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2-Thiocytosinium chloride

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Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.003 Å
R factor = 0.037
wR factor = 0.107
Data-to-parameter ratio = 19.4

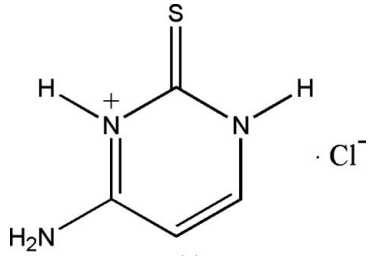
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound (systematic name: 4-amino-2-thioxo-2,3-dihydropyrimidin-1-ium chloride), $C_4H_6N_3S^+\cdot Cl^-$, has two cations and two anions in the asymmetric unit. The two cations have nearly the same structure. Both are nearly planar, the largest distance from the non-H atoms to the least-squares plane through the six-membered ring atoms being 0.010 (2) Å. Both Cl^- ions serve as hydrogen-bond acceptors. One thiocytosinium cation forms N—H···Cl hydrogen bonds with three Cl^- anions and the other one with four Cl^- ions, giving a sheet parallel to (101). There is also an N—H···S intermolecular hydrogen bond.

Comment

In order to acquire more information on the mechanism and the range of electron/hole transfer processes and the role of base stacking in DNA, we have studied charge transfer in well defined single crystals of nucleobases (Sanković *et al.*, 1988, 1996; Herak *et al.*, 1994, 1997; Matković-Čalogović & Sanković, 1999; Matković-Čalogović *et al.*, 2002).

A DNA model system was made by crystallizing 2-thiocytosine in hydrochloric acid. The structural differences between the title compound, (I), and 2-thiocytosine (Furberg & Jensen, 1970) are described here.



(I)

Both compounds crystallize in the monoclinic crystal system with two crystallographically independent molecules with $Z' = 2$. In general, the lengths of most of the corresponding bonds in the two crystallographically independent cations of (I) agree very well with those of thiocytosine. The largest difference is in the S2—C2 bond, which is longer in thiocytosine by 0.046 Å. Most of the angles are also closely similar, the largest difference being 5.85° for the S2—C2—N1 angle, which is greater in (I). Both of these differences involve S2, which forms two hydrogen bonds in thiocytosine, while in (I) it forms only one hydrogen bond. In both structures, the two crystallographically independent molecules or cations are nearly planar, the distances from the non-H atoms to the least-squares plane through the six-membered ring atoms being

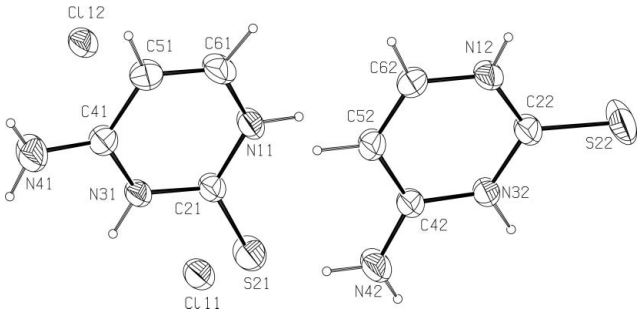


Figure 1
The asymmetric unit of the title compound, with the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

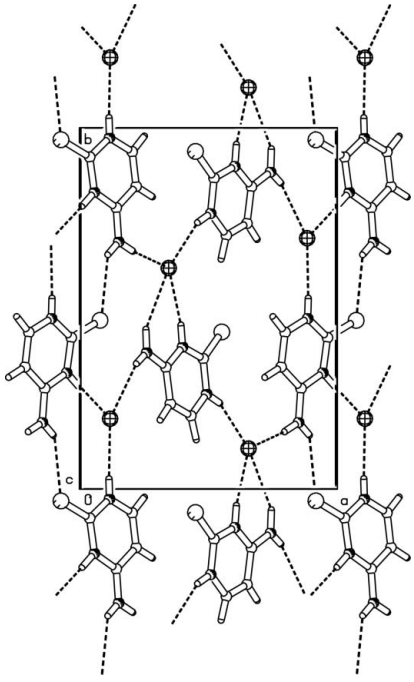


Figure 2
Packing of the ions in the unit cell. Hydrogen bonds are indicated by dashed lines.

