CHAPTER 1

INTRODUCTION TO THE TITLE

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Abstract
The first chapter introduces the basics and overview of polymers, chelating polymers, polychelates, classification and types of polychelates, bonding theories, basic properties of lanthanides (III) and applications of polychelates. The d-block elements are dominating in the area of coordination polymers; therefore, the present work is being extended on 4f-block elements. Further, the objective of the work done has been outlined in brief.
1.1 Introduction

The basic features of the coordination compounds were elucidated by the Danish chemist S. M. Jorgenson (1837-1914) and the Swiss Chemist Alfred Werner (1866-1919). They synthesized coordination compounds to find out the manner in which the saturated compounds (the metal salts and the ligands) unite to form coordination compounds. As Werner was able to give theory for these compounds which explained and correlated a large number of observation, these compounds are called the Werner’s complexes. He developed the idea of the coordination sphere for explaining the chemical activity, electrical conductivity and isomerism in these compounds. Metal complexes, in which a metal atom or ion is surrounded by several atoms or ions, play an important role in inorganic chemistry especially for elements of the d and f-blocks. The class of solids defined as coordination polymers is one of the most exciting fields in solid state chemistry. The stunning variety of structures, compositions and properties as well as their easy tailoring has attracted many researchers. As a result of all this activity the field has now moved in several different directions depending on the particular property being investigated.

The field of coordination polymer research is now vast, and one of the fastest growing areas of chemistry in recent times, with important work being done on a large variety of different aspects (1). A coordination polymer consists essentially of metal and ligands, although they often include guests and counter ions. The metal ions are usually transition metals and/or lanthanides. For transition metals, the field is dominated by the first-row elements (plus Zn, Cd, Hg, Ag and, to a lesser extent, Au, Pd, Pt), due to their kinetic lability and ready availability and stability. Generally, transition metals have been more popular, due in part to the more predictable nature of their coordination geometries; however, lanthanides have attracted increased attention recently, with their higher connectivity leading to interesting topologies, in addition to other inherent properties of interest (e.g. luminescence). These metals are commonly used as their halide, nitrate, perchlorate, tetrafluoroborate, hexafluorophosphate, hexafluorosilicate or trifluoromethanesulfonate salts; ‘non-coordinating’ anions are usually preferred.
1.1.1 Polymers

The word *polymer* is derived from classical Greek word ‘*poly*’ meaning “many” and ‘*meres*’ meaning “parts.” Thus a polymer is a large molecule (macromolecule) built up by the repetition of small chemical units. To illustrate this, Figure 1.1 shows the formation of the polymer polystyrene.

![Figure 1.1 Formation of polystyrene from styrene](image)

The styrene molecule contains a double bond. Chemists have devised methods of opening this double bond so that literally thousands of styrene molecules become linked together. The resulting structure, enclosed in square brackets, is the polymer polystyrene. Styrene itself is referred to as a *monomer*, which is defined as any molecule that can be converted to a polymer by combining with other molecules of the same or different type. The unit in square brackets is called the *repeating unit*. Notice that the structure of the repeating unit is not exactly the same as that of the monomer even though both possess identical atoms occupying similar relative positions. The conversion of the monomer to the polymer involves a rearrangement of electrons. The residue from the monomer employed in the preparation of a polymer is referred to as the *structural unit*. In the case of polystyrene, the polymer is derived from a single monomer (styrene) and, consequently, the structural unit of the polystyrene chain is the same as its repeating unit. Other examples of polymers of this type are polyethylene, polyacrylonitrile, and polypropylene. However, some polymers are derived from the mutual reaction of two or more monomers that are chemically similar but not identical. For example, poly(hexamethylene adipamide) or nylon 6,6 is made from the reaction of hexamethylenediamine and adipic acid (2).

1.1.2 Chelating polymers

Chelating polymers are the polymers which contain the pendent functional groups and are able to bind with the metal ions by forming coordination bond. These kinds
of polymers are the specialty polymers having such ability. They are used as precursor for the synthesis of polychelates.

The diverse nature of coordination and geometry of element offers the possibility of accessing polymers with unusual conformational, mechanical and morphological characters (3, 4). The incorporation of metals into the polymer chain offers potential for the preparation of processable materials with various applications, which differ significantly from those of conventional organic polymers. Metal ions can be incorporated into the chelating polymeric structure by three possible ways (Figure 1.2),

1. Metals can be either in the side-group structure
2. Directly in the main chain
3. Polymers with metals in both the side group and in the main chain, dendrimers/hyperbranched polymers.

![Structural classes of metal containing polymers](image)

**Figure 1.2** Structural classes of metal containing polymers

The sorption and desorption properties of the chelate-forming resin, poly(8-hydroxyquinoline 5,7-diylmethylene) towards La$^{3+}$, Ce$^{3+}$, Nd$^{3+}$, Sm$^{3+}$ and Gd$^{3+}$ metal ions were studied by a static batch equilibration technique as a function of pH and contact time was carried out by Ebraheem *et al.*, (5). Samal *et al.*, (6) have synthesized chelating resins (o-HAP-DDE-HCHO and o-HAP-DDE-FFD) having multiple functional groups by condensation of o-hydroxyacetophenone-4,4′-diaminodiphenylether(o-HAP-DDE) with formaldehyde and furfuraldehyde.
respectively and the extent of loading of metal ions Cu(II) and Ni(II) was studied in both competitive and non-competitive conditions varying the contact time.

Vijayalakshmi et al., (7) have carried out synthesis and metal uptake studies on poly (8-hydroxy-5-azoquinolinephenylacrylate-formaldehyde) resin and its metal complexes with the aqueous solution of Cu(II) and Ni(II). Shah et al., have derived phenolic resin from 8-hydroxyquinoline-formaldehyde-catechol using formaldehyde as a cross linking agent at 120±2ºC in DMF solution and the total cation exchange capacity, effect of pH and metal ion concentration on ion exchange capacity were also studied. The rate of cation exchange reactions and distribution coefficient values in tartaric acid media at different pH were studied using batch equilibration method (8).

