metal-organic compounds

[1-(5-Bromo-2-oxidobenzylidene)thio-semicarbazidato-κ^3O,N^1,S](pyridine-κN)nickel(II)

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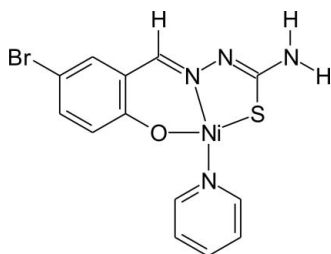Correspondence e-mail: adriano@daad-alumni.de

The reaction of 5-bromosalicylaldehyde thiosemicarbazone with nickel acetate tetrahydrate and pyridine yielded the title compound, [Ni(C$_8$H$_6$BrN$_3$OS)(C$_5$H$_5$N)]. The Ni^{II} atom is four-coordinated in a square-planar environment by one deprotonated dianionic thiosemicarbazone ligand, acting in a tridentate chelating mode through N, O and S atoms forming two metalla-rings, and by one pyridine molecule. The complex molecules are linked into dimers by pairs of centrosymmetrical N—H···N interactions. In addition, molecules are connected through intermolecular Br···Br interactions [3.545 (1) Å], forming chains along the b-axis direction.

Related literature

For the synthesis of 5-bromosalicylaldehyde thiosemicarbazones and for the antibacterial activity of their complexes, see: Joseph *et al.* (2010). For the crystal structure of 5-bromo-salicylaldehyde thiosemicarbazone, see: Kargar *et al.* (2010). For the crystal structure of an Ni^{II} complex with a similar coordination environment, see: Güveli *et al.* (2009). For the coordination chemistry of thiosemicarbazone derivatives, see: Lobana *et al.* (2009).

Experimental

Crystal data

[Ni(C$_8$H$_6$BrN$_3$OS)(C$_5$H$_5$N)]	V = 1447.46 (8) Å^3
M_r = 409.94	Z = 4
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
a = 12.2447 (4) Å	μ = 4.25 mm^{-1}
b = 4.1135 (1) Å	T = 293 K
c = 31.1380 (11) Å	0.93 × 0.10 × 0.05 mm
β = 112.646 (1)°	

Data collection

Nonius KappaCCD diffractometer	13946 measured reflections
Absorption correction: multi-scan (Blessing, 1995)	3224 independent reflections
T_{min} = 0.443, T_{max} = 0.830	2697 reflections with $I > 2\sigma(I)$
	R_{int} = 0.051

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.031	190 parameters
$wR(F^2)$ = 0.083	H-atom parameters constrained
S = 1.05	$\Delta\rho_{max}$ = 0.61 e Å^{-3}
3224 reflections	$\Delta\rho_{min}$ = −0.66 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N3—H1···N2^i	0.78	2.31	3.095 (3)	178

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

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; 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).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: ZL2486).

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supplementary materials

[1-(5-Bromo-2-oxidobenzylidene)thiosemicarbazidato-*κ*³*O*,*N*¹,*S*](pyridine-*κN*)nickel(II)

Fernanda Rosi Soares Pederzolli, Leandro Bresolin, Johannes Beck, Jörg Daniels and Adriano Bof de Oliveira

Comment

Thiosemicarbazone derivatives have a wide range of applications in biological inorganic chemistry and a very interesting coordination chemistry (Lobana *et al.*, 2009). For example, Cu^{II} and Ni^{II} complexes with 5-bromosalicylaldehyde thiosemicarbazone show antibacterial activity against *Staphylococcus aureus* and *Escherichia coli* (Joseph *et al.*, 2010). As part of our study of thiosemicarbazone derivatives, we report herein the synthesis and the crystal structure of a new Ni^{II} complex with 5-bromosalicylaldehyde thiosemicarbazone. In the title compound, in which the molecular structure unit matches the asymmetric unit, the Ni^{II} ion is coordinated in a square planar environment by one deprotonated dianionic 5-bromosalicylaldehyde thiosemicarbazone and one pyridine ligand (Fig. 1). The selected bond angles formed between donor atoms trough the Ni atom are N1—Ni1—N4 = 177.00 (10)° and O1—Ni1—S1 = 176.46 (6)°, and show a slightly distorted coordination environment. The thiosemicarbazone ligand is coordinated to the Ni^{II} ion in a tridentate chelating mode, forming five- and six-membered rings, as a "NOS" donor with the O/S atoms *trans* to each other, while the N1 azomethine atom is *trans* to the N4 atom from the pyridine ligand.

