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# Inclusion Compounds of Thiourea and Peralkylated Ammonium Salts. Part V. Hydrogen-Bonded Host Lattices Built of Thiourea and Acetate Ions

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**Abstract.** New inclusion complexes $(C_2H_5)_4N^+CH_3CO_2^- \cdot 4(NH_2)_2CS$ (**1**), $(n\text{-}C_3H_7)_4N^+[(CH_3CO_2)_2H]^- \cdot 2(NH_2)_2CS$ (**2**), $(n\text{-}C_4H_9)_4N^+[(CH_3CO_2)_2H]^- \cdot 2(NH_2)_2CS$ (**3**) and $(CH_3)_4N^+CH_3CO_2^- \cdot (NH_2)_2CS$ (**4**) have been prepared and characterized by X-ray crystallography. Crystal data, Mo$K_\alpha$ radiation: **1**, space group $C2/c$, $a$ = 28.702(4), $b$ = 8.457(1), $c$ = 22.906(7) Å, $\beta$ = 98.91(1)°, $Z$ = 8, and $R_F$ = 0.048 for 2587 observed data; **2**, space group $P2/n$, $a$ = 8.536(2), $b$ = 8.613(1), $c$ = 18.360(2) Å, $\beta$ = 90.66(2)°, $Z$ = 2, and $R_F$ = 0.045 for 1637 observed data; **3**, space group $P\bar{1}$, $a$ = 8.771(3), $b$ = 10.720(1), $c$ = 16.742(2) Å, $\alpha$ = 99.08(6), $\beta$ = 94.07(2), $\gamma$ = 95.25(2)°, $Z$ = 2, and $R_F$ = 0.063 for 2736 observed data; **4**, space group $P2_1/n$, $a$ = 8.421(3), $b$ = 16.532(6), $c$ = 8.628(3) Å, $\beta$ = 90.25(3), $Z$ = 4, and $R_F$ = 0.050 for 1507 observed data. In the crystal structure of **1**, the thiourea molecules and acetate ions constitute two channel systems aligned parallel to the [110] and [$\bar{1}$10] directions, with the tetraethylammonium cations accommodated in a single column within each channel. In the crystal structure of **2**, hydrogen-bonded centrosymmetric thiourea dimers and acetate dimers are alternately arranged to form a zigzag, puckered ribbon running parallel to [10$\bar{1}$], and the stacked columns of cations are sandwiched between undulatory wave layers constructed from the parallel arrangement of $[((NH_2)_2CS)_2((CH_3CO_2)_2H)^-]_\infty$ ribbons. In the crystal structure of **3**, zigzag hydrogen-bonded thiourea ribbons are linked by dimeric acetate anions existing in two different conformations to generate puckered layers matching the (002) planes, and the $(n\text{-}C_4H_9)_4N^+$ cations occupy the intervening space. In compound **4** the cations are accommodated in 'pseudo-channels' generated from infinitely extended thiourea-acetate composite ribbons.

**Key words.** Thiourea, tetraalkylammonium salt, acetate, acetate dimer, hydrogen bonding, inclusion compound.

**Supplementary Data** relating to this article have been deposited with the British Library as Supplementary Publication No. SUP 82231 (63 pages)

## 1. Introduction

Numerous studies on the classical inclusion compounds formed between urea or thiourea and various guest molecules have been undertaken since their accidental discovery in 1940 [1] and 1947 [2], respectively. Thiourea adducts crystallize in two space-group types: rhombohedral $R\bar{3}2/c$ [3], $R3c$ [4], $R\bar{3}c$ [5,6] or $R\bar{3}$ [7] and

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less commonly monoclinic $P2_1/a$ [8–10] which, in the latter case, exist only at reduced temperatures except for those containing squalene or aromatic guests [11]. In these inclusion compounds the host structure is built of thiourea molecules in an extensively hydrogen bonded lattice that contains parallel channels or tunnels with a free diameter of about 6.1 Å, which can enclose a variety of guest species such as branched-chain alkanes and their derivatives, haloalkanes, 5-, 6- and 8-membered ring compounds, condensed aromatic ring systems, and even ferrocene and other metallocenes [12]. Recent examples of appropriate guest molecules that have been investigated include cyclohexane and some of its derivatives such as chlorocyclohexane and bromocyclohexane [13, 14], as well as some organometallics such as (benzene)$Cr(CO)_3$ and (1,3-cyclohexadiene)$Fe(CO)_3$ [15].

We became interested in the generation of new host lattices by the combined use of thiourea and other molecular species as the building blocks. Several years ago we reported the crystal structures of a series of thiourea-peralkylammonium halide complexes [16] in which each thiourea molecule interacts with adjacent thiourea molecules *via* N—H$\cdots$S hydrogen bonds to give a ribbon-like arrangement, and also forms a pair of ‘chelating’ N—H$\cdots$X hydrogen bonds with a halide ion, resulting in an anionic host framework or composite ribbon as a principal component in the crystal packing. In our design of new thiourea-anion host lattices, some simple trigonal planar anions that can easily form O$\cdots$H—N acceptor hydrogen bonds such as $CO_3^{2-}$, $NO_3^-$, $HCO_3^-$, and $H_2BO_3^-$ have been used, and the crystal structures of thiourea-bicarbonate [17] and nitrate [18] complexes have been reported by us recently.

The structure of acetic acid ($CH_3COOH$) has been investigated in the vapor phase by electron diffraction [19], in solution by IR spectroscopy [20], and in the solid state by single crystal X-ray diffraction [21]. It is found that the acetic acid molecules are linked together to form cyclic planar dimers of $C_{2h}$ symmetry in the gaseous state, infinite zigzag chains in the solid state, and both cyclic and acyclic units in the pure liquid [22]. In the rational design of new thiourea–anion lattices that can accommodate peralkylated ammonium cations of different sizes, we consider the acetate ion which can easily form O$\cdots$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:

$(C_2H_5)_4N^+CH_3CO_2^- \cdot 4(NH_2)_2CS$ (**1**)
$(n\text{-}C_3H_7)_4N^+[(CH_3CO_2)_2H]^- \cdot 2(NH_2)_2CS$ (**2**)
$(n\text{n-}C_4H_9)_4N^+[(CH_3CO_2)_2H]^- \cdot 2(NH_2)_2CS$ (**3**)
$(CH_3)_4N^+CH_3CO_2^- \cdot (NH_2)_2CS$ (**4**)

## 2. Experimental

Tetramethylammonium hydroxide pentahydrate (99%) and tetraethylammonium hydroxide (25% wt. aqueous solution) were obtained from Aldrich and Eastman Kodak, respectively, whereas tetrapropyl- and tetrabutylammonium hydroxide were prepared from their corresponding chloride salts by reaction with moist silver(I) oxide [23].

Each hydroxide and thiourea were mixed in molar ratios of 1 : 3, 1 : 2.5, 1 : 3 and 1 : 2, respectively. A minimum quantity of water was used to dissolve the solid in each case, and glacial acetic acid (100%) was added to the solution in a 1 : 1 molar ratio for hydroxide : acid. After stirring for about half an hour, the solution was subjected to slow evaporation at room temperature in a desiccator charged with Drierite. Colorless crystals appeared in the form of small blocks (**1**, **2** and **3**) and thin plates (**4**). Strongly hygroscopic complex **1** was sealed in a 0.5 mm Lindemann glass capillary.

Information concerning crystallographic data and structure refinement of the four compounds is summarized in Table I. Intensities were collected in the variable-scan technique [24] on a Siemens R3m/V diffractometer using Mo$K_\alpha$ radiation ($\lambda$ = 0.71073Å) at 291 K. The raw data were processed with a learned-profile procedure [25], and empirical absorption correction based on $\psi$-scan data was also applied.

All calculations were performed on a PC 486 computer with the SHELXTL-PLUS program package [26]. 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. 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 [27]. The refinement of the coordinates and anisotropic thermal parameters of the non-hydrogen atoms was carried out by the full-matrix least-squares method, and the final $R$ indices and other parameters are listed in Table I.

## 3. Results and Discussion

The final positional and equivalent isotropic thermal parameters of **1**, **2**, **3** and **4** are listed in Table II, III, and IV, respectively. Anisotropic temperature factors, hydrogen coordinates, and structure factors have been deposited as Supplementary Data.

