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Transition metal complexes with thiosemicarbazide-based ligands. XXXIX. [Benzoylacetone 3-methylisothiosemicarbazonato(2–)-O,N^1,N^4](pyridine-*N*)nickel(II)

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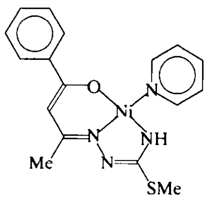
Abstract

The square-planar title complex of formula $[Ni(C_{12}H_{13}N_3OS)(C_6H_5N)]$ or [Ni(*L*)(py)] (*L* is the dianion of the *O*,*N*,*N*-terdentate benzoylacetone *S*-methylisothiosemicarbazone ligand and py is pyridine) has structural characteristics of the ligand *L* somewhat different from those reported previously for the square-planar $[Ni(HL)(NH_3)]I$ complex, which involves the same ligand in its monoanionic form. The differences are in the different electronic delocalization in the isothiosemicarbazide moiety, and the *trans* orientation of the S—Me group and the imido N atom. The effect of H-atom repulsion on the orientation of the phenyl ring with respect to the coordination plane of the complex and the effect of the pyridine ring on the crystal packing are also described.

Comment

Because of their biological activity and analytical applications, thiosemicarbazides and their metal complexes have been the subject of much research. This is evident from the large number of original scientific papers and several reviews (Campbell, 1975; Singh *et al.*, 1978; Padhye & Kauffman, 1985; Malinovskii *et al.*, 1985; West *et al.*, 1991). The thiosemicarbazide ligand presents two potential donor atoms (S and N) in the $-C(=S)-NH_2$ fragment and the S atom is mainly involved in coordination. However, in the case of the *S*-alkyl derivatives, the ligand is coordinated to the metal through the N atom of the fragment (Malinovskii *et al.*, 1985).

In our previous work (Galešić & Leovac, 1989), we described the synthesis and structure of the square-planar Ni^{II} complex of formula $[Ni(HL)(NH_3)]I$. It contains the monoanion of the *O*,*N*,*N*-terdentate benzoylacetone *S*-methylisothiosemicarbazone (H*L*) ligand, which is formed by deprotonation of the benzoylacetone moiety. As a continuation of our structural investigations of the title ligand, we present here the structure of another square-planar Ni^{II} complex, [Ni(*L*)(py)], (I), which contains the dianionic form of the ligand, formed by an additional deprotonation of the NH group of the $-NH-C(=NH)-SCH_3$ fragment.



(I)

The square-planar coordination around the Ni atom of (I) is formed by the O and two N (N1 and N3) atoms of the *L* ligand, and the pyridine N atom (N4). The best plane formed by the Ni, N1, N3, N4 and O atoms does not deviate from planarity by more than 0.016 Å. The six- and five-membered chelate rings are also almost planar, and the Ni—*L* bond lengths are practically identical to those observed in $[Ni(HL)(NH_3)]I$ (Galešić & Leovac, 1989). The $Ni-N_{py}$ bond [1.916 (2) Å] is somewhat longer than the same bond [1.87 (1) Å] in the square-planar $[Ni(HL^1)(py)]ClO_4\cdot MeOH$ complex (HL^1 is the monoanion of salicylaldehyde *S*-methylisothiosemicarbazone; Simonov *et al.*, 1992).

The phenyl (Ph) ring forms an angle of 15.05 (10)° with the best plane of the chelate rings. The torsion angle about the C6—C7 bond (C5—C6—C7—C8) is 14.5 (3)°. It is interesting that the Ph ring is shifted toward the O atom, as shown by the angles C7—C6—O of 114.2 (2)° [compared with C7—C6—C5 of 121.8 (2)°] and C6—C7—C12 of 120.3 (2)° [compared with C8—C7—C6 of 122.3 (2)°]. Such a position of the Ph ring can be explained by two effects: (i) repulsion between the H atoms bonded to C8 and C5 (H5···H8 2.09 Å), and (ii) existence of the C12—H···O hydrogen bond (H12···O 2.43 Å). In other words, of all the possible rotational positions of the Ph ring, the observed position is an energy compromise between repulsion of the H atoms and formation of the C12—H···O bond.

