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Crystal structure and Hirshfeld surface analysis of bis{(*Z*)-*N*′-[(*E*)-(furan-2-yl)methylidene]carbamohydrazonothioato}nickel(II) methanol disolvate

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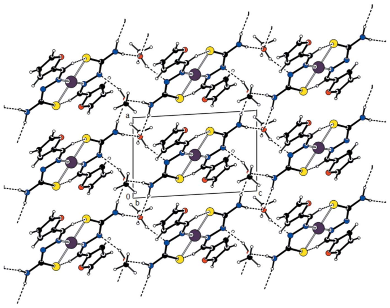
In the title complex, $[Ni(C_6H_6N_3OS)_2]\cdot 2CH_3OH$, the Ni^{II} atom is coordinated by the S and N atoms of two *N*′-[(*Z*)-(furan-2-yl)methylidene]carbamohydrazonothioic acid ligands in a distorted square-planar geometry. The two mutual ligands bound to Ni^{II} are also connected by C—H···S interactions, while the H atoms of the NH$_2$ group of the ligands form $R_4^4(8)$ motifs with the O atoms of the solvent ethyl alcohol molecules. At the same time, the OH groups of the solvent ethyl alcohol molecules form parallel layers to the (011) plane by the O—H···N interactions with the ligand N atom that is not bonded to the Ni^{II} atom.. The layers are connected by van der Waals interactions. A Hirshfeld surface analysis indicates that the most important contacts are H···H (37.7%), C···H/H···C (14.6%), O···H/H···O (11.5%) and S···H/H···S (10.6%).

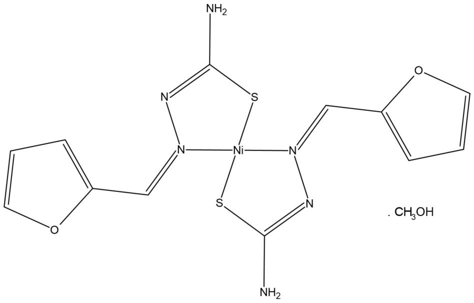


1. Chemical context

Hydrazones have been used extensively as substrates in organic synthesis (Polyanskii *et al.*, 2019; Shikhaliyev *et al.*, 2019; Safavora *et al.*, 2019; Zubkov *et al.*, 2018) and multidentate ligands (Gurbanov *et al.*, 2020*a*,*b*; Gurbanov *et al.*, 2022) while their complexes have been found to possess a wide variety of useful properties. Thus, they can be used as sensor or analytical reagents, catalysts and building blocks in crystal engineering (Ma *et al.*, 2021; Mahmudov *et al.*, 2010; Mahmoudi *et al.*, 2017*a*,*b*). Not only because of their coordination ability, but also the attached substituents, the intermolecular non-covalent interactions direct the functional properties as well as the supramolecular chemistry of hydrazones (Abdelhamid *et al.*, 2011; Khalilov *et al.*, 2021; Kopylovich *et al.*, 2011; Mahmudov *et al.*, 2015;). In fact, hydrogen and chalcogen bonds and other types of weak interactions have been well employed in the decoration of the secondary coordination sphere of transition-metal complexes (Mahmoudi *et al.*, 2019; Mahmudov *et al.*, 2012, 2022). We have synthesized a new Ni^{II} complex of a (*E*)-2-(furan-2-ylmethylene)hydrazine-1-carbothioamide ligand and studied its crystal structure.

2. Structural commentary

Fig. 1 shows the arrangement of the complex molecules in the unit cell. The Ni^{II} atom is coordinated by the S and N atoms of two *N*′-[(*Z*)-(furan-2-yl)methylidene]carbamohydrazonothioic acid ligands in a distorted square-planar geometry. The ligands assume a *trans* arrangement with respect to each other around the Ni^{II} ion, which lies on a crystallographic inversion centre at ($-x + 1$, $-y$, $-z + 1$). The Ni—S [2.1818 (6) Å] and Ni—N [1.9055 (17) Å] bond lengths lie within the range of those found in related structures.



3. Supramolecular features and Hirshfeld surface analysis

In the crystal, the two mutual ligands bound to Ni^{II} are also linked by C—H⋯S interactions, while the H atoms of the NH$_2$ group of the ligands form $R_4^4(8)$ motifs (Bernstein *et al.*, 1995; Tables 1 and 2; Fig. 2) with the O atoms of the solvent ethyl alcohol molecules. At the same time, the OH groups of the solvent ethyl alcohol molecules form parallel layers to the (011) plane by the O—H⋯N interactions with the ligand N atom that is not bonded to the Ni^{II} atom (Figs. 2, 3 and 4). These layers are connected by van der Waals interactions.

