been prepared and characterized by X-ray crystallography. Crystal data, MoKα radiation: space group $Pna2_1$, $Z = 4$, $a = 8.549(4)$, $b = 12.585(2)$, $c = 12.587(2)$ Å, and $R_F = 0.064$ for 1160 observed reflections. In the crystal structure **1**, a single column of choline ions is accommodated in each channel of the two-component urea-allophanate host lattice, with O-H...O hydrogen bonds formed between the guest hydroxyl groups and host allophanate O atoms. X-ray analysis has shown that ethyl allophanate $NH_2CONHCOOC_2H_5$ (**2**) has molecular symmetry m in the crystalline state. Crystal data, MoKα radiation: space group $C2/m$ (No. 12), $Z = 4$, $a = 14.455(3)$, $b = 6.920(1)$, $c = 7.097(1)$ Å, $\beta = 115.80(3)°$, and $R_F = 0.073$ for 408 observed reflections.

Keywords: ????

INTRODUCTION

The understanding of weak intermolecular interactions is becoming of central interest in diverse fields of chemistry.[1] In this regard, host-guest relationships of the coronate/cryptate type have helped to clarify some of the existing problems in molecular inclusion.[2] More than ten years ago, host-guest compounds of the lattice inclusion type[3] appeared to be potentially useful for the study of weak intermolecular interactions and practical applications in separating the components of mixtures.[4–6]

Urea forms non-stoichiometric crystalline inclusion compounds (space group $P6_122$ or $P6_522$) comprising an extensively hydrogen-bonded honeycomb-like host lattice that contains linear, parallel, non-intersecting, cylindrical channels within which a wide variety of straight-chain aliphatic guest molecules are accommodated. Previous structural characterization of urea inclusion compounds, generally by X-ray diffraction[7] and solid state NMR techniques,[8] has confirmed that they are incommensurate, that is, there exist no small integers m

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and n that satisfy $mc_h = nc_g$, where c_h and n_g are the host and guest repeat distances along the channel axis. Interchannel ordering of n-alkane guest molecules have been experimentally and theoretically studied.[9]

In a typical n-alkane inclusion compound, the urea molecules form a three-dimensional hydrogen-bonded network, in which each oxygen is linked to four nitrogen atoms, and each nitrogen to two oxygen atoms of adjacent urea molecules.[10] Hydrogen bonds are also responsible for the helical grouping of the urea molecules in the channel wall and thus for the helicity of the respective inclusion lattice.[11] Direct binding of guest molecules to the channel wall *via* hydrogen bonding occurs, however, only in very exceptional cases. Recently, very interesting stress-induced domain reorientation has been observed in commensurate ($3c_h = 2c_g$) 2,10-undecanedione/urea (1:9), whose lattice symmetry is lowered to $C222_1$ by hydrogen-bonding interaction between the guest molecules and every third urea molecule along a channel wall.[12]

The host-guest interaction can be enhanced if particular donor substituents (e.g. specific functional groups) facing corresponding acceptor groups of the host molecules are incorporated into the guest, and *vice versa*. For instance, in the hydrogen-bonded host lattices built of urea or thiourea molecules, with or without the incorporation of various anionic components, guest species containing hydroxyl group may be expected to form donor O-H...O or O-H...S hydrogen bonds with the host, so that both van der Waals interactions and hydrogen bonding contribute to the stability of the inclusion compound.

The (2-hydroxyethyl)trimethylammonium cation, commonly known as choline, has been used in a study of guest-exchange for adducts of a bisresorcinol derivative of anthracene, and it has been recognized that, in addition to hydrophobic and van der Waals interactions, host-guest hydrogen-bonding must at least partially be responsible for the complexion in an aqueous medium.[13,14] It has also been inferred from the infrared spectrum of choline fluoride that the hydroxyl group of the choline cation is tightly bound to the fluoride ion by an interaction which appears to be intermediate between the electrostatic and covalent types of hydrogen bonds.[15]

