ADDIS ABABA UNIVERSITY

SCHOOL OF GRADUATE STUDIES

SYNTHESIS AND CHARACTERIZATION OF METAL COMPLEXES OF A NEW HETEROCYLCIC LIGAND

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Abstract

N,N'-bis(3-quinoxaline-2-one)diaminopropane, (BQxDP) , and its complexes with metal ions of Cd(II), Ni(II) ,Zn(II), Fe(II), Cr(III), Mn(II) and VO^{+2} were prepared and characterized by IR, ^1H & ^{13}C NMR, electronic spectra and elemental analysis. The IR, ^1H NMR, electronic spectra and elemental analysis are consistent with the formation of the ligand (BQxDP). The elemental analysis, IR, electronic spectra are also consistent with the formation of Fe(II) complex. The structures of metal complexes are proposed by the IR spectra, quantitative tests of metals, chlorides sulphates and elemental analysis of the ligand. The IR spectra of all complexes indicate that the metal ions are coordinated to the azomethine nitrogen.

Abbreviations

BQxDP = N,N'-bis(quinoxaline-2,3-dione)diaminopropane

QxD = quinoxaline -2,3-dione

QPQ = The fusion of two quinoxalines with porphyry(quinoxaline porphyrin quinoxaline)

XT-btpa =(xanthene-bis(tris(2-pyridylmethyl)amine)

The XT-bterpy =xanthene-bisterpyridin

Introduction

1.1 Heterocycles, Quinoxaline and its derivatives

The heterocycles can be conveniently defined as cyclic organic compounds in which one or more of the ring carbon atoms have been replaced by another element such as N, O, or S. They may be either simple aromatic rings or non-aromatic rings. Some examples are pyridine (C_5H_5N), pyrimidine ($C_4H_4N_2$) and dioxane ($C_4H_8O_2$). More than half of the compounds produced by nature have heterocyclic rings incorporated in their structure. Heterocycles are found in fossil fuels, much to the chagrin of environmentalists. Heterocycles containing sulfur and/or nitrogen atoms are useful as components of functional materials since heteroatoms in their rings are helpful to stabilize ions or ion-radical species, and extended π-conjugation decreases columbic repulsion. In addition intermolecular interactions caused by heteroatom contacts can be expected to form novel molecular assemblies (1).

Heterocyclic nitrogens play in turn an important role in coordination chemistry. Imidazole, for instance, is an abundant ligand in chemical and biological systems as it appears as such in proteins, and, together with its derivatives, has been extensively employed for modeling in a wide range of inorganic subject areas, from biological applications to electronic devices and materials (2).

Ring-fused heterocycles which contain more than one nitrogen atom are key structures in a large variety of biochemical processes. For example, purines, pteridines and flavines as well as their metal complexes play an important role in many enzymatic reactions. These quinoxaline-type ligands can act as either neutral or anionic chelators and, in addition, could possibly act as bridging ligands. This leads one to expect that these ligands will exhibit various coordination modes in metal complexes and it is even possible that they can function as controlling ligands in catalytic reaction (3).

Quinoxaline is one of the benzo-fused six-membered heterocycles, which is related to naphthalene in the same way as pyridine with benzene. The fusion of a benzene ring, however, causes decrease in the aromaticity due to the bond alternation (4).

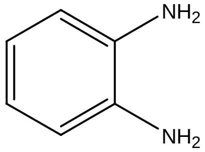
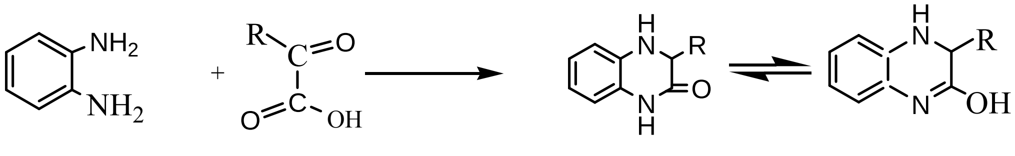


Fig 1 Quinoxaline

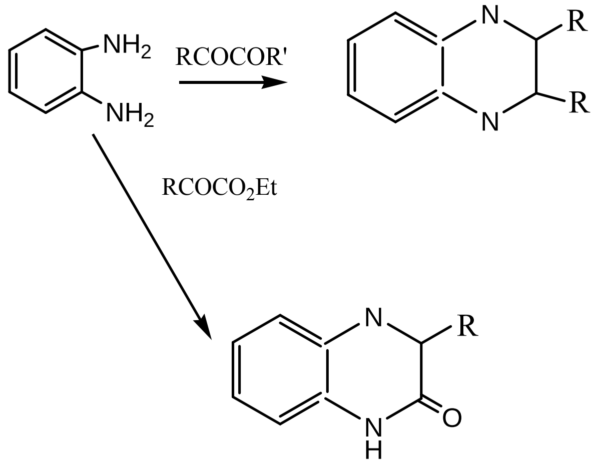
Numerous quinoxaline derivatives are important as antibacterial, antifungal, anticancer, antidepressant and anti-inflammatory agents. On the other hand, there are reports that benzoquinoxalinediones and pyridoquinoxalinediones as tricyclic analogues of 5,8-quinoxalinediones exhibited antitumor activity on L1210 leukemia and sarcoma 180 cell lines. These previous findings on heterocyclic quinones suggested that quinoxaline derivatives might be expected to have antitumor activity. A few papers have appeared in the literature on the antitumor activity of quinoxaline derivatives (5).

The quinoxalines or benzopyrazines are the products formed by the spontaneous condensation of aromatic o-diamines with 1,2-dicarbonyl compounds. Hydroxy quinoxalines-although the α-hydroxyquinoxalines are generally regarded as ketohydrohyquinoxalines, they can exist in the enolic form as true quinoxalines, and it is convenient to consider them members of the latter system for classification purposes.2-hydroxy-3-alkylquinoxalines are readily prepared by condensing α-keto acids or their esters with aromatic o-diamines under conditions similar to those of the classical quinoxaline synthesis.



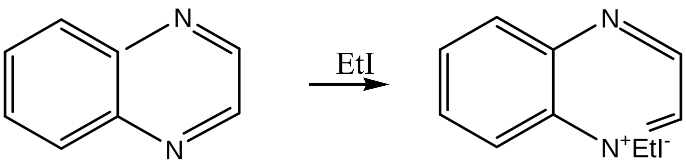
The 2,3-dihydroxyquinoxalines are readily prepared by the condensation of oxalic acid or its esters with aromatic o-diamines in HCl (6).

The standard method of quinoxaline synthesis uses the type of the skeleton as in the interaction of o-phenyldiamine with α-diketones.

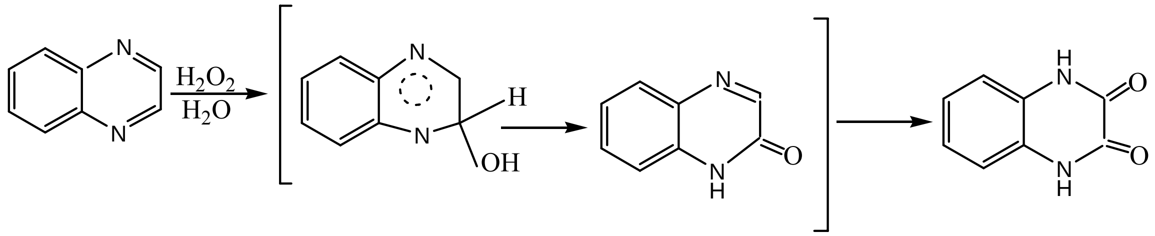


Scheme 1. Condensation of 2, 3-dihydroxyquinoxalines with oxalic acid

Quinoxaline is like pyrazine and also quinoline in many of its reactions. Monoquaternary salts are formed by the action of alkyl halides or dialkylsulfates, but bisquaternary salts are apparently not known.



