CHAPTER 1

INTRODUCTION

1.1. General Remarks
In recent years, there have been interesting developments in inorganic chemistry inspired by the understanding of structure and bonding in the broad class of coordination complexes. The chemistry of coordination compounds occupies a major part of the current research in inorganic chemistry and reports of newer and exotic complexes are appearing in the recent publications. Indeed there are now special journals devoted exclusively to a description of the chemistry of coordination compounds.

Development of sophisticated instrumentation techniques provides powerful methods of investigating the thermal, spectral and magnetic properties of coordination compounds, thereby helping to understand their stereochemistries. Studies on the reaction mechanisms have provided stimulating problems to be resolved in the exciting field of catalysis by transition metal complexes (1,2). Recent advances in bioinorganic chemistry are centered on the role of coordination compounds in biological systems (2,3).
1.2. Some Aspects of the Coordination Chemistry of 3d-Transition Metals.

1.2.1. Electronic configuration, orbital splitting and structural considerations.

Transition elements may be, strictly, defined as those which have partially filled d or f shells in their commonly occurring oxidation states (2). The main transition series include those elements which have partially filled \((n-1)d\) shells. General electronic configuration of the 3d-transition series is \([\text{Ar}]3d^{n}4s^{2}\). Because of the extra stability associated with empty, half-filled and filled subshells, there are some apparent anomalies in the electronic arrangements in the transition series. Thus the outer electronic configurations of chromium and copper are \(3d^{5}4s^{1}\) and \(3d^{10}4s^{1}\) respectively.

In free metal ions, the d orbitals are five-fold degenerate. However, the d orbitals are split in various ligand fields (octahedral, tetrahedral, square planar etc.), owing to their particular shapes and spatial orientation (1-3). As a consequence of this splitting, the electronic and magnetic properties of the complexes will be different. The
structural changes of the complexes will be reflected in the values of their magnetic moments. This enables one to predict their stereochemistries (4,5).

Electronic transitions occurring between the split d levels of the central atom give rise to d-d or ligand field spectra. Absorption bands due to these transitions are generally observed in the near infrared and visible regions of the spectra of transition metal complexes. The study of absorption spectra of these complexes has provided major contributions towards an understanding of their stereochemistries (6,7). The electronic spectra could be interpreted with the help of Tanabe-Sugano diagrams. Tanabe-Sugano diagrams are employed for both strong and weak ligand fields, while Orgel diagrams are used generally in the case of weak ligand fields. But for the more commonly found ligand fields of intermediate strength, either of these could be used (3,6).

Infrared absorptions of the complexes generally occur in the region $4000–200 \text{ cm}^{-1}$ and they provide valuable information about the bonding present in complexes by studying the frequency shifts of ligand vibrations upon coordination (8). The appearance or disappearance of certain bands has been used to deduce structural information.
The concept of hard and soft acids and bases has been useful in predicting the relative stability of the complexes of a given ligand with various metal ions (9). One of the earliest stability correlations was the 'Irving-Williams' series (10) in which complexes of divalent transition metals are arranged in the following order of increasing stability: Mn(II) < Fe(II) < Co(II) < Ni(II) < Cu(II) > Zn(II). The increasing stability is a measure of the increasing inherent 'acidity' of the metals due to decreasing size. Superimposed upon this is a hardness-softness factor in which the softer species (with greater number of d electrons) favour ligands in the order S > N > O (3).

Complexes of transition metals have been well documented (2,11,12). Coordination complexes find application in diverse fields from industrial catalysis to biological systems. Oxidation of ethylene to acetaldehyde, hydroformylation of olefins, methanol carbonylation and polymerisation of olefins are some of the industrial processes catalysed by transition metal complexes (2,13,14).

1.2.2. Complexes of transition metals with oxygen containing ligands.

Transition metals form a wide range of coordination compounds
with various types of ligands. However, complexes with nitrogen, oxygen and sulfur containing ligands are abundant. Several reviews have appeared on the complexes with such ligands (11,12,15). Since an oxygen donor ligand, embelin, was selected for our studies, the present discussion will be limited to a few oxygen containing ligands only.

A great many bi- and multi-dentate ligands contain the phenolate and/or carbonyl functional group as the donors. Much work has been reported on the complexes with several Schiff bases (16). Copper(II) complexes with N-isopropyl and N-sec-butylsalicylideneamine were studied by Sacconi and Ciampolini (17). They found these complexes to be isomorphous with the analogous complexes of cobalt(II), nickel(II), and zinc(II). Manganese(II) complexes with Schiff bases derived from salicylaldehyde and tri- or tetra- amines(18) and trinuclear copper(II) complexes involving catechol aldehyde and hetero-aromatic amines have been recently investigated (19). All the above mentioned Schiff bases coordinated to the metal through nitrogen and oxygen atoms. Metal complexes of the Schiff's base derived from salicylhydrazine and biacetylmonoxime were found to coordinate via carbonyl oxygen, azomethine nitrogen and phenolic hydroxyl group with the replacement of proton by metal ions (20). There are exceptions where the phenolate
oxygen remains uncoordinated. In the dimeric N,N-dimethyl salicylaldimine-nickel(II) complex containing one molecule of catechol mono-anion per metal ion, the unionised phenolic group is not coordinated. The coordinated catechol oxygen in this case acts as a bridge between the two metal atoms (21). Bridging of O-H group has been proposed for a novel trinuclear copper(II) hydroxo complex (22).

