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SYNTHESIS AND CHARACTEIZATION OF METAL COMPLEX WITH NINHYDRIN AND O-PHENYLENEDIAMINE DERIVATIVE

BY: TAYE TILAHUN

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By

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LIST OF ABBREVATIONS AND SYMBOLS

B.M.	Bohor magneton
DMSO	Dimethylsulfoxide
DEPT	Distortionless Enhancement by Polarization Transfer
IR	Infrared
THF	Tetrahydrofuran
CuL_2	Copper complex of NHOPD
S	Simens
M.pt	Melting point
UV-Vis	Ultraviolet-Visible
Rp	Ruhemann's Purple
Λ_M	Molar conductance
NHOPD	Ninhydrin o-phenylenediamine derivative

Abstract

A new quinoxaline derivative (NHOPD) was synthesized by a one step reaction between ninhydrin and o-phenylenediamine . It formed metal complex when reacted with $CuCl_2.2H_2O$ in ethanolic chloroform medium .The quinoxaline derivative(NHOPD) was characterized on the basis of IR,NMR,MS and UV-VIS spectral data.

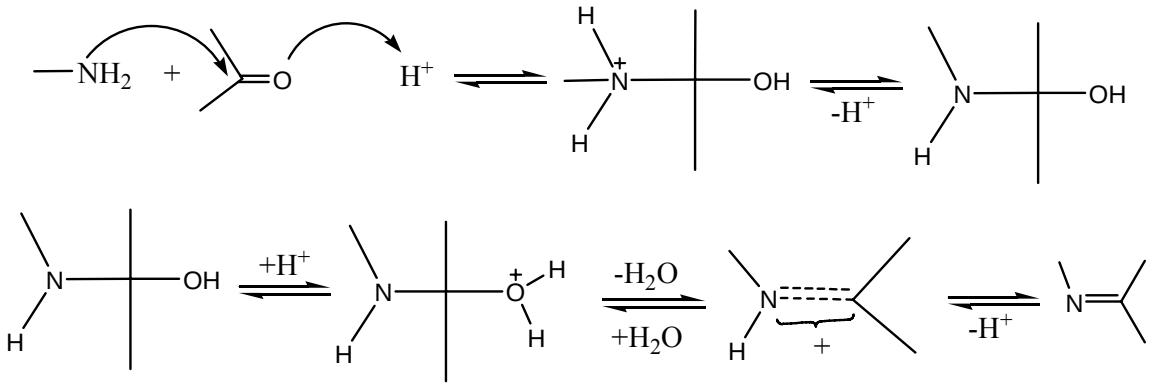
The Cu-NHOPD complex was characterized by analytical, conductivities, spectral (AAS,IR,UV-VIS) and magnetic data. Involvement of exocyclic carbonyl oxygen and one of the quinoxaline nitrogen in coordination was concluded, such that the ligand behaved as a neutral ON bidentate. Conductance measurement indicates a 1:2 electrolytic nature of the complex .Electronic spectral and magnetic susceptibility data suggest square planar geometry for the complex with molecular formula $[CuL_2]Cl_2.2H_20$ (L=NHOPD)

1. INTRODUCTION

Transition metal cations have tendencies to form complexes with several ligands such as neutral molecules (NH_3, H_2O, etc), anions (CN^-, Cl^-) and exceptionally cations like NO^+. These ligands possess invariably lone pairs of electrons which they donate to the transition metal cations in the formation of complex compounds. The metal-ligand bond stabilities derive contributions from sigma-pi interactions which influences the thermodynamic and kinetic characteristics of the complexes. [1]

A Schiff base (or azomethine) is a potential metal binding function due to σ, π– interacting capability towards metal ions. This functional group contains a carbon-nitrogen double bond with the nitrogen atom connected to an aryl or alkyl group. 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. Most commonly Schiff bases have NO or N_2O_2 donor atoms but NS, NN, ONO, NNO, donor sequences are also possible.

There are several reaction pathways to synthesize Schiff bases .The most common one is an acid catalyzed condensation reaction of amine and aldehyde or ketone as shown in **scheme 1**.



Scheme 1. Acid catalyzed Schiff base formation reaction

Schiff bases can be synthesized from an aromatic amine and a carbonyl compound by nucleophilic addition forming a hemiaminal, followed by dehydration to generate an imine. [2-4]

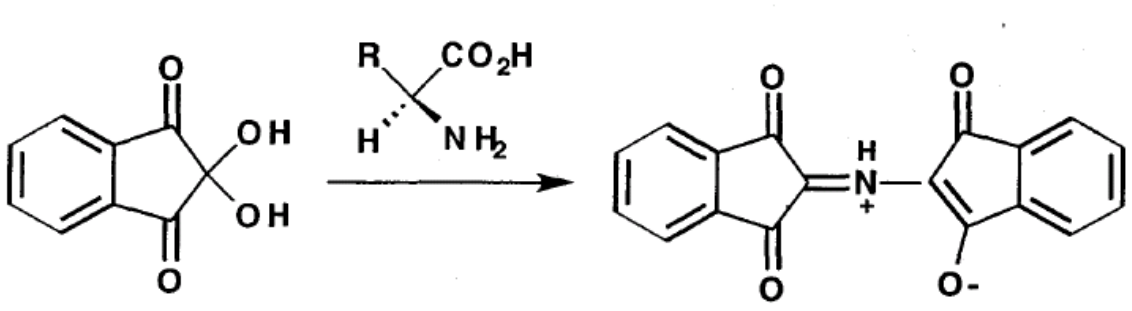
A large number of Schiff bases and their complexes have been studied for their interesting and important properties, e.g., their ability to reversibly bind oxygen, catalytic activity in hydrogenation of olefins and transfer of an amino group, photochromic properties, and complexing ability towards some toxic metals. [5]

The high affinity for the chelation of the Schiff bases towards the transition metal ions is utilized in preparing their solid complexes.

In the present investigation focus has been made on the synthesis of a new multidentate ligand (derived from ninhydrin and o-phenylenediamine) and its complexation properties. Hence a brief coverage of related systems is presented in the following section.

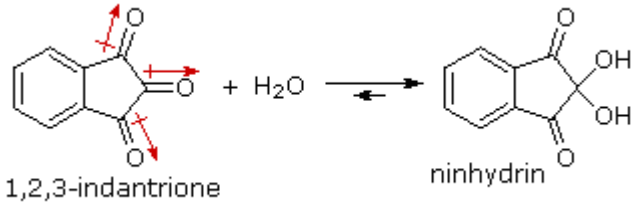
1.1 Ninhydrin

Ninhydrin was first made in 1910 by an English chemist Siegfried Ruhemann, who also investigated its reaction with amines and amino acids to form a colored compound. The product of this reaction is a compound known as Ruhemann's purple (Rp), which has an absorption maximum at 570 nm. [6-8]



Scheme 2. Rp formation reaction

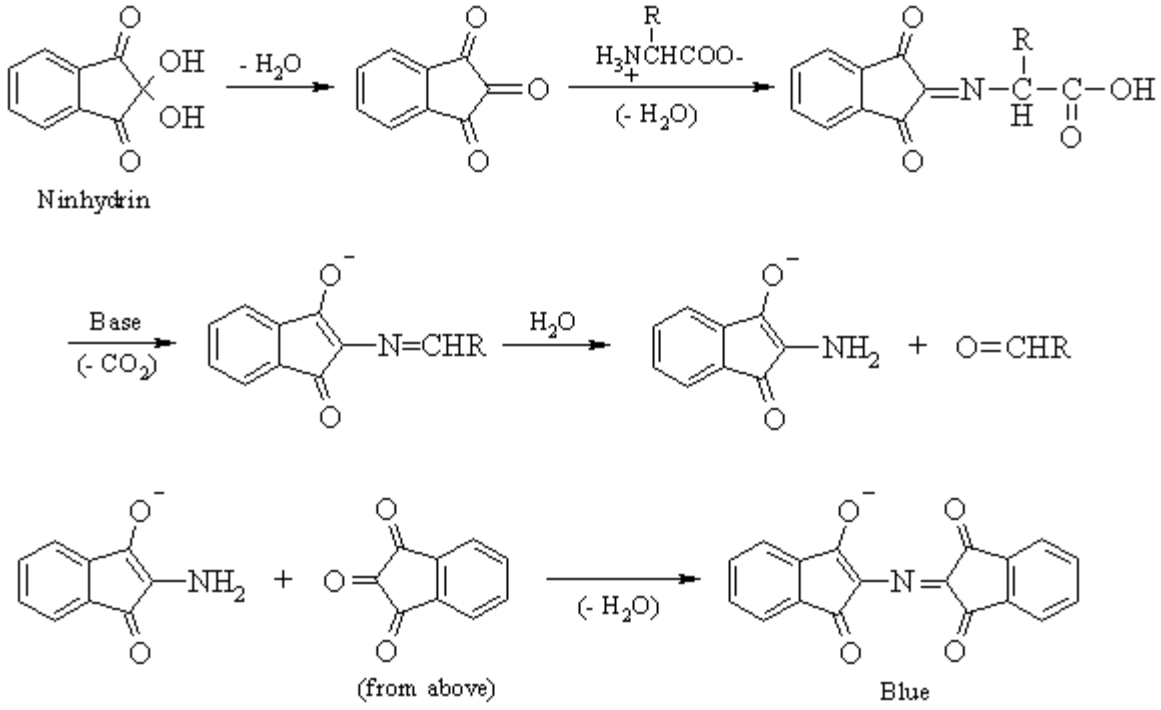
Ninhydrin is a stable hydrate form of its parent carbonyl compound (1,2,3-indantrione). The strong electron withdrawing groups on αC(alpha carbon) destabilizes an adjacent carbonyl group because of repulsion of adjacent positive charges. Hydrate formation overcomes the forces of repulsion. Therefore, the hydrate of the middle carbonyl group of ninhydrin removes both pairs of repulsions.



