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Bis{(*Z*)-[(*E*)-2-(pyridin-2-ylmethylidene)-hydrazin-1-ylidene][(pyridin-2-yl)methylsulfanyl]methanethiolato}nickel(II)

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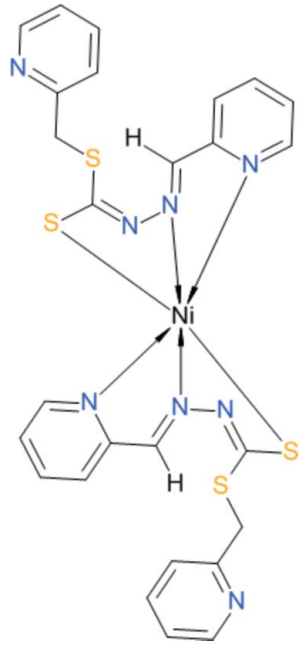
Key indicators: single-crystal X-ray study; T = 150 K; mean σ(C–C) = 0.016 Å; R factor = 0.045; wR factor = 0.121; data-to-parameter ratio = 11.7.

The title compound, $[Ni(C_{13}H_{11}N_4S_2)_2]$, was obtained by the reaction of *S*-2-picolyldithiocarbazate and pyridine-2-carbaldehyde with nickel(II) acetate. The Ni^{II} atom is located on a twofold rotation axis and is bonded to four N atoms at distances of 2.037 (8) and 2.109 (9) Å, and to two S atoms at a distance of 2.406 (3) Å, leading to a distorted octahedral coordination. The angle between the mean planes of the coordinating moieties of the two symmetry-related tridentate ligands is 83.3 (2)°. In the crystal, complex molecules are linked by weak C—H···S hydrogen bonds, π–π interactions between the pyridine rings [centroid–centroid distance = 3.775 (9) Å] and C—H···π interactions. The hydrogen-bonding interactions lead to the formation of layers parallel to (010); π–π interactions link these layers into a three-dimensional network.

Related literature

For biological applications of Schiff base ligands and complexes derived from dithiocarbazates, see: Hossain *et al.* (1996); Tarafder *et al.* (2002); Crouse *et al.* (2004). For a related structure, see: Omar *et al.* (2012).



Experimental

Crystal data

$[Ni(C_{13}H_{11}N_4S_2)_2]$
M_r = 633.49
Monoclinic, $C2/c$
a = 26.0501 (4) Å
b = 8.0057 (1) Å
c = 13.0743 (2) Å
β = 103.8993 (9)°
V = 2646.80 (7) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 1.08 mm^{-1}
T = 150 K
0.04 × 0.03 × 0.02 mm

Data collection

Nonius Kappa CCD diffractometer
Absorption correction: multi-scan (*DENZO/SCALEPACK*; Otwinowski & Minor, 1997)
T_{min} = 0.97, T_{max} = 0.98
5912 measured reflections
3030 independent reflections
2066 reflections with $I > 3\sigma(I)$
R_{int} = 0.020

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.045
$wR(F^2)$ = 0.121
S = 1.08
2066 reflections
177 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.81 e Å^{-3}
$\Delta\rho_{min}$ = −0.74 e Å^{-3}

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

Cg is the centroid of the pyridine ring (C9–C13/N4).

D—H···A	D—H	H···A	D···A	D—H···A
C8—H7···S2^{i}	0.94	2.72	3.644 (9)	166
C4—H4···S2^{i}	0.95	2.92	3.862 (11)	175
C6—H6···Cg^{ii}	0.98	2.98	3.750 (12)	136

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

Data collection: *COLLECT* (Nonius, 2001); cell refinement: *DENZO/SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO/SCALEPACK*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003); molecular graphics: *Mercury*

(Macrae *et al.*, 2006); 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: WM2742).

