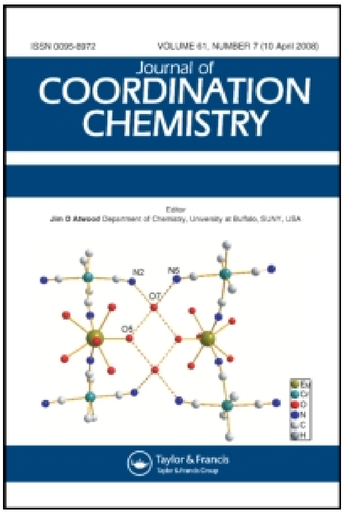

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The complex $[Ni(HL^1)_2]Cl_2$, **1**, (HL^1 = methyl(2-pyridyl)ketone thiosemicarbazone) has been prepared by reaction of HL^1 with nickel(II) chloride and the complex $[Ni(L^1)NCS]$, **2**, has been prepared by transmetallation of $[Pb_2(HL^1)(L^1)(NCS)_3]$ with an excess of nickel(II) chloride. The new complexes have been characterized by spectroscopic techniques and the crystal and molecular structure of $[Ni(L^1)NCS]$ has been determined. The nickel atom has square-planar geometry with three donor atoms (NNS) belonging to L^1; the fourth coordination site is occupied by an isothiocyanate ion. This results in a planar tricyclic ligating system containing one heterocyclic and two five-membered chelate rings.

Keywords: Thiosemicarbazone; nickel(II); Schiff bases; square-planar complexes; X-ray structure

INTRODUCTION

We have previously reported complexes of copper, cobalt, nickel, zinc and cadmium with benzil-based macrocyclic thiosemicarbazone ligands and

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palladium with benzil*bis*(thiosemicarbazone),[1] in which the ligands are chelated through the thione sulfur and nitrogen atoms, in neutral or anionic form. The complexes containing deprotonated ligands have demonstrated the facility to form intermolecular hydrogen bonds using the non-coordinated nitrogen atoms; this is an important factor in the reactivity of the thiosemicarbazone derivatives.[2–4] The introduction of a heteroatom in the aromatic ring, as in the case of the pyridine compound (methyl(2-pyridyl)-ketone thiosemicarbazone), represents a new kind of NNS thiosemicarbazone ligand and results in modified reactivity of the resulting complexes incorporating this so-called "pyridine pincer". Recent work has demonstrated that derivatives of methyl(2-pyridyl)ketone thiosemicarbazone containing Cu(II) presents interesting structural properties.[5]

To extend knowledge in this research field, particularly with respect to the coordination properties of heterocyclic thiosemicarbazones and the stereochemistry and molecular structures of the complexes, we now report the synthesis and characterization of new nickel(II) complexes with methyl-(2-pyridyl)ketone thiosemicarbazone (HL^1) together with the single crystal structure of isothiocyanato(methyl(2-pyridyl)ketone thiosemicarbazonato)-nickel(II), $[Ni(L^1)NCS]$, **2**. The isolation and characterization of the latter, obtained by transmetallation, is significant since it reveals the behaviour of the ligand methyl(2-pyridyl)ketone thiosemicarbazonato as a planar NNS donor set with a deprotonated thiol tautomeric form.

EXPERIMENTAL

Measurements

Infrared spectra (KBr discs) were recorded on a Bomen–Michelson spectrophotometer (4000–400 cm^{-1}); electronic spectra, in DMF solution, were recorded on an Ati-Unicam UV2 spectrophotometer. Elemental analyses (C, H, N and S) were carried out by the Servicio Interdepartamental de Investigación (SIDI) of the Universidad Autónoma de Madrid.

Materials

Thiosemicarbazide, methyl(2-pyridyl)ketone and nickel(II) chloride were commercially available (Fluka-Chemie) and used without further purification. Lead(II) thiocyanate was prepared according to standard procedures.

Preparations

Methyl(2-pyridyl)ketone thiosemicarbazone (HL^1) was prepared using published procedures.[6]

[Ni(HL^1)$_2$]Cl$_2$ To a methanolic solution (25 cm^3) of HL^1 (0.39 g, 2 mmol) was added dropwise with stirring a methanolic solution (25 cm^3) of $NiCl_2 \cdot 6H_2O$ (0.24 g, 1 mmol) at room temperature. After 2 h stirring the solution changed to red-brown. A red solid was isolated after slow evaporation of the solvent, washed with MeOH and Et_2O and dried *in vacuo*; yield = 88%. Found: C, 37.15; H, 3.91; N, 21.41; S, 12.53%. $C_{16}H_{20}Cl_2NiN_8S_2$ requires C, 37.09; H, 3.86; N, 21.63; S, 12.36%.

