Chapter I

Origin of Present Work & Literature Survey
1.1 Introduction:

The field of coordination chemistry is passing through such a rapid advance that many of the ideas and theories of the past two decades have been modified or discarded. Coordination chemistry have been grown to most active research field of inorganic chemistry and the complex formation reactions are applied as ‘key’ in studying the analytical\(^{1,3}\), bioinorganic\(^{4,5}\), clinical\(^{6-8}\) and biochemical\(^{9,10}\) aspects.

The importance of mixed-ligand chelates in various field of human interest has led to large number of reports on the studies of formation and stabilities\(^ {11-16}\). The recent concept of free radicals\(^ {17}\), antioxidants\(^ {18}\) and metal toxicity\(^ {19-21}\) involves the coordination properties of trace element metal ions in the body. Now a days a quick and precise detection of toxic metals is performed by IHMT\(^ {22}\) test which involves chelate formation.

Reactions of the metallo-enzyme have been shown to involve the formation of ternary complexes with biologically important molecules which provides simple model for understanding more complicated biological reactions\(^ {23-24}\). Chemical aspects of therapeutics have shown that some enzymes are activated by metal ion\(^ {25}\). Many complexes and complex forming compounds are known to be used as drug\(^ {26-27}\). Removal of undesirable metal ion from the body and removal of coagulated proteins by chelate therapy\(^ {28}\) involves equilibria of metal ion with proteins, enzymes and microcyclic ligands\(^ {29-31}\). British anti-lewisite is 2,3-di-mercapto propanol which is used in clinical chemistry to test the Hg, As, Sb, Bi, Au contamination. Titan yellow, magnon, 8-HQSA is used for estimation of Cerium, Magnesium. TESSOL is used in testing the heavy metal contamination due to paints, disposable metal containers, tinned food which is based on formation of coloured complexes\(^ {32,33}\). Use of 2,2-dimethyl thiazolede-4-carboxylic acid is well known for treatment of Wilson disease.
Chelation decreases the polarity of the metal ion which further leads to enhancement of lipophilicity of the complex. Since the micro-organism cells are surrounded by membrane which favours the passage of lipid soluble material on complexation results in increasing the penetration power of complex through the membrane and deactivates the active enzyme sites of the micro-organisms\textsuperscript{34-35}.

The mixed-ligand complexes have wide application in micro-electronic industry, Chemical vapour deposition of metals and metal-ion catalyzed reactions\textsuperscript{36,37}, in the study of toxic effect of metals, drug designing\textsuperscript{38}.

The impact of metal ion in life process of living systems and the effect on health and well beings has become increasingly known during last fifty years leading to fast development in bioinorganic chemistry. Now a days the inorganic constituent of biological systems is receiving increasing attention.

pH-dependent functioning of haemoglobin and photochemical excitation in magnesium porphyrin complex is well known. The application mainly involves structural aspects and knowledge of equilibria for the complex formation reaction\textsuperscript{39}. The knowledge of formation constants\textsuperscript{40}, pH of formation\textsuperscript{41}, stability\textsuperscript{42}. disproportion are very essential from the point of view of studying the application of complexes in any field.

1.2 Complex Formation Equilibria & Dependence of Stabilities of Mixed-Ligand Complexes

The coordination of different ligands to the same metal ion in almost overlapping steps indicating a slight difference in the affinities of the ligands for the metal ion:
The mixed-ligand complex formation may also result by the interaction of the initially formed different binary species of the metal ion with different ligand molecules at higher pH.

During the mixed systems, where no mixed-ligand complex is formed, the following possibilities may arise:

a) The metal ion may form a binary complex with one of the ligands leaving the other ligands in uncoordinated form.

b) Two or three different binary species of the metal ion with different ligands individually may result instead of a mixed-ligand species.

c) Formation of only one ternary complex with any of the two ligands leaving the third one in uncomplexed form.

