

Photo-physical properties of Pr (III) chelates of substituted nitrobenzoic acid and nitrophenols

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Abstract

Electronic absorption and emission spectra were recorded for chelates of Pr (III) with 2-hydroxy-4-nitrobenzoic acid, 3-hydroxy-4-nitrobenzoic acid, 4-hydroxy-3-nitrobenzoic acid, 4-methyl-2-nitrophenol, 4-chloro-2-nitrophenol and 5-fluoro-2-nitrophenol in various M: L stoichiometry and for different pH. Intensity and energy of intraconfigurational $4f^n$ transitions have been determined from the absorption spectra. The spectroscopic parameters like Slater-Condon (F_k), Racah (E^k), Lande (ζ_{4f}) and Judd-Oflet parameters Ω_λ ($\lambda=2, 4, 6$) have been computed using statistical method like partial regression method. The Judd-Oflet intensity parameters and fluorescence spectra have been used to calculate radiative life time (τ) of two excited states 3P_0 and 1D_2 . From the fluorescence spectra of the chelates, effective line width ($\Delta\lambda_{eff}$) spontaneous emission probability (A), fluorescence branching ratio (β) and stimulated emission cross section (σ) have been determined for three optical transition 3P_0 - 3H_4 , 3P_0 - 3H_5 and 1D_2 - 3H_4 . Spectroscopic and intensity parameters were studied with respect to the ligand field symmetry and degree of bond covalency.

Keywords: Praseodymium, Substituted nitrobenzoic acid, Substituted nitrophenols, Photo physical properties, Judd Oflet parameter, Laser parameter.

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Introduction

Rare earth metal complexes in the recent days are tools for various emerging fields from ranging from laser technology to bio-medical arenas [1-9]. As a part of systematic investigation, the complexes of hydroxy nitrobenzoic acid (2-hydroxy-4-nitrobenzoic acid, 3-hydroxy-4-nitrobenzoic acid and 4-hydroxy-3-nitrobenzoic acid) and substituted nitrophenols (4-methyl-2-nitrophenol, 4-chloro-2-nitrophenol, and 5-fluoro-2-nitrophenol) with rare earth metal ions were studied in detail for their photo-physical properties as literature survey indicates little work on these complexes [10-25].

In the current pursuit, Pr (III) chelates of hydroxy nitrobenzoic acid and substituted nitrophenols were selected for study and their absorption and emission spectra were recorded and analyzed for various spectroscopic parameters (energy, intensity and laser parameters). Praseodymium exhibits characteristic f-f absorption spectrum which corresponds to transitions from the ground state multiplet to the excited state multiplet. These transitions have a fixed

spectral position but their intensity and fine structure may vary with embedding matrix. The intensity of these multiplet-to-multiplet transitions has been successfully described by the Judd-Oflet theory [26-27]. According to Judd-Oflet theory, mixing between $4f^n$ configuration and another configuration having opposite parity may be occurred by the crystal field potential and cause $4f$ - $4f$ transitions to be allowed by the induced electric dipole. The spectra of Praseodymium consist of four peaks spectra with narrow bands with in the visible regions, representing the transition between 3H_2 (ground state) to 1D_2 , 3P_0 , 3P_1 , 3P_2 (excited states). The primary object of this investigation is to determine the Judd-Oflet* intensity parameters from the oscillator strength of absorption peaks and to examine how intensity parameters respond to the minor changes in the ligand environment. In addition to this, spectroscopic parameters Slater-Condon [28-29] (F_k), Racah [30-33] (E^k), Lande (ζ_{4f}) were also determined to study degree of covalency in the metal-ligand interaction. Using the Judd-Oflet intensity parameters Ω_λ ($\lambda=2, 4, 6$) and fluorescence spectra of the complexes, laser parameters like radiative lifetime of excited states, spontaneous emission probability,

fluorescence branching ratio and stimulated emission cross section of optical transitions were also evaluated to examine the alteration in fluorescence properties in conjunction with that of structure of the complex.

Experimental Studies

Hydroxy nitrobenzoic acid [2-hydroxy-4-nitrobenzoic acid, 3-hydroxy-4-nitrobenzoic acid and 4-hydroxy-3-nitrobenzoic acid] and substituted nitrophenols [4-methyl-2-nitrophenol, 4-chloro-2-nitrophenol, and 5-fluoro-2-nitrophenol] were obtained from Acros-Organics and used directly. Acetate salts of Praseodymium were obtained from Indian Rare Earths Ltd., India. All other chemicals were obtained from Ranbaxy, India ltd. All solutions were prepared prior to the experiments in double distilled deoxygenated water. Stock solutions of 0.01 M ligand and 0.01 M metal ions were also prepared in deoxygenated water. The absorption studies were carried out with the sample solutions of metal and ligands in stoichiometric ratio (M:L) of 1:1, 1:2, 1:3 and 1:4 to record the spectra. The absorption spectra of the sample solutions were recorded at the room temperature in the range of 400-700nm using Systronic-119 spectrophotometer with a scan speed 600 nm/min. The pH of 1:2 M:L solution has been altered in the range of 4.5-7.5 to obtain optimum pH range. The fluorescence spectra were recorded at room temperature on Hitachi Fluorescence spectrophotometer model F-3000 having a xenon lamp and spectral range of 200-900nm at the excitation wavelength of 443.5 nm.

Theory of Rare earth Spectroscopy

The effective Hamiltonian [33-35] of rare earth metal ion under the influence of a ligand field is composed of four terms

$$H = H_c + H_e + H_m + H_L$$

$$H = \sum_{i=1}^N \left(-\frac{\hbar^2}{2m_e} \Delta^2_i - \frac{Ze^2}{4\pi\epsilon_0} \right) + \sum_{i>k=1}^N \frac{e^2}{4\pi\epsilon_0 r_{ik}} + \sum_{i=k}^N \frac{Ze^2 \hbar^2}{8\pi\epsilon_0 C^2 m_e^2 r_i^3} \vec{S}_i \cdot \vec{l}_i + \sum_{i=1}^N \sum_{i=1}^M \frac{Ze^2}{d_{ii}} \dots 1.1$$

Here, first term H_c represents the undisturbed Hamiltonian (central field approximation), the second term H_e represents columbic interactions which were calculated by Slater [28], shortely, Codon [29] and Racah [30-32] using tensor operated methods and are expressed in terms of Slater Codon (F_2, F_4, F_6) and Racah parameters (E_1, E_2, E_3). The third term H_m gives spin orbit interactions, expressed as Lande parameter (ζ_{4f}). The final term H_L is the ligand field Hamiltonian (configuration interaction) which is expressed as interaction parameters (α).

