

Inclusion Compounds of Thiourea and Peralkylated Ammonium Salts. Part II. Hydrogen-Bonded Host Lattices Built of Thiourea and Cyclic Dimeric Bicarbonate Moieties

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Abstract. New inclusion complexes $R_4N^+HCO_3^- \cdot x(NH_2)_2CS \cdot yH_2O$ (**1**, $R = C_2H_5$, $x = 1$, $y = 1$; **2**, $R = n-C_3H_7$, $x = 2$, $y = 0$; **3**, $R = n-C_4H_9$, $x = 3$, $y = 0$) have been prepared and characterized by X-ray crystallography. Crystal data, MoK α radiation: **1**, space group $Pbca$, $Z = 8$, $a = 8.839(2)$, $b = 14.930(3)$, $c = 24.852(5)$ Å, and $R_F = 0.063$ for 1419 observed data; **2**, space group $C222_1$, $Z = 8$, $a = 8.521(3)$, $b = 16.941(4)$, $c = 32.022(7)$ Å, $R_F = 0.054$ for 1689 observed data; **3**, space group $P\bar{1}$, $Z = 2$, $a = 9.553(2)$, $b = 12.313(3)$, $c = 14.228(4)$ Å, $\alpha = 90.44(2)$, $\beta = 103.11(2)$, $\gamma = 110.12(2)^\circ$, $R_F = 0.044$ for 3925 observed data. In the crystal structure of **1**, the thiourea molecules form hydrogen-bonded zigzag ribbons running parallel to the a axis, and the cyclic dimeric bicarbonate moieties $(HCO_3^-)_2$ together with water molecules behave likewise. A puckered layer is formed by further lateral hydrogen bonding between these two types of ribbons, and the $(C_2H_5)_4N^+$ cations occupy the space between adjacent layers. In the crystal structure of **2**, the thiourea ribbons are cross-linked orthogonally by $(HCO_3^-)_2$ units via N—H \cdots O hydrogen bonds to form a composite double layer. Half of the cations are enclosed within and the other half sandwiched between these double layers. In the crystal structure of **3**, the thiourea molecules form puckered double ribbons running in the [110] direction. The host framework is constructed by cross-linking the double ribbons with bridging bicarbonate dimers, yielding two channel systems aligned parallel to [100] and [111] that accommodate the cationic guests. The structural relationship between the present complexes and the classical thiourea channel adducts is discussed.

Supplementary Data relating to this article have been deposited with the British Library as Supplementary Publication No. SUP 82178 (44 pages).

Key words: Thiourea, tetraalkylammonium salt, bicarbonate dimer, hydrogen bonding, inclusion compound.

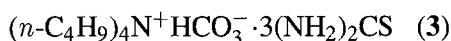
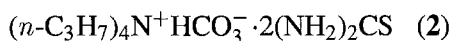
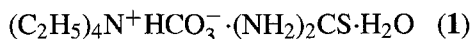
1. Introduction

The inclusion compounds of urea and thiourea are classical examples of crystalline host–guest systems [1–4]. Thiourea inclusion compounds feature an extensively

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hydrogen bonded thiourea host lattice that contains parallel channels or tunnels [5–7] with a free diameter of about 6.1 Å, which can enclose a variety of guest species such as branched-chain alkanes and their derivatives, haloalkanes, 5-, 6- and 8-membered ring compounds, condensed aromatic ring systems, and even ferrocene and other metallocenes [8]. Recent examples of appropriate guest molecules that have been investigated include cyclohexane and some of its derivatives [9], certain compounds containing organometallics [10], as well as fragments of polymers containing either phenyl groups or sugar rings [11]. Another well-known class of inclusion compounds are the tetraalkylammonium salt hydrates, which were found to be clathrates with a rich variety of three-dimensional hydrogen-bonded host structures built of water molecules and anionic moieties such as halide ions [12–14], CH_3COO^- [15] and $[\text{B}_5\text{O}_6(\text{OH})_4]^-$ [16].

Several years ago we reported the crystal structures of a series of thiourea-halide complexes, namely $(n\text{-C}_4\text{H}_9)_4\text{N}^+\text{F}^- \cdot 3(\text{NH}_2)_2\text{CS}$, $(n\text{-C}_4\text{H}_9)_3(\text{CH}_3)\text{N}^+\text{X}^- \cdot 2(\text{NH}_2)_2\text{CS}$ ($\text{X} = \text{Cl}, \text{Br}$) and $(n\text{-C}_3\text{H}_7)_4\text{N}^+\text{I}^- \cdot (\text{NH}_2)_2\text{CS}$ [17], in which the thiourea molecules are alternately linked by pairs of $\text{N}—\text{H} \cdots \text{S}$ hydrogen bonds to give a ribbon which in turn forms additional hydrogen bonds with the halide ions, thereby resulting in an anionic host framework or composite ribbon as a principal component in the crystal packing. In the design of new thiourea-anion host lattices, we consider the simple trigonal planar anions CO_3^{2-} , NO_3^- and HCO_3^- (if the proton is neglected from its molecular framework) that can easily form $\text{O} \cdots \text{H}—\text{N}$ acceptor hydrogen bonds. The HCO_3^- ion is particularly versatile as it can function as both donor and acceptor in hydrogen bonding. Accordingly we have carried out parallel studies employing these anions and thiourea in the construction of new host lattices that can accommodate peralkylated ammonium cations of different sizes. In the present work, we report the preparation and structural characterization of the following complexes:



2. Experimental

Tetraethylammonium hydroxide (25 wt.-% aqueous solution) was obtained from Eastman Kodak, whereas tetrapropyl- and tetrabutyl-ammonium hydroxide were prepared from their corresponding chloride salts by reaction with moist silver(I) oxide [18].

Each hydroxide and thiourea were mixed in molar ratios of 1 : 1, 1 : 1.5 and 1 : 2, respectively, and a minimum quantity of water was added to dissolve the solid in each case. After carbon dioxide gas (from dry ice) was allowed to bubble through

the solution for about half a hour, the latter was subjected to slow evaporation at room temperature in a desiccator charged with Drierite. Colorless crystals appeared in the form of thin plates (crystal **1**) and small blocks (crystal **3**), respectively. Complex **2** was obtained initially as very thin needles, which were 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 three compounds is summarized in Table I. Intensities were collected in the variable ω -scan technique [19] 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 [20], an empirical absorption correction based on ψ -scan data was also applied.

