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Bis(2-amino-5-methyl-1,3,4-thiadiazole- κN^3)dichloridocobalt(II)

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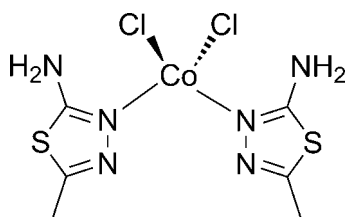
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Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(C-C) = 0.006$ Å; R factor = 0.045; wR factor = 0.110; data-to-parameter ratio = 20.5.

In the monomeric title complex, $[CoCl_2(C_3H_5N_3S)_2]$, the Co^{II} atom is tetracoordinated by two chloride anions and two N atoms from two monodentate 2-amino-5-methyl-1,3,4-thiadiazole ligands, giving a slightly distorted tetrahedral stereochemistry [bond angle range about $Co = 105.16$ (12)– 112.50 (10) $^\circ$]. In the complex, the dihedral angle between the 1,3,4-thiadiazole planes in the two ligands is 72.8 (1) $^\circ$. There are two intramolecular $N-H \cdots Cl$ interactions in the complex unit, while in the crystal, intermolecular $N-H \cdots N$ and $N-H \cdots Cl$ hydrogen bonds link these units into a two-dimensional layered structure parallel to (011).

Related literature

For potential applications of complexes containing 2,5-disubstituted 1,3,4-thiadiazoles, see: Katritzky *et al.* (2010); Seed *et al.* (2007). For the preparation of the 2-amino-5-methyl-1,3,4-thiadiazole ligand, see: Chubb & Nissenbaum (1959). For complexes with this ligand, see: Lynch & Ewington (2001); Neverov *et al.* (1986); Antolini *et al.* (1988).



Experimental

Crystal data

 $[CoCl_2(C_3H_5N_3S)_2]$
 $M_r = 360.15$

 Monoclinic, $P2_1/c$
 $a = 9.124$ (2) Å

 $b = 20.180$ (5) Å
 $c = 7.2767$ (19) Å
 $\beta = 99.479$ (5) $^\circ$
 $V = 1321.5$ (6) Å 3
 $Z = 4$

 Mo $K\alpha$ radiation
 $\mu = 2.01$ mm $^{-1}$
 $T = 296$ K
 $0.20 \times 0.20 \times 0.20$ mm

Data collection

 Bruker SMART APEX
 diffractometer
 Absorption correction: multi-scan
 (SADABS; Sheldrick, 1996)
 $T_{min} = 0.670$, $T_{max} = 0.676$

 8978 measured reflections
 3194 independent reflections
 2125 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.052$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.045$
 $wR(F^2) = 0.110$
 $S = 1.04$
 3194 reflections

 156 parameters
 H-atom parameters constrained
 $\Delta\rho_{max} = 0.47$ e Å $^{-3}$
 $\Delta\rho_{min} = -0.60$ e Å $^{-3}$
Table 1

 Hydrogen-bond geometry (Å, $^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$N1-H1A \cdots Cl1$	0.86	2.49	3.281 (4)	153
$N2-H2A \cdots Cl2$	0.86	2.66	3.445 (4)	152
$N2-H2B \cdots N6^i$	0.86	2.32	3.114 (5)	153
$N1-H1B \cdots Cl2^i$	0.86	2.65	3.387 (4)	144

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

Data collection: SMART (Bruker, 2001); cell refinement: SAINT (Bruker, 2001); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: OLEX2 (Dolomanov *et al.*, 2009); software used to prepare material for publication: publCIF (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: ZS2204).

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Bis(2-amino-5-methyl-1,3,4-thiadiazole- κ N³)dichloridocobalt(II)

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S1. Comment

Recently, metal complexes with 2,5-disubstituted 1,3,4-thiadiazoles have received considerable attention, as they have a wide range of potential applications in the fields of medicine and material science (Katritzky *et al.*, 2010; Seed *et al.*, 2007). The 2-Amino-5-methyl-1,3,4-thiadiazole (amtz) ligand, which contains one S and three N coordination sites is recognized as a potential multidentate ligand to construct some interesting compounds (Lynch *et al.*, 2001; Neverov *et al.*, 1986; Antolini *et al.*, 1988). Herein, the title complex [CoCl₂(C₃H₅N₃S)₂] has been synthesized and characterized structurally.