(a) Calculation of Energy parameters:

The Taylor series expansion method used by Wong [34-38] and other workers has been utilized for the evaluation of the spectroscopic parameters from the observed spectra [figure

1.1-1.3 and 2.1-2.3] for different M:L ratios and for different pH values. The energy E_j of the j^{th} level is given by the equation

$$E_j(F_k, \zeta_{4f}) = E_{0j}(F_k, \zeta_{4f}) + \sum_{k=2,4,6} \frac{\partial E_j}{\partial F_k} \Delta F_k + \frac{\partial E_j}{\partial \zeta_{4f}} \Delta \zeta_{4f} \dots 1.2$$

where E_{0j} = Zero order energy of the j^{th} level and ΔF_k & $\Delta \zeta_{4f}$ are the small changes in the corresponding parameters. The values of zero order energy E_{0j} and partial derivatives for the observed values of Pr(III) calculated by Wong has been used in the current evaluation. The values of ΔF_k & $\Delta \zeta_{4f}$ have been calculated by partial regression method. The values of F_k and ζ_{4f} are then calculated using following equations [Table 1.1 and Table 2.1].

$$[F_k = F_k^0 + \Delta F_k] \quad k=2, 4, 6 \quad \dots 1.3$$

$$\zeta_{4f} = \zeta_{4f}^0 + \Delta \zeta_{4f} \quad \dots 1.4$$

where F_k^0 and ζ_{4f}^0 are the zero order values of the corresponding parameters. The Racah parameters E_k have been calculated from F_k parameters using following equations

$$E^1 = \frac{[70F_2 + 231F_4 + 2002F_6]}{9} \quad \dots 1.5$$

$$E^2 = \frac{[F_2 - 3F_4 + 7F_6]}{9} \quad \dots 1.6$$

$$E^2 = \frac{[5F_2 + 6F_4 - 91F_6]}{3} \quad \dots 1.7$$

Using the computed F_k and ζ_{4f} values, the E_j values (E_c) have been calculated for Pr (III) complexes with three ligands [and are listed in Table 1.1 and Table 2.1]. The nephelauxetic effect and bonding parameter, important tools for determination of degree of covalency, have also been evaluated using the following equations 1.8.

$$\beta = \frac{F_k^C}{F_k^f} \quad \text{and} \quad b^{1/2} = \left[\frac{(1-\beta)}{2} \right]^{1/2} \quad \dots 1.8$$

where f and c refer to the free ion and complex respectively. The values of Slater-Codon (F_2, F_4, F_6) and Racah parameters (E^1, E^2, E^3) Lande (ζ_{4f}) along with nephelauxetic effect and bonding parameters are listed in Table 1.2 and Table 2.2.

(b) Calculation of oscillator strength and intensity parameter

The experimental oscillator strength (P_{exp}) of the observed bands have been calculated by using the relation

$$P_{exp} = 4.318 \times 10^{-9} \int \epsilon(\tilde{\nu}) d\tilde{\nu} \quad \dots 1.9$$

where $\epsilon(\nu)$ is the molar absorption coefficient at the energy ν and the integral corresponds to the area of the absorption band for certain transition. The theoretical oscillator strength P_{cal} were calculated by employing Judd-Oflet theory taking into account that f-f transitions are predominately induced electric dipole transitions. According to Judd-Oflet the oscillator strength of a transition between initial J manifold and terminal J'

manifold, is given by

$$P_{cal} = \left(\frac{8\pi^2 m c \nu (n^2 + 2)^2}{3h(2J+1)9n} \right) \sum_{\lambda=2,4,6} \Omega_{\lambda} \left| \langle f^N(\alpha, S, L) J \parallel U^{(\lambda)} \parallel f^N(\alpha', S', L') J' \rangle \right|^2 \quad \dots 2.0$$

where $\|U^{(\lambda)}\|$ represents the square of the reduced matrix elements of the unit tensor operator $U^{(\lambda)}$ connecting the initial and final states, summing over the three values $\lambda=2,4,6$. In the above equation the Ω_{λ} quantities, called as the Judd-Oflet intensity parameters were obtained from the least square analysis of the observed oscillator strength by employing the following equation.

$$P_{exp} = \Omega_2 \nu [U^2]^2 + \Omega_4 \nu [U^4]^2 + \Omega_6 \nu [U^6]^2 \quad \dots 2.1$$

where ν is the energy of the band in cm^{-1} . The values of judd-Oflet intensity parameters are listed in table 1.3 and table 2.3 for all the three kinds of chelates.

(c) Calculation of laser parameters:

Judd-Ofelt intensity parameters calculated above were used for the determination of radiative properties of rare earth metal complexes. Thus the Ω_{λ} values thus obtained from the absorption measurements are used to calculate the spontaneous emission probability (A), branching ratios, radiative life time and stimulated emission cross section as per equations given below where the symbols have usual meanings [42-43].

(i) **Spontaneous emission probability (A)**-The spontaneous emission probability from an initial J manifold to terminal J' manifold is given by

$$A = \frac{64\pi^4 e^2}{3h(2J'+1)\lambda_p^3} n \left[\frac{(n^2+2)^2}{9} \right] \times \sum_{\lambda=2,4,6} \Omega_{\lambda} \left| \langle f^N(\alpha', S', L') J' \parallel U^{(\lambda)} \parallel f^N(\alpha, S, L) J \rangle \right|^2 \quad \dots 2.2$$

The A values for different emission transitions, are calculated by substituting the emission wave length λ_p reduced matrix elements for the relevant transition and the values of Ω_{λ} parameters

(ii) **Fluorescence branching ratio (β)**-The fluorescence branching ratio for the transitions originating from a specific manifold is defined by

$$\beta = \frac{A}{\sum_{\alpha, S, L, J} A} \quad \dots 2.3$$

the values depend upon Ω_4 and Ω_6 parameters which in turn depend upon the coordination environment.

(iii) **Radiative lifetime (τ)**-The radiative life time τ for a transition is reciprocal of spontaneous emission probability A. For radiative decay from the initial J' manifold $|f^N(\alpha', S', L') J' \rangle$ it is given by

$$\tau = A^{-1} \quad \dots 2.4$$

(iv) **Stimulated emission cross-section (σ_p)**-The stimulated emission cross-section (σ_p) for transition from an initial J

manifold $|f^N(\alpha', S', L') J' \rangle$ to terminal J manifold $|f^N(\alpha, S, L) J \rangle$ is expressed as

$$\sigma_p = \frac{\lambda_p^4}{8\pi c n^2 \Delta\lambda_{eff}} A \quad \text{and} \quad \Delta\lambda_{eff} = \frac{\int I(\lambda) d\lambda}{I_{max}} \quad \dots 2.5$$

where λ_p the peak fluorescence is wave length of the emission band and $\Delta\lambda_{eff}$ is the effective fluorescence line width and $I(\lambda)$ is fluorescence intensity at wavelength λ . The rate of energy extraction from a laser material is dependent on the stimulated emission cross-section σ_p . This parameter is most important among laser parameters and is generally used to predict laser action. The values of above mention laser parameters for Praseodymium chelates are listed in table 1.4 and table 2.4.

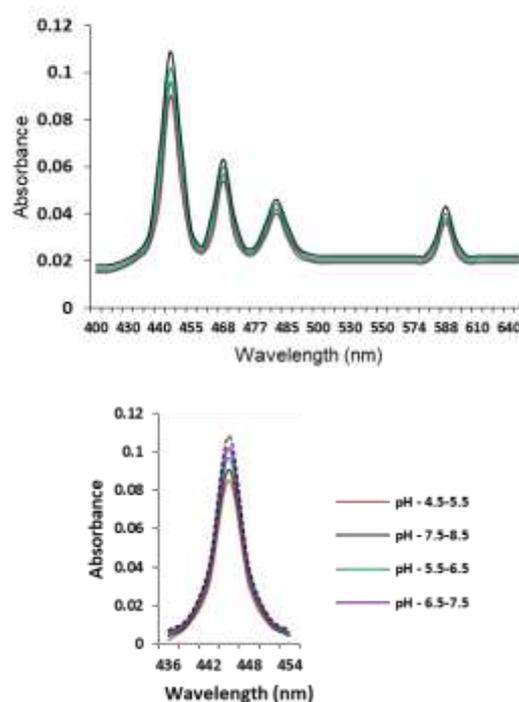
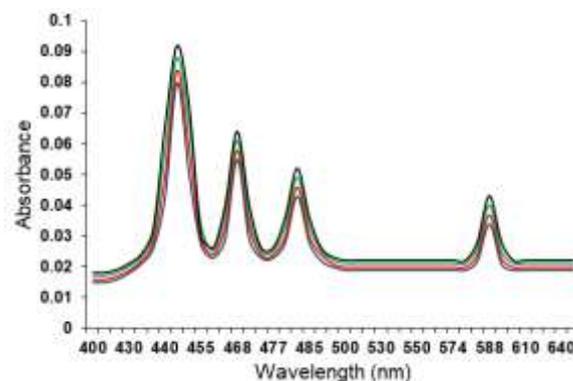