1.1.3 Polychelates
Polychelates are composed of synthetic polymer and metal ions, where the metal ions are bounded through the chelating groups of polymeric ligand by a coordinate covalent bond (9). A polymeric ligand contains coordinating sites like nitrogen, oxygen and/or sulphur obtained either by polymerization of monomer possessing the coordinating site or by a chemical reaction between a polymer and a low molecular weight compound having coordinating ability, which are capable of breaking the coordination bond but would not rupture the polymeric backbone (10). The coordination bonds are an integral part of the polymer backbone. The fact that the metal–ligand bonds are formed reversibly and variety of metal ions are forming suitable polymers is the advantage of coordination polymers (11).

The synthesis of coordination polymer results in an organic polymer with inorganic functions. The metal atoms attached to polymer backbone are bound to exhibit characteristic catalytic, antimicrobial and thermal behavior etc., which are distinctly different from their low molecular weight analogue. Thus polychelates are a novel type of materials possessing a combination of physical properties of an organic polymer and chemical properties of the attached metal ions.

1.2 Classification of polychelates
The methods include chelation between a ligand function anchored on a polymer matrix and metal ion, reaction of a multifunctional ligand with metal ion and polymerization of metal containing monomers. The polychelates are classified into
different groups according to the position occupied by the metal, which is decided by the methods of preparation.

(I) Chelation of polymeric ligands
(II) Chelation of multifunctional ligands
(III) Polymerization of metal containing monomers

1.2.1 Chelation of Polymeric Ligands

The polychelates are prepared by the chemical reactions of polymers having chelating sites with metal ions. Some examples are given as in Table 1.1.

Generally, the reaction of polymeric ligand with metal ion or stable metal complex, in which one coordination site remains vacant, results in different structures that can be grouped into pendant and inter/intra-molecular bridged polychelates (12).

**Pendent metal chelates:** A pendant metal chelate is one in which the metal ion is attached to the polymeric ligand function, which is appended to the polymeric chain. After chelation, abilities of ligands pendant chelates are classified as monodentate or polydentate polychelates. The monodentate pendant polychelates are formed from a metal ions or stable metal chelates in which the central metal ion is already masked with low-molecular weight ligands except for one coordinating site that remains vacant. In these chelates, the effects of polymer chains are exhibited clearly and the polychelates are often insoluble in water or in organic solvents, since it contains few bridged structures which reduce their solubility.

The reaction between metal ion or metal chelate and the polymeric ligand is carried out with excess of the metal or metal chelate, the probability of the substitution of the second labile ligand of the metal ion would be very less, resulting in a predominantly monodentate type complex (Figure 1.3) (13).

![Figure 1.3 Monodentate pendant polychelate](image-url)
### Table 1.1 Some chelate forming polymeric groups

<table>
<thead>
<tr>
<th>Coordinating groups</th>
<th>Repeating units of polymeric ligands</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Alcohols – OH; Carboxylic acids – COOH</td>
<td>![Chemical structure]</td>
</tr>
<tr>
<td>2. Thiols – SH</td>
<td>![Chemical structure]</td>
</tr>
<tr>
<td>3. Amines – NH₂, &gt;NH, &gt;N-</td>
<td>![Chemical structure]</td>
</tr>
<tr>
<td>4. Nitrogen of heterocyclic</td>
<td>![Chemical structure]</td>
</tr>
<tr>
<td>5. Schiff base &gt;C = N-</td>
<td>![Chemical structure]</td>
</tr>
<tr>
<td>6. Ketons esters, amides &gt;C =O</td>
<td>![Chemical structure]</td>
</tr>
<tr>
<td>7. Aminopoly carboxylic acids</td>
<td>![Chemical structure]</td>
</tr>
<tr>
<td>8. Phosphoric acids –PO(OH)₂</td>
<td>![Chemical structure]</td>
</tr>
</tbody>
</table>
Even if the metal ion or the metal complex has more than two labile ligands, it is possible to form a monodentate chelate by selecting an appropriate reaction conditions. When the polymer backbone contains multidentate ligands the structure of polychelate can be represented in **Scheme 1.1**.

**Scheme 1.1** Coordination structure of polychelate

Polydentate ligands often result in the formation of stable metal chelates with bridged structure (**Figure 1.4**) (14). Most of the chelating resins fall under this category. They are characterized by their relatively well defined coordination structure. Here the effect of the polymeric chain is more predominant (15).

**Figure 1.4** Polydentate polychelate

**Inter/intra-molecular bridged polychelates**: When a polymeric ligand is associated directly with metal ion possessing four or six coordinate bonding sites, the resulting polychelate may be of the intra-polymer chelate or inter polymer chelate type as shown in **Scheme 1.2**.

**Scheme 1.2** Inter/Intra-molecular bridge polychelates
The structure of polychelate in this type is not clear and it is often difficult to distinguish between inter/intra-molecular bridging. Intra-polymer chelate is sometimes soluble while inter-polymer chelate results precipitation of the linear polychelates as exemplified by poly(acrylic acid)-Cu(II) complexes (16). Thus, it is not easy to elucidate the polymer effect in studying the characteristics of the polychelates.

1.2.2 Chelation of polymeric ligands

Coordination polymers have been used since before restored history, though not recognized as such until recently. For instance, the tanning of leather depends on the coordination of metal ions with the proteins. These protein–metal ion complexes resist bacterial attack, which befall in non-tanned animal skins. Metals bound to other natural polymers including proteins, affect numerous enzymatic and membrane interactions (17). Multifunctional ligands capable of forming this type of coordination polymers are classified into linear coordinated polymers and network-coordinated polymers (Parquet). A low molecular weight compound with multifunctional ligands on both ends of the molecules grows into a linear network polymer. The polymer chain is composed of coordinate bonds and the ligand is the bridging unit as per the following representation (Scheme 1.3).

