

S,S'-(Pyridazine-3,6-diyl)dithiuronium dichloride methanol monosolvate

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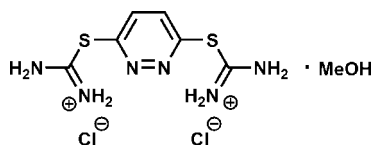
Received 5 May 2011; accepted 16 May 2011

Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å;
 R factor = 0.030; wR factor = 0.075; data-to-parameter ratio = 16.1.

In the title compound, $\text{C}_6\text{H}_{10}\text{N}_6\text{S}_2^{2+} \cdot 2\text{Cl}^- \cdot \text{CH}_3\text{OH}$, the pyridazine ring is almost planar, the greatest deviation from the mean plane being 0.025 (2) Å for one of the ring N atoms. The two thiuronium substituents are tilted out of this plane by 60.87 (6) and 57.94 (7)°. The thiuronium cations and the chloride anions are linked by strong $\text{N}-\text{H} \cdots \text{Cl}$ hydrogen bonds. The methanol solvent molecule interacts with both the chloride ion (through an $\text{O}-\text{H} \cdots \text{Cl}$ hydrogen bond) and the cation (through an $\text{N}-\text{H} \cdots \text{O}$ hydrogen bond), resulting in a three-dimensional supramolecular arrangement.

Related literature

For pharmacological applications of pyridazine derivatives, see: Cignarella & Barlocco (2002). For details of the preparation, see: Kumagai (1960); Steck & Brundage (1959).



Experimental

Crystal data

$\text{C}_6\text{H}_{10}\text{N}_6\text{S}_2^{2+} \cdot 2\text{Cl}^- \cdot \text{CH}_4\text{O}$
 $M_r = 333.26$
Triclinic, $P\bar{1}$
 $a = 6.7457$ (2) Å
 $b = 9.0234$ (3) Å
 $c = 13.0165$ (4) Å

$\alpha = 104.148$ (2)°
 $\beta = 98.066$ (2)°
 $\gamma = 108.695$ (2)°
 $V = 706.81$ (4) Å³
 $Z = 2$
Mo $K\alpha$ radiation

$\mu = 0.75$ mm⁻¹
 $T = 293$ K

$0.45 \times 0.10 \times 0.05$ mm

Data collection

Stoe IPDS 2 diffractometer
Absorption correction: integration
(*X-RED*; Stoe & Cie, 2002)
 $T_{\min} = 0.739$, $T_{\max} = 0.959$

3234 measured reflections
3234 independent reflections
2765 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.071$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.030$
 $wR(F^2) = 0.075$
 $S = 1.03$
3234 reflections
201 parameters

H atoms treated by a mixture of
independent and constrained
refinement
 $\Delta\rho_{\max} = 0.27$ e Å⁻³
 $\Delta\rho_{\min} = -0.33$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$\text{O1G}-\text{H1G} \cdots \text{Cl1}^{\text{i}}$	0.89 (3)	2.22 (3)	3.1038 (15)	171 (3)
$\text{N3}-\text{H3A} \cdots \text{Cl2}$	0.92 (3)	2.28 (3)	3.1746 (17)	166 (2)
$\text{N3}-\text{H3B} \cdots \text{O1G}$	0.89 (3)	1.95 (3)	2.839 (2)	171 (3)
$\text{N4}-\text{H4A} \cdots \text{Cl1}$	0.86 (3)	2.70 (3)	3.3950 (16)	139 (2)
$\text{N4}-\text{H4B} \cdots \text{Cl1}^{\text{i}}$	0.91 (3)	2.36 (3)	3.2522 (15)	167 (2)
$\text{N5}-\text{H5A} \cdots \text{Cl1}$	0.89 (2)	2.39 (2)	3.2614 (16)	170 (2)
$\text{N5}-\text{H5B} \cdots \text{Cl2}^{\text{ii}}$	0.90 (3)	2.25 (3)	3.1413 (17)	173 (2)
$\text{N6}-\text{H6A} \cdots \text{Cl2}^{\text{iii}}$	0.83 (3)	2.36 (3)	3.1878 (19)	175 (3)
$\text{N6}-\text{H6B} \cdots \text{O1G}^{\text{iv}}$	0.90 (3)	2.17 (2)	2.891 (2)	136 (2)

