ADDIS ABABA UNIVERSITY
SCHOOL OF GRADUATE STUDIES

TEMPLATE SYNTHESIS AND CHARACTERIZATION OF Cu (II) AND Co(II) COMPLEXES DERIVED FROM QUINOXALIN-2,3-DIONE AND 2,4-DIHYDROXY-5-ACETYLACETOPHENONEDIHYDRAZONE

By:
Seble Argaw

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GRAGUATE PROJECT SUBMITTED TO THE SCHOOL OF GRADUATE STUDIES OF ADDIS ABABA UNIVERSITY

In partial fulfillment of the requirements for the degree of Masters of Science in Chemistry

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AAS	Atomic Absorption Spectroscopy
IR	Infrared
M.pt	Melting point
NMR	Nuclear magnetic resonance
EA	Elemental analysis
ppm	parts per million
DAAP	2, 4-Dihydroxy-5-Acetylacetophenone
DAAD	2, 4-Dihydroxy-5-Acetylacetophenonedihydrazon
QXD	2, 3-Quinoxalinedione

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Abstract

In this study the template synthesis and characterization of two metal ion complexes, Cu (II) and Co (II), are presented. In order to do so, 2, 4-dihydroxy-5-acetylacetophenone (DAAP) was prepared first then 2, 4- dihydroxy-5-acetylacetophenonedihydrazon (DAAD) was synthesized by the condensation of 2 , 4-dihydroxy-5-acetylacetophenone (DAAP) with hydrazine hydrate and finally 2, 3-Quinoxalinedione(QXD) was prepared.

A new complexes of type $[M(L)(H_2O)_2]$ where M=Cu(II) and Co(II), L is tetra dentate Schiff base ligand, formed by the condensation of 2,4- dihydroxy-5-acetylacetophenonedihydrazon (DAAD) and 2,3-Quinoxalindione by template method. The complexes are formulated as: [M (L) (H_2O)] on the basis of elemental analysis, IR spectra and AAS studies in which the ligand "L" is formed by 1:1 condensation of QXD and DAAD. The ligand behaves as tridentate ONO system and coordinates through one of the two imine nitrogen atoms formed up on condensation of -NH2 of 2,4- dihydroxy-5-acetylacetophenonedihydrazon with -C=O group in 3-position of, 2, 3-Quinoxalinedione and one OH of 2,4- dihydroxy-5-acetylacetophenonedihydrazon after deprotonation.

The new metal complexes have been characterized with the help of IR spectra, elemental analysis and AAS. Both complexes were expected to have square planar geometry.

KEY WORDS: 2, 4- dihydroxy-5-acetylacetophenonedihydrazon, 2, 3-Quinoxalinedione, Template method and Schiff base.

1. Introduction

A metal complex is a compound in which a central metal ion or atom is attached to a group of surrounding molecule or ions by co-ordinate covalent bond [1, 2, 3]. Atoms, molecules, or ions attached to the metal ion are called ligands [4]. Ligands can be neutral molecules with unshared pairs of electrons (like H_2O), or they can be anions (like Cl^- or OH^-) [2, 3]. The atom in the ligand that actually provides the electron pair is called the donor atom [1, 3]. The formation of metal complex is a Lewis acid- base interaction in which the ligand act as Lewis base, or electron pair donors, and the central metal ion behave as a Lewis acid, an electron pair acceptor. The number of ligand donor atoms that surround central metal ion in a complex is called the co-ordination number of the metal. Metal complexes have characteristic shapes that depend on the metal ion`s coordination number [1, 4].

1.1. Multi dentate ligands and metal chelate system

Ligands can be classified as mono dentate or poly dentate, depending on the number of ligand donor atoms that bind to the metal. A pair of a single donor atom is called mono dentate ligands. Those that bind through electron pairs on more than one donor atom are termed as poly dentate ligands [1, 2, 3, 4, 5, 6].

Ligands are also grouped traditionally as O- donors and N-donors in which the division is based on selection of metal ions for complexation. The N-donor ligands complex well with the smaller transition metal ions derived from Sc, Te, V, Cr, Mn, Fe, Co, Ni and Cu. The O-donor ligands tend to complex with metal ions such as the larger alkali, alkaline earth metal ions and large post transition metal ions [7, 8].

Some unidentate ligands have two or different donor sites so that the possibility of linkage isomerism arises. Some important ligands of this type called ambidentate ligands. SCN (thiocyanate) is ambidentate ligands which can attach at either the sulfur atom or the nitrogen atom [5, 6].

Ligands attached to the central metal by more than one point of attachment are called chelating ligands and these ligands are called multi-dentate, and their complexes are called chelates. Multi-dentate ligands form more stable complexes than mono dentate [9]. A stable chelate usually contains five or six membered ring [10].

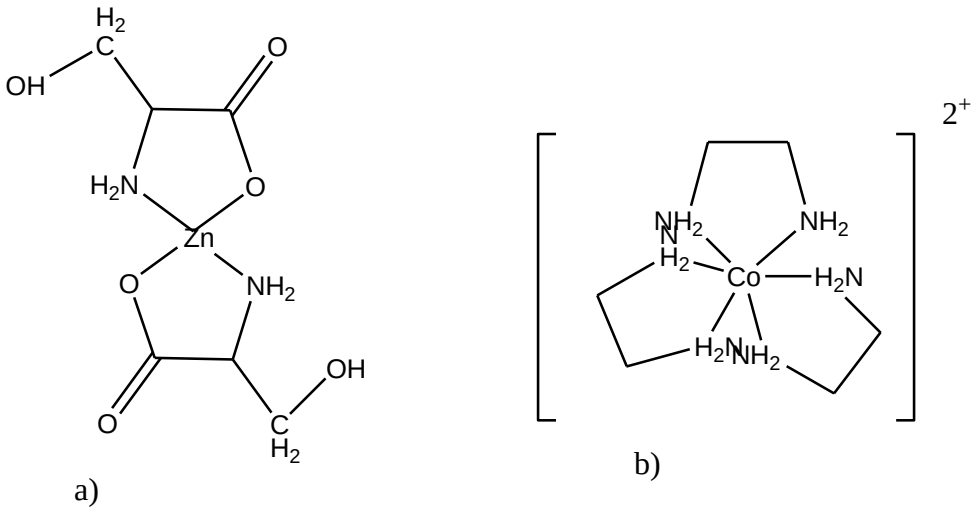


Figure 1: metal chelate of a) Serine b) ethylenediamine

The ligands in figure 1 are bound to the metal through two or more different ligand atoms and thus form parts of heterocyclic rings in which the metal is one of the members. The heterocyclic rings formed in this manner are termed chelate rings and a metal complex which contains one or more chelate rings is called metal chelate. The stereochemistry of some ligands doesn't allow all the binding sites to be simultaneously bonded to the same metal. Thus, although serine is potentially tridentate (NH_2, OH and CO_2), in figure 1a it functions only as a bidentate ligand/donor. Some typical chelating ligands are given in figure 2 [11].

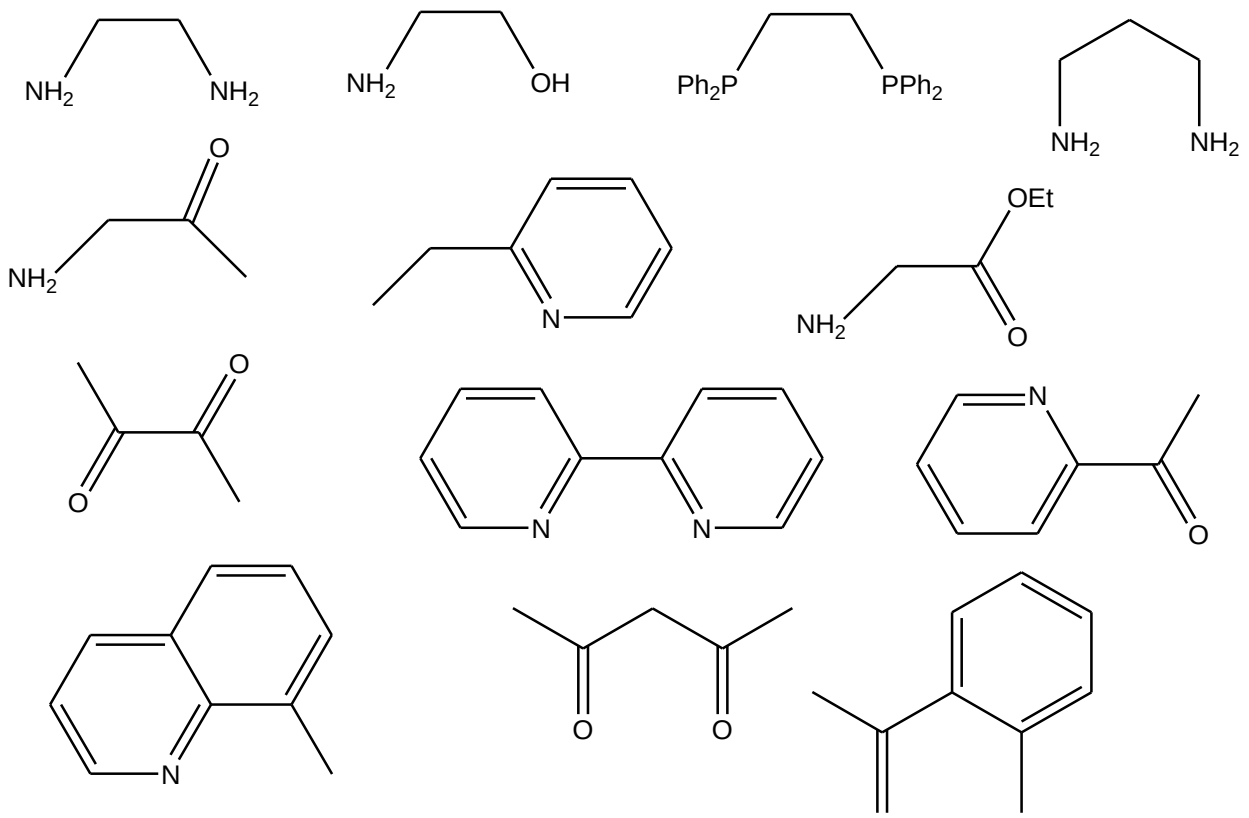


Figure 2: some typical chelating ligands

1.2Schiff Bases

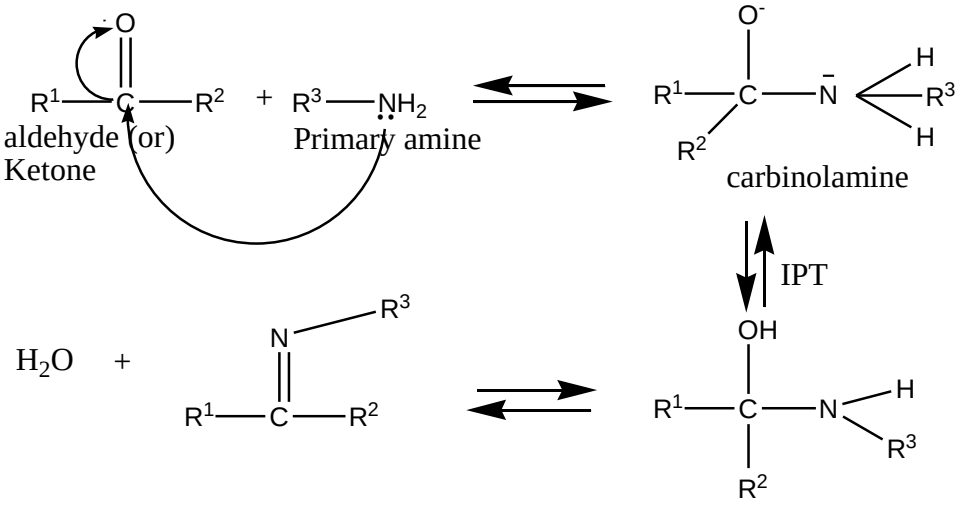
Schiff bases have been widely used as ligands in the formation of transition metal complexes. Schiff base ligands containing various donor atoms like O, N, and S show broad biological activity and are of special interest because of the variety of ways in which they are bonded to the transition metal ions [12]. It has been proved that biologically active Schiff base compounds indicate greater activity when treated as metal complexes than as free compounds [13].

