# metal-organic compounds

# Transition metal complexes with thiosemicarbazide-based ligands. XLII.[1] Bis(S-methylisothiosemicarbazido-$N^1$,$N^4$)bis(pyrazole-$N^2$)nickel(II) diiodide

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In the title compound, $[Ni(C_2H_7N_3S)_2(C_3H_4N_2)_2]I_2$, the $Ni^{II}$ ion assumes a centrosymmetric distorted octahedral geometry. The two molecules of *S*-methylisothiosemicarbazide are coordinated as bidentate ligands *via* the terminal N atoms, forming five-membered chelate rings. The I atoms are approximately in the equatorial plane of the chelate rings at a similar distance from both. The five-membered chelate rings are almost planar and exhibit flattened envelope conformations. There is a weak intermolecular interaction between the lone pair of electrons of the S atom and the center of the pyrazole ring.

## Comment

Up to now, X-ray structure analysis has been used to characterize a number of $Ni^{II}$ complexes with thiosemicarbazide (TSC), some of which present an octahedral geometry (Hazell, 1968, 1976; Ballard *et al.*, 1974; Kumar *et al.*, 1991; Burrows *et al.*, 1996), the others having a square-planar geometry (Gronbaek & Rasmussen, 1962; Hazell, 1968, 1972; Burrows *et al.*, 1996). Structures have also been reported with an uncoordinated TSC moiety (Andreetti *et al.*, 1970; Gubin *et al.*, 1984; Waskowska, 1998). In the $Ni^{II}$–TSC complexes, TSC is coordinated as a neutral ligand, (I). *S*-Methylisothiosemicarbazide [ITSC, (II)] also coordinates as a neutral ligand, forming either square-planar (Divjaković & Leovac, 1979; Divjaković *et al.*, 1983; Divjaković, 1984; Obadović *et al.*, 1997)

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[1] Part XLI: Bogdanović *et al.* (2001).

or octahedral complexes (Bourosh *et al.*, 1987) with $Ni^{II}$. However, in contrast to TSC, which is coordinated *via* the $N^1$ and S atoms, ITSC is coordinated *via* the terminal $N^1$ and $N^4$ atoms.
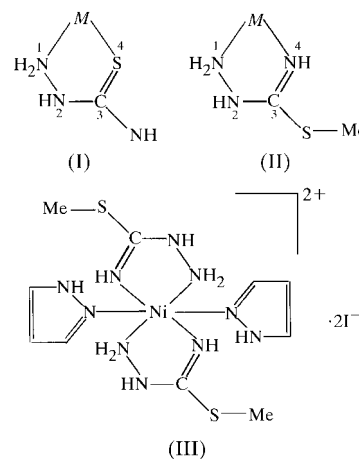


A consequence of the different coordination modes of these two ligands is the difference in the electronic delocalization in the $N^2$—$C^3$—$N^4$ fragment. Namely, the $N^2$—$C^3$ bond is about 0.05 Å longer than the $C^3$—$N^4$ bond for the ITSC complexes, whereas these two bonds are approximately equal in the TSC complexes. Thus, the ratio of bond lengths does not depend on the type of Ni complex (octahedral or planar). However, there is a significant difference in the metal–ligand distance depending on the metal coordination polyhedron. On the one hand, the Ni—$N^1$ distance of the square-planar complexes is about 0.07 Å shorter then in the octahedral complexes, whereas the Ni—$N^1$ distance is approximately the same in complexes (TSC and ITSC) of the same coordination number. On the other hand, the Ni—$N^4$ distances in the ITSC complexes are always shorter by 0.05–0.06 Å than the Ni—$N^1$ distances. This can be explained by the different hybridization
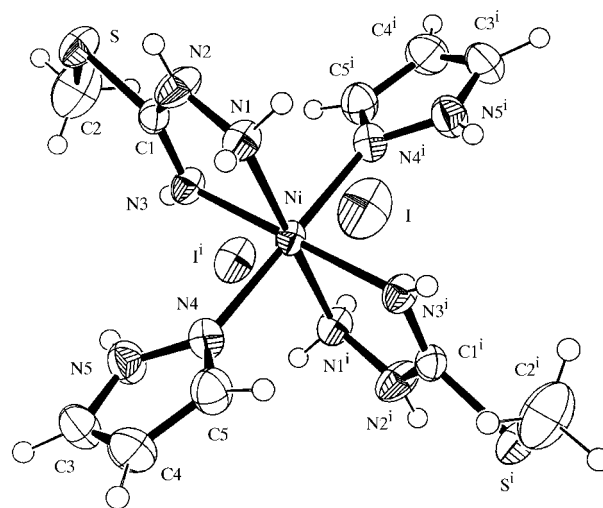


