



5-Methyl-2-hydroxy-acetophenone-thiosemicarbazone and its nickel(II) complex: Crystallographic, spectroscopic (IR, NMR and UV) and DFT studies



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ABSTRACT

A new 5-methyl-2-hydroxy-acetophenone-thiosemicarbazone ligand (L) and its nickel(II) complex [Ni(L)(PPh₃)] were synthesized. The crystal structure of free ligand and its complex has been determined by single crystal X-ray diffraction technique. In the complex, thiosemicarbazone ligand is coordinated to nickel through ONS mode. The structures were also characterized by elemental analysis, IR, ¹H NMR and UV–Vis. spectroscopies. In addition, the molecular geometries, vibrational frequencies and gauge-independent atomic orbital (GIAO) ¹H NMR chemical shift values of the compounds in the ground state have been calculated using the density functional theory (B3LYP) method with 6-311G(d,p) basis set for C, H, N, O, P, S atoms and LANL2DZ basis set for Ni atom. Electronic transitions were calculated using the time-dependent density functional theory (TD-DFT) formalism and the experimental spectra of the compounds have been discussed.

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1. Introduction

Thiosemicarbazone derivatives form an important class of organic compounds due to their structural chemistry and biological activities, such as, antibacterial, antiviral, antitumor, antiamebic and antimalarial activities [1–4]. Sulfur and oxygen containing thiosemicarbazones have been the subjects of extensive investigation because of their use for the biological applications [5,6]. Thiosemicarbazones, as well as their transition metal complex, has been the subject of great interest of many researchers for a number of years.

Phosphine ligands play a central role in many reactions catalyzed by transition metals [7], so research on metal-phosphine complexes containing thiosemicarbazones have raised considerable interest. But there have been only very few reports concerning the metal complexes containing both thiosemicarbazone and triphenylphosphine.

Such pharmacological activities are with biologically important metal ions such as Fe, Cu, Ni and their reductive capacities [8–13]. Nickel complexes have drawn much attention due to their environmental toxicity, carcinogenic nature and chemotherapeutic property in the past years [14]. It has been found that these

complexes can inhibit DNA repair by interfering with enzymes or proteins involved in DNA replication and/or DNA repair [15].

A new thiosemicarbazone ligand (L) and its nickel(II) complex [Ni(L)(PPh₃)] were synthesized and determined by single crystal X-ray diffraction technique. In the present study, it is planned to have a joint experimental and theoretical investigation of FT-IR, UV–Vis and ¹H NMR spectra. The geometrical parameters, fundamental frequencies, ¹H NMR chemical shifts and electronic absorption spectra in the ground state have been calculated by using DFT method with B3LYP/6-311G (d,p) basis set for both molecules and LANL2DZ (Ni) basis set was also used in calculations of the complex, and the results are compared with the experimental ones.

2. Materials and methods

2.1. Instrumentation

The elemental analyses were determined on a Carlo-Erba 1106 Elemental Analyser. The FT-IR spectrum of the compounds was recorded in the 4000–400 cm⁻¹ region with a Bruker Vertex 80V FT-IR spectrometer using KBr pellets. The ¹H NMR spectra (in CDCl₃, relative to SiMe₄) were recorded by a Bruker Avance-500 model spectrometer. UV–vis. spectra were obtained with a Shimadzu 2600 UV–Vis Spectrometer as 1.0 × 10⁻⁵ M solutions in MeOH.

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2.2. Synthesis

2.2.1. Synthesis of (L)

The ethanolic solution of thiosemicarbazide (0.91 g, 10 mmol) was added to the solution of 5-methyl-2-hydroxy-acetophenone (1.5 g, 10 mmol, in 10 mL absolute ethanol). The mixture was refluxed for 6 h and it was then allowed to stand at room

temperature. The crude product was filtered off and it was washed several times with small amounts of cold ethanol. The ligand was recrystallised from ethanol and dried under vacuum. The color; m.p. (°C); yield (%) and elemental analysis data of the ligand were given as follows: Cream; 201.4–202.8; 88; Analytical data for C₁₀H₁₃N₃OS (223.29 g), found (calc.): C, 53.65 (53.79), H, 5.74 (5.87), N, 18.67 (18.87), S, 14.20 (14.36).

