ADDIS ABABA UNIVERSITY
GRADUATE PROGRAM
DEPARTMENT OF CHEMISTRY

Synthesis and Structural Studies of a New Polydentate Ligand and its Ni (II) and Zn (II) Complexes

By: Tsegaye Fekadu

February, 2015

Synthesis and Structural Studies of a New Polydentate Ligand and its Ni (II) and Zn (II) Complexes

Tsegaye Fekadu

Thesis Submitted to

The Department of Chemistry

Presented in Partial Fulfillment of the Requirement for the Degree of Master of Science in Chemistry (Inorganic Chemistry)

Addis Ababa University

Addis Ababa, Ethiopia

February, 2015

Addis Ababa University
Graduate Program

This is to certify that the thesis prepared by Tsegaye Fekadu, entitled: ‘‘*Synthesis and Structural Studies of a New Polydentate Ligand and its Ni (II) and Zn (II) Complexes*’’ and submitted in fulfillment of the requirements for the Degree of Master of Science (Inorganic Chemistry) complies with the regulations of the University and meets the accepted standards with respect to originality and quality

Signed by the Examining Committee:

Examiner ________________________Signature _________Date _________

Examiner ________________________Signature _________Date _________

Advisor ________________________Signature _________Date _________

Abstract

A new polydentate ligand N-(2-hydroxyphenyl)-2-[(2-aminophenylamino)] acetamide, (HPAPAA) has been synthesized in the reaction between N-(2-hydroxyphenyl)-2-chloroacetamide and o-phenylenediamine. The Ni (II) and Zn (II) complexes of the ligand were synthesized and characterized on the basis of their spectral (IR, NMR, UV-Vis, and AAS), elemental analyses, conductivity and magnetic susceptibility measurements. The Ni (II) and Zn (II) metal complexes were synthesized in methanolic media. Metal-to-ligand ratios were found to be 1:1 for both complexes. Conductivity measurements suggested that both complexes were non-electrolytes. Binuclear Ni (II) complex exhibited subnormal magnetic moments indicating the possibility of antiferromagnetic interaction through a possible super exchange mechanism. The ligand behaves as dibasic tridentate, employing ONO donor sequence in chelation including phenoxide bridging. Based on the analytical, infrared, conductivity, magnetic susceptibility and electronic spectral data it may be concluded that octahedral geometry for Ni (II) complex and, square planar geometry for Zn (II) complex was suggested.

Key words: polydentate ligand, Ni (II) and Zn (II) complexes, HPAPAA

ACKNOWLEDGEMENTS

Since my first step in life till now a lot of people guide me through my education journey, my parents, my teachers in preschool, at primary school, at intermediate school, at secondary school, my lecturers at university, my supervisor in master degree . So many people have helped me along this journey. It is impossible to name everyone whose effort has allowed me to achieve my goals and dreams.

I would like to take this opportunity to acknowledge people who have helped me in a number of ways to make this dissertation a reality. First, I would like to express my deepest and truthful gratitude and respect to my advisor Dr. Yonas Chebude for his significant observations and direction, invaluable advice and guidance, continuous supervision and encouragement, assistance and support that greatly encouraged me to accomplish this thesis work.

I would like to thank my parents who have always supported all my decisions and have been a source of constant energy to me. I would also like to thank my brothers and sisters, Ashenafi, Mitku, Dawit, Sisay, Alemtsehay and Mihret, whose encouragement has always kept me going.

I would like to thank the financial support and also for giving me this opportunity for Arbaminch University, AMU. I gratefully acknowledge Addis Ababa University, AAU for providing all the necessary facilities and equipments for this work. I would like to express my heartfelt gratitude to W/o Mihret G/ Meskel for her cooperation and willingness when I was in need of her continuous moral support. I appreciate Ato Sahile Micheal, for his fast response in supplying chemicals and apparatus. I also thank Ato Yisak for running UV-Vis spectra, Ato Henok for running atomic absorption spectra, and W/o Woinshet Gebeyehu for running the IR spectra of the synthesized compounds and also PhD students for their supports and guidances while I was working in the lab.

Finally, I am also thankful to all my friends for their continuous encouragement.

TABLE OF CONTENT

List of Figures

List of Tables

List of Schemes

List of Appendixes

List of Abbreviations and Symbols

DMF	Dimethyl formamide
DMSO	Dimethyl sulfoxide
MeOH	Methanol
EtOH	Ethanol
M.Pt.	Melting point
IR	Infrared
UV-VIS	Ultraviolet-Visible
NMR	Nuclear magnetic resonance
DEPT	Distortionless Enhancement by Polarization Transfer
HPCA	N-(2-hydroxyphenyl)-2-chloroacetamide
HPAPAA	N-(2-hydroxyphenyl)-2-[(2-aminophenylamino)] acetamide
OPD	O-Phenylenediamine
AAS	Atomic absorption spectroscopy
TLC	Thin layer chromatography
CT	Charge transfer
br	Broad band
w	Weak band
Λ_M	Molar conductivity
μeff	Magnetic moment
B.M.	Bohr magneton

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 [1-7].

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, Ti, 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 [1, 2, 5].

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 [8].

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 [9,10].

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.

Transition metal bound organic compounds are structurally 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. 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 [11, 12, 13].

The coordination chemistry of amide ligands is an important part of a number of chemical problems. The review of Sigel and Martin clearly shows that, research interest is centered on the structure and stability of metal ion complexes of amide, oligopeptides and related ligands. Of special interest are the deprotonation process and the species thereby formed. The amide group offers two potential binding atoms, the oxygen and nitrogen, for complexation of metal ions. A number of complexes have been reported with amide group ligands, which exhibit diverse coordinating behavior with different metal ions [14].

Furthermore, development in the field of bioinorganic chemistry has also led to an increased interest in complexes of N, O-donor ligands since it has been recognized that many of these complexes may serve as models for biologically important species having N and O as bonding sites [15].

A literature survey reveals that the synthesis and characterization of metal complexes with N-(2-hydroxyphenyl)-2-[(2-aminophenylamino)] acetamide and its derivatives have not been reported. This report presents the synthesis and structural studies of a new polydentate ligand and its Ni (II) and Zn (II) complexes.

1.1. Chemistry of o-Aminophenol

2-Aminophenol is an organic compound with the formula C_6H_4 (OH) NH_2. Along with its isomer 4-aminophenol, it is an amphoteric molecule and a reducing agent. It is a useful reagent for the synthesis of dyes and heterocyclic compounds.

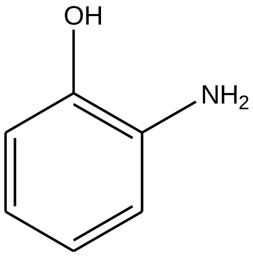


Figure 1: Structure of ortho-aminophenol

Table 1: Properties of 2-Aminophenol

Molecular Formula	C_6H_7NO
Molar Mass	109.13 g/mol
Appearance	White orthorhombic pyramidal needles
Density	1.328 g/cm³
Melting point	174 °C
Solubility in water	slightly soluble in cold water, soluble in hot water

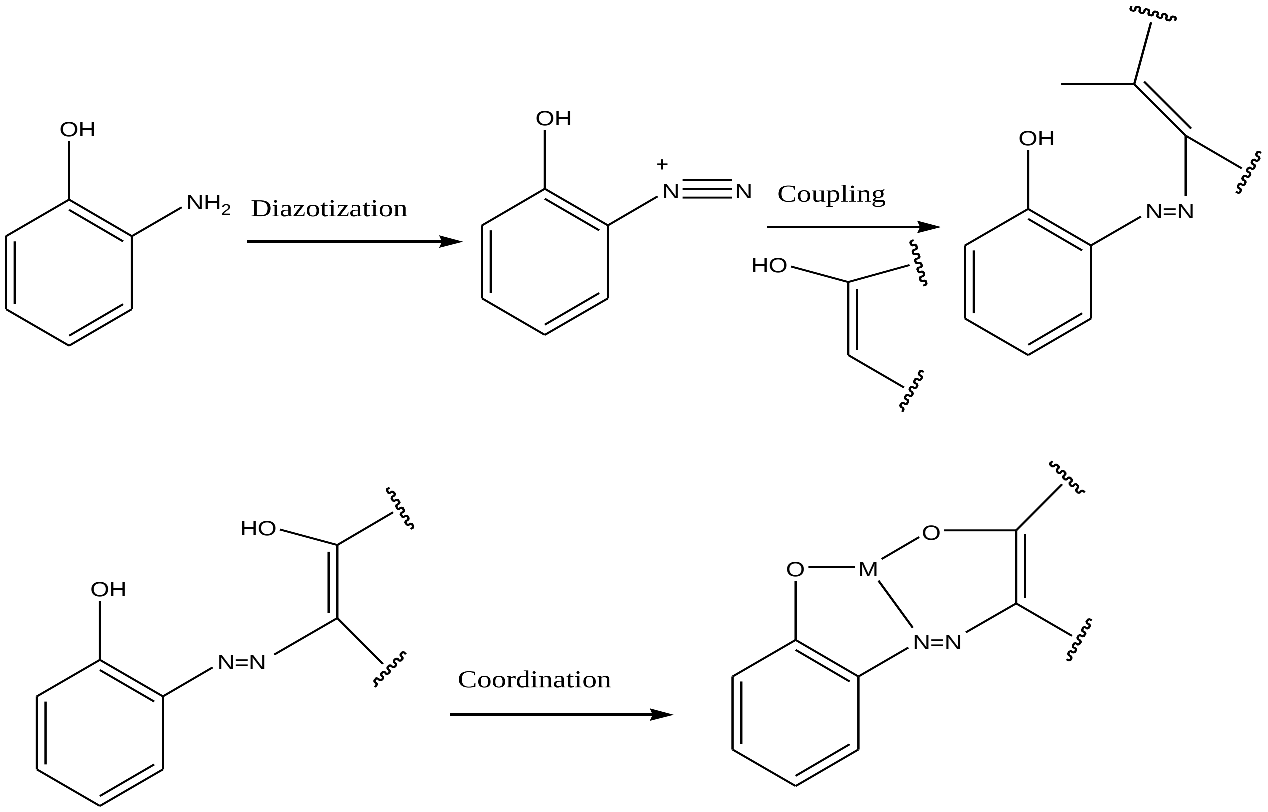
1.1.1. Synthesis and structure

2-Aminophenol (and its isomer, 4-aminophenol) is industrially synthesized by reducing the corresponding nitrophenol by hydrogen in the presence of various catalysts. The nitrophenols can also be reduced with iron.

The compound exhibits intra- and intermolecular hydrogen bond involving the neighbouring amine and hydroxyl groups. As a result, 2-aminophenol has a rather high melting point compared to other compounds with a similar molecular mass such as methylphenol.

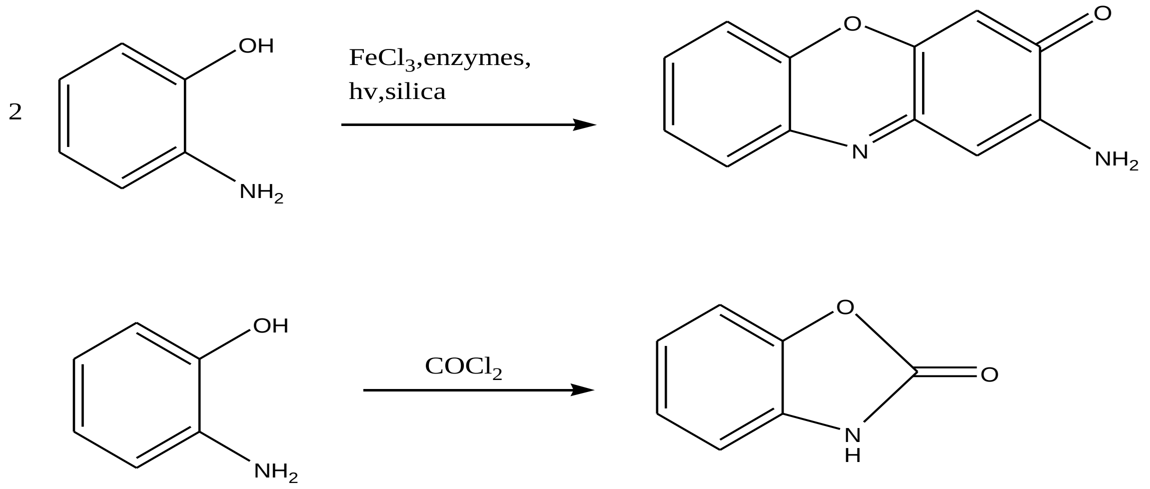
1.1.2. Applications

2-Aminophenol has a variety of uses. As a reducing agent, it is marketed under the names of Atomal and Ortol to develop black-and-white photographs. 2-Aminophenol is an intermediate in the synthesis of dyes. It is particularly useful in yielding metal-complex dyes when diazotized and coupled to a phenol, naphthol, or other aromatic or resonant dye species. Metal complex dyes using copper or chromium are commonly used for producing dull colors. Tridentate ligand dyes are useful because they are more stable than their bi- or mono-dentate counterparts.



Scheme 1: Formation of metal complex dyes

Due to the adjacency of the amino and hydroxyl groups, 2-aminophenol readily forms heterocycles. These heterocycles, such as benzoxazoles, can be biologically active and useful in the pharmaceutical industry [16].



Scheme 2: Formation of heterocycles

1.2. The chemistry of chloroacetyl chloride

Chloroacetyl chloride is a chlorinated acyl chloride. It is a bifunctional compound, making it a useful building block chemical.

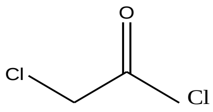


Figure 2: Structure of chloroacetylchloride

Table 2: Properties of Chloroacetyl chloride

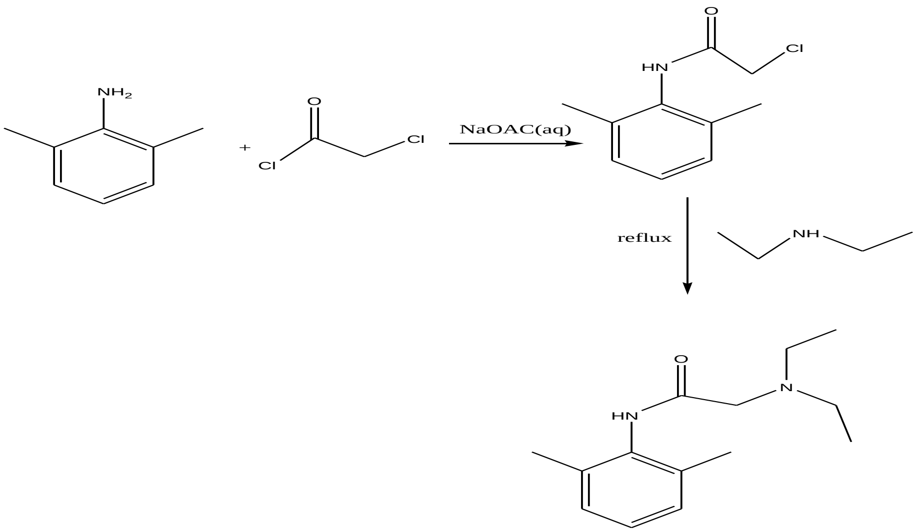
Molecular formula	$C_2H_2Cl_2O$
Molar mass	112.94 g mol^{-1}
Appearance	Colorless liquid
Density	1.42 g/Ml
Melting point	−22 °C (−8 °F; 251 K)
Boiling point	106 °C (223 °F; 379 K)
Solubility	Water: insoluble

1.2.1. Production

Industrially, it is produced by the carbonylation of methylene chloride, oxidation of vinylidene chloride, or the addition of chlorine to ketene. It may be prepared from chloroacetic acid and thionyl chloride, phosphorus pentachloride, or phosgene.

