

ADDIS ABABA UNIVERSITY  
SCHOOL OF GRADUATE STUDIES



A NEW POLYDENTATE LIGAND AND  
IT'S Cu (II) COMPLEX - SYNTHESIS  
AND CHARACTERIZATION

By: Desta W/Tsadik

August 2007

**A NEW POLYDENTATE LIGAND AND IT'S Cu (II) COMPLEX -  
SYNTHESIS AND CHARACTERIZATION**

**GRAGUATE PROJECT (CHEM.774) SUBMITTED TO THE  
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Chemistry**

By: Desta W/Tsadik

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## Table of contents

Acknowledgements.....	i
Table of contents.....	ii
List of Tables.....	iv
List of Figures.....	v
List of Schemes.....	vi
List of Abbreviations and Acrynomns.....	vii
List of Appendices.....	viii
Abstract.....	ix
1. INTRODUCTION.....	1
1.1 Multidentate Ligands and Their Metal Chelate System.....	1
1.2 Schiff Bases.....	4
1.3 The Chemistry of Imidazole.....	5
1.4 Some Synthetic Aspects of Imidazole Derivatives.....	7
1.5 Some Imidazole Derivative Multidentate Ligands with O, N and N, N Donor System.....	11
1.6 Copper(II) Complexes Of Imidazole Derivative Multidentate Ligands with O, N and N, N Donor.....	13
1.7. Aim and Scope of the Present Investigation.....	18
2. MATERIALS AND METHODS.....	19
2.1. Chemicals.....	19
2.2. Instruments.....	19
2.3. Methods.....	20
2.3.1. Qualitative Test.....	20

2.3.2. Quantitative Determinations .....	20
3. EXPERIMENTAL PART .....	22
3.1. Synthesis of 2, 4-Dihydroxy-5-Acetylacetophenone (DAAP) .....	22
3.2. Synthesis of 2, 4-Dihydroxy-5-Acetylacetophenone Dihydrazone (DAAD) .....	22
3.4. Synthesis of metal complex .....	24
4. RESULTS AND DISCUSSION .....	25
4.1. Physical Characteristics .....	25
4.2 IR Spectra of DAAP, DAAD, and BIMHEBD .....	26
4.2.1 IR Spectrum of DAAP .....	26
4.2.2 IR Spectrum of DAAD .....	27
4.3 IR Spectrum of the Metal Complex .....	28
4.4 Molar Conductivity of the Metal Complex .....	29
4.5 Atomic Absorption Spectroscopy of Metal Complex .....	29
4.6 Chloride Analysis Data .....	30
4.7 Magnetic Susceptibility of Metal Complex .....	31
4.8 UV-VIS Spectrum of BIMHEBD .....	32
4.9 UV-VIS Spectrum of the Cu(II) Complex .....	32
5. CONCLUSION .....	33
6. REFERENCES .....	34

## List of Tables

Table. 1 Some typical chelating ligands .....	3
Table. 2 physical properties of DAAP, DAAD, BIHEBD and Cu(II)complex.....	25
Table. 3 Solubility check for DAAP, DAAD, BIMHEBD and Cu(II) complex with some selected solvents.....	26
Table. 4 Characteristics vibrational frequencies of DAAP and DAAD .....	27
Table. 5 Characteristics vibrational frequencies of BIMHEBD and Cu(II) complex.....	29
Table. 6 percentage composition of copper in the complex .....	30
Table. 7 Percentage composition of chloride in the complex.....	31

## List of Figures

Figure. 1 Metal chelates of a) ethylenediamine b) serine .....	1
Figure. 2 Delocalization of charge on bidentate chelating anions .....	3
Figure. 3 a) Dipyromethene anion b) Bivalent metal chelate of dipyromethene anion .....	4
Figure. 4 General mechanistic aspects of Schiff base preparation .....	5
Figure. 5 Proposed structure of the Cu(II) Complex. ....	33

## List of Schemes

Scheme. 1 Some resonance structures of imidazole .....	6
Scheme. 2 Synthesis of imidazole .....	6
Scheme. 3 a) tris - (2-imidazolyl) carbinol (2-TIC) b) tris - [4(5) imidazolyl] carbinol (4-TIC) .....	7
Scheme. 4 Some bis(imidazol-2-yl) derivatives of dipeptides .....	12
Scheme. 5 Dinuclear Cu(II) complex coordinated through a) (NH <sub>2</sub> , CO and N(IM)) .....	14
Scheme. 6 Dinuclear Cu(II) complex coordinated through a) (NH <sub>2</sub> , N <sup>-</sup> and N(IM)) .....	15
Scheme. 7 Cu(II) complex coordinated through (NH <sub>2</sub> , N <sup>-</sup> , N <sup>-</sup> , N(HisIm)) .....	15
Scheme. 8 Dinuclear, trinuclear and tetranuclear Cu(II) complexes .....	17
Scheme. 9 Synthesis of DAAP .....	22
Scheme. 10 Synthesis of DAAD .....	23
Scheme. 11 Synthesis of BIMHEBD .....	24

## List of Abbreviations and Acrynomns

NH <sub>3</sub>	Ammonia
en	ethylene diamine
°C	Degree centigrade
IMAC	Immobilised Metal Affinity Chromatography
BIM	Bis(imidazol-2-yl) methane
BIMA	Bis(imidazol-2-yl) methyl amine
2-TIC	Tris - (2-imidazolyl) carbinol
2-TIC	Tris - [4(5) – imidazolyl] carbinol
PhSSPh	Diphenyldisulfide
DMSO	Dimethylsulfoxide
AAS	Atomic Absorption Spectroscopy
IR	Infrared
MS	Mass spectroscopy
M.pt	Melting point
$\Lambda_M$	Molar conductance
$\chi_g$	Gram Susceptibility
$\chi_m$	Molar Susceptibility
$\mu_{\text{eff}}$	Effective magnetic moment
$\Omega$	Ohm
ppm	parts per million
DAAP	2, 4-Dihydroxy-5-Acetylacetophenone
DAAD	2, 4-Dihydroxy-5-Acetylacetophenone Dihydrazone
BIMHEBD	4,6 – Bis { [ ( (imidazo-5-yl) methyl) hydrazo] ethyl } -benzene-1,3- diol

## List of Appendices

Appendix 1. IR spectrum of DAAP .....	37
Appendix 2. IR spectrum of DAAD .....	38
Appendix 3. IR spectrum of BIMHEBD .....	39
Appendix 4. Mass spectrum of BIMHEBD .....	40
Appendix 5. IR spectrum of Cu(II) Complex .....	41
Appendix 6. Electronic spectrum of BIMHEBD .....	42
Appendix 7. Electronic spectrum of Cu(II) Complex .....	43

## **Abstract**

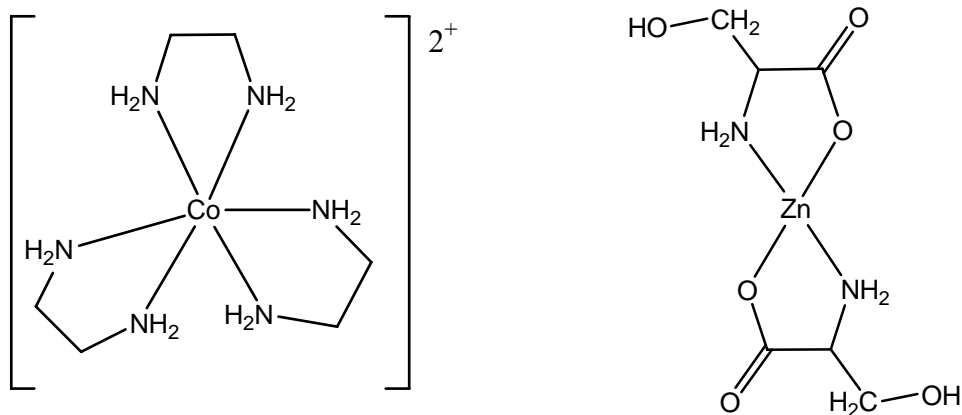
Dinuclear Copper (II) complex of a bis-chelating 4,6 – Bis{[(imidazo-5-yl) methyl] hydrazo] ethyl }-benzene-1,3-diol was synthesized and characterized by using conductivity, magnetic susceptibility measurement, IR and UV-VIS spectra. BIMHEBD was synthesized by the condensation of 2, 4-dihydroxy-5-acetylacetophenone dihydrazone (DAAD) with 4(5) – imidazo carboxo aldehyde. The ligand behaves as dibasic bis-tridentate chelating system through ONN-ONN donor sequence. Subnormal magnetic moment of the complex indicates the possibility of antiferromagnetic interaction through a possible superexchange mechanism.

# 1. INTRODUCTION

A metal complex is a chemical species which consists of a central metal atom or ion surrounded by a set of ions or molecules which have one or more atoms bearing lone pair of electrons. The ions or molecules that are bounded or coordinated with the metal are called ligands <sup>[1-4]</sup>. These donor atoms are bound electrostatically and covalently to the metal ion. In non-transition metal complexes such as  $\text{Na}^+(\text{aq})$ , which can be approximately formulated as  $[\text{Na}(\text{H}_2\text{O})_6]^+$ , the binding is largely electrostatic, while in transition metal complexes there is a significant metal-ligand covalency <sup>[2,5]</sup>.

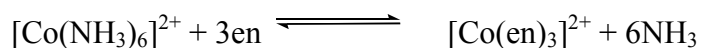
## 1.1 Multidentate Ligands and Their Metal Chelate System

The number of potential metal binding sites in a ligand is indicated by use of terms monodentate, bidentate, tridentate, etc. Polydentate ligands, which are flexible enough so that two or more of their donor atoms can wrap around and bind to same metal are called chelating ligands. Metal complexes of chelating ligands (fig1) are stabilized through effects which are basically entropy related.



**Figure. 1** Metal chelates of a) ethylenediamine b) serine

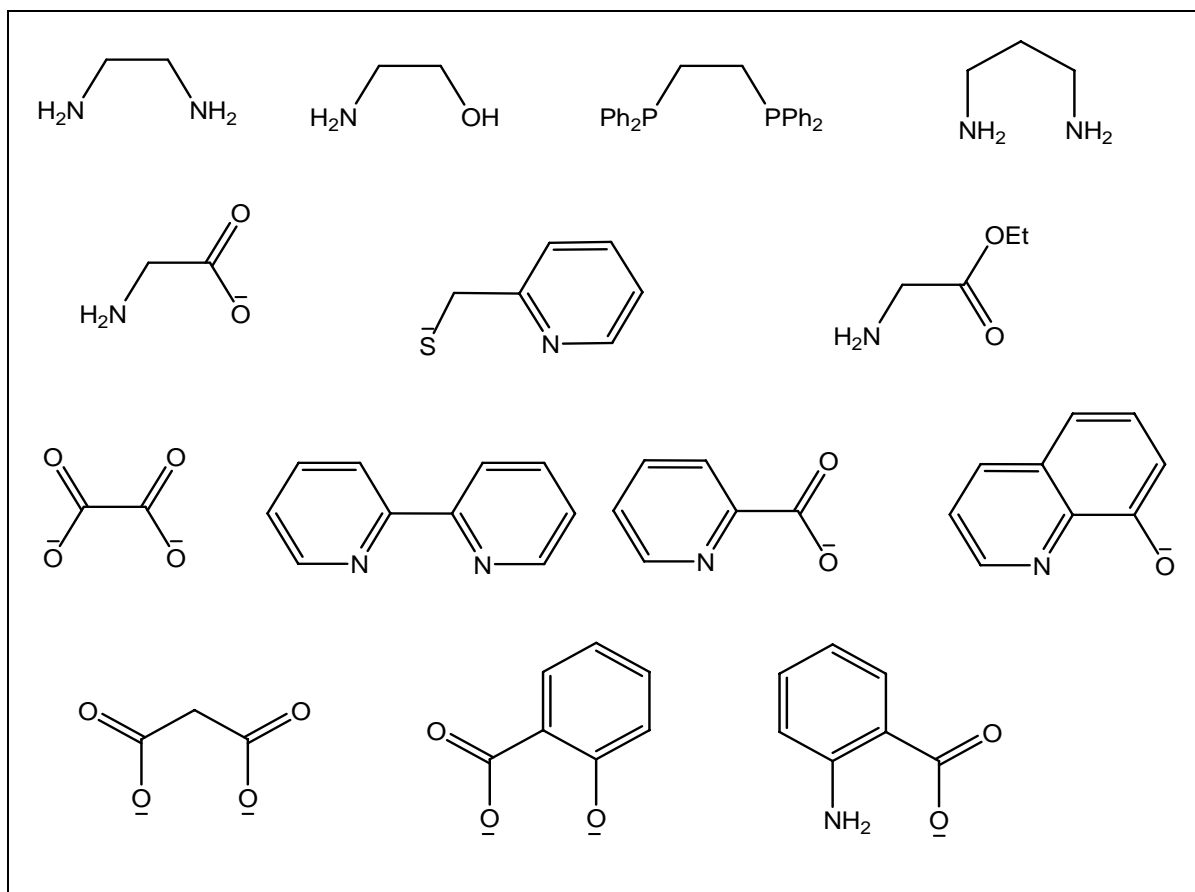
Chelate effect is an effect which happens when simple ligands like  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{Cl}$  etc..... are replaced by multidentate ligands like EDTA or ethylenediamine <sup>[1,2]</sup>. Consider the reaction below



Both the reactant and product complex contain six cobalt-nitrogen bonds. On the other hand, there are four molecules to the left and seven to the right, so there is greater potential for disorder to the right. Therefore the driving force, that is dominant factor is  $\Delta G$ , is the very positive change. If one end of a bidentate ligand becomes detached from the metal ion, there is a strong probability that it will re-attach itself before the other end becomes separated if the chain connecting the two ends is quite short. If the chain is long, the loose end can draft from the metal ion and the probability of reattachments is diminished <sup>[3,6]</sup>.