All calculations were performed on a PC 486 computer with the SHELXTL PC program package [21]. Direct methods yielded the positions of all non-hydrogen atoms. The thioamido, methylene, and methyl H atoms were generated geometrically (C—H fixed at 0.96 \AA) and allowed to ride on their respective parent atoms. The hydrogen atoms of the bicarbonate ions in **1** and **3** were located from subsequent difference Fourier syntheses, but that in **2** was not located and inserted at the centre of the hydrogen bond linking two O atoms. The hydrogen atoms of the water molecule in **1** were generated based on 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 [22]. 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.

3. Results and Discussion

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

3.1. CRYSTAL STRUCTURE OF **1**

The structure of **1** is comparable to those obtained in our previous work on a series of urea-water-tetraethylammonium halide inclusion complexes [23]. The layer structure may be conveniently described with reference to the hydrogen bonding scheme shown in Figure 1 and Table V. The thiourea molecules are alternately linked by pairs of N—H \cdots S hydrogen bonds to form an approximately planar ribbon oriented parallel to a . The bicarbonate ions occur as centrosymmetric cyclic dimers each consolidated by a pair of O—H \cdots O hydrogen bonds, and together with the water molecules they form a highly puckered zigzag $[(\text{HCO}_3^-)_2(\text{H}_2\text{O})_2]_\infty$

TABLE I. Data collection and processing parameters of thiourea-tetraalkylammonium bicarbonate complex

Complex	1	2	3
Molecular formula	$(C_2H_5)_4N^+ HCO_3^- \cdot CS(NH_2)_2 \cdot H_2O$	$(C_3H_7)_4N^+ HCO_3^- \cdot 2CS(NH_2)_2$	$(C_4H_9)_4N^+ HCO_3^- \cdot 3CS(NH_2)_2$
Molecular weight	285.40	399.60	531.85
Crystal system	Orthorhombic	Orthorhombic	Triclinic
Space group	<i>Pbca</i> (No. 61)	<i>C222</i> ₁ (No. 20)	<i>P</i> $\bar{1}$ (No. 2)
Unit cell parameters			
<i>a</i> , Å	8.839(2)	8.521(3)	9.553(2)
<i>b</i> , Å	14.930(3)	16.941(4)	12.313(3)
<i>c</i> , Å	24.852(5)	32.022(7)	14.228(4)
α , °	90	90	90.44(2)
β , °	90	90	103.11(2)
γ , °	90	90	110.12(2)
<i>V</i> , Å ³	3280(1)	4622(2)	1530.0(7)
<i>Z</i>	8	8	2
<i>F</i> (000)	1248	1744	580
Density (floatation in <i>n</i> -hexane/ <i>CCl</i> ₄), g cm ⁻³	1.159	1.123	1.152
Density (calcd.), g cm ⁻³	1.156	1.148	1.154
Absorption coefficient, cm ⁻¹	0.208	0.252	0.273
Crystal size, mm	0.52 × 0.62 × 0.68	0.18 × 0.48 × 0.52	0.42 × 0.64 × 0.68
Mean μ_r	0.05	0.04	0.08
Transmission factors	0.845 to 0.896	0.862 to 0.922	0.838 to 0.906
Scan speed (deg min ⁻¹)	2.0 to 29.3	4.0 to 60.0	3.5 to 19.5
Scan range (below <i>K</i> α ₁ to above <i>K</i> α ₂)	0.60 to 0.60	0.60 to 0.60	0.80 to 0.80
Background counting	stationary counts for one-half of scan time at each end of scan		
$2\theta_{max}$, °	45	52	50
Unique data measured	2583	3018	5413
Observed data	$ F_o > 6\sigma(F_o)$, 1419	$ F_o > 3\sigma(F_o)$, 1689	$ F_o > 4\sigma(F_o)$, 3925
Number of variables, <i>p</i>	163	227	299
$R_F = \sum F_o - F_c / \sum F_o $	0.063	0.054	0.044
Constant <i>g</i> in weighting scheme			
$\omega = [\sigma^2(F_o) + g F_o^2]^{-1}$	0	0.0008	0.002
$R_G = [\sum \omega(F_o - F_c)^2 / \sum F_o ^2]^{1/2}$	0.061	0.062	0.054
$S = [\sum \omega(F_o - F_c)^2 / (n - p)]^{1/2}$	1.22	1.32	1.82
Residual extrema in final difference map, e Å ⁻³	+0.40 to -0.25	+0.33 to -0.28	+0.22 to -0.18
Largest and mean Δ/σ	0.000, 0.000	0.029, 0.001	0.002, 0.000

ribbon by O··H—O(1W) hydrogen bonding. For these two types of ribbons, the extent of deviation from planarity can be seen from the relevant torsion angles: C(1a)—N(1a)··S(1)—C(1) = 5.7, C(1)—N(1)··S(1b)—C(1b) = -5.7;

TABLE II. Atomic coordinates ($\times 10^4$) and thermal parameters ($\text{\AA}^2 \times 10^3$) of $(\text{C}_2\text{H}_5)_4\text{N}^+\text{HCO}_3^-\cdot\text{CS}(\text{NH}_2)_2\cdot\text{H}_2\text{O}$ (1).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq} or U	Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq} or U
Thiourea-bicarbonate-water host lattice					Tetraethylammonium ion				
S(1)	1812(2)	4389(1)	2754(1)	74(1)	N(3)	5687(5)	7122(3)	1235(1)	62(1)
C(1)	1835(5)	4567(3)	2071(2)	56(2)	C(3)	7085(8)	6518(4)	1198(2)	99(3)
N(1)	3090(5)	4489(3)	1796(2)	78(2)	C(4)	8569(8)	7007(7)	1285(3)	135(4)
H(N1A)	3961	4348	1963	80	C(5)	5792(8)	7893(4)	850(2)	88(2)
H(N1B)	3081	4583	1439	80	C(6)	5920(9)	7641(5)	266(3)	123(3)
N(2)	590(5)	4778(3)	1812(2)	65(1)	C(7)	5578(8)	7515(4)	1796(2)	97(3)
H(N2A)	-290	4837	1991	80	C(8)	5441(11)	6834(5)	2249(2)	132(4)
H(N2B)	622	4968	1454	80	C(9)	4320(9)	6543(4)	1117(3)	111(3)
C(2)	1808(8)	4742(3)	416(2)	67(2)	C(10)	2798(8)	7023(7)	1155(3)	146(4)
O(1)	575(4)	4969(3)	635(1)	77(1)					
O(2)	2957(5)	4564(3)	672(1)	108(2)					
O(3)	1873(5)	4691(3)	-111(1)	85(1)					
H(O3)	1022	4808	-263	80					
O(1W)	4078(6)	5957(3)	-514(3)	179(3)					
H(1WA)	3433	5586	-392	80					
H(1WB)	4993	5800	-558	80					

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

The exponent of the isotropic temperature factor takes the form $-8\pi^2 U \sin^2 \theta / \lambda^2$.

but $\text{O}(1\text{W}) \cdots \text{O}(1) - \text{C}(2) - \text{O}(2) = -61.3$, $\text{C}(2) - \text{O}(1) \cdots \text{O}(1\text{W}) \cdots \text{O}(2\text{c}) = 91.4^\circ$, respectively. The parallel arrangement of these two kinds of complementary ribbons facilitates cross-linkage by pairs of $\text{N}-\text{H} \cdots \text{O}$ hydrogen bonds to form a puckered layer normal to the b axis (Figure 1).

