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SYNTHESIS AND STRUCTURAL STUDIES ON METAL COMPLEX BASED ON MULTIDENTATE LIGAND DERIVED FROM SALICYLALDEHYDE AND RESDIACETOPHENONE-DIHYDRAZONE

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AUGUST 2007

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DEDICATION TO

MY FAMILY AND MY WEL-WISHERS

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Abstract

Copper (II) complex of N, N-Bis (salicylidene)-2, 4-dihydroxy-5-acetylacetophenone dihydrazone (BSDAAD) was synthesized and characterized by conductivity and magnetic susceptibility measurements, analytical data, IR, UV-Vis and AAS spectroscopic techniques. The Schiff base BSDAAD, was synthesized by the condensation of 2, 4-dihydroxy-5-acetylacetophenone dihydrazone (DAAD) and salicylaldehyde, and characterized by MS, IR, and UV-Vis spectroscopic techniques. The ligand behaves as symmetric, tetrabasic bis-tetradentate system through ONNO donor sequence. The coordination results in a distorted (elongation) octahedral geometry. Subnormal magnetic moment of the dinuclear complex suggests antferromagnetic interaction between the metal ion centers through a possible super exchange mechanism.

List of Abbreviations and Acronyms

NH_3	Ammonia
^{O}C	degree centigrade
%	Percentage
cm	centimeter
nm	nanometer
OL	overlapped
DMSO	dimethylsulfoxide
DMF	dimethalforamne
UV-vis	Ultraviolet-visible region
AAS	Atomic Absorption Spectroscopy
IR	Infrared
MS	Mass spectroscopy
Mol.Wt	molecular weight
M.pt	Melting point
Dec.temp	decomposing temperature
B.M.	Bohr Magneton
Λ_M	Molar conductance
χ_g	Gram Susceptibility
χ_m	Molar Susceptibility
μ_{eff}	Effective magnetic moment
M/z	mass to charge ratio
S	siemens
ppm	parts per million
DAAP	2, 4-Dihydroxy-5-Acetylacetophenone
DAAD	2, 4-Dihydroxy-5-Acetylacetophenone Dihydrazone
BSDAAD	N, N-Bis (salicylidene)-2, 4-dihydroxy-5-acetylacetophenone dihydrazone

1. Introduction

A metal complex consists of a central metal atom or ion surrounded by a set of ligands that have one or more atom(s) bearing lone pairs of electron(s). These 'donor' atoms are bound electrostatically and covalently to the metal ion. In non-transition metal complexes, the binding is largely electrostatic, while in transition metal complexes there is significant covalency. Generally ligands are Lewis bases that have lone pairs on nitrogen, oxygen, sulphur, etc and that bind transition metals that are Lewis acids. These Lewis bases (ligands) can be divided into unidentate, bidentate and multidentate types, according to whether one, two or more atom(s) is (are) involved in such bonding [1-8].

Ligands are also grouped traditionally as O- donors and N-donors in which the division is based on selection of metal ions for complexation. The N-donor ligands complex well with the smaller transition metal ions derived from Sc Te, V, Cr, Mn, Fe, Co, Ni and Cu. The O-donor ligands tend to complex with metal ions such as the larger alkali, alkaline earth metal ions and large post transition metal ions [2, 5, 6, 9].

Some ligands are bonded to the metal through two or more different ligand atoms and thus form parts of heterocyclic ring (usually five and six member) in which the metal is one of the members. Such metal complex is termed as metal chelate. But sometimes, the stereochemistry of some ligands does not allow all the binding sites to be simultaneously bonded to the same metal, i.e. a ligand potentially tridentate ligand, may function only as a bidentate ligand [10, 11].

Large numbers of suitably substituted aliphatic heterocyclic and aromatic metal binding sites have provided an integrated approach towards a branch that can be classified as coordination chemistry. Multidentate ligands, which possess 'NO', 'ON', 'ONNO' and 'NS' donor systems, are of considerable structural interest as some of them may be involved in bridging two or more metal ions and generate unpaired spin-spin interactions on centers [12,13].

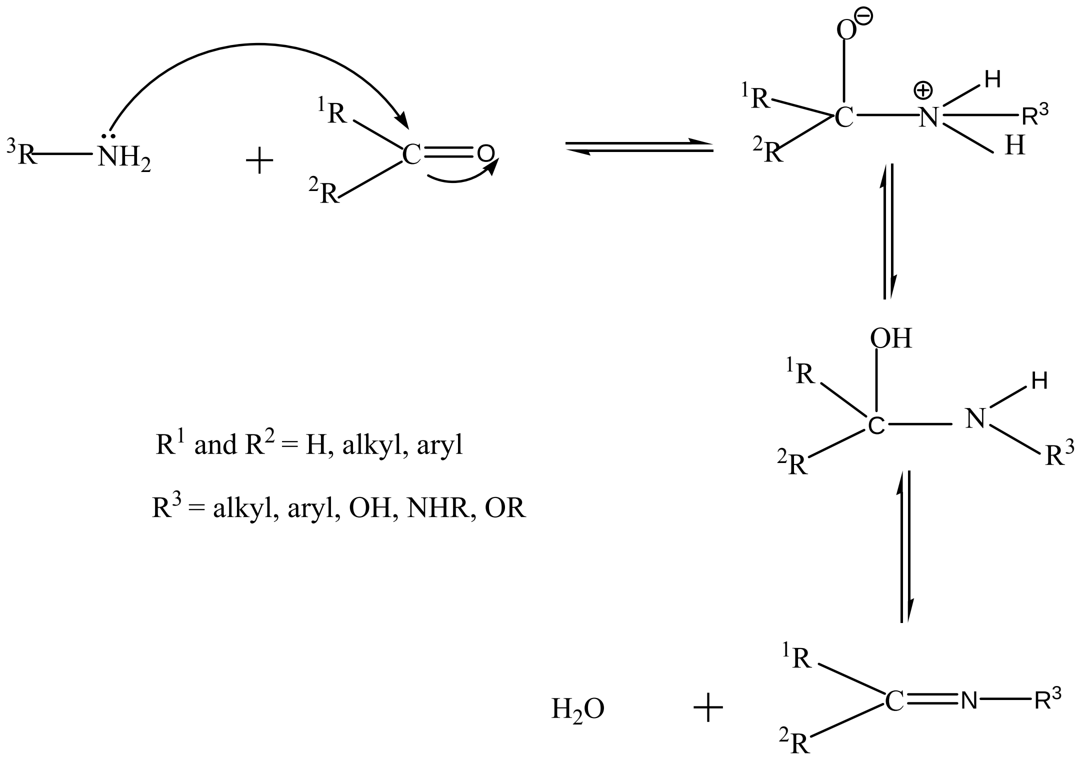
Transition metal bound organic compounds are structural known to possess considerable potential in many applications including biological, clinical, analytical, catalytic, microbial, insecticidal, antibiotics, growth factors, food additive, tumor inhibitors and cell division [14-16]. This is due to the unused coordination sites present on the metal and ligand systems, or due to the selective oxidation state of the complexed metal ions in the coordination sphere [17].

1.1 Schiff base

A large number of multidentate ligands have been synthesized and investigated for metal binding characteristics. Several such ligands possessing **C=N** or azometine grouping are known as Schiff bases [18, 19].

A Schiff base (or azomethine), named after Hugo Schiff, is a functional group that contains a carbon-nitrogen double bond with the nitrogen atom connected to an aryl or alkyl group—but not hydrogen. Schiff bases are of the general formula $R_1R_2C{=}N{-}R_3$, where R_3 is a phenyl or alkyl group that makes the Schiff base a stable imine [18, 19, 20].

Schiff bases can be synthesized from an aromatic amine and an active carbonyl (aldehyde) compound by nucleophilic addition forming a hemiaminal, followed by a dehydration to generate an imine. Moreover the reaction to prepare Schiff base is reversible [21, 22]. However, ketones will form Schiff bases, but the reactions tend to occur less rapidly than with aldehydes [23, 24]



R^1 and R^2 = H, alkyl, aryl

R^3 = alkyl, aryl, OH, NHR, OR

Scheme 1: The reaction to prepare Schiff base

Schiff bases which are effective as coordinating ligands have a functional group –OH, -NH_2, -SH, etc, sufficiently close to azomethine function such that a stable 5- or 6-membered chelate ring is formed on the reaction with metal ion. 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 [25].

Moreover a wide variety of ligands may be obtained via the Schiff base condensation reactions that vary in denticity, flexibility, and nature of donor atoms and in electronic properties [26]. Their metal complexes were investigated for fungicidal and bactericidal activity. Analytical applications of the Schiff bases as colorimetric reagents and as metal ion indicators in complexometric titration were reported [22, 27].

Salicylaldehyde was the carbonyl precursor first used by Pfeiffer and Tsumaki for the synthesis of Schiff bases. Some important classes of ligands derived from salicyl-aldehyde are shown below in their anionic (deprotorated) form [19].

