

CHAPTER - 1

INTRODUCTION

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When a metal ion combines with an electron donor, the resulting substance is said to be a complex or coordination compound. If the substance, ligand which combines with the metal contains two or more donor groups forming one or more rings with the metals, the resulting structure is said to be a chelate compound or metal chelate and the ligand is said to be a chelating agent.

The earliest quantitative determination of formation constants was pioneered by workers such as Euler¹ and Bodlander². The stepwise hydrolysis constants of Cr(III) were reported by N. Bjerrum³. The measurement of step wise stability constants for monodentate ligands in aqueous solution, was initiated by J. Bjerrum⁴. Here Bjerrum used excess of ligand to prevent hydrolysis and precipitation. Stability work in chelate compounds began with the seminal paper by Calvin and Wilson⁵. Some ligands are attached to the metal atom by more than one donor atom in such a manner as to form a hetrocyclic ring. This type of ring has been given a special name chelate ring and the molecule or ion from which it is formed is known as a chelating agent. The process of forming a chelate ring is known as chelation. The first chelating molecule discovered were those with two donor atoms and it was the caliper like mode of attachment of the molecules to the metal atom that led Morgan and Drew⁶ to suggest the name chelate, which was derived from the Greek word meaning lobster's claw. Any metal complex in which one or more chelate rings are present is defined as metal chelate. Electrically neutral metal chelates were originally called "inner complex metallic salts", as name

generally attributed to Ley⁷ who first used it in the title of a paper dealing with bis (glycinato) copper (II).

Metal chelates may be examined from two points of view

- (1) The central metal atom
- (2) The chelating molecule

(1) **The Central metal atom** :- As might be expected the properties of a metal complex are influenced to a considerable extent by the nature and oxidation state of central metal atom. One method of studying this influence is to compare the compounds formed by a series of different metal atoms in a given oxidation state with a particular chelating agent. The structure and properties of the complexes formed by a metal are influenced by its state of oxidation, in other words by its oxidation number. This number has been defined by Pauling (1948) as follows : "In a covalent compound of known structure the oxidation number of each atom is the charge remaining on the atom when each shared electron pair is assigned completely to the more electronegative of the two atoms sharing it. A pair shared by two atoms of the same element is split between them.

Metal ions exist in aqueous solution as aquo complexes. It is not always certain how many water molecules are involved, though for many metals it is probably four or six. Replacement of these water molecules by other molecules (including chelating molecules or ions) may stabilize an otherwise unstable oxidation state. For example, $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ is unstable in aqueous solution and is so powerful an oxidising agent that it oxidizes water to oxygen, $[\text{Co}(\text{NH}_3)_6]^{3+}$ and the corresponding ethylenediamine complexes are stable in aqueous solution. The hexaquo $[\text{Co}(\text{H}_2\text{O})_6]^{++}$ is stable in aqueous solution but replacement of the water molecules by five cyanide ions results in a complex

$[\text{Co}(\text{CN})_5]^{3-}$ that is capable of reducing water to hydrogen. The ion $[\text{Co}(\text{H}_2\text{O})_6]^+$ can not survive in aqueous solution. However, cobalt exists in aqueous solution in the +1 state if it is coordinated with three molecules of 2, 2'-bipyridine (Waind and Martin, 1958).

Coordination number of the metal atom has been defined as the number of donor ligand atoms directly bound to a central metal atom which is not necessarily fixed and invariable for each metal. Sometimes it depends on the nature of the donor atom; at other times it depends on the oxidation state of the metal. The halogen atoms Cl, Br and I participate in chelate ring formation in bridged, polynuclear complexes which are not usually thought of as metal chelates.

The coordination number of some metals in a given oxidation state is, in their stable compounds, fixed and characteristic. With very rare exceptions, if any, the metal Co(III), Cr(III), Pt(IV) and Pd(IV) have a coordination number of six. In contrast to the above metals, those whose coordination number for a given oxidation state varies usually with the nature of the ligand atoms include Fe(II) (four with Cl^- and six with CN^-) Zn(II) (six with NH_2 , CH_2 , CH_2 , NH_2 , and four with CN^-) and Cu(II) (2 with Cl^- and four with AsEt_3).

(2) **Chelating Molecules** :- The two conditions necessary for a molecule to function as a chelating agent are i) it must possess at least two appropriate functional groups, the donor atoms of which are capable of combining with a metal atom by donating a pair of electrons. These electrons may be contributed by basic coordinating groups such as $-\text{NH}_2$ or acidic groups that have lost a proton. ii) the functional groups must be so situated in the molecule that they permit the formation of a ring with a metal atom as the closing member.

Steric factors occasionally influence chelation. One chelating molecule may attach itself to a metal atom readily enough, but the addition of a second and third is hindered or even prevented by the fact that there is clash between the first and parts of the second and third when the latter move into the positions required for attachment.

According to the number of donor atoms capable of combining with a metal atom, these are called tridentate, quadridentate, quinquedentate, sexadentate and octadentate chelating molecules.

Chelating agents form more stable complexes than non-chelating agents which may be illustrated qualitatively by considering the two compounds $[\text{Ni}(\text{en})_3]\text{Cl}_2$ and $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$. The latter is rapidly hydrolysed in water.

