IUCrData

ISSN 2414-3146

mer-Bis(quinoline-2-carboxaldehyde 4-ethylthiosemicarbazonato)nickel(II) methanol 0.33-solvate 0.67-hydrate

Raudhatul Nadhirah Awang Adam, Natasha Ann Keasberry and Malai Haniti Sheikh Abdul Hamid*

Chemical Sciences, Faculty of Science, Universiti Brunei Darussalam, Jalan Tungku Link, Gadong, BE1410, Brunei.
*Correspondence e-mail: haniti.hamid@ubd.edu.bn

Received 14 March 2024
Accepted 17 April 2024

Edited by S. Bernès, Benemérita Universidad Autónoma de Puebla, México

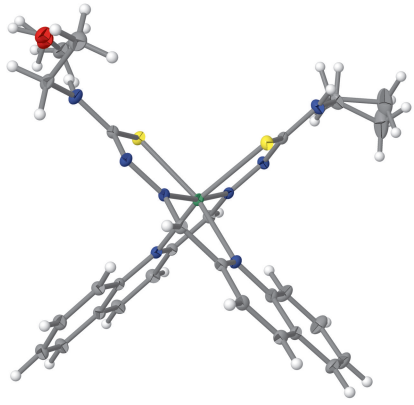
Keywords: crystal structure; nickel(II); quinoline; octahedral geometry; meridional coordination.

CCDC reference: 2331984

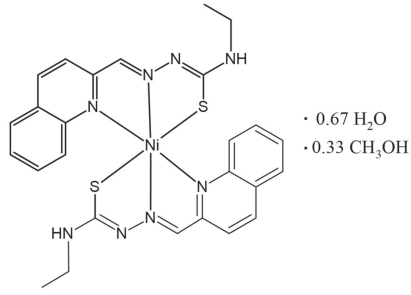
Structural data: full structural data are available from iucrdata.iucr.org

In the title compound, $[Ni(C_{13}H_{13}N_4S)_2]\cdot 0.33CH_3OH\cdot 0.67H_2O$, the Ni^{II} atom is coordinated by two tridentate quinoline-2-carboxaldehyde 4-ethylthiosemicarbazonate ligands in a distorted octahedral shape. At 100 K, the crystal symmetry is monoclinic (space group $P2_1/n$). A mixture of water and methanol crystallizes with the title complex, and one of the ethyl groups in the coordinating ligands is disordered over two positions, with an occupancy ratio of 58:42. There is intermolecular hydrogen bonding between the solvent molecules and the amine and thiolate groups in the ligands. No other significant interactions are present in the crystal packing.

3D view



Chemical scheme



Structure description

Thiosemicarbazones are a type of Schiff base ligand formed by the condensation of thiosemicarbazides with carbonyl compounds (Arulmurugan *et al.*, 2010). They commonly behave as *N*,*S*- or *N*,*N*′,*S*-chelating agents, coordinating the metal through the imine N and S atoms. They frequently feature more than two covalent sites, the number depending on the aldehyde used during the synthesis and on the tautomeric equilibrium of the thiosemicarbazone (Latheef *et al.*, 2021; Osman *et al.*, 2021). The versatility of the compounds, along with their metal complexes, have attracted significant interest in the fields of chemistry and biology. They exhibit a broad spectrum of biological properties, including antibacterial, anticancer, antiproliferative and antiviral activities (Chaturvedi, 2012; Damit *et al.*, 2021; Montalbano *et al.*, 2023; Kumar *et al.*, 2023; Arif *et al.*, 2024). For instance, a series of quinoline-2-carboxaldehyde thiosemicarbazone derivatives and their Cu^{II} and Ni^{II} complexes have been reported by Bisceglie *et al.* (2015) for biological survey studies.

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

D—H···A	D—H	H···A	D···A	D—H···A
N4—H4···O1W	0.84 (2)	2.10 (3)	2.936 (12)	174 (2)
N4—H4···O1S	0.84 (2)	2.08 (4)	2.91 (3)	170 (2)
O1S—H1S···S2^{i}	0.84	2.46	3.24 (2)	154
N8—H8···N3^{ii}	0.85 (2)	2.29 (2)	3.1349 (19)	174 (2)

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

Ni^{II} complexes having sulfur donors have been studied, receiving considerable attention due to the identification of a sulfur-rich coordination environment in biologically relevant nickel ompounds, such as the active sites of certain ureases, hydrogenases, as well as dehydrogenases, that may play a role in the supposed mutagenicity of nickel compounds (Latheef *et al.*, 2021). The coordination chemistry of nickel is thus of interest with respect to its important roles in biological systems (Jayakumar *et al.*, 2022; Sankar & Sharmila, 2023). This is due to the ability of nickel to adopt different coordination environments, such as tetrahedral, square planar and octahedral. The nickel ion can also bind to soft and hard donor ligands, which allows its coordination chemistry to encompass a variety of coordination environments, coordination numbers and oxidation states (Jayakumar *et al.*, 2022).

The asymmetric unit of the title compound contains one complex with formula $C_{26}H_{26}N_8S_2Ni$ and a mixture of water and methanol. The structure of the title compound is confirmed to be in a 2:1 ligand–metal complex, where the two ligands are perpendicular to each other in a distorted octahedral shape, coordinating in a *meridional* fashion (Fig. 1). This aligns with the methyl analogue of the complex found in the literature, which has methyl groups in place of the ethyl groups (Bisceglie *et al.*, 2015), with its two ligands coordinating as anionic deprotonated molecules. In the structure reported herein, one of the ethyl groups is disordered over two positions, with an occupancy ratio refined as 58:42. The occupancy ratio of the solvent molecules, methanol and water, was refined to 1/3:2/3.

