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Unsymmetrical Quaternary Ammonium Cations $R_3R'N$ as Guest Templates for the Generation of Novel Host Lattices Constructed from Thiourea and Oxocarbon Anions

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Unsymmetrical Quaternary Ammonium Cations $R_3R'N^+$ as Guest Templates for the Generation of Novel Host Lattices Constructed from Thiourea and Oxocarbon Anions

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New inclusion complexes $(n\text{-}C_4H_9)_3(CH_3)N^+HC_2O_4^- \cdot (NH_2)_2CS \cdot (1/2)H_2C_2O_4$ (1), $[(C_2H_5)_3(n\text{-}C_3H_7)N^+]_2CO_3^{2-} \cdot 6(NH_2)_2CS$ (2) and $2[(CH_3)_3(C_6H_5)N^+]_2CO_3^{2-} \cdot 11(NH_2)_2CS \cdot H_2O$ (3) have been prepared and characterized by X-ray crystallography. Crystal data, MoKα radiation: 1, space group *Fdd*2, $a = 18.603(3)$, $b = 63.661(8)$, $c = 7.830(1)$ Å, $Z = 16$, and $R_F = 0.0648$ for 1297 observed data; 2, space group $P\bar{1}$, $a = 12.593(2)$, $b = 13.075(2)$, $c = 16.238(2)$ Å, $\alpha = 76.16(1)$, $\beta = 71.17(1)$, $\gamma = 66.32(1)°$, $Z = 2$, and $R_F = 0.041$ for 4570 observed data; 3, space group $P\bar{1}$, $a = 11.605(2)$, $b = 17.059(3)$, $c = 22.779(5)$ Å, $\alpha = 109.46(3)$, $\beta = 92.72(3)$, $\gamma = 107.07(3)°$, $Z = 2$, and $R_F = 0.081$ for 5105 observed data. In the crystal structure of 1, the thiourea molecules, hydrogen oxalate ions and oxalic acid molecules build a three-dimensional network containing two fused channel systems that are arranged alternately along the [101] and [10$\bar{1}$] directions, with the tri-*n*-butylmethylammonium cations arranged in a zigzag column within each channel. Compound 2 features a three-dimensional open host structure in which two channel systems extend parallel to the [100] and [010] directions, which accommodate stacked columns of triethyl-*n*-propylammonium cations. In the crystal structure of 3, infinite thiourea chains and thiourea-carbonate layers are connected to generate a unidirectional channel host lattice that accommodates straight columns of trimethylphenylammonium cations.

Keywords: Thiourea, tetraalkylammonium salt, carbonate, oxalate, hydrogen bonding, inclusion compound

INTRODUCTION

Several years ago we reported the crystal structures of a series of thioureatetraalkylammonium halide complexes [1] in which each thiourea molecule interacts with adjacent thiourea molecules *via* N—H...S hydrogen bonds to give a ribbon-like arrangement, and also forms a pair of 'chelating' N—H...X hydrogen bonds with a halide ion. The resulting anionic host framework or composite ribbon, together with the bulkyl hydrophobic organic cations, constitute the principal components in the crystal packing. In our design of new thiourea-anion host lattices, some simple trigonal planar

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anions that can easily form N —H...O acceptor hydrogen bonds such as CO_3^{2-}, HCO_3^- and NO_3^- have been used, and the crystal structures of thiourea-bicarbonate [2] and thiourea-nitrate [3] complexes have been reported by us recently. Some monocarboxylic acid radicals, such as HCO_2^-[4] and $CH_3CO_2^-$[5], and dicarboxylic acid radicals, such as oxalate $C_2O_4^-$ or hydrogen oxalate $HC_2O_4^-$ and hydrogen fumarate $HC_4H_2O_4^-$ have also been used in our series of studies.

We have extended our studies to the unsymmetrical quaternary ammonium cations ($R_3R'N^+$) in order to explore the variation in shape and size of the enclosed cationic guests for the generation of novel anionic host lattices. Here we report the preparation and structural characterization of the following new crystalline inclusion compounds:

$$(n\text{-}C_4H_9)_3(CH_3)N^+HC_2O_4^- \cdot (NH_2)_2CS \cdot (1/2)H_2C_2O_4 \qquad (1)$$

$$[(C_2H_5)_3(n\text{-}C_3H_7)N^+]_2CO_3^{2-} \cdot 6(NH_2)_2CS \qquad (2)$$

$$2[(CH_3)_3(C_6H_5)N^+]_2CO_3^{2-} \cdot 11(NH_2)_2CS \cdot H_2O \qquad (3)$$

RESULTS AND DISCUSSION

Crystal Structure of $(n\text{-}C_4H_9)_3(CH_3)N^+HC_2O_4^- \cdot (NH_2)_2CS \cdot (1/2)H_2C_2O_4$ (1)

In complex **1**, the thiourea molecules, hydrogen oxalate ions and oxalic acid molecules generate a three-dimensional host network containing two channel systems that are arranged alternately in the [101] and [10$\bar{1}$] directions; these channels are rather unusual as their boundaries are not clearly demarcated but fused into a continuum, as shown in Figure 1. Structural details of the thiourea-anion ribbon and the linkage of ribbons may be conveniently described with reference to the hydrogen bonding scheme shown in Figure 2 and Table II.

The hydrogen oxalate ions adopt a synplanar O ═ C —O —H conformation and are interlinked by O —H...O hydrogen bonds to generate an infinite zigzag $(HC_2O_4)_\infty$ chain, in which the hydrogen oxalate skeletons lie alternately on both sides of the connecting line as only a single O —H...O hydrogen bond exists between two adjacent ions. The values of both the torsion angle between two adjacent hydrogen oxalate ions, C(2) —O(2)...O(4b) — C(3b) = 147.7°, and the dihedral angle between the two planar CO_2 fragments of the same hydrogen oxalate ion (28.1°) indicate that this chain has a twisted configuration. The only thiourea molecule in the asymmetric unit fits into a groove on one side of the chain by forming four N —H...O hydrogen bonds with three adjacent hydrogen oxalate ions, thereby generating a thiourea-hydrogen oxalate ribbon. For this slightly puckered thiourea-anion ribbon, the extent of deviation from planarity can be seen from the relevant torsion angles: C(1b) — N(1b)...O(1) —C(2) = −39.5, C(1b) —N(1b) ...O(4b) —C(3b) = 37.5 and C(1a) —N(2a) ...O(3) —C(3) = 163.1°. These thiourea-hydrogen oxalate ribbons are arranged in layers along the *b* axis and their main planes are parallel to the (10$\bar{1}$), (202), (20$\bar{2}$) and (101) families of planes (Fig. 1). They are further cross-linked by oxalic acid molecules, which lie on the crystallogrypic two-fold axes, to form a three-dimensional framework *via* N —H...O and O —H...S hydrogen bonds (Fig. 2).

