Chapter - 1

Introduction
1. Introduction

1.1 Coordination Polymers

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]. During the last fifteen years the number of publications concerning coordination polymers has dramatically increased from 100 articles per year to 1000 in 2004.

Coordination polymers are light in weight and possess high thermal stability. [2] Polymeric metal complexes have a variety of geometries that are not observed in organic polymers; some combine the properties of anisotropy with photo responsive behaviour 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. [3-5]

Coordination polymers have served humankind since before recorded history. The tanning of leather and generation of selected 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 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, microelectronics, nonlinear optics,
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. [7,8]

Polymeric coordination networks syntheses could be considered as “construction games”: the final architecture depends on the building modules, (organic ligands, metal centres, their counter ions, solvent molecules) and their compatibilities. Analyses of the final geometries, of the diverse interactions and optimization of the growth processes, are described as crystal engineering. In appropriate circumstances, crystals can be considered as the sum of a series of reproducible molecular recognition events. This means that control of the overall arrangement of the modules can be conceivable with prediction of topology and dimensionality, but not of the exact crystal structure (cell parameters). This approach could be compared to the supramolecular chemistry and self-assembly feature, if crystals are regarded as single chemical entities. Self assembly is based on complementary and explicit interactions between the building blocks in order to generate the final product. [9]

One such area in which this ligand having s-triazine and 8-hydroxy quinoline (an analytical reagent) has not been received any attention. Thus the present work describe in this direction. Fig.1
Coordination polymers contain utilized since before recorded history, though not recognized as such until recently. For instance, the tanning of leather depends on the coordination of metal ions by the proteins which make up the hide. These protein-metal ion complexes resist bacterial attack, wear and weathering which befall nontanned animal skins, affect many enzymatic and membrane interactions.

Metals can be coordinated with organic ligands to form a polymer or to form a coordination complex within an already formed polymer. The reactions forming coordination polymers can be like those which form polymers throughout condensation route. Here we consider polymers created through chelation of metal and nonorganic metal-containing ions and polymer complexation of metal ions. For prepared correlation of product structure with belongings it is best that the coordination polymer contains a repeat unit with one metal ion per unit. Even so there exist a larger number of synthesized coordination polymers where the exact structure is both unknown and probably varies within a single polymer chain.

Coordination polymers can be prepared by a number of routes, 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) Co-ordination of metal ion with a polymer containing chelating groups Figure-3.

c) Polymer formation during reaction of metal donor atom co-ordination Figure-4.
A listing of polymers utilized to form coordination polymers through route $b$ appears as Tables 1.1. Table 1.2 contains a listing of families of chelating compounds utilized to form coordination polymers through route $c$. Polymers formed through routes $a$ and $c$ naturally contain definable, “exact” repeat units while structures of polymers formed through route $b$ differ depending on the reaction conditions including solvent, temperature, nature of reactants and concentration ratio of the two reactants; and the structure will vary within a given chain for such polymers.

The synthesis and characterization of coordination polymers was supported by the US Air Force in a search for materials which show high thermal stabilities. However, attempts to prepare stable, mannerly coordination polymers which would simulate the exceptional thermal and/or chemical stability of model monomeric coordination compounds such as copper ethylenediaminobisacetylacetonate (II) or copper phthalocyanine (II) have been disappointing. Typically, only short chains are formed, and the thermally stable “monomers” lost most of their stability when linked by the metals into polymeric units.

Bailar listed a number of principles in designing coordination polymers briefly,
1) little flexibility is imparted by the metal ion on its instantaneous environment, thus, flexibility must arise from the organic moiety;

2) metal ions just stabilize ligands in their immediate vicinity, thus the chelates should be strong and close to the metal atom;

3) thermal, oxidative, hydrolytic stability are not directly related, thus, polymers must be designed specifically for the properties desired;

4) metal-ligand bonds have sufficient ionic-character to permit them to rearrange more readily than typical “organic bonds”,

5) flexibility increases because the covalent nature of the metalligand bond increases;

6) coordination number and stereochemistry of the metal ion determine polymer structure (such as square planar; linear; planar or three-dimensional);

7) complex formation is favored throughout use of pure reactants in stoichiometric amounts; and

8) If a solvent is used for the polymerization, it must not form a strong complex with either the metal ion or chelating agent. Several of these points should be self-evident to higher level undergraduate students since they are simple extensions of material typically obtainable in intermediate level inorganic courses.


