

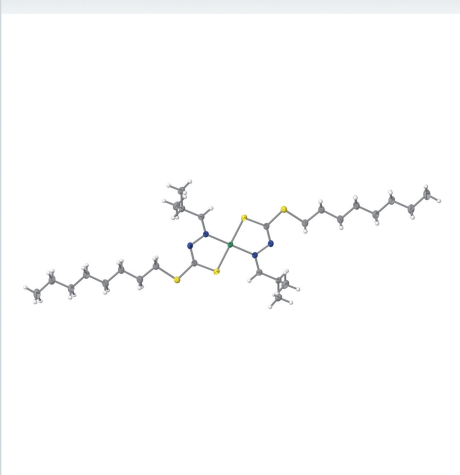
Bis[S-octyl 3-(2-methylpropylidene)dithiocarbazato- κ^2N^3,S]nickel(II)

Sultana Shakila Khan,^a Md. Belayet Hossain Howlader,^{a*} Md. Chanmiya Sheikh,^b Ryuta Miyatake^c and Ennio Zangrando^d

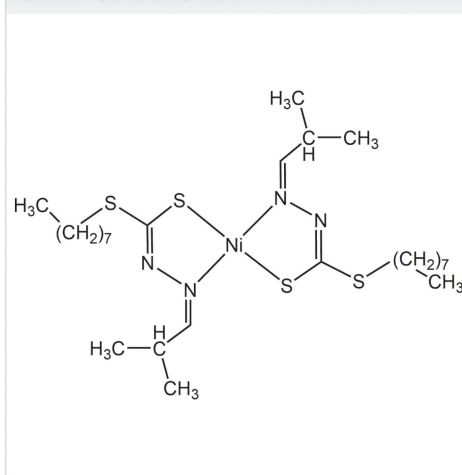
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The central Ni^{II} atom in the title complex, [Ni(C₁₃H₂₅N₂S₂)₂], is located on an inversion center and adopts a roughly square-planar coordination environment defined by two chelating *N,S* donor sets of two symmetry-related ligands in a *trans* configuration. The Ni–N and Ni–S bond lengths are 1.9193 (14) and 2.1788 (5) Å, respectively, with a chelating N–Ni–S bond angle of 86.05 (4)°. These data are compared with those measured for similar dithiocarbazato ligands that bear *n*-octyl or *n*-hexyl alkyl chains. Slight differences are observed with respect to the phenylethylidene derivative where the ligands are bound *cis* relative to one another.

3D view



Chemical scheme



Structure description

Dithiocarbazate Schiff base derivatives have emerged as prospective ligands in medicinal chemistry as a result of their various pharmaceutical and biological activities (Gou *et al.*, 2022; Low *et al.*, 2016; Malik *et al.*, 2020). For some years, we have been undertaking a study of *N,S*-chelating dithiocarbazato ligands and their corresponding metal complexes, which were observed to crystallize with ligands both in *trans* and *cis* configurations (Begum *et al.*, 2020). Considering the above aspects, and in a continuation of our research, we report herein a novel Ni^{II} complex with a dithiocarbazato Schiff base ligand bearing an octyl alkyl chain.

In the title complex (Fig. 1), [Ni(C₁₃H₂₅N₂S₂)₂], the Ni^{II} atom is located on an inversion center and exhibits a square-planar coordination environment, defined by two negatively charged *N,S*-chelating ligands in a *trans* configuration. The Ni–N1 and Ni–S1 bond lengths are 1.9193 (14) and 2.1788 (5) Å, respectively, with a chelating N1–Ni–S1 bond angle of 86.05 (4)°. With the exception of methyl groups C1 and C2, all

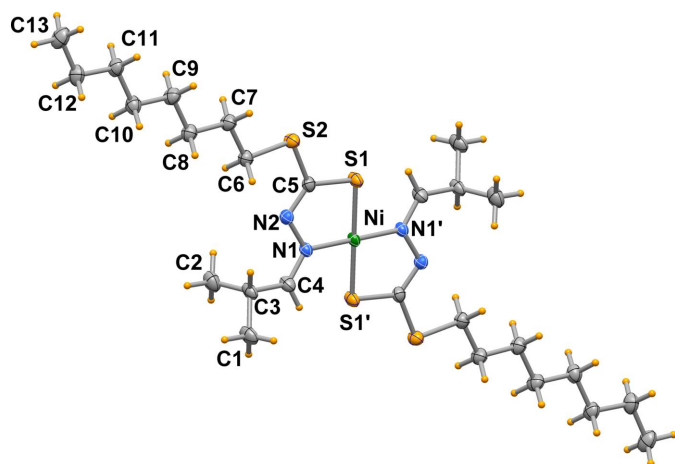


Figure 1
Molecular structure of the title complex $[\text{Ni}(\text{C}_{13}\text{H}_{25}\text{N}_2\text{S}_2)_2]$ with displacement ellipsoids drawn at the 50% probability level.

