Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

2-Thioureido-1*H*-benzimidazol-3-ium chloride monohydrate

C. N. Sundaresan,[a]* Dheeraj Kumar Singh[a] and Jagadeesh Babu Nanubolu[b]

[a]Department of Chemistry, Sri Sathya Sai Institute of Higher Learning, Brindavan Campus, Kadugodi, Bangalore 560 067, India, and [b]X-ray Crystallography Division, Indian Institute of Chemical Technology, Hyderabad 500 007, India
Correspondence e-mail: cnsundaresan@sssihl.edu.in

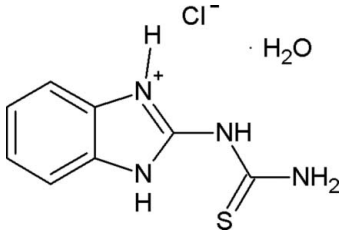
Received 20 March 2014; accepted 27 March 2014

Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.002 Å; R factor = 0.032; wR factor = 0.083; data-to-parameter ratio = 14.4.

In the title compound, $C_8H_9N_4S^+\cdot Cl^-\cdot H_2O$, the cation is approximately planar, with a dihedral angle of 7.71 (8)° between the mean planes of the benzoimidazole ring system and the thiourea unit. In the crystal, cations, anions and water molecules of crystallization are linked by O—H···Cl, N—H···O, N—H···Cl and N—H···S hydrogen bonds into a three-dimensional network. π–π stacking is observed between the benzene and imidazole rings of neighbouring molecules, the centroid–centroid distance being 3.5774 (11) Å.

Related literature

For the synthesis and biological activity of benzimidazoles, see: Siva & Subhash (2011); Sharghi *et al.* (2008); Refaat (2010); Puratchikody *et al.* (2008); Achar *et al.* (2010); Starcevic *et al.* (2007). For hydrogen-bond classification, see: Jeffrey *et al.* (1985).



Experimental

Crystal data

$C_8H_9N_4S^+\cdot Cl^+\cdot H_2O$
M_r = 246.72
Monoclinic, $P2_1/c$
a = 9.3027 (6) Å
b = 8.7038 (5) Å
c = 14.5503 (8) Å
β = 109.143 (3)°
V = 1112.97 (11) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.51 mm^{-1}
T = 293 K
0.33 × 0.19 × 0.14 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)
T_{min} = 0.850, T_{max} = 0.932
10318 measured reflections
1958 independent reflections
1818 reflections with $I > 2\sigma(I)$
R_{int} = 0.021

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.083
S = 1.07
1958 reflections
136 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.25 e Å^{-3}
$\Delta\rho_{min}$ = −0.20 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1*O*···Cl1^{i}	0.81	2.29	3.0991 (15)	179
O1—H2*O*···Cl1	0.87	2.30	3.1443 (14)	165
N1—H1*N*···O1	0.86	2.32	3.064 (2)	145
N1—H2*N*···O1^{ii}	0.86	2.14	3.000 (2)	174
N2—H2···O1	0.86	2.03	2.8667 (19)	165
N3—H3*N*···S1	0.80	2.43	3.0146 (14)	131
N4—H4*N*···Cl1	0.83	2.28	3.1055 (15)	175

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

Data collection: *SMART* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *publCIF* (Westrip, 2010).

We thank the Director, IICT, Hyderabad, India, for the XRD data and Dr Anand Solomon for his guidance.

Supporting information for this paper is available from the IUCr electronic archives (Reference: XU5781).

References

Achar, K. C., Hosamani, K. M. & Seetharamareddy, H. R. (2010). *Eur. J. Med. Chem.* **45**, 2048–2054.
Bruker (2001). *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2007). *SAINT* and *SMART*. Bruker AXS Inc., Madison, Wisconsin, USA.
Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
Jeffrey, G. A., Maluszynska, H. & Mitra, J. (1985). *Int. J. Biol. Macromol.* **7**, 336–348.
Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466–470.
Puratchikody, A., Nagalakshmi, G. & Doble, M. (2008). *Chem. Pharm. Bull.* **56**, 273–281.
Refaat, H. M. (2010). *Eur. J. Med. Chem.* **45**, 2949–2956.
Sharghi, H., Asemani, O. & Khalifeh, R. (2008). *Synth. Commun.* **38**, 1128–1136.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Siva, S. P. & Subhash, C. J. (2011). *Synth. Commun.* **41**, 729–735.
Starcevic, K., Kralj, M., Ester, K., Sabol, I., Grce, M., Pavelic, K. & Karminski-Zamola, G. (2007). *Bioorg. Med. Chem.* **15**, 4419–4426.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

supporting information

Acta Cryst. (2014). E**70**, o553 [doi:10.1107/S1600536814006837]

