Chapter 1

INTERODUCTION

1. INTRODUCTION

1.1 Coordination Polymers

One of the fascinating areas of coordination chemistry is the developing branch of coordination polymers. These systems with metal complexes bound or stacked together in wide variety of structural dispositions have been of intense interest to chemists, physicists, material scientists and theoreticians alike. Their concerted efforts backed by the skill of synthetic chemists have yielded multitudes of interesting and novel polymeric materials which find extensive applications. Unlike pure organic or inorganic polymers the coordination polymers have the mix of properties of both of them. Often this imparts unique and novel properties to the molecular systems formed which go on to make them very useful materials in the form of molecular ferromagnets, synthetic metallic conductors, non-linear optical materials, ferroelectrics, and one-dimensional conductors. The produced thesis is in connection with the aspect of coordination polymers of bis 8-hydroxy quinoline. So the brief review about the coordination polymers and 8-hydroxy quinoline has been given below.

The expression “Coordination Polymer” was first used by J. C. Bailar in 1967, when he compared organic polymers with inorganic compounds which can be considered as polymeric species. In comparison he established rules for the building and the required properties of new species involving metal ions and organic ligands\(^1\).

Coordination polymers are defined as high molecular weight molecules formed by the repetition of monomeric units linked with covalent bonds. In comparison, coordination polymers are infinite systems build up with metal ions and organic ligands as main elementary units linked via coordination bonds and other weak chemical bonds.
These compounds are also named metal-organic coordination networks or metal-organic frameworks (MOF)\(^2\).

The research on synthesis and applications of coordination polymers have become a popular field since the past 20 years because of the excellent properties, such as molecular recognition, ion exchange, catalysis, microelectronics, nonlinear optics, porous materials etc. \(^3\)\(^-\)\(^9\). Therefore, it is important to get an object with the expected structure and function through a reasonable choice and control of metal ions, organic ligands and other synthesis conditions. Transition metal ions are easy to coordinate with nitrogen and oxygen atoms, and the coordination numbers are mainly focus on 4 or 6, so it is relatively simple for their coordination geometries \(^10\)\(^-\)\(^16\).

The coordination polymer building is principally directed by the coordination bonding. Coordination bonds are the donation of a lone pair electron of the ligand (Lewis base) to the metal cation (Lewis acid). The energy of such interaction is usually evaluated around 50 kJ.mol\(^{-1}\). Weaker interactions also strongly influence the formation of coordination polymers.

In other word coordination polymers are metalloorganic entities composed of metal centers bridged by organic connectors. In marked contrast with coordinating polymers, i.e. polymers bearing sites allowing the coordination of metals, for coordination polymers, metal centers are incorporated within the structure of the polymer behaving thus as structural knots. Because metal offer a vast variety of coordination geometry as well as different oxidation states, the design and preparation of coordination polymers with controlled structures and thus, properties are currently under active investigation. The strategy for the formation of coordination polymers may be based on iterative assembling processes between metals and organic ligands. In this context, the design of the organic part has special importance. In order to allow the interconnection between metallic centers and ligands in which the coordination sites are oriented outwardly (exo-ligands) are needed \(^18\)\(^-\)\(^19\).Coordination polymers have served humankind since before recorded history.The tanning of leather and generation of select colored pigments depend on the coordination of metal ions.
A number of biological agents, including humans, owe their existence to coordination polymers have unknown and/or irregular structures.

The drive for the synthesis and characterization of synthesized coordination polymers were catalyzed by work supported and conducted by the United States Air Force in a search for materials which exhibited high thermal stabilities. Attempts to prepare stable, tractable coordination polymers which would stimulate the exceptional thermal and/or chemical stability of model monomeric coordination compounds such as copper ethylene diaminobisacetylacetate (II) or copper phthalocyanine (I) have been disappointing at best. Typically only short chains were formed and the thermally stable “monomers” lost their stability when linked to the metals resulting into polymeric units.

Coordination polymers are possessing high thermal stability. Polymeric metal complexes have a variety of geometries that are not observed in organic polymers, some combine the properties of anisotropy with photo responsive behavior that give rise to applications in areas such as optical storage, optical switching, diffractive optical elements, non-linear optical devices, liquid crystal displays (LCD’s) etc. Metal containing polymers have important applications in medical sciences; they play an important role in controlled drug delivery systems, artificial organs and protein synthesis.

 필드 listed a number of principles that can be considered in designing coordination polymers. Briefly these are as follows:

I. Little flexibility is imparted by the metal ion or within its immediate environment; thus, flexibility must arise from the organic moiety. Flexibility increase as the covalent nature of metal-ligand bond increases.

II. Metal ions only stabilize ligands in their immediate vicinity, thus the chelates should be strong and close to the metal atom.

III. Thermal, oxidative and hydrolytic stability are not directly related, thus, polymers must be designed specifically for the properties desired.

IV. Metal-ligand bonds have enough ionic-character to permit them to rearrange more readily than typical “organic bonds”.
V. Flexibility increases as the covalent nature of the metal ligand bond increases.

VI. Polymer structure (such as square planar, linear, octahedral, planar or three-dimensional) is dictated by the coordination number and stereochemistry of the metal ion or chelating agent.

VII. If a solvent is used for the polymerization, it must not form a strong complex with either the metal ion or chelating agent.