Figure 1.1 Absorption spectra of Pr(III)-2H4NBA for different molar ratios and for different pH



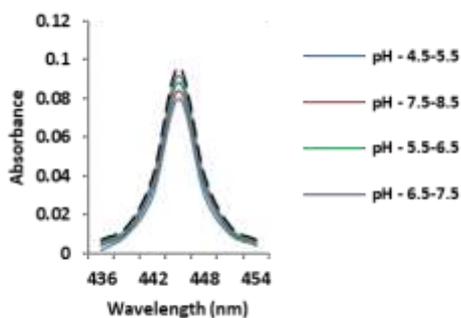


Figure 1.2: Absorption spectra of Pr(III)-3H4NBA for different molar ratios and for different pH

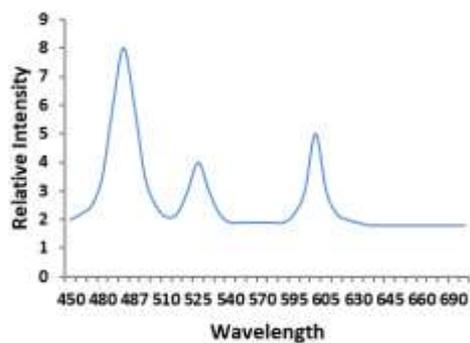


Figure 1.5: Fluorescence spectra of Pr(III) -3H4NBA

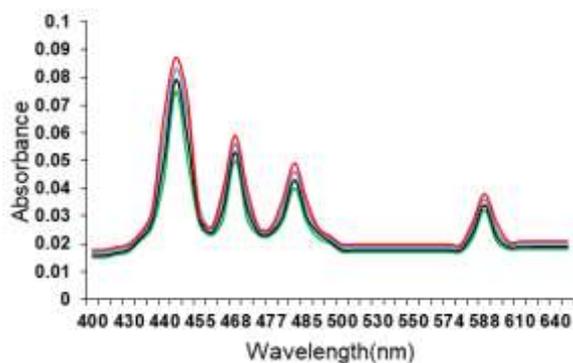


Figure 1.3 Absorption spectra of Pr(III)-4H3NBA for different molar ratios and for different pH

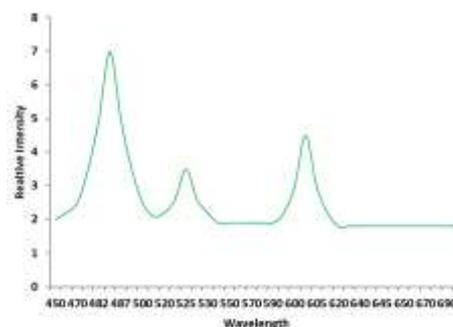
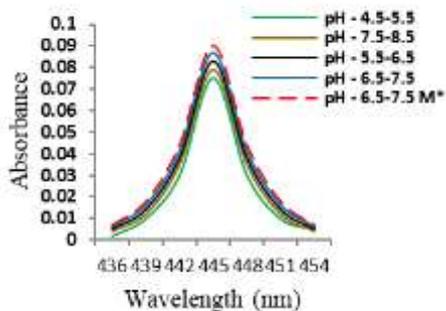


Figure 1.6: Fluorescence spectra of Pr(III) - 4H3NBA

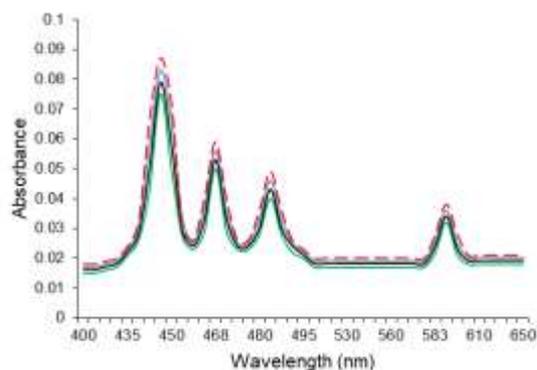


Figure 2.1: Absorption spectra of Pr(III)-4M2NP for different molar ratios and for different pH

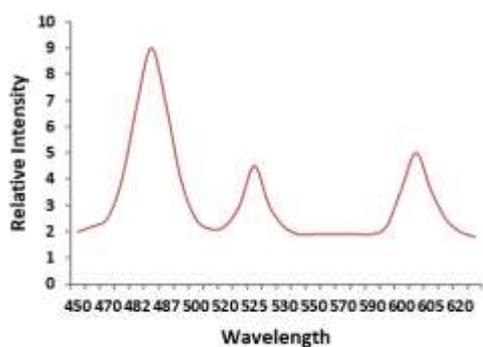
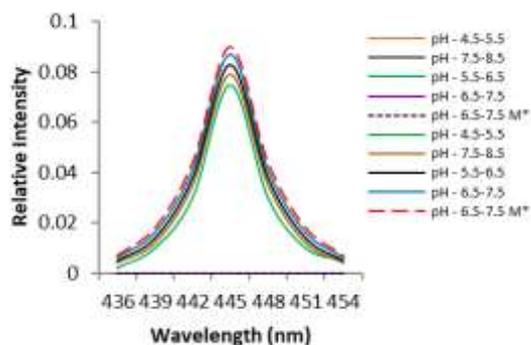


Figure 1.4: Fluorescence spectra of Pr(III) -2H4NBA



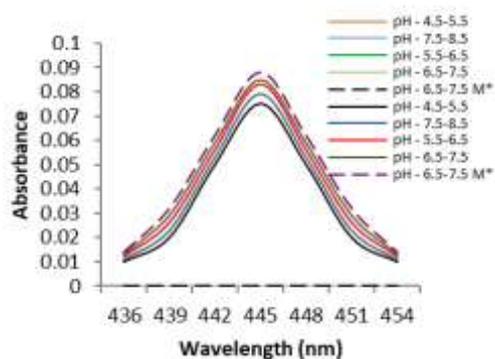
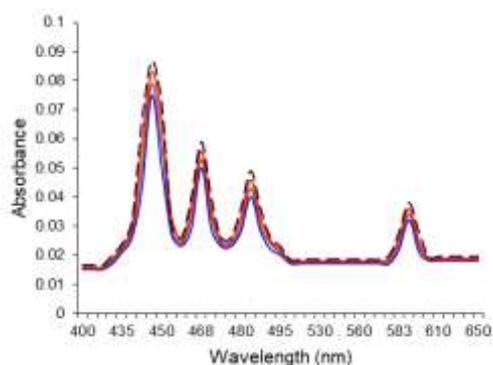


Figure 2.2: Absorption spectra of Pr(III)-4C2NP for different molar ratios and for different pH

