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[1-(2-Oxidobenzylidene)-4-phenylthiosemicarbazonato-κ^3S,N^1,O](pyridine-κN)nickel(II)

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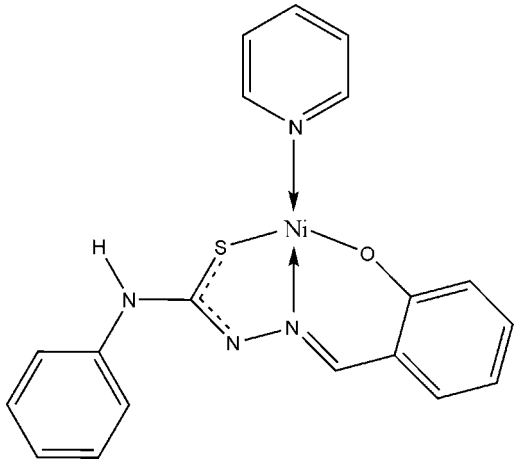
Key indicators: single-crystal X-ray study; T = 295 K; mean σ(C–C) = 0.011 Å; R factor = 0.037; wR factor = 0.089; data-to-parameter ratio = 15.5.

In the title complex, $[Ni(C_{14}H_{11}N_3OS)(C_5H_5N)]$, the Ni^{II} atom is *N*,*O*,*S*-chelated by the deprotonated salicylaldimine-4-phenylthiosemicarbazide dianion and is also coordinated by a pyridine molecule, the coordinating atoms giving rise to a square-planar geometry for the Ni atom. The asymmetric unit contains two molecules. The mononuclear units are linked into a chain structure along the *b* axis by intermolecular N—H···S hydrogen bonds and weak π–π stacking interactions between the pyridine rings [centroid–centroid = 3.758 (3) Å].

Related literature

For other metal derivatives of *N*-salicylaldimine-4-phenylthiosemicarbazide, see: Milanesio *et al.* (2000) for vanadium, Prabhakaran *et al.* (2005) and Soriano-García *et al.* (1985) for nickel, Naik *et al.* (2003) and Thomas *et al.* (2004) for copper, Deng *et al.* (2007) for zinc.



Experimental

Crystal data

$[Ni(C_{14}H_{11}N_3OS)(C_5H_5N)]$
M_r = 407.13
Monoclinic, *Pc*
a = 5.7294 (11) Å
b = 12.924 (3) Å
c = 23.683 (5) Å
β = 95.64 (3)°
V = 1745.2 (6) Å^3
Z = 4
Mo *K*α radiation
μ = 1.25 mm^{-1}
T = 295 (2) K
0.35 × 0.24 × 0.17 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
T_{min} = 0.669, T_{max} = 0.816
16815 measured reflections
7370 independent reflections
4892 reflections with $I > 2\sigma(I)$
R_{int} = 0.044

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.089
S = 1.06
7370 reflections
475 parameters
4 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.60 e Å^{-3}
$\Delta\rho_{min}$ = −0.57 e Å^{-3}
Absolute structure: Flack (1983), with 3366 Friedel pairs
Flack parameter: 0.029 (17)

Table 1
Selected geometric parameters (Å, °).

Ni1—N1	1.849 (4)	Ni2—N5	1.845 (4)
Ni1—O1	1.859 (4)	Ni2—O2	1.863 (4)
Ni1—N4	1.909 (4)	Ni2—N8	1.911 (4)
Ni1—S1	2.1547 (15)	Ni2—S2	2.1507 (15)
N1—Ni1—O1	95.77 (17)	N5—Ni2—O2	95.19 (17)
N1—Ni1—N4	177.51 (19)	N5—Ni2—N8	178.16 (19)
O1—Ni1—N4	85.93 (17)	O2—Ni2—N8	85.50 (17)
N1—Ni1—S1	87.31 (14)	N5—Ni2—S2	87.57 (13)
O1—Ni1—S1	175.83 (13)	O2—Ni2—S2	176.29 (13)
N4—Ni1—S1	91.08 (13)	N8—Ni2—S2	91.81 (14)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3*N*···S2^{i}	0.86 (4)	2.77 (4)	3.605 (4)	163 (5)
N7—H7*N*···S1^{ii}	0.86 (4)	2.80 (2)	3.627 (4)	161 (5)

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

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NG2284).

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supplementary materials

Acta Cryst. (2007). E**63**, m1961-m1962 [**doi:10.1107/S1600536807029698**]

[1-(2-Oxidobenzylidene)-4-phenylthiosemicarbazonato-κ^3S,N^1,O](pyridine-κN)nickel(II)

Z.-Y. Cao, Z.-P. Deng and S. Gao

Comment

Up to now, a number of metal complexes of *N*-salicyldimine-4-phenylthiosemicarbazide have been synthesized, and most of them are mononuclear (Milanesio *et al.*, 2000; Prabhakaran *et al.*, 2005; Soriano-García *et al.*, 1985; Naik *et al.*, 2003; Thomas *et al.*, 2004). Recently, a dinuclear complex has been reported (Deng *et al.*, 2007). In these complexs, the hydrazone ligand chelates in a terdentate manner. In the title mononuclear complex, [Ni($C_{14}H_{11}N_3OS$)(C_5H_5N)], the ligand binds in a similar mode. As shown in Fig. 1, the Ni^{II} atom is N,*O*,*S*-chelated by deprotonated salicylaldimine-4-phenylthiosemicarbazide dianion. It is also coordinated by pyridine molecule, and a square planar geometry results. The mononuclear units are linked into a chain structure along *b* axis by N—H···S intermolecular hydrogen bonds and weak π-π stacking interactions between the pyridine rings [centroid···centroid = 3.758 (3) Å] (Fig. 2).