The interlayer spacing of $b/2 = 7.465 \text{ \AA}$ is slightly larger than the corresponding values for similar layer structures with tetraethylammonium cations accommodated in the urea-water-halide lattice ($b/2 = 7.278 \text{ \AA}$, in monoclinic $(\text{C}_2\text{H}_5)_4\text{N}^+\text{Cl}^- \cdot (\text{NH}_2)_2\text{CO} \cdot 2\text{H}_2\text{O}$) [23] and the acetate-water lattice ($1/b^* = 7.39 \text{ \AA}$, in triclinic $(\text{C}_2\text{H}_5)_4\text{N}^+\text{CH}_3\text{COO}^- \cdot 4\text{H}_2\text{O}$) [15], as may be expected in view of the larger size of the S atom.

The tetrahedral $(\text{C}_2\text{H}_5)_4\text{N}^+$ cation is well ordered and nearly attains its idealized 222 molecular symmetry. Its averaged dimensions are $\text{N}-\text{C} = 1.517(9)$, $\text{C}-\text{C} = 1.523(10) \text{ \AA}$, $\text{C}-\text{N}-\text{C} = 109.5(5)$, and $\text{N}-\text{C}-\text{C} = 114.9(6)^\circ$. Individual bond distances and angles are given in the Supplementary Data. A stereo view of the crystal structure is illustrated in Figure 2. It is seen that the cations are located in the space between the layers, which correspond to the (020) family of planes.

TABLE III. Atomic coordinates ($\times 10^4$) and thermal parameters ($\text{\AA}^2 \times 10^3$) of $(\text{C}_3\text{H}_7)_4\text{N}^+\text{HCO}_3^- \cdot 2\text{CS}(\text{NH}_2)_2$ (**2**).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq} or U	Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq} or U
Thiourea–bicarbonate host lattice					Tetra-<i>n</i>-propylammonium ion				
S(1)	667(2)	6903(1)	1055(1)	69(1)	N(5)	5000	2621(3)	2500	63(1)
C(1)	676(6)	5967(3)	1263(1)	57(1)	C(4)	5895(6)	3127(3)	2189(2)	75(1)
N(1)	1983(5)	5627(3)	1375(1)	69(1)	C(5)	5017(3)	3743(3)	1955(2)	88(1)
H(N1A)	2901	5884	1347	100	C(6)	6087(7)	4163(3)	1661(2)	98(1)
H(N1B)	1964	5136	1482	100	C(7)	6167(7)	2120(3)	2735(2)	88(1)
N(2)	-642(5)	5571(3)	1299(2)	78(1)	C(8)	7083(7)	1529(3)	2488(3)	113(1)
H(N2A)	-1536	5799	1211	100	C(9)	8098(8)	1033(4)	2761(3)	150(1)
H(N2B)	-664	5080	1407	100	N(6)	5854(7)	0	0	80(1)
S(2)	618(2)	1173(1)	939(1)	82(1)	C(10)	4833(7)	-700(4)	-121(2)	94(1)
C(2)	650(6)	2108(3)	1128(2)	67(1)	C(11)	3779(7)	-1037(4)	218(2)	119(1)
N(3)	1949(5)	2492(3)	1202(2)	79(1)	C(12)	3089(7)	-1806(5)	88(3)	135(1)
H(N3A)	2885	2264	1153	100	C(13)	6863(7)	-193(3)	378(2)	83(1)
H(N3B)	1906	2988	1303	100	C(14)	7952(7)	-905(4)	325(2)	113(1)
N(4)	-654(5)	2481(3)	1211(2)	102(1)	C(15)	9045(7)	-965(4)	677(2)	115(1)
H(N4A)	-1584	2252	1156	100					
H(N4B)	-622	2977	1312	100					
C(3)	584(6)	3962(3)	1913(2)	73(1)					
O(1)	340(7)	4586(2)	2113(2)	161(1)					
O(2)	440(6)	3331(2)	2119(1)	116(1)					
O(3)	923(5)	3994(2)	1540(1)	92(1)					
H(O3)	-659	450	124	50					

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

The exponent of the isotropic temperature factor takes the form $-8\pi^2 U \sin^2 \theta / \lambda^2$.

3.2. CRYSTAL STRUCTURE OF **2**

The atom-labeling scheme and hydrogen-bonding interactions are shown in Figure 3. In the crystal structure of **2**, both independent thiourea molecules are involved in forming zigzag, puckered ribbons (torsion angles $\text{C}(2)\text{—N}(4)\cdots\text{S}(1c)\text{—C}(1c) = 48.4$, $\text{C}(1)\text{—N}(2)\cdots\text{S}(2a)\text{—C}(2a) = -47.3^\circ$) running parallel to *a*, and these ribbons are aligned in such a way that they lie approximately in layers that are normal to the *c* axis. The bicarbonate ions form cyclic $(\text{HCO}_3^-)_2$ dimers of symmetry 2, and each exocyclic O atom forms four acceptor hydrogen bonds with two adjacent thiourea ribbons belonging to the same layer. As a consequence of this unusual type of orthogonal cross-linkage, a composite *double layer*, whose thickness equals the longest dimension of the $(\text{HCO}_3^-)_2$ dimer, emerges as the principal component of the organized hydrogen-bonded host lattice (Figure 4).