1.2.2. Reactions

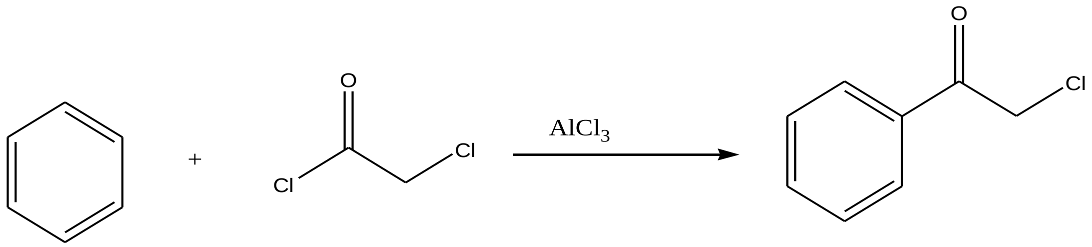
Chloroacetyl chloride is a bifunctional the acyl chloride easily forms esters and amides, while the other end of the molecule is able to form other linkages, e.g. with amines. The use of chloroacetyl chloride in the synthesis of lidocaine is illustrative.



Scheme 3: Bifunctional properties of chloroacetylchloride

1.2.3. Applications

The major use of chloroacetyl chloride is as an intermediate in the production of alachlor and butachlor (herbicides); an estimated 100 million pounds are used annually. Some chloroacetyl chloride is also used to produce phenacyl chloride, another chemical intermediate, also used as a tear gas. Phenacyl chloride is synthesized in a Friedel-Crafts acylation of benzene, with an aluminium chloride catalyst [17].



Scheme 4: Friedel-Crafts acylation of benzene

1.3. The chemistry of o-phenylenediamine

O-phenylenediamine (1,2-diaminobenzene) is a compound with the formula $C_6H_4(NH_2)_2$.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 covalent bond with proton. In addition it is a binucleophile molecule that forms a variety of compounds [18].

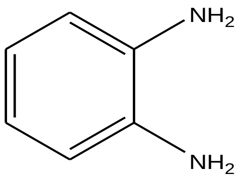


Figure 3: Structure of o-phenyldiamine

O-Phenylenediamine, can act as sigma donor and π-acceptor in a complex, which predominantly form covalent bond. The balance of donor and acceptor interaction and the effective negative charge on these ligands to a high degree depends on the overall 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**.**

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 [19].

In coordination chemistry o- phenylenediamine is an important ligand precursor. Schiff bases derived from salicylaldehyde, are excellent chelating ligands. O-phenylenediamine condenses with ketones and aldehyde 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 macro cyclic compounds and fused ring compounds. 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 drops dramatically [20, 21, 22].

1.4. Concept of tautomerization

Tautomers are interconvertible structural isomers. This reaction commonly results in the formal migration of a hydrogen atom or proton, accompanied by a switch of a single bond and adjacent double bond. Because of the rapid interconversion, tautomers are generally considered to be the same chemical compound.

In solutions in which tautomerization is possible, a chemical equilibrium of the tautomers will be reached. The exact ratio of the tautomers depends on several factors, including temperature, solvent, and pH [23].

The defference between resonance and tautomerism are; resonance is structures differ in the positions of electrons, where as tautomerism involves the movement of H or another atom and may result in changes in molecular geometry. Tautomerism can affect chemical reactions; as an example, the oxidation of a ketone by a strong oxidizing agent can proceed via tautomerization to the enol. In solution, enolization is enhanced by acid or base catalysis. Tautomeric equilibria can be shifted to favor one of the tautomers through the use of different substituents with electron-donating or electron-accepting properties. Tautomerism can be important in biochemical reactions, even though the relative amount of the reactive tautomer may be small, an example being the base pairing in deoxyribonucleic acid (DNA) or ribonucleic acid (RNA). Different tautomers may also have different pharmaceutical effects.

Prototropy is the most common form of tautomerism which involves the relocation of an H atom and a double bond. One example of prototropic tautomerism is that between keto and enol forms (Fig. 4). The keto tautomer possesses a CO group, while the enol form has a vinylic alcohol structure. Increasing acidity of the ά-H affects this tautomerism, favoring-the enol form. Conjugated double bonds and intermolecular H-bonds can also stabilize the enol form [24].

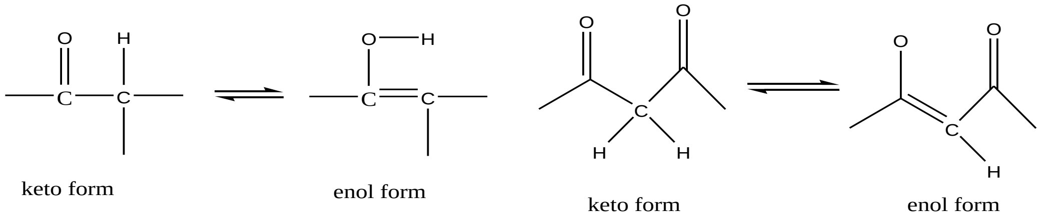


Figure 4: Keto-enol tautomerism and stabilization of the enol form through the intramolecular H-bonding.

Other types of prototropic tautomerism are amine-imine tautomerism (e.g. in adenines, amide-imidic acid tautomerism (related to asparagine-linked glycosylation) and, as a special case, lactam-lactim tautomerism (present in uracil and thymine) (Fig. 5).

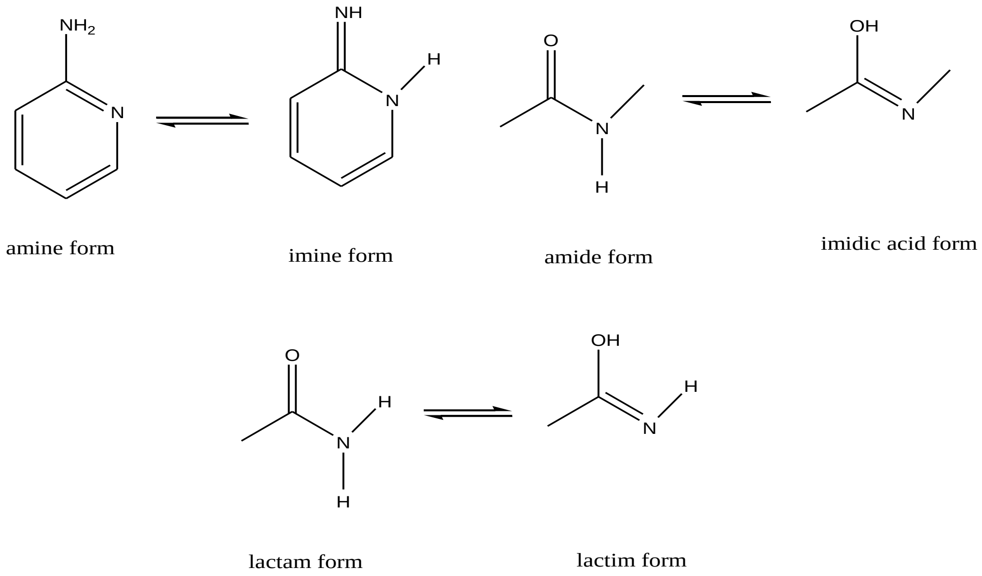


Figure 5: Other types of prototropic tautomerism

1.5. The chemistry of metal complexes

The coordination chemistry of transition metal ions is considered in this work: Ni (II) and Zn (II) will be presented in terms of their d^n configuration [25].

1.5.1. Nickel (II) complexes

The electronic configuration of the Ni (II) is d^8. Octahedral Ni (II) complexes having $^3A_{2g}$ ground state are expected to have three spin allowed transitions $^3A_{2g}\rightarrow{}^3T_{2g}$, $^3A_{2g}\rightarrow{}^3T_{1g}(P)$ and $^3A_{2g}\rightarrow{}^3T_{1g}(F)$ in the range of 7000-13000, 11000-20000 and 19000-27000 cm^{-1}, respectively. In addition to these three transitions, two spin-forbidden transitions $^3A_{2g}\rightarrow{}^1E_g$ and $^3A_{2g}\rightarrow{}^1T_{2g}$ are also observed one at near the second spin-allowed transition and another band between second and third spin-allowed transitions. Five coordinate Ni (II) complexes have structures, which are generally near to one of the two limiting geometries, namely the square pyramid and the trigonal bipyramid. The electronic ground state of Ni (II) in the five coordinate complexes can be either a spin singlet (low-spin) or a spin triplet (high-spin). Low–spin trigonal bipyramidal Ni (II) species, which exhibit three transitions, namely ${}^1A_1 \rightarrow {}^1B_1$, ${}^1A_1 \rightarrow {}^1E$ and ${}^1A_1 \rightarrow A_2$ lie in the region 15000-18000, 21000-24000 and 27000-29000 cm^{-1}, respectively.

The majority of four coordinate Ni (II) complexes are square-planar and diamagnetic, while other are pseudo tetrahedral Ni (II) complexes have spectral transitions in the visible region with a much greater intensity than the octahedral ones. Tetrahedral Ni (II) complexes with ${}^3T_1$ ground state generally exhibit four transitions. They are ${}^3T_1 \rightarrow {}^3A_2$, ${}^3T_1 \rightarrow {}^1E$, ${}^3T_1 \rightarrow {}^3T_1$ (P) and ${}^3T_2 \rightarrow {}^1T_1$. The band ${}^3T_1 \rightarrow {}^3T_1$ (P) is a strong band of high intensity when compared with others. In square planar Ni (II) complexes, three spin allowed d-d bands corresponding to ${}^1A_{1g} \rightarrow {}^1A_{2g}$, ${}^1A_{1g} \rightarrow {}^1B_{1g}$ and ${}^1A_{1g} \rightarrow {}^1Eg$ transitions are expected. Majority of the square planar Ni (II) complexes exhibit strong absorptions in 15000-25000 and 23000-30000 cm^{-1} region. The square planar Ni (II) complexes don't have any absorption band below 10000 cm^{-1}, due to large crystal field splitting. Hence they can be clearly distinguished from octahedral and tetrahedral complexes [2].

1.5.2. Zinc (II) complexes

The Zn^{2+} ion has a filled d^{10} shell and is very similar to Mg^{2+} ion in many respects. However, in addition to the regular octahedral coordination, Zn^{2+} ion has a strong tendency to adopt regular tetrahedral coordination. Zinc in mixed coordination is found in a number of zinc minerals. Zinc sometimes also adopts the trigonal bipyramidal or square pyramidal coordination. As a result, the structural chemistry of zinc minerals is also rather complex [26].

The divalent zinc ion is exceptionally stable with respect to oxidation and reduction and so it does not participate in redox reactions, in contrast to Mn, Fe, and Cu. The d^{10} configuration of Zn^{2+} indicates that zinc complexes are not subject to ligand field stabilization effects and so coordination number and geometry is only dictated by ligand size and charge. In enzymes, zinc shows a strong preference for tetrahedral coordination, which enhances both the Lewis acidity of a zinc center and the Brønsted acidity of a coordinated water molecule. Zinc is an element of borderline hardness, so that nitrogen, oxygen and sulfur ligands can all be accommodated, in contrast to magnesium and calcium, which favor binding to oxygen. Therefore, zinc binds strongly to many proteins [27].

1.6. Stability of complexes

The formation of a metal complex is dictated by its stability. The stability of the metal complex depends both on the metal ion and the ligand. In general, stability of the complex increases with decreasing size and increasing electron affinity of the central metal. Thus highly polarizing transition metal ions have greater tendency to form complex, regardless of the nature of the ligand, the stability of the bivalent transition metal complexes increase in the 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.

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 π-back donation from the filled metal orbital to the vacant π^* orbitals of the ligand. Therefore, ligands with weak sigma donor/strong π 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 [1].

1.7. Aim of the present investigation

Metal complexes of multidentate ligands with amide functionality have a wide range of analytical and catalytic applications in the areas of agriculture, pharmacy and polymers. In view of this, the present investigation is aimed at the synthesis and structural studies of a new polydentate ligand containing an amide function and its Ni (II) and Zn (II) complexes.

Literature survey shows, no work has been reported so far about the synthesis and characterization of N-(2-hydroxyphenyl)-2-[(2-aminophenylamino)] acetamide and its Ni (II) and Zn (II) complexes. Thus, the objectives of this study are:

- To synthesize the precursor (HPCA), the ligand (HPAPAA) and its metal complexes.
- To study HPCA, HPAPAA and the metal complexes by using various physical, chemical and instrumental techniques.
- Interpretation of physical and spectroscopic data.
- Structural elucidation of the ligand and the metal complexes.
- Proposing the geometries of the complexes.

2. Materials and Methods

2.1. Chemicals

All the chemicals used in the investigation were of AnalaR grade. These include orthoaminophenol, chloroacetylchloride and 1, 2-phenylenediamine. The metal salts used to synthesize the complexes are : $NiCl_2 \cdot 6H_2O$ and $ZnCl_2$. Solvents used during the investigation include; MeOH, EtOH, C_6H_6, THF, DMSO, DMF, $CHCl_3$, H_2O, CH_3CN, petroleum ether, diethyl ether, ethylacetate, dimethylglyoxime and 1,4-dioxane.Other chemicals used also include: HCl, HNO_3, $AgNO_3$, NaOH and NH_4OH.

2.2. Instrumentation

UV-Vis spectrophotometric measurements were made in the range 200-750 nm using Spectronic Genesys 2PC spectrophotometer. Determinations of melting points or decomposition temperatures 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 Spectrum 65 spectrophotometer in the range 4000-400 $cm^{-1}$with samples prepared using KBr pellets. Magnetic susceptibility measurements were performed using MSB Auto, Sherwood. The molar conductivity measurements were carried out using EC 214 Bench type conductivity meter (Hanna Instrument). The metal complexes were analyzed for their metal contents using Analytik Jena Model Zeenit 700P atomic absorption spectrometer. The purity of the complex was checked by thin layer chromatography (TLC). Elemental analyses of the complexes were carried out on Elemental analyzer EA 1112 (CE instruments).

2.3. Methods

2.3.1. Qualitative Tests

2.3.1.1. Thin Layer Chromatography (TLC)

TLC was used exhaustively to check the purity of the compounds and to control the progress of the reaction. For this purpose 2x4 cm silica coated aluminum plates were used and a suitable solvent or mixtures of solvents such as CH_3CN/ MeOH (1:1) for the precursor and ethyl acetate/MeOH (1:1) for both the ligand and its metal complexes were used as mobile phase. Observation of a single spot indicated the purity of the compound.

2.3.1.2. Chloride Test

Compounds (samples) decomposed/ 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 0.1 M $AgNO_3$. Absence of white precipitate formation after addition of $AgNO_3$ (0.1 M) solution indicated the absence of chloride in the sample.

2.3.1.3. Test for Nickel

20 mg of nickel complex was digested in nitric acid, and then a few ml.of an alcoholic solution of dimethylglyoxime was added, followed by neutralization with aqueous ammonia. A typical pink-red precipitate showed the presence of nickel.

2.3.1.4. Test for Zinc

20 mg of the zinc complex was digested in nitric acid. Then a few drops of deionized water solution of K_4 [Fe $(CN)_6$] was added. The formation of a light green precipitate confirmed the presence of zinc in the sample.

2.3.2. Quantitative Determinations

2.3.2. 1. Chloride ion estimation

20 mg of the sample was weighed and placed in an Erlenmeyer flask. Nitric acid (10 ml) was added to it. A magnetic stirrer was introduced and the contents were heated on hot plate while stirring until a few drops of the solution remained in the flask. Another 10 ml portion of Nitric acid was added to it and heated to almost dryness. The solution was then cooled to room temperature by adding 3 ml of 0.2 M HNO_3 followed by 2 ml of distilled water. $AgNO_3$ (0.5 M) was added to the solution and kept overnight at room temperature. White precipitate of AgCl was formed and the presence of chloride ion was confirmed. The precipitate was filtered through a previously dried and weighed sintered crucible, dried in a desiccator and weighed. The mass of the precipitate and the amount of chloride in the sample was obtained from the stoichiometric calculations.

