Synthesis, Characterization and Antimicrobial Analysis of Nickel and Cobalt Complexes of Condensates of Salicylaldehyde and 2-Hydroxy Aniline

Abstract

This study on the synthesis, characterization and antimicrobial analysis of Nickel and Cobalt complexes of condensates of salicylaldehyde and 2-hydroxy aniline constitutes an attempt towards the development of new molecular compounds that could destroy the barrier of resistance of pharmaceutical products. The ligands of 2-phenyliminomethylphenol (PMP) and 2,2-hydroxy benzylidene aminophenol (HAP) were first prepared by separately reacting Aniline with Salicylaldehyde on the one hand, and 2-aminophenol with Salicylaldehyde on the other hand.The unmixed metal complexes were prepared by reacting either of 0.29 mmol 2-phenyliminomethylphenol ligand with the metal salt or 0.29mmol 2,2-hydroxybenzylideneaminophenol ligand with the metal salt while the mixed metal complexes were prepared by addition of equimolar amount of ligands of 2-phenyliminomethylphenol and 2,2-hydroxybenzylideneaminophenol into the metal salt. The molecular structures of the ligands and their complexes have been determined and characterized using GC-MS, FTIR, UV-Vis, ^{1}H-NMR, and X-ray diffraction techniques. The melting point and solubility of the ligands and synthesized complexes were equally determined. Antimicrobial studies were carried out with ligands PMP and HAP and the metal complexes using clinical isolates of Gram Positive Bacteria (*Staphylococcus aureus* and *Bacillus substilis*), Gram Negative Bacteria (*Escherichia coli* and *Pseudomonas aeruginosa*) and Fungi (*Candida albicans* and *Aspergillus niger*). All complexes and ligands were found to be soluble in dimethylsulfoxide (DMSO). Asymmetric Octahedral geometry is observed for Nickel (II) and Cobalt (II) complexes with PMP, HAP, and the mixed ligands. A bidentate ligand is coordinated to metal ions through oxygen atoms of carbonyl groups and nitrogen atoms of two imine groups for Nickel (II) and Cobalt (II)complexes. The findings from the XRD pattern indicate that the ligand and metal complexes are crystalline with a high crystallite size of 119.23nm to 638.67nm. The FTIR spectra for 2-phenyliminomethylphenol (PMP) showed IR absorption band at 1569.2cm^{-1}suggesting the stretching vibration of the C=C bond in the benzene rings, while the bands at 1613.9 cm-^{1}indicated the =C-N stretching in the benzene ring. The complexes showed electronic spectra which suggestthat energy was absorbed in the ultraviolet/visible region, producing changes in the electronic energy of the compound and resulting from the transition of valence electrons in the complexes. The XRD findings reveal that the crystal formed by the ligands and their respective complexes are large. The ligands were found to be larger in size than the complexes and this could be due to the complexation reactions. The X-ray diffractograms of the metal complexes produced good intense peaks that suggest high crystallinity. The ligand of 2-phenyliminomethylphenol (PMP) and 2,2-hydroxy benzylidene aminophenol (HAP) showed partial inhibitory action on the clinical isolates of Gram Postive, Gram Negative and zero inhibitory effect on the fungi while the divalent metal complexes of both mixed and unmixed ligandsexhibited either stronger or strongest inhibition. The study concludes that the synthesized ligands and their metal complexes are purely crystalline as revealed by the chemical analysis, exhibited inhibitory actions on Gram Positive, Gram Negative and fungi species.

Keywords:PMP, HAP,Metal complexes, Salicylaldehyde, 2-hydroxyaniline, Ligands

1. Introduction

Coordination chemistry emerged from the work of Alfred Werner, a Swiss chemist who examined different compounds composed of Cobalt (III) Chloride and Ammonia. Upon the addition of Hydrochloric acid, Werner observed that Ammonia could not be completely removed. He then proposed that the Ammonia must be bound more tightly to the central cobalt ion. However, when aqueous silver nitrate was added, one of the products formed was solid silver chloride. The amount of silver chloride formed was related to the number of ammonia molecules bound to the Cobalt (III) Chloride. For example, when silver nitrate was added to $CoCl_3\cdot 6NH_3$, all three chlorides were converted to Silver Chloride. However, when Silver Nitrate was added to $CoCl_3\cdot 5NH_3$, only 2 of the 3 Chlorides formed Silver Chloride. When $CoCl_3\cdot 4NH_3$ was treated with silver nitrate, one of the three chlorides precipitated as silver chloride. The resulting observations suggested the formation of complexes or coordination compounds. In the inner coordination sphere, which is also referred to in some texts as the first sphere, ligands are directly bound to the central metal. In the outer coordination sphere, sometimes referred to as the second sphere, other ions are attached to the complex ion. Werner was awarded the Nobel Prize in 1913 for his coordination theory (Oxtoby *et al.*, 2008). A coordination complex is a chemical compound consisting of a central atom or ion, which is usually metallic and is called the *coordination centre*, and a surrounding array of bound molecules or ions, that are in turn known as ligands or complexing agents (Lawrence *et al.*, 2010). Many metal-containing compounds, especially those that include transition metals form coordination complexes (Greenwood *et al.*, 1997). Coordination refers to the "coordinate covalent bonds" (dipolar bonds) between the ligands and the central atom. Originally, a complex implied a reversible association of molecules, atoms, or ions through chemical bonds. Coordination compounds have been studied extensively because of what they reveal about molecular structure and chemical bonding, as well as because of the unusual chemical nature and useful properties of certain coordination compounds. The substances in the class may be composed of electrically neutral molecules or of positively or negatively charged species (Kleinberg *et al.*, 2008).

Coordination Chemistry is the study of compounds formed between metal ions and other neutral or charged molecules called Ligands. It refers to chemistry of coordination compounds and complexes (Lawrence *et al.*, 2012). Coordination compounds on the other hand are a class of substances with chemical structures in which a central metal atom is surrounded by non-metal atoms or groups of atoms, called ligands, joined to it by chemical bonds. Coordination compounds include such substances as vitamin B_{12}, hemoglobin, and chlorophyll, dyes and pigments, and catalysts used in preparing organic substances. Naturally occurring coordination compounds are vital to living organisms. Metal complexes play a variety of important roles in biological systems. Many enzymes, the naturally occurring catalysts that regulate biological processes, are metal complexes, metalloenzymes for example, carboxypeptidase, a hydrolytic enzyme important in digestion, contains a zinc ion coordinated to several amino acid residues of the protein. Another enzyme, catalase, which is an efficient catalyst for the decomposition of hydrogen peroxide, contains iron-porphyrin complexes. In both cases, the coordinated metal ions are probably the sites of catalytic activity. Haemoglobin also contains iron-porphyrin complexes, its role as an oxygen carrier being related to the ability of the iron atoms to coordinate oxygen molecules reversibly. Other biologically important coordination compounds include chlorophyll (a Magnesium-porphyrin complex) and vitamin B_{12}, a complex of Cobalt with a macrocyclic ligand known as Corrin (Lippard *et al.*, 1994 and Oxtoby *et al.*, 2008).

Coordination complexes are so pervasive and interesting that their structures and reactions are extensively investigated. The central atom or ion, together with all ligands, comprise the coordination sphere. Coordination number is the term proposed by Werner to denote the total number of bonds from the ligands to the metal atom. Coordination numbers generally range between 2 and 12, with 4 (tetracoordinate) and 6 (hexacoordinate) being the most common (Myers *et al.*, 1981). Werner referred to the central atom and the ligands surrounding it as the coordination sphere. The coordination number should be distinguished from oxidation number. The oxidation number, designated by an Arabic number with an appropriate sign or sometimes by a Roman numeral in parentheses, is an index derived from a simple and formal set of rules and is not a direct indicator of electron distribution or of the charge on the central metal ion or compound as a whole. For the hexaamminecobalt(3+) ion, $[Co(NH_3)_6]^{3+}$, and the neutral molecule triamminetrinitrocobalt(3+), $[Co(NO_2)_3(NH_3)_3]$, the coordination number of cobalt is 6 while its oxidation number is +3 (Cotton *et al.*, 1999). There are some donor atoms or groups which can offer more than one pair of electrons. Any donor atom will give a pair of electrons. There are some donor atoms or groups which can offer more than one pair of electrons. Such are called bidentate (offers two pairs of electrons) or polydentate (offers more than two pairs of electrons). In some cases, an atom or a group offers a pair of electrons to two similar or different central metal atoms or acceptors—by division of the electron pair into a three-center two-electron bond. These are called bridging ligands (Cotton *et al.*, 2006). The chemistry of transition metal complexes is dominated by interactions between S and P molecular orbitals of the donor atoms in the ligands and the d orbitals of the metal ions. The S, P, and d orbitals of the metal can accommodate 18 electrons (Miessler *et al.*, 1999). The maximum coordination number for a certain metal is thus related to the electronic configuration of the metal ion, to be more specific, the number of empty orbitals and to the ratio of the size of the ligands and the metal ion. Large metals and small ligands lead to high coordination numbers, for example $[Mo(CN)_8]^{4-}$. Metals with small size lead to low coordination numbers, for example $Pt[P(CMe_3)]_2$. Metal with large sizes such as lanthanides, actinides, and early transition metals tend to have high coordination numbers (Jeremy *et al.*, 1984). Most structures follow the points-on-a-sphere pattern or, as if the central atom were in the middle of a polyhedron where the corners of that shape are the locations of the ligands, where orbital overlap between ligand and metal orbitals and ligand-ligand repulsions tend to lead to certain regular geometries, but there are many cases that deviate from a regular geometry, due to the use of ligands of diverse types which results in irregular bond lengths, the coordination atoms do not follow a points-on-a-sphere pattern, due to the size of ligands, or due to electronic effects(Wells, 1984).

Complex formation involves an exchange of coordinated molecule, directly bonded to the central metal ion, for ligands on the condition that the ligand has an affinity for the metal ion strong enough to compete with that of the coordinated molecule.Coordination compounds are molecules that possess one or multiple metal centres that are bound to ligands (atoms, ions, or molecules that donate electrons to the metal). They are generally prepared by common methods such as substitution reactions, redox reactions and by the direct combination of the reactants.These complexes can be neutral or charged. When the complex is charged, it is stabilized by neighbouring counter-ions (Jackson *et al.*, 2004).A metal ion in solution does not exist in isolation, but in combination with ligands such as solvent molecules or simple ions or chelating groups, giving rise to complex ions or coordination compounds. These complexes contain a central atom or ion, often a transition metal, and a cluster of ions or neutral molecules surrounding it. Ligands are ions or neutral molecules that bond to a central metal atom or ion. Ligands act as Lewis bases (electron pair donors), and the central atom acts as a Lewis acid (electron pair acceptor). Ligands have at least one donor atom with an electron pair used to form covalent bonds with the central atom. The complexation of metals with ligands can drastically change the physicochemical and biological properties of the metal species (Gua *et al*., 1999).This present study aims to advance the growing interest in the synthesis of novel materials by the combination of organic and inorganic compounds by seeking to synthesize and characterize Ni(II) and Co(II) mixed ligand complexes of 2-phenyliminomethylphenol (PMP) and 2,2-hydroxybenzylideneaminophenol (HAP) and to investigate into the antimicrobial inhibitory action of the synthesized complexes.

2. Experimental Procedures

2.1 Synthesis of the ligand 2-phenyliminomethylphenol

A solution of 0.02M aniline in 20mL absolute ethanol was mixed with a solution of salicylaldehyde (0.02M) in 20 mL absolute ethanol in a 100mL round bottomed flask. Few drops of glacial acetic acid was then added and the mixture was heated under reflux at 50^{o}C with continuous magnetic stirring for 3 hours. The content was cooledto room temperature, producing a yellow precipitate which was washed several times using deionized water and then cold ethanol. Recrystallization was carried out with hot ethanol and the crystals were left to dry in the air.

2.2 Synthesis of the ligand 2,2-hydroxybenzyleneaminophenol

Salicylaldehyde (5.3 g) was refluxed with 2-aminophenol (5.5 g) in ethanol for 2 hours and an orange solution was obtained. The solution was reduced under suction and an orange precipitate was obtained. The precipitate was filtered under suction, washed with ethanol and recrystallized from ethanol. It was dried over silica gel in a desiccator.

2.3 Synthesis of mononuclear metal-ligand complexes of 2-phenyliminomethylphenol (PMP)

The metal complexesNi(II) andCo(II) were synthesized by adding 2-phenyliminomethylphenol ligand of 0.29 mmol into 30 mL of ethanol with the metal salts ($NiCl_2$ and $CoCl_2$) of 0.22 g, 1 mmol each. The solution was thoroughly mixed and the resulting mixture was refluxed at 60°C for 3 hours and allowed to cool. The crystals formed were then collected and purified by washing with ethanol and diethyl ether and finally air dried.

2.4 Synthesis of mononuclear metal ligand complexes of 2,2-hydroxybenzylideneaminophenol (HAP)

The metal complexes of Ni(II) and Co(II) were prepared by adding 2,2-hydroxybenzylideneaminoPhenol ligand of 0.29 mmol into 30 mL of ethanol with the metal salts ($NiCl_2$ and $CoCl_2$) of 0.22 g, 1 mmol. The solution was mixed thoroughly and the resulting mixture was refluxed at 60°C for 3 hours and allowed to cool. The crystals produced were then collected and purified by washing with ethanol and diethyl ether and finally air dried.

2.5 Synthesis of mononuclear metal mixed ligand complexes of 2-phenyliminomethylphenol (PMP) and 2,2hydroxybenzylideneaminophenol (HAP)

The metal complexes of Ni^{2+} and Co^{2+} were prepared by adding 2-phenyliminomethehylphenol ligand(PMP) of 0.29 mmol and 2,2-hydroxybenzylideneaminophenol (HAP) of 0.29mmole into 30 mL of ethanol with the metal salts ($NiCl_2$and $CoCl_2$) of 0.22 g, 1 mmol each. The solution, after thorough mixing, was heated under reflux at 60°C for 3 hours and allowed to cool. The crystals formed were collected and purified by washing with ethanol and diethyl ether and finally air dried.

2.6 Molar conductivity, Infrared, UV and X-ray diffractometric analyses of synthesized metal complexes

A 0.001 M solution of each complex was prepared in dimethyl sulfoxide (DMSO) as solvent to measure the molar conductance. The molar conductance of the complexes was then determined using the conductivity meter of Model EQ664 with inbuilt magnetic stirrer. The infrared spectra of the ligands and complexes were recorded in KBr pellets in the range (400 - 4000 cm-^{1}) on IR Affinity-1S FT-IR spectrophotometer. The UV spectrawere recorded on Aquamate Scientific spectrophotometer, model V 4.60. The X-Ray diffraction analysis of the mixed ligand complexes powder form was carried out on X-Ray diffractometer, Smartlab (Model VT/VRH/PXRD350), using CuKa radiation (α=1.54059A), the applied voltage and the tube current was 40Kv.

2.7 Proton nuclear magnetic resonance (H-NMR) spectral analysis

Proton NMR spectral analyses were recorded on NMR Spectrometer. Exactly 10mg of the recrystallized 2-phenyliminomethylphenol (PMP) and 2,2-hydroxybenzylideneaminophenol (HAP) were dissolved in a minimum amount of dimethyl sulphide and introduced into the NMR Spectrometer. The spectra were run at about 300MHz while the chemical shifts were quoted delta and related to that of the solvent.

2.8 GC-MS analysis

The GCMS analyses were carried out on Agilent GC 7890A coupled with a triple axis detector 5975 C single quadrupole mass spectrometer. The chromatographic column was an Agilent HP 5MS column (30 m × 0.25 mm × 0.25 μm film thickness), with high-purity helium as the gas carrier at a flow rate of 1 mL/min. The injector temperature was set at 250°C, and it was equipped with a splitless injector at 20:1. Other analytical conditions include a source temperature of MS at 230°C, quad temperature at 150°C, oven temperature at 40°C (held for 1 min) which then was increased to 150°C at 10°C min^{-1}(held for 1 minute), and then increased further to 300°C at10°C min^{-1} for 1 minute, injection volume of 1 μL, and a scan range of 50–800mass ranges at 70 eV electron energy and the solvent delay of 3 minutes. Subsequently, the unknown compounds were identified by comparing the spectra with that of the NIST 2008 (National Institute of Standard and Technology library). The total time required for analyzing a single sample was 30 minutes.

2.9 Antimicrobial studies

The clinical isolates of *Staphylococcus aureus* and *Bacillus substilis* representative of Gram-Positive Bacteria, then *Escherichia coli* and *Pseudomonas aeruginosa* representative of Gram-

Negative Bacteria then *Candida albicans* and Aspergillus niger representative of Fungi were collected. The isolates were subcultured on Sterile Nutrient agar. The antimicrobial activity of the Ni^{2+} and Co^{2+} complexes was antiseptically dropped into the agar wells, the already inoculated nutrient agar plates containing the test microbes were incubated at $37^{o}C$ for 24hours for the development of zones of inhibition, the zones of inhibition were observed and recorded.

3. Results and Discussion

3.1 Melting point and solubility characterization of metal complexes

The melting points(liquefaction points) of the prepared ligands and their complexes have been presented in Table 1, while the solubility characteristics of the prepared ligands and their complexes are presented in Table 2.

Table1. Ligands and complexes and their melting points

Ligands and Complexes	**Melting Point**
PMP	50°C
HAP	106°C
$[Ni(PMP)_2.Cl_2]$	77°C
$[Ni(HAP)_2.Cl_2]$	96°C
$[Ni(PMP+HAP).Cl_2]$	73°C
$[Co(PMP)_2.Cl_2]$	91°C
$[Co(HAP)_2.Cl_2]$	89°C
$[Co(PMP+HAP)_2.Cl_2]$	67°C

The melting point were significantly higher than ligand which was higher than the ligands 2-Phenyliminomethylphenol (PMP), 50°C and 2,2-hydroxy benzylidene aminophenol (HAP) 106°C except for 2,2-hydroxy benzylidene aminophenol (HAP) whose melting point is higher than some complexes with exception of Platinum complexes. The ligands 2-Phenyliminomethylphenol (PMP) and 2,2-hydroxybenzylideneaminophenol (HAP) have melting points higher than the melting points of all the complexes except one of the Nickel complexes$[Ni(HAP)_2.Cl_2]$ whose melting point was higher than that of ligand PMP.The decreases in melting point can be attributed to the increase in mass of the formed complexes and thus provided evidence for the formation of metal complexes. The melting points of the complexes were differently lower than that of the ligand 2,2-hydroxybenzylideneaminophenol (HAP) which may also be due to complexation (Ogwuegbu *etal.*, 1998). It is also observed that the melting points of mixed complexes were slightly lower than the unmixed complexes. This could be attributed to atomic size contraction as it is observed with a decrease in atomic number of the bivalent first transition series.

Solubility is the property of a substance that fundamentally depends on its physical and chemical properties and those of the solvent as well as on temperature, pressure and presence of other chemicals including changes to the pH of the solution. The data in Table 2 show the solubility of the prepared ligands and their metal complexes.

Table 2. Melting point and solubility values of the metal complexes

	Melting Point	Ac	MeOH	EtOH	Diethyl-ether	N-Hexane	CCl_4	Water	CS_2	DMSO
PMP	50°C	SS	SS	SIS	SS	IS	IS	IS	SS	SS
HAP	106°C	SS	MS	SIS	MS	IS	IS	IS	SIS	SS
[Ni(PMP)$_2$.Cl$_2$]	96°C	IS	IS	IS	SIS	IS	IS	IS	IS	SS
[Ni(HAP)$_2$.Cl$_2$]	73°C	MS	SIS	IS	IS	IS	IS	IS	IS	SS
[Ni(PMP+HAP).Cl$_2$]	72°C	MS	SIS	IS	IS	IS	IS	IS	IS	SS
[Co(PMP)$_2$.Cl$_2$]	91°C	SIS	IS	IS	IS	IS	IS	IS	IS	SS
[Co(HAP)$_2$.Cl$_2$]	89°C	IS	IS	IS	IS	IS	IS	IS	IS	SS
[Co(PMP+HAP)$_2$.Cl$_2$]	67°C	IS	IS	IS	IS	IS	IS	IS	IS	SS

SS: **Strongly Soluble;** MS: **Moderately Soluble;** IS: **Insoluble;** SIS: **Slightly Insoluble**

All the complexes formed as well as the two ligands were strongly soluble in dimethylysulfoxide (DMSO), but insoluble in n-Hexane, carbon tetrachloride, water, ethanol and carbon disulphide except the ligands which were at variance in ethanol and carbon disulphide. The ligand HAP was slightly insoluble in both ethanol and carbon disulphide while ligand PMP was slightly insoluble in ethanol but strongly soluble in carbon disulphide.The ligand PMP was strongly soluble in acetone, methanol and diethyl ether, while the ligand HAP was strongly soluble in acetone but moderately soluble in methanol and diethyl ether. All cobalt complexes were insoluble in acetone, methanol and diethyl ether, except complex [Co(PMP)$_2$.Cl$_2$] which was slightly insoluble in acetone. The Nickel complex [Ni(HAP)$_2$.Cl$_2$]and its mixed ligand complex [Ni(PMP+HAP).Cl$_2$]exhibited moderate solubility only in acetone and methanol.The results of the solubility of the Ligand and complexes formed provided information on the right solvent to be used for dissolution for further analysis and research.

