Thiourea-Halide Lattices. Part 1. Crystal Structures of $(n\text{-}C_4H_9)_4N^+F^-\cdot3(NH_2)_2CS$, $(n\text{-}C_4H_9)_3(CH_3)N^+X^-\cdot2(NH_2)_2CS$ (X = Cl, Br), and $(n\text{-}C_3H_7)_4N^+I^-\cdot(NH_2)_2CS^\star$

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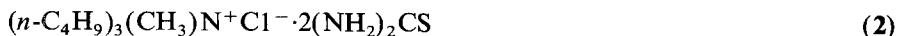**Abstract.** The title complexes (**1**, X = F; **2**, X = Cl; **3**, X = Br and isomorphous with **2**; **4**, X = I) have been prepared and characterized by X-ray crystallography. Crystal data, Mo $K\alpha$ radiation: **1**, space group Cc, $Z = 4$, $a = 12.017(3)$, $b = 14.263(5)$, $c = 17.210(7)$ Å, $\beta = 103.06(2)°$, and $R_F = 0.053$ for 2044 observed data; **2**, space group Cc, $Z = 4$, $a = 12.817(3)$, $b = 11.072(2)$, $c = 16.781(5)$ Å, $\beta = 90.74(2)°$, $R_F = 0.044$ for 2249 data; **3**, $a = 12.873(4)$, $b = 11.119(2)$, $c = 16.957(2)$ Å, $\beta = 89.11(2)°$, $R_F = 0.049$ for 2059 data; **4**, space group $P2_1/n$, $Z = 4$, $a = 8.858(2)$, $b = 14.358(3)$, $c = 15.379(3)$ Å, $\beta = 93.88(1)°$, $R_F = 0.068$ for 3119 data. In all four structures each thiourea molecule interacts with adjacent thiourea molecules via N—H···S hydrogen bonds to give a ribbon-like arrangement, and also forms a pair of 'chelating' N—H···X hydrogen bonds with a halide ion, resulting in an anionic framework (in **1–3**) or composite ribbon (in **4**) as a component in the crystal packing. The measured ranges of N···X distances are: 2.819(5)–2.994(7) Å for **1**, 3.252(3)–3.291(3)Å for **2**, 3.353(6)–3.459(6)Å for **3**, and 3.564(5)–3.680(5) Å for **4**.

Key words. Thiourea, hydrogen bonding, ribbon structure, tetraalkylammonium halide.

1. Introduction

Recently we reported the crystal structure of an isomorphous series of ternary complexes $(C_2H_5)_4N^+X^-\cdot(NH_2)_2CO\cdot2H_2O$ (X = Cl, Br, CN). in which the tetraethylammonium ions are sandwiched between hydrogen-bonded urea-water–halide/pseudohalide puckered layers [1]. Parallel studies employing bulkier cations and thiourea in place of urea yielded the series of anhydrous complexes **1–4**, whose structural characterization constitutes the essence of the present report. A simplified description of the crystal structure of **1** has appeared in a recent communication [2].

$$(n\text{-}C_4H_9)_4N^+F^-\cdot3(NH_2)_2CS \tag{1}$$

$$(n\text{-}C_4H_9)_3(CH_3)N^+Cl^-\cdot2(NH_2)_2CS \tag{2}$$

$$(n\text{-}C_4H_9)_3(CH_3)N^+Br^-\cdot2(NH_2)_2CS \tag{3}$$

$$(n\text{-}C_3H_7)_4N^+I^-\cdot(NH_2)_2CS \tag{4}$$

★ Dedicated to Dr D. W. Davidson in honor of his great contributions to the sciences of inclusion phenomena.

2. Experimental

Each of the binary complexes was prepared from slow evaporation of an aqueous solution containing stoichiometric amounts of quaternary ammonium salt and thiourea. New phases were not obtained by variation of the molar ratios.

Measurement of the crystal data and reflection intensities on a Nicolet R3m diffractometer using Mo$K\alpha$ radiation ($\lambda = 0.71069$ Å) followed the procedure described previously [3], and the relevant parameters are summarized in Table I.

Absorption corrections were applied by fitting a pseudoellipsoid to the azimuthal scan data of two strong reflections spread over a range of 2θ-values [4, 5]. The structure of 1 was derived by direct phase determination guided by negative quartets [6], whereas those of 2 and 4 were solved by Patterson and Fourier methods. The terminal CH_3—CH_2— leg of one n-butyl group in 1 exhibits disorder, and its scattering power was represented by half-carbon atoms C(18A), C(19A), C(18B) and C(19B). All non-hydrogen atoms except these disordered ones were subjected to anisotropic refinement. The thioamido, methylene, and methyl H atoms were generated geometrically; those of the first two types were allowed to ride on their respective parent N and C atoms, and the methyl groups were treated as rigid groups. Isotropic temperature factors (about 20% larger than those of the corresponding parent atoms) were assigned to the H atoms.

Computations were performed on a Data General Nova 3 minicomputer using the SHELXTL program package [7]. Analytic expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated [8]. Blocked-cascade least-squares refinement [9] coverged to the R indices and other parameters listed in Table I.

3. Results and Discussion

The final positional and thermal parameters of 1, the isomorphous pair 2 and 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. Bond distances and bond angles are given in Table V.

