Inclusion Compounds of Thiourea and Paralkylated Ammonium Salts. Part VII. Hydrogen-Bonded Host Lattices Constructed from Thiourea and Anionic Species Derived from Benzoic Acid

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Abstract. New inclusion complexes $(n\text{-}C_3H_7)_4N^+C_6H_5CO_2^-$ · $3(NH_2)_2CS$ (**1**), $(n\text{-}C_4H_9)_4N^+[(C_6H_5CO_2)_2H]^-$·$6(NH_2)_2CS$ (**2**) and $(C_2H_5)_4N^+C_6H_5CO_2^-$·$(NH_2)_2CS$ (**3**) have been prepared and characterized by X-ray crystallography. Crystal data, Mo$K\alpha$ radiation: **1**, space group $P2_12_12_1$, $Z = 4$, $a = 8.544(3)$, $b = 14.588(4)$, $c = 24.448(4)$ Å, and $R1 = 0.062$ for 1536 observed data; **2**, space group $Pbcn$, $Z = 4$, $a = 24.938(3)$, $b = 8.911(1)$, $c = 23.733(9)$ Å, and $R1 = 0.055$ for 2132 observed data; **3**, space group $P2_12_12_1$, $Z = 4$, $a = 9.996(2)$, $b = 10.122(4)$, $c = 18.350(2)$ Å, and $R1 = 0.049$ for 1180 observed data. In the crystal structure of **1**, the $(n\text{-}C_3H_7)_4N^+$ cations are stacked in a single column and accommodated within each channel built up by wide thiourea ribbons and benzoate ions *via* N—H· · ·O hydrogen bonds. In the crystal structure of **2**, the tetrabutylammonium cations are arranged in a zigzag column within each channel built of parallel corrugated thiourea layers that are inter-linked by dimeric $[(C_6H_5CO_2)_2H]^-$ groups through N—H· · ·O hydrogen bonds. In compound **3** the $(C_2H_5)_4N^+$ cations are accommodated in 'pseudo-channels' generated from infinitely extended thiourea-benzoate composite ribbons.

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

1. Introduction

Thiourea inclusion compounds crystallize in several space groups in two crystal systems: rhombohedral $R\bar{3}2/c$ [1], $R3c$ [2], $R\bar{3}c$ [3], $R\bar{3}$ [4] and monoclinic $P2_1/a$ [5–7]. In the last space group, the adducts exist only at reduced temperatures except for those containing squalene or aromatic guests [8]. In the most common type of thiourea inclusion compounds (space group $R\bar{3}c$; $a \approx 15.5$–16.2 Å, $c = 12.5$–12.5 Å in the hexagonal setting with $Z = 6$) the host structure is built of thiourea molecules in an extensively hydrogen-bonded lattice that contains parallel channels of non-uniform cross section, showing constrictions (minimum diameter = 5.8 Å) at $z = 0$, $\frac{1}{2}$ and bulges (minimum diameter = 7.1 Å) at $z = \frac{1}{4}$, $\frac{3}{4}$ [9]. In these typical
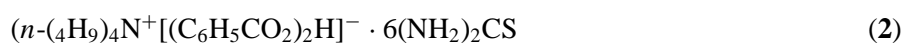
thiourea inclusion compounds, hydrogen bonds are also responsible for the helical grouping of the thiourea molecules in the channel wall and thus for the helicity of the respective inclusion lattice [10].

We have carried out a systematic study on the generation of new urea/thiourea-anion inclusion compounds in which the host lattices are formed by the combined use of urea or thiourea molecules and various anions as the building blocks [11] including halide [12], some simple trigonal planar anions such as HCO_3^- [13] and NO_3^- [14], some monocarboxylic acid radicals such as HCO_2^- [15] and $CH_3CO_2^-$ [16], as well as some dicarboxylic acid radicals such as $HC_2O_4^-$ [17, 18] $C_4H_2O_4^{2-}$ (fumarate) and $HC_4H_2O_4^-$ (hydrogen fumarate) [18].

The crystal structure of benzoic acid, $C_6H_5CO_2H$, consists of centrosymmetric dimers, in which the molecules are linked in pairs by a pair of hydrogen bonds between their carboxyl groups [19]. Benzoic acid as the guest molecule has been shown to complex well with α- [20] and β-cyclodextrin by different techniques [21]. In the crystal structure of the complex $C_6H_5COOTl \cdot 4(NH_2)_2CS$, each benzoate ion is strongly hydrogen-bonded to surrounding amino groups belonging to the thiourea molecules (N—H$\cdots$O = 2.92 ± 0.02 and 3.03 ± 0.02 Å) [22].

Parallel studies employing the benzoate anions and thiourea in the construction of new host lattices that can accommodate peralkylated ammonium cations of different size have been carried out in our laboratory. In the present work, we report the preparation and structural characterization of the following complexes:

$$(n\text{-}C_3H_7)_4N^+C_6H_5CO_2^- \cdot 3(NH_2)_2CS \tag{1}$$

$$(n\text{-}(_4H_9)_4N^+[(C_6H_5CO_2)_2H]^- \cdot 6(NH_2)_2CS \tag{2}$$

$$(C_2H_5)_4N^+C_6H_5CO_2^- \cdot (NH_2)_2CS \tag{3}$$

2. Experimental

Tetraalkylammonium hydroxide aqueous solutions and crystalline benzoic acid were obtained from Aldrich. Each hydroxide, benzoic acid and thiourea were mixed in molar ratios of $1:1:2$, $1:1:3$ and $1:1:3$ for **1**, **2** and **3**, respectively. A minimum quantity of deionized water was added to dissolve the solid in each 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 thin plates (**1**) and small blocks (**2** and **3**).

Information concerning the crystallographic data and structure determination of the three compounds is summarized in Table I. Intensities were collected in the variable ω-scan technique [23] on a Siemens P4 diffractometer using Mo$K\alpha$ radiation ($\lambda = 0.71073$ Å) at 291 K, and empirical absorption correction based on ψ-scan data [24] was applied.