Scheme 3 .Hydrate formation reaction

Ninhydrin reaction is used to detect the presence of α-amino acids and proteins containing free amino groups. When heated with ninhydrin, these molecules give characteristic deep blue color (or occasionally pale yellow**).** [9]

The chemistry of the reaction of ninhydrin with amino acids has been studied by several workers. The mechanism however was not well understood and this gives rise for a series of theories as reviewed by McCaldine. A simplified form of the mechanism proposed by Filippovich and McCaldinis is shown in **scheme 4**. It has a condensation step that leads to a Schiff base formation followed by decarboxylation, hydrolysis and finally further condensation with another ninhydrin molecule to give the final product, Ruhemann purple. Schiff base derived from ninhydrin and an α-aminoacid acts as a tridentate ligand forming two stable five membered rings on complexation. [10]



Scheme 4. The reaction of Ninhydrin with α -Amino Acids

Ninhydrin has found wide utility as a reagent for the spectrophotometric determination of amino acids as well as primary and secondary aliphatic amines. Aromatic amines are known to give colored condensation products with ninhydrin. Most of these compounds have color intensity so low that the reaction is usable only as a spot test if the aromatic amine is present in high concentration. Of the compounds investigated only p-phenylenediamines and p-aminophenols give colors sufficiently intense for the spectrophotometric determination of trace amounts**.** [11]

Since its discovery, extensive efforts have been made to apply manual and automated ninhydrin reactions as well as ninhydrin spray reagents to the detection, isolation, and analysis of numerous compounds of interest across a broad spectrum of disciplines. These include agricultural, biochemical, clinical, environmental, food, forensic, histochemical, microbiological, medical, nutritional, plant, and protein sciences.[12]

1.2 O-phenylenediamine

O-phenylenediamine (1,2-diaminobenzene) is a compound with the formula $C_6H_4(NH_2)$. This aromatic diamine is an important precursor to many heterocycles. It is isomeric with *m*-phenylenediamine and *p*-phenylenediamine. It is a weak base like ammonia and because of the unshared electron pair on nitrogen; it can form a coordinate bond with proton. In addition it is a binucleophile molecule that forms a variety of compounds. [13]

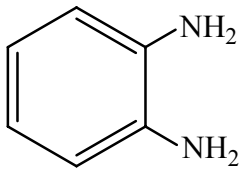
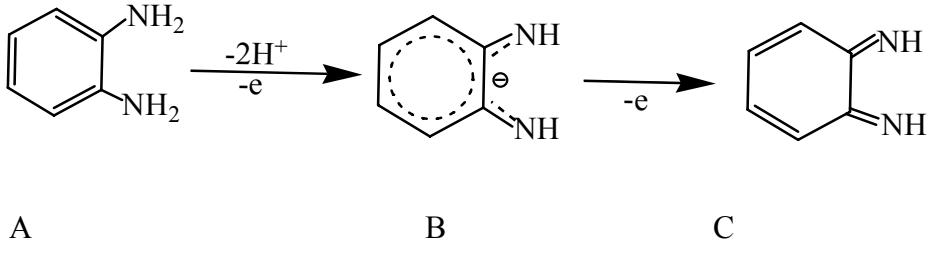


Figure. 1 Structure of o-phenylenediamine

O- phenylendiamine is grouped under non –innocent ligand. Generally ligands of this type can act as σ donors and π acceptors in a complex with predominantly covalent bond. The balance of donor and acceptor interaction and the effective negative charge on these ligands to a high degree depends on the over all electrons available. For example with a high number of such electrons, it is difficult if not impossible to establish the oxidation state of the central atom**.** [14]

In this case *o*-phenylenediamine shows three stable oxidation states: these are o-phenylenediamine (A), semiquinonediimine (B) and quinonediimine (C) forms as shown in the **Scheme 5**.

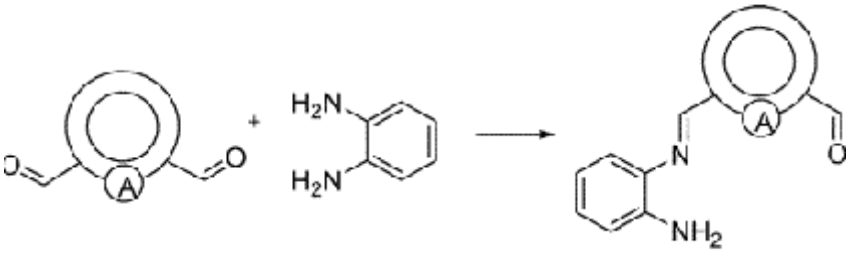


Scheme 5. O-Phenylenediamine with various oxidation states

O-phenylenediamine has many applications. It is an intermediate used in the production of fungicides, corrosion inhibitors, and various pigments and in the production of some pharmaceuticals. O-phenylenediamine is also used to remove sulfur from ores and to remove coloration by aldehydes in polymeric products. [15]

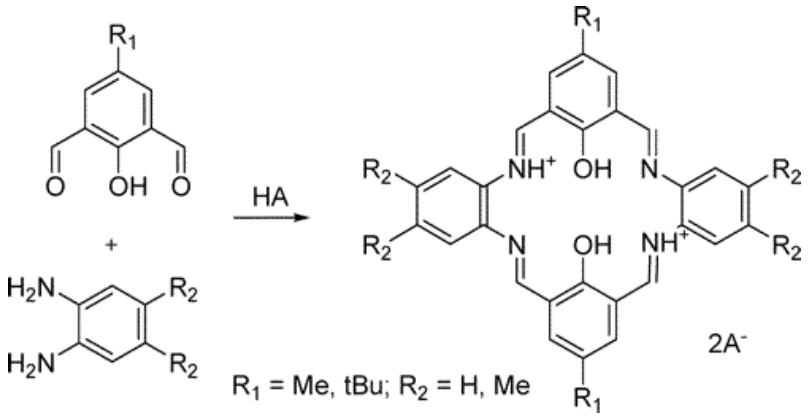
In coordination chemistry,o- phenylenediamine is an important ligand precursor. Schiff base derivatives, such as those derived from salicylaldehyde, are excellent chelating ligands.

O-phenylenediamine condenses with ketones and aldehydes to give rise to Schiff bases. Reactions of this aromatic diamine and its derivatives with aromatic dicarbonyl compounds have been most investigated because of the formation of macrocyclic compounds [16] and fused ring compounds. [17] During the formation of macrocyclic compounds both amino groups of *o*-phenylenediamine are involved in direct conjugation, but the reactivity of the second amino group after the end of condensation of the first one dramatically drops . As a result, [1+1]-Schiff base will be formed as shown in **Scheme 6**.