[Ni(L^2)NCS] Since previous studies had indicated a high degree of lability of Pb(II), in order to synthesize new nickel complexes we tried transmetallation reactions as follows. To a hot (60°C) methanolic suspension (25 cm^3) of lead(II) thiocyanate (0.32 g, 1 mmol) was added dropwise with stirring a methanolic solution (25 cm^3) of HL^1 (0.19 g, 1 mmol). After 2 h stirring a yellow solid was isolated for which the elemental analysis and mass spectrum corresponded to the complex $[Pb_2(HL^1)L^1(NCS)_3]$; yield = 75%. Found C, 23.3; H, 1.80; N, 15.95%; *m/z* 977; calc.: C, 23.35; H, 1.95; N, 15.80%. The required complex **2** was obtained by stirring a methanolic suspension of $[Pb_2(HL^1)L^1(NCS)_3]$ (0.99 g, 1 mmol) with a methanolic solution of $NiCl_2 \cdot 6H_2O$ (1.42 g, 6 mmol) at room temperature. After 2 h stirring a red-brown solution was obtained. After slow evaporation of the solvent to half volume, the solution was kept in cool place. In a few weeks, good red-brown crystals suitable for X-ray analysis were obtained; yield = 67%. Found: C, 34.88; H, 2.95; N, 22.22; S, 20.16%. $C_9H_9NiN_5S_2$ requires C, 34.87; H, 2.91; N, 22.60; S, 20.67%.

Crystal data and structure solution

Single crystal data collection was performed on a Siemens R3m/V diffractometer. Unit cell parameters were calculated by least-squares refinement of 25 well-centred reflections in the range $15° < 2\theta < 45°$. Intensities of four check reflections measured after every 120 min showed a decay in intensity of *ca.* 2%. The data were corrected for Lorentz and polarization effects. Absorption correction was applied *via* an empirical ψ scan. The structure was solved by direct methods and subsequent Fourier syntheses with the SHELXTL PC V5 program.[7] All non-hydrogen atoms were refined anisotropically in the final cycles of refinement. The positions of the hydrogen atoms were calculated and refined riding on the previous atoms. The maximum residual peak in the ΔF map was $2.22\,e\,Å^{-3}$, located in the

TABLE I Experimental data for the crystallographic analysis of complex **2**

Formula	$C_9H_9N_5NiS_2$
M	310.04
Temperature/K	293(2)
λ (Mo-Kα)/Å	0.71069
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	7.929(5)
b/Å	8.394(5)
c/Å	9.583(5)
α/°	94.796(5)
β/°	105.003(5)
γ/°	102.571(5)
U/Å^3	594.6(6)
Z	2
D_c/mg m^{-3}	1.732
μ/mm^{-1}	1.965
$F(000)$	316
Crystal size/mm	0.1 × 0.5 × 0.08
θ Range/°	2.22–30.00
hkl Ranges	−1 to 11, −11 to 11, −13 to 13
Reflections collected	3691
Independent reflections	3460 [R(int) = 0.2335]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2600/0/155
Goodness-of-fit on F^2	1.070
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.079$, $wR2 = 0.183$
R indices (all data)	$R1 = 0.137$, $wR2 = 0.290$

neighbourhood of the nickel atom. Neutral atomic scattering and dispersion factors were those included in the SHELXTL PC V5 package. Crystal data and details of refinement are given in Table I; the poor quality of the crystal is responsible for the relatively high estimated standard deviations of the positions for some of the atoms in the present structure. Selected bond lengths and angles are listed in Table II.

