

## ELECTRONIC SPECTRAL STUDIES OF Pr (III) AND Nd (III) WITH MIXED LIGAND SYSTEM.

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Some biprotic acids, namely, salicylic acid, tartaric acid & lactic acid and a few amino acids like glycine and  $\beta$ -alanine were chosen for mixed ligand system (biprotic acids as primary ligands & amino acids as secondary ligands). These were interacted with metal ion, Pr (III) or Nd (III) in different molar ratios & their electronic absorption spectra were recorded in aqueous solution. The various energy parameters such as Slater-Condon ( $F_k$ ), Racah ( $E^k$ ), Lande ( $\zeta_{4f}$ ) & intensity parameters such as, oscillator strength (P), Judd-Ofelt parameters ( $\Omega_\lambda$ ) have been computed using partial & regression statistical methods. The bonding parameter ( $b^{1/2}$ ) & nephelauxetic ratio ( $\beta$ ) have also been evaluated to ascertain the covalency in the metal-ligand bond.

**Key words:-** amino acids, biprotic acids, rare earth metals, mixed ligand system, energy & intensity parameters, bonding parameters, nephelauxetic ratio.

### INTRODUCTION:

Recent decades have witnessed a growing interest in the investigations of the trivalent rare earth metal ions [especially Pr(III) and Nd (III) complexes] due to their special photo physical properties which make them useful material for molecular lighting devices, lasers, optical telecommunications, quantum dot nanocrystals, diode pumped lasers and in various bioanalytical methods<sup>1-15</sup>. The photo physical properties like luminescence of rare earth metals ions could be enhanced through chelation with appropriate organic ligand. Fortunately, trivalent rare earth metal ions can form stable coordination compounds or chelates (with a variety of organic ligands) exhibiting high stability & strong luminescence.

Among the rare earth metal ions, Pr(III) & Nd(III) show emission spectra which extends from the blue to the near infrared region. Although much work has done on binary chelates of metals with single ligand system like Schiff bases, crown ethers, calixarenes, podents etc, but the literature survey has indicated that little work has been done on the ternary or mixed ligand chelates involving two ligands, especially, one having a biprotic acid & other as amino acid. The earlier studies associated with the amino acids and rare earth metals [Pr (III) and Nd (III)] includes work by A. Kuliev<sup>16</sup> who studied spectral and thermal properties of mixed ligand complexes of Pr (III) with glycine, methionine and tartaric acid. T.D. Singh and others<sup>17</sup> have conducted spectral investigation of the Nd (III) complexes with glutathione in presence and absence of Zn (II) in aquated organic solvents. Spectroscopic study of the interaction of Nd (III) with amino acids like L-aspartic acid, L-histidine, DL-malic acid and aspartame in aqueous solution was done by Soraya Jerico et.al<sup>18</sup>. The mixed ligand complexes of some biologically important polyamine polycarboxylic acids with Nd (III) and Pr (III) have been studied by Prashant N. Bhatt and others<sup>19</sup> They investigated spectral characteristics like oscillator strength,  $T_\lambda$  and Judd-Ofelt intensity parameters of the  $4f-4f$  transitions through absorption spectroscopy. H. Debecca Devi and others<sup>20</sup> have investigated spectral parameters (energy and intensity) of Nd (III) complexes with amino acids like DL-valine, DL-alanine and  $\beta$ -alanine in presence and absence of  $Ca^{2+}/Zn^{2+}$  in aqueous and different aquated organic solvents. Reda A Ammar et. al<sup>21</sup> have determine the stability constants of mixed ligand complexes of adenine and amino acids with Ni (III) complexes by potentiometric method. However spectral investigation on mixed ligand system of biprotic acids like Salicylic acid, Tartaric acid & Lactic acid and simple amino acids like Glycine &  $\beta$ -Alanine still needs to be explored and hence in the current pursuit, mixed ligand system of biprotic acids and amino acids were interacted with metal ions- Pr (III) & Nd (III)

in different molar ratios. The spectral studies were carried out in aqueous solution which provides information about energy levels of different transitions, coordinating environment (symmetry) & extent of metal-ligand interaction which has been expressed in terms of energy, intensity & bonding parameters.