Experimental

N-salicldimine-4-phenylthiosemicarbazone ligand was synthesized by condensing salicylaldehyde with 4-phenylthiosemicarbazide in ethonal for 2.5 h, and the hydrazone ligand was isolated as yellow crystals from the resulting solution. The title compound was prepared by the addition of nickel(II) acetate tetrahydrate (1 mmol) and pyridine (1 ml) to a methanol solution (15 ml) of the ligand (1 mmol). The mixture was refluxed for 1 h, cooled slowly to room temperature and filtered. Red-brown crystals were isolated from the solution after three days. Analysis calculated for $C_{19}H_{16}N_4OSNi$: C 56.06, H 3.96, N 13.76%; found: C 56.01, H 3.94, N 13.79%.

Refinement

C-bound H atoms were placed in calculated positions, with C—H = 0.93 and U_{iso}(H) = 1.2U_{eq}(C), and were included in the refinement in the riding-model approximation. H atoms on the N atoms were located in Fourier difference maps and refined with the restraints N—H = 0.86 (1) Å, and with U_{iso}(H) = 1.2U_{eq}(N). The Flack parameter was refined from 3366 Friedel paris.

Figures

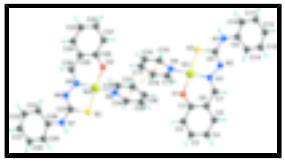

Fig. 1. **Figure 1**. A view of complex (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

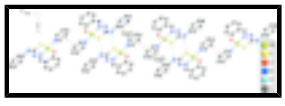

Fig. 2. **Figure 2**. The chain structure of (I), viewed along the *b* axis. Green dashed lines indicate N–H···S hydrogen bonds. H atoms not involved in hydrogen bonding have been omitted. *Cg*1 and *Cg*2 represent the centroids of adjacent pyridine rings, as defined in the comment.

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Crystal data

$[Ni(C_{14}H_{11}N_3OS)(C_5H_5N)]$	F_{000} = 840
M_r = 407.13	D_x = 1.550 Mg m^{-3}
Monoclinic, *Pc*	Mo *K*α radiation λ = 0.71073 Å
Hall symbol: P -2yc	Cell parameters from 11939 reflections
a = 5.7294 (11) Å	θ = 3.0–27.5º
b = 12.924 (3) Å	μ = 1.25 mm^{-1}
c = 23.683 (5) Å	*T* = 295 (2) K
β = 95.64 (3)º	Prism, colorless
V = 1745.2 (6) Å^3	0.35 × 0.24 × 0.17 mm
Z = 4	

Data collection

Rigaku R-AXIS RAPID diffractometer	7370 independent reflections
Radiation source: fine-focus sealed tube	4892 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.044
Detector resolution: 10.000 pixels mm^{-1}	θ_{max} = 27.5º
T = 295(2) K	θ_{min} = 3.0º
ω scans	*h* = −6→7
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)	*k* = −16→16
T_{min} = 0.669, T_{max} = 0.816	*l* = −30→30
16815 measured reflections	

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)]$ = 0.037	$w = 1/[\sigma^2(F_o^2) + (0.022P)^2 + 0.9787P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2)$ = 0.089	$(\Delta/\sigma)_{max}$ = 0.001
S = 1.06	$\Delta\rho_{max}$ = 0.60 e Å^{-3}
7370 reflections	$\Delta\rho_{min}$ = −0.57 e Å^{-3}
475 parameters	Extinction correction: none
4 restraints	Absolute structure: Flack (1983), with 3366 Friedel pairs
Primary atom site location: structure-invariant direct methods	Flack parameter: 0.029 (17)
Secondary atom site location: difference Fourier map	