As the separation between one layer of infinite ribbons running through the structure in the [101] direction and another layer of ribbons oriented in the same direction but shifted laterally with respecte to each other, the unit cell of compound **1** has one unusually long edge [$b = 63.661(8)$ Å], which is rarely found in both thiourea and thiourea anion inclusion compounds.

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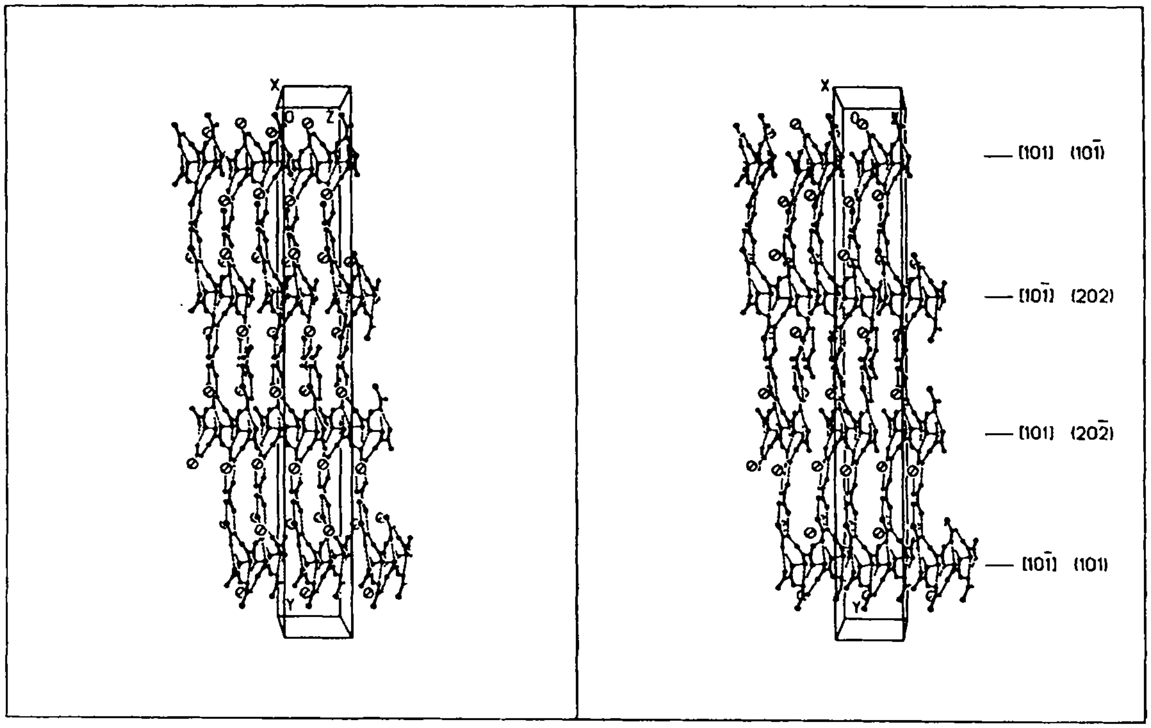

FIGURE 1 Stereodrawing of the crystal structure of $(n\text{-}C_4H_9)_3(CH_3)N^+HC_2O_4^- \cdot (NH_2)_2CS \cdot (1/2)H_2C_2O_4$ (1) showing two fused channel systems extending parallel to the [101] and [10$\bar{1}$] directions and the enclosed cations. Broken lines represent hydrogen bonds, and atom types are distinguished by size and shading. For clarity the enclosed $(n\text{-}C_4H_9)_3(CH_3)N^+$ ions are represented by large shaded circles.

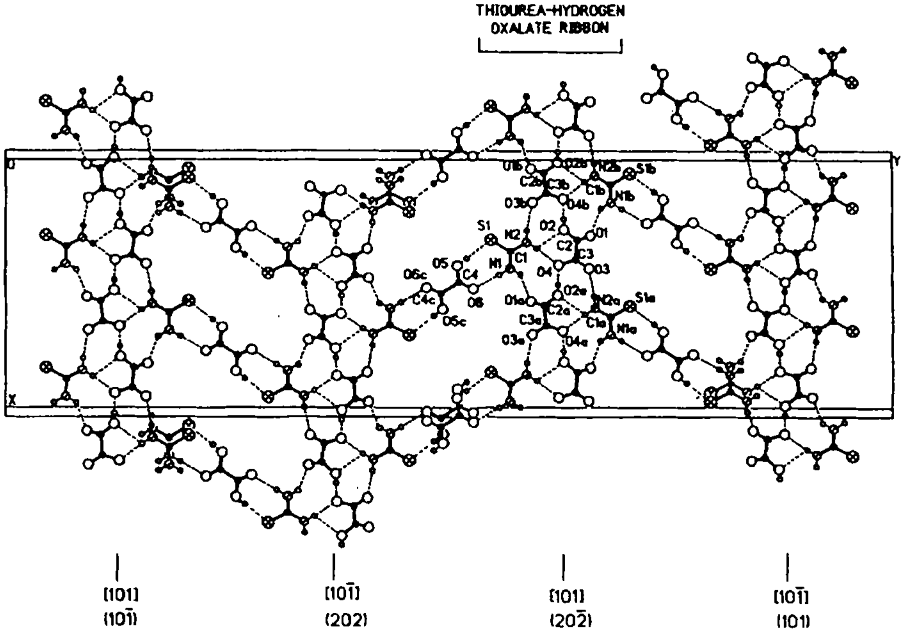

FIGURE 2 Hydrogen-bonded layer in 1 formed by thiourea-hydrogen oxalate ribbons cross-linked by oxalic acid molecules. The direction and orientation of each ribbon are indicated. The atom labels correspond to those given in Table II. Broken lines represent hydrogen bonds. Symmetry transformations: (a): $0.25+x$, $1.25-y$, $0.25+z$; (b): $-0.25+x$, $1.25-y$, $-0.25+z$; (c): $1-x$, $1-y$, z.

