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Transition-Metal Complexes with Thiosemicarbazide-Based Ligands. VIII. Structure of Ammine(benzoylacetone *S*-methylisothiosemicarbazonato)nickel(II) Iodide

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Abstract. $[\text{Ni}(\text{C}_{12}\text{H}_{14}\text{N}_3\text{OS})(\text{NH}_3)]\text{I}$, $M_r = 450.96$, monoclinic, $P2_1/c$, $a = 6.198$ (2), $b = 17.401$ (5), $c = 15.343$ (4) Å, $\beta = 96.54$ (3)°, $V = 1644.0$ (8) Å³, $Z = 4$, $D_m = 1.81$, $D_x = 1.822$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 31.66$ cm⁻¹, $F(000) = 888$, $T = 293$ K, final $R = 0.038$ for 1804 observed reflections. The Ni coordination environment is a slightly distorted square determined by the O, N(1) and N(4) atoms from the terdentate ligand and the ammonia N atom with corresponding bond lengths of 1.817 (5), 1.824 (6), 1.847 (6) and 1.918 (6) Å, respectively. The complex cation shows deviations of its non-H atoms within ± 0.32 (1) Å from planarity. All nitrogen H atoms are involved in weak N–H...I hydrogen bonds ranging from 3.609 (6) to 3.841 (7) Å.

Introduction. The synthesis and structural investigations of a considerable number of transition-metal complexes with *S*-alkylisothiosemicarbazides and *S*-alkylisothiosemicarbazones have recently been reported (Padhye & Kauffman, 1985, and references therein; Leovac, Divjaković, Petrović, Argay & Kálmán, 1983,

and references therein; Leovac & Češljević, 1987). A common feature of the complexes is that the N atom of the *S*-alkylthioamido group takes part in coordination, while the S atom remains uncoordinated.

As far as the authors are aware only two exceptions have been noticed. Biyushkin, Gerasimov & Rozhdestvenskaya (1986) reported the structure of an Ni^{III} complex with chlorine and diacetylmonoxime *S*-methylisothiosemicarbazone where Ni is coordinated by N atoms of hydrazine and oxime and by chlorine, while neither N nor S atoms from the *S*-methylthioamido group take part in the coordination. Chandra & Singh (1986) supposed that thiosemicarbazones of acetone and methyl ethyl ketone, coordinated to the Ni^{II} atom through S and hydrazine N atoms, do not change the coordinating atoms after alkylation of the S atom.

In the crystal structure of the $[\text{Ni}(\text{HL})(\text{NH}_3)]\text{I}$ complex, where HL is $\text{C}_6\text{H}_5\text{C}(\text{O})=\text{CHC}(\text{CH}_3)=\text{NNHC}(\text{SCH}_3)=\text{NH}$, the *S*-methylthioamido group is attached to the Ni^{II} by an N atom, thus showing the usual mode of metal coordination.

Experimental. Dark-brown crystals of the title complex are obtained by reaction of ethanolic solutions of stoichiometric amounts of Ni^{II} iodide, benzoylacetone, *S*-methylisothiosemicarbazide-hydrogen iodide and aqueous ammonia. *D_m* by flotation in a mixture of CCl₄ and CHBr₃. Intensity data collected from a crystal of dimensions 0.34 × 0.20 × 0.21 mm on a Philips PW 1100 four-circle diffractometer using graphite-monochromatized Mo *K*α radiation, ω-2θ scanning technique, scan width 1.80°, scan rate 0.04° s⁻¹. Unit-cell parameters obtained from least-squares analysis of 18 reflections within 2θ range 12–28°. From absent reflections *h*0*l*, *l* ≠ 2*n* and 0*k*0, *k* ≠ 2*n* the *P*₂/*c* space group was determined. 2686 reflections were scanned within a quadrant ±*h*, *k*, *l* (*h* ± 8, *k* 24, *l* 21) up to (sinθ)/λ = 0.70 Å⁻¹. Three standard reflections (340, 1,0,10, 067) measured every 2 h showed an average variation of 1%. Corrections applied for Lorentz and polarization effects. No corrections for absorption or extinction. The I and Ni atoms were located by the heavy-atom method, all other non-H atoms from Fourier maps and H atoms from difference maps. Full-matrix least-squares refinement on *F* for 1804 unique reflections with *I* > 3σ(*I*) using anisotropic thermal parameters for non-H atoms. Isotropic temperature factors of H atoms taken to be 15% greater than those belonging to corresponding carrier atoms, kept constant.