Table I. Crystal data and parameters of refinement

Complex	1	2	3
Molecular formula	$(n\text{-}C_3H_7)_4N^+C_6H_5CO_2^-$ $\cdot 3(NH_2)_2CS$	$(n\text{-}C_4H_9)_4N^+[(C_6H_5CO_2)_2H]^-$ $\cdot 6(NH_2)_2CS$	$(C_2H_5)_4N^+C_6H_5CO_2^-$ $\cdot(NH_2)_2CS$
Molecular weight	535.8	942.4	327.5
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$ (No. 19)	$Pbcn$ (No. 60)	$P2_12_12_1$ (No. 19)
Unit cell parameters			
a, Å	8.544(3)	24.938(3)	9.996(2)
b, Å	14.588(4)	8.911(1)	10.122(4)
c, Å	24.448(4)	23.733(9)	18.350(2)
V, Å^3	3047(1)	5274(2)	1856.7(8)
Z	4	4	4
$F(000)$	1160	2024	712
Density (calc.), g cm^{-3}	1.168	1.187	1.172
Crystal size, mm	$0.35 \times 0.40 \times 0.42$	$0.42 \times 0.50 \times 0.50$	$0.24 \times 0.24 \times 0.32$
Scan speed (deg min^{-1})	5.0	4.0 to 29.0	4.0 to 29.0
$2\theta_{max}$, °	52	50	50
Unique data measured	3388	4118	1689
Observed data	I > 2σ(I), 1536	I>2σ(I), 2132	I > 2σ(I), 1180
Number of variables, p	307	267	199
$R1$(obs.)	0.062	0.055	0.049
$wR2$(obs.)	0.116	0.117	0.110
Constant g in weighting scheme $w = 1/[\sigma^2(F_0^2) + (g\mathrm{P})^2]$ where $\mathrm{P} = (F_0^2 + 2F_c^2)/3$	0.0567	0.0855	0.0617
S(obs.)	1.108	1.092	1.065
Residual extrema in final difference map, eÅ^{-3}	+0.31 to −0.25	+0.22 to −0.34	+0.16 to −0.18
Largest and mean Δ/σ	0.000, 0.000	0.000, 0.000	0.000, 0.000

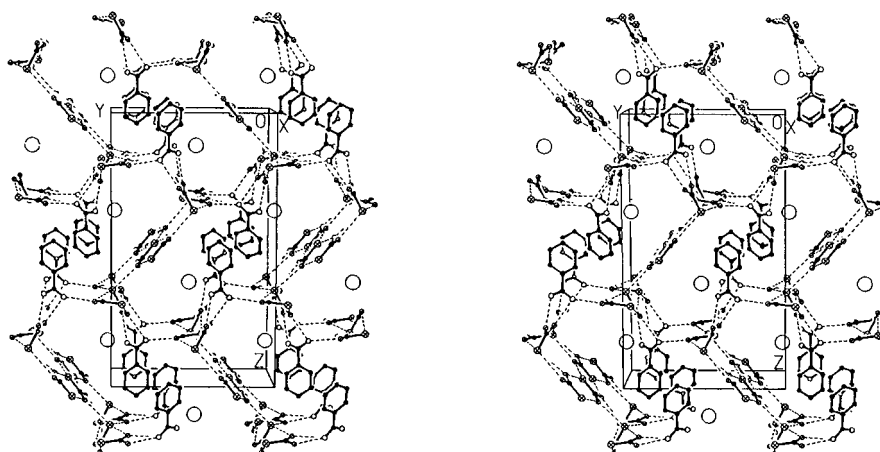*Figure 1.* Three-dimensional host framework containing parallel channels in the crystal structure of $(n\text{-}C_3H_7)_4N^+C_6H_5CO_2^- \cdot 3(NH_2)_2CS$ (**1**), viewed along the *a* axis. Broken lines represent hydrogen bonds, and atom types are distinguished by size and shading (open circles for O, filled circles for C, shaded circles for N, and cross-hatched circles for S). The tetraalkylammonium ions are represented by larger open circles.

The structures were solved by direct methods and all non-hydrogen atoms were refined with anisotropic thermal parameters. The amido, methylene, and methyl H atoms were generated geometrically (C—H distance fixed at 0.96 Å, N—H at 0.90 Å) and allowed to ride on the carbon atoms to which they are bonded. The hydrogen atoms of the hydroxyl H of the benzoic ion in **3** 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. All computations were performed on an IBM compatible PC with the SHELXL-93 [25] for full-matrix least-squares refinement against F^2 and SHELXTL-PLUS program package [26] for preparing the diagrams. Analytic expressions of atomic scattering factors were employed, and anomalous dispersion corrections were incorporated [27], 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 and hydrogen coordinates have been deposited at the Cambridge Crystallographic Data Center (CCDC No. 102384, 102385, 102386).

Table II. Atomic coordinates ($\times 10^4$) and thermal parameters* ($\text{Å}^2 \times 10^3$) of (n-C_3H_7)$_4$N$^+$C$_6$H$_5$CO$_2^-$ $\cdot$ 3(NH$_2$)$_2$CS (**1**)

Atom	x	y	z	U(eq)
S(1)	0.2280(2)	0.50575(12)	0.34202(6)	0.0519(5)
C(1)	0.2271(9)	0.5610(4)	0.2804(2)	0.042(2)
N(1)	0.0967(6)	0.5677(4)	0.2520(2)	0.054(2)
N(2)	0.3559(7)	0.5971(4)	0.2591(2)	0.057(2)
S(2)	0.7253(3)	0.56093(13)	0.31582(8)	0.0631(6)
C(2)	0.7222(10)	0.4457(5)	0.3260(2)	0.049(2)
N(3)	0.8531(7)	0.3983(4)	0.3327(2)	0.060(2)
N(4)	0.5876(7)	0.3990(4)	0.3249(2)	0.059(2)
S(3)	0.2595(3)	0.76322(13)	0.51701(8)	0.0779(7)
C(3)	0.2569(12)	0.6905(4)	0.4635(3)	0.057(2)
N(5)	0.3860(9)	0.6605(5)	0.4401(3)	0.072(2)
N(6)	0.1225(9)	0.6618(5)	0.4422(3)	0.071(2)
C(4)	0.6057(9)	0.2250(5)	0.4517(3)	0.059(2)
C(5)	0.5585(11)	0.2240(6)	0.5057(3)	0.081(3)
C(6)	0.6082(13)	0.1536(7)	0.5391(3)	0.090(3)
C(7)	0.7005(12)	0.0851(6)	0.5192(3)	0.084(3)
C(8)	0.7454(10)	0.0867(5)	0.4658(3)	0.060(2)
C(9)	0.7008(8)	0.1566(4)	0.4316(2)	0.040(2)
C(10)	0.7557(9)	0.1575(5)	0.3730(3)	0.049(2)
O(1)	0.6961(6)	0.2124(3)	0.3401(2)	0.0612(15)
O(2)	0.8567(7)	0.0983(4)	0.3606(2)	0.094(2)
N(7)	0.7023(6)	0.4779(4)	0.1229(2)	0.0440(15)
C(11)	0.5431(10)	0.4600(6)	0.1455(4)	0.093(3)
C(12)	0.4616(13)	0.3767(8)	0.1300(5)	0.136(5)
C(13)	0.3221(16)	0.3569(10)	0.1619(5)	0.230(9)
C(14)	0.8104(10)	0.3963(6)	0.1328(3)	0.080(3)
C(15)	0.8241(14)	0.3649(7)	0.1883(4)	0.117(4)
C(16)	0.9259(12)	0.2842(6)	0.1970(4)	0.116(4)
C(17)	0.7713(11)	0.5611(4)	0.1503(2)	0.072(2)
C(18)	0.7087(12)	0.6501(5)	0.1403(3)	0.086(3)
C(19)	0.7706(11)	0.7242(5)	0.1764(3)	0.088(3)
C(20)	0.6924(10)	0.4927(6)	0.0616(3)	0.078(3)
C(21)	0.8338(11)	0.5122(6)	0.0308(3)	0.092(3)
C(22)	0.8010(11)	0.5272(5)	−0.0294(3)	0.091(3)