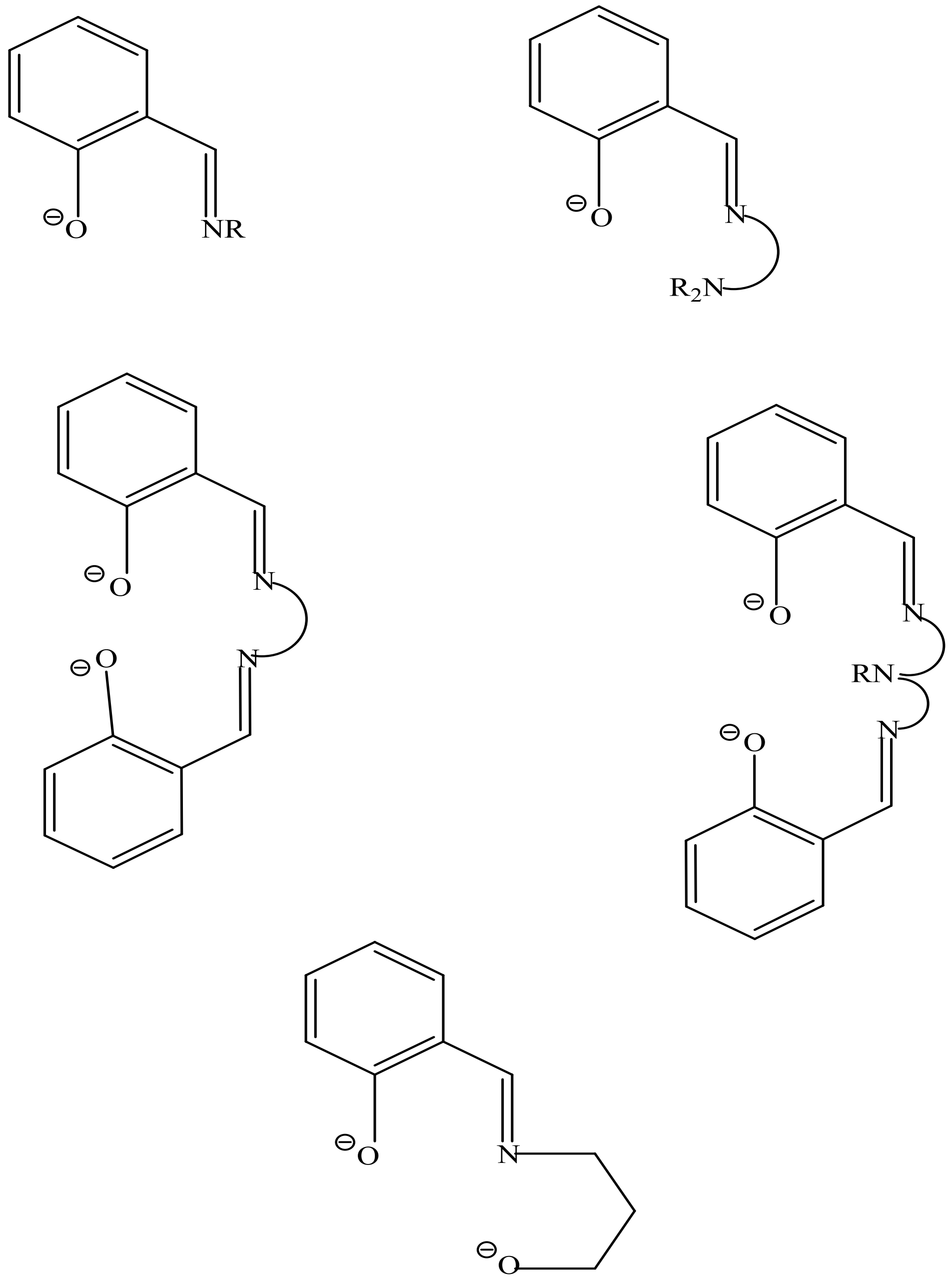


Figure 1: Important ligands derived from salicylaldehyde

Within each class subtle alteration in coordination characteristics can be achieved by variation in the nature and position on of substitutents (R) on the phenyl ring. A wide diversity of coordination geometries and magnetic behavior has been exhibited [28].

Moreover derivatives of salicyladhydes are known to have tautomeric structures as shown in the figure 2.

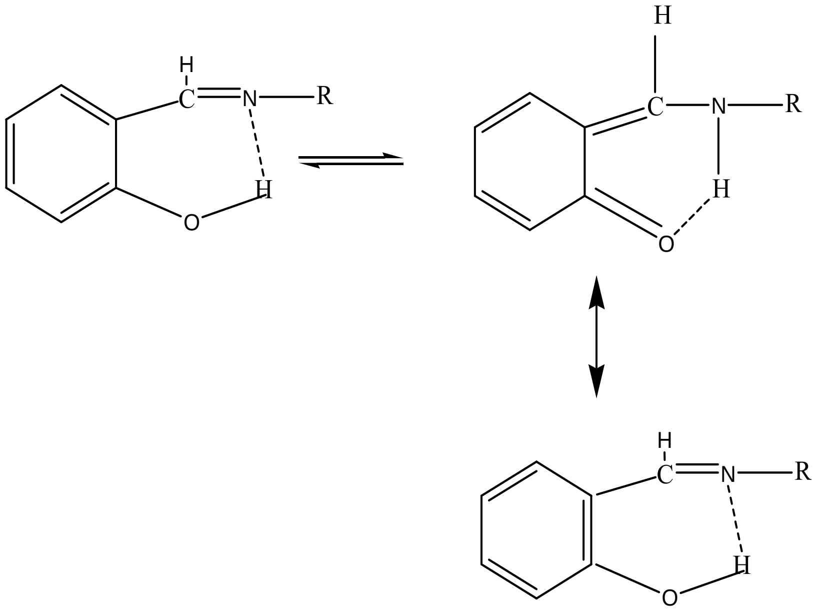


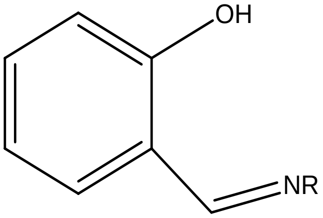
Figure 2: Tautomeric structure of derivatives of salicylaldehyde

The IR spectra are very similar in the region above 2500 cm^{-1}. They all display a rather broad band at 3550 cm^{-1} that may be assigned to free or weakly hydrogen-bonded hydroxyl group. From 3500 to 2500 cm^{-1}, there is a very broad and strong absorption due to strongly hydrogen-bonded hydroxyl, groups. The ratio of the intensities of hydrogen bonds may also occur [19].

The electronic spectra show two absorptions probably corresponding to n—∏* (415 nm) and ∏—∏* (320 nm) transitions. The ∏—∏* transition involves molecular orbital essentially localized on the azomethine group [19].

Because of the great synthetic flexibility of the Schiff base formation, many ligands of varied structural types can be and have been synthesized and their ligation properties have been extensively studied [29-31].

Many tridentate Schiff bases have been utilized as anionic ligands having NNO and NOO donor sets. Some of them are shown below; these ligands derived from substituted acetophenone with three or more metal binding substitutents are of great synthetic interest as they can produce polynuclear complexes [32].



R=CH_2COOH

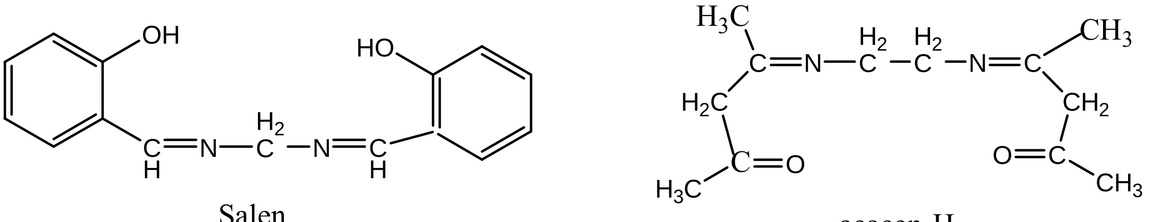
R=$(CH_2)_nC_6H_4OH$ (n=1,2)

R=2-$C_6H_4NH_2$

R=$(CH_2)_n$ X (n=2,3, X=OH,NMe_2,NEt_3,NH_2)

Figure 3: Tridentate Schiff bases

However, tetradentate Schiff bases with ONNO donor set have been widely studied. The condensation of two moles of salicylaldehyde with one mole of ethylenediamine or of their substituted analogues gives tetradentate Schiff bases like Salen and the condensation of two moles of acetylacetone with one mole of ethylenediamine gives tetradentate Schiff base like acacen-H_2 (fig 4.). The derivates of acetylacetone, salicyl aldehyde and hydroxyl methane were some of the ligands, which received extensive investigation [19].



Salen

acacen-H_2

Figure 4: Examples of tetradentate Sciff bases

The potentially pentadentate Schiff bases can also be synthesized and act as bis-tridentate ligands with respect to a single metal center giving binuclear complexes.

Moreover, the hexadentate ligands can be derived from salicylaldehyde and triethylenetetramine. In a variety of metal complexes, it is forming a distorted octahedral arrangement around the metal ion.

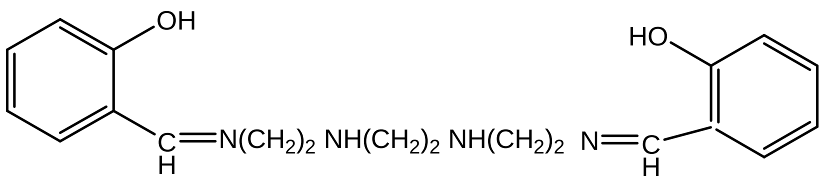


Figure 5: Hexadentate ligand

1.2 Multidentate ligands having O, N donors

Literature survey on multidentate ligands having oxygen and nitrogen donor systems reveals an extensive investigation on a number of 'ONN', and 'ONO' donor sequences which result in the formation of multidentate metal chelates. These metal chelates have been significantly understood with various types of oxygen bridging, alkoxide oxygen bridging, exhibiting characteristics spectra and magnetic properties.

The term bis-chelates was brought in to denote two chelating ligands producing metal complexes with metal to ligand ratio as 1:2. A class of ligand with more than one independent chelating sequence substituted on a single phenyl function exemplifies bis-chelating ligands that can bind two metal ions simultaneously and form dinuclear complexes.

The bis-chelating ligands can be classified into symmetric and unsymmetrical systems. They can be bidentate tridentate, tetradentate bis- chelating systems. 2,4-dihydroxy, -5-acetyl acetophenone (DAAP), which behaves as bis-bidentate 'OO,' 'OO' donor resulting in the formation of polynuclear metal complexes, is an example of symmetric bis-chelating system. This system can be transformed into two or more symmetric bis-bidentate systems, i.e. the dihydrazone and dioxime. Its dioxime and dihydrazone have been observed to be bis-bidenate 'ON', 'ON' donors [19].