Our interest in urea adducts stems from an attempt to generate different inclusion topologies, and we have been studying a series of inclusion compounds built of urea/thiourea-anion host lattices,[16–18] in which hydrophobic guest cations are enclosed in box-like cages, accommodated in an open, parallel channel system or sandwiched between puckered layers. In all these cases the interaction between host and guest is of the van der Waals type. In the present work, we report the preparation and structural characterization of a novel crystalline complex, $(CH_3)_3N^+(CH_2)_2OH{\cdot}NH_2CONHCO_2^-{\cdot}(NH_2)_2CO$ (**1**), in which the choline ions are accommodated in, and hydrogen-bonded to, a host lattice built of urea molecules and allophanate ions. In the nomenclature proposed by Weber, **1** can be described as a "coordinatoclathrate in a coordination-assisted host lattice".[19]

RESULTS AND DISCUSSION

The three-dimensional, open-channel host framework of **1** viewed along the c direction is presented in Fig. 1. It can be seen that the choline cations are arranged in a single column about a 2_1 axis so that their hydroxyl groups point toward opposite channel walls to form donor hydrogen bonds with O(4) atoms of the allophanate ions. This hydrogen bond is rather strong, as its length of 2.69(1) Å lies closer to the short side of general O-H...O hydrogen bonds in the range 2.40–3.10 Å.[20]

A pair of hydrogen-bonded zigzag chains, composed of allophanate ions related by a 2_1 axis, constitute two opposite walls of a hexago-

