Preparation and Characterization of Co (III) and Ni (II) Complexes of the New Chiral Schiff Base (z)-1-(Pyridine-2-Ylmethylene) Thiosemicarbazide

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Abstract: Two new complexes of (z)-1-(pyridine-2-ylmethylene) thiosemicarbazide that abbreviated as PMTC was synthesized and characterized by reaction of this novel ligand with CoCl₂.6H₂O and Ni(CH₃COO).4H₂O. These new ligand and complexes were characterized by microanalyses, FT-IR.

Key words: (z)-1-(pyridine-2-ylmethylene) thiosemicarbazide • Co (III) complex • Ni (II) complex • Synthesis • FT-IR • Schiff chiral bases • Metal complexes • Aromatic aldehydes

INTRODUCTION

Schiff bases derived from the reaction of aromatic aldehydes and aliphatic or aromatic amines represent an important series of widely-studied organic ligands. The chemistry of Schiff bases is a field that is being noticed. A large number of Schiff bases compounds are often used as ligands in coordination chemistry by considering their metal binding ability. Schiff bases form a significant class of compounds in medicinal and pharmaceutical chemistry with several biological applications that include antibacterial [1-6], antifungal and antitumor activity [7, 8]. Due to their multiple implications, the transition metal complexes with Schiff bases, as ligands, are of paramount scientific interest. Schiff base complexes have been used as drugs. Moreover, it is well known that some drug activities, when administered as metal complexes, are being increased [3]. Schiff base metal complexes have been widely studied because they have industrial, antibacterial, anticancer and herbicidal applications. They serve as models for biologically important species and find applications in biomimetic catalytic reactions. Nitrogen-containing ligands such as Schiff bases and their metal complexes played an important role in the development of coordination chemistry resulting in an enormous number of publications, ranging from pure synthetic work to physicochemical and biochemically relevant studies of metal complexes [9-13] and found wide range of applications. Other kinds of nitrogen-containing ligands are well-known pyrimidine systems such as purine analogues that exhibit a wide range of biological activities. Metal complexes make these compounds effective as stereospecific catalysts towards oxidation, reduction, hydrolysis, biological activity and other transformations of organic and inorganic chemistry. Chelating ligands containing N, S and O donor atoms show broad biological activity and are of special interest because of the variety of ways in which they are bonded to metal ions. It is known that the existence of metal ions bonded to biologically active compounds may enhance their activities. The variety of possible Schiff base metal complexes with wide choice of ligands and coordination environments, has prompted us to undertake research in this area. Zinc can function as active site of hydrolytic enzymes, where it is ligated by hard donors (N or O). It has long been recognized as an important co-factor in biological molecules, either as a structural template in protein folding or as a Lewis acid catalyst that can readily adopt the coordination numbers 4, 5, or 6. The catalytic role of Zn comprises Lewis acid activation of substrate, generation of a reactive nucleophile (Zn-OH) and stabilization of the leaving group. We are reporting the synthesis and characterization of Co (III) and Ni (II) complexes of the Schiff base ligand (z)-1-(pyridine-2-ylmethylene) thiosemicarbazide.

MATERIALS AND METHODS

All reagents were supplied by Merck and were used without further purification. Melting point was determined...
Fig. 1: FTIR spectrum of PMTC (KBr Disk)

Fig. 2: FTIR spectrum of Co (PMTC) (KBr Disk)

Fig. 3: FTIR spectrum of Ni (PMTC) (KBr Disk)
in an Electrothermal 9200. The FT-IR spectra were recorded in the range 400-4000 cm\(^{-1}\) by KBr disk using a Bruker Tensor 27 M 420 FT-IR spectrophotometer.

**Synthesis of the PMTC Ligand:** Pyridine carbaldehyde (1.516g, 17mmol) and thiosemicarbazone (1.516g, 17mmol) were dissolved. The mixture was refluxed for 2.5 h at 65°C and then the resulting white precipitate was filtered. Mp212°C Yield: 77%. Anal. Calc. for C\(_4\)H\(_6\)NS: C, 46.66; H, 4.44; N, 31.11%. Found: C, 46.75; H, 4.56; N, 31.20%. FTIR (KBr pellet, cm\(^{-1}\)): 3431.70 (m, NH), 2805.15 (w, =CH); 3122.70 (m, NH), 2689.89 (m, =CH), 1617.06 (w, =CH), 1574.77 cm\(^{-1}\). The IR spectra of the Schiff base show characteristic bands due to \(\nu_\text{C=N}\), \(\nu_\text{=CH}\), \(\nu_\text{C-N}\) and \(\nu_\text{C=S}\) in the region 3122.70 cm\(^{-1}\), 2805.15 (w, =CH), 1617.06 (w, C-N), 1574.77 cm\(^{-1}\) (Figure 1).

**Synthesis of the Co (PMTC):** PMTC (0.36g, 1mmol) and CoCl\(_2\).6H\(_2\)O (0.24g, 1mmol) were dissolved in CH\(_3\)CN. The mixture was stirred for 2 h to give a clear solution. The resulting green-brown mixture was filtered. Yield: 80%. Anal. Calc. for C\(_6\)H\(_6\)NSCo: C, 35.15; H, 3.34; N, 13.02%. Found: C, 35.25; H, 3.45; N, 13.15%. FTIR (KBr pellet, cm\(^{-1}\)): 3421.70 (w, NH), 2929.60 (w, =CH); 1674 (s, =CH), 1625 (s, C=N) in the region 3431.70 cm\(^{-1}\), 1154.22 (s, C=N), 1607.54 (m, C=N) and 1111 (s, C-N) respectively.

