Chapter – I

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1.1 Coordination Polymers

The study of coordination polymers, which was systematically initiated far decades ago, is now regarded as one of the developing frontier areas of coordination chemistry. One of the most important and interesting areas of chemical research today is the study of the properties of coordination compounds. It promises many contributions to science as well as to mankind. The scope of this field is increasing because of the use of these compounds as catalysts in industrial processes are growing and these compounds play a vital role in a number of biological processes. Coordination chemistry plays an important role in life itself. Coordination polymer often termed as chelate polymer, in general, can be defined as polymer in which metal ions are linked together with di- or poly-functional ligands. The metal ions in the coordination polymer are expected to contribute high thermal resistivity, electrical conductivity and thermal stability. A large number of reports describing the preparation and characterization of coordination compounds of transition and non-transition elements with the variety of ligands still appear in recent periodicals.
1.2 Application of Coordination Compounds

The coordination compounds of arylhydrozones have been reported to act as inhibitors for enzymes\(^1\). The coordination complexes of the schiff bases have been widely investigated due to their manifestation of novel structural features, unusual magnetic properties and relevance to biological processes\(^2\)\(^-\)\(^5\).

Coordination compounds, apart from having academic importance possess great technical significance because of its properties in diverse areas including industrial and medicinal fields. The most important application of coordination compounds is in catalysis\(^6\). Metal carbonyls and their derivatives play a wide role in this context. Some of the compounds have been used as dyes and pigments. Prussian blue is used as a paint pigment. Phthalocyanines and metalised azo dyes are common in textile industry. Platinum complexes containing diphosphines and other chelating ligands containing asymmetric carbon atoms have found use in chemical industry as stereo specific catalysts.

The study of coordination compounds has emerged as one of the major center of attraction for inorganic chemist. It covers a comprehensive range of theoretical applications. In industry, coordination compounds play key role in homogenous\(^7\)\(^-\)\(^2\) and heterogeneous catalysis\(^13\)\(^-\)\(^15\) and also purification of water, analytical chemistry, solvent extraction, photography,
metallurgy and electrochemistry. They are used as dyes and also used for the formulation and improvement of semi conductors, super conductors, advanced ceramic materials and pharmaceuticals.

Coordination compounds find application in analytical chemistry for the identification and extraction of metal ions in cation exchange resins, in solvent extraction for the separation of a variety of metals including radioactive ones and in the estimation of metals. Coordination compounds of many metals are involved in life process. Complexes of even alkali and alkaline earth and noble metals have found use in the treatment of diseases. Many coordination compounds are being used as therapeutic agents. Copper (II) complexes of thiosemicarbazones are found to be highly active as an anti fungal and anti-tumor agents. Metal chelates of salicylic acid-formaldehyde polymer are reported to be useful in photographic development and for pressure-sensitive copy paper. Schiff bases are important class of ligands and have got wide applications in various fields.

1.3 Polymeric Ligands

The polymeric ligands can be obtained by the polymerization of monomers containing coordinating groups or by the introduction of low-molecular weight ligands by polymer analogous reactions. The study of the
complexation behaviour of polymeric ligands has received increased interest in the various branches of chemistry, chemical technology and biology. Among the various ligands, amines, dithiocarbamates, iminodiacetic acids, schiff bases and amidoxime are widely used for the collection of heavy metal ions. The specific bindings of metal ion by metal-ion template-crosslinked polymers have been reported. If the coordination stereo structure of a polymer-metal complex is not destroyed, that polymer will preferentially complex the metal ion which was initially present.