The most familiar chelating agents are the organic polyamines, polycarboxylic acids, aminoacids, hydroxyacids and β -diketones. For a chelate ring of single bonds only, the five membered ring is usually most stable⁸ where as, six membered rings have maximum stability where there are two double bonds in the ring. Four membered chelate rings are relatively rare. From a study of x-ray crystal analysis it has been established that carbonatotetramine Co(II) bromide contains four membered chelate ring. It is further observed that out of the two similar chelating agents, that which forms greater number of chelate rings with a given metal ion, forms the more stable complex. For example, the stability constant of ethylenediamine Cu(II) is 10.8 while that of diethylenetriamine-Cu(II) is 16.0. Calvin and Wilson⁵ from a study of closely related chelating agents reported that the greater the basic strength (pK_a), the greater is the stability of the metal chelate. Substitution in the chelating molecule also influences chelation. It can be shown that the complexes of 8-hydroxyquinoline are less stable than those of 8-hydroxyquinoline,

despite the fact that the former chelating molecule is the stronger base of the two. This is attributed to the effect of steric hindrance arising from the chelation of 8-hydroxy quinaldine. The nature of the donor atoms have marked influence on chelation. The electron accepters are divided broadly into three classes, namely class (a), class (b) and intermediate by Ahrland, Chatt and Davis⁹ which is some what connected with the electronegativities. Class (a) alkaline earths, rare earths, Th(IV), Mn(II), Cr(III), U(IV) accepters can form most stable complexes with the first ligand atom of each family (N, O and F) where as class (b) Pt(II), Au(II) and (III), Cu(I), Ag(I) and Hg(II) accepter can form most stable complexes with the second or subsequent ligand atom of each family. Each oxidation state of a metal is regarded as a different acceptor and for this reason many metals are placed in the third group of intermediate, which includes Mo, W, Mn, Te, Re, Fe, Co, Ni, Ru, Rh, Os, Ir, Cu, Zn, Cd, Pb, Bi, Po etc.

Pearson¹⁰ and schwarzenbach¹¹ proposed the second approach in the form of hard and soft acids and base (HSAB concept). "Hard" metal ions behave like proton in their stability to coordinate with the ligands, possess small size and high positive oxidation states and have no valence shell electrons to be easily removed or distorted. "Soft" metal ions are comparatively large with low and zero oxidation state and have valence electrons to be easily removed or distorted. The ligand in which the coordinating atom has low Polarizability and high electronegativity is called "hard" base and others with high Polarizability and low electronegativity are called "soft" bases. Hard acids prefer to coordinate with hard bases and soft acids prefer to coordinate with soft bases. A cation which is a relatively hard acid or border line can be made softer by coordination with soft ligand and thus achieves greater ability to coordinate more number of soft

ligands. According to Pearson, Cr^{3+} , Fe^{3+} , Mn^{2+} , alkali, alkaline earth and rare earth metal ions prefer oxygen donor atoms. Ag^+ , Pb^{2+} and Hg^{2+} prefer nitrogen donors while Mn^{2+} , Zn^{2+} , Co^{2+} , Ni^{2+} , Cd^{2+} and Cu^{2+} etc. favour mixed oxygen and nitrogen donors.

The reverse phenomena is also true. It is important to note that complexes formed between hard acids and soft bases do exist and are thermodynamically stable to hydrolysis.

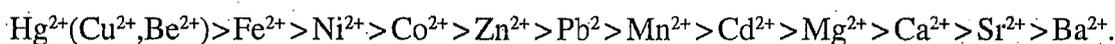
Historical Evolution of Computational Methods

Although methods of determining stability constants have been described in several books, the monograph by Rossotti and Rossotti¹² still stands today as the authority on pre-computer methods of data reduction involving many types of equilibrium data.

With the advent of computer, the situation changed dramatically. With this new tool, the equilibrium-coordination chemists became able to include in their treatment of data, all of the equilibrium constants simultaneously. Currently a number of computer programs are available¹⁴⁻¹⁶ but no single program seems to have outstanding advantages over the others. A review by Gans¹⁷ is an excellent survey of the field and the pitfalls in the application of computer to experimental data.

Several investigators have tried to correlate stability constants of complexes with the physical characteristics (ionisation potential, ionic radius and atomic number etc.) of metal ions. From a study of salicylaldehyde, glycine and oxine complexes, Mellor and Maley¹⁸ reported a stability order as $\text{Pd}^{2+} > \text{Cu}^{2+} > \text{Ni}^{2+} > \text{Co}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+} > \text{Fe}^{2+} > \text{Mn}^{2+} > \text{Mg}^{2+}$.