Parameters of non-H atoms and coordinates of H atoms refined separately in the subsequent cycles except *y* of H(31N) and *x* coordinates of H(32N) and H(33N) atoms which were kept fixed on account of their unrealistic shifts during refinement (181 and 49 parameters refined, respectively); *R* and *wR* = 0.038; function minimized $\sum w(|F_o| - |F_c|)^2$ with *w* = 1/σ²(*F_o*) giving *S* = 1.06; (Δ/*σ*)_{max} = 0.13. Final difference map revealed residuals between -0.51 and 0.39 e Å⁻³ except two maxima near I and one near Ni of 0.93, 0.79 and 0.56 e Å⁻³, respectively. Scattering factors of Cromer & Mann (1968) for non-H and those of Stewart, Davidson & Simpson (1965) for H atoms; anomalous-dispersion factors from Cromer & Liberman (1970). Calculation performed mainly with XRAY76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) on a Univac 1110 computer at the University Computing Center in Zagreb.

Discussion. The final atomic parameters for non-H atoms are listed in Table 1 and selected bond lengths and angles involving non-H atoms in Table 2.* The

* Lists of structure factors, anisotropic thermal parameters, mean planes, H-atom parameters, remaining bond lengths and angles and geometry of hydrogen bonds have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51634 (32 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional positional parameters (× 10⁴; × 10⁵ for I) for non-H atoms and equivalent isotropic temperature factors (Å² × 10³)

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
I	66151 (9)	12548 (3)	102915 (3)	4.47 (2)
Ni	893 (1)	1256 (1)	7903 (1)	3.57 (3)
S	-4523 (4)	2893 (1)	7476 (1)	4.72 (7)
O	3270 (8)	725 (3)	7650 (3)	4.4 (2)
N(1)	502 (9)	1746 (3)	6845 (4)	3.3 (2)
N(2)	-1264 (10)	2260 (4)	6792 (4)	4.2 (2)
N(3)	1278 (10)	757 (4)	9025 (4)	4.6 (2)
N(4)	-1486 (10)	1820 (4)	8149 (4)	3.8 (2)
C(1)	1569 (13)	1676 (5)	6153 (5)	4.3 (3)
C(2)	1018 (16)	2150 (7)	5357 (6)	7.9 (5)
C(3)	-2295 (12)	2274 (4)	7519 (5)	3.7 (3)
C(4)	-5054 (17)	2896 (6)	8581 (6)	8.5 (5)
C(5)	3333 (13)	1157 (5)	6205 (5)	4.7 (3)
C(6)	4118 (12)	724 (4)	6903 (5)	4.2 (3)
C(7)	6024 (12)	201 (4)	6904 (5)	4.1 (3)
C(8)	6727 (14)	-219 (5)	7639 (6)	5.4 (3)
C(9)	8549 (17)	-672 (5)	7678 (7)	6.8 (4)
C(10)	9717 (14)	-722 (6)	6972 (9)	7.2 (5)
C(11)	9015 (16)	-324 (6)	6227 (8)	7.5 (4)
C(12)	7203 (15)	133 (5)	6180 (6)	6.0 (4)

Table 2. Selected bond lengths (Å) and angles (°)

Ni-O	1.817 (5)	N(1)-C(1)	1.320 (10)
Ni-N(1)	1.824 (6)	N(2)-C(3)	1.347 (10)
Ni-N(3)	1.918 (6)	N(4)-C(3)	1.304 (9)
Ni-N(4)	1.847 (6)	C(1)-C(2)	1.482 (12)
S-C(3)	1.747 (8)	C(1)-C(5)	1.413 (11)
S-C(4)	1.764 (10)	C(5)-C(6)	1.354 (11)
O-C(6)	1.314 (10)	C(6)-C(7)	1.491 (11)
N(1)-N(2)	1.408 (8)		
O-Ni-N(1)	94.4 (2)	N(1)-C(1)-C(2)	121.5 (7)
O-Ni-N(3)	86.6 (3)	N(1)-C(1)-C(5)	118.0 (7)
O-Ni-N(4)	178.4 (3)	C(2)-C(1)-C(5)	120.4 (8)
N(1)-Ni-N(3)	178.9 (3)	S-C(3)-N(2)	115.3 (5)
N(1)-Ni-N(4)	84.6 (3)	S-C(3)-N(4)	129.6 (6)
N(3)-Ni-N(4)	94.4 (3)	N(2)-C(3)-N(4)	115.1 (7)
C(3)-S-C(4)	101.5 (4)	C(1)-C(5)-C(6)	127.4 (8)
Ni-O-C(6)	127.0 (5)	O-C(6)-C(5)	123.0 (7)
Ni-N(1)-N(2)	111.8 (4)	O-C(6)-C(7)	113.3 (7)
Ni-N(1)-C(1)	130.1 (5)	C(5)-C(6)-C(7)	123.7 (8)
N(2)-N(1)-C(1)	118.0 (6)	C(6)-C(7)-C(8)	120.3 (8)
N(1)-N(2)-C(3)	113.7 (6)	C(6)-C(7)-C(12)	122.3 (7)
Ni-N(4)-C(3)	114.7 (5)		