**Table 1.1**

**Ligands Utilized in the Synthesis of Co-ordination Polymers**

\[
\begin{align*}
\begin{array}{c}
\text{--- (CH}_2\text{-CH) ---} \\
\text{NH}_2 \\
\end{array}
\begin{array}{c}
\text{--- (CH}_2\text{-CH) ---} \\
\text{OH} \\
\end{array}
\end{align*}
\]

\[
\begin{align*}
\begin{array}{c}
\text{--- (CH}_2\text{-CH) ---} \\
\text{C=O} \\
\text{O} \\
\end{array}
\begin{array}{c}
\text{--- (CH}_2\text{-CH) ---} \\
\text{C=O} \\
\text{-HO} \\
\end{array}
\end{align*}
\]

\[
\begin{align*}
\begin{array}{c}
\text{--- (CH}_2\text{-CH) ---} \\
\text{HO-P=O} \\
\text{OH} \\
\end{array}
\begin{array}{c}
\text{--- (CH}_2\text{-CH) ---} \\
\text{S-H} \\
\end{array}
\end{align*}
\]

\[
\begin{align*}
\begin{array}{c}
\text{--- (CH}_2\text{-CH) ---} \\
\text{C=O} \\
\text{H}_2\text{N} \\
\end{array}
\begin{array}{c}
\text{--- (CH}_2\text{-CH-N) ---} \\
\text{H} \\
\end{array}
\end{align*}
\]

\[
\begin{align*}
\begin{array}{c}
\text{--- SO}_2\text{-HC}=\text{N-OH} \\
\end{array}
\begin{array}{c}
\text{--- N=CH-HO} \\
\end{array}
\end{align*}
\]
<table>
<thead>
<tr>
<th>Chelates Group</th>
<th>Representative Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Bis-1,2-amino acids</strong></td>
<td><img src="image" alt="Bis-1,2-amino acids diagrams" /></td>
</tr>
<tr>
<td><strong>Bis-o-amino-phenols</strong></td>
<td><img src="image" alt="Bis-o-amino-phenols diagrams" /></td>
</tr>
<tr>
<td><strong>Bis-diamines</strong></td>
<td><img src="image" alt="Bis-diamines diagrams" /></td>
</tr>
<tr>
<td><strong>Bis-b-diketones</strong></td>
<td><img src="image" alt="Bis-b-diketones diagrams" /></td>
</tr>
</tbody>
</table>

*Table-1.2: Ligands Utilized in the Synthesis of Coordination Polymers through Chelation with Metal Ions*
**Bis-1,2-dioximes**

![Bis-1,2-dioximes Diagram]

**Bis-dithiocarbates**

![Bis-dithiocarbates Diagram]

**Bis-a-hydroxy acids**

![Bis-a-hydroxy acids Diagram]

**Bis-o-hydroxyazos**

![Bis-o-hydroxyazos Diagram]

**Bis-hydroxy nitrogen heteroaromatics**

![Bis-hydroxy nitrogen heteroaromatics Diagram]
Bis-o-hydroxy Schiff bases

\[
\begin{align*}
\text{N} & = \text{CH} \quad \text{R} \quad \text{N} \\
\text{H} & = \text{O}
\end{align*}
\]

Bis-imides

\[
\begin{align*}
\text{O} & \quad \text{R} \\
\text{H-N} & \quad \text{N-H} \\
\text{O} & \quad \text{O}
\end{align*}
\]

Bis-thiooxamides

\[
\begin{align*}
\text{H} & \quad \text{S} \quad \text{S} \quad \text{H} \\
\text{N} & \quad \text{C} \quad \text{C} \quad \text{N}
\end{align*}
\]

Bis-thiopicolin amides

\[
\begin{align*}
\text{R} & \quad \text{N} \quad \text{C} - \text{N} \quad \text{R} \\
\text{S} & \quad \text{H} \\
\text{H} & \quad \text{S}
\end{align*}
\]

Bis-thiosemicarbazones

\[
\begin{align*}
\text{R} & \quad \text{N} \quad \text{C} - \text{N} \quad \text{N} = \text{CH} \quad \text{R} \\
\text{H}_2\text{N} & \quad \text{S} \quad \text{H} \\
\text{H} & \quad \text{S}
\end{align*}
\]
Bis-xanthanes

Cyclophosphazenes
(with chelating groups)

Dicarboxylates

Phosphinous anions

Bis-o-nitrites ad 1,2-dinitriles
1.2 Review literature

Following are short 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 formed, containing metals as Al, Be, Co, Cr, Ti, Ni and Zn. Some of the products give films with tensile strengths of several thousand psi, and thermal stabilities to 450°C. Thermal degradation commences by loss of the aryl or alkyl groups which in turn attacks other phosphinate groups. Film-forming characteristics are improved by use of plasticizers. Fig.5

![Single bridge](image1.png)

![Double bridged](image2.png)

![Triple bridged](image3.png)