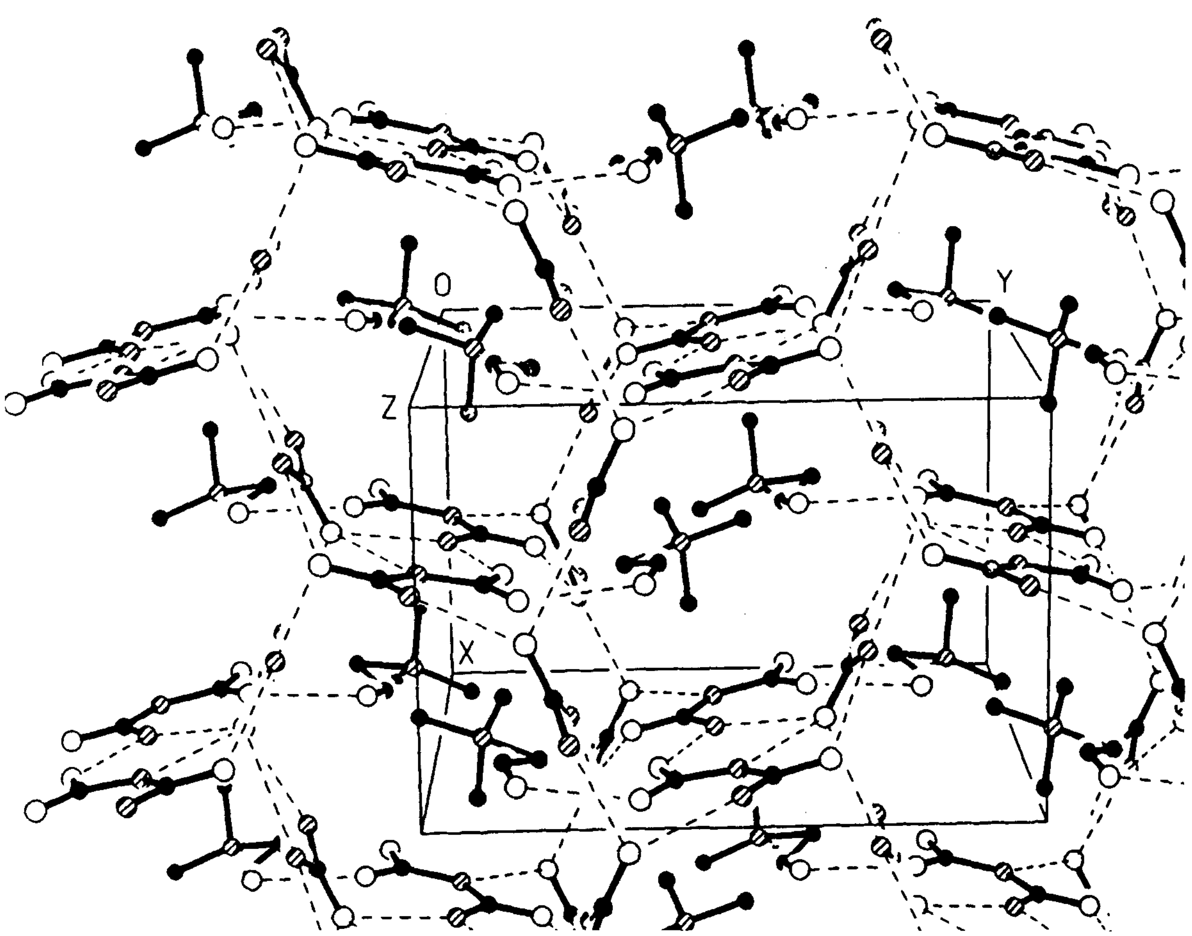

FIGURE 1 Three-dimensional host framework containing open channels in the crystal structure of $(CH_3)_3N^+(CH_2)_2OH \cdot NH_2CONHCO_2^- \cdot (NH_2)_2CO$ (**1**), viewed in a direction that makes a small inclined angle with respect to the *c* axis. Broken lines represent hydrogen bonds, and atom types are distinguished by size and shading (open circles for O, shaded circles for N, and filled circles for C).

nal channel extending along the [001] direction. In the hydrogen bonding scheme shown in Fig. 2, the allophanate ions are connected to form a nearly planar ribbon, as illustrated by the value of the torsion angle C(2)-N(3)...O(3c)-C(3c) = −175.6°. Urea molecules related by the *a* glide are alternately linked by hydrogen bonds in a head-to-tail mode to generate an undulated chain extending along the [100] direction. Since the angle between two successive urea molecular planes along this chain is 129.0°, two families of parallel urea chains directed along [001] crosslink the chains of allophanate ions to form a three-dimensional host framework containing open channels whose cross section is a distorted hexagon, of which the three independent interior angles are 103.0, 128.0 and 129.0° respectively (Fig. 1).

The channel-type host structure of **1** can be compared with those of the classical urea inclusion compounds, in which the separation between the centers of two adjacent channels is 8.2 Å, leading to an effective cross-sectional diameter of 5.2 Å for the inclusion of aliphatic guest molecules. On the other hand, these two corresponding values in the host lattice of **1** are 8.5 Å