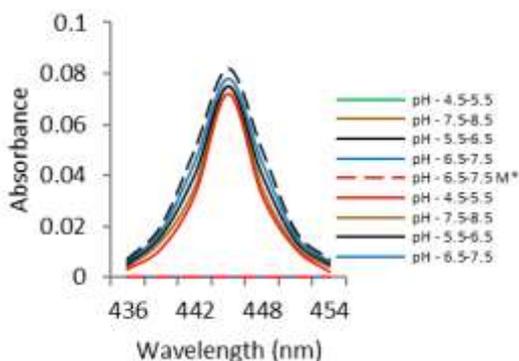
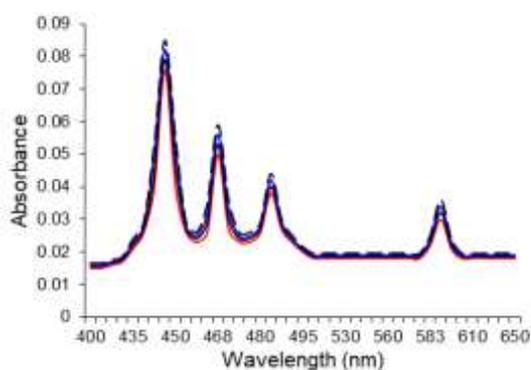


Figure 2.3: Absorption spectra of Pr(III)-4F2NP for different molar ratios and for different pH

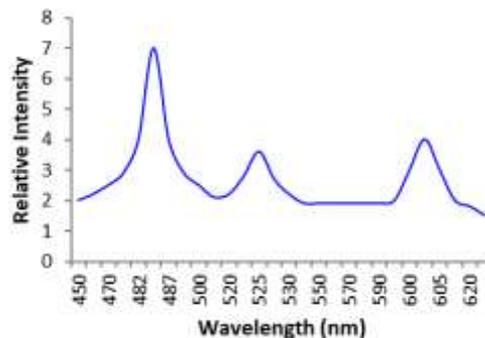


Figure 2.4: Fluorescence spectra of Pr(III)-4M2NP

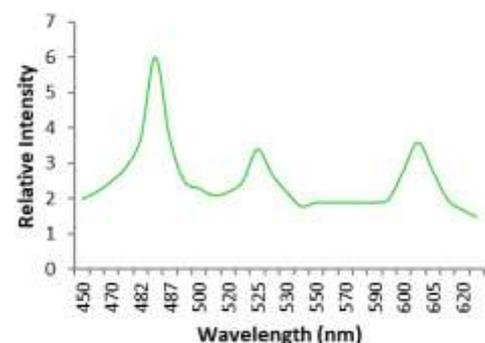


Figure 2.5: Fluorescence spectra of Pr(III)-4C2NP

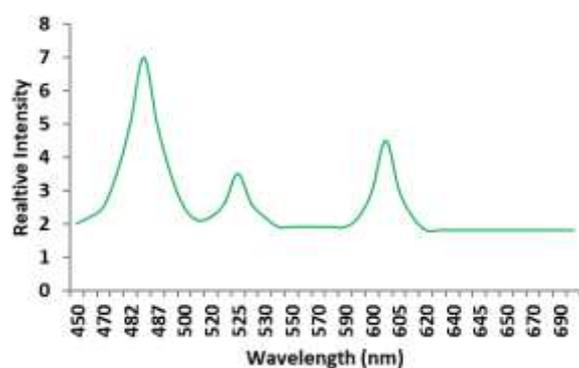


Figure 2.6: Fluorescence spectra of Pr(III)-5F2NP

Result and Discussion

(a) Oscillator Strength:

The absorption spectra of Praseodymium chelate in the wave length range of 400-650 nm at room temperature containing substituted nitrobenzoic acid (2H4NBA, 3H4NBA, 4H3NBA) are given in figure 1.1-1.3 and for the substituted nitrophenols (4M2NP, 4C2NP, 5F2NP) in the figure 2.1-2.3. The solution spectra have been analysed 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 which are a measure of intensities of specific electronic transitions or degree, to which a specific transition is allowed, show marked dependence on the cation environment. The four distinct bands in the visible region can be attributed to the excitation

from the ground state (3H_4) to various excited states (1D_2 , 3P_0 , 3P_1 , $^3P_2^*$). To ascertain the molar ratio for optimum molecular stacking in solution, absorbance of complexes was recorded for four different ratios (1:1, 1:2, 1:3 and 1:4) and oscillator strength was calculated (table 1.1 for series A and table 2.1 for series B). For different molar ratios, value of absorbance was found to be in order $1:1 < 1:4 < 1:3 < 1:2$ showing the bidentate nature of ligand and metal complex can be abbreviated as $[Pr(nba)_2](CH_3COO)_3$ and $[Pr(np)_2](CH_3COO)_3$ [where $nba=2H_4NBA$, $3H_4NBA$, $4H_3NBA$ and $np=4M_2NP$, $4C_2NP$, $5F_2NP$]. To understand the effect of pH on complexation, the absorption spectra of metal chelate were recorded in the wave length 430-460 nm for different pH range [4.5-5.5, 5.5-6.5, 6.5-7.5, and 7.5-8.5]. The absorbance value for a particular pH range represents the weighted average of three values measured at three different points (for example three pH points 4.5, 5.0, 5.5 were selected for pH range 4.5-5.5). The absorbance of metal chelates was found to be in the order $4.5-5.5 < 5.5-6.5 < 6.5-7.5 > 7.5-8.5$ (see figure 1.2 and 2.2). The decrease in value at higher pH can be attributed to the precipitation of metal chelate as turbidity appeared in solution after pH 7.5

(b) Energy Parameters:

The E_j values using Wong Equation 1.2 have been calculated for all the observed transitions of Pr(III) complexes with 2 series of ligands for different pH range. The values in table 1.2 (for ligands of series A) and in table 2.2 (for ligands of series B) is the average of three measurements done at various pH points for a given pH range and their value has been listed in Table 1.2 and 2.2. The low value of $r. m. s.$ between the experimental and theoretical values of energy for the observed transitions suggests the suitability of above relation. It is the non-centro-symmetrical interactions of metal ion with surrounding ligands that would cause the mixing of electronic states with even parity, thus f-f transitions become allowed ones as induced electric dipole transitions [26-27, 36-41]. During current investigation it has been observed that ligand 2H₄NBA (for ligands of series A) and ligand 4M₂NP (for ligands of series B) produces greater amount of vibronic coupling with central metal ion. The nature of metal-ligand bond can be analyzed in terms of Slater-Condon parameters (F_k and E^k) which represent the magnitude of interelectronic repulsions in metal ions. The decrease in value of these parameters in metal complexes (Table 1.2-series A and Table 2.2-series B) as compared to free aqua ion indicates expansion of f electron cloud which can be attributed in terms of degree of complexation.

The value of these parameters (F_K , E^k and ζ_{4f}) have been computed for different pH range and it was found that value decreases with increase in pH and was found to be lowest for the range 6.5-7.5. Thus, this range appears to be optimum pH range for the molecular stacking in solution. Among two series of chelates, the decrease in value of Slater and Codon parameters (F_k and E^k) is more for series A containing substituted nitro benzoic acids than series B.

For three ligands of nitrobenzoic series (series A), the value

of F_k and E^k [see table 1.2] were chosen to determine the order of complexation tendency. The values were found to be lowest for the complex $[Pr(nba)_2](CH_3COO)_3$ {where $nba=2H_4NBA$ } as compared to other two chelates. This is probably due to adjacent attachment of hydroxyl to carboxylic group and meta position of nitro group as compared with hydroxy group in 2H₄NBA. In case of series B (containing hydroxy nitro-phenols), the value of F_k and E^k is lowest for $[Pr(np)_2](CH_3COO)_3$ {where $np=4M_2NP$ } [see table 2.2], this probably due to fact the electron withdrawing effect is more pronounced in halogens (F and Cl) than methyl group. The decrease in the value of ζ_{4f} (as compared with free ion) clearly suggests the decrease in spin-orbit interactions indicating a general red shift in case of metal chelates. It has been found that the nephelauxetic ratio (β) for all the systems is less than one indicating that the metal-ligand interaction is not ionic but there is a mixing of metal and ligand orbitals i.e., the metal-ligand bonding in these chelates is not mere ionic but there is covalency in them.