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Ni1	0.42415 (9)	0.92246 (4)	0.75792 (3)	0.03968 (16)
Ni2	0.30864 (10)	0.32924 (4)	0.63710 (3)	0.03927 (16)
S1	0.1296 (2)	1.01932 (11)	0.72961 (6)	0.0479 (4)
S2	0.6011 (3)	0.23095 (11)	0.66440 (6)	0.0486 (4)
O1	0.6638 (8)	0.8306 (2)	0.78157 (17)	0.0491 (11)
O2	0.0683 (7)	0.4217 (2)	0.61431 (17)	0.0479 (11)
N1	0.5015 (8)	1.0198 (3)	0.81387 (19)	0.0399 (10)
N2	0.3641 (8)	1.1071 (3)	0.8204 (2)	0.0444 (11)
N3	0.0183 (8)	1.1876 (4)	0.78621 (19)	0.0464 (11)
H3N	−0.096 (6)	1.185 (4)	0.7596 (16)	0.056*
N4	0.3432 (8)	0.8267 (3)	0.69777 (19)	0.0372 (11)
N5	0.2299 (7)	0.2349 (3)	0.57989 (19)	0.0381 (10)
N6	0.3675 (8)	0.1466 (3)	0.57220 (19)	0.0451 (11)
N7	0.7084 (8)	0.0632 (4)	0.60734 (18)	0.0464 (11)
H7N	0.825 (6)	0.066 (4)	0.6330 (17)	0.056*
N8	0.3873 (8)	0.4238 (3)	0.69807 (19)	0.0380 (11)
C1	0.8281 (16)	0.8445 (6)	0.8244 (4)	0.0414 (19)
C2	0.995 (2)	0.7658 (7)	0.8368 (4)	0.057 (3)
H2	0.9801	0.7038	0.8169	0.069*
C3	1.176 (2)	0.7786 (8)	0.8771 (4)	0.062 (3)
H3	1.2856	0.7256	0.8826	0.075*
C4	1.2076 (16)	0.8661 (7)	0.9108 (4)	0.054 (2)
H4	1.3329	0.8726	0.9387	0.065*
C5	1.0409 (13)	0.9432 (6)	0.9004 (3)	0.053 (2)
H5	1.0548	1.0034	0.9220	0.064*
C6	0.8511 (12)	0.9335 (5)	0.8582 (3)	0.0424 (16)
C7	0.6850 (9)	1.0158 (4)	0.8509 (2)	0.0404 (12)
H7	0.7103	1.0723	0.8750	0.049*
C8	0.1818 (9)	1.1111 (4)	0.7833 (2)	0.0390 (12)
C9	0.0002 (17)	1.2640 (6)	0.8284 (4)	0.041 (2)
C10	−0.2062 (17)	1.3186 (6)	0.8283 (5)	0.051 (2)
H10	−0.3307	1.3035	0.8014	0.062*
C11	−0.2306 (14)	1.3955 (5)	0.8679 (3)	0.0557 (19)
H11	−0.3713	1.4315	0.8670	0.067*
C12	−0.0527 (15)	1.4192 (6)	0.9080 (4)	0.057 (2)
H12	−0.0701	1.4715	0.9342	0.068*
C13	0.1552 (17)	1.3640 (7)	0.9090 (5)	0.061 (3)
H13	0.2778	1.3783	0.9366	0.074*
C14	0.1808 (17)	1.2872 (6)	0.8688 (4)	0.047 (2)
H14	0.3217	1.2513	0.8694	0.056*
C15	0.4957 (11)	0.8095 (4)	0.6593 (3)	0.0456 (14)
H15	0.6289	0.8508	0.6602	0.055*
C16	0.4640 (11)	0.7341 (4)	0.6189 (2)	0.0508 (15)
H16	0.5721	0.7253	0.5925	0.061*
C17	0.2700 (11)	0.6712 (5)	0.6180 (2)	0.0537 (14)

