Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

2-Thiocytosinium bromide

Krešimir Sanković,[a] Biserka Prugovečki[b] and Dubravka Matković-Čalogović[b]*

[a]Department of Biophysics, Faculty of Pharmacy and Biochemistry, University of Zagreb, Ante Kovačića 1, 10000 Zagreb, Croatia, and [b]Laboratory of General and Inorganic Chemistry, Department of Chemistry, Faculty of Science, University of Zagreb, Horvatovac 102a, 10000 Zagreb, Croatia

Correspondence e-mail: biserka@chem.pmf.hr

Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.004 Å
R factor = 0.032
wR factor = 0.082
Data-to-parameter ratio = 20.3

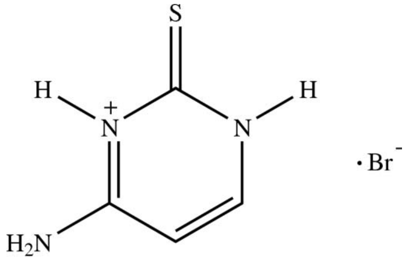
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 12 October 2005
Accepted 18 October 2005
Online 27 October 2005

The structure of the title compound (systematic name: 6-amino-2-thioxo-2,3-dihydropyrimidin-1-ium bromide), $C_4H_6N_3S^+\cdot Br^-$, has two 2-thiocytosinium cations and two Br^- anions in the asymmetric unit and is isostructural with 2-thiocytosinium chloride. Both six-membered rings are essentially planar. S atoms and Br^- anions serve as hydrogen-bond acceptors, forming sheets parallel to (101).

Comment

During our electron paramagnetic resonance investigations of the influence of ionizing radiation on DNA, we have used crystals of DNA bases as model systems (Sanković *et al.*, 1988, 1996, 2003; Herak *et al.*, 1994, 1997). It was found that not only spacial distribution and stacking of DNA bases, but also their environment in the crystal structure, plays a significant role in electron/hole long-range migration processes. We are currently investigating the influence of different base arrangements and different environments on the mechanism and range of these transfer processes. Knowledge of the crystal structure is essential for such a study (Matković-Čalogović & Sanković, 1999; Matković-Čalogović *et al.*, 2002; Prugovečki *et al.*, 2005). Here, we report the structure of 2-thiocytosinium bromide, (I), another model system appropriate for the study of long-range charge migration.



(I)

Compound (I) is isostructural with 2-thiocytosinium chloride (Prugovečki *et al.*, 2005) (Fig. 1), with two cations and two anions in the asymmetric unit. The replacement of Cl^- with Br^- ions does not change the hydrogen-bonding pattern. Both Br^- ions in (I) serve as hydrogen-bond acceptors. One thiocytosine cation forms hydrogen bonds of the type N—H···Br with three Br^- anions and the other with four Br^- ions, interconnecting them in the plane parallel to (101). There is also an intermolecular N42—H···S22 hydrogen bond (Table 2 and Fig. 2).

Parallel layers with closest contacts are shown in Fig. 3. Similar to what is observed in 2-thiocytosinium chloride, there is no stacking of the pyrimidine rings, but Br11 forms contacts

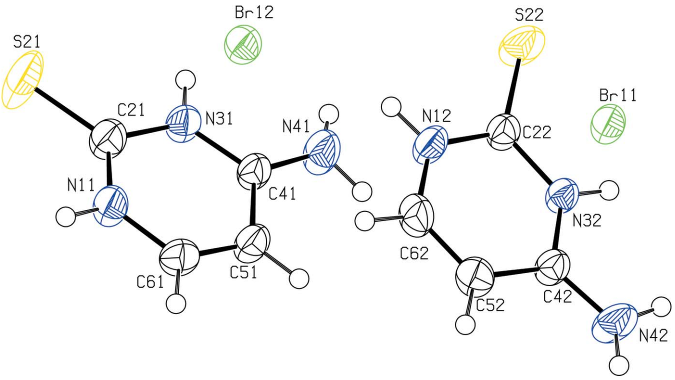


Figure 1
The asymmetric unit of (I), with the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