* 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 $-8\pi^2 U \sin^2 \theta / \lambda^2$.

Table III. Atomic coordinates ($\times 10^4$) and thermal parameters* ($\text{Å}^2 \times 10^3$) of (n-C$_4$H$_9$)$_4$N$^+$[(C$_6$H$_5$CO$_2$)$_2$H]$^-$ · 6(NH$_2$)$_2$CS (**2**)

Atom	x	y	z	U(eq)
S(1)	0.31838(5)	0.37451(14)	0.49089(4)	0.0826(4)
C(1)	0.2892(2)	0.5395(5)	0.5080(2)	0.0652(11)
N(1)	0.2874(2)	0.6495(4)	0.4711(2)	0.0911(12)
N(2)	0.26729(14)	0.5609(4)	0.55792(14)	0.0814(11)
S(2)	0.32362(5)	0.62262(13)	0.33133(4)	0.0672(3)
C(2)	0.2866(2)	0.4677(5)	0.3154(2)	0.0566(10)
N(3)	0.2817(2)	0.3574(4)	0.35225(15)	0.0821(11)
N(4)	0.26099(13)	0.4562(4)	0.26724(14)	0.0744(10)
S(3)	0.28214(4)	0.69881(14)	0.16132(4)	0.0640(3)
C(3)	0.34890(15)	0.7374(5)	0.1601(2)	0.0573(10)
N(5)	0.37561(12)	0.7454(5)	0.11207(14)	0.0872(13)
N(6)	0.37563(12)	0.7624(4)	0.20690(13)	0.0745(10)
C(4)	0.5489(2)	−0.0976(7)	0.0643(2)	0.105(2)
C(5)	0.5854(3)	−0.0641(8)	0.0220(2)	0.125(2)
C(6)	0.6348(3)	−0.0137(6)	0.0366(3)	0.107(2)
C(7)	0.6488(2)	0.0033(6)	0.0914(3)	0.097(2)
C(8)	0.6125(2)	−0.0314(5)	0.1333(2)	0.0770(13)
C(9)	0.5621(2)	−0.0822(5)	0.1204(2)	0.0657(11)
C(10)	0.5222(2)	−0.1181(5)	0.1650(2)	0.0727(12)
O(1)	0.47744(13)	−0.1634(6)	0.15238(14)	0.128(2)
O(2)	0.53672(11)	−0.1016(4)	0.21548(12)	0.0827(9)
N(7)	0.5000	0.3577(5)	0.2500	0.0743(14)
C(11)	0.5156(2)	0.4574(6)	0.2010(2)	0.0881(15)
C(12)	0.5312(3)	0.3775(8)	0.1476(3)	0.128(2)
C(13)	0.5344(4)	0.4677(10)	0.0983(3)	0.163(3)
C(14)	0.5417(3)	0.3820(12)	0.0463(4)	0.233(5)
C(15)	0.45378(15)	0.2553(5)	0.2339(2)	0.0792(13)
C(16)	0.4020(2)	0.3337(6)	0.2170(2)	0.102(2)
C(17)	0.3619(2)	0.2219(9)	0.1941(3)	0.132(2)
C(18)	0.3717(2)	0.1599(9)	0.1395(3)	0.153(3)

* 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 $-8\pi^2 U \sin^2\theta/\lambda^2$.

Table IV. Atomic coordinates ($\times 10^4$) and thermal parameters* ($\mathring{A}^2 \times 10^3$) of $(C_2H_5)_4N^+C_6H_5CO_2^- \cdot (NH_2)_2CS$ (**3**)

Atom	x	y	z	U(eq)
S(1)	0.26161(15)	0.14538(14)	0.60854(7)	0.0593(4)
C(1)	0.3745(4)	0.1495(5)	0.6769(2)	0.0385(11)
N(1)	0.4028(4)	0.2605(4)	0.7127(2)	0.0439(10)
N(2)	0.4393(4)	0.0409(4)	0.6978(2)	0.0518(12)
C(2)	0.8189(5)	0.2672(5)	0.9222(3)	0.0512(13)
C(3)	0.9086(6)	0.2717(5)	0.9796(3)	0.064(2)
C(4)	0.9291(6)	0.1612(6)	1.0222(3)	0.064(2)
C(5)	0.8598(6)	0.0478(6)	1.0075(3)	0.0582(15)
C(6)	0.7727(5)	0.0406(5)	0.9492(3)	0.0508(13)
C(7)	0.7506(4)	0.1529(4)	0.9065(2)	0.0375(10)
C(8)	0.6525(4)	0.1495(6)	0.8435(2)	0.0421(11)
O(1)	0.6167(4)	0.2568(3)	0.8174(2)	0.0552(10)
O(2)	0.6145(4)	0.0392(3)	0.8215(2)	0.0757(13)
N(3)	0.3325(4)	0.1162(5)	0.3617(2)	0.0524(12)
C(9)	0.3581(6)	−0.0179(5)	0.3957(3)	0.0629(15)
C(10)	0.2918(7)	−0.1320(7)	0.3572(4)	0.095(2)
C(11)	0.3823(5)	0.1197(6)	0.2839(3)	0.067(2)
C(12)	0.5288(6)	0.0980(7)	0.2737(3)	0.083(2)
C(13)	0.4036(6)	0.2167(6)	0.4076(3)	0.066(2)
C(14)	0.3950(7)	0.3586(6)	0.3824(4)	0.090(2)
C(15)	0.1829(5)	0.1456(7)	0.3591(3)	0.0598(15)
C(16)	0.1131(5)	0.1470(7)	0.4315(3)	0.072(2)

* 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 $-8\pi^2 U \sin^2 \theta / \lambda^2$.

