

*Synthesis and characterization of transition metal complexes with
thiosemicarbazone ligands*

A Dissertation

Submitted in partial fulfillment

**FOR THE DEGREE OF
MASTER OF SCIENCE IN CHEMISTRY**

Under Academic Autonomy

**NATIONAL INSTITUTE OF TECHNOLOGY,
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**NATIONAL INSTITUTE OF TECHNOLOGY
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CERTIFICATE

This is to certify that the dissertation entitled “Synthesis and characterization of transition metal complexes with thiosemicarbazone ligands” submitted by Purabi Rani Pradhan of the Department of Chemistry, National Institute of Technology, Rourkela for the degree of Master of Science in Chemistry is based on the result obtain in the bonafide project work carried out by her under my guidance and supervision.

I further certify that to the best of my knowledge Purabi Rani Pradhan bears a good moral character.

Date: 30/04/2011

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1. INTRODUCTION

Thiosemicabazones $\{R^1R^2C=N^3-N^2H-C(=S)-NR^3R\}$ possess several donor atoms and generally bind to metals via N^2 , S or N^3 , S donor atoms forming four or five membered rings, respectively.

Thiosemicarbazones (TSC), as well as their metal complexes, has been the subject of great interest of many researchers for a number of years. Apart from their diverse chemical and structural characteristics, the interest on these compounds also stems from their wide spectrum biological activity, which is already well established. Their biological importance is evidenced by a wide range of antibacterial, antimalarial, antiviral, antineoplastic and antileprotic activities.¹⁻² Such pharmacological activities are due to the strong chelating ability of these ligands with biologically important metal ions such as Fe, Cu, Ni and their reductive capacities.³⁻⁸

In this dissertation we have reported several thiosemicarbazone ligands and their corresponding complexes. The ligands and their corresponding complexes were successfully characterized by IR, UV-VIS, NMR spectroscopy.

2. Experimental:

Synthesis of thiosemicarbazones:

All the four thiosemicarbazones were prepared by stirring methanolic solution of the required thiosemicabazide with required aldehyde or ketone, which are schematically shown below:

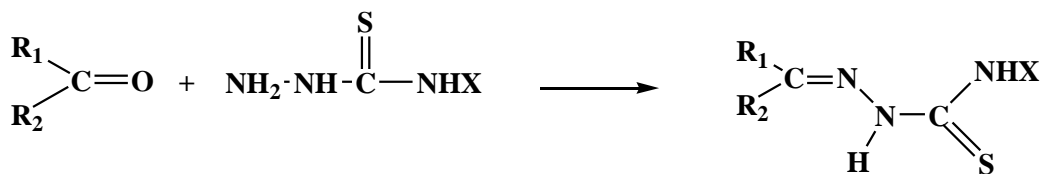
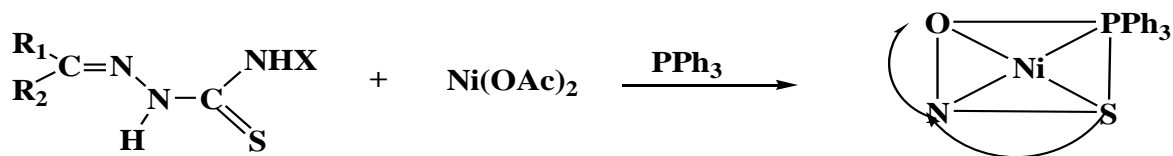


Figure 1

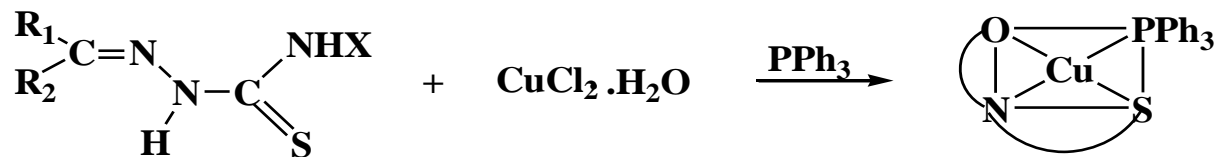
Synthesis of metal complexes

All the complexes were prepared following a similar method by stirring the ethanolic solutions of the metal precursor and ligand. PPh₃ was added as a co-ligand. Preparations of the metal complexes are described below.

Complex I:



Complex II:



3. Spectral Characteristics:

IR spectra

The IR spectra of all the ligands contains characteristic bands at around 3727 cm^{-1} , 3448 cm^{-1} and 1117 cm^{-1} due to $\nu(\text{OH})$, $\nu(\text{NH})$ and $\nu(\text{C}=\text{S})$ respectively. In the IR spectra of the corresponding metal complexes band at around 3727 cm^{-1} due to $\nu(\text{OH})$ disappears as the ligand coordinates as deprotonated enol and the band at around 1578 cm^{-1} due to $\nu(\text{C}=\text{S})$ also disappears as the S of C=S coordinates to the metal as S^- .

UV-VIS SPECTRA

The electronic absorption spectra (in DMSO) of all the complexes display a shoulder in 370- 424 nm region and two strong absorptions are located in the 267–360 nm range, which are assignable to L–M($d\pi$) LMCT and intraligand transitions respectively.

NMR spectra of the ligands and their corresponding metal complexes

The ^1H NMR spectra of all the ligands contain characteristic peaks at around 11.5 ppm, 10.5 ppm and from 7-9 ppm for OH, NH and aromatic protons respectively.

The peaks at around 3.5 and 2.5 are for water and solvent i.e. DMSO respectively.

In the proton NMR spectra of the corresponding metal complexes peaks at around 11.5 ppm and 10.5 ppm disappears as they undergo deprotonation.

In the ^{13}C NMR spectra, there is no change for the metal complexes.

The ^{31}P NMR spectra of the complexes contain characteristic peaks at around 21 ppm for PPh_3 .

4. Conclusion

In this dissertation several thiosemicarbazone ligands and their corresponding copper and nickel complexes has been synthesized and the ligands and their metal complexes has been characterized by IR, UV vis and NMR spectroscopy. The x-ray quality crystals of some synthesized complexes have been sent for structure determination using single crystal X-ray crystallography.

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