Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.40$, $T_{\max} = 0.48$
9084 measured reflections
8455 independent reflections
5456 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.067$
$\theta_{\max} = 29.96°$
$h = -18 \rightarrow 18$
$k = 0 \rightarrow 22$
$l = 0 \rightarrow 19$
3 standard reflections
frequency: 60 min
intensity decay: 2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.096$
$S = 0.96$
8455 reflections
379 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0484P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.009$
$\Delta\rho_{\max} = 0.87$ e Å^{-3}
$\Delta\rho_{\min} = -1.08$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Re1—O3	1.679 (4)	Re1—Cl1	2.365 (1)
Re1—O2	1.971 (4)	S1—C7	1.726 (5)
Re1—O1	1.984 (3)	S1—C13	1.728 (5)
Re1—N2	2.136 (4)	S2—C26	1.720 (6)
Re1—N1	2.144 (4)	S2—C20	1.732 (5)
O3—Re1—O2	103.6 (2)	O1—Re1—N1	81.3 (1)
O3—Re1—O1	165.0 (2)	N2—Re1—N1	95.0 (2)
O2—Re1—O1	85.0 (1)	O3—Re1—Cl1	101.2 (1)
O3—Re1—N2	86.9 (2)	O2—Re1—Cl1	85.8 (1)
O2—Re1—N2	90.1 (1)	O1—Re1—Cl1	91.5 (1)
O1—Re1—N2	80.8 (1)	N2—Re1—Cl1	171.5 (1)
O3—Re1—N1	91.4 (2)	N1—Re1—Cl1	87.2 (1)
O2—Re1—N1	164.4 (1)		

H atoms were fixed geometrically and refined using constraints with one overall isotropic displacement factor (except for the H atoms of the disordered molecule).

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *NRCVAX* (Gabe *et al.*, 1989). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *NRCVAX*. Software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1478). Services for accessing these data are described at the back of the journal.

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(2-Benzoylpyridine-*N* thiosemicarbazonato-N^1,*S*)chloronickel(II)

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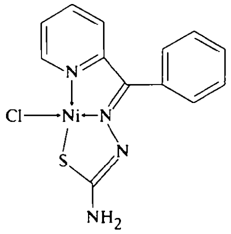
Abstract

In the title compound, [Ni($C_{13}H_{11}N_4S$)Cl], the coordination geometry about the Ni^{II} atom is distorted square planar, involving the pyridine N atom, the S atom and the imino N atom from the thiosemicarbazone ligand, and one Cl atom.

Comment

Thiosemicarbazones belong to a large group of thiourea derivatives, the properties of which are functions of the parent aldehyde or ketone (Podhye & Kauffman, 1985; Liberta & West, 1992; Duan *et al.*, 1996). It has been postulated that many N-heterocyclic carbaldehyde thiosemicarbazones act as tridentate ligands with *N*, *N'* and *S* donors, which bond to Fe or Cu in the synthesis of precursors of DNA (West *et al.*, 1993; Liu *et al.*, 1995). Moreover, it has been reported that transition metal complexes of thiosemicarbazones have the potential ability to show second harmonic generation effects (Long, 1995; Tian *et al.*, 1997; Liu *et al.*, 1999). In the present paper, we report the crystal structure of a new nickel(II) complex with 2-benzoylpyridine thiosemicarbazone, (I).



(I)

The Schiff base in (I) loses a proton from its tautomeric thiol form and acts as a tridentate ligand coordinating to Ni^{II} *via* the mercapto S and β-N atoms. The Ni^{II} coordination is square planar, with a mean deviation of the pyridine N4, imino N3, thiosemicarbazone S1 and chloride Cl1 atoms from their own plane of 0.003 (2) Å. The complex has an *E* configuration about C2—N3, but a *Z* configuration about C1—N2. The bond distances of formal single and double bonds in the thiosemicarbazone point to extensive electron delocalization over the entire group. In the crystal of (I), pairs of molecules related by crystallographic inversion centres form dimers, held together by hydrogen bonds of the type N1—H1N*B*···N2^{i} (Fig. 1); the N···N separation is 3.056 (6) Å and the N—H···N angle is 170 (4)° [symmetry code: (i) $2-x$, $1-y$, $-z$].

Experimental

The title compound was synthesized by refluxing a methanol solution of nickel(II) dichloride hexahydrate, sodium acetate and 2-benzoylpyridine thiosemicarbazone. The resulting orange crystalline solid was isolated and dried under vacuum. Good quality single crystals of (I) were obtained by slow evaporation of a methanol solution.

Crystal data

[Ni($C_{13}H_{11}N_4S$)Cl]
M_r = 349.48
Monoclinic
$P2_1/n$
a = 11.611 (5) Å
b = 10.297 (6) Å
c = 13.165 (3) Å
β = 115.58 (3)°
V = 1419.7 (10) Å^3
Z = 4
D_x = 1.635 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 36 reflections
θ = 6.34–12.01°
μ = 1.695 mm^{-1}
T = 293 (2) K
Block
0.35 × 0.35 × 0.30 mm
Dark brown