In (I), there is electronic delocalization in the N2—C1—N3 fragment different from that observed in the monoanionic form of the ligand in the $[Ni(HL)(NH_3)]I$ complex; the C1—N2 bond [1.300 (3) Å] is shorter than the C1—N3 bond [1.332 (3) Å], while in the monoanionic form of the ligand, the C1—N2 bond [1.347 (10) Å] is longer than the C1—N3 bond [1.304 (9) Å]. This different behaviour in (I) is obviously a consequence of deprotonation of the imino

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form (N2H group) of the monoanionic ligand in the [Ni(H*L*)(NH_3)]I complex inducing an increased electronic density, especially between the N2 and C1 atoms. Analogous distances [C1—N2 1.333 (9) and C1—N3 1.30 (1) Å] were found in the structure of the square-planar Ni^{II} complex with the *O,N,N*-terdentate dianion of 2,4-pentanedione *S*-methylisothiosemicarbazone (L^2), [Ni(L^2)(NH_3)]·$2H_2O$ (Leovac *et al.*, 1993). The other bond lengths in the *L* ligand are practically identical to those observed in the [Ni(H*L*)(NH_3)]I complex. However, the methyl group on the S atom is *trans* to the N3 atom with respect to the C1—S bond (Fig. 1). It can be supposed that the *trans* orientation of the CH_3 group and the N3 atom is also a consequence of deprotonation of the N2 atom, due to the fact that no repulsion can take place with the methyl group.

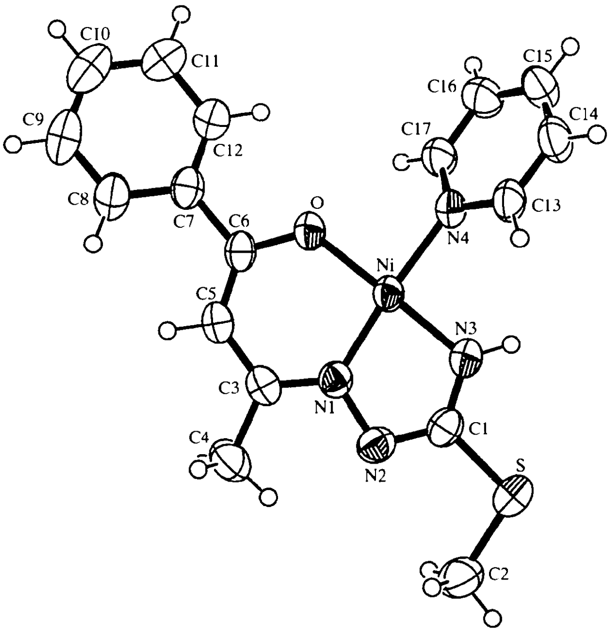

Fig. 1. A view of the title compound (50% probability displacement ellipsoids) with the atom-numbering scheme.

The crystal-packing arrangement in the [Ni(*L*)(py)] complex (along the *a* axis) consists of two types of layer, one of which is formed by the molecules in positions (i) and (ii), and the other by the molecules in positions (iii) and (iv) [symmetry codes: (i) *x*, *y*, *z*; (ii) $-x$, $-y$, $-z$; (iii) $-x+\frac{1}{2}$, $y+\frac{1}{2}$, $-z$; (iv) $x+\frac{1}{2}$, $-y+\frac{1}{2}$, *z*]. These layers form an angle of 52° (Fig. 2), which is equal to the angle between the best plane passing through the pyridine ring and the coordination plane of the complex. Viewing down the *b* axis, it is possible to notice three layers appearing alternately in the crystal lattice. The first consists of the S—Me fragments arranged alternately above one another in the S—Me...Me—S...S—Me sequence; there is a very weak hydrogen bond [C2—H···S^{v} 3.13 Å; symmetry code: (v) $-x+\frac{1}{2}$, $y-\frac{1}{2}$, $-z$] between the S—Me fragments. The second layer is non-polar, composed of the Ph rings, whereas the third is composed of the parallel alternately arranged thiosemicarbazide parts of the complex and neighbouring pyridine rings, with a shortest distance Ni···C15^{vi} of 3.421 (3) Å [symmetry code: (vi) $x-\frac{1}{2}$, $-y+\frac{1}{2}$, *z*].

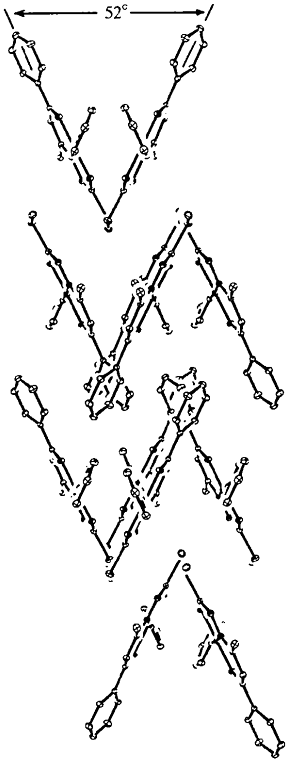

Fig. 2. The packing of (I) viewed down the *a* axis.

Experimental

The dark-red monocrystals of the title complex were obtained by the reaction of a warm EtOH solution of [Ni(H*L*)(NH_3)]I and pyridine (Leovac *et al.*, 1991).

