STRUCTURAL, SPECTRAL, BIOLOGICAL AND ELECTROCHEMICAL STUDIES OF SOME 3d TRANSITION METAL COMPLEXES OF O-N-S AND N-N-S DONOR LIGANDS

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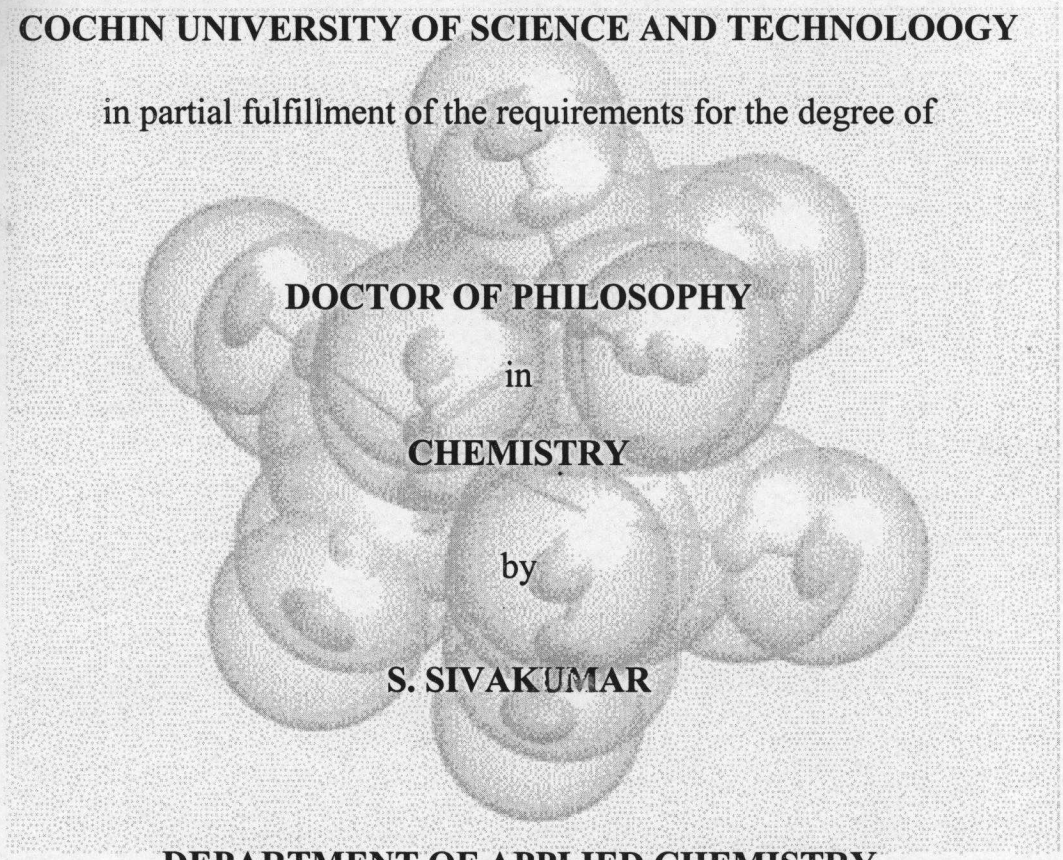

DOCTOR OF PHILOSOPHY

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CERTIFICATE

This is to certify that the thesis entitled STRUCTURAL, SPECTRAL, BIOLOGICAL AND ELECTROCHEMICAL STUDIES OF SOME 3d TRANSITION METAL COMPLEXES OF O-N-S AND N-N-S DONOR LIGANDS submitted by Mr.S.SIVAKUMAR, in partial fulfillment of the requirements of the degree of Doctor of Philosophy, to the Cochin University of Science and Technology, Kochi is an authentic and bonafied record of the original research work carried out by him under my guidance and supervision. Further, the results embodied in this thesis, in full or in part, have not been submitted for the award of any other degree.

M. R. Prathapachandra Kurup

(Supervisor)

CONTENTS

SPECTRAL, BIOLOGICAL (STRUCTURE – ACTIVITY RELATION) AND ELECTROCHEMICAL STUDIES OF Ni(II) COMPLEXES WITH N_2S DONOR LIGANDS AND SINGLE CRYSTAL X-RAY DIFFRACTION STUDIES OF $[Ni(HL4A)_2](ClO_4)_2 . H_2O$

PREFACE

The work embodied in this thesis was carried out by the author in the Department of Applied Chemistry during 1999-2003. The primary aim of these investigations was to probe the spectroscopic, electrochemical, biological and single crystal X-ray diffraction studies of some selected transition metal complexes of ^{4}N-monosubstituted thiosemicarbazones.

The chemistry of thiosemicarbazones has received considerable attention due to their proliferate applications. The transition metal complexes of them found applications in biology, medicine and industry. The present investigation is confined to the spectral, electrochemical, biological and single crystal X-ray diffraction studies of Cu(II), V(IV), V(V), Fe(III), Mn(II), Ni(II) and Zn(II) complexes of mono anionic tridentate thiosemicarbazones with O-N-S and N-N-S donor atoms.

The work embodied in the thesis is divided in to nine chapters. Chapter 1 gives a brief introduction about metal complexes of thiosemicarbazones, including their structural and bonding properties. Chapter 2 deals with the syntheses and single crystal X-ray diffraction studies of various thiosemicarbazones used up for the present investigations and various characterization techniques. Chapter 3 deals with spectral, biological and electrochemical studies of Cu(II) complexes with N-N-S donor thiosemicarbazones. Chapter 4 deals with spectral, biological and electrochemical studies of Cu(II) complexes with O-N-S donor thiosemicarbazones. Chapter 5 includes spectral, biological electrochemical and single crystal studies of vanadyl and vanadate complexes. Chapter 6 deals with spectral, biological and electrochemical studies of low spin Fe(III)complexes. Chapter 7 includes spectral, biological electrochemical and single crystal X-ray diffraction studies of Mn(II)complexes. Chapter 8 deals with spectral, biological, (structure activity relation) electrochemical and single crystal X-ray diffraction studies of Ni(II) complexes. Chapter 9 includes spectral, and biological studies of Zn(II) complexes.

Chapter

1

THIOSEMICARBAZONES AND THEIR TRANSITION METAL COMPLEXES

1.1 Introduction

Thiosemicarbazones belong to a group of thiourea derivatives; have been studied due to their wide range of potential biological uses, wide application in industry and analytical determination of various metal ions. Biological properties of thiosemicarbazones have been studied since 1956 when Brockman *et al* reported the antitumoral properties of thiosemicarbazones derived from 2-formylpyridine. Followed by this, considerable numbers of thiosemicarbazones derivatives have been reported as antibacterial, antiviral and antiproliferative [1]. The broad spectrum of medicinal properties of this class of compounds has been studied for activity against tuberculosis, leprosy, psoriasis, rheumatism, trypanosomiasis and coccidiosis [2].

Certain thiosemicarbazones in particular showed a selective inhibition of herpes simplex virus (HSV) infection *in vitro* and thiosemicarbazones were active inhibitors of *in vivo* HSV genital infection. The effect of thiosemicarbazones against human immuno deficiency virus (HIV) was also reported [3]. Studies on antifungal properties of heterocyclic thiosemicarbazones have been published recently. Thiosemicarbazones derived from 2-formylpyridine and 2-acetylpyridine have been extensively studied. The literature relates that the presence of bulky group at the terminal ^{4}N increases the biological activity. It is reported that anti smallpox activity of metal complexes of thiosemicarbazones depends on the group at ^{4}N position [4].

The transition metal complexes are far more biologically active than uncoordinated thiosemicarbazone and their enhanced biological activity has been an active area of investigation among medicinal researchers [5]. In general,

thiosemicarbazones as chelating ligands with transition metal ions by binding through the thioketo sulphur and hydrazine nitrogen atoms and therefore this type of compounds can coordinate *in vivo* to metal ions. Because of such coordination, the thiosemicarbazones moiety undergoes a sterical reorientation that could favour its biological activity. The biological activity of thiosemicarbazones is also considered to involve the inhibition of ribonucleotide reductase, an obligatory enzyme in DNA synthesis. Ribonucleotide reductase, the enzyme that converts ribonucleotides to deoxy ribonucleotides, is a vital enzyme in DNA synthesis and a key target for the development of antineoplastic agents.

There is also growing consensus on the involvement of toxic oxygen species, such as superoxide and hydroxyl radicals, in many of the disease states for which thiosemicarbazones have been shown to be effective. Recent study has revealed the potential of using copper(II) bis(thiosemicarbazones) as superoxide dismutase (SOD)-like drug at the inter cellular sites [6].

The extreme insolubility of most thiosemicarbazones in water causes difficulty in the oral administration in clinical practice. The introduction of an unprotected carbohydrate moiety as a substituent in the thiosemicarbazones should increase its water solubility and at the same time, its cell membrane permeability. Khadem reported the synthesis of D-arabino-hexos-ulose disemicarbazone. Horton *et al* reported the synthesis of 3-deoxy–aldos-2-ulose-bis (thiosemicarbazones) [7]. Similarly when the ^{4}N substituted thiosemicarbazones moiety is attached to an amide carbon greater solubility in polar solvents is realized.

Thiosemicarbazones can coordinate to metal as neutral molecules or after deprotonation, as anionic ligands and can adopt a variety of different coordination modes. The possibility of their being able to transmit electronic effects between a reduce unit and a metal centre is suggested by the delocalization of the π bonds in the thiosemicarbazone chain [8]. Transition metal complexes with thiosemicarbazone exhibit a wide range of stereochemistry, biomimic activity and have potential application as sensors.

Recently radionuclides have attracted considerable attention in nuclear medicine because they include isotopes with both diagnostic and therapeutic potential [9]. They are becoming increasingly available to the medicinal community using generator systems and improvements in small cyclotron production. It is reported that Ga(III) complexes of 2-acetylpyridine thiosemicarbazones gained more attention because they offer a convenient source of γ-ray emitters for position emission tomography imaging in institutions that do not have a site cyclotron [10]. Recently Kepper *et al* developed gallium complexes which showed profound antiviral and antitumor activity with energy, which make them useful for medical diagnostic agent [11]. There appeared some reports on the synthesis and single crystal studies of thiosemicarbazones of aluminum.

Thiosemicarbazones exhibit significant antimycobacterial activity against both tubercle and leprosy bacilli *in vivo*. The antibacterial activity of thiosemicarbazones against mycobacterium tuberculosis *in vitro* was first reported by Domagk *et.al* and later confirmed *in vivo*. The most important one is thiacetazone (p-acetamido benzaldehyde) thiosemicarbazones. The drawbacks such as toxic effects including hemolytic anemia, edema, excessive skin eruptions and hepatic dysfunctions and development of resistance to the drugs are overcome by coupling thiacetazone with other antitubercular drugs, especially isoniazide. Dobek *et al* reported [12] the synthesis of certain thiosemicarbazones derived from 2-acetylpyridine, having substantial clinical significance for human beings.

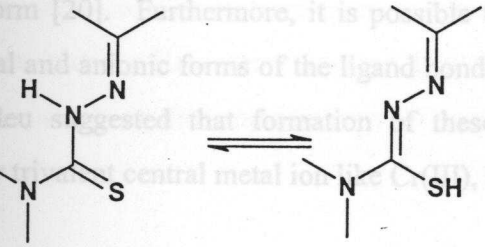
Recently it is reported that thiosemicarbazones of 2-acetylpyridine possess antileprotic activity and ribonucleotide diphosphate reductase (RDR) activity. This series of compounds correlates well with the observed antileprotic properties in mycobacterial systems suitable for *in vitro* testing [13]. The strong metal chelating ability of tridentate thiosemicarbazones is thought to be responsible for their biological activity and any alteration that hinders this chelation leads to loss of activity. Recently there appeared a report on the biological effects of thiosemicarbazones on Friend erytholeukemia cells by an *in vitro* test [14].

The structural and biological studies of copper(II) complexes with thiosemicarbazones are reported by West *et al* [15]. Concerning the exact mechanism by which the Cu(II) complexes exert the anti tumor activity is not clear due to large number of potential sites of action within the cell and the difficulties associated with monitoring and unequivocally assigning a reaction to a particular step. One of the proposed mechanisms is the interaction of the copper(II) drug with the thiol containing enzyme ribionucleoside diphosphate reductase, which is required for the synthesis of DNA precursors [16].

The nature of the substituent attached at ^{4}N can influence the biological activity, while the acid character of the ^{3}NH allows the ligand to be anionic and conjugation to be extended to include the thiosemicarbazones moiety. It has been proposed that this conjugated system enhances the antitumor activity. Extensive literatures on the antitumor properties of many heterocyclic carboxaldehyde thiosemicarbazones having uncommon coordination geometries are now available

1.2 Structure, bonding and stereochemistry

Owing to availability of NH-C=S group, thiosemicarbazones exhibit thione – thiol tautomerism. In solid they exist in thione form but in solution they exist as an equilibrium mixture of thione and thiol forms as shown in the Figure 1.1. Presence of N=C, made them to exist as E and Z stereo isomers. Considering the thermodynamic stability, E isomer will predominate in the mixture [17]. In that case, the compound may act as a monodentate ligand, it will coordinate through sulphur alone, and if the sulphur centre is substituted, the compound may act as a bidentate ligand, coordinating through hydrazine nitrogen and the amide nitrogen. Detailed studies have revealed that the steric effects of the various substituents in the thiosemicarbazones moiety considerably decide the stereochemistry of the ligand. It is proved that during complexation the compound is in the Z form because of the extra stability associated with electron delocalization in chelated complexes.



thione thiol

Fig 1.1

The existence of two forms of E isomer *viz* E^{1} and E^{11} is reported. The E^{1} isomer has more intermolecular hydrogen bonding than E^{11} [18]. The isomers are represented in the Figure.1.2

The E and Z isomers of 2-formylpyridine thiosemicarbazones as well as those of other heterocyclic thiosemicarbazones have been separated and characterized [19]. The subtle difference in stereochemistry between isomers was based upon the degree of shielding observed for the ^{2}N proton of the Z isomer, (δ=14.15 ppm).

However in most complexes thiosemicarbazones coordinate as bidentate ligand *via* the azomethine nitrogen and thione-thiol sulphur. When additional coordination functionality is present in the proximity of the donating centers, the ligands will coordinate in a tridentate manner. This either can be accomplished by the neutral molecule or by the monobasic anion upon loss of hydrogen.

Besides the denticity variation, consideration of the charge distribution is complicated in thiosemicarbazones due to the existence of thione and thiol tautomers. Although the thione form predominates in the solid state, solutions of thiosemicarbazone molecules show a mixture of both tautomers. As a result, depending upon the preparative conditions, the metal complex can be cationic neutral or anionic. Most of the earlier investigations of metal thiosemicarbazone complexes have involved ligands in the uncharged thione form, but a number of recent reports

have featured complexes in which the ^{2}N-hydrogen is lost, and thiosemicarbazones coordinate in the thiol form [20]. Furthermore, it is possible to isolate complexes containing both the neutral and anionic forms of the ligand bonded to the same metal ion. Ablov and Gerbeleu suggested that formation of these mixed "tautomer" complexes is promoted by trivalent central metal ion like Cr(III), Fe(III), and Co(III).

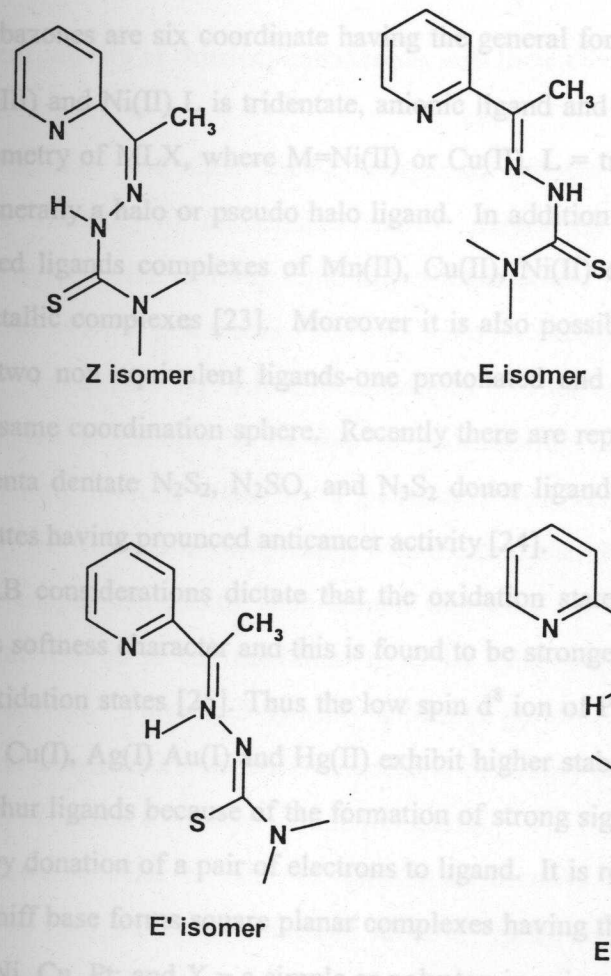


Fig 1.2

Recent reports on transition metal complexes of 2-heterocyclic thiosemicarbazones suggest that stereochemistry adopted by these complexes often depend upon the anion of the metal salt used and nature of the ^{4}N substituents [21]. Further, as indicated previously, the charge on the ligand is dictated by the thione –

thiol equilibrium which in turn is influenced by the solvent and pH of the preparative medium Many of the reported complexes have been prepared in mixed aqueous solvents, often with bases added. However, there are few reports [22] in which workers have varied the nature of their preparations to explore more about the potential diversity of these ligands

The most common stoichiometries encountered with 2-heterocyclic thiosemicarbazones are six coordinate having the general formula ML_2^{n+}, where M is Fe(III), Co(III) and Ni(II) L is tridentate, anionic ligand and n=0,.1, and planar with the stoichiometry of MLX, where M=Ni(II) or Cu(II), L = tridentate, anionic ligand and X is generally a halo or pseudo halo ligand. In addition to this there are reports on the mixed ligands complexes of Mn(II), Cu(II), Ni(II) etc and even homo and hetero bimetallic complexes [23]. Moreover it is also possible to isolate complexes containing two non equivalent ligands-one protonated and the other deprotonated with in the same coordination sphere. Recently there are reports on complexes with tetra and penta dentate N_2S_2, N_2SO, and N_3S_2 donor ligand in the monoanionic or dianionic states having prounced anticancer activity [24].

HSAB considerations dictate that the oxidation state of a metal affects the degree of its softness character and this is found to be stronger for transition metal in the lower oxidation states [25]. Thus the low spin d^8 ion of Pd(II), Pt(II) and Au(III) and d^{10} ions Cu(I), Ag(I) Au(I) and Hg(II) exhibit higher stability constants with this class of sulphur ligands because of the formation of strong sigma bonds as well as $d\pi$ - $d\pi$ bonds by donation of a pair of electrons to ligand. It is reported that pyridine-2-aldehyde Schiff base forms square planar complexes having the formula [M(NNS)X] where M = Ni, Cu, Pt; and X = a simple or polyatomic anions, octahedral complexes having the general formula $[M(NNS)_2]$. Certain manganese complexes are reported to have octahedral and polymeric structures [26]. Iron forms complexes having the formula $[Fe(NNS)_2]ClO_4$ $[Fe(NNS)_2][FeCl_4]$. Existence of two types of iron is confirmed with Mössbauer spectral studies.

PDMS (Plasma desorption mass spectroscopy) of various complexes of thio and selenosemicarbazones of 2-acetylpyridine with transition metal ions have been reported recently and found to posses the general structure $[ML_2]^+$ $[Z]^-$ where L is a monoanioic tridentate ligand. The cations in such complexes found to have octahedral geometry and these structures are entirely in accordance with structure assigned by Akbar Ali [27].

1.3 Biological activity of thiosemicarbazones and their complexes

Thiosemicarbazones and their metal complexes possess a range of biological applications. Heterocyclic thiosemicarbazones exercise their beneficial therapeutic properties in mammalian cells by inhibiting ribonucleotide reductase, a key enzyme in the synthesis of DNA precursors. The non heme iron subunit has been shown to be inhibited or inactivated by thiosemicarbazones. Their ability to provide this inhibitory action is thought to be due to coordination of iron *via* their N-N-S tridentate ligating system, either by a performed iron complexes binding to the enzyme or by the free ligand complexing with the iron charged enzyme [28]. Studies of iron and copper complexes have shown that they can be more active in cell destruction as well as in the inhibition of DNA synthesis, than the uncomplexed thiosemicarbazones. Further, 5-hydroxy 2-formyl pyridine thiosemicarbazone has been shown to cause lesions in DNA. Therefore, there may be a second site of action in addition to inhibition of ribonucleotide reductase.

The antimicrobial activity of thiosemicarbazones against mycobacterium tuberculosis *in vitro* and later confirmed *in vivo*. Since the causative organism of leprosy, one of the world's six major disease, thiosemicarbazones have also been used as second line drug in the chemotherapy of leprosy. Besides this they were also inhibit growth of both fungi and protozoa [29]. Wiles and Supunchuk reported that heterocyclic derivatives of thiosemicarbazide are active against the growth of *Aspergillus niger* and *Chactomiumglobsum* in concentrations as low as 10/mg (μ

g)/mL. Since then, several workers have reported the antimicrobial activity of thiosemicarbazones against selected plant pathogenic and saprophytic fungi [30]. The antiviral effect of thiosemicarbazones was first demonstrated by Hamre *et al* who showed that p-aminobenzaldehyde -3-thisemicarbazone and several of its derivatives were active against vaccinia virus in mice [31]. These studies were extended to include thiosemicarbazones of isatin, benzene, thiophene, pyridine and quinoline derivatives, which also showed activity against vaccinia – induced encephalitis. Later Bauer and co-workers isolated isatin-3-thiosemicarbazone having greatest activity against vaccinia virus. Thiosemicarbazones have also been tested against a variety of other viral infections including herpes virus, adenovirus, poliovirus, rhinovirus and RNA tumor virus with mixed results [32]. An extensive series of thiosemicarbazones obtained from 2-acetylpyridine was tested by Klayman *et al* for antimalarial activity against plasmodium berghi in mice. Recently, it has been shown that 2-formylpyridine thiosemicarbazones inhibited adenosine uptake in rodent erythrocytes and reticulocytes parasitized with plasmodium berghi. The thiosemicarbazone derived from 2-formylpyridine showed mild antileukemic activity against 1-1210 tumor in mice [33]. These observations have provided an impetus to the synthesis of large number of transition metal complexes of heterocyclic thiosemicarbazones.

