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Crystal structure of *cis*-bis[4-phenyl-2-(1,2,3,4-tetrahydronaphthalen-1-ylidene)hydrazinecarbothioamidato-κ^2N^1,S]nickel(II) monohydrate tetrahydrofuran disolvate

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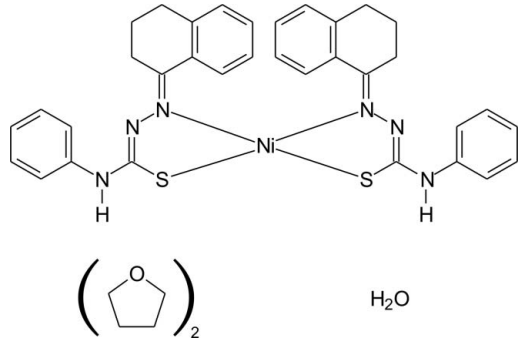
The reaction of Ni^{II} acetate tetrahydrate with the ligand 4-phenyl-2-(1,2,3,4-tetrahydronaphthalen-1-ylidene)hydrazinecarbothioamide in a 2:1 molar ratio yielded the title compound, $[Ni(C_{16}H_{16}N_3S)_2]\cdot 2C_4H_8O\cdot H_2O$. The deprotonated ligands act as *N*,*S*-donors, forming five-membered metallacycles with the metal ion exhibiting a *cis* coordination mode unusual for thiosemicarbazone complexes. The Ni^{II} ion is four-coordinated in a tetrahedrally distorted square-planar geometry. *Trans*-arranged anagostic C—H···Ni interactions are observed. In the crystal, the complex molecules are linked by water molecules through N—H···O and O—H···S hydrogen-bonding interactions into centrosymmetric dimers stacked along the *c* axis, forming rings of graph-set $R_4^4(12)$. Classical O—H···O hydrogen bonds involving the water and tetrahydrofuran solvent molecules as well as weak C—H···π interactions are also present.

1. Chemical context

Thiosemicarbazone ligands are *N*,*S*-donors that show a wide range of coordination modes (Lobana *et al.*, 2009). As a part of our ongoing project on the synthesis and structures of thiosemicarbazone derivatives and their metal complexes, the crystal structure of an Ni^{II} complex of 2-(1,2,3,4-tetrahydronaphthalen-1-ylidene)-4-phenyl-hydrazinecarbothioamide is reported. The crystal structure of the free ligand was published recently by our group (de Oliveira *et al.*, 2014), but one of the first reports on the synthesis of thiosemicarbazone derivatives was done by Freund & Schander (1902). The complex shows a *cis* coordination mode, which is unusual for this ligands, and two *trans*-arranged anagostic interactions between C—H groups and the metal ion are also observed. These interactions are typical for several complexes with catalytic applications (Brookhart *et al.*, 2007).



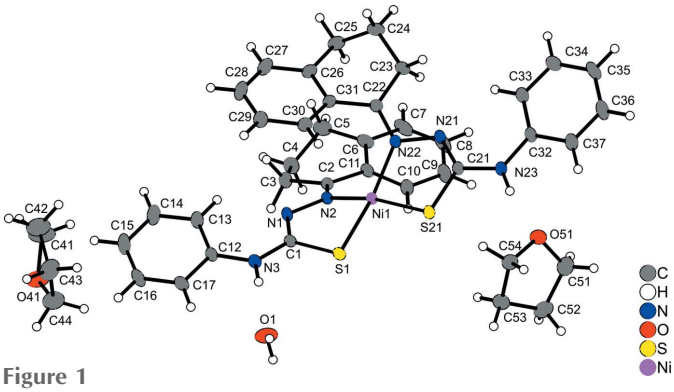


Figure 1
The molecular structure of the title compound with displacement ellipsoids drawn at the 40% probability level.

2. Structural commentary

In the crystal structure of the title compound, the Ni^{II} cation is four-coordinated by two crystallographically independent deprotonated ligands into discrete complexes that are located in general positions (Fig. 1). The metal displays a remarkable tetrahedrally distorted square-planar coordination geometry (maximum displacement 0.5049 (13) Å for atom N2) with the ligands showing an uncommon *cis* N^1,*S*-coordination mode. The values of the Ni—N and N—S bond lengths (Table 1) and N2—Ni1—S21 and N22—Ni1—S1 bond angles [164.04 (5) and 162.63 (4)°, respectively] confirm the distortion from the ideal coordination geometry. In the complex molecule significant structural changes of the N–N–C–S fragment are observed. For the non-coordinating2-(1,2,3,4-tetrahydronaphthalen-1-ylidene)-4-phenyl-hydrazinecarbothioamide ligand, the N—N, N—C and C—S bond lengths amount to 1.385 (2), 1.364 (2) and 1.677 (2) Å. These lengths indicate the double-bond character of the N═N and C═S bonds, and the single-bond character of the N–C bond (de Oliveira *et al.*, 2014). In contrast, in the title complex the acidic hydrogen of the hydrazine fragment is removed and the negative charge is delocalized over the N–N–C–S fragment. Therefore, the N—N, N—C and C—S bond lengths amount to 1.405 (2), 1.304 (2) and 1.757 (2) Å respectively in one ligand and 1.401 (2), 1.298 (3) and 1.761 (2) Å in the other. The N—C bond lengths indicate a considerable double-bond character, while the N—N and C—S bond distances are consistent with an increased single-bond character. It is worth noting that two *trans*-arranged anagostic interactions between aromatic C—H groups and the metal ion are observed (Fig. 2). For a three-centre–two-electron *M*···H—C agostic interaction, the *M*···H distance should range between 1.8 and 2.3 Å and the *M*···H—C angle should range between 90 and 140°. For an anagostic interaction these values should range from 2.3 to 2.9 Å and from 110 to 170°, respectively (Brookhart *et al.*, 2007). The title complex shows Ni1···H30 and Ni1···H10 contacts of 2.61 and 2.45 Å [both values are shorter than the sum of the van der Waals radii for Ni (1.63 Å; Bondi, 1964) and H (1.10 Å; Rowland & Taylor, 1996)], and C30—H30—Ni1 and C10—H10—Ni1 angles of 118 and 121°, in agreement with the presence of anagostic interactions.