1.3 Metal complexes of salicylaldehyde and relative ligands

Monomeric copper (II) complexes of a redox active tetradentate Schiff base ligand bis-(2, 5 dihydroxy acetophenone) ethylenediamine have been reported. The spectral data suggests a distorted tetragonal geometry for Cu (II) ion in the complex. The formation of a dimer is supported by low paramagnetic moment of 1.49B.M.

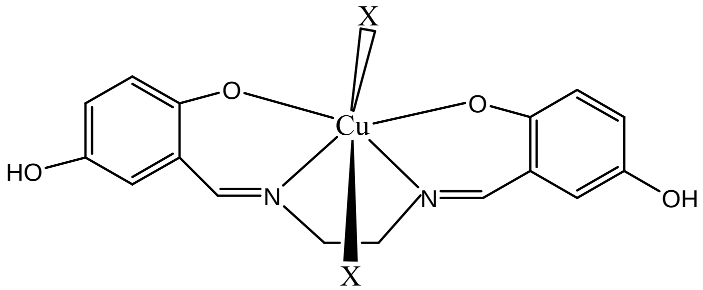


Figure 6: Cu (II) complex with bis- (2, 5-dihydroxy acetophenone) ethylenediamine

A Schiff base derived from 2, 4, dihydroxy acetophenone and ethanolamine with ONO donor sequence has been reported. Its complexes have polynuclear and binuclear structures. In the case of Cu (II) complex, the ligand acts as monobasic and tridentate with the alcoholic oxygen coordinating without deportonation whereas in the case of Ni(II), Co (II) and Fe (III) it acts as dibasic tridentate. Cu (II) and Fe (III) complexes have low magnetic moments as compared to spin only values, due to antiferromagnetic interaction [17].

Some of the ligand derivates of salicylaldhyde and diamines were found to form polymeric complexes with various metal ions. Copper (II) complex of (4-O-hydroxyl phenyl amino-3-pentene-one) is shown to have a dimeric structure (fig 7.). The dimer as a whole is essential, the subnormal magnetic moments of this and related complexes can now be rationalized on the basis of a dimeric structure [17].

While DAAP is dibasic bis-bidentate ‘OO’, ‘OO’ donor, its dioxime and dihydrazone have been observed to be dibasic bis-bidentate ‘ON’, ‘ON’ donors.

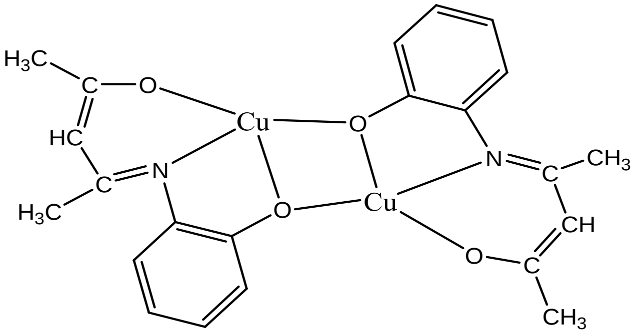


Figure 7: Dimeric structure of (4-O-hydroxylphenylamino-3-pentene-one) Cu (II)

Some more examples of bis-denticity are provided by derivatives of 2, 3-dihydrazone quenoxaline (DHQ). DHQ is a symmetric dibasic bis-tridentate ligand while; its azomethine derivative with salicyladehyde is a symmetric dibasic bis-tridentate ‘NNO’, ‘NNO’ donor. Besides this ligand, H_2-BSDHQ exhibits ambidenticity in the sense that it behaves as a dibasic tetradentate ‘ONNO’ donor as well as bis-tetradentate. It is reported that the ligand H_2-BSDHQ behaves as bis-tridentate towards Mn (II), Ni (II), Cu (II) and as tetradentate with Fe (III) [17].

The Mn (II) complex with SALEN, (Mn-SALEN) (where SALEN is a ligand derived from salicylaldehyde and ethylene diamine) has been the subject of a number of studies [33] and all of them have significantly indicated the presence of antiferromagnetic interactions.

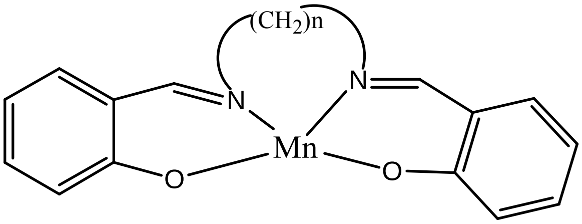


Figure 8: Mn-SALEN

1.4 Cu (II) chemistry

The Cu (II) ion with its d^9 configuration in octahedral and tetrahedral environment is highly susceptible to Jahn-Teller distortion.

Octahedral complexes without any distortion are expected to have only one d-d absorption band corresponding to $^2E_g \rightarrow {}^2T_{2g}$ Transition, while for distorted octahedral complexes several weak absorption bands are observed around 16000 cm^{-1} and often a broad band in the near IR region.

Cu (II) is usually found in tetragonal coordination environment, with four short equatorial bonds and one or two axially elongated bonds due to the Jahn-Teller effect, though some four coordinate tetrahedral and planar complexes are known.

The tetragonally distorted Cu (II) complex shows three absorption bands corresponding to the transitions $^2B_1 \rightarrow {}^2A_1$, $^2B_1 \rightarrow {}^2B_2$ and $^2B_1 \rightarrow {}^2E$. However, tetrahedral complexes are expected to give a single, broad band corresponding to $^2T_2 \rightarrow {}^2E$ transition in the near IR region.

For square planar, three d-d bands corresponding to $^2B_{1g} \rightarrow {}^2B_{2g}$, $^2B_{1g} \rightarrow {}^2A_{1g}$ and $^2B_{1g} \rightarrow {}^2Eg$ are observed. The transitions for the latter geometries (square planar and distorted tetragonal) are generally not well resolved.

The Cu (II) ion is classified as a borderline hard acid; therefore nitrogen and oxygen donors followed by chlorine and sulphur have dominated its coordination chemistry. Magnetic moments of monomeric Cu (II) complexes are generally in the rage 1.7 to 2.2 B.M. [34].

1.5 Stability of complexes

The formation of a metal complex is dictated by its stability. This stability of metal complexes depends both on the metal ion and the ligand. In general, stability of a complex increases with decreasing size and increasing electron affinity of the central metal ion. Thus highly polarizing transition metal ions have the greatest tendency to form complexes, regardless of the nature of the ligand. Thus the stability of bivalent transition metal complexes increases in order $Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} < Zn^{2+}$. This order can be correlated with decrease in size of metal ions across the series and in part with the ligand field effect [5, 35].

The synergic effect exhibited by the ligand field effect employed for the formation of coordinate compounds plays pronounced role in the stability of the complex. It is attributed to the fact that metal to ligand affinity increases with the ability of the ligand to lower electron density on the metal. This is possible as long as sigma electron donation by the ligand atom is counter balanced by ∏-back donation from the filled metal orbital to the vacant ∏ orbitals of the ligand. Therefore, ligands with weak sigma donor/strong ∏ acceptors abilities are more favorable in the formation of stable metal complexes.

Moreover, the stability of metal complexes can be treated in terms of the HSAB principle. According to this principle, the hard metal ions (called hard acids) prefer to complex well with O, N and F that have a high charge density (called hard bases). While soft metal ions are soft acids and prefer to form complexes with soft ligands (soft bases) such as S, P, As, etc, which have low charge density [5, 35].

1.6 Objectives and scope of the present investigation

Literature review reveals that a lot of work has been done on metal complexes of different bis-bidentates having N and O donor sites. This is due to their wide range of applications in agriculture, pharmaceutical, analytical fields, polymer chemistry and catalysis and binding ability to the transition metal ions.

Some bis-bidentate and multidentate systems may be obtained by condensing 2,4-dihydroxy-5-acetylacetophenone (DAAP) with bases like 2- amino aniline, 2-hydroxyaniline, alkanol amines, hydrazine alcohol, hydrazine ethylcarbazates, etc. which may behave either as symmetrical bis-chelants or unsymmetrical bis-chelants towards transition metal ions.

In view of these applications, this paper presents an investigation, in general devoted to the study of the coordination chemistry of N, N-Bis (salicylidene)-2, 4-dihydroxy-5-acetylacetophenone dihydrazone (BSDAAD) with Cu (II).

The ligand will be synthesized in the following steps;

(I) Synthesis of 2, 4-dihydroxy-5-acetylacetophenone (DAAP)

(II) Synthesis of 2, 4-dihydroxy-5-acetylacetophenone dihydrazone (DAAD)

(III) Synthesis of the ligand, N, N-Bis (salicylidene)-2, 4-dihydroxy-5-acetylacetophenone dihydrazone (BSDAAD).

In this study Cu (II) metal ion has been chosen for the synthesis of the metal complex. The starting materials, the ligand as well as the metal complex will be characterized on the basis of the elemental analysis, spectral (IR, UV-Vis, AAS) studies, melting or decomposition temperature, conductivity and magnetic measurements.

1.7 Materials, Methods and Instruments

1. 7.1 Chemicals

All the chemicals used for synthesis of the ligand precursors; the ligand and the metal complex were of Analar grade. The chemicals used in the synthesis were resorcinol (MERCK), acetic anhydride (BDH), zinc chloride (BDH), hydrated hydrazine ($H_2N-NH_2.H_2O$) (BDH), charcoal (BDH), hydrochloric acid (REACHIM), salicylaldehyde (ALDRICH), hydrated copper (II) chloride ($CuCl_2.2H_2O$) (Riedel-de Haen), sodium acetate (BDH) and sodium hydroxide (BDH). Solvents used during the investigation include; MeOH (Scharau), petroleum ether (ALDRICH), EtOH (Scharau), DMSO (BDH), THF (BDH), DMF (BDH), $CHCl_3$ (BDH), o-dichlorobenzene (ALDRICH), nitrobenzene (Riedel-de Haen), nitro methane (BDH), HNO_3, $AgNO_3$, and KBr.