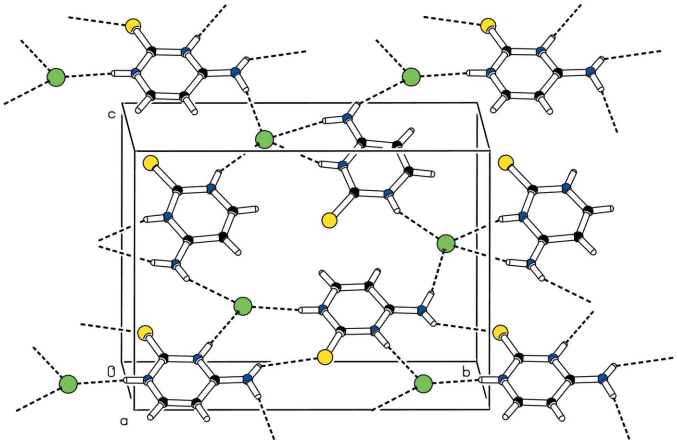


Figure 2
The packing of the ions of (I) in the unit cell. Hydrogen bonds are indicated by dashed lines.

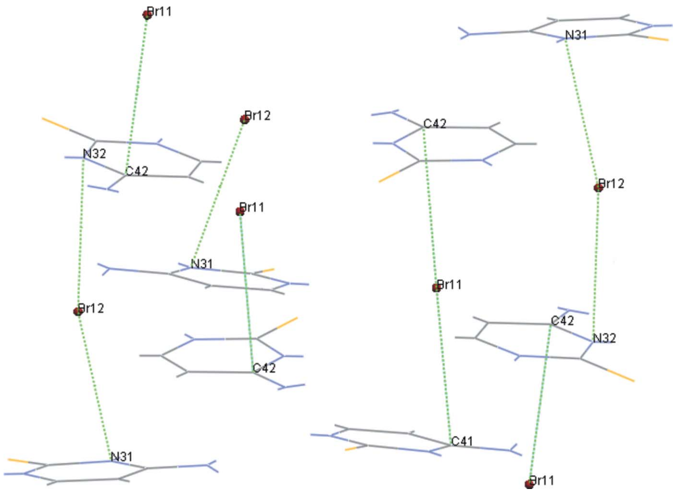


Figure 3
Four layers of (I), with the closest interlayer contacts shown as broken lines.

with atoms C41 and C42 [Br11$\cdots$C41($2-x$, $1-y$, $2-z$) 3.508 (2) and Br11$\cdots$C42($x, \frac{1}{2}-y, \frac{1}{2}+z$) 3.513 (2) Å], whereas Br12 forms contacts with atoms N31 and N32 [Br12$\cdots$N31(x, $\frac{1}{2}-y$, $-\frac{1}{2}+z$) 3.609 (2) and Br12$\cdots$N32($1-x$, $1-y$, $-z$) 3.443 (2) Å].

Experimental

Single crystals of (I) were grown from a saturated solution of 2-thiocytosine (Merck) in 1 *M* HBr (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 for months when exposed to the atmosphere.

Crystal data

$C_4H_6N_3S^+\cdot Br^-$
$M_r = 208.09$
Monoclinic, $P2_1/c$
$a = 10.1400$ (8) Å
$b = 14.2835$ (9) Å
$c = 10.4195$ (7) Å
$\beta = 97.480$ (6)°
$V = 1496.26$ (18) Å^3
$Z = 8$
$D_x = 1.847$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 1059 reflections
$\theta = 8.0$–26.0°
$\mu = 5.69$ mm^{-1}
$T = 295$ (2) K
Prism, colourless
0.38 × 0.34 × 0.17 mm

Data collection

Oxford Diffraction Xcalibur CCD diffractometer
ω scans
Absorption correction: numerical (CrysAlis RED; Oxford Diffraction, 2003)
$T_{\min} = 0.131$, $T_{\max} = 0.382$
19999 measured reflections
4311 independent reflections
3371 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.026$
$\theta_{\max} = 30.0°$
$h = -14 \rightarrow 14$
$k = -20 \rightarrow 19$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.082$
$S = 1.11$
4311 reflections
212 parameters
Only H-atom displacement parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0377P)^2 + 0.681P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 1.02$ e Å^{-3}
$\Delta\rho_{\min} = -1.00$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 1997)
Extinction coefficient: 0.0020 (3)

Table 1
Selected geometric parameters (Å, °).