Crystal data

[Ni($C_{12}H_{13}N_3OS$)(C_5H_5N)]
$M_r = 385.12$
Monoclinic
$P2_1/a$
$a = 11.848\ (2)$ Å
$b = 7.9903\ (15)$ Å
$c = 18.290\ (7)$ Å
$\beta = 95.59\ (3)°$
$V = 1723.3\ (8)$ Å^3
$Z = 4$
$D_x = 1.484$ Mg m^{-3}
D_m not measured

Mo *K*α radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 11.80–17.76°$
$\mu = 1.258$ mm^{-1}
$T = 293\ (3)$ K
Prismatic
0.29 × 0.29 × 0.25 mm
Dark red

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
5481 measured reflections
5011 independent reflections
2984 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.010$
$\theta_{\rm max} = 29.97°$
$h = -16 \rightarrow 16$
$k = 0 \rightarrow 11$
$l = -25 \rightarrow 17$
2 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.090$
$S = 1.194$
5011 reflections
217 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0453P)^2 + 0.6101P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.486$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.360$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Ni—O	1.830 (2)	N3—C1	1.332 (3)
Ni—N3	1.831 (2)	N2—C1	1.300 (3)
Ni—N1	1.847 (2)	C1—S	1.765 (2)
Ni—N4	1.916 (2)	C3—C5	1.413 (3)
N1—C3	1.321 (3)	S—C2	1.782 (3)
N1—N2	1.405 (2)	C6—C5	1.365 (3)
O—C6	1.308 (2)		
O—Ni—N3	177.85 (7)	O—Ni—N4	88.62 (7)
O—Ni—N1	96.10 (7)	N3—Ni—N4	93.01 (8)
N3—Ni—N1	82.28 (8)	N1—Ni—N4	175.28 (7)

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: local modification of *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*III (Burnett & Johnson, 1996). Software used to prepare material for publication: *SHELXL*93 and *PARST* (Nardelli, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1411). Services for accessing these data are described at the back of the journal.

References

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

Campbell, M. J. M. (1975). *Coord. Chem. Rev.* **15**, 279–319.

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

Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf–Nonius, Delft, The Netherlands.

Galešić, N. & Leovac, V. M. (1989). *Acta Cryst.* C**45**, 745–747.

Leovac, V. M., Češljević, V. I., Gerbeleu, N. V., Simonov, Yu. A., Dvorkin, V. M. & Arion, V. B. (1993). *Transition Met. Chem.* **18**, 309–311.

Leovac, V. M., Češljević, V. I. & Nešić, S. M. (1991). *Z. Anorg. Allg. Chem.* **592**, 217–223.

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

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

Padhye, S. & Kauffman, G. B. (1985). *Coord. Chem. Rev.* **63**, 127–160.

Sheldrick, G. M. (1985). *SHELXS*86. *Program for the Solution of Crystal Structures*. University of Göttingen, Germany.

Sheldrick, G. M. (1993). *SHELXL*93. *Program for Refinement of Crystal Structures*. University of Göttingen, Germany.

Simonov, Yu. A., Yampolskaya, M. A., Zavodnik, V. E., Leovac, V. M., Gerbeleu, N. V. & Malinovskii, T. I. (1992). *Zh. Neorg. Khim.* **37**, 790–795.

Singh, R. B., Garg, B. S. & Singh, R. P. (1978). *Talanta*, **25**, 619–632.

West, D. X., Padhye, S. B. & Sopawane, P. B. (1991). *Struct. Bonding (Berlin)*, **76**, 1–50.

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Dichloro[(cyclopentadienyl)tris(dimethylphosphito-*P*)cobalt(III)-*O*,*O*′,*O*″]oxomolybdenum(V)†

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Abstract

In the title compound, $[(C_5H_5)Co\{P(O)(OCH_3)_2\}_3MoOCl_2]$, an oxomolybdenum(V) unit binds to two chloro ligands and one tripodal oxygen-donating ligand. The coordination geometry around the Mo atom is a distorted octahedron.

Comment

The oxochloromolybdenum complex $[(C_5H_5)MoOCl_2]$ (Cousins & Green, 1964) was obtained from $[(C_5H_5)MoCl_4(thf)]$ (thf is tetrahydrofuran) and its structure was suggested on the basis of infrared spectroscopy. $[HB(pyrazol\text{-}1\text{-}yl)_3MoOCl_2]$ (Lincoln & Koch, 1986) was produced by the reaction of $[HB(pyrazol\text{-}1\text{-}yl)_3MoCl_3]$ with O_2 in dry CH_2Cl_2 and fully characterized by X-ray diffraction analysis. $[HB(3,5\text{-}dimethylpyrazol\text{-}1\text{-}yl)_3MoCl_2]$ (Cleland *et al.*, 1987) was also isolated but was not fully characterized. More recently, $[CpCo\{P(O)(OMe)_2\}_3]WOBr_2$ (Kläui *et al.*, 1995) was identified

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† Systematic name: dichloro-1κ^2*Cl*-[2(η^5)-cyclopentadienyl]tris-[μ-dimethoxyoxophosphato(1−)-1:2κ^2*O*:*P*](oxo-1κ*O*)cobalt(III)-molybdenum(V).