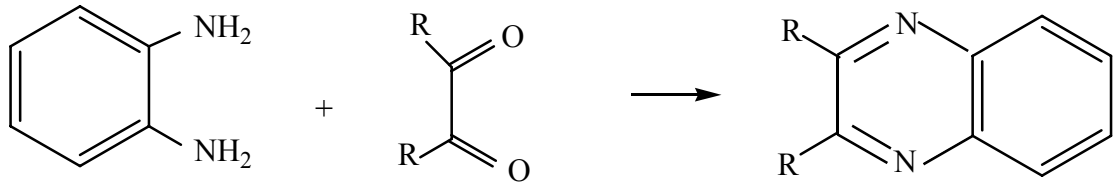
Scheme 6. [1+1]-Schiff base formation reaction

Thus, reactions of *o*-phenylenediamine and its derivatives with diformyl derivatives of phenols, pyrroles, or polypyrroles proceed smoothly only in the presence of acids to give salts of [2+2]-macrocycles. In the case of pyrrole derivatives, free macrocyclic bases were isolated by treating with triethylamine .[18]



Scheme 7. [2+2]-macrocycle Schiff base formation reaction

A good example for ring fused compounds is quinoxaline. Most quinoxaline derivatives have been prepared by condensation of *o*-phenylenediamine with 1,2-dicarbonyl compound. [19]



Scheme 8. Quinoxaline formation reaction

Quinoxaline is one of the benzo-fused six membered hetrocycles, which is related to naphthaline in the same way as pyridine with benzene. The fusion of a benzene ring, however, causes decrease in the aromaticity due to the bond formation. [20]]

Quinoxaline derivatives are interesting class of compounds possessing a broad spectrum of biological activity .They are well known for their antibacterial, antiviral antifungal, antispasmodic, or even anti cancer properties. Bidentate heteroatom sites are important building blocks in constructing bimetallic coordination compounds. Thus, some quinoxaline derivatives for example 2,3- bis 2-pyridylquinoxaline and 2,3- bis- l- furanyl quinoxaline form complexes with transition metals (Cu, Co, Ru, Rh, Pt) cations. [21]

1.3 Chemistry of copper

Cu (d^9) has a well defined aqueous chemistry. There are a large number of salts of various anions many of which are water soluble in addition to a wealth of complexes. The (d^9) configuration subject to Jahn Teller distortion if placed in an environment of cubic (regular octahedral or tetrahedral) symmetry, and this has a profound effect on all its stereochemistry. In octahedral symmetry the distortion usually leads to an elongation of the bonds giving four short and two long Cu-X (X is ligand) bond or more rarely two short and four long ones. The distortion in the limit results square planar arrangement about the copper which can often be induced on the copper by using large organic ligand that blocks the approach of the last two long bond forming ligands. The electronic spectra of Cu (II) ion in its complex could be explained based on Jahn Teller effect .In this case The Eg and T_2g states of the octahedral Cu (II) ion split under the influence of tetragonal distortion. The distortion creates three transitions $^2B_{1g} \rightarrow {}^2A_{1g}$,$^2B_{1g} \rightarrow {}^2B_{2g}$ and $^2B_{1g} \rightarrow {}^2E_{g,}$ which are unresolved in the spectra due to their closer energies. Generally all complexes and compounds of copper (II) are blue or green. Exceptions are caused by strong UV – charge transfer bands –tailling of into the blue end of the visible spectrum thus causing the substance appear red or brown. The magnetic moments of single Cu (II) complexes (those lacking Cu-Cu interactions) are generally in the range of 1.75 to 2.2 B.M .regardless of stereochemistry. [22-23]

Copper (II) forms many complexes with nitrogen donors. The four- coordinate complexies is usually much more stable than the six –coordinate ones, although many of these exist. For example $[Cu(NH_3)_4]^{+2}$ and $[Cu(en)_2]^{+2}$ are very stable whereas $[Cu(NH_3)_6]^{+2}$ and $[Cu(en)_3]^{+2}$ are less stable. Multidentate ligands such as N,N ‘-bis[4-(benzeneazo) salicylaldehyde]-o-phenylenediamine and 5-Hydroxysalicyliden-*p*-aminoaceto phenone oxime form complex with it.

Glycine containing both nitrogen and oxygen donors, reacts with copper (II) to give square planar diglycinecopper ($NH_2CH_2CO_2$) Cu. There are numerous complexes with chelating oxygen donors, such as β- diketones and β- diketoesters.[24,25,26]

1.4 Literature review

Studies on the synthesis, characterization and antimicrobial activity of new Co (II), Ni (II) and Zn ((II) complex of Schiff base derived from ninhydrin and glycine

For the first time, Co(II), Ni(II) and Zn(II) complexes were synthesized involving an intermediate Schiff base, indane-1,3-dione-2-imine-N-acetic acid the condensed product of ninhydrin and glycine. These colored complexes were characterized by elemental analysis, molar conductivity, thermogravimetric analyses/differential thermal analysis, infrared, magnetic susceptibility, NMR and electronic spectral studies. Mechanisms for their formation was proposed. The experimental studies revealed that the complexes possessed octahedral stereochemistry wherein the Schiff base behaved as a monobasic tridentate ligand. A molecular structure for the metal complexes was also proposed. A comparative study of the antimicrobial activity of ninhydrin and the corresponding metal complexes against Escherichia coli, Proteus mirabilis, Staphylococcus aureus and Streptococcus faecalis was undertaken and the results were discussed. [27]

Structure and electrochemical behavior of Bis [N-(4-methylphenyl) salicylaldimine] copper (II) N,N'dimethylformamide solvate

In recent years research on many newly synthesized Cu (II) Schiff base complexes has received importance . Here the effect of substitutent was studied. The structure of the R group bonded to the imine nitrogen significantly effects the coordination of the complex formed between ON types of Schiff base and transition metal ions.

It is reported in the literature that the steric structure of the R group affects the coordination geometry. It has been stated that when the R_2-group (**fig.2**) is a large group like t-butyl, then a tetrahedral complex is formed with Ni (II) and Cu (II). On the other

hand if the R_2-group is small or planar then a square-planar coordination with *trans*-structure can be formed. [28]

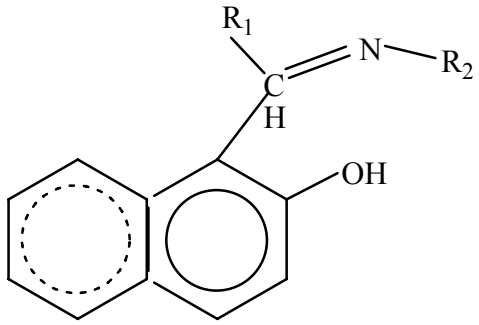


Figure. 2 ON type Schiff base

Template synthesis and characterization of highly unsymmetrical tetradentate Schiff base complexes of Ni (II) and Cu (II).

Nickel (II) and copper (II) complexes of a highly unsymmetrical tetradentate Schiff base have been synthesized by the template reaction of half-units N-(1-hydroxy-2-acetonaphtone) -1-amino-2-phenyleneimine (HL) and N-(2-hydroxya cetophenone)- 1-amino-2-phenyleneimine (HL_1) with the glyoxalphenylhydrazone.

The complexes have been characterized by elemental analyses, conductance,IR, ^{1}H NMR and UV- VIS spectroscopy. In this case the synthesis of mono-Schiff bases N-(1-hydroxy-2-acetonaphtone)-1-amino-2-phenyleneimine (HL) and N-(2-hydroxy acetophenone)-1-amino-2-phenyleneimine (HL_1) takes place by condensation of o-phenylenediamine with 1-hydroxy-2-acetonaphtone and o-hydroxyacetophenone respectively **(fig.3)**. Non-symmetric Schiff base complexes were then obtained by the reaction of half-units with glyoxalmono-phenylhydrazone (HL_2) in methanol in the presence of the desired metal acetate **(fig.4)**. [29]

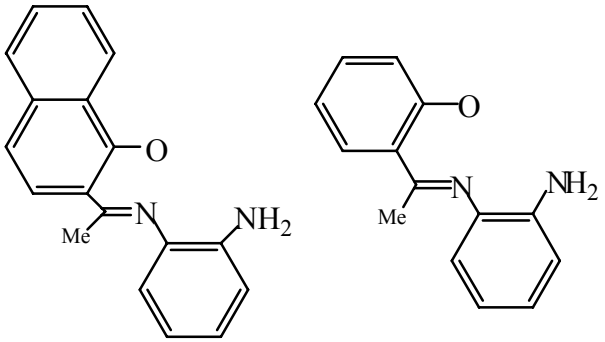


Figure .3 Half- unit structures for 2- phenyleneimine derivative ligand

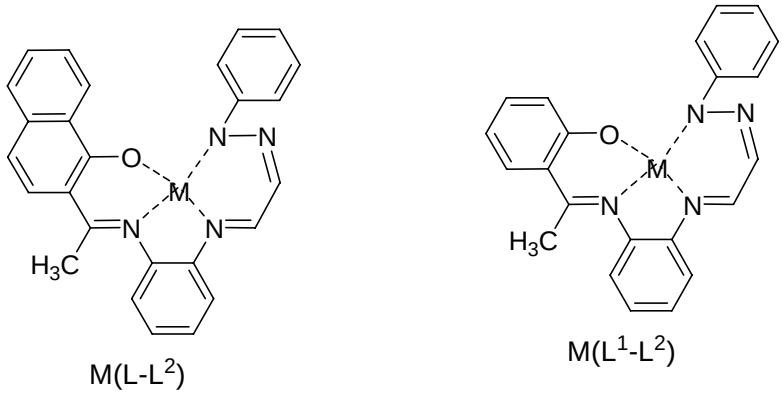


Figure .4 Structure of highly unsymmetrical Schiff base complex (M=Cu,Ni)

1.5 General objectives of the present investigation

Schiff bases have been widely used as bidentate ligands in the field of coordination chemistry. The Schiff base complexes have been used in catalytic reactions and as models for biological systems. In recent years many Copper complexes of Schiff bases were prepared [30] Literature survey reveals that the complexation behaviors of ligands derived from ninhydrin and di-or poly amines have not been much investigated. In view of the possible variation in the reactivities of different carbonyl groups in ninhydrin ,it is worthwhile to investigate its reactivities towards di-or polyamines and employ the products in metal complexation reactions**.** So in this investigation it was aimed to

1. Synthesize the Schiff base ligand derived from ninhydrin and o- phenyenediamine
2. Study the complex formed from dihydrated copper chloride and the ligand
3. Elucidiate the structure of the complex derived from dihydrated copper chloride and the ligand.