A similar order of increasing stability $Zn^{2+} < Cu^{2+} > Ni^{2+} > Co^{2+} > Mn^{2+}$ proposed by Irving and Williams¹⁹ holds irrespective of the nature of the ligand. This order has been explained on the basis of the increasing second ionisation potential and electronegativity value and decreasing ionic radii in the same transition metal series. Van-uitert *et al*²⁰ from a study of several substituted β - diketone complexes in 75% dioxane-water solution (stability constant Vs electronegativity) reported an order of stability values as :



Moeller *et al*²¹ in their review, "The coordination chemistry of Yttrium and Rare earth metal ions", indicated the stability order of lanthanide complexes. Since there is a regular decrease in the crystal radii of the rare earth metal ions, simple electrostatic theory suggesting that these ions form ionic complexes predict a direct relationship between the atomic number of the rare earth metal ion and the magnitude of the formation constant. From a study of large number of rare earth complexes it has been observed that this simple relationship holds good in the light rare earth region (La-Eu) and fails in the heavy rare earth region (Tb - Lu). The trends in the formation constants data in the heavy rare earth region has been divided qualitatively into three types²¹. For the first group of ligands like glycolic acid, lactic acid, iminodiacetic acid, nitrilotriacetic acid, ethylenediaminetetraacetic acid a regular increase of formation constant with respect to $1/r$ is observed.

The second group of ligands like acetic acid, mercaptoacetic acid, methoxyacetic acid, acetylacetone and dipicolinic acid etc. form complexes for which the formation constants of heavy rare earths have nearly the same value from gadolinium to lutetium.

The third group of ligands like 2 - 2' bis ([di-(carboxy methyl) amino] diethyl ether and diethylene triamine - N, N, N', N', N'', - pentaacetic acid form complexes for which the formation constants increase with the first element beyond gadolinium and then show a slight decrease to lutetium.

For all ligands which have been studied the gadolinium complex is less stable than would be expected from simple electrostatic model. This behaviour has been called the "Gadolinium break"²¹. This has been ascribed to the change in coordination number from 8 to 9 at around Gd(III) by Yatsimirski & others²¹.

The position of yttrium with respect to the magnitude of the formation constants of its complexes is quite striking. On the basis of the simple electrostatic model, yttrium should be positioned between holmium and thulium. But it is observed that the behaviour of yttrium is erratic. The formation constant with respect to first group of ligands discussed above, yttrium lies in the heavy rare earth region, while for the second group of ligands, it lies in the light rare earth region²¹.

Recent Developments :-

Three important developments have occurred recently in solution coordination chemistry which provide a key role for stability constant determinations and related information in the further development of the field. These new processes are :-

- 1) The development of chemistry of macrocyclic and macrobicyclic ("Cryptand") complexes, with the new challenges to ligand design and synthesis, potential achievements in the study of new complexes with high stabilities and important applications.

2) Development of the new fields of bioinorganic chemistry and inorganic environmental chemistry, both of which require knowledge of the complexes formed in multicomponent systems containing many ligands and metal ions, and

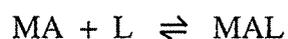
3) The development of computational methods for processing equilibrium data to provide more accurate and more rapid determination of stability constants, and the extension of the method to multidentate ligands and to systems of many metal ions and ligands that are too complex to have been investigated previously by classical methods.

MIXED LIGAND COMPLEXES :-

Mixed ligand formation has received wide spread interest in the past three decades because of the involvement of mixed chelation in many biological processes²², analytical method and industrial operations¹⁴. Importance of mixed chelation of antibiotics with the biologically active metal ions during their antibiotic activity has been emphasized in a review article by Chakrawarti²². Statistical considerations indicate favoured formation of ternary complexes²³ in many cases. Mixed ligand complexes involving unidentate ligands have been reviewed by Marcus and coworkers²⁴. Mixed ligand complexes involving polydentate ligands have been reviewed by Bhattacharya²⁵.

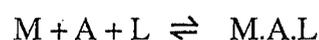
Watters and coworkers²⁶ determined the stability constants of M. ethylenediamine oxalate (M = metal) systems using P^H - metric and spectrophotometric methods. Martell and coworkers²⁷ suggested a P^H - metric method for the determination of stability constants for the system, Cu - tetramethylene diamine salicylic acid and mixed ligand chelates of U(IV)²⁸. Formation constants for the system, M-dipyridyl. L,

was reported by sigel and Griesser²⁹ considering the reaction to be of the type $M.dipy + L \rightleftharpoons M.dipy.L$. Thompson and Lorass³⁰ determined the formation constants of the complexes formed by M. aminopolycarboxylate. L systems, considering the reaction to be

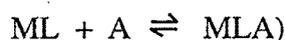
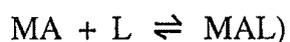
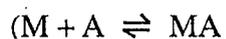


Bhattacharya and coworkers applied the Irving - Rossotti P^H - titration technique for binary complexes of the systems, M.dipyridyl.L³¹ and M.aminopolycarboxylate.L³². Here (M(dipy) or M.(aminopolycarboxylate) behaves as the metal ion and combines with the secondary ligand, mimicking binary systems.

In a system containing one metal ion M^{n+} and two bidentate ligands AH_2 and LH_2 with significant difference in the coordinating tendencies, simple complex, MA is formed²⁸, by the combination of more complexing ligand A and the metal ion. The other ligand remains unbound in the solution. However, if there is only a small difference in the complexing tendencies of the two ligands, ligand complexation occurs as shown in the following equation.



This reaction may be assumed to proceed through either of the following equilibria.