In addition to chelating polymers, polymers attached to macro cyclic ethers have been shown to complex metal ions. Recently, three different types of polymeric ethers, crown ethers, cryptands and podands have been introduced as new classes of neutral ligands to replace the conventional ion exchangers. The ion chelating properties of these neutral ligands have led to their selective application in extraction or separation of trace metals, isotopes and organic solutes. In the development of chelating resins for metal ion separation, the variation in matrix structure significantly affects ion diffusion and ion selectivities. The variation in reaction conditions and the influence of resin performance have gained much attention. The ability of a polymer-supported ligand to form complexes depends on the nature of the main chain. The matrix effect on ion binding is clearly evident when low molecular ligands and their polymeric analogues are compared as in the case of iminodiacetic acid ligand supported on polystyrene and
polyacrylamide \ A cross-linked polymeric ligand often forms a stable metal complex than a linear polymer and it shows a definite selectivity for metal ions due to its characteristic structure. A high degree of cross linking results in a low metal ion intake and a lower stability of the resulting metal complex by making the polymer chain more rigid. In the copper complexes of poly (4-vinylpyridine)s with 4-6 mole% DVB cross links a conversion of planar coordination centers to tetrahedral ones occur towards high cross linking$^{44,45}$.

A polymeric catalyst is a conventional catalytic species supported on a macromolecular backbone, which is used in catalytic quantities and can be reused many times without loss of activity. The performance of a catalyst is influenced by the chemical and physical properties of the support. Heterogenation of homogeneous catalysts by attaching them to polymers leads to improved stability and selectivity since the catalysts produced combine the advantages of the heterogeneous and homogeneous catalysts. The distribution and accessibility of the active sites controls the activity of the catalyst. The use of ion exchange resins as acidic / basic catalysts has been reported for a wide range of organic reactions in which acids and bases are used as catalysts in various reactions$^{4,6}$.

The application of polymeric photosensitizers for the excitation of molecules has received considerable interest owing to their potential use in
solar energy storage. In these processes, the polymeric sensitizer is excited by high energy into the triplet state and can then activate the substrate molecule while the sensitizer itself returns to the ground state. Polymer bound rose-bengal has been used for the photo-oxidation of olefins. The concept of heterogeneous catalysis has recently been introduced to aqueous-organic phase reaction by employing a polymeric catalyst in which both the catalyst and each of a pair of reactants are located in separate phases.

1.4 Polymeric Metal Complexes

The introduction of polymer supported metal complexes provides further advances in the already branch of polymer chemistry. A polymer can be defined as a substance in which many structural units are connected by valence bonds in many possible ways. A polymer metal complex is composed of a synthetic polymer and a metal ion. The synthesis represents an attempt to give an organic polymer with inorganic functions. The use of many synthetic polymer bound metal complexes exhibit high catalytic efficiency. Synthesis and characterization of more and more new polymer bound metal complexes may lead to the development of very useful heterogeneous catalysis.

A polymer-metal complex is composed of synthetic polymer and metal ions bound to the polymer ligand by a coordinate bond. A polymer
ligand contains anchoring sites like nitrogen; oxygen or sulfur obtained by the polymerization of the monomer possessing the coordinating site or by a chemical reaction between a polymer and a low molecular weight compound having the coordinating ability. The use of polymers as supports for metal complexes and synthetic reagents have grown tremendously since Merrifield demonstrated the application of polystyrene in peptide synthesis.

Tsuichida et al. have reported pendent type polymer metal complexes by coordinating a polymer ligand to a vacant site of a previously prepared stable low molecular weight metal complex. The stability and shape of polymer chelates are characterized from the results obtained for the equilibrium complexation of polymer with a liable metal ion. It was reported that a pendent type polymer Co(III) complex is one of the most suitable compounds for a quantitative study of the effects of a polymer ligand on the reactivity of a polymer complex. The polymer bound complexes are currently being investigated for application in molecular electronics, chemical sensors and catalysis. Metal complexes extensively catalyze organic reactions. If a polymer ligand was used as one component of a metal complex catalyst, its properties may affect the catalytic action of metal ion. Loutsch et al. reported the first example of catalysis by a
polymer metal complex. It has been found that in metalo enzymes such as oxidase and hemoglobin, the macromolecular protein part controls the reactivity of polymer metal complexes.

