

# Crystal structure of bis(azido- $\kappa$ N)bis[2,5-bis(pyridin-2-yl)-1,3,4-thiadiazole- $\kappa^2$ N<sup>2</sup>,N<sup>3</sup>]nickel(II)

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Reaction of 2,5-bis(pyridin-2-yl)-1,3,4-thiadiazole and sodium azide with nickel(II) triflate yielded the mononuclear title complex, [Ni(N<sub>3</sub>)<sub>2</sub>(C<sub>12</sub>H<sub>8</sub>N<sub>4</sub>S)<sub>2</sub>]. The Ni<sup>II</sup> ion is located on a centre of symmetry and is octahedrally coordinated by four N atoms of the two bidentate heterocyclic ligands in the equatorial plane. The axial positions are occupied by the N atoms of two almost linear azide ions [N—N—N = 178.8 (2)°]. The thiadiazole and pyridine rings of the heterocyclic ligand are almost coplanar, with a maximum deviation from the mean plane of 0.0802 (9) Å. The cohesion of the crystal structure is ensured by  $\pi$ – $\pi$  interactions between parallel pyridine rings of neighbouring molecules [centroid-to-centroid distance = 3.6413 (14) Å], leading to a layered arrangement of the molecules parallel to (001).

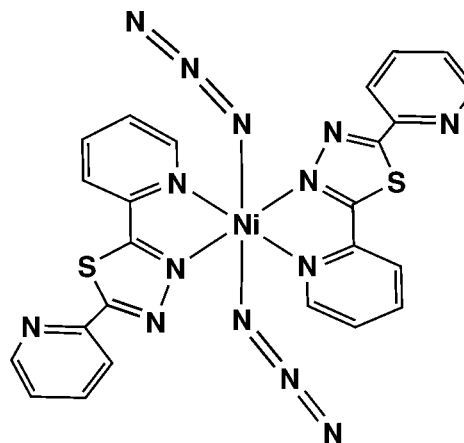
**Keywords:** crystal structure; mononuclear nickel(II) complex; 1,3,4-thiadiazole; azide ligand;  $\pi$ – $\pi$  interactions.

**CCDC reference:** 1042351

## 1. Related literature

2,5-Bis(pyridin-2-yl)-1,3,4-thiadiazole has been used as a bidentate or tetradentate ligand forming mononuclear (Bentiss *et al.*, 2004, 2011a, 2012; Zheng *et al.*, 2006) or dinuclear complexes (Laachir *et al.*, 2013). Coordination of the azide ion to transition metals results in compounds with interesting magnetic properties (Machura *et al.*, 2011; Świtlicka-Olszewska *et al.*, 2014). The iron salt with the same heterocyclic ligand and thiocyanate as the pseudohalide was

reported by Klingele *et al.* (2010). For the crystal structure of the related tetrafluoridoborate salt of [Ni(C<sub>12</sub>H<sub>8</sub>N<sub>4</sub>S)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>], see: Bentiss *et al.* (2011b). For the synthesis of the heterocyclic ligand, see: Lebrini *et al.* (2005).



## 2. Experimental

### 2.1. Crystal data

[Ni(N<sub>3</sub>)<sub>2</sub>(C<sub>12</sub>H<sub>8</sub>N<sub>4</sub>S)<sub>2</sub>]  
 $M_r = 623.34$   
 Monoclinic,  $P2_1/c$   
 $a = 7.7981$  (3) Å  
 $b = 8.2410$  (3) Å  
 $c = 20.1555$  (7) Å  
 $\beta = 93.141$  (2)°

$V = 1293.33$  (8) Å<sup>3</sup>  
 $Z = 2$   
 Mo  $K\alpha$  radiation  
 $\mu = 0.96$  mm<sup>-1</sup>  
 $T = 296$  K  
 $0.39 \times 0.31 \times 0.18$  mm

### 2.2. Data collection

Bruker APEXII CCD  
 diffractometer  
 Absorption correction: multi-scan  
 (SADABS; Bruker, 2009)  
 $T_{\min} = 0.640$ ,  $T_{\max} = 0.747$

15710 measured reflections  
 3077 independent reflections  
 2643 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.033$

### 2.3. Refinement

$R[F^2 > 2\sigma(F^2)] = 0.036$   
 $wR(F^2) = 0.100$   
 $S = 1.04$   
 3077 reflections

187 parameters  
 H-atom parameters constrained  
 $\Delta\rho_{\max} = 1.25$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.35$  e Å<sup>-3</sup>

Data collection: APEX2 (Bruker, 2009); cell refinement: SAINT (Bruker, 2009); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEP-3 for Windows (Farrugia, 2012); software used to prepare material for publication: WinGX (Farrugia, 2012).

