Inclusion Compounds of Thiourea and Peralkylated Ammonium Salts. Part IV. Hydrogen-Bonded Host Lattices Built of Thiourea and Formate Ions

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Abstract. New inclusion complexes $(C_2H_5)_4N^+ HCO_2^- \cdot (NH_2)_2CS \cdot H_2O$ (**1**), $[(C_2H_5)_4N]_2^+ [(HCO_2)_2H]^- (HCO_2^-) \cdot 2(NH_2)_2CS$ (**2**), $(n\text{-}C_3H_7)_4N^+ HCO_2^- \cdot 3(NH_2)_2CS \cdot H_2O$ (**3**) and $(n\text{-}C_4H_9)_4N^+ [(HCO_2)_2H]^- \cdot 2(NH_2)_2CS$ (**4**) have been prepared and characterized by X-ray crystallography. Crystal data, MoK_α radiation: **1**, space group $P2_1/c$, $a = 7.199(2)$, $b = 16.851(2)$, $c = 13.044(2)$ Å, $\beta = 100.13(2)°$, $Z = 4$, and $R_F = 0.065$ for 1011 observed data; **2**, space group $Pca2_1$, $a = 25.803(5)$, $b = 7.190(2)$, $c = 17.394(2)$ Å, $Z = 4$, and $R_F = 0.073$ for 1515 observed data; **3**, space group $P2_1/n$, $a = 8.533(2)$, $b = 9.423(5)$, $c = 33.517(7)$ Å, $\beta = 90.44(2)°$, $Z = 4$, and $R_F = 0.052$ for 2521 observed data; **4**, space group $Pbca$, $a = 17.389(3)$, $b = 16.622(2)$, $c = 20.199(3)$ Å, $Z = 8$, and $R_F = 0.056$ for 1910 observed data. In both **1** and **2** the tetraethylammonium ions are sandwiched between puckered layers, which are constructed by the cross-linkage of a parallel arrangement of infinite chains. In **1** each chain is composed of twisted (thiourea–formate)$_2$ tetramers bridged by water molecules, whereas in **2** it comprises an alternate arrangement of thiourea dimers and protonated formate trimers each formed by the linkage of a hydrogen diformate ion, $[(HCO_2)_2H]^-$, to a formate ion *via* a C—H$\cdots$O hydrogen bond. In compound **3** two independent thiourea molecules are used to construct a hydrogen-bonded puckered layer normal to the c axis, whereas the remaining thiourea molecule, together with the formate ion and water molecule, generate another puckered layer that is parallel to the first one. Hydrogen bonding between these two types of layers gives rise to a network containing channels running parallel to the [100] direction, and the cations are stacked regularly within each column. In the crystal structure of **4**, the thiourea molecules form hydrogen-bonded zigzag ribbons running parallel to the b axis, which are cross-linked by the dimeric formate moieties $[(HCO_2)_2H]^-$ to form a puckered layer, and the $(n\text{-}C_4H_9)N^+$ cations occupy the space between adjacent layers.

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

1. Introduction

The channel-type inclusion compounds of urea and thiourea are well-known classical examples of crystalline host-guest systems [1–4]. Thiourea adducts [5–7] have

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a cross-sectional 'channel diameter' ranging from about 5.8 to 7.1 Å [8], which can accommodate 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 [9]. Recent examples of appropriate guest molecules that have been investigated include cyclohexane and some of its derivatives [10], certain compounds containing organometallics [11], as well as fragments of polymers containing either phenyl groups or sugar rings [12].
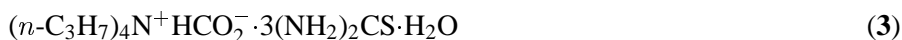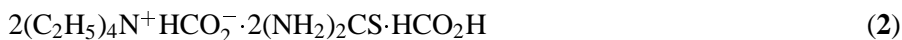
Another well-known class of inclusion compounds are the tetraalkylammonium salt hydrates, which were found to be clathrates with a rich variety of three-dimensional hydrogen-bonded host structures built of water molecules and anionic moieties such as halide ions [13–15], CH_3COO^- [16] and $[B_5O_6(OH)_4]^-$ [17].

C—H$\cdots$X hydrogen bonds are much weaker interactions than O—H$\cdots$O bonds and they have been investigated by various experimental and theoretical methods [18]. Recently, a study of weak but crucial polar interactions between the surface of a cyclodextrin cavity and a cluster of polar guest molecules indicates that the guest molecules are ordered and the inclusion geometry is stabilized by a cooperative system of host–guest O—H$\cdots$O, C—H$\cdots$O and C—H$\cdots\pi$ contacts [19]. An X-ray diffraction study of β-D-cellotetraose hemihydrate led to the conclusion that, besides normal O—H$\cdots$O hydrogen bonds, the more numerous C—H$\cdots$O and H$\cdots$H contacts as a whole contribute significantly to the stability of the crystal structure, and these weak intermolecular interactions are of importance in fine-tuning the packing arrangement of the flat, lath-shaped molecules [20]. It is now well recognized that C—H$\cdots$O hydrogen bonds occur when other packing forces and stereochemical constraints bring C—H bonds and acceptor O atoms within the range of electrostatic interactions at about 3.0 Å [18], and the structural parameters of authenticated C—H$\cdots$O hydrogen bonds are in the range H$\cdots$O = 2.3–2.8 Å, C$\cdots$O = 3.3–3.8 Å and C—H$\cdots$O = 130–180°.

The crystal structure of formic acid was determined by Holitzberg *et al.* [21] and later refined by Nahringbauer using low-temperature (98 K) data [space group $Pna2_1$, with $a = 10.241(1)$, $b = 3.544(1)$, $c = 5.356(1)$ Å, $Z = 4$]. It was reported that the formic acid molecules appear in the catemer motif, being inter-linked by O—H$\cdots$O bonds, and the resulting catemer chains are tightly packed to form (100) layers, in which the formyl H atom is not involved in any hydrogen bond so that the interaction between the chains is apparently of the van der Waals type [22, 23]. Recent *ab initio* calculations [24] have shown that the weakest form of hydrogen-bonding interaction, represented by the C—H$\cdots$O bond in a cyclic adduct of formic acid with formamide, still contributes a significant amount of 10–15 kJ/mol to the complex interaction energy, and a clear indication was found that the formyl proton may indeed participate in hydrogen bonding, despite the fact that the H$\cdots$O bond length may be extended up to 2.50Å.

Our interest in thiourea/urea adducts stems from an attempt to generate different inclusion topologies, and we have been studying a series of inclusion compounds

built of thiourea/urea-anion host lattices, in which hydrophobic guest cations are enclosed in box-like cages, accommodated in open parallel channel systems, or sandwiched between puckered layers [25, 26]. In our design of new thiourea-anion host lattices, some simple trigonal planar oxo-anions that can easily form $O \cdots H$—N acceptor hydrogen bonds have been used, such as CO_3^{2-}, NO_3^- [27] HCO_3^- [28] and $H_2BO_3^-$. As a natural extension of this work, we consider the simplest of all carboxylate ions, namely the formate ion, whose formyl proton may be involved in construction of the hydrogen-bonded host lattice. In the present study, we report the preparation and structural characterization of the following new thiourea-formate inclusion compounds:

$$(C_2H_5)_4N^+HCO_2^- \cdot (NH_2)_2CS \cdot H_2O \qquad\qquad (\mathbf{1})$$

$$2(C_2H_5)_4N^+HCO_2^- \cdot 2(NH_2)_2CS \cdot HCO_2H \qquad\qquad (\mathbf{2})$$

$$(n\text{-}C_3H_7)_4N^+HCO_2^- \cdot 3(NH_2)_2CS \cdot H_2O \qquad\qquad (\mathbf{3})$$

$$(n\text{-}C_4H_9)_4N^+[(HCO_2)_2H]^- \cdot 2(NH_2)_2CS \qquad\qquad (\mathbf{4})$$

2. Experimental

Tetraethylammonium hydroxide (25 wt.-% aqueous solution) was obtained from Eastman Kodak, whereas tetrapropyl- and tetrabutylammonium hydroxide were prepared from their corresponding chloride salts by reaction with moist silver(I) oxide [29].

