Chapter - 1

INTRODUCTION
1.1 General:

The first co-ordination compound was made by Tassaert in 1798. Who sought to precipitate cobalt hydroxide by the addition of ammonia to a solution of a cobalt salt. The discovery of other metal amines soon followed, and before long, other types of “complex inorganic compounds” were reported. The observation that hexamine cobalt(III)chloride can be converted readily to the aquo-pentamine chloride (through the intermediate formation of the chloro-pentamine chloride) links the hydrates and amines into a single family and the properties of the double salts seemed. In addition to the amines, hydrates and “double salts” many other classes of compounds have been found to fit into the co-ordination scheme. These include the metal carbonyls, nitrosyls, porphyrins, metalloproteins, metal-containing enzymes etc.

According to the theory of sidgwick and lowery a co-ordinate bond consists of the union of an atom, molecule or ion, which is able to donate a pair of electrons. In co-ordination compounds a metal ion is the electron pair acceptor and usually is able to accept more than one pair. The number of electron pairs which can be used in bonding called the co-ordination number (C.N.). The donor atom is usually non-metallic and is often part of molecule capable of
independent existence. This may be neutral or negative ion or occasionally a positive ion. The donor molecule or ion is called the ligand. The resulting complex may be either a positive or negative ion or neutral molecule depending on the balance of the metal and ligand charges.

Most complex compounds are ionic being made up of a complex cation and a simple anion, e.g., hexaminocobalt(III)chloride, \([\text{Co(NH}_3\text{)}_6]\text{Cl}_3\) or vice versa e.g., sodium hexanitrocobaltate(III) \(\text{Na}_3[\text{Co(NO}_2\text{)}_6]\) (old name: sodium cobaltinitrate), both ions may be complex, e.g., as in \([\text{Co(NH}_3\text{)}_6]\), \([\text{Co(NO}_2\text{)}_6]\). In a complex ion, the central metal ion is surrounded by usually four or six ions or molecules, called ligands (Latin word ligare means to bind) For example, in the hexacyanoferrate(II)ion, \([\text{Fe(CN)}_6]^{4-}\) the central ferrous ion \(\text{Fe}^{+2}\) is surrounded by six ligands have been arranged octahedrally around the central metal ion with four ligands a tetrahedral or square planar configuration is possible and both of these are found.

1.2 Characteristics of the transition elements:

Transition metals are all metals and characterized by high density, high melting and high boiling points. These properties suggest strong forces between the metal atoms in the metal lattice, as compared with weaker forces in non-transition elements. These strong force arises because the number of valence electrons available for binding a particular atom to its neighbours is much larger. Transition metals often form alloys with one another. They
also readily adsorb gases, the adsorption often being chemical in nature i.e., chemisorption, hence transition metals and their compounds are frequently used in heterogeneous catalysis. Another property of transition element is the formation of interstitial compounds with small non-metallic atoms.

Most complex compounds are ionic, being made up of a complex cation and atoms which are accommodated thus are commonly hydrogen, carbon and nitrogen. Hence the hydrides, carbides and nitriles of the transition metals are often non-stoichiometric, interstitial compounds. For example, titanium takes up nitrogen so readily that it must be refined in an atmosphere of argon (a larger atom not taken into the lattice). Again, iron takes up carbon interstitially, when this happens, the ability of the iron atoms to slide over one another is prevented by the interstitial carbon atoms which 'lock' the structure. Hence the iron becomes harder and stronger i.e., it becomes steel.

Chemical Behaviour

(a) Variable valency: The transition metals exhibit two or more valencies (oxidation states). Consider iron, cobalt and nickel, the first has two states, ferrous(Fe⁺²) and ferric(Fe⁺³) both common. Nickel commonly appears as nickel(II), e.g. in nickel sulphate(NiSO₄) and nickel chloride(NiCl₄) i.e. as the ion Ni⁺². In the oxide NiO₂, it is nickel(IV). The compound nickel carbonyl [Ni(CO)₄] has also been mentioned. Cobalt exhibit a common oxidation state of two, e.g. cobalt(II)
sulphate\((\text{CoSO}_4)\) and cobalt(II) chloride\((\text{CoCl}_2)\) but can be oxidized to the \(\text{Co}^{+3}\) state, though complex formation must take place to make this state stable. Since the cobalt(III) ion is a very powerful oxidizing agent. The variable oxidation state means that transition metal ions exhibit oxidation-reduction behavior and can often act as catalysts in solution, behaving as electron-transfer agents. The maximum oxidation number for manganese ion may be +7 and the compound which contains Mn(VII) is generally act as a strong oxidizing agents like KMnO\(_4\). Generally the compounds having Mn\(^{+2}\) have the highest stability. The compounds containing Mn\(^{+3}\) are least stable and can be reduced to Mn\(^{+2}\). The compounds like MnF\(_4\) has the Mn(IV) are also least stable. Copper ion generally known with +1 and +2 oxidation states. Generally the compounds having Cu(II) is more stable. The stability of the complexes of Cu(II) and Cu(I) is more depends on the ligand, dielectric constant of solution and neighbouring atoms of the copper ion.

(b) Paramagnetism: Paramagnetism arises from the presence of unpaired electrons and in the transition metal ions, the partly field inner shell often contains unpaired electrons.

(c) Complexes: From what has been said already, it is clear that transition metal ions form a wide variety of complexes and is perhaps their most outstanding property.
1.3 Biochemistry of manganese:

Deficiency of manganese in human body may cause some serious problems like effect on hair colour, growth and hypocholesterolemia. It is true that some enzymes required Mn$^{+2}$ or Mg$^{+2}$ for activation and that's why, in certain cases, there appears to be high specificity. For Mn$^{+2}$ and Mg$^{+2}$, there is still doubt over the physiological requirement of manganese.

Reviews are available on the physiology and biochemistry of manganese in mammals(1) and on manganese nutrition in ruminants(2). Manganese is bound in serum as Mn$^{III}$, β-globulin and in erythrocytes as a manganese porphyrin. It is present in rat serum as manganese transferrin. These again emphasize similarities with iron.