## Acknowledgements

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Supporting information for this paper is available from the IUCr electronic archives (Reference: WM5108).

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## References

- Bentiss, F., Capet, F., Lagrenée, M., Saadi, M. & El Ammari, L. (2011a). *Acta Cryst.* **E67**, m1052–m1053.
- Bentiss, F., Capet, F., Lagrenée, M., Saadi, M. & El Ammari, L. (2011b). *Acta Cryst.* **E67**, m834–m835.
- Bentiss, F., Lagrenée, M., Vezin, H., Wignacourt, J. P. & Holt, E. M. (2004). *Polyhedron*, **23**, 1903–1907.
- Bentiss, F., Outirite, M., Lagrenée, M., Saadi, M. & El Ammari, L. (2012). *Acta Cryst.* **E68**, m360–m361.
- Bruker (2009). *APEX2, SAINT and SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
- Klingele, J., Kaase, D., Klingele, M. H., Lach, J. & Demeshko, S. (2010). *Dalton Trans.* **39**, 1689–1691.
- Laachir, A., Bentiss, F., Guesmi, S., Saadi, M. & El Ammari, L. (2013). *Acta Cryst.* **E69**, m351–m352.
- Lebrini, M., Bentiss, F. & Lagrenée, M. (2005). *J. Heterocycl. Chem.* **42**, 991–994.
- Machura, B., Świtlicka, A., Nawrot, I., Mroziński, J. & Michalik, K. (2011). *Polyhedron*, **30**, 2815–2823.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Świtlicka-Olszewska, A., Machura, B. & Mroziński, J. (2014). *Inorg. Chem. Commun.* **43**, 86–89.
- Zheng, X.-F., Wan, X.-S., Liu, W., Niu, C.-Y. & Kou, C.-H. (2006). *Z. Kristallogr.*, **221**, 543–544.

## supporting information

*Acta Cryst.* (2015). E71, m24–m25 [doi:10.1107/S2056989015000201]

## Crystal structure of bis(azido- $\kappa N$ )bis[2,5-bis(pyridin-2-yl)-1,3,4-thiadiazole- $\kappa^2 N^2, N^3$ ]nickel(II)

Abdelhakim Laachir, Fouad Bentiss, Salaheddine Guesmi, Mohamed Saadi and Lahcen El Ammari