2-Thioureido-1*H*-benzimidazol-3-ium chloride monohydrate

C. N. Sundaresan, Dheeraj Kumar Singh and Jagadeesh Babu Nanubolu

S1. Comment

In recent years, Benzimidazole moiety has gained increased interest in drug industry worldwide, as an important pharmocophore exhibiting a wide spectrum of biological and pharmaceutical activities. They act as anti-HIV agents, anti cancer agents (Refaat, 2010), anti-tumor agents (Starcevic *et al.*, 2007), anti-microbial agents (Puratchikody *et al.*, 2008) analgesic and anti-inflammatory agents (Achar *et al.*, 2010).

The title compound (Fig. 1), $C_8H_{11}ClN_4OS$, crystallized in monoclinic $P2_1/c$ space group with Z=4 (Fig. 2). Two chloride anions and two water molecules are acting as a bridge to connect four molecules of the title compound which resulted in infinite layered type supramolecular architecture. The title compound is mainly stabilized by N—H···O, N—H···Cl, O—H···Cl intermolecular hydrogen bonding which resulted in generating of ring motifs R^2_2 (8) and R^1_2 (6). The intramolecular ring motif S^1_1 (6) is also generated due to intramolecular N—H···S hydrogen bonding.

S2. Experimental

A mixture of 5-amino-3*H*-1, 2, 4-dithiazole-3-thione (1.5 g, 0.01 mol) and *o*-phenylenediamine (1.08 g, 0.01 mol) in absolute ethanol (25 ml) was refluxed for 24 h. The solvent was removed under reduced pressure and the residue was treated with aqueous sodium hydroxide (1 N, 3 × 20 ml) and then filtered after an hour. The filtrate was adjusted to pH 5 by addition of aqueous hydrochloric acid (1 N) and left in a refrigerator overnight. The precipitate (1.8 g, 74%) was collected, washed with water and dried. The title compound was recrystallized from formic acid-propanol mixture to yield small crystals. The melting point was recorded as 248–251°C.

S3. Refinement

The structure refinements were performed by full-matrix least-squares on F2. The H positions bound to C atoms were calculated after each cycle of refinement using a riding model C—H = 0.93 Å and U_{iso}(H) = 1.2U_{eq}(C). H atoms bound to N and O atoms were located in a difference Fourier map and refined in riding mode, U_{iso}(H) = 1.2U_{eq}(N) and 1.5U_{eq}(O).