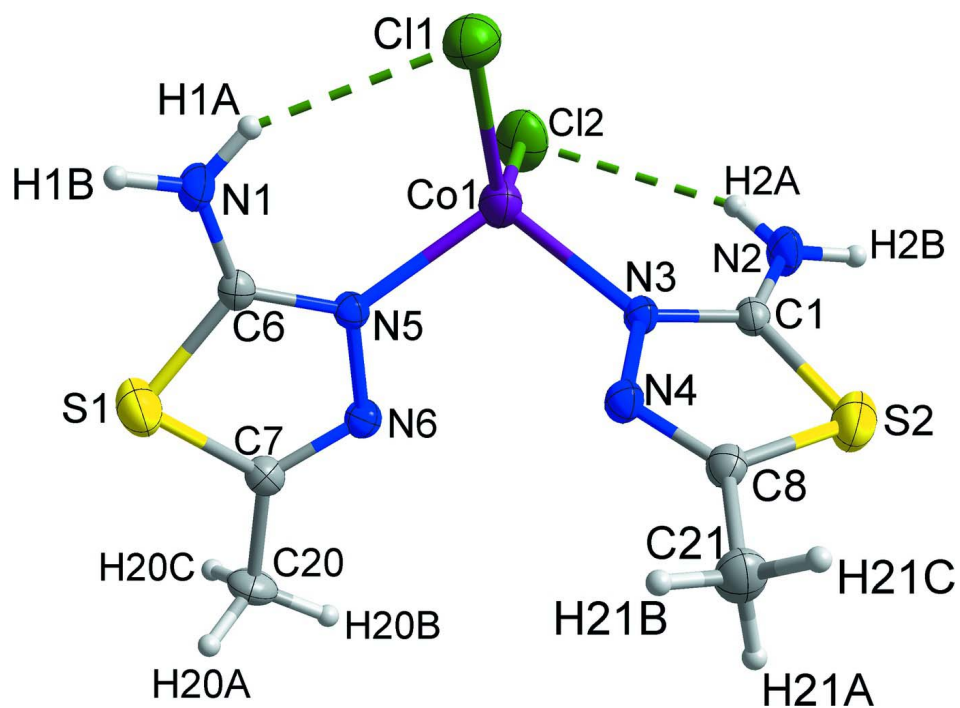
In the title monomeric complex, [CoCl₂(C₃H₅N₃S)₂], the Co^{II} is tetracoordinated by two chlorine anions and two nitrogen atoms from two monodentate 2-amino-5-methyl-1,3,4-thiadiazole ligands, giving a slightly distorted tetrahedral stereochemistry [bond angle range, 105.16 (12)–112.50 (10)°; bond lengths: Co—N = 2.004 (3) and 2.009 (3) Å; Co—Cl = 2.2416 (12) and 2.2590 (12) Å]. Since the intramolecular N—H⋯Cl interactions exist between the NH₂ group and Cl anions (Table 1), the Co—Cl bonds deviate from the thiadiazole ring planes (Antolini *et al.*, 1988). In the crystal, the complex molecules are connected by intermolecular N—H⋯Cl and N—H⋯N hydrogen-bonding interactions, forming a two-dimensional layered structure which extends along the (011) plane (Fig. 2).

S2. Experimental

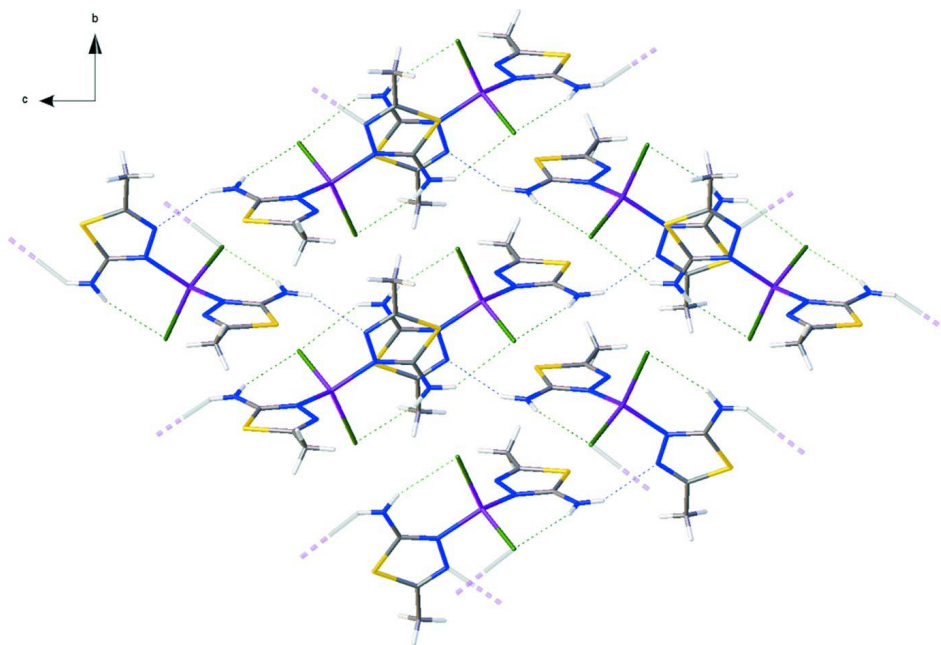
2-Amino-5-methyl-1,3,4-thiadiazole (amtz) was prepared according to a previously reported procedure (Chubb & Nissenbaum, 1959). 1 mmol of CoCl₂ · 6H₂O (0.237 g) dissolved in 20 ml of ethanol–water (1:1, v/v) containing 1 mmol of 2-amino-5-methyl-1,3,4-thiadiazole (0.115 g). The resulting solution was stirred continuously for about 2 h. Upon slow partial evaporation of the solvent, dark blue crystals formed after 5 days. Yield: 35% (based on CoCl₂ · 6H₂O).

