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SYNTHESIS AND CHARACTERIZATION OF SCHIFF BASE COMPLEXES DERIVED FROM 2,4-DIHYDROXYBENZOPHENONE, 2-HYDROXY-4-METHOXYBENZOPHENONE AND HYDRAZIN

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Synthesis and characterization of Schiff base complexes derived from 2,4-dihydroxy benzophenone, 2-hydroxy-4-methoxybenzophenone and hydrazin.

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This is to certify that the thesis prepared by Shewaye Temesgen, entitled: *Synthesis and characterization of Schiff base complexes derived from 2,4-dihydroxy benzophenone, 2-hydroxy-4-methoxybenzophenone and hydrazine* and submitted in partial fulfillment of the requirements for the degree of Master of Science complies with the regulations of the university and meets the accepted standards with respect to originality and quality. Signed by the Examining Committee:

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ABSTRACT

Synthesis and characterization of Schiff base complexes derived from 2,4-dihydroxy benzophenone, 2-hydroxy-4-methoxybenzophenone and hydrazine

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Addis Ababa University, 2013

Metal complexes of Ni (II) and Cu (II) with Schiff base 2,4-DHBPAM derived from the condensation of 2,4-dihydroxy benzophenone with hydrazine have been synthesized and characterized on the basis of elemental analyses, infrared studies, molar conductance, magnetic susceptibility measurements, and UV-Vis spectroscopy. The Schiff base ligand acts as a tetradentate coordinating through the oxygen atom of the deprotonated phenolic group and the nitrogen atom of azomethine group. This is confirmed by IR spectral data. The analysis of magnetic susceptibility and UV-Vis spectral data indicate octahedral geometry for the Cu (II) and Ni (II) complexes. Similar synthesis and characterization have been done for Ni (II) and Co (II) complexes derived from 2-hydroxyl-4-methoxybenzophenone and hydrazine using template method under different reflux time. The ligand in these complexes acts as tetradentate coordinates through oxygen atom of the deprotonated phenolic group and the terminal nitrogen of hydrazone which is supported by the IR spectral data.

Keywords: Schiff base, 2,4-dihydroxy benzophenone, 2-hydroxyl-4-methoxybenzophenone, template method .

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List of Abbreviations

2,4-DHBP	2,4-dihydroxy benzophenone
2,4-DHBPAM	2,4-dihydroxy benzophenone azomethine
2-H-4-MBP	2-hydroxy-4-methoxy benzophenone
2-H-4-MBPAM	2-hydroxy-4-methoxy benzophenone azomethine
2-H-4-MBPH	2-hydroxy-4-methoxy benzophenone hydrazone
EtOH	ethanol
MeOH	methanol
DMSO	dimethylsulfoxide
THF	tetrahydrofuran
DMF	dimethylformamide
DMG	dimethylglyoxime
TLC	thin layer chromatography
IR	infra-red
^{1}H NMR	proton nuclear magnetic resonance
^{13}C NMR	carbon nuclear magnetic resonance
UV-Vis	ultraviolet-visible
μeff	effective magnetic moment
χM	molar susceptibility
χg	gram susceptibility

1. Introduction

Schiff - base transition metal complexes play an important role in the field of coordination chemistry and find extensive applications in different fields. The understanding of relationship between metals and various biological systems is a subject of great interest for researchers [1]. The investigation done on the relationship of metal with various biological systems brings an introduction of Schiff base metal complexes application in different fields, like in agriculture sector for insect pest management, in human biology, in medicine for therapeutic activity [1-3].

From the survey of existing literature, it appears that benzyl mono phenyl hydrazone and its related compounds have been extensively used as biologically active complexing agents and analytical reagents [4]. To the best of my knowledge, no works have been done on the complexation of 2,4-dihydroxy benzophenone and 2-hydroxy-4-methoxy benzophenone with hydrazine. Therefore, in this work, we report the results of our studies on the synthesis, spectral properties of Co (II), Ni (II), Cu (II) and Zn (II) complexes of those Schiff bases.

1.1 The Chemistry of Schiff base

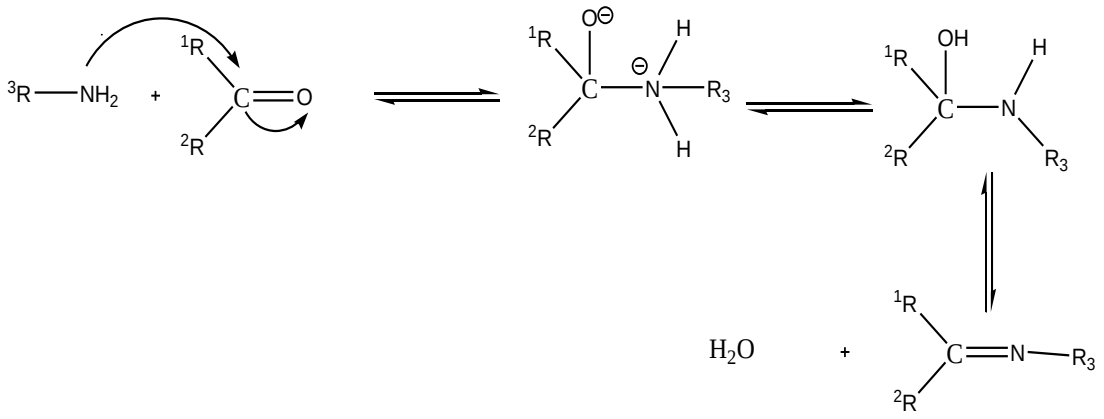
Schiff bases are compounds containing a carbon-nitrogen double bond (azomethine group), (C=N-) with the nitrogen atom connected to an aryl or alkyl group but not hydrogen. Schiff bases are of the general formula R1R2C=N-R3, where R3 is an aryl or alkyl group that makes the Schiff base a stable imine [5].

Schiff bases named after Hugo Schiff described the condensation between an aldehyde and an amine. Schiff base ligands are able to coordinate metals through imine nitrogen and another group usually linked to aldehyde [6] as shown in scheme 1.

Schiff bases have been studied for their important properties in catalysis [7]. They show catalytic activity in hydrogenation of olefins [8]. They find applications in biomimetic catalytic reactions.

Several studies [9, 10] showed that the presence of a lone pair of electrons in sp^2 hybridized orbital of nitrogen atom of the azomethine group is of considerable chemical and biological importance. Because of the relative easiness of preparation, synthetic flexibility, and the special property of C=N group, Schiff bases are generally excellent chelating agents,[9-12] especially

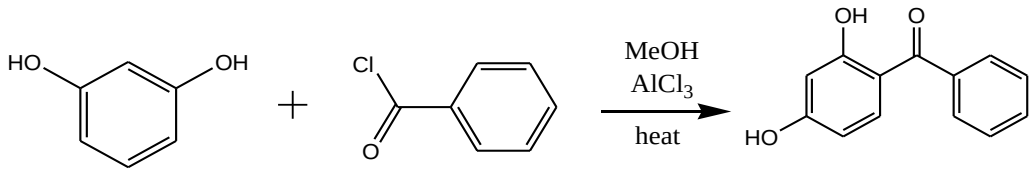
when a functional group like –OH or –SH is present close to the azomethine group so as to form a five or six membered ring with the metal ion.



Scheme 1 The reaction to prepare Schiff base

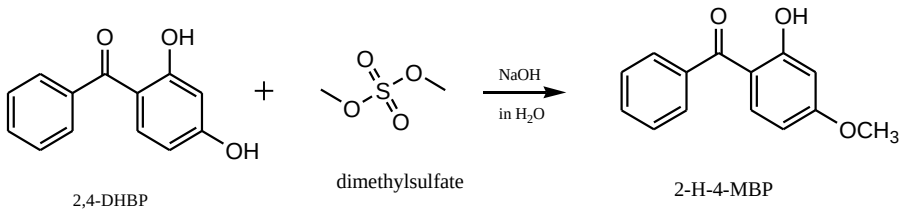
1.2 Chemistry of 2,4-Dihydroxybenzophenone and its derivatives

The well-known Ultraviolet light stabilizer, 2,4-dihydroxybenzophenone is synthesized by Friedel-Crafts acylation of resorcinol with benzoyl chloride in the presence of $A1C1_3$ or by adding benzotrichloride to a solution of resorcinol in aqueous methanol followed by heating [13].



Scheme 2 Synthesis of 2,4-dihydrohybenzophenone

When a solution of 2,4-dihydroxybenzophenone in aqueous sodium hydroxide is treated with dimethylsulfate, 2-hydroxy-4-methoxybenzophenone is produced which also occurs naturally in flower pigments and it synthesized for use in sunscreens, as a UV stabilizer in various cosmetic products, and in plastic surface coatings and polymers [14].

