SYNTHESIS AND CHARACTERIZATION OF 1,4-DIHYDRO-QUINOXALINE -2, 3-DIONE DERIVATIVES-BASED Zn (II) AND Cd (II) COMPLEXES.

BY

SHIBABAW BEKELE

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This is to certify that the project prepared by Shibabaw Bekele entitled: Synthesis and characterization of 1, 4-dihydro-quinoxaline -2, 3-dione derivatives-based Zn (II) and Cd (II) complexes and submitted in partial fulfillment of requirements for the degree of master of science in chemistry complies with the regulation of the University and meets the accepted standards with respect to originality and quality.

Signed by the Examining Board:

Advisor Dr Yonas Chebude Signature--------------------Date---------------------

Examiner Dr Negash Getachew Signature----------------Date---------------------

Examiner Dr Girum Ayalneh Signature----------------Date----------------------

ABSTRACT

Coordination compounds play vital roles in biology, biochemistry and medicine, controlling the structure and function of many enzymes and their metabolism. They find varied application in many industrial processes and in the development of new materials with specifically designed properties. Thus, synthesis and study of the complexes is very important. In this work, equimolar quantities of o-phenylene diamine and oxalic acid were ground with pestle in a mortar to produce 1,4-dihydro-quinoxaline 2,3-dione, which behaves as a bidentate O,N donor ligand by solvent free method. The new ligand 3-(2-hydroxy-phenylalanine) qunioxaline-2-one was synthesized by mixed equimolar ratio of 1,4-dihydro-quinoxaline-2,3-dione with 2-amonphenol by conventional method. Zn (II) and Cd (II) complexes were synthesized from mixed the ligand 1,4-dihydro-quinoxaline-2,3-dione derivative ligand with salts of anhydrous Zn(II) nitrate and anhydrous Cd(II) chloride by template method. These complexes and ligand have been characterized with the help of various spectra technique, such as AAS, IR, UV/VIS spectroscopic techniques as well as molar conductance, chloride test and melting point measurements have been done as supports to conclude the structures of the complexes. The square planer geometry was proposed for Zn-L complex and tetrahedron geometry was proposed for Cd-L complex.

Keyword:1,4-hydroquinoxaline2,3dione,2-aminophenol, 3-(2-hydroxylphenylalanine) qunioxaline2-one.

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Symbols and Abbreviations

AMPA= antagonist of amino propanoic acid

HIV=Human imino viral

R=alkyl, cycloalkyl, aryl or heterocyclic group

ROP=ring opening properties

PL=photo luminescent absorption

LMCT=Ligand to metal charge transfer

OLED=Organic light emitting diode

MeOH=methanol

EtOH=ethanol

DMSO=Dimethylsulphoxide

DMF=Dimethylformamide

UV=ultraviolet

IR=Infrared

AAS=atomic absorption spectroscopy

QXD=Quinoxaline dione

QXDA=Amino quinoxaline dione

CT=Charge transfer

ATNR=amine terminated liquid natural rubber

a.m.u= atomic mass unite

ppm= parts per mil

1. INTRODUCTION

Coordination compounds exhibit different characteristic properties which depend on the metal ion to which they are bound, the nature of the metal as well as the type of ligands. These metal complexes have found extensive application in various fields of human interest [1]. Schiff bases play important roles in coordination chemistry as they easily form stable complexes with most transition metal ions [2]. Schiff base complexes have remained an important and popular area of research due to their simple synthesis, versatility, and diverse range of applications. Schiff's bases are the compounds containing azomethine functional group (-C=N-). They are condensation products of ketones or aldehydes with primary amines and were first reported by Hugo Schiff in 1864.Schiff's bases of aliphatic aldehydes are relatively unstable and are readily polymerized while those of aromatic aldehydes, having an effective conjugation system, are more stable. Formation of Schiff base generally takes place under acid or base catalysis or with heat. Bases obtained from amines and aldehydes have applications in various disciplines of chemistry [3].

Schiff bases are important chelating agents which offer great versatility in the design of useful, interesting and commercial ligands system[4]. Schiff bases have been used extensively as versatile ligands with transition metals which are able to form very stable complexes because they donate electrons into the vacant d-orbital's of the metal atoms ions. This versatility of Schiff base ligands is shown in the biological, analytical and industrial applications of their metal complexes. This also makes further investigations in this area highly desirable and as such, current researches dealing with metal complexes of hetero atoms in Schiff bases have expanded their applications enormously to include a vast diverse fields of human endeavors. Many Schiff bases and their complexes are known to show promising antifungal, antibacterial, antiviral including anti HIV and anticancer activities. Schiff-base ligands with heterocyclic molecule and/or containing hetero atoms such as N, O, and S show a broad biological activity and are of special interest because of the variety of ways in which they are interacted to transition metal ions. In addition, some Schiff bases containing N & O donor atoms are also effective anti-corrosion agents and serve in many other analytical purposes in organic and inorganic chemistry fields, hence their wide applications in industries[5].In this project work first synthesis 1,4-didhydroquinoaxlin 2,3 dione from mixed equimolar amount of o-phenylene diamine and oxalic acid in the mortar and grinding with pestle and then the resulting product mixed with 2-aminophenol to synthesize the newly mixed ligands 3-(2-hydroxyleamino)quninoxaline-2-one and finally use the mixed Schiff base for the synthesis of Zn(II) and Cd(II) metal complexes.

1.1. Statement of the problem

Nowadays there are shortages of different chemicals used in different application such as biological activities and in different industry serve as raw materials. Chemicals used such activities are mostly synthesis transition metal complexes of C=N and C=O functional group, that why most researcher are focusing on these group. My study also depends on these functional group and their transition metal complexes. To began the research, there was a research done by Gemechu Lemisa to fulfill his MA degree in chemistry in 2018 on the title synthesis and characterization of new metal complexes derived from 1,4-Dihydro-qunioxalin 2,3- Dione, orthophenylene diamine and Hydroquinone used by the template method. When I reviewed his study the method used to synthesized 1,4-Dihydro-qunosaline 2,3-dione was conventional method but the rest was a little bit similarity in procedure the experiment done with the current research, but the current research differ from Gemechu's research modified the methods of synthesized the desire ligand by using solvent free method and the types of reagent used when I was synthesized the complexes metals and the new complex ligand.

1.2. Objectives

1.2.1. General Objective

General Objective of this project work was to synthesize and characterize Zn (II) and Cd (II) complexes from Schiff base derived from 1,4-dihydroquinoxaline-2,3-dione and 2-aminophenol.

1.2.2. Specific Objective

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

1.3. Significance of the study

Synthesis of ligands and metal complexes are very important for different filed of human interest. Nowadays different researchers give great attention to synthesize heterocyclic ligands and their metal complexes. Thus this research may have the following significance

1. It helps other researcher to use as a guide to study deeply on ligands and metal complexes.
2. It helps to synthesize raw materials for different industries as starting materials.
3. It helps to develop modified experimental procedure for future use.

1.4. Delimitation of the study

This study was delaminated to examine heterocyclic ligands specially nitrogen content and their metal complexes of Zn (II) and Cd(II) metals. Studying this area widely is good, but because of deficiency of time, chemicals and laboratory equipment. Thus the study was focusing on the title of synthesis and characterization of 1,4- dihydro-quinoxalin 2,4-dione derivate ligand and an hydrous salt of zinc nitrate and cadmium chloride because the researcher got sufficient chemicals and reagents in this area of study.

2. LITERATURE REVIEW

2.1. Schiff Base

The Schiff base are compounds that contain carbon nitrogen double bond backbone$R_3R_2C{=}NR_1$. The substituent's R_1, R_2 and R_3 may be alkyl, aryl, hetero aryl or hydrogen. These organic compounds occur in various derivatives and can be found in nature like many organic compounds which exist naturally. Schiff base compounds are found to be useful as ligands for preparation of metal complexes and as bioactive agents in medicinal fields [6].

2.1.1. Schiff Base Ligands

Schiff base ligands can be obtained as products after condensation of primary amines with aldehydes or ketones. These reactions generally occur under reflux in the presence of acid or base as the catalyst and drying agents such as sodium sulphate, molecular sieves or magnesium sulphate for water removal which is produced as a by-product [6]. Figure 1 shows the detailed mechanism for the condensation reaction where acid/base reaction protonation the carbonyl group to be active and more susceptible to attack by a neutral nucleophiles nitrogen of the primary amine. The attack from the nitrogen nucleophiles to the electrophonic carbonyl carbon group is followed by pi electrons going to the oxygen which becomes positively charged. The removal of the proton neutralizes the positive charge on the nitrogen and forms the carbinol amine intermediate. Then protonation followed to generate water molecule which is a good leaving group (dehydration process). The nucleophilic of the nitrogen helps to push out the leaving group (water molecule) forming an iminium ion. Deprotonation of the iminium nitrogen generate imines product and regenerates the acid catalyst [6].

Schiff base ligands have the ability to coordinate as mono-dentate to multidentate such as tetra-dentate, tri-dentate, bi-dentate and chelating abilities in the presence of donor sites [7].They normally coordinate to the metal center through nitrogen or phosphate lone pair of electrons. Some of the Schiff base ligands are stable, solid and can be carefully purified with minimum loss of the desired product [6,7]. The variation of substituent's on the Schiff base ligands are often used to induce substrate chirality and enhancing the solubility and stability of the resultant complexes[8]. The derivative, imidazole containing substituent's on Schiff base ligands behave as monodentate ligands at lower pH and as bridging ligands at higher pH in accordance with the flexibility of the compound [9]. The properties of Schiff base ligands vary based on substituent bonded to the imines functional group. The mechanism on figure demonstrates condensation of primary amines with aldehydes to form Schiff base compounds under acidic conditions.

FIG

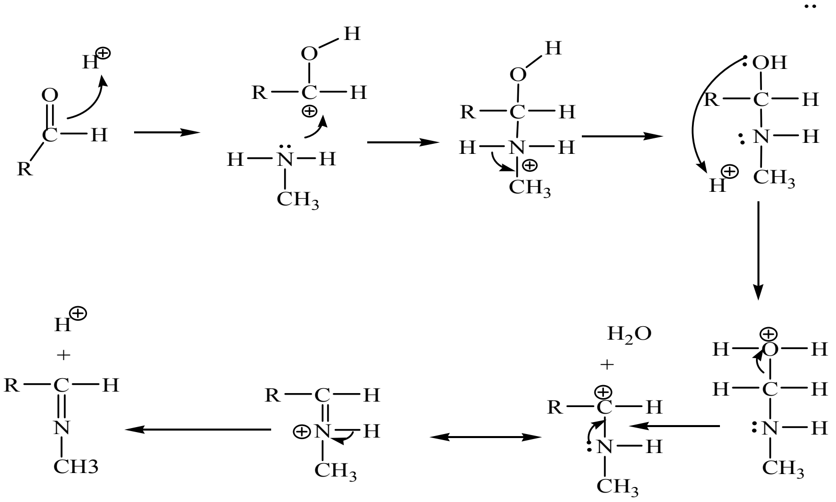


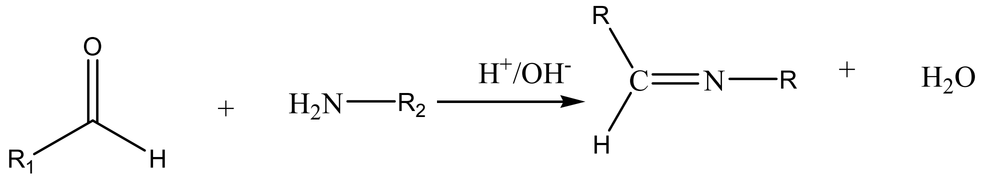
Figure 1 Mechanism for condention of primery amine with aldehydes to form schiff basecompound

2.1.2 Synthesis of Schiff's Bases

Different synthetic strategies have been reported for the preparation of Schiff bases [10].