The most extensively studied ligands among the carbonyl compounds are $\beta$-diketones (23,24). They are effective in the formation of 5-membered chelate rings and the deprotonated ligand neutralizes the charge on the metal ions in the complexes. Chelate ring electron delocalisation through conjugation within the enolate ion can lead to extra stability of these complexes. Coordination of the carbonyl group is indicated by the lowering of carbonyl stretching frequency in the infrared spectra of the complexes. Similar shifts in C=O frequencies have been observed for some metal $\beta$-diketonates (25) and several other complexes containing this group (26-30).

In the case of iron(III) chelates of salicylaldehyde-semithiosemi-, and S-methylthiosemi-carbazones, the coordination through phenolic oxygen was observed for all the complexes
and the carbonyl group was found to coordinate in the semicarbazone based ligand (31). The coordination behaviour of neutral, mononegative and dinegative forms of N-
(thiophene-2-carboxamido) salicylaldimine(H TCS) towards 3d-metal ions has been investigated (32). Spectral studies indicate that H TCS behaves as a neutral bidentate ligand (bonding sites being carbonyl oxygen, azomethine nitrogen), as a mononegative tridentate ligand (bonding sites being deprotonated phenolic oxygen, carbonyl oxygen and azomethine nitrogen) and as a binegative tridentate ligand (bonding through phenolic oxygen, enolic oxygen and azomethine nitrogen). However, the phenolic group participation with the ligand behaving neutrally has been observed for the copper(II) and nickel(II) complexes of 5,8-diethyl-7-hydroxy-6-dodecanone oxime. In this case the deprotonated ligand forms polymeric complexes whereas the neutral ligand forms monomeric complexes (33).

Spectral behaviour of the polymeric metal chelates of several hydroxyquinoid ligands has been investigated (34-35). 2,5-dihydroxy-1,4-benzoquinone acts as a tetradeionate ligand coordinating through its carbonyl and phenolic oxygens (34).

Complexes of quinizarin or 1,4-dihydroxyanthraquinone with manganese(II), cobalt(II), copper(II), zinc(II) and
ruthenium(II) have been prepared and characterised by the use of infrared and electronic spectra and magnetic studies (36). Magnetic moment vs. temperature data were used to calculate the interaction parameter (2J). The thermal and spectral properties of the chelates of lawsone (2-hydroxy-1,4-naphthoquinone) and juglone (6-hydroxy-1,4-naphthoquinone) with divalent cobalt, nickel, copper and zinc ions were investigated and compared with the complexes of 2,5-dihydroxy-1,4-benzoquinone (37). Oxygen coordination was observed in all the complexes. The chelates of several hydroxy quinoid ligands have been investigated recently (38,39). The monoanionic form of 1,2-dihydroxy-9,10-anthracenedione acts as a bidentate ligand using one carbonyl and one phenolic oxygen for coordination with metal ions. The chelate rings thus formed were expected to be stabilised by considerable delocalisation of \( \pi \) electron density (38).

1.3. Some Aspects of the Chemistry of Lanthanides.

1.3.1. General remarks

In the past few decades there has been considerable progress in the science and technology of the rare earth compounds (40). Some of the recent advances in this area are directed
towards development of improved methods of catalysis as well as of newer techniques in organometallic and biochemical studies. Application of rare earth oxides in catalysis has been reviewed by Rosynek (41) and Minachev (42). Rare earth compounds have been used for improving the activity of some methanation catalysts (43). The catalytic properties of rare earth oxides in the dehydrogenation of cyclohexane, the dehydrocyclisation of heptane, the cracking of butane, the hydrogenation and isomerisation of olefins, the dehydrogenation, dehydration and ketonisation of alcohols and the oxidation of propylene have also been reported (42). Dependence of catalytic activity on the magnetic moment values of the trivalent rare earth ions has been observed for the oxidation of carbon monoxide (44). Polymerisation of acetylene by rare earth coordination catalysts has been investigated (45). Rare earth ions are used to replace the acid sites in zeolites and for making them extremely effective for petroleum processing, particularly for the formation of gasoline fractions (46).

The commercial use of rare earth phosphors in colour television tubes has received much attention in electronics. The red phosphor produced by europium activated yttrium vanadate is well known for its clarity, intensity and other
desirable characteristics (47). Lanthanide complexes with sterically hindered \( \beta \)-diketones exhibit anti-knock activity (48) and may catalytically eliminate some undesirable combustion products of fuels (49). The properties of lanthanide chelates of 2,2,7-trimethyl-3,5-octane dione, for use in the fields such as extraction of metal ores, vapour deposition of metals and fuel combustion modification has been reported (50).

The potential use of rare earth cations as reporter sites in biological systems requiring calcium has been suggested on the basis of their comparable physico-chemical properties. Since rare earth ions are classified as typical hard acids (9) and have sizes comparable to \( \text{Ca}^{++} \), it is not surprising that biological activity due to lanthanide ions is observed in a number of calcium enzymes. The studies on calcium(II) sites in proteins require the application of special techniques due to spectroscopic inertness of this ion. Substitution of lanthanide ions for calcium(II) in proteins is employed for spectroscopic studies (51). Lanthanide cations were also reported as excellent NMR probes of their immediate environment in enzymes (52).