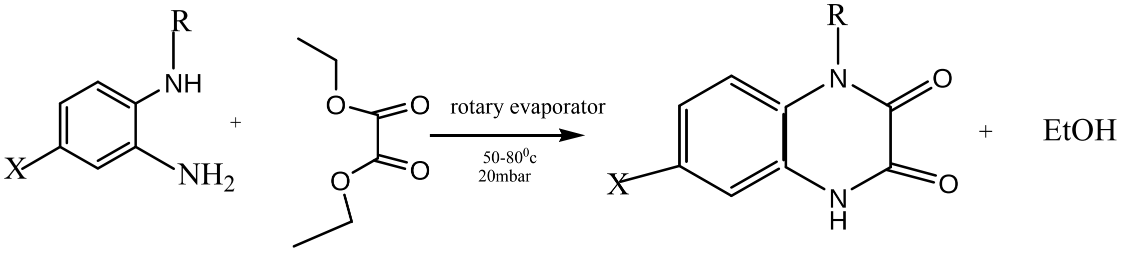
Oxidation of unsubstituted 2-&3-positions competes with n-oxide formation in these reactions. Thus if an aqueous solution is used for peroxidation of quinoxaline, quinoxaline-2, 3-dione is formed, probably via nucleophilic attack and further oxidation.



Scheme 2. Condensation of aromatic diamines

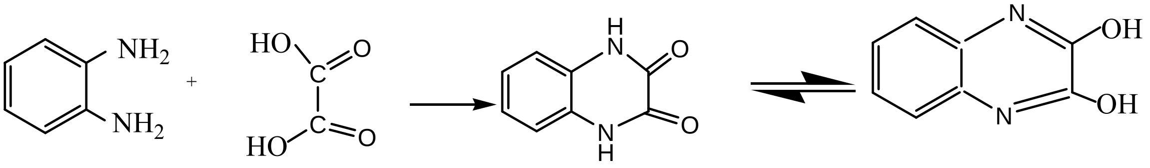
In recent years, polyfunctionalised quinoxalines have been prepared and studied because of their interesting biological activities. Heterocyclic quinones containing nitrogen have been developed for their antitumor and biological activities. Specifically, aminoquinones have attracted attention because of their excellent anticancer activities. Studies on structure activity relationship proved that the number and position of nitrogen in the nucleus play important roles in antitumor activity. For example, 6,7-dichloro-5, 8-quinoxalinedione showed higher antitumor activity than 2,3-dichloro-1,4-naphthoquinone or 6,7-dichloro-5,8-quinolinedione (7).

Quinoxaline-2,3-diones and quinoxaline-2-ones are mainly prepared by condensation of o-phenylenediamines with various ketoacid derivatives , although they can be prepared by other reactions, such as the photorearrangement of quinoxaline-1,4-dioxides. Several general methods are available for preparing o-phenylenediamine derivatives. The ring closure of an o-phenylenediamine with oxalate derivatives, used to form the six-member paradiazine ring of a quinoxaline-2,3-dione, is usually the last and crucial step (8).

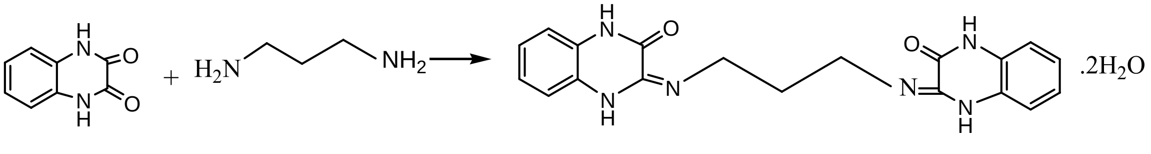


Scheme3. Condensation of o-phenylenediamines with ketoacid derivatives

Here, in the synthesis of the ligand, orthophenydiamine and oxalic acid in the Phillips condensation reaction condense to form quinoxaline-2,3-dione.



This dione is then treated with 1,3-diaminoprppane to form BQxDP(bisquinoxaline diaminopropane).The lignad, BQxDP is expected to be bis –ON donor or ONN donor system to form stable metal complexes of different geometries depending on the nature of coordination of the metal.



N,N-bis(3-imino quinoxaline-2-one)propylenediamine

Scheme 4. Condensation of o-phenyldiamine with oxalic acid followed by 1, 3-diaminopropane

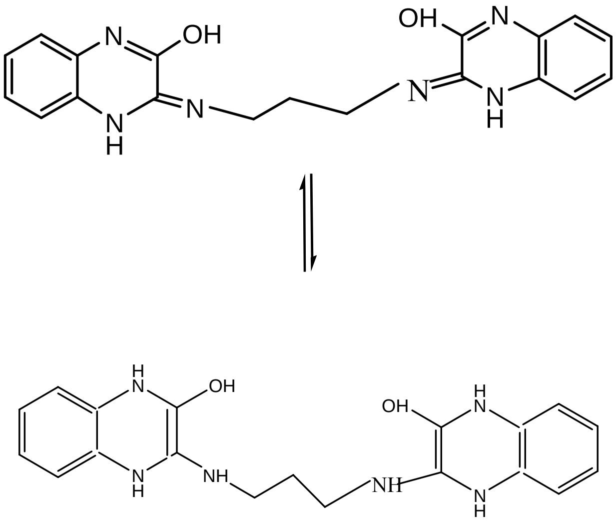


Fig 2. Tautomeric forms of the ligand BQxDP

1.2 The chemistry of metal complexes

Chromium (III) complexes

Cr^{3+} (d^3) – is the most stable and most important oxidation state of the metal, due to the kinetic inertness that many complex species can be isolated as solids and that they persist for relatively long periods in solution. It forms mostly hexacoordinate and sometimes four coordinated complexes. Polynuclear complexes do exist as well. Chromium has a behavior very similar to that of the elements U, W and Mo (which are homologies), but furthermore shows some similarities with the elements of sub-group 6/a, of which sulfur is a characteristic example. d^3 complexes must have 3 unpaired electrons irrespective of the strength of the ligand field and this has been confirmed for all known mononuclear complexes (9).

Chromium, with its coordination number 6, forms hexacoordinate complexes with a large number of ions and molecules, such as aquo, sulfato, and oxalate complexes. These complexes have an octahedral configuration and can give rise to cis- and transisomerism. They are mostly easily soluble in water. A number of organic compounds give rise to chromium chelates. Some of these chelates are insoluble, others form characteristic colors (10).

Cr(III) complexes of octahedral geometry are quite uncomplicated. Octahedral complexes must have three unpaired electrons irrespective of the strength of the ligand field. Magnetic moments should be very close to the spin-only value of 3.88BM. In the spectra of Cr(III) –three spin-allowed transitions are expected, and these have been observed in a considerable number of complexes. These bands are found at 17400, 24700 & 37000cm^{-1} configuration with ^4F ground term. Also in rubby, spin forbidden transitions from the $^4A_2$ ground state to the doublet states arising from the ^2G state of the free ion are observed. These are the $^4A_2 \rightarrow ^2E$ and $^4A_2 \rightarrow ^2T_1$ which give rise to extremely sharp lines because of the slopes of the energy lines for these states are the same as that for the ground state (except in extremely weak fields) (9).

Nickel(II) complexes

Ni^{2+} (d^8) – forms a large number of complexes, the main structural types being octahedral, tetrahedral or square planar. Octahedral nickel(II) complexes having $^3A_{2g}$ ground state are expected to have three allowed transitions. $^3A_{2g} \rightarrow ^3T_{2g}$, $^3A_{2g} \rightarrow ^3T_{1g}(P)$ and $^3A_2g \rightarrow ^3T_{1g}(F)$ in the range of 7000-13000,11000-20000 and 19000-27000cm^{-1} respectively. Two spin-forbidden transitions are also possible, $^3A_{2g} \rightarrow ^1E_g$ and $^3A_{2g} \rightarrow ^1T_{2g}$. The tetrahedral nickel (II) complexes with $^3T_1$ ground state generally exhibit four transitions.$^3T_1 \rightarrow ^3A_2$, $^3T_1 \rightarrow ^1E$, $^3T_1 \rightarrow ^3T_1(P)$ and $^3T_2 \rightarrow ^1T_1$. The band $^3T_1 \rightarrow ^3T_1(P)$ is a strong band of high intensity when compared with others. Square planar nickel(II) complexes don’t have any absorption band below 10000cm^{-1}, due to large crystal field splitting. Hence they can be clearly distinguished from octahedral and tetrahedral complexes (9).

Iron(II) complexes

Fe(II), d^6 –forms a number of complexes, most of them octahedral. Fe(II) complexes are oxidized into Fe(III) complexes. Hexacyanoferrate (II) ion is an extremely stable & well-known complex of iron (II). Hemoglobin (oxygen carrying protein molecule of blood, is another useful complex of iron (II). The electronic spectra of iron (II) has ground state ^5D Fe(II), iron complexes withd^6 configurations are very useful due to their rich and versatile redox chemistry, in addition to their usually favorable kinetic properties and stability.