1.4 Biochemistry of Iron:

In adults, iron present in the largest amounts. About 70 % of the working iron in mammals is in the form of porphyrin complexes heames. The well known example of coordination compound is Heamin, which is an iron complexes. Which is responsible for the transport of the oxygen in human body. Haemoglobin is a conjugated protein having a molecular weight of 64,500. Each haemoglobin molecule has four haeme groups bound to the globin on its surface. For each haeme unit of haemoglobin, four co-ordination position of Fe(II) are occupied by the four
nitrogen of the protoporphyrin with the fifth coordination position of Fe(II) occupied by the imidazole nitrogen of a histidine residue of the protein(globin) chain and the sixth coordination position of Fe(II) occupied by molecule of water. Haemoglobin takes up a large volume of oxygen from the lungs to tissues and it is also concerned with the transport of CO$_2$. 1 gm haemoglobin can absorb maximum 1.39 ml of oxygen. In human body blood of a normal male contains 0.15 gm haemoglobin per 100 ml and is in the red blood cells it contains 0.347 % Fe and thus there are about 50 mg Fe per 100 ml blood.

Anemia is most important nutritional disease which is caused due to deficiency of iron. Deficiency is accompanied by fatigue, palpitation on exertion sore tongue, tinnitus, headaches, cold hands and feet, 'spoon nails', in patients with classic migraine headaches, treatment for iron deficiency may decrease the frequency of attacks. Human child having age less than two years requires the highest amount of iron. The richest dietary sources of total iron are organ meats (liver and kidney), egg yolk, dried legumes, corn molasses and parsley. Liver is particularly valuable because of the high absorbability of its iron.

1.5 Biochemistry of cobalt:

The occurrence of cobalt on earth is rare, but generally it is found in fertile soil and plants. Vitamin-B$_{12}$ or cyanocobalamin and corresponding coenzymes are the best examples of cobalt in nature. Although Co(II) can be
substituted for Zn(II) in a number of coenzymes without change in activity, no such replacement is known to occur in nature. Several vitamin-B\textsubscript{12} model compounds have been studied\textsuperscript{(3)}. The molecule is built around a corrin ring containing a cobalt(III) ion co-ordinatively bound to the four planar nitrogen of the corrin ring, with the fifth and sixth coordination positions of the cobalt being occupied by a nitrogen atom of an imidazole ring of a side chain of the corrin ring and a cyanide ion respectively. Vitamin-B\textsubscript{12} is the only vitamin known to contain a metal. The adult human body contains 2.5 mg of vitamin-B\textsubscript{12} and its derivatives, mainly in liver. Some bacteria may synthesize it and is involved in the formation of methane by certain bacteria and is also responsible for the formation of the highly toxic methyl-mercury cation (H\textsubscript{3}C-Hg\textsuperscript{+}). The bonding to the sixth coordination position of cobalt in vitamin-B\textsubscript{12} is rather labile and the ligand attached to this position is indeed variable, which result in other B\textsubscript{12}-coenzyme.

Vitamin B\textsubscript{12} reacts with adenosinetriphosphate (ATP) lead to the formation of vitamin-B\textsubscript{12}. Co-enzyme, in which ATP is bound to the sixth co-ordination position of the Co(III).

1.6 Biochemistry of Nickel:

Nickel is now firmly established\textsuperscript{(4)} as an essential nutritional requirement for many eukaryotic and prokaryotic organisms. It is particularly well known as a component of the enzyme urease in plant cells growing on
urea as a nitrogen source. This is a famous enzyme, as it was the first enzyme protein to be recrystallized and for many years it represented the only example of a biological function for nickel. Nickel is required for the synthesis of active urease in plant and other cells. The activity of the enzyme is directly proportional to the nickel content. Suggesting an essential role for nickel in enzyme. The requirement for nickel by methamogenic bacteria was long over looked, partly because the stainless steel needles used in the anaerobic culture technique allowed enough nickel dissolve to sustain growth.

1.7 Biochemistry of Copper:

Highest loads of copper in human body are found in the liver, brain, lung and kidney in decreasing amounts. Actually copper is widely distributed at trace levels in living systems. High concentrations are also found in pigmented part of the eye associated with melanins. Copper is also present in a number of small proteins. Copper is present in the adult human body in the largest amounts. Copper is the third most abundant heavy metal in the human body. Copper has an essential role in a number of enzymes, notably those involved in the catalysis of electron transfer and in the transport of dioxygen and the catalysis of its reactions. Copper is also present in number of small proteins, characterized by an intense blue colour, that catalyze the transfer of dextrose. Copper sulphate recommended to strengthen man to stimulate the heart and
blood vessels, to increase deposition of fat and to treat anemia. Deficiency of copper produces defects in the structural stabilization of the fibrous protein of connective tissue in a number of animals. Due to high concentration of copper in blood some other diseases may associates are lukemia, lymphomas, rheumatoid, arthritis, psoriasis, nephritis and hodgkins disease.

1.8 Biochemistry of Zinc:

The most essential element for normal function in all forms of life is zinc. The biological importance of zinc has emerged only during the last few decades. Zinc was found to be indispensable for the growth of Aspergillus niger(5) and its presence in plants and animals was established within a two decade(6,7). An increasing number of disease entities are providing to be related to zinc deficiency both in animals and human beings(8-12). Such as loss of appetite, skeletal and hair abnormalities, skin lesion and inhibition of sexual maturation, low zinc levels may results in mental lethargy and depression. In DNA replication, transcription and in protein synthesis zinc plays important role. Zinc therapy has enhanced graft acceptance in children with major burns. Zinc levels decreases due to anesthessia and due to surgical injury causes. Zinc act as an active sites of the enzymes that catalyze. Some reactions such as hydrolysis, hydration and decarboxylation for a variety of compounds. Zinc is present in adult human body in largest amount.
1.9 APPLICATIONS

The co-ordination chemistry has become a bridge to combine closely physical, analytical, organic and biochemical chemistry with inorganic chemistry. Mixed-ligand complexes play a central role in development of co-ordination chemistry. Mixed-ligand complexes playing a vital role in chemical industry and life itself. Mixed-ligand complexes are widely used as catalyst in chemical and petrochemical industries, thermal stabilizer, semiconductive materials, moisture and water repellent, polymer additives, fungicides etc. Mixed-ligand complexes are also used in the nuclear fuel cycle, radiopharmacy, photography, electrochemistry, dyes, pigments, food industries, pollution control etc.