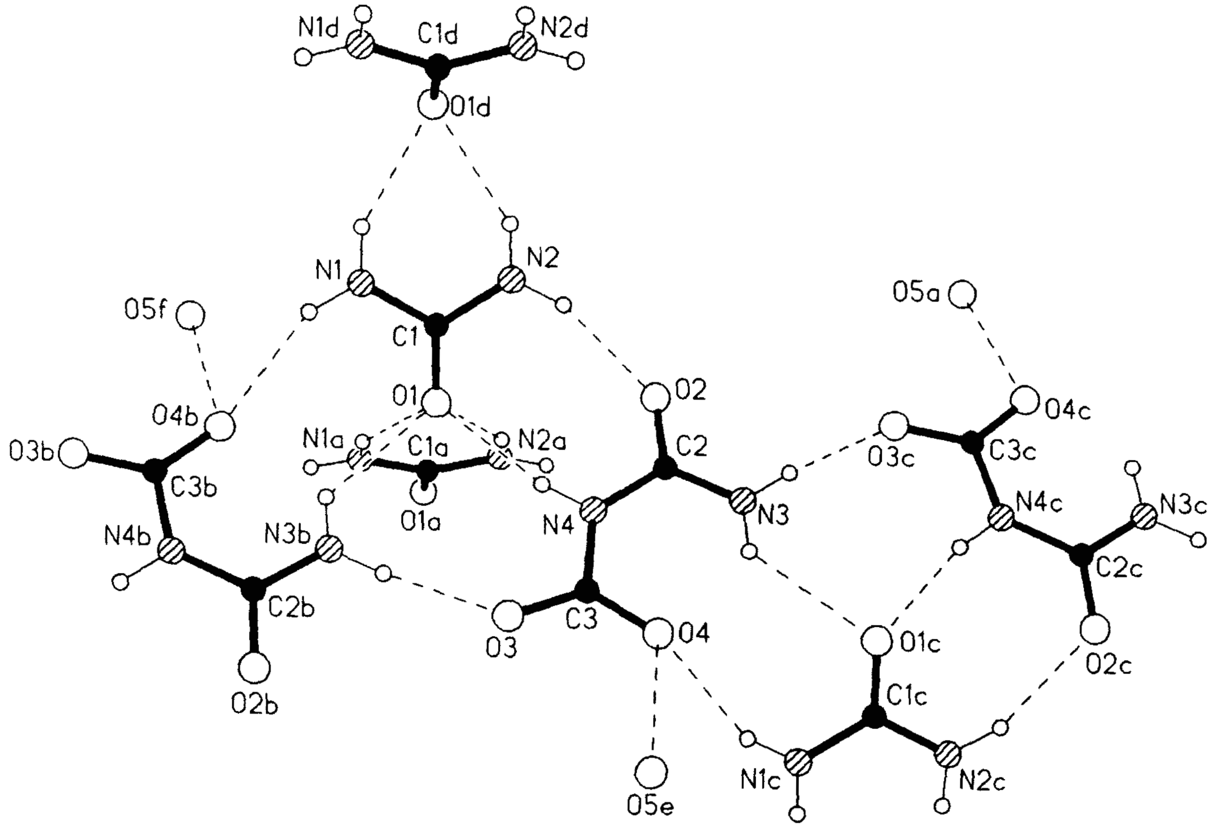

FIGURE 2 Perspective view of a portion of the cross linkage of a head-to-tail urea chain and a zigzag allophanate ribbon in **1**. Symmetry transformations: a: $-0.5 + x, 0.5 - y, z$; b: $-x, 1 - y, -0.5 + z$; c: $-x, 1 - y, 0.5 + z$; d: $0.5 + x, 0.5 - y, z$; e: $0.5 - x, 0.5 + y, -0.5 + z$; f: $-0.5 + x, 0.5 - y, -1 + z$.

and 5.5 Å, respectively, which are consistent with the greater bulk of the quaternary ammonium group in the choline cation. In the related urea-allophanate host lattice in $(n\text{-}C_3H_7)_4N^+ \cdot NH_2CONHCO_2^- \cdot 3(NH_2)_2CO$, the channel has an approximately elliptical shape with effective major and minor axes of 5.2/2 and 6.0/2 Å, respectively, and neighbouring channels are separated by about 8.2 and 10.1 Å.[18]

The measured molecular dimensions of the allophanate ion in compound **1** (Fig. 2), which adopts a planar configuration that facilitates the formation of an intermolecular N-H...O hydrogen bond, agree well with those in the related tetramethyl- and tetra-*n*-propyl-ammonium urea/allophanate inclusion compounds.[18] The ethyl ester **2** (Fig. 3) has crystallograthically-imposed *m* symmetry and molecular dimensions similar to those of the allophanate anion in **1**, except that the bond length C(3)-O(3) is significantly shorter than C(2)-O(3), showing that the latter is effectively a single bond with negligible participation in the extensive π-electron delocalization over the rest of the molecule.