During quaternary complex formation, the secondary and tertiary ligands will involve themselves in the coordination process, provided there is enough space available in the electron shell of the central metal ion for the accommodation of electron pairs from the ligands and also if the metal ion radius is large enough to allow
attachment of the additional ligands (secondary and tertiary ones). However, mixed-ligand complex formation mainly depends upon the following factors:

i) Electronic structure of the metal ion.

ii) Ionic potential of the metal ion.

iii) Availability of the vacant d or f-orbitals on the central metal ion.

iv) Ionic radius of the central metal ion.

v) Availability of the bonding electrons in the ligand molecules.

vi) Basicities and the dentateness of the ligands, and

vii) Number of fused rings present in the resulting chelates.

Apart from this, combinations of ligands in hetero-ligand chelate formation is also important. Ligand-Ligand interaction reduces the repulsive forces due to distribution of electron density in molecular orbitals of either ligand-ligand or even metal-ligand. Literature survey reveals the contribution of many other factors in stabilizing the mixed-ligand complexes.

A new approach of astatistical parameters ($\Delta \log K$, $\Delta\Delta \log K$) and percentage relative astatistical stabilisation (% RAS) is helpful in explaining the extra stabilities of hetero-ligand chelates which may be described as contribution of astatistical factors and total effects.

Further, the soft-soft or hard-hard acid base interaction favours the greater stability of the resulting species.

The relative stabilization of the mixed-ligand species in comparison to that of the parent binary species depends upon the following factors:

1. **Extra – molecular effect:**

   This effect is caused by the nature of solvent, ionic strength, pH and temperature of the medium.


2. Intra – molecular effect or statistical effect:

This effect involves the nature of bonding between the ligands of different types or asymmetry of the ligand field.

The best characterization of complexes formed in solution equilibria, can be made by evaluating their stability constants and other thermodynamic parameters. In fact the knowledge of stability constants rationalizes our understanding towards the behaviour of metal-complexes in solution.

The determination of overall equilibrium constant (βₙ) for a generalized equilibrium may be expressed as:

\[
M + iL + jL' \rightleftharpoons ML_iL'j
\]

\[
βₙ = \frac{[ML_iL']}{[M][L][L']}
\]

(for ternary species)

and

\[
M + iL + jL' + kL'' \rightleftharpoons ML_iL'_jL'\kappa
\]

\[
βₙ = \frac{[ML_iL'_jL'\kappa]}{[M][L][L'][L'']}
\]

(for quaternary species)

where M is the central metal ion (charge omitted), L, L’ and L’’ are the ligands and i, j and k are indices. The sum of indices, n = (i + j) or (i + j + k), which is termed as co-ordination level and should not exceed the co-ordination number N.(N-n) coordination sites, is left vacant are then occupied by the polar solvent molecules.

The following two approaches may be applied for the determination of the stability of mixed-ligand complexes:

1. In the first approach the different ligands are added, separated over a wide range of concentration and data are obtained as a function of two or three variables of free
ligand concentrations. Thus the value of overall formation constant ($\beta_n$) for the complexes depends on the free metal ion and free ligand concentrations.

2. According to the second approach the ligand concentration is selected so as to keep the coordination $N$ at the constant values of $n = i + j$ or $n = (i + j + k)$ and the replacement reaction of the type,

$$ML_{(i+p)}\, \text{L}', \, \, \, j+qL' \rightleftharpoons ML\, \text{L}', \, j+qL$$

is studied as a function of the ratio of free ligand concentration, $R = L/L'$. Assuming that there is no difference in the energies of reactants and products in the reaction equilibrium of the type,

$$ML_4 + ML_4' \rightleftharpoons 2ML_2L_2'$$

the value of equilibrium constant,

$$K_{ML_1L_1'} = \frac{[ML_2L_2']^2}{[ML_4][ML_4']}$$

can also be determined statistically and denoted by $K_{stat}$.

The stabilization constant ($K_{stab}$), a measure of stabilizing effect in the formation of mixed-ligand complex is the ratio of the observed equilibrium constant ($K_{ML_1L_1'}$) to the statistically calculated one ($K_{stat}$). The positive and negative values of log $K_{stab}$ indicates the formation and non-formation of hetero-ligand species respectively.

Bjerrum$^{43}$ classified the factors, affecting the formation of mixed-ligand complexes depending on the following effects:

(a) Statistical effect

(b) Ligand effect
The ligand effects are further sub-divided as:

(i) Electrostatic effect

(ii) Rest effect.