H17	0.2463	0.6180	0.5916	0.064*
C18	0.1127 (10)	0.6887 (4)	0.6568 (2)	0.0484 (14)
H18	−0.0200	0.6473	0.6571	0.058*
C19	0.1518 (10)	0.7674 (4)	0.6951 (2)	0.0459 (13)
H19	0.0405	0.7802	0.7202	0.055*
C20	−0.0943 (17)	0.4123 (6)	0.5718 (4)	0.0416 (19)
C21	−0.2597 (18)	0.4920 (7)	0.5611 (4)	0.050 (2)
H21	−0.2470	0.5516	0.5832	0.059*
C22	−0.4421 (19)	0.4834 (7)	0.5179 (4)	0.059 (3)
H22	−0.5520	0.5361	0.5115	0.071*
C23	−0.4570 (17)	0.3963 (8)	0.4851 (5)	0.061 (3)
H23	−0.5804	0.3898	0.4567	0.074*
C24	−0.2986 (14)	0.3196 (6)	0.4926 (3)	0.052 (2)
H24	−0.3117	0.2624	0.4687	0.062*
C25	−0.1122 (12)	0.3246 (5)	0.5364 (3)	0.0417 (17)
C26	0.0501 (9)	0.2410 (4)	0.5421 (2)	0.0439 (13)
H26	0.0254	0.1862	0.5168	0.053*
C27	0.5462 (10)	0.1413 (4)	0.6101 (2)	0.0403 (13)
C28	0.7199 (17)	−0.0134 (6)	0.5662 (4)	0.0381 (19)
C29	0.9279 (18)	−0.0694 (6)	0.5667 (4)	0.047 (2)
H29	1.0531	−0.0532	0.5933	0.057*
C30	0.9513 (14)	−0.1482 (6)	0.5287 (3)	0.057 (2)
H30	1.0917	−0.1845	0.5298	0.069*
C31	0.7675 (15)	−0.1739 (6)	0.4886 (4)	0.052 (2)
H31	0.7825	−0.2272	0.4628	0.062*
C32	0.5649 (16)	−0.1191 (6)	0.4881 (4)	0.051 (2)
H32	0.4408	−0.1366	0.4616	0.061*
C33	0.5341 (17)	−0.0390 (6)	0.5250 (4)	0.045 (2)
H33	0.3936	−0.0026	0.5229	0.054*
C34	0.5814 (9)	0.4822 (4)	0.7015 (2)	0.0435 (13)
H34	0.6953	0.4691	0.6770	0.052*
C35	0.6158 (11)	0.5614 (5)	0.7404 (2)	0.0534 (15)
H35	0.7476	0.6035	0.7407	0.064*
C36	0.4544 (11)	0.5779 (5)	0.7788 (2)	0.0548 (14)
H36	0.4754	0.6311	0.8053	0.066*
C37	0.2619 (11)	0.5145 (4)	0.7774 (2)	0.0509 (15)
H37	0.1531	0.5223	0.8038	0.061*
C38	0.2330 (11)	0.4391 (4)	0.7362 (2)	0.0443 (14)
H38	0.1008	0.3971	0.7349	0.053*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.0444 (4)	0.0343 (3)	0.0392 (4)	0.0006 (3)	−0.0018 (3)	−0.0047 (3)
Ni2	0.0437 (4)	0.0347 (3)	0.0380 (4)	0.0012 (3)	−0.0026 (3)	−0.0043 (3)
S1	0.0541 (9)	0.0433 (7)	0.0433 (8)	0.0063 (7)	−0.0103 (7)	−0.0090 (6)
S2	0.0550 (9)	0.0426 (7)	0.0452 (9)	0.0087 (7)	−0.0105 (7)	−0.0087 (7)
O1	0.057 (3)	0.043 (2)	0.044 (3)	0.0073 (17)	−0.007 (2)	−0.0095 (16)