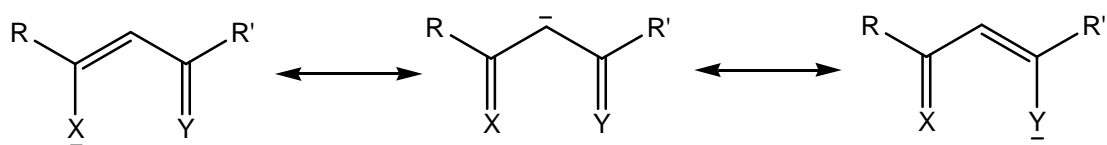
The ligands in figure 1 are bound to the metal through two or more different ligand atoms and thus form parts of heterocyclic rings in which the metal is one of the members. The heterocyclic rings formed in this manner are termed chelate rings and a metal complex which contains one or more chelate rings is called metal chelate. The stereochemistry of some ligands doesn't allow all the binding sites to be simultaneously bonded to the same metal. Thus, although serine is potentially tridentate ( $\text{NH}_2$ ,  $\text{OH}$  and  $\text{CO}_2^-$ ), in figure 1b it functions only as a bidentate.

Bidentate ligands can  $\sigma$  - bond with a metal through two distinct ligand atoms. If the stereochemistry of the ligand allows both these atoms to bond simultaneously to the same metal then coordination results in metal chelate. Some typical chelating ligands are given in table1 <sup>[1-4, 6]</sup>.



**Table. 1** Some typical chelating ligands

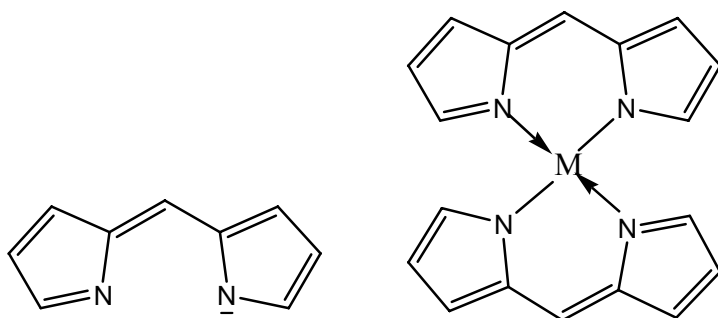
For a ligand to form a 5 or 6 membered chelate ring the two ligand atoms must be separated by two and three atoms respectively. These other atoms are usually, but not necessarily, carbon atoms in either an  $sp^2$  or  $sp^3$  hybridization, as shown by all the structures in table 1. It should be noted that with all the anionic ligands in the table in which only one of the ligands bears a negative charge, this charge can't be delocalized by resonance on the other ligand atom, even in those ligands where the two ligand atoms are separated by  $sp^2$  three hybridized carbon atom. There are, however, a number of important bidentate chelating anions in which delocalization of the charge can occur as shown in figure 2.



**Figure. 2** Delocalization of charge on bidentate chelating anions

Included in this category are the anions of pentane-2, 4-dione(acetylacetonone), ethyl acetate and salicylaldehyde and the various analogues obtained by replacing one or both of the ligands oxygen atoms in these anions by either S or NR<sup>[1, 4, 7]</sup>.

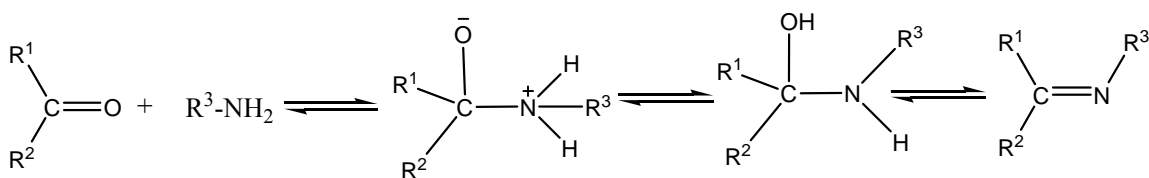
Another example of bidentate chelating anions in which delocalization of the negative charge occurs over ten of the constituent atoms is dipyrromethene anion. This anion, which is invariably in the form of substituted derivatives, forms neutral chelates with most of the bivalent metals.



**Figure. 3** a) Dipyrromethene anion b) Bivalent metal chelate of dipyrromethene anion

## 1.2 Schiff Bases

Many reports have been made on the synthesis and metal binding characteristics of multidentate ligands. Several multidentate ligands possessing C=N or azomethine group are known as Schiff bases. Schiff bases are compounds containing an imine or azomethine group (R-C=N-) and usually prepared by the condensation of a primary amine with an active carbonyl group. The reaction to prepare Schiff bases is reversible, progresses through a carbinol amine intermediate and requires the removal of water.<sup>[8]</sup>



**Figure. 4** General mechanistic aspects of Schiff base preparation

$R^1$  and  $R^2 = H, \text{ aryl}$ ;  $R^3 = \text{alkyl, aryl, OH, NHR, OR, NH}_2, \text{ SH} \dots$  etc functional groups near the site of condensation of Schiff base form effective coordinating ligands by forming five or six membered chelate rings on reaction with metal ions.

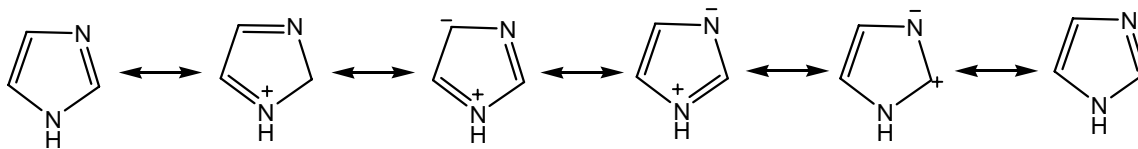
Schiff bases have played an important role in the development of coordination chemistry as they readily form stable complexes with most of the transition metals. Interest on Schiff base metal complexes has been growing in the area of bio-inorganic chemistry due to the role of such complexes in providing synthetic models for the metal containing sites in metalloproteins and enzymes. A huge number of Schiff bases which differ in denticity, flexibility, nature of donor atoms and in electronic properties can be obtained through the condensation reactions.<sup>[8-9]</sup>

Because of the great synthetic flexibility of Schiff base formation, many ligands of varied structural types can be and have been synthesized and their ligational properties have been extensively studied.<sup>[8]</sup>

### 1.3 The Chemistry of Imidazole

Imidazole is a heterocyclic aromatic organic compound, which belongs to the class of five membered planar ring containing one azomethine nitrogen centre.<sup>[10,11]</sup> The simplest member of the imidazole family is imidazole itself, a compound with molecular formula  $C_3H_4N_2$ . Imidazole, the parent compound  $C_3H_4N_2$ , is a white or pale yellow solid which is soluble in water and polar solvents with a relative high melting ( $90^\circ\text{C}$ ) and boiling points ( $256^\circ\text{C}$ ).<sup>[12]</sup> While imidazoles are a class of heterocycles with similar ring structure

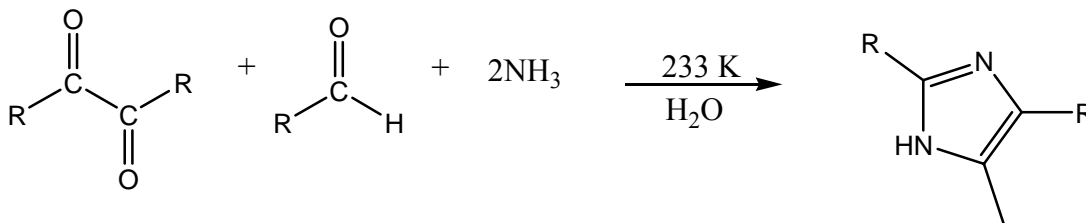
but varying substituents have shown a little deviation as compared with the parent compound. Some resonance structures of imidazole are shown in scheme 1.



**Scheme. 1** Some resonance structures of imidazole

Imidazole is a base and an excellent nucleophile. It reacts at the NH nitrogen, attacking alkylating and acylating compounds. It is not particularly susceptible to electrophilic attacks at the carbon atoms, and most of these reactions are substitutions that keep the aromaticity intact. From the resonance structure the carbon-2 is the carbon most likely to have a nucleophilic attack, but in general nucleophilic substitutions are difficult with imidazoles.<sup>[10,13]</sup>

Imidazole was first synthesized by H. Debus in 1858. His synthesis, as shown in scheme 4, used glyoxal and formaldehyde in ammonia to form imidazole. This synthesis, while producing relatively low yields, is still used for creating C-substituted imidazoles.



**Scheme. 2** Synthesis of imidazole

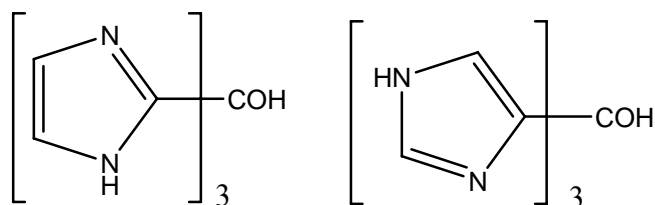
Besides the Debus's method, imidazole can be synthesized by numerous other methods. Many of these syntheses can also be applied to different substituted imidazoles and imidazole derivatives simply by varying the functional groups on the reactants.

In literature, these methods are commonly categorized by which and how many bonds form to make the imidazole rings. The imidazole ring system is present in important biological building blocks such as histidine, and the related hormone histamine. Imidazole can act as a base and as a weak acid. One of the applications of imidazole is in the purification of His-tagged proteins in immobilised metal affinity chromatography (IMAC).<sup>[10]</sup> Imidazole is used to elute tagged proteins bound to Ni ions attached to the surface of beads in the chromatography column. An excess of imidazole is passed through the column, which displaces the His-tag from nickel co-ordination, freeing the His-tagged proteins. Imidazole has become an important part of many pharmaceuticals. Synthetic imidazoles are present in many fungicides and antifungal, antiprotozoal, and antihypertensive medications. Imidazole is part of the theophylline molecule, found in tea leaves and coffee beans, which stimulates the central nervous system. It is present in the anticancer medication mercaptopurine, which combats leukemia by interfering with DNA activities.

Another application of imidazole is in corrosion inhibition process on certain transition metals, such as copper. Preventing copper corrosion is important, especially in aqueous systems, where the conductivity of the copper decreases due to corrosion.<sup>[14]</sup>

#### 1.4 Some Synthetic Aspects of Imidazole Derivatives<sup>[15]</sup>

Three decades ago the synthesis of two isomeric chelating ligands, tris - (2-imidazolyl) carbinol (2-TIC) and tris - [4(5) – imidazolyl] carbinol (4-TIC) have been reported.

