CHAPTER I

INTRODUCTION
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1. COORDINATION CHARACTERISTICS OF LANTHANIDES

The lanthanides are class 'a' acceptors\(^1\), or 'hard-acids'\(^2\). They possess the non-bonding core \((n-1) (f^1-f^{13}) ns^2 np^6\), where \(n=4\). The hard-hard and soft-soft interactions being more facile, the lanthanides form appreciably stable complexes with highly electronegative donor atoms like oxygen.

The lanthanide metal ions differ from each other in the number of electrons in the 4f - orbitals, which are effectively shielded from interactions with ligand orbitals by electrons in the 5s and 5p orbitals. Covalent bonding must involve normally unoccupied higher energy orbitals (5d, 6s and 6p), and such participation can be expected only with the most strongly coordinating ligands. Lewis et al.\(^3\) have shown from \(0^{17}\) NMR shifts in aqueous solutions of rare-earth ions that the formation of covalent bond in the hydrated ions involves only the lanthanide 6s orbitals. This implies that the 4f, 5d and 6p orbitals play, at most, a minor role in the
bonding. The metal-ligand interactions are, thus, largely electrostatic in character.

The absence of significant interactions between ligand orbitals and 4f-orbitals is supported by observation that complexing groups have only a small effect on the permanent magnetic moments of the tripositive LN$^{3+}$ ions$^{4-9}$, or upon the positions of sharply defined characteristic absorption bands in the UV and visible regions$^{10-12}$. The ligand field stabilization in the lanthanide complexes is small (ca. 1 Kcal/mole). Their large ionic radii (Appendix -I) also minimize covalent interactions. Their polarizing power at short interionic distances is relatively lower, which enables them to combine more strongly with less polarizable donors, resulting in the formation of predominantly ionic complexes.

The lanthanides are highly electropositive and they have little or no tendency to form complexes with $\pi$-bonding ligands due to non-availability of the 4f - orbitals for bonding. Their coordination chemistry is limited mainly to complexes with oxygen and oxygen-nitrogen donors.

In the case of d-block elements the ligand perturbations acting upon a set of d-electrons to
remove the degeneracy of the d-orbitals lie in the order
\[ e^2/r \sim V_{\text{oct}} \gg \lambda \cdot L \cdot S \gg V_{\text{tetrag}} \gg kT. \]

For the lanthanides, however, the sequence is
\[ e^2/r \gg \lambda \cdot L \cdot S \gg V_{\text{oct}} \sim kT. \]

That is, in the lanthanides the inter electronic repulsions are larger than the effect of spin-orbit coupling and low symmetry ligand-field components which, in turn, are greater than the cubic ligand field in an octahedral complex, the latter being approximately of the same order of magnitude as the thermal energy available to an atomic system at room temperature. Because of this, there is little or no destruction of the orbital angular momentum associated with the ground state and there is no change of ground term multiplicity.

The problem of geometry (coordination number and stereochemistry) of complexes in aqueous solutions is rather complex because of the unknown degree of coordination by water molecules and a strong competition by them to the incoming ligands during complexation. Only the species formed by very strong coordinating ligands may exist as definite entities in aqueous solutions.
Although the older literature suggests a coordination number six for the lanthanides, the recent data indicate that larger coordination numbers are very common\textsuperscript{13-17}, and six may be possible only in exceptional cases. The large cation size of the lanthanides makes available increased space around them which facilitates large coordination numbers. The following few complexes illustrate the variety of stereochemistries and coordination numbers that exist:

<table>
<thead>
<tr>
<th>C.N.</th>
<th>COMPLEX</th>
<th>STEREOCHEMISTRY</th>
<th>REF.</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>[ Er (NCS)\textsubscript{6} ]</td>
<td>Octahedral</td>
<td>18</td>
</tr>
<tr>
<td>7</td>
<td>[ Y (acac)\textsubscript{3}H\textsubscript{2}O ]</td>
<td>mono-capped trigonal prism</td>
<td>18</td>
</tr>
<tr>
<td>8</td>
<td>[ La (acac)\textsubscript{3}(H\textsubscript{2}O)\textsubscript{2} ]</td>
<td>square-antiprism</td>
<td>18</td>
</tr>
<tr>
<td>9</td>
<td>[ Nd (diglycolate)\textsubscript{3}(H\textsubscript{2}O)\textsubscript{6} ]</td>
<td>-</td>
<td>19</td>
</tr>
<tr>
<td>9</td>
<td>[ Nd (H\textsubscript{2}O)\textsubscript{9} ]\textsuperscript{3+} Br\textsubscript{3}\textsuperscript{-}</td>
<td>tricapped trigonal prism</td>
<td>18,20</td>
</tr>
<tr>
<td>9</td>
<td>[ La (edta) (H\textsubscript{2}O)\textsubscript{3} ]\textsuperscript{-}</td>
<td>-</td>
<td>21</td>
</tr>
<tr>
<td>10</td>
<td>[ La (edta.H) (H\textsubscript{2}O)\textsubscript{4} ]</td>
<td>-</td>
<td>18,20</td>
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<tr>
<td></td>
<td>edta.H = monoprotonated edta ion</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>La\textsubscript{2} (SO\textsubscript{4})\textsubscript{3} \cdot 9H\textsubscript{2}O</td>
<td>eicosahedral</td>
<td>18</td>
</tr>
</tbody>
</table>

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2. **SURVEY OF LITERATURE ON LANTHANIDE COMPLEXES**

The earlier work on the complexes of lanthanides has been reviewed by several authors including Cotton and Wilkinson\(^{22}\), Vickery\(^{23}\), Moeller\(^{24}\), Ryabchikov and Ryabukhin\(^{25}\), Eyring\(^{26}\), Sinha\(^{27}\), Bailar\(^{28}\) and Ashcroft and Mortimer\(^{29}\). Recent literature on the coordination chemistry of lanthanides is summarized in the following paragraphs.

(A). **SOLID COMPLEXES**

Since the lanthanides are so highly electropositive, they have very little or no tendency to form complexes with the \(\pi\)-bonding ligands. However, several \(\text{LN}\)-complexes derived from weakly basic nitrogen donors, such as 1-10 phenanthroline\(^{30}\), dipyridyl\(^{31-32}\) and terpyridyl\(^{33}\) have been isolated.

The number of neutral ligands coordinated to the lanthanide ion depends upon the coordinating ability of the anion present. When the anion is strongly chelating viz., 1-3 diketone or acetates, only mono-substituted complexes are obtained. The dipyridyl or phenanthroline are known to enter the coordination sphere of the \(\text{LN-(thd)}_3\) chelate\(^{34}\), \[\text{thd} = 2,2,6,6\text{ tetramethyl, 3-5 heptane, 3-5 dione}\] indicating the
ability of LN-ions to form high-coordinating complexes.

Utilization of the s, p and d orbitals in the valency shell of the lanthanides accounts for a maximum coordination number of nine, but higher a coordination number would require either the participation of 4f-orbitals or bond order less than one\textsuperscript{35}.

The proof of the LN-N bonding is found in the crystal structure of $\left[ \text{Eu (acac)}_3 \text{phen} \right]_{36}$ in which the LN$^{3+}$ ion is eight coordinate with a slightly distorted square-antiprismatic arrangement of O-N donor atoms. Bis-phenanthroline and dipyridyl complexes are obtained when the anion is chloride, nitrate or salicylate\textsuperscript{37-39}. Coordination number ten in the species like La (dipy)$_2$ (NO$_3$)$_2$ has been reported\textsuperscript{40} and verified on the basis of crystal structure determination.

Solid adducts of anhydrous LN-chlorides with ammonia and several mono-dentate amines have been reported\textsuperscript{41-43}. Although the weakly basic nitrogen donors donot displace the NO$_3^-$, Cl$^-$, anions from the coordination sphere, two phenanthroline or dipyridyl ligands are accommodated in the coordination sphere owing to the small steric requirments of anions. The IR spectra of the species LN-L$_2$. (5CN)$_3$, where L = dipyridyl,
indicate coordination of selenocyanate groups through $\text{N}$—with coordination number nine$^{44}$. Maximum coordination by the neutral donors is obtained when the anion is the weakly coordinating perchlorate group. Octacoordinate $\text{LN}-(\text{phen})_4 (\text{ClO}_4)_3$ and nine-coordinate $\text{LN}-(\text{terpy})_3(\text{ClO}_4)_3$ species have also been reported$^{45-46}$. Spectral investigations of solid LN-dipyridyl complexes have been carried out by Sinha$^{47}$, and others$^{48}$. Hexacoordinate complexes of LN with phenO$_2$ (where phenO$_2$ = 1–10 phenanthroline–N–N' dioxane) of the type $\text{LN} \cdot (\text{phenO}_2)_2 (\text{NO}_3)_2 \cdot \text{NO}_3$ have also been reported$^{49}$.

