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Key indicators

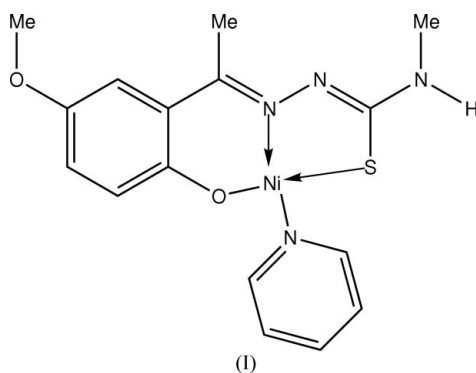
Single-crystal X-ray study
 $T = 291$ K
Mean $\sigma(\text{C}-\text{C}) = 0.005$ Å
 R factor = 0.047
 wR factor = 0.083
Data-to-parameter ratio = 17.7For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.(5-Methoxy-2-oxidoacetophenone 4-methylthio-
semicarbazonato- $\kappa^3\text{O},\text{N},\text{S}$)pyridinenickel(II)

In the title compound, $[\text{Ni}(\text{C}_{11}\text{H}_{13}\text{N}_3\text{O}_2\text{S})(\text{C}_5\text{H}_5\text{N})]$, the Ni^{II} ion is in a distorted square-planar geometry, with the $\text{C}_{11}\text{H}_{13}\text{N}_3\text{O}_2\text{S}$ ligand coordinated in a dianionic tridentate fashion; the pyridine molecule occupies the fourth position. The molecules are linked by $\text{N}-\text{H}\cdots\text{S}$ interactions about an inversion center.

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Comment

The title compound, (I), was synthesized with a view to studying the hydrogen-bonding interactions of the NH group in coordinated thiosemicarbazones. The Ni atom in (I) exhibits a coordination number of four with a distorted square-planar geometry, as indicated by the distances and angles around the metal ion (Table 1). The 5-methoxy-2-hydroxybenzaldehyde 4-methylthiosemicarbazonato ligand coordinates to the Ni^{II} ion in a tridentate fashion *via* the thiolate S, the azomethine N and the phenoxy O atom. The pyridine molecule coordinates in the fourth position. According to the relevant torsion angles, the thiosemicarbazone is almost planar; the methyl group on N3 and the methoxy group on the benzene ring are coplanar with the rest of the ligand (Table 1). The pyridine ring forms an angle of $57.5(1)^\circ$ with the mean plane of the rest of the molecule.



Several similar compounds have been reported: ammine-(salicylaldehyde thiosemicarbazonato)nickel(II) (Gyepes & Głowiak, 1989), (II), ammine(salicylaldehyde 4-phenylthiosemicarbazonato)nickel(II) (Soriano-García *et al.*, 1985), (III), ammine(2-hydroxy-1-naphthaldehyde 4-piperidylthiosemicarbazonato)nickel(II) (Martínez *et al.*, 2002), (IV), and ammine(2-hydroxy-1-naphthaldehyde 4-methylthiosemicarbazonato)nickel(II) (Valdés-Martínez *et al.*, 2004), (V). The geometry of these compounds is very similar. The bond distances and angles around the Ni^{II} atom in (I) are within the ranges of values observed in (II)–(V), except for the Ni–O

bond, which is shorter, and the Ni–N1 bond, which is longer than the distances observed in the other structures (1.83–1.86 and 1.84–1.86 Å, respectively).

There is only one unique hydrogen bond. The molecules are linked by a pair of hydrogen bonds about an inversion center (Table 2 and Fig. 1). In those related structures where there is no steric hindrance blocking N2, as in (II), (III) and (V), atom N2 acts as the acceptor of an N–H···N hydrogen bond.

