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Inclusion Compounds of Thiourea and Peralkylated Ammonium Salts. VI. Hydrogen-Bonded Host Lattices Constructed From Thiourea and Anions of Oxalic Acid and Fumaric Acid

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Abstract

New inclusion complexes tetra-*n*-butylammonium hydrogen oxalate–thiourea (1/2), $(n\text{-}C_4H_9)_4N^+.HC_2O_4^-.2[(NH_2)_2CS]$ (1), tetramethylammonium hydrogen fumarate–thiourea (1/1), $(CH_3)_4N^+.HC_4H_2O_4^-.(NH_2)_2CS$ (2), di(tetraethylammonium) fumarate–thiourea (1/2), $[(C_2H_5)_4N^+]_2.C_4H_2O_4^{2-}.2[(NH_2)_2CS]$ (3) and tetra-*n*-propylammonium hydrogen fumarate–thiourea–water (1/1/2), $(n\text{-}C_3H_7)_4N^+.HC_4H_2O_4^-.(NH_2)_2CS.2H_2O$ (4) have been prepared and characterized by X-ray crystallography. Crystal data, Mo $K\alpha$ radiation: (1), space group $P2_1/n$, $a = 8.854\,(6)$, $b = 9.992\,(3)$, $c = 32.04\,(2)$ Å, $\beta = 97.34\,(3)°$, $Z = 4$, $R_F = 0.055$ for 2261 observed data; (2), space group $P\bar{1}$, $a = 6.269\,(2)$, $b = 8.118\,(4)$, $c = 14.562\,(8)$ Å, $\alpha = 104.79\,(4)$, $\beta = 91.72\,(4)$, $\gamma = 101.30\,(4)°$, $Z = 2$, $R_F = 0.078$ for 1543 observed data; (3), space group $P2_1/n$, $a = 11.340\,(2)$, $b = 9.293\,(6)$, $c = 14.619\,(2)$ Å, $\beta = 102.41\,(2)°$, $Z = 2$, $R_F = 0.050$ for 1856 observed data; (4), space group $P2/n$, $a = 16.866\,(4)$, $b = 8.311\,(1)$, $c = 17.603\,(2)$ Å, $\beta = 104.94\,(1)°$, $Z = 4$, $R_F = 0.048$ for 2785 observed data. In the crystal structure of (1) the tetra-*n*-butylammonium ions are sandwiched between puckered layers, which are constructed from thiourea–hydrogen oxalate ribbons. In the crystal structure of (2), zigzag O—H···O and C—H···O hydrogen-bonded hydrogen fumarate ribbons are linked by thiourea dimers to form a wide puckered ribbon and the crystal structure is built of a packing of these thiourea–anion composite ribbons and the cationic columns. In the layer-type crystal structure of (3) a series of thiourea–fumarate layers match the (002) planes and the $(C_2H_5)_4N^+$ cations occupy the intervening space. In the crystal structure of (4) the thiourea, hydrogen fumarate ions and water molecules are connected by hydrogen bonds to form wide puckered ribbons, which are crosslinked to generate a three-dimensional host framework containing open channels aligned parallel to the *a* axis, with the tetra-*n*-propylammonium cations accommodated in a single column within each channel.

1. Introduction

Thiourea adducts crystallize in several space groups in two crystal systems: rhombohedral $R\bar{3}2/c$ (Lenné, 1954), $R3c$ (Schlenk, 1951), $R\bar{3}c$ (Hough & Nicholson, 1978; Harris & Thomas, 1990), $R\bar{3}$ (Fait, Fitzgerald, Caughlan & McCandless, 1991) and monoclinic $P2_1/a$ (Nicolaides & Laves, 1965; Chatani & Nakatani, 1976; Garneau, Raymond & Brisse, 1995). In the last space group the adducts exist only at reduced temperatures, except for those containing squalene or aromatic guests (Clement, Jegoudez & Mazieres, 1974). In this type of classical inclusion compound the host structure is built of thiourea molecules in an extensively hydrogen-bonded lattice, which contains parallel channels or tunnels with a free diameter of *ca* 6.1 Å, which can accommodate a variety of guest species, such as single-ring aromatics, cyclohexane and some of its derivatives (Schofield, Harris, Shannon & Rennie, 1993), ferrocene and other organometallics (Anderson, Calabrese, Tam & Williams, 1987), as well as fragments of polymers containing either phenyl groups or sugar rings (Tonelli, 1992).

This work arises from our systematic study on the generation of new host lattices by the combined use of thiourea and various molecular anions as the building blocks. The crystal structures of thiourea–bicarbonate (Li & Mak, 1995) and nitrate (Li & Mak, 1996*a*) complexes have been reported by us recently. Some monocarboxylic acid radicals, such as HCO_2^- (Li & Mak, 1996*b*) and $CH_3CO_2^-$ (Li & Mak, 1996*c*), have also been used in our series of studies.

α-Oxalic acid crystallizes in space group *Pbca* (Derissen & Smit, 1974), in which the molecules are interlinked by O—H···O bonds in the catemer motif to generate a *bc* hydrogen-bonded layer. On the other hand, the β form of oxalic acid belongs to space group $P2_1/c$ (Derissen & Smit, 1974) with hydrogen-bonded chains running parallel to the *a* axis. The available structural data show that the C—C bonds in oxalic acid and the oxalate ion are both significantly longer than the normal C—C single bond in aliphatic compounds.

Fumaric acid is dimorphic [$P\bar{1}$, $Z = 1$; $P2_1/c$, $Z = 6$ (Bednowitz & Post, 1966; Brown, 1966)] and the molecules are arranged in layers in its two crystal forms. Moreover, these layers are isostructural, being related by 2_1 axes in the monoclinic structure and by translation in the triclinic structure. Since intramolecular forces favor the synplanar C═C—C═O conformer, the antiplanar C═C—C═O conformation of fumaric acid must be due primarily to intralayer, *i.e.* C—H···O(carbonyl), interaction. An atom–atom potential analysis of the packing characteristics of fumaric acid indicated that the C—H···O(carbonyl) interaction plays an important role in stabilizing the observed layer structure (Berkovitch-Yellin & Leiserowitz, 1982).

In the rational design of new thiourea–anion lattices that can accommodate peralkylated ammonium cations of different sizes, we consider the oxalate and fumarate ions each containing two carboxyl groups which can easily form O···H—N hydrogen bonds with thiourea molecules. In the present work, we report the preparation and structural characterization of the following complexes that contain new types of thiourea–anion host lattices

$$(n\text{-}C_4H_9)_4N^+.HC_2O_4^-.2[(NH_2)_2CS] \qquad (1)$$

$$(CH_3)_4N^+.HC_4H_2O_4^-.(NH_2)_2CS \qquad (2)$$

$$[(C_2H_5)_4N^+]_2.C_4H_2O_4^{2-}.2[(NH_2)_2CS] \qquad (3)$$

$$(n\text{-}C_3H_7)_4N^+.HC_4H_2O_4^-.(NH_2)_2CS.2H_2O. \qquad (4)$$

2. Experimental

Tetramethylammonium hydroxide pentahydrate (99%) and tetra-*n*-butylammonium hydroxide (1 *M* in methanol) were obtained from Aldrich and tetraethylammonium hydroxide (25% wt aqueous solution) was obtained from Eastman Kodak, whereas tetra-*n*-propylammonium hydroxide was prepared from its chloride salt by reaction with moist silver(I) oxide (Morrison & Boyd, 1992).