Accordingly $K_{MLL'}$ may be related as:

$$\log K_{MLL'} = \log K_{\text{stat.}} + \log K_{EL} + \log K_R.$$ 

If the complex formation proceeds statistically, then

$$K_{\text{stat.}} = K_{MLL'}$$

$K_{EL}$ = the stabilization of the complex due to the electrostatic effect and $K_R$ = additional stabilization due to the rest effect.

### 1.3 Importance of Stability Complex Equilibria:

In application of coordination compounds the first and foremost requirement is the knowledge of thermal and kinetic stability of the chelates. It is in principle to calculate the equilibrium concentration of each of the species present under known set of experimental conditions. The rapidity with which the stability constant determination have gained importance can be judged from numerous reviews published since 1950 and from proceedings of series of international conferences. An immense number of data is tabulated in two volumes of “Stability Constant” published by Chemical Society, London (1964) and in book of “Instability Constant of Complex Compound” by “Yatsimirskii and Vasil’ev”. The determination of stability constant has led to important discoveries, structures, reactivity and application of complex compound. An enormous amount of information concerning complex equilibria has been available along with thousands of papers and excellent reviews have been appeared. The stability constant of ternary complex are of great interest for
understanding the role of metal ion and the nature of two ligands in determining the
stability of ternary complex\textsuperscript{47}.

The study of formation, stabilities and reactivities of ternary complex\textsuperscript{48} is an
active and challenging field of research even today.

1.4 Evidences for Complex Formation in Solution:

pH-metric studies provides the simplest and accurate method for detecting the
formation of complexes between metal ion and the acidic and basic ligand group in
solutions\textsuperscript{49}. Metal complexes may be formed by displacing one or more usually weak
acidic proton of ligand by metal ion\textsuperscript{50}.

The absence of precipitation by usual reagent was an indication of complex
formation by Ryabchikov and Torent'eva\textsuperscript{51}. Turner and Anderson\textsuperscript{52} found that
absorption spectra of solution containing metal ion and sulphosalicylic acid varies
considerably with pH due to complexation. Jaques\textsuperscript{53} was first to point out that
stoichiometric stability constant and formation of complexes present in solutions can be
determined from series of electrode potential measurement.

Increase in pH of hydrolysis of metal in presence of complexing agent in
solution is also evidence for complex formation in solution\textsuperscript{54,55}.

1.5 Mixed-Ligand Complexes of Transition Metal / Lanthanides:

Mixed-ligand complexes of transition metal have gained lot of importance
during recent past\textsuperscript{56,57} due to their wide applicability in many branches of pure and
applied chemistry. The tremendous interest in studying Lanthanides with various
complexing agents have lead to rapid accumulation of information regarding stepwise
and simultaneous formation studies in solution. The Lanthanides are studied widely
with respect to the analytical utility of the ions and mixed-ligand chelates in the field of analytical chemistry. The trivalent Lanthanides have been chosen for the present study are very important elements in analytical chemistry. Optical purity of indacrinone by PMR spectroscopy using chiral Lanthanide chelates, sequential determination of oligo-peptides by variation of pH with and without Lanthanide salt have been attempted. Lanthanide probe spectroscopy for determination of aminoglycoside, antibiotics have been attempted. Neomycin, streptomycin, gentamycin, tobramycin, amikacin, kanamycin have been attempted by using Lanthanides.

Base specific and enantioselective studies for the DNA binding and Fe(II) mixed-ligand chelates containing 1,10 phenonthroline and dipyrido phenazine indicates the electrostatic interaction of binding. Lanthanides have been used to improve colours of sulphide, oxalate, precursor in studying some ternary and quaternary system based on γCe₂S₃ using oxalate complexes. Complex flame spectra of Rare earth and closely related elements have been developed by use of organic extract of chelate and is applied for the determination of Rare earth group. Spectral simplification in PMR spectroscopy is done by chiral and achiral Lanthanide complexes.

