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Inclusion Compounds of Thiourea and Peralkylated Ammonium Salts. III. Hydrogen-Bonded Host Lattices Built of Thiourea and Nitrate Ions

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Abstract

The new inclusion complexes tetraethylammonium nitrate–thiourea (1:3), $(C_2H_5)_4N^+.NO_3^-.3(NH_2)_2CS$ (1), tetra-*n*-propylammonium nitrate–thiourea–water (1:3:1), $(n\text{-}C_3H_7)_4N^+.NO_3^-.3(NH_2)_2CS.H_2O$ (2), tetramethylammonium nitrate–thiourea (1:1), $(CH_3)_4N^+.NO_3^-.(NH_2)_2CS$ (3), tetra-*n*-propylammonium nitrate–thiourea (1:1), $(n\text{-}C_3H_7)_4N^+.NO_3^-.(NH_2)_2CS$ (4), and tetra-*n*-butylammonium nitrate–thiourea (1:1), $(n\text{-}C_4H_9)_4N^+.NO_3^-.(NH_2)_2CS$ (5) have been prepared and characterized by X-ray crystallography. Crystal data, Mo $K\alpha$: (1), space group $P\bar{1}$, $a = 10.300\,(2)$, $b = 14.704\,(3)$, $c = 15.784\,(4)$ Å, $\alpha = 75.30\,(3)$, $\beta = 86.98\,(3)$, $\gamma = 72.25\,(3)°$, $Z = 4$ and $R_F = 0.039$ for 5034 observed data; (2), space group $P2_1/n$, $a = 8.433\,(2)$, $b = 9.369\,(2)$, $c = 34.361\,(7)$ Å, $\beta = 91.01\,(3)°$, $Z = 4$ and $R_F = 0.050$ for 2475 observed data; (3), space group $Pnma$, $a = 15.720\,(3)$, $b = 8.218\,(2)$, $c = 8.709\,(2)$ Å, $Z = 4$ and $R_F = 0.073$ for 579 observed data; (4), space group $P2_1/n$, $a = 8.784\,(2)$, $b = 14.421\,(3)$, $c = 15.078\,(3)$ Å, $\beta = 92.31\,(3)°$, $Z = 4$ and $R_F = 0.046$ for 2507 observed data; (5), space group $Pna2_1$, $a = 19.934\,(3)$, $b = 12.680\,(2)$, $c = 9.092\,(3)$ Å, $Z = 4$ and $R_F = 0.047$ for 1646 observed data. In the crystal structure of (1) infinite chains each composed of an alternate arrangement of a twisted thiourea trimer and a nitrate ion are cross-linked to form a puckered layer and further hydrogen bonding between such layers leads to a channel host framework for accommodation of the cationic guests. In the crystal structure of (2) two independent thiourea molecules are used to construct a hydrogen-bonded puckered layer normal to the c axis, whereas the remaining thiourea molecule, together with the nitrate ion and water molecule, generate another puckered layer that is parallel to the first. Hydrogen bonding between these two types of layers gives rise to a channel system running parallel to the [100] direction and the cations are stacked regularly within each column. Compounds (3), (4) and (5) have closely related crystal structures in which the cations are separated by one-dimensional, infinitely extended thiourea–nitrate composite ribbons in a sandwich-like packing arrangement.

1. Introduction

Thiourea is known to form crystalline inclusion compounds with a range of guest molecules of appropriate size and shape (Takemota & Sonoda, 1984; Fetterly, 1964; Harris & Thomas, 1990; Harris, Smart & Hollingsworth, 1991; Harris, 1993; Mak & Zhou, 1992). With only a few exceptions (Otto, 1972; Hollingsworth, Santarsiero & Harris, 1994; Hollingsworth, Brown, Santarsiero, Huffman & Goss, 1994; Brown & Hollingsworth, 1995), inclusion compounds of this type crystallize in space group $P6_122$ or $P6_522$ and the host structure is built of thiourea molecules that are linked by hydrogen bonds to form helical ribbons, which are woven together to generate an array of parallel channels with a free diameter of ~ 6.1 Å (Tonelli, 1992; Schofield, Harris, Shannon & Rennie, 1993; Anderson, Calabrese, Tam & Williams, 1987).

Another well known class of inclusion compounds are the tetraalkylammonium salt hydrates, which were found to be clathrates with a rich variety of three-dimensional hydrogen-bonded host structures built of water molecules and anionic moieties such as halide ions (McMullan, Mak & Jeffrey, 1966; McLean & Jeffrey, 1967, 1968), CH_3COO^- (Mak, 1986) and $[B_5O_6(OH)_4]^-$ (Michael, Clemens, Juergen & Guenter, 1993).

Several years ago we reported the crystal structures of a series of thiourea–peralkylammonium halide complexes (Mak, 1990, part I of this series) in which 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 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···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 three thiourea bicarbonate complexes have been reported by us recently (Li & Mak, 1995, part II of this series). In the present study we chose the nitrate anion, which has been subjected to experimental studies, using tech-

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niques such as Raman spectrophotometry and X-ray scattering, on its hydrogen-bonding interactions with water molecules in aqueous solution (Rodgers & Plane, 1975; Caminiti, Licheri, Piccaluga & Pinna, 1978). The formation of hydrogen bonds between NO_3^- and H_2O has also been investigated by means of semiempirical and *ab initio* quantum mechanical methods (Shen, Xie, Schaefer & Deakyne, 1990; Lee, Keesee & Castleman, 1980; Howell, Sapse, Singman & Snyder, 1975). Furthermore, in the molecular inclusion complex [16-pyrimidinium crown-4]$(NO_3)_4$, one nitrate anion has been found to function as a guest species wedged between opposite pyrimidinium rings while interacting with two macrocyclic cations (Cramer *et al.*, 1991). In the present work we report the preparation and structural characterization of the following complexes that contain new types of thiourea–anion host lattices

$(C_2H_5)_4N^+.NO_3^-.3(NH_2)_2CS$ (1)
$(n\text{-}C_3H_7)N^+.NO_3^-.3(NH_2)_2CS.H_2O$ (2)
$(CH_3)_4N^+.NO_3^-.(NH_2)_2CS$ (3)
$(n\text{-}C_3H_7)_4N^+.NO_3^-.(NH_2)_2CS$ (4)
$(n\text{-}C_4H_9)_4N^+.NO_3^-.(NH_2)_2CS$. (5)

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 (Morrison & Boyd, 1992).

Each hydroxide and thiourea were mixed in molar ratios of 1:2, 1:3, 1:2, 1:2.5 and 1:3, respectively. A minimum quantity of water was used to dissolve the solid in each case and nitric acid (70%) was added to the solution in a 1:1 molar ratio for hydroxide:acid.

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 (1, 3 and 5) and small blocks (2 and 4).

Information concerning crystallographic data and structure refinement of the five compounds is summarized in Table 1. Intensities were collected using 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/PC* 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 Å) and allowed to ride on their respective parent atoms. The H atoms of the water molecule in (2) were located from a subsequent difference-Fourier synthesis. All H atoms were assigned appropriate isotropic temperature factors and included in the structure-factor calculations. Analytical expressions of atomic scattering factors were employed and anomalous dispersion corrections were incorporated (*International Tables for X-ray Crystallography*, 1974, Vol. IV). The refinement of the coordinates and anisotropic thermal parameters of the non-H atoms was carried out by the full-matrix least-squares method 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), (2) and (3)–(5) are listed in Tables 2, 3 and 4, respectively.*

3.1. *Crystal structure of* $(C_2H_5)_4N^+.NO_3^-.3(NH_2)_2CS$ *(1)*

A stereoview of the crystal structure of (1) along the [$\bar{1}$10] direction is presented in Fig. 1. The thiourea molecules and nitrate ions are arranged in a 3:1 ratio to build a channel-like host lattice and the tetraethylammonium cations are accommodated in a single column within each channel. The thiourea–anion lattice comprises parallel undulate layers connected by hydrogen bonds between some molecules which are oriented almost perpendicular to the layers and the molecules which have the same environment in a neighboring layer. The layer structure may be conveniently described with

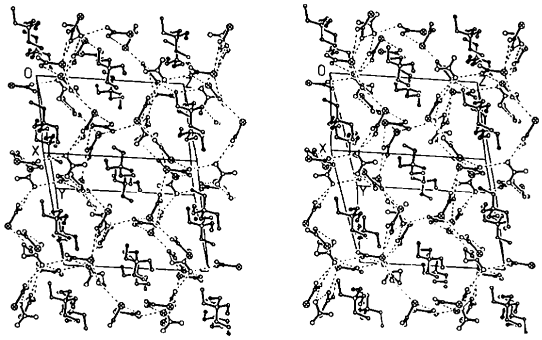

Fig. 1. Stereodrawing of the crystal structure of (1) showing the channels extending parallel to the [$\bar{1}$10] direction and the enclosed cations. Broken lines represent hydrogen bonds and atom types are distinguished by size and shading.