![Scheme 1.3 Metal chelated monomeric ligands](image)

Linear coordinated polymers can be of two types. In the first type the polymer chain is composed of bifunctional ligand and metal ion, as exemplified by copper complex of poly(thiosemicarbazide) (Figure 1.5) (18, 19).

![Figure 1.5 Copper complex of poly (thiosemicarbazide)](image)

In the other case a simple compound or ion can function as a bridging ion, to give a polymeric structure, same as in case of copper complex of poly(α-amino acids) (Figure 1.6) (20).
Parquet polymers are flat, netlike organic macromolecules in which a metal is completely enmeshed. This type of polychelate is formed by “template reaction” between two functional groups of the ligand induced by their coordination to metal ions, resulting in following type of polychelates (Scheme 1.4).

**Scheme 1.4** Parquet polymers

Polyporphyrinato copper(II) complex is formed by the reaction of copper(II) acetylacetonate with tetracyanoethylene at 200°C under vacuum (21). Polyporphyrinato copper(II) complex is formed by the reaction of pyromellite dianhydride, cupric chloride and urea in presence of a catalyst at 180°C (22). The colour of the complex varies from green to black and has molecular weight up to 4000 gm/mole. These polymers are very important because of their thermal stability, potential electrical properties and due to similarities with haemoproteins. Polyporphyrinato copper (II) (Figure 1.7A) and polyporphyrinato copper (II) (Figure 1.7B) complexes are the most common examples.
1.2.3 Polymerization of metal containing monomers

These type of polychelates are known for their clear coordination structure. Polymerization occurs by radical or ionic initiation to form a polymer of high molecular weight as depicted below (Figure 1.8).

![Figure 1.8 Polymerization of metal containing monomers](image)

Cu-complex with Schiff base ligand containing vinyl group (Figure 1.9) has been reported (16).

![Figure 1.9 Cu-complex of vinyl group containing ligand](image)

Methacrylate can coordinate with amines Co(III) complexes to form methacrylato-pentamine-Co(III) perchlorate (Figure 1.10A) and cis-dimethacrylato-tetramine-Co(III) perchlorate (Figure 1.10B). Homo and co-polymerization of these polychelates with methacrylic acid have been carried out using redox initiators (23).

![Figure 1.10 Metal chelated monomeric ligands](image)
1.3 Basic concepts of coordination compounds

The fundamental theories and concepts described herein are vital for understanding coordination compounds, polychelates and organometallic compounds. The whole description is given in brief to co-ordinate with the modern development in chemical bonding.

**Hard and soft acids and bases (HSAB) classification**

Ralph Pearson had introduced the HSAB principle in the early 1960s (24) as an attempt to unify inorganic and organic reaction chemistry (25). The HSAB concept is an acronym for hard and soft acids and bases. Also known as the Pearson acid base concept, HSAB is widely used in chemistry for explaining stability of compounds, reaction mechanisms and pathways. It assigns the term 'hard' or 'soft' and 'acid' or 'base' to chemical species. The term 'Hard' applied to species which are small, have high charge and are weakly polarizable. While term 'Soft' applied to species which are big, have low charge and are strongly polarizable (26). This principal is used in contexts where a qualitative rather than quantitative description would help in understanding the predominant factors which drive chemical properties and reactions. This is especially in transition metal chemistry, where numerous experiments have been done to determine the relative ordering of ligands and transition metal ions in terms of their hardness and softness. HSAB classification is also useful in predicting the products of metathesis reactions. Recently it has been shown that even the sensitivity and performance of explosive materials can be explained on the basis of HSAB concept (27). It implies making use of ‘Lewis’ definition of an acid (electron pair acceptors; metal ions and the proton) and a base (electron-pair donors; ligands). The soft acids react faster and form stronger bonds with soft bases, whereas hard acids react faster and form stronger bonds with hard bases (28). Hard-hard interaction is predominantly ionic. Soft-soft interaction cannot be ionic, as the Madelung energy for a pair of bigger ions will be very small.

Hard acids and hard bases tend to have

- Small size
- High oxidation state
- Low polarizability
- High electronegativity
• Low-lying HOMO (Highest Occupied Molecular Orbitals) energy (bases) and
  High-lying LUMO (Lowest Unoccupied Molecular Orbitals) energy (acids)

Examples of hard acids are: H⁺, alkali ions, Ti⁴⁺, Cr³⁺, Cr⁶⁺ and BF₃ etc.
Examples of hard bases are: OH⁻, F⁻, Cl⁻, NH₃, CH₃COO⁻ and CO₃²⁻. The affinity of
hard acids and hard bases for each other is mainly ionic in nature.

Soft acids and soft bases tend to have
• Large size
• Low or zero oxidation state
• High polarizability
• Low electronegativity
• High-lying HOMO (Highest Occupied Molecular Orbitals) energy (bases) and
  Low-lying LUMO (Lowest Unoccupied Molecular Orbitals) energy (acids)

Examples of soft acids are: CH₃Hg⁺, Pt⁴⁺, Pd²⁺, Ag⁺, Hg²⁺, Hg₂²⁺, Cd²⁺ and BH₃.
Examples of soft bases are: H⁻, R₃P, SCN⁻ and I⁻. The affinity of soft acids and bases
for each other is mainly covalent in nature.

There are number of borderline cases, therefore, this classification has been
used as a guideline rather than a law, but the general rule is that hard acids prefer
hard bases and vice versa. This is useful for many organic reactions (29). The
selected Hard/Borderline/Soft acids and bases are shown in Table 1.2.

