Synthesis and characterization of mixed nickel thiosemicarbazone complexes

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ABSTRACT

Three nickel thiosemicarbazone mixed ligands complexes have been synthesized. Complexes with the formula \([\text{NiL(PPh}_3\text{)}\text{Cl, [Ni}_2\text{L}_2\text{(Phen)}, [\text{Ni}_2\text{L}_2\text{(Bpy)}] \text{(where L= 2,3,4-trihydroxybenzaldehydethiosemicarbazone, PPh}_3\text{=} \text{Triphenylphosphine, Phen=1,10-phenanthroline, Bpy= 2,2 –Bipyridine)}\) have been characterized by IR spectroscopy, as well as elemental analysis. The structure of \([\text{NiL (PPh}_3\text{)}\text{Cl}\) has been determined by X-ray crystallography. The crystal structure of this complex shows that the Schiff base ligand functions as an N,O,S chelating anion to the phosphine – coordinated nickel(II) atom, which exists as a distorted square – planar geometry.

1. INTRODUCTION

Metal complexes are often prepared with an aim to bring out specific physiochemical properties. Choosing appropriate donor atoms and the design of the ligands are imperative in achieving such objectives. Sulfur, nitrogen and oxygen donor atoms are commonly encountered in metal complexes exhibiting interesting stereochemical, electrochemical and electronic properties[1]. Thiosemicarbazone and its derivatives are amongst the widely studied sulfur, nitrogen and oxygen donor ligands[2-5]. The real impetus towards synthesis of thiosemicarbazone and its coordination compounds is the broad range of applications in several chemical disciplines. Among these applications, the biological activities of thiosemicarbazone and its derivatives have received considerable attention because they possess a wide variety of biological activities such as antimalarial, antifungal, antibacterial, antiviral, anticancer and antitumor[6-10]. It has been shown that their biological properties are often enhanced upon complexation[11,12]. Thiosemicarbazones exist in two tautomeric forms, the thione and the thiol forms (Scheme 1.0) and coordinated to a metal ion in neutral or deprotonated form as N,S-bidentate ligands. However, the presence of an additional donor atom (X) like NH$_2$, OH, SH in the thiosemicarbazone moiety, normally results in X,N,S- tridentate ligands.

Mixed ligand complexes of thiosemicarbazone containing anionic and neutral compounds as second ligand are of current interest in view of their solid state structure and their key role in biological chemistry owing the fact that several enzymes have been shown to contain a metal ion in the active site with a variety of ligand environments[13].

Scheme 1  Tautomeric forms of Thiosemicarbazone

Besides many applications in catalysis, the coordination chemistry of nickel is of interest with respect to its important roles in biological systems. The biological importance of nickel has been increasingly realized in recent years because of the identification of nickel in many enzymes involved in ureolysis, hydrogen metabolism and acetogenesis[14]. The capacity of nickel to bind to soft and hard donor ligands allow its coordination chemistry to encompass a variety of geometries, coordination numbers and oxidation states[15]. Thiosemicarbazones derived from salicylaldehyde and their mixed complexes have been the subject of extensive investigation[16] because of their wide variation in modes of bonding and stereochemistry whereas the polyhydroxybenzaldehyde analogs have received much less attention. Herein, we report the synthesis and characterization of three nickel(II) mixed complexes with 2,3,4-trihydroxybenzaldehydethiosemicarbazone type
ligand. Two bidentate bases namely 2,2'-bipyridine(bipy), 1,10-phenanthroline(Phen) and one monodentate triphenylphosphine were used as auxiliary ligands for coordination with nickel metal.

2. EXPERIMENTAL

2.1 Materials, method and instruments

The solvents were purchased from Merck and the reactants for syntheses were from Sigma. [NiCl₂(PPh₃)₂] [17] and 2,3,4-trihydroxybenzaldehydethiosemicarbazone[18] were prepared by following the literature methods. FT-IR spectra were recorded on a Perkin-Elmer Spectrum RX-1 spectrophotometer as KBr pellets in the frequency range of 400 – 4000 cm⁻¹. Elemental analyses were performed on a Thermo Finnigan Eager 300 CHNS elemental analyzer.

2.2 Preparation of Ni(II) complexes of the type [Ni₂L₂Y]

Nickel chloride hexahydrate (0.24 g, 1 m mol) and 2,2'-bipyridine (0.16 g, 1 m mol) or 1,10-phenanthroline (0.18 g, 1 m mol) were heated in methanol (20 ml) for 1 hour followed by addition of 2,3,4-trihydroxybenzaldehyde thiosemicarbazone, H₄T (0.23 g, 1 mmol) in hot methanol (20 ml) and the mixture was refluxed for another 3 hours. The green complexes that formed were filtered, washed with cold methanol and ether, dried in air and kept in a desiccator over silica gel.

