Absorption Spectral Study of Pr(III) Complexes with L-Alanyl-L-Glutamine and N-Acetyl-L-Glutamine: Interaction Parameters, Bonding and Judd-Ofelt Intensity

N. Ranjana Devi, Sumitra Ch. and N. Rajmuhon Singh[*]

Department of Chemistry, Manipur University, Canchipur-795 003, India

*Corresponding author: E-mail: rajmuhon@yahoo.co.in

The chemical binding of Pr(III) complexes with L-alanyl-L-glutamine (Ala-Gln) and N-acetyl-L-glutamine (NAG) have been carried out in aqueous and different aquated organic solvents like CH_3OH, CH_3CN, dioxane, DMF and their equimolar mixtures by using absorption difference and comparative absorption spectroscopy involving 4f-4f transitions spectra as probe. The results of least squares fit of the energy levels and intensities of the bands are reported in terms of energy interaction and intensity parameters. Various energy interaction parameters like Slater Condon (F_k), Racah (E_k), Lande (ξ_{4f}), nephelauxetic effect (β), bonding ($b^{1/2}$) and per cent covalency (δ) parameters have been computed to explain the nature of complexation. The changes in the values of oscillator strength (P) and Judd-Ofelt parameters (T_λ, λ = 2, 4, 6) have been used to investigate the specific correlation between relative intensities and mode of binding for the interaction of Pr(III)-Ala-Gln and Pr(III)-NAG complexes. The comparative absorption difference of different 4f-4f transitions for Pr(III) complexes in different solvents and their equimolar mixtures has also been studied to investigate for the involvement of solvents in complexation.

**Key Words: Peptides, Nephelauxetic effect, Judd-Ofelt, 4f-4f Transitions, Pseudohypersensitive.**

INTRODUCTION

The study of chemical bonding between trivalent lanthanide ions and amino acids or peptides has its origin in the interest in using these ions as structural probes in biological systems, particularly in those reactions which contain Ca^{2+} ion in their structure[1,2] and also more important for the exploration of the structural functions of biomolecular reactions[3-5]. Substitution of Ca(II) by Ln(III) ion allows the investigation of the interaction of metal ions with peptides which acquire particular importance in view of the similarities in the sizes of Ca(II) and Ln(III) ions and their preference for oxygen donor atoms in complex formation[6]. Studies on lanthanide complexes with some amino acids in solution have been carried out using NMR, luminescence and titration methods to determine the thermodynamic stability constants[7,8]. Shah and Shah[9] studied comparative 4f-4f transition spectra of Pr(III) complexes with lysozyme by using the energy interaction parameters to explain the behaviour of binding between them. In our previous work[10-13], we have reported the spectral analysis of hypersensitive and pseudo-hypersensitive transitions of Pr(III)/Nd(III) complexes with many amino acids, polypeptides and other O/N-donor ligands in aqueous and different aquated organic solvents by using 4f-4f absorptions spectra as probe and analyzed them to calculate energy interaction parameters like

Slater Condon (F_k), Racah (E_k), Lande (ξ_{4f}), nephelauxetic effect (δ), bonding ($b^{1/2}$) and per cent covalency (δ) parameters. The oscillator strength and Judd-Ofelt intensity parameters have also been calculated to support the intensity data.

As lanthanide ions being hard acids, they prefer hard donor atoms and interact with ligands possessing oxygen-nitrogen donor atoms. Its coordination chemistry serves as a model for binding of endogenous metal ions by larger peptides and proteins. The dipeptide, L-alanyl-L-glutamine (Ala-Gln) offering as potential donor sites as one carboxylate, one amino, one peptide linkage and one terminal amide group. In both the ligands, both the carbonyl and the carboxyl groups are involved in bonding and play a major role in determining the binding behaviour of metal ions[14]. The peptides containing an amino acid, glutamine exhibits numerous beneficial effects in experimental and clinical studies.

In this paper, we intend to use L-alanyl-L-glutamine and N-acetyl-L-glutamine as the ligands for interaction with the Pr(III) ion and analyzed them to calculate the energy interaction and intensity parameters. It would be of interest to compare the parameters in different aquated organic solvents like CH_3OH, CH_3CN, dioxane, DMF and their equimolar mixtures with the parameters of aqua ion. The ligand structures are shown in Fig. 1.
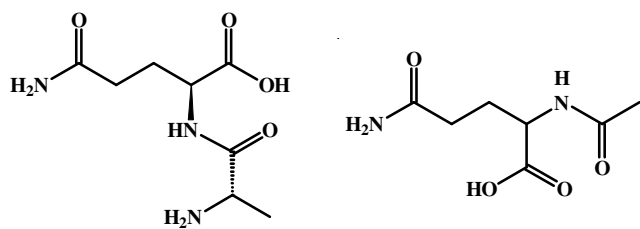
(a) L-Alanyl-L-glutamine (Ala-Gln)   (b) N-Acetyl-L-glutamine (NAG)

Fig. 1. Ligand structures

EXPERIMENTAL

$Pr(NO_3)_3 \cdot 6H_2O$ of 99.9 % purity was purchased from Central Drug House, Pvt. Ltd., New Delhi and the ligands (L-alanyl-L-glutamine and N-acetyl-L-glutamine) were obtained from SISCO Research Laboratories Pvt. Ltd., Mumbai and used without further purification. The solvents CH_3CN, CH_3OH, DMF and dioxane of A/R grade from Merck were used for spectral analysis. The solutions of Pr(III) complexes with N-acetyl-L-glutamine and L-alanyl-L-glutamine were prepared in the order of 1×10^{-2} M in different aquated organic solvents (50 % v/v). All the spectra of the complexes were recorded in 400-620 nm spectral region on Perkin Elmer Lambda 35 UV-visible spectrophotometer at 298 K.

For Pr(III) complexes, the energy of the bands arise due to forbidden transitions within the $4f^2$ configurations. They are assigned in terms of the intensity distribution of the observed bands. Carnal1 *et al.*[15] have successfully applied the Judd-Ofelt[16] theory for the assignments of the bands in the case of Ln(III) aquo-ions. In the present work the assignments of the bands to different transitions are based on comparison with the aquo-ion spectra. Transitions with larger matrix elements, $U^{(\lambda)}$ were assigned to a relatively intense absorption band.

To a first order approximation, the energy level of the $4f^n$ configuration may be considered to arise from electrostatic and magnetic interactions between the $4f$-electrons. The electrostatic interaction energy, E_e, can be expressed in terms of Slater-Condon parameters.