Classically

This method involves the condensation of an aldehydes and a primary amine under acidic or basic conditions.



Where R_1 and R_2aliphatic or aromatic group

Scheme 1.General synthesis of Schiff bases

The synthesis of a Schiff base from an aldehyde or a ketone is a reversible reaction. Preparation of Schiff bases under acidic conditions involves the following steps:-

Deprotonation of weak acid

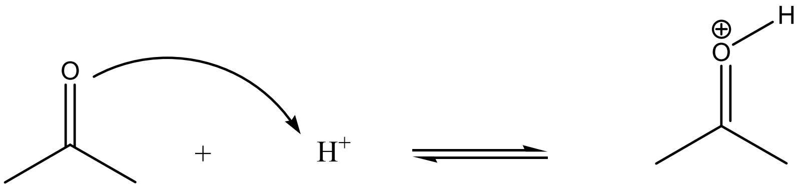
In the first step deprotonation of acid takes place and it dissociates into positive and negative ions.

$$HB \rightleftharpoons H^+ + B^-$$

Scheme2. Deprotonation of acid

Protonation of carbonyl group

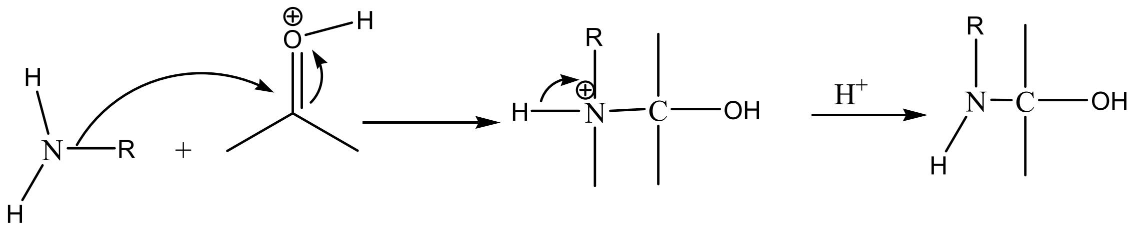
The deprotonated proton is taken up by the oxygen of the carbonyl group which produces a positive charge on it



Scheme3. Protonation of a carbonyl group

Nucleophilic attack of nitrogen

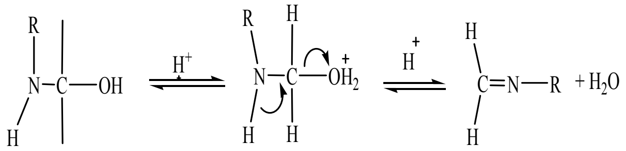
Protonation of carboxylic oxygen causes the electron density to shift away from carbon atom. As a result partial positive charge on this carbon of the carbonyl group increases, thus it becomes susceptible to nucleophilic attack. The nitrogen of amine group being nucleophilic in nature, attacks on the carboxylic carbon which results in the production of carbinolamine.



Scheme4. Nucleophilic attack of nitrogen

Removal of water

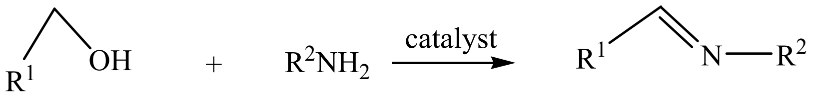
Acid used as a catalyst to accelerate nucleophilic attack of amines on carbonyl carbon also serves as a dehydrating agent for removal of water to obtain a Schiff base.



+

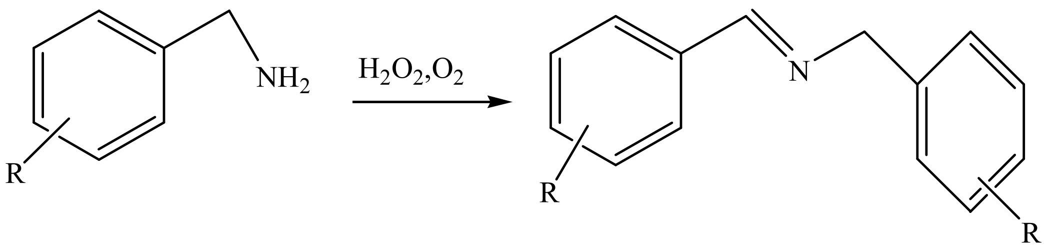
Scheme5. Removal of water

Aerobic oxidative preparation of Schiff bases from alcohol and primary amines [11]



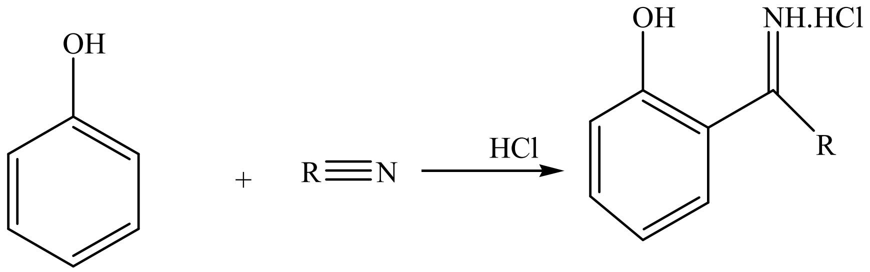
Scheme6. Aerobic oxidative preparation of Schiff bases

Aerobic oxidative preparation of Schiff bases from primary amine derivatives [11]



Scheme7. Oxidative preparation of imines from primary amines

Preparation of ketimines from phenol and nitrile demonstrates another route to Schiff base formation in the presence of hydrochloric acid [11]



Scheme 8. Preparations of ketimines

2.1.3. Some Synthesis Method of Schiff Base

Synthesis of Schiff base is often carried out using acid or base catalysts and generally by refluxing the mixture of aldehydes or ketones and amines in organic medium. The conventional method has been modified to obtain high yields of the Schiff bases by using aprotic non-polar solvents azotropic distillation of water in a Dean-Stark apparatus, and by adding suitable dehydrating agents [12].Environmentally benign synthetic methods have been receiving considerable attention and some solvent-free protocols have also been developed [13]. Microwave induced enhancement of organic reactions is currently a focus of attention for chemists due to the decreased reaction time, improved yields and easier work up as compared to conventional methods. In microwave synthesis, to avoid accidents, low boiling, toxic and poisonous solvents are often avoided. The use of microwave for the synthesis of organic compounds has proved to be efficient, safe and environmentally benign techniques with shorter reaction time [14]

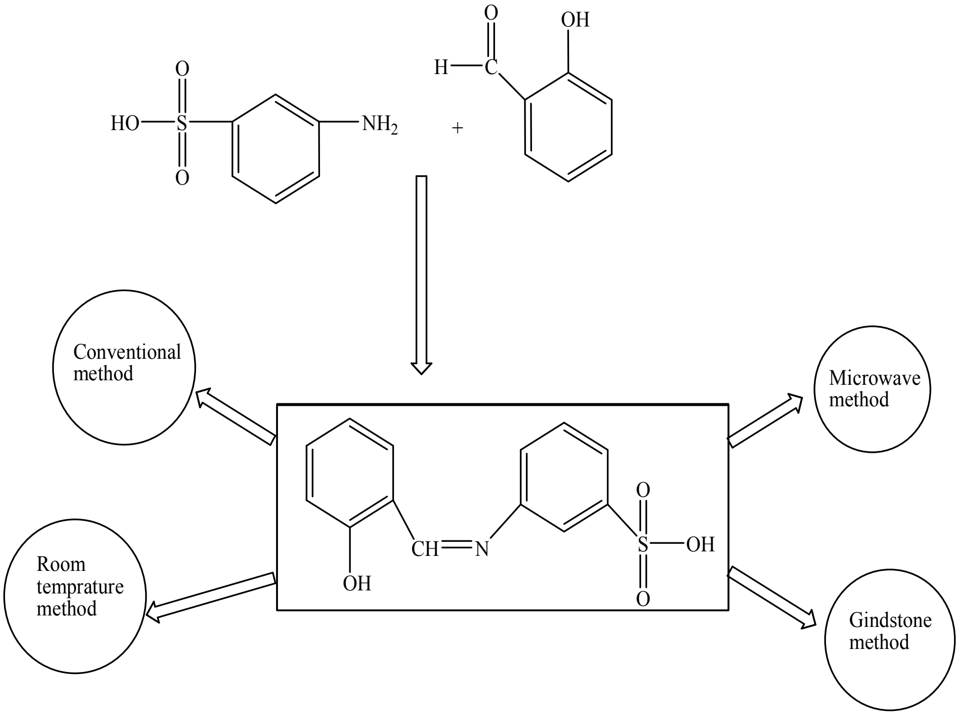


Figure2. Synthesis of Schiff base

- ✓ Temperature controlled method – used to reduce reaction time and give high yield
- ✓ Reflux method-conventional method for formation of Schiff base
- ✓ Room temperature method (stirring)-conventional for preparation of Schiff base
- ✓ Grindstone method – green method of synthesis of Schiff base, newly developed Process

Table 1 clearly shows that microwave irradiation is the simple way to synthesis this Schiff base. Microwave irradiation, which replaces the classical one, is becoming an increasingly popular method of heating because it is proved to be a clean, cheap and convenient method. Frequently, it affords higher yields and results in lesser reaction time. A result also shows that grindstone technique is better as compared to conventional method. In addition no organic solvent required, reaction finished within 20-40 minutes with pure products in good percent yield[15]

Table 1: the comparison of various methods of Schiff base synthesis

Approach	Reaction condition	Reaction time	Yield
1	Conventional method	4hr	60%
2	Room temperature method(stir)	1hr	75%
3	Grindstone method	20-40 minutes	65%
4	Microwave method	2-3minutes	93%

2.2. Application of Schiff bases and Their Metal Complexes

Schiff bases derived from an amino and carbonyl compound are an important class of ligands. The C=N linkage is essential for biological activity, several azomethine were reported to possess remarkable antibacterial, antifungal, anticancer and diuretic activities. Schiff bases have wide applications in food industry, dye industry, analytical chemistry, catalysis, and agrochemical. Schiff-base complexes are considered to be among the most important stereo chemical models in main group and transition metal coordination chemistry due to their preparative accessibility and structural variety. Considerable numbers of Schiff-base complexes have potential biological interest, being used as more or less successful models of biological compounds. Not .only have they played a seminal role in the development of modern coordination chemistry, but also they can also be found at key points in the development of inorganic biochemistry, catalysis and optical materials [16] The Schiff base ligands properties make them to be good candidates for use in industries for oxygenation, hydrolysis, electro -reduction and decomposition; in agricultural sectors for plant regulation as insecticides and are medicinally used as antiviral, antibacterial and antitumor agent [17].Medicinal and some other application of Schiff base and their metal complexes are as follows.

2.2.1. Antimicrobial Activities

Schiff base derived from indoline-2, 3-dione and 2-aminobenzoic acid and its Tin complex showed antibacterial activity against Staphylococcus aurous. The Zn complex showed a wide range of bactericidal activities against the Gram positive and Gram negative bacteria, were potent than or similar with commercial antibiotics [18].The following are Schiff base and metal complex application under antimicrobial activity.