## EXPERIMENTAL

### (a) Preparation of sample solutions:

Pr (III) & Nd (III) acetates (IREL, India) have been used for the preparation of metal-ion solutions (0.01 M) in double-distilled water which were duly standardized by the conventional methods<sup>22</sup>. The sample solutions were prepared in different molar-ratio [M: L<sub>1</sub>: L<sub>2</sub>] viz., 2:0.5:0.5, 2:0.7:0.7, 2:1:0.5 etc., where M=Pr (III) or Nd (III), L<sub>1</sub>=primary ligand-biprotic acid & L<sub>2</sub>=secondary ligand -amino acid. The electronic absorption spectra of these sample solutions have been recorded on a double beam spectrophotometer Systronic-119 in the range of 350-900 nm.

### (b) Evaluation of Spectroscopic Parameters:

The recorded spectra have been analysed and interpreted in terms of the various electronic spectral parameters (energy, intensity & bonding) which give useful information regarding spin-orbital interactions, inter electronic repulsion, nephelauxetic effect & bonding in the complexes. The values these have been calculated by using partial & multiple regression methods involving the various theories given by Slater-Condon<sup>23</sup>, Racah<sup>24-26</sup>, Slater<sup>27</sup>, Wybourne<sup>28</sup>, Dieke<sup>29</sup> & Judd-Ofelt<sup>30-31</sup>. The various energy parameters like Slater-Condon (F<sub>k</sub>) & Lande (ζ<sub>4f</sub>) factors have been calculated using following equation (1.1-1.3) as proposed by Wong<sup>32-33</sup>.

$$E_j(F_k, \zeta_{4f}) = E_{oj}(F_k, \zeta_{4f}) + \sum_{k=2,4,6} \frac{\partial E_j}{\partial F_k} \Delta F_k + \frac{\partial E_j}{\partial \zeta_{4f}} \Delta \zeta_{4f} \quad \dots 1.1$$

$$[F_k = F_k^0 + \Delta F_k]_{k=2, 4, 6} \quad \dots 1.2$$

$$\zeta_{4f} = \zeta_{4f}^0 + \Delta \zeta_{4f} \quad \dots 1.3$$

The energy and other spectroscopic parameters for different peaks observed during experimental studies have been summarized in Table-1.3 and 1.4 for Pr (III) & Nd (III) chelates corresponding to [M: L<sub>1</sub>: L<sub>2</sub>=2:0.5:0.5] molar ratios. The bonding parameter (b<sup>1/2</sup>) & nephelauxetic ratio (β) were calculated by following relations

$$\beta = \frac{F_K^c}{F_K^f} \quad \text{and} \quad b^{1/2} = \left[ \frac{(1-\beta)}{2} \right]^{1/2} \quad \dots 1.4$$

and the values of these calculated for [M:L<sub>1</sub>:L<sub>2</sub> ratios=2:0.5:0.5] for both the metal ion [Pr(III) and Nd(III)] system have been tabulated in Table-1.4. The oscillator strength of each band has been computed using following equation (1.5),

$$P_{obs} = 4.6 \times 10^{-9} \times \epsilon_{max} \times \Delta \nu_{1/2} \quad \dots 1.5$$

where Δν<sub>1/2</sub> is half band width & ε<sub>max</sub> is molar extinction coefficient. The solution spectra have been analyzed by resolving each band into gaussian curve shape to enable evaluation of oscillator strength. The bands for different transitions have been identified by comparing the values of energies with corresponding energy level in free metal-ion. The oscillator strength values besides several minor interactions are composed of prominently three main parameters known as Judd-Ofelt parameters Ω<sub>λ</sub> (λ=2, 4, 6). The Judd-Ofelt equation for experimentally observed oscillator strength is given by,

$$P_{\text{exp}} = \Omega_2 \nu [U^2]^2 + \Omega_4 \nu [U^4]^2 + \Omega_6 \nu [U^6]^2 \quad \dots 1.6$$

where,  $\nu$  is energy of the band ( $\text{cm}^{-1}$ ) &  $\Omega_2$ ,  $\Omega_4$  &  $\Omega_6$  are Judd-Ofelt intensity parameters. The values of energy and oscillator strength of absorption band and their intensity parameters are listed in Table-1.1 & 1.2 for Pr (III) & Nd (III) metal-chelates having [M:L<sub>1</sub>:L<sub>2</sub> =2:0.5:0.5 ratio].