S3. Refinement

All H-atoms were placed in calculated positions with N—H = 0.86 Å and C—H = 0.96 Å and were allowed to ride in the refinement, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$ and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$.

**Figure 1**

The structure and atom-numbering scheme for the title complex, with displacement ellipsoids drawn at the 30% probability level for non-H atoms. N—H...Cl interactions are shown as dashed lines.

**Figure 2**

A packing diagram viewed down the *a*-axis of the unit cell, showing the two-dimensional layered structure.

Bis(2-amino-5-methyl-1,3,4-thiadiazole- κ N³)dichloridocobalt(II)*Crystal data*[CoCl₂(C₃H₅N₃S)₂] $M_r = 360.15$ Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

 $a = 9.124 (2) \text{ \AA}$ $b = 20.180 (5) \text{ \AA}$ $c = 7.2767 (19) \text{ \AA}$ $\beta = 99.479 (5)^\circ$ $V = 1321.5 (6) \text{ \AA}^3$ $Z = 4$ $F(000) = 724$ $D_x = 1.810 \text{ Mg m}^{-3}$ Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 5643 reflections

 $\theta = 0.7\text{--}0.7^\circ$ $\mu = 2.01 \text{ mm}^{-1}$ $T = 296 \text{ K}$

Block, blue

 $0.20 \times 0.20 \times 0.20 \text{ mm}$ *Data collection*

Bruker SMART APEX

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: $8.192 \text{ pixels mm}^{-1}$ ω - 2τ scans

Absorption correction: multi-scan

(SADABS; Sheldrick, 1996)

 $T_{\min} = 0.670$, $T_{\max} = 0.676$

8978 measured reflections

3194 independent reflections

2125 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.052$ $\theta_{\max} = 28.2^\circ$, $\theta_{\min} = 2.0^\circ$ $h = -9 \rightarrow 12$ $k = -26 \rightarrow 26$ $l = -8 \rightarrow 9$ *Refinement*Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.045$ $wR(F^2) = 0.110$ $S = 1.04$

3194 reflections

156 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

 $w = 1/[\sigma^2(F_o^2) + (0.047P)^2 + 0.1324P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} < 0.001$ $\Delta\rho_{\max} = 0.47 \text{ e \AA}^{-3}$ $\Delta\rho_{\min} = -0.60 \text{ e \AA}^{-3}$ *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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Co1	0.15275 (5)	0.62934 (2)	0.21631 (7)	0.02936 (16)
S2	0.52153 (11)	0.77737 (5)	0.39642 (15)	0.0386 (3)
S1	0.26820 (12)	0.44424 (5)	-0.08418 (15)	0.0391 (3)
Cl1	0.06975 (11)	0.58762 (5)	0.46557 (14)	0.0410 (3)