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supporting information

Acta Cryst. (2013). E**69**, m323–m324 [doi:10.1107/S1600536813013032]

Bis{(*Z*)-[(*E*)-2-(pyridin-2-ylmethylidene)hydrazin-1-ylidene][(pyridin-2-yl)methylsulfanyl]methanethiolato}nickel(II)

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S1. Comment

In the last few decades an increasing interest in the potential benefits of dithiocarbazates has arisen which has led to the synthesis of several Schiff base ligands and complexes that can be derived from dithiocarbazates (Tarafder *et al.*, 2002; Hossain *et al.*, 1996). S-2-picolyl dithiocarbazate (S2PDTC) is one type of a dithiocarbazate compound that has been synthesized recently, and its Schiff bases and complexes have proven to possess antimicrobial and anticancer activities (Crouse *et al.*, 2004). Due to these potential medicinal properties of S2PDTC-derived Schiff bases and complexes, the title compound was synthesized and structurally analyzed.

The Ni^{II} atom is situated on a twofold rotation axis and is bonded to four nitrogen atoms [Ni—N3 = 2.037 (8) Å; Ni—N4 = 2.109 (9) Å] and two sulfur atoms [Ni—S2 = 2.406 (3) Å] in a distorted octahedral coordination environment as exemplified by the angle N4—Ni1—S2 = 158.4 (2)° (Fig. 1). The bond length of C7—S2 is 1.723 (10) Å, similar to that of C7—S1 of 1.746 (10) Å, which indicates that the ligand bonds to the Ni^{II} ion in its thiol tautomer *via* the deprotonated S atoms.

The angle between the mean plane defined by (Ni1—S2—C7—N2—N3—N4—C8) and that of the symmetry-related ligand is 83.3 (2)° which shows that the two ligands are nearly orthogonal to each other. The Ni—N bond lengths of the title complex are very similar to that of a previously reported related structure (Omar *et al.*, 2012) [2.013 (2) Å for Ni—N, 2.179 (2) Å for Ni—N where this N atom belongs to the pyridine ring; 2.426 (7) Å for Ni—S] which might indicate that the values of such bond lengths are typical of nickel(II) complexes derived from dithiocarbazates. The pyridine ring (C1—C2—C3—C4—C5—N1) is nearly perpendicular to the rest of the molecule with a torsion angle of C5—C6—S1—C7 = 84.0 (8)°.

The molecules in the crystal are stabilized by weak intermolecular C—H···S hydrogen bonding interactions (Table 1; Fig. 2). Moreover, the pyridine rings (C1—C2—C3—C4—C5—N1) at (*x*, *y*, *z*) and (3/2 - *x*, 1/2 - *y*, 2 - *z*) are stacked parallel to each other and form $\pi\cdots\pi$ interactions (Fig. 3) with a centroid-centroid separation of 3.775 (9) Å and a shift distance of 1.878 (17) Å while the distance between the planes of the rings is 3.275 (12) Å. There are also C—H···π interactions (Table 1; Fig. 4).

S2. Experimental

The nickel complex was synthesized according to a modified procedure reported by Crouse *et al.* (2004): 0.02 mole of S-picolyl dithiocarbazate were added to a beaker containing 40 ml of absolute ethanol followed by heating the mixture on a heating plate with constant stirring in order to ensure complete dissolving. Similarly, 0.02 mole of pyridine-2-carbaldehyde were dissolved in a separate beaker containing 40 ml of absolute ethanol followed by heating and stirring

of the mixture. The reactants were later mixed and 2–4 drops of concentrated H_2SO_4 were added to the mixture followed by heating of the mixture for 5 minutes. The mixture was cooled to 273 K in an ice-bath until the precipitation of the Schiff base ligand was achieved, and this was followed by filtration of the precipitated Schiff base ligand *via* suction filtration, washing it with cold ethanol and drying over silica gel.

0.0076 mole of the synthesized Schiff base ligand were dissolved in 50 ml of absolute ethanol followed by the addition of an equimolar amount of KOH and the mixture was heated over a heating plate and stirred until the compounds had been completely dissolved. The solution was then treated with a stoichiometric amount of nickel(II) acetate (0.0038 moles) dissolved in 50 ml of absolute ethanol followed by heating for 5 minutes and then kept in an ice-salt bath. Finally, the obtained product was isolated *via* suction filtration, washed with ethanol and dried over silica gel.