2. MATERIAS AND METHODS

2.1 Chemicals

Most chemicals used in the investigation were of AnalaR grade. Chemicals like ninhydrin (Pharmacos), o-phenylenediamines (Pharmacos), and $CuCl_2.2H_2O$ were used. Other reagents and solvents used in this investigation were silver nitrate, nitric acid and ammonia solution. Absolute ethanol and chloroform were used as the solvents through out the investigation. Solvents like DMSO, DMF, acetonitrile, methanol, carbon tetrachloride, THF, and distilled water were also used.

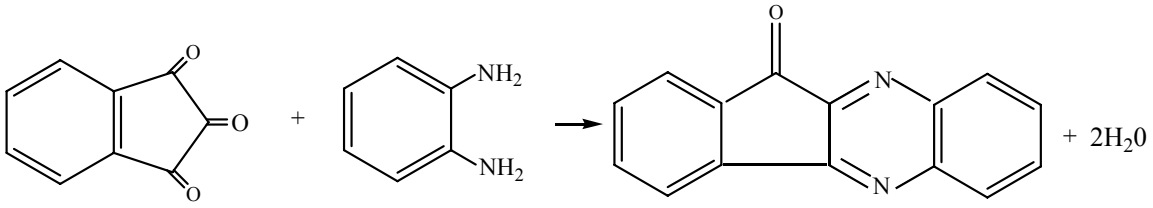
2.2. Instruments

UV-Vis spectrophotometric measurements were made in the range 200-750 nm using spectronic Genesys 2PC spectrophotometer. Determinations of melting point or decomposition temperature of the products were done with Stuart SMP3 Digital Melting Point apparatus. Nuclear magnetic resonance data were collected using BRUKER ARX 400 NMR spectrometer. Infrared (IR) spectra were recorded using a Perkin Elmer FT-IR BX spectrophotometer in the range 4000-400 $cm^{-1}$with samples prepared using KBr pellets. . Magnetic susceptibility measurements were performed using MSB Auto, (Sherwood Scientific). The molar conductivity measurements were carried out using EC 214 Bench type conductivity meter (Hanna Instrument). The metal complex was analyzed for its metal content using Buck Model Scientific 210 VGB atomic absorption spectrometer. MS data of the ligand were obtained on a ThermoFinigan High Temperature Direct Insertion Prob instrument. The sample was ramped from RT to 300^0c. Several other common laboratory equipments were also used during the investigation.

2.3 Preparation of the ligand

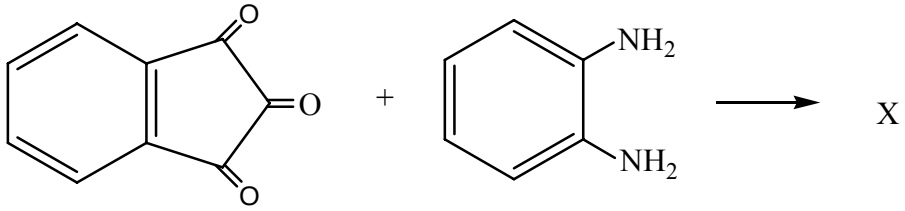
Ninhydrin (1.1m mol, 0.2 gm) in 15 ml ethanol was mixed with o-phenylenediamine (1.1m mol, 0.12gm) in 15 ml ethanol. The solution was stirred for 30 minutes. The resulting yellow precipitate was filtered off under sunction and repeatedly washed with ethanol. The product was then dried in open air and stored in a desiccator.

Yield: 89% mp 223-225 ^{o}C

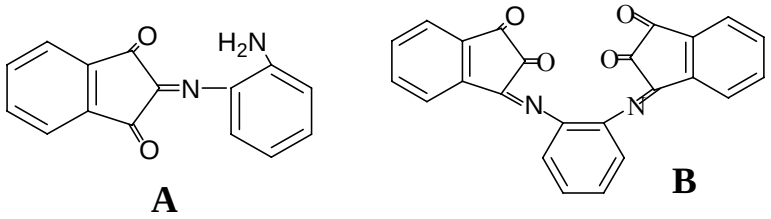


Scheme 9. Reaction of Ninhydrin with O-Phenylenediamine

Structural elucidation of the product was done based on experimental evidence (IR, NMR etc). The other possible products of this reaction are as follows



Where X is A or B as shown below



2.4 Preparation of the complex

$CuCl_2.2H_2O$ (0.35m mol, 0.6gm) in 15 ml ethanol was mixed with the ligand NHOPD (0.7m mol, 0.16gm) in 15 ml chloroform. The solution was refluxed through stirring for about 11 hours. After cooling the resulting dark brown solid product was filtered, washed with a mixture of ethanol and chloroform (1:1,30ml) dried in air and stored in desiccator Yield: 40% mp 323-325 ^oC

3 RESULTS AND DISCUSSION

3.1 Characterization of the ligand

3.1.1 Physical properties of the ligand

The ligand is stable at room temperature having yellow color. It is soluble in chloroform, benzene and hot ethanol, but partially soluble in DMSO and acetonitrile.

3.1.2 IR spectrum of the ligand

Ninhydrin shows three bands in the C=O stretching region, 1768, 1754, and 1720 cm^{-1} .The 1754 and1720 cm^{-1} bands are characteristic of its 1,3 –dicarbonyl functional group and 1768 cm^{-1} band is characteristic of the intermediate carbonyl in the tricarbonyl species which is in equilibrium with the dihydroxy species .The disappearance of the two carbonyl bands and the appearance of only one band at 1724 cm^{-1} indicates **(Appendix7)** the involvement of two carbonyl groups of ninhydrin in azomethine formation . On the other hand o-phenylenediamine has sharp NH_2 bands at 3386 cm^{-1} and 3364 cm^{-1} that are assigned as asymmetric and symmetric stretching vibration, respectively .But these bands did not appear in the spectrum which indicates the derivatization of these groups. Absorption frequency at 1570 cm^{-1} is assigned for C=N stretching mode of vibration. Absorption frequencies observed at 1337, and 1185 cm^{-1} are assigned to C-N stretching [31]

3.1.3 Electronic spectrum

The electronic spectrum of the ligand **(Appendix 4**) shows absorption bands at 26041 cm^{-1} (384nm) and 30,959 cm^{-1} (323nm). From these bands the one at 30,959 cm^{-1} is attributed to C=O group of $n\rightarrow\pi^*$ transition and the band at 26,041cm^{-1} can be attributed to the $n\rightarrow\pi^*$ transition of the C=N functional group .Absorption in the range 40,000 cm^{-1} are due to $\pi\rightarrow\pi^*$transitions of aromatic system.

3.1.4 ^{1}H and ^{13}C NMR spectrum

I) ^{1}H NMR Spectra:

The ^{1}H NMR results for ligand (**Appendix 1)** is summarized in **table 1** below.

Table 2. **^{1}H NMR data for ligand**

Compound	Type of Proton(s)	Number of Proton(s)	δ in ppm	Solvent
LIGAND	H 7	1H(d)	8.5	$CDCl_3$
	H9-10	2H(d,d)	8.15-8.1	
	H11	1H(d)	7.95	
	H15	1H(dd)	7.85	
	H12-13	2H(dd,dd)	7.8-7.75	
	H14	1H(dd)	7.65-7.6	

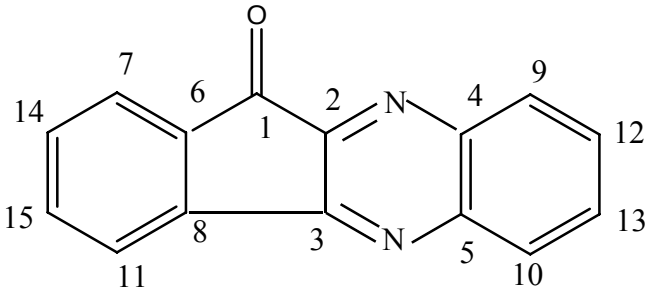


Figure .5 Structure of the ligand

II) ^{13}C NMR data for ligand

^{13}C NMR (**Appendix 2)** shows fifteen non-equivalent carbons for the ligand as given in **table 2**. The DEPT spectra(**Appendix 3)** shows no CH_2 group and from the fifteen non-equivalent carbons of the ligand seven are quaternaries and the other eight refers to methine carbon