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* Lists of atomic coordinates, anisotropic displacement parameters and structure factors have been deposited with the IUCr (Reference: CR0511). 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)	(5)
Crystal data					
Chemical formula	$C_8H_{20}N^+.NO_3^-$.- $3CH_4N_2S$	$C_{12}H_{28}N^+.NO_3^-$.- $3CH_4N_2S.H_2O$	$C_4H_{12}N^+.NO_3^-$.- CH_4N_2S	$C_{12}H_{28}N^+.NO_3^-$.- CH_4N_2S	$C_{16}H_{36}N^+.NO_3^-$.- CH_4N_2S
Chemical formula weight	420.60	494.70	212.30	324.51	380.60
Cell setting	Triclinic	Monoclinic	Orthorhombic	Monoclinic	Orthorhombic
Space group	$P\bar{1}$	$P2_1/n$	$Pnma$	$P2_1/n$	$Pna2_1$
a (Å)	10.300 (2)	8.433 (2)	15.720 (3)	8.784 (2)	19.934 (3)
b (Å)	14.704 (3)	9.369 (2)	8.218 (2)	14.421 (3)	12.680 (2)
c (Å)	15.784 (4)	34.361 (7)	8.709 (2)	15.078 (3)	9.092 (3)
α (°)	75.30 (3)				
β (°)	86.98 (3)	91.01 (3)		92.31 (3)	
γ (°)	72.25 (3)				
V (Å^3)	2201.5 (7)	2714 (1)	1125.1 (6)	1908 (1)	2298.2 (9)
Z	4	4	4	4	4
D_x (Mg m^{-3})	1.269	1.211	1.253	1.129	1.100
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
No. of reflections for cell parameters	25	25	25	25	25
θ range (°)	6–14	6–14	6–14	6–14	6–14
μ (mm^{-1})	0.363	0.307	0.280	0.184	0.162
Temperature (K)	291	291	291	291	291
Crystal form	Plate	Block	Block	Block	Plate
Crystal size (mm)	0.44 × 0.40 × 0.22	0.45 × 0.42 × 0.38	0.42 × 0.40 × 0.32	0.60 × 0.58 × 0.50	0.62 × 0.54 × 0.52
Crystal color	Colorless	Colorless	Colorless	Colorless	Colorless
Data collection					
Diffractometer	Siemens $R3m/V$	Siemens $R3m/V$	Siemens $R3m/V$	Siemens $R3m/V$	Siemens $R3m/V$
Data collection method	ω scans	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)	ψ scan (Kopfmann & Huber, 1968)
T_{min}	0.875	0.772	0.841	0.600	0.845
T_{max}	0.921	0.804	0.905	0.666	0.889
Scan speed (° min^{-1})	2.0–60.0	3.0–60.0	2.0–29.3	2.0–29.3	4.0–29.0
Scan range (°) below $K_{\alpha 1}$ to above $K_{\alpha 2}$	0.6–0.6	0.6–0.6	0.6–0.6	0.6–0.6	0.6–0.6
No. of measured reflections	7718	5606	1948	3586	2368
No. of independent reflections	6464	4270	955	3361	2368
No. of observed reflections	5034	2475	579	2507	1646
Criterion for observed reflections	$\|F_o\|>3\sigma(\|F_o\|)$	$\|F_o\|>4\sigma(\|F_o\|)$	$\|F_o\|>4\sigma(\|F_o\|)$	$\|F_o\|>4\sigma(\|F_o\|)$	$\|F_o\|>4\sigma(\|F_o\|)$
R_{int}	0.021	0.0351	0.1077	0.0283	Unnecessary
θ_{max} (°)	23.5	24	22.5	22.5	26
Range of h, k, l	$-1 \rightarrow h \rightarrow 11$ $-15 \rightarrow k \rightarrow 15$ $-17 \rightarrow l \rightarrow 17$	$-1 \rightarrow h \rightarrow 9$ $0 \rightarrow k \rightarrow 10$ $-39 \rightarrow l \rightarrow 39$	$0 \rightarrow h \rightarrow 18$ $0 \rightarrow k \rightarrow 9$ $0 \rightarrow l \rightarrow 9$	$0 \rightarrow h \rightarrow 10$ $0 \rightarrow k \rightarrow 17$ $-17 \rightarrow l \rightarrow 17$	$0 \rightarrow h \rightarrow 24$ $-15 \rightarrow k \rightarrow 14$ $0 \rightarrow l \rightarrow 11$
No. of standard reflections	3	2	2	2	3
Frequency of standard reflections	Every 97 reflections	Every 98 reflections	Every 98 reflections	Every 98 reflections	Every 97 reflections
Intensity decay (%)	±1.2	±1.1	±1.1	1.1	1.1
Refinement					
Refinement on	F	F	F	F	F
R	0.039	0.050	0.073	0.046	0.047
wR	0.049	0.056	0.080	0.052	0.053
S	1.52	1.28	1.34	1.18	1.44
No. of reflections used in refinement	5034	2475	579	2507	1646
No. of parameters used	452	271	71	191	226
H-atom treatment	H atoms refined using a riding model	H atoms refined using a riding model	H atoms refined using a riding model	H atoms refined using a riding model	H atoms refined using a riding model
Weighting scheme	$w = 1/[\sigma^2(F_o) + 0.0003\|F_o\|^2]$	$w = 1/[\sigma^2(F_o) + 0.0005\|F_o\|^2]$	$w = 1/[\sigma^2(F_o) + 0.0001\|F_o\|^2]$	$w = 1/[\sigma^2(F_o) + 0.0001\|F_o\|^2]$	$w = 1/[\sigma^2(F_o) + 0.0004\|F_o\|^2]$
$(\Delta/\sigma)_{max}$	0.012	0.010	0.038	0.0	0.0
$\Delta\rho_{max}$ (e Å^{-3})	0.23	0.28	0.66	0.25	0.21
$\Delta\rho_{min}$ (e Å^{-3})	−0.22	−0.19	−0.29	−0.23	−0.13
Extinction method	None	None	None	None	None
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)	*International Tables for X-ray Crystallography* (1974, Vol. IV)

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

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

	x	y	z	$U_{\rm eq}$
Thiourea–bicarbonate host lattice				
S(1)	0.5987 (1)	0.4470 (1)	0.1363 (1)	0.071 (1)
C(1)	0.7001 (2)	0.4761 (2)	0.1995 (1)	0.045 (1)
N(1)	0.8320 (2)	0.4263 (1)	0.2129 (1)	0.054 (1)
N(2)	0.6501 (2)	0.5501 (1)	0.2387 (1)	0.053 (1)
S(2)	0.3219 (1)	0.6977 (1)	0.1984 (1)	0.050 (1)
C(2)	0.2763 (2)	0.7191 (2)	0.0911 (2)	0.042 (1)
N(3)	0.3312 (2)	0.6523 (1)	0.0462 (1)	0.056 (1)
N(4)	0.1849 (2)	0.8027 (1)	0.0511 (1)	0.055 (1)
S(3)	0.0391 (1)	0.9722 (1)	0.1705 (1)	0.065 (1)
C(3)	0.1704 (2)	0.9867 (2)	0.2207 (2)	0.048 (1)
N(5)	0.1509 (2)	1.0618 (2)	0.2582 (1)	0.061 (1)
N(6)	0.2960 (2)	0.9258 (2)	0.2240 (1)	0.061 (1)
S(4)	−0.0775 (1)	0.5362 (1)	0.3614 (1)	0.049 (1)
C(4)	0.0337 (2)	0.5863 (2)	0.2970 (1)	0.041 (1)
N(7)	0.1473 (2)	0.5304 (1)	0.2697 (1)	0.052 (1)
N(8)	0.0094 (2)	0.6841 (1)	0.2729 (1)	0.052 (1)
S(5)	0.1942 (1)	0.2806 (1)	0.3164 (1)	0.050 (1)
C(5)	0.2332 (2)	0.2629 (2)	0.4241 (1)	0.038 (1)
N(9)	0.1771 (2)	0.3320 (1)	0.4669 (1)	0.049 (1)
N(10)	0.3210 (2)	0.1791 (1)	0.4683 (1)	0.050 (1)
S(6)	0.4700 (1)	−0.0017 (1)	0.3600 (1)	0.043 (1)
C(6)	0.5687 (2)	0.0592 (2)	0.2928 (1)	0.039 (1)
N(11)	0.6881 (2)	0.0103 (1)	0.2674 (1)	0.054 (1)
N(12)	0.5276 (2)	0.1578 (1)	0.2651 (1)	0.049 (1)
N(15)	0.8327 (2)	0.2088 (1)	0.1720 (1)	0.047 (1)
O(1)	0.8450 (2)	0.1850 (1)	0.2530 (1)	0.063 (1)
O(2)	0.9078 (2)	0.2520 (1)	0.1253 (1)	0.064 (1)
O(3)	0.7415 (2)	0.1897 (1)	0.1361 (1)	0.058 (1)
N(16)	−0.3440 (2)	0.7670 (1)	0.3176 (1)	0.047 (1)
O(4)	−0.3739 (2)	0.7843 (2)	0.2410 (1)	0.099 (1)
O(5)	−0.4031 (2)	0.7239 (2)	0.3756 (1)	0.083 (1)
O(6)	−0.2474 (2)	0.7936 (1)	0.3405 (1)	0.051 (1)
Tetraethylammonium ion				
N(13)	0.2486 (2)	0.7472 (1)	0.5066 (1)	0.043 (1)
C(7)	0.0962 (2)	0.7747 (2)	0.5155 (2)	0.071 (1)
C(8)	0.0155 (3)	0.8407 (2)	0.4318 (2)	0.094 (1)
C(9)	0.3110 (2)	0.6859 (2)	0.5962 (2)	0.063 (1)
C(10)	0.4640 (3)	0.6507 (2)	0.6016 (2)	0.088 (1)
C(11)	0.2950 (2)	0.8383 (2)	0.4771 (2)	0.058 (1)
C(12)	0.2484 (3)	0.9112 (2)	0.5339 (2)	7.09 (1)
C(13)	0.2951 (2)	0.6890 (2)	0.4382 (2)	0.064 (1)
C(14)	0.2666 (3)	0.5894 (2)	0.4586 (2)	0.079 (1)
N(14)	0.2594 (2)	0.2436 (1)	0.0009 (1)	0.046 (1)
C(15)	0.4037 (2)	0.2136 (2)	−0.0316 (2)	0.065 (1)
C(16)	0.5032 (2)	0.1277 (2)	0.0296 (2)	0.085 (1)
C(17)	0.2564 (2)	0.2726 (2)	0.0870 (2)	0.055 (1)
C(18)	0.3144 (3)	0.3558 (2)	0.0851 (2)	0.080 (1)
C(19)	0.1785 (2)	0.3305 (2)	−0.0704 (2)	0.061 (1)
C(20)	0.0306 (2)	0.3742 (2)	−0.0516 (2)	0.079 (1)
C(21)	0.1984 (2)	0.1588 (2)	0.0178 (2)	0.052 (1)
C(22)	0.1892 (2)	0.1197 (2)	−0.0612 (2)	0.070 (1)