The acidic hydrogen of the hydrazine fragment is lost by the reaction with KOH, which is in agreement with thiosemicarbazone derivatives prepared from aldehydes or ketones. The negative charge is delocalized over the C—N—N—C—S fragment as indicated by their intermediate bond distances. The imine and thioamide C—N distances indicate considerable double bond character, while the C—S distance is consistent with increased single bond character. These distances are C7—N1 = 1.295 (3) Å, N1—N2 = 1.403 (3) Å, N2—C8 = 1.289 (4) Å and C8—S1 = 1.735 (3) Å. The hydrogen of the hydroxyl group is also deprotonated with KOH, resulting in the dianionic form of the ligand.

The ligand shows a Z—E—E—Z conformation for the donor atoms about the C1—C7/C7—N1/N1—N2/N2—C8 bonds and the mean deviations from the least squares planes for the chelated fragments Ni1/N1/C7/C1/C2/O1 and Ni1/N1/N2/C8/S1 amount to 0.0286 (15) Å for N1 and 0.0170 (12) Å for N1, respectively, and the dihedral angle between the two planes is 2.97 (11)°. The Z—E—E—Z conformation is also observed for the free ligand (Kargar *et al.*, 2010) as well as for a complex with similar coordination environment (Güveli *et al.*, 2009).

Both ligands are almost planar (Fig. 1 and Fig. 2) and the maximum deviation from the least squares plane through all non-hydrogen atoms for the deprotonated thiosemicarbazone fragment C1/C2/C3/C4/C5/C6/C7/C8/Br1/N1/N2/N3/O1/S1 and for the pyridine molecule C9/C10/C11/C12/C13/N4 amount to 0.0668 (25) Å for C7 and 0.0059 (21) Å for C9, respectively, and the dihedral angle between the two planes is 61.15 (6)°.

The molecules are linked by pairs of centrosymmetrical N—H···N interactions (Fig. 2 and Table 1; N3—H5···N2ⁱ) forming a dimeric molecular structure, which stabilizes the crystal packing. Symmetry codes: (i) -*x*, -*y* + 1, -*z*.

The crystal structure shows that molecules are additionally connected through intermolecular Br⋯Br interactions into chains along the crystallographic *b* direction (Fig. 3). The Br⋯Br distances amount to 3.545 (1) Å, which are shorter than the sum of the van der Waals radii for Br atoms (3.70 Å).

Experimental

Starting materials were commercially available and were used without further purification. The synthesis of 5-bromo-salicylaldehyde thiosemicarbazone was adapted from a procedure reported previously (Joseph *et al.*, 2010). 5-Bromo-salicylaldehyde thiosemicarbazone (0.5 mmol) was dissolved in tetrahydrofurane (50 ml) and treated with one KOH pellet. After 30 min stirring under slight warming to 333 K, the solution was filtered and added to a nickel acetate tetrahydrate (0.5 mmol) solution in pyridine (10 ml). The reaction mixture was refluxed for 4 h under continuous stirring and showed a brown-red colour. Brown-red crystals of the complex, suitable for X-ray analysis, were obtained after six weeks by adding a 3:1 mixture of dimethylformamide and toluene (80 ml) to the reaction solution.

Refinement

H atoms attached to C atoms were positioned with idealized geometry and were refined isotropic with $U_{eq}(H)$ set to 1.2 times of the $U_{eq}(C)$ using a riding model with C—H = 0.93 Å. H atoms attached to N atoms atoms were positioned with idealized geometry and were refined isotropically with $U_{eq}(H)$ set to 1.2 times of $U_{eq}(N)$ using a riding model with N3—H1 = 0.7822 Å and N3—H2 = 0.8025 Å.