Each hydroxide was mixed with thiourea in molar ratios of 1 : 2 for **1** and **2**, and 1 : 3 for **3** and **4**, respectively. A minimum quantity of water was used to dissolve the solid in each case, and formic acid (88%) was added to the solution in a 1 : 1 molar ratio for hydroxide : acid. After stirring for about 30 min, 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 (**2**) or small blocks (**1**, **3** and **4**).

Information concerning crystallographic data and structure refinement of the four compounds is summarized in Table I. Intensities were collected in the variable ω-scan technique [30] on a Siemens R3m/V diffractometer using MoK_α radiation ($\lambda = 0.71073$ Å) at 291 K. The raw data were processed with a learnt-profile procedure [31], and empirical absorption correction based on ψ-scan data was also applied.

All calculations were performed on a PC 486 computer with the SHELXTL-PLUS program package [32]. 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 Å) and allowed to ride on their respective parent atoms. The hydrogen atoms of the water molecule in **3** were located from a

Table I. Data collection and processing parameters of thiourea- tetraalkylammonium formate complexes.

Complex	1	2	3	4
Molecular formula	$(C_2H_5)_4N^+HCO_2^-$ $\cdot CS(NH_2)_2\cdot H_2O$	$2(C_2H_5)_4N^+HCO_2^-$ $\cdot 2CS(NH_2)_2\cdot HCO_2H$	$(n\text{-}C_3H_7)_4N^+HCO_2^-$ $\cdot 3CS(NH_2)_2\cdot H_2O$	$(n\text{-}C_4H_9)_4N^+[(HCO_2)_2H]^-$ $\cdot 2CS(NH_2)_2$
Molecular weight	269.4	548.8	477.8	485.7
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Orthorhombic
Space group	$P2_1/c$ (No. 14)	$Pca2_1$ (No. 29)	$P2_1/n$ (No. 14)	$Pbca$ (No. 61)
Unit cell parameters				
a, Å	7.199(2)	25.803(5)	8.533(2)	17.389(3)
b, Å	16.851(2)	7.190(2)	9.423(5)	16.622(2)
c, Å	13.044(2)	17.394(2)	33.517(7)	20.199(3)
α, °	90	90	90	90
β, °	100.13(2)	90	90.44(2)	90
γ, °	90	90	90	90
V, Å^{-3}	1557.8(5)	3227.0(9)	2695(2)	5852(1)
Z	4	4	4	8
$F(000)$	592	1200	1040	2128
Density (calcd.), g cm^{-3}	1.149	1.130	1.177	1.098
Absorption coefficient, mm^{-1}	0.211	0.205	0.303	0.211
Crystal size, mm	0.36 × 0.40 × 0.50	0.30 × 0.40 × 0.40	0.36 × 0.40 × 0.42	0.32 × 0.36 × 0.42
Mean μr	0.07	0.06	0.06	0.05
Transmission factors	0.922 to 0.892	1.000 to 0.820	0.856 to 0.825	0.912 to 0.883
Scan speed (deg min^{-1})	5.0 to 60.0	2.0 to 29.3	6.0 to 60.0	2.0 to 29.30
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	0.60 to 0.60

Background counting	stationary counts for one-half of scan time at each end of scan			
$2\theta_{max}$, °	48	48	46	46
Reflections measured	2614	2193	4042	5153
Unique data measured	2407	2193	3747	5153
Observed data	$|F_o| > 4\sigma(|F_o|)$, 1011	$|F_o| > 4\sigma(|F_o|)$, 1515	$|F_o| > 4\sigma(|F_o|)$, 2521	$|F_o| > 4\sigma(|F_o|)$, 1910
Number of variables, p	155	325	262	281
$R_F = \sum \| |F_o| - |F_c| \| / \sum |F_o|$	0.065	0.073	0.052	0.056
Constant g in weighting scheme				
$\omega = [\sigma^2(F_o) + g|F_o|^2]^{-1}$	0.0004	0.0001	0.0003	0.0001
$R_G = [\sum \omega(|F_o| - |F_c|)^2 / \sum |F_o|^2]^{1/2}$	0.068	0.086	0.059	0.055
$S = [\sum \omega(|F_o| - |F_c|)^2/(n-p)]^{1/2}$	1.66	1.90	1.66	1.55
Residual extrema in final difference map, $e\,\text{Å}^{-3}$	+0.20 to −0.19	+0.32 to −0.20	+0.43 to −0.40	+0.20 to −0.22
Largest and mean Δ/σ	0.072, 0.004	0.005, 0.001	0.021, 0.001	0.000, 0.000

subsequent difference Fourier synthesis. The hydrogen atoms of the water molecule in **1** and the formate molecules in **2** failed to appear in the difference maps, and their positions were derived from the overall 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 [33]. 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** plus **2**, **3**, and **4** 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 $(C_2H_5)_4N^+HCO_2^-\cdot(NH_2)_2CS\cdot H_2O$ (**1**) AND $2(C_2H_5)_4N^+HCO_2^-\cdot 2(NH_2)_2CS\cdot HCO_2H$ (**2**)

Although the same molar ratio of thiourea to tetraethylammonium hydroxide was used in the preparation of compounds **1** and **2**, which have closely related crystal structures in which the cations are separated by thiourea-anion puckered layers in a sandwich-like packing mode, distinct types of thiourea-anion layers are formed by the incorporation of different crystallized solvent molecules as the third component, namely water and formic acid for **1** and **2**, respectively.

In compound **1** the layer structure may be conveniently described with reference to the hydrogen bonding scheme shown in Figure 1 and Table V. The independent thiourea molecule and formate ion in the asymmetric unit are connected by a pair of N—H$\cdots$O hydrogen bonds to form a cyclic dimer which, together with its centrosymmetrically-related partner, generate a (thiourea-formate)$_2$ tetramer consolidated by a pair of N—H$\cdots$S hydrogen bonds. The moieties of this tetrameric unit are almost coplanar, as can be shown by the torsion angles C(1b)—N(1b) $\cdots$S(1)—C(1) = -13.1, C(1)—N(1) $\cdots$O(2)—C(2) = -22.0, and C(1)—N(2) $\cdots$O(1)—C(2) = $-18.5°$, and the mean atomic deviation from the least-squares plane is 0.091 Å. Bridged alternately by donor O—H$\cdots$O hydrogen bonds from the water molecules, the tetramers form a zigzag ribbon running parallel to the b axis. Successive water molecules lie 0.911 Å alternately above and below the main plane of the ribbon. The parallel arrangement of these ribbons facilitates their cross-linkage by N—H$\cdots$O hydrogen bonds to generate a puckered layer normal to the a axis (Figure 1).

The tetrahedral $(C_2H_5)_4N^+$ cation is well ordered and nearly attains its idealized 222 molecular symmetry. Its averaged dimensions are N—C = 1.491(6), C—C =

Table II. Atomic coordinates ($\times 10^4$) and thermal parameters* ($\mathring{A}^2 \times 10^3$) of $(C_2H_5)_4N^+HCO_2^- \cdot CS(NH_2)_2 \cdot H_2O$ (**1**) and $[(C_2H_5)_4N]_2^+[(HCO_2)_2H](HCO_2) \cdot 2(NH_2)_2CS$ (**2**).