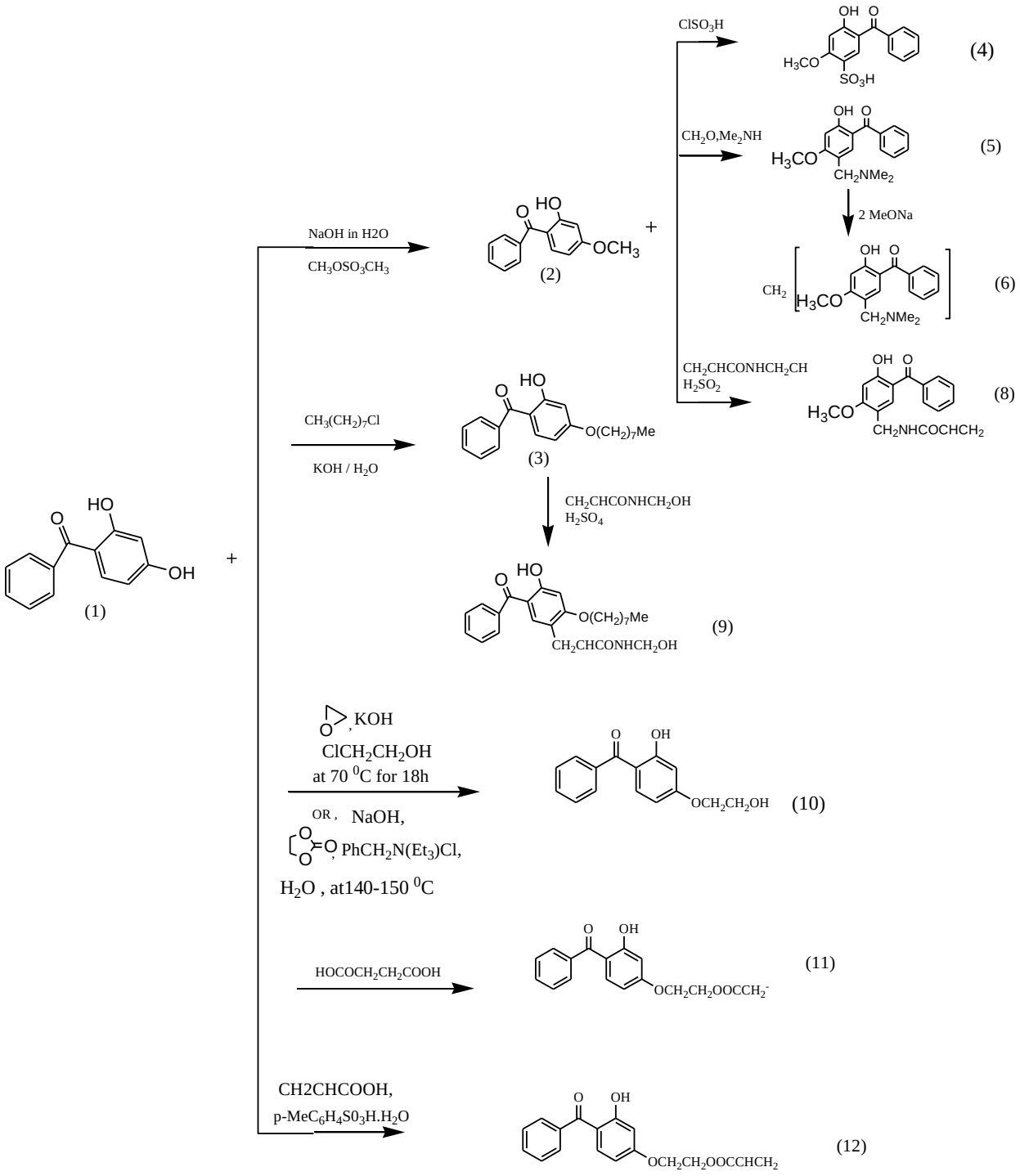


2,4-DHBP dimethylsulfate 2-H-4-MBP

Scheme 3 Synthesis of 2-hydroxy-4-methoxy benzophenone

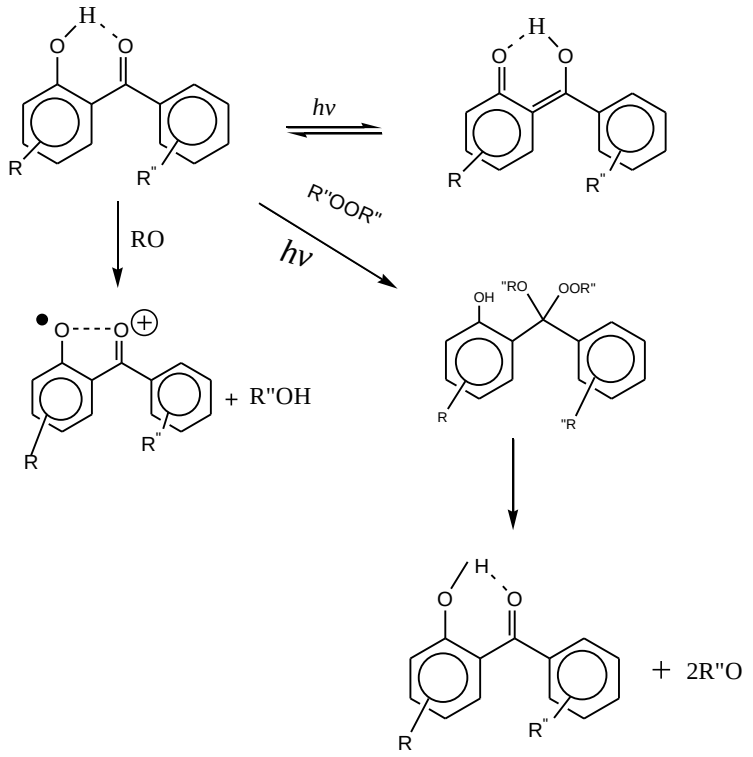
There are a number of compounds derived from 2,4-dihydroxybenzophenone, mainly it reacts with electrophiles at the para- position of the hydroxyl group as shown in Scheme 4.

Literature reveals that 2,4-dihydroxy benzophenone itself is employed sometimes, some of its derivatives are used more frequently as the practical ultraviolet absorbers to prevent materials from photo-degradation or photo-crosslinking caused by ultraviolet light presented in sunlight and artificial light source[15].



Scheme 4 Reactions of 2,4-DHBP

It has been proposed that, when ultraviolet light is irradiated, the proton of their 2-hydroxy group transfers to the oxygen of carbonyl group affording the excited form and it can migrate back again to provide the former phenolic structure under giving out heat (see Scheme 5), fluorescence, or phosphorescence [13].



Scheme 5 Ultraviolet absorbers of 2-hydroxybenzophenone type

1.3 Reactivity of Hydrazine

Hydrazine is a convenient reductant because the by-products are typically nitrogen gas and water. Thus, it is used as an antioxidant, an oxygen scavenger, and a corrosion inhibitor in water boilers and heating systems. It is also used to reduce metal salts and oxides to the pure metals in electro-less nickel plating and plutonium extraction from nuclear reactor waste. Some colour photographic processes also use a weak solution of hydrazine as a stabilizing wash, as it scavenges dye coupler and unreacted silver halides [16].

There are a number of processes reported for the commercial production of hydrated hydrazine. Some of those are Olin Raschig process, the Ketazine process, the peroxide process and

Pechiney-Ugine-Kuhlmann process. The Raschig process involves oxidation of ammonia to chloramine with sodium hypochlorite then further reaction of the chloramine with excess ammonia and sodium hydroxide to produce an aqueous solution of hydrazine with sodium chloride as a by-product. Fractional distillation of the product yields hydrazine hydrate solutions [17].

$$NH_2Cl + NH_3 + NaOCl \rightarrow H_2N\text{-}NH_2\,(aq.) + NaCl$$

Anhydrous hydrazine is the formulation used in rocket fuels and is produced by dehydration of the hydrate by azeotropic distillation with aniline as an auxiliary fluid [16].The chemistry of hydrazine derivatives had its beginnings in 1863 when Hofmann successfully converted azobenzene to hydrazobenzene thus synthesizing the first hydrazine derivative.

Hydrazine is the versatile ligand and it offers the possibility of different modes of coordination towards transition metal ions [18, 19]. It can function as a mono dentate or bidentate ligand [20]. Thermal reactivity of the metal carboxylates with hydrazine is of increasing interest, since they serve as precursors to fine particle oxide materials [21].

1.4 Transition metal complexes of Multidentate N and O donor Schiff base ligands

Schiff bases and their transition metal complexes continue to be of interest even after over a hundred years of study. Schiff bases have a chelating structure and are in demand because they are straightforward to prepare and are moderate electron donors with easily-tunable electronic and steric effects thus being versatile. Schiff base metal complexes are still widely used in catalysis but increasingly with a slightly modified concept [22].

Schiff base complexes have been extensively used in a variety of applications including biological, clinical and analytical [23-25]. Nowadays, the research field dealing with Schiff base coordination chemistry has expanded enormously. The importance of Schiff base complexes for bioinorganic chemistry, biomedical applications, supra molecular chemistry, catalysis and

material science, separation and encapsulation processes, and formation of compounds with unusual properties and structures has been well recognized and reviewed [26].

Even though the condensation reaction can be retarded or totally hindered by steric effects of the carbonyl compound and amine, it is important to be able to synthesize sterically hindered metal complexes. These complexes have a significant impact on catalyst design as the ligand substituents can have a prominent effect on the catalytic activity of the prepared metal complex [27].

The coordination chemistry of nitrogen-oxygen donor ligands is an interesting area of research [28]. They have played an important role in the development of coordination chemistry, as they readily form stable complexes with most of transition metal elements [29].

Complexes of substituted hydrazine such as hydrazine, thiosemicarbazide, hydrazone and diacylhydrazine are of general interest as models for bioinorganic processes [30 - 33]. The interest has been centered on the role of such complexes in providing synthetic models for metal-containing sites in metallo-proteins and enzymes [29].

The effective role of Schiff base ligands is well documented in biological, pharmacological, clinical and analytical applications. Schiff bases are capable of forming coordinate bonds with many of metal ions through either/both azomethine nitrogen and phenolic oxygen. A large number of Schiff bases and their complexes are of significant interest and attention because of their biological activity including anti-tumor, antibacterial, fungicidal, anti-carcinogenic and catalytic activity [34, 35].

1.5 Metal complex synthesis methods

Synthesis of the metal-ligand complex can be carried out in two methods. Synthesizing the full ligand from different precursors accompanied by introduction of the metallic species of interest constitutes one of these methods and this is known as direct method. In the other method, the different precursors and the metallic species or one of the precursor along with the metallic

substance followed by addition of another precursor after some times are allowed to undergo complex formation. This method is known as the template method [36].

In template method, the reaction is fundamentally enhanced by a particular geometrical orientation that is imposed by metal coordination. The effect recognizes molecular organization because it involves organization of an assembly of atoms with respect to one or more geometrical positions so as to achieve a particular linkage between atoms [37].

A template can be called either positive or negative. In a positive template, two reactive parts of a single molecule can be brought together while negative template keeps the reactive groups apart, thus, suppressing the desired reaction and favoring the intermolecular one.

Metal-template reactions offer simple ways to obtain organic molecules which otherwise involve complicated organic routes, high amount of solvents, small yields and high costs. In such cases, organic molecules act as ligands and the high stability of the complex allows the reaction at the coordinated ligands without complex distraction [38].

2. Objective

2.1 General objectives

The main aim of this work is to synthesize and characterize new metal complexes of Ni (II) and Cu (II), Co (II) and Zn (II) from a Schiff base, derived from the condensation of 2,4-dihydroxy benzophenone and 2-hydroxy-4-methoxy benzophenone with hydrazine.

The characterization of both the ligands and metal complexes was carried out using NMR, (only for ligand and Zn (II) complex), elemental analyses (C, H, N), infrared spectroscopy, molar conductance, magnetic susceptibility measurements, and UV-Vis spectroscopy.

2.2 Specific objectives

- To synthesize and characterize Schiff base ligand derived from the condensation of 2,4-DHBP with hydrazine.
- To synthesize and characterize metal complexes of Ni (II), Cu (II) and Zn (II)) of Schiff base by both direct and template synthesis methods.
- To synthesize and characterize metal complexes of Co (II) and Ni (II) complex of 2-H-4-MBP and hydrazine under template synthesis methods.

3. Experimental

3.1 Chemicals

All the chemicals used for the synthesis of the ligand precursors the metal complexes were of Analar grade. Chemicals used in the syntheses of 2,4-DHBPAM were 2,4-dihydroxybenzophenone, hydrazine monohydrate, and for the metal complexes, 2,4 DHBPAM, 2,4-DHBP, 2-H-4-MBPH, hydrazine, $NiI_2 \cdot 6H_2O$ and $CuCl_2 \cdot H_2O$, $CoCl_2 \cdot 6H_2O$, and $ZnCl_2$.
Solvents and reagents used during the investigation include; MeOH, EtOH, DMSO, THF, DMF, $CHCl_3$, iso-propanol, chloroform, acetone, acetonitrile, benzene, 1,4-dioxine, diethylether, ammonium hydroxide, acetic acid, HCl, HNO_3, DMG, $AgNO_3$, and KCl.

3.2 Instrumentation

Purity of the ligand was tested by thin layer chromatography (TLC). For this purpose, a mixture of benzene, ammonia and acetic acid were used to develop chromatograms. Electrothermal IA 9200, digital melting point apparatus was used to determine the melting point of the ligands, and metal complexes. The ^{1}H NMR, ^{13}C NMR and DEPT spectra were recorded on BRUKER 400 Ultra-shield NMR (400 and 100.6 MHz for ^{1}H and ^{13}C, respectively). ^{1}H NMR, ^{13}C NMR and DEPT spectra of 2,4-DHBP was recorded using $CDCl_3$ as a solvent and $DMSO.d_6$ was used for 2,4-DHBPAM. The IR spectra of the ligands and the complexes were recorded using KBr pellets (4000–400 cm^{-1}) on Perkin-Elmer BTX FT-IR spectrometer.

Molar conductance of the metal complexes was determined in MeOH, EtOH and DMF at room temperature using a Hanna Digital conductometer (HI86304 reads EC from0.00-19.99ms/cm). The UV-Vis spectra's were recorded in the range of 200-900 nm region using SPECTRONIC GENESYS 2 PC. The Uv-vis spectrum of the ligand as well as their metal complexes was studied in MeOH, EtOH and DMF. Magnetic susceptibility measurements were carried out on Sherwood Scientific Magnetic susceptibility balance at room temperature ($22^{0}C$). The metal contents & chloride contents of the complexes were determined according to the common analytical procedures.

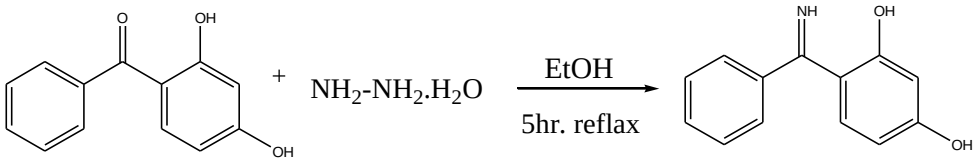
3.3 Method

The metal complexes of the Schiff base ligand was synthesized using both direct and template synthesis method. The metal to ligand ratio of Ni (II), Co (II) and Cu (II) complexes were determined by gravimetric analyses using the most known reagents DMG, NH_3SCN and $NH_3$for Ni^{+2}, Co^{+2} and Cu^{+2} tests, respectively.

3.4 Synthesis of the ligands

3.4.1 Synthesis of 2,4-dihydroxy benzophenone azomethine (2,4-DHBPAM)

The Schiff base has been synthesized by adding 2.5 ml (0.05 mol) of monohydrate hydrazine in ethanolic solution of 2, 4-DHBP (10.7 g, 0.05 mol) in equimolar ratio followed by the addition of $CuCl_2 \cdot 2H_2O$ (4.26 g) dissolved in the same solvent with 3 ml pipridine. The reaction mixture was continuously stirred for about 12 hours at room temperature. The chocolate color precipitate was discarded and the filtrate was left to evaporate at room temperature. The yield of the product, after recrystallization through benzene and a mixture of diethylether and water, was 34% (3.68 g) and melts at 328^0C.