Each hydroxide and thiourea were mixed in molar ratios of 1:3, 1:2, 1:2.5 and 1:3 for (1), (2), (3) and (4), respectively. A minimum quantity of water was used to dissolve the solid in each case and crystalline oxalic acid was added to the solution in a 1:1 hydroxide:acid molar ratio for (1); crystalline fumarate acid was added in a similar manner for (2), (3) and (4). After stirring for ~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 [(3)] and small blocks [(1), (2) and (4)].

Information concerning crystallographic data and structure refinement of the four compounds is summarized in Table 1. Intensities were collected in the variable ω-scan technique (Sparks, 1976) on a Siemens *R3m/V* diffractometer using Mo $K\alpha$ radiation (λ = 0.71073 Å) at 291 K. The raw data were processed with a learnt-profile procedure (Kopfmann & Huber, 1968) and an empirical absorption correction based on ψ-scan data was also applied.

All calculations were performed on a PC 486 computer with the *SHELXTL-Plus* program package (Sheldrick, 1982). Direct methods yielded the positions of all non-H atoms. The thioamido, methylene and methyl H atoms were generated geometrically (C—H fixed at 0.96, N—H at 0.90 Å) and allowed to ride on their respective parent atoms. The $(CH_3)_4N^+$ cation in (2) exhibits twofold orientational disorder and the scattering power of the methyl groups was represented by fractional C atoms C(n) and C(n') (Table 3); the H atoms of the disorderd cation were not included in the structural model. All H 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 (*International Tables for X-ray Crystallography*, 1974, Vol. IV). Refinement of the coordinates and anisotropic thermal parameters of the non-H atoms was carried out by full-matrix least-squares and the final R indices and other parameters are listed in Table 1.

3. Results and discussion

The final positional and equivalent isotropic thermal parameters of (1) and (2)–(4) are listed in Tables 2 and 3, respectively.*

3.1. *Crystal structures of thiourea–oxalate inclusion compound* $(n\text{-}C_4H_9)_4N^+.HC_2O_4^-.2[(NH_2)_2CS]$ *(1)*

Compound (1) features a sandwich-like crystal structure built up from undulate layers (Fig. 1). In the thiourea–hydrogen oxalate layer structure, as shown in the hydrogen-bonding scheme (Fig. 2), the anions are interlinked by O—H···O hydrogen bonds to generate an infinite $(HC_2O_4)_\infty$ chain running parallel to the [010] direction. Although the O—H group of the hydrogen oxalate ion adopts a synplanar O=C—O—H conformation, the chain is not straight but a zigzag type in which successive oxalate moieties are alternately arranged left and right of the single O—H=O hydrogen bond between them. Within this chain all atoms are essentially co-planar, the torsion angle C(4^{ii})—O(3^{ii})···O(1)—C(3) being −171.1°, and the mean atomic deviation from the plane of two adjacent oxalate ions is 0.21 Å. Two independent thiourea molecules are linked by N—H···S hydrogen bonds in a head-to-tail mode to generate a dimer. These thiourea dimers together with the hydrogen oxalate chains form a broad, virtually unpuckered ribbon in which the thiourea molecule C(2) [composed of atoms S(2), C(2), N(3) and N(4)] fits an indent in the chain and forms four N—H···O hydrogen bonds with three adjacent hydrogen oxalate ions. Within this ribbon the other independent thiourea molecule C(1) [composed of S(1), C(1), N(1) and N(2)] forms one

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* Lists of atomic coordinates, anisotropic displacement parameters and structure factors have been deposited with the IUCr (Reference: HR0032). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Experimental details*

	(1)	(2)	(3)	(4)
Crystal data				
Chemical formula	$(C_4H_9)_4N^+.C_2HO_4^-$.-$2[CS(NH_2)_2]$	$(CH_3)_4N^+.C_4H_3O_4^-$.-$CS(NH_2)_2$	$2(C_2H_5)_4N^+.C_4H_2O_4^{2-}$.-$2[CS(NH_2)_2]$	$(C_3H_7)_4N^+.C_4H_3O_4^-$.-$CS(NH_2)_2.2H_2O$
Chemical formula weight	483.7	265.3	526.8	413.6
Cell setting	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$P2_1/n$	$P2/n$
a (Å)	8.854 (6)	6.269 (2)	11.340 (2)	16.866 (4)
b (Å)	9.992 (3)	8.118 (4)	9.293 (6)	8.311 (1)
c (Å)	32.04 (2)	14.562 (8)	14.619 (2)	17.603 (2)
α (°)		104.79 (4)		
β (°)	97.34 (3)	91.72 (4)	102.41 (1)	104.94 (1)
γ (°)		101.30 (4)		
V (Å^3)	2812 (3)	700.1 (4)	1504.5 (9)	2384.0 (9)
Z	4	2	2	4
D_x (Mg m^{-3})	1.143	1.259	1.163	1.152
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
No. of reflections for cell parameters	25	25	25	25
θ range (°)	6–14	6–14	6–14	6–14
μ (mm^{-1})	0.221	0.239	0.212	0.169
Temperature (K)	291	291	291	291
Crystal form	Block	Block	Plate	Block
Crystal size (mm)	0.50 × 0.45 × 0.42	0.38 × 0.32 × 0.22	0.62 × 0.60 × 0.40	0.42 × 0.36 × 0.32
Crystal color	Colorless	Colorless	Colorless	Colorless
Data collection				
Diffractometer	Siemens *R3m/V*	Siemens *R3m/V*	Siemens *R3m/V*	Siemens *R3m/V*
Data collection method	ω scans	ω scans	ω scans	ω scans
Absorption correction	ψ scan (Kopfmann & Huber, 1968)	ψ scan (Kopfmann & Huber, 1968)	ψ scan (Kopfmann & Huber, 1968)	ψ scan (Kopfmann & Huber, 1968)
$T_{\min}$	0.787	0.882	0.891	0.925
$T_{\max}$	0.856	0.987	1.000	0.959
No. of measured reflections	4225	2452	4665	3865
No. of independent reflections	3931	2222	2349	3728
No. of observed reflections	2261	1543	1856	2785
Criterion for observed reflections	$F_o>4\sigma(F_o)$	$F_o>4\sigma(F_o)$	$F_o>4\sigma(F_o)$	$F_o>4\sigma(F_o)$
$R_{\rm int}$	0.020	0.015	0.016	0.030
$\theta_{\max}$ (°)	25	25	25	25
Range of h, k, l	$0 \rightarrow h \rightarrow 9$ $0 \rightarrow k \rightarrow 11$ $-35 \rightarrow l \rightarrow 34$	$0 \rightarrow h \rightarrow 7$ $-9 \rightarrow k \rightarrow 9$ $-16 \rightarrow l \rightarrow 16$	$-12 \rightarrow h \rightarrow 12$ $0 \rightarrow k \rightarrow 10$ $-16 \rightarrow l \rightarrow 16$	$0 \rightarrow h \rightarrow 19$ $0 \rightarrow k \rightarrow 9$ $-20 \rightarrow l \rightarrow 19$
No. of standard reflections	3	2	3	3
Frequency of standard reflections	Every 97 reflections	Every 98 reflections	Every 97 reflections	Every 97 reflections
Intensity decay (%)	1.1	1.1	1.1	1.1
Refinement				
Refinement on	F	F	F	F
R	0.055	0.078	0.050	0.048
wR	0.056	0.089	0.057	0.057
S	1.63	1.41	1.11	1.72
No. of reflections used in refinement	2261	1543	1856	2785
No. of parameters used	281	195	154	245
H-atom treatment	See text	See text	See text	See text
Weighting scheme	$w = 1/[\sigma^2(F_o) + 0.0003\|F_o\|^2]$	$w = 1/[\sigma^2(F_o) + 0.00002\|F_o\|^2]$	$w = 1/[\sigma^2(F_o) + 0.00005\|F_o\|^2]$	$w = 1/[\sigma^2(F_o) + 0.0003\|F_o\|^2]$
$(\Delta/\sigma)_{\max}$	0.001	0.019	0.001	0.001
$\Delta\rho_{\max}$ (e Å^{-3})	0.33	0.67	0.65	0.17
$\Delta\rho_{\min}$ (e Å^{-3})	−0.26	−0.39	−0.20	−0.28
Extinction method	$F_{\rm corr} = F_c(1 + 0.002 \times \chi F_c^2/\sin 2\theta)^{-1/4}$	None	None	None
Extinction parameter	$\chi = 2.8 \times 10^{-4}$	–	–	–
Source of atomic scattering factors	*International Tables for X-ray Crystallography* (1974, Vol. IV)	*International Tables for X-ray Crystallography* (1974, Vol. IV)	*International Tables for X-ray Crystallography* (1974, Vol. IV)	*International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 2. *Fractional atomic coordinates and equivalent isotropic displacement parameters* ($Å^2$) *for (1)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Thiourea–oxalate host lattice				
S(1)	0.5495 (2)	0.6170 (1)	0.4422 (1)	0.058 (1)
C(1)	0.5306 (3)	0.4577 (3)	0.4246 (1)	0.047 (1)
N(1)	0.4913 (3)	0.3607 (3)	0.4495 (1)	0.078 (1)
N(2)	0.5525 (3)	0.4222 (3)	0.3857 (1)	0.062 (1)
S(2)	0.5450 (2)	0.0613 (1)	0.3940 (1)	0.076 (1)
C(2)	0.5960 (3)	−0.0329 (3)	0.3545 (1)	0.041 (1)
N(3)	0.6230 (3)	0.0206 (3)	0.3186 (1)	0.063 (1)
N(4)	0.6127 (3)	−0.1650 (3)	0.3587 (1)	0.051 (1)
C(3)	0.7156 (3)	0.5384 (3)	0.2871 (1)	0.049 (1)
C(4)	0.6900 (3)	0.3864 (3)	0.2794 (1)	0.053 (1)
O(1)	0.7696 (3)	0.5987 (2)	0.2584 (1)	0.093 (1)
O(2)	0.6855 (3)	0.5870 (2)	0.3198 (1)	0.070 (1)
O(3)	0.7311 (3)	0.3422 (2)	0.2446 (1)	0.071 (1)
O(4)	0.6357 (3)	0.3189 (2)	0.3049 (1)	0.081 (1)
Tetra-*n*-propylammonium ion				
N(5)	1.1075 (3)	0.8071 (3)	0.3862 (1)	0.056 (1)
C(5)	1.2066 (3)	0.8512 (3)	0.4262 (1)	0.056 (1)
C(6)	1.1200 (3)	0.9012 (3)	0.4609 (1)	0.075 (1)
C(7)	1.2310 (3)	0.9433 (3)	0.4989 (1)	0.075 (1)
C(8)	1.3070 (4)	1.0756 (3)	0.4939 (2)	0.094 (1)
C(9)	0.9978 (3)	0.6974 (3)	0.3953 (2)	0.069 (1)
C(10)	1.0684 (3)	0.5739 (3)	0.4171 (2)	0.079 (1)
C(11)	0.9496 (4)	0.4724 (3)	0.4233 (2)	0.098 (1)
C(12)	1.0103 (4)	0.3536 (3)	0.4481 (2)	0.132 (1)
C(13)	1.0125 (3)	0.9234 (3)	0.3663 (2)	0.068 (1)
C(14)	1.1004 (3)	1.0473 (3)	0.3575 (2)	0.086 (1)
C(15)	1.0028 (4)	1.1555 (3)	0.3386 (2)	0.110 (1)
C(16)	1.0893 (4)	1.2813 (3)	0.3293 (2)	0.134 (1)
C(17)	1.2181 (3)	0.7565 (3)	0.3572 (1)	0.064 (1)
C(18)	1.1501 (4)	0.6987 (3)	0.3154 (2)	0.095 (1)
C(19)	1.2743 (4)	0.6433 (4)	0.2918 (2)	0.134 (1)
C(20)	1.2268 (4)	0.5705 (4)	0.2560 (2)	0.178 (1)