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TABLE I Data collection and processing parameters of selenourea-tetraalkylammonium halide complexes

Complex	1	2	3
Molecular formula	$(n\text{-}C_4H_9)_3(CH_3)N^+HC_2O_4^- \cdot (NH_2)_2CS \cdot (1/2)H_2C_2O_4$	$[(C_2H_5)_3(n\text{-}C_3H_7)N^+]_2CO_3^{2-} \cdot 6(NH_2)_2CS$	$2[(CH_3)_3(C_6H_5)N^+]_2CO_3^{2-} \cdot 11(NH_2)_2CS \cdot H_2O$
Molecular weight	410.5	805.3	1520.2
Crystal system	Orthorhombic	Triclinic	Triclinic
Space group	*Fdd*2 (No.43)	$P\bar{1}$ (No.2)	$P\bar{1}$ (No.2)
Unit cell parameters			
a, Å	18.603(3)	12.593(2)	11.605(2)
b, Å	63.661(8)	13.075(2)	17.059(3)
c, Å	7.830(1)	16.238(2)	22.779(5)
α, °	90.00	76.16(1)	109.46(3)
β, °	90.00	71.17(1)	92.72(3)
γ, °	90.00	66.32(1)	107.07(3)
V, Å^3	9274(2)	2298.8(6)	4012(1)
Z	16	4	2
F(000)	3568	872	1620
Density (calcd.), g cm^{-3}	1.176	1.163	1.259
Absorption coefficient, cm^{-1}	0.173	0.339	0.360
Crystal size, mm	0.28 × 0.30 × 0.32	0.30 × 0.32 × 0.48	0.48 × 0.50 × 0.60
Mean μr	0.04	0.07	0.09
Transmission factors	0.789 to 0.892	0.832 to 0.923	0.768 to 0.993
Scan speed (deg min^{-1})	4.0 to 29.3	5.3 to 29.3	3.0 to 29.3
Scan range (below $K\alpha_1$ to above $K\alpha_2$)	0.60 to 0.60	0.60 to 0.60	0.60 to 0.60
Background counting	stationary counts for one-half of scan time at each end of scan		
$2\theta_{max}$, °	48	46	48
Unique data measured	1655	6398	12019
Observed data	$\|F_o\| > 4\sigma(\|F_o\|)$, 1297	$\|F_o\| > 4\sigma(\|F_o\|)$, 4570	$\|F_o\| > 6\sigma(\|F_o\|)$, 5105
Number of variables, p	239	433	774
$R_F = \Sigma\|\|F_o\|-\|F_c\|\|/\Sigma\|F_o\|$	0.068	0.041	0.081
Constant g in weighting scheme $\omega = [\sigma^2(F_o) + g\|F_o\|^2]^{-1}$	0.00005	0.0003	0.0001
$R_G = [\Sigma\omega(\|F_o\|-\|F_c\|)^2/\|F_o\|^2]^{1/2}$	0.072	0.046	0.091
$S = [\Sigma\omega(\|F_o\| - \|F_c\|)^2/(n-p)]^{1/2}$	1.06	1.41	1.16
Residual extrema in final difference map, eÅ^{-3}	+0.44 to −0.30	+0.21 to −0.19	+0.68 to −0.50
Largest and mean Δ/σ	0.000, 0.000	0.001, 0.000	0.010, 0.000

The tri-*n*-butylmethylammonium cation $(n\text{-}C_4H_9)_3(CH_3)N^+$ is well ordered except for one carbon atom of a *n*-butyl fragment which exhibits twofold disorder. When these cations are arranged in a zigzag column within each channel, each has its three-fold symmetry axis pointed toward the main planes of the thiourea-hydrogen oxalate ribbons, so that the *n*-butyl groups are accommodated in the wider region of the channel.

Crystal Structure of $[(C_2H_5)_3(n\text{-}C_3H_7)N^+]_2CO_3^{2-} \cdot 6(NH_2)_2CS$(2)

As shown in Figures 3 and 4, compound 2 has two open channel systems extending parallel to the [100] and [010] directions. This three-dimensional host framework is built of an alternate arrangement of layers of two types of thiourea double ribbons running in the corresponding channel directions, which are bridged by cabonate ions *via* N—H...O hydrogen bonds. Structural details of the thiourea double ribbons may be conveniently described with reference to the hydrogen bonding scheme shown in Figures 5(a), (b), and Table II.

The two types of double ribbons lie in layers at $z = (1/2)$ (Type I) and $z = 0$ (Type II) and extend parallel to the [100] and [010] directions, respectively. In each type of double ribbon, three independent thiourea molecules generate a

TABLE II Selected bond distances (Å), bond angles (°) and torsion angles (°) in the thiourea-anionic systems *

$(n\text{-}C_4H_9)_3(CH_3)N^+HC_2O_4^- \cdot (NH_2)_2CS \cdot (1/2)H_2C_2O_4$(1)			
(i) Thiourea, hydrogen oxalate and oxalic molecules			
S(1) —C(1)	1.711(7)	C(1) —N(1)	1.309(7)
C(1) —N(2)	1.331(9)	C(2) —C(3)	1.566(6)
C(2) —O(1)	1.190(8)	C(2) —O(2)	1.290(8)
C(3) —O(3)	1.205(9)	C(3) —O(4)	1.283(9)
C(4) —O(5)	1.282(7)	C(4) —O(6)	1.196(9)
C(4) —C(4A)	1.512(14)		
S(1) —C(1) —N(1)	121.7(6)	S(1) —C(1) —N(2)	119.8(4)
N(1) —C(1) —N(2)	118.5(6)	C(3) —C(2) —O(1)	121.5(6)
C(3) —C(2) —O(2)	112.8(5)	O(1) —C(2) —O(2)	125.7(5)
C(2) —C(3) —O(3)	118.3(6)	C(2) —C(3) —O(4)	114.2(6)
O(3) —C(3) —O(4)	127.5(5)	O(5) —C(4) —O(6)	125.0(7)
O(5) —C(4) —C(4A)	113.5(7)	O(6) —C(4) —C(4A)	121.4(6)
(ii) Hydrogen bonding			
O(5)...S(1)	3.040	N(1b)...O(1)	2.927
N(2)...O(2)	2.920	N(2b)...O(3)	3.011
N(2)...O(4)	2.976	O(2a)...O(4)	2.482
N(1)...O(6)	3.013		
O(5)...S(1) —C(1)	111.6	N(1b)...O(1) —C(2)	140.1
N(2)...O(2) —C(2)	118.7	N(2a)...O(3) —C(3)	132.0
N(2)...O(4) —C(3)	123.3	O(2a)...O(4) —C(3)	110.1
N(1)...O(6) —C(4)	124.6		
C(2)...O(2)...O(4b) —C(3b)	147.7	C(1) —N(1)...O(6) —C(4)	1.7
C(4) —O(5)...S(1) —C(1)	3.5	C(1b) —N(1b)...O(1) —C(2)	−39.5
O(1) —C(2) —C(3) —O(3)	27.9	O(5) —C(4)...C(4c) —O(6c)	−49.6
$[(C_2H_5)_3(n\text{-}C_3H_7)N^+]_2CO_3^{2-} \cdot 6(NH_2)_2CS$ (2)			
(i) Thiourea and carbonate molecules			
S(1) —C(1)	1.705(3)		
		S(2) —C(2)	1.722(3)
S(3) —C(3)	1.715(3)		
		S(4) —C(4)	1.707(3)
S(5) —C(5)	1.720(4)		
		S(6) —C(6)	1.686(4)
(ii) Hydrogen bonding			
N(4)...S(1)	3.512	N(6d)...S(1)	3.445
N(2)...S(2)	3.373	N(2b)...S(2)	3.281
N(3)...S(2)	3.436	N(3)...S(3)	3.502
N(1a)...S(3)	3.386	N(1b)...S(3)	3.561
N(9)...S(4)	3.592	N(12g)...S(4)	3.510
N(7)...S(5)	3.463	N(11)...S(5)	3.523
N(11)...S(5)	3.308	N(12i)...S(5)	3.767
N(8f)...S(6)	3.587	N(10)...S(6)	3.990
N(3)...O(1)	2.869	N(8)...O(1)	2.903
N(10)...O(1)	2.812	N(5)...O(2)	2.744
N(7)...O(2)	2.778	N(4)...O(3)	2.829
N(6)...O(3)	2.879	N(9)...O(3)	2.881
N(6d)...S(1) —C(1)	102.2	N(4)...S(1) —C(1)	97.3
N(4)...S(1)...N(6d)	159.5	N(2)...S(2)...N(2b)	66.2
N(2b)...S(2)...N(3)	114.5	N(2)...S(2)...N(3)	164.2
N(1a)...S(3)...N(1b)	99.6	N(1b)...S(3)...N(3)	81.9
N(3)...S(3)...N(1a)	163.9	N(9)...S(4) —C(4)	92.5
N(12g)...S(4) —C(4)	94.3	N(7)...S(5)...N(11)	154.1
N(11)...S(5)...N(11d)	67.1	N(7)...S(5)...N(11i)	112.9
N(8f)...S(6) —C(6)	93.5	N(3)...O(1)...N(8)	136.6
N(3)...O(1)...N(10)	109.1	N(8)...O(1)...N(10)	92.0
N(4)...O(2)...N(6)	98.9	N(4)...O(2)...N(10)	104.0
N(6)...O(2)...N(9)	131.3	N(5)...O(3)...N(7)	130.8
C(3d) —N(6d)...S(1) —C(1)	−41.7	C(1) —N(2)...S(2) —C(2)	−49.8