Table 1
Selected bond lengths (Å).

Ni1—N2	1.9313 (14)	Ni1—S21	2.1524 (5)
Ni1—N22	1.9417 (14)	Ni1—S1	2.1664 (5)

Table 2
Hydrogen-bond geometry (Å, °).

*Cg*1 and *Cg*2 are the centroids of the C32–C37 and C12–C17 rings, respectively.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H1*N*···O1	0.88	2.06	2.934 (2)	172
N23—H2*N*···O51	0.88	2.02	2.895 (2)	171
O1—H1*O*1···S1^{i}	0.84	2.63	3.4609 (16)	170
O1—H2*O*1···O41^{ii}	0.84	2.00	2.836 (2)	173
C27—H27···*Cg*1^{iii}	0.95	2.80	3.595 (2)	142
C54—H54*B*···*Cg*2^{iv}	0.99	2.67	3.633 (2)	164

Symmetry codes: (i) $-x+2, -y+1, -z+1$; (ii) $-x+2, y-\frac{1}{2}, -z+\frac{1}{2}$; (iii) $x, -y+\frac{3}{2}, z-\frac{1}{2}$; (iv) $x, -y+\frac{1}{2}, z+\frac{1}{2}$.

3. Supramolecular features

The asymmetric unit of the title complex contains one water and two tetrahydrofurane solvate molecules. The water molecules bridge the complex molecules through N—H···O and O—H···S hydrogen bonds (Table 2) into centrosymmetric dimers arranged along the *c* axis, forming rings of graph-set $R_4^4(12)$ (Fig. 3). In addition, classical O—H···O hydrogen

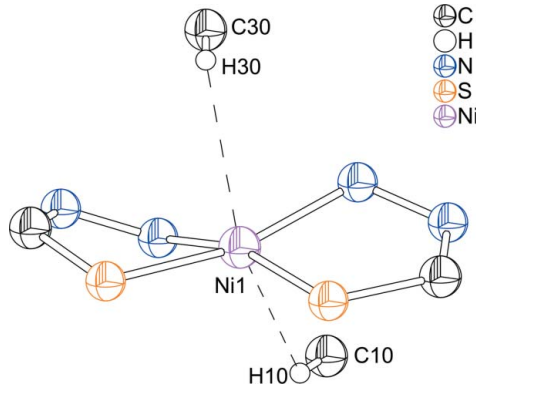


Figure 2
Coordination environment of the metal ion showing the C—H···*M* anagostic interactions (dashed lines).

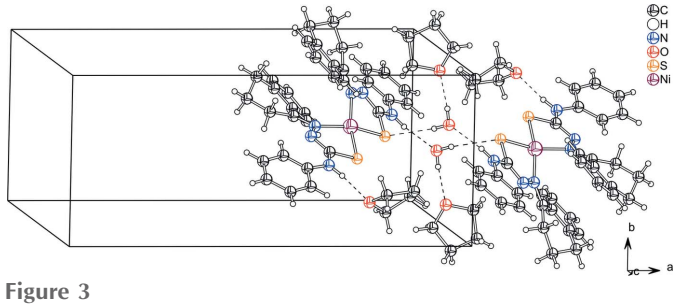


Figure 3
Molecules of the title compound connected through inversion centres *via* pairs of N—H···O and O—H···S interactions. Intermolecular N—H···O and O—H···O hydrogen bonds are also shown. Hydrogen bonds are shown as dashed lines.

Table 3
Experimental details.

Crystal data	
Chemical formula	$[Ni(C_{16}H_{16}N_3S)_2]\cdot 2C_4H_8O\cdot H_2O$
M_r	809.71
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	200
a, b, c (Å)	20.9248 (13), 8.7872 (5), 21.2833 (15)
β (°)	92.841 (8)
V (Å^3)	3908.6 (4)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.65
Crystal size (mm)	0.19 × 0.15 × 0.10
Data collection	
Diffractometer	Stoe *IPDS1*
Absorption correction	Numerical (*X-SHAPE* and *X-RED32*; Stoe & Cie, 2008)
T_{min}, T_{max}	0.787, 0.941
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	40358, 8412, 7107
R_{int}	0.064
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.639
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.038, 0.090, 1.04
No. of reflections	8412
No. of parameters	488
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.32, −0.48

Computer programs: *X-AREA* and *X-RED32* (Stoe & Cie, 2008), *SHELXS97* and *SHELXL97* (Sheldrick, 2008), *DIAMOND* (Brandenburg, 2006) and *publCIF* (Westrip, 2010).

bonds between tetrahydrofurane and water molecules and weak C—H···π interactions are observed (Table 2).