The characteristic colour of co-ordination complexes would indicate their utility as dyes. This use was discovered accidentally in ancient times. For a long time, the co-ordination compounds were considered as a rare and special class but now they have been recognized as the most familiar type of compounds which help the nature to convert simple inorganic molecules into organic matter. For intense CO₂ and H₂O are converted into sugars by a co-ordination compound called chlorophyll [Mg(II) complex]. A similar iron complex called haemoglobin operates in the red blood cells as a carrier of oxygen. Among the uses of complexes and chelates in particular, it may be maintain about their property of acting as reservoirs for metal atoms to prevent the convenient precipitation of metals. At some stage in
industries, in the purification of rare metals and pharmacological uses. The chelating agents which forms metal chelates, are used intensively in both quantitative and qualitative analysis. Chelates pigments such as the phthalocyanins are now widely used. Further developments in the application of chelating agent in connection, in which cation exchange resin and solvent extraction have been particularly useful in the separation of radioactive metals. It has been discovered that some complexing agents can influence the course of polymerization so as to give plastics desirable properties such as higher softening temperatures and greater strength. The complexing agents are also used in photography(13,14).

The Schiff bases derived from salicylaldehyde and diamines are exceptionally useful in food industries. The metal complexes of Schiff base derived from salicylaldehyde and diamine has an excellent light resisting capacity, storage ability and does not allow to degrade the food in the presence of acidic gases such as CO$_2$. Hence they are exceptionally useful in food industries.

Anils or azomethines from an important class of compounds and have varied applications(15). This includes their used as catalysts(16-19), stabilizers(20,21), in polymers(22,23), pigments, dyes(24-27), photography(28-30), and various biological systems(31-34). Some Schiff bases have been also used as a analytical reagent(35), as inhibitors against corrosion(36) and as flocculants(37).
In metallurgical process and electrodeposition process many cyanocomplexes are used. Electroplating is the process which is used for achieving the final objective of a bright, smooth, fine grained metal deposits generally metals like Cu, Ag, Au etc are used for electroplating using a solution of their complex ions. Nickel can be purified by formation of co-ordination complex by mond's process.

The biochemists are also interested in the effect of metal ions in the form of complexes on biological process. Many enzymes are active only if trace amounts of metal ions are present and in many cases the active site of the enzyme is at a co-ordination position of the metal.

1. Application of co-ordination compounds in medicine:

Mixed-ligand complexes of schiff base are important class of compound on account of their values as an anticancer and antitumor agents. It is well known fact that reactive group of Schiff bases is a azomethine. The intermediate of the azomethine shows, biological importance in larger number of the enzymetic reacions. Chelation therapy may be the only effective treatment for metal poisoning. Mixed-ligand complexes can be used in treatment and diagnosis of disease specifically one can be define following principles areas of the use of co-ordination compounds in medicine.

a) The use of co-ordination compound to treat disease.
b) The use of chelating agent to treat metabolic dyes-function.
c) The use of chelating agents to remove metal poison from body.

d) The use of co-ordination compound to transport metals to specific sites in the body to aid on imaging.

2. Application of co-ordination compounds in agriculture:

Manganese complexes are also employed in agriculture as a fungicide. The most important complexes are 1,2-ethane-diylbis(carbamodithioato)manganese, which is generally sold under the trade name 'maneb'(38). It is applied either to the foliage directly or to the seed prior to planting. It can be used on many plants and trees but may cause injury to certain varieties of cherries, apples and tobaccos.

\[ \text{Fe(S}_2\text{NMe}_2\text{)}_3 \] is an important fungicide sold under the trade name 'Ferbam'(39). Ferbam is less phytotoxic than maneb, though it causes rusting in one kind of apple. It can be used widely with many fruits, vegetables, root, crops and berries as well as with melons, almonds and tobacco and it control a wide range of plant diseases. ‘Ferbam’ should not be used in connection with time of mercury or copper compounds. It is used together with menals and the tine fungicide, ‘tiram’. Another iron fungicide in use is the triammine methylarsonate sold under the trade name ‘Neo-asozin’(40). Neo-asozin is of much more limited application than Febram, apparently being restricted to rice and grapes.
3. Application of coordination compounds in polymer chemistry:

Iron compounds are effective smoke retarders for some polymers. Thus, tris(acetylacetonato)iron, \( \text{FeSO}_4, \text{Fe}_2(\text{SO}_4)_3 \) and \( \text{Fe}_2\text{O}_3 \) are all roughly equal in combustion tests on poly(vinyl chloride)\(^{41}\).

The manganese complexes of 2[Cl-hydroxy-2-naphthalenyl]carbonyl]benzoic acid are reported to be effective photostabilizers for polymers\(^{42}\) and manganese phthalocyanine shows smoke retarding properties in polystyrene\(^{43}\).

Cobalt complexes find various applications as additives for polymers. Thus cobalt phthalocyanine act as a smoke retardent for styrene polymers\(^{43}\). The cobalt complex of the benzoic acid derivatives act as an antioxidant for butadiene polymers\(^{44}\). Stabilization of poly(vinyl chloride)-polybutadiene rubber blends against UV light is provided by dicyclohexylthiophosphinate cobalt\(^{45}\). The complexes \([\text{CuCS}_2(\text{NEt}_2)_2]\) and \([\text{CuS}_2\text{P(Opr)}_2]_2\) have been shown to be extremely effective scavengers for peroxyl radicals and can be used to inhibit the auto oxidation of hydrocarbons\(^{46}\). Copper phthalocyanine is more effective as a smoke retardent for polystyrene than most such complexes of the first row transition metal\(^{47}\). Other copper compounds which are effective smoke retardants for poly(vinyl chloride) are \( \text{Cu}_2\text{O}, \text{CuO}, \text{CuI} \) and \( \text{CuSO}_4 \)\(^{48,49}\). Zinc complexes are important as additives for rubber polymer. The diamyl and diethyl dithiocarbamate complexes
have been found to inhibit the hardening of asphalt, but the effect appears too weak to be useful(50). The di-n-butylidithiocarbamate complex is important in the vulcanization and injection molding of rubber(51) as a stabilizer against photolytic and thermal degradation of styrene-butadiene-styrene copolymer, thermoplastic rubber(52) and as an inhibitor of the photodegradation of urethane polymers(53).

