

# Crystal structures of 5-amino-*N*-phenyl-3*H*-1,2,4-dithiazol-3-iminium chloride and 5-amino-*N*-(4-chlorophenyl)-3*H*-1,2,4-dithiazol-3-iminium chloride monohydrate

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**Keywords:** crystal structure; hydrogen bonding; dithiazole ring; salt

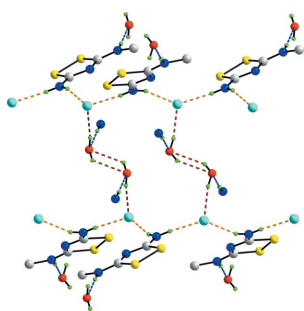
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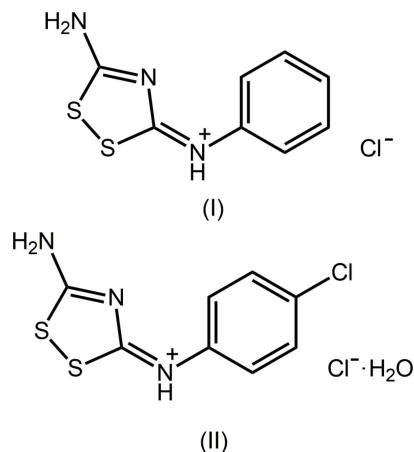
The crystal and molecular structures of the title salt,  $C_8H_8N_3S_2^+ \cdot Cl^-$ , (I), and salt hydrate,  $C_8H_7ClN_3S_2^+ \cdot Cl^- \cdot H_2O$ , (II), are described. The heterocyclic ring in (I) is statistically planar and forms a dihedral angle of  $9.05(12)^\circ$  with the pendant phenyl ring. The comparable angle in (II) is  $15.60(12)^\circ$ , indicating a greater twist in this cation. An evaluation of the bond lengths in the  $H_2N-C-N-C-N$  sequence of each cation indicates significant delocalization of  $\pi$ -electron density over these atoms. The common feature of the crystal packing in (I) and (II) is the formation of charge-assisted amino- $N-H \cdots Cl^-$  hydrogen bonds, leading to helical chains in (I) and zigzag chains in (II). In (I), these are linked by chains mediated by charge-assisted iminium- $N^+ - H \cdots Cl^-$  hydrogen bonds into a three-dimensional architecture. In (II), the chains are linked into a layer by charge-assisted water- $O-H \cdots Cl^-$  and water- $O-H \cdots O$ (water) hydrogen bonds with charge-assisted iminium- $N^+ - H \cdots O$ (water) hydrogen bonds providing the connections between the layers to generate the three-dimensional packing. In (II), the chloride anion and water molecules are resolved into two proximate sites with the major component being present with a site occupancy factor of 0.9327 (18).

## 1. Chemical context

The title salts were isolated as a part of a research programme into the crystal engineering aspects and biological potential of phosphanegold(I) carbonimidothioates, *i.e.* molecules of the general formula  $R_3PAu[SC(OR')=NR'']$ ;  $R, R', R'' =$  aryl and/or alkyl. While earlier work focussed on supramolecular aggregation patterns (Kuan *et al.*, 2008) and solid-state luminescence (Ho *et al.*, 2006), more recent endeavours have focussed upon biological studies. For example, the  $Ph_3PAu[SC(O-alkyl)=N(p-tolyl)]$  compounds prove to be very potent against Gram-positive bacteria (Yeo, Sim *et al.*, 2013). In addition,  $Ph_3PAu[SC(O-alkyl)=N(aryl)]$  compounds exhibit significant cytotoxicity and kill cancer cells by initiating a variety of apoptotic pathways (Yeo, Ooi *et al.*, 2013; Ooi, Yeo *et al.*, 2015). A focus of recent synthetic efforts has been to increase the functionality of the thiocarbamide molecules in order to produce gold complexes of higher nuclearity. During this work bipodal  $\{1,4-[MeOC(=S)N(H)]_2C_6H_4\}$  was synthesized along with its binuclear phosphanegold(I) complexes (Yeo *et al.*, 2015). As an expansion of these studies, the 1:2 reactions of thiourea with arylisothiocyanates were undertaken which, rather than yielding bipodal molecules, gave the 1:1 cyclization products, isolated as salts. These and related compounds have been described in the patent litera-

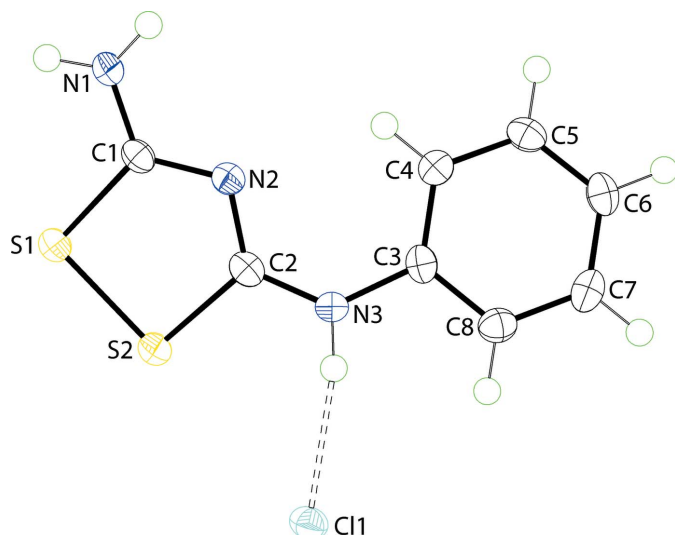


ture as having a range of biological properties, *e.g.* as bactericides, fungicides and plant-growth inhibitors (Röthling *et al.*, 1989). Herein, the crystal and molecular structures of two examples of these products, *i.e.* the salt,  $[\text{C}_8\text{H}_8\text{N}_3\text{S}_2]^+\text{Cl}^-$  (I), and the salt hydrate  $[\text{C}_8\text{H}_7\text{ClN}_3\text{S}_2]^+\text{Cl}^- \cdot \text{H}_2\text{O}$  (II), are described.



## 2. Structural commentary

The asymmetric unit of (I), comprising a cation and chloride anion, is shown in Fig. 1. The five-membered 1,2,4-dithiazole ring of the cation in (I) is strictly planar with the maximum deviation being less than  $\pm 0.003$  (2) Å. However, the entire cation is not planar with the dihedral angle between the rings being  $9.05$  (12)°. Selected geometric parameters are collected in Table 1. While the S—S and S—C bond lengths correspond to single bonds, an evaluation of the C—N bonds, internal and external to the ring, suggest a high level of delocalization of  $\pi$ -electron density across these atoms. The angles subtended at the S atoms are nearly right-angles. The trigonal angles around the C1 atom are all approximately 120° but there is a range of



**Figure 1**  
The asymmetric unit for (I), showing the atom-labelling scheme and displacement ellipsoids at the 70% probability level. The dashed lines indicate hydrogen bonds.