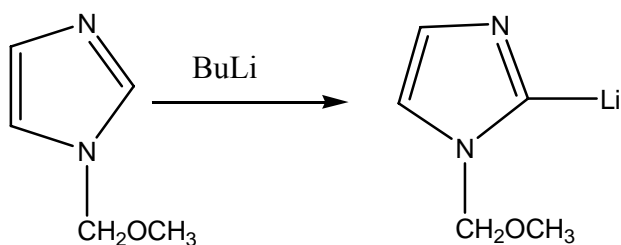


**Scheme. 3** a) tris - (2-imidazolyl) carbinol (2-TIC) b) tris - [4(5) imidazolyl] carbinol (4-TIC)

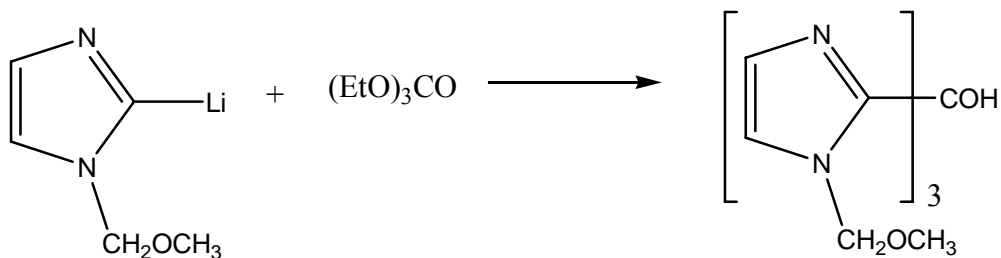
## Mechanistic Aspects of the Tris(2-imidazolyl)carbinol and Tris[4(5)-imidazolyl]carbinol synthesis

### I) Tris(2-imidazolyl)carbinol (2-TIC)

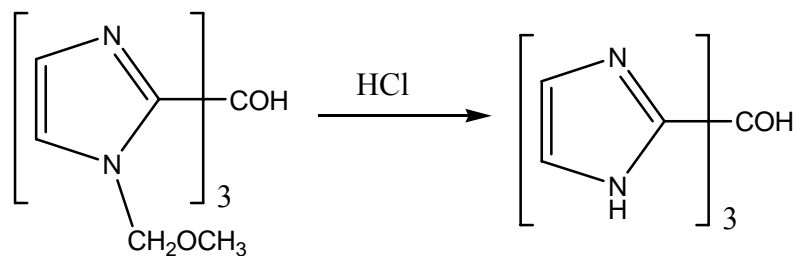
Metallating N-methoxy methyl imidazoles using BuLi at C-2;



Reacting the lithio derivative with diethyl carbonate afford the tris N-methoxy methyl imidazoles carbinol adduct,



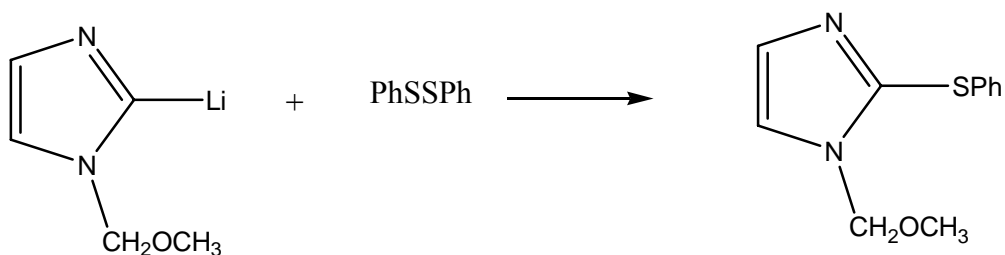
Deprotecting the tris N-methoxy methyl imidazoles carbinol adducts with hydrochloric acid yield, 2-TIC;



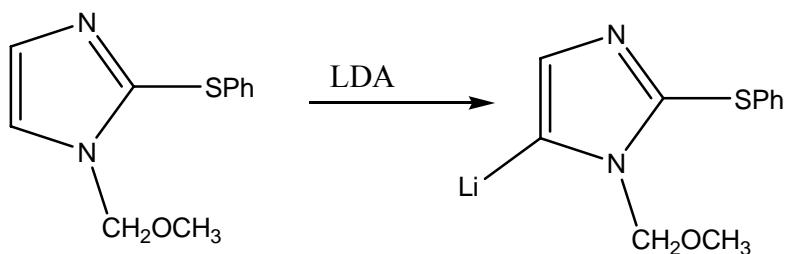
## II) Tris[4(5)-imidazolyl] carbinol (4-TIC)

The synthesis of 4-TIC is more challenging than 2-TIC. All attempts to make organometallic reagents from N-protected 4(5)-bromo imidazole failed, leading either to reduction or to C-2 metallated derivatives.

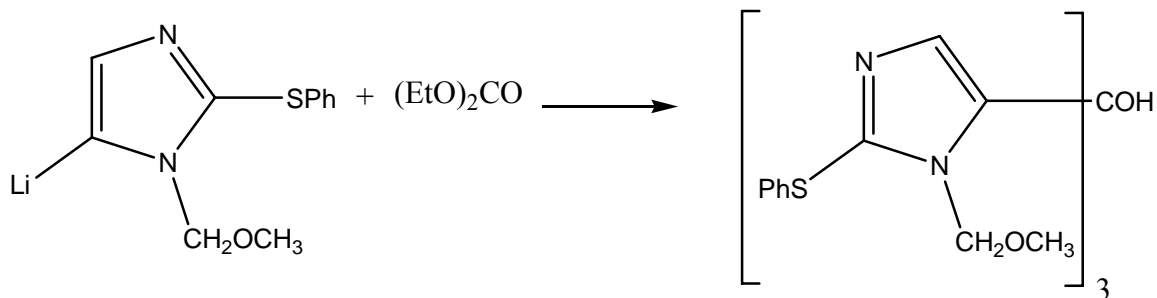
Reacting the lithio N-methoxy methyl imidazole with diphenyldisulfide affords the thiophenyl derivative.



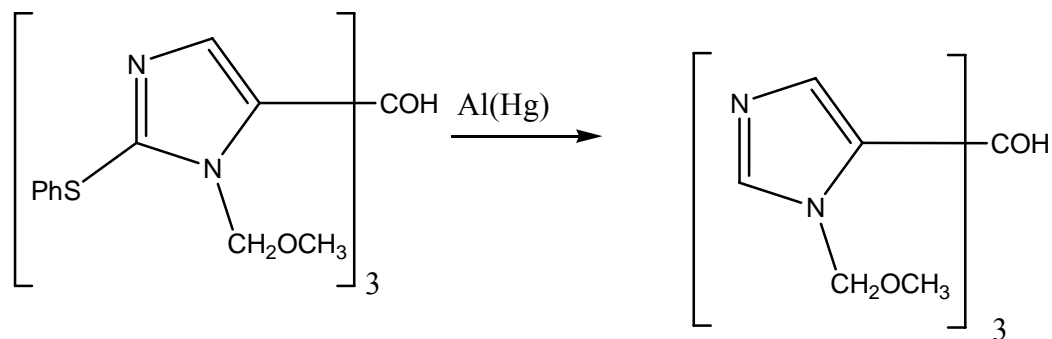
Metallating the thiophenyl derivative with lithiodiisopropylamide yield C-5 lithio N-methoxy methyl imidazole thiophenyl derivative.



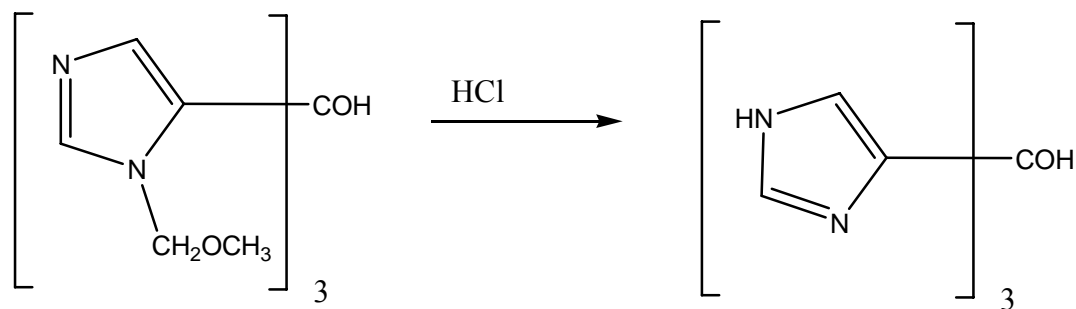
Reacting C-5 lithio derivative with diethylcarbonate yield the tris- N-methoxy methyl imidazole thiophenyl carbinol derivative.



Treating the tris N-methoxy methyl imidazole thiophenyl carbinol with aluminium amalgam in aqueous ethanol gave good yields of tris- N-methoxy methyl imidazole carbinol.



Reacting the tris- N-methoxy methyl imidazole carbinol with HCl produce, the Tris[4(5)-imidazolyl] carbinol (4-TIC).



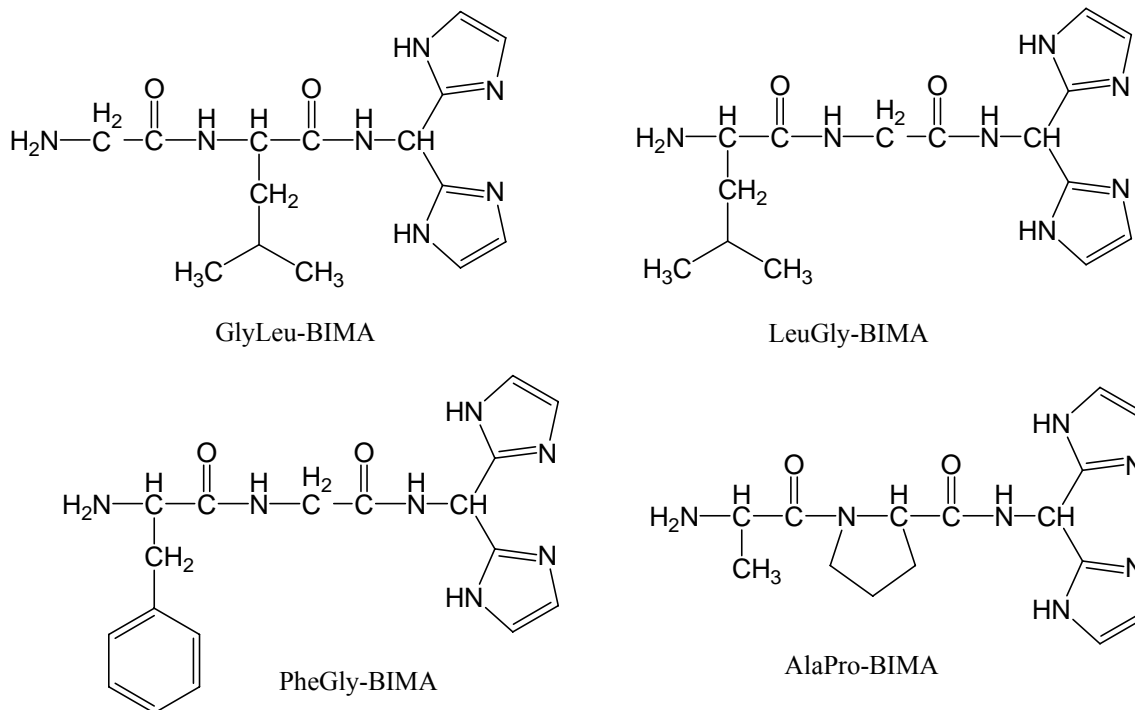
### 1.5 Some Imidazole Derivative Multidentate Ligands with O, N and N, N Donor System

The simplest representatives of polyimidazole ligands are the derivatives of bis(imidazol-2-yl) methane (BIM), in which two imidazole rings are linked *via* a single tetrahedral carbon atom. The bis(imidazol-2-yl)methyl group was reported to be a very effective complexing agent for a great variety of transition metal ions forming stable six-membered chelates *via* the coordination of imidazole nitrogen atoms.<sup>[16]</sup> The coordination chemistry of the ligands containing two imidazole rings is more versatile when the chelating nitrogen donors are linked to other chelating ligands creating multi- and/or ambi-dentate ligands.<sup>[17]</sup>

The metal complexes of multidentate ligands containing the bis(imidazol-2-yl)methyl residues at the C- or N-termini of amino acids or peptides have been reported. From these studies it has been inferred that the imidazole nitrogen donor atoms are the primary metal binding sites in the copper(II), nickel(II) and zinc(II) complexes of these molecules.

Very stable dinuclear complexes were obtained from equimolar solutions of copper(II) and bis(imidazol-2-yl)methyl derivatives of amino acids, in which all metal ions were co-ordinated by [NH<sub>2</sub>, N, N(Im) (Im = imidazolyl)] donors and the metal centres were joined *via* imidazole bridging. The presence of the histidyl side chain in His-bis(imidazol-2-yl)methylamine, however, resulted in a further increase in the versatility of the complex formation reactions. Deprotonation of the imidazole N(1)H donor functions was detected under slightly alkaline conditions. Peptide derivatives of the bis(imidazol-2-yl)-methyl ligands can, however, easily saturate the co-ordination sphere of all metal ions and may provide stable conditions for the formation of imidazolato bridged polynuclear complexes.<sup>[18]</sup>

Some investigators had reported spectroscopic studies on the copper(II), nickel(II) and zinc(II) complexes of GlyLeu- BIMA, LeuGly-BIMA, PheGly-BIMA and AlaPro-BIMA (Scheme 4).