A Hirshfeld surface analysis was carried out using *CrystalExplorer 17.5* (Spackman *et al.*, 2021) to analyse the intermolecular interactions. The three-dimensional Hirshfeld surface mapped over the normalized contact distance ($d_{\rm norm}$) is shown in Fig. 5. The bright-red spots indicate shortened contacts, and correspond to the O—H⋯N and N—H⋯O intermolecular hydrogen bonds.

The two-dimensional fingerprint plots show the H⋯H (Fig. 6*b*; 37.7%) contacts to be the most common, followed by C⋯H/H⋯C (Fig. 6*c*; 14.6%), O⋯H/H⋯O (Fig. 6*d*; 11.5%) and S⋯H/H⋯S (Fig. 6*e*; 10.6%) contacts. The N⋯H/H⋯N (8.5%), O⋯C/C⋯O (4.9%), Ni⋯H/H⋯Ni (3.2%), O⋯N/N⋯O (2.2%), N⋯C/C⋯N (1.9%), C⋯C (1.8%), S⋯C/C⋯S (1.1%), S⋯S (0.7%), O⋯O (0.7%),S⋯O/O⋯S (0.5%) and Ni⋯C/C⋯Ni (0.2%) contacts have little directional influence on the molecular packing.

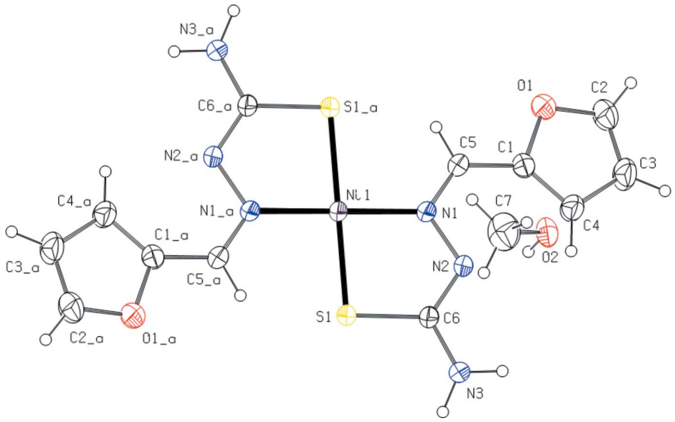


Figure 1
The molecular structure of the title compound, with atom labelling. The displacement ellipsoids are drawn at the 30% probability level.

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

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
O2—H2*O*⋯N2	0.90	1.94	2.788 (3)	156
N3—H3*A*⋯O2^{i}	0.90	2.07	2.964 (3)	173
N3—H3*B*⋯O2^{ii}	0.90	2.12	3.009 (3)	171
C5—H5⋯S1^{iii}	0.93	2.51	3.102 (3)	121

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

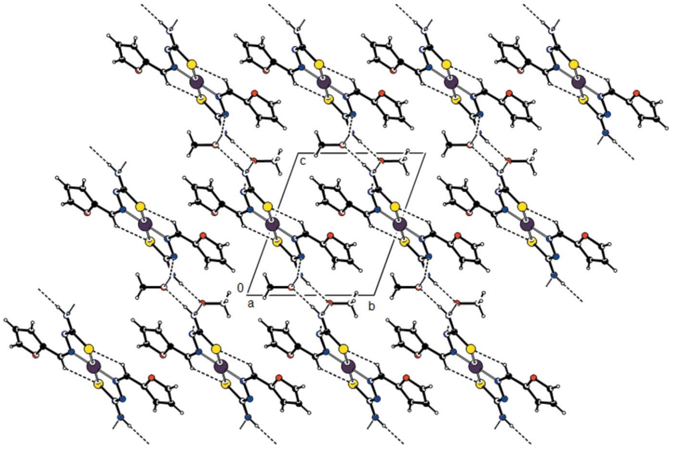


Figure 2
A view along the *a* axis of the crystal packing of the title compound. The O—H⋯N, N—H⋯O and C—H⋯S hydrogen bonds are shown as dashed lines.

