

UDC 548.73:547.13:546.74

COORDINATIVE PROPERTIES OF THE PYRIDINE-2-CARBALDEHYDE THIOSEMICARBAZONE LIGAND TOWARDS NI(II)**C. Graiff, S. Canossa, G. Predieri***Dipartimento di Chimica, Università di Parma, Parma, Italy*
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Received October, 7, 2012

Revised November, 6, 2012

Three crystal structures of Ni compounds containing bis(pyridine-2-carbaldehyde thiosemicarbazone) ligand (HL), namely (pyridine-2-carbaldehyde thiosemicarbazonato)(pyridine-2-carbaldehyde thiosemicarbazone) nickel(II) nitrate hydrate $[\text{Ni}(\text{HL})\text{L}][\text{NO}_3] \cdot (\text{H}_2\text{O})$ (**1**), bis(pyridine-2-carbaldehyde thiosemicarbazone) nickel(II) dinitrate $[\text{Ni}(\text{HL})_2][\text{NO}_3]_2$ (**2a**), and bis(pyridine-2-carbaldehyde thiosemicarbazone) nickel(II) dinitrate dihydrate $[\text{Ni}(\text{HL})_2][\text{NO}_3]_2 \cdot 2(\text{H}_2\text{O})$ (**2b**) are determined by X-ray diffraction methods. Comparative structural studies are carried out.

Keywords: nickel, thiosemicarbazone complexes, crystal structure.**INTRODUCTION**

The study of thiosemicarbazones and their metal complexes has become a fruitful area of the coordination chemistry due to the interesting properties exhibited by these compounds, in particular those dealing with the biological activity. Thiosemicarbazones have been known for many years to show a broad spectrum of therapeutic properties with antibacterial, antiviral and antitumour activities against a range of diseases. Metal complexes derived from thiosemicarbazone ligands show interesting antiproliferative characteristics, as pointed out in the recent reports [1, 2]. Usually thiosemicarbazone acts as a *N,N,S* terdentate ligand and gives rise to rigid planar systems. The reaction between $\text{Ni}(\text{NO}_3)_2 \cdot 6(\text{H}_2\text{O})$ and pyridine-2-carbaldehyde thiosemicarbazone in equimolar amounts in EtOH leads to the formation of two Ni(II) complexes different because of the presence of neutral and deprotonated forms of the pyridine-2-carbaldehyde thiosemicarbazone ligand. Comparative structural studies have been carried out on the nickel(II) complexes obtained.

EXPERIMENTAL

General. The starting reagent $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, pyridine-2-carbaldehyde thiosemicarbazone and the solvent ethanol were pure commercial products (Aldrich, Fluka, and C. Erba) and were used as received. The C, H, N elemental analyses were carried out using a Carlo Erba EA1108 microanalyzer. FTIR spectra ($4000\text{--}400\text{ cm}^{-1}$) were recorded with a Nicolet Nexus spectrophotometer equipped with a Smart Orbit HATR accessory (diamond).

Reaction of $\text{Ni}(\text{NO}_3)_2 \cdot 6(\text{H}_2\text{O})$ and pyridine-2-carbaldehyde thiosemicarbazone. *Method a:* An ethanol solution of equimolar amounts of $\text{Ni}(\text{NO}_3)_2 \cdot 6(\text{H}_2\text{O})$ (300 mg, 1 mmol) and pyridine-2-carbaldehyde thiosemicarbazone (HL) (183 mg, 1 mmol) was stirred at 50°C for 1 h. The color of the solution turned to red. A brownish precipitate formed, which was filtered and dried; it was recognised as rough $[\text{Ni}(\text{C}_7\text{H}_8\text{N}_4\text{S})_2](\text{NO}_3)_2$ **2a** by IR spectroscopy, through a comparison with the IR spectrum of