3.2 NMR Analysis

The spectral data obtained from the proton NMR spectroscopic analysis of the ligands are presented in Appendix 1 and 2. The Schiff base ligands exist in enol tautomeric form and this is evident in the non-splitting of the methine proton and the appearance of the phenolic protons. The phenolic hydroxyl proton in the aldehyde moiety of the ligands appears as a broad singlet downfield at 8 - 9 ppm, while the broad signal at 9.79 - 9.77 ppm can be attributed to the hydroxyl proton of the *ortho*-aminophenol moiety. The broadness of the signals can be accounted for by a strong hydrogen bonding existing between the nitrogen atom of the imine and the hydroxyl protons. All the aromatic protons absorbed in the neighborhood of 6.50 - 7.50 ppm and amine NH_2 ($\delta = 3 – 4$ ppm); in the ligands spectra.

3.3 GC-MS Analysis

The results of the GC-MS characterization have been presented in Tables 3–10. The GC-MS reveals the structure-activities-functions of complexes following the fragmentation pattern and matching them with clinically relevant therapeutic molecules present. The gas chromatogram is presented in Appendix 3 to 22

Table 3.GC-MSfragments of sample A (PMP); Molecular ion of 2-Phenyliminomethylphenol (PMP) = 197.23g/mol

S/N	RT (min)	Area (Pct)	Name of Compounds	*m/z*	Mol. Weight	Mol. Formula
1	7.115	67,000	Mercaptamine	59	77.149g/mol	C_2H_7NS
2	9.909	45,000	Aniline	97	93.13 g/mol	$C_6H_5NH_2$
3	11.718	97,000	Benzaldehyde, 2-hydroxy-	96	122.1213g/mol	$C_7H_6O_2$
4	12.360	102,000	Benzaldehyde, 2-hydroxy-	94	122.1213g/mol	$C_7H_6O_2$
5	16.017	52,000	Fumaramic acid	37	116.07g/mol	$C_4H_4O_4$
6	20.978	94,000	Propanamide, N-acetyl-N-(3-Methylbutyl) acetamide	38	129.2001g/mol	$C_7H_{15}NO$
7	22.142	96,000	Decane	64	142.28g/mol	$C_{10}H_{22}$
8	26.493	120,000	7-Heptadecene, 1-chloro-	30	272.9g/mol	$C_{17}H_{33}Cl$
9	31.723	803,000	Salicylidene aniline	98	**197.23g/mol**	$C_{13}H_{11}NO$
10	32.094	11,000	Salicylidene aniline	95	197.23g/mol	$C_{13}H_{11}NO$
11	32.642	48,000	Hexadecanoic acid, ethyl ester	90	284.4772g/mol	$C_{18}H_{36}O_2$
12	33.487	726,000	9-Octadecenoic acid (Z)-, 2-hydroxy-1-(hydroxymethyl)ethyl ester	93	356.5g/mol	$C_{21}H_{40}O_4$
13	33.653	559,000	17-Pentatriacontene	96	490.9303g/mol	$C_{35}H_{70}$
14	33.989	115,000	9-Octadecenoic acid	94	282.5g/mol	$C_{18}H_{34}O_2$
15	34.172	46,000	5-Eicosene, (E)-	78	280.5316g/mol	$C_{20}H_{40}$
16	34.287	240,000	9-Octadecenamide, (Z)-	95	281.4766g/mol	$C_{18}H_{35}NO$
17	34.970	267,000	9-Octadecenoic acid (Z)-, 2,3-dihydroxypropyl ester	90	356.5399g/mol	$C_{21}H_{40}O_4$
18	35.097	133,000	1H-Indene, 5-butyl-6-hexyloctahydro-	60	264.5g/mol	$C_{19}H_{36}$
19	35.912	3,999,000	9-Octadecenamide, (Z)-	96	281.4766g/mol	$C_{18}H_{35}NO$
20	36.138	383,000	Octadecanamide	93	283.5g/mol	$C_{18}H_{37}NO$
21	36.766	1,997,000	Oleic Acid	80	282.5g/mol	$C_{18}H_{34}O_2$

Table 4. Showing GC-MS fragments of Sample B (HAP); Molecular Ion of 2,2-Hydroxybenzylideneaminophenol (HAP) = 214.34g/mol

S/N	RT (min)	Area (Pct)	Name of Compounds	*m/z*	Mol. Weight	Mol. Formula
1	5.817	267,000	2-Hexanol, 3-methyl-	53	116.2013g/mol	$C_7H_{16}O$
2	10.888	209,000	Ethanol, 2-bromo-	38	124.96g/mol	C_2H_5BrO
3	13.522	162,000	3-Pentanone, dimethylhydrazone	50	128.22g/mol	$C_7H_{16}N_2$
4	20.845	246,000	4-Hexenoic acid, 6-hydroxy-4-methyl-, methyl ester, (E)-	40	158.19g/mol	$C_8H_{14}O_3$

5	32.7164	1,144,360	Undecanoic acid, ethyl ester	49	**214.3443g/mol**	$C_{13}H_{26}O_2$
5	29.087	863,000	2-Methyl-Z,Z-3,13-octadecadienol	78	280.5g/mol	$C_{19}H_{36}O$
6	32.094	37,000	Hexadecanoic acid, methyl ester	60	270.4507g/mol	$C_{17}H_{34}O_2$
7	32.643	90,000	Hexadecanoic acid, ethyl ester	64	284.4772g/mol	$C_{18}H_{36}O_2$
8	33.482	220,000	9,17-Octadecadienal, (Z)-	83	264.4g/mol	$C_{18}H_{32}O$
9	33.674	46,000	Heptadecanoic acid, heptadecyl ester	55	354.6g/mol	$C_{23}H_{46}O_2$
10	34.000	187,000	9-Octadecenoic acid	95	282.5g/mol	$C_{18}H_{34}O_2$
11	34.179	106,000	Oleic Acid	41	282.5g/mol	$C_{18}H_{34}O_2$
12	35.107	1,098,000	Octadecanal	83	268.4778g/mol	$C_{18}H_{36}O$
13	35.755	6,420,000	17-Pentatriacontene	95	490.9303g/mol	$C_{35}H_{70}$
14	36.772	51,000	cis-13-Octadecenoic acid	53	282.5g/mol	$C_{18}H_{34}O_2$

Table 5. Showing GC-MS fragments of Sample I [Ni(PMP)$_2$.Cl$_2$] Molecular Ion of [Ni(PMP)$_2$.Cl$_2$] = 615.69g/mol

S. no.	RT (min)	Area (Pct)	Name of Compounds	*m/z*	Mol. Weight	Mol. Formula
1	6.0805	205,200	Urethane	35	89.09g/mol	$C_3H_7NO_2$
2	7.0637	183,530	3-Heptafluorobutyroxydodecane	22	348.26g/mol	$C_{14}H_{15}F_7O_2$
3	8.3915	107,620	Diglycolamine	50	105.14g/mol	$C_4H_{11}NO_2$
4	9.6157	149,190	Urethane	59	89.09g/mol	$C_3H_7NO_2$
5	10.9067	129,710	Buthanal, 3-hydroxyl-	64	88.11g/mol	$C_4H_8O_2$
6	11.5843	144,660	Tetrahydro-4H-pyran-4-ol	70	102.13g/mol	$C_5H_{10}O_2$
7	12.1851	135,590	8-[N-Aziridylethylamino]-2,6-dimethyloctene-2	52	142.28g/mol	$C_{10}H_{22}$
8	12.848	122,140	Succinamic acid	47	118.09g/mol	$C_4H_6O_4$
9	14.6672	90,190	Bis(dimethylamino)phosphinic chloride	47	170.58g/mol	$C_4H_{12}CIN_2OP$
10	15.6973	143,650	Cyclohexanone, dimethylhydrazone	53	140.23g/mol	$C_8H_{16}N_2$
11	16.7621	49,060	Thiophene-3-ol, tetrahydro-,1,1-dioxide	43	136.17g/mo	$C_4H_8O_3S$
12	17.6913	112,850	Metanephrine	47	197.23g/mol	$C_{10}H_{15}NO_3$
13	19.2269	120,870	N-(3,5-Dinotropyridin-2-yl)-L-aspartic acid	53	300.18g/mol	$C_9H_8N_4O_8$
14	20.3436	29,870	Butylated Hydroxytoluene	96	220.35g/mol	$C_{15}H_{24}O$
15	20.9675	114,300	Metaraminol	53	167.20g/mol	$C_9H_{13}NO_2$
16	22.9912	105,120	N-Methoxy-1-ribofuranosyl-4-imadazolecarboxylic amide	53	273.24g/mol	$C_{10}H_{15}N_3O_6$

17	25.2286	149,270	Thiophene-3-ol, tetrahydro-,1,1-dioxide	53	136.17g/mol	$C_4H_8O_3S$
18	26.4786	136,590	5-Nitro-3-cyano-2(1H)-pyridone	43	149.11g/mol	$C6H3N3O_2$
19	28.0972	153,760	2-Oxo-3-methyl-cis-perhydro-1,3-benzoxazine	59	169.22g/mol	$C_9H_{15}NO_2$
20	29.255	28,900	Pentadecanoic acid, 14-methyl-, methyl ester	98	270.5g/mol	$C_{17}H_{34}O_2$
21	29.7656	10,660	1,2-Benzenedicarboxylic acid, bis(2-methylpropyl) Ester	86	278.34g/mol	$C_{16}H_{22}O_4$
22	30.0121	155,970	Hexadecanoic acid, ethyl ester	98	284.5g/mol	$C_{18}H_{36}O_2$
23	30.783	343,740	Oleic acid	60	282.5g/mol	$C_{18}H_{34}O_2$
24	30.8918	335,970	9,12-Octadecadienoic acid, methyl ester	99	294.4721g/mol	$C_{19}H_{34}O_2$
25	30.9341	200,360	9-Octadecenoic acid (Z)-, methyl ester	99	296.5g/mol	$C_{19}H_{36}O_2$
26	31.1297	14,000	Tetradecanoic acid, 12-methyl-, methyl ester	90	256.4g/mol	$C_{16}H_{32}O_2$
27	31.4124	198,870	Ethyl Oleate	98	310.51g/mol	$C_{20}H_{38}O_2$
28	31.5822	72,420	Octadecanoic acid, ethyl ester	98	310.5g/mol	$C_{20}H_{38}O_2$
29	32.0118	108,590	6-Octadecenoic acid, (Z)-	53	282.5g/mol	$C_{18}H_{34}O_2$
30	32.2306	55,780	cis-Vaccenic acid	62	282.5g/mol	$C_{18}H_{34}O_2$
31	32.4127	86,580	Oleic acid	45	282.46g/mol	$C_{18}H_{34}O_2$
32	32.5863	76,510	Oleic acid	50	282.46g/mol	$C_{18}H_{34}O_2$
33	32.7131	117,960	Octadecanoic acid, ethyl ester	43	312.53g/mol	$C_{20}H_{38}O_2$
33	32.8399	159,410	4,4-diaminodichloro N-tritriacontanoic acid	30	**615.69g/mol**	$C_{33}H_{56}Cl_2N_2O_4$
34	33.6725	2,839,010	Oleic acid	25	282.46g/mol	$C_{18}H_{34}O_2$
35	34.9587	214,830	Oleic acid	60	282.46g/mol	$C_{18}H_{34}O_2$
36	35.4475	269,210	6-Octadecenoic acid, (Z)-	59	282.5g/mol	$C_{20}H_{38}O_2$
37	35.7957	321,660	Trichothec-9-en-4-ol, 7,8:12,13-diepoxy-, 2-butenoate, [4.beta.(Z)]	60	250.33g/mol	
38	36.3829	2,065,820	Z-8-Pentadecen-1-ol acetate	48	268.4g/mol	$C_{17}H_{32}O_2$

Table 6. Showing GC-MS Fragments Of Sample J [Ni(HAP).Cl_2]; Molecular Ion of [Ni(HAP).Cl_2] = 649.69g/mol

S. no.	**RT (min)**	**Area (Pct)**	**Name of Compounds**	***m/z***	**Mol. Weight**	**Mol. Formula**
1	6.0223	420,660	Aniline	97	93.13g/mol	C_6H_7N
2	6.9871	160,830	Cyclohexene, 1-methyl-5-(methylethenyl)-	53	136.23g/mol	$C_{10}H_{16}$

3	7.5623	253,600	Benzaldehyde, 2-hydroxyl-	97	122.12g/mol	$C_7H_6O_2$
4	7.8441	200,520	Benzaldehyde, 2-hydroxyl-	94	122.12g/mol	$C_7H_6O_2$
5	8.5732	7,730	2-(Oxan-3-yl)ethanamine	43	227.34g/mol	$C_{13}H_{25}NO_2$
6	8.6896	48,650	.beta.-Chloroethylurea	46	185.05g/mol	$C_5H_{10}Cl_2N_2O$
7	8.7184	44,170	Levonordefrin	25	183.20g/mol	$C_9H_{13}NO_3$
8	9.3041	83,620	Ethanone, 1-phenyl-, o-(4-coumarinyl)oxime	50	135.16g/mol	C_8H_9NO
9	9.6296	13,840	N,N'-Dicarbethoxy-N-[2,4-diamino-6-hydroxy -5-pyrimidinyl]hydrazine	38	169.14g/mol	$C_5H_7N_5O_2$
10	9.6947	32,100	Urethane	27	89.09g/mol	$C_3H_7NO_2$
11	9.7255	25,570	N,N-Dimethylacetoacetamide	47	129.16g/mol	$C_6H_{11}NO_2$
12	11.2708	34,960	Diglycolamine	43	105.136g/mol	$C_4H_{11}NO_2$
13	11.2894	24,030	1,2,4-Triazole, 4-[N-(2-hydroxyethyl)-N-nitro] amino-	37	173.13g/mol	$C_4H_7N_5O_3$
14	12.7477	14,900	1-Dodecanamine	47	185.35g/mol	$C_{12}H_{27}N$
15	12.8211	72,640	1-Octanamine	53	129.24g/mol	$C_8H_{19}N$
16	14.2078	38,820	Thiophene-3-ol, tetrahydro-,1,1-dioxide	43	136.17g/mol	$C_4H_8O_3S$
17	14.2253	8,390	Tetrahydro-4H-pyran-4-ol	47	102.13g/mol	$C_5H_{10}O_2$
18	14.2652	21,230	N-Methoxy-1-ribofuranosyl-4-imidazolecarboxylic amide	72	273.24g/mol	$C_{10}H_{15}N_3O_6$
19	14.2816	17,260	2-(Oxan-3-yl)ethanamine	64	129.20g/mol	$C_7H_{15}NO$
20	14.8692	75,860	1-Pentanol, 4-amino-	50	143.65g/mol	$C_5H_{14}CINO$
21	14.9356	17,850	Cycloserine	47	102.09g/mol	$C_3H_6N_2O_2$
22	15.6756	72,780	N,N-Dimethylacetamide	53	87.12g/mol	C_4H_9NO
23	15.723	19,510	Propanenitrile, 3-amino-2,3-di(hydroxymino)-	50	84.12g/mol	$C_4H_5N_2$
24	16.3878	76,510	1-Decanamine	43	157.30g/mol	$C_{10}H_{23}N$
25	16.7592	12,180	Benzaldehyde, 4-ethoxy-	47	150.17g/mol	$C_9H_{10}O_2$
26	17.9326	42,170	1-hexadecanesulfonamide, N-(2-aminoethyl)-	53	349.6g/mol	$C_{18}H_{39}NO_3S$
27	17.9669	16,520	Propanenitrile, 3-amino-2,3-di(hydroxymino)-	47	84.12g/mol	$C_4H_5N_2$
28	19.5522	102,320	Benzenepropanamine, .alpha.-methyl-	46	149.23g/mol	$C_{10}H_{15}N$
29	20.3521	16,570	Butylated Hydroxytoluene	98	220.35g/mol	$C_{15}H_{24}O$
30	21.4043	41,400	N-Formyl-di-alanine	50	117.10g/mol	$C_4H_7NO_3$

31	21.4616	29,870	Bis(dimethylamino)phosphinic chloride	50	170.58g/mol	$C_4H_{12}ClN_2OO$
32	23.3563	31,250	Pterin-6-carboxylic acid	52	207.15g/mol	$C_7H_5N_5O_3$
33	23.4097	13,900	Urea, formyltrimethyl-	50	130.15g/mol	$C_5H_{10}N_2O_2$
34	23.4307	26,720	Ethanedial, bis(dimethylhydrazone)	47	142.20g/mol	$C_6H_{14}N_4$
35	24.9611	69,830	Dimefox	59	154.125g/mol	$C_4H_{12}FN_2OP$
36	26.2829	61,360	1,2-Benzenediol, 4-(2-amino-1-hydroxypropyl)-	30	183.20g/mol	$C_9H_{13}NO_3$
37	26.3399	29,040	Propanenitrile, 3-(methylamino)-	43	84.12g/mol	$C_4H_8N_2$
38	28.1873	662,820	Salicylidene aniline	99	197.23g/mol	$C_{13}H_{11}NO$
39	28.4433	17,960	Salicylidene aniline	98	197.23g/mol	$C_{13}H_{11}NO$
40	28.4963	58,760	Salicylidene aniline	97	197.23g/mol	$C_{13}H_{11}NO$
41	28.5294	44,440	Salicylidene aniline	95	197.23g/mol	$C_{13}H_{11}NO$
42	28.5834	48,970	Salicylidene aniline	91	197.23g/mol	$C_{13}H_{11}NO$
43	29.264	26,450	Hexadecanoic acid, methyl ester	97	270.45g/mol	$C_{17}H_{34}O_2$
44	30.0195	112,840	Hexadecanoic acid, ethyl ester	98	284.5g/mol	$C_{18}H_{36}O_2$
45	30.853	5,240	Oleic acid	46	282.46g/mol	$C_{18}H_{34}O_2$
46	30.9019	40,040	9,12-Octadecadienoic acid, methyl ester	99	294.5g/mol	$C_{19}H_{36}O$
47	30.9437	110,360	9-Octadecenoic acid (Z)-, methyl ester	99	296.5g/mol	$C_{19}H_{36}O$
48	31.1364	26,230	Methyl stearate	95	298.5g/mol	$C_{19}H_{38}O_2$
49	31.1799	4,930	Oleic acid	78	282.46g/mol	$C_{18}H_{34}O_2$
50	31.4197	2,391,630	(E)-9-Octadecenoic acid, ethyl ester	91	310.5g/mol	$C_{20}H_{38}O_2$
51	31.5832	522,590	Octadecanoic acid, ethyl ester	99	310.5g/mol	$C_{20}H_{38}O_2$
52	32.4145	3,660	9-Oxabicyclo[6.1.0]nonane, cis-	35	140.18g/mol	$C_8H_{12}O_2$
53	32.5934	2,820	Oleic acid	64	282.46g/mol	$C_{18}H_{34}O_2$
54	32.7185	9,840	Oleic acid	80	282.46g/mol	$C_{18}H_{34}O_2$
55	33.6825	35,350	Cyclohexadecane, 1,2-diethyl-	72	280.5g/mol	$C_{20}H_{40}$
56	33.7865	15,410	Z-8-Pentadecen-1-ol acetate	46	282.5g/mol	$C_{18}H_{34}O_2$
57	33.8921	83,240	Oleic acid	56	282.46g/mol	$C_{18}H_{34}O_2$
58	34.3625	895,110	Oleic acid	64	282.46g/mol	$C_{18}H_{34}O_2$
59	34.3883	102,870	Oleic acid	46	282.46g/mol	$C_{18}H_{34}O_2$
60	34.4146	177,680	Z-6-Pentadecen-1-ol acetate	38	268.4g/mol	$C_{17}H_{32}O_2$
61	34.4512	591,000	9-Octadecenoic acid (Z)-, 2,3-dihydroxypropyl			

			ester	20	372.5g/mol	$C_{21}H_{40}O_5$
61	34.4878	413320	2,4-diaminodichloro(N-pentatriaconnanoic acid)	38	**649.69g/mol**	$C_{35}H_{66}Cl_2N_2O_4$
62	35.4627	63,340	Z-8-Pentadecen-1-ol acetate	55	268.4g/mol	$C_{17}H_{32}O_2$
63	35.4923	12,330	Z-8-Pentadecen-1-ol acetate	66	268.4g/mol	$C_{17}H_{32}O_2$
64	35.5402	29,180	Oleic acid	38	282.46g/mol	$C_{18}H_{34}O_2$
65	35.5632	14,260	Ethanol, 2-bromo-	27	124.96g/mol	C_2H_5BrO
66	35.6222	43,380	Z-6-Pentadecen-1-ol acetate	47	268.4g/mol	$C_{17}H_{32}O_2$
67	35.8091	359,060	1,5,9-Undecatriene, 2,6,10-trimethyl-, (Z)-	86	192.34/mol	$C_{14}H_{24}$
68	36.0246	488,860	Z-10-Pentadecen-1-ol acetate	53	226.40g/mol	$C_{15}H_{30}O$
69	36.044	74,740	Z-8-Pentadecen-1-ol acetate	52	268.4g/mol	$C_{17}H_{32}O_2$
70	36.0806	174,310	6-Octadecenoic acid, (Z)-	50	282.5g/mol	$C_{18}H_{34}O_2$
71	36.1092	471,140	9-Octadecenoic acid (Z)-, 2,3-dihydroxypropyl ester	35	372.5g/mol	$C_{21}H_{40}O$

Table 7. Showing GC-MS fragments of Sample K [Ni(PMP+HAP)$_2$.Cl$_2$]; Molecular Ion of [Ni(PMP+HAP)$_2$.Cl$_2$] =632.69g/mol