Compounds containing an azomethine group (-CH=N-) known as Schiff bases [14, 15, 16]. Several studies showed that the presence of a lone pair of electrons in sp ^{2} hybrid orbital of nitrogen atom of the azomethine group is of considerable chemical and biological importance. Ligands containing sp^2hybridized nitrogen atoms, particularly those in which the N-atom is a part of the aromatic system, show very extensive coordination chemistry. Because of the relative easiness of preparation, synthetic flexibility, and the special property of C=N group, Schiff bases are considered as excellent chelating agents 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 chelate ring with the metal ion[17].

The Schiff bases formed by the condensation of a primary amine with a carbonyl compound were first reported by Hugo Schiff in 1864. [15, 16, 17, 18]. Schiff bases are generally bi-or tri-dentate ligands capable of forming very stable complexes with transition metals [14, 16, 19]. In organic synthesis, Schiff base reactions are useful in making carbon-nitrogen bonds [14, 19]. The formation of a Schiff base is reversible and the formation is generally driven to the completion by separation of the product or removal of water or both.

Schiff bases having chelation with oxygen, nitrogen etc. donors and their complexes have been used as drugs and reported to possess a wide variety of biological activities against bacteria, fungi, and certain type of tumors and also, they have many biochemical, clinical and pharmacological properties. Imine or azomethine groups are present in various natural, naturally derived and non- natural compounds [19].

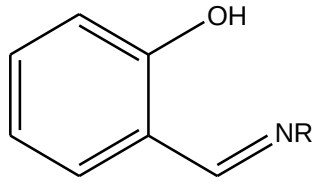


R^1 and R^2=H, alkyl, aryl
R^3=alkyl, aryl, OH, NHR, OR

Scheme 1:General mechanistic aspects of schiff base preparation

.

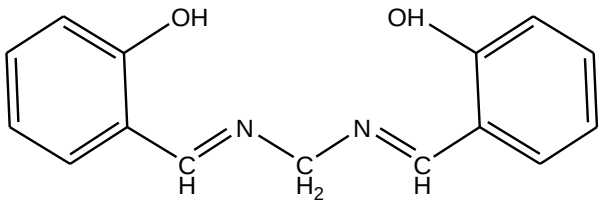
Many tridentate Schiff bases have been utilized as anionic ligands having NNO and NOO donor sets. Some of them are shown below; these ligands derived from substituted acetophenone with three or more metal binding substituents are of great synthetic interest as they can produce polynuclear complexe [20]



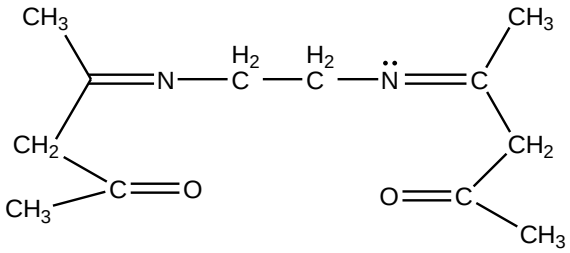
R=CH_2COOH
R=$(CH_2)_nC_6H_4OH$ (n=1,2)
R=$2C_6H_4NH_2$
R=$(CH_2)_nX$ (n=2,3, X=OH, NMe_2, Net_3, NH_2)

Figure 3: Tridentate schiff base

However, tetra dentate Schiff bases with ONNO donor set have been widely studied. The condensation of two moles of 2, 3-Quinoxalinedione and one mole of 2,4-dihydroxy-5-acetyl acetophenonedihydrazone in the presence of metal salts gives a bis tetra dentate Schiff bases with ONNO donor set.



Salen



Acacen-H_2

Figure 4: Tetra dentate schiff bases

1.3 Chemistry of Quinoxaline

Quinoxaline derivatives are an important class of nitrogen containing benzo heterocyclic compounds containing a ring complex made up of a benzene ring and a pyrazine ring [21,22]. Quinoxaline is formed by the fusion of two aromatic rings, benzene and pyrazine. For this reason it is called benzopyrazine. It is also known as 1, 4-benzodiazine, benzoparadiazine, phenpiazine [22 23]. Quinoxaline is an isomer of cinnolines, phthalazines and quinazolines.

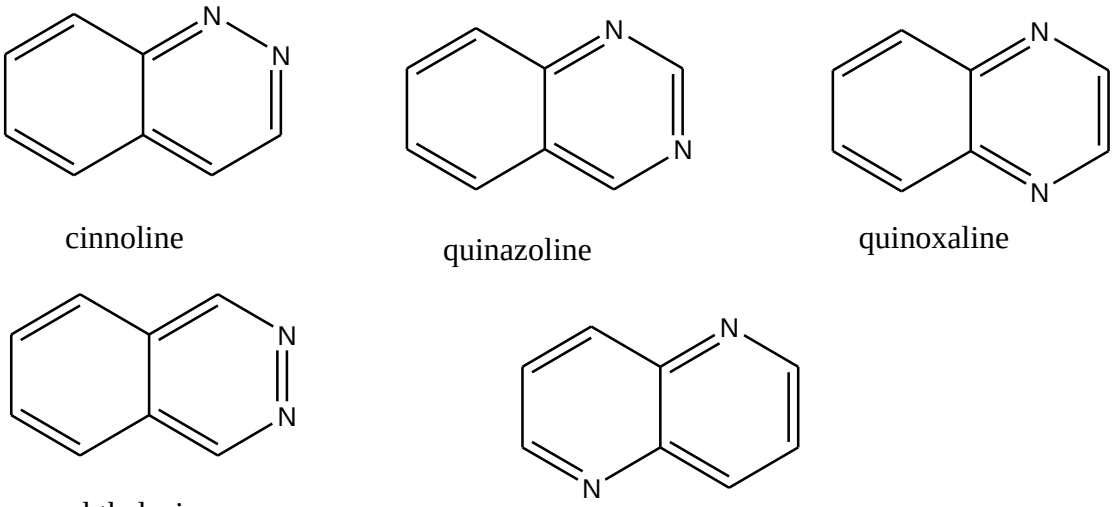


Figure 5: Structures of isomeric diazanaphthalenes

All these compounds have 10-π electrons that are located in five molecular orbitals that can be regarded as linear combination of 2p-atomic orbitals, one atomic orbital and one π- electron coming from each atom of the ring skeleton. There are also two non-bonding orbitals that lie in the molecular plane and largely are confined to the nitrogen atoms, each of these orbitals contains an electron pair and these electrons are responsible for the basic properties of the group of compounds [24].

According to several previous studies, the variation of the substituent on the quinoxaline core, could improve the biological activity, also some quinoxalines fused with other moieties such as triazole have been proved as antimicrobial agents [25].

Quinoxaline is numbered as shown and the 2 and 3 positions which are equivalent are also designated as α −positions [23, 26].

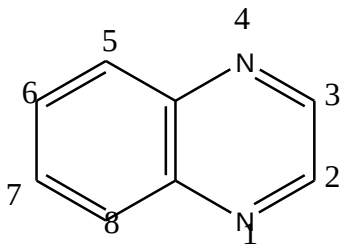


Figure 6: Structure of quinoxaline

1.4 Synthesis

Studies on the synthesis of new quinoxalines have been of considerable importance because of their interesting chemical as well as biological properties [26]. Quinoxalines are, in general easy to prepare and numerous derivatives have been reported in literature designed to produce biologically active compounds [26, 27].Various quinoxaline derivatives have been prepared by the following methods:[26]

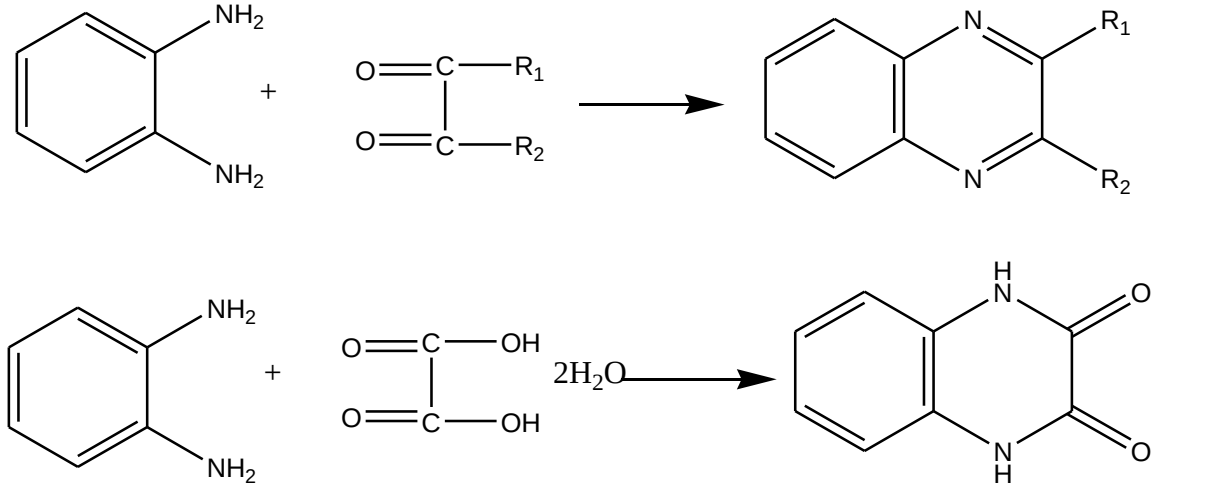
(i) Condensation of aromatic diamines and dicarbonyl compounds.

(ii) Intramolecular cyclisation of N-substituted aromatic ortho-diamines.

(iii) Ring transformation.

(iv) Condensation of benzofurazan-l-oxide and o-quinone dioximes to form quinoxaline-N-oxides.

One of the ligand that used for synthesizing the desired metal complexes is 2 , 3-quinoxalinedione.It is prepared by the condensation of aromatic diamines and di carbonyl compounds.



1,4-dihydroquinoxaline-2,3-dione

Scheme 2: synthesis of quinoxaline derivative by condensation of aromines and dicarbonyl compounds.

Many quinoxaline derivatives are known in the pharmaceutical industry and wide area of biological activities including anti-virus, anti-diabetic, anti-HIV, antifungal, antiparasitic, anti-cancer, anti-bacterial and anti-depression has been reported in the literature for this compound. Quinoxaline ring is part of the structure of some anti-biotic such as Actinomycin, Lomacin and Actinolite that is known as a preventer agent of growing of Gram-positive bacteria and active compound against different migratory tumor [28].

1.5. 2, 4-dihydroxy-5-acetylacetophenone

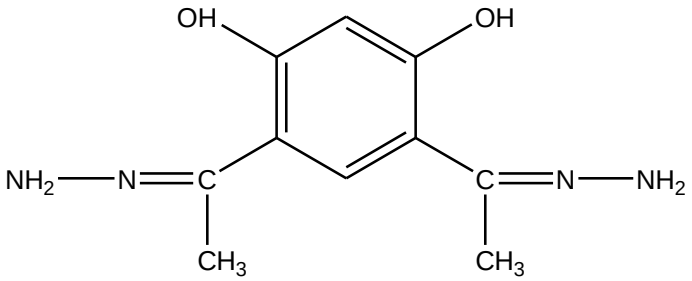
2, 4-dihydroxy-5-acetylacetophenone is a precursor used for the synthesis of 2, 4-dihydroxy-5-acetylacetophenonedihydrazone, in order to form the desired metal complex.

