

Dichloridobis(thiourea- κ S)nickel(II)

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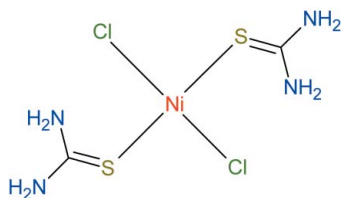
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 Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{N}-\text{C}) = 0.003$ Å; R factor = 0.017; wR factor = 0.045; data-to-parameter ratio = 12.8.

The title complex, $[\text{NiCl}_2(\text{CH}_4\text{N}_2\text{S})_2]$, has been synthesized from the previously reported (diaminomethylidene)sulfonium chloride–thiourea (3/2) salt [Zouihri (2012*b*). *Acta Cryst.* **E68**, o257]. The Ni^{II} ion is coordinated in a distorted tetrahedral geometry by two molecules of thiourea [$\text{Ni}-\text{S} = 2.3079$ (7) and 2.3177 (6) Å] and two chloride anions [$\text{Ni}-\text{Cl} = 2.2516$ (7) and 2.2726 (7) Å]. The bond angles at the Ni atom lie between 96.69 (2) and 115.40 (3)°, while the dihedral angle between the mean planes of the two thiourea ligands is 6.36 (15)°. The crystal structure is characterized by intra- and intermolecular $\text{N}-\text{H}\cdots\text{Cl}$ hydrogen bonds, which lead to the formation of two-dimensional networks lying parallel to the ab plane. The networks are linked *via* classical $\text{N}-\text{H}\cdots\text{Cl}$ and $\text{N}-\text{H}\cdots\text{S}$ hydrogen bonds, forming a three-dimensional arrangement.

Related literature

For the synthesis and the crystal structure of (diaminomethylidene)sulfonium chloride thiourea (3/2), see: Zouihri (2012*b*). For related structures, see: Ambujam *et al.* (2007); Zouihri (2012*a*). For related literature on the coordination complexes of Ni^{II} salts with thiourea, see: Asif *et al.* (2010).



Experimental

Crystal data

 $[\text{NiCl}_2(\text{CH}_4\text{N}_2\text{S})_2]$
 $M_r = 281.85$

 Monoclinic, Cc
 $a = 8.1578$ (3) Å

 $b = 11.8183$ (5) Å
 $c = 10.8526$ (6) Å
 $\beta = 103.869$ (2)°
 $V = 1015.81$ (8) Å³
 $Z = 4$

 Mo $K\alpha$ radiation
 $\mu = 2.79$ mm⁻¹
 $T = 100$ K
 $0.42 \times 0.37 \times 0.17$ mm

Data collection

 Bruker APEXII CCD detector
 diffractometer
 Absorption correction: multi-scan
 (SADABS; Sheldrick, 2004)
 $T_{\text{min}} = 0.322$, $T_{\text{max}} = 0.622$

 4883 measured reflections
 1695 independent reflections
 1678 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.022$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.017$
 $wR(F^2) = 0.045$
 $S = 1.08$
 1695 reflections
 132 parameters
 10 restraints

 All H-atom parameters refined
 $\Delta\rho_{\text{max}} = 0.25$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.15$ e Å⁻³
 Absolute structure: Flack (1983),
 745 Friedel pairs
 Flack parameter: 0.069 (10)