pure recrystallized **2a** (*vide infra*). In fact, taking advantage of its high solubility in water, the brownish precipitate was recrystallized giving brown crystals of **2a**. The reddish ethanol filtrate solution was led to evaporation and red crystals of **1** were obtained in two days. FTIR (Diamond crystal HATR): **1** = 3411 (m), 3291 (m), 3180 (m), 1596 (s), 1396 (vs), 1303 (vs), 1286 (vs), 1152 (s), 1131 (s), 862 (m), 496 (m) cm^{-1} ; An. El. calcd for **1** (497.78): C 33.75, H 3.44, N 25.32; found C 33.12, H 3.71, N 25.01. FTIR (Diamond crystal HATR): **2a** = 3291 (m), 3162 (br), 1591 (s), 1385 (vs), 1288 (vs), 1230 (vs), 1186 (s), 920 (m), 494 (m) cm^{-1} ; An. El. calcd for **2a** (542.76): C 30.95, H 2.97, N 25.80; found C 31.02, H 2.18, N 26.01.

Method b: An ethanol/water solution containing equimolar amounts of $\text{Ni}(\text{NO}_3)_2 \cdot 6(\text{H}_2\text{O})$ (300 mg, 1 mmol) and pyridine-2-carbaldehyde thiosemicarbazone (HL) (183 mg, 1 mmol) was stirred at room temperature for 1 h. Brown crystals of **2b** were obtained by slow evaporation of the solution. FTIR (Diamond crystal HATR): **2b** = 3356 (m), 3188 (br), 1587 (s), 1400 (vs), 1278 (vs), 1266 (vs), 1132 (s), 1111 (s), 892 (m), 491 (m) cm^{-1} ; An. El. calcd for $[\text{Ni}(\text{HL})_2][\text{NO}_3]_2 \cdot 2(\text{H}_2\text{O})$ (578.78): C 29.03, H 3.48, N 24.19; found C 29.15, H 3.55, N 24.33.

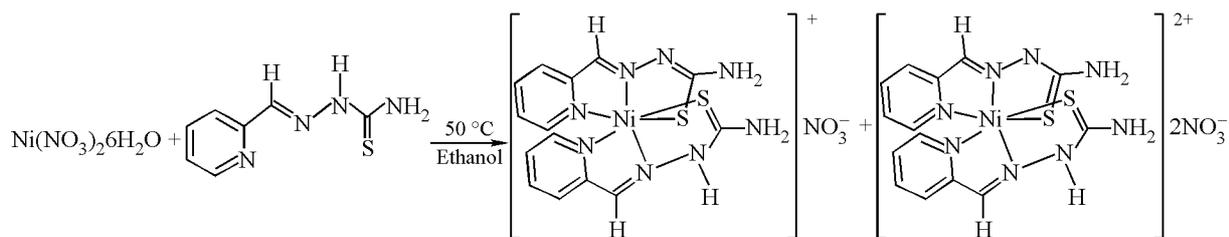
X-ray data collection, structure solution and refinement for complexes 1, 2a, and 2b. The intensity data were collected at room temperature on Bruker APEX II (compound **1**) and Bruker AXS Smart 1000 (compounds **2a** and **2b**) diffractometers, equipped with an area detector using graphite-monochromated MoK_α radiation. The Bruker program package was used to determine the unit cell parameters and for data collection. Crystallographic and experimental details for structures are summarized in Table 1.

The structures were solved by Patterson and Fourier methods and refined by full-matrix least-squares procedures (based on F_0^2) [3–6] with anisotropic thermal parameters in the last cycles of the refinement for all the non-hydrogen atoms. In compound **1** the crystallization water molecule was found disordered in two positions which were refined with a site occupancy factor of 0.80 and 0.20 respectively. The hydrogen atoms in all the three structures were introduced into the geometrically calculated positions and refined as riding on the corresponding parent atoms, excepting the hydrogen atoms of the 0.80 water molecule of crystallization in **1** which were found in ΔF and refined isotropically and excepting the hydrogen atoms of the water molecules of crystallization in **2b** in which they have been omitted in the calculation.