1.5 Polymer Supported Ligands and Complexes

The chemistry and technology of reactive functional polymers is an area, which has achieved rapid progress in the recent past. The chemistry and applications of these functionalized polymers depend largely on the characteristics of the specific active functional groups. Polymer supported metal complexes have wide range of applications. Organic synthesis using functional polymers\(^\text{63}\), design of polymeric reagents\(^\text{64}\) and polymeric catalysts\(^\text{63}\), complexation and separation of metal ions using polymeric ligands\(^\text{66}\), understanding of the specificity of biological reactions of naturally occurring macromolecules\(^\text{67}\), biomimetic chemistry\(^\text{68}\), enzyme immobilization\(^\text{69}\), controlled release formulations\(^\text{70}\), conductive polymers\(^\text{71}\), polymeric surfactants\(^\text{72}\), stabilizers\(^\text{71}\) and polymeric liquid crystals\(^\text{71}\) are some of the important fields where in the chemistry of functionalized polymers bears relevance.

Functionalized polymers are useful in the removal of industrial effluents. These effluents may be removed from the polymer matrix by a suitable treatment and polymer can be reused economically. These insoluble polymer-supported complexes have the advantages over their
soluble counter part of easy separation from the reaction mixture leading to operational flexibility, facile regenerability and higher stability\textsuperscript{25}. The most important advantage of polymer-supported strategy is the simplification of product work up, easy separation and isolation. Automation of the process is possible leading to industrial significance. The attachment of functional groups to insoluble cross-linked polymers can bring about significant reactivity changes by possible restricted interaction of functional groups. The insolubility makes the functional groups mutually inaccessible. The polymer acts as an insolubilizing medium for the attached species.

Now a days polymer supported metal complexes are widely used in metal ion removal studies. It has got wide application in water purification and treatment of effluents. Metal ions are removed from hazardous waste streams by this method. The polymer supported inorganic complexes are used for preparation of ion selective electrodes\textsuperscript{76}. Thus detection and removal of trace metal ions are possible using polymer supported metal complexes.

Metal ion removal studies are carried out using polymer-supported ligands. Heavy metal ions such as Cu(II), Hg(I), Fe(II), Fe(III), Cr(III), Ni(II), and U(IV), etc can be removed by using polymer supported reagents. These are removed either by complexation or by absorption. Leaching can collect these metal ions. Even trace metal ions present in water can be collected by this method. This technique has great industrial application in
water purification and recovery of metal ions from effluent. Most of the polymer ligands and polychelates were characterized by IR spectra and elemental analysis, magnetic measurements and visible reflectance spectra were reported.  

1.6 Oxime Ligands and Complexes - A Brief Review

Oximes are formed by the condensation of hydroxylamine with aldehydes or Ketones. Organic chelating ligands containing oxime functional group have been extensively used in analytical chemistry for the detection and separation of metals. In recent years considerable interest has been shown in the co-ordination chemistry of bivalent transition metals with o-hydroxy oximes because of their application as analytical reagents in solvent extraction systems and in hydrometallurgy. However most of the studies were concerned with kinetic and equilibrium extraction properties and relatively little work have been reported on the isolation and characterization of the extracted species. Reports are available on the synthesis and characterization of a set of oxime complexes.

Winslow et.al have reported the synthesis and characterization of polychelates of salicylaldehyde, formaldehyde and 2,4-dihydroxy benzaldehyde oxime polymers with various metal ions. Sykora and Dubsky have prepared a selective cation exchanger by condensing...
2,4-dihydroxy acetophenoneoxime, resorcinol and formaldehyde in an alkaline medium. They have measured the exchange capacity of the resin for Cu$^{2+}$, Al$^{3+}$, Fe$^{3+}$ and many other metal ions. The selectivity of the resin was tested by selectivity coefficient determination. In 1973, Sen Budhadev et.al$^{104}$ have reported [3-furfuraldoxime complexes of Cr(III), Fe(III), Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) with the general formula ML$_2$Cl$_2$. Complexes with the general formula ML$_2$Cl$_2$ were assigned to Mn(II), Co(II), Ni(II) and Zn(II) chelates, where the ligand coordinates through oxygen of furan and nitrogen of the oxime groups.

The synthesis and studies of ortho substituted derivatives of benzophenone oxime$^{103}$ is important, in view of pharmacological, analytical, mechanistic and stereo chemical utility of oximes$^{106,10}$. Patel et.al$^{111}$ synthesized Ni(II), Cu(II) and Co(II) complexes of acetaldoxime and a-benzaldoxime. The complexes were characterized on the basis of conductivity studies, magnetic moment, IR and electronic spectral data analysis. Nitrogen atom of the ligand molecule acts as the coordination site. Ni(II) and Co(II) complexes have the general formula ML$_2$X$_2$ and are assigned six coordinate structure and Cu(II) complex has tetragonally distorted structure.