Atom	x	y	z	U_{eq} or U
(i) $(C_2H_5)_4N^+HCO_2^- \cdot CS(NH_2)_2 \cdot H_2O$ (1)				
Thiourea-formate-water host lattice				
S(1)	−42(2)	4566(1)	6629(1)	80(1)
C(1)	−86(4)	3729(3)	5899(3)	56(1)
N(1)	178(4)	3756(2)	4920(3)	72(1)
N(2)	−357(4)	3022(2)	6287(3)	68(1)
C(2)	5(4)	1772(3)	4053(4)	94(1)
O(1)	76(4)	1662(2)	4993(3)	113(1)
O(2)	−185(4)	2384(2)	3548(3)	94(1)
O(1W)	−1446(5)	114(4)	5368(4)	159(1)
Tetraethylammonium ion				
N(3)	4819(4)	3722(2)	2361(3)	69(1)
C(3)	6219(5)	3638(3)	1644(4)	117(1)
C(4)	5381(5)	3515(4)	498(4)	195(1)
C(5)	3521(4)	4417(3)	2049(4)	98(1)
C(6)	4492(5)	5208(3)	2107(4)	154(1)
C(7)	5956(4)	3813(3)	3417(4)	101(1)
C(8)	4853(5)	3904(3)	4307(4)	147(1)
C(9)	3592(4)	3016(3)	2288(4)	101(1)
C(10)	4599(5)	2215(3)	2516(4)	128(1)
(ii) $2(C_2H_5)_4N^+HCO_2^- \cdot 2CS(NH_2)_2 \cdot HCO_2H$ (2)				
Thiourea-formate host lattice				
S(1)	2915(1)	864(2)	5462	94(1)
C(1)	3304(2)	596(2)	6240(2)	65(1)
N(1)	3800(2)	193(2)	6190(2)	78(1)
N(2)	3111(2)	816(2)	6957(2)	82(1)
S(2)	4545(1)	−47(2)	4542(1)	92(1)
C(2)	4169(2)	321(2)	3762(2)	65(1)
N(3)	3677(2)	646(2)	3826(2)	78(1)
N(4)	4368(2)	251(2)	3060(2)	77(1)
C(3)	3247(2)	1433(2)	1904(2)	103(1)
O(1)	2992(2)	1201(2)	2453(2)	101(1)
O(2)	3717(2)	1416(2)	1837(2)	149(1)
C(4)	4272(2)	86(2)	8121(2)	111(1)
O(3)	4512(2)	37(2)	7512(2)	106(1)
O(4)	3807(2)	259(2)	8193(2)	168(1)
C(5)	3752(2)	537(2)	10012(2)	164(1)
O(5)	3603(2)	1482(2)	9507(2)	179(1)
O(6)	3868(2)	−1078(2)	9984(2)	193(1)
O(5')	3696(2)	2137(2)	9976(2)	176(1)
O(6')	3665(2)	−746(2)	9592(2)	135(1)

Table II. Continued.

Atom	x	y	z	U_{eq} or U
Tetraethylammonium ion				
N(5)	2448(2)	5779(2)	3724(2)	70(1)
C(6)	2485(2)	7127(2)	3049(2)	123(1)
C(7)	2569(2)	6172(2)	2282(2)	149(1)
C(8)	2947(2)	4732(2)	3817(2)	113(1)
C(9)	3420(2)	5805(2)	3955(2)	167(1)
C(10)	2328(2)	7009(2)	4372(2)	121(1)
C(11)	2264(2)	5859(2)	5165(2)	177(1)
C(12)	2051(2)	4392(2)	3561(2)	118(1)
C(13)	1503(2)	5259(2)	3375(2)	167(1)
N(6)	5067(2)	4779(2)	6306(2)	80(1)
C(14)	5221(2)	6061(2)	5622(2)	98(1)
C(15)	5198(2)	5060(2)	4856(2)	141(1)
C(16)	5452(2)	3175(2)	6365(2)	102(1)
C(17)	6000(2)	3713(2)	6504(2)	152(1)
C(18)	5105(2)	6030(2)	7004(2)	97(1)
C(19)	4972(2)	5015(2)	7763(2)	137(1)
C(20)	4550(2)	3986(2)	6194(2)	100(1)
C(21)	4105(2)	5253(2)	6107(2)	126(1)

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

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

Atom O(1W) represents an inversional disordered H_2O molecule and has an occupancy of 1/2.

Atoms O(5)–O(6′) belong to an orientational disordered fomate anion and the site occupancy of them are: O(5) = 0.52; O(5′) = 0.48; O(6) = 0.73 and O(6′) = 0.27.

1.522(7) Å, C—N—C = 109.5(4), and N—C—C = 115.6(3)°. Individual bond distances and angles are given in the Supplementary Data. A perspective view of the crystal structure is illustrated in Figure 2. It can be seen that the cations are located in the space between the layers, which correspond to the (010) family of planes.

In the crystal structure of **2**, C—H···O hydrogen bonds play an important role in the construction of a three-component anionic layer. As shown in Figure 3, two independent thiourea molecules are connected by a pair of N—H···S hydrogen bonds to form a dimer, while a pair of formate ions are bridged by a single proton to form a hydrogen diformate species, $[(HCO_2)_2H]^-$. The hydrogen diformate ion and a formate ion are furthered consolidated by a C—H···O hydrogen bond of length 3.238 Å to generate a protonated formate trimer. The middle formate

Table III. Atomic coordinates ($\times 10^4$) and thermal parameters* ($\text{Å}^2 \times 10^3$) of $(n\text{-}C_3H_7)_4N^+HCO_2^- \cdot 3CS(NH_2)_2 \cdot H_2O$ (**3**).

Atom	x	y	z	U_{eq} or U
Thiourea-formate-water host lattice				
S(1)	−509(1)	916(1)	2212(1)	62(1)
C(1)	−435(4)	2650(4)	2340(1)	47(1)
N(1)	932(3)	3321(3)	2378(1)	68(1)
N(2)	−1727(3)	3406(3)	2395(1)	59(1)
S(2)	4641(1)	1735(1)	2349(1)	53(1)
C(2)	4593(4)	917(4)	1894(1)	47(1)
N(3)	3242(3)	580(3)	1720(1)	68(1)
N(4)	5911(3)	597(3)	1704(1)	57(1)
S(3)	1938(2)	−4050(2)	366(1)	116(1)
C(3)	649(5)	−2778(5)	311(1)	87(1)
N(5)	-734(4)	−2931(5)	121(1)	107(1)
N(6)	850(5)	−1506(4)	471(1)	111(1)
C(4)	4610(5)	−759(4)	782(1)	71(1)
O(1)	5935(4)	−457(4)	887(1)	97(1)
O(2)	3380(4)	−694(4)	957(1)	103(1)
O(1W)	7898(4)	−158(4)	277(1)	137(1)
Tetra-n-propylammonium ion				
N(7)	8127(3)	−237(3)	3831(1)	47(1)
C(5)	7265(4)	1161(4)	3838(1)	55(1)
C(6)	6460(5)	1602(4)	3452(1)	74(1)
C(7)	5588(5)	2958(4)	3505(2)	95(1)
C(8)	9353(4)	−241(4)	3499(1)	59(1)
C(9)	10558(5)	936(5)	3524(1)	79(1)
C(10)	11870(5)	654(6)	3237(2)	103(1)
C(11)	6994(4)	−1449(4)	3742(1)	55(1)
C(12)	5723(5)	−1684(4)	4044(2)	82(1)
C(13)	4670(5)	−2873(5)	3925(2)	101(1)
C(14)	8905(4)	−450(4)	4237(1)	57(1)
C(15)	9879(5)	−1772(5)	4278(1)	84(1)
C(16)	10387(5)	−2046(5)	4701(2)	101(1)

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

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

moiety is steeply inclined to the plane containing the terminal moieties of the trimeric unit, as can be seen from the values of the torsion angles C(5)—O(5) ⋯O(4)—C(4) = −60.0 and O(5)—C(5) ⋯O(2b)—C(3b) = 65.2°. The thiourea