Thus,

$$E_e = \sum_{k=0}^{6} f^k F_k \qquad (1)$$

where f_k is the angular coefficient and F_k is given by

$$F_k = \frac{1}{D_k} \int_0^\infty \int_0^\infty \frac{r_<^k}{r_>^{k+1}} R_i^2(r_i) R_j^2(r_j) dr_i dr_j \qquad (2)$$

where i and j refer to the ith and jth electron, respectively. The denominators D_k are given by Condon and Shortley[17] and the angular coefficients are tabulated by Nielson and Koster[18].

Among the magnetic interactions, the energy, E_{so} of the spin-orbit interaction is given by

$$E_{so} = A_{so} \xi_{4f} \qquad (3)$$

where A_{so} represents the angular part and ξ_{4f} is known as the Lande's parameter.

Under the influence of the electric field of the solution matrix, the changes in the parameters F_k and ξ_{4f} are very small, so, to a first order approximation, the energy E_j of the jth level may be expressed[19] in terms of the changes in the parameters by a Taylor-series expansion. Thus,

$$E_j(F_k, \xi_{4f}) = E_{oj}(F_k^o, \xi_{4f}^o) + \sum_{k=2,4,6} \frac{\partial E_j}{\partial F_k} \Delta F_k + \frac{\partial E_j}{\partial \xi_{4f}} \Delta \xi_{4f} \qquad (4)$$

where E_{oj} is the zero-order energy of the jth level and $\partial E_j/\partial F_k$ and $\partial E_j/\Delta \xi_{4f}$ are the partial derivatives.

By using zero order energies and partial derivatives of Pr(III) as calculated by Wong[19] the above eqn. (4) can be solved by least square technique and the values of ΔF_k and ξ_{4f} can be evaluated. From these values, the values of F_2, F_4, F_6 and ξ_{4f} are obtained by using relation

$$\xi_{4f} = \xi^o_{4f} + \Delta \xi_{4f}$$

$$F_k = F_k^o + \Delta F_k \qquad (5)$$

The least squares fit method used to evaluate these parameters leads to RMS deviations of 120 and 128 cm^{-1} of N-acetyl-L-glutamine and L-alanyl-L-glutamine, respectively for Pr^{3+} solutions. This is in good agreement with the calculations reported[15,20-21] earlier. The computed values of the parameters have also been used to evaluate the nephelauxetic ratio β, given by

$$\beta = \frac{F_k^c}{F_k^f} \text{ or } \frac{E_c^k}{E_f^k} \qquad (6)$$

and the bonding parameter $b^{1/2}$ given by Henrie *et al.*[22]

$$b^{1/2} = \left[\frac{1-\beta}{2} \right]^{1/2} \qquad (7)$$

where $b^{1/2}$ is a measure of partial covalency. F_k^c and F_k^f refer to the complex and free-ions, respectively. The per cent covalency are calculated as

$$\delta\% = \left(\frac{1-\beta}{\beta} \right) \times 100 \qquad (8)$$

The intensities of intra f^n transitions are predominantly electric dipole in character which are in accordance with the theoretical treatment derived by Judd and Ofelt[16]. The oscillator strength of an induced electric-dipole transition from the ith component of the ground state of an ion to the jth component of an excited state is given by

$$P = \chi(8\pi^2 m\nu/h) \left| \left\langle i \left| D_q^{(1)} \right| j \right\rangle \right|^2 \qquad (9)$$

where, m is the mass of an electron, h is Planck's constant and ν is the frequency of the line.

The factor χ is related to the refractive index of the medium by the relation

$$\chi = \frac{(\eta^2 + 2)^2}{9\eta} \qquad (10)$$

To have non-zero values of the matrix elements given in eqn. 9, Judd and Ofelt[16] assumed mixing of the wave functions of opposite parity associated with at least one of the two *J* levels involved in the transition. Thus, in their notation,

$$P = \sum_{\lambda=2,4,6} T_\lambda \nu \left| \left\langle f^N \psi_J \left\| U^{(\lambda)} \right\| f^N \acute{\psi}_{\acute{J}} \right\rangle \right|^2 \qquad (11)$$

where $U^{(\lambda)}$ is the matrix element given by Carnall *et al.*[15]. Judd-Ofelt parameters, T_λ are complex expressions relating the radial wave function of the states, the refractive index of the medium and the ligand-field parameters which characterize the environmental field. In principle they can be calculated, but in practice they are treated as parameters to be determined from the experimental data.

The intensity of 4f-4f bands can also be evaluated, using the following equation:

$$P = 4.31 \times 10^{-9} \left[\frac{9\eta}{(\eta^2+2)^2} \right] \int \varepsilon_{max} \nu \partial \nu \qquad (12)$$

ε_{max} is the molar extinction coefficient, ν is the energy of transition in cm^{-1} and η is the refractive index of the medium. The experimental values of oscillator strength (P_{obs}) of absorption band were given by Gaussian curve analysis as

$$P_{obs} = 4.6 \times 10^{-9} \times \varepsilon_{max} \times \Delta\bar{\nu}_{1/2} \qquad (13)$$

where $\Delta\bar{\nu}_{1/2}$ (cm^{-1}) is the half band width. From these values, the values of T_2, T_4 and T_6 are calculated by using Judd-Ofelt expression

$$\frac{P_{obs}}{\bar{\nu}} = [(U^2)]^2 T_2 + [(U^4)^2 T_4 + [(U^6)]^2 T_6 \qquad (14)$$

RESULTS AND DISCUSSION

Pr(III) ions observed four energy bands ($^3H_4 \rightarrow {}^3P_2$, $^3P_1$, $^3P_0$ and $^1D_2$) in the visible spectral region. These transitions do not obey the selection rules for hypersensitive transition, yet, they have been found to exhibit substantial sensitivity towards even minor coordination changes around Ln(III) ion, due to the difference in the binding behaviour and changes in the immediate coordination environment around Ln(III) ion. Such transitions are regarded as ligand mediated pseudo hypersensitive transitions. For Pr(III) complexes, the binding of Pr(III) ion with L-alanyl-L-glutamine and N-acetyl-L-glutamine bring about changes in the energies of various bands which cause the degree of lowering in the energy interaction parameters like Slater Condon inter electronic repulsion (F_k), Racah (E_k), Lande's parameter (χ_{4f}) which leads to nephelauxetic effect and intensities of 4f-4f electronic transitions.