2.3.2. 2. Determination of metal in the complex

Atomic absorption spectrometry (AAS) is an analytical technique that measures the concentrations of elements. It is commonly used for determining the concentration of a particular metal element within a sample. A number of reference standard solutions of each metal were prepared in various concentration ranges. Absorbances of these solutions were measured at the specific wavelength of each metal using background correction technique. Calibration graphs were plotted for metals solutions. The concentrations of unknown solutions were calculated from their respective absorbances by using the standard values.

The metal percentage was estimated by decomposing 20 mg of the metal complex through digestion in 10 ml conc. HNO_3 until a clear solution was obtained. The solution was diluted to 50 ml in a volumetric flask, to separately prepare solutions of known concentration. The metal content was recorded using Analytik Jena Model Zeenit 700P Atomic Absorption Spectrometer. The experimental percentage of metal in the complex was calculated as:

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

2.3.2.3. Molar conductance measurement

The molar conductance was determined from conductivity measurements of one milli molar solution of the complex in MeOH/ DMF and the determination of cell constant using the following relation:

$$\Lambda_M = \frac{\mathbf{1000K}}{\mathbf{C}}$$

Where Λ_M = Molar conductance

C= concentration of the sample (10^{-3})

κ= specific conductivity of the complex

2.3.2.4. Magnetic moment measurement

MSB Auto, (Sherwood Scientific) 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.

$$\text{Molar magnetic susceptibility } (\chi_M) = \chi_g \text{ . Molecular wt. of the compound}$$

$$\text{Magnetic moment } (\mu_{eff}) = 2.84\, (\chi_M^{corr} . \text{T})^{½}$$

From the effective magnetic moment value obtained, the number of unpaired electron was calculated by using the relation

$$\mu_{eff} = [n(n+2)]^{1/2}$$

Where n is number of unpaired electron.

2.4. Synthesis of the precursor, ligand and metal complexes

2.4.1. Synthesis of the precursor

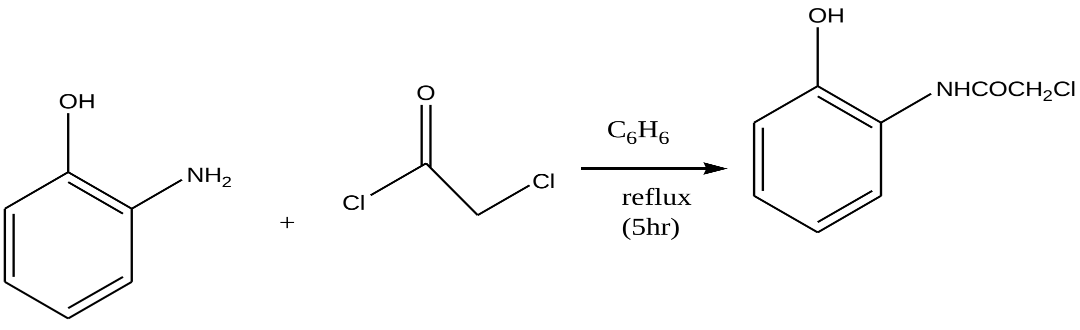
To 5.5 g (0.05mol) of o-aminophenol in benzene, 4.5 ml of chloroacetylchloride was slowly added drop wise with continuous stirring. It was then refluxed for about 5 hours with stirring on water bath. The precipitate of the product was filtered, washed with benzene and diethyl ether and then dried in air.

Yield: 7.95 g (85%),

Color: bright white

Appearance: crystalline product,

Melting point: 141-142 ^{0}C.



o-aminophenol **chloroacetylchloride** **HPCA**

Scheme 5: Synthesis of HPCA

2.4.2. Synthesis of the ligand

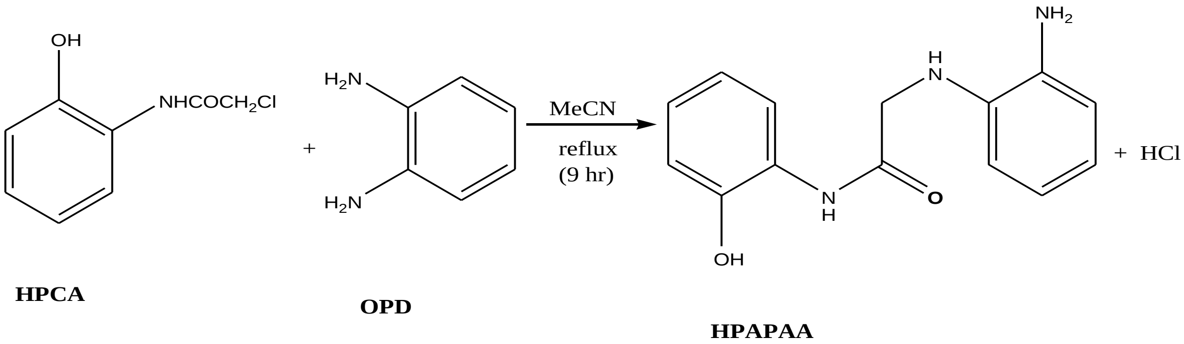
N-(2-hydroxyphenyl)-2-chloroacetamide (0.004 mol, 0.7 g) in 20 ml MeCN was mixed with o-phenylenediamine (0.004 mol, 0.42 g) in 20 ml MeCN. The solution was refluxed for about 9 hours with stirring on water bath and then concentrated. The resulting deep red product was filtered and repeatedly washed with MeCN and ether. The product was then dried in open air and stored in a desiccator.

Yield: 62 %

Color: deep red

Appearance: solid product,

Decomposes partially: 194-195 ^{o}C.



Scheme 6: Synthesis of HPAPAA

2.4.3. Synthesis of Ni (II), and Zn (II) complexes

A solution of metal chloride $NiCl_2{\cdot}6H_2O$ (0.238 g, 0.001mol) and anhydrous $ZnCl_2$ (0.137 g, 0.001 mol) was prepared in MeOH (20mL) in a round bottom flask. To this, a solution of ligand (0.257 g, 0.001 mol) in 20 mL of MeOH was added. The pH of the resultant solution was 3. As a result, the following color changes were observed: (dark greenish for Ni (II) and off white for Zn (II)).The pH of the mixture was raised to 5 by drop-wise addition of 1% NH_4OH solution in methanol. The mixture was stirred while heating on hot water bath for 7hours at 55-60 ^{0}C. The metal complexes thus synthesized were concentrated. Then they were washed with methanol and diethyl ether and dried. Yield: Ni (II) complex, 0.33 g (85.5 %) and Zn (II) complex, 0.2 g (59 %).

3. Results and Discussion

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

3.1. Characterization of N-(2-hydroxyphenyl)-2-chloroacetamide

3.1.1. General Properties of HPCA

O-hydroxyphenyl chloroacetanilide (HPCA, $C_8H_8NO_2Cl$, molar mass 185.7 g/mol) is a bright white crystalline powder. It does melt at 141-142 ^{0}C. It is soluble in solvents, such as DMSO and CH_3CN and also sparingly soluble in H_2O, MeOH, EtOH and $CHCl_3$.

3.1.2. Elemental Analysis

The experimentally obtained C, H and N percent elemental analysis shows a good agreement with the theoretically calculated value. Accordingly the structure of the precursor can be presented as in figure below.

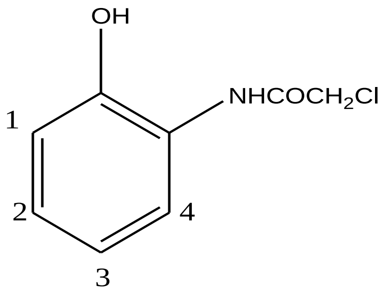


Figure 6: Structure of HPCA

Table 3: Elemental analysis results of the precursor (HPCA)

Precursor	calculated (found) %		
$C_8H_8NO_2Cl$	C	H	N
	51.4 (51.5)	4.4 (4.3)	7.5 (7.5)

3.1.3. IR Spectrum of HPCA

The IR spectrum (appendix 2) of the precursor HPCA shows a sharp band at 3368 cm^{-1} due to υ-NH stretching. The broad band at 3180 shows the presence of hydrogen bonded OH (phenolic OH) in the compound. The bands at 1657, 1551, 1442, 1270 and 752 cm^{-1} are because of C=O (amide), C =C, CH_2 (bending), C-OH (phenolic group) and C-Cl (halide group) or 1, 2 disubstituted (-Ar) respectively. Structural differences between orthoaminophenol and HPCA are listed out in table 4.

Table 4: Comparison of AP and HPCA IR absorption frequencies (in cm^{-1})

Compounds	$\nu_{NH,NH2}$	ν_{OH}	$\nu_{C=O}$	$\nu_{C=C}$	ν_{CH2}	ν_{C-OH}	$\nu_{C-Cl/-Ar}$
AP	3376,3269	3053	__	1513	__	1268	742
HPCA	3368(m,s)	3180(b)	1657(s,s)	1551(s)	1442	1270	750

3.1.4. NMR Spectra

The NMR data were obtained in CD_3CN solution for HPCA. The chemical shifts, integral values, and DEPT patterns of HPCA confirm the expected structures shown in figure 6.

3.1.4.1 .^{1}H NMR Spectrum of HPCA

The ^{1}H NMR spectrum (appendix 6) of the precursor HPCA was measured in CD_3CN. The spectrum could be resolved in to seven different region of proton broad singlet at δ 4.3 (S,2H,CH_2), at δ 4.85 (S,1H,OH), at δ 8.3 (S,1H,NH) , δ 6.90 (D,1H,CH),at δ 7.84 (D,1H,CH) , at δ 6.95 (t,1H,CH) and at δ 7.1 (t,1H,CH) which is in agreement with the proposed structure

Table 5: ^{1}H NMR spectrum of HPCA

	Types of proton (s)	Number of Proton(s)	δ in ppm (appearance)	Solvent
HPCA	CH_2	2(s)	4.3	CD_3CN
	OH	1(s)	4.85	
	NH	1(s)	8.3	
	CH^1	1(d)	6.9	
	CH^2	1(t)	7.1	
	CH^3	1(t)	6.95	
	CH^4	1(d)	7.84	

where s=singlet,d=doublet,t=triplet

3.1.4.2 .^{13}C NMR Spectrum of HPCA

The ^{13}C NMR spectrum (appendix 7) of the precursor HPCA was also recorded in CD_3CN.At δ 44.12 (CH_2), at δ 117.02-126.63 (arom. C), at δ 126.54 (C-NH), at δ 148.21 (C-OH) and at δ 166.13(C=O, amide).

3.1.4.3. The DEPT spectrum

The DEPT spectrum (appendix 8) show that there are 1CH_2 group downfield at (44.07), 4 CH group up field between (116.97-126.58).

Table 6: ^{13}C NMR and DEPT spectrum of HPCA

	Types of carbon(s)	δ in ppm (appearance)	DEPT Data (δ in ppm)	Remarks	Solvent
HPCA	CH_2	44.12	44.07	$C-H_2$	CD_3CN
	C-NH	126.54	_______	Quaternary	
	C-OH	148.21	_______	Quaternary	
	C=O(amide)	166.13	_______	Quaternary	
	^1CH	117.02	116.97	C-H	
	^2CH	122.35	126.58	C-H	
	^3CH	118.36	121.00	C-H	
	^4CH	121.05	122.30	C-H	

3.2. Characterization of the ligand

3.2.1 .General Properties of HPAPAA

N-(2-hydroxyphenyl)-2-[(2-aminophenylamino)]acetamide (HPAPAA,$C_{14}H_{15}N_3O_2{\cdot}HCl$, molar mass 293.5 g/mol) is a deep red solid. It is soluble in solvent such as MeOH, EtOH, CD_3CN and DMSO. It is insoluble in diethylether, C_6H_6 and $CHCl_3$.

3.2.2. Chloride Test

HPAPAA decomposed/dissolved in nitric acid were subjected to chloride identification. Presence of white precipitate formation after addition of 0.1 M $AgNO_3$ solution indicated the presence of chloride in the sample. This might be because of presence of HCl along with the expected product. It may be recalled that HPAPAA is formed by the reaction between HPCA and OPD, in which HCl is also a product.

3.2.3. Elemental Analysis

The experimental and calculated values of the elemental composition of H and N analysis data are in good match with the molecular formula of HPAPAA $C_{14}H_{15}O_2N_3{\cdot}HCl$. Elemental analysis results of the ligand are presented in table 7.

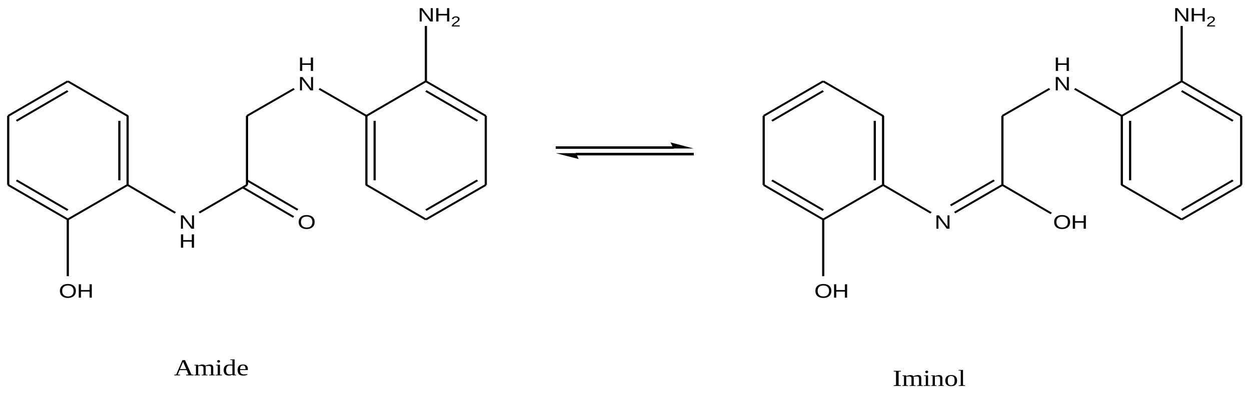
Table 7: Elemental analysis results of the ligand (HPAPAA)

Ligand	calculated (found) %		
$C_{14}H_{15}O_2N_3 \cdot HCl$.	C	H	N
	—	5.45 (5.45)	14.28 (14.3)

From the above table, the experimentally obtained H and N percentages are in good agreement with the theoretically calculated value. However, inconsistent deviations were observed between the theoretical and experimental values of carbon. This might be because of incomplete decomposition of the ligand with respect to its carbon content during the estimation. However in view of satisfactory IR, ^{1}H NMR and ^{13}C NMR results, the formation of HPAPAA as HCl adduct was concluded.

3.2.4. IR Spectrum of the ligand

The IR spectrum (appendix 3) of the ligand HPAPAA shows broad band at 3401cm^{-1} indicating the presence of OH group while at 3200 -3000 cm^{-1} confirm the presence of secondary amine. The presence of OH band is indicative of the possible tautomerization (Scheme 8) in the ligand. Strong band at 1661 cm^{-1} indicated the presence of amide moiety also and thus further supports the existence of the two possible tautomers (either keto-enol or amide-iminol) with the amide tautomer as the dominant one. A weak band at 2925 cm^{-1}, which is due to $\upsilon_{\text{C-H}}$ aromatic. The bands at 1401 and 1305 cm^{-1} are due to CH_2 (bending) and (C-OH) respectively. The medium sharp band at 1506 cm^{-1} indicated the presence of conjugated (C=C) as a characteristic band of aromatic system, while a strong absorption peak at 750 cm^{-1} was assigned to 1,2 disubstituted (C-Ar) bond absorption frequency. The IR data of the spectra of the ligand is presented in table 8.



Scheme 7: Amide-iminol tautomerism in the ligand.