Lanthanide ions are characterised by the gradual filling up of the 4f subshells. The electronic configuration for the
lanthanides is \([\text{Xe}]4f\,5d\,6s\). However there are certain exceptions to this arrangement. Europium(II) and ytterbium(II) are stabilised by \([4f^7]\) and \([4f^{14}]\) configurations. Such a system having a maximum number of parallel spins will be stabilised by the exchange energy resulting from their more favourable spatial distribution compared to that of paired electrons.

The free lanthanide metals are more reactive, and in this respect these could be compared more with alkali or alkaline earth metals than 3d-transition metals. These have lower ionisation energies and heats of atomisation than 3d metals.

An important feature of the chemistry of rare earth elements is the lanthanide contraction. It is the manifestation of a steady and significant decrease in the size of atoms and ions with increasing atomic number, that is from La to Lu. This contraction is caused by the imperfect shielding of one 4f electron by another, owing to the shapes of the orbitals (2). Consequently the effective nuclear charge experienced by the 4f electrons increases with increasing atomic number (La to Lu), thus causing a reduction in size. The observed trends
in the chromatographic separation of lanthanides as well as in the stability of their complexes can be regarded as the summation of the effects of lanthanide contraction(3). The striking similarity in the properties of yttrium to those of the lanthanides is another consequence of the lanthanide contraction. The atomic and ionic radii of yttrium are very close to those of terbium and dysprosium. The resulting resemblance in size coupled with equality in ionic charge accounts reasonably for the invariably natural occurrence of yttrium with the heavier lanthanides (53).

The magnetic (54) and spectroscopic properties (55) of lanthanides are entirely different from the d block elements because the 4f electrons are well shielded from the external ligand fields by the 5s2 5p6 octet. Hence these properties are mostly independent of the stereochemistries of the lanthanide complexes.

The coordination chemistry of lanthanides is receiving increasing attention and there has been considerable progress in this area in the past two decades. Several review articles on various aspects of the coordination chemistry of lanthanides have been published during this period (56-64).
### 1.3.2. Comparison of transition metal ions and lanthanide ions (64).

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1.3.3. Features of lanthanide ions which determine their coordination behaviour.

(a) Electronic configuration
The most common oxidation state of lanthanides is +3. The trivalent lanthanide ion possesses the electronic configuration \([\text{Xe}]^{26}4f^n5s^25p^6\). The 4f orbitals seem to be buried so deeply within the atom that they are unaffected by the environment to any great degree. Hence these orbitals are expected to have only very weak interactions with the ligand orbitals. Usually the higher energy orbitals are only available for bond formation. This restricts the possibilities of complex formation. Ligand field stabilisation energies of lanthanides are too low as compared to those of 3d-metal ions.

(b) Ionic size
The trivalent lanthanide ions are somewhat larger than the other tripotent ions. This minimises the electrostatic nature of the metal-ligand interaction. Increasing covalency is expected with decrease in size (La to Lu) of the metal ions.

(c) Ligand exchange reactions
Ligand exchange reactions of lanthanide ions are very rapid.
This limits the number of isolable complexes. The composition of a complex in the solid state may not be the same as that in solution, and once the solid complex is dissolved, it may remain unrecoverable.

(d) Coordination number and stereochemistry
Since the ligand field stabilisation energies of lanthanide complexes are negligible, greater flexibility in geometry and coordination number is observed (59). The change in LFSE will be very small, when the complex transforms from one geometry to another. Lack of directional bonding due to electrostatic nature of the metal-ligand interactions is also responsible for the observed flexibility in geometries. Coordination number is mostly determined by the spatial accommodation of the ligands around the metal ion, and in the solution it may be different from that in crystals. In many cases the geometry of the complexes has been reported ignoring the possibility of the coordination with solvent molecules like water, benzene, alcohol, etc.(61).

(e) Donor atoms
Lanthanides are regarded as hard acids, and are expected to interact strongly with hard bases (9,65). The general
preference for bonding to donor atoms is in the order $O > N > S$. Majority of the complexes are formed with oxygen donor ligands, especially anionic ones such as carboxylates and $\beta$-diketonates.

(f) Complexation of lanthanides in aqueous media
The coordination of water molecules with lanthanides has been observed in many of its complexes (59,62); under alkaline conditions the $OH^-$ ion is an even stronger ligand than the water molecule. Thus in aqueous media these two ligands compete with each other for complexation thereby limiting the number and types of isolable complexes from aqueous media. In general, the complexation of lanthanide ions in aqueous media is governed by the molar ratio of the ligand to cation, the nature and concentration of starting material, hydrolysis of the product formed, and finally the pH and temperature of the solution (61).

1.3.4. Lanthanide complexes with oxygen containing ligands
Majority of the lanthanide complexes are prepared from oxygen donor ligands. Earlier studies have devoted more attention to the isolation of lanthanide complexes with carboxylates and $\beta$-diketonates (56). Koppikar et al have reviewed the complexes of lanthanides with neutral oxygen donor ligands (62). Moeller et al. (58) and Forsberg (60) have reviewed the complexes of lanthanides with non oxygen-donor ligands.
Information on a large number of lanthanide complexes with C=O group ligands is available (56,61). The ligand to metal ratio is often found to be larger for the complexes in the presence of non-coordinating anions. Thus the ratio of $L:M$ for the complexes of N,N-dimethylformamide with lanthanide nitrates, lanthanide chlorides and lanthanide acetates are 4:1, 2:1 and 1:1 respectively (62). The ligand to the metal ratio for the complexes of N,N-dimethylacetamide with lanthanide perchlorates is also found to decrease from eight for La(III)-Nd(III) to six for Tm(III)-Lu(III), apparently due to the decrease in cationic size (66). However the complexes of this ligand with lanthanide bromides do not exhibit a similar behaviour (67).