Cl2	-0.02720 (11)	0.68410 (5)	0.02491 (16)	0.0457 (3)
C1	0.3446 (4)	0.75138 (19)	0.3006 (5)	0.0320 (8)
N3	0.3324 (3)	0.68679 (14)	0.2864 (4)	0.0302 (7)
N5	0.2217 (3)	0.55309 (15)	0.0748 (4)	0.0303 (7)
N6	0.3037 (3)	0.56944 (15)	-0.0648 (5)	0.0337 (7)
N4	0.4654 (3)	0.65406 (15)	0.3519 (5)	0.0352 (8)
C6	0.1944 (4)	0.48894 (18)	0.0809 (5)	0.0293 (8)
C7	0.3353 (4)	0.5187 (2)	-0.1557 (5)	0.0336 (9)
C8	0.5721 (4)	0.69334 (19)	0.4114 (5)	0.0355 (9)
N1	0.1191 (4)	0.46049 (16)	0.2013 (5)	0.0434 (9)
H1A	0.0845	0.4842	0.2825	0.052*
H1B	0.1050	0.4183	0.1981	0.052*
N2	0.2347 (4)	0.79357 (16)	0.2434 (5)	0.0460 (9)
H2A	0.1488	0.7789	0.1933	0.055*
H2B	0.2494	0.8355	0.2565	0.055*
C20	0.4198 (5)	0.5212 (2)	-0.3141 (6)	0.0453 (11)
H20A	0.4970	0.4884	-0.2961	0.068*
H20B	0.4632	0.5643	-0.3198	0.068*
H20C	0.3538	0.5125	-0.4285	0.068*
C21	0.7265 (5)	0.6726 (2)	0.4872 (7)	0.0552 (13)
H21A	0.7922	0.6872	0.4051	0.083*
H21B	0.7307	0.6252	0.4976	0.083*
H21C	0.7563	0.6920	0.6081	0.083*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.0291 (3)	0.0241 (3)	0.0352 (3)	-0.0010 (2)	0.0060 (2)	-0.0012 (2)
S2	0.0437 (6)	0.0292 (5)	0.0425 (6)	-0.0096 (4)	0.0060 (5)	-0.0050 (5)
S1	0.0487 (6)	0.0273 (5)	0.0421 (6)	0.0026 (4)	0.0100 (5)	-0.0051 (5)
Cl1	0.0442 (5)	0.0428 (6)	0.0381 (6)	-0.0072 (4)	0.0129 (4)	-0.0008 (5)
Cl2	0.0433 (6)	0.0360 (6)	0.0541 (7)	0.0069 (5)	-0.0029 (5)	0.0033 (5)
C1	0.039 (2)	0.0279 (19)	0.031 (2)	-0.0037 (17)	0.0099 (17)	-0.0030 (17)
N3	0.0303 (16)	0.0216 (15)	0.0387 (19)	0.0003 (13)	0.0054 (13)	0.0001 (14)
N5	0.0328 (16)	0.0271 (17)	0.0315 (18)	0.0015 (13)	0.0066 (13)	0.0005 (14)
N6	0.0374 (17)	0.0279 (17)	0.0368 (19)	-0.0001 (14)	0.0092 (14)	0.0041 (15)
N4	0.0330 (17)	0.0275 (16)	0.045 (2)	-0.0003 (14)	0.0046 (15)	0.0001 (16)
C6	0.0294 (18)	0.0277 (19)	0.029 (2)	0.0011 (15)	-0.0004 (15)	0.0013 (16)
C7	0.035 (2)	0.035 (2)	0.031 (2)	0.0025 (17)	0.0041 (16)	0.0003 (18)
C8	0.038 (2)	0.033 (2)	0.036 (2)	-0.0038 (17)	0.0065 (17)	0.0000 (18)
N1	0.057 (2)	0.0255 (17)	0.050 (2)	-0.0062 (16)	0.0168 (18)	0.0004 (16)
N2	0.047 (2)	0.0247 (17)	0.065 (3)	0.0031 (16)	0.0032 (18)	-0.0034 (18)
C20	0.044 (2)	0.058 (3)	0.037 (2)	0.008 (2)	0.0165 (19)	0.000 (2)
C21	0.041 (2)	0.054 (3)	0.067 (3)	0.003 (2)	-0.003 (2)	-0.005 (3)

Geometric parameters (Å, °)