1.7.2 Instruments

Determination of melting point or decomposition temperature of the ligand precursors; the ligand and the metal complex was done with Stuart SMP3 Digital Melting Point apparatus.

Infrared (IR) spectra were recorded using a Perkin Elmer Spectrum BX FT-IR spectrophotometer in the range 4000 - 400 cm^{-1} with samples prepared using KBr pellet.

UV-Vis spectrophotometric studies were done in the range 200-750nm using spectronic Genesys 2PC spectrophotometer.

Magnetic susceptibility measurements were performed using MSB Auto, (Sherwood sciencetific).

Mass spectrum of the ligand was obtained on Thermo Firrigan High Temperature Direct Insertion Probe instrument with a facility to ramp the temperature from RT up to $300^{O}C$.

The molar conductivity measurements were carried out using Jenway Digital conductivity-meter in DMSO.

Several other common laboratory equipment were also used during the investigation.

1.8 Analytical procedures

1.8.1) Chloride estimation

50 mg of the metal complex was dissolved in 10 ml concentrated nitric acid that is diluted to 100 ml using deionized water after evaporating nitric acid and digesting for one hour. To the digested solution, 0.1N of silver nitrate ($AgNO_3$) was added and allowed to settle. The solution, when treated with 0.1N $AgNO_3$ did not form any precipitate indicating that the absence of chloride in the sample.

1.8.2) Metal determination

The metal content in the complexes were determined spectroscopically using Atomic Absorption Spectroscopy (AAS). Metal percentage along with C, H, N, O percentages was used to arrive at the metal-ligand ratio in the complex. The experimental percentage of metal in the complexe was found as:

$$M\,(\%) = \text{Absorbance (A, ppm)} \times \frac{\text{Volume diluted to}}{\text{Mass of sample taken}} \times \frac{100}{1000}$$

The result obtained was corrected by the blank measurement taken as a control.

1.8.3) Molar conductance measurement

The molar conductance was determined from conductivity measurements of one mill-molar solution of the complex in DMSO and the determination of cell constant using the following relation:

$$\Lambda_M = \frac{1000\,L}{C}$$

Where, L= specific conductance

C= morality

1.8.4) Electronic spectra measurement

About 2 mg of each the ligand and the copper complex were dissolved in 15 ml of DMSO.

1.8.5) Magnetic moment measurement

MSB Auto, (Sherwood sciencetific) magnetic balance can generate gram susceptibilities (χ_g) data for a given paramagnetic substance. The following calculations were made to arrive at the magnetic moments.

Molar magnetic susceptibility (χ_M) = χ_g . Molecular wt. of the compound

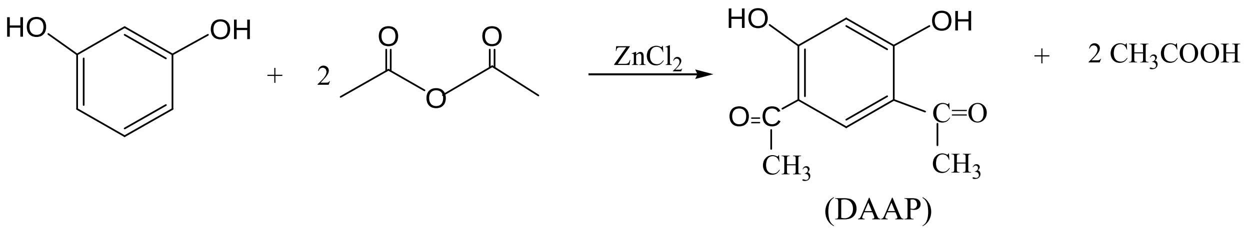
And the Magnetic moment (μ_{eff}) = 2.84 ($\chi_M^{corr.}$. T) ^{½}

2. Experimental Part

2.1. Synthesis of 2, 4-Dihydroxy-5-acetylacetophenone (DAAP) [36]

To a mixture of fused and crushed $ZnCl_2.2H_2O$ (10g) and acetic anhydride (17.3 ml, 1.8 mmol), 10g (0.9 mmol) of resorcinol were added gradually while stirring. The resulting brown solution was refluxed for 30 minutes oil bath at 140°C-160°C and was left over night. It was hydrolyzed with 80 ml dilute hydrochloric acid (HCl/ H_2O being 1:1 v/v) in an ice bath. The solid obtained was filtered, washed thoroughly with distilled water using suction filtration and was left open for drying. The desired product was repeatedly recrystallized using methanol as a solvent and charcoal as a decolorizing agent.
Yield: 2.696g (15%)

The over all reaction was:

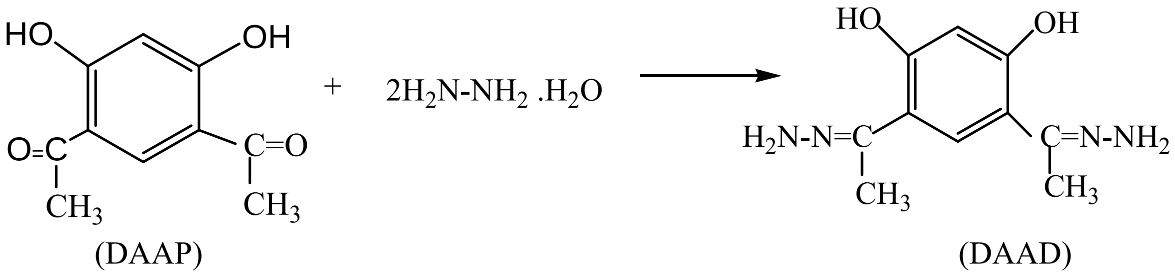


Scheme 2: Synthesis of DAAP

2.2. Synthesis of 2, 4-Dihydroxy-5-acetylacetophenone Dihydrazone (DAAD) [36]

A solution of hydrazine hydrate (0.3 ml, 5.2 mmol) in methanol was added to a hot methanolic solution of DAAP (0.5g, 2.6mmol). The resulting solution was refluxed on a water bath for 3 hours. The greenish yellow product was filtered, and washed successively using suction filtration with methanol and petroleum ether and then dried in open air. Yield: 0.36g (63 %)

The expected reaction would be:



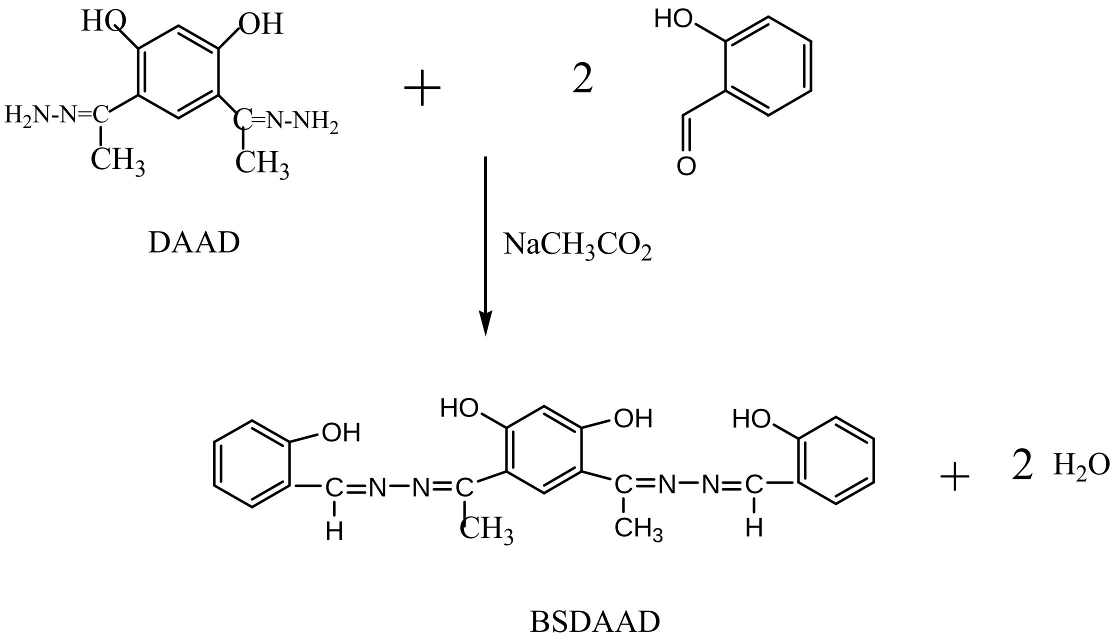
Scheme 3: Synthesis of DAAD

2.3. Synthesisof N, N-Bis (salicylidene)-2, 4-dihydroxy-5-acetylacetophenone dihydrazone (BSDAAD)

A solution of sodium acetate (0.5g, 61 mmol)) in water was added to a solution of DAAD (0.15g, 0.676 mmol) in acetic acid. To the prepared solution, a solution of salicylaldehyde (0.15g, 1.35 mmol) in acetic acid was added while stirring for 15 minutes, and then was refluxed in oil bath at 120^{O}C for 4 hours. The yellowish product left overnight, and was filtered and washed thoroughly with water. The product obtained was then collected and dried.

Yield: 0.20g (69%)

The expected reaction would be:



Scheme 4: Synthesis of the ligand, BSDAAD

2.4. Synthesis of Metal complex

The complex of Cu (II) was synthesized using a general procedure. The mole ratio of the ligand to metal taken was 1:2. A solution of NaOH (0.5g) in 100 ml of methanol was prepared and a minimum amount of this solution was added to a solution of the ligand, BSDAAD (0.2g, 0.47 mmol) in o-dichlorobenzene. Metal salt, $CuCl_2.2H_2O$ (0.16g, 0.94 mmol) dissolved in methanol was added to the solution. The reaction mixture was then refluxed for about 20 hours on an oil bath. The dark brown product obtained was filtered and washed thoroughly with o-dichlorobenzene and methanol. The product was then dried in an open air.