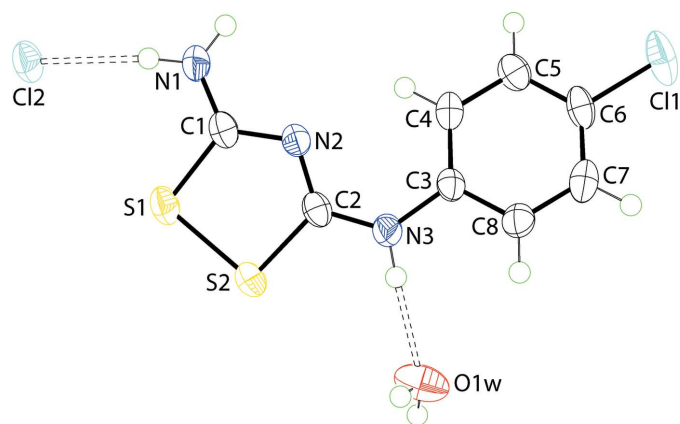
**Table 1**  
Geometric data (Å, °) for (I) and (II).

Parameter	(I)	(II)
S1—S2	2.0669 (10)	2.0657 (12)
S1—C1	1.769 (3)	1.749 (3)
S2—C2	1.772 (3)	1.763 (3)
N1—C1	1.309 (3)	1.305 (4)
N2—C1	1.328 (3)	1.337 (4)
N2—C2	1.317 (3)	1.312 (4)
N3—C2	1.328 (3)	1.332 (4)
N3—C3	1.418 (3)	1.424 (4)
C1—S1—S2	92.63 (9)	92.68 (11)
C2—S2—S1	92.72 (10)	92.85 (11)
C2—N2—C1	115.1 (2)	115.1 (2)
C2—N3—C3	130.4 (2)	128.0 (3)
N1—C1—N2	122.5 (2)	120.8 (3)
N1—C1—S1	117.8 (2)	119.5 (2)
N2—C1—S1	119.7 (2)	119.8 (2)
N2—C2—N3	125.2 (2)	123.4 (3)
N2—C2—S2	119.8 (2)	119.6 (2)
N3—C2—S2	115.1 (2)	117.0 (2)

10° for the angles about the C2 atom, with the widest angle being N2—C2—N3, consistent with double-bond character in the C—N bonds. The widest angle in the molecule is that subtended at the N3 atom, an observation that correlates with the C2=N3 double bond and the presence of the small H atom on the N3 atom.

The asymmetric unit of (II), comprising a cation, a chloride anion and a water molecule of crystallization, is illustrated in Fig. 2. As for (I), the cation is almost planar with the maximum deviation being 0.010 (2) Å for the N2 atom; the r.m.s. deviation for the fitted atoms is 0.010 Å. A greater overall twist in the molecule is evident, as seen in the dihedral angle of  $15.60$  (12)° formed between the rings. In terms of bond lengths, Table 1, the discussion above for (I), holds true for (II). Similarly, for the bond angles except that the range of angles about the C2 atom is narrower at 6°.

Fig. 3 presents an overlay diagram of the cations in each of (I) and (II) which highlights the similarity in their molecular structures.



**Figure 2**  
The asymmetric unit for (II), showing the atom-labelling scheme and displacement ellipsoids at the 70% probability level. The dashed lines indicate hydrogen bonds.

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N1-H1N\cdots Cl1^i$	0.87 (2)	2.36 (2)	3.215 (2)	170 (3)
$N1-H2N\cdots Cl1^{ii}$	0.88 (2)	2.29 (2)	3.131 (3)	159 (3)
$N3-H3N\cdots Cl1$	0.88 (2)	2.22 (2)	3.084 (2)	169 (2)

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

**Table 3**  
Hydrogen-bond geometry (Å, °) for (II).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N1-H1N\cdots Cl2^i$	0.88 (3)	2.30 (3)	3.144 (3)	161 (3)
$N1-H2N\cdots Cl2$	0.88 (2)	2.22 (1)	3.089 (2)	172 (4)
$N3-H3N\cdots O1W$	0.88 (2)	2.06 (2)	2.927 (4)	174 (3)
$O1W-H2O\cdots O1W^{ii}$	0.84 (3)	2.29 (4)	2.884 (4)	128 (3)
$O1W-H1O\cdots Cl2^{iii}$	0.85 (3)	2.16 (3)	3.005 (3)	170 (3)

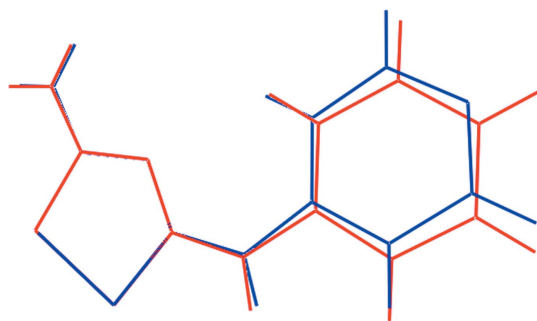
Symmetry codes: (i)  $x, -y + 2, z - \frac{1}{2}$ ; (ii)  $-x + 1, -y + 1, -z + 1$ ; (iii)  $-x + \frac{3}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$ .

### 3. Supramolecular features

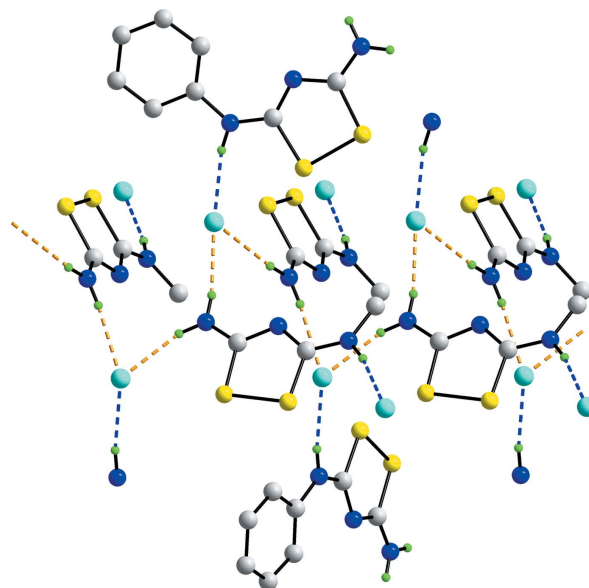
Geometric parameters characterizing the intermolecular interactions operating in the crystal structures of (I) and (II) are collected in Tables 2 and 3, respectively.