S3. Refinement

The H atoms were all located in a difference map, but those attached to carbon atoms were repositioned geometrically. The H atoms were initially refined with soft restraints on the bond lengths and angles to regularize their geometry (C—H in the range 0.93–98 Å) and isotropic temperature factors (U_{iso}(H) in the range 1.2–1.5 times U_{eq} of the parent atom), after which the positions were refined with riding constraints.

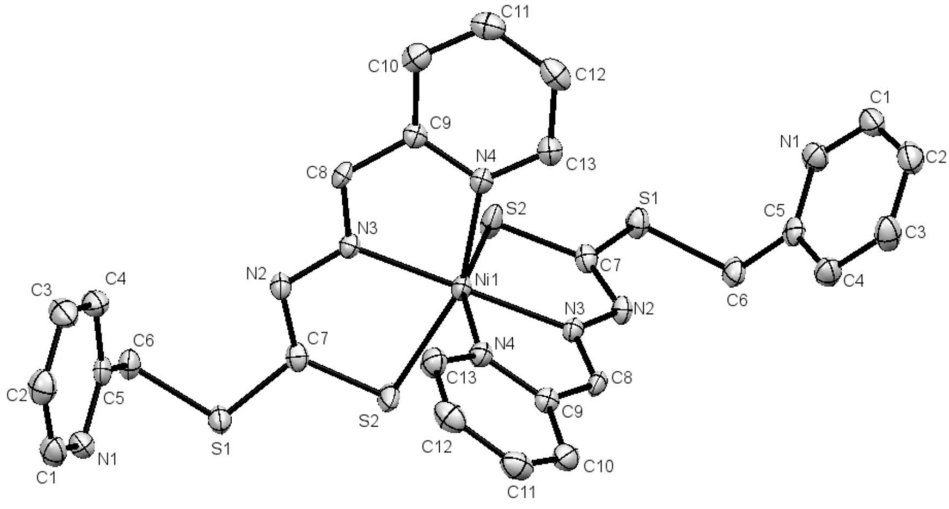

Figure 1

The molecular structure of the title compound showing 50% probability displacement ellipsoids in addition to the atomic numbering scheme. Hydrogen atoms were omitted for clarity. The second ligand is related to the first by symmetry code x, $-y$, $z + 1/2$.