For spectral studies on the structures of coordination compounds of lanthanides in solution, Jorgensen and Ryan[23] noticed the dependence of nephelauxetic effect on the coordination number. It was suggested that shortening in the metal-ligand distance occurs with decrease in the coordination number. To interpret the correlation and analysis of the relationship between nephelauxetic effect and geometry, energy parameters have been derived and evaluated for complex compounds using the angular overlap model, the value of 'n' is proportional to the nephelauxetic effect as

$$n = \left[\frac{1-\beta^{1/2}}{\beta^{1/2}} \right] \qquad (15)$$

It may also be expressed as

$$n = \frac{H_L^2}{(H_M - H_L)^2} (S \times R)^2 N \qquad (16)$$

where, N is the coordination number, H_M and H_L are coulomb integrals of atomic orbital, S is the overlap integral, R is the radius of the orbit. For compounds with ligand coordinated through identical donor atoms, the term of eqn. 16 is a constant and becomes

$$n = constant (S \times R)^2 N \qquad (17)$$

Eqn. 17 represents the nephelauxetic effect as a function of two variables, $S \times R$ and N which vary with changes in metal-ligand bond distance in opposite directions. However, any variation in the value of R leads to a larger change in $(S \times R)^2$ compared to that in N. As a result, the nephelauxetic effect increases when the coordination number decreases. The Ln-O distance shortens in spite of the addition nature of β and decreases in the number of coordinating ligand.

The interaction of Pr(III) ion with L-alanyl-L-glutamine and N-acetyl-L-glutamine is generally predominant with carboxylic groups of N-acetyl-L-glutamine and L-alanyl-L-glutamine and basically electrostatic in nature. Therefore, they bring about the lowering of the energy interaction parameters. Table-1 gives the values of energy interaction parameters like Slater Condon (F_k), Racah (E_k), Lande (ξ_{4f}), nephelauxetic ratio (β), bonding parameter ($b^{1/2}$) and percentage covalency (δ) parameters for Pr(III); Pr(III): Ala-Gln; Pr(III):Ala-Gln:Ca(II) and Pr(III):Ala-Gln:Zn(II) and Pr(III):NAG; Pr(III):NAG: Ca(II) and Pr(III):NAG:Zn(II) in aqueous and different aquated organic solvents. From these values, it has been observed that in all the systems, there is decrease in the energy interaction parameters like Slater Condon (F_k), Racah (E_k) and spin-orbit interaction (ξ_{4f}) which indicates lowering of both coulombic (F_k) and spin-orbit interaction (ξ_{4f}) parameters thus leading to the expansion of the central metal ion orbital when ligand is added to Pr(III) ion. Further, it has also been observed that the decrease values in energy is more in case of complexes when DMF is used as the organic solvent or DMF as one of the organic solvents in their equimolar mixtures whereas CH_3OH is the least. For Pr(III) complexes, the values of nephelauxetic ratio (β) in all the systems is less than unity and the values of bonding parameter ($b^{1/2}$) are found to be positive which correlates covalent bonding.

However, the changes in the energy interaction parameters and nephelauxetic effect are not apparently significant. We have given more emphasis to quantitative f-f transition intensity analysis because changes in intensities are more significant compared to energy changes. Table-2 gives the values of oscillator strength (P) and Judd-Ofelt intensity (T_λ) parameters, determined in aqueous and different aquated organic solvents for Pr(III) complexes with L-alanyl-L-glutamine and N-acetyl-L-glutamine. The analysis of the oscillator strengths and Judd-Ofelt intensity parameters are used in the investigation of formation and nature of Pr(III)-L-alanyl-L-glutamine and Pr(III)-N-acetyl-L-glutamine complexes. Judd and Ofelt have suggested three phenomenological parameters (T_2, T_4, T_6) which are sensitive towards the changes in the immediate coordination environment (T_2) and symmetry

TABLE-1

CALCULATED VALUES OF ENERGY INTERACTION PARAMETERS FOR Pr(III), Pr(III): L (1:1), Pr(III): L:Ca(II) (1:1:1) and Pr(III): L:Zn(II) (1:1:1), WHERE L = L-ALANYL-L- GLUTAMINE (ALA-GLN) AND N-ACETYL-L-GLUTAMINE (NAG) IN AQUEOUS AND AND DIFFERENT AQUATED ORGANIC SOLVENTS (50:50V/V)