Hydrolysis of the species MA, ML and even of M leading to the formation of $MA(OH)_n$, $ML(OH)_n$ may take place. There also exists the possibilities of the formation of other species like the binary complexes, MA_2 and ML_2 . The species MA_2 and ML_2

may undergo repropotionation into MAL or MLA or may disproportionate into MA_2 and ML_2 . In the case of mixed ligand complexes involving acidic ligands, the ligand ion may still hold some protons and give rise to complex species of the type M.H.A.L, MAL.H or MAH.LH.

In the case of hexacoordinated metal ions, species present in the solution could be M, MA, MA_2 , MA_3 , ML, ML_2 , MLA, MLA_2 , MAL_2 and also the hydroxo species and complexes with protonated ligands.

In common bidentate ligands, the protons get liberated on the coordination of the ligand with the metal ion. It has been shown that MLA will be formed in preference to $MA(OH)_2$, or $ML(OH)$ if $K_{MAL}^{MA} / K_{MAOH}^{MA}$ and K_{MAOH}^{MA} are greater than 10^{10} . Formation of hydroxo complexes can be ignored in such cases. In dilute solutions, it can also be presumed that the polymeric species do not exist. In such cases, equilibria involving protonated ligands, hydroxo complexes and polymers can be ignored.

It is therefore necessary to consider all the species in solution for calculating the formation constants of ternary complexes if the two ligands A and L have similar coordinating tendencies and combine simultaneously with the metal ion. However, if the ligand A has much higher complexing tendencies than L, formation of mixed ligand complex, in a solution containing M, A and L takes place in two distinctly separate steps.



The species present in solution of such systems are MA and MAL. Only one mixed ligand formation constant K_{MAL}^{MA} characterises the second step

$$K_{MAL}^{MA} = \frac{[MAL]}{[MA][L]}$$

The necessary condition for such system is that the two ligands must combine with the metal ion in different P^H -ranges. The formation of MA should complete in the lower P^H -range and MA should be stable in the higher P^H -range where the combination of L starts. The tendency of MA to form hydroxo complex, MA(OH) should be less compared to the formation of MAL.

The values of stability constants of the ternary complexes, MAL, involving tertiary amine (where A = dipyridyl or O-phenanthroline) have been shown to be comparatively higher than values of the corresponding binary complexes, ML^{33} . An explanation to this was extended by Sigel²⁹ and Bhattacharya³¹ attributing lower negative $\Delta \log K$ or positive $\Delta \log K$ ($\Delta \log K = \log K_{MAL}^{MA} - \log K_{ML}^M$) to the special nature of tertiary diamine. These ligands are bound to the metal ion by $N \rightarrow M$ (M = metal) σ bond. Besides, there is also $M \rightarrow N \pi$ bond formation by the back donation of electrons from the metal $d\pi$ orbital to the vacant delocalized $P\pi$ orbitals over the ligand. The $d\pi - P\pi$ interaction does not allow the concentration of electrons on the metal ion to increase significantly. In other words, the positive charge on the metal ion or its electronegativity in $M(\text{dipy})^{2+}$ is almost same as in $(M.aq)^{2+}$ ion and hence $K_{M.dipy.L}^{M.dipy} \approx K_{ML}^M$. The value of $K_{M.dipy.L}^{M.dipy}$ is much higher than $K_{ML_2}^{ML}$ due to the difference in π bonding, electrostatic repulsion and charge neutralisation in the formation of $M.dipy.L$ and ML_2 .

Sigel and coworkers³⁴⁻³⁶ and also Bhattacharya and coworkers³⁷⁻³⁸ observed the difference between the values of K_{ML}^M and $K_{M.dipy.L}^{M.dipy}$ and concluded that i) the difference is more if coordination in the secondary ligand is through two nitrogen atoms (aliphatic diamine) ii) the difference is less when the secondary ligand atoms are one oxygen and one nitrogen (amino acid) and iii) it is least when the secondary ligand has two oxygen atoms (catechol, oxalic acid and salicylic acid etc.) Sigel³⁴ also observed that a

'cooperative effect' exists between the π - systems of two ligands bound to the same metal atom. Due to this cooperative effect the ternary complex is stabilised.

The steric effect factor has also observed in $M.dipy.L$ where L is aliphatic diamine³⁹. In such systems, $\Delta \log K$ is less negative as expected from π - bonding in $M-dipy$ bond. However, $\Delta \log K$ becomes more if L is N -alkyl substituted ethylenediamine. This is because of the steric hindrance due to N -alkyl group during the coordination of the diamine with $(M-dipy)^{2+}$. Martin and Coworkers⁴⁰ have also shown the influence of steric effect on the value of $\Delta \log K$.

If the primary ligand is a charged ion the K_{MAL}^{MA} value is significantly lower compared to the value of K_{ML}^M . This is due to the repulsion between the already existing charged ion (iminodiacetic acid (-2)), nitriloacetic acid (-3) and ethylenediamine tetraacetic acid (-4) and the secondary ligands L^n . Thus, the tendency of the secondary ligand L^n to combine with the MA^n ion will be less than to combine with the $M(H_2O)_n^{2+}$. This results in lowering of the value of K_{MAL}^{MA} . The values of $K_{ML}^M - K_{MAL}^{MA}$ increases with the increase of charges on L^n and A^n . For the complexes $[MAL]^n$, with different A^n the following order holds good.

$$K_{M.Hist.L}^{M.Hist} > K_{M.IMDA.L}^{M.IMDA} > K_{M.NTA.L}^{M.NTA} > K_{M.EDTA.L}^{M.EDTA}$$

This can be explained by considering that the electrostatic repulsion between the primary ligand and secondary ligand goes on increasing with increase in charge on the primary ligand. This also depends on the size of the metal ion, and the steric hindrance offered by the primary ligand to the incoming secondary ligand.