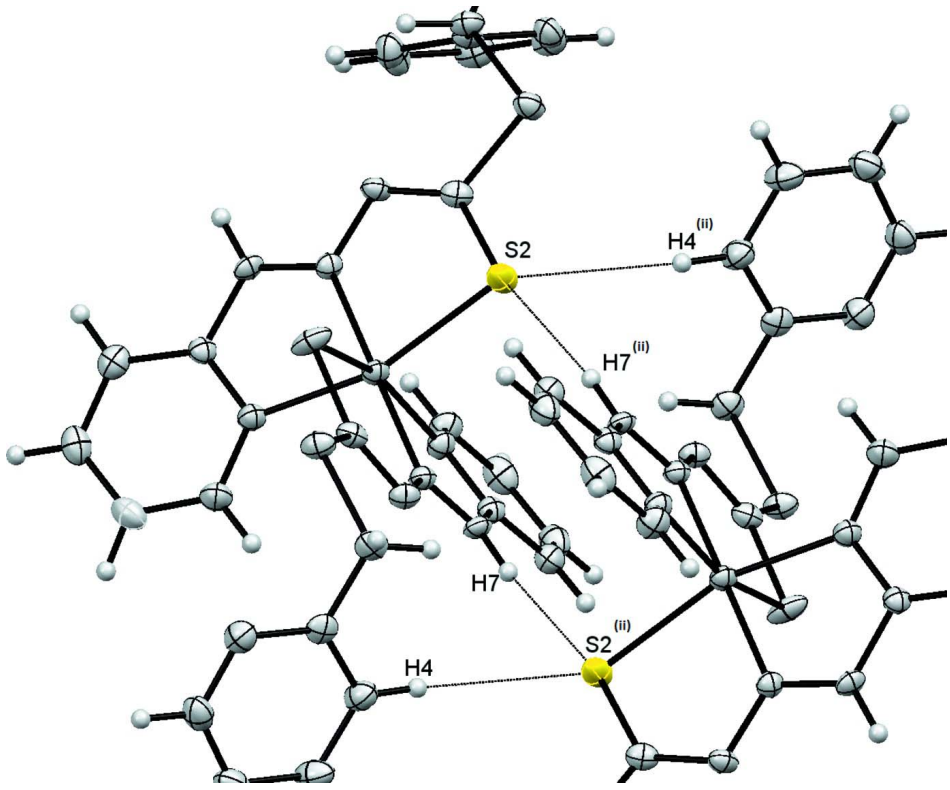

Figure 2

The molecules in the structure are stabilized by intermolecular C—H···S hydrogen bonding interactions. Probability function as in Fig. 1. [Symmetry code: (ii) *x*, -*y*, *z* + 1/2.]

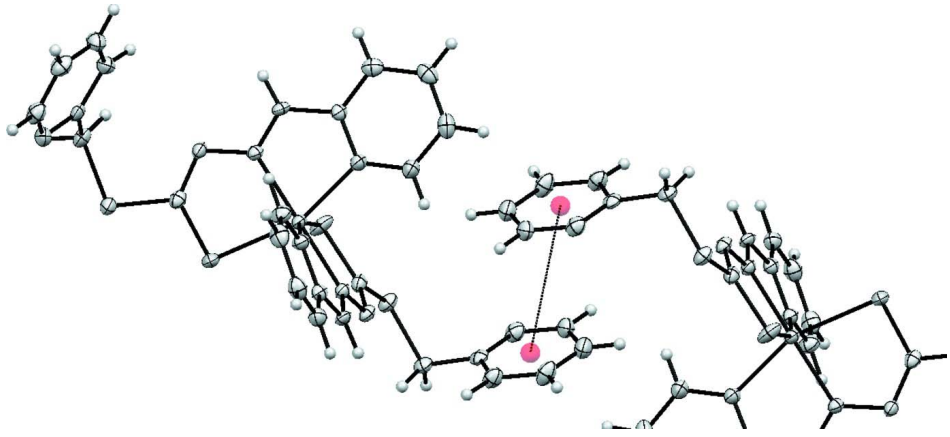

Figure 3

The molecules in the structure are also linked by $\pi\cdots\pi$ interactions between pairs of pyridine rings with a centroid···centroid distance of 3.775 (9) Å. Probability function as in Fig. 1. [Symmetry code: 3/2 - *x*, 1/2 - *y*, 2 - *z*.]