Table 1.2 Selected Hard/Borderline/Soft Acids and Bases

<table>
<thead>
<tr>
<th>Nature</th>
<th>Acids</th>
<th>Bases</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soft</td>
<td>Cu⁺, Ag⁺, Au⁺, Cd²⁺, Pd²⁺, Pt²⁺, Tl³⁺</td>
<td>RSH, R₂S, I⁻, CN⁻</td>
</tr>
<tr>
<td>Borderline</td>
<td>Fe²⁺, Ni²⁺, Zn²⁺</td>
<td>Br⁻, NO₂⁻</td>
</tr>
<tr>
<td>Hard</td>
<td>H⁺, Na⁺, K⁺, Be²⁺, Mg²⁺, Sr²⁺, Sc³⁺, Fe³⁺, Ln³⁺</td>
<td>H₂O, NH₃, R₂O, Cl⁻, NO₃⁻</td>
</tr>
</tbody>
</table>

To explain and understand the nature of chemical bond between two atoms
within the molecules, Valance bond, Molecular orbital, Crystal field and Ligand
field theories have been put by various researchers.

Valence bond (VB) theory
This theory was introduced by L Pauling in 1930-31 to explain bonding in
complexes. It is simple, qualitative and approximation method applicable to
covalent bonding. It deals with ground state of atoms or central metal ion in case of metal complexes. In this theory, it is considered that, the atoms are maintaining their individuality. The bond formation takes place from the interaction of the valance electrons as the atoms come together for complete combining. It explains the nature of a chemical bond in molecule in terms of atomic valencies (30).

\[ \text{A}^\circ + \text{B}^\circ \rightarrow \text{A} - \text{B} \quad \text{A and B two atoms} \]

\[ \text{A:B} \quad \text{Shared pair of electrons} \]

\[ \text{A-B} \quad \text{Covalent bond formation} \]

This is the central idea of the VB theory. The role of inner electrons is totally ignored or not considered, is the major drawback of the theory.

**Molecular orbital (MO) theory**

The MO theory determines molecular structure in which electrons are not assigned to individual bonds between atoms but are treated as moving under the influence of nuclei in the whole molecule (31). The \( c_{ij} \) coefficients may be determined numerically by substitution of this equation into the Schrodinger equation and application of the variation principle. This method is called the linear combination of atomic orbitals (LCAO) approximation. In this theory, each molecule has a set of molecular orbitals. The molecular orbital wave function \( \Psi \) may be written as a simple weighted sum of the n constituent atomic orbitals \( \chi_i \) (32). MO theory was developed in the years, after valence bond theory (1927) had been established, primarily through the efforts of Friedrich Hund, Robert Mulliken, John C Slater and John Lennard-Jones (33). It was originally called the Hund-Mulliken theory. The word *orbital* was introduced by Mulliken in 1932 (34). By 1933, the MO theory had become valid, popular and a useful theory (35). By 1950, molecular orbitals were completely defined as eigen functions (wave functions) of the self-consistent field Hamiltonian and it became fully rigorous and consistent (36).

**Crystal field theory**

Crystal field theory (CFT) is a model that describes the electronic structure of coordination compounds. It was developed by physicists Hans Bethe and John Hasbrouck Van Vleck in 1930s (37). According to CFT, the interaction between metal and ligands arises from the attraction between the positive charge of metal cation and negative charge of the non-bonding electrons of the ligand. In this theory,
• Ligands are treated as point charges
• There is no attraction between metal orbitals and ligand orbitals
• The ‘d’ orbitals on the metal ion are degenerate in the free atom

However, during a complex formation, the degeneracy of ‘d’ orbital disappears.

**Ligand field theory**

Ligand field theory was developed during the 1930s and 1940s as an extension of crystal field theory (CFT). Ligand field theory, in a sense, is combination of CFT and molecular orbital theory. CFT does not describe bonding but describe specific properties of coordination compounds which are based on a model that emphasizes electrostatic interactions between ligand electrons with electrons on the metal ions, while LFT describes the bonding in coordination compounds (38).

**1.4 Structure and reactivity of polychelates**

Although several reports discuss the structure and reactivity of polychelates, most of these polychelates are too complicated to be discussed quantitatively due to their non uniformity in their structures. These compounds include not only “chelates of macromolecules” but also the structurally labile “metal chelates”. Before detailed information can be obtained about the properties of polychelates, especially about the reactivity and catalytic activity, their structure must be elucidated. A polychelate having a uniform structure may be defined as follows:

• The structure within the coordination sphere is uniform, i.e. the species and the composition of the ligand and its configuration should be identical in any complex unit existing in the polychelate.

• The primary structure of the polymeric ligand must be known.

If the structure within the coordination sphere is identical in a polychelate and a monomeric chelate, their reactivity ought to be the same even though the chelate is bound to a polymer chain. However, it is clear that the reactivity is sometimes strongly affected by the polymer ligand that exists outside the coordination sphere and surrounding the metal chelates. The effect of polymer ligands can be explained in terms of two factors:

• The special environment constituted by a polymer ligand domain.
• The steric effect, which is determined by the conformation and density of the polymer ligand chain.
Hence, it is possible to prepare polychelates having variety of applications by varying the polymer chain, nature of the ligand and the metal ion (39).

**1.5 Applications of polychelates**

**Catalytic activity**

A catalyst, by definition, increases or decreases the rate of a chemical reaction without undergoing any change in its own composition or being consumed in the reaction. In homogeneous catalysis, catalysts are used in solution. However, heterogeneous catalysis offers the advantage of ease of separation from products and lack of corrosiveness.