(c) Intensity Parameters:

The effect of host matrix on local environment for a given rare earth ion can be elucidated using the Judd-Oflet theory by studying changes in the experimentally fitted Judd-Oflet intensity parameters [Ω_λ ($\lambda=2, 4, 6$)]. It has been shown that among the three intensity parameters the Ω_2 is very sensitive to the structural details and chemical environment of the ligand environment. During current investigation, it is found that value of Ω_2 , decrease with upon complexation and it is more pronounced for 1:2 M:L ratio for the given ligand. The decrease is more pronounced for series A [substituted nitrobenzoic acid] than for series B [substituted nitrophenols]. The value is lowest for 2H₄NBA among nitrobenzoic acid and for 4M₂NP among nitrophenols.

(d) Radiative Properties and Fluorescence Spectra:

The fluorescence spectra of three chelates recorded at room temperature using a xenon laser with excitation wavelength of 443.5 nm is shown in figures 1.4-1.6. The spectra consist of three transitions corresponding to $^3P_0-^3H_4$, $^3P_0-^3H_5$ and $^1D_2-^3H_4$ arising from two excited states 1D_2 and 3P_0 . Using the Ω_λ values thus obtained from the absorption measurements are used to calculate spontaneous emission probability, branching ratios, radiative life time and stimulated emission cross section for the metal chelates as per the equations given above. Transitions having spontaneous emission probability (A) greater than 500 sec⁻¹ and fluorescence branching ratio (β) ~ 0.5 are considered to be good radiation transition. It has been observed that among three transitions, value of spontaneous emission probability is maximum for the transition $^3P_0-^3H_4$ for both series of ligands. The value is 722.633 for Pr(III)-2H₄NBA, 620.089 for Pr(III)-3H₄NBA and 562.093 cm⁻¹ for Pr(III)-4H₃NBA. This trend clearly indicates that spontaneous emission probability is related to structural dynamics of chelates. In the case of Pr (III) chelates of nitrophenols, the stimulated emission probability (A) for the transition $^3P_0-^3H_4$ was found to be 606.287 with ligand 4M₂NP, 597.944

with ligand 4C2NP and 589.613 with ligand 5F2NP. These values clearly indicate that among two ligand series, ligands of first category have higher value of stimulated emission probability, probably because they have higher degree of covalency in the metal -ligand linkage.

The luminescence branching ratio (β) is a critical parameter, to the laser designer, because it characterizes the possibility of attaining stimulated emission from any specific transition and among three transitions observed in two series of ligands, only transition ${}^3P_0\text{-}{}^3H_4$ have the adequate value of branching ratio. For the Pr (III) chelates of nitrobenzoic acid and nitrophenols, the observed values are very close (~ 0.76 for the nitrophenols and ~ 0.75 for the nitrobenzoic acid). These values indicate that two kinds of ligands have similar branching ratio for the transition ${}^3P_0\text{-}{}^3H_4$.

Stimulated emission cross section (σ) is most important laser parameter. Its value signifies the rate of energy extraction from the laser material. Value of σ for the Pr (III) chelates with nitrobenzoic series ranges from 1.62-1.39 for the transition ${}^3P_0\text{-}{}^3H_4$, 0.81-0.84 for the transition ${}^3P_0\text{-}{}^3H_5$ and 0.21-0.22 for the ${}^1D_2\text{-}{}^3H_4$. For the Pr (III) chelates with nitrophenols, the observed value ranges from 1.42-1.61 for the transition ${}^3P_0\text{-}{}^3H_4$, 0.78-0.85 for the transition ${}^3P_0\text{-}{}^3H_5$ and 0.24-0.26 for the ${}^1D_2\text{-}{}^3H_4$. Thus, among three transitions observed with both series of ligand ${}^3P_0\text{-}{}^3H_4$ has the maximum value of stimulates emission cross section.

The fluorescence life time (τ) for a transition is reciprocal of A. The minimum value of τ has been obtained for the transition ${}^3P_0\text{-}{}^3H_4$ for the two series of Pr (III) chelates. This fact coupled with other laser parameters clearly indicate that the transition ${}^3P_0\text{-}{}^3H_4$ to be most probable laser transition and 3P0 level to be efficient fluorescence level respectively for two series of metal chelates.

Conclusion

In the present pursuit, the equilibrium, spectroscopic and luminescence studies of Pr(III) metal-chelates have been carried out with two series of ligands. The first series consist of substituted nitrobenzoic acids (2-hydroxy-4-nitrobenzoic acid [2H4NBA], 3-hydroxy-4-nitrobenzoic acid [3H4NBA], and 4-hydroxy-3-nitrobenzoic acid [4H3NBA]) and second series consist of substituted nitrophenols (includes 4-methyl-2-nitrophenol [4M2NP], 4-chloro-2-nitrophenol [4C2NP], and 5-fluoro-2-nitrophenol [5F2NP]). It can be concluded that both series of ligands shows chelation with Praseodymium (III) metal salt and chelation is more pronounced for substituted nitrophenols than substituted nitrobenzoic acids and optimum pH range is found to be 6.5-7. From various energy and intensity parameters, it can be concluded that among substituted nitrobenzoic acids 2H4NBA is more effective in coordination and in substituted nitrophenols 4M2NP show maximum chelation. The Laser parameters also follows the same trend.

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Table-1.1: Observed and computed values of oscillator strengths (P) & energies (E) of Pr(III) chelates containing hydroxy nitrobenzoic acid

| 1:2 M:L ratio | pH | Energy Wavelength and Oscillator Strength | Energy levels | | | | $\sigma_{r.m.s.}$ deviation |
|------------------|-------------|---|---------------|---------|---------|---------|--------------------------------|
| | | | $^3P_2^*$ | 3P_1 | 3P_0 | 1D_2 | |
| 2H4NBA | 6.5- 7.5 | $E_{expt} (cm^{-1})$ | 22538 | 21358 | 20725 | 17016 | 91.55 |
| | | $E_{cal} (cm^{-1})$ | 22450 | 21257 | 20725 | 17140 | |
| | | $P_{expt} \times 10^6$ | 15.730 | 7.869 | 3.581 | 3.991 | 1.47 $\times 10^{-6}$ |
| | | $P_{cal} \times 10^6$ | 15.730 | 5.759 | 5.652 | 3.991 | |
| 3H4NBA | 6.5- 7.5 | $E_{expt} (cm^{-1})$ | 22553 | 21397 | 20731 | 17025 | 96.33 |
| | | $E_{cal} (cm^{-1})$ | 22476 | 21276 | 20733 | 17155 | |
| | | $P_{expt} \times 10^6$ | 14.784 | 6.920 | 3.178 | 3.845 | 1.28 $\times 10^{-6}$ |
| | | $P_{cal} \times 10^6$ | 14.784 | 5.080 | 4.983 | 3.845 | |
| 4H3NBA | 6.5- 7.5 | $E_{expt} (cm^{-1})$ | 22554 | 21400 | 20773 | 17054 | 83.25 |
| | | $E_{cal} (cm^{-1})$ | 22485 | 21298 | 20774 | 17166 | |
| | | $P_{expt} \times 10^6$ | 13.989 | 6.362 | 2.800 | 3.325 | 1.23 $\times 10^{-6}$ |
| | | $P_{cal} \times 10^6$ | 13.989 | 4.606 | 4.526 | 3.325 | |