Table 8: Important IR absorption frequencies (in cm^{-1}) of the ligand

Ligand	ν_{OH}	$\nu_{NH,NH2}$	$\nu_{C=O}$	$\nu_{C=C}$	ν_{CH2}	ν_{C-OH}	ν_{C-Ar}	ν_{C-N}
HPAPAA	3401 (b)	3200-3000	1661 (s)	1506 (m)	1401	1305	750 (s)	1121

3.2.5. NMR Spectra

The NMR data were obtained in CD_3CN solution for HPAPAA. The chemical shifts, integral values, and DEPT patterns of HPAPAA confirm the expected structures shown in scheme 7

3.2.5.1. ^{1}H NMR Spectrum of HPAPAA

In the ^{1}H-NMR spectrum (appendix 9), the signals between 7.9 and 6.6 ppm with their characteristic proton couplings indicate the presence of aromatic protons. The singlet at 8.9 ppm indicates the presence of an amide-iminol tautomerism in the target molecule, while a singlet at 3.9 ppm represented the presence of CH_2. The broad singlet (2H) at 4.3 ppm is assigned to NH_2 protons. From the spectral data, it is concluded that the ligand involves tautomerism in solution phase (in CD_3CN) with the amide form being a dominant tautomer.

Table 9: ^{1}H NMR spectrum of HPAPAA

	Types of proton(s)	Number of Proton(s)	δ in ppm (appearance)	Solvent
HPAPAA	CH_2	2(s)	3.9	CD_3CN
	NH_2	1(s)	4.3	
	OH/NH	1(s)	8.9	
	CH^1	1(d)	6.6	
	CH^2	1(t)	6.65	
	CH^3	1(t)	6.75	
	CH^4	1(d)	6.7	
	CH^5	1(d)	7.9	
	CH^6	1(t)	6.95	
	CH^7	1(t)	7.1	
	CH^8	1(d)	6.9	

3.2.5.2. ^{13}C NMR Spectrum of HPAPAA

The ^{13}C NMR spectrum (appendix 10) of the ligand HPAPAA was also measured in CD_3CN. At δ 43.12 (CH_2), atδ 120.02-125.63 (arom.C), at δ 126.54 (C-NH), at δ 134.0 may be (C=N, tautomeric), at δ 147.21 (C-OH), and at δ 165.2 (C=O, amide).

3.2.5.3. The DEPT spectrum

The DEPT spectrum (appendix 11) of the ligand HPAPAA was measured in the same solvent from the above The DEPT spectra show that there are 1CH_2 group downfield at (43.20), 8CH group up field between (116.75-126.68).

Table 10: ^{13}C NMR and DEPT spectrum of HPAPAA

	Types of carbon(s)	δ in ppm (appearance)	DEPT Data (δ in ppm)	Remarks	Solvent
HPAPAA	CH_2	43.12	43.20	$C\text{-}H_2$	CD_3CN
	C-NH	126.54	______	Quaternary	
	C=N	134.0	______	Quaternary	
	C-OH	147.21	______	Quaternary	
	C=O(amide)	165.23	______	Quaternary	
	^{1}CH	119.02	116.97	C-H	
	^{2}CH	120.08	126.58	C-H	
	^{3}CH	121.44	121.00	C-H	
	^{4}CH	117.02	116.71	C-H	
	^{5}CH	125.68	124.28	C-H	
	^{6}CH	121.02	121.00	C-H	
	^{7}CH	124.54	125	C-H	
	^{8}CH	119.05	122.30	C-H	

3.3 Characterization of Ni (II) and Zn (II) complexes

3.3.1. General Properties of the metal complex

The metal complexes form colored compounds. They are soluble in hot (MeOH, EtOH, CD_3CN) and DMSO. It is insoluble in diethyl ether, C_6H_6 and $CHCl_3$. Some of the important physical properties of the metal complexes are summarized in the following table 11.

Table 11: Some physical characteristics of the metal complexes

Complexes	$NiL\cdot 4H_2O$	$ZnL\cdot H_2O$
Mol. Formula	$NiC_{14}H_{15}O_2N_3\cdot 4H_2O$	$ZnC_{14}H_{15}O_2N_3\cdot H_2O$
Mol Weight (g/mol)	385.69	338.38
Color	Dark greenish	Off white
Appearance	Solid	Solid
Yield (%)	85.5	59
M.P/Decom.temp (^oC)	101-102 (melt)	262 (Decomposed)

3.3.2. Elemental Analysis of the metal complex

The experimental and the calculated values of the elemental composition of C, H, and N of the metal complexes are presented in table 12.

Table 12: Elemental analysis results of Ni (II) and Zn (II) complexes

Metal Complexes	calculated (found) %		
	C	H	N
$NiC_{14}H_{15}O_2N_3\cdot 4H_2O$	—	5.4 (5.4)	10.48 (10.89)
$ZnC_{14}H_{15}O_2N_3\cdot H_2O$	—	4.0 (4.4)	12.0 (12.4)

Results obtained from the elemental analyses of Ni (II) and Zn (II) complexes, respectively, given as experimental (calculated) were % H 5.4 (5.4) and % H 4.0 (4.4) N

10.48 (10.89) and % N 12.0 (12.4). However, deviations were observed between the theoretical and experimental values of carbon. This may be due to incomplete decomposition of the complex during the analysis. As such, the formulae were matched with N, H and metal percentages.

3.3.3. Quantitative Determinations of the metal complexes

3.3.3. 1. Chloride ion estimation

Samples of the complexes were well digested in concentrated nitric acid. When 0.1M solution of silver nitrate was added to the cooled acid solutions and left overnight, there was no formation of any precipitate. This observation leads to the conclusion that the complexes do not contain any chloride ion in their structures.

3.3.3.2. Metal Estimation using AAS

The molar ratios of the metal to ligand of both the complexes were obtained from absorbance measurements using atomic absorption spectroscopy. The results obtained are tabulated as follows.

Table 13: Estimation of metals in HPAPAA-metal complexes by AAS

Element	$\lambda_{\text{absorbance}}$ (nm)	(%) of Metal cal (exp)	Metal to ligand ratio
Nickel	232	15.69 (15.21)	1:1
Zinc	213	19.32 (19.59)	1:1

The results show that, theoretical and experimental (AAS) values are in good agreement, suggesting a metal to ligand ratio of 1:1 in both complexes according to the proposed structures.

3.3.3.3. Molar Conductance Measurement of the metal Complexes

The molar conductance (Λ_m) values were calculated from conductivity measurements in MeOH and DMF. Specific conductance (Sc) is a measure of how well solution conducts electricity. Conductibility increases with increasing concentration and mobility of ions. These ions come from the breakdown of a compound and conduct electric current because they are positively and negatively charged when dissolved in the solvent. The specific conductance of 0.001M solution of Ni (II) and Zn (II) complexes were measured in MeOH and DMF at 21^0C and found to be 25.49μScm^{-1} and 60.3μScm^{-1} respectively. The molar conductance of each complex was calculated from the following equation.

$$\boldsymbol{\Lambda_M = \frac{1000K}{C}}$$

Where Λ_M = Molar conductance

C= concentration of the sample (10^{-3})

κ= specific conductivity of the complex

The molar conductance values which summarized in table-14 indicate that both Ni (II) Zn (II) complexes are non-electrolytes. In view of the non-electrolytic nature, absence of chloride in both the complexes, it is concluded that the ligand undergoes enolization and subsequent deprotanation of enolic and phenolic hydrogens to form a dinegative anion $(ONO)^{2-}$ during complexation. As such the enol form of the ligand is proposed for chelation. This derives further support from spectral and magnetic data.

Table 14: Conductivity data for the metal complexes

Complexes	Solvent	Molar conductance, Scm^2mol^{-1}	Ions ratio	Type
$NiL\cdot4H_2O$	DMF	25.49	___	Non-electrolyte
$ZnL\cdot H_2O$	MeOH	49.18	___	Non-electrolyte

3.3.3.4. Magnetic susceptibility of the metal Complexes

Magnetic susceptibility measurements were recorded at room temperature (23 ^{0}C). The gram magnetic susceptibility measurements for Ni (II) complex is 4.416 x 10^{-6}. The result indicates Ni (II) complex is paramagnetic with magnetic moment values 2.0 (BM).This value is significantly sub-normal and can be explained on the basis of substantial anti-ferromagnetic interaction at room temperature [28, 29]. Zn (II) (d^{10}) complex is diamagnetic. Octahedral geometry for the Ni (II) complex and square planar geometry for the Zn (II) complex have been proposed.

The experimentally obtained gram magnetic susceptibility (χ_g), calculated magnetic moment and nature of complexes are summarized in table 15.

Table 15: Magnetic moments of the metal complexes

Complexes	χ_g X10^{-6}	$\chi_m = \chi_g$MW	$\mu = 2.824[T\ \chi_m]^{1/2}$	Nature of the complex
NiL·4H_2O	4.416	0.00225	2.0 (BM)	Paramagnetic
ZnL·H_2O	___	___	___	Diamagnetic

3.3.4. Infrared spectra of the metal complexes

The IR spectra of the complexes were compared with those of the free ligand in order to determine the coordination sites that may be involved in coordination (appendix 3-5). The spectrum of HPAPAA (ligand), show some characteristic bands. The main bands are in the regions corresponding to ν_{OH} and $\nu_{C=O}$ functions besides, $\nu_{C=C}$,ν_{C-H} and other related bands. An intense broad band centered at 3401 cm^{-1} observed due to ν_{OH} in the spectrum of the free ligand was absent in the spectra of metal complexes. However, more intense and broad bands were observed at 3468-3500 cm^{-1} in the metal complexes spectra. They are assignable to ν_{OH}, due to H_2O molecules which are present in both the complexes.

Comparison of the free ligand and metal complexes spectra indicates that the ligand undergoes tautomerization to iminol form (scheme 7) during complexation. Strong bands at 1661 and 1506 cm^{-1}in free ligand assignable to $\nu_{C=O}$ and $\nu_{C=C}$ are replaced by intense

,Sharpe and multiple bands in the regions 1656-1487 cm^{-1} in Ni (II) and 1657-1508 cm^{-1} in Zn (II) complexes. The band multiplicity is more explicit in the spectrum of Zn (II) complex. These bands are assignable to $\nu_{C=N}$, $\nu_{C=C}$, δ_{NH2}, δ_{H2O} of the enol tautomer and of H_2O present in the complexes. The absorptions around 1500 cm^{-1} in the complex can be attributed to $\nu_{C=C}$ stretching vibration of aromatic carbon, which is in agreement with previous observations. The bands at 1402 and 750 cm^{-1} are due to CH_2 (bending) and 1, 2 disubstituted (-Ar) respectively.

The phenolic $\nu_{C\text{-}O}$ stretching vibrations appeared at 1305 cm $^{-1}$ in the free ligand, undergo a shift towards lower frequencies (1251 and 1261cm $^{-1}$) in the complexes. This shift confirms the participation of oxygen in the formation of C-O-M bond. Significant lowering of $\nu_{C\text{-}O}$ may be attributed to the involvement of deprotonated phenolic oxygen in bonding and bridging interaction. The is proposed as the reason for sub-normal magnetic moment of Ni (II) complex, leading to metal- metal interaction via phenoxide bridging.

The band at 1121 cm^{-1} assigned for C–N stretching side chain in the free ligand is shifted to lower wave number (1107 and 1117 cm^{-1}) in the complexes. This suggests that the nitrogen atom of the ligand is involved in coordination with the metal ions.

Further evidence for bonding by nitrogen and oxygen atoms is provided by far IR spectra of complexes. Due to interference of skeletal vibrations of ligands with M-N and M-O vibrations, definite assignments of bands are difficult. Therefore only tentative assignments are made on the basis of information available in literature. Spectra of both complexes showed week bands at 600-550 cm^{-1}and 480-450 cm^{-1}vibrations, which may be assigned to the $\nu_{M\text{-}N}$ and $\nu_{M\text{-}O}$ stretching [30, 31]

The presence of coordinated water in Ni (II) complex was suggested by very broad absorption centered around 3468 cm^{-1} in the infrared spectrum. Some of the weak bands between 640-400 cm^{-1} are due to the wagging mode of water and those between 1038-750 cm^{-1} are assigned for rocking mode of coordinated water. Based on geometrical consideration four water molecules are assumed to be in coordination sphere while the remaining is in lattice sites. But in the case of Zn (II) complex a broad band that appears in the region 3500 cm^{-1} shows the existence of water molecule in the outer sphere. In the spectrum of Zn (II) complex, the sharp band at 3208 cm $^{-1}$ is due to ν_{NH} stretching vibration.

Based on IR data, it is proposed that the ligand behaves as dibasic tridentate, employing ONO donor sequence in chelation. Deprotonated phenolic oxygen, imine nitrogen and deprotonated iminolic oxygen are proposed for the chelation. The donor sequence will form complexes with bicyclic structural components, in which a five membered ring and a four membered ring combindly stabilize the chelate, while gaining further support from phenoxide bridging. This appears to be a unique feature of this metal-ligand interaction. The IR data of the spectra of the ligand and their metal complexes are presented in Table 16.

Table 16: IR absorption frequencies (in cm^{-1}) of HPAPAA and its metal complexes

Band assignments	HPAPAA/cm^{-1}	Ni (II) complex/cm^{-1}	Zn (II) complex/cm^{-1}
$\nu_{(OH)}$	3401	3500	3468
$\nu_{(NH,NH2)}$	3200-3000	3100	3208
$\nu_{(C=O)}$	1661 (s)	—	—
$\nu_{(C=N)}$	—	1656	1657
$\nu_{(C=C)}$	1506	1487	1508
$\nu_{(CH2)}$	1401	1403	1401
$\nu_{(C-OH)}$	1305	1251	1261
$\nu_{(C-N)}$	1121	1107	1117
$\nu_{(C-Ar /C-Cl)}$	750	752	750
ν_{M-N} ,ν_{M-O}	—	600-550, 480-450	600-550, 480-470

3.3.5. UV-VIS Spectrum of HPAPAA and its metal complexes

Electronic spectra measurements are very useful for assigning the stereochemistry of the complex based on the position and number of d-d transitions. The electronic absorption spectra of the complexes were recorded at room temperature using the solvent methanol.

The UV-Vis spectrum of the ligand is characterized mainly by two absorption bands at 396 nm (25253 cm^{-1}), and 286 nm (34965cm^{-1}). The first band in the spectrum of the ligand was assigned to transition due to extended conjugation of the ligand (HPAPAA). The second band was attributed to transition due to aminophenol chromophore moiety (Appendix 12-14).

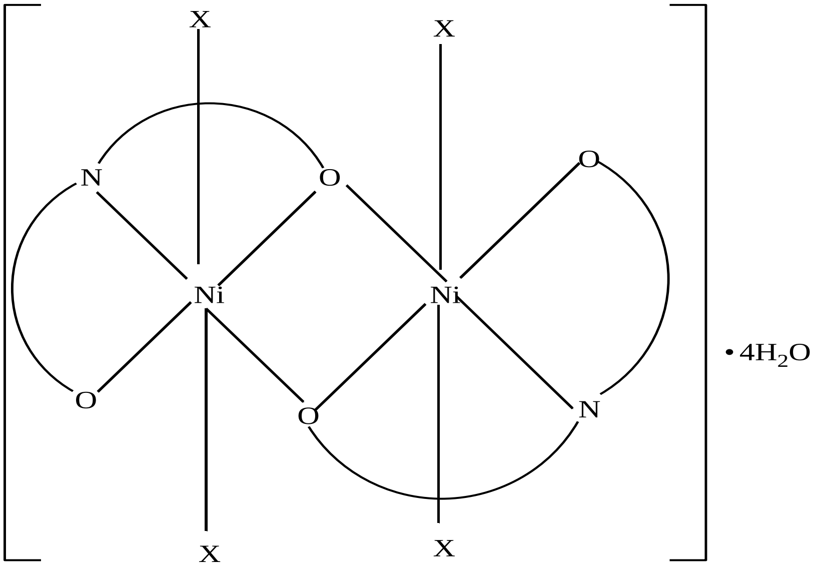
In general, there is a wave length shift of both $\pi \rightarrow \pi^*$and $n \rightarrow \pi^*$ bands, which suggest modifications in electronic distribution of complexation. The electronic spectrum of Ni (II) complex shows characteristic bands in visible/near IR region which are assignable to d-d transition but in our case there is experimental limitation. However, Ni (II) complex have three spin allowed transitions $^3A_{2g} \rightarrow {}^3T_{2g}(F)$,$^3A_{2g} \rightarrow {}^3T_{1g}(F)$, and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ in the range of 7000-13000, 11000-20000 and 19000-27000 cm^{-1} only two spin allowed transitions are observed in our case $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ at, 23923 and 27770 respectively. $^3A_{2g} \rightarrow {}^3T_{2g}$ (F) transition has not been resolved under the experimental condition. Based on the data presented in table 17 along with assignment of transitions, octahedral geometry has been assigned to Ni (II) complex [1].