1.4 Objective and scope of the present work

Transition metal complexes with thiosemicarbazones exhibit a wide range of stereochemistries and possess potential biological activity. Metal complexes of thiosemicarbazones are proved to have improved pharmacological and therapeutic effects because of the following factors.

- Considerable reduction of drug resistance on complexation.
- Form complexes with biologically essential elements.

- Metal complexes may act as a vehicle for the activation of ligand, which is the principal cyctotoxic agent.
- The long-term side effects of therapeutic agents can be avoided.

Their biological activity can be altered by 1) varying the nature and size of the carbonyl moiety, 2) changing the ^{4}N.substituent, 3) modifying the sulphur centre by alkylation, 4) replacing the sulphur of the thiocarbonyl group by oxygen, selenium, imine or oxime, and 5) shifting the thiosemicarbazones moiety's point of coordination to the heterocyclic ring.

Motivated by the proliferate functionality of thiosemicarbazones, we have decided to prepare some O-N-S and N-N-S donor ligands and synthesize metal complexes of first transition series with them.

We have taken the task with the following objectives

- Explore the structure of ligands and complexes by single crystal XRD studies.
- Investigate the antimicrobial activity against clinical pathogens.
- The changes in biological activity upon complexation with metal ions.
- The effect of ^{4}N substituent on biological activity in various thiosemicarbazones and their complexes.
- The redox behaviour of coordinated metal ions.

The studies are conducted to bring about a fair understanding of the structure activity relationship and to develop certain effective and economical metal-based antimicrobial agents.

We assumed following strategy to tackle our objectives. We prepared three N-N-S donors from 2-acetylpyridine and two O-N-S donors from salicylaldehyde and 2-hydroxy acetophenone. Using N-N-S donors, we synthesized twelve Cu(II), two oxovanadium(1V), two dioxovanadium(V), four iron(III), two manganese(II), five nickel(II), three zinc(II) complexes. Thirteen copper(II) and two manganese(II) complexes are prepared with O-N-S donors. All of them are characterized by using various physico-chemical techniques and screened for their antimicrobial activities.

Electrochemical studies of thirty-six complexes and single crystal XRD investigation of two N-N-S, donor ligands and three complexes were accomplished.

1.5 Concluding remarks

An extensive literature survey is made on the versatile properties of thiosemicarbazones. Studies showed that these thiosemicarbazones have antibacterial, antiviral and antiproliferative properties and hence used against tuberculosis, leprosy, psoriasis, rheumatism, trypanosomiasis and coccidiosis. Certain thiosemicarbazones showed a selective inhibition of HSV and HIV infections. The extreme insolubility of most thiosemicarbazones in water causes difficulty in the oral administration in clinical practice. The nature of the substituent attached at ^{4}N influences the biological activity, while the acid character of the ^{2}NH allows the ligand to be anionic or neutral. Transition metal complexes are found to have more activity than uncombined thiosemicarbazones. They exhibit a variety of denticity and can be varied by proper substitution. The stereochemistry assumed by the thiosemicarbazones during coordination with transition metal ions depends on the factors such as preparative conditions and availability of additional bonding site in the ligand moiety and charge of the ligand. The resulting complexes exhibited a wide range of stereo chemistries and have biomimic activity and potential application as sensors.

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Chapter

2

SYNTHESES, CHARACTERISATION OF LIGANDS AND EXPERIMENTAL TECHNIQUES

2.1 Introduction

Thiosemicarbazones of heterocyclic ketones and aldehydes possess a broad spectrum of potentially useful chemotherapeutic activities and their importances have been discussed in Chapter 1. The antimalarial, antibacterial and antiviral properties of this class have been explored by Klayman *et al.* The antileishmanial activity of a series of acetyl β-carboline thiosemicarbazones was recently described by Dodd *et al.* A recent study discusses the synthesis of certain hydrophilic thiosemicarbazones from carbohydrates by the use of microwave [1].

This chapter describes the synthesis of thiosemicarbazones and various physico chemical methods employed for the characterization of them and their transition metal complexes. Details of the synthesis of metal complexes are given in appropriate chapters.

2. 2 Synthesis of ligands

We synthesized three N-N-S and two O-N-S donor ligands.

The N-N-S donor ligands that we synthesized were,

1) 2-Acetylpyridine ^{4}N – morpholine thiosemicarbazone

(Morpholine-4-thiocarboxylic acid 2[1-(2-pyridinyl) ethylidene] hydrazide), HL4M

2) 2-Acetylpyridine ^{4}N -pyrrolidine thiosemicarbazone

(Pyrrolidine-4-thiocarboxylic acid 2[1-(2-pyridinyl) ethylidene] hydrazide), HL4P

3) 2-Acetylpyridine ^{4}N –hexahydroazepine thiosemicarbazone

(Hexahydroazepine-4-thiocarboxylic acid 2-[1-(2-pyridinyl) ethylidene] hydrazide), HL4A

The O-N-S donor ligands that we synthesized were,

4) Salicylaldehyde ^{4}N –pyrrolidine thiosemicarbazone

(N-Pyrrolidine-2- [1-(2-hydroxy) benzylidine] hydrazine carbothioamide), H_2SAP

5) 2-Hydroxyacetopheone ^{4}N –pyrrolidine thiosemicarbazone

(N-Pyrrolidine [1-(2- hydroxy methyl benzylidine] hydrazine carbothioamide), H_2APP

2.3 Experimental techniques

Followings are some of the general experimental methods for the synthesis of thiosemicarbazones.

Method-1. It involves the condensation of thiosemicarbazide with appropriate simple or substituted carbonyl compounds.

Method-2. It involves replacement of the S-methyl group of the compound formed from the condensation of a carbonyl compound with methyl hydrazine carbodithioate by an appropriate amine; the rate of transamination depends on the basicity of the amine.

Method-3. It involves a condensation between a carbonyl compound and isothiocyanate.

Method-4. Holmberg and Psilanderhielm originally reported it and later refined by J. P. Scovill [3]. In this, carboxymethyl –N-methyl –N-Phenyl dithiocarbamate formed by the reaction between carbon disulphide, N-methylaniline, sodium hydroxide and sodium chloroacetate is treated with hydrazine hydrate to get N-methyl –N-phenyl thiosemicarbazide. It is then condensed with an appropriate carbonyl compound and then transaminated with a suitable amine into desired thiosemicarbazones. Using a suitable solvent both condensation and transamination

can be manifested in a single step. We followed this method for the synthesis of all thiosemicarbazones.

2.4 Materials

2-Acetylpyridine, morpholine, hexamethyleneimine, pyrrolidine (Fluka), salicylaldehyde (Lancaster), 2-hydroxyacetophenone (Merck), carbon disulphide (Fluka), N-methylaniline (Merck), hydrazine hydrate (98%, Glaxo fine Chemicals) were used as received. The solvents were purified and dried by using standard procedure. Acetonitrile (S.D.fine) was dried overnight and distilled over activated alumina. Methanol and ethanol were dried over fused $CaCl_2$ and distilled in presence of magnesium isopropoxide.

2.5 Synthesis of thiosemicarbazones

Step-1:- Synthesis of carboxymethyl - N-methyl-N-phenyl dithiocarbamate

A mixture consisting of 12.0 mL (15.2 g, 0.20 mol) of carbon disulphide and 21.6 mL (21.2 g, 0.20 mol) of N- methylaniline was treated with aqueous solution of 8.4 g (0.21 mol) of NaOH in 250 mL. After stirring at room temperature for 4 h, the organic layer had disappeared. At this point, the straw-coloured solution was treated with 23.2 g (0.20 mol) of sodium chloroacetate and allowed to stand overnight (17 h). The solution was acidified with 25 mL. of Conc. HCl and the solid which separated was collected and dried. This afforded 39.5 g (81%) of the buff coloured carboxymethyl N-methyl- N-phenyl dithiocarbamate, mp 198°C.

Step-2:- Synthesis of 4-methyl-4-phenyl-3-thiosemicarbazide

This procedure is an improvement of the method of Stanovnik and Tisler [4]. To a mixture of 17.7 g (0.0733 mol) of carboxymethyl –N-methyl-N-phenyldithiocarbamate in 20 mL of 98% hydrazine hydrate was added 10 mL of water and heated. After 3 minutes crystals began to separate. Heating was continued

an additional 22 minutes. The crystals were collected by filtration, washed well with water and dried under a heat lamp. The crude product was recrystallised from a mixture of 50 mL of ethanol and 25 mL of water. This gave 10.8 g (81%) of stout colourless rods of 4-methyl-4-phenyl-3-thiosemicarbazide, mp 124°C.

Step.3:- Synthesis of morpholine-4-thiocarboxylic acid 2 [1-(2-pyridinyl) ethylidene] hydrazide, HL4M.

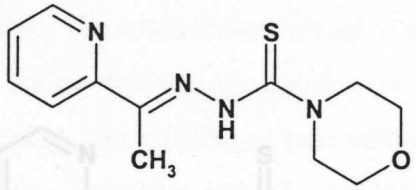


Fig. 2.1 Structural formula of HL4M

A solution 1 g (5.52 mmol) of 4-methyl-4-phenyl-3-thiosemicarbazide.in 5 mL of acetonitrile was treated with 480 mg (5.52 mmol) of morpholine and 668 mg (5.52 mmol) of 2-acetylpyridine. .The solution was heated at reflux for 15 minutes. The solution was chilled and the crystals that separated were collected and washed well with acetonitrile. This afforded 850 mg (58%) of stout yellow rods of morpholine-4-thiocarboxylic acid 2[1-(2-pyridinyl) ethylidene] hydrazide, Fig. 2.1. The compound was recrystallised from methanol, mp 188°C.

Synthesis of pyrrolidine-4-thiocarboxylic acid 2[1-(2-pyridinyl) ethylidene] hydrazide, HL4P

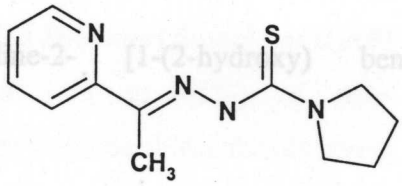


Fig. 2.2 Structural formula of HL4P

A solution 1 g (5.52 mmol) of 4-methyl-4-phenyl-3-thiosemicarbazide.in 5 mL of acetonitrile was treated with 392 mg (5.52 mmol) of pyrrolidine and 668 mg (5.52

mmol)of 2-acetylpyridine. The solution was heated at reflux for 15 minutes. The solution was chilled and the crystals that separated were collected and washed well with acetonitrile. This afforded 893 mg (61%) of stout yellow rods of pyrrolidine-4-thiocarboxylic acid 2[1-(2-pyridinyl) ethylidene] hydrazide, Fig. 2.2. The compound was recrystallised from methanol, mp 148°C.

Synthesis of hexahydroazipine-4-thiocarboxylic acid 2[1-(2-pyridinyl) ethylidene] hydrazide, HL4A

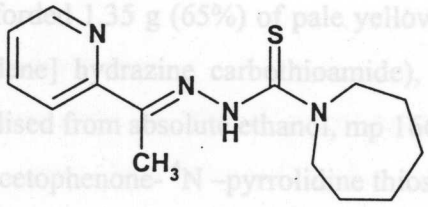


Fig. 2.3 Structural formula of HL4A

A solution 1 g (5.52 mmol) of 4-methyl-4-phenyl-3-thiosemicarbazide,.in 5 mL of acetonitrile was treated with 532 mg (5.52 mmol) of hexamethyleneimine (hexahydroazepine) and 668 mg (5.52 mmol) of 2-acetylpyridine. The solution was heated at reflux for 15 minutes. The solution was chilled and the crystals that separated were collected and washed well with acetonitrile. This afforded 880 mg (60%) of stout yellow rods of hexahydroazipine-4-thiocarboxylic acid 2- [1-(2-pyridinyl) ethylidene] hydrazide, Fig. 2.3. The compound was recrystallised from methanol, mp 162°C.

Synthesis of N-pyrrolidine-2- [1-(2-hydroxy) benzylidene] hydrazine carbothioamide), H_2SAP

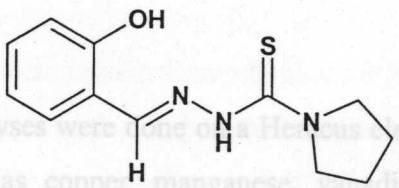


Fig. 2.4 Structural formula of H_2SAP

A solution 1 g, (5.52 mmol) of 4-methyl-4-phenyl-3-thiosemicarbazide, .in 5 mL of methanol was treated with 392 mg (5.52 mmol) of pyrrolidine and 678 mg (5.52 mmol) of 2-salicylaldehyde. The solution was heated at reflux for 20 minutes. The solution was chilled and the crystals that separated were collected and washed well with methanol. This afforded 1.35 g (65%) of pale yellow rods of N-pyrrolidine-2-[1-(2-hydroxy) benzylidene] hydrazine carbothioamide), H_2SAP. Fig. 2.4. The compound was recrystallised from absolute ethanol, mp 166°C.

Synthesis of 2-hydroxyacetophenone- ^4N –pyrrolidine thiosemicarbazones, H_2APP

A solution 1 g (5.52 mmol) of 4-methyl-4-phenyl-3-thiosemicarbazide.in 5 mL of methanol was treated with 392 mg (5.52 mmol) of pyrrolidine and 664 mg (5.52 mmol) of 2-hydroxyacetophenone. The solution was heated at reflux for 20 minutes. The solution was chilled and the crystals that separated were collected and washed well with

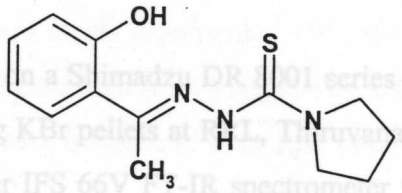


Fig. 2.5 Structural formula of H_2APP

methanol. This afforded 1.35 g (65%) of pale yellow rods of 2-hydroxyacetophenone- ^3N –pyrrolidine thiosemicarbazones, H_2APP Fig. 2.5. The compound was recrystallised from absolute ethanol, mp 178°C.

2.6 Analytical methods

The partial elemental analyses were done on a Heracus elemental analyzer at CDRI, Lucknow. Metals such as copper, manganese, vanadium were estimated after decomposing the organic part of the complexes in Conc. nitric acid, by atomic absorption spectroscopy in a Perkin Elmer analyzer 700, at Spices Board, Kochi. Usual gravimetric procedures [5] were used for the estimation of nickel, and iron. Copper content in some of the copper complexes was estimated iodometrically. Zinc was estimated complexometrically [6].

2.6.1 Magnetic moment measurements

Magnetic moment measurements at 298 K were conducted at CUSAT in the polycrystalline state in a simple Gouy balance [7] using cobalt mercuric thiocyanate, $Hg[Co(SCN)_4]$, as reference substance, as suggested by Figgis and Nyholm

2.6.2 Conductance measurements

The molar conductance of the complexes in dimethylformamide (10^{-3} M) solution was measured at 298 K with a Systronic model 303 direct-reading conductivity bridge at CUSAT. (Cell constant 0.9999 cm^{-1})

2.6.3 I R spectra

IR spectra were measured on a Shimadzu DR 8001 series FT-IR spectrometer in the 4000-400 cm^{-1} range using KBr pellets at RRL, Thiruvananthapuram. Far IR spectra were recorded on a Bruker IFS 66V FT-IR spectrometer using polyethylene pellets over 500-100 cm^{-1} at the RSIC, IIT, Chennai, India.

2.6.4. Electronic spectra

Diffuse reflectance spectra at room temperature in magnesium oxide diluents were recorded at our centre with Ocean Optics DRS spectrophotometer. Electronic spectra in different solvents were recorded with Hitachi 1050 UV-Visible spectrophotometer at the Department of Chemical Oceanography, CUSAT, Kochi.

2.6.5. NMR spectra

^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX 300 in $CDCl_3$ /DMSO-d^6 ($CHCl_3$, δ = 7.26 and $^{13}CDCl_3$, δ = 77) with TMS as internal reference at RRL, Thiruvananthapuram. COSY homonuclear and HMQC heteronuclear spectra were recorded with AMX 400 at I. I. Sc. Bangalore.

2.6.6 EPR spectra

The EPR spectra were recorded on Varian E-112 X-band spectrometer operating with 100 KHz modulation frequency using TCNE (g=2.00277) as field marker at RSIC, IIT, Bombay.

2.6.7 Mössbauer spectra

The Mössbauer spectra were recorded with a constant velocity Mössbauer spectrometer with a multi channel analyzer CMCA-1000A supplied by M/s Wiessel Germany. [Source ^{57}Co (Rh)] at I.I.C, I.I.T, Roorkee.

2.6.8 Cyclic voltammetry

Cyclic voltammetry is the electrochemical equivalent of spectroscopy. It is a useful tool for studying electrochemical reversibility and the effects of follow up chemical reactions. It is the single most powerful tool for examining the electrochemical properties of a chemical substance or material. Both thermodynamic and kinetic information are available in a single experiment. The properties of both reactants and products can frequently be discerned from a single voltammogram or from a series of voltammograms obtained as a function of scan rate, concentration, pH, solvent type temperature and so forth [8].

The cyclic voltammetric measurements were performed on a Cypress system model CS-1090/ model CS -1087 computer controlled electro analytical system at RRL Thiruvananthapuram. Measurements were made on the degassed (N_2 bubbling for 10 min) solutions in dimethylformamide (10^{-3} M) containing 0.1 M tetrabutyl ammonium fluroborate as the supporting electrolyte. The three electrode system consisted of glassy carbon (working) platinum wire (counter) and Ag/AgCl (reference) electrode or SCE.

2.6.9 X - ray diffraction studies

Single crystal X-ray diffraction studies were made by using Mo-Kα radiation with a detector distance of 4 cm and swing angle of -35°. in a Siemens SMART CCD area detector diffractometer at X-ray crystallography unit, School of Physics, Universiti Sains Malaysia and at I.I.T, Bombay. A hemisphere of the reciprocal space was covered by combination of three sets of exposures; each set had a different of angle and each exposure of 30 s covered 0.3° in ω. The structures were refined by direct methods and refined by least square on F^2_0 using the SHELXTL [9] (Sheldrick, 1997) soft ware package. We also used the following softwares, SMART (Siemens 1996), Cell refinement. SAINT (Siemens, 1996),

2.6.10 Biological studies

Anti microbial activity including MIC, against nine-gram negative and two-gram positive bacteria of all ligands and complexes were performed at the Biotechnology department of CUSAT. Details of the studies are appended in Chapter 3.

2.7 Results and discussion

2.7.1 Synthesis of thiosemicarbazones

The synthesis of thiosemicarbazones from 4-methyl-4-phenyl thiosemicarbazide in a single step involves two simultaneous processes such as condensation and transamination. The former involves condensation with an appropriate carbonyl compound and later involves replacement of N-methylaniline (weaker the base better is its leaving ability) from the mother thiosemicarbazide by the amine present in the solution. It is assumed that amine used up for transamination also functions as a catalyst. It has been found that stronger the base added, better will be its transamination ability. The rate and extent of reaction are also be influenced by the acidity of added base. The solvent also plays a very important role in shaping the product and the rate of reaction. In the synthesis of N-N-S donor ligands, acetonitrile was found to be very efficient but for O-N-S donors ligands, methanol. It is assumed

that the condensation reaction is initiated at the beginning and later the transamination surpasses the condensation in the presence of solvent. It is reported that condensation of carbonyl compound with 4-methyl-4-phenyl-3-thiosemicarbazide results in the formation of thiosemicarbazones and attack of the thiocarbonyl group of it by an amine gives a tetrahedral intermediate. Loss of N-methyl aniline from these intermediate results in reformation of the thiocarbonyl group and completes the transamination process. It is also noticed that deactivated amines decelerates transamination process and in such cases, the major product is the non-transaminated one. Refluxing time also plays a major role in shaping the product. Longer refluxing time produces a mixture of transaminated and non-transaminated product and even dithiourea derivatives [10].

The percentage of tautomer in the mixture of product depends on the mode of preparation and basicity of the medium. The more polar the medium and higher the pH of the product, more will be the percentage of thiol tautomer in the mixture. However re-crystallization from the solvent increases the percentage of thione tautomer. The appearance of the crystals depends on the nature of the solvent used and method adopted for their crystallization. To certain extent the shades of the product depends on the amine used up for transamination. Our attempts to effect the transamination with pyridine, piperidine and pyrimidine in methanol remained unsuccessful.

2.8 Characterization of ligands

The colours, melting points and partial elemental analyses of the ligands are listed in Table 2.1. All N-N-S donor ligands are pleasant yellow non-hygroscopic crystalline substances and O-N-S donors are pale yellow non-hygroscopic crystalline substances.

2.8.1 IR spectral characterization

The tentative assignments of the IR spectral bands to establish the structural identity of the ligands are listed in Table 2.2

The Schiff bases contain thioamide function –NH-C(S)-NR_2, consequently they exhibit thione–thiol tautomerism.