The steric hindrance to coordination caused by the bulkiness of the ligand molecules also affects the stoichiometry of the complexes. For example, complexes of lanthanide perchlorate with N,N-dimethylformamide have a $L:M$ ratio of 8:1, but the corresponding diphenylformamide complexes have a ratio of only 6:1 (68).

Complexes of antipyrine derivatives have been studied extensively by several authors (69-73). Nair and co-workers have reported the complexes of lanthanide perchlorates (69)
and nitrates (70,71) with 4-aminoantipyrine. The coordination of the ligand to the metal ion takes place through the carbonyl rather than the nitrogen of amino group. The phenolic group is coordinated in the 4-aminoantipyrine Schiff base complexes of lanthanides (72). Phenolic oxygen was also found to be a potential donor site in the rare earth iodide complexes of 4-N-(2-hydroxy-1-naphthylidine) aminoantipyrine (73).

Complexes of lanthanide perchlorates with 2-N-(pyridyl) benzamide were studied (74). Coordination through oxygen of the amide group and nitrogen of the heterocyclic ring were observed and hexacoordinated geometry was proposed for the complex.

Much work has been done on the lanthanide complexes with 1,3-diketone ligands (61,62). The neutral tris-chelates of these ligands are commonly precipitated as solvates. eg. \[ \text{Ln(diket) } n\text{H}_2\text{O} \] where \( n = 1-3 \). Unsolvated tris-chelates are obtained with bulky organic ligands such as dipivaloylmethane (57). In many of these complexes the lanthanide ion exhibits 8-coordination. It is interesting to note that some of these chelates with bulky diketonate ligands exhibit volatility (50). This is due to the
minimised interaction of metal ion with ligands which is caused by the shielding of the bulky alkyl groups. Early methods used for preparation of lanthanide tris $\beta$-diketonates have been critically examined by Moeller et al (56). Some of the $\beta$-diketonate complexes prepared from aqueous ethanolic mixtures showed undesirable compositions. Based on such observations, the advantages of synthesising lanthanide complexes in non-aqueous media using metal alkoxides as starting materials have been proposed (61).

The participation of phenolic oxygen in coordination at certain ligand to metal ratios has been observed for some lanthanide isopropoxide complexes with mendelic acid and salicylic acid (75). In the crystal structure determination for aquo-tris-salicylato samarium, Burns and Baldwin (76) have found that there are no discrete molecules and instead each metal atom is linked to six different salicylato ions through a variety of donation modes in which both the carboxylic and phenolic oxygen atoms participate. Lanthanide complexes of the composition Ln(Sal)$_3$ (where Sal corresponds to salicylaldehyde) for the lighter lanthanides are obtained by complexation with salicylaldehyde. Heavier lanthanides give the hydroxy derivatives corresponding to the composition Ln(Sal) OH. Phenolic oxygen is found to coordinate in these
complexes (77).

The physico-chemical properties of the lanthanide benzohydroxamates have been studied by Schelokov et al (78). The complexes correspond to the composition $M(C_6H_5CONHO)_3$ where $M$ is La(III) to Lu(III). Infrared spectra of these complexes show that there is bidentate cyclic coordination of the benzohydroxamate ion. Absence of phenolic O-H vibration in the complexes and the shift in carbonyl group frequency indicate the participation of these groups in the coordination. Octahedral geometry is proposed for the complexes. New lanthanide complexes with salicyloylhydrazide-salicylaldehyde Schiff base and anthranilic acid-salicylaldehyde Schiff base were synthesised and characterised(79). Infrared spectra of these complexes reveal the bidentate binding of both the Schiff base ligands to lanthanide ions.

1.4. Some Aspects of the Coordination Chemistry of Actinides, particularly Thorium and Uranium

The actinides are characterised by a general electronic configuration $^{n\circ}5f^66d^27s^2$. The $5f$ electrons are effectively shielded by $6s6p$ octet. The main difference between the $4f$ and $5f$ orbitals seems to depend upon the relative energies and spatial distribution of the orbitals. The $4f$ electrons
are deeply buried in the atom, whereas the 5f electrons are available for bonding. Consequently, the binding energies of 4f electrons in lanthanides are much greater than the binding energies of 5f electrons in actinides. The 5f electrons can be removed more easily, thus causing the actinides to possess positive oxidation states as high as a value equal to the sum of the 7s, 6d and 5f electrons.

Similar to that of lanthanide contraction, actinide contraction is also the result of imperfect shielding of the 5f electrons leading to increased nuclear charge and concomitant reduction in size. Actinide contraction initially parallels that of lanthanides, but the elements from curium onwards are smaller than might have been expected, probably resulting from poorer shielding of 5f electrons in these elements.

Thorium and uranium are the most abundant elements among the actinides in nature. They are now regarded mainly as the potential source of nuclear energy. A large number of complexes have been reported for uranium and thorium.

The loosely bound nature and the less effective shielding of the 5f electrons make the actinides more susceptible to
complex formation. The complex forming tendency is controlled by factors such as ionic size and charge so that the order is generally $M^{4+} > M^{2+} > M^{3+} > M^{2+}$.