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

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED32* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP* (Siemens, 1994); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

This work was performed within the Cluster of Excellence "Structure Design of Novel High-Performance Materials *via* Atomic Design and Defect Engineering (ADDE)" that is financially supported by the European Union (European Regional Development fund) and by the Ministry of Science and Art of Saxony (SMWK). LI is grateful to the DFG for a travel grant.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FJ2416).

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supporting information

Acta Cryst. (2011). E67, o1477 [https://doi.org/10.1107/S1600536811018514]

***S,S'*-(Pyridazine-3,6-diyl)dithiouronium dichloride methanol monosolvate**

Jörg Hübscher, Lidiya Izotova, Samat Talipov, Felix Katzsch and Edwin Weber

S1. Comment

Pyridazine derivatives are important compounds for pharmacological applications, among them 3,6-dithiopyridazine being a secondary substance of the title compound (Cignarella & Barlocco, 2002).

In the title compound (Fig. 1), the pyridazine ring is almost planar, with maximal deviation from the mean plane 0.025 (2) Å. Dihedral angles between the pyridazine plane and thiourea substitutes are different (S2 C6 N5 N6 - 60.87 (6)° and S1 C5 N3 N4 - 57.94 (7)°).

The structure is formed by a (C₆H₁₀N₆S₂)²⁺ cation and two Cl⁻ anions, connected through strong N—H···Cl⁻ hydrogen bonds [H3A···Cl2 = 2.28 (3) Å, N3—H3A···Cl2 = 166 (2)°; H4A···Cl1 = 2.70 (3) Å, N4—H4A···Cl1 = 139 (2)°; H5A···Cl1 = 2.39 (3) Å, N5—H5A···Cl1 = 170 (2)°], and one solvate CH₃OH molecule bonded to the anion through a hydrogen bond [H3B···O1G = 2.839 (2) Å, N3—H3B···O1G = 171 (3)°]. Intermolecular hydrogen bonds link the Cl⁻ anions and the solvate MeOH molecule to two additional cations (Table 1) resulting in a three-dimensional supramolecular arrangement (Fig.2).

S2. Experimental

The title compound has been obtained as an intermediate substance of the synthesis of 3,6-dithiopyridazine involving the reaction of 3,6-dichloropyridazine with thiourea in methanol solution and was isolated before alkaline treatment (Steck & Brundage, 1959); (Kumagai, 1960). The colourless plate-type single crystals are stable in the air.

S3. Refinement

All H-atoms, except H-atoms involved in H-bonding, were positioned geometrically and allowed to ride on their parent atoms, with C—H=0.95 Å and $U_{\text{iso}} = 1.2\text{--}1.5 U_{\text{eq}}$ (parent atom). The rest H-atoms were located in a difference map and fully refined