The exponent of the isotropic temperature factor 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)*

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

	x	y	z	$U_{\rm eq}$
Thiourea–nitrate–water host lattice				
S(1)	0.4611 (1)	0.3104 (1)	0.2374 (1)	0.053 (1)
C(1)	0.4524 (4)	0.3995 (3)	0.1942 (1)	0.047 (1)
N(1)	0.5841 (3)	0.4319 (3)	0.1757 (1)	0.057 (1)
N(2)	0.3172 (3)	0.4361 (3)	0.1779 (1)	0.066 (1)
S(2)	0.5525 (1)	0.8967 (1)	0.2778 (1)	0.063 (1)
C(2)	0.5447 (4)	0.7201 (4)	0.2675 (1)	0.047 (1)
N(3)	0.6749 (3)	0.6442 (3)	0.2627 (1)	0.059 (1)
N(4)	0.4089 (3)	0.6525 (3)	0.2646 (1)	0.066 (1)
S(3)	0.1768 (2)	0.9030 (1)	0.0415 (1)	0.085 (1)
C(3)	0.0437 (4)	0.7738 (4)	0.0331 (1)	0.059 (1)
N(5)	−0.0840 (4)	0.7939 (4)	0.0112 (1)	0.080 (1)
N(6)	0.0593 (4)	0.6456 (3)	0.0493 (1)	0.075 (1)
N(7)	0.4536 (4)	0.5641 (3)	0.0826 (1)	0.063 (1)
O(1)	0.3289 (3)	0.5627 (3)	0.1009 (1)	0.088 (1)
O(2)	0.5834 (3)	0.5611 (3)	0.0992 (1)	0.083 (1)
O(3)	0.4470 (4)	0.5686 (4)	0.0469 (1)	0.110 (1)
O(1*w*)	0.7701 (4)	0.5028 (3)	0.0228 (1)	0.099 (1)
Tetra-*n*-propylammonium ion				
N(8)	0.8076 (3)	0.5257 (3)	0.3847 (1)	0.045 (1)
C(4)	0.8825 (4)	0.5420 (3)	0.4249 (1)	0.054 (1)
C(5)	0.9777 (5)	0.6772 (4)	0.4315 (1)	0.081 (1)
C(6)	1.0281 (5)	0.6919 (4)	0.4733 (1)	0.087 (1)
C(7)	0.7185 (4)	0.3859 (3)	0.3843 (1)	0.051 (1)
C(8)	0.6430 (4)	0.3449 (4)	0.3455 (1)	0.069 (1)
C(9)	0.5584 (5)	0.2036 (4)	0.3489 (1)	0.083 (1)
C(10)	0.9331 (4)	0.5267 (4)	0.3535 (1)	0.056 (1)
C(11)	1.0520 (4)	0.4080 (4)	0.3560 (1)	0.074 (1)
C(12)	1.1754 (5)	0.4296 (5)	0.3254 (2)	0.105 (1)
C(13)	0.6972 (4)	0.6500 (3)	0.3758 (1)	0.055 (1)
C(14)	0.5716 (5)	0.6770 (4)	0.4053 (1)	0.082 (1)
C(15)	0.4651 (5)	0.7954 (4)	0.3932 (2)	0.110 (1)

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

reference to the hydrogen bonding scheme shown in Fig. 2 and Table 5.

As shown in Fig. 1, the channel is composed of highly undulate layers whose mean planes are positioned at $z = \frac{1}{4}$ and $\frac{3}{4}$. Each layer possesses two analogous types of infinite chains running through the structure in the [$\bar{1}$10] direction, one being generated by thiourea molecules C(1) [composed of atoms C(1), S(1), N(1) and N(2), and hereafter conveniently referred to as C(1)], C(2), C(3) with a nitrate anion N(15) [composed of atoms N(15), O(1), O(2) and O(3)] and the other by C(4), C(5) and C(6), together with another nitrate anion N(16) (Fig. 2). In each chain three independent thiourea molecules, connected sequentially in the order described, constitute a trimeric unit of which the terminal molecules, C(1) and C(3) or C(4) and C(6), are essentially coplanar, as the dihedral angle between the plane of molecule C(1) and the plane of molecule C(3) is 6.4°, and the relevant dihedral angle between molecules C(4) and C(6) is 6.1°. However, the middle thiourea molecule of each trimer is inclined with respect to the main plane of the chain: the dihedral angles between pairs of thiourea molecules in the sequence C(1), C(2), C(3) are 42.7 and 46.9°, and the corresponding dihedral angles for C(4), C(5), C(6) are 70.1 and 68.7°, respectively. The alternate arrangement of nitrate anions and thiourea trimers are consolidated by O···H—N hydrogen bonds to form a highly twisted chain, as shown by the torsion angles C(1)—N(1)···O(2)—N(15) = −63.5, C(3)—N(5)···O(1$^{\rm ii}$)—N(15$^{\rm ii}$) = −60.2, C(4)—N(8)···O(6)—N(16) = −54.4, C(6)—N(11)···O(6$^{\rm v}$)—N(16$^{\rm v}$) = 56.5°. The two types of twisted chains, lying side by side in an alternate arrangement and extending in the [$\bar{1}$10] direction, are linked by lateral 'chelating' N—H···O and N—H···S hydrogen bonds to form a puckered layer,

Table 4. *Fractional atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for (3), (4) and (5)*