Computing details

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); 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).
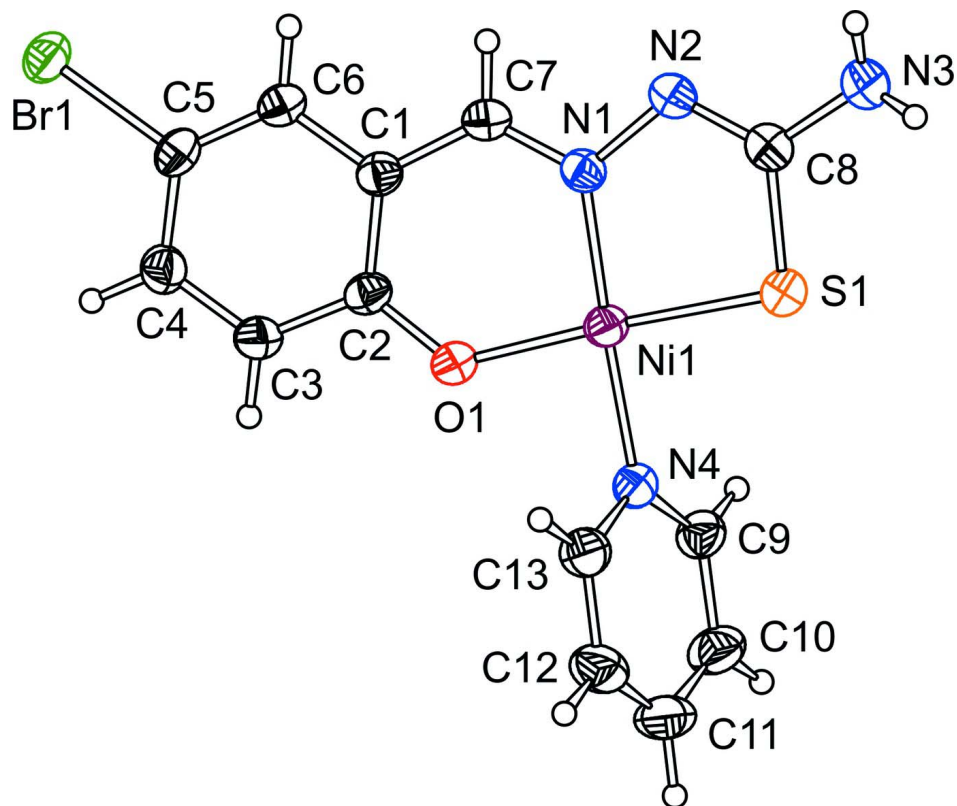
Figure 1