### 3.1. CRYSTAL STRUCTURE OF $(C_2H_5)_4N^+CH_3CO_2^- \cdot 4(NH_2)_2CS$ (**1**)

In complex **1**, the thiourea molecules and acetate ions build a three-dimensional host lattice in a 4 : 1 ratio, generating two channel systems that are arranged alternately

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

| Complex | **1** | **2** | **3** | **4** |
|---|---|---|---|---|
| Molecular formula | $(C_2H_5)_4N^+CH_3CO_2^- \cdot 4CS(NH_2)_2$ | $(n\text{-}C_3H_7)_4N^+[(CH_3CO_2)_2H]^- \cdot 2CS(NH_2)_2$ | $(n\text{-}C_4H_9)_4N^+[(CH_3CO_2)_2H]^- \cdot 2CS(NH_2)_2$ | $(CH_3)_4N^+CH_3CO_2^- \cdot CS(NH_2)_2$ |
| Molecular weight | 493.8 | 457.7 | 513.8 | 209.3 |
| Crystal system | Monoclinic | Monoclinic | Triclinic | Monoclinic |
| Space group | $C2/c$ (No. 15) | $P2/n$ (No. 13) | $P\bar{1}$ (No. 2) | $P2_1/n$ (No. 14) |
| Unit cell parameters | | | | |
| $a$, Å | 28.702(4) | 8.536(2) | 8.771(3) | 8.421(2) |
| $b$, Å | 8.457(1) | 8.613(1) | 10.720(1) | 16.532(3) |
| $c$, Å | 22.906(7) | 18.360(2) | 16.742(2) | 8.628(4) |
| $\alpha$, ° | 90 | 90 | 99.08(6) | 90 |
| $\beta$, ° | 98.91(1) | 90.66(2) | 94.07(2) | 90.25(3) |
| $\gamma$, ° | 90 | 90 | 95.25(2) | 90 |
| $V$, Å$^3$ | 5493(2) | 1349.7(4) | 1542.1(6) | 1201.1(6) |
| $Z$ | 8 | 2 | 2 | 4 |
| $F(000)$ | 2128 | 500 | 564 | 456 |
| Density (calcd.), g cm$^{-3}$ | 1.194 | 1.126 | 1.107 | 1.157 |
| Absorption coefficient, mm$^{-1}$ | 0.372 | 0.226 | 0.205 | 0.249 |
| Crystal size, mm | 0.40 × 0.42 × 0.62 | 0.40 × 0.40 × 0.46 | 0.30 × 0.36 × 0.40 | 0.42 × 0.42 × 0.50 |
| Mean $\mu r$ | 0.08 | 0.05 | 0.04 | 0.05 |
| Reflections for cell measurement | 25 | 25 | 25 | 25 |
| $\theta$ range (°) | 5 to 12.5 | 5 to 12.5 | 5 to 12.5 | 6 to 14 |
| Transmission factors | 0.936 to 0.805 | 0.819 to 0.784 | 0.889 to 0.845 | 0.921 to 0.875 |
| Scan speed (deg min$^{-1}$) | 6.0 to 60.0 | 6.0 to 60.0 | 6.0 to 60.0 | 3.0 to 23.40 |
| 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 | 0.70 to 0.70 |
| Background counting | stationary counts for one-half of scan time at each end of scan | | | |
| $2\theta_{\max}$, ° | 46 | 48 | 46 | 50 |
| No. of standard reflections | 3 | 3 | 3 | 2 |
| Reflections measured | 7541 | 2276 | 4645 | 2262 |
| Unique data measured | 3818 | 2119 | 4310 | 2116 |
| Observed data | $\|F_o\| > 4\sigma(\|F_o\|)$, 2587 | $\|F_o\| > 4\sigma(\|F_o\|)$, 1637 | $\|F_o\| > 4\sigma(\|F_o\|)$, 2736 | $\|F_o\| > 4\sigma(\|F_o\|)$, 1507 |
| Number of variables, $p$ | 263 | 133 | 297 | 118 |
| $R_F = \Sigma \|\| F_o\| - \|F_c\| \| / \Sigma\|F_o\|$ | 0.048 | 0.045 | 0.063 | 0.050 |
| Constant $g$ in weighting scheme $\omega = [\sigma^2(F_o) + g\|F_o\|^2]^{-1}$ | 0.0002 | 0.0003 | 0.0005 | 0.0001 |
| $R_G = [\Sigma\omega(\|F_o\| - \|F_c\|)^2/\Sigma\|F_o\|^2]^{1/2}$ | 0.055 | 0.054 | 0.077 | 0.053 |
| $S = [\Sigma\omega(\|F_o\| - \|F_c\|)^2/(n-p)]^{1/2}$ | 1.79 | 1.64 | 1.88 | 1.52 |
| Residual extrema in final difference map, $e$ Å$^{-3}$ | +0.37 to −0.26 | +0.22 to −0.20 | +0.49 to −0.24 | +0.29 to −0.23 |
| Largest and mean $\Delta/\sigma$ | 0.000, 0.000 | 0.000, 0.000 | 0.001, 0.000 | 0.005, 0.001 |

Table II. Atomic coordinates ($\times 10^4$) and thermal parameters[*] ($Å^2 \times 10^3$) of $(C_2H_5)_4N^+CH_3CO_2^- \cdot 4CS(NH_2)_2 \cdot$ (**1**).

| Atom | $x$ | $y$ | $z$ | $U_{eq}$ or $U$ |
|---|---|---|---|---|
| Thiourea-acetate host lattice | | | | |
| S(1) | 5286(1) | 1487(2) | 4224(1) | 67(1) |
| C(1) | 5397(1) | −30(4) | 3783(2) | 53(1) |
| N(1) | 5055(1) | −885(4) | 3489(1) | 73(1) |
| N(2) | 5840(1) | −404(4) | 3718(1) | 63(1) |
| S(2) | 6826(1) | 1573(2) | 4449(1) | 65(1) |
| C(2) | 6704(1) | 1396(4) | 5146(2) | 53(1) |
| N(3) | 6263(1) | 1225(3) | 5251(1) | 59(1) |
| N(4) | 7042(1) | 1444(4) | 5614(1) | 70(1) |
| S(3) | 7077(1) | 5929(2) | 8155(1) | 66(1) |
| C(3) | 7185(1) | 4437(4) | 7701(2) | 57(1) |
| N(5) | 7615(1) | 4141(4) | 7591(2) | 69(1) |
| N(6) | 6835(1) | 3536(4) | 7434(2) | 82(1) |
| S(4) | 5706(1) | 3573(1) | 7724(1) | 60(1) |
| C(4) | 5611(1) | 5108(4) | 8170(2) | 54(1) |
| N(7) | 5956(1) | 5974(4) | 8446(2) | 71(1) |
| N(8) | 5174(1) | 5466(4) | 8261(2) | 72(1) |
| C(5) | 6109(2) | −414(5) | 7276(2) | 91(1) |
| C(6) | 6218(2) | 411(5) | 6732(2) | 61(1) |
| O(1) | 5892(1) | 755(5) | 6338(1) | 97(1) |
| O(2) | 6644(1) | 704(4) | 6695(1) | 71(1) |
| Tetraethylammonium ion | | | | |
| N(9) | 3621(1) | 6266(4) | 9547(1) | 59(1) |
| C(7) | 3263(2) | 7305(6) | 9182(2) | 97(1) |
| C(8) | 2826(2) | 6447(6) | 8867(2) | 111(1) |
| C(9) | 3406(2) | 5461(5) | 10029(2) | 84(1) |
| C(10) | 3214(2) | 6554(6) | 10453(2) | 105(1) |
| C(11) | 4033(2) | 7318(5) | 9806(2) | 85(1) |
| C(12) | 4435(2) | 6475(6) | 10188(2) | 108(1) |
| C(13) | 3790(2) | 4988(5) | 9173(2) | 103(1) |
| C(14) | 4019(2) | 5592(7) | 8670(2) | 152(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 III. Atomic coordinates ($\times 10^4$) and thermal parameters* ($Å^2 \times 10^3$) of $(n\text{-}C_3H_7)_4N^+[(CH_3CO_2)_2H]^- \cdot 2CS(NH_2)_2$ (**2**) and $(n\text{-}C_4H_9)_4N^+[(CH_3CO_2)_2H]^- \cdot 2CS(NH_2)_2$ (**3**).

| Atom | $x$ | $y$ | $z$ | $U_{eq}$ or $U$ |
|---|---|---|---|---|
| (i) $(n\text{-}C_3H_7)_4N^+[(CH_3CO_2)_2H]^- \cdot 2CS(NH_2)_2$ (**2**) | | | | |
| Thiourea-acetate host lattice | | | | |
| S(1) | 2637(1) | 5832(1) | 4596(1) | 52(1) |
| C(1) | 3925(3) | 6494(3) | 3979(1) | 41(1) |
| N(1) | 3447(2) | 7277(3) | 3390(1) | 51(1) |
| N(2) | 5449(3) | 6254(3) | 4048(1) | 58(1) |
| C(2) | 5825(3) | 8554(4) | 791(2) | 72(1) |
| C(3) | 5959(3) | 8323(3) | 1598(1) | 48(1) |
| O(1) | 7360(2) | 8097(3) | 1837(1) | 63(1) |
| O(2) | 4811(2) | 8364(2) | 1986(1) | 58(1) |
| Tetra-$n$-propylammonium ion | | | | |
| N(3) | 2500 | 2444(3) | 2500 | 41(1) |
| C(4) | 1312(3) | 3501(3) | 2858(1) | 47(1) |
| C(5) | −27(4) | 2710(4) | 3242(2) | 71(1) |
| C(6) | −1160(4) | 3912(4) | 3508(2) | 86(1) |
| C(7) | 1719(3) | 1377(3) | 1943(1) | 45(1) |
| C(8) | 787(4) | 2177(3) | 1350(2) | 67(1) |
| C(9) | 100(5) | 1009(4) | 834(2) | 96(2) |
| (ii) $(n\text{-}C_4H_9)_4N^+[(CH_3CO_2)_2H]^- \cdot 2CS(NH_2)_2$ (**3**) | | | | |
| Thiourea-acetate host lattice | | | | |
| S(1) | 2423(1) | −609(1) | 5059(1) | 66(1) |
| C(1) | 2559(2) | 881(2) | 4832(2) | 45(1) |
| N(1) | 1322(2) | 1430(2) | 4644(2) | 64(1) |
| N(2) | 3904(2) | 1544(2) | 4831(2) | 61(1) |
| S(2) | 7388(1) | −542(1) | −148(1) | 70(1) |
| C(2) | 7605(2) | 1054(2) | −104(2) | 53(1) |
| N(3) | 8983(2) | 1692(2) | −48(2) | 72(1) |
| N(4) | 6400(2) | 1711(2) | −131(2) | 66(1) |
| C(3) | 2704(2) | 5980(2) | 4404(2) | 105(1) |
| C(4) | 2755(2) | 4606(2) | 4356(2) | 67(1) |
| O(1) | 1642(2) | 3864(2) | 4075(2) | 93(1) |
| O(2) | 4003(2) | 4224(2) | 4621(1) | 78(1) |
| C(5) | 6968(2) | 6391(2) | 790(2) | 118(1) |
| C(6) | 7924(2) | 5403(2) | 496(2) | 80(1) |
| O(3) | 7501(2) | 4305(2) | 489(2) | 122(1) |
| O(4) | 9203(2) | 5833(2) | 270(2) | 100(1) |