Yield: 0.16g (51%)

3. Results and Discussion

In this part, physical properties and the results related to, spectral studies such as IR, UV-Vis, AAS, melting or decomposition temperature, conductivity and magnetic measurements of the ligand precursors, the ligand as well as the metal complex will be discussed.

3.1. Physical properties

The ligand precursors (DAAP and DAAD) were prepared using reported procedures [36]. Moreover the Schiff base ligand was prepared through the condensation process of the carbonyl group of the salicylaldehyde and the unreacted –NH_2 group of the hydrazone precursor. The metal, Cu (II) complex was prepared through the procedure, using metal salt and the ligand in 2:1 mole ratios and the p^H of the reaction mixture was adjusted to 8 by adding aqueous NaOH.

The prepared ligand is sparingly soluble in solvents like methanol, ethanol DMF, acetonitrile whereas partially soluble in DMSO and chloroform. However, it was found that its solubility in benzene, o-dichlorobenzene and nitromethane was much better. The ligand was observed to decompose above 320^OC.

The metal complex was found to be stable in atmospheric conditions. However, it was found to be very sensitive to water, it hydrolyses to the parent carbonyl compounds and hydrazone [11]. Moreover it was hardly soluble in ethanol, methanol and chloroform, but partially soluble in DMSO and DMF. However the metal complex was found to be insoluble in benzene, nitrobenzene and nitromethane. It was also found that it decompose above 350^OC.

The physical properties of the ligand precursors, the ligand as well as the metal complex are summarized in table 1.

Table 1: Some physical properties of the ligand precursors, the ligand and the complex

Compound	Mol. Formula	Mol.Wt (g/mol)	Appearance	Color	M.Pt/Dec. temp(^{O}C)	% Yield
DAAP	$C_{10}H_{10}O_4$	194	Needle like Crystal	White	182	15
DAAD	$C_{10}H_{14}O_2N_4$	222	Fine Powder	Greenish yellow	>300	63
BSDAAD	$C_{24}H_{22}O_4N_4$	430	Fine Powder	Yellow	>320	69
Cu (II) complex	$Cu_2C_{24}H_{32}O_{10}N_4$	671	Fine Powder	Dark brown	>350	51

3.2 AAS data

The amount of copper in the complex was 19.12 %(experimental value), and it was found to correspond with 19.21 %(calculated value). Therefore, one can say that the experimental value is in a good agreement with the calculated value for the molecular formula $Cu_2C_{24}H_{32}O_{10}N_4$.

Table 2: AAS data of Copper complex

Element	Mol. Formula	Complex (MW,estm) (g/mol)	λ_{absor} (nm)	Conc.(M)	Sample absor	Element (μg/L)	% Metal
Cu(II)-complex	$Cu_2C_{24}H_{32}O_{10}N_4$	671	324.7	1.9×10^{-4}	1.1506	26.77	19.21 $(19.12)^{*}$

$(\ )^{*}$ is the calculated value

3.3 Conductance data

Molar conductance was determined from conductivity measurement of the complex in DMSO at $24^{O}C$. By using the relation Λ_M =1000L/C, the molar conductance of the complex was calculated and it was found that molar conductance is 50 S cm^2 mol^{-1} which is lower than those indicated for an electrolyte. Therefore the measurement indicates that the complex is a non-electrolyte. In view of the absence of any other ions like Cl^- in the complex, it is concluded that the ligand behaves as tetrabasic chelant towards the metal ion.

3.4. Mass spectrum

The mass spectrum of the ligand reveals that the ligand may contain acetic acid (CH_3COOH). Once the acetic acid removed, it is observed the molecular ion peak at
m/z = 430 appears in the spectrum. The base peak is formed at m/z = 240 (see appendix 6).

3.5. IR Spectra

3.5.1) DAAP

The IR spectrum of DAAP (appendix 1) shows characteristic bands assignable to O-H, C=O, C-O and C=C which are indications of the functional group of the target molecule.
The broad band from 3500 to 2700 cm^{-1} is due to the strong intra and intermolecular hydrogen bonded O-H stretching frequency of the phenolic group, which is also supported by the medium band at 1243 cm^{-1} of its bending mode frequency [37, 38].
The band at 3020 cm^{-1} is assigned to C-H stretching frequency of the aromatic group, besides its bending mode is observed at 839 cm^{-1}, which is a relatively sharp band. However, the band at 2925 cm^{-1} can be assigned to CH stretching of the methyl group and its bending mode is observed at 1370 cm^{-1}.

The strong band at 1646 cm^{-1} corresponds to C=O stretching frequency of the carbonyl group. The shift to a lower frequency from the expected value is probable due to the formation of hydrogen bonding between the phenolic O-H and the ketonic C=O [37,38].

The bands that appeared at 1588 and 1490 cm^{-1} can be assigned to C=C of the benzene aromatic ring.

The strong band that is located at 1258 cm^{-1} can be assigned to C-O stretching of the phenolic group.

3.5.2) DAAD

The IR spectrum of DAAD (appendix 2) has shown the characteristic bands of its functional group.

The band at 3367 cm^{-1} can be assigned to symmetric stretching of N-H of the hydrazine group. However its asymmetric stretching is probably submerged in the O-H stretching frequency.

The broad band in the range of at 3440 to 2860 cm^{-1} is due to the phenolic O-H that is involved in intra and intermolecular hydrogen bonding whereas it’s bending mode frequency is observed at 1282 cm^{-1}.

The strong band at 1617 cm^{-1} may be assigned for the newly formed C=N stretching. While the band at 1507 cm^{-1} corresponds to C=C stretching of the aromatic ring.

The band at 1229 cm^{-1} may be assigned to C-O stretching. The band at 1049 cm^{-1} can be assigned to N-N stretching while the band at 876 cm^{-1} corresponds to the N-H rocking vibration and the bending frequency of C-H of the ring [38].

The formation of new bands (in this spectrum) at the frequencies 3367 cm^{-1} (N-H), 1617 cm^{-1} (C=N), 1049 cm^{-1} (N-N) as well as their corresponding bending frequencies could be the sign for the formation the desired product. Moreover this is supported by the absences of the vibration frequency band for C=O (carbonyl) group.

3.5.3) BSDAAD

The IR spectrum of the ligand (appendix 3) shows the characteristic bands of the vibration frequencies of the functional groups such as O-H, C=N, C-O, N-N, C=C.

The broad band that appearing in the region 3550 to 2850 cm^{-1} can be assigned to the phenolic O-H. The lower frequency and the broadness of the band in comparison with the expected O-H frequency (around 3600 cm^{-1}) are due to the intra and intermolecular hydrogen bonding.

The small bands at around 3050 and 2950 cm^{-1} could be assigned to C-H stretching frequency of the benzene ring and the methyl group respectively.

The sharp bands that located at 1621 cm^{-1} and 1572 cm^{-1} are attributed to C=N stretching of the azomethine group. While the C=C stretching of the aromatic ring is observed at 1488 cm^{-1}.

The band at 1271 cm^{-1} may be assigned to C-O stretching of the phenolic group and the band at 1034 cm^{-1} can be assigned to N-N stretching. While those bands at 1205 and 750 cm^{-1} correspond to the bending frequencies of O-H phenolic group and C-H of the aromatic ring.

Comparing the spectrum of the ligand with that of the previous ligand precursor, in the ligand spectrum there is no vibrational frequencies of N-H of the hydrazide group instead there is a broad band that could be assigned to the phenolic O-H. This may indicate the formation the desired ligand through the condensation of the hydrazone group of the precursor and the carbonyl of the other reactant, salicylaldehyde.

3.5.4) Cu (II) complex

The metal complex shows observable changes in the spectrum (appendix 4), which can be attributed to the involvement of the four phenolic oxygens, and the two azomethine nitrogen in the metal binding process.

The lower frequency components at 1605 and 1543 cm^{-1} (comparing with ligand spectrum) could be assignable to the C=N stretching frequency. This downward shift is consistent with metal binding through the two azomethine nitrogens.

Moreover the deprotonation subsequently leads to metal binding through the phenoxide function, which is supported by the upward shift in the C-O stretching frequency in the range 1256 to 1323 cm^{-1}. The positive shifts are in the range of 15 to 30cm^{-1}. These upward shifts again confirm metal binding through the deprotonated phenolic oxygen.

The spectrum of the complex records broad band in the range 3430 to 2850 cm^{-1}, which can be attributed to the components of coordinated water molecules which are expected to form hydrogen bonding with nearby oxygen and nitrogen.

Furthermore the spectral data also shows non-ligand bands in the range of 600-400 cm^{-1} assignable to M-O and M-N stretching. Therefore it can be said that the ligand binds to the metal ion through a ONNO donor system.

The infrared spectra of the ligand precursors, the ligand as well as the metal complex are summarized in table 3.

Table 3: Infrared spectra results of the precursors, the ligand and the complex

Band assignments	**DAAP /cm^{-1}**	**DAAD /cm^{-1}**	**BSDAAD /cm^{-1}**	**Cu(II)Comp. /cm^{-1}**
$\upsilon_{\text{O-H}}$	3500-2700	3400-2860	3550-2950	3430-2850
υ_{NH2} sym	-	3367	-	-
υ_{NH2} asym	-	OL	-	-
$\upsilon_{\text{Ar-C-H/ Me-C-H}}$	3020/ 2925	OL/ 2924	3050/ 2850	OL/ 2922
$\upsilon_{\text{(C=N)}}$	-	1617	1621,1572	1605,1534
$\upsilon_{\text{(C=O)}}$	1646	-	-	-
$\upsilon_{\text{(C=C) (phe)}}$	1588,1490	1507	1572,1488	1534,1466
$\upsilon_{\text{(C-O)}}$	1258	1229	1271	1323-1256
$\upsilon_{\text{(N-N)}}$	-	1049	1031	1040

OL = overlapped

3.6 Magnetic Susceptibility

The effective magnetic moment was calculated using the formula $\mu_{eff} = 2.824\ (\chi_M T)^{1/2}$

From the measurement, it was found that Cu (II) complex has magnetic moment of 1.34B.M./Cu (II) ion, which is below the expected magnetic moment value (1.73B.M.). This result can be explained on the basis of metal-metal interaction and pairing of electrons on adjacent copper centers, most likely through the $d_{x^2-y^2}$ orbital. This is explained on the basis of antiferomagnetic interaction due to super-exchange phenomenon. Further, the back donation of electrons due to electron rich metal ions will facilitate spin pairing via the delocalized π-electron cloud. In other word, this is possibly occurring due to the extensive conjugation through which electrons delocalizing between the two copper centers and resulting in appreciable metal-metal interactions that lead to antiferomagnetism [1, 5, 39]. However, addition studies on variable temperature magnetic susceptibilities are needed to draw final conclusion.