Simultaneous determination of ciproflaxacin and tetracycline in biological fluids is based on dual Lanthanide sensitised luminescence. Terbium and Europium have been used as a dry reagent. Mixed-ligand complexes of Platinum(II) with methionine and 2,4-disubstituted pyrimidines and other amino acids have been attempted by Badar Taqui Khan et al. Ligand substitution and formation of mixed-ligand complexes have been studied. Ligand containing sulphur as donor atom and diamino carboxylic acids have been studied to support the chelation through nitrogen atom of amino acids. Mixed solvent mixed-ligand chelates with sulphur containing
molecules have been reported. Lanthanides have been extensively studied for their catalytic activity on hydrogenation of chloronitro benzene.

Sigel et al. reported that the stability of ternary complex (MLL') is more than that of binary complex, because of the association of second ligand to ML is more facile than that to the aquocomplexes and this may be due to the existence of interligand π-interaction. The dependence of stabilities of mixed-ligand complexes on the nature of ligand has been thoroughly investigated. The nature of metal-ligand bond (σ or π), mutual polarisibility of the central metal ion and the ligand also plays a significant role in formation of mixed-ligand complexes. The π-bonding promotes the mixed-ligand complex formation because the destabilization caused by ligand–ligand repulsion is smaller in biligand or triligand complexes as compared to parent binary ones, and secondly by lowering the electron density on central metal ion due to the process of bonding interaction (back donation). In addition to the above factors chelate formation, conjugate effect and geometry of the complexes including dentateness of ligands also plays an important role in mixed-ligand complex formations. Further the soft-soft and hard–hard acid-base interactions favours the greater stability of the resulting species. The relative stabilization of mixed-ligand species in comparison to that of parent binary species depends on the factors like extra molecular effect caused by nature of solvent, ionic strength, pH and temperature of the medium and intramolecular effect, due to nature of the bonding between the ligands of different types or asymmetry of the ligand field.

Mercus introduced the polarized ion model to explain extrastabilisation of ternary complexes as compared to binary ones.

Electrostatic effect, numbers and size of chelate rings formed are of equal importance in determining the stability of mixed-ligand complexes.
The complex formation of higher order often shows ligand dependence\textsuperscript{91}. Complex formation always occurs with replacement of coordinated water molecule to the central metal ion\textsuperscript{92}. The presence of ligand other than water molecule in inner coordination sphere affects the lability of remaining water molecule\textsuperscript{93,94}. The degree of enhancement of water loss is especially great for those ligands containing delocalized \(\pi\)-orbitals or ligand where interligand \(\pi\)-interaction occurs\textsuperscript{95} and thus reflecting on the more positive entropy changes associated with formation of mixed-ligand complexes\textsuperscript{96}.

It is obvious that aliphatic, aromatic ligands coordinating through oxygen atoms gives the complexes of higher stabilities as compared to those formed by aliphatic, aromatic ligand coordinating through O-N atoms\textsuperscript{97-101}. The higher stabilities of ternary complexes (MAL), where A=Amino-polycarboxylic acid and L = Oxygen donor, reflects on the tendency of Rare earth ions to expand the coordination number\textsuperscript{102-105} originally suggested by Andergg\textsuperscript{106} et al.

It is space consuming and also out of context to cite all literature pertaining to the studies of mixed-ligand complexes, hence the attempt have been made in the following few pages to cite the literature only in context of the present work.

1.6 Literature Survey:

For the systematic and informative study the literature is cited below under different headings on only the mixed-ligand complexes.

A] Mixed-Ligand Complexes (MLL') where L and L' are oxygen donors:

The formation of mixed-ligand complexes by a metal ion with two competing ligands have attracted the interest\textsuperscript{107}. Among the oxygen donors the carboxylic
(-COOH) and phenolic (-OH) group offers a potential side for coordination.