Figure-5
The metal phosphinates are prepared from metal salts and dialkyl or diarylphosponic acids utilizing melt or solution systems. The metal polyphosphimates are utilized as additives, e.g., chromium (III) polyphosphinates thicken silicones to greases 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 have synthesized what may be considered as platinum coordination polymers as antitumoral 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 cells in the presence of platinum electrodes. A major case of this inhibition to cell growth division is cis-dichlorodiamine platinum II, C-DDP, which was recently licensed as an antineoplast drug. It is currently successfully used 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. Fig. 6
Allcock and coworkers attached C-DDP to a preformed, water-soluble polymer, poly [methiamine] phosphazene], that bears coordination sites on both the side group and chain nitrogen atoms. The compound reacts with $K_2PtCl_4$ and 18-crown-6-ether in organic media yielding a coordination complex, containing C-DDP. This complex shows tumor inhibitory activity against mouse P388 lymphocytic leukemia and in the Ehrlich Ascites tumor regression test. Fig. 7

Carraher and coworkers included the cis-dihaloplatinum diamine into polymers using diamine-containing reactants including aromatic, aliphatic, pyrimides, pyridines, purines [10]. These polymers show a wide variety of biological activities. At concentrations of 10 to 20 mg/ml they can suppress, enhance or have no effect on the replication of viruses.
such as poliovirus type I, a L RNA virus, but none of the polymers show activity towards any of the tested cell lines, including L929 (mouse), HeLa and wish at these concentrations. At concentrations of 30 mg/ml and above most of the platinum polyamines inhibit tumoral cell growth. Further, mice can tolerate dosages in excess of 20 mg/gram weight with no apparent ill effect.

Figure 8

\[ \text{K}_2\text{PtX}_4 + \text{H}_2\text{NRNH}_2 \rightarrow \text{Pt}(\text{H}_2\text{NRNH}_2^+) \]

Where, \( X = \text{Cl}, \text{Br}, \text{I} \)

**Figure-8**

Carrather and coworkers have also utilized formation of coordination polymers as a model for uranyl ion retrieval for both environmental and industrial purposes. Selected salts of diacids, dioximes, etc. are capable of removing the uranyl ion to \( 10^{-4} \) to \( 10^{-8} \) \( M \) \((11,12) \) (The uranyl ion is the most common natural-occurring water soluble form of uranium.) This has been extended to removal utilizing salts of polyacrylic acids, polyacrylic acid itself, and a wide variety of carboxylic acid sulfonate and sulfate containing resins \([13]\). Almost all of these compounds containing the complexed uranyl moiety have greatly reduced toxicities to a wide range of bacteria and fungi compared to UNHH itself \([14]\). Thus the toxicity has been significantly reduced through chelation of the uranyl ion.

Figure-9
Using resins to remove and detect metal ions, including the uranly ion, has been practiced for some time [15]. Reactions, in which metal-containing coordination polymers are formed, are critical analytical and chromatographic reactions, but are often not recognized as involving coordination polymer chemistry in its broadest sense.

Further, there are a number of plants which are known to chelate various ions [15-17]. Currently studies are underway concerning the complexation of the uranyl ion by such plants, specifically sphagnum fimbriatatum and spagnum recurrum mosses [18]. Thus future efforts at identification, separation and isolation of metal containing moieties might include use of natural occurring reagents.

The most widely studied coordination polymer family is that derived from bis-\(\text{b-diketones}\). The diketones utilized are usually of two structural types
with the alkylene vrudge occurring either between the
two sets of carboxyls or to one side of the

carboxyls.Fig.10

Such polymers are formed through the bulk
polymerization of the bis-\(b\)-diketone with metal
acetates or metal acetylacetonates (2,19,20). Thermal
decomposition of polymers occurs in the range of 225
to 350\(^{\circ}\)C Figure-11.

Of the many coordination polymers studied by
Bailar and Marvel and coworkers, those derived from
bisthiopicolinamides showed the best thermal
stabilities. The zinc II derivatives showed the best
thermal stability and could be heated at 300\(^{\circ}\)C for 6
hours without appreciable loss in weight or change in
the infrared spectra [21]. The zinc II derivatives of bis-
salicaldimines also show the best thermal stability [22].
A reason [21] cited for the often found superior thermal
stability of zinc II derivatives is that zinc possesses only one (common) oxidation state. Transition metals, etc. can be oxidized to higher states, catalyzing the decomposition of the polymer chains. There are number of latest reference including book in the area of coordination polymer [23-25].