Scheme 5 Reaction of 2,4-DHBP with hydrazine

3.5 Synthesis of metal complexes

3.5.1 Template Synthesis of Co (II) and Ni (II) complex of 2-H-4-MBPH

Each metal salt of 5 mmol (1.19 g of $CoCl_2 \cdot 6H_2O$,1.19 g of $NiCl_2.6H_2O$) dissolved in hot propanol (25 ml) was mixed to 2.28 g (14 mmol) of 2-hydroxy-4-methoxy benzophenone dissolved in the same solvent followed by the addition of 0.7 ml (14 mmol) of hydrazine dropwise. The reaction mixture was refluxed for 24 hours and 1 hour, respectively. The product was filtered off after cooling of the reaction mixture, and then dissolved in ethanol and left until

a yellow precipitate was formed. The yellow precipitate was discarded; while the ethanolic solution was evaporated at room temperature.

3.5.2 Direct Synthesis of Ni (II) and Cu (II) complex of 2,4-DHBPAM

2,4-DHBPAM (0.08 g, 0.352 mmol and 0.25 g, 1.096 mmol) dissolved in hot propanol (25 ml) with 3 ml of pyridine was added to each metal salt solution of propanol (0.13 g, 0.548 mmol of $NiCl_2 \cdot 6H_2O$, 0.03 g, 0.176 mmol $CuCl_2 \cdot 2H_2O$), respectively. The reaction mixture then refluxed for 30 hours at 85-90^{0}C. The reaction mixture was concentrated using rotary evaporator. Then the product was recrystallized with ethanol several times.

4. Results and Discussion

4.1 General

In this study, we tried to synthesize the Schiff bases, 2,4-DHBPAM, and its metal complexes of Co (II), Ni (II), Cu (II) and Zn (II) using both template and direct synthesis methods. The Schiff base synthesis was not successful without the usage of $CuCl_2.2H_2O$. The metal complex synthesis of 2,4-DHBP and hydrazine using the template synthesis method was not effective for all metals listed above. The Co (II) and Ni (II) complex synthesis of 2-H-4-MBP and hydrazine was successful under the same method. The metal complex synthesis of 2,4-DHBP and hydrazine using the same method was not effective for all metals listed above, which is supported by the elemental analyses we made in table 6. In addition, Cu (II) complex synthesis of 2-H-4-MBP with hydrazine was not successful in complexation. Rather the single crystals obtained from the synthesis revealed the formation of the azomethine (2-H-4-MBPAM (2-hydroxy-4-methoxy benzophenone azomethine) and its dimer (see Appendix 14).The solved structure of these crystals are A and B shown in Figures 2 and 3, respectively. Therefore, the discussion we made later is concerning only the successful results.

The metal complexes synthesized in this work was soluble in DMF, 1,4-dioxine, and slightly in methanol, THF, acetonitrile. The analytical data of ligands and there metal complexes are listed in Table 1.

Table 1 Analytical data of the precursors, the Schiff Base Ligands and metal complexes

Compound name	Color	Decomposition (^{0}C)	Yield (%)	$\mu_{effe.}$ B.M
DHBP	light yellow	>145	-	-
DHBPAM	orange	>318	34	-
$[Co(C_{14}H_{12}N_2O_2)_2]\cdot 2H_2O$	Dark green	>267	82	3.41
$[Cu(C_{13}H_{10}NO_2)_2]\cdot 2H_2O$	brown	>205	89	
$[Ni(C_{13}H_{10}NO_2)_2]\cdot 2H_2O$	Dark yellow	>318	86	3.01
$[Ni(C_{14}H_{12}N_2O_2)_2\cdot 2H_2O$	White green	>350	80	2.92

4.2 Structural study of the Schiff base ligand

4.2.1 IR Spectrum of 2,4-DHBPAM

The IR spectrum of the starting compound (2,4-DHBP) shows basic characteristic bands at 3183, 1629 and 1282 cm^{-1} , which are associated with *ν*O−H, *ν*C=O and *ν*C−H, respectively (appendix 1). Upon condensation, the band at 3183 cm^{-1} was shifted to 3315 cm^{-1}.This is due to the overlapped stretching of both N−H and O−H. The carbonyl stretching at 1629 cm^{-1} disappears and new band appears at 1616 cm^{-1}. This is attributed to the formation of azomethine(C=N). The strong band at 1242 cm^{-1} is the C−O stretching of the phenolic OH. The absence of any new band in the region 1080-950 cm^{-1} is due to the absence of N−N stretching of hydrazone and the rest shows the same pattern as shown in the starting compound (precursor ligand) except change in intensity (Appendix 2) [39, 40].

Table 2 Summary of the IR bands of the Schiff base ligand

compound	ν_{N-H} cm^{-1}	ν_{O-H} cm^{-1}	$\nu_{C=O}$ cm^{-1}	$\nu_{C=N}$ cm^{-1}	ν_{C-O} cm^{-1}	ν_{C-N}, ν_{N-N} cm^{-1}
2,4-DHBP	-	3183	1629	-	1282	-
2,4-DHBPAM	3315	-	-	1616	1242	-

4.2.2 NMR Spectra of 2,4-DHBPAM

The NMR spectrum of 2,4-DHBPAM was obtained from DMSO.d_6. The ^{1}H NMR spectrum showed the presence of aromatic protons appearing in the region between 6-8 ppm. A singlet appearing at 6.1 ppm (1H) is due to H*e* (see figure 1). The one appearing at 6.2 ppm (1H) is more likely due to H*c*. This proton was found to couple with a proton appearing at 6.6 ppm (1H). The broad singlet found at 7.3 ppm (2H*A*) is due to the symmetrical proton ortho to the terminal carbon of the mono-substituted benzene. The remaining three hydrogen atoms in the ring were found in broad singlet at 7.6 ppm. In addition, the spectrum also reveals the presence of phenolic hydrogen appearing at 10.2 and 12 ppm. The one that appears at 12 ppm (1H) is accounted for the OH ortho to the azomethine group (H*g*) (appendix 3).

The ^{13}C spectrum shows eleven signals at 103.26, 108.08, 111.68, 128.03, 129.32, 129.49, 133.71, 134.74, 135.8, 162.45 and 169.80 ppm (appendix 4). The phenolic carbons are seen at 103.26, 108.08, 111.68, 133.71, 135.80, 162.44 ppm. As shown from the DEPT spectrum (appendix 5), only three signals at 103.26, 108.08, and 133.71ppm appear (see figure 1 and table 3), which implies that carbons of the phenol bears hydrogen (C-H). The carbon bearing azomethine appears at 169.80 ppm. The terminal carbon of the mono substituted benzene appears at 134.74 ppm and the rest three are for the rest benzene carbons [41, 42].

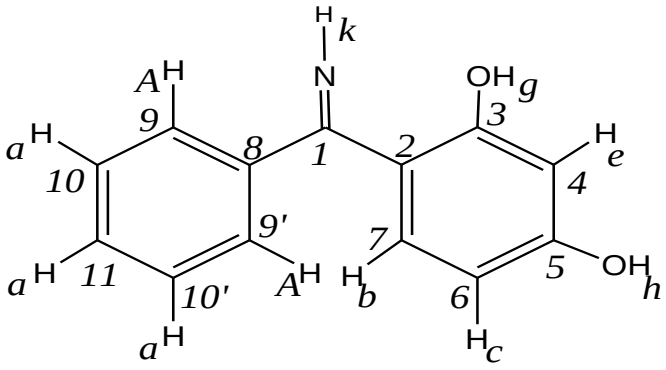


Figure 1 The structure of synthesized 2,4-DHBPAM

Table 3 Chemical shift value of ^{13}C and DEPT of 2,4-DHBPAM

Chemical Shift (ppm)	^{13}C	DEPT
C1	169.80	Q
C2	134.74	Q
C3	135.80	Q
C4	103.26	103.26
C5	162.44	Q
C6	108.08	108.08
C7	133.71	133.72
C8	111.68	Q
C9	129.49	129.49
C10	129.32	129.32
C11	128.03	128.03

4.3 Characterization of the Metal Complexes

4.3.1 IR spectra of Cu (II) and Ni (II) complex of 2,4-DHBPAM

In order to study the binding mode of Schiff base to metal in the complexes, IR spectrum of the free ligand was compared with the spectra of the metal complexes. 2,4- dihydroxy benzophenone azomethine shows its characteristics absorption bands in the 3315, 1615, and 1242 cm^{-1} regions, assignable to O–H, C=N and C-O stretching vibrations, respectively (see appendix 2). The band at 1615 cm^{-1} due to the azomethine group of the Schiff base underwent a shift to lower frequency (1605 cm^{-1}) after complexation, indicating the coordination of azomethine nitrogen to metal atom. In the spectra of both complexes, the broad band at 3420 and 3324 cm^{-1}, together with new band at 689 cm^{-1} and 692 cm^{-1} indicating the presence of coordinated water [39, 40].

The nature of metal– ligand bonding is confirmed by the newly formed non ligand band below 459 cm^{-1}, 430 cm^{-1} and 520 cm^{-1}, 515 cm^{-1} in the spectra of the Cu (II) and Ni (II) complexes, which are tentatively assigned to M-O and M–N stretching vibration of Cu (II) and Ni (II) [43], respectively (appendix 6 &7).

Table 4 summary of Cu (II) and Ni (II) complex of 2,4-DHBPH IR spectra

	νOH	ν**C**=N	νC-O	νM-N	νM-O
Ligand	3315(sh, m)	1615 (s)	1242(s)	-	-
Cu Complex	3420(b, m)	1605(s)	1241(m)	520	>459
Ni Complex	3324(b, m)	1605(s)	1241 (m)	515	430

b- broad, m- medium, sh- sharp, s- strong, w- weak

4.3.2 IR spectrum of Co (II) and Ni (II) complex of 2-H-4-MBPH

IR spectrum of the free precursor ligand was compared with the spectrum of the cobalt complex. 2-hydroxy-4-methoxybenzophenonhydrazone shows its characteristic absorption bands in the regions 3064-2631, 1636, 1260 and 1113 cm^{-1}, assignable to O–H, C=O, C-O-H and C-O-C stretching vibrations, respectively (see appendix 8). After complexation, the Co (II) complex showed new characteristic bands at 3391, 3322, 1621, 1246, 1035, 600-532 and 460-404 cm^{-1} which can be explained as follows:

The band at 1636 cm^{-1} is due to the carbonyl group of the precursor ligand shifts to lower frequency (1621 cm^{-1}), indicating the formation of azomethine. The broad band at 3391 cm^{-1} is due to the stretching of N-H of hydrazone (see appendix 10). The band at 1260 cm^{-1}on the precursor ligand due to the phenolic hydroxyl group is shifted to the lower frequency with medium intensity (1246 cm^{-1}), is the conformation of the involvement of the phenolic hydroxyl group coordinated to the metal ion through oxygen. This is also supported by the multiple new bands appearing in the region 460-404 cm^{-1}[43]. The weak peak at 980 cm^{-1} is associated with the stretching of N-N of the hydrazone.

The appearance of weak and broad peak centered at 3435 cm^{-1}, in the Ni(II) complex (appendix 9), is due to the stretching of NH of the hydrazone, indicating the involvement of terminal nitrogen of hydrazone in coordination with the metal. The peak in the double bond region shows slight change in comparison to the precursor ligands (1636 → 1630 cm^{-1}), which confirms the formation of C=N. The band at 1261 cm^{-1}, due to the stretching of C-O of the phenol and the band at 1113 cm^{-1} is the stretching of C-O-C of the methoxy group, the stretching of N-N bond of hydrazone is assigned by the new weak peak at 979 cm^{-1} [39, 40]. The weak peak at 408 cm^{-1} is due to the M-O stretching. The details of basic characteristic bands are summarized on the following table.