4. Synthesis and crystallization

Starting materials were commercially available and were used without further purification. The synthesis of the ligand was adapted from a procedure reported previously (Freund & Schander, 1902) and its structure is already published (de Oliveira *et al.*, 2014). 2-(1,2,3,4-Tetrahydronaphthalen-1-ylidene)-4-phenyl-hydrazinecarbothioamide was dissolved in THF (2 mmol/40 ml) with stirring maintained for 30 min until the solution turned yellow. At the same time, a solution of nickel acetate tetrahydrate (1 mmol/40 ml) in THF was prepared under continuous stirring. A mixture of both solutions was maintained with stirring at room temperature for 6 h. Crystals suitable for X-ray diffraction were obtained by the slow evaporation of the solvent.

5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. The imine and water H atoms were located in difference Fourier map, and were refined as riding with N—H = 0.88, O—H = 0.84 Å, and with U_{iso}(H) = 1.2 U_{eq}(N) or 1.5 U_{eq}(O). All other H atoms were positioned with idealized geometry and refined using a riding model approximation, with C—H = 0.95-0.99 Å and with U_{iso}(H) = 1.2 U_{eq}(C). An outlier (17 0 20) was omitted in the last cycles of refinement.

Acknowledgements

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Crystal structure of *cis*-bis[4-phenyl-2-(1,2,3,4-tetrahydronaphthalen-1-ylidene)hydrazinecarbothioamidato-κ^2N^1,S]nickel(II) monohydrate tetrahydrofuran disolvate

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Computing details

Data collection: *X-AREA* (Stoe & Cie, 2008); cell refinement: *X-AREA* (Stoe & Cie, 2008); data reduction: *X-RED32* (Stoe & Cie, 2008); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010).

cis-Bis[4-phenyl-2-(1,2,3,4-tetrahydronaphthalen-1-ylidene)hydrazinecarbothioamidato-κ^2N^1,S]nickel(II) monohydrate tetrahydrofuran disolvate

Crystal data

$[Ni(C_{16}H_{16}N_3S)_2]\cdot 2C_4H_8O\cdot H_2O$
$M_r = 809.71$
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a = 20.9248\ (13)$ Å
$b = 8.7872\ (5)$ Å
$c = 21.2833\ (15)$ Å
$\beta = 92.841\ (8)°$
$V = 3908.6\ (4)$ Å^3
$Z = 4$
$F(000) = 1712$
$D_x = 1.376$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 40358 reflections
$\theta = 2.5–27.0°$
$\mu = 0.65$ mm^{-1}
$T = 200$ K
Prism, red
0.19 × 0.15 × 0.10 mm

Data collection

Stoe IPDS-1 diffractometer
Radiation source: fine-focus sealed tube, Stoe IPDS-1
Graphite monochromator
φ scans
Absorption correction: numerical (*X-SHAPE* and *X-RED32*; Stoe & Cie, 2008)
$T_{min} = 0.787$, $T_{max} = 0.941$
40358 measured reflections
8412 independent reflections
7107 reflections with $I > 2\sigma(I)$
$R_{int} = 0.064$
$\theta_{max} = 27.0°$, $\theta_{min} = 2.5°$
$h = -26\rightarrow26$
$k = -11\rightarrow11$
$l = -27\rightarrow27$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.090$
$S = 1.04$
8412 reflections
488 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

$w = 1/[\sigma^2(F_o^2) + (0.0495P)^2 + 1.531P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.32$ e Å^{-3}
$\Delta\rho_{min} = -0.48$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0043 (6)

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 $F^2 > \sigma(F^2)$ 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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Ni1	0.763345 (10)	0.57702 (2)	0.542635 (10)	0.01599 (8)
S1	0.85498 (2)	0.51110 (5)	0.50807 (2)	0.02150 (10)
C1	0.84794 (8)	0.63429 (18)	0.44282 (8)	0.0176 (3)
N1	0.80744 (7)	0.74626 (15)	0.43901 (6)	0.0193 (3)
N2	0.77215 (7)	0.75911 (15)	0.49300 (6)	0.0176 (3)
C2	0.74873 (8)	0.89550 (17)	0.50036 (8)	0.0176 (3)
C3	0.75309 (9)	1.01216 (19)	0.44862 (8)	0.0239 (4)
H3A	0.7289	0.9747	0.4106	0.029*
H3B	0.7984	1.0230	0.4381	0.029*
C4	0.72730 (9)	1.16776 (19)	0.46591 (9)	0.0272 (4)
H4A	0.7214	1.2308	0.4275	0.033*
H4B	0.7585	1.2197	0.4950	0.033*
C5	0.66362 (10)	1.1516 (2)	0.49709 (10)	0.0312 (4)
H5A	0.6470	1.2536	0.5076	0.037*
H5B	0.6320	1.1016	0.4677	0.037*
C6	0.67272 (9)	1.05810 (19)	0.55612 (9)	0.0249 (4)
C7	0.64126 (10)	1.0929 (2)	0.61052 (11)	0.0339 (5)
H7	0.6105	1.1724	0.6094	0.041*
C8	0.65380 (11)	1.0144 (2)	0.66589 (11)	0.0380 (5)
H8	0.6306	1.0376	0.7019	0.046*
C9	0.70038 (11)	0.9014 (2)	0.66901 (10)	0.0334 (4)
H9	0.7103	0.8502	0.7076	0.040*
C10	0.73221 (9)	0.8639 (2)	0.61548 (8)	0.0249 (4)
H10	0.7646	0.7880	0.6177	0.030*
C11	0.71703 (8)	0.93683 (18)	0.55811 (8)	0.0204 (3)
N3	0.88815 (7)	0.60673 (16)	0.39553 (7)	0.0219 (3)
H1N	0.9185	0.5384	0.4020	0.026*
C12	0.88886 (8)	0.67796 (19)	0.33607 (8)	0.0208 (3)

