Spectral, Electrochemical and Structural Studies of Some Copper and Molybdenum Complexes of Malonoyl-, Succinoyl- and Adipoyl–Dihydrazones

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SUMMARY

CHAPTER I

INTRODUCTION AND LITERATURE SURVEY

This chapter presents a brief account of importance of the metal ions selected in the present study i.e. copper and molybdenum. It also presents a pertinent literature on the transition and non-transition metal complexes of acyl-, aroyl- and pyridoyl dihydrazines and their dihydrazones derived from their condensation with various aldehydes and ketones and related ligands. An attempt has been made to survey literature on all these ligands up-to-date.

CHAPTER II

EXPERIMENTAL

The experimental details regarding the preparation of malonoyl-, succinoyl- and adipoyl dihydrazines and the ligands disalicylaldehyde malonoyl-, succinoyl- and adipoyldihydrazones (H_4slmh, H_4slsh and H_4slah), respectively, have been described in this chapter. Procedures for elemental analyses, physico-chemical techniques and instruments used are also described in this chapter.

CHAPTER III

Synthesis, characterization and electrochemical studies of mononuclear copper(II) complexes derived from disalicylaldehyde malonoyl-, succinoyl- and adipoyldihydrazones.

This chapter deals with the synthesis and characterization of monometallic copper(II) complexes derived from polyfunctional disalicylaldehyde malonoyl-, succinoyl- and adipoyldihydrazones.

The complexes are of the following compositions:

$[Cu(H_4L)]SO_4$ (where H_4L = H_4slsh (**311**), H_4slah (**312**) and $[Cu(H_2L)]$ (where H_4L = H_4slmh (**313**), (H_4slsh) (**314**) and (H_4slah) (**315**)), have been described.

The copper complexes are intense coloured being green or dark brown, respectively, they are air-stable and decompose above 300 ^{0}C. All the complexes are non-electrolytic in nature. All complexes are normal paramagnetic. Apart from the ligand bands, all the complexes show a single broad band in the region 627-675 nm with a very low molar extinction coefficient suggesting that all of them have square-planar geometry.

All complexes have been characterized by EPR spectra. The magnetic parameters for the complexes fall in the region $g_{||} > g_{\perp} > 2.0023$ suggesting that the unpaired electron is present in d_{x2-y2} orbital of copper centre.

The IR spectra of the ligands show two bands in the region 3065-3277 cm^{-1} and medium to strong band in the region 3436-3449 cm^{-1}, respectively. The essential feature of this band suggests that they arise from phenolic -OH and >NH groups. A strong band in the region 1666 – 1779 cm^{-1} is due to ν (>C=O) group while those in the region 1619-1626 cm^{-1} is due to ν (>C=N-) group.

The essential features of the IR spectra of the complexes **(311)** and **(312)** in the region 3000 – 3600 cm^{-1} is almost same as that of the ligands. The negative shift of υ(>C=O) band in the complexes (**311**) and (**312**) is a clear indication of coordination of both the υ(>C=O) to the metal centre in keto form whereas this band disappears in the complexes (**313**) to (**315**) indicating the destruction of amide structure and their bonding to the metal centre through enolic C-O group. The ligands show strong bands at 1626 and 1619 cm^{-1} due to stretching vibration of >C=N groups which shift to lower position indicating strong coordination of the ligands to the metal centre through >C=N groups. The most crucial feature of IR spectra of the complexes (**313**) to (**315**) is the presence of a strong band in the region 1509-1520 cm^{-1}, which arise usually due to νNCO$^-$ vibration resulted from enolisation of hydrazide ligands.

All complexes show strong intramolecular hydrogen bonding involving phenolic-OH groups. The non-ligand band occurring in the region 451- 483 cm^{-1} is assigned to νM-O

(enolised carbonyl). Mass spectrometric behaviour of the complex (**311**) suggests that the complexes are monomeric in nature.

The redox behaviors of copper(II) complexes (**311**) to (**315**) have been studied with the help of cyclic voltammetry.

Based on physico-chemical data and spectral studies, the tentative structures of the complexes have also been suggested at the end of the chapter.

CHAPTER IV

Synthesis, characterization and electrochemical studies of homotrinuclear copper(II) complexes derived from disalicylaldehyde malonoyl-, succinoyl- and adipoyldihydrazones.

This chapter deals with the synthesis and characterization of homotrimetallic copper(II) complexes derived from disalicylaldehyde malonoyl-, succinoyl- and adipoyldihydrazones.

The complexes have the general composition $[Cu_3^{II}(L)(\mu_2\text{-}Cl)_2]$ and $[Cu_3^{II}(L)(Cl)_2(A)_2]$ where [H_4L = H_4slmh (**411**), H_4slsh (**416**), H_4slah (**421**) and A = pyridine, 2-picoline, 3-picoline and 4-picoline]

The complexes are either green, black, brown or dark brown and decompose above 300 °C without melting. The molar conductance value for the complexes in DMSO lies in the region 2.71-3.81 $ohm^{-1}\,cm^2\,mol^{-1}$ indicating their non-electrolytic nature in this solvent.

The magnetic moment values indicates considerable amount of interaction between the copper(II) ions in the complexes (**411**), (**416**) and (**421**) as compared to their pyridine counterparts. This is attributed due to the presence of both oxido- and chlorido-bridge in these complexes. The electronic spectra of the complexes show a new non-ligand shoulder at 403-405 nm which have high molar extinction coefficient. This band has been assigned to arise due to ligand-metal charge transfer (LMCT) transition. All of the complexes display a relatively less intense broad band in the region 638-675 nm with low molar extinction coefficient that arise from the d-d transition in copper(II).

The EPR spectra of the complexes (**411-415**) in the present study are isotropic at room temperature and LNT in powder form. All of the complexes show anisotropic spectra at LNT characteristic of the systems having axial symmetry. LNT EPR spectra are typical for S = ½ spin systems. Magnetic parameters fall in the order $g_{\parallel} > g_{\perp} > 2.0023$ suggesting d_{x2-y2} orbital constitutes the ground state in these complexes. Further, the $g_{\parallel}/A_{\parallel}$ values are also found to lie in agreement with the proposed distorted square planar geometry around copper atom. The $g_{\parallel}/A_{\parallel}$ values for the present complexes are found to lie in the range 219–252 slightly higher than that required for a square-planar geometry. For all the complexes $g_{\parallel}/A_{\parallel}$ quotient is more than 135 which suggests that the complexes are appreciably distorted from square-planar geometry towards tetrahedrality.

The υ(-OH) and υ(>NH) vibrations disappear in the complexes indicating the coordination of -OH group via deprotonation and involvement of >NH group in coordination via enolization. The disappearance of band due to >C=O group and appearance of new band in the region 1499-1542 cm^{-1} due to newly created (NCO^-) group further support the enolization of the ligands molecule upon coordination with the metal centre. The bands due to azomethine (>C=N) group split into two bands in all of the complexes which appear in the regions 1592-1623 cm^{-1}. The νC=N bands shifts to lower frequencies in the complexes by 3 to 32 cm^{-1} which indicates the coordination of azomethine nitrogen atoms to the metal centre. The pyridine bases are bonded to metal centres in the complexes. A band observed in the region 275-290 cm^{-1} is assigned to ν(M-N) stretching vibration due to coordination of pyridine bases to the metal centre. The present complexes show a medium to strong band in the region 332-360 cm^{-1} not observed either in the IR spectra of the ligand nor in those of the monometallic complexes. Hence, these bands are assigned to νCu-Cl vibrations.

The mass spectra of the complexes suggests that all of the complexes are monomeric in nature. The redox behavior of copper(II) complexes (**411**) to (**425**) have been examined by cyclic voltammetry.

On the basis of various physico-chemical data and spectral studies, the tentative structures of the complexes have been suggested at the end of the chapter.

CHAPTER V

Synthesis, spectral and electrochemical characterization of molybdenum (VI) complexes of disalicylaldehyde malonoyl-, succinoyl- and adipoyldihydrazones.

This chapter deals with the synthesis, characterization and structural assessment of fifteen monometallic molybdenum(VI) complexes derived from the tetrabasic octadentate ligands disalicylaldehyde malonoyl-(H_4slmh), succinoyl-(H_4slsh) and adipoyldihydrazones (H_4slah). In the beginning, a brief account of its biological and technological relationship of molybdenum with copper has been presented.

The complexes described in this chapter are as follows:

$[(\mu_2\text{-}O)_2(MoO_2)_2(H_4slmh)_2].2A$ (where, A = H_2O (**511**), py (**512**); 2-pic (**513**); 3-pic (**514**) and 4-pic (**515**));

$[(\mu_2\text{-}O)_2(MoO_2)_2(H_4slsh)_2].2A$ (where, A = H_2O (**516**), py (**517**); 2-pic (**518**); 3-pic (**519**) and 4-pic (**520**));

$[(\mu_2\text{-}O)_2(MoO_2)_2(H_4slah)_2].2A$ (where, A = H_2O (**521**), py (**522**); 2-pic (**523**); 3-pic (**524**) and 4-pic (**525**)).

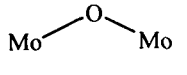
The complexes are orange, yellow, yellow orange, green and white, respectively, in colour. All of the complexes are air-stable solid powder and decompose without melting above 300 °C. They are all insoluble in common organic solvents such as ethanol, methanol, acetone, benzene, acetonitrile and ether. But all of them are soluble in highly coordinating solvents such as DMSO and DMF. All of the complexes are non-electrolyte. The mass spectral behavior of these complexes suggests that these are all dimeric in nature. Molar conductance values for the complexes (**511**) to (**525**) lie in the range 0.5 - 3.9 Ω^{-1} cm^2 mol^{-1} which are consistent their non-electrolytic nature in DMSO. All of the complexes are diamagnetic, consistent with the +6 oxidation state of molybdenum in them.

The essential features of the ligand band in the electronic spectra of the complexes suggest that the ligands are bonded to the metal centre in the same configuration as in the uncoordinated dihydrazones i.e. *anti-cis* configuration. The electronic spectra of all of the complexes, in addition to the intraligand bands exhibit a couple of bands in the region 402 – 405 nm. These bands are assigned to ligand-to-metal charge transfer transition.

In the ^{1}H NMR spectra of the complexes (**511**) to (**525**) two proton signals observed in the region δ 11.25-11.64 ppm have been assigned to δ(OH) protons in the free dihydrazones, however, these signals are downfield shifted in these complexes. The signals in the region δ 8.28 – 9.01 ppm have been assigned to azomethine (-CH=N) protons, whereas a multiplet in the region δ 6.63-7.95 ppm to phenyl protons.

The essential features of the ^{1}H NMR spectra of the complexes are similar to that of the uncoordinated dihydrazones and this suggests that the conformation of the dihydrazone remains unaltered on complexation. The significant difference of the ^{1}H NMR spectra of the complexes (**511**) to (**525**) as compared to that of the free dihydrazones is that the δ(-CH=N) signals show an average down field shift by 0.06-0.67 ppm and this suggests the involvement of azomethine group in coordination to the metal centre. The appearance of δ(OH) and δ(NH) proton signals in the form of doublets or two singlets in all of the complexes suggests their non-involvement in coordination to the metal centre. The co-ligand molecules such as pyridine and substituted pyridines are uncoordinated to the metal centre in all of the complexes.

The uncoordinated dihydrazones show a strong band in the region 1666-1679 cm^{-1} which is assigned to ν(C=O) stretching vibration. The ν(C=O) band remains either unshifted in positon or shifts to higher frequency. Such a feature associated with the ν(C=O) band in the IR spectra of these complexes rules out the possibility of coordination of >C=O group to the metal centre because the >C=O group absorbs at almost in the same region in the complexes in which uncoordinated >C=O group have been reported to absorb in dihydrazone metal complexes. The ν(C=N) bands observed in the region 1626-1619 cm^{-1} in the free dihydrazones remain unshifted in the complexes (**515, 521** and **525**) and shifts to lower frequency by 6-13 cm^{-1} in the remaining complexes indicating coordination of N-atom of >C=N group to the metal centre. The appearance of strong to medium intensity bands in the region 857 - 956 cm^{-1} in the IR spectrum of the complexes (**511**) to

(**525**) clearly indicates the presence of *cis*-MoO_2^{2+} group in these complexes. The complex (**511-520**) show an additional strong band in the region 850-864 cm^{-1} which is assigned to the bridging of υMo=O.....Mo vibration. On the otherhand, the complexes (**511-515**) and (**521-525**) show strong band in the 758-771 cm^{-1} indicating the presence of a bent  bridging. In the present study, the complexes show a new medium to weak intensity band in the region 397 - 404 cm^{-1}. This band either appears almost unshifted in position or shifts to lower position indicating pyridine non-coordinated to the metal centre present in the complexes. Moreover, these complexes donot show any band in the region 200-300 cm^{-1} ruling out the possibility of coordination of pyridine molecules to the metal centres.

The electron transfer reactions of the complexes have also been studied with the help of cyclic voltammetry.

At the end of the chapter, the tentative structures for the complexes have been suggested.

CHAPTER VI

Synthesis and characterisation of homobimetallic molybdenum(VI) complexes derived from malonoyl-, succinoyl- and adipoyldihydrazones.

The present chapter describes the synthesis, characterization and structural assessment of fifteen homobimetallic molybdenum(VI) complexes derived from disalicylaldehyde malonoyl-, succinoyl- and adipoyldihydrazones, respectively. After presenting in brief the rationality for its relevance in relation to the fifth chapter, this chapter deals with the importance of multimetallic enzymes in various fields. Subsequently, it describes the synthesis of the complexes followed by result and discussion.

The complexes described in this chapter were found to have the following general composition:

$[(MoO_2)_2(L)(D)_2]$ and $[[(MoO_2)_2(L)(D)_2].H_2O$ where (H_4L = H_4slmh (**611**), H_4slsh (**616**) and H_4slah (**621**) ; D = H_2O, py, 2-pic, 3-pic and 4-pic).

The complexes are light yellow, yellow, light green, green, orange and yellowish orange, respectively. All of the complexes are air-stable solid powder and decompose above 300 °C without melting. All of the complexes are insoluble in water and common organic solvents such as ethanol, methanol, acetone, benzene, acetonitrile, chloroform and ether. But all of the complexes are soluble in DMSO and DMF.

All of the complexes are non-electrolyte in DMSO. All of the complexes are diamagnetic consistent with the presence of molybdenum in +6 oxidation state in these complexes with d^0 electronic configuration. The mass spectral behavior of the complexes suggest that the complexes are bimetallic monomeric and do not undergo dimerization even under the condition of study by mass spectrometry.

The electronic spectra of the complexes exhibit red as well as blue shift of ligands bands which is a good evidence of chelation of the ligands to the metal centre. The electronic spectra of the complexes in addition to the ligands band exhibit a new band centred at 403 nm on the UV-Vis borderline which are assigned to originate from ligand-to-metal charge transfer transition (LMCT).

The two proton signals observed in the of region δ 11.25-11.64 ppm in the ^{1}H NMR spectra of the free dihydrazones are absent in the ^{1}H NMR spectra of the complexes indicating collapse of amide structure of the ligands and its involvement in coordination in enol form through phenolate oxygen atoms via deprotonation and carbonyl oxygen atoms via enolization cum deprotonation. The most crucial feature of the ^{1}H NMR spectra of the complexes (**611**) to (**625**) is the merger of the doublets corresponding to δ(-CH=N) protons in the free ligands into a single resonance on complexation. This suggests that the dihydrazones, which exist in the *anti-cis* configuration in uncoordinated state, isomerize to *staggered* configuration in these complexes. The co-ligand molecules such as pyridine and substituted pyridines are coordinated to the metal centre as they show downfield shift with respect to the free pyridine molecules.

IR spectra of the complexes support the conclusions drawn from ^{1}H NMR spectroscopy regarding bonding of the ligands to the metal centre. All of the dioxomolybdenum complexes show two strong to very strong bands in the region 857 - 956 cm^{-1}. This indicates the presence of *cis*-MoO_2^{2+} group in these complexes.

In the low frequency IR the complexes (**616**), (**617**), (**621**) and (**622**) show new bands in the region 306-344 cm^{-1}. These new bands occur in almost in the same region in which the ν(M-N) bands have seen reported to occur metal complexes of hydrazine derivatives. Hence, these bands are assigned to ν(M-N) stretching vibration due to coordinated >C=N group. Further, all of the complexes show new bands in the region 433-489 and 640-671 cm^{-1} except the complex (**611**), (**616**) and (**620**). These bands are assigned to arise due to in-plane and out-of plane ring deformation modes of coordinated pyridine/ substituted pyridines. An additional medium intensity band is observed at ~240 m which is absent in the IR spectra of the complexes (**611**), (**616**) and (**621**). Hence, this bands is assigned arise due to ν(M-N) stretching frequency due to coordination of pyridyl ring nitrogen atom to the metal centre .

Some of the complexes have been characterized by cyclic voltammetry. The tentative structures for the complexes have been proposed at the end.

Chemistry

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MEGHALAYA (INDIA)

May, 2010

DEDICATED

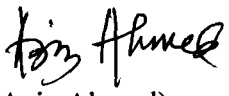
TO

MY BELOVED PARENTS

DECLARATION

I, Aziz Ahmed, hereby declare that the subject matter of the thesis entitled "*Spectral, Electrochemical and Structural Studies of Some Copper and Molybdenum Complexes of Malonoyl-, Succinoyl- and Adipoyl–Dihydrazones*" is the record of work done by me and the content of this thesis didn't form the basis of the award of any previous degree to me or to anybody else to the best of my knowledge and that the thesis has not been submitted by me for any research degree in any other University/ Institution.

This is being submitted to the North-Eastern Hill University for the degree of Doctor of Philosophy in Chemistry.



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CERTIFICATE

This is to certify that the thesis entitled "**Spectral, Electrochemical and Structural Studies of Some Copper and Molybdenum Complexes of Malonoyl-, Succinoyl- and Adipoyl–Dihydrazones**" submitted by Aziz Ahmed for the degree of Doctor of Philosophy of North-Eastern Hill University, Shillong-22, embodies the record of original investigation carried out by him under my supervision. He has been duly registered and the thesis presented is worthy of being considered for the Ph.D degree in Chemistry.

The work described in this thesis is original and has not been submitted for any other degree or diploma in this or any other University.

Ralal 28/5/16

(Prof. R. A. Lal)
SUPERVISOR

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CONTENTS

Acknowledgement

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Aziz Ahmed

(Aziz Ahmed)

Date: 28/05/10

Place: Shillong

PREFACE

Studies on synthesis, physico-chemical characterization and structural assessment of Cu(II) and Mo(VI) complexes derived from polyfunctional nitrogen and oxygen donor ligands and their incorporating some coligands is the focal theme of the work described in the present thesis. The entire thesis is divided over six chapters (**Chapter I-VI**) and Summary. Each chapter is virtually completed in itself. The description of the results of work undertaken for the present research work are presented in **Chapter-III** to **Chapter-VI**. These **Chapters (III-VI)** include a short introduction justify the specific objective of the work followed by a section on experimental describing the synthesis then result and discussion and finally the tentative structure of the complexes.

The first chapter (**Chapter-I**) deals with introduction provides a background in pertaining to work described in the thesis. The significance, interest and scope of some polyfunctional Schiff bases have been portrayed in this chapter with citations from contemporary literature. Diversity of structures, synthetic procedures and characterization of coordination compounds have been found particular attention in this chapter.

Chapter-II, includes the details of instruments used, synthetic methods of preparation of ligands and analytical methods for characterization of the synthesized complexes.

Chapter-III of this thesis is concerned with synthesis, characterization and assessment of the structure of Cu(II) complexes of disalicylaldehyde malonoyl-, succinoyl- and adipoyldihydrazones. The complexes reported here are of the type $[Cu(H_4slsh)]SO_4$ (**311**), $[Cu(H_4slah)]SO_4$ (**312**), $[Cu(H_2slmh)]$ (**313**), $[Cu(H_2slsh)]$ (**314**) and $[Cu(H_2slah)]$ (**315**)

The fourth Chapter (**Chapter-IV**) deals with "Synthesis, characterization, electrochemical studies and structural assessment of homotrinuclear copper(II) complexes derived from disalicylaldehyde malonoyl-, succinoyl- and adipoyldihydrazones. The complexes described in this chapter are of the type $[Cu_3(slmh)(\mu_2\text{-}Cl)_2]$ (**411**), $[Cu_3(slmh)(Cl)_2(py)_2]$ (**412**), $[Cu_3(slmh)(Cl)_2(2\text{-}pic)_2]$ (**413**), $[Cu_3(slmh)(Cl)_2(3\text{-}pic)_2]$ (**414**), $[Cu_3(slmh)(Cl)_2(4\text{-}pic)_2]$ (**415**), $[Cu_3(slsh)(\mu_2\text{-}Cl)_2]$ (**416**), $[Cu_3(slsh)(Cl)_2(py)_2]$ (**417**), $[Cu_3(slsh)(Cl)_2(2\text{-}pic)_2]$ (**418**), $[Cu_3(slsh)(Cl)_2(3\text{-}pic)_2]$ (**419**), $[Cu_3(slsh)(Cl)_2(4\text{-}pic)_2]$ (**420**), $[Cu_3(slah)(\mu_2\text{-}Cl)_2]$ (**421**), $[Cu_3(slah)(Cl)_2(py)_2]$ (**422**), $[Cu_3(slah)(Cl)_2(2\text{-}pic)_2]$ (**423**), $[Cu_3(slah)(Cl)_2(3\text{-}pic)_2]$ (**424**), $[Cu_3(slah)(Cl)_2(4\text{-}pic)_2]$ (**425**)

Chapter-V of this thesis presents an account of synthesis, characterization, electrochemical studies and structural assessment of Mo(VI) complexes of disalicylaldehyde malonoyl-, succinoyl- and adipoyl-dihydrazones and the coligands pyridine, 2/3/4-picoline molecules, respectively. The reported complexes of the type

$[(\mu_2\text{-}O)_2(MoO_2)_2(H_4L)_2].2A$, (where, H_4L = H_4slmh, A = H_2O (**511**), py (**512**), 2-pic (**513**), 3-pic (**514**) and 4-pic (**515**); H_4slsh, A = H_2O (**516**), py (**517**), 2-pic (**518**), 3-pic (**519**) and 4-pic (**520**) and H_4slah, A = H_2O (**521**), py (**522**), 2-pic (**523**), 3-pic (**524**) and 4-pic (**525**).

The last chapter but not the least **Chapter-VI** deals with synthesis, characterization, electrochemical behavior of homobimetallic Molybdenum(VI) complexes derived from malonoyl-, succinoyl- and adipoyl-dihydrazones and the coligands pyridine, 2/3/4-picoline respectively. The complexes in this chapter are of the type

$[(MoO_2)_2(L)(D)_2]$ and $[(MoO_2)_2(L)(D)_2].H_2O$ (where H_4L = H_4slmh, D = H_2O (**611**), pyridine (py, **612**), 2-picoline (2-pic, **613**), 3-picoline (3-pic, **614**), 4-picoline (4-pic, **615**); H_4slsh, D = H_2O (**616**), pyridine (py, **617**), 2-picoline (2-pic, **618**), 3-picoline (3-pic, **619**), 4-picoline (4-pic, **620**) and H_4slah, D = H_2O (**621**) pyridine (py, **622**), 2-picoline (2-pic, **623**), 3-picoline (3-pic, **624**) and 4-picoline (4-pic, **625**)

CHAPTER I

INTRODUCTION AND LITERATURE SURVEY

Introduction

The present thesis embodies the results of investigations of reactions of disalicylaldehyde malonoyl-, succinoyl- and adipoyldihydrazones, $Cu(oAc)_2.H_2O$, $CuCl_2.2H_2O$, $CuSO_4.5H_2O$, $MoO_2(acac)_2$ and the characterization of the resulting complexes. The structural assessment of the complexes described in this thesis is based on the data obtained from elemental analyses, mass spectroscopy, IR, ^1H NMR, ESR, conductivity measurements, magnetic susceptibility measurements, electronic and cyclic voltammetry measurements. Accordingly, the present chapter gives a brief account of the importance of copper and molybdenum in monometallic, homobimetallic and homotrimetallic systems followed by description of bonding modes of dihydrazone ligands and literature survey on metal complexes of dihydrazones.

Copper is a relatively 'modern' element [**1, 2**], having become bioavailable only about 1.7 billion years ago with the advent of an oxygen atmosphere [**3**]. The oxidizing environment generated by photosynthetic organisms not only allowed the conversion of Cu(I) to Cu(II), which is more soluble and bioavailable, but also led to the need for a redox-active metal with potentials between 0 and 800 mV [**2**]. The Cu(I)/Cu(II) redox pair fits this requirement and as a result, many copper-containing enzymes function in O_2 binding, activation and subsequent substrate oxidation. These enzymes include monooxygenases, dioxygenases, oxidases and play an essential role in biological processes such as peptide hormone activation, biosynthesis of melanin pigments, iron homeostasis and methane oxidation. The O_2-reactive centres are mononuclear (type 2), dinuclear (type 3) or trinuclear (type 2 and type 3). Copper containing enzymes that react with O_2 play a key role in many biological processes. Mononuclear, dinuclear and trinuclear copper centers function in O_2 binding, activation and subsequent substrate oxidation. In the structural biology of O_2 activating copper enzymes range from the identification of novel copper centres, such as that of particulate methane

monooxygenase, to the elucidation of the details of O_2 binding and reacitivity in peptidyglycine α-hydrooxylating monooxygenase.

Copper occurs in several enzymes and metalloproteins **[4]** like ascorbate oxidase, copper dioxygenase, copper monooxygenase, super dismutase, cytochrome oxidase and 'blue' oxidase **[5-10]** etc. Copper is an essential bioelement responsible for numerous catalytic processes in living organism where it is often present in di- or tri nuclear assemblies **[11]**. Polynuclear copper centres are widespread in biological systems, occurring in type 3 cuproproteins, such as tyrosinase and hemocyanin **[12]**.

Molybdenum is the only element of the second transition series, being essential for life **[13, 14]**. The element molybdenum is present in two types of enzymes, one of these is nitrogenase **[15]** which is found in free living and symbiotic microorganisms and catalyses the reduction of dinitrogen to ammonia. The other category of molybdenum enzymes consists of hydroxylases or oxotransferases **[16]** which catalyses a variety of two electron oxidation-reduction reactions. As a constituent of enzymes, molybdenum also participates in redox reactions, viz., oxidation of aldehydes, xanthine and other purines **[17]**, and reduction of nitrate to molecular nitrogen **[18, 19]**. Molybdenum's biochemical role is based on its ability to facilitate electron exchanges and to form stable complexes with oxygen, nitrogen and sulphur containing ligands **[14]**.

It is well-known that metalloproteins often use binuclear metal centers to perform catalytic functions. Moreover, the well-known anagonistic function of the molybdenum ion with regard to copper in ruminants **[20]** has raised interest in the interaction of Cu ions with ligated molybdenum species. However, most of the Mo-Cu mixed-metal complexes reported till now **[21]** employ mainly $(MoS_4)^{2-}$ as the source of the molybdenum component, moreover, these Mo-Cu mixed-metal complexes involve Mo-Cu(I) metal pairs in which the Mo most often exhibits a VI oxidation state. Mo(VI)-Cu (I) Schiff-base complexes having cubane-like cores of the formula $Mo_2Cu_2O_4$ in which Mo and Cu retain +6 and +2 oxidation states, respectively, have not been reported in the literature.

Mixed metal-molybdenum oxides are used as efficient and selective catalysts for partial oxidation of light alkanes in petrochemistry **[22]**. The molybdenum compound $[NH_3Pr^i][Mo_7O_{24}].3H_2O$ (PM-8) is proved to be significant in tumor growth suppression in bearing several human tumors and has shown anti-tumour activity against human gastric cancer **[23]**. The polyoxomolybdenum anions have potential applications in catalysis, solid-state technology and medicine, including antitumor, antibacterial and antivirus (HIV) activity **[24, 25]**.

The molecular complexes derived from transition and inner-transition metals having the same or different metal ions are of interest in areas like homogeneous catalysis **[26]** and heterogeneous catalysis **[27]**. In homogeneous catalysis, a heterobimetallic complex containing an electron deficient metal atom and an electron rich metal atom presents the possibility of Lewis acid activation of a substrate molecule bound to the electron rich metal centre. The heterobimetallic complexes which have such types of properties are usually derived from widely divergent metal **[28]**. Further, the heterobimetallic complexes have the potential to mediate certain chemical reactions of industrial relevance either more efficiently or in different manner to isolated metal centres **[29]**. They exhibit distinct reactivity pattern as compared to their monometallic and homobimetallic complexes.

LITERATURE SURVEY

The dihydrazones are examples of polyfunctional ligands which can bind two metals in close proximity to one another. The work on metal complexes of polyfunctional ligands has recently created much interest among chemists, because the magneto and electro chemical properties of complexes derived from them show promise in developing theories whereby electron transport phenomena can be understood **[30]**. Acyl-, aroyl-, and pyridoyl-, dihydrazones are some of the few examples of ligands which can yield binuclear, heteronuclear and polynuclear complexes of transition and inner-transition metals, possessing interesting magnetic and electro chemical properties **[31]** and which can serve as models in bioinorganic chemistry **[33]**. Acyl-, aroyl-, and pyridoyl-, dihydrazones derived from the condensation of o-hydroxyaromatic aldehydes and ketones and acyl- and aroyl- dihydrazines in which two hydrazone groups are separated from each other by methylene chains of varying length or phenyl group, or pyridoyl group and those derived from condensation of monohydrazines with dialdehydes, constitute a special class of molecules. This class of molecules reacts in the keto-enol forms **[36]** depending upon the mode of preparation of the complexes, the nature of the reaction medium, the pH of the reaction medium, the nature of the metal salt and the molar ratio of the metal salt and the ligand employed ad can act as mono-, di-, tri-, and tetrabasic hexadentate ligands and give rise to polymeric complexes through both ligand bridging due to their flexibility in three-dimensional space and oxo-bridging through the phenolic atoms.

The dihydrazones can be obtained from condensation of acyl-, aroyl-, and pyridoyl-, dihydrazines [$R(CONHNH_2)_2$]; (R = O, $-(CH_2)_n-$, $C_6H_4<$, $C_6H_3N<$) with o-hydroxyaromatic aldehydes and ketones. Another category of the dihydrazones can be obtained from condensation of dialdehydes [$R(CR'O)_2$]; (R = O, $-(CH_2)_n-$, $C_6H_4<$, $C_6H_3N<$, R' = alkyl groups) with monoacyl-, aroyl-, pyridoyl- and quinaldenoyl-, hydrazines. Accordingly, the literature survey is presented under the following two major sections.

A) Complexes of dihydrazones derived from condensation of acyl-, aroyl-, and pyridoyl-, dihydrazines with simple and o-hydroxyaromatic aldehydes and ketones.

B) Complexes of dihydrazones derived from condensation of dialdehydes with monoacyl-, aroyl-, pyridoyl- and quinaldinoyl-, hydrazines.

Sacconi **[34]** has isolated a seies of diamagnetic dinuclear nickel(II) complexes of dihydrazones obtained from condensation of aliphatic dicarboxylic acid dihydrazides with salicylaldehyde, 2-hydroxy-1-naphthaldehyde, *o*-aminobenzaldehyde, and *o*-hydroxyacetophenone. He showed that the hydrazones react in their enol forms with $Ni(OAc)_2$ in aq. alc. ammonia as bis-tridentate complexing agents.