Organic reactions are extensively catalyzed by polychelates (40). A polymer-supported group often has catalytic properties analogous to that of the same group used in homogeneous catalysis. The catalytic cycle of a polychelate catalyzed reaction is illustrated by the following equations:

\[
\begin{align*}
ML_n + S & \leftrightarrow L_{n-1} M - S \\
M'L_n + S^* & \leftrightarrow L_{n-1} M' - S^*
\end{align*}
\]

Where, M is the metal ion, L the ligand and S the substrate.

In the first step the substrate coordinates to a metal catalyst forming an intermediate mixed complex (transition state). The substrate is then activated by metal ions and dissociates from the catalyst. The complex catalyst, having accomplished its purpose, is regenerated to the original complex. The catalytic action of a metal ion depends substantially on the nature of the ligands in the intermediate mixed complex. The catalytic activities of the polychelates possess the following features:

- The economy and convenience of heterogeneous catalysis.
- Polymer-bound catalyst can be employed under conditions comparable to those of conventional homogeneous catalyst (i.e.) at temperatures below 100 °C and at ambient pressures.
- Homogeneous catalytic activity is retained by metal chelates or binding to the resin.
- The steric environment of the catalyst is altered and substrate selectivity is increased.
• The catalytic sites (single metal atom) can be separated by binding to the rigid region of the support. By avoiding the formation of ligand-bridged complexes greater catalytic activity is gained.

**Oxidative reactions**

Oxidative reactions of organic compounds with molecular oxygen take place with high efficiency and selectivity in presence of Werner-type metal complexes used as catalysts. A metal chelate catalyzes oxidation of compounds having mobile hydrogens, such as hydroquinone, ascorbic acid, phenols and amines, in presence of molecular oxygen. In this reaction a substrate coordinates to metal catalyst and then one-electron of the substrate is oxidized by the metal ion with higher valency.

\[
2 \text{AH}_2 + \text{O}_2 \xrightarrow{\text{M}^+} 2 \text{A} + 2 \text{H}_2\text{O}
\]

The catalytic properties of this polymer–Fe(III) porphyrin complex were compared with Fe(III) porphyrin in the oxidative reaction of phenylenediamine. Metalloporphyrin was linked to a poly (phenyl alanine) chain by peptide bond. The catalytic activity of the polychelate was twice as large as that for the corresponding analog as reported by Lautsch et al, (41). Polychelates often exhibit high catalytic efficiency in the decomposition of \(\text{H}_2\text{O}_2\): Poly(β-diketone)-Cu(II) (42), poly(acetylhydroxamic acid)-Cu(II) (43), various poly(amino acid)– Cu(II) (44) and poly(4-vinylpyridine)–Co(II) (45). Hojo et al., (46) employed Cu(II) poly (vinyl alcohol) as the catalyst for the decomposition of \(\text{H}_2\text{O}_2\) and reported that the relation between the initial rate and initial concentration of \(\text{H}_2\text{O}_2\) varied in accordance with the rate expression of Michaelis–Menten type.

Lei and Wang (47) reported the selective oxidation of ethylbenzene, \(n\)-propylbenzene and \(n\)-butylbenzene catalysed by organic polymer supported Ru(II) complexes under oxygen or air in the absence of solvent in heterogeneous phase. The reaction gives the corresponding ketone and alcohol in good yield. The catalytic selectivity of total ketone and alcohol ranged from 98 to 100% with different ruthenium polymer-bound 2, 2’-bipyridine complexes.

Kaliyappan and Kannan synthesized the poly(2-hydroxy-4-acryloyloxy benzaldehyde)-Cu(II)/Ni(II) complexes and used as the catalyst for the oxidation of cyclohexanol to cyclohexanone with higher conversion (48). Oxidation of ascorbate and hydroquinone by molecular oxygen was found to be enhanced by
poly(amine-organosiloxane) (PAOS)-Cu(II) complex. In contrast to Cu(II) catalyzed reaction, the PAOS–Cu(II) catalyzed reaction becomes zero order in the substrate concentration at a relatively low concentration of the substrate exhibiting Michaelis–Menten kinetics (49).

**Hydrogenation reactions**

Bis-benzonitrile dichloropalladium(II) was supported on two copolymers containing carboxyl and bipyridyl groups and employed as catalyst for hydrogenation of olefins under mild conditions. The coordination environment and the nature of the metal species on the polymers were studied. On the basis of environmental evidences it was proposed that polymer–palladium complexes initially contain palladium atoms with chloride atom bridges, which are cleaved in activation. The catalyst was found to be active towards the hydrogenation of olefins under ambient conditions. The kinetic and mechanistic aspects of the hydrogenation of styrene and acrylonitrile and the recycling capacity data have also been reported (50).

A very high catalytic activity was observed for the hydrogenation of olefins catalyzed by poly (acrylic acid)-Rh(II) complexes in homogenous solution. The catalyst effected preferential reduction of the olefinic bond in case of substrates having additional functional groups such as diallylether, allylaldehyde and cyclohexene-1-one. In addition greater substrate selectivity and sensitivity to the size of the alkene was also observed in the above reduction (51). Card et al., (52) reported poly (styryl)bipyridine Pd(II)acetate to be useful catalyst for the hydrogenation of alkenes and alkynes. More substituted or sterically bulky groups got reduced rapidly than the less hindered olefins. In case of alkynes, preferential reduction to alkenes in good yield without isomerization was achieved by stopping the reaction after consumption of one equivalent of hydrogen.