0.043 and 0.010 (2) Å, respectively, for thiocytosine and (I). However, the chloride ions completely change the hydrogen-bond network, resulting in different packing in the unit cell of (I) (Fig. 2) in comparison with thiocytosine. There is greater similarity with the hydrogen-bond network in cytosine hydrochloride (Mandel, 1977), where each cytosinium cation forms hydrogen bonds with three Cl^- ions. In (I), the 2-thiocytosinium cations and Cl^- anions are linked together by eight hydrogen bonds into layers parallel to (101) (Table 2). Four parallel layers with the closest contacts are shown in Fig. 3. There is no stacking of the pyrimidine rings, but Cl11 forms contacts with atoms N31 and N32 [Cl11$\cdots$N31($x, \frac{1}{2}-y, z-\frac{1}{2}$) = 3.346 (2) Å and Cl11$\cdots$N32($1-x, 1-y, 1-z$) = 3.496 (2) Å] and Cl12 forms two contacts with atoms C41 and C42 [Cl12$\cdots$C41($-x, 1-y, -z$) = 3.359 (2) Å and Cl12$\cdots$C42($x, \frac{1}{2}-y, z-\frac{1}{2}$) = 3.382 (2) Å]. In guaninium dichloride (Matković-Čalogović & Sanković, 1999), the guaninium cation and chloride anions lie in a crystallographic mirror plane and are also interconnected by multiple

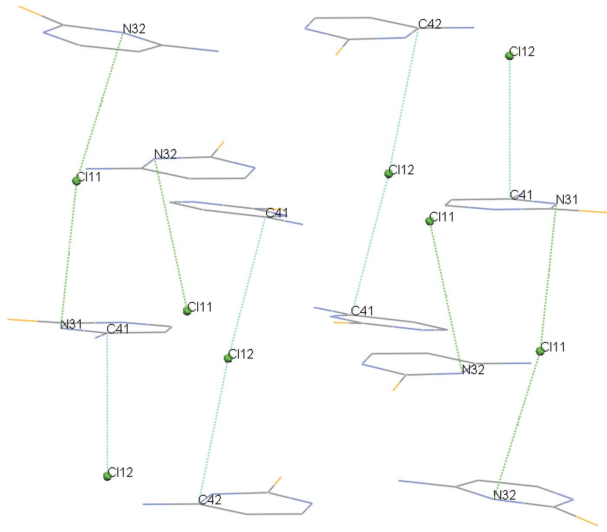


Figure 3
Four layers of (I) with the closest interlayer contacts shown as broken lines.

hydrogen bonds. The distance between the planes is 3.2905 Å. The distances in (I) are greater since it contains sulfur.

Experimental

Single crystals of (I) were grown from a saturated solution of 2-thiocytosine (Merck) in 1 *M* HCl (Kemika) by slow evaporation at 300 K. The vessel containing the solution was covered with a watch glass to reduce evaporation. Crystals were obtained after two months and these were stable when exposed to the atmosphere.

Crystal data

$C_4H_6N_3S^+\cdot Cl^-$
M_r = 163.63
Monoclinic, $P2_1/c$
a = 9.969 (2) Å
b = 13.8855 (18) Å
c = 10.2272 (17) Å
β = 98.704 (16)°
V = 1399.5 (4) Å^3
Z = 8
D_x = 1.553 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 52 reflections
θ = 10.4–17.3°
μ = 0.75 mm^{-1}
T = 295 (2) K
Prism, colourless
0.60 × 0.60 × 0.54 mm