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TABLE II (Continued)

C(2) —N(3)...S(3) —C(3)	-67.4	C(3) —N(5)...S(2) —C(2)	−62.2
C(2) —N(4)...S(1) —C(1)	-54.8	C(1) —N(1)...S(3d) —C(3d)	−46.1
C(1) —N(1)...S(3b) —C(3b)	-96.8	C(1) —N(2)...S(2b) —C(2b)	−110.1
C(6g) —N(12g)...S(4) —C(4)	-71.5	C(4) —N(7)...S(5) —C(5)	−68.6
C(5) —N(9)...S(4) —C(4)	-60.8	C(4) —N(8)...S(6g) —C(6g)	−68.0
C(6i) —N(11i)...S(5) —C(5)	98.2	C(6) —N(11)...S(5) —C(5)	−41.3
$2[(CH_3)_3(C_6H_5)N^+]_2CO_3^{2-} \cdot 11(NH_2)_2CS \cdot H_2O$(3)			
(i) Thiourea and carbonate molecules			
S(1) —C(1)	1.718(3)	S(2) —C(2)	1.701(3)
S(3) —C(3)	1.710(3)	S(4) —C(4)	1.707(3)
S(5) —C(5)	1.722(3)	S(6) —C(6)	1.676(4)
S(7) —C(7)	1.714(3)	S(8) —C(8)	1.719(5)
S(9) —C(9)	1.653(3)	S(10) —C(10)	1.711(3)
S(11) —C(11)	1.707(4)		
(ii) Hydrogen bonding			
N(2g)...S(1)	3.449	N(3)...S(1)	3.577
N(1)...S(2)	3.434	N(5)...S(2)	3.396
N(4)...S(3)	3.471	N(8)...S(3)	3.425
N(6)...S(4)	3.388	N(9)...S(4)	3.519
N(7)...S(5)	3.341	N(10h)...S(5)	3.467
N(13)...S(6)	3.505	N(12)...S(7)	3.374
N(12c)...S(7)	3.417	N(20)...S(8)	3.427
N(18f)...S(8)	3.371	N(19)...S(9)	3.524
N(17)...S(10)	3.455	N(17f)...S(10)	3.305
N(14)...S(11)	3.438	N(11c)...S(11)	3.403
N(1)...O(1g)	2.897	N(13)...O(1)	2.832
N(11e)...O(1)	2.719	N(15)...O(2)	2.770
N(2)...O(2g)	2.970	N(14)...O(2)	2.860
N(16)...O(3)	2.805	N(22b)...O(3)	2.937
N(4)...O(4a)	2.862	N(18)...O(4)	2.730
N(19)...O(4)	2.925	N(3)...O(5a)	2.929
N(20)...O(5)	2.918	N(21)...O(5)	2.714
N(9)...O(6b)	3.099	N(10)...O(6b)	3.042
N(16a)...O(6)	3.069	N(22)...O(6)	2.890
C(33e)...O(1W)	3.371		
C(1g) —N(2g)...S(1) —C(1)	−13.7	C(1) —N(1)...S(2) —C(2)	23.0
C(2) —N(4)...S(3) —C(3)	−13.7	C(3) —N(6)...S(4) —C(4)	11.5
C(4) —N(7)...S(5) —C(5)	36.4	C(5) —N(10)...S(5h) — C(5h)	8.3
C(6) —N(12)...S(7) —C(7)	−34.1	C(7) —N(13)...S(6) —C(6)	−49.0
C(10) —N(19)...S(9) —C(9)	−31.9	C(9) —N(17)...S(10) —C(10)	−16.4

* Symmetry transformations:

1,	a $(0.25+x, 1.25-y, 0.25+z)$;	b $(-0.25+x, 1.25-y, -0.25+z)$;	c $(1-x, 1-y, z)$
2,	a $(-1+x, y, z)$;	b $(1-x, 1-y, 1-z)$;	c $(-x, 2-y, -z)$;
	d $(1+x, y, z)$;	e $(-x, 2-y, 1-z)$;	f $(x, 1+y, z)$;
	g $(x, 1+y, -z)$;	h $(1-x, 2-y, -z)$;	i $(1-x, 1-y, -z)$
3,	a $(-1+x, y, z)$;	b $(1-x, y, z)$;	c $(-x, -y, 1-z)$;
	d $(-x, 1-y, -z$;	e $(1-x, -y, 1-z)$;	f $(1-x, 1-y, -z)$;
	g $(1-x, 1-y, 1-z)$;	h $(1-x, 2-y, 1-z)$	

Standard deviations in hydrogen bond lengths and bond angles:

1, $\sigma(l) \approx 0.005$ Å, $\sigma(\theta) \approx 0.3°$;
2, $\sigma(l) \approx 0.009$ Å, $\sigma(\theta) \approx 0.9°$;
3, $\sigma(l) \approx 0.004$ Å, $\sigma(\theta) \approx 0.3°$.