System	F_2	F_4	F_6	ξ_{4f}	E_1	E_2	E_3	β	$b^{1/2}$	δ	r.m.s.
1. H₂O											
Ligand-Ala-Gln											
Pr(III)	309.3741	42.7091	4.6715	722.4326	3512.8343	23.7720	615.0563	0.9471	0.1627	5.5895	102.50
Pr(III):L	309.3663	42.7080	4.6714	722.4103	3512.7461	23.7714	615.0408	0.9470	0.1627	5.5924	102.76
Pr(III):L:Ca(II)	309.3543	42.7064	4.6712	722.4168	3512.6095	23.7704	615.0169	0.9470	0.1628	5.5939	102.79
Pr(III):L:Zn(II)	309.3470	42.7054	4.6711	722.4049	3512.5271	23.7699	615.0025	0.9470	0.1628	5.5960	102.71
Ligand-NAG											
Pr(III):L	309.3280	42.7027	4.6709	722.4806	3512.3115	23.7684	614.9647	0.9470	0.1627	5.5933	101.25
Pr(III):L:Ca(II)	309.3095	42.7002	4.6706	722.4848	3512.1008	23.7670	614.9278	0.9470	0.1628	5.5960	101.06
Pr(III):L:Zn(II)	309.2928	42.6979	4.6703	722.5070	3511.9115	23.7657	614.8947	0.9470	0.1628	5.5971	101.02
2. CH₃OH											
Ligand-Ala-Gln											
Pr(III)	309.2895	42.6974	4.6703	722.4697	3511.8737	23.7655	614.8881	0.9470	0.1628	5.6004	101.14
Pr(III):L	309.2573	42.6930	4.6698	722.3534	3511.5084	23.7630	614.8241	0.9468	0.1630	5.6146	101.89
Pr(III):L:Ca(II)	309.2393	42.6905	4.6695	722.3536	3511.3039	23.7616	614.7883	0.9468	0.1631	5.6175	101.93
Pr(III):L:Zn(II)	309.2298	42.6892	4.6694	722.3107	3511.1957	23.7609	614.7694	0.9468	0.1631	5.6223	101.87
Ligand-NAG											
Pr(III):L	309.3234	42.7021	4.6708	722.0017	3512.2585	23.7681	614.9554	0.9467	0.1633	5.6307	106.48
Pr(III):L:Ca(II)	309.3125	42.7006	4.6706	721.9416	3512.1350	23.7672	614.9338	0.9466	0.1633	5.6370	107.07
Pr(III):L:Zn(II)	309.2972	42.6985	4.6704	721.8966	3511.9612	23.7661	614.9034	0.9466	0.1634	5.6430	107.80
3. CH₃CN											
Ligand-Ala-Gln											
Pr(III)	309.2569	42.6929	4.6698	722.4649	3511.5044	23.7630	614.8234	0.9469	0.1629	5.6061	103.33
Pr(III):L	309.2220	42.6881	4.6693	722.3429	3511.1080	23.7603	614.754	0.9468	0.1631	5.6211	104.27
Pr(III):L:Ca(II)	309.2087	42.6863	4.6691	722.2526	3510.9563	23.7593	614.7275	0.9467	0.1633	5.6302	104.67
Pr(III):L:Zn(II)	309.1968	42.6846	4.6689	722.1815	3510.8210	23.7583	614.7038	0.9466	0.1634	5.6376	104.81
Ligand-NAG											
Pr(III):L	309.3056	42.6996	4.6705	722.4350	3512.0565	23.7667	614.9201	0.9470	0.1628	5.6005	103.44
Pr(III):L:Ca(II)	309.2707	42.6948	4.6700	722.1297	3511.6611	23.7640	614.8509	0.9467	0.1632	5.6295	107.79
Pr(III):L:Zn(II)	309.2442	42.6912	4.6696	721.9415	3511.3594	23.7620	614.798	0.9465	0.1635	5.6482	110.12
4. DMF											
Ligand-Ala-Gln											
Pr(III)	308.9231	42.6468	4.6647	719.2022	3507.7141	23.7373	614.1598	0.9442	0.1670	5.9105	128.24
Pr(III):L	308.8987	42.6435	4.6644	719.2771	3507.4372	23.7354	614.1113	0.9442	0.1670	5.9088	128.15
Pr(III):L:Ca(II)	308.8811	42.6410	4.6641	719.2932	3507.2365	23.7341	614.0762	0.9442	0.1670	5.9104	128.21
Pr(III):L:Zn(II)	308.8653	42.6388	4.6639	719.3272	3507.0571	23.7329	614.0447	0.9442	0.1670	5.9104	128.41
Ligand-NAG											
Pr(III):L	308.9632	42.6524	4.6653	719.8949	3508.1693	23.7404	614.2395	0.9447	0.1662	5.8508	120.94
Pr(III):L:Ca(II)	308.9546	42.6512	4.6652	719.8613	3508.0720	23.7397	614.2224	0.9447	0.1663	5.8548	120.96
Pr(III):L:Zn(II)	308.9439	42.6497	4.6651	719.8131	3507.9496	23.7389	614.201	0.9446	0.1664	5.8602	120.80
5. Dioxane											
Ligand-Ala-Gln											
Pr(III)	309.2178	42.6875	4.6692	721.9937	3511.0602	23.7600	614.7456	0.9465	0.1635	5.6485	107.03
Pr(III):L	309.1744	42.6815	4.6685	721.7488	3510.5673	23.7566	614.6593	0.9463	0.1639	5.6743	111.11
Pr(III):L:Ca(II)	309.1484	42.6779	4.6681	721.4822	3510.2721	23.7546	614.6076	0.9461	0.1642	5.6989	113.94
Pr(III):L:Zn(II)	309.1344	42.6760	4.6679	721.3797	3510.1135	23.7535	614.5799	0.9460	0.1643	5.7090	114.29
Ligand NAG											
Pr(III):L	309.2379	42.6903	4.6695	722.0299	3511.2880	23.7615	614.7855	0.9466	0.1634	5.6425	107.35
Pr(III):L:Ca(II)	309.2315	42.6894	4.6694	722.1114	3511.2159	23.7610	614.7729	0.9466	0.1633	5.6373	105.91
Pr(III):L:Zn(II)	309.1775	42.6820	4.6686	721.4713	3510.6022	23.7569	614.6654	0.9461	0.1641	5.6950	114.38
6. DMF + dioxane											
Ligand-Ala-Gln											
Pr(III)	309.0418	42.6632	4.6665	720.3809	3509.0616	23.7464	614.3957	0.9452	0.1656	5.8007	119.45
Pr(III):L	309.0175	42.6599	4.6662	720.3180	3508.7853	23.7446	614.3473	0.9451	0.1657	5.8095	119.20
Pr(III):L:Ca(II)	309.0043	42.6581	4.6660	720.2226	3508.6363	23.7436	614.3212	0.9450	0.1658	5.8189	119.25
Pr(III):L:Zn(II)	308.9958	42.6569	4.6658	720.1142	3508.5389	23.7429	614.3042	0.9449	0.1659	5.8286	119.55
Ligand-NAG											
Pr(III):L	309.0464	42.6639	4.6666	720.3346	3509.1141	23.7468	614.4049	0.9451	0.1656	5.8035	120.29
Pr(III):L:Ca(II)	309.0404	42.6630	4.6665	720.2538	3509.0462	23.7463	614.393	0.9451	0.1657	5.8106	120.59
Pr(III):L:Zn(II)	309.0401	42.6630	4.6665	720.1662	3509.0418	23.7463	614.3922	0.9450	0.1658	5.8174	121.03

| 7. CH$_3$OH + DMF										
Ligand-Ala-Gln										
Pr(III)	309.0549	42.6650	4.6667	720.2888	3509.2107	23.7474	614.4218	0.9451	0.1656	5.8056	117.76
Pr(III):L	309.0399	42.6630	4.6665	720.3296	3509.0404	23.7463	614.392	0.9451	0.1656	5.8049	117.65
Pr(III):L:Ca(II)	309.0330	42.6620	4.6664	720.3144	3508.9618	23.7458	614.3782	0.9451	0.1657	5.8072	117.60
Pr(III):L:Zn(II)	309.0261	42.6611	4.6663	720.2992	3508.8833	23.7452	614.3645	0.9451	0.1657	5.8095	117.55
Ligand-NAG										
Pr(III):L	309.1147	42.6733	4.6676	720.7055	3509.8899	23.7520	614.5407	0.9455	0.1651	5.7639	113.91
Pr(III):L:Ca(II)	309.1021	42.6715	4.6674	720.6997	3509.7466	23.7511	614.5156	0.9455	0.1651	5.7664	113.89
Pr(III):L:Zn(II)	309.1617	42.6798	4.6683	721.6561	3510.4225	23.7556	614.634	0.9462	0.1640	5.6835	100.54