The molecular structure of the title compound with labeling and displacement ellipsoids drawn at the 40% probability level.
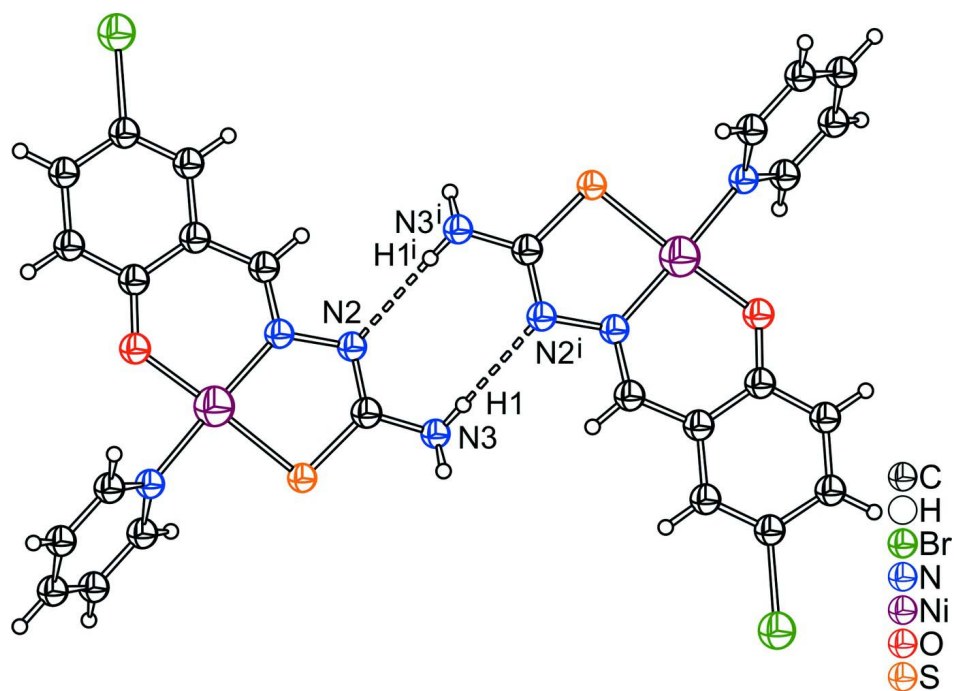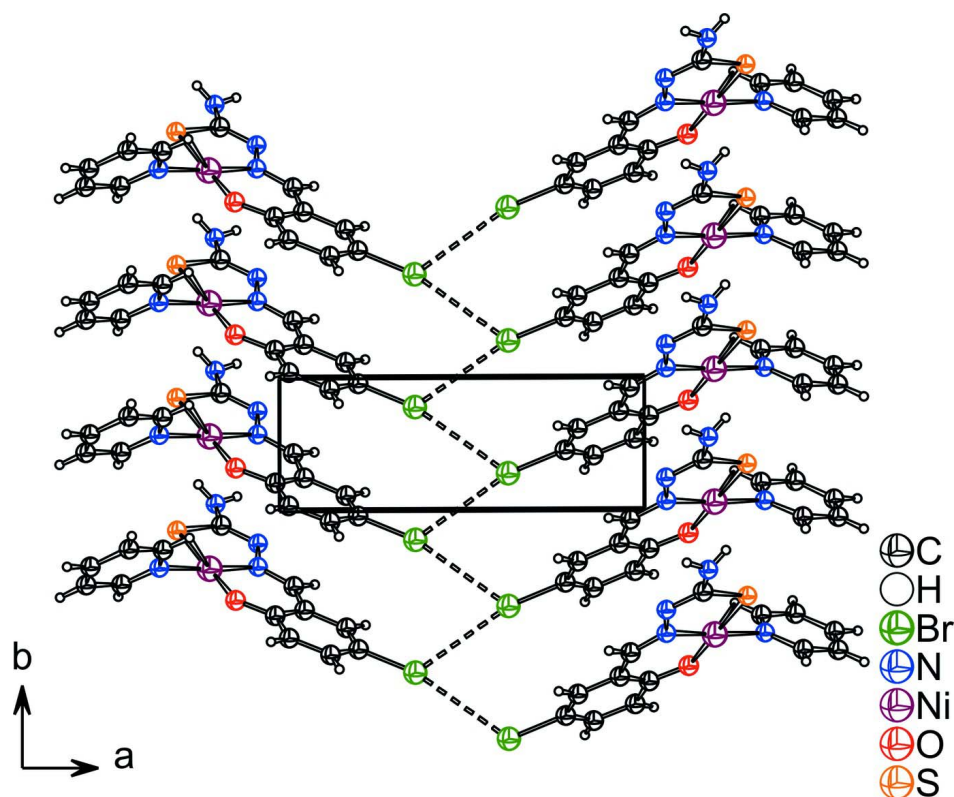
Figure 2

Molecules of the title compound connected through pairs of inversion symmetric N—H···N interactions. Hydrogen bonding is indicated by dashed lines. Symmetry code: (i) -*x*, -*y* + 1, -*z*.

Figure 3

Molecules of the title compound connected through intermolecular Br···Br interactions into chains along the crystallographic *b* direction. The Br···Br distances amount to 3.545 (1) Å and the interactions are indicated by dashed lines.

[1-(5-Bromo-2-oxidobenzylidene)thiosemicarbazidato- *κ³O,N¹,S*](pyridine-*κN*)nickel(II)

Crystal data

[Ni(C$_8$H$_6$BrN$_3$OS)(C$_5$H$_5$N)]	$F(000) = 816$
$M_r = 409.94$	$D_x = 1.881$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 17227 reflections
$a = 12.2447$ (4) Å	$\theta = 2.9–27.5°$
$b = 4.1135$ (1) Å	$\mu = 4.25$ mm^{-1}
$c = 31.1380$ (11) Å	$T = 293$ K
$\beta = 112.646$ (1)°	Needle, red
$V = 1447.46$ (8) Å^3	$0.93 \times 0.10 \times 0.05$ mm
$Z = 4$	