**Hydrolysis**

The catalytic hydrolysis of oligophosphates by poly (I-lysine)-Cu(II) complexes (PLL–Cu(II)) has been reported, the PLL-Cu(II) complex showed strong catalytic activity and attacked pentaphosphate exclusively, thus producing orthophosphate as the main product. This result was explained by the chelate structure of PLL–Cu(II) (53). Kaliyappan et al., (54) reported the good catalytic hydrolysis of ethyl acetate by poly (2-hydroxy-4-(meth)acryloyloxybenzophenone. Nozawa et al., (55)
found that poly(L-lysine)-Cu(II) complex exerted a symmetrically selective catalysis of the hydrolysis of phenyl alanine ester, whereas Cu(II) ions and bis(bipyridyl) Cu(II) had no catalytic activity. The improved stability of the intermediate PLL-Cu(II) complex with the d-ester was considered responsible for the catalytic activity. Gomez et al., (56) studied the hydrolysis of p-nitrophenylacetate spectrophotometrically in ethanol–water at 26°C and pH 8 in absence and presence of poly(4-vinylimidazole) and Cu(II). First order kinetics in p-nitrophenyl acetate was observed. The rate was increased by addition of <10^{-6} M Cu(II).

**Hydrosilylation**

Kinetic and catalytic studies were carried out to evaluate the role of polymeric organosilicon support of rhodium phosphine catalysts for hydrosilylation of -C=C- bonds. All kinetic data showed that modification of Wilkinson’s complex by polysiloxylalkylphosphine (insoluble) and silylalkylphosphine (soluble) ligand essentially had no effect on the kinetic parameters and mechanism of the hydrosilylation of 1-hexene (57).

Capaka et al., (58) reported that the polymer-supported Rh and Pt complexes catalyse the hydrosilylation reaction. The rate of hydrosilylation reaction decreases as the electron withdrawing substituent groups are substituted on the alkene molecule. Although hydrosilylation with triethoxysilane proceed uniformly with all supported catalyst complexes, which are good catalysts for hydrosilylation with Et₃SiH are poor catalysts for the reaction with Cl₃SiH and vice versa. The reaction conditions for hydrosilylation using a polymeric catalyst are mild and comparable to those with homogeneous catalysts such as chloroplatinic acid. Heterogenous poly(9-10-anthralenevinylene)-Pt complex was prepared. Hydrosilylation of CH₂=CHCH₂–OPh with (EtO)₃SiH in the presence of the catalyst gave 81% PhO(CH₂)₃Si(OEt)₃ (59).

**Initiation of polymerization**

Acrylic acid–styrene copolymer-supported Nd showed high catalytic activity and stereospecificity for butadiene polymerization. The cis-1,4 content of poly(butadiene) was 98.7%. The system was also used for isoprene polymerization to give poly(isoprene) with 95% cis-1,4-content (60).
Tsuchida and Nishide (61) used Cu/Mn poly(4-vinylpyridine) complexes as initiator for the preparation of phenolic polymers. The rate of the reaction, yield and molecular weight of the polymer were high. The polymerization of d-vinylpyrrolidone was initiated by poly(2-hydroxy-4-methacryloyloxybenzaldehyde) Cu(II)/Ni(II) complexes reported (62). Water soluble poly(vinylphosphate)–Cu(II)complex was active as a free radical initiator for the polymerization of styrene in presence of carbon tetrachloride. The maximum conversion was observed at neutral pH (63).

**Environmental Protection**

Geckeler (64) has reported the concept of chemoremediation in the liquid homogeneous phase using polymer reagents as a green technology. It is based on the retention of their molecular size by using membrane filtration. The fundamentals of metal ion interaction with respect to enrichment and separation procedures are discussed and the role of polychelates is assessed.

**Antimicrobial Agents**

The polychelates possess good antimicrobial activity compared to conventional organic polymers. So that polychelates are used as biocidal coatings and are widely applied to prevent growth of microorganisms on surfaces e.g. in antifouling paints (65). Various research groups have worked on the antimicrobial activity of transition and inner transition metal chelated polychelates (66-69).

**1.6 Chemistry of lanthanides, their properties and applications**

The lanthanides are the elements found in the sixth row between groups IIA and IVB along the bottom of the periodic table, separated from the main body of the periodic table (Figure 1.11), which represents the lanthanides like Lanthanum (La), Cerium (Ce), Praseodymium (Pr), Neodymium (Nd), Promethium (Pm), Samarium (Sm), Europium (Eu), Gadolinium (Gd), Terbium (Tb), Dysprosium (Dy), Holmium (Ho), Erbium (Er), Thulium (Tm), Ytterbium (Yb) and Lutetium (Lu). The lanthanides were once called "rare earths". In fact, many of them are available in large quantity like other familiar elements (70).

The lanthanides and actinides are actually a part of the larger family known as transition metals. These elements are known as ‘inner’ transition elements. The lanthanide series consists of 15 elements, from atomic number 57 (La) to 71 (Lu) (71), while the actinide series comprises of another 15 elements, from atomic
number 90 to 103. They are set aside from the periodic table due to similarities in their properties. Specifically, the lanthanides and actinides are the only elements with filled $f$-orbitals. The lanthanide series is usually combined with La which has an atomic number 57, under the general heading of lanthanides. As their name indicates, members of the lanthanide series share certain characteristics with La; hence the collective term "lanthanides" is commonly used.

In these elements, however, the outermost $d$ and $f$ subshells lie close together in energy, leading to some irregularities in electronic structure. These irregularities in turn lead to some uncertainty regarding their position in the periodic table. La has no electrons in their $4f$ subshell and it fits best with the elements of group III. Cerium also has no $f$ electrons but is considered member of the inner transition metal series. A common arrangement is to place the inner transition metals between groups IIA and IVB (72).

**Properties of lanthanides**

These metals are distinctive in terms of size, valence orbitals, electrophilicity, magnetic and electronic configurations. Some members of the series are currently used as best metals for specific applications. Their unusual combination of physical properties can be exploited to accomplish new types of chemical transformations which are not possible with transition and main group metals.
The lanthanides are some of the largest non-radioactive metals in the periodic table. Trivalent metal ions are stable and used in various reactions. The lanthanides 4f valence orbitals have a limited radial extension. As a result, orbital factors do not affect the chemistry as much as in transition metal chemistry. Hence, substrates can approach the metal center in a variety of orientations and the reaction pathways are not orbitally forbidden. The lanthanides are electropositive and have a high affinity for oxygen and halides. Therefore, lanthanides are utilized in the catalytic converters of automobiles and in fuel cells.