• **Coordination Polymers of Bis (8-Quinolinol)s**

So many literature surveys have been described in this subject on based on 8-hydroxyquinoline moieties. The some of the literature give information of coordination polymers based on bis-8-hydroxy quinoline derivatives, H Juerjea and Roth Hermann reported [26] that reaction between CMQ and urea/guanidine afforded the following products Figure-12.

\[
\text{N,N'-bis(8-hydroxyquinolin-5-yl methyl) urea}
\]

\[
\text{1,3-N,N'-bis(8-hydroxyquinolin-5-yl methyl) guanidine}
\]

**Figure-12**
As CMQ also has reactive group, number of ion-exchange resins has been prepared by reaction of CMQ with reactive group of polymers. The cellulose is a high molecular weight natural polymer and its reaction with CMQ affords the 8-hydroxyquinoline - cellulose product which is a good ion exchanger [27-29]. The well-known polymer say polystyrene and/or styrene divinyl benzene copolymer were aminated and these on treatment with CMQ afford good ion-exchangers [30].

Polyethylene amine, polyethylene polyamine and poly-xylene polyamines also reacts with CMQ [31]. The authors suggested that these products are good metal chelating agents [32]. Ulkelov et al [32] reported the ion-exchange resin by condensation of CMQ and poly thiocyanato aniline. Taken et al [33] 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 [34]. The chelate resin obtained by the reaction between CMQ and acrylonitrile-divinyl benzene-ethylene ,diamine copolymer has been patented [35]. 8-hydroxyquinoline terminated polyether was prepared by the reaction between amino terminated polyether and CMQ [35, 36]. Various scientists have reported the bis-8-hydroxy quinolines, prepared from CMQ and their co-ordination polymers based on structures are given below [37-39] Figure-13.
L. Feng et al [40] reported synthesis and photo physics of novel 8-hydroxy quinoline 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 [41]. 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 [42-46].

S. C. Panchani et al [47] recently reported coordination polymeric chain assemblies of some metal ions containing 8-hydroxyquinoline moieties, They also studied thermal behavior of this polychelates Figure-14.
K. D. Pateli et al. [48] have reported some coordination polymeric chains of metal ions containing 8-hydroxyquinoline moiety. A. D. Patel et al. [49] also reported some coordination polymers based on 5-chloromethyl-8-hydroxyquinoline (CMQ).

E. Horowitz et al. [50] have reported thermal stability of bis (8-hydroxy-5-quinolyl)-methane coordination polymers containing Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) metal ions.

H. S. Patel et al. [51] have reported a various coordination polymers based on bis 8-hydroxyquinoline moieties with various metal ions.

S. P. Patel et al. [52] have reported a various coordination polymers based on bis 8-hydroxyquinoline moieties have been extensively investigated for their gripping properties.
8-hydroxyquinoline is one of the well-known N-O bidentate ligand and most widely utilized as a chelating agent industrially and analytically. The complexing capacity with metal ions of this ligand has been further enhanced by preparing its bis form such bis ligand from a may afford a linear chain coordination polymers arrayed with metal ions in the reporting units. These linear chain coordination polymers are of short chain lengths with the hydroxyl end groups as shown below Figure-16

![Figure-16](image)

However, they are found to be very resistant to temperature and can be melted without decomposition. Bailar and his coworkers initiated the work on preparation of variety of coordination polymers based on bis-8-hydroxyquinoline and its derivative [53]. A variety of coordination polymers of bis oxines and its derivative were prepared and investigated for their thermal stability. They observed that bis (8-hydroxyquinoline) sulphone ligand appeared to give the most stable coordinated
system up to the temperature 280°C in addition to 330°C for Copper (II) and Zinc metal ions respectively. Following the pattern Korshak et al [54] reported the synthesis of coordination polymers of bis (8-hydroxyquinolyl) methane of the first-row transition metal ions and explored their thermo-chemical properties, molecular weight and crystallinity. Later on, Berg and Alam [55] discussed the synthesis of coordination polymers of 8,8′-dihydroxy-5,5′-biquinolinol and the use of ligand as an analytical reagent for detecting metal ions in the microgram range [55]. The thermal stability of these polymers was studied by heating the samples at different temperatures in air and observing changes in colour and in infrared spectra. Infrared study of the products of polymerization gives the evidence of coordination between metal ions and bis ligand.