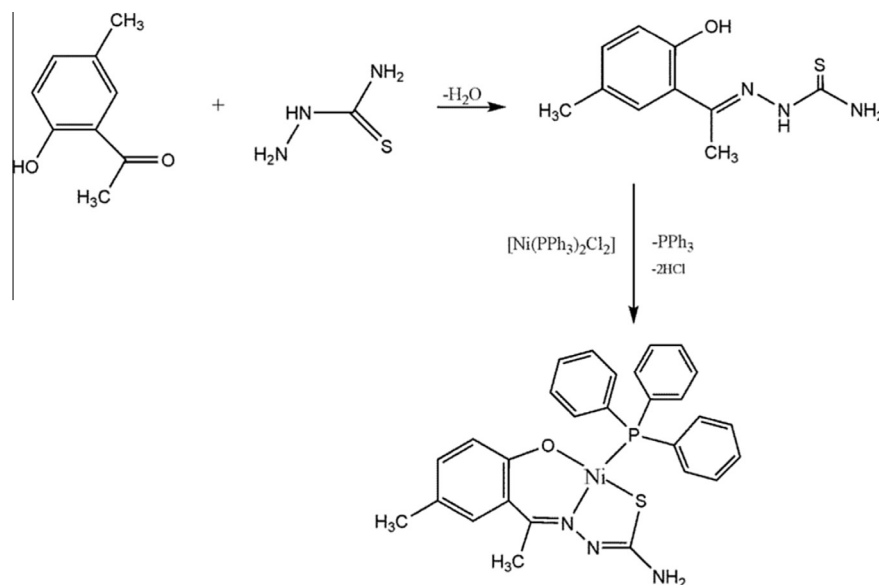


Fig. 1. The formation of the (L) and [Ni(L)(PPh₃)] compounds.

Table 1

Crystal data and structure refinement parameters for (L) and [Ni(L)(PPh₃)].

| | (L) | [Ni(L)(PPh ₃)] |
|--|---|--|
| CCDC deposition number | 1421542 | 1421541 |
| Chemical formula | C ₁₀ H ₁₃ N ₃ OS | C ₂₈ H ₂₆ N ₃ NiOPS |
| Color/shape | cream/prismatic plate | dark red/prismatic plate |
| Formula weight | 223.29 | 542.26 |
| Crystal size (mm) | 0.47 × 0.19 × 0.16 | 0.56 × 0.24 × 0.07 |
| Wavelength (Å) | Mo Kα, λ = 0.71073 | Mo Kα, λ = 0.71073 |
| Temperature (K) | 296 | 296 |
| Crystal system | monoclinic | monoclinic |
| Space group | P2 ₁ /c | P2 ₁ /n |
| <i>Unit cell parameters</i> | | |
| a (Å) | 7.3814(4) | 13.0204(8) |
| b (Å) | 11.8583(6) | 8.0188(4) |
| c (Å) | 12.2368(7) | 24.5770(17) |
| α (°) | 90 | 90 |
| β (°) | 91.706(5) | 98.446(6) |
| γ (°) | 90 | 90 |
| V (Å ³) | 1070.62(10) | 2538.2(3) |
| Z | 4 | 4 |
| Density (Mg m ⁻³) | 1.385 | 1.419 |
| μ (mm ⁻¹) | 0.279 | 0.936 |
| Absorption correction | integration | analytical |
| T _{min} , T _{max} | 0.877, 0.965 | 0.733, 0.947 |
| F(000) | 472 | 1128 |
| Diffractometer/meas. meth. | STOE IPDS 2/ω-scan | Xcalibur Eos/ω-scan |
| θ range for data collection (°) | 2.761 ≤ θ ≤ 28.948 | 2.992 ≤ θ ≤ 26.372 |
| Index ranges | -10 ≤ h ≤ 10, -16 ≤ k ≤ 16, -16 ≤ l ≤ 16 | -15 ≤ h ≤ 16, -9 ≤ k ≤ 10, -30 ≤ l ≤ 30 |
| Reflections collected | 10543 | 12585 |
| Independent/observed reflections | 2819/1999 | 5168/3897 |
| R _{int} | 0.089 | 0.035 |
| Data/restraints/parameters | 2819/0/154 | 5168/2/325 |
| Goodness of fit (GOF) on F ² | 1.013 | 1.050 |
| Final R indices [I > 2σ(I)] | 0.0563, 0.1352 | 0.0477, 0.0944 |
| Δρ _{max} , Δρ _{min} (e Å ⁻³) | 0.36, -0.38 | 0.43, -0.35 |

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