TABLE IV. Atomic coordinates ($\times 10^4$) and thermal parameters ($\text{\AA}^2 \times 10^3$) of $(\text{C}_4\text{H}_9)_4\text{N}^+\text{HCO}_3^-\cdot 3\text{CS}(\text{NH}_2)_2$ (3).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq} or U	Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq} or U
Thiourea–bicarbonate host lattice									
S(1)	7757(1)	11868(1)	2781(1)	62(1)	C(4)	6247(2)	6175(2)	1109(2)	57(1)
C(1)	7789(2)	12207(2)	3944(2)	52(1)	O(1)	6657(2)	5429(2)	755(1)	81(1)
N(1)	8835(2)	13169(2)	4450(2)	67(1)	O(2)	7079(2)	6983(2)	1726(1)	80(1)
H(N1A)	9537	13652	4173	80	O(3)	4796(2)	6101(1)	774(1)	72(1)
H(N1B)	8840	13340	5065	80	H(03)	4339	5449	124	100
N(2)	6766(2)	11533(2)	4381(2)	70(1)	Tetra-<i>n</i>-butylammonium ion				
H(N2A)	6029	10883	4056	80	N(7)	6937(2)	7350(1)	7775(1)	48(1)
H(N2B)	6799	11726	4997	80	C(5)	5299(2)	6604(2)	7257(2)	58(1)
S(2)	1377(1)	5348(1)	3522(1)	58(1)	C(6)	5291(2)	5517(2)	6671(2)	66(1)
C(2)	-49(2)	5622(2)	2707(2)	50(1)	C(7)	3493(2)	4907(2)	6113(2)	93(1)
N(3)	-1262(2)	4766(2)	2194(2)	59(1)	C(8)	3103(2)	3742(2)	5649(2)	91(1)
H(N3A)	-1348	4023	2270	80	C(9)	7669(2)	6608(2)	8414(2)	54(1)
H(N3B)	-2001	4928	1770	80	C(10)	9260(2)	7245(2)	9053(2)	65(1)
N(4)	24(2)	6707(2)	2570(2)	68(1)	C(11)	9866(2)	6406(2)	9638(2)	74(1)
H(N4A)	831	7312	2903	80	C(12)	11506(2)	6976(2)	10205(2)	114(1)
H(N4B)	-739	6833	2139	80	C(13)	7914(2)	7831(2)	7057(2)	57(1)
S(3)	3880(1)	8965(1)	3331(1)	70(1)	C(14)	7302(2)	8484(2)	6284(2)	67(1)
C(3)	4715(2)	8266(2)	2726(2)	53(1)	C(15)	8558(2)	9219(2)	5819(2)	89(1)
N(5)	5947(2)	8835(2)	2413(2)	76(1)	C(16)	9690(2)	10271(2)	6441(2)	116(1)
H(N5A)	6396	9613	2524	80	C(17)	6878(2)	8364(2)	8362(2)	58(1)
H(N5B)	6347	8429	2096	80	C(18)	6081(2)	8036(2)	9182(2)	76(1)
N(6)	4119(2)	7130(2)	2518(2)	68(1)	C(19)	6168(2)	9096(2)	9768(2)	93(1)
H(N6A)	3265	6717	2704	80	C(20)	7711(3)	9743(2)	10383(2)	141(1)
H(N6B)	4566	6766	2197	80					

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

The exponent of the isotropic temperature factor takes the form $-8\pi^2 U \sin^2 \theta / \lambda^2$.

Figure 3 shows the crisscross arrangement of molecules and details of the hydrogen bonding between them. The four acceptor hydrogen bonds formed by O(3) with two molecules of thiourea resemble those formed by the carbonyl O atom in crystalline urea [24] and its normal inclusion compounds [25]. In the present structure the four N—H \cdots O hydrogen bonds have an average bond length of about 3.01 Å and are approximately coplanar; the angles between them are: N(1) \cdots O(3) \cdots N(2) = 43.7, N(2) \cdots O(3) \cdots N(4) = 116.5, N(3) \cdots O(3) \cdots N(4) = 43.4, and N(1) \cdots O(3) \cdots N(3) = 126.4°, respectively, with a sum of 330.0°. The values of the torsion angles between the bridging bicarbonate dimer and thiourea ribbons, C(3)—O(3) \cdots N(1)—C(1) = -91.7 and C(3)—O(3) \cdots N(3)—C(2) = 80.7,

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

(C ₂ H ₅) ₄ N ⁺ HCO ₃ ⁻ · CS(NH ₂) ₂ · H ₂ O (1)			
<i>(i) Thiourea and bicarbonate molecules</i>			
S(1)—C(1)	1.720(4)	S(1)—C(1)—N(1)	120.8(3)
C(1)—N(1)	1.307(6)	S(1)—C(1)—N(2)	120.7(3)
C(1)—N(2)	1.312(6)	N(1)—C(1)—N(2)	118.5(4)
C(2)—O(1)	1.265(7)	O(1)—C(2)—O(2)	123.2(4)
C(2)—O(2)	1.228(8)	O(2)—C(2)—O(3)	118.0(5)
C(2)—O(3)	1.313(6)	O(1)—C(2)—O(3)	118.8(5)
<i>(ii) Hydrogen bonding</i>			
N(1a) ··· S(1)	3.479	N(1) ··· O(2)	2.799
N(2b) ··· S(1)	3.557	N(2) ··· O(3)	2.913
O(3) ··· O(1d)	2.564	O(1) ··· O(1W)	2.900
O(2) ··· O(1Wc)	2.761		
C(1a)—N(1a) ··· S(1)—C(1)	5.7	C(1b)—N(2b) ··· S(1)—C(1)	-37.3
(C ₃ H ₇) ₄ N ⁺ HCO ₃ ⁻ · 2CS(NH ₂) ₂ (2)			
<i>(i) Thiourea and bicarbonate molecules</i>			
S(1)—C(1)	1.721(5)	S(2)—C(2)	1.696(5)
C(1)—N(1)	1.304(6)	C(2)—N(3)	1.307(7)
C(1)—N(2)	1.314(7)	C(2)—N(4)	1.306(7)
C(3)—O(1)	1.254(7)	C(3)—O(2)	1.260(6)
C(3)—O(3)	1.231(7)		
S(1)—C(1)—N(1)	121.1(4)	S(2)—C(2)—N(3)	123.0(4)
S(1)—C(1)—N(2)	120.1(4)	S(2)—C(2)—N(4)	120.8(4)
N(1)—C(1)—N(2)	118.7(4)	N(3)—C(2)—N(4)	116.3(5)
O(1)—C(3)—O(2)	115.7(5)	O(1)—C(3)—O(3)	119.8(5)
O(2)—C(3)—O(3)	124.5(5)		
<i>(ii) Hydrogen bonding</i>			
N(1) ··· S(2b)	3.522	N(1) ··· O(3)	2.957
N(2) ··· S(2a)	3.540	N(2) ··· O(3)	3.083
N(3) ··· S(1d)	3.354	N(3) ··· O(3)	2.900
N(4) ··· S(1c)	3.322	N(4) ··· O(3)	3.081
O(1) ··· O(1e)	2.543	O(2) ··· O(2e)	2.556
C(1)—N(1) ··· S(2b)—C(2b)	64.6	C(2)—N(2) ··· S(1d)—C(1d)	-46.1
C(1)—N(2) ··· S(2a)—C(2a)	-47.3	C(2)—N(4) ··· S(1c)—C(1c)	48.4

TABLE V. Continued.