Thorium is the second member of the actinide series, and is less basic than the trivalent lanthanides. Nevertheless, it resembles lanthanides in the physical properties of many of its compounds (53).

Among the best known complexes of thorium are those with β-diketones. The acetyl acetonato complex, Th(acac)$^4$ has been extensively studied (80,81). Complexes of 8-quinolinol (82,83) and some oxalates (80) have been synthesised and characterised.

A ten coordinate oxobridged thorium complex $\mu$-oxo-bis [aquanitrato (2,9-diformyl-1,10-phenanthroline-disemicarbazone- Th(IV) nitrate] with an unusual polyhedron was synthesised and characterised (84). A coordination number of 10 has also been proposed for the complexes $\left[\text{NH}_4\text{Th}(L)\text{H}_2\text{O}\right]^+ \text{H}_2\text{O}$ and $\text{Li}\left[\text{Th(trop)}\text{H}_2\text{O}\right]^+\text{H}_2\text{O}$ where $\text{NH}_4\text{L} = \text{cupferron}$ and trop = tropolone anion (85,86).

An oxygen coordinated complex of pyridine N-oxide with Th(NCS)$^4$ having the composition $\left[\text{Th(NCS)}(\text{PyO})\text{H}_2\text{O}\right]^+$ has been
reported (87). An 8-coordinated structure has been suggested for this complex. Some polymeric complexes of Th(NO$_3$)$_4$ with N-methylpiperazine and 2-methylpiperazine are reported (88). A coordination number higher than 10 was proposed for these complexes. Complexes of thorium(IV) with 2,6-lutidine-N-oxide and tetramethylenesulfoxide were reported to have coordination through oxygen and the coordination number varied from 6-10, depending upon the nature of anions (89).

Uranium(VI) complexes, particularly the uranyl complexes, represent the most extensively studied among the complexes of uranium. Preparation of several \(\beta\)-diketanato complexes have been reported in the literature (90,91). Mixed nitrogen and oxygen coordination is well illustrated in some uranyl complexes with polyaminopolycarboxylates (92,93). Several uranyl complexes with sulfur donor ligands have been recently investigated (94). Several workers have reported uranyl complexes with Schiff base ligands (72,95,96). Eight coordinated complexes of dioxo uranium with 8-quinolinol-5-sulphonic acid (H$_2$L) with the composition Na\(\left[UO_2L\right]_2H_2O\) and \(K\left[UO_2L\right]_2O_5H_2O\) have been reported (97). Mixed oxygen and nitrogen bonding from 3 bidentate ligands are observed for these complexes. Spectral studies on uranyl complexes with 3-benzamidophthodanine and its derivatives show the bidentate coordination of the ligand through amide nitrogen and
carbonyl oxygen (98). Dioxouranium complex with N-phenylbenzoylhydroxamate has been prepared and characterised (85). Two bidentate hydroxamato ligands and one methanol molecule are equatorially bonded to the linear uranyl group in the pentagonal bipyramidal geometry. Uranyl complexes with isonicotinamido salicylaldimine were found to coordinate through the carbonyl oxygen, phenolic oxygen, azomethine nitrogen and ring nitrogen (99). Uranyl complexes of glycine, aniline and aminobutanoic acid were prepared and characterised (100). The uranyl group is equatorially bonded to the bidentate carboxylate groups of the 3 molecules of the organic ligand forming a distorted hexagonal bipyramidal coordination geometry around the metal.

1.5. Coordination Polymers

1.5.1. Nature of coordination polymers

Most of the metal complexes of embelin (101) and 2,5-dihydroxy-1,4-benzoquinone (34) are polymeric in nature. Hence it would be relevant to have a discussion here on the nature of coordination polymers. The term coordination polymer has been used to describe any macromolecular entity which contains coordinate covalent bonds (102). The concept of coordination polymer is restricted to the limitation that
a metal ion has to be involved in the coordinate covalent bond. They are generally classified as inorganic polymers. The ligands commonly incorporated are mostly organic in nature. Two types of coordination polymers are usually investigated, one in which the metallic part functions as the backbone of the macromolecular unit and the other in which the metallic elements are coordinated to a polymer repeating unit containing donor groups. Metal complexes of embelin belong to the former group.

1.5.2. Thermal stability of some coordination polymers
Simple organic compounds are greatly stabilised by coordination with metal ions (103,104). In several cases, it has been found that coordination increases the thermal stability of the ligand (105,106). However there are instances where the pyrolysis behaviour of certain complexes is not in conformity with the above statement. The complexes of acetyl acetone decomposes significantly at 270°C whereas the ligand has got only very little decomposition under similar conditions (107,108). Usually it is found that the coordination polymers are thermally more stable than their monomeric types. Here also some exceptions are noticed. The complexes of Schiff bases and phthalocyanines are thermally more stable than their highly polymerised analogs (109-111).
Coordination polymers of hydroxyquinones are generally more stable than their monomeric ligands. It has long been known that the hydroxyl and carboxyl groups readily form bridges between metal ions, thus forming polymeric species (112). Dihydroxyquinones are ligands which can attach itself simultaneously to two metal ions.

Frank and co-workers (113) were able to synthesise the metal complexes of 2,5 dihydroxy-1,4-benzoquinone. They considered these complexes as simple monomeric types. However, complexes of 2,5-dihydroxy-1,4-benzoquinone with copper(II), nickel(II) and cobalt(II) were shown to have polymeric nature (114).

