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Bis[1-hydroxy-3-methylpyridine-2(1*H*)-thionato-*O,S*]nickel(II)

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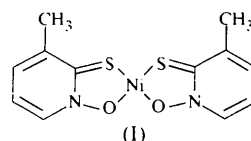
Abstract

In the structure of the title compound, [Ni(C₈H₆NOS)₂], the Ni atom is coordinated by a slightly distorted planar array of two S and two O atoms. The two 1-hydroxy-3-methylpyridine-2(1*H*)-thione (3-Me-HPT) ligands adopt a *cis* configuration. The average Ni—O and Ni—S bond lengths are 1.868 (2) and 2.130 (1) Å, respectively.

Comment

Owing to their useful bactericidal and antifungal activities, transition metal complexes of 1-hydroxypyridine-2(1*H*)-thione (HPT) have been widely investigated. Moreover, HPT exhibits unusual versatility in coordi-

nating to metals (Barnett *et al.*, 1977; West *et al.*, 1988). On the other hand, the simulation of many metallo-enzymes involving the thiolate group has also received considerable attention, particularly the assessment of the antitumor activity of some nickel complexes with chelating ligands (West *et al.*, 1993). As part of our studies of metal complexes of HPT (Xiong *et al.*, 1996; Song *et al.*, 1996), we now report the crystal structure of bis[1-hydroxy-3-methylpyridine-2(1*H*)-thionato-*O,S*]nickel(II), (I).



The complex is formed with *cis*-oriented 1-hydroxy-3-methylpyridine-2(1*H*)-thione (3-Me-HPT) ligands and shows nearly planar geometry. The Ni atom is coordinated by the S and O atoms of the two ligands and has a distorted square-planar geometry. The whole molecule exhibits a pseudo-*C*_{2v} symmetry, with the *C*₂ axis passing through the Ni atom and the midpoints of S1—S2 and O1—O2. When comparing the title compound with the analogue [Ni(PT)₂] (Chen *et al.*, 1991), the Ni—S and Ni—O bond distances in the two complexes are essentially the same within experimental error. However, the C—S bond lengths in (I) [average 1.728 (3) Å] are significant longer than those in the latter (average 1.710 Å) and the N—O bond lengths [average 1.320 (4) Å] are somewhat shorter than those in the latter (average 1.350 Å), which may be the result of steric hindrance of the 3-methyl group. The two O—Ni—S bite angles are nearly equal and close to 90°, as is found in [Ni(PT)₂], where PT is pyridine-2-thione. In the title complex, the two five-membered chelate rings are nearly planar, with maximum deviations of 0.024 (4) Å for C1 and 0.021 (4) Å for C11. The dihedral angle between these two planes is 5.3 (1)°. The complete molecule is almost planar. The Ni atom deviates by 0.002 (1) Å from the basal plane formed by the

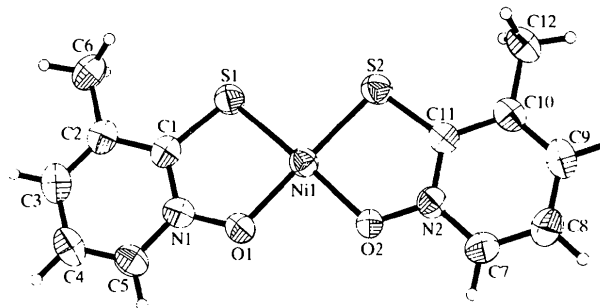


Fig. 1. A displacement ellipsoid plot (50% probability level) of the title molecule showing the atom-numbering scheme.

S and O atoms. The presence of C—H... π interactions and stacking between the glide-related molecules enhances the packing of the molecules, apart from any van der Waals interactions; $Cg2 \cdots Cg4(x, \frac{1}{2} - y, z - \frac{1}{2})$ 3.93, $Cg3 \cdots Cg3(-x + 1, -y, -z + 2)$ 3.55 and $Cg4 \cdots Cg4(x, \frac{1}{2} - y, z + \frac{1}{2})$ 3.73 Å (where $Cg2$ is the centroid of the five-membered chelate ring containing atoms Ni1, O2, N2, S2 and C11, and $Cg3$ and $Cg4$ are the centroids of the six-membered N1- and N2-containing rings, respectively).

