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Transition metal complexes with thiosemicarbazide-based ligands. XV. A square-pyramidal Ni^{II} complex with an asymmetric coordination of 2,6-diacetylpyridine bis(*S*-methylisothiosemicarbazone)

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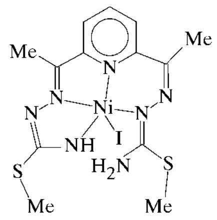
The title compound, [diacetylpyridine bis(*S*-methylisothiosemicarbazonato)]iodonickel(II), $[Ni(C_{13}H_{18}N_7S_2)I]$, is the first example of a complex involving the ^{2}N coordination of the isothiosemicarbazide moiety. 2,6-Diacetylpyridine bis(*S*-methylisothiosemicarbazone), as a potentially pentadentate ligand (N_5), is coordinated as a tetradentate species, whereby one (deprotonated) isothiosemicarbazide moiety is coordinated in the usual way (^{1}N^{4}N), but the other (neutral) is bonded *via* the ^{2}N atom only, the fourth ligator being the pyridine nitrogen. The difference in coordination mode of the isothiosemicarbazide moiety is reflected in the ^{1}N—^{2}N bond lengths of 1.359 (4) and 1.379 (3) Å in the deprotonated and undeprotonated moieties, respectively. The structure contains three fused chelate rings in a 5:5:6 arrangement. The six-membered ring has a non-planar conformation.

Comment

Up to now, more than 60 metal complexes with isothiosemicarbazides and isothiosemicarbazones of different denticity have been characterized by X-ray analysis (Malinovskii *et al.*, 1985; Obadović *et al.*, 1997; Bogdanović *et al.*, 1999). Consequently, it has been found that the isothiosemicarbazone moiety is coordinated *via* the terminal N atoms ^{1}N and ^{4}N. To our knowledge, the only exceptions are the Ni^{II} complex with diacetyl monoxime *S*-methylisothiosemicarbazone (Biyuskin *et al.*, 1986) and the Pd^{II} complex with salicylaldehyde *S*-methylisothiosemicarbazide (Revenko *et al.*, 1996), in which the isothiosemicarbazide moiety is coordinated *via* ^{1}N, and *via* ^{1}N plus the alkylated S atom, respectively.

The common ^{1}N^{4}N coordination mode of both isothiosemicarbazide moieties has also been found in the pentagonal–bipyramidal Mn^{II} complex with 2,6-diacetylpyridine bis(*S*-methylisothiosemicarbazone) (*L*) as a pentadentate ligand (N_5) of the formula [Mn(NCS)*L*(MeOH)]NCS (Leovac *et al.*, 1997).

The crystal structure of the Ni^{II} complex with the monoanion of this ligand (L—H), (I), described in the present work, represents the first example of a new mode of coordination of this class of ligands, *i.e.* one isothiosemicarbazide moiety is coordinated only through the ^{2}N atom which, together with the common ^{1}N^{4}N coordination of the other (deprotonated) isothiosemicarbazide moiety and the pyridine nitrogen, gives rise to a tetradentate character for this ligand (Fig. 1).



(I)

The consequence of such an asymmetric coordination is seen most clearly as the difference in the N1—N2 and N1′—N2′ bond lengths, which are 1.379 (3) and 1.359 (4) Å, as well as the location of the H atom in the neutrally coordinated isothiosemicarbazide fragment; if the isothiosemicarbazide moiety is coordinated in its neutral form in the usual way, one of the H atoms is always bonded to ^{2}N, $=^{1}N-^{2}NH-^{3}C(-SR)=^{4}NH$ (imido form), so that this fragment has an *E* configuration. Such an instance has also been found in the structure of the previously mentioned Mn^{II} complex with *L*, in which a bidentate coordination (^{1}N^{4}N) in the imido form has been observed for both isothiosemicarbazide fragments. In contrast to this, the neutral free ligands (Argay *et al.*, 1983; Bourosh *et al.*, 1987, 1989; Simonov *et al.*, 1990) are characterized by a *Z* configuration with both H atoms located on the ^{4}N atom, $=^{1}N-^{2}N=^{3}C(-SR)-^{4}NH_2$ (amido form). Because of the absence of the coordinated N3 atom in the title Ni^{II} complex, the undeprotonated isothiosemicarbazide fragment from this complex retains a *Z* configuration and the amido form as in the case with the non-coordinated ligands (contrary to the coordinated ligands).

The Ni atom is located in a pseudo-square-pyramidal surrounding (with the tetradentate ligand around the central ion in the basal plane and the I atom in the apical position). The Ni—I bond of 3.485 (2) Å is very elongated, and can be considered as an electrostatic interaction between the two atoms. However, considering that the iodine is situated in the regular apical position, with angles to the corresponding coordinated atoms from the basal plane of less than 100.4°, it can be supposed that the Ni atom is in a pseudo-square-pyramidal environment. The basal coordination plane is slightly puckered, showing a tetrahedral distortion with a maximum displacement of 0.097 (3) Å, while the Ni atom is displaced by 0.0495 (13) Å from this plane towards the apical iodine.