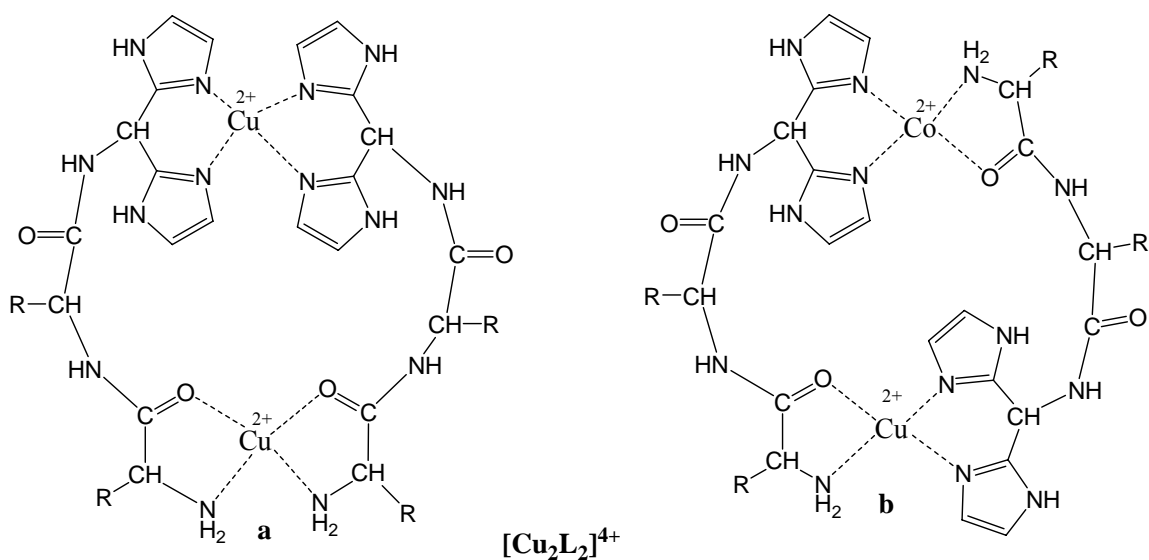
**Scheme. 4** Some bis(imidazol-2-yl) derivatives of dipeptides

The ligands have three dissociable protons and the protonation constants are similar to those of the corresponding bis(imidazol-2-yl)methyl ligands and the most common dipeptides. The  $pK$  values of the imidazole nitrogens are very similar to each other and to those of the amino acid derivatives. This means that the increase in the length of the side chains connected to the bis(imidazol-2-yl)methyl moiety and the presence of the bulky phenyl or alkyl group in the peptide does not effect the acid–base properties of the imidazole rings. Basicity of the terminal amino group is, however, significantly influenced by the amino acid sequence of the ligands. The bulky aromatic ring of N-terminal phenylalanine with a strong electron withdrawing effect decreases, while the presence of proline in the second position slightly increases the  $pK$  values of amino groups. <sup>[19]</sup>

## 1.6 Copper(II) Complexes Of Imidazole Derivative Multidentate Ligands with O, N and N, N Donor

The structures of the three ligands (GlyLeu-BIMA, LeuGly-BIMA and PheGly-BIMA) are very similar to each other and **five nitrogen** donors can be potential metal binding sites: two imidazole nitrogens can form six-membered chelate ring, while the binding of terminal amino, two deprotonated amide and one of the imidazole nitrogens results in the formation of stable fused chelate rings. The prolyl residue of the fourth compound (AlaPro-BIMA) is, however, considered as a “breakpoint” in the peptide chain, because the secondary amide nitrogen cannot be a metal binding site. Former studies on the peptides containing proline in an intermediate position led to the conclusion that proline breaks the metal ion co-ordination to the subsequent amide nitrogen atoms, but it does not necessarily stop further metal–peptide binding. <sup>[19]</sup>

The formation of bis(ligand) complexes is not hindered by the length of the peptide chain connected to the bis(imidazol-2-yl)methyl group. The unusually broad absorption bands with maxima around  $\lambda_{max} = 620$  nm, which is characteristic of copper (II) complexes coordinated by two bis(imidazol-2-yl)-methyl groups, Probably derive from a mixture of various copper(II) complexes containing two, three and/or four N donor atoms in the coordination sphere. These observations can be explained by the assumption of a ligand bridged dimeric structure for the species  $[\text{Cu}_2\text{L}_2]^{4+}$ , which can exist in the form of two isomers, (Scheme 5).



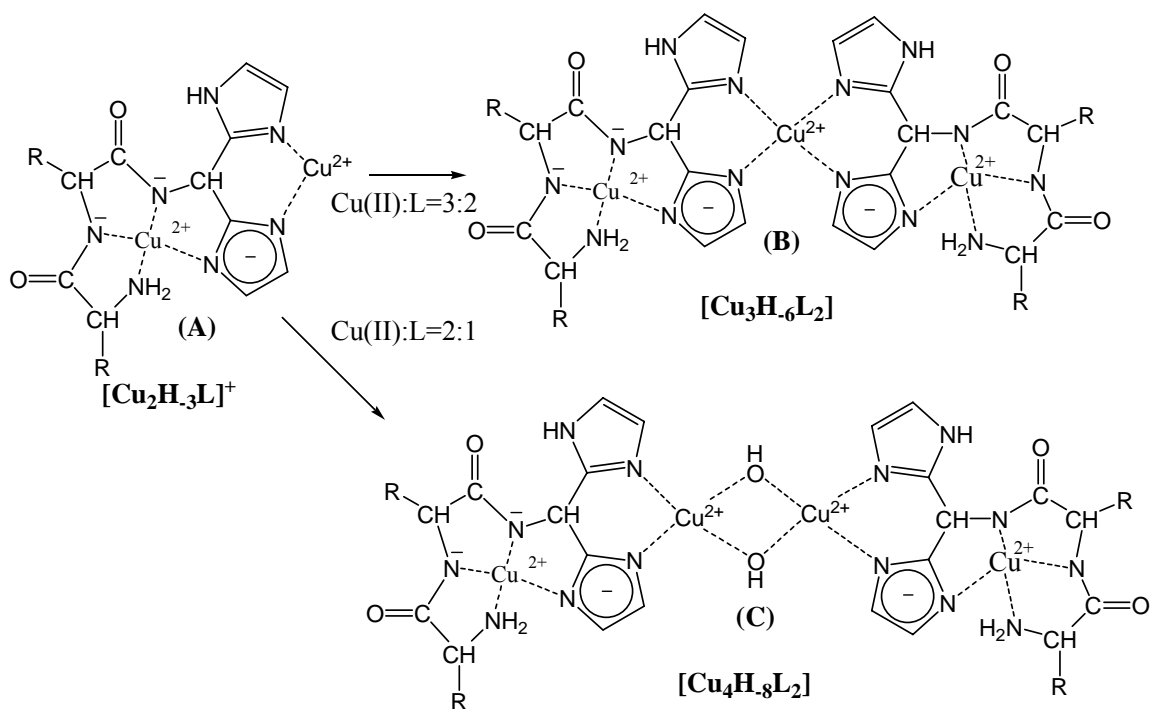
**Scheme. 5** Dinuclear Cu(II) complex coordinated through a) ( $\text{NH}_2$ , CO and N(IM))

In the case of the copper(II) complexes of GlyLeu-BIMA, LeuGly-BIMA, PheGly-BIMA, an extra base consuming process starts above pH 6 and it is accompanied by the shift of absorption maxima to lower wavelengths. The deprotonation and co-ordination of one of the amide nitrogens and the formation of  $[\text{Cu}_2\text{H}_2\text{L}_2]^{2+}$  complex can be concluded. The change of absorption maxima from  $\approx 620$  nm to  $\approx 540$  nm, upon the transformation of  $[\text{Cu}_2\text{L}_2]^{4+}$  to  $[\text{Cu}_2\text{H}_2\text{L}_2]^{2+}$ , however, indicates an increase in the number of co-ordinated nitrogen atoms, suggesting the deprotonation is not able to break the ligand bridged structure of  $[\text{Cu}_2\text{L}_2]^{4+}$ , but the conversion of ( $\text{NH}_2$ , CO) chelate (Scheme 5) to ( $\text{NH}_2$ , N $^-$ ) chelate (Scheme 6) takes place in the dinuclear species.<sup>[19,20]</sup>



Another base consuming process takes place under strongly alkaline conditions ( $\text{pH} > 10$ ), which may correspond to the deprotonation of pyrrole type nitrogen of imidazole ring or the formation of mixed hydroxo complexes. Taking into account the decrease of  $\lambda_{max}$ , the formation of  $[\text{CuH}_3\text{L}]^-$  should be the result of deprotonation of the N(1)H group (Scheme 7). The stable 4N structure with a saturated co-ordination sphere around the copper(II) ions hinders the hydrolysis of the complex and the appearance of precipitation. The deprotonation of the N(1)H group of the imidazole ring was observed in alkaline solutions of copper(II) complexes of various ligands containing histidyl residues.[18,20] The deprotonation generally took place in the pH range 8–12 resulting in the formation of polymeric structures in some cases. The blue shift of the absorption maxima was also observed in parallel with the deprotonation of the pyrrole type N(1)H group.

The multidentate character of the ligands makes it possible to bind more than one metal ion and it is important to note that the N(1)H deprotonation creates a new chelating site, too. As a consequence, precipitation was not observed even in slightly basic solution up to 2: 1 Cu(II): L ratio and the formation of various polynuclear complexes was suggested that the species  $[\text{Cu}_2\text{H}_3\text{L}]^+$ ,  $[\text{Cu}_3\text{H}_6\text{L}_2]$  and  $[\text{Cu}_4\text{H}_8\text{L}_2]$  are the major polynuclear complexes in alkaline solutions and their formation is represented by Scheme 8. Following the binding of the second amide group in  $[\text{CuH}_2\text{L}]$  the imidazole nitrogen atoms get to a sterically favourable position which promotes the deprotonation of the pyrrole type N(1)H group resulting in the formation of the  $[\text{Cu}_2\text{H}_3\text{L}]^+$  species (Scheme 8a.). It is also clear from the structure of  $[\text{Cu}_2\text{H}_3\text{L}]^+$ , that the co-ordination sphere of the metal ion is not saturated yet, and this results in the formation of tri- or tetra-nuclear complexes depending on the metal to ligand ratio.



**Scheme. 8** Dinuclear, trinuclear and tetranuclear Cu(II) complexes

At 3 : 2 metal to ligand ratio the trinuclear complex  $[\text{Cu}_3\text{H}_6\text{L}_2]$  predominates above pH 7, in which all copper(II) ions are coordinated by 4 N donor atoms (Scheme 8b), while at 2 : 1 metal to ligand ratio a mixed hydroxo complex  $[\text{Cu}_4\text{H}_8\text{L}_2]$  is formed connecting the  $[\text{Cu}_2\text{H}_3\text{L}]^+$  moieties *via* hydroxo bridges (Scheme 8c).<sup>[19]</sup>

## 1.7. Aim and Scope of the Present Investigation

Literature review reveals that the synthesis and applications of amino acid and peptide containing Bis and Tris (imidazolyl) ligands and their coordination chemistry have been extensively studied. But in all cases, the imidazole rings are connected by one, two or three aliphatic carbons. Bis - chelating ligands derived from the condensation of 4(5) - imidazole carboxo aldehyde and 2, 4-Dihydroxy-5-acetylacetophenone (DAAP) have not been attempted for studies on metal complexation.

The ligand aimed for study will have an aromatic back-bone on which imidazoles, N-C=N, conjugated C=N and hydroxyl group of the phenol functional group are grafted to achieve bis-multidenticity towards metal ions. The ligands will be synthesized in the following steps.

- i) synthesis of DAAP
- ii) synthesis of DAAD
- iii) synthesis of 4,6 - Bis{[(imidazo-5-yl) methyl] hydrazo] ethyl }-benzene-1,3-diol

For this investigation  $\text{Cu}^{2+}$  has been chosen for the synthesis of the metal complex. The ligand will be characterized using IR, UV-VIS and MS spectra where as the metal complex will be characterized on the basis of analysis, spectra (IR and UV -VIS), conductance, magnetic susceptibility and AAS data.

## **2. MATERIALS AND METHODS**

### **2.1. Chemicals**

All the chemicals used were of AnalaR grade. Metal salts used for synthesizing the complex and as a catalyst were  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  and  $\text{ZnCl}_2 \cdot 2\text{H}_2\text{O}$  respectively. Chemicals that were used for the preparation of the two precursors (DAAP and DAAD) and the ligand (BDIHEBD) were resorcinol, acetic anhydride, fused and crushed zinc chloride,  $\text{H}_2\text{N-NH}_2 \cdot \text{H}_2\text{O}$ , sodium acetate and 4(5) - imidazole carboxo aldehyde. Solvents used include MeOH, EtOH, acetic acid and distilled water. Other chemicals used were charcoal,  $\text{AgNO}_3$ , HCl,  $\text{HNO}_3$  and  $\text{NH}_4\text{OH}$ .

### **2.2. Instruments**

Infrared (IR) spectra were recorded using a Perkin Elmer Spectrum BX FT-IR spectrophotometer in the range  $4000 - 400\text{cm}^{-1}$  using pressed pellet sampling technique /KBr discs/. The melting points and decomposition temperatures were determined using Stuart SMP3 Digital Melting Point apparatus. UV-Vis spectrophotometric measurements were done in the range 200-1000nm using Spectronic Genesys 2PC spectrophotometer. Magnetic susceptibility data was recorded using MSB-AUTO, (Sherwood Scientific) Magnetic Balance. The molar conductivity measurement was carried out using EC 214 Bench type conductivity meter (Hanna Instrument). The metal content was estimated using Buck Model Scientific 210 VGB Atomic Absorption Spectrometer. During the study, several other common laboratory equipments were also used. The MS data of the ligand was generated on Thermofinnigan High Temperature Direct insertion Probe Instrument. The sample was ramped from RT up to  $300^{\circ}\text{C}$ .

## **2.3. Methods**

### **2.3.1. Qualitative Test**

#### **I) Chloride Test**

Compounds (samples) dissolved in nitric acid were subjected to chloride identification. The presence of chloride in the sample was confirmed by the formation of a curdy white precipitate on the addition of  $\text{AgNO}_3$  (0.1N).