Aggarwal and coworkers **[35]** isolated complexes of the compositions $[VO(LH_2)]SO_4$, $[VO(LH_2)]Cl_2$, $[VO(LH_2)py]SO_4$ from reaction of vanadyl sulphate and chloride and metal (II) chloride with bis(acetone)oxaloyldihydrazone, bis(acetone)malonoyldihydrazone and bis(acetone)succinoyldihydrazones in alcoholic medium. The complexes $[VO(LH_2)]SO_4$ and $[VO(LH_2)]Cl_2$ were proposed to have square pyramidal stereochemistry while the remaining complexes were proposed to have octahedral stereochemistry.

Iskander and coworkers **[36]** isolated the metal (II) complexes of the composition $M(LH_3)X.nH_2O$, $M_2(LH_2)X_2.nH_2O$, $M(LH_2).nH_2O$ and $M(LH_3)_2.nH_2O$ (where M = Cu(II), Ni(II) and Co(II); X = Cl^-, Br^-, I^-)from reaction of the metal(II) salts with dihydrazones (LH_4) derived from condensation of salicyaldehyde with acyldihydrazines with the methylene backbone varying from 1 to 5 under different experimental conditions. They assigned a pseudo-octahedral stereochemistry for the nickel(II) complexes $[Ni(LH_3)X].nH_2O$ (X = Cl^-, Br^-, I^-) and $[Ni_2(LH_2)Cl_2].2H_2O$ on the basis of magnetic moment data and spectral studies. The latter complexes change to penta-coordinated state on dehydration. However, five coordinate structure was proposed for the nickel(II) complexes $Ni(LH_2).nH_2O$ as against a distorted octahedral structure for the corresponding cobalt(II) analogues. On the other hand, Kapoor and coworkers **[37]** suggested that the nickel(II) complexes $Ni(LH_2).nH_2O$ have octahedral stereochemistry. Anomolous magnetic behaviour of the nickel complexes $Ni_2(L).nH_2O$ (μ_{eff} values lying in the range 1.65-1.70 BM) is ascribed to arise due to the presence of two magnetically non-equivalent sites in the same unit cell. This is confirmed from electronic spectral study of the complexes as well which show bands characteristic of octahedral and square planar nickel(II) sites in the complexes. All the cobalt(II) complexes are proposed to have

octahedral stereochemistry. The copper complexes $Cu(LH_3)X.nH_2O$ and $Cu_2(LH_2)X_2.nH_2O$ are proposed to have square pyramidal stereochemistry. The low magnetic moment values than the spin only value is attributed to superexchange interactions through the oxygen bridges. The complex $Cu(LH_2).nH_2O$has been suggested to have square planar stereochemistry.

Narang and Lal **[38]** have described complexes of disalicyaldiminesuccinamide (H_2L) and N,N-Bis(o-hydroxyacetophenoneimine)succinamide (H_2J)of the types ML, MJ, M(HL)Cl, M(HJ)Cl and M'$(HL)_2$ (where M = Cu(II), Ni(II), or Co(II) and = Ni(II) or Co(II) and M' = Ni(II) or Co(II)). The complexes are proposed to have either octahedral stereochemistry or square planar stereochemistry.

Narang and Lal **[39]** have reported mono and binuclear zinc(II) complexes Zn(HL)Cl and Zn_2(L-2H) derived from multidentate acyldihydrazone ligands. The reaction medium, zinc salts and ligand geometry are shown to influence the composition and stereochemistry of the complexes. The zinc centres were proposed to have octahedral as well as tetrahedral stereochemistry.

Polymeric metal (II) complexes **[40]** of the type M_2L derived from dihydrazones obtained from condensation of oxaloyldihydrazide, succinoyldihydrazide and phthaloyldihydrazide with salicylaldehyde or o-hydroxyacetophenone have been described by the above authors. Copper complexes and few nickel and cobalt complexes are proposed to have square planar stereochemistry while other nickel and cobalt complexes are proposed to have distorted octahedral and square pyramidal stereochemistry. The anomalously low magnetic moments of some complexes are related to M-M interactions via oxo-bridge structure.

Narang and Lal **[41]** have prepared and characterized the metal(II) complexes $M(H_2J)$, $M(H_2K)$, $M(H_3J)Cl$, $M(H_3K)Cl$; M_2J, M_2K and M_2 (HK) (CH_3COO) (where M = Cu(II), Ni (II) and Co(II)) derived from di(salicylaldimine}malonamide(H_4J) and di(o-hydroxyacetophenoneimine}malonamide(H_4K) and the zinc(II) complexes ZnH_2L and Zn_2L from a number of multidentate acyldihydrazones (H_4L). The copper complexes are shown to have square pyramidal and pseudo-octahedral stereochemistry. The cobalt complexes are shown to have square planar, square pyramidal, mixed octahedral and

tetrahedral and distorted octahedral stereochemistry in the solid state whereas zinc complexes have octahedral and tetrahedral stereochemistry.

Narang and coworkers **[42]** synthesized new series of polymeric cobalt (II) complex of the type $Co_2(L).nH_2O$ from reaction of metal(II) acetate and dihydrazone (LH_4) where LH_4 is bis(o-hydroxyacetophenone)oxaloyldihydrazone, bis(salicylaldehyde) oxaloyldihydrazone, bis(o-hydroxyacetophenone)succinoyldihydrazone in the ratio 4: 1 (metal: ligand) in ethanol under reflux. The complexes have been proposed to have polymeric structure with strong Co-Co interactions with planar disposition of donor atoms around metal centres.

Sahni and coworkers **[43]** synthesized and characterized complexes of the type $[M(LH_2)]X_3$ (where M = Cr(III), Mn(III), Fe(III) or Co(III); X =Cl^-, NO_3 or OAc) from reaction of metal (III) salts with N-N-dibenzylidene dipicolinic acid hydrazone (LH_2) in ethanol medium. The ligand acts as a pentadentate unit having coordination sites at pyridine nitrogen, amide oxygen and hydrazinic nitrogens or azomethine nitrogens. In this context, it is important to mention that these authors **[44]** have also claimed that dipicolinic acid dihydrazine behaves as pentadentate ligand. On the otherhand, Dutta and Sarkar **[45]** have argued in favour of neutral tridentate behaviour of this ligand in which it can function either as a (NNN) or as a (ONO) donor.

Kapoor and coworkers **[46]** have studied reaction of vanadyl chloride and dipicolinic acid dihydrazone in presence of acetylacetone or other β-diketones in ethanol and acetic acid. They isolated brown solid complexes of macrocylic ligand bis(β-diketone) dipicolinoyldihydrazones. On the other hand they isolated a non-macrocyclic pyrazole derivative when reaction of vanadyl chloride was carried out with the preformed bis(β-diketone) dipicolinic acid dihydrazone. Similar products **[47]** were isolated in case of zirconium(IV) also.

Teotia and Rana **[48]** synthesized complexes $[M(L).2H_2O]$ (M = Cu(II), Ni(II) and Co(II)) of the above macrocyclic ligands by treating a methanol solution containing a mixture of acetylacetone and 2, 6-dipicolinic acid hydrazide and the appropriate metal chloride. The IR spectra indicated condensation of both the oxygen atoms of

acetylacetone with NH groups of dihydrazine. The electronic spectral bands agree reasonably well with five coordinate geometry.

Kapoor and coworkers **[49]** synthesized a number of metal (II) and metal (III) complexes from reaction of metal (II) and metal (III) salts with dihydrazones obtained from condensation of salicylaldehyde with oxaloyldihydrazine, malonoyldihydrazine and succinoyldihydrazine under different experimental conditions. The trivalent metal ions are found to yield complexes having compositions $[M_2LX_2].nH_2O$ and $[M_2(LH_2)X_4]$ $.nH_2O$ (M= Cr(III), Fe (III) and Mn(III)) (X= Cl^-, NO_3^-, OAc, OH) while the bivalent metal ions were found to form complexes having compositions $[M(LH_2)]$ and $[ML(H_2O)_4]$ (M= Mn(II) and Fe(II)). The dihydrazones are suggested to function as dibasic and tetrabasic hexadentate binucleating ligands. Iron(III) complexes were characterized by Mossbauer spectroscopy as well. The complexes have been suggested to have distorted octahedral stereochemistry.

Narang and Yadav **[50]** studied reaction of aluminium(III) salts with several dihydrazone ligands in aqueous medium at controlled pH and characterized the resulting complexes by infrared spectroscopy. The complexes are suggested to be polymeric with dihydrazones coordinated in the keto form.

Narang and Dubey **[51]** have described Zn(II), Cu(II), Ni(II) and Co(II) complexes of solid polymers derived from glyoxal and organic acid dihydrazides. They have discussed the structure of the complexes in light of magnetic moment, electronic and IR spectral studies.

Yacouta and coworkers **[52]** studied the complexation behaviour of uranyl ion with various dihydrazides and their diydrazones obtained from condensation of simple and *o*-hydroxyaromatic aldehydes and ketones with dihydrazides. They isolated several monometallic and bimetallic uranyl complexes and characterised by various physico-chemical data and spectroscopic studies. They also studied the effect of excess acetate ion on complex formation.

Lal and coworkers **[53]**, have prepared several homotrinuclear complexes having general formula $[M_3LCl_2(H_2O)_3]$ (M= Mn(II), Co(II) or Ni(II)) from bis(acetophenone)-2,6-dipicolinoyldihydrazone(LH_4) in alcoholic medium by adjusting pH to ~8 by KOH. The

complexes show low μ_{eff} values much less than those expected for the high-spin metal ions possibly due to metal-metal interaction and anti- ferromagnetic exchange. The complexes are proposed to have mixed six-coordinate octahedral and five coordinate square pyramidal stereochemistry.

Narang and Singh **[54]** have synthesized polymeric complexes M(L-2H).nH_2O (where M = Fe(II), Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II), L=A,B) from bis (2-hydroxy-1naphthaldehyde)oxaloyldihydrazone (A) and bis(2-hydroxy-1naphthaldehyde) malonoyldihydrazone(B) by solid-solution reaction. All of the complexes were suggested to have distorted octahedral stereochemistry.

Lal and coworkers **[55]** studied reaction of uranyl acetate with the above dihydrazones (H_4L) in aqueous-alcoholic media and isolated complexes of the type $(UO_2)_2L.6H_2O$. The dihydrazones coordinate to the metal centre in enol form. They have studied the effect of complexation on the coupling of >C=O vibrations, in an enolized form and of ligand coordination to the uranyl ion as a function of the number of methylene groups by comparing the asymmetric stretching vibrations of the uranyl ion in various complexes recorded under identical conditions.

Lal and Das **[56]** studied reaction of uranyl nitrate and acetate with dihydrazones (H_4L) (where H_4L = disalicylaldehydeoxaloyldihydrazone(H_4A), -malonoyldihydrazone(H_4B), -succinoyljihydrazone(H_4C), -glutoyldihydrazone(H_4D), -adipoyldihydrazone (H_4E), and phthaloyldihydrazone (H_4F) in 3: 1 molar ratio in alcoholic medium. The complexes $[(UO_2)_2(H_2L)\ (NO_3)_2\ (H_2O)_4].2H_2O$ and $[(UO_2)_2(H_2L)(CH_3COO)_2(C_2H_5OH)_2]\ .C_2H_5OH$ have been isolated and characterized.

Lal and coworkers **[57]** synthesized copper(II) complexes $Cu_2(L).nH_2O$ and dioxouranium(VI) complexes $[(UO_2)_2(H_2L)(C_2O_4)].2nH_2O$ of the above dihydrazones. The $C_2O_4^{2-}$ group is suggested to cooordinate to the uranium centre retaining its D_{2h} symmetry.

Lal and coworekers **[58]** synthesized a series of uranyl complexes of the composition $[UO_2(H_3L)_2].nH_2O$ from above dihydrazones from reaction of uranyl nitrate with salicylaldehyde and acyl- and aroyl- dihydrazines in 1:4:2 molar ratio in ethanol medium.

Lal and coworkers **[59]** studied reactions of disalicylaldehyde adipoyldihydrazone with uranyl njtrate and uranyl acetate in aqueous and ethanol media under different experimental conditions. The resulting complexes of the compositions $[UO_2(H_2L)(H_2O)]_n$, $[UO_2(H_2L)_2]_n.3nH_2O$, $[UO_2(H_3L)(CH_3COO)]_n.3nH_2O$, $[UO_2Zn(L)(H_2O)_2]_n.2nH_2O$, $[(UO_2)_2(H_2L)(C_2O_4)].nH_2O$, $[(UO_2)_2(L)(py)_2(H_2O)_4]$, $[(UO_2)_2(HL)(CH_3COO)(H_2O)_3]_3.nH_2O$ $[(UO_2)_3(L)(CH_3COO)_2(H_2O)_2]_n.2nH_2O$, $[(UO_2)_2(L)(py)_2(H_2O)_2]_n.xnH_2O$, (where py = pyridine or α-, β-, γ-picoline, X=0, 1) have been isolated and characterized. In the complexes the ligand functions as a bridging monobasic tetradentate, dibasic hexadentate and tetrabasic hexadentate ligand and exhibits keto-enol tautomerism. In the heterobimetallic complexes $[UO_2Zn(L)(H_2O)_2]_n.2nH_2O$, the uranium and zinc atoms are considered to have hexagonal bipyramidal and tetrahedral stereochemistry respectively.

Lal and coworkers **[60]** have described dioxouranium(VI) and Zn(II) complexes $[M(H_2L)(H_2O)_2]_2.2nH_2O$ (where M= UO_2^{2+}, Zn^{2+}) of bis(*o*-hydroxynaphthaldehyde) oxaloyldihydrazone(H_4L). The complexes are obtained from reaction of metal acetate with oxaloyldihydrazine in 1: 1 molar ratio in ethanol followed by reaction of excess *o*-hydroxynaphthaldehyde under reflux. Dioxouranium(VI) complex is proposed to be eight coordinate involving coordination of dihydrazone in the enolic form with *cis*-configuaration while the zinc complex is proposed to be octahedral involving coordinated dihydrazone in enolic form in the staggered configuration. The naphtholic-OH are proposed to be non-coordinated. They **[61]** have, further, synthesized dioxouraninum(VI) complexes $[UO_2(H_2L)]_n.2nH_2O$ and $[(UO_2)_2(L)(H_2O)_6]_n$ from reaction of uranyl nitrate with preformed dihydrazone bis (*o*-hydroxynaphthaldehyde)oxaloyldihydrazone in a 3:1 molar ratio in aqueous and ethanol media, respectively, under reflux. Based on the splitting of the δ NH signal in monometallic complex and δ CH=N in both complexes into quartet as compared to the singlet in free dihydrazone, the complexes are proposed to exist in chair formation with the *anti-cis*-configuration of dihydrazone involving eight and nine coordinated uranium atoms, respectively.

The complexes **[62]** $Na_4[(UO_2)_4(L)_2(CH_3COO)_4(H_2O)_4].4H_2O$ and $Na_4[(UO_2)_4(L)_2F_4(H_2O)_4]$ have been obtained from the same ligand have also been described by them.

Patil and Kulkarni **[63]** and others **[64]** obtained complexes of the type $[UO_2L].nH_2O$ from interaction of uranyl acetate disalicylaldehyde thiocarbohydrazone(H_2L) and established their structure by ^1H NMR and IR spectroscopic studies.

Kapoor and coworkers **[65]** studied reaction of malonoyldihydrazine and phthaloyldihydrazine with β-diketones in presence of the dioxouraninum(VI) cation which appears to function as a metal template. This facilitates condensation of dihydrazide with diketones resulting in the formation of several dioxouranium(VI) complexes of macrocylic ligands. The formation of a macrocyclic ring was confirmed from infrared spectroscopic studies. However, when dioxouranium(VI) nitrate is treated with the condensation product of phthaloyldihydrazine and acetylacetone, an entirely different pyrazole derivative is formed.

Sahoo and coworkers **[66]** have synthesized several first series transition metal complexes from several dihydrazones. The complexes were characterized by elemental analyses, physico-chemical data and spectral studies.

Pandey **[67]** reported a number of organometallic complexes derived from pyridoyldihydrazones. In this study, he showed from IR spectral data that dihydrazones coordinate to the metal centre in keto form through both >C=O and >C=N groups.

Mahale and Havanur **[68]** studied dioxomolybdenum(VI) complexes of the composition $(MoO_2)_2(L)(py)_2$ synthesized from dihydrazones(H_4L) obtained from condensation of the several acyl dihydrazines and substituted salicylaldehyde.

Panda and coworkers **[69]** synthesized heterobimetallic complexes $[MNiM(BTDO)_2X_2(H_2O)_4].nH_2O$ (where M= Ni(II), Co(II) and Cu(II); X = Cl^-, NO_3^-, n = 0 or 0.5 and BTDO = 1,8-Bis(2'-oxophenyl)-2,3, 6,7-tetraza-4,5-dimethyl-1,3,5,7-octatetraene) from the precursor nickel complex nickel[bis(diacetyldihydrazone)]. The metal centres have been proposed to have octahedral stereochemistry.

Gopinathan and coworkers **[70]** synthesized a tin complex of disalicylaldehyde malonoyldihydrazone and studied its structure by X-ray crystallography.

Sacconi **[71]** studied reactions of biacetyl-bis(benzoylhydrazone) with nickel(II) acetate in alcohol in the presence of concentrated ammonia and isolated orange coloured

biacetylbis(benzoylhydrazonato)nickel(II) complex and studied its reaction with pyridine **[72]**. The formation constant of complexes formed between biacetylbis(benzylhydrazonato)nickel(II) and various alkyl amines **[73]** have been studied. Complexes of lead(II), lead(IV) and tin(IV) of the types [Pb(L)], [$ph_2Pb(L)$], [$Sn(L)_2$], [phSn(L)Cl] and [$ph_2Sn(L)$] have been obtained by mixing methanol solutions of the appropriate metal salts and the ligand **[74]** .

Pelizzi and coworkers **[75]** have studied reaction of copper(II) chloride dihydrate with 2,6-diacetylpyridinebis(picoloylhydrazone) (LH_2) in refluxing ethanol yielding dark green crystal of $Cu_2(L)CI_2.H_2O$. IR spectral data indicate coordination of all the three pyridine nitrogens. The ligand behaves as an octadentate bridging (NONNNNNN) donor. The authors have established the square pyramidal structure of the complex unequivocally by X-ray crystallography. The environment about one Cu(II) is made up of a basal plane consisting of a chloride, two nitrogen atoms from the ligand (LH_2), an oxygen atom from second adjacent ligand molecule and another nitrogen from the same adjacent ligand molecule taking up the axial position. The environment around the second Cu(II) is made up of four nitrogen atoms from the first ligand molecule, while a chlorine ion takes up the apical site. Same authors **[76]** have isolated another series of complexes of the type $M(LH_2)C1_2.nH_2O$ (M=Mn(II), Co(II), Ni(II) and Cu(II)) by mixing chloroform solution of LH_2 and ethanolic solution of the metal chlorides in 1: 1 molar ratio. Another Mn(II) compound $MnL.9H_2O$ was obtained by adding dropwise, a dilute NaOH solution to a warm ethanol-water solution containing LH_2 and $MnC1_2.4H_2O$(1:1) molar ratio until pH~ 8.0. The compounds were characterized by magnetic moment data, electronic and IR spectroscopic studies.

The complex $Mn(LH_2)Cl_2.5H_2O$ was shown to have pentagonal bipyramidal stereochemistry by X-ray crystallography **[77]**. On the basis of similarity of IR spectra of Cu(II), Ni(II) and Zn(II) complexes with that of Mn(II) complexes, a similar pentagonal bipyramidal stereochemistry was proposed for them also with ligand acting as ONNNO donor and chloride or water molecules occupying apical positions. The complex $MnL.9H_2O$ was also characterized by X-ray crystallography and shown to have pentagonal bipyramidal stereochemistry.

Curtis and coworkers **[78]** and others **[79]** studied Cu(II) and Ni(II) complexes of acetylacetonebis(picoloylhydrazone) and acetylacetonebis(isonicotinoylhydrazone). They carried out X-ray structural analysis of copper(II) complex of acetylacetonebis(isonicotinoylhydrazone) obtained from reaction of metal(II) salt, isonicotinoylhydrazine and acetyl acetone and confirmed the square pyramidal stereochemistry.

Giordano and coworkers **[80]** isolated cobalt(II) and nickel(II) complexes of compositions $[Co(LH_2)(H_2O)(NO_3)]NO_3$ and $[Ni(LH_2)(H_2O)_2](NO_3)2.2H_2O$ from reaction of metal nitrates with 2,6-diacetylpyridine bis(benzoylhydrazone) (LH_2) in 95% ethanol. The X-ray crystallographic study confirmed that the metal atoms are in a pentagonal bipyramidal arrangement in the structural unit of the complexes.

Palenik and coworkers **[81]** isolated lanthanum complex of composition $[La(LH_2)(NO_3)_3]$ from reaction of lanthanum nitrate and the ligand in ethanol at 55 ^{0}C in the presence of water. The complex was studied by infrared spectroscopy and X-ray crystallographic studies. They showed lanthanum to be eleven coordinated in these complexes. A decahedral arrangement of the donor atoms of the ligand is proposed around the lanthanum atom in the complexes.

Paolucci and coworkers **[82]** prepared a series of dioxouranium(VI) complexes of 2,6-acetylpyridine bis(4-methoxy benzoylhydrazone)(H_2dapmb). The neutral compound of the composition UO_2(dapmb) was formed in two different crystalline forms, α andβ depending upon the experimental conditions. The geometry of $[UO_2(dapmb)]$ which was formed in two forms is very similar, the only significant difference being the difference in the conformation of carbon atoms in a methoxy group. Seven fold coordination of uranium(VI) was established with the five donor nitrogen atoms in the equatorial plane.

Pelizzi and coworkers **[83]** isolated tin(IV) complexes of the composition $[Snpr_2(LH_2)]$ from reaction of n-propyltinchloride in anhydrous acetone, under nitrogen atmosphere with boiling suspension of 2, 6-diacylpyridinebis(salicylhydrazone) (LH_4) in dry methanol. X-ray crystal structure study has established that tin atom is seven coordinated in the complex with pentagonal bipyramidal arrangement of ligand atoms. The -OH groups remain uncoordinated.

Teotia and coworkers **[84]** have studied reactions of metal(II) salts (M = Cu(II), Ni(II)) with picolinoyl/isonicotinoylhydrazine in presence of acetylacetone. They isolated complexes of the compositions [M(LH)X] (M = Ni(II), Cu(II), X = Cl^-, Br^- NO_3^- and NCS, LH_2 = acetylacetonebis(picolinoylhydrazone) or acetylacetonebis(isonicotinoylhydrazone). All the complexes have been established to have square pyramidal stereochemistry. Complexes $[M(LH)X_2]$ [X= Cl^-, Br^- NO_3^- and NCS for M=Cu(III); X= OAc, Cl^-, Br^-, NCS for Mn(III) and OH for Co(III) were also prepared similarly **[85]** by them. The complexes have been suggested to have six-coordinate tetragonal structure.

Paolucci and coworkers **[86]** synthesized several complexes of 2, 6-diformylphenolbis(benzoylhydrazone) and its substituted derivatives with the bivalent metal ions (M= Co(II), Ni(II), Cu(II) and Zn(II) and established their molecular structure by various physico chemical techniques. A fascinating aspect of these ligands is the coordinating and bridging ability of phenolic-OH of the 2, 6-formylphenol moiety plus the very subtle behaviour of acidic protons.

Dutta and coworkers **[87]** isolated complexes of the composition [VO(L)] from reaction of $VO(acac)_2$ with acetylacetonebis(benzoylhydrazone) (LH_2) in acetone. The same ligand on reaction with CoX_2 (X= Cl^-, Br^-) in anhydrous medium yield blue coloured tetrahedral polymeric complexes $[Co(LH_2)X_2]$ **[88]**. However, in the presence of lattice water, bromide salt yields pink coloured pseudo-octahedral $[Co(LH_2)Br_2]$ complexes.

The dihydrazone reacts with nickel(II) chloride in rectified spirit and yields diamagnetic, orange yellow complex [Ni(L)] **[89]**. However reaction with anhydrous $NiCl_2$ in warm anhydrous methanol gives a paramagnetic complex $[Ni(LH_2)Cl_2]$ having a *trans*-dichloro pseudo-octahedral structure. When this complex is exposed to moist atmosphere and over KOH, the partial dechlorination occurs giving the complex [Ni(LH)Cl]. This complex is proposed to have a five-coordinate structure. They also isolated complexes [Zn(L)], $[Cd(L)].2H_2O$ and [Pb(L)] from the interaction of appropriate metal acetate with the ligand in ethanol.

Snow and coworkers **[90]** studied the reaction of bis(acetylacetonato)oxovanadium(IV) with benzoylhydrazine in dry ethanol under dry nitrogen. They isolated bis(acetylacetone benzoylhydrazonato)vanadium(IV). A trigonal prismatic geometry was verified for this complex.

Dutta and coworkers **[91]** showed that the reaction of $VO(acac)_2$ with benzoylhydrazine and related ligands in methanol, ethanol and methyl acetate yielded violet or almost black coloured bis(acetylacetonebenzoylhydrazonato)vanadium(IV) whereas reaction in acetone or methylethylketone yielded (acetylacetonebenzoylhydrazonato)oxovanadium(IV). While in the former complex, the abstraction of oxo-group has been suggested to occur, in the latter complex it is retained.

Lanthanide complexes **[92]** of the type $[Ln(L)(OH)(H_2O)]$ (Ln = La(III), Pr(III), Nd(III), Sm(III), Gd(III), Ho(III), Er(III)) have been obtained in situ by refluxing biacetyl, benzoylhydrazine and the appropriate metal chloride in ethanol in the presence of a regulated quantity of NH_4OH. The ligand acts as a quadridentate ONNO donor in its enol form.

Pelizzi and coworkers **[93]** have isolated a new series of metal(II) complexes of the type $[M(LH_2)(OH_2)Cl]$ (M = Co(II), Ni(II), Mn(II), Cu(II) and Zn(II)) by mixing ethanol solutions of LH_2 with ethanol solutions of metal(II) chloride in 1:1 molar ratio. With metal(II) acetates, the compounds of the type [ML] are obtained. The ligand reacts with metal centres in keto form in complexes $[MLH_2(OH_2)Cl]Cl$ and enol form in complexes [ML]. Some of the complexes are characterized by X-ray crystallographic method as well. The complexes are shown to have pentagonal bipyramidal stereochemistry.

Dutta and coworkers **[94]** have studied the reaction of $MoO_2(acac)_2$ with benzoylhydrazine and related ligands in different solvents. They isolated the complex (benzoylhydrazine) (benzoylhydrazido) (acetylacetonato)molybdenum(VI) in dry methanol while in ordinary methanol the complexes (acetylacetonato) (*cis*-dioxo)molybdenum(VI)-μ-diol-(benzoylhydrazino) (*cis*-dioxo)molybdenum(VI) dihydrate was isolated. They have shown that in dry methanol acetylacetone and hydrazines condense to give Schiff base complexes whereas no Schiff base formation occurs in ordinary methanol. The Schiff bases derived from acetylacetone and 2-

picolinoylhydrazide or isonicotinoylhydrazide are similar to above, but they give complexes of the $[UO_2L]Cl$ (where LH = Schiff base), in which Schiff bases coordinate through both azomethine nitrogen and pyridine nitrogen (in the case of 2-picolinoylhydrazone) or carbonyl oxygen (in the case of isonicotinoylhydrazone) **[95]**.

On the basis of IR and conductivity data Day et al **[96]** have reported the formation of $[UO_2(LH_2)](NO_3)_2$ (where LH_2 represents 1,2-dimethyl bis(4-methoxybenzoylhydrazone)). Similarly they have reported the formation of $[UO_2(LH_2)(NO_3)]NO_3$ upon acidification of $[UO_2L]$ with HNO_3. Ligands are proposed to coordinate to the metal centres in keto as well as enol forms. Interaction of these complexes with neutral mono and bidentate ligands lead to the formation of $[UO_2L(A)_2]$ and $[UO_2L(AA)]$ (where A = pyridine, picoline, methylamine, aniline, ph_3 PO; AA = en, ph, phen).

Marangoni and coworkers **[97]** synthesized mercury(II) complex with 2,6-diacetylpyridine bis(2-pyridoylhydrazone). They carried out X-ray structural analysis of the complex, and confirmed its pentagonal bipyramidal stereochemistry.

Pelizzi and coworkers **[98]** synthesized nickel(II) complex $[\{Ni(H_2apsh)(OH_2)(I)\}_2C1_2].2dmf.5H_2O$, and cobalt(II) and copper(II) complexes, viz., $[Co(H_2dpsah)(OH_2)_2]Cl.4H_2O$ of 2,6-diacetylpyridinebis[2-(semicarbozono)propionyl-hydrazone] (H_4apsh) and H_2dpsah = 2,6-diacetylpyridinebis[2-(semicarbazono)-acetophenoylhydrazone] (H_2dpash) respectively. In the nickel complex, the four atoms of the semicarbazone system are involved in coordination while in the cobalt complex, semicarbazone system does not participate in coordination. They established the structure of the complexes by IR spectroscopy and X-ray crystallography.

Pelizzi and coworkers **[99]** studied the structure of a tetranuclear copper(II) complex $[Cu_2(dappc)(OH_2)_3]_2$, $[Cu_2(dappc)(OH_2)_2(ClO_4)]_2(ClO_4)_6.2H_2O$ (I) and $[(Cu_2(dapip)Br]_2$ (II) derived from the polyfunctional ligand 2, 6-diacetylpyridinebis(2-pyridine carbonylhydrazone) (H_2dappc) and 2,6 -diacetylpyridinebis(2-(2-pyridinecarbonylhydrazone phenylacetohydrazone] (H_4dapip) respectively . The structure of compound (I) is built up of complex cations of formula $[Cu_2(dappc)(OH_2)_3]_2$ and $[Cu_2(dappc)(OH_2)_2\ ClO_4]^{2+}$. ClO_4 anions and uncoordinated H_2O molecule while that of

the compound (II) consists of neutral unit of formula $[Cu_2(dapip)Br]_2$ and solvating H_2O molecules. In both compounds, two metal atoms for one hydrazone molecule are present and the ligand is bideprotonated in complex (I) and trideprotonated in complex (II).

A monoperoxo complex of Schiff base (H_5C_6C= N-NHC(S).$SCH_2C_6H_5)_2$, (LH_2) has been reported by Tarafder et al **[100]**. The complex $[UO_2(O_2)L]$ was prepared by treating uranyl nitrate with the Schiff base dissolved in a solution of KOH in 30% H_2O_2. The Schiff base behaves as dibasic NNSS tetradentate ligand, while peroxo group is bonded to the metal centre as bidentate chelating ligand.

Toshev and coworkers **[101]** reported the dioxouranium complex of diacetylbis (thio-benzoylhydrazone) in which uranium has a distorted pentagonal bipyramidal structure with the uranyl oxygen atoms at the axial positions.

Pelizzi and coworkers **[102]** synthesized copper complexes of di-2-pyridylketone(phenylsemicarbazone)acetylhydrazone (H_2psah) and studied their structure by X-ray crystallography. They showed that the copper complex $[Cu_2(psah)Cl].H_2O$ consists of a pair of structurally distinct metal centres with different environments bound to the heptadentate hydrazone ligand and held together by a -N-N- bridge.