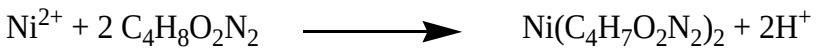
Table 5 Summary of Co (II) and Ni (II) complex IR characteristic bands

	*V*N-H cm^{-1}	*V*O-H cm^{-1}	*V*C=O cm^{-1}	*V*C=N cm^{-1}	*V*C-O cm^{-1}	*V*C-O-C cm^{-1}	*V*N-N cm^{-1}	*V*M-O
Precursor Ligand	-	3064-2631(w)	1636(s)	-	1260(s)	1113(m)	-	-
Co(II) complex	3391(w)	3322(w)	-	1621(m)	1246(m)	1114(m)	980(w)	404(w)
Ni(II) complex	3435(w)	3285(s)	-	1630(m)	1261(s)	1113(m)	979(w)	408(w)

b- broad, m- medium, sh- sharp, s- strong, w- weak

4.4 Metal analysis

The quantity of nickel ions in a sample is determined by precipitating the ions with dimethylglyoxime in an ammonium hydroxide solution.



$$Ni^{2+} + 2\ C_4H_8O_2N_2 \longrightarrow Ni(C_4H_7O_2N_2)_2 + 2H^+$$

The red precipitate is due to formation of bis (dimethylglyoximato) nickel (II), Ni $(C_4H_7O_2N_2)_2$. All Nickel complexes of 2,4-DHBPAM and 2-H-4-MBPH form red precipitation.

4.5 Chloride ion estimation in the metal complexes

This test was achieved by using aqueous solution of silver nitrate of 0.01M and diluted nitric acid. The test shows that, none of the metal complexes form a white precipitate, indicating the absence of chloride in the inner sphere as well as in their outer sphere.

4.6 Elemental analysis

The elemental analysis of Ni and Cu complexes synthesized by template method are summarizes in the following table.

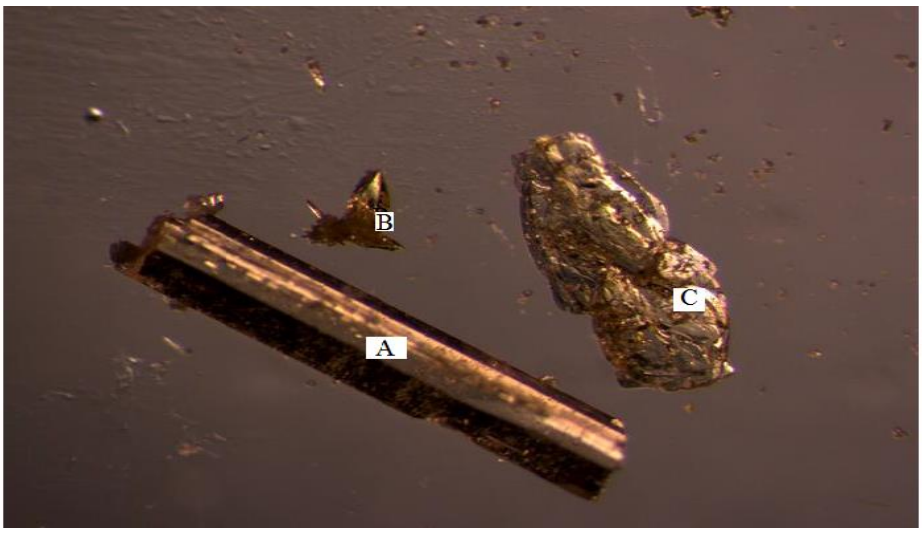
Table 6 summary of C, H, N analysis in some complex

	Elemental analyses (%)							
	C		H		N		metal	
	Cal.	found	Cal.	found	Cal.	found	Cal.	found
2,4-DHBPH of Cu	60	1.57	4.15	5.35	5.26	0.01	11.93	
2,4-DHBPH of Ni	59.2	1.75	4.17	4.22	5.31	27.32	11.13	29.8
2-H-4-MBPH of Ni	52.09	49.78	4.3	5.01	8.68	9.82	9.09	10.1
2-H-4-MBP of Cu	59.79	73.59	4.98	5.32	4.98	0.18	11.29	

Cal. Calculated value

The Ni complex of 2-H-4-MBPH is in good agreement with the molecular formula given in the conclusion.

The Cu (II) complex synthesis of 2-H-4-MBP has showed an excess of Carbon and Hydrogen, and insignificant percent of Nitrogen. It has a crystal structure depicted in the photograph below.



The crystals on the left (pale yellow square columns, **A**) are the best ones in terms of crystal quality and size. It was took a preliminary set of data in order to check that they were compatible with the expected molecule. It was checked in the CCDC database that these cell parameters did not correspond to the structure of an already published compound. As the search in the database did not give any result, collected the full data set and solved the structure, finding that the molecule was not the copper complex but a fragment of the ligand:

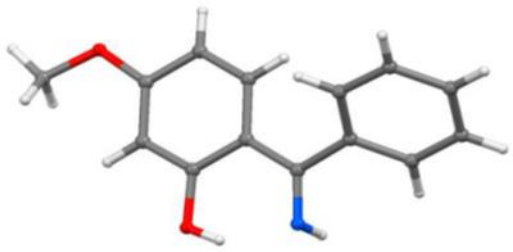


Figure 2 structure of crystal A

As there were two other crystal types, It was tried next the type **B** crystals, collecting again the cell parameters and checking the database and compatibility of these parameters with the proposed molecule. As they were also compatible with the expected coordination compound, and different from the once obtained for crystal sample **A**, It collected the full data set. All of the crystals of type **B** are very small but the collected data were good enough to solve the structure, and the result was a dimer of the species present in crystal **A**:

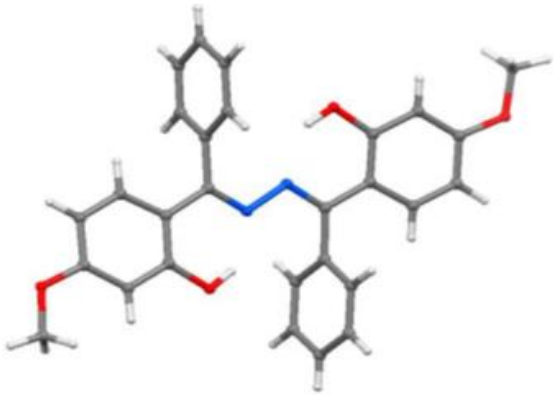


Figure 3 structure of crystal B

Finding again that the crystals were not from the copper complex, it was tried crystals of the type **C**. They are extremely thin plates that form clusters and need to be previously cut in order to obtain a single crystal domain. Unfortunately, the data from the preliminary set only allowed to know that they are a different crystalline solid, with different unit cell parameters (also not

previously published), but they do not give enough diffraction signal to allow the structure solution.

4.7 Molar conductivity

The molar conductivity measurements of Ni (II), Cu (II), and Co (II) complex were carried out by using MeOH and DMF as solvents, respectively. The result shows that all the complexes were non-electrolytes.

4.8 Magnetic susceptibility measurements of the metal complexes

The magnetic susceptibility measurements of all complexes were measured at room temperature (22^0C). The effective magnetic moment of Ni complexes of 2,4-DHBPAM and 2-H-4-MBPH was 3.01 BM and 2.92 BM, respectively. These values are in good agreement with the μeff value of Ni (II) complexes in the literature, which range from 2.9 BM to 3.9 BM. Therefore, these values are for two unpaired electrons. The cobalt complex of 2-H-4-MBPH has a magnetic moment of 3.41BM which is less than the expected value ranging from 4.1 BM to 5.2 BM for Co^{+2}. Although there is significant decrease in its magnetic moment, the number of unpaired electron calculation indicates the presence of three unpaired electrons around the metal atom. Therefore, cobalt in this complex most likely is in + 2 oxidation state [44-46].

Table 7 Summary of magnetic susceptibility of Ni and Co complexes

	MW g/mol	χ_g at 22^oc 10^{-6} g/cm^{-3}	χ_M 10^{-3} g/mol^{-3}	$\mu_{effe.}$ B.M	n
Ni(II)2,4-DHBPAM	527	7.289	3.84	3.01	2.17
Ni(II)2-H-4-MBPH	645	5.609	3.62	2.92	2.08
Co(II)2-H-4-MBP	593	8.30	4.92	3.41	2.55

4.9 Uv-visible studies

The Uv- visible absorption spectra of the Schiff base and its Cu (II) and Ni (II) complexes of 2,4-DHBPAM were recorded at room temperature using DMF and methanol as solvents, respectively. The Uv-vis spectrum of the ligand shows two bands at 318 and 387 nm. Those

bands are associated with π-π* and n-π* transitions, respectively. The Uv-vis spectra of the Cu (II) and Ni (II)complexes display slightly different absorption spectra from the ligand which are shifted to lower wavelengths with shoulders besides a decrease of the band of n-π* transition, which confirm the coordination through azomethine nitrogen. On the other hand, π-π* transition disappear due to complexation in Cu (II) complex, but it appears at 312nm with small absorption in the case of Ni (II) complex. Although d-d transition in this type of complexes may appear above 400 nm, it does not appear due to the low intensity of the d-d transition (appendix 11-13). Therefore, the data support the octahedral geometry of the complexes [47, 48].

5. Conclusion

The synthesis and characterization of metal complexes of N, O-donor Schiff base ligand have been described in this paper. The ligand reported in this work introduces a new feature Schiff base. The definition given for schiff base in many literatures [5], is disproved here, since in the existing literature it is stated as ‘‘nitrogen of the azomethine is restricted to connected only with any aryl or alkyl but not with hydrogen’’. But we found that the azomethine nitrogen can be connected with hydrogen as depicted in figure 1 and 2.

In addition, the spectroscopic data and the elemental analyses data of the Co and Ni complexes have shown a seven membered ring around the metal ion which is also a new outcome of this investigation.

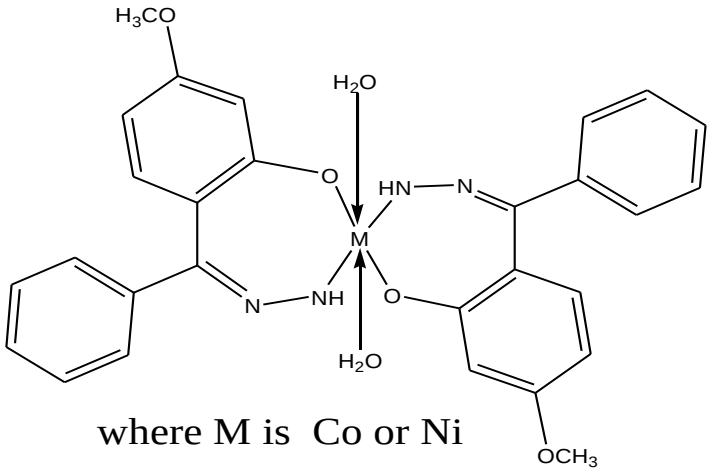
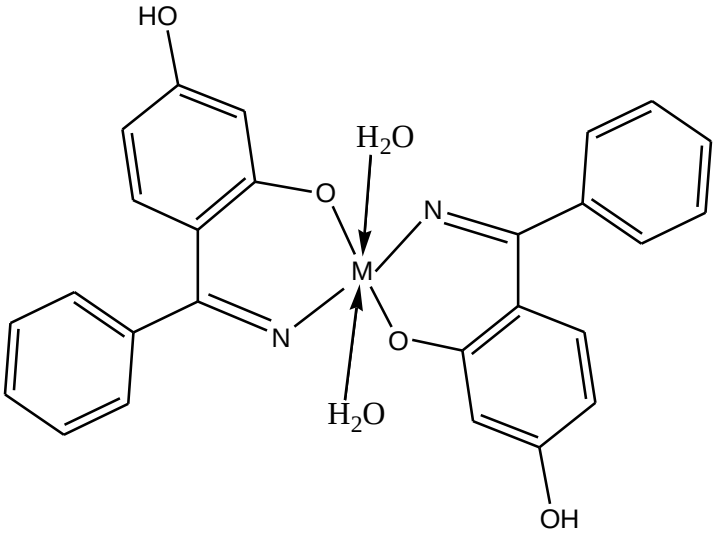


Figure 4 proposed structure of Co (II) and Ni (II) complexes of 2-H-4-MBPH

The spectroscopic data in addition to the magnetic susceptibility value of the Cu and Ni complexes of the schiff base give good evidence for the proposed structures below.



