

Bis{methyl N^β -[4-(dipropylamino)benzylidene]-dithiocarbazato}nickel(II)

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Key indicators

Single-crystal X-ray study

$T = 293\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.004\text{ \AA}$

R factor = 0.060

wR factor = 0.144

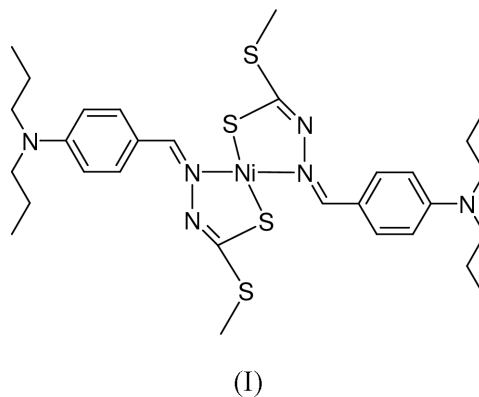
Data-to-parameter ratio = 20.9

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

The Schiff base ligand in the title complex, $[\text{Ni}(\text{C}_{15}\text{H}_{22}\text{N}_3\text{S}_2)_2]$, lost a proton from its tautomeric thiol form and coordinated to Ni(II) *via* the mercapto S and β -N atoms. The geometry around the Ni atom is square planar with two equivalent Ni–N and Ni–S bonds. The two phenyl rings and the coordination moieties are in one plane forming an extensive electronic delocalization system. The structure is governed by C–H \cdots S and C–H \cdots N hydrogen bonds, leading to the formation of centrosymmetric dimers.

Comment

There has been continuous interest in the chemistry of the metal complexes of Schiff bases containing N and S donor atoms. The thio derivatives of the Schiff bases, $\text{RCH}=\text{NNHCSSR}'$, are known to coordinate readily with transition metals to give stable complexes, forming a long π -conjugated system by deprotonation on complex formation (Podhlye & Kauffman, 1985; Tian, Duan, Lu *et al.*, 1996); they have also been shown to possess biological activity (Martinez & Toscano, 1995; Pérez *et al.*, 2001) and non-linear optical (NLO) properties (Zhao *et al.*, 1989; Tian, Duan, Lu & You, 1996). As part of our studies on these thio-Schiff-base-metal complexes, we report the title structure, (I), which is nickel(II) complexed with *S*-methyl dithiocarbazate derived from 4-(dipropylamino)benzaldehyde.



In the title complex, (I), the asymmetric unit consists of one half of the complex molecule. The other half is related by an inversion center at Ni1. The nickel atom is coordinated in a distorted *trans* square-planar geometry. The distortion is evident from the reduction of the N–Ni–S angle to $85.98(6)^\circ$ in the chelate ring (from the ideal value of 90°). The Schiff base loses a proton from its tautomeric thiol form and acts as a singly charged bidentate ligand, coordinating to Ni1 *via* the mercapto S and β -N atoms. The Ni1 atom is displaced

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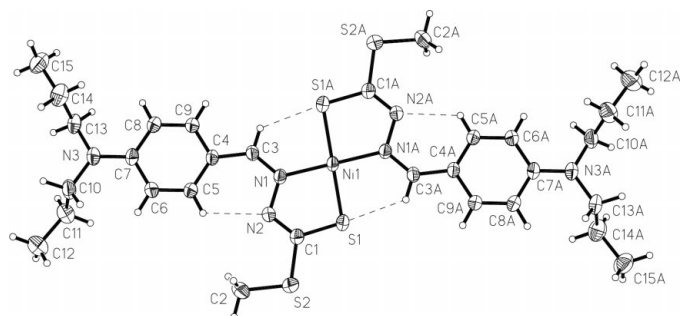


Figure 1
The structure of (I) showing 50% probability displacement ellipsoids and the atom-numbering scheme.

by 0.284 (1) Å from the plane through N1, N2, S1, C1. All bond distances in the side chain are intermediate between a single bond and a double bond. This has been documented before (Duan *et al.*, 1998), indicating the high electron delocalization in the π -system of the whole molecule. The mean plane defined by N1, N2, C1, S1 and S2 makes an angle of 14.2 (1)° with the plane of the phenyl ring, whereas in the uncoordinated molecule it is 5.55 (5)° (Fun *et al.*, 1996).

In the crystal lattice, two intramolecular C—H \cdots S and C—H \cdots N interactions form S1A—Ni1—N1—C3—H3, N2—N1—C3—C4—C5—H5 closed rings, and the molecules are stacked parallel in columns along the *b* axis (Fig. 2).