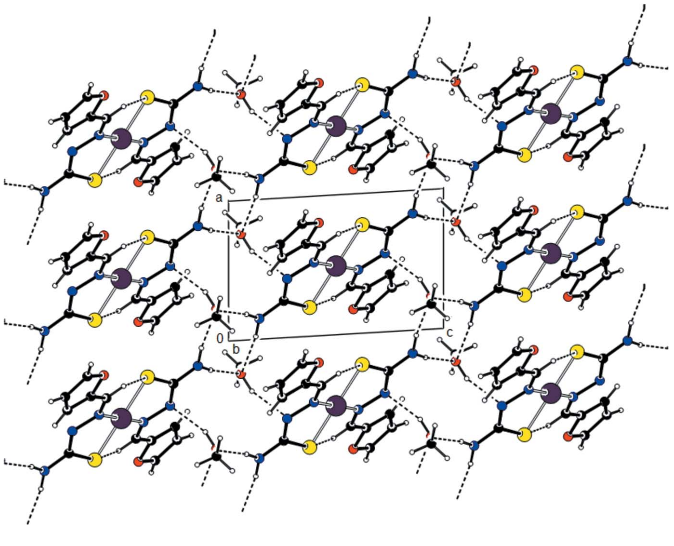


Figure 3
A view along the *b* axis of the crystal packing of the title compound, with hydrogen bonds indicated by dashed lines.

Table 2
Summary of short interatomic contacts (Å) in the title compound.

Contact	Distance	Symmetry operation
S1···C5	3.55	$-1 + x, y, z$
H2···O1	2.78	$2 - x, 1 - y, 1 - z$
N2···H2*O*	1.94	x, y, z
H3*B*···O2	2.12	$-1 + x, y, z$
H3*A*···O2	2.07	$1 - x, 1 - y, 1 - z$
C1···C1	3.51	$1 - x, 1 - y, 1 - z$
H3*B*···H3*A*	2.55	$-x, 1 - y, -z$
H7*C*···H7*C*	2.38	$2 - x, -y, -z$

4. Database survey

A search of the Cambridge Structural Database (ConQUEST version 2022 3.0; Groom *et al.*, 2016) for one of the Ni atoms plus ligands in the title compound yielded 14 structures that have the same framework as the title compound. FUTRAN (Puranik *et al.*, 1987) appears to be the same structure, without any solvent, and NOQCUS (Rodríguez-Argüelles *et al.*, 2009) is the same with a dimethyl sulfoxide solvent molecule; the other 12 have alkyl or phenyl groups attached.

In the crystal of FUTRAN, Ni ^{II} is in the distorted square planar ligand field of the N_2S_2 chromophore. The thiosemicarbazonato group is planar with Ni—S = 2.149 (1) Å and Ni—N(2) = 1.921 (2) Å. The coordination around Ni is *trans* planar with respect to the two S and two N atoms. The furan ring plane is at an angle of 3(1)° to the coordination plane. In the crystal of NOQCUS, the coordination environment around the nickel(II) ion is totally planar, as the NiN_2S_2

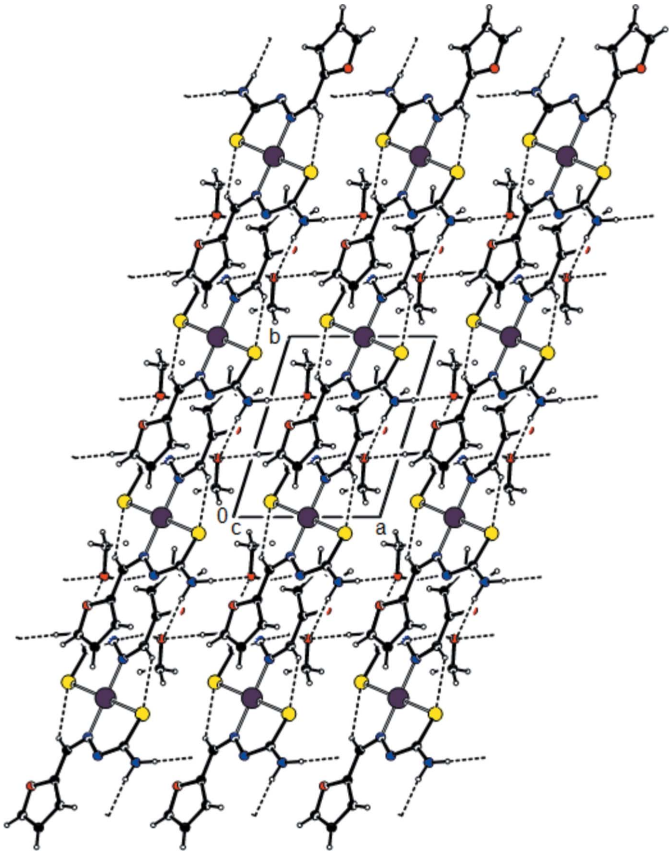


Figure 4
A view along the *c* axis of the crystal packing of the title compound, with hydrogen bonds indicated by dashed lines.