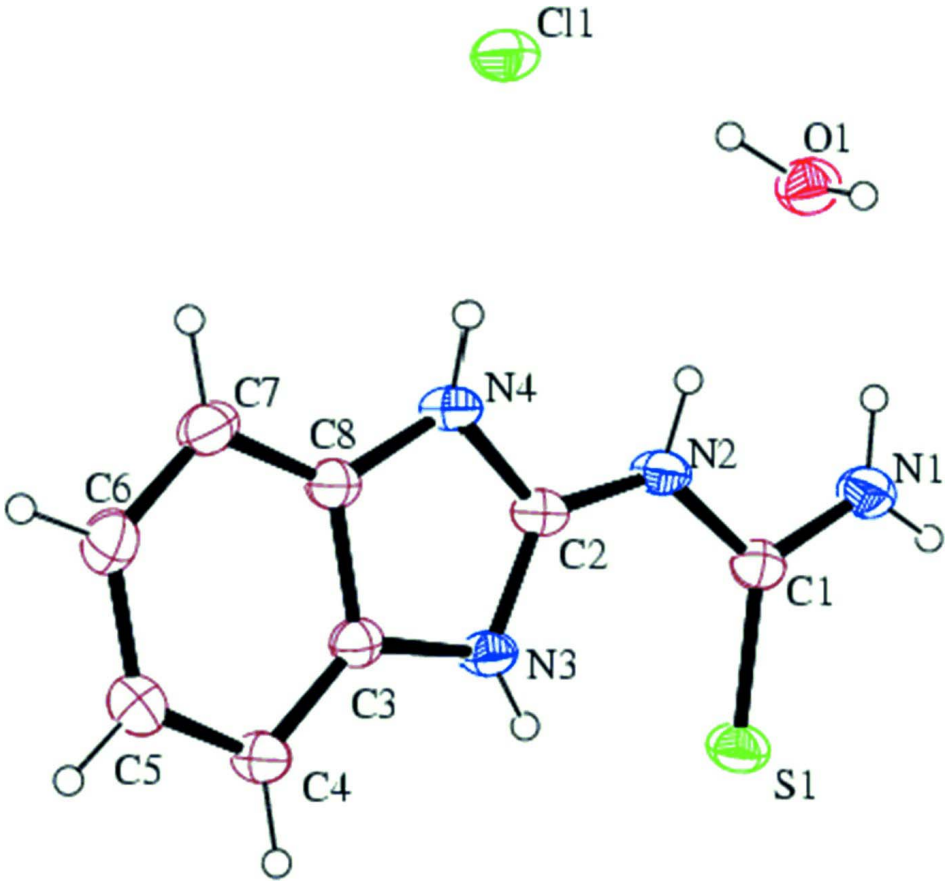


Figure 1

ORTEP diagram of 1-(1*H*-benzo[*d*]imidazol-2-yl)thiourea salt hydrate (Thermal ellipsoids are drawn at 30% probability level).

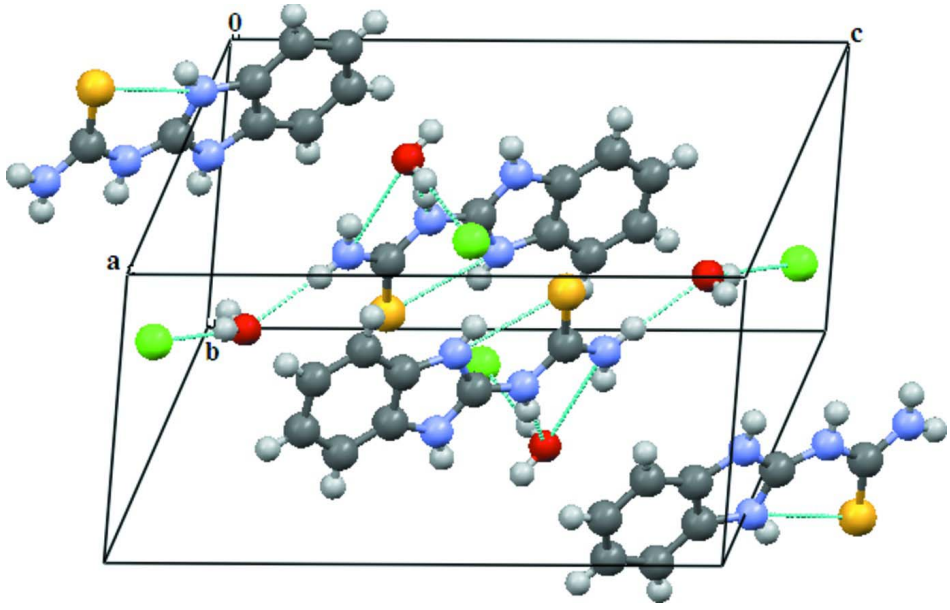


Figure 2

Crystal packing diagram of the title compound (I).

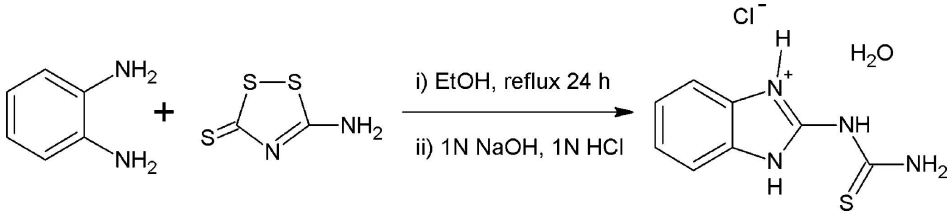


Figure 3

Synthetic scheme of the title compound (I).