C13	0.84043 (10)	0.7741 (2)	0.31185 (9)	0.0281 (4)
H13	0.8049	0.7976	0.3362	0.034*
C14	0.84464 (12)	0.8354 (2)	0.25151 (9)	0.0358 (5)
H14	0.8116	0.9004	0.2351	0.043*
C15	0.89587 (12)	0.8032 (2)	0.21546 (10)	0.0384 (5)
H15	0.8985	0.8465	0.1748	0.046*
C16	0.94352 (10)	0.7069 (3)	0.23938 (9)	0.0358 (5)
H16	0.9787	0.6832	0.2146	0.043*
C17	0.94061 (9)	0.6444 (2)	0.29920 (9)	0.0273 (4)
H17	0.9738	0.5790	0.3150	0.033*
S21	0.77040 (2)	0.40904 (5)	0.61626 (2)	0.02150 (10)
C21	0.69687 (8)	0.45636 (18)	0.64762 (8)	0.0189 (3)
N21	0.65424 (7)	0.54193 (16)	0.61843 (7)	0.0214 (3)
N22	0.67275 (7)	0.58376 (15)	0.55827 (6)	0.0179 (3)
C22	0.62487 (8)	0.63338 (18)	0.52238 (8)	0.0185 (3)
C23	0.56144 (8)	0.6663 (2)	0.55078 (9)	0.0265 (4)
H23A	0.5686	0.7398	0.5857	0.032*
H23B	0.5451	0.5710	0.5689	0.032*
C24	0.51066 (9)	0.7303 (2)	0.50437 (10)	0.0314 (4)
H24A	0.4914	0.6466	0.4787	0.038*
H24B	0.4763	0.7789	0.5276	0.038*
C25	0.54023 (9)	0.8468 (2)	0.46163 (10)	0.0298 (4)
H25A	0.5068	0.8908	0.4325	0.036*
H25B	0.5599	0.9303	0.4871	0.036*
C26	0.59041 (9)	0.7688 (2)	0.42476 (9)	0.0244 (4)
C27	0.59580 (11)	0.7956 (2)	0.36072 (9)	0.0350 (4)
H27	0.5691	0.8697	0.3402	0.042*
C28	0.63934 (11)	0.7161 (3)	0.32660 (9)	0.0376 (5)
H28	0.6429	0.7375	0.2832	0.045*
C29	0.67788 (10)	0.6050 (2)	0.35546 (9)	0.0306 (4)
H29	0.7070	0.5487	0.3317	0.037*
C30	0.67348 (9)	0.57702 (19)	0.41940 (9)	0.0233 (4)
H30	0.6994	0.5005	0.4392	0.028*
C31	0.63103 (8)	0.66085 (18)	0.45479 (8)	0.0195 (3)
N23	0.68631 (7)	0.39556 (17)	0.70534 (7)	0.0229 (3)
H2N	0.7178	0.3384	0.7209	0.027*
C32	0.62840 (9)	0.38489 (19)	0.73636 (8)	0.0221 (3)
C33	0.57121 (9)	0.4550 (2)	0.71649 (9)	0.0285 (4)
H33	0.5697	0.5192	0.6806	0.034*
C34	0.51621 (10)	0.4305 (2)	0.74952 (10)	0.0339 (4)
H34	0.4772	0.4776	0.7354	0.041*
C35	0.51734 (10)	0.3391 (2)	0.80225 (10)	0.0356 (5)
H35	0.4795	0.3227	0.8242	0.043*
C36	0.57417 (11)	0.2718 (2)	0.82274 (10)	0.0357 (5)
H36	0.5755	0.2098	0.8594	0.043*
C37	0.62939 (10)	0.2937 (2)	0.79037 (9)	0.0298 (4)
H37	0.6682	0.2464	0.8050	0.036*
O1	0.99770 (7)	0.40290 (16)	0.41952 (8)	0.0417 (4)