Horowitz and Perros [56] prepared coordination polymers of bis (8-hydroxy-5-quinolinyl) methane ligand with Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) by solution polymerization and thermal polymerization. The thermal stability of each polymer in vacum and in air was studied by thermogravimetric analyses and found to be closely related to periodic properties of the metal ion incorporated in the backbone of polymer infrared spectral studies of the coordination polymers provide information about the nature of the metal-ligand bond at the C-O metal site.
Later on various attempts have been made for the synthesis of coordination polymers of bis(8-hydroxy-5-quinolinyl) methane ligand with transition alkali and alkaline earth metals [54,56-58] and their characterization by elemental analysis, IR and electronic spectrum studies. Magnetic moment, molecular formula determination and thermal behaviour at high temperature. These report also indicated that the thermal stability of coordination polymers derived from schiff base by condensation of 5-formyl-8-hydroxyquinoline with methane dianiline and subsequently refluxing it with transition metal acetate. Report also mentioned that the metal coordinated in the polymer backbone is one of the significant factor in governing the thermobackbone is one of the major factor in governing the thermo stability. Additional report also indicate that bis Schiff base ligand prepared by condensation of 5-amino-8-hydroxyquinoline with teraphthaldehyde and coordinated with different metal ions [58-65].

Metal chelates of novel bis Schiff base were prepared by refluxing a mixture of 5-formyl oxine, benzidine and metal acetate (2:1:1) in DMF. The metallic compound of formula ML₂H₂O [M=Cu (II), Co (II), Mn (II) and Zn(II)] obtained are highly colored colored amorphous powders. The presence of Schiff base has been confirmed by infrared spectral data. Thermal studies of these metal chelates indicated that they start decomposing at 325-375°C and Zn (II) chelate is observed to be thermally most stable [66].
Patel and his coworkers [67] 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 by elemental analyses, IR and diffuse reflectance spectral studies and magnetic moment. They also have investigated the thermal behavior of each of coordination polymer by TGA in air upto 700°C. The order increasing thermal stability as under.

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

A new bis-(8-quinolinol)s bidentate ligand namely 7,7’-[1,4-N,N’-dimethylene piperazine-8-quinolionol] has been synthesized by employing Mannich base reaction of oxine with formaldehyde and piperazine dihydrochloride in presence of acid catalyst [68]. The coordination polymers of this ligand with different metal ions [Cu(II), Zn(II), Co(II), polymers of this ligand with different metal ions [Cu(II), Zn(II), Co(II), Mg(II), Mn(II) and Cd(II)] were prepared and their thermal. Electrical and magnetic properties and metal to ligand stoichiometry were investigated for each of the polymer. The molecular structure of coordination polymer is shown.

The thermal studies of these coordination polymers and parent ligand revealed that each of the coordination polymer sample decompose very slowly initially upto 350°C and are more stable than the parent ligand. The data of magnetic
moment show that coordination polymers of Cu(II), Mn(II), Cd(II) and Co(II) are paramagnetic while those of Zn(II), and Hg(II) are diamagnetic.

Tobinaga Et al [69] obtained polymer chelate of copper form bis (5-ethyl-8-hydroxy-7-quinolyl) alkanes by Friedel-crafts acylation of 5-ethyl 8-quinolinol with acyl chloride (CICO(CH₂)n-2(COCI) with susequent Wolff-Kishner reduction of the product and treatment with copper acetate. The resultant polymers were found to have polymeric trans planner structure Figure-17.

![Figure-17](image)

Recently N. Manolova [70] reported water soluble metal complexes of oxine obtained by chemical modification of poly (ethylene glycol) a useful for plant nutrition. They modified poly(ethylene glycol)s by binding 8-quinolionl moiety through their hydroxyl group at 8-position resulting polyether was water soluble. Polyethers with terminal 8-hydroxyquinoline were complex with Cu(II), Ni(II), Zn(II), Cd(II), Mn(II) and Fe(II). The structure of all poly(oxyethylene) complexes were established by determining metal to legend stoichiometry and the stability constants and
further confirmed by H-NMR studies. The thermal stability of this polymer was investigated by estimating their $T_g$ and $T_m$ by DSC. The proposed structure of poly (oxyethylene) s bearing 8-quinolinoxy groups (POE) Figure-18.

![Figure-18](image)

In addition to this, these authors have reported the synthesis, complexing ability and biological activity of various polymers and copolymers with end or pendent groups of 8-quinolinol [71,72].

Beside this research, several scientists of many nations are also engaged in the co-ordination polymer research. These types of polymers are studied recently. Their structures and reference names are given below. [73-76] Figure-19
Recently our research coworker [77-80] reported the novel co-ordination polymers of Bis-(8-quinolinol)s as well as Bis-(8-quinolinol)s containing amide bridge.

1.3 Coordination Polymers based on Triazine base moiety

The triazine structure is a heterocyclic ring, analogous to the six-membered benzene ring goal with three carbons mittal by nitrogens. The three isomers of triazine are distinguished from each other by the positions of their Atoms nitrogen, and are referred to as 1,2,3-triazine, 1,2,4-triazine and 1,3,5-triazine. Other aromatic nitrogen heterocycles are pyridine ring with one nitrogen atom, nitrogen diazines with 2 Atoms in the
ring and tetrazines with 4 ring nitrogen Atoms. Triazines are weaker bases than pyridine.