RESULTS AND DISCUSSION

Infrared scanning,[8] in KBr disc (Table III), of the free ligand exhibits the ν(C=S) thioamide IV vibration at *ca.* 850 cm^{-1} indicating the presence of the thione form. The negative shift of this band upon complexation in complex **1** can be interpreted in terms of coordination through the sulfur atom in the thione form of the thioamide group. Further evidence in support of the coordination through sulfur and nitrogen iminic atoms is provided by the red shift of ν(C=N) and the ν(asym) and ν(sym) NH stretching

TABLE II Selected bond lengths (Å) and angles (°)

Ni–N(23)	1.847(4)	C(5)–C(6)	1.356(9)
Ni–N(1A)	1.858(5)	C(21)–N(23)	1.310(7)
Ni–N(1)	1.908(5)	C(21)–C(22)	1.500(7)
Ni–S(26)	2.137(2)	N(23)–N(24)	1.380(6)
N(1)–C(6)	1.336(7)	N(24)–C(25)	1.318(6)
N(1)–C(2)	1.357(7)	C(25)–N(27)	1.338(7)
C(2)–C(3)	1.386(8)	C(25)–S(26)	1.750(5)
C(2)–C(21)	1.451(7)	N(1A)–C(1A)	1.134(7)
C(3)–C(4)	1.371(9)	C(1A)–S(1A)	1.634(5)
C(4)–C(5)	1.392(10)		
N(23)–Ni–N(1A)	176.9(2)	N(1)–C(2)–C(3)	121.2(5)
N(23)–Ni–N(1)	83.6(2)	C(4)–C(3)–C(2)	119.2(6)
N(1A)–Ni–N(1)	97.8(2)	C(3)–C(4)–C(5)	119.1(6)
N(23)–Ni–S(26)	87.22(14)	C(6)–C(5)–C(4)	118.9(6)
N(1A)–Ni–S(26)	91.6(2)	N(1)–C(6)–C(5)	123.0(6)
N(1)–Ni–S(26)	170.32(14)	C(1A)–N(1A)–Ni	167.3(5)
C(6)–N(1)–C(2)	118.6(5)	N(1A)–C(1A)–S(1A)	179.4(6)

TABLE III Selected vibrational bands (cm^{-1}) of HL^1 and Ni(II) complexes

	HL^1	1	2
ν(NH)	3362,3256	3320,3248	3391,3298
ν(NH···N)	3186	3128	3153
ν(SCN)			2096
ν(CN)	1607	1612	1634
δ(NH$_2$)	1607	1612	1600
py ν(CN) + ν(CC)	1584	1566	1560
Thioamide I	1500	1554	1510
Thioamide IV	850	808	840
py ring (o.p.)	624	634	634
py ring (in p.)	404	409	412

frequencies of the thioamide group. However, metal coordination of complex **2** occurs through the thiol form *via* deprotonation of the –SH group. This can be inferred from the absence of any ν(SH) and the weakness of the ν(C=S) vibrations. The SNNN mode of coordination is ascertained from the red shift of the ν(C=N) and pyridine (ring deformation out of plane and ring deformation in plane) vibrations and by the presence of a new band at 2096 cm^{-1} indicating *N*-coordination of the thiocyanate group.[9] The well resolved band at *ca.* 3153 cm^{-1} has been assigned to strong N–H···N intermolecular hydrogen bonding.

A drawing of the complex **2** with the atom numbering scheme is shown in Figure 1. The nickel(II) atom has square-planar geometry surrounded by one sulfur atom and three nitrogen atoms, the L^1 ligand showing *E* configuration about N(24)–C(25) bond. The organic molecule acts as a

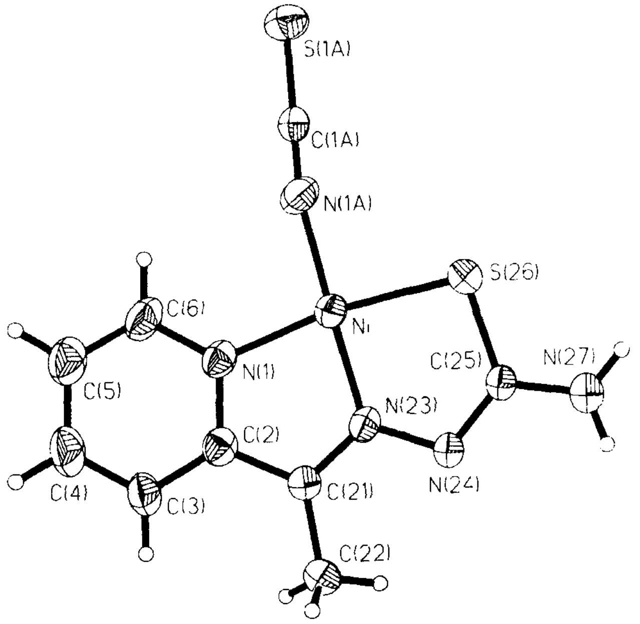

FIGURE 1 Structure of the complex [Ni(L^1)NCS], **2**, showing atom numbering scheme.