S. no.	RT (min)	Area (Pct)	Name of Compounds	*m/z*	Mol. Weight	Mol. Formula
1	5.8520	169,760	Methyl 4,6-decadienyl ether	27	168.28g/mol	$C_{11}H_{20}O$
2	5.8516	109,610	Formic acid, 1-methylpropyl ester	22	102.1317g/mol	$C_5H_{10}O$
3	6.6012	141,080	1-Nonanamine	38	143.2697g/mol	$C_9H_{21}N$
4	6.6329	61,560	2-(Oxan-3-yl)ethanamine	45	129.2g/mol	$C_7H_{15}NO$
5	7.9142	164,210	2-(Oxan-3-yl)ethanamine	50	129.2g/mol	$C_7H_{15}NO$
6	9.2011	127,320	Benzeneethanamine,2-fluoro-.beta.,3-dihydroxy-N-methyl-	47	185.20g/mol	$C_9H_{12}FNO_2$
7	9.2404	56,740	Diglycolamine	47	105.1356g/mol	$C_4H_{11}NO_2$
8	10.5349	46,120	dl-Allo-cystathionine	32	222.26g/mol	$C_7H_{14}N_2O_4S$
9	10.5827	67,540	N,N-Dimethylethanesulfonamide	43	137.20g/mol	$C_4H_{11}NO_2S$
10	12.0762	55,180	5-Nonanone, dimethylhydrazone	45	184.32g/mol	$C_{11}H_{24}N_2$
11	12.1741	87,880	2-Amino-4-dimethylaminomethylenepentane dinitrile	53	126.20g/mol	$C_7H_{14}N_2$
12	13.5582	141,440	Uramil-N,N-diacetic acid	43	259.17g/mol	$C_8H_9N_3O_7$

13	15.0609	93,350	2-Methylaminomethyl-1,3-dioxolane	58	117.15g/mol	$C_5H_{11}NO_2$
14	17.1209	100,790	3-Azabicyclo[3.3.1]nonan-9-one, 3-methyl-	52	139.19g/mol	$C_8H_{13}NO$
15	18.9062	120,430	3,6-Dimethylpiperazine-2,5-dione	53	142.16g/mol	$C_6H_{10}N_2O_2$
16	20.3525	272,020	Butylated Hydroxytoluene	92	220.35g/mol	$C_{15}H_{24}O$
17	21.7223	146,110	Imidazole, 2-amino-5-[(2-carboxy)vinyl]-	49	153.14g/mol	$C_6H_7N_3O_2$
18	24.7809	137,580	Benzenemethanol, .alpha.-[(methylamino)methyl]-	47	165.2322g/mol	$C_{10}H_{15}NO$
19	267475	281,890	E-15-Heptadecenal	95	252.4354g/mol	$C_{17}H_{32}O$
20	28.5323	139,970	Phenylephrine	50	167.20 g/mol	$C_9H_{13}NO_2$
21	28.6025	84,430	Phenylephrine	53	167.20 g/mol	$C_9H_{13}NO_2$
22	29.2581	41,730	Hexadecanoic acid, methyl ester	97	270.4507g/mol	$C_{17}H_{34}O$
23	30.0167	527,620	Hexadecanoic acid, ethyl ester	98	284.4772g/mol	$C_{18}H_{36}O$
24	30.4165	477,090	Oleic acid	51	282.46g/mol	$C_{18}H_{34}O_2$
25	30.8994	29,820	9,12-Octadecadienoic acid, methyl ester	99	294.4721g/mol	$C_{19}H_{34}O_2$
26	30.9419	71,670	9-Octadecenoic acid (Z)-, methyl ester	99	296.4879g/mol	$C_{19}H_{36}O_2$
27	31.4168	498,290	Ethyl Oleate	91	310.5g/mol	$C_{20}H_{38}O_2$
28	31.5865	186,770	Octadecanoic acid, ethyl ester	99	312.5304g/mol	$C_{20}H_{40}O_2$
28	31.7562	311,520	4,4-diaminodichloro-pentatriaconanoic acid	86	**632.69g/mol**	$C_{34}H_{61}Cl_2N_2O_4$
29	32.0171	172,970	cis-Vaccenic acid	93	282.5g/mol	$C_{18}H_{34}O_2$
30	32.0661	49,220	Oleic acid	95	282.46g/mol	$C_{18}H_{34}O_2$
31	32.2392	220,020	6-Octadecenoic acid, (Z)-	64	282.4614g/mol	$C_{18}H_{34}O$
32	32.5924	1,234,590	cis-11-Eicosenoic acid	89	310.5145g/mol	$C_{20}H_{38}O_2$
33	32.7164	1,144,360	Undecanoic acid, ethyl ester	49	214.3443g/mol	$C_{13}H_{26}O_2$
34	37.0392	2,023,430	n-Propyl 11-octadecenoate	55	324.5g/mol	$C_{21}H_{40}O$
35	37.0613	717,390	cis-9-Octadecenoic acid, propyl ester	38	324.5g/mol	$C_{21}H_{40}O_2$

Table 8. Showing GC-MS fragments of Sample L [Co(PMP)$_2$.Cl$_2$]; Molecular Ion of [Co(PMP)$_2$.Cl$_2$] = 523.93g/mol

S. no.	**RT (min)**	**Area (Pct)**	**Name of Compounds**	***m/z***	**Mol. Weight**	**Mol. Formula**
1	5.739	58,000	2-Hexanol, 3-methyl-	38	116.20g/mol	$C_7H_{16}O$
2	5.804	78,000	2-Decanol	47	158.28g/mol	$C_{10}H_{22}O$
3	8.309	122,000	1-Methoxymethoxy-hexa-2,4-diene	38	142.20g/mol	$C_8H_{14}O_2$
4	8.386	85,000	(4-Methoxymethoxy-hex-5-ynylidene) –			

			cyclohexane	2	222.32g/mol	$C_{14}H_{22}O_2$
5	9.967	738,000	Aniline	97	93.13g/mol	$C_6H_5NH_2$
6	11.788	465,000	Benzaldehyde, 2-hydroxy-	94	122.1213g/mol	$C_7H_6O_2$
7	17.994	92,000	Benzeneethanamine, .alpha.,2,6-trimethyl-, (.+/-.)-	22	163.26g/mol	$C_{11}H_{17}N$
8	18.036	36,000	Ethyl 3-methyl-8-[p-sulfamylbenzylamino]pyrido[2,3-b] pyrazin-6-carbamate	27	416.5g/mol	$C_{18}H_{20}N_6O_4S$
9	24.780	190,000	Oxacycloheptadecan-2-one	60	254.41g/mol	$C_{16}H_{30}O_2$
10	30.776	9,000	Pentadecafluorooctanoic acid, dodecyl ester	35	582.3873g/mol	$C_{20}H_{25}F_{15}O_2$
11	31.705	1,073,000	Salicylidene aniline	98	197.23g/mol	$C_{13}H_{11}NO$
12	32.093	304,000	Hexadecanoic acid, methyl ester	83	270.4507g/mol	$C_{17}H_{34}O_2$
13	32.507	2,133,000	n-Propyl 9-hexadecenoate	86	296.5g/mol	$C_{19}H_{36}O_2$
14	32.628	876,000	Hexadecanoic acid, ethyl ester	97	284.4772g/mol	$C_{18}H_{36}O_2$
15	33.480	141,000	(S)(+)-Z-13-Methyl-11-pentadecen-1-ol acetate	78	282.5 g/mol	$C_{18}H_{34}O_2$
16	33.660	68,000	cis-13-Octadecenoic acid	78	282.5g/mol	$C_{18}H_{34}O_2$
17	33.992	476,000	9-Octadecenoic acid	94	282.5g/mol	$C_{18}H_{34}O_2$
18	34.176	276,000	Octadecanoic acid, ethyl ester	89	312.5304g/mol	$C_{20}H_{40}O_2$
19	34.592	2,718,000	2-Methyl-Z,Z-3,13-octadecadienol	84	280.5g/mol	$C_{19}H_{36}O$
20	35.008	2,442,000	2,3-diaminodichloro (Heptacosanonic acid)	67	**523.93g/mol**	$C_{27}H_{36}Cl_2N_2O_4$
20	35.966	42,000	Oleic Acid	70	282.5g/mol	$C_{18}H_{34}O_2$
21	36.173	7,000	Oleic Acid	86	282.5g/mol	$C_{18}H_{34}O_2$
22	36.200	7,000	Oleic Acid	53	282.5g/mol	$C_{18}H_{34}O_2$
23	36.451	4,000	Oleic Acid	93	282.5g/mol	$C_{18}H_{34}O_2$
24	36.595	1,000	Disparlure	49	282.5 g/mol	$C_{19}H_{38}O$

Table 9. Showing GC-MS fragments of Sample M [Co(HAP)$_2$.Cl$_2$]; Molecular Ion of [Co(HAP)$_2$.Cl$_2$] = 557.93g/mol

S. no.	**RT (min)**	**Area (Pct)**	**Name of Compounds**	***m/z***	**Mol. Weight**	**Mol. Formula**
1	5.350	346,000	2-Hexanol, 3-methyl-	40	116.2013g/mol	$C_7H_{16}O$
2	6.027	195,000	2-Octanol, (R)-	43	130.23g/mol	$C_8H_{18}O$
3	7.231	333,000	Ethanamine, 2-propoxy-	52	103.16g/mol	$C_5H_{13}NO$
4	9.800	160,000	(9Z,12Z,15Z)-2,3-Dimethoxypropyl octadeca-9,12,15-trienoate	43	380.5613g/mol	$C_{23}H_{40}O_4$
5	13.887	455,000	Ethanol, 2-bromo-	46	124.96g/mol	C_2H_5BrO
6	14.992	203,000	2(1H)-Benzocyclooctenone, decahydro-4a-methyl-, trans-(-)-	59	194.31g/mol	$C_{13}H_{22}O$
7	21.441	242,000	1,2,4-Triazole, 4-[N-(2-hydroxyethyl)-N-nitro]			

			amino-	14	173.13g/mol	$C_4H_7N_5O_3$
8	29.274	1,054,000	1-Pentadecene	92	210.40g/mol	$C_{15}H_{30}$
9	30.789	5,000	8-Bromooctanoic acid, ethyl ester	38	251.16g/mol	$C_{10}H_{19}BrO_2$
10	31.830	116,000	Dodecyl propyl ether	43	228.4140g/mol	$C_{15}H_{32}O$
11	31.830	111,000	Hexadecanoic acid, methyl ester	78	270.4507g/mol	$C_{17}H_{34}O_2$
12	32.641	461,000	Hexadecanoic acid, ethyl ester	95	284.4772g/mol	$C_{18}H_{36}O_2$
13	33.489	1,835,000	cis-Vaccenic acid	90	282.5g/mol	$C_{18}H_{34}O_2$
14	33.846	4,484,000	2-Methyl-Z,Z-3,13-octadecadienol	84	280.5g/mol	$C_{19}H_{36}O$
15	34.203	2,649,000	4,4-diaminodichloro Nonacosanoic acid	90	**557.93g/mol**	$C_{29}H_{46}Cl_2N_2O_4$

Table 10. Showing GC-MS fragments of Sample N [Co(PMP+HAP).Cl_2]; Molecular Ion of [Co(PMP+HAP).Cl_2] = 540.93g/mol

S. no.	RT (min)	Area (Pct)	Name of Compounds	*m/z*	Mol. Weight	Mol. Formula
1	7.180	192,000	2-Hexanol	38	102.17g/mol	$C_6H_{14}O$
2	10.786	182,000	2-Propanol, 1-bromo-	43	138.99g/mol	C_3H_7BrO
3	11.802	100,000	Benzaldehyde, 2-hydroxy-	95	122.1213g/mol	$C_7H_6O_2$
4	12.126	135,000	Benzaldehyde, 2-hydroxy-	90	122.1213g/mol	$C_7H_6O_2$
5	18.149	111,000	Acetic acid, cyano-	43	85.06g/mol	$C_3H_3NO_2$
6	26.041	330,000	E,E-1,9,17-Docasatriene	38	304.6g/mol	$C_{22}H_{40}$
7	29.958	-5,000	Bis(2-ethylhexyl) phthalate	72	390.6g/mol	$C_{24}H_{38}O_4$
8	30.122	32,000	Diisooctyl phthalate	35	390.6g/mol	$C_{24}H_{38}O_4$
9	30.790	133,000	Estra-1,3,5(10)-trien-17.beta.-ol	76	256.3826g/mol	$C_{18}H_{24}O$
10	31.841	3,44				
12	33.481	57,000	Palmitoleic acid	62	254.41g/mol	$C_{16}H_{30}O_2$
13	33.670	14,000	Heptadecanoic acid, heptadecyl ester	70	354.6g/mol	$C_{23}H_{46}O_2$
14	33.999	41,000	9-Eicosenoic acid, (Z)-	93	310.5145g/mol	$C_{20}H_{38}O_2$
15	34.179	28,000	Octadecanoic acid, ethyl ester	83	312.5304g/mol	$C_{20}H_{40}O_2$
16	34.970	33,000	6-Octadecenoic acid, (Z)-	60	282.4614g/mol	$C_{18}H_{34}O_2$
17	35.099	22,000	Oleic Acid	70	282.5g/mol	$C_{18}H_{34}O_2$
18	36.810	1,335,000	Squalene	97	410.7g/mol	$C_{30}H_{50}$
19	37.163	3,772,000	17-Pentatriacontene	89	490.9303g/mol	$C_{35}H_{70}$
20	37.516	2,437,000	2,4-diaminodichlorooctacosanoic acid	65	**540.93g/mol**	$C_{28}H_{41}Cl_2N_2O_4$

All complexes were identified and confirmed by matching their molecular ion, mass fragmentation pattern with respect to mass to charge ratio of the chromatograms. The detected compounds/fragments belonged to unsaturated phenolic moiety, an indication of potential activity. Database used for the elucidation of constituents employed Shaimadzu GC-MS library Class-5000, ver2.0(1996) software and NIST Mass Spectral Search Program for the NIST/EPA/NIH Mass Spectral library ver.16d(06/24/1998), Gaithersburg MD, USA. Available literature revealed that a number of the identified constituents were pharmacologically active compounds and proved to possess therapeutic activities which may contribute to the antimicrobial inhibitory potency observed and recorded. The constituents could also possibly possess anticancer, antitumor, antimutagenic anti-inflammatory properties. Again, the identified fragmented compounds in the complexes serve as the basis for the determination of bioactive therapeutic constituents present and other possible health benefits of the metal complexes, leading to further pharmaceutical and biological studies regarding their anticancer, antimutagenic, antitumor and anti-inflammatory applications.

3.4 FTIR Spectra

Tables 11–18 show the FTIR spectra of the ligands, their metal complexes and the mixed ligand metal complexes.

Table 11. Showing the FTIR spectrum data for the ligand 2-phenyliminomethylphenol (PMP) of the characteristics of infrared absorption frequencies

Assignment of Bond	**Frequency Range in cm^{-1}**	**Functional Group Type**
vC=N stretching	1569.2	Aromatic Amines
C-H bending	1613.9	Aromatic Amines
C-H bending	1833.3	Aromatic ring
C-H bending	1919.6	Aromatic ring
vC=N stretching	2109.7	Aromatic Amines
vC-H stretching	2653.9	Aromatic ring
vC-H stretching	2713.5	Aromatic ring
vC-H stretching	2851.4	Aromatic ring
vC-H stretching	2991.9	Aromatic ring
vC-H vibrations in ring	3056.4	Aromatic ring
vO-H	3213.0	Phenolic
vO-H	3652.8	Phenolic

Table 12. Showing the FTIR spectrum data for the ligand2,2-hydroxy benzylidene aminophenol (HAP) of the characteristics infrared absorption frequencies

Assignment of Bond	**Frequency Range in cm^{-1}**	**Functional Group Type**
vC-H stretching	1528.2	Aromatic ring
vC-H stretching	1804.8	Aromatic ring
vC-H stretching	1848.0	Aromatic ring
vC-H vibrations in ring	1990.4	Aromatic ring
vC-H stretching	2113.4	Aromatic ring
vC-H stretching	2374.3	Aromatic ring
vC-H stretching	2542.0	Aromatic ring
vC-H stretching	2691.1	Aromatic ring

vC-H stretching	2851.4	Aromatic ring
vC-H stretching	2926.0	Aromatic ring
vC-H vibrations in ring	3045.2	Aromatic ring
vO-H	3634.2	Phenolic
vO-H	3678.9	Phenolic

Assignment of Bond	**Frequency Range in cm^{-1}**	**Functional Group Type**
vC=C aromatic	1569.2	Aromatic Alkenes
vC=N bending	1613.9	Aromatic Amines
vC=N bending	1796.6	Aromatic Amines
C-H bending (aromatic)	1882.3	Aromatic Ring
C-H bending (aromatic)	1949.4	Aromatic Ring
vC=N stretching	2109.7	Aromatic Amines
vC=N stretching	2370.6	Aromatic Amines
vC-H stretching	2650.1	Aromatic Ring
vO-H	3324.9	Phenolic
vO-H	3652.8	Phenolic
vO-H	3712.4	Phenolic
vO-H	3753.4	Phenolic

Table 13. Showing the FTIR spectrum data for 2-phenyliminomethylphenol Nickel(II)chloride complex of the characteristics infrared absorption frequencies

Table 14. Showing the FTIR spectrum data for 2,2-hydroxy benzylidene aminophenol Nickel(II) chloride complex of the characteristics infrared absorption frequencies

Assignment of Bond	**Frequency Range in cm^{-1}**	**Functional Group Type**
vC=C aromatic	1617.7	Aromatic Alkenes
C-H bending	1871.1	Aromatic Alkenes
vC=N stretching	2109.7	Aromatic Amines
vC=N stretching	2339.7	Aromatic Amines
vO-H	3112.4	Phenolics
vO-H	3753.4	Phenolics

Table 15. Showing the FTIR spectrum data for mixed ligand of PMP+HAP Nickel(II) chloride complex of the characteristics infrared absorption frequencies

Assignment of Bond	**Frequency Range in cm^{-1}**	**Functional Group Type**

vC=C aromatic	1550.6	Aromatic Alkenes
vC-N	1617.7	Aromatic Amines
C-H bending (aromatic)	1871.4	Aromatic Ring
vC=N stretching	2119.4	Aromatic Amines
vC=N stretching	2922.2	Aromatic Amines
vO-H	3056.4	Phenolic
vO-H	3369.5	Phenolic
vO-H	3570.8	Phenolic
vO-H	3652.8	Phenolic
vO-H	3712.4	Phenolic
vO-H	3753.4	Phenolic

Table 16. Showing the FTIR spectrum data for 2-phenyliminomethylphenol Cobalt(II)chloride complex of the characteristics infrared absorption frequencies

Assignment of bond	**Frequency Range in cm^{-1}**	**Functional group type**
vC-H stretching	1610.2	Aromatic Amines
vC-H stretching	1900.9	Aromatic Ring
vC=N stretching	2109.7	Aromatic Amines
vC=N stretching	2344.0	Aromatic Ring
vC=N stretching	2374.0	Aromatic Ring
vC=N stretching	2791.8	Aromatic ing
vO-H vibrations	3052.7	Phenolic
vO-H	3350.9	Phenolic
vO-H	3652.8	Phenolic

Table 17. Showing the FTIR spectrum data for 2,2-hydroxybenzylideneaminophenol cobalt(II)chloride complex of the characteristics infrared absorption frequencies

Assignment of bond	**Frequency Range in cm^{-1}**	**Functional group type**
vC=C vibrations	1543.1	Aromatic Ring
vC=C vibrations	1580.4	Aromatic Ring
vC-H stretching	1994.1	Aromatic Ring
vC=N stretching	2109.7	Aromatic Amines
vC=N stretching	2374.3	Aromatic Amines
vC=N stretching	2564.4	Aromatic Amines
vO-H	3056.4	Phenolic
vO-H	3341.1	Phenolic

Table 18. Showing the FTIR spectrum data formixed ligand of PMP+HAP cobalt(II)chloride complex of the characteristics infrared absorption frequencies

Assignment on bond	Frequency Range in cm^{-1}	Functional group type
vC=C stretching	1528.2	Aromatic Ring
vC=C stretching	1580.4	Aromatic Ring
vC-H stretching	1990.4	Aromatic Ring
vC=N stretching	2113.4	Aromatic Amines
vC=N stretching	2568.1	Aromatic Amines
vC=N stretching	2922.2	Aromatic Amines
vO-H	3041.6	Phenolic
vO-H	3678.9	Phenolic

The FTIR spectra for the ligand and metal complexes are presented in Appendix 11 to 18 while the data and assignment for interpretation are presented in Tables 11 to 18. The FTIR spectra for 2-phenyliminomethylphenol (PMP) is presented in Appendix 11. The absorption band at 1569.2 cm^{-1} indicated the stretching vibration of C=C bond in the benzene rings andthe bands at 1613.9 cm^{-1} indicated =C-N stretching in the benzene ring. Furthermore, vC-H stretching was also seen in the neighborhood of 2653.9–2851.4 cm^{-1}, vC-H vibrations in ring was seen at 3056.4 while vO-H stretching of phenol was revealed by the band at 3213 and 3652.8 cm^{-1} respectively. The IR spectra for 2-phenyliminomethylphenol (PMP) were in agreement with previous reports by Turhan and Yaşar (2020). FTIR spectra for 2,2-hydroxybenzylideneaminophenol (HAP) is presented in Appendix 12 and the Spectral interpretation is presented in Table 12. The vibrational stretching absorption due to C-H bond could be observed in the neighborhood of 2691.1–2926.0cm^{-1}; a vibrational C-H band within the benzene ring was indicated by the absorption at 1804.6 cm^{-1}, 1848.8 cm^{-1}, 1990.4 cm^{-1}and 3045.2 cm^{-1} respectively, C=C stretching vibrations within the benzene ring and C=N stretching vibrations were seen at 1528.2 cm^{-1} and 1610.2 cm^{-1} respectively. vO-H stretching of phenol was also assigned to the band at 3634.2 cm^{-1} and 3678.0 cm^{-1} respectively.