2.2.2. Catalysts

Co (II), Fe (III) and Run (III) complexes of Schiff bases derived from hydroxyl benzaldehyde are used in oxidation of cyclohexane into cyclohexanol and cyclohexane one in presence of hydrogen peroxide. Binucleation complexes, Co, Ni, and Zn, with Schiff base sneytral bis (iminopyridyl) benzene and monoanionic bis (iminopyridyl) phenolate acts as catalyst [19].

2.2.3. Anti fertility and Enzymatic Activity

About 20 zinc enzymes are known in which zinc is generally tetrahedrally four coordinate and bonded to hard donor atoms such as nitrogen or oxygen. The Schiff base complexes of 2-pyridinecarboxaldehyde and its derivatives have been reported to possess high super oxide dismutase activities [20]

2.2.4. Dyes

Chromium azomethine complexes, cobalt complex Schiff base unsymmetrical complex 1:2 chromium. Dyes give fast colors to leathers, food packages, wools etc. Azo groups containing metal complexes are used for dying cellulose polyester textiles. Some metal complexes are used to mass dye poly fibers [21].

2.2.5. Polymer

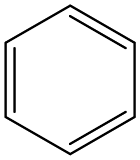
Photochemical degradation of natural rubber yield amine terminated liquid natural rubber (ATNR) when carried out in solution, in presence of ethylene diamine. ATNR on reaction with glyoxal yield poly Schiff base, which improves aging resistance.Organocobalt complexes with tridentate Schiff base act as initiator of emulsion polymerization and co-polymerization of dienyl and vinyl monomer [22].

2.2.6. Miscellaneous Applications

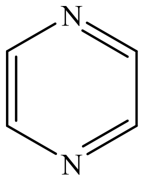
Zinc (II) complexes with benzothiazoles, which are oxidized forms of benzothiazolines, are luminescent. Zinc (II) and Cadmium (II) complexes with N_2S_2 Schiff base ligands are a new class of luminescent compounds, and the careful derivatization of the substituent on the pendent phenyl rings permits fine tuning of the emission wavelength [23]

2.3. Quinoxaline

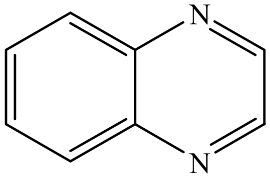
Quinoxalines are a versatile class of nitrogen containing heterocyclic compounds and they constitute useful intermediates in organic synthesis. Quinoxaline, also called a benzopyrazine, in organic chemistry, is a heterocyclic compound containing a ring complex made up of a benzene ring and a pyrazine ring and they are isomeric with phthalazines and quinazolines (24).



Benzene



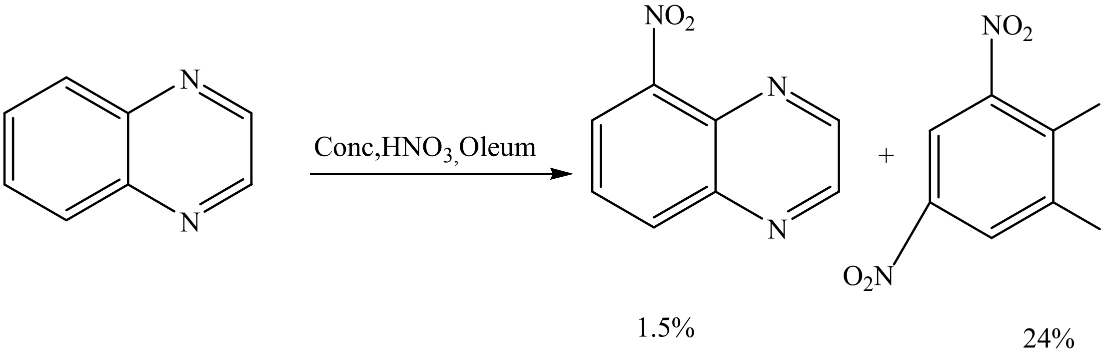
Pyrazine



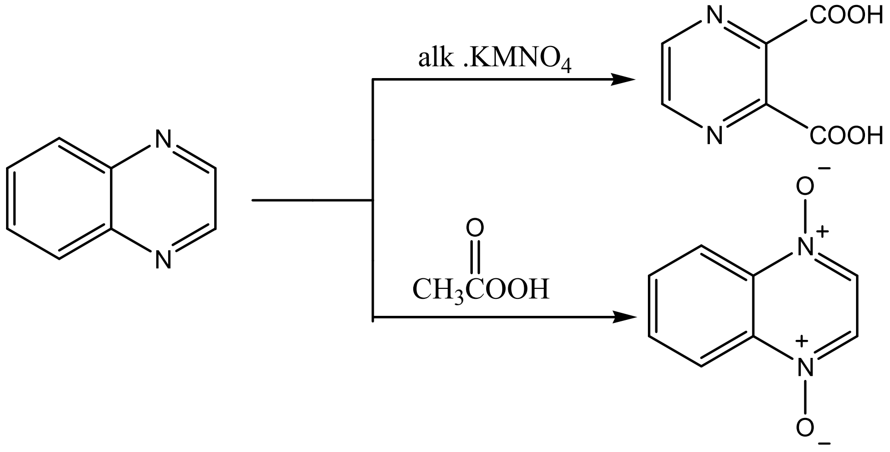
Quinoxaline nucleus

2.3.1. Chemistry of Quinoxalines

Quinoxaline is a low melting solid, m.p 29-30˚C and is miscible with water. It is weakly basic .Quinoxaline forms salts with acids. Nitration occurs only under forcing conditions (Conc. HNO_3, Oleum, 90°C) to give 5-nitroquinoxaline (1.5%) and 5, 7-dinitro- quinoxaline (24%) [24].



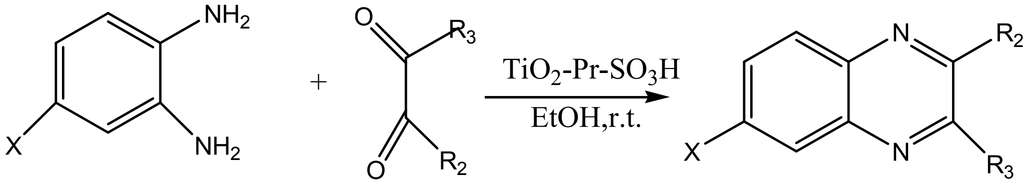
Oxidation of quinoxaline results in the formation of the product depending on the nature of the oxidizing agent employed. With alkaline potassium permanganate pyrazine2, 3-dicarboxylic acid is formed, while with per acid quinoxaline di-N-oxide results [24].



It is a wonderful nucleus which gives almost all type of biological activity. So due to diversity in biological activity it attracts the researchers to find out more its biological activity. But its traditional synthesis suffers from variety of disadvantage such as pollution, high cost, low yield, tedious work-up and long reaction time. Recently different methods have been developed for synthesis of quinoxaline derivatives by use of microwave and catalyst. Quinoxaline is important nitrogen containing heterocyclic compound containing ring complex made up of a benzene ring and a pyrazine ring in medicinal chemistry [24].

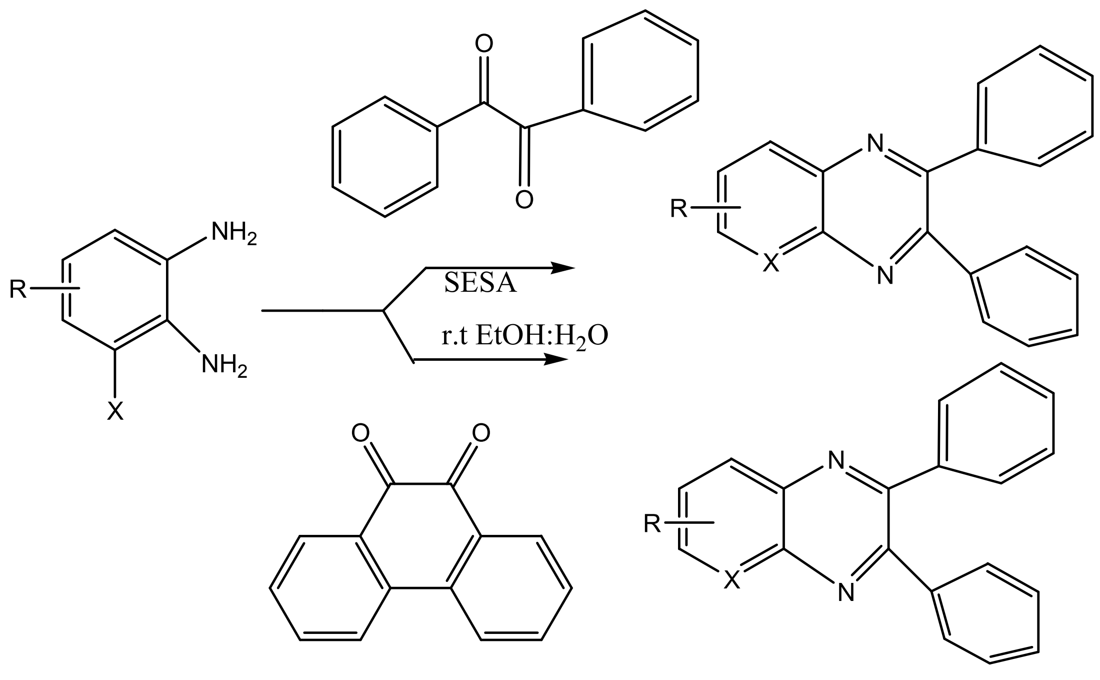
2.4.2. Synthesis of Quinoxaline

The reaction of 1,2-phenylenediamine (1 mmol) with benzyl (1 mmol) in various solvents (EtOH, THF, Me CN, EtOAc, and toluene) and also under solvent-free classical heating conditions in the presence of different amounts of the catalyst. The best result was achieved by carrying out the reaction in the presence of 10 mg of TiO2-Pr-SO3H in EtOH [24].



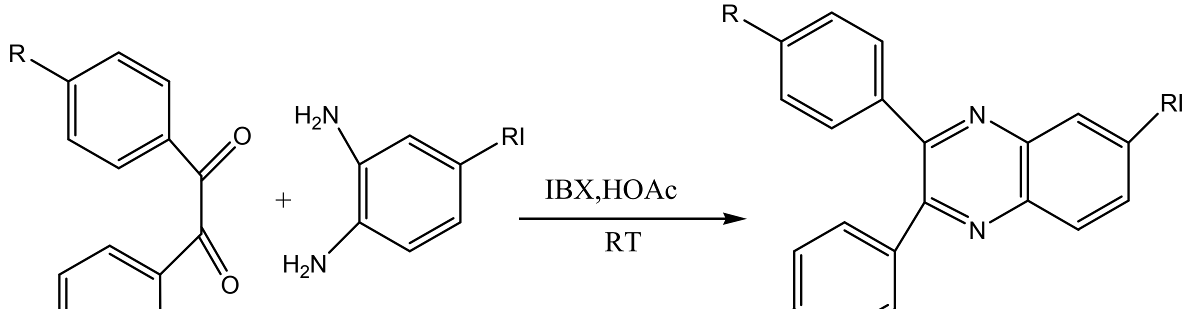
X=H,NO_2 X=H,NO_2

Eco-friendly and efficient method for the preparation of quinoxaline derivatives\in high yields via a one-pot condensation of aromatic diamine and 1,2-dicarbonyl compounds in the presence of [2-(sulfooxy) ethyl] sulfuric acid (SESA)[24]



X=CH,N

A readily available hypervalent iodine (V) reagent, was found to be highly effective in synthesis of quinoxaline derivatives, from 1,2-diketonesandophenylenediamines at room temperature in very high yields[24].