(C ₄ H ₉) ₄ N ⁺ HCO ₃ ⁻ · 3CS(NH ₂) ₂ (3)			
<i>(i) Thiourea and bicarbonate molecules</i>			
S(1)—C(1)	1.702(2)	C(2)—N(4)	1.332(3)
C(1)—N(1)	1.330(2)	S(3)—C(3)	1.704(3)
C(1)—N(2)	1.327(3)	C(3)—N(5)	1.323(3)
S(2)—C(2)	1.712(2)	C(3)—N(6)	1.318(3)
C(2)—N(3)	1.324(2)	C(4)—O(2)	1.234(2)
C(4)—O(1)	1.258(3)	C(4)—O(3)	1.331(3)
S(1)—C(1)—N(1)	121.2(2)	S(2)—C(2)—N(4)	120.9(1)
S(1)—C(1)—N(2)	121.6(1)	N(3)—C(2)—N(4)	117.8(2)
N(1)—C(1)—N(2)	117.2(2)	S(3)—C(3)—N(5)	121.9(2)
S(2)—C(2)—N(3)	121.3(2)	S(3)—C(3)—N(6)	120.9(2)
N(5)—C(3)—N(6)	117.2(2)	O(1)—C(4)—O(2)	125.8(2)
O(1)—C(4)—O(3)	117.1(2)	O(2)—C(4)—O(3)	117.1(2)
<i>(ii) Hydrogen bonding</i>			
N(3f) ··· S(1)	3.525	C(2f)—N(3f) ··· S(1)—C(1)	52.6
N(1b) ··· S(2)	3.495	C(1)—N(2) ··· S(3)—C(3)	42.8
N(1c) ··· S(2)	3.447	C(3)—N(6) ··· S(2)—C(2)	83.1
N(4) ··· S(3)	3.685	C(2)—N(4) ··· O(2g)—C(4g)	-37.9
N(3) ··· O(1)	2.851	C(2)—N(3) ··· O(1g)—C(4g)	-52.6
N(5) ··· O(2)	3.080	C(3)—N(5) ··· O(2)—C(4)	56.3
O(3) ··· O(1h)	2.649		
C(1c)—N(1c) ··· S(2)—C(2)	59.2	C(1c)—N(1c) ··· S(2)—C(2)	59.2
C(2)—N(4) ··· S(3)—C(3)	50.6	C(2)—N(4) ··· S(3)—C(3)	50.6
C(3)—N(5) ··· S(1)—C(1)	42.7	C(3)—N(5) ··· S(1)—C(1)	42.7

*Symmetry transformations:

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

2, a (0.5 + x, -0.5 + y, z); b (-0.5 + x, -0.5 + y, z); c (0.5 + x, 0.5 + y, z); d (-0.5 + x, 0.5 + y, z); e (-x, y, 1.5 - z)

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

Standard deviations in hydrogen bond lengths and bond angles:

1, $\sigma(l) \simeq 0.009 \text{ \AA}$, $\sigma(\theta) \simeq 0.6^\circ$;

2, $\sigma(l) \simeq 0.009 \text{ \AA}$, $\sigma(\theta) \simeq 0.6^\circ$;

3, $\sigma(l) \simeq 0.005 \text{ \AA}$, $\sigma(\theta) \simeq 0.4^\circ$.

clearly show their nearly orthogonal relationship in the construction of the double layer.

Both well-ordered tetrapropylammonium cations in the asymmetric unit occupy special positions of site symmetry 2: atoms N(5) and N(6) are situated at Wyckoff positions 4(b) at $(\frac{1}{2}, y, \frac{1}{4})$ and 4(a) at $(x, 0, 0)$, respectively. Figure 4

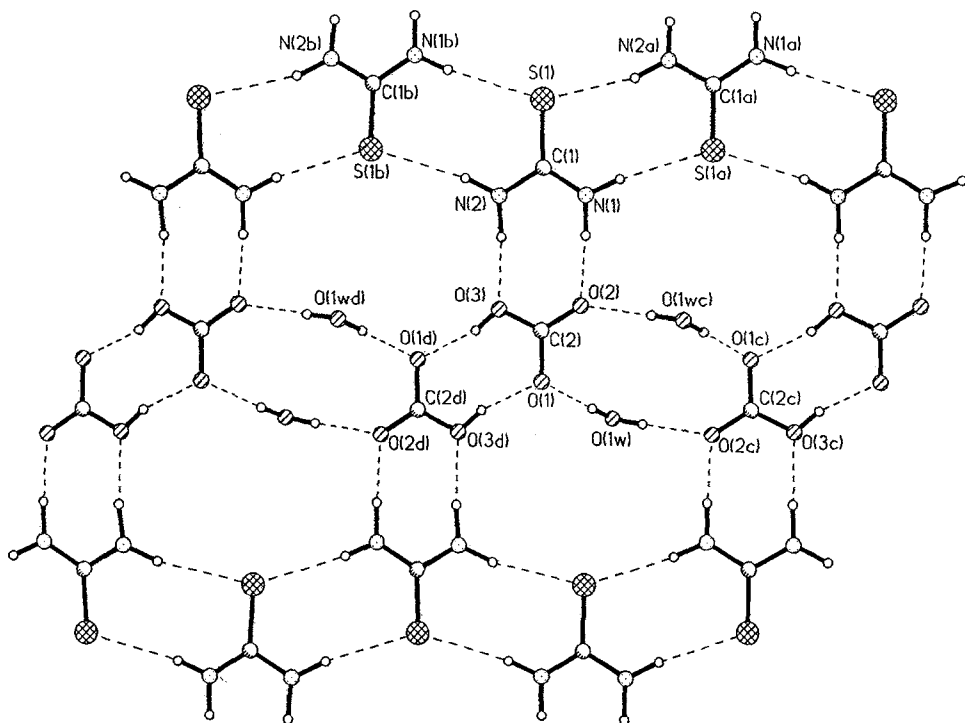


Fig. 1. Hydrogen-bonded layer in $(\text{C}_2\text{H}_5)_4\text{N}^+\text{HCO}_3^- \cdot (\text{NH}_2)_2\text{CS} \cdot \text{H}_2\text{O}$ (**1**) formed by the cross-linkage of thiourea ribbons and $[(\text{HCO}_3^-)_2 \cdot \text{H}_2\text{O}]_\infty$ ribbons. The atom labels correspond to those given in Tables II and V. Broken lines represent hydrogen bonds. Symmetry transformations: a: $-\frac{1}{2} + x, y, \frac{1}{2} - z$; b: $\frac{1}{2} + x, y, \frac{1}{2} - z$; c: $1 - x, 1 - y, -z$; d: $-x, 1 - y, -z$.