As expected for a d^{10} electronic configuration, the electronic spectrum of zinc (II) complex does not show any d-d transition. The observed bands are due to the ligand and charge transfer transitions. The bands at 354 nm (28248 cm^{-1}) and 279 nm (35842 cm^{-1}) are assigned to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ intraligand transition. The other band located at 414 nm (24154 cm^{-1}), may be assigned to ligand to metal charge transfer transition. Except this, the complex shows no appreciable absorption in the region above 450 nm, due to d^{10} electronic configuration of the Zn (II) ion. Although Zn^{2+} ion has a strong tendency to adopt regular tetrahedral coordination, the ligands affect its geometry as a result it become square planar geometry.

Table 17: UV-VIS Spectrum of HPAPAA and its metal complexes

Compounds	Abs. nm (cm^{-1})	Assignment of Transition
HPAPAA	396 (25253) 286 (34965)	Bands of extended conjugation Bands of aminophenol chromophore moiety
$NiL\cdot4H_2O$	418 (23923) 360 (27770)	$^3A_{2g} \rightarrow {}^3T_{1g}(F)$, $^3A_{2g} \rightarrow {}^3T_{1g}(P)$,
$ZnL\cdot H_2O$	354 (28248) 279 (35842) 414 (24154)	$n \rightarrow \pi^*$ (Intraligand) $\pi \rightarrow \pi^*$ (Intraligand) LMCT

Based on the analytical, infrared, conductivity, magnetic susceptibility and electronic spectral data, octahedral geometry for Ni (II) complex and square planar geometry for Zn (II) complex was suggested and the proposed schematic structures are presented in figures 7 and 8.



Where X=H_2O

Figure 7: proposed schematic structure of Ni (II) complex

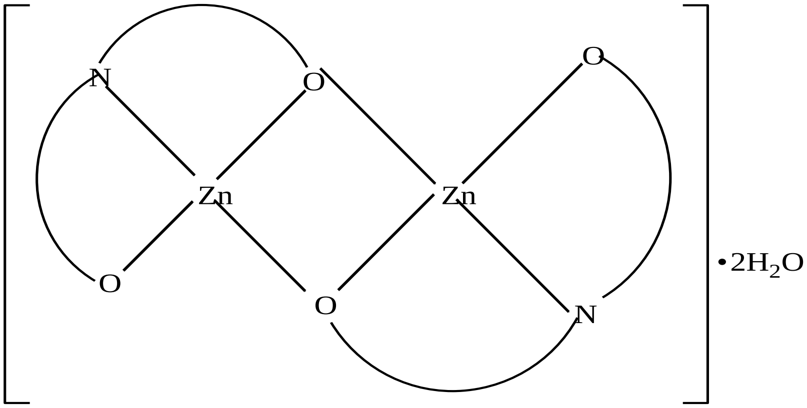


Figure 8: proposed schematic structure of Zn (II) complex.

4. Conclusion

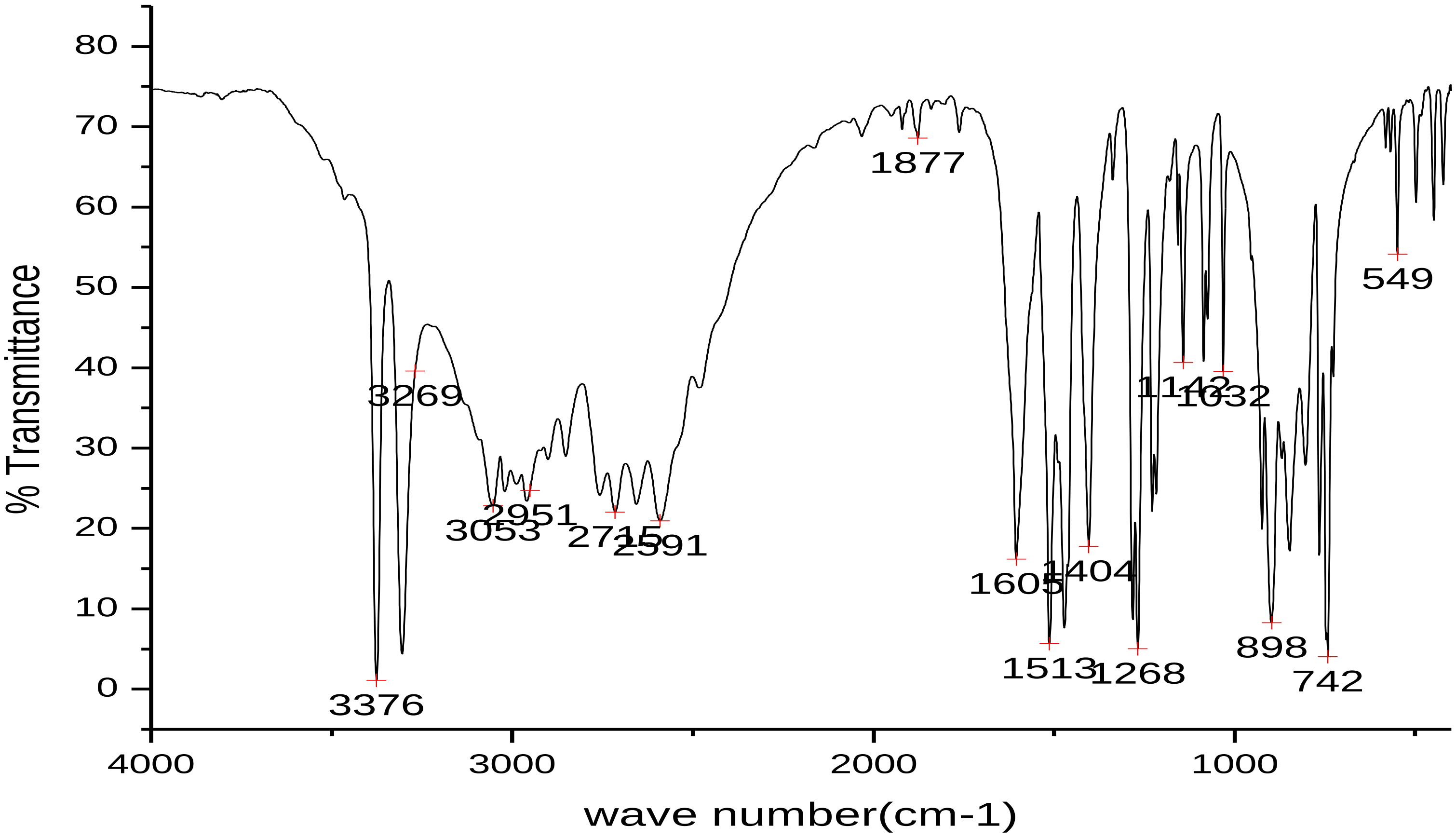
A new polydentate ligand N-(2-hydroxyphenyl)-2-[(2-aminophenylamino)] acetamide, (HPAPAA), has been synthesized in the reaction between N-(2-hydroxyphenyl)-2-chloroacetamide and o-phenylenediamine. The Ni (II) and Zn (II) complexes of the ligand were synthesized from methanolic media and subjected to structural elucidation based on spectral (IR, NMR, UV-VIS, AAS), conductivity and magnetic studies. The conductivity data revealed that both of the complexes are non-electrolytes. In view of the non-electrolytic nature, absence of chloride in both the complexes, it is concluded that the ligand undergoes enolization and subsequent deprotanation to form a dinegative anion (ONO) $^{2-}$ during complexation. The atomic absorption spectral data revealed metal to ligand ratio 1:1 for both Ni (II) and Zn (II) complexes. Binuclear Ni (II) complex exhibited subnormal magnetic moment indicating the possibility of antiferromagnetic interaction through a possible super exchange mechanism. Based on IR data, it is proposed that the ligand behaves as dibasic tridentate, employing ONO donor sequence in chelation including phenoxide bridging.

5. References

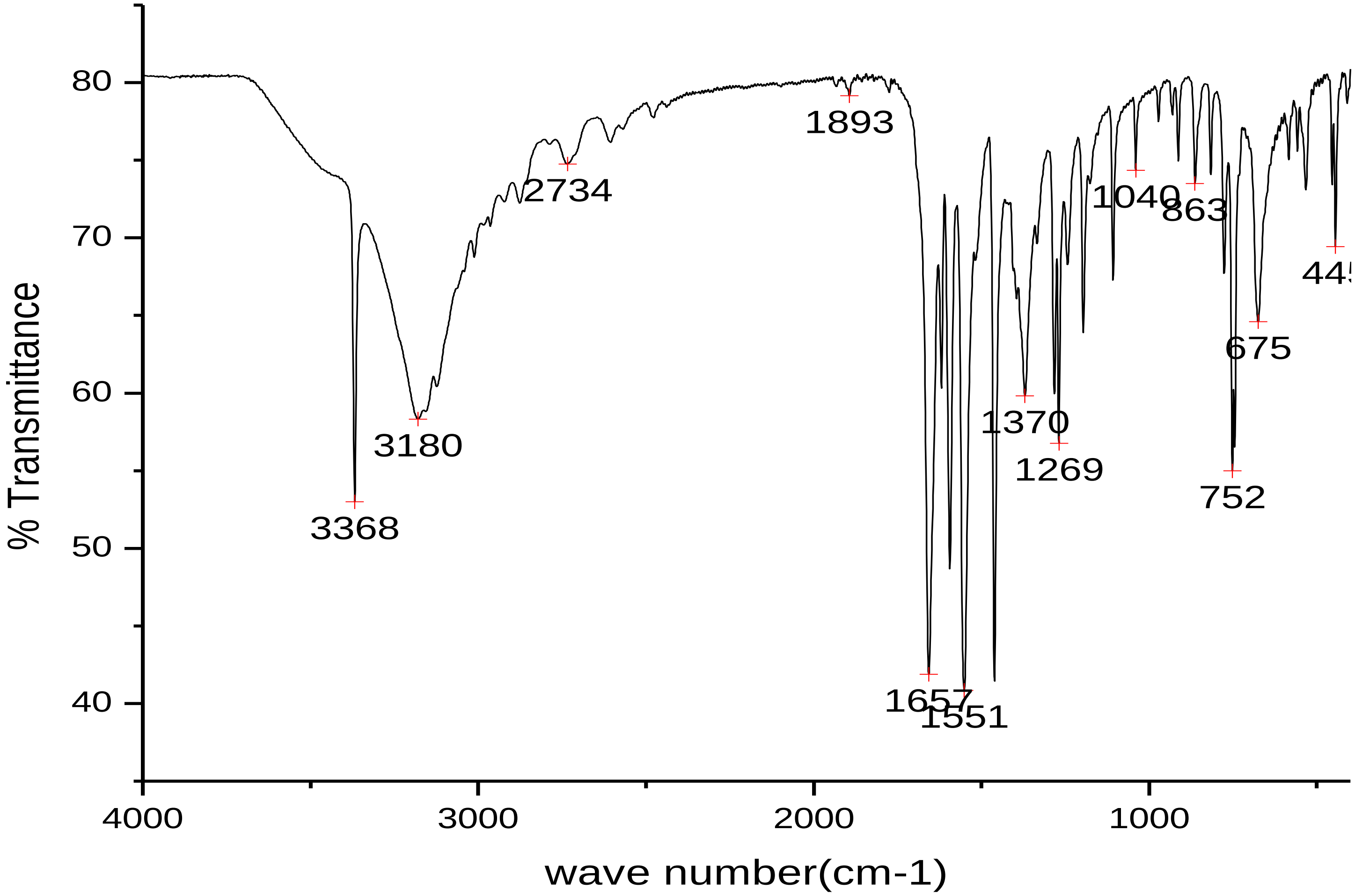
1. Huheey, J.E.; Keiter, E.A.; Keiter, R.L. *Inorganic Chemistry*, 4th ed., Harper Collins college publishers: New York; **1993**.
2. Murilla, C.A.; Cotton, F.A.;Wilkinson,G.; Bochmann M. *Advanced Inorganic Chemistry*, 6th ed., Wiley India Pvt. Ltd: India; **2007.**
3. Atkins, P.W.*Shriver and Atkins inorganic chemistry*. 5th ed., Oxford University Press:UK; **2010.**
4. Lee, J.D. *A New Concise Inorganic Chemistry*, 3th ed., Oxford University Press: UK; **2013.**
5. Miessler,G.L.; Fischer, P.J.; Tarr, D.A. *Inorganic Chemistry*, 5th ed., Prentice Hall Inc; **2013.**
6. Canham, G.R. *Descriptive Inorganic Chemistry*, 2nd ed., W.H.Freeman and company: USA; **2000.**
7. Gavrilova, A.L.; Bosnich, B. *Principles of mononucleating and binucleating ligand design*, Chem. Rev. **2004**, 104, 349-383.
8. http://en.wikipedia.org/wiki/Coordination_complex.
9. El-Sonbati, A.Z.; El-Bidarry, A.A. *Polish.J.Chem*.**2000**, 74, 621-630.
10. Carneiro, T.M.G.; Beraldu, H. *J.Braz.Chem.Soc*. **1999**, 10, 184-188.
11. Raman, N.; Muthuraj, V.; Ravichandrand, S.; Kulandasamy, A. *Proc.India, Acad.Sci*.**2003**, 115, 3.
12. Raman, N.; Pitchaikani, Y.; Kulandasamy, A. *Proc. India, Acad. Sci*. **2001**, 113.
13. Assayehegn,E. *Synthesis and Structural Studies on metal complex based on multidentate ligand derived from salicylaldehyde and resdiacetophenone-dihydrazone*, M.Sc. Thesis, Addis Ababa University, Addis Ababa, Ethiopia, **2007.**.
14. Gudasi, K.B.; Patil S.A.; Vadavi, R.S.; Shenoy, R.V.; Patil M.S. *J.Serb.Chem.Soc.* **2006**, *71* (5), 529–542.
15. Sisay, G. *Synthesis and Characterization of Some Transition Metal Complexes with O,N,O and O,O donor ligands,*M.Sc. Thesis, Addis Ababa University, Addis Ababa, Ethiopia, **2012.**

16. http://en.wikipedia.org/wiki/2-Aminophenol
17. http://en.wikipedia.org/wiki/Chloroacetyl_chloride
18. Troll,W.; Keith, R. *Cannan, a Modified Photometric Ninhydrin Method for the Analysis of Amino and Imino acids*, **2007**.
19. Amare, M. *Synthesis and Characterization of a Quinoxaline Derivative and its Ni (II) and Co (II) Complexes*, M.Sc. Thesis, Addis Ababa University, Addis Ababa, Ethiopia, **2010.**
20. Kumar, N.; Sharma, P.; Pareek, A.; AVGS, P.*Int.J.Chem.pharm.Sci*.**2013**, 4 (1), 12-18.
21. Siddappa, K; Mana, S.B.*Int.J.pharma.Sci*.**2013**.5, 725-732.
22. Venegas-Yazigi, D.; Campos-Vallette, M.; Lever, A.B.P.; Costamagna, J.; Latorre R.O.; Hernández G.W,*A Family of Ruthenium Complexes containing the non inocent ligand O-Benzoquinonneddiamine, An Infrared Structural Interpretation.* **2003.**
23. http://en.wikipedia.org/wiki/Tautomer
24. Martiskainen, O. *Tautomerism and Fragmentation of Biologically active Hetero atom (O, N) Containing Acyclic and Cyclic Compounds Under Electron Ionization*, PhD.Thesis, University of Turku, **2009.**
25. Douglas, B.; McDaniel, D.; Alexander, John. *Concepts and Model of Inorganic Chemistry*, 3rd ed., John Wiley and Sons: USA; **1993.**
26. Sönmez, M. *Turk.J.Chem*. **2001,** 25, 181-185.
27. Raman, N.; Pitchaikani Y, R.; Kulandaisamy A. *Proc. Indian Acad.Sci*. **2001**, 113, 3, 183-189.
28. Siddappa, K.; Reddy, T.; Mallikarjun, M.; Reddy,C.V. *E-Journal of Chemistry*, **2008,** 5.1, 155-162.
29. Girobami, G.S.; Rauchfuss, T.B.; Angelici, R.J.; *Synthesis technique in InorganicChemistry*, 3rd ed., a laboratory manual.
30. Ferraro, J.R. *Low Frequency Vibrations of Inorganic and Coordination Compounds* Springer Verlag, **2012**.
31. Godara, M.; Maheshwari, R.;Varshney.S.; Varshney, A.k. *J. Serb. Chem. Soc.* **2007**, *72* (4), 367–374.

