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SPECTROSCOPIC STUDY OF PR^{3+}-AMINO ACID TERNARY COMPLEXES IN AQUO SOLUTION

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ABSTRAC

The absorption spectra of four ternary complexes of Pr^{3+} having glycine, valine, leucine or tryptophan as primary ligand and ethane 1,2 diol as secondary ligand have been studied. From these spectra Slater-Condon (F_k), Racah (E^k) and Lande (ξ_{4f}) parameters and Judd-Ofelt intensity parameters have been computed and discussed.

RESUMEN

Se estudió el espectro de absorción de cuatro complejos ternarios de Pr^{+3} teniendo glycine, valine, leucine o tryptophan como ligantes primarios y etano 1,2 diol como ligante secundario. Basado en estos espectros se computaron y discutieron los parámetros Slater-Condon (F_k), Racah (E^k) y Landé (ξ_{4f}) y parámetros de intensidad Judd-Ofelt.

INTRODUCTION

The amino acid complexes have a potential for their use in therapy and diagnosis. Binary amino acid complexes of rare-earths were studied by Misumi et al[1] but their ternary complexes have been studied only recently in this laboratory[2-6].

The present communication reports absorption spectra of Pr^{3+} ternary complexes of glycine, valine, leucine and tryptophan as primary ligands and ethane 1,2 diol as secondary ligand. From these the various spectroscopic parameters, like interaction parameters viz. Slater-Condon (F_k), Lande(ξ_{4f}) parameters and Judd-Ofelt intensity parameters (T_λ) have been computed.

EXPERIMENTAL

The ternary complexes of the type $Pr^{3+}M_2M'$ were prepared using the standard method described earlier[4], where M stands for the primary ligand [Glycine (G), valine (V), leucine (L) and stryptophan (T)] and M'stands for the secondary ligand [Ethane 1,2 diol (ED)].

Pr^{3+} chloride was obtained from Indian Rare Earths Ltd. and the ligands were of A.R. grade. Triple distilled water was used for making solution of the purified complexes.

The absorption spectra, wavelength (nm) vs optical density (O.D.) were recorded on Carl-Zeiss VSU-2P spectrophotometer.

RESULTS AND DISCUSSION

The absorption spectra are given in Figs. 1-4. The energies E_{obs} for different peaks are given in Table 1, while the observed intensities P_{obs} of the various peaks in terms of oscillator strength are given in table 2.

INTERACTION AND BONDING PARAMETERS: The interaction parameters like Slater-Condon (F_k, k= 2,4,6) and spinorbit iteraction parameter known as Landé parameter (ξ_{4f}) have been computed by partial regression method. The detailed calculation of these parameters have been discussed earlier[7].

The energy of a level is given by[8],

$$E_j(F_k, \xi_{4f}) = E_{oj}(F_k^o, \xi_{4f}^o) + \sum_{k=2,4,6} \frac{\partial E_j}{\partial F_k} F_k + \frac{\partial E_j}{\partial \xi_{4f}} \xi_{4f} \qquad \ldots(1)$$

where E_{oj} are zero order energies of level j and $\partial E_j/\partial F_k$ and $\partial E_j/\partial \xi_{4f}$ are partial derivatives, whose values, given by Wong[8], have been used.

Here difficulty in calculation arises because the number of levels observed is just the same as number of parameters to be evaluated.

The radial eigenfunction for Pr^{3+} has been reasonably assumed to be hydrogenic for which F_4 and F_6 can be evaluated in terms of F_2 by the relation,

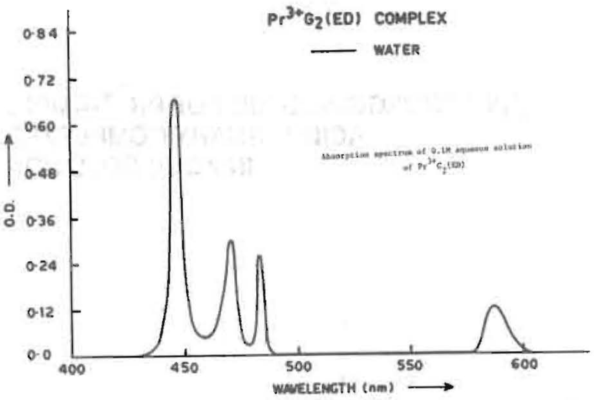

FIG. 1.