3.1. CRYSTAL STRUCTURE OF 1

Figure 1 illustrates the atom labelling and the hydrogen-bonding interactions among the thiourea molecules and the fluoride ions. Each thiourea molecule is linked by a pair of N—H⋯S hydrogen bonds to another thiourea molecule on either side while forming donor hydrogen bonds to the fluoride ion in a bidentate chelating mode. Three independent thiourea molecules, connected sequentially in the manner described, constitute a trimeric unit which is repeated by the symmetry operation $(1 + x, -y, \frac{1}{2} + z)$ to generate an extended twisted ribbon. Ribbons running in different directions [as related by the symmetry operations (x, y, z), $(x, -y, -\frac{1}{2} + z)$ and $(\frac{1}{2} + x, \frac{1}{2} + y, z)$] are bridged by the fluoride ions to form an open framework which accommodates the tetrabutylammonium ions (Figure 2).
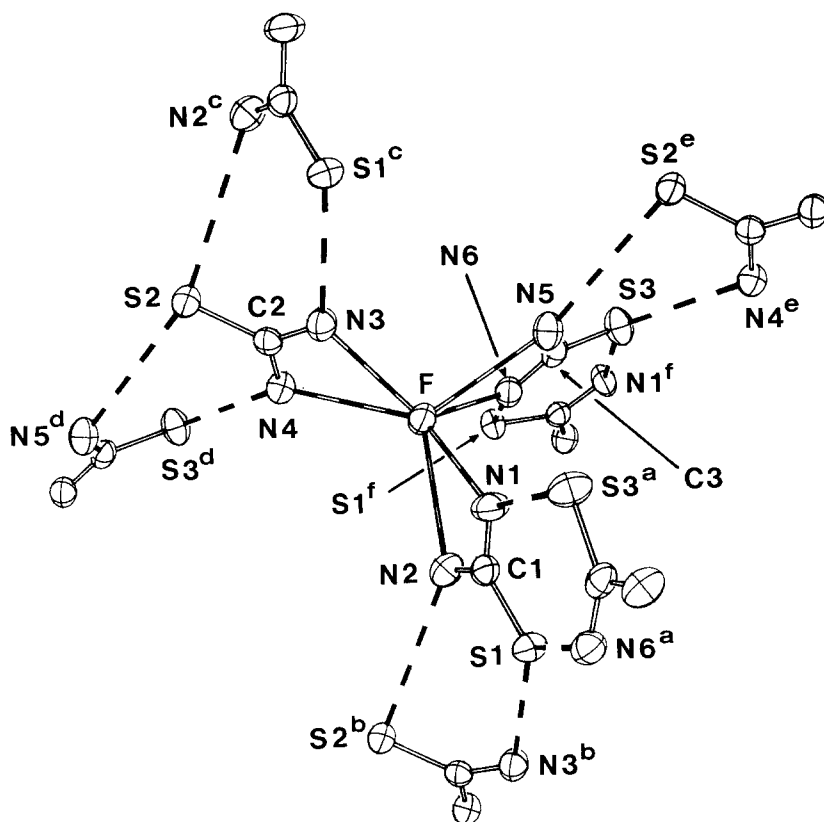
Fig. 1. Perspective view of a portion of the thiourea–fluoride lattice in $(n\text{-}C_4H_9)_4N^+F^-\cdot3(NH_2)_2CS$ (1). The thermal ellipsoids are drawn at the 25% probability level. The atom labels correspond to those given in Tables II and V. Symmetry transformations: $^a x, -y, \frac{1}{2}+z$; $^b -\frac{1}{2}+x, -\frac{1}{2}+y, z$; $^c \frac{1}{2}+x, \frac{1}{2}+y, z$; $^d -\frac{1}{2}+x, \frac{1}{2}+y, z$; $^e \frac{1}{2}+x, -\frac{1}{2}+y, z$; $^f x, -y, -\frac{1}{2}+z$.

3.2. CRYSTAL STRUCTURE OF 2 AND 3

The atom labelling and the hydrogen-bonding interactions among its components are shown in Figure 3. The thiourea molecules are alternately linked by pairs of N—H···S hydrogen bonds to form a slightly buckled ribbon (Figure 4). The resulting two criss-crossing ribbon systems (related by the c-glide and pointing in the [110] and [1$\bar{1}$0] directions) are bridged by the halide ions to generate an open anionic lattice which accommodates the tributylmethylammonium ions (Figures 4 and 5).

3.3. CRYSTAL STRUCTURE OF 4

The atom labelling and hydrogen-bonding interactions are shown in Figure 6. The thiourea molecules are connected by pairs of N—H···S hydrogen bonds, each arranged about an inversion center, to form a slightly buckled ribbon running

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

Complex	1	2	3	4
Molecular formula	$(n\text{-}C_4H_9)_4N^+F^-$ $\cdot 3(NH_2)_2CS$	$(n\text{-}C_4H_9)_3(CH_3)N^+Cl^-$ $\cdot 2(NH_2)_2CS$	$(n\text{-}C_4H_9)_3(CH_3)N^+Br^-$ $\cdot 2(NH_2)_2CS$	$(n\text{-}C_3H_7)_4N^+I^-$ $\cdot (NH_2)_2CS$
Molecular weight	489.82	388.08	432.53	389.38
Cell parameters				
a, Å	12.017(3)	12.817(3)	12.873(4)	8.858(2)
b, Å	14.263(5)	11.072(2)	11.119(2)	14.358(3)
c, Å	17.210(7)	16.781(5)	16.957(2)	15.379(3)
β,°	103.06(2)	90.74(2)	89.11(2)	93.88(1)
V, Å^3	2873 (1)	2381.3(8)	2426.8(8)	1951.5(5)
Z	4	4	4	4
$F(000)$	1072	848	920	780
Density (flotation in CCl$_4$/n-hexane, g cm^{-3}	1.15	1.107	1.185	1.334
Density (calcd.), g cm^{-3}	1.132	1.082	1.184	1.325