TABLE-2

COMPUTED AND OBSERVED VALUES OF OSCILLATOR STRENGTHS AND JUDD-OFELT PARAMETERS FOR Pr(III), Pr(III): L (1:1), Pr(III): L:Ca(II) (1:1:1) and Pr(III): L: Zn(II) (1:1:1), WHERE L = L-ALANYL-L- GLUTAMINE (ALA-GLN) AND N-ACETYL-L-GLUTAMINE (NAG) IN AQUEOUS AND DIFFERENT AQUATED ORGANIC SOLVENTS (50:50V/V)

System	$^3H_4 \rightarrow {}^3P_2$		$^3H_4 \rightarrow {}^3P_1$		$^3H_4 \rightarrow {}^3P_0$		$^3H_4 \rightarrow {}^1D_2$		T$_2$	T$_4$	T$_6$
	Pobs	Pcal	Pobs	Pcal	Pobs	Pcal	Pobs	Pcal			
1. H$_2$O											
Ligand-Ala-Gln											
Pr(III)	2.4499	2.4499	0.8113	0.6052	0.3929	0.5958	0.7949	0.7949	17.569	1.661	7.5831
Pr(III):L	2.5548	2.5548	0.7316	0.5657	0.3936	0.557	0.6	0.6	-33.33	1.5526	7.9559
Pr(III):L:Ca(II)	2.5504	2.5504	0.701	0.5492	0.3912	0.5407	0.6857	0.6857	-13.57	1.5073	7.9538
Pr(III):L:Zn(II)	2.5434	2.5434	0.7107	0.5522	0.3876	0.5437	0.6321	0.6321	-25.26	1.5157	7.9288
Ligand-NAG											
Pr(III):L	2.903	2.903	0.9401	0.7005	0.4539	0.6898	0.6632	0.6632	-42.3	1.9231	8.9991
Pr(III):L:Ca(II)	2.431	2.431	0.9205	0.684	0.4406	0.6735	0.6468	0.6468	-15.07	1.8778	7.4668
Pr(III):L:Zn(II)	2.511	2.511	0.9852	0.7172	0.4422	0.7061	0.7727	0.7727	8.1387	1.969	7.703
2. CH$_3$OH											
Ligand-Ala-Gln											
Pr(III)	2.8123	2.8123	0.8896	0.6517	0.4074	0.6417	0.8636	0.8636	9.2073	1.7893	8.7384
Pr(III):L	2.7194	2.7194	0.8236	0.6118	0.3938	0.6024	0.7813	0.7813	-3.216	1.6799	8.4646
Pr(III):L:Ca(II)	2.8313	2.8313	0.8018	0.5991	0.3904	0.5899	0.7302	0.7302	-22.09	1.6453	8.8413
Pr(III):L:Zn(II)	2.8595	2.8595	0.7737	0.5834	0.387	0.5744	0.6919	0.6919	-32.57	1.602	8.9457
Ligand-NAG											
Pr(III):L	2.4842	2.4842	0.7306	0.5602	0.3839	0.5517	0.703	0.703	-5.278	1.5379	7.7296
Pr(III):L:Ca(II)	2.5941	2.5941	0.768	0.582	0.3899	0.5731	0.7607	0.7607	0.5426	1.5977	8.074
Pr(III):L:Zn(II)	2.4879	2.4879	0.7723	0.5912	0.4038	0.5821	0.855	0.855	28.868	1.623	7.7196
3. CH$_3$CN											
Ligand-Ala-Gln											
Pr(III)	2.7412	2.7412	0.8552	0.6379	0.4141	0.6281	0.8135	0.8135	2.6263	1.7515	8.5149
Pr(III):L	2.6506	2.6506	0.8632	0.6407	0.4119	0.6309	0.8128	0.8128	8.4246	1.7597	8.2164
Pr(III):L:Ca(II)	2.6689	2.6689	0.8182	0.6209	0.4171	0.6114	0.8867	0.8867	24.056	1.7052	8.2913
Pr(III):L:Zn(II)	2.7615	2.7615	0.872	0.648	0.4175	0.6381	0.8667	0.8667	13.368	1.7798	8.5753
Ligand-NAG											
Pr(III):L	2.6395	2.6395	0.9455	0.6777	0.4036	0.6673	0.8147	0.8147	9.4231	1.8605	8.1519
Pr(III):L:Ca(II)	2.6535	2.6535	0.9557	0.6861	0.41	0.6755	0.8876	0.8876	25.107	1.8834	8.1921
Pr(III):L:Zn(II)	2.6229	2.6229	0.9027	0.6524	0.3959	0.6423	0.8823	0.8823	26.081	1.7911	8.1168
4. DMF											
Ligand-Ala-Gln											
Pr(III)	2.8906	2.8906	0.8509	0.6808	0.5032	0.6708	0.9292	0.9292	19.467	1.8714	8.9883
Pr(III):L	2.9196	2.9196	0.8395	0.6775	0.508	0.6676	0.7797	0.7797	-16.46	1.8625	9.0865
Pr(III):L:Ca(II)	3.236	3.236	0.92	0.735	0.5419	0.7242	0.8514	0.8514	-21.09	2.0206	10.083
Pr(III):L:Zn(II)	3.3517	3.3517	0.9562	0.7519	0.5396	0.7409	0.8808	0.8808	-22.05	2.0672	10.451
Ligand-NAG											
Pr(III):L	3.3484	3.3484	0.878	0.7088	0.5316	0.6983	0.8177	0.8177	-36.22	1.9481	10.47
Pr(III):L:Ca(II)	3.4263	3.426	0.930	0.751	0.564	0.7407	0.993	0.993	-1.62	2.0664	10.694
Pr(III):L:Zn(II)	3.3104	3.3104	0.9061	0.7236	0.5332	0.713	0.8624	0.8624	-23.61	1.9892	10.335
5. Dioxane											
Ligand-Ala-Gln											
Pr(III)	2.4802	2.4802	0.7399	0.5677	0.3895	0.559	0.8457	0.8457	27.33	1.559	7.7131
Pr(III):L	2.5502	2.5502	0.7374	0.5679	0.3922	0.5591	0.8359	0.8359	20.621	1.5595	7.9426
Pr(III):L:Ca(II)	2.557	2.557	0.7046	0.5502	0.3898	0.5418	0.8587	0.8587	25.474	1.5111	7.9783
Pr(III):L:Zn(II)	2.539	2.539	0.7203	0.5665	0.4065	0.5579	0.8441	0.8441	23.295	1.5561	7.9079