2.3.3. Application of Quinoxaline

Nitrogen containing heterocyclic compounds are indispensable structural units for both the chemists and biochemists. Among the various classes of benzene fused six-membered nitrogen containing heterocyclic compounds, quinoxaline derivatives form an important class of pharmacologically activity. Numerous quinoxaline derivatives have important biological activity such as antibacterial, anticancer, anti-inflammatory agents antimycobial and anticandida, cytotoxic, Antioxidant, Anticonvulsant, antiviral, protein-specific kinase-1, inhibitor activity. In addition, quinoxaline compounds possess in agriculture field herbicides, fungicides and insecticides. They are also used quinoxaline derivatives are in formation of dyes, efficient electron luminescent materials, organic semiconductor, cavitands and dehydoannulenes [25].

2.4. Some Derivatives of Quinoxaline

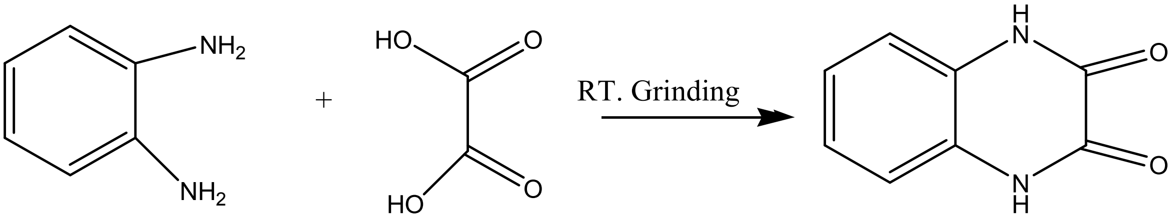
2.4.1. Quinoxaline-Dione

2.4.1.1 Chemistry of Quinoxaline-Dione

Quinoxaline-dione is an organic compound with the formula $C_6H_4\,(NH)_2(CO)_2$. It is a colorless solid that is soluble in polar organic solvents. Various quinoxaline-diones are drugs. Melting point: > 300 °C (572 °F; 573 K).Quinoxaline-dione and their derivatives are important members of heterocyclic compounds that are widely applied in many fields, as curatorial intermediates, bacteriocides and insecticides. It is one of the main classes of known antagonists of amino propanoic acid (AMPA). The quinoxaline moiety is also present in peptide antibiotics. Due to their wide range of applications, these compounds have received a great deal of attention in connection with their synthesis. One-pot efficient synthesis of quinoxaline-dione derivatives may permit the development of novel therapies for the treatment of epilepsy pain and other neurodegenerative disorders. Many synthetic methods for these heterocyclic compounds have been reported which include the use of catalysts and/or some special techniques. However, many of these methods are associated with several shortcomings such as long reaction times, expensive reagents, harsh conditions, and low-product yields, occurrence of several side products and difficulties in recovery and reusability of the catalysts [26].Quinoxalines. which represent an important category among heterocyclic of medical, biological and industrial interests, are 1, 4-benzodiazine derivatives 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, ditriazolo, have been proved as antimicrobial agents [27].

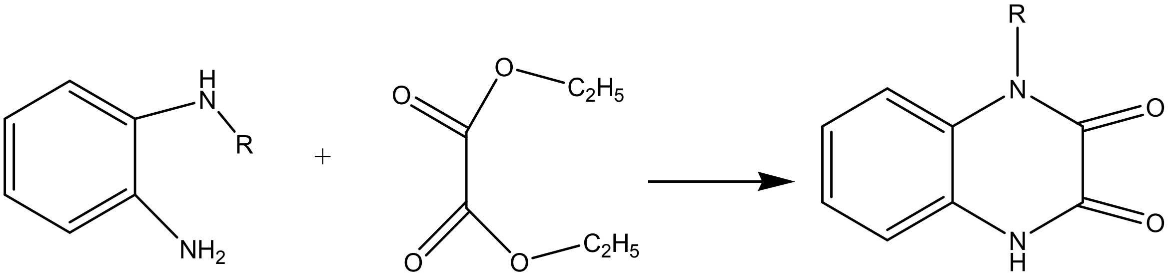
2.4.1.2. Synthesis of 1, 4-dihydroquinoxalin-2, 3-Dione

On the development of newer and cleaner processes for organic reaction attention is drawn to the synthesis of these potential pharmacophore 1,4-dihydro-quinoxaline-2,3-dione derivatives report simple solid phase grinding of the two reactants at room temperature in an open atmosphere to get the product in good yield. Solvent-free method has an operationally simple procedure. In a typical experiment, a mixture of oxalic acid dehydrates and o-phenylene diamine is thoroughly ground with a pestle in a mortar at room temperature in an open atmosphere until the mixture turned into a melt. The mixtures continue to be ground occasionally for different periods; then the melt is crystallizing from water or water/ethanol mixture to get the pure products [26].



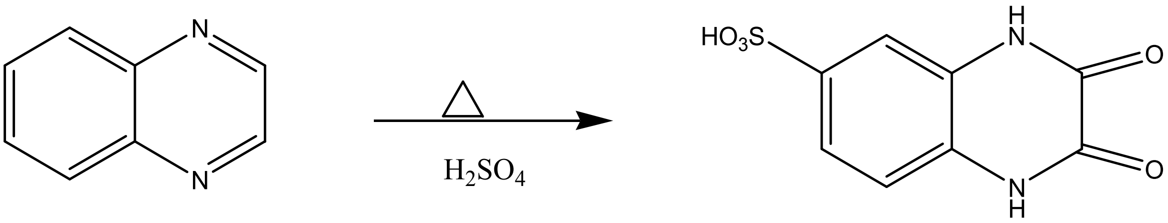
Scheme9. Synthesis of -1, 4-dihydroquinoxalin-2, 3-dione by solvent free method

Various N-substituted quinoxaline-2, 3-diones were synthesized by rotavaporation of 1, 2-diamino aromatic compounds in diethyl oxalate at 50-60^{0}C [26].



Scheme10. Various N-substituted quinoxaline-2, 3-diones synthesis

Electrophilic substitution of aromatic ring of quinoxaline usually occurs at 6th and7th position of aromatic ring of quinoxaline. Thus saponification of quinoxaline 2, 3-dione with fuming sulphuric acid yields the sulphounic acid derivative of quinoxaline-dione.



Scheme11. Synthesis of quinoxaline 2, 3-dione Electrophilic substitution of aromatic ring of quinoxaline

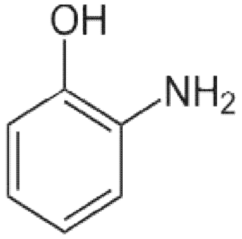
2.4.1.3. Application of Quinoxaline 2, 3-Dione Derivative

Quinoxaline-2, 3-dione derivatives are important classes of nitrogen-containing heterocyclic, as they constitute useful intermediates in organic synthesis. In particular, quinoxaline scaffolds are found as a core unit in a number of biologically active compounds. Quinoxaline including their fused ring derivatives display diverse pharmacological activities such as neuroprotective agents, antifungal, antibacterial, radio protective, anticonvulsant, antimalarial, anticancer, potent antithrombotic, analgesic, anti-inflammatory, antiglaucoma, antiparasite, antituberculosis, hypoglycemic, antiviral, anti-HIV, anthelmintic activities, antidepressant, and antimalarial activities. Literatures are described different series of AMPA receptor antagonistic, one of which is based on the quinoxaline-2, 3-dione structure which have high affinity and selectivity [27]

2.5. 2-Amino Phenol

2.5.1. Chemistry of 2-Aminophenol

2-Aminophenol is an intermediate in the synthesis of dyes. It is particularly useful in yielding metal-complex dyes when diazotized and coupled to a phenol, naphthol, or other aromatic or resonant dye species.2-Aminophenol is an organic compound with the formula C_6H_7NO and soluble in cold water. Along with its isomer 4-aminophenol, it is an amphoteric molecule and a reducing agent. It is a useful reagent for the synthesis of dyes and heterocyclic compounds. Reflecting its slight hydrophilic character, white powder is moderately soluble in alcohols.



Scheme 12.Structure of 2-aminophenol

The compound exhibits intra- and intermolecular hydrogen bonding involving the neighboring amine and hydroxyl groups. As a result, 2-aminophenol has a relatively high melting point (174 °C) compared to other compounds with a similar molecular mass; for example, 2-methylphenol melts at 31 ° Extensive studies have been conducted on complexation of Schiff bases with metals due to the attractive physicochemical properties of metal complexes and broad range of utilization in various areas of science. Such types of complexes have paved the way for exploration and findings of a variety of metal complexes in recent years. [28]

2.5.2. Applications 2-Aminophenol

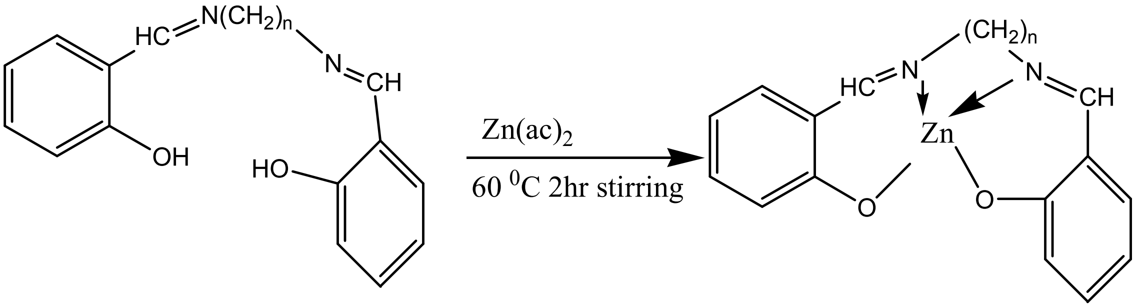
Transition metal complexes of 2-aminophenol based Schiff bases have been the subject of extensive investigation because of their wide use in various fields. These Schiff base complexes have wide applications in biological field, as antidepressants, antimicrobial, antitumor, nematocide, and other medicinal agents have been reported based on these compounds. Furthermore these complexes have good catalytic role in many reactions. The data available for 2-aminophenol based Schiff bases in the literature embraces very wide and diversified subjects, comprising vast areas of organo-metallic compounds and multiple aspects of bioinorganic chemistry [29]. 2-Aminophenol has a variety of uses. As a reducing agent, it is marketed under the names of Atomal and Ortol to develop black-and-white photographs.2-Aminophenol is an intermediate in the synthesis of dyes and in yielding metal-complex dyes when diazotized and coupled to a phenol, naphthol, or other aromatic or resonant dye species. Metal complex dyes using copper or chromium are commonly used for producing dull colors. Tridentate ligands dyes are useful because they are more stable than their bi- or mono-dentate counterparts [30]

2.6. Chemistry of Zinc

Zinc is a metallic element with atomic number 30 and stable isotopes of mass 66, 67, 68, and 70, average 65.38 a.m.u. The terrestrial chemistry of Zn is that of Zn (II) rather than Zn(0).The Zn (II) ion has an electron configuration of $1s^{2}$, $2s^{2}$, $2p^{6}$, $3d^{10}$, and therefore lacks unfilled *d* sub shells in the well-known oxidation state, the requisite criterion for true transition metals. Zinc (II) has an ionic radius comparable with Mg (II) but Lewis acidity more like that of the smaller Cu (II) ion. Zinc is an essential element for terrestrial life since it is required as either a structural component or reaction site in numerous proteins, the zinc-binding portions of which are highly conserved among species. Zinc sites in proteins consist of Zn polyhedral with apical S, N, or O, associated with cysteine, histidine, glutamic acid, aspartic acid, and water. Coordination numbers for zinc range from four in the case of structural Zn associated with four thiol groups derived from cysteine to six in the case of a number of reactive sites containing O and N as apices [31].Literature survey has shown that zinc complexes are very effective in the treatment of athlete foot, ring worm, dry skin, atopic dermatitis, vitiligo, UVB induced sunburn, anaphylactic Shocks etc. Therefore it is widely used in creams, lotions, shampoo, wipes, pad, and ointments [32].