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

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters* ($Å^2$) *for (2), (3) and (4)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
(i) $(CH_3)_4N^+.HC_4H_2O_4$.$(NH_2)_2CS$ (2)				
Thiourea–fumarate host lattice				
S(1)	1.2213 (2)	0.3264 (2)	0.4417 (1)	0.073 (1)
C(1)	1.0254 (5)	0.2842 (4)	0.3509 (3)	0.050 (1)
N(1)	0.8337 (4)	0.3268 (4)	0.3635 (2)	0.061 (1)
N(2)	1.0594 (4)	0.2045 (4)	0.2624 (2)	0.060 (1)
O(1)	0.5178 (4)	0.2394 (4)	0.1937 (2)	0.063 (1)
O(2)	0.7948 (4)	0.2262 (4)	0.1060 (2)	0.094 (1)
C(2)	0.6011 (5)	0.2380 (4)	0.1176 (3)	0.057 (1)
C(3)	0.4691 (5)	0.2496 (5)	0.0340 (3)	0.072 (1)
C(4)	0.2664 (5)	0.2411 (5)	0.0272 (3)	0.067 (1)
C(5)	0.1395 (5)	0.2466 (5)	−0.0593 (3)	0.080 (1)
O(3)	−0.0678 (4)	0.2348 (5)	−0.0540 (2)	0.135 (1)
O(4)	0.2217 (4)	0.2628 (5)	−0.1308 (2)	0.107 (1)
Tetramethylammonium ion				
N(3)	0.6313 (4)	0.2300 (4)	0.6910 (2)	0.069 (1)
C(6)	0.7031 (5)	0.3980 (5)	0.7777 (4)	0.097 (1)
C(7)	0.8432 (5)	0.2153 (5)	0.6476 (5)	0.111 (1)
C(8)	0.4410 (5)	0.2374 (5)	0.6327 (4)	0.150 (1)
C(9)	0.5778 (5)	0.0778 (5)	0.7391 (4)	0.072 (1)
C(6′)	0.5027 (5)	0.3788 (5)	0.6997 (5)	0.092 (1)
C(7′)	0.7471 (5)	0.2161 (5)	0.5959 (4)	0.094 (1)
C(8′)	0.7897 (6)	0.2595 (6)	0.7757 (4)	0.234 (1)
C(9′)	0.4608 (6)	0.0556 (5)	0.6775 (5)	0.166 (1)