The best known 1,3,5-triazine derivative is melamine with three amino substituents used in the manufacture of resins. Another triazine extensively used in resins is benzoguanamine. Triazine compounds are often used as the basis for various herbicides such as cyanuric chloride (2,4,6-trichloro-1,3,5-triazine). Chlorine-substituted triazines are also used as reactive dyes. These compounds react through a chlorine group with hydroxyl groups present in cellulose fibres in nucleophilic substitution, the other triazine positions contain chromophores. Mixtures of Triazines and water are also used to remove $H_2S$ from natural gas.

A series of 1,2,4-triazine derivatives known as BTPs have been considered in the liquid-liquid extraction community as possible extractants for use in the advanced nuclear reprocessing of used fuel. BTPs are molecules containing a pyridine ring bonded to two 1,2,4-triazin-3-yl groups. Triazine-based molecules have been used as bridging ligands to bind three dinuclear arene ruthenium (or osmium) compounds to form metallaprisms. S-Triazine derivatives represent an important class of compounds due to their potential to be biologically active. They are known to be anti-protozoals, [81] anticancer agents, estrogen receptor modulators, antimalarials, cyclindependent kinase odulators, [82] and antimicrobials. Cyanuric chloride, an inexpensive, easily available reagent, of low toxicity and less corrosive than other similar reactants, has been widely used in organic reactions. 1,3,5-triazines (or s-triazines) are a class of compounds well known for a long time and still continue the object of considerable interest mainly due to their application in different fields, including the production of herbicides and
polymer photostabilizers. Some 1,3,5-triazines display important biological properties; for example hexamethylmelamine (HMM, (a) & 2-amino-4-morphlino-s-triazine (b) are used clinically due to their antitumor properties to treat lung, breast and ovarian cancer, respectively. [83] The diverse biological activities observed for different molecule containing the 1,3,5-triazine unit have been further explored in order to discover other new potential molecules through the synthesis of libraries by combinatorial approaches. Certain 1, 3, 5-triazine derivatives are also used as chiral stationary phases, for example, the chiral solvating agent(c) for the determination of enantiometric excess by NMR spectroscopy and determination of absolute configuration by circular dichroism.

Thus owing to the above stated importance of this ligand having s-triazine and 8-hydroxyquinoline (8-HQ) and their systematic literature survey we were interested to synthesize coordination polymers based on ligands prepared from s-triazine-ether, 5-amino 8-Hydroxyquinoline and various phenol.

I.B.Johns and H. R. Dipietro [84] reported structure of trimer of salicylonitrile, 2,4,6-tris(2-hydroxy phenyl)-s-triazine suggest that it should be coordinate with divalent tetracoordinate metal ion to form polymeric products Figure-20.
Patrick Gamez, Paul de Hoog and Olivier Roubeau [85] work on Copper(II) nitrate reacts with the rigid polydentate triple-connecting dpyatriz ligand in acetonitrile to an unprecedented infinite molecular ladder in which five-coordinated copper pseudo-dimers are bridged by nitrate anions and the coordination polymer chains are linked by hexacoordinated copper ions leading to the formation of large guest cavities.

Megumu Munakata and Ming Wen and Yusaku Suenaga [86] work on carbon and nitrogen coordinated silver (I) polymers of 2,4,6-triphenoxy-1,3,5-triazine. For the purpose of furthering the understanding of steric structure effects upon
coordination behavior and exploring the possibility of non-planar complexation in the triazine system for formation of extended polymeric structures, 2,4,6-triphenoxy-1,3,5-triazine(tpotz) has been reacted with silver(I) perchlorate and trifluoromethanesulfonate. The crystal structures of [Ag2(tpotz)3(ClO4)2] and [Ag2(tpotz)2(CF3SO3)2(THF)] have been determined by single-crystal X-ray diffraction. Tpotz is rich in organic components that can offer potential sites for complexation, which can be utilized to generate an interesting array of organometallic compounds with one-dimensional chains Figure-22.

![Schematic view of anion coordinated chain](image)

**Figure-22**

Patrick Gamez, Paul de Hoog and Martin Lutz [87] studied on coordination compounds from 1,3,5-triazine derived multidirectional ligands which useful for oxidation catalysis. A series of 1,3,5-triazine- and 2,2-dipyridylamine-based ligands have been prepared and the crystal structure from one of them was solved. The coordination of these dendritic multidirectional ligands with various metal salts led to attractive supramolecular architectures Figure-23.
Differential reactivity of 1,3,5-triazines

Ligands prepared and tested in catechol oxidase activity

Figure-23

Jonathan T. Maeyer, T. Jason Johnson and Amy K. Smith [88] studied pyrimidine, pyradazine, quinazoline, phthalazine
and triazine coordination polymers of copper (I) halides. The coordination of diazine and triazine bridging ligands (B = pyrimidine (Pym), quinazoline (Qnz), pyridazine (Pdz), phthalazine (Ptz), and 1,3,5-triazine (Trz)) with CuX and CuXL (X=Cl, Br, I; L=PPh\(_3\), P(OPh)\(_3\)) has been investigated Figure-24.