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

Atom	x	y	z	U_{eq} or U
Thiourea–dimeric formate host lattice				
S(1)	8082(1)	5371(1)	7755(1)	84(1)
C(1)	7740(2)	5459(3)	6977(2)	77(1)
N(1)	7700(2)	6167(2)	6676(2)	91(1)
N(2)	7490(2)	4837(2)	6638(2)	93(1)
S(2)	8166(1)	8031(1)	7322(1)	91(1)
C(2)	7848(3)	7943(3)	8108(2)	75(1)
N(3)	7482(2)	8521(2)	8411(2)	96(1)
N(4)	7954(2)	7270(2)	8450(2)	92(1)
C(3)	6662(3)	5217(3)	4864(3)	168(1)
O(1)	6818(3)	5002(3)	5410(2)	216(1)
O(2)	6614(3)	5929(3)	4651(2)	179(1)
C(4)	7162(3)	7580(3)	5247(3)	152(1)
O(3)	7191(3)	7727(3)	4676(2)	192(1)
O(4)	6978(3)	6921(3)	5506(2)	172(1)
Tetra-n-butylammonium ion				
N(5)	5510(2)	8483(2)	3132(2)	68(1)
C(5)	6109(2)	8854(2)	3583(2)	73(1)
C(6)	5832(3)	9503(3)	4037(2)	105(1)
C(7)	6450(3)	9845(3)	4446(2)	107(1)
C(8)	6226(3)	10509(3)	4900(3)	138(1)
C(9)	5161(2)	9104(2)	2686(2)	83(1)
C(10)	5722(3)	9586(3)	2276(2)	113(1)
C(11)	5320(3)	10159(3)	1794(3)	144(1)
C(12)	5007(3)	9750(3)	1273(3)	179(1)
C(13)	5917(2)	7845(2)	2738(2)	75(1)
C(14)	5458(3)	7427(3)	2205(2)	97(1)
C(15)	5912(3)	6782(3)	1875(2)	113(1)
C(16)	5514(3)	6385(3)	1327(2)	157(1)
C(17)	4854(2)	8128(3)	3527(2)	81(1)
C(18)	5056(3)	7520(3)	4041(2)	113(1)
C(19)	4353(3)	7258(3)	4416(2)	135(1)
C(20)	4472(3)	6822(3)	4987(3)	191(1)

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

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

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

$(C_2H_5)_4N^+ HCO_2^- \cdot CS(NH_2)_2 \cdot H_2O$ (1)

(i) Thiourea and formate molecules

S(1)—C(1)	1.700 (5)	C(1)—N(1)	1.324 (6)
C(1)—N(2)	1.323 (6)	C(2)—O(1)	1.232 (6)
C(2)—O(2)	1.218 (6)		

S(1)—C(1)—N(1)	121.3(4)	S(1)—C(1)—N(2)	121.5(3)
N(1)—C(1)—N(2)	117.2(4)	O(1)—C(2)—O(2)	130.2(5)

(ii) Hydrogen bonding

N(1b)···S(1)	3.465	N(2)···O(1)	2.895
N(1)···O(2)	2.908	O(1W)···O(1)	2.904
N(2e)···O(2)	3.010	O(1c)···O(1W)	3.212

N(1b)···S(1)—C(1)	110.7	N(2)···O(1)—C(2)	118.2
N(2)···O(1)···O(1W)	122.0	O(1W)···O(1)—C(2)	110.6
N(1)···O(2)—C(2)	110.6	N(2e)···O(2)—(2)	108.6
N(1)···O(2)···N(2e)	140.1		

C(1b)—N(1b)···S(1)—C(1)	−13.1	C(1)—N(1)···O(2)—C(2)	−22.0
C(1)—N(2)···O(1)—C(2)	−18.5	C(1e)—N(2e)···O(2)—C(2)	−6.3

$2(C_2H_5)_4N^+[HCO_2(HCO_2)_2H]^{2-} \cdot 2CS(NH_2)_2$ (2)

(i) Thiourea and formate molecules

S(1)—C(1)	1.696(4)	C(1)—N(1)	1.315(6)
C(1)—N(2)	1.352(5)	S(2)—C(2)	1.689(4)
C(2)—N(3)	1.296(6)	C(2)—N(4)	1.325(5)
C(3)—O(1)	1.171(5)	C(3)—O(2)	1.219(7)
C(4)—O(3)	1.228(5)	C(4)—O(4)	1.212(6)
C(5)—O(5)	1.177(5)	C(5)—O(6)	1.200(3)

S(1)—C(1)—N(1)	123.3(3)	S(1)—C(1)—N(2)	120.3(3)
N(1)—C(1)—N(2)	116.4(4)	S(2)—C(2)—N(3)	121.4(3)
S(2)—C(2)—N(4)	120.8(4)	N(3)—C(2)—N(4)	117.8(4)
O(1)—C(3)—O(2)	129.4(4)	O(3)—C(4)—O(4)	126.3(4)
O(5)—C(5)—O(6)	127.6(4)		

(ii) Hydrogen bonding

N(3)···S(1)	3.463	N(1)···S(2)	3.456
N(3)···O(1)	2.998	N(4)···O(2)	2.838
N(2f)···O(1)	2.988	C(5a)···O(2)	3.238
N(1)···O(3)	2.944	N(2)···O(4)	2.830
N(4d)···O(3)	3.050	O(5)···O(4)	2.504

N(3)···S(1)—C(1)	108.3	N(1)···S(2)—C(2)	109.9
N(3)···O(1)—C(3)	109.7	N(2f)···O(1)—C(3)	108.2
N(4)···O(2)—C(3)	121.4	C(5a)···O(2)—C(3)	97.1
N(4)···O(2)···C(5a)	131.4	N(1)···O(3)—C(4)	111.0
N(4d)···O(3)—C(4)	102.1	N(1)···O(3)···N(4d)	146.9
N(2)···O(4)—C(4)	124.3	O(5)···O(4)—C(4)	109.8
N(2)···O(4)···O(5)	120.7		

Table V. Continued.

(ii) Hydrogen bonding (Continued)

C(1)—N(1)···S(2)—C(2)	−3.2	C(2)—N(3)···S(1)—C(1)	3.4
C(1)—N(1)···O(3)—C(4)	11.4	C(1)—N(2)···O(4)—C(4)	10.5
C(2)—N(3)···O(1)—C(3)	-13.5	C(2)—N(4)···O(2)—C(3)	−21.7
C(1)—N(2)···O(1e)—C(3e)	-11.4	C(2)—N(4)···O(3c)—C(4c)	0.3
C(5)—O(5)···O(4)—C(4)	-60.0	O(5)—C(5)···O(2b)—C(3b)	65.2

$(n\text{-}C_3H_7)_4N^+ HCO_2^- \cdot 3CS(NH_2)_2 \cdot H_2O$ (3)

(i) Thiourea and formate molecules

S(1)—C(1)	1.690(4)	C(1)—N(1)	1.332(5)
C(1)—N(2)	1.327(5)	S(2)—C(2)	1.708(4)
C(2)—N(3)	1.327(5)	C(2)—N(4)	1.332(5)
S(3)—C(3)	1.637(5)	C(3)—N(5)	1.343(6)
C(3)—N(6)	1.324(6)	C(4)—O(1)	1.216(6)
C(4)—O(2)	1.209(6)		
S(1)—C(1)—N(1)	121.0(3)	S(1)—C(1)-N(2)	121.7(3)
N(1)—C(1)—N(2)	117.4(3)	S(2)—C(2)-N(3)	121.0(3)
S(2)—C(2)—N(4)	121.0(3)	N(3)—C(2)-N(4)	118.0(3)
S(3)—C(3)—N(5)	124.2(4)	S(3)—C(3)-N(6)	122.1(4)
N(5)—C(3)—N(6)	113.6(4)	O(1)—C(4)-O(2)	131.0(4)