Fe(II) with ground state ^5D is split by octahedral and tetrahedral ligand fields into $^5T_2 \rightarrow {}^5E$ states. There are no other quintet states; hence only one spin-allowed d-d transition occurs. All tetrahedral complexes are high spin and typically occur at 4000cm^{-1} The magnetic moments are normally 5.0 to 5.2 BM owing to the spins of the four uncoordinated electron and a small second order orbital contribution. For octahedral high spin complexes the $^5T_2g \rightarrow {}^5Eg$ transition occurs in the visible or near IR region(1000cm^{-1}) and is broad or even resolvably split to the Jahn-Teller effect in the excited state that derives from a $t_{2g}^3e_g^3$ configuration. Magnetic moments are ~5.2BM in magnetically dilute compounds (9).

Manganese (II) complexes

Mn^{2+} (d^{5+}) is important and stable, resistant to oxidation. Its complexes have tetrahedral or square planar geometries for four coordination. The geometry of 6coordination is octahedral. In the electronic spectra it's high spin complex of water [Mn $(H_2O)_6$] has

1. Weak bands and pale color complexes
2. Large number of bands
3. Greater variation in the width of bands with one extremely narrow band

It has similar structure in other complexes. The ground state has ^6S which do not split by the ligand field and hence weak bands (9).

Vanadium (IV) complexes

$VO^{+2}(d^1)$ -ion dominates the vanadium (IV) chemistry. Almost all compounds containing VO^{+2} unit are blue and display two other characteristic physical properties. 1) an epr spectrum with characteristic g values and ^{51}V hyper fine coupling and 2) a strong V=O stretching in the range of 950-1000cm^{-1} because VO^{+2} complexes may be five or six coordinate with the additional ligand (trans to V=O bond) showing various degrees of interaction, all of the spectral features reflect the exact nature of the ligand set. In some solid compounds the V=O units are stacked to give V=O.....O=V chains.

The VO bonds can be regarded as multiple ones, with the π-component arising from the flow of electron density O (p π) →V (d π). Pentacoordinate complexes have been shown to take up a sixth ligand quite readily becoming octahedral with donors such as pyridine or $PPh_{3.}$ because of the strong VO π bonding in oxovanadium (IV) compounds, the interpretation of the electronic spectra isn't as simple as it would be for an ordinary octahedral complex and at present there are some unresolved differences of opinion as to the interpretation of the spectra of the exact ordering of the orbitals (9).

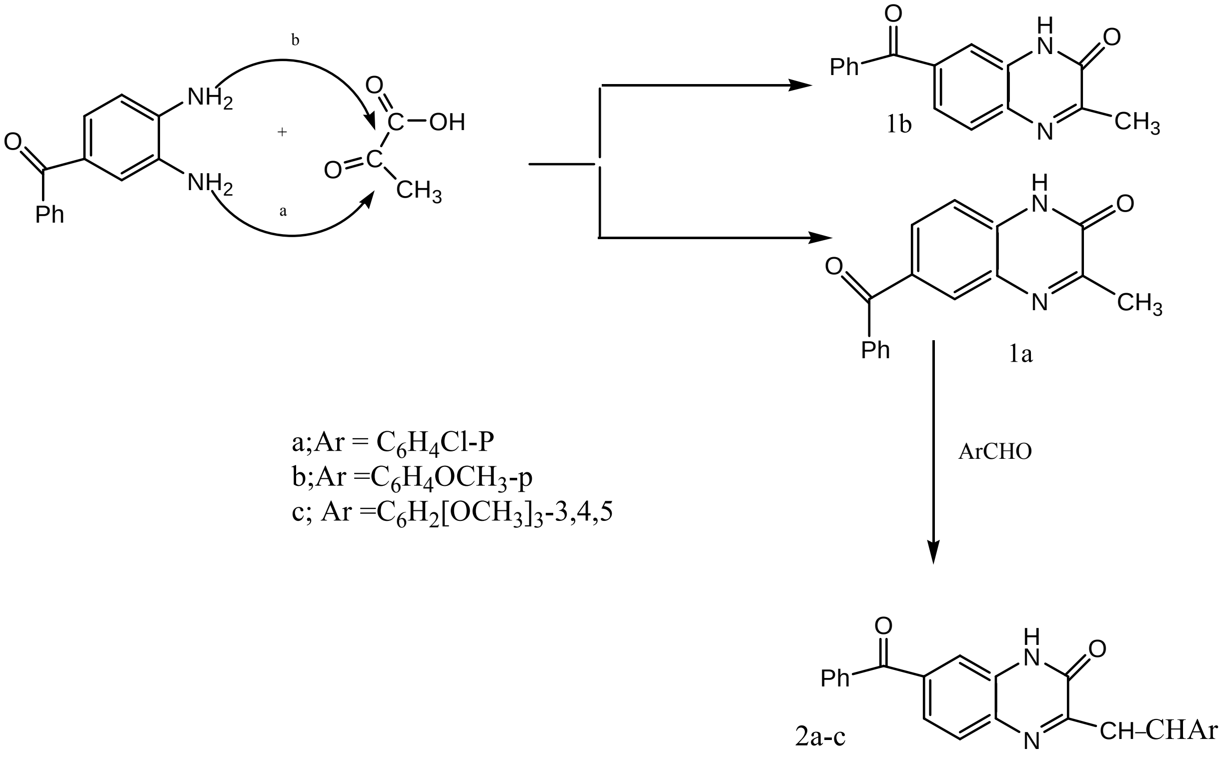
Zinc (II) and Cadmium (II) complexes

There are no ligand field stabilization effects in Zn^{2+}, and Cd^{2+} ions because of their completed d-shells. Thus the stereochemistry of their compounds is determined solely by consideration of size, electrostatic forces and covalent bonding forces. The effect size is to make Cd^{+2} more likely than to assume coordination number of six. In their complexes, Zn & Cd often have coordination number six, but four is more common. The dithiocarbamates form 5-coordinate 1:1 complexes with amines; a similar Cd complex is probably the only example of a 5-coordinated Cd^{+2} complex. These metal ions are diamagnetic and don't possess' d-d transition due to a d^{10} configuration (9).

1.3 Literature survey

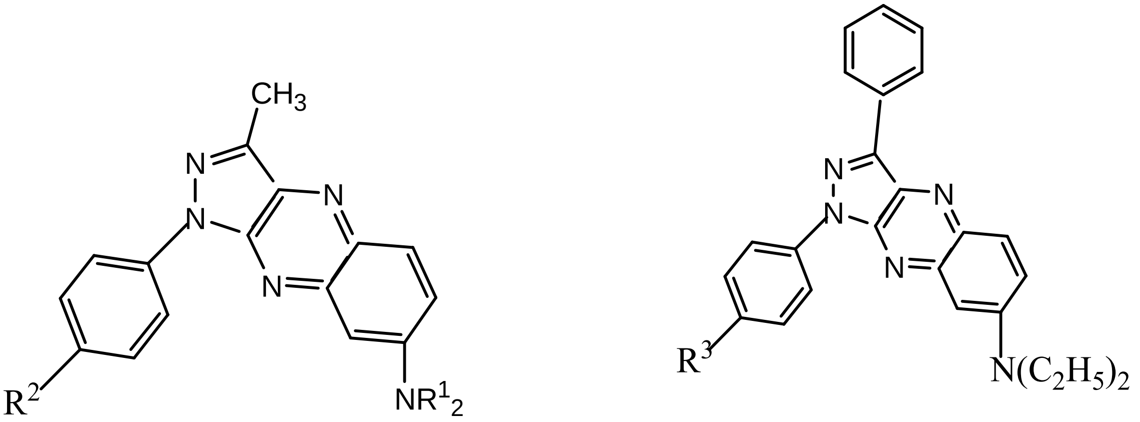
Numerous quinoxaline derivatives are important as antibacterial, antifungal, anticancer, antidepressant and anti-inflammatory agents. From this point of view, it was of interest to synthesize some quinoxalinone derivatives with the aim of investigating their antimicrobial properties. Condensation of 4-benzoyl-1,2-phenylenediamine with sodium pyruvate in acetic acid at room temperature furnished two products which showed analytical and spectral data in good agreement with the 3-methylquinoxalinone structures

1a,**b**. The reaction proceeds due to the (–R) effect of the benzoyl group which deactivates the p-amino group, thus the m-amino group initiates the reaction to give 6-benzoyl-3-methyl-2(1H) quinoxalinone **1a** as the main product (60%). The second isomer was obtained in 30% yield and identified as 7-benzoyl-3-methyl-2(1H) quinoxalinone **1b** (11).