The details of the crystal structure investigations are deposited to the Cambridge Crystallographic Data Centre as supplementary publications no. CCDC-906026 (**1**), no. CCDC-906027 (**2a**), no. CCDC-906028 (**2b**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: int. code + 44(1223)336-033, e-mail: deposit@ccdc.cam.ac.uk].

RESULTS AND DISCUSSION

The reaction between $\text{Ni}(\text{NO}_3)_2 \cdot 6(\text{H}_2\text{O})$ and pyridine-2-carbaldehyde thiosemicarbazone (HL) in equimolar amounts in EtOH, at 50 °C leads to the formation of two Ni(II) complexes: ethanol soluble red complex $[\text{Ni}(\text{HL})\text{L}][\text{NO}_3]$ (**1**) and water soluble brownish complex $[\text{Ni}(\text{HL})_2][\text{NO}_3]_2$ (**2**) [**2a**]. The ORTEP view of compounds **1** and **2a** are reported in Figs. 1 and 2, together with the atomic numbering scheme.



Scheme

Summary of crystallographic data for compounds **1**, **2a**, and **2b**

Parameter	1	2a	2b
Formula	[Ni(C ₇ H ₈ N ₄ S)(C ₇ H ₇ N ₄ S)](NO ₃)·H ₂ O	[Ni(C ₇ H ₈ N ₄ S) ₂](NO ₃) ₂	[Ni(C ₇ H ₈ N ₄ S) ₂](NO ₃) ₂ ·2H ₂ O
FW	498.20	543.20	579.23
Crystal system	C2/c	P-1	P2 ₁ /c
Space group	Monoclinic	Triclinic	Monoclinic
a, b, c, Å	21.951(3), 14.891(2), 13.5105(13)	8.825(2), 11.639(3), 12.356(3)	21.417(3), 16.756(2), 13.5733(17)
α, β, γ, deg.	90, 111.559(2), 90	70.251(6), 88.104(4), 71.512(5)	90, 105.195(2), 90
V, Å ³	4107.2(9)	1128.9(4)	4700.7(10)
Z	8	2	8
D _{calcd} , g·cm ⁻³	1.611	1.598	1.637
F(000)	2048	556	2384
Crystal size, mm	0.20×0.18×0.15	0.19×0.18×0.15	0.18×0.16×0.15
Crystal colour	Red	Brown	Brown
Crystal shape	Prism	Prism	Prism
μ, mm ⁻¹	1.190	1.098	1.066
θ range	1.69—30.59	1.76—28.07	0.99—28.01
Rfins collected / unique	33067 / 6304	13295 / 5291	55518 / 11237
rfins obsv [I > 2σ(I)]	4125 [R _{int} = 0.0626]	3328 [R _{int} = 0.0262]	5694 [R _{int} = 0.0803]
Parameters	289	298	631
R indices [I > 2σ(I)]	R1 = 0.0407, wR2 = 0.0940	R1 = 0.0347, wR2 = 0.0702	R1 = 0.0423, wR2 = 0.0869
R indices (all data)	R1 = 0.0734, wR2 = 0.1067	R1 = 0.0678, wR2 = 0.0775	R1 = 0.1160, wR2 = 0.1040
GOOF	1.019	0.832	0.907
Residual density max.	0.389	0.317	0.442

$$R1 = \frac{\sum||F_0| - |F_c||}{\sum|F_0|}, \quad wR2 = \frac{[\sum[w(F_0^2 - F_c^2)^2]}{\sum[w(F_0^2)^2]}.$$

Complex **2** in its dihydrated form [Ni(HL)₂][NO₃]₂·2(H₂O) (**2b**) is also obtained by slow evaporation of a water/ethanol solution.

Comparative structural studies have been carried out on Ni(II) complexes **1** and **2**. In Table 2 a list of the most important bond distances and angles are reported for the compounds.