H1O1	1.0309	0.4309	0.4401	0.062*
H2O1	1.0030	0.3084	0.4169	0.062*
O41	0.97593 (8)	0.58636 (16)	0.08169 (9)	0.0448 (4)
C41	0.90931 (12)	0.5585 (3)	0.07052 (16)	0.0538 (7)
H41A	0.8912	0.6291	0.0381	0.065*
H41B	0.8864	0.5735	0.1097	0.065*
C42	0.90244 (13)	0.3977 (3)	0.04853 (15)	0.0531 (7)
H42A	0.8981	0.3930	0.0020	0.064*
H42B	0.8645	0.3492	0.0661	0.064*
C43	0.96318 (13)	0.3203 (3)	0.07266 (12)	0.0455 (6)
H43A	0.9842	0.2683	0.0380	0.055*
H43B	0.9540	0.2443	0.1053	0.055*
C44	1.00526 (12)	0.4463 (2)	0.10005 (13)	0.0448 (6)
H44A	1.0089	0.4382	0.1465	0.054*
H44B	1.0487	0.4394	0.0838	0.054*
O51	0.78020 (7)	0.19400 (17)	0.76536 (7)	0.0344 (3)
C51	0.81446 (12)	0.2516 (3)	0.82019 (11)	0.0467 (6)
H51A	0.8107	0.1802	0.8558	0.056*
H51B	0.7967	0.3512	0.8323	0.056*
C52	0.88412 (11)	0.2691 (3)	0.80450 (11)	0.0408 (5)
H52A	0.9120	0.2021	0.8314	0.049*
H52B	0.8985	0.3758	0.8103	0.049*
C53	0.88546 (10)	0.2222 (2)	0.73570 (10)	0.0347 (4)
H53A	0.8835	0.3122	0.7077	0.042*
H53B	0.9245	0.1630	0.7278	0.042*
C54	0.82624 (9)	0.1255 (2)	0.72640 (10)	0.0297 (4)
H54A	0.8106	0.1259	0.6817	0.036*
H54B	0.8351	0.0192	0.7395	0.036*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.01618 (12)	0.01577 (11)	0.01627 (11)	0.00208 (7)	0.00338 (8)	0.00228 (7)
S1	0.0184 (2)	0.0223 (2)	0.0243 (2)	0.00532 (15)	0.00491 (16)	0.00550 (15)
C1	0.0171 (8)	0.0168 (7)	0.0191 (7)	−0.0003 (6)	0.0028 (6)	−0.0024 (6)
N1	0.0229 (7)	0.0191 (6)	0.0164 (6)	0.0042 (5)	0.0067 (6)	−0.0001 (5)
N2	0.0176 (7)	0.0197 (6)	0.0157 (6)	0.0022 (5)	0.0035 (5)	−0.0018 (5)
C2	0.0175 (8)	0.0163 (7)	0.0189 (8)	0.0006 (6)	0.0019 (6)	−0.0006 (6)
C3	0.0301 (9)	0.0188 (8)	0.0234 (8)	0.0055 (7)	0.0056 (7)	0.0026 (6)
C4	0.0326 (10)	0.0158 (8)	0.0335 (10)	0.0048 (7)	0.0065 (8)	0.0019 (7)
C5	0.0275 (10)	0.0212 (8)	0.0451 (11)	0.0079 (7)	0.0031 (9)	−0.0016 (8)
C6	0.0211 (9)	0.0185 (8)	0.0358 (10)	−0.0011 (6)	0.0064 (8)	−0.0077 (7)
C7	0.0285 (10)	0.0273 (9)	0.0473 (12)	−0.0029 (7)	0.0167 (9)	−0.0147 (8)
C8	0.0411 (12)	0.0367 (11)	0.0384 (11)	−0.0119 (9)	0.0229 (10)	−0.0165 (9)
C9	0.0423 (12)	0.0348 (10)	0.0242 (9)	−0.0111 (8)	0.0117 (9)	−0.0071 (8)
C10	0.0308 (10)	0.0237 (8)	0.0204 (8)	−0.0057 (7)	0.0049 (7)	−0.0052 (7)
C11	0.0209 (8)	0.0191 (7)	0.0217 (8)	−0.0034 (6)	0.0062 (7)	−0.0051 (6)
N3	0.0213 (7)	0.0228 (7)	0.0220 (7)	0.0063 (6)	0.0054 (6)	−0.0005 (6)