The presence of charge-assisted  $N-H\cdots Cl^-$  and  $N^+-H\cdots Cl^-$  hydrogen bonds are crucial in establishing the three-dimensional architecture in the crystal structure of (I). The structure is conveniently described as comprising columns of cations aligned along the  $a$  axis connected through hydrogen bonds to rows of chloride ions, also aligned along the  $a$  axis. As illustrated in Fig. 4, charge-assisted amino- $N-H\cdots Cl^-$  hydrogen bonds lead to helical chains along [100], being generated by  $2_1$  screw symmetry. The chains are linked to neighbouring chains by charge-assisted iminium- $N^+-H\cdots Cl^-$  hydrogen bonds, that in themselves lead to chains aligned along [011]. In this way, a three-dimensional architecture is constructed as shown in projection in Fig. 5.

A more complicated pattern of hydrogen bonding occurs in the crystal structure of (II). The amino-H atoms form charge-assisted  $N-H\cdots Cl^-$  hydrogen bonds while the iminium-H atom forms a charge-assisted  $N^+-H\cdots O$  hydrogen bond to the water molecule of crystallization. The water molecule also

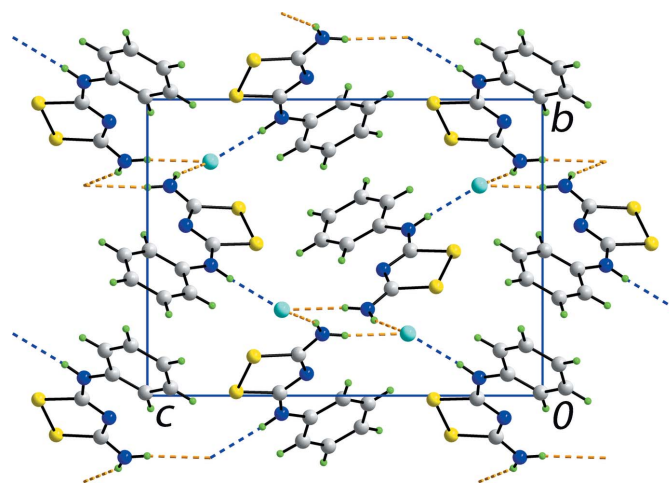


**Figure 3**  
Overlay diagram of the cations in (I), red image, and (II), blue image. The cations have been overlapped so that the five-membered rings are coincident.

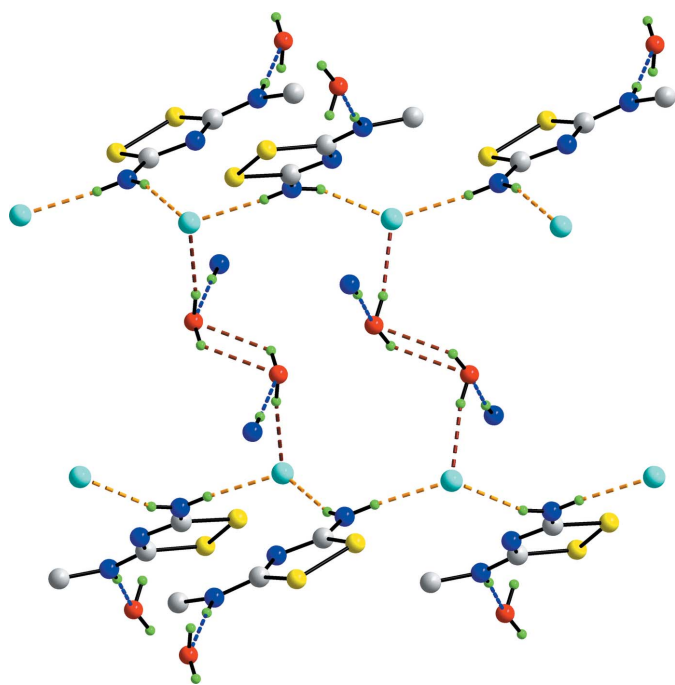


**Figure 4**  
Detail of the hydrogen bonding operating in the crystal structure of (I). The charge-assisted amino- $N-H\cdots Cl^-$  hydrogen bonds are shown as orange dashed lines and lead to helical chains along [100]. The charge-assisted imino- $N^+-H\cdots Cl^-$  hydrogen bonds are shown as blue dashed lines and lead to chains along [011]. For reasons of clarity, H atoms not involved in hydrogen bonding have been omitted and only one of the chains along [011] is shown.

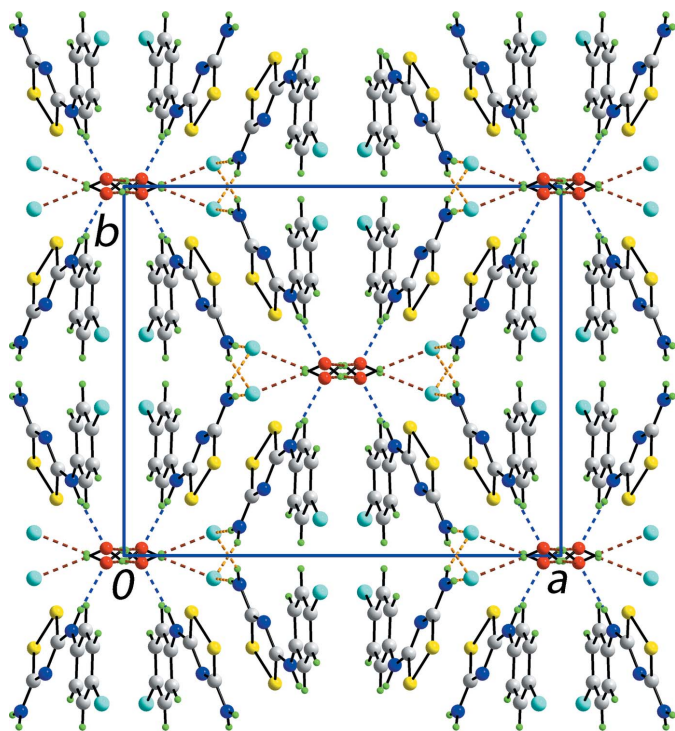
forms two donor interactions, one to another water molecule and the second, charge-assisted, to the chloride anion. Hence, all donor atoms participate in the hydrogen-bonding scheme and each of the chloride and water species forms three hydrogen bonds. A diagram showing the detail of the hydrogen bonding is shown in Fig. 6. The amino- $N-H\cdots Cl^-$  bridges clearly persist, as for (I), but lead to zigzag chains (glide symmetry) along the  $c$  axis. As pairs of water molecules are linked *via* water- $O-H\cdots O$ (water) hydrogen bonds across a centre of inversion and each forms a charge-assisted water-



**Figure 5**  
Unit-cell contents for (I) shown in projection down the  $a$  axis. The charge-assisted amino- $N-H\cdots Cl^-$  and imino- $N^+-H\cdots Cl^-$  hydrogen bonds are shown as orange and blue dashed lines, respectively.