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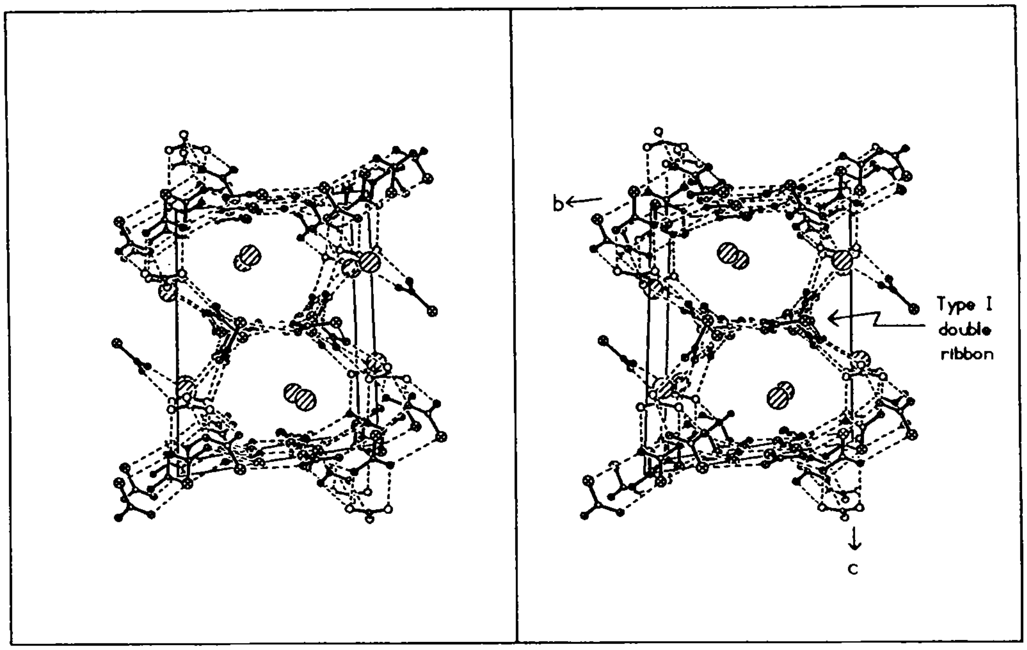

FIGURE 3 Stereodrawing of the crystal structure of $[(C_2H_5)_3(n\text{-}C_3H_7)N^+]_2CO_3^{2-}\cdot 6(NH_2)_2CS$ (**2**) showing the channels extending parallel to the [100] direction and the enclosed cations. The origin of the unit cell lies at the upper right corner, with *a* towards the reader, *b* pointing from right to left and *c* downwards. Broken lines represent hydrogen bonds, and atom types are distinguished by size and shading. For clarity the enclosed $(C_2H_5)_3(n\text{-}C_3H_7)N^+$ ions are represented by large shaded circles.

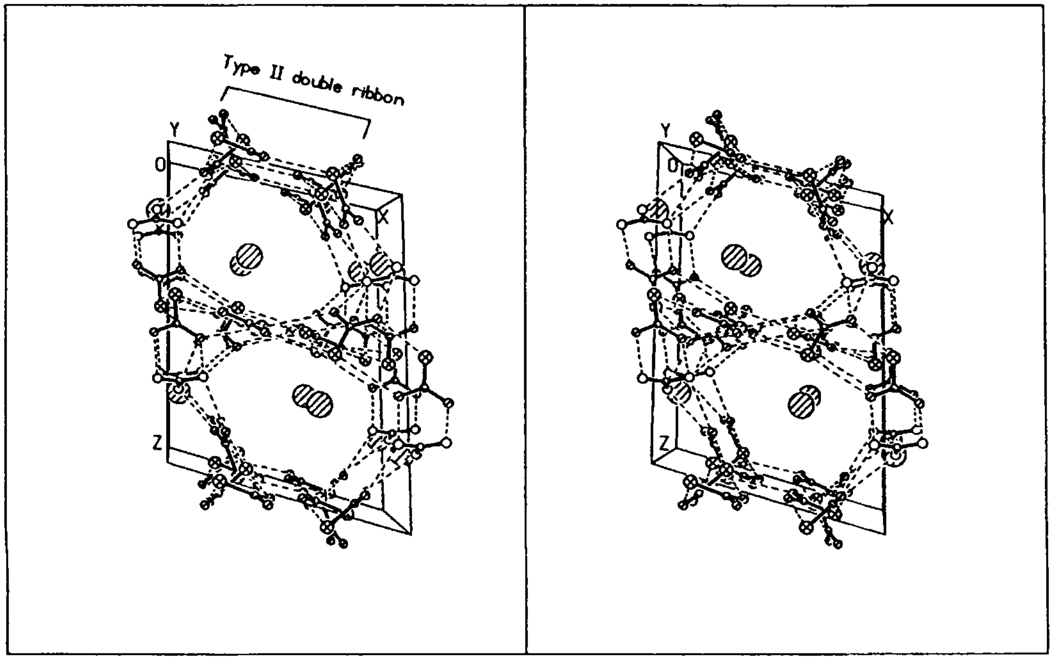

FIGURE 4 Stereodrawing of the crystal structure of **2** showing the channels extending parallel to the [010] direction and the enclosed cations. Broken lines represent hydrogen bonds, and atom types are distinguished by size and shading. For clarity the enclosed $(C_2H_5)_3(n\text{-}C_3H_7)N^+$ ions are represented by large shaded circles.