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N1}-\text{H1A}\cdots\text{Cl1}$	0.84 (3)	2.60 (3)	3.388 (3)	157 (3)
$\text{N1}-\text{H1B}\cdots\text{Cl2}^{\text{i}}$	0.83 (3)	2.56 (3)	3.365 (3)	164 (3)
$\text{N2}-\text{H2A}\cdots\text{Cl2}^{\text{i}}$	0.83 (3)	2.75 (3)	3.499 (2)	150 (3)
$\text{N2}-\text{H2B}\cdots\text{Cl2}^{\text{ii}}$	0.81 (2)	2.64 (2)	3.432 (2)	166 (3)
$\text{N3}-\text{H3A}\cdots\text{Cl1}^{\text{iii}}$	0.86 (3)	2.83 (5)	3.423 (3)	128 (5)
$\text{N3}-\text{H3B}\cdots\text{Cl2}^{\text{iv}}$	0.86 (4)	2.47 (4)	3.317 (3)	168 (4)
$\text{N4}-\text{H4A}\cdots\text{S2}^{\text{v}}$	0.84 (3)	2.70 (3)	3.366 (2)	137 (3)
$\text{N4}-\text{H4B}\cdots\text{Cl1}$	0.86 (3)	2.60 (3)	3.448 (3)	168 (3)

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

Data collection: APEX2 (Bruker, 2005); cell refinement: SAINT (Bruker, 2005); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: PLATON (Spek, 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: FJ2518).

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 Zouihri, H. (2012*b*). *Acta Cryst.* **E68**, o257.

supplementary materials

Acta Cryst. (2012). E68, m314 [doi:10.1107/S1600536812006174]

Dichloridobis(thiourea- κ S)nickel(II)**Hafid Zouihri****Comment**

Nickel^(II), which has a d⁸ configuration, commonly exhibits octahedral, square planar and tetrahedral coordination geometries depending upon the nature of the ligands and the Crystal Field Splitting Parameter value.

In our case, the coordination complexes of Ni^(II) salts with thiourea show a variety of compositions and types of coordination (octahedral, tetragonal, square-planar and tetrahedral) (Asif *et al.* 2010). In general, the predominant coordination geometries for the Ni^(II)-Ligand-*X* (*X* = Cl, Br and I) are Tetragonal (Ni^(II)L₄)X₂ and Octahedral (Ni^(II)L₆)X₂. Tetrakis coordination of thiourea about Nickel Ni(Th)₄Cl₂ has been found in centered tetragonal symmetry class I4 by K. Ambujam (Ambujam *et al.* 2007).

In former work we have reported the synthesis and crystal structure of the *catena*-poly[[chlorido(thiourea- κ S)copper(I)]- μ -thiourea- κ^2 S:S] complexe (Zouihri, 2012*a*). In this paper we report the crystal structure of [Ni^(II)(Th)₂] 2Cl which has been synthesized from the (Diaminomethylidene)sulfonium chloride-thiourea (3/2) (Zouihri, 2012*b*).

In the title complex compound, (SCN₂H₄)₂Ni^(II)Cl₂, The Ni^(II) atom is four coordinated in a tetrahedral geometry by two molecules of thiourea (average Ni—S distance = 2.3079 (7) to 2.3177 (6) Å) and two chloride anions (average Ni—Cl distance = 2.2516 (7) to 2.2726 (7) Å) with average (S, Cl)—Ni^(II)—(S, Cl) torsion angles between 96.69 (2)° and 115.40 (3)°. The dihedral angle between the two thiourea Ligands is: 6.36 (15)°.

The crystal structure is characterized by intramolecular and intermolecular N—H...Cl hydrogen bonds which lead to the formation of two-dimensional networks lying parallel to the *ab* plane (Fig. 2 and Table 1). The networks are linked *via* classical intermolecular N—H...Cl and N—H...S hydrogen bonds, forming a three-dimensional arrangement (Fig. 3 and Table 1).