Experimental

A solution of $NiCl_2 \cdot 6H_2O$ (0.499 g, 2.1 mmol) in EtOH (20 ml) was dropped slowly into a solution of 3-Me-HPT (0.533 g, 4.2 mmol) in hot EtOH (20 ml). The mixed solution was stirred for 1 h at 313 K and then cooled to room temperature to give brown microcrystals, which were collected by filtration, washed successively with H_2O , EtOH and ethyl ether, and dried *in vacuo*. The product was then evaporated slowly from dimethylformamide over a period of a few weeks, after which time, thick brown plate-like crystals suitable for X-ray analysis were obtained.

Crystal data

$[Ni(C_6H_6NOS)_2]$
 $M_r = 339.07$
 Monoclinic
 $P2_1/c$
 $a = 7.3437(3)$ Å
 $b = 24.6375(8)$ Å
 $c = 7.4493(3)$ Å
 $\beta = 93.295(1)^\circ$
 $V = 1345.58(9)$ Å³
 $Z = 4$
 $D_x = 1.674$ Mg m⁻³
 D_m not measured

Mo $K\alpha$ radiation
 $\lambda = 0.71073$ Å
 Cell parameters from 7131 reflections
 $\theta = 2.78$ – 38.60°
 $\mu = 1.749$ mm⁻¹
 $T = 293(2)$ K
 Plate
 $0.44 \times 0.30 \times 0.14$ mm
 Brown

Data collection

Siemens SMART CCD area-detector diffractometer
 ω scans
 Absorption correction: empirical (SADABS; Sheldrick, 1996)
 $T_{min} = 0.513$, $T_{max} = 0.792$
 7820 measured reflections
 2341 independent reflections

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.055$
 $wR(F^2) = 0.148$
 $S = 1.107$
 2341 reflections
 174 parameters
 H-atom parameters constrained

2039 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.079$
 $\theta_{max} = 25^\circ$
 $h = -8 \rightarrow 8$
 $k = 0 \rightarrow 29$
 $l = 0 \rightarrow 8$
 $w = 1/[\sigma^2(F_o^2) + (0.0809P)^2 + 0.8304P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} < 0.001$
 $\Delta\rho_{max} = 1.223$ e Å⁻³
 $\Delta\rho_{min} = -0.539$ e Å⁻³
 Extinction correction: none
 Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. Selected geometric parameters (Å, °)

Ni1—O1	1.866(3)	S1—C1	1.726(4)
Ni1—O2	1.869(3)	S2—C11	1.731(4)
Ni1—S1	2.130(1)	O1—N1	1.316(5)
Ni1—S2	2.130(1)	O2—N2	1.323(5)
O1—Ni1—O2	89.4(1)	S1—Ni1—S2	93.5(1)
O1—Ni1—S1	88.7(1)	C1—S1—Ni1	97.0(2)
O2—Ni1—S1	176.2(1)	C11—S2—Ni1	96.9(1)
O1—Ni1—S2	175.7(1)	N1—O1—Ni1	118.4(3)
O2—Ni1—S2	88.6(1)	N2—O2—Ni1	118.5(2)

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

D—H...A	D—H	H...A	D...A	D—H...A
C5—H5A...O1 ⁱ	0.93	2.41	3.303(6)	160
C6—H6B... π (Cg3 ⁱⁱ)	0.96	2.68	3.552	151
C12—H12C... π (Cg2 ⁱⁱⁱ)	0.96	2.83	3.653	145

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

Data collection: SMART (Siemens, 1996a). Cell refinement: SAINT (Siemens, 1996b). Data reduction: SAINT. Program(s) used to solve structure: SHELXTL (Sheldrick, 1997). Program(s) used to refine structure: SHELXTL. Molecular graphics: SHELXTL. Software used to prepare material for publication: SHELXTL, PARST (Nardelli, 1995) and PLATON (Spek, 1990).

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