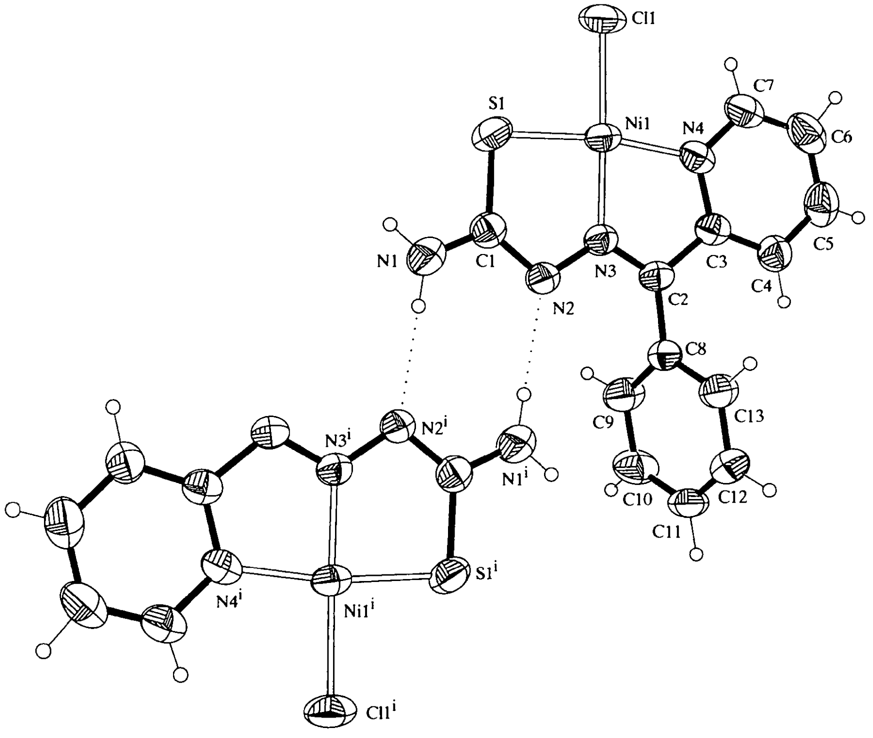


Fig. 1. The two molecules of the title compound, showing the atom-numbering scheme and displacement ellipsoids at the 50% probability level. Dotted lines indicate the hydrogen bonding across the crystallographic inversion centre [symmetry code: (i) $2-x$, $1-y$, $-z$].

Data collection

Siemens *P*4 diffractometer
$2\theta/\omega$ scans
Absorption correction:
  ψ scan (North *et al.*, 1968)
  $T_{min} = 0.562$, $T_{max} = 0.595$
3254 measured reflections
2505 independent reflections
1821 reflections with $I > 2\sigma(I)$
$R_{int} = 0.027$
$\theta_{max} = 25.04°$
$h = -1 \rightarrow 13$
$k = -1 \rightarrow 12$
$l = -15 \rightarrow 14$
3 standard reflections
  every 197 reflections
  intensity decay: 13.6%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.091$
$S = 1.024$
2504 reflections
225 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0330P)^2 + 0.2173P]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.262$ e Å^{-3}
$\Delta\rho_{min} = -0.278$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Ni1—N3	1.864 (3)	N1—C1	1.336 (5)
Ni1—N4	1.924 (3)	N2—C1	1.331 (4)
Ni1—S1	2.143 (1)	N2—N3	1.385 (4)
Ni1—Cl1	2.173 (1)	N3—C2	1.307 (4)
S1—C1	1.741 (4)		
N3—Ni1—N4	83.86 (13)	N4—Ni1—Cl1	97.26 (10)
N3—Ni1—S1	87.08 (10)	S1—Ni1—Cl1	91.80 (5)
N4—Ni1—S1	170.93 (9)	C1—S1—Ni1	95.54 (14)
N3—Ni1—Cl1	178.85 (10)	C1—N1—H1N*B*	121 (3)

All H atoms were found from a difference map and refined isotropically; C—H distances are in the range 0.87 (4)–0.97 (4) Å.

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *SHELXTL* (Siemens, 1995). Program(s) used to solve structure: *SHELXTL*. Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*. Geometric calculations: *PARST* (Nardelli, 1983).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: HA1262). Services for accessing these data are described at the back of the journal.

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Tris[3,6-bis(2-pyridyl)pyridazine-N^1,N^6]-nickel(II) diperchlorate 0.11-hydrate

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Abstract

The structure of the title complex, $[Ni(C_{14}H_{10}N_4)_3](ClO_4)_2\cdot0.11H_2O$, consists of well separated mononuclear tris[3,6-bis(2-pyridyl)pyridazine]nickel(II) cations and perchlorate anions. There are two crystallographically independent cations, in which the Ni atoms are surrounded in a distorted octahedral arrangement by three bulky organic ligands, with four possible N-donor atoms each, acting as bidentate chelates. The Ni—N distances range from 2.045 (4) to 2.094 (3) Å and the bite angles range from 77.6 (1) to 78.4 (1)°. The lattice water molecule is hydrogen bonded to two perchlorate anions.

Comment

Ligands that contain a delocalized π system and which can serve as molecular bridges between metal centres give inorganic chemists access to a wide variety of transition metal complexes with various structures. One such ligand is 3,6-bis(2-pyridyl)pyridazine (dppa), which has been used to synthesize many mono-, bi- and polynuclear complexes, *e.g.* mononuclear $[RuCl_2(CO)_2(dppa)]$ (De Munno *et al.*, 1988), $[Cu(dppa)_2Cl]Cl\cdot5H_2O$ (Lanfredi *et al.*, 1982) and $[Mn(dppa)_2(NO_3)_2]$ (Andrew *et al.*, 1975), binuclear $[Cu_2Cl_4(H_2O)(dppa)]$ (De Munno & Bruno, 1984) and $[Ni_2(dppa)_2(H_2O)_4](ClO_4)_4$ (Ball & Blake, 1969), and polynuclear $\{[Cu_2(dppa)Cl_2(H_2O)(OH)]Cl\}_n\cdot2nH_2O$ (Dapporto *et al.*, 1983). We report here