 Coordination polymers can be prepared by a number of routes, with the three most common being:

a) Preformed metal complexes polymerized through functional groups where the actual polymer forming step may be a condensation or addition reaction.

b) Metal chelating ligands. The monomers produced by dupont consist of copolymers of ethylene with a small portion of methacrylic acid. The polymer chains are cross linked by addition of metal ions. These polymers exhibit good thermal stability and flame retardance.

Coordination polymer of metal ion containing chelating groups.
c) Polymer formation through reaction of metal-containing moiety with an appropriate donor atom (Lewis-base) containing reactant.

These three different reactions resulting into formation of coordination polymers are referred as the coordination reactions. Thus the syntheses of coordination polymers involve the formation of coordination complexes within the performed polymers. A wide variety of methods for preparing coordination polymer have been discussed in detail and among these the three principal methods are shown below:

(i) Preformed metal complexes or monomers containing coordinated metal ions are polymerized through the functional groups either by condensation or by addition reaction (shown in (4) and (5)).
The equation (4) and (5) shows the polymerization of a typical vinyl monomer containing metal atom in a chelating ring. These equations,

\[ R - X \]

\[ Y \]

represent a chelate group and \( R_1 \) is an aromatic, alicyclic or acyclic radical. The reactions (1) and (4) will be lead to the formation of linear or branched polymers, while reaction (5) forms three dimensional or highly branched polymer structures. The formation of coordination polymers by the method (4) and (5) has not been widely reported as these polymers are of low thermal stability.

(ii) Coordination of a metal ion with multidentate ligands through chelating groups.
The possibility of using reaction of this type depends primarily upon the fact that transition metals are polyfunctional in character and therefore are capable of accepting more than one pair of electrons yielding the cross linked or polymer chain containing ring polymeric structures. This is illustrated by the reaction of β-diketone.

\[
\begin{align*}
&\text{O=C}\\
&\text{C-Y-C=O} \\
&\text{R} \\
&\text{O=C} \\
&\text{C-Y-C=O} \\
&\text{M}^{2+} \\
&\text{R'} \\
&\text{R'} \\
&\text{O=C} \\
&\text{C-Y-C=O} \\
&\text{R} \\
&\text{O=C} \\
&\text{C-Y-C=O} \\
&\text{M}^{n} \\
&\text{R'} \\
&\text{R'} \\
&\text{n}
\end{align*}
\]

(6)

In many cases it has been observed empirically that chelation with metal ions greatly enhances the thermal stability of organic ligand. The degree of cross linking in any polymer of this type is governed by the coordination number of metal and number of coordinating centers of the ligand.

(iii) Formation of coordination polymers by reaction of metal ions with preformed polymeric ligands capable of coordinating to metal atoms.

In such reactions the metal atom acts as crosslinking units between the adjacent chains as shown in following:

\[
\begin{align*}
&\text{R} \\
&\text{X} \\
&\text{Y} \\
&\text{H} \\
&\text{H}_2 \\
&\rightarrow \\
&\text{M}^{n} \\
&\text{R} \\
&\text{X} \\
&\text{Y} \\
&\text{H} \\
&\text{H}_2
\end{align*}
\]

(7)
In addition to this, the chelating ability of ligand may be enhanced by using bis (bidentate) type ligands such as bis-β-diketone, dithiooximido, bis (8-hydroxyquinoline) etc. However, to obtain linear polymers with bis (bidentate) chelating agents the metal atom must have a coordination number at least four \(^{30-31}\). Bis (8-hydroxyquinoline) can also used as bis (bidentate) chelating agents with four or six coordinate divalent transition metal ions \(^{32}\) to give polymer of the type (8)

\[
\begin{align*}
\text{Where } Y &= -\text{CH}_2-, -\text{C(CH}_3)_2-, -\text{SO}_2\text{ and } M = \text{Metal ions} \\
\end{align*}
\]

(8)

Polymeric Schiff's bases have also been cross linked by this method. Lions and Martin \(^{33}\) prepared such bases from diamines and pyridine-2,6-dialdehyde and crosslinked with Fe(II) ions to give an insoluble heat-stable polymer of the structure (9)

(9)
General properties and industrial perspective

Carracher has reported the following general properties of coordination polymers\textsuperscript{34}.

- Coordination polymers are soluble in few solvents and often insoluble in organic solvents such as hydrocarbons and chloroform.
- Most of the coordination polymers are in the form of powder, which may be cast to give films or fibers with difficulty.
- They are typically hydrophobic and resistance to hydrolysis until suitable wetting agents or solvent added.
- Many of these polymers are semiconductors to near semiconductors exhibiting bulk resistivity's of the order of $10^3$ to $10^{13}$ ohm cm.
- Thermal degradation of organometallic polymer occurs typically through a series of kinetically dependent and/or independent on stability plateaus characteristic due to presence of bonds of different thermal stabilities compared to classical polymers, which undergo thermally induced weight losses. Further in addition to this, coordination polymer may or may not undergo melting prior to initial degradation.

Coordination polymers are considered as the polymers for multifunctional application, because of their special properties such as thermal stability, catalytic activity, biocidal, optical, semiconductors and chemical resistance properties.