### **2.3.2. Quantitative Determinations**

#### **I) Chloride determination**

For Quantitative determination of Chloride, 20mg of the sample (metal complex) was dissolved in 10ml of conc.  $\text{HNO}_3$  and heated on a hot plate. 4-5 ml of conc.  $\text{HNO}_3$  were added, repeatedly and heating was continued until all the organic matter decomposed and only the chloride contents (metal chloride), were left over.

The aqueous extract with a few ml of  $\text{HNO}_3$  added was diluted to about 100ml. And  $\text{AgNO}_3$  solution was added until precipitation of  $\text{AgCl}$  was completed. It was digested on a steam bath and left to cool overnight. Then the precipitate formed was filtered through a sintered crucible which was initially cleaned, dried and weighed. The sintered crucible was dried to a constant weight in an oven at  $110^\circ\text{c}$ . The amount of chloride was determined from the weight difference.

#### **II) Metal determination**

The metal percentage was estimated by decomposing 20mg of the metal complex through digestion in 10ml conc.  $\text{HNO}_3$  until a clear solution observed. The clear solution was diluted to 25ml volumetric flask to make solutions of known concentration and the metal content was recorded using Buck Model Scientific 210 VGB Atomic Absorption Spectrometer.

### **III) Molar conductance measurement**

One millimolar solution of metal complex was prepared in acetic acid and molar conductance was calculated from conductivity recording.

### **IV) Magnetic Susceptibility**

The gram susceptibility of the complex was determined using MSB-AUTO, (Sherwood Scientific) Magnetic Balance. The magnetic moment was calculated after converting gram susceptibility into molar susceptibility and incorporating diamagnetic corrections.

### 3. EXPERIMENTAL PART

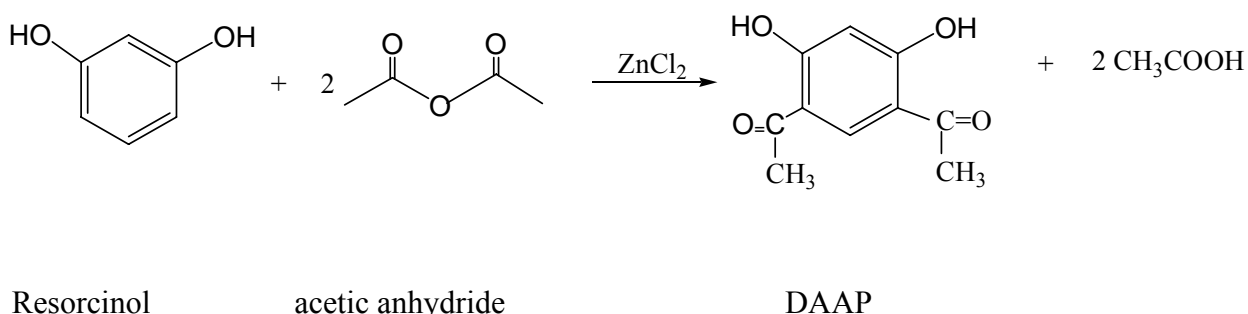
#### 3.1. Synthesis of 2, 4-Dihydroxy-5-Acetylacetophenone (DAAP)

To a mixture of fused (made by heating on direct flame) and crushed zinc chloride (10g) and acetic anhydride (17.3ml), 10g of resorcinol was added gradually while stirring. The resulting pink solution was refluxed for 30 minutes on an oil bath in temperature range of 140°C -160 °C and was left overnight. It was hydrolyzed with dilute hydrochloric acid (HCl/ H<sub>2</sub>O being 1:1 v/v) in an ice bath. During hydrolysis deep-red mud like material was formed which was filtered, washed thoroughly with distilled water and was left open for drying. The dried product was repeatedly recrystallized to purify from impurities using methanol as a solvent and charcoal as a decolorizing agent.

Yield: 2.7g (15%)

Color: white

Appearance: needle-like crystal



**Scheme. 9** Synthesis of DAAP

#### 3.2. Synthesis of 2, 4-Dihydroxy-5-Acetylacetophenone Dihydrazone (DAAD)

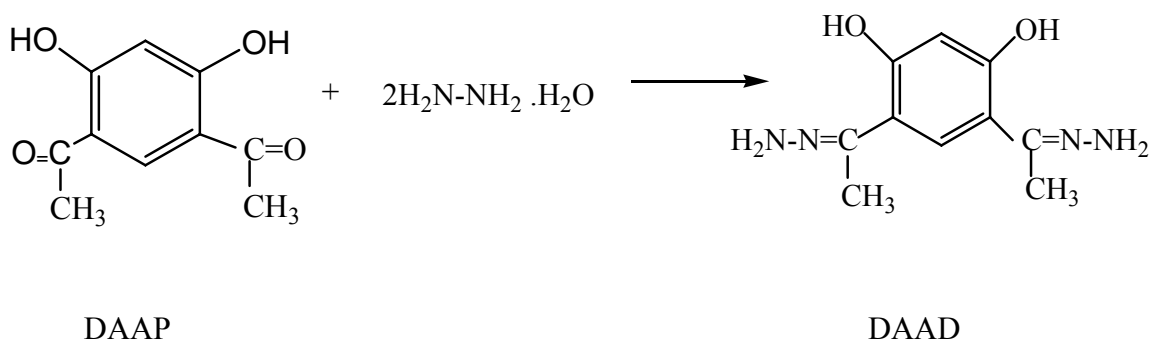
A solution of hydrazine hydrate (0.3ml, 5.2mmol) in methanol (5.15ml) was added to a hot methanolic solution (5.15ml) of DAAP (0.5g, 2.6mmol). The resulting solution was

refluxed on a water bath for 3 hours. The bright - yellow crystalline product was filtered, and washed successively with methanol and petroleum ether and then dried in open air.

Yield: 0.3917g (78 %)

Color: bright - yellow

Appearance: Crystalline



**Scheme. 10** Synthesis of DAAD

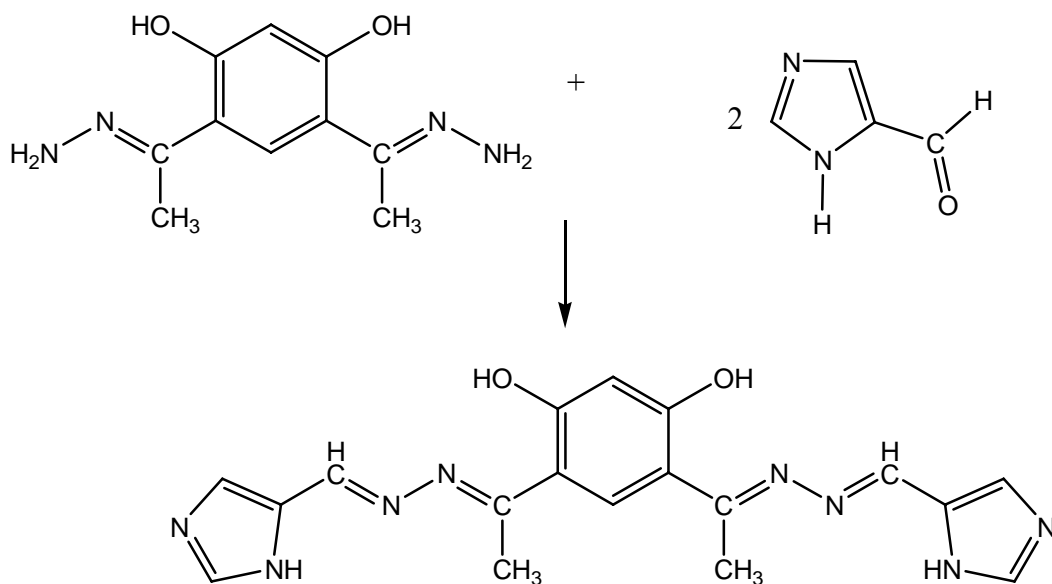
### 3.3. Synthesis of 4,6 – Bis{[(imidazo-5-yl) methyl] hydrazo} ethyl }-benzene-1,3- diol (BIMHEBD)

A solution of [4(5)-Imidazole carboxo aldehyde] (0.206g , 1.6 mmol ) dissolved in 10ml of acetic acid was added drop wise with stirring to a mixture of (0.15g ,0.676 mmol ) DAAD in the same solvent and 0.5% aqueous sodium acetate. The bright-yellow solution was refluxed for 4 hours over an oil bath at 130<sup>o</sup>C and was left over night. The product obtained was filtered, washed thoroughly with distilled water and acetone.

Yield: 0.153g (60 %)

Color: yellow

Appearance: powder



**Scheme. 11** Synthesis of [BIMHEBD](#)

### **3.4. Synthesis of metal complex**

To a methanolic solution (1%) of the ligand (0.05 g, 0.132 [mmol](#)) a methanolic solution of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (0.045g, 0.265 [mmol](#)) was added. The pH of the solution was adjusted to 6.5-7.0 using a methanolic sodium hydroxide solution and the contents were refluxed for 48 hours. The separated metal complex was filtered, washed thoroughly with methanol and then dried in open air.

Yield: [0.052 \(56 %\)](#)

Color: green

Appearance: powder

## 4. RESULTS AND DISCUSSION

Three active compounds were initially prepared; from which the two precursors DAAP and DAAD were reported earlier and the third **BIMHEBD** was synthesized for the first time. The IR spectra of DAAP and DAAD were reproduced. Beside the IR spectrum and the mass spectrum were generated for the newly synthesized compound, **BIMHEBD**.

### 4.1. Physical Characteristics

Some of the important physical characteristics of the compounds DAAP, DAAD, BIMHEBD and Cu(II)complex are listed in table 2

**Table. 2** Physical properties of DAAP, DAAD, BIMHEBD and Cu(II)complex.

Compound	Mol. formula	Mol. Weight(g/mol)	appearance	color	M.Pt (°C)	Yield (%)
DAAP	C <sub>10</sub> H <sub>10</sub> O <sub>4</sub>	194	Needle-like crystals	White	179-184	15
DAAD	C <sub>10</sub> H <sub>14</sub> O <sub>2</sub> N <sub>4</sub>	222	Crystalline	bright-yellow	> 320	78
<b>BIMHEBD</b>	C <sub>18</sub> H <sub>18</sub> O <sub>2</sub> N <sub>8</sub>	378	Fine-powder	<b>yellow</b>	243 (Decomp)	<b>60</b>
Cu(II) complex	C <sub>18</sub> H <sub>34</sub> O <sub>11</sub> N <sub>8</sub> Cl <sub>2</sub> Cu <sub>2</sub>	736	<b>Fine-powder</b>	green	321 (Decomp)	56

**Table. 3** Solubility check for DAAP, DAAD, BIMHEBD and Cu(II) complex with some selected solvents

compound	Methanol	Ethanol	Water	Acetonitrile	Chloroform	THF	DmsO	Acetic acid
DAAP	soluble	-	insoluble	-	soluble	insoluble	soluble	insoluble
DAAD	insoluble	-	insoluble	-	Partially soluble	Partially soluble	Partially soluble	soluble
BIMHEBD	soluble	soluble	insoluble	insoluble	Partially soluble	insoluble	Partially soluble	insoluble
Cu(II) complex	insoluble	Partially soluble	insoluble	insoluble	insoluble	insoluble	insoluble	insoluble

## 4.2 IR Spectra of DAAP, DAAD, and BIMHEBD

### 4.2.1 IR Spectrum of DAAP

The broad band centered at  $3421\text{ cm}^{-1}$  is assigned to OH stretching of phenolic functional group. The CH stretching mode of the methyl group is located at  $2925\text{ cm}^{-1}$  and it's overlapped by CH stretching mode of the ring.<sup>[21]</sup> The C=C stretching mode of the ring is located at  $1588\text{ cm}^{-1}$ . The strong band at  $1646\text{ cm}^{-1}$  correspond to C=O stretching.<sup>[22]</sup> The strong band at  $1243\text{ cm}^{-1}$  can be assigned to C-O stretching of the phenolic group. The band at  $1355\text{ cm}^{-1}$  may be assigned to the CH bending mode of methyl functional group. The strong band at  $1370\text{ cm}^{-1}$  can be assigned to OH deformation vibration of the phenolic functional group. The band at  $1183\text{ cm}^{-1}$  may be assigned to the aromatic CH in plane deformation vibration of 1, 2, 4, 5-tetra substituted aromatic ring. The band at  $951\text{ cm}^{-1}$  can be assigned to N-N stretching. The strong band at  $839\text{ cm}^{-1}$  may be assigned to the aromatic CH out of plane deformation vibration of 1, 2, 4, 5-tetra substituted aromatic ring. The strong band at  $578\text{ cm}^{-1}$  may be assigned to the C-CO-C in plane deformation vibration. The weak band at  $455\text{ cm}^{-1}$  may be assigned to in plane bending vibration of aromatic C-OH bond.<sup>[21]</sup>