The equilibrium studies on mixed-ligand complex formation of Nd(III) with carboxymethylsuccinic acid and simple, substituted dicarboxylic acid has been reported pH-metrically \(^{108}\). Jahagirdar\(^ {109} \) et al reported the mixed-ligand complex formation of \( \text{UO}_2^{2+} \) and \( \text{VO}^{2+} \) with catechol as primary and adipic, itaconic, phthalic, sulphosalicylic acids as secondary ligands. The effect on the stabilities of mixed-ligand complexes formed when both the donors are dicarboxylic acids, one dicarboxylic acid and other phenolic acid, both phenolic acid, have been discussed by investigating the mixed-ligand complex formation with succinic, malonic, itaconic sulphosalicylic acid potentiometrically by Mali\(^ {110} \) et al. Solution studies on ternary complex formation involving dicarboxylic acid and glutamic acid as one of the ligands have been reported\(^ {111} \). Biligand complex formation of Zn with citric, malonic, oxalic, tartaric, malic, succinic acid have been carried out\(^ {112} \). Stability constants of some metal-phthalate with fumaric, maleic and salicylic acid has been determined\(^ {113} \). Ternary complex formation of some metal ions with simple and substituted dicarboxylic acids have been thoroughly investigated by Santappa\(^ {114,115} \) and co-workers. Complexing tendencies of aliphatic dicarboxylic acids with 1:1 metal-methylmalonic acid, characterization of their bonding modes have been studied by Shelke\(^ {116} \).

Agrawal\(^ {117} \) et al has reported the 1:1:1 complexes of \( \text{Cd}^{2+} \) with gluconic, itaconic and citraconic acids polarographically. Ternary complexes of dicarboxylic acids and some aliphatic hydroxy acids with \( \text{Be}^{(II)} \) has been studied\(^ {118,119} \). Lingaiah\(^ {120} \) and co-workers reported the complexes of Rare earth ions with phthalic, maleic, fumaric, succinic, salicylic acid and pyrocatechol. Mixed-ligand complexes of Dioxouranium\(^{(IV)} \)\(^ {121} \) with aliphatic and aromatic oxygen donors has been reported by
same workers. Bhobe et al reported the mixed-ligand complexes involving oxalic, phthalic acid as oxygen donor by polarographic technique.

The extra stabilized nature of ternary complexes due to enhancement in the ligand field strength, effective transmission of electronic effect due to presence of double bond in ligand structure and strengthening of olefinic linkage with metal ion has been studied by many workers. Adducts of transition metals with carboxylates of unsaturated acid as one of the ligands has been reported extensively. The enhanced stability of Cd(II)-itaconate-citraconate over Cd(II)-gluconate-citraconate has been investigated polarographically and has been interpreted in terms of π-bonding between metal ion and ligands. The preferential formation of ternary complexes than binary ones between Nd(III) ions and oxygen donor ligands have been explained on the basis of stabilization parameter (Δ log K) and basicity. Kuznik investigated the formation of Zn-oxalate-glycollate / lactate complexes by solubility method.

Studies on effect of structural changes of ligands on the stability of mixed-ligand complexes shows that O-O coordination is favourable to the parent binary complexes.

B] Mixed–Ligand Complexes (MLL’) where L=Aminopolycarboxylate ion and L’ is oxygen donor.

a) L’-as Aliphatic Oxygen Donor:

Ternary complexes of Rare earth ions with several multidentate complexones and number of bidentate ligands have been studied spectrophotometrically by Poluektov et al. Mixed-ligand chelates of U(IV) with NTA as primary ligand and
some hydroxy acids as secondary ligands have been reported by Carey and Martell. pH-metric investigations on 1:1:1 complex formation of Yttrium(III) with NTA, HEDTA, EDTA as primary ligands and acetylacetone, kojic acid as secondary ligands has been reported by Munshi et al. Garg et al have reported the mixed-ligand complex formation of Lanthanides with β-isopropyl tropolone in solution. Potentiometric and spectrophotometric studies of mixed-ligand complexes of some Rare earth ions including Ho(III) with some complexones, acetylacetone β-isopropyltropolone and kojic acid has been carried out by Shetty et al. La(III) / Nd(III) / Ho(III) / Er(III) – EDTA – lactic acid / CO3^2- complexes have been reported. Abou Ali Samir et al carried out the pH–metric investigations on Lanthanide(III)- EDTA- malic acid complex formation. Martell and Intorre reported mixed-ligand complex forming tendencies of Zr(IV) with HEDTA and some bidentate hydroxy acids. Dobrynina investigated the formation of Rare earth-EDTA-tartaric acid complexes. Potentiometric investigations on mixed-ligand complex formation between La(III), Pr(III), Nd(III) with HEDTA, DTPA and some dicarboxylic acids has been reported by Sharma et al. Rare earth-DTPA-ketoglutarate formation in solution has been reported. Polarographic investigation on Cd(III)-DTPA-tartaric acid complex formation has been carried out by Mahajani et al.