A class of ligands with more than one independent chelating sequence substituted on a single phenyl function exemplifies bischelating ligands that can bind two metal ions simultaneously and form dinuclear complexes. The bis-chelating ligands can be classified into symmetric and unsymmetrical systems. They can be bi dentate, tri dentate, tetra dentate bis- chelating systems. 2, 4-Dihydroxy-5-acetylacetophenone (DAAP) is a symmetric bisbidentate, 'O.O'-'O.O' donor [29].

1.6. 2, 4-dihydroxy-5-acetylacetophenonedihydrazone

2, 4-dihydroxy-5-acetylacetophenonedihydrazone is one of the ligand used for metal complex formation. Some bis bidentate or multidentate ligands can be synthesized by condensing DAAP with different amines i.e. Hydrazinehydrate and dioxime. Its dioxime and hydrazine hydrate have been observed to be bis-bidenate'ON, ON'donors. In fact some of these ligands can be tailor made or designed to drive metal ions into suitable / preferred coordination geometries.

As the proposed ligand possess hydroxy functions which can be deprotonated they constitute acidic metal binding centres which when associated with tri or other multidentate sequences are likely to form metal complexes of significant structural characteristics. Deprotonated phenolic groups can lead to bridging interactions with two or more metal ions and results in the formation of complexes which may exhibit exceptional magnetic properties. DAAD is a bis-bidentate 'ON ,'ON donor Schiff base[29].



(DAAD)

Figure 7: Structure of DAAD

1.7. Cu (II) chemistry

The Cu (II) ion with its d^9 configuration in octahedral and tetrahedral environment is highly susceptible to Jahn-Teller distortion. Octahedral complexes without any distortion are expected to have only one d-d absorption band corresponding to $^2T_{2g} \leftarrow {}^2E_g$ transition, while for distorted octahedral complexes several weak absorption bands are observed around 16000 cm^{-1} and often a broad band in the near IR region.

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

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

For square planar, three d-d bands corresponding to $2B_{1g} \rightarrow {}^2B_{2g}$, $^2B_{1g} \rightarrow {}^2A_{1g}$ and $^2B_{1g} \rightarrow {}^2E_g$ are observed. The Cu (II) ion is classified as a borderline hard acid; therefore nitrogen and oxygen donors followed by chlorine and sulphur have dominated its coordination chemistry. Magnetic moments of monomeric Cu (II) complexes are generally in the range 1.7 to2.2 B.M [30].

1.8. Cobalt (II) chemistry

Cobalt (III) is relatively unstable in simple compounds but the low spin complexes are exceedingly numerous and stable, especially where the donor atoms (usually N) make strong contribution to the ligand field. There are also some important complexes of Co (I) , this oxidation state is better known for cobalt than for any other element of the first transition series except copper .Divalent cobalt forms numerous complexes of various stereo chemical types. Octahedral and tetrahedral ones are the common, but there are a fair number of square ones as well as some which are five coordinated. Co (II) forms tetrahedral complexes more readily than any other transition metal ion. This is in accord with the fact that for a d^7 ion, ligand field stabilization energies disfavor the tetrahedral configuration relative to the octahedral one to a smaller extent than for any other d^n $(1 \leq n \leq 9)$ configuration, although it should be carefully noted

that this argument is valid only in comparing the behavior of one metal ion to another and not for assessing the absolute stability of the configuration for any particular ion[5].

1.9. Stability of complexes

The formation of a metal complex is dictated by its stability. This stability of metal complexes depends both on the metal ion and the ligand. In general, stability of a complex increases with decreasing size and increasing electron affinity of the central metal ion. Thus highly polarizing transition metal ions have the greatest tendency to form complexes, regardless of the nature of the ligand. Thus the stability of bivalent transition metal complexes increases in order Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} < Zn^{2+}. This order can be correlated with decrease in size of metal ions across the series and in part with the ligand field effect [8, 31].

The synergic effect exhibited by the ligand field effect employed for the formation of coordinate compounds plays pronounced role in the stability of the complex. It is attributed to the fact that metal to ligand affinity increases with the ability of the ligand to lower electron density on the metal. This is possible as long as sigma electron donation by the ligand atom is counter balanced by Π-back donation from the filled metal orbital to the vacant Π orbitals of the ligand. Therefore, ligands with weak sigma donor/strong Π acceptors abilities are more favorable in the formation of stable metal complexes [8, 31].

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

1.10 Objectives and scope of the present investigation

Literature review reveals that a lot of work has been done on metal complexes of quinoxaline derivative. This is due to their potential diverse applications for chemotherapy, insecticides, fungicides….etc. Also a lot of works has been done on metal complexes of different bis bidentates having N and O donors sites. This is due to their wide range of applications in pharmaceutical, catalysis, agricultural and binding ability of the transition metal ion. However no work has been reported on the template synthesis of Cu (II) and Co (II) complexes with 2, 4-dihydroxy-5-acetylacetophenonedihydrazone and quinoxaline -2,3-dione.

The present study is aimed at investigating the template synthesis of the divalent ions Cu (II) and Co (II) complexes with 2, 4-dihydroxy-5-acetylacetophenonedihydrazone and quinoxaline -2,3-dione.Preparation of complexes and their characterization will be the main tasks addressed.

The objectives of the study are as follows

- Synthesis of 2, 4-dihydroxy-5-acetylacetophenone, which is the precursor for 2,4-dihydroxy-5-acetylacetophenonedihydrazone.
- Synthesis of 2, 4-dihydroxy-5-acetylacetophenonedihydrazone, which is one of the reactants for the synthesis of the desired complexes.
- Synthesis of quinoxaline -2,3-dione, which is one of the reactants for the synthesis of the desired complexes.
- Template synthesis of the Cu (II) and Co (II) complexes with condensed 2, 4-dihydroxy-5-acetylacetophenonedihydrazone and quinoxaline -2,3-dione.
- Characterization of these products (like melting point, elemental analysis, IR, NMR, etc.)
- Interpretation of physical data's like IR, NMR, elemental analysis, AAS.
- Explanation of their properties.
- Elucidation of the possible structural formula of the complexes on the basis of correlation of IR spectra, elemental analysis and AAS.

2 Materials and methods

2.1 Chemicals

All the chemicals used for synthesis of the ligand precursors; the ligand and the metal complex were of Analar grade. **Metal salts used for** synthesizing the complexes were $CuCl_2 \cdot 2H_2O$, $CoCl_2 \cdot 2H_2O$ and $ZnCl_2 \cdot 2H_2O$ used as a catalyst. Chemicals that were used for the preparation of DAAP, DAAD, QXD and metal complexes were resorcinol, acetic anhydride, fused and crushed zinc chloride, $H_2N\text{-}NH_2 \cdot H_2O$ and orthophenylenediamine. Solvents used include distilled MeOH, petroleum ether, diethyl oxalate, THF and distilled water. Other chemicals used were charcoal, $AgNO_3$, HCl, HNO_3 and NaOH.

2.2. Instruments

Infrared (IR) spectra were recorded using a Perkin Elmer Spectrum BX FT-IR spectrophotometer in the range 4000 - 400cm^{-1} using pressed pellet sampling technique /KBr discs/.

The melting points and decomposition temperatures were determined using Stuart SMP3 Digital Melting Point apparatus.

Metal contents of the complexes Cu (II) were determined using ZEEnit 700 P (analytik jena)-Flame AAS. After digesting a known amount of sample in HNO_3.

The ^{1}H NMR, ^{13}C NMR & DEPT spectra were recorded on Bruker Arx 400 NMR spectrometer using TMS as internal standard. ^{1}H NMR, ^{13}C NMR & DEPT spectra of DAAP is recorded using $CDCl_3$ as a solvent. During the study, several other common laboratory equipment's were also used.

2.3 Methods

2.3.1 Chloride Test

Compounds (samples) dissolved in10 ml of nitric acid and digest the sample repeatedly by adding 5 ml nitric acid until a clear solution is formed. To the digested solution, 0.1N of silver nitrate (AgNO3) was added and allowed to settle. The solution, when treated with 0.1N AgNO3 did not form any precipitate indicating that the absence of chloride in the sample.

2. 3.2 Metal content determination

The metal contents in the complexes were determined using atomic absorption spectroscopy (AAS). The experimental percentage of metal in the complex was found as:

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

3. Experimental part

3.1. Synthesis of 2, 4-Dihydroxy-5-acetylacetophenone (DAAP) [32]

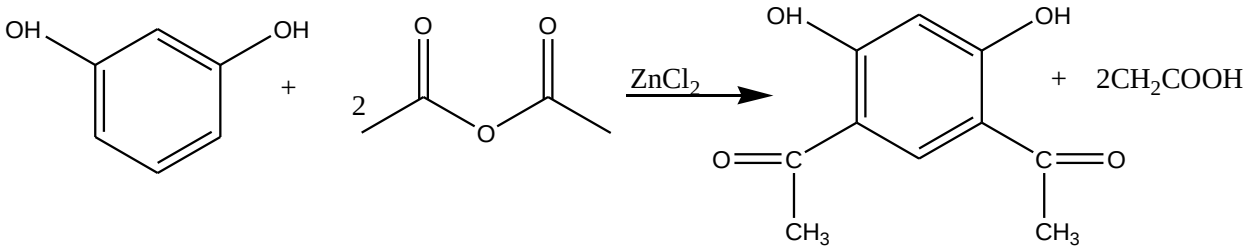
To a mixture of fused and crushed $ZnCl_2 \cdot 2H_2O$ (10g) and acetic anhydride (17.3 ml, 1.8 mmol), 10g (0.9 mmol) of resorcinol were added gradually while stirring. The resulting brown solution was refluxed for 30 minutes in oil bath at 140°C-160°C and was left over night. It was hydrolyzed with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

Yield: 2.78 g (16%)

Color: White

Appearance: needle like crystal

The overall reaction was



(DAAP)

Scheme 3: Synthesis of DAAP

3.2. Synthesis of 2, 4-Dihydroxy-5-Acetylacetophenone **Dihydrazone (DAAD)** [32]

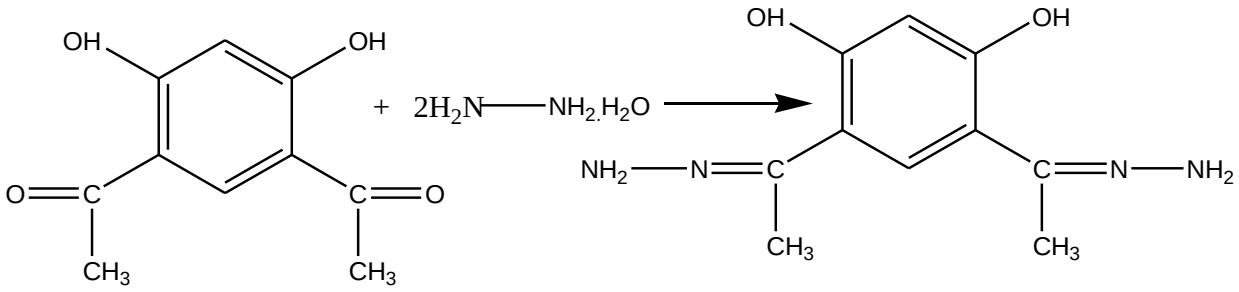
A solution of hydrazine hydrate (0.3ml, 5.2mmol) in methanol (5.15ml) was added to a hot methanolic solution (5.15ml) of DAAP (0.5g, 2.6mmol). The resulting solution was refluxed on a water bath for 3 hours. The bright - yellow crystalline product was filtered, and washed successively with methanol and petroleum ether and then dried in open air.

Yield: 0.49 g (84.89%)

Color: bright - yellow

Appearance: Crystalline

The overall reaction was



Scheme 4: Synthesis of DAAD

3.3 Synthesis of Quinoxaline-2, 3-dione (QXD) [33]

A solution of orthophenylene diamine (5.4g) in diethyl oxalate (50ml) was evaporated in vacuum using rotary evaporator in water bath at 80^0c for 3hrs. Then additional 50ml diethyl oxalate was added and evaporated for 3hrs again. The silvery white solid crystalline product was washed several time with diethyl ether and dried in vacuum.