Co1—N3	2.004 (3)	N4—C8	1.275 (5)
Co1—N5	2.009 (3)	C6—N1	1.330 (5)
Co1—C11	2.2416 (12)	C7—C20	1.490 (5)
Co1—C12	2.2590 (12)	C8—C21	1.486 (5)
S2—C1	1.731 (4)	N1—H1A	0.8600
S2—C8	1.756 (4)	N1—H1B	0.8600
S1—C6	1.725 (4)	N2—H2A	0.8600
S1—C7	1.735 (4)	N2—H2B	0.8600
C1—N3	1.311 (5)	C20—H20A	0.9600
C1—N2	1.329 (5)	C20—H20B	0.9600
N3—N4	1.395 (4)	C20—H20C	0.9600
N5—C6	1.320 (4)	C21—H21A	0.9600
N5—N6	1.397 (4)	C21—H21B	0.9600
N6—C7	1.277 (5)	C21—H21C	0.9600
N3—Co1—N5	105.16 (12)	N6—C7—S1	114.7 (3)
N3—Co1—C11	112.50 (10)	C20—C7—S1	120.9 (3)
N5—Co1—C11	107.63 (9)	N4—C8—C21	125.1 (4)
N3—Co1—C12	110.78 (9)	N4—C8—S2	113.7 (3)
N5—Co1—C12	108.41 (9)	C21—C8—S2	121.2 (3)
C11—Co1—C12	111.99 (5)	C6—N1—H1A	120.0
C1—S2—C8	87.17 (18)	C6—N1—H1B	120.0
C6—S1—C7	87.32 (18)	H1A—N1—H1B	120.0
N3—C1—N2	124.2 (3)	C1—N2—H2A	120.0
N3—C1—S2	113.2 (3)	C1—N2—H2B	120.0
N2—C1—S2	122.5 (3)	H2A—N2—H2B	120.0
C1—N3—N4	112.7 (3)	C7—C20—H20A	109.5
C1—N3—Co1	130.6 (3)	C7—C20—H20B	109.5
N4—N3—Co1	116.2 (2)	H20A—C20—H20B	109.5
C6—N5—N6	112.5 (3)	C7—C20—H20C	109.5
C6—N5—Co1	131.1 (3)	H20A—C20—H20C	109.5
N6—N5—Co1	116.2 (2)	H20B—C20—H20C	109.5
C7—N6—N5	112.4 (3)	C8—C21—H21A	109.5
C8—N4—N3	113.2 (3)	C8—C21—H21B	109.5
N5—C6—N1	124.5 (4)	H21A—C21—H21B	109.5
N5—C6—S1	113.1 (3)	C8—C21—H21C	109.5
N1—C6—S1	122.4 (3)	H21A—C21—H21C	109.5
N6—C7—C20	124.3 (4)	H21B—C21—H21C	109.5
C8—S2—C1—N3	0.3 (3)	C6—N5—N6—C7	−0.4 (4)
C8—S2—C1—N2	−178.0 (4)	Co1—N5—N6—C7	−175.9 (3)
N2—C1—N3—N4	178.2 (3)	C1—N3—N4—C8	−0.3 (5)
S2—C1—N3—N4	−0.1 (4)	Co1—N3—N4—C8	−173.4 (3)
N2—C1—N3—Co1	−10.0 (6)	N6—N5—C6—N1	179.7 (3)
S2—C1—N3—Co1	171.75 (19)	Co1—N5—C6—N1	−5.7 (6)
N5—Co1—N3—C1	145.3 (3)	N6—N5—C6—S1	0.2 (4)

Cl1—Co1—N3—C1	-97.9 (3)	Co1—N5—C6—S1	174.85 (18)
Cl2—Co1—N3—C1	28.3 (4)	C7—S1—C6—N5	0.0 (3)
N5—Co1—N3—N4	-43.2 (3)	C7—S1—C6—N1	-179.5 (3)
Cl1—Co1—N3—N4	73.7 (3)	N5—N6—C7—C20	179.1 (3)
Cl2—Co1—N3—N4	-160.1 (2)	N5—N6—C7—S1	0.3 (4)
N3—Co1—N5—C6	137.7 (3)	C6—S1—C7—N6	-0.2 (3)
Cl1—Co1—N5—C6	17.5 (4)	C6—S1—C7—C20	-179.0 (3)
Cl2—Co1—N5—C6	-103.8 (3)	N3—N4—C8—C21	-179.3 (4)
N3—Co1—N5—N6	-47.8 (3)	N3—N4—C8—S2	0.6 (4)
Cl1—Co1—N5—N6	-168.0 (2)	C1—S2—C8—N4	-0.5 (3)
Cl2—Co1—N5—N6	70.7 (2)	C1—S2—C8—C21	179.4 (4)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1 <i>A</i> ...Cl1	0.86	2.49	3.281 (4)	153
N2—H2 <i>A</i> ...Cl2	0.86	2.66	3.445 (4)	152
N2—H2 <i>B</i> ...Cl1 ⁱ	0.86	2.90	3.331 (4)	113
N2—H2 <i>B</i> ...N6 ⁱⁱ	0.86	2.32	3.114 (5)	153
N1—H1 <i>B</i> ...Cl2 ⁱⁱⁱ	0.86	2.65	3.387 (4)	144
N1—H1 <i>A</i> ...Cl1 ^{iv}	0.86	2.88	3.341 (3)	115

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