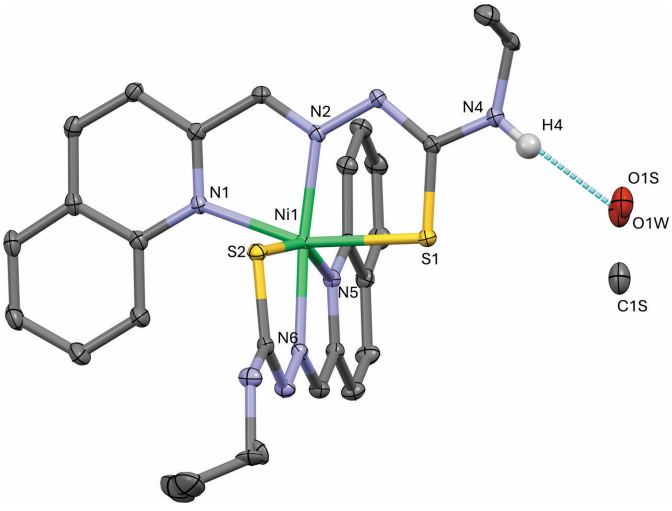


Figure 1
The molecular structure of the title compound with the more abundant ethyl-group positions. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity (with the exception of H4). Atoms C1S, O1S and O1W are for the disordered solvent molecules, methanol and water. The dashed bond is the intermolecular hydrogen bond between the complex and the methanol molecule (Table 1, entry 2).

Each methanol/water molecule bridges two neighbouring complexes through intermolecular N4—H4···O(solvent) and OH(solvent)···S2^{i} hydrogen bonds (Table 1). The crystal structure is further stabilized by weaker intermolecular N8—H8···N3^{ii} hydrogen bonds, forming a tri-periodic supramolecular network (Fig. 2). No other significant interactions are present in the crystal packing of the title compound. In contrast, in the case of the methyl analogue complex, no solvent is present in the unit cell (Bisceglie *et al.*, 2015). Furthermore, this methyl complex also features intermolecular interactions of C—H groups with the quinoline π-system, which are not observed in the structure reported herein. The Ni—N bond lengths are in good agreement with those observed in other octahedral $[Ni(N,N',S)_2]^{2+}$ complexes retrieved from the Cambridge Structural Database (CSD, Version 5.45; Groom *et al.*, 2016): refcodes NOTWEA (Min *et al.*, 2014), and JUKRAK and JUKQUD (Bisceglie *et al.*, 2015). To the best of our knowledge, no quinoline-2-carboxaldehyde 4-ethylthiosemicarbazonate–nickel(II) complexes have been deposited in the CSD so far.

In the title compound, no H peaks were located on N3 and N7 in a difference map. Additionally, the C11═N3 and C24═N7 bond lengths are 1.3438 (19) and 1.3355 (19) Å, respectively, which confirms that significant double-bond character is present, and that the ligand is in its deprotonated form. Spectroscopic and mass spectrometry analyses of the complex further confirm that the 2:1 deprotonated ligand–metal complex is present.

Synthesis and crystallization

The title Ni^{II} complex was synthesized by dissolving quinoline-2-carboxaldehyde 4-ethylthiosemicarbazone (0.050 g,

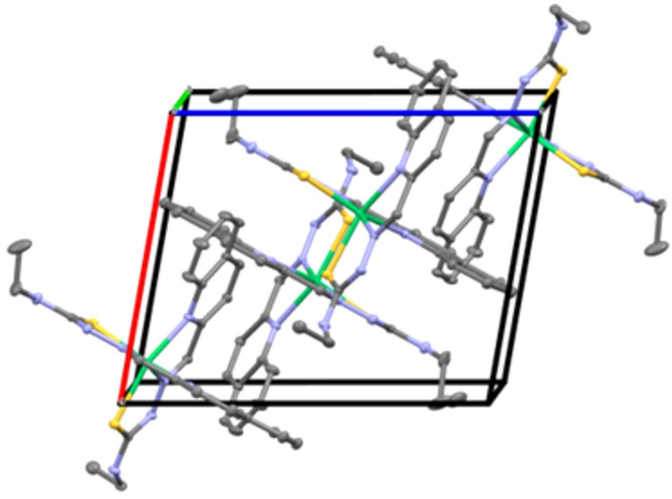


Figure 2
Perspective view of the crystal packing of the title compound approximately along the *b* axis. Solvent molecules and H atoms have been omitted for clarity.

Table 2
Experimental details.

Crystal data	
Chemical formula	$[Ni(C_{13}H_{13}N_4S)_2]\cdot 0.33CH_4O\cdot 0.67H_2O$
M_r	595.97
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	100
a, b, c (Å)	10.0560 (6), 21.3696 (9), 12.5648 (6)
β (°)	100.161 (2)
V (Å^3)	2657.7 (2)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.93
Crystal size (mm)	0.13 × 0.13 × 0.10
Data collection	
Diffractometer	Bruker D8 Venture
Absorption correction	Multi-scan (*SADABS*; Krause *et al.*, 2015)
T_{min}, T_{max}	0.710, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	143112, 8094, 7523
R_{int}	0.076
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.714
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.036, 0.083, 1.08
No. of reflections	8094
No. of parameters	385
No. of restraints	36
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.46, −0.48

Computer programs: *APEX4* and *SAINT* (Bruker, 2016), *SHELXT2018* (Sheldrick, 2015*a*), *SHELXL2019* (Sheldrick, 2015*b*), *Mercury* (Macrae *et al.*, 2020) and *publCIF* (Westrip, 2010).