	Cc	Cc	Cc	$P2_1/n$
Space Group	Cc	Cc	Cc	$P2_1/n$
Absorption coefficient, cm^{-1}	2.71	3.34	18.83	17.18
Crystal size, mm	$0.44 \times 0.40 \times 0.36$	$0.56 \times 0.56 \times 0.50$	$0.52 \times 0.40 \times 0.40$	$0.40 \times 0.40 \times 0.32$
Mean μr	0.050	0.066	0.500	0.297
Transmission factors	0.876–0.899	0.807–0.864	0.238–0.266	0.420–0.442
Scan type and speed	$\omega - 2\theta$; 2.02–8.37 deg min^{-1}			
Scan range	1° below $K\alpha_1$ to 1° above $K\alpha_2$			
Background counting	stationary counts for one-half of scan time at each end of scan			
$2\theta_{max}$, °	50	55	50	55
Unique data measured	2329	2539	2235	3942
Observed data with $\|F_0\| > 3\sigma(\|F_0\|)$, n	2044	2249	2059	3119
Number of variables, p	276	218	218	175
$R_F = \Sigma \||F_0|-|F_c|\|/\Sigma|F_0|$	0.053	0.044	0.049	0.068
Constant g in weighting scheme $w = [\sigma^2(F_0) + g|F_0|^2]^{-1}$	0.0015	0.0008	0.0010	0.0008
$R_G = [\Sigma w(|F_0| - |F_c|)^2/\Sigma w|F_0|^2]^{1/2}$	0.066	0.051	0.062	0.084
$S = [\Sigma w(|F_0| - |F_c|)^2/(n-p)]^{1/2}$	1.336	1.275	1.541	2.107
Residual extrema in final difference map, e Å^{-3}	+0.35 to −0.21	+0.32 to −0.23	+0.34 to −0.50	+1.29 to −1.17

Table II.   Atomic coordinates ($\times 10^4$ for ordered atoms; $\times 10^3$ for disordered atoms)[a] and thermal parameters[b] ($\mathring{A}^2 \times 10^3$) of $(n\text{-}C_4H_9)N^+F^-\cdot 3(NH_2)_2CS$ (1)

Atom	x	y	z	U_{eq} or U
(i) Thiourea-fluoride lattice				
F	0	1844(2)	0	75(1)*
S(1)	1417(1)	−580(1)	1692(1)	73(1)*
C(1)	−998(5)	309(4)	1162(3)	65(2)*
N(1)	43(4)	657(4)	1360(4)	88(2)*
H(N1A)	266	1150	1047	108
H(N1B)	579	417	1817	108
N(2)	−1686(5)	672(4)	529(3)	83(2)*
H(N2A)	−1420	1165	237	102
H(N2B)	−2454	444	359	102
S(2)	119(1)	5352(1)	244(1)	75(1)*
C(2)	74(4)	4159(4)	132(3)	60(2)*
N(3)	911(4)	3624(3)	505(3)	79(2)*
H(N3A)	874	2958	423	95
H(N3B)	1562	3897	861	95
N(4)	−792(4)	3728(3)	−348(3)	71(2)*
H(N4A)	−782	3059	−406	87
H(N4B)	−1430	4085	−673	87
S(3)	1953(2)	−183(1)	−1712(1)	86(1)*
C(3)	1359(5)	532(3)	−1128(3)	65(2)*
N(5)	1969(5)	839(3)	−423(3)	85(2)*
H(N5A)	1625	1251	−104	89
H(N5B)	2749	646	−239	89
N(6)	299(4)	824(3)	−1341(3)	73(2)*
H(N6A)	−1	1236	−997	104
H(N6B)	−177	626	−1839	104
(ii) Tetra-n-butylammonium ion				
N(7)	1766(4)	3586(3)	−2059(2)	61(1)*
C(4)	2506(5)	3312(4)	−1260(3)	77(2)*
C(5)	3716(7)	3623(6)	−1065(5)	105(3)*
C(6)	4349(8)	3156(9)	−234(6)	143(5)*
C(7)	5501(10)	3483(12)	49(9)	200(8)*
C(8)	2248(5)	3212(3)	−2745(3)	65(2)*
C(9)	2368(6)	2163(4)	−2775(4)	82(2)*
C(10)	3059(7)	1891(5)	−3382(5)	100(3)*
C(11)	3129(10)	877(6)	−3477(6)	141(5)*
C(12)	601(4)	3180(3)	−2081(3)	62(2)*
C(13)	−295(5)	3327(4)	−2831(3)	73(2)*
C(14)	−1460(5)	3029(4)	−2689(4)	82(2)*
C(15)	−2381(6)	3144(5)	−3418(5)	99(3)*
C(16)	1695(6)	4651(4)	−2165(4)	79(2)*
C(17)	1147(11)	5178(5)	−1581(6)	134(5)*
C(18A)	133(4)	619(1)	−190(2)	216(15)
C(18B)	78(2)	621(1)	−185(1)	137(7)
C(19A)	115(4)	701(3)	−142(2)	248(16)
C(19B)	197(2)	650(2)	−146(1)	136(6)