Table III. Continued

| Atom | $x$ | $y$ | $z$ | $U_{\mathrm{eq}}$ or $U$ |
|---|---|---|---|---|
| Tetra-$n$-butylammonium ion | | | | |
| N(5) | 3606(2) | −2443(2) | −2517(1) | 55(1) |
| C(7) | 3048(2) | −3578(2) | −3158(2) | 61(1) |
| C(8) | 2346(2) | −4745(2) | −2855(2) | 74(1) |
| C(9) | 1812(2) | −5822(2) | −3531(2) | 99(1) |
| C(10) | 1150(2) | −6986(2) | −3238(2) | 113(1) |
| C(11) | 4737(2) | −2808(2) | −1882(2) | 58(1) |
| C(12) | 6086(2) | −3443(2) | −2204(2) | 79(1) |
| C(13) | 7018(2) | −3917(2) | −1559(2) | 84(1) |
| C(14) | 8373(2) | −4561(2) | −1855(2) | 104(1) |
| C(15) | 2275(2) | −1953(2) | −2078(2) | 65(1) |
| C(16) | 997(2) | −1582(2) | −2613(2) | 94(1) |
| C(17) | −322(2) | −1008(2) | −2236(2) | 70(1) |
| C(18) | 227(2) | 413(2) | −2014(2) | 102(1) |
| C(17′) | 160(2) | −577(2) | −1928(2) | 99(1) |
| C(18′) | −980(2) | 11(2) | −2416(2) | 124(1) |
| C(19) | 4383(2) | −1451(2) | −2945(2) | 64(1) |
| C(20) | 4873(2) | −160(2) | −2428(2) | 87(1) |
| C(21) | 5520(2) | 761(2) | −2935(2) | 120(1) |
| C(22) | 5925(2) | 2083(2) | −2481(2) | 149(1) |

*For non-hydrogen atoms, equivalent isotropic temperature factor $U_{\mathrm{eq}}$ defined as 1/3 of the trace of the orthogonalised **U** matrix.
The exponent of the isotropic temperature factor takes the form $-8\pi^2 U \sin^2\theta/\lambda^2$.

along the [110] and [$\bar{1}$10] directions, as shown in Figures 1 and 2, respectively. The tetraethylammonium cations are accommodated in a single column within each channel. The thiourea-anion lattice comprises zigzag ribbons running parallel to the [110] and [$\bar{1}$10] directions, and parallel undulatory layers connected by hydrogen bonds which are oriented almost perpendicular to the ribbons and parallel to the (110) family of planes. As shown in Figure 1, the mean planes of these highly undulatory layers are positioned at $z$ = 1/4 and 3/4. Features of the ribbons and relation between ribbons and layers may be conveniently described with reference to the hydrogen bonding scheme shown in Figure 3(a) and Table V.

The infinite chains running through the structure in the [110] and [$\bar{1}$10] directions, which form a pair of opposite walls of the corresponding channels, are generated by two independent thiourea molecules, **C(1)** [composed of atoms C(1), S(1), N(1) and N(2), and hereafter conveniently referred to as **C(1)**; other thiourea molecules are designated in the same manner] and **C(2)**, together with an acetate anion **C(6)** [composed of atoms C(6), C(5), O(1), O(2)]. Thiourea molecules **C(1)**

Table IV. Atomic coordinates ($\times 10^4$) and thermal parameters* (Å$^2$ $\times$ $10^3$) of $(CH_3)_4N^+CH_3CO_2^- \cdot CS(NH_2)_2$ (**4**).

| Atom | $x$ | $y$ | $z$ | $U_{eq}$ or $U$ |
|---|---|---|---|---|
| Thiourea-acetate host lattice | | | | |
| S(1) | 2499(1) | 41(1) | −958(1) | 60(1) |
| C(1) | 2499(3) | 672(2) | 599(3) | 45(1) |
| N(1) | 1155(3) | 931(2) | 1230(3) | 54(1) |
| N(2) | 3844(3) | 929(2) | 1231(3) | 55(1) |
| C(2) | 2501(5) | 2454(3) | 6070(4) | 84(1) |
| C(3) | 2491(4) | 1969(2) | 4599(3) | 56(1) |
| O(1) | 1217(3) | 1789(2) | 4029(3) | 98(1) |
| O(2) | 3786(3) | 1788(2) | 4027(3) | 98(1) |
| Tetra methylammonium ion | | | | |
| N(3) | 7502(3) | 1222(1) | 6088(3) | 53(1) |
| C(4) | 6054(4) | 1122(3) | 7055(4) | 84(1) |
| C(5) | 8948(4) | 1123(3) | 7054(4) | 84(1) |
| C(6) | 7497(7) | 615(3) | 4854(6) | 113(2) |
| C(7) | 7490(5) | 2042(2) | 5404(5) | 76(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 $-8\pi^2 U \sin^2\theta/\lambda^2$.

and **C(2)** are linked by a pair of N—H···S hydrogen bonds in a shoulder-to-shoulder fashion while **C(2)** is further linked to an acetate ion via two N—H···O donor hydrogen bonds to generate a trimer (Figure 3(a)). Two centrosymmetrically-related trimers constitute a hexamer consolidated by a pair of N—H···O hydrogen bonds between **C(2)** and its symmetry equivalent partner **C(2d)**. With this hexamer as a repeating unit, formation of hydrogen bonds of the type between **C(1)** and **C(6c)** generates a wide ribbon running through the structure in the direction of [110]. At a location which is one-half translation away along the $c$ axis, there is a similar ribbon which extends in the [$\bar{1}$10] direction. In this ribbon the molecules originating from thiourea **C(2)** and acetate **C(6)** of the hexamer are essentially coplanar, as shown by the torsion angles C(2)—N(4)···O(2)—C(6) = −1.4 and C(2)—N(3)···O(1)—C(6) = −13.1°. However, those derived from thiourea **C(1)** are inclined with respect to the main plane of the ribbon, and the relevant torsion angles are C(1)—N(2)···S(2)—C(2) = 53.1 and C(1)—N(1)···O(1c)—C(6c) = 121.1°, respectively.

The acetate ion **C(6)** also contributes to the construction of a layer built of the other two thiourea molecules: thiourea molecules of type **C(3)** related by a $2_1$ axis