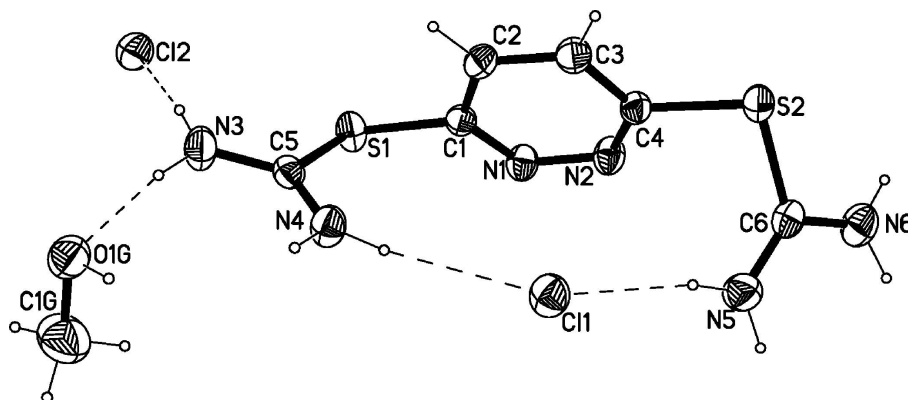


Figure 1

Perspective view of the title compound, showing 50% probability displacement ellipsoids for the non-H atoms. Dashed lines represent hydrogen bond.

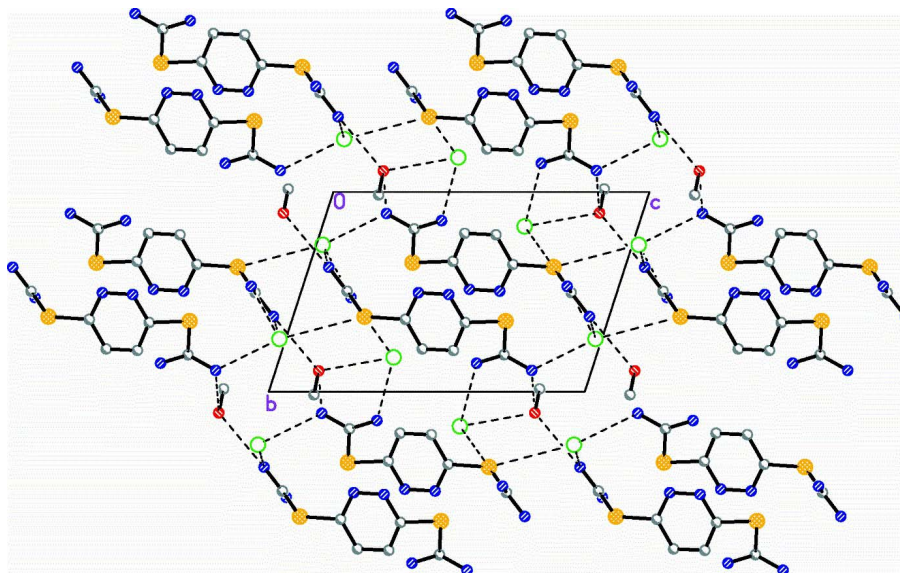


Figure 2

Packing diagram of the title compound viewed down the *a* axis. The weak hydrogen bonds are shown as dashed lines. H-atoms are omitted for clarity

{Amino[(6-{[amino(iminiumyl)methyl]sulfanyl}pyridazin-3-yl)sulfanyl]methylidene}azanum dichloride methanol monosolvate

Crystal data

$\text{C}_6\text{H}_{10}\text{N}_6\text{S}_2^{2+} \cdot 2\text{Cl}^- \cdot \text{CH}_4\text{O}$

$M_r = 333.26$

Triclinic, $P\bar{1}$

Hall symbol: $-P\ 1$

$a = 6.7457(2)\ \text{\AA}$

$b = 9.0234(3)\ \text{\AA}$

$c = 13.0165(4)\ \text{\AA}$

$\alpha = 104.148(2)^\circ$

$\beta = 98.066(2)^\circ$

$\gamma = 108.695(2)^\circ$

$V = 706.81(4)\ \text{\AA}^3$

$Z = 2$

$F(000) = 344$

$D_x = 1.566\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 32534 reflections

$\theta = 1.7\text{--}29.6^\circ$

$\mu = 0.75\ \text{mm}^{-1}$

$T = 293$ K
Plate, colourless

$0.45 \times 0.10 \times 0.05$ mm

Data collection

Stoe IPDS 2
diffractometer
Radiation source: sealed X-ray tube, long-fine
focus
Plane graphite monochromator
Detector resolution: 6.67 pixels mm^{-1}
rotation method scans
Absorption correction: integration
(*X-RED*; Stoe & Cie, 2002)