0.194 mmol) in hot acetonitrile (10 ml), which was mixed with a hot solution of nickel(II) acetate tetrahydrate (48.2 mg, 0.194 mmol) in methanol (10 ml) on a steam bath, and left to reflux at 355 K for 40 min. On standing overnight at room temperature, dark-brown crystals suitable for X-ray diffraction were obtained [yield: 0.0164 g; m.p. 541 K (decomposition)]. Elemental analysis calculated (%) for $C_{26.33}H_{28.65}N_8NiOS_2$: C 53.06, H 4.85, N 18.8; found: C 53.22, H 4.75, N 19.14. IR (ν, cm^{-1}): 3280, 3217 (N—H), 2965, 2921 (CH aryl), 1600 (C═N), 1530, 1469 (C═C arom.), 831 (C—S). UV–Vis (DMSO), λ_{max}: 118, 389, 474 nm. HR ESI–MS: calculated for $[M + H]^+$: 573.1165; found 573.1087 (M is the unsolvated complex).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. One ethyl group (C25—C26) was modelled for disorder over two parts. Displacement parameters for this group were restrained to be similar and site occupancies were refined to 0.58 (2) and 0.42 (2). The last residual peaks in the difference maps were modelled as a mixture of water and methanol sharing a single site, and displacement parameters for these atoms (C1*A*, O1*A* and O1*W*) were constrained to be identical. Occupancies for water and methanol were refined to 0.672 (6) and 0.328 (6), respectively. The H atoms of the solvent molecules could not be located from a difference map and were thus placed in calculated positions. The H atoms of the amine groups (H4 and H8) were refined freely (positions and isotropic displacement parameters), while other H atoms were placed in calculated positions.

Acknowledgements

We are grateful for the support of the Chemical Sciences, Faculty of Science at Universiti Brunei Darussalam and the National University of Singapore for running the elemental, NMR, MS and single-crystal X-ray diffraction analyses.

Funding information

Funding for this research was provided by: Government of Brunei Darussalam (scholarship to Raudhatul Nadhirah Awang Adam; grant No. UBD/RSCH/1.4/FICBF(b)/2022/043 to Natasha Ann Keasberry; grant No. UBD/RSCH/1.4/FICBF(b)/2020/024 to Malai Haniti Sheikh Abdul Hamid).

References

Arif, R., Akrema, , Pulaganti, M., Rubab, U., Ali, A., Khan, M. S. & Uddin, R. (2024). *Chem. Pap.* **78**, 2867–2883.
Arulmurugan, S., Kavitha, H. P. & Venkatraman, B. R. (2010). *Rasayan J. Chem.* **3**, 385–410.
Bisceglie, F., Musiari, A., Pinelli, S., Alinovi, R., Menozzi, I., Polverini, E., Tarasconi, P., Tavone, M. & Pelosi, G. (2015). *J. Inorg. Biochem.* **152**, 10–19.
Bruker (2016). *APEX4* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Chaturvedi, D. (2012). *Tetrahedron*, **68**, 15–45.
Damit, N. S. H. H., Hamid, M. H. S. A., Rahman, N. S. R. H. A., Ilias, S. N. H. H. & Keasberry, N. A. (2021). *Inorg. Chim. Acta*, **527**, 120557.
Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* B**72**, 171–179.
Jayakumar, K., Seena, E. B., Kurup, M. R. P., Kaya, S., Serdaroğlu, G., Suresh, E. & Marzouki, R. (2022). *J. Mol. Struct.* **1253**, 132257.
Krause, L., Herbst-Irmer, R., Sheldrick, G. M. & Stalke, D. (2015). *J. Appl. Cryst.* **48**, 3–10.
Kumar, R., Singh, A. A., Kumar, U., Jain, P., Sharma, A. K., Kant, C. & Haque Faizi, M. S. (2023). *J. Mol. Struct.* **1294**, 136346.
Latheef, L., Kurup, M. R. P. & Suresh, E. (2021). *Chem. Data Coll.* **35**, 100758.
Macrae, C. F., Sovago, I., Cottrell, S. J., Galek, P. T. A., McCabe, P., Pidcock, E., Platings, M., Shields, G. P., Stevens, J. S., Towler, M. & Wood, P. A. (2020). *J. Appl. Cryst.* **53**, 226–235.
Min, R., Fan, X.-R., Zhou, P., Yan, J., Zhou, J.-L. & Zhang, S.-C. (2014). *Chin. J. Inorg. Chem.* **30**, 1771–1777.
Montalbano, S., Buschini, A., Pelosi, G. & Bisceglie, F. (2023). *Molecules*, **28**, 2778.
Osman, U. M., Silvarajoo, S., Kamarudin, K. H., Tahir, M. I. M. & Kwong, H. C. (2021). *J. Mol. Struct.* **1223**, 128994.
Sankar, R. & Sharmila, T. M. (2023). *Results Chem.* **6**, 101179.
Sheldrick, G. M. (2015*a*). *Acta Cryst.* A**71**, 3–8.
Sheldrick, G. M. (2015*b*). *Acta Cryst.* C**71**, 3–8.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

full crystallographic data

IUCrData (2024). **9**, x240339 [https://doi.org/10.1107/S2414314624003390]

mer-Bis(quinoline-2-carboxaldehyde 4-ethylthiosemicarbazonato)nickel(II) methanol 0.33-solvate 0.67-hydrate

Raudhatul Nadhirah Awang Adam, Natasha Ann Keasberry and Malai Haniti Sheikh Abdul Hamid

