ADDIS ABABA UNIVERSITY

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SYNTHESIS AND CHARACTERIZATION OF NEW METAL COMPLEXES DERIVED FROM 1,4-DIHYDROQUINOXALINE -2, 3- DIONE, ORTHOPHENYLENEDIAMINE AND HYDROQUINONE.

BY

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Addis Abeba, Ethiopia

April 2018

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A THESIS SUBMITTED TO THE SCHOOL OF GRADUATE STUDIES OF ADDIS ABABA UNIVERSITY IN PARTIAL FULFILLMENT OF THE REQUIREMENT FOR THE DEGREE OF MASTER OF SCIENCE IN CHEMISTRY

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COLLEGE OF NATURAL AND COMPUTATIONAL SCIENCE

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Dr. Yonas Chebude	_____	_____

April 2018

Declaration

I hereby declare that this thesis entitled **"Synthesis and characterization of new metal complexes derived from 1,4-dihydroquinoxaline-2,3-dione, orthophenylenediamine and hydroquinone''** is an authentic research work carried out by me under the guidance of **Dr**. **Negash Getachew.** No part of this work shall be published in scientific journals or reported in the media without the knowledge and consent of my advisor.

Acknowledgements

I would like to express my deepest gratitude to my advisor, **Dr. Negash Getachew** for his fruitful advice, encouragement and contribution in the course of my work. I am surely privileged to have his as my advisor in this thesis work. I thank the department and all members of the Chemistry department, who have played an important role in my successful completion of this thesis work.
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Table of content

List of figures

List of schemes

List of tables

Symbols and abbreviation used

OPD = orthophenylenediamine

QXD = 1,4-dihydroquinoxaline-2,3-dione

H Q = hydroquinone

DMF = dimethylformamide

DMSO = dimethyl sulfoxide

MeOH = methanol

EtOH = ethanol

L = ligand

M = molarity

AAS = atomic absorption spectroscopy

m.pt = melting point

M-L = metal-ligand complex

^{1}HNMR = proton nuclear magnetic resonance

^{13}CNMR = carbon nuclear magnetic resonance

IR = infrared

TLC = thin layer chromatography

υ = stretching

Ins.= insoluble

Sol.= soluble

Appendices

1. IR Spectrum of QXD (dione)

2. IR spectrum of expected Ligand

3. IR spectrum of Zn-L complex

4. IR spectrum of Zn (QXD) (HQ) complex

5. IR spectrum of hydroquinone

6. IR spectrum of orthophenylenediamine

7. ^{1}NMR spectrum of Zn (QXD) (HQ) complex

8. ^{13}CNMR spectrum of Zn (QXD) (HQ) complex

9. ^{1}HNMR spectrum of Zn-L complex

10. ^{13}CNMR spectrum of Zn-L complex

11. UV-Visible spectrum of Zn-L complex

12. UV-Visible spectrum of Zn (QXD) (HQ)

13. UV-Visible spectrum of hydroquinone

14. UV-Visible spectrum of orthophenylenediamine

Abstract

Metal complex of the type [$MLCI_2$], M=Zn(II), L=tetra- dentate cyclic ligand, has been prepared through the condensation of orthophenylenediamine and 1,4-dihydroquinoxaline-2,3-dione in the presence of $ZnCl_2$ (template system). The ligand coordinates through the four imine nitrogen atoms formed up on condensation of $–NH_2$ function of orthophenylenediamine with C=O groups in 2-position of quinoxaline -2,3-dione. Another metal complex of zinc (II) was synthesized with 1,4-dihydroquinoxaline-2,3-dione and hydroquinone with behaving as mixed ligand system. These complexes have been characterized with the help of various spectral technique, such as ^{1}H and $^{13}CNMR$, FT-IR, AAS elemental analysis and measurement of molar conductance in $1x\ 10^{-3}$ M solutions of DMSO. Furthermore, the determination of chloride test in metal content supports the concluded structures. The octahedral geometry was proposed for Zn-L complex and square planar for Zn (QXD) (HQ) complex.

1.INTRODUCTION

A metal complex consists of central metal atom and ion surrounded by set of ligand, anions or neutral molecules, which have one or more atoms bearing a lone pairs of electrons (1). The binding of these donor atoms with metal ion is electrostatic and/or covalent. In non-transition metal complexes, the binding is largely electrostatic, while in transition metal complexes there is significant covalent. Generally, ligands are Lewis bases that have lone pair on nitrogen, oxygen, Sulphur, etc. and that bind with transition metals (Lewis acids). Ligands can be divided into unidentate, bidentate and multidentate types, according to the availability of one, two or more donor atoms bonding with metal [2]. Multidentate ligands which are bonded to the metal through their two or more atoms form heterocyclic ring(s) (usually five or six member) in which the metal is one of the members. Such a metal complex is termed as metal chelate. Metal complexes are of great interest for many years. It is well known that N, S and O atoms play a key role in the coordination of metals at the active sites of numerous metal biomolecules. Chelating ligands containing O, N and S donor atoms show broad spectrum of biological activities and are of special interest in the variety of ways in which they are bonded to metal ions [4]. The development of the field of bioinorganic chemistry has increased the interest in Schiff base complexes, since it has been recognized that these complexes may serve as models for biologically important species [5]. Schiff bases possessing azomethine group (RHC=NR'), first reported by Hugo Schiff in 1864, are condensation products of carbonyl compounds and primary amines. The presence of a dehydrating agent normally favors the formation of Schiff bases. Though the Schiff bases are stable solids, care should be taken in the purification steps as it undergoes degradation. Presence of a lone pair of electrons in 2p orbitals of nitrogen atom of the azomethine group is of considerable chemical importance and imparts excellent chelating ability especially when used in combination with one or more donor atoms close to the azomethine group. This chelating ability of the Schiff bases combined with the ease of preparation and flexibility in varying the chemical environment about the C=N group makes it an interesting ligand in coordination chemistry.

Schiff bases are important class of ligands in coordination chemistry and find extensive application in different fields [6]. Schiff base ligands and their complexes have been extensively studied for

their structures and applications. Schiff bases derived from the carbonyl compounds and ethylene diamine are well known polydentate ligands forming neutral complexes [7]. Metal complexes of the Schiff bases are generally prepared by treating metal salts with Schiff base ligands under suitable experimental conditions [8]. However, for some catalytic application the Schiff base metal complexes are prepared in situ in the reaction system [9]. The interactions of these donor ligands with metal ions give complexes of different geometries which are potentially biologically active. Thus, in recent years' metal complexes of Schiff bases have attracted considerable attention due to their remarkable antifungal, antibacterial, antitumor and anticancer activities [10]. Transition metal complexes with Schiff bases have expanded enormously and embraced wide and diversified subject comprising vast areas of bio-organic compounds. Many studies have been done on transition metal complexes of Schiff bases due to the fact that Schiff bases offer opportunities for inducing substrate chirality, tuning metal centered electron factor, enhancing the solubility and stability of either homogenous or heterogeneous catalyst [12]. Schiff base ligands are able to coordinate many different metals and stabilize them in various oxidation states [13]. Transition metal complexes of N-donor ligands (Schiff bases) showed anti-*Candida* activities [14]. Transition metal complexes of Schiff base have become important due to their ability to serve as polymeric ultraviolet stabilizers, as Laster dyes and molecular switches in logic or memory circuits. The first row transition metal complexes such as Zn(II), Ni(II), Cu(II) have been found to exhibit fungicidal, bactericidal and antiviral activity [15]. Ketoazomethines, a class of Schiff bases, possessing adjoining azomethine (RHC=N-R') and ketone (C=O) groups, well known for their biological properties, dyeing characteristics and analytical applications, have been identified as novel ligands in forming complexes of isomeric structures, unusual stereo chemistries and iso- and poly nuclear species [16].

The coordination activity of the carbonyl group of the ketones derived from primary substituted aromatic amines generally depends upon the nature and position of the substituent(s), which is another interesting feature of these compounds as ligands.

1.2 Objective of the study

1.2.1 General objective

General Objective of the Study was to synthesizing and characterizing of Zn (II) complexes with 1,4-dihydroquinoxaline-2,3-dione and orthophenylenediamine as well as with 1,4-dihydroquinoxaline-2,3-dione and hydroquinone ligand.

1.2.2 Specific objective

- Synthesis of desired Schiff base derived from-1,4-dihydroquinoxaline-2,3-dione and orthophenylenediamine.
- Synthesis of Zn^{2+} metal complex with mixed ligand Schiff base derived from 1,4-dihydroquinoxaline-2,3-dione and orthophenylenediamine by template method.
- Synthesis of mixed ligand of Zn^{+2} with 1,4-dihydroquinoxaline-2,3-diones and hydroquinone.
- Characterization of these Zn^{+2} complexes.

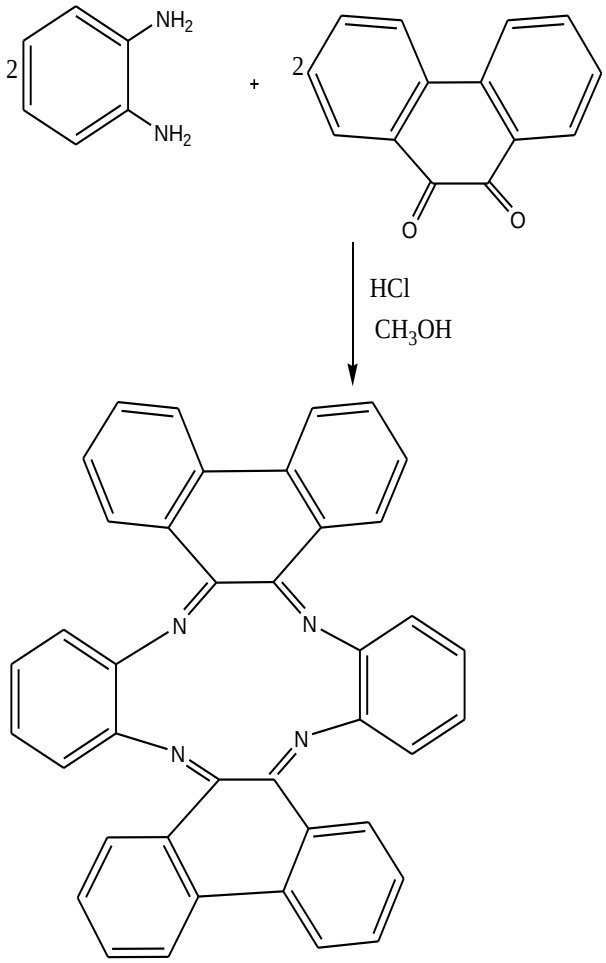
2. LITERATURE REVIEW

2.1 Synthesis of Schiff's Bases (azomethine ligand)

Many reports have been made on the synthesis and metal binding characteristics of multidentate ligands. Several multidentate ligands possessing C=N or azomethine group are known as Schiff bases. Schiff bases are compounds containing an imine (-C=N-) or azomethine group (R-C=N-) and usually prepared by the condensation of a primary amine with an active carbonyl group. The reaction to prepare Schiff bases is reversible, progresses through a carbinol amine intermediate and requires the removal of water [17].

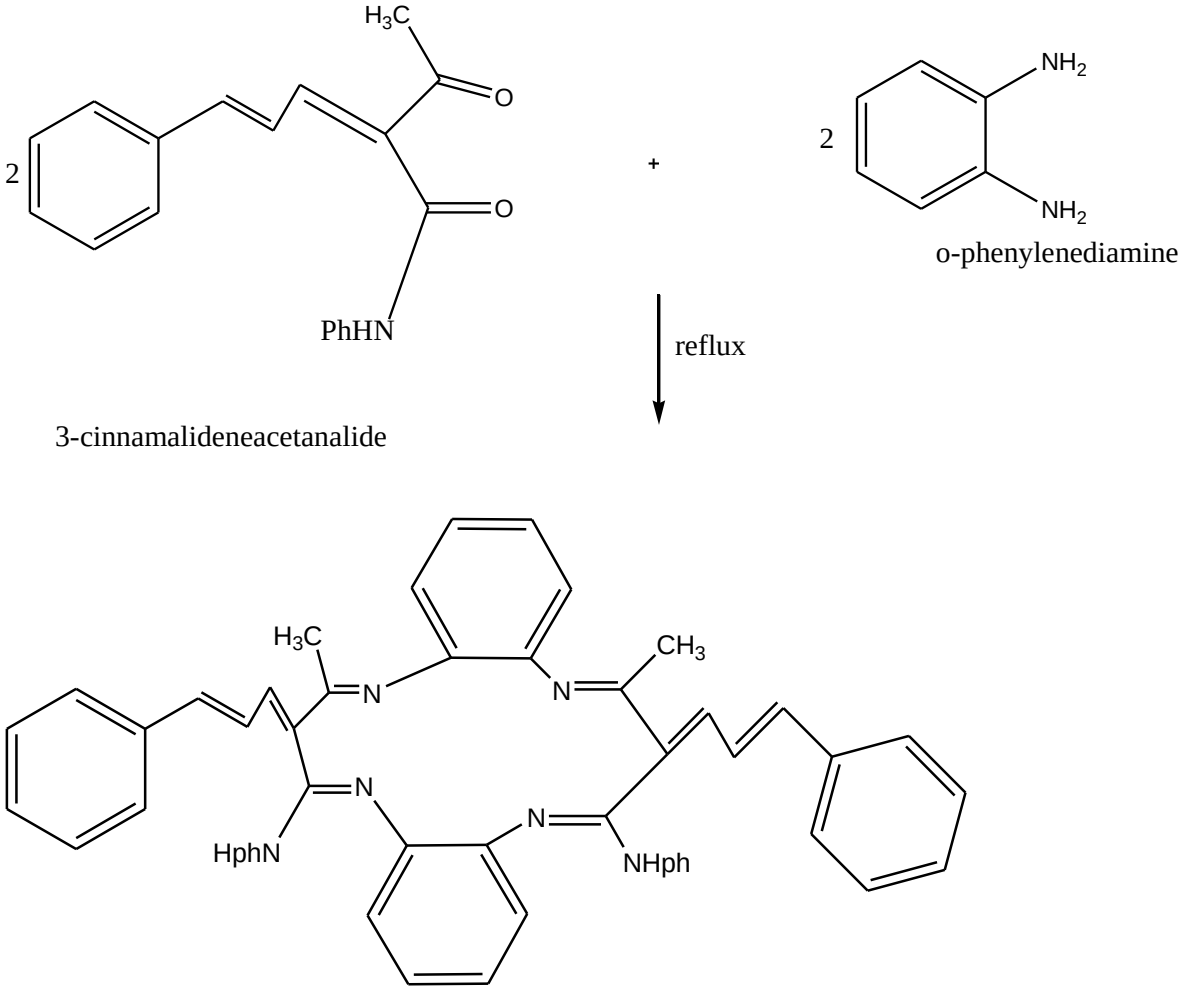
2.1.1 Synthesis of macrocyclic ligand

Schiff base tetra-azamacrocyclic ligand, was synthesized by the condensation of orthophenylenediamine and quinoxaline derivatives [18]**.**



Scheme1. Structure of macrocyclic ligand (L)

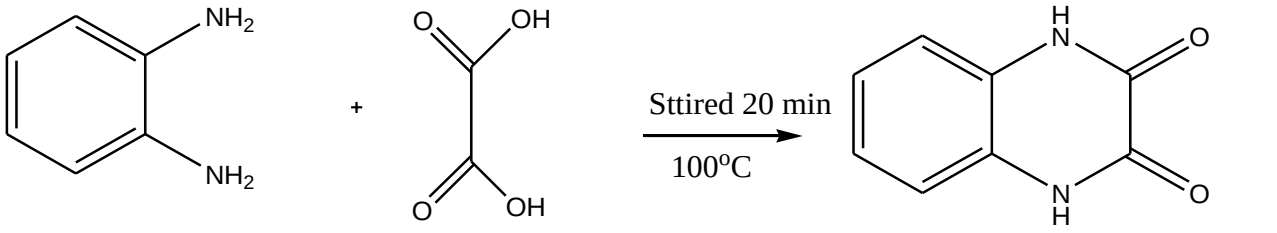
Raman et al have reported the synthesis of a macrocyclic Schiff base derived from 3-cinnamalideneacetanalide and orthophenylenediamine which acts as a tetra dentate and strongly conjugated ligand to form a cationic solid complex with Cu (II), Ni (II), Co (II) and Zn (II) [19]



Scheme 2. Macrocyclic Schiff base derived from cinnamalide and o-phenylenediamine

2.1.2 Synthesis of 1,4 –dihydroquinoxaline-2,3-dione [20]

A solution of oxalic acid dehydrate (0.238 mol, 30g) in H_2O (100 ml) was heated to 100^oC and concentrated HCl ml was added, followed by orthophenylenediamine (0.204 mol, 22g) with constant stirring adjusting the temperature at 100 ^oC for 20 min. The mixture was cooled in ice bath and Precipitate was formed and washed with water repeatedly. Product was recrystallized from ethanol.