In summary, we have shown that the elusive allophanate ion can be generated *in situ* and stabilized by urea in a crystalline environment, and the allophanate O atoms of the resulting hydrogen-bonded hydrophilic host lattice can form acceptor hydrogen bonds with the hydroxyl groups of choline guests [Fig. 4(b)]. This may be contrasted with the classical urea or thiourea inclusion compounds formed by self-assembly, as well as inclusion compounds built of urea or thiourea together with various anions, in which the hydrophobic guest species are retained by

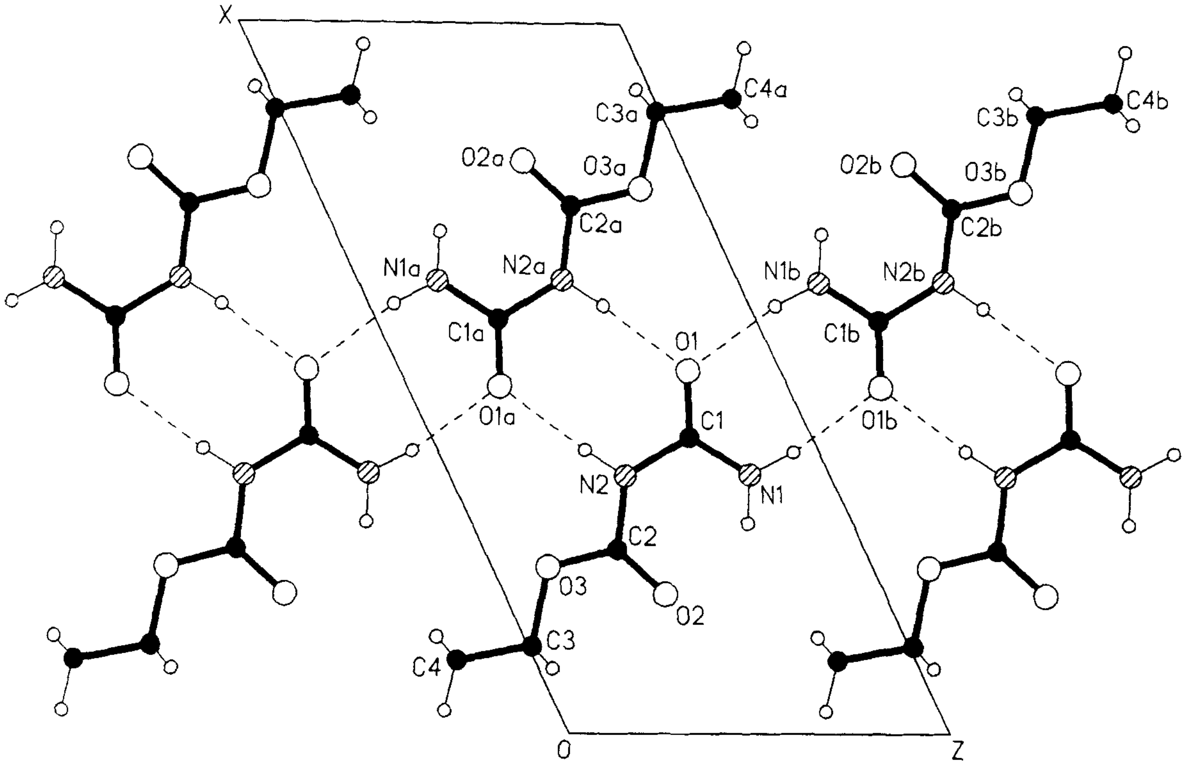

FIGURE 3 The crystal structure of **2** projected along the *b* axis, showing a planar ethyl allophanate ribbon running parallel to the [001] direction; broken lines represent hydrogen bonds. Symmetry transformations: a: $1 - x, y, 1 - z$; b: $1 - x, y, 2 - z$.

steric barriers formed by the hydrogen-bonded host lattice [Fig. 4(a)].

EXPERIMENTAL

The ethyl allophanic ester $NH_2CONHCOOC_2H_5$ (**2**) was synthesized by the action of ethyl chloroformate on urea in a 1:2.1 molar ratio.[21] The white powdery product **2** was recrystallized from tetrahydrofuran. Subsequently choline hydroxide (50 wt. % solution in water from Aldrich) and **2** were mixed in equal molar amounts and a minimum quantity of water was added to dissolve the solid. When the solution was heated at about 80°C and stirred for half an hour, generation of the allophanate ion from the hydrolysis of **2** by warm alkali was effectively complete.[22] Then another molar equivalent of urea was dissolved in the solution, and the latter was allowed to evaporate at room temperature in a desiccator charged with drierite to yield colorless crystals of **1**.