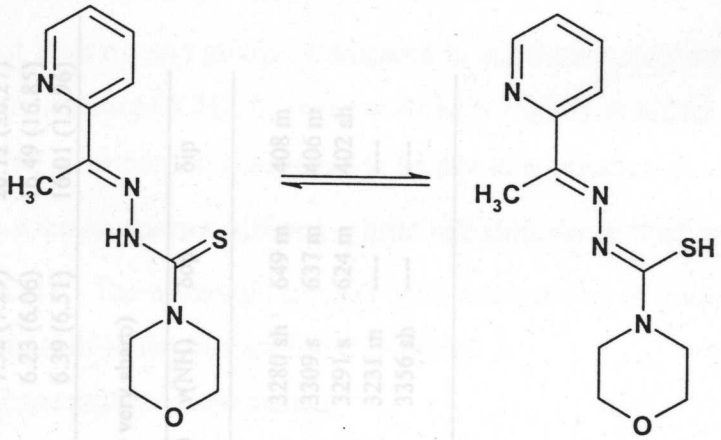


Fig. 2.6 Thione-thiol tautomers of HL4M

In the solid state, the compounds remain in the thione form because none contains ν(S-H) band expected to be at *ca* 2570 cm^{-1}. A sharp ν(^{2}N-H) band is observed at 3280, 3309 and 3291 cm^{-1} for various N-N-S donor ligands and for O-N-S donors ligands , ν(^{2}N-H) band is observed at 3310 and 3290 cm^{-1}. These results support the existence of thione tautomer in the solid state. However, this band is vivid in N-N-S donors and the same is rather obscured in O-N-S donors due to phenolic stretching vibration *ca* 3500 cm^{1}. A sharp ν(C=S) band and a medium or shoulder of low intensity δ(C=S) band are seen in these compounds respectively in the range 1357-1380 cm^{-1} and 838-892 cm^{-1}. For O-N-S donor ligands sharp ν(O-H) band appears in the range 3434-3471 cm^{-1} and δ(O-H) band appears in the range 1400-1555 cm^{-1}. Azomethine stretching vibration for the various donor ligands found in the range 1587-1627 $cm.^{-1}$ The bands in the region 1350-1460 cm^{-1} are due to ν(^{2}N-C),and ν(^{4}N-C) stretching vibrations. This region is partially obscured by combination with the aromatic ν(C=C) vibrations. The ν(N-N) band is observed with medium intensity in the range 998-1010 cm^{-1}, for N-N-S donor ligands . For O-N-S donor ligands, ν(N-N) band appears at 993 and 999 cm^{-1}.

Table 2.1
Analytical data, colours, melting point and yield for ligands.

Compound	Empirical formula	Colour	Mel.point(^{0}C)	Yield (%)	Analytical data Found (calcd) %		
					C	H	N
HL4M	$C_{12}H_{16}N_4OS$	Yellow	188	59	54.44 (54.52)	6.20 (6.10)	21.27 (21.19)
HL4P	$C_{12}H_{16}N_4S$	Yellow	148	58	58.21 (58.03)	6.57 (6.49)	22.39 (22.56)
HL4A	$C_{14}H_{20}N_4S$	Yellow	162	60	60.71 (60.84)	7.32 (7.29)	20.12 (20.27)
H_2SAP	$C_{12}H_{15}N_3OS$	PaleYellow	I35	65	57.52 (57.81)	6.23 (6.06)	16.49 (16.85)
H2APP	$C_{13}H_{17}N_3OS$	PaleYellow	149	65	59.44 (59.29)	6.39 (6.51)	16.01 (15.96)

Table 2.2.
Selected IR bands (cm^{-1}) with tentative assignments for ligands. (s =sharp, m =medium, sh shoulder, vs = very sharp)

compound	$\nu(^7C{=}^1N)$)	$\nu(^2N^9C)$ $\nu(^3N^8C)$	$\nu(^1N^2N)$ $\nu(^2N^3N)$	ν(C=S)	δ(C=S)	ν(C=O)	ν(CCO)/ ν(COC)/	$\nu(^9CN)$	ν(O-H)	ν(NH)	δop	δip
HL4M	1627 s	1480 s	1010 m	1371 s	892 m	------	------	----	----	3280 sh	649 m	408 m
HL4P	1604 s	1493 s	998 m	1380 s	843 sh	-----	-------	-----	-----	3309 s	637 m	406 m
HL4A	1601 s	1487 s	1003 m	1563 s	867 m	-----	-------	------	------	3291 s	624 m	402 sh
H_2SAP	1634 s	1560 s	1040 m	139_1 m	804 m	1290 s	1169 m	1472 s	3383m	3231 m	----	----
H2APP	1615 m	1546 s	996 m 1027 m	1382 s	827 m	1228 s	1117 m	1462m	3410 s	3356 sh	----	----

Table 2.3.
UV-Visible spectral assignments for ligands (All absorptions are given in nm)

Compound	$\pi \rightarrow \pi^*$	$n \rightarrow \pi^*$
HL4M	292 sh (3.97)	331 sh (4.01); 301 sh (4.14)
HL4P	291.sh (4.11)	332 sh (3.96) ; 310 sh (4.08)
HL4A	291 sh (4.10)	330.sh (4.01) ; 310 sh (3.99)
H_2SAP	261 sh (4.05)	337 (3.89) ; 314 sh (3.94)
H_2APP	263 sh (3.97)	331 sh (4.02) ; 317 sh (4.09)

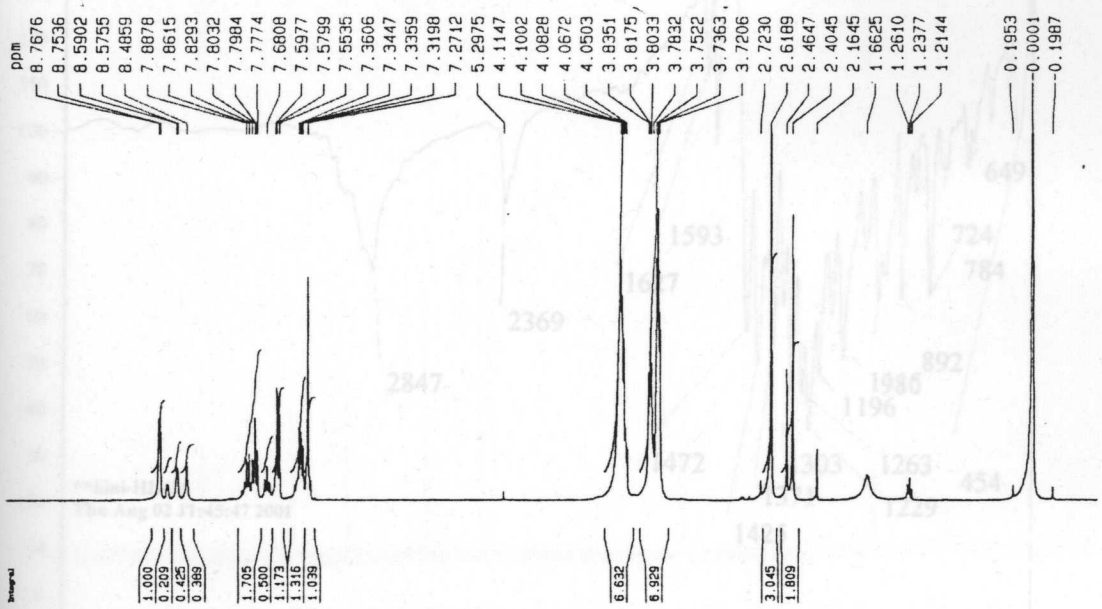
[a] Log ε in paranthesis; [a] = ε is expressed in l $mol^{-1}cm^{-1}$ (sh = shoulder)

2.8.2 Electronic spectroscopy

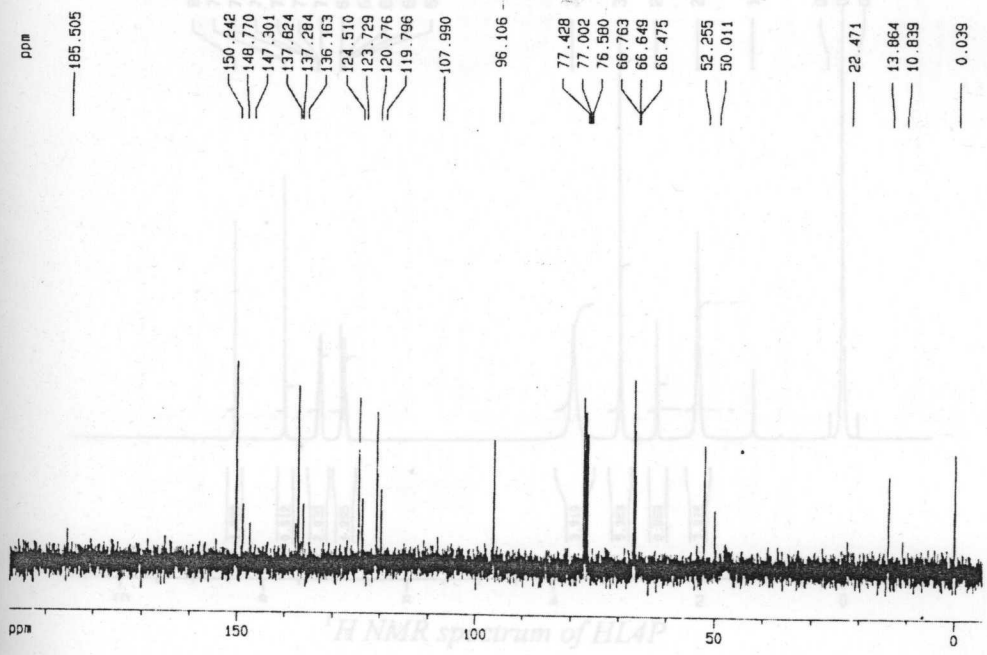
The electronic spectra of various ligands in solution registered bands in the region 261-292 nm and 310-331 nm, which are attributed to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions, respectively of thiocarbonyl group. Compared to solid-state electronic spectra, the solution spectra (methanol/CH_2Cl_2) registered bands slightly at higher energies (blue shift) for $n \rightarrow \pi^*$ transition. It is assumed to be due to enolisation of the compounds. Similarly the solution spectra suffered a little red shift for $\pi \rightarrow \pi^*$ transition when compared to DRS. The electronic spectral band assignments of various N-N-S and O-N-S donor ligands in solution are listed in Table 2.3.

2.8.3.^{1}H NMR spectral characterization

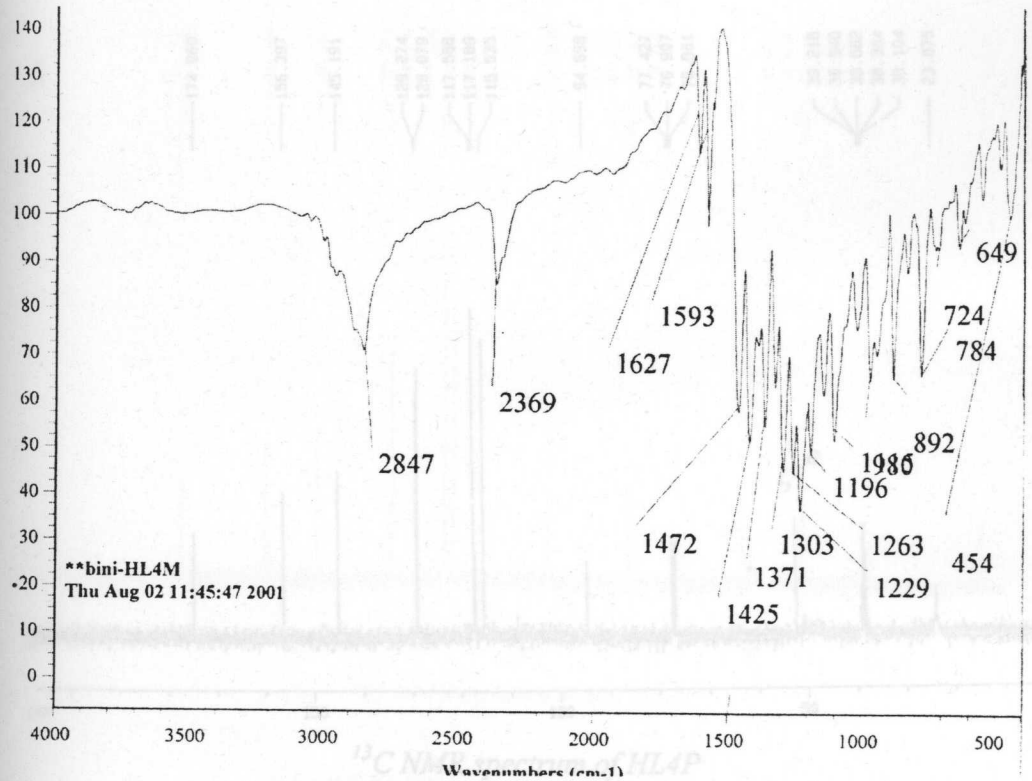
The NMR spectra of 2-acetylpyrdine thiosemicarbazones in $CDCl_3$ show no resonance peak at 4. 11 ppm assignable to S-H proton but they do show a peak in the region δ.77-9.01 ppm ($CDCl_3$) assignable to the secondary N-H protons. It also supports the fact that in solution the predominant tautomer is thione form. The low values of the signals due to N-H proton in the ^{1}H NMR spectra indicate that the compounds are predominantly in the E′ form. A singlet of three protons at δ 2.6 ppm was attributed to the methyl protons which are chemically and magnetically equivalent. The high δ values observed for O-H and N-H proton for O-N-S donor ligands were assumed to be due to intermolecular hydrogen bonding with solvent DMSO. For O-N-S donor ligands signals at δ 11.7, 10.9 and 8.3 ppm correspond to O-H, N-H and –C-H= protons respectively. Aromatic protons appear as multiplet at 7.2-7.7 ppm range. The ^{1}H NMR assignments given in Table 2.4 are in agreement with values in earlier reports [12].



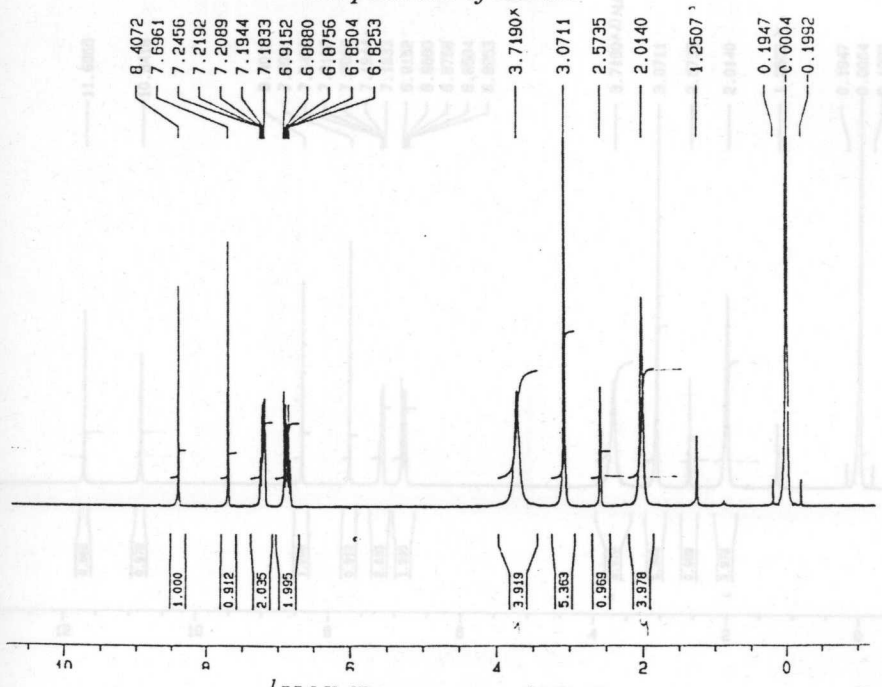
[1]HNMR spectrum of HL4M



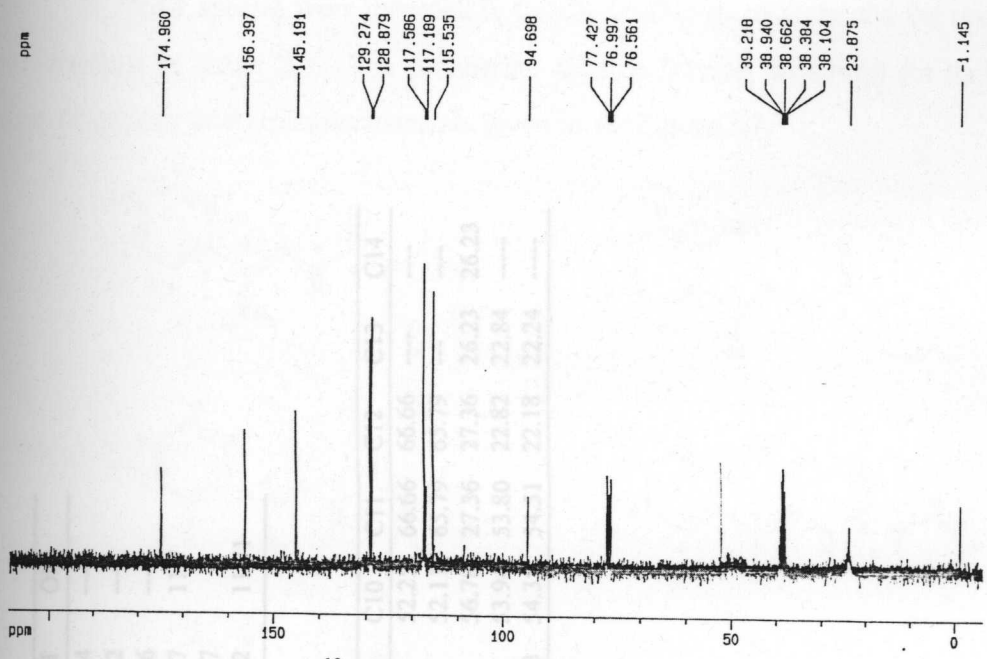
[13]C NMR spectrum of HL4M



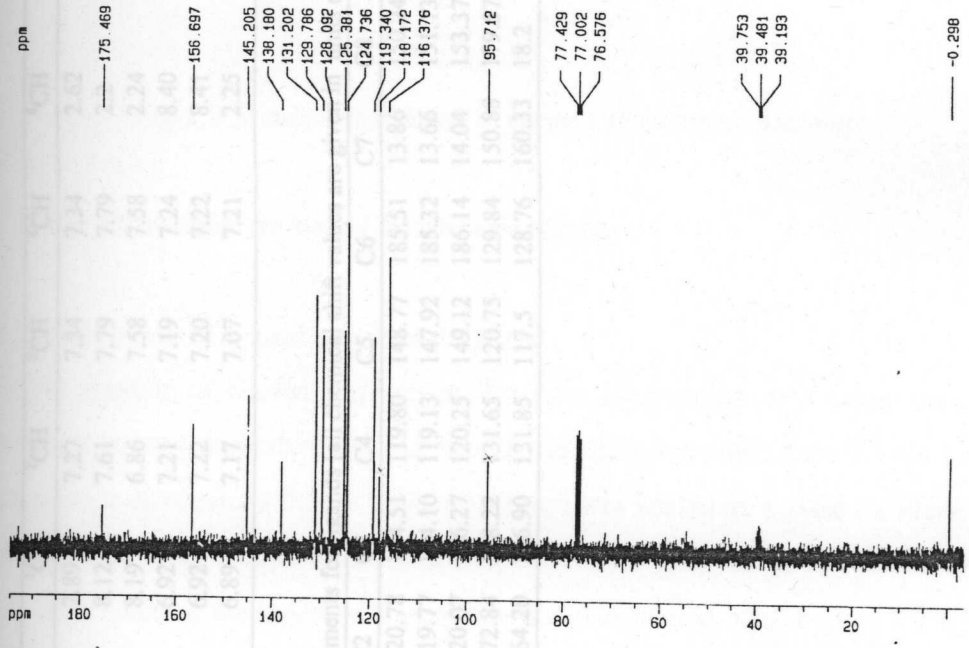
IR spectrum of HL4M



^{1}H NMR spectrum of HL4P



^{13}C NMR spectrum of H_2SAP



^{13}C NMR spectrum of H_2APP

Table 2.4
^{1}H NMR assignments for ligands. [All chemical shift values are given in units of ppm]

Compound	^{3}NH	^{1}CH	^{2}CH	^{3}CH	^{4}CH	^{8}CH	$^{9\text{-}12,13}$ CH	OH
HL4M	8.77	7.89	7.27	7.34	7.34	2.62	3.72-3.84	----
HL4P	8.63	8.12	7.61	7.79	7.79	2.2	3.48-3.62	----
HL4A	9.01	8.19	6.86	7.58	7.58	2.24	1.51-2.56	----
H2SAP	10.84	6.92	7.21	7.19	7.24	8.40	2.01-2.57	11.7
D_2Oexchange	----	6.92	7.22	7.20	7.22	8.41	2.01-2.57	
H2APP	10.92	6.89	7.17	7.07	7.21	2.25	2.24-2.32	11.71

Table 2.5.
^{13}C NMR spectral assignments for ligands [all chemical shift values are given in units of ppm]

Compound	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11	C12	C13	C14
HL4M	137.82	120.78	124.51	119.80	148.77	185.51	13.86	150.24	52.25	52.25	66.66	66.66	----	----
HL4P	137.19	119.77	124.10	119.13	147.92	185.32	13.66	151.13	52.11	52.11	65.79	65.79	---	----
HL4A	138.04	120.07	126.27	120.25	149.12	186.14	14.04	153.37	56,78	56.78	27.36	27.36	26.23	26.23
H_2SAP	124.32	172.84	118.22	131.65	120.75	129.84	150.88	179.57	53.94	53.94	53.80	22.82	22.84	-----
H_2APP	125.4	164.20	116.90	131.85	117.5	128.76	160.33	18.2	178.93	54.35	54.51	22.18	22.24	-----

^{13}C NMR spectra were recorded in $CDCl_3$-DMSO-d_6 mixture and the results are presented in Table 2.5. The numbering scheme (crystal structure) for carbon atoms of various thiosemicarbazones are given in the Figure 2.7.