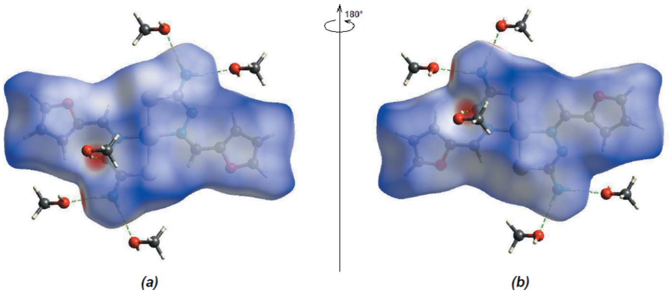


Figure 5
(*a*) Front and (*b*) back sides of the three-dimensional Hirshfeld surface of the title compound mapped over $d_{\rm norm}$.

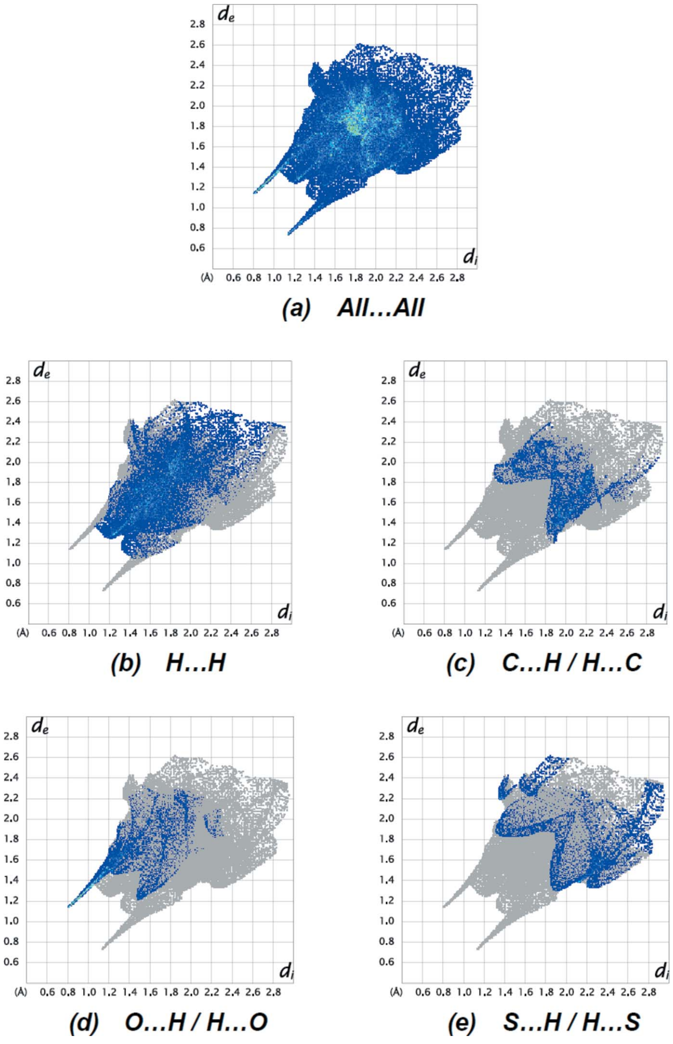


Figure 6
The two-dimensional fingerprint plots of the title compound, showing (*a*) all interactions, and delineated into (*b*) H···H, (*c*) C···H/H···C, (*d*) O···H/H···O and (*e*) S···H/H···S interactions. [d_e and d_i represent the distances from a point on the Hirshfeld surface to the nearest atoms outside (external) and inside (internal) the surface, respectively].

Table 3
Experimental details.

