CHAPTER-5

COORDINATION POLYMERS AND CHARACTERIZATION TECHNIQUES
This chapter gives a brief introduction of coordination polymers, classification, its applications, recent advances in coordination polymers, objective of the work and research question. It also highlights experimental techniques which were not included in Chapter 2.
This chapter is briefly divided into two sections.

1. Introduction of coordination polymers
2. Characterization techniques for coordination polymers

SECTION: I

5.1. INTRODUCTION OF COORDINATION POLYMERS

One of the fascinating areas of coordination chemistry is the developing branch of coordination polymers (CPs). These systems with metal complexes bound or stacked together in wide variety of structural arrangements are of great interest to chemists, physicists, material scientists and theoreticians. Their concerted efforts backed by the skill of synthetic chemists have yielded multitudes of interesting and novel polymeric materials which have extensive applications. Unlike pure organic or inorganic polymers, the coordination polymer shows mixed properties of both of them. Often this imparts unique and novel properties to the molecular systems which make them very useful materials like molecular ferromagnets, synthetic metallic conductors, non-linear optical materials, ferroelectrics, and conductors.

A CP is defined as a polymeric substance containing a coordination compound or metal complex in its repeating unit. A polymer ligand contains nitrogen, oxygen or sulphur acquired either by the polymerization of monomer (having the coordinating site) or by a chemical reaction between a polymer and a low molecular weight material (having the coordinating site) [1]. The coordination polymer building is principally directed by the coordination bonding. Coordination bonds are the donor of a lone pair electron of the ligand (Lewis base) to the metal cation (Lewis acid).

In recent years, the design and construction of CPs have attracted increasing attention [2]. CP sometimes referred to as metal-organic frameworks (MOFs) are composed of metal ions or clusters connected by polytopic organic linkers via strong coordination bonds. CPs may form its zero, one, two, and three dimensional infinite networks.
A tentative hierarchy of CPs and metal–organic frameworks is given as under [3].

![Diagram of CP hierarchy]

**Figure 5.1: A tentative hierarchy of coordination polymers & MOFs**

### 5.2. CLASSIFICATION OF COORDINATION POLYMERS [4]

The transition metal coordination polymers are classified into various groups according to the arrangement of a metal in the macromolecule as is under:

1. Mono valent metal is attached as a pendent to ligand moiety
2. Di/tri valent metal is a cross linking between two/three polymeric ligands
3. Metal is enmeshed in a polymer (parquet polymers)
4. Metal is an integral part of the polymer back bone
5. Stacked metal chain complexes
6. Miscellaneous

#### 5.2.1. Mono valent metal is attached as a pendent to ligand moiety

Polymers containing metal as a part of the pendent or substituent group may be formed using functionalized ligands which undergo addition polymerization. Thus obtained polymer acts as a ligand and is complexed by a metal atom or ion e.g. 1 1'-disubstituted ferrocenes undergo cyclopolymerization to form polymer (Figure 5.2). Polymer bound catalysts also have metal-containing pendent groups.
Figure 5.2: 1,1'-disubstituted ferrocene undergo cycopolymerization to form polymer

5.2.2. Di/trivalent metal cross linked between two/three polymeric ligands

The condensation of several substituted ferrocenes results in the formation of linear polymer chains cross-linked by ferrocene moieties e.g. condensation of ferrocene with acetone in presence of ZnCl₂ and HCl at 56 °C yields a soluble polymer (Figure 5.3) containing semiconducting properties [5].

Figure 5.3: Polymer obtained from ferrocene & acetone

The polymer is obtained by the treatment of ferrocene with diazonium salt of p-amino salicylic acid followed by reaction with di/trivalent metals (Figure 5.4).

Figure 5.4: Polymer obtained from ferrocene & diazonium salt of p-amino salicylic acid

Another black semiconducting polymer that function as bands and produce metal cross-linked polymer as shown in figure 5.5.
5.2.3. Parquet polymers

Parquet polymers are flat net like organic macromolecules in which a metal is completely enmeshed. Polyphthalocyanato and polyporphyrinato complexes are the most common examples. These polymers are of interest because of their thermal stability, potential electrical properties, and similarities to homo proteins.