[a] Atoms C(18A), C(18B), C(19A) and C(19B) each has a site occupancy factor of 1/2.
[b] Asterisk indicates 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 $-8\pi^2 U \sin^2 \theta / \lambda^2$.
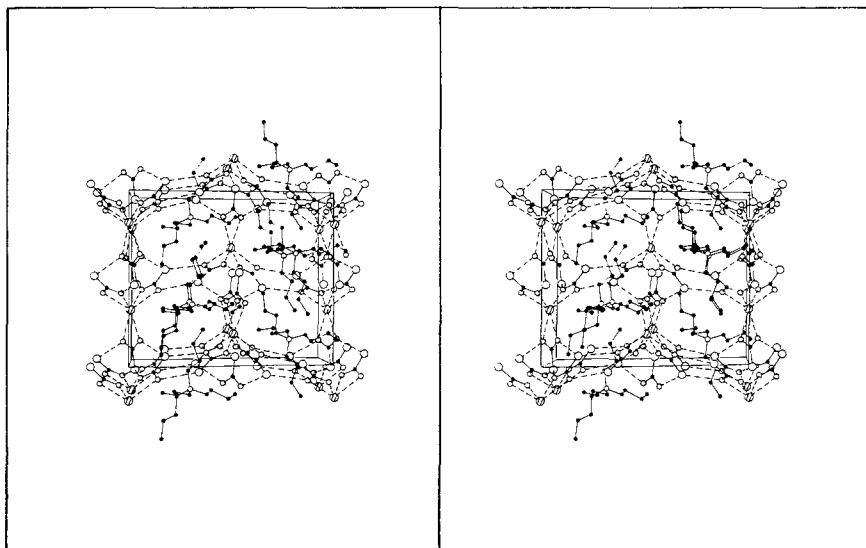
Fig. 2. Stereo drawing of the crystal structure of **1**. The origin of the unit cell lies at the upper left corner, with *a* pointing towards the reader, *b* downwards, and *c* from left to right. Broken lines represent hydrogen bonds, and atom types are distinguished by size and shading in all stereo drawings.
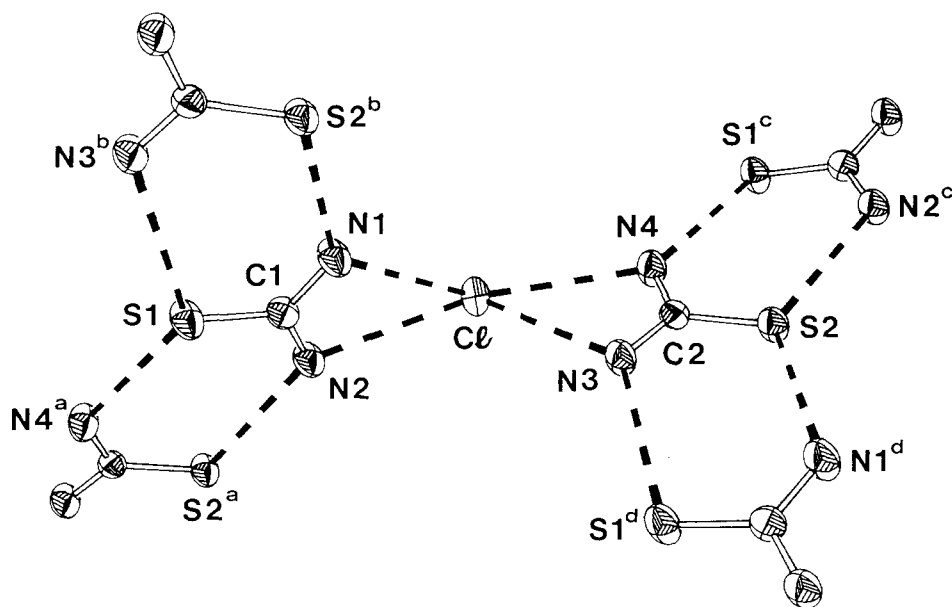

Fig. 3. Perspective view of a portion of the thiourea–chloride lattice in $(n\text{-}C_4H_9)_3(CH_3)N^+Cl^- \cdot$ $2(NH_2)_2CS$ (**2**). The thermal ellipsoids are drawn at the 30% probability level. The atom labels correspond to those given in Tables III and V. Symmetry transformations: $^a -\frac{1}{2} + x, 1\frac{1}{2} - y, -\frac{1}{2} + z$; $^b x,$ $2 - y, -\frac{1}{2} + z$; $^c \frac{1}{2} + x, 1\frac{1}{2} - y, \frac{1}{2} + z$; $^d x, 2 - y, \frac{1}{2} + z$.

Table III.   Atomic coordinates ($\times 10^5$ for Br; $\times 10^4$ for other atoms) and thermal parameters[a] ($\text{Å} \times 10^4$ for Cl and Br; $\times 10^3$ for other atoms) of $(n\text{-}C_4H_9)_3(CH_3)N^+X^-\cdot2(NH_2)_2CS$ (X = Cl, **2**; X = Br, **3**)

Atom	Complex **2** (X = Cl)				Complex **3** (X = Br)			
	x	y	z	U_{eq} or U	x	y	z	U_{eq} or U
(i) Thiourea-halide lattice								
X	0	6994(1)	0	752(4)*	0	68806(6)	0	715(2)*
S(1)	−1721(1)	9331(1)	−2550(1)	71(1)*	−1768(2)	9313(2)	−2562(1)	72(1)*
C(1)	−1194(3)	8622(3)	−1748(2)	55(1)*	−1260(5)	8591(6)	−1776(4)	55(2)*
N(1)	−249(3)	8915(3)	−1460(2)	74(1)*	−349(5)	8886(6)	−1496(4)	75(2)*
H(N1A)	20	8515	−1023	89	−94	8490	−1064	84
H(N1B)	130	9517	−1699	89	39	9481	−1737	84
N(2)	−1694(3)	7751(3)	−1375(2)	67(1)*	−1784(5)	7732(6)	−1399(4)	68(2)*
H(N2A)	−1389	7381	−940	80	−1498	7360	−969	82
H(H2B)	−2345	7514	−1550	80	−2430	7504	−1569	82
S(2)	1153(1)	8705(1)	2933(1)	61(1)*	1111(1)	8749(2)	2929(1)	61(1)*
C(2)	799(3)	8190(3)	2009(2)	49(1)*	759(5)	8214(5)	2036(4)	54(2)*
N(3)	−24(2)	8656(3)	1625(2)	66(1)*	−52(4)	8659(6)	1651(3)	64(2)*
H(N3A)	−214	8367	1130	79	−222	8353	1166	76
H(N3B)	−401	9268	1855	79	−443	9268	1872	76
N(4)	1312(3)	7319(3)	1657(2)	68(1)*	1281(5)	7331(6)	1681(3)	68(2)*

