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Hydrogen bonding in coordinated thiosemicarbazones: ammine[2-hydroxy-1-naphthaldehyde 4-methylthiosemicarbazonato]nickel(II)

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In the title compound, [Ni($C_{13}H_{11}N_3OS$)(NH_3)], the Ni atom is four-coordinate, with a distorted square-planar geometry. The 2-hydroxy-1-naphthaldehyde 4-methylthiosemicarbazonate ligand coordinates in a tridentate manner through the S, imine-N and O atoms, the ammonia molecule completing the coordination. The molecules are connected by N—H···N hydrogen bonds, through *c*-glide-plane translations, forming extended chains.

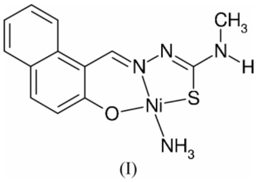
Key indicators

Single-crystal X-ray study
T = 291 K
Mean σ(C–C) = 0.005 Å
R factor = 0.034
wR factor = 0.080
Data-to-parameter ratio = 12.4

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Metal complexes of thiosemicarbazones continue to attract the interest of inorganic and medicinal chemists due to their potential pharmacological activity (Labisabal *et al.*, 2003). To understand the biological activity of thiosemicarbazones may also require an understanding of their supramolecular chemistry. Ammine[2-hydroxy-1-naphthaldehyde 4-methylthiosemicarbazonato]nickel(II), (I), was synthesized with a view to studying the hydrogen-bonding interactions of the N—H group in the coordinated thiosemicarbazone (TSC) and how it competes with other possible interactions, in this case the hydrogen bonding of the coordinated ammonia molecule.



(I)

The Ni atom in (I) exhibits a coordination number of four. The loss of the hydroxy proton, as well as the one from N2 of the thiosemicarbazone moiety, produces a terdentate dianionic ligand which coordinates *via* the thiolate S, the azomethine N and the naphthoxy O atom. The ammonia molecule coordinates in the fourth position. The coordination, as indicated by the distances and angles around the metal ion

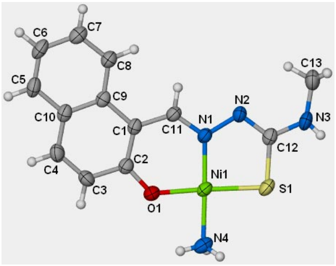


Figure 1
View of the molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by circles of arbitrary size.

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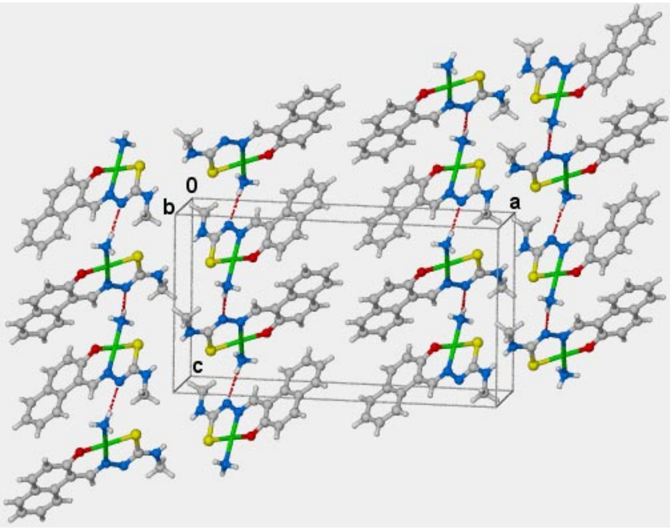

Figure 2
The molecular packing of (I), viewed approximately along the *b* axis. Hydrogen bonds are indicated as dashed lines

(see Table 1), is distorted square planar. The coordinated thiosemicarbazone ligand is almost planar and the angle between the Ni1/S1/N1/N2/C12 and Ni1/O1/N1/C1/C2/C11 chelate rings is 4.4 (2)°. The angle between the Ni1/S1/N1/N2/C12 chelate ring and the mean plane of the naphthalene rings is 10.03 (14)°. The methyl group, C13, is in the same plane as the rest of the ligand, the torsion angle N2—C12—N3—C13 being −0.7 (6)°.