Table 3. (*cont.*)

	x	y	z	U_{eq}
(ii) $[(C_2H_5)_4N^+]_2.C_4H_2O_4^{2-}$.$2(NH_2)_2CS$ (3)				
Thiourea–fumarate host lattice				
S(1)	0.3503 (1)	1.1832 (1)	−0.0413 (1)	0.060 (1)
C(1)	0.2846 (2)	1.0368 (3)	−0.0028 (2)	0.045 (1)
N(1)	0.1728 (2)	1.0417 (3)	0.0111 (2)	0.054 (1)
N(2)	0.3409 (2)	0.9111 (3)	0.0131 (2)	0.067 (1)
C(2)	0.0567 (3)	0.5141 (4)	0.0082 (2)	0.066 (1)
C(3)	0.1071 (3)	0.6658 (3)	0.0263 (2)	0.054 (1)
O(1)	0.0407 (2)	0.7756 (2)	0.0152 (2)	0.071 (1)
O(2)	0.2172 (2)	0.6691 (2)	0.0531 (2)	0.084 (1)
Tetraethylammonium ion				
N(3)	0.4998 (2)	0.5796 (3)	0.7818 (2)	0.052 (1)
C(4)	0.6334 (2)	0.5813 (4)	0.8265 (2)	0.062 (1)
C(5)	0.7166 (3)	0.5895 (5)	0.7599 (3)	0.092 (2)
C(6)	0.4635 (3)	0.7168 (4)	0.7252 (2)	0.067 (1)
C(7)	0.4879 (4)	0.8559 (4)	0.7783 (3)	0.089 (2)
C(8)	0.4340 (3)	0.5676 (4)	0.8609 (2)	0.064 (1)
C(9)	0.2998 (3)	0.5651 (6)	0.8334 (3)	0.100 (2)
C(10)	0.4692 (3)	0.4545 (4)	0.7140 (2)	0.067 (1)
C(11)	0.4988 (4)	0.3066 (4)	0.7548 (3)	0.083 (1)
(iii) $(n\text{-}C_3H_7)_4N^+.HC_4H_2O_4^-$.$(NH_2)_2CS.2H_2O$ (4)				
S(1)	0.4929 (1)	0.4321 (1)	0.3756 (1)	0.049 (1)
C(1)	0.4037 (2)	0.3573 (3)	0.3892 (2)	0.037 (1)
N(1)	0.3477 (1)	0.2928 (3)	0.3306 (1)	0.046 (1)
N(2)	0.3858 (1)	0.3654 (3)	0.4583 (1)	0.050 (1)
O(1)	0.5676 (1)	0.1015 (3)	0.0767 (1)	0.073 (1)
O(2)	0.6234 (1)	0.1767 (3)	0.1988 (1)	0.076 (1)
C(2)	0.5632 (2)	0.1515 (3)	0.1460 (2)	0.049 (1)
C(3)	0.4790 (2)	0.1777 (3)	0.1528 (2)	0.046 (1)
C(4)	0.4124 (2)	0.1506 (3)	0.0961 (2)	0.043 (1)
C(5)	0.3269 (2)	0.1862 (3)	0.1019 (2)	0.042 (1)
O(3)	0.2701 (1)	0.1696 (3)	0.0410 (1)	0.058 (1)
O(4)	0.3178 (1)	0.2296 (3)	0.1666 (1)	0.065 (1)
O(1*W*)	0.6651 (1)	0.2627 (3)	0.3602 (1)	0.074 (1)
O(2*W*)	0.7893 (1)	0.0739 (3)	0.4448 (1)	0.087 (1)
Tetra-*n*-propylammonium ion				
N(3)	1/4	0.3113 (3)	3/4	0.038 (1)
C(6)	0.2011 (2)	0.4212 (3)	0.6860 (1)	0.046 (1)
C(7)	0.1489 (2)	0.3402 (4)	0.6140 (2)	0.060 (1)
C(8)	0.1054 (3)	0.4633 (5)	0.5570 (2)	0.093 (2)
C(9)	0.3056 (2)	0.2014 (3)	0.7183 (2)	0.044 (1)
C(10)	0.3663 (2)	0.2820 (4)	0.6808 (2)	0.061 (1)
C(11)	0.4193 (2)	0.1584 (4)	0.6557 (2)	0.071 (1)
N(4)	1/4	−0.2267 (3)	1/4	0.037 (1)
C(12)	0.3008 (2)	−0.1183 (3)	0.3141 (2)	0.042 (1)
C(13)	0.3517 (2)	−0.2032 (3)	0.3859 (2)	0.058 (1)
C(14)	0.4013 (2)	−0.0846 (4)	0.4437 (2)	0.066 (1)
C(15)	0.3052 (2)	−0.3352 (3)	0.2167 (2)	0.046 (1)
C(16)	0.3606 (2)	−0.2491 (4)	0.1749 (2)	0.060 (1)
C(17)	0.4130 (2)	−0.3676 (5)	0.1455 (2)	0.088 (2)

The exponent of the isotropic displacement parameter takes the form $-8\pi^2 U \sin^2\theta/\lambda^2$. Atoms C(6)–C(9′) belong to a disordered tetramethylammonium ion in (2) with s.o.f. 0.602 for C(6)–C(9) and 0.398 for C(6′)–C(9′).

N—H···O donor hydrogen bond with a hydrogen oxalate anion and an additional S···H—N acceptor hydrogen bond with C(2) belonging to a neighboring thiourea dimer. In this wide, approximately planar thiourea–anion ribbon, the extent of deviation of its components from planarity can be seen from the relevant torsion angles: C(2^{ii})—N(3^{ii})···O(1)—C(3) = 36.2, C(1)—N(2)···O(2)—C(3) = 171.5 and C(2)—N(3)···O(4)—C(4) = 160.7°. With these thiourea–anion ribbons arranged side by side, pairs of inter-ribbon N—H···S hydrogen bonds are generated between C(1) molecules across inversion centers to build a two-dimensional infinite layer.

As shown in Fig. 1, the distance separating two adjacent thiourea–hydrogen oxalate layers is 7.703 Å and between them there is a layer composed of stacked columns of cations. The tetra-*n*-butylammonium cations $(n\text{-}C_4H_9)_4N^+$ are well ordered and have normal dimensions, except that one methyl group located at the end of an alkyl chain deviates from the idealized $\bar{4}2m$ (D_{2d}) conformation.

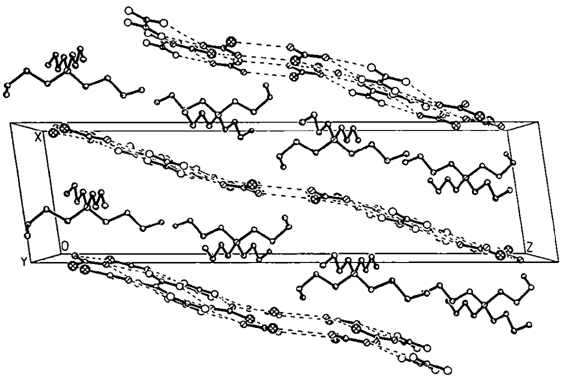

Fig. 1. Perspective view of the layer structure of $(n\text{-}C_4H_9)_4N^+.HC_2O_4^-.2[(NH_2)_2CS]$ (1). Dashed lines represent hydrogen bonds and atom types are distinguished by size and shading.

3.2. *Crystal structures of thiourea–fumarate inclusion compounds*

3.2.1. *Crystal structure of* $(CH_3)_4N^+.HC_4H_2O_4^-.(NH_2)_2CS$ *(2).* The atom labeling and hydrogen-bonding scheme for (2) are shown in Fig. 3. One carboxyl group of the hydrogen fumarate ion, $HC_4H_2O_4^-$, exhibits distinct carboxyl and carbonyl C—O bonds: C(5)—O(3) = 1.286 *versus* C(5)=O(4) = 1.207 Å. Unlike those in the crystal structure of the pure acid, the hydrogen fumarate ions are interlinked by a pair of C—H···O hydrogen bonds and a O—H···O hydrogen bond in the antiplanar O=C—O—H conformation, generating a co-planar $(HC_4H_2O_4^-)_\infty$ chain running parallel to the *a* axis. The lengths of these hydrogen bonds, C(3^{vi})···O(3) = 3.219, C(4^{vii})···O(2) = 3.195 and O(3^{vii})···O(2) = 2.522 Å, are slightly shorter than