The infrared spectra of FTIR spectra for 2-phenyliminomethylphenol Nickel(II) chloride complex [Ni(PMP)$_2$.Cl$_2$], 2,2-hydroxybenzylideneaminophenol Nickel(II)chloride complex [Ni(HAP)$_2$.Cl$_2$] and mixed ligand of PMP and HAP of Nickel(II)chloride[Ni(PMP+HAP).Cl$_2$] are presented in Appendices13, 14 and 15 and the spectral interpretation is given in Tables13, 14 and 15 respectively. The spectra for the metal complexes were compared with that of the original ligand PMP and HAP. The original ligand and complexes showed dissimilarity in their spectra suggesting the bonding of Ni^{2+} with PMP and HAP and Cl^{-}. For [Ni(PMP)$_2$.Cl$_2$], vC=C stretching was noticed at bands of 1569.2cm^{-1}, vC=N bending was found at 1613.9cm-^{1} and 1796.6cm-^{1} respectively, vC=N stretching was observed at 2109.7cm^{-1}bands and vO-H stretching were found at 3324.9 cm^{-1} and 3753.4cm^{-1} bands. For [Ni(HAP)$_2$.Cl$_2$].The vC=C stretching was found at 1617.7cm^{-1} bands while vC=N stretching was at bands 2109.7cm^{-1} and 2339.7cm^{-1} respectively, and vO-H stretching was between 3112.4cm^{-1} and 3753.4cm^{-1}. For the mixed ligands of [Ni(PMP+HAP).Cl$_2$]. vC=C vibrations were found at 1550.6cm^{-1} bands, vC=N stretching were found at 2119.4cm^{-1} and 2922.2cm^{1} bands respectively, and vO-H stretching were noticed at 3056.4cm^{-1} and -3753.4cm^{-1}. The broad absorption band at the 3753.4 cm^{-1} for the mixed Ni^{2+} which was present in the spectra of the metal complexes of Ni^{2+} was assigned to vOH of the enol form of the ligand (Chris and John, 2007).

The infrared spectra of FTIR spectra for 2-phenyliminomethylphenol Cobalt(II)Chloride complex [Co(PMP)$_2$.Cl$_2$], 2,2-hydroxybenzylideneaminophenol Cobalt(II) chloride complex [Co(HAP)$_2$.Cl$_2$] and mixed ligand of PMP and HAP of Cobalt(II) chloride [Co(PMP+HAP).Cl$_2$] are presented in Appendices16, 17 and 18 and the spectral interpretation is given in Tables16, 17 and 18 respectively. The spectra for the metal complexes were compared with that of the original ligand PMP and HAP. The original ligand and complexes showed dissimilarity in their spectra suggesting the bonding of Co^{2+} with PMP and HAP and Cl$^-$. For [Co(PMP)$_2$.Cl$_2$], vC=N stretching were observed at bands of 2105.0cm-^{1} -2370.6cm^{-1}, were observed vC=N vibrations noticed at 2109.7cm^{-1}-2791.8cm^{-1} and vO-H stretching were found at 3052.7 -3652.8cm^{-1} bands. For [Co(HAP)$_2$.Cl$_2$]. The vC=C stretching were found at 1543.1cm^{-1} and 1580.4cm^{-1} bands while vC=N stretching were at bands 2109.7cm^{-1} and 2564.4cm^{-1} bands respectively, the vC-H and vO-H stretching were between 3056.4cm^{-1} and 3341.1cm^{-1}.For the mixed ligands of [Co(PMP+HAP).Cl$_2$], vC=C stretching was found at 1528.2cm^{-1}bands,vC-H stretching was seen at 1990.4cm^{-1}bands, vC=N stretching was found at 2113.4cm^{-1} to 2922.2cm^{-1} bands, and vO-H stretching were noticed at 3041.6cm^{-1} to 3678.9cm^{-1} . The broad absorption band at the 3678.9 cm^{-1} for the mixed Co^{2+} which were present in the spectra of the metal complexes of Co^{2+} was assigned to vOH of the enol form of the ligand (Chris & John, 2007). However, the broad band appearing in the 3041.6 cm^{-1} of the FTIR spectra region for Pt^{2+} complexes have been attributed to vOH of the adduct of water molecules coordinated to the central metal ion or residing in the crystal lattices of the complexes (Ogwuegbu *et al.*, 2019). Furthermore, the absorption band at 2922.2 cm^{-1} due to C=N vibration in the spectrum of 2-phenyliminomethylphenol was shifted in the spectra of the prepared complex. This shows that the coordination of [Co(PMP)$_2$.Cl$_2$] is between N of the C=N (imine) group and the metal of the complex.

3.5 Electronic Spectra

The electronic spectra of the complexes formed are presented in Appendices19 to 24 while the spectral data were listed in Table 19.

Table 19.UV-Visible spectra for mixed ligand nickel and cobalt(II) chloride complexes

Compounds	**Wavelength (nm)**	**Elemental transition**
[Ni(PMP)$_2$.Cl$_2$]	325	π → π*
[Ni(HAP)$_2$.Cl$_2$]	369	π → π*
[Ni(PMP+HAP).Cl$_2$]	420	π → π*
[Co(PMP)$_2$.Cl$_2$]	355	π → π*
[Co(HAP).Cl$_2$]	357	π → π*
[Co(PMP+HAP).Cl$_2$]	342	π → π*

The energy absorbed in the UV-Vis region gives rise to changes in the electronic energy of the compound resulting from transition of valence electrons in the complexes. These electronic transitions consist of the excitation of an electron from an occupied molecular orbital usually a non-bonding (n) or a bonding (π) molecular orbital to an unoccupied molecular orbital. Normally, not all transitions from occupied to unoccupied molecular orbitals is allowed(Waheb & Adedibu, 2003; Ogwuegbu *et al.*, 2017).The UV-Vis spectrum of the complexes were characterized mainly by one absorption and thus appear to have virtually identical spectra, and absorb in the near visible region around λ_1=325nm, 369nm, 420nm, 355nm, 357nm and 342nm for [Ni(PMP)$_2$.Cl$_2$], [Ni(HAP)$_2$.Cl$_2$], [Ni(PMP+HAP)$_2$.Cl$_2$], [Co(PMP)$_2$.Cl$_2$], [Co(HAP)$_2$.Cl$_2$] and [Co(PMP+HAP).Cl$_2$] complexes. These absorptions are ascribed to $\pi \rightarrow \pi^*$. The close absorption spectra of the ligand and the metal complexes suggest that the π -bonding system of the free nitro group is intact in the ligand of the metal complexes (Ogwuegbu & Maseka, 1998),indicating that there are no interaction between the metal ions and π-bonding system of the ligand. The coordination between the ligand and the metal ions is therefore through bond formation between the metal ions and the O atom of the hydroxyl group of the ligand.

3.6 XRD Analysis

X-ray diffraction analysis (XRD) was deployed to determine the crystallographic structure of the synthesized complexes. The XRD spectral (powder study) for the different synthesized ligands PMP and HAP and the $Ni^{2+}$and Co^{2+}complexes are presented in Appendices25 to 32 and the spectral interpretation given in Tables 20 to 27.The X-Ray Diffractograms of the metal complexes investigated showed good intense peaks indicating high crystallinity. The 2-phenylenyliminomethylphenolNickel(II) complex had reduced and broadened peak indicating it is less crystalline. Similar observation was made for Cobalt(II) complexes of 4(4-(dimethylamino) benzylideneamino)benzoic acid (Khan *et al.*, 2013). Crystalline nature of the complexes was indicated by comparing the diffractograms with their respective ligands and results showed marked differences, indicating that complexation have really taken place.

Table 20. FWHM Values, Average Crystallite Sizes Calculated Using Scherrer's Formula, D-Spacing, And Bragg's Diffraction Degree of 2-Phenyliminomethylphenol Ligand Synthesized

Bragg's diffraction [°2Ɵ]	**Full width at half maximum (FWHM) (degrees)**	**d-spacing [Å]**
PMP		
9.8808	0.1574	8.95195
11.7117	0.1574	7.55628
12.4831	0.1968	7.09100
12.9439	0.1378	6.83958
13.8742	0.4723	6.38301
15.4647	0.1378	5.72993
16.7218	0.2362	5.30191
17.1345	0.1181	5.17511
18.4386	0.1181	4.81192
18.8751	0.1181	4.70163
19.0686	0.0984	4.65435
21.4763	0.1771	4.13768
23.7810	0.2362	3.74164
25.6052	0.3936	3.47907
27.6052	0.6298	3.23139
28.0226	0.1181	3.18420
28.8981	0.1181	3.08970
29.3573	0.2755	3.04240
30.4013	0.3149	2.94026
34.2139	0.0787	2.62084
38.0036	0.1574	2.36776

38.8284	0.3149	2.31934
39.7807	0.2362	2.26599
44.2773	0.1968	2.04574
48.1090	0.4723	1.89138
49.9102	0.3936	1.82726
64.4521	0.3149	1.44570

Average crystallite size = 459.09 nm

Table 21.FWHM values, average crystallite sizes calculated using Scherrer's formula, d-spacing, and Bragg's diffraction degree of 2,2-hydroxybenzylideneaminophenol ligand synthesized

Bragg's diffraction [°2Ɵ]	Full width at half maximum (FWHM) (degrees)	d-spacing [Å]
HAP		
8.5287	0.4723	10.36788
9.3516	0.0984	9.45732
9.6897	0.2362	9.12802
13.2924	0.1378	6.66104
13.6907	0.2755	6.46813
14.7029	0.1181	6.02507
15.1847	0.1771	5.83495
15.3412	0.1181	5.77577
19.3409	0.4723	4.58943
20.8612	0.6298	4.25827
22.5581	0.9446	3.94164
24.3965	0.1181	3.64864
27.2967	0.1574	3.26721
34.2415	0.1181	2.61879
35.5234	0.6298	2.52717
38.0154	0.1968	2.36705
39.7603	0.1181	2.26710
44.2581	0.0787	2.04659
45.8873	0.4723	1.97764
49.5299	0.2362	1.84040
64.4553	0.1181	1.44564
68.8234	0.2362	1.36416

Average crystallite size = 473.52 nm

Table 22.FWHM values, average crystallite sizes calculated using Scherrer's formula, d-spacing, and Bragg's diffraction degree of 2-phenylaminomethylphenol Nickel(II) Chloride complex synthesized

Bragg's diffraction [°2Ɵ]	Full width at half maximum	d-spacing [Å]

	(FWHM) (degrees)	
[$Ni(PMP)_2.Cl_2$]		
8.44	0.59	10.47
15.079	0.15	5.871
16.647	0.128	5.321
17.094	0.185	5.183
18.963	0.156	4.6762
23.59	0.55	3.768
25.052	0.074	3.5516
27.806	0.143	3.2058
33.249	0.161	2.6924
33.763	0.16	2.6526
34.162	0.198	2.6226
37.690	0.051	2.3848
38.038	0.154	2.3637
39.747	0.12	2.2660
44.236	0.170	2.0459
49.601	0.20	1.8364
64.47	0.24	1.4442
68.86	0.16	1.3624
Average crystallite size = 597.83 nm		

Table 23.FWHM values, average crystallite sizes calculated using Scherrer's formula, d-spacing, and Bragg's diffraction degree of 2,2-hydroxybenzylideneaminophenol Nickel(II)chloride complex synthesized

Bragg's diffraction [°2Θ]	Full width at half maximum (FWHM) (degrees)	d-spacing [Å]
[$Ni(HAP)_2.Cl_2$]		
5.72	0.24	15.45
7.25	0.30	12.19
8.471	0.534	10.430
9.144	0.253	9.664
9.622	0.37	9.185
18.50	3.7	4.79
22.13	0.57	4.013
24.23	0.58	3.670
27.29	0.44	3.265
37.999	0.189	2.3661
44.248	0.21	2.0453
Average crystallite size = 266.18 nm		

Table 24.FWHM values, average crystallite sizes calculated using Scherrer’s formula, d-spacing, and Bragg’s diffraction degree of mixed ligand (PMP+HAP) Nickel(II) chloride complex synthesized

Bragg’s diffraction [°2Ɵ]	**Full width at half maximum (FWHM) (degrees)**	**d-spacing [Å]**
[Ni(PMP+HAP).Cl$_2$]		
8.33	3.05	10.60
37.992	0.169	2.3665
44.239	0.14	2.0457
Average crystallite size = 478.67 nm		

Table 25.FWHM values, average crystallite sizes calculated using Scherrer’s formula, d-spacing, and Bragg’s diffraction degree of 2-phenyliminomethylphenol Cobalt(II) chloride complex synthesized

Bragg’s diffraction [°2Ɵ]	**Full width at half maximum (FWHM) (degrees)**	**d-spacing [Å]**
[Co(PMP)$_2$.Cl$_2$]		
9.8076	0.1968	9.01857
19.0158	0.4723	4.66716
28.0908	0.9446	3.17662
Average crystallite size = 220.79 nm		

Table 26.FWHM values, average crystallite sizes calculated using Scherrer’s formula, d-spacing, and Bragg’s diffraction degree of 2,2-hydroxybenzylideneaminophenol Cobalt(II) chloride complex synthesized

Bragg’s diffraction [°2Ɵ]	**Full width at half maximum (FWHM) (degrees)**	**d-spacing [Å]**
[Co(HAP)$_2$.Cl$_2$]		
10.2236	0.4723	8.65256
18.3028	0.9446	4.84733
26.3041	0.7872	3.38819
Average crystallite size = 229.85nm		

Table 27.FWHM values, average crystallite sizes calculated using Scherrer's formula, d-spacing, and Bragg's diffraction degree of mixed ligand (PMP+HAP) Cobalt(II) chloride complex synthesized

Bragg's diffraction [°2Ɵ]	**Full width at half maximum (FWHM) (degrees)**	**d-spacing [Å]**
[Co(PMP+HAP).Cl_2]		
10.2236	10.2236	10.2236
18.3028	18.3028	18.3028
26.3041	26.3041	26.3041
Average crystallite size = 119.23 nm		

The average crystal size of the synthesized ligands and metal complexes were determined from the most intense peaks using Debye–Scherrer's equation. The Debye–Scherrer's equation is given as Equation (1)

$$D = \frac{k\lambda}{\beta \cos\theta} \qquad (1)$$

where K = 0.94 is Scherrer's constant, λ = 1.54 nm is the X-ray wavelength, θ is Bragg's diffraction angle, and β is the full width at half maximum (FWHM). Values for θ and β can be found in Table 20 to Table 27. The results for average crystallite size of the synthesized ligands and metal complexes are presented in Table 20 to 27. The sizes were 459.05 nm, 473.52 nm, 597.83 nm, 266.18 nm, 478.67 nm, 220.79 nm,229.85nm and 119.23 nm for PMP, HAP, [Ni(PMP)$_2$.Cl_2], [Ni(HAP)$_2$.Cl_2], [Ni(PMP+HAP)$_2$.Cl_2], [Co(PMP)$_2$.Cl_2], [Co(HAP).Cl_2] and [Co(PMP+HAP).Cl_2] respectively. These results indicate the crystal formed by the ligands and their respective complexes are large. However, the ligands had higher size compared to the complexes formed, which could be due to the complexation reactions. In comparison with other studies, lower average crystallite sizes were obtained for Ni^{2+} complexes derived from a new schiff base 2-((Z)-(3-methylpyridin-2-yleimino)methyl)phenol 30.1 to 54.3 nm (Orojloo *et al.*, 2015) and 2.61 to 44.4 nm for a dimeric complexes with *bis* bidentate ON–NO donor azo dye ligands (Maha Patra *et al.*, 2013). However, the results were comparable with the crystallite size of 101 to 599 nm reported for Cu^{2+} and Co^{2+} complexes of 3-(N- phenyl) thiourea-pentanone-2 (Mishra *et al.*, 2012).

3.7 Microbial Chemistry and Antimicrobial Activities of the Synthesized Ligands and Metal Complexes

The results obtained from this study as regards the antimicrobial activities of the ligands PMP and HAP and the metal complexes of $Ni^{2+}$and Co^{2+}, both mixed and unmixed ligands complexes have been presented in Table 28.

Table 28. Showing inhibitory action of Nickel and Cobalt metal complexes across different classes of micro-organisms

	PMP	**HAP**	**[Ni(PMP)$_2$.Cl_2]**	**[Ni(HAP)$_2$.Cl_2]**	**[Ni(PMP+HAP).Cl_2]**	**[Co(PMP)$_2$.Cl_2]**	**[Co(HAP)$_2$.Cl_2]**	**[Co(PMP+HAP)$_2$.Cl_2]**
Gram Positive Bacteria								
Staphylococcus aureus	+	+	+	++	+++	+	+++	+++
Bacillus substilis	+	+	++	++	+++	++	+++	+++

- shows no inhibitory action, + shows weak or partial inhibitory action, ++ shows stronger inhibitory action, +++ shows strongest inhibitory action, – shows no inhibition.

The results showed that the PMP and HAP ligands showed weak inhibitory activity, but when complexed with the divalent metals, they got stronger with improved inhibitory action against Gram-Positive, Gram-Negative Bacteria and Fungi when sensitivity test on these microbes were conducted. PMP and HAP showed partial inhibitory action on *Staphylococcus aureus* and *Bacillus substilis* of Gram-Positive Bacteria. Furthermore, PMP and HAP showed weak inhibitory action on Pseudomonas aeruginosa, while HAP showed stronger inhibitory action on *Escherichia Coli* but PMP showed partial inhibitory action of the Gram-Negative Bacteria. The sensitivity on the Fungi have different inhibitory action as to PMP and HAP showed no inhibitory action on Candida albicans while HAP showed weak inhibitory action on the Fungi specie: *Aspergillus niger*, PMP showed no inhibitory action. The complex [Ni(PMP)$_2$.Cl$_2$] showed weak inhibition on *Staphylococcus aureus*, but only stronger inhibition on *Bacillus substilis* of Gram Negative Bacteria, for Gram Negative Bacteria it showed stronger sensitive on *Escherichia coli* but partial inhibition on *Pseudomonas aeruginosa* and showed weak inhibition on both *Candida albicans* and Aspergillus niger of Fungi species. [Ni(HAP)$_2$.Cl$_2$] showed only stronger inhibition on both *Staphylococcus aureus* and *Bacillus substilis* of Gram Positive bacteria while it showed weak inhibition on Escherichia but stronger inhibitory action on *Pseudomonas aeruginosa* of Gram Negative Bacteria, on the fungi species it showed stronger inhibition on *Aspergillus niger* and only weak inhibition on *Candida albicans*. The mixed ligand complexes of Nickel. [Ni(PMP+HAP)$_2$.Cl$_2$] showed strongest inhibition on both *Staphylococcus aureus* and *Bacillus substilis* of Gram Positive Bacteria and *Escherichia coli* and *Pseudomons aeruginosa* of gram Negative Bacteria, on the Fungi species it showed only stronger inhibitory action on *Candida albicans* but strongest inhibition on *Aspergillus niger*.

The complex [Co(PMP)$_2$.Cl$_2$] showed weak inhibition on *Staphylococcus aureus* but only stronger inhibitory action on *Bacillus substilis* while [Co(HAP)$_2$.Cl$_2$] and mixed ligand [Co(PMP+HAP)$_2$.Cl$_2$] of Cobalt showed strongest inhibition both Staphylococcus aureus and *Bacillus substilis* of Gram Positive Bacteria and *Escherichia coli* and *Pseudomonas aeruginosa* of Gram Negative Bacteria, on the Fungi species [Co(PMP)$_2$.Cl$_2$] showed partial inhibition on *Candida albicans*, only stronger inhibitory action on *Aspergillus niger* but [Co(HAP)$_2$.Cl$_2$] showed only strongest inhibitory action on *Aspergillus niger* while the mixed ligand of Cobalt

$[Co(PMP+HAP)_2.Cl_2]$ showed strongest inhibition on *Candida albicans* and *Aspergillus niger* of Fungi species.

4. Conclusion

From the results, the following conclusions can be drawn;

The complexes involving 2-phenyliminomethylphenol (PMP) i.e $[Ni(PMP)_2.Cl_2]$, $[Co(PMP)_2.Cl_2]$, $[Ni(HAP)_2.Cl_2]$, $[Co(HAP)_2.Cl_2]$, $[Ni(PMP+HAP).Cl_2]$ and $[Co(PMP+HAP)_2.Cl_2$, had been synthesized and the following melting points 96°C, 91°C, 73°C, 89°C, 72°C and 67°Crespectively, which was higher than the ligand (50°C). The increases in melting point are attributed to the increase in mass of the formed complexes and thus provide evidence for complexation. However, for the 2,2-hydroxybenzylideneaminophenol (HAP) with melting point of 106°C, was higher than its metal complexes with 73°C, 89°C, 72°C and67°C for $[Ni(HAP)_2.Cl_2]$, $[Co(HAP)_2.Cl_2]$, $[Ni(PMP+HAP).Cl_2]$ and $[Co(PMP+HAP)_2.Cl_2$respectively. All complexes formed as well as their ligands were strongly soluble in dimethylsulfoxide (DMSO). The two divalent metal complexes were found to exhibit octahedral geometry with 2-phenyliminomethylphenol and octahedral with 2,2-hydroxybenzylideneaminophenol distorted-octahedral with the mixed ligands. The ligand behaves as a bidentated ligand coordinated to the metal ions via oxygen atom of carbonyl group and nitrogen atoms of two imine groups for the complexes ofNi^{2+} and Co^{2+} ions. It was evident in the XRD pattern that the ligand and metal complexes are crystalline in nature and exhibited large crystallite size. The ligands 2-phenyliminomethylphenol(PMP) and 2,2-hydroxybenzylideneaminophenol(HAP) exhibited weak inhibitory action on the Clinical isolates of Gram Positive Bacteria, Gram Negative and no inhibition on Fungi species while the metal complexes of Ni^{2+} and Co^{2+}showed either stronger or strongest inhibition.