H(N4A)	1101	7050	1162	82	1075	7061	1195	81
H(N4B)	1884	6977	1906	82	1849	6994	1918	81

(ii) Tri-*n*-butylmethylammonium ion

N(5)	3408(3)	1850(3)	3825(2)	70(1)*	3331(5)	1891(5)	3795(4)	68(2)*
C(3)	2971(5)	2421(5)	3074(3)	96(2)*	2906(9)	2498(8)	3080(6)	96(4)*
C(4)	4374(3)	1096(4)	3632(3)	81(2)*	4283(6)	1136(7)	3575(6)	78(3)*
C(5)	4255(4)	261(4)	2920(3)	88(2)*	4144(7)	289(8)	2867(6)	89(3)*
C(6)	5233(5)	-452(5)	2805(4)	110(2)*	5101(8)	-438(8)	2728(7)	111(4)*
C(7)	5186(7)	-1187(6)	2065(5)	138(3)*	5031(13)	-1167(11)	2014(8)	145(6)*
C(8)	2559(3)	1070(4)	4178(3)	68(1)*	2466(5)	1124(7)	4153(5)	67(2)*
C(9)	2785(4)	498(4)	4974(3)	77(2)*	2680(7)	532(8)	4918(5)	82(3)*
C(10)	1907(5)	-313(5)	5203(4)	109(2)*	1812(10)	-278(10)	5177(7)	109(4)*
C(11)	2086(8)	-899(6)	5999(4)	151(4)*	1961(13)	-910(12)	5949(7)	139(6)*
C(12)	3745(4)	2859(4)	4388(3)	83(2)*	3696(7)	2851(8)	4347(6)	85(3)*
C(13)	2924(4)	3709(4)	4643(3)	95(2)*	2880(7)	3730(8)	4621(6)	85(3)*
C(14)	3316(5)	4625(5)	5237(4)	101(2)*	3310(9)	4578(9)	5233(6)	97(4)*
C(15)	2491(5)	5492(5)	5480(4)	103(2)*	2490(10)	5493(8)	5532(6)	105(4)*

[a] Asterisk indicates 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 ($\times 10^5$ for I; $\times 10^4$ for other atoms) and thermal parameters[a] ($\text{Å}^2 \times 10^4$ for I; $\times 10^3$ for other atoms) of $(n\text{-}C_3H_7)_4N^+I^-\cdot(NH_2)_2CS$ (4)

Atom	x	y	z	U_{eq} or U
(i) Thiourea-iodide chain				
I	28936(6)	35097(3)	45042(3)	736(2)*
S	2445(2)	−495(1)	4989(1)	64(1)*
C(1)	2500(6)	659(4)	4774(4)	48(2)*
N(1)	3757(6)	1085(4)	4574(4)	59(2)*
H(N1A)	3743	1740	4446	72
H(N1B)	4683	740	4556	72
N(2)	1257(6)	1182(4)	4785(4)	68(2)*
H(N2A)	1302	1834	4652	76
H(N2B)	317	906	4926	76
(ii) Tetra-n-propylammonium ion				
N(3)	2154(5)	1742(3)	1590(3)	43(1)*
C(2)	1022(9)	2543(5)	1459(5)	82(3)*
C(3)	470(10)	3007(6)	2151(7)	101(4)*
C(4)	−367(13)	3886(7)	1960(6)	105(4)*
C(5)	1483(11)	1014(5)	2146(8)	115(5)*
C(6)	142(10)	594(7)	2032(8)	119(5)*
C(7)	−403(12)	−63(6)	2655(7)	102(4)*
C(8)	2347(10)	1345(9)	711(5)	107(4)*
C(9)	3105(14)	1726(9)	69(7)	126(5)*
C(10)	3138(12)	1289(8)	−787(7)	106(4)*
C(11)	3626(9)	2076(9)	1976(6)	119(5)*
C(12)	4943(11)	1588(10)	2119(9)	153(7)*
C(13)	6297(10)	1947(9)	2564(9)	146(6)*

[a] Asterisk indicates 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 $-8\pi^2 U \sin^2\theta/\lambda^2$.
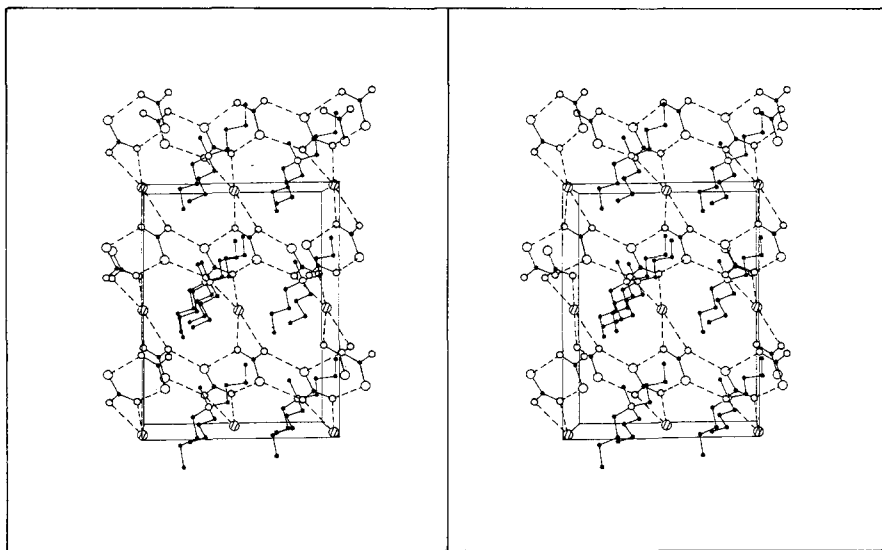

