ABSTRACT

Owing to the incompletely filled f-orbitals lanthanides exhibit very interesting chemical properties. Since 4f-orbitals in lanthanides are too far inside to be influenced by the coordinating ligands, it is difficult for them to be involved in coordination. However, they have the inherent tendency to expand their coordination number around them. Moreover, the lanthanides show toxic behaviour towards animals and man. In aqueous solution the coordination sites of lanthanides are occupied by water molecules and only the strong ligands can coordinate with them. In addition, they act as anti blood coagulants. They accumulate mainly in liver and are eliminated very slowly.

Nitrogen and sulphur containing ligands are known to have toxic effect. Their toxicity increases on complexation with lanthanide metals. In view of this an attempt has been made to synthesize and characterise a variety of such complexes in order to study the nature and relative toxicological behaviour of such ligands and their lanthanide complexes towards insects.

Lanthanide chelates (1M:3L) of the Schiff bases derived from the condensation of sulphapyridine with salicylaldehyde (SB I) and sulphamerazine with salicylaldehyde (SB II) and N,N-dimethylaminobenzaldehyde (SB III) have been synthesized.
However, Schiff base obtained from sulphapyridine and \(N, N\)-dimethylaminobenzaldehyde did not yield stable complexes with \(La(III)\), \(Ce(III)\), \(Pr(III)\), \(Nd(III)\), \(Gd(III)\), \(Dy(III)\), \(Ho(III)\) and \(Er(III)\). Being hard acids, lanthanides prefer to coordinate with hard bases such as oxygen containing ligands than those of the ligands containing nitrogen donor sites. The \(^1\text{H NMR-}\) and \(IR-\) spectral data indicate the coordination of the metal through phenolic oxygen and azomethine nitrogen of \(SB\ I\) and \(II\) along with two water molecules rendering the metals eight coordinated. In the case of \(SB\ II\), the lanthanides have been observed to coordinate through imino- and pyridyl-nitrogens. Presence of three molecules of water suggests that the lanthanide chelates of \(SB\ III\) are also eight coordinated.

New Schiff bases namely, bis-barbituric acid-1, 3-diaminopropane (I) and bis-5,5-diethylbarbituric acid-1, 3-diaminopropane(II) have been synthesized. Since the reaction of (I) proceeds only at \(pH = 6.0 - 6.5\), it was maintained by adding requisite volume of perchloric acid. The chelates formed in 1:1 (MIL) ratio have been found to coordinate through two C=N and two NH nitrogens with the replacement of imino proton by the metal. Two molecules of water are bonded to each chelate maintaining coordination number seven. A sharp band at around 1070 cm\(^{-1}\) in the IR spectra of bis-barbituric acid-1, 3-diaminopropane complexes indicated the presence of tetrahedral perchlorate ion. Since the complexes are insoluble, their molar conductance could not be measured which would have
confirmed the nature of the perchlorate ion.

Solution study of the chelates of above two series has been made potentiometrically at 25°, 30° and 35°C at 0.1M ionic strength maintaining the total volume at 50 ml by adding calculated volume of water. The stability constants of the chelates follow the order La(III) < Ce(III) < Pr(III) < Nd(III) < Gd(III) < Dy(III) < Ho(III) < Er(III). It seems that the log K is inversely proportional to ionic radii of lanthanide ions. A plot of log K versus e²/r shows roughly a linear relationship suggesting ionic character for the metal-ligand bond in solution. The negative value of free energy (-ΔG) shows that the formation of the complexes is thermodynamically favourable. It has also been found that the stability of the complexes decreases with the increase in temperature.

As a part of this project mixed-ligand complexes of lanthanides with cyclopentanone thiazolidine-4-one, thiobarbituric acid(I); cyclohexanone thiazolidine-4-one, barbituric acid(II) have been studied. Lanthanides yielded complexes of the type LML'Cl.3H₂O, where L = cyclopentanone thiazolidine-4-ones and L' = barbituric acids. Coordination occurs after deprotonation of the ligands which has been ascertained by analytical and infrared spectral data. Carbonyl oxygen and imino nitrogen of both thiazolidine-4-ones and barbituric acids...
together with three molecules of water are bonded to lanthanide rendering them eight coordinated.

Insecticidal investigations of the ligands and their complexes (in chapter IV and V) have been made against cockroaches. The per cent mortality has been evaluated in terms of probit. From the \( LD_{50} \) it has been observed that the toxicity of the ligands increases after chelation with lanthanides.

As an extension of this work novel metal complexes have been exploited as ligands in order to study their chelating behaviour towards lanthanide ions. These multi-dentate ligands were synthesised in two steps: (i) Synthesis of bis (1,3-diaminopropane) \( M(II) \) chloride (\( M = Cu^{2+} \) or \( Zn^{2+} \)) and (ii) subsequent synthesis of tetrakis (Salicylaldehyde) bis (1,3-diaminopropane) \( M(II) \) chloride. This ligand may also be synthesised via a different route. When Schiff base derived from 1,3-diaminopropane and salicylaldehyde was treated with \( Cu(II) \), it did not yield the desired ligand. Since the \( Cu(II) \) is bonded to phenolic C-O and the azomethine nitrogen atom they are not available for further coordination with lanthanides. A comparison of the spectra of the metal containing ligands with those of their chelates indicated that coordination of the lanthanides occurs by the replacement of phenolic proton by the metal preceeded by the formation of lanthanide-oxygen bond.

- iv -
Visible spectra of all chelates have been analysed and nephelauxetic ratio (β), nephelauxetic effect (1-β), bonding parameter (b^{1/2}) and Sinha covalency parameter(β) were evaluated. The positive values of these bonding parameters indicated that the complexes are covalent. The conductivity measurements of soluble complexes showed that sulphadrug Schiff base complexes are covalent while the chelates of metal containing ligands are ionic in nature. The magnetic moment measurements have shown that the f-orbitals of lanthanide do not participate in bond formation as they are shielded by 5s^26p^6 levels.

From the above studies it has been concluded that the lanthanides form covalent bond with the ligands and the absorption originating within f-f orbitals is greatly influenced by the approaching ligands. Moreover, the f-orbitals find difficult to be involved in coordination. Though the lanthanide (III) salts are hygroscopic, their chelates are air stable and non-hygroscopic. However, the stability of the chelates increases with the increase in atomic number of lanthanides as a result of lanthanide contraction.