

Syntheses and Characterization of Trivalent Lanthanide Complexes with Heterocyclic Amines and Schiff Bases. Optical Absorption and NMR Spectroscopic Studies

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The NMR spectra of paramagnetic trivalent lanthanides whose binding to a ligand induce frequency shifts in the NMR spectrum of the ligands. The lanthanide induced paramagnetic shifts have two contributions: (1) Fermi contact (δ_C) which is induced through-bonds and (2) dipolar or pseudocontact shifts (δ_{pC}). The predominant shift in the case of trivalent lanthanides is pseudocontact in nature, arising through space.

The dipolar shift is limited by the geometry of the complex species and is given by the equation:

$$[\Delta V/V_0] = D [3\cos^2\theta - 1 / r^3]$$

In this equation r is the length of a vector which joins the metal atom and the nucleus being examined, θ is the angle this vector makes with z magnetic axis, ϕ is the angle which the projection of r into the xy plane makes with the x magnetic axis.

The electronic spectra of lanthanide(III) complexes have been studied to give information regarding structure and bonding in these complexes. Most of the sharp lines like $4f-4f$ transitions originating within the $4f$ configuration of the lanthanide(III) ions are little affected by the environment about the lanthanide ions. A few, however, are very sensitive to the environment and are more intense when the ion is complexed than they are in the corresponding aqua-ions. The oscillator strength and band shape of these transitions in lanthanide(III) complexes are especially sensitive to the structural details and the chemical nature of the ligand environment. Such transitions have been called *hypersensitive* transitions and the phenomenon is generally referred to as *hypersensitivity*. The oscillator strength and band shapes of the hypersensitive transitions in the absorption spectra of the lanthanides have been correlated to the complex formation, coordination numbers, coordination geometry, ligand structure, chelate solvent interactions and symmetry of the field around lanthanide ion.

The intensity of an absorption band is measured by its oscillator strength, which is directly proportional to the area under the absorption curve. The oscillator strength P can be expressed in terms of the molar extinction coefficient ϵ , the energy of the transition in wave number ν , and the refractive index of the medium η , by the

relationship

$$P = 4.31 \times 10^{-9} [9\eta / (\eta^2 + 2)^2] \int \epsilon(\nu) d\nu$$

The spectra of the lanthanide complexes show the shift of spectral bands towards lower energy as compared to the position in the respective ions. These red shifts have been called the nephelauxetic effect and have long been regarded as a measure of covalency. This shift, as described by Jorgensen, is due to coulombic interaction between the f-electrons on the lanthanide atoms: that is expansion of electron clouds. The nephelauxetic parameter, the covalency parameter and the bonding parameter of the complexes have been calculated and discussed.

The **aims and objects** presented in this thesis are three-fold:

to enhance our knowledge of the coordination chemistry of the trivalent lanthanides ions,

to study absorption spectra (in the visible region) of praseodymium, neodymium, dysprosium, holmium and erbium complexes containing weakly basic nitrogen donors in different solvents; to examine hypersensitivity of 4f-4f transitions; to demonstrate the sensitivity of the oscillator strengths and band shapes between the complexes in different environment and

to examine the nature of paramagnetic shift, to correlate the observed shift and hypersensitivity to structural characterization.

The optical absorption, NMR and thermal studies of 1,10-phenanthroline complexes of trivalent lanthanide chlorides have been investigated and discussed. The ^1H NMR spectra of the paramagnetic complexes show that the phen resonances have been shifted to lower as well as higher fields, which is a manifestation of dipolar interaction. The phen signals of methanol solution of diamagnetic lanthanum complex have been found to shift to lower fields compared with free phen, which is a strong evidence that the aromatic amine remains coordinated to the metal ion in methanol solution. The H (2) protons of the heterocyclic amine display broad resonances. The degree of broadening in Pr, Nd, and Yb complexes follows the order $\text{Pr} < \text{Nd} < \text{Yb}$. The inter and intramolecular shift ratios have been calculated which show that the paramagnetic shift is predominantly due to dipolar interaction.

The electronic spectra of Pr, Nd, Ho and Er complexes have been studied in methanol, pyridine, DMSO and DMF. The oscillator strength and covalency parameters (β , $b^{1/2}$ and δ) have been calculated from the spectra of these complexes and discussed. The oscillator strength for the hypersensitive and non-hypersensitive transitions have been determined and variation in the oscillator strengths and band shapes with respect to

solvent type is rationalized. The interelectronic repulsion parameter β which is less than one and the covalency parameters ($b^{1/2}$ and δ) which are positive show covalent nature of bonding between the metal and the ligand.