(ii) Hydrogen bonding

N(4a)···S(1)	3.499	N(3)···S(1)	3.624
N(1)···S(2)	3.502	N(2c)···S(2)	3.478
N(1b)···S(2)	3.381	N(2b)···S(2)	3.704
N(3)···O(2)	2.828	N(5e)···S(3)	3.434
N(6)···O(2)	2.801	O(1W)···O(1)	2.668
N(5c)···O(1W)	2.910	N(6c)···O(1W)	2.891
N(3)···S(1)—C(1)	99.7	N(4a)···S(1)—C(1)	103.7
N(3)···S(1)···N(4a)	122.8	N(1)···S(2)—C(2)	101.6
N(2c)···S(2)—C(2)	105.0	N(1b)···S(2)—C(2)	79.0
N(1)···S(2)···N(2c)	127.6	N(2b)···S(2)—C(2)	80.4
N(1)···S(2)···N(1b)	105.4	N(1)···S(2)···N(2b)	142.0
N(2c)···S(2)···N(1b)	123.3	N(2c)···S(2)···N(2b)	86.9
N(5e)···S(1)—C(1)	110.7	N(6)···O(2)—C(4)	111.8
O(1W)···O(1)—C(4)	113.0	N(5c)···O(1W)···N(6c)	45.3
C(1)—N(1)···S(2)—C(2)	56.9	C(2)—N(3)···S(1)—C(1)	55.6
C(1)—N(1)···S(2d)—C(2d)	87.1	C(1)—N(2)···S(2d)—C(2d)	−83.2
C(3)—N(6)···O(2)—C(4)	62.5	C(3e)—N(5e)···S(3)—C(3)	−3.9

$(n\text{-}C_4H_8)_4N^+ [(HCO_2)_2H]^- \cdot 2CS(NH_2)_2$ (4)

(i) Thiourea molecules and formate dimers

S(1)—C(1)	1.686(5)	C(1)—N(1)	1.330(6)
C(1)—N(2)	1.315(6)	S(2)—C(2)	1.687(5)
C(2)—N(3)	1.307(6)	C(2)—N(4)	1.330(6)
C(3)—O(1)	1.190(7)	C(3)—O(2)	1.265(7)
C(4)—O(3)	1.182(6)	C(4)—O(4)	1.257(7)

Table V. Continued.

(i) Thiourea molecules and formate dimers (Continued)

S(1)—C(1)—N(1)	121.4(3)	S(1)—C(1)—N(2)	122.2(3)
N(1)—C(1)—N(2)	116.3(4)	S(2)—C(2)—N(3)	122.4(3)
S(2)—C(2)—N(4)	121.2(3)	N(3)—C(2)—N(4)	116.4(4)
O(1)—C(3)—O(2)	127.7(6)	O(3)—C(4)—O(4)	126.8(5)

(ii) Hydrogen bonding

N(3a)$\cdots$S(1)	3.495	N(4)$\cdots$S(1)	3.470
N(1)$\cdots$S(2)	3.464	N(2a)$\cdots$S(2)	3.502
N(2)$\cdots$O(1)	2.756	N(3c)$\cdots$O(2)	3.065
N(4c)$\cdots$O(3)	2.807	N(1)$\cdots$O(4)	2.957
O(2)$\cdots$O(4)	2.472		
N(3a)$\cdots$S(1)—C(1)	109.3	N(4)$\cdots$S(1)—C(1)	106.0
N(3a)$\cdots$S(1)$\cdots$N(4)	129.2	N(1)$\cdots$S(2)—C(2)	101.5
N(2a)$\cdots$S(2)—C(2)	109.8	N(1)$\cdots$S(2)$\cdots$N(2a)	123.1
N(2)$\cdots$O(1)—C(3)	163.8	N(3c)$\cdots$O(2)—C(3)	121.7
N(4c)$\cdots$O(3)—C(4)	151.9	N(1)$\cdots$O(4)—C(4)	126.5
N(1)$\cdots$O(4)$\cdots$O(2)	112.5	C(4)—O(4)$\cdots$O(2)	111.0
C(1)—N(1)$\cdots$S(2)—C(2)	−37.8	C(2)—N(3)$\cdots$S(1a)—C(1a)	−5.0
C(1a)—N(2a)$\cdots$S(2)—C(2)	18.9	C(2)—N(4)$\cdots$S(1)—C(1)	−15.6
C(1)—N(1)$\cdots$O(4)—C(4)	−163.7	C(1)—N(2)$\cdots$O(1)—C(3)	37.3
C(2)—N(3)$\cdots$O(2b)—C(3b)	145.1	C(2)—N(4)$\cdots$O(3b)—C(4b)	−87.5
C(3)—O(2)$\cdots$O(4)—C(4)	159.2		

* **Symmetry transformations:**

1, a $(x, 0.5 − y, 0.5 + z)$;   b $(−x, 1 − y, 1 − z)$;   c $(−x, −y, 1 − z)$;
    d $(−x, 0.5 + y, 1.5 − z)$;   e $(x, 0.5 − y, −0.5 + z)$;   f $(−x, 1 − y, 1 − z)$;

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

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

4, a $(1.5 − x, 0.5 + y, z)$;   b $(x, 1.5 − y, 0.5 + z)$;   c $(x, 1.5 − y, −0.5 + z)$.

Standard deviations in hydrogen bond lengths and bond angles:
1, $\sigma(l) \approx 0.006$ Å, $\sigma(\theta) \approx 0.4°$;
2, $\sigma(l) \approx 0.006$ Å, $\sigma(\theta) \approx 0.3°$;
3, $\sigma(l) \approx 0.006$ Å, $\sigma(\theta) \approx 0.3°$;
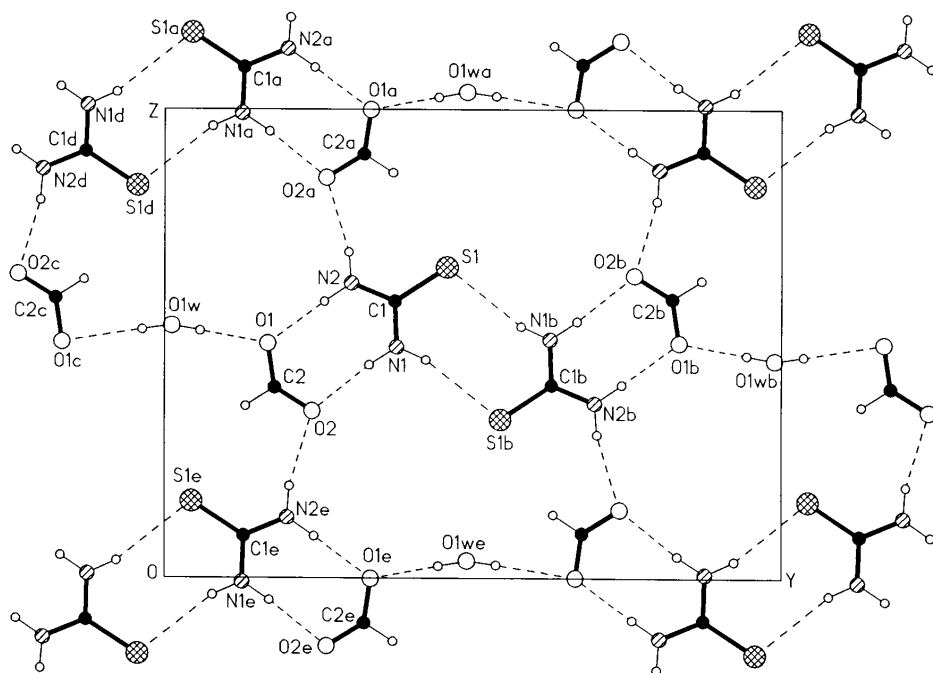**4**, $\sigma(l) \approx 0.006$ Å, $\sigma(\theta) \approx 0.4°$.