O2	0.053 (3)	0.040 (2)	0.048 (3)	0.0083 (17)	−0.010 (2)	−0.0123 (16)
N1	0.043 (3)	0.036 (2)	0.041 (3)	0.002 (2)	0.000 (2)	0.000 (2)
N2	0.044 (3)	0.033 (2)	0.054 (3)	0.011 (2)	−0.009 (2)	−0.007 (2)
N3	0.048 (3)	0.043 (3)	0.045 (3)	0.009 (2)	−0.012 (2)	−0.005 (2)
N4	0.038 (3)	0.034 (2)	0.039 (3)	0.0015 (19)	0.001 (2)	−0.0015 (19)
N5	0.038 (3)	0.031 (2)	0.044 (3)	0.0033 (19)	−0.001 (2)	−0.0020 (19)
N6	0.049 (3)	0.037 (2)	0.048 (3)	0.008 (2)	−0.001 (2)	−0.008 (2)
N7	0.046 (3)	0.046 (3)	0.043 (3)	0.009 (2)	−0.014 (2)	−0.009 (2)
N8	0.043 (3)	0.035 (2)	0.036 (3)	0.002 (2)	0.002 (2)	−0.0005 (19)
C1	0.039 (4)	0.044 (4)	0.041 (4)	0.009 (3)	−0.001 (3)	0.009 (3)
C2	0.075 (7)	0.051 (5)	0.044 (5)	0.019 (4)	−0.004 (4)	−0.013 (4)
C3	0.072 (6)	0.068 (5)	0.045 (5)	0.034 (4)	−0.004 (4)	0.005 (4)
C4	0.047 (4)	0.071 (5)	0.042 (5)	0.014 (4)	−0.008 (4)	−0.006 (4)
C5	0.048 (4)	0.060 (4)	0.049 (4)	0.004 (3)	−0.009 (4)	−0.005 (3)
C6	0.044 (4)	0.042 (3)	0.040 (4)	0.002 (3)	0.001 (3)	−0.003 (3)
C7	0.038 (3)	0.041 (3)	0.041 (3)	0.000 (2)	−0.005 (2)	−0.007 (2)
C8	0.045 (3)	0.032 (3)	0.039 (3)	0.006 (2)	−0.002 (2)	0.003 (2)
C9	0.049 (5)	0.036 (4)	0.036 (4)	−0.001 (3)	0.001 (3)	0.000 (3)
C10	0.037 (4)	0.053 (4)	0.061 (5)	0.012 (3)	−0.007 (4)	0.003 (4)
C11	0.053 (5)	0.056 (4)	0.060 (5)	0.015 (4)	0.011 (4)	0.003 (4)
C12	0.062 (6)	0.052 (4)	0.059 (5)	0.007 (4)	0.017 (4)	−0.008 (3)
C13	0.063 (6)	0.062 (5)	0.058 (6)	−0.005 (4)	0.002 (5)	−0.022 (4)
C14	0.046 (4)	0.046 (4)	0.047 (5)	0.013 (3)	−0.002 (3)	−0.005 (3)
C15	0.043 (4)	0.045 (3)	0.049 (4)	0.002 (3)	0.005 (3)	0.003 (3)
C16	0.062 (4)	0.048 (3)	0.042 (3)	0.015 (3)	0.007 (3)	−0.004 (3)
C17	0.068 (4)	0.042 (3)	0.049 (3)	0.006 (3)	−0.007 (3)	−0.008 (3)
C18	0.054 (3)	0.044 (3)	0.047 (3)	−0.010 (3)	0.003 (3)	−0.009 (3)
C19	0.049 (3)	0.046 (3)	0.042 (3)	−0.001 (3)	0.004 (3)	−0.005 (3)
C20	0.054 (5)	0.043 (3)	0.027 (3)	0.000 (3)	0.000 (3)	−0.003 (3)
C21	0.059 (6)	0.045 (4)	0.043 (4)	0.020 (4)	−0.005 (4)	0.000 (3)
C22	0.066 (6)	0.064 (5)	0.045 (5)	0.025 (4)	−0.009 (4)	−0.002 (4)
C23	0.052 (4)	0.076 (6)	0.052 (5)	0.018 (4)	−0.018 (4)	−0.009 (4)
C24	0.052 (5)	0.057 (4)	0.044 (4)	0.009 (3)	−0.013 (3)	−0.015 (3)
C25	0.043 (4)	0.043 (3)	0.038 (4)	0.007 (3)	0.001 (3)	0.000 (3)
C26	0.046 (3)	0.040 (3)	0.043 (3)	−0.002 (2)	−0.006 (3)	−0.007 (2)
C27	0.046 (3)	0.036 (3)	0.037 (3)	0.003 (2)	−0.004 (2)	0.000 (2)
C28	0.045 (4)	0.030 (3)	0.040 (4)	0.005 (3)	0.007 (3)	0.006 (3)
C29	0.049 (4)	0.049 (4)	0.044 (4)	0.003 (3)	0.003 (3)	−0.007 (4)
C30	0.056 (5)	0.059 (5)	0.057 (5)	0.020 (4)	0.005 (4)	0.001 (4)
C31	0.070 (6)	0.044 (4)	0.043 (4)	0.010 (3)	0.010 (4)	−0.006 (3)
C32	0.052 (5)	0.054 (5)	0.043 (5)	0.012 (4)	−0.009 (4)	−0.010 (4)
C33	0.037 (4)	0.045 (4)	0.052 (5)	0.002 (3)	−0.004 (3)	−0.008 (4)
C34	0.044 (3)	0.048 (3)	0.038 (3)	−0.003 (3)	0.002 (2)	−0.004 (3)
C35	0.055 (4)	0.053 (4)	0.051 (3)	−0.005 (3)	−0.002 (3)	−0.003 (3)
C36	0.067 (4)	0.044 (3)	0.051 (4)	0.009 (3)	−0.004 (3)	−0.014 (3)
C37	0.057 (4)	0.053 (3)	0.044 (3)	0.008 (3)	0.012 (3)	0.002 (3)
C38	0.045 (4)	0.045 (3)	0.042 (3)	−0.003 (3)	0.000 (3)	0.002 (3)

Geometric parameters (Å, °)

Ni1—N1	1.849 (4)	C12—C13	1.387 (12)
Ni1—O1	1.859 (4)	C12—H12	0.9300
Ni1—N4	1.909 (4)	C13—C14	1.394 (12)
Ni1—S1	2.1547 (15)	C13—H13	0.9300
Ni2—N5	1.845 (4)	C14—H14	0.9300
Ni2—O2	1.863 (4)	C15—C16	1.366 (8)
Ni2—N8	1.911 (4)	C15—H15	0.9300
Ni2—S2	2.1507 (15)	C16—C17	1.375 (8)
S1—C8	1.744 (5)	C16—H16	0.9300
S2—C27	1.736 (5)	C17—C18	1.367 (8)
O1—C1	1.327 (10)	C17—H17	0.9300
O2—C20	1.308 (10)	C18—C19	1.367 (7)
N1—C7	1.302 (6)	C18—H18	0.9300
N1—N2	1.393 (6)	C19—H19	0.9300
N2—C8	1.297 (6)	C20—C21	1.406 (12)
N3—C8	1.368 (7)	C20—C25	1.407 (11)
N3—C9	1.415 (10)	C21—C22	1.392 (11)
N3—H3N	0.86 (4)	C21—H21	0.9300
N4—C19	1.334 (6)	C22—C23	1.366 (13)
N4—C15	1.341 (7)	C22—H22	0.9300
N5—C26	1.298 (6)	C23—C24	1.343 (12)
N5—N6	1.410 (5)	C23—H23	0.9300
N6—C27	1.295 (6)	C24—C25	1.415 (10)
N7—C27	1.378 (7)	C24—H24	0.9300
N7—C28	1.397 (10)	C25—C26	1.424 (8)
N7—H7N	0.86 (4)	C26—H26	0.9300
N8—C38	1.340 (7)	C28—C29	1.393 (13)
N8—C34	1.340 (6)	C28—C33	1.410 (11)
C1—C6	1.400 (11)	C29—C30	1.375 (12)
C1—C2	1.406 (12)	C29—H29	0.9300
C2—C3	1.348 (12)	C30—C31	1.386 (11)
C2—H2	0.9300	C30—H30	0.9300
C3—C4	1.386 (13)	C31—C32	1.359 (12)
C3—H3	0.9300	C31—H31	0.9300
C4—C5	1.386 (12)	C32—C33	1.377 (12)
C4—H4	0.9300	C32—H32	0.9300
C5—C6	1.409 (10)	C33—H33	0.9300
C5—H5	0.9300	C34—C35	1.379 (7)
C6—C7	1.426 (8)	C34—H34	0.9300
C7—H7	0.9300	C35—C36	1.376 (8)
C9—C14	1.372 (11)	C35—H35	0.9300
C9—C10	1.377 (13)	C36—C37	1.371 (8)
C10—C11	1.382 (12)	C36—H36	0.9300
C10—H10	0.9300	C37—C38	1.378 (8)
C11—C12	1.358 (11)	C37—H37	0.9300
C11—H11	0.9300	C38—H38	0.9300