3.1. CRYSTAL STRUCTURE OF $(n\text{-}C_3H_7)_4N^+C_6H_5CO_2^- \cdot 3(NH_2)_2CS$ (**1**)

As shown in Figure 1, the crystal structure of compound **1** features channels that extend parallel to the *a* axial direction. This channel framework is built up by wide thiourea ribbons and benzoate ions *via* N—H$\cdots$O hydrogen bonds. Structural characteristics of these wide thiourea ribbons, which are formed by two types of thiourea ribbons (designated type I and type II), may be conveniently described with reference to the hydrogen bonding scheme shown in Figure 2 and Table V.

The type I ribbon is composed of thiourea molecules **C(1)** [for simplicity the thiourea molecule composed of atoms C(1), S(1), N(1) and N(2) is designated as **C(1)**; other thiourea molecules are designated in the same manner] and **C(2)**. Two independent thiourea molecules are alternately linked by pairs of N—
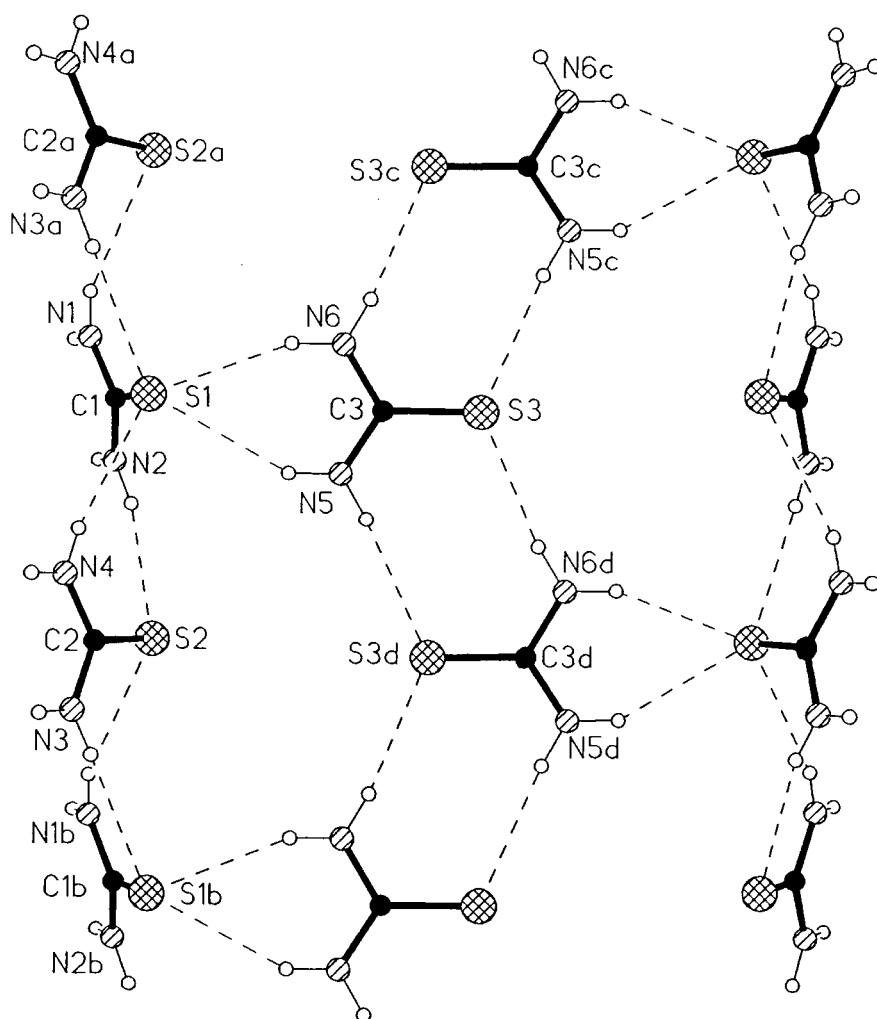
Figure 2. Perspective view of a portion of the wide thiourea ribbon in **1**. Symmetry transformations: (a) $-1 + x$, y, z; (b) $1 + x$, y, z; (c) $-0.5 + x$, $1.5 - y$, $1 - z$; (d) $0.5 + x$, $1.5 - y$, z; (e) $1 - x$, $-0.5 + y$, $0.5 - z$.

H$\cdots$S hydrogen bonds in the usual shoulder-to-shoulder manner to form zigzag, puckered ribbons running parallel to the a axis. The relevant torsion angles in each thiourea ribbon, C(1)—N(2)$\cdots$S(2)—C(2) = 46.9, C(2)—N(4)$\cdots$S(1)—C(1) = 70.8, C(1b)—N(1b)$\cdots$S(2)—C(2) = -76.8 and C(2)—N(3)$\cdots$S(1b)—C(1b) = $-58.4°$, indicate that this ribbon has a highly twisted configuration.