The absorption spectra$^{50-54}$ of lanthanide ions have been a subject of several investigations. The nephelauxetic effect$^{55-56}$ (red-shift), which is caused due to the inter-electronic repulsions, has been used as a measure of metal-ligand covalent interactions. Recently, Megh Singh$^{57}$ and co-workers have concluded, on the basis of nephelauxetic effects, a decrease of covalency from Pr to Er, in the LN-complexes of O-phenanthroline-tris-trifluoacetates.

The earlier observation, that the cationic complexes derived from N-donors could not be isolated from $\text{N}$ aqueous medium, was regarded as an indication, that these species are thermodynamically unstable in aqueous solutions, and the LN–N interactions are weaker.
than LN -O inter-actions\textsuperscript{58}.

Amongst the pyridine and quinoline carboxylic acids, the spectral data indicate, that 4-, 6-, 8-quinoline carboxylic acids form O-bidentate structures, where as structures involving the nitrogen-atom probably occur for the chelates of 2-quinoline carboxylic acid\textsuperscript{59}.

It has been inferred from the IR spectra of LN-picolinates\textsuperscript{60} that a covalent bond exists between the LN and the carboxylate ion, and the chelate possesses an octahedral configuration involving three nitrogen atoms and three chelating oxygens as in Ni (II) picolinate\textsuperscript{61}.

Spectrochemical studies of the structure of LN-aminopolycarboxylate complexes\textsuperscript{62} s have confirmed that EDTA behaves in these as a hexadentate ligand with three to four water molecules included in the coordination sphere indicating the coordination number 9–10. Several solid adducts containing (LN-EDTA)\textsuperscript{-} ion have been reported\textsuperscript{63–65}. Some more solid adducts with DDPA\textsuperscript{66}, H\textsubscript{6}TTHA\textsuperscript{67}, TMMA\textsuperscript{68} and other nitrogen donors, viz, DMG\textsuperscript{69}, have also been isolated.

A coordination number of nine has been assigned for the LN (thmd)\textsubscript{3} (ClO\textsubscript{4})\textsubscript{3}\textsuperscript{70} (thmd = N,N,N',N', tetra-
methyl pyridine dicarboxylamide, LN = Pr, Nd, Ho and Er), on the basis of electronic spectral data. The IR spectra suggest the coordination of ligand through oxygen atom of amide and the pyridine nitrogen atom, and the ionic bonding of perchlorates.

B-diketones such as acetylacetone, dibenzoyl-methane and thenoyl trifluoroacetone form complexes of stoichiometry LN-(B-diketone)$_3$ which generally crystallize with solvent indicating coordination number above six$^{71}$. Several other LN-acetylacetonates have been reported where the coordination number above six has been assigned$^{72,73}$. Nitrato complexes of some lanthanides, with 2(2'-pyridyl) Benzimidazole and 2(2' hydroxybenzyl) Benzimidazole have been characterised by Mishra and Singh$^{74}$.

In addition, other donor atoms eg., S, Se, P, As can bond to lanthanide ion under the conditions of zero or, minimal complexation$^{75,76}$. The earlier work records the readily hydrolyzable tris-dithiocarbamates as perhaps the only LN-complexes of S-ligands. However, several new complexes of sulphur donors$^{77}$ with neighbouring N$^{78,79}$, and O$^{80}$, sites have been characterized in recent years.
(B). **COMPLEXES IN SOLUTIONS**:

Much of the earlier data describe the determination of stoichiometry and/or stability constants of the binary complexes with the hydroxy-, saturated-, or, unsaturated- carboxylic acids, phenols, aminocids, aminopolycarboxylic acids, thio-acids, β-diketones, heterocyclic N-O donors, and halides, sulphates, nitrates and polyphosphates.

(I). **BINARY COMPLEXES**:

An attempt has been made to in-corporate below a classified account, as far as possible, of the LN-complexes based on the nature of the donor atoms of the ligands.