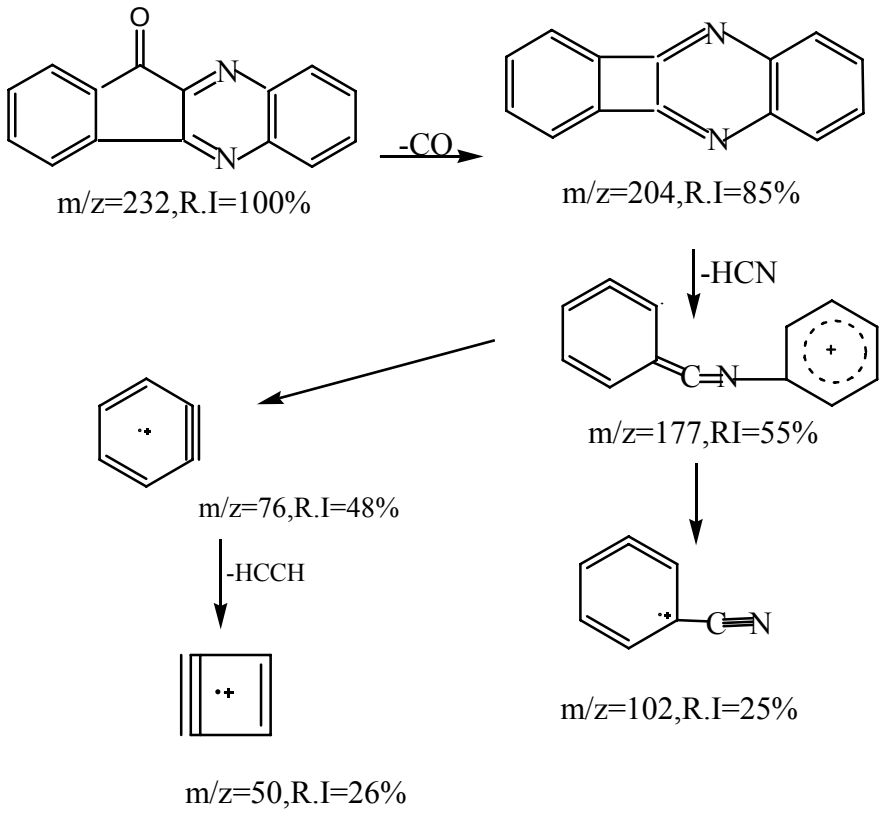
Table 3**.** ^{13}C NMR data for ligand

Compound	Type of Carbon(s)	Number of Carbon(s)	δ in ppm	Solvent
LIGAND	C-1	1	189.93	$CDCl_3$
	C-2	1	156.62	
	C-3	1	149.27	
	C-4	1	143.14	
	C-5	1	142.65	
	C-6	1	141.56	
	C-7	1	136.82	
	C-8	1	136.68	
	C-9	1	132.52	
	C-10	1	132.45	
	C-11	1	131.6	
	C-12	1	130.29	
	C13	1	129.28	
	C14	1	124.79	
	C15	1	122.52	

The ^{1}HNMR spectrum shows chemical shifts and coupling interactions. This data together with DEPT and ^{13}C NMR patterns confirm the above **(fig. 5)** structure of the ligand.

3.1.5 Mass Spectrum

The mass spectrum of NHOPD shows (**Appendix 6)** a molecular ion peak with m/z = 232 which shows up a base peak. This precisely corresponds with the molecular mass, exactly matching with molecular formula $C_{15}H_8N_2O$. This is in supportive evidence for the structural conclusions drawn on the basis of IR, NMR and UV-VIS spectra .Subsequently fragmentation can be explained on the basis of the formation of this molecular ion. The fragmentation is revealed by the formation of species with m/z = 204, 177, 150, 116, 102, 76, 63, and 50.The molecular ion and the fragment obtained by cleavage in different position are shown in **scheme 10**.



Scheme 10. Molecular ion fragmentation

3.2 Characterization of the complex

3.2.1. Physical characteristics of metal complex

The metal complex of Cu (II) was synthesized by reacting the ligand NHOPD with the salt of metal chloride in 1: 0.5 mole ratios.

This metal complex of Cu (II) has formed dark brown colored compound. The metal complex is insoluble in ethanol, benzene and chloroform. However, it is soluble in acetonitrile and DMSO. Some of the important physical properties of the metal complex are summarized in the following **table 3.**

Table 4.. **Physical characteristics of the metal complex**

compound	**appearance**	**color**	**M.pt temperature (^{o}C)**	**Yield (%)**
Cu-complex	Fine powder	dark-brown	323-325	40

.

3.2.2. Qualitative Test

I) Chloride Test

The compound (sample) dissolved in nitric acid was subjected to chloride identification. A curdy white precipitate formed in the solution after addition of $AgNO_3$ (0.1N sliver nitrate) solution indicated the presence of chloride in the sample.

Dissolution of the precipitate (AgCl) in aqueous ammonia and reprecipitation by adding concentrated nitric acid confirmed the presence of chloride.

3.2.3. Quantitative Determination

I) Metal determination (Atomic absorption spectral estimation)

The metal content in the complex was determined spectroscopically using atomic absorption spectroscopy (AAS). Metal percentage along with C, H, N, O percentages was used to arrive at the metal-ligand ratios in the complex. The experimental percentage of metal in the complex was found as:

$$M(\%) = \text{Absorbance(A, ppm)} \frac{\text{X volume diluted to X} \quad 100}{\text{Mass of the sample} \quad 1000}$$

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

Procedure:

20 mg of Cu (II) complex was placed in a clean and dry beaker, to which 10 ml portion of conc. HNO_3 was added and the content was heated gently in a hood until a few drops remained in the beaker. Then 10 ml of additional conc. HNO_3 was added in the beaker and heated slowly until a few drops remained. The latter procedure was repeated for three times until all the organic portion of the complex was decomposed. Then the residue was dissolved and diluted using deionized water in a 50 ml flask. The solution was subjected to AAS studies after appropriate dilutions. Based on the absorbance data, the concentration of Cu (II) complex was calculated.

The metal percentage obtained from this calculation was used to arrive at the metal to ligand ratio in the complex as shown in the **Table 4**.The variation of calculated an found mass may be connected with the presence of impuities.

Table 4.. **Metal determination data**

Metal complex	Found (%mass)	Calculated (%mass)	Metal to ligand ratio
CuL_2	8.41	10.12	1:2

(II) Chloride Estimation

20mg of the complex was dissolved in 5ml concentrated nitric acid and digested for complete oxidations of organic component which is diluted to 100 ml using deionized water after evaporation of HNO_3 and digested for 2 hours. To the digested solution 0.1N of $AgNO_3$ was added until precipitation was complete. The content was further digested on steam bath for one hour. The AgCl precipitate was filtered through a previously dried and weighed sintered glass crucible, washed with $0.1HNO_3$ and dried to a constant weight at 110^0c .The percentage of chloride was calculated using the weight of AgCl precipitates. This indicates **(Table5**) the presence of two chlorides in the complex.

Table 5. **Chloride estimation data found (calculated)**

Complex	Cu(II)
Weight of AgCl found	11mg
% of chloride in the complex	10.8(11.2)

3.2.4. Molar Conductivity of the metal complex

The molar conductance was determined from conductivity measurements of the one millimolar solution of the complex in acetonitrile at 25 ^{o}C .The determination of cell constant was made using the following relation:

$$\Lambda_M = \frac{1000\ \kappa}{C}$$

The molar conductivity value of Cu (II) complex is 226 S cm^2 mol^{-1} , indicating its electrolytic nature. This suggests that the chlorides in the complex are in the ionization sphere. The molar conductivity of the metal complex is summarized in **Table 6**.

Table 6. **Molar conductivity of the metal complex**

Compound	**Λ_M (molar conductivity) S cm^2 mol^{-1}**
Cu(II)-complex	226

3.2.5 IR spectrum

When the IR spectrum of the metal complex (**Appendix 8**) was compared with that of the free ligand, certain shifts were found. The band corresponding to C=N shifts to a lower frequency (**Table 7) indicating** its involvement in complex formation .The shift of carbonyl band from 1724 cm^{-1} to 1715 cm^{-1} indicates the movement of electron density

from the C=O to the metal. 1337 Absorption frequency observed at 3081 cm^{-1} and 3055 cm^{-1} are assigned to aromatic C-H, 1615 cm^{-1} and 1464 cm^{-1} to aromatic ring. The shift of band from cm^{-1} to1341 cm^{-1} indicates the change of electron density of C-N bond due to complex formation. Other bands like 3435 cm^{-1} represent the presence of water in the complex. The new band at 554 cm^{-1} and 435 cm^{-1} are assigned for M-O and M-N bonds respectively.