In 1982, Parmer et.al$^{112}$, have synthesized 2,4-dihydroxyacetophenoneoxime-formaldehyde resins in acidic medium and
studied their chelation ion-exchange properties. Sangal et al.\textsuperscript{113} have reported the synthesis and characterization of Pyrazine-2-amidoxime complexes of Cu(II), Ni(II), Co(II), Fe(II) and Mn(II). Bonding in these complexes takes place through the pyrazine ring nitrogen and oxime nitrogen. In 1987, Masoud et al.\textsuperscript{114} have reported the coordinating behaviour of dimethyl glyoxime, salicylaldoxime, a-benzoinoxime, 4-pentanedione dioxime, barbituric acid oxime and thiobarbituric acid oxime towards Co(II), Ni(II), and Cu(II). Metal complexes with oximes have received much attention during recent years\textsuperscript{115-118}. Reports are available on bis and tris complexes of Co(II), Ni(II) and Cu(II). The ligands are capable of co-coordinating through oxygen and nitrogen to give homo and hetero poly nuclear encapsulated and macro cyclic metal complexes\textsuperscript{119}. The complexes were characterized by conductivity measurements\textsuperscript{120,121}, proton NMR spectra and TGA. The complexes were of the types M(HL)\textsubscript{2}X\textsubscript{2}2H\textsubscript{2}G, where M=Zn, X=OAc and ML\textsubscript{2}X\textsubscript{2}2H\textsubscript{2}O, where M=Cd, Hg, X=OAc. The ligand was found to be monodentate in Zn complex and bidentate in the other complexes\textsuperscript{122}. 

Dhar et al.\textsuperscript{123}, have reported the synthesis and characterization of lanthanide complexes of o-vanillin. Based on the characterization studies such as elemental and thermal analysis, magnetic moment studies and spectral analysis. They assigned a general formula Ln(C\textsubscript{6}H\textsubscript{5}N\textsubscript{0}\textsubscript{3})X.H\textsubscript{2}O tor these complexes (where X=2,3…) Here the ligand behaves as abidendate
one, coordinating through oxygen and nitrogen. In 1989, Revenkar and Mehela have reported the synthesis and characterization of complexes of 2-acetyl-benzimidazole oxime (AcBzOxH$_2$) and 2-benzoyl-benzimidazole oxime (BzBzOxH$_2$) with Co(II), Ni(II), and Cu(II). Patel et.al, have reported the synthesis of chelating ion-exchange resins 2,4-dihydroxy propiophenonoxime-formaldehyde (2,4-DPPO-F) and their ion-exchange properties. The resins have been characterized by elemental analysis, IR spectra, viscosity and TGA. The molecular weights of resins have been determined by non-aqueous conductometric titrations and vapour pressure osmometry (VPO). Chelating ion-exchange properties have also been studied employing the batch equilibrium method. Prasad et.al have reported the synthesis and characterization of ternary complexes of 3d metal(II) ions such as Mn, Co, Ni, Cu, Zn, and VO with acetyl acetone and salicylaldoxime. The complexes have been synthesized and characterized on the basis of conductivity, electronic, magnetic, IR and ESR spectral data. Ni(II) complex exhibits a square planar octahedral equilibrium where all other complexes have octahedral stereochemistry. Reddy reported the synthesis and structural studies of complexes of Fe(II), Fe(III), Co(II), Co(III), Ni(II) and Cu(II) complexes with o-vanillin oxime. The complexes were characterized on the basis of elemental, thermal and spectral studies. The reaction of some oxime derivatives of 5-formyl vanillin with Ni(II) and Cu(II) halides were studied by Zular et.al. Ramesh et.al have reported the metal chelates of 2,3-dioximes of some acetoaryl amides.
The complexes have the general formula MU where M=Hg, Cu; HL=2,5-dioximes of aceto acetanilide, o-aceto toluene, 2,4-acetoacetoxylidine. Mehta et.al[1] studied the transition metal complexes of 2-hydroxy-n-naphthaldehyde oxime and 2-acetyl-1-naphthol oxime.