**Figure 1**
A view of the molecular structure of $[Ni(ITSC)_2(pz)_2]I_2$ showing the atom-labeling scheme. Displacement ellipsoids are at the 50% probability level. [Symmetry code: (i) $1 - x$, $-y$, $1 - z$.]

character of the $N^1$ ($sp^3$) and $N^4$ ($sp^2$) atoms, due to the partial $\pi$-character of the Ni—$N^4$ bond.

The novel $Ni^{II}$ complex presented in this work, [Ni(ITSC)$_2$(pz)$_2$]I$_2$ (pz is pyrazole), (III), has an octahedral centrosymmetric coordination. The chelate rings are almost planar, displaying a flattened envelope conformation. The Ni atom is 0.324 (6) Å out of the mean plane defined by the other ring-forming atoms (N1, N2, C1 and N3). The puckering parameters (Cremer & Pople, 1975) for the five-membered chelate ring are $Q$ = 0.155 Å and $\varphi$ = 186.57°. The ITSC ligand is coordinated *via* the two terminal N atoms [Ni—N1 = 2.120 (3) Å and Ni—N3 = 2.053 (3) Å]. Therefore, as observed previously for other ITSC complexes, the Ni—N3 bond is about 0.07 Å shorter than the Ni—N1 bond. Iodine is not involved in metal coordination, the shortest Ni···I distance being 4.556 (2) Å.

Due to the formation of five-membered rings, the coordination around nickel is characterized by deformed equatorial angles [N1—Ni—N3 = 79.00 (12)°]. The I atoms are in the equatorial plane of the chelate ligand (Fig. 1) and lie on the line which approximately bisects the N1—Ni—N3′ angle [100.8 (2)°]; they form weak hydrogen bonds with the N1H$_2$ and N2H groups (Table 2).

The S atom is directed to the center ($M$) of the pyrazole ring at $-x$, $-y$, $1 - z$, at a distance of 3.45 Å. The angle between the plane through the C1—S—C2 fragment and the mean plane of the pyrazole ring is 89.5 (2)°. Considering these geometrical parameters and also the fact that the angles C2—
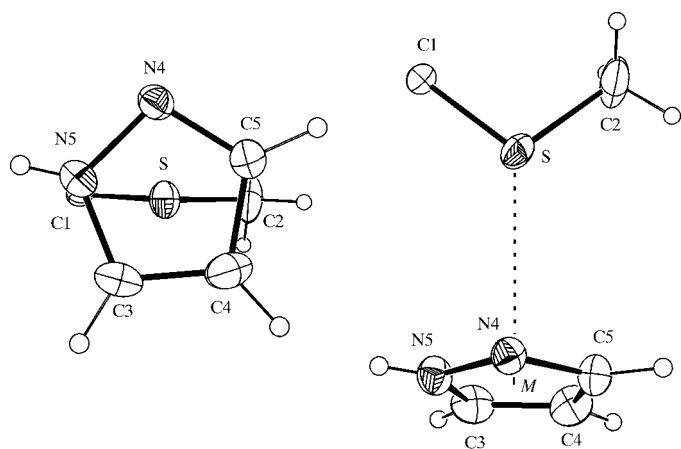


**Figure 2**
Two projections of the crystal structure fragments showing a potential weak interaction between the S atom and center of the pyrazole ring ($M$).

S—$M$ (128.3°) and C1—S—$M$ (128.8°) are almost identical, it is obvious that some kind of interaction exists between the S atom and the pyrazole ring (Fig. 2). The free electron pair of the S atom is ideally oriented toward the ring center, probably due to a partial positive complex cation charge located on the pyrazole ring. This interaction is weak, but it cannot be coincidental due to the probability of free rotation of the pyrazole ring around the Ni—N4 bond.