Data collection

Nonius KappaCCD diffractometer	Absorption correction: multi-scan (Blessing, 1995)
Radiation source: fine-focus sealed tube, Bruker Kappa CCD	$T_{min} = 0.443$, $T_{max} = 0.830$
Graphite monochromator	13946 measured reflections
Detector resolution: 9 pixels mm^{-1}	3224 independent reflections
CCD rotation images, thick slices scans	2697 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.051$

$\theta_{max} = 27.6°$, $\theta_{min} = 3.3°$

$h = -15 \rightarrow 15$

$k = -5 \rightarrow 5$

$l = -40 \rightarrow 40$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.031$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.083$	
$S = 1.05$	H-atom parameters constrained
3224 reflections	$w = 1/[\sigma^2(F_o^2) + (0.0442P)^2 + 0.6555P]$ where $P = (F_o^2 + 2F_c^2)/3$
190 parameters	
0 restraints	$(\Delta/\sigma)_{max} = 0.001$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{max} = 0.61$ e Å^{-3}
	$\Delta\rho_{min} = -0.66$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ 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	$U_{iso}*/U_{eq}$
Br1	1.37247 (2)	0.72025 (7)	0.228104 (10)	0.04622 (11)
Ni1	0.80812 (3)	−0.06339 (9)	0.089703 (11)	0.03527 (11)
S1	0.71884 (6)	−0.35252 (19)	0.02859 (2)	0.04380 (17)
O1	0.87955 (16)	0.1736 (5)	0.14418 (7)	0.0419 (4)
N1	0.93997 (18)	−0.0757 (5)	0.07408 (7)	0.0339 (4)
N2	0.9399 (2)	−0.2507 (6)	0.03540 (8)	0.0403 (5)
N3	0.8245 (2)	−0.5541 (7)	−0.02746 (9)	0.0519 (6)
H1	0.8831	−0.6069	−0.03	0.062*
H2	0.7769	−0.6986	−0.0334	0.062*
N4	0.67067 (19)	−0.0743 (6)	0.10494 (8)	0.0383 (5)
C1	1.0684 (2)	0.2490 (6)	0.13889 (9)	0.0350 (5)
C2	0.9877 (2)	0.2887 (6)	0.16117 (9)	0.0357 (5)
C3	1.0269 (2)	0.4575 (7)	0.20359 (10)	0.0423 (6)
H3	0.9751	0.4858	0.2187	0.051*
C4	1.1399 (2)	0.5829 (7)	0.22359 (10)	0.0428 (6)
H4	1.1642	0.6923	0.2519	0.051*
C5	1.2167 (2)	0.5430 (6)	0.20077 (9)	0.0377 (5)
C6	1.1830 (2)	0.3830 (7)	0.15955 (10)	0.0377 (5)
H6	1.2358	0.3616	0.1448	0.045*
C7	1.0394 (2)	0.0704 (7)	0.09658 (9)	0.0380 (6)
H7	1.0971	0.0579	0.0841	0.046*
C8	0.8393 (2)	−0.3869 (7)	0.01258 (9)	0.0390 (6)
C9	0.5660 (2)	0.0532 (7)	0.07772 (10)	0.0439 (6)
H9	0.558	0.1437	0.0493	0.053*