The thiourea molecules of type **C(3)** are arranged along a 2_1 axis in a shoulder-to-shoulder mode and are linked by hydrogen bonds to generate a type II thiourea ribbon. This ribbon is essentially planar as can be assessed by the relevant torsion angles: C(3c)—N(5c)$\cdots$S(3)—C(3) = 2.5 and C(3)—N(6)$\cdots$S(3c)—C(3c) =
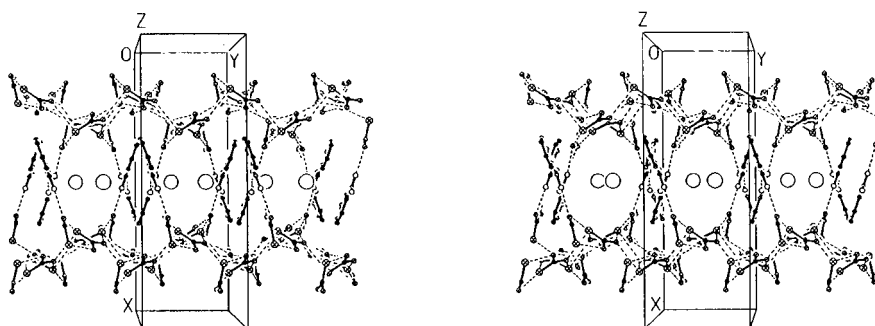
Figure 3. Stereodrawing of the crystal structure of $(n\text{-}C_4H_9)_4N^+[(C_6H_5CO_2)_2H]^- \cdot 6(NH_2)_2CS$ (**2**). Broken lines represent hydrogen bonds, and atom types are distinguished by size and shading. The tetraalkylammonium ions are represented by larger open circles.

$-4.1°$. Each thiourea molecule is further linked to a sulfur atom of **C(1)** *via* two additional N—H$\cdots$S donor hydrogen bonds that extend outward on either side of the ribbon in a head-to-tail fashion. As a result a wide thiourea ribbon is formed by one type II and two type I thiourea ribbons, which are almost perpendicular to each other (Figure 2).

These wide ribbons are located about half of the 2_1 axes running parallel to *a* and separated by columns of benzoate ions located about the other half of the 2_1 axes. When two hydrogen bonds, $N(2e)\cdots O(1) = 2.986$ and $N(1e)\cdots O(2) = 2.816$ Å, are formed between N atoms of the neighboring thiourea molecule and each O atom of the benzoate ion, as well as two hydrogen bonds, $N(3)\cdots O(1) = 3.021$ and $N(4)\cdots O(1) = 2.899$ Å, between the same O(1) atom and the N atoms of a thiourea molecule belonging to another wide ribbon, a three dimensional network containing channels that run parallel to the [100] direction is formed.

The tetra-*n*-propylammonium cations nearly attain idealized $\bar{4}2m$ molecular symmetry. The crystal structure of **1** viewed parallel to the *a* axis (Figure 1) shows that the $(n\text{-}C_3H_7)_4N^+$ cations are stacked in a single column and accommodated within each channel.

3.2. CRYSTAL STRUCTURE OF $(n\text{-}C_4H_9)_4N^+[(C_6H_5CO_2)_2H]^- \cdot 6(NH_2)_2CS$ (**2**)

As illustrated in Figure 3, the dominant feature of compound **2** is a channel system extending parallel to the [001] direction, which is built of corrugated thiourea layers that are interlinked by dimeric $[(C_6H_5CO_2)_2H]^-$ groups through N—H$\cdots$O hydrogen bonds. Structure characteristics of the thiourea layers may be conveniently described with reference to the hydrogen bonding scheme shown in Figure 4 and Table V.

Two independent thiourea molecules **C(1)** and **C(2)** are consolidated by a pair of N—H$\cdots$S hydrogen bonds in the usual shoulder-to-shoulder fashion to yield a thiourea dimer. These dimers are arranged in a broadside manner and interlinked

Table V. Selected bond distances (Å), bond angles (°) and torsion angles (°) in the thuiourea-anionic systems*

$(n\text{-}C_3H_7)_4N^+C_6H_5CO_2^-\cdot3(NH_2)_2CS$ (**1**)

(i) *Thiourea and benzoate ion*

S(1)–C(1)	1.709(6)	C(1)–N(1)	1.316(7)
C(1)–N(2)	1.326(8)	S(2)–C(2)	1.699(7)
C(2)–N(3)	1.325(8)	C(2)–N(4)	1.337(9)
S(3)–C(3)	1.685(7)	C(3)–N(5)	1.316(9)
C(3)–N(6)	1.329(9)	C(4)–C(9)	1.377(9)
C(4)–C(5)	1.380(9)	C(5)–C(6)	1.379(11)
C(6)–C(7)	1.363(11)	C(7)-C(8)	1.362(9)
C(8)–C(9)	1.373(8)	C(9)–C(10)	1.507(8)
C(10)–O(1)	1.244(7)	C(10)–O(2)	1.258(8)
N(1)–C(1)–N(2)	117.8(5)	N(1)–C(1)–S(1)	120.3(6)
N(2)–C(1)–S(1)	122.0(5)	N(3)–C(2)–N(4)	117.5(6)
N(3)–C(2)–S(2)	121.4(6)	N(4)–C(2)–S(2)	121.0(6)
N(5)–C(3)–N(6)	116.7(6)	N(5)–C(3)–S(3)	122.3(7)
N(6)–C(3)–S(3)	120.9(7)	C(9)–C(4)–C(5)	120.4(7)
C(6)–C(5)–C(4)	119.0(8)	C(7)–C(6)–C(5)	120.8(8)
C(8)–C(7)–C(6)	119.5(8)	C(7)–C(8)–C(9)	121.3(8)
C(8)–C(9)–C(4)	119.0(6)	C(8)–C(9)–C(10)	119.9(7)
C(4)–C(9)–C(10)	121.1(6)	O(1)–C(10)–O(2)	124.5(7)
O(1)–C(10)–C(9)	119.4(7)	O(2)–C(10)–C(9)	115.9(7)

(ii) *Hydrogen bonding* (*donor atom listed first*)

N(3a)···S(1)	3.573	N(4)···S(1)	3.470
N(5)···S(1)	3.560	N(6)···S(1)	3.462
N(1b)···S(2)	3.538	N(2)···S(2)	3.487
N(5c)···S(3)	3.538	N(6d)···S(3)	3.437
N(2e)···O(1)	2.986	N(3)···O(1)	3.031
N(4)···O(1)	2.899	N(1e)···O(2)	2.816
N(3a)···S(1)···N(4)	126.1	N(4)···S(1)···N(5)	91.7
N(5)···S(1)···N(6)	37.4	N(3a)···S(1)···N(5)	131.4
N(4)···S(1)···N(5)	95.8	N(4)···S(1)···N(6)	127.6
N(1b)···S(2)···N(2)	129.2	N(5c)···S(3)···N(6d)	128.9
N(2e)···O(1)···N(3)	121.4	N(2e)···O(1)···N(4)	112.2
N(3)···O(1)···N(4)	45.1		
C(3c)–N(5c)···S(3)–C(3)	2.5	C(3)–N(6)···S(3c)–C(3c)	−4.1
C(1b)–N(1b)···S(2)–C(2)	−76.8	C(2)–N(3)···S(1b)–C(1b)	−58.4
C(1)–N(2)···S(2)–C(2)	46.9	C(2)–N(4)···S(1)–C(1)	70.8
C(3)–N(5)···S(1)–C(1)	100.3	C(3)–N(6)···S(1)–C(1)	−97.5
C(1e)–N(1e)···O(2)–C(10)	−44.7	C(1e)–N(2e)···O(1)–C(10)	−60.5