of the non-H atoms of the title complex are coplanar, with Ni1 (+0.16 Å) and S1 (−0.15 Å) deviating the most from the least-squares plane (r.m.s. deviation of fitted atoms = 0.073 Å). The long alkyl chain is in a staggered conformation with torsion angles along the chain between 178.20 (19) and 179.81 (15)°. The molecular structure is stabilized by an intramolecular non-conventional C4—H4···S1ⁱ hydrogen bond with a C4···S1ⁱ distance of 3.0965 (16) Å and a C4—H4···S1ⁱ angle of 121° [symmetry code: (i): 1 − x, 1 − y, 1 − z].

A number of Ni^{II} complexes with ligands bearing *n*-octyl or *n*-hexyl alkyl chains have been structurally characterized and a comparison of relevant bond lengths and angles is compiled in Table 1. The corresponding values reported above are

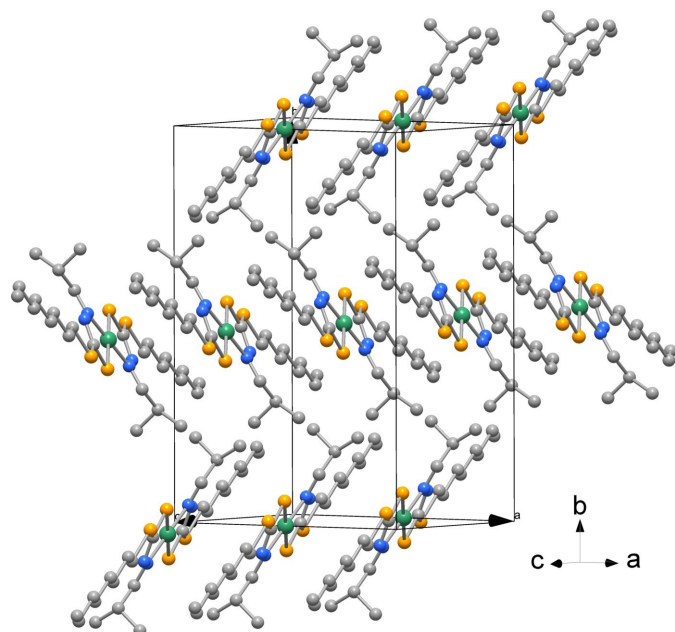


Figure 2
View of the crystal packing of the title complex $[\text{Ni}(\text{C}_{13}\text{H}_{25}\text{N}_2\text{S}_2)_2]$ in a view along [102]; H atoms are not shown for clarity.

Table 1
Comparative geometrical parameters (Å, °) for bis-chelated Ni complexes with dithiocarbazato ligands bearing an *S*-octyl/*S*-hexyl (*n*) alkyl chain.

Complex	CSD Refcode	<i>n</i>	Ni—N	Ni—S	N—Ni—S
This work	—	8	1.9193 (14)	2.1788 (5)	86.05 (4)
1	BIQTIH	8	1.9310 (19)	2.1796 (6)	85.67 (5)
2	MIMTIG	8	1.9168 (19)	2.1735 (7)	85.88 (6)
3, ligand 1	QIVYUT	8	1.9318 (16)	2.1506 (6)	86.26 (5)
3, ligand 2	QIVYUT	8	1.9392 (16)	2.1573 (6)	86.40 (5)
4	LUBYAK	6	1.933 (3)	2.1775 (10)	86.04 (9)
5, ligand 1	JUYCAJ	6	1.9112 (12)	2.1785 (4)	85.74 (3)
5, ligand 2	JUYCAJ	6	1.9177 (12)	2.1812 (4)	86.03 (4)
6	WEGKEB	6	1.915 (2)	2.1788 (8)	85.58 (8)
7	TILVUJ	6	1.9295 (10)	2.1600 (4)	85.68 (3)

Notes: Complex **1** (Begum *et al.*, 2018); **2** (Kahn *et al.*, 2023a); **3** (Kahn *et al.*, 2023b); **4** (Howlader *et al.*, 2015); **5** (Begum *et al.*, 2016); **6** (Begum *et al.*, 2017); **7** (Begum *et al.*, 2020). Complexes **3** and **7** show a *cis* configuration of ligands.

consistent with those measured in bis-chelated Ni^{II} complexes

Table 2
Experimental details.