Bottei and Gerace had prepared and characterised the copper(II), nickel(II) and cobalt(II) complexes of naphthazarin (5,8-dihydroxy-1,4-naphthoquinone) (115). Copper(II) complex was recognised as anhydrous and other complexes were dihydrates. The metal to ligand ratio was 1:1 for all chelates except for copper complex for which it was 3:4. The thermal stability of the naphthazarin chelates was found to decrease in the order Ni > Zn > Cu > Co. The greater thermal stability found for the nickel(II) complex is attributed to the spatial arrangement of the polymer in which metal ion appears to be more planar in nature. The greater
stability of naphthazarin chelates over 2,5-dihydroxy-1,4-benzoquinone chelates is due to the greater unsaturation of the organic ligand leading to increased stabilisation of metal-oxygen bonds through electron delocalisation.

Knobloch and Rauscher (116) have used various techniques to prepare coordination polymers; they prepared quinizarin (1,4-dihydroxyanthraquinone) complex of copper (II) using an aqueous solution of Cu(NH₃)₄²⁺ and quinizarin solution in benzene. Synthesis and characterisation of some polymeric transition metal chelates of quinizarin has been recently reported (117).

Studies on the thermal and spectral properties of some polymeric chelates of chloranilic acid (2,5-didroxy-3,6-dichloro-1,4-benzoquinone) rhodizonic acid and 2,3,5,6-tetrahydroxyparabenzquinone were also reported (118). The chelate of chloranilic acid is thermally much more stable than those of rhodizonic acid and of tetrahydroxyquinone. The lowest lying carbonyl peak in the infrared spectra of these complexes was also found for the chloranilic acid chelate and this was attributed to the inductive effect due to the steric hindrance of the chloride ions.
Coble and Holtzclaw have studied the thermal stability of polymeric copper(II) chelates of 2,5-dihydroxy-1,4-benzoquinone, 5,8-dihydroxy-1,4-naphthoquinone, 1,4-dihydroxy-anthraquinone, 1,5-dihydroxyanthraquinone, 1,2,5,8-tetrahydroxyanthraquinone and 6,11-dihydroxynaphthoquinone (35). The compounds were prepared under similar conditions and the relative thermal stabilities were determined by differential thermal analysis. The thermal stability is not related to thermodynamic stability as indicated by the shift in carbonyl absorption frequency, but is almost found to be a linear function of the number of fused rings in the ligand portion of the chelate.

1.5.3. Applications of coordination polymers
It has long been known that coordination polymers have got some applications in industrial processes. Tanning of leather, which is an ancient art depends on the coordination of metal ions with the polypeptides of the hide(112). The complexes which are thus formed are more resistant to bacterial attack, weather and wear than the original hide.

Coordination polymerisation is involved in the formation of a water repellent basic chromic stearate, basic chromic acrylate and an analogous hydrophobic, and oleophobic
perfluorocarboxylate. The monomers of these substances are soluble in alcohol and they are applied to the surfaces to be protected. When the material is heated, a strong protection of the coordination polymer is formed on the surface of the material (112).

Other applications include the use of coordination polymers as viscosity stabilizers for oil and grease thickeners, as antistatic agents and also as corrosion resistant coatings for metals (112). Chelating resins with multi-dentate ligands in the polymeric matrix are used as metal ion collectors in the field of environmental chemistry. In view of this application, preparation and chelating properties of polymeric and matrix bound ligands have been reported (119,120). Corley has patented the application of coordination polymers as a combustion modifier for propellants and it has been reported that the burning rate of a propellant is increased by the addition of a certain amount of the copper complex of 2,5-dihydroxy-1,4-benzoquinone to the propellant(121).

Catalytic applications of the coordination polymers are also receiving considerable importance in industrial processes. It has long been known that the chemistry of the adsorbed
molecules and the chemistry of coordination compounds are intimately related. Several examples can be cited to illustrate the use of transition metal complexes as catalysts for several conversions (13,14). Coordination polymers are finding use in heterogenising homogeneous catalysts. If a homogeneous catalyst is attached to a polymer which is insoluble in the reaction medium, it may still retain the selectivity of the homogeneous catalyst, but like other heterogeneous catalysts, it can be recovered readily by filtration. Catalysts bound to polymers do not loose selectivity and in some cases are more active than the parent homogeneous catalyst. Polymeric rhodium carbonyl complexes are effective and highly selective in the hydroformylation of olefins (112). Bruner and Bailar used polymeric diphenylbenzylphosphine polymer with coordinated platinum(II) chloride or palladium(II) chloride in the selective hydrogenation of olefins (122).

In the Wacker process, the oxidation of ethylene to acetaldehyde in aqueous media is catalysed by a solution containing palladium(II) chloride and copper(II) chloride. Nevertheless, organic quinone polymers containing sulfonic acid functional groups combined with palladium(II) were found to function as heterogeneous catalysts for the oxidation of ethylene to acetaldehyde without any co-catalyst such as copper(II) chloride (123).
1.6. A Brief Review of the Constitution, Biological Aspects and Analytical Applications of Embelin.