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

| | | | |
|---|---|---|---|
| $(C_2H_5)_4N^+CH_3CO_2^-\cdot 4CS(NH_2)_2$ (**1**) | | | |
| (i) Thiourea and acetate molecules | | | |
| S(1)—C(1) | 1.694(4) | C(1)—N(1) | 1.315(5) |
| C(1)—N(2) | 1.341(5) | S(2)—C(2) | 1.693(4) |
| C(2)—N(3) | 1.332(5) | C(2)—N(4) | 1.331(5) |
| S(3)—C(3) | 1.694(4) | C(3)—N(5) | 1.323(5) |
| C(3)—N(6) | 1.332(5) | S(4)—C(4) | 1.700(4) |
| C(4)—N(7) | 1.314(5) | C(4)—N(8) | 1.337(5) |
| C(5)—C(6) | 1.504(6) | C(6)—O(1) | 1.230(5) |
| C(6)—O(2) | 1.262(5) | | |
| S(1)—C(1)—N(1) | 121.8(3) | | |
| S(1)—C(1)—N(2) | 120.9(3) | | |
| N(1)—C(1)—N(2) | 117.3(3) | S(2)—C(2)—N(3) | 121.4(3) |
| S(2)—C(2)—N(4) | 121.7(3) | N(3)—C(2)—N(4) | 116.9(4) |
| S(3)—C(3)—N(5) | 121.6(3) | S(3)—C(3)—N(6) | 120.8(3) |
| N(5)—C(3)—N(6) | 117.6(4) | S(4)—C(4)—N(7) | 122.4(3) |
| S(4)—C(4)—N(8) | 120.6(3) | N(7)—C(4)—N(8) | 117.1(4) |
| C(5)—C(6)—O(1) | 119.1(4) | C(5)—C(6)—O(2) | 118.3(3) |
| O(1)—C(6)—O(2) 122 | 6(4). | | |
| (ii) Hydrogen bonding | | | |
| N(3)···S(1) | 3.376 | N(7a)···S(1) | 3.543 |
| N(8a)···S(1) | 3.375 | N(2)···S(2) | 3.484 |
| N(4d)···S(2) | 3.680 | N(7)···S(3) | 3.384 |
| N(5i)···S(3) | 3.398 | N(6)···S(4) | 3.408 |
| N(8)···S(4) | 3.501 | N(1g)···S(4) | 3.570 |
| N(2g)···S(4) | 3.499 | N(1c)···O(1) | 2.881 |
| N(3)···O(1) | 2.882 | N(4)···O(2) | 2.949 |
| N(5h)···O(2) | 2.805 | N(6)···O(2) | 3.935 |
| N(3)···S(1)—C(1) | 98.8 | N(7a)···S(1)—C(1) | 89.6 |
| N(8a)···S(1)—C(1) | 101.3 | N(3)···S(1)···N(7a) | 86.2 |
| N(3)···S(1)···N(8a) | 119.3 | N(2)···S(2)—C(2) | 98.0 |
| N(4d)···S(2)—C(2) | 113.0 | N(2)···S(2)···N(4d) | 148.9 |
| N(7)···S(3)—C(3) | 113.5 | N(5i)···S(3)—C(3) | 101.6 |
| N(7)···S(3)···N(5i) | 114.8 | N(1g)···S(4)—C(4) | 92.6 |
| N(2g)···S(4)—C(4) | 101.8 | N(6)···S(4)—C(4) | 111.7 |
| N(8e)···S(4)—C(4) | 82.6 | N(6)···S(4)···N(8e) | 119.4 |
| N(1g)···S(4)···N(6) | 132.5 | N(1g)···S(4)···N(8e) | 103.2 |
| N(2g)···S(4)···N(6) | 96.2 | N(2g)···S(4)···N(8e) | 139.9 |
| N(1g)···S(4)···N(2g) | 37.4 | N(6)···O(2)—C(6) | 102.6 |
| N(5h)···O(2)—C(6) | 121.5 | N(4)···O(2)—C(6) | 127.0 |
| N(6)···O(2)···N(5h) | 89.5 | N(4)···O(2)···N(6) | 104.4 |
| N(4)···O(2)···N(5h) | 103.4 | | |
| C(2)—N(3)···S(1)—C(1) | 61.5 | C(1)—N(2)···S(2)—C(2) | 53.1 |
| C(2)—N(4)···S(2d)—C(2d) | −22.0 | C(4a)—N(7a)···S(1)—C(1) | 109.8 |
| C(4a)—N(8a)···S(1)—C(1) | −75.0 | C(4)—N(7)···S(3)—C(3) | −10.6 |
| C(3)—N(6)···S(4)—C(4) | 10.0 | C(4)—N(8)···S(4e)—C(4e) | −83.0 |
| C(2)—N(3)···O(1)—C(6) | −13.1 | C(2)—N(4)···O(2)—C(6) | −1.4 |
| C(3)—N(6)···O(2)—C(6) | 165.9 | C(3)—N(5)···O(2i)—C(6i) | 174.3 |

Table V. Continued

| | | | |
|---|---|---|---|
| $(n\text{-}C_3H_7)_4N^+[(CH_3CO_2)H]^-\cdot 2CS(NH_2)_2$ (**2**) | | | |
| (i) Thiourea and acetate molecules | | | |
| S(1)—C(1) | 1.687(3) | C(1)—N(1) | 1.334(3) |
| C(1)—N(2) | 1.322(3) | C(2)—C(3) | 1.498(4) |
| C(3)—O(1) | 1.284(3) | C(3)—O(2) | 1.218(3) |
| S(1)—C(1)—N(1) | 121.3(2) | S(1)—C(1)—N(2) | 122.1(2) |
| N(1)—C(1)—N(2) | 116.6(2) | C(2)—C(3)—O(1) | 114.7(2) |
| C(2)—C(3)—O(2) | 121.4(2) | O(1)—C(3)—O(2) | 123.9(2) |
| (ii) Hydrogen bonding | | | |
| N(2d)···S(1) | 3.464 | N(2a)···O(1) | 2.954 |
| O(1a)···O(1) | 2.445 | N(1)···O(2) | 2.992 |
| N(1e)···O(2) | 3.008 | | |
| N(2d)···S(1)—C(1) | 110.6 | N(2a)···O(1)—C(3) | 119.2 |
| O(1a)···O(1)—C(3) | 114.8 | O(1a)···O(1)···N(2a) | 119.5 |
| N(1)···O(2)—C(3) | 144.9 | N(1e)···O(2)—C(3) | 127.2 |
| N(1)···O(2)···N(1e) | 74.5 | | |
| C(1d)—N(2d)···S(1)—C(1) | 2.2 | C(1)—N(2)···O(1a)—C(3a) | 153.6 |
| C(3)—O(1)···O(1a)—C(3a) | −160.7 | N(2)···O(1a)···O(1)—C(3) | 47.8 |
| $(n\text{-}C_4H_8)_4N^+[(CH_3CO_2)H]^-\cdot 2CS(NH_2)_2$ (**3**) | | | |
| (i) Thiourea and acetate molecules | | | |
| S(1)—C(1) | 1.695(2) | C(1)—N(1) | 1.323(3) |
| C(1)—N(2) | 1.320(2) | S(2)—C(2) | 1.693(2) |
| C(2)—N(3) | 1.323(2) | C(2)—N(4) | 1.325(3) |
| C(3)—C(4) | 1.467(3) | C(4)—O(1) | 1.217(2) |
| C(4)—O(2) | 1.278(3) | C(5)—C(6) | 1.457(3) |
| C(6)—O(3) | 1.200(3) | C(6)—O(4) | 1.278(3) |
| S(1)—C(1)—N(1) | 121.5(1) | S(1)—C(1)—N(2) | 121.6(2) |
| N(1)—C(1)—N(2) | 117.0(2) | S(2)—C(2)—N(3) | 121.4(2) |
| S(2)—C(2)—N(4) | 121.2(1) | N(3)—C(2)—N(4) | 117.4(2) |
| C(3)—C(4)—O(1) | 120.8(2) | C(3)—C(4)—O(2) | 117.6(2) |
| O(1)—C(4)—O(2) | 121.6(2) | C(5)—C(6)—O(3) | 120.6(2) |
| C(5)—C(6)—O(4) | 113.6(2) | O(3)—C(6)—O(4) | 125.7(2) |
| (ii) Hydrogen bonding | | | |
| N(1a)···S(1) | 3.413 | N(2c)···S(1) | 3.462 |
| N(1)···O(1) | 2.912 | N(2)···O(2) | 2.943 |
| O(2b)···O(2) | 2.434 | N(3g)···S(2) | 3.530 |
| N(4e)···S(2) | 3.531 | N(3)···O(3) | 3.221 |
| N(4)···O(3) | 2.863 | N(3h)···O(4) | 3.055 |
| O(4h)···O(4) | 2.467 | | |
| N(1a)···S(1)—C(1) | 107.8 | N(2c)···S(1)—C(1) | 107.5 |
| N(1a)···S(1)···N(2c) | 144.5 | N(1)···O(1)—C(4) | 117.4 |
| N(2)···O(2)—C(4) | 117.3 | O(2b)···O(2)—C(4) | 85.8 |
| N(2)···O(2)···O(2b) | 119.9 | N(3g)···S(2)—C(2) | 110.1 |
| N(4e)···S(2)—C(2) | 112.6 | N(3g)···S(2)···N(4e) | 134.7 |
| N(3)···O(3)—C(6) | 133.8 | N(4)···O(3)—C(6) | 159.6 |
| N(3)···O(3)···N(4) | 43.1 | N(3h)···O(4)—C(6) | 141.7 |
| O(4h)···O(4)—C(6) | 114.0 | N(3h)···O(4)···O(4h) | 104.2 |
| C(1a)—N(1a)···S(1)—C(1) | 14.2 | C(1)—N(2)···S(1c)—C(1c) | −9.8 |
| C(1)—N(1)···O(1)—C(4) | −33.8 | C(1)—N(2)···O(2)—C(4) | −15.3 |

Table V. Continued

| | | | |
|---|---|---|---|
| $(CH_3)_4N^+CH_3CO_2^-\cdot CS(NH_2)_2$ (**4**) | | | |
| (i) Thiourea and acetate molecules | | | |
| C(4)—O(2)· · ·O(2b)—C(4b) | −180.0 | C(2g)—N(3g)· · ·S(2)—C(2) | −3.6 |
| C(2)—N(4)· · ·S(2e)—C(2e) | −13.4 | C(2)—N(3)· · ·O(3)—C(6) | −160.7 |
| C(2)—N(4)· · ·O(3)—C(6) | 102.0 | C(2)—N(3)· · ·O(4h)—C(6h) | −143.8 |
| C(6)—O(4)· · ·O(4h)—C(6h) | 180.0 | | |
| S(1)—C(1) | 1.702(3) | C(1)—N(1) | 1.329(3) |
| C(1)—N(2) | 1.324(3) | C(2)—C(3) | 1.501(5) |
| C(3)—O(1) | 1.216(4) | C(3)—O(2) | 1.236(4) |
| N(3)—C(4) | 1.490(4) | N(3)—C(5) | 1.481(4) |
| N(3)—C(6) | 1.463(6) | N(3)—C(7) | 1.479(4) |
| S(1)—C(1)—N(1) | 121.6(2) | S(1)—C(1)—N(2) | 121.3(2) |
| N(1)—C(1)—N(2) | 117.1(2) | C(2)—C(3)—O(1) | 118.3(3) |
| C(2)—C(3)—O(2) | 117.8(3) | O(1)—C(3)—O(2) | 123.9(3) |
| (ii) Hydrogen bonding | | | |
| N(1b)· · ·S(1) | 3.478 | N(2a)· · ·S(1) | 3.481 |
| N(1)· · ·O(1) | 2.801 | N(2)· · ·O(2) | 2.799 |
| N(1b)· · ·S(1)—C(1) | 109.5 | N(2a)· · ·S(1)—C(1) | 109.8 |
| N(1b)· · ·S(1)· · ·N(2a) | 124.4 | N(1)· · ·O(1)—C(3) | 119.0 |
| N(2)· · ·O(2)—C(3) | 119.1 | | |
| C(1a)—N(2a)· · ·S(1)—C(1) | −21.1 | C(1)—N(1)· · ·S(1b)—C(1b) | −21.2 |
| C(1)—N(1)· · ·O(1)—C(3) | 5.0 | C(1)—N(2)· · ·O(2)—C(3) | −4.9 |