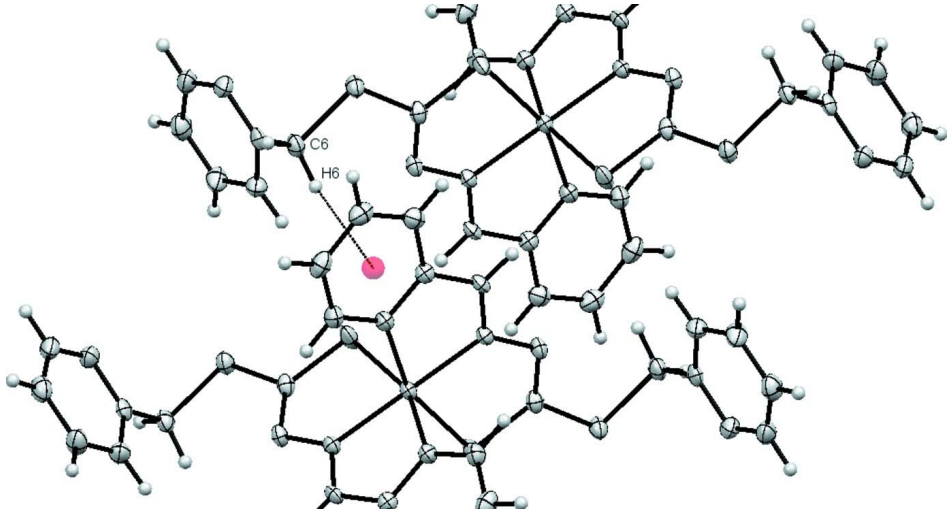

Figure 4

Diagram showing the C—H···π interaction between the molecules in the structure. Probability function as in Fig. 1. [Symmetry code: 1 - *x*, - *y*, 2 - *z*.]

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Crystal data

$[Ni(C_{13}H_{11}N_4S_2)_2]$
M_r = 633.49
Monoclinic, *C*2/*c*
Hall symbol: -C 2yc
a = 26.0501 (4) Å
b = 8.0057 (1) Å
c = 13.0743 (2) Å
β = 103.8993 (9)°
V = 2646.80 (7) Å^3
Z = 4
F(000) = 1304
D_x = 1.590 Mg m^{-3}
Mo *K*α radiation, λ = 0.71073 Å
Cell parameters from 3175 reflections
θ = 1–27°
μ = 1.08 mm^{-1}
T = 150 K
Plate, dark green
0.04 × 0.03 × 0.02 mm

Data collection

Nonius Kappa CCD diffractometer
Graphite monochromator
ω scans
Absorption correction: multi-scan (*DENZO*/*SCALEPACK*; Otwinowski & Minor, 1997)
T_{min} = 0.97, T_{max} = 0.98
5912 measured reflections
3030 independent reflections
2066 reflections with $I > 3\sigma(I)$
R_{int} = 0.020
θ_{max} = 27.5°, θ_{min} = 2.7°
h = −33→33
k = −10→10
l = −16→16

Refinement

Refinement on *F*
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.045
$wR(F^2)$ = 0.121
S = 1.08
2066 reflections
177 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
Method = Quasi-Unit *w*eights W = 1.0 or 1./2*F*

$(\Delta/\sigma)_{max}$ = 0.000256
$\Delta\rho_{max}$ = 0.81 e Å^{-3}
$\Delta\rho_{min}$ = −0.74 e Å^{-3}

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

	x	*y*	*z*	U_{iso}*/U_{eq}
H1	0.8234	0.1314	1.0674	0.0390*
H2	0.8039	0.3461	1.1740	0.0419*
H3	0.7243	0.3331	1.2252	0.0430*
H4	0.6648	0.1115	1.1674	0.0380*
H5	0.6999	−0.2613	1.0830	0.0320*
H6	0.6483	−0.1561	1.0864	0.0320*
H7	0.5288	0.1849	1.0417	0.0250*
H8	0.4519	0.3855	1.0530	0.0351*
H9	0.3830	0.5632	0.9638	0.0430*
H10	0.3638	0.5694	0.7768	0.0412*
H11	0.4110	0.4002	0.6869	0.0369*
C1	0.7910 (4)	0.1272 (16)	1.0890 (8)	0.0279
C2	0.7800 (5)	0.2562 (16)	1.1526 (9)	0.0301
C3	0.7328 (5)	0.2491 (16)	1.1824 (9)	0.0304
C4	0.6977 (4)	0.1170 (16)	1.1487 (8)	0.0266
C5	0.7126 (4)	−0.0081 (14)	1.0863 (7)	0.0204
C6	0.6789 (4)	−0.1619 (14)	1.0548 (8)	0.0229
C7	0.5986 (4)	−0.0675 (13)	0.8762 (8)	0.0197
C8	0.5162 (4)	0.1936 (13)	0.9682 (7)	0.0177
C9	0.4708 (4)	0.2967 (13)	0.9196 (7)	0.0178
C10	0.4431 (4)	0.3919 (15)	0.9783 (8)	0.0243
C11	0.4023 (4)	0.4963 (15)	0.9253 (9)	0.0281
C12	0.3908 (4)	0.4991 (15)	0.8152 (9)	0.0284
C13	0.4192 (4)	0.3980 (16)	0.7618 (8)	0.0253
S1	0.65548 (10)	−0.1902 (4)	0.9126 (2)	0.0223
S2	0.56873 (11)	−0.0826 (4)	0.7438 (2)	0.0273
N1	0.7591 (3)	−0.0039 (12)	1.0560 (7)	0.0250
N2	0.5828 (3)	0.0209 (11)	0.9494 (6)	0.0185
N3	0.5379 (3)	0.1138 (11)	0.9056 (6)	0.0168
N4	0.4582 (3)	0.2990 (11)	0.8126 (6)	0.0196
Ni1	0.5000	0.1151 (3)	0.7500	0.0172