Scheme 5. Quinoxaline derivatives with antimicrobial properties

Organic light-emitting devices (OLEDs) have received much attention because of their potential applications in flat-panel displays. It has been shown that doping a suitable dye into a host layer can improve both the efficiency and the stability significantly. Thus, it becomes a very important task to search for doping dyes with desired properties, such as high emission quantum yield, high thermal and photochemically stability, good color purity etc. For example, doping highly fluorescent dyes,such as coumarin derivatives, quinacridone and its derivatives, into a host, such as tris(8-hydroxyquinolinato)aluminum (Alq3) can remarkably improve the efficiency and hue of green-emitting devices. Several new 1H-pyrazolo quinoxaline derivatives with N,N-dialkylamino as the electron donating group were prepared; their photoluminescence in solution and electroluminescence have been investigated; they show emission at about 520–540 nm with a fluorescence quantum yield close to unity in solution; devices fabricated by using these compounds as dopants show green emission with efficiencies of 7.5–9.7 cd A21 and a narrow bandwidth of 65–70nm peaking at 530–545 nm. More recently, some pyrazolo[3,4b]quinoxaline derivatives have been prepared and used as photoinitiators.

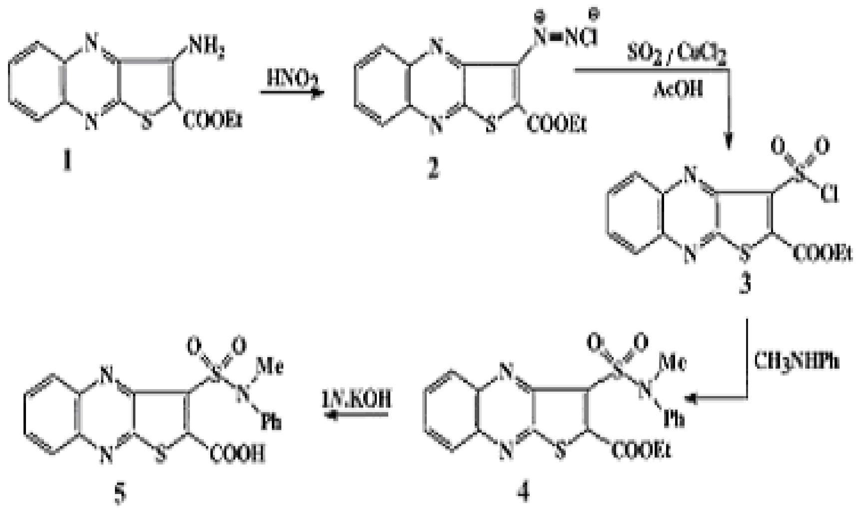


1 $R^1 = CH_3$, $R^2 = CH_3$
2$R^1 = C_2H_5$, $R^2 = H$
3$R^1 = C_2H_2$, $R^2 = CH_3$

4 X = N, Y = C, $R^3 = H$
5 X =N, Y = N, $R^3 = CF_3$

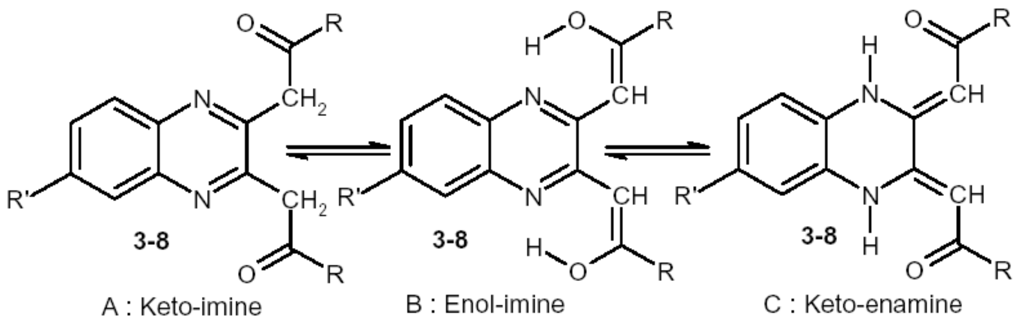
Scheme 6. Quinoxalinederivatives which can be used as photoinitiators

Among the wide variety of quinoxaline derivatives that have been explored for developing pharmaceutically important molecules for examples, imidazoquinoxalines ribonucleosides as linear of antiviral, pyrazoloquinoxaline showed a relatively high antibacterial activity wherein MIC value was 25μ g/mL against Bacillus Licheniformis and Cellulomonas, quinoxaline-1,4-di-N-oxides for treatment of tuberculosis, pyrimido[4,5-b]quinoxaline used as anti-hypertensive and blood platelet antiaggregating agents, also some quinoxaline derivatives have a cytotoxic effects on human cancer cell lines, commercially important as agrochemicals, herbicides, hypoxic-cytoxic agents, antivirus (HepatitisB), antimicrobial, and amebicides (12).



Scheme 7. Pharmaceutically important molecules

It is aimed to synthesize some different heterocycles systems fused with thieno[2,3-b]quinoxaline hoping that they may be highly biologically active. The reaction of 3-amino-2-ethoxycarbonylthieno [2,3-b]quinoxaline with nitrous acid and then sulfur dioxide and cupric chloride in acetic acid gave the 2-ethoxycarbonylthieno[2,3-b]quinoxaline- 3-sulfonylchloride 3 via the diazonium salt. The reaction of 3 with N-methylaniline afforded the 3-sulfamoylthienoquinoxaline 4, whose hydrolysis provided the 3- sulfamoyl-2-carboxylic acid 5 (Scheme 7). In modern times, the treatment of wastewater constitutes a crucial part of most industrial processes. Efficient separation of metal ions by solvent extraction either from industrial wastes or from raw materials is gaining importance as the most common technique used. The literature is well documented with the use of α-diketones and quinoxalines as chelating ligands in solvent extraction. Previous studies focused on the extraction of lanthanoids by 1-phenyl-3-isoheptyl-1,3-propanedione and a-diketones, which have been extensively used as extractants in the separation of metal ions. Also, quinoxaline derivatives are currently being studied as chemical chelants and have been employed extensively as analytical reagents in the determination of metal ions by liquid-liquid extraction (13).



Scheme 8. Different tautomeric forms of quinoxaline derivatives

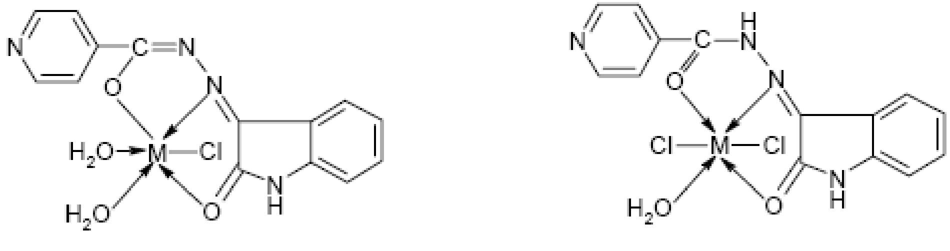
Ni/Fe hydrogenase catalyzes the formation / consumption of molecular hydrogen and is one of the most important Ni enzymes. It is interesting not only for its biological importance but also for its potential relevance to bio-energy applications in the future. Sulfur ligated Ni and NiFe complexes are often useful in modeling the active Ni sites for the corresponding hydrogenases. Geometric structure and electronic structure are the two major interesting aspects concerning metal complexes (14).

Metal complexes of Schiff bases have played a central role in the development of coordination chemistry. From the survey of existing literature, it appears that benzil monophenylhyrazone and its related compounds have been extensively used as biologically active complexing agents and analytical reagents. Keeping the above facts in mind transition metal (II) complexes with Schiff bases in the synthesis and characterization of Cu(II), Co(II), Ni(II) and Zn(II) complexes of Schiff base derived from the condensation of benzil-2,4-dinitrophenylhydrazone with aniline, the IR spectrum of the free ligand was compared with the spectra of the metal complexes. Benzil-2,4-dinitrophenylhydrazone shows its characteristics absorption bands in the

3100, 1645,1620 and 920 cm^{-1} regions, assignable to N–H, C=O, C=N and N–N vibrations respectively. The appearance of a band at 19240 cm^{-1} due to $^3A_2g \rightarrow {}^3T_{1g}(P)$ transition favors an octahedral geometry for the Ni(II) complex. The absence of any band below 10,000 cm^{-1} eliminates the possibility of a tetrahedral environment in this complex (15).