Yield: 92%

Color: silvery white

Appearance: Crystalline

3.4. Synthesis of metal complex

Both metal complexes were synthesized by the template method by the condensation of 2,4-dihydroxy-5-acetylacetophenonedihydrazone with quinoxaline 2,3-dione in the presence of hydrated salts of the respective divalent metal ion $CuCl_2 \cdot 2H_2O$ and $CoCl_2 \cdot 2H_2O$(in methanolic media)

The mole ratio of quinoxaline 2, 3-dione, 2, 4-dihydroxy-5-acetylacetophenonedihydrazone, metal salts ($CuCl_2 \cdot 2H_2O$ and $CoCl_2 \cdot 2H_2O$) and sodium hydroxide pellet taken was 2:1:2:2 mole ratios respectively.

A solution of NaOH (1mmol) in 10 ml methanol was prepared and added to DAAD solution (0.5mmol) in dry THF (30ml) .A solution of 1mmol of the metal salts where taken in 10 ml of methanol and added to a quinoxaline 2,3-dione solution (1mmol) in methanol(30 ml) . The resulting solution was refluxed for 30 minutes in a water bath. To this solution a basic DAAD solution was added. The resulting solution was refluxed for 6hrs.The precipitate obtained was filtered off and washed thoroughly with methanol and THF. The product was then dried in an open air.

4. Results and discussion

In these part physical properties like melting or decomposition temperature, solubility, spectral studies such as IR, NMR, AAS and elemental analysis of the ligand precursors, the ligand as well as the metal complex will be discussed

4.1. Physical properties

Some of the important physical properties of DAAP, DAAD, QXD, Cu (II) and Co (II) complex are listed in table 1

Table.1 Physical properties of DAAP, DAAD, QXD, Cu (II) and Co (II) complex

Compound	Mol. Formula	Mol. Weight (g/mol)	Appearance	Color	M.Pt(^{o}c)/ Decomposition tem.	Yield (%)
DAAP	$C_{10}H_{10}O_4$	194	Needle-like Crystals	White	184	16
DAAD	$C_{10}H_{14}O_2N_4$	222	Crystalline	Bright yellow	Dose not melt until 320	90
QXD	$C_8H_6O_2N_2$	162	Crystalline	Silvery white	Dose not melt until 350	92
Cu(II) complex	$Cu_3(C18H18O4N6)_2$	954.5	Crystalline	Dark gray	Dose not melt until 350	61
C0(II) complex	$Co_3(C_{18}H_{18}O_4N_6)_2$	941	Crystalline	Dark green	Dose not melt until 350	70

Table.2 Solubility check for DAAP, DAAD, QXD, Cu (II) and Co (II) complex with some solvents

Compound	Methanol	Ethanol	DMSO	Chloroform	THF	Acetic acid	Dietylether
DAAP	Soluble	-	Partially soluble	Soluble	insoluble	Insoluble	Partially soluble
DAAD	Insoluble	-	Partially soluble	-	soluble	Soluble	-
QXD	Partially soluble	Insoluble	insoluble	Insoluble	insoluble	Insoluble	Insoluble
Cu(II) complex	Insoluble	Insoluble	Partially soluble	Insoluble	insoluble	Insoluble	Insoluble
Co(II) complex	Insoluble	Insoluble	Partially soluble	Insoluble	insoluble	Insoluble	Partially soluble

4.2 IR Spectra of DAAP and DAAD

4.2.1 IR spectrum of DAAP

The IR spectrum data of DAAP is almost similar with the reported data of Elias Assayehegn project work. [34]

The IR spectrum of DAAP (appendix 1) shows characteristic bands assignable to O-H, C=O, C-O, C-H and C=C which are indications of the functional group of the target product.

The broad band centered at 3436cm^{-1} is due to the strong intra and inter molecular hydrogen bonded O-H stretching frequency of the phenolic group, which is also supported by the medium band at 1243 cm^{-1}of its bending mode frequency[36].

The band at 3083 cm^{-1} is assigned to CH stretching frequency of the aromatic group, besides its bending mode is observed at 840 cm^{-1}, which is a relatively sharp band

A band located at 2924cm^{-1} is assigned to the CH stretching mode of the methyl group and its bending mode is observed at 1370cm^{-1}.

The strong band at 1645cm^{-1} is due to C=O stretching frequency of the carbonyl group. The shift to a lower frequency from the expected value is probably due to the formation of hydrogen bonding between the phenolic O-H and the ketonic C=O [36]

The strong band at 1258cm^{-1} is due to C-O stretching of the phenolic group.

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

4.2.2 IR spectrum of DAAD

The IR spectrum data of DAAD is almost similar with the reported data of Elias Assayehegn project work. [34]

The IR spectrum of DAAD (appendix 2) shows the characteristic bands assignable to O-H, C=N, N-H which are indications of the functional group of the target molecule.

A band at 3460cm^{-1} is assigned asymmetric stretching of N-H group

A band at 3364cm^{-1} is assigned symmetric stretching of N-H group.

The band that is broad due to hydrogen bonding and obscured by the NH_2 group, appears in the region of 3400-2850 cm^{-1}can be assigned to the OH stretching of the phenolic group.

The band at 3060 cm^{-1} can be assigned to CH stretching of methyl group. The strong band that appears at 1616cm^{-1} may be assigned for C=N stretching of the of the azomethine group. The band at 1506cm^{-1} may be due to C=C of the ring. The strong band at 1228cm^{-1} may be assigned to C-O stretching of phenolic functional group. The band at 1050 cm^{-1} can be assigned to N-N stretching. The band at 877 cm^{-1} corresponds to the NH rocking vibration.

The formation of new bands at 3364cm-1(stretching frequency of N-H) , 1616cm^{-1}(C=N) and 1040cm-1(N-N) could be the sign of the formation of the desired product .Moreover this is supported by the disappearance of the vibrational frequency band for C=O(carbonyl group).

4.2.3 IR spectrum of QXD

The IR spectrum data of QXD is almost similar with the reported data of Gojje Gamo project work. [33]

The IR spectrum of QXD (appendix 3) has shown the characteristic bands assignable to O-H/N-H, C=O which are indications of the functional group of the target product.

The strong band at 1682cm^{-1} is due to C=O stretching frequency of the carbonyl group.

A band located at 3048cm^{-1} is assigned to aromatic sp^{2}C-H stretching.

The band at 3442 cm^{-1} can be assigned to –NH/OH stretching due to its tautomer form.

The formation of new bands at 1682cm^{-1}(stretching frequency of C=O) and 3442cm^{-1}(–NH/OH stretching due to its tautomer form) could be the sign of the formation of the desired product. Moreover this is supported by the disappearance of the vibrational frequency band for NH2 groups of O-phenylenediamine at 3386 cm^{-1} and 3364 cm^{-1} (i.e. stretching modes of starting materials)

4.3. Elemental analysis for DAAD

Table. 3 elemental analysis data of DAAD

Molecular formula	$C_{10}H_{14}N_4O_2$	
	C	H
Calculated (%)	54.05	6.31
Experimental (%)	54.05	6.05

4.4 NMR spectrum of DAAP

The NMR spectrum data of DAAP is almost similar with the reported data of Engidayehu Asrate project work. [35]

The ^{1}H and ^{13}C NMR spectrum for DAAP was recorded in $CDCl_3$. The observation obtained from the chemical shifts, coupling interactions and the DEPT spectra confirm the expected structure.

4.4.1 ^{1}H NMR spectrum

The ^{1}H NMR spectra of DAAP indicate the presence of four different protons. Each exists as a singlet peaks. The ^{1}H NMR spectra and^{13}C NMR spectral result of DAAP is summarized below in table 3 and 4.

Table 4 the ^{1}H NMR spectral data of DAAP

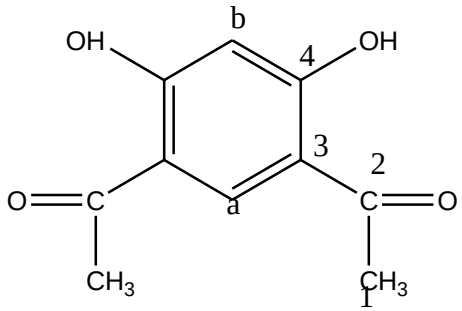
Types of proton (s)	Number of proton(s)	Chemical shift	Solvent
CH_3	6	2.2(s)	$CDCl_3$
H_a	1	6.44(s)	
H_b	1	8.22(s)	
OH	2	12.94(s)	

4.4.2 ^{13}C NMR spectrum of DAAP

The ^{13}C NMR spectra of DAAP shows six nonequivalent carbons

Table 5 ^{13}C NMR spectral data of DAAP

Type of Carbon(s)	Number of carbon(s)	Chemical shift (ppm)	Solvent
C_a	1	104.94	$CDCl_3$
C_b	1	113.58	
C_1	2	26.05	
C_2	2	202.43	
C_3	2	136.22	
C_4	2	168.85	



(DAAP)

Figure 8: Structure of DAAP

4.5 NMR spectrum of QXD

The ^{1}H and ^{13}C NMR spectrum for QXD was recorded in $CDCl_3$. The observation obtained from the chemical shifts, coupling interactions and the DEPT spectra confirm the expected structure.

4.5.1 ^{1}H NMR spectrum of QXD

The ^{1}H NMR spectra of QXD indicates the presence of four different protons. A multiple signal from 7.04-7.16ppm is due to the different proton of aromatic benzene ring. A peak around 12ppm is the OH proton due to its tautomer and singlet around 3.5 is due to the hydrazine NH proton of the ring.

4.5.2 ^{13}C NMR spectrum of QXD

The ^{13}C NMR spectra of QXD show the presence of four non –equivalent carbons. A peak at 155.64ppm is due to carbon bonded to carbonyl oxygen. Signals at 126ppm is carbon bonded to cyclic nitrogen, signal at 123ppm is the middle carbon of benzene ring as well as peak at 115ppm is the end carbon of the benzene ring.

4.6 Characterization of metal complexes

4.6.1 IR spectra of metal complexes

The IR spectra of Co (II) and Cu (II) complexes are almost similar. But they show significant changes when compared with the ligands DAAD and QXD.

The broad band presenting at 3419cm^{-1}for Cu (II) and 3424cm^{-1} for Co (II) complex can be assigned to the OH stretching of the coordinated water. The band at2924cm^{-1} for Cu (II) and 2924cm^{-1} for Co (II) complex is due to CH stretching of the methyl group. Whereas it's bending mode frequency is observed at 1360cm^{-1} and 1362cm^{-1} respectively. In both complex No strong absorption band was observed near 1685-1670 cm^{-1} indicating the absence of C=O of quinoxaline-2, 3-dione at 2-position, this confirms the condensation of carbonyl group of quinoxaline 2, 3-dione and amino groups of 2,6-dihydroxy-5-acetylacetophenonedihydrazone. The band at 1542cm^{-1} for Cu (II) and 1561cm^{-1} for Co(II) may be attributed to the C=N group. The stretching frequency of C=N for the ligand DAAD was 1616 cm^{-1}. This down ward shift confirms that complexation of one of the two azomethine group with the metal ion. The band at 1244cm^{-1} for Cu (II) and 1246cm^{-1} for Co (II) may be assigned to the stretching frequency of C-O. The stretching frequency of C-O for the ligand DAAD was 1228 cm^{-1}. This upward shift of C-O stretching confirms the deprotonating of the phenolic group and subsequent comp laxation of through phenoxide. NH_2 asymmetric stretching frequencies for the complexes were overlapped with OH stretching frequency of the coordinated water. This confirms the presence of uncondensed NH_2 group in the complex. Furthermore the spectral data shows non ligand bands in the range of 600-400cm^{-1} assignable to M-O and M-N stretching. So infrared spectra revealed that nitrogen atom of imine group and oxygen atom of carbonyl participate in coordinating with the central metal ions

The infrared spectra of the ligand precursors, the ligand as well as the metal complexes are summarized in table 6.

