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Bis(2-formylpyridine semicabazonato)nickel(II)

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Key indicators

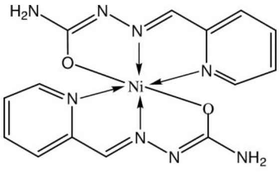
Single-crystal X-ray study
T = 193 K
Mean σ(C–C) = 0.004 Å
R factor = 0.026
wR factor = 0.056
Data-to-parameter ratio = 14.0

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

The Ni atom in the title complex, $[Ni(C_7H_7N_4O)_2]$, is octahedrally coordinated by two mono-deprotonated Schiff bases that are derived from the condensation of pyridine-2-carbaldehyde and semicarbazide; the Schiff bases act as meridional tridentate ligands, each of them coordinating the metal with the deprotonated amidate oxygen [Ni—O = 2.0909 (15) and 2.0959 (15) Å], imine nitrogen [Ni—N = 1.9892 (18) and 1.9822 (18) Å] and pyridine nitrogen [Ni—N = 2.100 (2) and 2.1317 (2) Å]. The dihedral angle formed by the mean planes of the bicyclic chelate systems of each of the ligands is equal to 87.69 (4)°. The crystal packing is stabilized by intermolecular hydrogen bonds involving N—H···O and C—H···O interactions.

Comment

Metal complexes of Schiff bases synthesized by the condensation of pyridine-2-carbaldehyde and thiosemicarbazide, semicarbazide and other amines (Chen *et al.*, 2003; Javier & Teofilo, 1999; Singh *et al.*, 2002; Wang *et al.*, 2004) have received attention owing to their antimicrobial, cytotoxic and antioxidant activities (Reddy *et al.*, 1999; Tarafder *et al.*, 2001). A number of such complexes have been crystallographically characterized (Alistair *et al.*, 1987; Kovala-Demertzi *et al.*, 1999; Wang *et al.*, 2004). However, so far, only a few studies on the synthesis, spectroscopic characterization and antimicrobial activities of metal complexes with Schiff bases derived from pyridine-2-carbaldehyde and semicarbazide (H-Pysc) have been reported (Iskander *et al.*, 1979; Liang *et al.*, 2002); as far as we are aware, no crystal structures of its transition metal complexes have been published. In order to investigate the coordination behavior of the H-Pysc ligand, we synthesized the title complex, (I), and determined its crystal structure (Fig. 1).



(I)

The Ni1 atom has a distorted octahedral coordination formed by two tridentate meridional ligands of H-Pysc; the dihedral angle formed by the mean planes of the bicyclic chelate nodes of the two ligands is equal to 87.69 (4)°. The Ni1—N1 [2.100 (2) Å] and Ni1—N5 [2.1317 (19) Å] bonds are similar to earlier reported Ni—N(pyridine) bonds [*e.g.* 2.101 Å in Drew *et al.*, 1972)]; the Ni1—N2 [1.9892 (18) Å],

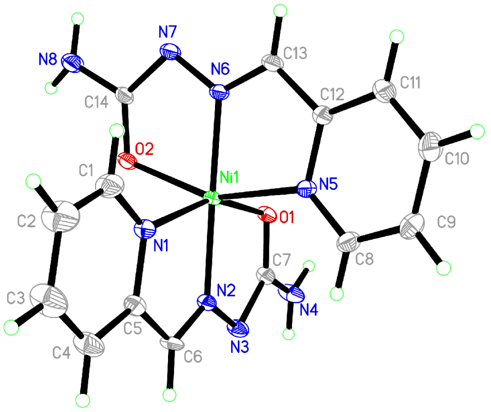


Figure 1
View of the title complex, showing 30% probability displacement ellipsoids and the atom-numbering scheme.

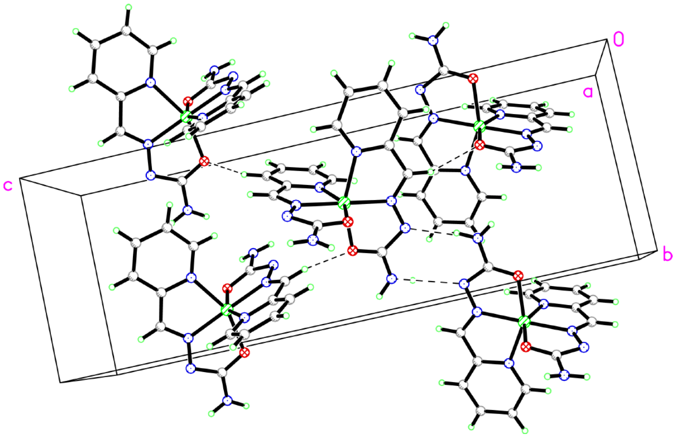


Figure 2
A packing diagram of the crystal structure of the title compound (dashed lines indicate hydrogen bonds).

Ni1—N6 [1.9822 (18) Å], Ni1—O1 [2.0909 (15) Å] and Ni1—O2 [2.0959 (15) Å] bonds are comparable to those reported for other nickel(II) complexes with semicarbazone fragments (Carcelli *et al.*, 1999; Kasuga *et al.*, 2001). The involvement of the O atom in the chelate formation shifts the keto–enolic equilibrium towards the enolic form, which is particularly evident in the the C—O bonds C7—O1 [1.265 (3) Å] and C14—O2 [1.266 (3) Å], significantly longer than C═O double bonds [*e.g.* C═O = 1.237 (4) Å (Liang *et al.*, 2002)]. Both pyridine-2-carbaldehyde semicarbazone ligands have the *E* configuration with respect to the azomethine double bond. As one can observe, the Ni—N bond distances involving the azomethine N atoms (N2 and N6) are significantly shorter than those involving the pyridyl N atoms (N1 and N5). This has been attributed to the fact that the negative charge due to the deprotonation of N3 and N7 is partially localized on the atoms N2 and N6 (Khalil *et al.*, 1994).