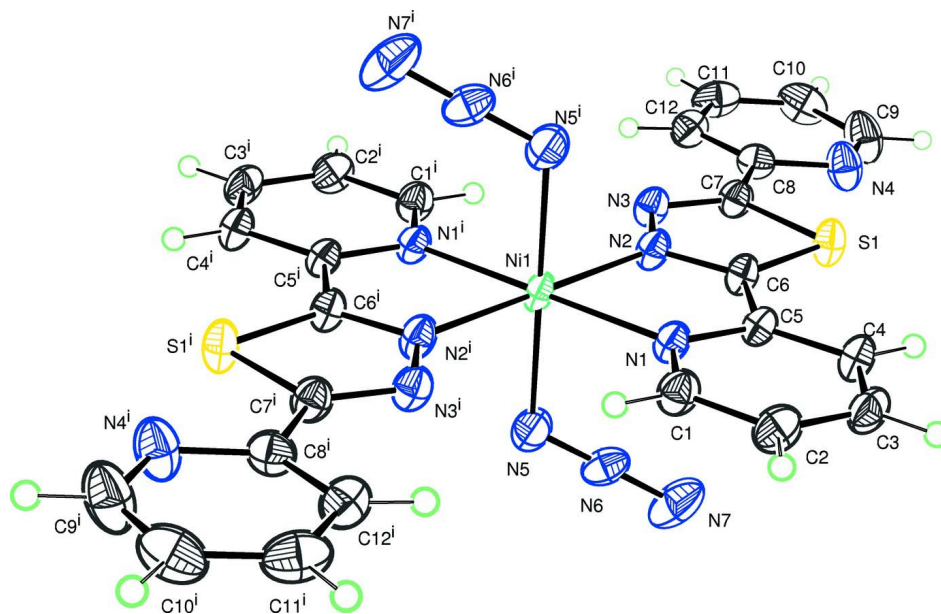
### S1. Experimental

The 2,5-bis(2-pyridyl)-1,3,4-thiadiazole ligand (noted *L*) was synthesized as described previously by Lebrini *et al.* (2005).  $Ni_2L_2(N_3)_2$  was obtained in bulk quantity by dropwise addition of an aqueous solution of  $NaN_3$  (0.4 mmol, 26 mg) to an ethanol/water solution of *L* (0.1 mmol, 24 mg) and  $Ni(O_3SCF_3)_2$  (0.1 mmol, 36 mg) under constant stirring at room temperature. An orange coloured solid was precipitated, filtered and washed with cold ethanol. Single crystals of  $Ni_2L_2(N_3)_2$  were grown by slow interdiffusion of a solution of  $Ni(O_3SCF_3)_2$  and *L* in acetonitrile into  $NaN_3$  dissolved in water. Orange block-shaped single crystals appeared after one month. The crystals were washed with water and dried under vacuum (yield 50%).

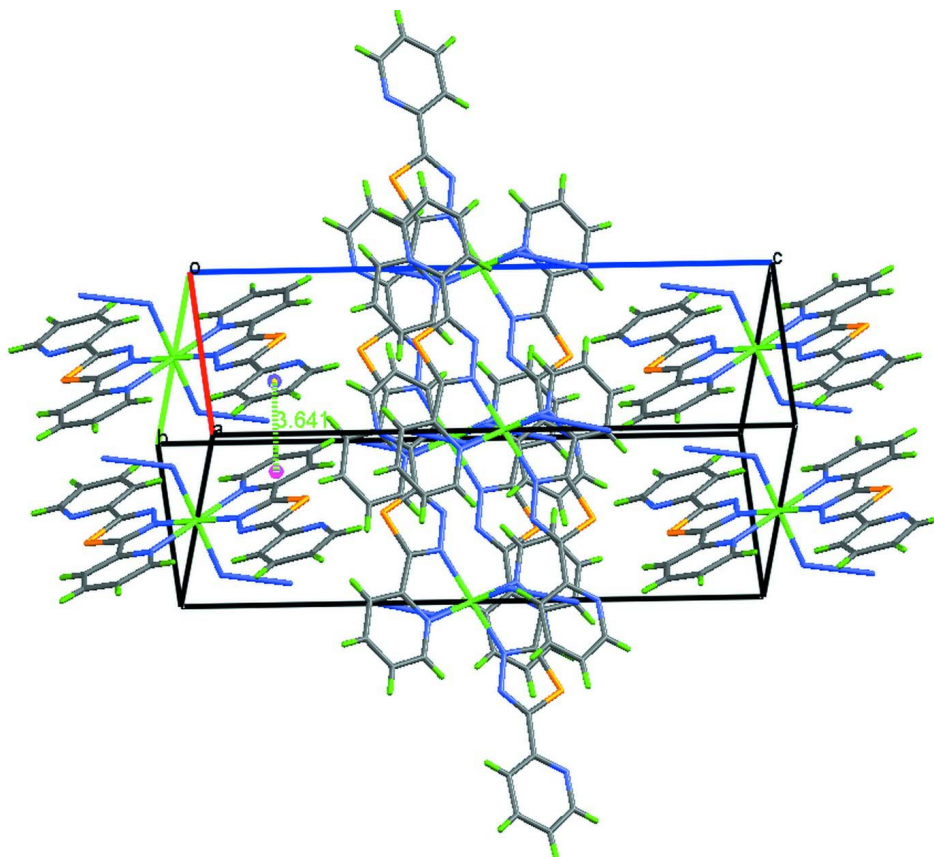
**CAUTION.** Azide compounds are potentially explosive. Only a small amount of material should be prepared and handled with care.