Katti and coworkers **[103]** synthesized a number of Palladium(II) complexes from series of phosphorous hydrazide and hydrazones. The complexes were characterized by elemental analyses. The structural assessment was carried out by NMR and IR spectroscopic studies. They established the structure of one complex by X- ray crystallography as well.

Lukyanenko and coworkers **[104]** have determined complex stability of Na^+, K^+, Rb^+, and Cs^+ ions with bis(benzo-15-crown-5) with acylhydrazide fragments in the linking chain in 95% aqueous methanol. In all cases, the formation of 1: 1 complex was observed. The studied bis-crown ethers form more stable complexes than benzo-15-crown-5. The stability of biscrown ether complexes is substantially determined by the length of the linking chain. Biscrown ether with a glutaric acid residue in the linking chain exhibits striking potassium selectivity. High selectivity and stability of the complexes are due to the increase of their sandwich structure rigidity resulting from the formation of H-bonds between acylhydrazide fragments.

Ji and coworkers **[105]** studied several dinuclear yttrium(III) and lanthanide(III) picrate complexes derived from acetylferrocenepyridine-2,6-diformylhydrazone having the stoichiometric formula $Ln_2L_2pic_6.n(1\text{-}C_3H_7OH).mH_2O$ (pic = picrate anion, Ln = Y, La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, n = 2, m = 4; Ln = Er, Tm, Yb, , n = 0, m = 2). These complexes were characterized by EA, IR, UV, ^1H NMR spectra and molar conductance data. It was found that the ligand coordinates in keto form to the lanthanide ions. All the complexes described in the present study are 1: 6 electrolyte in methanol.

Xianzeng and coworkers **[106]** synthesized zinc(II) complex $[Zn_2L(CH_3COO)_2].CH_3CH_2OH$, from binucleating ligand L, 2,6-diformylpyridine N-oxidebis(benzoylhydrazone) via template reaction in alcohol. They characterized the complex by X-ray crystalljographic studies. The dihydrazone ligand was found to be present in doubly deprotonated form. They established that all the coordinated atoms of the Schiff base ligand and two zinc atoms with the same bond length of 2.24(1) A^0. The two acedtato ions act as bidentate ligands linking two zinc atoms. Both the zinc atoms have a distorted trigonal-bipyramidal environment. The complex crystallizes in the triclinic space group P1.

Pelizzi and coworkers **[107]** synthesized six complexes of copper(II), nickel (II), and iron(II) from a chiral ligand 2,6-diacetyl pyridinebis{[DL-hydroxy-(phenyl)acetic]hydrazone (H_4dapm) and characterized them by spectroscopic studies. They established the structure of the nickel complex $[Ni(H_4dapm)\text{-}(H_2dapm)].13H_2O$ by X-ray diffraction methods. The complex crystallizes in the monoclinic space group C2/c. The complex has a two fold crystallography imposed symmetry with the nickel atom in a distorted octahedral environment consisting of six nitrogen atoms from two ligand molecules. With the help of ^1H NMR spectroscopic studies, the existence of the ligand in therr forms i.e the meso DL and the two enantiomeric DD and LL ones were established. They attributed the doublets at 6.40 and 5.58ppm to the OH groups. The ^1H NMR spectrum of the complex $[Ni(H_4dapm)(H_2dapm)].13H_2O$ showed the presence of two inequivalent ligand molecules i.e. one in meso form and the other in the DD or LL form. The complexes were characterized by IR spectroscopic studies.

Rana and cowoekers **[108]** synthesized several manganese(II), iron(II), cobalt(II), nickel (II), and copper(II) complexes of 2, 6-diacetylpyridine(benzylacetone)hydrazone (H_2L).

The complexes have been shown to have composition $[M(H_2L)X_2]$ (where M = Mn, Fe, Co, Ni and Cu; X = Cl, Br, NO_3, SCN) and have been characterized by molar conductance, magnetic moment data, infrared, and electronic spectroscopy. The dihydrazone has been shown to function as a tridentate ligand bonding to the metal centre through pyridyl nitrogen and azomethine nitrogen atoms. All the complexes have been proposed to be five coordinate having trigonal bipyramidal stereochemistry in which the dihydrazone donor atoms occupy equatorial position while the anions occupy axial positions.

Paolucci and coworkers **[109]** studied the interactions of potentially binucleating ligand, 2, 6-diacetylpyridine-bis(1-phthalazinylhydrazone) (H_2dapz), containing only nitrogen donor atoms, with nickel(II), copper(II), and zinc(II) salts. They showed that depending on the nature of the counter ions, Ni(II) and Cu(II) ions, selectivelyenter in one of the two compartments present in the ligand. They isolated five series of mononuclear complexes [dapzM], $[H_2dapzMCl_2]$, [HdapzMCl], $[(H_2dapz)_2M][ClO_4]_2$, $[HdapzM][ClO_4]$, from reactions of metal acetates, metal chlorides and metal perchlorates, respectively and the ligand. They established that the dihydrazone is present in the bisdeprotonated, monodeprotonated and undeprotonated forms, respectively in the complexes. They also studied some interconversion reactions. The complexes were characterized by analytical techniques and spectroscopic methods. Some tentative stereochemical assignments of these compounds are reported on the basis of their physico-chemical properties. Different behaviour has been observed in the case of zinc(II) chloride and perchlorate. Crystal structure analysis on the bisdeprotonated complex $[dapzNI]_2$ shows that the compound is dimeric with the metal ions octahedrally coordinated into the upper compardtment and the pyridine nitrogens bridging the two nickel atoms.

Maurya and coworkers **[110]** synthesized binuclear dioxotungsten(VI) complexes of the type $[(WO_2)_2L]$, where L is a flexibly bridged hexadentate tetra anionic Schff base derived from the condensation of methylene or dithiobissalicylaldehyde with isonicotinoylhydrazine, benzoylhydrazine, *p*-nitrobenzoylhydrazine and furoylhydrazine are reported. The IR and NMR spectral data suggest an oligomeric structure for these complexes in which each tungsten atom achieves a pseudo-octahedral structure via W—O→W bridging. Cyclic voltammetric measurements indicate irreversible to

quasireversible reduction of the dioxotungsten(VI) complexes to oxotungsten(V) with a cathodic reduction potential of -1.0 to -1.1V vs SCE at the scan rate of 500 mV/s. The bridging methylene ($-CH_2$) or dithio (-S-S-) group has very little effect on the thermodynamic stability of the complexes.

Lal and coworkers **[111]** synthesized the bimetallic manganese(II, III) and dioxouranium(VI) complexes $[Mn_4(H_2L)(OAc)_4].4H_2O$, $[Mn_4(L)_2(H_2O)_8].4H_2O$, $K_4[Mn_4(L)_2F_6(H_2O)_2].2H_2O$, $[UO_2(H_2O)_4[Mn_4(L)_2(OAc)_4].4H_2O$, and $K_4[(UO_2)Mn_3(L)_2F_5(H_2O)_3]$ from bis(2-hydroxy-1-naphthaldehyde)oxaloyldihydrazone (H_4L). The complexes have been characterized by physical and spectral data. IR spectral data indicate that the dihydrazone coordinates to the metal centres in keto as well as in enol forms in the *anti-cis*-configuration in all of the complexes.

Lal and Adhikari **[112]** synthesized the compound $[(MoO_2)_2(L)(H_2O)].2H_2O$ from the reaction of $MoO_2(acac)_2$ with bis(2-hydroxy-1-naphthaldehyde)oxaloyldihydrazone (H_4L) in ethanol-acetonitrile in 3:1 molar ratio under reflux. The complex is proposed to be a hexamer in which ligands are arranged in sets of three in two parallel planes one above the other. The intra-planer metal atoms are bonded to each other by naphthoxo-bridges whereas the inter-planer metal atoms are bonded to each other by M = O...Mo type bridging. The *anti-cis*-configuration of the dihydrazone moieties leads to the chair conformation of the complexes.

Lal and coworkers **[113]** isolated the homobimetallic complex $[(MoO_2)_2(L)].4H_2O$ from bis(2-hydroxy-1-naphthaldehyde)oxaloyldihydrazone (H_4L) in the solid state. It reacts with Lewis bases pyridine and 3-picoline to form the complexes $[\{\mu_2\text{-}O)MoO_2\}MoO_2(H_2L)].2D.4H_2O$ (where D = pyridine(py) (2), 3-picoline(3-pic) (3) and with proton bases salicyloylhydrazine ($sylshH_3$) and isonicotinoylhydrazine ($inhH_3$) to yield the Mo(V) compounds $[Mo_2(L)(sylsh)_2].\ 5H_2O$ (4) , and $[Mo_2(L)(inh)_2(H_2O)_2].\ 3H_2O$ (5), respectively. The complexes have been characterized by elemental analysis, molecular weight determinations, molar conductance, magnetic moment, ESR, electronic, infrared, and ^1H NMR spectral studies. IR and ^1H NMR data indicate that the dihydrazone coordinates to the metal centre in and *anti-cis*-configuration in all the complexes. The dihydrazone is present in the enol form in the complexes (1). (4), and (5)

but in the keto form in the complexes (2) and (3). The complexes (4) and (5) are paramagnetic to the extent of 3.02 and 3.16 μ_B respectively.

Lal and coworkers **[114]** have synthesized the complexes of the type $[(UO_2)_4(L)_2(H_2O)_8].4H_2O$ (1), $K_4[(UO_2)_4(L)_2(OAc)_4(H_2O)_4].4H_2O$ (2), and $K_4[(UO_2)_4(L)_2F_4(H_2O)_4]$ (3), from bis(2-hydroxy-1-naphthaldehyde)oxaloyldihydrazone (H_4L) and characterized by elemental analyses, molecular weight determinations, molar conductance, electronic, IR and ^1H NMR spectroscopic studies. The dihydrazone coordinates to the metal centre in the *anti-cis*-configuration in enol form in the complexes (1) and (3) which contain water and fluoro groups as co-ligands in the coordination sphere functioning as terminal monodentate ligand. The dihydrazone isomerizes to *syn-cis*-configuration when the bridging bidentate acetate group is introduced into the first coordination sphere in the complex (2). The coordination of both azomethine groups of the dihydrazone to the same metal centre in *anti-cis*- configuration in complexes (1) and (3) leads to coupling between azomethine protons suggesting their chair conformation. However, no such coupling occurs when different hydrazone parts of the dihydrazone coordinates to different metal centres in *syn-cis*-configuration in complex (2) eliminating the possibility of its existence in chair conformation.

Lal and Kumar **[115]** have synthesized an unstable monomeric yellow complex of the type $[(MoO_2)_2(CHsalmlhH_4)(H_2O)_2].H_2O$ {complex (A)} from the reaction between bis(acetylacetonato)dioxomolybdenum(VI) and disalicylaldehyde malonoyldihydrazone ($CH_2salmlhH$) in ethanol. This is transformed into an intermediate complex $[(MoO_2)_2(CHsalmlhH)(H_2O)]_2.4H_2O$ {complex (AB)} after sometime. Ultimately a stable brown isomer complex $[(MoO_2)_2(CH_2salmlh)(H_2O)_2].4H_2O$ {complex (AB)} is obtained. All the products have been characterized by various physico-chemical techniques and IR and ^1H NMR spectroscopic studies.

Lal and coworkers **[116]** isolated the complexes of the composition $[UO_2(H_3salligh)(OAc)].3H_2O$ and $[UO_2Zn(salligh)(H_2O)_2].2H_2O$, where $H_4salligh$ refers to disalicylaldehydeoxaloyldihydrazone ($H_4saloxlh$), malonoyldihydrazone ($H_4salmlh$), succinoyldihydrazone ($H_4salsuch$), glutaroyldihydrazone ($H_4salgluth$), and phthaloyldihydrazone ($H_4salphth$). The complexes have been characterized by molar conductance and spectral data.

Lal and coworkers **[117]** have synthesized the complexes, $Na_4[(UO_2)_4(L)_2(OAc)_4(H_2O)_4].4H_2O$ (1) and $Na_4[(UO_2)_4(L)_2F_4(H_2O)_4]$ (2) from bis(*o*-hydroxynaphthaldehyde)oxaloyldihydrazone (napoxlhH_4) and characterized by elemental analysis, molar conductance, electronic, IR and ^1H NMR spectroscopic studies. On the basis of these studies, it is suggested that the fluoro complex exists in chair conformation in which coordination of both azomethine nitrogen atoms of the dihydrazone in *cis*-configuration to the same metal centre leads to coupling between azomethine protons. In the acetato complex, the coordination of two hydrazone parts of the dihydrazone even in *cis*-configuration to different metal centres eliminates the possibility of azomethine proton coupling and thus, its existence in chair conformation. All the complexes involves eight-coordinated uranium atom with the dihydrazone in the enol form.

Lal and coworkers **[118]** have synthesized the monometallic complexes of the type $[Zn_2(H_4L)_2(SO_4)_2]$ (1), $[Zn_2(H_2L)_2(H_2O)_2]$ (2), $K_2[Zn_2(H_2L)_2F_2]$ (2a), and the heterometallic complexes of the type compound $[(UO_2)_2Zn_2(H_2O)_6]$ (3), $[(UO_2)_2Zn_2(L)_2F_4(H_2O)_2]$ (3a), $[Cu_2Zn_2(L)_2(H_2O)_4]$ (4), $K_4[Cu_2Zn_2(L)_2F_4(H_2O)_2]$ (4a), and characterized by analytical, molar conductance and magnetic moment data and electronic, ESR, IR, and ^1H NMR spectroscopic studies. All of the complexes have been proposed to be dimmer on the basis of molecular weight determinations. Monometallic complexes have been shown to contain the coordinated dihydrazone in *syn-cis*-configuration while the heterobimetallic complexes contain the coordinated dihydrazone in the *anti-cis*-configuration. In these complexes, copper and zine metal centres have been shown to be five coordinate square-pyramidal whereas uraniumcentres have been shown to be eight-coordinate hexagonal bipyramidal.

Ma Yongxiang and coworkers **[119]** synthesized the chelates $Na_2[Ln(C_{34}H_{28}N_8O_8)Cl].nH_2O$ of the malonoyl dihydrazone of salicylaldehyde with the lanthanides and characterized them by elemental analysis, IR, UV, molar conductance and TGA. They showed that the ligand coordinates to the central ion with one hydrazone unit in the keto form and one chloride ion participates in coordination to the metal ion. These chelates are 1:2 electrolytes in DMF and are more thermostable than their ligand due to the formation of chelate rings.

Bolgar and coworkers **[120]** synthesized a series of dihydrazone and substituted dihydrazone derivatives of biacetyl and of hydrazine and phenylhydrazine derivatives of 2-acetylpyridine. They studied the reactions of those dihydrazones with $[Ru(bipy)_2 Cl_2]$ and isolated the products of the composition $[Ru(bipy)_2(L—L)][PF_6]_2$ {bipy = 2,2'-bipyridine; L—L = biacetyl di(phenylhydrazone) 1a, biacetyl di[methyl(phenyl)hydrazone] 1b, biacetyl di(o-tolylhydrazone) 1c, biacetyl di(methylhydrazone) 1d, biacetyl dihydrazone) 1e, biacetyl di(benzaldehyde azine) 1f, 2-acetylpyridinephenylhydrazone 1g, or 2-acetylpyridinehydrazone 1h}. The structures of all complexes were determined using IR, UV/Vis, H^1 NMR and microanalysis. The proton NMR spectra of 1a-1c showed an unusual dependence on probe temperature with broadened aromatic resonances, sharpening at both high and low temperatures in the case of 1b and 1c. No emission was observed for complexes with two hydrazone moieties, whereas it was observed for 1g and 1h with one hydrazone. The molecular structure of 1a was determined and it was shown that a hydrazone phenyl group lies over each of the bipyridyl rings: space group C2/c, a = 25.895(3), b= 10.505 (1), c= 17.431(2) Å, β = 106.03 (2)° and Z= 4.

Khan and coworkers **[121]** synthesized a new class of tetraiminetetraamide macrocyclic (Ph_4[20]tetraene, N_8O_4, and Ph_6[20]tetraene, N_8O_4) complexes through the metal ion controlled reaction of 1,2-diphenylethane-1,2-dione dihydrazone (DPEDDH) with succinic acid $[ML_1X_2]$ or phthalic acid $[ML_2X_2]$ [M = Co, Ni, Cu or Zn; X = Cl or NO_3]. They elucidated the structure of the complexes on the basis of IR, ^1H NMR, EPR and electronic spectral data and conductance, as well as magnetic, properties. An octahedral geometry was assigned for all the complexes, involving coordination of all the imine nitrogens.

Labib and coworkers **[122]** synthesized a series of polyacylhydrazones by condensing diacetyl with oxalic, malonic, succinic, glutaric and adipic dihydrazides and characterized them by conventional spectroscopic studies. They reacted these dihydrazones of general formula $\{[Cu_2(L)(OAc)_2(OH)(H_2O)_2].yH_2O\}_n$, $\{[Cu(L)(AcO)_2(HO)(H_2O)].yH_2O\}_n$, $\{[Ni_2(L)(AcO)_2(HO)_2].yH_2O\}_n$, $\{[Ni(L)(AcO)(HO)].yH_2O\}_n$, where L refers to the neutral dihydrazone unit. Magnetic susceptibility measurements in the 4.2-300 K range indicated significant antiferromagnetic coupling between the Cu^{II} centers in the

metallopolymers. The results might indicate the presence of two polymer chains crosslinked by bis-μ-acetatocopper(II) bridges. Based on IR, spectral and magnetic measurements, tentative structures of the Cu^{II} and Ni^{II} metallopolymers were proposed. The dihydrazone units in these polymers were found to be coordinated to the metal(II) via the azomethine nitrogen(s) whereas the amide group was found to remain uncoordinated. Each Cu^{II} is penta-cordinated in a distordted square pyramidal environment and is neutralized by one bridged acetate and a hydroxide ion, while the fifth coordination site is occupied by a water molecule. In the nickel(II) metallopolymers, the metal ions were in a tetrahedral environment and were coordinated to azomethine nitrogen, two bridged acetate oxygens and to the hydroxide ion.

Larin and coworkers **[123]** synthesized the dinuclear copper(II) complexes with 2-hydroxypropiophenone, 2-hydroxy-5-methyl and 5-chloro-2-hydroxyacetophenone acyldihydrazones (H_4L) having the composition [$Cu_2L.mPy$], where L ligand contains the polymethylene chain with different lengths (from two to five units). The crystal and moljjecular structure of the 2-hydroxypropiophenone adipoylhydrazone complex [$Cu_2L.4Py$].Py were established by X-ray diffraction analysis. Copper atoms were found to be separated from one another by a distance of 8.212Å. Their nearest environment were found to have tetragonal pyramidal geometry. The ESR spectra of solutions of the complexes based on acyldihydrazones of succinic , malonic ,glutaric, and adipic acids contain seven HFS lines with the constant ~ 40×10^{-4} $cm^{-1}$from two equivalent copper atoms. The spectra were interpreted as a result of the spin-spin exchange interaction of two unpaired electrons. An increase in the polymethylene chain length of five units prevents exchange interactions. The ESR spectrum of the complex with acyldihydrazone of pimelic acid contains a signal of four HFS lines with A_{Cu} = 73.4×10^{-4} cm^{-1}, which is typical of mononuclear copper(II) complexes.

Andelkovic and coworkers **[124]** synthesized complexes of Zn(II), Pd(II) and Pt(II) with 2'-[1-(2-pyridinyl)ethylidene]oxamohydrazide (Hapsox). The complexes were characterized and their structures were determined. All the complexes were found to be neutral type with two apsox ligands coordinating to Zn(II) and one apsox ligand coordinating to Pd(II) or Pt(II). In each case, the polydentate ligand was coordinated via pyridine and hydrazone nitrogens and α-oxyazine, forming an octahedral geometry

around Zn(II), and a square planer one around Pd(II) and Pt(II). The structure determination was performed by IR, ^{1}H NMR and ^{13}C NMR spectroscopy, and for the Zn (II) complex by X-ray structure analysis.

Para et al **[125]** synthesized dialdehyde starch dihydrazone DASHZ from reaction of dialdehyde starch with hydrazine . The dihydrazone (DASHZ) coordinated to Ca, Cd, Co (II), Cu(II), Fe(II), Mg, Mn (II), Ni (II), Pb(II), and Zn ions. The nitrogen atoms of the >C=N moiety in dihydrazone as well as the oxygen atom of the fomer pyranose ring were the coordination sites. Metal ions were chelated to a different extent. One mole of a metal ion could coordinate with 3 [Cu(II)] to 50 [Mn(II)] mole of the DASHZ units. The ligand DASHZ and the metal complexes decomposed thermally in four steps but the rates of decomposition of the ligand and chelates in relevant steps were different. Except the complex with Mg, these rates for complexes were lower.

Zhao and coworkers **[126]** synthesized polynuclear manganese(II), cobalt(II)/(III), iron(II)/(III) and nickel(II) complexes of a group of flexible polydentate dihydrazone ligands, based on pyridine-2,6-dipicolinic (A), oxalic (B) and malonic (C) subunits. They reported the structural details for the linear dinuclear complexes $[Ni_2(2poap)_2(H_2O)_2](NO_3)_2.2CH_3OH.2H_2O$(1),$[Mn_2(pttp)_2(NO_3)_2(CH_3OH)_2(H_2O)_2](NO_3)_2.2H_2O$ (2), and $[Mn_2(mapttp)_2(NO_3)_2(H_2O)_2](NO_3)_2.10H_2O$ (3), a square tetranuclear complex $[Co_4(pttp)_4]Br_6.9H_2O$, a tetranuclear tetrahedral complex $[Ni_4(pttp)_6](BF_4)_6F_2.14H_2O$ (7), and a mixed spin state tetranuclear Ni(II) complex $[(2pyoap)_2Ni_4(CH_3OH)_4].1.5CH_3OH$ (10), with a diamond-like arrangement of metal ions. The paramagnetic metal centres are well separated in each case, leading to weak antiferromagnetic coupling or non-existent spin exchange.

Tirosh and coworkers **[127]** synthesized the cadmium (II) complex $[Cd(C_4H_{10}N_4)_3(ClO_4)_2]$ from the reaction of $Cd(ClO_4)_2.H_2O$ with biacetyl dihydrazone in methanol. They established the structure of the compound with the help of X-ray crystallography. The cation was found to be located on a 3 axis and was characterized by an approximate octahedral geometry, with each of the ligands occupying two coordination sites around the metal.

Carcelli and coworkers **[128]** synthesized a novel series of lanthanide (III) complexes with two potentially hexadentate ligands containing a rigid phenanthroline moiety and two flexible hydrazonic arms with different donor atom sets (NNN'N'OO and NNN'N"N", respectively. These hydrazones , (2,9-diformylphenanthroline)bis (benzoyl)hydrazone (H_2L^1), (2,9-diformylphenanthroline)bis(2-pyridyl)hydrazone (H_2L^2). They prepared both both nitrate and acetate complexes of H_2L^1 with La, Eu, Gd, and Tb and fully characterized. They presented the X-ray crystal structure of the complex $[Eu(HL^1)(CH_3COO)_2].5H_2O$. The stability constants of the equilibria $Ln^{3+} + H_2L^1 = [Ln(H_2L^1)^{3+}$ and $Ln^{3+} + (L^1)^{2-} = [Ln(L_1)^+$ (Ln = La(III), Eu(III), Gd(III), and Tb(III) were determined by UV spectrophotometric titrations in DMSO at t = 25°C. They also synthesized the nitrate complex of H_2L^2 with La, Eu, Gd and Tb. The X-ray crystal structure of the complex $[La(H_2L^2)(NO_3)_2(H_2O)](NO_3)$, $[Eu\ (H_2L^2)(NO_3)_2](NO_3)$ and $[Tb(H_2L^2)(NO_3)_2](NO_3)$ were also established.

Salem **[129]** synthesized a series of acyldihydrazones, H_2L^n from condensation of ethylpyruvate with oxalic, malonic, succinic, glutaric and adipic dihydrazides. The author isolated dicopper(II) complexes of the general formula $[Cu(L'^n).H_2O].xH_2O$, where L'^n refers to the quadruply deprotonated pyruvic acid dihydrazone ligand and n refers to the number of carbon atoms of the aliphaticspacer between the two acylhydrazone units. The isolated complexes were characterized by elemental analyses, infrared spectra, mass spectra and variable temperature magnetic susceptibility measurements. Magnetic susceptibility measurements in the 4.2-298 K range indicate significant antiferromagnetic coupling between copper(II) centers and suggest association of the coordinated copper(II) units Cu(ONO) via oxazine oxygen bridges. This leads to a polymeric structure where the dimeric units are connected together with aliphatic spacer. From the best fit values of the mole fraction of paramagnetic uncoupled copper(II) centers (ρ), the degree of association in these polynuclear copper(II) complexes were estimated.

Elengoz et al **[130]** synthesized the zinc complex tris(biacetyl dihydrazone-κ^2N,N')zinc(II) bis(perchlorate) at 110 K and determined its crystal structure precisely.The metal-organic cation, which is located on a 3 axis, is characterized by an approximate octahedral geometry, with each of the ligands occupying two coordination sites around the metal. The title compound, crystallizes in the trigonal space group P3c1

with two units of the $[Zn(C_4H_{10}N_4)_3]^{2+}$ cationic complex and four ClO_4^- anions in the unit cell. The Zn^{II} atom is located on a 3axis, while the perchlorate anion is located on a theefole rotation axis. The cation is characterized by perfect 3 symmetry, in which three chelating ligands occupy the octahedral coordination sites of the zinc metal ion. The imine N atoms of the lignd provide the coordination sites to the central metal ion. The conformation about the central C—C bond of the ligand is cis, with the two C=N bonds being nearly coplanar, to direct the two imine coordinating sites towards the metal centre. The N—Zn—N bond angle involving two coordinating N atoms of a given ligand is 74.33 (11)°. In the free form of the ligand, the N—N=C—C=N—N backbone adopts a planer anti conformation (Hauer et al, 1987).

V. P. Singh and P. Gupta **[131]** synthesized and characterized the Complexes of diacetyl salicylaldehyde oxalic acid dihydrazone, $CH_3COC(CH_3)$= NNHCOCONHN=$CHC_6H_4(OH)$,(dsodh) and diacetyl salicylaldehyde malonic acid dihydrazone $CH_3COC(CH_3)$=NNHCOCH_2CONHN=$CHC_6H_4(OH)$, (dsmdh) by elemental analyses, molar conductance, magnetic moments, electronic, ESR and infrared spectra and X-ray diffraction data and were found to have the general compositions [M(L)]Cl, [M'(L)Cl], [M(L')]Cl and [M'(L')Cl] (where M= Co(II), Cu (II), Zn (II), Cd (II) and M'= Ni(II); HL=dsodh and HL' =dsmdh). With the help of magnetic moments and electronic spectral data they predicted a six-coordinate octahedral geometry for Co(II) and square planar geometry for Ni(II) complexes. They also found that the ESR spectral data of Cu(II) complexes in DMF solution reveal a tetragonally distorted octahedral geometry. Both ligands bond through >C=O, >C=N and deprotonated phenolate groups in all octahedral complexes and through >C=N and deprotonated phenolate groups in Ni(II) square planar complexes. The lattice parameters for Cu(dsodh) and Co(dsmdh) correspond to an orthorhombic and Ni(dsodh) corresponds to a tetragonal crystal lattice. The complexes were found to exhibit significant antifungal activity against a number of pathogenic fungi viz. Stemphylium, Myrothecium and Alternaria. The antibacterial activity was studied against Pseudomonas fluorescence (gram -ve) and Clostridium thermocellum (gram +ve).

C. T. Yang and coworkers **[132]** synthesized the complexes of dioxouranium(VI) with four dipyridoxal hudrazone ligands H_{4PL}^n and characterized them by various analytical

and spectroscopic methods including X-ray crystallography. The ligands and the UO_2^{VI} complexes were also tested for cytotoxicity. They found that the solid-state structure of $[(UO_2)_4(PL')_2(H_2O)_4].12H_2O$ is a cyclic tetramer.

M. F. Iskander and coworkers **[133]** synthesized and characterized two series of dicopper(II) complexes derived from bis(N-salicylidine)dicarboxylic acid dihydrazides ($H4L^n$) of general formula $[Cu_2(L_n).xH_2O]$ .yH_2O and $[Cu_2(H_2L^n)Cl_2.xH_2O].yH_2O$ where n refers to the number of carbon atoms in the aliphatic spacer between the two N-salicylideneacylhydrazine units. Magnetic susceptibility measurements for neutral dicopper(II) complexes $[Cu_2(L^n).xH_2O].yH_2O$ indicate significant antiferromagnetic coupling between copper(II) centers. The –2J values obtained from the Bleany–Bowers equation are within the range 121–223cm^{-1}, suggesting association of the coordinated copper(II) units Cu(ONO) via phenoxy bridges. This leads to a polynuclear structure in which the dimeric units are connected with the aliphatic spacer. From the best-fit values of the mole fraction of paramagnetic uncoupled copper(II) centers (ρ), the degree of association in these polynuclear copper(II) complexes has been estimated. The chloro dicopper(II) complexes $[Cu_2(H_2L^n)Cl_2.\ xH_2O].yH_2O$ with n= 0, 2 and 3 also show strong antiferromagnetic exchange coupling (-2J=215–423cm^{-1}), suggesting a polynuclear structure in which the copper(II) is in a distorted square-pyramidal environment, bound in the equatorial plane with a monoanionic ONO tridentate acylhydrazone unit and the μ-phenoxy oxygen and the axial site occupied by a chloride. The dicopper(II) complexes with n¼1 and 4 show weak antiferromagnetic exchange coupling (-2J=16–20 cm^{-1}). In these complexes the chloride ion may occupy the fourth equatorial site while the μ-phenoxy is in the apical position.

V. P. Singh and P. Gupta **[134]** synthesized and characterized the Complexes of diacetyl salicylaldehyde oxalic acid dihydrazone, $CH_3COC(CH_3)$= $NNHCOCONHN=CHC_6H_4(OH)$,(dsodh) and diacetyl salicylaldehyde malonic acid dihydrazone $CH_3COC(CH_3)=NNHCOCH_2CONHN=CHC_6H_4(OH)$, (dsmdh) of general compositions[M(L)]Cl, [M'(L)Cl], [M(L')]Cl and [M'(L')Cl] (where M= Co(II), Cu(II), Zn(II), Cd(II) and M' = Ni(II); HL = dsodh and HL' = dsmdh) were prepared and characterized by elemental analyses, molar conductance, magnetic moments, electronic, ESR and infrared spectra and X-ray diffraction data. The magnetic moments and

electronic spectra indicate six-coordinate octahedral geometry for Co(II) and square planar geometry for Ni(II) complexes. The ESR spectral data of Cu(II) complexes in DMF solution reveal a tetragonally distorted octahedral geometry. Both ligands bond through >C=O, >C=N and deprotonated phenolate groups in all octahedral complexes and through >C=N and deprotonated phenolate groups in Ni(II) square-planar complexes. The lattice parameters for Cu(dsodh) and Co(dsmdh) correspond to an orthorhombic and Ni(dsodh) corresponds to a tetragonal crystal lattice. The complexes were found to exhibit significant antifungal activity against a number of pathogenic fungi viz. *Stemphylium, Myrothecium and Alternaria.* The antibacterial activity was studied against *Pseudomonas fluorescence* (gram -ve) and *Clostridium thermocellum* (gram +ve)

V. P. Singh and co-workers **[135]** isolated the metal(II) complexes of the general formula [M(Bsodh)]Cl and [MBsmdh]Cl where M = Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) (HBsodh = benzyl salicylaldehyde oxalic acid dihydrazone and HBsmdh = benzyl salicylaldehyde malonic acid dihydrazide) and characterized them by elemental analyses, molar conductance, magnetic moment, ESR, IR and X-ray diffraction studies. The ligands and their metal complexes were found to exhibit significant antibacterial activity against Bacilus subtilis and Pseudiomonas fluiorescens.