SUGGESTED STRUCTURES

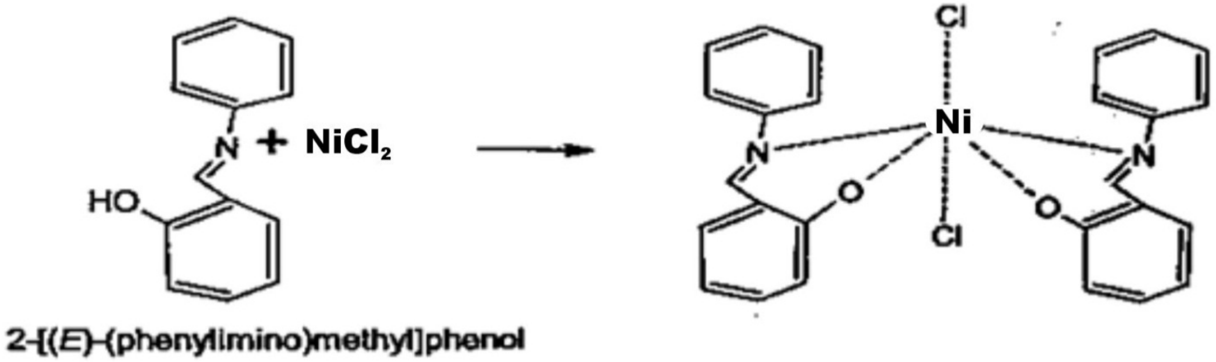


Figure 1. 2-phenyliminomethylphenol of Nickel (II) complex

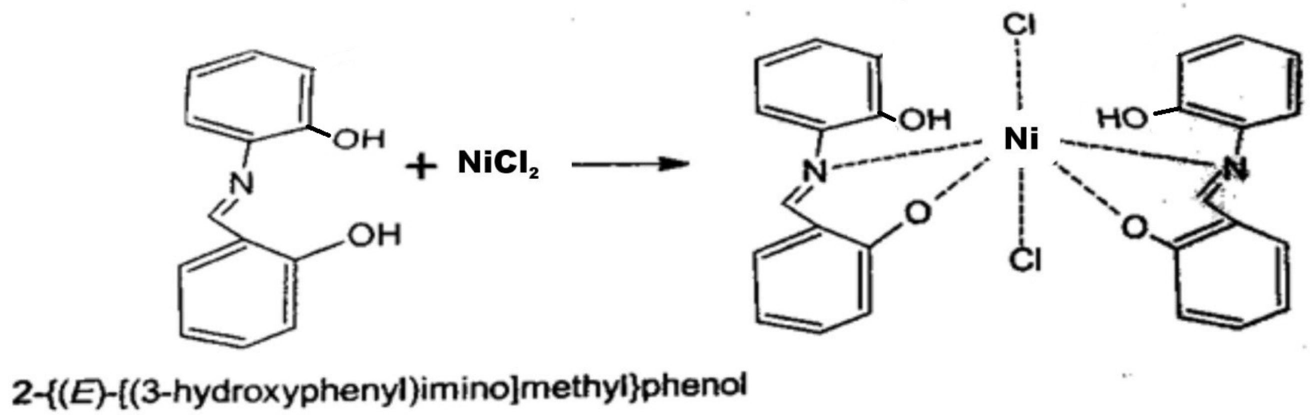


Figure 2. 2,2-hydroxybenzylideneaminophenol of Nickel(II) complex

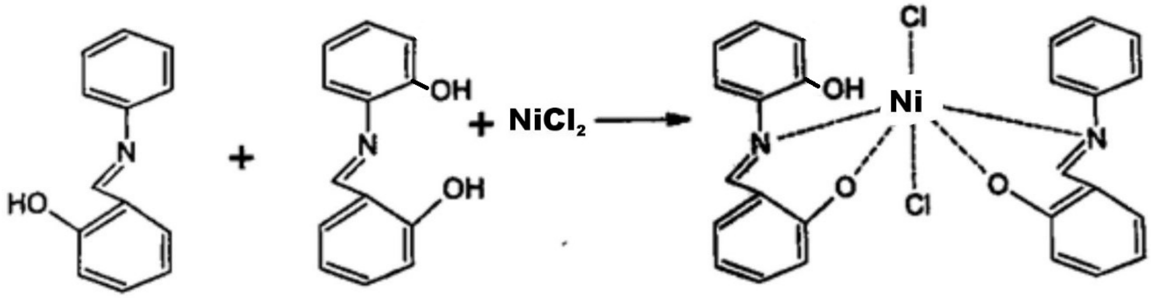


Figure 3. mixed ligand (PMP+HAP) of Nickel(II) complex

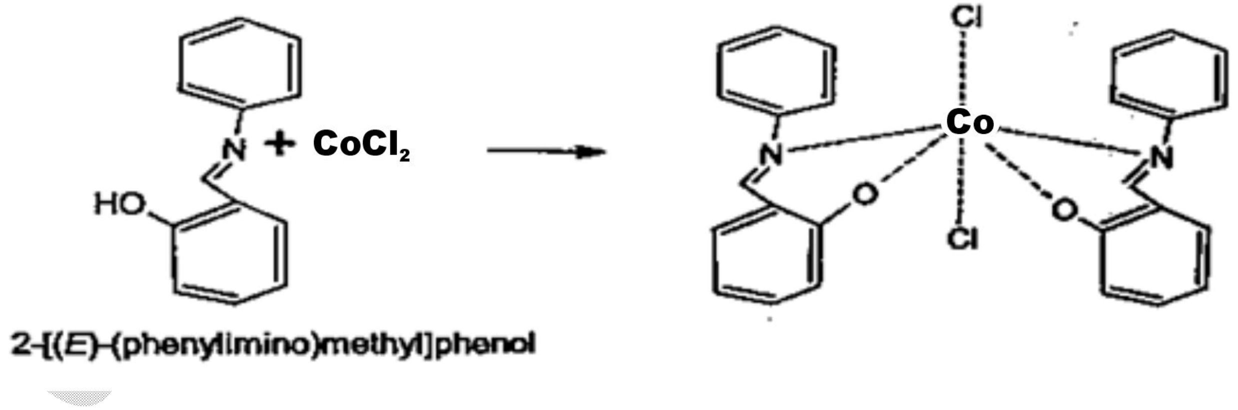


Figure 4. 2-phenyliminomethylphenol of Cobalt(II) complex

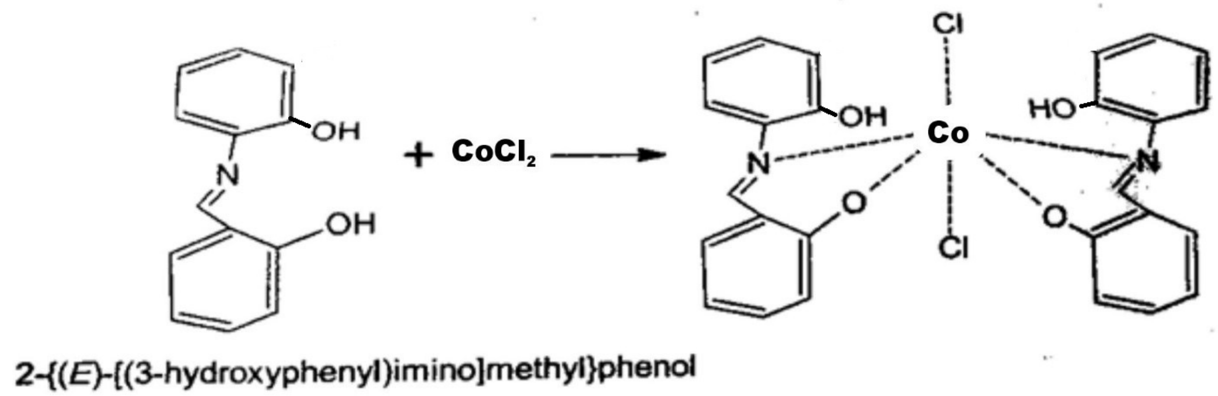


Figure 5. 2,2-hydroxybenzylideneaminophenol of Cobalt(II) complex

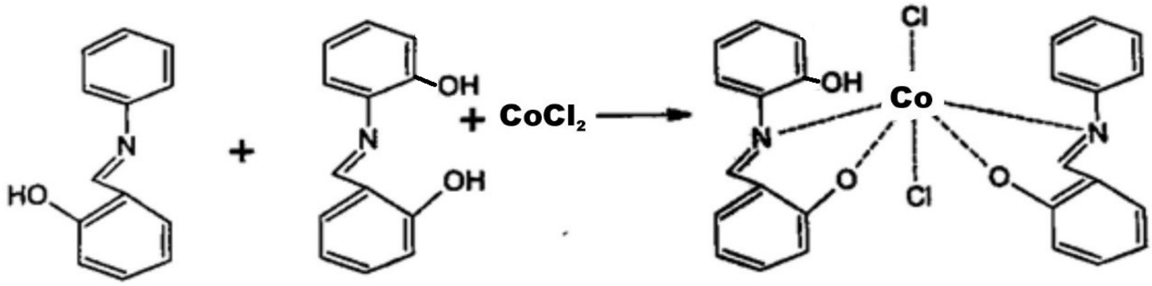
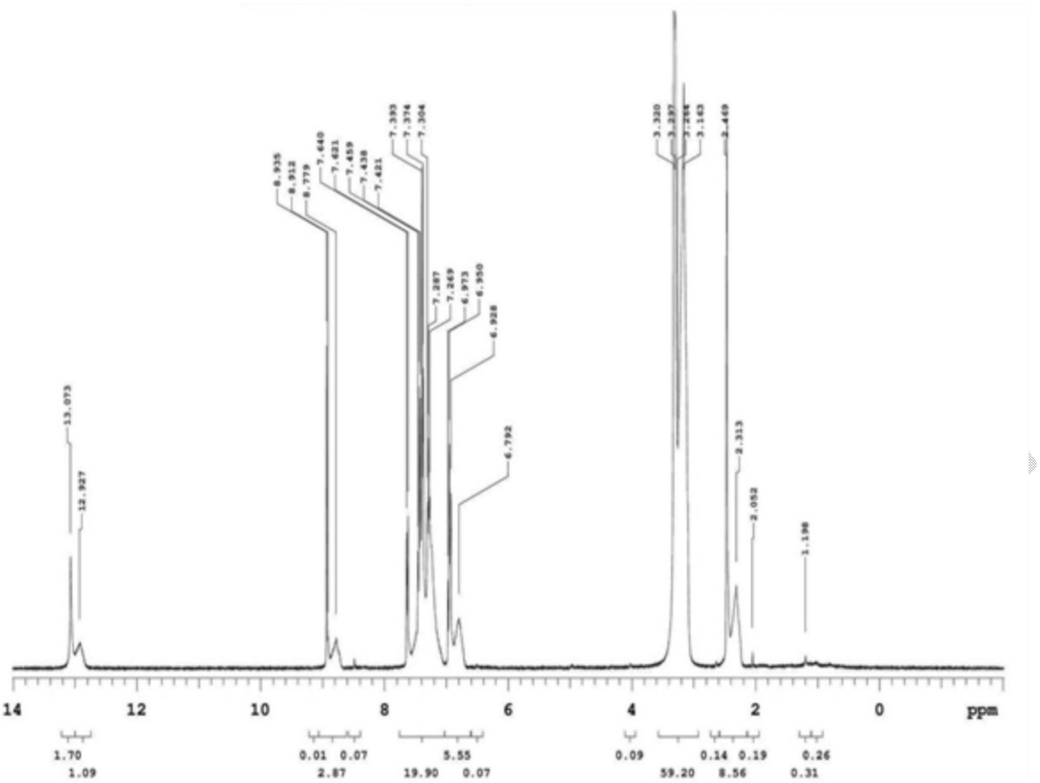
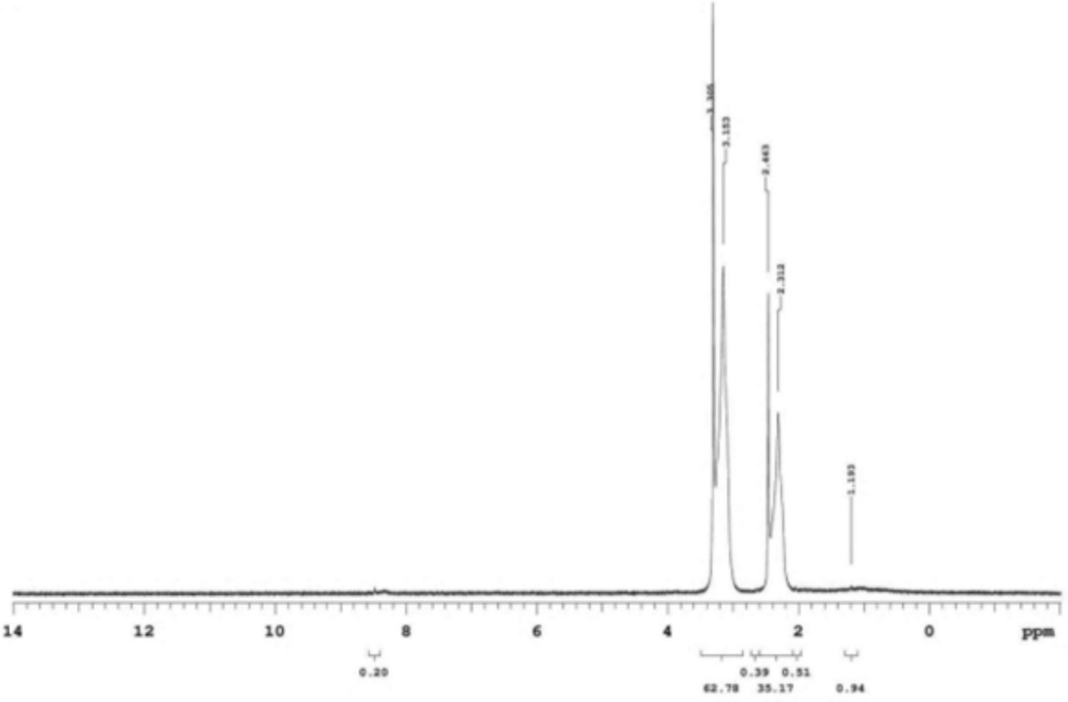


Figure 6. mixed ligand (PMP+HAP) of Cobalt(II) complex

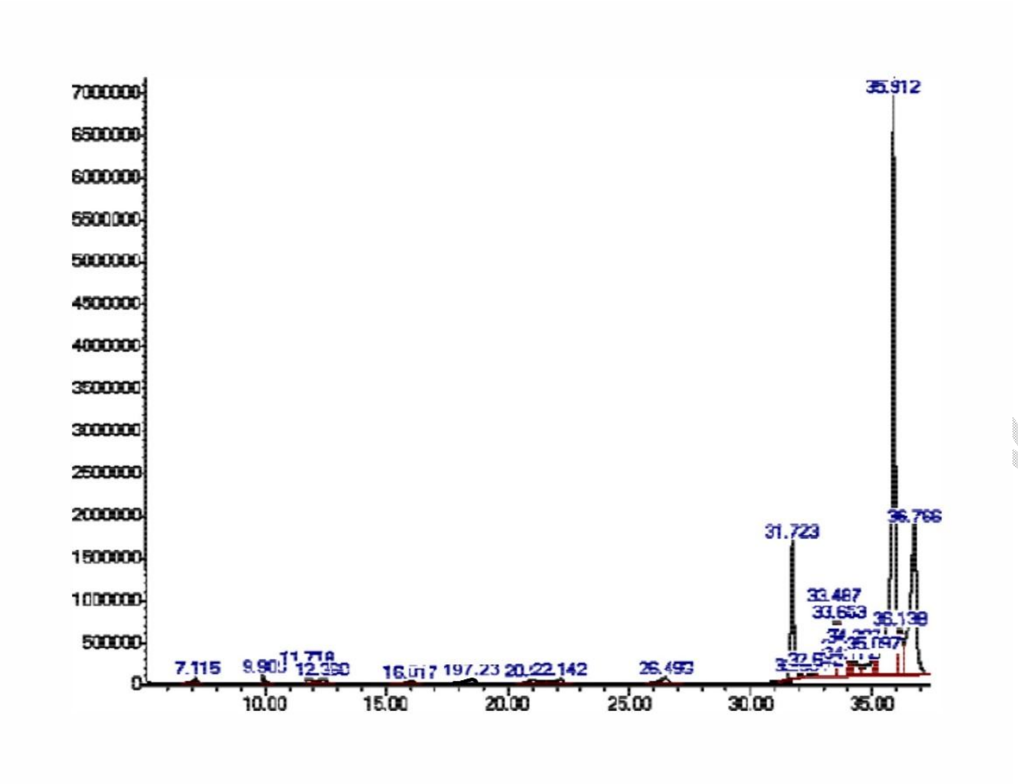
APPENDICES



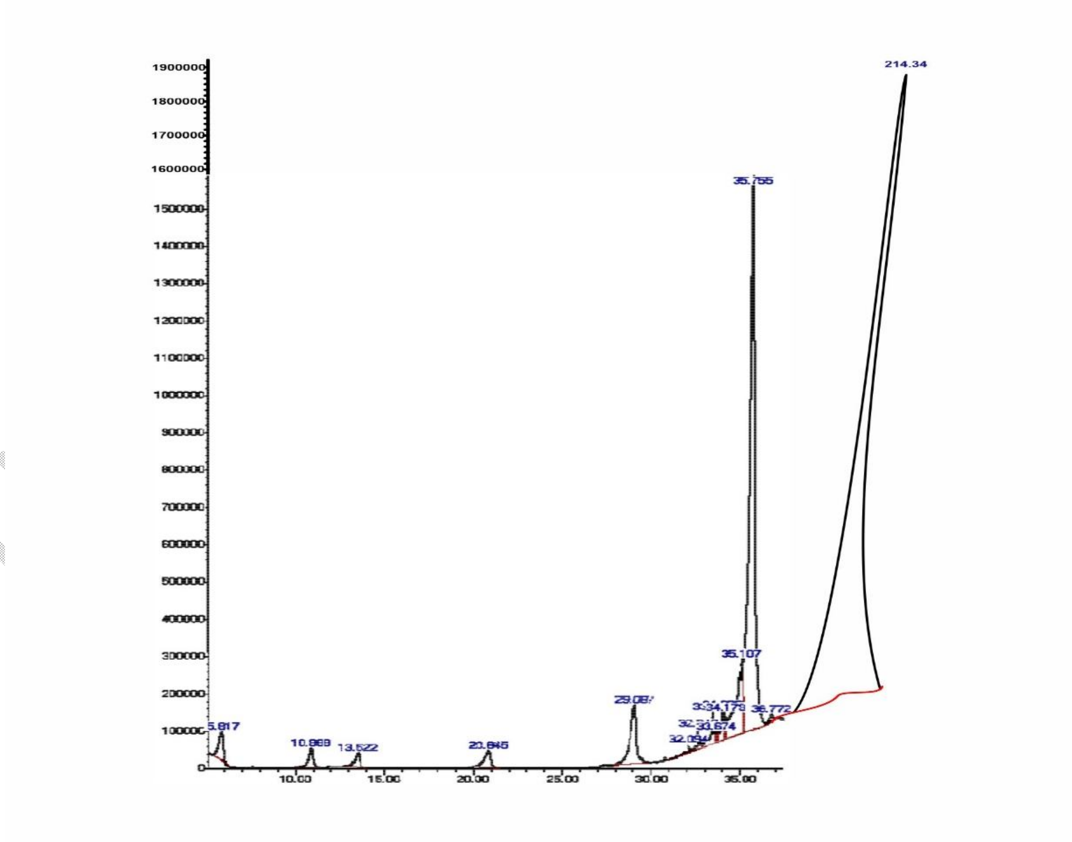
Appendix 1: Showing Proton ^{1}HNMR Spectra for 2-Phenyliminomethylphenol (PMP)



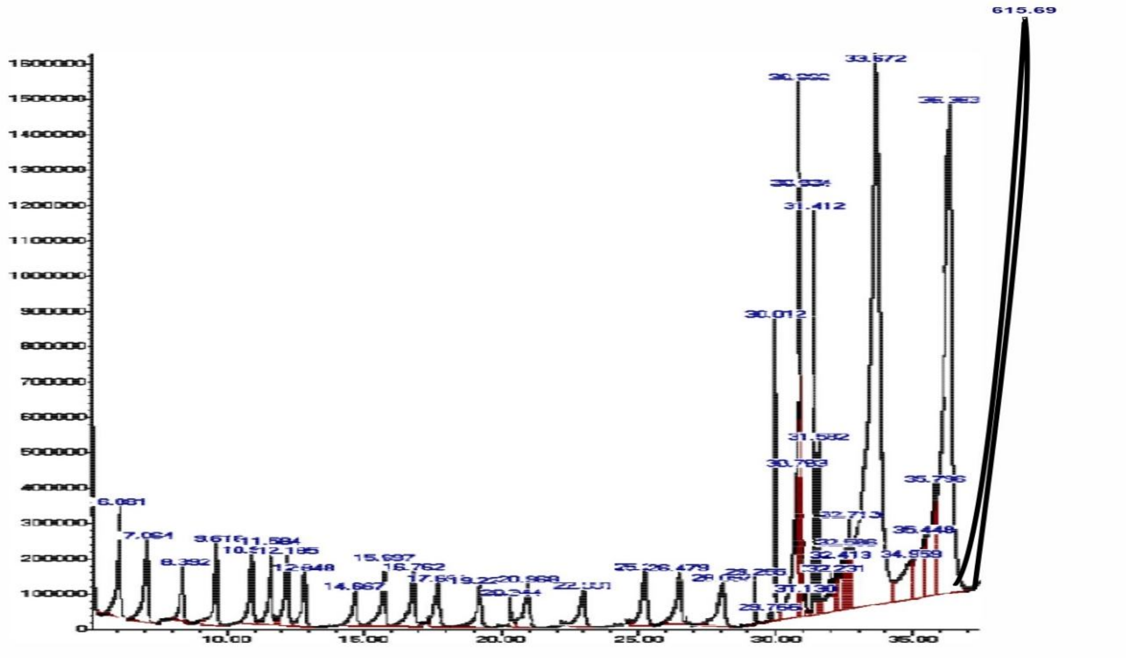
Appendix 2: Showing Proton ^{1}HNMR Spectra for 2,2-Hydroxybenzylideneaminophenol(HAP)