Typical current and potential uses of such materials are as below’

- **Electronic and photo industries:**
  - (i) Photochromic properties (in electric multicolor display panel and in photocopying devices) \textsuperscript{35}.
  - (ii) Bulk resistivity's of the semiconductors (as semiconductors in electronic device and gas sensors materials) \textsuperscript{36}.
  - (iii) Ability to absorb and transfer energy (electronic transfer processes of laser) in manufacturing of functionalized electrodes, specialized electrodes and sensor development \textsuperscript{37-42}.

- **Space industry:**
  - (i) Excellent flame retardant and thermal properties \textsuperscript{43}.
  - (ii) Exhibiting intense absorption of UV radiation \textsuperscript{43}.
Chemical industry:

(i) Catalytic activity (in terms of better efficiency, selectivity and separation catalysis) used as polymer supported catalysis in organic reaction such as oligomerization of olefins, hydrogenation, hydroformylation and decarboxylation etc.

(ii) The properties such as film forming and high thermal stability provide coordination polymers used as thickening agent for silicon greases.

Medicine:

It shows antibacterial and/or antifungal activity suggests their use in specially bandages and topical medical applications offer also a ready avenue as delivery agents for biologically active agents. Metal containing polymers show a wide range of biological activity and hence used as cell strains.

Following are brief discussions of several families of coordination polymers

Polymeric metal phosphinates have been extensively studied by Block and his coworkers. Single-, double- and triple-bridge phosphinate polymers have been produced, containing metals as Al, Be, Co, Cr, Ni, Ti and Zn. Some of the products give films with tensile strengths of several thousand psi, and thermal stabilities to 450ºC. Thermal degradation commences with loss of the aryl or alky groups which in turn attacks other phosphinate groups. Film-forming characteristics are enhanced by use of plasticizers.
The metal phosphinates are prepared from metal salts and dialkyl or diarylphosphonic acids utilizing melt or solution systems. The metal polyphosphinates are utilized as additives, e.g., chromium (III) polyphosphinates thicken silicones to grease and improve their high pressure physical properties. Chromium and titanium polyphosphinates impart antistatic properties to a wide range of plastic.

Allcock, Carraher and their coworkers $^{50-51}$ have synthesized platinum coordination polymers as antitumor agents. Malignant neoplasms are the second leading cause of death. In 1964 Rosenberg and coworkers discovered that bacteria failed to divide, but continued to grow giving filamentous $^{52}$ cells in the presence of platinum electrodes. A major case of this inhibition to cell growth division is c-DDP (cis-dichlorodiamineplatinum (II)) employing nitrogen-
containing Lewis bases. This was recently licensed as an antineoplast drug. Currently it is used successfully in conjunction with other drugs in the treatment of a wide variety of tumors. The use of c-DDP is complicated due to a wide number of negative side effects. Allcock and Carraher recognized that a number of these side effects may be overcome if the platinum is present in a polymer which can both act as a long-acting controlled-release agent and be prevented from entering catastrophically into the human circulatory and excretion system.

\[
K_2PtX_4 + H_2NRNH_2 \rightarrow \text{Pt} - X - \text{NRNH}_2
\]

where $X = \text{Cl, Br or I}$

(13)

Many of the coordination polymers studied by Martin, Marvel and coworkers, those derived from bisthiopicolinamides showed the best thermal stabilities. The zinc(II) derivatives showed the best thermal stability, no appreciable weight loss have been seen at 300° C for 6 hour and no significant changes found in the infrared spectra. The zinc(II) derivatives of bis-salicaldimines also show the best thermal stability. A reason cited for the often found superior thermal stability of zinc (II) derivatives is that zinc possesses only one (common) oxidation state. Transition metals can be oxidized to higher states, catalyzing the decomposition of the polymer chains.

Consequently the research in coordination polymers have been stimulated in the last four decades because of demands for new polymeric material with high thermal and chemical stability for various applications, such as phase transfer catalysts, photo responsive materials and electron transferring agents; for removal of heavy metal ions from effluents and recovery of rare earth metal ions. The remarkable progress in this direction is mainly attributed to the fact that much information about the structure and properties of coordination polymers.

1.2 A Review on 8-Hydroxyquinoline Derivatives

Among the class of hydroxyquinolines, the chemistry of 8- hydroxyquinoline (BHQs) has attracted special interest due to their diverse biological properties
such as antimalarials, antibiotics, antifungals and anticancer agents. 8HQ shows remarkable effects similar to the antibiotic, lomofugin, which rapidly and selectively inhibits the RNA synthesis in yeast. Iron bound to the lipophilic chelator, 8HQ, and causes substantial DNA strand breakage of cultured human lung cells. Additionally, quinoline derivatives find use in the synthesis of fungicides, virucides, biocides, alkaloids, rubber chemicals and flavoring agents. They are also used as polymers, catalysts, corrosion inhibitors, preservatives, and as solvent for resins and terpenes. Furthermore, these compounds find applications in chemistry of transition-metal catalyst for uniform polymerization and luminescence chemistry. Quinoline derivatives also act as antifoaming agent in refineries.

8-Hydroxyquinoline and its derivatives find wide application in coordination chemistry, pharmaceutical chemistry and materials chemistry. The syntheses and properties of 8-hydroxyquinoline derivatives and their complexes have attracted much research.