***mer*-Bis(quinoline-2-carboxaldehyde 4-ethylthiosemicarbazonato)nickel(II) methanol 0.33-solvate 0.67-hydrate**

Crystal data

$[Ni(C_{13}H_{13}N_4S)_2]\cdot 0.328CH_4O\cdot 0.672H_2O$
M_r = 595.97
Monoclinic, $P2_1/n$
a = 10.0560 (6) Å
b = 21.3696 (9) Å
c = 12.5648 (6) Å
β = 100.161 (2)°
V = 2657.7 (2) Å^3
Z = 4
$F(000)$ = 1242
D_x = 1.489 Mg m^{-3}
Melting point: 541 K
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9658 reflections
θ = 2.6–30.4°
μ = 0.93 mm^{-1}
T = 100 K
Rod, dark brown
0.13 × 0.13 × 0.10 mm

Data collection

Bruker D8 Venture diffractometer
Radiation source: Microfocus Sealed Tube
φ and ω scans
Absorption correction: multi-scan (SADABS; Krause et al., 2015)
T_{min} = 0.710, T_{max} = 0.746
143112 measured reflections
8094 independent reflections
7523 reflections with $I > 2\sigma(I)$
R_{int} = 0.076
θ_{max} = 30.5°, θ_{min} = 3.0°
h = −14→14
k = −30→30
l = −17→17

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.083
S = 1.08
8094 reflections
385 parameters
36 restraints
Primary atom site location: dual
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0226P)^2 + 3.305P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.46 e Å^{-3}
$\Delta\rho_{min}$ = −0.47 e Å^{-3}

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Ni1	0.37125 (2)	0.34643 (2)	0.54815 (2)	0.01053 (5)	

S1	0.58288 (4)	0.34892 (2)	0.48937 (3)	0.01341 (8)
S2	0.23953 (4)	0.30891 (2)	0.37971 (3)	0.01339 (8)
N1	0.21681 (13)	0.31495 (6)	0.63795 (11)	0.0125 (2)
N2	0.44276 (13)	0.26050 (6)	0.60052 (10)	0.0113 (2)
N3	0.55983 (13)	0.23412 (6)	0.58182 (11)	0.0126 (2)
N4	0.74864 (14)	0.25342 (7)	0.50791 (12)	0.0156 (3)
H4	0.791 (2)	0.2775 (11)	0.4735 (19)	0.024 (6)*
N5	0.44660 (13)	0.41468 (6)	0.67711 (10)	0.0119 (2)
N6	0.31246 (13)	0.42947 (6)	0.47570 (10)	0.0117 (2)
N7	0.24729 (13)	0.43707 (6)	0.37230 (11)	0.0130 (2)
N8	0.14719 (14)	0.38603 (7)	0.21967 (11)	0.0159 (3)
H8	0.125 (2)	0.3518 (11)	0.187 (2)	0.025 (6)*
C1	0.10008 (15)	0.34256 (7)	0.65722 (13)	0.0143 (3)
C2	0.07119 (17)	0.40507 (8)	0.62318 (15)	0.0202 (3)
H2	0.132819	0.427501	0.588242	0.024*
C3	−0.04576 (18)	0.43326 (9)	0.64064 (17)	0.0244 (4)
H3	−0.064523	0.475099	0.617169	0.029*
C4	−0.13860 (17)	0.40102 (9)	0.69295 (16)	0.0220 (3)
H4A	−0.219476	0.421041	0.703837	0.026*
C5	−0.11204 (16)	0.34105 (8)	0.72788 (14)	0.0188 (3)
H5	−0.174306	0.319666	0.763675	0.023*
C6	0.00747 (15)	0.31046 (8)	0.71120 (13)	0.0148 (3)
C7	0.03928 (16)	0.24885 (8)	0.74760 (13)	0.0161 (3)
H7	−0.020396	0.226208	0.784164	0.019*
C8	0.15664 (16)	0.22215 (7)	0.72970 (13)	0.0146 (3)
H8A	0.180217	0.181002	0.754807	0.018*
C9	0.24290 (15)	0.25634 (7)	0.67338 (12)	0.0124 (3)
C10	0.36676 (15)	0.22762 (7)	0.65212 (12)	0.0124 (3)
H10	0.390954	0.186202	0.675312	0.015*
C11	0.63063 (15)	0.27363 (7)	0.53007 (12)	0.0124 (3)
C12	0.80517 (16)	0.19107 (8)	0.53084 (14)	0.0172 (3)
H12A	0.786655	0.177009	0.601868	0.021*
H12B	0.904409	0.193044	0.535614	0.021*
C13	0.74744 (19)	0.14358 (8)	0.44520 (16)	0.0228 (3)
H13A	0.790999	0.102944	0.462710	0.034*
H13B	0.764093	0.157600	0.374460	0.034*
H13C	0.649940	0.139539	0.443148	0.034*
C14	0.51401 (15)	0.40752 (7)	0.78126 (12)	0.0123 (3)
C15	0.54723 (16)	0.34674 (7)	0.82233 (13)	0.0147 (3)
H15	0.524935	0.311347	0.776942	0.018*
C16	0.61140 (16)	0.33856 (8)	0.92725 (13)	0.0164 (3)
H16	0.632372	0.297488	0.953940	0.020*
C17	0.64651 (17)	0.39034 (8)	0.99577 (14)	0.0181 (3)
H17	0.689126	0.383985	1.068662	0.022*
C18	0.61934 (17)	0.44984 (8)	0.95752 (13)	0.0173 (3)
H18	0.645279	0.484621	1.003611	0.021*
C19	0.55302 (16)	0.45990 (7)	0.85004 (13)	0.0142 (3)
C20	0.52339 (17)	0.52050 (8)	0.80729 (13)	0.0171 (3)