In both complexes the nickel ion adopts a distorted octahedral coordination geometry; the ligand is tridentate in its E configuration about the C=N azomethine group, binding to the metal through the N_{pyridine}, N_{azomethine}, and S atoms. In complex **2** (anhydrous **2a** and hydrated form **2b**) the ligand is present in its neutral form HL, whereas in complex **1** one ligand molecule is coordinated in its anionic deprotonated form, L⁻. The structure of **1** consists of discrete [Ni(HL)L]⁺ cations, NO₃⁻ anions, and water molecules. The water molecule is involved in a weak hydrogen bond with the N7 atom of the deprotonated molecule [N7···O1o 3.178(2) Å, N7···H1w—O1o 132.89°]. Compound **2** crystallizes in two forms **2a** and **2b**, both containing discrete [Ni(HL)₂]²⁺ cations and two NO₃⁻ anions. Form **2b** differs from **2a** because of the presence of two independent Ni complex cations and two co-crystallized water molecules.

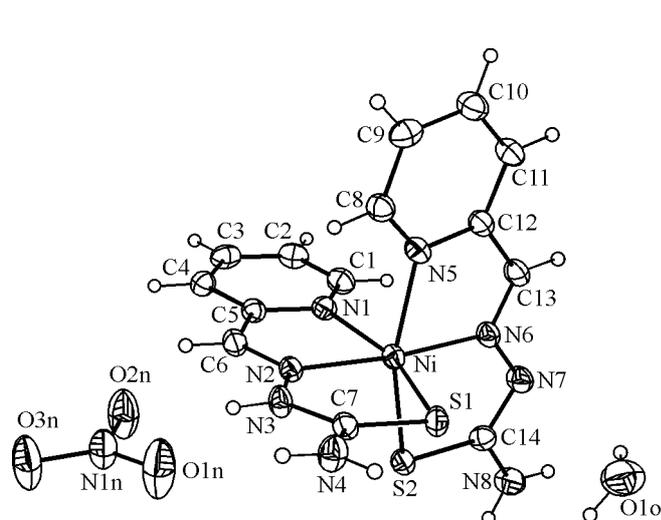


Fig. 1. View of the molecular structure of compound **1** with the atomic labelling scheme. The thermal ellipsoids are drawn at the 30 % probability level

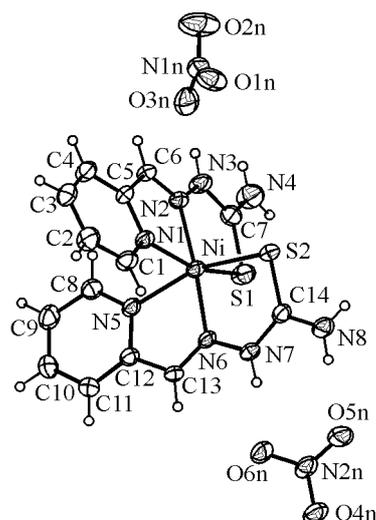


Fig. 2. View of the molecular structure of compound **2a** with the atomic labelling scheme. The thermal ellipsoids are drawn at the 30 % probability level

T a b l e 2

Selected bond distances (Å) and angles (deg.) for compounds 1, 2a, and 2b

Atoms	1	2a	2b (molecule A)	2b (molecule B)
Ni—S1	2.4310(7)	2.4270(8)	2.4395(10)	2.4189(10)
Ni—S2	2.3808(7)	2.4143(8)	2.4353(10)	2.4196(10)
Ni—N1	2.1185(18)	2.1068(19)	2.116(3)	2.114(3)
Ni—N2	2.0281(17)	2.0119(17)	2.022(3)	2.028(2)
Ni—N5	2.0999(18)	2.1034(19)	2.103(3)	2.120(3)
Ni—N6	2.0117(17)	2.0184(17)	2.020(3)	2.025(3)
S1—C7	1.692(2)	1.682(2)	1.688(3)	1.681(3)
S2—C14	1.720(2)	1.686(2)	1.682(4)	1.689(4)
S1—Ni—N1	159.13(5)	158.29(5)	158.77(8)	158.26(8)
S2—Ni—N5	160.84(5)	158.11(5)	158.94(8)	158.52(8)
N2—Ni—N6	174.01(7)	175.29(8)	174.48(11)	174.56(10)