N1—Ni1—O1	95.77 (17)	C9—C14—C13	120.6 (10)
N1—Ni1—N4	177.51 (19)	C9—C14—H14	119.7
O1—Ni1—N4	85.93 (17)	C13—C14—H14	119.7
N1—Ni1—S1	87.31 (14)	N4—C15—C16	122.9 (5)
O1—Ni1—S1	175.83 (13)	N4—C15—H15	118.5
N4—Ni1—S1	91.08 (13)	C16—C15—H15	118.5
N5—Ni2—O2	95.19 (17)	C15—C16—C17	119.0 (6)
N5—Ni2—N8	178.16 (19)	C15—C16—H16	120.5
O2—Ni2—N8	85.50 (17)	C17—C16—H16	120.5
N5—Ni2—S2	87.57 (13)	C18—C17—C16	118.5 (5)
O2—Ni2—S2	176.29 (13)	C18—C17—H17	120.8
N8—Ni2—S2	91.81 (14)	C16—C17—H17	120.8
C8—S1—Ni1	95.46 (18)	C19—C18—C17	119.5 (6)
C27—S2—Ni2	95.30 (18)	C19—C18—H18	120.2
C1—O1—Ni1	126.3 (4)	C17—C18—H18	120.2
C20—O2—Ni2	127.8 (4)	N4—C19—C18	122.7 (5)
C7—N1—N2	112.7 (4)	N4—C19—H19	118.7
C7—N1—Ni1	125.2 (4)	C18—C19—H19	118.7
N2—N1—Ni1	122.1 (3)	O2—C20—C21	119.2 (7)
C8—N2—N1	112.6 (4)	O2—C20—C25	122.6 (8)
C8—N3—C9	129.6 (5)	C21—C20—C25	118.3 (8)
C8—N3—H3N	114 (4)	C22—C21—C20	121.2 (9)
C9—N3—H3N	116 (4)	C22—C21—H21	119.4
C19—N4—C15	117.4 (5)	C20—C21—H21	119.4
C19—N4—Ni1	123.1 (4)	C23—C22—C21	118.9 (9)
C15—N4—Ni1	119.1 (4)	C23—C22—H22	120.5
C26—N5—N6	112.1 (4)	C21—C22—H22	120.5
C26—N5—Ni2	125.9 (4)	C24—C23—C22	121.9 (10)
N6—N5—Ni2	122.0 (3)	C24—C23—H23	119.0
C27—N6—N5	111.5 (4)	C22—C23—H23	119.0
C27—N7—C28	129.1 (5)	C23—C24—C25	121.0 (8)
C27—N7—H7N	115 (4)	C23—C24—H24	119.5
C28—N7—H7N	116 (4)	C25—C24—H24	119.5
C38—N8—C34	118.3 (5)	C20—C25—C24	118.6 (7)
C38—N8—Ni2	118.8 (4)	C20—C25—C26	123.1 (7)
C34—N8—Ni2	122.6 (4)	C24—C25—C26	118.3 (6)
O1—C1—C6	124.6 (7)	N5—C26—C25	125.3 (5)
O1—C1—C2	118.6 (8)	N5—C26—H26	117.4
C6—C1—C2	116.8 (8)	C25—C26—H26	117.4
C3—C2—C1	121.2 (9)	N6—C27—N7	119.8 (5)
C3—C2—H2	119.4	N6—C27—S2	123.5 (4)
C1—C2—H2	119.4	N7—C27—S2	116.7 (4)
C2—C3—C4	123.8 (10)	C29—C28—N7	117.4 (8)
C2—C3—H3	118.1	C29—C28—C33	118.2 (9)
C4—C3—H3	118.1	N7—C28—C33	124.4 (8)
C5—C4—C3	115.8 (9)	C30—C29—C28	121.1 (9)
C5—C4—H4	122.1	C30—C29—H29	119.5
C3—C4—H4	122.1	C28—C29—H29	119.5
C4—C5—C6	122.2 (8)	C29—C30—C31	120.7 (8)