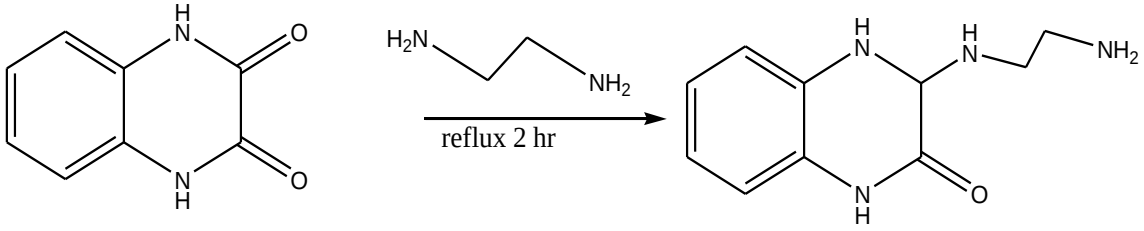


ortophenylenediamine Oxalic acid 1,4-dihydroquinoxaline-2,3-dione

Scheme 3. Synthesis of 1,4-dihydroquinoxaline-2,3-dione

2.1.3 Synthesis of quinoxaline derivatives [21]

A mixture of the 1,4-dihydroquinoxaline-2,3-dione (0.062 mmol, 10.04 g), ethylene diamine (1 mol, 50 ml) and water (50 ml) was heated under reflux for 2 hours, then cooled to room temperature, the precipitate was filtered, washed with water repeatedly and recrystallized from 2-ethanol.

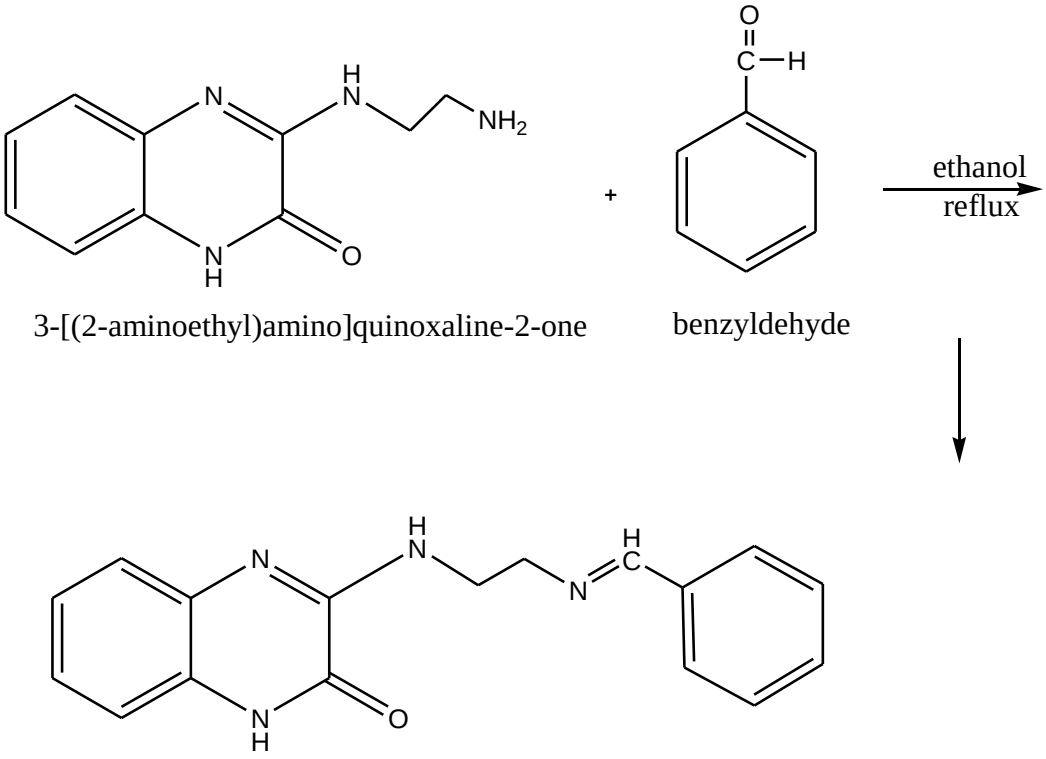


1,4-dihydroquinoxaline-2,3-dione

3-[(2-aminoethyl) amino] quinoxaline-2-one

Scheme 4. Synthesis of quinoxaline derivatives

2.1.4 Synthesis of a substituted aromatic Schiff base using quinoxaline derivatives [22]



3-[(2-aminoethyl)amino]quinoxaline-2-one benzyldehyde

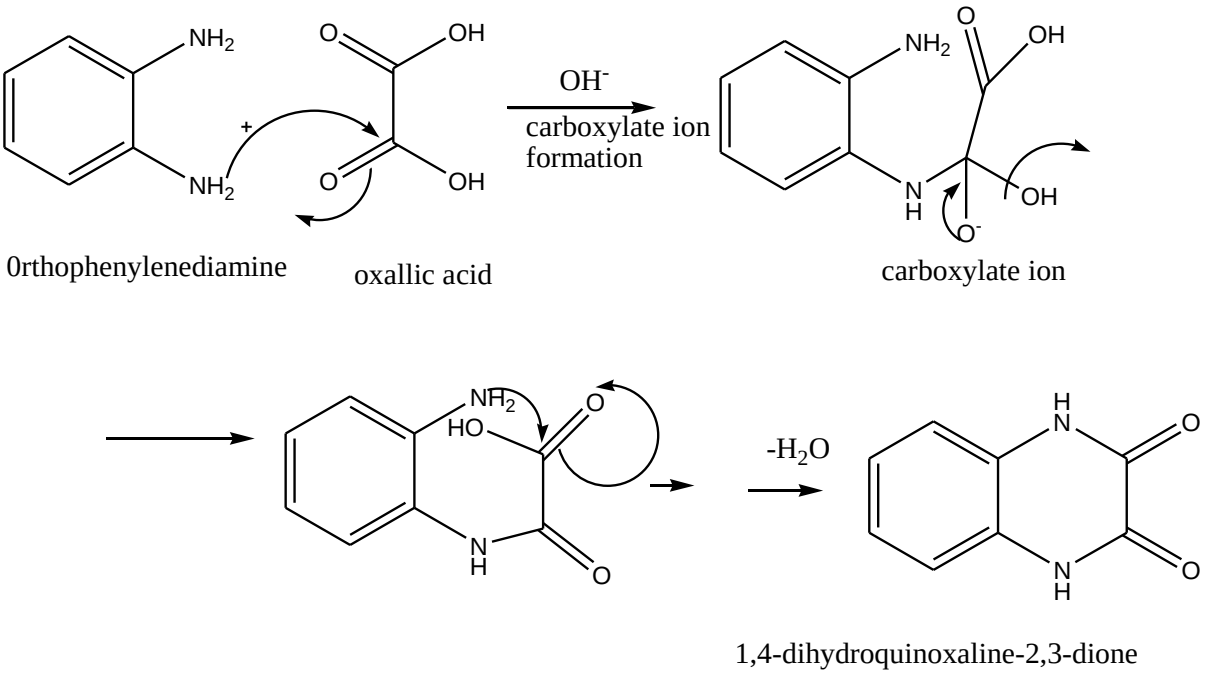
Schiff base substituted quinoxaline-2-one

Scheme 5. Synthesis of Schiff base substituted quinoxaline-2-one

Proposed mechanism for the formation of 1,4-dihydroquinoxaline-2,3-dione [23]

Synthesis of 1,4-dihydroquinoxaline-2,3-dione and orthophenylenediamine condense with oxalic acid to form the heterocyclic compound 1,4-dihydroquinoxaline-2,3-dione via **Phillip's** condensation reaction.

Condensation reaction: A chemical reaction in which two molecules or moieties combine to form a single molecule with loss of a small molecules, usually water. In this step, lone pairs from the amine of orthophenylenediamine attacks the partial positive carbon of carbonyl group from oxalic acid as follows.

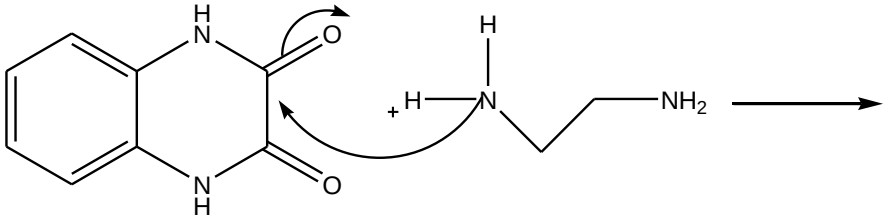


Scheme 6. proposed mechanism of 1,4-dihydroquinoxaline-2,3-dione

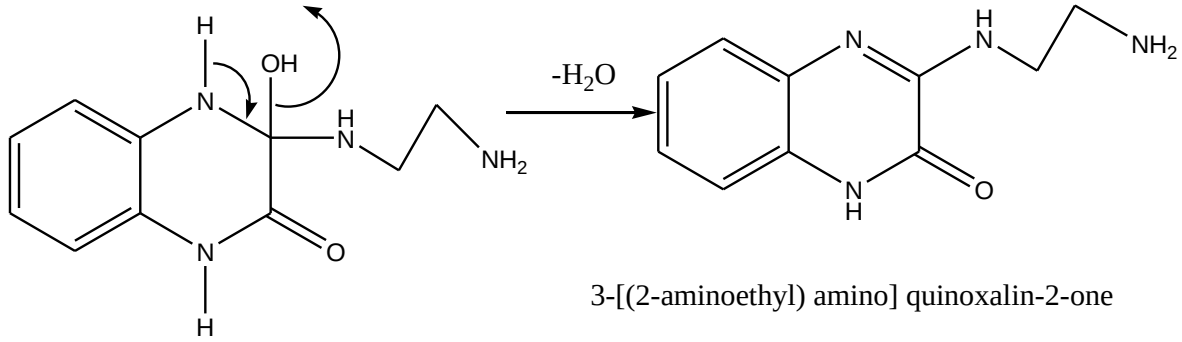
proposed mechanism for the formation of 3-[(2-aminoethyl) amino] quinoxalin-2-one [24]

The quinoxaline 1,4-dihydroquinoxaline-2,3-dione in the presence of ethylene diamine undergoes substitution reaction at the position of three and gives 3-[(2-aminoethyl) amino] quinoxalin-2-one with the loss of one water molecule.

Here the electron rich Centre of ethylene diamine targets the electron deficient carbonyl carbon of quinoxaline ring which leads to the substitution of carbonyl oxygen by amine with the loss of one water molecule.



1,4-dihydroquinoxaline-2,3-dione ethelenediamine

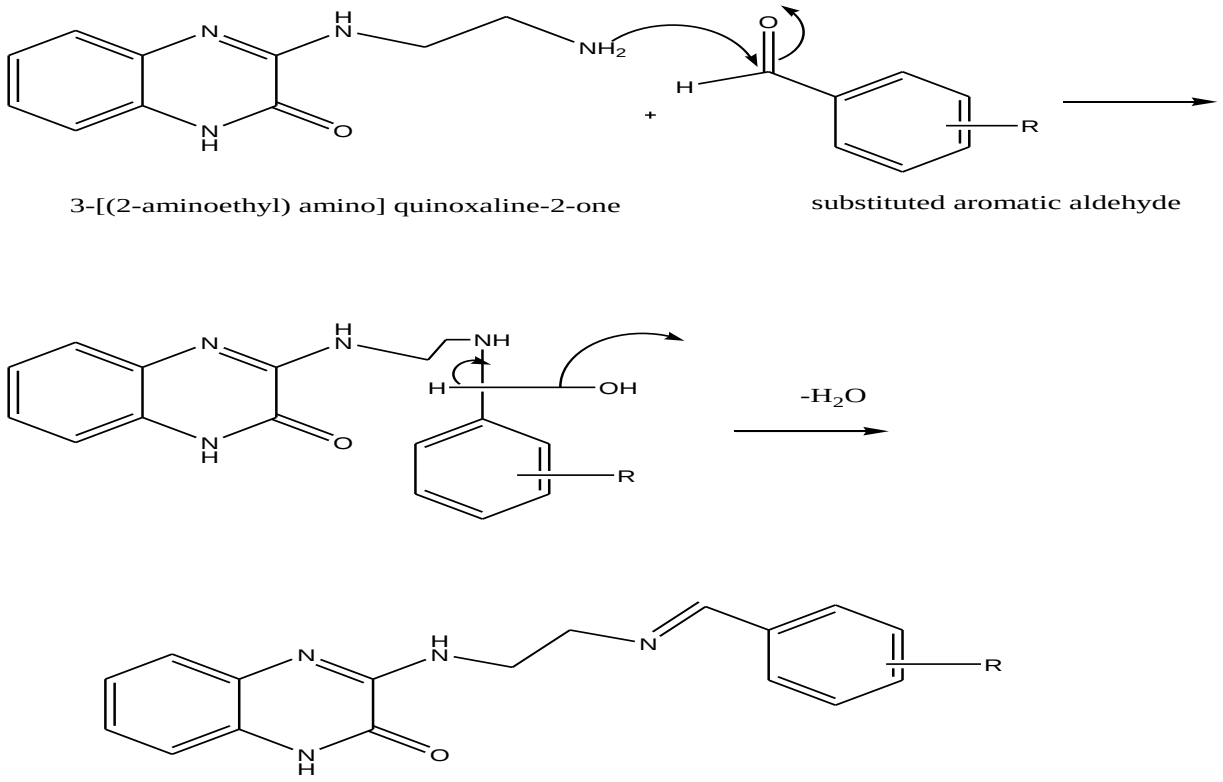


3-[(2-aminoethyl) amino] quinoxalin-2-one

Scheme 7. Proposed mechanisms of 3-[(2-aminoethyl) amino] quinoxaline-2-one

Proposed mechanism of 3-[(-{[(E)-(substituted phenyl) methylidene] amino] quinoxaline-2-one [25]

When 3- [(amino ethyl) amino] quinoxalin-2-one is made to react with aromatic aldehyde it results as follows; condensation of primary amine of ethylene diamine with carbonyl group of aromatic aldehyde takes place by nucleophilic addition followed by dehydration which results in the formation of imine (C=N) functional moiety that is formation of Schiff base. Schiff base [named after Hugo Schiff; (1834-1915 German chemist]. Which gives 3-[(2-{[E)-(substituted phenyl) methylidene] amino} ethyl) amino] quinoxalin-2-one.

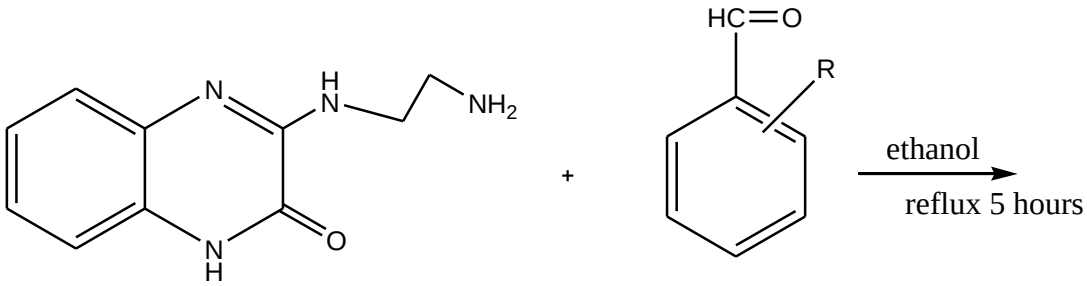


Scheme 8. proposed mechanism of Schiff base of substituted quinoxaline-2-one

2.1.5 Conventional and microwave synthesis of quinoxaline derivatives

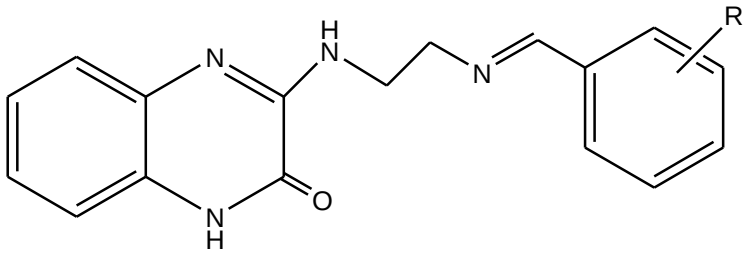
2.1.5.1 Conventional synthesis [26]

In this method, compound 3-[(2-aminoethyl) amino] quinoxalin-2-one and the corresponding aromatic aldehyde (0.01mol of each) in ethanol as the solvent (20 ml) was refluxed for 5 hours. Upon cooling, the precipitate was obtained, filtered, dried and recrystallized from ethanol.