Construction of these polymers is done by polymerization of the organic net without altering the environment of the metal or through coordination of one organic net to a neighboring metal atom, thereby increasing the coordination number of the metal while retaining the monomeric organic unit. The common examples of parquet polymers formed by polymerization of the organic net [6] are depicted in (Figure 5.6).

5.2.4. Polymers with back bone metals

Polymers containing transition metals as part of their backbones are formed by using ligands that can simultaneously coordinate to two different metal atoms or
that have the potential to undergo addition or condensation thereby linking monomeric units. The most common example of this type of polymer is gold cyanide AuCN obtained by heating H[Au(CN)₂] at 110 °C is a yellow powder that is slightly soluble in water, ethanol, and ether and very soluble in aqueous cyanide solutions. Like the analogous colorless AgCN, it forms infinite linear polymer chains (Figure 5.7). Other examples of planar polymeric structure are shown in figure 5.8.

![Figure 5.7: Linear polymer obtained from gold cyanide](image)

**Figure 5.7: Linear polymer obtained from gold cyanide**

**Figure 5.8: Planar polymers**

### 5.2.5. Stacked metal chain complexes

Stacked metal chain complexes are a mixed-valence square planar coordination complex of platinum and cyanide bonded through linear platinum metal chains. Tetracyanoplatinate-stacked complexes resemble the metal phthalocyanine polymeric structure except that coordinating macro cycles which do not chelate each metal atom. Instead of stacks of square planar Pt(CN)₄⁻ units are formed with anions between the stacks. The cyano groups surrounding Pt are staggered with respect to those coordinating the adjacent Pt atoms.

### 5.2.6. Miscellaneous

#### 5.2.6.1. Magnus green salt

Due to one-dimensional structure of Magnus green salt [Pt(NH₃)₄][PtCl₄] is of great interest for material science chemist and solid-state physicists. It consists of
a linear chain of alternating \([\text{PtCl}_4]^{2-}\) and \([\text{Pt(NH}_3)_4]^{2+}\), in which the platinum atoms are separated by 3.25 Å [7] and are used as a semi-conductor. The deep green colored complex was obtained by mixing aqueous solutions of \([\text{Pt(NH}_3)_4]^{2+}\) and \([\text{PtCl}_4]^{2-}\) [8].

### 5.2.6.2. Polymetallocenes

Metalloocene is a compound typically consisting of two cyclopentadienyl anions bound to a metal center in the oxidation state II. Metalloccenes are a subset of a broader class of organometallic compounds called sandwich compounds. There are two major classes of organometallic polymers existing with transition metals in the main chain. The first type of poly(metallocenes) targeted in the early 1960’s were of low molecular weight but they were with very poorly defined structures. High molecular weight examples have been found to possess a range of interesting properties. The second major class comprising of rigid rod polymers such as metal acetylides or poly(yne) materials are also now well known which are seen to be quite stable, presumably because of the \(M(d\pi)\) and acetylide\((p\pi)\) interaction which can effectively strengthen the \(M-C\) bonds.

### 5.2.6.3. Poly(yne)s

An unusual class of organometallic polymers is the transition-metal poly(yne) polymers, which contain transition metals bound to carbon within the main chain and which might vaguely be considered as coordination polymers. The Pt and Pd copolymer of this class have rod like structures.

### 5.2.6.4. Shiskabob polymers

The Shiskabob approach yields another class of coordination polymer of stacked macro cyclic metal complexes. Here macro cyclic complexes are linked together by axial coordination of bridging ligands.

- O-bridged polymeric compounds: Shiskabob macromolecules with the stacked metal phthalocyanine polymers containing, bridging ligands between the metal atoms \((M=\text{Si, Ge})\) conduct electricity through their metal-ligand-metal linkages [9]. Dehydration of phthalocyanine complexes of Si, Ge
and Sn produces face to face stacks of oxygen bridged metal phthalocyanine units.