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

	x	y	z	U_{eq}
(i) $(CH_3)_4N^+.NO_3^-.(NH_2)_2CS$ (3)				
Thiourea–nitrate host lattice				
S(1)	0.5407 (2)	1/4	−0.0454 (3)	0.072 (1)
C(1)	0.5135 (4)	1/4	0.1441 (8)	0.055 (1)
N(1)	0.5036 (3)	0.1119 (5)	0.2192 (5)	0.070 (1)
N(2)	0.3868 (5)	1/4	0.5551 (8)	0.082 (1)
O(1)	0.4191 (6)	0.1276 (8)	0.5220 (7)	0.186 (1)
O(2)	0.3220 (7)	1/4	0.6250 (12)	0.198 (1)
Tetramethylammonium ion				
N(3)	0.2439 (4)	1/4	1.0169 (7)	0.063 (1)
C(2)	0.2968 (4)	0.1013 (7)	0.9932 (8)	0.100 (1)
C(3)	0.1728 (6)	1/4	0.9106 (12)	0.103 (1)
C(4)	0.2115 (8)	1/4	1.1774 (10)	0.113 (1)
(ii) $(C_3H_7)_4N^+.NO_3^-.(NH_2)_2CS$ (4)				
Thiourea–nitrate host lattice				
S(1)	0.2533 (1)	0.5020 (1)	0.5390 (1)	0.061 (1)
C(1)	0.2453 (2)	0.5059 (1)	0.4265 (1)	0.052 (1)
N(1)	0.1135 (2)	0.5076 (1)	0.3803 (1)	0.063 (1)
N(2)	0.3705 (2)	0.5078 (2)	0.3799 (1)	0.073 (1)
N(3)	0.2304 (2)	0.4904 (1)	0.1477 (1)	0.060 (1)
O(1)	0.1225 (2)	0.4632 (2)	0.1900 (1)	0.108 (1)
O(2)	0.3335 (2)	0.5359 (1)	0.1854 (1)	0.079 (1)
O(3)	0.2412 (2)	0.4691 (1)	0.0690 (1)	0.084 (1)
Tetra-*n*-propylammonium ion				
N(4)	0.8448 (2)	0.8188 (1)	0.4122 (1)	0.043 (1)
C(2)	0.9374 (2)	0.8177 (1)	0.4998 (1)	0.047 (1)
C(3)	0.9572 (3)	0.7242 (2)	0.5437 (2)	0.071 (1)
C(4)	1.0468 (3)	0.7342 (2)	0.6311 (2)	0.075 (1)
C(5)	0.9215 (2)	0.7614 (1)	0.3424 (1)	0.054 (1)
C(6)	1.0762 (3)	0.7935 (2)	0.3171 (2)	0.077 (1)
C(7)	1.1352 (2)	0.7367 (3)	0.2436 (2)	0.118 (1)
C(8)	0.6885 (2)	0.7768 (2)	0.4220 (1)	0.054 (1)
C(9)	0.5886 (3)	0.8210 (2)	0.4890 (2)	0.072 (1)
C(10)	0.4443 (3)	0.7644 (3)	0.4954 (3)	0.103 (1)
C(11)	0.8332 (2)	0.9205 (1)	0.3850 (1)	0.045 (1)
C(12)	0.7547 (3)	0.9400 (2)	0.2957 (1)	0.057 (1)
C(13)	0.7454 (3)	1.0437 (2)	0.2816 (2)	0.075 (1)
(iii) $(C_4H_9)_4N^+.NO_3^-.(NH_2)_2CS$ (5)				
Thiourea–nitrate host lattice				
S(1)	0.0317 (1)	0.4990 (1)	0.3459	0.069 (1)
C(1)	−0.0484 (1)	0.4552 (1)	0.3429 (2)	0.052 (1)
N(1)	−0.0794 (1)	0.4362 (1)	0.2160 (2)	0.064 (1)
N(2)	−0.0825 (1)	0.4399 (1)	0.4649 (2)	0.071 (1)
N(3)	−0.2579 (1)	0.4324 (1)	0.2860 (2)	0.077 (1)
O(1)	−0.2255 (1)	0.4068 (2)	0.1756 (2)	0.117 (1)
O(2)	−0.2277 (1)	0.4437 (2)	0.4041 (2)	0.101 (1)
O(3)	−0.3178 (1)	0.4462 (2)	0.2840 (2)	0.127 (1)
Tetra-*n*-butylammonium ion				
N(4)	0.3369 (1)	0.7470 (1)	0.1946 (2)	0.048 (1)
C(2)	0.2698 (1)	0.6989 (1)	0.2379 (2)	0.056 (1)
C(3)	0.2189 (1)	0.7758 (2)	0.3013 (2)	0.067 (1)
C(4)	0.1553 (1)	0.7207 (2)	0.3413 (2)	0.087 (1)
C(5)	0.1046 (1)	0.7894 (2)	0.4119 (2)	0.104 (1)
C(6)	0.3274 (1)	0.8361 (1)	0.0842 (2)	0.051 (1)
C(7)	0.2883 (1)	0.8098 (2)	−0.0530 (2)	0.062 (1)
C(8)	0.2764 (1)	0.9063 (2)	−0.1465 (2)	0.070 (1)
C(9)	0.2339 (1)	0.8841 (2)	−0.2792 (2)	0.091 (1)
C(10)	0.3708 (1)	0.7945 (1)	0.3273 (2)	0.051 (1)
C(11)	0.3903 (1)	0.7191 (2)	0.4481 (2)	0.062 (1)
C(12)	0.4242 (1)	0.7783 (2)	0.5711 (2)	0.065 (1)
C(13)	0.4539 (1)	0.7074 (2)	0.6857 (2)	0.085 (1)
C(14)	0.3780 (1)	0.6584 (1)	0.1297 (2)	0.056 (1)
C(15)	0.4505 (1)	0.6847 (2)	0.0912 (2)	0.065 (1)
C(16)	0.4874 (1)	0.5868 (2)	0.0428 (2)	0.091 (1)
C(17)	0.5594 (1)	0.6051 (2)	−0.0009 (2)	0.114 (1)

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

Table 5. *Selected bond distances (Å), bond angles (°) and torsion angles (°) in the thiourea–anionic systems*

$(C_2H_5)_4N^+.NO_3^-.3(NH_2)_2CS$ (1)			
(i) Thiourea and nitrate molecules			
S(1)—C(1)	1.693 (3)	C(1)—N(1)	1.331 (3)
C(1)—N(2)	1.341 (4)	S(2)—C(2)	1.707 (3)
C(2)—N(3)	1.326 (4)	C(2)—N(4)	1.327 (3)
S(3)—C(3)	1.697 (3)	C(3)—N(5)	1.341 (4)
C(3)—N(6)	1.325 (3)	S(4)—C(4)	1.703 (2)
C(4)—N(7)	1.330 (3)	C(4)—N(8)	1.338 (3)
S(5)—C(5)	1.704 (3)	C(5)—N(9)	1.330 (3)
C(5)—N(10)	1.332 (2)	S(6)—C(6)	1.709 (3)
C(6)—N(11)	1.321 (3)	C(6)—N(12)	1.339 (3)
N(15)—O(1)	1.240 (3)	N(15)—O(2)	1.243 (3)
N(15)—O(3)	1.257 (4)	N(16)—O(4)	1.207 (3)
N(16)—O(5)	1.221 (3)	N(16)—O(6)	1.272 (4)
S(1)—C(1)—N(1)	121.6 (2)	S(1)—C(1)—N(2)	121.1 (2)
N(1)—C(1)—N(2)	117.3 (3)	S(2)—C(2)—N(3)	120.6 (2)
S(2)—C(2)—N(4)	120.6 (2)	N(3)—C(2)—N(4)	118.7 (2)
S(3)—C(3)—N(5)	120.8 (2)	S(3)—C(3)—N(6)	122.2 (3)
N(5)—C(3)—N(6)	117.1 (3)	S(4)—C(4)—N(7)	121.7 (2)
S(4)—C(4)—N(8)	120.4 (2)	N(7)—C(4)—N(8)	117.9 (2)
S(5)—C(5)—N(9)	121.3 (1)	S(5)—C(5)—N(10)	120.9 (2)
N(9)—C(5)—N(10)	117.8 (2)	S(6)—C(6)—N(11)	120.8 (2)
S(6)—C(6)—N(12)	120.9 (2)	N(11)—C(6)—N(12)	118.3 (2)
O(1)—N(15)—O(2)	121.4 (3)	O(1)—N(15)—O(3)	119.4 (2)
O(2)—N(15)—O(3)	119.2 (2)	O(4)—N(16)—O(5)	122.4 (3)
O(4)—N(16)—O(6)	120.0 (3)	O(5)—N(16)—O(6)	117.6 (2)
(ii) Hydrogen bonding			
N(3)···S(1)	3.449	N(3$^{\mathrm{iii}}$)···S(1)	3.496
N(2)···S(2)	3.405	N(6)···S(2)	3.408
N(7)···S(2)	3.410	N(8)···S(2)	3.414
N(4)···S(3)	3.437	N(1)···S(4$^{\mathrm{iv}}$)	3.470
N(9)···S(4)	3.433	N(2$^{\mathrm{v}}$)···S(4)	3.419
N(7)···S(5)	3.441	N(10)···S(6)	3.448
N(12)···S(5)	3.518	N(5$^{\mathrm{i}}$)···S(6)	3.490
N(6$^{\mathrm{i}}$)···S(6)	3.418	N(5$^{\mathrm{vi}}$)···O(1)	3.112
N(1)···O(2)	3.090	N(4$^{\mathrm{iii}}$)···O(3)	2.994
N(11)···O(3)	3.089	N(12)···O(3)	2.982
N(8)···O(6)	2.950	N(9$^{\mathrm{vii}}$)···O(6)	3.122
N(11$^{\mathrm{ii}}$)···O(6)	2.975		
C(1)—N(1)···S(4$^{\mathrm{iv}}$)	100.9	C(1)—N(1)···O(2)	110.4
C(1)—N(2)···S(4$^{\mathrm{iv}}$)	103.1	S(2)···N(2)···S(4$^{\mathrm{iv}}$)	136.4
C(2)—N(3)···S(1)	120.2	C(2)—N(3)···S(1$^{\mathrm{iii}}$)	157.5
S(1)···N(3)···S(1$^{\mathrm{iii}}$)	81.8	C(2)—N(4)···O(3$^{\mathrm{iii}}$)	100.5
C(2)—N(4)···S(3)	118.2	O(3$^{\mathrm{iii}}$)···N(4)···S(3)	136.1
C(3)—N(5)···S(6$^{\mathrm{viii}}$)	100.1	C(3)—N(5)···O(1$^{\mathrm{ii}}$)	112.1
S(6$^{\mathrm{vii}}$)···N(5)···O(1$^{\mathrm{ii}}$)	145.9	C(3)—N(6)···S(2)	115.6
C(3)—N(6)···S(6$^{\mathrm{viii}}$)	103.9	S(2)···N(6)···S(6$^{\mathrm{viii}}$)	131.1
C(4)—N(7)···S(2)	100.8	C(4)—N(7)···S(5)	117.6
S(2)···N(7)···S(5)	140.8	C(4)—N(8)···S(2)	100.4
C(4)—N(8)···O(6)	113.3	S(2)···N(8)···O(6)	143.6
C(5)—N(9)···S(4)	118.0	C(5)—N(9)···O(6$^{\mathrm{vii}}$)	99.8
S(4)···N(9)···O(6$^{\mathrm{vi}}$)	136.3	C(5)—N(10)···S(6)	118.7
C(5)—N(10)···S(6$^{\mathrm{ix}}$)	160.6	S(6)···N(10)···S(6$^{\mathrm{ix}}$)	80.7
C(6)—N(11)···O(3)	96.2	C(6)—N(11)···O(6$^{\mathrm{v}}$)	112.2
O(3)···N(11)···O(6$^{\mathrm{v}}$)	150.8	C(6)—N(12)···O(3)	100.7
C(6)—N(12)···S(5)	116.8	O(3)···N(12)···S(5)	139.9
N(15)—O(1)···N(5$^{\mathrm{v}}$)	95.2	N(15)—O(2)···N(1)	94.5
N(15)—O(3)···N(4$^{\mathrm{iii}}$)	107.8	N(15)—O(3)···N(11)	105.4
N(15)—O(3)···N(12)	109.6	N(4$^{\mathrm{iii}}$)···O(3)···N(11)	124.6
N(4$^{\mathrm{iii}}$)···O(3)···N(12)	142.5	N(11)···O(3)···N(12)	44.1
N(16)—O(6)···N(9$^{\mathrm{vi}}$)	103.5	N(16)—O(6)···N(8)	108.5
N(16)—O(6)···N(11$^{\mathrm{ii}}$)	107.8	N(9$^{\mathrm{vii}}$)···O(6)···N(8)	93.5
N(9$^{\mathrm{vi}}$)···O(6)···N(11$^{\mathrm{ii}}$)	129.8	N(8)···O(6)···N(11$^{\mathrm{ii}}$)	111.9
N(3)···S(1)—C(1)	110.2	N(3$^{\mathrm{iii}}$)···S(1)—C(1)	131.5
N(3)···S(1)···N(3$^{\mathrm{iii}}$)	98.2	N(2)···S(2)—C(2)	110.6
N(6)···S(2)—C(2)	104.0	N(2)···S(2)···N(6)	109.7
N(7)···S(2)—C(2)	93.7	N(8)···S(2)—C(2)	93.8
N(7)···S(2)···N(8)	39.1	N(4)···S(3)—C(3)	105.9
N(1$^{\mathrm{v}}$)···S(4)—C(4)	97.4	N(2$^{\mathrm{v}}$)···S(4)—C(4)	110.5
N(9)···S(4)—C(4)	93.1	N(1$^{\mathrm{v}}$)···S(4)···N(2$^{\mathrm{v}}$)	38.7
N(1$^{\mathrm{v}}$)···S(4)···N(9)	96.0	N(2$^{\mathrm{v}}$)···S(4)···N(9)	129.2
N(7)···S(5)—C(5)	93.3	N(10)···S(6)—C(6)	97.2