Table-1.2: Computed values of (F_k), (ζ_{4f}), (E^k) (in cm^{-1}), (β) and ($b^{1/2}$) parameters of Pr (III) chelate containing hydroxy nitrobenzoic acid in various metal-ligand stoichiometries and at different pH

| M:L Ratio | pH | chelates | Slater-Condon parameters (F_k) | | | Lande parameter ζ_{4f} | Racah parameters (E^k) | | | Nephelauxetic β | Bonding parameter $b^{1/2}$ |
|--------------|-------------|----------|---------------------------------------|--------|-------|------------------------------------|----------------------------|--------|---------|--------------------------|-----------------------------------|
| | | | F_2 | F_4 | F_6 | | E^1 | E^2 | E^3 | | |
| 1:1 | 6.5- 7.5 | 2H4NBA | 310.406 | 42.851 | 4.690 | 705.023 | 4557.320 | 23.839 | 460.766 | 0.9637 | 0.1346 |
| | | 3H4NBA | 310.542 | 42.870 | 4.692 | 705.473 | 4559.326 | 23.849 | 460.969 | 0.9641 | 0.1338 |
| | | 4H3NBA | 311.109 | 42.948 | 4.700 | 704.416 | 4567.649 | 23.893 | 461.811 | 0.9659 | 0.1305 |
| 1:2 | 4.5- 5.5 | 2H4NBA | 310.155 | 42.816 | 4.686 | 707.579 | 4553.638 | 23.819 | 460.394 | 0.9629 | 0.1361 |
| | | 3H4NBA | 310.260 | 42.831 | 4.688 | 708.364 | 4555.17 | 23.827 | 460.550 | 0.9632 | 0.1355 |
| | | 4H3NBA | 310.996 | 42.933 | 4.699 | 704.517 | 4565.988 | 23.884 | 461.643 | 0.9655 | 0.1312 |
| | 5.5- 6.5 | 2H4NBA | 310.065 | 42.804 | 4.685 | 708.649 | 4552.326 | 23.813 | 460.261 | 0.9626 | 0.1366 |
| | | 3H4NBA | 310.180 | 42.820 | 4.686 | 708.515 | 4554.002 | 23.821 | 460.431 | 0.9630 | 0.1359 |
| | | 4H3NBA | 310.929 | 42.923 | 4.698 | 704.405 | 4565.000 | 23.879 | 461.543 | 0.9653 | 0.1316 |
| | 6.5- 7.5 | 2H4NBA | 309.976 | 42.792 | 4.683 | 709.718 | 4551.015 | 23.806 | 460.129 | 0.9623 | 0.1371 |
| | | 3H4NBA | 310.031 | 42.799 | 4.684 | 713.948 | 4551.821 | 23.810 | 460.210 | 0.9625 | 0.1368 |
| | | 4H3NBA | 310.882 | 42.917 | 4.697 | 704.320 | 4564.315 | 23.875 | 461.474 | 0.9652 | 0.1319 |
| | 7.5- 8.5 | 2H4NBA | 310.318 | 42.839 | 4.688 | 704.869 | 4556.039 | 23.832 | 460.637 | 0.9634 | 0.1351 |
| | | 3H4NBA | 310.360 | 42.845 | 4.689 | 702.878 | 4556.649 | 23.835 | 460.698 | 0.9635 | 0.1349 |
| | | 4H3NBA | 310.952 | 42.927 | 4.698 | 704.575 | 4565.344 | 23.881 | 461.578 | 0.9654 | 0.1314 |
| 1:3 | 6.5- 7.5 | 2H4NBA | 310.246 | 42.829 | 4.687 | 706.452 | 4554.972 | 23.826 | 460.529 | 0.9632 | 0.1355 |
| | | 3H4NBA | 310.295 | 42.836 | 4.688 | 708.235 | 4555.692 | 23.830 | 460.602 | 0.9633 | 0.1353 |
| | | 4H3NBA | 311.022 | 42.936 | 4.699 | 704.672 | 4566.376 | 23.886 | 461.682 | 0.9656 | 0.1310 |
| 1:4 | 6.5- 7.5 | 2H4NBA | 310.303 | 42.837 | 4.688 | 706.163 | 4555.809 | 23.831 | 460.614 | 0.9634 | 0.1352 |
| | | 3H4NBA | 310.344 | 42.843 | 4.689 | 708.146 | 4556.417 | 23.834 | 460.675 | 0.9635 | 0.1350 |
| | | 4H3NBA | 311.087 | 42.945 | 4.700 | 704.082 | 4567.330 | 23.891 | 461.778 | 0.9658 | 0.1306 |

| | | | | | | | | |
|---------------|---------|--------|-------|---------|----------|--------|---------|--|
| Free aqua ion | 322.090 | 44.460 | 4.867 | 741.000 | 4729.000 | 24.740 | 748.140 | |
|---------------|---------|--------|-------|---------|----------|--------|---------|--|

Table-1.3: computed values of Judd-Ofelt (Ω_i) intensity parameters for Pr (III) chelates containing hydroxy nitrobenzoic acid for different metal-ligand stoichiometries and for different pH

| M:L Ratio | pH | Parameters ($\Omega_i \times 10^9$) | Pr (III) - 2H4NBA | Pr (III) - 3H4NBA | Pr (III) - 4H3NBA | |
|-----------|---------|---------------------------------------|-----------------------|-------------------|-------------------|----------|
| 1:1 | 6.5-7.5 | Ω_2 | -14.3015 | -17.2159 | -19.9995 | |
| | | Ω_4 | 1.3119 | 1.2921 | 1.21562 | |
| | | Ω_6 | 4.1226 | 4.0948 | 3.91060 | |
| | | Ω_4 / Ω_6 | 0.3182 | 0.3155 | 0.31085 | |
| 1:2 | 4.5-5.5 | Ω_2 | -11.8053 | -13.4723 | -14.0019 | |
| | | Ω_4 | 1.4230 | 1.3669 | 1.2900 | |
| | | Ω_6 | 4.3673 | 4.2269 | 4.0435 | |
| | | Ω_4 / Ω_6 | 0.3258 | 0.3233 | 0.3190 | |
| | 5.5-6.5 | Ω_2 | -11.3025 | -12.2095 | -12.7652 | |
| | | Ω_4 | 1.4332 | 1.3920 | 1.3149 | |
| | | Ω_6 | 4.3854 | 4.2710 | 4.0887 | |
| | | Ω_4 / Ω_6 | 0.3268 | 0.3259 | 0.3215 | |
| | 6.5-7.5 | Ω_2 | -10.3445 | -10.9524 | -11.5282 | |
| | | Ω_4 | 1.4292 | 1.4148 | 1.3398 | |
| | | Ω_6 | 4.3398 | 4.3154 | 4.1333 | |
| | | Ω_4 / Ω_6 | 0.3293 | 0.3278 | 0.3241 | |
| | | 7.5-8.5 | Ω_2 | -11.5555 | -12.6991 | -13.3771 |
| | | | Ω_4 | 1.4279 | 1.3795 | 1.3025 |
| | | | Ω_6 | 4.3765 | 4.2489 | 4.0659 |
| | | | Ω_4 / Ω_6 | 0.3262 | 0.3246 | 0.3203 |
| 1:3 | 6.5-7.5 | Ω_2 | -12.2089 | -14.7203 | -17.5204 | |
| | | Ω_4 | 1.3916 | 1.3421 | 1.2652 | |
| | | Ω_6 | 4.2732 | 4.1829 | 3.9991 | |
| | | Ω_4 / Ω_6 | 0.3256 | 0.3208 | 0.3163 | |
| 1:4 | 6.5-7.5 | Ω_2 | -13.0713 | -15.9532 | -18.7639 | |
| | | Ω_4 | 1.3363 | 1.3172 | 1.2404 | |
| | | Ω_6 | 4.1663 | 4.1380 | 3.9550 | |
| | | Ω_4 / Ω_6 | 0.3207 | 0.3183 | 0.3136 | |