Experimental

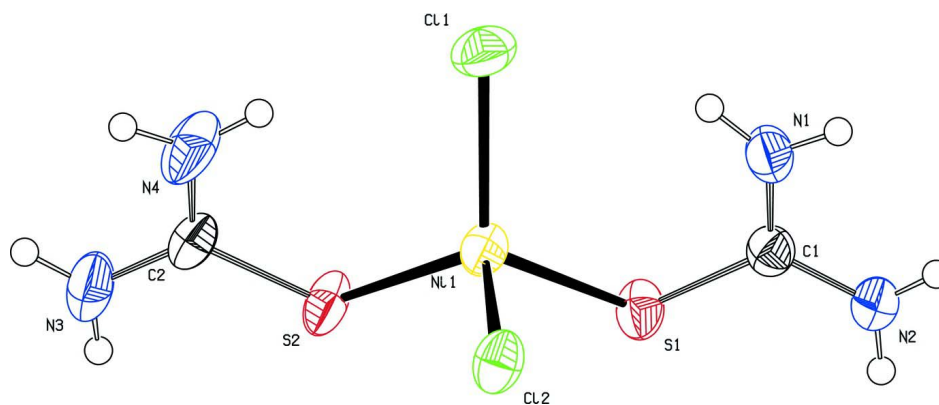
To a 10 ml aqueous solution of NiCl₂ (2 mmol) was added 10 ml EtOH solution of (Diaminomethylidene)sulfonium chloride-thiourea (3/2) (Zouihri, 2012*b*) (1.0 mmol). Colourless crystal were obtained after about one week.

Refinement

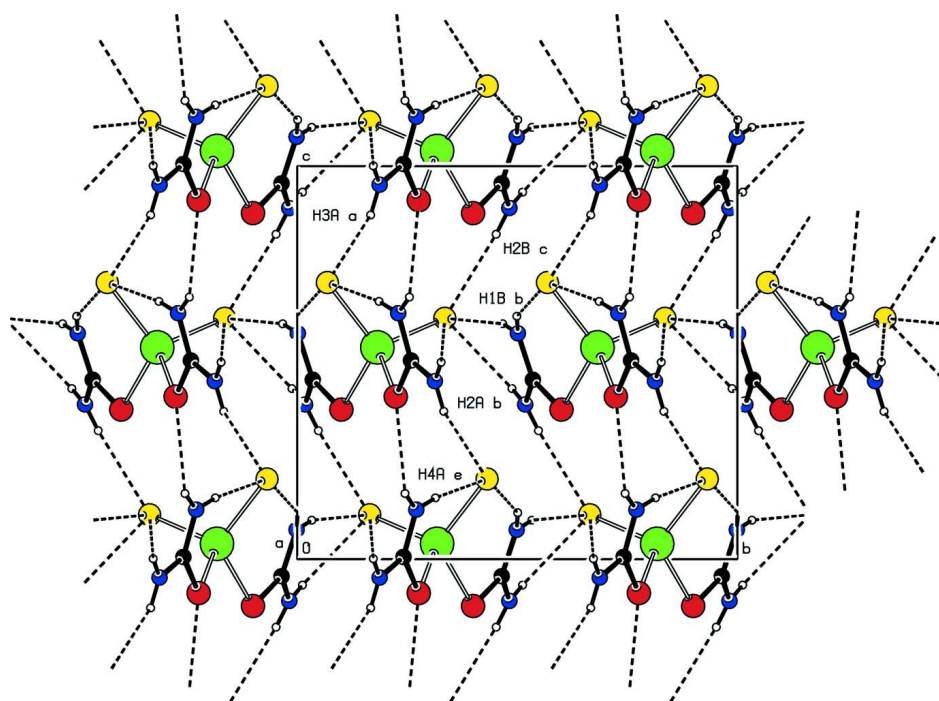
All H atoms were located from difference Fourier maps and refined isotropically, with restrained distance N—H = 0.86 (2) Å.