Crystal data	
Chemical formula	$[\text{Ni}(\text{C}_{13}\text{H}_{25}\text{N}_2\text{S}_2)_2]$
M_r	605.65
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	173
<i>a</i> , <i>b</i> , <i>c</i> (Å)	11.5962 (4), 18.4606 (5), 7.8973 (2)
β (°)	106.532 (7)
<i>V</i> (Å ³)	1620.71 (10)
<i>Z</i>	2
Radiation type	Mo $K\alpha$
μ (mm ^{−1})	0.88
Crystal size (mm)	0.18 × 0.06 × 0.02
Data collection	
Diffractometer	Rigaku R-Axis RAPID
Absorption correction	Multi-scan (ABSCOR; Rigaku, 1995)
T_{\min} , T_{\max}	0.781, 0.983
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	15550, 3702, 2920
R_{int}	0.049
$(\sin \theta/\lambda)_{\text{max}}$ (Å ^{−1})	0.649
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.036, 0.072, 1.04
No. of reflections	3702
No. of parameters	163
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ^{−3})	0.37, −0.21

Computer programs: RAPID-AUTO (Rigaku, 2018), SHELXT (Sheldrick, 2015a), SHELXL (Sheldrick, 2015b), DIAMOND (Brandenburg, 1999) and WinGX publication routines (Farrugia, 2012).

built with similar ligands bearing a methoxybenzylidene (Begum *et al.*, 2018) or thiophenemethylidene (Khan *et al.*, 2023a) ligand. On the contrary, in the phenylethylidene complex (Khan *et al.*, 2023b) the two independent Ni—N bond lengths are 0.02 Å longer with respect to those calculated in the present work, while the Ni—S ones are shorter by ca 0.02 Å. It is worth noting that the latter complex exhibits a *cis* configuration of the ligands. A similar trend is also observed in the complex with the *S*-*n*-hexyl 3-(1-phenylethylidene)dithiocarbazate ligand (Begum *et al.*, 2020). Nickel(II) and copper(II) complexes with dithiocarbazato ligands have been reported to crystallize in both *cis* and *trans* configurations,

although the latter are slightly more frequent (Begum *et al.*, 2020). However, the chelating *N,S* bond angles in these complexes are similar within their standard deviations and fall into the range 85.67 (5)–86.40 (5)°.

The packing of the complex is shown in Fig. 2; the complexes stack with an Ni··Ni separation of 7.8973 (2) Å along the *c* axis.

Synthesis and crystallization

A solution of Ni(CH₃COO)₂·4H₂O (0.124 g, 0.5 mmol) in 10 ml of methanol was added to a solution of *S*-octyl-3-(2-methylpropylidene)dithiocarbamate (0.274 g, 1.0 mmol) in 30 ml of methanol. The resulting mixture was stirred at room temperature for 5 h. The green precipitate that formed was filtered off, washed with methanol and dried *in vacuo* over anhydrous CaCl₂. Green single crystals of the title compound suitable for X-ray diffraction were obtained by slow evaporation from a mixture of chloroform and acetonitrile (1:1, *v/v*) after 7 d.

Yield: 72%; m. p. 333–334 K. FT-IR (KBr discs, cm⁻¹): ν(C–H, alkyl) 2964, 2922, ν(C=N–N=C) 1634. ¹H NMR (400 MHz, CDCl₃, p.p.m.) δ: 6.99 (*d*, 2×1H, C-4, CH=N), 3.29 (*m*, 2×1H, C-3), 2.98 (*t*, 2×2H, C-6, –SCH₂), 1.65 (*m*, 2×2H, C-7), 1.38–1.12 (*m*, 2×10H, C-8, 9, 10, 11, 12), 1.00 (*d*, 2×6H, C-1, 2, CH₃), 0.87 (*t*, 2×3H, C-13, CH₃). HRMS (FAB) Calculated for C₂₆H₅₀N₄NiS₄ [*M* + H]⁺: 605.23494, found [*M* + H]⁺: 605.23445.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Acknowledgements

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full crystallographic data

IUCrData (2024). **9**, x240186 [<https://doi.org/10.1107/S241431462400186X>]