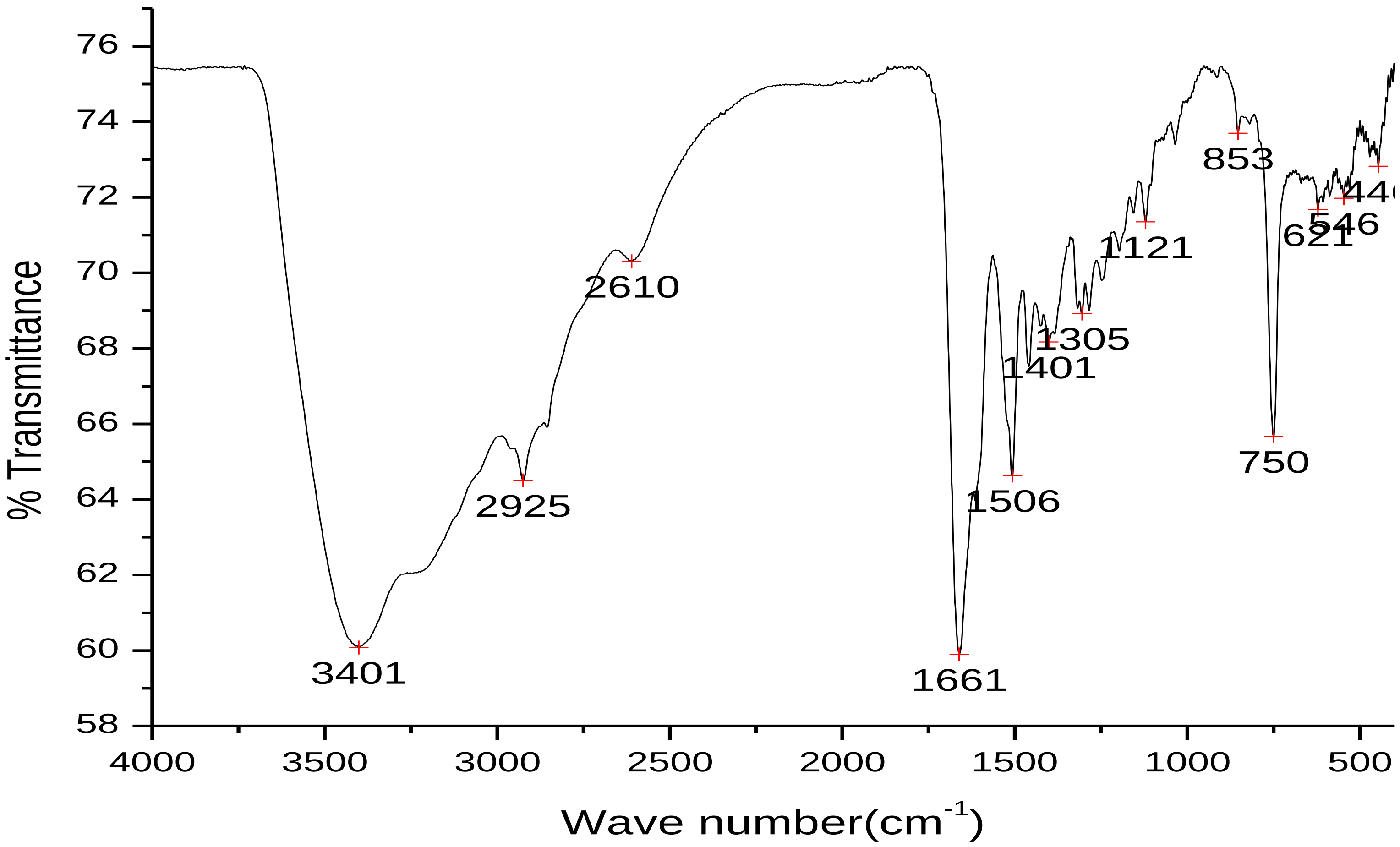
6. Appendices



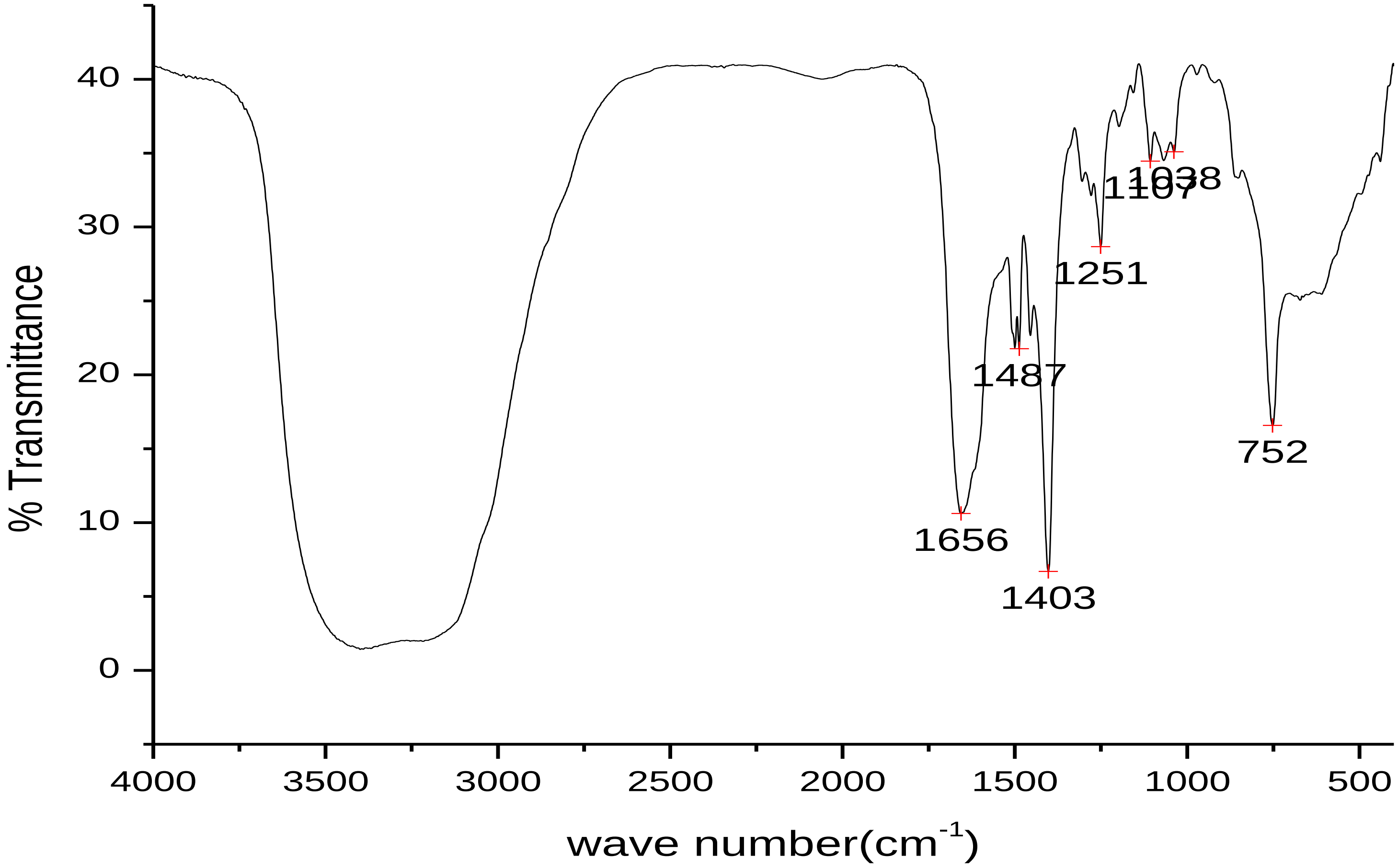
Appendix 1: IR spectrum of 2-AP



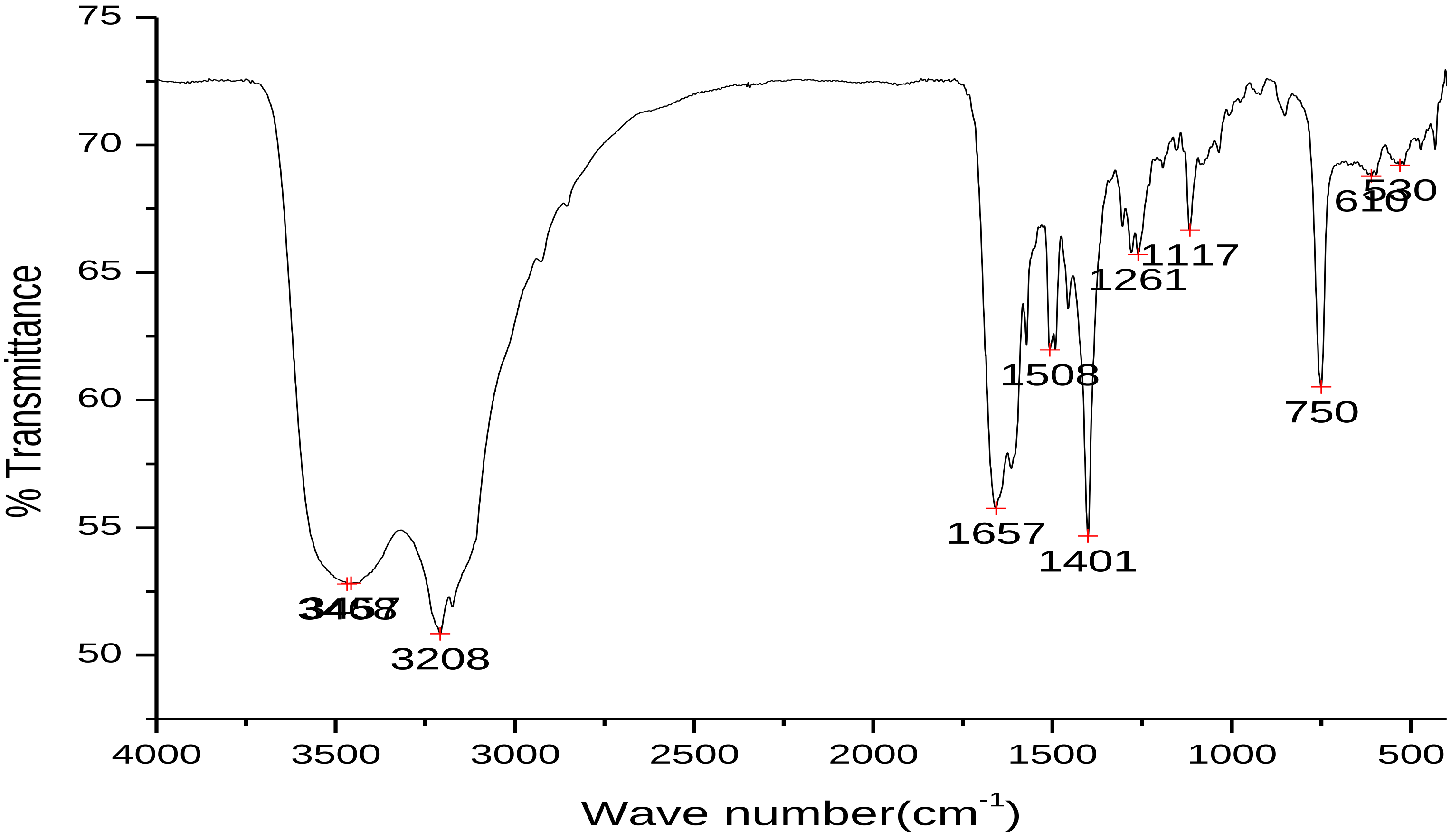
Appendix 2: IR spectrum of HPCA



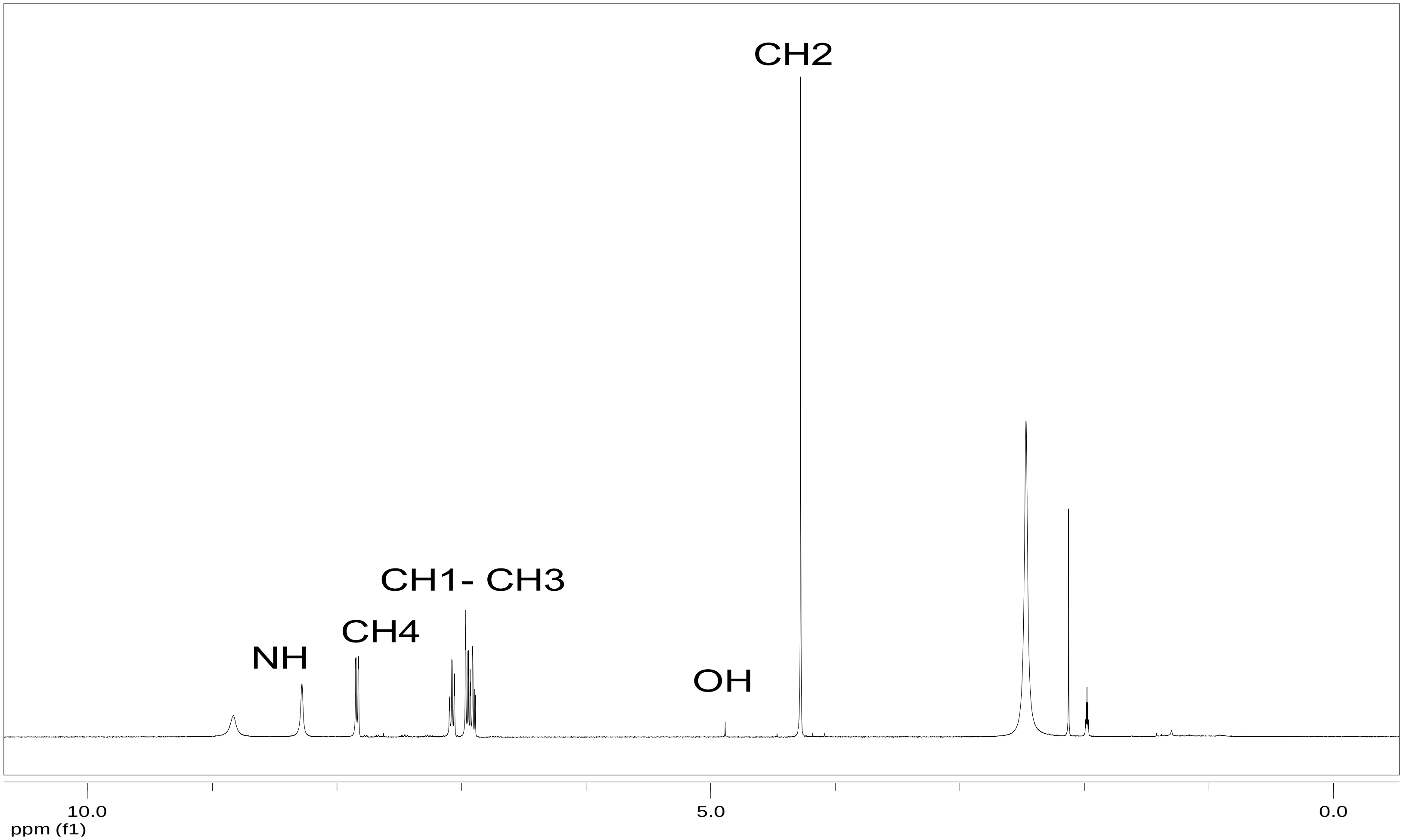
Appendix 3: IR spectrum of HPAPAA



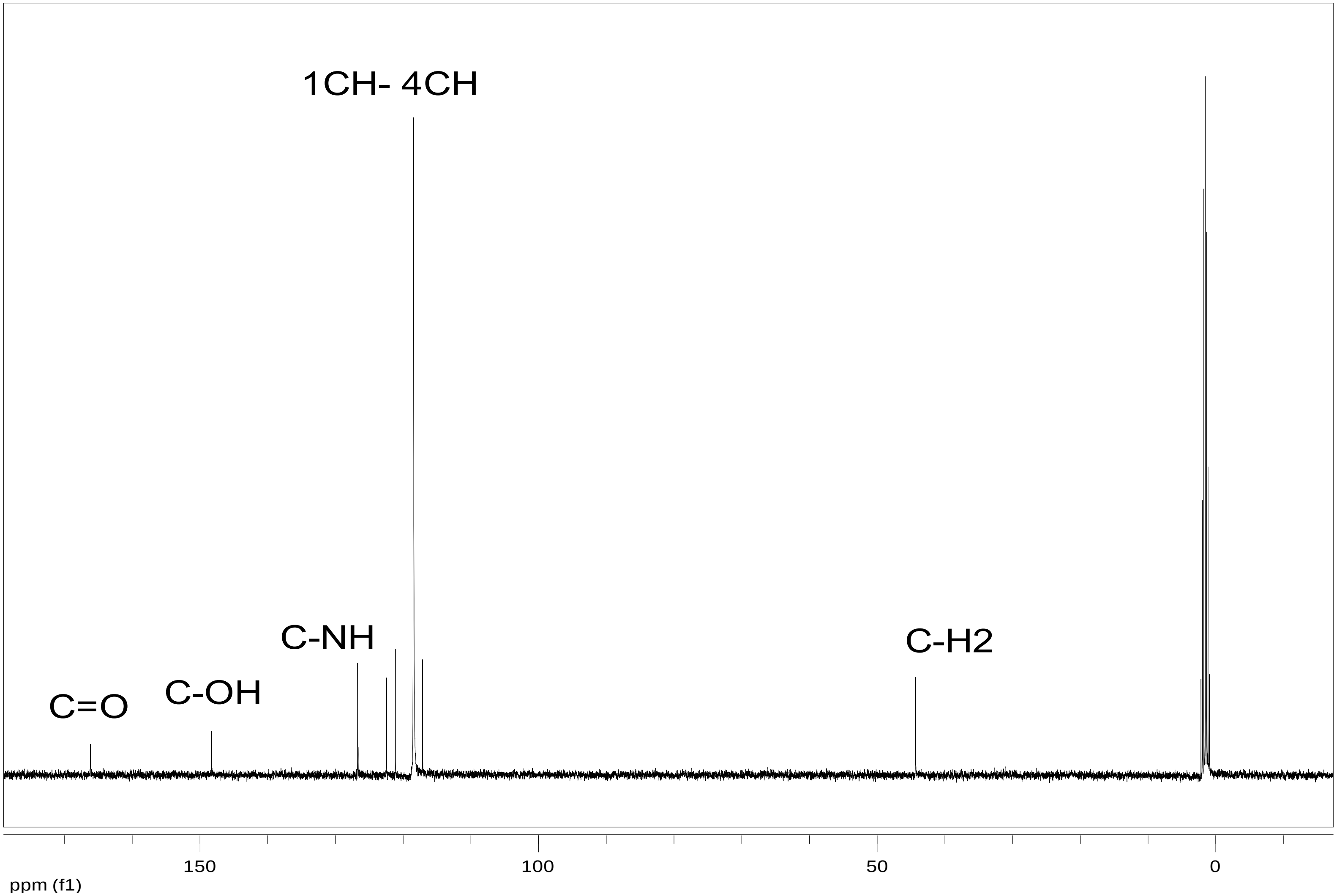
Appendix 4: IR spectrum of Ni (II) complex



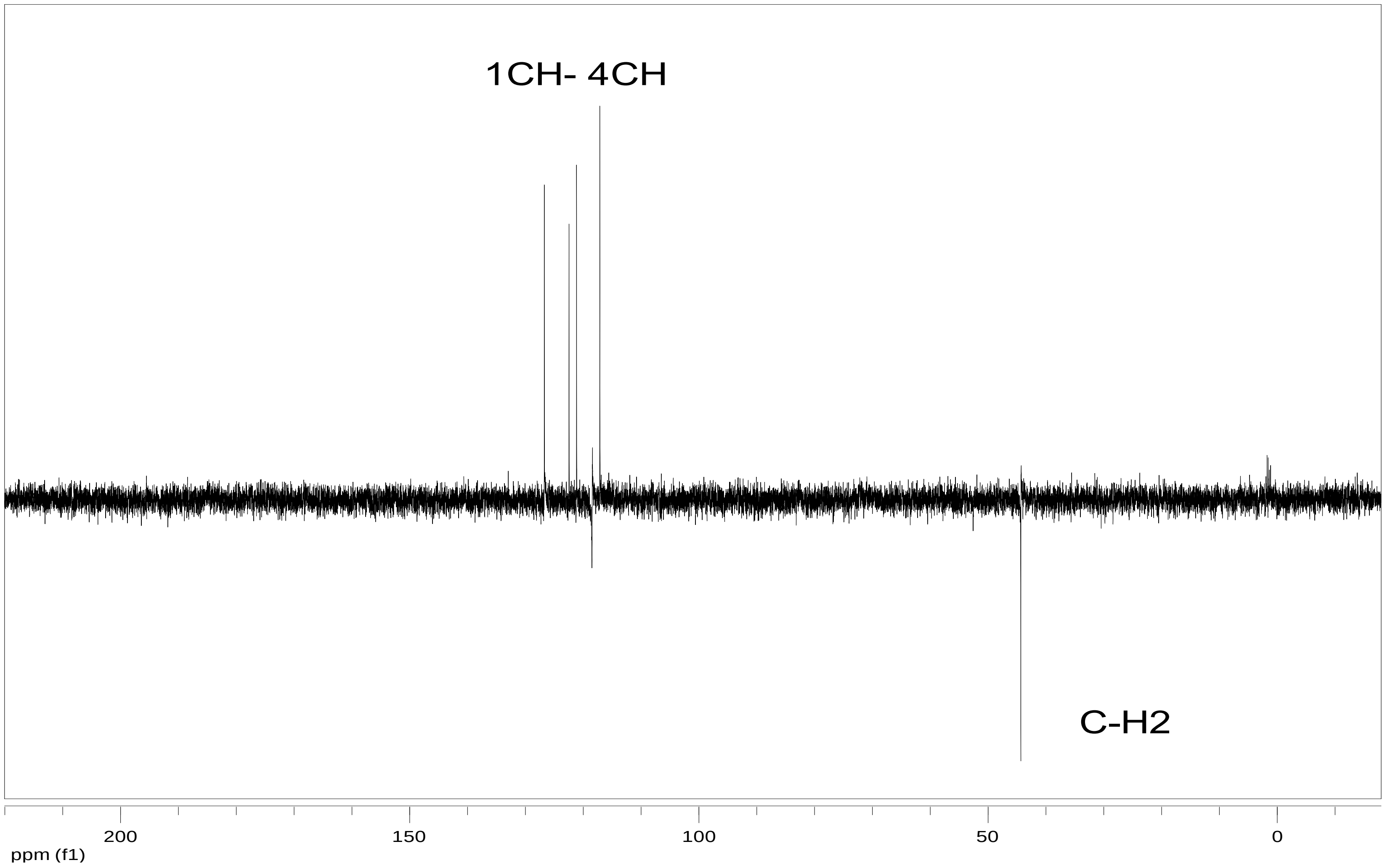
Appendix 5: IR spectrum of Zn (II) complex