Table 6 infrared spectral data of DAAP, DAAD, QXD and metal complexes

Band assignment	DAAP/cm^{-1}	DAAD/cm^{-1}	QXD/cm^{-1}	Cu(II) complex/ cm^{-1}	Co(II) complex/ cm^{-1}
υ O-H	3550-2750	3420-2850	3442	3419	3424
$\upsilon NH2\ sym$	-	3864-3460	-	-	-
υNH2 assy	-	OL	-	OL	OL
υAr-C-H/Me-C-H	2924	OL	-	2922	2922
$\upsilon(C=N)$	-	1616	1614	1542	1561
$\upsilon(C=O)$	1645	-	1682	1597	1611
$\upsilon(C-O)$	1258	1228	-	1244	1246

OL=overlapped

4.6.2 Atomic Absorption Spectroscopy of Metal Complex

0.01gm of the metal complex dissolved in 10 ml of concentrated nitric acid was digested with gradual and repeated addition of 5 ml portions of the acid until the organic content of the complexes decomposes. After the decomposition only the metal salts remain in the solution. The residue was diluted to 50 ml volumetric flask using deionized water and subjected to analysis. The experimental percentage of metal in the complex was obtained from the AAS data:

4.6.3 Elemental analysis

The elemental analysis (C, H, Metal percentages) of metal coplexes are presented in table 7.

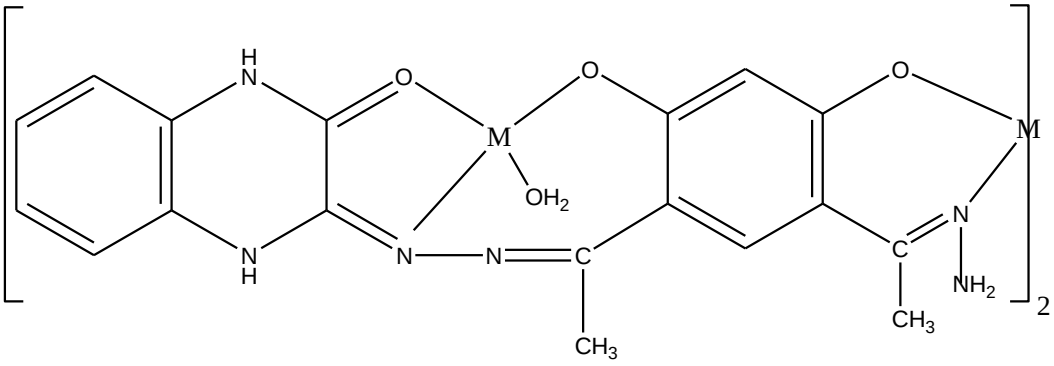
The data supports the formation of Co (II) and Cu (II) complexes with the molecular formula M L (H_2O) (L=$C_{18}H_{16}O_3N_6$, M=Cu (II) or Co (II). This formula justifies the absence of chloride ions in the complexes, as verified by qualitative analysis. It also verifies the diatomic nature of the ligand, formed by 1:1 condensation of QXD and DAAD in basic aqueous MeOH and THF media, in the presence of metal ions (in a template method)

Table.7 Elemental analysis (C, H, Metal percentages) of metal complexes

Molecular Formula	$CuC_{18}H_{18}O_4N_6$		
	% C	%H	% Cu(II)
Practical value	45.15	3.87	17.46
Calculated value	45.26	3.77	19.96
Molecular Formula	$CoC_{18}H_{18}O_4N_6$		
	% C	% H	
Practical value	39.7	3.77	
Calculated value	45.91	3.83	

5. Conclusion

New copper (II) and Co(II) complexes were prepared from the template condensation of 2,4-dihydroxy-5-acetylacetophenondihydrazone and quinoxalin-2,3-dione with the corresponding metal salts $CuCl_2 \cdot 2H_2O$ and $CoCl_2 \cdot 2H_2O$.The complexes were characterized on the basis of elemental analysis, IR,AAS and other data.. Square planar geometry was proposed for the metal complexes. Further studies on electronic spectra, magnetic susceptibilities thermal analysis and XRD of the complexes can lead to confirmation of the proposed structure.



Where, M=Co(II) or Cu(II)

Figure 9: The proposed structure of the Cu(II) and Co(II) complex with DAAD and QXD

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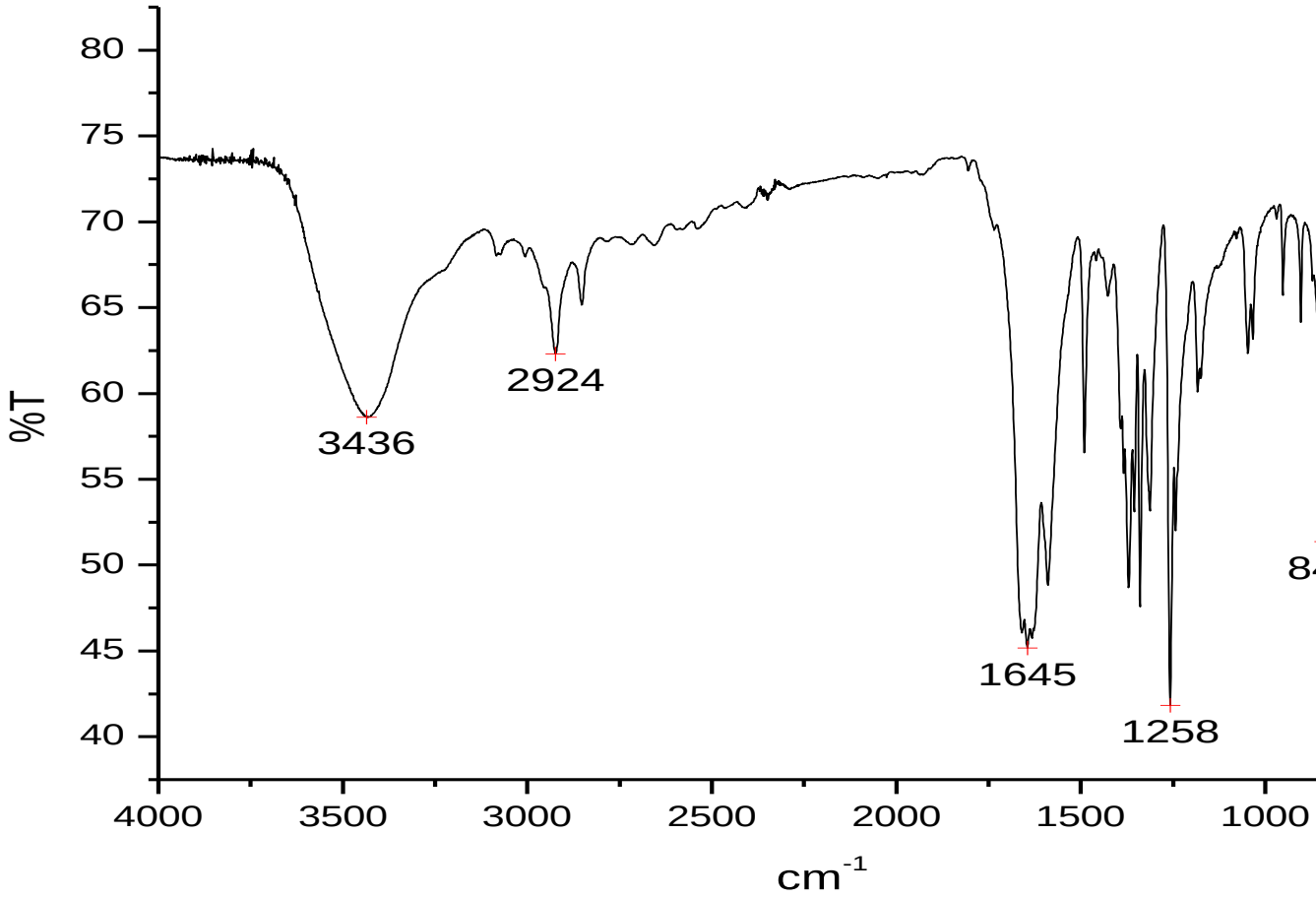
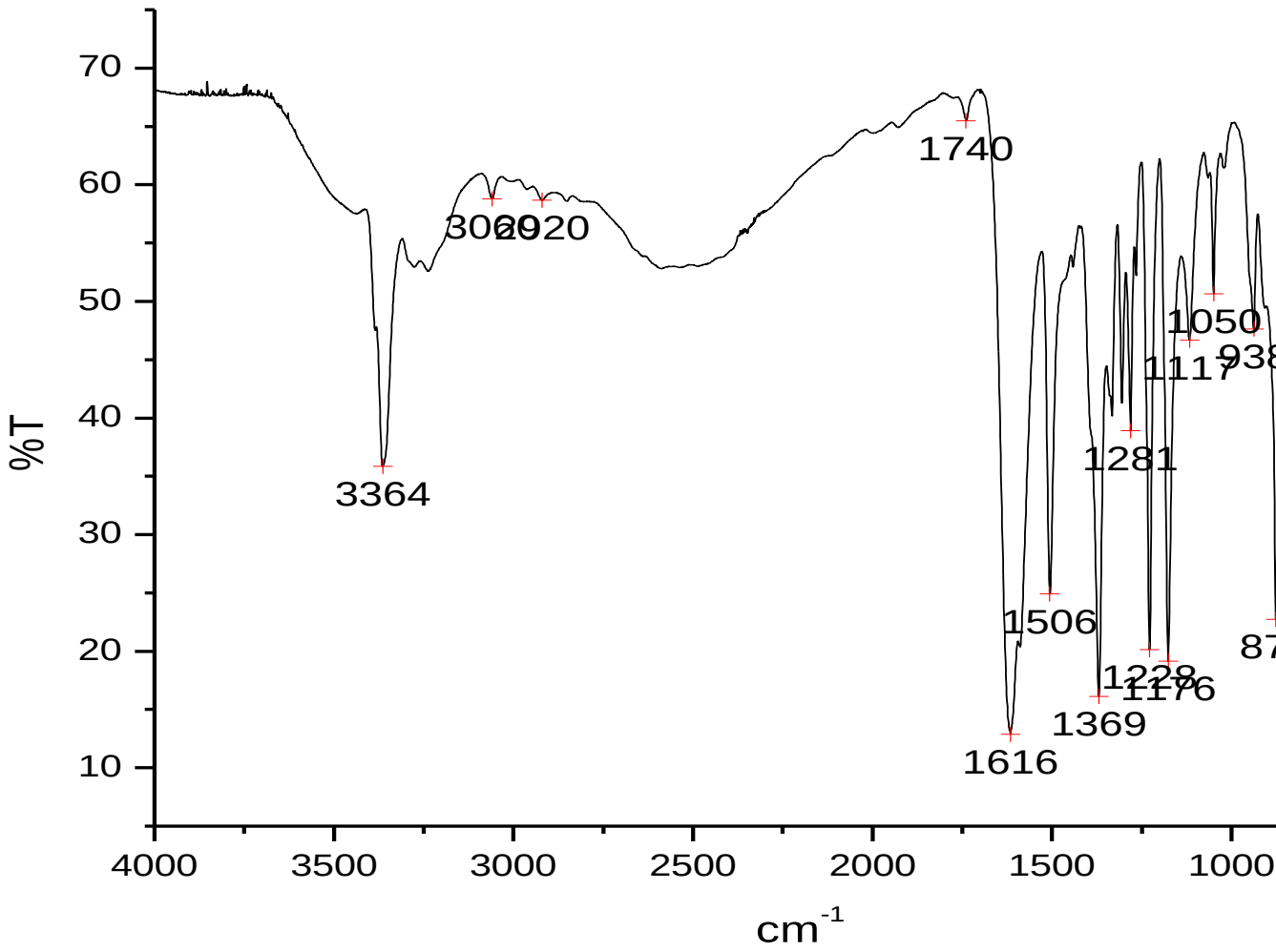
7. Appendices