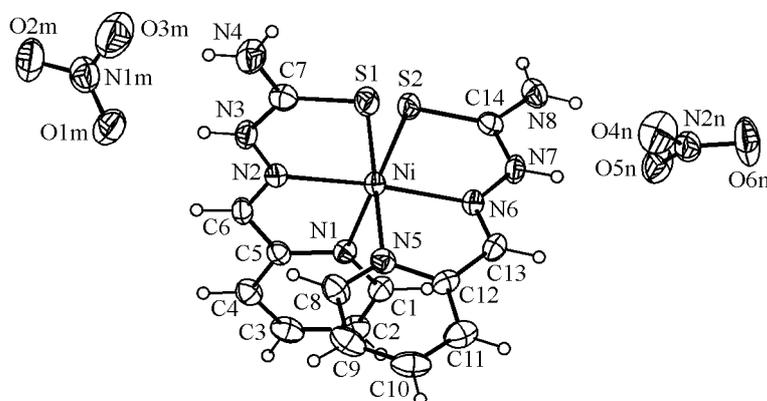


Fig. 3. View of the molecular structure of molecule A of compound **2b** with the atomic labelling scheme. The thermal ellipsoids are drawn at the 30 % probability level

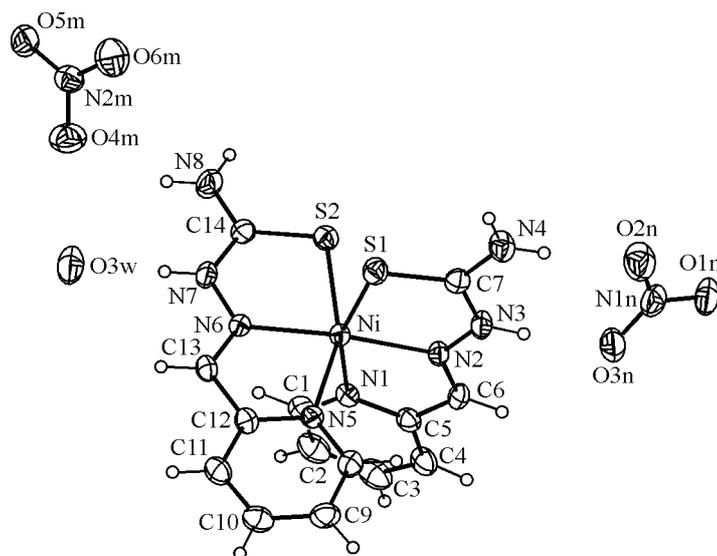


Fig. 4. View of the molecular structure of the molecule B of compound **2b** with the atomic labelling scheme. The thermal ellipsoids are drawn at the 30 % probability level

In the three structures the Ni—N bond distances are in the range 2.012(2)—2.212(3) Å in agreement with those found in seven parent Ni(II)[*N,N,S*]₂²⁺ structures (the mean Ni—N bond distance 2.063 Å) [CSD entry codes: CAGCOD, DIRYAF, EFOPIY, OHUHII, POKDAV, YAPKEG, YAPKIK, CSD version updates August 2012] [7]. It is interesting to remark that compound **1** allows a comparison of the bonding parameters in neutral and anionic thiosemicarbazone molecules coordinated to the same metal cation. In this regard the values of the C=S (1.720(2) Å) and Ni—S (2.381(1) Å) bond distances in the anionic form L[−] appear significantly different from those displayed by the corresponding distances in the neutral form HL (1.692(2) Å and 2.431(1) Å respectively). Indeed the mean values of C=S and Ni—S distances found for the seven HL molecules reported in the present work (1.685(3) Å and 2.426(4) Å) are in good agreement with the mean values (1.687(3) Å and 2.427(1) Å) calculated by using the seven parent Ni complexes cited above [7]. Regarding packing all the Ni(II) cationic complexes, nitrates anions and water molecules are linked each other via N—H⋯O and O—H⋯O hydrogen bonds into a three dimensional supramolecular network.

Acknowledgements. University of Parma is gratefully acknowledged.

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