* Symmetry transformations:

**1**, a $(x, 1-y, 1-z)$; b $(x, 1-y, -0.5+z)$; c $(1-x, -y, 1-z)$;
d $(1.5-x, 0.5-y, 1-z)$; e $(1-x, y, 1.5-z)$; f $(x, 1-y, 0.5+z)$;
g $(x, -y, 0.5+z)$; h $(1.5-x, -0.5+y, 1.5-z)$; i $(1.5-x, 0.5+y, 1.5-z)$

**2**, a $(1.5-x, , 0.5-z)$; b $(1+x, y, z)$; c $(-1+x, y, z)$;
d $(1-x, 1-y, 1-z)$; e $(0.5-x, y, 0.5-z)$;

**3**, a $(-x, -y, 1-z)$; b $(1-x, 1-y, 1-z)$; c $(1-x, -y, 1.5-z)$;
d $(x, 1+y, z)$; e $(1-x, -y, -z)$; f $(1-x, 1-y, -z)$;
g $(2-x, -y, -z)$; h$(2-x, 1-y, -z)$; i $(1-x, y, z)$

**4**, a $(1-x, -y, -z)$; b $(-x, -y, -z)$; c $(-1+x, y, z)$;

Standard deviations in hydrogen bond lengths and bond angles:

**1**, $\sigma(l) \approx 0.06$ Å, $\sigma(\theta) \approx 0.5°$;

**2**, $\sigma(l) \approx 0.46$ Å, $\sigma(\theta) \approx 0.2°$;

**3**, $\sigma(l) \approx 0.03$ Å, $\sigma(\theta) \approx 0.2°$;

**4**, $\sigma(l) \approx 0.05$ Å, $\sigma(\theta) \approx 0.3°$;

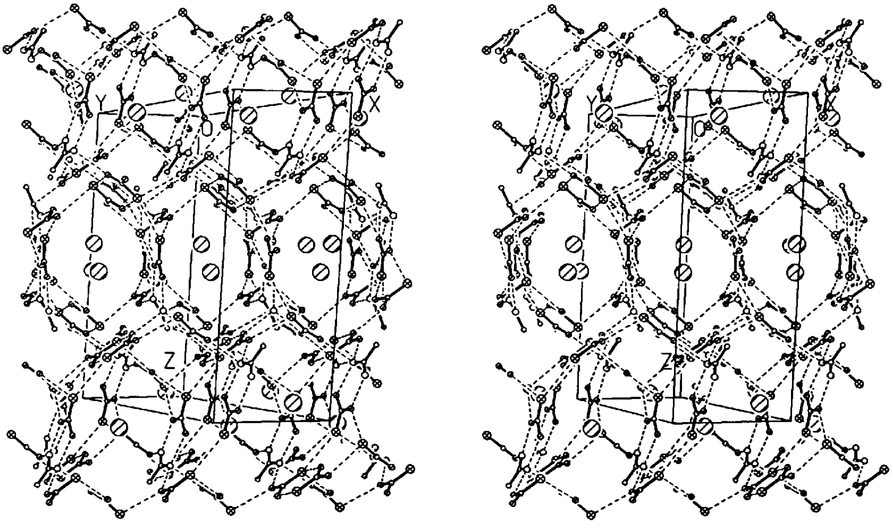

*Figure 1.* Stereodrawing of the crystal structure of $(C_2H_5)_4N^+CH_3CO_2^- \cdot 4(NH_2)_2CS$ (**1**) showing the channels extending parallel to the [110] direction and the enclosed cations. Broken lines represent hydrogen bonds, and atom types are distinguished by size and shading. For clarity the enclosed $(C_2H_5)_4N^+$ ions are represented by large dotted circles.

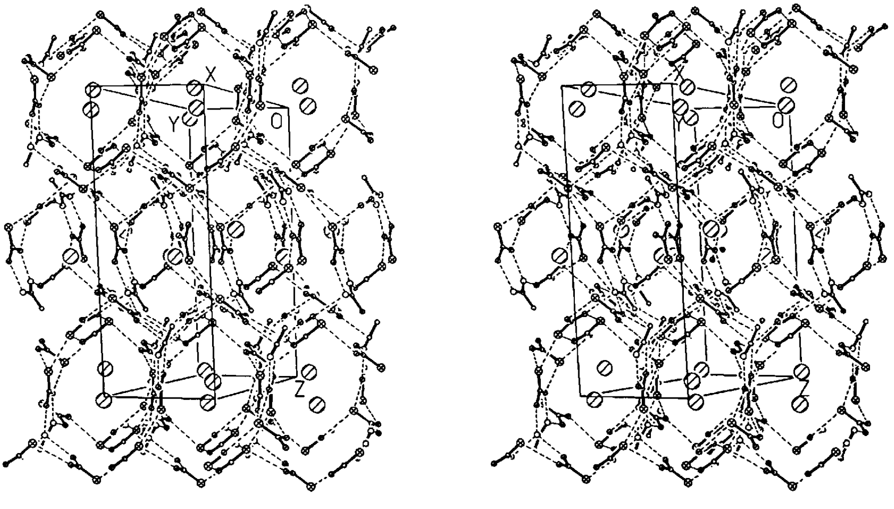

*Figure 2.* Stereodrawing of the crystal structure of **1** showing the channels extending parallel to the [$\bar{1}$10] direction and the enclosed cations. Broken lines represent hydrogen bonds, and atom types are distinguished by size and shading. For clarity the enclosed $(C_2H_5)_4N^+$ ions are represented by large dotted circles.

are alternately linked by hydrogen bonds nearly in a head-to-tail mode to generate a highly twisted zigzag ribbon extending along the [010] direction, as shown by the torsion angle C(3)—N(5)···S(3i)—C(3i) = −63.7° (Figure 3(b)). Only one

N—H···S hydrogen bond is formed between adjacent molecules along the ribbon, so that each pair of thiourea molecules is also bridged by N—H···O hydrogen bonds with the O(2) atom belonging to an acetate ion. Two thiourea molecules **C(4)** related by a 2 axis are linked by a pair of hydrogen bonds in the shoulder-to-shoulder fashion to form a rare dimer, in which they are almost mutually orthogonal, as shown by the torsion angle C(4)—N(8)···S(4e)—C(4e) = −83.0°. The twisted zigzag ribbons lying side by side in an alternate arrangement are cross-linked by the thiourea dimers via N—H···S hydrogen bonds of the type between **C(3)** and **C(4)** to form a puckered layer as shown in Figure 3(b). Cross-linkage of the ribbons and layers positioned at $z = 1/4$ and 3/4 generates a three-dimensional host lattice containing two open channel systems running parallel to the [110] and $[\bar{1}10]$ directions, as illustrated in Figures 1 and 2, respectively.

The tetrahedral $(C_2H_5)_4N^+$ cation is well ordered and nearly attains its idealized 222 molecular symmetry. Its averaged dimensions are N—C = 1.515(4), C–C = 1.522(5) Å, C—N—C = 109.5(2)°, and N—C—C = 114.9(3)°. Individual bond distances and angles are given in the Supplementary Data. These cations are accommodated in a zigzag column within each channel.

## 3.2. CRYSTAL STRUCTURES OF $(n\text{-}C_3H_7)_4N^+[(CH_3CO_2)_2H]^-\cdot 2(NH_2)_2CS$ (**2**) AND $(n\text{-}C_4H_9)_4N^+[(CH_3CO_2)_2H]^-\cdot 2(NH_2)_2CS$ (**3**)

Unlike the case in **1**, a pair of acetate ions are bridged by a single proton, which lies on a 2 axis in **2** or an inversion center in **3**, to form a dimeric $[(CH_3CO_2)_2H]^-$ anionic system, as shown in Figures 4, 6(a) and 6(b). These dimers combine with the thiourea molecules in different modes so that very different host lattices are generated in the two complexes despite their analogous stoichiometry.

Compound **2** features a sandwich-like crystal structure built up from undulatory layers. The plane wave like layer structure may be conveniently described with reference to the hydrogen bonding scheme shown in Figure 4 and Table V. 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 all atoms are essentially co-planar (mean deviation 0.002 Å). The thiourea dimers and $[(CH_3CO_2)_2H]^-$ anions occupying a site of symmetry 2 are linked in a broadside-on manner by pairs of N—H···O hydrogen bonds to form a zigzag, puckered $[((NH_2)_2CS)_2((CH_3CO_2)_2H)^-]_\infty$ ribbon running parallel to the $[10\bar{1}]$ direction. Within this ribbon each S atom forms only one acceptor hydrogen bond, and the N(1) and O(2) atoms which lie at both edges of the ribbon can form other hydrogen bonds to neighboring ribbons. With these ribbons in a parallel arrangement side by side, their cross-linkage by N—H···O(1) hydrogen bonds generates a wave-like layer. Finally, the corrugated layers are alternately stacked parallel to the (010) family of planes, such that the “crests” and “troughs” of each layer are concentrated at $z = 1/4$ and 3/4, respectively.