3-[(2-aminoethyl) amino] quinoxaline-2-one

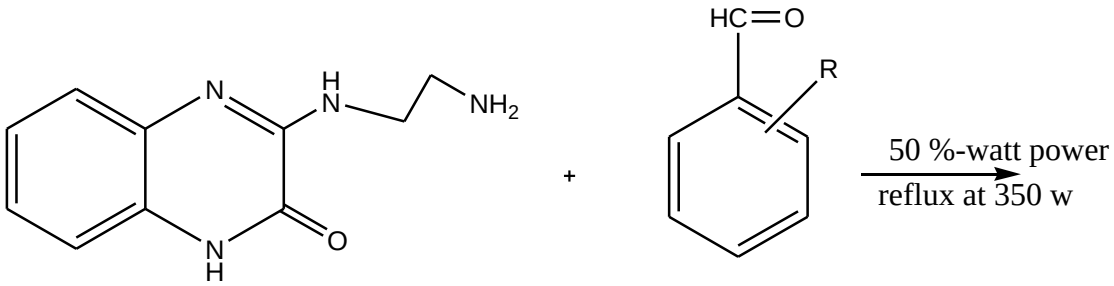
aromatic aldehyde



Schiff base of substituted quinoxaline-2-one

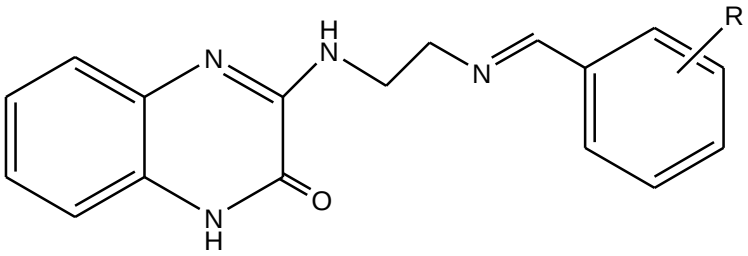
2.1.5.2 Microwave synthesis [27]

In this method, compound 3- [(2-amino ethyl) amino] quinoxalin-2-one and the corresponding aromatic aldehyde (0.01 mol of each) in the ethanol as solvent (20 ml) was added to it and irradiated with micro waves at 50 %, 350 W. After specific time, depending of the derivative, the precipitate obtained was recrystallized using ethanol.



3-[(2-aminoethyl) amino] quinoxaline-2-one

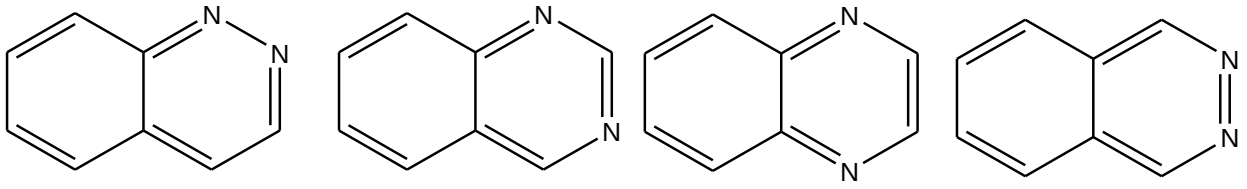
aromatic aldehyde



Schiff base of substituted quinoxaline-2-one

2.2 Chemistry of Quinoxaline

Quinoxaline (benzo pyrazines) derivatives are an important class of nitrogen containing heterocyclic compound containing a ring complex made up of a benzene ring and pyrazine ring, they are isomeric with the cinnolenes, phthalazines and quinolones. All these are class of heterocyclic compound known as diazanaphthalenes, that may have the two heteroatoms in the same or different rings.



cinnoline quinazoline quinoxaline pthalazine

Figure. 1 Structures of some aromatic heterocyclic compounds

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 [27]. The primary synthesis of quinoxaline may be accomplished by cyclization of benzene substrates already bearing appropriate substituents; by cyclocondensation of benzene substrates with acyclic synthons to provide one or more of the ring atoms required to complete the pyrazine ring; by analogous processing of preformed pyrazine substrates; or by rearrangement, ring expansion/contraction, degradation, or modification of appropriate derivatives of other heterocyclic systems [28]. Quinoxaline are readily made from 1,2-dicarbonyl compounds and aromatic 1,2-diamines. A well-known route to quinoxaline is the reaction of orthophenylene diamine with a 1,2 –dicarbonyl compound [29].

The condensation of ketone or aldehyde with a primary amine leads to the formation of an imine linkage with the liberation of water molecule. The N-atom carries a lone pair of electrons and can function as a Lewis base, forming complexes with transition metal ions [30].

In this literature review I described a conventional as well as microwave assisted extremely rapid Schiff bases synthesized of quinoxaline. The procedure is simple convenient and does not required any aqueous work up, thereby the generation of waste and many contribute to the area of green chemistry

2.2.1 Quinoxaline derived from orthophenylenediamine

The orthophenylenediamine and its derivatives were used as the starting material to react with carbonyl compounds through thermo-reaction and microwave irradiation, and the benzo-fused multi-membered hetero aromatic compounds including benzimidazoles, quinoxaline and benzodiazepines were obtained in good yields [31]. Quinoxaline are very useful functional groups amenable to a wide variety of chemical transformations. Indeed, they have been used to prepare a number of heterocyclic compounds, such as dihydropyrazines, imidazoles, and pteridines. The quinoxaline skeleton has been used as a synthetic intermediate for the preparation of numerous compounds with interesting biological properties. Due to their conformational rigidity and their wide range of properties, such heterocyclic systems play an essential role as scaffolds in biologically active compounds.

For example, ring-fused heterocycles that contain more than one nitrogen atom are key structures in a large variety of biochemical processes. During the last few years, quinoxaline have been of special interest due to their biological activity. This has led to the development of a new class of structural elements for mycobacteriostatic drugs based on 2,3-diaminoquinoxalines [32]. Quinoxaline 1,4-dioxides are known as potent anti-bacterial agents, and sub therapeutic levels have been used to promote growth and improve efficiency of feed conversion in animal feed.

On the other hand, several authors have reported about photo allergic and mutagenic effects of some quinoxaline derivatives. Quinoxaline may also cause the development of antibiotic-resistant bacteria and influence the horizontal transfer of virulence genes between bacteria [33].

The present report shows that the synthetic quinoxaline species are used as electrochemical extraction of Zn (II). Quinoxaline-2,3-diones and quinoxaline-2-ones are mainly prepared by condensation of orthophenylenediamine with various keto acid derivatives [34].

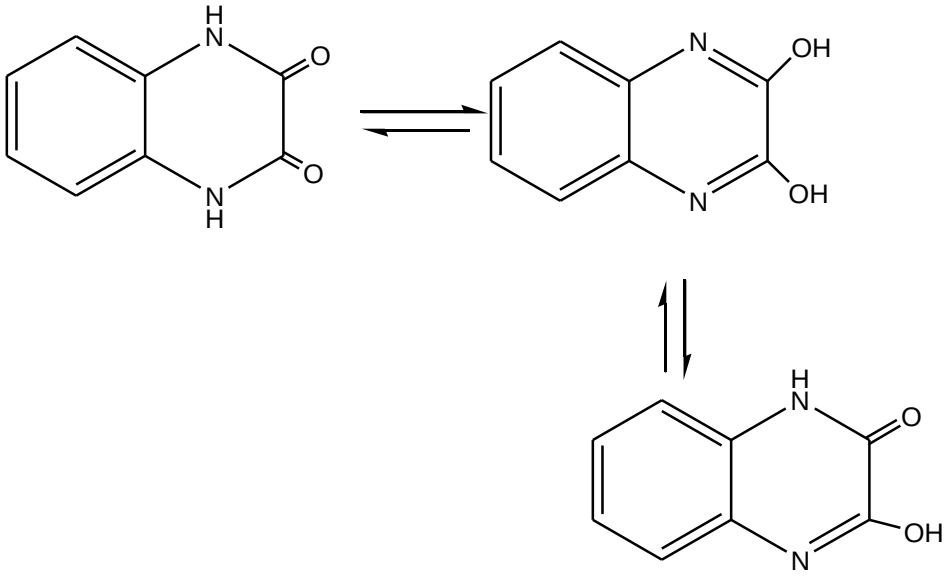
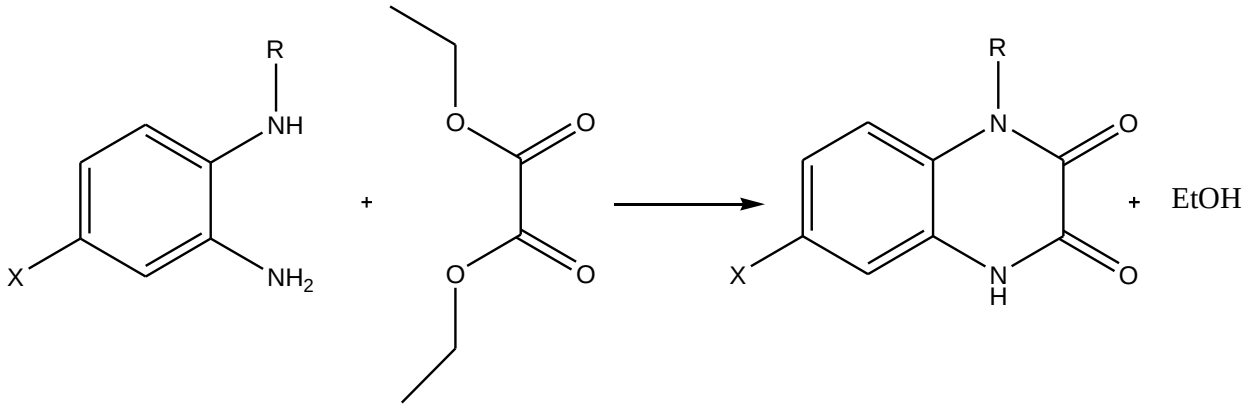


Figure. 2 Tautomeric form of 1,4-dihydroquinoxaline-2,3-dione

Several general methods are available for preparing orthophenylenediamine derivatives [35]. The ring closure of an orthophenylenediamine with oxalate derivatives, used to form the six-member paradiazine ring of a 1,4-dihydroquinoxaline-2,3- dione, is usually the last and crucial step. Normally, this step is carried out using the method of Phillip's [36] under the catalysis of strong acid or at elevated temperatures [37]. Sometimes a solvent is also used [38]. With the structural modifications at other sites on 1,2- diaminobenzene completed in the previous steps, it is desirable to perform the ring closure in the synthesis of quinoxaline- 2,3-dione under mild reaction

conditions in order to avoid any side reactions. The general Phillip's reaction carried out under harsh conditions, as commented by **Piguet** [39], needs be modified for various reasons.

If possible, catalysts and solvents should not be used, because any such substances are potential impurities in the final product.



Scheme 9. Synthesis of derivatives of quinxaline-2,3-diones

Ligands of orthophenylenediamine and its complexes have a variety of applications including biological, clinical and analytical. Earlier work has shown that some drugs showed increased activity when administered as metal chelates rather than as organic compounds, and that the coordinating possibility of orthophenylenediamine has been improved by condensing with a variety of carbonyl compounds.

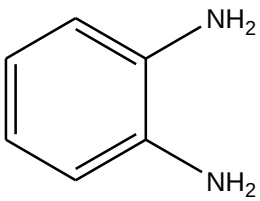


Figure 3. Structure of orthophenylenediamine

A search through literature reveals that some work has been done on the transition metal complexes of the ligand derived from orthophenylenediamine and quinoxaline-2,3-dione. In this paper, I report the synthesis of a type of tetra-dentate ligand formed by the condensation of orthophenylenediamine with 1,4-dihydroquinoxaline-2,3-dione in the presence of Zn^{2+} [40] and another complex derived from 1,4-dihydroquinoxaline-2,3-diones and hydroquinone.

2.3 Chemistry of Zinc

Zinc is the heaviest member of the first row transition series of elements, consisting of Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu and Zn, and belongs to group 12 of the periodic table, along with Cd and Hg. The element has an atomic number of 30, an atomic mass of 65, one main oxidation state (+2) and five naturally occurring isotopes (^{64}Zn, ^{66}Zn ,^{67}Zn, ^{68}Zn and ^{70}Zn), of which ^{64}Zn, ^{66}Zn and ^{68}Zn are the most abundant at 48.6%, 27.9% and 18.8% respectively of the total mass.

In general Zinc has a specific role in bioinorganic processes because of the unique properties of the coordination compounds of the zinc (II) ions. One, zinc (II) can easily be 4-, 5-, or 6-coordinated, without a marked preference for six coordination. The electronic configuration of zinc (II) is $3d^{10}$. In coordination compounds, there is no ligand-field stabilization energy, and the coordination number is determined by a balance between bonding energies and repulsion among the ligands. Tetrahedral four-coordinate complexes have shorter metal-donor distances than five-coordinate complexes, and the latter have shorter ones than six-coordinate complexes, whereas the ligand repulsion increases in the same order. Thus zinc (II) forms four coordinated tetrahedral complexes. Two, as a catalyst, zinc in enzymes is exposed to solvents, which is most often, water. A coordinated water molecule exchanges rapidly, because ligands in zinc complexes are kinetically labile. This, again, can be accounted for by lack of preference for a given coordination number by the Zinc ion. Zinc (II) is an ion of borderline hardness and displays high affinity for N and O-donor atoms as well as for sulfur [41].

2.4 Chemistry of Zinc Complexes

2.4.1 Zn (II) Complex of Macrocyclic system and quinoxaline derivatives

Zinc is chemically similar to magnesium because its ion is of similar size and its only common oxidation state is +2. The Zn^{2+} ion has a filled d^{10} shell. The divalent zinc ion is exceptionally stable with respect to oxidation and reduction and so it does not participate in redox reactions, in contrast to the first row transition series. The d^{10} configuration of Zn^{2+} indicates that zinc complexes are not subject to ligand field stabilization effects and so coordination number and geometry is only indicated by ligand size and charge. Zinc is an element of borderline hardness, so that nitrogen, oxygen and sulfur ligands can all be accommodated, in contrast to magnesium and calcium, which favor binding to oxygen. This allows for the formation of four covalent bonds by accepting four electron pairs and thus obeying the octet rule. The stereochemistry is therefore tetrahedral and the bonds may be described as being formed from sp3 hybrid orbitals on the zinc ion. In its complexes Zn (II) ion will commonly have coordination numbers four, five, and six, the coordination number five is common for zinc. This metal ion is diamagnetic and does not possess any d-d transition state [42].

2.4.2 Metal complexes of a ligand derived from 2,3-quinoxalinedithiol and 2,6-bis (bromomethyl) pyridine

The synthesis of a new ligand containing quinoxaline and pyridine subunits is described. The reaction of 2,3-quinoxalinedithiol with 2,6-bis (bromomethyl) pyridine leads to the isolation of bis (2-thio-3-mercaptoquinoxalino)-2,6-dimethylpyridine (**L**), which is a macrocyclic ligand precursor. The reaction of transition metal ions with **L** gives [M (L) X] X complexes (where M =Zn (II) and X=Cl or Br.

The compounds were characterized by physical and spectroscopic measurements which indicated that the ligand is probably acting as a penta-dentate NS_4 chelating agent. On the assumption that four sulfur atoms and one nitrogen atom of the ligand are coordinated to the metal, as seems likely from an inspection of molecular models, it follows that the complexes would be five coordinate with respect to the ligand. As the ligand is potentially penta- dentate, it is quite feasible that the metal ions are six coordinate with one halide ion at the vertices of an octahedron.

When the energy of the complexes was minimized, the reasonable bond distances and bond angles around the metal were obtained, suggesting that an octahedral or distorted octahedral configuration around the metal is possible. The possibility of a square pyramidal configuration around the metal has been discarded from the conductivity measurements, which show that the complexes are 1:2 electrolytes [43]

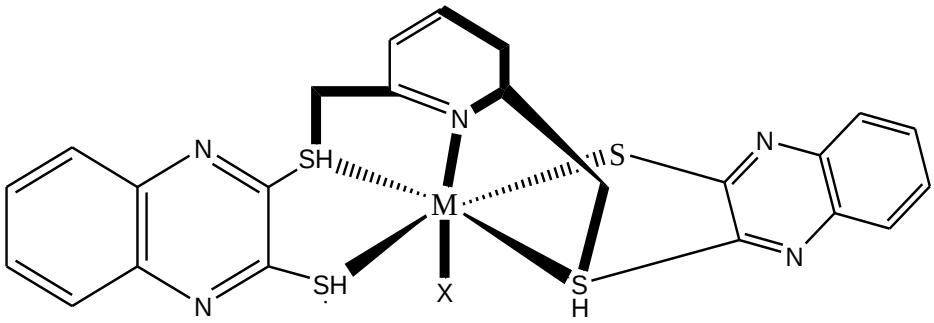
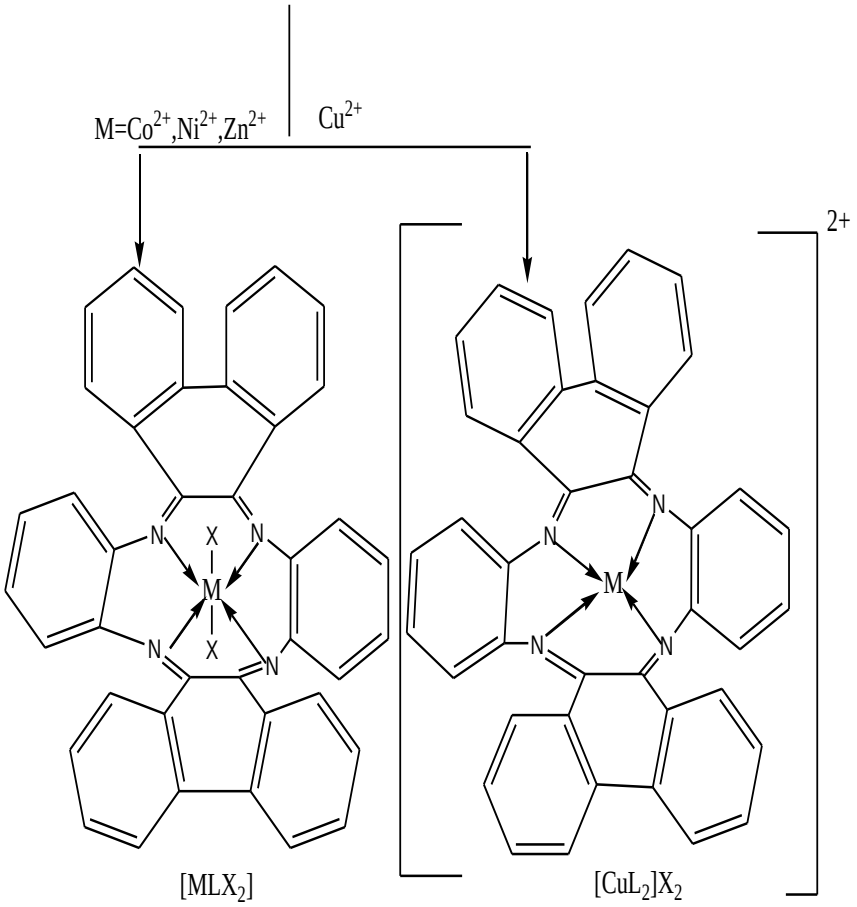