**Figure 6**  
Detail of the hydrogen bonding operating in the crystal structure of (II). The charge-assisted amino-N-H...Cl<sup>-</sup> hydrogen bonds are shown as orange dashed lines and lead to zigzag chains along [001]. The charge-assisted imino-N<sup>+</sup>-H...O(water) hydrogen bonds are shown as blue dashed lines and both water-O-H...Cl<sup>-</sup> and water-O-H...O(water) hydrogen bonds are shown as brown dashed lines. For reasons of clarity, H atoms not involved in hydrogen bonding have been omitted.

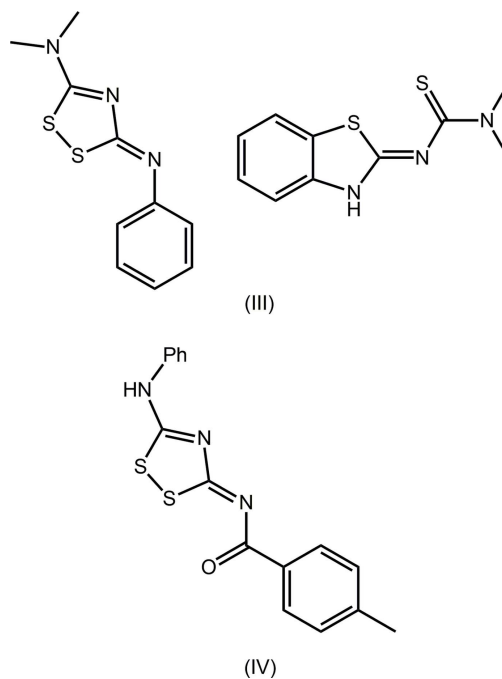


**Figure 7**  
Unit cell contents for (II) shown in projection down the *c* axis. The charge-assisted amino-N-H...Cl<sup>-</sup> (orange), imino-N<sup>+</sup>-H...Cl<sup>-</sup> (blue), water-O-H...Cl<sup>-</sup> (brown) and water-O-H...O(water) (brown) hydrogen bonds are shown as dashed lines.

O-H...Cl<sup>-</sup> hydrogen bond, the water molecules form links between the zigzag chains resulting in supramolecular layers. Finally, the water molecules accept charge-assisted imino-N<sup>+</sup>-H...O(water) hydrogen bonds, providing links between the layers so that a three-dimensional architecture ensues. As seen from Fig. 7, globally, the structure may be described as comprising layers of cations parallel to [001] that define rectangular channels parallel to [001] incorporating the anions and internalized water molecules. Not shown in Fig. 5, are indications of close Cl1...Cl1<sup>i</sup> contacts of 3.3510 (10) Å which occur within layers rather than between layers; symmetry operation (ii): 1 - *x*, *y*, - $\frac{1}{2}$  - *z*.

#### 4. Database survey

A search of the Cambridge Structural Database (Groom & Allen, 2014), revealed there are no direct analogues of (I) and (II) in the crystallographic literature. The structure of a closely related neutral species, *i.e.* 5-(dimethylamino)-3-(phenylimino)-1,2,4-dithiazole, characterized in its 1:1 co-crystal with 2-(dimethylcarboxamido-imino)benzothiazole, (III) in the scheme below, has been reported (Flippen, 1977), along with several benzoyl derivatives, as exemplified by 3-(4-methylbenzoylimino)-5-phenylamino-3*H*-1,2,4-dithiazole (IV) (Kleist *et al.*, 1994). An evaluation of the bond lengths in the N-C-N-C-N sequences in these molecules suggests a greater contribution of the canonical structure with formal C=N bonds, *i.e.* N-C=N-C=N. This difference is traced to the influence of the formal charge on the iminium-N atom.



#### 5. Synthesis and crystallization

**Synthesis of (I).** To thiourea (Merck, 5 mmol, 0.38 g) in acetonitrile (20 ml) was added 50% *w/v* NaOH (10 mmol,

**Table 4**  
Experimental details.

	(I)	(II)
Crystal data		
Chemical formula	$C_8H_8N_3S_2^+ \cdot Cl^-$	$C_8H_7ClN_3S_2^+ \cdot Cl^- \cdot H_2O$
$M_r$	245.74	298.20
Crystal system, space group	Orthorhombic, $P2_12_12_1$	Monoclinic, $C2/c$
Temperature (K)	100	100
$a, b, c$ (Å)	6.5702 (4), 10.8637 (7), 14.4964 (10)	17.0581 (7), 14.1660 (7), 10.3215 (4)
$\alpha, \beta, \gamma$ (°)	90, 90, 90	90, 101.084 (4), 90
$V$ (Å <sup>3</sup> )	1034.70 (12)	2447.61 (19)
$Z$	4	8
Radiation type	Mo $K\alpha$	Mo $K\alpha$
$\mu$ (mm <sup>-1</sup> )	0.73	0.85
Crystal size (mm)	0.15 × 0.02 × 0.02	0.20 × 0.10 × 0.05
Data collection		
Diffractometer	Bruker SMART APEX CCD diffractometer	Agilent SuperNova Dual diffractometer with an Atlas detector
Absorption correction	Multi-scan ( <i>SADABS</i> ; Sheldrick, 1996)	Multi-scan ( <i>CrysAlis PRO</i> ; Agilent, 2012)
$T_{min}, T_{max}$	0.898, 1.000	0.748, 1.000
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	9875, 2378, 2185	19709, 2821, 2142
$R_{int}$	0.044	0.064
$(\sin \theta/\lambda)_{max}$ (Å <sup>-1</sup> )	0.650	0.650
Refinement		
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.028, 0.058, 1.07	0.046, 0.102, 1.02
No. of reflections	2378	2821
No. of parameters	136	167
No. of restraints	3	6
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å <sup>-3</sup> )	0.29, -0.21	0.76, -0.64
Absolute structure	Flack $x$ determined using 842 quotients [[ $I^+$ )-( $I^-$ )]/[( $I^+$ )+( $I^-$ )] (Parsons <i>et al.</i> , 2013).	-
Absolute structure parameter	0.08 (5)	-

Computer programs: *CrysAlis PRO* (Agilent, 2012), *APEX2* and *SAINTE* (Bruker, 2008), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *ORTEP-3 for Windows* (Farrugia, 2012), *QMol* (Gans & Shalloway, 2001), *DIAMOND* (Brandenburg, 2006) and *pubCIF* (Westrip, 2010).