4. Application of co-ordination compounds in organic chemistry:

The organic chemists often uses co-ordination compounds in preparative reactions. The Friedel crafts reaction employs metal chloride (Al₂Cl₆, Fe₂Cl₆ etc.) in many alkylation reactions the metal chloride complex behaving primarily as a Lewis acid. Other familiar examples are the grignard reactions using RMgX and the sandmeyer reactions which employs cuprous halides and no doubt involves complexation of the metal ion in the area of catalysis. Metal complexes are employed in the polymerization of ethylene (ziegler type catalysts, Ti⁺³ alkyles) and in homogenous hydrogenation of olefines using (I-C₄H₉)₃ Al and Co(acac)₃.

5. Application of co-ordination compounds in physical chemistry:

In physical chemistry, complexes have provided suitable compounds for testing and expanding the theories
in the areas of bonding, electrolytic behavior of iron, magnetic behaviour, solution thermodynamics and theories of kinetic behaviour.

6. Application of co-ordination compounds in analytical chemistry:

Co-ordination compounds are very widely useful in analytical chemistry in both quantitative analysis and qualitative analysis.

- All the metal ions are precipitated in qualitative analysis using the principle of co-ordination chemistry.
- Dimethylglyoxime which is used for the detection of Ni^{2+}.
- Separation of Na^+ and K^+ is made by sodium cobaltinitrate.
- Some metals precipitated by using different ligand which can be further analyzed gravimetrically. e.g. Oxine(8-hydroxy quinoline) is used for Mg, Cu, Fe, Pd, Al etc, cupferron for Fe, Ti, V, Sn etc. 2- Benzoinoxime(cupron) for Cu, Mo, Ni, anthranilic acid for Cd, Zn, Ni, Co, Cu etc.
- Shrivastav et al.(54) have reported 5,5'-thiodisalicylic acid as an analytical reagent. 2,5-Dihydroxy-p-benzoquinone has been used in the determination(55) of Th and its seperation from some of the rare earths, the determination of Zr and its seperation from Ti, in the gravimetric determination(56) of Ce(III & IV), La(III), Y(III), U(IV) and Ti(III) and in the determination(57) of Zr in presence of common metals. Naphthazarin was used for detection(58) of Al, Be and Mg.
- Some organic ligands are used in removal of interference in gravimetric estimations.
- In volumetric analysis, complexometric titrations are the most important application of co-ordination chemistry. Here EDTA is used as a titrating agents. Here metal indicators and metallochromic indicators are used.
- Some co-ordination compounds are also useful in photometric titration, amperometric titration etc.

Some co-ordination compounds are also useful as masking and demasking agents.

1.10 INORGANIC POLYMER:

The thousands of organic polymers are already available, yet the scientists are interested in the synthesis of inorganic polymers. Now the question arises “why”? The reasons for this fall into two categories:

First, most of the known organic polymers represented a compromise in properties compared with the “ideal” materials sought by engineers and medical researchers. For example, many organic backbone polymers react with oxygen or ozone over a long period of time and lose their advantageous properties. Most organic polymers burn, often with the release of toxic smoke. Many polymers degrade when exposed to ultraviolet or gamma radiation. Organic polymers sometimes soften at unacceptably low temperatures, or they swell or dissolve in organic solvents, oils, or hydraulic fluids. At the environmental level, few organic polymers degrade at an acceptable rate in the
biosphere. Finally the suspicion exists that the availability of many organic polymers may one day be limited by the anticipated scarcities of petroleum. It is generally accepted that polymers that contain inorganic elements in the molecular structure may avoid some or all of these problems.

The second set of reasons for the burgeoning interest in inorganic-based macromolecules is connected with their known or anticipated difference from their totally organic counterparts. Inorganic elements generate different combinations of properties in polymers than do carbon atoms. For one thing, the bonds formed between inorganic elements are often longer, stronger, and more resistant to free radical cleavage reactions than are bond formed by carbon. Thus, the incorporation of inorganic elements into the backbone of a polymer can change the bond angles and bond torsional mobility and this in turn can change the material's properties to a remarkable degree. Inorganic elements can have different valencies than carbon, and this means that the number of side groups attached to a skeletal atom may be different from the situation in an organic polymer. This will affect the flexibility of the macromolecule, its ability to react with chemical reagents, its stability at high temperatures and its interactions with solvents and with other polymer molecules. Moreover, the use of non-carbon elements in the backbone provides opportunities for tailoring the chemistry in ways that are not possible in totally organic macromolecules. The future development of
polymer chemistry and polymer engineering may well depend on the inorganic aspects of the field for the introduction of new molecular structures, new combinations of properties, and new insights into the behaviour of macromolecules in solution and in the solid state.

Thus, inorganic polymers provide an opportunity for an expansion of fundamental knowledge and at the same time, for the development of new materials that will assist in the advancement of technology. For example, the superb thermal stability of several poly(organosiloxanes) can be understood in terms of their fundamental chemistry. The controlled hydrolytic degradability of certain polyphosphazenes, which depends on molecular design to favour specific hydrolysis mechanisms, is the basis for their prospective use as pharmaceutical drug delivery systems. The unusual energy absorption characteristics of polysilanes is indicative of surprising electronic structures, and this underlies the interest in some of these materials for use in integrated circuit fabrication.

CLASSIFICATION OF INORGANIC POLYMERS:

1. Homoatomic Inorganic Polymers: These are the inorganic polymers, which have atoms of only one element in their backbones.