- S-bridged polymeric compounds: A change in the bridging ligand was made in an attempt to get some information on the mechanism of electrical conductivity of chalcogen bridged IVB metals with phthalocyanine as macrocycle [10]. Sulphur instead of oxygen was used to see if the better d-orbital overlap has any influence on the conductivity before and after doping. In comparison with [PcGeO]ₙ polycrystalline samples of [PcGeS]ₙ do not show a pronounced increase in electrical conductivity.

- F-bridged polymeric compounds: Polymeric stacks of bridged metallofluorophthalocyanines, [PcMF]ₙ with M=Al, Ga, Cr were prepared [11]. PcAlCl and PcGaCl were converted with NH₄OH or pyridine into PcAlOH and PcGaOH respectively which react with concentrated aqueous (48%) HF to form [PcMF]ₙ.

- Alkynyl-bridged polymers: Alkynyl-bridged ligands other than O⁻² and S⁻² have also been used to prepare polymeric stacked metallomacrocyles. But it is less known about metal-carbon bonds in metallophthalocyanine compounds and synthesized polytrans ethynylphthalocyaninato silicon. These are obtained by reacting phthalocyaninato metal dichlorides with appropriate Grignard reagents [12].

### 5.3. METAL-ORGANIC FRAMEWORKS (MOFs)

#### 5.3.1. Choice of ligand

What is ligand? A common delusion prevails with the term ligand. To obtain a coordination complex, a ligand is a molecule that attaches to a central metal atom. Bonding explains the molecular orbital theory utilizing formalism. Ligands in a complex state the reactivity of the central atom, including rate and reactivity of the ligand substitution [13].

#### 5.3.2. Choice of metal

First-row transition metals are most commonly employed as the metal ions of MOFs due to their availability, cost, fixed coordination geometry, and thorough
understanding of chemical bonding. Additionally, the functionality or properties of the MOF is directly related to the metal ion used. The nature of the metal has also been shown to have an effect on the adsorption properties of MOFs with respect to certain gases. The metal with the known catalytic function should be incorporated if the constructed MOF is to have the desired catalytic property. To optimize the intended application, the judicious choice of both ligand and metal is important.

5.3.3 Synthetic conditions

MOFs are typically synthesized by means of a solvothermal reaction where both the metal salt and organic ligand are combined and heated at relatively low temperatures until crystal growth has completed. The polar solvent having high boiling point such as water, dialkyl formamides, dimethyl sulfoxide, and dimethylacetamide is commonly used. Synthesized MOFs include the judicious choice of solvent, the ratio of the ligand to metal, the pH of the solution, and the solubility of the organic ligand and metal salt employed in the reaction system.

Occasionally the addition of small amounts of acid or base is necessary to promote good crystal growth. Especially in this case, carboxylate ligands are employed in the reaction. As previously mentioned, deprotonation is necessary for the oxygen to form bonds to the metal centers. In some instances a base (amines, alcohols, or pyridine) needs to be added to promote the deprotonation.

5.4. APPLICATIONS OF COORDINATION POLYMERS

The properties of coordination polymers are a complex function of their chemical, electronic and architectural structures. Bridging the gap between molecular characteristics and bulk properties remains a continuing challenge to both chemical and material sciences. Most important applications of such coordination polymers are as under:

- Gas storage [14]
- light harvesting [15]
- catalysis [16]
proton conduction [17]
chemical sensing [18]
drug delivery [19]
superabsorbent polymers [20]
soft and wet interfaces of polymer gels have been found to show adhesion of polymer gels by supramolecular interactions [21]

5.5. LITERATURE REVIEW

This literature review deals specifically with the application of the coordination polymers. The structures of MOFs are greatly depending upon the structure of the organic ligands, the coordinative geometry of metal ions, metal–ligand ratio and other factors [22].