2-Thioureido-1*H*-benzimidazol-3-ium chloride monohydrate

Crystal data

$C_8H_9N_4S^+·Cl^+·H_2O$
M_r = 246.72
Monoclinic, $P2_1/c$
Hall symbol: -p 2ybc
a = 9.3027 (6) Å
b = 8.7038 (5) Å
c = 14.5503 (8) Å
β = 109.143 (3)°
V = 1112.97 (11) Å^3
Z = 4
$F(000)$ = 512
D_x = 1.472 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 5220 reflections
θ = 2.3–27.9°
μ = 0.51 mm^{-1}
T = 293 K
Block, yellow
0.33 × 0.19 × 0.14 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)
T_{min} = 0.850, T_{max} = 0.932
10318 measured reflections
1958 independent reflections
1818 reflections with $I > 2\sigma(I)$

R_{int} = 0.021
θ_{max} = 25.0°, θ_{min} = 2.3°
h = −11→11
k = −10→10
l = −17→17

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.083
S = 1.07
1958 reflections
136 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.041P)^2 + 0.391P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.25 e Å^{-3}
$\Delta\rho_{min}$ = −0.20 e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	y	z	U_{iso}*/U_{eq}
S1	0.37873 (6)	−0.13735 (5)	0.83964 (4)	0.05278 (17)
N1	0.45104 (18)	0.12730 (17)	0.77931 (11)	0.0483 (4)
H1N	0.4545	0.2261	0.7785	0.058*
H2N	0.4887	0.0771	0.7417	0.058*
N2	0.33167 (17)	0.15159 (16)	0.89088 (10)	0.0415 (3)
H2	0.3490	0.2470	0.8830	0.050*
N3	0.25238 (15)	−0.02567 (16)	0.99381 (10)	0.0372 (3)
H3N	0.2705	−0.1020	0.9695	0.045*
N4	0.22253 (15)	0.22080 (16)	1.00973 (10)	0.0394 (3)
H4N	0.2267	0.3140	0.9987	0.047*
C1	0.38850 (19)	0.0537 (2)	0.83586 (12)	0.0383 (4)
C2	0.27105 (19)	0.11420 (19)	0.96112 (12)	0.0366 (4)
C3	0.19110 (17)	−0.00866 (19)	1.06892 (11)	0.0348 (4)
C4	0.1550 (2)	−0.1157 (2)	1.12841 (13)	0.0421 (4)
H4	0.1668	−0.2207	1.1213	0.051*
C5	0.1006 (2)	−0.0573 (2)	1.19897 (14)	0.0475 (4)
H5	0.0780	−0.1248	1.2418	0.057*
C6	0.0785 (2)	0.1001 (2)	1.20790 (14)	0.0487 (4)
H6	0.0397	0.1343	1.2556	0.058*
C7	0.11296 (19)	0.2059 (2)	1.14772 (13)	0.0445 (4)
H7	0.0972	0.3106	1.1531	0.053*
C8	0.17212 (18)	0.14874 (18)	1.07901 (12)	0.0360 (4)

O1	0.44295 (16)	0.44905 (15)	0.86287 (10)	0.0522 (3)
H1O	0.5262	0.4440	0.9042	0.078*
H2O	0.3841	0.4980	0.8881	0.078*
Cl1	0.23786 (6)	0.57314 (5)	0.98063 (4)	0.05321 (17)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0756 (4)	0.0303 (3)	0.0653 (3)	−0.0048 (2)	0.0406 (3)	−0.0053 (2)
N1	0.0621 (10)	0.0372 (8)	0.0539 (9)	−0.0004 (7)	0.0303 (8)	0.0037 (7)
N2	0.0569 (9)	0.0264 (7)	0.0446 (8)	−0.0004 (6)	0.0210 (7)	0.0028 (6)
N3	0.0462 (8)	0.0258 (7)	0.0404 (7)	0.0011 (6)	0.0152 (6)	−0.0025 (6)
N4	0.0479 (8)	0.0243 (7)	0.0456 (8)	0.0015 (6)	0.0150 (6)	0.0010 (6)
C1	0.0400 (9)	0.0361 (9)	0.0372 (8)	−0.0004 (7)	0.0104 (7)	0.0009 (7)
C2	0.0411 (9)	0.0288 (8)	0.0372 (8)	0.0000 (7)	0.0092 (7)	0.0006 (7)
C3	0.0347 (8)	0.0307 (8)	0.0371 (8)	0.0004 (6)	0.0094 (7)	−0.0016 (7)
C4	0.0455 (9)	0.0320 (9)	0.0489 (10)	0.0001 (7)	0.0156 (8)	0.0012 (7)
C5	0.0490 (10)	0.0459 (10)	0.0513 (11)	−0.0029 (8)	0.0214 (9)	0.0050 (8)
C6	0.0484 (10)	0.0511 (11)	0.0529 (11)	0.0017 (8)	0.0248 (9)	−0.0047 (9)
C7	0.0445 (10)	0.0356 (9)	0.0531 (10)	0.0049 (7)	0.0156 (8)	−0.0057 (8)
C8	0.0358 (8)	0.0313 (9)	0.0389 (9)	0.0001 (6)	0.0096 (7)	0.0001 (7)
O1	0.0616 (8)	0.0418 (7)	0.0558 (8)	0.0010 (6)	0.0227 (6)	−0.0045 (6)
Cl1	0.0654 (3)	0.0333 (3)	0.0646 (3)	0.0053 (2)	0.0264 (2)	0.0047 (2)