3.7 Electronic spectroscopy

The electronic absorption spectra of the Schiff base and the metal complex were recorded at room temperature using DMSO as solvent and the graphs are presented in appendix 5.

3.7.1 UV-Vis spectrum of the ligand

The electronic spectrum of the ligand shows a high intensity band at 28,248 cm^{-1} (with shoulder at 26,666 cm^{-1}) which may be assigned to a combination of $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transition characteristic of the azomethine chromophore. Another important absorption band was recorded at 33,333 cm^{-1} which indicates the $n \rightarrow \pi^*$transition of the substituted benzene moieties. Furthermore the multiple bands that are observed in the range of 43,478 – 38,461 cm^{-1} indicate absorption due to $n \rightarrow \pi^*$ transitions associated with the aromatic group.

3.7.2. UV-Vis spectrum of the metal complex

In comparison with the free ligand spectrum, the metal complex spectrum reveals characteristic features. The electronic spectrum of the copper (II) complex shows bathochromic shifts in the absorption frequencies of phenolic and azomethine chromophores. The band structure observed between 33,333 – 26,666 cm^{-1} in free ligand spectrum appears to shift to 31,152 - 21,739 cm^{-1}. This is a consequence of the involvement of phenoxide and azomethine functions in chelation.

Besides there is an unresolved non ligand electronic spectral band observed in the spectrum of the metal complex which can be assigned to the d-d transitions characteristic of the electronic configuration and the geometry around the metal ion. The band positioned around 16,666 – 13,333 cm^{-1}, the d-d transition characteristic, could be attributed to the transitions $^2B_1 \rightarrow {}^2A_1$, $^2B_1 \rightarrow {}^2B_2$ and $^2B_1 \rightarrow {}^2E$ corresponds with distorted (most probably elongated) octahedral geometry. The distortion can be attributed to electronic degeneracy and Jahn-Teller effect. The H_2O ligands occupying axial positions are expected to be present at longer distances than the ONNO chelants sequence.

Table 4: UV-Vis data for the ligand and metal complex

Compound	λ_{max} (cm^{-1})	Type of transition
Ligand, BSDAAD	28,248	$\pi\rightarrow\pi^*$ $n\rightarrow\pi^*$ (Azomethine)
	33,333	$n\rightarrow\pi^*$ (Phenoxide)
	43,478 – 38,461	$\pi\rightarrow\pi^*$ (Aromatic ring)
Cu (II)-complex	16,666 – 13,333	$^2B_1 \rightarrow {}^2A_1$, $^2B_1 \rightarrow {}^2B_2$, $^2B_1 \rightarrow {}^2E$

The proposed geometry with the formula [Cu (II) L (IV) $(H_2O)_4$].$2H_2O$ is given in fig 9.

3.8 Conclusion

The Copper (II) complex, which was synthesized by using the Schiff base, N, N-Bis (salicylidene)-2, 4-dihydroxy-5-acetylacetophenone dihydrazone (BSDAAD) (formed by the condensation of 2, 4-dihydroxy-5-acetylacetophenone dihydrazone (DAAD) and Salicylaldehyde) was characterized on the basis of analytical data, IR, UV-VIS spectra, conductivity, and magnetic susceptibility measurements, distorted (elongated) octahedral geometry has be proposed.

The multidentate ligand containing O and N donor systems is found to behave as symmetric tetrabasic bis-tetradentate system employing two ONNO donor sequences. This novel chelation generating a dinuclear Cu (II) complex exhibits subnormal magnetic moment, which can be justified on the basis of antiferromagnetic behavior.