Among various organic ligands, multicarboxylate ligands are often used as multifunctional organic ligands, not only because of their various coordination modes to the metal ions, but also because of their ability to act as H-bond acceptors and donors assembling supramolecular structures [23]. For example, 1,2,4,5-benzenetetra carboxylate, 3,3′,4,4′-biphenyltetracarboxylic acid [24], 1,1′-biphenyl-2,3′,3,4′-tetracarboxylicacid [25] and methylene diiso phthalic acid [26] have been extensively used for the synthesis of various coordination polymers. Zhao et al. [27] had synthesized Metal–organic frameworks based on transition-metal carboxylate.

Zheng et al. [28] had synthesized zinc (II) coordination polymers based on a benzene dicarboxylic acid derivative. Zuo et al. [29] had synthesized series of coordination polymers with 2,2′-bipyridyl-4,4′-dicarboxylic acid. Mihalcea et al. [30] had synthesized coordination polymers from different ditopic aromatic dicarboxylates. Ma et al. [31] had synthesized lanthanide (III) coordination polymers from benzimidazole-5,6-dicarboxylic Acid and 1,10-phenanthroline.

Xue et al. [32] had reported structural diversity and properties of coordination polymers from a rigid octadentenate carboxylic acid. Cai et al. [33] had synthesized Ba(II) coordination polymers based on imidazole-based dicarboxylate ligands. Gai et al. [34] had reported lanthanide–organic coordination
polymers based on hydroxyquinoline–carboxylate ligands. Decadt et al. [35] had synthesized carboxylate based rare-earth coordination polymers.


Zhao et al. [41] had synthesized metal–organic frameworks constructed from a V-shaped tripodal carboxylate ligand. Wang et al. [42] had reported metal–organic frameworks based on chains with mixed carboxylate and azide. Liu et al. [43] had synthesized metal–organic frameworks from metal aromatic sulfonate–carboxylate. Yu et al. [44] had reported lanthanide coordination polymers with hexa-carboxylate ligands.

On the other hand, the use of auxiliary N-containing ligands is also an effective method for the framework formation of coordination polymers owing to the fact that they can satisfy and even mediate the coordination needs of the metal center and consequently generate more meaningful architectures [45]. In our laboratory, Patel et al. [46] had reported synthesis and characterization of various coordination polymers and their microbicidal studies. Our Indian scientists had reported about the study of complexes of phthalamic acids [47].

5.6. RESEARCH GAP

Owing to the published work on these topics and a long–standing interest of our laboratory in the study of coordination polymers, a more exploration has been undertaken. Coordination polymers are prepared by polymerization of bisligand and metal ions. The coordination polymers based on bisamic acid of pyromellitic dianhydride has not attracted any attention; hence with the aim of investigating the influence of bisligands (containing carboxylic and amide containing group) on the frameworks of coordination polymers, it was thought to undertake the study for the reaction of transition metal (II) salts with various novel bisligands.
5.7. OBJECTIVES OF THE PRESENT WORK

In view of above review and looking to the research gap, the prime intentions of the present thesis are mainly focused on,

- Synthesis and characterization of bisligand from pyromellitic dianhydride and various amines
- Synthesis and characterization of coordination polymers derived from synthesized bisligand and transition metal (II) acetates viz., Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II). (Scheme 2)
- Antimicrobial activity of the synthesized bisligands and their coordination compounds.

5.8. RESEARCH METHODOLOGY

Literature survey development has been made by referring library volumes and using internet facilities through Google and other search engines. After the thorough literature survey, research topic was deeply studied. Synthesis of compounds was carried out by taking support of various organic and polymer books. Data analysis was carried out by using available techniques and data interpretation was done by referring various published books and research articles. Reporting of the data was accomplished by using Microsoft office tools.
SECTION: II

5.9. EXPERIMENTAL TECHNIQUES

Coordination polymers were characterized by physicochemical, thermo-gravimetric and spectroscopic techniques. Electronic spectral analysis and magnetic measurement studies were taken into account for the geometry of coordination polymers. Polymeric analysis was also carried out.