H20	0.548570	0.556342	0.850925	0.020*	
C21	0.45851 (17)	0.52724 (7)	0.70315 (13)	0.0163 (3)	
H21	0.438725	0.567711	0.673239	0.020*	
C22	0.42098 (15)	0.47294 (7)	0.64009 (12)	0.0128 (3)	
C23	0.35131 (16)	0.47991 (7)	0.52932 (13)	0.0136 (3)	
H23	0.334804	0.520070	0.497294	0.016*	
C24	0.21181 (15)	0.38279 (7)	0.32265 (12)	0.0121 (3)	
C25	0.1078 (15)	0.4456 (8)	0.1591 (14)	0.021 (2)	0.58 (2)
H25A	0.161021	0.480574	0.196717	0.025*	0.58 (2)
H25B	0.130426	0.442171	0.085764	0.025*	0.58 (2)
C26	−0.0373 (7)	0.4598 (3)	0.1497 (11)	0.0455 (18)	0.58 (2)
H26A	−0.055776	0.501394	0.117810	0.068*	0.58 (2)
H26B	−0.062309	0.458858	0.221588	0.068*	0.58 (2)
H26C	−0.090205	0.428441	0.103356	0.068*	0.58 (2)
C25A	0.1242 (19)	0.4421 (11)	0.1610 (18)	0.017 (2)	0.42 (2)
H25C	0.181819	0.443287	0.104807	0.021*	0.42 (2)
H25D	0.149015	0.478010	0.210232	0.021*	0.42 (2)
C26A	−0.0277 (10)	0.4477 (6)	0.1064 (12)	0.041 (2)	0.42 (2)
H26D	−0.043953	0.489086	0.073039	0.061*	0.42 (2)
H26E	−0.085129	0.442191	0.161080	0.061*	0.42 (2)
H26F	−0.049072	0.415319	0.050730	0.061*	0.42 (2)
O1W	0.9174 (12)	0.3352 (4)	0.3991 (10)	0.0262 (8)	0.672 (6)
H1W	0.926373	0.363814	0.449173	0.039*	0.672 (6)
H2W	0.999607	0.326761	0.391031	0.039*	0.672 (6)
O1S	0.924 (3)	0.3269 (10)	0.394 (2)	0.0262 (8)	0.328 (6)
H1S	1.007535	0.322428	0.413664	0.039*	0.328 (6)
C1S	0.8922 (6)	0.3926 (3)	0.3797 (5)	0.0262 (8)	0.328 (6)
H1A	0.828778	0.404763	0.426964	0.039*	0.328 (6)
H1B	0.851011	0.400377	0.304168	0.039*	0.328 (6)
H1C	0.975225	0.417242	0.398023	0.039*	0.328 (6)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.00948 (9)	0.00951 (9)	0.01260 (9)	0.00096 (6)	0.00196 (7)	0.00092 (7)
S1	0.01215 (16)	0.01128 (16)	0.01730 (18)	0.00052 (12)	0.00392 (13)	0.00194 (13)
S2	0.01316 (16)	0.01044 (15)	0.01588 (17)	0.00003 (12)	0.00072 (13)	0.00007 (13)
N1	0.0099 (5)	0.0132 (6)	0.0148 (6)	0.0006 (4)	0.0033 (5)	0.0001 (5)
N2	0.0094 (5)	0.0121 (5)	0.0122 (6)	0.0006 (4)	0.0012 (4)	−0.0004 (4)
N3	0.0100 (5)	0.0128 (6)	0.0152 (6)	0.0021 (4)	0.0031 (5)	0.0008 (5)
N4	0.0120 (6)	0.0154 (6)	0.0202 (7)	0.0020 (5)	0.0054 (5)	0.0030 (5)
N5	0.0104 (5)	0.0125 (6)	0.0130 (6)	−0.0002 (4)	0.0025 (4)	0.0002 (4)
N6	0.0100 (5)	0.0131 (6)	0.0122 (6)	0.0018 (4)	0.0022 (4)	0.0007 (4)
N7	0.0137 (6)	0.0126 (6)	0.0122 (6)	0.0010 (4)	0.0004 (5)	0.0006 (5)
N8	0.0180 (6)	0.0141 (6)	0.0142 (6)	−0.0001 (5)	−0.0012 (5)	−0.0008 (5)
C1	0.0117 (6)	0.0154 (7)	0.0155 (7)	0.0011 (5)	0.0018 (5)	−0.0005 (5)
C2	0.0163 (7)	0.0166 (7)	0.0297 (9)	0.0037 (6)	0.0094 (7)	0.0032 (6)
C3	0.0182 (8)	0.0192 (8)	0.0377 (10)	0.0053 (6)	0.0104 (7)	0.0014 (7)