L. D. Popov and co-workers **[136]** synthesized the dihydrazone ligand 2, 6-diformyl-4-tert-butylphenol bis(8-quinolylhydrazone) and its transition meta complexes of the compositions $[Cu_2(H_2L)Cl]Cl_2$, $[Ni_2(H_2L)Cl_3]$ and $[Mn_2(H_2L)Cl_3]$, where H_2L is the monodeprotonated form of the hydrazone. They studied the conformations of sthe bis-hydrazone, geometries of the complexes, and parameters of exchange coupling between the ferromagnetic centres using quantum–chemical calculations. They also compared the calculated results with the results of the physicochemical study of the complexes.

S. Naskar and D. Mishra **[137]** synthesized a Ni(II) complex of 2, 6-diacetyljpyridine bis(anthraniloyl hydrazone) and characterized it by various physico-chemical methods. The structure of the complex was determined by X-ray crystallography. They also found that, in the solid state, the compound exist as a dimer and two coordinated ligand moieties form a double helix around the two metal ions.

R. M. Issa and co-workers **[138]** studied the thermal stabilities of bis salicylidine adipic dihydrazone derivatives and their complexes with divalent Mn, Ni, Cu and Zn ions and discussed them in terms of structure and type of metal ions. They also found that, the TG curves display mostly four steps of thermal decomposition.

V. F. Shulgin and co-workers **[139]** synthesized and characterized dinuclear copper(II) complexes with acyldihydrazones of 2-hydroxy-5-nitroacetophenone (H_4L) of the composition $Cu_2(py)_xL.mEtOH$. It was found that, in the complexes, the coordination polyhedra ofs the copper atoms are linked to each other by a polymethylene chain of different lengths, from one to five monomer units. They also established the structure for [$Cu_2L.4Mrf$] complex (where Mrf is morpholine) based on acyldihydrazone of malonic acid by X-ray diffraction.

M. Salavati-Niasari and A. Sobhani **[140]** isolated the monomer transition metal complexes, [ML] (M = Mn(II), Co(II), Ni(II) and Cu(II)) from the reaction of metal acetates with bis(salicylaldehyde)oxaloyldihydrazone (H_2L) in 1 : 1 molar ratio in ethanol under reflux. It was suggested that, in all of the complexes, the principal dihydrazone ligand coordinate to the metal centres in the *anti-cis* configuration. These metal complexes were entrapped in the nano cavity of zeolite-Y. The new Host-Guest Nano Composite Materials (HGNM) were characterized by chemical analysis and spectroscopic methods. They also reported the catalytic activities for the oxidation of cyclohexane with HGNM.

Da-Yu Wu and co-workers **[141]** isolated three ligands, di(2-pyridylcarbaldehyde)-6, 6'-dicarboxylic acid hydrazone-2, 2'-bipyridine (H_2L^1), di(2-acetylpyridyl)-6, 6'-dicarboxylic acid hydrazone-2, 2'-bipyridine (H_2L^2) and di(2-pyridyketone)-6, 6'-dicarboxylic acid hydrazone-2, 2'-bipyridine (H_2L^3) with flexible bis-terdentate coordination sites and their cobalt complexes. The complexes were obtaine via self-assembly and their structures were determined by FT-IR, elemental analyses, ESI-MS and X-ray diffraction method.

Lal and coworkers **[142]** synthesized the complexes $[(UO_2)(CH_2L)(H_2O)_4].4H_2O$, $[M_4(H_2L)_2(H_2O)_4].4H_2O$ (M = Zn, Cu), $(M')_2[(UO_2F)(CH_2L)(H_2O)_2]$ [M' = K, Na], $M'[(UO_2)_2(CH_2L)(OAc)(H_2O)_2]$ [M' = K, Na], $K_4[(MF)_2(CH_2L)_2].4H_2O$ [M Zn, Cu]

from the reaction of appropriate metal salts with bis(2-hydroxy-1-naphthaldehyde)oxaloyldihydrazone (CH_2LH_4) under different experimenatal conditions in ethanol/methnol media. The complexes have been characterized by elemental analyses, molecular weight, molar conductance, magnetic and EPR data. The structural assessment of the complexes have been carried out on the basis of electronic, infrared, ^1H NMR and ^{13}C NMR sprectral studies.

Lal and coworkers **[143]** synthesized and characterized zinc(II), copper(II), nickel(II) and manganese(II) complexes derived from bis(2-hydroxy-1-naphthaldehyde)malonoyldihydrazone. In their study, they have shown that the reaction of different salts of the same metal with sterically crowded dihydrazone bis(2-hydroxy-1-naphthaldehyde)malonoyldihydrazone (CH_2LH_4) in ethanol/aqueous media gives complexes of different stereochemistry. While the reaction of Zn(II) and copper(II) sulphate with dihydrazone yields tetrahedral complexes, the zinc(II) and copper(II) chlorides give square-pyramidal and distorted octahedral complexes respectively. On the other hand, nickel(II) sulphate and chloride, both gave high-spin octahedral complexes. They also investigated the reaction of these complexes with KF. All of the products were characterized by analytical, magnetic moment and molar conductance data. The structure of the complexes have been established by spectroscopic studies.

Lal and coworkers **[144]** synthesized the monomer molybdenum(VI) complex $[MoO_2(napoxlhH_2)].2H_2O$ (1) from the reaction of $MoO_2(acac)_2$ with bis(2-hydroxy-1-naphthaldehyde)oxaloyldihydrazone ($napoxlhH_4$) in 1: 1 molar ratio in ethanol under reflux. This complex on reaction with pyridine /3-picoline /4-picoline yielded the dimmer molybdenum(VI) complex $[Mo_2O_4(napoxlhH_2)(A)_2].2H_2O$ (A = py (2), 3-pic(3), 4-pic(4)), whereas the reaction with isonicotinoyl hydrazine ($inhH_3$) and salicyloyl hydrazine ($sylshH_3$) led to the reduction of the metal centre yielding monomeric molybdenum(V) complexes $[Mo(napoxlhH_2)(hzid)].2H_2O$ (where $hzidH_3 = inhH_3$ (5) and ($sylshH_3$ (6)). The complexes have been characterized by elemental analyses, molecular weight determinations, molar conductance data, magnetic moment data, electronic, IR, ESR and ^1H NMR spectroscopic data.

From the survey of literature presented above, it is evident that although mono and bimetallic complexes of various types of dihydrazones have been synthesized and

characterised, in some detail, those derived from dihydrazones containing bulky fragments in their molecular skeleton have much less been studied. In view of limited number of investigations on metal complexes of dihydrazones containing bulky fragments in their molecular skeleton, the project has been undertaken. It is quite possible to extend and develop such a study, with the help of variety of metal ions into a major field, but because of time factor, it has been restricted to monometallic and homobimetallic complexes of disalicylaldehyde malonoyl-, succinoyl- and adipoyldihydrazones with copper(II) and molybdenyum(VI). Part of the work is under consideration for publications.

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CHAPTER –II

EXPERIMENTAL

This chapter deals with experimental details regarding synthesis of ligands, methods of analyses and the instrument employed for studying the ligands as well as the complexes. The details about preparation of complexes are given in the respective chapters.

Materials

The metal salts, ammonium molybdate $[(NH_4)_6Mo_7O_{24}.4H_2O]$, $Cu(OAc)_2.H_2O$, $CuCl_2.2H_2O$, $CuSO_4.5H_2O$, diethylmalonate $CH_2(CO_2Et)_2$, hydrazine hydrate $(N_2H_4.H_2O)$, salicylaldehyde $(C_6H_4(OH)CHO)$, diethylsuccinate $(CH_2)_2(COOEt)_2$, diethyladipate $(CH_2)_4(COOEt)_2$ were E-Merck or equivalent grade reagents and were used without further purification. Acetylacetone, pyridine, 2-picoline, 3-picoline and 4-picoline were Lanchaster or equivalent grade reagents. Bis(acetylacetonato)dioxomolybdenum(VI), $MoO_2(acac)_2$ was prepared by literature method **[1]**. The organic solvents viz., ethanol, methanol, diethylether, acetone, dimethylsulphoxide (DMSO) and dimethylformamide (DMF) were purified by standard literature procedures.

Preparation of ligands

The ligand disalicylaldehyde malonoyl-, succinoyl and adipoyldihydrazones were prepared in two steps. In the Ist step, malonoyl-(H_6mh), succinoyl-(H_6sh) and adipoyldihydrazines(H_6ah) were prepared by reacting diethylmalonate, diethylsuccinate and diethyladipate with hydrazine hydrate in 1:2 molar ratio. In the second step, malonoyl-, succinoyl- and adipoyldihydrazine thus obtained were allowed to react with salicylaldehyde in 1:2.2 molar ratio in ethanol which yielded the ligands H_4slmh, H_4slsh and H_4slah respectively.

1. Preparation of Malonoyl-, succinoyl- and adipoyldihydrazine $(CH_2)_n(CONHNH_2)_2$, n = 1, 2, 4

Malonoyldihydrazine (MDH) was prepared by reacting diethylmalonate (10 mL) and hydrazine hydrate (7 mL) in 1:2 molar ratio under reflux for 30 min. This yielded white precipitate which was filtered in cold condition and washed 3-4 times with hot ethanol and dried. The precipitate was recrystallized from dilute ethanol. Yield: 88-85%

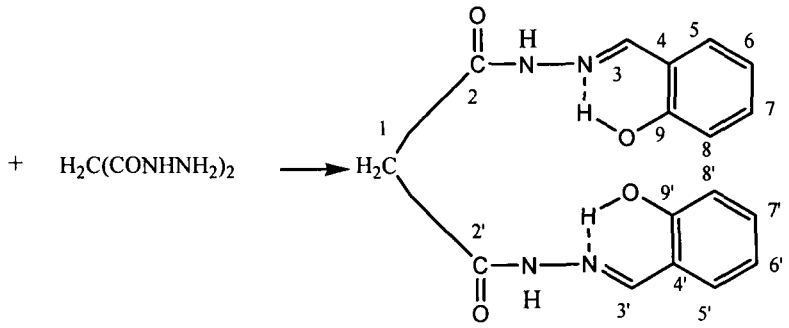
$$H_2C(COOEt)_2 + 2N_2H_4 \rightarrow H_2C(CONH\text{-}NH_2)_2 + 2EtOH$$

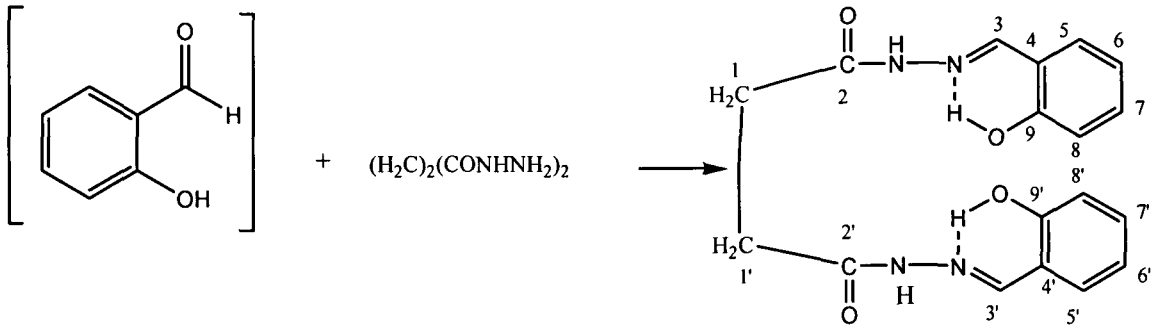
Succinoyldihydrazine (SDH) and adipoylhydrazine (ADH) were also preparared by essentially the above method using diethyl succinate and adipate instead of diethyl malonate, respectively.

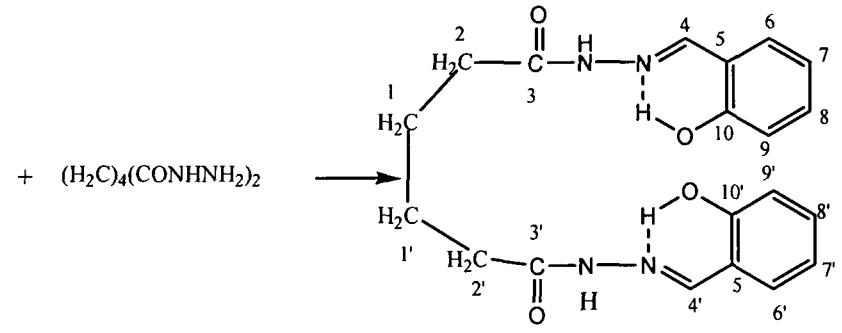
2. Preparation of disalicylaldehyde malonoyl- (H_4slmh), succinoyl- (H_4slsh) and adipoyldihydrazones (H_4slah)

In order to prepare disalicylaldehyde malonoyldihydrazone, the dihydrazine (MDH = 2 g, 5.882 mmol), in dilute ethanol (60 mL) was allowed to react with salicylaldehyde (4.07 mL, 46.642 mmol) in ethanol (30 mL) over hot plate at 70 °C with constant gentle stirring for 30 - 45 min. The yellow white polycrystalline precipitate thus obtained was purified by repeated washing with hot ethanol and dried over anhydrous $CaCl_2$.

Disalicylaldehyde succinoyldihydrazone and adipoyldihydrazone were also prepared by essentially the above method using succinoyldihydrazine and adipoyldihydrazine instead of malonoyldihydrazine.







Estimation of metals

The estimation of various metals was done by following standard literature procedures [2] as given below.

Estimation of Molybdenum

Molybdenum content of the complexes was determined by the following procedure.

About 0.4 g of the complex was accurately weighed in a 250 mL capacity conical flask. To this, 100 mL water and 1.0 g of NaOH were added. The solution was boiled for 2 h.

This decomposed the complex which passed into solution. The solution was neutralized with 0.1 M H_2SO_4 using methyl red indicator and then further acidified with few drops of 0.1 M H_2SO_4. Subsequently 5 mL of 2.0 M ammonium acetate solution was added to it and the solution was diluted to 100 mL. The resulting solution was boiled and then oxine solution in dilute acetic acid was added to it until the supernatant liquid became perceptibly yellow. The solution was further boiled and stirred for 3 min. This yielded precipitate which was filtered through a sintered glass crucible (G-4). The precipitate was washed several times with water until free from oxine and dried to constant weight at 130-140 °C and is weighed as $MoO_2(C_9H_6ON)_2$.

Estimation of Copper

The copper content of the complexes were estimated gravimetrically as copper(I) thiocyanate. About 0.4 g of copper complexes was heated in a silica crucible at high temperature to remove organic part. This was then added in a beaker containing 50 mL of water. To this 20-30 mL hydrochloric acid was added and then diluted to about 200 mL. The mixture was heated to boiling and slowly with constant stirring from a burette until present in slight excess. The precipitate of copper(I) thiocyanate should be white; the mother liquor should be colourless and smell of the sulphur dioxide. Allow to stand overnight. Filter through a weigh filtering crucible and wash the precipitate 10-15 times with cold solution prepared by adding to every 100 mL of water, 1 mL of a 10 percent solution of ammonium thiocynate and 5-6 drops of saturated sulfurious acid solution and finally several times with 20% ethanol to remove ammonium thiocynate. Dry the precipitate to constant weight. Weigh as CuSCN.

Estimation of Chloride

Accurately weighed 0.2 g of chloro complex was digested with 0.5 g of NaOH for about 2 h the solution thus obtained was filtered and filtrate was treated with nitric acid. Any undissolved material was rejected by filtration. To this solution 0.1(N) $AgNO_3$ solution was added keeping it slight excess. The precipitate so obtained was allowed to settle for 2 h in dark, white precipitate of AgCl was filtered through a gooch crucible and dried to constant weight at 110°C [2]

Estimation of Sulphate

Acurately weighed about 0.3 g of sulphato complex was taken and dissolved in conc.HCl and diluted to 225 mL. The solution was heated to boiling and 55mL barium chloride solution was added dropwise with constant stirring. The precipitate was allowed to settle and was filtered by filter paper (Whatman, No.40). The precipitate on filter paper was washed for eight to ten times with hot water. The precipitate was collected and dried and placed in silica crucible, which is previously ignited, cooled and weighed. The crucible was gradually heated to red hot and allowed to cool in dessicator and finally weighed. The percentage of SO_4^{2-} was then catculated.

Physico-Chemical Measurement

CHN Analysis

Elemental Analysis (CHN) was performed by Perkin-Elmer 2400 CHNS/O Analyser 11. Water, ethanol, pyridine, 2-Picoline, 3-picoline and 4-picoline molecules were determined by heating the samples in an electric oven at 110 °C or 180 °C or 220 °C respectively, or in the temperature range 80-250 °C and determining the weight loss. Water molecules were identified by passing the vapours through a test tube containing anhydrous copper sulfate which turn blue, while pyridine, 3-picoline and 4-picoline molecules were determined by passing the vapours through a test tube (a) a solution of sodium hydroxide and iodine; (b) a solution of $CHCl_3$ containing a drop of 5 M NaOH solution and (c) a test tube containing cyanogens bromide solution which turn green-violet and blue respectively in case of 3-picoline and 4-picoline molecules respectively **[3]**.

Room temperature magnetic susceptibility measurements were carried out on Sherwood Scientific Magnetic susceptibility Balance MBS-Auto. The molar conductance of the complexes at 10^{-3} M dilution in DMSO solution were measured on Wayne Kerr Precision Component Analyser 6440B with a dip-type conductivity cell at room temperature. Infrared spectra were recorded on Bomen 1) A-8FT-IRSpectrophotometer in the range 4000-450 cm^{-1} and 2) Spectrum-BX Perkin Elmer in KBr discs. Low frequency infrared spectra were recorded in the range 600-30 cm^{-1} on Perkin Elmer Spectrum 400 in CsI

discs. The electronic spectra were recorded on a Perkin Elmer Lamda 25 UV/Vis spectrophotometer using DMSO solution. The mass spectra of the complexes were recorded on Liquid Chromatoghaphy-Mass Spectrometer Model: Waters ZQ-4000. The electronic paramagnetic resonance (EPR) spectra of the complexes in powder as well as solution state were recorded at X-Band frequency on Variance E-112E-Line Century Series ESR Spetrometer using TCNg (g = 2.0027) as an internal field marker. The ^1H NMR spectra were recorded on AMX-400 MHz and Varian 400 MHz in DMSO-d_6 using TMS as internal standard. The Cyclic Voltammetric measurement of the complexes in DMSO (10^{-3} M) was done using CH Instruments Electrochemical Analyser under nitrogen atmosphere. The electrolytic cell comprises of 3-electrodes. The working electrode was a glassy carbon disk from BAS and the reference electrode was a aqueous SCE or Ag/AgCl separated from the sample solution by a salt bridge, 0.1 M TBAP was used as the supporting electrolyte.

Table 1: Melting Point and C, H, N Analyzer of ligands.

Ligands	Formula	M.P(^{0}C)	Analysis : Found (Calcd) %		
			C	H	N
Disalicyldehyde malonoyldihydrazone (H_4slmh)	$C_{17}H_{16}N_4O_4$	230	60.37 (60.00)	4.71 (4.74)	16.28 (16.46)
Disalicyldehyde succinoyldihydrazone (H_4slsh)	$C_{18}H_{18}N_4O_4$	250	61.23 (61.01)	5.15 (5.12)	15.69 (15.81)
Disalicyldihyde adipoyldihyrazone (H_4slah)	$C_{20}H_{22}N_4O_4$	>300	62.69 (62.82)	5.79 (5.80)	14.59 (14.64)

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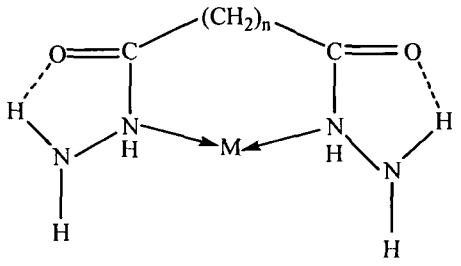
CHAPTER –III

Synthesis, characterization and electrochemical studies of mononuclear copper(II) complexes derived from disalicylaldehyde malonoyl-, succinoyl- and adipoyldihydrazones.

Introduction

The ligands which have been employed for the synthesis of the complexes in the present chapter have been derived from condensation of malonoyl-, succinoyl-and adipoyl-dihydrazines with salicylaldehyde. Hence, it is relevant to briefly mention the type of complexes formed by acyl-, aroyl- and pyridoyl-dihydrazines and their dihydrazones and examine their bonding modes. Dutta and Sengupta [1] and Sahni et al [2] reported that acyl and aroyldihydrazines derived from aliphatic dicarboxylic acids, containing two –$CONHNH_2$ groups have been reported to coordinate as a neutral bidentate ligand through two imino nitrogens (>NH) although the potentially strong donor functions like >C=O and $-NH_2$ are present. It has been suggested that strong intramolecular hydrogen bonding, as follows (I), probably makes them unavailable for coordination [3, 4].



(I)

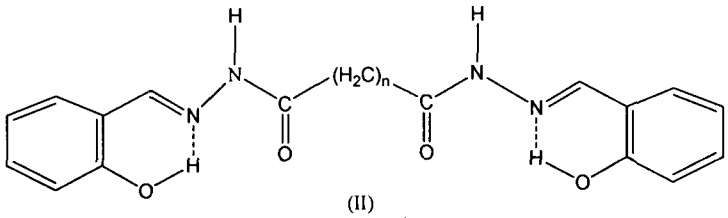
However, when methylene or phenyl functions are substituted by pyridyl functions in dihydrazines, the resulting picolinoyldihydrazine coordinates to the metal centre as a neutral pentadentate ligand through pyridyl nitrogen atom, two >C=O and two $-NH_2$ groups [5]. It appears that these ligands, because of the presence of pyridyl nitrogen atom, make >C=O and $-NH_2$ groups reactive.

Maki and coworkers [6] synthesized dioxouranium(VI) complexes of some dicarboxylic acid dihydrazines in ethanol medium in the presence or absence of NaOAc. The

dihydrazides were found to coordinate in a tetradentate fashion in the enol form except adipic acid dihydrazide which coordinates in the keto form. The existence of dihydroxo bridges for the complexes isolated in the presence of NaOAc or basic medium ($-NH_2$) was also established.

When the terminal $-NH_2$ groups of dihydrazides are condensed with aldehydes, Schiff bases are obtained which possess >C=O and >C=N- groups instead of >C=O and $-NH_2$ groups in the parent dihydrazides. Further, in such Schiff bases, above type of hydrogen bonding is likely to disappear also. Aggarwal and coworkers [7] synthesized 1:1 (metal: ligand) neutral and cationic complexes from reaction of the first row transition metal ions with dihydrazones derived from condensation of acyldihydrazide and simple aldehydes and ketones. They have established that the dihydrazones behave either as a dibasic tetradentate ligand or neutral tetradentate ligand coordinating through carbonyl oxygen and azomethine nitrogen atoms.

On the other hand, if the dihydrazones are derived from condensation of acyl-, aroyl- and pyridoyl-dihydrazines with *o*-hydroxy aromatic aldehydes and ketones, they possess –OH group in addition to >C=O and >C=N group [**8, 9**]. In such dihydazones, the possibility of existence of new hydrogen bonding in solid, as shown in (II) can't be ruled out.



(II)

Such dihydrazones existing in keto-enol form offer several alternate bonding sites and can act as potentially multidentate coordinating or chelating ligands resulting in the formation of complexes having different stoichiometries under different experimental con ditions. The molecular model of the dihydrazones indicates their flexible nature in space due to which they are able to offer planar as well as the tetrahedral set of donor atoms depending upon the different stereochemical disposition of the metal valences, nature of

the R-groups and the bonds formed in the coordination process. The various donor sites in the ligands can bind either to the same metal atom or to the different metal atoms leading to a monomeric or polymeric structure of the complexes [**8**]. However, polymerization may also arise due to oxo-bridged structures [**9, 10**].

The ligands disalicylaldehyde malonoyl-, succinoyl- and adipoyldihydrazones selected in the present study have been derived from condensation of malonoyl-, succinoyl- and adipoyldihydrazines with salicylaldehyde in 1:2 molar ratio. The ligand disalicylaldehyde malonoyldihydrazone (H_4slmh) contains active methylene function flanked by keto groups in addition to other functional groups like amide, azomethine and phenol functions, each in duplicate. These ligands may exist in diketo, keto-enol and dienol forms, respectively and are among examples of few ligands which offer chemically flexible ligand framework, which permit free rotation of two hydrazone groupings about C-C bonds. The ligand disalicylaldehyde malonoyldihydrazone in addition, may undergo keto-enolization involving active methylene protons as well [**11**]. This is, in contrast, to aroyl and pyridoyl-dihydrazones in which the central phenyl and pyridyl rings between the two hydrazone groupings impose planarity on them. Evidently, the ligands can assume monobasic, dibasic, tribasic, tetrabasic or even pentabasic character in forming metal complexes either in *staggered* configuration or *syn-cis* configuration or *anti-cis* configuration [**12**].

A survey of literature has disclosed that few complexes of the first row transition metal ions, dioxouranium(VI) and dioxomolybdenum(VI) with the dihydrazones derived from condensation of salicylaldehyde and related *o*-hydroxy aromatic aldehydes and ketones with malonoyldihydrazine and other acyldihydrazines, aroyldihydrazines and pyridoyl dihydrazines have been reported [**13**]. In these studies, the metal complexes have been synthesized from reaction of metal chloride, nitrates and acetates with dihydrazones. The complexes were characterized by analytical, molar conductance and magnetic moment data. The structures of the complexes were discussed in the light of the spectroscopic studies. Further, some zinc(II) and dioxouranium(VI) complexes of dihydrazones have been synthesized by template methods and characterized. In these studies it was shown that the dihydrazone containing bulky napthyl fragments in its molecular skeleton coordinated in *staggered* and *anti-cis* configuration in zinc(II) and dioxouranium(VI)

complexes [**14**], respectively, while those containing less bulky salicylaldehyde fragments in their molecular skeleton reacted in *staggered* configuration even in dioxouranium(VI) complexes [**15**]. However, no such study have been reported on the complexes of other metals derived from salicylaldehyde dihydrazones. Moreover, the literature survey further indicated that copper(II) complexes derived from the reaction of $CuSO_4.5H_2O$ with preformed disalicylaldehyde malonoyldihydrazone in 3:1 molar ratio in aqueous medium having 2:1 (metal: ligand) ratio has been synthesized and its structure established [**4**]. But there appears to be virtually no study on reaction of copper sulphate with other dihydrazones. In addition, the work on metal complexes of dihydrazones derived by template synthesis is scanty [**16, 17**].

In view of the importance of copper in biological system, in magnetochemistry and meagre amount of work on synthesis and characterization of copper(II) complexes derived from reaction of copper(II) sulphate with dihydrazones and those synthesized by template method, it was imperative to study the reaction of copper(II) sulphate with the dihydrazones and to isolate the product and to characterize them and establish their structures. Further, in view of meagre amount of work on the copper(II) complexes synthesized by template method, it was interesting to synthesize the copper(II) complexes and characterize them and establish their structures. Hence, in the present chapter, copper(II) complexes of the title dihydrazones have been synthesized by the reaction of copper(II) sulphate with disalicylaldehyde succinoyldihydrazone and adipoyldihydrazone by template method in aqueous-alcoholic media are described. The composition of the isolated complexes has been judged mainly from the elemental analyses. The structure of the copper(II) complexes have been discussed in the light of the molar conductance, magnetic moment, mass, electronic, infrared, cyclic voltammetry and ESR spectroscopic data.

Experimental

The complexes were synthesized by the following two general methods:

Preparation of $[Cu(H_4L)]SO_4$ (H_4L = H_4slsh (311), H_4slah (312))

$CuSO_4.5H_2O$ (2.10 g, 8.42 mmol) was dissolved in methanol-water mixture (70 mL + 25 mL) by slight warming. H_4slsh (1.00 g, 2.83 mmol) suspended in methanol-water mixture

(20 mL+ 60 mL) under hot condition was added to $CuSO_4$ solution and stirred for 30 mins. The resulting solution was refluxed for 6 h. The precipitate so obtained was washed three times with each of the solvents methanol-water mixture (40 mL + 40 mL), methanol, ether and vacuum dried. Yield: 0.79 g

The complex (**312**) was also prepared essentially by the above method using adipoyldihydrazine (H_4slah) instead of succinoylhydrazine (H_4slsh). Yield: 0.81 g

Preparation of [Cu(H_2L)] (H_4L = H_4slmh (313), H_4slsh (314), H_4slah (315))

Copper acetate monohydrate, $Cu(OAc)_2.H_2O$ (1.51 g, 7.74 mmol) in MeOH (60 mL) and malonoyldihydrazide (1.0 g, 7.58 mmol) in H_2O (20 mL) were separately dissolved by warming. $Cu(OAc)_2.H_2O$ solution in hot condition was added to malonoyldihydrazide solution slowly and slowly over a period of half an hour accompanied by gentle stirring. The resulting solution was refluxed for 1 h which yielded a light green precipitate in suspension. The suspension was added drop by drop to salicylaldehyde (2.03 mL) in MeOH (30 mL), accompanied by gentle stirring over a period of 1 h. The resulting solution was refluxed for 1 h. This precipitated a dark green compound which was filtered in hot condition and washed three times with methanol and ether (40 mL each) and dried under vacuum. Yield: 0.81 g

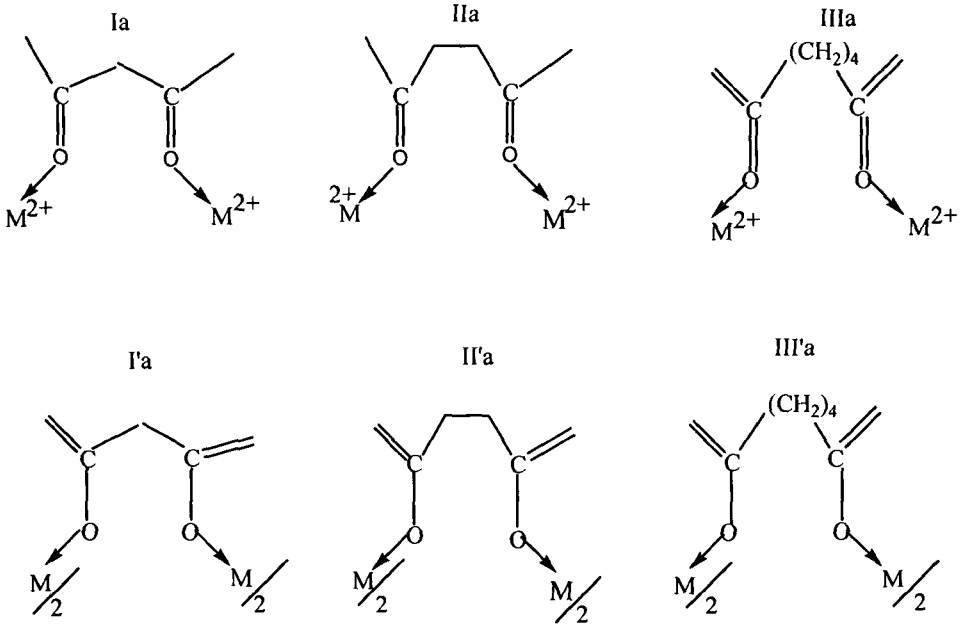
The complexes (**314**) and (**315**) were prepared essentially by the above method using succinoyl- and adipoyldihydrazide instead of malonoyldihydrazide. Yield: 0.74 to 0.81g

Results and Discussion.