Schiff bases of p-substituted aniline and its complexes have a variety of applications in biological, clinical and analytical, fields. Earlier work has shown that some drugs show increased activity when administered as metal chelates rather than as organic compounds. The Ni (II) complex shows absorption in the region 20,000 cm^{-1} assigned to $1A_{1g} \rightarrow 1B_{1g}$ transition that suggests square-planar geometry. The electronic absorption spectra of the Schiff base and its Cu (II), Co (II) and Ni (II) complexes were recorded at room temperature using DMSO as the solvent. The electronic spectrum of the free ligand shows a band at 25,706 cm^{-1} that is assigned as intra-ligand charge transfer band (INCT) (16).

For metals of Zn, Cd, and Hg complexes [M (LH) Cl_2 (H_2O)], the data indicates the implication of the oxygen atom in coordination. In the IR spectra of the complexes [MLCl (H_2O) $_2$], the hydrazidic C=O band disappears. Moreover, in the IR spectra are observed new absorption bands at 1188─1191 cm^{-1}; these new bands are assigned to the vibrations of the C-O-M bonds (17).



[MLCl(H_2O)$_2$]

[M(LH)Cl_2H_2O]

M = Zn(II), Cd(II), Hg(II),
LH = isatin isonicotinoyl hydrazone

Fig 3. Possible geometries of the metals based on conductivities, IR & electronic spectra

In search for rationally designed dimanganese complexes that catalyze four-electron oxidation of water to dioxygen, two xanthene-based dinucleating ligands were developed, XT-btpa and XT-bterpy

The XT-btpa (xanthene-bis(tris(2-pyridylmethyl)amine) ligand has two metal-binding sites that are located in a well-defined geometry determined by the rigid xanthene spacer. The manganese complex was found to have an $[Mn_2(\mu\text{-}O)_2]$ core. The XT-bterpy ligand also has two metal-binding sites with a well-defined geometry, and has two terpyridine units which provide more rigid and less decomposition-prone organic environment. Three manganese complexes, $[(\text{XT-bterpy})Mn_2Cl_4]$, $[(\text{XTbterpy})\ Mn_2(\text{tropolonato})_2](ClO_4)_2$, and $[(\text{XT-bterpy})Mn_2(\text{2-picolinato})_2](ClO_4)_2$, were prepared. Any of these three complexes catalyzed disproportionation of H_2O_2 to water and dioxygen, with much higher activity than the related mononuclear complex [(terpyridine) $MnCl_2$ (18).

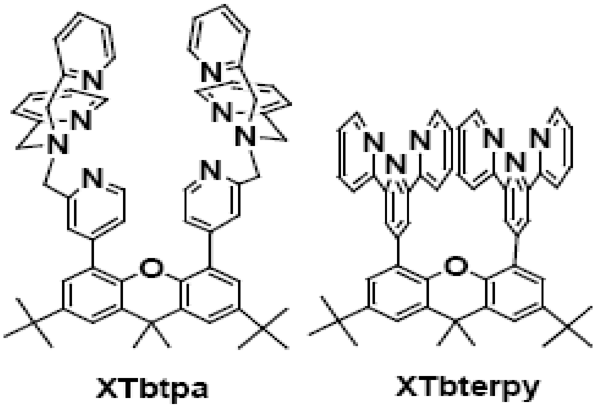
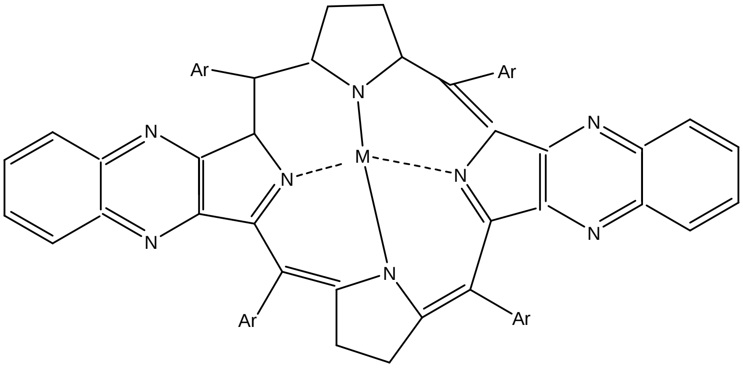


Figure 4. Two xanthene-based binucleating ligands.

The hydrolysis of ATP and ADP by ecto-nucleoside troposphere diphosphohydrolase 1 (CD39) requires divalent cations, like Ca^{2+} and Mg^{2+}. When VO^{2+} was used as a substitute for Ca^{2+}, the ATPase activity of soluble CD39 was 25% of that with Ca^{2+} as cofactor. Protein ligands of the VO^{2+}-nucleotide complex bound to the catalytic site of soluble CD39 were characterized by electron paramagnetic resonance (EPR) spectroscopy. The EPR spectrum contained one species designated T with VO^{2+}-AMPPNP as ligand. Two species D1 and D2 were observed when VO^{2+}-AMPCP was bound to soluble CD39. The results suggest that species D1 and D2 represent the metal-

ADP complexes at the catalytic site of soluble CD39 corresponding to the intermediate formed during ATP hydrolysis and the substrate for further hydrolysis, respectively.VO^{2+} can functionally substitute for Ca^{2+} as a cofactor of sCD39, and it produces four different EPR features when bound in the presence of different nucleotides or in the absence of nucleotide (19).

The electrochemistry of t-butyl-tetraphenylporphyrin and t-butyl-tetraphenyl-quinoxalinoporphyrin, represented as (P)M and (PQ)M were investigated in the different nonaqueous solvents. Electrochemical data showed that the fusion of an electroactive quinoxaline group to an electroactive porphyrin (P_PQ) results in easier reductions of the porphyrin part of the molecule while the quinoxaline-centered redox processes shifts to more negative potentials. The fusion of two quinoxaline groups either on the opposite side of porphyrin (P_QPQ) or on the corner side of the porphyrin (P_PQ2) both result in even easier reductions with the shift in $E_{1/2}$ amount to 20 to 200 mV. (QPQ)M is the most reducible among these four kinds of complexes. The average HOMO-LUMO gaps for the (PQ2)M and (QPQ)M derivatives is 2.03 ± 0.02 V and 1.93 ± 0.03 V, respectively (20).



M=Cu, Zn, Ni, Pd

QPQ

Figure 5. Structures of the investigated complex.

2. Experimental

2.1 Materials **and methods**

All metal salts and other reagents were of AR grade. Distilled MeOH, EtOH and DMSO solvents were used. Melting points were determined using LEICA GALEN (III) compound microscope as well as Electro thermal melting point apparatus. IR spectra were recorded by Perkin Elmer BX between the range of 400-4000 nm using KBr discs as reference compound. Electronic spectra were recorded using spectronic genesys 2pcin DMSO solutions in the range of 200-1100 nm at room temperature. Magnetic susceptibility measurements were carried out using MSB Auto, Sherwood and elemental analysis was carried out using Flash FA 1112 Elemental analyzer

2.2 Synthesis

2.2.1 Synthesis of quinoxaline-2, 3-Dione

To synthesize QxD, o-phenylenediamine (10mmol), oxalic acid (10mmol) and 6ml of 4N HCl were refluxed in 4N HCl for15 mins. A pale blue crystalline solid was formed which was cooled, collected, washed with water and alkali and then acidified with HCl. Its yield was 58%.

2.2.2 Synthesis of N, N'-bis (3-quinoxaline-2-one) diaminopropane (BQxDP)

The ligand was prepared by adding 5mmol of quinoxaline-2, 3-dione and 29.9 mmol (2.5ml) diaminopropane and refluxed for about 2 hrs and cooled. The precipitate was filtered off, washed with ethanol and dried. It yielded 46%.

2.2.3 Synthesis of the complexes.

The complexes were prepared by using 0.5mmol of the ligand(BQxDP) in hot methanol (10ml) and 0.5mmol of metal ion salt solutions were added to it. The reaction mixtures were refluxed for 8-12 hrs.The solid products obtained were filtered, washed in methanol, and dried.