Where, M is Ni or Cu

Figure 5 proposed structure of NI (II) and Cu (II) complex of 2,4-DHBPAM

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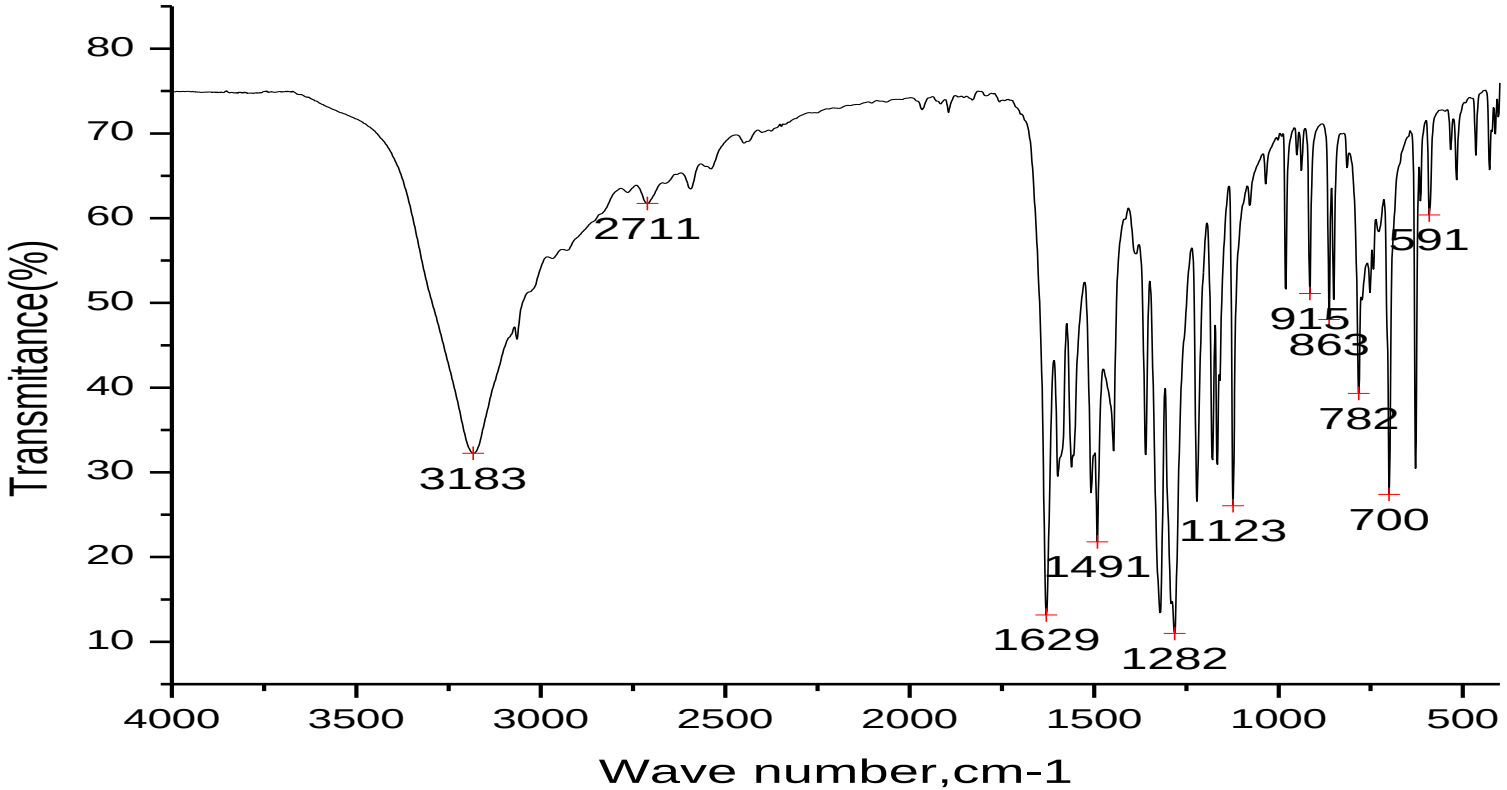
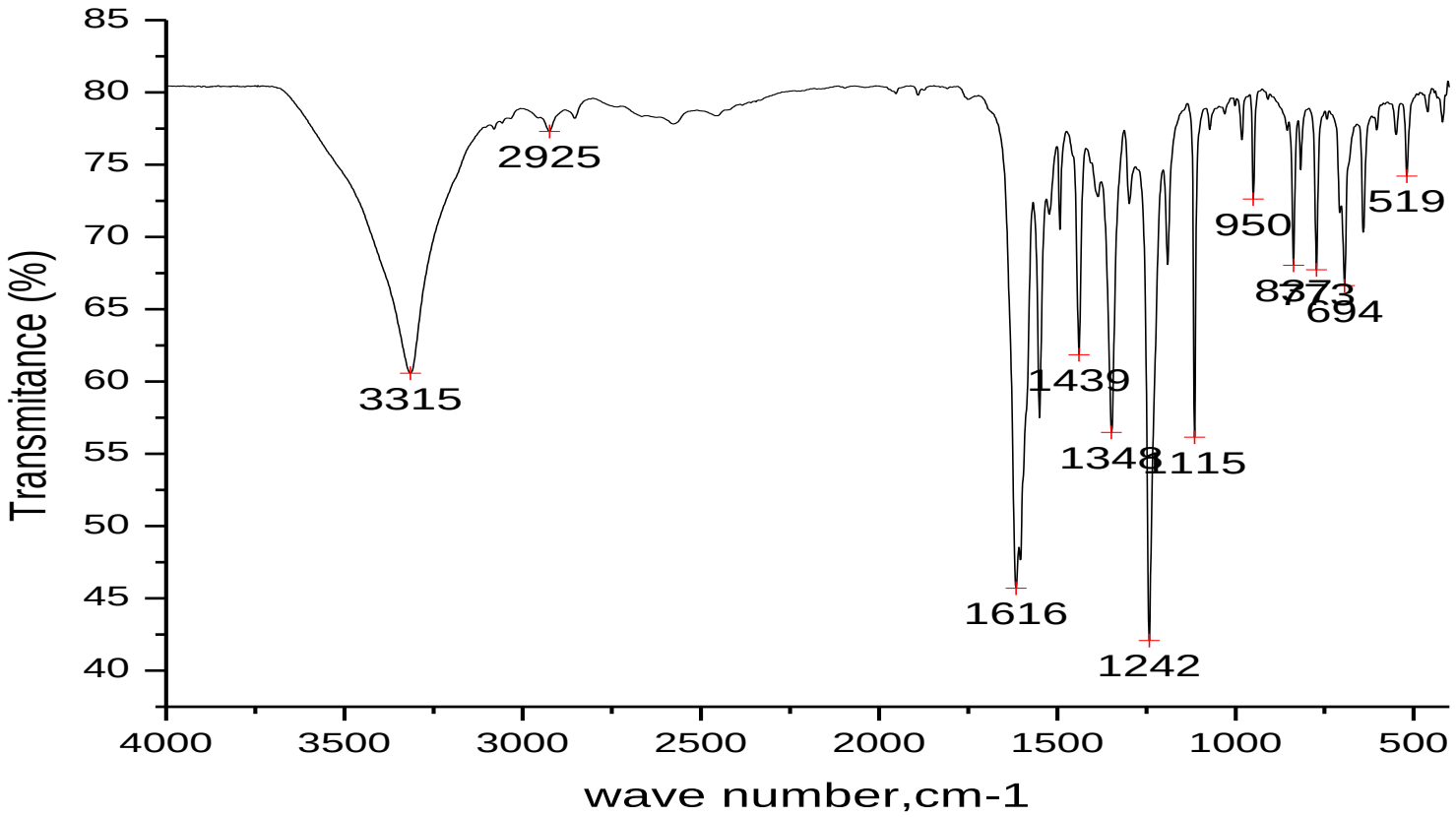
7. Appendix