C4—C5—H5	118.9	C29—C30—H30	119.7
C6—C5—H5	118.9	C31—C30—H30	119.7
C1—C6—C5	120.1 (7)	C32—C31—C30	118.1 (8)
C1—C6—C7	121.3 (7)	C32—C31—H31	121.0
C5—C6—C7	118.6 (6)	C30—C31—H31	121.0
N1—C7—C6	126.6 (5)	C31—C32—C33	123.3 (9)
N1—C7—H7	116.7	C31—C32—H32	118.3
C6—C7—H7	116.7	C33—C32—H32	118.3
N2—C8—N3	120.3 (5)	C32—C33—C28	118.7 (9)
N2—C8—S1	122.4 (4)	C32—C33—H33	120.7
N3—C8—S1	117.3 (4)	C28—C33—H33	120.7
C14—C9—C10	118.5 (9)	N8—C34—C35	121.4 (5)
C14—C9—N3	122.8 (9)	N8—C34—H34	119.3
C10—C9—N3	118.7 (8)	C35—C34—H34	119.3
C9—C10—C11	120.8 (9)	C36—C35—C34	119.7 (6)
C9—C10—H10	119.6	C36—C35—H35	120.1
C11—C10—H10	119.6	C34—C35—H35	120.1
C12—C11—C10	121.2 (8)	C37—C36—C35	118.9 (5)
C12—C11—H11	119.4	C37—C36—H36	120.6
C10—C11—H11	119.4	C35—C36—H36	120.6
C11—C12—C13	118.7 (8)	C36—C37—C38	118.7 (6)
C11—C12—H12	120.7	C36—C37—H37	120.7
C13—C12—H12	120.7	C38—C37—H37	120.7
C12—C13—C14	120.2 (10)	N8—C38—C37	122.8 (5)
C12—C13—H13	119.9	N8—C38—H38	118.6
C14—C13—H13	119.9	C37—C38—H38	118.6
N1—Ni1—S1—C8	−3.0 (2)	C9—C10—C11—C12	−0.3 (13)
N4—Ni1—S1—C8	178.9 (2)	C10—C11—C12—C13	−0.6 (13)
N5—Ni2—S2—C27	2.4 (2)	C11—C12—C13—C14	1.2 (14)
N8—Ni2—S2—C27	−179.4 (2)	C10—C9—C14—C13	0.2 (15)
N1—Ni1—O1—C1	−2.1 (6)	N3—C9—C14—C13	179.3 (8)
N4—Ni1—O1—C1	176.1 (6)	C12—C13—C14—C9	−1.1 (15)
N5—Ni2—O2—C20	1.4 (6)	C19—N4—C15—C16	−1.0 (8)
N8—Ni2—O2—C20	−176.9 (6)	Ni1—N4—C15—C16	172.3 (4)
O1—Ni1—N1—C7	5.3 (5)	N4—C15—C16—C17	−1.3 (8)
S1—Ni1—N1—C7	−177.5 (5)	C15—C16—C17—C18	1.7 (8)
O1—Ni1—N1—N2	−174.8 (4)	C16—C17—C18—C19	0.0 (9)
S1—Ni1—N1—N2	2.3 (4)	C15—N4—C19—C18	2.9 (8)
C7—N1—N2—C8	179.8 (5)	Ni1—N4—C19—C18	−170.1 (4)
Ni1—N1—N2—C8	−0.1 (6)	C17—C18—C19—N4	−2.4 (8)
O1—Ni1—N4—C19	108.6 (4)	Ni2—O2—C20—C21	−179.2 (7)
S1—Ni1—N4—C19	−68.5 (4)	Ni2—O2—C20—C25	1.4 (12)
O1—Ni1—N4—C15	−64.3 (4)	O2—C20—C21—C22	−177.1 (9)
S1—Ni1—N4—C15	118.6 (4)	C25—C20—C21—C22	2.4 (15)
O2—Ni2—N5—C26	−3.7 (5)	C20—C21—C22—C23	−1.0 (17)
S2—Ni2—N5—C26	178.8 (5)	C21—C22—C23—C24	−1.2 (17)
O2—Ni2—N5—N6	175.2 (4)	C22—C23—C24—C25	2.0 (16)
S2—Ni2—N5—N6	−2.4 (4)	O2—C20—C25—C24	177.9 (8)
C26—N5—N6—C27	180.0 (5)	C21—C20—C25—C24	−1.6 (12)