However, these are not numerous. A homoatomic inorganic polymer may be represented as follows:

---- X — X — X — X — X ----

Where X is an element.
The silicon, phosphorous and sulphur can form homoatomic inorganic polymers. For example, sulphur forms chains or rings when in the elemental form and also in several types of compounds. The unique property of carbon to form large homoatomic chains is possible due to its electronegativity being such that of all the other elements, its tendency to accept and yield electrons is the least. The groups IV.B elements germanium and tin, among the heavier elements have been most suited for homoatomic polymer formation. Homoatomic inorganic polymers so far reported have not been found to have exceptionally high molecular weight (hmw) and therefore they do not have any appreciable practical value.

In organic polymers the carbon-to-carbon single bond strength is 330.96 to 347.8 J/mole whereas the single bond strengths in homoatomic inorganic polymers are 218.4 to 252 J/mole for sulphur, about 222.6 J/mole for silicon, 210.6 to 222.6 J/mole for phosphorous, about 189 J/mole for germanium and about 163.8 J/mole for tin.

2. **Heteroatomic Inorganic Polymers:** These are the inorganic polymers, which have more than one element in their backbones. In these polymers, there are various combinations of non-metallic elements, e.g.,

\[ \text{---X--Y--X--Y-- OR --X--Y--Z--X--Y--Z--} \]

If Y is more electronegative than carbon and X and Z are less electronegative than carbon the stable heteroatomic inorganic polymers would be produced provided the difference in electronegativities of the elements
being not so large as to make covalent bond formation impossible. In fact, the closer the electronegativities of the two groups are to carbon, stable would be the heteroatomic chain due to strong covalent bond formation.

For the formation of stable heteroatomic chains, atoms of elements like B, Al, C, Si, Ti, Ge, P and As are suitable for X and Z while atoms of elements like O, N and S are suitable for Y.

The heteroatomic polymers having a framework made up of atoms of elements of groups III and V occupying alternate positions in the chain are very interesting because these offer the following advantages:

(i) Such a combination has been found to be isoelectronic with a framework, which is built up of atoms of Group IV elements. For instance, \(--\text{Al}--\text{N}--\text{Al}--\text{N}--\text{Al}\) \(\text{N}--\text{has been found to be isoelectronic with}\)--\(\text{Si}--\text{C}--\text{Si}--\text{C}--\text{Si}--...\) while \(...--\text{B}--\text{N}--\text{B}--\text{N}--\text{B}--...\) has been found to be isoelectronic with \(...--\text{C}--\text{C}--\text{C}--\text{C}--...\)

(ii) When combinations of such elements of low atomic number take place, strong covalent bonds are expected to be formed which result in a strong framework for building the polymer.

(iii) In order to get strong covalent bonding and hence a strong framework for polymer formation, the electronegativities are kept small by using combinations of such elements which belong either to the same or adjacent periods of the periodic Table.
(iv) In order to bring about changes in the properties of the polymer, the usual practice is to attach a wide variety of terminal groups to the various sites or inactive terminal groups, it is sulfur-containing polymers might logically fit the definition of partially inorganic.

3. CO-ORDINATION POLYMER

A co-ordination polymer is one in which a metal ion is co-ordinated with organic ligand so as to form polymer in which there is a metallic atom or ion for each monomer unit.

The co-ordination polymers offer academic interest as well as materials of desired and superior quality when compared with the conventional organic polymers.

Co-ordination polymers can be synthesized by the addition of apparently saturated molecules to each other. These are polymeric materials which contain metal atoms are of two types.

1. First type includes those co-ordination polymers in which the metal atom (ion) is an integral part of the polymer framework.

2. Second type includes those co-ordination polymers in which the metal atom bound to a polymer having suitable donor groups in the framework.

Lewis(59) considered the phenomenon of coordination of metal ion with donor atoms or groups to be
similar to neutralization of an acid (electron acceptor) with a base (electron donor).

The growing knowledge in the fields of coordination chemistry lead the foundation for the attempts of workers to produce the inorganic polymers with modified and desired properties. To be assigned a high polymers, there must be sufficiently large units (degree of polymerization) to exhibit considerable mechanical strength and capability of forming fibers, plastics etc. However, their molecular weight determination becomes difficult due to their insolubility in different solvents, which is the characteristic property of such polymers.

In the co-ordination polymers, metal is expected to contribute thermal stability and electrical and thermal conductivity, whereas the organic part would supply the plasticity, toughness and fabricability. There existed examples of the stabilization of inorganic compounds against thermal or chemical attack by co-ordination with a metal ion.

Sowerby and Audrich(60) preferred to discuss co-ordination polymers apart from condensation and addition polymers, since they could not be readily classified into one or other of these categories by their method of formation. Bailar(61) has pointed out, however, that co-ordination polymers may be formed through both addition and condensation reactions. Quick formation of polymeric palladous is an example of addition polymerization.
The formation of cis-hydroxy-[tetra-aminecobalt(III)]
ion from the hydroxoaquo-amine, however, is a case of condensation polymerization.

\[
\begin{align*}
\text{nPdCl}_2 & \rightarrow \begin{array}{c}
\text{Pd} \\
\text{Cl} & \text{Cl} & \text{Cl} & \text{Cl}
\end{array} \\
& \begin{array}{c}
\text{Pd} \\
\text{Cl}
\end{array} \\
& \begin{array}{c}
\text{Pd} \\
\text{Cl}
\end{array} \\
& \begin{array}{c}
\text{Pd} \\
\text{Cl}
\end{array}
\end{align*}
\]

The dimers of aluminium chloride and ferric chloride, which are found in the vapour stage, may be classified as such, as also may the polymers of cuprous(62,63) palladous chloride and silicon sulphide. The number of bridging groups between the metal atoms in co-ordination polymers depends on the number of co-ordination sites available on the metal atom concerned. Silver and gold, which have only two co-ordination positions, which produce linear polymers with suitable bidentate ligand e.g. Cyanides, with one bridging group between every two metal atoms.

\[
\begin{align*}
2 \text{[NH}_3\text{]}_4\text{Co} & \quad \text{H}_2\text{O} \\
\rightarrow & \begin{array}{c}
\text{NH}_3\text{]}_4\text{Co} \\
\text{OH} & \text{Co (NH}_3\text{)]}_4 & \quad \text{OH}
\end{array} \quad + 2\text{H}_2\text{O}
\end{align*}
\]

Divalent Pd, Pt, Ni and Cu, on the other hand, have four co-ordination sites per metal atoms and are, therefore, capable of forming co-ordination polymers with cyanide ions consisting of infinite layer(64).
If the metal atom is capable of adopting an octahedral configuration, three dimensional co-ordination polymers can be formed. A typical example is the formation of purssion blue by the addition of transition metal ions to solutions of alkali and alkaline earth ferrocyanides. The structure of such highly coloured precipitates has been discussed by Wells(65) and it is apparent that in these materials three dimensional arrangement occurs with the cyanide groups acting as metal-metal bridges.