(1). **COMPLEXES WITH OXYGEN DONORS**:

Roulet and coworkers\(^1\) have reported the formation of 1:1 and 1:2 complexes of lanthanides with malic, maleic and methylnsuccinic acids. The equilibrium constants of the complexation reactions of Y(III) and rare-earths with malic\(^2\), gluconic\(^3\),\(^4\) and maleic\(^5\) acids have been investigated including the deprotonation studies.

Potentiometric determination of the stability constants of 1:2 LN-complexes has been carried out with malonate, succinate and maleate, as well as their derivatives\(^6\),\(^7\),\(^8\).
The formation constants of 1:2 and 1:3 mandelate complexes of La$^{3+}$, Ce$^{3+}$, Pr$^{3+}$, Nd$^{3+}$ and Sm$^{3+}$, have been evaluated at the ionic strengths of 0.1 M and 1.0 M, (NaClO$_4$)$^{90}$, and 0.1 M and 1.0 M KNO$_3$. A medium of 2.0 M (NaClO$_4$) was employed by Choppin$^{92}$ and Grenthe$^{93}$ for comparison of thermodynamic values with analogous data of other $\alpha$-hydroxy carboxylates. Choppin and DeGischer$^{94}$ have compared the formation constants of 1:1 and 1:2 LN-malonate complexes for $\mu = 0.1$ M and 2.0 M (NaClO$_4$).

Choppin et al. have worked out the formation constants and thermodynamic parameters of lanthanide complexes with propionate, $\alpha$-hydroxypropionate$^{95-97}$, iso-butyrate, fumarate and maleate$^{98}$. The formation constants of the 1:4 complexes with other hydroxy acids such as glycolic$^{99}$, lactic$^{99}$, $\alpha$-hydroxy butyric$^{100}$ and mandelic and atrolactic$^{101,102}$ acids using potentiometric titration technique at $\mu = 0.1$ M (NaClO$_4$) have also been reported. The variation of log$K$ (stability constants) with Z (atomic number) has been studied for the complexes with malic$^{103}$ acid and other ligands.$^{104,105}$

Complexing tendencies of ethanediol, propane 1-2 diol and glycerol have been compared with water$^{106}$ by Manku and Chadha.$^{107}$
The thermodynamic parameters of the LN-squarate complexes have been computed at \( \mu = 0.1 \text{ M} (\text{NaClO}_4) \) by potentiometric and calorimetric titrations. It has been concluded that these complexes are weaker than analogous complexes with other hydroxy or keto ligands due to more endothermic enthalpy of complexation.

Evaluation of formation constants for the \( \text{Sm}^{3+} \) acetates and propionates systems has been done taking into consideration the formation of polymeric species and the hydrolysis of the complexes.

Bhuyan and Dubey have worked out the formation constants of 1:2 lanthanide chelates with catechol at different ionic media, viz., 0.35, 0.20, and 0.05 (\( \text{NaClO}_4 \)). They have calculated the extrapolated thermodynamic stability constants also for \( \mu \rightarrow 0.00 \text{ M} \). Thermodynamic parameters of these complexes at \( \mu = 0.2 \text{ M} (\text{NaClO}_4) \) have also been reported.

Proton - ligand stability constants of phloroglucinol and metal - ligand stability constants of its 1:1 \( \text{Ln}^{3+} \) complexes (\( \text{IN}^{3+} = \text{La}^{3+}, \text{Ce}^{3+}, \text{Pr}^{3+}, \text{Nd}^{3+} \) and \( \text{Sc}^{3+}, \text{Y}^{3+} \)) have been determined by Makhijani and Sengal at three different temperatures, at \( \mu = 0.2 \text{ M} (\text{NaClO}_4) \). Bhargav and Dhinsa have worked out the formation
constants of 1:1 LN–B-resorcyclic acid complexes. Fazal and Ali\textsuperscript{117} have reported the LN–protocatechuic acid complexes. Formation of protonated complexes in the systems LN–salicylic acid and its derivatives has been studied\textsuperscript{118}. LN–complexes with di-iodosalicylates have been investigated by Koppikar and Sounderrajan\textsuperscript{119}. Complexes of La\textsuperscript{3+}, Pr\textsuperscript{3+}, and Nd\textsuperscript{3+} with hydroxy-naphtoic acids in partial aqueous media have been investigated, by Deshpande and Jahagirdar\textsuperscript{120}. Pyrogallol, pyrocatechol violet and tiron have also been used as ligands\textsuperscript{121,122}.