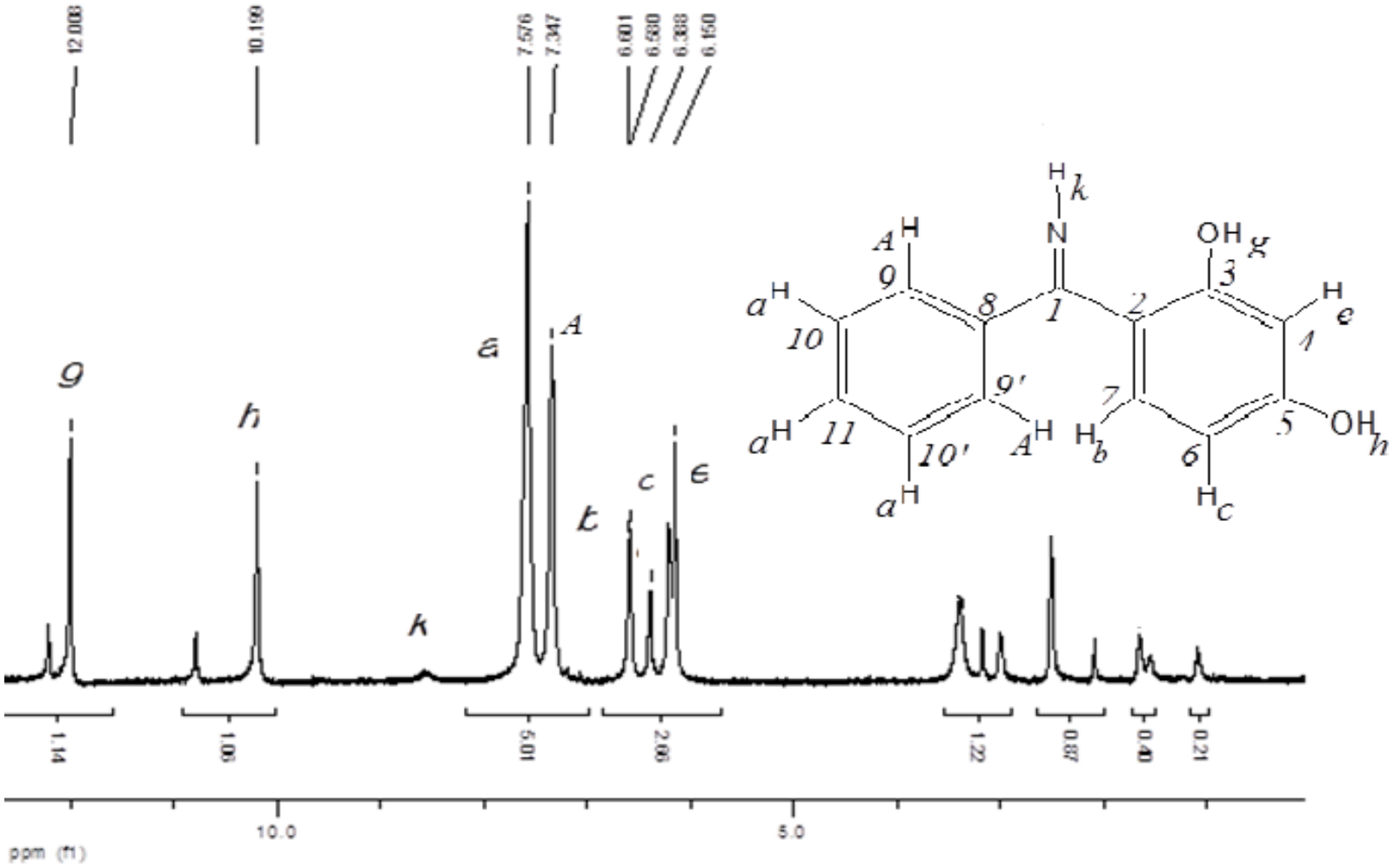
Appendix 1 IR spectrum of 2,4-DHBP



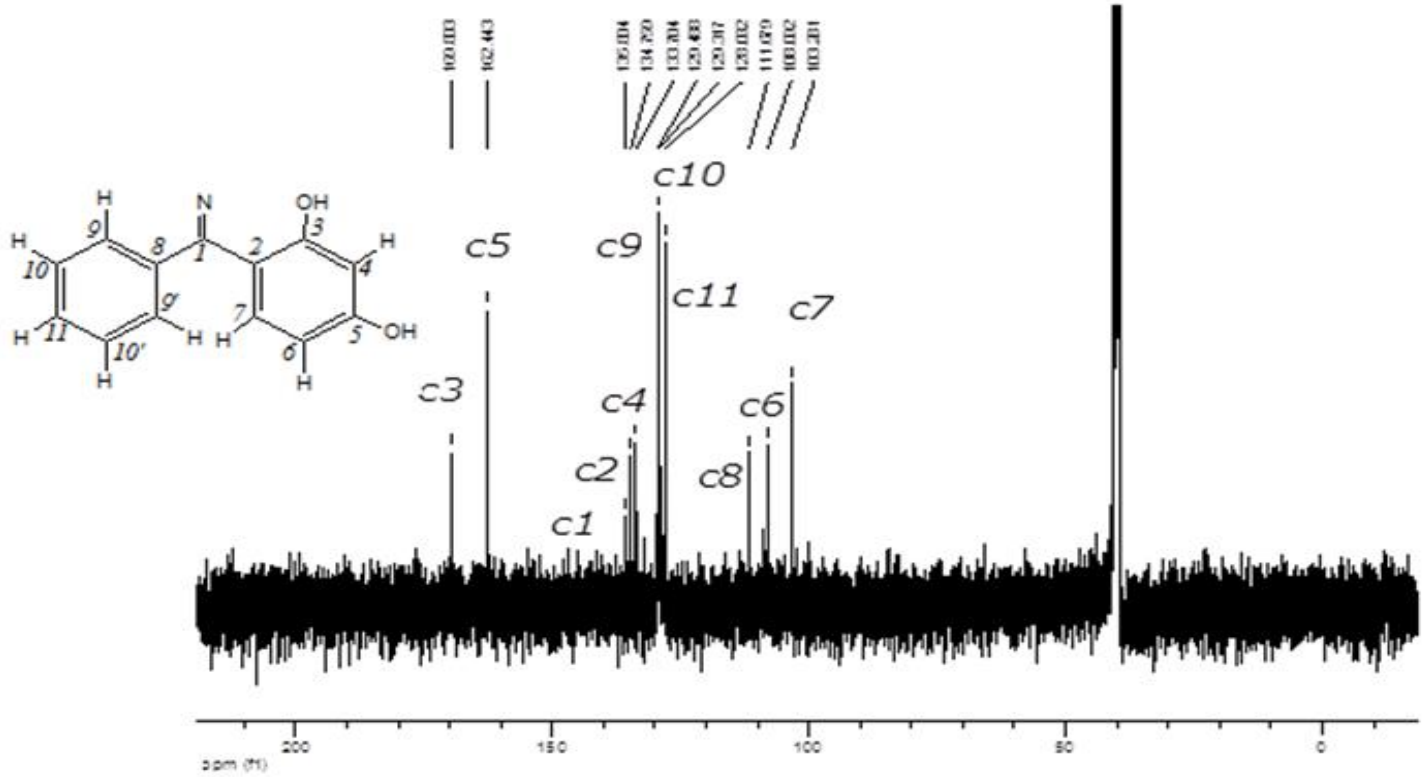
Appendix 2 IR spectra of 2,4-DHBPAM



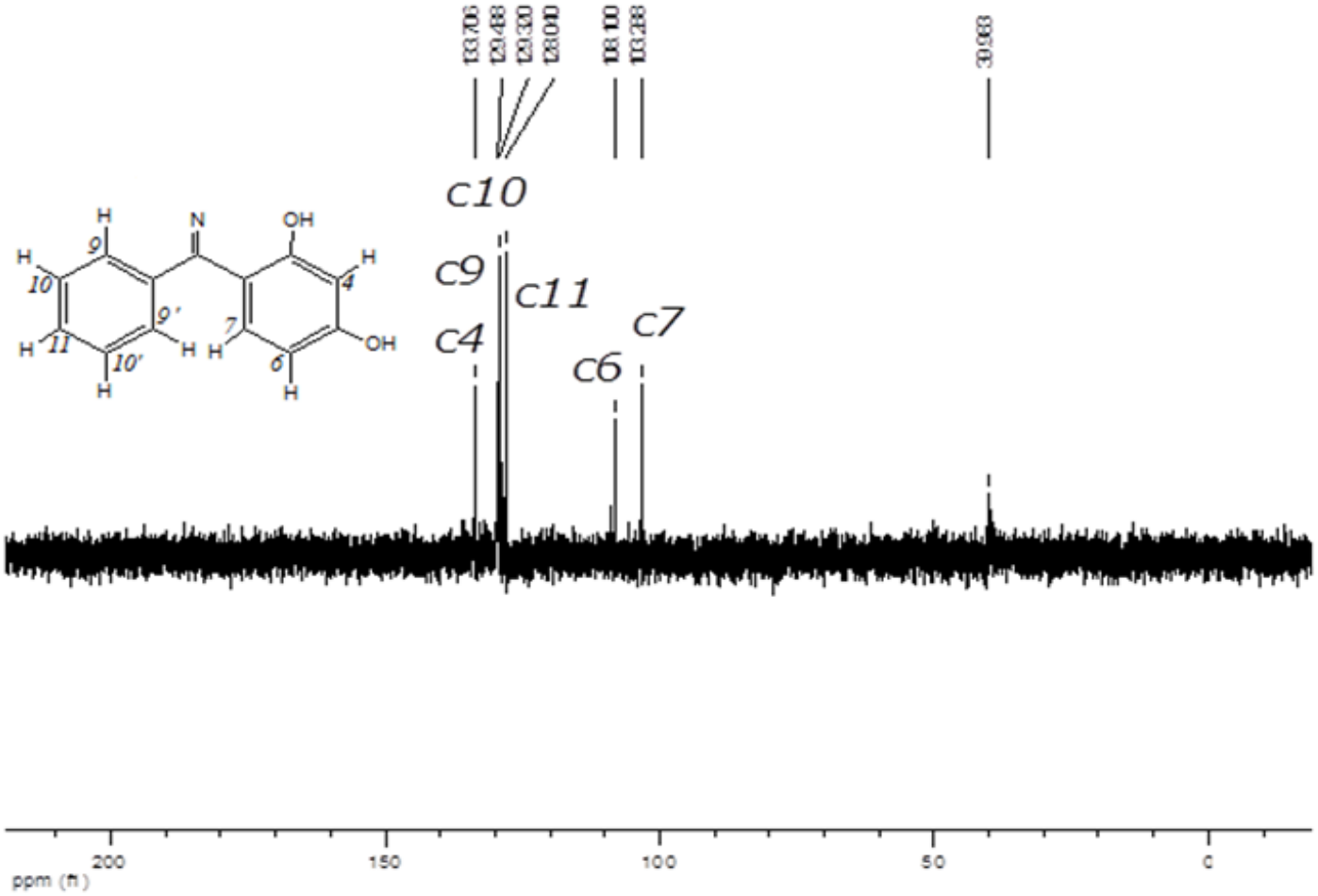
Appendix 3 ^{1}H NMR spectra of 2,4-DHBPAM



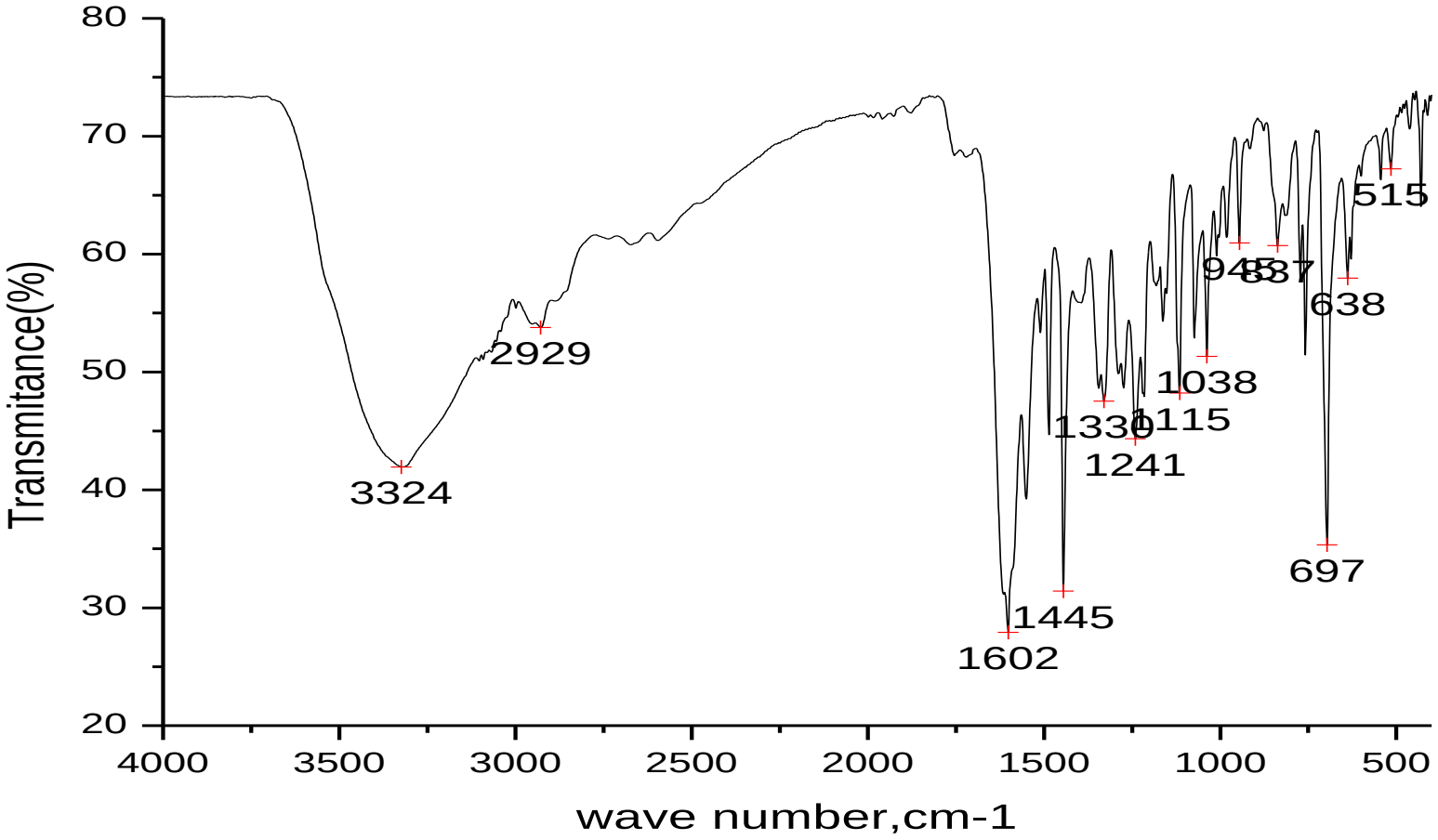
Appendix4 ^{13}C NMR spectra of 2,4-DHBPAM