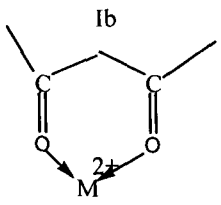
Disalicylaldehyde malonoyl-, succinoyl- and adipoyl-dihydrazones are polyfunctional ligands containing functional groups like amide, azomethine and phenol each in duplicate. They have been derived from condensation of malonoyl-, succinoyl- and adipoyldihydrazides with salicylaldehyde. Two hydrazone groupings are joined to each other through (-CH_2-), (-CH_2-CH_2-) and (-CH_2-CH_2-)$_2$ groupings in malonoyl-, succinoyl- and adipoyldihydrazones, respectively. It is not out of context to compare the reactivity of these dihydrazones and the stability of the complexes resulting from interaction of metal ions with them.

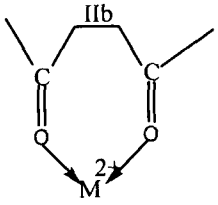
Weatherburn et al [**18**] and Bosnich et al [**19**] have reported the effect of ring size on the stability of polyamine complexes containing linked consecutive rings from their studies. They have concluded that 5-membered ring becomes sterically constrained on coordination to a metal and that the replacement of 5-membered ring by a 6-membered ring can reduce steric constraints and lead to considerable increase in the stability of the complexes. The size of this increase depends upon the configurational requirements of the metal. In general, a six-membered chelate ring is much more sterically stable than the five-membered chelate ring.

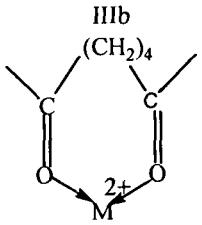
During the course of reaction of the dihydrazones with the metal ions, the aldimine parts of the dihydrazones would always form 6-membered chelate ring in each case while the central parts would give either no ring or rings of different sizes depending upon whether it would react either with the different metal ions or the same metal ion. If the carbonyl oxygens of the central part of the dihydrazone ligands coordinate either as such or in the enolized form to the different metal as shown below, this would result in the complexes which would be expected to have almost the equal stability.

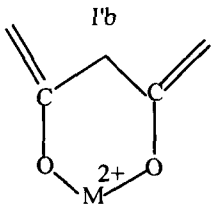


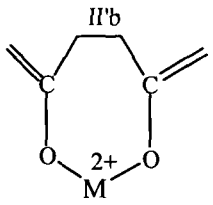
On the other hand, if the coordination occurs to the same metal ion, the different stability of the resulting complexes would be expected.

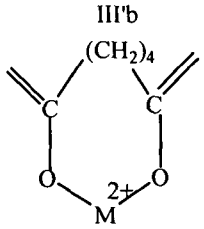










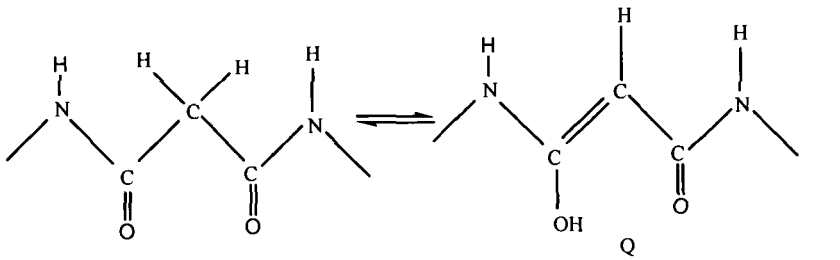


Six-membered ring Seven-membered ring Nine-membered ring

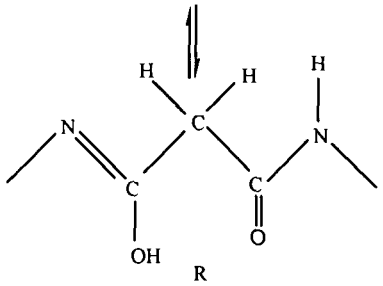
The above representations explicitly show that the malonoyl-, succinoyl- and adipoyldihydrazide based dihydrazones result in 6-, 7- and 9-membered metal chelate rings, respectively. The formation of 7- and 9-membered metal chelate ring system is sterically less favoured as compared to the 6-membered chelate ring system.

In the light of the above views and discussion, it can be reasoned that central parts of the various dihydrazones would lead to their different reactivity and would, thus, give complexes having different stability. As the central part of the malonoyldihydrazide based dihydrazones form 6-membered chelate ring having more stability than 7- and 9-membered chelate rings, such dihydrazones would react more readily with metal ions and would yield more stable complexes than the other dihydrazones. Out of the three dihydrazones, the one derived from malonoyldihydrazide has active methylene groups flanked by keto groups while normal methylene groups are present in the dihydrazones derived from succinoyldihydrazide and adipoyldihydrazide. Thus, by virture of having active methylene groups, the malonoyldihydrazone can undergo enolization involving active methylene protons in addition to those involving secondary amine protons similar to those undergone by succinoyldihydrazone and adipoyldihydrazone. The fact that malonoyldihydrazone involves active methylene group in enolization as compared to

succinoyl dihydrazone and adipoyldihydrazone is confirmed from ^{1}H NMR spectra of the dihydrazones. Thus, H_4slmh and H_4slah show four signals (two doublets) corresponding to -OH groups in the region δ 11.25-11.60 ppm while H_4slsh show only two signals in the region δ 11.27-11.64 ppm corresponding to -OH groups. The four signals in the region δ 11.25-11.60 ppm in H_4slmh do have signals resulting from enolization of active methylene and secondary -NH protons as shown below.



P Q



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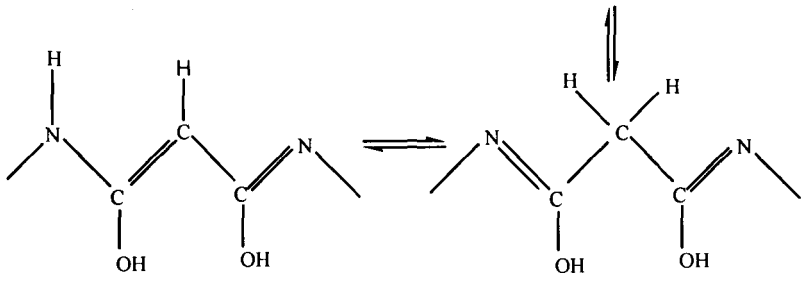
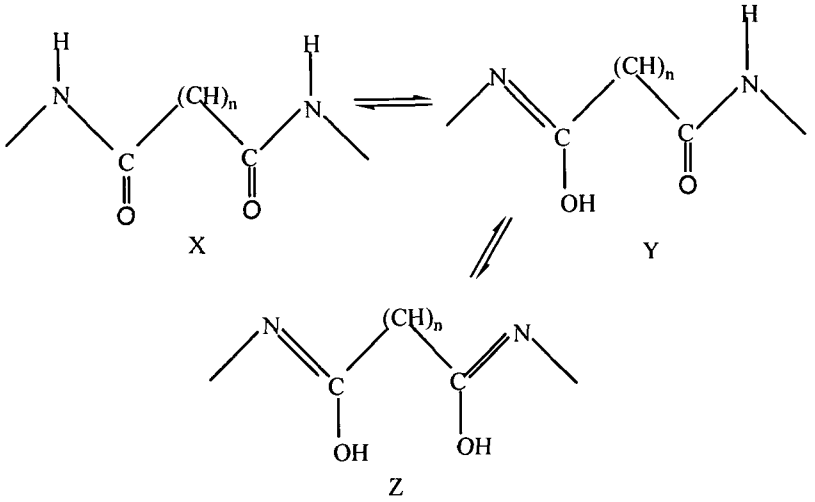


T S

On the other hand, enolization processes in H_4slsh and H_4slah involving secondary –NH proton only may be represented, as below, in which there is no involvement of methylene protons.



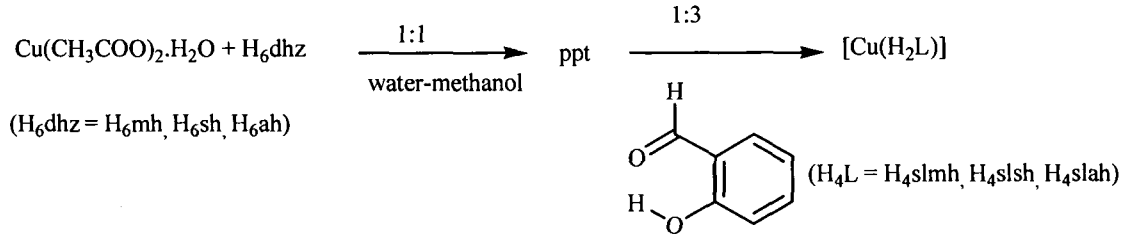
Further, because of the presence of eight bonding sites, the ligands can bind to metal ions in several different modes, as a monobasic bidentate ligands coordinating through *o*-hydroxyl oxygen and one azide group nitrogen, as a monobasic tridendate or dibasic tridentate ligands coordinating through one hydroxyl oxygen, azide group nitrogen and >C=O group while the other half of the molecule remains unbonded as a neutral bidentate ligand coordinating either through two carbonyl oxygen atoms or two secondary amine nitrogen atoms with the -OH groups remaining intact hydrogen bonded in the complexes as dibasic tetradentate ligand coordinating through the two hydroxyl oxygen and the two azide group nitrogen atoms and as dibasic hexadentate ligands bonding to the same metal ion through the two hydroxyl oxygen, two azide group nitrogen and two carbonyl oxygen in the keto form. Further, these ligands may undergo enolization affording newer bonding possibilities leading to the formation of the binuclear or polynuclear complexes. All the above possibilities can actually be realized in practice if the metal salt, concentration of metal ion and ligands, reaction medium, pH and temperature are varied.

When $CuSO_4.5H_2O$ is allowed to react with preformed dihydrazones in 3:1 molar ratio, complexes of the composition $[Cu(H_4L)]SO_4$ are obtained in case of H_4slsh and H_4slah.

$$CuSO_4.5H_2O + H_4L \xrightarrow{3:1} [Cu(H_4L)]SO_4 + 5H_2O$$

(H_4L = H_4slsh (311), H_4slah (312))

On the other hand, the treatment of the dihydrazides (H_6dhz = H_6mh, H_6sh, H_6ah) with copper(II) acetate under reflux followed by reaction with salicylaldehyde in 1:1:3 molar ratio in water-methanol mixture resulted into precipitation of the complexes [Cu(H_2L)] (H_4L = H_4slmh (**313**), H_4slsh (**314**) and H_4slah (**315**))



On the basis of elemental analyses, the complexes have been suggested to have composition:

[Cu(H_4L)]SO_4 (where H_4L = H_4slsh (**311**), H_4slah (**312**) and [Cu(H_2L)] (where H_4L = H_4slmh (**313**), H_4slsh (**314**) and H_4slah (**315**))

The complexes together with their characterization data are set out in **Table 3.1**. The copper(II) complexes are either green or dark brown, respectively. They are all air stable and decompose above 300 °C. They are insoluble in water and common organic solvents such as ethanol, methanol, acetone, CCl_4, $CHCl_3$, diethylether, benzene, dichloromethane, acetonitrile except in the highly coordinating solvents like DMSO and DMF in which they dissolve in hot condition. All of the complexes showed weight loss neither at 110 °C nor at 180 °C ruling out the possibility of presence of water molecules either in their lattice structure or in the first coordination sphere around the metal centre.

Mass Spectroscopy

The complex [Cu(H_2slsh)] (**314**) was characterized by mass spectrometry as representative example in order to make assessment of the molecularity of the complexes studied in the present chapter. This complex shows a peak at m/z values of 476.4. This m/z value is close to the mass of molecular ion $[Cu(slsh\text{-}CH_2)(DMSO)]^+$ (478.08). This suggests that the complex is monomeric. Such mass spectrometric behaviour of this

complex suggests that the complexes are monomeric in nature. The mass spectrum of the complex (**314**) is shown in Fig: **3.01**.

Molar conductance

The standard molar conductance value for 1:1 electrolyte in DMSO is reported to be 35 Ω^{-1} cm^2 mol^{-1} whereas the value as low as 23 Ω^{-1} cm^2 mol^{-1} and as high as 42 Ω^{-1} cm^2 mol^{-1} for individual compounds have also been recorded for the compound $[Ru(en)_2(H_2O)N_2][B(C_6H_5)_4]_2$, suggested to be 2:1 electrolyte, the value found is 35 Ω^{-1} cm^2 mol^{-1} which is exactly the value for standard 1:1 electrolytes but could be explained by the low ionic mobility of anionic coordination sphere [**20**]. Further, for 3:1 electrolyte in DMSO, the molar conductance value recorded in the literature is 109 Ω^{-1} cm^2 mol^{-1}. Molar conductance value for the complexes of different electrolyte types depend on the nature of the solvent. Some of the molar conductance (Λ_M) values reported at 10^{-3} M dilution for the complexes of different electrolyte types in aqueous and non-aqueous solvents are given in the following **Table 3.0.**

Table 3.0

Solvent	Electrolyte Type (Ω^{-1} cm^2 mol^{-1})			
	1:1	2:1	3:1	4:1
Water	95	225-270	380-452	above520
Nitromethane	75-95	150-180	220-260	above 520
Nitrobenzene	20-30	50-60	70-82	90-100
Acetone	100-140	160-200	270-?	360-?
Acetonitrine	120-160	220-300	340-420	500-?
DMF	65-90	130-170	200-240	300-?
Methanol	80-115	160-220	290-350	450-?
Ethanol	35-45	70-90	120-?	160-?
DMSO	35-70	_	109-?	

The molar conductance values for the complexes (**311**) to (**315**) lie in the range 2.2-2.6 Ω^{-1} cm^2 mol^{-1} are shown in **Table 3.1**. A comparison of molar conductance data

for the complexes (**311**) to (**315**) with the values in above table suggests that these complexes are non- electrolyte in DMSO [**21**].

Magnetic Moment

Copper(II) complexes show magnetic moment values in the range 1.75-1.87 BM **Table 3.1**. This value is close to the spin-only value of 1.73 BM [**22**]. This indicates the absence of any appreciable spin-spin coupling between unpaired electrons belonging to different copper atoms. According to Figgis [**23**], a magnetic moment value >1.90 BM indicates a tetrahedral stereochemistry while <1.90 BM is indicative of square planar as well as octahedral stereochemistry. This shows that the magnetic susceptibility is not of much use in deciding on the stereochemistry of Cu(II) complexes.

Electronic Spectra

The electronic absorption spectra of the ligands and their complexes along with molar extinction coefficient were recorded at room temperature using DMSO as the solvent. The important electronic spectral bands for dihydrazone ligands H_4slmh, H_4slsh and H_4slah and their monometallic complexes alongwith molar extinction coefficients have been given in **Table 3.2**. The electronic spectra for the dihydrazones H_4slmh, H_4slsh, H_4slah and some of their complexes (**311**) and (**315**) have been shown in Fig: **3.02** to **3.04**, **3.05** and **3.06**

The electronic spectra are used to assign the stereochemistry of the metal ion in the complexes based on the position and number of d-d transition bands. The absorption spectra of the ligands H_4slmh, H_4slsh and H_4slah are characterized by two bands in the regions 280-285 and ~323 nm, respectively. These bands are assigned to arise due to intraligands $\pi \rightarrow {}^{*}\pi$ and $n \rightarrow {}^{*}\pi$ transition due to >C=N and >C=O groups in the ligands [**24**]. The band at ~323 nm is considered as characteristic band for salicylaldimine fraction of the ligands as has been observed in monoacylhydrazones [**16**]. Both these bands undergo splitting into either two or three components out of which one component is blue shifted while the other components are red-shifted. The first split component corresponding to the bands in the region 280 - 285 nm shifts to shorter wavelength by 11

-16 nm in the complexes (**311**), (**313**) and (**315**) and appears in the region 269 – 273 nm. The other bands are shifted to longer wavelength by 6 – 10 and 24 – 25 nm and appear in the regions 286 – 290 and 304 – 305 nm, respectively. The band at ~323 nm is also split into two components. First component is blue shifted by 3 – 6 nm and appears in the region 318 – 320 nm while the second component shows considerably high red shift by 20 – 24 nm and appears in the region 372 – 386 nm. Such a splitting of the ligand bands in the spectra of the complexes suggests bonding of the ligands to the metal centre. The complexes show an additional strong shoulder in the region 402 – 404 nm. Further, this shoulder has very high molar extinction coefficient lie in the region 3100 – 9500 dm^3 mol^{-1} cm^{-1}. In view of its very high molar extinction coefficient it is assigned to have its charge transfer character arising from the transfer of charge from ligand to metal centre, most probably, from phenolate oxygen atoms.

All the complexes show a single broad band in the region 627-675 nm with a comparatively very low molar extinction coefficient in the range 55-160 dm^3 mol^{-1} cm^2. Hence, this band is assigned to arise due to d-d transition [**25**]. In the octahedral [**26, 27**] and tetrahedral [**28**] complexes of copper(II), the band due to d-d transition occurs at ~800 nm and ~1200 nm, respectively. In octahedral complexes, the band at ~800 nm is considerably blue shifted due to Jahn-Teller distortion and in extreme case, it falls in the range 600-700 nm reported for the square-planar complexes [**29**]. Thus, the band in the range 627-675 nm with a low molar extinction coefficient is assigned to have its origin due to d-d transition. The essential feature of this band suggests that it is the combination of three transition ($^2B \rightarrow {}^2A_{1g}$, $^2B_{1g} \rightarrow {}^2B_{2g}$ and $^2B_{1g} \rightarrow {}^2E_g$). Thus, it may be concluded that all of the copper(II) complexes have square-planar geometry.

Electron Spin Resonance Spectroscopy

All of the monometallic complexes have been studied by ESR spectroscopy at LNT in glassy state. The ESR parameters for the complexes have been set out in **Table 3.3** . Some of the ESR spectra of the complexes (**311**), (**314**) and (**315**) are shown as the representative examples in Fig: **3.07**, **3.08** and **3.09.** All of the complexes show anistropic spectra and have almost similar ESR spectral features. The $g_{\|}$ value for the complexes lies in the region 2.273–2.472 while $g_{\perp}$ value lies in the region 2.093-2.242. The $g_{\|}$ and $g_{\perp}$ values depart considerably from the free ion value. The shifting of g values from

2.0023 in transition metal complexes is due to mixing, via spin-orbit coupling of the metal orbitals containing the unpaired electron(s), with the empty or filled ligand orbials. When the mixing is with empty ligand orbitals, the result is negative g shift, whereas the mixing with the filled ligand orbitals leads to a positive g value shift. The shift depends on the amount of unpaired electron density at the donor sites of the ligands i.e., on the degree of covalency of the complex. The ESR spectra of the complexes (**311**) and (**312**) show splitting in the g|| region while complex (**315**) shows splitting in the g⊥ region due to copper-hyperfine coupling. In g|| as well as g⊥ region only two split weak signals are observed. The nuclear quantum number of copper is 3/2, hence it should show four signals. However, all the signals are not observed in the complexes. Kivelson and Neiman [**30**] have reported that g|| value in copper complexes can be used as a measure of the nature of the metal-ligand bond. If this value is more than 2.3, the environment is essentially ionic and values less than this limit are indicative of a covalent character. The fact that g|| values in the present complexes (**313**), (**314**) and (**315**) are more than 2.3 indicates that the metal-ligands bonds have considerable ionic nature. On the other hand, g|| values for the complexes (**311**) and (**312**) are less than 2.3. This indicates that the metal-ligand bonds in these complexes have covalent character. Also the shape of the ESR lines indicate that the geometry around the copper(II) ion is not trigonal bipyramidal in these complexes since the low field side of the ESR spectrum is less intense than the high field side and the order of g⊥ values are not in accordance with the range suggested for trigonal bipyramidal complexes [**31**] (2.00 > g|| > g⊥). The magnetic parameters indicate g|| > g⊥ > free spin (2.0023) which shows that the unpaired electron is in the d_{x2-y2} orbital of the Cu (II) centre. The in-plane α covalency parameter, α^2_{Cu} was calculated for the Cu(II) complexes using the following equations [**32-34**] and the values obtained are listed in the **Table 3.3**

$$\alpha_{Cu}^2 = -(A_{||}/P) + g_{||} - 2.0023) + 3/7\,(g_{\perp} - 2.0023) + 0.04$$

where $P = 0.036\ cm^{-1}$

The α^2_{Cu} value accounts for the fraction of unpaired electron density on the copper ion. Smaller the value of α^2_{Cu}, more covalent is the bonding nature. For example $\alpha^2_{Cu} = 0.5$ indicates complete covalent bonding, but $\alpha^2_{Cu} = 1.0$ suggests complete ionic bonding.

The α^2_{Cu} values for the mononuclear Cu(II) complexes are in the range of 0.794– 0.882 < 1 indicating that the Cu(II) complexes have considerable amount of covalent character.

Suresh Babu et al reported [**35**] that $g_{||} > 2.4$ for copper-oxygen bonds and 2.3 for copper–nitrogen bonds. The Cu(II) complexes (**311-315**) have $g_{||}$ values between 2.2 – 2.4 and are in agreement with the presence of mixed copper-oxygen and copper-nitrogen bonds.

The nature of the ligand forming the complex is evaluated from G values obtained by using the following equation:

$G = (g_{||}-2)/ (g_{\perp}-2)$

If G < 4.0, the ligand forming the complex is regarded as a strong field ligand. For the square planar complexes G is usually in the range [**34**] of 2.03-2.45. G value for the complexes (**311**)-(**315**) lies in the range 1.950 - 3.443 at LNT which suggests that the dihydrazone ligands sufficiently strong field in complexes.

Infrared spectroscopy

Some structurally significant IR bands for the Schiff base ligands H_4slmh, H_4slsh and H_4slah and their complexes (**311**) to (**315**) have been summarized in the **Table 3.4**. The IR spectra of the ligands H_4slmh, H_4slsh and H_4slah alongwith some of the complexes (**312**) to (**314**) have been given in Fig: **3.10** to **3.12** and **3.13** to **3.15,** respectively.

When a ligand is coordinated to a metal ion, the metal atom is introduced into the ligands vibrating system and the IR spectra of the coordinated ligands will, thus, be different from that of the free ligands. The spectra of the complexes may differ from that of the ligands in band positions, band intensities and the appearance of new weak bands and splitting of some of the bands of the free ligands. But it is not always possible to assign unequivocally all the observed bands in the spectra of the complexes. Practically, we therefore, compare the spectra of the complexes with that of the free ligands and the changes are interpreted in the light of the structure of the complexes.

IR spectra of the complexes $[Cu(H_4slsh)]SO_4$ (311) and $[Cu(H_4slah)]SO_4$ (312) in which the ligands (H_4slsh and H_4slah) exist in the keto form.

The IR spectra of the Schiff base ligands H_4slmh, H_4slsh and H_4slah are very much complicated due to overlapping of the bands arising from several groups occurring in the same region. However, some typical bands have been selected for the location of bonding sites of the ligands. The solution spectra of the ligands could not be investigated due to their insolubility in most of the common organic solvents. Hence, it has not been possible to eliminate the effect of intramolecular hydrogen bonding by comparing the solid state spectra of the complexes with the solution spectra of the parent ligands.

The uncoordinated ligands show medium intensity band in the region 3065-3277 cm^{-1} and medium to strong band in the region 3436-3449 cm^{-1}. The band in the region 3436-3449 cm^{-1} is assigned to νOH of salicylaldehydato part of the dihydrazones, while lower frequency band is assigned to arise from secondary >NH. All of the dihydrazones show a very strong intensity band in the region 1666-1679 cm^{-1} which is assigned to νC=O stretching vibration [**36**].

The essential features of IR spectra of the complexes consist of bands at 3502, 3383 and 3423, 3230 cm^{-1} in the region 3000-3600 cm^{-1} which are similar to those of the uncoordinated ligands but they are slightly broadened. The band at 3502 and 3423 cm^{-1} is assigned to νOH vibration of uncoordinated phenolic-OH groups while the band at 3383 and 3230 cm^{-1} is assigned to arise due to νNH vibration. These bands are shifted to higher frequency by 179 and 26 cm^{-1} as compared to their position in the uncoordinated dihydrazones. Such features of νOH and νNH bands in the ligands rule out the possibility of the involvement of phenolic –OH and secondary –NH groups in bonding with the metal centre. Further, the presence of νNH band in the spectra indicate that the ligands coordinate to the metal centre in keto form. Another prominent feature of IR spectra of the complexes is the appearance of a cluster of medium intensity band in the region 2400-2800 cm^{-1} in the complexes. This band is characteristic of occurrence of stronger intramolecular H-bonding in the complexes involving –OH groups [**37**].

The ligand bands appearing at 1666 and 1672 cm^{-1} due to >C=O vibration show large negative shift by 87 and 56 cm^{-1} in the complexes (**311**) and (**312**), respectively. In the

complex (**312**), the υC=O band appears at 1616 cm^{-1} as a very strong band. On the other hand, in the complex (**311**), νC=O band merges with νC=N band and appears at 1579 cm^{-1}. This shows coordination of both the >C=O group to the metal centre [**38**]. The ligands show strong bands at 1626 and 1619 cm^{-1} which arise due to stretching vibration of >C=N groups. These bands are shifted to lower frequency by 47 and 33 cm^{-1}, respectively. The lower shift of νC=N band by such a large frequency indicates strong coordination of the ligands to the metal centre through >C=N groups [**39**]. The amide II band appearing at ~1566 cm^{-1} is shifted to lower frequency by 36 cm^{-1} and appears as a strong shoulder band at 1530 cm^{-1} in the complex (**311**) but it does not show its independent appearance in the complex (**312**). The negative shift of amide II band in the complexes suggests coordination of >C=O group to the metal. The most crucial feature of IR spectra of the complexes is the absence of a new strong band in the region 1500-1530 cm^{-1}, which arises usually due to νNCO^{-} resulted from enolization of hydrazide ligands. This ruled out the possibility of enolization of ligands in the complexes and suggested the co-ordination of dihydrazones to the metal centre in the keto form.

The νN-N band is observed at 1049 and 1036 cm^{-1} in the free ligands H_4slsh and H_4slah, respectively. These bands shift to higher frequency by 5- 8 cm^{-1} and appear at 1054 cm^{-1} and 1044 cm^{-1}, respectively, as shoulder. This indicates the involvement of only one of the nitrogen atoms of the >C=N-N=C< group in coordination to the Cu(II) centre in the complexes. The complexes (**311**) and (**312**) show a new very strong band at 1161 and 1128 cm^{-1}, respectively. These bands appear at almost the same frequency region in which ionic sulphates have been reported to absorb [**40**]. Further, these bands don't show any splitting in the complexes which rules out the possibility of coordination of sulphato group to the metal centre. These complexes also show a single medium intensity band at 611 and 624 cm^{-1}, respectively. The position and essential features of these bands suggest that sulphato group is present in ionic form in the complexes.

Low frequency region 600-450 cm^{-1}

Low frequency IR spectra of the metal complexes provide very useful information regarding the type of metal-ligand bond arising from coordination of ligands to the metal centre. However, the IR spectra of the ligands containing aromatic rings which show bands due to out-of-plane ring [**41**] deformation and out-of-plane

deformation C-H bonding [**42**] in the low frequency region, complicate the spectral features. The ligands H_4slsh and H_4slah absorb at 614m, 552m, 516w, 470w, 552w, 486w, 430w and 605w, 565w, 486w respectively. These bands occur at almost the same frequencies in the IR spectra of the metal complexes or slightly shifted as compared to those in the corresponding free dihydrazones. However, few new bands arise which may be assigned to metal-ligand vibrations.

The present ligands are the combination of malonoyl-, succinoyl- and adipoyl-hydrazide and salicyladimine parts. From a stereochemical consideration of the ligands, it might be expected that a maximum of four kinds of metal-ligand vibrations may arise viz, ν(M-O)(phenolate), ν(M-O)(M-O-C< or M←O=C<) and ν(M-N) in the complexes. The ν(M-O)(phenolate) is expected at higher frequency because of differences in the bond order. Further, the low frequency IR spectra is expected to show bands due to coordination of dihydrazones, water molecules and pyridine bases. A review of literature related with metal-phenolate [**43**] metal-enolates (M←O=C< and M-O-C<) [**44**] and metal hydrazine ν(M-N) [**45**] indicates that the various metal-ligand stretching frequencies occur in the overlapping regions. In metal acetylacetonates [**46**] and oxalates [**47**], ν(M-O) is observed in the 470-420 cm^{-1} and 446-419 cm^{-1} regions, respectively, while in metal salicyaldimines, the ν(M-O) is observed in the 600-490 cm^{-1} region [**48**]. The ν(M-N) in salicylaldimine complexes has been reported to occur in the 440-360 cm^{-1} range. Keeping all the assignments in view, the ν(M-L) bands have been assigned in the metal complexes in the present study. The complexes don't show any new band in the region 500-600 cm^{-1} which could be assigned to ν(M-O)(phenolate). This ruled out the possibility of coordination of phenolate oxygen to the metal centres. The complexes show a new weak band at 451 and 474 cm^{-1} which could be assigned to ν(M-O) carbonyl indicating the coordination of carbonyl oxygen form in the metal complexes.

IR spectra of the complexes (313)–(315) in which the ligands (H_4slmh, H_4slsh and H_4slah) exist in the enolized form:

Coordination of H_4slmh, H_4slsh and H_4slah through >C=O and >C=N results in lowering of the group stretching frequencies. In the event of enolization, the >C=O and >NH groups are destroyed resulting in –C(OH):N- groups in which νOH, νC-O and

νC=N should appear. Reaction with metal ions in the enol form results in –N=C-O and >C=N-N=C< group vibrations. The coordination of dihydrazone from imine group has little effect on >C=O and >NH group vibrations.

The medium νNH band appearing in the 3204-3277 cm^{-1} region in the free ligands disappears in the IR spectra of the complexes (**313**), (**314**) and (**315**). Further, a medium to strong broad band appears in the region 3000-3600 cm^{-1} in these complexes. However, the intensity of the band in this region is considerably decreased as compared to that in the other complexes. The destruction of >NH band in this region suggests destruction of amide structure of the ligands in complexes and its binding to the metal centre through enolic C-O group. This is also corroborated by the fact that the amide I bands originally present in the region 1666-1679 cm^{-1} in the ligands have disappeared in the complexes. The medium intensity band due to amide II + ν(C-O) observed at 1566 cm^{-1} in the free ligands shifts to lower frequency in the complexes (**313**) and (**314**) and appears at 1538 and 1533 cm^{-1}, respectively. The negative shift of this band rules out the possibility of bonding between phenolic C-O group and metal centre because it has been established that whenever phenolic C-O group is bonded to the metal centre, the νC-O shows either no shift or shifts to higher frequency [**49**]. Further, in these complexes a very strong new band is observed in the region 1509-1520 cm^{-1} not observed in the IR spectra of the complexes (**311**) and (**312**). Hence, this band has been assigned to νNCO stretching vibration as a result of enolisation [**50**].