8-Hydroxyquinoline-like biological and pharmacological chelating agent-based ligands and chelates are in progress in coordination studies with increasing interest and also in the field of metal extraction. 8HQs exert the above-mentioned activities, possibly due to their ability to chelate with the metal ions, which essential for metabolism, where the –OH group of 8HQ acts as an acid, dissociating to –O–. Bivalent cations are bounded by the dissociated acid group and the lone pair of electrons borne by the nitrogen atom. The metal chelates of 8HQs (oxinates) have been reported biologically active due to their lipid solubility and have comparable activity against bacteria and fungi. The activity of oxinates was explained by assuming that these complexes first penetrate the cell wall due to lipid solubility and at the site of action undergoes dissociation to 1: 1, 8HQ: complex, which then becomes a toxic entity by combining with the metal binding sites of enzymes as well as by blocking the same.

8-hydroxyquinoline (8-HQ) and its derivatives have received attention due to their applications in various areas such as in wastewater treatment for metal recovery, in proactive coatings, as an in vitro and in vivo anticarcinogenic agent,
and for potential biological activity 78-83. In addition, fluorescence enhancement occurs by cation binding as in metal chelates of 8-HQ, which exhibited intense fluorescence activity 84-85.

A literature survey has revealed a promising method to enhance the chelating ability of 8-quinolinol compounds for the formation of coordination polymers by using a bidentate 8-quinolinol in which two 8-hydroxyquinolinyl end groups were joined by a linear aliphatic bridge, usually at the 5,5’-positions 86-87. Recently, we have also reported the synthesis and characterization of coordination polymers based on a novel 8-hydroxyquinoline bis(bidentate) ligand containing a dimethyleneoxide (-CH₂-O-CH₂-)₉₈ aliphatic bridge. Researchers have published a series of papers 89-91 on polymers and copolymers of 8-quinolinol either present as end group or as pendant group with a view to study their complexing ability and biological activity.

8-Hydroxyquinoline, a monoprotonbidentate chelating agent, has received increased attention recently because its most representative metalloquinolate, aluminum tris (8-hydroxyquinoline) (AlQ3), have served as the emitting material in organic light emitting diodes (OLEDs) 92. Many derivatives of 8-hydroxyquinoline (for example, substituted at 2, 5, or 7 position, or coordinated with different metal ions) have also attracted considerable interest because due to their high thermal stability, excellent electron-transport properties and unique luminescent properties 93.In most recent published literatures 94-96, the 8-hydroxyquinoline has been present to be a mixed type inhibitor by the formation of a complex chelate, blocking the active sites of the aluminium alloy surface. Additionally, the inhibitory action of 8-hydroxyquinoline on the copper corrosion process has been investigated and was showing the formation of the protective film composed by Cu(II)–hydroxyquinoline complexes on the copper surface and hindered the action of aggressive ions in solution, such as Cl⁻ or OH⁻ 97. 8-hydroxyquinoline and its derivatives has been designed and identified as an effective pharmacophore for the development of better antifungal agents 98-99. A series of compounds derived from 8-hydroxyquinoline as potential HIV-1 integrase inhibitors were synthesized recently 100.
8-Hydroxyquinoline might be thought to function as a phenol, but out of the 7 isomeric hydroxyquinolines only 8-hydroxyquinoline exhibits significant antimicrobial activity. It is only isomer has the capacity to form chelate. If the hydroxyl group is blocked, the compound is unable to form chelate. The relationship between chelation and activity of 8-hydroxyquinoline has been investigated \textsuperscript{101-103}. 8-hydroxyquinoline and its derivatives are widely used as analytical reagents and anti-amoebic agents. 8-Hydroxyquinoline, in its deprotonated form, is a bidentatechelator; forming complexes with a number of metal ions. The deprotonated O atom and the ring N atom are involved in the metal chelation. Metal chelation has been implicated in the biological activity of derivatives of 8-hydroxyquinoline.

8-hydroxyquinoline itself is inactive and exerts activity by virtue of the metal chelates produced in its reaction with metal ions in the medium. 8-hydroxyquinoline and its sulfate (Chinosol) or benzoate used in antiseptics, the effect being bacteriostatic and fungi static rather than microbiocidal. Inhibitory action is more pronounced upon gram-positive than gram-negative bacteria \textsuperscript{104-105}. The 8-hydroxyquinoline benzoate was the most active antifungal agent in a series of 24 derivatives of quinoline tested \textsuperscript{106-107}. Iron and cupric salts were found to prolong the antibacterial effect of 8-hydroxyquinoline on teeth \textsuperscript{108}. Certain halogen derivatives of 8-Hydroxyquinoline have a record of therapeutic efficacy in the treatment of coetaneous fungus infections and also for amebic dysentery. Among these are 5-Chloro-7-iodo-8-quinolinol (iodochlorhydroxyquinol, Vioform); 5,7-diiodo-8-hydroxyquinoline (diiodohydroxyquinolone) and sodium 7-Iodo-8-hydroxyquinoline-5-sulfonate(chiniofon) \textsuperscript{109-111}. Halogenated derivatives of 8-hydroxyquinoline (14) have been widely used in the treatment of various intestinal and vaginal infections. Greatest success was achieved with iodinated 8-hydroxyquinolines among which the commonly used drugs are iodoquinol (IQN) (15) and clioquinol (CQN) (16). Copper 8-quinolinolinate (copper oxinate) (17) is employed as an industrial preservative for a variety of purposes, including the protection of wood and textiles against fungus-caused rotting and food plants. It has 25 times greater antifungal activity than 8-hydroxyquinoline \textsuperscript{112}. 
One of the derivatives of 8-hydroxyquinoline, 5-chloromethyl-8-hydroxyquinoline (CMQ) is also active in various fields. The literature survey reveals that 5-chloromethyl-8-hydroxyquinoline (CMQ) is a versatile derivative of 8-hydroxyquinoline. It can be easily prepared at room temperature by the reaction of 8-hydroxyquinoline, formaldehyde, conc.HCl and dry HCl gas. It is stable in hydrochloride form otherwise it hydrolyzes to methyl group. The reports included a number of derivatives of CMQ by the reaction of CMQ with alcohols and secondary amines. Aristov et al has documented several reports about a number of 5-substituted derivatives from CMQ having the structures as follows.