Fig. 4. Stereo drawing of the crystal structure of **2**. The origin of the unit cell lies at the upper left corner, with a pointing from left to right, b towards the reader, and c downwards.
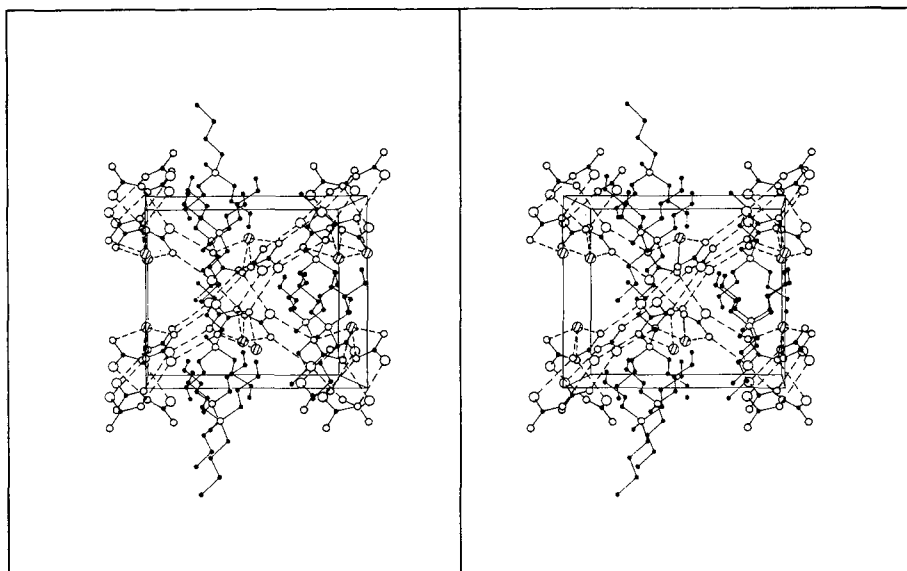
Fig. 5. Stereo drawing of the crystal structure of **3**. The origin of the unit cell lies at the lower left corner, with a pointing from left to right, b upwards, and c towards the reader.
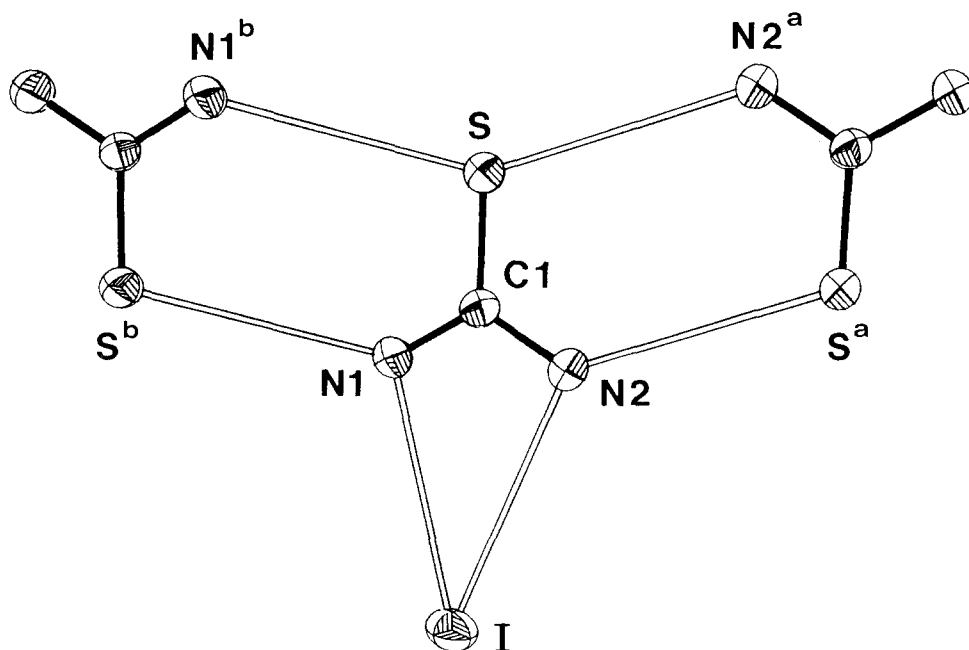

Fig. 6. Perspective view of a portion of the thiourea–iodide chain in $(n\text{-}C_3H_7)_4N^+I^-\cdot(NH_2)_2CS$ (**4**). The thermal ellipsoids are drawn at the 30% probability level. The atom labels correspond to those given in Tables IV and V. Symmetry transformations: [a] $-x, -y, 1-z$; [b] $1-x, -y, 1-z$.
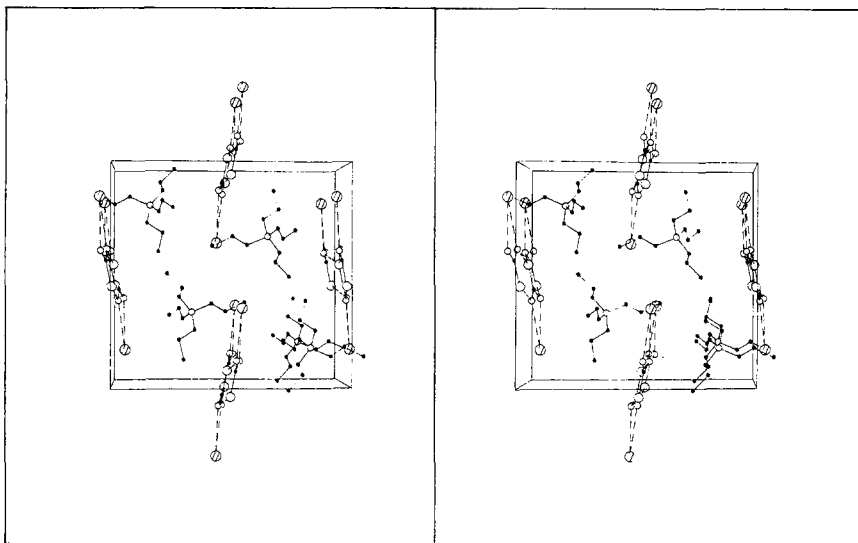
Fig. 7.   Stereo view of the crystal structure of **4**. The origin of the unit cell lies at the upper left corner, with *a* pointing towards the reader, *b* downwards, and *c* from left to right.

parallel to the [100] direction, with the iodide ions attached to it on both sides via N—H⋯I interactions. The crystal structure is built of a packing of these anionic composite ribbons and the tetrapropylammonium ions (Figure 7).