Crystal data	
Chemical formula	$[Ni(C_6H_6N_3OS)_2]\cdot 2CH_4O$
M_r	459.19
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	296
a, b, c (Å)	6.5394 (11), 8.9611 (15), 10.2020 (15)
α, β, γ (°)	67.965 (5), 79.666 (6), 70.349 (6)
V (Å^3)	520.92 (15)
Z	1
Radiation type	Mo $K\alpha$
μ (mm^{-1})	1.16
Crystal size (mm)	0.26 × 0.21 × 0.12
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2008)
T_{min}, T_{max}	0.735, 0.861
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	8497, 2134, 1633
R_{int}	0.046
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.626
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.032, 0.088, 1.04
No. of reflections	2134
No. of parameters	125
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.25, −0.21

Computer programs: *APEX4* (Bruker, 2008), *SAINT* (Bruker, 2008), *SHELXT2016/6* (Sheldrick, 2015*a*), *SHELXL2016/6* (Sheldrick, 2015*b*, *ORTEP-3 for Windows* (Farrugia, 2012), *PLATON* (Spek, 2020).

chromophore lies on its least-squares calculated plane and the four angles formed by the metal centre with the four donor atoms add up to exactly 360°. The Ni—N and Ni—S distances are within the usual range. This plane forms a 18° angle with the uncoordinated furan ring, which is also highly planar.

5. Synthesis and crystallization

17 mg (0.1 mmol) of (*E*)-2-(furan-2-ylmethylene)hydrazine-1-carbothioamide were dissolved in 30 mL of methanol then 13 mg (0.05 mmol) of *Ni*$(OOCCH_3)_2\cdot 4H_2O$ were added. The reaction mixture was kept in air at room temperature for slow evaporation. After *ca* 2–3 d, orange crystals, suitable for X-ray analysis, were formed.

Yield 81%, soluble in DMSO, ethanol and dimethylformamide and insoluble in non-polar solvents. Elemental analysis: $C_{14}H_{20}N_6NiO_4S_2$ (M = *459*.17); C 36.61 (calc. 36.62); H 4.35 (4.39); N 18.26 (18.30) %. IR (KBr): 3372 ν(OH), 2965 and 2854 ν(NH), 1643 ν(C═N) cm^{-1}.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. C-bound H atoms were positioned geometrically (C—H = 0.93 and 0.96 Å) and refined using a riding model with U_{iso}(H) = 1.2 or 1.5U_{eq}(C). O- and N-bound H atoms were located in difference Fourier maps [O2—H2*O* = 0.90 Å, N3—H3*A* = 0.90 Å, N3—H3*B* = 0.90 Å] and refined with U_{iso}(H) = 1.2U_{eq}(N) and 1.5U_{eq}(O), with their positions fixed. Two reflections (001) and (010), affected by the beam stop, were omitted in the final cycles of refinement.

Acknowledgements

The author's contributions are as follows. Conceptualization, MA and AB; synthesis, ANA and GZM; X-ray analysis, ANA, GZM, STÇ and MA; writing (review and editing of the manuscript) STÇ, MA and AB; funding acquisition, ANA and GZM; supervision, MA and AB.

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supporting information

Acta Cryst. (2023). E**79**, 669-673 [https://doi.org/10.1107/S2056989023005182]

Crystal structure and Hirshfeld surface analysis of bis{(*Z*)-*N*′-[(*E*)-(furan-2-yl)methylidene]carbamohydrazonothioato}nickel(II) methanol disolvate

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Computing details

Data collection: *APEX4* (Bruker, 2008); cell refinement: *SAINT* (Bruker, 2008); data reduction: *SAINT* (Bruker, 2008); program(s) used to solve structure: *SHELXT2016/6* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2016/6* (Sheldrick, 2015b; molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *PLATON* (Spek, 2020).

Bis{(*Z*)-*N*′-[(*E*)-(furan-2-yl)methylidene]carbamohydrazonothioato}nickel(II) methanol disolvate

Crystal data

$[\mathrm{Ni(C_6H_6N_3OS)_2}]\cdot 2\mathrm{CH_4O}$
$M_r = 459.19$
Triclinic, $P\overline{1}$
$a = 6.5394\ (11)$ Å
$b = 8.9611\ (15)$ Å
$c = 10.2020\ (15)$ Å
$\alpha = 67.965\ (5)°$
$\beta = 79.666\ (6)°$
$\gamma = 70.349\ (6)°$
$V = 520.92\ (15)$ Å^3
$Z = 1$
$F(000) = 238$
$D_x = 1.464$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 2724 reflections
$\theta = 2.7$–$26.4°$
$\mu = 1.16$ mm^{-1}
$T = 296$ K
Prism, orange
0.26 × 0.21 × 0.12 mm