Table-1.4: The Spontaneous emission probability (A), fluorescence branching ratio (β), total spontaneous probability (A_T), measured $[\tau]$ and radiative fluorescence life time $[\tau_R]$ for Pr (III) chelates containing hydroxy nitrobenzoic acid with fluorescence peak value.

| Metal chelates | Parameters | $^3P_0 \rightarrow ^3H_4$ | $^3P_0 \rightarrow ^3H_5$ | $^1D_2 \rightarrow ^3H_4$ |
|----------------|----------------------------|---------------------------|---------------------------|---------------------------|
| Pr(III)-2H4NBA | λ_p (nm) | 486 | 525.8 | 602.6 |
| | $\Delta\lambda_{eff}$ (nm) | 22.05 | 15.46 | 20.22 |
| | A (sec^{-1}) | 722.633 | 184.397 | 36.378 |
| | B | 0.765855 | 0.195547 | 0.038598 |
| | A_T (sec^{-1}) | 942.981 | | |
| | τ (μs) | 138.5 | 542.3 | 2747.5 |
| | τ_R (μs) | 106.1 | | |
| | σ (pm^2) | 1.622 | 0.810 | 0.211 |
| Pr(III)-3H4NBA | λ_p (nm) | 488 | 526 | 602.9 |
| | $\Delta\lambda_{eff}$ (nm) | 21.22 | 13.32 | 18.45 |
| | A (sec^{-1}) | 620.0869 | 163.7574 | 33.23951 |
| | B | 0.758902 | 0.200417 | 0.040681 |
| | A_T (sec^{-1}) | 817.083 | | |
| | τ (μs) | 161.3 | 610.7 | 3008.5 |
| | τ_R (μs) | 122.4 | | |
| | σ (pm^2) | 1.461 | 0.842 | 0.212 |
| Pr(III)-4H3NBA | λ_p (nm) | 487.1 | 527.2 | 602 |
| | $\Delta\lambda_{eff}$ (nm) | 20.07 | 11.04 | 18.45 |
| | A (sec^{-1}) | 562.093 | 152.591 | 31.491 |
| | β | 0.753299 | 0.204497 | 0.042204 |

| | | | | |
|--|-----------------------------|---------|-------|--------|
| | A_T (sec ⁻¹) | 746.175 | | |
| | τ (μ s) | 177.9 | 655.3 | 3175.5 |
| | τ_R (μ s) | 134.0 | | |
| | σ (pm ²) | 1.390 | 0.812 | 0.211 |

Table-2.1: observed and computed values of oscillator strengths (P) & energies (E) of Pr(III) chelates containing substituted nitrophenols

| 1:2 M:L ratio | pH | Energy Wavelength and Oscillator Strength | Energy levels | | | | σ r.m.s. deviation |
|---------------------|-------------|---|-------------------------------|-----------------------------|-----------------------------|-----------------------------|------------------------------|
| | | | ³ P ₂ * | ³ P ₁ | ³ P ₀ | ¹ D ₂ | |
| 4M2NP | 6.5- 7.5 | E _{expt} (cm ⁻¹) | 22558 | 21404 | 20732 | 16969 | 78.19 |
| | | E _{cal} (cm ⁻¹) | 22446 | 21257 | 20733 | 17139 | |
| | | P _{expt} x 10 ⁶ | 13.783 | 6.400 | 3.765 | 3.341 | 0.82 x 10 ⁻⁶ |
| | | P _{cal} x 10 ⁶ | 13.783 | 5.120 | 5.020 | 3.341 | |
| 4C2NP | 6.5- 7.5 | E _{expt} (cm ⁻¹) | 22507 | 21358 | 20730 | 16998 | 96.22 |
| | | E _{cal} (cm ⁻¹) | 22425 | 21242 | 20732 | 17128 | |
| | | P _{expt} x 10 ⁶ | 13.483 | 6.190 | 3.581 | 3.155 | 0.89 x 10 ⁻⁶ |
| | | P _{cal} x 10 ⁶ | 13.483 | 4.917 | 4.832 | 3.155 | |
| 5F2NP | 6.5- 7.5 | E _{expt} (cm ⁻¹) | 22503 | 21354 | 20730 | 16996 | 95.97 |
| | | E _{cal} (cm ⁻¹) | 22420 | 21239 | 20731 | 17125 | |
| | | P _{expt} x 10 ⁶ | 13.184 | 5.980 | 3.398 | 2.970 | 0.88 x 10 ⁻⁶ |
| | | P _{cal} x 10 ⁶ | 13.184 | 4.719 | 4.637 | 2.970 | |

Table-2.2: Computed values of (F_k), (ζ_{4f}), (E_k) (in cm⁻¹), (β) and (b^{1/2}) parameters of Pr(III) chelates containing substituted nitrophenols in various metal-ligand stoichiometries and at different pH

| M:L Ratio | pH | chelates | Slater-Condon parameters (F _k) | | | Lande parameter ζ_{4f} | Racah parameters (E ^b) | | | Nephelauxetic β | Bonding parameter b ^{1/2} |
|--------------|-------------|----------|--|----------------|----------------|------------------------------------|------------------------------------|----------------|----------------|--------------------------|--|
| | | | F ₂ | F ₄ | F ₆ | | E ¹ | E ² | E ³ | | |
| 1:1 | 6.5- 7.5 | 4M2NP | 310.510 | 42.866 | 4.691 | 703.809 | 4558.858 | 23.847 | 460.922 | 0.9640 | 0.1340 |
| | | 4C2NP | 310.636 | 42.883 | 4.693 | 696.906 | 4560.702 | 23.856 | 461.108 | 0.9644 | 0.1333 |
| | | 5F2NP | 310.692 | 42.891 | 4.694 | 697.080 | 4561.529 | 23.861 | 461.192 | 0.9646 | 0.1330 |
| 1:2 | 4.5- 5.5 | 4M2NP | 310.456 | 42.858 | 4.690 | 703.104 | 4558.061 | 23.843 | 460.841 | 0.9638 | 0.1343 |
| | | 4C2NP | 310.596 | 42.877 | 4.693 | 697.024 | 4560.120 | 23.853 | 461.049 | 0.9643 | 0.1335 |
| | | 5F2NP | 310.580 | 42.875 | 4.692 | 697.183 | 4559.875 | 23.852 | 461.025 | 0.9642 | 0.1336 |
| | 5.5- 6.5 | 4M2NP | 310.334 | 42.841 | 4.689 | 704.522 | 4556.262 | 23.833 | 460.659 | 0.9635 | 0.1350 |
| | | 4C2NP | 310.474 | 42.860 | 4.691 | 698.442 | 4558.321 | 23.844 | 460.868 | 0.9639 | 0.1342 |
| | | 5F2NP | 310.512 | 42.866 | 4.691 | 697.074 | 4558.889 | 23.847 | 460.925 | 0.9640 | 0.1340 |
| | 6.5- 7.5 | 4M2NP | 310.300 | 42.836 | 4.688 | 704.277 | 4555.765 | 23.831 | 460.609 | 0.9633 | 0.1352 |
| | | 4C2NP | 310.440 | 42.856 | 4.690 | 698.198 | 4557.823 | 23.841 | 460.817 | 0.9638 | 0.1344 |
| | | 5F2NP | 310.466 | 42.859 | 4.691 | 696.991 | 4558.207 | 23.843 | 460.856 | 0.9639 | 0.1343 |

