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Transition metal complexes with thiosemicarbazide-based ligands. Part LVI: Nickel(II) complex with 1,3-diphenylpyrazole-4-carboxaldehyde thiosemicarbazone and unusually deformed coordination geometry

Vukadin M. Leovac [a], Slađana B. Novaković [b], Goran A. Bogdanović [b], Milan D. Joksović [c,*], Katalin Mészáros Szécsényi [a], Valerija I. Češljević [a]

[a] *Faculty of Sciences, University of Novi Sad, Trg D.Obradovića 3, 21000 Novi Sad, Serbia*
[b] *VINČA Institute of Nuclear Sciences, P.O. Box 522, Belgrade 11001, Serbia*
[c] *Faculty of Sciences, University of Kragujevac, R. Domanovica 12, 34000 Kragujevac, Serbia*

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Abstract

Synthesis of a new nickel(II) complex, [Ni($Ph_2PzTSC-H$)$_2$] with 1,3-diphenylpyrazole-4-carboxaldehyde thiosemicarbazone (Ph_2PzTSC), is described. The compounds have been characterized by elemental and thermal analysis, molar conductivity and spectral (UV–Vis, IR, ^1H NMR, and ^{13}C NMR) measurements. In the case of complex the magnetic measurement has been also performed. Crystal and molecular structures of both the free ligand and the complex have been determined by single crystal X-ray analysis. It was found that the ligand coordinates in a bidentate NS fashion, in its deprotonated thioenolato form. The *cis*-square-planar geometry of the complex is significantly distorted tetrahedrally. The Cambridge Structural Database (CSD) study has been performed to obtain geometrical and structural informations on similar nickel(II) complexes in order to compare structural data.

Keywords: Nickel(II) complex; Thiosemicarbazone; Spectroscopic and TA studies; Crystal structure; CSD study

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1. Introduction

A number of *N*-heterocyclic thiosemicarbazones and their metal ion complexes have attracted considerable interest in chemistry and biology, owing to their potentially beneficial biological activities (antibacterial, antimalarial, antiviral, etc.), which have often been related to a chelation phenomenon with trace of metal ions [1–5]. Heterocyclic thiosemicarbazones are believed to exercise their beneficial therapeutic properties in mammalian cells by inhibiting ribonucleotide reductase in the synthesis of DNA precursors [4].

On the other side, many pyrazole derivatives are known to exhibit also a wide range of biological properties. Particularly, arylpyrazoles are important in medicinal and pesticidal chemistry [6]. Recently, some arylpyrazoles were reported to have non-nucleoside HIV-1 reverse transcriptase inhibitory activity [7]. Extensive studies have been devoted to arylpyrazole derivatives such as Celecoxib, a well-known cyclooxygenase-2 inhibitor [8–11]. More recently, pyrazole derivatives as high affinity and selective A2B adenosine receptor antagonists have been reported [12].

The well-documented biological activities of *N*-heterocyclic thiosemicarbazones have prompted further investigation on the coordination chemistry of such ligands during the last period [5,13] with the recommendation that

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[*] Corresponding author. Tel.: +381 34336223; fax: +381 34335040.
E-mail address: mjoksovic@kg.ac.yu (M.D. Joksović).

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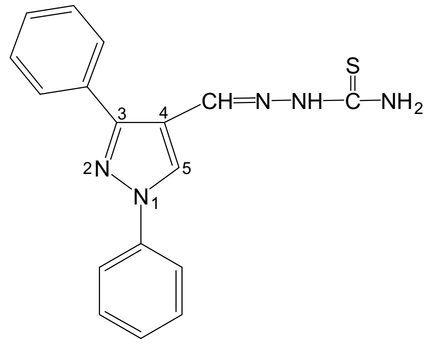

Fig. 1. Chemical structure of Ph_2PzTSC.

structural variation on the heterocyclic ring might bring out significant enhancement in their biological effects, especially in corresponding metal complexes, often with novel structural information. Synthesis and spectroscopic characterization of nickel(II) complexes with some pyrazolyl thiosemicarbazones, such as 5-methyl-3-formylpyrazole-3-substituted thiosemicarbazones have been reported by other authors [14–16]. As a part of our investigation toward synthesis and structural characterization of new compounds containing biorelevant pyrazolyl thiosemicarbazones, the present paper reports the synthesis, spectroscopic, and structural properties of 1,3-diphenylpyrazole-4-carboxaldehyde thiosemicarbazone ligand (Ph_2PzTSC, Fig. 1) and its nickel(II) complex.

2. Experimental

2.1. Reagents and starting materials

Solvents and reagents were obtained from commercial sources. The solvents were purified using the established method [17]. Thiosemicarbazide and nickel(II) acetate tetrahydrate were purchased from Aldrich Chemicals, USA. 1,3-Diphenylpyrazole-4-carboxaldehyde was synthesized according to Rathelot et al. procedure [18].