3. Results and discussion

3.1 Characterization of the ligand

3.1.1 Physical properties of the ligand

The ligand is stable at room temperature having pale rose color and a decomposition temperature of >360^{o}c. The ligand is soluble in DMSO but slightly soluble in $CHCl_3$

3.1.2 Elemental analysis

Elemental analysis result showed that there is a direct correlation between the calculated and the experimentally found values indicating the formation of the ligand with the formula $C_{19}H_{22}O_4$(BQxDP.$2H_2O$)

Table 1. Elemental analysis data of the ligand

H (%) Cal(found)	N (%) Cal(found)	C (%) Cal(found)
5.52(5.61)	21.10(20.89)	57.28(56.85)

3.1.3 IR spectra

The IR spectrum of quinoxaline 2,3-dione(QxD) shows a strong absorption at 1680cm^{-1} corresponding to the C =O stretching mode of vibration. The ν C= O of the ligand (BQxDP) appears at 1653cm^{-1}, which is a lower frequency than the quinoxaline 2,3-dione(QxD). This lowering of frequency is due to the H-bonding interactions existing with in the ligand. The peak observed at 1506cm^{-1} is due to the N─H bending mode of vibration, and another peak observed at 1603cm^{-1} is assigned for C=N stretching mode of vibration. Absorption frequencies observed at 3089cm^{-1} is assigned to N-H aromatic stretching, 2967cm^{-1} to ν aromatic C-H, 2864cm^{-1}to CH_2 asymmetric & 2894cm^{-1}correspond to ν CH_2 symmetric stretching. Absorption bands between 1225─950cm^{-1} are assigned to the inplane bending and bands below 950cm-1 are assigned for out of plane bending of the phenyl group (21).

Table 2. IR spectrum of the ligand(BQxDP) and QxD

Compound	ν NH(exo+ring) + ν OH	νC=O	ν C=N
QxD	3500-2870	1681	----
Ligand(BQxDP)	3500-2800	1654	1588

3.1.4 Electronic spectra

The electronic spectrum of the ligand (BQxDP) shows absorption bands at 32154cm^{-1}, 30959cm^{-1}, 29325cm^{-1} and 27624cm^{-1}.Out of these bands the band at 32154cm^{-1} may be assigned to $\pi \rightarrow \pi^*$ transition of the benzene ring and the peak observed at 29325cm^{-1} is assigned for the $n \rightarrow \pi^*$ transition of the carbonyl(C=O) functional group. The band at 30959cm^{-1} is due to the azomethine group in the ligand.

3.1.5 ^{1}H and ^{13}C NMR

The ^{1}H NMR spectrum shows a quintet peak at δ 1.5ppm due to the middle CH_2 and a triplet at δ 2.1ppm due to the terminal CH_2 groups bonded to the azomethine. The peak at δ 7.1ppm is assigned to aromatic protons and at δ11.8ppm due to N-H protons.

3.2 Characterization of metal complexes

3.2.1 Physical properties

Complexes of Fe(II), Zn(II), Cd(II), Ni(II) and Cr(III) are soluble in DMSO but Mn(II) and VO^{+2} complexes are almost insoluble in most organic solvents. A mixture of DMF with nitro methane slightly dissolves VO^{+2} complex. Complexes of Ni^{2+} and Cr^{3+} have pale yellow color, Zn^{2+} and Cd^{2+} have white color, Fe^{2+} red, Mn^{2+} pale black, Vo^{2+} yellowish green. All the metal complexes donot melt until $340^{O}{}_{C}$.

3.2.2 Elemental analysis

Table 4. Elemental analysis of Fe(II) complex

Compound	H (%)cal (found)	N (%) cal (found)	C (%) cal (found)	M (%)cal
Fe(II) complex	3.75(5.10)	15.78(16.88)	42.85(46.63)	10.52

Complex	% calculated	% experimental
Cd^{+2}	19.27	17.28
Cr^{+3}-1	11.60	18.53
Fe^{+2}-1	10.52	7.93

The elemental analysis result of Fe(II) complex shows the formation of Fe(II) with the ligand and is consistent with the expected hexacoordinate complexation.

3.2.3 IR Spectrum

Table 5.IR spectrum data of metal complexes (cm^{-1})

Compound	ν NH(exo+ring) + ν (HOH)	νC=O	ν C=N	Non-ligand bands
NiLCl	3500-2890	1682	1501	944,855,759,639,582,459
ZnL	3580-2890	1682	1501	943,855,759,639,581,459
CdLCl	3600-2900	1720	1566	608,419,409
FeL	3580-2890	1670-1720	1552	944,854,639,581,471
MnL	3500-2800	1700-1586	1550	917,737,716,658,605
$VO^{2+}L$	3450-2850	1680	1500	943,854,639,581
CrL	3400-2700	1720-1590	1501	943,855,759,639,581,458

The IR spectra of metal complexes have strong bands in the range 1700—1650cm^{-1} attributed to the C=O stretching mode of vibration .The C=O absorption frequency of the ligand shifted from 1654cm^{-1} to 1680-1682cm^{-1} in the metal complexes. Where as the C=N band of the ligand shifts from 1588cm^{-1}to a lower frequency between 1500-1566cm^{-1} in the metal complexes. These two values suggest that metal ligand interaction has taken place to stabilize metal complexes. The lowering of the absorption frequency of the azomethine nitrogen in the metal complexes can be explained by the donation of electrons from nitrogen to the empty d-orbital of the metal atoms. New bands observed in the region 640-400cm^{-1} are assigned to ν M-O and ν M-N frequencies. Some of the bands between 640-400cm^{-1} are due to the wagging mode of water and those between 960-792cm^{-1} are assigned for rocking mode of coordinated water (21).

3.2.4 Electronic spectra

Table 6. Electronic spectra of metal complexes

Complex	Electronic spectra bands (cm^{-1})	Assignment
$Ni^{+2}L$	23,600, 18,000, 18,450, 14,900,	$^3A_2g\rightarrow{}^3T_1(P)$ $^3A_2\rightarrow{}^3T_1(F)$ $^3A_2\rightarrow{}^3T_2$
$Fe^{+2}L$	21008	$^5T_2g\rightarrow{}^5Eg$
$Cr^{+3}L$	32154,30674,25125,18450,15576	$^4A_2(F)\rightarrow{}^4T_2(F)$ $^2E\rightarrow{}^2T_1$ $^4A_2\rightarrow{}^4T_1$
$VO^{+2}L$	40485,32573,28901	

L = ligand

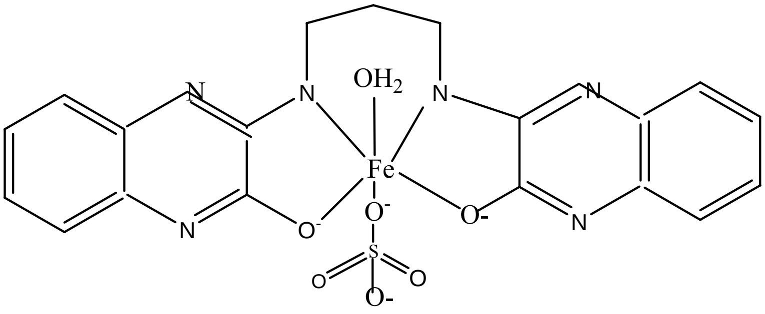
In the electronic spectra of VO^{+2} complex, a broad band from 380 to 450 nm is observed. It doesn't show any d-d transition in the visible region, this may be due to the oxidation of V^{4+} to V^{5+}. This broad absorption in the visible region is due to ligand-to-metal charge transfer. Ni^{+2} has absorption band at 23600cm^{-1}, which is more intense than other bands. This may be due to $^3A_2g\rightarrow{}^3T_1(P)$ transition and the remaining at 18450cm^{-1} is due to $^3A_2\rightarrow{}^3T_1(F)$ transition implying an octahedral geometry. The electronic spectra of Fe^{+2} complex are broad or resolvably split owing to a Jahn-Teller effect in the excited state. It shows a broad absorption in the visible region due to d-d transition. The bands 25125 cm^{-1} of Cr(III) complex indicates the LMCT of Cr(III) complex. Other bands at 18450 & 15576 cm^{-1} are due to $^4A_2(F) \rightarrow {}^4T_2(F)$ & $^2E \rightarrow {}^2T_1$ transitions respectively indicating octahedral geometry.