\[
\begin{align*}
\text{R} &= \text{Alkyl, Cycloalkyl, Benzyl} \\
\end{align*}
\]
The derivatives were monitored for their activity as anthelmintics, rematacides and fungicides. The coumarin ring containing derivatives (22) have also been reported from CMQ hydroxycoumarin.

\[ R = \text{Me, Et, isobutyl} \]

Victor et al. reported that CMQ derivatives (23, 24) act as dental plaque inhibitors.
The fungicidal active compound has been prepared from bis-8-hydroxyquinoline moiety from the reported method. D. Pennelolce reported the corbostyriss derivatives containing 8-hydroxy quinoline. The tetrakis 8-hydroxyquinoline methyl ethylene alkyl diamine (25) shown below has been prepared for their complexation.

![Chemical Structure](image1)

(25)

Similarly the glycine ester from CMQ has also been reported. The patent has been reported about the 5-methylpiperazinyl derivative (26) for Fschamia treatment. Some reports about the metal analysis complexation and electro analysis of these derivatives are also found.

![Chemical Structure](image2)

(26)

Se bastien Madonna et al. reported structure activity relationships and mechanism of action of antitumor bis 8-hydroxyquinoline substituted benzyl amines. They reported that, a series of twenty six structurally related 8-hydroxyquinoline substituted amines were synthesized to evaluate the effects of structural changes on antitumor activity and understand their mechanism of action. The studies were performed on a wide variety of cancer cell lines within glioma and carcinoma models. The results obtained from chemical models and biological techniques such as microarrays suggest the following hypothesis that a quinonemethode intermediate which does not react with DNA but gives covalent
protein thiol adducts. Micro-array analysis showed that the drugs induce the expression of a variety of stress related genes responsible for the cytotoxic and cytostatic effects in carcinoma and glioblastoma cells respectively. The described analogues could represent new promising anti-cancer candidates with specific action mechanisms, targeting accessible thiols from specific proteins and inducing potent anti-cancer effects.

B. Ghosh et al.,\(^{130}\) recently synthesized 8-quinolinol and N-substituted piperazine in one combined molecule and studied in vivo activity which indicates potential application in symptomatic and neuroprotective therapy for Parkinson’s disease.

R. Peng et al.,\(^{131}\) synthesized fluorescent sensors for Fe\(^{3+}\) containing 8-hydroxyquinoline (27). They reported that a series of 5-dialkyl (aryl) aminomethyl-8-hydroxyquinoline derivatives were synthesized and their fluoroionophoric properties toward representative alkali ions, alkaline earth ions and transition metal ions were investigated. Among the selected ions, Fe\(^{3+}\) caused considerable quenching of the fluorescence, while Cr\(^{3+}\) caused quenching to some extent. The absence of any significant fluorescence quenching effects of the other ions examined, especially Fe\(^{2+}\), renders these compounds highly useful Fe\(^{3+}\) selective fluorescent sensors.

F. Wang et al.,\(^{132}\) reported that a series of bidentate 8-hydroxyquinoline (8-HQ) and 5-dialkyl (aryl) aminomethyl-8-HQ derivatives were synthesized and their fluoroionophoric properties toward representative alkali, alkaline earth, group IIIA and transition metal ions were investigated. Among the selected ions, Zn (II) enhanced the fluorescence of N-di-(methoxycarbonyl) ethyl aminoethyl-3-[4-(8-hydroxyquinolin-5-ylmethyl) piperazin-1-yl]-propanoic amide] (28) by 31-fold,
while Al(III) caused enhancement to some extent. The absence of any significant fluorescence enhancement by the other ions examined, renders a highly useful Zn(II)-selective fluorescent sensor.

They also reported in vitro antimicrobial, thermal and spectral studies of mixed ligand Cu (II) heterochelates of clioquinol and coumarin derivatives.  

1.3 Coordination polymers based on bis-8-hydroxyquinoline derivatives

Literature surveys have been described on 8-hydroxyquinoline moiety. The some of the literature give information about coordination polymers based on bis-8-hydroxyquinoline derivatives. H Juerjea and Roth Hermann reported that the reaction between CMQ and urea/ guanidine afforded the following products. 

![Diagram of N,N'-bis(8-hydroxyquinolin-5-yl methyl) urea](image)
Polyethylene amine, polyethylene polyamine and polyxylene polyamines also react with CMQ\textsuperscript{135}. The authors suggested that these products are good metal chelating agents\textsuperscript{135}. Ulkelov et al \textsuperscript{136} reported the ion-exchange resin by condensation of CMQ and poly thiocyanato aniline. Taken et al.\textsuperscript{137} reported the important aspect about florescent chelate based on reaction product of CMQ and water soluble polymers.