The basal coordination plane is characterized by the very deformed angles between the coordinated atoms and the metal atom. The largest deviation is seen for the angle N2—Ni—N3′, which is a consequence of the steric hindrance between the N3′H and N3H2 groups, with a closest distance of 2.31 (5) Å between the H atoms. The N1′/N2′/C1′/N3′ fragment is nearly planar with a torsion angle of 3.4 (4)°, which is commonly observed for the isothiosemicarbazide ligands. However, in contrast, the corresponding N1/N2/C1/N3 fragment is not planar, the torsion angle being 167.5 (3)°. This difference is also a consequence of the ligand tendency to diminish the repulsion of the N3′H and N3H2 groups. The Ni—N1′ distance is significantly shorter than the distances to the other N atoms, which could be related to the distribution of the negative charge on the deprotonated isothiosemicarbazide fragment to which N1′ belongs.

The five-membered rings are almost planar. Their total puckering amplitudes are 0.074 (3) and 0.052 (2) Å for Ni/N1′/N2′/C1′/N3′ and Ni/N1′/C3′/C9/N4, showing half-chair and envelope conformations, respectively. The six-membered chelate ring is puckered and assumes a conformation between half-chair and envelope, which can be explained in terms of the $^6S_7$ form (Boeyens, 1978) (the Ni atom was taken as the first atom in the ring). The puckering parameters (Cremer & Pople, 1975) for the Ni/N4/C5/C3/N1/N2 sequence are q^2 = 0.210 (3) Å, q^3 = −0.079 (3) Å, Q = 0.224 (3) Å, θ = 110.7 (9)° and φ = 139.4 (8)°. The maximum deviation from the best plane is 0.292 (3) Å for the N2 atom.

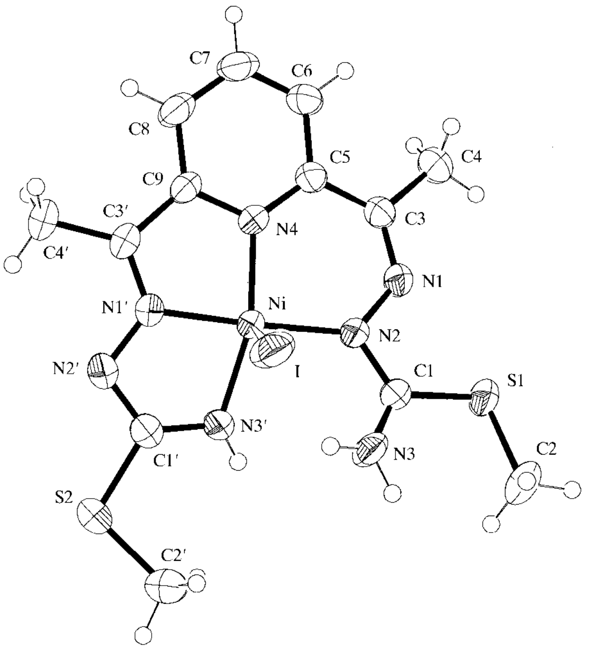


Figure 1
A view of the molecular structure of (I) showing the atom labels. Displacement ellipsoids are shown at the 50% probability level.

The crystal-packing arrangement in (I) consists of parallel layers with a shortest distance C1′···C8$^{\rm i}$ of 3.455 (5) Å [symmetry code: (i) $-x+1, -y+1, -z+1$]. Inside the layers, the shortest contact is between the S atoms: S2···S2$^{\rm ii}$ = 3.364 (2) Å [symmetry code: (ii) $-x+1, -y+1, -z$].

Experimental

The dark brown diamagnetic monocrystals of the title complex result from a template synthesis, *i.e.* the reaction of equimolar amounts of warm MeOH solutions (reflux, 40 min) of NiL'_2I$_2$ (L' = 3-methylisothiosemicarbazide; Leovac *et al.*, 1980) and 2,6-diacetylpyridine.