The optical absorption NMR and thermal studies of 2,2'-bipyridyl complexes of trivalent lanthanide chlorides have also been investigated. Both bis- and tris bpy complexes have been isolated in ethanol under normal conditions. The NMR spectra of paramagnetic complexes exhibit lower as well as higher field shifts of bpy resonances, which reflect change in geometry and reveals importance of the geometric factor ($3\cos^2\theta - 1$) in changing sign of the shift. The paramagnetic shifts recorded, for these complexes, have been analysed and the intramolecular shift ratios suggest that the paramagnetic shift is predominantly dipolar in origin.

The electronic absorption spectra of the complexes have been studied in different non-aqueous solvents. The solvents differ with respect to their atoms. The results indicate that the chemical environment around the lanthanide ion has great impact on $f-f$ transitions and any change in the environment brings about large spectral changes both in terms of oscillator strength and band shapes. The oscillator strength for the hypersensitive and non-hypersensitive transitions have been determined and changes in the oscillator strength and band shape with respect to solvent type is rationalized in terms of ligand (solvent) structure and coordination properties. Change in the counter anion from thiocyanate to chloride increases the oscillator strength. However, a change in the heterocyclic amine from phen to bpy decreases the oscillator strength of the transitions. A rigidly planar phen is expected to bring more deal of covalency in the complex and, therefore, increase the oscillator strength. Pyridine is an exception where actually the oscillator strength has increased, the ring current effect of both pyridine and bpy may be responsible for this increase. The results of electronic spectra clearly show that the pyridine is the most effective in promoting $f-f$ spectral intensity. The nephelauxetic and covalency parameters of the complexes have been calculated which show covalent nature of bonding between the metal and the ligand.

A study has been carried out that deals with the absorption spectroscopic studies on the mixed-ligand complexes of Pr (III) Nd (III) Ho (III) and Er (III) with 2,2'-bipyridyl and thiocyanate in pyridine, DMSO, DMF and methanol. The oscillator strengths for the hypersensitive and non-hypersensitive transitions have been calculated and variation in the oscillator strength and band shapes with respect to solvent type is rationalized in terms of solvent structures and coordinating properties. Pyridine has been found most effective in promoting $4f-4f$ intensity and the increase in the oscillator strength in this solvent is due to dynamic ligand polarization mechanism. Comparing the oscillator strength of $[\text{Pr}(\text{bpy})_3(\text{SCN})_3]$ with that of $[\text{Pr}(\text{phen})_3(\text{SCN})_3]$ reveals that the values are larger for the phen complex in methanol, DMSO and pyridine solutions indicating the role of the difference in specific bonding relations of the praseodymium atom and the two ligands. It seems that the rigidly planar phen ligand is especially effective in promoting $4f-4f$ electric dipole intensity. The occurrence of different band shapes for the two complexes is indicative of different symmetries i.e. different geometrical

arrangement of the ligands about the lanthanide ion. The ${}^5G_6 \leftarrow {}^5I_8$ transition of Ho complex is 46%, 81%, 172% and 303% more intense in methanol, DMSO, DMF and pyridine, respectively, compared with Ho^{3+} aqua-ion. This reflects strongly hypersensitive behaviour of this transition in Ho(III) systems. The spectra of all the complexes in all solvents have been found to shift towards longer wavelength (red shift) as compared to the position in the respective aqua-ion.

This study also includes syntheses and characterization of trivalent lanthanide complexes of bis(thiourea)acetylacetonate. The ligand and complexes were characterized by elemental analyses, molar conductances, melting points, TG analyses and infrared spectra. The molar conductance of the complexes is in the range $15\text{--}50 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$, which suggests that the complexes are non-electrolyte and the three chloride ions are inside coordination sphere. The infrared spectra of the complexes show coordination through free amino groups as well as azomethine nitrogens. Thus the ligand acts as a tetradentate. The electronic spectra of the complexes have been studied in methanol and in some cases in ethanol also. The oscillator strengths and the covalency parameters have been calculated from the spectra. The values of the covalency parameters suggest covalent nature of bonding between the metal and the ligand. The oscillator strength of the hypersensitive transitions show larger variation as compared to the non-hypersensitive transitions.