Table 7. **Important characteristic IR bands of the metal complex**

Compound	$\nu_{OH\ in}$ cm^{-1}	$\nu_{C=O}$ in cm^{-1}	$\nu_{C=N\ in}$ cm^{-1}	$\nu_{C-N\ in}$ cm^{-1}	New bands
Cu(II)-complex	3435(b)	1715(vs)	1560(S)	1341(S)	554(M-O) 435(M-N)

3.2.6 UV-VIS spectrum of the metal complex

The electronic spectrum of the complex was recorded in acetonitrile at room temperature. In comparison with the free ligand spectrum, the metal complex shows characteristic features which can be attributed to electron density reorganization and metal ligand bonding through specific metal binding centers. The major features of the spectrum are explained below. The spectrum**(Appendex5)** indicates bathochromic shift of absorptions due to carbonyl and azomethine functions. Additionally the spectrum shows an intense band at 22729 cm^{-1} which is assignable to ligand → metal charge transfer. Other bands of low intensity observed at 20,747 19417 cm^{-1} are assignable to two of the three possible electronic transitions characteristic of square planar geometries.[32] The bands are assigned to the transitions $^2B_{1g} \rightarrow {}^2B_{2g}$ and $^2B_{1g} \rightarrow {}^2E_{g..}$ **(table 8**)

Table 8. **Electronic spectrum of the complex**

compound	Absorption bands (cm^{-1})	Transition
Cu complex	22573(443nm)	LMCT
	20,746(482nm)	$^2B_{1g} \rightarrow {}^2B_{2g}$
	19,417(515nm)	$^2B_{1g} \rightarrow {}^2E_g$

3.2.7 Magnetic Susceptibility

The gram susceptibility (χ_g) for a given paramagnetic substance has been measured. The following calculations were made to arrive at the magnetic moments. Molar magnetic susceptibility (χ_M) = χ_g × Molecular weight of the compound χ_M is subjected to diamagnetic correction to obtain corrected molar magnetic susceptibility ($\chi_M^{corr.}$), from which the magnetic moment is finally calculated.

$$\text{Magnetic moment } (\mu_{eff}) = 2.84(\chi_M^{coor} \text{ X T})^{1/2} \text{ (in B.M.)}$$

.

The magnetic moment at the given temperature for Cu (II) a complex is given in **table 9** below. The experimental room temperature magnetic moment (B.M.) represents paramagnetism due to Cu (II) metal ions in the complex. Variation of magnetic moment from spin-only value could be explained by considering the contribution of orbital motion (Russel-Saunders coupling) or spin-orbit coupling of electrons. In this investigation the value of magnetic moment is a little higher than theoretical value. This variation indicates the presence of spin-orbit coupling, which arises because of the mixing of ground state orbital with higher orbital of degenerate states.[33]

Table 9**.** Magnetic susceptibility of the metal complex

Compound	**μ_{eff} found (B.M.)**	**μ_{eff} experimental (B.M.)**
Cu(II)-complex	2.3	1.7-2.2

3.2.8. CONCLUSION

Based on IR, UV-VIS, NMR, MS, molar conductance, and magnetic data of the ligand and the complex, the following structure of the complex was proposed. This suggests that the square planar geometry around the metal ion and supports the neutral bidentate ON donor behavior of the ligand. The proposed structure is given in **fig.6**.

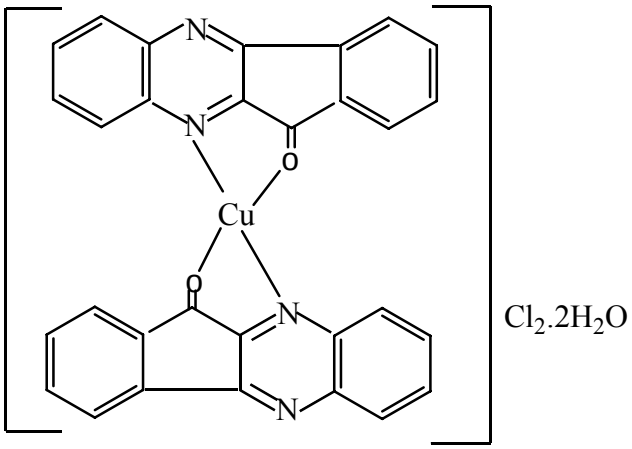


Figure . 6 Proposed structure of Copper complex

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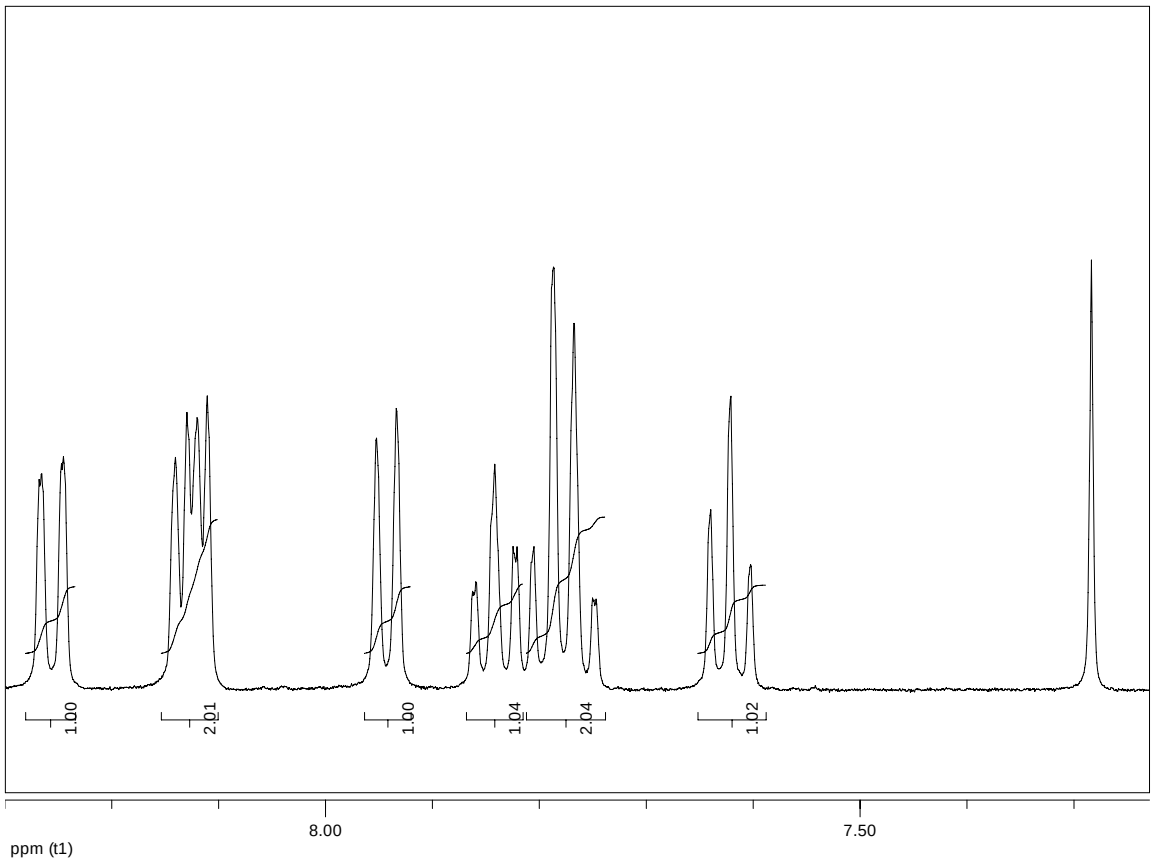
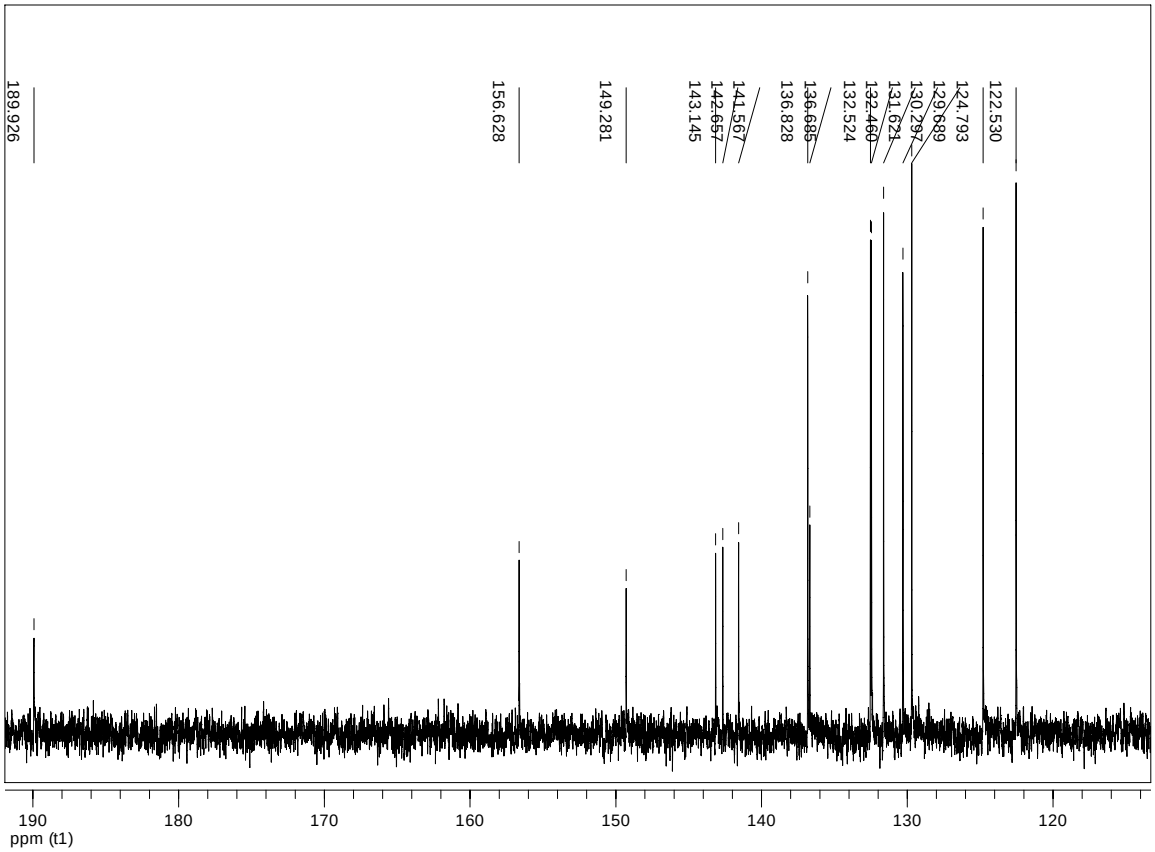
APPENDICES