## RESULTS & DISCUSSIONS:

The absorption spectra of the Pr(III)-metal chelates show four bands corresponding to the four transitions from the ground state ( $^3\text{H}_4$ ) to various excited state ( $^1\text{D}_2$ ,  $^3\text{P}_0$ ,  $^3\text{P}_1$ ,  $^3\text{P}_2$ ), & the Nd(III)-metal chelates show ten bands originating from the ground state  $^4\text{I}_{9/2}$  to various excited states ( $^4\text{F}_{3/2}$ ,  $^4\text{F}_{5/2}$ ,  $^4\text{F}_{7/2}$ ,  $^4\text{F}_{9/2}$ ,  $^4\text{G}_{5/2}$ ,  $^5\text{G}_{7/2}$ ,  $^2\text{G}_{9/2}$ ,  $^4\text{G}_{11/2}$ ,  $^2\text{P}_{1/2}$ ) in the visible region. The bands for different transitions have been identified by comparing the values of energies with corresponding value in a free metal-ion. The spectra have been analyzed and the various parameters have been evaluated. The values of these parameters for Pr (III) & Nd (III)-metal chelates have been summarized in Table -1.3 & 1.4, respectively, in different metal-ligands molar-ratio.

The spectral or photo-physical properties of rare earth metal chelates depend upon intra-configurational transitions that take place through magnetic dipole, induced electric dipole or electric quadrupole transitions (governed by Laporte & spin-multiplicity rule). The magnetic dipole transitions are spectroscopically allowed but their intensity is independent of surrounding matrix, on the other hand induced electric dipole transitions are spectroscopically forbidden but in a coordinating environment these become allowed as asymmetric ligand field mixes the electronic states with opposite parity within  $4f^n$  configuration. The theoretical method for energy calculation of different  $4f^n$  transitions was initially developed by Slater & Codon<sup>17, 21</sup> but it could not be applied to configurations higher than  $4f^2$ . Later on Racah<sup>24-26</sup> developed a tensor-operated method which was extended by Judd<sup>30</sup>, Wybourne<sup>28</sup> Dieke<sup>29</sup> & others. Here interactions among  $4f$  electrons were expressed in term of Slater-Codon ( $F_k$ ), Racah( $E^k$ ) & Lande( $\zeta_{4f}$ ) parameters. These parameters are collectively referred to as energy parameters. Judd<sup>30</sup> & Ofelt<sup>31</sup> independently developed a theory for calculating induced electric dipole matrix elements and the effect of the coordinating environment on the intensity of spectral peaks were expressed in terms of the Judd-Ofelt intensity parameters ( $\Omega_\lambda$ ,  $\lambda=2,4,6$ ). The intensity parameters along with nephelauxetic effect ( $\beta$ ) & bonding parameter ( $b^{1/2}$ ) are indicative of covalency in a metal-ligand bond. Thus, the study of these parameters (energy, intensity & bonding) provides useful information regarding coordination & bonding in rare earth metal chelates.

### (1) ENERGY PARAMETERS

#### (a) Racah Parameter (E) & Slater-Condon Parameter ( $F_k$ ):

The Racah parameters can be expressed as the linear combination of Slater-Condon parameter ( $F_k$ ). The Racah parameters may be calculated by the following relations<sup>28, 35</sup>.

$$E^1 = (70 F_2^2 + 231 F_4 + 2002 F_6) / 9 \quad \dots(1.7a)$$

$$E^2 = (F_2 - 3F_4 + 7F_6) / 9 \quad \dots(1.7b)$$

$$E^3 = (5 F_2 + 6 F_4 - 91 F_6) / 3 \quad \dots(1.7c)$$

The trend of values both Racah parameters(E) & the Slater-Condon ( $F_k$ ) is same for all the metal chelates and were found to be  $E^1 > E^3 > E^2$  and  $F_2 > F_4 > F_6$  which is in conformity with the earlier findings<sup>36, 37</sup>.