### S2. Refinement

H atoms were located in a difference map and treated as riding with  $C-H = 0.96 \text{ \AA}$  and with  $U_{iso}(H) = 1.2U_{eq}(C)$ . The highest electron density was found  $1.65 \text{ \AA}$  from atom H1. The vicinity of this peak to the H1 atom and the requirement for electroneutrality made it seem possible that this electron density might be associated with an underoccupied water molecule. However, the  $U_{eq}$  value of the so modelled O atom (occupancy  $< 0.05$ ) refined to negative values and hence this electron density was not considered in the final model.

**Figure 1**

The molecular structure of the title compound. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented as spheres of arbitrary radius. [Symmetry code: (i)  $-x + 2, -y + 1, -z + 2$ .]

**Figure 2**

The crystal packing of the title compound, showing intermolecular  $\pi$ - $\pi$  interactions between pyridyl rings (dashed green lines).

**Bis(azido- $\kappa$ N)bis[2,5-bis(pyridin-2-yl)-1,3,4-thiadiazole- $\kappa^2$ N<sup>2</sup>,N<sup>3</sup>]nickel(II)**

*Crystal data*

[Ni(N<sub>3</sub>)<sub>2</sub>(C<sub>12</sub>H<sub>8</sub>N<sub>4</sub>S)<sub>2</sub>]

$M_r = 623.34$

Monoclinic,  $P2_1/c$

Hall symbol: -P 2ybc

$a = 7.7981$  (3) Å

$b = 8.2410$  (3) Å

$c = 20.1555$  (7) Å

$\beta = 93.141$  (2)°

$V = 1293.33$  (8) Å<sup>3</sup>

$Z = 2$

$F(000) = 636$

$D_x = 1.601$  Mg m<sup>-3</sup>

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

Cell parameters from 3077 reflections

$\theta = 2.6$ – $27.9$ °

$\mu = 0.96$  mm<sup>-1</sup>

$T = 296$  K

Block, orange

$0.39 \times 0.31 \times 0.18$  mm

*Data collection*

Bruker APEXII CCD  
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

$\varphi$  and  $\omega$  scans

Absorption correction: multi-scan  
(*SADABS*; Bruker, 2009)

$T_{\min} = 0.640$ ,  $T_{\max} = 0.747$

15710 measured reflections

3077 independent reflections

2643 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.033$   
 $\theta_{\text{max}} = 27.9^\circ$ ,  $\theta_{\text{min}} = 2.6^\circ$   
 $h = -10 \rightarrow 9$

$k = -10 \rightarrow 10$   
 $l = -26 \rightarrow 26$

*Refinement*

Refinement on  $F^2$   
 Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.036$   
 $wR(F^2) = 0.100$   
 $S = 1.04$   
 3077 reflections  
 187 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  
 $w = 1/[\sigma^2(F_o^2) + (0.0522P)^2 + 0.8063P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 1.25 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.35 \text{ e } \text{\AA}^{-3}$

*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  $F^2 > 2\sigma(F^2)$  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>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	1.3016 (3)	0.4676 (3)	0.90640 (11)	0.0356 (5)
H1	1.3538	0.4022	0.9392	0.043*
C2	1.3853 (3)	0.4935 (3)	0.84813 (12)	0.0397 (5)
H2	1.4916	0.4460	0.8423	0.048*
C3	1.3091 (3)	0.5902 (3)	0.79925 (10)	0.0380 (5)
H3	1.3630	0.6089	0.7599	0.046*
C4	1.1511 (3)	0.6589 (3)	0.80960 (10)	0.0350 (4)
H4	1.0966	0.7246	0.7774	0.042*
C5	1.0759 (2)	0.6281 (2)	0.86873 (9)	0.0292 (4)
C6	0.9114 (3)	0.6956 (3)	0.88563 (9)	0.0304 (4)
C7	0.6422 (2)	0.8193 (2)	0.90011 (10)	0.0313 (4)
C8	0.4793 (3)	0.9088 (3)	0.89219 (11)	0.0336 (4)
C9	0.3101 (4)	1.0642 (4)	0.82288 (15)	0.0575 (7)
H9	0.2915	1.1167	0.7823	0.069*
C10	0.1844 (3)	1.0747 (3)	0.86751 (15)	0.0536 (7)
H10	0.0843	1.1332	0.8575	0.064*
C11	0.2099 (3)	0.9966 (3)	0.92746 (14)	0.0498 (6)
H11	0.1274	1.0021	0.9590	0.060*
C12	0.3601 (3)	0.9095 (3)	0.94026 (11)	0.0401 (5)
H12	0.3799	0.8534	0.9800	0.048*
N1	1.1488 (2)	0.5333 (2)	0.91692 (8)	0.0298 (4)
N2	0.8473 (2)	0.6603 (2)	0.94235 (8)	0.0313 (4)