Crystal data

[Ni($C_{13}H_{18}N_7S_2$)I]
M_r = 522.07
Triclinic, $P\overline{1}$
a = 7.713 (2) Å
b = 10.653 (3) Å
c = 12.535 (3) Å
α = 108.08 (5)°
β = 101.01 (4)°
γ = 101.51 (6)°
V = 923.4 (4) Å^3
Z = 2
D_x = 1.878 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 23 reflections
θ = 12.10–16.56°
μ = 2.959 mm^{-1}
T = 293 (3) K
Prismatic, dark brown
0.34 × 0.29 × 0.28 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: by integration (*ABSORB*; DeTitta, 1985)
$T_{\rm min}$ = 0.363, $T_{\rm max}$ = 0.437
4230 measured reflections
3325 independent reflections
2926 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.020
$\theta_{\rm max}$ = 25.30°
$h = -9 \rightarrow 9$
$k = -12 \rightarrow 12$
$l = -14 \rightarrow 15$
2 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.027
$wR(F^2)$ = 0.070
S = 1.356
3325 reflections
229 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0337P)^2 + 0.0788P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max}$ = 0.79 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.71 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ni—N1′	1.844 (2)	N2′—C1′	1.339 (4)
Ni—N4	1.879 (2)	N3′—C1′	1.315 (4)
Ni—N3′	1.890 (3)	N1—C3	1.286 (4)
Ni—N2	1.893 (3)	N1—N2	1.379 (3)
N1′—C3′	1.300 (4)	N2—C1	1.343 (4)
N1′—N2′	1.359 (4)	N3—C1	1.308 (4)
N1′—Ni—N4	83.92 (12)	N1′—Ni—N2	176.51 (11)
N1′—Ni—N3′	80.91 (12)	N4—Ni—N2	93.21 (12)
N4—Ni—N3′	162.78 (12)	N3′—Ni—N2	102.21 (12)
C3—N1—N2—Ni	21.4 (4)	N2—Ni—N4—C5	7.8 (3)
N4—Ni—N2—N1	−21.0 (3)	Ni—N4—C5—C3	5.3 (4)
N2—N1—C3—C5	−2.6 (5)	N1—C3—C5—N4	−11.3 (5)

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

D—H$\cdots$$A$	D—H	H$\cdots$$A$	$D$$\cdots$$A$	D—H$\cdots$$A$
N3—H11$\cdots$I	0.84 (6)	2.97 (5)	3.635 (4)	138 (4)
N3—H12$\cdots$I^{i}	0.86 (4)	2.83 (5)	3.583 (4)	147 (4)

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

All H atoms were found in difference Fourier maps, but those connected to C atoms were placed at calculated positions using a riding model [isotropic displacement parameters equal to 1.2 (or 1.5 for methyl H atoms) times the equivalent isotropic displacement parameter of the parent atom].

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: a local modification of *MolEN* (Fair, 1990); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*III (Burnett & Johnson, 1996); software used to prepare material for publication: *SHELXL*97 and *PARST* (Nardelli, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1472). Services for accessing these data are described at the back of the journal.

References

Argay, Gy., Kálmán, A., Ribár, B., Leovac, V. & Petrović, A. (1983). *Monatsh. Chem.* **114**, 1205–1211.

Biyuskin, V. N., Gerasimov, V. I. & Rozhelestvenskaya, I. V. (1986). *Koord. Khim.* **12**, 1270–1275.

Boeyens, J. C. A. (1978). *J. Cryst. Mol. Struct.* **8**, 317–320.

Bogdanović, G. A., Spasojević-de Biré, A., Leovac, V. M. & Češljević, V. I. (1999). *Acta Cryst.* C**55**, 1656–1658.

Bourosh, P., Gerbeleu, N., Revenko, N., Simonov, Yu., Beljskiy, V. & Virtosu, N. (1987). *Zh. Neorg. Khim.* **32**, 2482–2488.

Bourosh, P., Simonov, Yu., Arion, V., Sobolv, A., Gerbeleu, N. & Pahopol, V. (1989). *Kristallographiya*, **34**, 637–641.

Burnett, M. N. & Johnson, C. K. (1996). *ORTEP*III. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.

Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.

DeTitta, G. T. (1985). *J. Appl. Cryst.* **18**, 75–79.

Enraf–Nonius (1989). *CAD*-4 *Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.

Fair, C. K. (1990). *MolEN.* Enraf–Nonius, Delft, The Netherlands.

Leovac, V. M., Babin, M., Canić, V. & Gerbeleu, N. V. (1980). *Z. Anorg. Allg. Chem.* **471**, 227–232.

Leovac, V. M., Ivegeš, E. Z., Češljević, V. I., Divjaković, V. & Klement, U. (1997). *J. Serb. Chem. Soc.* **62**, 837–845.

Malinovskii, T. I., Simonov, Yu. A., Gerbeleu, N. V., Yampolskaya, M. A., Revenko, M. D. & Shova, S. G. (1985). *Probl. Kristallokhim. Nauk. Mosk.* pp. 39–68.

Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.

Obadović, D. Z., Divjaković, V. & Leovac, V. M. (1997). *Polyhedron*, **16**, 695–699.

Revenko, M. D., Bulmaga, P. I., Ketrash, P. M., Simonov, Yu. A. & Bel'skii, V. K. (1996). XIIth Conference of Physical Methods in Coordination and Supramolecular Chemistry, Kishinew, Moldova, Book of Abstracts, p. 138.

Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.

Simonov, Yu., Gerbeleu, N., Bourosh, P., Arion, V., Garnovskiy, A., Sobolv, A. & Alekseenko, V. (1990). *Zh. Strukt. Khim.* **31**, 199–202.