Figure 4. Suggested structure for the metal complexes of a new multidentate quinoxaline derivative

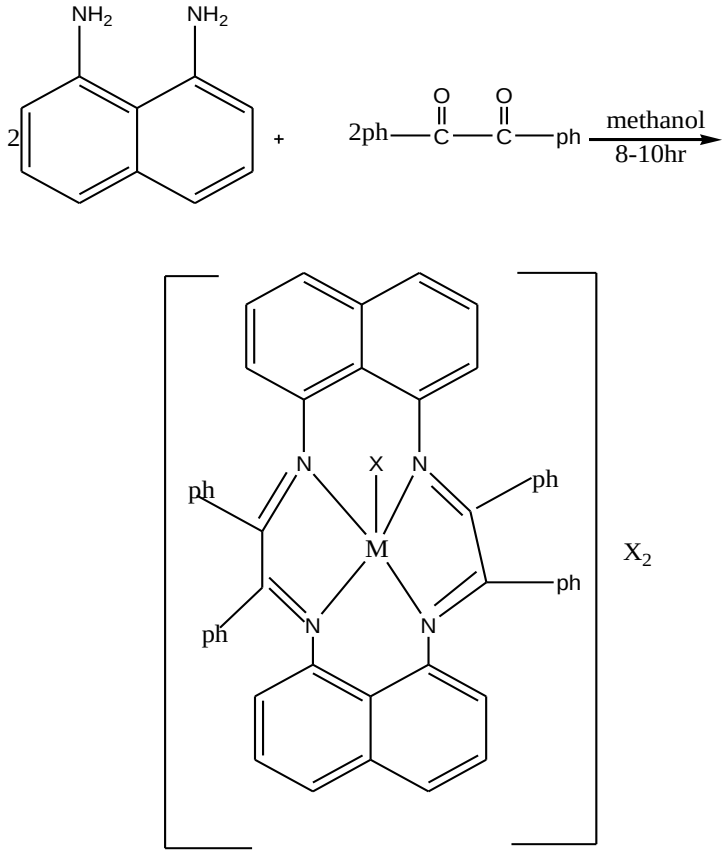
2.4.3 Metal complex of macrocyclic ligand (L) synthesis from orthophenylenediamine and quinoxaline [44]



Where X=Cl^{-1}, NO_2^- where X=Cl^{-1}, NO_3^-

Scheme 10. Metal complex of macrocyclic ligand

Singh and coworkers have reported the synthesis of a novel series of macrocyclic complexes by template condensation of 1,8-diamino naphthalene and benzyl ketone in the presence of trivalent metal salts in methanoic medium [45]



Scheme 11. Complex formed from 1,8-diaminonaphthalene and benzyl ketone

2.4.4 Dichlorodiquinoxaline zinc (II) complex

In complex [ZnC_{l2} $(C_8H_6N_2)_2$], two quinoxaline ligands are mono-coordinated to a Zn (II) atom with two chloride ions, they form a distorted tetrahedral coordination geometry. The combination of π stacking interactions between inversion-related quinoxaline ligands and the coordination to Zinc creates layer parallel to the two quinoxaline ligand [46]

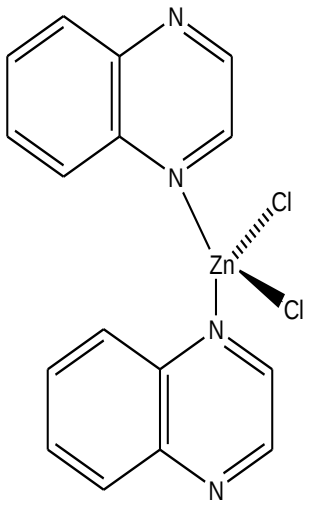


Figure 5. Structure of $ZnCl_2$ $(C_8H_6N_2)_2$ complex

2.4.5 Macrocyclic zinc complex with quinoxaline bridging

The tricyclic derivatives containing an additional quinoxaline ring, which in principle could also coordinate with the Zinc ion have been reported. The ^{1}HNMR spectrum of the complex showed that only one phenolate group coordinates to the Zn atom, thus indicating that the quinoxaline acts as a monoanionic ligand. This was confirmed by X-ray crystallography. Rather surprisingly, the complex exhibits a 36-membered macrocyclic ring system composed of six monomeric units. All Zinc ions are tetrahedral has coordinated with the quinoxaline ligand bridging two zinc cations. Both the imine nitrogen N_2 and the amide nitrogen N_1 in the quinoxaline binds to one zinc center to form a five-membered chelate ring. In addition, the amine nitrogen N_5 acts as a bridging donor to connect two Zinc centers. This results in the formation of an unusual macrocyclic system in which six Zinc ions in a chair conformation are linked by six quinoxaline ligands [47]

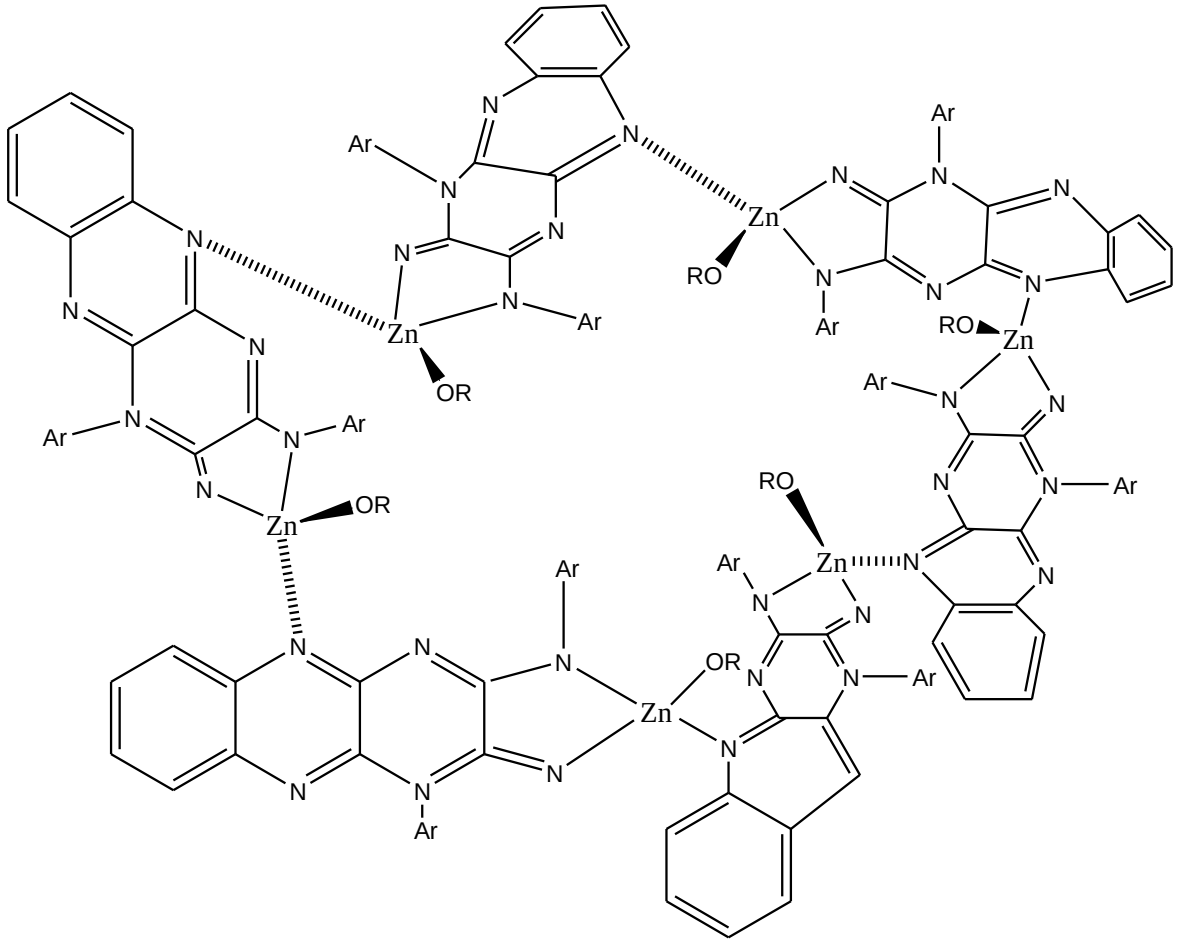
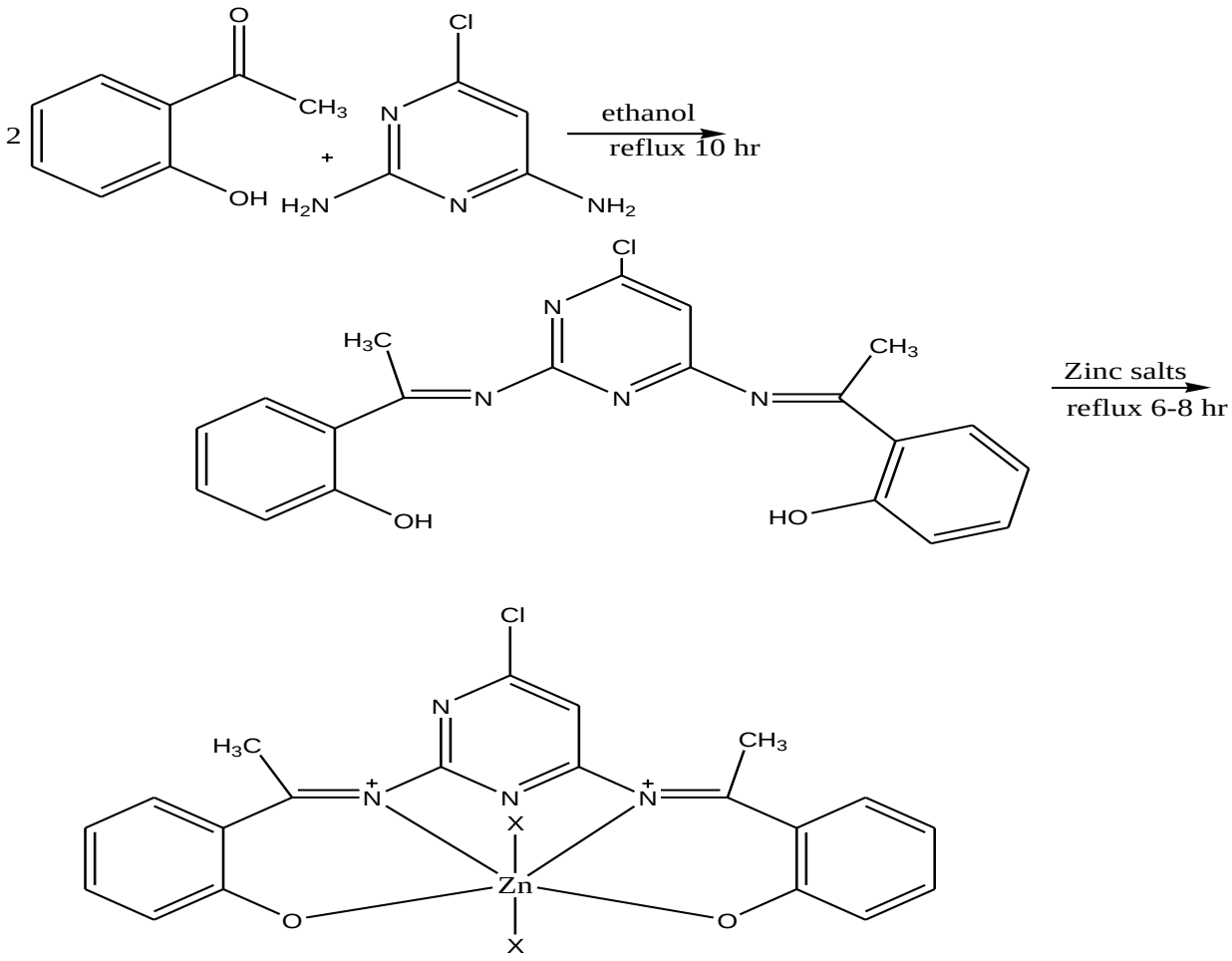


Figure 6. Macrocyclic zinc complex with quinoxaline bridging

2.4.6 Synthesis of Schiff base complexes by direct interaction.

The Schiff's base can be synthesized without using the metal ion and then followed by addition of the transition metal salt for complex formation. This can be easily described by the following example [48].



Scheme 12. Synthesis of Schiff base complex by direct method

3. MATERIALS AND METHODS

3.1 Chemicals and reagents

The chemicals used for the synthesis of metal complexes were of Analytical grade. These included anhydrous salts of the divalent metal $ZnCl_2$, oxalic acid dihydrated ($C_2H_2O_4.2H_2O$) and the ligands such as hydroquinone ($C_6H_6O_2$) as well as orthophenylenediamine ($C_6H_8N_2$). Analytical grade reagents like conc. HNO_3 and solvent such as methanol (MeOH), ethanol (EtOH), acetone (CH_3COCH_3), dimethylsulphoxide (DMSO), dimethylformamide (DMF) and chloroform ($CHCl_3$) were used for various purposes.

3.2 Apparatus and Instruments

For different purposes of this study, various ordinary laboratory glassware has been used. Instruments such as FT-IR Spectrophotometer (for running the IR spectra of the complexes using the KBr pellets method), Atomic Absorption Spectrometer (for determination of metal in complex), Conductivity meter (for conductivity measurements), ^{1}H and ^{13}CNMR and Digital melting point apparatus (to determine the melting point of the metal complexes) were utilized for analyzes of the various products obtained from different preparations as described in the experimental section.

3.3 Experimental methods and procedures

Synthesis of the desired Schiff basses, and metal complexes by template method was carried out in the Chemistry Laboratories of Addis Ababa University. In addition, the analytical works such as atomic absorption spectroscopy, elemental analysis, ^{1}H and ^{13}CNMR interpretation, conductivity measurements and FT-IR spectra of the as-synthesized complexes were conducted at Addis Ababa University, Department of chemistry.

3.3.1 Qualitative Test

3.3.1.1 Chloride Test

30 mg of each Zn-L and Zn (QXD) (HQ) complexes were dissolved in 10 ml of concentrated nitric acid and heated on hot plate until the organic compound decomposed and few drops are left. When 0.1 M solution of silver nitrate was added to the cooled acid solutions and left overnight, there was no formation of any precipitate in Zn (QXD) (HQ) solution, but there was white precipitate in

Zn-L solution. These suggests that chloride is coordinated in inner sphere of the Zn-L complex. These observation leads to the conclusion that the Zn (QXD) (HQ) complex does not contain any chloride, but Zn-L complex contain chloride in inner of its structure.

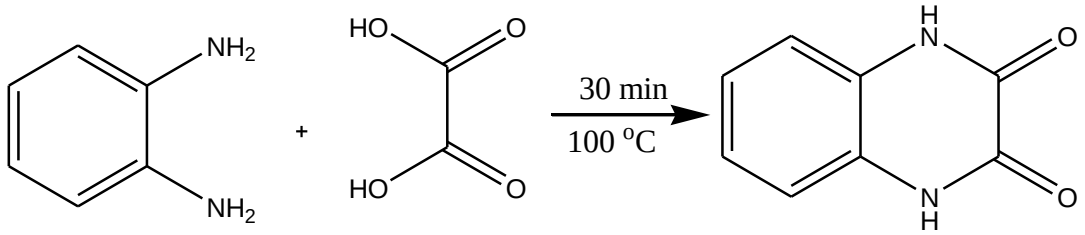
3.3.1.2 TLC test

The TLC test of the complexes, Zn (QXD) (HQ) complex and Zn-L complex exhibit single spot on silica coated aluminum plate as stationary phase and chloroform as mobile phase. A single spot in both samples indicates the complexes are pure or homogeneous.

3.4 Synthesis

3.4.1 Synthesis of 1,4-dihydroquinoxaline-2,3-diones [20]

A solution of oxalic acid dihydrated (0.033 mol, 4.1 g) in H_2O (20 ml) was heated to 100 ^oC and concentrated HCl (2 M) was added, followed by orthophenylenediamine (0.028 mol, 3g) with constant stirring, keeping the temperature at 100 ^oC for 30 min. The mixture was cooled by addition of ice. The precipitate formed and washed with distilled water repeatedly and ethanol, then dried in air. The product was weighed to be 2.23 g, yield 29.6 % and melting point greater than 350 ^oC.