A quantitative approach to stability co-relation of some Lanthanide–EDTA-aliphatic hydroxy acid complexes have been attempted by Saxena et al. Entropy stabilized nature of the 1:1:1 complexes of Lanthanides with aliphatic oxygen donors have been discussed on the basis of results obtained from pH–metric studies. The stabilized nature of mixed-ligand complexes (MLL') where L' is unsaturated oxygen donor ligand has been investigated by Munshi et al. Effect of ring size due to
secondary ligand on the stability of ternary complexes of La_{(III)}, Ce_{(III)}, Nd_{(III)} and Sm_{(III)} has been thoroughly discussed\(^{169}\).

**b) L’-as Aromatic Oxygen Donor:**

Potentiometric investigations on 1:1:1 ternary complex formation with aromatic oxygen donors have been most extensively studied\(^{170,171}\). Chaturvedi\(^{172}\) et al. carried out the pH–metric investigations on ternary complexes formation of Rare earth–NTA / HEDTA–catechol and other oxygen donors. Complexing tendencies of Y_{(III)}, La_{(III)}, Pr_{(III)}, Nd_{(III)}, Sm_{(III)} with NTA, HEDTA, EDTA and some diphenoxyl compounds have been studied pH–metrically\(^{173-176}\). Tandon\(^{177}\) et al. investigated the formation of mixed-ligand complexes of some Lanthanide ions with NTA and hydroxamic acid. Ternary complexes formation of Pr_{(III)} with aromatic oxygen donor ligands have been thoroughly investigated\(^{178,179}\). Formation constants of biligand complexes with nitrilotriacetate and some bidentate donors are reported by Israeli\(^{180}\). Solution studies on mixed–ligand complex formation of Y_{(III)} using NTA / HEDTA / EDTA as primary ligand and some aromatic oxygen donors as secondary ligands have been reported by Munshi\(^{181}\) et al. Complex forming tendencies of some metal ions with NTA and EDTA as primary ligands and dinitro, dibromo-derivatives of salicylic acid, cresotic acid as secondary ligands have been studied by Dey\(^{182,183}\) et al. Spectrophotometric investigations on Ho_{(III)}–EDTA-5-sulphosalicylic acid complex have been carried out by Taketatsu\(^{151,152}\) and co-workers. Importance of oxygen donors and five membered ring structure in formation of Ho_{(III)}–EDTA-tiron complex have been studied by Shetty\(^{150}\) et al. Mixed ligand complexes of Th_{(IV)} with DTPA and some oxygen donors have been studied potentiometrically\(^{184}\). pH–metric investigations on mixed–ligand complex formation using NTA\(^{185,186}\), HEDTA\(^{187}\), EDTA\(^{188}\) and DTPA\(^{157-159}\) with aromatic oxygen donor ligands have been studied extensively. Swamy M. Abu\(^{189}\)
reported the trends in stabilities of mixed-ligand complexes of some Lanthanide ions with aminopolycarboxylates and aromatic oxygen donors. Entropy stabilized nature of Lanthanide - EDTA - aromatic oxygen donors have been discussed on the basis of results obtained from pH-metric studies by Saxena et al.

C] Quaternary Complexes of the type MLL’L” and origin of the present work:

Systematic survey of literature shows that there is a growing interest in investigating mixed-ligand chelates of transition and inner transition metal ion in view of studying the effect of ligand characteristics in mixed-ligand formation. Most of the work reported is on binary and ternary complexes. We thought to extend the idea to study the higher order mixed-ligand systems to get some new information.

As compared to ternary complexes very little work has been reported on quaternary complexes. The field of studies in mixed-ligand quaternary complexes gained the importance in this decade. During 1960-80 most of the work reported is on the binary and ternary complexes.

Quaternary complex formation during the determination of fluoride ions has been reported by Belchor et al. Satynarayana et al reported the quaternary complex formation during the extraction of Lanthanides. Krishna and Plane reported the quaternary complex formation of Zn(II) and Cd(II) with chloride, thiocynate and glycine. Strelow reported the quaternary complexes of Thallium(III). Quaternary complex forming tendencies of Fe(III), Co(III), and Ni(II) with number of ligands have been investigated.
Mali et al. reported the potentiometric investigations on the 1:1:1:1 quaternary complexes in solution. Quaternary complexes of Dioxouranium with hydroxamic acid as one of the ligand have been reported by Janardhan Rao et al.