C4	0.0127 (7)	0.0245 (8)	0.0298 (9)	0.0040 (6)	0.0067 (6)	−0.0035 (7)
C5	0.0114 (7)	0.0242 (8)	0.0219 (8)	−0.0004 (6)	0.0062 (6)	−0.0036 (6)
C6	0.0103 (6)	0.0195 (7)	0.0148 (7)	−0.0008 (5)	0.0025 (5)	−0.0015 (6)
C7	0.0140 (7)	0.0202 (7)	0.0147 (7)	−0.0026 (6)	0.0040 (5)	0.0010 (6)
C8	0.0138 (7)	0.0152 (7)	0.0148 (7)	−0.0019 (5)	0.0026 (5)	0.0023 (5)
C9	0.0127 (6)	0.0131 (6)	0.0113 (6)	−0.0006 (5)	0.0017 (5)	0.0000 (5)
C10	0.0122 (6)	0.0107 (6)	0.0144 (7)	0.0005 (5)	0.0024 (5)	0.0010 (5)
C11	0.0112 (6)	0.0133 (6)	0.0124 (6)	0.0006 (5)	0.0015 (5)	0.0000 (5)
C12	0.0131 (7)	0.0189 (7)	0.0198 (8)	0.0066 (6)	0.0037 (6)	0.0035 (6)
C13	0.0232 (8)	0.0183 (8)	0.0269 (9)	0.0053 (6)	0.0041 (7)	0.0009 (7)
C14	0.0098 (6)	0.0141 (6)	0.0133 (7)	−0.0001 (5)	0.0024 (5)	0.0002 (5)
C15	0.0155 (7)	0.0136 (7)	0.0146 (7)	0.0011 (5)	0.0017 (5)	−0.0003 (5)
C16	0.0159 (7)	0.0159 (7)	0.0168 (7)	0.0021 (5)	0.0015 (6)	0.0020 (6)
C17	0.0171 (7)	0.0202 (7)	0.0155 (7)	0.0005 (6)	−0.0012 (6)	0.0001 (6)
C18	0.0183 (7)	0.0170 (7)	0.0153 (7)	−0.0018 (6)	−0.0009 (6)	−0.0024 (6)
C19	0.0137 (7)	0.0143 (7)	0.0145 (7)	−0.0012 (5)	0.0020 (5)	−0.0006 (5)
C20	0.0209 (8)	0.0134 (7)	0.0160 (7)	−0.0019 (6)	0.0009 (6)	−0.0020 (6)
C21	0.0201 (7)	0.0117 (6)	0.0170 (7)	−0.0008 (5)	0.0030 (6)	−0.0004 (5)
C22	0.0119 (6)	0.0124 (6)	0.0140 (7)	−0.0002 (5)	0.0026 (5)	0.0000 (5)
C23	0.0144 (7)	0.0115 (6)	0.0146 (7)	0.0010 (5)	0.0021 (5)	0.0019 (5)
C24	0.0093 (6)	0.0132 (6)	0.0138 (7)	0.0006 (5)	0.0022 (5)	0.0006 (5)
C25	0.030 (5)	0.014 (2)	0.017 (2)	0.004 (3)	−0.002 (3)	0.0074 (18)
C26	0.028 (2)	0.031 (2)	0.068 (4)	0.0062 (17)	−0.017 (3)	0.003 (3)
C25A	0.010 (3)	0.022 (4)	0.016 (3)	0.001 (3)	−0.006 (2)	−0.003 (3)
C26A	0.030 (3)	0.037 (4)	0.049 (5)	0.002 (3)	−0.011 (3)	0.020 (3)
O1W	0.0180 (11)	0.033 (2)	0.0285 (12)	−0.0032 (15)	0.0077 (8)	−0.0046 (16)
O1S	0.0180 (11)	0.033 (2)	0.0285 (12)	−0.0032 (15)	0.0077 (8)	−0.0046 (16)
C1S	0.0180 (11)	0.033 (2)	0.0285 (12)	−0.0032 (15)	0.0077 (8)	−0.0046 (16)

Geometric parameters (Å, º)

Ni1—N6	2.0339 (13)	C12—C13	1.518 (2)
Ni1—N2	2.0384 (13)	C12—H12A	0.9900
Ni1—N1	2.1808 (13)	C12—H12B	0.9900
Ni1—N5	2.2120 (13)	C13—H13A	0.9800
Ni1—S1	2.3731 (4)	C13—H13B	0.9800
Ni1—S2	2.4264 (4)	C13—H13C	0.9800
S1—C11	1.7303 (15)	C14—C15	1.416 (2)
S2—C24	1.7359 (15)	C14—C19	1.426 (2)
N1—C9	1.3395 (19)	C15—C16	1.373 (2)
N1—C1	1.3730 (19)	C15—H15	0.9500
N2—C10	1.2935 (19)	C16—C17	1.408 (2)
N2—N3	1.3625 (17)	C16—H16	0.9500
N3—C11	1.3438 (19)	C17—C18	1.370 (2)
N4—C11	1.3376 (19)	C17—H17	0.9500
N4—C12	1.457 (2)	C18—C19	1.413 (2)
N4—H4	0.84 (2)	C18—H18	0.9500
N5—C22	1.3381 (19)	C19—C20	1.413 (2)

N5—C14	1.3720 (19)	C20—C21	1.363 (2)
N6—C23	1.294 (2)	C20—H20	0.9500
N6—N7	1.3578 (18)	C21—C22	1.418 (2)
N7—C24	1.3355 (19)	C21—H21	0.9500
N8—C24	1.343 (2)	C22—C23	1.451 (2)
N8—C25A	1.40 (2)	C23—H23	0.9500
N8—C25	1.499 (15)	C25—C26	1.474 (15)
N8—H8	0.85 (2)	C25—H25A	0.9900
C1—C2	1.417 (2)	C25—H25B	0.9900
C1—C6	1.422 (2)	C26—H26A	0.9800
C2—C3	1.373 (2)	C26—H26B	0.9800
C2—H2	0.9500	C26—H26C	0.9800
C3—C4	1.412 (3)	C25A—C26A	1.56 (2)
C3—H3	0.9500	C25A—H25C	0.9900
C4—C5	1.366 (3)	C25A—H25D	0.9900
C4—H4A	0.9500	C26A—H26D	0.9800
C5—C6	1.416 (2)	C26A—H26E	0.9800
C5—H5	0.9500	C26A—H26F	0.9800
C6—C7	1.412 (2)	O1W—H1W	0.8700
C7—C8	1.365 (2)	O1W—H2W	0.8700
C7—H7	0.9500	O1S—C1S	1.44 (2)
C8—C9	1.416 (2)	O1S—H1S	0.8400
C8—H8A	0.9500	C1S—H1A	0.9800
C9—C10	1.455 (2)	C1S—H1B	0.9800
C10—H10	0.9500	C1S—H1C	0.9800