$T_{\min} = 0.739$, $T_{\max} = 0.959$
3234 measured reflections
3234 independent reflections
2765 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.071$
 $\theta_{\max} = 27.5^\circ$, $\theta_{\min} = 2.5^\circ$
 $h = -8 \rightarrow 8$
 $k = -11 \rightarrow 11$
 $l = 0 \rightarrow 16$

Refinement

Refinement on F^2
Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.030$
 $wR(F^2) = 0.075$
 $S = 1.03$
3234 reflections
201 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 atoms treated by a mixture of independent
and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0481P)^2 + 0.1092P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.27 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.33 \text{ e } \text{\AA}^{-3}$
Extinction correction: *SHELXL97* (Sheldrick,
2008), $F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.055 (4)

Special details

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'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 $F^2 > 2\sigma(F^2)$ 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 ($\text{\AA}^2$)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cl1	0.46287 (7)	0.17255 (5)	0.64021 (3)	0.03256 (12)
Cl2	0.10144 (7)	0.26455 (6)	0.02016 (4)	0.03622 (12)
O1G	0.5002 (2)	−0.10500 (17)	0.13659 (11)	0.0364 (3)
C1G	0.7040 (4)	0.0147 (3)	0.1460 (2)	0.0570 (6)
H1G1	0.7251	0.1146	0.2013	0.085*
H1G2	0.7098	0.0358	0.0775	0.085*
H1G3	0.8152	−0.0251	0.1658	0.085*
H1G	0.518 (5)	−0.132 (4)	0.197 (2)	0.059 (8)*
H4B	0.434 (4)	0.053 (3)	0.357 (2)	0.048 (7)*
H5A	0.436 (4)	0.388 (3)	0.780 (2)	0.037 (6)*
H6B	0.410 (4)	0.684 (3)	0.992 (2)	0.040 (6)*
H3A	0.201 (4)	0.137 (3)	0.138 (2)	0.046 (6)*