Embelin (2,5-dihydroxy-3-undecyl-2,5-cyclohexadiene-1,4-dione), an orange pigment isolated from the berries of the Indian shrub Embelia ribes is of great medicinal importance because of its anthelmintic properties (124). In Bengali and Sanskrit Embelia ribes is known as 'Vidanga', as 'Baberang' in Hindustani and as 'Vizhalari' in Malayalam. Charaka recommended the use of the berries of Embelia ribes in dyspepsia, flatulence, gripes etc; Hakkims regarded it as an anthelmintic, particularly for the expulsion of tape worms (125).

Embelia ribes is a large scandent shrub growing mainly in the valleys of the Vindhya hills. It bears fruit towards the end of autumn. The fruit is intense pink in colour and globular in shape. On drying, it becomes shrivelled up and the colour changes to dark brown.
Heffter and Feuerstein (126) showed that natural embelin contained a side chain $C_{11}H_{23}$ as they were able to isolate n-lauric acid by oxidation. They also prepared a dibenzoyl derivative and showed that embelin condensed with primary amines in the same way as did benzoquinone. Fieser and Chamberlin (124) synthesised embelin using lauryl peroxide for the alkylation of 2,5-dihydroxy-1,4-benzoquinone and compared its properties with pure natural embelin. Constitution and preparations were also studied in detail by Kaul et al. (125). The embelin content in embelia ribes was estimated after extracting it with solvent ether. The crude embelin thus obtained as such or after some purification was subjected to chemical analysis by gravimetric or colorimetric techniques. Sarin and Ray estimated embelin in embelia ribes based on a colour reaction between aniline and embelin (127). Bheema Sankara Rao and Venkateswarlu (128) estimated embelin after precipitating it as Vilangin (2,5-dihydroxy-4-undecyl-3,6-benzoquinone) using 5% formaldehyde solution in methylalcohol. On an average, the embelin content in the berries was found to be ~ 2.5%.

1.6.1. Biological studies on embelin
Quinones and their substituted derivatives have long been known to possess numerous chemically and biologically significant properties with many important applications in
several areas (129-131). The quinoid metabolites are found to inhibit the growth and metabolism of a range of bacterial genera and it has been reported that the antibiotic activity of 2,5-dihydroxy-1,4-benzoquinone derivatives depends on the nature of substituents at the 3 and 6 positions (132). Hence some of these biological activities could also be expected in the case of embelin.

The biological aspects and medicinal importance of embelin have received much attention during the last few years. Antifertility activity of embelia ribes have been studied by Krishnaswami et al. (133,134). The effect of embelin was tested in rats for estrogenic and anti-estrogenic activities. Embelin dosage upto 100 mg/kg did not increase or decrease any of the estrogen sensitive parameters like uterine weight, uterine glycogen and uterine alkali phosphatase levels. Dixit and Khanna (135) have patented the isolation of embelin as a male antifertility drug. Phosphatase activity in the testis and prostate of rats dosed with embelin were studied by Chawhan and Agarwal (136). The acid and alkali phosphatase levels in rats were elevated on administering embelin. Biochemical changes in the uterus and cervix of rats treated with embelin have been investigated (137).

The analgesic activity of embelin was studied in rats and mice (138). Embelin was shown to exhibit an activity
entirely different from other opiates. There was no precipitation of abstinence syndrome as observed with morphine. A peripheral site of action of the drug is ruled out, as it lacks any demonstrable antiinflammatory action. The high oral efficacy and nonnarcotic property of embelin is expected to make it more acceptable than morphine. Effect of embelin on the germination rates of maize (or corn) and cowpea were also investigated (139). Embelin reduced the germination rates of corn and cowpea at 100 ppm and 250 ppm levels and stimulated germination at 50 ppm level. Data on respiratory rate and catalase activity indicate that such compounds inhibit respiration rates.

1.6.2. Analytical applications of embelin

The use of embelin as an analytical reagent for the precipitation and separation of various metals has been reported by Venkateswarlu and Bheema Sankara Rao (140-142). However, information regarding actual composition and stereochemistry of the complexes with some divalent metal ions has been reported only very recently (101).

The formation of water insoluble chelate complexes of embelin with many metals under suitable pH conditions have been observed (140). Most of the divalent metal ions form 1:1 complexes.
Complexes of uranium and thorium and their separation using embelin were also investigated (141a). Embelin precipitated uranium (VI) at pH 6.5 and thorium (IV) from a 0.3 to 0.4N HCl solution. Both the precipitates were ignited to oxides for weighing. Thorium(IV) can be separated from uranium (VI), rare earths and some other divalent metal ions using this method. Titanium and iron showed interference in the determinations.

Separation of aluminium and beryllium and their estimations were also reported (141b). Aluminium was precipitated with an alcoholic solution of embelin at pH 4 to 4.5. The precipitate was filtered, ignited and weighed as Al₂O₃. Since the beryllium complex is soluble in alcohol, the removal of excess alcohol by boiling was suggested.

Estimation of copper and cadmium and their separation have also been studied (142). Copper(II) was separated from cadmium(II) by its precipitation with embelin at pH 2.5-3.0. Cadmium(II) precipitates at pH 6.0 - 6.5. Precipitation of divalent calcium, barium, strontium and magnesium using embelin were also carried out under controlled pH conditions using ammonium acetate-acetic acid buffer (141c).
1.7. Coordination of Metal Ions with Biologically Important Ligands.

Our studies are mainly centered on the coordination behaviour of various metal ions towards embelin. Embelin is quite well known for its anthelmintic, antifertilitic and analgesic activities. Therefore, a brief discussion on biologically active ligands as well as their metal complexes would not be out of place in the present context.