Table V. (continued)

$(n\text{-}C_4H_9)_4N^+[(C_6H_5CO_2)_2H]^-\cdot 6(NH_2)_2CS$ (**2**)

(i) *Thiourea and benzoate ion*

S(1)–C(1)	1.691(5)	C(1)–N(1)	1.316(5)
C(1)–N(2)	1.318(5)	S(2)–C(2)	1.703(4)
C(2)–N(4)	1.314(5)	C(2)–N(3)	1.321(5)
S(3)–C(3)	1.700(4)	C(3)–N(6)	1.315(4)
C(3)–N(5)	1.322(4)	C(4)–C(9)	1.380(6)
C(4)–C(5)	1.389(7)	C(5)–C(6)	1.356(8)
C(6)–C(7)	1.356(7)	C(7)–C(8)	1.379(7)
C(8)–C(9)	1.369(5)	C(9)–C(10)	1.487(6)
C(10)–O(1)	1.225(5)	C(10)–O(2)	1.260(5)
N(1)–C(1)–N(2)	118.5(4)	N(1)–C(1)–S(1)	120.1(3)
N(2)–C(1)–S(1)	121.3(3)	N(4)–C(2)–N(3)	118.2(4)
N(4)–C(2)–S(2)	121.3(3)	N(3)–C(2)–S(2)	120.4(3)
N(6)–C(3)–N(5)	117.6(3)	N(6)–C(3)–S(3)	121.1(3)
N(5)–C(3)–S(3)	121.3(3)	C(9)–C(4)–C(5)	121.3(5)
C(6)–C(5)–C(4)	118.9(6)	C(5)–C(6)–C(7)	121.1(5)
C(6)–C(7)–C(8)	119.9(5)	C(9)–C(8)–C(7)	121.0(5)
C(8)–C(9)–C(4)	117.9(4)	C(8)–C(9)–C(10)	121.8(4)
C(4)–C(9)–C(10)	120.3(4)	O(1)–C(10)–O(2)	122.1(4)
O(1)–C(10)–C(9)	120.5(4)	O(2)–C(10)–C(9)	117.3(4)

(ii) *Hydrogen bonding* (*donor atom listed first*)

N(1b)···S(1)	3.347	N(3)···S(1)	3.418
N(5e)···S(1)	3.384	N(1)···S(2)	3.445
N(3a)···S(2)	3.395	N(6)···S(2)	3.458
N(2d)···S(3)	3.482	N(2c)···S(3)	3.393
N(4)···S(3)	3.357	N(4a)···S(3)	3.569
N(5f)···O(1)	2.833	N(6f)···O(1)	2.925
O(2)···O(2e)	2.457		
N(1b)···S(1)···N(3)	68.1	N(3)···S(1)···N(5e)	156.5
N(1b)···S(1)···N(5e)	105.2	N(1)···S(2)···N(3a)	67.3
N(3a)···S(2)···N(6)	101.1	N(1)···S(2)···N(6)	153.5
N(2d)···S(3)···N(2c)	82.6	N(2c)···S(3)···N(4)	94.9
N(4)···S(3)···N(4a)	80.7	N(2d)···S(3)···N(4)	150.2
N(2c)···S(3)···N(4a)	156.2	N(2d)···S(3)···N(4a)	89.7
N(5f)···O(1)···N(6f)	46.1		
C(1)–N(1)···S(2)–C(2)	50.6	C(2)–N(3)···S(1)–C(1)	48.0
C(1b)–N(1b)···S(1)–C(1)	−115.7	C(2a)–N(3a)···S(2)–C(2)	−113.6
C(2)–N(4)···S(3)–C(3)	38.9	C(1c)–N(2c)···S(3)–C(3)	−47.4
C(10)–O(2)···O(2e)–C(10e)	165.2		

Table V. (continued)

$(C_2H_5)_4N^+C_6H_5CO_2^- \cdot (NH_2)_2CS$ (**3**)

(i) *Thiourea and benzoate ion*

S(1)–C(1)	1.687(4)	C(1)–N(1)	1.332(6)
C(1)–N(2)	1.333(6)	C(2)–C(7)	1.374(6)
C(2)–C(3)	1.383(7)	C(3)–C(4)	1.380(7)
C(4)–C(5)	1.367(7)	C(5)–C(6)	1.381(7)
C(6)–C(7)	1.398(6)	C(7)–C(8)	1.517(6)
C(8)–O(1)	1.239(5)	C(8)–O(2)	1.246(6)
N(1)–C(1)–N(2)	116.7(4)	N(1)–C(1)–S(1)	122.0(4)
N(2)–C(1)–S(1)	121.3(4)	C(7)–C(2)–C(3)	120.6(5)
C(4)–C(3)–C(2)	120.0(5)	C(5)–C(4)–C(3)	119.6(5)
C(4)–C(5)–C(6)	121.1(5)	C(5)–C(6)–C(7)	119.4(5)
C(2)–C(7)–C(6)	119.3(4)	C(2)–C(7)–C(8)	120.0(4)
C(6)–C(7)–C(8)	120.8(4)	O(1)–C(8)–O(2)	124.9(4)
O(1)–C(8)–C(7)	117.4(4)	O(2)–C(8)–C(7)	117.7(4)

(ii) *Hydrogen bonding* (*donor atom listed first*)

N(1)$\cdots$O(1)	2.875	N(2b)$\cdots$O(1)	2.943
N(1a)$\cdots$O(2)	2.896	N(2)$\cdots$O(2)	2.867
N(1)$\cdots$O(1)$\cdots$N(2b)	77.4	N(2)$\cdots$O(2)$\cdots$N(1a)	78.3
C(1)–N(1)$\cdots$O(1)–C(8)	−21.0	C(1)–N(2)$\cdots$O(2)–C(8)	−17.1
C(1)–N(1)$\cdots$O(2b)–C(8b)	43.0	C(1)–N(2)$\cdots$O(1a)–C(8a)	39.4