ORTEP diagram (Johnson, 1965) showing the complex with the corresponding atom numbering is shown in Fig. 1.

The Ni coordination environment is a slightly distorted square determined by the benzoylacetone O atom, the N(1) and N(4) atoms from the *S*-methylisothiosemicarbazide moiety and the ammonia N(3) atom. The bond lengths at the Ni atom, ranging from 1.817 (5) Å toward the O to 1.918 (6) Å toward the N(3) atom (Table 2), are in accord with those found in the structures of compounds containing similar coordinating groups with square-planar coordination around the Ni atom (Bart, Bassi, Calcaterra & Pieroni, 1978; Renkema, Lute & Stam, 1979; Simonov, Bel'skii, Gerbeleu, Shova & Arion, 1985; Leovac, Divjaković,

Češljević & Engel, 1987; Leovac, Češljević & Galešić, 1988). The coordinating atoms deviate from their mean plane within ± 0.007 (7) Å while the Ni atom is 0.015 (2) Å apart from it.

Of the two chelate rings formed by the Ni atom and the terdentate ligand (Fig. 1), the five-membered ring is planar within ± 0.005 (6) Å while the six-membered ring shows greater atom deviations which are within ± 0.034 (8) Å from planarity. All non-H atoms of the complex cation deviate from their mean plane within ± 0.32 (1) Å showing its approximate planarity.

The isothiosemicarbazide moiety is considerably affected by electron delocalization. Thus it shows shortened single bonds N(1)–N(2) 1.408 (8) and N(2)–C(3) 1.347 (10) Å and a lengthened double bond C(3)=N(4) 1.304 (9) Å. These bond lengths are in accord with those in similar nickel isothiosemicarbazide complexes with a formally sp^3 -hybridized N(2) atom (Divjaković & Leovac, 1979; Simonov *et al.*, 1985).

The methyl group at S and the N(4) atom are *cis* with respect to the C(3)–S bond (Fig. 1). An increase in the bond angle S–C(3)–N(4) 129.6 (6)° accounts for S–C(3)–N(2) 115.3 (5)°, possibly by releasing repulsion between the H(4N) and H(42) atoms resulting in a contact of 2.36 (11) Å between them. A similar

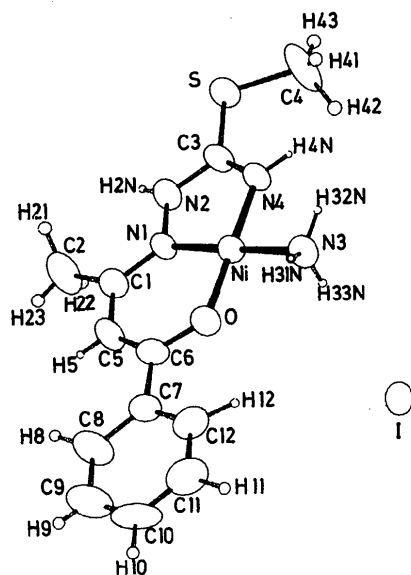


Fig. 1. Diagram showing the complex and corresponding atom numbering. Ellipsoids are at the 50% probability level.

effect is characteristic of isothiosemicarbazide complexes with such a *cis* orientation (Leovac, Češljević & Galešić, 1988, and references therein).

The complex cation and I show mutual interaction through weak N–H...I hydrogen bonds ranging from 3.609 (6) to 3.841 (7) Å where all nitrogen H atoms are involved. The H...I⁻ separations ranging from 2.84 (6) to 2.96 (6) Å are considerably shorter than 3.35 Å, taken as the sum of the corresponding van der Waals radii (Hamilton & Ibers, 1968). The N–H...I⁻ angles range from 148 to 162 (6)°.

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