Table 5 (*cont.*)

N(5$^{\mathrm{i}}$)···S(6)—C(6)	108.9	N(6$^{\mathrm{i}}$)···S(6)—C(6)	105.3
N(10)···S(6)···N(5$^{\mathrm{i}}$)	86.0	N(5$^{\mathrm{i}}$)···S(6)···N(6$^{\mathrm{i}}$)	38.4
N(10)···S(6)···N(6$^{\mathrm{i}}$)	124.1		

C(2)—N(3)···S(1)—C(1)	−34.6	C(1)—N(2)···S(2)—C(2)	−37.4
C(3)—N(6)···S(2)—C(2)	69.6	C(4)—N(7)···S(2)—C(2)	−99.0
C(4)—N(8)···S(2)—C(2)	98.8	C(2)—N(4)···S(3)—C(3)	50.0
C(3)—N(5)···O(1$^{\mathrm{ii}}$)—N(15$^{\mathrm{ii}}$)	−60.2	C(5)—N(9)···S(4)—C(4)	--75.7
C(6)—N(12)···S(5)—C(5)	74.3	C(4)—N(7)···S(5)—C(5)	−74.6
C(5)—N(10)···S(6)—C(6)	68.8	C(1)—N(1)···O(2)—N(15)	−63.5
C(6)—N(11)···O(3)—N(15)	106.9	C(6)—N(12)···O(3)—N(15)	−96.6
C(4)—N(8)···O(6)—N(16)	−54.4		

$(C_3H_7)_4N^+.NO_3^-.3(NH_2)_2CS.H_2O$ (2)

(i) Thiourea and nitrate molecules

S(1)—C(1)	1.703 (4)	C(1)—N(1)	1.325 (4)
C(1)—N(2)	1.307 (5)	S(2)—C(2)	1.694 (4)
C(2)—N(3)	1.321 (4)	C(2)—N(4)	1.311 (4)
S(3)—C(3)	1.672 (4)	C(3)—N(5)	1.315 (5)
C(3)—N(6)	1.329 (5)	N(7)—O(1)	1.235 (5)
N(7)—O(2)	1.226 (4)	N(7)—O(3)	1.230 (5)

S(1)—C(1)—N(1)	120.4 (3)	S(1)—C(1)—N(2)	121.8 (3)
N(1)—C(1)—N(2)	117.8 (3)	S(2)—C(2)—N(3)	121.6 (3)
S(2)—C(2)—N(4)	121.2 (3)	N(3)—C(2)—N(4)	117.2 (3)
S(3)—C(3)—N(5)	122.4 (3)	S(3)—C(3)—N(6)	121.3 (3)
N(5)—C(3)—N(6)	116.2 (3)	O(1)—N(7)—O(2)	121.6 (3)
O(1)—N(7)—O(3)	119.0 (3)	O(2)—N(7)—O(3)	119.4 (3)

(ii) Hydrogen bonding

N(4)···S(1)	3.370	N(3$^{\mathrm{xii}}$)···S(1)	3.442
N(4$^{\mathrm{x}}$)···S(1)	3.451	N(1$^{\mathrm{xiii}}$)···S(2)	3.443
N(2$^{\mathrm{xi}}$)···S(2)	3.513	N(5$^{\mathrm{xiv}}$)···S(3)	3.455
N(2)···O(1)	2.912	N(6)···O(1)	2.962
N(1)···O(2)	2.901	O(1*w*)···O(3)	2.927
O(1*w*)···O(3$^{\mathrm{iii}}$)	3.063	N(5$^{\mathrm{iv}}$)···O(1*w*)	3.021
N(6$^{\mathrm{iv}}$)···O(1*w*)	2.914		

N(3$^{\mathrm{xii}}$)···S(1)—C(1)	104.2	N(4)···S(1)—C(1)	76.9
N(4$^{\mathrm{x}}$)···S(1)—C(1)	99.6	N(3$^{\mathrm{xii}}$)···S(1)···N(4$^{\mathrm{x}}$)	127.6
N(4$^{\mathrm{x}}$)···S(1)···N(4)	106.9	N(1$^{\mathrm{xiii}}$)···S(2)—C(2)	102.8
N(2$^{\mathrm{xi}}$)···S(2)—C(2)	99.2	N(1$^{\mathrm{xiii}}$)···S(2)···N(2$^{\mathrm{xi}}$)	125.4
N(5$^{\mathrm{xiv}}$)···S(3)—C(3)	111.0	C(1)—N(1)···S(2$^{\mathrm{xii}}$)	120.3
C(1)—N(1)···O(2)	122.7	C(1)—N(2)···S(2$^{\mathrm{x}}$)	124.2
O(2)···N(1)···S(2$^{\mathrm{xii}}$)	116.6	O(1)···N(2)···S(2$^{\mathrm{x}}$)	118.8
C(1)—N(2)···O(1)	117.0	C(2)—N(3)···S(1$^{\mathrm{xiii}}$)	119.9
C(2)—N(3)···S(1)	94.7	C(2)—N(4)···S(1)	111.2
S(1)···N(3)···S(1$^{\mathrm{xiii}}$)	144.3	S(1)···N(4)···S(1$^{\mathrm{xi}}$)	121.7
C(2)—N(4)···S(1$^{\mathrm{xi}}$)	125.5	C(3)—N(5)···O(1$^{\mathrm{v}}$)	97.8
C(3)—N(5)···S(3$^{\mathrm{xiv}}$)	126.5	C(3)—N(6)···O(1)	123.5
S(3$^{\mathrm{xiv}}$)···N(5)···O(1*w*$^{\mathrm{v}}$)	136.3	O(1)···N(6)···O(1*w*$^{\mathrm{v}}$)	134.6
C(3)—N(6)···O(1*w*$^{\mathrm{v}}$)	101.8	N(6)···O(1)—N(7)	110.3
N(2)···O(1)—N(7)	120.6	N(1)···O(2)—N(7)	115.0
N(2)···O(1)···N(6)	127.8	O(1*w*$^{\mathrm{iii}}$)···O(3)—N(7)	142.5
O(1*w*)···O(3)—N(7)	104.4	O(1*w*)···O(3)···O(1*w*$^{\mathrm{iii}}$)	106.2

