



Crystallographic, spectroscopic and theoretical investigations on Ni(II) complexes of a tridentate NNS donor thiosemicarbazone



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ABSTRACT

Five new nickel(II) complexes [Ni(L)NCS] (**1b**), [Ni(L)N₃] (**2**), [Ni(L)N(CN)₂] (**3**), [Ni(L)OAc] (**4**) and [Ni(HL)SO₄] (**5**) of a thiosemicarbazone HL (where HL = 2-benzoylpyridine-N(4)-phenylthiosemicarbazone) including pseudohalides like thiocyanate, azide and dicyanamide have been synthesized and characterized by elemental analysis, magnetic susceptibility, FT-IR, electronic and NMR spectroscopic techniques. The interesting amido-iminol tautomerism enables the pro-ligand to exist in amido form as well as deprotonated iminol form thereby functioning as tridentate NNS donor, coordinating through pyridyl nitrogen atom, azomethine nitrogen atom and amido/imino sulfur atom in the complexes. The crystal structures were established by single crystal XRD analysis. Two different single crystals of the compound thiocyanato complex were obtained with and without DMF solvent molecule having triclinic and monoclinic lattices with *P*1 and *P*2₁/*n* space groups respectively. Also, the compound **2** is having a monoclinic lattice with *P*2₁/*n* space group. Nickel(II) exists in distorted square planar geometry in all the complexes. Further DFT calculations were carried out at B3LYP/TZVP level of theory to obtain an insight on the stability and the nature of frontier orbitals. Finally, electrostatic potential plots mapped on optimized geometries substantiate the noncovalent interactions found in their respective crystal structures.

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1. Introduction

Thiosemicarbazones (TSCs) and their metal complexes show a lot of applications in pharmacology and therefore they have been extensively studied due to which there are now a considerable number of coordination compounds in which TSCs behave as neutral or anionic ligands with transition or non-transition metals [1–6]. The chelation property exhibited by these thiosemicarbazones with metal ions is responsible for the biological activities [7]. Also the ability of the thiosemicarbazone moiety to coordinate in the anionic form as C=N–N=C–S⁽⁻⁾–N increases the biological activity of these compounds [8]. These thiourea derivatives find substantial applications in different facets of contemporary scientific research such as in enzyme modeling mechanism, corrosion inhibitory studies [9–11], etc. These TSCs being NNS donors show carcinostatic efficiency and *in vivo* activity against tumor cells [12–14]. It is also evidenced that some structural variations on the TSCs due to their chelation may damage or decrease its

therapeutic value [15]. Nickel is an essential nutrient and act as the active site in some enzymes seen in plants. Various nickel(II) complexes find a potential application in the production of anti-cancer agents.

In the present study, a tridentate NNS donor, HL = 2-benzoylpyridine-N(4)-phenylthiosemicarbazone has been used to synthesize five different Ni(II) complexes viz., [Ni(L)NCS] (**1b**), [Ni(L)N₃] (**2**), [Ni(L)N(CN)₂] (**3**), [Ni(L)OAc] (**4**), [Ni(HL)SO₄] (**5**). The chosen ligand shows both anionic coordination (iminol form) in complexes **1–4**, as well as neutral coordination (amido form) in the complex **5**.

2. Experimental

2.1. General remarks

Commercially available AR grade reagents and chemicals were used as received without further purification. The ligand was prepared *in situ* through an equimolar (1:1) condensation reaction of 2-benzoylpyridine with N(4)-phenyl-3-thiosemicarbazide and one pot method was adopted for the syntheses of all the complexes.

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