Perrin and Coworkers⁴¹ observed that the formation of ternary complex between copper - serine and ethylenediamine or histidine was favoured due to the possible

hydrogen bonding between the amino hydrogen and the oxygen of the hydroxyl group of serine.

Various other factors which influence the formation of the mixed ligand complexes are i) increased polarisation of metal ions in the fields of more than one type ii) charge neutralisation with decreased solvation and iii) asymmetry of the ligand field.

Sigel⁴² observed that the linear relationship between the basicity of the ligand L, and the value of K_{MAL}^{MA} for complexes of the type MAL existed in the same way as in binary complexes,

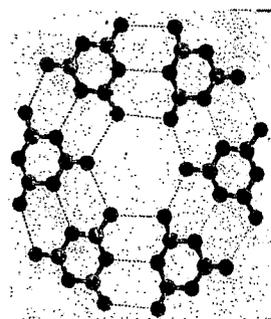
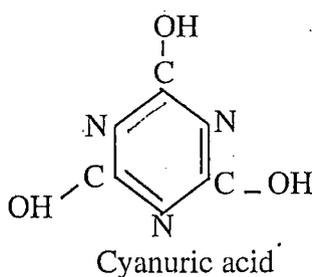
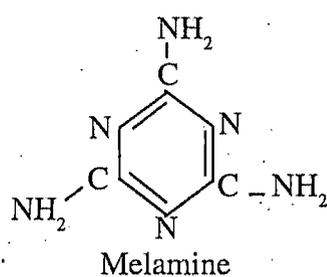
Interest in multidentate acyclic / macrocyclic compounds is continually increasing⁴³⁻⁵² because of their unique properties and use in the synthesis of polynuclear metal complexes which mimic metallobisites, magnetically concentrated systems and molecules exhibiting catalytic activity. Sahkir et al have reported the synthesis of azamacrocyclic complexes⁵³⁻⁵⁴. The macrocyclic complexes may bear different functional groups such as azomethines, amides, polyamides, hydroxyketones and pyridyl methyl groups. Goeta⁵⁵ et al have reported the elegant synthesis of Cu(II) complexes of the isomeric tetra azamacrocyclic ligands I, II - and 1, 8-bis (2 pyridyl methyl) - 1, 4, 8, 11 tetra azocyclotetra decane and examined their crystal structure. Novel applications of macrocyclic rings as catalysts⁵⁵⁻⁵⁷, as models for metallobiosites⁵⁸⁻⁶⁰ and the study of cation-cation interaction over short interatomic distances⁶¹⁻⁶² have led to the synthesis of new macrocycles⁶³.

Supramolecular structural ligands

Supramolecular chemistry based on the self-assembly of molecular units has provided a powerful means for designing molecular systems with novel structures and properties (Haiduc). The molecular units are held together in the self-assembly by weak forces such as hydrogen bonding and Vander Waals interaction (C.N.R. Rao). Some

supramolecular copper complexes possess great potential as models for bioinorganic system⁶⁶ as catalyst⁶⁷ and as molecular magnets⁶⁸.

A supramolecular rosette structure of hydrogen bonded adduct of cyanuric acid and melamine (From Ranganathan Pedireddi and Rao; *J. Am. Chem. Soc.* 121, 1752, 1999) is mentioned below.



The Fe-Mo cofactor of the nitrogenase enzyme mimics the topology found in the native systems such as multi-copper oxidases⁶⁹. The method employed in the synthesis of polymetallic coordination compounds are the self assembly of metal centres and ligand species, both coordination and bridging into polymetallic arrays⁷⁰⁻⁷¹ or the direct incorporation of metal ions into preformed polydentate ligands.

Rotaxanes are molecular motors which are molecular assemblies in which some part can be set in motion by an external signal such as proton, electron or photon transfer while other parts remain motionless. The energy introduced by external stimulation allows the system to undergo some kind of continuous motion. The artificial motors intensively explored are the transition metal containing systems⁷²⁻⁷⁵. The synthesis of such a copper complex rotaxane has been presented by Kern et al⁷⁶. On oxidation or reduction the system can be set to equilibrium. The ligands employed include catenanes and rotaxanes where the constituents are mechanically linked together. Catenanes have interlocked macrocycles. Rotaxanes are found to be a macrocycle encircling a single dumbbell component having a large blocking group at each end of linear end. In such a molecule rotation or translation can be reversibly manipulated. The gliding of one ring

with the other in a two copper catenane could be electronically or photochemically triggered⁷⁷. Well arranged metal containing macrocycles have unusual structures⁷⁸ with special functional properties such as luminescence⁷⁹, redox activity⁸⁰ and magnetism⁸¹.