C(1)—N(1)···S(2$^{\mathrm{xii}}$)—C(2$^{\mathrm{xii}}$)	61.4	C(1)—N(2)···O(1)—N(7)	9.5
C(1)—N(2)···S(2$^{\mathrm{x}}$)—C(2$^{\mathrm{x}}$)	−55.1	C(2)—N(3)···S(1$^{\mathrm{xiii}}$)—C(1$^{\mathrm{xiii}}$)	56.0
C(2)—N(4)···S(1)—C(1)	−85.8	C(2)—N(4)···S(1$^{\mathrm{xi}}$)—C(1$^{\mathrm{xi}}$)	−58.2
C(3)—N(5)···S(3$^{\mathrm{xiv}}$)—C(3$^{\mathrm{xiv}}$)	−5.2	C(3)—N(6)···O(1)—N(7)	−64.7
O(3)···O(1*w*)···N(6$^{\mathrm{iv}}$)—C(3$^{\mathrm{iv}}$)	−69.7	O(3)···O(1*w*)···N(5$^{\mathrm{iv}}$)—C(3$^{\mathrm{iv}}$)	127.7
C(1)—N(1)···O(2)—N(7)	−10.6		

$(CH_3)_4N^+.NO_3^-.(NH_2)_2CS$ (3)

(i) Thiourea and nitrate molecules

S(1)—C(1)	1.705 (8)	C(1)—N(1)	1.319 (6)
N(2)—O(1)	1.163 (8)	N(2)—O(2)	1.188 (13)

S(1)—C(1)—N(1)	120.6 (3)	N(1)—C(1)—N(1$^{\mathrm{xv}}$)	118.7 (6)
O(1)—N(2)—O(2)	120.1 (5)	O(1)—N(2)—O(1$^{\mathrm{xv}}$)	119.7 (10)

(ii) Hydrogen bonding

N(1)···O(1)	2.955	N(1$^{\mathrm{xvi}}$)···S(1)	3.409

C(1)—N(1)···O(1)	117.3	C(1)—N(1)···S(1$^{\mathrm{xvii}}$)	123.8
N(1$^{\mathrm{xvi}}$)···S(1)—C(1)	112.2	N(1)···O(1)—N(2)	117.0

C(1)—N(1)···O(1)—N(2)	10.7	C(1$^{\mathrm{xvi}}$)—N(1$^{\mathrm{xvi}}$)···S(1)—C(1)	−20.9

$(C_3H_7)_4N^+.NO_3^-.(NH_2)_2CS$ (4)

(i) Thiourea and nitrate molecules

S(1)—C(1)	1.696 (2)	C(1)—N(1)	1.327 (3)
C(1)—N(2)	1.329 (3)	N(3)—O(1)	1.228 (3)
N(3)—O(2)	1.237 (3)	N(3)—O(3)	1.233 (3)

S(1)—C(1)—N(1)	121.7 (2)	S(1)—C(1)—N(2)	121.9 (2)
N(1)—C(1)—N(2)	116.4 (2)	O(1)—N(3)—O(2)	119.8 (2)
O(1)—N(3)—O(3)	120.7 (2)	O(2)—N(3)—O(3)	119.4 (2)

(ii) Hydrogen bonding

N(1)···S(1$^{\mathrm{vii}}$)	3.493	N(2)···S(1$^{\mathrm{xviii}}$)	3.481
N(1)···O(1)	2.943	N(2)···O(2)	2.965

C(1)—N(1)···S(1$^{\mathrm{vii}}$)	127.8	C(1)—N(1)···O(1)	117.0
S(1$^{\mathrm{vii}}$)···N(1)···O(1)	113.1	C(1)—N(2)···S(1$^{\mathrm{xviii}}$)	127.5
C(1)—N(2)···O(2)	117.8	S(1$^{\mathrm{xviii}}$)···N(2)···O(2)	114.7
N(1$^{\mathrm{vii}}$)···S(1)—C(1)	110.3	N(2$^{\mathrm{xviii}}$)···S(1)—C(1)	110.7

C(1$^{\mathrm{vii}}$)—N(1$^{\mathrm{vii}}$)···S(1)—C(1)	−1.9	C(1)—N(2)···S(1$^{\mathrm{xviii}}$)—C(1$^{\mathrm{xviii}}$)	−2.3
C(1)—N(1)···O(1)—N(3)	−37.4	C(1)—N(2)···O(2)—N(3)	−44.0

$(C_4H_9)_4N^+.NO_3^-.(NH_2)_2CS$ (5)

(i) Thiourea and nitrate molecules

S(1)—C(1)	1.691 (2)	C(1)—N(1)	1.332 (2)
C(1)—N(2)	1.316 (3)	N(3)—O(1)	1.236 (3)
N(3)—O(2)	1.240 (2)	N(3)—O(3)	1.207 (3)

S(1)—C(1)—N(1)	120.8 (1)	S(1)—C(1)—N(2)	121.5 (2)
N(1)—C(1)—N(2)	117.7 (2)	O(1)—N(3)—O(2)	118.7 (2)
O(1)—N(3)—O(3)	122.8 (2)	O(2)—N(3)—O(3)	118.5 (2)

(ii) Hydrogen bonding

N(1$^{\mathrm{xix}}$)···S(1)	3.592	N(2$^{\mathrm{xx}}$)···S(1)	3.691
N(1)···O(1)	2.959	N(2)···O(2)	2.947

C(1)—N(1)···S(1$^{\mathrm{xx}}$)	130.3	C(1)—N(1)···O(1)	126.0
S(1$^{\mathrm{xx}}$)···N(1)···O(1)	100.0	C(1)—N(2)···S(1$^{\mathrm{xix}}$)	128.2
C(1)—N(2)···O(2)	110.3	S(1$^{\mathrm{xix}}$)···N(2)···O(2)	116.2
N(2$^{\mathrm{xx}}$)···S(1)—C(1)	108.2	N(1$^{\mathrm{xix}}$)···S(1)—C(1)	109.9
N(1)···O(1)—N(3)	112.3	N(2)···O(2)—N(3)	129.6

C(1)—N(1)···S(1$^{\mathrm{xx}}$)—C(1$^{\mathrm{xx}}$)	10.4	C(1)—N(2)···S(1$^{\mathrm{xix}}$)—C(1$^{\mathrm{xix}}$)	−4.8
C(1)—N(1)···O(1)—N(3)	12.1	C(1)—N(2)···O(2)—N(3)	18.8

Symmetry codes: (i) $x, y-1, z$; (ii) $x-1, 1+y, z$; (iii) $1-x, 1-y, -z$; (iv) $1+x, y, z$; (v) $x-1, y, z$; (vi) $1+x, y-1, z$; (vii) $-x, 1-y, 1-z$; (viii) $x, 1+y, z$; (ix) $1-x, -y, 1-z$; (x) $\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$; (xi) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; (xii) $\frac{3}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$; (xiii) $\frac{3}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; (xiv) $-x, 2-y, -z$; (xv) $x, \frac{1}{2}-y, z$; (xvi) $1-x, \frac{1}{2}+y, -z$; (xvii) $1-x, y-\frac{1}{2}, -z$; (xviii) $1-x, 1-y, 1-z$; (xix) $-x, 1-y, \frac{1}{2}+z$; (xxi) $-x, 1-y, z-\frac{1}{2}$. Standard deviations in hydrogen bond lengths and angles: (1) $\sigma(l) \simeq 0.005$ Å, $\sigma(\theta) \simeq 0.3°$; (2) $\sigma(l) \simeq 0.006$ Å, $\sigma(\theta) \simeq 0.4°$; (3) $\sigma(l) \simeq 0.009$ Å, $\sigma(\theta) \simeq 0.6°$; (4) $\sigma(l) \simeq 0.004$ Å, $\sigma(\theta) \simeq 0.3°$; (5) $\sigma(l) \simeq 0.007$ Å, $\sigma(\theta) \simeq 0.5°$.

as shown in Fig. 2. Finally, a channel framework is generated by N—H···O and N—H···S hydrogen bonds involving those thiourea molecules and nitrate anions that tilt out of the mean plane of each individual layer.

In the present host lattice the S atoms form different numbers of acceptor N—H···S hydrogen bonds: S(3) forms only one, S(1) and S(5) each forms two, S(4) and S(6) each has three, whereas S(2) has four, two of which being formed with adjacent molecules in the same chain and the other two with a single molecule in the neighboring chain. The lengths of all these hydrogen bonds are close to the expected value of ~ 3.431 Å, except that three are significantly longer at N(5$^{\mathrm{i}}$)···S(6) = 3.490, N(3$^{\mathrm{iii}}$)···S(1) = 3.496 and N(12)···S(5) = 3.518 Å.