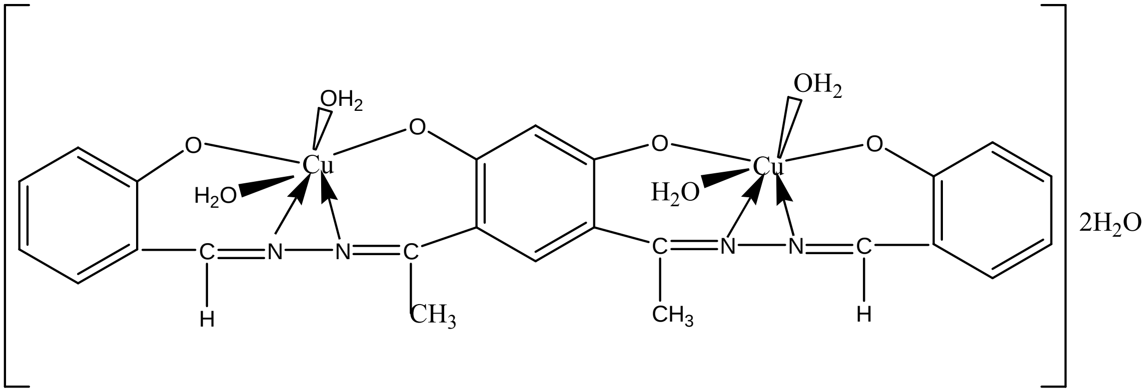


Figure 9: The proposed structure of the Cu (II) complex with BSDAAD

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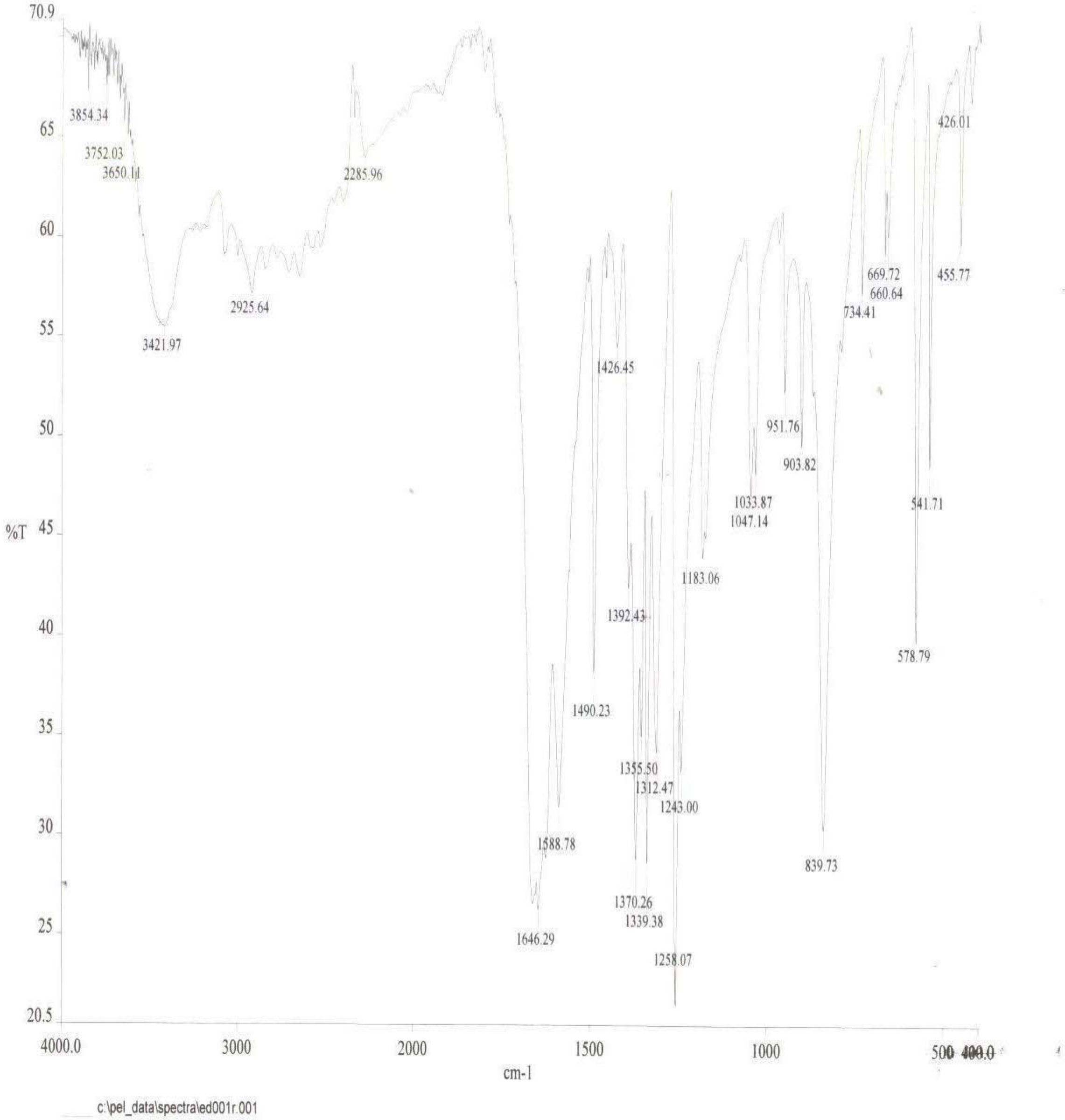
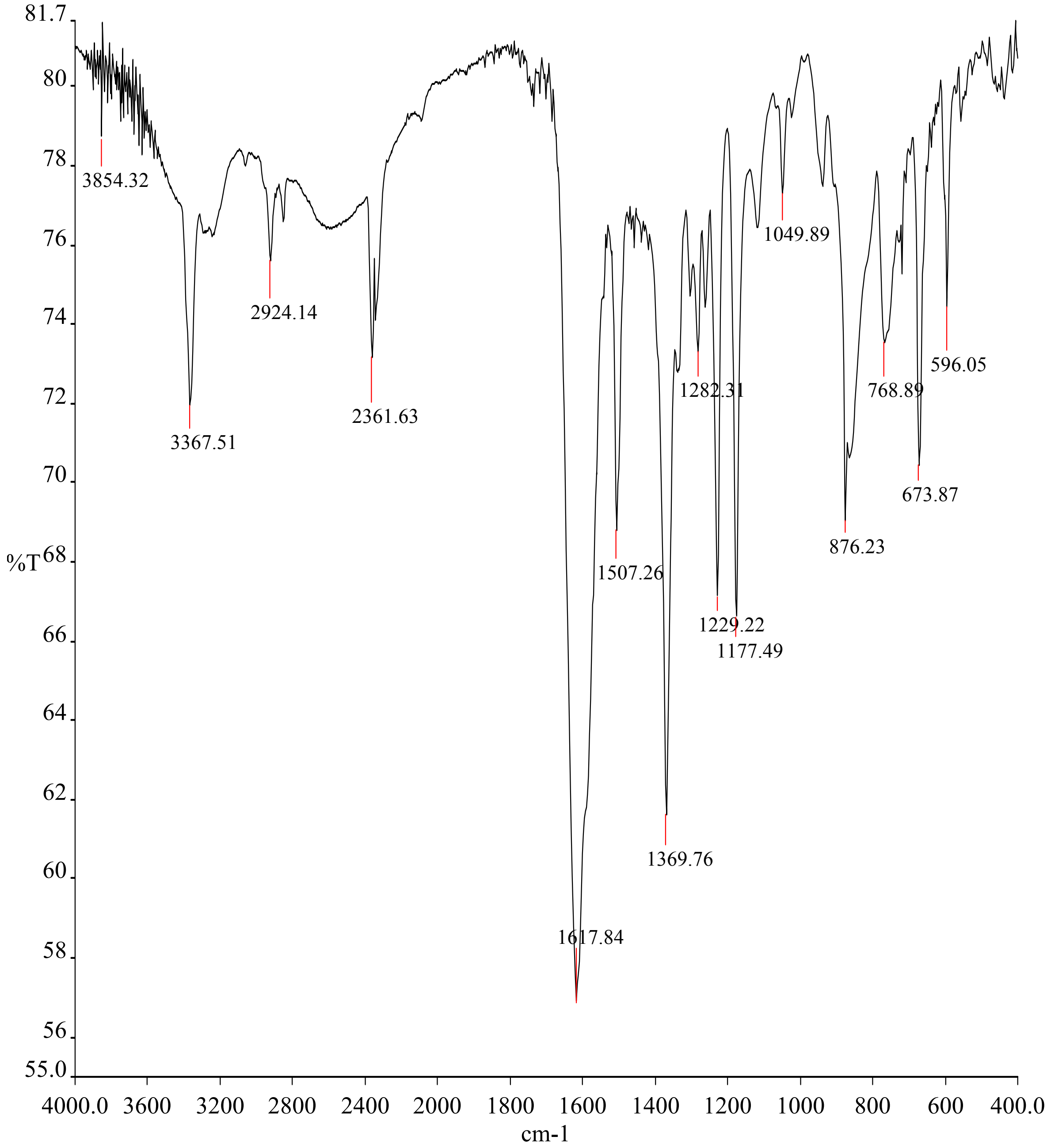
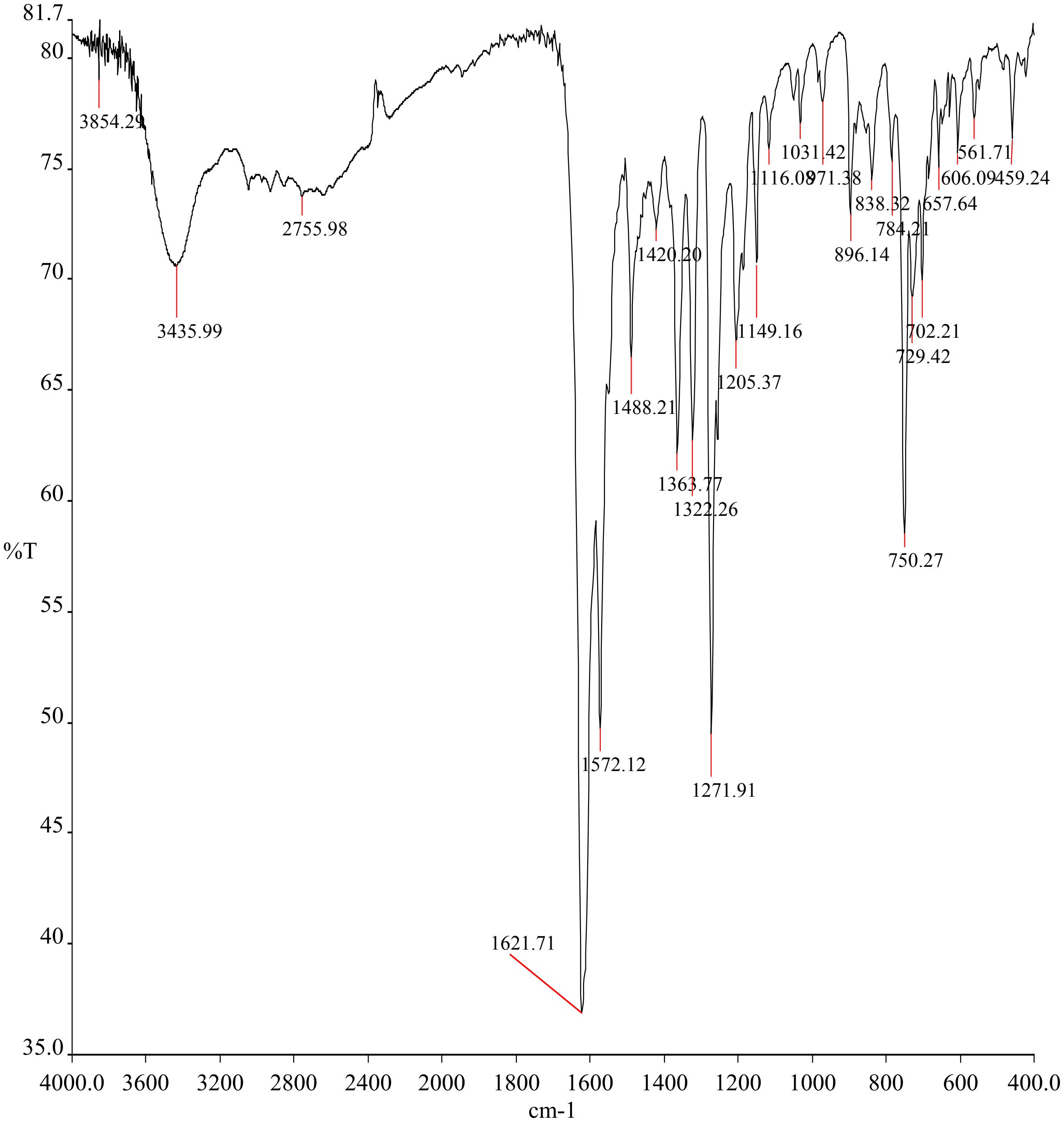


