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Tetra-*n*-butylammonium Chloride–Thiourea (1/2), a Layer-Type Inclusion Compound

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Abstract

The structure of a new layer-type inclusion compound, tetra-*n*-butylammonium chloride–thiourea (1/2), $[(^nC_4H_9)_4N^+.Cl^-].2[(NH_2)_2CS]$, is reported. The thiourea molecules and Cl^- ions form nearly planar layers with the ordered tetra-*n*-butylammonium ions sandwiched between them. The layers, which correspond to the (101) family of planes, result from parallel hydrogen-bonded thiourea ribbons that are cross-bridged by Cl^- anions.

Comment

Several years ago, we reported the crystal structures of an isomorphous series of ternary complexes $[(C_2H_5)_4N^+.X^-].(NH_2)_2CO.2H_2O$ (X = Cl, Br, CN) (Mak & McMullan, 1988) and a parallel study of a series of anhydrous adducts formed by thiourea and tetraalkylammonium halides (Mak, 1990). In the urea inclusion compounds, the cations are sandwiched between hydrogen-bonded urea–water–halide/pseudohalide puckered layers. However, in all four thiourea–halide lattices, 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; this results in an anionic framework or composite ribbon as a component in the crystal packing. As part of our ongoing investigation of the properties and molecular packing of adducts of thiourea/urea with peralkylated ammonium salts, the new adduct $[(^nC_4H_9)_4N^+.Cl^-].2[(NH_2)_2CS]$, (I), was prepared and characterized by single-crystal X-ray analysis.

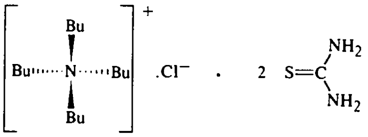
(I)

Fig. 1 shows a portion of a thiourea–chloride layer consolidated by hydrogen bonding. Both independent thiourea molecules have normal planar configurations and dimensions (see, for example, Mak & Lau, 1978; Truter, 1967; Elcombe & Taylor, 1968). Each thiourea molecule couples with two neighbors related to it by a 2_1 screw axis to generate a slightly buckled ribbon running parallel to the b axis; these two resulting ribbons are each nearly planar, as indicated by the torsion angles $C(1^{ii})—N(2^{ii})\cdots S(1)—C(1) = -15.2(4)$ and $C(1^{i})—N(1^{i})\cdots S(1)—C(1) = -9.6(5)°$ for one ribbon and $C(2^{iv})—N(3^{iv})\cdots S(2)—C(2) = -5.9$ and $C(2^{v})—N(4^{v})\cdots S(2)—C(2) = -2.2(5)°$ for the other. Adjacent ribbons are nearly coplanar and aligned in such a way that each has a thiourea molecule forming donor hydrogen bonds to the same Cl^- ion in a bidentate chelating mode. The resulting puckered layer, which corresponds to the (101) family of planes, is thus generated by hydrogen-bonded thiourea ribbons and bridging Cl^- ions. As shown in Fig. 1, an open octagon lies between a pair of Cl^- ions in each layer. This thiourea–halide lattice can be contrasted with that of the compound $[(^nC_4H_9)_3(CH_3)N^+.Cl^-].2[(NH_2)_2CS]$ (Mak, 1990) in which each thiourea ribbon is constructed from two independent thiourea molecules and the ribbons are arranged in a crisscross fashion.

A stereoview of the crystal structure is presented in Fig. 2. It can be seen that the ordered $(^nC_4H_9)_4N^+$ cations are sandwiched between hydrophilic layers with one alkyl leg pointing toward a neighboring octagonal void. The interlayer spacing is about 9.31 Å which is larger than the corresponding value for a similar layer structure with tetra-*n*-butylammonium cations accommodated in a urea–bicarbonate lattice $\{[(^nC_4H_9)_4N^+.HCO_3^-].3[(NH_2)_2CO]$ (triclinic, $1/a^*$ = 8.32 Å; Li & Mak, 1995)}, as may be expected in view of the larger size of the S atom.