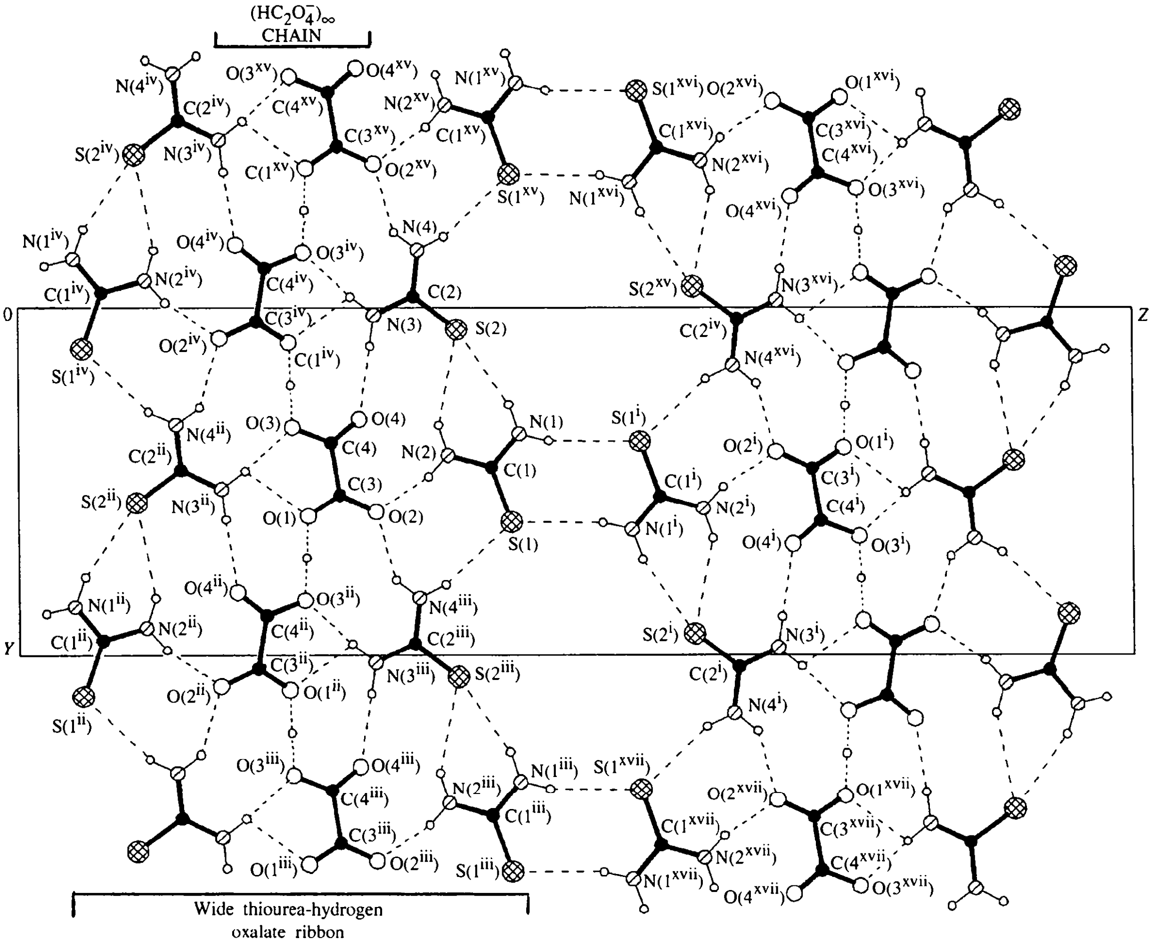

Fig. 2. Projection drawing of the thiourea–hydrogen oxalate anionic layer parallel to (100) in the crystal structure of (1). The atom labels correspond to those given in Tables 2 and 4. Dashed lines represent hydrogen bonds.

the average distances for both known crystalline forms of fumaric acid [C—H· · ·O = 3.44 and O—H· · ·O = 2.680 Å, respectively (Bednowitz & Post, 1966; Brown, 1966)]. The thiourea molecule together with its centrosymmetrically related partner are consolidated by a pair of N—H· · ·S hydrogen bonds to yield a cyclic dimer, in which there is an appreciable dihedral angle between the molecular planes, as shown by the torsion angle C(1^{v})—N(1^{v})· · ·S(1)—C(1) = 22.9°. The thiourea dimers located at inversion centers each crosslinks two hydrogen fumarate chains with three N—H· · ·O hydrogen bonds on each side, two in the synplanar and one in the antiplanar conformation, to generate a wide composite ribbon whose cross-section resembles the tilde symbol '∼', as shown in Fig. 4.

The $(CH_3)_4N^+$ cations are accommodated in a straight column and the crystal structure is built of a packing of thiourea–anion composite ribbons and cationic columns.

3.2.2. *Crystal structure of* $[(C_2H_5)_4N^+]_2.C_4H_2O_4^{2-}.2[(NH_2)_2CS]$ *(3).* Compound (3) features a sandwich-like crystal structure built up from undulate layers. The layer structure may be conveniently described with reference to the hydrogen-bonding scheme shown in Fig. 5 and Table 4. The fumarate dianion is located at a site of symmetry 1. The thiourea molecule together with its centrosymmetrically related partner are consolidated by a pair of N—H· · ·S hydrogen bonds to yield a cyclic dimer. Each thiourea molecule forms a pair of N—H· · ·O donor hydrogen bonds in the synplanar manner with one carboxylate group of the fumarate ion and also one antiplanar-type hydrogen bond with the carboxylate group that is related to the first one by inversion symmetry. The cyclic arrangement of four hydrogen bonds about one set of inversion centers generates a series of infinite thiourea–anion layers matching the (002) family of planes. For each layer the extent of deviation of its molecular components from planarity can be seen from the relevant torsion angles: C(1^{ix})—N(2^{ix})· · ·S(1)—C(1) = 14.0, C(1)—N(1)· · ·O(1)—C(3) = 16.6, C(1)—N(2)· · · O(2)—C(3) = 23.9 and C(1^{x})—N(1^{x})· · ·O(1)—C(3) = 24.1°.

The interlayer spacing of $c/2$ = 7.309 Å is slightly smaller than the corresponding values for a similar layer structure with tetraethylammonium cations accommodated in the thiourea–bicarbonate–water

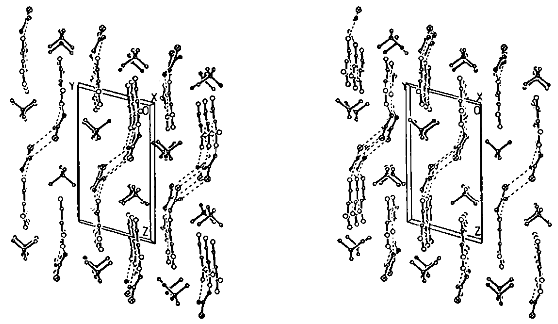

Fig. 4. Stereodrawing of the crystal structure of (2) showing the packing of $(CH_3)_4N^+$ ions between the wide ribbons. The origin of the unit cell lies at the upper right corner, with a towards the reader, b pointing from right to left and c downwards. Dashed lines represent hydrogen bonds and atom types are distinguished by size and shading.