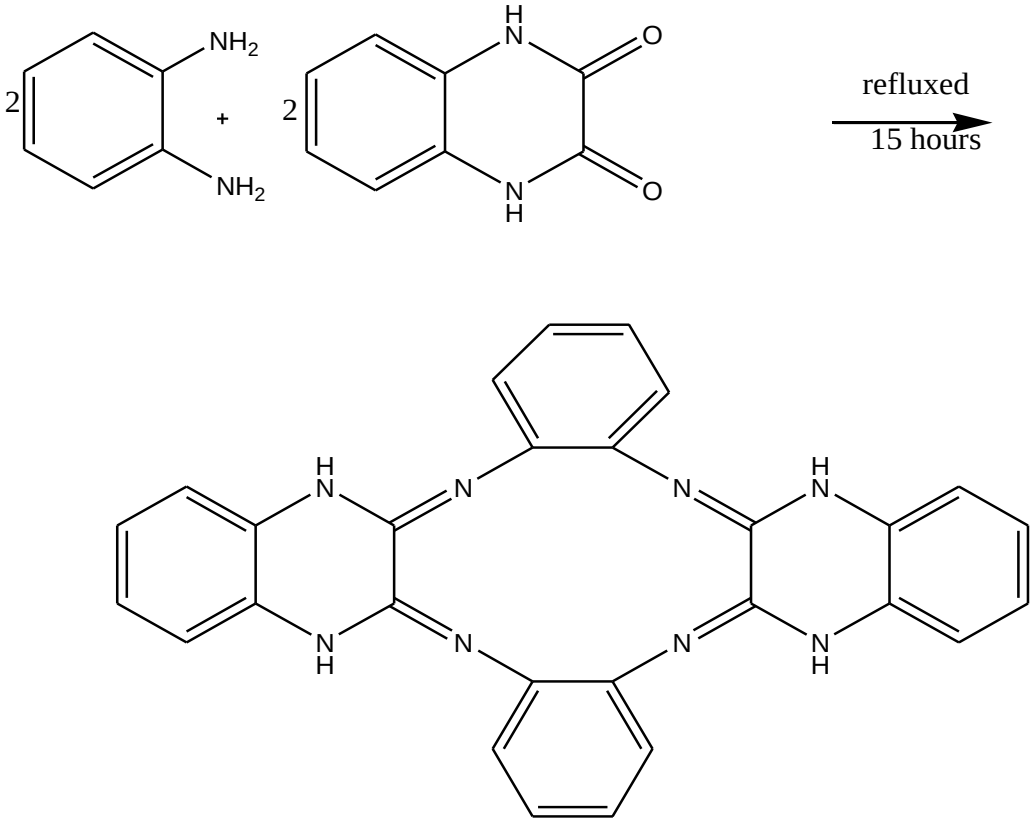


orthophenylenediamine oxalic acid 1,4-dihydroquinoxaline-2,3-dione

Scheme 13. Synthesis of 1,4-dihydroquinoxaline-2,3-dione

3.4.2 Synthesis of the ligand (L)

Attempts to prepare the ligand were made with the following procedure. Methanol solution of 1,4-dihydroquinoxaline-2,3-dione (2 mmol, 0.324 g) and methanol solution of orthophenylenediamine (2 mmol ,0.216 g) were refluxed for 15 hours. A color crystalline solid appeared which was cooled, collected, washed with methanol repeatedly and dried. Yield 12.5 % melting point greater than 350 ^{o}C. The possible products of this reaction is as follows



Scheme 14. Structure of expected ligand (L)

As the structural studies indicated that the expected ligand were not formed, instead the reactants were regenerated. The synthesis of the metal complexes was subsequently done using template method in which quinoxaline-2,3-dione and orthophenylenediamine were reacted in the presence of metal ion.

3.4.3 Synthesis of metal complexes

Metal complexes were synthesized by the template method according to the procedure described in [38], by the condensation of 1,4-dihydroquinoxaline-2,3- dione ($C_8H_6N_2O_2$) and orthophenylenediamine ($C_6H_6N_2$) and by the mixed ligand of 1,4-dihydroquinoxaline-2,3-dione and hydroquinone in the presence of anhydrous salt of the respective divalent metal ion $ZnCl_2$ (in ethanol medium).

3.4.3.1 Synthesis of Zn-L complex

To an aqueous solution (10 ml) of anhydrous Zinc (II) chloride (0.14 g, 1 mmol), hot ethanoic solution (10 ml) of 1,4-dihydroquinoxaline-2,3-dione (0.324 g, 2 mmol) was added. The mixture was stirred and kept in a boiling water bath for 40 min. To this hot solution, hot ethanoic solution (10 ml) of orthophenylenediamine (0.216 g, 2 mmol) was added with constant stirring. The mixture was again refluxed for 7 hours in a water bath. The complexes were obtained by raising pH of the reaction mixture by adding a drop of sodium hydroxide solution to maintain the PH value between 6.5 and 7.5. The mixture was cooled and solid complex obtained was filtered, washed with water followed by ethanol. The complexes thus prepared were white grey in color. Yield 59.99 % and the melting point is 346 ^oC. The possible chemical reaction of this experiment is;

$$ZnCl_2(aq) + 2C_8H_6N_2O_2(EtOH) \xrightarrow[\text{reflux}]{\text{40 min}} 2C_6H_8N_2(EtOH) \xrightarrow[\text{reflux 7 hour}]{} ZnC_{28}H_{2O}N_8Cl_2$$

3.4.3.2 Synthesis of Zn (QXD) (HQ) complex

To an aqueous solution (10 ml) of Zinc (II) chloride anhydrous (1 mmol, 0.14 g), hot ethanoic solution (10 ml) of 1,4-dihydroquinoxaline-2,3-dione (2 mmol, 0.324 g) was added. The mixture was stirred and kept in a boiling water bath for 40 min. To this hot solution, ethanol solution (10 ml) of hydroquinone (2 mmol, 0.220 g) was added with constant stirring. The mixture was again refluxed for 4 hours in a water bath. The complexes were obtained by raising pH of the reaction mixture by adding a drop of sodium hydroxide solution to maintain the PH value between 6.5 and 7.5. The mixture was cooled and solid complex obtained was filtered, washed with water followed by ethanol. Yield 42.8 %, and the melting point is 346 ^{o}C.

$$ZnCl_2\,(aq) \;-\; 2C_8H_6N_2O_2\,(EtOH) \xrightarrow[\text{reflux}]{\text{40 min}} \xrightarrow[\text{reflux 4 hour}]{2C_6H_6O_2\,(EtOH)} ZnC_{28}H_{22}N_4O_8$$

3.5 Results and discussion

The Zn-L or Zn (QXD) (OPD) and Zn (QXD) (HQ) complexes were obtained as powders with high melting points and low solubility in organic solvents. Both complexes are color. They are air and moisture stable solids, both complexes are soluble in DMSO. The solubility in other solvents are listed in **table.1**. The conductivity values of the complexes measured in DMSO at room temperature fall in the range 2-20 $\Omega\ cm^2\ mol^{-1}$ that indicates both are non-electrolytes. The chloride test indicates the presence of chloride in Zn (QXD) (OPD) or Zn-L but the absence of chloride in Zn (QXD) (HQ) complex. Attempts to prepare the ligand (L) was unsuccessful.

3.5.1 Solubility of QXD and complexes in different solvents

Solubility test was done to identify the best suitable solvent for the following analytical and spectroscopic measurement**.** The experimentally observed solubility of the ligand and metal complexes are summarized in **table.1.**

Table 1 Solubility of QXD, and metal complexes.

compound	Solvent						
	water	ethanol	methanol	DMSO	DMF	acetonitrile	chloroform
QXD	Ins.	Partial sol.	Partial sol.	Sol.	Partial sol.	Ins.	Ins.
Zn-L complex	Ins.	Ins	Ins.	Sol.	Partial sol.	Ins.	Partial sol.
Zn(QXD)(HQ)	Ins.	Ins,	Ins.	Sol.	Sol.	Ins.	Partial sol

3.5.2 Determination of Molar Conductivity

The complexes were dissolved in DMSO and the molar conductivities of $1x10^{-3}$ M of their solutions at 22 ^{o}C were measured. The values were in the range of 2-20 Ω^{-1} cm^2 mol^{-1}. These values are lower than those expected for an electrolyte. These observations indicate that; the complexes are non-electrolytes in DMSO ($1x10^{-3}$ M) at room temperature. The measured values are given in **table .2.**

Table.2 conductivity values of complexes

solvent	complexes	Molar conductance(Ωcm^2mol^{-1})	Types of electrolytes
DMSO	Zn (QXD) (HQ)	3.45	Non-electrolyte
DMSO	Zn-L	2.18	Non-electrolyte

Table.3 Some physical properties of the ligand and the complexes

Compounds	**color**	**Empirical formula**	**M.Wt (g/mol.)**	**m.pt**	**Analytical data found(calculated)**		
					C %	**H %**	**N %**
QXD	Light green	$C_8H_6N_2O_2$	162	>350 ^oC	-	-	-
Zn-L	White grey	$ZnC_{28}H_{20}N_8Cl_2$	604.38	>350 ^oC	-	-	-
Zn $(QXD)_2H_4O_2$	white	$ZnC_{26}H_{12}N_4O_6$	421.38	346 ^oC	54.89 (45.6**)**	4.02 (2.85**)**	10.08 (13.3**)**

3.5.3 Infrared spectra

3.5.3.1 Infrared spectra of 1,4-dihydroquinoxaline-2,3-dione (QXD)

The IR spectra of the 1,4-dihydroquinoxaline-2,3-dione (QXD) shows three characteristic bands at 3443 cm^{-1},1392 cm^{-1} and 1682 cm^{-1} are the region for stretching vibration of υ (N-H), υ (C-N) and υ (C=O) respectively. The band at 3047 cm^{-1}, 2882 $cm^{-1}$and 2865 cm^{-1} are the characteristics region of υ (C-H) stretching vibration of benzene. The band at 753 cm^{-1} and 855 cm^{-1} are the characteristics region of out plane bending vibration of (C-H) in benzene (**fig.9**).

3.5.3.2 Infrared spectra of Zn $(QXD)_2$

The IR spectra of metal complex can provide valuable information as to whether or not reaction has occurred. In order to study the binding mode of the ligand to the metal ion in the Zn $(QXD)_2$ complexes, the IR spectrum of the free ligand must be compared with the spectra of the complexes. In the complex the band at 1682 cm^{-1} υ (C=O) of 1,4-dihydroquinoxaline-2,3-dione is increase to 1688 cm^{-1} υ (C=O), which indicates the 1,4-dihydroquinoxaline-2,3-dione, donates a pair of electron to the metal. The three characteristic band at 3049 cm^{-1},2967 cm^{-1} and 2865 cm^{-1} is the characteristics region for stretching vibration of (C-H) in benzene. The –OH vibrations are generally measured between 3600-3200 cm^{-1}. Therefore, the band observed at 3362 cm^{-1} is the characteristic region for stretching vibration of (-OH) on water molecules. The band observed 1411 cm^{-1} is the characteristic region for stretching vibration of both (C-C) and (C=C), because the two functional group are called semicircle stretching vibration, usually occur in the region 1625-1400 cm^{-1}. The band observed at 1193 cm^{-1} is the characteristic region for stretching vibrational of (C-N) in 1,4-dihydroquinoxaline-2,3-dione. The band observed at 766 cm^{-1} is the region for out plane bending vibration of (C-H) in benzene ring and in hydroquinone. The far IR spectra show bands in the region 584-464 cm^{-1} corresponding to υ Zn-O vibrations (**fig.12**).

3.5.3.3 Infrared spectra of Zn-L complex

The IR spectra of cyclic metal complexes (Zn-L) has shown the presence condensed functional groups $–NH_2$ and C=O of orthophenylenediamine and 1,4-dihydroquinoxaline-2,3-dione (i.e. stretching modes of starting materials) which confirm the formation of the proposed cycle organic moiety involving imine (C=N) groups. The appearance of strong absorption band in the region 1629 cm^{-1} corresponds to υ C=N (imine) stretching frequency. A strong absorption recorded in the regions 3385 cm^{-1} may be corresponds to υ N-H in 1 and 4 positions of 1,4-dihydroquinoxaline-2,3-dione ring. Furthermore, no strong absorption band was observed near 1682 cm^{-1}-1660 cm^{-1} indicating the absence of C=O of 1,4-dihydroquinoxalin-2,3-dione at two position, this confirms the condensation of carbonyl group of 1,4-dihydroquinoxaline-2,3-dione and amino groups of orthophenylenediamine. These results provide strong evidence for the formation of cyclic frame. The lower values in the wave numbers of υ (C=N) may be explained on the basis of drift of lone pair density of imine nitrogen towards metal atoms. In the presence of metal salts, a tetra dentate cyclic system is formed which coordinates through four imine nitrogen atom.

The far IR spectra show bands in the region 495 cm^{-1} to 444 cm^{-1} corresponding to υ Zn-N vibrations. C=N supports the coordination of organic group with disappearance of strong bands at 1682-1660 cm^{-1}. Thus, the cyclic tetra dentate ligand behaves as N4 system is formed. Furthermore, the strong band observed at 822 cm^{-1} -768 cm^{-1} shows the out plane bending of C-H stretching vibration in benzene ring (**fig.11**).

Table.4 Infrared Data of QXD and Metal Complexes

compounds	υ(CH) cm^{-1}	υ (-OH)	υN-H cm^{-1}	υC=O cm^{-1}	υC=N cm^{-1}	υC-N cm^{-1}	υC=C cm^{-1}	υC-O cm^{-1}	υ M-O cm^{-1}	υ M-N
QXD	2882 3047		3423	1682	-	1392	1411	-	-	-
Zn-L	-		3385	-	1629	1364 to 1319	1411	-	-	444 to 495
Zn(QXD) (HQ)	2865 3049	3362		1688	-	-		1193	464 to 584	-

3.5.4 NMR spectra

3.5.4.1 ^{1}HNMR Zn (QXD) (HQ)

The ^{1}H NMR spectrum of Zn (QXD) (HQ) complex shows a multiple signals observed at δ 7.071-7.142 ppm that may be attributed to C-H of the terminal aromatic protons. The singlet observed in the region 12 ppm may be assigned to the deshielded of -OH protons on water that are affected strongly by the electronic withdrawing of Zn (II) ion. The singlet absorption in the 3.5 ppm corresponds to N-H of pyrazine ring. The singlet observed at 6.5 ppm corresponds to C-H of the aromatic proton next to terminal aromatic proton. The singlet observed at 8.51ppm corresponds to C-H of the hydroquinone proton. The chemical shifts in the region 3.5 ppm of the N-H confirms the presence of C=O of pyrazine ring, thus support the expected structure of the Zn (II) complex (**fig.16**).

3.5.4.2 ^{13}CNMR Zn (QXD) (HQ)

the ^{13}C NMR spectrum of Zn $(QXD)_2.2H_2O$ complex displays resonances at 40, (115.58, 116.10), (123.47,126.05),150.18 and 155.62 ppm that are attributed to CH_3(DMSO), C=C (Ar-), C=C (HQ), C-N, and C=O groups respectively (**fig.17**)

3.5.4.3 ^{1}HNMR Zn-L

The ^{1}HNMR spectrum of Zn-L complex show a multiple signal peak at 7.074-7.143 ppm is attributed to C-H of the terminal different aromatic proton. A singlet signal observed at 3.5 ppm is assigned to N-H proton of pyrazine ring. A singlet observed at 12 ppm may be show the -OH proton that formed due to impurities (**fig.18**)

3.5.4.4 ^{13}CNMR Zn-L

the^{13}CNMR spectrum of Zn-L complexes displays resonance at 40,115.59,123.51,126.03 and 155.63 ppm that attributed to CH_3(DMSO), C=C-(Ar), C-N (pyrazine ring), C=N (imine) group respectively (**fig.19**)

3.5.5 AAS determination of metal in complex

3.5.5.1 AAS determination of Zinc in Zn-L complex

The Zinc metal percentage was estimated by decomposing 10 mg of the Zn-L complex through digestion in 10 ml conc. HNO_3 until a clear solution observed. The clear solution was diluted to 50 ml volumetric flask to make solutions of known concentration. The known solution again diluted by 10 ml, and finally the metal content was recorded using Atomic Absorption Spectrometer.

$$\% \text{ Zn} = \frac{Absorbance(PPM) x volume\ diluted(50ml)(10ml)x100}{\text{Mass of sample taken}}$$

$$= \frac{2.676\ \text{mg/L x50mlx10ml x100}}{0.01g}$$

$$= 13.38\%$$

3.5.5.2 AAS determination of Zinc in Zn (QXD) (HQ) complex

The Zinc metal percentage was estimated by decomposing 10 mg of the Zn (QXD) (HQ) complex through digestion in 10 ml conc. HNO_3 until a clear solution observed. The clear solution was diluted to 50 ml volumetric flask to make solutions of known concentration. The known solution again diluted by 80 ml, and finally the metal content was recorded using Atomic Absorption Spectrometer.

$$\% \text{ Zn} = \frac{Absorbance(PPM) x volume\ diluted(50ml)(80ml)x100}{\text{Mass of sample taken}}$$

$$= \frac{0.2286\text{mg/L x50mlx80ml x100}}{0.01g}$$

$$= 9.144\%$$

Table.5 AAS data for Zn-L and Zn (QXD) (HQ) complexes

	Metal content found and expected		
Complexes	%Zn expected(cal.)	%Zn found	Empirical formula of complexes
Zn $(QXD)_2$	10.84	9.144	$ZnC_{28}H_{22}N_4O_8$
Zn-L	10.82	13.38	$ZnC_{28}H_{20}N_8Cl_2$

3.5.6 Electronic spectra of complexes

3.5.6.1 Electronic spectra of Zn-L complex

As expected for a d^{10} electronic configuration, the electronic spectrum of Zn-L complex does not show any d-d transition. The two transition in the electron spectrum of the ligands are n-π* (transition that shifts to shorter wave length) and π-π* (transition that shifts to longer wave length). The observed bands are due to the ligand and charge transfer transitions, i.e. the bands at 296.5 nm and 250 nm are assigned to n-π* transition of imine (C=N) and π-π* transition of benzene ring, respectively. This transition also found in the spectrum of complex i.e. since zinc ion has d^{10} configuration, the absorption at 294.5 nm, 296.50 nm and 320.50 nm could be assigned to a charge transfer transition. The green color of the complex may be conjured as having arisen from this absorption in the ultraviolet region (**fig.20**)

3.5.6.2 Electronic spectra of Zn (QXD) (HQ)

Since Zn (II) ion has d^{10} electronic configuration, the electronic spectrum of Zn (QXD) (HQ) complex does not show any d-d transition. The observed bands are due to the ligand and charge transfer transitions. The bands at 298 nm and 249.50 nm are assigned to n-π* transition of carbonyl group and π-π* transition of benzene ring, respectively. The absorption at 295 nm,298 nm and 321.5 nm could be assigned to charge transfer transition. The blue color of the complex may be conjured as having arisen from this absorption in the ultraviolet region (**fig.21**)

Table.6 Electronic spectral data of the complexes recorded in DMSO solution.