W. R. David suggested that polymers of olefin bearing bidentate ligands are useful as protective coating and primers. Thus he prepared such polymer by reaction between poly (2-hydroxy-ethylmethacrylate) and CMQ\textsuperscript{138}. The chelate resin obtained by the reaction between CMQ and acrylonitrile-divinyl benzene-ethylene diamine copolymer has been patented\textsuperscript{139}. 8-hydroxyquinoline terminated polyether was prepared by the reaction between amino terminated polyether and CMQ\textsuperscript{139-140}. Various scientists have reported the bis-8-hydroxy quinolines, prepared from CMQ and their co-ordination polymers based on structures are given below i.e. (31)\textsuperscript{141-144}. 

![Chemical Structure](image-url)
Patel and his coworkers \(^{88}\) reported the coordination polymers of bis (8-hydroxy-5-quinolinyl methylene) sulphide with Zn (II), Cu (II), Ni (II), Co (II) and Mn(II) ions and characterized them by elemental analyses, IR, diffuse reflectance spectral studies and magnetic moment. They also have investigated the thermal behavior of each of the coordination polymer by TGA in air upto 700°C. The order of increasing thermal stability of metal containing coordination polymers are as under.

\[ \text{Cu} < \text{Ni} < \text{Co} < \text{Mn} \]

L. Feng et al., \(^{145}\) reported synthesis and photo physics of novel 8-hydroxyquinoline aluminum metal complex with fluorine units.

Discovery of a new family of bis-8-hydroxyquinoline substituted benzyl amines give a pro-apoptotic activity in cancer cells and their synthesis, structure-activity relationship and action mechanism studies has been reported by V. moret et al. \(^{146}\). One of the derivative of 8-hydroxyquinoline, 5-chloromethyl 8-quinolinol (CMQ) can be synthesize easily and studied for number of useful compounds and polymers \(^{147-153}\).

S. C. Panchani et al., \(^{154}\) recently reported coordination polymeric chain assemblies of some metal ions containing 8-hydroxyquinoline moieties (32). They also studied thermal behavior of this polychelates.
G. J. Kharadi et al.,\textsuperscript{155} also reported some coordination polymeric chains of metal ions containing 8-hydroxyquinoline moiety (33).

A. D. Patel et al.,\textsuperscript{156} also reported thermal stability and number-average molecular weights of all of the coordination polymers containing metal ions Zn(II), Cu(II), Ni(II), Co(II) and Mn(II).
Patel and his coworkers\textsuperscript{157} reported the coordination polymers of 1,6-bis(8-hydroxyquinolin-5-yl)-2,5-dioxahexane with Zn(II), Cu(II), Ni(II), Co(II) and Mn(II) ions and characterized them by elemental analyses, IR, diffuse reflectance spectral studies and magnetic moment. They also have investigated the thermal stability and number-average molecular weights of all of the coordination polymers.

![Diagram](image1)

\[ M = \text{Cu(II), Ni(II), Co(II), Mn(II) and Zn(II)} \]

(35)

D. J. Patel et al.,\textsuperscript{158} reported coordination polymers containing 1H-indole and its antimicrobicidal activity.

![Diagram](image2)

Where \( M = \text{Cu(II), Ni(II), Co(II), Mn(II) and Zn(II)} \)

(36)

Jianlin Shi et al.,\textsuperscript{159} also reported a new soluble tris(8-hydroxyquinoline) aluminium (AlQ3)-based coordination polymer named CP-B8QBA-Al does not
crystallize and can be fabricated into amorphous films by conventional spin-coating.

Chudasama et al.,\textsuperscript{160} reported the coordination polymer based on the basic dyes containing 8-hydroxyquinoline (8 HQ) moiety.

Where M = Cu(II), Ni(II), Co(II), Mn(II) and Zn(II)

\[(37)\]
1.4 A Review on 2, 2’-(alkylazanediyl) diethanol

Alkylalkanolamines are versatile, polyfunctional molecules that combine the characteristics of amines and alcohols. This makes them useful intermediates in the synthesis of numerous products. They are of major importance in the pharmaceutical, water treatment, fabric treatment, coatings and gas treatment industries.

Gary T. Rochelle et al.,\textsuperscript{161} studied the piperazine (PZ)/ methyldiethanolamine (MDEA)/water/carbon dioxide system. The experimental solubility of CO\textsubscript{2} and model predictions presented in this work suggest that PZ-activated MDEA blends offer a lower equilibrium partial pressure of CO\textsubscript{2} at low loading than DEA/MDEA blends. Partial pressures at low loading are, however, seen to be higher than those in MEA-promoted MDEA. This is due to the carbamate stability of each of these promoters.

Tadeusz Spychaj,* et al.,\textsuperscript{162} studied Waste poly (ethylene terephthalate) can be readily degraded to low-molecular-weight or oligomeric products by tertiary alkanolamines at temperatures above 190°C. These products comprise mixtures of aminoesters of terephthalic acid. The products of PET aminoglycolysis are viscous liquids with different viscosities and hydroxyl values. Higher viscosities and lower hydroxyl values were found as the temperature and reaction time were increased. These features are results of the side reactions, including dehydration, that occur in the PET/tert-alkanolamine system at high temperatures above 190 °C. Some products of PET chemical degradation with tertiary alkanolamines can be used as epoxy resin hardeners for curing at elevated temperature. The most active PET aminoglycolysates are terephthalic derivatives of N-methyl- and N-ethyldiethanolamines, triethanolamine, and bis(2hydroxyethyl)piperazine.