Lanthanides react rapidly with hot water or more slowly with cold water to form hydrogen gas. They are quite reactive with oxygen and combustion takes place readily in air. When lanthanides react with another reagent to form a compound, it usually loses three of its outer most electrons to form tripositive ions with positive electric charge of +3. This is the most stable ionic form of lanthanides. The less stable +2 or +4 oxidation states are also known for some of the lanthanides. Lanthanides tend to form ionic compounds or compounds containing either positive or negative ions with other elements e.g. fluorine. The lanthanide ions are primarily in the +3 oxidation state because electrons in outer most orbitals significantly shield the 4f electrons. Other stable oxidations states observed with lanthanide ions include +2 (Eu and Yb) and +4 (Ce and Tb) corresponding to vacant, half filled or filled 4f sublevels. The size of the +3 lanthanide ions is similar due to the lanthanide contraction within the range from 1.06 Å for La(III) to 0.848 Å for Lu(III) (73). Due to the decreasing size of the lanthanide ions across the series, the charge density (Z/r) of the ion increases across the series. The primary hydration sphere number changes from 9 [La(III) to Nd(III)] and 8 [Tb(III) to Lu(III)] due to the decrease in ionic radius and the increase in charge density. Nd(III) to Tb(III) ions have either 8 or 9 water molecules of hydration. Because of the similar charge and size, lanthanide(III) ions behave physically and chemically in similar manner.

The lanthanides in their +3 oxidation state begin to hydrolyze above pH 6 and the hydroxide can readily compete for coordination of the metal ion at higher pH. Lanthanide(III) ions can form both inner and outer sphere complexes. An inner sphere complex forms through an Eigen mechanism as the outer sphere complex replaces one or more primary hydration sphere water molecules. The coordination
number 6 is a common coordination number N for lanthanides. Actually, N = 8, 9, 10 or even 12 seems to be far more typical depending on properties of the ligand, solvent, concentration and other factors (74).

**Lanthanide contraction**

This is the name given to an unusual phenomenon encountered in the series of rare-earth elements. The radii of the atom of the members of this series decrease slightly as the atomic number increases. As the charge on the nucleus increases across the rare-earth series, all electrons are pulled in closer to the nucleus so that the radii of the rare-earth ions decrease slightly as we go across the rare-earth series. However, the lattice parameters become smaller and the crystals denser as the compounds proceed across the series. This decrease of the ionic radii is known as the lanthanide contraction (75).

In single-electron atoms, the average separation of an electron from the nucleus is determined by the subshell, it belongs to and decreases with increasing charge on the nucleus; this in turn leads to a decrease in atomic radius. In multi-electron atoms, the decrease in radius brought about by increase in nuclear charge is partially offset by electrostatic repulsion among electrons. Particularly, a "shielding effect" operates: i.e., as electrons are added in outer shells, electrons already present, shield the outer electrons from nuclear charge making them experience a lower effective charge on the nucleus. The shielding effect exerted by the inner electrons decreases in order $s > p > d > f$. Usually in a period, as particular subshell is filled up, atomic radii continue on decreasing. This effect is particularly pronounced in case of lanthanides, as their 4f subshells are being filled across the period and are unable to shield outer (5th and 6th) shell electrons. Thus, the shielding effect is ineffective in countering the decrease in radius due to increasing nuclear charge, which leads to "lanthanide contraction" (Table 1.3). Radius decreases from 1.034Å to 0.848Å in case of Ce(III) to Lu(III) respectively.

As a result of the increased attraction of the outer shell electrons across the lanthanide period, the following effects are observed. Each of these effects is sometimes referred to as the lanthanide contraction:

- The atomic radii of the lanthanides are smaller than would normally be expected.
• The ionic radii of the lanthanides decrease from 1.06 Å La(III) to 0.848 Å Lu(III) in lanthanide series.

• The third row of d block elements has only marginally larger atomic radii than the second transition series.

• The radii of the elements following the lanthanides are smaller than would be expected if there were no f-transition metals.

• There is a general trend of increasing Vickers hardness, Brinell hardness, density and melting point from Ce to Lu (with Yb being the most notable exception). Lu is the hardest and most dense lanthanide and has the highest melting point.