N3	0.6911 (2)	0.7303 (2)	0.95059 (8)	0.0320 (4)
N4	0.4563 (3)	0.9844 (2)	0.83359 (11)	0.0463 (5)
N5	0.8723 (3)	0.3030 (2)	0.95247 (9)	0.0427 (4)
N6	0.8332 (2)	0.3118 (2)	0.89483 (9)	0.0385 (4)
N7	0.7973 (3)	0.3188 (3)	0.83827 (11)	0.0645 (7)
S1	0.78523 (7)	0.82456 (7)	0.83744 (3)	0.03745 (15)
Ni1	1.0000	0.5000	1.0000	0.02650 (12)

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C1	0.0333 (11)	0.0420 (11)	0.0319 (10)	0.0063 (9)	0.0056 (8)	0.0008 (9)
C2	0.0340 (11)	0.0477 (13)	0.0387 (12)	0.0036 (9)	0.0120 (9)	-0.0044 (9)
C3	0.0386 (11)	0.0478 (13)	0.0288 (10)	-0.0037 (10)	0.0128 (8)	-0.0036 (9)
C4	0.0374 (11)	0.0451 (12)	0.0228 (9)	0.0007 (9)	0.0050 (8)	0.0023 (8)
C5	0.0301 (9)	0.0351 (10)	0.0226 (9)	0.0005 (8)	0.0046 (7)	-0.0011 (7)
C6	0.0309 (9)	0.0385 (11)	0.0219 (9)	0.0017 (8)	0.0008 (7)	0.0026 (8)
C7	0.0290 (9)	0.0367 (10)	0.0283 (9)	0.0022 (8)	0.0027 (7)	0.0006 (8)
C8	0.0291 (10)	0.0329 (10)	0.0385 (11)	0.0033 (8)	0.0006 (8)	-0.0013 (8)
C9	0.0508 (15)	0.0563 (16)	0.0656 (17)	0.0155 (13)	0.0046 (13)	0.0247 (14)
C10	0.0362 (12)	0.0439 (14)	0.081 (2)	0.0158 (11)	0.0015 (12)	-0.0001 (13)
C11	0.0355 (12)	0.0543 (15)	0.0608 (16)	-0.0010 (10)	0.0129 (11)	-0.0183 (12)
C12	0.0398 (12)	0.0451 (13)	0.0354 (11)	-0.0025 (10)	0.0021 (9)	-0.0026 (9)
N1	0.0312 (8)	0.0357 (9)	0.0229 (8)	0.0022 (7)	0.0045 (6)	0.0003 (6)
N2	0.0298 (8)	0.0410 (9)	0.0235 (8)	0.0063 (7)	0.0045 (6)	0.0019 (7)
N3	0.0283 (8)	0.0407 (9)	0.0271 (8)	0.0072 (7)	0.0029 (6)	0.0014 (7)
N4	0.0380 (10)	0.0508 (12)	0.0507 (12)	0.0098 (9)	0.0090 (9)	0.0182 (9)
N5	0.0501 (11)	0.0467 (11)	0.0315 (9)	-0.0058 (9)	0.0040 (8)	-0.0017 (8)
N6	0.0304 (9)	0.0464 (11)	0.0387 (10)	0.0060 (8)	0.0015 (7)	-0.0129 (8)
N7	0.0631 (15)	0.0907 (19)	0.0379 (12)	0.0154 (13)	-0.0121 (10)	-0.0185 (12)
S1	0.0343 (3)	0.0496 (3)	0.0289 (3)	0.0091 (2)	0.00513 (19)	0.0117 (2)
Ni1	0.02602 (19)	0.0358 (2)	0.01789 (17)	0.00586 (14)	0.00320 (12)	0.00259 (13)