The tetrahedral $(C_2H_5)_4N^+$ cations are well ordered and almost attain idealized 222 molecular symmetry. The average 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)° for cation N(13); N—C = 1.520 (4), C—C = 1.511 (5) Å, C—N—C = 109.5 (2) and N—C—C = 115.5 (2)° for cation N(14), respectively. Individual bond distances and angles are given in the supplementary data.* In the stereoview of the crystal structure illustrated in Fig. 1, the stacked columns of cations within each channel at $z = 1/2$ are formed by cations N(13) and those at $z = 0$ are formed by cations N(14), respectively.

3.2. *Crystal structure of* $(n\text{-}C_3H_7)_4N^+.NO_3^-.3(NH_2)_2CS.H_2O$ *(2)*

As shown in Fig. 3, the crystal structure of (2) also features one-dimensional channels that extend parallel to the *a* axial direction. This channel framework is built up of two types of layers interlinked by N—H···O(nitrate) hydrogen bonds. One layer is composed of thiourea molecules C(1) and C(2), which are alternately linked by pairs of N—H···S hydrogen bonds in a shoulder-to-shoulder fashion to form zigzag puckered ribbons running parallel to the *a* axis. The relevant torsion angles in each thiourea ribbon are: C(1)—N(1)···S(2^{xii})—C(2^{xii}) = 61.4, C(1)—N(2)···S(2^{x})—C(2^{x}) = −55.1, C(2)—N(3)···S(1^{xiii})—C(1^{xiii}) = 56.0 and C(2)—N(4)···S(1^{xi})—C(1^{xi}) = −58.2°, so that each S atom forms two acceptor hydrogen bonds with its neighbors. With these ribbons arranged side by side, half of the thiourea molecules [molecule C(2) and its symmetry equivalents] may be considered to constitute a main plane and the S(1) atom of molecule C(1) forms an acceptor hydrogen bond with the N(4) atom of molecule C(2) belonging to an adjacent ribbon to yield a puckered layer that is normal to the *c* axis (Fig. 4). On the other hand, the O(3) atom of the nitrate anion and the water molecule are involved in forming a cyclic centrosymmetric hydrogen-bonded $(NO_3^-)_2(H_2O)_2$ tetramer, as shown in Fig. 5. The third thiourea molecule C(3), together with

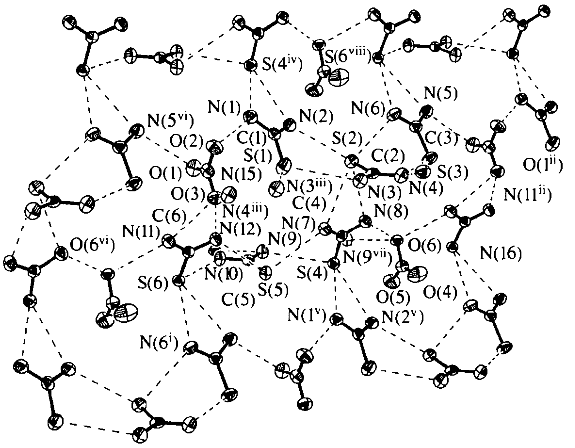

Fig. 2. The hydrogen-bonding scheme in the thiourea–anion host lattice of $(C_2H_5)_4N^+.NO_3^-.3(NH_2)_2CS$ (1). The atom labels correspond to those given in Tables 2 and 5, and the thermal ellipsoids are drawn at the 35% probability level. Broken lines represent hydrogen bonds. Symmetry codes: (i) $x, 1 + y, z$; (ii) $-x, 1 - y, 1 - z$; (iii) $x - 1, y, z$; (iv) $1 + x, y, z$; (v) $1 + x, y - 1, z$; (vi) $1 - x, 1 - y, -z$; (vii) $x - 1, 1 + y, z$; (viii) $x, y - 1, z$.

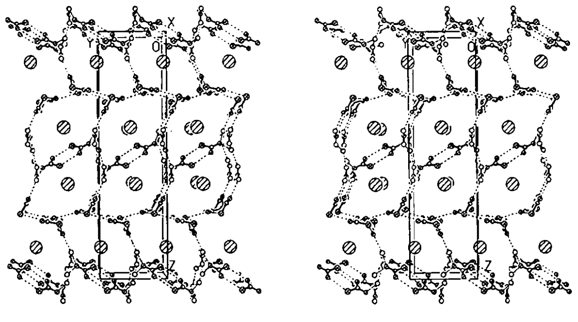

Fig. 3. Stereodrawing of the crystal structure of $(n\text{-}C_3H_7)_4N^+.NO_3^-.3(NH_2)_2CS.H_2O$ (2). The origin of the unit cell lies at the upper-right corner, with *a* towards the reader, *b* pointing from right to left and *c* downwards. For clarity the enclosed $(n\text{-}C_3H_7)_4N^+$ ions are represented by large stippled circles.

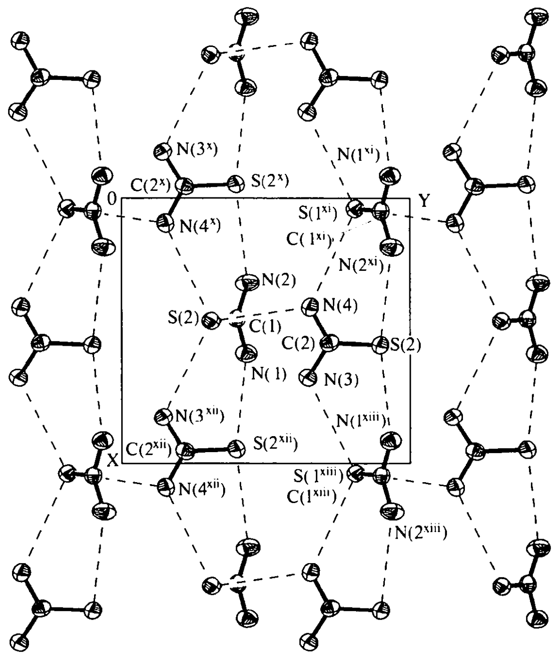

Fig. 4. Hydrogen-bonded layer in (2) formed by thiourea ribbons. The atom labels correspond to those given in Tables 3 and 5, and the thermal ellipsoids are drawn at the 35% probability level. Broken lines represent hydrogen bonds. Symmetry codes: (i) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$; (ii) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (iii) $\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (iv) $\frac{3}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$.

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* See deposition footnote on p. 990.

its centrosymmetrically related partner, are consolidated by a pair of N—H···S hydrogen bonds to yield a cyclic dimer. These dimers link with the tetramers by N—H···O(nitrate) hydrogen bonds to form the second type of highly puckered layer. The two types of layers are alternately stacked parallel to the (001) family of planes and further cross-linked by N—H···O hydrogen bonds to generate a three-dimensional network containing channels that run parallel to the [100] direction.

The stacked columns of well ordered tetrahedral (n-$C_3H_7)_4N^+$ cations are arranged in a single column within each channel to form a typical channel-like structure.

3.3. *Crystal structures of* $(CH_3)_4N^+.NO_3^-.(NH_2)_2CS$ *(3),* $(n\text{-}C_3H_7)_4N^+.NO_3^-.(NH_2)_2CS$ *(4) and* $(n\text{-}C_4H_9)_4N^+.NO_3^-.(NH_2)_2CS$ *(5)*

Compounds (3), (4) and (5) have essentially the same type of crystal structure as illustrated in Figs. 6, 7 and 8, respectively, although they belong to different space groups. 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 *b* axis in (3), the *a* axis in (4) or the *c* axis in (5). The ribbon is essentially planar in (4) and (5), as can be assessed by the relevant torsion angles: $C(1)—N(1)\cdots S(1^i)—C(1^i) = -1.9$, $C(1)—N(2)\cdots S(1^{ii})—C(1^{ii}) = -2.3°$ for (4), and the corresponding values for (5) are −5.8 and 10.6°. However, in structure (3) the ribbon is rather more undulatory, as can be verified by the value of the torsion angle between two adjacent thiourea molecules, $C(1)—N(1)\cdots S(1^{iii})—C(1^{iii}) = 20.9°$. Each thiourea molecule is further linked to a nitrate ion *via* two additional N—H···O donor hydrogen bonds that extend outward on either side of the ribbon, so that these ribbons can also be regarded as being constructed from a thiourea–anion dimeric building block. The orientation of the NO_3^- group with respect to the thiourea ribbon can be described by torsion angles $C(1)—N(1)\cdots O(1)—N(2) = 10.7$ for (3), $C(1)—N(1)\cdots O(1)—N(3) = -37.4$ and 13.2° for (4) and (5), respectively.