C10	0.4699 (3)	0.0547 (9)	0.09040 (12)	0.0553 (8)
H10	0.3986	0.1475	0.0711	0.066*
C11	0.4810 (3)	−0.0826 (9)	0.13187 (12)	0.0586 (8)
H11	0.4172	−0.0845	0.1411	0.07*
C12	0.5869 (3)	−0.2171 (8)	0.15973 (11)	0.0569 (8)
H12	0.5955	−0.3131	0.1879	0.068*
C13	0.6808 (3)	−0.2087 (8)	0.14557 (10)	0.0476 (7)
H13	0.7528	−0.2985	0.1647	0.057*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.03290 (15)	0.0510 (2)	0.05011 (18)	−0.00359 (11)	0.01082 (12)	−0.00312 (13)
Ni1	0.03052 (17)	0.0412 (2)	0.03447 (17)	0.00019 (13)	0.01296 (13)	0.00106 (13)
S1	0.0378 (3)	0.0507 (4)	0.0424 (4)	−0.0046 (3)	0.0148 (3)	−0.0052 (3)
O1	0.0321 (9)	0.0540 (12)	0.0406 (10)	−0.0025 (8)	0.0151 (8)	−0.0049 (9)
N1	0.0352 (10)	0.0337 (11)	0.0336 (10)	0.0034 (8)	0.0141 (9)	0.0010 (9)
N2	0.0419 (12)	0.0419 (13)	0.0399 (12)	0.0010 (10)	0.0189 (10)	−0.0039 (10)
N3	0.0488 (14)	0.0583 (17)	0.0502 (14)	−0.0046 (12)	0.0210 (12)	−0.0152 (12)
N4	0.0346 (11)	0.0443 (13)	0.0356 (11)	−0.0030 (9)	0.0130 (9)	−0.0002 (9)
C1	0.0327 (12)	0.0355 (13)	0.0367 (13)	0.0030 (10)	0.0132 (10)	0.0025 (10)
C2	0.0297 (11)	0.0387 (14)	0.0389 (13)	0.0030 (10)	0.0134 (10)	0.0046 (11)
C3	0.0359 (13)	0.0526 (17)	0.0410 (13)	0.0018 (12)	0.0179 (11)	−0.0023 (12)
C4	0.0387 (13)	0.0475 (16)	0.0393 (13)	0.0025 (12)	0.0118 (11)	−0.0041 (12)
C5	0.0289 (11)	0.0358 (14)	0.0438 (14)	0.0008 (10)	0.0089 (10)	0.0030 (11)
C6	0.0311 (12)	0.0391 (14)	0.0443 (14)	0.0020 (10)	0.0159 (11)	0.0018 (11)
C7	0.0348 (12)	0.0405 (15)	0.0426 (14)	0.0023 (11)	0.0191 (11)	0.0007 (11)
C8	0.0431 (14)	0.0363 (14)	0.0376 (13)	0.0049 (11)	0.0157 (11)	0.0021 (11)
C9	0.0365 (13)	0.0535 (18)	0.0393 (14)	0.0004 (12)	0.0120 (11)	0.0060 (12)
C10	0.0349 (14)	0.072 (2)	0.0588 (18)	0.0048 (14)	0.0179 (13)	0.0068 (16)
C11	0.0478 (17)	0.076 (2)	0.064 (2)	−0.0003 (16)	0.0339 (16)	0.0031 (17)
C12	0.062 (2)	0.071 (2)	0.0460 (17)	−0.0009 (17)	0.0303 (16)	0.0069 (16)
C13	0.0418 (14)	0.0607 (19)	0.0390 (14)	0.0018 (13)	0.0141 (12)	0.0074 (13)

Geometric parameters (Å, º)

Br1—C5	1.909 (3)	C2—C3	1.403 (4)
Ni1—N1	1.858 (2)	C3—C4	1.380 (4)
Ni1—O1	1.8576 (19)	C3—H3	0.93
Ni1—N4	1.917 (2)	C4—C5	1.390 (4)
Ni1—S1	2.1516 (8)	C4—H4	0.93
S1—C8	1.735 (3)	C5—C6	1.358 (4)
O1—C2	1.311 (3)	C6—H6	0.93
N1—C7	1.295 (3)	C7—H7	0.93
N1—N2	1.403 (3)	C9—C10	1.378 (4)
N2—C8	1.289 (4)	C9—H9	0.93
N3—C8	1.373 (4)	C10—C11	1.367 (5)
N3—H1	0.7822	C10—H10	0.93
N3—H2	0.8025	C11—C12	1.369 (5)
N4—C9	1.341 (4)	C11—H11	0.93