*Geometric parameters (Å, °)*

C1—N1	1.336 (3)	C9—N4	1.324 (3)
C1—C2	1.391 (3)	C9—C10	1.369 (4)
C1—H1	0.9300	C9—H9	0.9300
C2—C3	1.376 (3)	C10—C11	1.374 (4)
C2—H2	0.9300	C10—H10	0.9300
C3—C4	1.382 (3)	C11—C12	1.386 (3)
C3—H3	0.9300	C11—H11	0.9300
C4—C5	1.380 (3)	C12—H12	0.9300
C4—H4	0.9300	N1—Ni1	2.1069 (17)
C5—N1	1.348 (2)	N2—N3	1.366 (2)
C5—C6	1.456 (3)	N2—Ni1	2.0885 (16)
C6—N2	1.305 (3)	N5—N6	1.187 (3)
C6—S1	1.714 (2)	N5—Ni1	2.1075 (19)

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C7—N3	1.295 (2)	N6—N7	1.160 (3)
C7—C8	1.470 (3)	Ni1—N2 <sup>i</sup>	2.0885 (16)
C7—S1	1.731 (2)	Ni1—N1 <sup>i</sup>	2.1069 (17)
C8—N4	1.339 (3)	Ni1—N5 <sup>i</sup>	2.108 (2)
C8—C12	1.379 (3)		
N1—C1—C2	122.4 (2)	C10—C11—H11	120.5
N1—C1—H1	118.8	C12—C11—H11	120.5
C2—C1—H1	118.8	C8—C12—C11	117.8 (2)
C3—C2—C1	119.3 (2)	C8—C12—H12	121.1
C3—C2—H2	120.4	C11—C12—H12	121.1
C1—C2—H2	120.4	C1—N1—C5	117.71 (18)
C2—C3—C4	118.9 (2)	C1—N1—Ni1	127.46 (15)
C2—C3—H3	120.6	C5—N1—Ni1	114.79 (13)
C4—C3—H3	120.6	C6—N2—N3	113.55 (16)
C5—C4—C3	118.63 (19)	C6—N2—Ni1	113.19 (13)
C5—C4—H4	120.7	N3—N2—Ni1	133.19 (13)
C3—C4—H4	120.7	C7—N3—N2	111.69 (16)
N1—C5—C4	123.14 (19)	C9—N4—C8	116.6 (2)
N1—C5—C6	113.27 (17)	N6—N5—Ni1	119.16 (16)
C4—C5—C6	123.58 (18)	N7—N6—N5	178.8 (2)
N2—C6—C5	120.32 (18)	C6—S1—C7	86.77 (9)
N2—C6—S1	113.49 (15)	N2—Ni1—N2 <sup>i</sup>	180.00 (7)
C5—C6—S1	126.18 (15)	N2—Ni1—N1	78.32 (6)
N3—C7—C8	125.80 (19)	N2 <sup>i</sup> —Ni1—N1	101.68 (6)
N3—C7—S1	114.47 (15)	N2—Ni1—N1 <sup>i</sup>	101.68 (6)
C8—C7—S1	119.72 (15)	N2 <sup>i</sup> —Ni1—N1 <sup>i</sup>	78.32 (6)
N4—C8—C12	123.7 (2)	N1—Ni1—N1 <sup>i</sup>	180.000 (1)
N4—C8—C7	113.74 (19)	N2—Ni1—N5	89.63 (8)
C12—C8—C7	122.5 (2)	N2 <sup>i</sup> —Ni1—N5	90.37 (8)
N4—C9—C10	124.4 (3)	N1—Ni1—N5	90.35 (7)
N4—C9—H9	117.8	N1 <sup>i</sup> —Ni1—N5	89.65 (7)
C10—C9—H9	117.8	N2—Ni1—N5 <sup>i</sup>	90.37 (8)
C9—C10—C11	118.3 (2)	N2 <sup>i</sup> —Ni1—N5 <sup>i</sup>	89.63 (8)
C9—C10—H10	120.8	N1—Ni1—N5 <sup>i</sup>	89.65 (7)
C11—C10—H10	120.8	N1 <sup>i</sup> —Ni1—N5 <sup>i</sup>	90.35 (7)
C10—C11—C12	119.1 (2)	N5—Ni1—N5 <sup>i</sup>	179.998 (1)

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