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.019 (5)	0.037 (7)	0.026 (5)	−0.004 (5)	0.002 (4)	0.004 (5)
C2	0.027 (6)	0.032 (6)	0.028 (6)	−0.007 (5)	0.000 (5)	−0.001 (5)
C3	0.025 (6)	0.034 (6)	0.029 (6)	0.004 (5)	0.002 (5)	−0.012 (5)
C4	0.022 (5)	0.034 (6)	0.023 (5)	0.002 (5)	0.005 (4)	−0.006 (5)
C5	0.019 (5)	0.024 (5)	0.015 (4)	0.004 (4)	−0.002 (4)	0.005 (4)
C6	0.022 (5)	0.026 (6)	0.018 (5)	0.001 (4)	−0.001 (4)	0.004 (4)
C7	0.019 (5)	0.017 (5)	0.020 (5)	−0.002 (4)	0.000 (4)	0.000 (4)

C8	0.022 (5)	0.020 (5)	0.010 (4)	−0.002 (4)	0.001 (4)	−0.002 (4)
C9	0.019 (5)	0.016 (5)	0.018 (5)	0.000 (4)	0.004 (4)	0.000 (4)
C10	0.026 (5)	0.025 (6)	0.023 (5)	−0.005 (5)	0.007 (4)	−0.002 (5)
C11	0.025 (5)	0.026 (6)	0.035 (6)	−0.002 (5)	0.012 (5)	−0.005 (5)
C12	0.021 (5)	0.025 (6)	0.039 (6)	0.003 (5)	0.005 (5)	0.004 (5)
C13	0.022 (5)	0.031 (6)	0.021 (5)	0.004 (5)	0.002 (4)	0.002 (5)
S1	0.0207 (12)	0.0238 (14)	0.0197 (12)	0.0040 (11)	−0.0003 (9)	−0.0014 (11)
S2	0.0276 (14)	0.0357 (17)	0.0145 (11)	0.0112 (12)	−0.0026 (10)	−0.0066 (11)
N1	0.019 (4)	0.032 (5)	0.023 (4)	0.005 (4)	0.003 (3)	−0.001 (4)
N2	0.018 (4)	0.019 (4)	0.016 (4)	0.002 (4)	−0.001 (3)	0.001 (3)
N3	0.017 (4)	0.018 (4)	0.014 (4)	−0.001 (4)	0.002 (3)	−0.002 (3)
N4	0.019 (4)	0.023 (5)	0.016 (4)	0.001 (4)	0.003 (3)	0.001 (4)
Ni1	0.0172 (9)	0.0210 (10)	0.0120 (8)	0.0000	0.0007 (6)	0.0000

Geometric parameters (Å, º)