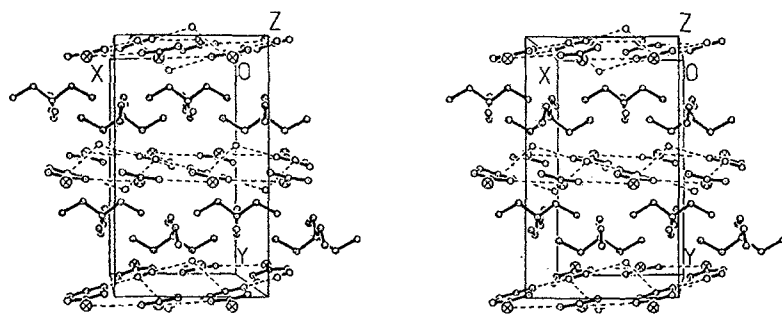


Fig. 2. Stereo drawing of the crystal structure of **1**. The origin of the unit cell lies at the upper right corner, with a pointing from right to left, b downwards, and c towards the reader. Broken lines represent hydrogen bonds, and atom types are distinguished by size and shading.

shows a honeycomb-like double layer at $z = \frac{1}{4}$ with large octagonal windows and $(n\text{-C}_3\text{H}_7)_4\text{N}(5)^+$ cations trapped within it. When the crystal structure of **2** is viewed parallel to the a axis (Figure 4), the $(n\text{-C}_3\text{H}_7)_4\text{N}(6)^+$ cations are seen to

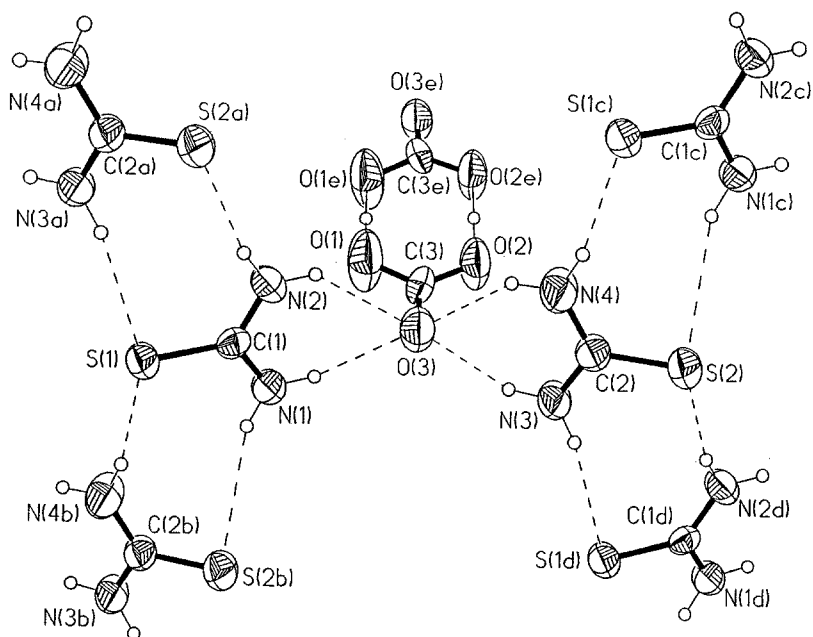


Fig. 3. Perspective view of a portion of the thiourea-bicarbonate lattice in $(n\text{-C}_3\text{H}_7)_4\text{N}^+\text{HCO}_3^- \cdot 2(\text{NH}_2)_2\text{CS}$ (**2**). The atom labels correspond to those given in Tables III and V. Symmetry transformations: a: $\frac{1}{2} + x, -\frac{1}{2} + y, z$; b: $-\frac{1}{2} + x, -\frac{1}{2} + y, z$; c: $\frac{1}{2} + x, \frac{1}{2} + y, z$; d: $\frac{1}{2} + x, \frac{1}{2} + y, z$; e: $-x, y, 1\frac{1}{2} - z$.

be concentrated about the (002) planes and sandwiched between adjacent double layers.

3.3. CRYSTAL STRUCTURE OF **3**

Figure 5 illustrates the atom labeling and the hydrogen-bonding interactions among the thiourea molecules and the dimeric bicarbonate ions. The three independent thiourea molecules in **3** are alternately connected by pairs of N—H··S hydrogen bonds to form a zigzag ribbon which, unlike those in **1** and **2**, has a highly twisted shape as shown by the torsion angles $\text{C}(2\text{f})\text{—N}(3\text{f})\text{··S}(1)\text{—C}(1) = 52.6$, $\text{C}(1)\text{—N}(2)\text{··S}(3)\text{—C}(3) = 42.8$ and $\text{C}(3)\text{—N}(6)\text{··S}(2)\text{—C}(2) = 83.1^\circ$. A pair of twisted ribbons, lying side by side and extending in the [110] direction, are linked by lateral N—H··S hydrogen bonds to form a puckered *double ribbon*. As shown in Figure 5, the twisted configuration of the thiourea ribbon facilitates the formation of inter-ribbon hydrogen bonds arranged about a row of inversion centers; one of the independent thiourea molecules is only involved in construction of the double ribbon, whereas the other two also partake in donor hydrogen bonding with the centrosymmetric bicarbonate dimers. Cross-linkage of the double ribbons by