As shown in Fig. 9, the zipper-like ribbons are aligned side by side in an almost coplanar layer without any interaction between the two adjacent ribbons. The distances between the two are different for each structure according to the sizes of the cations, being 8.709 Å (length of the *c* axis) for structure (3), 15.078 Å (length

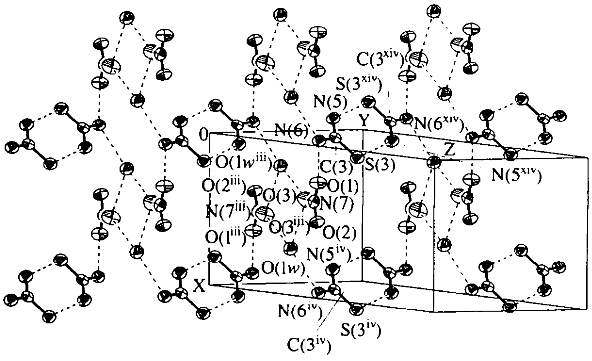

Fig. 5. Hydrogen-bonded layer in (2) formed by the cross-linkage of thiourea dimers and $(NO_3^-)_2(H_2O)_2$ tetramers. The atom labels correspond to those given in Tables 3 and 5, and the thermal ellipsoids are drawn at the 35% probability level. Broken lines represent hydrogen bonds. Symmetry codes: (i) $1 - x$, $1 - y$, $-z$; (ii) $1 + x$, y, z; (iii) $-x$, $2 - y$, $-z$.

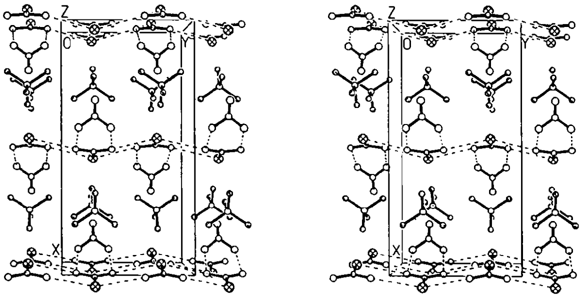

Fig. 6. Stereodrawing of the crystal structure of $(CH_3)_4N^+.NO_3^-.(NH_2)_2CS$ (3). The origin of the unit cell lies at the upper-left corner, with *a* downwards, *b* pointing from left to right and *c* towards the reader. Broken lines represent hydrogen bonds and atom types are distinguished by size and shading.

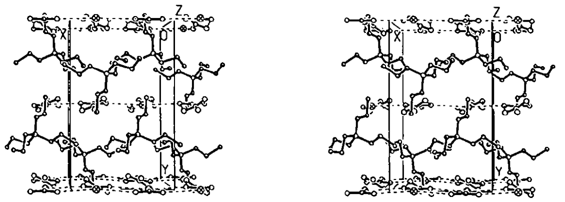

Fig. 7. Stereodrawing of the crystal structure of $(n\text{-}C_3H_7)_4N^+.NO_3^-.(NH_2)_2CS$ (4). The origin of the unit cell lies at the upper-right corner, with *a* pointing from right to left, *b* downwards and *c* towards the reader. Broken lines represent hydrogen bonds and atom types are distinguished by size and shading.

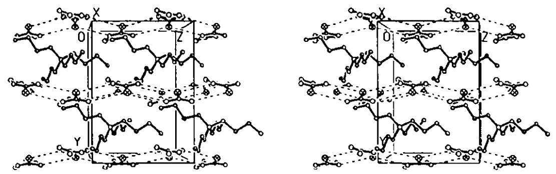

Fig. 8. Stereodrawing of the crystal structure of $(n\text{-}C_4H_9)_4N^+.NO_3^-.(NH_2)_2CS$ (5). The origin of the unit cell lies at the upper-left corner, with *a* towards the reader, *b* downwards and *c* pointing from left to right. Broken lines represent hydrogen bonds and atom types are distinguished by size and shading.

of the *c* axis) for structure (4) and 19.983 Å (length of the *a* axis) for structure (5), respectively.

The tetraalkylammonium cations are well ordered and have normal dimensions, of which the $(n\text{-}C_3H_7)_4N^+$ and $(n\text{-}C_4H_9)_4N^+$ cations nearly attain $\bar{4}2m$ (D_{2d}) conformation. These cations are separated by layers of the one-dimensional infinitely extended thiourea–nitrate composite ribbons in a sandwich-like packing arrangement (see Figs. 6, 7 and 8). Although the tetrabutylammonium ion is much larger than the tetrapropylammonium ion, the molecular volume of $(C_3H_7)_4N^+$ and $(C_4H_9)_4N^+$ being 221 and 287 Å^3, respectively (Mingos & Rohl, 1991; Gavezzotti, 1983), the separation between two ribbon layers in (5) ($b/2$ = 6.359) is smaller than that in structure (4) ($b/2$ = 7.211). This is caused by the different orientation of the cations with respect to the corresponding ribbon layers: in (5) the shortest symmetry axis of the tetrabutylammonium ion is almost parallel to the *b* axis (Fig. 8), but in (4) one pseudo-C_3 axis of the tetrapropylammonium ion is aligned in the *b* direction so that one alkyl leg penetrates into an adjacent ribbon layer (Fig. 7). Interestingly, (3) containing the smallest $(CH_3)_4N^+$ cation has the largest interlayer separation ($a/2$ = 7.860), which is caused by the out-of-plane attachment of the nitrate ions to the mean plane of each ribbon layer (Fig. 6).

3.4. *General structural features*

The present series of thiourea–quaternary ammonium nitrate complexes exhibit two distinctly different types of thiourea–anion lattices depending on the stoichiometric ratio of thiourea to nitrate ions. Compounds (1) and (2) (3:1) are novel channel inclusion compounds, whereas (3), (4) and (5) (1:1) are each characterized by an anionic composite ribbon composed of a zigzag arrangement of thiourea molecules with nitrate ions attached to both sides. The channel-type host structure of (1) and (2) can be compared with those of the classical thiourea inclusion compounds, in which the separation between the centers of two adjacent channels is ~ 9.3 Å, corresponding to an effective cross-sectional diameter of ~ 6.1 Å for the inclusion of guest molecules. On the other hand, the effective cross-sectional diameter of (1) is ~ 6.5 Å and the cross-section of a channel in the host lattice of (2) has an approximately elliptical shape (Fig. 3), with effective minor and major axes of 5.42 and 6.12 Å, respectively. The latter values are almost equal to the related values (5.22 and 6.02 Å) of the channel-type inclusion compound $(n\text{-}C_3H_7)_4N^+.NH_2CONHCO_2^-.3(NH_2)_2CO$, in which the cations are accommodated in the host lattice constructed from urea and allophanate building blocks (Mak, Yip & Li, 1995).

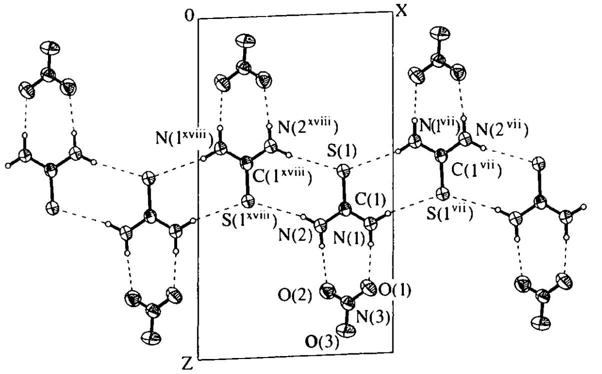

Fig. 9. The zipper-like composite ribbons in (4) formed by the attachment of nitrate ions to both sides of each thiourea ribbon. The atom labels correspond to those given in Tables 4 and 5, and the thermal ellipsoids are drawn at the 35% probability level. Broken lines represent hydrogen bonds. Symmetry codes: (i) $-x$, $1 - y$, $1 - z$; (ii) $1 - x$, $1 - y$, $1 - z$; (iii) $1 - x$, $1 - y$, $-z$; (iv) $-x$, $1 - y$, $-z$. A similar ribbon exists in the crystal structures of (3) and (5). In (3) the nitrate ion is attached to the thiourea ribbon in an out-of-plane fashion.

In comparing this series of compounds with the thiourea–bicarbonate inclusion compounds (Li & Mak, 1995, part II of this series), it is noted that the O atoms of the NO_3^- ion, unlike the HCO_3^- ion, can only form acceptor hydrogen bonds with other potential donors. Therefore, the construction of a two- or three-dimensional host framework requires a higher thiourea:nitrate molar ratio, with or without co-crystallized water molecules, as is the case in complexes (1) and (2). The resulting ribbons generally adopt a twisted configuration so that the thiourea molecules can form additional donor hydrogen bonds with atoms in adjacent ribbons. In the 1:1 complexes (3), (4) and (5) only a parallel arrangement of separate ribbons can be constructed from the thiourea and nitrate building blocks.

The versatility of thiourea as a key component in the construction of channel-type host lattices is clearly demonstrated by the occurrence of (i) the twisted thiourea trimeric units that are alternately bridged by the nitrate ions to from an infinite chain (Fig. 2), (ii) the cross-linkage of twisted thiourea ribbons to form a puckered layer (Fig. 4) and (iii) the assembly of centrosymmetric thiourea dimers and cyclic $(NO_3)_2(H_2O)_2$ tetramers into a puckered layer (Fig. 5).

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