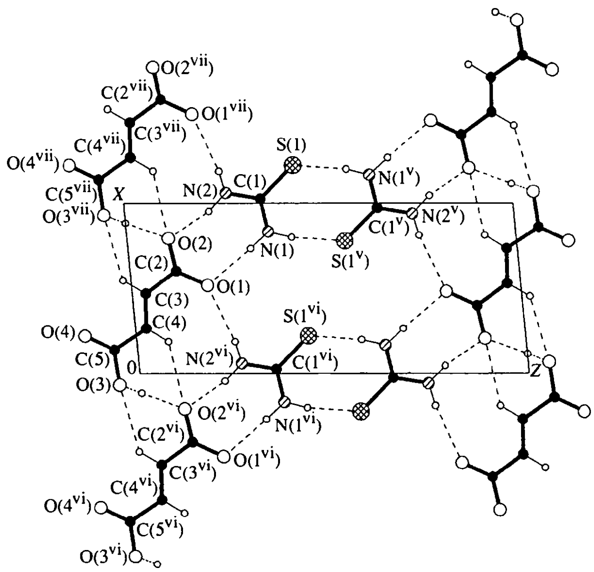

Fig. 3. The hydrogen-bonding scheme in a thiourea–fumarate wide ribbon in the crystal structure of $(CH_3)_4N^+.HC_4H_2O_4^-.(NH_2)_2CS$ (2). The atom labels correspond to those given in Tables 3 and 4. Dashed lines represent hydrogen bonds.

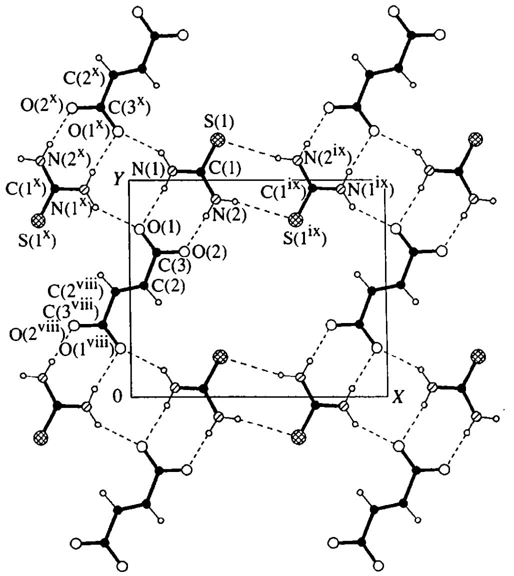

Fig. 5. Projection drawing of a hydrogen-bonded thiourea–acetate anionic layer parallel to (001) in $[(C_2H_5)_4N^+]_2.C_4H_2O_4^-.2[(NH_2)_2CS]$ (3). The atom labels correspond to those given in Tables 3 and 4. Dashed lines represent hydrogen bonds.

Table 4. *Selected bond distances (Å), angles (°) and torsion angles (°) in the thiourea–anionic systems*

$(n\text{-}C_4H_9)_4N^+.HC_2O_4^-.2[(NH_2)_2CS]$ (1)			
(i) Thiourea and hydrogen oxalic molecules			
S(1)—C(1)	1.690 (3)	C(1)—N(1)	1.329 (5)
C(1)—N(2)	1.335 (5)	S(2)—C(2)	1.686 (4)
C(2)—N(3)	1.315 (5)	C(2)—N(4)	1.334 (4)
C(3)—C(4)	1.551 (4)	C(3)—O(1)	1.245 (5)
C(3)—O(2)	1.214 (5)	C(4)—O(3)	1.292 (5)
C(4)—O(4)	1.206 (5)		
S(1)—C(1)—N(1)	120.6 (3)	S(1)—C(1)—N(2)	122.8 (3)
N(1)—C(1)—N(2)	116.6 (3)	S(2)—C(2)—N(3)	121.7 (2)
S(2)—C(2)—N(4)	120.8 (3)	N(3)—C(2)—N(4)	117.5 (3)
C(4)—C(3)—O(1)	114.7 (3)	C(4)—C(3)—O(2)	119.1 (3)
O(1)—C(3)—O(2)	126.2 (3)	C(3)—C(4)—O(3)	114.9 (3)
C(3)—C(4)—O(4)	120.2 (3)	O(3)—C(4)—O(4)	124.9 (3)
(ii) Hydrogen bonding			
$N(1^{i})\cdots S(1)$	3.540	$N(4^{iii})\cdots S(1)$	3.549
$N(1)\cdots S(2)$	3.544	$N(2)\cdots S(2)$	3.617
$O(3^{ii})\cdots O(1)$	2.436	$N(3^{ii})\cdots O(1)$	2.866
$N(2)\cdots O(2)$	3.033	$N(4^{iii})\cdots O(2)$	2.884
$N(3^{ii})\cdots O(3)$	3.103	$N(3)\cdots O(4)$	3.017
$N(1^{i})\cdots S(1)—C(1)$	111.6	$N(4^{iii})\cdots S(1)—C(1)$	110.2
$N(1^{i})\cdots S(1)\cdots N(4^{iii})$	138.2	$N(1)\cdots S(2)—C(2)$	156.2
$N(2)\cdots S(2)—C(2)$	119.5	$N(1)\cdots S(2)\cdots N(2)$	36.9
$O(3^{ii})\cdots O(1)—C(3)$	120.9	$N(2)\cdots O(2)—C(3)$	122.0
$N(4^{iii})\cdots O(2)—C(3)$	143.4	$N(3^{ii})\cdots O(3)—C(4)$	123.6
$N(3^{ii})\cdots O(3)\cdots O(1^{iv})$	123.1	$O(1^{iv})\cdots O(3)—C(4)$	112.1
$N(3)\cdots O(4)—C(4)$	132.7		
$C(1^{i})—N(1^{i})\cdots S(1)—C(1)$	−6.1	$C(1)—N(1)\cdots S(2)—C(2)$	3.3
$C(1)—N(2)\cdots S(2)—C(2)$	−170.3	$C(2^{ii})—N(3^{ii})\cdots O(1)—C(3)$	36.2
$C(4^{ii})—O(3^{ii})\cdots O(1)—C(3)$	−171.1	$C(1)—N(2)\cdots O(2)—C(3)$	171.5
$C(2)—N(3)\cdots O(4)—C(4)$	160.7		
$(CH_3)_4N^+.HC_4H_2O_4^-.(NH_2)_2CS$ (2)			
(i) Thiourea and hydrogen fumarate molecules			
S(1)—C(1)	1.697 (4)	C(1)—N(1)	1.320 (4)
C(1)—N(2)	1.329 (5)	O(1)—C(2)	1.237 (5)
O(2)—C(2)	1.249 (4)	C(2)—C(3)	1.486 (6)
C(3)—C(4)	1.258 (4)	C(4)—C(5)	1.484 (6)
C(5)—O(3)	1.291 (4)	C(5)—O(4)	1.201 (5)
S(1)—C(1)—N(1)	122.7 (3)	S(1)—C(1)—N(2)	120.7 (3)
N(1)—C(1)—N(2)	116.6 (3)	O(1)—C(2)—O(2)	123.4 (4)
O(1)—C(2)—C(3)	120.0 (3)	O(2)—C(2)—C(3)	116.6 (3)
C(2)—C(3)—C(4)	126.4 (4)	C(3)—C(4)—C(5)	124.6 (4)
C(4)—C(5)—O(3)	116.4 (4)	C(4)—C(5)—O(4)	123.0 (3)
O(3)—C(5)—O(4)	120.6 (4)		
(ii) Hydrogen bonding			
$N(1^{v})\cdots S(1)$	3.529	$N(1)\cdots O(1)$	2.966
$N(2^{vi})\cdots O(1)$	3.056	$N(2)\cdots O(2)$	2.839
$O(3^{vii})\cdots O(2)$	2.522	$C(4^{vii})\cdots O(2)$	3.195
$C(3^{vi})\cdots O(3)$	3.219		
$N(1^{v})\cdots S(1)—C(1)$	113.1	$N(1)\cdots O(1)—C(2)$	114.9
$N(2^{vi})\cdots O(1)—C(2)$	137.2	$N(2)\cdots O(2)—C(2)$	118.5
$O(3^{vii})\cdots O(2)—C(2)$	117.8	$C(4^{vii})\cdots O(2)—C(2)$	163.7
$N(2)\cdots O(2)—O(3^{vii})$	123.7	$N(2)\cdots O(2)\cdots C(4^{vii})$	76.9
$O(3^{vii})\cdots O(2)\cdots C(4^{vii})$	47.0	$C(3^{vi})\cdots O(3)—C(5)$	160.7
$C(3^{vi})\cdots O(3)\cdots O(2^{vi})$	45.9		
$C(1^{v})—N(1^{v})\cdots S(1)—C(1)$	22.9	$C(1)—N(1)\cdots O(1)—C(2)$	−29.8
$C(1)—N(2)\cdots O(2)—C(2)$	−31.5	$C(5^{vii})—O(3^{vii})\cdots O(2)—C(2)$	170.8
$[(C_2H_5)_4N^+]_2.C_4H_2O_4^{2-}.2[(NH_2)_2CS]$ (3)			
(i) Thiourea and fumarate molecules			
S(1)—C(1)	1.704 (3)	C(1)—N(1)	1.327 (3)
C(1)—N(2)	1.328 (4)	C(2)—C(3)	1.524 (4)
$C(2)—C(2^{viii})$	1.283 (6)	C(3)—O(1)	1.258 (4)
C(3)—O(2)	1.226 (4)		