2.2. Preparation of Ph_2PzTSC

The Ph_2PzTSC ligand was prepared by refluxing the mixture of the 1,3-diphenylpyrazole-4-carboxaldehyde (1.24 g, 5 mmol) and thiosemicarbazide (0.45 g, 5 mmol) in ethanol (20 cm^3) for 4 h. One drop of glacial acetic acid was previously added into the mixture. After cooling, the white precipitate was filtered, washed with cold chloroform in order to remove the traces of unchanged aldehyde, and dried over anhydrous calcium chloride. Yield: 1.25 g, 78%. The suitable crystals for X-ray analysis were obtained by recrystallization of the ligand from the mixture of acetone and methanol (1:1 v/v).

Anal. Calc. for $C_{17}H_{15}N_5S$: C, 63.53; H, 4.70; N, 21.79. Found: C, 63.75; H, 4.62; N, 21.55%. UV–Vis spectra ($cm^{-1}/\log\varepsilon$): 31950 (4.0); ~30000 (4.0).

^1H NMR (200 MHz, DMSO-d_6): 7.38–7.70, m (8H, Ar); 7.80, br s (1H, NH_2); 7.90, d (2H, Ar, $J = 7.86$ Hz, *ortho*-H, N-substituted phenyl); 8.22, s (1H, Pz); 8.27, br s (1H, NH_2); 9.19, s (1H, CH=N); 11.34, br s (1H, NH).

^{13}C NMR (200 MHz, DMSO-d_6): 117.43; 118.66; 127.15; 127.85; 128.30; 128.75; 128.91; 129.85; 132.28; 135.10; 139.20; 151.52; 177.72.

IR (KBr pellets): 3326, 3257, 3140, 1618, 1598, 1543, 1500, 1221, 1098, 1064, 831, 807, 755, 704, 687 cm^{-1}.

2.3. Preparation of $[Ni(Ph_2PzTSC\text{-}H)_2]$

$Ni(CH_3COO)_2 \cdot 4H_2O$ (0.25 g, 1 mmol) was dissolved in methanol (10 cm^3) under heating and the solution was mixed with a warm solution of Ph_2PzTSC (0.32 g, 1 mmol) in acetone (20 cm^3). The heating was continuated for several minutes. After 10 h of standing, the brown crystals were filtered and washed with acetone and dried over anhydrous calcium chloride Yield: 0.16 g, 46%.

Anal. Calc. for $C_{34}H_{28}N_{10}NiS_2$: C, 58.38; H, 4.03; N, 20.02; Ni, 8.39. Found: C, 58.42; H, 3.98; N, 20.12; Ni, 8.42%. $\lambda_M(DMF) = 3.3\ S\ cm^2\ mol^{-1}$. UV–Vis: ($cm^{-1}/\log\varepsilon$): ~33300 (4.0); 30210 (4.3); 25500 sh (3.7); 19300 sh (2.1). sh (shoulder).

^1H NMR (200 MHz, DMSO-d_6): 6.97–7.19, m (7H; 5H, phenyl and 2H, NH_2); 7.49, s (1H, Pz); 7.50, d (1H, Ar, $J = 7.36$Hz, *para*-H, N-substituted phenyl); 7.65, t, (2H, Ar, $J = 7.66$Hz, *meta*-H, N-substituted phenyl); 8.03, d, (2H, $J = 7.77$Hz, *ortho*-H, N-substituted phenyl); 9.84, s (1H, CH=N, azomethine).

^{13}C NMR (200 MHz, DMSO-d_6): 114.29; 119.89; 127.62; 127.86; 128.44; 128.83; 129.88; 130.10; 130.89; 139.23; 150.17; 152.68; 173.46.

IR (KBr pellets): 3466, 3284, 3067, 1626, 1596, 1526, 1513, 1504, 1219, 956, 705, 672 cm^{-1}.

2.4. Physical measurements

Elemental (C, H, N) analysis of the samples was carried out by standard micromethods in the Center for Instrumental Analysis, Faculty of Chemistry, Belgrade. Nickel content was determined by the complexometric titration with EDTA method, upon the destruction of complex with the mixture of concentrated H_2SO_4 and HNO_3. Molar conductivity of freshly prepared 1×10^{-3} mol dm^{-3} solution was measured on a Jenway 4010 conductivity meter. IR spectra were recorded on a Perkin Elmer Spectrum One FT-IR spectrometer with a KBr disc. ^1H and ^{13}C NMR spectra were obtained using a Varian Gemini 200 spectrometer. Electronic spectra were recorded on a Secomam (Anthelie 2, Advanced, for the range 270–900 nm) and on a Thermo Nicolet instrument (NEXUS 670 FT-IR, for the range 900–1400 nm) in $(1–2) \times 10^{-3}$ mol dm^{-3} DMF solutions of the ligand and complex. Thermal analysis in argon and air gas carriers with a 15 dm^3/min flowing rate and a heating rate of 10 K/min were carried out using a DuPont 1090 TA system. For thermogravimetric