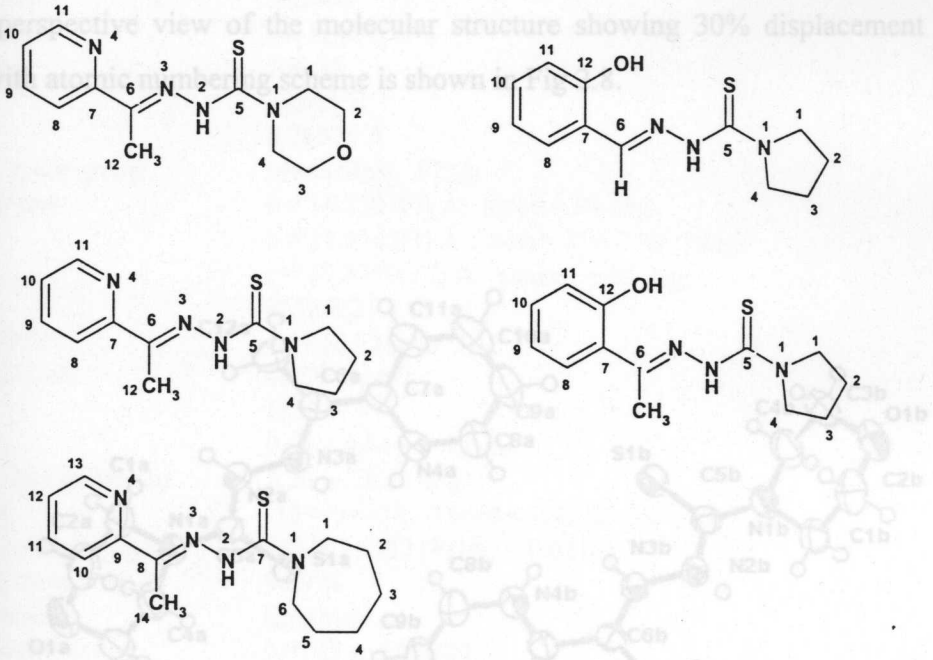


Fig.2.7 Numbering scheme of various thiosemicarbazones

2.9 X-ray diffraction studies of HL4M and HL4A

2.9 1 Description of crystal structure of HL4M

Suitable crystals of HL4M were grown by slow evaporation of a dilute methanol solution at room temperature. A deep yellow monoclinic crystal of the HL4M having approximate dimensions 0.64 × 0.44 × 0.40 mm was sealed in a glass capillary, and intensity data were measured at room temperature (293 K) on an Siemens SMART CCD area detector equipped with graphite-monochromated MoKα (λ = 0.71073Å) radiation. The crystallographic data along with details of structure solution refinements are given in Table 1. Unit cell dimensions were obtained using 25 centered reflections in the θ range 1.74 –24.93° . The intensity data were collected by

ω-scan mode within $1.190 < \theta < 24.92°$ for hkl ($-3 \leq h \leq 18$, $-14 \leq k \leq 14$, $-23 \leq l \leq 23$) in monoclinic system. Absorption corrections were employed using Psi-Scan ($T_{max} = 1.000$ and $T_{min} = 0.991$).

A perspective view of the molecular structure showing 30% displacement ellipsoid with atomic numbering scheme is shown in Fig 2.8.

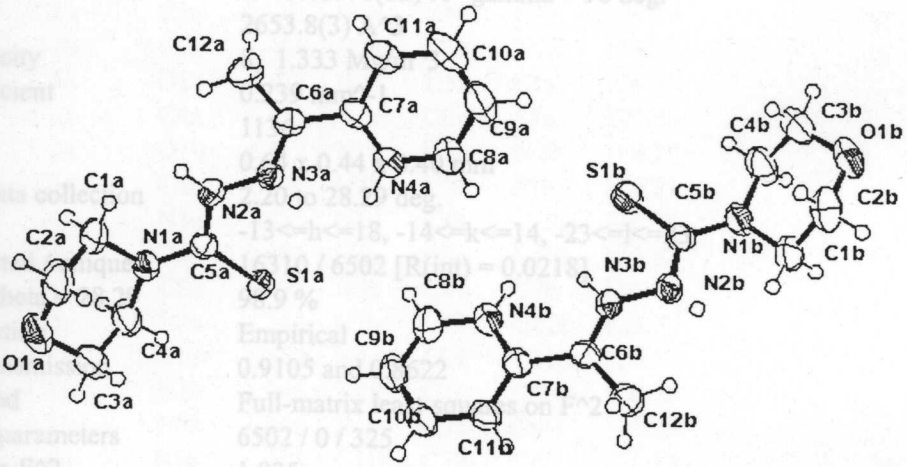


Fig 2.8. ORTEP diagram of Compound HL4M indicating H- bonding interactions between the molecules. Displacement ellipsoids are drawn at the 30% probability level and hydrogen atoms are shown as small spheres of arbitrary radii.

HL4M crystallizes in to monoclinic lattice with a non –centrosymmetric space group $P_{21/c}$ and the system belongs to C_s molecular point group. The molecular packing of the molecule in a unit cell is shown in Fig 2.10. The unit cell contains eight molecules. The molecule exists as E conformation in which the C5-N bond of the pyridine ring is *cis* to the azomethine bond and the thiosemicarbazones moiety directed away from the pyridyl nitrogen. The structure reveals quasi coplanarity and

Table 2.6
Crystal data and structure refinement for HL4M

Identification code	HL4M
Empirical formula	$C_{12}\ H_{18}\ N_4\ O\ S$
Formula weight	266.36
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P21/c
Unit cell dimensions	a = 14.1581(9) A alpha = 90 deg. b = 11.0745(7) A beta = 108.776(1) deg. c = 17.8770(12) A gamma = 90 deg.
Volume	2653.8(3) A^3
Z, Calculated density	8, 1.333 Mg/m^3
Absorption coefficient	0.239 mm^-1
F(000)	1136
Crystal size	0.64 x 0.44 x 0.40 mm
Theta range for data collection	2.20 to 28.29 deg.
Limiting indices	-13<=h<=18, -14<=k<=14, -23<=l<=23
Reflections collected / unique	16310 / 6502 [R(int) = 0.0218]
Completeness to theta = 28.29	98.9 %
Absorption correction	Empirical
Max. and min. transmission	0.9105 and 0.8622
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6502 / 0 / 325
Goodness-of-fit on F^2	1.035
Final R indices [I>2sigma(I)]	R1 = 0.0541, wR2 = 0.1418
R indices (all data)	R1 = 0.0842, wR2 = 0.1613
Largest diff. peak and hole	0.244 and -0.552 e.A^-3

Table.2.7
Selected bond lengths [Å] and bond angles [deg]

list of bond lengths (Å).			list of bond angles(Degree)			
C1b	N1b	1.469	O1a	C2a	C1a	112.11
C1b	C2b	1.486	O1b	C2b	C1b	111.58
C2a	O1a	1.423	O1b	C3b	C4b	112.24
C2a	C1a	1473	N1a	C4a	C3a	109.81
C2b	C1b	1.486	N2a	C5a	N1a	114.24
C3a	O1a	1.423	N2a	C5a	S1a	124.37
C3a	C4a	1.481	N1a	C5a	S1a	121.38
C3a	O1b	1.417	N1b	C5b	N2b	114.29
C3a	C4b	1.475	N2b	C5b	S1b	124.21
C4a	N1a	1.451	N3a	C6a	C12a	119.79
C4a	C3a	1.481	C7a	C6a	C12a	123.82
C4b	C3b	1.475	N3b	C6b	C7b	116.69
C5a	N2a	1.344	C7b	C6b	C12b	123.25
C5a	N1a	1.352	N4a	C7a	C11a	121.77
C5b	N1b	1.346	N4a	C7a	C6a	116.25
C5b	N2b	1.346	N4b	C7b	C6B	116.29
C5a	S1b	1.713	C11b	C7b	C6b	121.58
C6a	N3a	1.300	N4a	C8a	C9a	123.33
C6a	N3b	1.297	C10a	C9a	C8a	118.47
C6b	C7b	1.472	C10b	C9b	C8B	118.70
C6b	C12b	1.477	C9a	C10a	C11a	119.35
C8a	N4a	1.334	C9b	C10b	C11b	119.63
C8a	C9a	1.373	C10a	C11a	C7a	118.63
C8b	N4b	1.325	C10b	C11b	C7b	117.84
C8b	C9b	1.374	C5a	N1a	C4a	124.59
C9b	C10b	1.364	C4a	N1a	C1a	111.99

the same exists as two crystallographically equivalent molecules assembled in an offset fashion via strong intra molecular H- bonding interactions in an asymmetric unit. In each monomer, the N-N distance is less than 1.44 Å accepted as a typical of single N-N bonds, and agrees well with those of similar thiosemicarbazones [13]. The C-S distance is intermediate between those of single and double C-S bonds, 1.82 and 1.56 Å respectively, showing partial double bond character, implied by the canonical structures usually considered for thiosemicarbazones in solution. The azomethine bond length is likewise short enough to imply a partial double bond character [14]. Pyridine moiety in monomer is almost planar but the thiosemicarbazones moiety is not exactly coplanar, because C (9) C (8) N (3) and C (8) N (3) N (2) angles are 116.99^0 and 124.75^0.

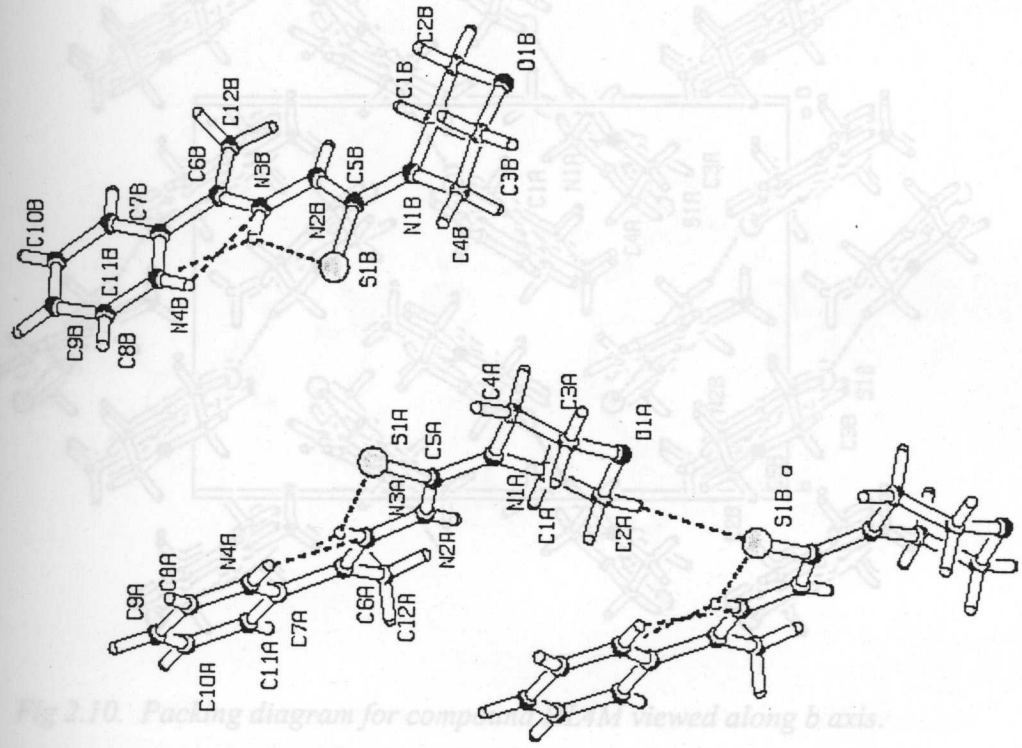


Fig 2.9. PLATON diagram of Compound HL4M, indicating H- bonding interactions between the molecules.

The morpholine moiety assumed almost chair conformation. The packing diagram shows that H of morpholino group is intermolecularly hydrogen bonded to

thione S in a molecule on one side and N (2) H to a pyridyl nitrogen of a second molecule on the opposite side (Fig 2.10). The molecules are packed into molecular columns to the *b* direction. Analysis of short ring interactions prove that the self assembly in the crystal lattice is controlled by intra and inter molecular H-bonding net works and not by the so called ring- ring interactions or herringbone interactions. Significant inter molecular hydrogen bonding (Fig 2.9) is consistent with high density [15]. Although an intermolecular N---H----S bond might be expected which crystallize in space group P_{21}/c, the N---S distance measured, 3.7 Å is well above the usual range 3.25Å.

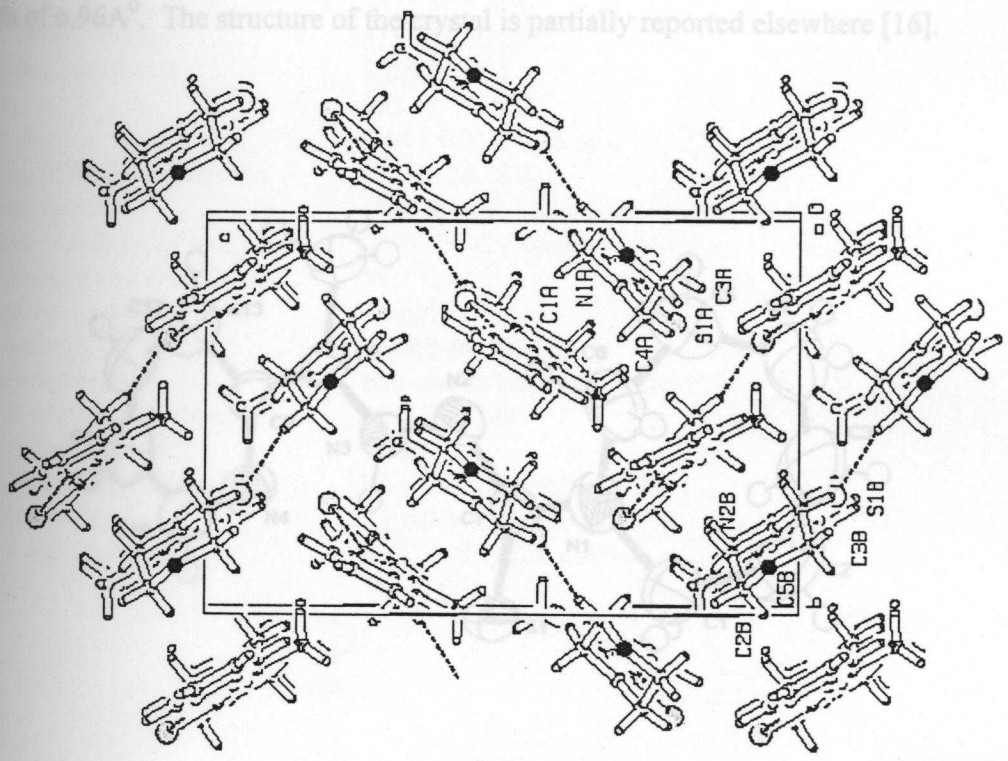


Fig 2.10. Packing diagram for compound HL4M viewed along b axis.

2.9.2 Description of crystal structure of HL4A

Suitable crystals of HL4A were grown by slow evaporation of a dilute solution of dichloromethane. Our intention was to develop the E or Z conformer of the

molecule, but what we got finally is the same E' tautomer. The crystal data, data collection and structural analysis/refinement information are summarized in Table.2.8. The bond lengths and bond angles are listed in Table 2.9

The cell dimensions for the crystals were determined using a substantial number of accurately centered reflections in a representative 2j. All non-hydrogen atoms were refined anisotropically. Refinement of the parameters was accomplished by full matrix least squares using riding model for hydrogen atoms. The idealized position of hydrogen atoms were generated from the geometries about the attached carbon atom and they were assigned fixed thermal parameters of u=0.06A^{02} and bond length of o.96A^{0}. The structure of the crystal is partially reported elsewhere [16].

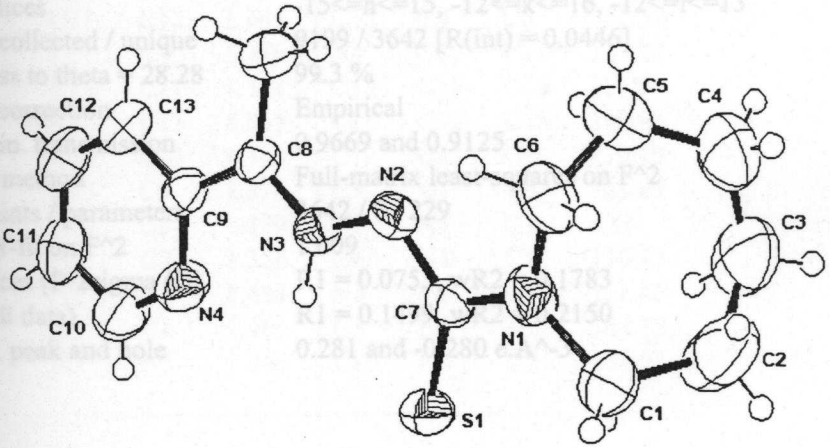


Fig 2.11 ORTEP diagram for compound HL4A, Displacement ellipsoids are drawn at the 55% probability level and hydrogen atoms are shown as small spheres of arbitrary radii.

A perspective view of HL4A is shown in Figure 2.11, intra molecular hydrogen bonding and packing of molecules are shown in fig.2.12 and 2.13 respectively. The compound HL4A crystallizes in monoclinic system and belongs to

Table 2.8.
Crystal data and structure refinement for HL4A

Identification code	HL4A
Empirical formula	C_{14} H_{20} N_4 S
Formula weight	276.40
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P21/c
Unit cell dimensions	a = 11.6605(9) A alpha = 90 deg. b = 12.5348(10) A beta = 99.437(2) deg. c = 10.2563(8) A gamma = 90 deg.
Volume	1478.8(2) A^3
Z, Calculated density	4, 1.241 Mg/m^3
Absorption coefficient	0.212 mm^-1
F(000)	592
Crystal size	0.44 x 0.31 x 0.16 mm
Theta range for data collection	2.40 to 28.28 deg.
Limiting indices	-15<=h<=15, -12<=k<=16, -12<=l<=13
Reflections collected / unique	9199 / 3642 [R(int) = 0.0446]
Completeness to theta = 28.28	99.3 %
Absorption correction	Empirical
Max. and min. transmission	0.9669 and 0.9125
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3642 / 0 / 229
Goodness-of-fit on F^2	1.009
Final R indices [I>2sigma (I)]	R1 = 0.0753, wR2 = 0.1783
R indices (all data)	R1 = 0.1499, wR2 = 0.2150
Largest diff. peak and hole	0.281 and -0.280 e.A^-3

Table 2.9
Selected bond lengths [Å] and bond angles [deg]

List of bond length(Å)			List of bond angles(degree)			
C1	N1	1.461	N1	C1	C2	115.46
C6	N1	1.454	C3	C2	C1	122.48
C6	C5	1.502	C4	C3	C2	119.75
C7	N2	1.352	C3	C4	C5	119.88
C7	N1	1.356	C4	C5	C6	116.61
C7	S1	1.711	N1	C6	C5	113.53
C8	N3	1.298	N2	C7	N1	114.04
C8	C9	1.472	N2	C7	S1	124.32
C8	C14	1.479	N1	C7	S1	121.64
C9	N4	1.339	N3	C8	C9	116.99
C9	C13	1.374	N3	C8	C14	120.22
C9	C8	1.472	C9	C8	C14	122.80
C10	N4	1.338	N4	C9	C13	122.48
C10	C11	1.380	N4	C9	C8	115.92
C11	C12	1.363	C13	C9	C8	121.59
C11	C10	1.380	N4	C10	C11	123.91
C12	C11	1.363	C12	C11	C10	117.59
C12	C13	1.365	C11	C12	C13	119.88
C13	C12	1.365	C12	C13	C9	119.19
C13	C9	1.374	C7	N1	C6	121.07
C14	C8	1.479	C7	N1	C1	122
N1	C7	1.356	C6	N1	C1	116.93
N1	C6	1.454	N3	N2	C7	111.80
N1	C1	1.461	C8	N3	N2	124.75
N2	N3	1.343	C10	N4	C9	116.93

Cs point group. The unit cell contains four molecules. The molecule exists as E tautomer with thiosemicarbazones moiety directed away from the pyridyl nitrogen. E tautomer exists in two forms *viz* E and E . However E form has a bifurcated structure, which is characterized by the following parameters.

a) A bright yellow colour, b) NMR signal of N (2) H at ca 14, 6 ppm and CH_3 (acetyl) at ca 2.48 ppm c) Intra molecular hydrogen bonding; N(2) H with thione S and pyridine Nitrogen. But E form has no intra molecular hydrogen bonding and its N(2) H signals at ca 7.58 ppm and CH3 (acetyl) at 2.41 ppm. The molecule packs with offset-hands-on type fashion along *a* axis. The packing diagram shows that N(2) H is not inter molecularly hydrogen bonded to a thione S in a molecule on one side and pyridyl nitrogen of a second molecule on the opposite side. There are no significant inter molecular interaction which is consistent with low density. Adjacent molecules are coplanar and involved only in intra molecular hydrogen bonding and existence of inter molecular hydrogen bonding remained speculative.

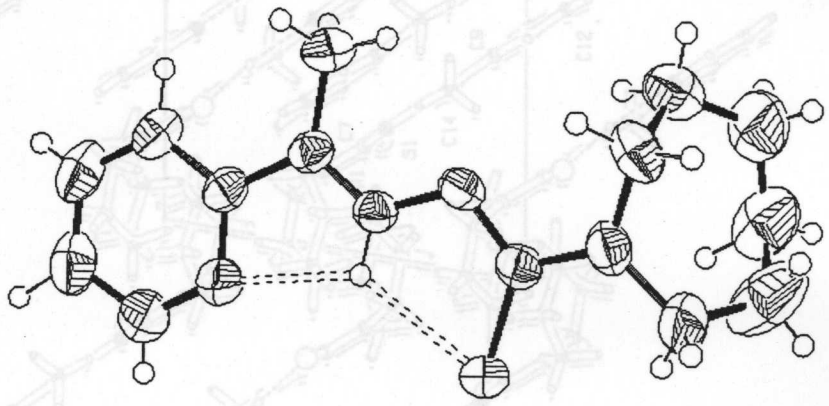


Fig. 2.12 ORTEP diagram of compound HL4A showing intra molecular H-bonding interactions.

We also noticed that C(8)-N(3)-N(2) bond angle is fairly large (124.75°) which is presumably characteristic of the E isomer. More over N(2) C(7) S(1) angle is larger (121.64°) compared to approximately 120°. This difference is attributed to the S atom's involvement in the bifurcated structure of E tautomer. The molecule is almost planar and the angle between the mean plane of the pyridine ring and thiosemicarbazones moiety is 1.43°.