Experimental

The ligand 5-methoxy-2-hydroxybenzaldehyde 4-methylthiosemicarbazone was obtained from the reaction of 5-methoxysalicylaldehyde (1.66 g, 10 mmol) and 4-methyl-3-thiosemicarbazide (0.93 g, 10 mmol) in boiling ethanol (100 ml) containing 1 ml of acetic acid. Compound (I) was prepared from the reaction of 5-methoxy-2-hydroxybenzaldehyde 4-methylthiosemicarbazone (1.20 g, 5 mmol) and nickel(II) nitrate hexahydrate (1.20 g, 5 mmol) in a 1:1 molar ratio in a boiling 10:1 methanol/ammonia solution (75 ml). Crystals of (I) were obtained by slow evaporation of the reaction mixture at room temperature.

Crystal data

$[\text{Ni}(\text{C}_{11}\text{H}_{13}\text{N}_3\text{O}_2\text{S})(\text{C}_5\text{H}_5\text{N})]$	$Z = 4$
$M_r = 389.11$	$D_x = 1.499 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 13.9017 (12) \text{ \AA}$	$\mu = 1.26 \text{ mm}^{-1}$
$b = 6.2419 (6) \text{ \AA}$	$T = 291 (2) \text{ K}$
$c = 20.3533 (18) \text{ \AA}$	Prism, red
$\beta = 102.453 (2)^\circ$	$0.40 \times 0.12 \times 0.08 \text{ mm}$
$V = 1724.6 (3) \text{ \AA}^3$	

Data collection

Bruker SMART APEX CCD area-detector diffractometer	16339 measured reflections
ω scans	3952 independent reflections
Absorption correction: numerical (<i>SHELXTL/PC</i> ; Sheldrick, 1997b)	2311 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.691$, $T_{\max} = 0.909$	$R_{\text{int}} = 0.049$
	$\theta_{\text{max}} = 27.5^\circ$

Refinement

Refinement on F^2	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.047$	$w = 1/[\sigma^2(F_o^2) + (0.030P)^2]$
$wR(F^2) = 0.083$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.88$	$(\Delta/\sigma)_{\text{max}} = 0.001$
3952 reflections	$\Delta\rho_{\text{max}} = 0.78 \text{ e \AA}^{-3}$
223 parameters	$\Delta\rho_{\text{min}} = -0.20 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Ni1–O1	1.820 (2)	Ni1–N4	1.920 (2)
Ni1–N1	1.869 (2)	Ni1–S1	2.1429 (8)
O1–Ni1–N1	95.32 (9)	O1–Ni1–S1	175.69 (7)
O1–Ni1–N4	86.12 (9)	N1–Ni1–S1	88.52 (7)
N1–Ni1–N4	174.18 (9)	N4–Ni1–S1	90.25 (7)

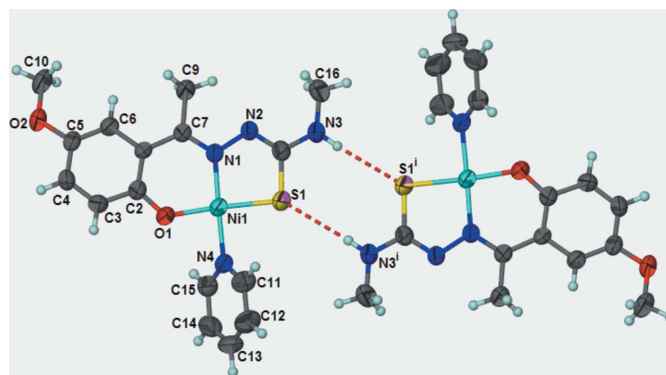


Figure 1

The structure of the hydrogen-bonded dimer of (I). Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by circles of arbitrary size. The dashed lines indicated hydrogen bonds. [Symmetry code: (i) $-x + 1, -y + 1, -z + 1$.]

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N3}-\text{H3A}\cdots\text{S1}^i$	0.849 (10)	2.728 (11)	3.569 (3)	171 (3)

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

The H atom attached to atom N3 was found in a difference Fourier map and its positional parameters were refined [$U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$]. H atoms attached to C atoms were located in calculated positions ($C-H = 0.93\text{--}0.96 \text{ \AA}$), and refined using a riding model with fixed displacement parameters [$U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$].

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINTE* (Bruker, 2000); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997a); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997a); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *enCIFer* (Allen *et al.*, 2004).

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