* Symmetry transformations:
1. (a) $(-1 + x, y, z)$; (b) $(1 + x, y, z)$; (c) $(-0.5 + x, 1.5 - y, 1 - z)$; (d) $(0.5 + x, 1.5 - y, z)$; (e) $(1 - x, -0.5 + y, 0.5 - z)$.
2. (a) $(0.5 - x, 0.5 + y, z)$; (b) $(0.5 - x, -0.5 + y, z)$; (c) $(x, 1 - y, -0.5 + z)$; (d) $(0.5 - x, 1.5 - y, -0.5 + z)$; (e) $(1 - x, y, 0.5 - z)$; (f) $(x, -1 + y, z)$; (g) $(1 - x, -1 + y, 0.5 - z)$.
3. (a) $(1 - x, -0.5 + y, 1.5 - z)$; (b) $(1 - x, 0.5 + y, 1.5 - z)$.
Standard deviations in hydrogen bond lengths and bond angles:
1. $\sigma(l) \approx 0.009$ Å , $\sigma(\theta) \approx 0.6$ °;
2. $\sigma(l) \approx 0.007$ Å, $\sigma(\theta) \approx 0.5$ °;
3. $\sigma(l) \approx 0.007$ Å, $\sigma(\theta) \approx 0.4$ °.

by pairs of lateral N–H$\cdots$S hydrogen bonds to generate a puckered, wide ribbon running parallel to the *b* axis; the deviation of its molecular moieties from co-planarity is shown by the torsion angles C(1)—N(1)$\cdots$S(2)—C(2) = 50.6 and C(2)—N(3)$\cdots$S(1)—C(1) = 48.0°. These wide ribbons are arranged side by side and cross-linked by other thiourea molecules derived from **C(3)**, each forming two N—H$\cdots$S donor and four S$\cdots$H—N acceptor hydrogen bond to four thiourea molecules in adjacent ribbons to generate corrugated layers extending parallel to the planes $x = \frac{1}{4}$ and $\frac{3}{4}$ with inter-layer spacing 12.469 (*a*/2) Å.
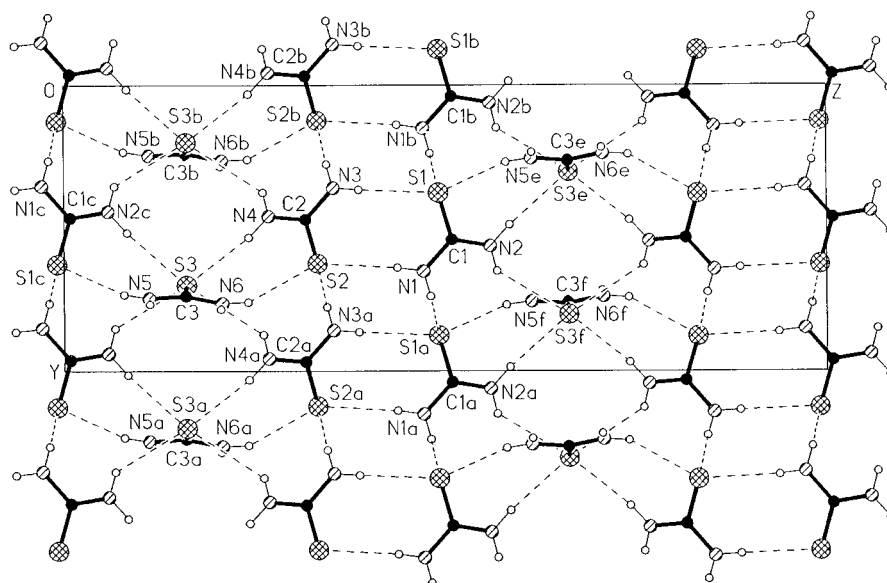
Figure 4. Hydrogen-bonded layer in **2** formed by two types of thiourea ribbons. Broken lines represent hydrogen bonds. Symmetry transformations: (a) $0.5 - x$, $0.5 + y$, z; (b) $0.5 - x$, $-0.5 + y$, z; (c) x, $1 - y$, $-0.5 + z$; (d) $0.5 - x$, $1.5 - y$, $-0.5 + z$; (e) $1 - x$, y, $0.5 - z$; (f) x, $-1 + y$, z; (g) $1 - x$, $-1 + y$, $0.5 - z$.

The benzoate ion together with its centrosymmetrically-related partner are bridged by a single proton in the synplanar conformation to form a hydrogen dibenzoate species, $[(C_6H_5CO_2)_2H]^-$. These anions are arranged in a zigzag column running parallel to the c axis and located between the corrugated thiourea layers. Note that the thiourea molecules of type **C(3)** protrude from both sides of each thiourea layer, thus facilitating formation of hydrogen bonds between their N atoms and the carboxyl oxygen atoms.

The tetrabutylammonium cations occupy special position of site symmetry 2: atom N(7) is situated at Wyckoff position $4(c)$ at $(0, y, \frac{1}{4})$. A stereoview of the crystal structure shows that the $(n\text{-}C_4H_9)_4N^+$ cations are arranged in a zigzag column within each channel (Figure 3).