Experimental

The title compound was prepared by mixing equal volumes (25 ml) of ethanol solutions of nickel acetate (1 mmol) and the ligand (2 mmol). The mixture was refluxed and stirred for 4 h. On cooling to room temperature, it yielded the crystalline complex. Single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of a dichloromethane solution of the complex containing ethanol.

Crystal data

$C_{30}H_{44}N_6NiS_4$	$D_x = 1.327 \text{ Mg m}^{-3}$
$M_r = 675.66$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 8192 reflections
$a = 12.3394 (1) \text{ \AA}$	$\theta = 1.8\text{--}28.3^\circ$
$b = 9.1468 (1) \text{ \AA}$	$\mu = 0.85 \text{ mm}^{-1}$
$c = 15.9725 (1) \text{ \AA}$	$T = 293 (2) \text{ K}$
$\beta = 110.335 (1)^\circ$	Block, black
$V = 1690.40 (3) \text{ \AA}^3$	$0.46 \times 0.38 \times 0.34 \text{ mm}$
$Z = 2$	

Data collection

Siemens SMART CCD area-detector diffractometer	3992 independent reflections
ω scans	2918 reflections with $I > 2\sigma(I)$
Absorption correction: empirical <i>SADABS</i> (Sheldrick, 1996)	$R_{\text{int}} = 0.084$
$T_{\text{min}} = 0.696$, $T_{\text{max}} = 0.761$	$\theta_{\text{max}} = 28.0^\circ$
11381 measured reflections	$h = -15 \rightarrow 16$
	$k = -12 \rightarrow 6$
	$l = -20 \rightarrow 20$

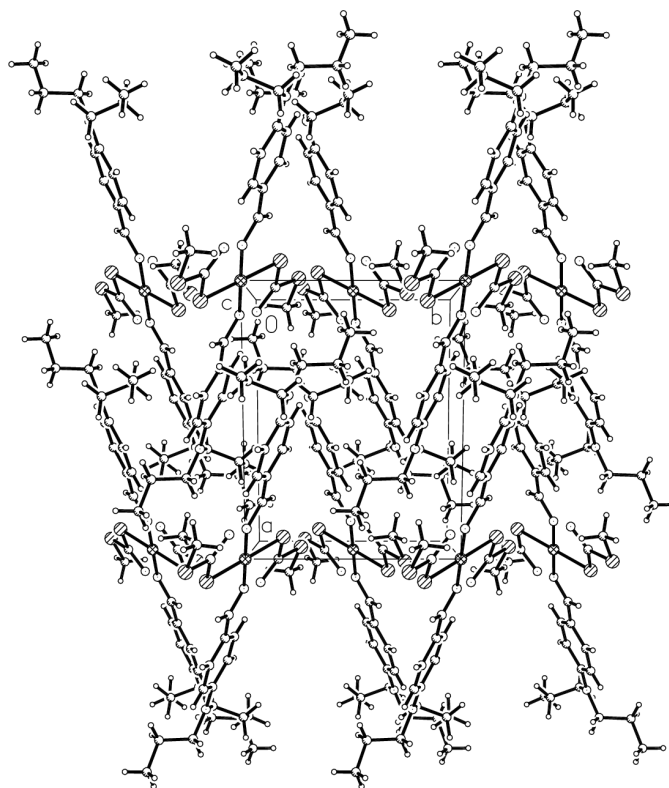


Figure 2
Packing diagram of the structure (I), viewed down the *c* axis.

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0713P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.060$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.144$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 0.95$	$\Delta\rho_{\text{max}} = 0.94 \text{ e \AA}^{-3}$
3992 reflections	$\Delta\rho_{\text{min}} = -0.84 \text{ e \AA}^{-3}$
191 parameters	Extinction correction: <i>SHELXTL</i>
H-atom parameters constrained	Extinction coefficient: 0.057 (4)

Table 1

Selected geometric parameters (Å, °).

Ni1—N1	1.928 (2)	S2—C1	1.746 (3)
Ni1—S1	2.1667 (7)	S2—C2	1.787 (3)
S1—C1	1.719 (2)		
Ni1 ⁱ —Ni1—S1	94.02 (6)	N1—Ni1—S1	85.98 (6)
C2—S2—C1—N2	−3.9 (3)	Ni1—N1—C3—C4	−178.6 (2)

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

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
C3—H3 \cdots S1 ⁱ	0.93	2.44	3.073 (3)	125
C5—H5 \cdots N2	0.93	2.33	2.897 (3)	119

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

After checking their presence in a difference map, all H-atoms were geometrically fixed and allowed to ride on the parent C atoms with C–H distances 0.93–0.97 Å and isotropic displacement parameters.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); 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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