Computing details

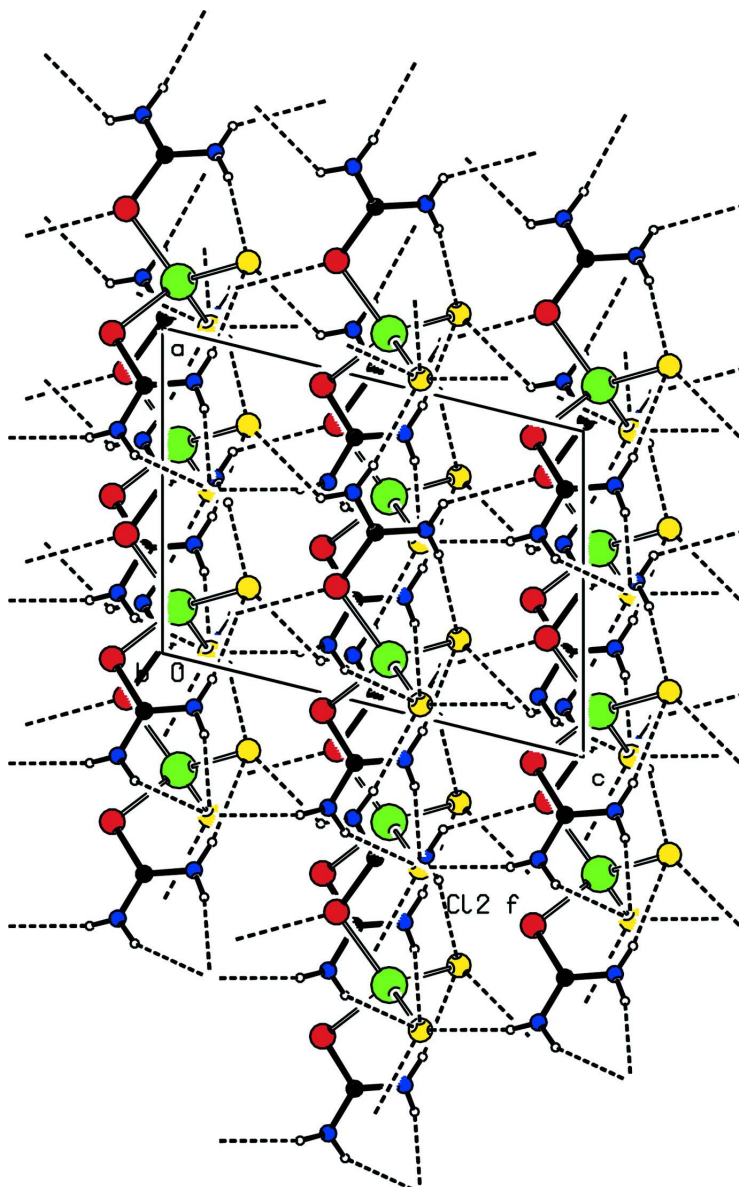
Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINTE* (Bruker, 2005); data reduction: *SAINTE* (Bruker, 2005); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *pubCIF* (Westrip, 2010).

**Figure 1**

Molecular view of the title compound showing displacement ellipsoids drawn at the 50% probability level.

**Figure 2**

Projection of the title compound along the *a* axis showing two-dimensional networks lying parallel to the *ab* plane, H-bonds are represented by dashed lines.

**Figure 3**

Projection of the title compound along the *b* axis showing the three-dimensional arrangement of the title complex, H-bonds are represented by dashed lines.

Dichloridobis(thiourea- κ S)nickel(II)

Crystal data

$[\text{NiCl}_2(\text{CH}_4\text{N}_2\text{S})_2]$

$M_r = 281.85$

Monoclinic, *Cc*

Hall symbol: *C* -2yc

$a = 8.1578$ (3) Å

$b = 11.8183$ (5) Å

$c = 10.8526$ (6) Å

$\beta = 103.869$ (2)°

$V = 1015.81$ (8) Å³

$Z = 4$

$F(000) = 568$

$D_x = 1.843$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 289 reflections