Table 4 (*cont.*)

S(1)—C(1)—N(1)	121.6 (2)	S(1)—C(1)—N(2)	122.2 (2)
N(1)—C(1)—N(2)	116.2 (2)	C(3)—C(2)—C(2$^{\mathrm{viii}}$)	123.0 (4)
C(2)—C(3)—O(1)	122.4 (3)	C(2)—C(3)—O(2)	113.4 (3)
O(1)—C(3)—O(2)	124.2 (3)		
(ii) Hydrogen bonding			
N(2$^{\mathrm{ix}}$)···S(1)	3.547	N(1)···O(1)	2.899
N(1$^{\mathrm{x}}$)···O(1)	2.914	N(2)···O(2)	2.778
N(2$^{\mathrm{ix}}$)···S(1)—C(1)	104.8	N(1)···O(1)—C(3)	113.3
N(1$^{\mathrm{x}}$)···O(1)—C(3)	161.3	N(1)···O(1)···N(1$^{\mathrm{x}}$)	85.3
N(2)···O(2)—C(3)	118.6		
C(1$^{\mathrm{ix}}$)—N(2$^{\mathrm{ix}}$)···S(1)—C(1)	14.0	C(1)—N(1)···O(1)—C(3)	16.6
C(1$^{\mathrm{x}}$)—N(1$^{\mathrm{x}}$)···O(1)—C(3)	24.1	C(1)—N(2)···O(2)—C(3)	23.9
$(n\text{-}C_3H_7)_4N^+.HC_4H_2O_4^-.(NH_2)_2CS.2H_2O$ (4)			
(i) Thiourea and hydrogen fumarate molecules			
S(1)—C(1)	1.701 (3)	C(1)—N(1)	1.319 (3)
C(1)—N(2)	1.328 (4)	O(1)—C(2)	1.309 (4)
O(2) C(2)	1.205 (3)	C(2)—C(3)	1.471 (4)
C(3)—C(4)	1.316 (3)	C(4)—C(5)	1.502 (4)
C(5)—O(3)	1.247 (3)	C(5)—O(4)	1.241 (4)
S(1)—C(1)—N(1)	121.3 (2)	S(1)—C(1)—N(2)	121.8 (2)
N(1)—C(1)—N(2)	116.8 (2)	O(1)—C(2)—O(2)	122.3 (3)
O(1)—C(2)—C(3)	114.3 (2)	O(2)—C(2)—C(3)	123.4 (3)
C(2)—C(3)—C(4)	124.4 (3)	C(3)—C(4)—C(5)	124.2 (3)
C(4)—C(5)—O(3)	117.3 (2)	C(4)—C(5)—O(4)	117.9 (2)
O(3)—C(5)—O(4)	124.8 (3)		
(ii) Hydrogen bonding			
N(2$^{\mathrm{i}}$)···S(1)	3.533	O(1*W*)···S(1)	3.300
O(1$^{\mathrm{xi}}$)···O(2*W*)	2.547	O(1*W*)···O(2)	2.838
N(2$^{\mathrm{xii}}$)···O(3)	3.095	O(2W^{xiii})···O(3)	2.712
N(1)···O(4)	2.848	N(1$^{\mathrm{xii}}$)···O(4)	2.854
O(2*W*)···O(1*W*)	2.731		
N(2$^{\mathrm{i}}$)···S(1)—C(1)	113.7	O(1*W*)···S(1)—C(1)	133.2
N(2$^{\mathrm{i}}$)···S(1)···O(1*W*)	86.4	O(1*W*)···O(2)—C(2)	139.3
N(2$^{\mathrm{xii}}$)···O(3)—C(5)	113.8	O(2W^{xiii})···O(3)—C(5)	115.5
N(2$^{\mathrm{xii}}$)···O(3)···O(2W^{xiii})	129.3	N(1)···O(4)—C(5)	162.2
N(1$^{\mathrm{xii}}$)···O(4)—C(5)	115.0	N(1)···O(4)···N(1$^{\mathrm{xii}}$)	82.3
O(2*W*)···O(1*W*)···O(2)	111.0	C(2)—O(1)···O(2W^{xi})	116.8
O(1$^{\mathrm{xi}}$)···O(2*W*)···O(3$^{\mathrm{xiv}}$)	115.5		
C(1$^{\mathrm{i}}$)—N(2$^{\mathrm{i}}$)···S(1)—C(1)	4.9	C(1$^{\mathrm{xii}}$)—N(1$^{\mathrm{xii}}$)···O(4)—C(5)	−35.7
C(1$^{\mathrm{xii}}$)—N(2$^{\mathrm{xii}}$)···O(3)—C(5)	−42.6	C(1)—N(1)···O(4)—C(5)	47.5

Symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $\frac{3}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; (iii) $x, 1+y, z$; (iv) $\frac{3}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$; (v) $2-x, 1-y, 1-z$; (vi) $x-1, y, z$; (vii) $1+x, y, z$; (viii) $-x, 1-y, -z$; (ix) $1-x, 2-y, -z$; (x) $-x, 2-y, -z$; (xi) $\frac{3}{2}-x, y, \frac{1}{2}-z$; (xii) $\frac{1}{2}-x, y, \frac{1}{2}-z$; (xiii) $x-\frac{1}{2}, -y, z-\frac{1}{2}$; (xiv) $\frac{1}{2}+x, -y, \frac{1}{2}+z$; (xv) $x, y-1, z$; (xvi) $1-x, -y, 1-z$; (xvii) $1-x, 2-y, 1-z$; (xviii) $1-x, -y, -z$; (xix) $x-\frac{1}{2}, -y, z-\frac{1}{2}$. Standard deviations in hydrogen bond lengths and bond angles: (1), $\sigma(l) \simeq 0.005$ Å, $\sigma(\theta) \simeq 0.3°$; (2), $\sigma(l) \simeq 0.005$ Å, $\sigma(\theta) \simeq 0.3°$; (3), $\sigma(l) \simeq 0.004$ Å, $\sigma(\theta) \simeq 0.3°$; (4), $\sigma(l) \simeq 0.003$ Å, $\sigma(\theta) \simeq 0.3°$.