H4A	0.441 (5)	0.205 (4)	0.439 (2)	0.059 (8)*
H5B	0.581 (4)	0.541 (3)	0.880 (2)	0.047 (7)*
H3B	0.330 (4)	0.032 (3)	0.169 (2)	0.056 (8)*
H6A	0.183 (5)	0.646 (3)	0.947 (2)	0.049 (7)*
S1	0.22215 (7)	0.35351 (5)	0.32279 (3)	0.02800 (11)
S2	0.02098 (7)	0.37603 (6)	0.77378 (3)	0.03286 (12)
C4	0.0693 (2)	0.36263 (19)	0.64195 (12)	0.0231 (3)
N1	0.2518 (2)	0.48701 (16)	0.53011 (11)	0.0265 (3)
N2	0.2047 (2)	0.49603 (17)	0.62795 (11)	0.0284 (3)
C3	−0.0424 (3)	0.2143 (2)	0.55821 (13)	0.0277 (3)
H3	−0.1409	0.1249	0.5703	0.033*
C1	0.1553 (2)	0.34686 (18)	0.44932 (12)	0.0220 (3)
N6	0.2904 (3)	0.6233 (2)	0.93770 (13)	0.0357 (3)
C6	0.2824 (3)	0.50356 (19)	0.85521 (13)	0.0261 (3)
C2	−0.0002 (3)	0.2071 (2)	0.45784 (13)	0.0271 (3)
H2	−0.0716	0.1135	0.3979	0.033*
N3	0.2723 (3)	0.1075 (2)	0.18987 (12)	0.0352 (3)
N5	0.4521 (3)	0.4721 (2)	0.83639 (13)	0.0335 (3)
N4	0.3980 (3)	0.1435 (2)	0.37169 (13)	0.0308 (3)
C5	0.3058 (2)	0.18519 (19)	0.29330 (13)	0.0232 (3)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0377 (2)	0.0308 (2)	0.0310 (2)	0.01700 (17)	0.00766 (16)	0.00711 (15)
Cl2	0.0359 (2)	0.0417 (2)	0.0307 (2)	0.01407 (18)	0.00600 (16)	0.01193 (17)
O1G	0.0373 (7)	0.0351 (7)	0.0328 (7)	0.0125 (5)	0.0048 (5)	0.0066 (5)
C1G	0.0417 (12)	0.0504 (13)	0.0699 (16)	0.0099 (10)	0.0192 (11)	0.0091 (11)
S1	0.0392 (2)	0.0296 (2)	0.0249 (2)	0.02017 (17)	0.01270 (15)	0.01233 (15)
S2	0.0286 (2)	0.0409 (2)	0.02151 (19)	0.00569 (17)	0.00775 (15)	0.00506 (16)
C4	0.0239 (7)	0.0251 (7)	0.0206 (7)	0.0111 (6)	0.0049 (5)	0.0048 (6)
N1	0.0314 (7)	0.0223 (6)	0.0244 (6)	0.0086 (5)	0.0073 (5)	0.0064 (5)
N2	0.0342 (7)	0.0230 (6)	0.0238 (6)	0.0080 (5)	0.0072 (5)	0.0031 (5)
C3	0.0261 (7)	0.0244 (7)	0.0266 (8)	0.0038 (6)	0.0067 (6)	0.0050 (6)
C1	0.0227 (7)	0.0237 (7)	0.0213 (7)	0.0114 (6)	0.0048 (5)	0.0066 (5)
N6	0.0434 (9)	0.0308 (7)	0.0275 (7)	0.0142 (7)	0.0051 (7)	0.0009 (6)
C6	0.0317 (8)	0.0237 (7)	0.0216 (7)	0.0090 (6)	0.0048 (6)	0.0075 (6)
C2	0.0259 (7)	0.0240 (7)	0.0228 (7)	0.0042 (6)	0.0030 (6)	0.0003 (6)
N3	0.0454 (9)	0.0423 (8)	0.0237 (7)	0.0263 (7)	0.0087 (6)	0.0063 (6)
N5	0.0305 (8)	0.0345 (8)	0.0320 (7)	0.0130 (6)	0.0045 (6)	0.0044 (6)
N4	0.0393 (8)	0.0321 (7)	0.0255 (7)	0.0203 (6)	0.0062 (6)	0.0077 (6)
C5	0.0230 (7)	0.0230 (7)	0.0243 (7)	0.0081 (5)	0.0085 (5)	0.0074 (6)

Geometric parameters (Å, °)

O1G—C1G	1.417 (3)	C1—C2	1.398 (2)
O1G—H1G	0.89 (3)	N6—C6	1.305 (2)
C1G—H1G1	0.9600	N6—H6B	0.90 (3)