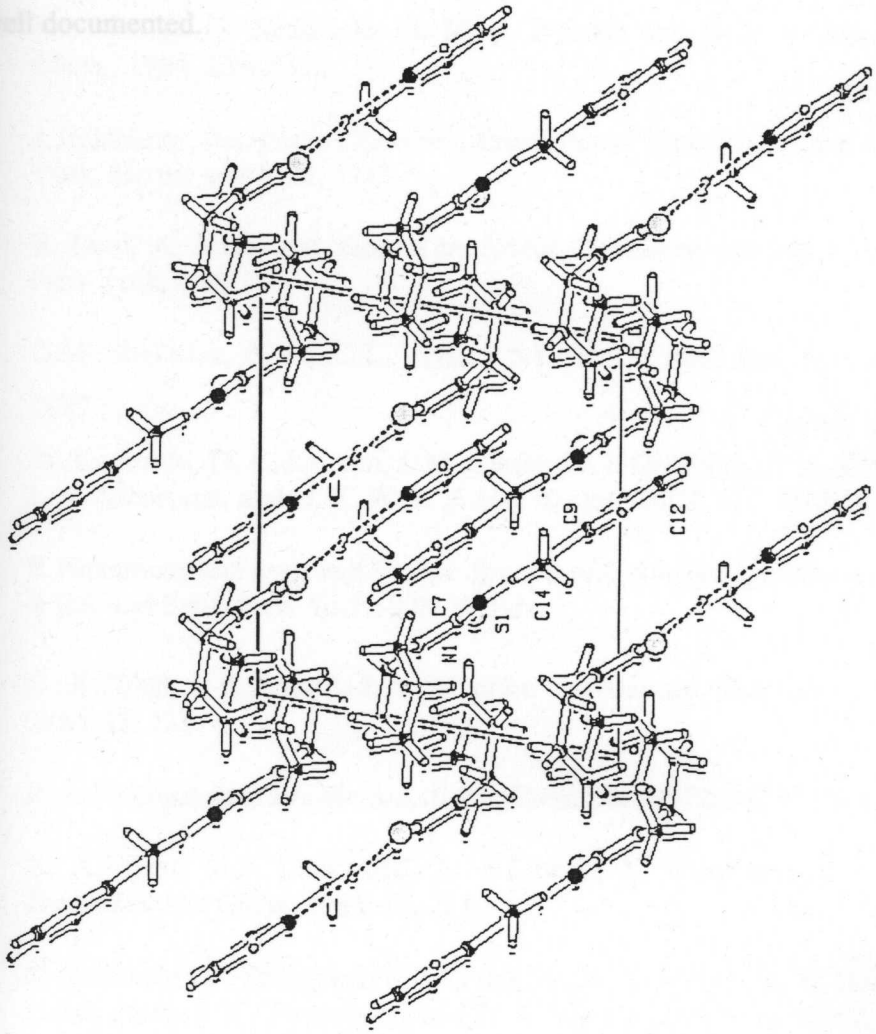


Fig 2.13. Packing diagram compound HL4A view along b axis

2.10 Concluding remarks.

Synthesized three N-N-S and two O-N-S donor ligands. They were characterized by IR, electronic, ^{1}H and, ^{13}C NMR techniques. X-ray diffraction studies of HL4M and HL4A were accomplished. Both were crystallized as monoclinic with space group P_{21}/c and existed in E conformation. HL4M had both inter and intra molecular hydrogen bonding where as HL4A had only intra molecular hydrogen bonding. The other spectral techniques used for the characterization of complexes, redox behavior of metal ion in complexes and antimicrobial activities of ligands and new complexes are well documented.

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Chapter

3

SPECTRAL, ELECTROCHEMICAL AND BIOLOGICAL STUDIES OF COPPER(II) COMPLEXES WITH N-N-S DONOR LIGANDS

3.1 Introduction

Copper with atomic number 29, atomic weight 63.546 and oxidation states from 0 to IV, has a wide variety of biochemical and physiological functions. Copper is one of the more abundant element, (20^{th} in the order of abundance), occurring at a concentration of about 100 g per ton of earth's crust [1]. It is the third most abundant transition metal element in the biological systems with an occurrence of 80-120 mg in the human body. It is a brownish red metallic element and probably the first metal from which useful articles were made. Copper objects have been found among the remains of many ancient civilizations, including those of Egypt, Asia Minor, China, South Eastern Europe, Cyprus (from which the word copper is derived) [2]. It is also found in the pure state and because of its many desirable properties such as its conductivity of electricity and heat, resistance to corrosion, malleability, beauty, and it has long been used in a wide variety of applications. Copper and its salts are highly toxic to lower organism, it is also poisonous to man in large quantities, and it is an essential constituent of proteins and enzymes [3]. Like other transition metals, copper is very important as a catalyst in the oxidation of organic molecules by atmospheric oxygen. Copper occurs in a range of oxidation states and the ions readily form complexes with extensive variety of stereochemistry and stoichiometry [4]. The copper(II) state is significantly more common and it is extensively involved as an intermediate oxidation state in mechanistic studies especially those involving

amino acid species. Under normal conditions it forms a wealth of simple compounds and coordination compounds and most prolific in the formation of good crystals [5]. Its major role in the biological systems is to trigger the reduction of oxygen to the substrate; it is acting as a biological catalyst [6] as a super oxide dismutase has a specific but important role of removing the highly reactive super oxide anion. The importance of copper(II) in oxygenation reaction has been reviewed [7]. The question of copper promoted reaction in aromatic chemistry and role of organometallic complexes in organic reaction has been widely investigated. In general the role of copper(II) is intimately involved and related to the presence of Cu(I) and Cu(II) oxidation states; although there is a little or no information on the stereochemistry of various Cu(I) and Cu(II) complexes or their mechanism of involvement [8]. Investigations in the magnetic properties of Cu(II) complexes show considerable interest. Magneto chemical and spectroscopic investigations are used to estimate molecular and electronic structures and to calculate the ligand field parameters and M-L chemical bond of Cu(II) coordination compounds [9].

Thiosemicarbazones and their copper complexes have been studied in recent years owing to their pharmacological interest. Thiosemicarbazones react as chelating ligands with transition metal ions by bonding through the thioketo sulphur and hydrazine nitrogen atoms. Therefore these types of compounds can coordinate *in* vivo to metal ion. Because of such coordination, the thiosemicarbazone moiety undergoes a sterical reorientation that could favor its biological activity.

Copper forms a variety of octahedral square planar square pyramidal, trigonal bipyramidal complexes with thiosemicarbazones. Electrochemical, structural and spectral investigations offer an insight in understanding various physico chemical properties such as stabilities, reaction pathways and structures and .such informationas are reported [10]. Biological activities of some N-N-S donor ligands have been screened and the results were appealing. Initial interest in such substituted derivatives of thiosemicarbazones derivatives arose from their marked antibacterial properties. It is reported that the nature of the substituent attached to the ^{4}N position

of thiosemicarbazone can influence the biological activity while the acid character of ^{2}NH allows the ligand to be anionic and conjugation to be extended to include the thiosemicarbazone moiety [11]. It has been proposed that this conjugated system enhances the antitumour activity. Most studies to date have focused on the metal free ligands; it has been shown that they are inactive or partially active than the metal free chelates. The thiosemicarbazones have been found to be more active against influenza protozoa, smallpox, and certain kinds of tumor. They have been suggested as possible pesticides and fungicides. Higher activity of these compounds has frequently been thought to be due to their ability to chelate free metals [12]. Petering *et al* showed that the active intermediate in the antitumour activity of 3-ethoxy – oxo butralehyde bis (thiosemicarbazone) was the copper(II) chelate. These findings have lead recently to an increased interest in the chemistry of copper chelate of thiosemicarbazones [13].

In this chapter, we have attempted to explore the magnetic, spectral, redox properties and antimicrobial studies of copper(II) complexes of 2-acetylpyridine ^{4}N-morpholine thiosemicarbazone, (HL4M) and 2-acetylpyridine ^{4}N- pyrrolidine thiosemicarbazone, (HL4P) having general composition, [Cu(L4M)X], [Cu(L4A)X] $[Cu(L4M)H_2O]ClO_4$ and $[Cu(HL4M)SO_4]$ where, (X = Cl, Br, I, NCS, NO_3, OAc, ClO_4, N_3, and H_2O etc). We expected coordination is most often *via* the pyridyl nitrogen, imine nitrogen and thiolate or thione sulphur when coordinating as the anionic or neutral ligand. In such investigations we used different spectral techniques such as IR, electronic and EPR to explore the geometry and stereochemistry of new complexes.

3.2 Experimental

3.2.1 Materials

The syntheses of HL4M and HL4P are described in Chapter.2. The solvents were of AR grade and purified by standard methods. Various copper(II) salts (GR, Qualigen's fine chemicals) were purified by standard methods. Copper perchlorate hexahydrate was obtained by treating GR copper carbonate with 1:1 perchloric acid, followed by evaporation and crystallization.

3.2.2 Syntheses of complexes

The method for isolation of Cu(II) complexes of HL4M and HL4P is described below.

Chloro[1H-morpholine-1-thiocarbohydrazonato-1-(2-pyridinyl)ethylidene] copper(II), [Cu(L4M)Cl], **1**

A solution of 1.0574 g (4 mmol) of HL4M in 25 mL of hot methanol was refluxed with 0.681 g (4 mmol) of copper chloride dihydrate in 25 mL of hot methanol for 3 h. The crystalline complex which separated on cooling was collected, washed well with hot water, methanol and ether and dried *in vacuo* over P_4O_{10}.

Bromo[1-H-morpholine-1-thiocarbohydrazonato-1(2-pyridinyl)ethylidene] copper(II), [Cu(L4M)Br], **2**

A solution of 1.0574 g (4 mmol) of HL4M in 25 mL of hot methanol was refluxed with 0.895 g (4 mmol) of copper bromide in 20 mL of hot methanol for 3 h. On cooling micro crystals of the respective compound in appreciable yield was crystallized out. The compound was filtered off, washed with hot water, methanol and, ether and dried *in vacuo* over P_4O_{10}.

Iodo [1-H morpholine-1-thiocarbohydrazonato -1 (2-pyridinyl) ethylidene]copper(II), [Cu(L4M)I], **3**

A solution of 0.6460 g (4 mmol) of copper nitrate dihydrate and 0.61 g (4 mmol) sodium iodide in methanol was boiled for 15 minutes and then chilled in ice. The precipitated sodium nitrate was filtered off and the filtrate was treated with a

solution of 1.0574 g (4 mmol) of HL4M in 25 mL hot methanol. The mixture is refluxed for 30 minutes and cooled, when micro crystals of compound in decent yield crystallized out. The compound was filtered off, washed with water, methanol and ether and dried *in vacuo* over P_4O_{10}.

Acetato[1-Hmorpholine-1-thiocarbohydrazonato-1(2-pyridinyl)ethylidene] copper(II) monohydrate, [Cu(L4M)Ac].H_2O, **4**

A solution of 1.0574 g (4 mmol) of HL4M in 25 mL hot methanol was refluxed with a solution of 0.798 g (4 mmol) of copper acetate monohydrate in 20 mL of hot methanol for 2 h. On cooling micro crystals of the respective compound in decent yield crystallized out. The compound was filtered off, washed with hot water methanol and ether and dried *in vacuo* over P_4O_{10}.

Nitrato[1-H-morpholine-1-thiocarbohydrazonato-1(2-pyridinyl)ethylidene]copper(II) [Cu(L4M)NO_3], **5**

A solution of 1.0574 g (4 mmol) of HL4M in 25 mL hot methanol was refluxed with a solution of 0.6460 g (4 mmol) of copper nitrate dihydrate in 20mL of hot methanol for 3 h. On cooling micro crystals of the respective compound in decent yield crystallized out. The compound was filtered off, washed with hot water, .methanol and ether and dried *in vacuo* over P_4O_{10}.

Thiocyanato[1-H-morpholine-1-thiocarbohydrazonato-1(2-pyridinyl)ethylidene] copper(II), [Cu(L4M)NCS], **6**

A solution of 2 mmol of. chloro [1H-morpholine-1-thiocarbohydrazonato-1-(2-pyridinyl) ethylidene] copper(II) in 100 mL of refluxing propionitrile was treated with a solution of 0.250 g (2.55 mmol) of KCNS in 30 mL of propionitrile. The solution was heated under reflux for 30 minutes and chilled. On cooling micro crystals of the compound in decent yield crystallized out. The compound was filtered off, washed with hot water, methanol and ether and dried in vacuo over P_4O_{10}.

Azido[1-H-morpholine-1-thiocarbohydrazonato-1-(2-pyridinyl)ethylidene]copper(II) [Cu(L4M)N_3], **7**

A solution of 2 mmol of. chloro [1H-morpholine-1-thiocarbohydrazonato-1-(2-pyridinyl) ethylidene] copper(II) in 100 mL of refluxing propionitrile was treated with a solution of 0.17 g (2.55 mmol) of sodium azide in 30 mL of propionitrile. The solution was heated under reflux for 30 minutes and chilled. On cooling micro crystals of the compound in decent yield crystallized out. The compound was filtered off, washed with hot water, methanol and ether and dried *in vacuo* over P_4O_{10}.

1-H-morpholine-1-thiocarbohydrazonato-1(2-pyridinyl)ethylidene]}sulphato copper(II), [Cu(HL4M)SO_4], **8**

A solution of 0.5287 g (2 mmol) of HL4M in 25 mL of hot methanol was refluxed with 0.50 g (2 mmol) of copper sulphate pentahydrate in 20 mL of hot methanol for 3 h. On cooling micro crystals of the respective compound in appreciable yield crystallized out. The compound was filtered off, washed with hot water, methanol, and ether and dried *in vacuo* over P_4O_{10}.

Aqua [1-H morpholine-1-thiocarbohydrazonato-1 (2-pyridinyl) ethylidene] copper(II) perchlorate, [Cu (L4M)H_2O] ClO_4, **9**

Copper perchlorate hexahydrate (1.12 g, 3 mmol) in methanol (15 mL) was added to a hot solution 3 mmol of HL4M in methanol. The solution was refluxed for 2 h and chilled. On cooling dark green micro crystals of the respective compound in appreciable yield crystallized out. The compound was filtered off, washed with water, methanol and ether and dried *in vacuo* over P_4O_{10}. Complexes such as [Cu(L4P)Cl]; **10,** [Cu(L4P)Br], **11** and [Cu(L4P)OAc]H_2O, **12** with HL4P have been prepared by the same procedure adopted for the preparation of copper(II) complexes with HL4M.

3.2.3 Measurements

Details regarding the analytical measurements and other characterization techniques used are reported in Chapter 2.

3.3 Results and discussion

The colours, molar conductivities, magnetic susceptibilities and partial elemental analyses of Cu(II) complexes with N-N-S donors are listed in Table 3.1. The complexes are monomeric with a 1:1:1 ratio of metal ion, thiosemicarbazone and gegenions. The colours of both series of complexes indicate that the thiosemicarbazones moiety determines the colour rather than the particular gegenions that occupy the fourth coordination position.

Thiosemicarbazones can coordinate metal ions as neutral ligands or as anionic species. The micro analytical data indicates that HL4M and HL4P enolise and deprotonate on complexation. The fourth coordination position is taken by mono or polyatomic anion or water molecule as confirmed by IR spectra of the complexes and their geometry is probably square planar. In contrast, complex **8** has one neutral ligand. The complexes **4** and **12** contain one water molecule, which is lattice water, as confirmed by IR data. The complexes are insoluble in most of the common polar and non-polar solvents. They are however soluble in propionitrile, dimethylformamide and dimethyl sulphoxide. Conductivity measurements at room temperature were made in dimethylformamide (10^{-3}M), showing non electrolytic nature of the complexes.

3.3.1 Magnetic susceptibility

Magnetic susceptibility measurements were carried out at room temperature using Gouy balance and calculations were made using computed values of Pascal's constants for diamagnetic corrections. The magnetic moments of the complexes are in 1.77 and 2.11 BM range. The room temperature magnetic moments of the copper(II)

Table 3.1
Analytical data, conductivity, magnetic moments, colours and yield of Cu(II) complexes with N-N-S donor ligands

Compound	Emp.formula [b]	Yield (%)	Colour	μ [c] (BM)	ΛM [d]	Analytical data Found (Calcd) %			
						C	H	N	Cu
CuL4MCl, **1**	$C_{12}H_{15}N_4OSClCu$	62	Brown	1.80	18	39.91 (39.78)	4.27 (4.17)	15.33 (15.46)	17.49 (17.50)
CuL4MBr, **2**	$C_{12}H_{15}N_4OSBrCu$	64	Green	1.92	21	35.34 (35.43)	3.95 (3.72)	13.94 (13.77)	15.64 (15.62)
CuL4MI, **3**	$C_{12}H_{15}N_4OSICu$	56	Green	1.77	19	31.44 (31.76)	3.03 (3.33)	12.18 (12.34)	14.12 (14.00)
CuL4MAc.H_2O, 4	$C_{14}H_{20}N_4O_4SCu$	69	Brown	1.88	21	41.64 (41.52)	5.11 (5.23)	14.02 (13.84)	15.72 (15.69)
CuL4MNO_3, **5**	$C_{12}H_{15}N_5O_4SCu$	63	Green	1.91	32	37.26 (37.06)	3.89 (3.88)	18.11 (18.01)	16.40 (16.35)
CuL4MNCS, **6**	$C_{13}H_{15}N_5OS_2Cu$	69	Green	2.01	24	40.01 (40.56)	3.85 (3.93)	18.15 (18.19)	16.54 (16.50)
CuL4MN_3, **7**	$C_{12}H_{15}N_7OSCu$	57	Green	1.82	11	39.12 (39.07)	3.98 (4.09)	26.46 (26.57)	17.25 (17.23)
CuHL4MSO_4, **8**	$C_{12}H_{18}N_4O_6S_2Cu$	60	Green	2.11	41	41.01 (40.87)	4.91 (4.72)	15.46 (15.89)	09.02 (09.01)
CuL4MH_2OClO_4, **9**	$C_{12}H_{17}N_4O_6SClCu$	63	Green	1.99	38	32.57 (32.44)	4.02 (3.86)	12.94 (12.61)	14.42 (14.30)
CuL4PCl, **10**	$C_{12}H_{15}N_4SClCu$	64	Brown	1.89	19	41.15 (41.61)	3.98 (4.36)	16.42 (16.18)	18.16 (18.35)
CuL4PBr, **11**	$C_{12}H_{15}N_4SBrCu$	60	Green	1.91	21	36.48 (36.88)	3.48 (3.87)	13.92 (14.33)	16.13 (16.26)
CuL4PAc.H_2O, **12**	$C_{14}H_{20}N_4O_3SCu$	63	Brown	2.01	20	43.53 (43.23)	5.36 (5.44)	14.63 (14.40)	16.31 (16.34)

[b] Emperical formula. [c] Magnetic moment [d] Molar conductivity, 10^{-3}M solution (DMF) at 298 K

complexes indicate that they are magnetically dilute and contains one unpaired electron as expected for Cu(II) complexes. The corrected magnetic moments are within the normal values for copper(II) complexes in a square planar tetra coordinated environment [14,15].

The molar conductivity values for the copper(II) complexes in dimethyl formamide fall well below 25 Ω cm^{-1} mol^{-1} for 1:1 electrolytes. It indicates that both gegnions and the monoanionic thiosemicarbazones are coordinated to the copper(II) ion. However, for nitrate and perchlorate complexes the values are higher than the values reported for 1:1 electrolytes, indicating non coordinated or ionisable nature of gegnions in the complexes.

3.3.2 Vibrational spectra

The significant IR bands with the tentative assignments of HL4M, HL4A and their copper(II) complexes in the region 4000-200 cm^{-1} are presented in the Table 3.2 and IR spectra of some of the representative complexes, in the 800–200 cm^{-1} regions are shown in Fig 3.1. The thiosemicarbazones contain the thioamide function -NH-C(S)-NH_2- and consequently they exhibit thione thiol tautomerism [16]. The vibrational spectra of the thiosemicarbazones, do not display any ν(S-H) band in the range 2600-2570 cm^{-1}, but exhibit the ν(NH) band at *ca* 3160 cm^{-1}, indicating that in the solid state they remain as thioketo tautomer.. However, when dissolved in the presence of copper(II) salts, they readily tautomerise to thiol form with concomitant formation of copper(II) complexes of deprotonated ligand [17]. The thiosemicarbazone ligands not only coordinate with metal ion in deprotonated form but protonated form also. It is found that with copper sulphate salt, the principal ligand yielded a copper(II) complex **8** containing the neutral form of the ligand and it contains ν(NH) band of the free ligand.

The higher bands at 1371 and, 1315 cm^{-1} and a lower bands at 869 and 892 cm^{-1} are considered to have significant contribution from the ν(C=S) band in HL4M and HL4P respectively. The substantial shift of these bands to lower energies is an

Table 3.2
Selected IR bands (cm^{-1}) with tentative assignments of Cu(II) complexes with N-N-S donor ligands

Compd	$\nu(^6C=^1N)$	$\nu(^1N\,^2N)$	ν(C=S)	ν(C=S)	δ_{op}	δ_{ip}	$\nu(Cu\,^2N(azo)$	$\nu(Cu\,N_{pyr})$	ν (Cu-S)	ν (Cu-X)	$\nu\,(^2N=^3C)$
HL4M	1627 s	1010 m	1371 m	892 m	649 m	408 m	----	----	----	----	----
CuL4MCl	1620 s	1040 m	1263 s	842 m	659 m	432 m	383 s	344 sh	328 w	331 s	1591 m
CuL4MBr	1640 s	1026 m	1279 s	837 m	667 m	434 m	412 s	341 w	341 sh	231 s	1592 s
CuL4MI	1607 s	1034 m	1243 m	839 m	661 m	431 m	391 m	334 m	337 s	----	1590 sh
CuL4MAc.H_2O	1607 s	1030 m	1276 m	829 m	670 m	432 m	390 m	332 w	333 s	318m,28m	1593 sh
CuL4MNO_3	1600 s	1013 m	1236 s	836 m	673 m	442 m	389 m	329 sh	320 s	309 w	1591 sh
CuL4MNCS	1607 s	1028 m	1270 s	826 m839m	663 m	421 m	396 m	328 sh	329 sh	321 sh	1601 sh
CuL4MN_3	1606 s	1046 m	1270 s	837 m	656 m	433 m	393 m	331 sh	341 sh	446 sh	1601 sh
CuHL4MSO_4	1609 s	1034 m	1236 s	886 m	663 m	431 m	395 m	332 sh	332 sh	337 m	1603 m
CuL4MH_2OClO_4	1607 s	1023 m	1236 s	829 m	676 m	434 m	397 m	339 sh	326 sh	320 m	1601 sh
HL4P	1598 s	1008 m	1315 s	869 m	624 m	409 m	----	----	----	----	
CuL4PCl	1580 s	1018 m	1277 s	814 m	641 m	430 sh	382 s	345 sh	339 w	331 sh	1571 sh
CuL4PBr	1589 s	1021 m	1290 s	807 m	644 m	432 m	414 s	341 w	334 w	247 m	1570 sh
CuL4PAc.H_2O	1607 s	1015 m	1288 s	829 m	640 m	431 m	389 m	326 s	340 sh	280w.319sh	1581 sh

$_s$ = strong, $_m$ = medium; $_w$ = weak; $_{sh}$ = shoulder.

indication of sulphur coordination and the results obtained are in agreement with the results reported by other workers [18].