(11). COMPLEXES WITH SULPHUR – OXYGEN DONORS:

Dubey and Puri\textsuperscript{123} have worked out the formation constants of LN–thiocarboxylic acid complexes. The stability constants of \(\alpha\)-and \(\beta\)-mercapto propionate LN–complexes have been determined by Choppin and co-workers\textsuperscript{124}.

Saxena and co-workers have reported the formation constants of LN–complexes (LN = La\textsuperscript{3+}, Ce\textsuperscript{3+}, Pr\textsuperscript{3+}, Sm\textsuperscript{3+}) with thiols\textsuperscript{125–127} and substituted mercapto-propionate\textsuperscript{128}. The stability data of the latter complexes have been used to verify Born’s relation. Murty and co-workers\textsuperscript{129} have reported the LN–thiourea complexes.
Dutt and Nag\textsuperscript{130} have worked out the formation constants of some LN-complexes (LN = La\textsuperscript{3+}, Ce\textsuperscript{3+}, Pr\textsuperscript{3+}, Nd\textsuperscript{3+}, Sm\textsuperscript{3+}, Gd\textsuperscript{3+}) with 3-merapto-1-phenyl buta-2-en-1-one at 0.1 M NaClO\textsubscript{4} and 30°C in 3:1 (v/v) acetone–water mixture. Effect of variation of ionic strength on the stability constants of monothio-dibenzoylmethane complexes and their thermodynamic parameters have been studied by Vishwanath\textsuperscript{131} and others. They have tested the validity of Born relation for these complexes.

(iii). **COMPLEXES WITH NITROGEN – OXYGEN DONORS**

Agrawal and co-workers have worked out the formation constants and the thermodynamic parameters of the glutamine\textsuperscript{132} and aspartic acid\textsuperscript{133,134} complexes of La\textsuperscript{3+} and Ce\textsuperscript{3+}. The stability constants of 1:3 N – N – dihydroxy ethylglycine complexes with Ce(III) and Ce(IV) have been reported by Agrawal and Kapoor\textsuperscript{135}. Chitale and Pitre\textsuperscript{136} have determined polarographically the formation constants of 1:1 La\textsuperscript{3+}, Pr\textsuperscript{3+} and Nd\textsuperscript{3+} complexes with glycine, IMDA and NTA in lower pH-region. They have shown that the order of stability (i.e., glycine < IMDA < NTA) depends on the dentate character of the ligands. Stability constants of 1:1 amino-acid complexes of Sc\textsuperscript{3+}, Y\textsuperscript{3+}, La\textsuperscript{3+}, Ce\textsuperscript{3+}, Pr\textsuperscript{3+} and Nd\textsuperscript{3+} with glycine, aspartic acid and glutamine, have been determined by Makhijani and Sengal\textsuperscript{137} using Irving–Rossotti pH-
pH-titration technique at 30°C and 0.2 M(NaClO₄). Sekhon and Chopra¹³⁸ have examined the validity of Born relation for the 1:1 complexes of Y³⁺, La³⁺ and Ce³⁺ with glutamine at three different ionic media of 0.1, 0.2 and 0.3 M (NaClO₄).

Correlation between the stability constants and reciprocal of ionic radius for LN-hydroxamic acid complexes (LN = La³⁺, Ce³⁺, Pr³⁺, Nd³⁺, Sm³⁺ and Gd³⁺) has been studied by Agrawal¹³⁹ at 35°C in 50% (v/v) dioxane/water medium. Thermodynamic parameters of LN-α-amino-butyric acid complexes have been reported by Shrivastava.¹⁴⁰ Several Schiff's bases complexes of lanthanides have also been studied in partial aqueous media.¹⁴¹-¹⁴⁵

Garg and Malik¹⁴⁶ have reported 1:1 complexes of La³⁺, Sm³⁺, Eu³⁺ and Yb³⁺ with DTPA, TTHA and TPHA in acidic medium using polarographic technique. The changes in the coordination sphere of LN-ions, as reflected from the entropy and enthalpy changes, during their complexation with amino acids, have been studied in detail by Choppin and Gradman¹⁴⁷. They have studied potentiometrically 1:1 LN-complexes with α-picoline, NTA, EDTA, HEDTA, DCTA and DTPA. It has been concluded that the hydration sphere of lighter lanthanides is 20% larger in magnitude than that of the heavier lanthanides.
The variation of $\Delta S$ with hydration number for LN-CDTA complexes has been studied by Nair.\textsuperscript{148}