3.3. CRYSTAL STRUCTURE OF $(C_2H_5)_4N^+C_6H_5CO_2^- \cdot (NH_2)_2CS$ (**3**)

The atom-labeling and hydrogen-bonding schemes of compound **3** are shown in Figure 5. Each thiourea molecule forms a pair of N—H$\cdots$O donor hydrogen bonds in the synplanar manner with the carboxylate group of the benzoate ion to generate a thiourea-benzoate dimer. With the formation of one additional antiplanar-type hydrogen bond between this thiourea molecule and the carboxylate group that is related to the first one by 2_1 symmetry, a thiourea-anion ribbon running parallel to the [010] direction is generated. For each ribbon the extent of deviation of its

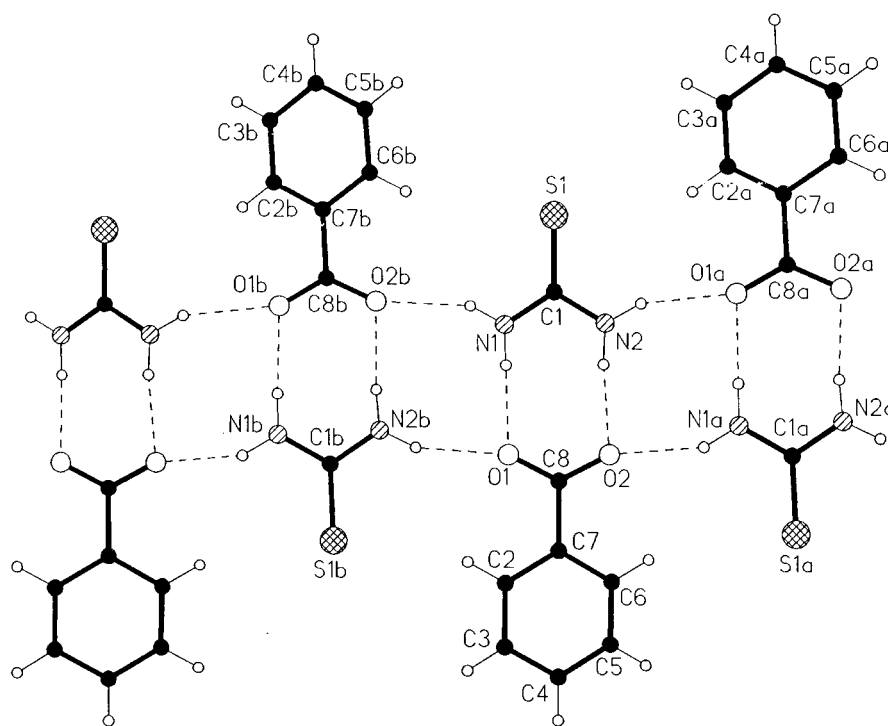*Figure 5.* Zipper-like composite ribbon in $(C_2H_5)_4N^+C_6H_5CO_2^- \cdot (NH_2)_2CS$ (**3**), formed by the attachment of benzoate ions to both sides of each thiourea ribbon. Symmetry transformations: (a) $1 - x, -0.5 + y, 1.5 - z$; (b) $1 - x, 0.5 + y, 1.5 - z$.

molecular components from planarity can be seen from the relevant torsion angles: $C(1)—N(1)\cdots O(2b)—C(8b) = 43.0$ and $C(1)—N(2)\cdots O(1a)—C(8a) = 39.4°$.

As shown in Figure 6, the zipper-like ribbon are arranged by operations of the corresponding $2_12_12_1$ symmetry elements to generate a "pseudo-channel" type of thiourea-anion lattice. The cross-section of a "pseudo-channel" takes the shape of a rectangle that has incompletely closed edges, with separations between its two pairs of walls measuring 7.2 and 13.9 Å. The tetraethylammonium cations are arranged in a zigzag column along the [010] direction, being accommodated between the "pseudo-channels" created by the herringbone arrangement of the thiourea-benzoate composite ribbons.

4. Structural Features and Relationships

It is notable that the mode of association of the wide thiourea ribbon in compound **1** differs distinctly from those in thiourea-anion host lattices reported previously [11]. As described in section 3.1, these wide thiourea ribbons are generated by linkage of pairs of N–H$\cdots$S hydrogen bonds in a head-to-tail fashion between two different
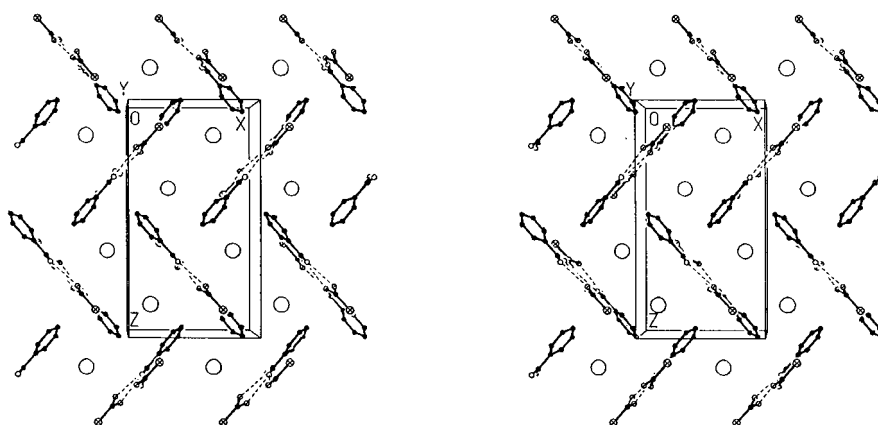
Figure 6. Stereodrawing of the crystal structure of **3**. Broken lines represent hydrogen bonds, and atom types are distinguished by size and shading. The tetraalkylammonium ions are represented by larger open circles.

types of thiourea ribbons which are built up by one or two independent thiourea molecules, respectively. Functioning as fundamental building blocks, these wide thiourea ribbons combine with benzoate anions to generate a novel channel-type host lattice.

The present series of thiourea-quaternary ammonium benzoate complexes exhibit two distinctly different kinds of thiourea-anion lattices depending on the stoichiometric ratio of thiourea to benzoate ion. Compounds **1** and **2** (3:1) are novel channel inclusion compounds whereas **3** is characterized by an anionic composite ribbon composed of a zigzag arrangement of thiourea molecules with benzoate ions attached to both sides.

In comparing this series of compounds with inclusion compounds in which the host lattices are built by thiourea and other monocarboxylic acid radicals, it is noted that the $C_6H_5CO_2^-$ ion has a bulky, hydrophobic benzenoid ring that takes no part in hydrogen bonding. Therefore, the construction of a two- or three-dimensional host framework requires a higher thiourea/benzoate molar ratio, as in the case of compounds **1** and **2**. The crystal structures of these two complexes can also be described by alternative models: a zigzag column of aromatic rings and two columns of tetrapropylammonium cations accommodated in a channel with a doubled cross-sectional area in **1**, or columns of rings and columns of cations arranged alternately and sandwiched between thiourea layers in **2**.

Finally, we note that in **1**–**3** the tetraalkylammonium ions of different sizes do not merely fill the voids in the anionic host lattices, but rather they play a key role in directing the organized assembly of the benzoate and thiourea species in the crystallization process.

Acknowledgements

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