Information concerning the crystallographic data and structure determination of the two compounds is summarized in Table I. Intensities were collected in the variable ω-scan technique[23] on a Siemens R3m/V diffractometer using MoKα radiation (λ = 0.71073 Å) at 291 K. The raw data were processed with a learnt-profile procedure,[24] 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.[25] The structures were solved by direct methods and all non-hydrogen atoms were re-

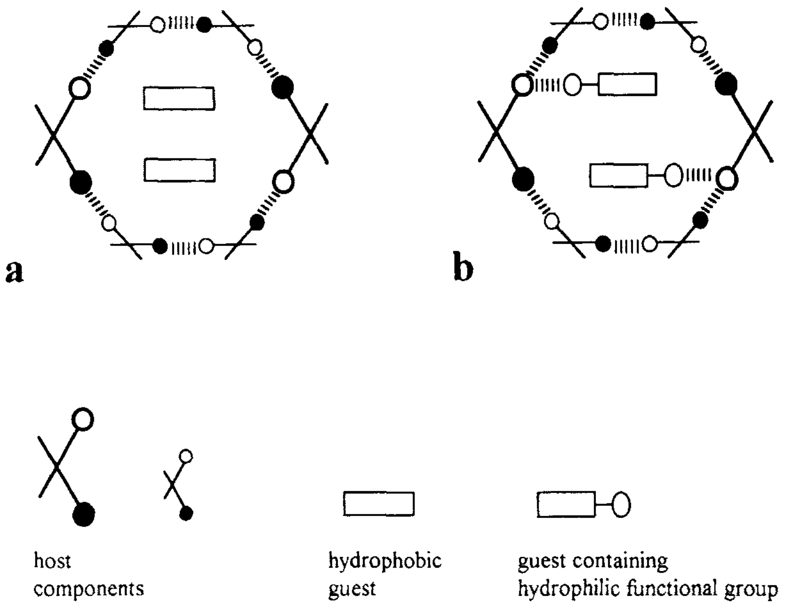

FIGURE 4 Diagrammatic (projection) representation of two different modes of channel inclusion involving hydrogen bonding interactions (indicated by broken lines): (**a**) guest molecules arranged in a zigzag chain are retained by steric barriers formed by the hydrogen-bonded host lattice (**b**) hydrogen bonds also exist between host and guest components, as in the case of **1**.

TABLE I Selected Crystal Data and Structure Refinement for **1** and **2**.

Complex	**1**	**2**
Molecular formula	$(CH_3)_3N^+(CH_2)_2OH \cdot NH_2CONHCO_2^- \cdot (NH_2)_2CO$	$NH_2CONHCOOC_2H_5$
Molecular weight	267.3	132.1
Crystal system	Orthorhombic	Monoclinic
Space group	$Pna2_1$	$C2/m$
Unit cell parameters		
a, Å	8.549(4)	14.455(3)
b, Å	12.583(2)	6.920(1)
c, Å	12.587(2)	7.097(1)
α, °	90.00	90.00
β, °	90.00	115.80(3)
γ, °	90.00	90.00
V, Å^3	1354.2(7)	639.1(3)
Z	4	4
$F(000)$	576	280
Density (calcd.), g cm^{-3}	1.311	1.373
Crystal size, mm	0.20 × 0.26 × 0.36	0.22 × 0.32 × 0.44
Scan speed (deg min^{-1})	3.0 to 29.0	2.0 to 29.3
$2\theta_{max}$, °	50	45
Unique data measured	2347	631
Observed data	$\|F_o\|>4\sigma(\|F_o\|)$, 1160	$\|F_o\|>4\sigma(\|F_o\|)$, 408
Number of variables, p	152	56
$R_F = \Sigma\|\|F_o\|-\|F_c\|\|/\Sigma\|F_o\|$	0.064	0.073
Constant g in weighting scheme		
$\omega = [\sigma^2(F_o) + g\|F_o\|^2]^{-1}$	0.0002	0.0001
$R_G = [\Sigma\omega(\|F_o\|-\|F_c\|)^2/\|F_o\|^2]^{1/2}$	0.067	0.079
$S = [\Sigma\omega(\|F_o\|-\|F_c\|)^2/(n-p)]^{1/2}$	1.53	1.26
Residual extrema in final difference map, eÅ^{-3}	+0.50 to −0.50	+0.22 to −0.37
Largest and mean Δ/σ	0.011, 0.001	0.000, 0.000