Ligand-NAG											
Pr(III):L	2.5053	2.5053	0.7189	0.5549	0.3849	0.5464	1.0483	1.0483	71.686	1.5237	7.8037
Pr(III):L:Ca(II)	2.4787	2.4787	0.7809	0.5848	0.3827	0.5758	0.7362	0.7362	2.5271	1.6058	7.6949
Pr(III):L:Zn(II)	2.4487	2.4487	0.7168	0.5537	0.3846	0.5452	0.9115	0.9115	44.563	1.5205	7.6197
6. DMF + dioxane											
Ligand-Ala-Gln											
Pr(III)	2.8914	2.8914	0.8705	0.6771	0.4765	0.667	0.806	0.806	-8.786	1.8604	8.9891
Pr(III):L	2.9842	2.9842	0.8347	0.6451	0.4487	0.6355	0.772	0.772	-22.5	1.7727	9.3177
Pr(III):L:Ca(II)	2.9649	2.9649	0.8439	0.6592	0.4674	0.6494	0.9345	0.9345	15.649	1.8115	9.2449
Pr(III):L:Zn(II)	2.9346	2.9346	0.8245	0.6473	0.4631	0.6377	1.1484	1.1484	66.304	1.779	9.1546
Ligand-NAG											
Pr(III):L	2.9751	2.9751	0.8574	0.6666	0.4686	0.6565	0.9401	0.9401	16.236	1.8312	9.272
Pr(III):L:Ca(II)	3.0359	3.0359	0.8031	0.6421	0.4739	0.6325	0.9136	0.9136	6.3093	1.7641	9.4898
Pr(III):L:Zn(II)	3.0555	3.0555	0.8554	0.6697	0.4767	0.6596	1.0341	1.0341	32.331	1.8398	9.5341
7. CH₃OH + DMF											
Ligand-Ala-Gln											
Pr(III)	3.0138	3.0138	0.9787	0.7249	0.464	0.714	0.9796	0.9796	22.407	1.9916	9.3572
Pr(III):L	2.9565	2.9565	0.9283	0.7143	0.4929	0.7037	0.9342	0.9342	15.881	1.9627	9.1773
Pr(III):L:Ca(II)	2.775	2.775	0.9205	0.7068	0.4858	0.6963	0.7986	0.7986	-2.997	1.9422	8.5876
Pr(III):L:Zn(II)	3.0231	3.0231	0.9288	0.7148	0.4934	0.7042	0.9557	0.9557	16.383	1.9642	9.3964
Ligand-NAG											
Pr(III):L	2.9581	2.9581	0.9064	0.7	0.4863	0.6896	0.9819	0.9819	26.579	1.9232	9.1901
Pr(III):L:Ca(II)	2.9868	2.9868	0.8787	0.6833	0.4806	0.6731	0.9949	0.9949	27.702	1.8772	9.2969
Pr(III):L:Zn(II)	2.9501	2.9501	0.9316	0.7033	0.4679	0.6928	1.2372	1.2372	84.589	1.9323	9.1623

(T_4, T_6). It has been observed that among the three T_λ, parameters, T_6 is the best-defined while T_2 is the least-defined parameter for Pr(III) complexes since by definition, $T_\lambda \geq 0$ and their order is $T_6 > T_4 > T_2$. Henrie and co-workers[22] have shown that the low magnitudes of oscillator strengths indicate outer sphere complexation while high values indicate inner sphere complexation. For the present complexs T_2, T_4 and T_6 parameters have low values, indicating thereby the predominance of outer sphere complexation. For most of the Pr(III) complexes, T_2 values are found negative and meaningless. This is because only $^3F_2 \rightarrow {}^3H_4$ transition has a significant $U^{(2)}$ matrix and it is not included in the data set of any of the complexes. The comparative absorption spectra of Pr(III); Pr(III):Ala-Gln; Pr(III):Ala-Gln:Ca(II) and Pr(III):Ala-Gln:Zn(II) is shown in Figs. 2 and 3 also shows the comparative absorption spectra of Pr(III); Pr(III):NAG; Pr(III):NAG:Ca(II) and Pr(III):NAG: Zn(II) in DMF. This clearly shows that the addition of Ala-Gln or NAG to Pr(III) ion results in significant enhancement in the oscillator strengths of different $4f$-$4f$ transitions. This further increases when Ca(II) and Zn (II) ions are added to the solution. As a consequence, we have observed noticeable increase in the magnitude of Judd-Ofelt intensity parameters. These suggest the binding of L-alanyl-L-glutamine and N-acetyl-L-glutamine to Pr(III) in solution state.

The effect of solvent on complexation is quite significant. DMF appears to induce the strongest complexation influence on Pr(III): Ala-Gln and Pr(III):NAG complex. The red shift is observed in the energies of all the four bands. Although we have found red shift in energies of all transitions, the effect is more pronounced in DMF. The red shift is due to the expansion of the metal ion orbital radius resulting in the decrease of interelectronic repulsion, which leads to the phenomenon of nephelauxetic effect. The sensitivities of the intensification of bands of the four transitions of Pr(III):Ala-Gln complexes are shown in Fig. 4. The relative sensitivity of solvents of all the
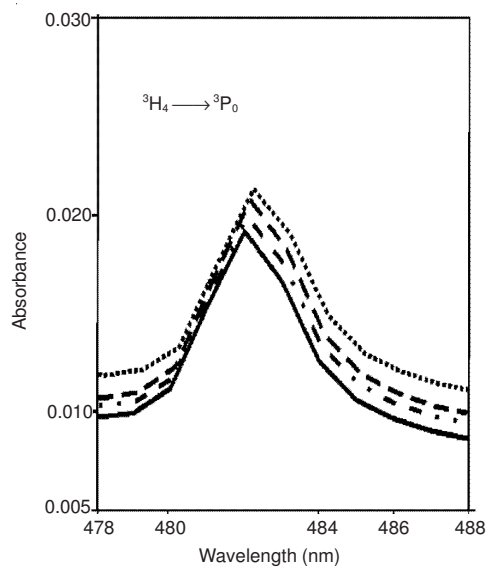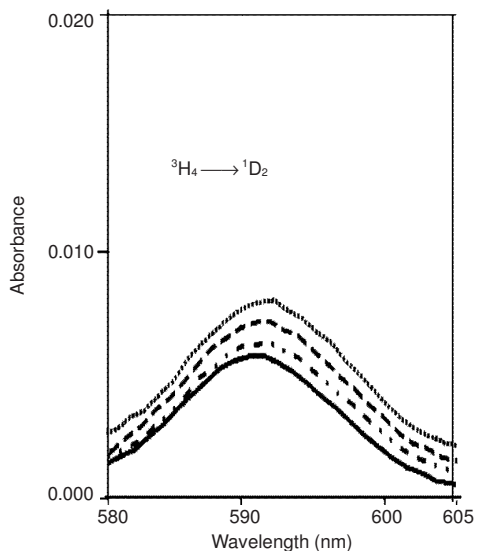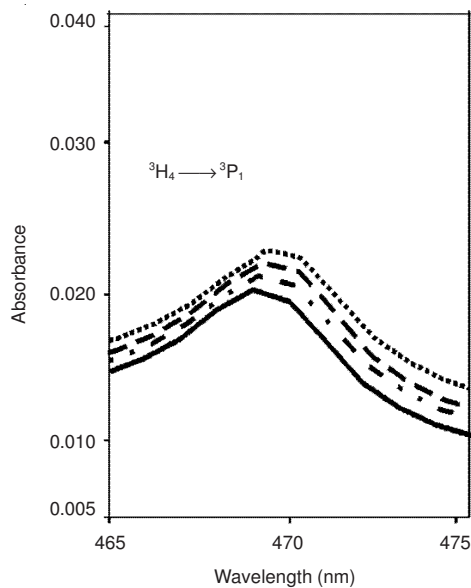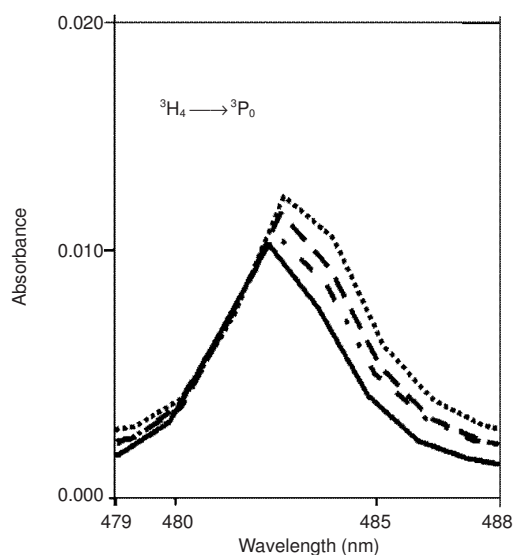