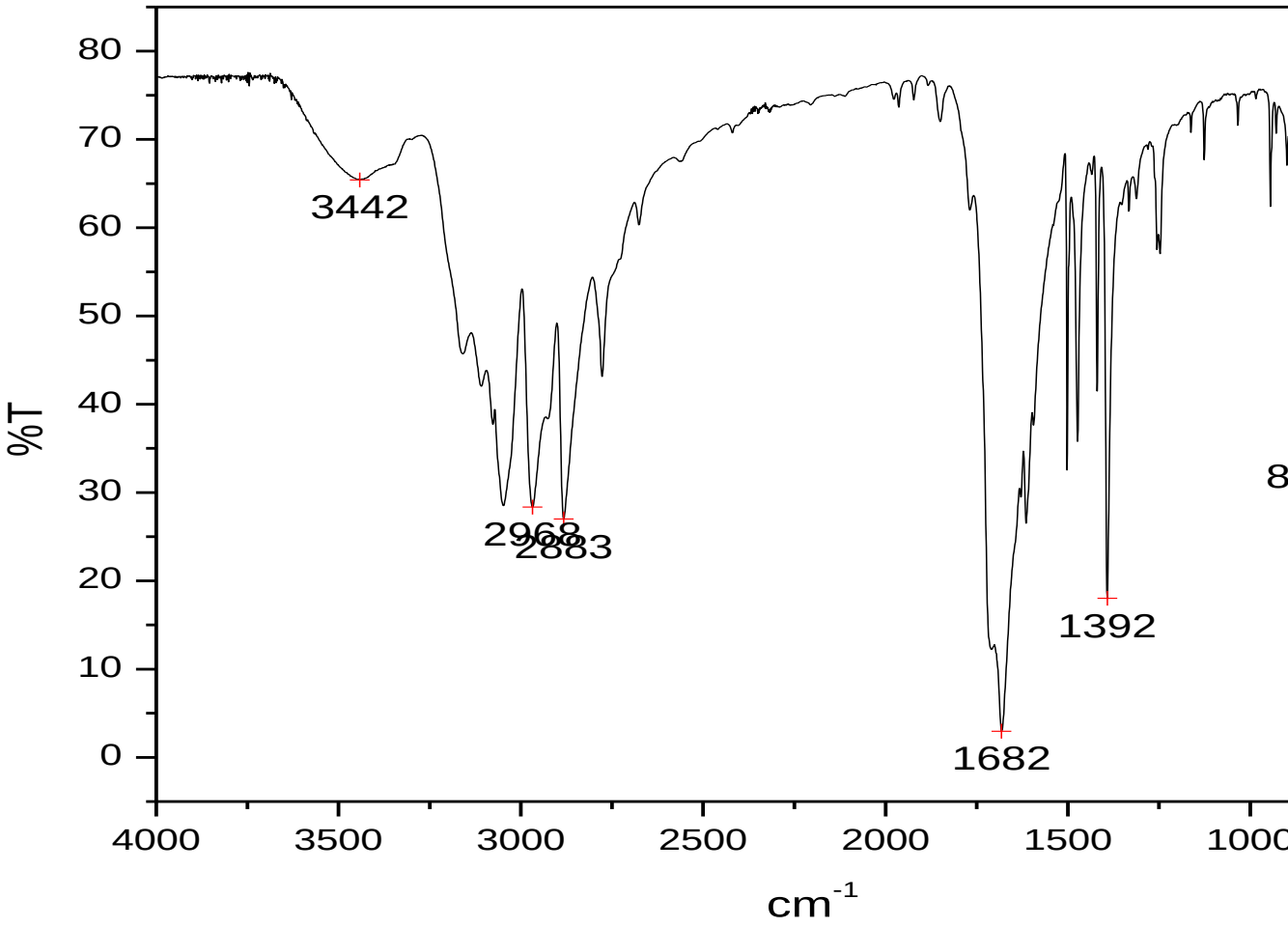
Appendix 1: IR spectra for DAAP



Appendix 2: IR spectra for DAAD



Appendix 3: IR spectra for QXD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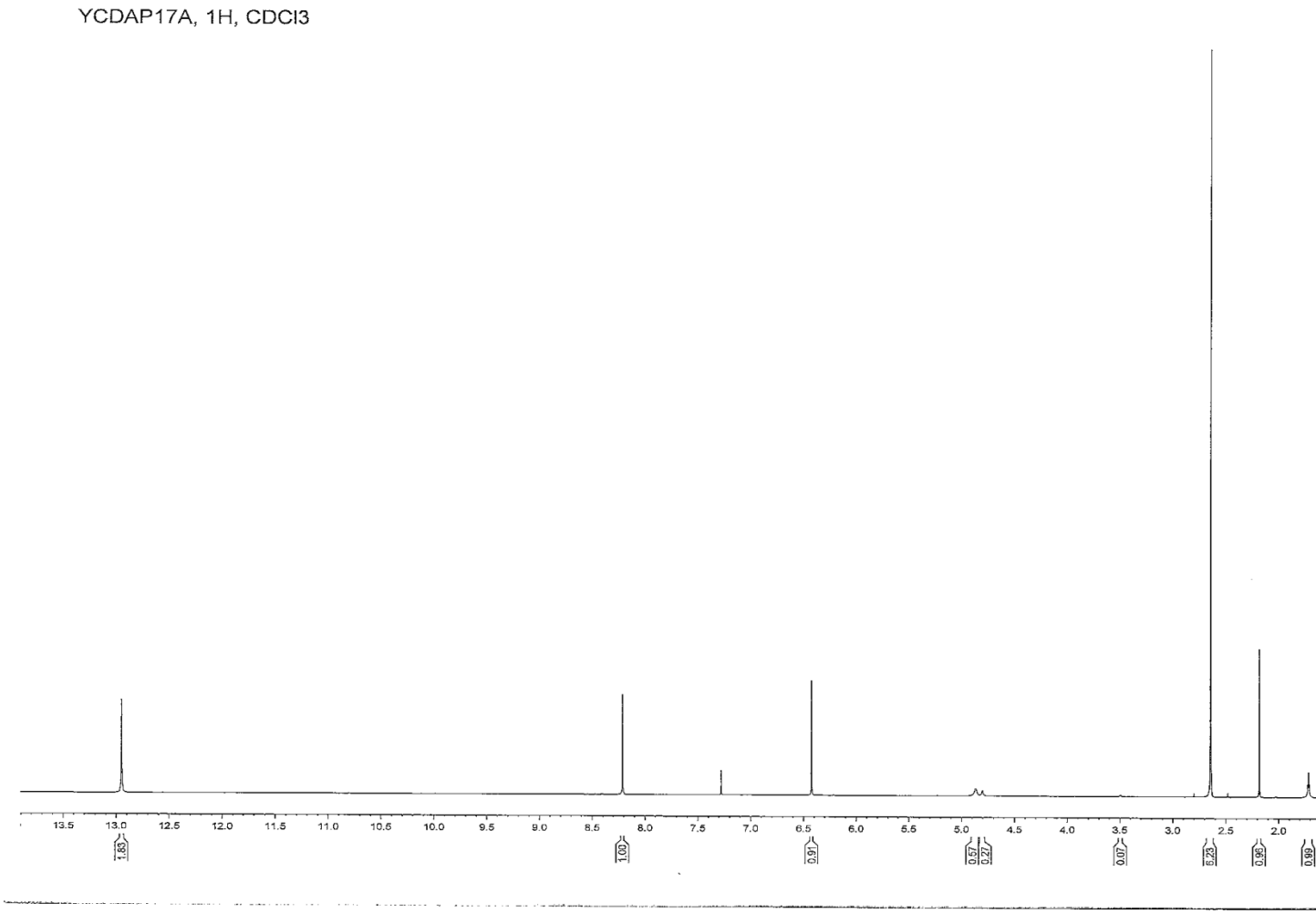
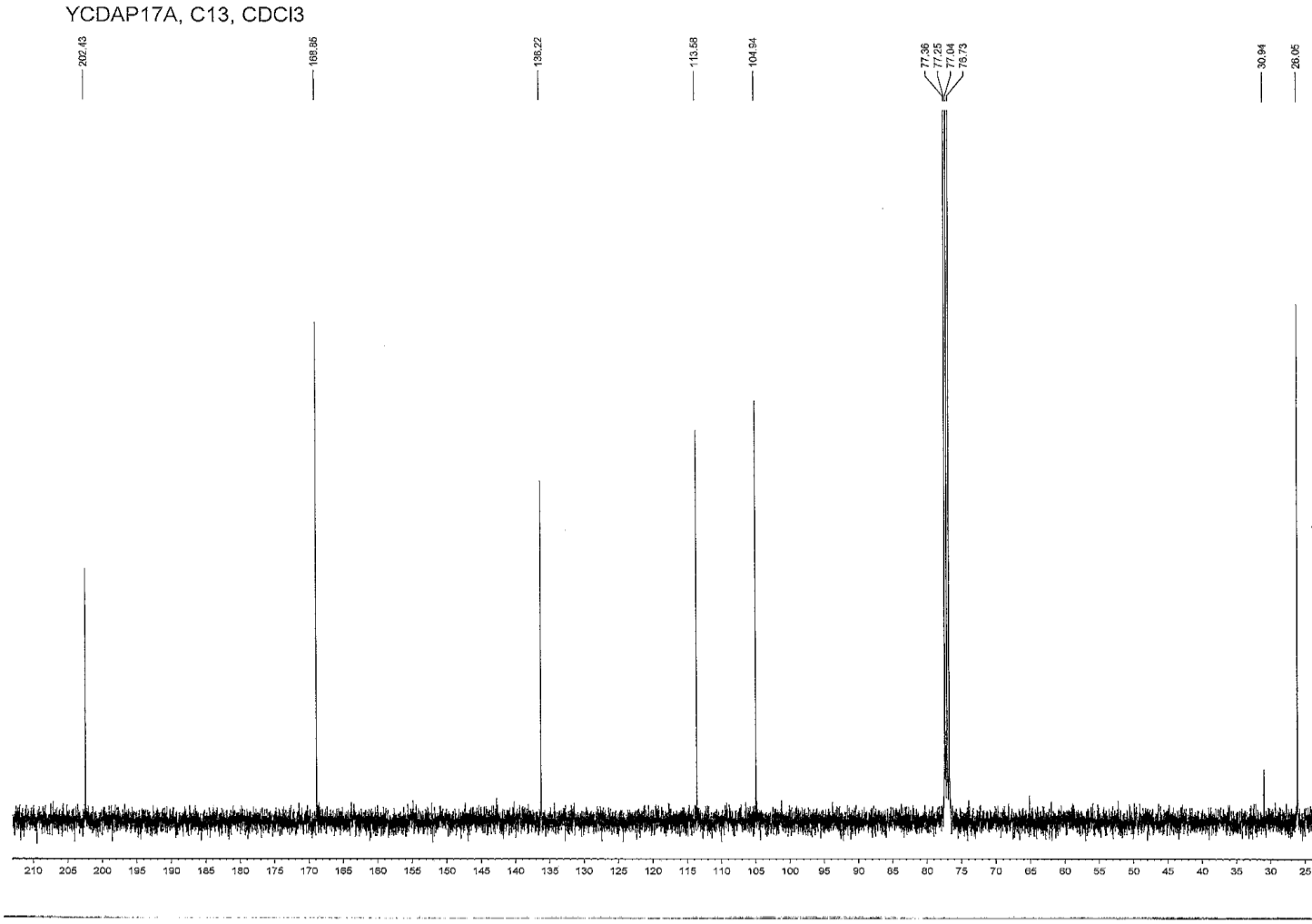
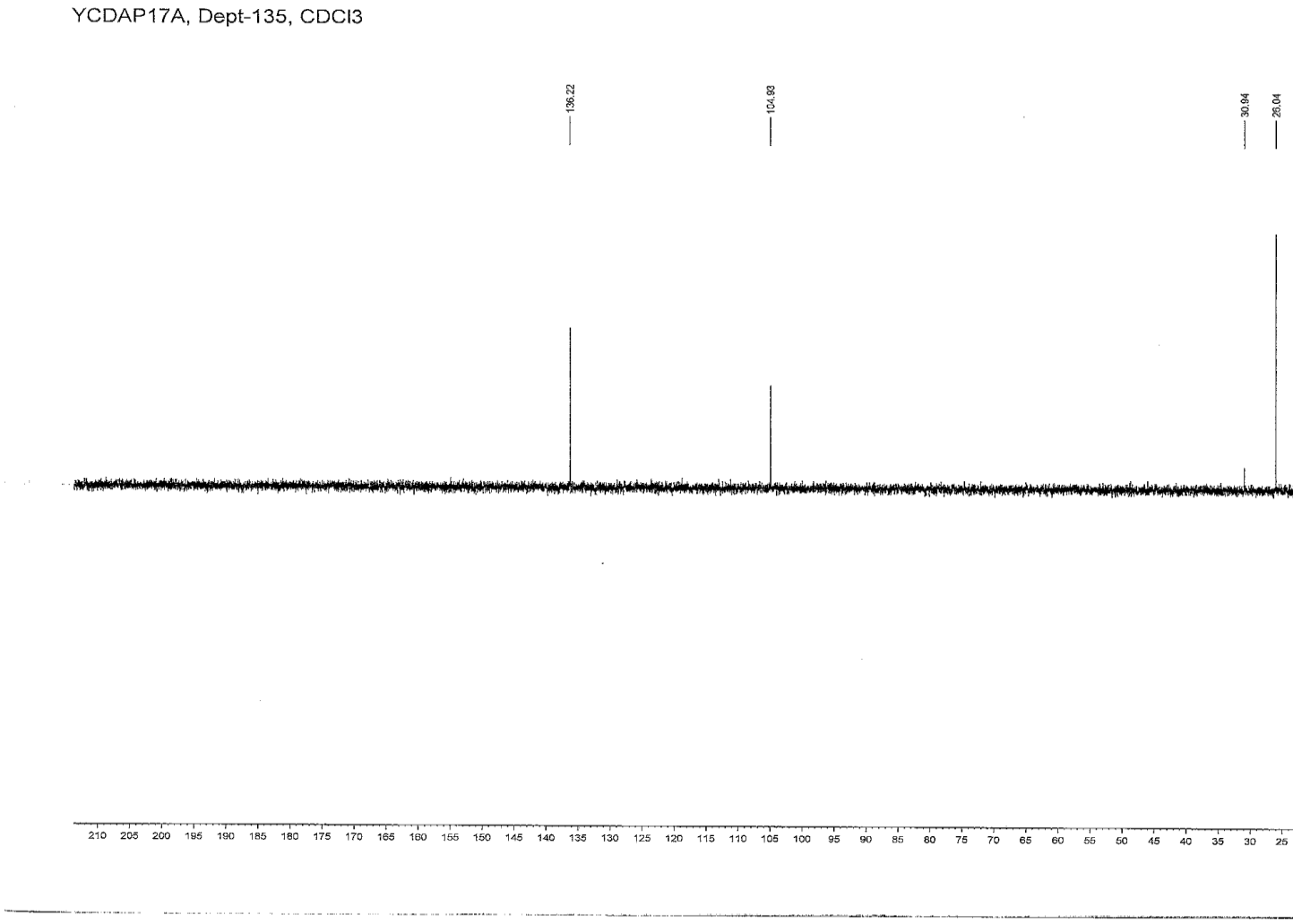
Appendix 4: ^{1}H NMR spectra of DAAP