#### 4.2.2 IR Spectrum of DAAD

The band at  $3367\text{ cm}^{-1}$  can be assigned to the symmetric stretching of  $\text{NH}_2$  group. The asymmetric stretching of  $\text{NH}_2$  group is not observed in the spectrum, this may be due to the overlap of this band with broad phenolic OH stretching in the range  $3400 - 2800\text{ cm}^{-1}$ . The broad range of the phenolic OH stretching is observed due to hydrogen bonding.<sup>[22]</sup> The band at  $2924\text{ cm}^{-1}$  can be assigned to CH stretching of methyl group. The strong band at  $1617\text{ cm}^{-1}$  can be assigned for C=N stretching. The band at  $1229\text{ cm}^{-1}$  may be assigned to C-O stretching of phenolic functional group. The strong band at  $1369\text{ cm}^{-1}$  may be assigned to phenolic OH bending. The band at  $1110\text{ cm}^{-1}$  may be assigned to OH out of plane bending. The weak band at  $1282\text{ cm}^{-1}$  may be assigned to aromatic CH in plane deformation vibration of 1, 2, 4, 5-tetra substituted aromatic ring. The band at  $949\text{ cm}^{-1}$  can be assigned to N-N stretching. The band at  $876\text{ cm}^{-1}$  corresponds to the aromatic vibration CH out of plane deformation vibration of 1, 2, 4, 5-tetra substituted aromatic ring. The band at  $1179\text{ cm}^{-1}$  may be assigned to the aromatic CH in plane deformation vibration of 1, 2, 4, 5-tetra substituted aromatic ring.<sup>[21]</sup>

**Table. 4** Characteristics vibrational frequencies of DAAP and DAAD

Compound	$\nu_{\text{OH}}$	$\nu_{\text{NH}_2}$ sym	$\nu_{\text{NH}_2}$ asym	$\nu_{\text{C-H}}$ , methyl	$\nu_{\text{C-H}}$ , benzene	$\nu_{\text{C=O}}$	$\nu_{\text{C=N}}$	$\nu_{\text{C-O}}$	$\nu_{\text{V-N}}$
DAAP	3500- 2850(br)		-	2925	overlapped with $\text{CH}_3$	1646	-	1243	-
DAAD	3400- 2700(br)	3367	-	2924	overlapped with $\text{CH}_3$	-	1617	1229	949

### 4.2.3 IR Spectrum of BIMHEBD

The broad band centered at  $3401\text{ cm}^{-1}$  is assigned to OH stretching of phenolic functional group. The N-H stretching of the imidazole functional group is not clearly observed this is due to the overlap of the N-H stretching band with broad phenolic OH stretching band. The band at  $2926\text{ cm}^{-1}$  can be assigned to CH stretching of methyl group. Multiple splitted strong bands in the range of  $1650 - 1570\text{ cm}^{-1}$  (specifically at 1647 and 1597) may be assigned to C=N-N=C stretching of the dihydrazone derivative.<sup>[21,23]</sup> The band at  $1491\text{ cm}^{-1}$  may be assigned to aromatic C=C stretching of the imidazole functional group. The band at  $1570\text{ cm}^{-1}$  may be assigned to N-C=N stretching of the imidazole functional group.<sup>[21,24]</sup> The band at  $1243\text{ cm}^{-1}$  corresponds to C-O stretching of phenolic functional group.

### 4.2.4 Mass spectrum of BIMHEBD

The mass spectrum reveals a peak at  $m/Z = 380$  and at  $m/Z = 379$  of relative low abundance, which is the di- and monoprotonated form of the ligand, BIMHEBD, with molecular formula 378 respectively. The base peak appears at  $m/Z = 129$  while other ions recorded in the spectrum correspond with  $m/Z = 293, 259, 241, 207$  .....

### 4.3 IR Spectrum of the Metal Complex

Comparing the spectrum of the free ligand with the metal complex, a significant shift with reduced multiplicities of characteristics bands were observed that can be correlated with complex formation. The band centered at  $3422\text{ cm}^{-1}$  can be assigned to the OH stretching of the coordinated water. The band at  $2924\text{ cm}^{-1}$  can be assigned to CH stretching of methyl group. The shift to a lower frequency of C=N multiple bands in the range  $1650 - 1597\text{ cm}^{-1}$  of the free ligand indicates the involvement of C=N-N=C in complexation.<sup>[25,26]</sup> The shift to a lower frequency of N-C=N stretching of the imidazole functional group from  $1570\text{ cm}^{-1}$  to  $1532\text{ cm}^{-1}$  indicates the involvement of N-C=N of the imidazole functional group in complexation. The positive shift of C-O stretching indicates the deprotonation of the phenolic group and subsequent complexation through phenoxide. The disappearance of the broad band due to  $\nu_{\text{OH}}$  also indicates the

deprotonation of the phenolic group. The down ward shift of N-N stretching in the complex further confirms the involvement of C=N in coordination.<sup>[26]</sup> Non-ligand bands in the range of 600-400 cm<sup>-1</sup> can be assigned to for M – N and M – O stretching.

**Table. 5** Characteristics vibrational frequencies of BIMHEBD and Cu(II) complex

Compound	$\nu_{OH}$	$\nu_{NH}$ sym	$\nu_{C-H}$ , methyl	$\nu_{C-H}$ , benzene	$\nu_{C=NN=C}$	$\nu_{N-C=N}$ Imidazole	$\nu_{C-O}$	$\nu_{V-N}$
<b>BIMHEBD</b>	3450-2650(br)	overlapped with OH	2926	overlapped with CH <sub>3</sub>	1647, 1597	1570	1243	949
<b>Cu(II) complex</b>	3550-3100(br)	overlapped with OH	2924	overlapped with CH <sub>3</sub>	1636, 1585	1532	1261	960

#### 4.4 Molar Conductivity of the Metal Complex

One mmol of metal complex was added in a flask that contains 25ml acetic acid and molar conductance was recorded. The molar conductance of the complex is below 5  $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ . The negligible molar conductivity value indicates the non-electrolytic nature of the metal complex and that the chloride ions in the metal complex are present in the inner sphere or coordination sphere.

#### 4.5 Atomic Absorption Spectroscopy of Metal Complex

The metal percentage was estimated by decomposing 20mg of the metal complex through digestion in 10ml conc. HNO<sub>3</sub> until a clear solution observed. The clear solution was diluted to 25ml volumetric flask to make solutions of known concentration. For sample analysis, three series of working standard metal solutions were prepared by appropriate

dilution of the metal stock solutions with water containing 1.5ml conc.HNO<sub>3</sub>. Calibration graph for copper using the prepared standard solutions was plotted. Even if the calibration graph was plotted, the concentration of the copper wasn't recorded since the concentration is out of the linear range. There fore, only the absorbance was recorded and from the absorbance the concentration was calculated.

The experimental percentage composition of the metal complex was determined using the following relation. <sup>[27]</sup>

$$\begin{aligned} \% \text{ of Cu} &= \frac{\text{absorbance (ppm)} \times \text{volume diluted} \times 100}{\text{Mass of sample taken} \times 1000} \\ &= \frac{34.5 \times 25\text{ml} \times 100}{5.3\text{mg} \times 1000} \\ &= 16.27\% \end{aligned}$$

**Table. 6** percentage composition of copper in the complex

complex	% of copper		Formula of the Cu(II) complex
	Cal.	Exp.	
Cu(II)	16.45	16.27	C <sub>18</sub> H <sub>34</sub> O <sub>11</sub> N <sub>8</sub> Cl <sub>2</sub> Cu <sub>2</sub>

The experimental and the calculated percentage composition of the metal is in good agreement with the formula of the complex taken as Cu<sub>2</sub>Cl<sub>2</sub>N<sub>8</sub>O<sub>11</sub>H<sub>34</sub>C<sub>18</sub>.

#### 4.6 Chloride Analysis Data

20 mg of the sample (metal complex) was dissolved in 10ml of conc. HNO<sub>3</sub> and heated on a hot plate. 10 ml of conc. HNO<sub>3</sub> were added, and heating was continued until all the organic matter decomposed and only the chloride contents (metal chloride), were left over.

The aqueous extract was diluted to 100ml and AgNO<sub>3</sub> solution was added to the hot solution until precipitation of AgCl was completed. It was digested on steam bath and left to cool overnight. Then the precipitate formed was filtered through a sintering glass crucible which was initially cleaned, dried and weighed. The sintered crucible was dried

in an oven at 110<sup>0</sup>c. The amount of chloride was determined from the weight difference AgCl.

**Table. 7** Percentage composition of chloride in the complex

complex	% of chloride		Formula of the Cu(II) complex
	Cal.	Exp.	
Cu(II)	8.96	9.19	$C_{18}H_{34}O_{11}N_8Cl_2Cu_2$

#### 4.7 Magnetic Susceptibility of Metal Complex

The effective magnetic moment of the complex was calculated using the formula

$$\mu_{\text{eff}} = 2.823\sqrt{\chi_M T}$$

Where  $\chi_M$  - is molar magnetic susceptibility which is derived from  $\chi_g$ , gram magnetic susceptibility and T is absolute temperature. The magnetic susceptibility measurement for a powdered sample of the metal complex was performed at 22<sup>0</sup>C. The magnetic moment ( $\mu = 0.72$  B.M.) of the copper complex deviates from the expected magnetic moment corresponding to one unpaired electron. This subnormal magnetic moment is expected to result from the anti ferromagnetic interaction associated with a bridged bi -nuclear metal complex which leads to super exchange phenomena. The unpaired electron on the first copper (II) centre interacts with the unpaired electron on the second copper(II) centre through extended conjugation between them due to the bridging ligand with the result the unpaired electron on the second copper center is aligned in an anti parallel manner with respect to that on the first copper. <sup>[2]</sup>

#### 4.8 UV-VIS Spectrum of BIMHEBD

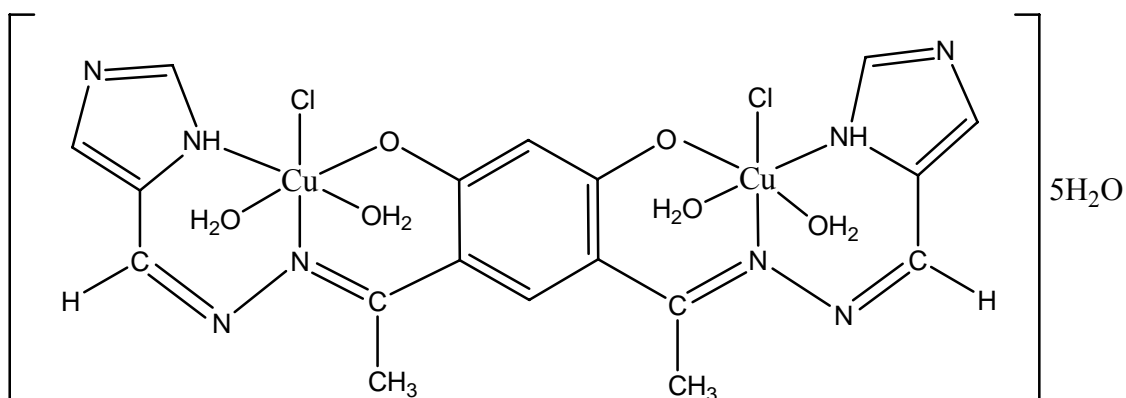
Corresponding to the expected structure of **BIMHEBD**, the electronic spectrum of **BIMHEBD** exhibits some electronic bands. The band at  $34602\text{ cm}^{-1}$  may be due to  $\pi \rightarrow \pi^*$  transition of the substituted benzene. The strong absorption band at  $31545\text{ cm}^{-1}$  and a weak band at  $28571\text{ cm}^{-1}$  can be attributed to  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transition of the conjugated C=N-N=C chromophore respectively. The  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transition of the imidazole N-C=N functional group may be overlapped with  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transition of the conjugated C=N-N=C chromophore.<sup>[28]</sup>

#### 4.9 UV-VIS Spectrum of the Cu(II) Complex

Beside significant modification in comparison with the absorption spectrum as the free ligand additional features due to **d-d** transitions are observed.  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transition of the C=N-N=C chromophore bathochromically shifted to  $30487\text{ cm}^{-1}$  and  $27397\text{ cm}^{-1}$  respectively. Considering the overlap of the  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transition of the imidazole C=N functional group with  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transition of the conjugated C=N-N=C chromophore there might be a bathochromic shift of the  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transition of the imidazole N-C=N functional group due to the coordination of the imidazole N-C=N with the metal. A broad band in the range of  $17605 - 12500\text{ cm}^{-1}$  is observed without any resolved components. The broadness of the band is assumed to be due to the combination of three possible transitions  ${}^2B_1 \rightarrow {}^2A_1$ ,  ${}^2B_1 \rightarrow {}^2B_2$  and  ${}^2B_1 \rightarrow {}^2E$  which are assignable for a distorted octahedral geometry due to Jahn-Teller effect.<sup>[26]</sup> The proposed structure of the complex is given in fig. 5.

## 5. CONCLUSION

The negligible molar conductivity value reveals the non-electrolytic nature of the metal complex and the chloride ions in the metal complex are coordinated in the inner sphere. The AAS data confirms the metal to ligand ratio as 2 : 1. The UV-VIS spectrum and magnetic moment suggest a distorted octahedral geometry for the Cu(II)-complex. The IR spectrum of the complex confirms the dibasic bis –tridentate chelating nature of the ligand towards the Cu(II). Subnormal magnetic moment of the complex indicates metal – metal interaction in solid state.