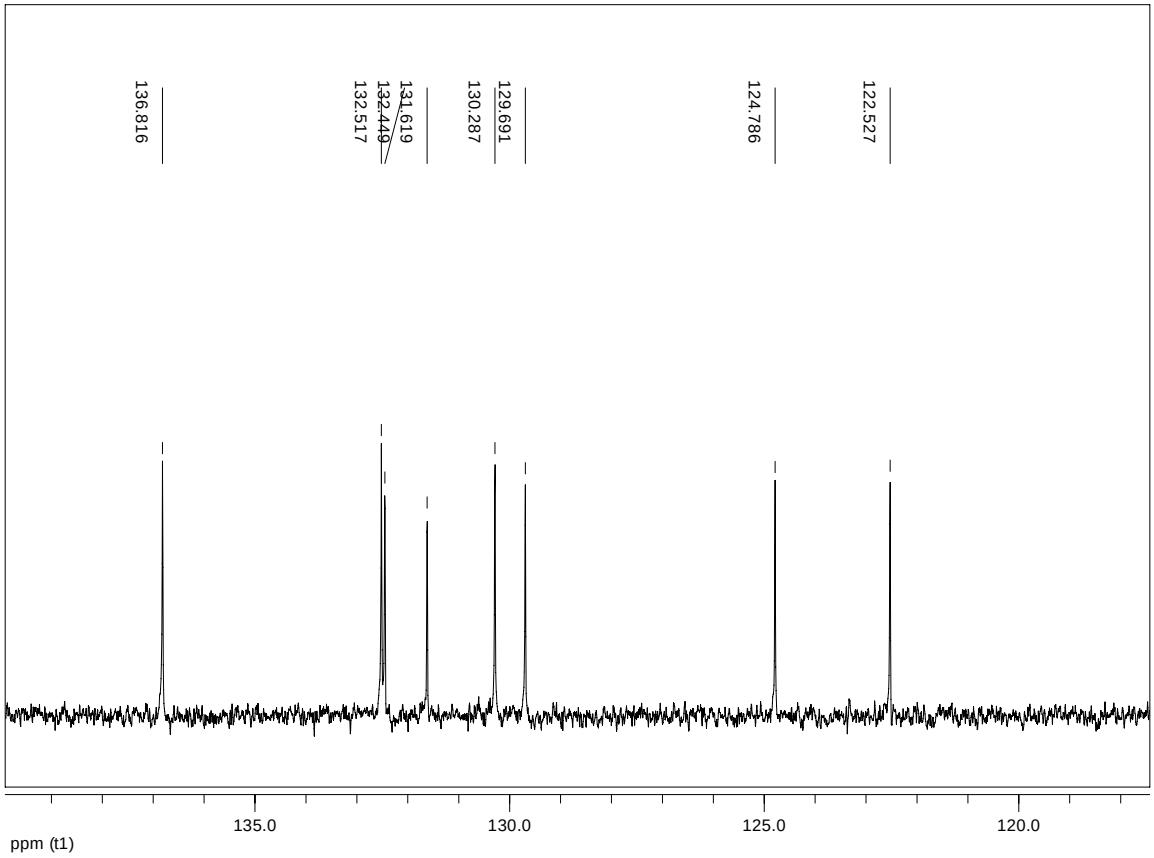
Appendix 1. ^{1}H NMR of NHOPD



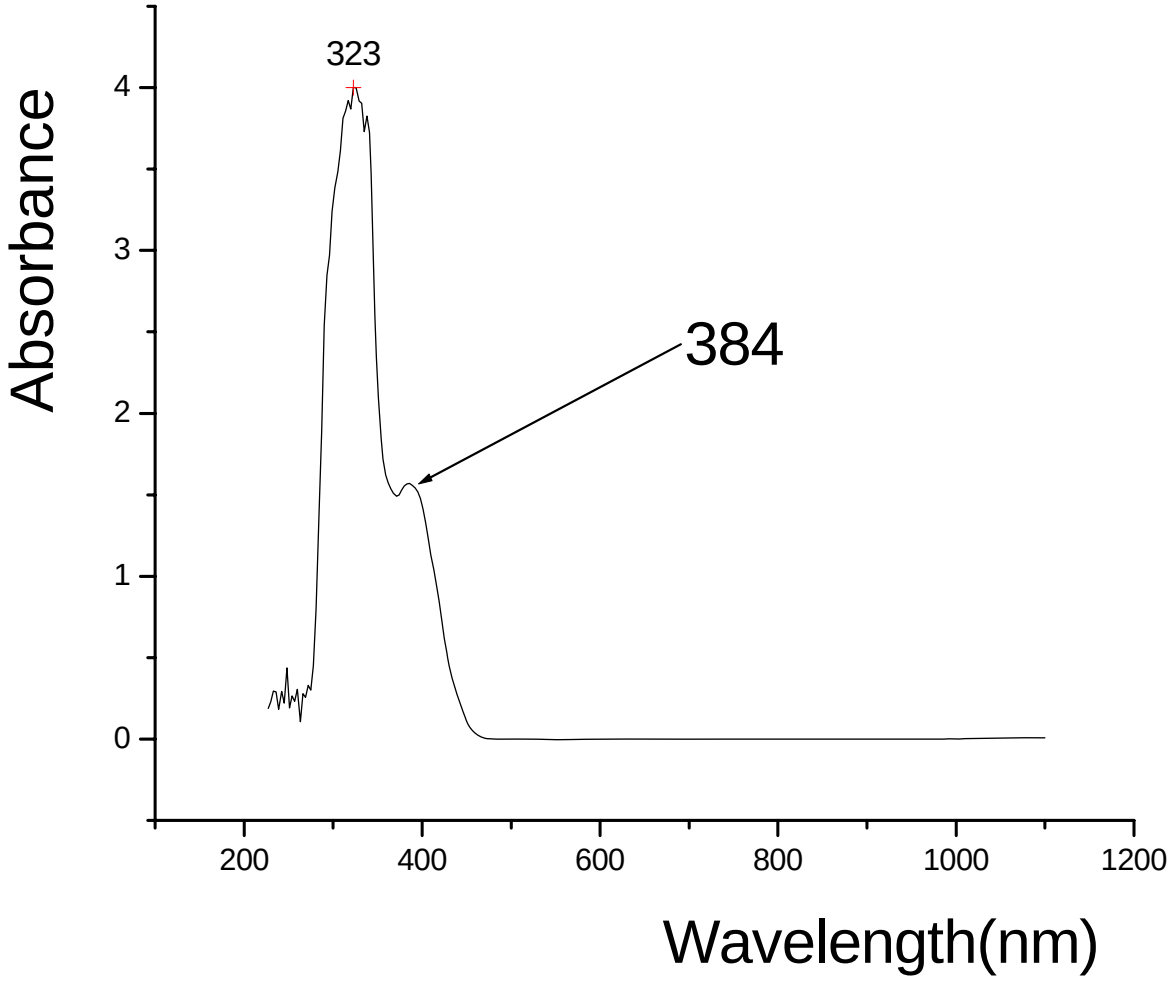
Appendix 2. ^{13}C NMR of NHOPD



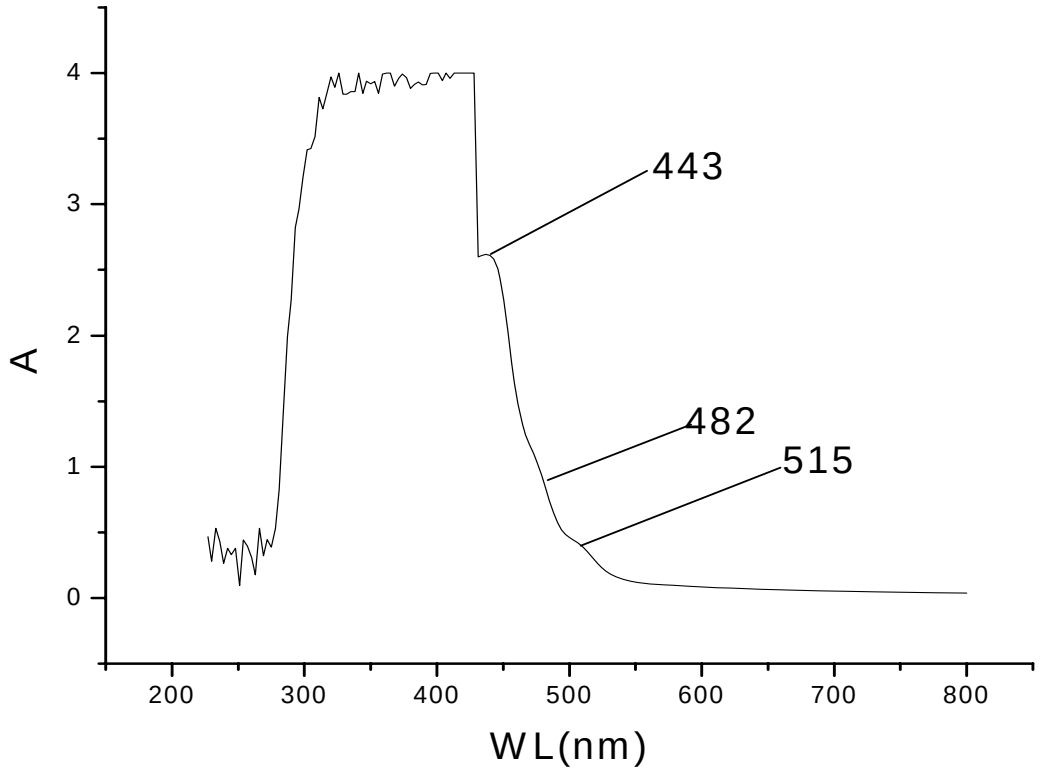
Appendix 3. DEPT-135 spectrum of NHOPD



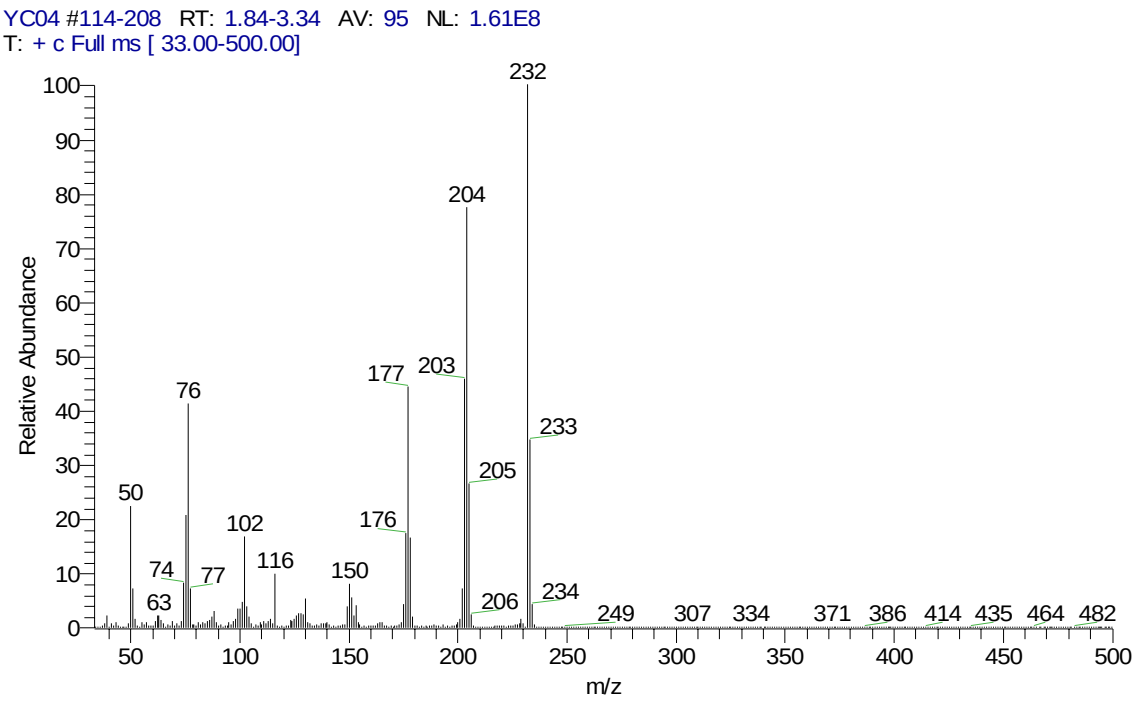