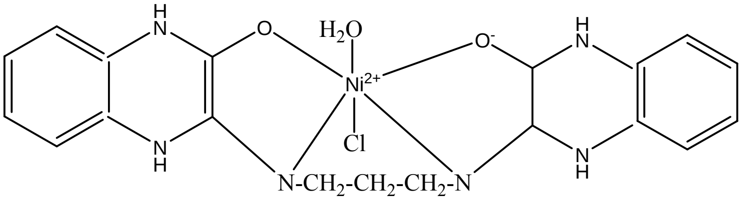
It was attempted to synthesize complexes of the above metal ions solutions with the ligand in the template method. The IR spectra, color and m.pts greatly vary from the previously synthesized complexes.

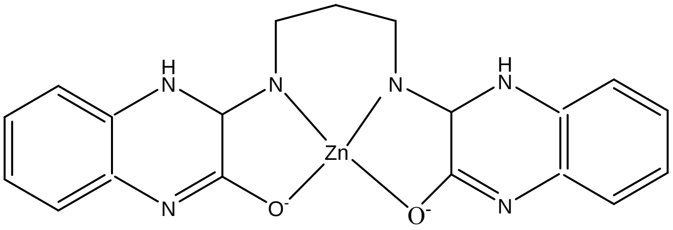
CONCLUSION

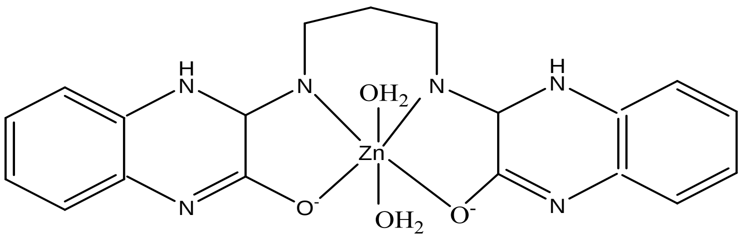
Based on IR, electronic spectra and elemental analysis, the ligand binds to the metal ions through donor atoms. It is proposed that the azomethine group of the ligand underwent a shift to lower frequency, and the carbonyl shifted towards a higher frequency indicating the coordination of azomethine nitrogen and the oxygen of the carbonyl to the metal ion and this can be explained by the donation of electrons from nitrogen and oxygen to the empty d-orbitals of the metal ion.

Possible geometries of metal complexes based on the IR, electronic spectra and elemental analysis and quantitative tests of chlorides and sulphates