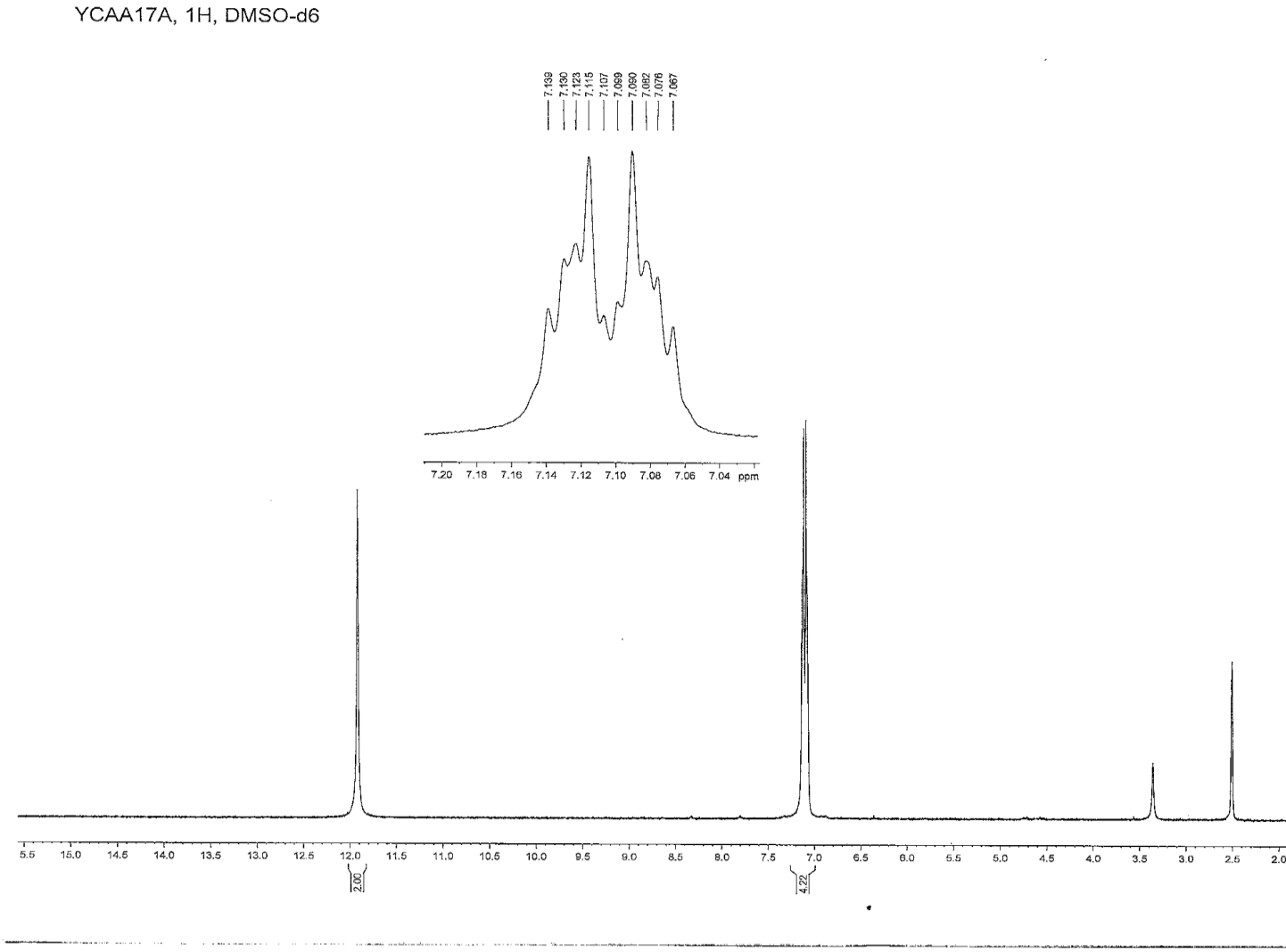
Appendix 5: ^{13}C NMR spectra of DAAP



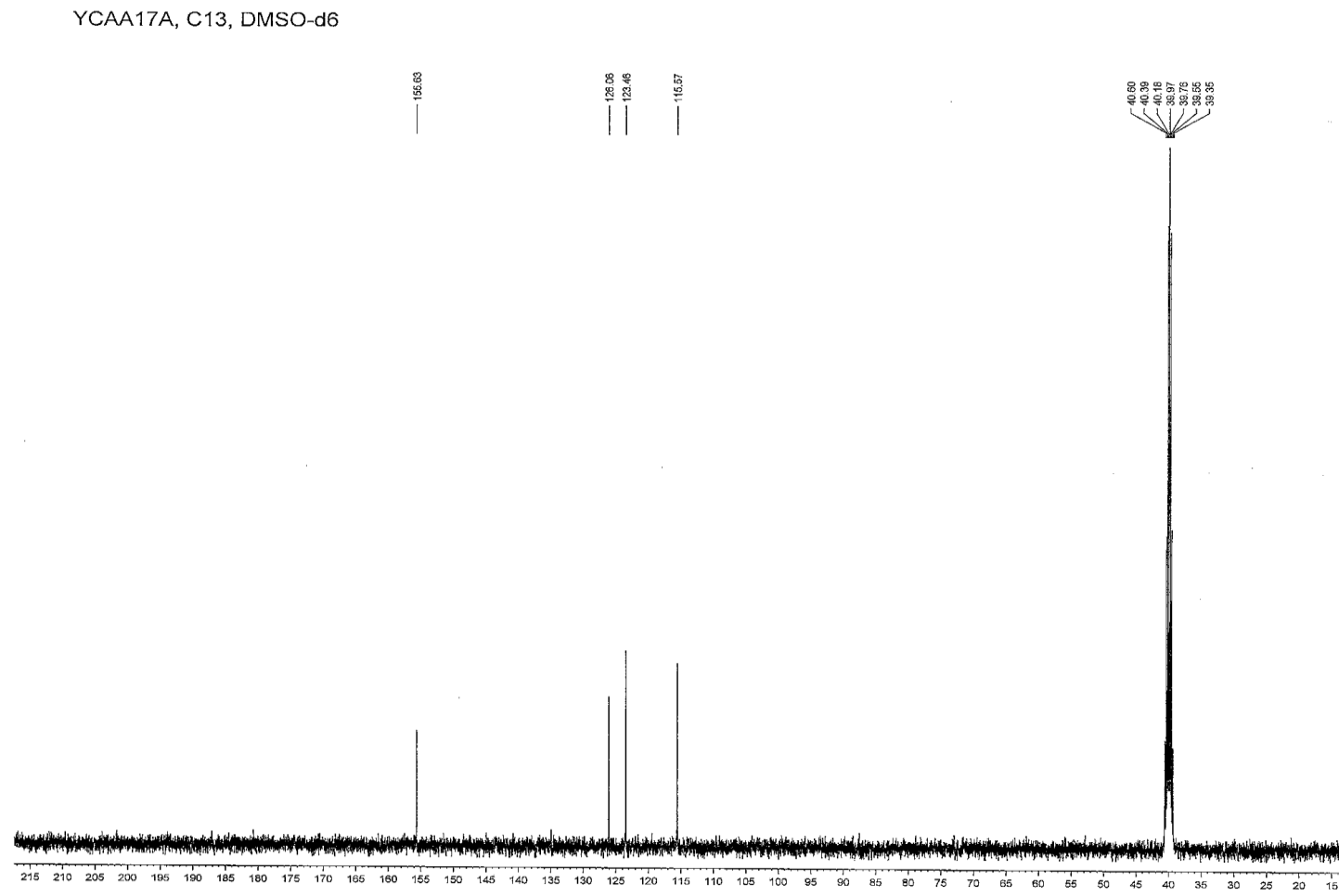
Appendix 6: DEPT-135 spectra of DAAP



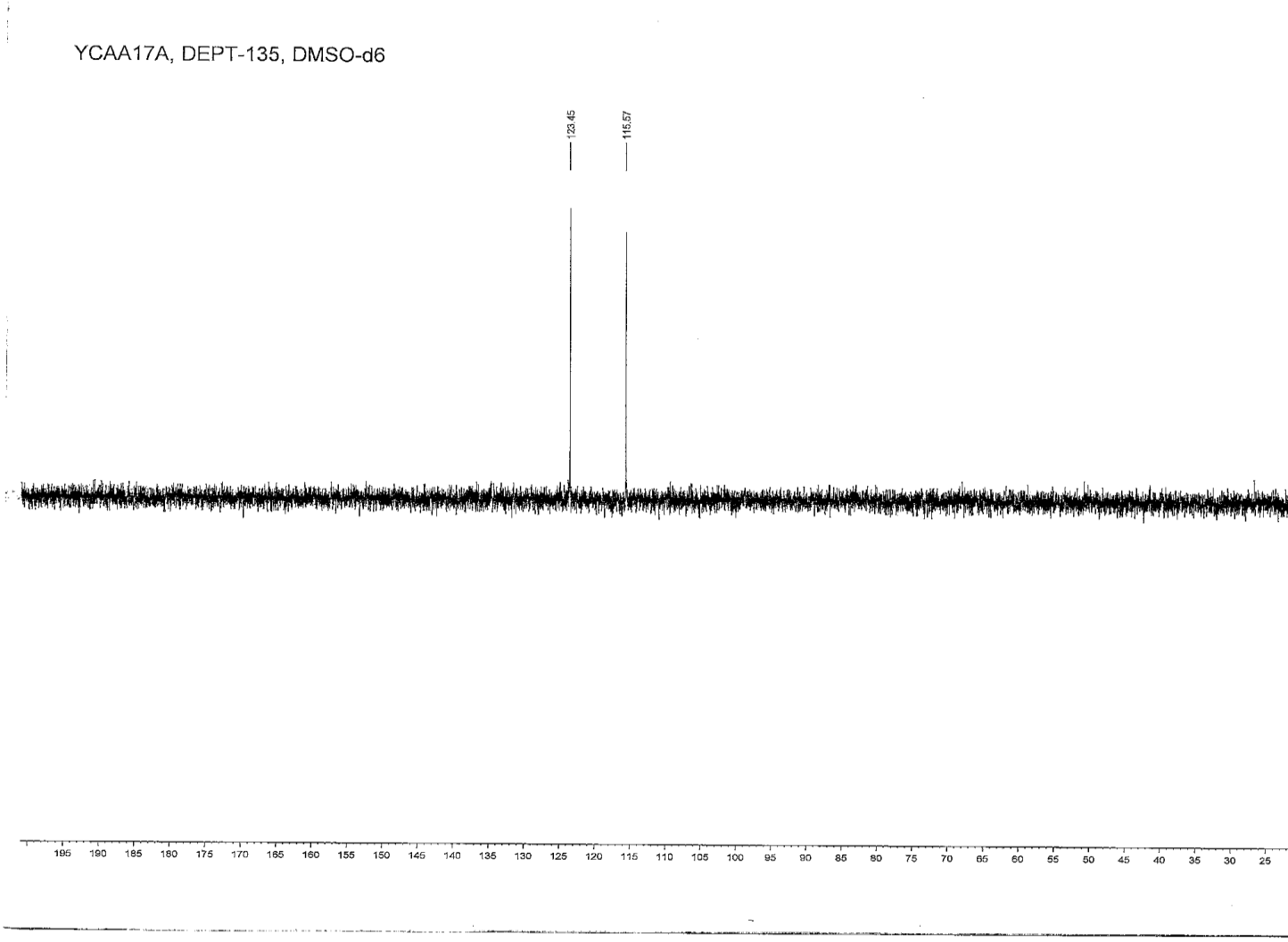
Appendix 7: ^{1}H NMR spectra of QXD



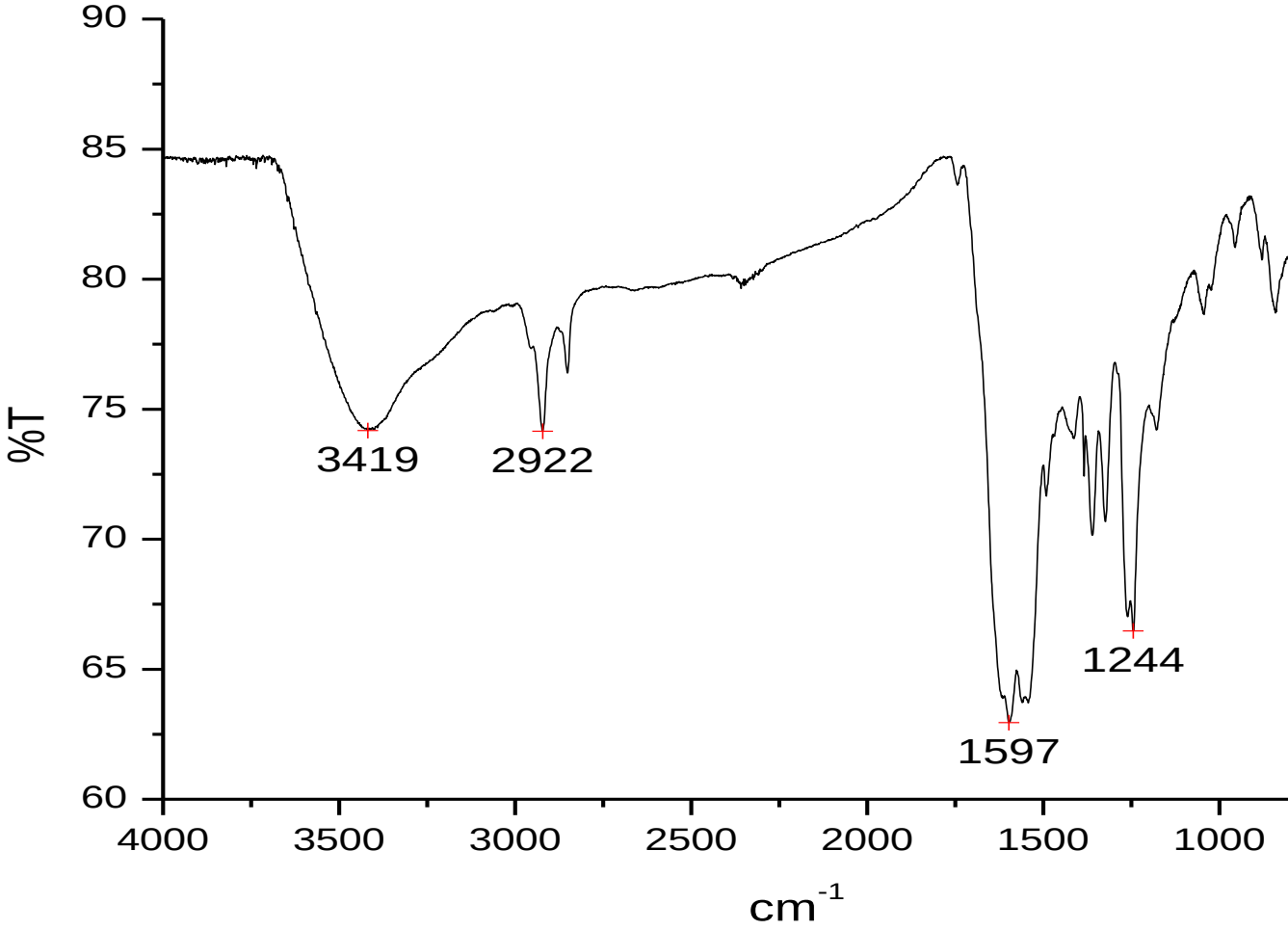