A strong band in the 1615-1613 cm^{-1} region appears, this band is attributed to arise due to >C=N-N=C< group. The very strong character of this band is attributed to arise due to reinforcement of the >C=N of the ligands by another >C=N band produced as a result of enolisation. This band shifts to lower frequency by 4 - 13 cm^{-1} as compared to those in the uncoordinated ligand indicating involvement of >C=N-N=N< group in coordination [**49**]

Similar to the complexes (**311**) and (**312**), these complexes also show a new medium intensity band in the region 2400–2800 cm^{-1}. This band is attributed to arise due to strong intramolecular hydrogen bonding in the complexes involving phenolic-OH groups.

Based on the literature and discussions given previously, it can be said that the ligands are bonded to the metal centre through enolic >C-O and >C=N group. The non ligand band occurring in the region 454-483 cm^{-1} is assigned to νM-O (enolised carbonyl)

Cyclic Voltammetry

The cyclic voltammogram of a 2 mm solution of the complexes (**311**) to (**315**) has been examined at a scan rate of 100 mV/s by cyclic voltammetry in DMSO solution due to their insolubility in common organic solvents with 0.1 M tetra n-butylammonium perchlorate (TBAP) as a supporting electrolyte. The data have been set out in **Table 3.5**. The potentials of the ligands and complexes were scanned in the potential range 2.4 to -2.4 V. The ligands were non-electroactive in this potential range. The complexes showed no redox activity either in the potential range +1.60 to +2.00 or -1.60 to -2.00 V. This is true regardless of the scanning direction i.e whether starting point is .00 or 2.00 V. It should be mentioned that the supporting electrolyte TBAP in DMSO did not show any redox activity in the potential range studied.

The cyclic voltammogram of the ligands along with complexes (**311**), (**313**) and (**315**) are shown in Fig: (**3.16 – 3.21**)

The copper(II) complexes exhibit well defined one electron transfer reduction waves in the range of +0.30 to -1.70 V. In the case of $[Cu(H_4slsh)]SO_4$ (**311**), the first irreversible one electron transfer peak at +0.21 and the second peak at -1.45 V are observed. The corresponding peaks in the complxes (**312**) are observed at -0.16 and -1.13 V, respectively. Corresponding to these reductive waves there is no oxidative waves in the anodic scan. This is attributed to some unstable species formed in solution which reverts back to original species. The cathodic reduction potential increases from -0.21 to -0.16 V and -1.45 to -1.13 V when a methylene group is introduced in the aliphatic chain. This behavior is typical of irreversible charge transfer processes and such behavior has been observed in other Schiff base complexes [**51**].

The neutral copper(II) complexes (**313**) - (**315**) show a reversible one electron redox process at +0.37, -0.24 and -0.60 V, respectively. The complexes (**313**) - (**315**) show an additional irreversible reduction peak at -0.83, -1.51 and -1.63 V while the complex (**314**)

and (**315**) shows an irreversible oxidation wave at +1.55, +0.55 and +0.30 V, respectively.

The reductive wave at +0.34, -0.27 and -0.56 V and corresponding oxidative waves at +0.40 , -0.21 and -0.50 V in the complexes (**313**) – (**315**) are attributed to arise due to Cu^{II}/Cu^{I} redox couple, respectively. The reductive waves at -0.83, -1.51 and -1.63 V in the complexes (**313**) - (**315**) and the oxidative waves at + 1.55, +0.50 and +0.25 V do not have their corresponding oxidative and reductive waves respectively, hence they are attributed to the formation of some unstable species which revert back to their original species.

Conclusion

Copper(II) complexes described in the present chapter have been synthesized by two different methods. On the basis of various physico-chemical and spectral studies, it has been concluded that the ligands succinoyl-(H_4slsh) and adipoyldihydrazones(H_4slah) coordinate as a neutral tetradentate ligand through azomethine nitrogen and carbonyl oxygen in the complexes (**311**) and (**312**) while as a dibasic tetradentate ligand through azomethine nitrogen and enolate oxygen atom in the complexes (**313**) to (**315**). The sulphato group remains uncoordinated in the complexes (**311**) and (**312**). All of the copper complexes are normal paramagnetic and donot possess any M-M interaction. The $d_{x^2-y^2}$ orbital constitutes the ground state in all of the complexes. All of the complexes have square-planar stereochemistry.

The electron transfer reaction of the complexes have been investigated with the help of cyclic voltammetry.

On the basis of the results and discussion given above, the structure of the complexes (**311**) and (**312**) have been proposed as shown in **Fig 3.00** and those of the complexes (**313**) to (**315**) have been proposed as shown in **Fig 3.00a** respectively.

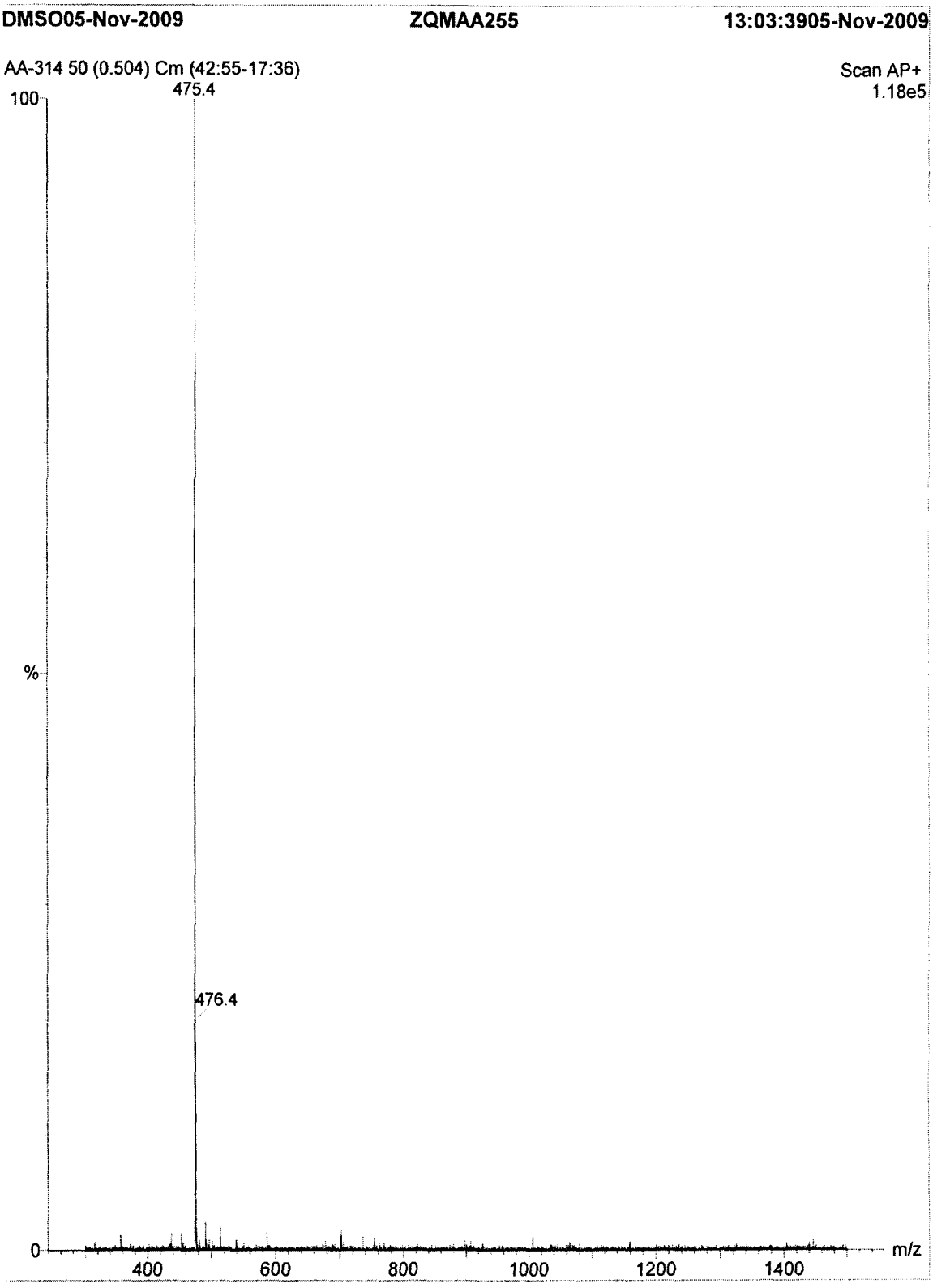
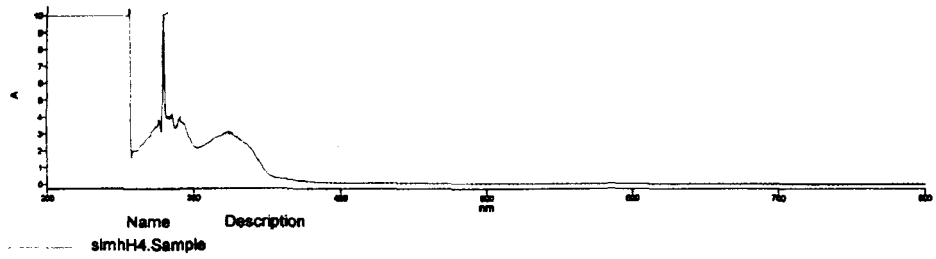


Fig: 3.01 Mass spectrum of [Cu(H_2slsh)] (**314**) in DMSO



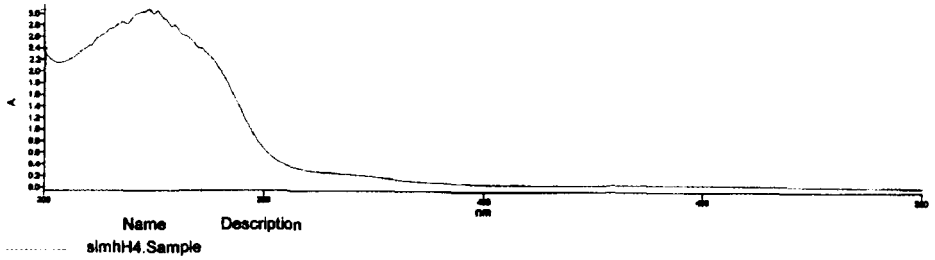


Fig: 3.02 Electronic Spectrum of Disalicylaldehydemalonoyldihydrazone (H_4slmh) in DMSO

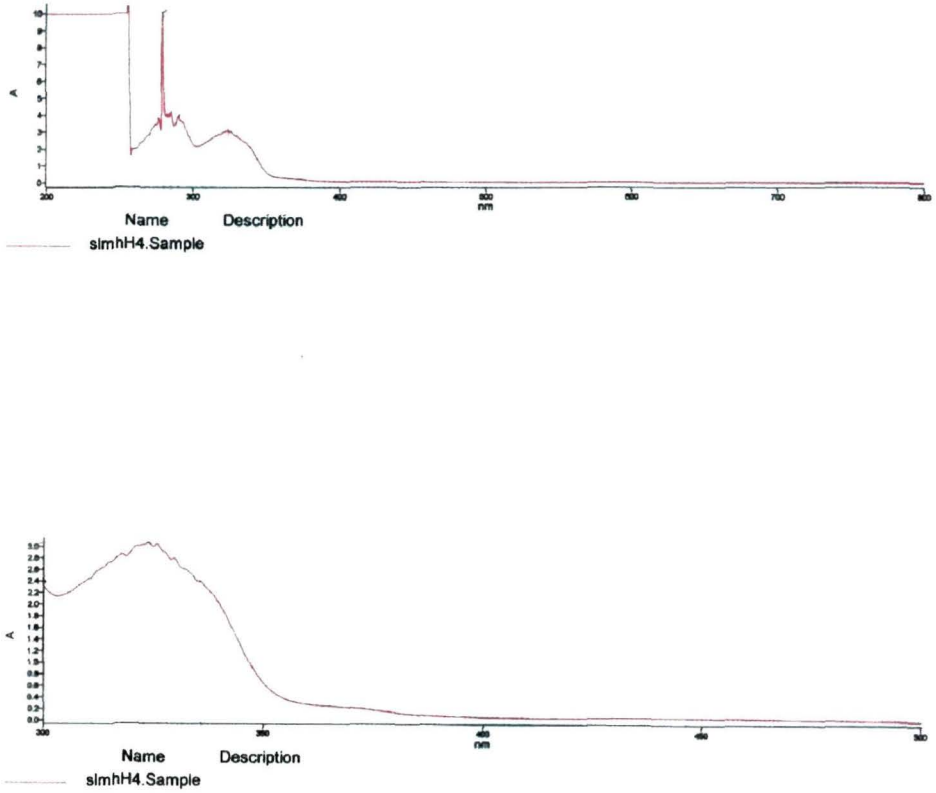


Fig: 3.02 Electronic Spectrum of Disalicylaldehydemalonoyldihydrazone (H_4slmh) in DMSO

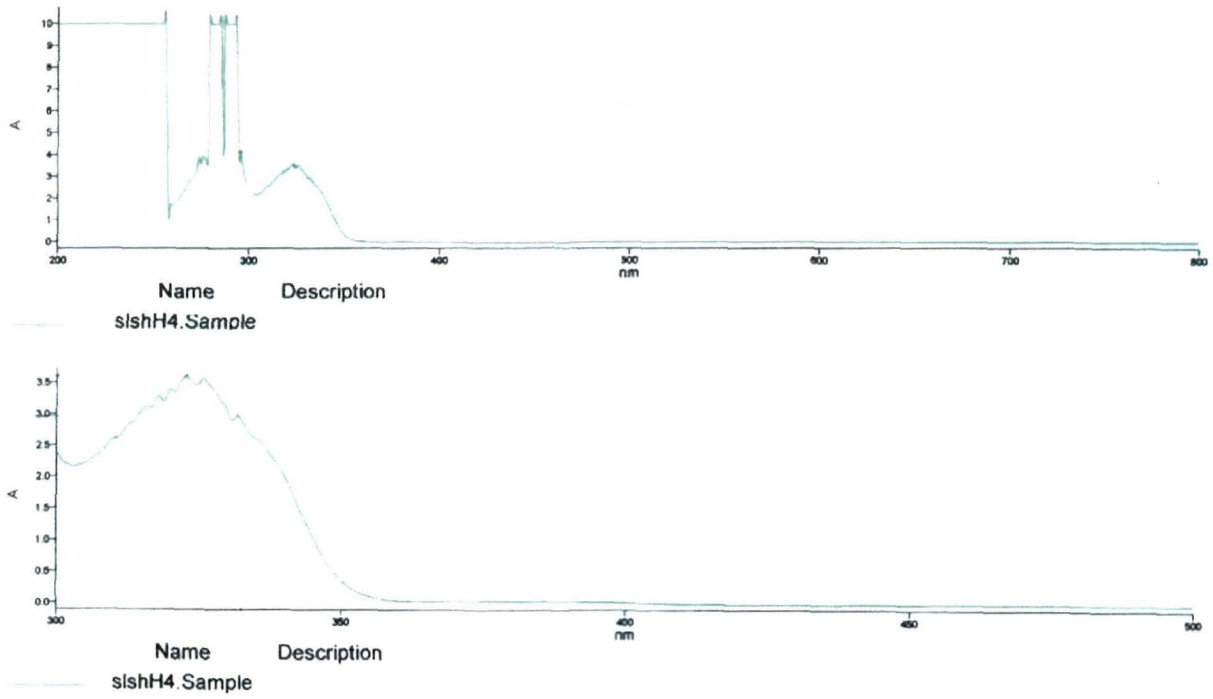


Fig: 3.03 Electronic Spectrum of Disalicylaldehydesuccinoyldihydrazone (H_4slsh) in DMSO

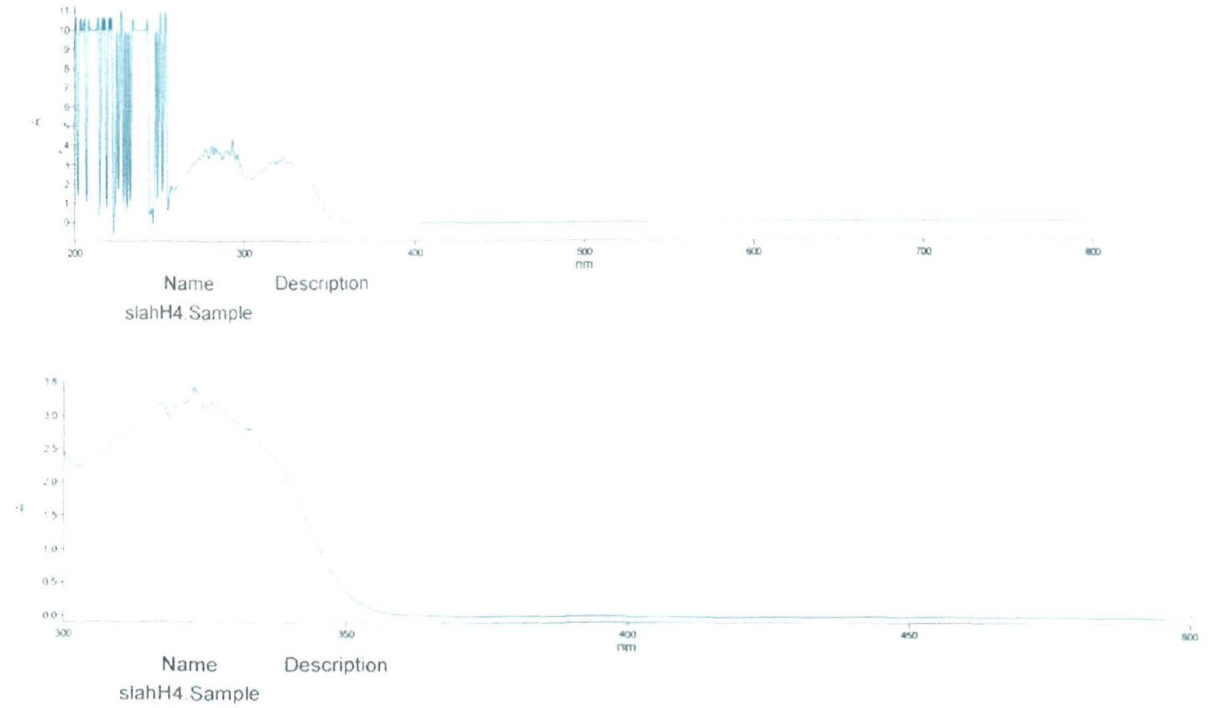


Fig: 3.04 Electronic Spectrum of Disalicylaldehydeadipoyldihydrazone (H_4slah) in DMSO

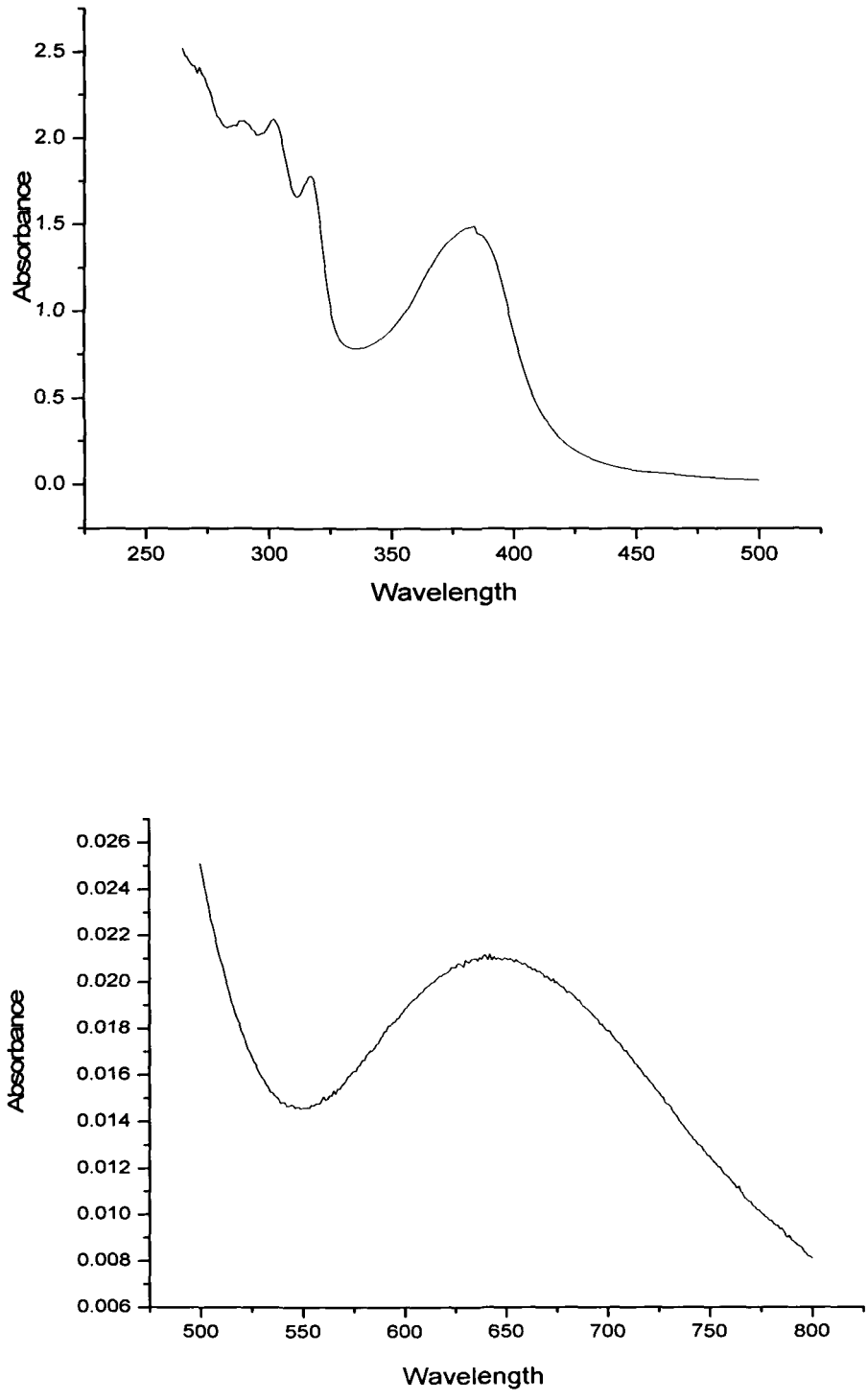


Fig: 3.05 Electronic Spectrum of $[Cu(H_4slsh)]SO_4$ **(311)** in DSMO

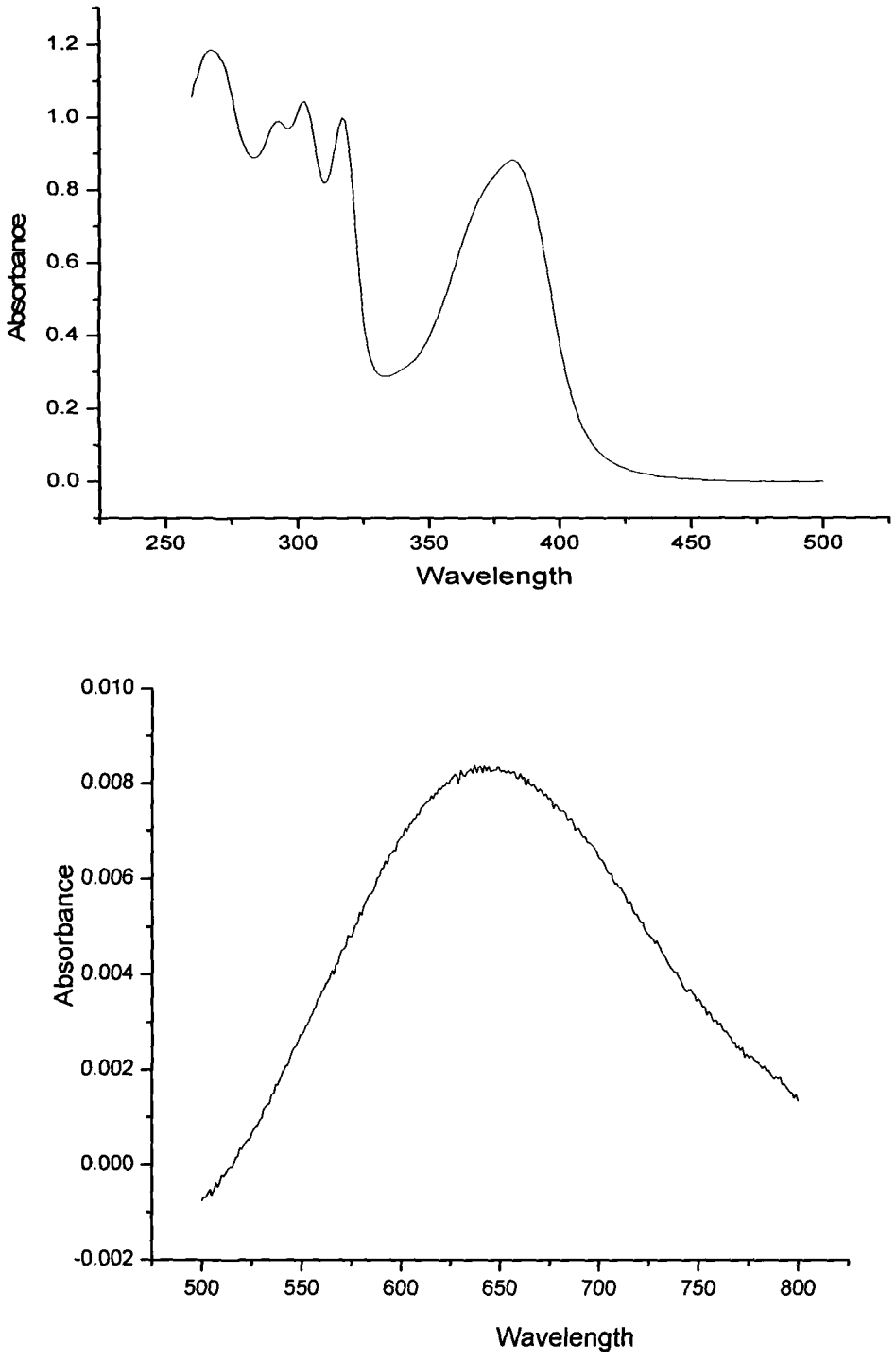


Fig: 3.06 Electronic Spectrum of [Cu(H_2slah)] (**315**) in DMSO

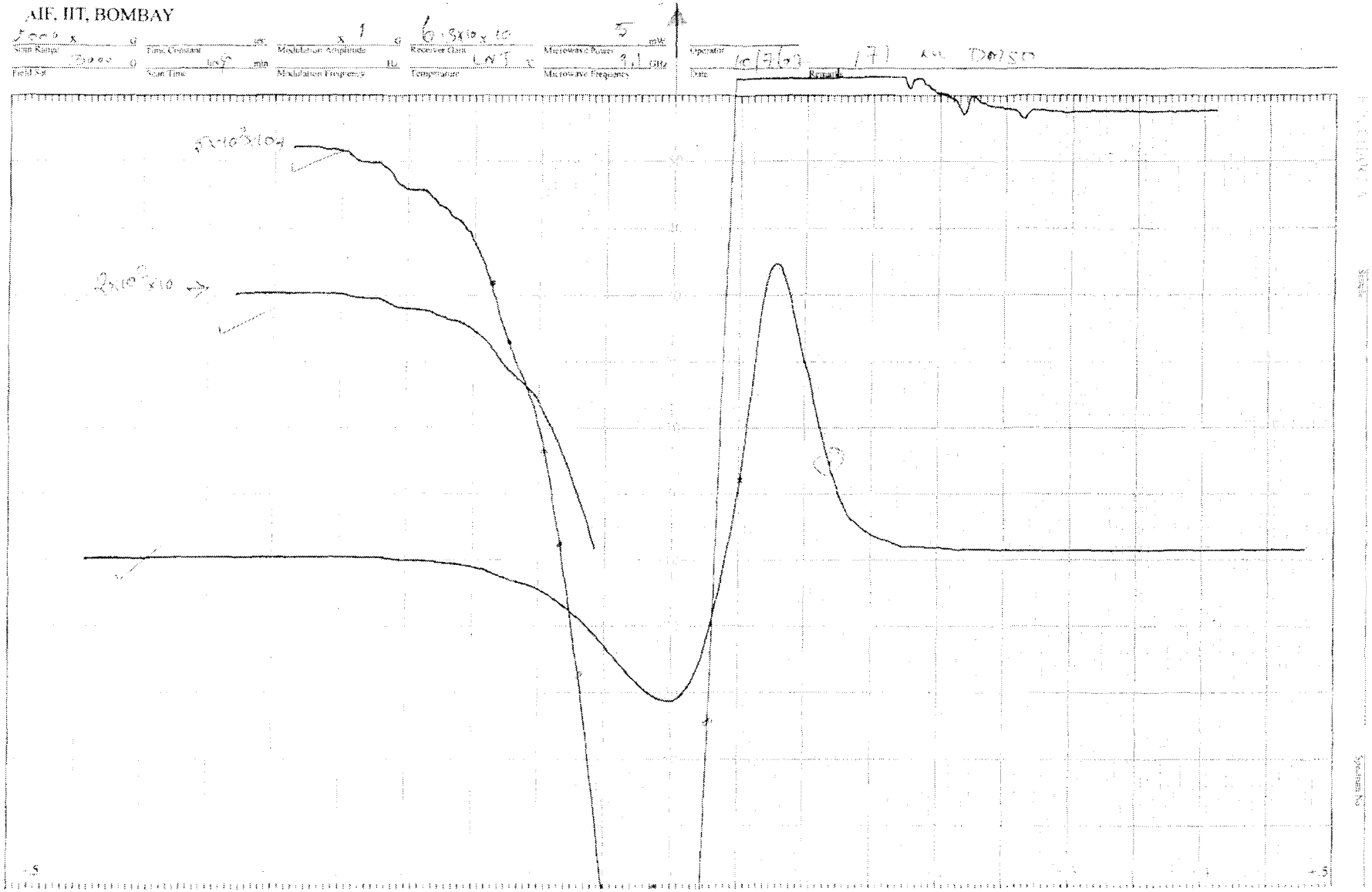


Fig: 3.07 ESR Spectrum of $[Cu(H_4slsh)]SO_4$ (**311**) in DMSO at LNT, Frequency 9.1GHz, Scan Range 2000 G and Field Set 3000 G