Mitra Ghassemzadeh, Forough Adhami and Abas Taeb [89] studies Coordination polymer from HAMTTO with Silver (I) (HAMTTO = 4-Amino-6-methyl-1,2,4triazine -3-thione-5-one). The reaction of 4-amino-6-methyl-1,2,4-triazine-3-thione-5-one, HAMTTO, with silver (I) nitrate in methanol led under deprotonation to the polymeric compound [(AMTTO)Ag]\(_n\). The coordination polymer [(Ag(HAMTTO))[ClO\(_4\)]\(_n\) 1 is synthesized from the reaction of the latter polymeric compound with perchloric acid. Both compounds were characterized by elemental analysis and IR spectroscopy. Single-crystal X-ray diffraction studies on compound 1 showed that HAMTTO acts as a bidentate ligand and chelates the silver atom \textit{via} its hydrazine nitrogen atom and its sulfur atom.

Yongquin wei, kechen wu and Ria broer [90] work on a polymeric cobalt compound [Co(DCNT)[H\(_2\)O]]\(_n\) with novel
topology: Synthesis, structure, luminescence, and magnetic property. The hydrothermal reaction of Co(NO\textsubscript{3})\textsubscript{2}. 6H\textsubscript{2}O and a new designed ligand H\textsubscript{2}DCNT yields a three-dimensional polymer [Co(DCNT) (H\textsubscript{2}O)]\textsubscript{\textit{n}} (1), H\textsubscript{2}DCNT=2,4-bis(4-carboxyphenylamino)-6-diethylamino-1,3,5-triazine. In the structure of 1, each DCNT\textsuperscript{2-} has three coordination sites, one nitrogen atom in the triazine ring coordinating to Co(II) and two carboxylates adopting bridging mode, which make the infinite Co(II) chains array uniformly and evenly toward crystallographic c-axis. Luminescent and magnetic properties of (1) were also studied Figure-25.

![Figure-25: The structure and synthetic route of H\textsubscript{2}DCNT](image)

Quilong Zhu, Tianlu Sheng and Ruibiao Fu [91] reported novel structures and luminescence properties of lanthanide coordination polymers with a novel flexible polycarbonate ligands. A series of lanthanide coordination polymers with a novel flexible hexapodal ligand, formulated as \([\text{Ln}_2(\text{TTHA})-(\text{H}_2\text{O})_4].9\text{H}_2\text{O} (\text{TTHA}=1,3,5-triazine-2,4,6-triamine hexaacetic acid; \text{Ln}=1, \text{Eu}; 2, \text{Tb}; 3, \text{Gd}; 4, \text{Dy})\) and \([\text{Yb}_2(\text{TTHA})-(\text{H}_2\text{O})_2]\) have been hydrothermally synthesized and characterized.
Catalin Maxim, Adil Matni [92] reported $C_3$ symmetric tris(phosphonate) -1,3,5-triazine ligand: homopolymetallic complexes and its radical anion Figure-26.

Zhu Q, Sheng T and Tan C [93] published formation of Zn(II) and Cd(II) coordination polymers assembled by triazine-based polycarboxylate and in-situ-generated pyridine-4-thiolate or dipyridylsulfide ligands: observation of an unusual luminescence thermochromism

Bruno Therrien [94] reported coordination chemistry of 2,4,6-tri(pyridyl)-1,3,5-triazine ligands. This review covers the rich coordination chemistry of 2,4,6-tri(pyridyl)-1,3,5-triazine ligands. These polypyridyl derivatives have been coupled to transition metals and lanthanides, and the complexes obtained have been used in various fields such as luminescent materials, for the preparation of coordination polymers and networks as well as for the synthesis of discrete metalla-assemblies. The synthetic and structural aspects of the different isomers of 2,4,6-tri(pyridyl)-1,3,5-triazine are presented, and a survey of their coordination chemistry is given.