Inorganic co-ordination polymers are highly thermal stable e.g. bis(acetylacetone)ethylenediamine is not so stable but its copper(II) complex is stable at high temperatures and is only decomposed at red heat. Martin (1958) obtained co-ordination polymers of good thermal stability by reacting bis(thio-picolylamides) with several metal ions like Cu, Ni, Zn etc. Some of these have stability up to 400 °C. In 1962 Block et al. reported the preparation
of chain polymers of the biphenyl phosphinates of Be, Cr, Zn etc. out of these polymers beryllium polymer can be heated up to 530 °C. In 1965, Thomson and Meyer reported the synthesis of some co-ordination polymers of bis(dithiocarbamato)ethylene and bis(dithiocarbamato)hexamethylene with Ni(II), Co(II), Cu(I) and Fe(III). All are starts decomposing above 200 °C. Berlin and coworkers (1959) reported that the stable sheet polymers can be derived by the reaction of Cu(II)-acetylacetonc with tetracyanoethylene \( \text{C}_2(\text{CN})_4 \). Similar polymers are also formed as films on the surface of metals like iron, copper or nickel by the direct reaction with \( \text{C}_2(\text{CN})_4 \).

**FACTORS AFFECTING THE FORMATION OF CO-ORDINATION POLYMERS:**

Bailar (1961) discussed the various factors, which must be kept in view for developing suitable co-ordination polymers. Some of these factors are as follows:

1. Degree of covalency of the metal-ligand bond: Very little ionic character of metal-ligand bond is preferable for getting good co-ordination polymers.
2. Number of negative groups in a ligand: Over all charge of polymeric chelate should be balanced.
3. Functionality of the ligand and the stereochemical requirements of the co-ordinated metal ion.
4. Chelation: This enhances the stability of a polymer.
APPLICATION OF THE POLYMERIC CHELATES:

Polymeric material possessing both high thermal and good mechanical properties are in demand for various components of high speed aircraft, rockets and a number of other industrial applications. Co-ordination polymer has been one such group of compounds with good potential.

Quite a lot of work has been done in the field of co-ordination polymers, which by virtue of their excellent qualities like high thermal and chemical stability have provided and supported the research to meet the present challenges of science and technology. Compared with most organic polymers, inorganic polymers are generally stronger, harder, more brittle and usually insoluble with few exceptions (for example sulphur), they do not burn and only soften or melt at very high temperatures. These characteristic features of high modulus, lack of ductility, insolubility and inertness to heat are typical of polymers with a highly cross linked network and may of the properties of inorganic polymers can be ascribed to their cross linked structure.

Many scientists have reviewed the different applications of polymers(66-69). One of the important applications of co-ordination polymers is their use as a catalysts in a large variety of organic reactions. Many workers have reported the catalytic activity of the polymeric chelates for various petrochemical reactions and oxidation-reduction reaction(70-78). Metal-5,5'-methylenebis(salicylaldehyde) has been used as catalyst in the decomposition of
hydrazine, isopropanol, formic acid, hydrogen peroxide and oxidation of cumene to its hydroxides (79, 80).

Remiraz et al. (81) have reported the synthesis of a polyacrolein deferoxamine copolymer for potential use in the extra corporal treatment of Fe poisoning.

The important application of the polymers as a dying material in the textile industries has been reviewed by Tater, Kenfrew and Tiefenthal (82). One of the widely used applications of the polymers are their use as a converters of solar energy into chemical fuels. Aizowa and Auruki have used the polymeric complexes in energy conversion systems (83). The application of metal polychelate coated electrodes have been reviewed by Japanese chemists (84). Applications of transition metal co-ordination compounds as light emission and light absorption sensitizers have been reviewed by Balletta (85). Various reviews dealing with the semi-conducting properties of polymeric chelates are available (86, 87). The chelate polymers are also found to facilitate the separation of metal ions (88). Several synthetic polymer metal complexes which are functioning as oxygen carrier have been reported (89, 90).

The properties as well as applications of the polymeric chelates depends upon the metal as well as the ligand used in the synthesis. Polymeric chelates of desired properties and application have been synthesized by different types of ligands containing nitrogen and oxygen donor atoms and different metal ions (91-93).
1.11 LITERATURE SURVEY:

Syamal and co-workers(94) have prepared the copper(II) complexes with the ligands derived from salicylaldehyde or 5-chlorosalicylaldehyde or 5-bromosalicylaldehyde or 3-methoxysalicylaldehyde or 2-hydroxy-1-naphthaldehyde and o-aminobenzyl alcohol. Physico-chemical and biological studies of metal complexes of bidentate Schiff bases derived from 2-hydroxy 1-naphthaldehyde and p-anisidine have been done by S. Mishra and G. K. Chaturvedi(95). P. R. Shukla and co-workers (96) have derived Schiff bases from aldehydes and ketones. C. P. Trivedi et al. have derived the Schiff base from glyoxal(97). Synthesis, spectral and magnetic studies of Ni(II) complexes with Schiff base of heterocyclic aldehyde have been done by Rajesh Dhakarey and Greesh Saxena(98) Smita Behra and B. Pradhan(99) have synthesized the monodentate and tridentate Schiff base and their complexes with Ni(II), Cu(II) and Mn(II). P. R. Shukla and co-workers(100) have derived the complexes of chromium(III), manganese(II), iron(II), cobalt(II) and nickel(II) with some tri, tetra and hexadentate Schiff bases. Dutta and De(101) have isolated the mixed-ligand complexes of Cu(II) containing 2,2'-bipyridyl or o-phenanthroline as primary ligand and glycine or α-alanine as secondary ligand. Pfeiffer and co-worker(102,103) have investigated the reaction of various metal ions with condensed system of salicylaldehyde and several diamines. Rana et al.(104) prepared five or six co-ordinated complexes of Cr(III), Mn(II) and Co(II) with tri or tetradeятate ligands
like o-hydroxyacetophenonepicoloyl hydrazone or o-hydroxyacetophenoneisonicotiohydrazone. The complexes of CuL$_2$·H$_2$O have been reported with 2-hydroxy acetophenone and 2-hydroxy propiophenone(105). Some octahedral complexes of Co(II) with Schiff bases derived from salicylaldehyde and amino acids have been prepared and characterized by Ramanujan and Sivasankar(106). Islam et al.(107) have prepared mixed-ligand complexes having the general formula[M(SB)(L)$_3$], where, M = Co(II) or Ni(II), H$_2$SB = tridentate Schiff base of glycine with o-hydroxybenzaldehyde, L = quinoline, isoquinoline, 2-picoline and pyridine and characterized on the basis of elemental analyses, conductivity, TLC, magnetic measurements, IR, electronic and $^1$H-NMR spectra. K. Dey and K. C. Ray(108) have synthesized the manganese(II) complexes of tridentate Schiff base derived from salicylaldehyde and o-aminophenol. Physico-chemical studies of the metal complexes of Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Pd(II), Cd(II) and UO$_2$(II) with N-(2-hydroxy-1-napthylidene) anthranilic acid and N-(2-hydroxy-1-napthylidene)β-alanine have been done by Mehta et al.(109). Mishra and Srivastav(110) prepared the complexes of Co(II), Ni(II) and Cu(II) with the Schiff base of thiophene-2-aldehyde and nicotinamide. Gaungbin wang characterized copper(II) and zinc(II) complexes of Schiff bases derived from aminoacids and 2,4-dihydroxybenzaldehyde(111). The nickel(II) complexes with tridentate N,N,O-donor ligands have been prepared by G. V. Karunakar and N. R. Sangeetha(112). Maya et al.(113)
reported the antimony(III) derivatives of the Schiff base derived from salicylaldehyde and 2-aminothiophenol. Complexes of nickel(II) and copper(II) with neutral bidentate Schiff base derived by the condensation of ethylenediamine with acetophenone or benaldehyde have been synthesized by Dey and Sen(114). Some complexes of Co(II), Ni(II), Cu(II) and Zn(II) with bidentate Schiff bases derived from salicylaldehyde and 2,4-dinitrophenylhydrazine have been prepared by Mishra(115). Shukla et al.(116) studied the complexes of Co(II), Ni(II) and Cu(II) with some Schiff bases derived from salicylaldehyde and aminophenols or anthranilic acid. The biological activity of hydrazides R-CO-NH-NH₂ and their corresponding aroylhydrazones, R-CO-NH-N=CH-R' and the dependence of their mode of chelation with transition metal ions, in the living system have been of significant interest in recent years(117-120).

Dey et al.(121-124) have synthesized and characterized the co-ordination chain polymers of some transition metal ions with different Schiff bases derived from terephthalaldehyde and semi carbazone or o-aminobenzioc acid or isonicotinic acid hydrazone or 4-phenylthiosemi-carbazone. P. L. Maurya and co-workers have also prepared some polychelates based on terephthalaldehyde and hydrazides(125). Co-ordination polymers of copper(II) with dihydroxyquinoid ligands have been prepared by H. D. Coble and H. F. Hulzclaw(126). The polymerization through co-ordination have been studied by Martin, K. V.(127). E. Horwitz and T. P. Perros(128) have studied the thermal
stability of some co-ordination polymers derived from bis(8-hydroxy-5-quinolyl)-methane. Co-ordination chain polymers are generally, thermally more stable than complexes (129,130). Aswar and co-workers have studied the synthesis, characterization, thermal stability and electrical conductivity(131). Karamparwala A. M. and his co-workers have studied the physico-chemical properties of the co-ordination chain polymers(132). Co-ordination polymers of Cu(II), Ni(II), Co(II), Mn(II) and Zn(II) with polySchiff base derived from 5,5'-methylene bis(3-nitrosalicylaldehyde) and 1,3-diaminopropane have been prepared(133). P. P. Patel(134) has prepared some polychelates of poly-Schiff bases using diamines such as ethylenediamine, 1,3-diamino propane, 1,4-diaminobutane, benzidine etc. Poly chelates of bissemicarbazone and bisthiosemicarbazone of 5,5'-methylene-bis-salicylaldehyde have been prepared(135) and their probable structures were determined using various experimental techniques. Synthesis and co-ordinating properties of 2(1-indolyl)benzothiazole towards Mn(II), Co(II), Ni(II) and Cu(II); have been studied by T. A. Khan and Shajahan(136). Mixed-ligand complexes of Co(II) and Cu(II) with pyrazolinic Mannich Bases and 2-aminobenzothiazole have been synthesized and characterized by O. Costisor et al.(137). Synthesis, characterization and thermal studies of thiosemicarbazones of N-ethyl N-ethylacetoacetanilide have been done by Deepa and Arvinda khan(138). Mohamed et. al.(139) have studied on preparation, chemical characterization and electronic spectra of 6-(2-pyridylazo)-3-
acetamideophenol and its metal complexes with Fe(II), Co(II), Ni(II), Zn(II) and Cd(II).

1.12 Present Work:

The present work described in the thesis is in connection with the synthesis of some mixed-ligand complexes and co-ordination chain polymers. The results of these investigations are presented in following chapters.