2.6.1. **Synthesis and Application of Zn (II) Metal Schiff Complexes**

Zn (II) ions have a high affinity towards nitrogen, oxygen and sulfur donor ligands. Zinc (II) ion provides a number of coordination compounds because of its affinity towards different types of ligands and flexible coordination number ranging from two to eight. In zinc complexes commonly found geometries are tetrahedral and octahedral. Among these tetrahedral geometry predominates. Six coordinate complexes may be octahedral or trigonal prismatic. Among the less common five coordinate complexes trigonal bipyramidal geometry predominates over square pyramidal geometry [33].Complexation with Zn II metal center usually results in complexes with 4-coordination number and a tetrahedral geometry. This is due to the fact that Zn is a late transition metal with full d valence electrons, which means that a stable 18-electron complex can be formed through 4-coordination number with its ligands. Due to this reason, 5-coordinate, Zn-complex is considered unusual and expected to be unstable [34]. A lot of zinc complexes supported by Schiff base ligands were synthesized and applied to catalyze the ROP of lactide with excellent catalytic performance. Zinc complexes are important as light-emitting materials as well as exhibit electron transport ability, light-emitting efficiency, high thermal and redox stability and tunable electronic properties, ternary complexes as electron transport and electroluminescent materials. Substituted Schiff base complexes with zinc metal exhibit good photo luminescent (PL) and electroluminescent properties. Luminescence properties of zinc (II) complexes originate from organic ligand rather than LMCT because d shell of central ion is completely filled .Molecular structures, degree of conjugation, and substitutes of ligands have a large effect on PL characteristics of zinc–Schiff base complexes. Zinc complexes based on salicylidimine to Schiff base ligands emit light in blue, green, and red region. These compounds show good color purity and there is a possibility to incorporate them in the list of electroluminescent complexes used for the fabrication of full colored OLEDs. Nonetheless, blue light-emitting zinc complexes are rare compared to green and yellow green light-emitting materials [35].



Scheme13. Synthetic route of metal complex

n=2, Bis (salicylidene) ethylene-1, 2-diaminatozinc (II) [Zn (salen)]

n=3, Bis (salicylidene) propylene-1, 3-diaminatozinc (II) [Zn (salpen)]

n=4, Bis (salicylidene) butylene-1, 4-diaminatozinc (II) [Zn (salbutene)]

n=6, Bis (salicylidene) hexylene-1, 6-diaminatozinc (II) [Zn (salhexene)]

n=7, Bis (salicylidene) heptylene-1, 7-diaminatozinc (II) [Zn (salheptene

2.7. Chemistry of Cadmium Metal

Cadmium is a transition metal located in the d-block and 12 group of the periodic table possessing an atomic number of 48 and an atomic mass of 112.411g. Cadmium was discovered in Germany in 1817, by a German scientist, Friedrich Strohmeyer. This element was very commonly used as a sacrificial anode to protect iron and steel from corroding and is also used in nickel cadmium batteries [36].Cadmium has total of eight naturally occurring isotopes. These are ^{106}Cd, ^{108}Cd, ^{110}Cd, ^{111}Cd, ^{112}Cd, ^{113}Cd, ^{114}Cd, ^{116}Cd. Of these eight isotopes, ^{114}Cd and ^{112}Cd are the most common with an abundance of 29% and 24% respectively. Cadmium metal is soft and malleable when pure and is used mostly for electroplating steel (corrosion resistance) and in the manufacture of bearings [37]. Cadmium compounds are also found in oil paints where they provide some brilliant colors (e.g., "cadmium yellow"). In its solid state, this metal is a silvery grey color. Cadmium is a very good electricity conductor, as well as very resistant to corrosion, making it an excellent sacrificial anode for metals such as iron and steel. Like zinc and tin, cadmium metal "cries" or emits a high pitched sound when bent rapidly. Most cadmium today is recovered as a by-product of the zinc refining. Cadmium never occurs in nature in its elemental form. It is always found in a compound with another element. The most common natural compounds of cadmium are cadmium sulfide and cadmium carbonate. Cadmium sulfide, also known as the mineral Greenockite, is the most well known source of cadmium. Cadmium is also found in the Earth's Crust in amounts of about 0.1 to 0.2 ppm, a very small amount. Most of the cadmium that is obtained through a process known as zinc refinement uses its different melting point. Cadmium is a very toxic metal, therefore needs to be handled with great caution. Cadmium can enter the human body through smoking cigarettes, contaminated water due to landfills, certain foods such as shellfish, and mostly through handling the metal itself. This metal when inhaled or digested can cause many health effects, including vomiting, nausea, diarrhea, dry throat, and headaches. More serious affects are still being investigated, but is thought to cause high blood pressure, cancer, heart and liver disease [38]

2.7.1. Synthesis and Application of Cd (II) Metal Schiff Base Complex

Luminescent organic/organometallic compounds have been attracting much attention in recent years because of their potential application in flat panel displays based on organic light emitting diodes (OLEDs). These materials have been shown to be useful in OLEDs because of their relatively high stability and efficiency . Among these materials, cadmium complexes have been especially important because of the simplicity in synthesis procedures and wide spectral response. Extensive research work is going on in various laboratories to synthesize new cadmium complexes containing new ligands to produce a number of novel luminescent cadmium complexes, as emitters and electron transporters in OLED research [39].Industrial production and the use of Cd element can cause environmental pollutions. On the other hand, some of this metal is present in trace amount as essential element for the biological systems and this metal ion also play an important role in bio-inorganic chemistry. In order to understand the role of this metal ion in biological systems, structural studied of the biological compound and his metal complexes is extremely important[40].

3. MATERIALS AND METHODS

3.1. Chemicals and Reagents

The chemicals used for the synthesis of metal complexes and a newly complex ligand were of analytical grade. These include anhydrous salts of the divalent metal of zinc nitrate (Zn $(NO_3)_2$), anhydrous salt of cadmium chloride ($CdCl_2$), oxalic acid dehydrated ($C_2H_2O_4$) and the ligand o-phenylene diamine ($C_6H_8N_2$). Analytical grade reagents like 2-aminophenol and solvent such as distilled water, methanol(MeOH), ethanol(EtOH) ,acetone(CH_3COCH_3),dimethylsulphoxide(DMSO),dimethylformamide(DMF),chloroform ($CHCl_2$) and acetonitrile were used for preparing solution and for washing apparatus.

3.2. Experimental Methods and Procedures

The desired Schiff base was synthesized by conventional method and the metal complexes were synthesized by using template method .The experiment was carried out in the Chemistry Laboratories of Addis Ababa University. In addition, analytical works such as atomic absorption spectroscopy, UV-visible spectrophotometer, conductivity measurements and FT-IR spectra of the synthesized complexes were conducted at Addis Ababa University in chemistry laboratory.

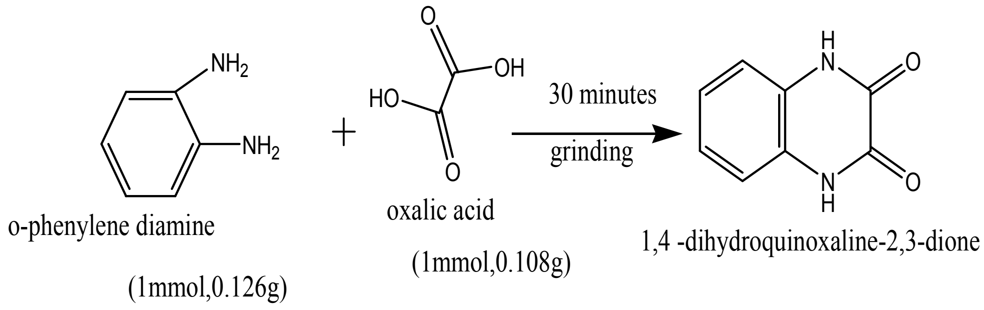
3.3. Apparatus and Instruments

To accomplish the purpose of this study, various ordinary laboratory equipments were used. Instruments such as FT-IR Spectrum 65 PerkinElmer (for running the IR spectra of the complexes using the KBr pellets method), the UV-T-60 UV-Visible spectrophotometer was used to determine the electronic transition of complexes ,Digital melting point apparatus was used to determine the melting point of the newly synthesized ligands and complexes, AAS was used to determine to know quantity of metal in the synthesized complex, the conductivity meter was used to determine the molar conductivity of the complexes. These instruments were utilized for analyzing various products obtained from different preparations as described in the experimental section.

3.3.1. Synthesis

3.3.1.1. Synthesis of 1, 4-Dihydroquinoxaline-2, 3-Dione

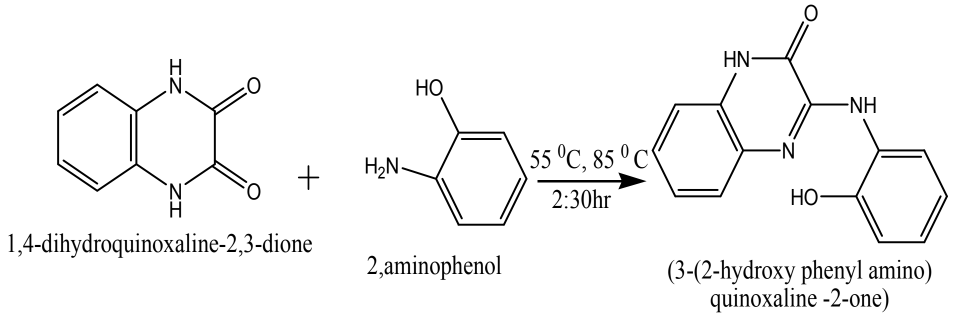
A mixture of solid oxalic acid dehydrate (1mmol,0.126g) and o-phenylene diamine (1mmol,0.108g) were thoroughly ground with pestle in a mortar at room temperature and an open atmosphere until the mixture turned in to melt for 30 minutes. The melted sample dissolved with 1:1 ratio of ethanol and water and concentrated with the temperature of 60^{0}C-65^{0}C and left the concentrated solution at room temperature and atmosphere for four days. After four days the needle shaped green brown color particles were formed.[26].



Scheme14. Synthesis and Structure of 1, 4-dihyroqunoxaline-2, 3-Dione

3.3.1.2 Synthesis of the new complex Ligand

The new complex ligand was prepared as the following procedure. Mixed (1mmol, 0.162g) of 1, 4-dihydroquinoxaline-2, 3-dione with (1mmol, 0.109 g) of 2-amino phenol and dissolved with the mixture of 15 ml of distilled water and 10 ml of methanol and then refluxed the solution at the begging with the temperature 55^{o}C because the boiling point of methanol is 65^{o}C and the temperature gradually increased till 85^{o}C for 2:30hr. The refluxed solution was changed its color from colorless in to pink red solution. This pink red solution was separated by using rot vapor. The newly extracted complex was pink red in its color and solid.