0.40 ml) and phenyl isothiocyanate (Merck, 10 mmol, 1.2 ml). The resulting mixture was stirred for 4 h at 323 K. 5 M HCl (20 mmol, 4.1 ml) was added and the mixture was stirred for another 1 h. The final product was extracted using chloroform (200 ml). The powder that formed after 2 weeks was redissolved in dichloromethane/acetonitrile (1:1 *v/v*, 200 ml), yielding yellow prisms after 3 weeks. Yield: 0.627 g (51%). M.p. 492–493 K. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, 298 K): 13.37 (*s, br*, 1H, NH), 10.73 (*s*, 1H, NH<sub>2</sub>), 10.66 (*s, br*, 1H, NH<sub>2</sub>), 7.74 (*d*, 2H, *o*-Ph-H,  $J = 7.96$  Hz), 7.45 (*dd*, 2H, *m*-Ph-H,  $J = 7.82$  Hz,  $J = 7.82$  Hz), 7.27 (*t*, 1H, *p*-Ph-H,  $J = 7.34$  Hz). <sup>13</sup>C NMR (400 MHz, DMSO-*d*<sub>6</sub>, 298 K): 182.9 [SC(=N)N], 176.1 [C(NH<sub>2</sub>)], 138.5 (*C*<sub>ipso</sub>), 129.7 (*C*<sub>meta</sub>), 126.5 (*C*<sub>para</sub>) 121.4 (*C*<sub>ortho</sub>). IR (cm<sup>-1</sup>): 3414 (*m*) (N–H),  $\nu$  3007 (*m*) (C–H),  $\nu$  1248 (*s*) (C–N).

**Synthesis of (II).** The *p*-chloro derivative (II) was prepared as described above but using 4-chlorophenyl isothiocyanate (Sigma–Aldrich) as the unique reagent. Yellow prismatic crystals were isolated after 4 weeks. Yield: 0.581 g (39%). M.p. 484–485 K. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, 298 K): 13.51 (*s, br*, 1H, NH), 10.72 (*s*, 1H, NH<sub>2</sub>), 10.41 (*s, br*, 1H, NH<sub>2</sub>), 7.77 (*d*, 2H, *m*-Ph-H,  $J = 8.60$  Hz), 7.52 (*d*, 2H, *o*-Ph-H,  $J = 8.52$  Hz), 3.48 (*br*, 2H, H<sub>2</sub>O). <sup>13</sup>C NMR (400 MHz, DMSO-*d*<sub>6</sub>, 298 K): 183.0 [SC(=N)N], 176.1 [CNH<sub>2</sub>], 137.4 (*C*<sub>ipso</sub>), 130.3 (*C*<sub>para</sub>),

129.6 (*C*<sub>meta</sub>), 122.9 (*C*<sub>ortho</sub>). IR (cm<sup>-1</sup>):  $\nu$  2965 (*br*) (O–H),  $\nu$  1250 (*s*) (C–N).

## 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 4. For (I) and (II), carbon-bound H atoms were placed in calculated positions (C–H = 0.95 Å) and were included in the refinement in the riding-model approximation, with  $U_{iso}(H)$  set to  $1.2U_{eq}(C)$ . The N-bound H atoms were located in a difference Fourier map but were refined with a distance restraint of N–H =  $0.88 \pm 0.01$  Å, and with  $U_{iso}(H)$  set to  $1.2U_{eq}(N)$ . For (I), owing to poor agreement, one reflection, *i.e.* (020), was omitted from the final cycles of refinement. For (II), disorder was noted in the structure, involving the Cl2 anion and water molecule of crystallization so that two proximate positions were resolved for the heteroatoms. The major component refined to a site occupancy factor of 0.9327 (18). The anisotropic displacement parameters for the pair of Cl2 anions and for the water-O atoms were constrained to be equal. Only the water-bound H atoms for the major component were resolved and these were assigned full weight with O–H  $0.84 \pm 0.01$  Å, and with  $U_{iso}(H) = 1.5U_{eq}(O)$ .

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## supporting information

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## Crystal structures of 5-amino-*N*-phenyl-3*H*-1,2,4-dithiazol-3-iminium chloride and 5-amino-*N*-(4-chlorophenyl)-3*H*-1,2,4-dithiazol-3-iminium chloride monohydrate

Chien Ing Yeo, Yee Seng Tan and Edward R. T. Tiekink

### Computing details

Data collection: *APEX2* (Bruker, 2008) for (I); *CrysAlis PRO* (Agilent, 2012) for (II). Cell refinement: *APEX2* (Bruker, 2008) for (I); *CrysAlis PRO* (Agilent, 2012) for (II). Data reduction: *SAINTE* (Bruker, 2008) for (I); *CrysAlis PRO* (Agilent, 2012) for (II). For both compounds, program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012), *QMol* (Gans & Shalloway, 2001) and *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010).

### (I) 5-Amino-*N*-phenyl-3*H*-1,2,4-dithiazol-3-iminium chloride

#### Crystal data

$C_8H_8N_3S_2^+Cl^-$	$D_x = 1.578 \text{ Mg m}^{-3}$
$M_r = 245.74$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
Orthorhombic, $P2_12_12_1$	Cell parameters from 2635 reflections
$a = 6.5702 (4) \text{ \AA}$	$\theta = 2.3\text{--}27.3^\circ$
$b = 10.8637 (7) \text{ \AA}$	$\mu = 0.73 \text{ mm}^{-1}$
$c = 14.4964 (10) \text{ \AA}$	$T = 100 \text{ K}$
$V = 1034.70 (12) \text{ \AA}^3$	Prism, yellow
$Z = 4$	$0.15 \times 0.02 \times 0.02 \text{ mm}$
$F(000) = 504$	

#### Data collection

Bruker SMART APEX CCD diffractometer	9875 measured reflections
Radiation source: fine-focus sealed tube	2378 independent reflections
Graphite monochromator	2185 reflections with $I > 2\sigma(I)$
$\varphi$ and $\omega$ scans	$R_{\text{int}} = 0.044$
Absorption correction: multi-scan ( <i>SADABS</i> ; Sheldrick, 1996)	$\theta_{\text{max}} = 27.5^\circ$ , $\theta_{\text{min}} = 2.3^\circ$
$T_{\text{min}} = 0.898$ , $T_{\text{max}} = 1.000$	$h = -8 \rightarrow 8$
	$k = -14 \rightarrow 14$
	$l = -18 \rightarrow 18$

#### Refinement

Refinement on $F^2$	2378 reflections
Least-squares matrix: full	136 parameters
$R[F^2 > 2\sigma(F^2)] = 0.028$	3 restraints
$wR(F^2) = 0.058$	Hydrogen site location: mixed
$S = 1.07$	

H atoms treated by a mixture of independent

and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0242P)^2 + 0.0389P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} < 0.001$$

$$\Delta\rho_{\max} = 0.29 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.21 \text{ e } \text{\AA}^{-3}$$

Absolute structure: Flack  $x$  determined using

842 quotients  $[(I^-)-(I^+)]/[(I^-)+(I^+)]$  (Parsons *et al.*, 2013).