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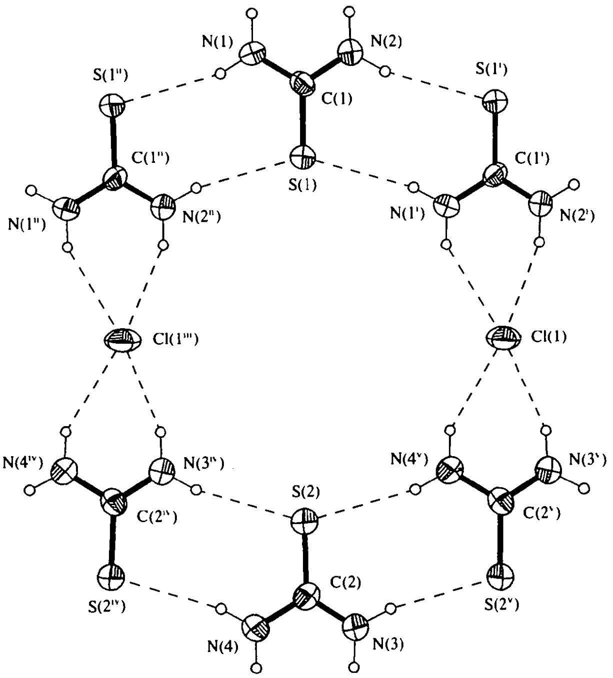

Fig. 1. Perspective view of a portion of a thiourea–chloride layer consolidated by hydrogen bonding in $[(^nC_4H_9)_4N^+.Cl^-].2[(NH_2)_2CS]$. The displacement ellipsoids are drawn at the 35% probability level.

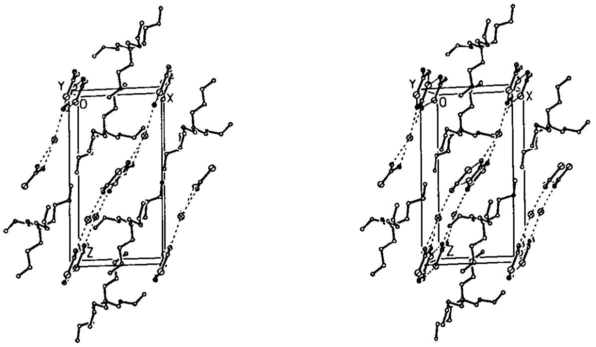

Fig. 2. Stereoview of the crystal structure of $[(^nC_4H_9)_4N^+.Cl^-].2[(NH_2)_2CS]$. The origin of the unit cell lies at the upper-left corner, with **a** pointing from left to right, **b** towards the reader, and **c** downwards.

Experimental

Tetra-*n*-butylammonium chloride and thiourea were mixed in a molar ratio of 1:2.5; a minimum quantity of water was added to dissolve the solid. 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 after ten days.

Crystal data

$C_{16}H_{36}N^+.Cl^-.2CH_4N_2S$
$M_r = 430.15$
Monoclinic
$P2_1$
$a = 8.754\,(2)$ Å
$b = 8.857\,(2)$ Å
$c = 16.748\,(3)$ Å
$\beta = 92.00\,(3)°$
$V = 1297.8\,(5)$ Å^3
$Z = 2$
$D_x = 1.101$ Mg m^{-3}
$D_m = 1.192$ Mg m^{-3}
D_m measured by flotation in *n*-hexane/CCl_4
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 5$–12.5°
$\mu = 0.320$ mm^{-1}
$T = 293\,(2)$ K
Transparent block
$0.48 \times 0.42 \times 0.32$ mm
Colorless