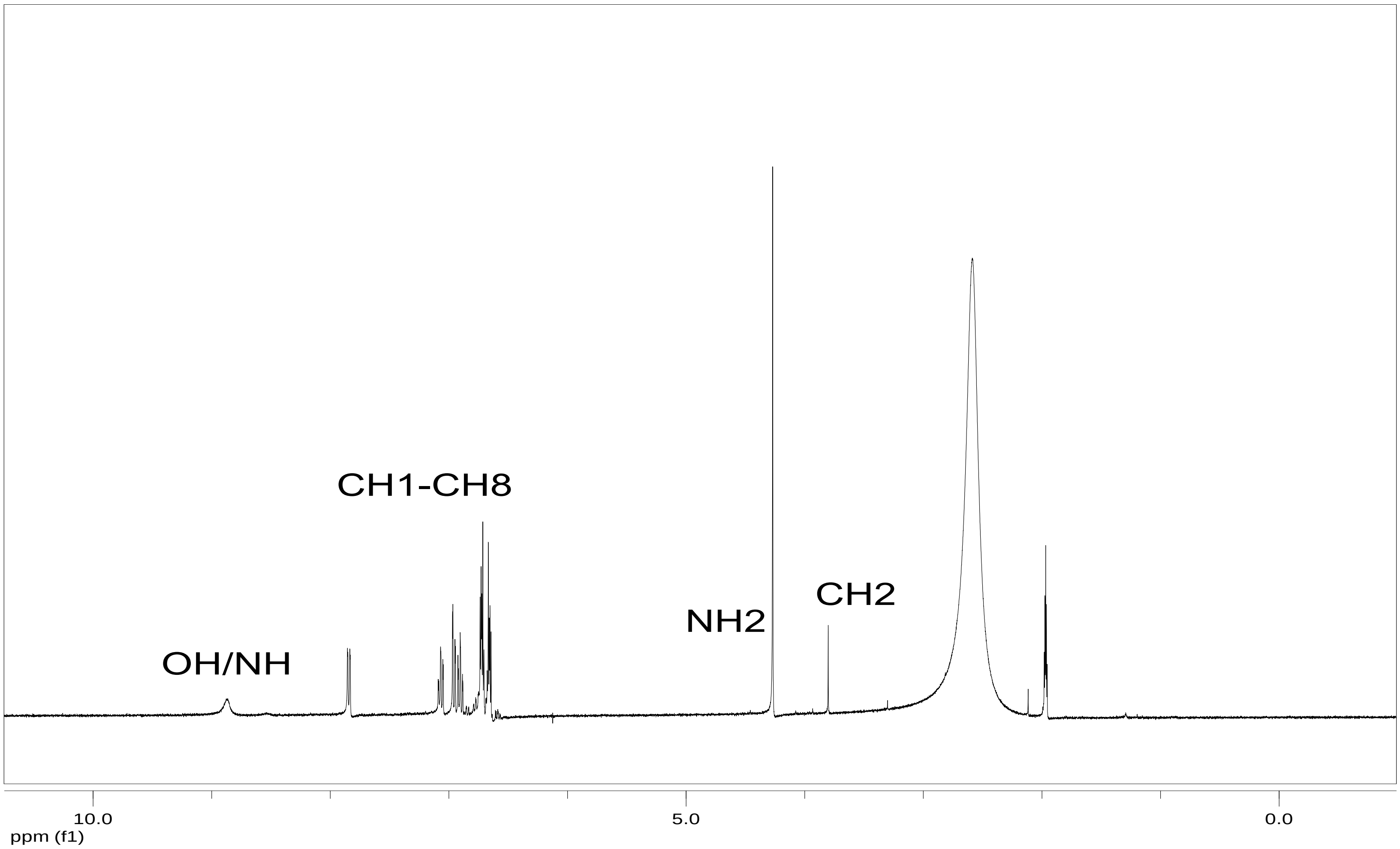
Appendix 6: ^{1}H NMR spectrum of HPCA



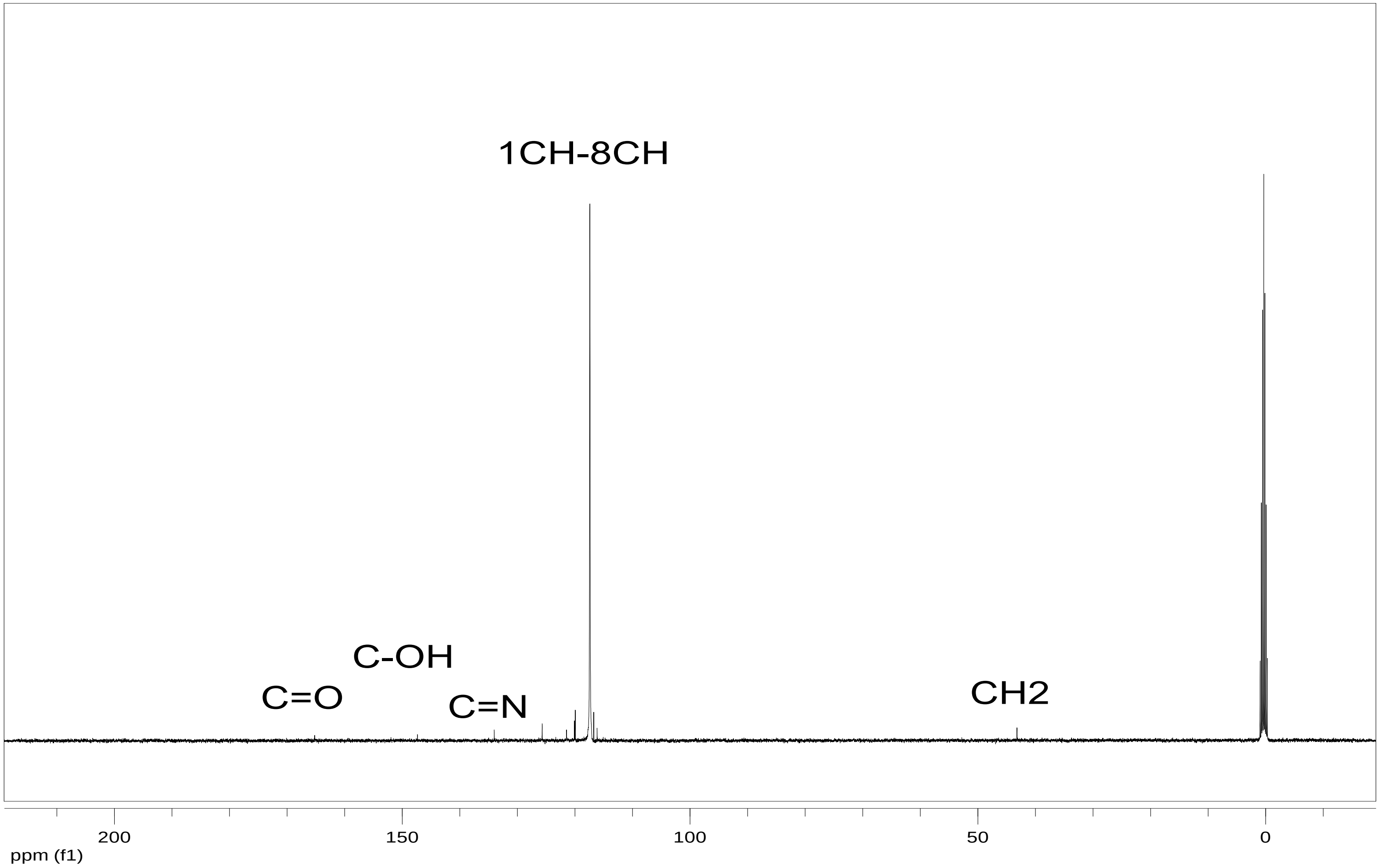
Appendix 7: ^{13}C NMR spectrum of HPCA



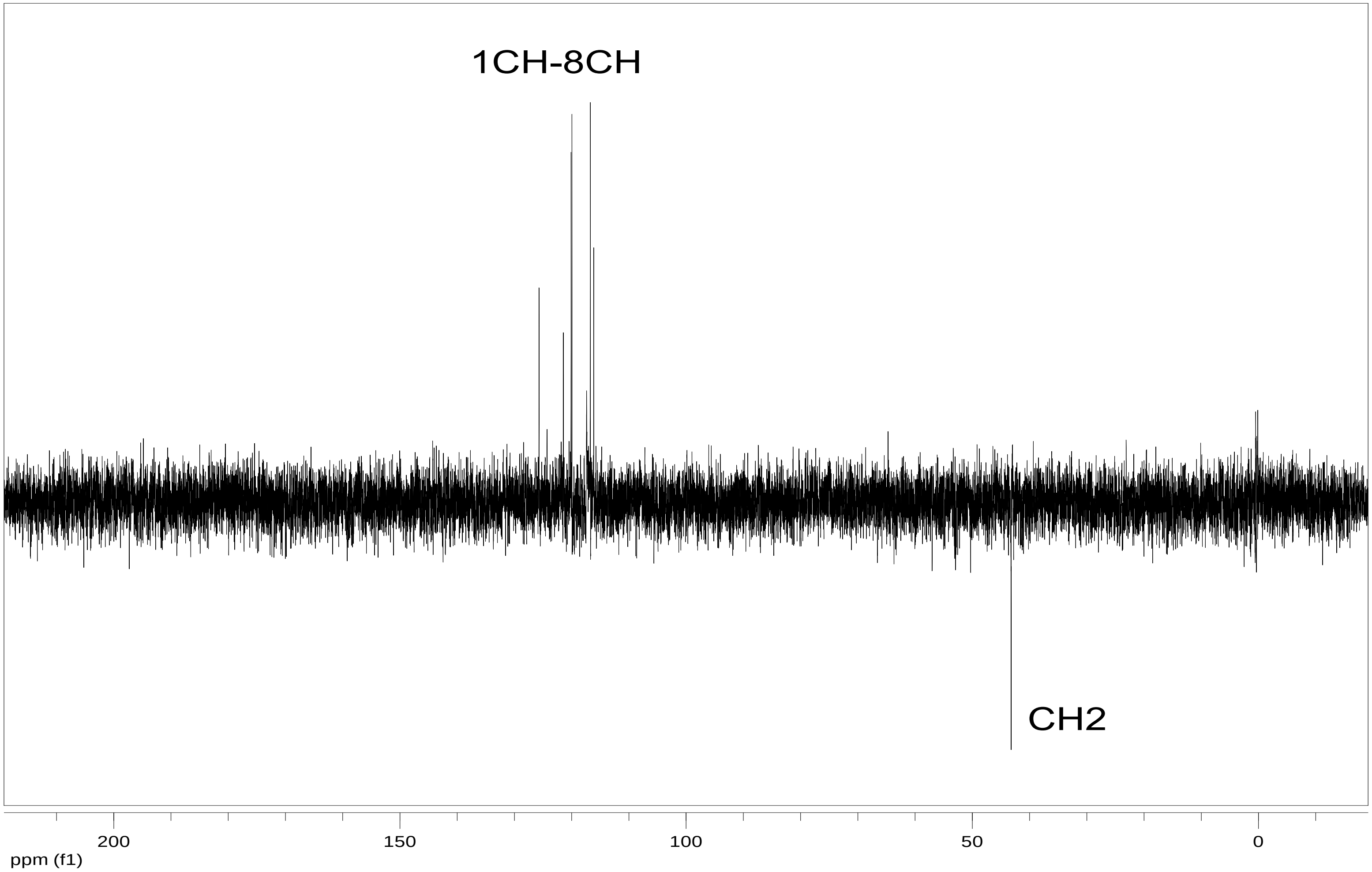
Appendix 8 : DEPT-135 NMR spectrum of HPCA



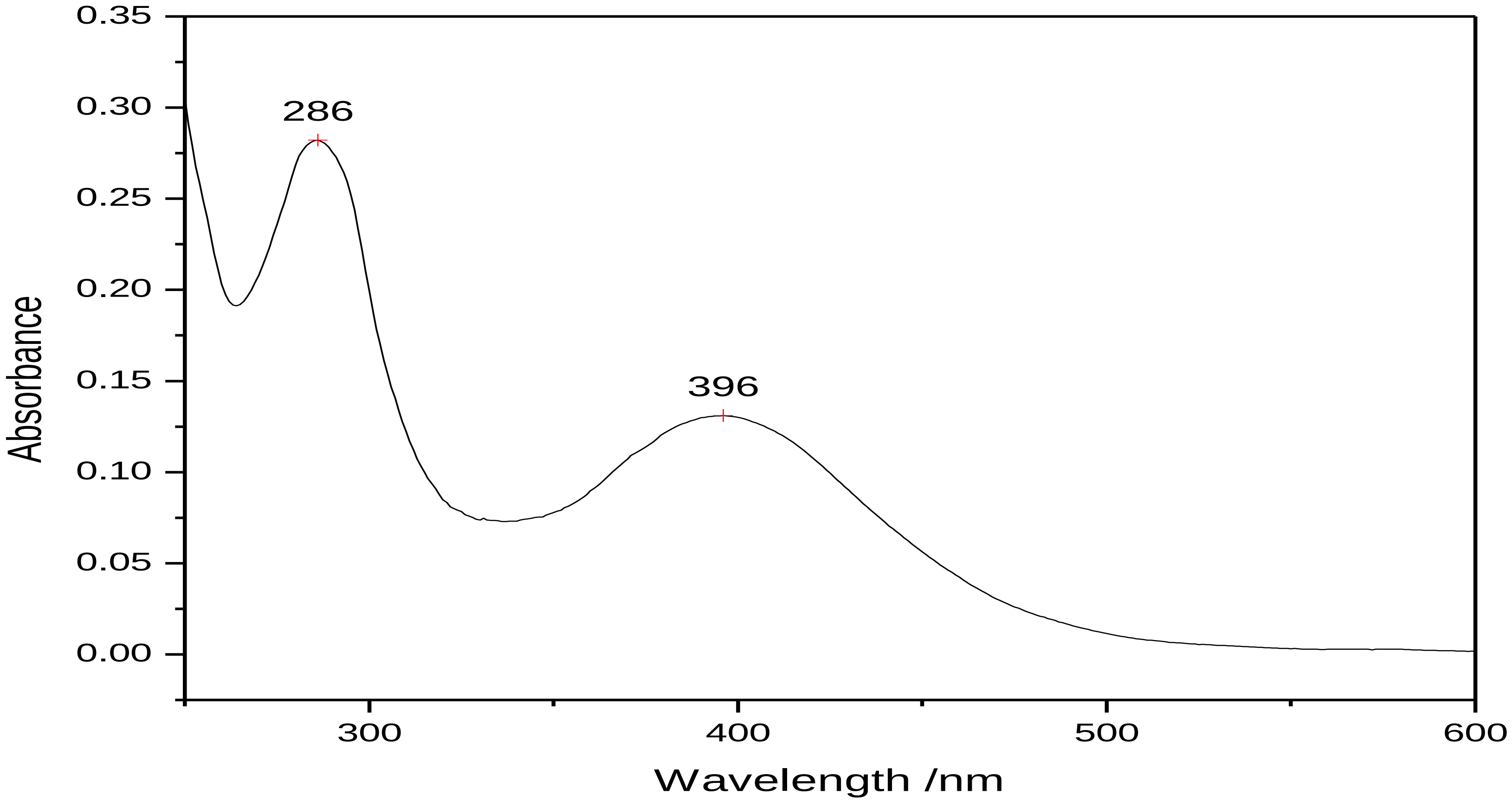
Appendix 9 : ^{1}H NMR spectrum of HPAPAA