Data collection

Philips PW1100 diffractometer updated by Stoe
ω–2θ scans
Absorption correction: integration (*X-RED*; Stoe & Cie, 1995)
T_{min} = 0.734, T_{max} = 0.772
7868 measured reflections
4084 independent reflections
2985 reflections with $I > 2\sigma(I)$
R_{int} = 0.042
θ_{max} = 30.0°
$h = -14 \rightarrow 14$
$k = -19 \rightarrow 19$
$l = -9 \rightarrow 14$
5 standard reflections
frequency: 90 min
intensity decay: 13.5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.107
S = 1.04
4084 reflections
211 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0465P)^2 + 0.5775P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.79 e Å^{-3}
$\Delta\rho_{min}$ = −1.04 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S21—C21	1.6537 (17)	C22—N12	1.351 (2)
C21—N11	1.360 (2)	C22—N32	1.361 (2)
C21—N31	1.368 (2)	N32—C42	1.360 (2)
C41—N41	1.311 (2)	C42—N42	1.305 (2)
C41—C51	1.417 (3)	C42—C52	1.420 (2)
C51—C61	1.346 (3)	C52—C62	1.339 (3)
C61—N11	1.362 (2)	C62—N12	1.364 (2)
S22—C22	1.6567 (19)		
N11—C21—N31	114.68 (15)	N12—C22—N32	115.59 (16)
N11—C21—S21	123.45 (13)	N12—C22—S22	122.58 (14)
N31—C21—S21	121.86 (13)	N32—C22—S22	121.81 (14)
C41—N31—C21	124.85 (15)	C42—N32—C22	124.32 (15)
N41—C41—N31	118.39 (17)	N42—C42—N32	119.35 (17)
N41—C41—C51	123.55 (17)	N42—C42—C52	122.75 (17)
N31—C41—C51	118.05 (16)	N32—C42—C52	117.89 (15)
C61—C51—C41	117.83 (17)	C62—C52—C42	117.92 (16)
C51—C61—N11	121.15 (17)	C52—C62—N12	121.25 (17)
C21—N11—C61	123.44 (16)	C22—N12—C62	123.00 (16)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N11—H11···Cl11	0.88 (3)	2.43 (3)	3.2567 (18)	157 (2)
N12—H12···Cl12^{i}	0.77 (3)	2.32 (3)	3.0822 (18)	174 (2)
N31—H31···Cl11^{ii}	0.85 (2)	2.38 (2)	3.2100 (16)	166 (2)
N32—H32···Cl12^{iii}	0.93 (3)	2.20 (3)	3.1270 (17)	178 (3)
N41—H411···Cl11^{ii}	0.89 (3)	2.68 (3)	3.474 (2)	150 (3)
N41—H412···Cl12^{iv}	0.77 (3)	2.61 (3)	3.340 (2)	160 (3)
N42—H421···S22^{v}	0.84 (3)	2.57 (3)	3.2344 (19)	137 (3)
N42—H422···Cl11^{vi}	0.89 (3)	2.42 (3)	3.293 (2)	171 (3)

Symmetry codes: (i) $x, y+1, z$; (ii) $-x+1, y+\frac{1}{2}, -z+\frac{3}{2}$; (iii) $-x, y+\frac{1}{2}, -z+\frac{1}{2}$; (iv) $x, y, z+1$; (v) $-x, y-\frac{1}{2}, -z+\frac{1}{2}$; (vi) $-x+1, y+\frac{1}{2}, -z+\frac{1}{2}$.

H atoms were found in a difference Fourier map and were refined isotropically. The deepest hole is 0.94 Å from atom S22. Five standard reflections show the continuous decay up to 13.5% during the data collection.

Data collection: *STADI4* (Stoe & Cie, 1995); cell refinement: *STADI4*; data reduction: *X-RED* (Stoe & Cie, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PLATON*.

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References

Furberg, S. & Jensen, L. H. (1970). *Acta Cryst.* B**26**, 1260–1268.
Herak, J. N., Sanković, K. & Hüttermann, J. (1994). *Int. J. Radiat. Biol.* **66**, 3–9.
Herak, J. N., Sanković, K., Krilov, D., Jaksić, M. & Hüttermann, J. (1997). *Radiat. Phys. Chem.* **50**, 141–148.
Mandel, N. S. (1977). *Acta Cryst.* B**33**, 1079–1082.
Matković-Čalogović, D., Bešić, E. & Sanković, K. (2002). *Acta Cryst.* C**58**, o568–o569.
Matković-Čalogović, D. & Sanković, K. (1999). *Acta Cryst.* C**55**, 467–469.
Sanković, K., Herak, J. N. & Krilov, D. (1988). *J. Mol. Struct.* **190**, 277–286.
Sanković, K., Krilov, D., Pranjić-Petrović, T., Hüttermann, J. & Herak, J. N. (1996). *Int. J. Radiat. Biol.* **70**, 603–608.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
Stoe & Cie, (1995). STADI4 (Version 1.05B) and *X-RED* (Version 1.05B). Stoe & Cie, Darmstadt, Germany.