$^3H_4 \longrightarrow {}^3P_2$

$^3H_4 \longrightarrow {}^3P_1$
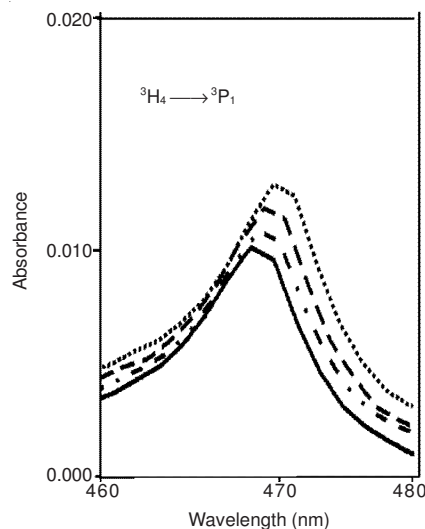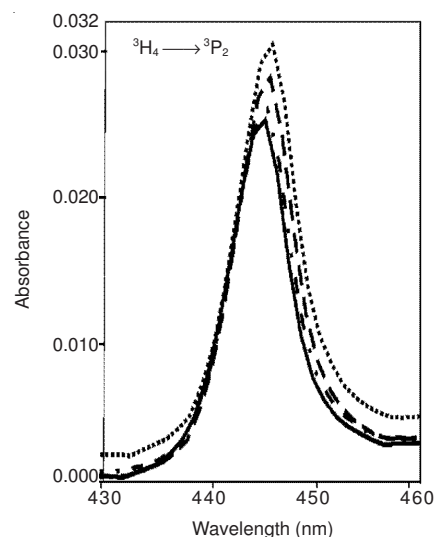
Fig. 2. Comparative absorption spectra of complexes (a) Pr(III) (———),
(b) Pr(III): Ala-Gln (1:1) (-- ---), (c) Pr(III): Ala-Gln:Ca(II) (1:1:1)
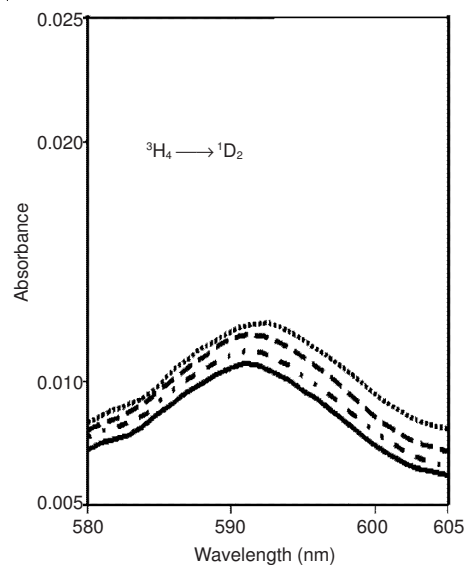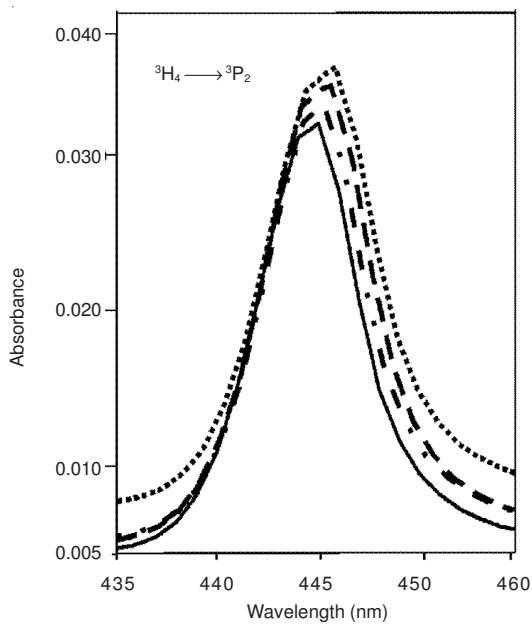(———) and (d) Pr(III): Ala-Gln:Zn(II) (1:1:) (-------) in DMF