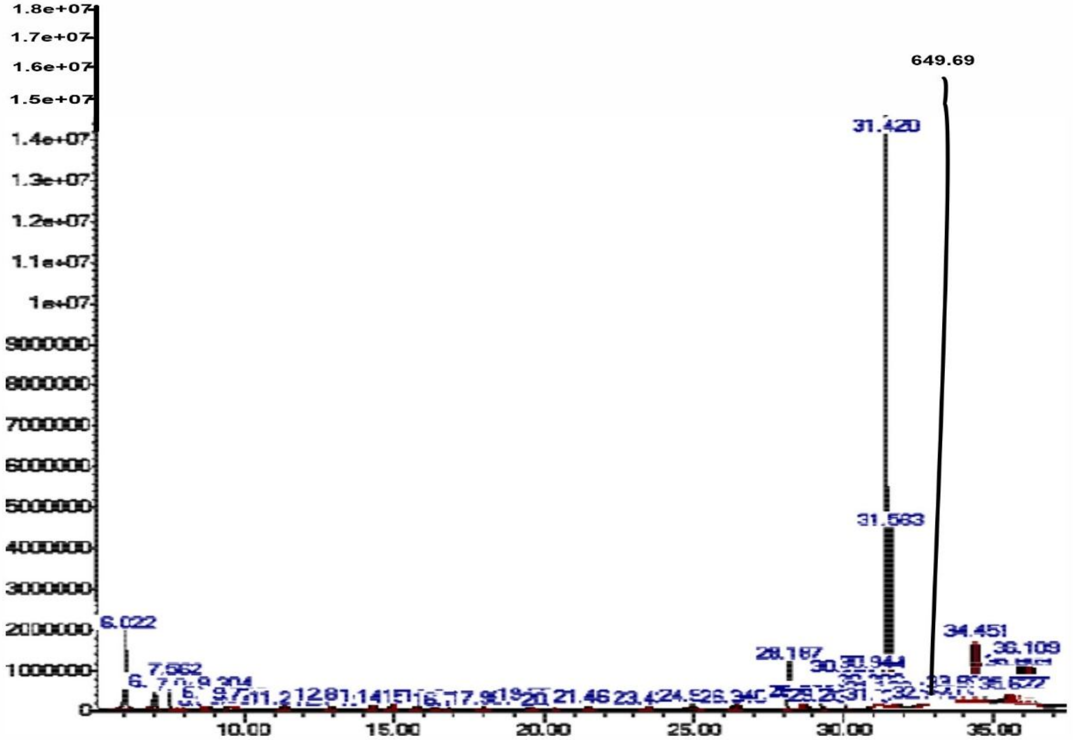
Appendix 3. Showing the GC-MS Spectrum of Sample A (PMP)



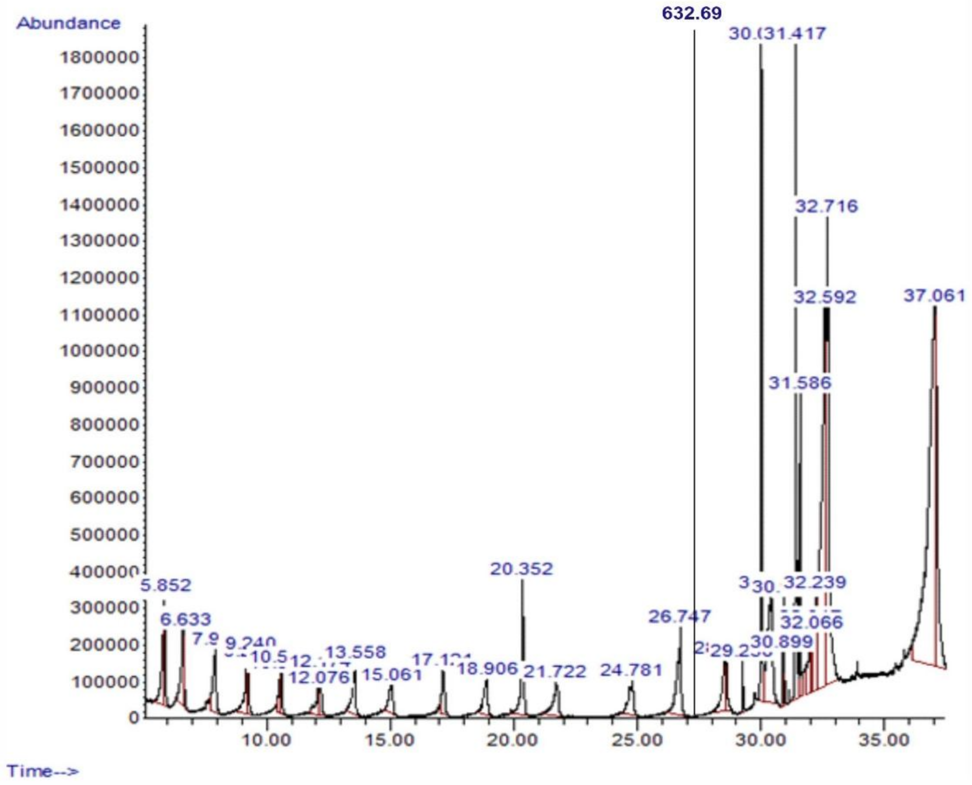
Appendix 4. Showing the GC-MS Spectrum of Sample B (HAP)



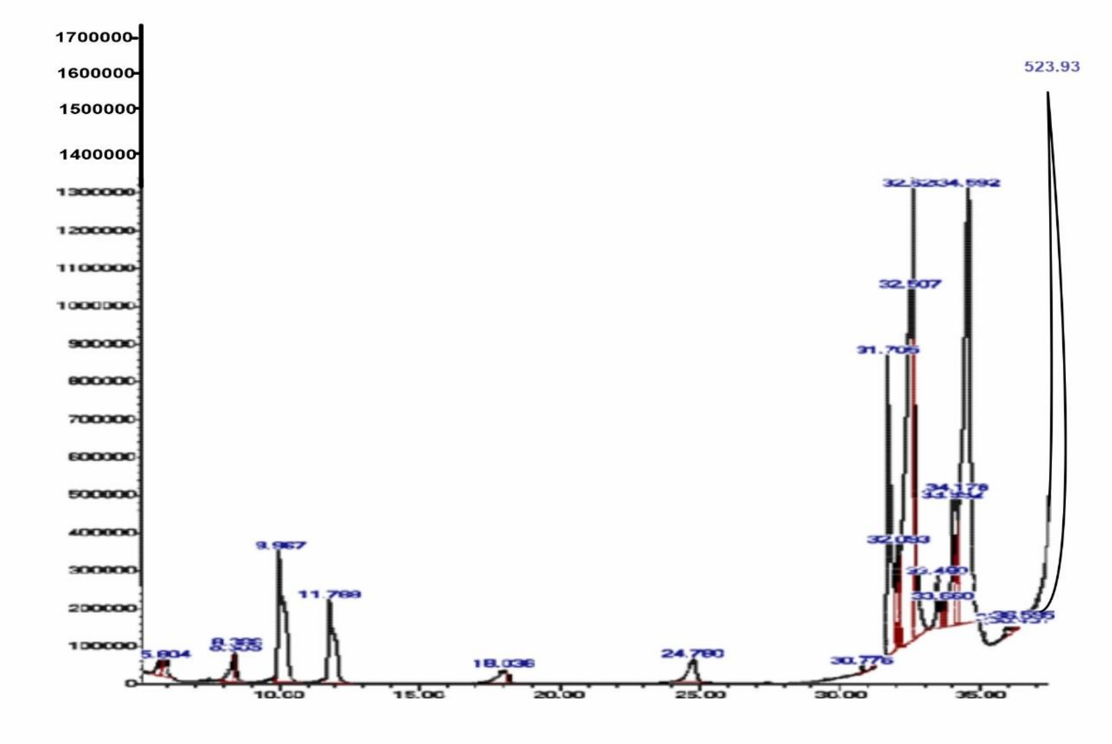
Appendix 5. Showing The GC-MS Spectrum of Sample I [Ni(PMP)$_2$.Cl$_2$]



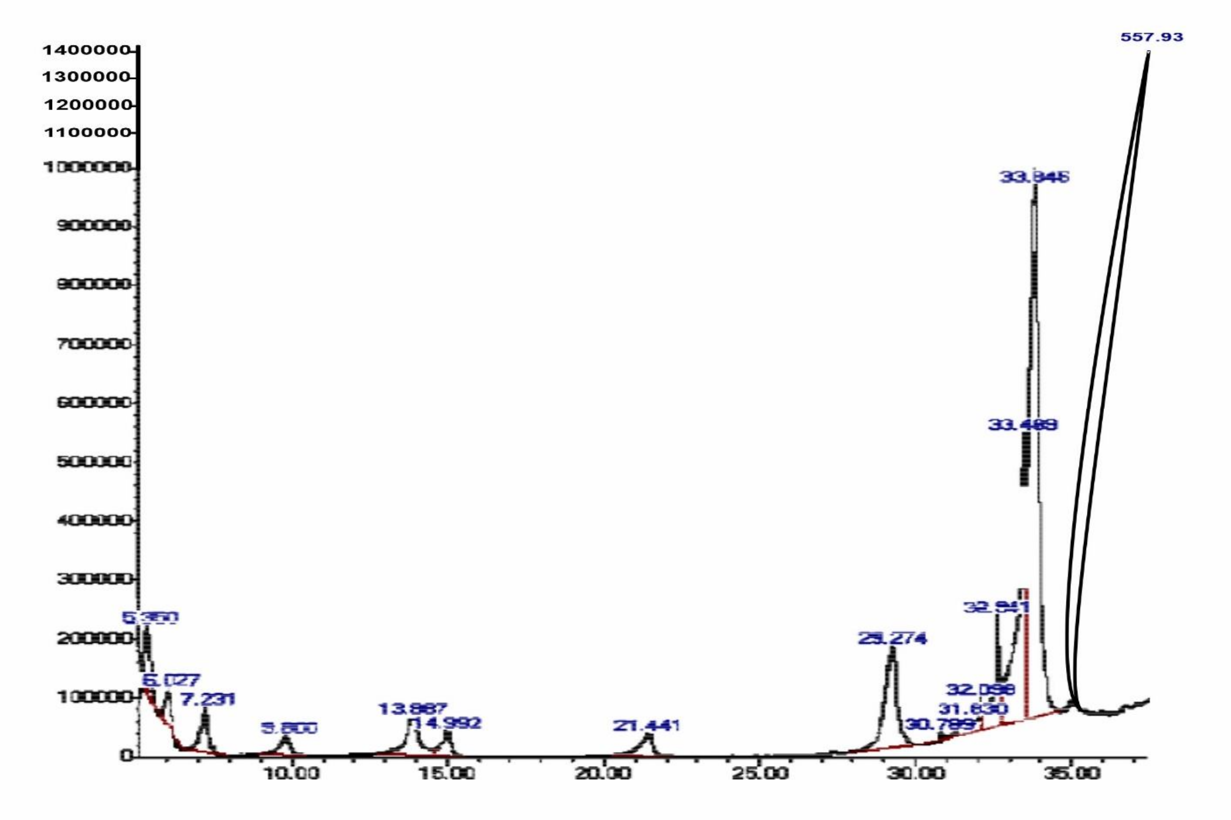
Appendix 6. Showing the GC-MS Spectrum Of Sample J [Ni(HAP)$_2$.Cl$_2$]



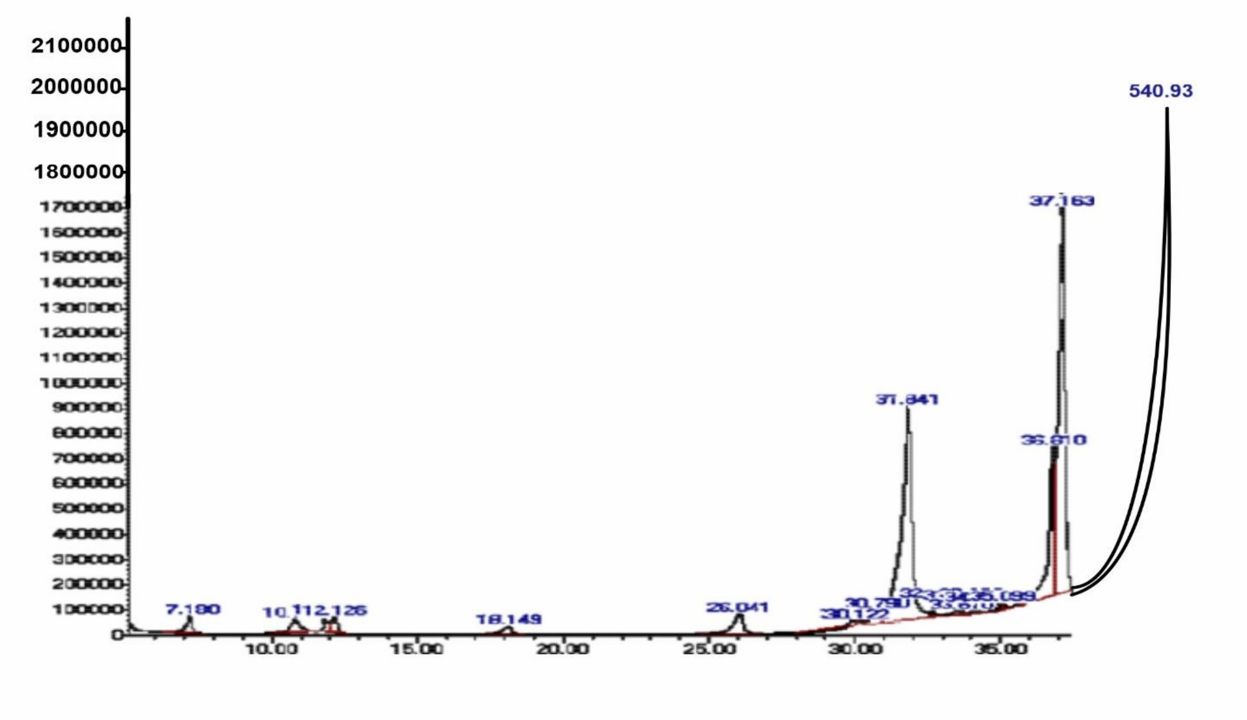
Appendix 7. Showing GC-MS Spectrum of Sample K [Ni(PMP+HAP).Cl_2]



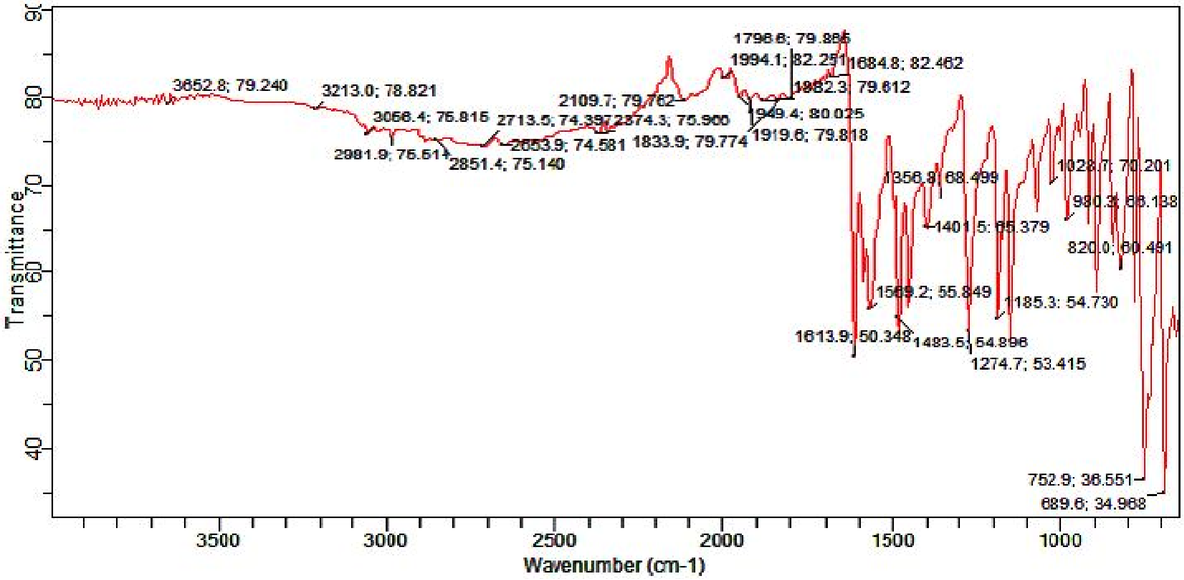
Appendix 8. Showing GC-MS Spectrum of Sample L [Co(PMP)$_2$.Cl$_2$]



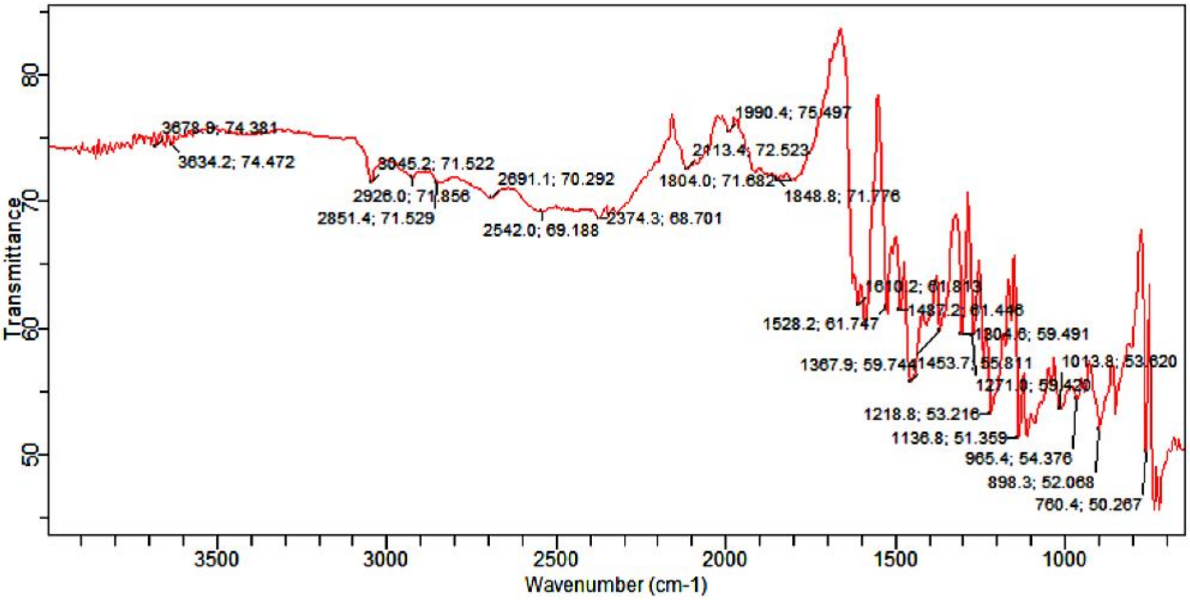
Appendix 9. Showing the GC-MS Spectrum of Sample M [Co(HAP)$_2$.Cl$_2$]



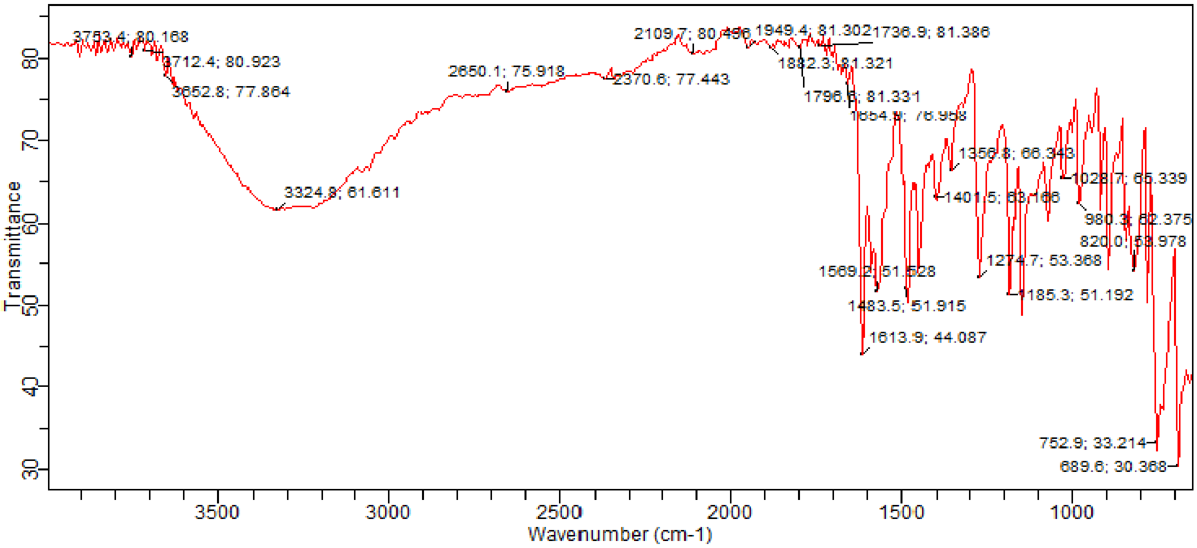
Appendix 10. Showing GC-MS Spectrum of Sample N [Co(PMP+HAP).Cl_2]