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Bis[S-octyl 3-(2-methylpropylidene)dithiocarbazato- κ^2N^3,S]nickel(II)*Crystal data*

[Ni(C₁₃H₂₅N₂S₂)₂]

$M_r = 605.65$

Monoclinic, $P2_1/c$

$a = 11.5962$ (4) Å

$b = 18.4606$ (5) Å

$c = 7.8973$ (2) Å

$\beta = 106.532$ (7)°

$V = 1620.71$ (10) Å³

$Z = 2$

$F(000) = 652$

$D_x = 1.241$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71075$ Å

Cell parameters from 11425 reflections

$\theta = 1.8$ – 27.5 °

$\mu = 0.88$ mm⁻¹

$T = 173$ K

Platelet, green

$0.18 \times 0.06 \times 0.02$ mm

Data collection

Rigaku R-AXIS RAPID

diffractometer

Detector resolution: 10.000 pixels mm⁻¹

ω scans

Absorption correction: multi-scan

(ABSCOR; Rigaku, 1995)

$T_{\min} = 0.781$, $T_{\max} = 0.983$

15550 measured reflections

3702 independent reflections

2920 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.049$

$\theta_{\max} = 27.5$ °, $\theta_{\min} = 2.2$ °

$h = -15 \rightarrow 15$

$k = -23 \rightarrow 23$

$l = -10 \rightarrow 9$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.036$