Compouds	Transtion	Absorption band (in nm)	Conductivity Ω cm^2mol^{-1}	Assigned complex	Magenetic propertty
QXD	π-π* (C=C)	249.50	-	-	
	n-π* (C=O)	298.0	-	-	
	π-π* (C=C)	250.0	-	-	
	n-π* (C=N)	296.00	-	-	
Zn-L	LMCT	277-320.50	2.18	Octahedral	non-electrolyte
Zn (QXD) (HQ)	LMCT	276.50-321.50	3.45	square planar	non-electrolyte

Conclusion

The absence of C=N stretching frequency on the IR spectrum of the expected ligand sample ruled out the formation of the ligand L but it was formed in the presence of metal salts by undergoing condensation between orthophenylenediamine and 1,4-dihydroquinoxaline -2,3-dione.

The modified route to obtain metal complex through template method was followed. The ligand which was formed in the presence of metal ion has several potential donor atoms, the ligand can provide a maximum of four donor atoms at any one time for coordinating to a metal. On assumption that the four nitrogen atoms of the ligand are coordinated to the metal with two chlorine ion and hence the complexes are six coordinates with respect to the ligand.

As the ligand is potentially tetra dentate, it is quite feasible that the Zn-L complex is six coordinate with N-donor ligand and two chlorine ion formed by template method. The Zn-L complex is six coordinates and Zn (QXD) (HQ) complex is four coordinate as shown below. The complexes were characterized on the basis of IR, AAS, elemental analysis NMR, UV-VIS and conductivity measurements. The following structure were proposed.

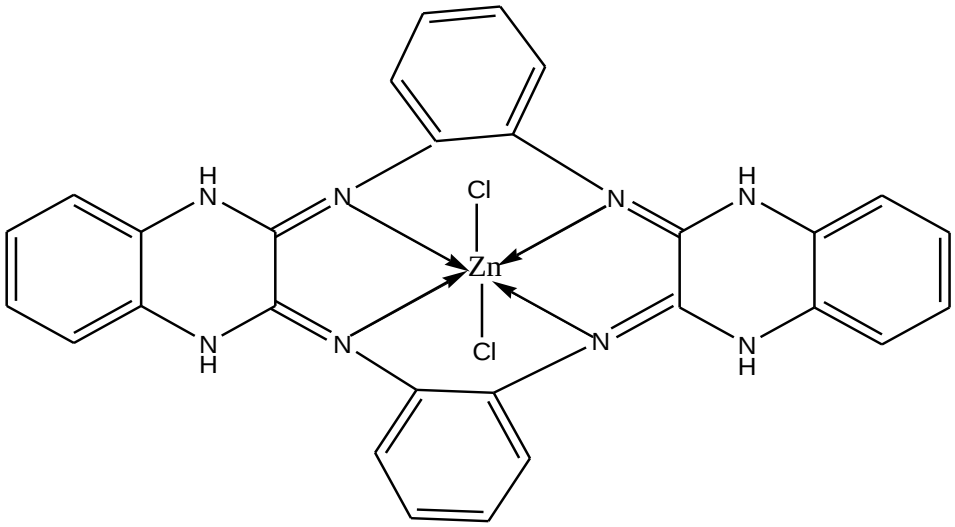


Figure .7 Suggested Structure of Zn-L complex

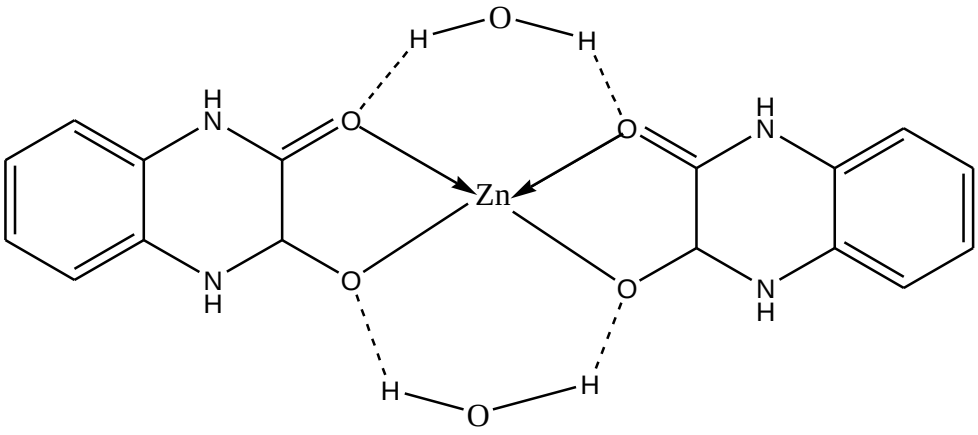


Figure.8 Suggested Structure of Zn (QXD) (HQ)

Recommendation

From the review literature point of view, if the optimization is done, surely the expected ligand, L is formed. Therefore, I invite the coming researcher to do this ligand by optimization process [13].

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Appendices

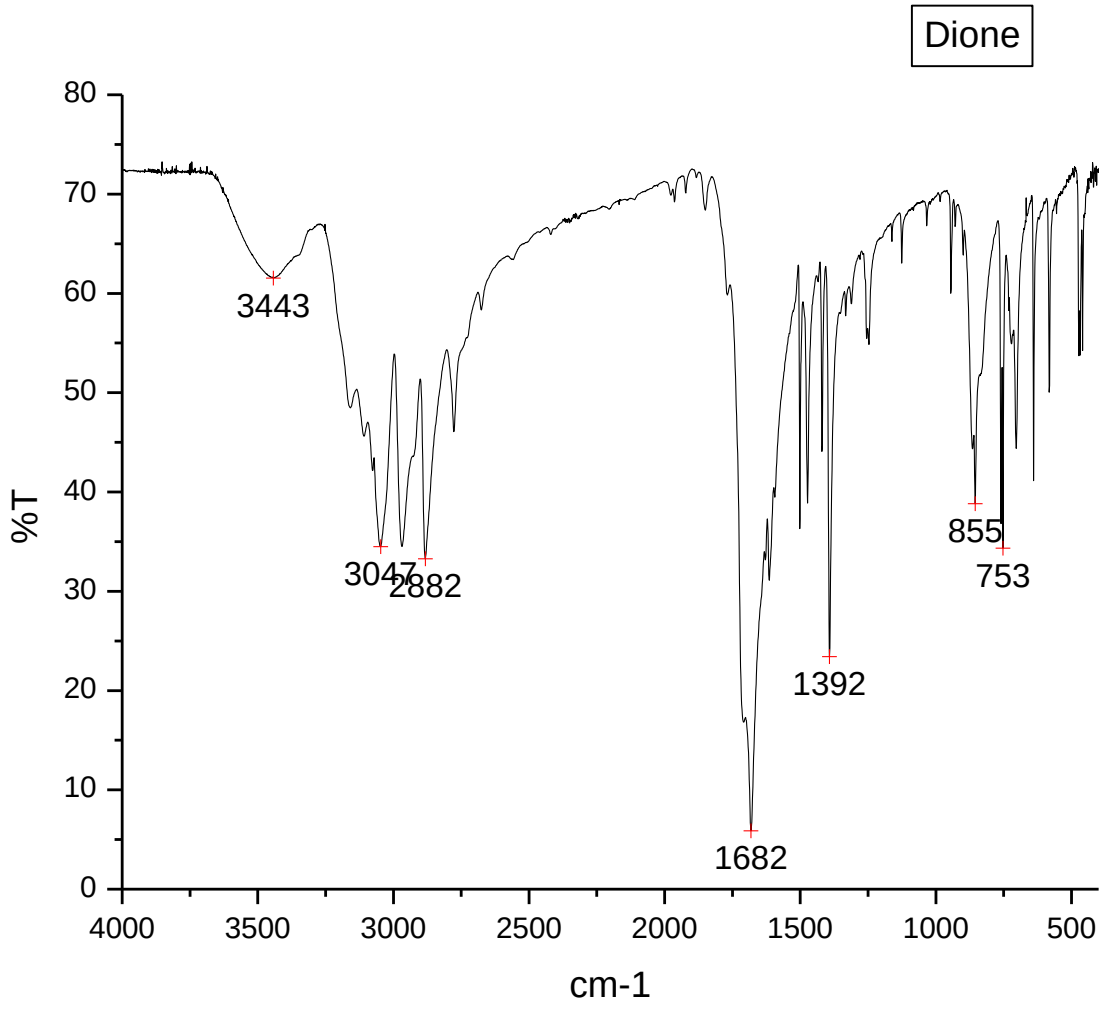

Figure 9. IR Spectrum of QXD (dione)