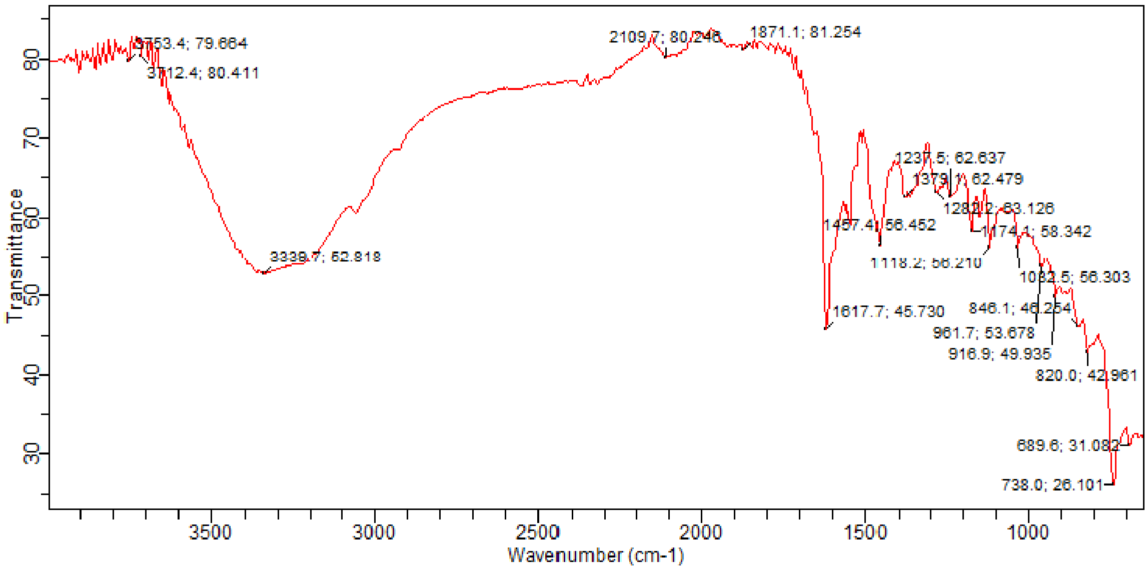
Appendix 11. Showing the FTIR Spectra For 2-Phenyliminomethylphenol (PMP)



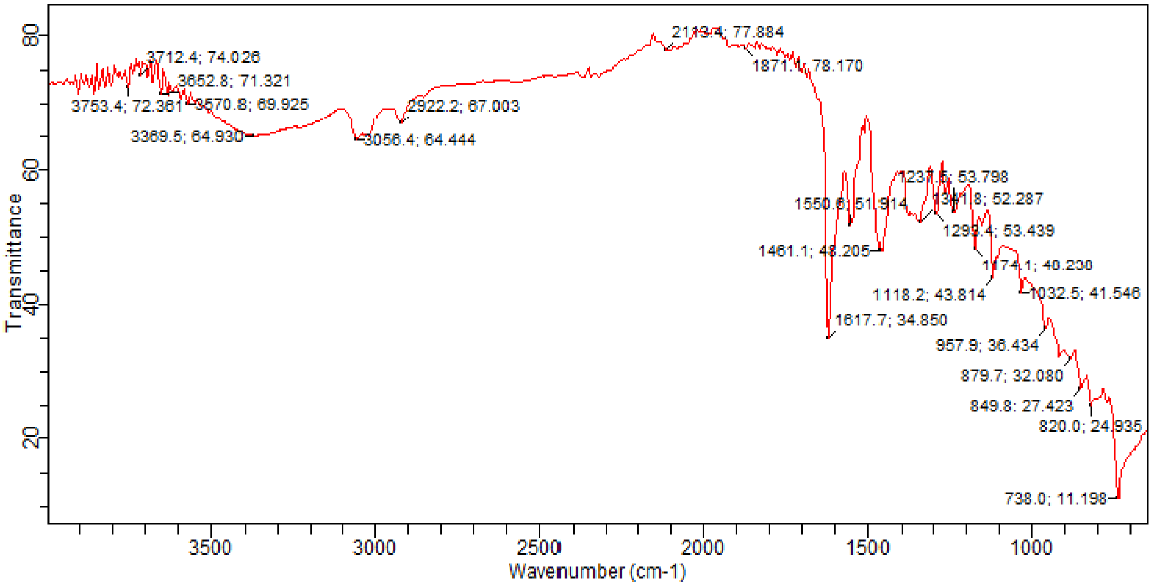
Appendix 12. Showing FTIR Spectra For 2,2-Hydroxybenzylideneaminophenol (HAP)



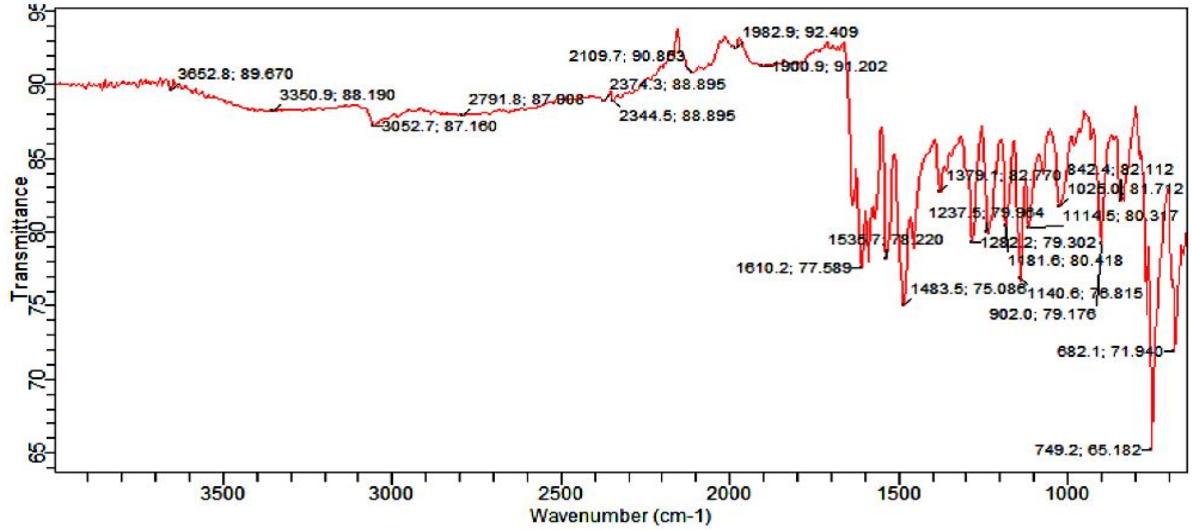
Appendix 13. Showing The FTIR Spectra For 2-Phenyliminomethylphenol Nickel(II) Chloride Complex, $[Ni(PMP)_2.Cl_2]$



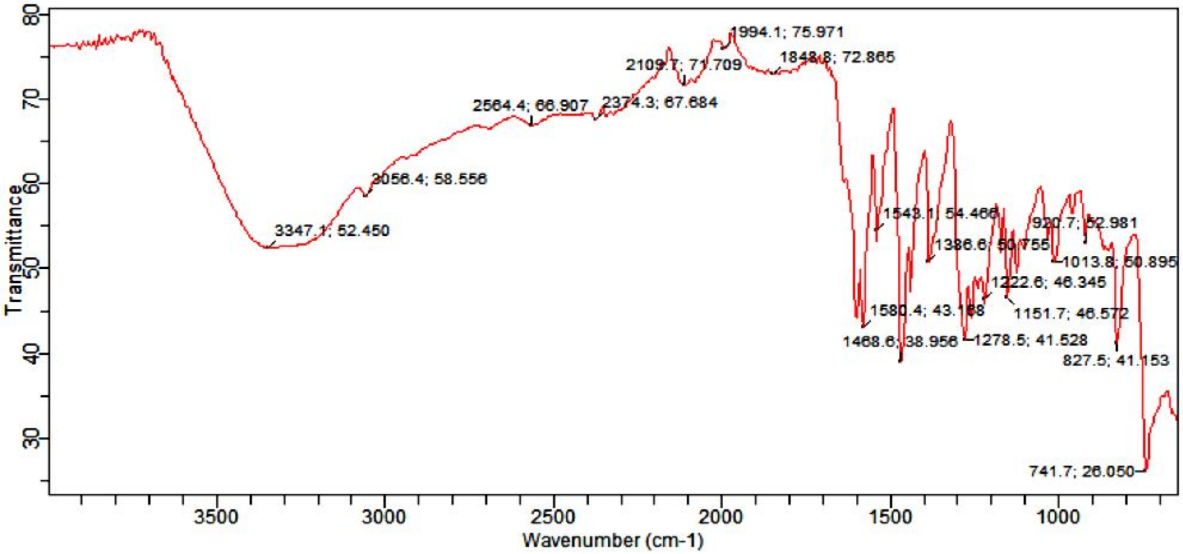
Appendix 14. Showing FTIR spectra for 2,2-hydroxybenzylideneaminophenol Nickel(II) chloride complex, $[Ni(HAP)_2.Cl_2]$.



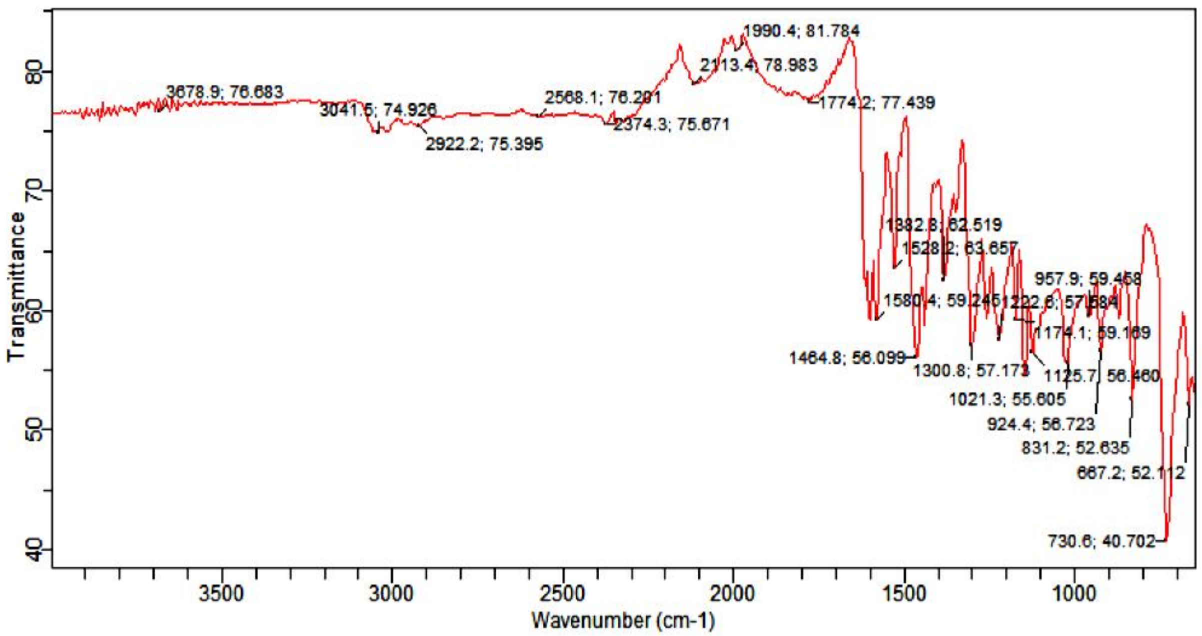
Appendix 15. Showing FTIR Spectra Mixed Ligand of PMP+HAP Nickel(II) chloride Complex, $[Ni(PMP+HAP).Cl_2]$



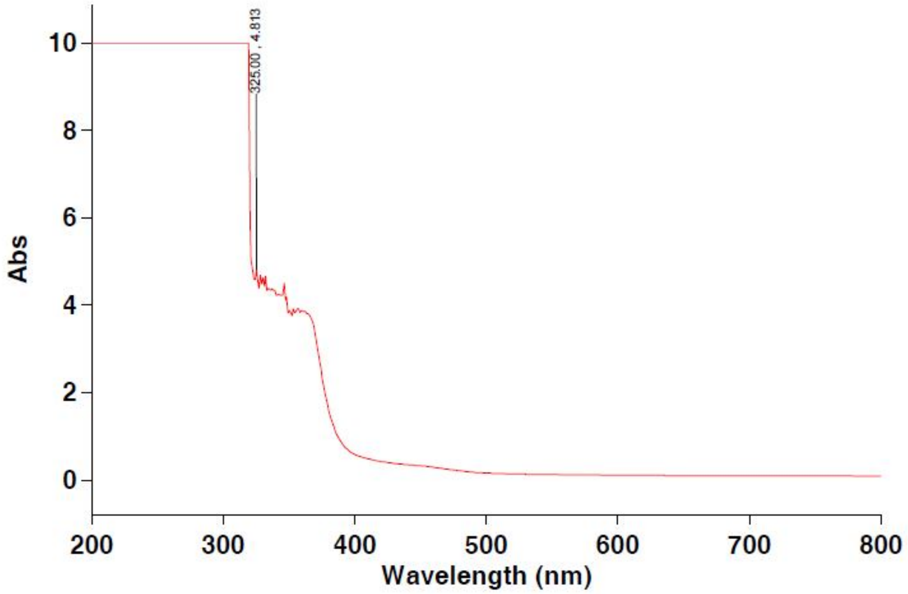
Appendix 16. Showing The FTIR Spectra For 2-Phenyliminomethylphenol Cobalt(II)Chloride Complex, [Co(PMP)$_2$.Cl$_2$]



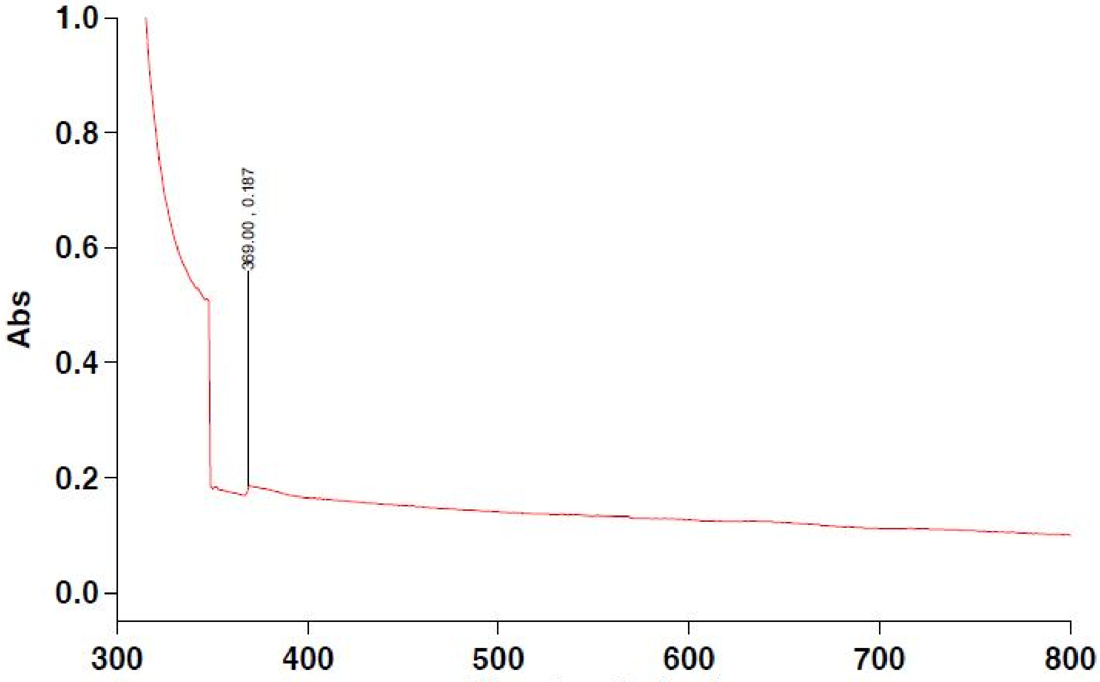
Appendix 17. Showing FTIR Spectra For 2,2-Hydroxybenzylideneaminophenol Cobalt(II) Chloride Complex, [Co(HAP)$_2$.Cl$_2$]



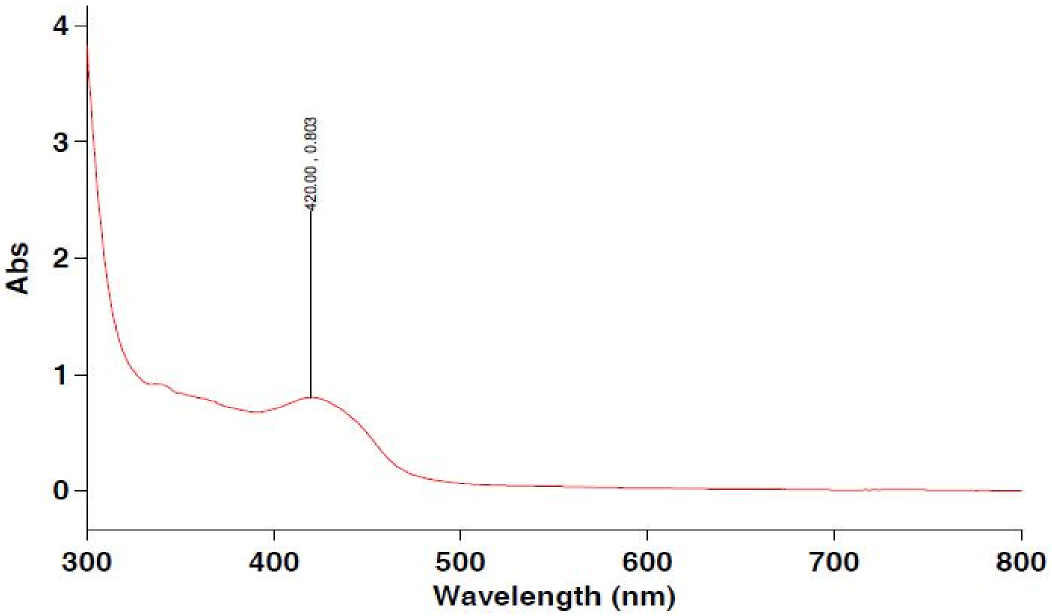
Appendix 18. Showing FTIR Spectra Mixed Ligand of PMP+HAP Cobalt(II)Chloride Complex, [Co(PMP+HAP).Cl_2]



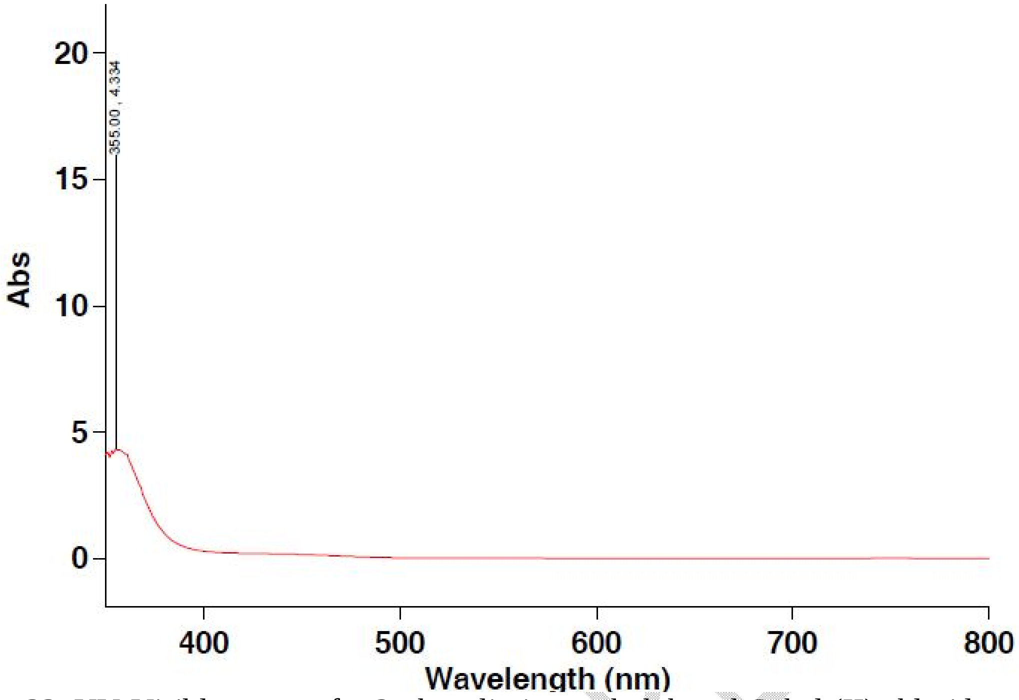
Appendix 19. UV-Visible Spectra For 2-Phenyliminomethylphenol Nickel(II) Chloride Complex, [Ni$(PMP)_2$.Cl_2]