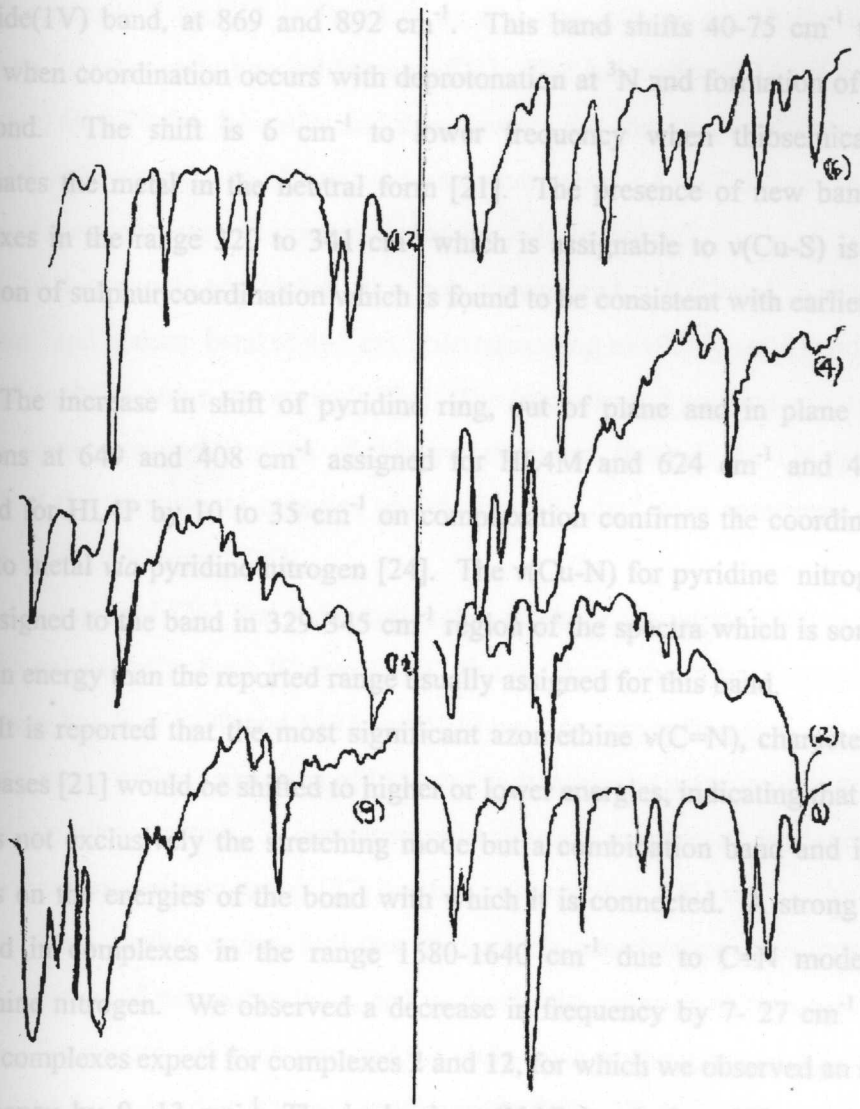


Fig. 3.1 Far IR spectra of the copper complexes in the region 50-500 cm^{-1}

Recent studies [19] have assigned a number of bands as having contributions from ν(C=S) in a complex but the many ring vibrations contribute to the complexity of the spectra in the thiosemicarbazones which makes band other than the thioamide (1V) band difficult to assign. It is reported that the thioamide bands are 1[β(NH)+

γ(CN)], 111[γ(CN) + β(NH)] and 1V[γ(C=S)] and usually these bands appear at 1579, 1275 and 877 cm^{-1} respectively. The uncomplexed thiosemicarbazones show the thioamide(1V) band, at 869 and 892 cm^{-1}. This band shifts 40-75 cm^{-1} to lower energy when coordination occurs with deprotonation at ^{3}N and formation of a single C-S bond. The shift is 6 cm^{-1} to lower frequency when thiosemicarbazone coordinates the metal in the neutral form [21]. The presence of new band in the complexes in the range 320 to 341 cm^{-1} which is assignable to ν(Cu-S) is another indication of sulphur coordination which is found to be consistent with earlier reports [20].

The increase in shift of pyridine ring, out of plane and in plane bending vibrations at 649 and 408 cm^{-1} assigned for HL4M and 624 cm^{-1} and 409 cm^{-1} assigned for HL4P by 10 to 35 cm^{-1} on complexation confirms the coordination of ligand to metal *via* pyridine nitrogen [24]. The ν(Cu-N) for pyridine nitrogen has been assigned to the band in 329-345 cm^{-1} region of the spectra which is some what higher in energy than the reported range usually assigned for this band.

It is reported that the most significant azomethine ν(C=N), characteristic of Schiff bases [21] would be shifted to higher or lower energies, indicating that ν(C=N) mode is not exclusively the stretching mode but a combination band and its value depends on the energies of the bond with which it is connected. A strong band is observed in complexes in the range 1580-1640 cm^{-1} due to C=N mode of the azomethine nitrogen. We observed a decrease in frequency by 7- 27 cm^{-1} for this band in complexes expect for complexes **2** and **12**, for which we observed an increase in frequency by 9- 13 cm^{-1}. The hydrazine ν(N-N) band also shifts to the lower wavenumbers consistent with azomethine nitrogen coordination [22]. Furthermore, coordination of azomethine nitrogen is confirmed by the presence of a new band at 383-414 cm^{-1} assignable to ν(Cu-N) for these complexes [29]. The presence of $\nu(CuN_{py})$, $\nu(Cu\text{-}N_{azomethine})$, and ν(Cu-S) in the ranges of 329-345 cm^{-1}, 383 to 414 cm^{-1} and 320-341 cm^{-1} respectively indicated that the ligands are coordinated *via* the azomethine nitrogen, pyridine nitrogen, and mercaptide sulphur atom.

The chloro complexes **1** and **10** of both ligands show a sharp ν(Cu-Cl) band at 331 cm,$^{-1}$indicating terminal rather than bridging chlorine. The ν(Cu-Br) band for the bromo complexes **2** and **11** is found at *ca* 231 and 247 cm^{-1}. These values are suggestive for terminally bonded bromine [23]. The ratio ν(Cu-Br) / ν(Cu-Cl) is in the range 0.69-0.70 for the solids and same results are consistent with usual values obtained for the complexes of first row transition series. As ν(Cu-I) is beyond the window of measurements, it is not assigned for iodo complex **3**.

The thiocyanato complex **6** has a very strong band at 2072 cm^{-1}, a strong band at 839 cm^{-1} and a sharp band at 485 cm^{-1} corresponding to ν(CN), ν(CS) and δ(NCS) modes of the NCS group respectively [24]. The intensity and position of these bands indicate unidentate coordination of thiocyanate group through the nitrogen. The ν(Cu-N) of the thiocyanato complex observed at 321 cm^{-1} is in agreement with the reported value of 325 cm^{-1} [25].

It is reported [26] that the coordination mode of the nitrate group cannot be deduced unequivocally from IR data alone. But we found that nitrato complex **5** has three strong bands at 1270 and 1391 and 1010 cm^{-1} corresponding to ν_1 ν_4 and ν_2 of the nitrato group with a separation of 121 cm,$^{-1}$ indicating the presence of a terminally monodentate nitrato group. A combination band $\nu_1+\nu_4$, considered as diagnostic for the monocordinate nitrato group [27] has been observed at 1761 cm^{-1}. The absence of a split band in this region indicates that strong coordination of nitrate ions is unlikely. We could not assign ν_3, ν_5 and ν_6 due to the richness of the spectra of the complex. For nitrato solids, it reported the ν(Cu-N) is in the range of 250-350 cm^{-1} and we identified a band at 309 cm^{-1} for this mode [28].

The acetato complexes **4** and **12** have bands at 1620 and 1395 cm^{-1} corresponding to asymmetric and symmetric COO^- stretching bands respectively, which are in agreement with the acetate group being monodentate. The ν(Cu-O) of acetate solids at *ca* 319 and 280 cm^{-1} is based on the assignment of Baldwin *et al.* A medium intensity broad band observed in the solid around 3329 cm^{-1} probably due to the presence of non-coordinated water.

The perchlorate complex **9** shows a single broad band at 1120 cm^{-1} and a strong band at 620 cm^{-1}, indicating the presence of ionic perchlorate [29]. The band at 1120 cm-^{1} is assignable to $\nu_3(ClO_4)$ and an unsplit band at 620 cm^{-1} assignable to $\nu_4(ClO_4)$. More over, no bands assignable to $\nu(930cm^{-1})$ or $\nu_2(460\ cm^{-1})$ are observable in its spectra. This along with unsplit ν_3 and ν_4 bands shows exclusive presence of non-coordinated perchlorate group having C_{3v} symmetry and it is supposed to be descended from T_d symmetry due to lattice effects [30]. Bands at 3317, 1627, 601 and 423 cm^{-1} attributable to ν(O-H), $\delta(OH_2)$, π, $w(OH_2)$, and ν(CuO) are of coordinated water. Accordingly, it appears that the water molecule occupies the fourth coordination position.

The azido complex **7**, shows a single broad band at 2047 cm^{-1} and a strong band at 1340 cm^{-1}. These are assigned to ν_a and ν_s. The broad band at 656 and 446 cm^{-1} are assigned to δ(N-N-N) and ν(Cu-N) bands. This suggests that Cu-N-N-N bond is linear.

For sulphato solid **8**, the bonding of the neutral ligand is to be considered. As usual the bonding of thiosemicarbazone moiety in **8** is through azomethine nitrogen, indicated by a substantial shift of the ν(C=N) to lower energy and pyridyl nitrogen, shift of $\delta_{(op)}$ and $\delta_{(ip)}$ to higher energy and third site would be by thione sulphur because $\nu(^{3}NH)$ is found in the region 3240-3320 cm^{-1} for the uncomplexed thiosemicarbazones (HL4M) remained undisturbed in the complex suggestive of unionized thiosemicarbazones. Coordination *via* thione sulphur atom is indicated by a decrease in frequency of the thioamide band by 6 cm^{-1} in the spectrum of complex. This fact can be due to a decrease in the double bond character of C=S bond and the change in the conformation along N-C bond on complexation [31]. The presence of a weak non-ligand band in the region 320-336 cm^{-1} further confirms sulphur coordination. The fourth coordination position is occupied by sulphate ion which is having T_d symmetry in the uncomplexed form and the symmetry would be descending to C_{2v} when coordinated as bidentate group. The sulphato complex

shows bands at *ca* 1270 cm^{-1}, 1115 cm^{-1}, 1034 cm^{-1} due to ν_3, 710 cm^{-1}, 649 cm^{-1}, 575 cm^{-1}, due to ν_4, 977 cm^{-1} due to ν_1 and 460 cm^{-1} due to ν_2 and these are assignable to a bidentatively coordinated sulphato group. Of the four fundamental vibrations two of them will be IR active in the free state but due to descending the symmetry, two of the Raman active vibrations would then become IR active [32] and we assigned four bands as mentioned above in the region between 500 and 1150 $cm.^{-1}$ Vibrations due to ν_1 and ν_2 appear with medium intensity. However, it is found that vibrations due to ν_3 and ν_4, each band splits in to three bands. These results can be interpreted in terms of lowering of symmetry from T_d to C_{2v} and which indicates bidentate coordination of the sulphate anion. The probable geometry of the compound will be a distorted square pyramidal.

3.3.3 Electronic spectra

The electronic spectra of copper(II) complexes is probably the most easily determined electronic property to measure but equally the most difficult from which to obtain useful structural information, due to flexible stereochemistry of the copper(II) ions [33]. The electronic states of several transition metal complexes have been extensively studied in the last two decades and detailed knowledge has been accumulated for octahedral complexes. An interesting review [34] gives the electronic states of biologically important complexes.

There is extraordinary amount of spectroscopic interaction available in the literature because of the general ease with which copper(II) complexes can be made By far the bulk of this consists of complexes with a single broad poorly resolved asymmetric band in the visible region. The copper(II) complexes of lower coordination number are also appear to exist in a wide range of stereo chemistries making it difficult to use electronic spectroscopy alone as a definitive tool for identifying structure [35]. .Although there is an enormous body of copper(II) electronic spectra in the literature [36] such of it is published with out full knowledge of the detailed structure of the complex concerned, and is therefore often ambiguous. We used average environment rule to predict copper(II) spectroscopic band centers.

Table.3.3
Electronic spectral data (nm) for the Cu (II) complexes with N-N-S donor ligands (€ are given in units of dm^3 mol^{-1} cm^{-1})

Compound	mode	d-d	CT	$n \rightarrow \pi^*$	$\pi \rightarrow \pi^*$
HL4M	Solid	----	----	393.	255.
	DMF	----	----	391 (3.96)	255 (4.02)
CuL4MCl	Solid	560., 640.sh	411, 430.	392, 340.	243
	DMF	588.sh (2.41)	450.(3.98)	392, 346 sh (4.02)	250., 256. sh (4.21)
CuL4MBr	Solid	570	381, 440 sh 473.	391, 388	265., 256
	DMF	582 sh (2.37)	452..(3.01)	394, 344.3 sh (4.11)	257.,251sh (4.16)
CuL4MI	Solid	590 s 609. sh	442..	352	264, 261
	DMF	554 s521. sh (2.15)	441, 411. sh (3.98)	392., 332 sh (4.05)	258, 242 sh (4.41)
CuL4MAc.H_2O	Solid	746.s 570	430, 427	360, 390.	252, 268
	DMF	561 s 571.sh (2.18)	420	396., 352 sh (3.06)	255 sh (4.21)
CuL4MNO_3	Solid	580., 549	435	352, 304.	257
	DMF	580.sh (2.31)	413, 415 sh (3.01)	396., 346.sh (4.01)	249, 257 sh (4.13)
CuL4MNCS	Solid	650, 570	437, 426	390	268, 254
	DMF	576 sh (2.25), 555.	429 sh (3.96)	393 (3.98)	257 sh (4.36)
CuL4MN_3	Solid	660, 524.	418.	383.	261., 255 sh
	DMF	562., 545 sh (2.36)	433 m, 411 sh (3.02)	394, 380. sh (4.02)	257 , 243.sh (4.14)
CuHL4MSO_4	Solid	590.s, 565	446 s, 427.	349.	254.
	DMF	589 s 567 sh (2.21)	416. (3.84)	392., 374 sh (4.05)	257., 253 sh (4.36)
CuL4MH_2OClO_4	Solid	589	428.	375, 318	291
	DMF	577 sh (2.16)	420, 405 sh (3.90)	304 (4.11)	259, 238 sh (4.27)
HL4P	Solid	----	----	360, 349.	255.
	DMF	----	----	329.(3.06)	259 (4.11)
CuL4PCl	Solid	585.	404 s 395.sh	334 , 294	276 vs 254.
	DMF	573.sh (2.26)	400, 390.sh (3.92)	331, 284 sh(4.09)	255., 237 sh (4.39)
CuL4PBr	Solid	575.	380	330, 312	257, 251.sh
	DMF	570.sh (3.94)	418.s 35 9sh (3.94)	287.(3.98)	255 sh (4.27)
CuL4PAc.H_2O	Solid	566	418.s, 359	328, 323 m	254. 248
	DMF	561sh (2.18)	438, 390.sh (3.90)	328 (4.01)	257.(4.12), 250 sh

The significant electronic absorption bands in the spectra of the complexes recorded in dimethylformamide solution and in the polycrystalline state are presented in the Table. 3.3

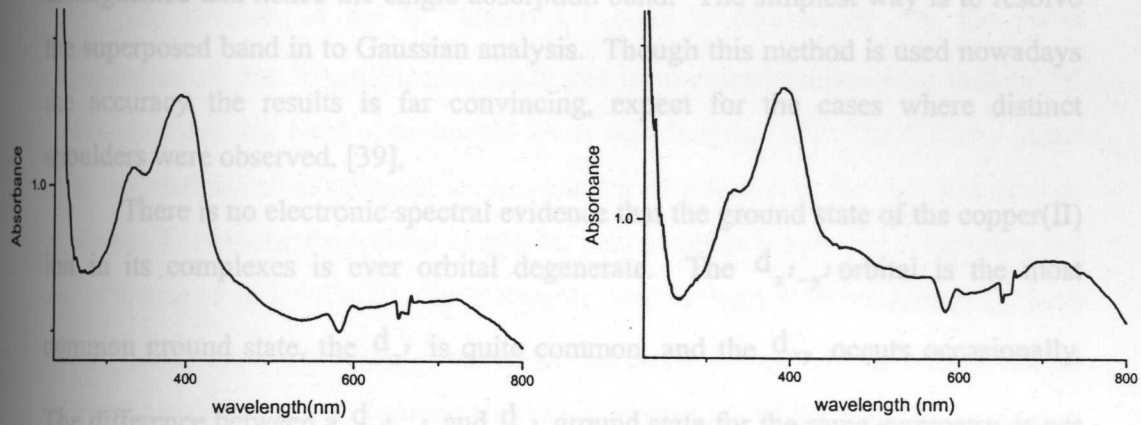


Fig 3.2 Uv-Vis Diffuse Reflectance Spectra of the copper complexes **1** *and* **9**

The electronic spectra of HL4M in solution consists of two broad bands at 410 and 255 nm and for HL4A, these bands appear at 349 & 255 nm. These two regions remained almost unshifted in the complexes showing that they are intra ligand.bands. The spectra of complexes at higher concentration consist of a high frequency broad band at *ca* 540- 680 nm with occasionally a low frequency shoulders. These spectra are consistent with square planar, elongated tetragonal or square pyramidal but not tetrahedral stereochemistry [37]. All copper complexes exhibit a d-d band frequently with shoulders in the visible region whose maximum of absorption lies in the visible region λ_{max} (550 to 630 nm). Such a feature is expected for a square planar chromophore in accordance with earlier reports. It is reported [38] that for square planar complexes with $d_{x^2-y^2}$ ground state, three spin allowed

transitions are possible $^2B_{1g} \rightarrow {}^2A_{1g}$, $^2B_{1g} \rightarrow {}^2B_{2g}$ and $^2B_{1g} \rightarrow {}^2B_{2g}$. These may also be represented respectively as $d_{x^2-y^2}, d_{z^2} \rightarrow d_{xy}$ and $d_{x^2-y^2} \rightarrow d_{xz}, d_{yz}$ and it is difficult to resolve it in to three bands. Since the four lower orbitals are often so close together in energy that individual transfer there from to the upper d level cannot be distinguished and hence the single absorption band. The simplest way is to resolve the superposed band in to Gaussian analysis. Though this method is used nowadays the accuracy the results is far convincing, expect for the cases where distinct shoulders were observed. [39].

There is no electronic spectral evidence that the ground state of the copper(II) ion in its complexes is ever orbital degenerate. The $d_{x^2-y^2}$ orbital is the most common ground state, the d_{z^2} is quite common, and the d_{xy} occurs occasionally. The difference between a $d_{x^2-y^2}$ and d_{z^2} ground state for the same symmetry, is not observable in the electronic spectra, but can be readily distinguished from the EPR data [40]

It is also observed that the diffuse reflectance spectra of the complexes are dominated by intense intra ligand and charge transfer bands. These intense bands cause the low energy bands to appear as weak shoulders. The high intensity bands in the region 240-265 nm is assignable to $\pi \rightarrow \pi^*$ transitions. An apparent bathochromic shift (red shift.) is observed to these bands in solution due to coordinating nature of solvent [41]. The copper(II) complexes have $n \rightarrow \pi^*$ bands at 314 and 333 nm. There is a slight shift in the energy of these bands on complexation. The $n \rightarrow \pi^*$ band associated with the pyridine ring at 333 nm in the solid state spectra of the thiosemicarbazones is often shifted in energy in solution, which is probably due to hydrogen bonding taking place between the thiosemicarbazones moiety and the solvent molecule. The molar absorptities are more than 10^4 which are consistent with previously studied heterocyclic thiosemicarbazones.

Two metal to ligand charge transfer (CT) bands are found at 370 and 434 nm for the copper(II)complexes with HL4M. These bands appear at .387 and 476 nm for the copper(II)complexes with HL4P. In accordance with the reported results the higher energy band is assigned to S $\rightarrow$ Cu(II) LMCT transition, which is tailing in to the visible region and the other to Pyridine $\rightarrow$ Cu(II) CT transition.

The position of the S $\rightarrow$ Cu(II) CT band is determined by the steric requirements of the ^{4}Nsubstituents, such that thiosemicarbazones with bulkier ^{4}N substituent have this band at somewhat lower wavelengths [42]. The CT may occur from the p orbital of coordinated ketonic sulphur or nitrogen to the vacant d orbitals of copper(II). Among the halide complexes, iodo complex is some what brown or red due to tailing of an I $\rightarrow$ Cu(II) charge transfer band through visible region.[43]. Such LMCT bands have also been observed in the electronic spectra of related N-N-S thiosemicarbazones. It is observed that the band maxima of the chloride complexes are lower in energy than those of the bromide complexes, as chloride ion lies above bromide in the spectrochemical series. This inversion may arise from the greater π bonding potential of bromide compared to chloride, as reflected in its higher position in the Nephelauxetic series.

The d-d bands of some of the copper(II) complexes are found at 715 and 588 nm, the later being seen as a very weak shoulder in the tail of the CT bands. These spectra are similar to copper(II) complexes with square planar geometry as reported by Ali and Tarafdar [44]. The diffuse reflectance spectra of representative complexes are given in Fig 3.2.