**Synthesis of the Ni (PMTC):** PMTC (0.4g, 1mmol) and Ni (CH\(_2\)COO).4H\(_2\)O (0.27g, 1mmol) were dissolved in CH\(_3\)CN. The mixture was stirred for 2 h to give a clear solution. The resulting yellow mixture was filtered. Yield: 85%. Anal. Calc. for C\(_6\)H\(_6\)NSNi: C, 35.19; H, 3.35; N, 23.46%. Found: C, 35.25; H, 3.45; N, 23.58%. FTIR (KBr pellet, cm\(^{-1}\)): 3478.15 (s, NH), 2689.89 (s, =CH); 1617.06 (w, C-N), 1372.75 (m, C=S) (Figure 2).

**Synthesis of the PMTC Ligand:** Pyridine carbaldehyde (1.516g, 17mmol) and thiosemicarbazone (1.516g, 17mmol) were dissolved. The mixture was refluxed for 2.5 h at 65°C and then the resulting white precipitate was filtered. Mp212°C Yield: 77%. Anal. Calc. for C\(_4\)H\(_6\)NS: C, 46.66; H, 4.44; N, 31.11%. Found: C, 46.75; H, 4.56; N, 31.20%. FTIR (KBr pellet, cm\(^{-1}\)): 3431.70 (m, NH), 2805.15 (w, =CH); 3122.70 (m, NH), 2689.89 (m, =CH), 1617.06 (w, =CH), 1574.77 cm\(^{-1}\). The IR spectra of the Schiff base show characteristic bands due to \(\nu_\text{v(NH)}, \nu_\text{v(=CH)}, \nu_\text{v(C=C)}\) and \(\nu_\text{v(C-N)}\) in the region 3431.70 cm\(^{-1}\), 1146.13 (w, C-N), 1361.05 (m, C=S), 1607.54 (m, C=N) in the region 1410.68 cm\(^{-1}\) respectively. In the case of Co (III) complex \(\nu_\text{v(C=C)}\) and \(\nu_\text{v(C=S)}\) in the region 3431.70 cm\(^{-1}\), 1146.13 (w, C-N), 1361.05 (m, C=S), 1607.54 (m, C=N) in the region 1410.68 cm\(^{-1}\) respectively.

**RESULTS AND DISCUSSION**

The Schiff base compounds constitute an important class of ligands which have been extensively studied in coordination chemistry. Schiff bases derived from the reaction of aromatic aldehydes and aliphatic or aromatic amines represent an important series of widely-studied organic ligands. The chemistry of Schiff bases is a field that is being noticed. Schiff bases are potentially capable of forming stable complexes with metal ions. Schiff bases form a significant class of compounds in medicinal and pharmaceutical chemistry with several biological applications that include antibacterial, antifungal and antitumor activity. Schiff base complexes play a vital role in designing metal complexes related to synthetic and natural oxygen carriers Cobalt (III) and Ni (II) salts react with Schiff base ligand in 1:1 (L/M) molar ratio in solvent to afford complexes. The ligand and complexes are stable at room temperature. In this paper, a direct, simple and one step method has been used to synthesize these compounds. The advantages of the method are; that there is no side product, the reaction is quite fast, there are mild conditions and the accompanied color change that provides visual means for ascertaining the progress of the reaction. In summary, the synthesis and characterization of complexes have been described. A complex of Co (III) was synthesized simply. Co (PMTC) was prepared by the reaction of PMTC and CoCl\(_2\).6H\(_2\)O. Ni (PMTC) was prepared by the reaction of PMTC and Ni (CH\(_2\)COO). 4H\(_2\)O. In this study we have reported the synthesis of a new thiosemicarbazidederivative and its Co (III) and Ni (II) complexes. The structural characterizations of synthesized compounds were made by using the elemental analysis and IR techniques. This PMTC ligand with Co (III) and Ni (II) compounds were obtained in relatively high yield, 77, 80 and 85% respectively. The infrared spectrum of complexes and ligand was obtained. The IR spectra of the Schiff base show characteristic bands due to \(\nu_\text{v(NH)}, \nu_\text{v(=CH)}, \nu_\text{v(C=C)}\) and \(\nu_\text{v(C-N)}\) in the region 3122.70 cm\(^{-1}\), 2857.57 cm\(^{-1}\), 1410.68 cm\(^{-1}\) and 1574.77 cm\(^{-1}\) respectively. In the case of Co (III) complex we observed characteristic bands due to \(\nu_\text{v(NH)}, \nu_\text{v(=CH)}, \nu_\text{v(C=C)}, \nu_\text{v(C-N)}\) and \(\nu_\text{v(C-S)}\) in the region 3431.70 cm\(^{-1}\), 2805.15 cm\(^{-1}\), 1607.54 cm\(^{-1}\), 1146.13 cm\(^{-1}\) and 1361.05 cm\(^{-1}\) respectively.

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**REFERENCES**