N6—Ni1—N2	171.31 (5)	N4—C12—H12B	109.1
N6—Ni1—N1	108.87 (5)	C13—C12—H12B	109.1
N2—Ni1—N1	78.34 (5)	H12A—C12—H12B	107.8
N6—Ni1—N5	77.74 (5)	C12—C13—H13A	109.5
N2—Ni1—N5	107.56 (5)	C12—C13—H13B	109.5
N1—Ni1—N5	90.43 (5)	H13A—C13—H13B	109.5
N6—Ni1—S1	92.69 (4)	C12—C13—H13C	109.5
N2—Ni1—S1	80.56 (4)	H13A—C13—H13C	109.5
N1—Ni1—S1	158.05 (4)	H13B—C13—H13C	109.5
N5—Ni1—S1	90.18 (4)	N5—C14—C15	119.67 (14)
N6—Ni1—S2	80.04 (4)	N5—C14—C19	121.82 (14)
N2—Ni1—S2	95.23 (4)	C15—C14—C19	118.50 (14)
N1—Ni1—S2	91.16 (4)	C16—C15—C14	120.50 (15)
N5—Ni1—S2	157.00 (4)	C16—C15—H15	119.7
S1—Ni1—S2	96.747 (15)	C14—C15—H15	119.7
C11—S1—Ni1	96.00 (5)	C15—C16—C17	120.78 (15)
C24—S2—Ni1	94.75 (5)	C15—C16—H16	119.6
C9—N1—C1	117.82 (13)	C17—C16—H16	119.6
C9—N1—Ni1	110.17 (10)	C18—C17—C16	120.13 (15)
C1—N1—Ni1	131.89 (11)	C18—C17—H17	119.9
C10—N2—N3	117.81 (13)	C16—C17—H17	119.9
C10—N2—Ni1	116.44 (10)	C17—C18—C19	120.52 (15)

N3—N2—Ni1	125.69 (10)	C17—C18—H18	119.7
C11—N3—N2	111.78 (12)	C19—C18—H18	119.7
C11—N4—C12	125.70 (14)	C18—C19—C20	122.34 (15)
C11—N4—H4	117.6 (16)	C18—C19—C14	119.52 (14)
C12—N4—H4	116.6 (16)	C20—C19—C14	118.15 (14)
C22—N5—C14	117.88 (13)	C21—C20—C19	119.66 (15)
C22—N5—Ni1	109.80 (10)	C21—C20—H20	120.2
C14—N5—Ni1	132.30 (10)	C19—C20—H20	120.2
C23—N6—N7	116.66 (13)	C20—C21—C22	119.02 (15)
C23—N6—Ni1	117.15 (10)	C20—C21—H21	120.5
N7—N6—Ni1	125.86 (10)	C22—C21—H21	120.5
C24—N7—N6	112.77 (12)	N5—C22—C21	123.45 (14)
C24—N8—C25A	123.8 (9)	N5—C22—C23	117.36 (13)
C24—N8—C25	124.9 (7)	C21—C22—C23	119.19 (14)
C24—N8—H8	117.5 (16)	N6—C23—C22	117.65 (14)
C25A—N8—H8	118.5 (19)	N6—C23—H23	121.2
C25—N8—H8	117.6 (17)	C22—C23—H23	121.2
N1—C1—C2	119.21 (14)	N7—C24—N8	116.68 (14)
N1—C1—C6	121.95 (14)	N7—C24—S2	125.94 (12)
C2—C1—C6	118.83 (14)	N8—C24—S2	117.37 (12)
C3—C2—C1	120.07 (16)	C26—C25—N8	112.6 (10)
C3—C2—H2	120.0	C26—C25—H25A	109.1
C1—C2—H2	120.0	N8—C25—H25A	109.1
C2—C3—C4	121.03 (17)	C26—C25—H25B	109.1
C2—C3—H3	119.5	N8—C25—H25B	109.1
C4—C3—H3	119.5	H25A—C25—H25B	107.8
C5—C4—C3	119.96 (16)	C25—C26—H26A	109.5
C5—C4—H4A	120.0	C25—C26—H26B	109.5
C3—C4—H4A	120.0	H26A—C26—H26B	109.5
C4—C5—C6	120.58 (16)	C25—C26—H26C	109.5
C4—C5—H5	119.7	H26A—C26—H26C	109.5
C6—C5—H5	119.7	H26B—C26—H26C	109.5
C7—C6—C5	122.16 (15)	N8—C25A—C26A	110.7 (14)
C7—C6—C1	118.33 (14)	N8—C25A—H25C	109.5
C5—C6—C1	119.50 (15)	C26A—C25A—H25C	109.5
C8—C7—C6	119.31 (15)	N8—C25A—H25D	109.5
C8—C7—H7	120.3	C26A—C25A—H25D	109.5
C6—C7—H7	120.3	H25C—C25A—H25D	108.1
C7—C8—C9	119.38 (15)	C25A—C26A—H26D	109.5
C7—C8—H8A	120.3	C25A—C26A—H26E	109.5
C9—C8—H8A	120.3	H26D—C26A—H26E	109.5
N1—C9—C8	123.19 (14)	C25A—C26A—H26F	109.5
N1—C9—C10	117.21 (13)	H26D—C26A—H26F	109.5
C8—C9—C10	119.61 (14)	H26E—C26A—H26F	109.5
N2—C10—C9	117.62 (13)	H1W—O1W—H2W	104.5
N2—C10—H10	121.2	C1S—O1S—H1S	109.5
C9—C10—H10	121.2	O1S—C1S—H1A	109.5
N4—C11—N3	117.59 (14)	O1S—C1S—H1B	109.5