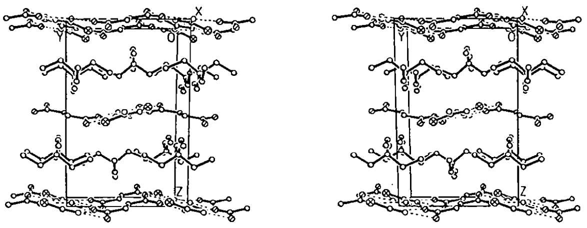

Fig. 6. Stereodrawing of the layer structure of (3). The origin of the unit cell lies at the upper right corner, with *a* towards the reader, *b* pointing from right to left and *c* downwards. Dashed lines represent hydrogen bonds and atom types are distinguished by size and shading.

lattice [*b*/2 = 7.465 Å, in orthorhombic $(C_2H_5)_4N^+.HCO_3^-.(NH_2)_2CS.H_2O$] (Li & Mak, 1995), as may be expected in view of the approximate co-planarity of layers in (3).

A stereoview of the crystal structure is illustrated in Fig. 6. It is seen that the tetrahedral $(C_2H_5)_4N^+$ cation, which is well ordered and nearly attains its idealized 222 molecular symmetry, occupies the space between the layers.

3.2.3. *Crystal structure of* $(n\text{-}C_3H_7)_4N^+.HC_4H_2O_4^-.(NH_2)_2CS.2H_2O$ *(4)*.

In the crystal structure of (4) the thiourea, hydrogen fumarate ions and water molecules

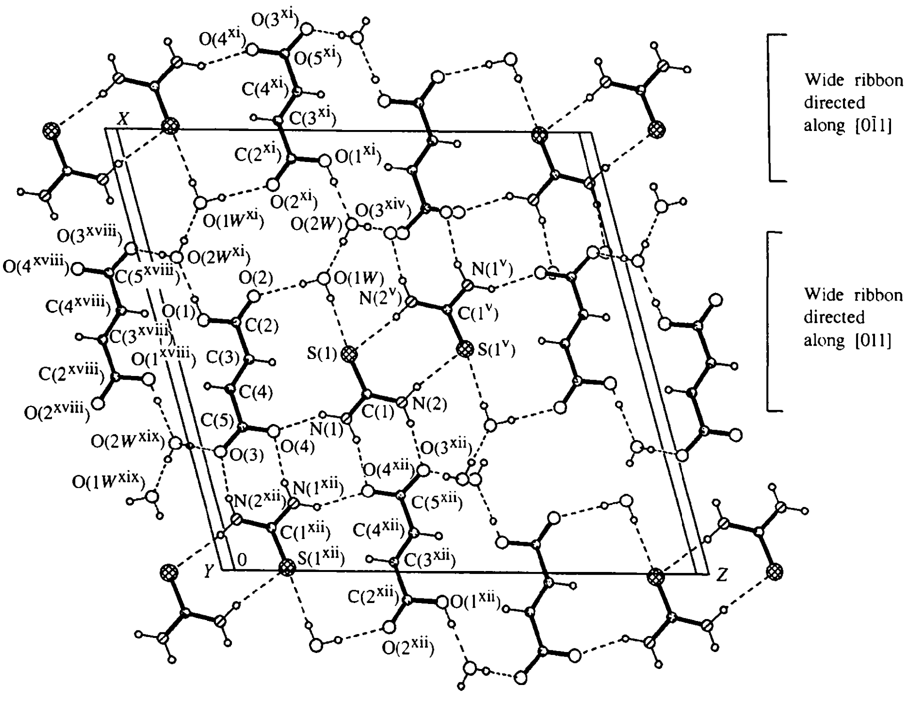

Fig. 7. Hydrogen-bonded layer in $(n\text{-}C_3H_7)_4N^+.HC_4H_2O_4^-.(NH_2)_2CS$ (4) formed by ribbons constructed from thiourea dimers and cyclic hydrogen fumarate–water tetramers. The atom labels correspond to those given in Tables 3 and 4. Dashed lines represent hydrogen bonds.

are interconnected by hydrogen bonds to form wide puckered ribbons, which are crosslinked to generate a three-dimensional host framework containing open channels. The hydrogen-bonding scheme is shown in Fig. 7. As in the case of compound (2), one carboxyl group of the hydrogen fumarate ion exhibits distinctly different C—O bonds orders with C(2)—O(1) = 1.309 and C(2)=O(2) = 1.205 Å. Two centrosymmetric thiourea molecules are connected by a pair of N—H···S hydrogen bonds to form a dimer and likewise the hydrogen fumarate ions and water molecules are organized into cyclic centrosymmetric tetramers each consolidated by pairs of O(hydroxyl)···O(2*W*) and O(2*W*)···O(carbonyl) hydrogen bonds. These dimers and tetramers are linked by N—H···O(carbonyl) hydrogen bonds and also bridged by the second water molecule O(1*W*), forming O(1*W*)···O(carbonyl) and O(1*W*)···S hydrogen bonds, to build a puckered ribbon running through the structure in the direction of [011]. At a location which is half a translation away along the *a* axis, there is a similar ribbon which extends in the [0$\bar{1}$1] direction. Pairs of N—H···O and O(2*W*)—H···O(1*W*) hydrogen bonds are formed between adjacent ribbons to link these two criss-cross series of ribbons into a three-dimensional framework containing open uni-directional channels, as shown in Fig. 8.

Two independent $(n\text{-}C_3H_7)_4N^+$ cations occupy special positions of site symmetry 2: atoms N(3) and N(4) are situated at $(\frac{1}{4}, y, \frac{3}{4})$ and $(\frac{1}{4}, y, \frac{1}{4})$, respectively. These well ordered cations are arranged in a single column within each channel to form a typical channel-like structure (Fig. 8).

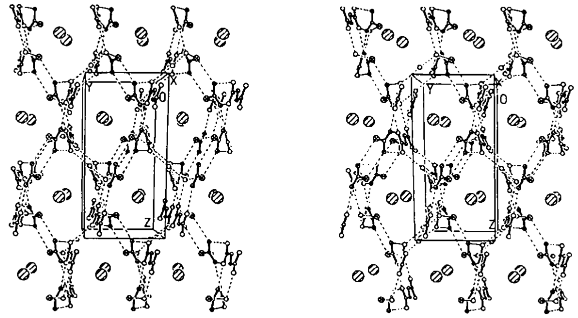

Fig. 8. Stereodrawing of the channel structure of (4). The origin of the unit cell lies at the upper right corner, with *a* towards the reader, *b* pointing from right to left and *c* downwards. Dashed lines represent hydrogen bonds and atom types are distinguished by size and shading. For clarity the enclosed $(n\text{-}C_3H_7)_4N^+$ ions are represented by large shaded circles.

3.3. *Structural features and relationships*

The present series of three thiourea–quaternary ammonium fumarate complexes exhibit thiourea–anion lattices, which are distinctly different from one another, depending on the stoichiometric ratio of thiourea to fumarate ion and the presence of co-crystallized water molecules. Compound (3) (2:1) has fumarate dianions incorporated into a two-dimensional host framework, whereas in (4) (1:1) hydrogen fumarate ions and co-crystallized water molecules are involved in building a three-dimensional channel-type host lattice, whereas in anhydrous complex (2) (1:1) only a parallel arrangement of separate ribbons can be constructed from the thiourea and hydrogen fumarate building blocks.

The hydrogen fumarate anions in (2) and (4) each contain a carboxyl fragment with distinct carbonyl and hydroxyl O atoms [average values C=O 1.207 and C—OH 1.298 Å are close to those in the triclinic and monoclinic modifications of fumaric acid, 1.225 and 1.292 Å (Leiserowitz, 1976)], and a carboxylate fragment with almost equal C—O bond lengths of average 1.241 Å.

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