Data collection

Siemens *R*3*m*/*V* four-circle diffractometer
ω scans
Absorption correction: ψ scan (Kopfmann & Huber, 1968)
$T_{\min} = 0.752$, $T_{\max} = 0.908$
2108 measured reflections
1959 independent reflections
1618 observed reflections $[I > 2\sigma(I)]$
$R_{\rm int} = 0.0511$
$\theta_{\max} = 23.04°$
$h = 0 \rightarrow 9$
$k = 0 \rightarrow 9$
$l = -18 \rightarrow 18$
2 standard reflections monitored every 100 reflections intensity decay: 2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0501$
$wR(F^2) = 0.1476$
$S = 1.061$
1959 reflections
234 parameters
H atoms riding, C—H 0.96 Å
$w = 1/[\sigma^2(F_o^2) + (0.0911P)^2 + 0.3415P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.389$ e Å^{-3}
$\Delta\rho_{\min} = -0.280$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Absolute configuration: Flack (1983)
Flack parameter = −0.2 (2)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^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*	$U_{\rm eq}$
S(1)	0.4626 (2)	0.6349	0.53077 (8)	0.0731 (5)
C(1)	0.5862 (5)	0.6337 (9)	0.4552 (3)	0.0534 (12)
N(1)	0.6214 (6)	0.7619 (7)	0.4176 (3)	0.069 (2)
N(2)	0.6511 (7)	0.5097 (7)	0.4308 (3)	0.0645 (14)
S(2)	0.0148 (2)	0.6347 (3)	0.96320 (9)	0.0794 (5)
C2	−0.0590 (5)	0.6312 (9)	1.0549 (3)	0.0574 (12)
N(3)	−0.0913 (7)	0.5054 (7)	1.0922 (3)	0.066 (2)
N(4)	−0.0869 (7)	0.7606 (8)	1.0942 (3)	0.072 (2)
N5	0.3412 (5)	0.4046 (6)	0.2268 (3)	0.0589 (12)
C(3)	0.1948 (7)	0.3356 (8)	0.2609 (4)	0.069 (2)
C(4)	0.1796 (8)	0.3384 (10)	0.3479 (5)	0.084 (2)
C(5)	0.0299 (8)	0.2703 (12)	0.3711 (4)	0.099 (2)
C(6)	0.0070 (9)	0.2683 (16)	0.4598 (5)	0.142 (5)
C(7)	0.4826 (6)	0.3229 (8)	0.2616 (3)	0.0624 (15)
C(8)	0.4933 (7)	0.1584 (10)	0.2421 (4)	0.089 (2)

C(9)	0.6489 (8)	0.0899 (11)	0.2636 (4)	0.100 (3)
C(10)	0.7631 (9)	0.1179 (17)	0.2064 (5)	0.139 (4)
C(11)	0.3566 (7)	0.5678 (8)	0.2544 (4)	0.069 (2)
C(12)	0.2273 (8)	0.6723 (9)	0.2258 (5)	0.093 (2)
C(13)	0.2408 (11)	0.8251 (11)	0.2621 (6)	0.112 (3)
C(14)	0.1911 (14)	0.8353 (13)	0.3456 (7)	0.140 (4)
C(15)	0.3286 (7)	0.3914 (10)	0.1367 (4)	0.079 (2)
C(16)	0.4686 (7)	0.4367 (12)	0.0938 (4)	0.090 (2)
C(17)	0.4419 (10)	0.4174 (15)	0.0052 (4)	0.117 (3)
C(18)	0.5751 (12)	0.4107 (18)	−0.0449 (5)	0.148 (4)
Cl(1)	0.2045 (2)	0.1146 (3)	0.73726 (9)	0.0874 (6)