terdentate ligand with the NNS donor set placed on the same side. The third nitrogen atom is provided by the isothiocyanate anion. Coordination of the thiosemicarbazone results in the formation of three rings, one heterocyclic and two five-membered (NiSCNN and NiNCCN) chelate rings, all of them are planar within experimental error. A careful examination of bond length data shows that the Ni–N bonds involving the iminic and isothiocyanate nitrogens (1.847 and 1.858 Å) are somewhat shorter than that involving the pyridine nitrogen (1.908 Å). This suggests that nickel(II) is small enough to perfectly fit in the ligand cavity and to bond effectively, by which the pyridine ring is required to flex inwards towards the metal ion.[10,11] This results in a small distortion to the ligand structure easily quantified by a consideration of the bite angles: N(23)–Ni–N(1) 83.6(2)°, N(23)–Ni–S(26) 87.22(14)°, N(1A)–Ni–S(26) 91.6(2)°, and N(1A)–Ni–N(1) 97.8(2)°. The Ni–S bond (2.137 Å) is comparable with those reported for other thiosemicarbazone nickel complexes[12,13] with strong coordination, attributable to the high basicity of the ligand. The loss of the proton originally bound to N(24) produces a negative charge, which is delocalized in the C(21)–N(23)–N(24)–C(25)–S(26) system, consistent with the bond distances C(25)–S(26) 1.750 Å, in the range of single-bond character, C(21)–N(23) 1.310 Å and

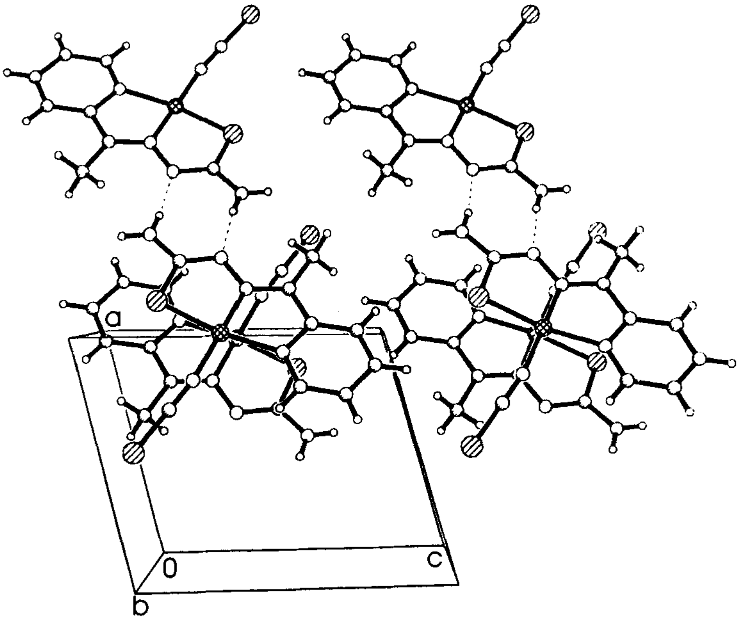

FIGURE 2 Packing arrangement for [Ni(L^1)NCS], **2**.

N(24)–C(25) 1.318 Å, intermediate between formal single and double bonds.[14–17] This substantiates the displacement of the tautomeric equilibrium to the thiol form. N(1A)–C(1A) 1.134 Å and C(1A)–S(1A) 1.643 Å in the thiocyanate ion are in the double bond range in agreement with *N*-coordination of the isothiocyanate group.

The essential characteristic of the crystal packing (Figure 2) is the hydrogen bonding between the complex molecules. This involves the nitrogen atoms [N(27)–H···$N(24)^{I}$ ($I = 3 - x, -y, 1 - z$) 3.062 Å and 171°] and supports the infrared stretching assignments given for NH.

The electronic absorption spectra of the complexes show intense bands centred at *ca.* 380 and 410, 375 and 450 nm for **1** and **2** respectively. The highest energy band is due to an intraligand $n \rightarrow \pi^*$ transition, while the other band includes $S \rightarrow Ni$ and $N \rightarrow Ni$ LMCT transitions.[18] Complex **2** reveals, in DMF, a simple ligand-field band at 490 nm consistent with planar geometry. The incorporation of other ligands to the coordination sphere, in complex **1**, results in the octahedral high-spin form. This is evidenced by a decrease in the intensity of the ligand-field bands at 415 nm and the appearance of two components of low intensity at *ca.* 810 and 1025 nm.

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