

*Synthesis and characterization of some new Cu(I) complexes
with thiosemicarbazone ligands*

A Dissertation

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CERTIFICATE

This is to certify that the dissertation entitled “*Synthesis and characterization of some new Cu(I) complexes with thiosemicarbazone ligands*” submitted by Poonam Kumari 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 bona fide project work carried out by her under my guidance and supervision. To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University/Institute for the award of any degree or diploma.

I further certify that to the best of my knowledge Poonam Kumari bears good moral character.

Date: 03/05/2012

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1.INTRODUCTION

Thiosemicarbazones (TSCs) have received significant attention due to their eventual therapeutic activities against bacterial and viral infections [1, 2], tuberculosis [3] and leprosy [4, 5]. The 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 [6, 7].

Thiosemicarbazone chemistry of copper(I) halides has been explored and in neutral form, they have exhibited different bonding modes: η^1 -S (mode A), μ_2 -S (mode B), N^3 , S-chelation (mode C), N^3 , S-chelation-cum-S-bridging (mode D) [8–10], and in the anionic form, there is only N^2 , S-chelation-cum-S-bridging (mode E) (Chart- 1) [11, 12].

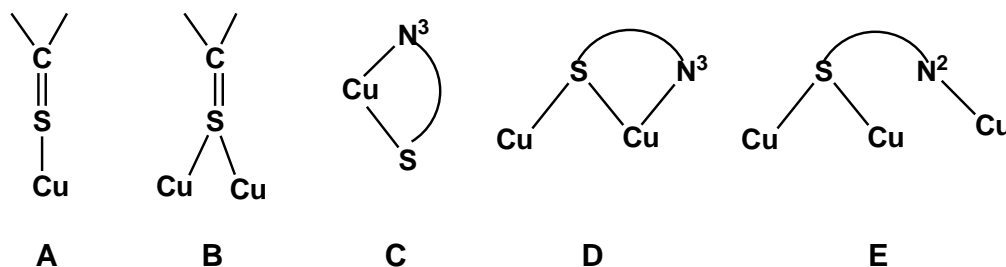


Chart -1

The present report deals with the chemistry of some new Cu(I) complexes of 4-(p-X-phenyl) thiosemicarbazone of naphthaldehyde {X=F, Cl, Br, OMe}, with particular reference to their synthesis and characterization

2. EXPERIMENTAL

Synthesis of ligands:

The thiosemicabazides were prepared from distilled substituted aniline by a known method reported earlier [13]. Schiff base ligands, of naphthaldehyde were prepared in 80-90% yield by stirring equimolar ratio of the substituted thiosemicabazide with naphthaldehyde in methanol medium by standard procedures [14]

Synthesis of metal complexes

All the complexes were prepared following a similar method. To a solution of CuBr in CH₃CN, solid PPh₃ was added and stirring was continued until the formation of white solid, followed by addition of HL¹ ligand. To this mixture, 5 mL of CH₂Cl₂ was added and the contents were stirred for a further period of 10 min. On slow evaporation, light yellow coloured crystals were obtained from filtrate.

3. RESULT AND DISCUSSION:

3.1. Spectral Characteristics:

IR spectra

The IR spectra of all the ligands as well as complexes contain characteristic bands at around 3322 cm⁻¹ and 3126 cm⁻¹ due to two ν(NH) present. The sharp band in 772 cm⁻¹ due to ν(C=S) stretching in the ligand is lowered by 10-15 cm⁻¹ in case of complex, indicating participation of the thione sulfur in coordination [15]. The characteristic ν(P-C) bands at 1090 and 1091 cm⁻¹ in complexes II and III respectively attributes to the presence of PPh₃.

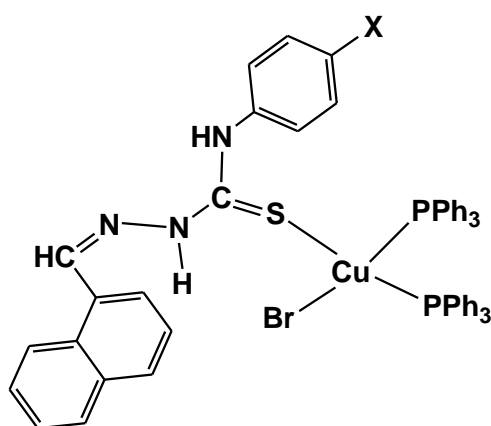
UV-VIS spectra

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 π) LMCT and intra ligand transitions respectively[16].

NMR spectra of the ligands

The ^1H NMR spectra of all the ligands contain characteristic peaks at around 12.03 ppm, 10.26 ppm and 9.12 ppm for two NH protons and one CH proton respectively. The aromatic protons are present in the range 8.46-7.43 ppm [17]. The peaks at around 3.5 ppm and 2.5 ppm are for water and solvent i.e. DMSO respectively.

4. EXPECTED STRUCTURE OF METAL COMPLEXES



5. CONCLUSION

In this dissertation four 4-(p-X-phenyl) thiosemicarbazone of naphthaldehyde {X=F, Cl Br, OMe} and their corresponding new Cu(I) complexes has been synthesized. The ligands and their metal complexes have been characterized by IR, UV-VIS and NMR spectroscopy. Full characterization of all complexes could not possible to report due to shortage of time. X-ray structure of complex II is done using single crystal X-ray crystallography.

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