The coordination behaviour of amide based ligands is very interesting⁸²⁻⁸⁵. In some Cu^{+2} complexes with amide based ligand, the amide oxygen atoms coordinate the central metal ion in acidic media, while in basic media, the deprotonated amide nitrogen atoms coordinate the metal ion. This type of structural conversion is also studied for a 13-membered dioxotetra azamacrocycle but it does not occur in smaller ring macrocycle⁸⁶. Graham et al⁸⁷ have reported the synthesis of some new macrocycles.

The sub-commission, V.6 on equilibrium data of the analytical division of IUPAC has published all the reported stability constant data in different volumes. These volumes have been written by some of the more active workers in the field such as Schwarzenbach, Sillen, Martell, Hogfeldt and Perrin⁸⁸⁻⁹³. Publications for equilibrium constant data in different series are also available in different volumes of the Journal of Pure and Applied Chemistry⁹⁴.

Lanthanides :

The co-ordination chemistry of lanthanides attracts interest both as a field of study in its own right⁹⁵⁻⁹⁷ and for its wide range of applications in various fields such as nuclear magnetic resonance imaging⁹⁸⁻¹⁰⁷, synthetic organic chemistry¹⁰⁸⁻¹⁰⁹, biochemistry¹¹⁰⁻¹¹², solvent extraction¹¹³⁻¹¹⁴, industrial applications¹¹⁵⁻¹¹⁷, radiopharmaceuticals¹¹⁸⁻¹¹⁹ and lanthanide ion selective reagents etc.¹²⁰⁻¹²².

Lanthanum ($z = 57$) and the next fourteen elements ($z = 58 - 71$) which follow it are called lanthanides or lanthanons. These fifteen elements closely resemble one another and they have been allotted single position in the periodic table on account of similarity in their electronic configuration and chemical properties.

The characteristic oxidation state of the lanthanide elements is +3. Lanthanum shows +3 oxidation state by the loss of two 6s and one 5d electron thereby attaining the stable electronic configuration of Xenon. The +2 and +4 oxidation states are shown by those elements which by doing so attain the stable $4f^0$, $4f^7$ and $4f^{14}$ configurations. For example cerium and terbium attain $4f^0$ and $4f^7$ configuration respectively when they go into +4 oxidation state. Similarly, europium and ytterbium acquire $4f^7$ and $4f^{14}$ configurations respectively when they change into +2 oxidation state¹²³. This argument becomes less convincing when we note that Sm and Tm give M^{2+} having f^6 and f^{13} configuration whereas Pr and Nd give M^{+4} ions in aqueous solution have a tendency to change readily into M^{+3} ions while Ce^{+4} is stable (kinetically) in water. Ce^{+4} is a very strong oxidising agent in aqueous solution ($E^0 = 1.74$ V) and is used as a volumetric standard in redox titrations. Some of its salts find application in organic chemistry as oxidizing agents¹²⁴. Although the f^0 , f^7 and f^{14} concept throws some light about the oxidation states of the lanthanide ions, there are other thermodynamic and kinetic factors which are of equal or greater importance in determining the stability of oxidation states¹²⁵ of lanthanide ions such as Nd^{2+} , Ce^{+2} and Pr^{+2} .

Lanthanide Contraction :

The radii of M^{3+} ions of lanthanides decreases from lanthanum to lutetium. As we proceed from La to Lu, the nuclear charge and the number of 4f electrons increase by one at each step. The shielding of one 4f electron by another is very imperfect owing to the shapes of the orbitals, so that at each increase the effective nuclear charge experienced by each 4f electron increases, thus causing a reduction in size of the entire $4f^n$ shell. The accumulation of these successive contractions is the total lanthanide contraction¹²⁵.

Coordination number :

In lanthanide compounds (both ionic crystals and in complexes) coordination number exceeding 6 are the general rule rather than the exception. Lanthanide compounds showing coordination number of 6 has been established to be small. Many lanthanide complexes are known to have solvent molecules bound to the metal leading to the common coordination number 7, 8 and 9. In solution the lighter members, La^{+3} - Nd^{+3} have 9-coordination where as the members from Gd^{+3} - Lu^{3+} have 8-coordination. However a smaller ion Gd^{+3} - Lu^{+3} due to their greater polarising power may lead to a greater solvated radius and hence promote greater co-ordination number¹²⁵. Recently Iftrkhar¹²⁶⁻¹²⁸ etal have prepared and characterised the complexes of the type $\text{Ln}(\text{Phen})_3(\text{SCN})_3$ where $\text{Ln} = \text{La}, \text{Pr}, \text{Nd}, \text{Sm}$ and Eu and $\text{Ln}(\text{Phen})_3(\text{SCN})_3 \cdot \text{H}_2\text{O}$ ($\text{Phen} = 1, 10$ Phenanthroline) where $\text{Ln} = \text{Dy}, \text{Ho}, \text{Er}$ and Yb . According to their observation the lighter lanthanides have 9-coordination and the heavier lanthanides have 10-coordination. $[\text{Ce}(\text{NO}_3)_6]^{3-}$ indicates 12-coordination for cerium.