Absolute structure parameter: 0.08 (5)

### Special details

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

### Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	1.07530 (11)	0.36767 (6)	0.26929 (5)	0.01784 (16)
S2	0.85079 (11)	0.48700 (7)	0.22480 (5)	0.01919 (17)
N1	1.0681 (4)	0.2920 (2)	0.44270 (15)	0.0173 (5)
H1N	1.027 (4)	0.297 (3)	0.4995 (11)	0.021*
H2N	1.182 (3)	0.255 (3)	0.4263 (19)	0.021*
N2	0.8085 (3)	0.4255 (2)	0.40293 (14)	0.0140 (5)
N3	0.5664 (4)	0.5602 (2)	0.33970 (16)	0.0175 (5)
H3N	0.540 (4)	0.605 (2)	0.2910 (14)	0.021*
C1	0.9739 (4)	0.3609 (2)	0.38220 (17)	0.0144 (6)
C2	0.7320 (4)	0.4904 (3)	0.33453 (18)	0.0156 (6)
C3	0.4216 (4)	0.5731 (2)	0.41161 (18)	0.0153 (6)
C4	0.4307 (4)	0.5100 (2)	0.49499 (18)	0.0162 (6)
H4	0.5415	0.4567	0.5083	0.019*
C5	0.2751 (4)	0.5264 (3)	0.55831 (19)	0.0173 (6)
H5	0.2780	0.4817	0.6146	0.021*
C6	0.1161 (4)	0.6061 (3)	0.54155 (19)	0.0194 (6)
H6	0.0121	0.6173	0.5863	0.023*
C7	0.1093 (5)	0.6702 (3)	0.45801 (19)	0.0202 (7)
H7	0.0006	0.7255	0.4458	0.024*
C8	0.2609 (4)	0.6529 (3)	0.39322 (19)	0.0180 (6)
H8	0.2554	0.6956	0.3361	0.022*
Cl1	0.53467 (10)	0.70982 (6)	0.15949 (4)	0.01812 (16)

### Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
S1	0.0186 (4)	0.0216 (3)	0.0133 (3)	0.0037 (3)	0.0025 (3)	0.0005 (3)
S2	0.0194 (4)	0.0250 (4)	0.0132 (3)	0.0046 (3)	0.0021 (3)	0.0022 (3)
N1	0.0167 (13)	0.0221 (12)	0.0131 (11)	0.0035 (12)	0.0024 (10)	0.0002 (10)
N2	0.0144 (13)	0.0146 (12)	0.0129 (11)	-0.0016 (10)	-0.0004 (9)	-0.0006 (9)
N3	0.0181 (12)	0.0194 (12)	0.0151 (11)	0.0040 (11)	0.0019 (11)	0.0045 (10)
C1	0.0150 (14)	0.0150 (13)	0.0133 (12)	-0.0036 (12)	0.0014 (11)	-0.0008 (11)
C2	0.0167 (14)	0.0161 (13)	0.0138 (12)	-0.0033 (12)	0.0005 (12)	-0.0019 (12)



C3	0.0134 (14)	0.0152 (13)	0.0172 (13)	-0.0023 (12)	0.0017 (12)	-0.0031 (11)
C4	0.0155 (14)	0.0155 (13)	0.0175 (13)	-0.0007 (13)	-0.0012 (12)	-0.0005 (10)
C5	0.0184 (15)	0.0195 (14)	0.0138 (13)	-0.0044 (12)	-0.0015 (11)	-0.0005 (11)
C6	0.0152 (16)	0.0220 (15)	0.0210 (15)	-0.0017 (12)	0.0044 (12)	-0.0035 (12)
C7	0.0166 (18)	0.0188 (14)	0.0252 (16)	0.0036 (12)	-0.0012 (12)	-0.0039 (12)
C8	0.0203 (16)	0.0162 (14)	0.0176 (14)	-0.0004 (12)	-0.0022 (12)	0.0003 (11)
Cl1	0.0179 (4)	0.0221 (3)	0.0144 (3)	-0.0015 (3)	-0.0009 (3)	0.0030 (3)

*Geometric parameters (Å, °)*

S1—C1	1.769 (3)	C3—C4	1.391 (4)
S1—S2	2.0669 (10)	C3—C8	1.392 (4)
S2—C2	1.772 (3)	C4—C5	1.386 (4)
N1—C1	1.309 (3)	C4—H4	0.9500
N1—H1N	0.869 (13)	C5—C6	1.378 (4)
N1—H2N	0.881 (13)	C5—H5	0.9500
N2—C2	1.317 (3)	C6—C7	1.398 (4)
N2—C1	1.328 (3)	C6—H6	0.9500
N3—C2	1.328 (3)	C7—C8	1.382 (4)
N3—C3	1.418 (3)	C7—H7	0.9500
N3—H3N	0.875 (12)	C8—H8	0.9500
C1—S1—S2	92.63 (9)	C8—C3—N3	115.5 (2)
C2—S2—S1	92.72 (10)	C5—C4—C3	118.7 (3)
C1—N1—H1N	117.0 (19)	C5—C4—H4	120.6
C1—N1—H2N	119 (2)	C3—C4—H4	120.6
H1N—N1—H2N	123 (3)	C6—C5—C4	121.6 (3)
C2—N2—C1	115.1 (2)	C6—C5—H5	119.2
C2—N3—C3	130.4 (2)	C4—C5—H5	119.2
C2—N3—H3N	116 (2)	C5—C6—C7	119.3 (3)
C3—N3—H3N	114 (2)	C5—C6—H6	120.3
N1—C1—N2	122.5 (2)	C7—C6—H6	120.3
N1—C1—S1	117.8 (2)	C8—C7—C6	119.9 (3)
N2—C1—S1	119.7 (2)	C8—C7—H7	120.1
N2—C2—N3	125.2 (2)	C6—C7—H7	120.1
N2—C2—S2	119.8 (2)	C7—C8—C3	120.1 (3)
N3—C2—S2	115.1 (2)	C7—C8—H8	120.0
C4—C3—C8	120.4 (3)	C3—C8—H8	120.0
C4—C3—N3	124.1 (2)		
C2—N2—C1—N1	179.8 (3)	C2—N3—C3—C4	0.2 (4)
C2—N2—C1—S1	0.4 (3)	C2—N3—C3—C8	-178.3 (3)
S2—S1—C1—N1	-179.9 (2)	C8—C3—C4—C5	1.2 (4)
S2—S1—C1—N2	-0.5 (2)	N3—C3—C4—C5	-177.2 (2)
C1—N2—C2—N3	179.2 (2)	C3—C4—C5—C6	-1.9 (4)
C1—N2—C2—S2	-0.1 (3)	C4—C5—C6—C7	1.2 (4)
C3—N3—C2—N2	-7.6 (5)	C5—C6—C7—C8	0.2 (4)
C3—N3—C2—S2	171.6 (2)	C6—C7—C8—C3	-0.9 (4)