Ya-Ping Wang, Ning Zhang and Xiang He [95] reported Poly [dinitrato $\mu_3$-2,4,6-tris(4-pyridyl)-1,3,5-triazine]cobalt(II)]. The solvo-thermal reaction of Co(NO$_3$)$_2$ and 2,4,6-tris(4-pyridyl)-1,3,5-triazine in dimethylformamide/ethanol mixed
solvent afforded the title coordination polymer, 
\[ \text{[Co(NO}_3\text{)]}_2(\text{C}_{18}\text{H}_{12}\text{N}_6)\text{]}_n, \] in which the Co\textsuperscript{II} atom is seven-coordinated by pyridyl groups of three different ligands and two chelating nitrate anions. The complex displays a nanosized porous metal–organic framework that belongs to a (10,3) topological network Figure-27.

**Figure-27**

Jing-Cheng Zhu and Shi-Jiang Liu [96] reported Crystal structure of a 1D Zn Coordination polymer based on 3-(4-carboxyphenyl)-propionic acid and 2,4,6-tri(2-pyridyl)-1,3,5-triazine, \( \text{C}_{28}\text{H}_{26}\text{N}_6\text{O}_7\text{Zn}. \) A mixture of 3-(4-carboxyphenyl)propionic acid (0.1 mmol, 19.4 mg), 2,4,6-tri-(2-pyridyl)-1,3,5-triazine (0.1 mmol, 31.2 mg), \( \text{Zn(OAc)}_2\cdot2\text{H}_2\text{O} \) (0.1 mmol, 22.0 mg), \( \text{NaOH} \) (0.1 mmol), and \( \text{H}_2\text{O} \) (6.0 ml) were placed in a 23ml Teflon lined stain less steel re-actor. The vessel was heated to 393K for 4 days, and then slowly cooled to room temperature. Colour less crystals were obtained and further crystals were filtered off, washed with the mother liquid, and dried under ambient conditions. Yield 56%.

Chaojun Shen, Tianlu Sheng and Chongbin Tian [97] reported two Mn\textsuperscript{II} coordination polymers with a triazine-based
polycarboxylate ligand: pH value influence, crystal structures and magnetic properties. Two new coordination compounds, \([\text{Mn}(HL)(\text{H}_2\text{O})_2]\)_n (1) and \([[\text{Mn12}(L)_8(\text{H}_2\text{O})_{30}]\cdot10\text{H}_2\text{O}]_n\) (2) were successfully synthesized by using a hydrothermal technique under different pH values and characterized by single-crystal X-ray diffraction.

1.4 Research lacks about work on Bis-(8-quinolinols) containing triazine base moiety

Number of co-ordination polymers based on 8-hydroxy quinoline has been reported for pharmaceutical application. However, the reaction between the 1.0 mole of 2,4-di chloro-6-phenoxy-1,3,5-triazine and 2.0 mole of 5-amino-8-hydroxy quinoline has not been reported except only certain reference [73,74] in which 2,4-di chloro-6-phenoxy-1,3,5-triazine derivatives used. These newly prepared bis-(8-quinolinols) containing triazine having phenoxy derivatives applied for metal complexation is not yet reported.

Hence, the present work has been undertaken. Schem.1
1.5 Objectives of the present work

The Bis-(8-quinolinols)-containing triazine moiety have not been utilized for co-ordination polymerization. Hence the objectives of proposed work are:

i) To synthesis and characterize Bis-(8-quinolinols)-containing triazine moiety.

ii) The Co-ordination polymerization study of above prepared bis-ligands

iii) To monitored the antimicrobial activity of all the synthesized novel Coordination polymers.
The present work

The work reported in proceeding sections has revealed that 8-hydroxy quinoline based metal complexes have found wide applications in different areas of science such as catalysis medicine, agriculture, paints etc. Therefore, the author thought to carry out systematic work regarding synthesis, characterization and microbial activity of novel coordination polymers of bis-(8-quinolinol)s containing triazine base moiety as mentioned in the following manner. The work bifurcated into following chapters.

The chapter-2 comprises the synthesis of various substituted 2,3-dichloro-6-phenoxy-1,3,5-triazine derivatives. These were then condensed with 5-amino-8-hydroxyquinoline. The resultant Bis(8-quinolinols) ligands designated as Bis-ligands [PBDQ-1 to PBDQ-6]. The differential scanning calorimetry (DSC) performed to identify the melting point. The details about the synthesis and DSC data of these ligands presented in chapter-2.

All the bis(8-quinolinols) ligands were characterized by elemental analysis, Infrared spectroscopy and Nuclear magnetic resonance spectroscopy. The number of hydroxyl group was determined. The details of the results are presented in chapter-3 of the thesis.

The co-ordination polymers from transition metal ions (i.e. Cu$^{+2}$, Co$^{+2}$, Ni$^{+2}$, Zn$^{+2}$, Mn$^{+2}$) of all the Bis(8-quinolinols) ligands (Mentioned in chapter-2) have been prepared and their elemental and metal contents have been determined. All these are included in chapter-4.