In 1993, Reddy has described the synthesis and structural studies of complexes of Fe(II), Fe(III), Co(III), Ni(II) and Cu(II) with syn-phenyl-a-pyridyl ketoxime. The complexes were characterized by elemental analysis, electronic spectra, magnetic moment, conductivity and IR data. Fe(II) and Co(III) have pseudo octahedral and octahedral geometry. Ni(II) complex has square pyramidal geometry and Cu(II) has a square pyramidal geometry and have binuclear nature. The ligand acts as uninegative bidentate by coordinating through azomethine nitrogen atom and heterocyclic ring nitrogen[13].

Synthesis and studies of some new arylazo oximes and their cobalt complexes were reported[2]. In 1995, Ali et.al synthesized three unsymmetrical vic-dioximes, namely, N-ethylaminophenylglyoxime, N-propylatninoglyoxime and N-butylaminoglyoxime. Its Co(II) and Ni(II) complexes were prepared and characterized[3]. Angelolf et.al., have reported the polydentate ligand 1,10-phenanthroline-2,9-dicarbaldehyde dioxime. This ligand and its complexes with Zn(II), Cu(II), Co(II) and Ni(II) were designed as potential agent for nucleic acid hydrolysis and were characterized by elemental analysis, NMR spectroscopy, ES-MS and X-ray
diffraction analysis. The ligand acts as a tridentate ligand in most cases, to form monomeric trigonal bipyramidal, square pyramidal structure\textsuperscript{134}.

In 1997, Sharma et al.\textsuperscript{135}, have reported the preparation and characterization of mixed ligand complexes of iron phthalimide and iron nitrite triacetate with oxime. Preparation and characterization of \(3\times\left\{2\times[1\times\text{methyl}\times3\times\text{oxobut-1-enyl}\times\text{amino}\times\text{ethyl}\times\text{-imino}\times]\text{butan-2-one}\times\text{oxime}\right\}\) and its mononuclear \(\text{Cu}^{II}\) and \(\text{Ni}^{II}\) dinuclear complexes involving \(\text{Cu}^{II}\times\text{Cu}^{II}, \text{Cu}^{II}\times\text{Ni}^{II}\) and \(\text{Cu}^{II}\times\text{Cr}^{III}\) were reported by Jean et al.\textsuperscript{136}.

In 1999, conventional chemical and direct electrochemical synthesis of \(\text{Cu, Co, Ni, and Zn chelates of 2-}\left\{\text{N-tosyl amino}\times\text{benzaldoxime}\times\right\}\times\text{and 2-}\left\{\text{N-tosyl amino}\times\text{benzal-o-methyl}\times\text{oximes}\right\}\times\text{where reported by Burlov et al.}\textsuperscript{137}. The complexes were characterized on the basis of elemental analysis, IR, EPR spectra and magnetic properties. Tas et al.\textsuperscript{138}, have reported the synthesis of \(9,10\times\text{bis(hydroxyimino)}\times-4,8,11,15\times\text{tetraaza-1,2,17,18-o-dibenzal octadecane}\) from \(1,2\times\text{o-benzal-4-aza-7-aminoheptane}\), which was prepared from reaction of \(1\times\text{chloro-2,3-o-benzalpropane}\times\text{and dichloroglyoxime}\). The complexes of \(\text{Co(II), Co(III), Cu(II), Ni(II)}\) and \(\text{U0}_2(V)\times\text{were prepared and characterized by elemental analysis, IR spectra, magnetic susceptibility measurements, TGA and DTA. Two tetraoximes, ethane 1,2\times\text{bis(thio-p-nitrophenyl glyoxime) and ethane 1,2-bis(thio-m-nitroglyoxime) have been synthesized from anti-p-nitro phenyl chloro glyoxime or m-nitotphenyl chloro glyoxime and 1,2-ethanedithiol. It’s polymeric complexes}
with Ni(II), Cu(II) and Co(III) ions have been prepared and reported by Chahit et.al\textsuperscript{139}.