Lanthanide (III) Complexes :

Lanthanide ions, inspite of high charge (+3) have low charge density because of their large size. Therefore they cannot cause much polarisation and consequently, they have a weak tendency to form complexes. Their complexes with unidentate ligands are few. However, their complexes with chelating ligands are fairly common. The lanthanides do not form complexes with π -bonding ligands such as CO, NO and CNR etc. The tendency to form complexes and their stability increases with increasing atomic number.

Lanthanides behaves as typical hard acids. The co-ordination chemistry of lanthanides was limited to strongly chelating ligands with oxygen as donor atoms. The 4f electrons of lanthanides are too well shielded to interact. Consequently each lanthanide ion is effectively an inert gas type ion like those of alkaline earth metals that attracts

ligands only by overall electrostatic forces. In presence of water, complexes with nitrogen, sulphur and halogen donors are comparatively less stable.

The interaction of lanthanides with chelating agents, H_4 EDTA (ethylene diamine tetra acetic acid), H_3 (HEDTA)(N-hydroxyethylene diamine triacetic acid), H_4 CDTA (1,2-diamino cyclohexane tetra acetic acid) have been explored extensively¹²⁹⁻¹³¹. Iftikhar *et al*¹²⁷⁻¹²⁸ have reported the preparation and characterisation of mixed ligand complexes of trivalent lanthanide ions with β -diketones and heterocyclic amines. Allen *et al*¹³² have prepared 4-coordinated complexes of lanthanides containing benzophenone as one of the ligands. The complexes have the composition $[LnL_3(Ph_2CO)]$ where $Ln = La, Eu, Tb, Yb$ or Y and $L = N(SiMe_3)_3$.

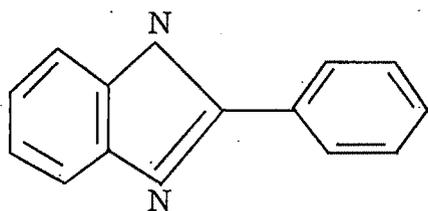
Schiff bases offer a versatile and flexible series of ligands capable of binding f-metal ions and to give the resulting complexes such properties as to make them suitable for theoretical studies and or practical applications¹³³⁻¹³⁶.

Macrocyclic and macroacyclic schiff bases are currently under intense scrutiny as contrast media in magnetic resonance imaging¹³⁷, as cleaving agent of RNA¹³⁸, and as components in molecular devices based on photochemical processes¹³⁹ or magnetic interactions¹⁴⁰. Recently, new lanthanide complexes $[Ln(L)(dmf)_2]$ with a Schiff base ligand, H_3L have been prepared by condensation of 2,6 - diformyl - 4 - chlorophenol and tris - (2 - aminoethyl) amine in the presence of $LnCl_3 \cdot nH_2O$ ($Ln = La, Gd$ and Dy) and NEt_3 ¹⁴¹.

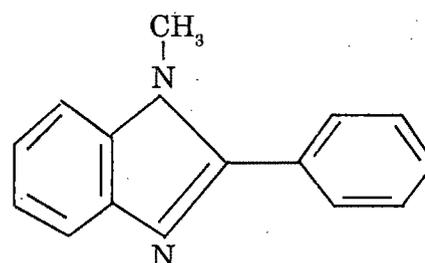
A large number of Ln (III) - carboxylates derived from aliphatic carboxylic acids are known¹⁴²⁻¹⁴³. Trivalent lanthanide complexes with anionic ligands containing oxygen as donor¹⁴⁴⁻¹⁴⁵ atoms and the complexes with synthetic ionophores stabilised by macrocyclic effect¹⁴⁶⁻¹⁴⁷ have been studied.

4-Acyl-bis-pyrazolones in which there are four oxygen donor atoms available for complexation are good chelating agents for lanthanides. They form mononuclear, polynuclear and heteronuclear complexes under differing conditions. Some lanthanide ions when combined with 4-acyl-bis-pyrazolone exhibit excellent fluorescence¹⁴⁸.

Imidazole and its derivatives are biologically significant. The preparation and characterization of lanthanide thiocyanate complexes of 2 - (2' - pyridyl) benzimidazole and 1 - methyl - 2 (2'-pyridyl) benzimidazole have been reported by Thakur *et al*¹⁴⁹.

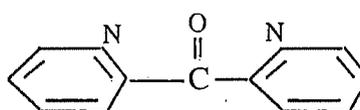


2 - (2' - pyridyl) benzimidazole



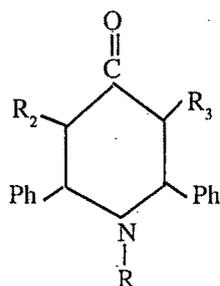
N - methyl - 2 - (2'-pyridyl) benzimidazole

Di - 2 - pyridyl Ketone a ligand having three potential donor sites namely two nitrogens of the pyridine rings and oxygen of the ketocarbonyl group has been used to form



complexes with lanthanide perchlorates¹⁵⁰. Lanthanides being hard acids would be expected to show preference to bonding via the ketocarbonyl oxygen. But the i.r spectral studies showed that the carbonyl group is not coordinated and only the ring nitrogens are coordinated. Studies on Samarium(III) complexes containing piperidine - 4 - ones have been made recently by selvraj *et al*¹⁵¹. They have also reported that the ligand coordinates the lanthanide ion through ring nitrogen and not through the carbonyl oxygen