On chelation, the values of  $F_2$  parameter reduces in the range of 2.85-3.70% for the Pr(III) metal-chelates as compared to the free/aquo ion value & in the range of 1.15-3.30% for the Nd(III) metal-chelates. This suggests that interaction of the  $4f$ -orbital of the metal ion with the ligand orbitals decreases in the order Pr (III) > Nd (III). The values of  $F_2$  parameters for the metal ions have been calculated by using the empirical relation<sup>38</sup>

$$F_2 = 12.4 (Z-34).$$

The  $F_2$  values calculated from this empirical relation were found to be 310.00 & 322.48 for the Pr (III) & Nd (III)-metal chelates, respectively, which are less than 1% of the computed values obtained from the observed spectra. The ratio  $F_4/F_2$  for Pr(III) metal chelates is 0.1381, but for Nd(III)-metal chelates varies from 0.1560 to 0.1611, respectively. These values are slightly higher than those calculated by assuming  $4f$ -wave function to be hydrogenic<sup>39</sup> wave function (~0.138) or by Hartee-Fock methdos<sup>40</sup> (~0.130). The  $F_6/F_2$  ratio for Pr (III) chelates have been found to be 0.0151 & for the Nd (III) chelates it varies from 0.1390 to 0.0183 which are nearly equal to that of hydrogenic wave function<sup>41</sup> (~0.0151). This justifies the approximation made in the case of Pr (III) chelates. In the case of Pr (III) chelates the number of levels observed is just equal to the number of parameter to be evaluated, so only  $F_2$  &  $\zeta_{4f}$  have been calculated and values of the  $F_4$  &  $F_6$  are calculated in term of  $F_2$  by the relations

$$F_4 = 0.1380 F_2 \text{ \& } F_6 = 0.0151 F_2.$$

From these equations it is clear that the ratio  $F_4/F_2$  &  $F_6/F_2$  are respectively equal to 0.1380 & 0.0151 & remains constant.

(b) *Lande ( $\zeta_{4f}$ ) Parameter:*

The spin-orbit coupling constants, Lande parameter ( $\zeta_{4f}$ ), for the aquo metal ion is given by<sup>42</sup> –

$$\zeta_{4f} = 142 (Z-7648).$$

The simple calculation gives the 748.14 & 497.00 value of  $\zeta_{4f}$ , for Pr (III) & Nd (III) aqua ion, respectively. The observed values lie between 686.51 & 681.42  $\text{cm}^{-1}$  for the Pr. (III) and 497.80, & 499.07  $\text{cm}^{-1}$ , for the Nd (III)-chelates, respectively, which are in close agreement with the empirical values. The energy ( $E_{\text{cal}}$ ) of various observed transitions for Pr (III) & Nd (III) chelates have been calculated using the computed values of  $F_k$  &  $\zeta_{4f}$  parameters & are summarized in Table 1.3 and 1.4. The  $\sigma_{\text{r.m.s}}$  deviation of the calculated & observed energy values are in ranges of  $1.32 - 1.65 \times 10^{-6}$  for Pr (III)-chelates & for the Nd (III)-chelates it is  $0.76 - 0.91 \times 10^{-6}$  & the small value of  $\sigma_{\text{r.m.s}}$  deviation shows validity of the Judd-Ofelt theory and the calculations made.

Finally, the reduction in the values of  $F_k$  &  $\zeta_{4f}$  with respect to free aquo ion is an evidence for the chelation. The lowering of these values further indicates the expansion of the metal orbitals on chelation. But this lowering is not significant with change in metal-ligands stiochiometries, thereby showing ligands have little effect on the spectral pattern & points towards outer sphere chelation<sup>43</sup> & the covalence of metal-ligand bond. The lowering in  $\zeta_{4f}$  values is more than that of the  $F_k$  values on chelation.

(2) INTENSITY PARAMETERS: *Oscillator strength (P) & Judd-Ofelt ( $\Omega_\lambda$ ) Parameters:*

The oscillator strength value is a measure of intensity & degree of allowance of a specific electronic transition and these values show the marked dependence on the cations environment. The oscillator strength is highest for the transition,  $^3\text{H}_4 \rightarrow ^3\text{P}_2$  suggesting it to be a hypersensitive transition for the Pr (III) chelates, and  $^4\text{I}_{9/2} \rightarrow ^4\text{G}_{5/2}^*$  appears to be hypersensitive transition in the Nd(III) chelates. The value of oscillator strength for hypersensitive transition is highest

for all the metal-chelates whenever the primary ligand is tartaric acid & secondary ligand is glycine. And the effect of secondary ligand is also clear from the data, the values of interelectronic shows more decrease for glycine than for  $\beta$ -alanine. The decrease in the value of  $\zeta_{df}$  as compared to free ion clearly suggest the decrease in spin-orbit interaction as also evident by the general red shift in case of all the metal chelates. The value of nephelauxetic ratio ( $\beta$ ) is less than one indicating that interaction is not merely ionic but there is some sort of mixing of metal-ligand orbitals.