Figure 1. Projection diagram showing a hydrogen-bonded layer constructed from (thiourea-formate)$_2$ tetramers in the crystal structure of $(C_2H_5)_4N^+HCO_2^- \cdot (NH_2)_2CS \cdot H_2O$ (**1**) The atom labels correspond to those given in Tables II and V. Broken lines represent hydrogen bonds. Symmetry transformations: a: $x, 0.5 - y, 0.5 + z$; b: $-x, 1 - y, 1 - z$; c: $-x, -y, 1 - z$; d: $-x, 0.5 + y, 1.5 - z$; e: $x, 0.5 - y, -0.5 + z$; f: $-x, 1 - y, 1 - z$.
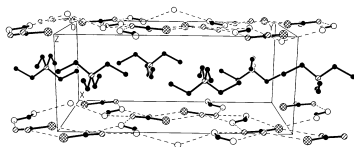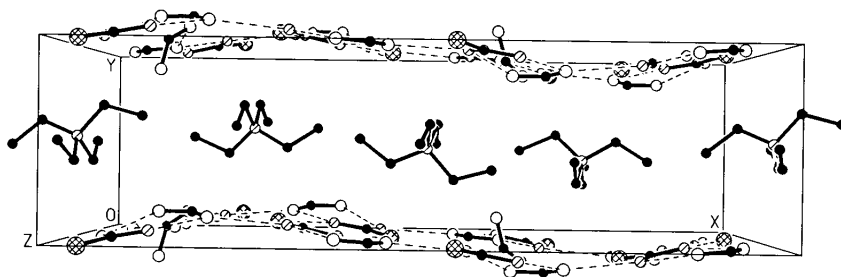

Figure 2. Perspective view of the layer-type crystal structure of **1**. Broken lines represent hydrogen bonds, and atom types are distinguished by size and shading.

dimers and the formate trimers are alternately arranged and linked by pairs of N—H$\cdots$O hydrogen bonds to form a zigzag ribbon oriented parallel to the c axis. In this ribbon the thiourea dimer and formate moieties at both ends of the trimer are nearly coplanar; the relevant torsion angles are: C(2)—N(3) $\cdots$S(1)—C(1) = 3.4, C(1)—N(1) $\cdots$S(2)—C(2) = −3.2, C(2)—N(3) $\cdots$O(1)—C(3) = −13.5, C(2)—N(4) $\cdots$O(2)—C(3) = −21.7, C(1)—N(1) $\cdots$O(3)—C(4) = 11.4, and C(1)—N(2) $\cdots$O(4)—C(4) = 10.5°, and the mean atomic deviation from the least-squares plane is 0.123 Å. With these ribbons lying side by side, additional N—H$\cdots$O hydrogen
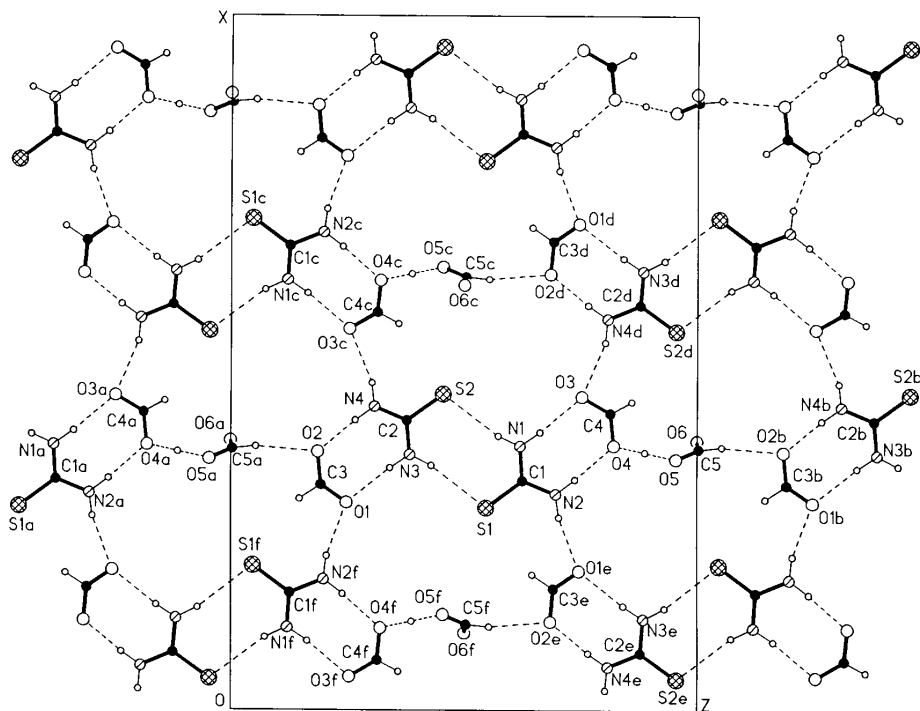
Figure 3. Hydrogen-bonded layer in $2(C_2H_5)_4N^+HCO_2^- \cdot 2(NH_2)_2CS \cdot HCO_2H$ (**2**) formed by ribbons contructed from thiourea dimers and protonated formate trimers. The atom labels correspond to those given in Tables II and V. Broken lines represent hydrogen bonds. Symmetry transformations: a: $x, y, -1 + z$; b: $x, y, 1 + z$; c: $1 - x, -y, -0.5 + z$; d: $1 - x, -y, 0.5 + z$; e: $0.5 - x, y, 0.5 + z$; f: $0.5 - x, y, -0.5 + z$.

bonds cross-link them together to generate a puckered layer normal to the b axis (Figure 3).

Figure 4 shows a perspective view of the crystal structure of **2** along the c axial direction. Both well-ordered tetraethylammonium cations in the asymmetric unit are arranged in two separate columns running parallel to the [001] direction; the columns of type $(C_2H_5)_4N(5)^+$ are located at $x = 1/4$ and 3/4, and those of type $(C_2H_5)_4N(6)^+$ at $x = 0$ and 1/2. The parallel, alternate arrangement of these two kinds of columns constitutes a cationic layer oriented parallel to the (010) family of planes and sandwiched between adjacent thiourea-anion layers.

In compounds **1** and **2**, the respective interlayer spacings of 7.199 ($= a$) and 7.190Å ($= b$) are slightly smaller than the corresponding value 7.465Å ($= b/2$) for tetraethylammonium cations accommodated in the layer-type thiourea-bicarbonate-water lattice of orthorhombic $(C_2H_5)_4N^+HCO_3^- \cdot (NH_2)_2CS \cdot H_2O$ [25], as may be expected in view of the better planarity of the anionic layers in the present compounds.

Figure 4. Perspective view of the layer-type crystal structure of **2**. Broken lines represent hydrogen bonds, and atom types are distinguished by size and shading.

3.2. CRYSTAL STRUCTURE OF $(n\text{-}C_3H_7)_4N^+HCO_2^- \cdot 3(NH_2)_2CS \cdot H_2O$ (**3**)

Compound **3** is isomorphous with $(n\text{-}C_3H_7)_4N^+NO_3^- \cdot 3(NH_2)_2CS \cdot H_2O$ (**3a**) [$P2_1/n$, $a = 8.433(2)$, $b = 9.369(2)$, $c = 34.361(7)$ Å, $\beta = 91.01(3)°$, $Z = 4$], which has been reported in our recent study on a series of inclusion complexes of thiourea with peralkylated ammonium nitrate salts [27], and changing the anion from nitrate to formate causes no marked variation in the structure of the thiourea-anionic host lattice.