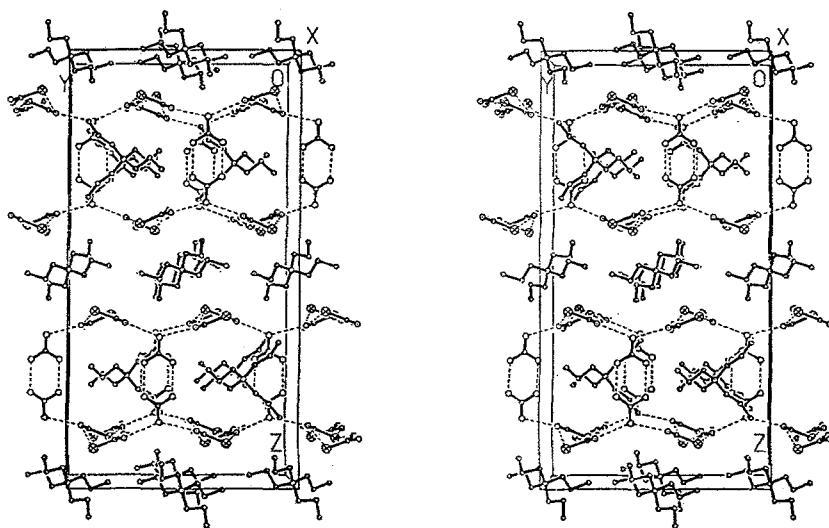


Fig. 4. Stereo drawing of the crystal structure of **2** showing the double layers and the two different types of enclosed cations. The origin of the unit cell lies at the upper right corner, with *a* pointing towards the reader, *b* from right to left, and *c* downwards. Broken lines represent hydrogen bonds.

$(\text{HCO}_3^-)_2$ units generates a three-dimensional host lattice with two open channel systems running parallel to the $[100]$ and $[111]$ directions, as illustrated in Figures 6 and 7, respectively.

In the present host lattice atoms S(2) and S(3) each forms acceptor H—N \cdots S hydrogen bonds with three different neighboring molecules of thiourea, but atom S(1) is linked with two neighboring molecules only. Within a double ribbon, all hydrogen bonds involving the same S atom are comparable in length. Considering S(3) as an example, N(2) \cdots S(3) = 3.450, N(2b) \cdots S(3) = 3.481 and N(4) \cdots S(3) = 3.685 Å, but one of the bond angles is markedly larger than the others: N(2) \cdots S(3) \cdots N(4) = 160.0°, but N(2) \cdots S(3) \cdots N(2b) = 87.1 and N(2b) \cdots S(3) \cdots N(4) = 82.4°. For atoms S(2) and S(1), the largest angle between two hydrogen bonds is N(1c) \cdots S(2) \cdots N(6) = 170.0 and N(3f) \cdots S(1) \cdots N(S) = 157.2°, respectively. Each bicarbonate dimer is consolidated by a pair of intramolecular hydrogen bonds, and there are four additional hydrogen bonds between this cyclic dianion and two neighboring thiourea molecules.

The stacked columns of ordered tetrahedral $(n\text{-C}_4\text{H}_9)_4\text{N}^+$ cations are arranged in a single column within each channel parallel to the $[111]$ direction, but in two parallel columns within each channel along the $[100]$ direction such that two successive $(n\text{-C}_4\text{H}_9)_4\text{N}^+$ cations in the same column are partitioned by a double ribbon.

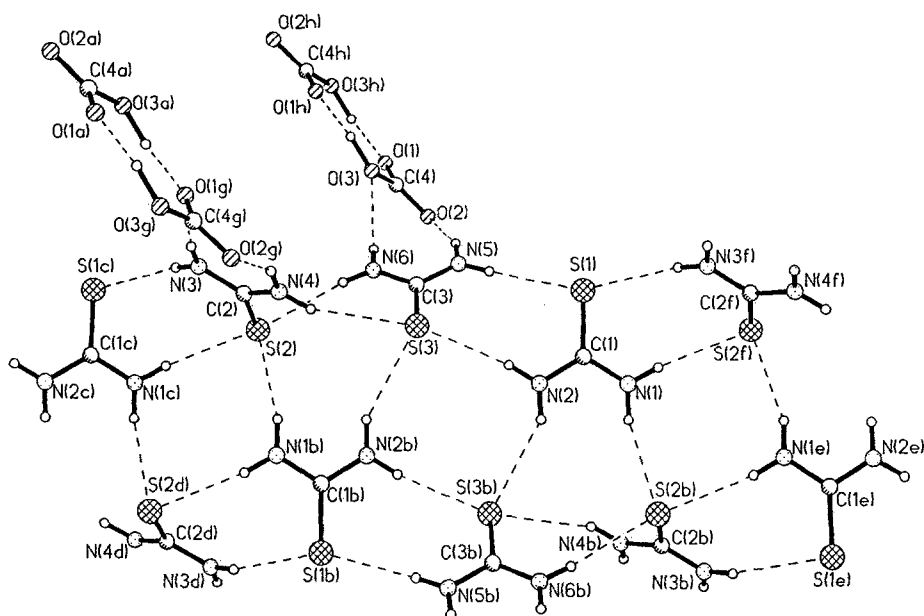


Fig. 5. Perspective view of a thiourea double ribbon linked to bicarbonate dimers in $(n\text{-C}_4\text{H}_9)_4\text{N}^+\text{HCO}_3^- \cdot 3(\text{NH}_2)_2\text{CS}$ (**3**). The atom labels correspond to those given in Tables IV and V. Symmetry transformations: a: $-x, -y, -z$; b: $1-x, 1-y, 1-z$; c: $-1+x, -1+y, z$; d: $-x, -y, 1-z$; e: $2-x, 2-y, 1-z$; f: $1+x, 1+y, z$; g: $-1+x, y, z$; h: $1-x, -y, -z$.

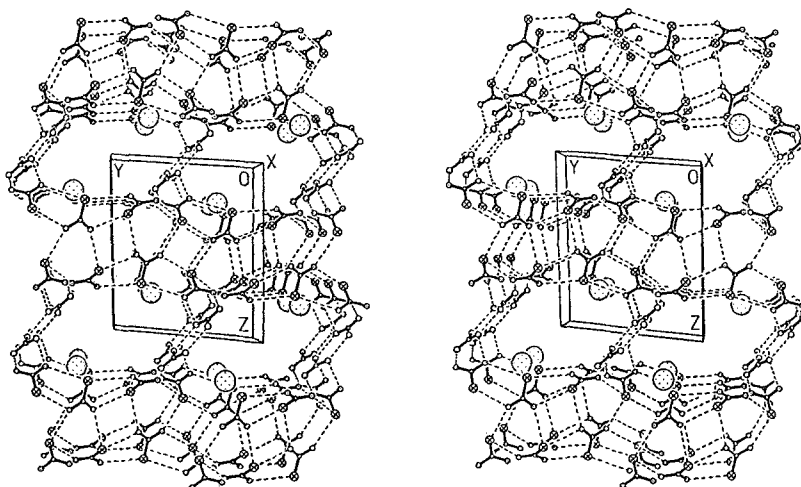


Fig. 6. Stereo drawing of the crystal structure of **3** showing the thiourea double ribbons running parallel to the $[110]$ direction and their linkage by bridging bicarbonate dimers to form channels extending parallel to this *a* axis. For clarity the enclosed $(n\text{-C}_4\text{H}_9)_4\text{N}^+$ ions are represented by large dotted circles.