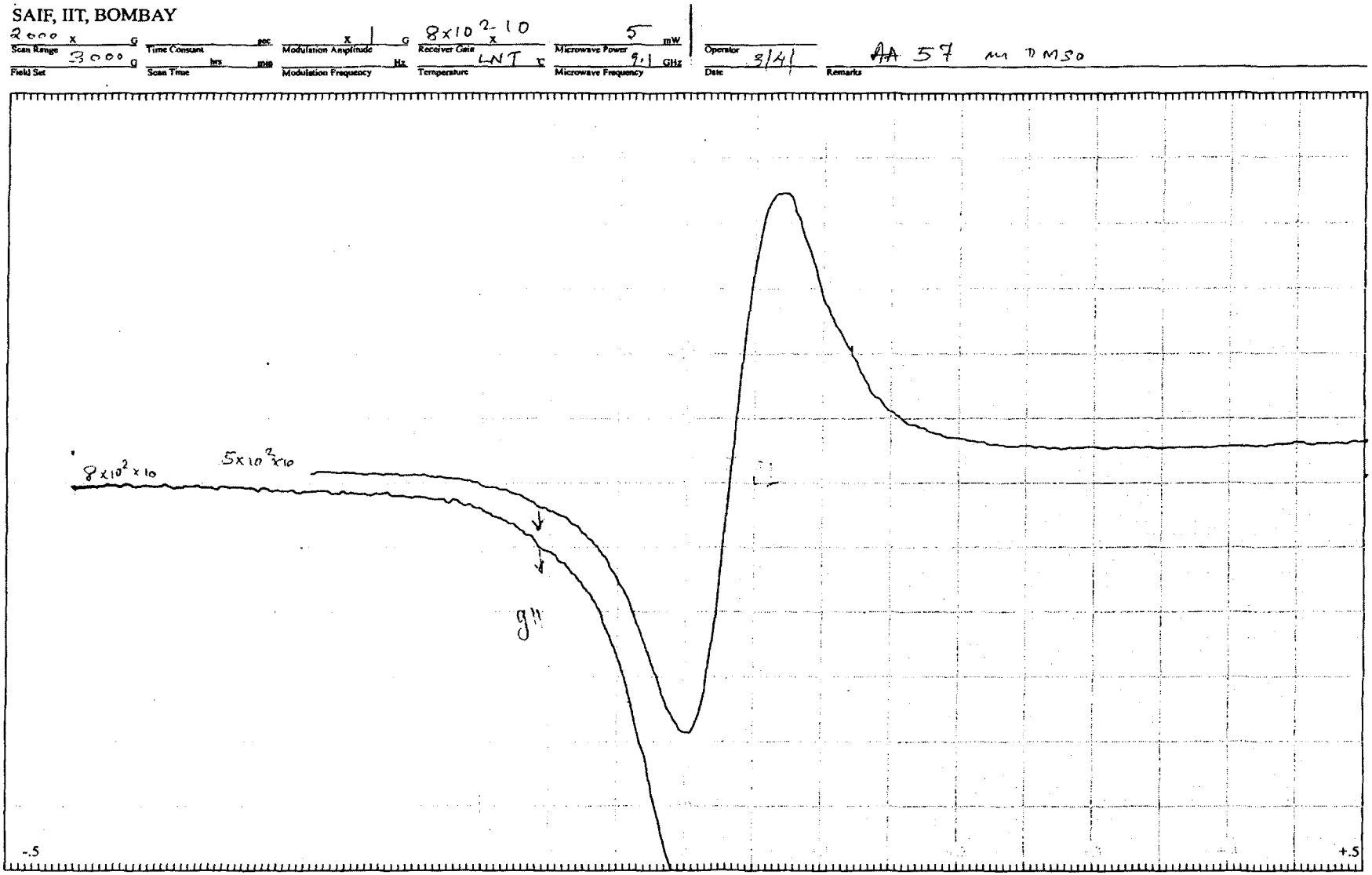


Fig: 3.08 ESR Spectrum of [Cu(H_2slmh)] (**313**) in DMSO at LNT, Frequency 9.1GHz, Scan Range 2000 G and Field Set 3000 G

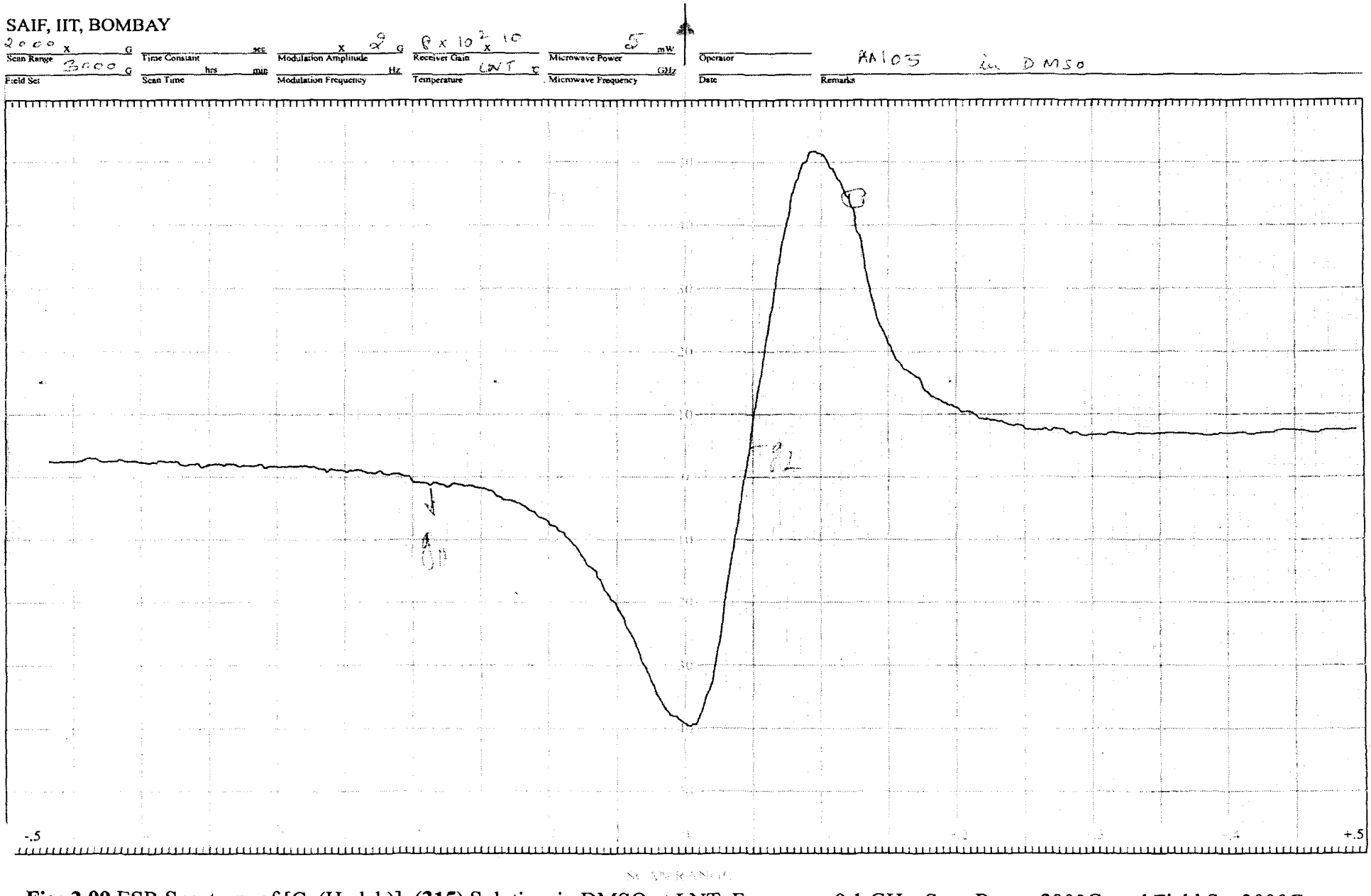


Fig: 3.09 ESR Spectrum of [Cu(H_2slah)] **(315)** Solution in DMSO at LNT, Frequency 9.1 GHz, Scan Range 2000G and Field Set 3000G

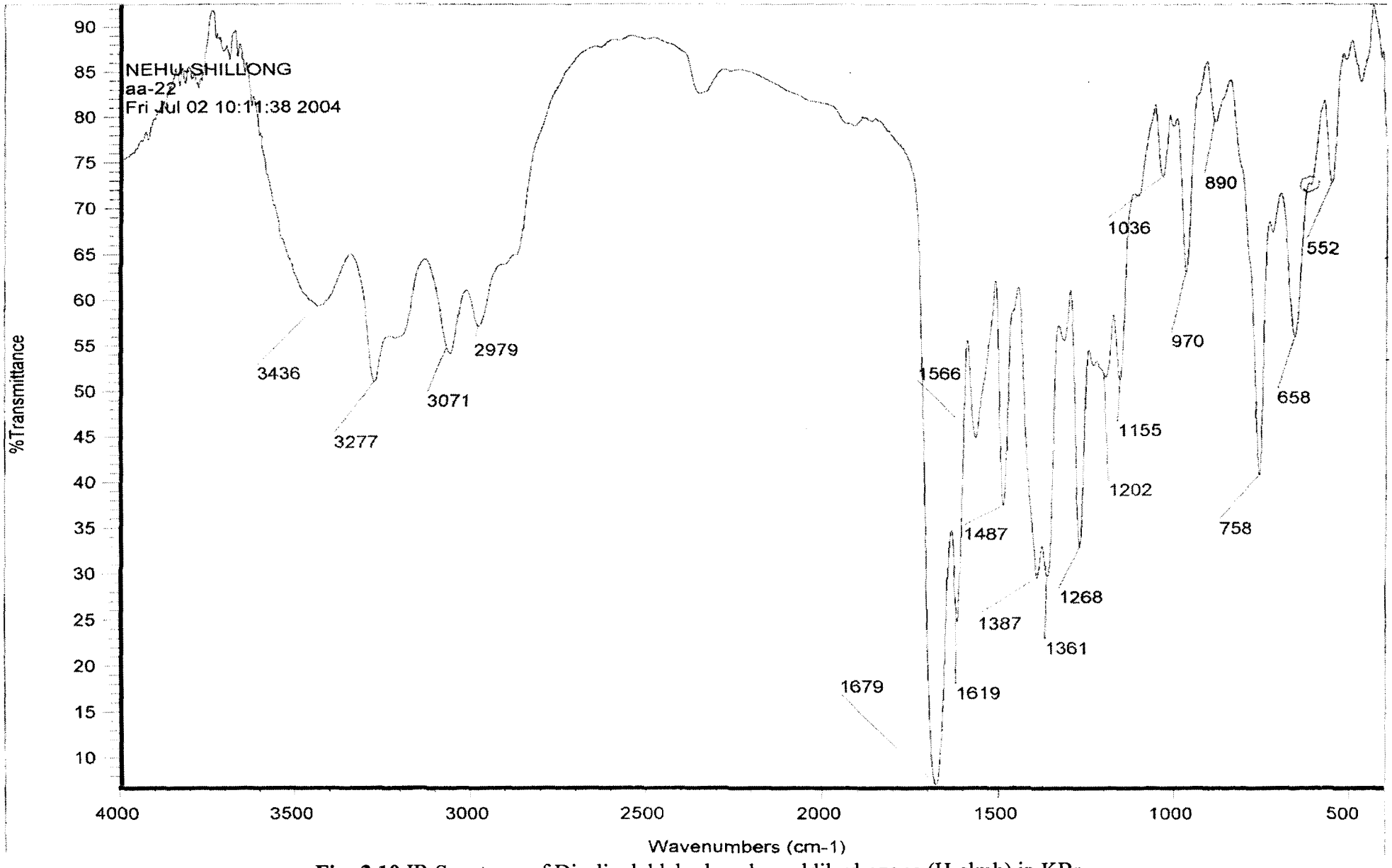


Fig: 3.10 IR Spectrum of Disalicylaldehydemalonoyldihydrazone (H_4slmh) in KBr

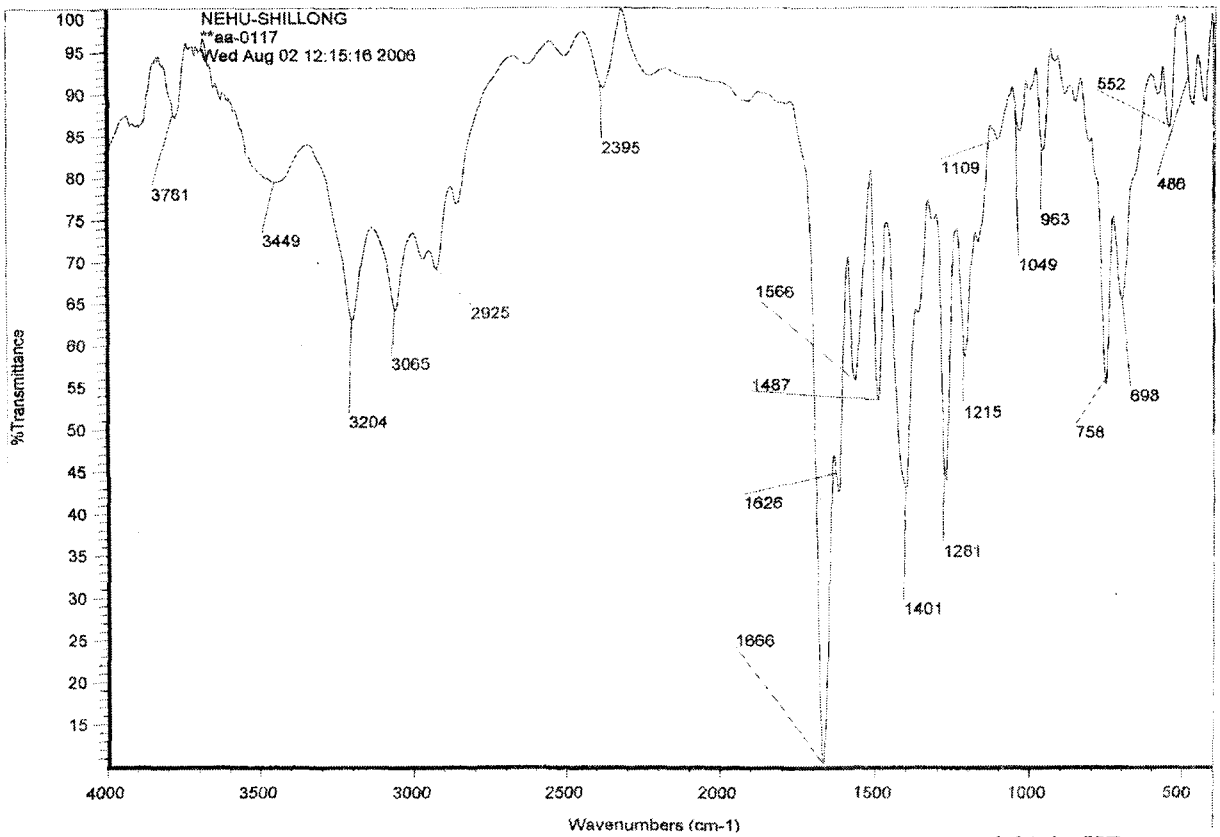


Fig: **3.11** IR Spectrum of Disalicylaldehydesuccinoyldihydrazone (H_4slsh) in KBr

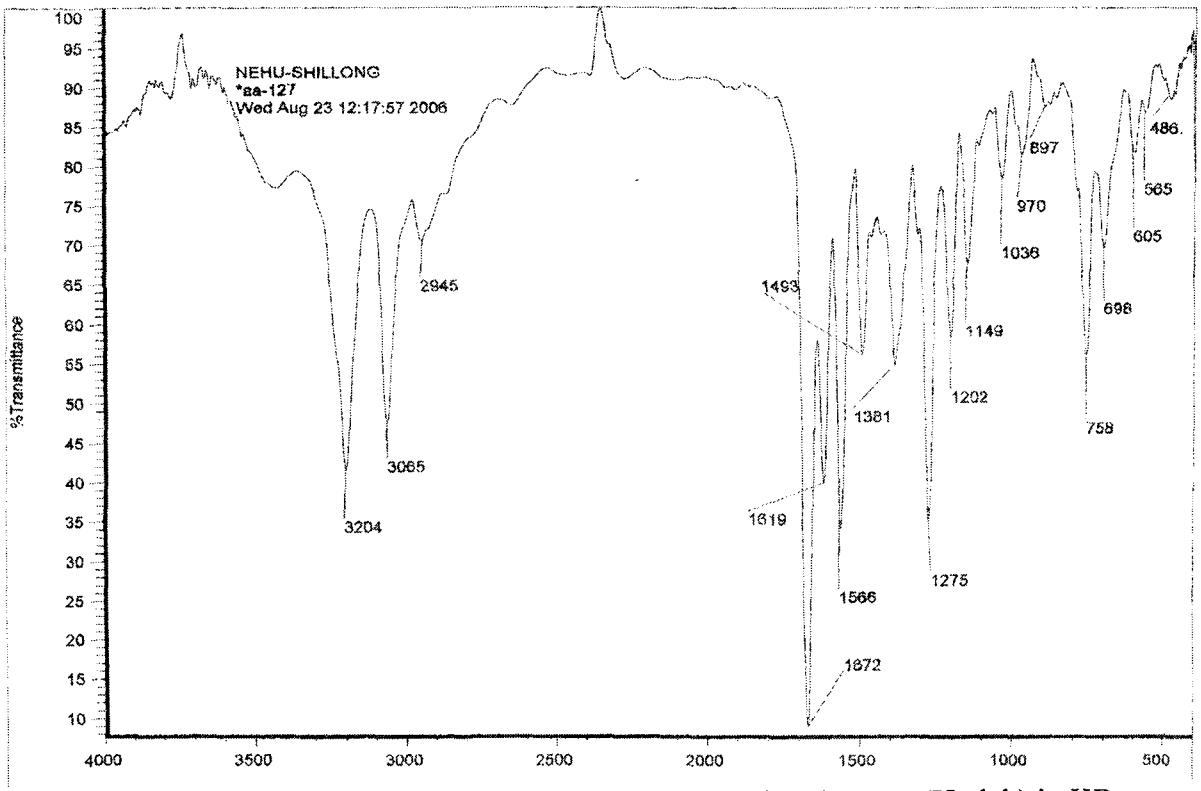


Fig: **3.12** IR Spectrum of Disalicylaldehydeadipoyldihydrazone (H_4slah) in KBr

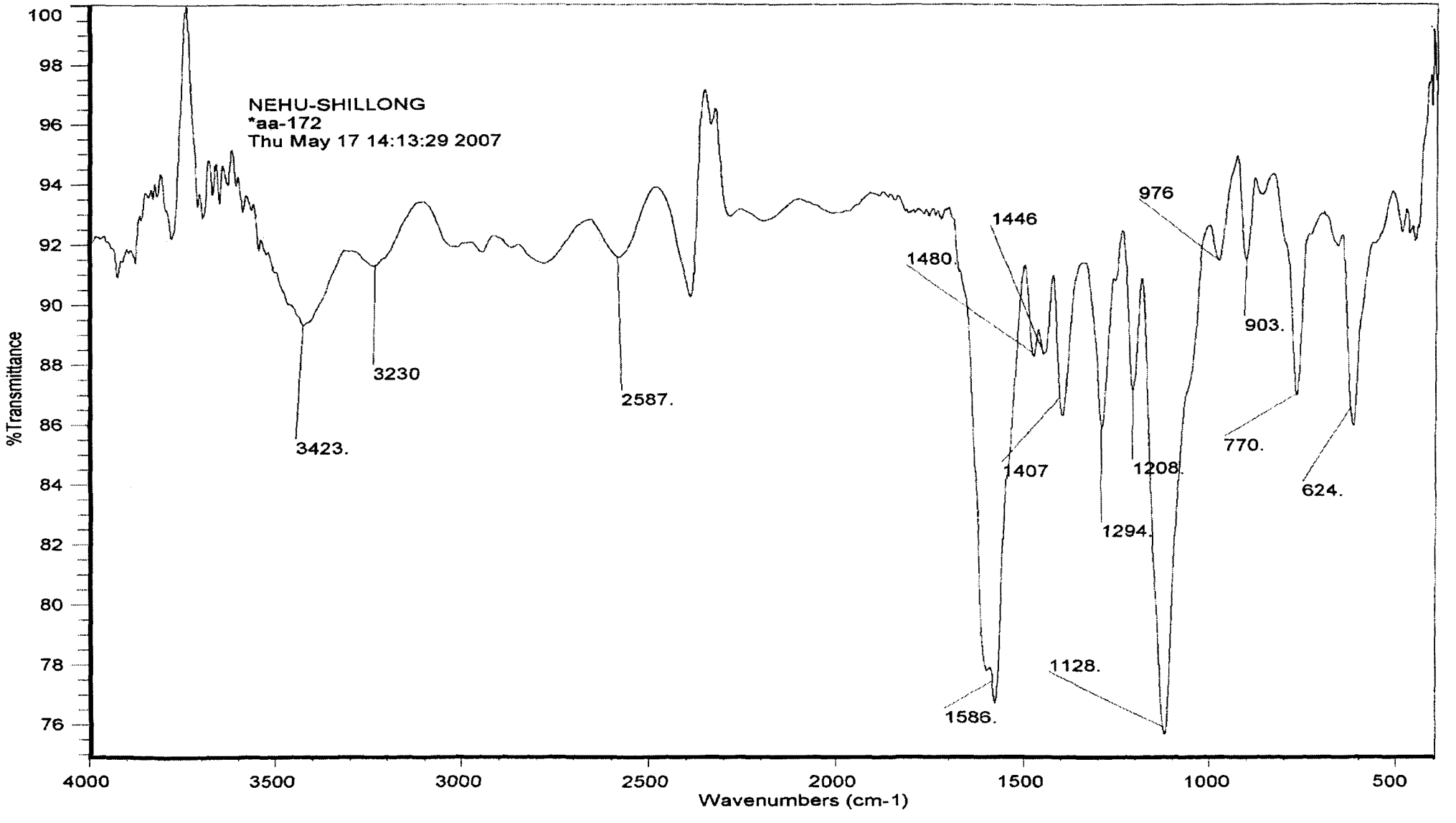


Fig: 3.13 IR Spectrum of $[Cu(H_4slah)]SO_4$ **(312)** in KBr

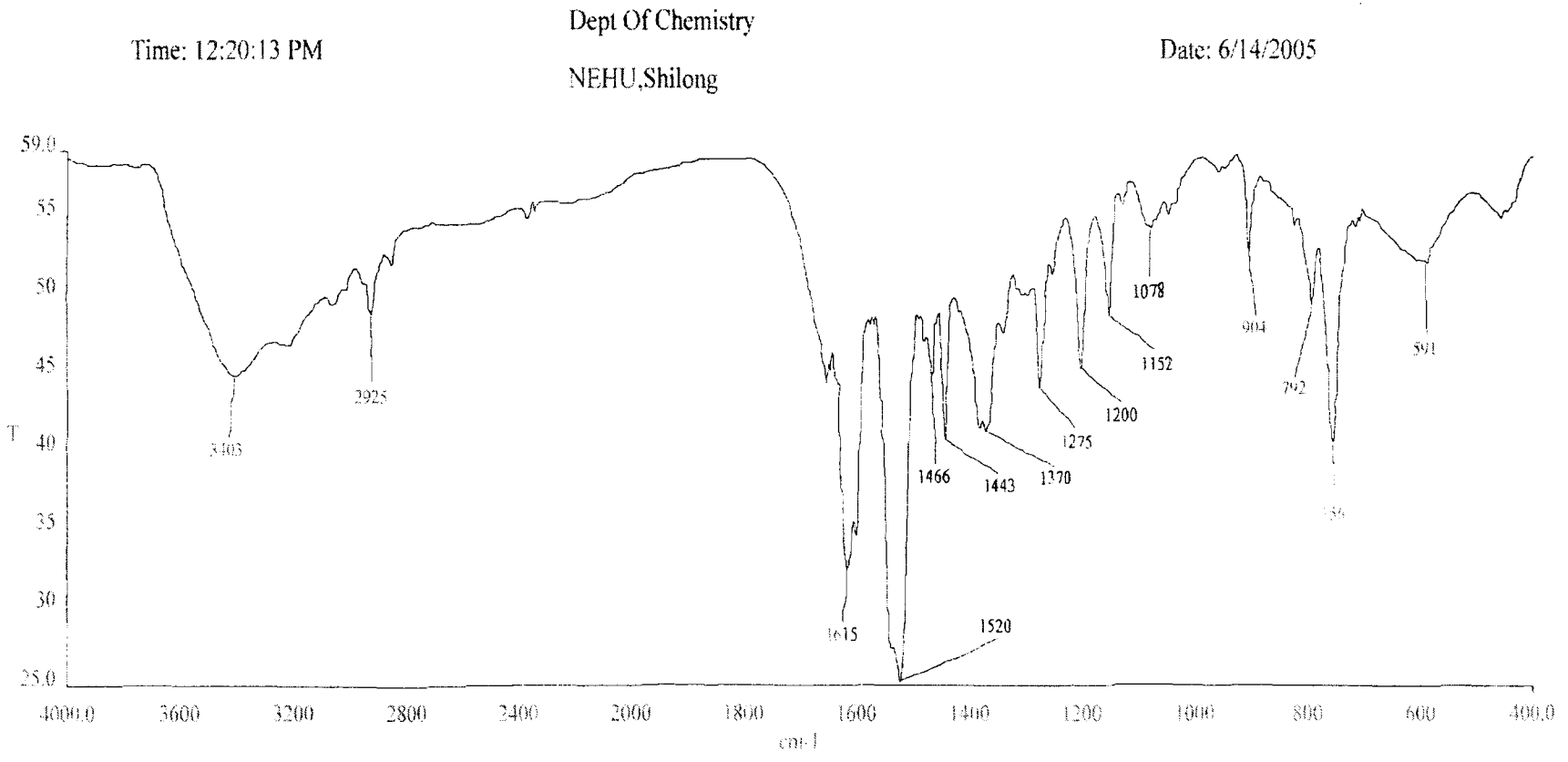


Fig: 3.14 IR Spectrum of [Cu(H_2slmh)] (**313**) in KBr

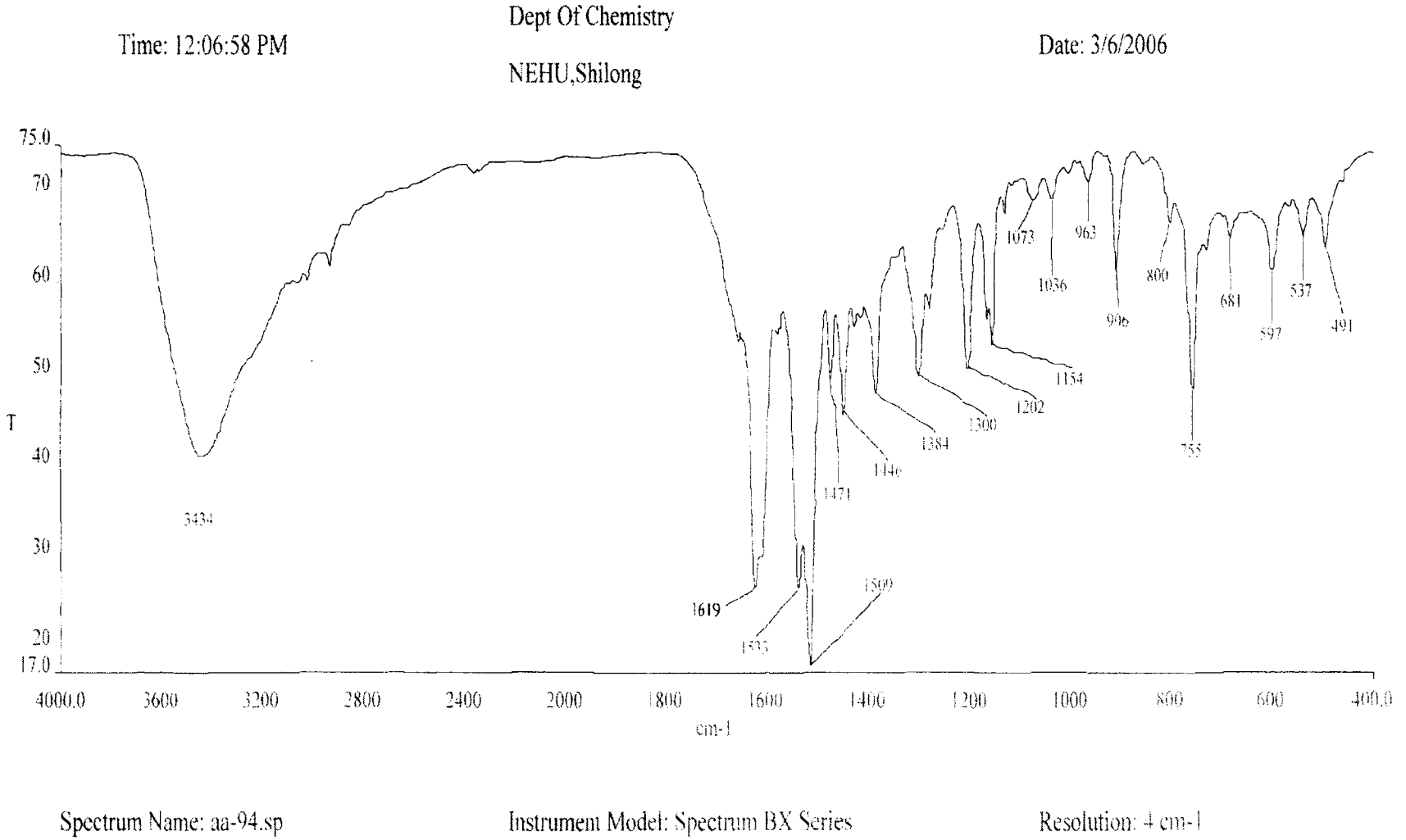


Fig: 3.15 IR Spectrum of [Cu(H_2slsh)] (**314**) in KBr

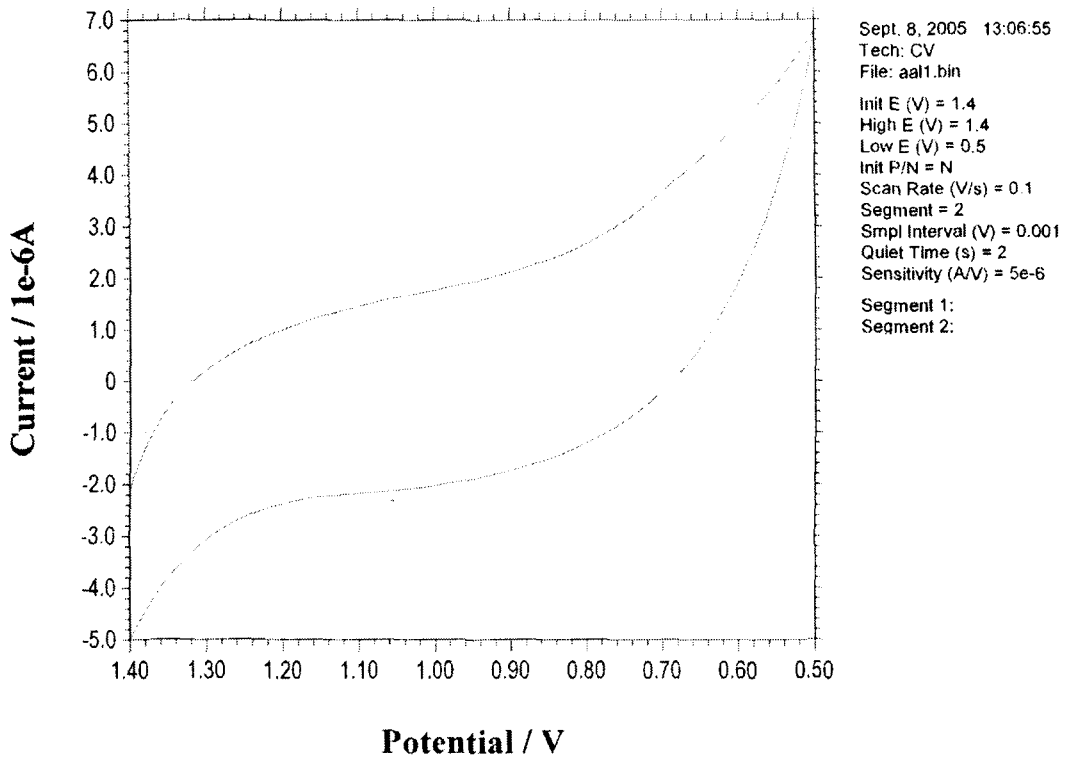


Fig: 3.16 Cyclic voltammogram of Disalicylaldehydemalonoyldihydrazone (H_4slmh) in DMSO