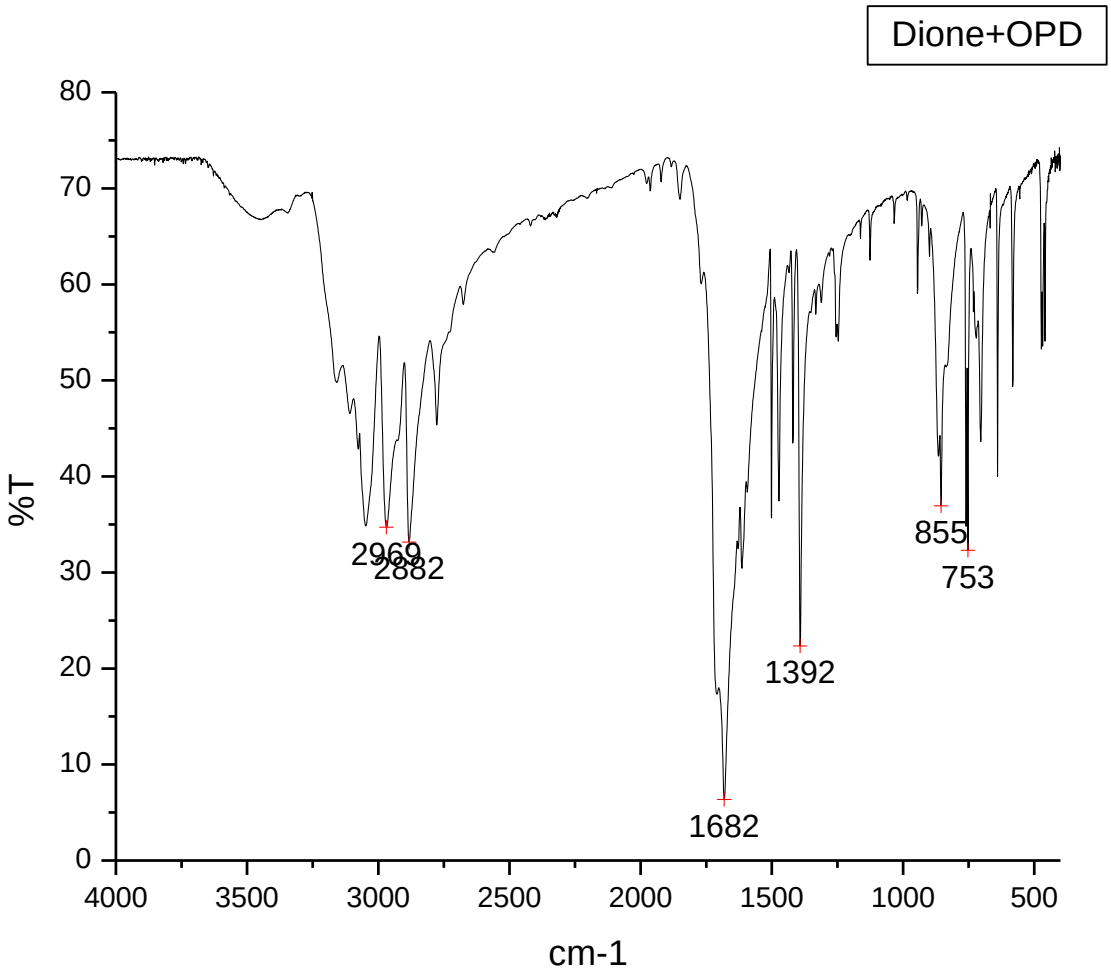

Figure 10.IR Spectrum of expected ligand

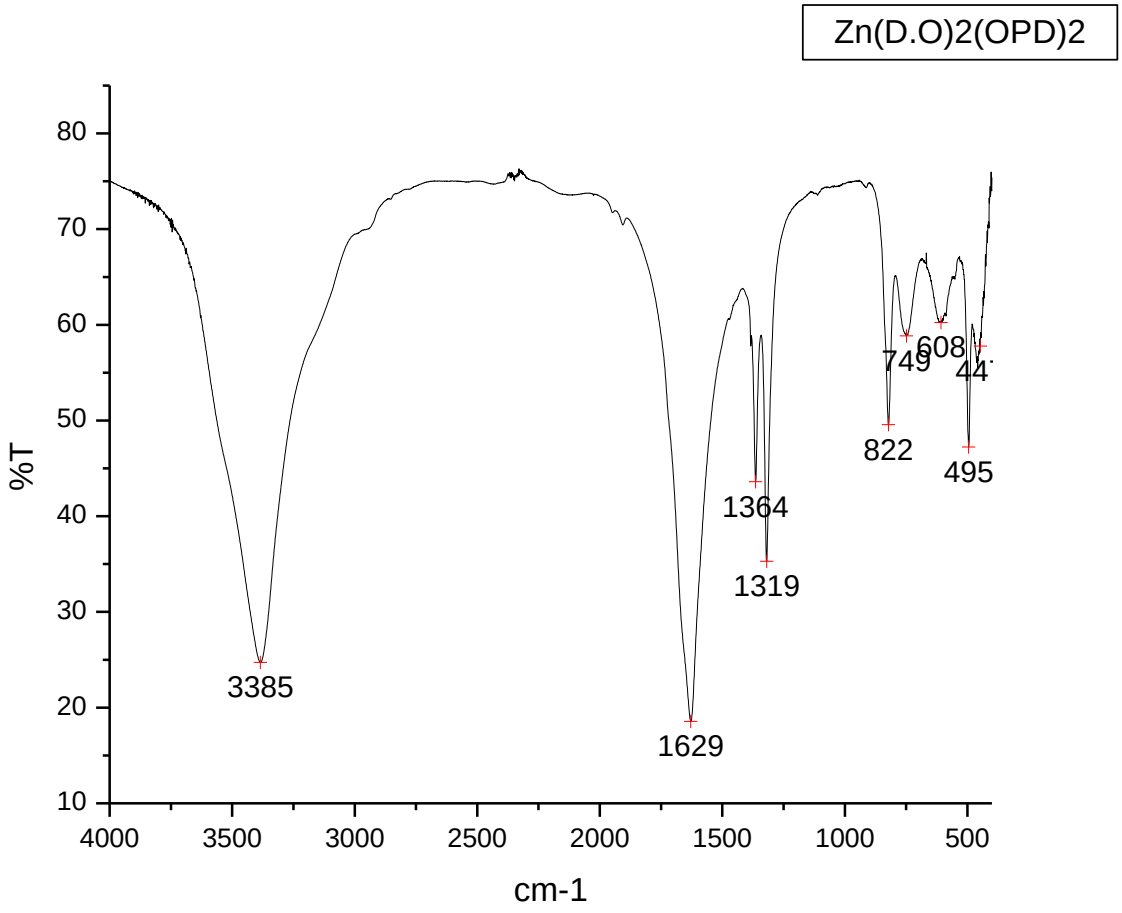

Figure 11. IR Spectrum of Zn +Dione +OPD or Zn-L complex

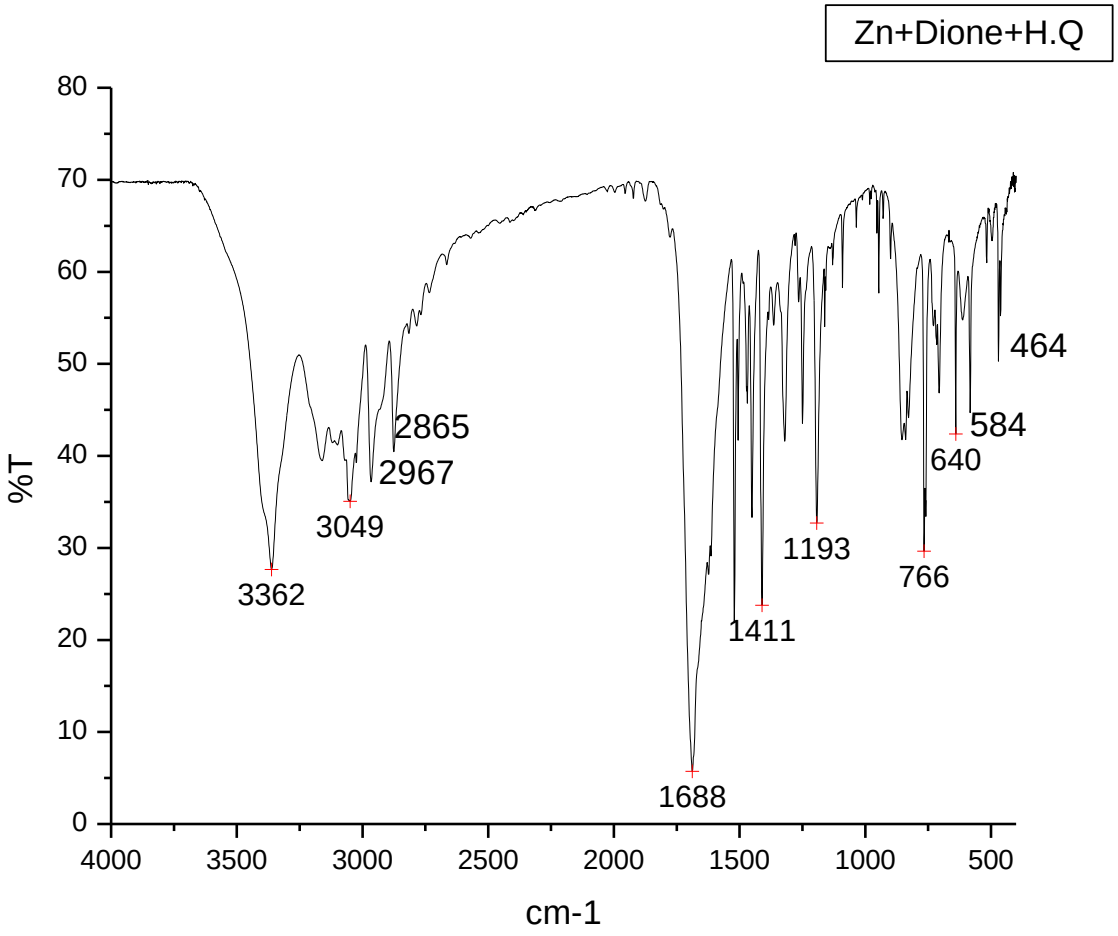

Figure 12. IR Spectrum of Zn +Dione +H Q or Zn (QXD) (HQ) complex

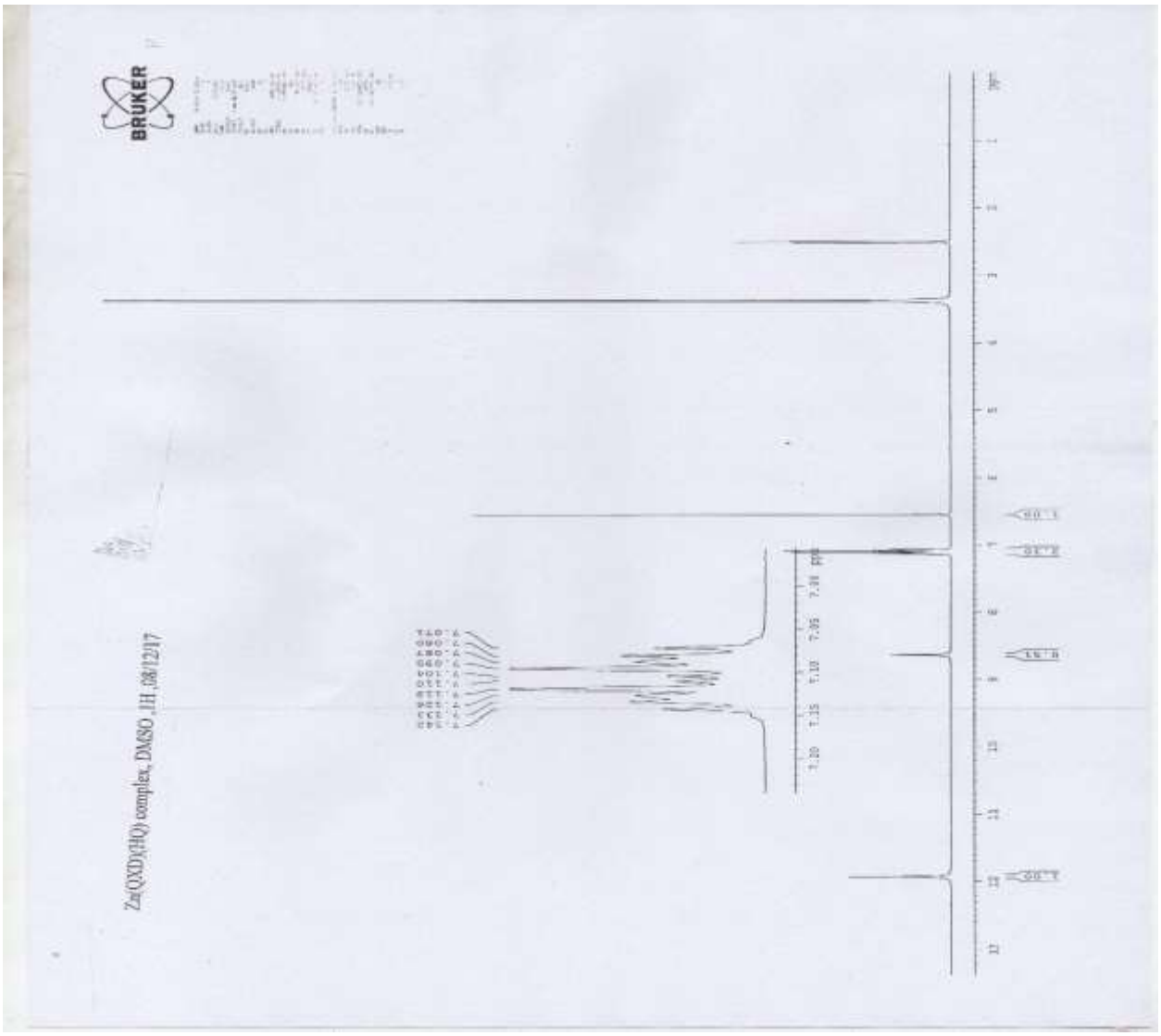

Figure 13. [1]HNMR spectrum of Zn (QXD) (HQ)