In the crystal structure, molecules are connected by N—H···N hydrogen bonds through *c*-glide-plane translations, to form extended chains (see Table 2). These chains are close-packed through van der Waals interactions, as shown in Fig. 2. There are two N atoms that can act as H donors, the ammonia N4, and N3 from the thiosemicarbazone. We can argue that the best acceptor is N2 on the TSC. Although the present results suggest that ammonia is a better donor compared to N3 of the TSC, this is not conclusive. In the crystal structure of ammine[2-hydroxy-1-naphthaldehyde 4-piperidylthiosemicarbazonato]nickel(II) (Valdés-Martínez *et al.*, 2002), the ammonia does not interact with N2 (possibly due to steric hindrance of the piperidyl group) and in ammine(salicylaldehyde thiosemicarbazonato)nickel(II) (Gyepes & Glowiak, 1989), and ammine[salicylaldehyde 4-phenylthiosemicarbazonato]nickel(II) (Soriano-García *et al.*, 1985), centrosymmetric N3—H···N2 hydrogen-bonded dimers are preferred to hydrogen bonds involving the ammonia molecule.

Experimental

The ligand 2-hydroxy-1-naphthaldehyde 4-methylthiosemicarbazone was obtained from a 1:1 molar ratio of 2-hydroxy-1-naphthaldehyde and 4-methylthiosemicarbazide in boiling ethanol containing 1 ml of acetic acid. Compound (I) was prepared from the 4-methylthiosemicarbazone and nickel(II) nitrate hexahydrate in a 1:1 molar ratio in a boiling methanol–ammonia solution. Crystals of (I) were obtained by slow evaporation, at room temperature, of the reaction mixture.

Crystal data

$[Ni(C_{13}H_{11}N_3OS)(NH_3)]$
$M_r = 333.05$
Monoclinic, $P2_1/c$
$a = 21.345$ (4) Å
$b = 5.387$ (1) Å
$c = 11.787$ (2) Å
$\beta = 90.48$ (1)°
$V = 1355.3$ (4) Å^3
$Z = 4$

$D_x = 1.632$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 42 reflections
$\theta = 1.9$–12.2°
$\mu = 1.59$ mm^{-1}
$T = 291$ (2) K
Plate, dark red
0.38 × 0.16 × 0.04 mm

Data collection

Siemens *P*4/*PC* diffractometer
ω scans
Absorption correction: analytical (*SHELXTL/PC*; Sheldrick, 1997*b*)
$T_{\min} = 0.783$, $T_{\max} = 0.940$
3374 measured reflections
2388 independent reflections
1737 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.036$
$\theta_{\max} = 25.0°$
$h = -25 \rightarrow 25$
$k = -6 \rightarrow 1$
$l = -1 \rightarrow 14$
3 standard reflections every 97 reflections intensity decay: <2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.080$
$S = 0.90$
2388 reflections
193 parameters

H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.04P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.38$ e Å^{-3}
$\Delta\rho_{\min} = -0.41$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ni1—O1	1.833 (2)	O1—C2	1.304 (4)
Ni1—N1	1.858 (3)	N1—C11	1.308 (4)
Ni1—N4	1.940 (3)	N1—N2	1.411 (4)
Ni1—S1	2.1506 (10)	N2—C12	1.301 (4)
S1—C12	1.751 (4)	N3—C12	1.353 (5)
O1—Ni1—N1	94.77 (11)	O1—Ni1—S1	177.35 (8)
O1—Ni1—N4	83.99 (13)	N1—Ni1—S1	87.88 (8)
N1—Ni1—N4	178.72 (14)	N4—Ni1—S1	93.36 (11)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N4—H4*A*···N2$^{\rm i}$	0.84 (5)	2.29 (5)	3.125 (5)	169 (4)

Symmetry code: (i) $x, \frac{3}{2} - y, \frac{1}{2} + z$.

All H atoms were initially located in a difference Fourier map. The ammonia H atoms were refined isotropically, the refined N—H distances ranging from 0.71 (4) to 0.85 (4) Å. H atoms attached to C atoms were included in calculated positions (C—H = 0.93–0.97 Å), and refined using a riding model, with fixed displacement parameters $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$.

Data collection: *XSCANS* (Siemens, 1994); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1997*b*); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*a*); molecular graphics:

X-Seed (Barbour, 2001); software used to prepare material for publication: *SHELXL*97.

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