$\theta = 1.8$ – 26.7 °

$\mu = 2.79$ mm⁻¹

$T = 100$ K $0.42 \times 0.37 \times 0.17$ mm
 Prism, colourless

Data collection

Bruker APEXII CCD detector	4883 measured reflections
diffractometer	1695 independent reflections
Radiation source: fine-focus sealed tube	1678 reflections with $I > 2\sigma(I)$
Graphite monochromator	$R_{\text{int}} = 0.022$
ω and φ scans	$\theta_{\text{max}} = 25.5^\circ$, $\theta_{\text{min}} = 3.1^\circ$
Absorption correction: multi-scan	$h = -9 \rightarrow 8$
(SADABS; Sheldrick, 2004)	$k = -14 \rightarrow 14$
$T_{\text{min}} = 0.322$, $T_{\text{max}} = 0.622$	$l = -13 \rightarrow 13$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	All H-atom parameters refined
$R[F^2 > 2\sigma(F^2)] = 0.017$	$w = 1/[\sigma^2(F_o^2) + (0.0205P)^2 + 0.1021P]$
$wR(F^2) = 0.045$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.08$	$(\Delta/\sigma)_{\text{max}} = 0.002$
1695 reflections	$\Delta\rho_{\text{max}} = 0.25 \text{ e } \text{\AA}^{-3}$
132 parameters	$\Delta\rho_{\text{min}} = -0.15 \text{ e } \text{\AA}^{-3}$
10 restraints	Absolute structure: Flack (1983), 745 Friedel pairs
Primary atom site location: structure-invariant direct methods	Flack parameter: 0.069 (10)
Secondary atom site location: difference Fourier map	

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	$U_{\text{iso}}^*/U_{\text{eq}}$
Ni1	0.15345 (3)	0.18215 (2)	0.53899 (3)	0.03234 (9)
Cl2	0.03840 (8)	0.33531 (5)	0.61305 (6)	0.03892 (15)
S2	0.33740 (7)	0.22386 (7)	0.41358 (6)	0.04019 (16)
S1	-0.05478 (8)	0.10041 (6)	0.38067 (5)	0.03680 (15)
Cl1	0.26641 (9)	0.06856 (6)	0.70409 (7)	0.04738 (16)
C1	-0.1912 (3)	0.03547 (18)	0.4566 (2)	0.0312 (5)
N1	-0.1424 (3)	0.0014 (2)	0.5748 (2)	0.0427 (5)
N2	-0.3484 (3)	0.0180 (2)	0.3936 (2)	0.0419 (5)
C2	0.5326 (3)	0.2585 (2)	0.5057 (2)	0.0341 (5)
N3	0.6387 (3)	0.3127 (2)	0.4532 (3)	0.0535 (7)
N4	0.5794 (3)	0.2294 (3)	0.6260 (2)	0.0562 (7)
H1A	-0.042 (3)	-0.001 (3)	0.618 (3)	0.054 (10)*
H2A	-0.412 (4)	-0.012 (3)	0.434 (3)	0.052 (9)*

H3A	0.597 (8)	0.333 (4)	0.376 (3)	0.13 (2)*
H4A	0.672 (3)	0.255 (3)	0.667 (3)	0.067 (11)*
H1B	-0.217 (4)	-0.033 (3)	0.599 (3)	0.048 (9)*
H2B	-0.392 (4)	0.048 (2)	0.327 (2)	0.039 (8)*
H3B	0.737 (4)	0.327 (4)	0.501 (5)	0.095 (17)*
H4B	0.513 (4)	0.186 (2)	0.656 (3)	0.046 (10)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.02675 (16)	0.03985 (16)	0.03008 (15)	-0.00044 (13)	0.00613 (11)	-0.00065 (13)
Cl2	0.0308 (3)	0.0446 (3)	0.0418 (3)	-0.0015 (2)	0.0094 (3)	-0.0120 (3)
S2	0.0226 (3)	0.0721 (4)	0.0250 (3)	-0.0055 (3)	0.0039 (2)	-0.0010 (3)
S1	0.0339 (3)	0.0500 (4)	0.0255 (3)	-0.0108 (3)	0.0052 (2)	-0.0026 (3)
Cl1	0.0441 (4)	0.0561 (4)	0.0385 (4)	0.0094 (3)	0.0032 (3)	0.0128 (3)
C1	0.0307 (12)	0.0278 (11)	0.0344 (13)	-0.0013 (9)	0.0063 (10)	-0.0036 (10)
N1	0.0366 (13)	0.0507 (13)	0.0385 (12)	-0.0128 (10)	0.0046 (10)	0.0096 (9)
N2	0.0301 (12)	0.0458 (14)	0.0462 (14)	-0.0054 (10)	0.0020 (10)	0.0098 (11)
C2	0.0230 (12)	0.0414 (13)	0.0366 (13)	0.0039 (10)	0.0045 (9)	-0.0070 (10)
N3	0.0270 (13)	0.0680 (18)	0.0648 (19)	-0.0072 (11)	0.0099 (13)	0.0030 (14)
N4	0.0326 (14)	0.095 (2)	0.0335 (13)	-0.0043 (14)	-0.0065 (11)	-0.0040 (14)