Table 2. *Selected geometric parameters (Å, °)*

S(1)—C(1)	1.694 (5)	S(2)—C2	1.688 (5)
C(1)—N(2)	1.308 (9)	C2—N(3)	1.312 (9)
C(1)—N(1)	1.340 (9)	C2—N(4)	1.347 (10)
N(2)—C(1)—N(1)	117.1 (4)	N(3)—C2—N(4)	116.4 (4)
N(2)—C(1)—S(1)	122.3 (5)	N(3)—C2—S(2)	123.0 (6)
N(1)—C(1)—S(1)	120.6 (5)	N(4)—C2—S(2)	120.6 (6)
$N(1^{i})\cdots S(1)$	3.500 (9)	$N(1^{i})\cdots Cl(1)$	3.321 (9)
$N(2^{ii})\cdots S(1)$	3.531 (9)	$N(2^{i})\cdots Cl(1)$	3.261 (9)
$N(3^{iii})\cdots S(2)$	3.483 (9)	$N(3^{iv})\cdots Cl(1)$	3.205 (9)
$N(4^{iv})\cdots S(2)$	3.514 (9)	$N(4^{iv})\cdots Cl(1)$	3.302 (9)
$N(1^{i})\cdots S(1)\cdots N(2^{ii})$	141.2 (5)	$Cl(1^{v})\cdots N(2^{ii})\cdots S(1)$	123.1 (5)
$N(2^{ii})\cdots Cl(1^{v})\cdots N(3^{iii})$	145.5 (5)	$Cl(1^{v})\cdots N(3^{iii})\cdots S(2)$	126.1 (5)
$N(3^{iii})\cdots S(2)\cdots N(4^{iv})$	141.1 (5)	$N(3^{iv})\cdots Cl(1)\cdots N(4^{iv})$	40.6 (5)
$N(4^{iv})\cdots Cl(1)\cdots N(1^{i})$	132.8 (5)	$N(4^{iv})\cdots Cl(1)\cdots N(1^{i})$	132.8 (5)
$Cl(1)\cdots N(1^{i})\cdots S(1)$	132.1 (5)	$N(1^{i})\cdots Cl(1)\cdots N(2^{i})$	40.1 (5)
$Cl(1)\cdots N(4^{iv})\cdots S(2)$	131.9 (5)		

Symmetry codes: (i) $1 - x, y - \frac{1}{2}, 1 - z$; (ii) $1 - x, \frac{1}{2} + y, 1 - z$; (iii) $-x, \frac{1}{2} + y, 2 - z$; (iv) $-x, y - \frac{1}{2}, 2 - z$; (v) $x, 1 + y, z$.

Data collection: Siemens diffractometer software. Cell refinement: Siemens diffractometer software. Data reduction: *SHELXTL/PC* (Sheldrick, 1990*a*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990*b*). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KH1101). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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2-(2,5-Dichlorophenylhydrazono)glutaric Acid and 2-(3,5-Dichlorophenylhydrazono)glutaric Acid

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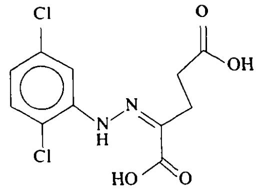
Abstract

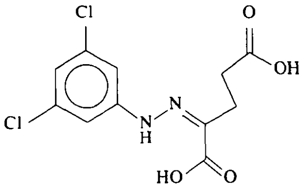
The title compounds, $C_{11}H_{10}Cl_2N_2O_4$, are constitutional isomers which exhibit similar molecular geometry. The configuration about the N=C bond is *E* in both molecules. The same packing pattern was found in both structures. Hydrogen-bonded dimers, formed around the inversion centres *via* O—H···O interactions of carboxyl groups, are connected into infinite chains. The intramolecular N—H···Cl hydrogen bond observed only in the 2,5-dichlorophenyl derivative contributes to the planarity of the molecule.

Comment

During the preparation of dihalogenated indole-3-acetic acids (Baldi, Slovin & Cohen, 1984), the title intermediates 2-(2,5-dichlorophenylhydrazono)glutaric acid, (1), and 2-(3,5-dichlorophenylhydrazono)glutaric acid, (2), were obtained. It is important that the two compounds should be identified unambiguously prior to bioactivity testing to avoid misinterpretation of bioassays. Hence, the crystal structures of the title compounds were solved and the results are reported here.



(1)



(2)

As part of a systematic study of the structure–activity correlations of the phytohormone indole-3-acetic acid, (3) (auxin), the series of monohalogenated and dihalogenated derivatives has been examined (Antolić, Kojić-Prodić, Tomić, Nigović, Magnus & Cohen, 1996; Nigović, Kojić-Prodić, Antolić, Tomić, Puntarec & Cohen, 1996). Our study includes structural character-