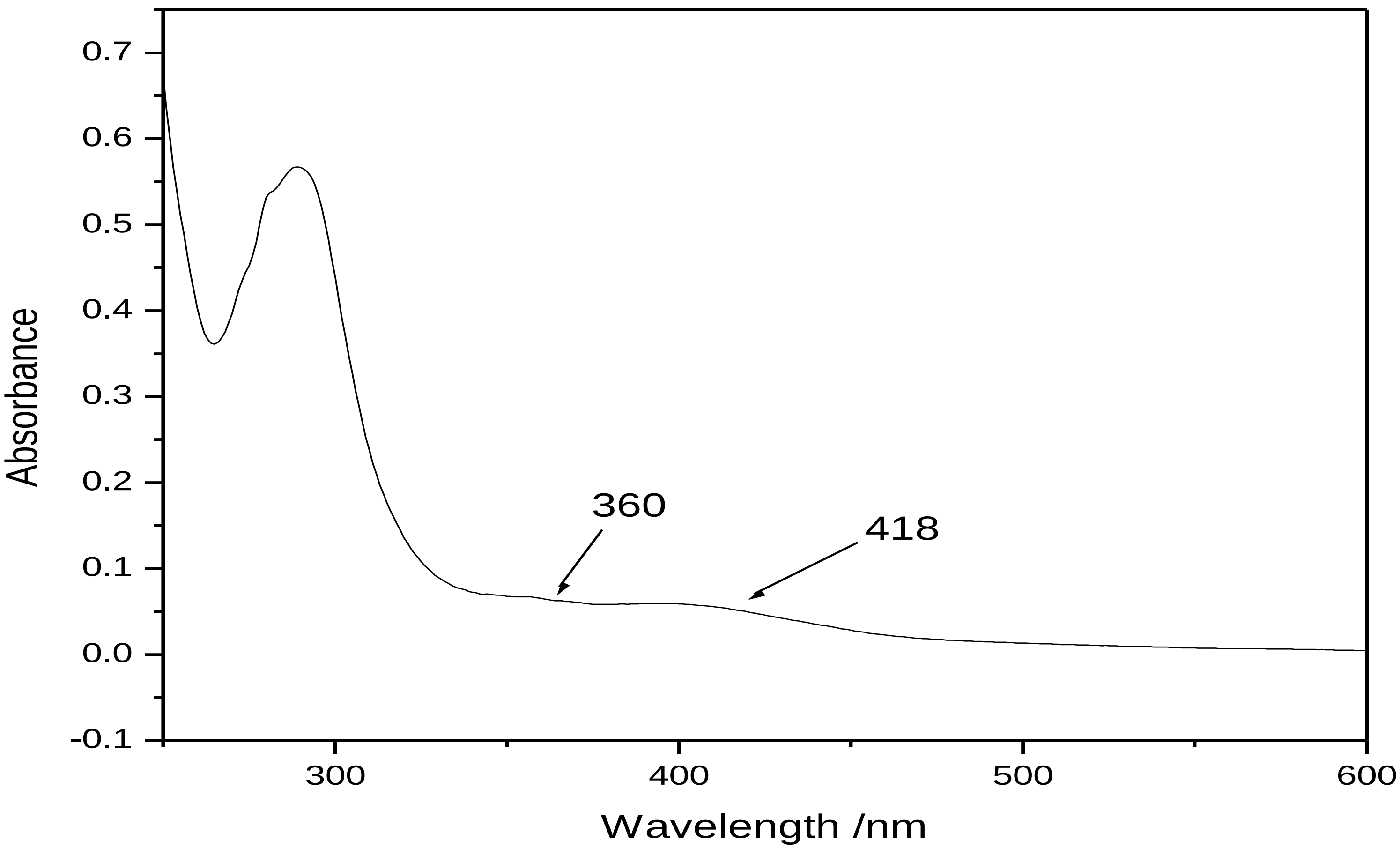
Appendix 10: ^{13}C NMR spectrum of HPAPAA



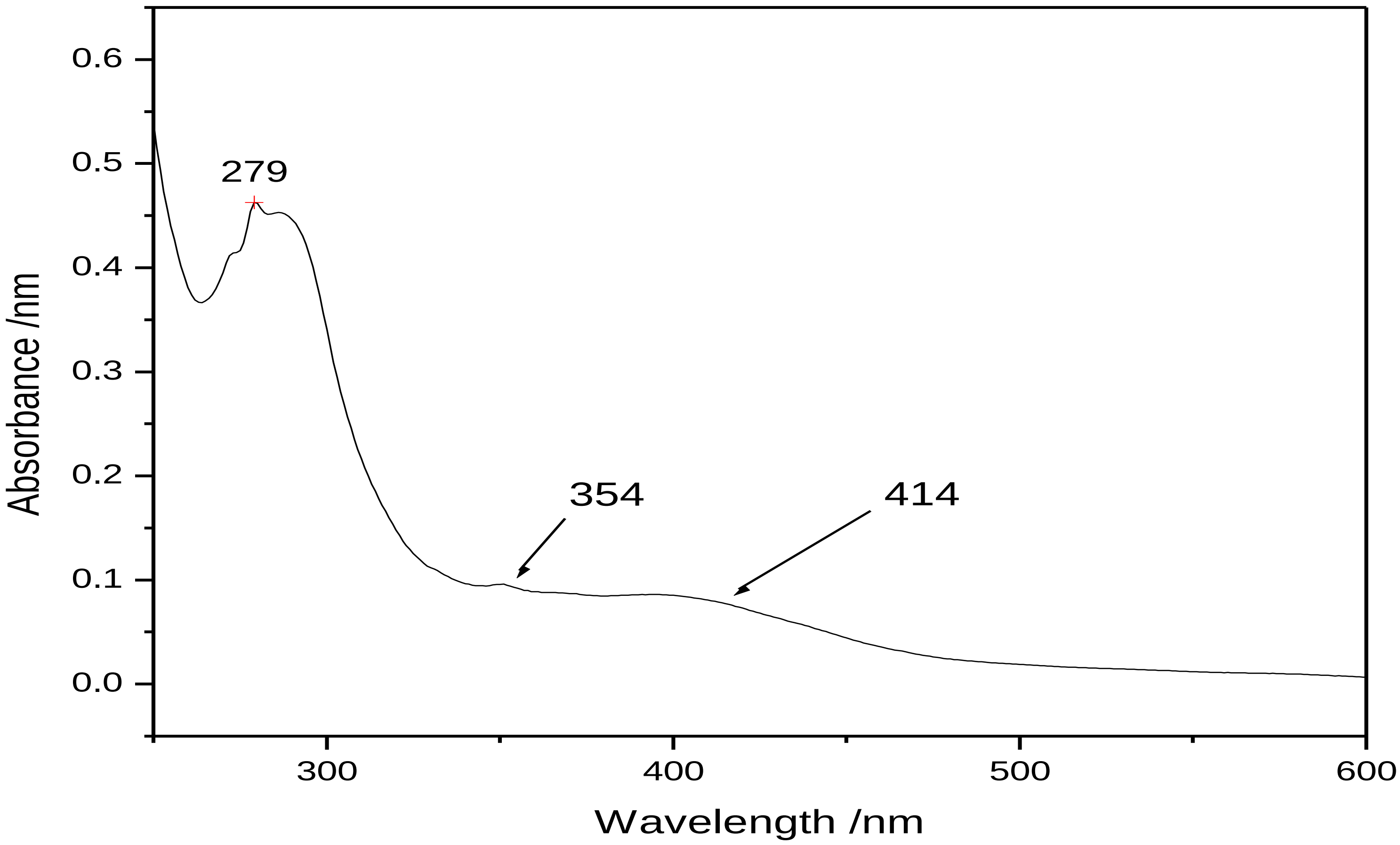
Appendix 11: DEPT-135 NMR spectrum of HPAPAA



Appendix 12: UV-VIS spectrum of HPAPAA



Appendix 13: UV-VIS spectrum of Ni (II) complex



Appendix 14: UV-VIS spectrum of Zn (II) complex