C12	0.0224 (8)	0.0216 (8)	0.0187 (8)	−0.0039 (6)	0.0055 (7)	−0.0036 (6)
C13	0.0348 (10)	0.0295 (9)	0.0205 (8)	0.0045 (8)	0.0073 (8)	0.0007 (7)
C14	0.0518 (13)	0.0330 (10)	0.0229 (9)	0.0043 (9)	0.0053 (9)	0.0045 (8)
C15	0.0557 (14)	0.0387 (11)	0.0217 (9)	−0.0103 (10)	0.0102 (9)	0.0022 (8)
C16	0.0345 (11)	0.0485 (12)	0.0258 (10)	−0.0151 (9)	0.0146 (8)	−0.0088 (9)
C17	0.0224 (9)	0.0340 (9)	0.0261 (9)	−0.0048 (7)	0.0068 (7)	−0.0081 (7)
S21	0.0219 (2)	0.0233 (2)	0.0197 (2)	0.00565 (15)	0.00496 (16)	0.00627 (15)
C21	0.0214 (8)	0.0183 (7)	0.0171 (7)	−0.0010 (6)	0.0026 (6)	0.0006 (6)
N21	0.0214 (7)	0.0243 (7)	0.0189 (7)	0.0009 (6)	0.0060 (6)	0.0042 (5)
N22	0.0197 (7)	0.0178 (6)	0.0164 (6)	0.0016 (5)	0.0029 (5)	0.0011 (5)
C22	0.0192 (8)	0.0160 (7)	0.0204 (8)	0.0006 (6)	0.0022 (6)	−0.0015 (6)
C23	0.0189 (8)	0.0323 (9)	0.0288 (9)	0.0031 (7)	0.0042 (7)	0.0005 (7)
C24	0.0186 (9)	0.0361 (10)	0.0394 (11)	0.0043 (7)	0.0004 (8)	−0.0007 (8)
C25	0.0258 (10)	0.0294 (9)	0.0338 (10)	0.0105 (7)	−0.0030 (8)	0.0006 (8)
C26	0.0239 (9)	0.0239 (8)	0.0250 (9)	0.0041 (7)	−0.0035 (7)	−0.0011 (7)
C27	0.0404 (12)	0.0388 (11)	0.0251 (9)	0.0109 (9)	−0.0056 (8)	0.0050 (8)
C28	0.0486 (13)	0.0465 (12)	0.0175 (9)	0.0073 (10)	−0.0003 (8)	0.0013 (8)
C29	0.0337 (11)	0.0358 (10)	0.0225 (9)	0.0028 (8)	0.0034 (8)	−0.0079 (7)
C30	0.0245 (9)	0.0214 (8)	0.0238 (8)	0.0026 (7)	−0.0004 (7)	−0.0041 (6)
C31	0.0196 (8)	0.0192 (7)	0.0194 (8)	0.0008 (6)	−0.0015 (6)	−0.0029 (6)
N23	0.0228 (8)	0.0277 (7)	0.0185 (7)	0.0042 (6)	0.0039 (6)	0.0058 (6)
C32	0.0261 (9)	0.0223 (8)	0.0183 (8)	−0.0021 (6)	0.0064 (7)	−0.0010 (6)
C33	0.0273 (10)	0.0348 (10)	0.0238 (9)	0.0009 (8)	0.0056 (8)	0.0047 (7)
C34	0.0248 (10)	0.0429 (11)	0.0343 (11)	−0.0005 (8)	0.0068 (8)	0.0019 (8)
C35	0.0335 (11)	0.0394 (11)	0.0355 (11)	−0.0082 (9)	0.0170 (9)	0.0019 (9)
C36	0.0443 (12)	0.0347 (10)	0.0294 (10)	−0.0021 (9)	0.0153 (9)	0.0080 (8)
C37	0.0347 (11)	0.0301 (9)	0.0252 (9)	0.0038 (8)	0.0077 (8)	0.0063 (7)
O1	0.0317 (8)	0.0309 (7)	0.0613 (11)	0.0075 (6)	−0.0092 (7)	−0.0028 (7)
O41	0.0357 (9)	0.0262 (7)	0.0711 (12)	−0.0026 (6)	−0.0108 (8)	0.0095 (7)
C41	0.0352 (13)	0.0342 (11)	0.090 (2)	0.0029 (9)	−0.0133 (13)	−0.0017 (12)
C42	0.0458 (14)	0.0434 (13)	0.0685 (18)	−0.0082 (11)	−0.0121 (13)	−0.0022 (12)
C43	0.0606 (16)	0.0306 (10)	0.0443 (13)	0.0010 (10)	−0.0074 (11)	−0.0035 (9)
C44	0.0422 (13)	0.0310 (10)	0.0602 (15)	0.0027 (9)	−0.0069 (11)	0.0046 (10)
O51	0.0256 (7)	0.0425 (8)	0.0351 (8)	0.0066 (6)	0.0017 (6)	0.0013 (6)
C51	0.0449 (14)	0.0643 (15)	0.0309 (11)	0.0098 (12)	0.0022 (10)	−0.0047 (11)
C52	0.0393 (12)	0.0409 (11)	0.0409 (12)	0.0005 (9)	−0.0103 (10)	−0.0025 (9)
C53	0.0279 (10)	0.0370 (11)	0.0395 (11)	0.0015 (8)	0.0039 (9)	0.0030 (9)
C54	0.0296 (10)	0.0266 (9)	0.0329 (10)	0.0055 (7)	0.0006 (8)	0.0016 (7)

Geometric parameters (Å, º)

Ni1—N2	1.9313 (14)	C24—H24B	0.9900
Ni1—N22	1.9417 (14)	C25—C26	1.506 (3)
Ni1—S21	2.1524 (5)	C25—H25A	0.9900
Ni1—S1	2.1664 (5)	C25—H25B	0.9900
S1—C1	1.7612 (17)	C26—C27	1.393 (3)
C1—N1	1.298 (2)	C26—C31	1.406 (2)
C1—N3	1.365 (2)	C27—C28	1.382 (3)