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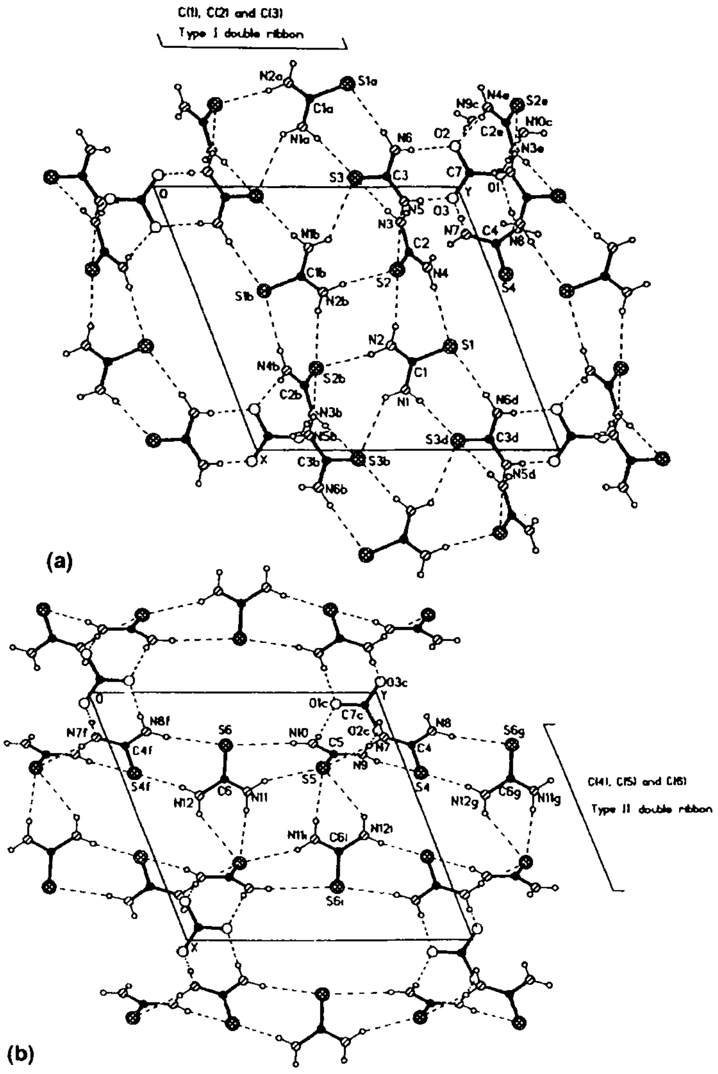

FIGURE 5 Hydrogen-bonded thiourea double ribbons in 2. (a) Type I double ribbon running parallel to the *a* axis at $z = 1/2$; (b) Type II double ribbon running parallel to the *b* axis at $z = 0$. The atom labels correspond to those given in Table II. Broken lines represent hydrogen bonds. Symmetry transformations: (a): $-1+x, y, z$; (b): $1-x, 1-y, 1-z$; (c): $-x, 2-y, -z$; (d): $1+x, y, z$; (e): $-x, 2-y, 1-z$; (f): $x, 1+y, z$; (g): $x, 1+y, -z$; (h): $1-x, 2-y, -z$; (i): $1-x, 1-y, -z$.

spiral chain similar to those found in the crystal structures of urea and thiourea. This kind of spiral chain also occurs in thiourea inclusion complexes such as the cyclohexane adduct [6].

As illustrated in Figure 5(a), the Type I thiourea chain is generated by a trimeric unit comprising thiourea molecules C(1) [composed of atoms C(1), S(1), N(1) and N(2), and hereafter conveniently referred to as C(1)], C(2) and C(3), and the C —N. . . S — C torsion angles between consecutive thiourea molecules are −41.7, - 49.8 and −67.4°. Two adjacent, parallel chains related by the inversive operation are cross-linked by pairs of N—H. . .S hydrogen bonds involving donor N atoms belonging to C(1) in one chain and acceptor S atoms belonging to C(2) and C(3) of the other chain, so that a double ribbon is formed. The torsion angles between two chains are C(1) —N(1)...S(2b) —C(2b) = −110.1 and C(1) —N(2)...S(3b) —C(3b) = −96.8°. These twisted thiourea double ribbons, lying side by side and extending parallel to the *a* axis, are located in the (002) plane as shown in Figures 3 and 5(a).

The Type II double ribbon is constructed from thiourea molecules **C(4)**, **C(5)** and **C(6)** and has essentially the same structure as type I, except that the torsion angles between **C(4)** and adjacent molecules have much larger values, namely C(6g) —N(12g)...S(4) —C(4) = −71.5 and C(4) —N(7)...S(5) —C(5) = −68.6°. These thiourea double ribbons run in the [010] direction and are arranged in a layer in the (001) plane, as showing in Figures 4 and 5(b).

The carbonate ion plays an important role in generating the host lattice. The O(1) and O(2) oxygen atoms each forms three acceptor hydrogen bonds in which two donor N atoms belong to adjacent double ribbons of the same type and one donor N atom belongs to a double ribbon of the other type: *e.g.*, in the O(1)...N(8), O(1)...N(10c) and O(1)...N(3) hydrogen bonds, N(8) and N(10c) belong to Type II but N(3) belongs to Type I (Fig. 5a). Thus a three-dimensional framework containing two open channel systems is built from two different types of thiourea double ribbons that are bridged by carbonate anions. Stacked columns of well-ordered **N(13)** $(C_2H_5)_3(n\text{-}C_3H_7)N^+$ cations are accommodated in channels extending in the [100] direction (Fig. 3), and likewise single columns of **N(14)** cations occupy channels extending in the [010] direction (Fig. 4).

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Crystal Structure of $2[(CH_3)_3(C_6H_5)N^+]_2CO_3^{2-}\cdot 11(NH_2)_2CS\cdot H_2O$ (3)

Compound 3 features a channel-type structure, which comprises infinite thiourea chains running parallel to the $[1\bar{1}1]$ direction, together with hydrogen-bonded thiourea-carbonate layers which are oriented almost perpendicular to the chains and parallel to the (022) family of planes, as shown in Figure 6.

Figure 7 shows a portion of the thiourea chain, in which five independent thiourea molecules in the asymmetric unit are linked by N —H...S hydrogen bonds in the usual shoulder-to-shoulder manner to form a pentamer, and an infinite thiourea chain is generated from similar linkage involving successive pairs of centrosymmetrically-related pentamers. All of the atoms in a chain are approximately co-planar, as can be assessed by the mean deviation of 0.14 Å from the least-squares plane of the five thiourea molecules.

The other six thiourea molecules in the asymmetric unit, together with two carbonate anions, are involved in forming a nearly planar hydrogen bonded layer. The atomlabeling scheme and hydrogen-bonding interactions in this layer are shown in Figure 8(a). Thiourea molecules **C(6)** and **C(7)** are connected by a pair of N —H...S hydrogen bonds to form a dimer, in which there is an appreciable dihedral angle between their molecular planes, as shown by the torsion angles C(6) —N(12)...S(7) —C(7) = −34.1 and C(7) —N(13)...S(6) —C(6) = −49.0°. Thiourea molecules **C(9)** and **C(10)** behave likewise, the corresponding torsion angles being C(9) —N(18)...S(10) —C(10) = −16.4 and C(10) —N(19)...S(9) —C(9) = −31.9°. The remaining thiourea molecules **C(8)** and **C(11)** each pairs up with a carbonate ion [**C(12)** and **C(13)**, respectively] to form a hetero-dimer consolidated by a pair of N —H...O hydrogen bonds. Each thiourea dimer is linked with a thiourea-carbonate hetero-dimer by a pair of N —H...O hydrogen bonds to yield a tetramer. These isostructural and independent tetramers (highlighted by shading in Fig. 8a) serve as building blocks to generate a thiourea-carbonate layer matching a (022) plane. Alternatively, the building blocks of this type of layer can be constructed from cyclic, centrosymmetric thiourea hexamers each having two protruding arms (highlighted by shading in Fig. 8b) that are bridged by the carbonate ions.