Appendix 4. UV-vis of the NHOPD



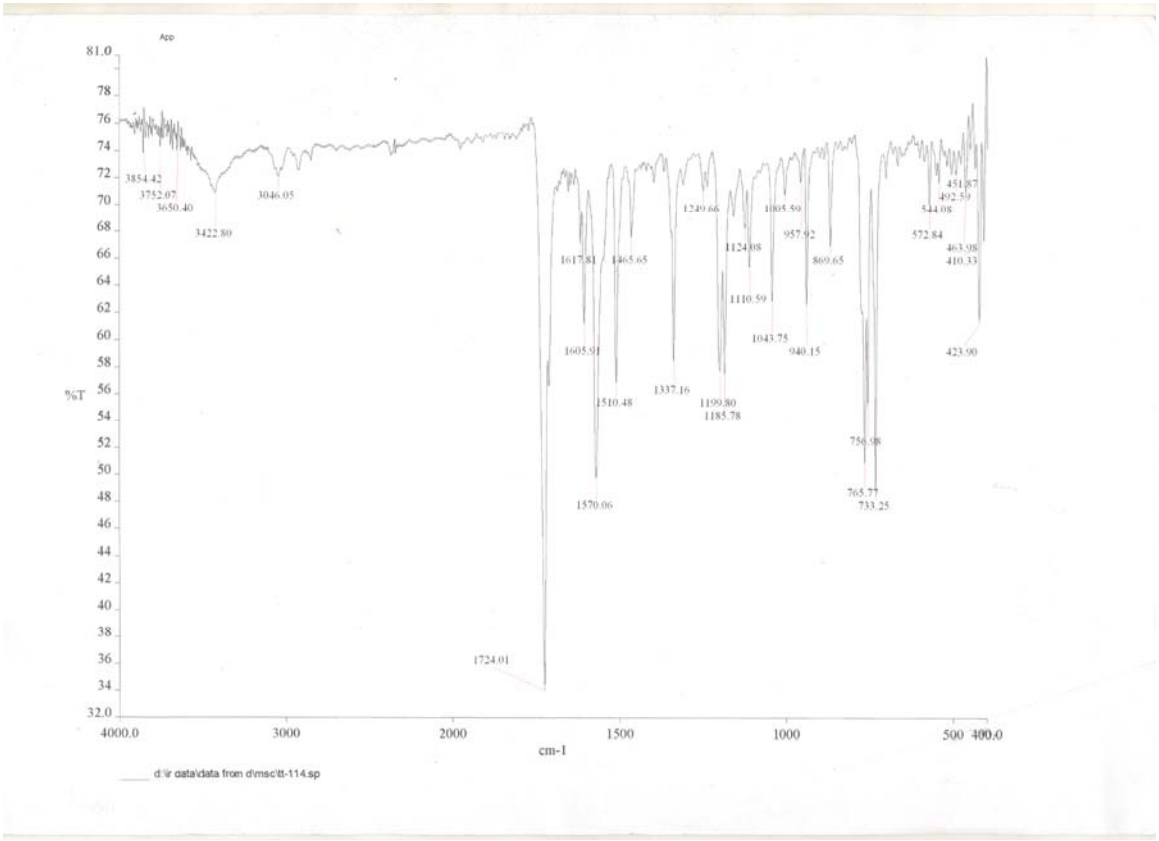
Appendix 5. UV-vis of the copper complex of NHOPD



Appendix 6. Mass spectrum of NHOPD



Appendix 7. IR spectrum of NHOPD



Appendix8.IR spectrum of Cu(II) complex of NHOPD