Table 1.3 The Decrease in Ionic Size of Lanthanides

<table>
<thead>
<tr>
<th>Atomic Number</th>
<th>Symbol</th>
<th>Electronic Configuration</th>
<th>Ionic Radii(Å)</th>
<th>Difference size (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>57</td>
<td>La</td>
<td>5d(^1)6s(^2)</td>
<td>1.061</td>
<td>---</td>
</tr>
<tr>
<td>58</td>
<td>Ce</td>
<td>4f(^2)6s(^2)</td>
<td>1.034</td>
<td>0.027</td>
</tr>
<tr>
<td>59</td>
<td>Pr</td>
<td>4f(^3)6s(^2)</td>
<td>1.013</td>
<td>0.021</td>
</tr>
<tr>
<td>60</td>
<td>Nd</td>
<td>4f(^4)6s(^2)</td>
<td>0.995</td>
<td>0.018</td>
</tr>
<tr>
<td>61</td>
<td>Pm</td>
<td>4f(^5)6s(^2)</td>
<td>0.979</td>
<td>0.016</td>
</tr>
<tr>
<td>62</td>
<td>Sm</td>
<td>4f(^6)6s(^2)</td>
<td>0.964</td>
<td>0.015</td>
</tr>
<tr>
<td>63</td>
<td>Eu</td>
<td>4f(^7)6s(^2)</td>
<td>0.950</td>
<td>0.014</td>
</tr>
<tr>
<td>64</td>
<td>Gd</td>
<td>4f(^7)5d(^1)6s(^2)</td>
<td>0.938</td>
<td>0.012</td>
</tr>
<tr>
<td>65</td>
<td>Tb</td>
<td>4f(^8)6s(^2)</td>
<td>0.923</td>
<td>0.015</td>
</tr>
<tr>
<td>66</td>
<td>Dy</td>
<td>4f(^9)6s(^2)</td>
<td>0.908</td>
<td>0.015</td>
</tr>
<tr>
<td>67</td>
<td>Ho</td>
<td>4f(^{10})6s(^2)</td>
<td>0.894</td>
<td>0.014</td>
</tr>
<tr>
<td>68</td>
<td>Er</td>
<td>4f(^{11})6s(^2)</td>
<td>0.881</td>
<td>0.013</td>
</tr>
<tr>
<td>69</td>
<td>Tm</td>
<td>4f(^{12})6s(^2)</td>
<td>0.869</td>
<td>0.012</td>
</tr>
<tr>
<td>70</td>
<td>Yb</td>
<td>4f(^{13})6s(^2)</td>
<td>0.858</td>
<td>0.011</td>
</tr>
<tr>
<td>71</td>
<td>Lu</td>
<td>4f(^{14})5d(^1)6s(^2)</td>
<td>0.848</td>
<td>0.010</td>
</tr>
</tbody>
</table>

Applications

Lanthanides are, however, difficult to extract due to their chemical similarity. Sometimes high levels of their reactivity and sensitivity to contamination are also responsible. Though some lanthanides have limited uses, members of this group are found in routine applications from cigarette lighters to TV screens, from
colored glass to control rods in nuclear reactors (76) and in radionuclide therapy (77, 78).

The limited radial extension of the 4f orbitals reduces vibronic broadening of optical transitions and this leads to sharp 4f-4f emission and absorption spectra. The sharp nature of these transitions leads to very precise and efficient optical process such that the lanthanides are often the components of choice in optical devices ranging from lasers (79), energy saving phosphors (A substance that glows when struck by electrons) (80), energy-saving lighting devices, displays, optical fibers, amplifiers, lasers, sensors (81), responsive luminescent stains for biomedical applications (82), to low weight high power magnets used in cars, aeroplanes and electromagnetic micro actuators (NdFeB and SmCo magnets) (83). Most lanthanides are widely used in lasers. It is known that they can deflect ultraviolet and infrared rays. Hence, they are commonly used in sunglasses. In addition, two of the lanthanides (Sm and Lu) have radioactive isotopes (147Sm and 176Lu) with long half-lives, and they are used for dating minerals and rocks from the Earth, Moon and Meteorites.

The best known lanthanide alloy Auer metal is a mixture of Ce and Fe that produces a spark when struck. It has long been used as a flint in cigarette and gas lighters. Auer metal is one of a series of mixed lanthanide alloys known as Misch metals. The Misch metals are composed of varying amounts of the lanthanide metals, mostly Ce and smaller amounts of others such as La, Nd and Pr. They have also been used to remove oxygen and sulfur impurities from various industrial systems, as hydrogen storage medium (84). The use of rare earth elements in modern technology has increased dramatically over the past years. For example, Dy has gained significant importance for its use in the construction of hybrid motorcars (85).

1.7 Objectives and a brief outline of the present work

Objectives

1. Synthesis of superior phenolic resins and their polychelates with La(III), Pr(III), Nd(III), Sm(III), Gd(III), Tb(III) and Dy(III).

2. Characterization of polychelates by elemental analysis, FTIR, 1H-NMR, UV-Visible spectroscopy and magnetic moment.
3. To study the catalytic properties of synthesized polychelates in the synthesis of important pharmaceutical intermediates.

4. To evaluate the antimicrobial activity of phenolic resins and polychelates with different micro-organisms.

5. Investigation of metal sorption properties of the phenolic resins employing batch equilibrium technique.

The synthesis of monomer, phenolic resins and their polychelates is discussed in the second chapter. The phenolic resins were synthesized by Friedel Craft’s polycondensation reaction of 2,4-dihydroy acetophenone and different diols such as 1,2-ethanediol, 1,2-propane diol, 1,3-propane diol, 1,3-butane diol and 1,4-butane diol in presence of Lewis acid catalyst. The synthesized phenolic resins possess pendant hydroxyl groups and carbonyl oxygen as donor sites with interesting properties. Polychelates of the synthesized phenolic resins were prepared with hydrated metal acetates of La(III), Pr(III), Nd(III), Sm(III), Gd(III), Tb(III) and Dy(III). These polychelates were characterized on the basis of elemental analysis, FTIR, $^1$H-NMR, UV-visible spectroscopy and magnetic moment.

In the third chapter, catalytic properties of selected polychelates in Biginelli three component, one-pot synthesis of 3,4-dihydropyrimidin-2(1H)-ones have been studied. These are very important and attractive organic derivatives, used in pharmaceuticals. Chapter four studies the antimicrobial activity of phenolic resins and their polychelates with different micro-organisms such as Escherichia coli, Bacillus subtilis, Staphylococcus aureus (bacteria) and Saccharomyces Cerevisiae (yeast).

In the last chapter, metal sorption properties of the phenolic resins were studied employing batch equilibrium technique. The comparative selectivity of these resins for different lanthanide ions from aqueous nitrate solution has been studied. Some important outcomes of ion-exchange separation like distribution ratio, effect of electrolytes, effect of pH on retention, and contact time on the metal-ion uptake are also discussed.

1.8 References


Drinkard WC, Bailar JC Jr. Journal of the American Chemical Society, 1959, 81, 4795.