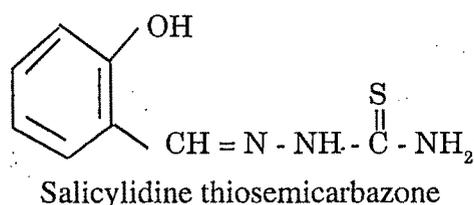
with the formula of the complexes as $[\text{Sm}(\text{L})(\text{NO}_3)_2(\text{H}_2\text{O})_2]\text{NO}_3 \cdot \text{H}_2\text{O}$



where L - Substituted piperidine - 4 - one

There have been limited efforts to study the coordination compounds of nitrogen and sulphur donor ligands with lanthanides¹⁵²⁻¹⁵³. The cause for this has been ascribed to the lower electronegativity and greater atomic radius of sulphur atom in comparison to oxygen. However, it has been shown that the synthesis of nitrogen and sulphur donor complexes of lanthanides may be effected either in the complete absence of solvent or in an anhydrous solvent of reduced polarity and donor strength¹⁵⁴⁻¹⁵⁵.

Thiosemicarbazones are among the most widely studied sulphur donor ligands. The lanthanide complexes containing salicylidine thiosemicarbazone (AH_2), 2-hydroxy-1-naphthalidine thiosemicarbazone (BH_2) and 2-hydroxy-1-acetophenone imine thiosemicarbazone (CH_2) have been prepared in the presence of anhydrous solvents¹⁵⁶. These thiosemicarbazones act as doubly negatively charged tridentate ligands by losing the protons from both the phenolic and mercapto groups of the tautomeric form. Recently, 3,4 - methylene dioxy benzaldehyde thiosemicarbazone (LH) has been used as a ligand in the preparation of lanthanide nitrate complexes¹⁵⁷. The spectral study of these complexes showed that two thiosemicarbazone ligands and two nitrate groups were bound to the lanthanide ion in a bidentate fashion.



et al
Agarwal *et al*¹⁵⁷ synthesized some lanthanide (III) complexes derived from 4 - [N - (4 - methoxy benzylidene) amino] antipyrine thiosemicarbazone and characterised them by different physico chemical methods. The general composition of the complex has been shown to be Ln (MBAA PTS) (NO₃)₃ (Where Ln = La, Pr, Nd, Sm, Gd, Tb, Dy & Ho)

Dithiocarbonates have also been used in the preparation of lanthanide complexes. These complexes have been prepared in an inert atmosphere using anhydrous lanthanide salts¹⁵⁸⁻¹⁶⁰.

In recent years, there has been considerable interest in lanthanide complexes containing macrocyclic ligands. macrocyclic polyethers so called crown ethers have been used for the preparation of lanthanide complexes¹⁶¹⁻¹⁶⁵. The lanthanide complexes with macrocyclic polyoxo and polyaza-polycarboxylates have also been studied¹⁶⁶⁻¹⁷⁰.

Aim and scope of the present investigation

The coordinating ability of 2-hydroxy-2-methyl propanoic acid towards various metal ions is well known. But the studies on its mixed ligand complexes involving EDTA as one of the ligands is conspicuously missing. The steric and inductive effect of the CH₃ - group of the acid on the values of stability constants have been discussed.

Similarly, any systematic study on the coordinating tendency of D(+) saccharic acid has been limited despite the advantages that it may offer for coordination with metal ions due to the availability of six potential coordinating sites (four-hydroxylic and two carboxylic acid groups) in its molecular structure. More over there has been no study on its mixed ligand complexes involving EDTA as one of the ligands.

In view of this the present investigation aims at potentiometric determination of formation constants for the M-L binary and MAL ternary complexes where M = Y³⁺,

La³⁺, Ce³⁺, Pr³⁺, Nd³⁺, Sm³⁺, Eu³⁺, Gd³⁺, Tb³⁺, Dy³⁺, Er³⁺ and Yb³⁺, Mn²⁺, Ni²⁺, Co²⁺, Cu²⁺, and Zn²⁺.

L = 2-Hydroxy - 2 methyl propanoic acid (HPa)

= D(+) - saccharic acid (H₂Sa)

and A = disodium salt of ethylenediamine tetraacetic acid (Na₂H₂EDTA)

by P^H - titration technique at 25^oc and 0.1 M ionic strength (NaClO₄) by Irving - Rossotti

P^H - titration technique as adopted by Bhattacharya and Chidambaram³¹.

The systems M-EDTA-Pa, M-Sa and M-EDTA-Sa have been studied for the first time and therefore the values of stability constants for the above systems are completely new. The stability constants of ML-binary systems have been determined by two separate methods such as Irving-Rossotti and Patnaik and Coworker method. The values obtained by two methods agree well each other (Table - A and B).

The values of stability constants for the systems M-EDTA-Pa an M-EDTA-Sa have been determined by a modified Irving-Rossotti method as followed by Bhattacharya etal³¹. In few cases the values have been evaluated by the method as followed by Thompson and Lorass³⁰ and the values obtained by these two methods are found to agree well with each other. (Table - C and D)