The intensity of the observed bands have been given in terms of the oscillator strength (P) & the Judd-Ofelt parameters  $\Omega_\lambda$  ( $\Omega_2$ ,  $\Omega_4$  &  $\Omega_6$ ) for all the metal – chelates & have been computed by using values of the oscillator strength. The matrix elements  $U^{(\lambda)}$  were taken as given by Carnell<sup>44</sup>. Out of these three parameters,  $\Omega_2$  parameters shows high sensitivity towards co-ordination while  $\Omega_4$  &  $\Omega_6$  have been found to exhibit more sensitivity towards symmetry changes around the metal-ion. The values of the intensity parameters for all the metal-chelates have been summarized in Tables 1.1 & 1.2. The value of  $\Omega_4/\Omega_6$  ranges from 0.151 to 0.301 for Pr (III)-chelates & 0.184 to 0.825 for Nd(III)-metal chelates, respectively, indicating similar symmetry of stereo environment around these metal-ions is through oxygen & nitrogen donor atom.

### (3) BONDING PARAMETERS: Nephelauxetic ( $\beta$ ) & Bonding ( $b^{1/2}$ ) Parameters:

The data summarized in Tables – 1.3 & 1.4 reveal that the values of nephelauxetic ratio for the Pr (III) & Nd (III) chelates are in the range of 0.963 to 0.967 & 0.960 to 0.970 ,respectively. From these values it has been found that the nephelauxetic ratio ( $\beta$ ) for the chelates of Pr (III) & Nd (III) follows the order Pr-SG > Pr-S $\beta$  > Pr-T $\beta$  > Pr-TG & Nd-LG < Nd-L $\beta$  < Nd-TG < Nd-S $\beta$  < Nd-SG, respectively. Similarly bonding parameter ( $b^{1/2}$ ) values for Pr (III) & Nd(III) chelates have been found between 0.136 to 0.131 & 0.122 to 0.137, respectively. These values for Pr(III) & Nd (III) chelates follows the order Pr-SG < Pr-LG < Pr-T $\beta$  < Pr-TG & Nd-SG < Nd-T $\beta$  < Nd-SG < Nd-TG < Nd-LG, respectively. Both the nephelauxetic ( $\beta$ ) & bonding ( $b^{1/2}$ ) parameters indicate that the covalency in metal-ligand bond is the highest in the Pr-TG chelate among all the Pr(III) and the lowest is in the Nd-TB chelate among all the Nd(III) chelates.

Based on these data it may be concluded that in all the chelates, the metal – ligand bond is not merely ionic but there is covalency up to some extent. The order of covalency, on the basis of these data, in all the metal-chelates with these ligands, is as follows Pr-TG > Pr-T $\beta$  > Pr-S $\beta$  > Pr-SG & Nd-LG > Nd-L $\beta$  > Nd-TG > Nd-SG > Nd-T $\beta$ . These data also suggests that ,in the present case ,in all the chelates, It is interesting to point out that the covalency decreases as the atomic number of rare earth metal ion increases .Thus the order of covalency in complexes will be Pr (III) > Nd (III).

### CONCLUSION:

For all the Pr (III) & Nd (III) metal-chelates, the value of interelectronic repulsion parameters especially, the Slater & Condon decreases from free ion value indicating complexation (Table 1.1 & 1.2). Among all the Pr (III) & Nd (III) metal-chelates, the decrease is more pronounced for group of Pr (III) & Nd (III) metal-chelates consists of tartaric acid as primary ligand & glycine or  $\beta$ -alanine as secondary ligands, respectively, probably due to more effective coordination sites provided by the two adjacent -COOH groups in tartaric acid as compared of group of Pr (III) & Nd (III) metal-chelates consists lactic acid or salicylic acid as primary ligands & , glycine or  $\beta$ -alanine as secondary ligands, respectively. The effect of secondary ligand is also clear from the data, the values of interelectronic shows more decrease for glycine than for  $\beta$ -alanine. The decrease in the value of, Lande parameter  $\zeta_{df}$  as compared to free ion clearly suggest the decrease in spin-orbit interaction as also evident by the general red shift in case of all the metal chelates. The value of nephelauxetic ratio ( $\beta$ ) is less than one indicating that interaction is not merely ionic but there is some sort of mixing of metal-ligand orbitals, i.e. co-valent.

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