Scheme15.Preparetion and Structure of the Ligand (3-(2-hydroxy phenyl amino) quinoxaline -2-one)

3.3.1.3. Synthesis of Zn (II) and Cd (II) Complexes

Metal complexes were synthesized by the conventional method by mixing the synthesized ligand 3-(2-hydroxy phenyl amino) quinoxaline-2-one with anhydrous salt of the respective divalent metal ion of Zn $(NO_2)_2$ and anhydrous $CdCl_2$ though condensation.

3.3.1.3.1. Synthesis of Zn (II) complex

30 mg of anhydrous Zinc (II) Nitrate (0.012mmol) was mixed (the ratio of ligand(s) to metal 2:1 due to increase chelating enhance the stability of the complex) with the synthesized ligand (3-(2-hydroxy phenyl amino) quinoxalin-2-one) (0.024mmol, 0.06g) and added 20 ml of the deionized water and shake the mixed sample and solvent. Then the solution changed into pale yellow color and made some precipitation settled at the bottom of the round flask at room temperature. To make the metal more reactive with the ligand, the solution was refluxed using oil base for 3hr at the temperature of 85^{0}C.The pale yellow color of the solution changed to red and left this red solution for 12hr at room temperature then white solid precipitate and pink red color solution was formed and separated the precipitation from red color solution by using filtration.

$$Zn(NO_2)_2.6H_2O + 2C_{14}H_{11}N_3O_2 \text{ solv.}H_2O \xrightarrow[\text{Reflux 3hr}]{} [ZnC_{28}H_{22}N_6O_4]$$

3.3.1.3.2. Synthesis of Cd (II) Complex

Cadmium (II) complex was synthesis by using a common procedure that mixed cadmium chloride and the organic ligand (QXDA) in equimolar ratio (1:1) due to the negatively charged ligand(s) could enhance the stability of the fourfold coordination geometry. Organic ligand (QXDA) dissolved with methanol and the solution of this organic ligand (0.119mmol, 30mg) was mixed with (0.119mmol, 0.027mg) of cadmium chloride with continuous stirring, the mixture was refluxed for 7hr and then orange color solution was formed. The orange color Cd (II) complex solution was concentrated. The concentrated solution was filtrated and the filtrated solid orange color was washed with methanol and cold water then dried in vacuum.

$$\mathrm{Cd\ (II)\ Cl_2} + \mathrm{C_{12}H_{11}N_3O_2} \xrightarrow[\text{Reflux 7hr}]{\text{solv. EtOH}} \mathrm{[Cd\ (C_{12}H_{11}N_3O_2)\ Cl_2]}$$

3.4. Determination of Molar Conductivity

Both complexes were dissolved in DMSO and then the molar conductivity of Zn (II) complex in 6.21×10^{-4} M of its solution at 22^0C was measured and also the molar conductivity of Cd (II) complex in1.096×10^{-6} M of its solution at 22^0C was measured.

3.5. Chloride Test

Zn (II) and Cd (II) complexes were dissolved in 10 ml of concentrated nitric acid and digested 2hr until the organic compound decomposed. When 0.1 M solution of silver nitrate was added to the cooled acid solution and left overnight. There was no formation of any precipitate in Zn (II) solution but there was precipitate in Cd (II) solution.

4.6. AAS Determination of Zn (II) and Cd(II) Metal in their Complexes

The zinc metal percentage was estimated by decomposing 6.5 mg of the Zn (II) complex through digestion in 10 ml concentration HNO_3 until a clear solution was observed. The clear solution was diluted more with distilled water in 50 ml of volumetric flask to make the solution of known concentration.

The Cd metal percentage was estimated by decomposing 8.7 mg of Cd (II) complex through digestion in 10 ml conc. HNO_3 until a clear solution observed. The clear solution was diluted more with distilled water in 50 ml of volumetric flask to make the solution of known concentration. The solution was again diluted by adding 4 ml of distilled water.

4. Results and Discussion

4.1. Characterization of the Ligands

4.1.1. Physical Properties of the Ligands

The green color of quinoxalin 2, 3-dione is moisture stable solid and the net mass of the sample extracted was weighed 258 mg (0.258g) and the calculated yield was 85% and the melting point was 384^0C and soluble with DMSO and slightly soluble with DMF but insoluble with water, ethanol, methanol, acetonitrile and chloroform. The pink color complex ligand (3-(2-hydroxy phenyl amino) quinoxalin -2-one) is moisture stable solid and the mass and the melting point were 0.22g and 298^0C respectively and the calculated yield was 25.3%.It was soluble with water, ethanol, methanol, DMSO and insoluble with DMF, acetonitrile, chloroform solvent.

4.2. Characterization of the Complexes

4.2.1. Physical Properties of the Complexes

Both Zn (II) and Cd (II) complexes were obtained as powders with high melting point. Zn (II) complex was insoluble in water, ethanol, methanol, DMF, acetonitrile but slightly soluble in DMSO and The melting point and mass of the newly extracted complex were $>390^0$C and 23mg respectively and the calculated yield was 40%. Cd (II) complex is soluble with DMSO and DMF but insoluble water, methanol, ethanol, acetonitrile and the mass and the melting point of the newly extracted metal complex were 19 mg, $>390^0$C respectively and the calculated yield was 63.27%. They are air and moisture stable solids. The molar conductivity values of each complex measured at room temperature fall in the range 0.0355-20 Ω^{-1} cm^2 mol^{-1} .These values are lower than those expected for an electrolyte in DMSO. These observations indicate that the complexes are non-electrolyte in DMSO at room temperature. The chloride test indicates that chloride coordinated in inner sphere of Cd (II) complex, but the absence of chloride in Zn (II) complex. These observation leads to the conclusion that the Zn (II) complex does not contain any chloride, but Cd (II) complex contain 17 % of chloride in inner sphere of its structure. Some physical properties of the ligands and complexes and the molar conductivity of Zn (II) and Cd (II) are summarizing the following table.

Table 2.Solublity of ligands and their derivative complexes

Compound	Solvent						
	Water	Methanol	ethanol	DMSO	DMF	Acetonitrile	chloroform
QXD	Insoluble	Insoluble	insoluble	Soluble	Partial soluble	Insoluble	insoluble
QXDA	Soluble	Soluble	soluble	Soluble	insoluble	Insoluble	insoluble
Zn-L complex	Insoluble	Insoluble	insoluble	slightly soluble	insoluble	Insoluble	insoluble
Cd-L complex	Insoluble	Insoluble	insoluble	Soluble	soluble	Insoluble	insoluble

Table3. Conductivity values of complexes

Solvent	complex	Molar Conductance	Types of electrolytes
DMSO	Zn-L	$3.55x10^{-2}\Omega^{-1}cm^{2}\,mol^{-1}$	Non electrolyte
DMSO	Cd-L	$20\ \Omega^{-1}cm^{2}\,mol^{-1}$	Non electrolyte

Table 4. Some physical properties of ligands and the complexes

compound	Color	Empirical formula	M.wt g/mol	M.Pt
QXD	Green	$C_8H_6O_2$	134	384^0C
QXDA	Pink	$C_{12}H_{11}N_3O_2$	253	298^0C
Zn-L	White	$[ZnC_{28}H_{22}N_6O_4]$	571	$>390^0C$
Cd-L	orange	$[Cd(C_{12}H_{11}N_3O_2)Cl_2]$	412	$>390^0C$

4.3. IR Spectra of Ligands

4.3.1. **IR Spectrum of 1, 4-Dihydroquinoxaline-2, 3-Dione**

The IR spectrum of the 1,4-dihydroquinoxaline-2,3-dione shows four characteristic bands at 3423cm^{-1},1586 cm^{-1},1513cm^{-1} and 1307cm^{-1} are the region for stretching vibration of υ(N-H), υ(C=O), υ (C-C) and υ (C-N) respectively. The band at 2861 cm^{-1} and 2601 cm^{-1} are the characteristics region of υ (C-H) stretching vibration of benzene. The band at 770 cm^{-1} is the characteristics region of out plane bending vibration of (C-H) in benzene (Figure 3)

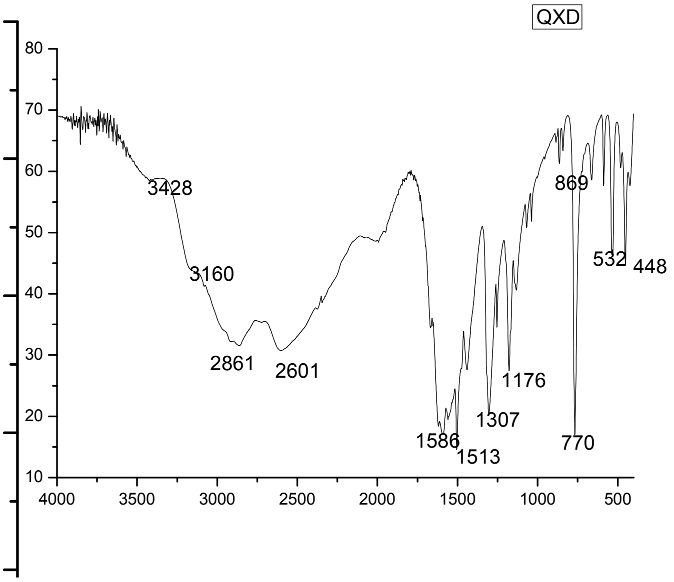


Figure3.IR spectrum of quninoxaline-2,3- dione

4.3.2. IR spectrum of 3-(2-hydrox phenyl amino) quinoxaline-2-one

The IR spectrum of 3-(2-hydrox phenyl amino) quinoxaline-2-one shows that the characteristic region of bands at 3436 cm^{-1}, 3205 cm^{-1}, 1746 cm^{-1}, 1635 cm^{-1}, 1545cm^{-1}and 1505cm^{-1},1471cm^{-1} and 1404cm^{-1} are the region for stretching vibration of υ (N-H), υ (O-H), υ (C=O), υ (C=N), υ (C=C), υ (C-C) respectively. The bands at 2922cm^{-1} and 2848 cm^{-1} are the characteristic region of υ (C-H) stretching vibration of benzene. The band at 1271cm^{-1} and 1276cm^{-1} is the characteristics region of υ (C-N) stretching vibration of in benzene. 741 cm^{-1}, 546 cm^{-1} are the characteristic region of out plane bending vibration of υ (C-H) of in benzene. (Figur4).