Data collection

Bruker APEXII CCD diffractometer
φ and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2008)
$T_{\min} = 0.735$, $T_{\max} = 0.861$
8497 measured reflections
2134 independent reflections
1633 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.046$
$\theta_{\max} = 26.4°$, $\theta_{\min} = 3.3°$
$h = -8 \rightarrow 8$
$k = -11 \rightarrow 11$
$l = -12 \rightarrow 12$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.088$
$S = 1.03$
2134 reflections
125 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Hydrogen site location: mixed
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0459P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$	$\Delta\rho_{min} = -0.21$ e Å^{-3}
$\Delta\rho_{max} = 0.25$ 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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Ni1	0.500000	0.000000	0.500000	0.03949 (16)
S1	0.21552 (9)	0.08780 (8)	0.37725 (6)	0.0544 (2)
O1	0.8206 (3)	0.4874 (2)	0.41926 (18)	0.0592 (5)
O2	0.7620 (3)	0.3261 (2)	0.05737 (16)	0.0534 (4)
H2O	0.634939	0.350050	0.108389	0.080*
N1	0.5375 (3)	0.2167 (2)	0.39689 (17)	0.0403 (4)
N2	0.4320 (3)	0.3178 (2)	0.27263 (18)	0.0428 (4)
N3	0.1595 (3)	0.3562 (2)	0.1429 (2)	0.0558 (6)
H3A	0.195718	0.448305	0.083360	0.067*
H3B	0.032648	0.349515	0.126510	0.067*
C1	0.6747 (4)	0.4539 (3)	0.3592 (2)	0.0446 (5)
C2	0.8207 (5)	0.6480 (3)	0.3424 (3)	0.0688 (8)
H2	0.905332	0.703098	0.359617	0.083*
C3	0.6847 (5)	0.7162 (3)	0.2396 (3)	0.0679 (8)
H3	0.658018	0.824589	0.173586	0.082*
C4	0.5872 (4)	0.5926 (3)	0.2494 (3)	0.0544 (6)
H4	0.483563	0.604491	0.191646	0.065*
C5	0.6538 (3)	0.2881 (3)	0.4311 (2)	0.0440 (5)
H5	0.732223	0.223902	0.511529	0.053*
C6	0.2750 (3)	0.2665 (3)	0.2568 (2)	0.0415 (5)
C7	0.8122 (6)	0.1616 (4)	0.0563 (3)	0.0883 (10)
H7A	0.683980	0.143664	0.039468	0.132*
H7B	0.864640	0.082516	0.146089	0.132*
H7C	0.922412	0.146101	−0.017494	0.132*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.0337 (2)	0.0371 (3)	0.0388 (2)	−0.01571 (17)	−0.00740 (15)	0.00392 (17)
S1	0.0428 (3)	0.0477 (4)	0.0586 (4)	−0.0248 (3)	−0.0200 (3)	0.0150 (3)
O1	0.0688 (12)	0.0533 (11)	0.0615 (11)	−0.0308 (9)	−0.0191 (8)	−0.0081 (8)
O2	0.0559 (10)	0.0439 (10)	0.0575 (10)	−0.0225 (8)	0.0064 (8)	−0.0116 (7)
N1	0.0346 (9)	0.0423 (10)	0.0352 (9)	−0.0157 (8)	−0.0070 (7)	0.0024 (8)
N2	0.0419 (10)	0.0435 (11)	0.0368 (10)	−0.0213 (8)	−0.0095 (8)	0.0040 (8)
N3	0.0505 (12)	0.0567 (13)	0.0511 (11)	−0.0293 (10)	−0.0223 (9)	0.0121 (10)
C1	0.0482 (13)	0.0444 (13)	0.0435 (12)	−0.0202 (10)	−0.0031 (10)	−0.0114 (11)
C2	0.087 (2)	0.0537 (17)	0.078 (2)	−0.0385 (15)	−0.0121 (16)	−0.0171 (15)