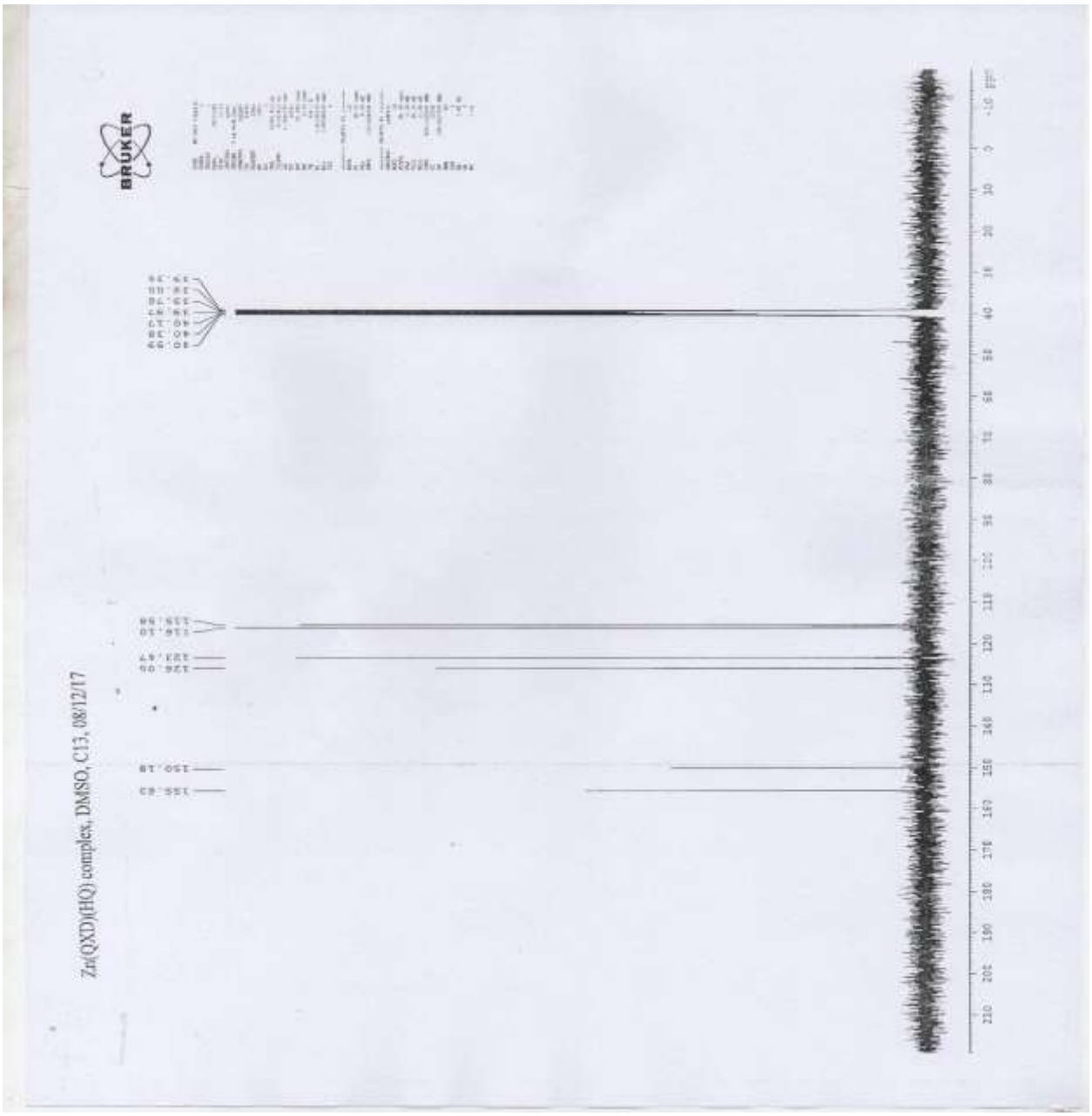

Figure14. ^{13}CNMR spectrum of Zn (QXD) (HQ) complex

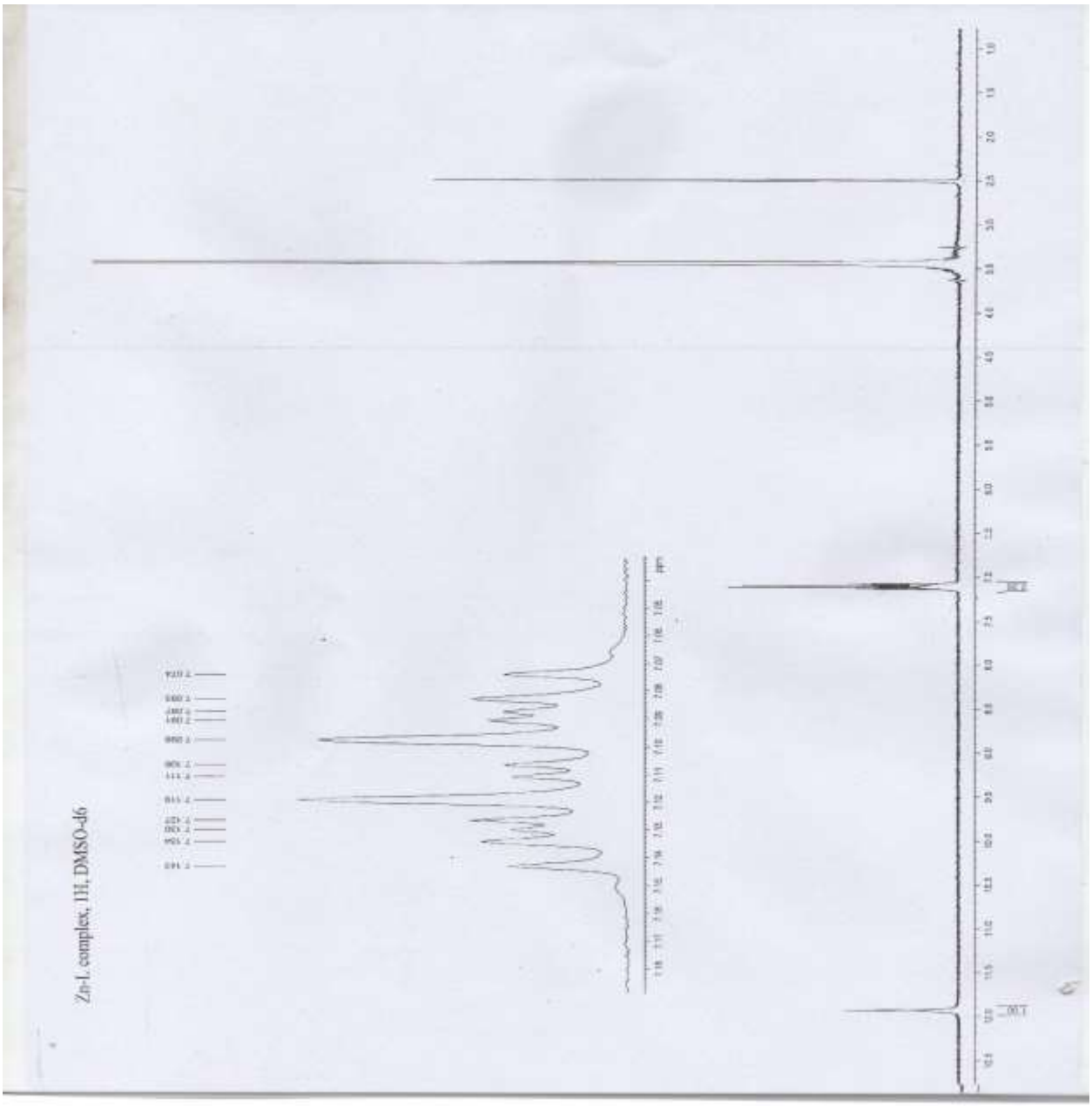

Figure 15. [1]HNMR spectrum of Zn-L complex

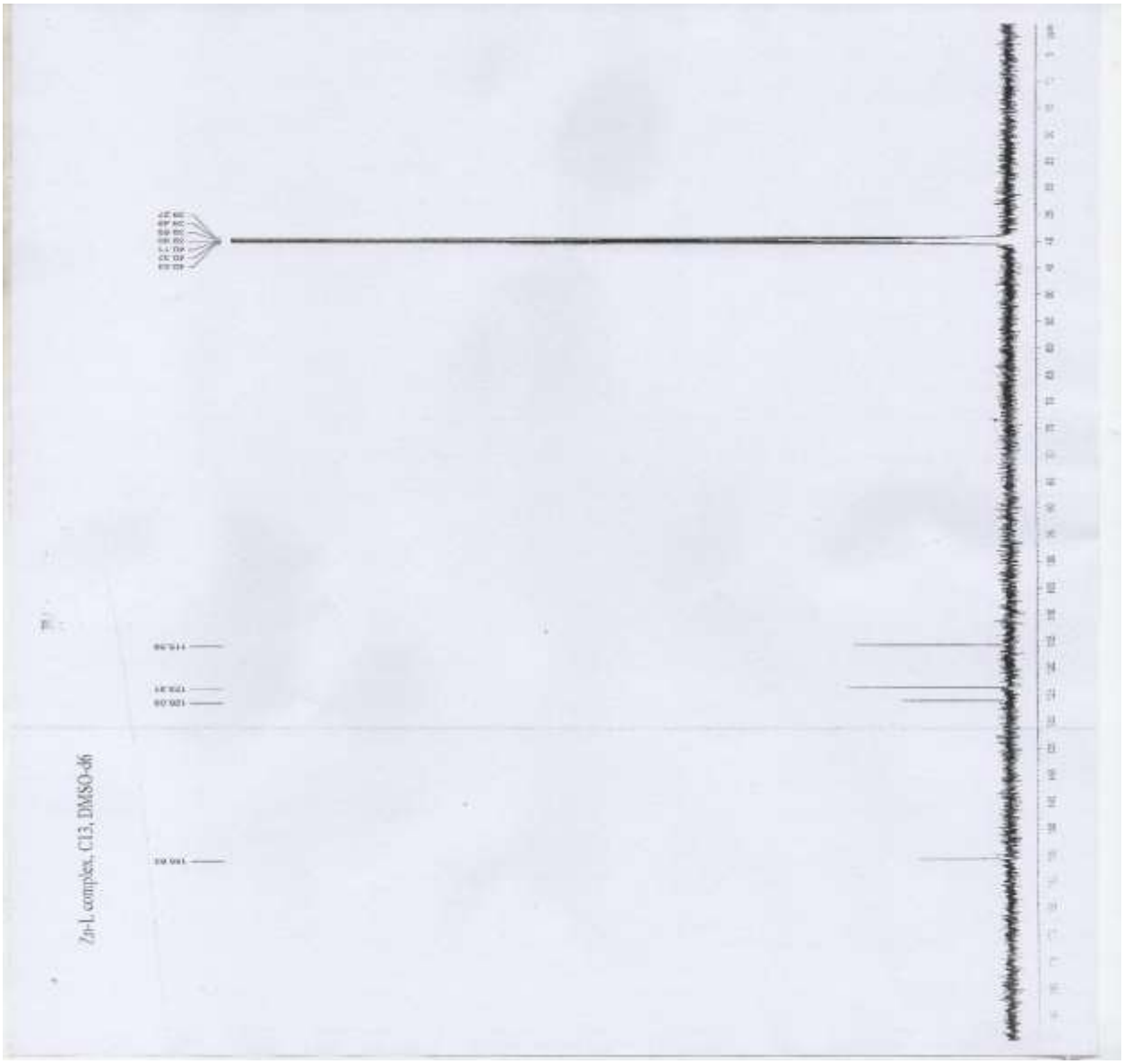

Figure 16. ^{13}CNMR spectrum of Zn-L complex

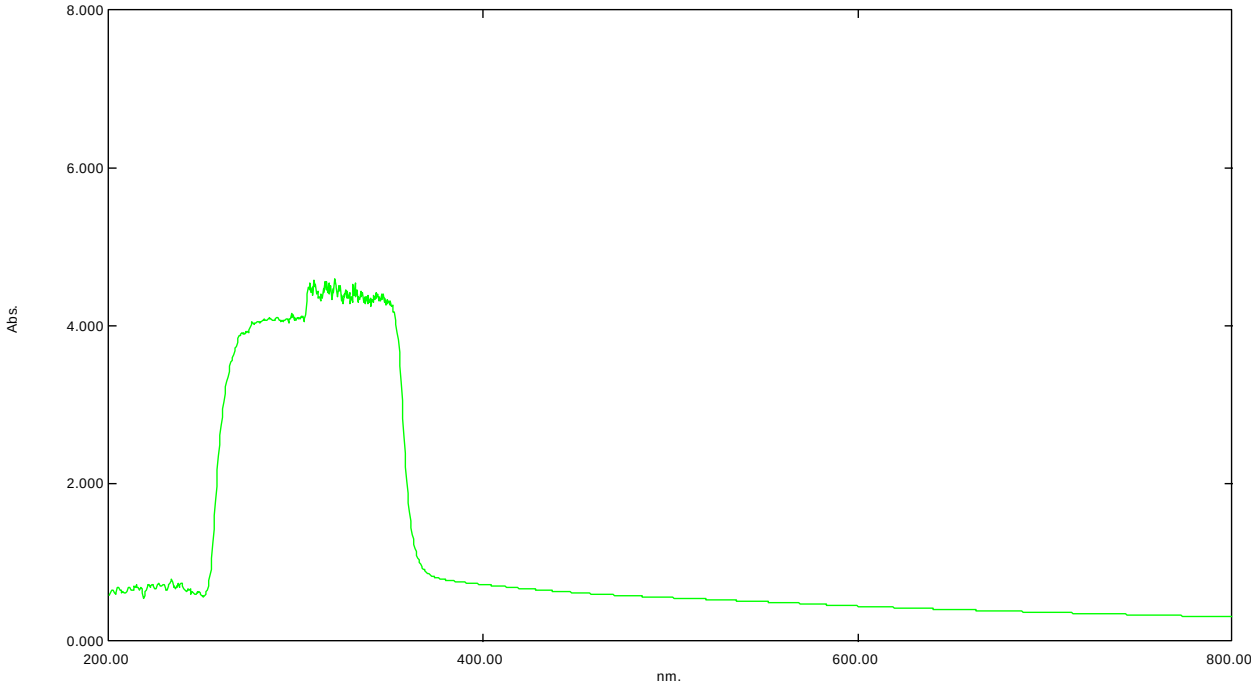

Figure 17. UV-VIS spectrum of Zn-L complex.

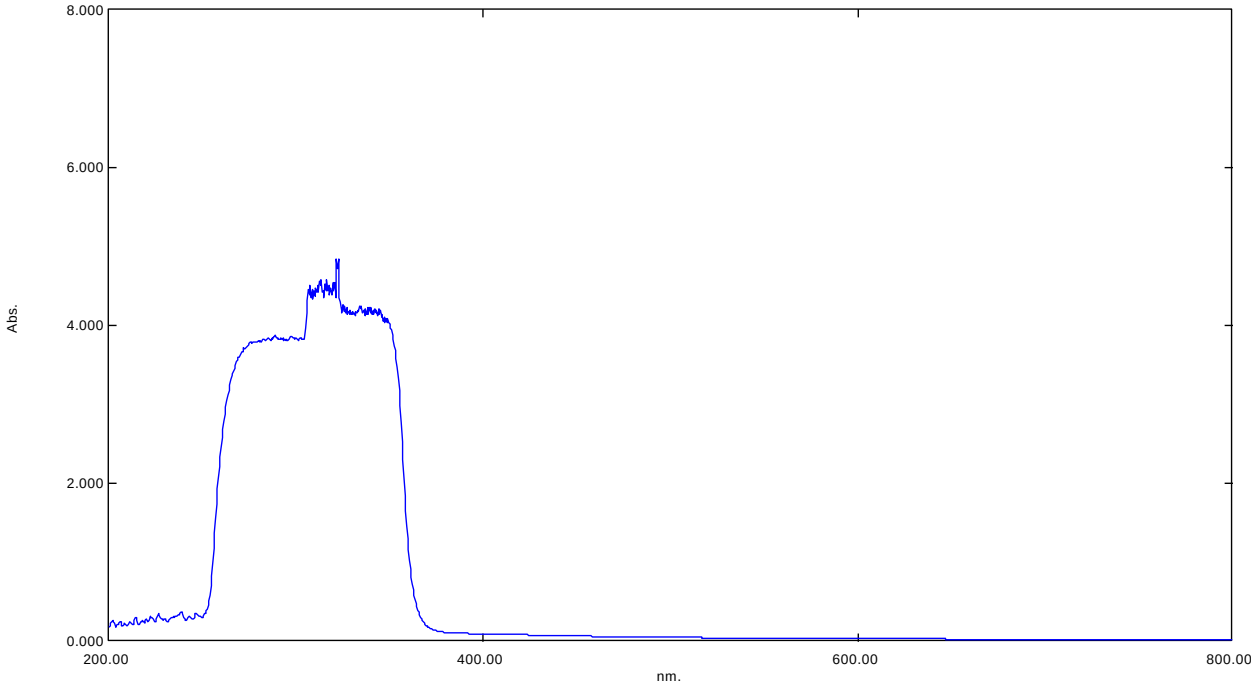

Figure 18. UV-VIS spectrum of Zn $(QXD)_2$.

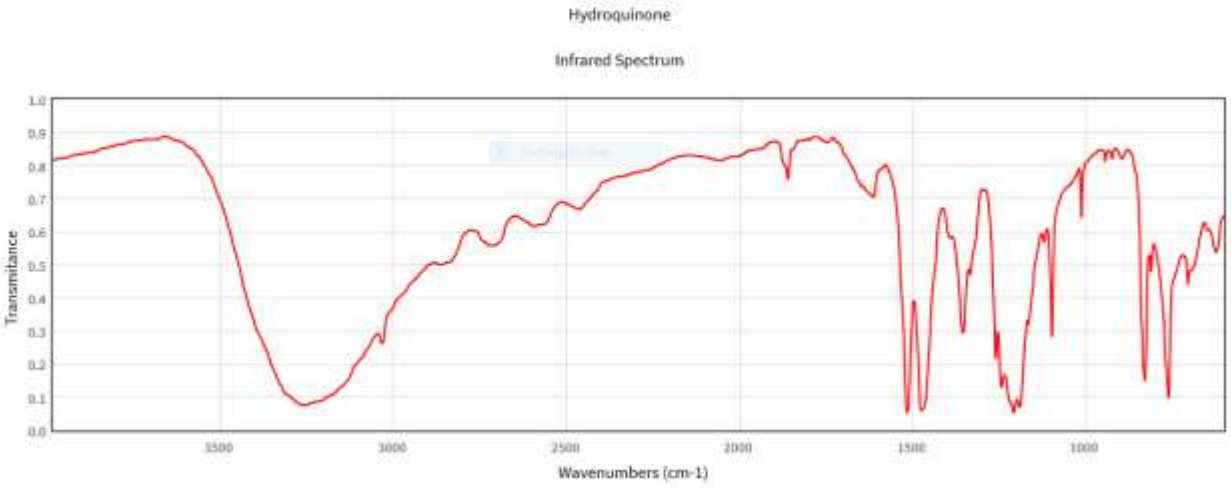

Figure 19. Infrared spectrum of hydroquinone

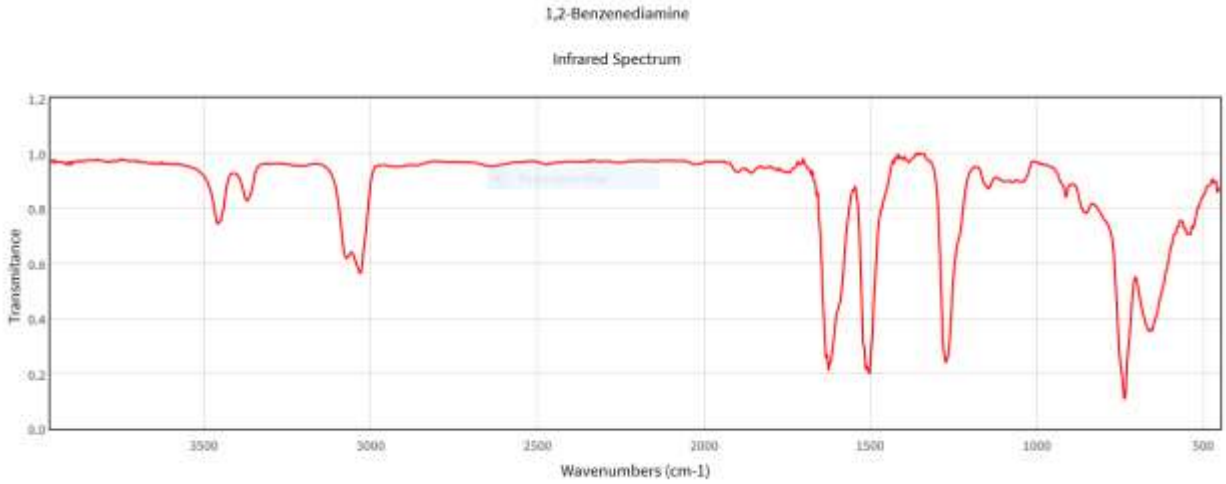

Figure 20. IR spectrum of orthophenylenediamine

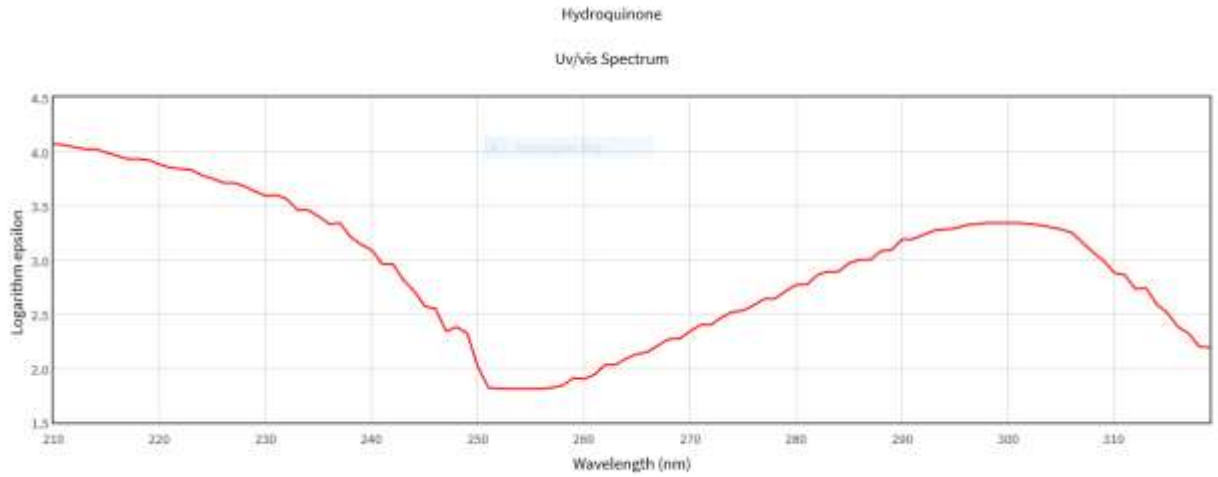

Figure 21. UV-Visible spectrum of hydroquinone

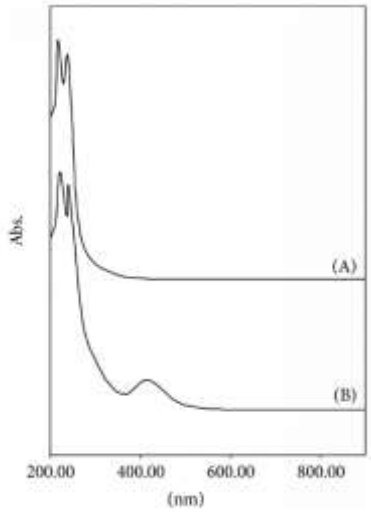

Figure 22. UV-Visible spectra of orthophenylenediamine (OPDA) (A) and it analogous polymer (POPDA) (B)

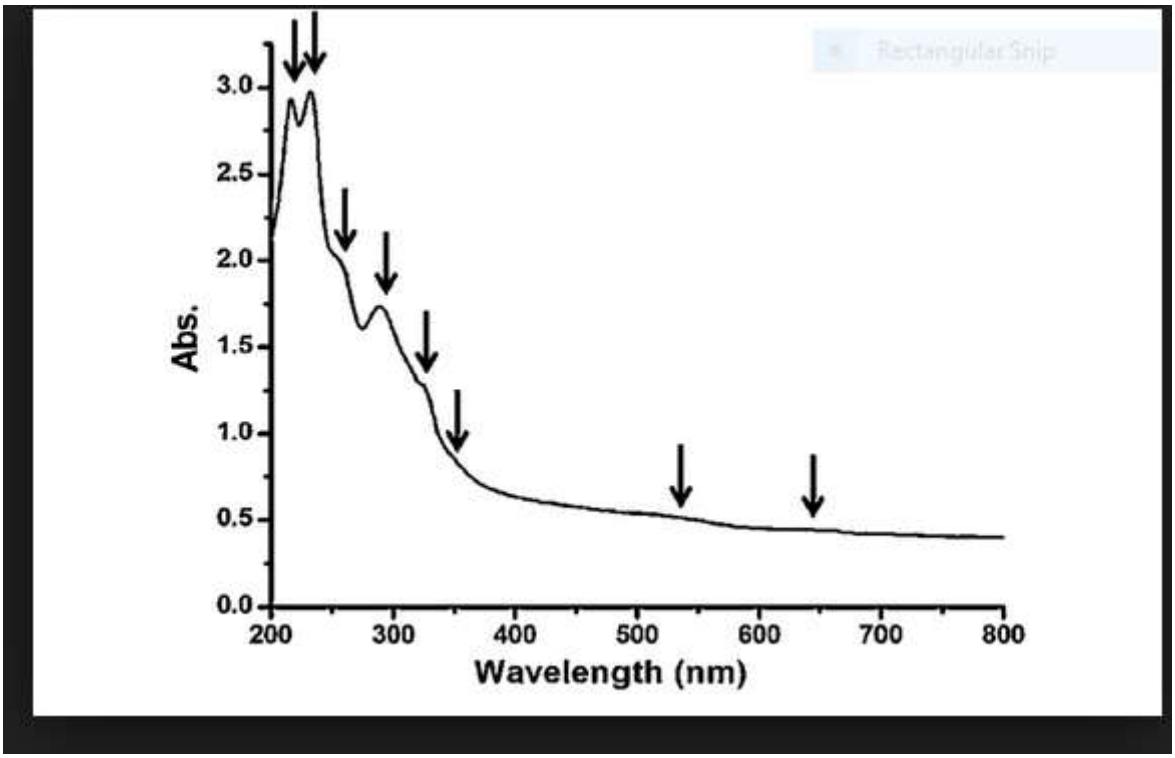

Figure 23. UV-VIS spectrum of 1,4-dihydroquinone-2,3-dione