Kinetic exchange between EDTA and DTPA for their Ce$^{3+}$ and Tb$^{3+}$ complexes has been investigated by Briicher and Banyai\textsuperscript{149}. A number of polyaminocarboxylate LN- complexes have been reported.\textsuperscript{150-151}

The formation constants of 1:1 LN-complexes with ethylenediaminediacetic acid (EDDA), TPHA and TTHA have been evaluated potentiometrically by Garg and co-workers.\textsuperscript{152}

Pandey and Munshi\textsuperscript{153} have studied the complexes of Y$^{3+}$ at 0.2 M(NaClO$_4$) ionic strength in partial aqueous medium with 8-hydroxy quinoline, 8-hydroxyquinoline-5-salphonic acid, 5-sulphosalicylic acid, 3,5- dinitro salicylic acid and Nitroso- R salt using Irving-Rossotti pH-titration technique.

Formation constants of 1:2 LN-complexes with heterocyclic carboxylic acids viz., quinaldinic acid, quinoline-8-carboxylic acid, quinoline-2-carboxylic acid and 3-hydroxy picolinic acid using Irving-Rossotti pH-titration technique have been reported by Dutt and Nag\textsuperscript{154}. Protonated complexes of 5-sulpho salicylic acid with Gd$^{3+}$\textsuperscript{155} have been studied in partial aqueous medium.
5-7-diiodo 8-hydroxyquinoline LN-complexes at $\mu = 0.1$ M (NaClO$_4$) and 35°C have also been reported.\textsuperscript{156}

Several other LN-complexes with a variety of ligands, viz., tyrosine\textsuperscript{157,158}, Lawson,\textsuperscript{159} Xylenol-orange\textsuperscript{160}, Alizarine-red-$S$\textsuperscript{161-163}, Methyl-thymol blue,$^ {164}$ Thoron$^ {165}$, Nitro-alizarine$^ {166}$, Aurine tricarboxylic acid$^ {167}$, Solochrome dyes$^ {168}$, TAN, or TAR$^ {169}$, PAN$^ {170}$, Maltol$^ {171}$, as worked out in aqueous or partial aqueous medium have been reported.

Some attempts have been made to examine the so-called 'Gd-break'\textsuperscript{172,173} and more recently observed 'tetrad effect'\textsuperscript{174,175} and 'double-double effect'\textsuperscript{176,177}. Sinha\textsuperscript{178} has generalised that 'inclined $W$' plots are obtained for the variations in stability constants of the LN-complexes with the total angular momentum of the LN-ions. These observations have been supported by some other workers\textsuperscript{179,180} too.

(II). TERNARY COMPLEXES:

Several polydentate aminopolycarboxylic acids have been used as primary ligands in studying biligand mixed complexes of the lanthanides. These include, IMDA, NTA, EDTA, DTPA and CDTA.

Formation constants and thermodynamic parameters
of 1:1:1 ternary complexes of the type (LN$^{3+}$-A-L) (where LN$^{3+}$ = La$^{3+}$, Br$^{3+}$, or Nd$^{3+}$, A = NTA$^{181}$, IMDA, HEDTA, EDTA$^{182}$ or CDTA$^{183}$ and L = 8-hydroxyquinoline, 8-hydroxyquinoline-5-sulphonic acid, or 2-picolinic acid, pyrocatechol, tiron, dihydroxynaphthalene sulphonic acid) have been reported by Tandon and co-workers$^{184}$. Mixed-ligand complexes (LN-CDTA-L) (where LN = La$^{3+}$,Pr$^{3+}$ or Nd$^{3+}$ and L = hydroxy acids$^{185}$, viz., lactic (LA), glycolic (GA), or malic acid (MA), or their thio-derivatives$^{186}$, have also been worked out. It has been shown that the stability of these complexes varies in the sequence MA $\supset$ LA $\supset$ GA, which is the order of basicity of these secondary ligands.