M. Lourdes Calzada* et al.,\textsuperscript{163} synthesized bismuth-based oxide thin films by using bismuth (III) and N-methyldiethanolamine for photosensitive application. The photo reactivity of this metal complex makes the formation of a metal–O–metal oxide skeleton possible in the deposited layer by excitation with...
UV light. This enables the stabilization and formation by low thermal annealing (350 °C) of the high-temperature cubic d-Bi$_2$O$_3$.

P.J.G. Huttenhuis et al. studies gas solubility of H$_2$S and CO$_2$ in aqueous solutions of N-methyldiethanolamine. An alkanolamine solution to remove acidic gases is determined by the acid gas solubility, the reaction rate and the mass transfer properties. In this study the experimental determined solubility data of CO$_2$ and H$_2$S in aqueous MDEA solutions. From these experiments it is concluded that an increasing methane partial pressure resulted in a higher acid gas partial pressure.

Abdelbaki Benamor et al. studies reactive absorption of CO$_2$ into aqueous mixtures of Methyl-diethanolamine and Diethanolamine. The effect of mixing a tertiary amine, N,N-Methyl-diethanolamine (MDEA), with a secondary amine, diethanolamine (DEA), on the kinetics of the reaction with carbon dioxide in aqueous media has been studied in a stirred cell reactor with a plane, horizontal gas-liquid interface. Temperature was varied from 293 to 313K over a range of blend composition and total mixture concentration ranging from one to two molars.
1.5 A Review on azo dyes based on bis-ethanolamine

Azo compounds which have versatile application in various fields, such as dyeing textile fiber, biological–pharmacological activities and advanced application in organic synthesis \(^{166-170}\).

Xie et al., \(^{171}\) prepared polyurethanes from the reaction of toluene 2,4-diisocyanate with N,N-di(2-hydroxyethyl)aniline containing azobenzene (Disperse Red-19, DR-19), azo-benzothiazole and bisazobenzene. Their second-order non-linear optical (NLO) properties have also been studied.

![Diagram of azo dyes]

A first rosin-based nonlinear optical polymer was synthesized by the condensation polymerization of rosin-maleic anhydride imidodicarboxylic acid with \((4'-\text{nitrophenylazo})-[\text{N,N-bis(2-hydroxyethyl)}]-\text{aniline}\) (DR 19). The polymer was amorphous and showed glass transition. Dipolar alignment of nonlinear optical chromophores was achieved by the contact poling at the transition temperature of the polymer \(^{172}\).
Two kinds of dual functional carbazole-based chromophores are synthesized to enhance the photorefractive (PR) performance of the polymers by attaching the electron-donating groups like \(N,N\)-diethanolaminophenyl and electron accepting groups like \(p\)-nitrophenyl or 5-nitrothiazole. Both chromophores exhibit a large hyperpolarizability in the Hyper-Rayleigh scattering experiment due to the extended chain length \(^{173}\).

![Diagram of a chromophore](image)

Patel et al. synthesized new monoazo disperse dyes by coupling of diazotized 2-amino-4-(2',4'-dichlorophenyl)-1,3 thiazole with various N-alkyl derivatives of substituted aniline and their dyeing performance on polyester fiber has been assessed. The dyed polyester fabric showed fair to very good light fastness and very good to excellent on washing and rubbing fastness properties with superior depth and levelness \(^{182}\).

![Diagram of a dye molecule](image)
1.6 Research gap about 2, 2’-(alkylazanediyl) diethanol,azo dyes based on bis-ethanolamine and 8-hydroxyquinoline

Looking to the systematic literature survey of 2,2’-(alkylazanediyl) diethanol, azo dyes (i.e. dispers dyes) based on diethanol and 8-hydroxyquinoline derivatives, it was found that numbers of azo dyes having diethanol (i.e. disperse dyes) were reported having good dyeing properties. But from the literature survey it was found that, one of the derivatization of such dyes by reaction of 8-hydroxyquinolines were not reported.

Hence, it was thought worthwhile to study coordination polymers based such dyes, 2, 2’-(alkylazanediyl) diethanol and 5-chloromethyl-8-hydroxyquinoline moiety.

1.7 Objectives

The objectives of the thesis are:
- To synthesized bis-ligand having CMQ (derivatives of 8-HQ) and 2, 2’-(alkylazanediyl) diethanol moieties.
- To synthesized bis-ligand having CMQ (derivatives of 8-HQ) and azo dyes (i.e. disperse dyes) based on bis-ethanolamine.
- Studies on coordination polymers based on the bis-ligands.
- Carry out antimicrobial activity of the synthesized bis-ligands and its coordination compounds.

Present Work

In view of the above objectives, the research work was carried and distributed into following chapters of the present thesis.

Chapter-2

Chapter-2 of the thesis comprises into two sections.

Section-A comprises the details about the techniques used for characterization of bis-ligands and their coordination polymers.

Section-B deals with the details about raw materials such
- (i) 5-chloromethyl 8-hydroxyquinoline
(ii) N-alkyl bis-ethanolamine
(iii) dyes containing bis-ethanolamine

Chapter 3

Chapter 3 of the thesis comprises into two sections.