| | | | | | | | | | | | |
|---------------|---------|-------|---------|--------|-------|---------|----------|--------|---------|---------|--------|
| | 7.5-8.5 | 4M2NP | 310.381 | 42.848 | 4.689 | 703.685 | 4556.951 | 23.837 | 460.729 | 0.9636 | 0.1348 |
| | | 4C2NP | 310.521 | 42.867 | 4.691 | 697.606 | 4559.010 | 23.848 | 460.937 | 0.9640 | 0.1340 |
| | | 5F2NP | 310.536 | 42.869 | 4.692 | 697.242 | 4559.233 | 23.849 | 460.960 | 0.9641 | 0.1339 |
| 1:3 | 6.5-7.5 | 4M2NP | 310.436 | 42.855 | 4.690 | 703.383 | 4557.773 | 23.841 | 460.812 | 0.9638 | 0.1344 |
| | | 4C2NP | 310.577 | 42.875 | 4.692 | 697.301 | 4559.832 | 23.852 | 461.020 | 0.9642 | 0.1336 |
| | | 5F2NP | 310.606 | 42.879 | 4.693 | 697.337 | 4560.261 | 23.854 | 461.064 | 0.9643 | 0.1335 |
| 1:4 | 6.5-7.5 | 4M2NP | 310.477 | 42.861 | 4.691 | 703.703 | 4558.363 | 23.844 | 460.872 | 0.9639 | 0.1342 |
| | | 4C2NP | 310.659 | 42.886 | 4.694 | 696.976 | 4561.03 | 23.858 | 461.142 | 0.9645 | 0.1332 |
| | | 5F2NP | 310.671 | 42.888 | 4.694 | 696.748 | 4561.212 | 23.859 | 461.160 | 0.9645 | 0.1331 |
| Free aqua ion | | | 322.090 | 44.460 | 4.867 | 741.000 | 4729.000 | 24.740 | 748.140 | 322.090 | |

Table-2.3: Computed values of Judd-Ofelt (T_{λ}) intensity parameters for Pr (III) chelates containing substituted nitrophenols for different metal-ligands stoichiometries and for different pH

| Stoichiometric ratio of M:L | pH | Parameters ($\Omega_{\lambda} \times 10^9$) | Pr (III) – 4M2NP | Pr (III) – 4C2NP | Pr (III) – 5F2NP |
|-----------------------------|-----------------------|---|------------------|------------------|------------------|
| 1:1 | 6.5-7.5 | Ω_2 | -20.8025 | -22.1557 | -23.2043 |
| | | Ω_4 | 1.1848 | 1.1605 | 1.1342 |
| | | Ω_6 | 3.7167 | 3.6856 | 3.6442 |
| | | Ω_4 / Ω_6 | 0.3187 | 0.3148 | 0.3112 |
| 1:2 | 4.5-5.5 | Ω_2 | -17.6318 | -18.6767 | -19.6258 |
| | | Ω_4 | 1.2632 | 1.2467 | 1.2233 |
| | | Ω_6 | 3.8396 | 3.8201 | 3.7836 |
| | | Ω_4 / Ω_6 | 0.3290 | 0.3263 | 0.3233 |
| | 5.5-6.5 | Ω_2 | -16.5676 | -17.6183 | -18.5772 |
| | | Ω_4 | 1.2894 | 1.2729 | 1.2495 |
| | | Ω_6 | 3.8805 | 3.8611 | 3.8255 |
| | | Ω_4 / Ω_6 | 0.3322 | 0.3296 | 0.3266 |
| | 6.5-7.5 | Ω_2 | -15.5121 | -16.5685 | -17.3158 |
| | | Ω_4 | 1.3156 | 1.2991 | 1.2810 |
| | | Ω_6 | 3.9219 | 3.9026 | 3.8749 |
| | | Ω_4 / Ω_6 | 0.3354 | 0.3328 | 0.3305 |
| 7.5-8.5 | Ω_2 | -17.2091 | -18.3620 | -19.2014 | |
| | Ω_4 | 1.2738 | 1.2547 | 1.2338 | |
| | Ω_6 | 3.8563 | 3.8329 | 3.8003 | |
| | Ω_4 / Ω_6 | 0.3303 | 0.32735 | 0.3246 | |
| 1:3 | 6.5-7.5 | Ω_2 | -18.6892 | -19.8343 | -20.8873 |
| | | Ω_4 | 1.2372 | 1.2180 | 1.1918 |
| | | Ω_6 | 3.7990 | 3.7754 | 3.7343 |
| | | Ω_4 / Ω_6 | 0.3256 | 0.3226 | 0.3191 |
| 1:4 | 6.5-7.5 | Ω_2 | -19.7448 | -20.8840 | -21.7324 |
| | | Ω_4 | 1.2109 | 1.1917 | 1.1709 |
| | | Ω_6 | 3.7577 | 3.7340 | 3.7016 |
| | | Ω_4 / Ω_6 | 0.3222 | 0.3191 | 0.3163 |

Table-2.4: The Spontaneous emission probability (A), fluorescence branching ratio (β), total spontaneous probability (A_T), measured [τ] and radiative fluorescence life time [τ_R] for Pr (III) chelates containing substituted nitrophenols with fluorescence peak value.

| Metal chelates | Parameters | $^3P_0 \rightarrow ^3H_4$ | $^3P_0 \rightarrow ^3H_5$ | $^1D_2 \rightarrow ^3H_4$ |
|----------------|-----------------------------|---------------------------|---------------------------|---------------------------|
| Pr(III)-4M2NP | λ_p (nm) | 485.8 | 525.7 | 603 |
| | $\Delta\lambda_{eff}$ (nm) | 20.1 | 13.23 | 14.22 |
| | A (sec ⁻¹) | 606.287 | 154.151 | 30.253 |
| | B | 0.767 | 0.194 | 0.0380 |
| | A_T (sec ⁻¹) | 790.691 | | |
| | τ (μ s) | 164.9 | 648.7 | 3305.4 |
| | τ_R (μ s) | 126.5 | | |
| | σ (pm ²) | 1.491 | 0.789 | 0.249 |
| Pr(III)-4C2NP | λ_p (nm) | 486 | 525.9 | 603.2 |
| | $\Delta\lambda_{eff}$ (nm) | 19.02 | 12.65 | 13.42 |
| | A (sec ⁻¹) | 597.944 | 152.610 | 30.051 |
| | β | 0.766 | 0.195 | 0.0384 |
| | A_T (sec ⁻¹) | 780.606 | | |
| | τ (μ s) | 167.2 | 655.3 | 3327.7 |
| | τ_R (μ s) | 128.1 | | |
| | σ (pm ²) | 1.556 | 0.819 | 0.263 |
| Pr(III)-5F2NP | λ_p (nm) | 486 | 525.9 | 603.2 |
| | $\Delta\lambda_{eff}$ (nm) | 18.07 | 12.03 | 13.11 |
| | A (sec ⁻¹) | 589.613 | 150.989 | 29.817 |
| | β | 0.765 | 0.195 | 0.0387 |
| | A_T (sec ⁻¹) | 770.420 | | |
| | τ (μ s) | 169.6 | 662.3 | 3353.8 |
| | τ_R (μ s) | 129.8 | | |
| | σ (pm ²) | 1.615 | 0.852 | 0.267 |