H1—C1	0.952	C5—N1	1.361 (13)
H2—C2	0.948	C6—S1	1.826 (10)
H3—C3	0.936	C7—S1	1.746 (10)
H4—C4	0.949	C7—S2	1.723 (10)
H5—C6	0.986	C7—N2	1.333 (13)
H6—C6	0.982	C8—C9	1.458 (14)
H7—C8	0.940	C8—N3	1.272 (13)
H8—C10	0.949	C9—C10	1.398 (14)
H9—C11	0.956	C9—N4	1.358 (12)
H10—C12	0.944	C10—C11	1.399 (16)
H11—C13	0.951	C11—C12	1.398 (16)
C1—C2	1.397 (17)	C12—C13	1.392 (16)
C1—N1	1.345 (15)	C13—N4	1.335 (13)
C2—C3	1.377 (16)	S2—Ni1	2.406 (3)
C3—C4	1.398 (17)	N2—N3	1.388 (11)
C4—C5	1.404 (15)	N3—Ni1	2.037 (8)
C5—C6	1.512 (15)	N4—Ni1	2.109 (9)
H1—C1—C2	118.2	H9—C11—C12	121.5
H1—C1—N1	117.1	C10—C11—C12	118.0 (10)
C2—C1—N1	124.6 (10)	C11—C12—H10	120.4
H2—C2—C1	121.6	C11—C12—C13	119.9 (10)
H2—C2—C3	120.9	H10—C12—C13	119.7
C1—C2—C3	117.5 (11)	H11—C13—C12	119.4
H3—C3—C2	119.8	H11—C13—N4	118.5
H3—C3—C4	120.0	C12—C13—N4	122.0 (10)
C2—C3—C4	120.2 (11)	C6—S1—C7	105.2 (5)
H4—C4—C3	121.2	C7—S2—Ni1	94.6 (4)
H4—C4—C5	120.7	C5—N1—C1	116.8 (9)
C3—C4—C5	118.1 (10)	C7—N2—N3	111.3 (8)
C4—C5—C6	121.0 (9)	N2—N3—C8	117.6 (8)
C4—C5—N1	122.8 (10)	N2—N3—Ni1	124.9 (6)

C6—C5—N1	116.1 (9)	C8—N3—Ni1	117.2 (7)
C5—C6—H5	108.8	C9—N4—C13	119.1 (9)
C5—C6—H6	108.9	C9—N4—Ni1	111.8 (7)
H5—C6—H6	108.4	C13—N4—Ni1	128.7 (7)
C5—C6—S1	114.1 (7)	N4—Ni1—N4^{i}	91.5 (5)
H5—C6—S1	107.4	N4—Ni1—S2	158.4 (2)
H6—C6—S1	109.1	N4^{i}—Ni1—S2	89.4 (2)
S1—C7—S2	112.5 (6)	N4—Ni1—S2^{i}	89.4 (2)
S1—C7—N2	119.4 (7)	N4^{i}—Ni1—S2^{i}	158.4 (2)
S2—C7—N2	128.0 (8)	S2—Ni1—S2^{i}	97.72 (17)
H7—C8—C9	122.4	N4—Ni1—N3	77.7 (3)
H7—C8—N3	121.3	N4^{i}—Ni1—N3	102.7 (3)
C9—C8—N3	116.3 (8)	S2—Ni1—N3	81.0 (2)
C8—C9—C10	122.7 (9)	S2^{i}—Ni1—N3	98.6 (2)
C8—C9—N4	115.2 (9)	N4—Ni1—N3^{i}	102.7 (3)
C10—C9—N4	122.1 (9)	N4^{i}—Ni1—N3^{i}	77.7 (3)
H8—C10—C9	120.4	S2—Ni1—N3^{i}	98.6 (2)
H8—C10—C11	120.6	S2^{i}—Ni1—N3^{i}	81.0 (2)
C9—C10—C11	119.0 (10)	N3—Ni1—N3^{i}	179.4 (5)
H9—C11—C10	120.5		

Symmetry code: (i) $-x+1, y, -z+3/2$.

Hydrogen-bond geometry (Å, º)

Cg is the centroid of the pyridine ring (C9–C13/N4).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C8—H7···S2^{ii}	0.94	2.72	3.644 (9)	166
C4—H4···S2^{ii}	0.95	2.92	3.862 (11)	175
C6—H6···*Cg*^{iii}	0.98	2.98	3.750 (12)	136

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