3.4. GENERAL STRUCTURAL FEATURES

The present series of complexes are characterized by ribbon-like arrangement of thiourea molecules alternately linked by pairs of N—H⋯S hydrogen bonds. The extent to which the ribbons in 1–4 deviate from planarity can be assessed by the measured values of the C—N⋯S—C torsion angle τ, which is zero for the idealized exactly planar zigzag configuration. The data in Table VI show that the ribbon in 1 has a twisted configuration, whereas those in the other complexes may be regarded as approximately planar. Every thiourea molecule forms an additional pair of donor hydrogen bonds with an adjacent halide ion in the manner of a bidentate chelate, and the number of such interactions per halide ion is faithfully reflected by the stoichiometry of the particular complex.

The bonding configuration at each of the N and S atoms is close to planar (Table VI), indicating that the NH_2 groups are favorably oriented for donor hydrogen bonding. The measured N⋯X distances increases monotonically from 1 to 4, but the N⋯S distances vary in the order 1 > thiourea > 4 > 3 > 2 (Table VI). The implication is that N—H⋯S bonding is quite weak in 1 but very strong in 2–4 in relation to orthorhombic thiourea [10] as a standard.* The N—H⋯F hydrogen

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* The three independent N⋯S distances in room-temperature orthorhombic thiourea (site symmetry *m*) are 3.397(3), 3.522(8) and 3.683(6) Å.

Table V.   Bond distances (Å) and selected bond angles (°) and torsion angles (°) in the anionic thiourea-halide systems[a]

$(n\text{-}C_4H_9)_4N^+F^-\cdot3(NH_2)_2CS$ (I)

(i) Urea molecules

C(1)—S(1)	1.702(6)	C(2)—S(2)	1.711(5)	C(3)—S(3)	1.697(6)
C(1)—N(1)	1.317(7)	C(2)—N(3)	1.310(7)	C(3)—N(5)	1.342(7)
C(1)—N(2)	1.317(7)	C(2)—N(4)	1.325(6)	C(5)—N(6)	1.311(8)
S(1)—C(1)—N(1)	121.4(4)	S(2)—C(2)—N(3)	121.5(4)	S(3)—C(3)—N(5)	120.9(5)
S(1)—C(1)—N(2)	122.0(4)	S(2)—C(2)—N(4)	122.2(4)	S(3)—C(3)—N(6)	122.6(4)
N(1)—C(1)—N(2)	166.6(5)	N(3)—C(2)—N(4)	116.3(5)	N(5)—C(3)—N(6)	116.5(5)

(ii) Thiourea-fluoride hydrogen-bonded interactions

F···N(1)	2.880(6)	F···N(3)	2.823(5)	F···N(6)	2.994(7)
F···N(2)	2.926(6)	F···N(4)	2.868(5)	F···N(6)	2.819(5)
N(1)···F···N(2)	45.4(1)	N(3)···F···N(4)	46.3(1)	N(5)···F···N(6)	45.5(1)
N(1)···F···N(3)	110.1(2)	N(3)···F···N(5)	103.5(2)	N(5)···F···N(1)	92.6(2)
N(2)···F···N(4)	112.3(2)	N(4)···F···N(6)	114.2(1)	N(6)···F···N(2)	100.7(2)
F···N(1)···S(3)[a]	137.8(3)	F···N(3)···S(1)[c]	134.2(3)	F···N(5)···S(2)[e]	144.1(3)
F···N(2)···S(2)[b]	141.4(3)	F···N(4)···S(3)[d]	136.2(3)	F···N(6)···S(1)[f]	132.5(3)

(iii) Hydrogen bonding between thiourea molecules (e.s.d.s of bond distances, bond angles and torsion angles are 0.007 Å, 0.4° and 0.5°, respectively)

N(1)···S(3)[a]	3.647	N(3)···S(1)[c]	3.579	N(5)···S(2)	3.764
N(2)···S(2)[b]	3.787	N(4)···S(3)[d]	3.521	N(6)···S(1)[f]	3.561
C(1)—N(1)···S(3)[a]	122.0	C(2)—N(3)···S(1)[c]	125.8	C(3)—N(5)···S(2)[e]	121.5
C(1)—N(1)···S(2)[b]	119.2	C(2)—N(4)···S(3)[d]	126.0	C(3)—N(6)···S(1)[f]	123.5
C(1)—S(1)···N(6)[a]	113.8	C(2)—S(2)···N(2)[c]	98.0	C(3)—S(3)···N(4)[e]	103.5
C(1)—S(1)···N(3)[b]	105.4	C(2)—S(2)···N(5)[d]	98.3	C(3)—S(3)···N(1)[f]	112.8
C(1)—N(1)···S(3)[a]—C(3)[a]	0.9	C(1)—S(1)···N(6)[a]—C(3)[a]	−24.1		
C(1)—N(2)···S(2)[b]—C(2)[b]	−64.8	C(1)—S(1)···N(3)[b]—C(2)[b]	−43.7		

Table V.   (continued)