Chapter-2 divided into seven sections

Section-A: This section describes the experimental methods used for preparation of the ligands and their mixed ligand complexes of the types [MA₂:B·H₂O (Where, M = Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II), A = salicylaldehyde and B = bis(benzylidene)ethylene diamine or bis(acetophenone)ethylene diamine] and [MA₂:B] [Where, M = Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II), A = 5-Bromosalicylidene aniline or 3,5-dibromosalicylidene aniline or 5-chlorosalicylidene aniline and B = bis(acetophenone)ethylene diamine.

Section-B: Elemental analyses.

Section-C: Magnetic measurements.

Section-D: Electronic spectra.

Section-E: Thermo gravimetric analysis.

Section-F: Anti microbial activity.

Section-G: IR-spectra.

Chapter-3 contains the synthesis and characterization of co-ordination polymers of some transition metal ions like Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) with N,N'-di(o-hydroxyphenyl)terephthalaldehyde-
diimine or 1-carboxy-1’-hydroxy-2,2’[1-isonitriloethelidynin-nitrilomethylidenephene]yl[diphenyl].

Chapter-4 describes the synthesis and characterization of co-ordination polymers of type \([\text{Ln(SB)}(\text{H}_2\text{O})(\text{NO}_3)]_n\cdot\text{XH}_2\text{O}\) where, \(\text{M} = \text{La(III)}, \text{Ce(III)}, \text{Nd(III)}, \text{Pr(III)}, \text{and Sm(III)}\)., \(\text{SB} = \text{N,N’-di(o-carboxyphenyl)terephthaldehydediimine or N,N’-di(o-hydroxyphenyl)terephthaldehydediimine}\).
REFERENCES

1. R. M. Lench,

2. M. Hidiroglou,

3. a D. Dalphin,

   b J. Halpern,

   C Y. Murakami,

   d L. G. Marzilli et. al.,

4. R. K. Thauer, G. Dickert and P. Schonheit,

5. J. Raulin,

6. G. Lechartier and F. Bellamy,

7. F. Raoult and H. Breton,

8. R. E. Bruch, H. K. I. Hahn and J. R. Sullivan,

9. J. A. Halsted, J. C. Smith and M. I. Irwin,

10. E. J. Moynahan,


47. L. P. Parts and J. T. Miller, Jr. (Monsanto Co.) US. Pat. 3825520(1974).


70. Cernia, E. M. and Graziani, M.,

71. Hatano, Mashiro, Yuki Gosei,
    Kugaku kyokai shi, 34(11), 837(1976).

72. Hirai, Hidefumi,

73. Hirai, Hidefumi,
    Kayaku zokan(Kyoto), 77, 121(1978).

74. Keneko, Masao,

75. Kriss, E. E., Kurbatova, G. T. and Yatsimirskii, K. B.,

76. Teyssie, ph., catal,

77. Tsuchida, E. and Nishide H.,

78. Tsuchida, E. and Kuneko, M.,

79. Inone, M., Kishito, M. and kubo, M.,


81. Ramirez, R. S. and Rade, J. D,

82. Taber, D., Renfrew, E. E. and Trifesthal, H. E.,
    Fibrereactive Dyes in E. M. Fettes(ed), chemical reactions of polymers, chap-15, Inter science publishers, a division

83. Aizwa, M. and Suzuki, S.,
Kagaku zokan(kyoto), 77, 297(1978).

84. Oyama, N. and Matsuda, H.,
Denki kayaku Oyohi kogyo Butsuri kuyaku, 47171,
Chem. Abstr. 95, 122765k(1981).

85. Boletta, F.,

86. Matsuda, Y. and Murakami, Y.,
kugaku zokan(kyoto), 77, 263(1978).

87. Sonogashira, K. and Hayihara, N.,
kagaku to kogyo(Tokyo), 32(4), 229(1979).

88. Tsuchida, E.,

89. Tsuchida, E.,

90. Tsuchida, E. and Shigehra, K.,

91. Haglhara, N. , Sonigashira, K. and Takahashi, S.
Advance in polymer science, 41, 949(1981). Springer
verlay, New York.

92. Kaneko, M. and Tsuchida, E.,

93. Woehrle, Dietor,

94. A. Syamal, K. S. Kale and S. Banerjee,
95. Smita Mishra and G. K. Chaturvedi,

96. P. R. Shulkla, Minakshi Mishra, A. K. Pathak and Gopal Narain,

97. C. P. Trivedi, Rena Vyas, Deepali Jain and Purnima Kapoor,

98. Rajesh Dhakarey and Greesh Saxena,

99. Smita Behra and B. Pradhan,

100. P. R. Shukla, Nihal Ahmed, Suresh Chandra, Sanjay Mishra, Roshan Rastogi and Gopal N.,

101. R. L. Dutta and Dhrubanada De,

102. P. Pfeiffer et al.,
Ann., 503, 84(1933).

103. P. Pfeiffer et al.,

104. V. B. Rana, J. N. Gurtu and M. P. Teotia,

105. D. P. Gradden and G. M. Mockler,

106. V. V. Ramanujan and B. Sivasankar,

107. M. Saidul Islam, Motahera Begum and Harendra Nath Roy,
108. K. Dey and K. C. Ray,  


110. A. P. Mishra and S. K. Srivastav,  

111. G. Wang,  

112. G. V. Karunakar and N. R. Sangeetha,  

113. M. S. Singh and R. K. Prasad,  

114. K. Dey and S. K. Sen,  

115. N. C. Mishra,  

116. P. R. shukla, V. K. Singh and A. M. Jaiswal,  

117. I. A. Tossidis, C. A. Bolos, P. N. Aslanidis and G. A. Katsonlos,  

118. J. A. Auten, D. Nichlis, J. M. Markopoulos and O. Markopoulous,  
Polyhedron, 6, 1075(1987).

119. A. Maiti and S. Ghosh,  

120. R. C. Agrawal, N. K. Singh and R. P. Singh,  


135. A. M. Karampurwala,  

136. T. A. Khan and Shahjahan,  

137. O. Costisor, M. Mracec, Z. Jori, I. Labadi and W. Linert,  

138. K. P. Deepa and K. K. Arvindakshan,  

139. G. C. Mohamed, E. A. Nadia El. Gamel and F. A. Nour El. Dien,  