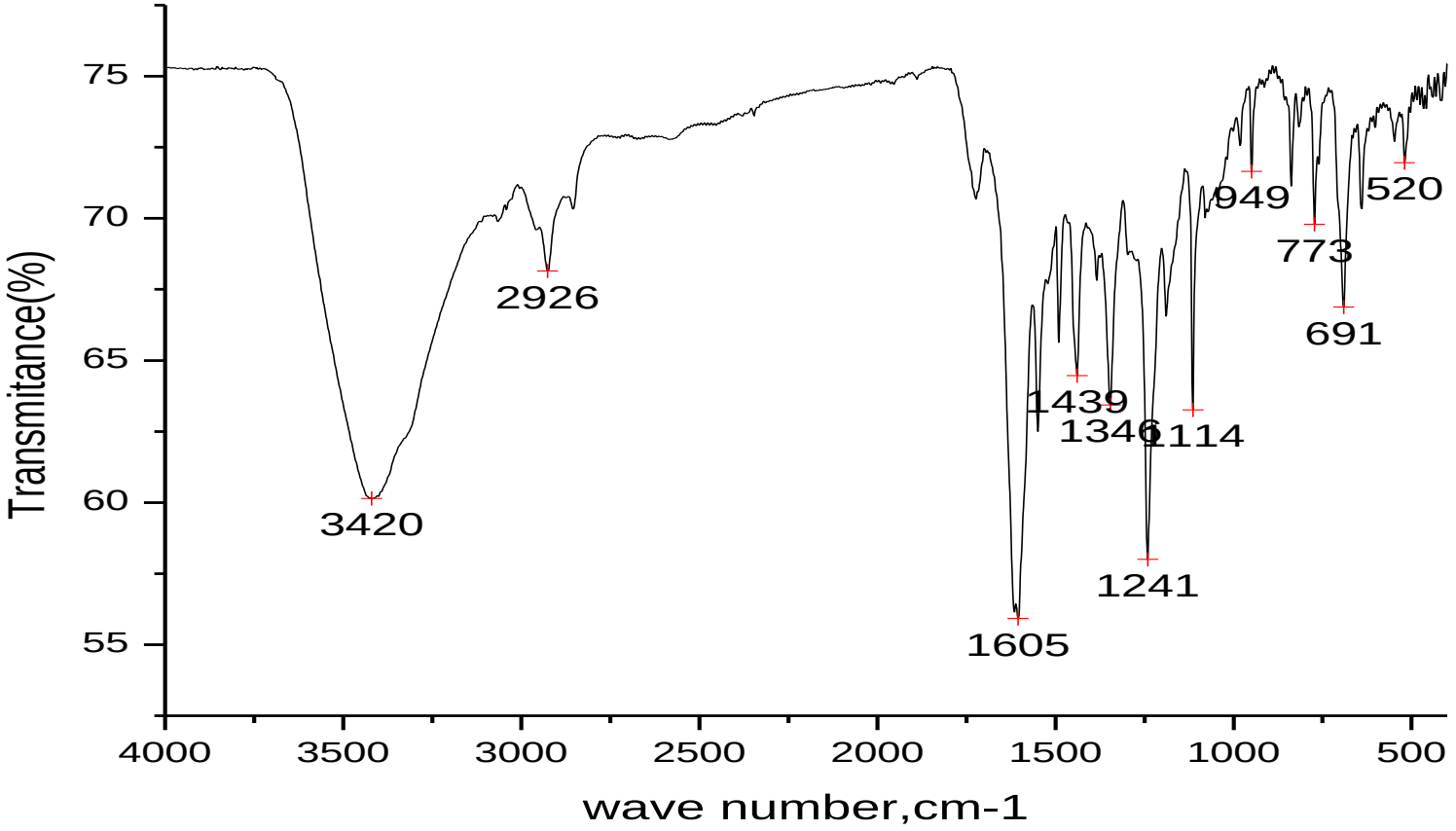
Appendix5 DEPT spectra of 2,4-DHBPAM



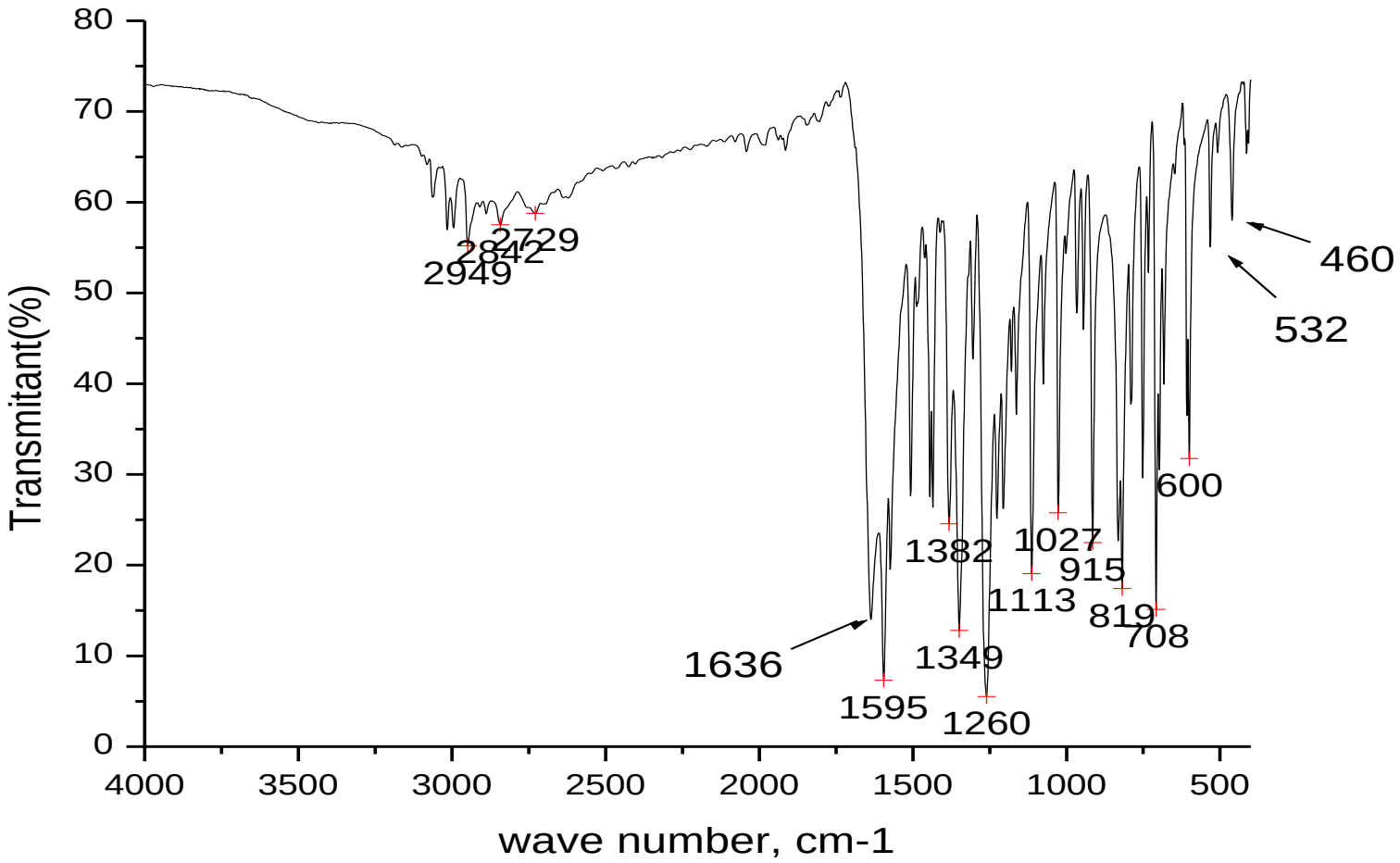
Appendix 6 IR spectra of Ni complex of 2,4-DHBPAM



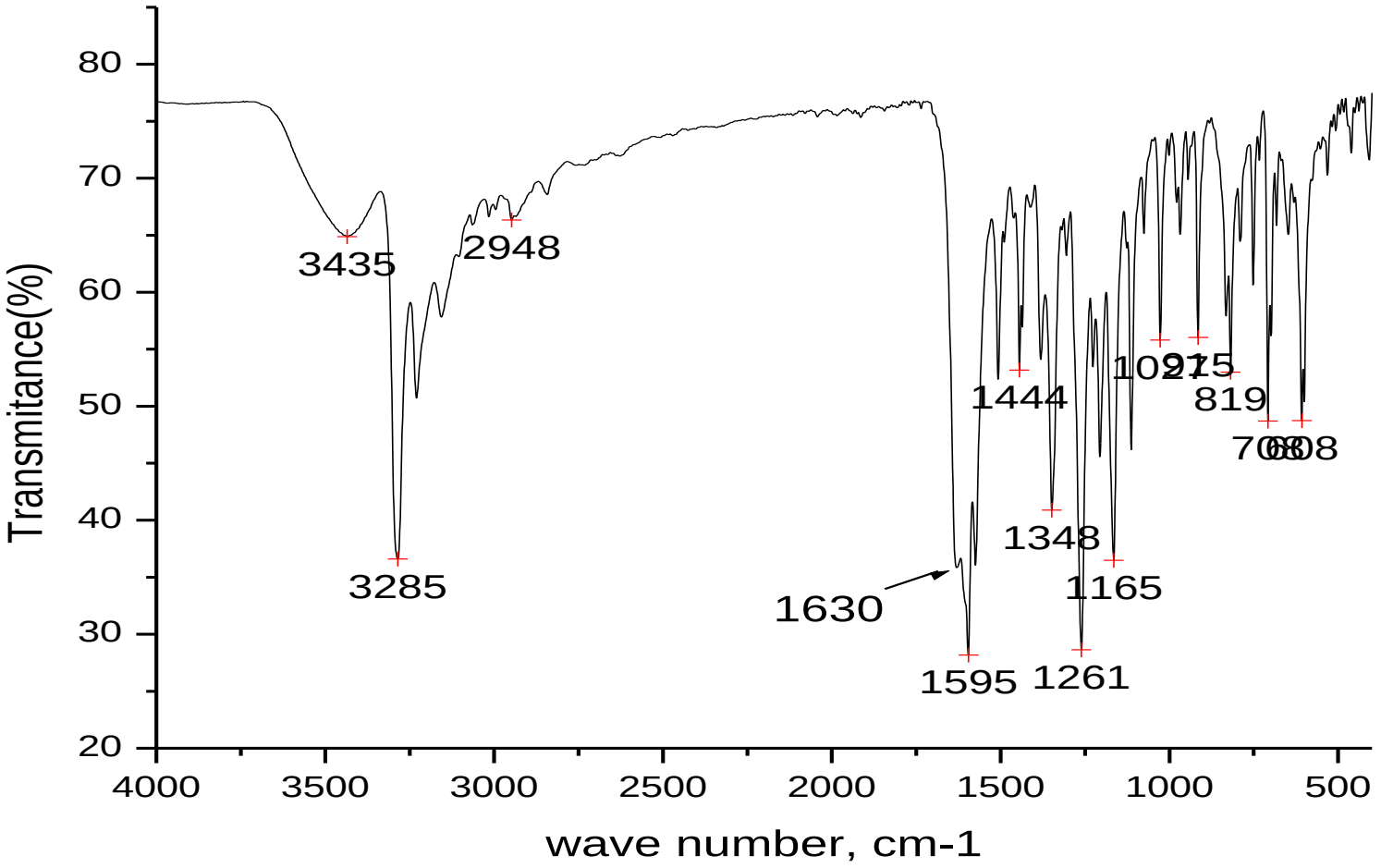
Appendix 7 IR spectra of Cu complex of 2,4-DHBPAM