$(n\text{-}C_4H_9)_3(CH_3)N^+X^-\cdot 2(NH_2)_2CS$
(iv) Urea molecules

	2 (X = Cl)	3 (X = Br)
C(1)—S(1)	1.692(4)	1.695(7)
C(1)—N(1)	1.338(5)	1.314(9)
C(1)—N(2)	1.320(5)	1.328(9)
S(1)—C(1)—N(1)	121.7(3)	121.6(5)
S(1)—C(1)—N(2)	121.7(3)	121.3(5)
N(1)—C(1)—N(2)	116.7(3)	117.1(6)
C(2)—S(2)	1.709(3)	1.696(7)
C(2)—N(3)	1.333(5)	1.335(9)
C(2)—N(4)	1.312(5)	1.327(9)
S(2)—C(2)—N(3)	120.5(3)	121.9(5)
S(2)—C(2)—N(4)	121.7(3)	121.6(5)
N(3)—C(2)—N(4)	117.8(3)	116.6(5)

(v) Thiourea-halide hydrogen-bonded interactions

X···N(1)	3.258(4)	3.413(7)
X···N(2)	3.257(3)	3.459(6)
X···N(3)	3.291(3)	3.427(6)
X···N(4)	3.252(3)	3.353(6)
N(1)···X···N(2)	40.6(1)	38.3(1)
N(3)···X···N(4)	40.5(1)	39.0(1)
N(1)···X···N(4)	128.0(1)	127.3(2)
N(2)···X···N(3)	115.5(1)	113.4(1)
N(1)···X···N(3)	104.8(1)	103.2(2)
N(2)···X···N(4)	155.5(1)	151.9(2)
X···N(1)···S(2)[b]	133.9(2)	130.3(3)
X···N(2)···S(2)[a]	130.7(2)	129.9(3)
X···N(3)···S(1)[d]	135.5(2)	134.8(3)
X···N(4)···S(1)[c]	130.8(2)	128.4(3)

(vi) Hydrogen bonding between thiourea molecules (e.s.d.s of bond distances, bond angles and torsion angles are 0.004, 0.2° and 0.4° for **2**, 0.008 Å, 0.4° and 0.6° for **3**, respectively)

N(1)···S(2)[b]	3.355	3.367
S(1)···N(3)[b]	3.419	3.414
N(2)···S(2)[a]	3.389	3.384
S(1)···N(4)[a]	3.373	3.377
C(1)—N(1)···S(2)[b]	124.5	126.0
C(1)—S(1)···N(3)[b]	112.0	111.4
C(1)—N(2)···S(2)[a]	125.7	126.3
C(1)—S(1)···N(4)[a]	110.5	109.9
C(2)—N(3)···S(1)[d]	124.1	124.1
C(2)—S(2)···N(1)[d]	113.6	112.2
C(2)—N(4)···S(1)[c]	126.7	127.0
C(2)—S(2)···N(2)[c]	111.0	110.9
C(1)—N(1)···S(2)[b]—C(2)[b]	-21.5	-18.8
C(1)—S(1)···N(3)[b]—C(2)[b]	-20.3	-19.5
C(1)—N(2)···S(2)[a]—C(2)[a]	1.5	-2.2
C(1)—S(1)···N(4)[a]—C(2)[a]	18.6	18.6

$(n\text{-}C_3H_7)_4N^+ I^- \cdot (NH_2)_2CS$ (**4**)

(vii) Urea molecule

C(1)—S	1.690(6)	C(1)—N(1)	1.325(8)	C(1)—N(2)	1.334(8)
S—C(1)—N(1)	122.3(4)	S—C(1)—N(2)	120.9(5)	N(1)—C(1)—N(2)	116.8(5)

(viii) Thiourea-iodide interactions

I···N(1)	3.564(5)	I···N(1)···S[b]	116.4(4)	N(1)···I···N(2)	36.4(3)
I···N(2)	3.680(5)	I···N(2)···S[a]	130.8(4)		

(ix) Hydrogen bonding between thiourea molecules (e.s.d.s of bond distances, bond angles and torsion angles are 0.006°, 0.3° and 0.6°, respectively)

N(1)···S[b]	3.490	C(1)—N(1)···S[b]	131.1	C(1)—S···N(1)[b]	103.6
N(2)···S[a]	3.464	C(1)—N(2)···S[a]	129.0	C(1)—S···N(2)[a]	109.8
C(1)—N(1)···S[b]—C(1)[b]	19.8	C(1)—N(2)···S[a]—C(1)[a]	6.3		

[a] Symmetry transformations for compounds **1**, **2** and **3**, and **4** are given in the legends for Figures 1, 3, and 6, respectively.

Table VI. Structural parameters of thiourea–thiourea and thiourea-halide interactions[a]

Compound	N···S (Å)	N···X (Å)	$|\tau|$ (°)	Σ_N (°)	Σ_S (°)
1	3.521(7)—3.787(7)	2.819(5)—2.994(7)	0.9—64.8	358.5—360.0	355.5—359.0
2	3.355(4)—3.419(4)	3.252(3)—3.291(3)	1.5—21.5	358.0—358.6	354.5—359.6
3	3.367(8)—3.414(8)	3.353(6)—3.459(6)	2.2—19.5	357.1—359.8	354.9—359.9
4	3.464(6)—3.490(6)	3.564(5)—3.680(5)	6.3—19.8	353.5—360.0	358.3

[a] τ is the C—N···S—C torsion angle. Σ_A is the sum of the bond angles at atom A, including hydrogen bonds but neglecting the H atoms.

bonding is concomitantly strong, so that to a good approximation the crystal structure of **1** can be described as a packing of $(n\text{-}C_4H_9)_4N^+$ ions and quasi-isolated $\{SC(NH_2)_2\}_3F^-$ units of trigonal-prismatic geometry [2].

The crystal structures of **1–4** can be rationalized in terms of the hydrophobic nature of thiourea, which favors direct bridging of the thiourea ribbons by halide ions. In contrast to this, the complexes of tetraalkylammonium salts with urea are generally hydrated [11], so that both halide ions and water molecules partake in bridging the analogous urea ribbons to generate an anionic lattice [1].

Acknowledgement

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