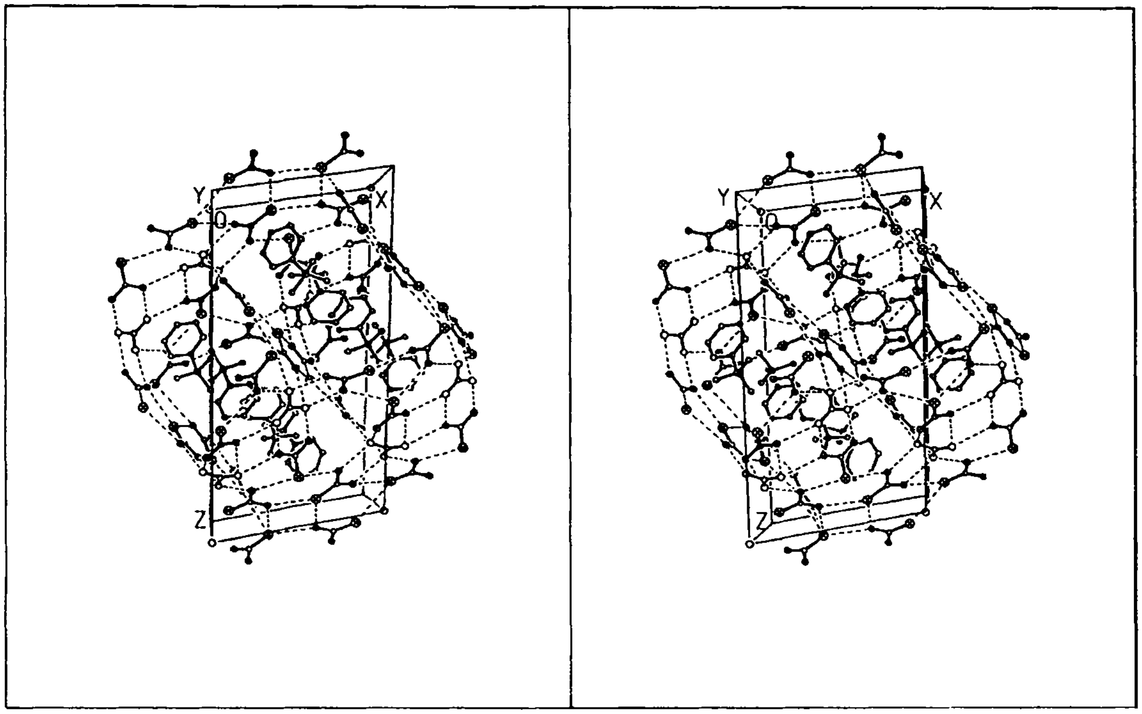

FIGURE 6 Stereodrawing of the crystal structure of $2[(CH_3)_3(C_6H_5)N^+]_2CO_3^{2-} \cdot 11(NH_2)_2CS \cdot H_2O$ (3). The origin of the unit cell lies at the upper left corner, with *a* pointing from left to right, *b* towards the reader and *c* downwards. Broken lines represent hydrogen bonds, and atom types are distinguished by size and shading.

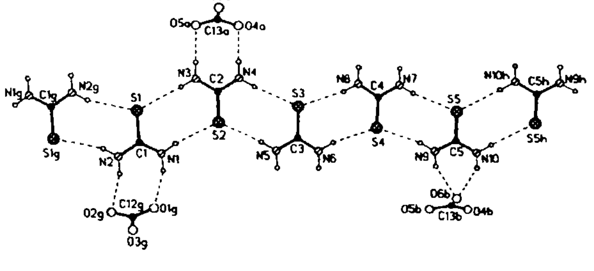

FIGURE 7 Portion of a zigzag thiourea ribbon running parallel to the $[1\bar{1}1]$ direction in 3, The atom labels correspond to those given in Table II. Symmetry transformations: (a): $-1+x, y, z$; (b): $1+x, y, z$ (g): $1-x, 1-y, 1-z$; (h): $1-x, 2-y, 1-z$;.

Finally, cross-linkage of the almost mutually perpendicular thiourea chains and thiourea-carbonate layers gives rise to a three-dimensional host lattice containing an open channel system running parallel to the $[1\bar{1}1]$ direction, as illustrated in Figure 6. All four trimethylphenylammonium cations in the asymmetric unit are arranged, sequentially and in an anti-parallel fashion, in a zigzag column with their phenyl groups oriented parallel to one another within each channel. The water molecule located at the origin makes no contribution in consolidating the hydrogen-bonded host lattice and its role is limited to that of a casual additional guest. The nearest contact between O(1 W) and its neighbors is that with methyl carbon atom C(33e) of the trimethylphenylammonium cation at 3.371(4) Å, and the shortest H...O(1W) distance is about 2.88 Å, which lies within the range H...O 1.5–3.0 Å for C—H...O hydrogen bonds [7]. Thus the water molecule fills a void between two centosymmetrically-related organic cations and is stabilized by a pair of diagonally-opposed C—H...O(1W) hydrogen bonds.