2.3 Preparation of [NiL(PPh₃)]Cl

[NiCl₂(PPh₃)₂] (0.65 g, 1 m mol) was heated in ethanol (20 ml) for 10 min followed by addition of 2,3,4-trihydroxybenzaldehydethiosemicarbazone, H₄T (0.23 g, 1 mmol) in hot methanol (20 ml) and the red mixture was refluxed for 24 hours. The clear solution was filtered, and kept for crystallization, the crystals which formed after two weeks filtered and washed with small amounts of cold methanol and ether and kept in a desiccator over silica gel.

3. RESULTS & DISCUSSION

3.1 Syntheses and characterization

The reaction of 2,3,4-trihydroxybenzaldehyde thiosemicarbazone with NiCl₂.6H₂O in presence of heterocyclic bases in a 1:1:1 molar ratio in ethanol yielded dinuclear complexes of the formula [Ni₂L₂Y]. On the other hand, the reaction of the ligand with [NiCl₂(PPh₃)₂] in methanol/ethanol mixture afforded mononuclear complex of the formula [NiL(PPh₃)]Cl. All the complexes are stable to air and light and soluble in organic solvents such as CH₃CN, CH₂Cl₂, DMF and DMSO. The elemental analyses obtained for the complexes are in good agreement with the proposed molecular formula Table 1. The main vibrational bands of the free ligand (2,3,4-trihydroxybenzaldehydethiosemicarbazone) and its nickel(II) complexes are compared in Table 2. The free ligand exists as thione tautomer in solid state due to the absence of any bands in the 2800 – 2500 cm⁻¹ region of the IR spectrum. The bands 3479, 3340 and 3187 cm⁻¹ are assigned to the ν(OH) , ν(N(4)-H) and ν(N(2)-H) vibrations of the free ligand[19]. The OH vibration is still seen in the spectra of the three nickel complexes indicating that only one of the phenolic OH of 2,3,4-trihydroxybenzaldehyde thiosemicarbazone ligand is deprotonated and involved in the coordination with nickel.
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The band at 3187 cm⁻¹ assigned to ν(N(2)-H) of the free ligand disappear in the spectra of the complexes [Ni₂L₂Y] indicates the deprotonation of the hydrazinic proton and the coordination with nickel in the thiol form. On the other hand, the spectra of the complex [NiL(PPh₃)]Cl shows ν(N(2)-H) band at 3056 cm⁻¹ indicates the coordination of the ligand in the thione form. The absorption due to νC=N of the free ligand appearing in the 1620 cm⁻¹ region undergoes a negative shift by 10-20 cm⁻¹ in the spectra of all the three complexes indicating the coordination of azomethine nitrogen to the nickel ion [20].

3.3. Crystallography

Single crystals of complex [NiL(PPh₃)]Cl (3) suitable for X-ray diffraction studies, were grown by slow evaporation of the reaction mixture. Complex 3 crystallized into an orthorhombic lattice with space group symmetry P2₁/n (No.4) with Z = 4. The Ellipsoidal plots of the complex are shown in Figure 2. The crystal data and structure refinement parameters for complex 3 are shown in Table 3. Selected bond lengths and angles are presented in Table 4. Complex 3 is formed by the chelation of the mono deprotonated thiosemicarbazone ligand to a nickel atom with one PPh₃ group attached (Fig. 2). The chelate structure of complex 3 consists of coordination of the ligand in the tridentate fashion through the O, N and S atoms, forming a five- and six-member chelate rings with O-Ni-N and N-Ni-S bite angles of 93.6(2)° and 88.61(19)° respectively. The PPh₃ ligand coordinates to nickel(II), and the fourth coordination site of the central atom is completed by the phosphorus atom. The donor atoms of the complex 3 are placed in the corners of a slightly distorted square plane geometry, like in the nickel–triphenylphosphine complex obtained from 2,3-dihydroxybenzaldehydehyde semicarbazone[22]. The Ni-O, Ni-N, NiS and Ni-P were found to be 1.849(5), 1.894(6), 2.131(2) and 2.228(2) respectively. The co-ordination bonds of both complexes are of approximately the same lengths, although the Ni1-S1 bond of complex 3 is slightly shorter than the equivalent bond of the other complex by approximately 0.06 Å.
4. CONCLUSIONS

This study shows that nickel (II) reacts with thiosemicarbazone of 2,3,4-trihydroxybenzaldehyde in presence of heterocyclic bases and triphenylphosphine giving mononuclear and binuclear complexes. In all these complexes the thiosemicarbazone coordinated to nickel(II) in a tridentate fashion afford Stable mixed-ligand complexes. The X-ray diffraction studies reveal that the thiosemicarbazone in the complex [NiL(PPh₃)]Cl is monodeprotonated and coordinated to the metal in the thione form.

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