Fig. 3. Comparative absorption spectra of complexes (a) Pr(III) (———),
(b) Pr(III): NAG (1:1) (-- ---), (c) Pr(III): NAG:Ca(II) (1:1:1) (———)
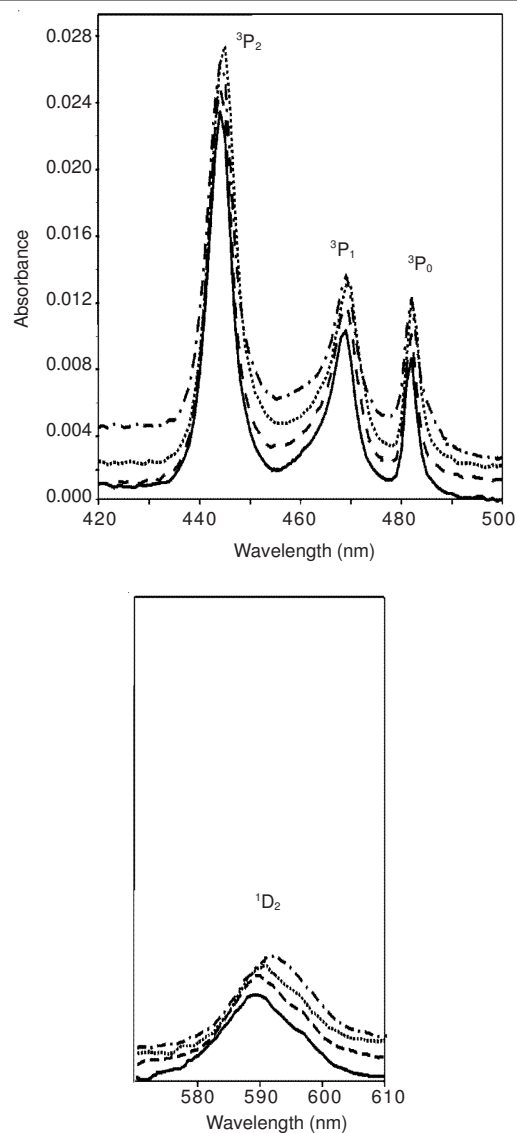and (d) Pr(III): NAG:Zn(II) (1:1:) (-------) in DMF

Fig. 4. Comparative absorption spectra of complexes (a) Pr(III) complexes with Ala-Gln in (a) DMF (–––), (b) dioxane (------), (c) CH₃CN (——) and (d) CH₃OH (——), solvents

four transitions is in the order DMF > dioxane > CH₃CN > CH₃OH. The influence of solvents like acetonitrile and dioxane are less on complexation of Pr(III): Ala-Gln and Pr(III):NAG complex. This indicates that DMF generally binds through oxygen and not nitrogen when it coordinates to hard acids like the lanthanide ions whereas CH₃CN binds through nitrogen. The higher intensification in DMF medium also reveals the stronger bonding capacity of oxygen than nitrogen. Methanol is a very weak donor.

Conclusion

From these investigations, it has been observed that the interaction of Pr(III) ions with L-alanyl-L-glutamine and

N-acetyl-L-glutamine has been determined spectroscopically using 4*f*-4*f* transitions. The magnitude and variation of spectral parameters show significant changes in the intensity parameters but less prominent changes in the coulombic and spin orbit interaction parameters. These points lead to the fact that the changes in the symmetry of the complex play a dominant role. The involvement of Ca(II) and Zn(II) ions in the Pr(III) complexes reveals more complexation, supported by comparative absorption spectra. Further, the effect of different organic solvents for the complexation of Pr(III) complexes with L-alanyl-L-glutamine and N-acetyl-L-glutamine has also been observed. Among the solvents used, DMF is found to be the most sensitive for the complexation of Pr(III) complexes with L-alanyl-L-glutamine and N-acetyl-L-glutamine.

REFERENCES

1.   J. Bruno, W.D. Horrocks and R.J. Zauhar, *Biochemistry*, **31**, 7016 (1992).
2.   E. Nieboer, *Struct. Bonding*, **22**, 1 (1975).
3.   R.B. Martin and F.S. Richardson, *Quart. Rev. Biophys.*, **12**, 181 (1979).
4.   S.N. Misra, G. Ramchandriah, M.A. Gagnani, R.S. Shukla and M.I. Devi, *Appl. Spectrosc. Rev.*, **38**, 433 (2003).
5.   J.C.G. Bunzli and G.R. Choppin, Lanthanide Probes in Life, Chemical and Earth Sciences, Elsevier, Amsterdam (1989).
6.   H.G. Brittan, F.S. Richardson and R.B. Martin, *J. Am. Chem. Soc.*, **98**, 8255 (1976).
7.   A.D. Sherry, C. Yoshida, E.R. Birnbaum and D.W. Darnall, *J. Am. Chem. Soc.*, **95**, 3011 (1973).
8.   J. Legendziewicz, E. Huskowska, Gy. Argay and A. Waskowska, *Inorg. Chim. Acta*, **95**, 57 (1984).
9.   K.J. Shah and M.K. Shah, *Bull. Pure Appl. Sci.*, **20C**, 81 (2001).
10. H.D. Devi, Th.D. Singh, N. Yaiphaba, Ch. Sumitra, M. Indira Devi and N.R. Singh, *Asian J. Chem.*, **16**, 412 (2004).
11. Ch. Victory Devi and N.R. Singh, *Spectrochim. Acta A*, **78**, 1180 (2011).
12. T. Moaienla, Th. David Singh, N.R. Singh and M.I. Devi, *Spectrochim. Acta*, **74**, 434 (2009).
13. Ch. Sumitra, Th. David Singh, M.I. Devi and N.R. Singh, *J. Alloys Com.*, **451**, 365 (2008).
14. R. Richardson and S. Murphym, *Toxicol. Appl. Pharmacol.*, **31**, 505 (1975).
15. W.T. Carnall, P.R. Fields and K. Rajnak, *J. Chem. Phys.*, **49**, 4424 (1968).
16. G.S. Ofelt, *J .Chem. Phys.*, **37**, 511 (1962); B.R. Judd, *Phys. Rev.*, **127**, 750 (1962).
17. E.U. Condon and G.H. Shortley, The Theory of Atomic Spectra (Cambridge: Cambridge UP) 178 (1957).
18. C.W. Nielson and G.F. Koster, Spectroscopic Coefficients for the pn, dn, fn Configurations, Cambridge, Massachusetts: MIT Press (1963).
19. E.Y. Wong, *J. Chem. Phys.*, **35**, 544 (1961); E.Y. Wong, *J. Chem. Phys.*, **38**, 976 (1963).
20. S.P. Tandon and P.C. Mehta, *J. Chem. Phys.*, **52**, 4313 (1970).
21. D.A. Wensky and W.G. Moulton, *J. Chem. Phys.*, **53**, 3957 (1970).
22. D.E. Henrie and G.R. Choppin, *J . Chem. Phys.*, **49**, 477 (1968).
23. C.K. Jorgensen and L. Ryan, *J. Phys. Chem.*, **70**, 2845 (1966).