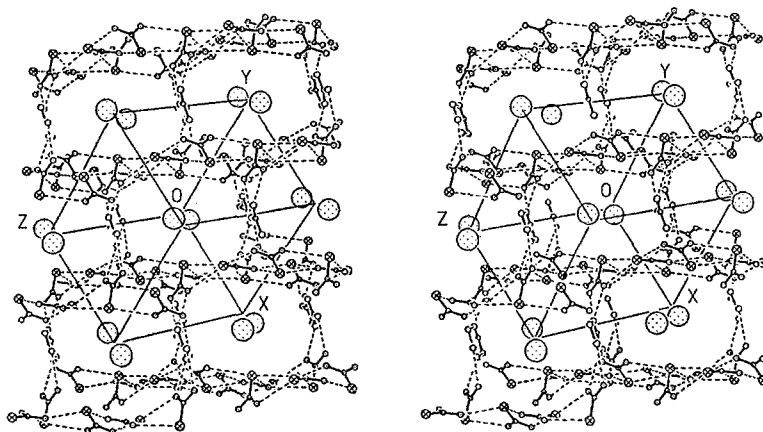


Fig. 7. Stereo drawing of the crystal structure of **3** showing the channels extending parallel to the $[111]$ direction and the enclosed cations (as large dotted circles).

3.4. STRUCTURAL FEATURES AND RELATIONSHIPS

Although the inclusion compounds **1–3** all contain thiourea ribbons and cyclic dimeric bicarbonate anions as building blocks, different modes of combination were utilized in the construction of the resulting hydrogen-bonded host lattices. The thiourea ribbons in **1** do not interact directly with one another, but are laterally linked with complementary $[(\text{HCO}_3^-)_2(\text{H}_2\text{O})_2]_\infty$ ribbons to form a layer structure. In **2** the separated thiourea ribbons are bridged in an orthogonal manner by $(\text{HCO}_3^-)_2$ units to give a novel double layer. Unlike those in **1** and **2**, the thiourea ribbons in **3** adopt a twisted configuration; they are further organized into puckered double ribbons which are cross-linked by $(\text{HCO}_3^-)_2$ moieties to generate a three-dimensional host framework containing two open channel systems. The close structural relationship between this host framework and that of the well-established thiourea channel adducts [5–7] can be appreciated by comparing Figure 7 with Figure 8. It is noted that three double ribbons of the type found in compound **3** (Figure 5) constitute the cylindrical wall of an open channel in a thiourea inclusion complex, whose channel system (Figure 8) is closely matched by a similar one (Figure 7) in the host framework of **3**.

It is interesting to note that the C—O bond distances in the bicarbonate anions differ from each other in the present inclusion compounds. In the centrosymmetric cyclic bicarbonate dimers of **1** and **3**, in which the hydrogen bonds link two different O atoms of each anion, the observed C(2)—O(3) bond lengths of 1.316 and 1.331 Å are shorter than the single bond value of 1.43 Å found in paraffinic alcohols [26], and the corresponding lengths of 1.266 and 1.258 Å for C(2)—O(1) are longer than the third C—O bond (1.226 and 1.234 Å for **1** and **3** respectively). The O(1) atom forms a strong acceptor hydrogen bond with O(3) so that the C(2)—O(3) bond corresponds to about 14% double bond character and the C(2)—O(1) bond to

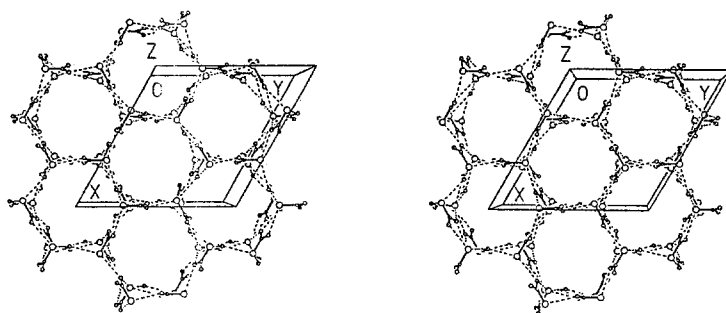


Fig. 8. Stereo drawing showing the pseudo-hexagonal ($R\bar{3}$) host structure of a typical thiourea inclusion compound. This plot was made with crystallographic data for the chlorocyclohexane/thiourea inclusion system given in Ref. 7.

about 48% double bond character [27]. But in crystal **2**, the bicarbonate dimer has site symmetry 2, and the intramolecular hydrogen bonds of the type O(1)—O(1e) and O(2)—O(2e) are symmetric and virtually equal in length. The bonds C(3)—O(1) = 1.254 and C(3)—O(2) = 1.260 Å would be predicted to have 50% double bond character, both being significantly longer than C(3)—O(3) = 1.231 Å. It is similar to the structure of potassium bicarbonate [28], in which the bicarbonate ions form hydrogen bonded dimers and both oxygen atoms involved in hydrogen bonding have similar carbon—oxygen bond distances, namely 1.32 and 1.33 Å, and the third carbon—oxygen distance is shorter at 1.28 Å.

In summary, the present study has demonstrated that the classical thiourea hydrogen-bonded host lattice can be modified in interesting ways by the incorporation of cyclic dimeric bicarbonate moieties (with water as an additional component in one example), and that novel host frameworks bearing different thiourea/guest molar ratios are generated by variation in the size of the hydrophobic, pseudo-spherical R_4N^+ guest species. In an idealized scheme of host design, the well-knit pseudo-hexagonal ($R\bar{3}$) thiourea channel framework is first divided into puckered double ribbons, which are next cleaved lengthwise to give single-strand, stretched-out ribbons. Hydrogen bonding between these two kinds of smaller structural units with suitable anionic and neutral species would then lead to new varieties of host systems.

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