**Figure. 5** Proposed structure of the Cu(II) Complex.

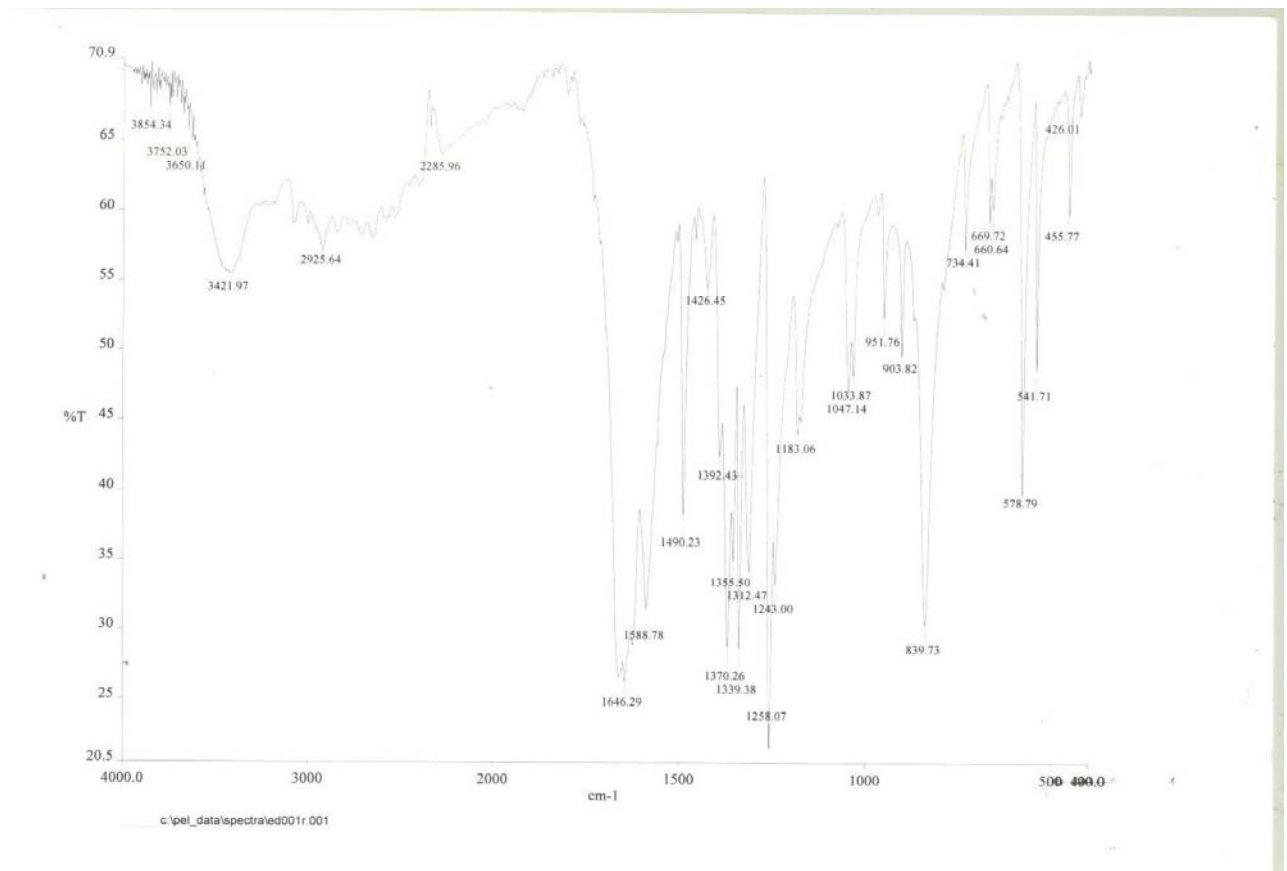
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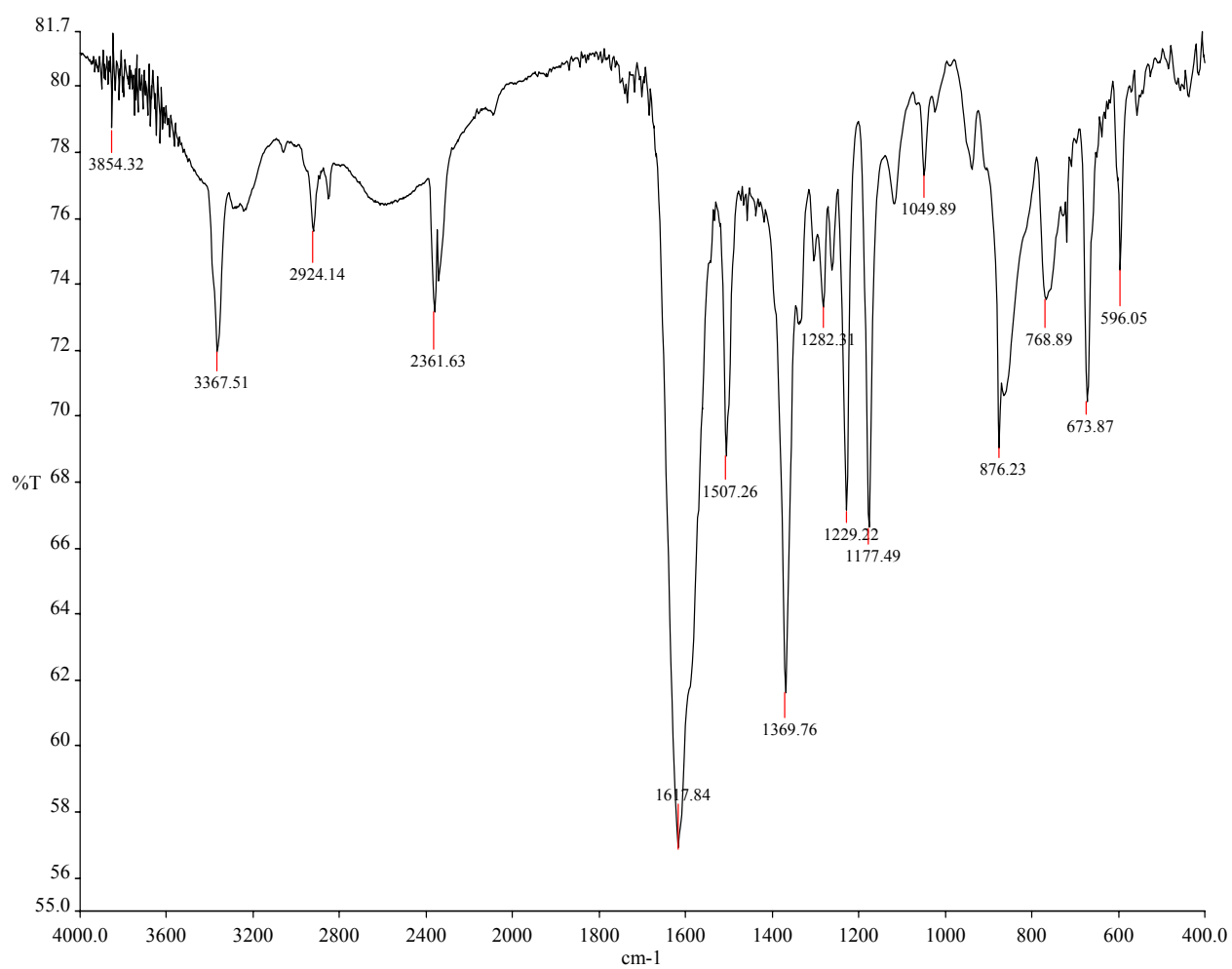
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# **APPENDICES**