Ramamooorthy & Santappa investigated the formation of triligand complexes with succinic, thiomalic, itaconic acids and reported the stability of quaternary complexes formed, depends more on the nature of ligands. pH-metric investigations on the 1:1:1:1 triligand complexes of UO$_2^{4+}$ has been reported by Chaturvedi$^{213-215}$ and others.

Equation for calculating the simultaneous equilibria involving attachment of two and three ligands to the central metal ion has been derived by Ramamoorthy and Santappa$^{214}$.

Kumar et al. suggested the modified method for evaluating the equilibria for formation of quaternary complexes. Triligand complex formation of Lanthanide ions with aminopolycarboxylates and malonic, citraconic, malic, tartaric acid have been investigated by Sharma and co-workers. 1:1:1:1 triligand complex formation of Cu$^{2+}$, Ni$^{2+}$ and Zn$^{2+}$ with picolinic, oxalic acid and catechol have been reported by Chaturvedi et al. Recently the quaternary complex formation of some Lanthanide with complexes and O-O donor ligands have been reported from this laboratory$^{222,223}$.

Extrastabilization of Lanthanide quaternary complexes than ternary have been explained on the basis of increased number of fused ring and ligand-ligand interaction using NTA, pyridine 2,6 dicarboxylic acid, furan-2-carboxylic acid has been studied potentiometrically$^{224,225}$. Hetero-ligand equilibria of La$^{3+}$, Pr$^{3+}$, Nd$^{3+}$, Gd$^{3+}$ and Dy$^{3+}$ with iminodiacetic acid and phthalic acid or malonic acid have been investigated and correlated with charged radius ratio$^{226,227}$. Multiligand multimetal complexes of
some transition metal ion have been studied on the basis of speciation curves to throw light on bridging bidentate coordination by studying 1:1:1:1 quaternary species formation equilibria\textsuperscript{192,228-230}. Formation structures and stability of multiligand complex with IMDA and Proline have been studied through COO\textsuperscript{-} and N atom\textsuperscript{192}. Existence of multiligand multimetal complexes with amino acid valine have been attempted on the basis of 1:1:1:1 quaternary species distribution curves\textsuperscript{229-232}.

R. C. Sharma et al have studied the quaternary complex formation in solution using EDTA, CDTA, pyridine 2-dicarboxylic acid, succinic acid to suggest the stability enhancing effect\textsuperscript{193,217,219} due to presence of aryl ring. Statistical aspects of Lanthanide mixed-ligand complex formation have been studied pH-metrically and involvement of statistical, electrostatic and other operative factors is described as total effect with same dicarboxylic acid and amino acid glycine\textsuperscript{194,233}.

Mali\textsuperscript{112,234,235} and co-workers reported the investigation on formation of mixed-ligand chelate of malonic, succinic, tartaric and glutaric acid and steric hindrance of ligand in the formation of mixed-ligand complexes have been discussed.

Recently number of reports\textsuperscript{163,217,236,237} are available on correlation of stabilities on the basis of astatistical factors like $\Delta \log K$, $\Delta \Delta \log K$, percentage relative astatistical stabilisation (% RAS) have been attempted for Lanthanides and some other transition metal ions using amino acid as ligand.

Influence of ionic strength\textsuperscript{96}, dielectric constant of medium\textsuperscript{238-239}, acoustic properties\textsuperscript{240} of some compounds have been extensively studied by Narwade\textsuperscript{241} et al with special interest with their physical parameters and complex formation equilibria in solution.
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218. Dwivedi, P. C., Tripathi, S. P. & Sharma, R. C.

219. Dwivedi, P. C., Tripathi, S. P. & Sharma, R. C.

220. Gahlaut, A., Dwivedi, P. C. & Sharma, R. C.


222. Raut, A. R. & Mhaske, T. H.

223. Raut, A. R. & Mhaske, T. H.

224. Yadav, S. S. & Sharma, R. C.