As shown in Figure 5, the crystal structure of compound **3** features one-dimensional channels extending parallel to the a axial direction. This channel framework is built up by two types of layers (designated type I and type II) inter-linked by N—H···O(formate) hydrogen bonds. The type I layer is composed of thiourea molecules **C(1)** [composed of atoms C(1), S(1), N(1) and N(2), and here-after conveniently referred to by naming the carbon atom] and **C(2)**, which are alternately linked by pairs of N—H···S hydrogen bonds in a shoulder-to-shoulder fashion to form zigzag, puckered ribbons running parallel to the a axis (Figure 6). The relevant torsion angles in each thiourea ribbon are: C(1)—N(1)···S(2)—C(2) = 56.9 and C(2)—N(3)···S(1)-C(1) = 55.6°, which are close to the corresponding values for **3a**, 61.4 and 56.0° respectively. With these ribbons arranged side by side, atom S(2) of molecule **C(2)** forms two acceptor hydrogen bonds with atoms N(1b) and N(2b) of molecule **C(1b)** belonging to an adjacent ribbon, such that this type of cross-linkage yields a puckered layer that is normal to the c axis (Figure 6). The dihedral angles between adjacent ribbons are quite large, as can be seen from the relevant torsion angles: C(1)—N(1)···S(2d)—C(2d) = 87.1, and C(1)—N(2)···S(2d)—C(2d) = $-83.2°$; the corresponding value for **3a** is $-58.2°$.

The type II layer is shown in Figure 7. As in the case of **3a**, the third thiourea molecule **C(3)**, together with its centrosymmetrically-related partner, are consolidated by a pair of N-H···S hydrogen bonds to yield a cyclic dimer. Water molecules and formate ions link these dimers into a wide chain running parallel to the a axis. The shortest distance between O atoms of water molecules and formate ions belonging to adjacent chains is 4.345Å, so that the type II layer just consists of chains
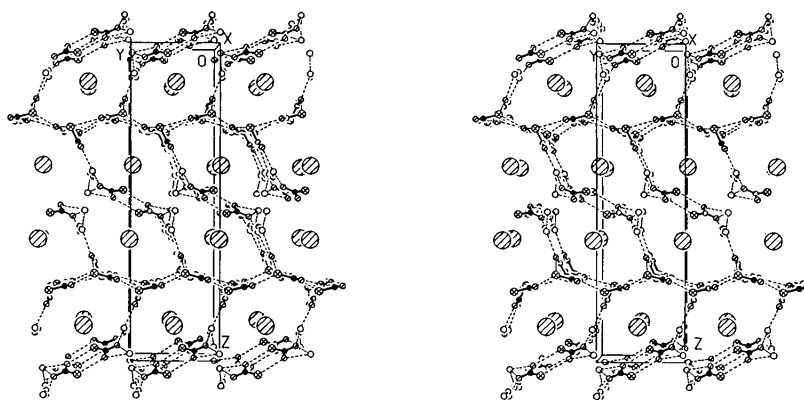
Figure 5. Stereodrawing of the channel-type crystal structure of $(n\text{-}C_3H_7)_4N^+HCO_2^-\cdot$ $3(NH_2)_2CS\cdot H_2O$ (**3**). The origin of the unit cell lies at the upper right corner, with a towards the reader, b pointing from right to left and c downwards. For clarity the enclosed $(n\text{-}C_3H_7)_4N^+$ ions are represented by large shaded circles.
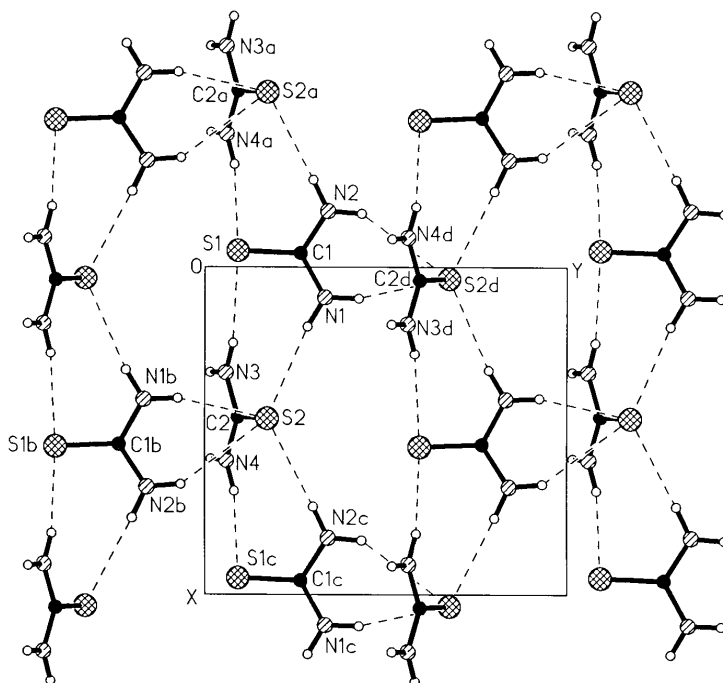

Figure 6. Type I hydrogen-bonded layer in **3**, formed by thiourea ribbons. The atom labels correspond to those given in Tables III and V. Broken lines represent hydrogen bonds. Symmetry transformations: a: $-1 + x,\ y,\ z$; b: $0.5 - x,\ -0.5 + y,\ 0.5 - z$; c: $1 + x,\ y,\ z$; d: $0.5 - x,\ 0.5 + y,\ 0.5 - z$.
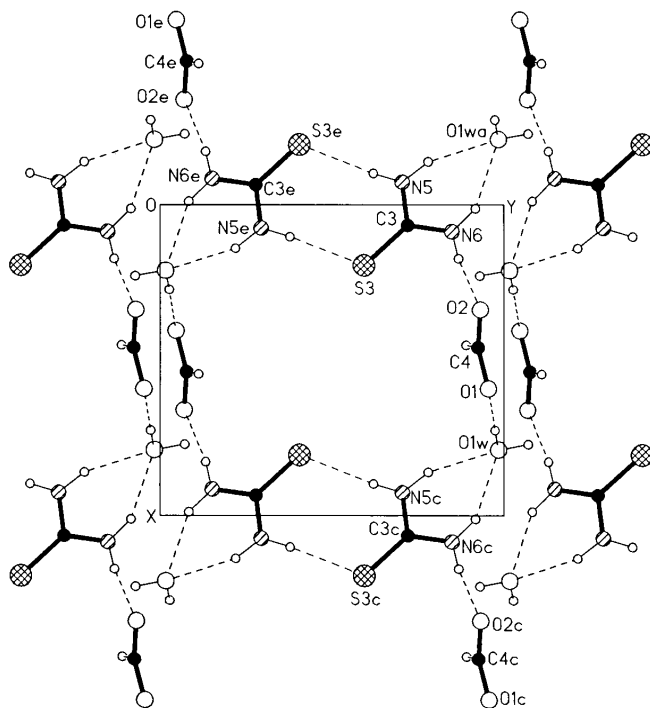
Figure 7. Type II layer composed of hydrogen-bonded wide chains in **3**, each formed by the cross-linkage of thiourea dimers, formate ions and water molecules. The atom labels correspond to those given in Tables III and V. Broken lines represent hydrogen bonds. Symmetry transformations: e: $-x$, $1-y$, $-z$; a, c same as those in Fig. 6.

aligned side by side in a highly puckered manner without any significant interaction between them.

As shown in Figure 5, the two types of layers are alternately stacked parallel to the (001) family of planes and further cross-linked by N—H···O hydrogen bonds to generate a three-dimensional network containing channels that run parallel to the [100] direction. The well-ordered tetrahedral $(n\text{-}C_3H_7)_4N^+$ cations are stacked in a single column within each channel, which has a partial opening at $z = 0$ or $1/2$, corresponding to the locations of layers of type II.