Appendix 8: ^{13}C NMR spectra of QXD



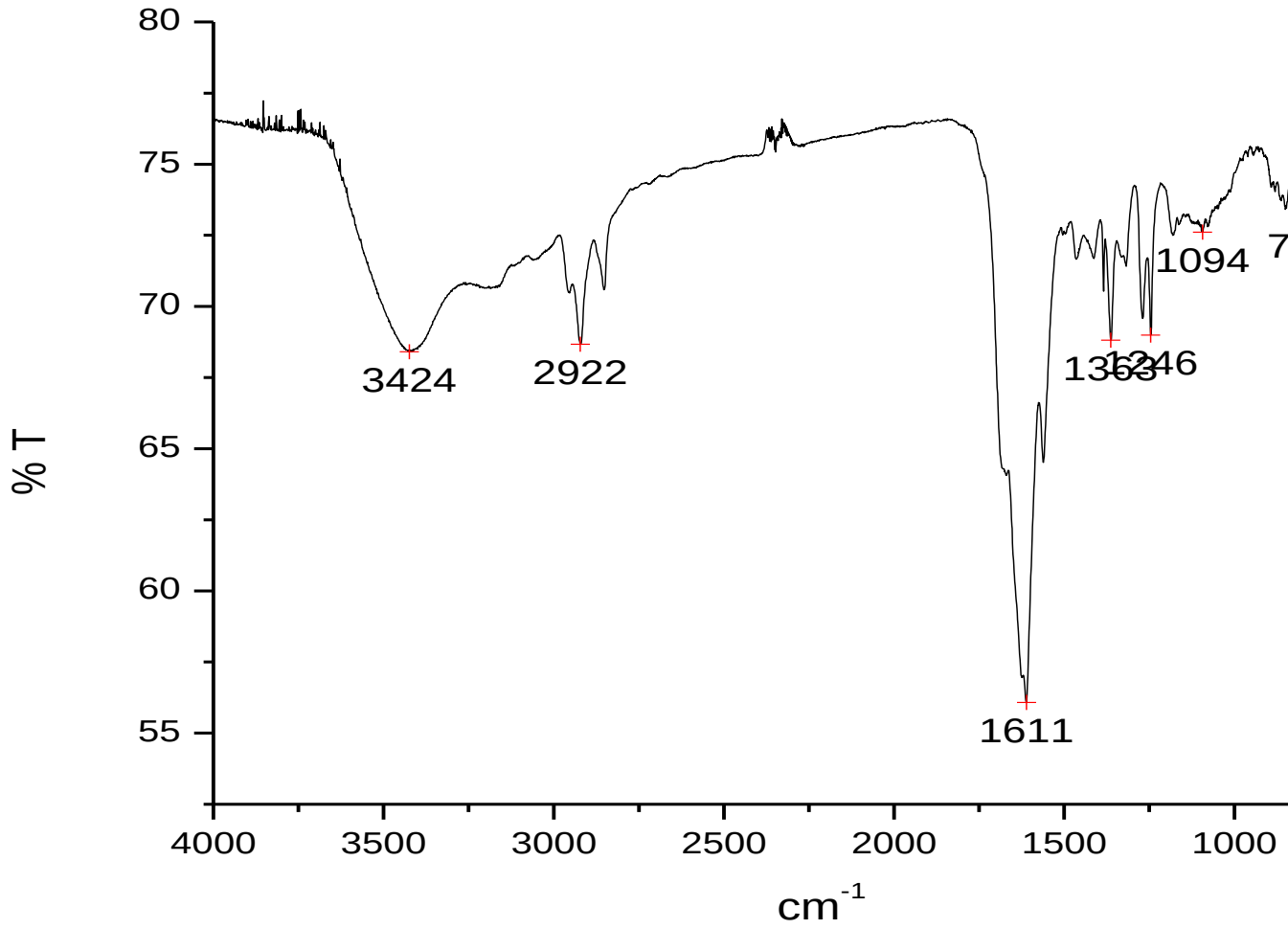
Appendix 9: DEPT-135 spectra of QXD



Appendix 10: IR spectrum of Cu (II) complex



Appendix 11: IR spectrum of Co (II) complex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