5.9.1. Elemental analysis, Spectral analysis: FT–IR, $^1$H NMR, $^{13}$C NMR

The details of Elemental analysis, Spectral analysis: FT–IR, $^1$H NMR, $^{13}$C NMR were given in Chapter 2: Techniques and Characterization.

5.9.2. U. V. visible / Electronic Spectral analysis

Ultraviolet–visible spectroscopy is associated to absorption spectroscopy in the ultraviolet-visible spectral region indicated the utilization of visible and adjacent (near–UV and near-IR) light. Molecules go through electronic transitions in the electromagnetic spectrum region. This method is corresponding to fluorescence spectroscopy, where fluorescence deals with transition from the excited state to the ground state, while absorption measures vice versa [48]. Especially those Organic compounds having high degree of conjugation absorb the light in the ultraviolet or visible regions of the electromagnetic spectrum. For these determinations, water is a solvent for water soluble compounds or ethanol is a solvent for organic soluble compounds. The absorption spectrum of an organic compound is influenced by the solvent polarity and pH.

Reflectance spectroscopy deals with the measurements of absorption of energy when electrons are promoted to higher energy level from ground energy level, this electron transition occur when electromagnetic radiation of the proper energy is provided. The structural information related to molecule such as different transitions, geometries, forces and nature are obtained from the electronic spectrum study. The physical and chemical behavior such as conformational analysis, configurationally correlation, electromagnetic and electrochemical of system has been suitably interpreted by bonding theories [48].
The d-orbitals of an isolated transition metal ion are degenerated. However, the electrostatic crystal field theory predicts that the complex formation will partially remove the d-orbital degeneracy, so transition within the d-levels become possible. For structures in which there is an inversion center, d-d transition are forbidden by the laporte rule [49] and can occur only because of transitory loss of the inversion center via molecular vibrations. Consequently d-d transitions are invariably weak ($\varepsilon < 200$), they generally occur in the visible or near infrared regions and are responsible for the colors of many complexes. The d-d absorptions are commonly referred to as ligands field bands. Charge transfer absorption bands always occur at higher energy level than d-d transitions and are frequently found in the blue or ultraviolet regions.

A colored compound owe their color to the presence of no more unsaturated groups responsible for electronic absorption, the group is called as chromophores; an oxochrome represents a saturated group containing unshared electron which when attached to a chromophore changes both the intensity as well as the wavelength of the absorption maximum.

Shift to maximum absorption of a longer wavelength is called bathochromic or red shift, while a Shift to maximum absorption of a shorter wavelength is called as hypsochromic or blue shift. The effect of increased absorption intensity is known as hyperchromic effect and vice versa is known as hypochromic effect. Electronic spectra of the samples were recorded on Shimadzu 160A UV-visible spectrophotometer using DMF as the solvent blank.

5.9.3. Magnetic moment

The magneto chemistry reveals the magnetic properties of material; it shows whether the material will be attracted or repelled by magnet. In this study there are several methodologies such as nuclear spin, electron spin, electron orbital motion; which are useful to generate magnetic fields in material. The raised magnetic fields interact with external magnetic field and each other. The interaction may vary from material to material. NMR and ESR are the spectroscopy used for measurements of interaction with nuclear spins.
Gouy's method for the measurements of magnetic susceptibility has been used in present study. In this methodology, a sample was hanged in between applied external magnetic field. The force exerted by the sample was measured by weighing technique on digital electronic balance. The measurement of magnetic susceptibility was done at 298 K using gouy balance (Citizen Balance, Japan). The Gouy tube was calibrated using mercury tetrathiocynate cobaltate (II) - Hg[Co(CNS)₄] \( (x_g = 16.44 \times 10^{-6} \text{ c.g.s. units at 298 K}) \).