C3	0.095 (2)	0.0426 (15)	0.0671 (18)	−0.0308 (15)	−0.0135 (16)	−0.0068 (13)
C4	0.0675 (16)	0.0402 (14)	0.0540 (15)	−0.0191 (12)	−0.0152 (12)	−0.0063 (12)
C5	0.0457 (12)	0.0435 (13)	0.0366 (12)	−0.0171 (10)	−0.0090 (9)	−0.0005 (10)
C6	0.0350 (11)	0.0408 (12)	0.0391 (12)	−0.0152 (9)	−0.0050 (9)	0.0017 (10)
C7	0.101 (3)	0.0552 (19)	0.111 (3)	−0.0192 (17)	−0.003 (2)	−0.0358 (19)

Geometric parameters (Å, º)

Ni1—N1	1.9055 (17)	N3—H3A	0.8997
Ni1—N1^{i}	1.9055 (17)	N3—H3B	0.9000
Ni1—S1	2.1818 (6)	C1—C4	1.354 (3)
Ni1—S1^{i}	2.1818 (6)	C1—C5	1.431 (3)
S1—C6	1.731 (2)	C2—C3	1.323 (4)
O1—C2	1.357 (3)	C2—H2	0.9300
O1—C1	1.384 (3)	C3—C4	1.419 (3)
O2—C7	1.402 (3)	C3—H3	0.9300
O2—H2O	0.9032	C4—H4	0.9300
N1—C5	1.305 (3)	C5—H5	0.9300
N1—N2	1.391 (2)	C7—H7A	0.9600
N2—C6	1.313 (3)	C7—H7B	0.9600
N3—C6	1.332 (3)	C7—H7C	0.9600

N1—Ni1—N1^{i}	180.0	C3—C2—H2	124.4
N1—Ni1—S1	85.69 (5)	O1—C2—H2	124.4
N1^{i}—Ni1—S1	94.31 (5)	C2—C3—C4	107.0 (2)
N1—Ni1—S1^{i}	94.31 (5)	C2—C3—H3	126.5
N1^{i}—Ni1—S1^{i}	85.69 (5)	C4—C3—H3	126.5
S1—Ni1—S1^{i}	180.0	C1—C4—C3	106.5 (2)
C6—S1—Ni1	95.83 (7)	C1—C4—H4	126.7
C2—O1—C1	106.13 (18)	C3—C4—H4	126.7
C7—O2—H2O	109.2	N1—C5—C1	127.45 (19)
C5—N1—N2	112.86 (16)	N1—C5—H5	116.3
C5—N1—Ni1	126.69 (14)	C1—C5—H5	116.3
N2—N1—Ni1	120.44 (13)	N2—C6—N3	117.99 (17)
C6—N2—N1	112.74 (15)	N2—C6—S1	122.47 (15)
C6—N3—H3A	116.5	N3—C6—S1	119.54 (16)
C6—N3—H3B	127.8	O2—C7—H7A	109.5
H3A—N3—H3B	114.4	O2—C7—H7B	109.5
C4—C1—O1	109.12 (19)	H7A—C7—H7B	109.5
C4—C1—C5	138.1 (2)	O2—C7—H7C	109.5
O1—C1—C5	112.71 (19)	H7A—C7—H7C	109.5
C3—C2—O1	111.2 (2)	H7B—C7—H7C	109.5

C5—N1—N2—C6	−163.93 (19)	N2—N1—C5—C1	2.4 (3)
Ni1—N1—N2—C6	15.0 (2)	Ni1—N1—C5—C1	−176.40 (17)
C2—O1—C1—C4	−0.7 (3)	C4—C1—C5—N1	5.6 (5)
C2—O1—C1—C5	−179.0 (2)	O1—C1—C5—N1	−176.8 (2)
C1—O1—C2—C3	0.3 (3)	N1—N2—C6—N3	178.56 (19)

O1—C2—C3—C4	0.2 (3)	N1—N2—C6—S1	−1.8 (3)
O1—C1—C4—C3	0.8 (3)	Ni1—S1—C6—N2	−8.9 (2)
C5—C1—C4—C3	178.5 (3)	Ni1—S1—C6—N3	170.73 (18)
C2—C3—C4—C1	−0.6 (3)		

Symmetry code: (i) −*x*+1, −*y*, −*z*+1.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2*O*···N2	0.90	1.94	2.788 (3)	156
N3—H3*A*···O2^{ii}	0.90	2.07	2.964 (3)	173
N3—H3*B*···O2^{iii}	0.90	2.12	3.009 (3)	171
C4—H4···N2	0.93	2.51	2.882 (3)	104
C5—H5···S1^{i}	0.93	2.51	3.102 (3)	121

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