1.7.1. Metal ions in living systems.

Transition metal ions in biological systems is receiving increasing attention, because of its wide application in the field of biochemistry and medicine(2,3,143). Metalloproteins are intimately involved in several metabolic processes. Binding sites on proteins have some chelation character, and stability is gained through coordination with a metal ion (143). The iron containing proteins hemoglobin, myoglobin, chlorocruorin and hemrythrin are associated with oxygen carriage. Oxygen utilisation in living systems is catalysed by cytochrome-c-oxidase which contains two iron atoms bound in a heme unit [an iron(II) porphyrin] and two copper atoms. Chlorophyll, participating in photosynthesis, is a magnesium(II) porphyrin ring system. Vitamin B$_{12}$ or cyanocobalamin is involved in the reduction of organic species. It also helps the acceptance of a methyl group and
its transfer in the biosynthesis of methionine which in turn is involved in trans methylation reactions in biosynthesis (3). The enzyme system nitrogenase in plants is known to contain both iron and molybdenum. It has been reported that the molecular nitrogen forms a dinitrogen complex with one of these metals and other serves as an electron source leading to the eventual reduction of nitrogen to ammonia (144). The discovery that molecular nitrogen was capable of forming stable complexes with transition metals led to extensive investigation of the possibility of nitrogen fixation via such complexes (3).

1.7.2. Metal ions and chelating agents in medicine.
Role of chelating agents in medicine has been discussed in detail by Hughes (145) and Perrin (146). An excess of highly toxic metal ion in the living system can be removed using a chelating agent. Certain drugs are good ligands which may bind with the native metal ions. Excessive calcium deposits, resulting in the formation of stones can be treated with EDTA. Chelating agents can seek out toxic metal ions to bind and excrete them as complexes, they may deliver the essential trace elements to tissues that require them. The most important complex forming species in animal and plant tissues are amino acids, peptides, carboxylic acids, phosphates and
the mercapto, dithio, amino, imidazole, phenolic and free carboxyl groups of proteins. The toxic effects of heavy metal ions are due to their strong complexing ability towards these active complexing groups on tissues. Hence a suitable chelating agent, more powerful than these groups is administered to remove the toxic cations. Chelated drugs are also finding application in the treatment of various diseases. The use of chelated drugs could represent a better route of administration associated with smaller risk of toxic effects (145,146). The copper dependence of rheumatoid arthritis is well established (147,148) and the observation that copper complexes involving anti-inflammatory drugs can be more effective and involve less gastrointestinal irritations than the free drug (149) has stimulated a great deal of investigations involving drug complexation(150). A physiological approach to treatment of inflammatory diseases using copper complexes has been given by Sorenson et al (151). Ligands such as anthranilic acid is inactive, but their copper complexes are found to be potent anti-inflammatory agents. Aspirin and D-pencillamine are also known to have therapeutic applications in rheumatoid arthritis (148,152). Nevertheless, their coper complexes are more effective than the free drugs lending credence to the hypothesis that the active metabolites of anti-arthritic
drugs are their copper complexes (151). The antibiotic action of tetracyclines is related to the ability of these compounds to form complexes with metal ions (145,153,154). Antifungal activity of thiosemicarbazones has been found to increase on complexing with transition metals (155).

1.7.3. Structural studies on chelated drugs
It is quite wellknown that metal complexes of ligands which have biological activity are more active than the free ligands (156,157). The study of stereochemistries and the chemical reactivity of the coordination compounds of the drugs will help to determine the nature and extent of the relationships existing between the chemical structure and biological activity (158).

Studies on complex formation of antibiotics (as ligands) such as cycloserine, 4-aminoisoxazolidin-3-one (159-161) and its derivative N,N'-terephthal-bis-cycloserine (162) have been reported. Harrison et al. have studied the complexes of iron(III), cobalt(II), nickel(II), copper(II) and zinc(II) with an antiinflammatory drug azapropazone(163). The preparation, characterisation and anti-tumour activity of some metal(II) chelates of 4-((m-aminophenyl)-2-formylpyridine thiosemicarbazone has been reported (164).
Complexes of manganese(III), iron(II), nickel(II), copper(II) and zinc(II) with Schiff bases of N,N-diethyl-diaminedithiocarbamates were prepared and characterised to study the effect of antifungal and antibacterial activities upon complexation, (165). Similar investigations on structural and biological aspects were also reported for the metal complexes with dicamba (166) and alkyl pyrazines (167). Pyrazine is a constituent of plants like Cocoa and Coffee.

Sarkar and Ghosh (168) have studied the complexes of uracil with manganese(II), iron(II), cobalt(II), nickel(II) and copper(II). Octahedral geometry is proposed for the complexes. Uracil is a constituent of RNA in biological system. Spectral and magnetic studies were carried out on some complexes of pyrazole derived carbohydrazide, a potential ligand of biological importance (169). Metal complexes of antiinflammatory drugs have also been investigated recently (170,171). In view of the above mentioned merits of the structural studies on chelated drugs, we are anticipating the role of metal complexes of embelin to function as possible basis for further studies on its medicinal properties. Very little is known on the behaviour of embelin towards transition metal ions. Hence, a
systematic study on the metal complexes of embelin is warranted and it is expected that the investigation reported herein would help provide a better insight into the relevant role of metal complexes in biological systems.