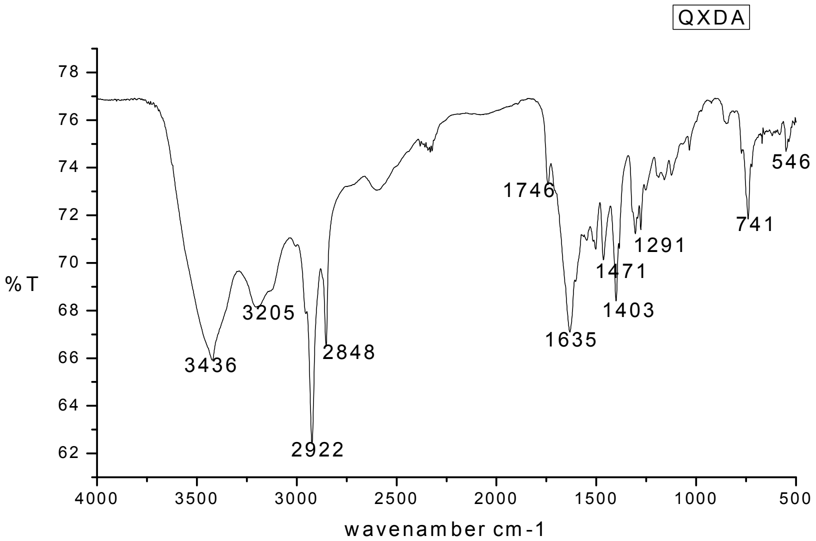


Figure 4. IR spectrum of the newly formed complex ligand

4.4. IR Spectra of Zn (II) and Cd (II) Complexes

4.4.1. IR Spectrum of Zn (II) Complex

In the complex the medium broad band at 3389cm^{-1} is the characteristic region of υ (N-H), the broad week band at 3153cm^{-1} is the characteristic region of υ (O-H), the sharp medium band at 1704cm^{-1} is the characteristic region of υ (C=O),strong sharp band at 1627cm^{-1} is the characteristic region of υ (C=N),the medium intensity at 1374 cm^{-1} and 1322 cm^{-1} are the characteristics region of υ(C-C) on the benzene ring, the medium sharp band at the 1240cm^{-1}and 1105cm^{-1} are assigned the characteristics region of υ(C-N),the strong sharp band at the 815cm^{-1}is the characteristics\ region of out plane the bending vibration of the υ(C-H) of the benzene ring. The additional bands observed at the region of 609cm^{-1},487cm^{-1}, 455cm^{-1} are assigned to ligand metal complex of stretching vibration (figure 6)

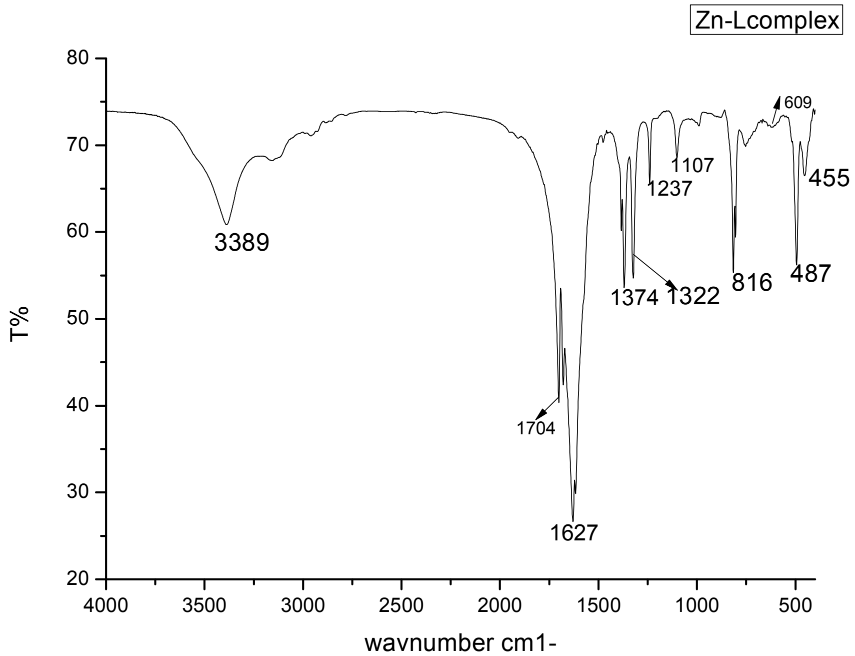


Figure 6.IR spectrum of Zn complex

4.4 1.1. Comparison of IR Spectrum Zn (II) Complex with the free ligand Spectrum

The IR spectrum of Zn (II) 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 (II) complex, the IR spectrum of the free ligand must be compared with the spectrum of the complex. When compared the spectra of metal complex with the free ligand, in the spectra of Zn (II) complex the strong sharp band appeared in the region at 1627cm^{-1} was assigned to υ (C=N) stretching vibration mode. In the corresponding free ligand this frequency for the same group was observed at 1635cm^{-1}. The downward shift of the band in the complex indicate that the υ (C=N) group of the ligand is coordinated to metal ion via its azomethine nitrogen. The weak sharp band in the region 1704cm^{-1} in the IR spectrum of Zn(II) complex was assigned to υ (C=O) stretching vibration . This bands in the corresponding ligand appeared in the region of 1746cm^{-1}, then the change the band position downward shift indicate that the υ(C=O) group of the ligand is coordinated to metal ion via its carbonyl oxygen. The sharp medium band in the region 1374cm^{-1} and 1322cm^{-1} in the IR spectrum of Zn (II) complex were assigned to υ(C-C) stretching vibration, these bands in the corresponding ligands appear in the region 1471cm^{-1} and 1403cm^{-1} the band position change downward shift indicates change in the distribution of electrons and molecular environment around the ligands due to introduction of metal ion cause shift in position. The same change occur the band position that assigned to υ(C-N) in the Zn (II) complex that compared to the corresponding ligand spectrum due to the changing the electron through resonance and the out plane bending vibration of υ(C-H) in Zn (II) complex increasing when it is compared with the corresponding ligand due to the delocalization of the electrons through benzene ring. The newly additional bands observed in the IR spectrum of Zn (II) complex at the region 609 cm^{-1},487 cm^{-1},455cm^{-1} assigned to (Zn-N) and υ (Zn-O) stretching vibrations respectively.

Table5. IR spectral data of free ligand and Zn (II) complex

Compound	N-H cm^{-1}	O-H cm^{-1}	C-H cm^{-1}	C=O cm^{-1}	C=N cm^{-1}	C=C cm^{-1}	C-C cm^{-1}	C-N cm^{-1}	C-H cm^{-1}	Zn-N cm^{-1}	ZN-O cm^{-1}
Free ligand	3436	3205	2922& 2848	1746	1635	1545 & 1507	1471& 1403	1291& 1276	741	-	-
Zn(II) Complex	3389	3153		1704	1627		1374& 1322	1237& 1107	816	609	487& 455

4.4.2. IR Spectrum of Cd (II) Complex

In the complex Cd (II) the sharp medium band at 3408 cm^{-1} the characteristic region of υ (N-H),the sharp week band at 3333cm^{-1} the characteristics region of υ (O-H), the sharp medium, week band at 2922cm^{-1},2856cm^{-1} and 2603cm^{-1} are the characteristics region of υ (C-H), medium sharp band at 1627cm-1 characteristic region of υ (C=O),the week bands at 1604 cm^{-1} the characteristic region of υ (N=C),the weak, strong sharp band at the1560 cm^{-1} and1500 cm^{-1} are the characteristics region of υ(C=C), the medium sharp bands at,1474cm^{-1} and1403cm^{-1} are the characteristics region υ (C-C) respectively, the medium sharp band at 1283cm^{-1},1187cm^{-1}and1128 cm^{-1} are the characteristics region of υ(C-N),the medium and strong sharp bands at the 852cm^{-1} and 755cm^{-1} are the characteristics region of the out plane bending vibration of the υ(C-H) in benzene ring. The additional bands observed at the region of 628cm^{-1},577cm^{-1}, 524cm^{-1},554cm^{-1} are assigned to ligand metal complex of stretching vibration (Figure 5).

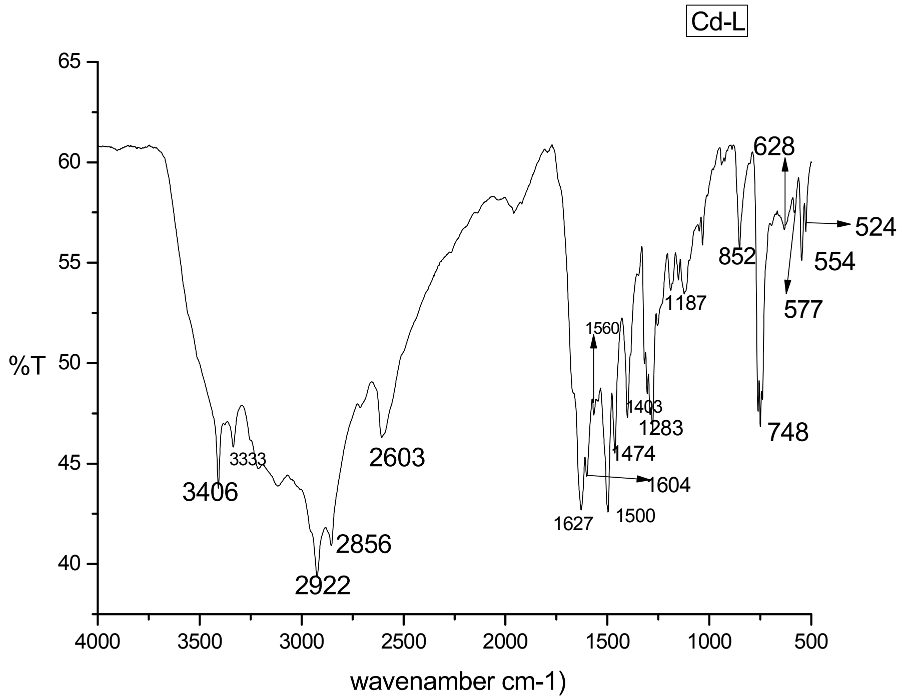


Figure 5 .IR spectrum of Cd complex

4.4.2.1. Comparison of IR Spectrum of Cd (II) Complex with the Free Ligand Spectrum

The IR spectrum of metal Cd (II) 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 Cd (II) complex, the IR spectrum of the free ligand must be compared with the spectra of the complexes. When the spectra of metal complex compared with the free ligand, in the spectrum of Cd (II) complex the medium sharp band appeared in the region at 1627cm^{-1} was assigned to υ (C=O) stretching vibration mode, in the corresponding ligand this frequency for the same group was observed at 1746 cm^{-1}. The downward shift of the band in the complex indicate that the υ (C=O) group of the ligand is coordinated to metal ion via its carbonyl oxygen. The week band in the region at1604cm^{-1} in the IR spectrum of Cd

(II) complex was assigned to υ(C=N) stretching vibration. This band in the corresponding ligand appear in the region of 1635 cm^{-1}, then the change the band position downward shift indicate that the υ(C=N) group of the ligand is coordinated to metal ion via its azomethine nitrogen. The medium and sharp bands at the region of 1471 cm^{-1} and 1404 cm^{-1} in the IR spectrum of Cd (II) complex were the characteristic stretching vibration of (C-C), compared with the corresponding ligand with same group there is no significant change in the band position. The sharp band at the region 1283 cm^{-1} and weak band at the region 1187 cm^{-1} were the characteristic stretching vibration of (C-N) in the Cd (II) complex. Comparing to the corresponding ligand spectra bands of the same group change the position of the bands downward shift indicate the changing the electron through resonance due to the introduction of metal ion. The out plane bending vibration of υ(C-H) in Cd (II) complex show small change compared with the corresponding ligand due to the delocalization of the electrons though benzene ring. The newly additional bands observed in the IR spectrum of Zn (II) complex at the region 628 cm^{-1},577 cm^{-1} and 554cm^{-1},524cm^{-1}assigned to υ(Zn-N) and υ(Zn-O) stretching vibrations respectively.