C1G—H1G2	0.9600	N6—H6A	0.83 (3)
C1G—H1G3	0.9600	C6—N5	1.305 (2)
S1—C5	1.7603 (16)	C2—H2	0.9300
S1—C1	1.7775 (15)	N3—C5	1.306 (2)
S2—C6	1.7709 (17)	N3—H3A	0.92 (3)
S2—C4	1.7738 (15)	N3—H3B	0.89 (3)
C4—N2	1.329 (2)	N5—H5A	0.89 (2)
C4—C3	1.399 (2)	N5—H5B	0.90 (3)
N1—C1	1.326 (2)	N4—C5	1.315 (2)
N1—N2	1.3450 (19)	N4—H4B	0.91 (3)
C3—C2	1.366 (2)	N4—H4A	0.86 (3)
C3—H3	0.9300		
C1G—O1G—H1G	103.6 (19)	C6—N6—H6A	122.6 (19)
O1G—C1G—H1G1	109.5	H6B—N6—H6A	114 (2)
O1G—C1G—H1G2	109.5	N6—C6—N5	123.12 (17)
H1G1—C1G—H1G2	109.5	N6—C6—S2	115.38 (14)
O1G—C1G—H1G3	109.5	N5—C6—S2	121.38 (13)
H1G1—C1G—H1G3	109.5	C3—C2—C1	116.94 (14)
H1G2—C1G—H1G3	109.5	C3—C2—H2	121.5
C5—S1—C1	100.19 (7)	C1—C2—H2	121.5
C6—S2—C4	99.98 (8)	C5—N3—H3A	120.2 (16)
N2—C4—C3	123.90 (14)	C5—N3—H3B	120.0 (18)
N2—C4—S2	117.88 (11)	H3A—N3—H3B	120 (2)
C3—C4—S2	118.18 (12)	C6—N5—H5A	119.1 (15)
C1—N1—N2	118.93 (13)	C6—N5—H5B	117.8 (16)
C4—N2—N1	119.05 (13)	H5A—N5—H5B	123 (2)
C2—C3—C4	116.86 (15)	C5—N4—H4B	121.2 (17)
C2—C3—H3	121.6	C5—N4—H4A	122 (2)
C4—C3—H3	121.6	H4B—N4—H4A	116 (3)
N1—C1—C2	124.05 (14)	N3—C5—N4	123.08 (15)
N1—C1—S1	114.57 (11)	N3—C5—S1	115.75 (13)
C2—C1—S1	121.20 (12)	N4—C5—S1	121.17 (12)
C6—N6—H6B	123.2 (15)		
C6—S2—C4—N2	−37.51 (14)	C5—S1—C1—N1	126.26 (12)
C6—S2—C4—C3	144.58 (13)	C5—S1—C1—C2	−58.54 (14)
C3—C4—N2—N1	−5.3 (2)	C4—S2—C6—N6	134.58 (13)
S2—C4—N2—N1	176.96 (11)	C4—S2—C6—N5	−49.21 (15)
C1—N1—N2—C4	2.6 (2)	C4—C3—C2—C1	1.9 (2)
N2—C4—C3—C2	2.9 (2)	N1—C1—C2—C3	−4.5 (2)
S2—C4—C3—C2	−179.32 (13)	S1—C1—C2—C3	−179.24 (12)
N2—N1—C1—C2	2.3 (2)	C1—S1—C5—N3	149.37 (13)
N2—N1—C1—S1	177.35 (11)	C1—S1—C5—N4	−31.32 (15)

Hydrogen-bond geometry (Å, °)

<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>
O1 <i>G</i> —H1 <i>G</i> $\cdots$ Cl1 ⁱ	0.89 (3)	2.22 (3)	3.1038 (15)	171 (3)
N3—H3 <i>A</i> $\cdots$ Cl2	0.92 (3)	2.28 (3)	3.1746 (17)	166 (2)
N3—H3 <i>B</i> $\cdots$ O1 <i>G</i>	0.89 (3)	1.95 (3)	2.839 (2)	171 (3)
N4—H4 <i>A</i> $\cdots$ Cl1	0.86 (3)	2.70 (3)	3.3950 (16)	139 (2)
N4—H4 <i>B</i> $\cdots$ Cl1 ⁱ	0.91 (3)	2.36 (3)	3.2522 (15)	167 (2)
N5—H5 <i>A</i> $\cdots$ Cl1	0.89 (2)	2.39 (2)	3.2614 (16)	170 (2)
N5—H5 <i>B</i> $\cdots$ Cl2 ⁱⁱ	0.90 (3)	2.25 (3)	3.1413 (17)	173 (2)
N6—H6 <i>A</i> $\cdots$ Cl2 ⁱⁱⁱ	0.83 (3)	2.36 (3)	3.1878 (19)	175 (3)
N6—H6 <i>B</i> $\cdots$ O1 <i>G</i> ^{iv}	0.90 (3)	2.17 (2)	2.891 (2)	136 (2)

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