In 2000, Razarta languri et.al\textsuperscript{140} have synthesized a series of cis-[Ru(bpy-oxime)]\textsuperscript{2+} complexes, cyclohexa dione dioxime, diphenyl glyoxime and 2-acetyl pyridine. The complexes were characterized by \textsuperscript{1}H and \textsuperscript{13}C NMR spectra, cyclic and differential pulse voltametry and using pKa determination. Kelkar et.al\textsuperscript{141}, have synthesized the oxime ligand using 2-hydroxy- 1-naphthaldehyde and 2,4-dihydroxy acetophenone. Co(II), Ni(II) and Cu(II) complexes of oxime were synthesized and characterized by their analytical parameters and various spectral features. The structures of the complexes were proposed from electronic absorption spectra and magnetic susceptibility data studies. Triorgano antimony(V) complexes with internally functionalized oximes have been prepared by the reaction of K\textsubscript{3}SbBr\textsubscript{5} with the corresponding oximes (R=Me, Pr) in 1:2 molar ratios in anhydrous benzene. The complexes have been characterized by elemental analysis, IR and NMR (\textsuperscript{1}H and \textsuperscript{13}C) spectroscopic studies\textsuperscript{142}.

Rai et.al\textsuperscript{143}, have reported isolation and characterization of a series of Co(II), Ni(II) and Cu(II) complexes with 9,10-phenanthroquinone dioxime along with nitrogen donor adducts with ammonia or pyridine. In 2001, Rai et.al have also reported the synthesis and characterization of Co(II) complexes with some new quinazolone oximes\textsuperscript{144} in continuation of their research work on transition metal complexes with oximes\textsuperscript{145,146}. Synthesis
and characterization of lanthanide complexes of schiff bases derived from 2,6-diacetyl pyridine mono oxime and diamino benzene were studied\textsuperscript{147}.

Vanadium complexes of oxime lignds have been synthesized and the structure reaction correlation studies have been carried out\textsuperscript{145} in 2003. Organotin coordination works have been carried out on oxime analogues of aminoacids and peptides\textsuperscript{149}. In 2004, Socorro et.al have synthesized and characterized certain macrocyclic complexes of the oxime class\textsuperscript{130}. Otter et.al, recently synthesized and studied the photochemistry of some cobalt complexes of oxime based ligands\textsuperscript{151}.

1.7 Scope of the Present Investigation

Polymcr-anchored ligands with chelating properties have created considerable research interest in recent years\textsuperscript{75, 152}. Such ligands itself and their complexes find applications in a variety of fields. The facile regenerability, higher stability and operational flexibility\textsuperscript{155} are the striking advantages of these co-ordination polymers. Chelating polymers are of considerable importance due to their inherent advantages over simple ion exchange resins\textsuperscript{154}.

Keeping these points, as part of the present investigations, tour different aldoxime urea formaldehyde based novel polymeric ligands (Schiffs bases) such as 4-hydroxybenzaldoxime urea formaldehyde (4-HBO-U-F), vanillin oxime urea formaldehyde (VO-U-F), anisaldoxime
urea formaldehyde (AO-U-F) and 2-nitrobenzaldoxime urea formaldehyde (2-NBO-U-F) polymeric ligands have been synthesized and characterized. The synthesized ligands have been developed as selective reagents for the removal of heavy metals from solution based on the principle of chelation. Thus 4-hydroxybenzaldoxime urea formaldehyde is developed as a reagent for the removal of Cu(II), vanillin oxime urea formaldehyde for Fe(III), anisaldoxime urea formaldehyde for Zn(II) and 2-nitrobenzaldoxime urea formaldehyde is developed for the removal of Cr(VI). Optimum experimental conditions have been established for the removal of all these metal ions and systematic analytical studies have been carried out. Each ligand has its own advantages with respect to the removal of the respective metal. The application of the presently developed reagents in the removal of metal ion from industrial effluent has also been established. Since complexation is the basis of the studies, the corresponding metal complexes have also been separated and an attempt is made for their characterization.

It is hoped that the presently developed reagents can be used for the removal of the corresponding metal ion from aqueous solutions, natural samples and industrial effluents.