3.3.4. EPR spectral investigations

EPR spectroscopy has been widely used in the study of paramagnetic complexes formed between metal ions and various ligands, as it offers the potential to define local structure as well as provide information on the chemical reactions. The EPR spectra (Fig 3.3); of polycrystalline sample at 298K, dimethylformamide solution at 298 and 77 K were recorded in the X band, using the 100-kHz field modulation. The

g factors were quoted relative to the standard marker TCNE. Spectral simulations were performed using computer programs described elsewhere [45]. The EPR parameters of copper(II) complexes obtained for the polycrystalline state at 298K, in solution at 298K and 77 K are presented in Table 3.4. The spin Hamiltonian parameters and other bonding parameters are listed in Table 3.5a and 3.5b.

To obtain information about the stereochemistry and the site of the metal ligand bonding and to determine the magnetic interaction in the metal complexes we recorded the EPR spectra of all complexes in the polycrystalline state at room temperature. The coordination environment around Cu(II) in the complexes and existence of different types of geometrical species are obtainable from such spectra. The powder EPR spectral profiles of complexes may be simple and consist of one, two or three g values in the region 2 to 2.5. Compounds **3**, **4**, **7** and **9** show only one broad signal. Such isotropic spectra, consisting of a broad signal, arise from extensive exchange coupling through misalignment of the local molecular axes between different molecules in the unit cell (dipolar broadening) and enhanced spin lattice relaxation. This type of spectra unfortunately gives no information on the electronic ground state of Cu(II) ion present in the complexes [46].

Compounds **1**, **5**, **6**, **11** and **12** show typical axial spectra with well-defined $g_{\parallel}$ features. The $g_{\perp}$ features are only poorly defined because of the broadening resulting from the smaller spin lattice relaxation time and large spin orbit coupling. The variation in the $g_{\parallel}$ and $g_{\perp}$ values indicates that the geometry of the compounds in the solid state is affected by the nature of the substituent at ^{4}N position. The value increases with the bulkiness of the substituent. Spectra consisting of two or three signals and hence two and three *g* values, respectively of axial and rhombic features do not rule out the possibility of exchange coupling [47].

Table 3. 4
EPR Spectral assignments of Cu(II) complexes with N-N-S donors (Experimentally determined, * A value $x10^{-4}$)

Compound	Solid(298 K)		DMF solution(298 K)			DMF solution(77 K)				
	$g_0 / g_{\|} / g_3$	$g_\perp / g_1 / g_2$	g_0 / g_{iso}	A_0 / A_{iso}*	A_N*	$g_{\|}$	$g_\perp$	G_{av}	$A_{\|}$ Cu *	$A_\perp$ Cu*
CuL4MCl	$g_{\|}$ 2.0941	$g_\perp$ 2.037	2.0591	86.08	15.5	2,1823	2.0493	2.0936	193. 7	16..5
CuL4MBr	g_3 2.0938	g_2 2.0407 g_1 2.0344	2.0596	83.5	16.3	g_3 2.17 g_1 2.0224 $g_{\|}$ 2.097	2.023	2.0483	156.5	16.1
CuL4MI	g_0 2.061	------	2.0724	80.5	16.5	2.1904	2.0572	2.0113	188	16..3
CuL4MAc.H_2O	g_0 2.0669	------	2.1043	83.5	160	2.1105	2.0514	2.1043	185.18	16..5
CuL4MNO_3	$g_{\|}$ 2.1283	$g_\perp$ 2.053	2.0819	82.89	171	2.1934	2.0403	2.0913	180.03	17..3
CuL4MNCS	$g_{\|}$ 2.1249	$g_\perp$ 2.050	2.0764	82.90	16.4	2.1949	2.0505	2.0753	186.27	16..22
CuL4MN_3	g_0 2.0669	------	2.0659	84.07	17.3	2.1900	2.0513	2.0975	194.2	16..07
CuHL4MSO_4	g_3 2.070	g_2 2.0372 g_1 2.0311	2.095	87.87	16.1	g_3 2.1938 g_1 2.046 $g_{\|}$ 2.1419	2.0949	2.1112	176	15.81
CuL4MH_2OClO_4	g_0 2.0669	------	2.0797	80.30	16.3	2.2123	2.0538	2.1066	182.5	16.22
CuL4PCL	g_3 2.1897	g_2 2.053 g_1 1.9812	2.0331	82.1	17.6	g_3 2.0672 g_1 2.0146 $g_{\|}$ 2.0762	2.0298	2.0452	155.08	15..2
CuL4PBr	$g_{\|}$ 2.1049	$g_\perp$ 2.041	2.0521	86.13	16.9	2.1926	2.0499	2.0974	170.4	15.6
CuL4PAc.H_2O	$g_{\|}$ 2.143	$g_\perp$ 2.032	2.071	86.02	17.4	2.132	2.034	2.080	164	17.00

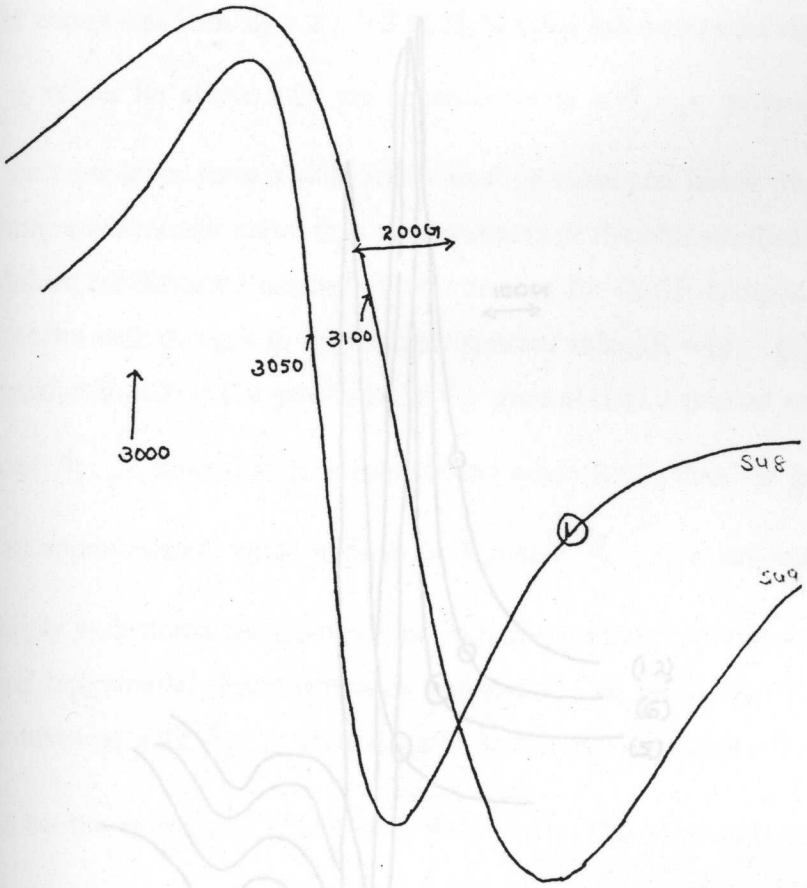


Fig 3.3(a) EPR spectra in polycrystalline state at 298 K of the complexes

The axial spectral parameter, G, where $G = [g_{\parallel} - 2.0023] / [g_{\perp} - 2.0023]$ for axial spectra, is a measures exchange interaction between copper centers in the polycrystalline solid. For rhombic spectra, $G = [g_3 \quad 2.0023] / [g_{\perp} \quad 2.0023]$ and $g_{\perp} = [g_1 + g_2]/2$. It is reported that G lies between 3 and 5. If $G > 4$, exchange interaction is negligible and if it is less than 4, considerable exchange interaction is indicated in the solid complex. The axial parameter G for the complexes is found to be in the range 3.2 to 4.2 indicating that the *g* value obtained in the polycrystalline samples are near to the molecular *g* values which indicate the fact that the unit cell of the compounds contain magnetically equivalent sites [48].

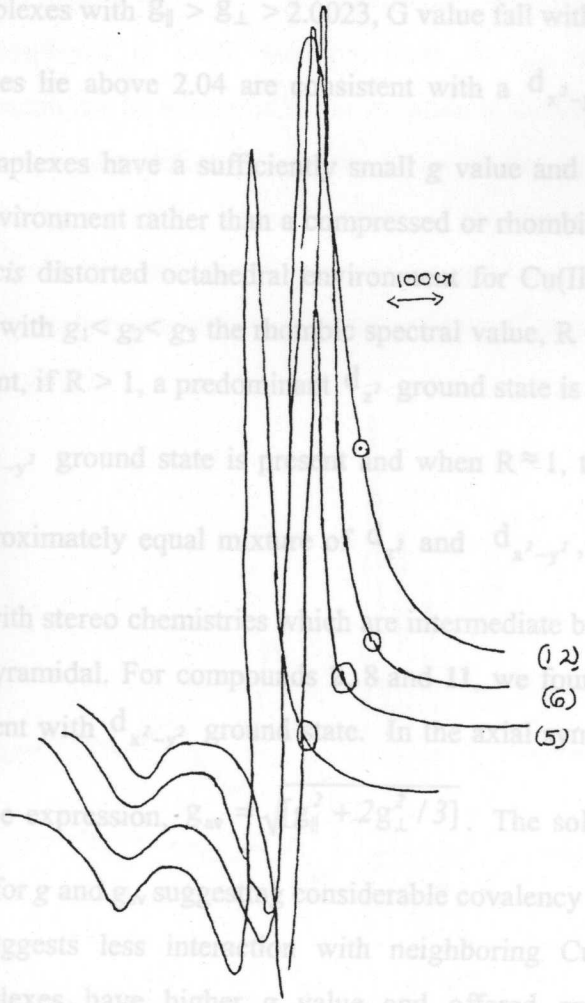


Fig 3.3(b) EPR spectra in polycrystalline state at 298 K of the complexes

Occasionally the EPR spectra of a polycrystalline sample of a complex which has axial or rhombic crystal g value may appear approximately isotropic due to much greater intensity of the signal associated with $g_{\perp}$ relative to that associated with $g_{\parallel}$.

Compounds **2**, **8** and **10** show typical rhombic features with three *g* values indicating some rhombic distortion in their geometry and that distortion are small because g_1 and g_2 are closer to one another. The G value calculated for those complexes in rhombic symmetry is found in the range 3 to 5 indicating that the exchange coupling

is small for complexes with $g_{\parallel} > g_{\perp} > 2.0023$, G value fall with in the range, and the observed g values lie above 2.04 are consistent with a $d_{x^2-y^2}$ ground state [49]. None of the complexes have a sufficiently small g value and hence we assigned a square planar environment rather than a compressed or rhombic octahedral, trigonal bipyramidal or *cis* distorted octahedral environment for Cu(II) complexes. In the rhombic spectra with $g_1 < g_2 < g_3$ the rhombic spectral value, $R = (g_3 - g_1) / (g_3 - g_2)$ may be significant, if R > 1, a predominant d_{z^2} ground state is present and if R>1 ,a predominant $d_{x^2-y^2}$ ground state is present and when $R \approx 1$, then the ground state involves an approximately equal mixture of d_{z^2} and $d_{x^2-y^2}$, a structure which is found to apply with stereo chemistries which are intermediate between square planar and trigonal bipyramidal. For compounds **2**, **8** and **11**, we found the value of R<1, which is consistent with $d_{x^2-y^2}$ ground state. In the axial symmetry the g_{av} values are related by the expression, $g_{av} = \sqrt{[g_{\parallel}^2 + 2g_{\perp}^2 / 3]}$. The solid-state EPR spectra have low values for *g* and g_{av} suggesting considerable covalency in the bonding. Low *g* value also suggests less interaction with neighboring Cu(II) centers. Five coordinate complexes have higher *g* value and offered greater intermolecular interactions [50].

The solution spectra of all complexes were recorded in dimethylformamide at 298 K. For all complexes spectra with isotropic features were obtained. It is assumed to be due to tumbling motion of the molecules in .dimethylformamide solution. The spectral features of **1**, **5**, **6**, **9**, **11**, and **12** clearly show four well resolved hyperfine lines ($^{63,\ 65}$Cu, I=3/2). The signal corresponding M_I =-3/2 splits clearly in to three peaks with a superhyperfine (shf) or ligand hyperfine coupling constant $A \approx 17$ G. This is characteristic of compounds bound through azomethine nitrogen and an indication that the bonding in solution state is dominated by the

thiosemicarbazones moiety rather than the gegenions. The small variation in the g_{av} value of the complexes in DMF solution from the g_{av} value calculated for polycrystalline spectra can be attributed to the variation in the geometric environment of the compounds upon dissolution. All spectra show similar A_0 and g_0 values of the complexes, suggesting similarity in the bonding of the thiosemicarbazones. The isotropic g value, g_0 is calculated at the centre of the spectrum of the four lines. The isotropic nuclear hyperfine constant, A_0 is expressed in cm^{-1} and is obtained from the mean of the splittings [51].

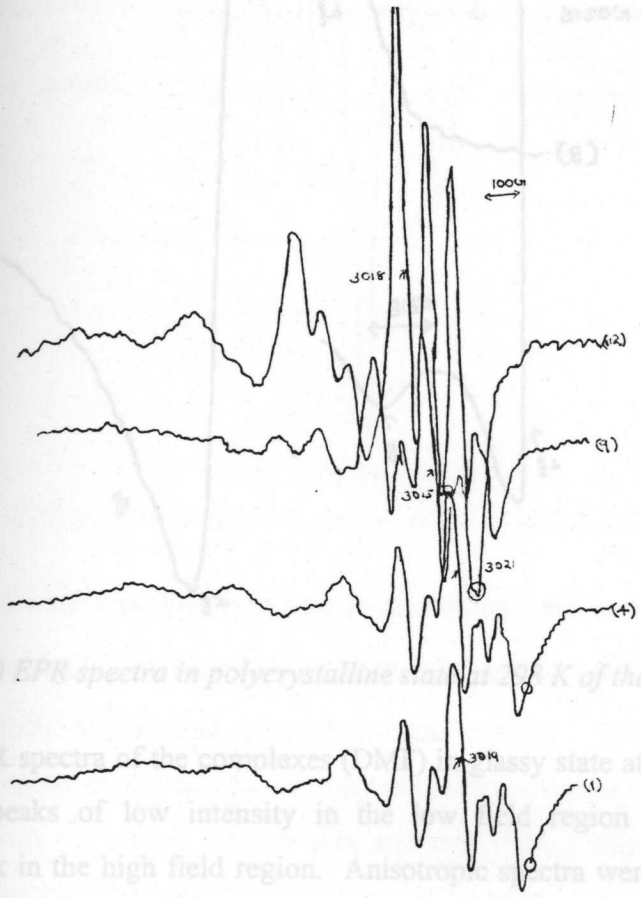


Fig 3.3(c) EPR spectra in solution state in DMF at 298 K of the complexes

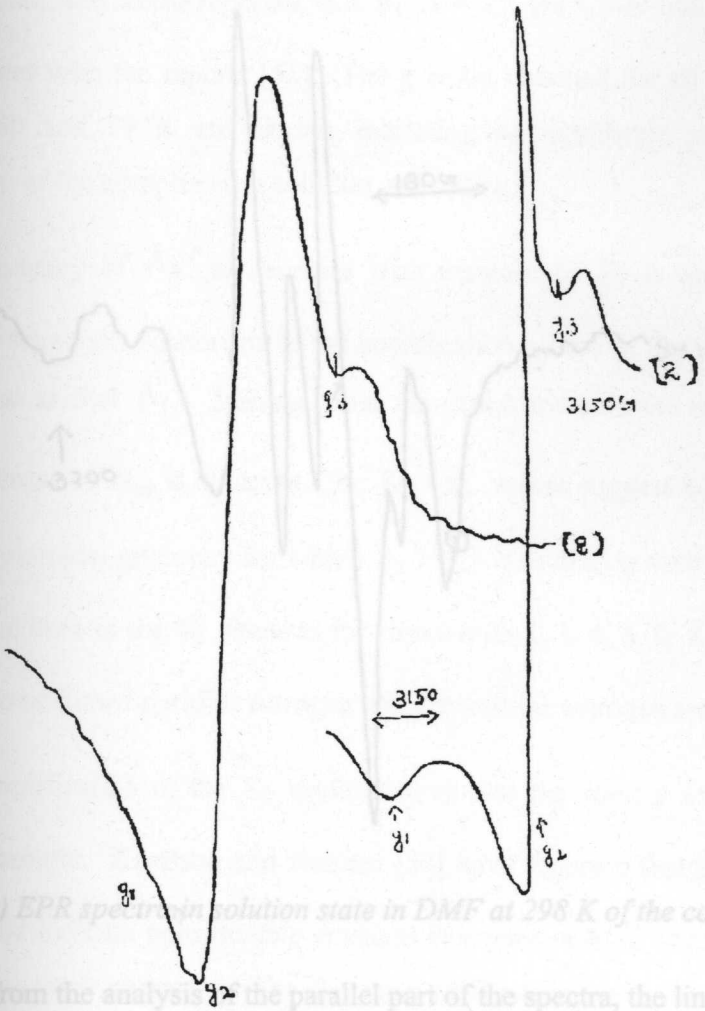


Fig 3.3(d) EPR spectra in polycrystalline state at 298 K of the complexes

The EPR spectra of the complexes (DMF) in glassy state at 77 K show three well-resolved peaks of low intensity in the low field region and one intense unresolved peak in the high field region. Anisotropic spectra were obtained for all complexes. The $g_{\|}$ and $A_{\|}$ values were calculated accurately from the spectrum while $g_{\perp}$ and $A_{\perp}$ values were evaluated using the following equations [52].

$$g_{\perp} = [3g_0 - g_{\|}] / 3 \text{ and } A_{\perp} = [3A_0 - A_{\|}] / 3$$

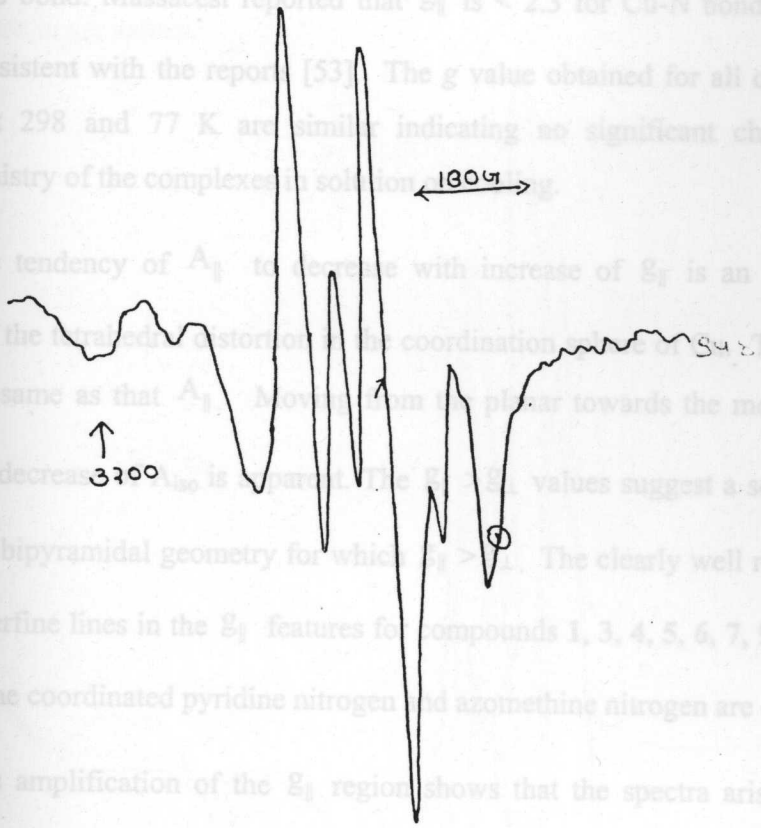


Fig 3.3(e) EPR spectrum in solution state in DMF at 298 K of the complexes

As is evident from the analysis of the parallel part of the spectra, the line width of the M_I =-3/2, component is small compared with the nitrogen coupling constants, leading to the appearance of nitrogen super hyperfine pattern. The splitting in the perpendicular region of the spectra can be attributed to interaction of an unpaired electron spin with the copper nuclear spin and two (^{14}N, I =1) donor nuclei. In addition, an extra overshoot line resulting from the angular dependence of the copper hyperfine lines in the perpendicular region is observed. The smaller $g_{\|}$ values for the complexes indicate increased delocalization of the unpaired electron spin density away from the copper nucleus and may be interpreted in terms of increased covalency

of the M-L bond. Massacesi reported that $g_{\|}$ is < 2.3 for Cu-N bond and we got results consistent with the reports [53]. The *g* value obtained for all complexes in solution at 298 and 77 K are similar indicating no significant change in the stereochemistry of the complexes in solution on cooling.

The tendency of $A_{\|}$ to decrease with increase of $g_{\|}$ is an index of an increase of the tetrahedral distortion in the coordination sphere of Cu. The trend for A_{iso} is the same as that $A_{\|}$. Moving from the planar towards the more distorted complex a decrease of A_{iso} is apparent. The $g_{\|} > g_{\perp}$ values suggest a square planar rather than bipyramidal geometry for which $g_{\|} > g_{\perp}$. The clearly well resolved five ligand hyperfine lines in the $g_{\|}$ features for compounds **1**, **3**, **4**, **5**, **6**, **7**, **9**, **10** and **12** show that the coordinated pyridine nitrogen and azomethine nitrogen are coplanar.

Less amplification of the $g_{\|}$ region shows that the spectra arise from one species in the sample. Kivelson and Neiman [54] have reported that the $g_{\|}$ values less than 2.3 and indicate considerable covalent character to M-L bond and greater than 2.3 indicate ionic character. The $g_{\|}$ value of the complexes found to be less than 2.3, which indicate considerable covalent character to M-L bond. The $g_{\|} > g_{\perp} > g_e$ (2.0023) trend observed for these complexes and $G = [g_{\|} - 2.0023] / [g_{\perp} - 2.0023]$ values are less than 4.2, suggest that the unpaired electron lies in the d_{x2-y2} orbital of Cu(II) ion. The higher G value suggests that there are no interactions between the copper centers in solution. For solids, the value is less than 4, suggesting interaction between copper centers exist slightly. It also indicates the presence of small exchange coupling. The g_{av} values of compounds **1**, **2** and **4** do not vary much, while the value increases for **3**, **5**, **9**, **12** and decreases for others from the g_{av} values observed for them in the solid state. The variation might be due to variation in the

overall geometry and resulting change in covalency of the bonds, which decreases with increase in g_{av} values.