## Experimental

*Crystal data*

| | |
|---|---|
| [Ni(C$_2$H$_7$N$_3$S)$_2$(C$_3$H$_4$N$_2$)$_2$]I$_2$ | $Z$ = 1 |
| $M_r$ = 659 | $D_x$ = 1.993 Mg m$^{-3}$ |
| Triclinic, $P\bar{1}$ | Mo $K\alpha$ radiation |
| $a$ = 7.911 (3) Å | Cell parameters from 25 |
| $b$ = 8.798 (3) Å | reflections |
| $c$ = 8.819 (2) Å | $\theta$ = 13.2–17.6° |
| $\alpha$ = 102.92 (3)° | $\mu$ = 3.90 mm$^{-1}$ |
| $\beta$ = 92.43 (2)° | $T$ = 293 (3) K |
| $\gamma$ = 112.05 (2)° | Prismatic, violet |
| $V$ = 549.1 (3) Å$^3$ | 0.36 × 0.29 × 0.25 mm |

*Data collection*

| | |
|---|---|
| Enraf–Nonius CAD-4 | $R_{int}$ = 0.014 |
| diffractometer | $\theta_{max}$ = 27.0° |
| $\omega/2\theta$ scans | $h$ = 0 → 10 |
| Absorption correction: Gaussian | $k$ = −11 → 10 |
| (Spek, 1990) | $l$ = −11 → 11 |
| $T_{min}$ = 0.361, $T_{max}$ = 0.469 | 2 standard reflections |
| 2556 measured reflections | frequency: 60 min |
| 2378 independent reflections | intensity decay: none |
| 2119 reflections with $I > 2\sigma(I)$ | |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | $w$ = 1/[$\sigma^2(F_o^2)$ + (0.0564$P$)$^2$ |
| $R[F^2 > 2\sigma(F^2)]$ = 0.035 | + 0.5270$P$] |
| $wR(F^2)$ = 0.095 | where $P$ = ($F_o^2$ + 2$F_c^2$)/3 |
| $S$ = 1.11 | $(\Delta/\sigma)_{max}$ < 0.001 |
| 2378 reflections | $\Delta\rho_{max}$ = 1.49 e Å$^{-3}$ |
| 135 parameters | $\Delta\rho_{min}$ = −1.07 e Å$^{-3}$ |
| H atoms treated by a mixture of | |
| independent and constrained | |
| refinement | |

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

| | | | |
|---|---|---|---|
| Ni—N1 | 2.120 (3) | N5—C3 | 1.334 (6) |
| Ni—N3 | 2.053 (3) | N5—N4 | 1.337 (4) |
| Ni—N4 | 2.122 (3) | C1—N2 | 1.343 (5) |
| N1—C2 | 1.407 (4) | C1—S | 1.754 (3) |
| N3—C1 | 1.287 (4) | C2—S | 1.780 (6) |
| N4—C5 | 1.328 (5) | | |
| | | | |
| C1—N3—Ni | 113.8 (2) | N3—Ni—N4 | 91.49 (12) |
| C1—N2—N1 | 118.7 (3) | N2—C1—N3 | 119.4 (3) |
| N1—Ni—N3 | 79.00 (12) | N2—N1—Ni | 107.4 (2) |
| N1—Ni—N4 | 89.57 (13) | | |

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N1—H2N1···I | 0.91 (7) | 2.96 (7) | 3.585 (3) | 128 (5) |
| N2—H1N2···I$^i$ | 0.77 (5) | 2.94 (5) | 3.548 (4) | 138 (4) |
| N3—H1N3···I$^{ii}$ | 0.92 (5) | 2.96 (5) | 3.695 (3) | 137 (3) |
| N5—H1N5···I$^{iii}$ | 0.75 (5) | 2.91 (5) | 3.536 (4) | 143 (5) |

Symmetry codes: (i) $-x$, $-1 - y$, $-z$; (ii) $1 - x$, $-y$, $1 - z$; (iii) $x$, $y + 1$, $z$.

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All H atoms were found in $\Delta F$ 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; C—H = 0.93 and 0.96 Å]. H atoms on N atoms were refined. A Gaussian-type absorption correction based on the crystal morphology was applied (Spek, 1990, 1998). The largest spurious peaks in the final difference Fourier map were located near the I atom.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994); 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).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1529). Services for accessing these data are described at the back of the journal.

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