The samples were weighed in presence and absence of applied magnetic field (4 amp and 6 amp), the \( \mu_{\text{eff}} \) and \( x_g \) were calculated using difference in weight according to reported calculations [50]. The molar susceptibility is obtained by multiplying the gram susceptibility \( x_g \) by the molecular weight of complexes. Pascal’s constant was used to apply diamagnetic corrections and corrected molar susceptibility \( x'_m \) had been obtained [51]. The effective magnetic moment \( \mu_{\text{eff}} \) was calculated according to following equation:

\[
\mu_{\text{eff}} = 2.84 \left( x'_m \times T \right)^{\frac{1}{2}}
\]

Where, \( T \) is absolute temperature in K.

5.9.4. Thermogravimetric analysis (TGA)

Thermogravimetric analysis of polymer is a very useful technique in assessing the thermal stability of polymers. The methods usually employed are Differential Scanning Calorimetry (DSC), Differential Thermal Analysis (DTA), Thermogravimetric Analysis (TGA) and Derivatographic Analysis [52] for comparative study of thermal behavior of related polymer samples.

Each sample is analyzed by any one or more of these methods of analysis under identical experimental conditions. For example TGA is carried out in air and in oxygen free nitrogen. It is carried out at different heating rates.

Using the TGA following can be done.

- Decomposition of metal salts and coordination polymers: In this study, the amount of byproducts and intermediates, final product and the composition of the material can be found [53].
Analysis of mixture: The studies show the difference between the behaviors of substances on heating and if those behaviors are significantly different on temperature scale, the individual reactions of substances may be identified and measured. The moisture content, total volatile content, metal content, organic matter content and ash content may be measured in coal, soil and natural material analysis [54].

Oxidation studies: The study concern with oxidation of organic compounds, oxidation of metal, alloy and their compounds [55].

Reduction studies: TGA measures continuously the composition of hydrogen during reaction, has given many useful data on catalyst preparation and allowed the detection of overlapping reactions and the study of kinetics [56].

5.9.5. Number average molecular weight ($\overline{M_n}$)

Number average molecular weight ($\overline{M_n}$) of coordination polymers was determined by non-aqueous conductometric titration. It was carried out in pyridine solution against standard tertiary–n–butyl ammonium hydroxide as titrant. The number average molecular weight of each sample was calculated according to method reported in literature [57].

5.9.6. General Remarks for the Experimental Techniques

All solvents used were distilled and dried. The purity of the compounds was checked by TLC. Column chromatography was performed on silica gel (60-120 mesh).

Infrared spectra (FT–IR) were obtained from KBr pellets in the range of 4000–400 cm$^{-1}$ with a Perkin Elmer spectrum GX spectrophotometer (FT–IR) instrument.

$^1$H NMR and $^{13}$C NMR spectra were acquired at 400 MHz on a Bruker NMR spectrometer using DMSO-d6 (residual peak at $\delta \sim 2.5$ or $\sim 39.5$ ppm, 300 K) as a solvent as well as TMS an internal reference standard.

Micro analytical (C, N, H) data i.e. C, H, N contents of all the compounds were recorded on Thermofinigen 1101 Flash elemental analyzer.
The solid diffuse electronic spectra were recorded on a Beckman DK–2A spectrophotometer with a solid reflectance attachment. MgO was employed as a reference.

Magnetic moments were determined by the Gouy method with mercury tetra thiocyanetocobaltate (II), [HgCo(NCS)4] as calibrant (Xg = 1644×10^{-6} cgs units at 20 °C), by Citizen Balance (at room temperature). Molar susceptibilities were corrected using Pascal’s Constant [50].

The thermogravimetric studies were carried out with a Perkin Elmer thermogravimetry analyzer at a heating rate of 10 °C min^{-1} in the temperature range of 50–700 °C under nitrogen.

The metal content of the coordination polymers was carried by decomposing a weighed amount of each coordination polymers with HClO₄, H₂SO₄ and HNO₃ (1:1.5:2.5) mixture followed by standard EDTA titration method.

Number average molecular weight (Mn) of coordination polymers was determined by non-aqueous conductometric titration [57].

Melting points (°C) of all the compounds were measured by open capillary method. All the melting points were uncorrected.
REFERENCES


Chapter 5