Table 6. IR spectral data of free ligand and Cd II complex

Compound	N-H cm^{-1}	O-H cm^{-1}	C-H cm^{-1}	C=O cm^{-1}	C=N cm^{-1}	C=C cm^{-1}	C-C cm^{-1}	C-N cm^{-1}	C-H cm^{-1}	Zn-N cm^{-1}	ZN-O cm^{-1}
Free ligand	3436	3205	2922& 2848	1746	1635	1545& 1507	1471& 1403	1291& 1276	741	-	-
Cd(II) complex	3408	3333	2922& 2856	1627	1604	1560& 1500	1474& 14 03	1283& 1187	852& 748	628& 577	554& 524

4.5. AAS results Zn(II) and Cd(II) Metal in their Complexes

4.5.1 AAS result of Zinc Metal in Zn (II) Complex

The metal content of the solution was determined with AAS and the recorded molar concentration was 12.85 mg/L. The percentage of the metal in the solution was calculated as follows

$$\%\ \mathrm{Zn} = \frac{\text{AAS result x volume of solvent use to dilute x100}}{\text{Mass of sample taken}}$$

$$\%\ \mathrm{Zn} = \frac{12.85\ \mathrm{mg/L} \times (50\mathrm{ml}) \times 100}{6.5\mathrm{mg}} = 9.88$$

% Zn = 9.8 this result show the percentage of Zn metal exist in Zn (II) metal complex

4.5.2. AAS result of Cadmium Metal in Cd (II) Complex

The metal content of the solution was determined with AAS and the recorded molar concentration was 9.446 mg/L. the percentage of metal in a solution was calculated as follow.

$$\%\ \mathrm{Cd} = \frac{\text{AAS result x volume of solvent use dilute x100}}{\text{Mass of sample taken}}$$

$$\%\ \mathrm{Cd} = \frac{9.446\ \mathrm{mg/L} \times (50\mathrm{ml}) \times 4\mathrm{ml})}{8.7\mathrm{mg}} \times 100 = 21.74$$

% Cd = 21.74 this result show the percentage of Cd metal exist in Cd (II) metal complex.

Table7. The percentage of the expected and found of Zn and Cd metals in their complexes

	Metal content found and expected		
Complexes	Theoretically	expected	Empirical formula of complexes
Zn(QXDA)2	11.43	9.88	$[ZnC_{28}H_{22}N_6O_4]$
Cd(QXDA)	27.18	21.74	$Cd(C_{12}H_{11}N_3O_2)Cl_2]$

4.6. Electronic Transition of Zn (II) and Cd (II) Complexes

As expected for a d^{10}electronic configuration, the electronic spectrum of Zn (II) complex does not have any d-d transition, but the expected transition was CT that shows the week band at 222 nm and 224 nm and the intense bands that show at 217 nm, 219 nm and 221 nm assigned to charge transfer transition shown as (Figure 8). The similarly Cd (II) ion complex has d^{10} electronic configuration does not show any d-d transition but the absorbed bands that show in the region at 210, 206 nm, 204 nm and 208 nm in Cd (II) complex assigned to a charge transfer transition as shown in (Figure 9). The bands in the region at 268nm and 273nm are assigned to $\pi - \pi *$ electronic transition of benzene ring and n-$\pi *$ electronic transition of carbonyl group as shown in (Figure 7)

Table8. Electronic transition of ligand, Zn (II) and Cd II complexes recorded in DMSO solution.

Compounds	Transition	absorption bands(nm)	Conductivity $\Omega^{-1}cm^2mol^{-1}$	geometry	Magnetic property
QXDA	$\pi - \pi *$ n-$\pi *$	268nm 273nm	-	-	-
Zn (QXDA)	LMCT	222nm-221nm	$3.55x10^{-2}$ $\Omega^{-1}cm^2\ mol^{-1}$	Square planer	non - electrolyte
$[Cd(QXDA)Cl_2]$	LMCT	210 nm-208nm	20 $\Omega^{-1}cm^2\ mol^{-1}$	Tetrahedron	non-electrolyte

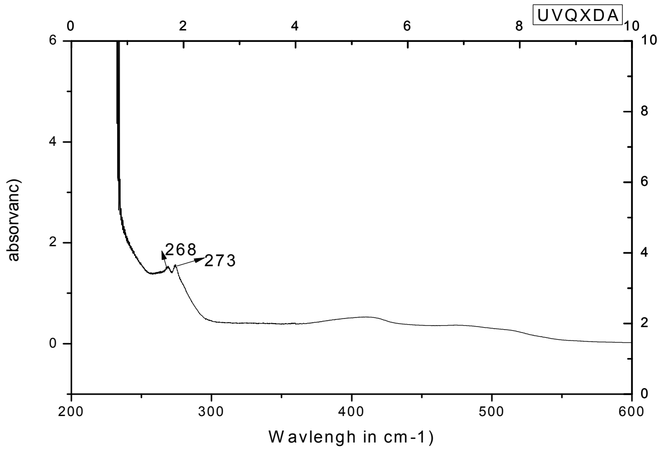


Figure 7. UV -visible spectrum of the ligand

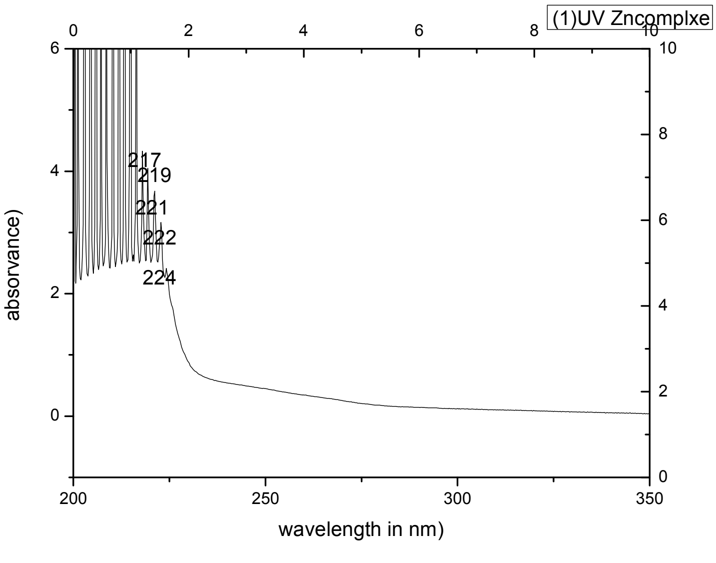


Figure 8. UV -visible spectrum of Zn-complex

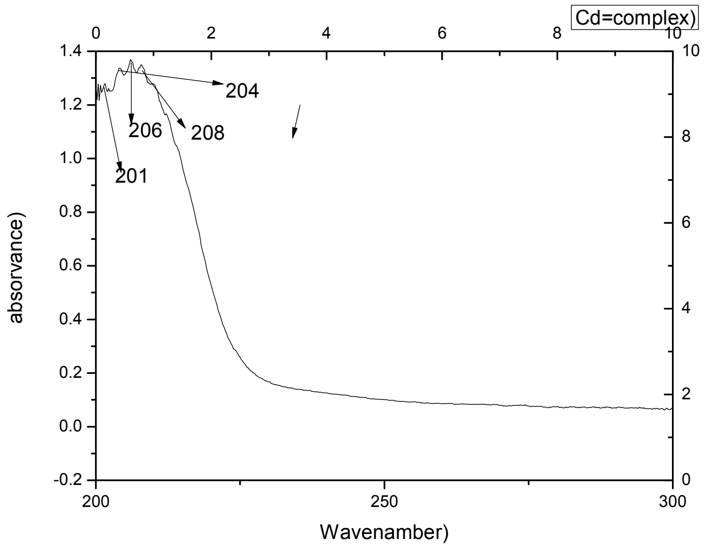
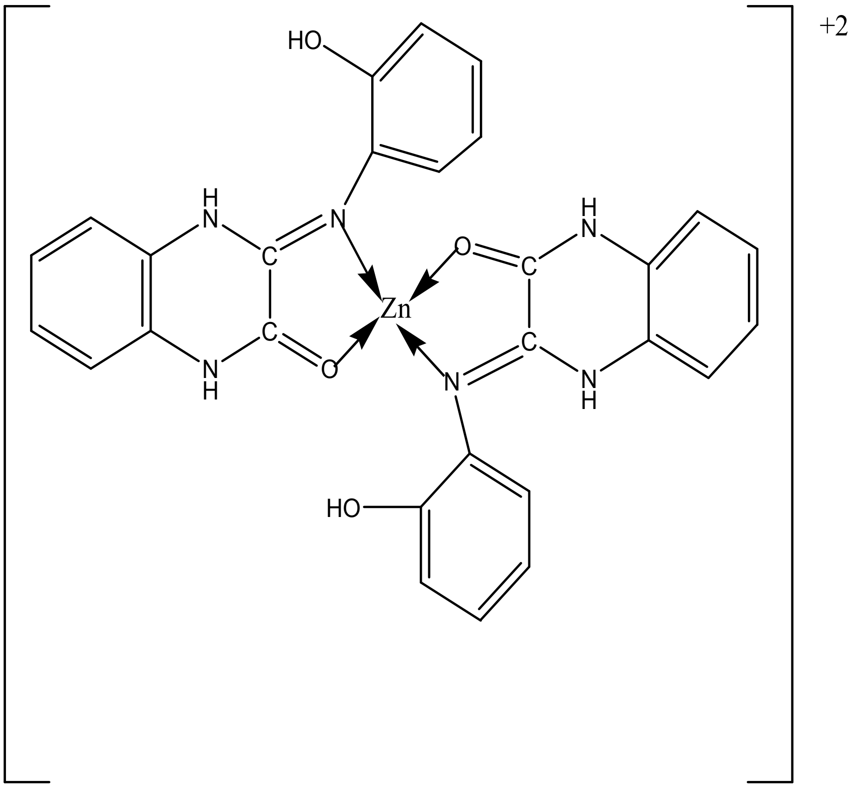


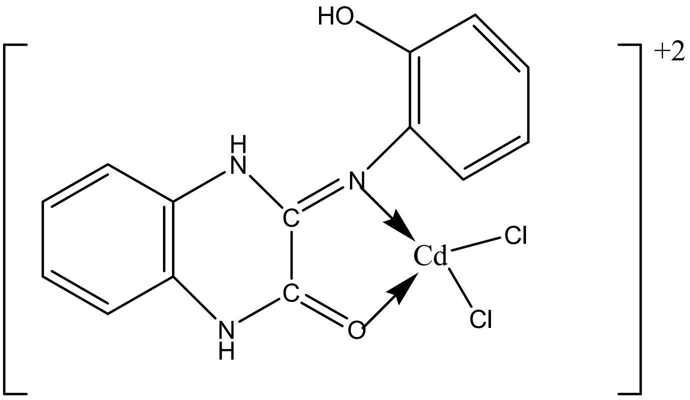
Figure 9.uv-visible spectrum of Cd –L complex

5. Conclusion and recommendation

Based on IR, electronic spectroscopy, AAS measurement results the ligand binds to the metal ions through O and N donor atoms. In the two complexes Zn (II) and Cd (II) the wave number of azomethine and carbonyl group shift downfield when comparing to the free ligand complex wave number of azomethine and carbonyl group, this show with other supportive measurements the ligand form coordination with the vacant orbital's of the metal ions of Zn (II) and Cd (II) .The structures of the newly expected synthesis complexes are as follows.



Scheme16. Structure of expected zinc (II) ligand complex



Scheme17.Structure of Expected Cd (II) metal complex

Recommendation

Coordination compounds have found extensive application in various filed of human interest. Therefore the synthesis, characterization and study of their properties are indispensable. The work done in this project work is not the final but the starting point of synthesis and analysis of the ligands and their metal complexes. In the present day researches of quinazolines derivatives are getting promising application for treatment of disease like anticancer activities and in other area like agriculture, dye industry, and luminescent materials. Therefore as far as the availability of the starting materials and simplified synthesis methods are concerned, further studies and works are immense importance's for their synthesis and divers application.

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