N1—N2	1.4008 (18)	C27—H27	0.9500
N2—C2	1.307 (2)	C28—C29	1.390 (3)
C2—C11	1.471 (2)	C28—H28	0.9500
C2—C3	1.511 (2)	C29—C30	1.390 (3)
C3—C4	1.522 (2)	C29—H29	0.9500
C3—H3A	0.9900	C30—C31	1.402 (2)
C3—H3B	0.9900	C30—H30	0.9500
C4—C5	1.524 (3)	N23—C32	1.412 (2)
C4—H4A	0.9900	N23—H2N	0.8800
C4—H4B	0.9900	C32—C33	1.393 (3)
C5—C6	1.505 (3)	C32—C37	1.401 (2)
C5—H5A	0.9900	C33—C34	1.395 (3)
C5—H5B	0.9900	C33—H33	0.9500
C6—C7	1.394 (3)	C34—C35	1.379 (3)
C6—C11	1.412 (2)	C34—H34	0.9500
C7—C8	1.379 (3)	C35—C36	1.379 (3)
C7—H7	0.9500	C35—H35	0.9500
C8—C9	1.390 (3)	C36—C37	1.388 (3)
C8—H8	0.9500	C36—H36	0.9500
C9—C10	1.388 (3)	C37—H37	0.9500
C9—H9	0.9500	O1—H1O1	0.8400
C10—C11	1.401 (3)	O1—H2O1	0.8397
C10—H10	0.9500	O41—C44	1.422 (3)
N3—C12	1.413 (2)	O41—C41	1.424 (3)
N3—H1N	0.8798	C41—C42	1.493 (3)
C12—C13	1.398 (3)	C41—H41A	0.9900
C12—C17	1.400 (2)	C41—H41B	0.9900
C13—C14	1.400 (3)	C42—C43	1.509 (4)
C13—H13	0.9500	C42—H42A	0.9900
C14—C15	1.378 (3)	C42—H42B	0.9900
C14—H14	0.9500	C43—C44	1.513 (3)
C15—C16	1.386 (3)	C43—H43A	0.9900
C15—H15	0.9500	C43—H43B	0.9900
C16—C17	1.391 (3)	C44—H44A	0.9900
C16—H16	0.9500	C44—H44B	0.9900
C17—H17	0.9500	O51—C51	1.431 (3)
S21—C21	1.7571 (17)	O51—C54	1.434 (2)
C21—N21	1.301 (2)	C51—C52	1.519 (3)
C21—N23	1.368 (2)	C51—H51A	0.9900
N21—N22	1.4050 (19)	C51—H51B	0.9900
N22—C22	1.304 (2)	C52—C53	1.523 (3)
C22—C31	1.470 (2)	C52—H52A	0.9900
C22—C23	1.513 (2)	C52—H52B	0.9900
C23—C24	1.522 (3)	C53—C54	1.508 (3)
C23—H23A	0.9900	C53—H53A	0.9900
C23—H23B	0.9900	C53—H53B	0.9900
C24—C25	1.521 (3)	C54—H54A	0.9900
C24—H24A	0.9900	C54—H54B	0.9900

N2—Ni1—N22	100.89 (6)	C26—C25—C24	108.67 (15)
N2—Ni1—S21	164.04 (5)	C26—C25—H25A	110.0
N22—Ni1—S21	85.90 (4)	C24—C25—H25A	110.0
N2—Ni1—S1	85.74 (4)	C26—C25—H25B	110.0
N22—Ni1—S1	162.63 (4)	C24—C25—H25B	110.0
S21—Ni1—S1	91.944 (18)	H25A—C25—H25B	108.3
C1—S1—Ni1	93.59 (5)	C27—C26—C31	118.83 (17)
N1—C1—N3	120.84 (15)	C27—C26—C25	121.67 (17)
N1—C1—S1	122.94 (12)	C31—C26—C25	119.43 (16)
N3—C1—S1	116.22 (12)	C28—C27—C26	121.06 (18)
C1—N1—N2	112.26 (13)	C28—C27—H27	119.5
C2—N2—N1	112.85 (13)	C26—C27—H27	119.5
C2—N2—Ni1	130.35 (11)	C27—C28—C29	120.40 (18)
N1—N2—Ni1	116.77 (10)	C27—C28—H28	119.8
N2—C2—C11	120.93 (14)	C29—C28—H28	119.8
N2—C2—C3	119.88 (14)	C28—C29—C30	119.46 (18)
C11—C2—C3	119.19 (14)	C28—C29—H29	120.3
C2—C3—C4	113.48 (14)	C30—C29—H29	120.3
C2—C3—H3A	108.9	C29—C30—C31	120.48 (17)
C4—C3—H3A	108.9	C29—C30—H30	119.8
C2—C3—H3B	108.9	C31—C30—H30	119.8
C4—C3—H3B	108.9	C30—C31—C26	119.68 (16)
H3A—C3—H3B	107.7	C30—C31—C22	121.87 (15)
C3—C4—C5	110.47 (15)	C26—C31—C22	118.36 (15)
C3—C4—H4A	109.6	C21—N23—C32	128.82 (16)
C5—C4—H4A	109.6	C21—N23—H2N	114.1
C3—C4—H4B	109.6	C32—N23—H2N	115.6
C5—C4—H4B	109.6	C33—C32—C37	118.67 (17)
H4A—C4—H4B	108.1	C33—C32—N23	124.97 (16)
C6—C5—C4	109.69 (16)	C37—C32—N23	116.34 (17)
C6—C5—H5A	109.7	C32—C33—C34	119.79 (18)
C4—C5—H5A	109.7	C32—C33—H33	120.1
C6—C5—H5B	109.7	C34—C33—H33	120.1
C4—C5—H5B	109.7	C35—C34—C33	121.2 (2)
H5A—C5—H5B	108.2	C35—C34—H34	119.4
C7—C6—C11	118.49 (18)	C33—C34—H34	119.4
C7—C6—C5	121.87 (17)	C34—C35—C36	119.13 (18)
C11—C6—C5	119.53 (16)	C34—C35—H35	120.4
C8—C7—C6	121.49 (19)	C36—C35—H35	120.4
C8—C7—H7	119.3	C35—C36—C37	120.63 (19)
C6—C7—H7	119.3	C35—C36—H36	119.7
C7—C8—C9	120.08 (18)	C37—C36—H36	119.7
C7—C8—H8	120.0	C36—C37—C32	120.52 (19)
C9—C8—H8	120.0	C36—C37—H37	119.7
C10—C9—C8	119.6 (2)	C32—C37—H37	119.7
C10—C9—H9	120.2	H1O1—O1—H2O1	102.5
C8—C9—H9	120.2	C44—O41—C41	107.61 (17)