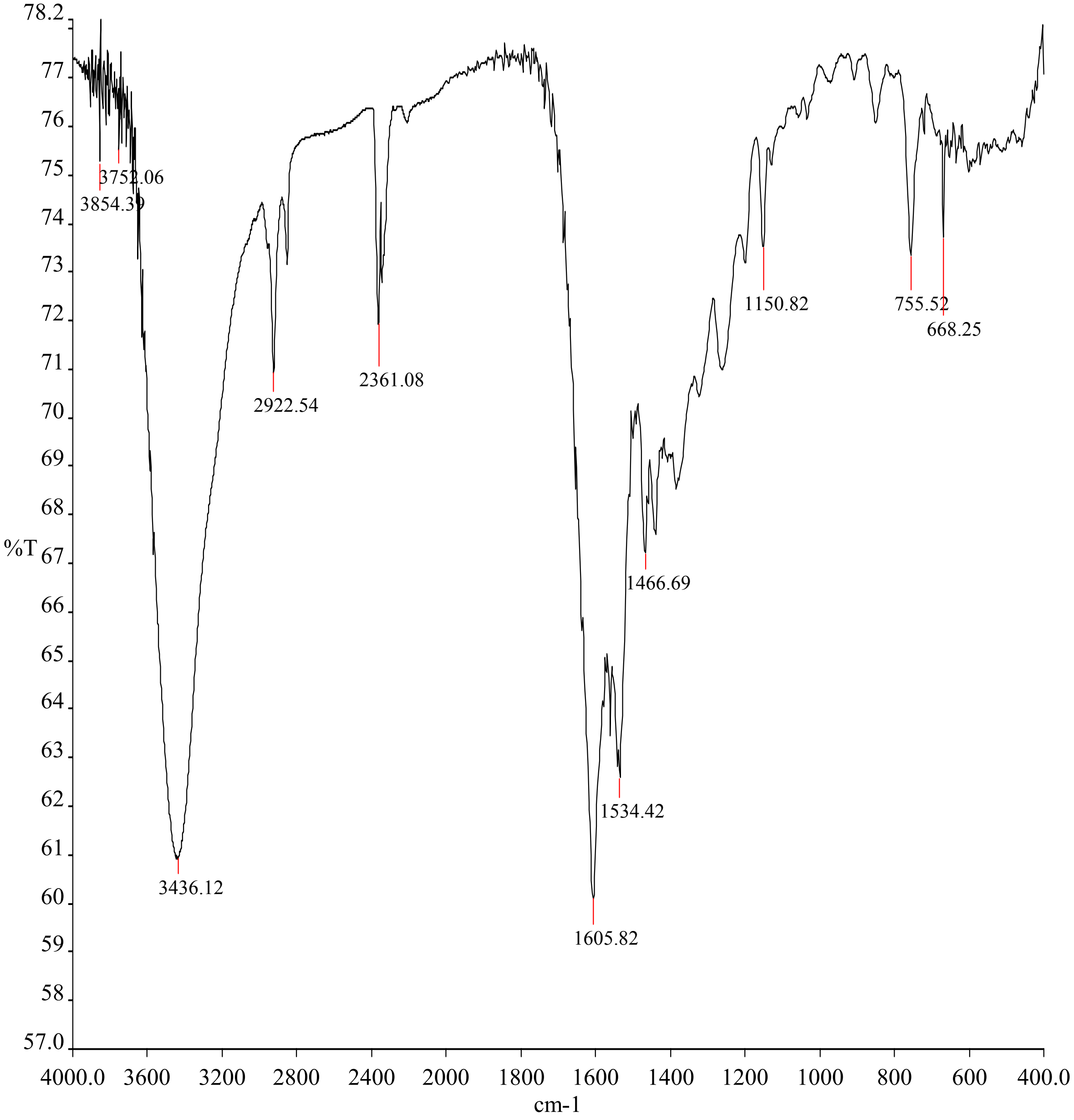
Appendix 1: IR spectrum of DAAP



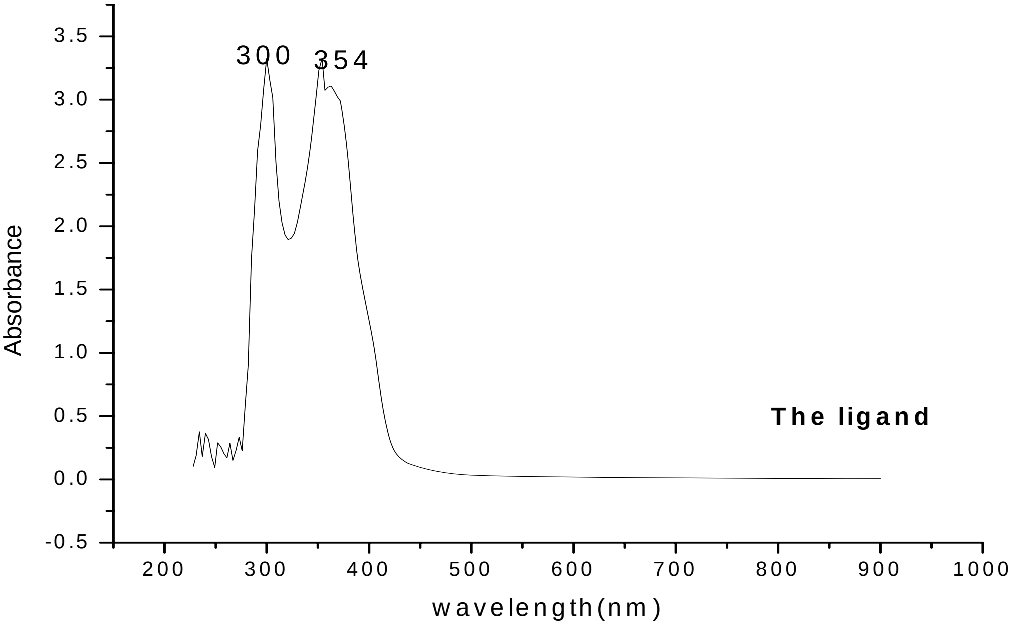
Appendix 2: IR spectrum of DAAD

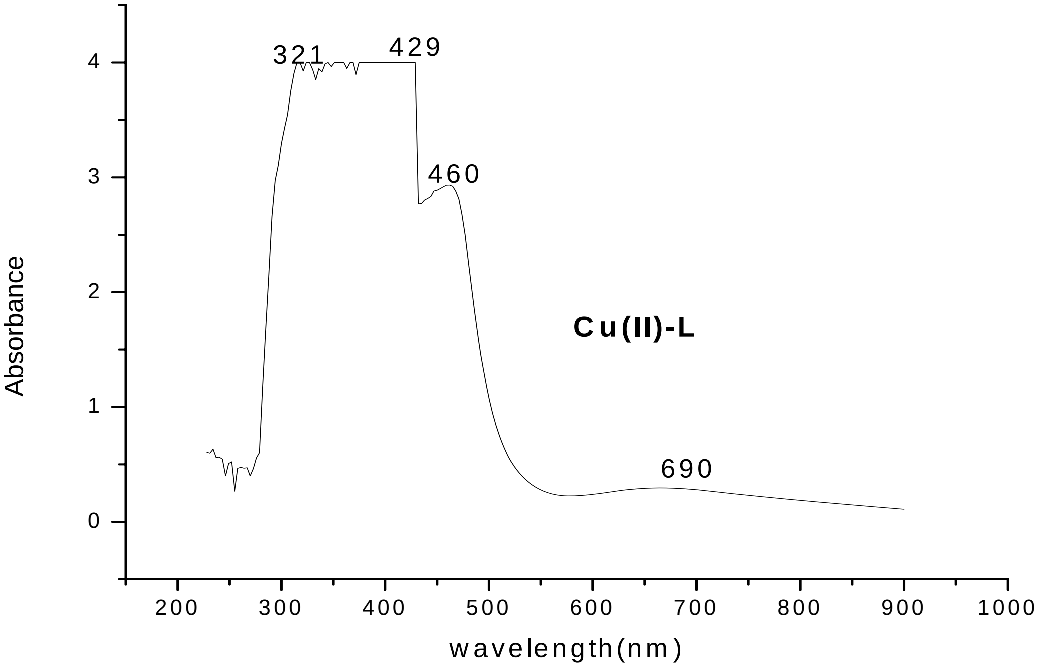


Appendix 3: IR spectrum of BSDAAD

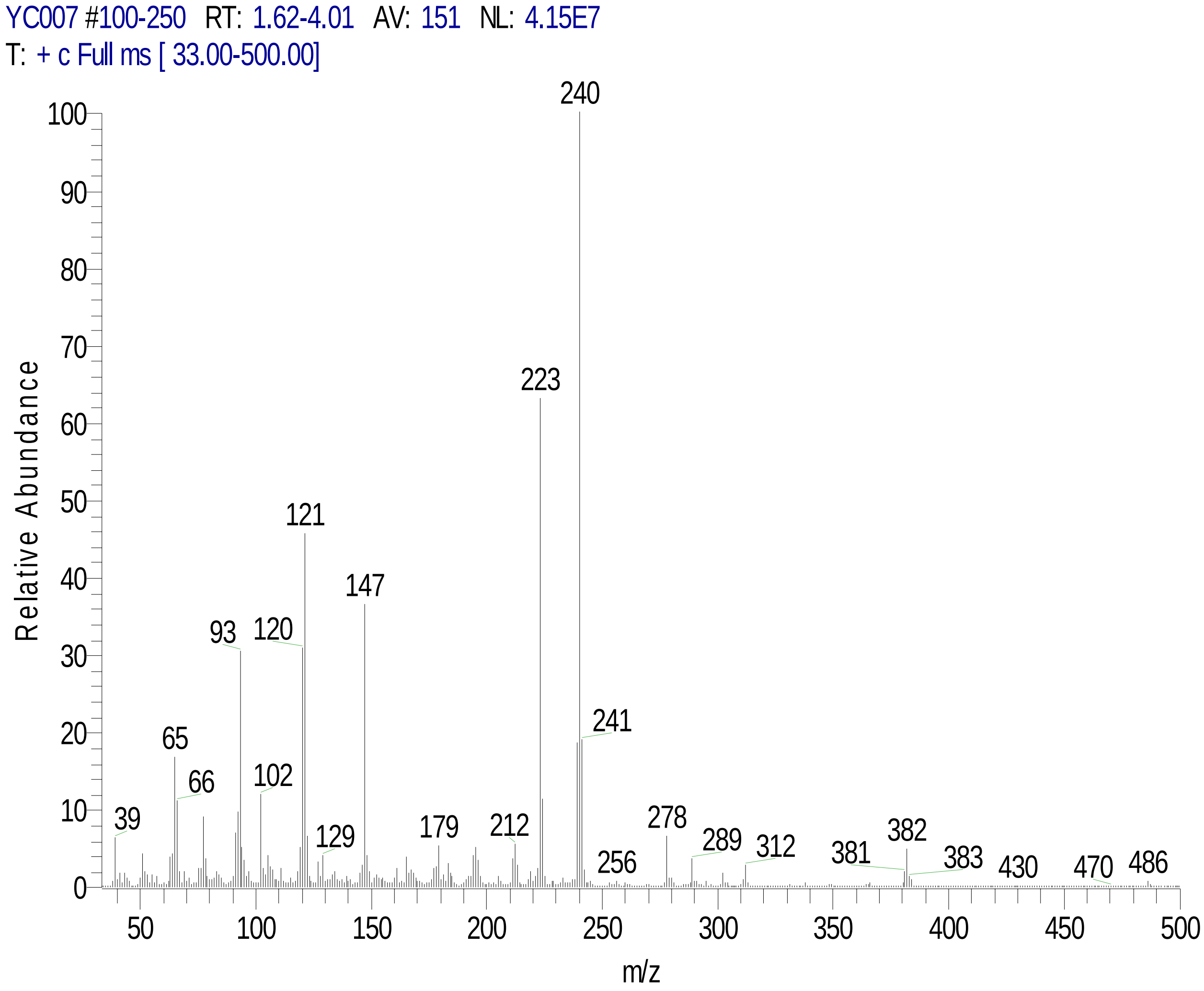


Appendix 4: IR spectrum of Cu (II) complex





Appendix 5: Uv-Vis spectra of the ligand and Cu (II) complex



Appendix 6: Mass spectrum of the ligand