3.3. CRYSTAL STRUCTURES OF $(n\text{-}C_4H_9)_4N^+[(HCO_2)_2H]^- \cdot 2(NH_2)_2CS$ (**4**)

As illustrated in Figure 8, compound **4** features a sandwich-like structure in which the $(n\text{-}C_4H_9)_4N^+$ ions are separated by thiourea-anion puckered layers. In the construction of the host layer, two independent thiourea molecules are alternately connected by hydrogen bonds in the usual shoulder-to-shoulder manner to form a zigzag ribbon running parallel to the b axis, which is essentially planar, as shown
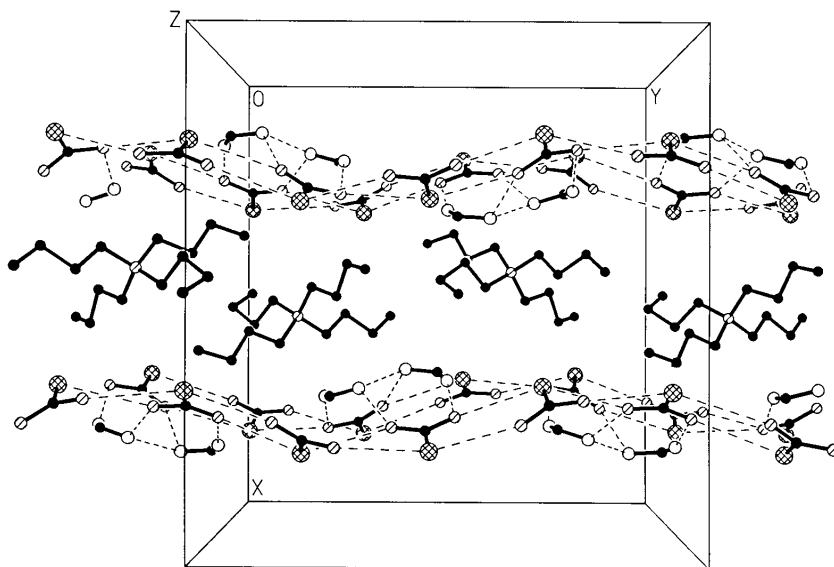
Figure 8. Perspective view of the layer-type crystal structure of $(n\text{-}C_4H_9)_4N^+[(HCO_2)_2H]^- \cdot 2(NH_2)_2CS$ (**4**). Broken lines represent hydrogen bonds, and atom types are distinguished by size and shading.

by the torsion angles C(2)—N(4) ···S(1)—C(1) = −15.6, C(1)—N(2) ···S(2a)—C(2a) = 18.9, C(2)—N(3) ···S(1a)—C(1a) = −5.0, C(1)—N(1) ···S(2)—C(2) = −37.8° (Figure 9). With these thiourea ribbons stacked broadside-on in the [001] direction, each thiourea molecule is further linked to a *syn*-planar hydrogen diformate ion, $[(HCO_2)_2H]^-$, via two additional N—H···O donor hydrogen bonds that extend outward on either side of the ribbon, so that a puckered layer oriented parallel to the (100) family of planes is formed.

In the cation $(n\text{-}C_4H_9)_4N^+$, a terminal methyl group deviates from the main plane through other carbon atoms of its parent butyl group, so that the cation does not attain its idealized $\bar{4}2m$ (D_{2d}) conformation, as illustrated in Figure 8. It can be seen that these cations are located in the space between the layers, which correspond to the (100) family of planes. The interlayer spacing of 8.695 Å ($= a/2$) can be compared with the corresponding value 8.371 Å ($= c/2$) for a similar layer structure with tetra-n-butylammonium cations accommodated in the thiourea-hydrogen diacetate lattice of monoclinic $(n\text{-}C_4H_9)_4N^+[(CH_3CO_2)_2H]^- \cdot 2(NH_2)_2CS$ [34].

3.4. GENERAL STRUCTURAL FEATURES

The present series of four thiourea-quaternary ammonium formate complexes exhibit two general types of host lattices depending on the stoichiometric ratio of thiourea to formate anion. Compounds **1**, **2** and **4** (1 : 1) adopt sandwich-like structures in which different types of layers are formed by various combinations of
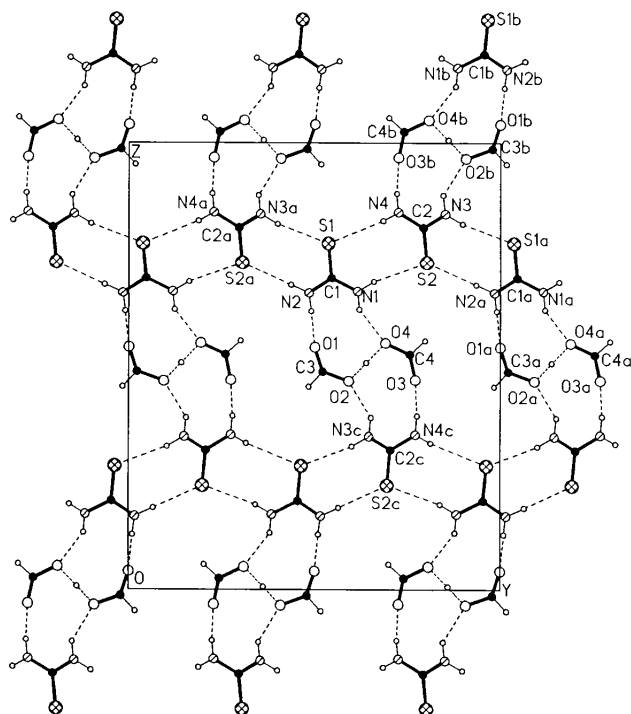
Figure 9. Hydrogen-bonded layer in **4**, formed by thiourea ribbons and hydrogen diformate anions. The atom labels correspond to those given in Tables IV and V. Broken lines represent hydrogen bonds. Symmetry transformations: a: $1.5 - x, 0.5 + y, z$; b: $x, 1.5 - y, 0.5 + z$; c: $x, 1.5 - y, -0.5 + z$.

thiourea and formate anions with or without complementary co-crystallized solvent molecules, whereas compound **3** (3 : 1) has a channel structure that is isostructural with the analogous nitrate complex **3a**.

It is interesting to note that the protonated formate trimer in compound **2**, and the terminal formate moieties are essentially coplanar, as the dihedral angle between the least-squares plane of formate **C(4)** and the plane of formate **C(3b)** is 10.4°, and they are involved in forming the main plane of the thiourea-anion layer. However, the middle formate moiety **C(5)** is rotated out of plane to a large extent, making dihedral angles of 69.8 and 76.3° with **C(4)** and **C(3b)**, respectively. The formyl H atom of **C(5)** forms a C—H···O hydrogen bond with the carboxy O atom of **C(3b)** with H···O = 2.303 Å, C—H···O = 3.213 Å and C—H···O = 157.9°. The H···O distance is shorter than the sum of the relevant van der Waals radii ($W_H + W_O = 2.4$ Å) and closer to the lower end of the H···O range of 2.16 to 2.65 Å for C—H···O=C hydrogen bonding established by accurate X-ray and neutron diffraction analyses [18], indicating that the formyl proton has a stronger donor capability.

In comparing the present series of compounds with the thiourea-bicarbonate [28] and nitrate [27] inclusion compounds, it is noted that the oxygen atoms of the HCO_2^- ion, like the NO_3^- ion, can only form acceptor hydrogen bonds with other potential donors. Therefore, the construction of a two- or three-dimensional host framework requires a higher thiourea/formate molar ratio, and the resulting ribbons generally adopt a twisted configuration so that the thiourea molecules can form additional donor hydrogen bonds with atoms in adjacent ribbons.

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