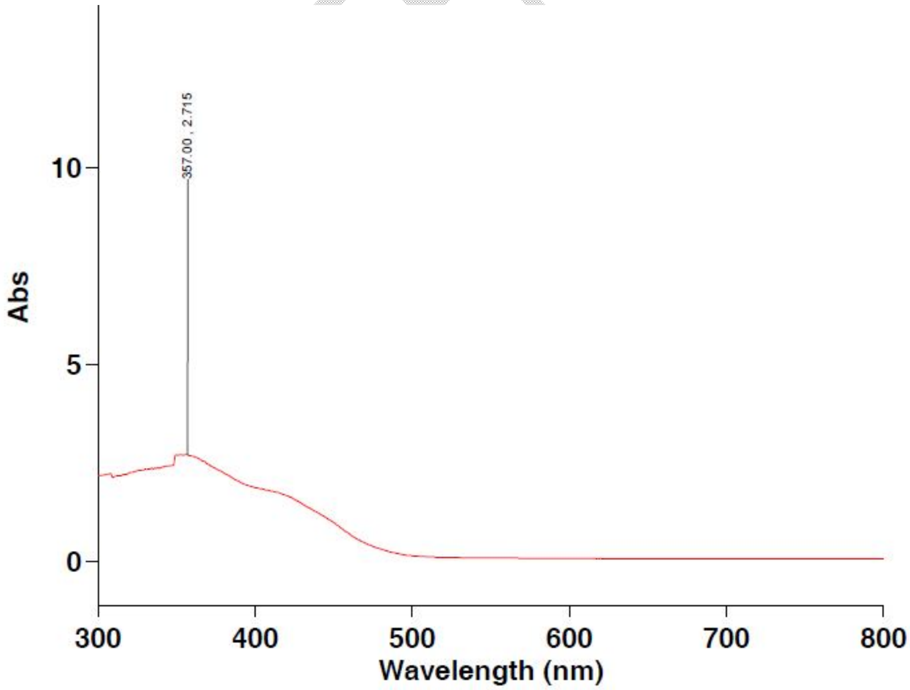
Appendix 20. UV-Visible spectra for 2,2-hydroxybenzylideneaminophenol Nickel(II) chloride complex, [Ni(HAP)$_2$.Cl$_2$]



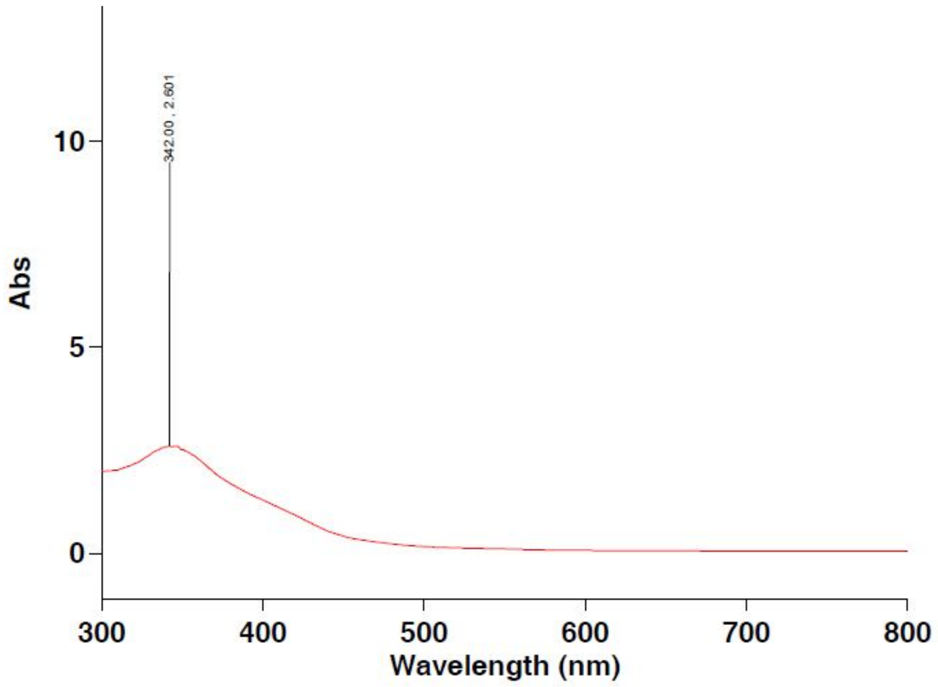
Appendix 21. UV-Visible spectra for mixed ligand (PMP+HAP) Nickel(II) chloride complexes, [Ni(PMP+HAP).Cl$_2$]



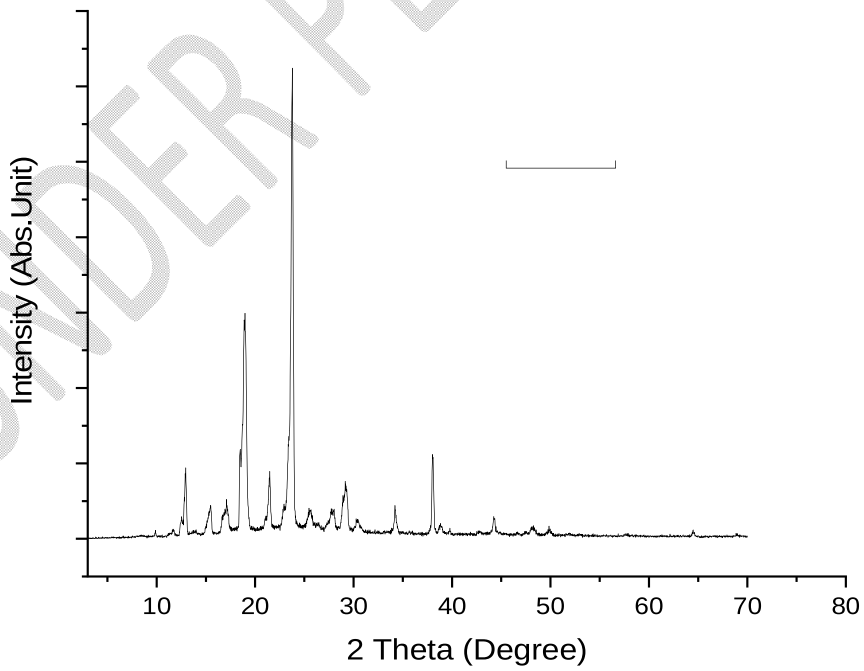
Appendix 22. UV-Visible spectra for 2-phenyliminomethylphenol Cobalt(II) chloride complex, [Co(PMP)$_2$.Cl$_2$]



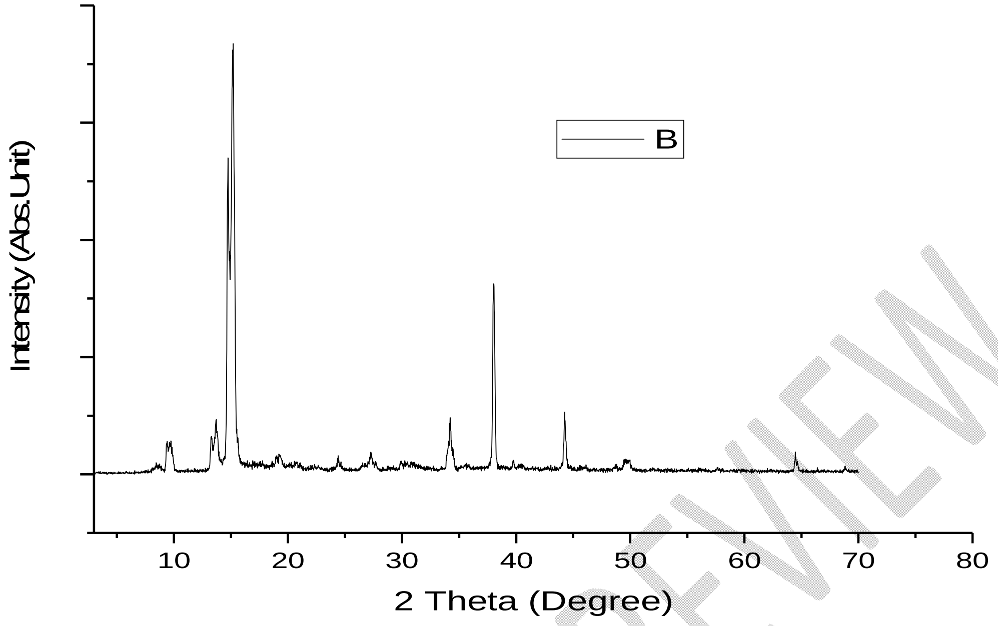
Appendix 23. UV-Visible spectra for 2,2-hydroxybenzylideneaminophenol Cobalt(II) chloride complex, [Co(HAP)$_2$.Cl$_2$]



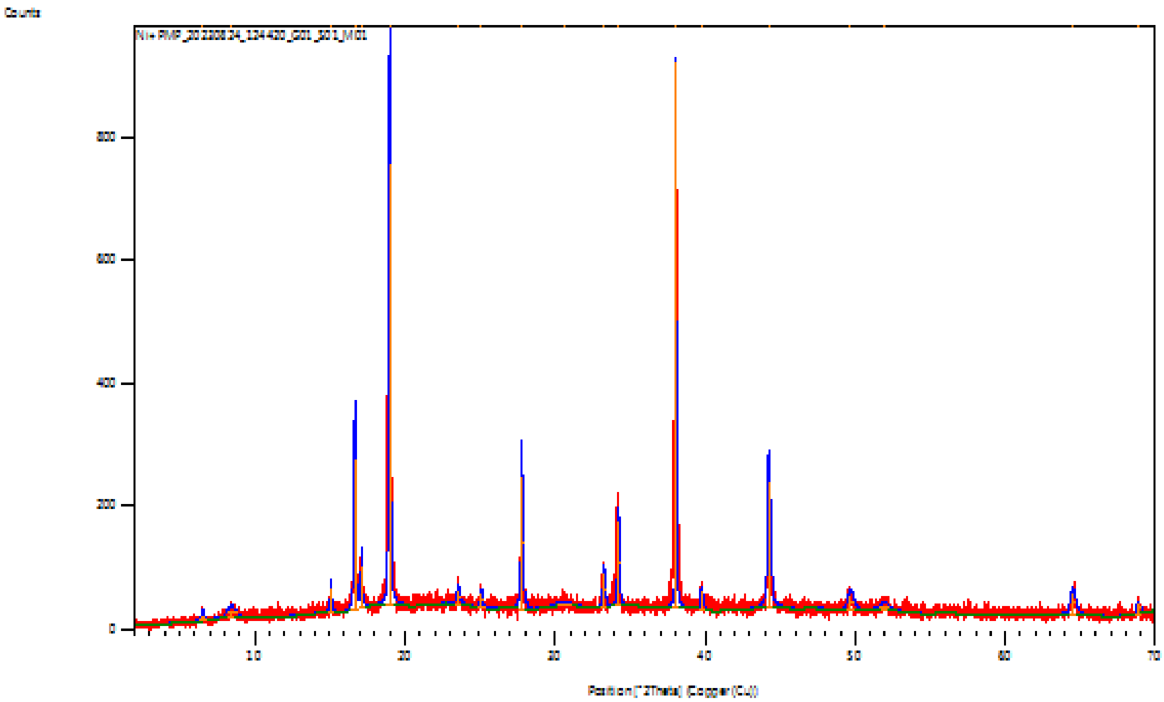
Appendix 24. UV-Visible spectra for mixed ligand (PMP+HAP) Cobalt(II) chloride complexes, [Co(PMP+HAP).Cl_2]



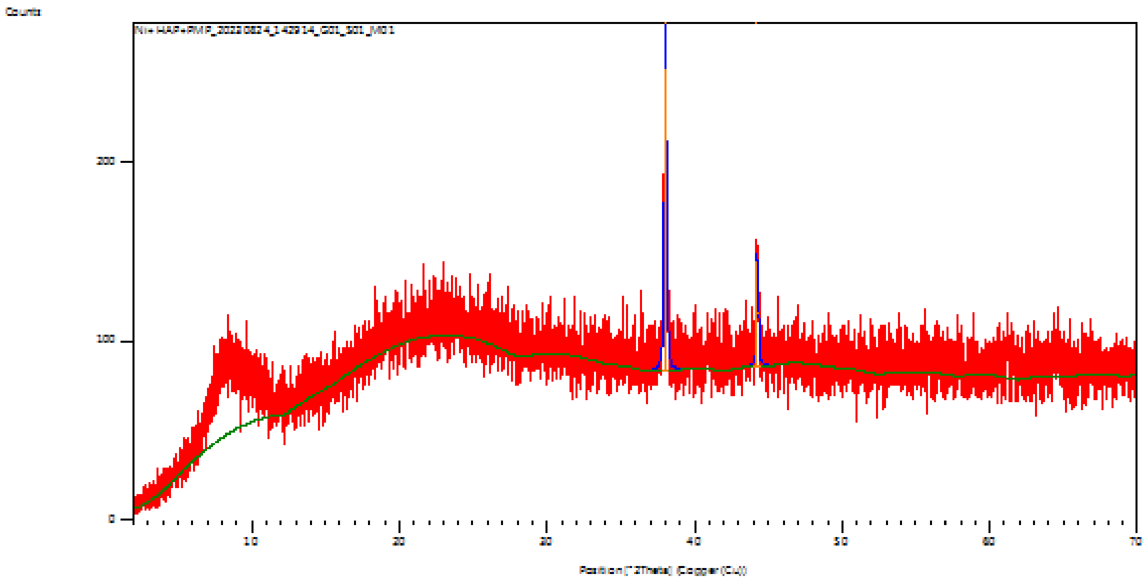
Appendix 25. XRD Spectra for 2-phenyliminomethylphenol ligand



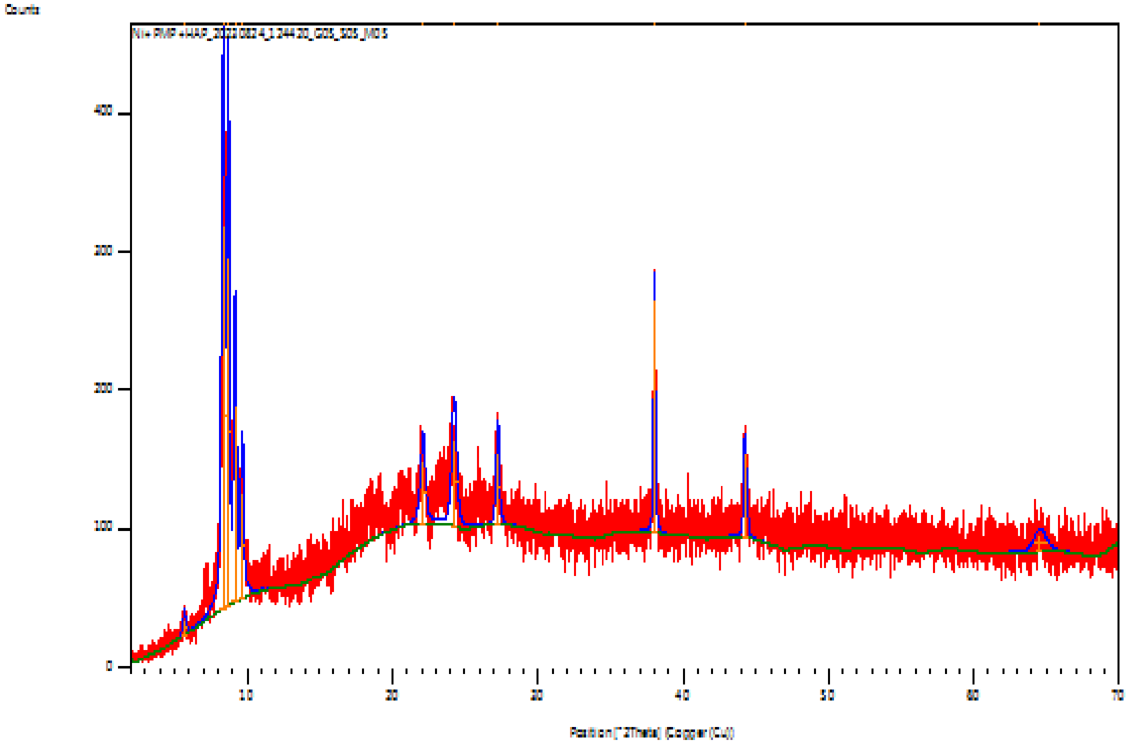
Appendix 26. XRD spectra for 2,2-hydroxybenzylideneaminophenol ligand



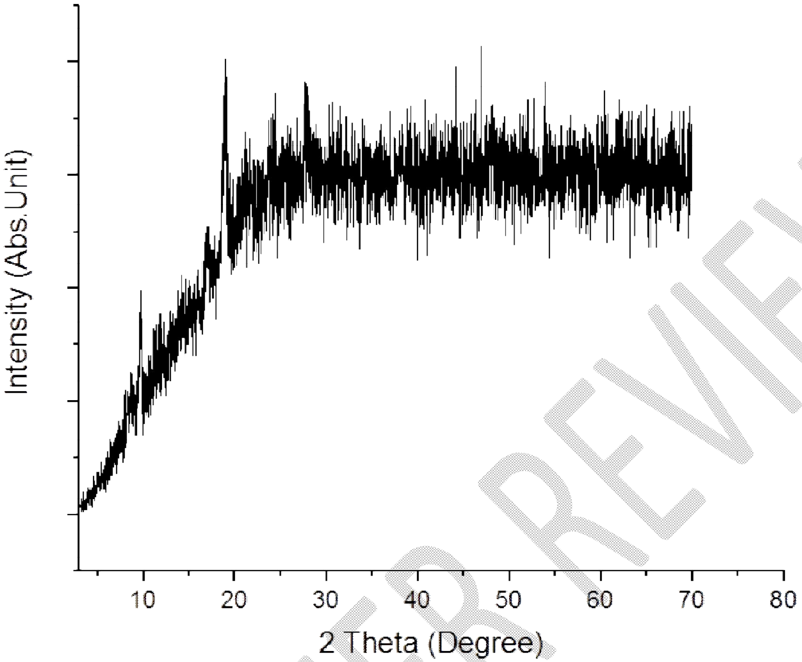
Appendix 27. XRD spectra for 2-phenyliminomethylphenol Nickel(II) chloride complex, [Ni(PMP)$_2$.Cl$_2$]



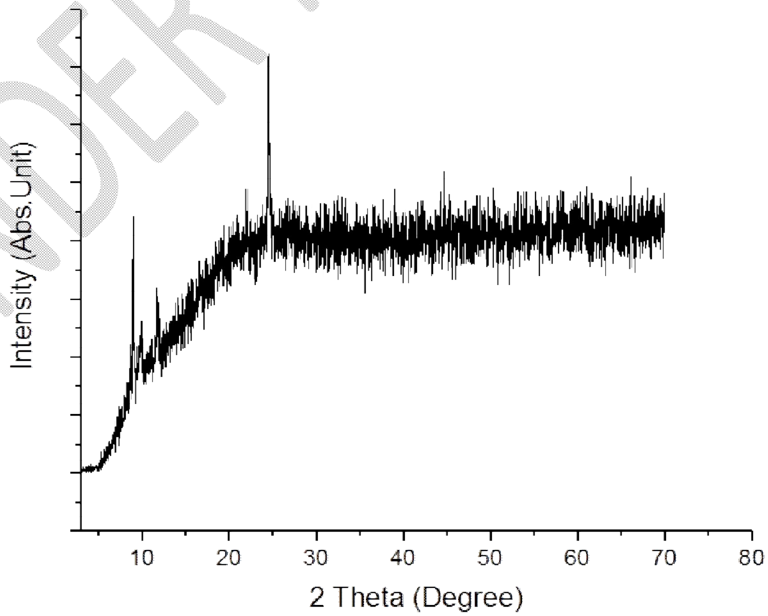
Appendix 28. XRD spectra for 2,2-hydroxybenzylideneaminophenol Nickel(II) chloride complex, $[Ni(HAP)_2.Cl_2]$



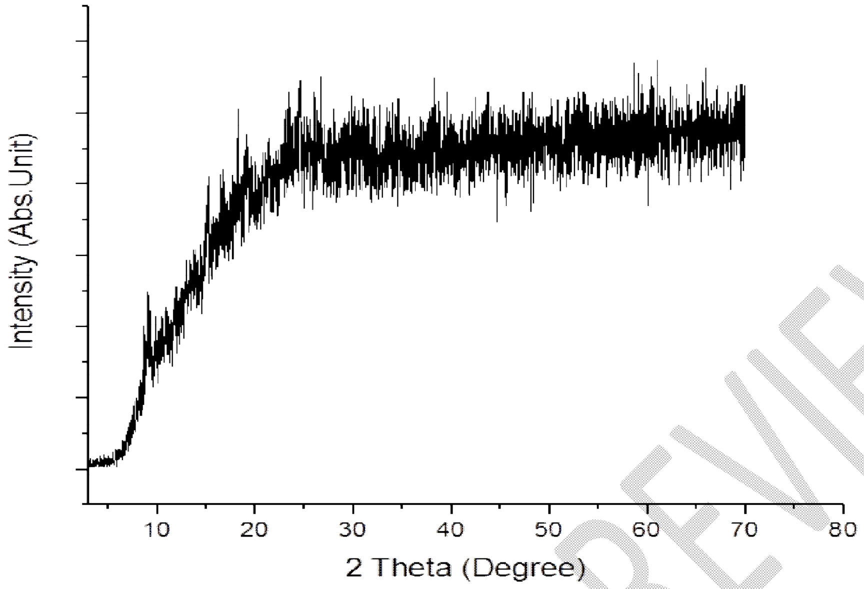
Appendix 29. XRD spectra for mixed ligand (PMP+HAP) Nickel(II) chloride complex, [Ni(PMP+HAP).Cl_2]



Appendix 30. XRD Spectra For 2-Phenyliminomethylphenol Cobalt(II) Chloride Complex, [Co$(PMP)_2$.Cl_2]



Appendix 31. XRD spectra for 2,2-hydroxybenzylideneaminophenol Cobalt(II) chloride complex, [Co$(HAP)_2$.Cl_2]



Appendix 32. XRD spectra for mixed ligand (PMP+HAP) Cobalt(II) chloride complex, [Co(PMP+HAP).Cl_2]

5. Recommendations

1. It is recommended that further research on other pharmaceutical and medicinal application such as anticancer, antitumor and antimutagenic investigations rather than antimicrobial activities of these complexes be done.
2. Investigation onindustrial applications such as catalysis, epoxidation reactions, metathesis, polymerization agents, metallocenes,etc of these complexes should be carried out.
3. Investigations on other economic viability of the complexes should be carried out.

6. References

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