Geometric parameters (Å, º)

S1—C1	1.6673 (18)	C3—C4	1.386 (2)
N1—C1	1.319 (2)	C3—C8	1.395 (2)
N1—H1N	0.8607	C4—C5	1.382 (3)
N1—H2N	0.8592	C4—H4	0.9300
N2—C2	1.359 (2)	C5—C6	1.397 (3)
N2—C1	1.387 (2)	C5—H5	0.9300
N2—H2	0.8606	C6—C7	1.379 (3)
N3—C2	1.339 (2)	C6—H6	0.9300
N3—C3	1.396 (2)	C7—C8	1.382 (2)
N3—H3N	0.7964	C7—H7	0.9300
N4—C2	1.332 (2)	O1—H1O	0.8112
N4—C8	1.393 (2)	O1—H2O	0.8651
N4—H4N	0.8304		
C1—N1—H1N	121.3	C4—C3—N3	131.46 (15)
C1—N1—H2N	120.4	C8—C3—N3	106.54 (14)
H1N—N1—H2N	118.4	C5—C4—C3	116.06 (16)
C2—N2—C1	128.15 (14)	C5—C4—H4	122.0
C2—N2—H2	118.3	C3—C4—H4	122.0
C1—N2—H2	113.1	C4—C5—C6	122.05 (18)
C2—N3—C3	108.39 (14)	C4—C5—H5	119.0
C2—N3—H3N	122.0	C6—C5—H5	119.0

C3—N3—H3N	129.5	C7—C6—C5	121.59 (17)
C2—N4—C8	108.90 (13)	C7—C6—H6	119.2
C2—N4—H4N	122.2	C5—C6—H6	119.2
C8—N4—H4N	128.9	C6—C7—C8	116.69 (17)
N1—C1—N2	113.04 (15)	C6—C7—H7	121.7
N1—C1—S1	123.02 (14)	C8—C7—H7	121.7
N2—C1—S1	123.94 (13)	C7—C8—N4	132.05 (15)
N4—C2—N3	109.79 (15)	C7—C8—C3	121.58 (16)
N4—C2—N2	121.94 (15)	N4—C8—C3	106.37 (14)
N3—C2—N2	128.26 (15)	H1O—O1—H2O	107.1
C4—C3—C8	121.98 (16)		

C2—N2—C1—N1	−174.63 (16)	C3—C4—C5—C6	2.0 (3)
C2—N2—C1—S1	5.7 (3)	C4—C5—C6—C7	−1.3 (3)
C8—N4—C2—N3	1.18 (19)	C5—C6—C7—C8	−0.8 (3)
C8—N4—C2—N2	−177.76 (15)	C6—C7—C8—N4	−177.98 (17)
C3—N3—C2—N4	−1.16 (18)	C6—C7—C8—C3	2.1 (2)
C3—N3—C2—N2	177.68 (16)	C2—N4—C8—C7	179.38 (17)
C1—N2—C2—N4	178.93 (15)	C2—N4—C8—C3	−0.71 (18)
C1—N2—C2—N3	0.2 (3)	C4—C3—C8—C7	−1.5 (3)
C2—N3—C3—C4	−177.73 (17)	N3—C3—C8—C7	179.93 (15)
C2—N3—C3—C8	0.69 (18)	C4—C3—C8—N4	178.62 (15)
C8—C3—C4—C5	−0.6 (2)	N3—C3—C8—N4	0.01 (17)
N3—C3—C4—C5	177.59 (16)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*O*···Cl1^{i}	0.81	2.29	3.0991 (15)	179
O1—H2*O*···Cl1	0.87	2.30	3.1443 (14)	165
N1—H1*N*···O1	0.86	2.32	3.064 (2)	145
N1—H2*N*···O1^{ii}	0.86	2.14	3.000 (2)	174
N2—H2···O1	0.86	2.03	2.8667 (19)	165
N3—H3*N*···S1	0.80	2.43	3.0146 (14)	131
N4—H4*N*···Cl1	0.83	2.28	3.1055 (15)	175

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*+2; (ii) −*x*+1, *y*−1/2, −*z*+3/2.