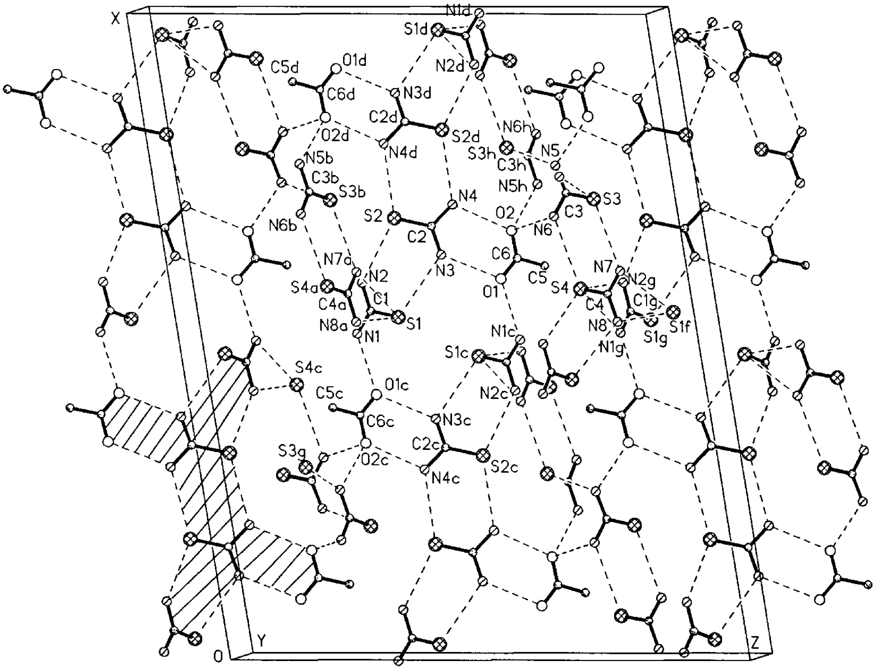

*Figure 3.* (a) The hydrogen bonding scheme in the thiourea-anion host lattice of **1**, in which a centrosymmetric hexameric structural unit is highlighted by shading. (b) Projection drawing of the hydrogen-bonded thiourea-acetate anionic layer parallel to the (001) family of planes in **1**. The atom labels correspond to those given in Tables II and V. Broken lines represent hydrogen bonds. Symmetry transformations: a: $x, 1-y, 1-z$; b: $x, 1-y, -0.5+z$; c: $1-x, -y, 1-z$; d: $1.5-x, 0.5-y, 1-z$; e: $1-x, y, 1.5-z$; f: $x, 1-y, 0.5+z$; g: $x, -y, 0.5+z$; h: $1.5-x, -0.5+y, 1.5-z$; i: $1.5-x, 0.5+y, 1.5-z$.

The stacked columns of well-ordered tetrahedral $(n\text{-}C_3H_7)_4N^+$ cations located on the 2 axis are arranged in a single column between the turning portions of the wavy layers to form a sandwich-like structure (Figure 5).

In the crystal structure of compound **3**, two independent thiourea molecules in the asymmetric unit are linked by N—H· · ·S hydrogen bonds with its own kind in the usual shoulder-to-shoulder manner to form a zigzag ribbon running parallel to the $a$ axis, at $z = 0$ and 1/2, respectively. All of the atoms in a ribbon are approximately co-planar since inversion centers are present between each pair of thiourea molecules, as can be assessed by the measured values of the relevant torsion angles: C(1a)—N(1a)· · ·S(1)—C(1) = 14.2, C(1)—N(2)· · ·S(1c)—C(1c) = −9.8, C(2g)—N(3g)· · ·S(2)—C(2) = −3.6, C(2)—N(4)· · ·S(2e)-C(2e) = −13.4°. Ribbons of the same kind are arranged in parallel and cross-linked by the dimeric $[(CH_3CO_2)_2H]^-$ groups to generate a thiourea-anion layer normal to the $c$ axis. Since the hydrogen bonding interaction between the acetate dimers and urea ribbons must allow for the spatial accommodation of the hydrophobic methyl groups, the

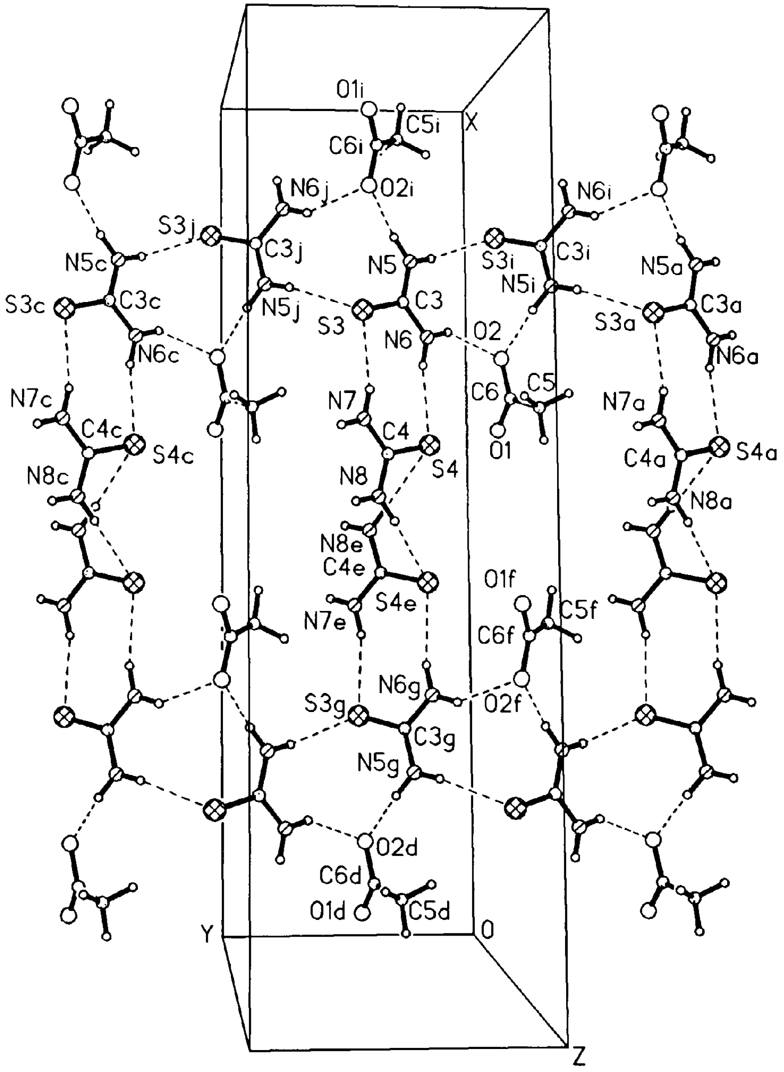

*Figure 3b.*

layer is rather undulatory, as can be verified by the value of the relevant torsion angles C(1)—N(1)· · ·O(1)-C(4) = −33.8, C(2)—N(4)· · ·O(3)—C(6) = 102.0°.

As illustrated in Figures 6(a) and 6(b), two different conformations of the acetate dimer are formed in successive layers: in the layer located at $z = 0$, the $[(CH_3CO_2)_2H]^-$ anion takes the synplanar form between the ribbons formed by **C(2)** molecules, as is the case in **2**, but the antiplanar form exists between ribbons formed by **C(1)** molecules in the layer at $z = 1/2$.

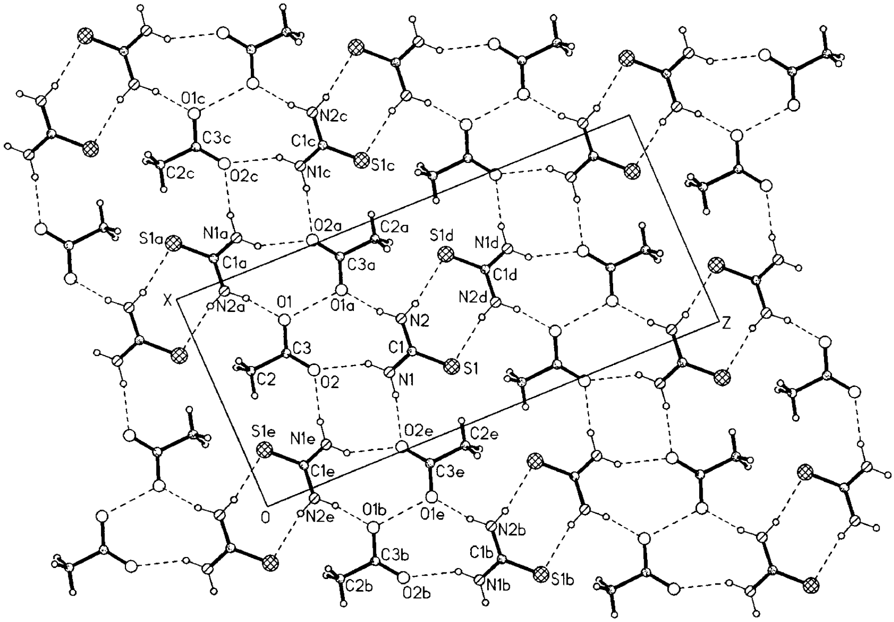

*Figure 4.* Hydrogen-bonded layer in $(n\text{-}C_3H_7)_4N^+[(CH_3CO_2)_2H]^- \cdot 2(NH_2)_2CS$ (**2**) formed by ribbons constructed from thiourea dimers and dimeric acetate anions. The atom labels correspond to those given in Tables III and V. Broken lines represent hydrogen bonds. Symmetry transformations: a: $1.5 - x, y, 0.5 - z$; b: $1 + x, y, z$; c: $-1 + x, y, z$; d: $1 - x, 1 - y, 1 - z$; e: $0.5 - x, y, 0.5 - z$.