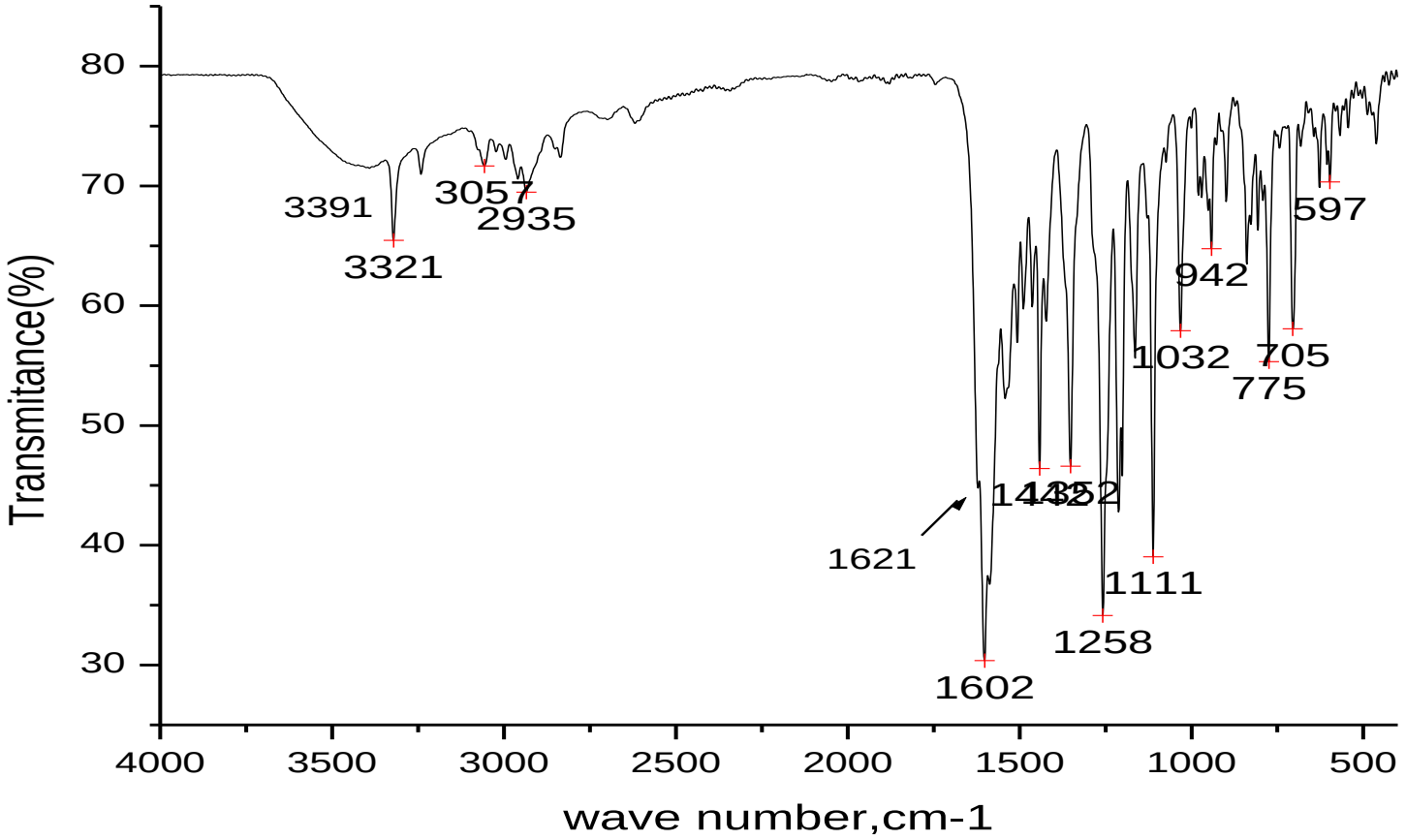
Appendix 8 IR spectrum of 2-H-4-MBP



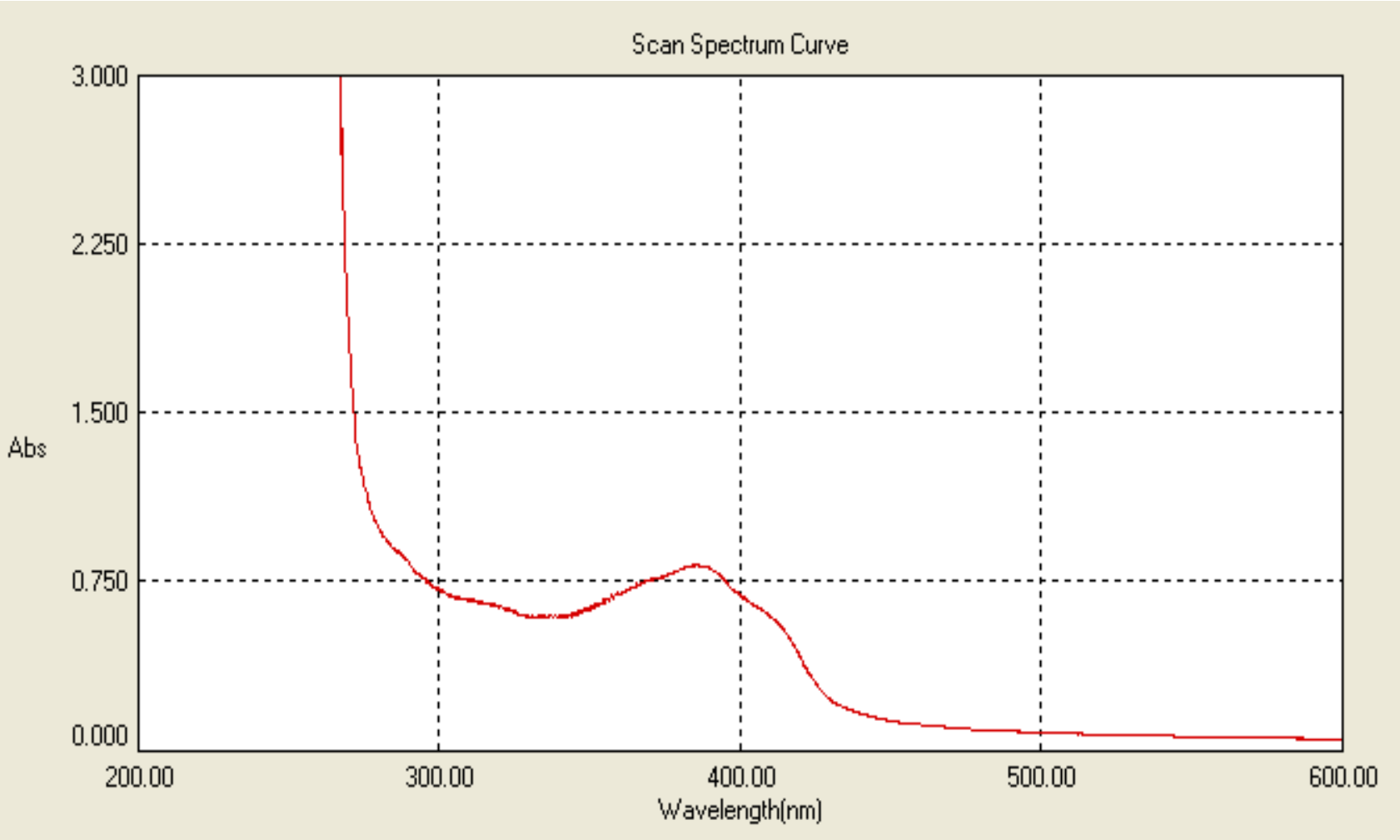
Appendix9 IR spectra of Ni complex of 2-H-4-MBPH



Appendix10 IR spectra of Co complex of 2-H-4-MBPH

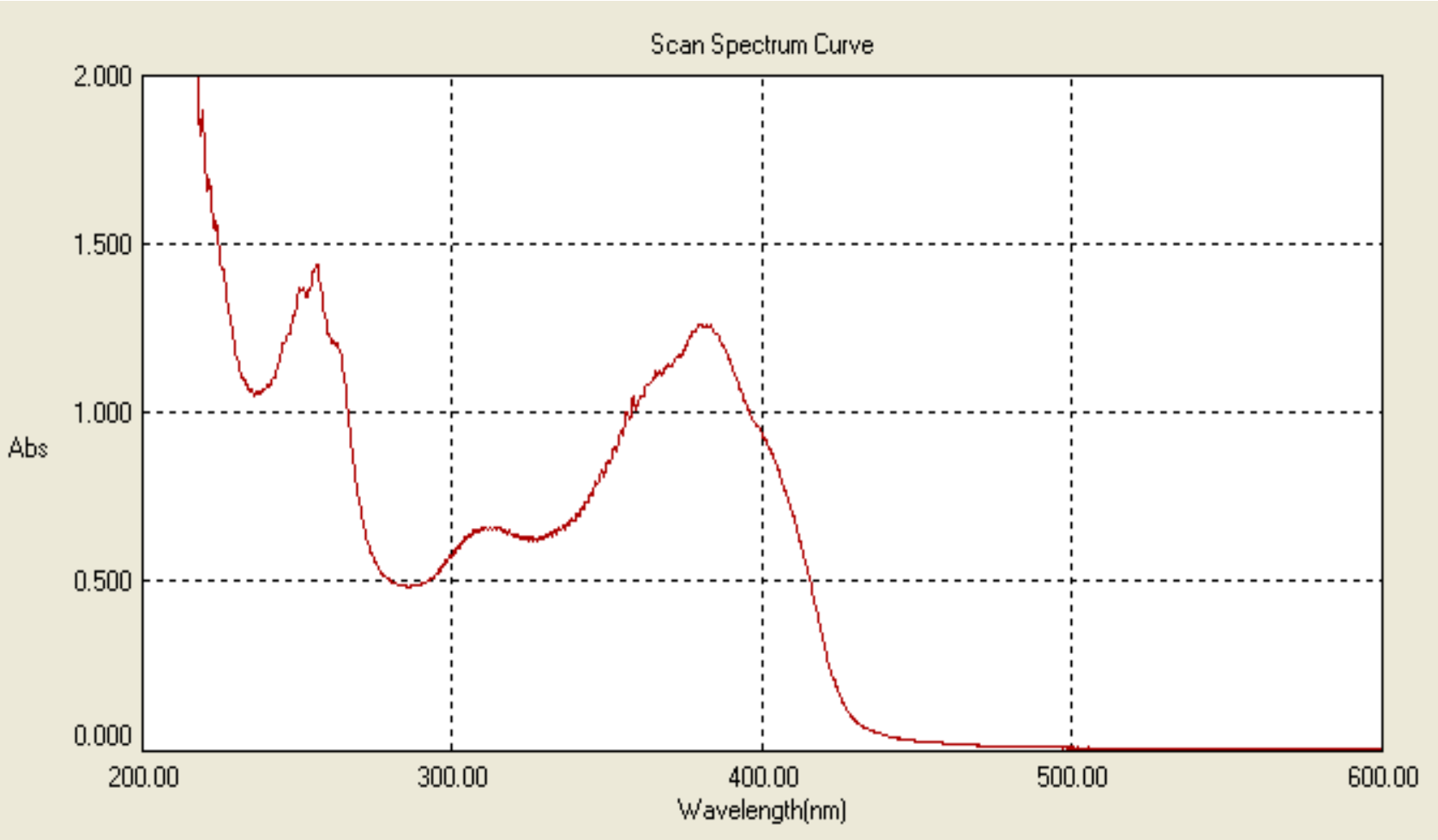


Appendix 11 Uv-vis of Cu (II) complex of 2,4-DHBPH



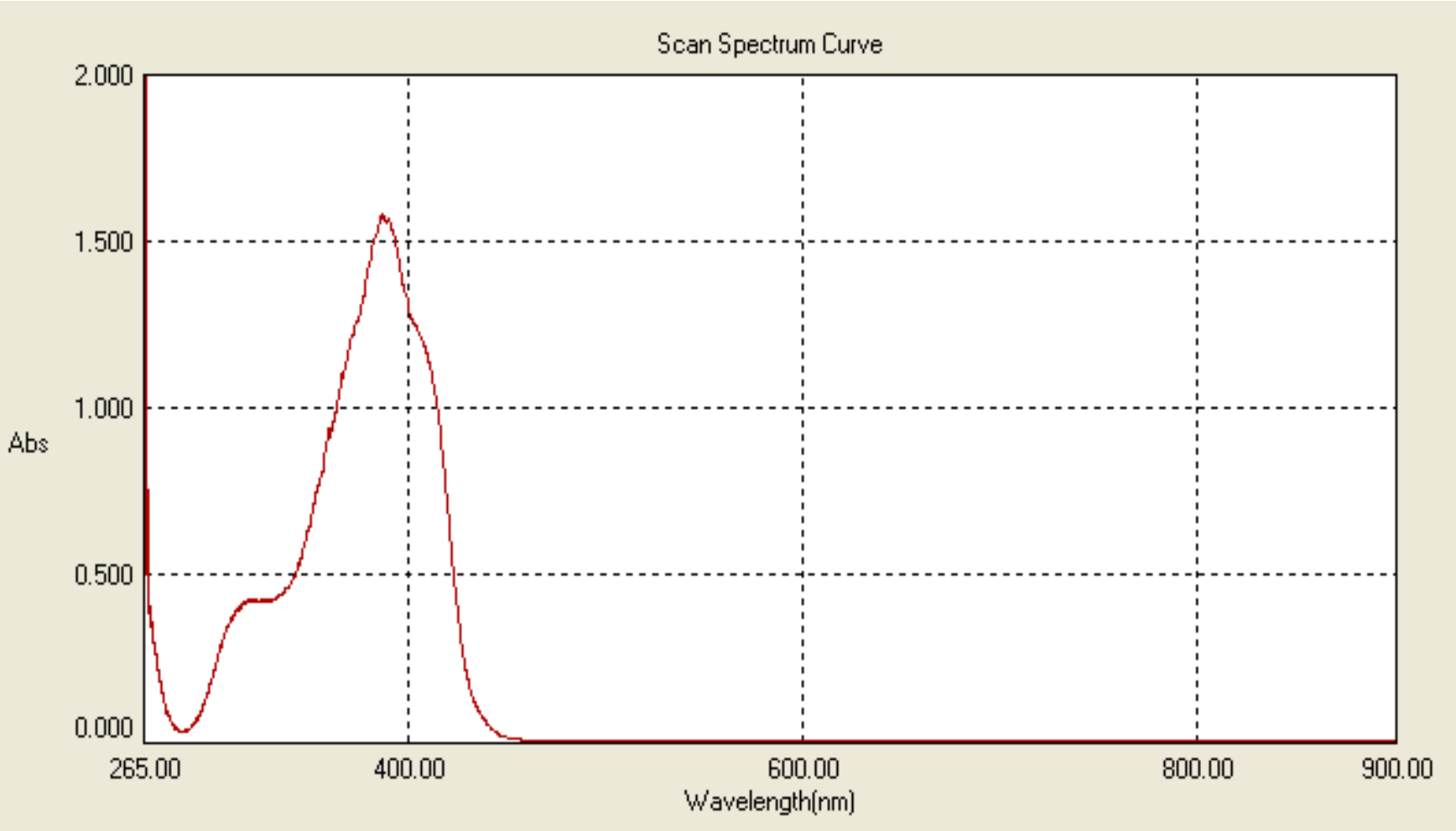
Maxima at 392nm and 423nm

Appendix 12 Uv-vis of Ni(II) complex of 2,4-DHBPH



Maxima at 262nm, 318nm and 389nm

Appendix 13 Uv-vis spectrum of 2,4-DHBPH



Maxima at 318 nm and 387 nm