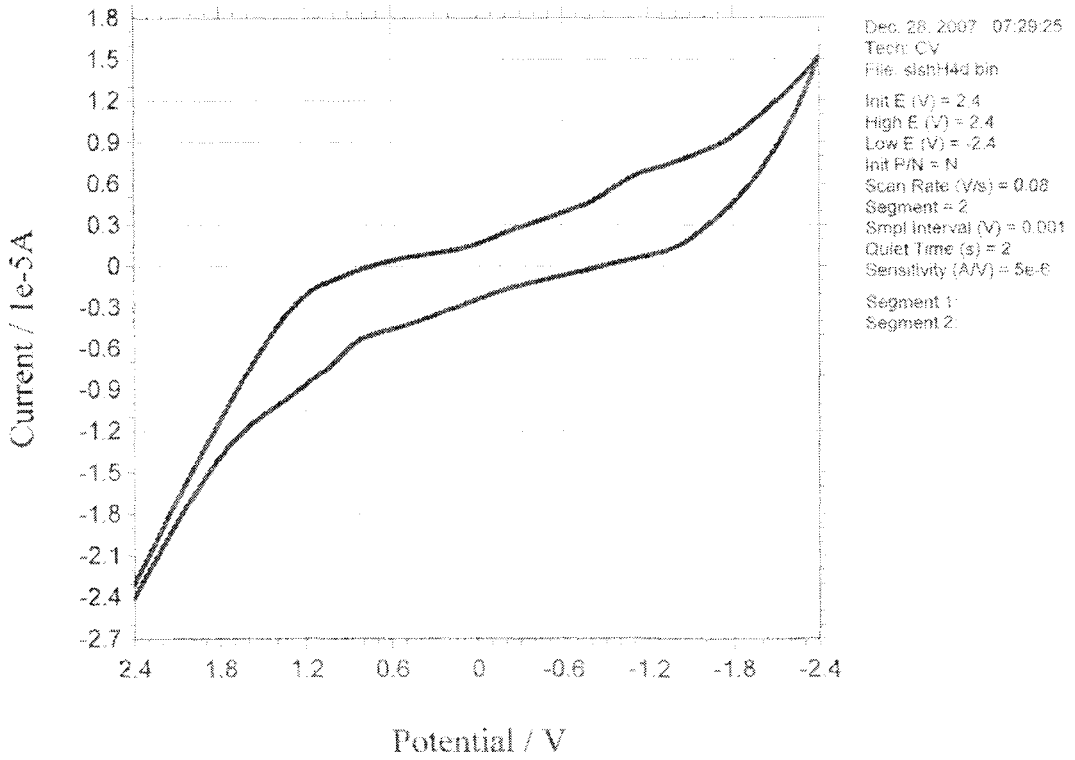


Fig: 3.17 Cyclic voltammogram of Disalicylaldehydesuccinoyldihydrazone (H_4slsh) in DMSO

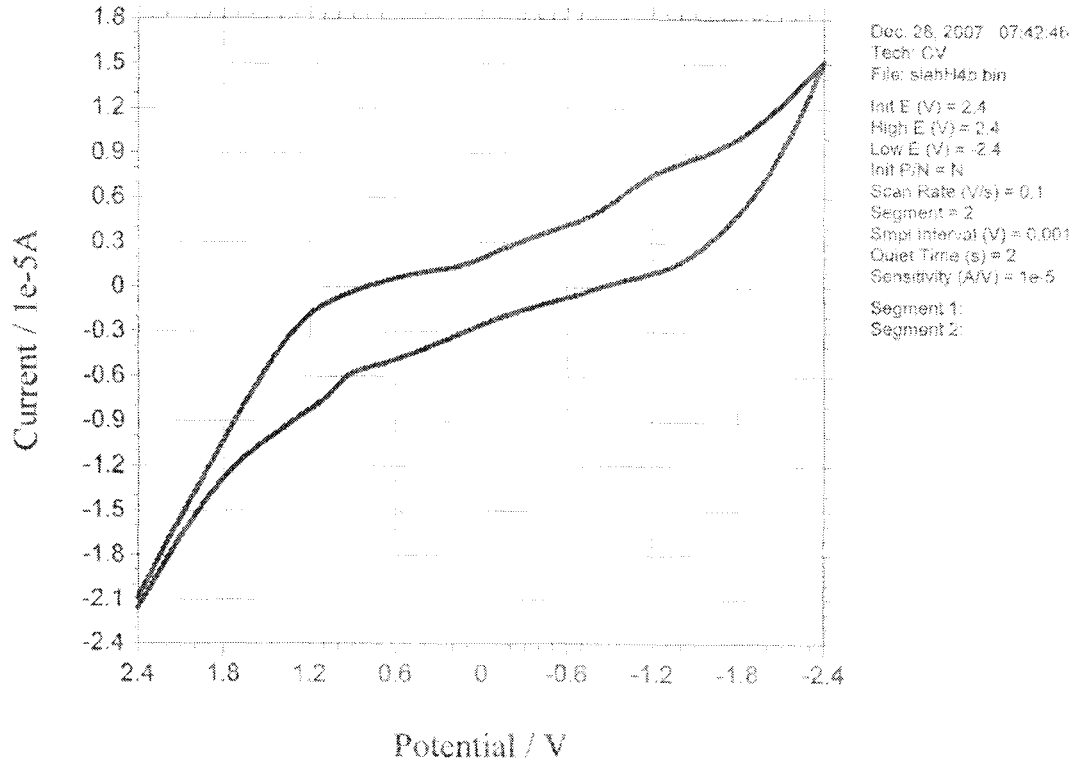


Fig: 3.18 Cyclic voltammogram of Disalicyldehydeadipoyldihydrazone (H_4slah) in DMSO

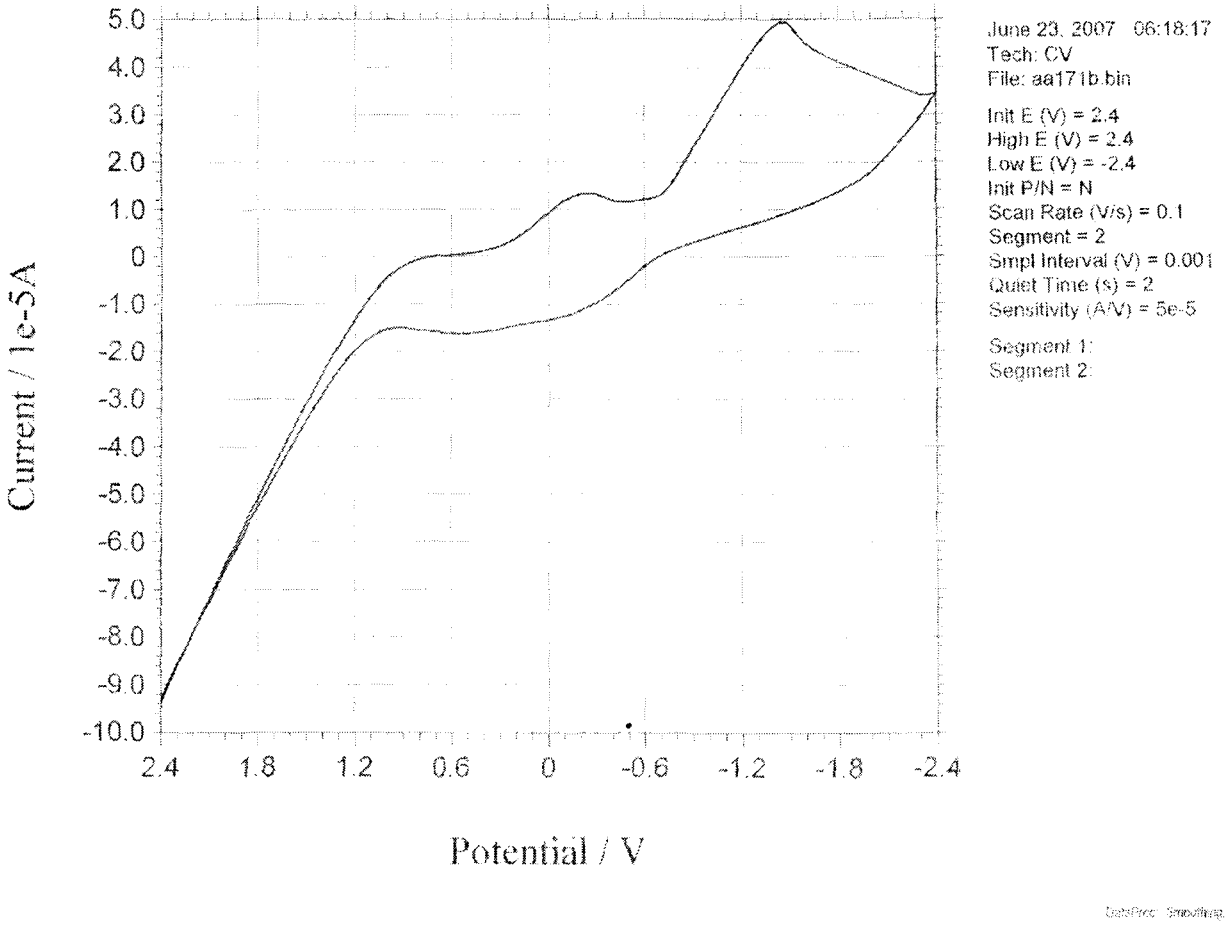


Fig: 3.19 Cyclic voltammogram of $[Cu(H_4slsh)]SO_4$ (**311**) in DMSO

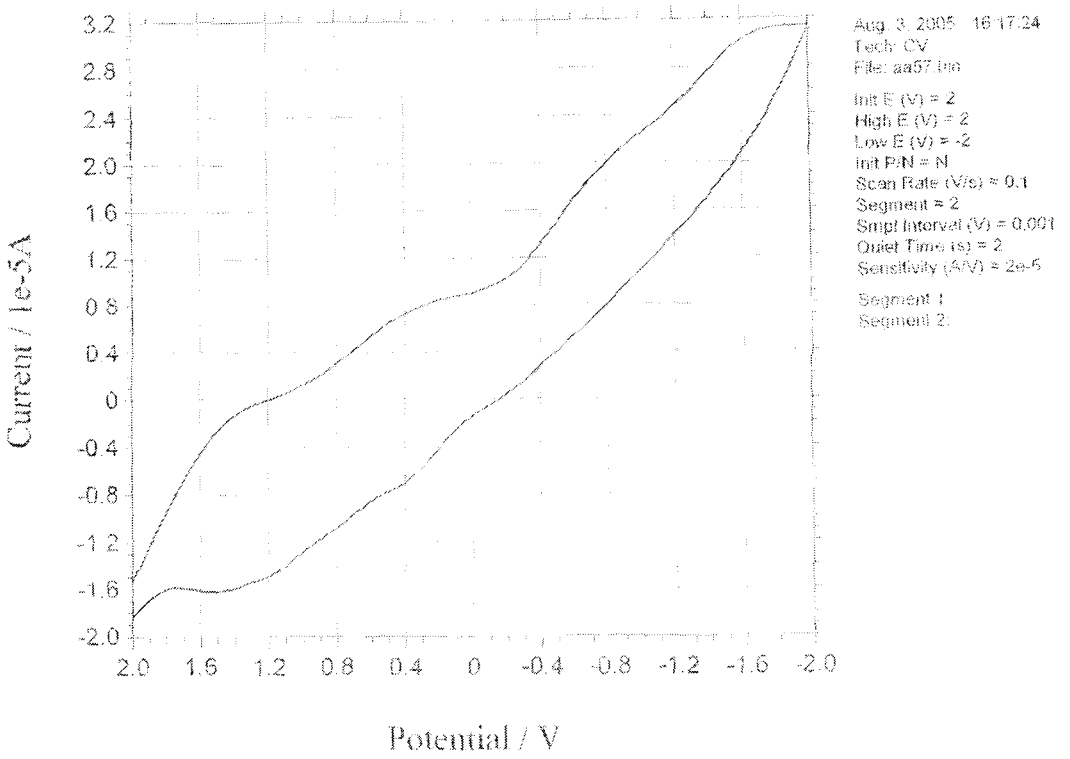


Fig: 3.20 Cyclic voltammogram of [Cu(H_2slmh)] (**313**) in DMSO

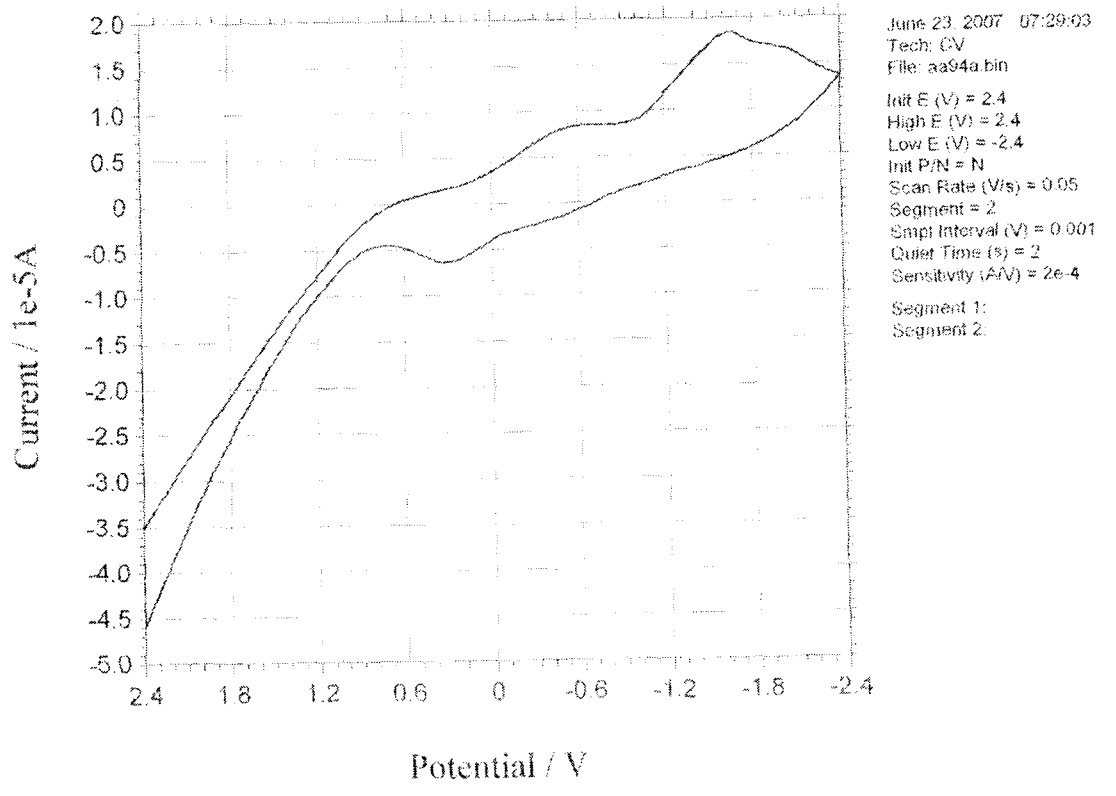


Fig: 3.21 Cyclic voltammogram of [Cu(H_2slah)] (**315**) in DMSO

Table 3.1

Complexes, colour, decomposition point, elemental analysis, magnetic moment and molar conductance for monometallic copper(II) complexes of disalicylaldehyde malonoyl-, succinoyl- and adipoyl-dihydrazones.

Sl.No	Complex and colour	D.P (^{0}C)	Yield (%)	**Elemental Analysis:Found(cal)%**				SO_4^{2-}	Magnetic moment	Molar Conductance ($\Omega^{-1}cm^2mol^{-1}$)
				Cu	C	H	N			
311	$[Cu(H_4slsh)]SO_4$ Green	>300	66	12.13 (12.36)	42.25 (42.06)	3.51 (3.54)	11.21 (10.90)	18.71 (18.69)	1.85	2.2
312	$[Cu(H_4slah)]SO_4$ Green	>300	63	11.51 (11.72)	44.71 (44.32)	4.07 (4.10)	10.52 (10.33)	18.03 (17.72)	1.87	2.6
313	$[Cu(H_2slmh)]$ Green	>300	68	16.13 (15.81)	51.21 (50.80)	3.49 (3.52)	13.69 (13.93)		1.83	2.5
314	$[Cu(H_2slsh)]$ Dark Brown	>300	59	15.20 (15.28)	52.23 (51.98)	3.87 (3.89)	13.23 (13.47)		1.78	2.3
315	$[Cu(H_2slah)]$ Green	>300	64	14.12 (14.31)	54.40 (54.11)	4.52 (4.55)	12.66 (12.61)		1.76	2.3

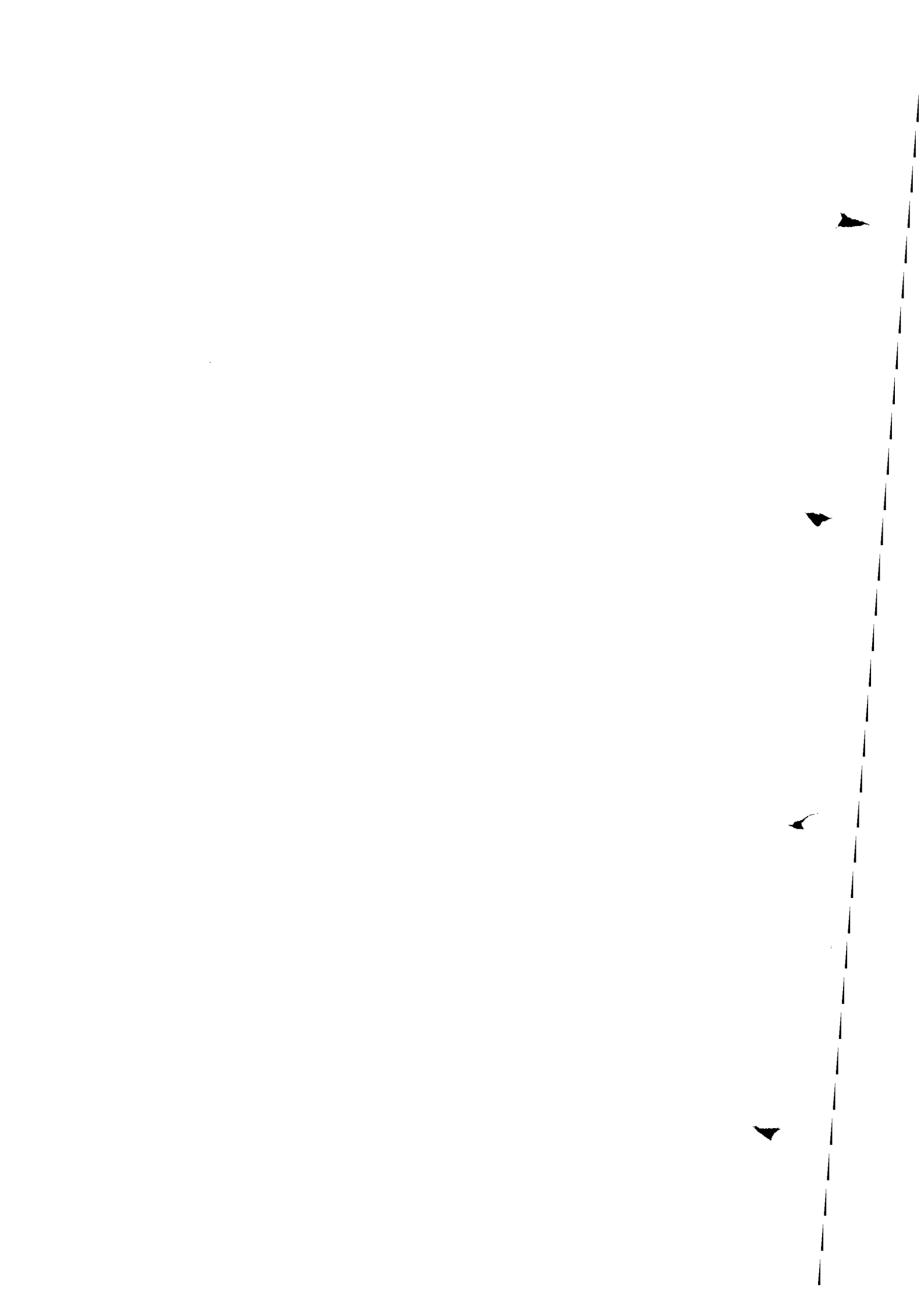


Table 3.2

Electronic spectral data for monometallic Cu(II) complexes of disalicylaldehyde *malonoyl-, succinoyl- and adipoyl-dihydrazones*

Sl. No.	Ligands/Complexes	Electronic spectral bands λ_{max} (nm), ε_{max} ($dm^3\ cm^{-1}\ mol^{-1}$)
1	H_4slmh	280(333367), 323(10267)
2	H_4slsh	283(33333), 322(11700)
3	H_4slah	285(39300), 322(32500)
311	[Cu(H_4slsh)]SO_4	271(2410), 305(2500), 318(8950), 383(7400), 402(8000), 648(105)
312	[Cu(H_4slah)]SO_4	290(1190), 304(1280), 318(10000), 382(10400), 403(4800), 650(109)
313	[Cu(H_2slmh)]	273(2560), 286(2980), 317(9133), 386(5906), 404(9500),675(55)
314	[Cu(H_2slsh)]	276(2340), 304(2500), 320(3850), 385(3250), 403(8000), 627(160)
315	[Cu(H_2slah)]	269(1110), 305(1500), 318(3380), 372(8800), 404(3100), 646(82)

Table 3.3

Magnetic parameters for monometallic Cu(II) complexes of disalicylaldehyde malonoyl-, succinoyl- and adipoyl-dihydrazones

Sl.No	Complexes	Temp	Solid/ Solution	g‖	g⊥	g_{av}	A‖ (G)	A⊥ (G)	G	α^2
311	$[Cu(H_4slsh)]SO_4$	LNT	Solution	2.273	2.097	2.155	160	-	2.814	0.794
312	$[Cu(H_4slah)]SO_4$	LNT	Solution	2.291	2.093	2.159	175	-	3.129	0.852
313	$[Cu(H_2slmh)]$	LNT	Solution	2.339	2.118	2.192	-	-	2.872	-
314	$[Cu(H_2slsh)]$	LNT	Solution	2.334	2.097	2.176	-	-	3.443	0.882
315	$[Cu(H_2slah)]$	LNT	Solution	2.472	2.242	2.318	120	37	1.950	-

Table 3.4

Structurally significant IR spectral data (in cm^{-1}) for disalicylaldehyde malonoyl-, succinoyl- and adipoyl-dihydrazones and their copper(II) complexes

Sl. No.	Ligands/Complexes	υOH+NH	υC=O	υC=N	AmideII +υC-O Phenyl	υNCO	υC-O	υN-N	Sulphato		υM-O Phenolic	υM-O Carbonyl
									ν_3	ν_4		
1	H_4slmh	3436m 3277m 3071m	1679vs	1619m	1566m	-	1268s	1036w	-	-	-	-
2	H_4slshH_4	3449s 3204m 3065m	1666vs	1626m	1566m	-	1281s	1049w	-	-	-	-
3	H_4slah	3204s 3065s	1672vs	1619s	1566s	-	1275s	1036w	-	-	-	-
311	[Cu(H_4slsh)]SO_4	3502s 3383m	-	1579vs	-	1530ssh	1294s	1054w	1161s 1002w	611m	-	451w
312	[Cu(H_4slah)]SO_4	3423m 3230w	1616vs	1586vs	-	-	1294s	1044w	1128vs 1028s 976w	624m	-	474w 439w
313	[Cu(H_2slmh)]	3403m (3650-3000)	-	1615s	1538vs	1520vs	1275m	-	-	-	-	475wbr

Sl. No.	Ligands/Complexes	υOH+NH	υC=O	υC=N	Amide II +υC-O Phenyl	υNCO	υC-O	υN-N	Sulphato		υM-O Phenolic	υM-O Carbonyl
									ν_3	ν_4		
314	[Cu(H_2slsh)]	-	-	1613vs	1533vs	1509vs	1238w	1031w	-	-	-	483wbr
315	[Cu(H_2slah)]	3423s 3065m	-	1613s	-	1513vs	1295m	1036w	-	-	-	454w

Table 3.5

The electrochemical parameters for the mononuclear copper(II) complexes (Pot Vs SCE) of disalicylaldehyde malonoyl-, succinoyl- and adipoyldihydrazones.

Sl. No	Complex	Epa/V	Epc/V	ΔEp
311	$[Cu(H_4slsh)]SO_4$	-	0.21 -1.45	-
312	$[Cu(H_4slah)]SO_4$	-	-0.16 -1.13	-
313	$[Cu(H_2slmh)]$	+0.40 - +1.55	+0.34 -0.83 -	60
314	$[Cu(H_2slsh)]$	-0.21 - +0.50	-0.27 -1.51 -	60
315	$[Cu(H_2slah)]$	-0.50 - +0.25	0.56 -1.63 -	-

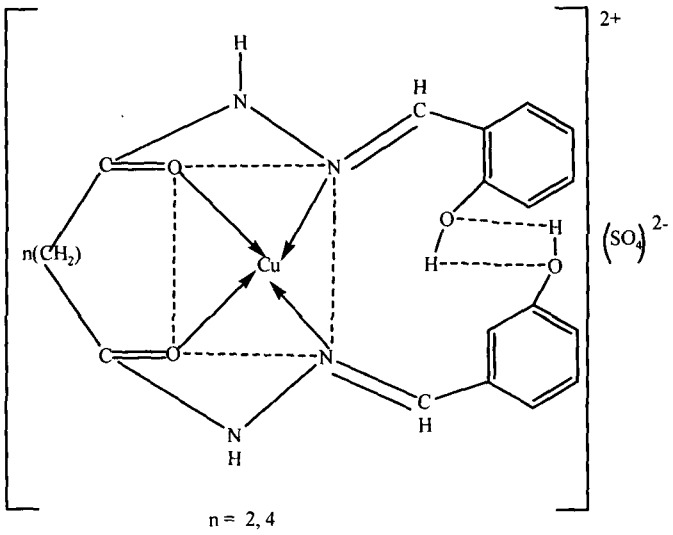


Fig: 3.00 Tentative structure for the complexes $[Cu(H_4L)]SO_4$ (H_4L = H_4slsh (**311**) and H_4slah (**312**))

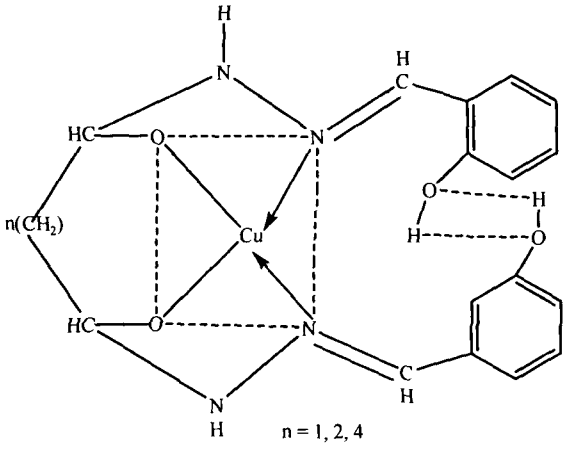


Fig : 3.00a Tentative structure for the complexes $[Cu(H_2L)]$ (H_2L = H_4slmh (**313**), H_4slsh (**314**) and H_4slah (**315**))

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CHAPTER-IV

Synthesis, characterization and electrochemical studies of homotrinuclear copper(II) complexes derived from disalicylaldehyde malonoyl-, succinoyl- and adipoyldihydrazones

Introduction

Chapter III describes the synthesis and characterization of monometallic copper(II) complexes of malonoyl-, succinoyl- and adipoyl dihydrazones synthesized by two different methods. The title ligands being polyfunctional ligand are capable of binding more than one metal atom if an excess of metal salt is used in the reaction. This is considered to be the most plausible possibility because copper occurs in the biological systems with few exceptions as binuclear or multinuclear systems. Hence, it was considered worthwhile to investigate the reactions of the title polyfunctional dihydrazone ligands with the excess of metal salt and to explore the structures of the resulting complexes. In fact, in the present study, monometallic complexes described in the previous chapter, have been used as a metal complex ligands and allowed to react with the excess of the metal salt and the products have been isolated and characterized. Hence ,it appears appropriate at this stage, before we proceed for the synthesis of multimetallic copper(II) complexes, to brief the importance of copper in multimetallic systems.

The importance of homobimetallic and polymetallic copper(II) complexes stems from the fact that copper is an essential bio-element responsible for numerous catalytic processes in living organism where it is often present in di- or trinuclear assemblies. The multinuclear arrays of copper centres at the active sites of copper oxidases and oxygen transport proteins are invariably present. Multinuclear copper oxidases are an important class of enzymes found in bacteria, fungi, plants and animals. Copper is present in enzymes in biological systems either alone or in combination with some other metal ions to discharge their biological functions. When copper is present alone in enzymes in biological systems, it occurs either as a couple of ions or more than a couple of ions. Thus, hemocyanin and tyrosinase contain binuclear copper sites while laccase, ascorbate oxidase, human ceruloplasmin, fungal laccase, FET 3 and phenoxazinase synthase etc.

contain more than two copper atoms. Ceruloplasmin (Cp) is the only multicopper oxidase found in human [ferroxidase iron (II): dioxidoreductase EC] in which it is present in combination with iron. The physiological role of Cp is still some what in dispute, however, a consensus is emerging that it is a plasma ferroxidase **[1-4]**. All multicopper oxidases utilize at least four Cu ions to couple the four electron reduction of O_2 to H_2O with four sequential one-electron substrate oxidations. Multicopper oxidases contain four copper ions of the following types: at least one blue copper or Type 1 site (T1) **[5]**, a normal or Type 2 site (T2) and a Type 3 copper pair (T3) involving strong antiferromagnetic coupling leading to the lack of EPR signal. The T2 and T3 site form a trinuclear cluster which is the site for dioxygen reduction. The function of the T1 site is to transfer electrons from substrate to the trinuclear cluster and this is the site for substrate oxidation. Substitution of the blue copper site by a redox innocent mercuric ion significantly impedes O_2 bond cleavage by the fully reduced trinuclear site. The absence of this fourth reducing equivalent stabilizes an intermediate in which dioxygen has been reduced by $2e^-$ to the peroxide level **[6]**. A $3e^-$ reduced O_2 species is apparently not thermodynamically preferred; as the peroxide is ligated directly to an easily oxidized Cu (I) species **[7]**. These data support the notion that dioxygen bond cleavage in the native trinuclear enzymes occur in two sequential $2e^-$ steps, with each of the four coppers providing $1e^-$ **[8]**.

Ceruloplasmin is unique among the multicopper oxidases in that it contains additional copper sites beyond the four required for oxidase activity. Huber and Frieden were among the first to establish that human Cp contains six copper per molecule, with an additional labile copper-binding site that does not alter the oxidase activity **[9]**. Ortel et al. **[10]** and later Messerschmidt and Huber **[11]** examined the sequence homology among the various multicopper oxidase and plastocyanin and noted that there are three putative T1 binding sites, one with a leucine in place of methionine. The crystal structure of Zeifseva et al confirms this basic stoichiometry of six integral coppers (a trinuclear cluster and seventh labile copper) distributed between the two cation binding sites **[12]**.

Despite the extensive number of multicopper oxidases that have been structurally and spectroscopically characterized, several functionally relevant questions regarding the chemical nature of the trinuclear Cu cluster remains. One has to do with the nature of the