Geometric parameters (\AA , $^\circ$)

Ni1—Cl1	2.2516 (7)	N1—H1B	0.822 (18)
Ni1—Cl2	2.2726 (7)	N2—H2A	0.840 (19)
Ni1—S2	2.3079 (7)	N2—H2B	0.806 (18)
Ni1—S1	2.3177 (6)	C2—N3	1.312 (4)
S2—C2	1.715 (2)	C2—N4	1.315 (4)
S1—C1	1.716 (2)	N3—H3A	0.87 (2)
C1—N1	1.312 (3)	N3—H3B	0.86 (2)
C1—N2	1.317 (3)	N4—H4A	0.836 (19)
N1—H1A	0.843 (19)	N4—H4B	0.865 (19)
Cl1—Ni1—Cl2	108.56 (3)	H1A—N1—H1B	120 (3)
Cl1—Ni1—S2	113.37 (3)	C1—N2—H2A	116 (3)
Cl2—Ni1—S2	114.86 (3)	C1—N2—H2B	124 (2)
Cl1—Ni1—S1	115.40 (3)	H2A—N2—H2B	117 (4)
Cl2—Ni1—S1	107.62 (3)	N3—C2—N4	119.7 (3)
S2—Ni1—S1	96.69 (2)	N3—C2—S2	118.7 (2)
C2—S2—Ni1	110.56 (9)	N4—C2—S2	121.6 (2)
C1—S1—Ni1	105.95 (8)	C2—N3—H3A	114 (4)
N1—C1—N2	119.3 (2)	C2—N3—H3B	117 (4)
N1—C1—S1	121.80 (19)	H3A—N3—H3B	128 (6)
N2—C1—S1	118.9 (2)	C2—N4—H4A	116 (3)
C1—N1—H1A	126 (3)	C2—N4—H4B	118 (3)
C1—N1—H1B	113 (3)	H4A—N4—H4B	126 (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> ···C11	0.84 (3)	2.60 (3)	3.388 (3)	157 (3)
N1—H1 <i>B</i> ···C12 ⁱ	0.83 (3)	2.56 (3)	3.365 (3)	164 (3)
N2—H2 <i>A</i> ···C12 ⁱ	0.83 (3)	2.75 (3)	3.499 (2)	150 (3)
N2—H2 <i>B</i> ···C12 ⁱⁱ	0.81 (2)	2.64 (2)	3.432 (2)	166 (3)
N3—H3 <i>A</i> ···C11 ⁱⁱⁱ	0.86 (3)	2.83 (5)	3.423 (3)	128 (5)
N3—H3 <i>B</i> ···C12 ^{iv}	0.86 (4)	2.47 (4)	3.317 (3)	168 (4)
N4—H4 <i>A</i> ···S2 ^v	0.84 (3)	2.70 (3)	3.366 (2)	137 (3)
N4—H4 <i>B</i> ···C11	0.86 (3)	2.60 (3)	3.448 (3)	168 (3)

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