The distortions of octahedral coordination of the Ni atom are caused by formation of the chelate rings and are manifested in the chelate bite angles being smaller than 90° [N2—Ni1—O1 = 76.40 (7)°, N2—Ni1—N1 = 79.14 (8)°, O2—Ni1—N6 = 76.75 (6)° and N5—Ni1—N6 = 78.60 (7)°], as well as the N1—Ni1—O1 [155.5 (7)°] and N5—Ni1—O2 [155.21 (7)°] angles deviating markedly from 180°. These values are comparable with those reported for other nickel(II) complexes containing semicarbazone Schiff base ligands (Kasuga *et al.*, 2001).

As shown in Fig. 2, the crystal packing is stabilized by intermolecular N—H⋯O hydrogen bonds and C—H⋯O interactions.

Experimental

The Schiff base of pyridine-2-carbaldehyde semicarbazone (H-Pysc) was prepared according to Gong *et al.* (1994). Single crystals of the title complex suitable for X-ray diffraction study were obtained by the reaction of $Ni(ClO_4)_2{\cdot}6H_2O$ with H-Pysc. $Ni(ClO_4)_2{\cdot}6H_2O$ (0.2 mmol), H-Pysc (0.4 mmol), methanol (0.6 ml) and CH_2Cl_2 (0.8 ml) were placed in a thick Pyrex tube (*ca* 20 ml). The tube was then cooled with liquid N_2, evacuated under vacuum and sealed with a torch. The tube was heated at 343 K for 3 d to yield a green block-shaped crystalline product in a yield of 65%.

Crystal data

$[Ni(C_7H_7N_4O)_2]$
$M_r = 385.04$
Tetragonal, $P4_3$
$a = 8.2766$ (12) Å
$c = 23.648$ (4) Å
$V = 1619.9$ (4) Å^3
$Z = 4$
$D_x = 1.579$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 8353 reflections
$\theta = 3.4$–27.5°
$\mu = 1.22$ mm^{-1}
$T = 193$ (2) K
Elongated octahedron, dark red
0.54 × 0.37 × 0.30 mm

Data collection

Rigaku Mercury CCD diffractometer
ω scans
Absorption correction: multi-scan (Jacobson, 1998)
$T_{\min} = 0.557$, $T_{\max} = 0.710$
18151 measured reflections

3413 independent reflections
3368 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.033$
$\theta_{\max} = 27.5°$
$h = -8 \rightarrow 10$
$k = -10 \rightarrow 10$
$l = -30 \rightarrow 25$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.026$
$wR(F^2) = 0.056$
$S = 1.12$
3413 reflections
243 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0203P)^2 + 0.748P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.19$ e Å^{-3}
$\Delta\rho_{\min} = -0.21$ e Å^{-3}
Absolute structure: Flack (1983); 1512 Friedel pairs
Flack parameter = 0.445 (10)

Table 1
Selected geometric parameters (Å, °).

Ni1—O1	2.0909 (15)	Ni1—N5	2.1317 (19)
Ni1—O2	2.0959 (15)	Ni1—N6	1.9822 (18)
Ni1—N1	2.100 (2)	C7—O1	1.265 (3)
Ni1—N2	1.9892 (18)	C14—O2	1.266 (3)
N1—Ni1—N2	79.14 (8)	N2—Ni1—O1	76.40 (7)
N1—Ni1—N5	89.77 (7)	N2—Ni1—O2	103.45 (7)
N1—Ni1—N6	101.95 (8)	N5—Ni1—O1	96.33 (6)
N2—Ni1—N5	101.25 (7)	N5—Ni1—O2	155.21 (7)
N2—Ni1—N6	178.90 (8)	N6—Ni1—O1	102.52 (7)
N5—Ni1—N6	78.60 (7)	N6—Ni1—O2	76.75 (7)
N1—Ni1—O1	155.50 (7)	O1—Ni1—O2	91.49 (6)
N1—Ni1—O2	92.80 (7)		

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

D—H$\cdots$$A$	D—H	H$\cdots$$A$	$D$$\cdots$$A$	D—H$\cdots$$A$
N4—H4$B$$\cdots$N7^{i}	0.88 (2)	2.09 (2)	2.959 (3)	170
N8—H8$A$$\cdots$N3^{ii}	0.88 (2)	2.12 (2)	2.993 (3)	171
C4—H4$\cdots$O1^{iii}	0.95	2.46	3.152 (3)	128
C9—H9$\cdots$O1^{iv}	0.94	2.59	3.487 (3)	156
C13—H13$\cdots$O2^{v}	0.95	2.26	3.150 (3)	154

Symmetry codes: (i) $y, -x, \frac{1}{4}+z$; (ii) $-y, x, z-\frac{1}{4}$; (iii) $1+y, 1-x, \frac{1}{4}+z$; (iv) $1+x, y, z$; (v) $1-y, x, z-\frac{1}{4}$.

H atoms bound to C atoms were positioned geometrically and included in the refinement in the riding-model approximation [C—H = 0.93 Å and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C)]. H atoms bound to atoms N4 and N8 were located in a difference map and refined isotropically subject to N—H distance restraints of 0.86 (1) Å. Due to a Flack (1983) parameter of 0.445 (1), the refinement was carried out based on the racemic twin model. The absolute structure is reversed and the space group $P4_1$ changed to $P4_3$.

Data collection: *CrystalClear* (Rigaku, 1999); cell refinement: *CrystalClear*; data reduction: *CrystalStructure* (Rigaku and Rigaku/MSC, 2000); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Siemens, 1994); software used to prepare material for publication: *SHELXTL*.

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