The tetraalkylammonium cations $(n\text{-}C_4H_9)_4N^+$ are well ordered and have normal dimensions, except that the two carbon atoms located at the end of an alkyl chain exhibit two-fold disorder. A stereoview of the crystal structure is illustrated in Figure 7. It is seen that the cations are located in the space between the layers, which correspond to the (002) family of planes.

### 3.3. CRYSTAL STRUCTURE OF $(CH_3)_4N^+CH_3CO_2^- \cdot (NH_2)_2CS$ (4)

The atom labeling and hydrogen bonding schemes are shown in Figure 8. In compound **4** the thiourea molecules are linked by N—H···S hydrogen bonds in the usual shoulder-to-shoulder manner to form a zigzag ribbon running parallel to the $a$ axis. But unlike those in **3**, the ribbon is rather more undulatory, and the extent of deviation from planarity can be seen from the measured values of the torsion angles between two adjacent thiourea molecules: C(1a)—N(2a)···S(1)—C(1) = −21.1, C(1)—N(1)···S(1b)—C(1b) = −21.2°, which are larger than the corresponding values of structure **3**, and the main plane of the ribbon is parallel to the (031) and $(03\bar{1})$ family of planes which are related by a $2_1$ axis. Each thiourea molecule is further linked to an acetate ion via two additional N—H···O donor hydrogen bonds that extend outward on either side of the ribbon, so that these

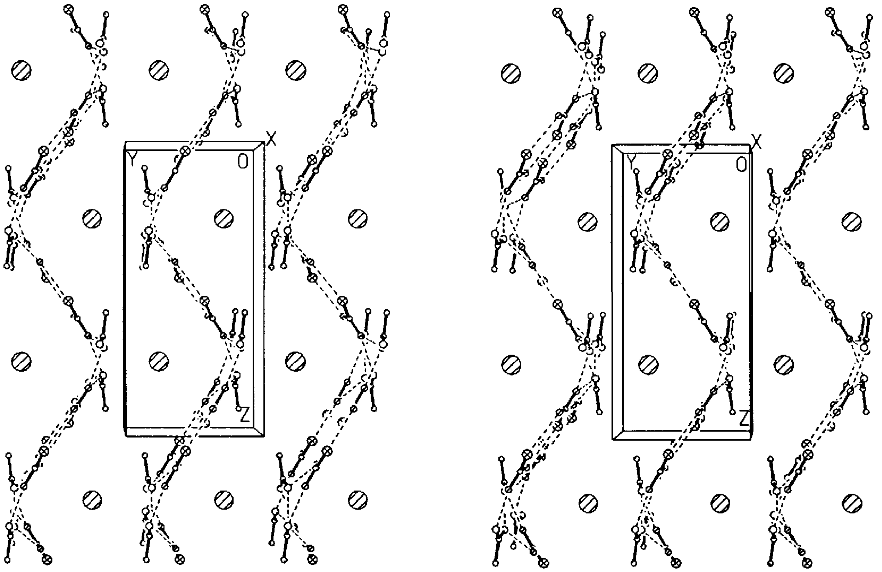

*Figure 5.* Stereodrawing of the crystal structure of **2**. The origin of the unit cell lies at the upper right corner, with $a$ towards the reader, $b$ pointing from right to left and $c$ downwards. Broken lines represent hydrogen bonds, and atom types are distinguished by size and shading. For clarity the enclosed $(n\text{-}C_3H_7)_4N^+$ ions are represented by large dotted circles.

ribbons can also be regarded as being constructed from a thiourea-anion dimeric building block that is very similar to that in the inclusion compounds of thiourea with tetramethyl-, tetrapropyl- and tetrabutyl-ammonium nitrate salts [16]. The orientation of the $CH_3COO^-$ group with respect to the thiourea ribbon can be described by the torsion angle C(1)—N(1)· · ·O(1)—C(3) = 5.0°.

As shown in Figure 9, the zipper-like ribbons are arranged by operations of the corresponding $2_1/n$ symmetry elements to generate a ‘pseudo-channel’ type of thiourea-anionic lattice, but without any interaction between adjacent ribbons, the shortest distances between two of them being 8.709(4) Å. The cross-section of a “pseudo-channel” is shaped approximately like a parallelogram, with distances between its two pairs of sides measuring 4.7 and 9.5 Å.

The independent tetramethylammonium cation is well ordered and its averaged dimensions are N—C = 1.478(4) Å, C—N—C = 109.5(3)°. These cations are arranged in a straight column along the [100] direction, and two parallel columns are separated by the one-dimensional infinitely extended thiourea-acetate composite ribbons in a channel-like packing arrangement (see Figure 9).

### 3.4. STRUCTURAL FEATURES AND RELATIONSHIPS

The present series of four thiourea–quaternary ammonium acetate complexes exhibit thiourea–anion lattices which are distinctly different from one another,

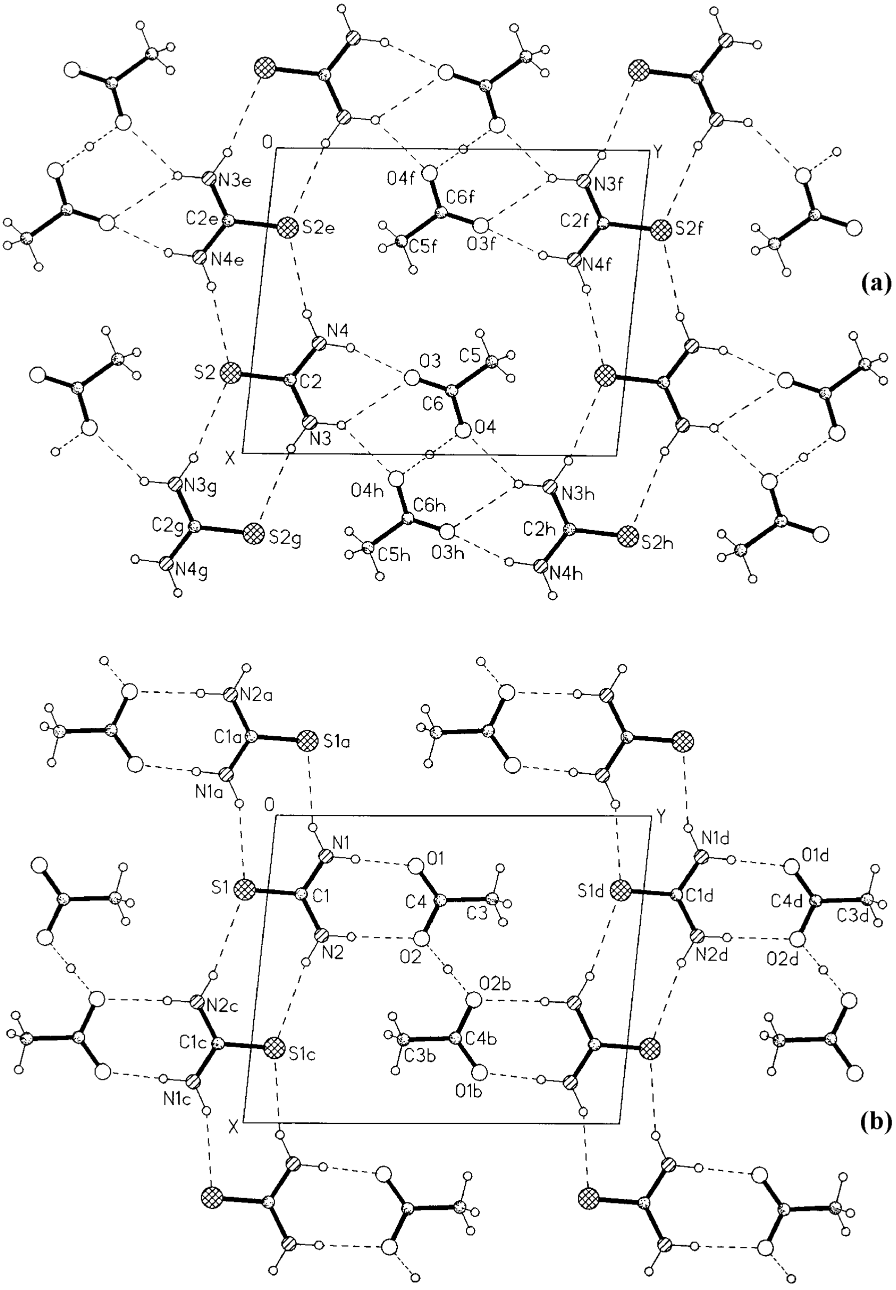

*Figure 6.* Hydrogen-bonded layer at (**a**) $z = 0$ and (**b**) $z = 1/2$ in $(n\text{-}C_4H_9)_4N^+$ $[(CH_3CO_2)_2H]^- \cdot 2(NH_2)_2CS$ (**3**), formed by thiourea ribbons and dimeric acetate anions. The atom labels correspond to those given in Tables III and V. Broken lines represent hydrogen bonds. Symmetry transformations: a: $-x, -y, 1-z$; b: $1-x, 1-y, 1-z$; c: $1-x, -y, 1-z$; d: $x, 1+y, z$; e: $1-x, -y, -z$; f: $1-x, 1-y, -z$; g: $2-x, -y, -z$; h: $2-x, 1-y, -z$; i: $1-x, y, z$.