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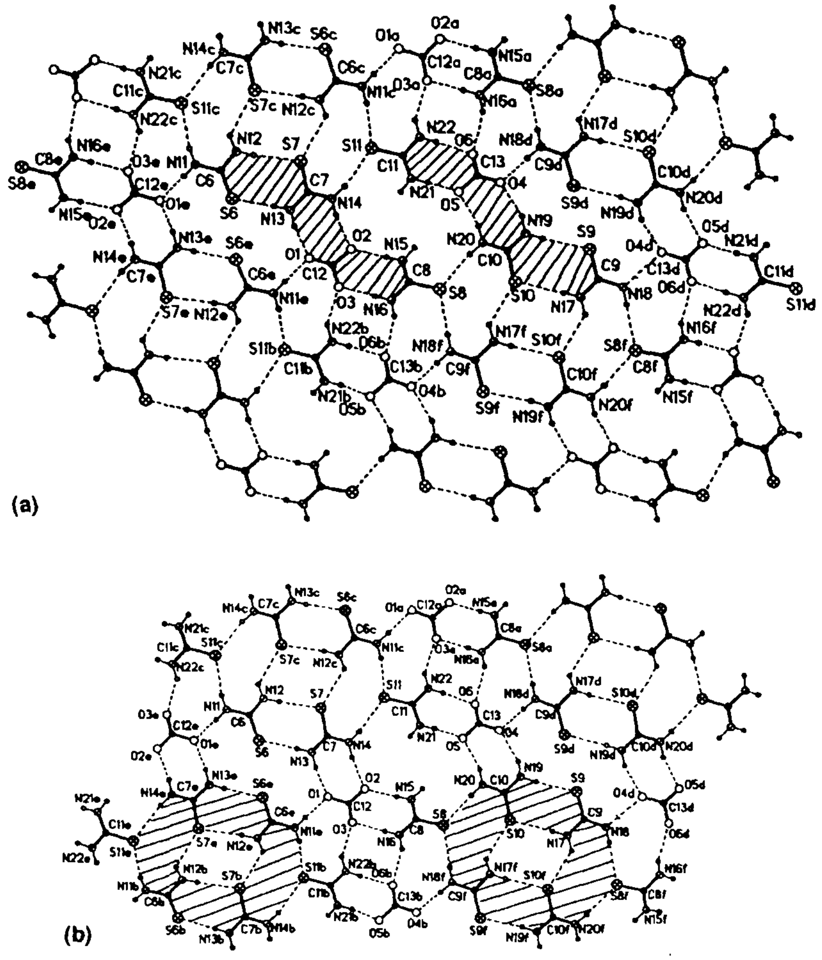

FIGURE 8 (a) Hydrogen-bonded layer in 3 formed by thiourea-carbonate tetramers. (b) Hydrogen bonded layer in 3 formed by cetrosymmetric thiourea hexamers linked by carbonate ions. The atom labels correspond to those given in Table II. Broken lines represent hydrogen bonds. Symmetry transformations: (a): $-1+x, y, z$; (b): $1+x, y, z$; (c): $-x, -y, 1-z$; (d): $-x, 1-y, -z$ (e): $1-x, -y, 1-z$; (f): $1-x, 1-y, -z$.

Structural Features and Relationships

The present thiourea-anion host lattices, generated from the template effect of unsymmetrical quaternary ammonium ions, exhibit distinctly different structural characteristics, depending on the size and shape of the hydrophobic cation and the nature of the anion. Compound 1 features a continuum of two fused channel systems to suit the $(n\text{-}C_4H_9)(CH_3)N^+$ cation which has a flattened trigonal pyramidal shape, whereas compound 2 possesses two open channel systems, and the channel-type host lattice of 3 is built up by thiourea-carbonate layers and infinite thiourea chains.

It is interesting to compare the modes of linkage of the thiourea molecules in compounds 2 and 3, both having a high stoichiometric ratio of thiourea to carbonate ion. The thiourea molecules in 2 are linked in the three-molecule spiral chain mode as found in neat thiourea and some thiourea inclusion complexes [6], which are further connected pairwise to form double ribbons. In compound 3 two novel linkage

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modes are found: five sequential independent thiourea molecules constitute a repeating unit to build an infinite thiourea chain, whereas the remaining six thiourea molecules interact with the carbonate ions to generate a nearly planar layer.

In comparing compounds **2** and **3** with the thiourea-bicarbonate [2] and thiourea-nitrate [3] inclusion compounds, it is noted that the carbonate ion CO_3^{2-} is more akin to NO_3^- than to HCO_3^-, as it can only form acceptor hydrogen bonds with other potential donors. Therefore, the relevant three-dimensional host frameworks have a higher than normal thiourea/carbonate molar ratio, and most oxygen atoms of the carbonate ions form three acceptor hydrogen bonds with nitrogen atoms of neighboring thiourea molecules. The only exceptions are O(3) in **2** and O(6) in **3**, each forming two accepted hydrogen bonds, and the O(3) atom in **3** which forms four O...H—N hydrogen bonds.

The two carboxylate fragments of both the hydrogen oxalate ion and the oxalic acid molecule in **1** are notably non-coplanar, the dihedral angles between them being 28.1 and 49.4°, respectively. This can be rationalized in terms of the abnormally long C—C single bond in $H_2C_2O_4$ (1.548 Å) [8], $HC_2O_4^-$ (1.550 Å) [9] and $C_2O_4^{2-}$ (1.567 Å) [10], which has a σ bond order less than unity [11]. As a result of the small barrier to rotation of the two carboxylate fragments about the central C—C bond, the hydrogen oxalate ion and oxalic acid molecule adopt the most favorable conformations to form hydrogen bonds with neighboring thiourea molecules in the host lattice. As shown in Figure 2, the oxalic acid molecule is located between two adjacent thiourea-anion ribbons that are extended in different directions, and the dihedral angle between its two carboxylate fragments (49.4°) results from optimal positioning of the oxygen atoms to form N—H...O and O—H...S hydrogen bonds.

EXPERIMENTAL

Tri-*n*-butylmethyl-, triethyl-*n*-propyl- and trimethylphenyl-ammonium hydroxides were prepared from their corresponding chloride or iodide salts by reaction with moist silver(I) oxide [12]. Each hydroxide and thiourea were mixed in molar ratios of 1:2, 1:3 and 1:4, respectively. A minimum quantity of water was used to dissolve the solid in each case, and crystalline oxalic acid was added to the solution in a 1:1 molar ratio for hydroxide: acid and stirred for about half an hour for **1**, while carbon dioxide (from dry ice) was allowed to bubble through the solution for about half an hour for **2** and **3**. Then the solution was subjected to slow evaporation at room temperature in a desiccator charged with drierite. Colorless crystals appeared in the form of thin plates (**1** and **3**) or small blocks (**2**). Complex **1** is highly hygroscopic and a selected single crystal was sealed in a 0.5 mm Lindemann glass capillary for the X-ray study.

Information concerning crystallographic data and structure refinement of the three compounds is summarized in Table I. Intensities were collected at 291 K in the variable ω-scan mode [13] on a Siemens R3m/V diffractometer using MoKα radiation ($\lambda = 0.71073$ Å). The raw data were processed with a learnt-profile procedure [14], 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 [15]. Direct methods yielded the positions of all non-hydrogen atoms. The thioamido, methylene, methyl, and aromatic H atoms were generated geometrically (C—H fixed at 0.96 Å) 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. The methyl groups of one independent cation in **3** exhibit two-fold orientational disorder, and their

X-ray scattering power was represented by half-carbon atoms C (n) and C (nA). Analytic expressions of atomic scattering factors were employed, and anomalous dispersion corrections were incorporated [16]. 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.

Acknowledgments

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