$wR(F^2) = 0.072$

$S = 1.04$

3702 reflections

163 parameters

0 restraints

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0305P)^2 + 0.4396P]$

where $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{\max} = 0.37$ e Å⁻³

$\Delta\rho_{\min} = -0.21$ e Å⁻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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Ni1	0.500000	0.500000	0.500000	0.02167 (9)
S1	0.60829 (5)	0.43196 (2)	0.71132 (6)	0.02979 (12)
S2	0.72948 (5)	0.47341 (3)	1.07771 (6)	0.02978 (12)
N1	0.50276 (14)	0.56970 (8)	0.68145 (18)	0.0234 (3)
N2	0.58197 (14)	0.56067 (8)	0.85404 (18)	0.0256 (3)
C1	0.3208 (2)	0.71961 (11)	0.7769 (3)	0.0404 (5)
H1A	0.324068	0.754490	0.871744	0.049*
H1B	0.258003	0.683641	0.773519	0.049*
H1C	0.302375	0.745114	0.663553	0.049*
C2	0.5430 (2)	0.73600 (11)	0.8188 (3)	0.0428 (5)
H2A	0.526392	0.761787	0.705932	0.051*
H2B	0.619737	0.710216	0.841194	0.051*
H2C	0.547434	0.770833	0.914072	0.051*
C3	0.44208 (19)	0.68158 (10)	0.8112 (2)	0.0313 (5)
H3	0.459840	0.655777	0.927134	0.038*
C4	0.43794 (19)	0.62718 (10)	0.6691 (2)	0.0296 (4)
H4	0.381339	0.636002	0.557753	0.035*
C5	0.63166 (16)	0.49751 (10)	0.8740 (2)	0.0236 (4)
C6	0.71997 (18)	0.54982 (10)	1.2175 (2)	0.0284 (4)
H6A	0.746134	0.594707	1.170536	0.034*
H6B	0.636015	0.556435	1.221253	0.034*
C7	0.80161 (19)	0.53402 (11)	1.4016 (2)	0.0318 (4)
H7A	0.774890	0.488545	1.445197	0.038*
H7B	0.884609	0.526391	1.394499	0.038*
C8	0.80273 (18)	0.59419 (11)	1.5335 (2)	0.0318 (4)
H8A	0.720371	0.600857	1.544146	0.038*
H8B	0.827396	0.640071	1.488945	0.038*
C9	0.88802 (19)	0.57782 (12)	1.7150 (2)	0.0348 (5)
H9A	0.864291	0.531126	1.756945	0.042*
H9B	0.970303	0.571941	1.703476	0.042*
C10	0.8907 (2)	0.63547 (11)	1.8535 (2)	0.0351 (5)
H10A	0.809207	0.640256	1.868614	0.042*
H10B	0.912217	0.682544	1.810629	0.042*
C11	0.97951 (19)	0.61888 (12)	2.0320 (2)	0.0349 (5)
H11A	0.956543	0.572383	2.075870	0.042*
H11B	1.060468	0.612554	2.015773	0.042*
C12	0.9864 (2)	0.67654 (12)	2.1710 (3)	0.0391 (5)
H12A	0.905293	0.683647	2.185985	0.047*
H12B	1.011361	0.722853	2.128801	0.047*
C13	1.0734 (2)	0.65819 (14)	2.3487 (3)	0.0470 (6)
H13A	1.153265	0.648814	2.334234	0.056*
H13B	1.045122	0.614956	2.396874	0.056*
H13C	1.078151	0.698927	2.429976	0.056*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.02940 (18)	0.01765 (16)	0.01852 (16)	0.00189 (14)	0.00771 (13)	-0.00255 (13)
S1	0.0423 (3)	0.0221 (2)	0.0226 (2)	0.0069 (2)	0.0055 (2)	-0.00327 (19)
S2	0.0348 (3)	0.0295 (2)	0.0225 (2)	0.0061 (2)	0.0041 (2)	-0.0013 (2)
N1	0.0317 (9)	0.0195 (7)	0.0187 (7)	0.0016 (6)	0.0066 (6)	-0.0007 (6)
N2	0.0314 (9)	0.0245 (8)	0.0193 (7)	0.0011 (6)	0.0050 (6)	-0.0028 (6)
C1	0.0578 (15)	0.0326 (11)	0.0314 (11)	0.0130 (10)	0.0134 (10)	-0.0055 (9)
C2	0.0600 (15)	0.0315 (11)	0.0382 (11)	0.0013 (10)	0.0159 (11)	-0.0078 (9)
C3	0.0490 (13)	0.0223 (9)	0.0220 (9)	0.0080 (9)	0.0091 (9)	-0.0031 (8)
C4	0.0434 (12)	0.0243 (9)	0.0203 (9)	0.0065 (8)	0.0080 (8)	0.0005 (8)
C5	0.0276 (9)	0.0232 (8)	0.0209 (8)	-0.0011 (8)	0.0082 (7)	-0.0016 (8)
C6	0.0313 (11)	0.0297 (10)	0.0244 (9)	0.0006 (8)	0.0083 (8)	-0.0027 (8)
C7	0.0351 (11)	0.0349 (11)	0.0234 (9)	0.0026 (9)	0.0051 (8)	-0.0035 (9)
C8	0.0354 (11)	0.0355 (10)	0.0236 (9)	-0.0011 (9)	0.0069 (8)	-0.0033 (9)
C9	0.0363 (11)	0.0414 (12)	0.0245 (9)	0.0019 (9)	0.0053 (8)	-0.0037 (9)
C10	0.0434 (13)	0.0330 (11)	0.0278 (10)	-0.0023 (9)	0.0082 (9)	-0.0041 (9)
C11	0.0360 (12)	0.0395 (11)	0.0281 (10)	-0.0012 (9)	0.0073 (9)	-0.0083 (9)
C12	0.0469 (13)	0.0388 (12)	0.0314 (10)	-0.0079 (10)	0.0110 (9)	-0.0087 (9)
C13	0.0447 (14)	0.0614 (15)	0.0323 (11)	-0.0070 (11)	0.0069 (10)	-0.0129 (11)

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

Ni1—N1	1.9193 (14)	C6—H6B	0.9900
Ni1—N1 ⁱ	1.9193 (14)	C7—C8	1.520 (3)
Ni1—S1 ⁱ	2.1788 (5)	C7—H7A	0.9900
Ni1—S1	2.1788 (5)	C7—H7B	0.9900
S1—C5	1.7295 (18)	C8—C9	1.522 (3)
S2—C5	1.7416 (18)	C8—H8A	0.9900
S2—C6	1.8138 (19)	C8—H8B	0.9900
N1—C4	1.288 (2)	C9—C10	1.520 (3)
N1—N2	1.420 (2)	C9—H9A	0.9900
N2—C5	1.290 (2)	C9—H9B	0.9900
C1—C3	1.526 (3)	C10—C11	1.521 (3)
C1—H1A	0.9800	C10—H10A	0.9900
C1—H1B	0.9800	C10—H10B	0.9900
C1—H1C	0.9800	C11—C12	1.514 (3)
C2—C3	1.530 (3)	C11—H11A	0.9900
C2—H2A	0.9800	C11—H11B	0.9900
C2—H2B	0.9800	C12—C13	1.516 (3)
C2—H2C	0.9800	C12—H12A	0.9900
C3—C4	1.496 (2)	C12—H12B	0.9900
C3—H3	1.0000	C13—H13A	0.9800
C4—H4	0.9500	C13—H13B	0.9800
C6—C7	1.521 (2)	C13—H13C	0.9800
C6—H6A	0.9900		