S1—S2—C2—N2	-0.2 (2)	C4—C3—C8—C7	0.2 (4)
S1—S2—C2—N3	-179.5 (2)	N3—C3—C8—C7	178.7 (2)

*Hydrogen-bond geometry* ( $\text{\AA}$ ,  $^\circ$ )

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
N1—H1N $\cdots$ C11 <sup>i</sup>	0.87 (2)	2.36 (2)	3.215 (2)	170 (3)
N1—H2N $\cdots$ C11 <sup>ii</sup>	0.88 (2)	2.29 (2)	3.131 (3)	159 (3)
N3—H3N $\cdots$ C11	0.88 (2)	2.22 (2)	3.084 (2)	169 (2)

Symmetry codes: (i)  $-x+3/2, -y+1, z+1/2$ ; (ii)  $-x+2, y-1/2, -z+1/2$ .**(II) 5-Amino-*N*-(4-chlorophenyl)-3*H*-1,2,4-dithiazol-3-iminium chloride monohydrate***Crystal data* $\text{C}_8\text{H}_7\text{ClN}_3\text{S}_2^+\cdot\text{Cl}^-\cdot\text{H}_2\text{O}$  $M_r = 298.20$ Monoclinic,  $C2/c$  $a = 17.0581$  (7)  $\text{\AA}$  $b = 14.1660$  (7)  $\text{\AA}$  $c = 10.3215$  (4)  $\text{\AA}$  $\beta = 101.084$  (4) $^\circ$  $V = 2447.61$  (19)  $\text{\AA}^3$  $Z = 8$  $F(000) = 1216$  $D_x = 1.618$   $\text{Mg m}^{-3}$ Mo  $K\alpha$  radiation,  $\lambda = 0.71073$   $\text{\AA}$ 

Cell parameters from 4628 reflections

 $\theta = 2.4$ – $27.5^\circ$  $\mu = 0.85$   $\text{mm}^{-1}$  $T = 100$  K

Prism, yellow

 $0.20 \times 0.10 \times 0.05$  mm*Data collection*

Agilent SuperNova Dual

diffractometer with an Atlas detector

Radiation source: SuperNova (Mo) X-ray

Source

Mirror monochromator

Detector resolution: 10.4041 pixels  $\text{mm}^{-1}$  $\omega$  scan

Absorption correction: multi-scan

(CrysAlis PRO; Agilent, 2012)

 $T_{\min} = 0.748$ ,  $T_{\max} = 1.000$ 

19709 measured reflections

2821 independent reflections

2142 reflections with  $I > 2\sigma(I)$  $R_{\text{int}} = 0.064$  $\theta_{\max} = 27.5^\circ$ ,  $\theta_{\min} = 2.4^\circ$  $h = -22 \rightarrow 22$  $k = -18 \rightarrow 18$  $l = -13 \rightarrow 13$ *Refinement*Refinement on  $F^2$ 

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.046$  $wR(F^2) = 0.102$  $S = 1.02$ 

2821 reflections

167 parameters

6 restraints

Hydrogen site location: mixed

H atoms treated by a mixture of independent

and constrained refinement

 $w = 1/[\sigma^2(F_o^2) + (0.0237P)^2 + 10.8824P]$ where  $P = (F_o^2 + 2F_c^2)/3$  $(\Delta/\sigma)_{\max} = 0.001$  $\Delta\rho_{\max} = 0.76$   $\text{e \AA}^{-3}$  $\Delta\rho_{\min} = -0.64$   $\text{e \AA}^{-3}$ *Special details*

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

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Cl1	0.55093 (5)	0.90087 (7)	-0.09408 (7)	0.0413 (2)	
Cl2	0.79427 (5)	0.93836 (6)	1.03317 (7)	0.0315 (2)	0.9327 (18)
Cl2'	0.8457 (8)	0.9762 (9)	1.0388 (10)	0.0315 (2)	0.0673 (18)
S1	0.70602 (5)	0.75085 (6)	0.81299 (7)	0.02725 (19)	
S2	0.65448 (5)	0.65361 (6)	0.67312 (7)	0.0304 (2)	
N1	0.73581 (17)	0.9221 (2)	0.7316 (2)	0.0307 (6)	
H1N	0.740 (2)	0.9640 (19)	0.671 (3)	0.037*	
H2N	0.7550 (19)	0.932 (3)	0.8156 (13)	0.037*	
N2	0.67993 (14)	0.81976 (17)	0.5669 (2)	0.0216 (5)	
N3	0.61963 (15)	0.70381 (19)	0.4213 (2)	0.0253 (6)	
H3N	0.5993 (18)	0.6468 (11)	0.415 (3)	0.030*	
C1	0.70728 (17)	0.8388 (2)	0.6944 (3)	0.0234 (6)	
C2	0.65147 (16)	0.7342 (2)	0.5421 (3)	0.0222 (6)	
C3	0.60695 (16)	0.7557 (2)	0.3010 (3)	0.0208 (6)	
C4	0.60976 (17)	0.8531 (2)	0.2941 (3)	0.0246 (6)	
H4	0.6230	0.8895	0.3726	0.029*	
C5	0.59310 (17)	0.8977 (2)	0.1718 (3)	0.0258 (6)	
H5	0.5950	0.9645	0.1662	0.031*	
C6	0.57366 (16)	0.8435 (2)	0.0582 (3)	0.0252 (7)	
C7	0.57171 (17)	0.7464 (2)	0.0638 (3)	0.0277 (7)	
H7	0.5593	0.7103	-0.0150	0.033*	
C8	0.58805 (17)	0.7020 (2)	0.1854 (3)	0.0258 (6)	
H8	0.5864	0.6351	0.1904	0.031*	
O1W	0.54036 (18)	0.5195 (2)	0.3920 (3)	0.0455 (7)	0.9327 (18)
H1O	0.5860 (11)	0.495 (3)	0.419 (4)	0.068*	
H2O	0.5075 (16)	0.493 (3)	0.430 (4)	0.068*	
O1W'	0.503 (2)	0.485 (3)	0.336 (4)	0.0455 (7)	0.0673 (18)

Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Cl1	0.0453 (5)	0.0588 (6)	0.0198 (4)	0.0229 (4)	0.0062 (3)	0.0110 (4)
Cl2	0.0394 (5)	0.0378 (5)	0.0172 (4)	0.0038 (4)	0.0051 (3)	0.0024 (3)
Cl2'	0.0394 (5)	0.0378 (5)	0.0172 (4)	0.0038 (4)	0.0051 (3)	0.0024 (3)
S1	0.0329 (4)	0.0323 (4)	0.0169 (4)	0.0045 (3)	0.0056 (3)	0.0028 (3)
S2	0.0432 (5)	0.0290 (4)	0.0193 (4)	-0.0042 (4)	0.0068 (3)	0.0052 (3)
N1	0.0455 (17)	0.0270 (15)	0.0170 (12)	-0.0015 (13)	-0.0003 (12)	-0.0009 (11)
N2	0.0220 (12)	0.0239 (13)	0.0183 (12)	0.0001 (10)	0.0027 (9)	0.0019 (10)
N3	0.0288 (14)	0.0279 (14)	0.0191 (12)	-0.0079 (11)	0.0040 (10)	0.0012 (10)
C1	0.0233 (15)	0.0290 (16)	0.0183 (13)	0.0042 (13)	0.0052 (11)	0.0025 (12)
C2	0.0201 (14)	0.0293 (17)	0.0184 (14)	0.0012 (12)	0.0070 (11)	0.0037 (12)
C3	0.0175 (13)	0.0280 (16)	0.0174 (13)	-0.0047 (12)	0.0045 (10)	0.0013 (11)
C4	0.0228 (15)	0.0331 (17)	0.0173 (14)	0.0008 (13)	0.0025 (11)	-0.0013 (12)
C5	0.0221 (15)	0.0301 (17)	0.0246 (15)	0.0049 (13)	0.0032 (12)	0.0049 (13)
C6	0.0167 (14)	0.0415 (19)	0.0171 (13)	0.0066 (13)	0.0025 (11)	0.0053 (13)

C7	0.0215 (15)	0.0423 (19)	0.0191 (14)	-0.0025 (14)	0.0034 (11)	-0.0055 (13)
C8	0.0241 (15)	0.0293 (17)	0.0240 (15)	-0.0074 (13)	0.0044 (12)	-0.0012 (12)
O1W	0.0394 (17)	0.0353 (17)	0.066 (2)	0.0025 (13)	0.0211 (15)	0.0151 (14)
O1W'	0.0394 (17)	0.0353 (17)	0.066 (2)	0.0025 (13)	0.0211 (15)	0.0151 (14)

*Geometric parameters (Å, °)*

C11—C6	1.746 (3)	C3—C8	1.399 (4)
S1—C1	1.749 (3)	C4—C5	1.390 (4)
S1—S2	2.0657 (11)	C4—H4	0.9500
S2—C2	1.763 (3)	C5—C6	1.387 (4)
N1—C1	1.306 (4)	C5—H5	0.9500
N1—H1N	0.876 (10)	C6—C7	1.377 (5)
N1—H2N	0.876 (10)	C7—C8	1.384 (4)
N2—C2	1.312 (4)	C7—H7	0.9500
N2—C1	1.337 (4)	C8—H8	0.9500
N3—C2	1.332 (4)	O1W—H1O	0.850 (10)
N3—C3	1.423 (4)	O1W—H2O	0.835 (10)
N3—H3N	0.876 (10)	O1W'—O1W <sup>ii</sup>	1.75 (9)
C3—C4	1.384 (4)		
C1—S1—S2	92.68 (11)	C8—C3—N3	115.8 (3)
C2—S2—S1	92.84 (11)	C3—C4—C5	119.8 (3)
C1—N1—H1N	119 (2)	C3—C4—H4	120.1
C1—N1—H2N	119 (2)	C5—C4—H4	120.1
H1N—N1—H2N	122 (3)	C6—C5—C4	119.4 (3)
C2—N2—C1	115.1 (2)	C6—C5—H5	120.3
C2—N3—C3	128.0 (3)	C4—C5—H5	120.3
C2—N3—H3N	117 (2)	C7—C6—C5	121.4 (3)
C3—N3—H3N	115 (2)	C7—C6—C11	120.0 (2)
N1—C1—N2	120.7 (3)	C5—C6—C11	118.7 (3)
N1—C1—S1	119.5 (2)	C6—C7—C8	119.4 (3)
N2—C1—S1	119.8 (2)	C6—C7—H7	120.3
N2—C2—N3	123.4 (3)	C8—C7—H7	120.3
N2—C2—S2	119.6 (2)	C7—C8—C3	119.9 (3)
N3—C2—S2	117.0 (2)	C7—C8—H8	120.0
C4—C3—C8	120.2 (3)	C3—C8—H8	120.0
C4—C3—N3	124.0 (3)	H1O—O1W—H2O	108.5 (17)
C2—N2—C1—N1	-178.8 (3)	C2—N3—C3—C8	167.1 (3)
C2—N2—C1—S1	1.9 (4)	C8—C3—C4—C5	0.5 (4)
S2—S1—C1—N1	179.7 (2)	N3—C3—C4—C5	-177.2 (3)
S2—S1—C1—N2	-1.0 (2)	C3—C4—C5—C6	0.1 (4)
C1—N2—C2—N3	178.0 (3)	C4—C5—C6—C7	-1.0 (4)
C1—N2—C2—S2	-1.9 (3)	C4—C5—C6—C11	178.7 (2)
C3—N3—C2—N2	-3.0 (5)	C5—C6—C7—C8	1.2 (4)
C3—N3—C2—S2	176.9 (2)	C11—C6—C7—C8	-178.5 (2)
S1—S2—C2—N2	1.1 (2)	C6—C7—C8—C3	-0.5 (4)

S1—S2—C2—N3	-178.9 (2)	C4—C3—C8—C7	-0.3 (4)
C2—N3—C3—C4	-15.1 (5)	N3—C3—C8—C7	177.6 (3)

Symmetry code: (i)  $-x+1, y, -z+1/2$ .

*Hydrogen-bond geometry (Å, °)*

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
N1—H1N...C12 <sup>ii</sup>	0.88 (3)	2.30 (3)	3.144 (3)	161 (3)
N1—H2N...C12	0.88 (2)	2.22 (1)	3.089 (2)	172 (4)
N3—H3N...O1W	0.88 (2)	2.06 (2)	2.927 (4)	174 (3)
O1W—H2O...O1W <sup>iii</sup>	0.84 (3)	2.29 (4)	2.884 (4)	128 (3)
O1W—H1O...C12 <sup>iv</sup>	0.85 (3)	2.16 (3)	3.005 (3)	170 (3)

Symmetry codes: (ii)  $x, -y+2, z-1/2$ ; (iii)  $-x+1, -y+1, -z+1$ ; (iv)  $-x+3/2, y-1/2, -z+3/2$ .