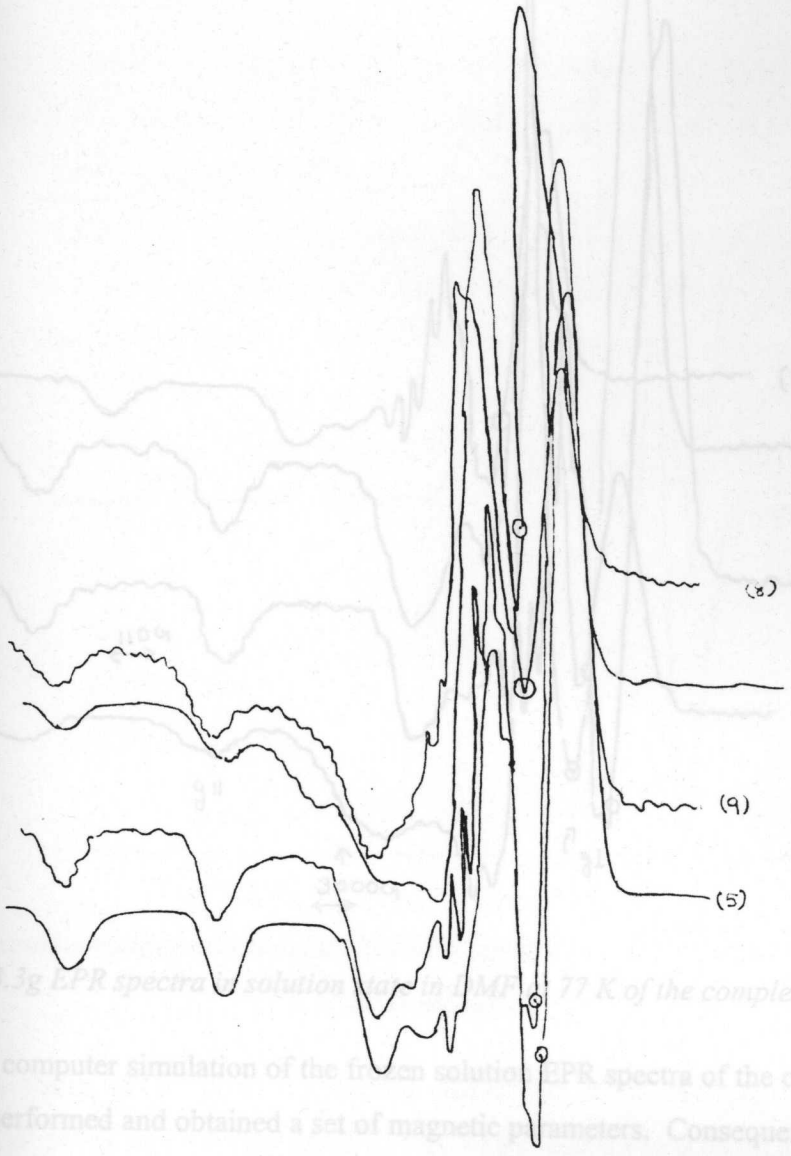


Fig 3.3(f) EPR spectra in solution state in DMF at 77 K of the complexes

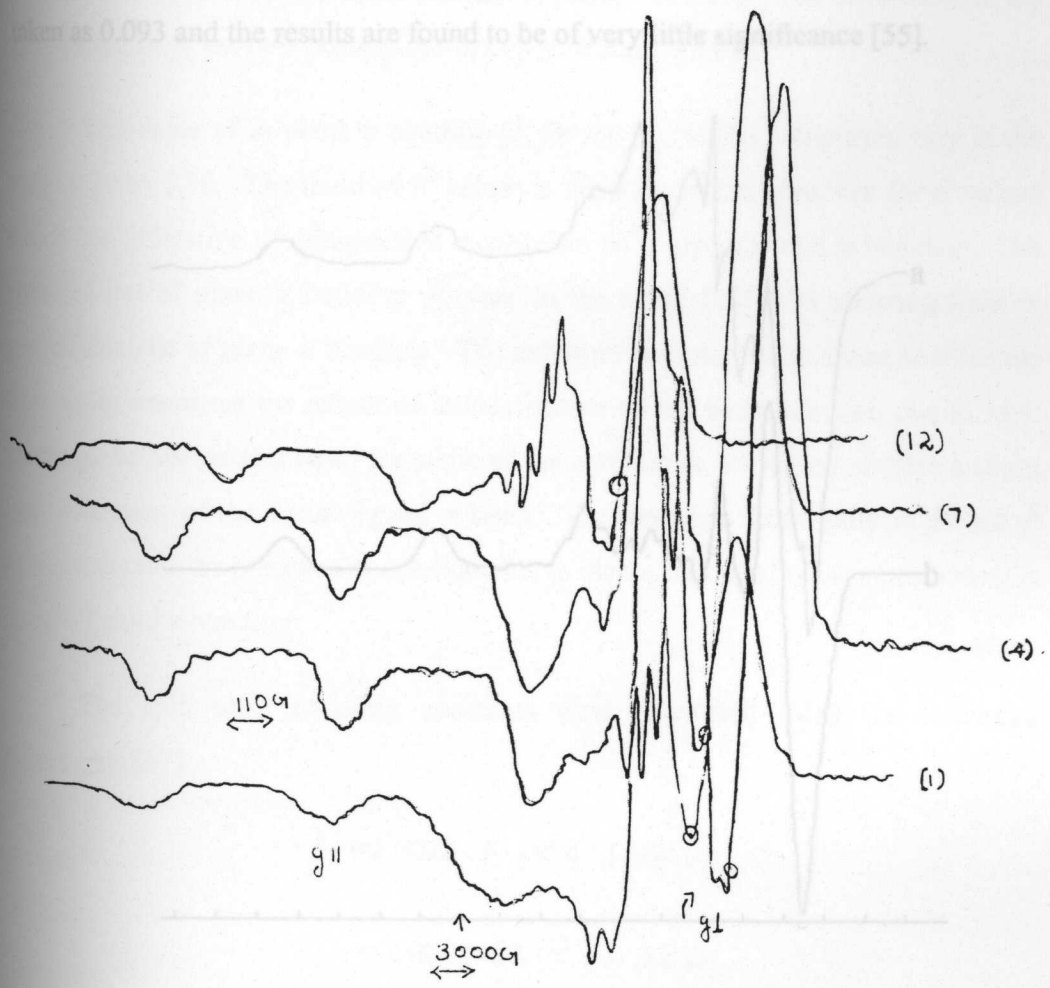


Fig 3.3g EPR spectra in solution state in DMF at 77 K of the complexes

The computer simulation of the frozen solution EPR spectra of the complexes have been performed and obtained a set of magnetic parameters. Consequently it has been possible to gain some insight in to the geometric arrangement at the metal site. The EPR parameters $g_{\|}$, $g_{\perp}$, g_{av}, $A_{\perp}$ and $A_{\|}$ and energies of d-d transitions were used to evaluate the bonding parameters α^2, β^2 and γ^2, which may be regarded as measures of covalency of the in plane σ bond, in plane π bond and out of plane π bond respectively. The out of plane σ-bond strength α'^2, was calculated by using the

relationship $\alpha'^2 = (\alpha^2 + \alpha'^2 - 2\ \alpha\ \alpha' S) = 1$ where S is the overlap integral which is taken as 0.093 and the results are found to be of very little significance [55].

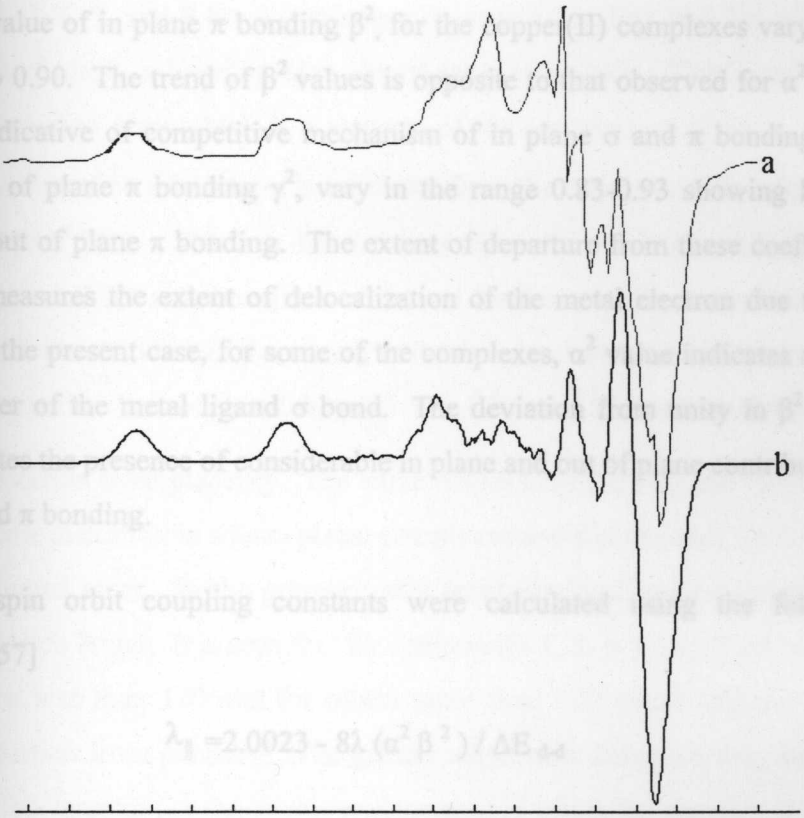


*Fig 3.4 Experimental(**a**) and simulated(**b**) EPR spectra in solution state in DMF at 77 K of the compound **3***

The value of in plane σ bonding parameter α^2 is estimated from the expression, $\alpha^2 = A_{\parallel} / 0.036 + [g_{\parallel} - 2.0023] + 3/7 [g_{\perp} - 2.0023] + 0.04$. This can also be calculated [56] by another expression $\alpha^2 = 1/8[-14(A+K)/p + 11(g_{\perp} - g_e) + 9(g_0 - g_e)$ where P = dipolar interaction coefficient (0.036 cm^{-1}) for free Cu(II) ion, K = represents the Fermi contact interaction term which is calculated by using the relation ship, $K = -A_0 + P(g_0 - g_e)$. The metal –ligand in plane in plane α^2 is completely ionic if $\alpha^2 = 1$ and it is completely covalent if $\alpha^2 = 0.5$. The observed values suggest that in

plane σ bonding is more covalent than the in plane π bonding. The differences in the α^2 obtained from the two expressions are only within the limits.

The value of in plane π bonding β^2, for the copper(II) complexes vary in the range 0.79 to 0.90. The trend of β^2 values is opposite to that observed for α^2 values which are indicative of competitive mechanism of in plane σ and π bonding. The value of out of plane π bonding γ^2, vary in the range 0.83-0.93 showing little to appreciable out of plane π bonding. The extent of departure from these coefficients from unity measures the extent of delocalization of the metal electron due to M-L bonding. In the present case, for some of the complexes, α^2 value indicates a slight ionic character of the metal ligand σ bond. The deviation from unity in β^2 and γ^2 values indicates the presence of considerable in plane and out of plane contribution in metal – ligand π bonding.

The spin orbit coupling constants were calculated using the following expressions [57]

$$\lambda_{\parallel} = 2.0023 - 8\lambda (\alpha^2 \beta^2) / \Delta E_{d\text{-}d}$$

$$\lambda_{\perp} = 2.0023 - 2\lambda (\alpha^2 \gamma^2) / \Delta E_{d\text{-}d}$$

The spin orbit coupling constants $\lambda_{\parallel}$, $\lambda_{\perp}$ suggest greater contribution from put of plane π bonding than in plane π bonding ($\lambda_{\parallel}$ = -789.87 cm^{-1} and $\lambda_{\perp}$ = -785.12 cm^{-1}) except for **1**, **2**, **6**, **7** and **8**. The orbital reduction factors were estimated using the following expressions [58].

$$K_{\parallel}^2 = (g_{\parallel} - 2.0023)\, \Delta E\, (d_{xy} - d_{x^2-y^2}) / 8\lambda_0.$$

$$K_{\perp}^2 = (g_{\perp} - 2.0023)\, \Delta E\, (d_{xy} - d_{x^2-y^2}) / 2\lambda_0$$ .where λ_0 is the spin orbit coupling constant and has a value of - 828 cm^{-1} for Cu(11) d^9 systems.

According to Hathaway [59], for pure σ bonding $K_{\parallel} \approx K_{\perp} \approx 0.77$, for in plane π bonding $K_{\parallel} < K_{\perp}$ while out of plane π bonding $K_{\parallel} > K_{\perp}$. It is seen that for compounds **1**, **2**, **6**, **7**, and **8** there is stronger in plane π bonding and for others, in-plane and out of plane π bonding have almost same magnitude. The Fermi contact hyperfine interaction term which is a measure of the contribution of the s electron density to the hyperfine interaction, is estimated from the expression, $K_0 = A_{iso} / P \beta^2 + [g_{av} - 2.0023] / \beta^2$ [60]. This is a dimensionless quantity and is generally found to have a value around 0.3 and the values calculated for the complexes are found to be in the range 0.3 which indicates the mixing of the 4s orbital with d orbitals possessing an unpaired electron. The empirical factor $f = g_{\parallel} / A_{\parallel}$ cm^{-1} is an index of tetrahedral distortion, distortion from planarity. The value ranges between 105 and 135 cm^{-1} for small to extreme distortion in square planar complexes and that depends on the nature of the coordinated atom. In the presence of a tetrahedrally distorted structure, the value can be much larger. It is seen that for compounds **1**, **3**, **4**, **6** and **7** the value of *f* is found to be less than 120 and for others more than 120 which indicate less to moderate distortion from planarity. The greater tetrahedral distortion may be due to the more flexible structure or the *in vivo* environment in which the complex located in solvent sysiem. Recent studies [61] have shown that the biological activity is related to the geometry at the metal site in terms of SOD like activity. Complexes with more tetrahedral distortion are reported to display higher activity.

Giordano and Bereman [62] suggest the identification of bonding groups from the values of the dipolar term P. The small reduction in P values from the free ion (0.036 cm^{1}) might be attributable to significant covalent bonding character. The k value calculated for the complexes is found to in the range (0.020 - 0.0222 cm^{-1}) which indicate significant covalent character. The value of α^2 calculated for these complexes supported our arguments. Giordino and Bereman have treated the parameter P as a variable to observe the effects of electron delocalization by use of

Table 3.5.a
Spin Hamiltonian parameters of Cu(II) complexes with N-N-S donors

comp d*	$g_{\|}/g_{zz}$	g_{xx}	$g_{\|}/g_{yy}$	Gav (77K)	Gav (solid)	$A_{\|}$ /Azz	Axx	$A_{\|}$ /Ayy	Aav	G (solid)	G (77k)	R
1	2.1823	2.0489	2.0493	2.0936	2.0591	193.71	16.51	16.51	75.57	3.697	3.860	--
2	2.1700	2.0684	2.023	2.0871	2.0584	156.39	13.4	13.40	78.93	---	5.041	.449
3	2.194	2.058	2.057	2.1013	2.061	187.93	14.54	14.52	72.32	---	3.5045	----
4	2.1100	2.050	2.051	2.0703	2.067	185.18	14.12	14.12	71.14	---	2.210	----
5	2.1934	2.0402	2.0403	2.0913	2.0786	180.03	19.33	19.33	72.89	2.4	5.028	----
6	2.195	2.0505	2.050	2.0986	2.0566	186.25	16.22	16.22	72.90	2.47	3.9975	----
7	2.1900	2.0512	2.0513	2.0975	2.0716	194.20	14.00	14.01	74.07	----	3.8384	----
8	2.1938	2.0989	2.046	2.1129	2.0909	176.00	13.81	13.81	67.87	----	4.480	.550
9	2.1934	2.0403	2.0403	2.0913	2.0669	182.46	14.22	14.22	70.30	----	5.020	----
10	2.0762	2.0449	2.0146	2.0423	2.0746	155.08	15.20	15.20	61.82	4.58	2.560	.968
11	2.0922	2.035	2.0237	2.0503	2.0989	154.06	16.81	16.81	62.56	3.53	4.200	----
12	2.O98	2.0253	2.0253	2.0495	2.099	161.00	17.44	17.44	65.49	2.3	3.877	----

* = Compound

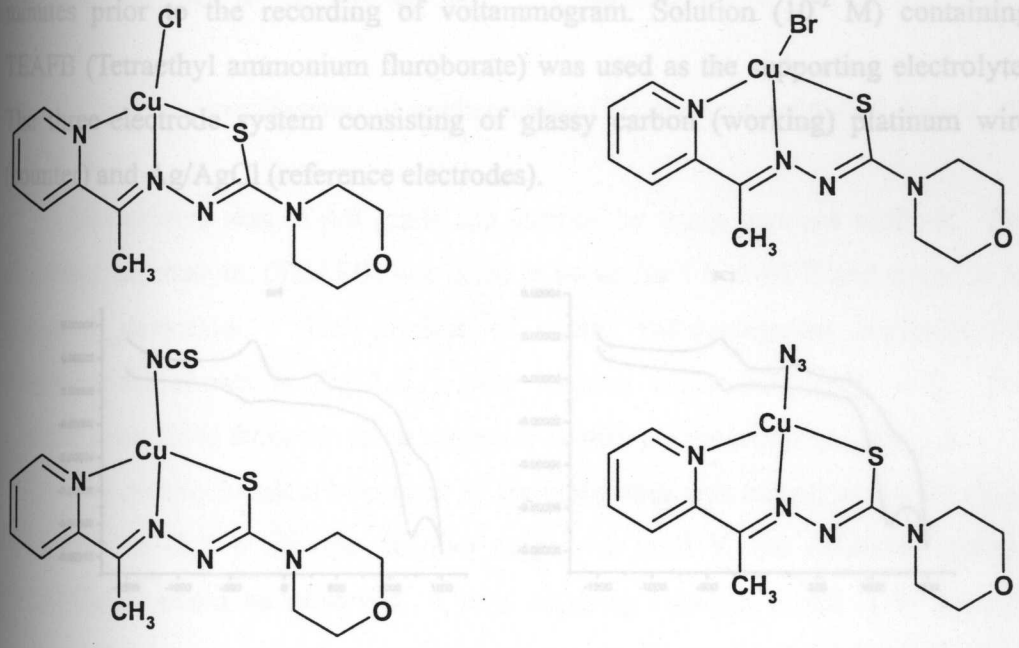
Table 3.5.b
Orbital reduction parameters of Cu(II) complexes with N-N-S donors

compounds *	α^2	β^2	γ^2	$K\parallel$	$K\perp$	K_0	$f$cm	p
1	.7701	.8292	.8471	.6386	.6524	..3051	112..65	.0248
2	.5784	.8516	.8125	.4926	.4700	..3125	134 .08	.0225
3	.7360	.7731	.8817	.6817	.5417	..2928	116. 53	.0229
4	.7838	.8718	.8415	.6828	.6597	..3122	119 .40	.0192
5	.7475	.9003	.8029	.673	.6002	..3015	121 .83	.0218
6	.7705	.9216	.9353	.7101	.7207	..3155	121 .83	.0241
7	.7881	.8188	.8366	.6453	.6595	..2584	112..72	.0239
8	6892	.8047	.8939	.5546	.6161	..2959	121..81	.0222
9	.7822	.8586	.8501	.6716	.6651	..3671	121. 24	.0194
10	.5735	.7050	.8593	.4042	.4927	..2146	133 .87	.0251
11	.5668	.8235	.8028	.4667	.4559	..2179	135..80	.0236
12	.6112	.8119	.7947	.4957	.4856	..2296	136..10	.0233

* = compounds

formula $P = (A_{\parallel} - A_{\perp}) / [(g_{\parallel} - 2) - 5 / 14 (g_{\perp} - 2) - 6/7$. Identification of the bonding groups may be obtained from the values of P. The observed value of P for the complexes is in the ranges .0.019 to 0.025 which favors the bonding of nitrogen to copper. The reduction of P values from the free ion value (0.036 cm^{-1}) might be attributed to the presence of covalent bonding. It is also worth noticing that there is a little covalency in the out of plane π bonds between both Cu and S and Cu and N and in plane, covalency is not negligible. Computer simulation of the EPR spectra had revealed differences in the magnetic parameters of the compound. The magnetic parameters used for simulation are reported in Table 3.5a and 3.5b. The experimental spectrum is shown in the Fig 3.4 and is paired with their best simulation.

Based on the molar conductance, magnetic moment, IR, electronic and EPR spectral data we suggest that complexes except **8** have square planar structures. The structures proposed for representative complexes are given in Fig 3.5.



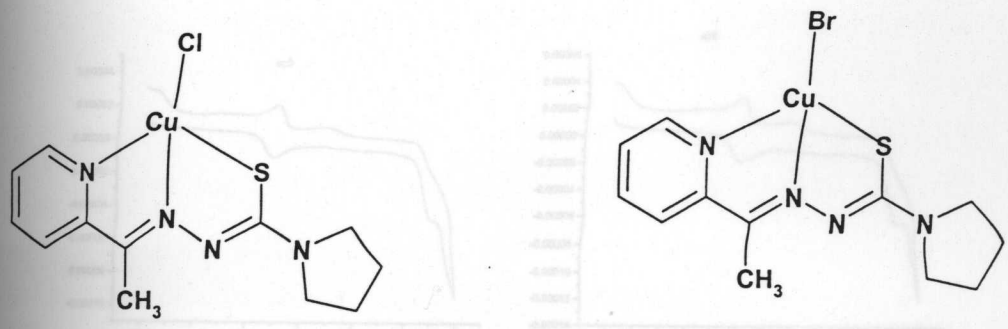


Fig 3.5 Structural formulae of the complexes

3.4 Electrochemical studies

In order to monitor spectral and structural changes accompanying electron transfer, the electrochemical properties of metal complexes particularly with sulphur donor atoms have been studied. The CV measurements were made on the degassed (all solution) was deoxygenated by passing nitrogen into DMF solution (10^{-3} M) for 10 minutes prior to the recording of voltammogram. Solution (10^{-2} M) containing TEAFB (Tetraethyl ammonium fluroborate) was used as the supporting electrolyte. The three-electrode system consisting of glassy carbon (working) platinum wire (counter) and Ag/AgCl (reference electrodes).