N1—Ni1—N1 ⁱ	180.0	C8—C7—C6	113.37 (16)
N1—Ni1—S1 ⁱ	93.95 (4)	C8—C7—H7A	108.9
N1 ⁱ —Ni1—S1 ⁱ	86.05 (4)	C6—C7—H7A	108.9
N1—Ni1—S1	86.05 (4)	C8—C7—H7B	108.9
N1 ⁱ —Ni1—S1	93.95 (4)	C6—C7—H7B	108.9
S1 ⁱ —Ni1—S1	180.00 (2)	H7A—C7—H7B	107.7
C5—S1—Ni1	95.74 (6)	C7—C8—C9	112.13 (16)
C5—S2—C6	103.11 (8)	C7—C8—H8A	109.2
C4—N1—N2	111.92 (14)	C9—C8—H8A	109.2
C4—N1—Ni1	127.63 (13)	C7—C8—H8B	109.2
N2—N1—Ni1	120.45 (11)	C9—C8—H8B	109.2
C5—N2—N1	111.59 (14)	H8A—C8—H8B	107.9
C3—C1—H1A	109.5	C10—C9—C8	114.43 (17)
C3—C1—H1B	109.5	C10—C9—H9A	108.7
H1A—C1—H1B	109.5	C8—C9—H9A	108.7
C3—C1—H1C	109.5	C10—C9—H9B	108.7
H1A—C1—H1C	109.5	C8—C9—H9B	108.7
H1B—C1—H1C	109.5	H9A—C9—H9B	107.6
C3—C2—H2A	109.5	C9—C10—C11	113.32 (17)
C3—C2—H2B	109.5	C9—C10—H10A	108.9
H2A—C2—H2B	109.5	C11—C10—H10A	108.9
C3—C2—H2C	109.5	C9—C10—H10B	108.9
H2A—C2—H2C	109.5	C11—C10—H10B	108.9
H2B—C2—H2C	109.5	H10A—C10—H10B	107.7
C4—C3—C1	110.15 (16)	C12—C11—C10	114.35 (17)
C4—C3—C2	109.32 (17)	C12—C11—H11A	108.7
C1—C3—C2	111.16 (17)	C10—C11—H11A	108.7
C4—C3—H3	108.7	C12—C11—H11B	108.7
C1—C3—H3	108.7	C10—C11—H11B	108.7
C2—C3—H3	108.7	H11A—C11—H11B	107.6
N1—C4—C3	127.07 (17)	C11—C12—C13	113.45 (18)
N1—C4—H4	116.5	C11—C12—H12A	108.9
C3—C4—H4	116.5	C13—C12—H12A	108.9
N2—C5—S1	124.84 (14)	C11—C12—H12B	108.9
N2—C5—S2	119.66 (13)	C13—C12—H12B	108.9
S1—C5—S2	115.50 (10)	H12A—C12—H12B	107.7
C7—C6—S2	107.68 (13)	C12—C13—H13A	109.5
C7—C6—H6A	110.2	C12—C13—H13B	109.5
S2—C6—H6A	110.2	H13A—C13—H13B	109.5
C7—C6—H6B	110.2	C12—C13—H13C	109.5
S2—C6—H6B	110.2	H13A—C13—H13C	109.5
H6A—C6—H6B	108.5	H13B—C13—H13C	109.5
C4—N1—N2—C5	169.13 (17)	C6—S2—C5—N2	5.12 (18)
Ni1—N1—N2—C5	-10.2 (2)	C6—S2—C5—S1	-174.45 (11)
N2—N1—C4—C3	1.5 (3)	C5—S2—C6—C7	179.27 (14)
Ni1—N1—C4—C3	-179.19 (15)	S2—C6—C7—C8	179.81 (15)
C1—C3—C4—N1	-154.1 (2)	C6—C7—C8—C9	-178.30 (18)

C2—C3—C4—N1	83.5 (2)	C7—C8—C9—C10	-178.72 (18)
N1—N2—C5—S1	1.2 (2)	C8—C9—C10—C11	-178.20 (19)
N1—N2—C5—S2	-178.29 (12)	C9—C10—C11—C12	178.39 (19)
Ni1—S1—C5—N2	6.18 (17)	C10—C11—C12—C13	178.8 (2)
Ni1—S1—C5—S2	-174.28 (9)		

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