Munshi and co-workers have studied the 1:1:1 ternary complexes of the type (Pr$^{3+}$-A-L), where, A = NTA, HEDTA, or EDTA and L = pyrogallol, pyrocatechol, protocatechuic acid, protocatechualdehyde$^{187}$, or dinitrosalicylic acid, iodo salicylic acid, polyhydroxy phenolic acid$^{188,189}$. Ternary complexes of Y$^{3+}$ using EDTA or HEDTA as primary ligand and 8-hydroxy quinoline, iodosalicylic acid, pyrogallol, protocatechuic acid or dinitro-salicylic acid as secondary ligands have also been reported by them$^{190}$. Influence of ionic strength and dielectric constants on the stability of Sm$^{3+}$ and Ho$^{3+}$
ternary complexes with Cy DTA as primary ligand and ARS, 8-hydroxy quinoline-5-sulphonic acid, or iminodiacetic acid as secondary ligands has been studied recently by Marathe and Munshi.\textsuperscript{191}

Formation constants and reproportionation constants for the ternary systems (LN\textsuperscript{3+}-NTA-isopropyltropolone) have been evaluated by Singh and co-workers.\textsuperscript{192,193}

Tripathi and co-workers have reported the formation of protonated ternary complexes of the type (LN\textsuperscript{3+}-A-L), where A = CDTA or DTPA and L = ketoglutaric acid\textsuperscript{194} or hydroxy acids\textsuperscript{195,196}. Some biologically active ternary complexes of La\textsuperscript{3+}, Ce\textsuperscript{3+}, Pr\textsuperscript{3+}, Nd\textsuperscript{3+}, Gd\textsuperscript{3+} and Dy\textsuperscript{3+} with picolinic acid as primary ligand and catechol and 8-hydroxy quinoline as secondary ligands have also been studied by them.\textsuperscript{197}

Taquikhan and Reddy\textsuperscript{198} have reported the formation constants of the complexes (LN\textsuperscript{3+}-EDTA-TPP) and (LN\textsuperscript{3+}-EDTA-ATP) (where TPP = tripolyphosphate and ATP = adenosine triphosphate). Ozer\textsuperscript{199} has worked out potentiometrically the ternary complexes of Y\textsuperscript{3+} with tiron, dihydroxy napthalene sulphonic acid and pyrocatechol using EDTA or HEDTA as primary ligand.
Dey and co-workers\textsuperscript{200} have reported the ternary complexes of some substituted salicylic acids with lanthanides in 0.1 M KNO\textsubscript{3} and 50\% (v/v) water-ethanol medium, using EDTA or ethylene glycol-Bis (\(\beta\)-amino ethyl ether) tetraacetic acid as primary ligand.

NMR studies of some paramagnetic ternary lanthanide complexes using EDTA as primary ligand and IMDA, methyl-IMDA or NTA as secondary ligands have been reported by Rosalind and co-workers\textsuperscript{201}

3. **AIM AND SCOPE OF THE PRESENT WORK**

A survey of literature on the coordination chemistry of lanthanides reveals that much work has been done on their binary complexes. Contrary to earlier belief, it is now accepted that (i) the lanthanides form complexes even with \(\alpha\) -donors, and (ii) their coordination number is almost always greater than six. The ligands that have been used are invariably carboxylic or aminocarboxylic acids including their derivatives. Although, recently some mixed-ligand complexes have been studied in solution, the data available are meagre as compared to those related to the d-block elements.
It was, therefore, considered worthwhile to undertake a systematic investigation on some ternary (biligand) lanthanide complexes in solution. The choice of lanthanides as central atoms has two additional advantages (i) their similar outer electronic configuration \((4f^n)\) enables a comparative study of their complexes where the variations in the stability may be caused largely by the changes in ionic radii, (ii) their ionic radii are much larger than the similarly charged d-block elements. These enable the lanthanides to have larger coordination numbers which are aptly suited for the studies of ternary complexes involving polydentate ligands.

Ethylene diamine tetraacetic acid (EDTA) has been used as primary ligand. The use of EDTA as primary ligand has the following advantages,

(i) EDTA behaves as a hexadentate ligand. Assuming coordination number eight (or, even nine) two (or, three) coordination positions are left for the secondary ligand,

(ii) the LN-EDTA complexes are very stable (see appendix IV). Therefore, there is little or no possibility of ligand displacement of the type, \(MA + L \rightarrow ML + A\) in the ternary system \((M = LN^{3+}, A = EDTA, L = Secondary ligands)\).
ligands).