**Section-A** deals with the synthesis and characterization of bis-ligands (i.e. \( H_2L_{1-4} \)) containing bis-ethanolamine bridge with alkyl group as a pendant group and their derivatives have been summarized.

- \( 5,5'\-(((\text{methylazanediyl})\text{bis(ethane-2,1diyl)})\text{bis(oxy)})\text{bis(methylene)}\text{bis(quinolin-8-ol)} \) [MBEDQ]
- \( 5,5'\-(((\text{ethylazanediyl})\text{bis(ethane-2,1diyl)})\text{bis(oxy)})\text{bis(methylene)}\text{bis(quinolin-8-ol)} \) [EBEDQ]
- \( 5,5'\-(((\text{propylazanediyl})\text{bis(ethane-2,1diyl)})\text{bis(oxy)})\text{bis(methylene)}\text{bis(quinolin-8-ol)} \) [PBEDQ]
- \( 5,5'\-(((\text{isopropylazanediyl})\text{bis(ethane-2,1diyl)})\text{bis(oxy)})\text{bis(methylene)}\text{bis(quinolin-8-ol)} \) [IPBEDQ]

**Section-B** deals with the synthesis and characterization of bis-ligands (i.e. \( H_2L_{5-8} \)) containing bis-ethanolamine with dye moiety as pendant group and their derivatives have been summarized.

- \( 5,5'\-(((4-(4-(\text{4-nitrophenyl})\text{diazenyl})\text{phenyl})\text{azanediyl})\text{bis(ethane-2,1diyl})\text{bis(oxy)})\text{bis(methylene)}\text{bis(quinolin-8-ol)} \) [NPBEMQ]
- \( 5,5'\-(((3-(\text{3-methyl-4-((4-nitrophenyl)\text{diazenyl})phenyl})\text{azanediyl})\text{bis(ethane-2,1diyl)})\text{bis(oxy)})\text{bis(methylene)}\text{bis(quinolin-8-ol)} \) [MEBMQ]
- \( \text{N-}(5-(\text{bis(2-((8-hydroxyquinolin-5-yl)methoxy)ethyl)amino)-2-((4-nitrophenyl)\text{diazenyl})phenyl})\text{acetamide} \) [BHQMNA]
- \( 5,5'\-(((3-\text{chloro-4-((2,6-dichloro-4-nitrophenyl)\text{diazenyl})phenyl})\text{azanediyl})\text{bis(ethane-2,1diyl)})\text{bis(oxy)})\text{bis(methylene)}\text{bis(quinolin-8-ol)} \) [CDEBMQ]

Chapter 4

Chapter 4 of the thesis comprises into two sections.

**Section-A** The various coordination polymers based bis-ligands containing bis-ethanolamine with alkyl as pendant group and first row transition metal ions
i.e., Cu(II), Ni (II), Co(II), Mn(II) and Zn(II) have been synthesized and characterized preliminary.

**Section- B**  
The various coordination polymers based bis-ligands containing bis-ethanolamine with dye moiety as pendant group and first row transition metal ions i.e., Cu(II), Ni (II), Co(II), Mn(II) and Zn(II) have been synthesized and characterized preliminary.

**Chapter-5**  
All the coordination Polymers of two series was characterization by metal: ligand ratio, spectral study, magnetic measurement and thermogravimetry. All the details are interpretation to be furnished in chapter-5.

**Chapter-6**  
Chapter-6 of the thesis comprises into two sections.  
**Section-A** all the prepared bis-ligands containing ethanolamine with alkyl as pendant group and their coordination polymers were screened for their antimicrobial activity. The common biospecies have been selected. The results of such study are discussed in thisSection.  
**Section- B** all the prepared bis-ligands containing ethanolamine with dye moiety as pendant group and their coordination polymers were screened for their antimicrobial activity. The common biospecies have been selected. The results of such study are discussed in this Section.
The entire general synthetic route for preparation of bis-ligands and its metal complexes:

**Scheme 1.1.** The synthetic route for the preparation of ligands and their coordination polymers

Where **R** = (a) CH₃  
(b) C₂H₅  
(c) n-C₃H₈  
(d) i-C₃H₈

Where **D** = (a) C₁₆H₁₈O₄N₄  
(b) C₁₈H₂₂O₅N₅  
(c) C₁₇H₂₁O₄N₄  
(d) C₁₆H₁₈O₄N₄Cl
Annexure

The annexure of the present thesis describes work on viscosity measurements of solutions of carboxymethyl phenol-formaldehyde (CMPF) resins were carried out in DMF at 30° ± 0.3°C by using Ubbelohde viscometer. CMPF resins were prepared by reported method. The viscosity data of the solution of CMPF resins signified that the decrease in concentration of solution increases reduced viscosity ($\eta_{\text{red}}$). This suggests the CMPF resins act as polyelectrolyte of anionic type. Therefore the viscosity of the solution in DMF is suppressed by adding water and KBr in DMF. Thus the viscosity measurements of solution of CMPF resins in DMF-Water-KBr (80:20:1%) gives the intrinsic viscosity. Also applying empirical equation:

$$\eta_{sp/C} = Z = [\eta] + \frac{K[\eta]}{C^{1/2}}$$

is able to represent the viscometric data for all the resins. It may be stated that as the equation is quite empirical.
1.7 References