TABLE II Selected bond distances (Å), bond angles (°) and torsion angles (°) in (**1**)*.

(i) Urea and allophanate molecules			
O(1)-C(1)	1.248(4)	C(1)-N(1)	1.353(5)
C(1)-N(2)	1.333(5)	O(2)-C(2)	1.233(5)
C(2)-N(3)	1.319(6)	C(2)-N(4)	1.387(6)
N(4)-C(3)	1.408(5)	C(3)-O(3)	1.221(5)
C(3)-O(4)	1.241(5)		
O(1)-C(1)-N(1)	120.8(3)	O(1)-C(1)-N(2)	122.3(3)
N(1)-C(1)-N(2)	116.9(3)	O(2)-C(2)-N(3)	121.8(4)
O(2)-C(2)-N(4)	118.1(4)	N(3)-C(2)-N(4)	119.9(4)
C(2)-N(4)-C(3)	128.6(4)	N(4)-C(3)-O(3)	115.5(4)
N(4)-C(3)-O(4)	119.1(4)	O(3)-C(3)-O(4)	125.4(4)
(ii) Hydrogen bonding (donor atom listed first)			
N(1a)...O(1)	3.009	N(2a)...O(1)	2.992
N(3b)...O(1)	3.003	N(4)...O(1)	2.966
N(2)...O(2)	2.975	N(3b)...O(3)	2.874
N(1c)...O(4)	3.046	O(5e)...O(4)	2.694
N(3b)...O(1)-C(1)	122.6	N(4)...O(1)-C(1)	114.5
N(2)...O(2)-C(2)	118.2	N(3b)...O(3)-C(3)	137.7
N(1c)...O(4)-C(3)	147.2		
C(1a)-N(1a)...O(1)-C(1)	107.9	C(1a)-N(2a)...O(1)-C(1)	−106.4
C(1)-N(2)...O(2)-C(2)	−56.8	C(2b)-N(3b)...O(3)-C(3)	−175.8
C(1c)-N(1c)...O(4)-C(3)	123.8		

*__Symmetry transformations:__ a $(-0.5 + x, 0.5 - y, z)$; b $(-x, 1 - y, -0.5 + z)$; c $(-x, 1 - y, 0.5 + z)$; d $(0.5 + x, 0.5 - y, z)$; e $(0.5 - x, 0.5 + y, -0.5 + z)$.

fined with anisotropic thermal parameters. The amido, methylene, and methyl H atoms were generated geometrically (C-H distance fixed at 0.96Å, N-H at 0.90 Å) and allowed to ride on their respective parent atoms. The hydrogen atoms of the hydroxyl H of the choline ion in **1** failed to appear in the difference map, and its position was derived from the scheme of hydrogen bonding. 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.[26] The choline ion was found to be two-fold disordered about a non-crystallographic mirror plane passing through the N, O and methyl C(4) atoms, and the scattering power of the other two methylene groups and the ethylene fragment was represented by half-carbon atoms C(5), C(6), C(7), C(8), C(5′), C(6′), C(7′) and C(8′). The refinement of the coordinates and anisotropic thermal parameters of the non-hydrogen atoms was carried out by the full-matrix least-squares method, and the final *R* indices and other parameters are listed in Table I.

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