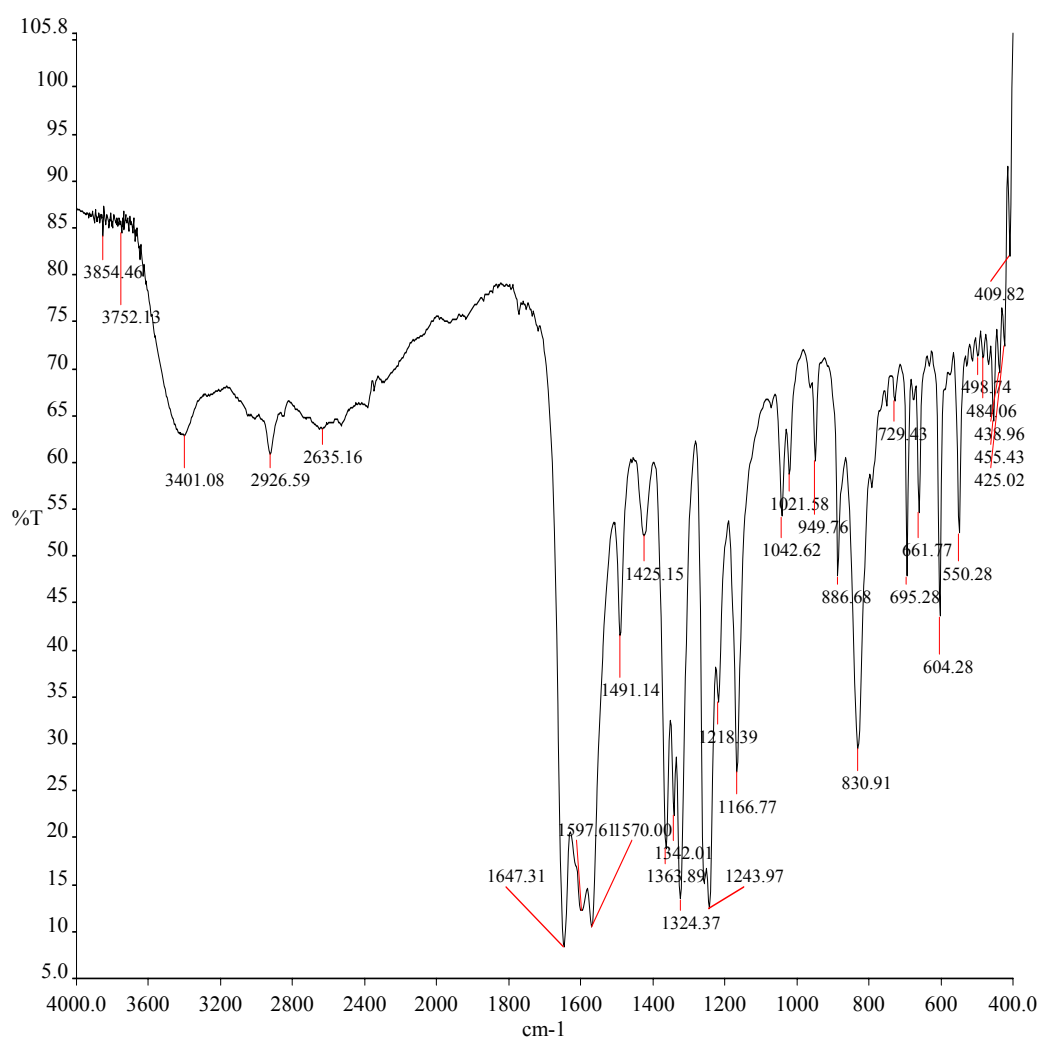
## Appendix 1. IR spectrum of DAAP



## Appendix 2. IR spectrum of DAAD

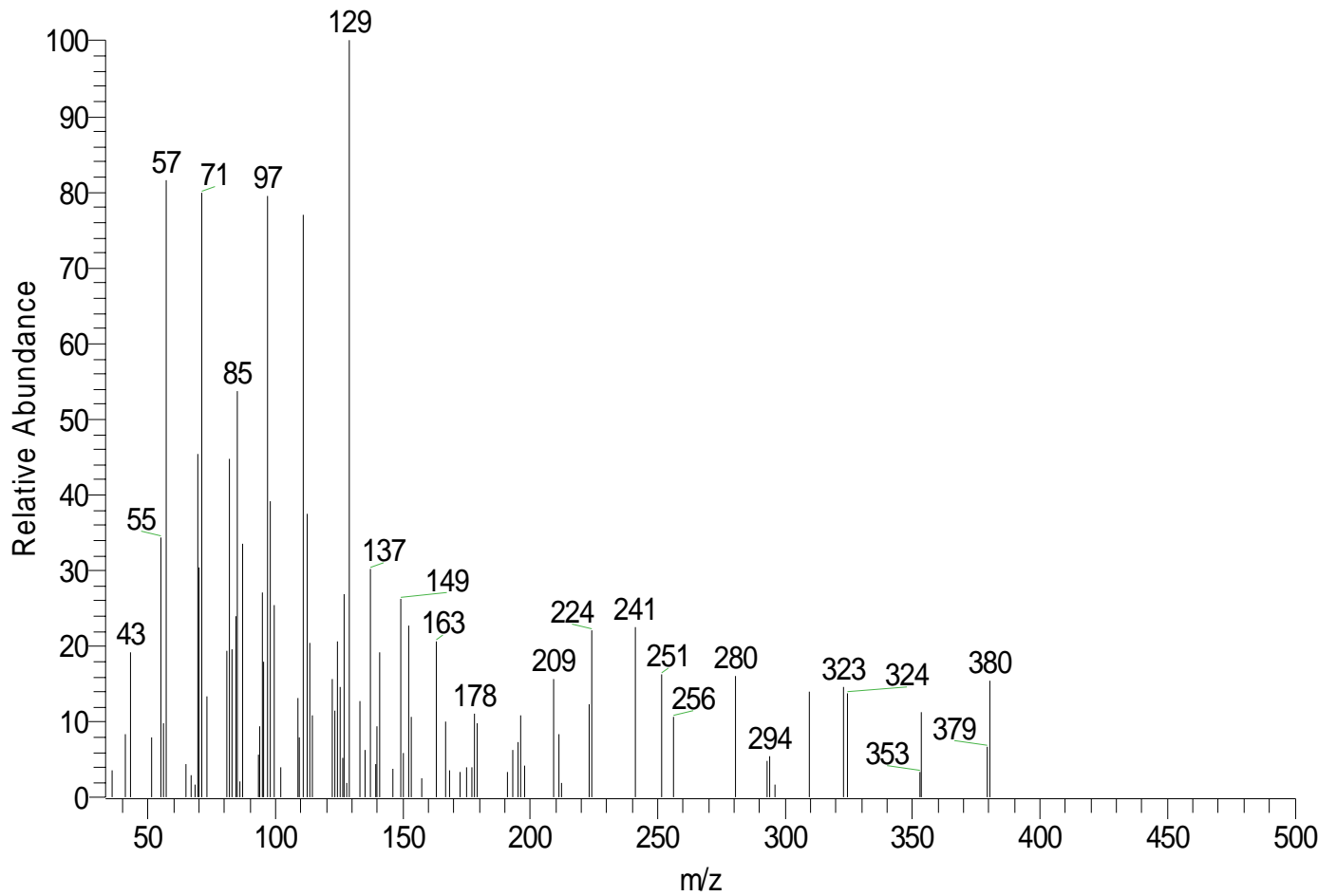


### Appendix 3. IR spectrum of BIMHEBD

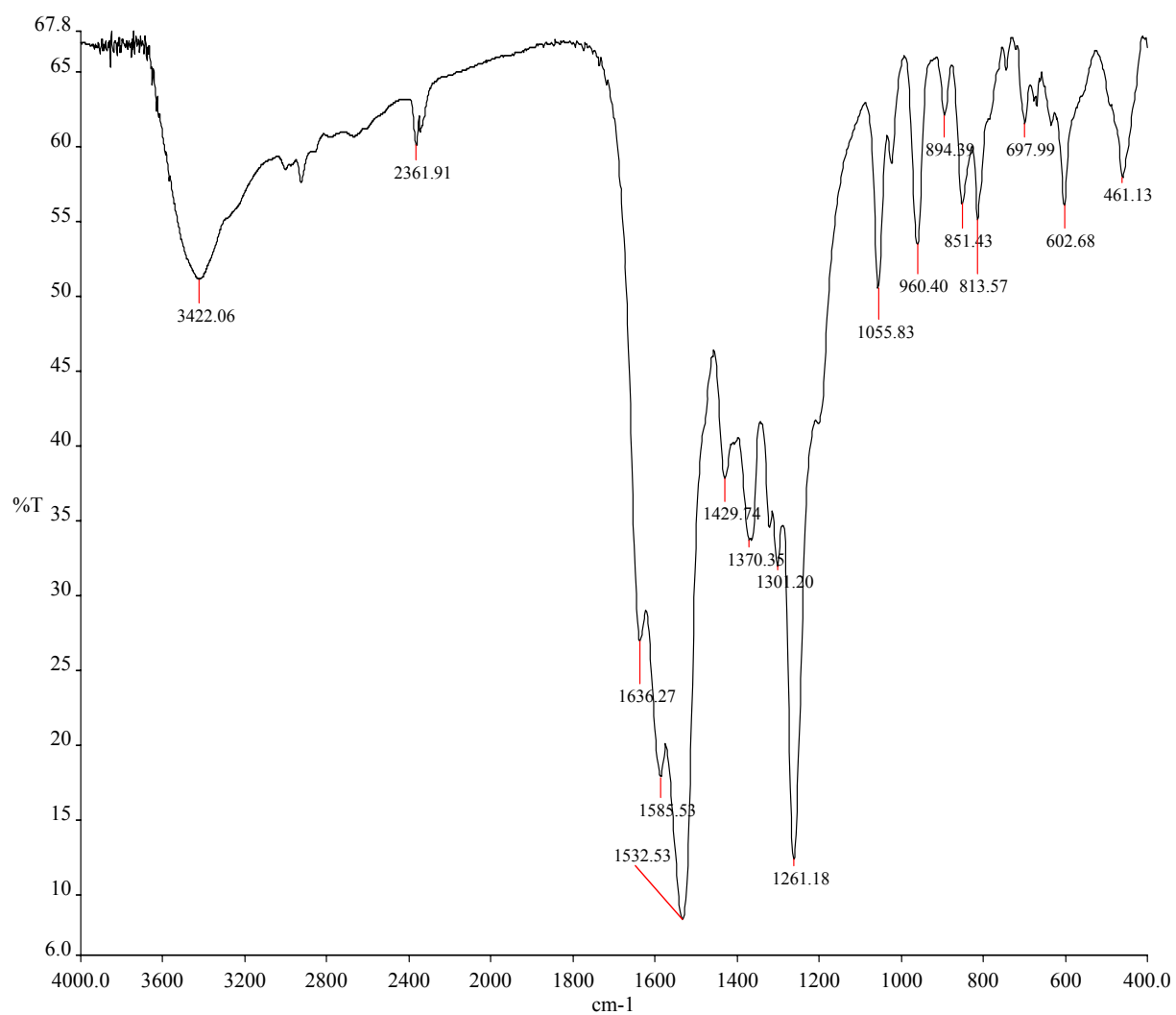


#### Appendix 4. Mass spectrum of BIMHEBD

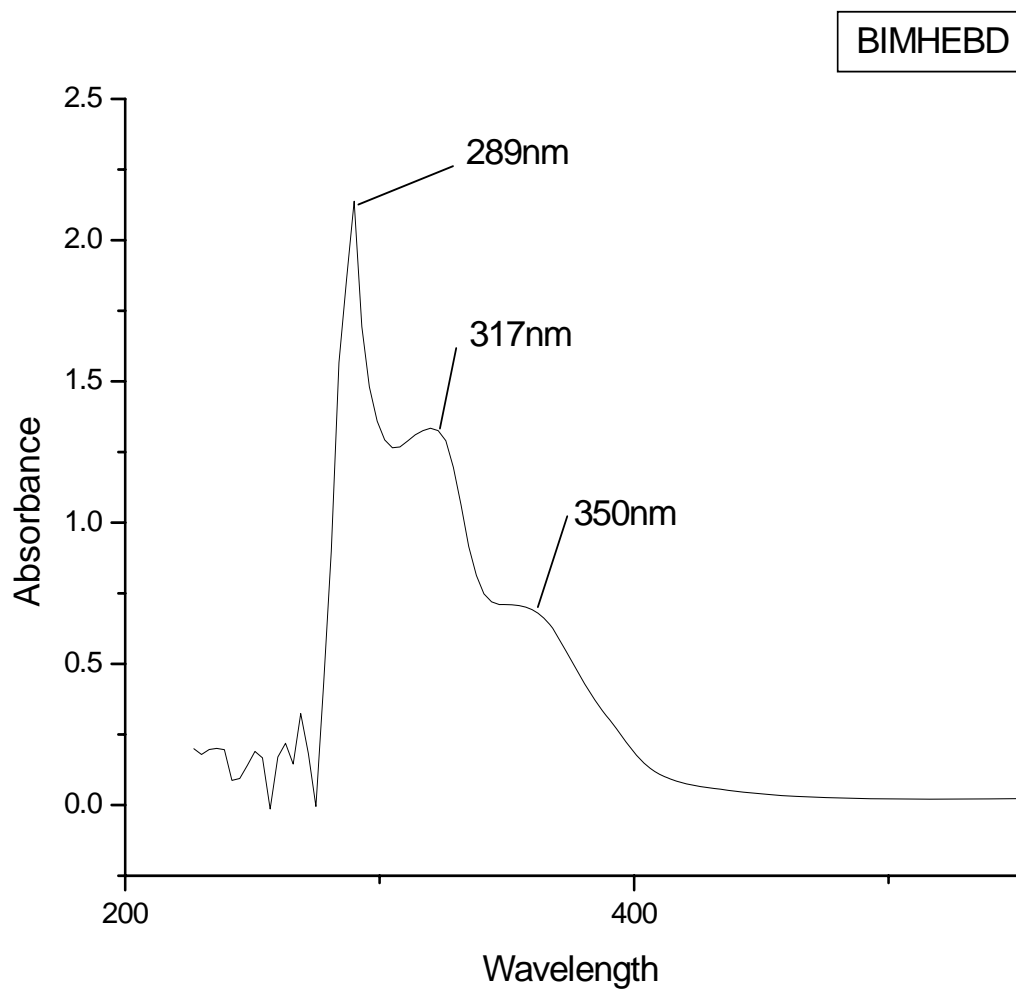
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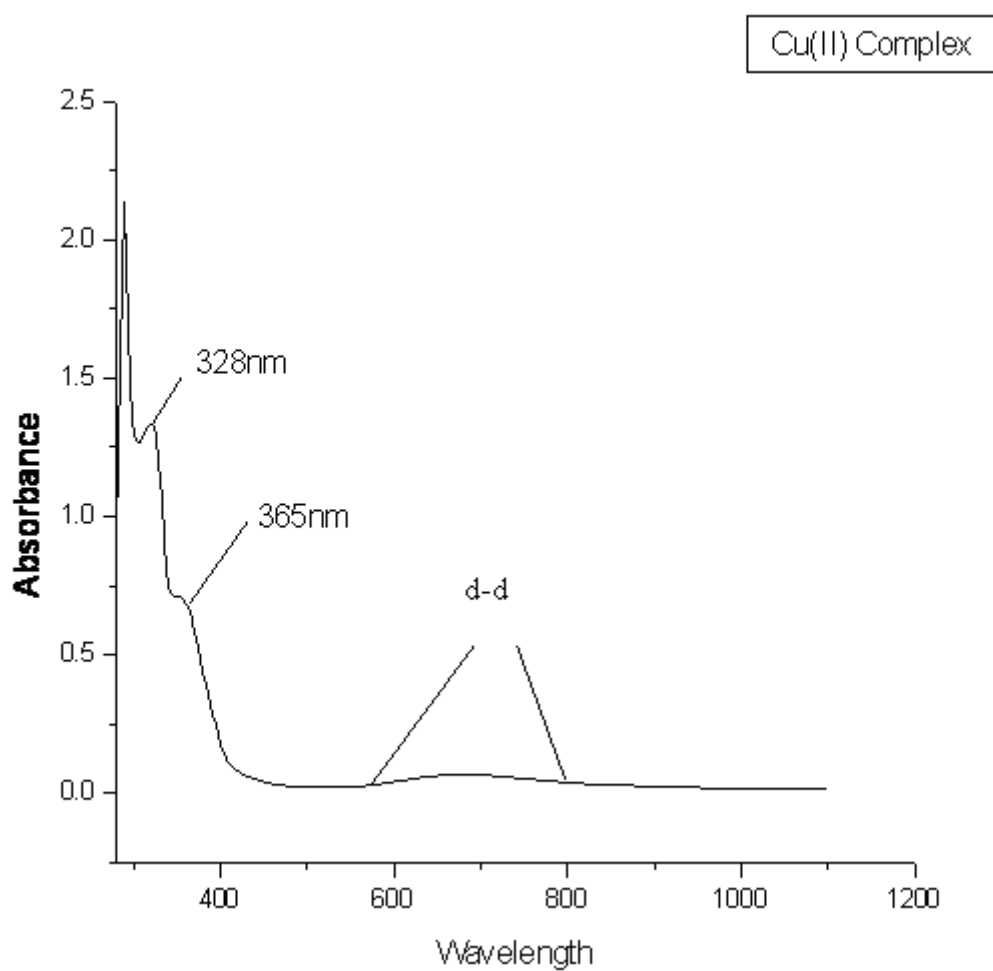
## Appendix 5. IR spectrum of Cu(II) Complex



**Appendix 6. Electronic spectrum of BIMHEBD**



## Appendix 7. Electronic spectrum of Cu(II) Complex



August 7, 2007

**Declaration**

I the Undersigned confirm the results reported in this work were obtained by research carried out by me under the supervision of my Advisor in the Faculty of Science, Department of Chemistry, Addis Ababa University in the academic year 2006-2007. No part of this work shall be published in scientific journals or reported in the media or presented at a conference without the knowledge and consent of my advisor, who is the principal scientist responsible for any publication. Furthermore if the work is published the institutional address given should be that of the Chemistry Department, AAU.

Name: \_\_\_\_\_

Signature: \_\_\_\_\_

This project work has been submitted for examination with my approval as a university advisor.

Advisor: \_\_\_\_\_

Signature: \_\_\_\_\_

Place and date of submission: School of Graduate Studies  
Addis Ababa University