C21—N11	1.346 (4)	C22—N12	1.354 (4)
C21—N31	1.363 (4)	C22—N32	1.364 (3)
C21—S21	1.650 (3)	C22—S22	1.647 (3)
C41—N41	1.299 (4)	C42—N42	1.309 (3)
C41—N31	1.349 (3)	C42—N32	1.360 (3)
C41—C51	1.428 (4)	C42—C52	1.415 (4)
C51—C61	1.330 (4)	C52—C62	1.339 (4)
C61—N11	1.360 (4)	C62—N12	1.360 (4)
N11—C21—N31	114.5 (2)	N32—C22—S22	121.7 (2)
N11—C21—S21	123.4 (2)	N42—C42—N32	118.8 (3)
N31—C21—S21	122.0 (2)	N42—C42—C52	123.5 (3)
N41—C41—N31	119.9 (2)	N32—C42—C52	117.7 (2)
N41—C41—C51	122.7 (3)	C62—C52—C42	118.1 (3)
N31—C41—C51	117.4 (2)	C52—C62—N12	121.0 (3)
C61—C51—C41	117.5 (2)	C21—N11—C61	123.4 (3)
C51—C61—N11	121.7 (3)	C41—N31—C21	125.4 (2)
N12—C22—N32	114.4 (2)	C22—N12—C62	123.8 (2)
N12—C22—S22	123.8 (2)	C42—N32—C22	125.0 (2)

Acta Cryst. (2005). E**61**, o3846–o3848 Sanković *et al.* • $C_4H_6N_3S^+\cdot Br^-$ **o3847**

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N11—H11⋯Br11^{i}	0.85 (3)	2.37 (3)	3.208 (2)	173 (2)
N12—H12⋯Br12^{ii}	0.83 (3)	2.62 (3)	3.377 (2)	153 (3)
N31—H31⋯Br11^{iii}	0.82 (4)	2.42 (4)	3.240 (2)	179 (6)
N32—H32⋯Br12	0.83 (4)	2.56 (4)	3.345 (2)	158 (3)
N41—H121⋯Br12^{iv}	0.85 (3)	2.60 (3)	3.427 (3)	166 (4)
N41—H122⋯S21^{v}	0.78 (4)	2.73 (4)	3.309 (3)	134 (4)
N42—H221⋯Br12	0.76 (4)	2.80 (4)	3.533 (3)	161 (3)
N42—H222⋯Br11^{vi}	0.87 (3)	2.58 (3)	3.415 (3)	162 (3)

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

H atoms were found in a difference Fourier map and refined isotropically. The highest peak and the deepest hole are 0.94 and 0.92 Å from S21, respectively.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2003); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2003); data reduction: *CrysAlis RED*; 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*.

The authors thank the Ministry of Science and Technology of the Republic of Croatia for financial support (grant Nos. 0006421 and 0119632).

References

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.

Matković-Čalogović, D., Bešić, E. & Sanković, K. (2002). *Acta Cryst.* C**58**, o568–o570.

Matković-Čalogović, D. & Sanković, K. (1999). *Acta Cryst.* C**55**, 467–469.

Oxford Diffraction (2003). *CrysAlis CCD* and *CrysAlis RED*. Versions 1.170. Oxford Diffraction Ltd., Abingdon, England.

Prugovečki, B., Matković-Čalogović, D. & Sanković, K. (2005). *Acta Cryst.* E**61**, o2706–02708.

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.

Sanković, K., Malinen, E., Herak, J. N., Medunić, Z. & Sagstuen, E. (2003). *Phys. Chem. Chem. Phys.* **5**, 1665–1670.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13

o3848 Sanković *et al.* • $C_4H_6N_3S^+ \cdot Br^-$ *Acta Cryst.* (2005). E**61**, o3846–o3848