N4—C13	1.342 (4)	C12—C13	1.381 (4)
C1—C6	1.411 (4)	C12—H12	0.93
C1—C2	1.419 (3)	C13—H13	0.93
C1—C7	1.429 (4)		
N1—Ni1—O1	95.87 (9)	C5—C4—H4	120.5
N1—Ni1—N4	177.00 (10)	C6—C5—C4	121.4 (2)
O1—Ni1—N4	86.32 (9)	C6—C5—Br1	119.63 (19)
N1—Ni1—S1	87.15 (7)	C4—C5—Br1	118.9 (2)
O1—Ni1—S1	176.46 (6)	C5—C6—C1	120.5 (2)
N4—Ni1—S1	90.60 (7)	C5—C6—H6	119.8
C8—S1—Ni1	95.77 (10)	C1—C6—H6	119.8
C2—O1—Ni1	127.26 (17)	N1—C7—C1	125.8 (2)
C7—N1—N2	113.1 (2)	N1—C7—H7	117.1
C7—N1—Ni1	125.23 (18)	C1—C7—H7	117.1
N2—N1—Ni1	121.70 (16)	N2—C8—N3	118.8 (2)
C8—N2—N1	112.4 (2)	N2—C8—S1	122.9 (2)
C8—N3—H1	115.1	N3—C8—S1	118.2 (2)
C8—N3—H2	114.2	N4—C9—C10	122.3 (3)
H1—N3—H2	112.6	N4—C9—H9	118.8
C9—N4—C13	118.4 (2)	C10—C9—H9	118.8
C9—N4—Ni1	123.42 (18)	C11—C10—C9	118.9 (3)
C13—N4—Ni1	118.17 (19)	C11—C10—H10	120.5
C6—C1—C2	119.3 (2)	C9—C10—H10	120.5
C6—C1—C7	118.2 (2)	C10—C11—C12	119.4 (3)
C2—C1—C7	122.5 (2)	C10—C11—H11	120.3
O1—C2—C3	119.0 (2)	C12—C11—H11	120.3
O1—C2—C1	123.2 (2)	C11—C12—C13	119.3 (3)
C3—C2—C1	117.8 (2)	C11—C12—H12	120.4
C4—C3—C2	122.0 (2)	C13—C12—H12	120.4
C4—C3—H3	119	N4—C13—C12	121.7 (3)
C2—C3—H3	119	N4—C13—H13	119.2
C3—C4—C5	118.9 (3)	C12—C13—H13	119.2
C3—C4—H4	120.5		
N1—Ni1—S1—C8	1.82 (11)	C3—C4—C5—C6	−0.3 (4)
N4—Ni1—S1—C8	−176.20 (12)	C3—C4—C5—Br1	179.4 (2)
N1—Ni1—O1—C2	1.9 (2)	C4—C5—C6—C1	−0.7 (4)
N4—Ni1—O1—C2	179.8 (2)	Br1—C5—C6—C1	179.7 (2)
O1—Ni1—N1—C7	−4.3 (2)	C2—C1—C6—C5	1.3 (4)
S1—Ni1—N1—C7	177.6 (2)	C7—C1—C6—C5	−177.2 (2)
O1—Ni1—N1—N2	175.74 (19)	N2—N1—C7—C1	−175.7 (2)
S1—Ni1—N1—N2	−2.40 (18)	Ni1—N1—C7—C1	4.3 (4)
C7—N1—N2—C8	−178.1 (2)	C6—C1—C7—N1	177.7 (3)
Ni1—N1—N2—C8	1.9 (3)	C2—C1—C7—N1	−0.7 (4)
O1—Ni1—N4—C9	119.2 (2)	N1—N2—C8—N3	177.0 (2)
S1—Ni1—N4—C9	−62.5 (2)	N1—N2—C8—S1	0.2 (3)
O1—Ni1—N4—C13	−58.9 (2)	Ni1—S1—C8—N2	−1.6 (3)
S1—Ni1—N4—C13	119.3 (2)	Ni1—S1—C8—N3	−178.4 (2)

Ni1—O1—C2—C3	−178.72 (19)	C13—N4—C9—C10	1.0 (4)
Ni1—O1—C2—C1	0.8 (4)	Ni1—N4—C9—C10	−177.1 (2)
C6—C1—C2—O1	179.6 (2)	N4—C9—C10—C11	−0.9 (5)
C7—C1—C2—O1	−2.0 (4)	C9—C10—C11—C12	0.1 (5)
C6—C1—C2—C3	−0.9 (4)	C10—C11—C12—C13	0.6 (5)
C7—C1—C2—C3	177.5 (2)	C9—N4—C13—C12	−0.2 (4)
O1—C2—C3—C4	179.5 (3)	Ni1—N4—C13—C12	178.0 (2)
C1—C2—C3—C4	0.0 (4)	C11—C12—C13—N4	−0.6 (5)
C2—C3—C4—C5	0.6 (4)		

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
N3—H1···N2[i]	0.78	2.31	3.095 (3)	178

Symmetry code: (i) −x+2, −y−1, −z.