N4—C11—S1	116.67 (12)	H1A—C1S—H1B	109.5
N3—C11—S1	125.74 (12)	O1S—C1S—H1C	109.5
N4—C12—C13	112.58 (14)	H1A—C1S—H1C	109.5
N4—C12—H12A	109.1	H1B—C1S—H1C	109.5
C13—C12—H12A	109.1		

C10—N2—N3—C11	−178.48 (14)	C22—N5—C14—C15	−177.83 (14)
Ni1—N2—N3—C11	4.53 (18)	Ni1—N5—C14—C15	0.2 (2)
C23—N6—N7—C24	179.47 (13)	C22—N5—C14—C19	1.7 (2)
Ni1—N6—N7—C24	6.23 (18)	Ni1—N5—C14—C19	179.77 (11)
C9—N1—C1—C2	178.43 (15)	N5—C14—C15—C16	−178.22 (15)
Ni1—N1—C1—C2	−6.1 (2)	C19—C14—C15—C16	2.2 (2)
C9—N1—C1—C6	−1.1 (2)	C14—C15—C16—C17	−0.6 (2)
Ni1—N1—C1—C6	174.43 (11)	C15—C16—C17—C18	−1.4 (3)
N1—C1—C2—C3	179.27 (17)	C16—C17—C18—C19	1.6 (3)
C6—C1—C2—C3	−1.2 (3)	C17—C18—C19—C20	−179.83 (16)
C1—C2—C3—C4	0.4 (3)	C17—C18—C19—C14	0.1 (2)
C2—C3—C4—C5	0.6 (3)	N5—C14—C19—C18	178.44 (14)
C3—C4—C5—C6	−0.6 (3)	C15—C14—C19—C18	−2.0 (2)
C4—C5—C6—C7	179.03 (16)	N5—C14—C19—C20	−1.6 (2)
C4—C5—C6—C1	−0.2 (3)	C15—C14—C19—C20	177.97 (15)
N1—C1—C6—C7	1.3 (2)	C18—C19—C20—C21	−179.63 (16)
C2—C1—C6—C7	−178.14 (15)	C14—C19—C20—C21	0.4 (2)
N1—C1—C6—C5	−179.35 (15)	C19—C20—C21—C22	0.6 (2)
C2—C1—C6—C5	1.2 (2)	C14—N5—C22—C21	−0.7 (2)
C5—C6—C7—C8	−179.50 (16)	Ni1—N5—C22—C21	−179.18 (12)
C1—C6—C7—C8	−0.2 (2)	C14—N5—C22—C23	179.15 (13)
C6—C7—C8—C9	−1.1 (2)	Ni1—N5—C22—C23	0.68 (17)
C1—N1—C9—C8	−0.3 (2)	C20—C21—C22—N5	−0.4 (2)
Ni1—N1—C9—C8	−176.77 (12)	C20—C21—C22—C23	179.71 (15)
C1—N1—C9—C10	179.83 (13)	N7—N6—C23—C22	179.89 (13)
Ni1—N1—C9—C10	3.41 (16)	Ni1—N6—C23—C22	−6.25 (18)
C7—C8—C9—N1	1.4 (2)	N5—C22—C23—N6	3.5 (2)
C7—C8—C9—C10	−178.73 (14)	C21—C22—C23—N6	−176.61 (14)
N3—N2—C10—C9	179.06 (13)	N6—N7—C24—N8	−179.73 (13)
Ni1—N2—C10—C9	−3.66 (18)	N6—N7—C24—S2	1.23 (19)
N1—C9—C10—N2	−0.1 (2)	C25A—N8—C24—N7	4.5 (11)
C8—C9—C10—N2	−179.93 (14)	C25—N8—C24—N7	−2.6 (8)
C12—N4—C11—N3	2.8 (2)	C25A—N8—C24—S2	−176.4 (11)
C12—N4—C11—S1	−177.32 (13)	C25—N8—C24—S2	176.5 (8)
N2—N3—C11—N4	179.34 (13)	Ni1—S2—C24—N7	−5.77 (14)
N2—N3—C11—S1	−0.52 (19)	Ni1—S2—C24—N8	175.20 (12)
Ni1—S1—C11—N4	177.62 (12)	C24—N8—C25—C26	−103.1 (11)
Ni1—S1—C11—N3	−2.52 (14)	C24—N8—C25A—C26A	−129.9 (12)
C11—N4—C12—C13	82.1 (2)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N4—H4···O1*W*	0.84 (2)	2.10 (3)	2.936 (12)	174 (2)
N4—H4···O1*S*	0.84 (2)	2.08 (4)	2.91 (3)	170 (2)
O1*S*—H1*S*···S2^{i}	0.84	2.46	3.24 (2)	154
N8—H8···N3^{ii}	0.85 (2)	2.29 (2)	3.1349 (19)	174 (2)

Symmetry codes: (i) *x*+1, *y*, *z*; (ii) *x*−1/2, −*y*+1/2, *z*−1/2.