Ni2—N5—N6—C27	1.0 (6)	O2—C20—C25—C26	−2.8 (12)
O2—Ni2—N8—C38	64.2 (4)	C21—C20—C25—C26	177.8 (8)
S2—Ni2—N8—C38	−118.3 (4)	C23—C24—C25—C20	−0.6 (13)
O2—Ni2—N8—C34	−109.7 (4)	C23—C24—C25—C26	−179.9 (8)
S2—Ni2—N8—C34	67.8 (4)	N6—N5—C26—C25	−175.6 (5)
Ni1—O1—C1—C6	−2.1 (12)	Ni2—N5—C26—C25	3.4 (9)
Ni1—O1—C1—C2	179.2 (7)	C20—C25—C26—N5	0.3 (11)
O1—C1—C2—C3	175.1 (10)	C24—C25—C26—N5	179.6 (6)
C6—C1—C2—C3	−3.8 (16)	N5—N6—C27—N7	−176.3 (4)
C1—C2—C3—C4	2.9 (19)	N5—N6—C27—S2	1.7 (7)
C2—C3—C4—C5	−0.9 (17)	C28—N7—C27—N6	3.9 (10)
C3—C4—C5—C6	−0.1 (14)	C28—N7—C27—S2	−174.2 (6)
O1—C1—C6—C5	−175.9 (8)	Ni2—S2—C27—N6	−3.0 (5)
C2—C1—C6—C5	2.8 (12)	Ni2—S2—C27—N7	175.1 (4)
O1—C1—C6—C7	4.2 (12)	C27—N7—C28—C29	166.5 (7)
C2—C1—C6—C7	−177.0 (8)	C27—N7—C28—C33	−14.8 (13)
C4—C5—C6—C1	−1.0 (13)	N7—C28—C29—C30	178.1 (7)
C4—C5—C6—C7	178.9 (7)	C33—C28—C29—C30	−0.6 (13)
N2—N1—C7—C6	175.4 (5)	C28—C29—C30—C31	0.0 (13)
Ni1—N1—C7—C6	−4.7 (9)	C29—C30—C31—C32	0.1 (12)
C1—C6—C7—N1	−0.6 (11)	C30—C31—C32—C33	0.5 (14)
C5—C6—C7—N1	179.5 (6)	C31—C32—C33—C28	−1.2 (15)
N1—N2—C8—N3	175.1 (4)	C29—C28—C33—C32	1.2 (14)
N1—N2—C8—S1	−3.3 (7)	N7—C28—C33—C32	−177.5 (8)
C9—N3—C8—N2	−6.5 (10)	C38—N8—C34—C35	−4.6 (7)
C9—N3—C8—S1	171.9 (6)	Ni2—N8—C34—C35	169.4 (4)
Ni1—S1—C8—N2	4.3 (5)	N8—C34—C35—C36	3.5 (8)
Ni1—S1—C8—N3	−174.1 (4)	C34—C35—C36—C37	0.1 (9)
C8—N3—C9—C14	14.8 (13)	C35—C36—C37—C38	−2.4 (9)
C8—N3—C9—C10	−166.2 (7)	C34—N8—C38—C37	2.2 (8)
C14—C9—C10—C11	0.4 (14)	Ni2—N8—C38—C37	−172.0 (4)
N3—C9—C10—C11	−178.6 (7)	C36—C37—C38—N8	1.3 (8)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3N···S2^{i}	0.86 (4)	2.77 (4)	3.605 (4)	163 (5)
N7—H7N···S1^{ii}	0.86 (4)	2.80 (2)	3.627 (4)	161 (5)

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

Fig. 1

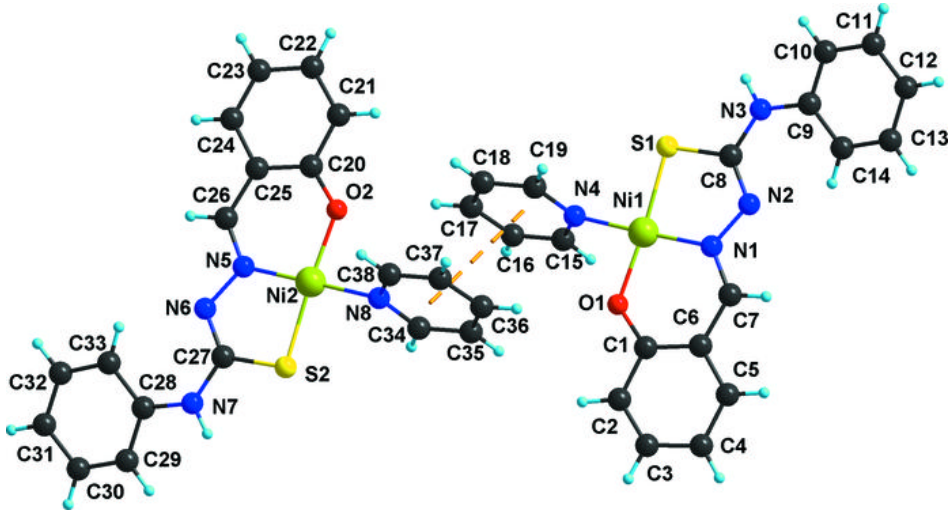
C22
C23
C21
C24
C20
C26
C25
O2
N5
Ni2
N6
C27
S2
C33
C32
C28
N7
C31
C29
C30
C37
C38
N8
C34
C36
C35
C18
C19
N4
C17
C16
C15
S1
Ni1
C8
N2
N1
O1
C6
C7
C1
C5
C2
C4
C3
C11
C10
C12
N3
C9
C13
C14

Fig. 2