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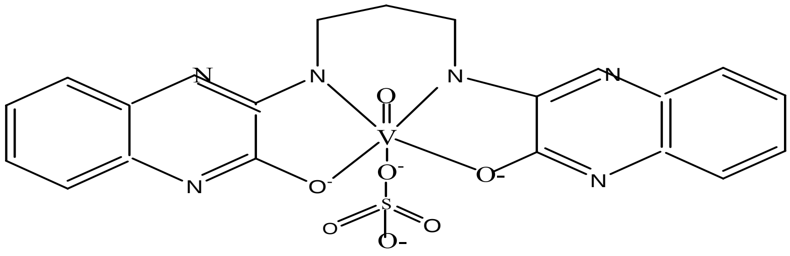
O-
N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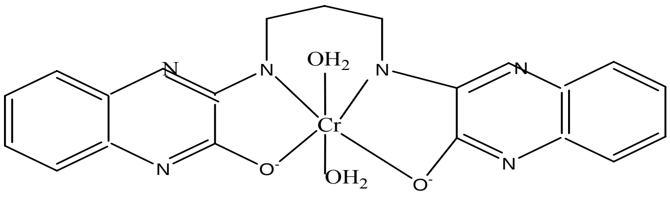
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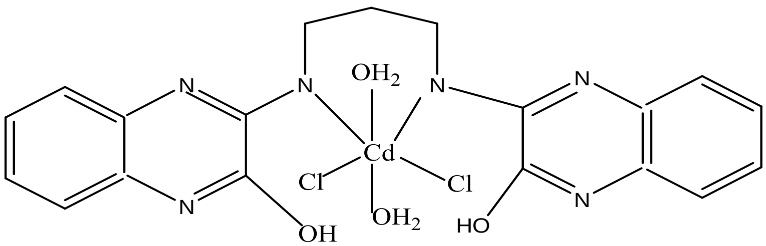
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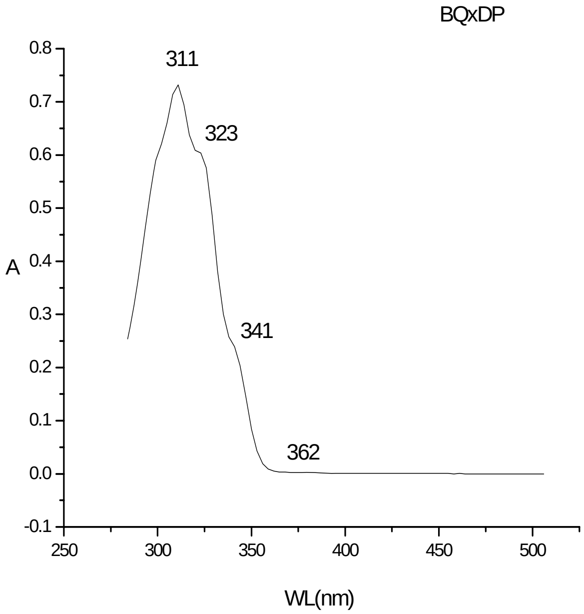
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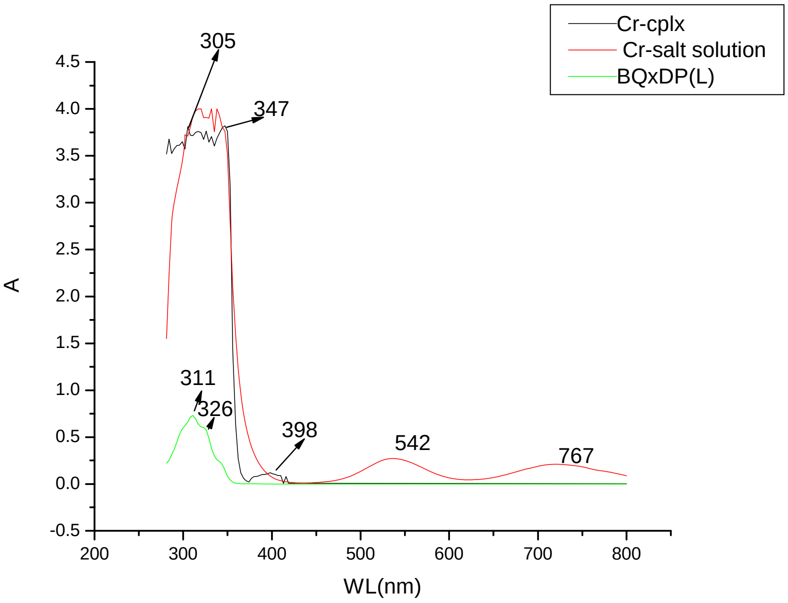
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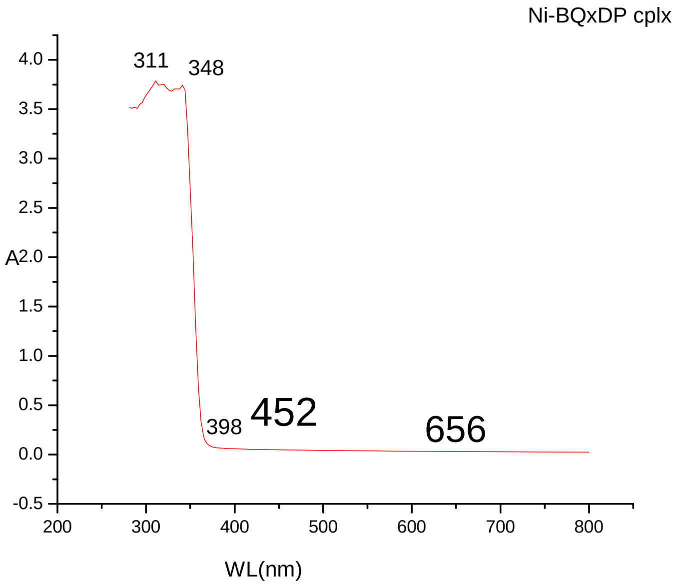
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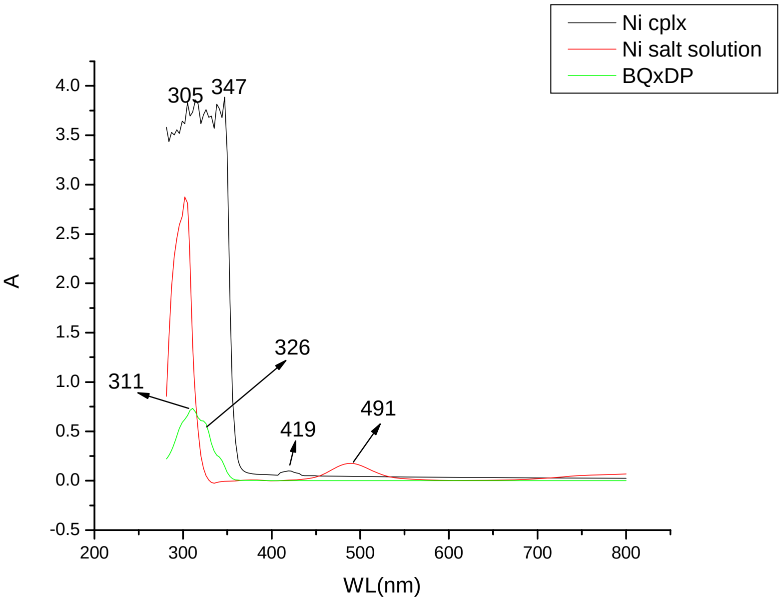
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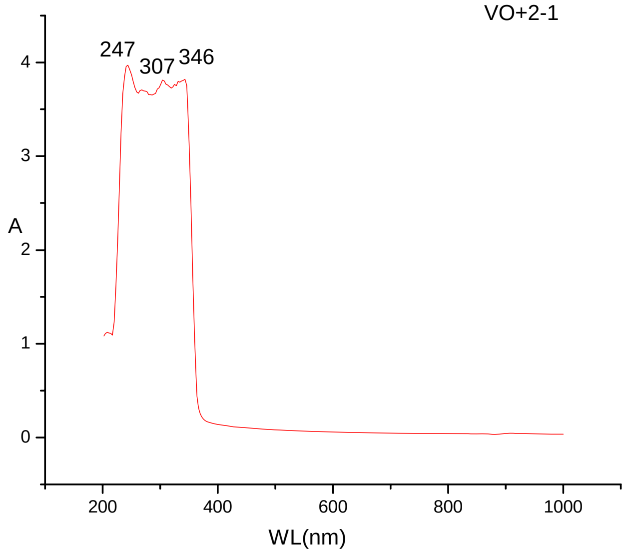
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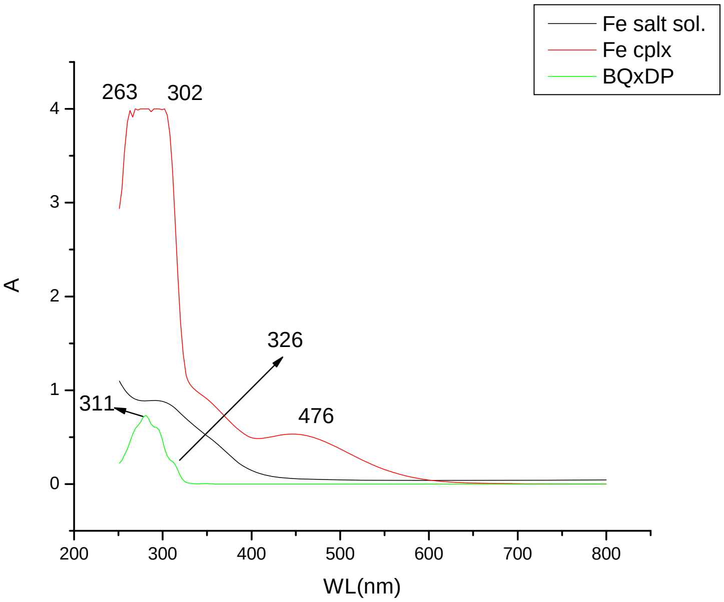
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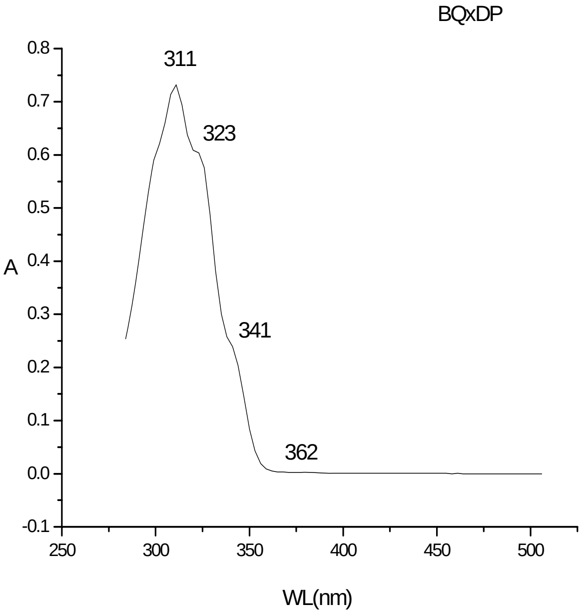
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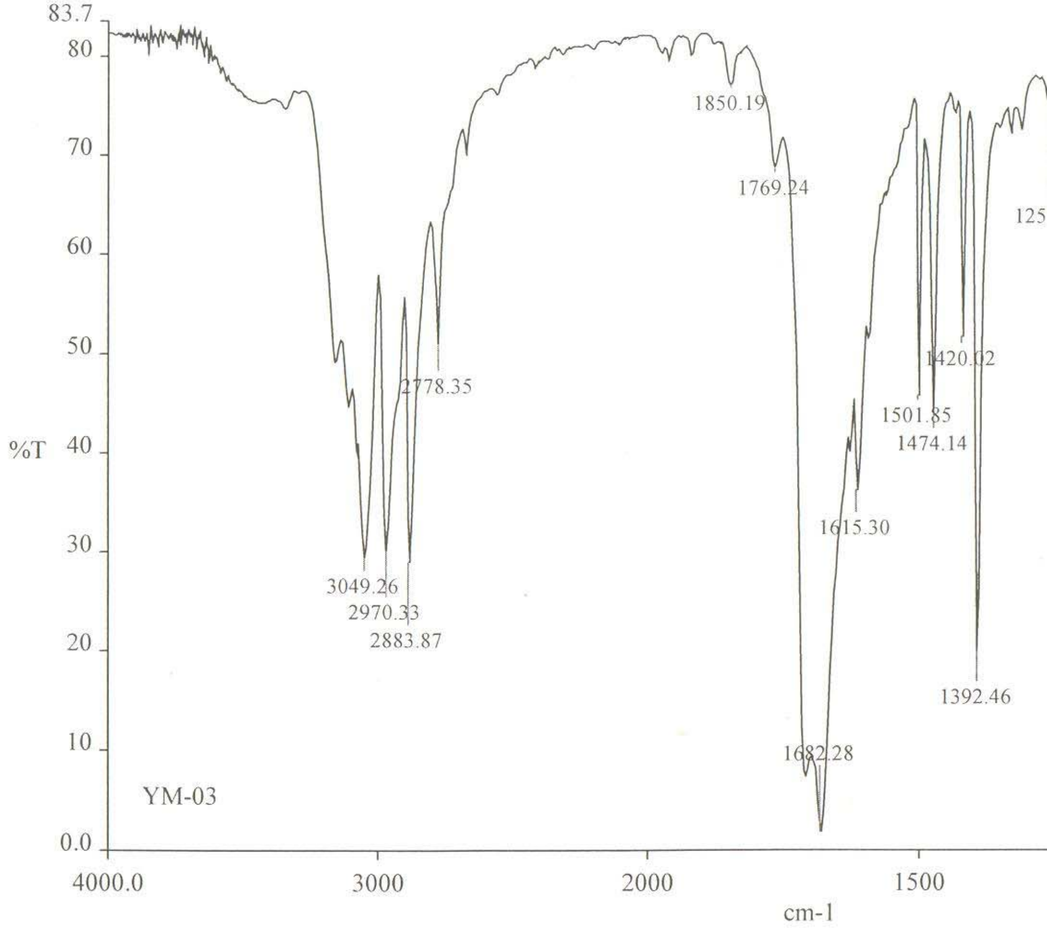
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125