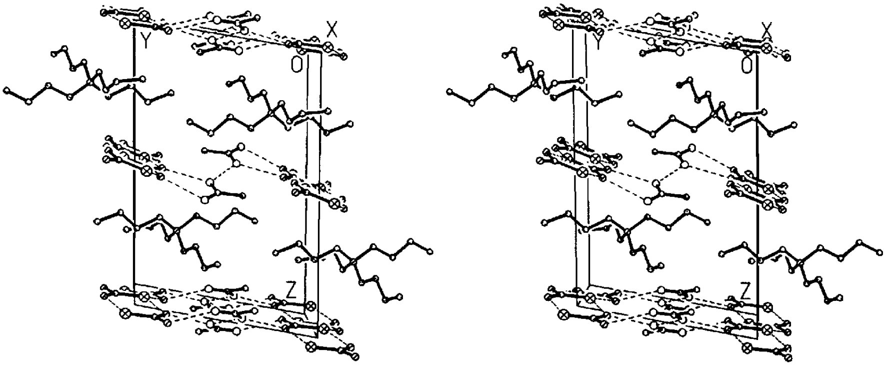

*Figure 7.* Stereodrawing of the crystal structure of **3**. The origin of the unit cell lies at the upper right corner, with $a$ towards the reader, $b$ pointing from right to left and $c$ downwards. Broken lines represent hydrogen bonds, and atom types are distinguished by size and shading.

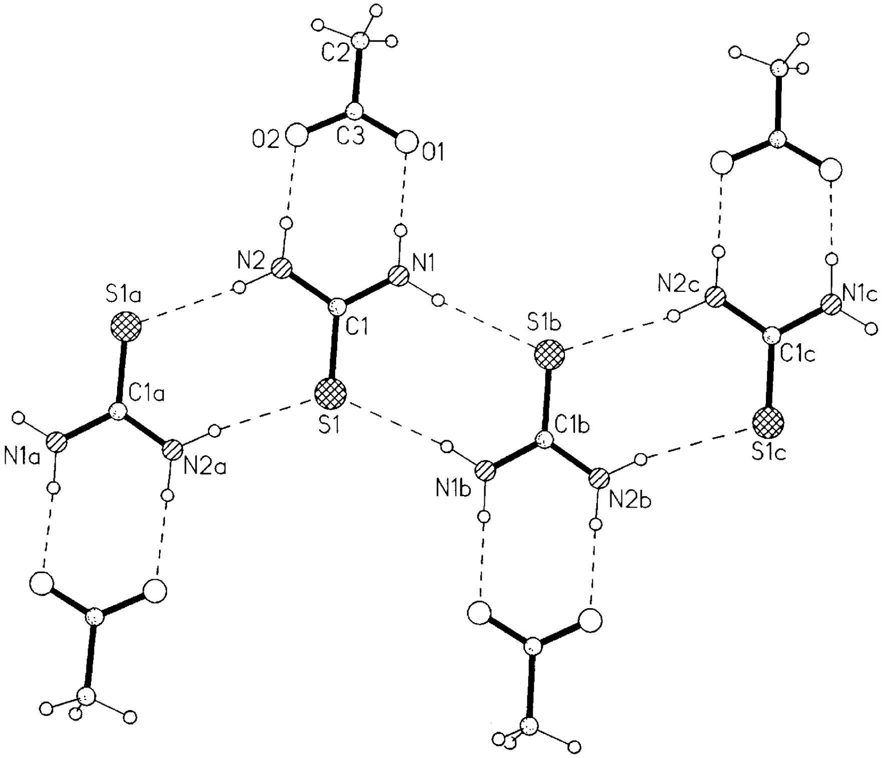

*Figure 8.* The zipper-like composite ribbons in $(CH_3)_4N^+CH_3CO_2^- \cdot (NH_2)_2CS$ (**4**), formed by the attachment of acetate ions to both sides of each thiourea ribbon. The atom labels correspond to those given in Tables VI and V. Symmetry transformations: a: $1 - x$, $-y$, $-z$; b: $-x, -y, -z$; c: $-1 + x$, $y$, $z$.

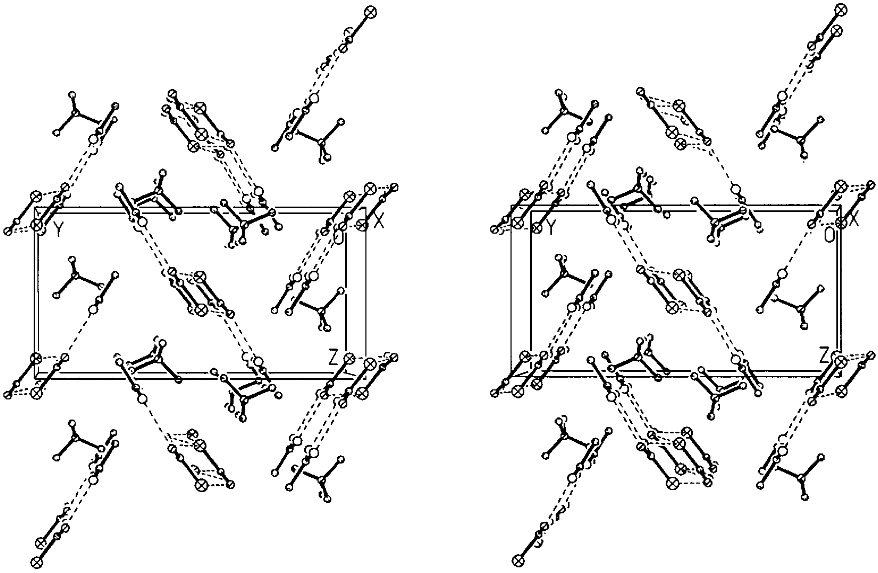

*Figure 9.* Stereodrawing of the crystal structure of **4**. The origin of the unit cell lies at the upper right corner, with *a* towards the reader, *b* pointing from right to left and *c* downwards. Broken lines represent hydrogen bonds, and atom types are distinguished by size and shading.

Table VI. Bond lengths for acetic acid, monomeric anion and dimeric anion

| | Dimeric anion | | | Monomeric | Acetic acid |
|---|---|---|---|---|---|
| | **2** | **3** ($z = 0$) | **3** ($z = 1/2$) | anion | chain |
| C═O | 1.218(3) | 1.200(3) | 1.217(2) | 1.230(5) | 1.24(2) |
| C—O | 1.284(3) | 1.278(3) | 1.278(3) | 1.262(5) | 1.29(2) |
| C—C | 1.498(4) | 1.457(3) | 1.467(3) | 1.504(6) | 1.54(2) |
| O· · ·H· · ·O | 2.445(4) | 2.467(4) | 2.434(4) | – | 2.61(2) |

depending on the stoichiometric ratio of thiourea to acetate ion and the modes of combination of thiourea molecules and dimeric acetate anions. Compound **1** (4 : 1) is a novel channel inclusion compound whereas **2** and **3** (2 : 2) have different layer-type structures, and **4** (1 : 1) is characterized by an anionic composite ribbon composed of a zigzag arrangement of thiourea molecules with acetate ions attached to both sides.

It is interesting to note that the singly hydrogen-bridged dimeric acetate anion is present in compounds **2** and **3**, and two different conformations co-exist in **3**. Its molecular dimensions are compared with those of crystalline acetic acid in Table VI. The most noteworthy trend is a decrease of the C═O bond length in the sequence acid chain, monomeric anion, dimeric anion and the shorter hydrogen bond length in the dimeric anion. The symmetric O· · ·H· · ·O hydrogen bond linking two acetate anions in the present complexes has an average length of 2.449(5)Å, which places it in the "very strong" category [28].

Although the inclusion compounds **2** and **3** both contain thiourea molecules and dimeric acetate anions as building blocks, different modes of combination are utilized in the construction of the resulting hydrogen-bonded host lattices. In compound **2**, the centrosymmetric thiourea dimeric units are alternately bridged by the acetate dimers to form an infinite $[((NH_2)_2CS)_2((CH_3CO_2)_2H)^-]_\infty$ ribbon (Figure 4), but the thiourea ribbons combine with the dimeric acetate anions to form puckered layers in **3** [Figures 6(a), 6(b)].

In comparing this series of compounds with the thiourea-bicarbonate [17], thiourea-nitrate [18], and thiourea-formate [29] inclusion compounds, it is noted that the $CH_3CO_2^-$ ion, unlike the $HCO_3^-$ ion, can only form acceptor hydrogen bonds with other potential donors and furthermore, unlike both $HCO_3^-$ and $NO_3^-$, it has only two oxygen atoms functioning as acceptors in the hydrogen-bonded host framework, and its hydrophobic methyl group must be accommodated. Therefore, the construction of a two- or three-dimensional host framework requires a higher thiourea/acetate molar ratio, as in the case in compound **1**, or the dimeric acetic anion necessarily takes the role of a building block as is the case in complexes **2** and **3**. The resulting ribbons generally adopt a twisted configuration so that the thiourea molecules can form additional donor hydrogen bonds with atoms in adjacent ribbons, or the more exposed oxygen atoms can form acceptor hydrogen bonds with nitrogen atoms of neighboring thiourea molecules. In the 1 : 1 complex **4** only a 'pesudo channel' arrangement of separate ribbons can be constructed from the thiourea and acetate building blocks.

## Acknowledgment

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