C9—C10—C11	120.61 (18)	O41—C41—C42	107.1 (2)
C9—C10—H10	119.7	O41—C41—H41A	110.3
C11—C10—H10	119.7	C42—C41—H41A	110.3
C10—C11—C6	119.45 (16)	O41—C41—H41B	110.3
C10—C11—C2	121.53 (15)	C42—C41—H41B	110.3
C6—C11—C2	118.94 (16)	H41A—C41—H41B	108.6
C1—N3—C12	128.03 (15)	C41—C42—C43	104.7 (2)
C1—N3—H1N	118.2	C41—C42—H42A	110.8
C12—N3—H1N	113.8	C43—C42—H42A	110.8
C13—C12—C17	119.16 (17)	C41—C42—H42B	110.8
C13—C12—N3	123.95 (15)	C43—C42—H42B	110.8
C17—C12—N3	116.85 (16)	H42A—C42—H42B	108.9
C12—C13—C14	119.57 (18)	C42—C43—C44	105.43 (19)
C12—C13—H13	120.2	C42—C43—H43A	110.7
C14—C13—H13	120.2	C44—C43—H43A	110.7
C15—C14—C13	121.2 (2)	C42—C43—H43B	110.7
C15—C14—H14	119.4	C44—C43—H43B	110.7
C13—C14—H14	119.4	H43A—C43—H43B	108.8
C14—C15—C16	119.09 (19)	O41—C44—C43	107.00 (19)
C14—C15—H15	120.5	O41—C44—H44A	110.3
C16—C15—H15	120.5	C43—C44—H44A	110.3
C15—C16—C17	120.95 (18)	O41—C44—H44B	110.3
C15—C16—H16	119.5	C43—C44—H44B	110.3
C17—C16—H16	119.5	H44A—C44—H44B	108.6
C16—C17—C12	120.02 (19)	C51—O51—C54	107.23 (16)
C16—C17—H17	120.0	O51—C51—C52	107.68 (18)
C12—C17—H17	120.0	O51—C51—H51A	110.2
C21—S21—Ni1	94.84 (6)	C52—C51—H51A	110.2
N21—C21—N23	121.14 (15)	O51—C51—H51B	110.2
N21—C21—S21	123.24 (13)	C52—C51—H51B	110.2
N23—C21—S21	115.61 (13)	H51A—C51—H51B	108.5
C21—N21—N22	111.90 (14)	C51—C52—C53	104.34 (18)
C22—N22—N21	112.50 (14)	C51—C52—H52A	110.9
C22—N22—Ni1	129.64 (12)	C53—C52—H52A	110.9
N21—N22—Ni1	117.63 (11)	C51—C52—H52B	110.9
N22—C22—C31	121.71 (15)	C53—C52—H52B	110.9
N22—C22—C23	119.56 (15)	H52A—C52—H52B	108.9
C31—C22—C23	118.72 (15)	C54—C53—C52	102.98 (17)
C22—C23—C24	114.16 (15)	C54—C53—H53A	111.2
C22—C23—H23A	108.7	C52—C53—H53A	111.2
C24—C23—H23A	108.7	C54—C53—H53B	111.2
C22—C23—H23B	108.7	C52—C53—H53B	111.2
C24—C23—H23B	108.7	H53A—C53—H53B	109.1
H23A—C23—H23B	107.6	O51—C54—C53	105.00 (16)
C25—C24—C23	110.19 (16)	O51—C54—H54A	110.7
C25—C24—H24A	109.6	C53—C54—H54A	110.7
C23—C24—H24A	109.6	O51—C54—H54B	110.7
C25—C24—H24B	109.6	C53—C54—H54B	110.7

C23—C24—H24B	109.6	H54A—C54—H54B	108.8
H24A—C24—H24B	108.1		

Hydrogen-bond geometry (Å, º)

*Cg*1 and *Cg*2 are the centroids of the C32–C37 and C12–C17 rings, respectively.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H1*N*···O1	0.88	2.06	2.934 (2)	172
N23—H2*N*···O51	0.88	2.02	2.895 (2)	171
O1—H1*O*1···S1^{i}	0.84	2.63	3.4609 (16)	170
O1—H2*O*1···O41^{ii}	0.84	2.00	2.836 (2)	173
C27—H27···*Cg*1^{iii}	0.95	2.80	3.595 (2)	142
C54—H54*B*···*Cg*2^{iv}	0.99	2.67	3.633 (2)	164

Symmetry codes: (i) −*x*+2, −*y*+1, −*z*+1; (ii) −*x*+2, *y*−1/2, −*z*+1/2; (iii) *x*, −*y*+3/2, *z*−1/2; (iv) *x*, −*y*+1/2, *z*+1/2.