(iii) there is almost no chance of the formation of 1:2 complex \([LN-(EDTA)]_2\) and hence the possibility of disproportionation is minimised in the ternary systems.

A number of secondary ligands of the type O-O donors, O-N donors and O-S donors have been selected for the ternary systems.

The major aim of the present investigations has been to seek co relations between the stability constants of the 1:1 binary and 1:1:1 ternary complexes and certain characteristics of the metal ions and ligands. These include:

(i) testing the validity of Born's relation

(ii) variation in the stability constants with the basic strengths of the secondary ligand,

(iii) the stability \(\text{aqqu}\) sequence with respect to the lanthanides (ionic radii or atomic number) and the closely related secondary ligands belonging to a particular series,

(iv) the trends in the values of \(\log K\)' in the ternary systems, \((LN\text{-EDTA-L})\),

(v) variation in the stability constants with the
ionization potentials, standard electrode potentials and standard entropies of the lanthanides,

(vi) correlation between the stability constants and the total angular momentum of the lanthanides,

(vii) evaluation of l.f.s.e. using the stability data of the binary edta complexes.

Mathematical relationships for some of the above correlations have been developed. An attempt has been made to explain some aspects of a possible model of these complexes.

The use of a limited number of lanthanides in the present work is due mainly to the non-availability of the remaining metal salts.

The ternary systems investigated have been classified as under:

<table>
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<tr>
<th>LN</th>
<th>Primary ligand</th>
<th>Donor atoms</th>
<th>Secondary ligands</th>
</tr>
</thead>
<tbody>
<tr>
<td>La$^{3+}$, Ce$^{3+}$, Pr$^{3+}$</td>
<td>Series I</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nd$^{3+}$, Sm$^{3+}$</td>
<td>EDTA 0 - 0</td>
<td>Malic, Lactic, Glycolic,</td>
<td>Gluonic acids</td>
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<td></td>
<td></td>
<td></td>
<td>Contd. ..</td>
</tr>
<tr>
<td>LN</td>
<td>Primary ligand</td>
<td>Donor atoms</td>
<td>Secondary ligands</td>
</tr>
<tr>
<td>--------</td>
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<td>---------------------------</td>
</tr>
<tr>
<td>La(^{3+}), Ce(^{3+}), Pr(^{3+})</td>
<td>EDTA</td>
<td>0 - S</td>
<td>Thiamallic, Thioglycolic acids</td>
</tr>
<tr>
<td>Nd(^{3+}), Sm(^{3+})</td>
<td>EDTA</td>
<td>0 - 0</td>
<td>Malonic, Succinic, Glutaric acids</td>
</tr>
<tr>
<td>La(^{3+}), Ce(^{3+}), Pr(^{3+})</td>
<td>EDTA</td>
<td>0 - 0</td>
<td>Maleic, Crotonic, Citraconic, Itaconic acids</td>
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<tr>
<td>Nd(^{3+}), Sm(^{3+})</td>
<td>EDTA</td>
<td>0 - N</td>
<td>Glycine, Leucine, α and, β-Alanine, Aspartic acid, Valine</td>
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<tr>
<td>La(^{3+}), Ce(^{3+}), Pr(^{3+})</td>
<td>EDTA</td>
<td>0 - 0</td>
<td>Salicylic, Phthalic, Anthranilic acid</td>
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<tr>
<td>Nd(^{3+}), Sm(^{3+})</td>
<td>EDTA</td>
<td>0 - 0</td>
<td>Catechol, Resorcinol, Phloroglucinol, Protocatechuic acid, β-Resorcylic acid</td>
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<th>Primary ligand</th>
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<tbody>
<tr>
<td>$\text{La}^{3+}$, $\text{Ce}^{3+}$, $\text{Pr}^{3+}$</td>
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<td>Series VIII</td>
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<tr>
<td>$\text{Nd}^{3+}$, $\text{Sm}^{3+}$</td>
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<td></td>
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<td>LLANE-</td>
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<td>OUS</td>
<td>1-(2-pyridylazo)-2-</td>
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<td>neptol, (PAN),</td>
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<td>4-(2-pyridylazo) resorcinol (PAR)</td>
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<td>166.</td>
<td>S.M.F.Rahman, Naseer Ahmad and V.Kumar, Indian J.Chem., 1974, 12, 899.</td>
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