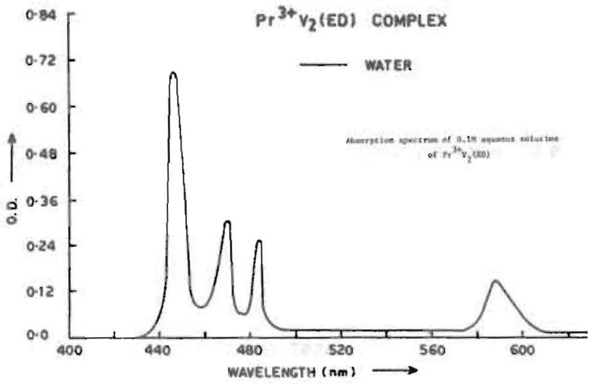

FIG. 2.

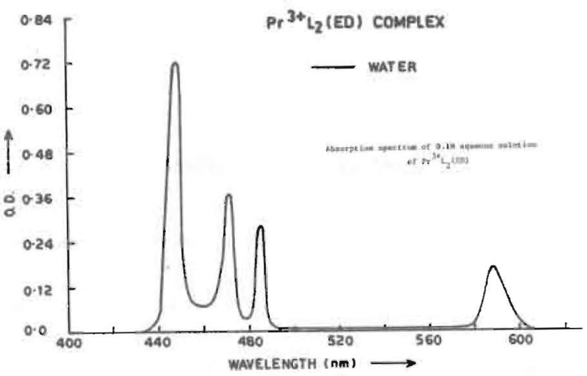

FIG. 3.

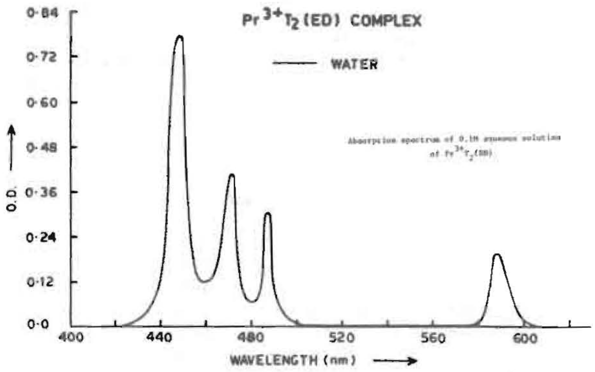

FIG. 4.

$$F_4 = 0.1380\ F_2, \quad F_6 = 0.01511\ F_2 \qquad \ldots(2)$$

Thus only two parameters F_2 and ξ_{4f} could be computed. The values of the parameters F_2, F_4, F_6 and ξ_{4f} have been given in table 3. The Racah parameters (E^k) can be expressed[9] as linear combinations of F_k's

$$E^1 = (70F_2 + 231F_4 + 2002F_6)/9 \qquad \ldots(3)$$

$$E^2 = (F_2 - 3F_4 + 7F_6)/9 \qquad \ldots(4)$$

$$E^3 = (5F_2 + 6F_4 - 91F_6)/3 \qquad \ldots(5)$$

The reduction of F_2 parameter in the case of Pr^{3+} complexes in comparison to its free ion value is 4.11%, which is more than that in the case of Nd^{3+} ternary complexes. This shows that 4f-orbital ligand interaction in Pr^{3+} complexes is stronger than Nd^{3+} complexes.

Empirically the spin-orbit coupling constant ξ_{4f} for aquo ion is given by[10]

$$\xi_{4f} = 142Z - 7648 \qquad \ldots(6)$$

where Z is the atomic number.

Simple calculation gives ξ_{4f} value as 730 cm^{-1} which agrees well with the observed value 704 cm^{-1}. The calculated values of energy levels, using the above discussed F_k and ξ_{4f} values, have been given in Table 1.

The low value of r.m.s. deviation (53.26-92.92 cm^{-1}) shows the validity of the calculations in the present case.

The nephelauxetic ratio, β, defined as

$$\beta = \frac{F_2^c}{F_2^f} \qquad \ldots(7)$$

is found to be less than 1.0 (Table 3) indicating covalent nature of the complexes under study which is in confirmity with the earlier findings of Tandon and co-workers[4,7].

The bonding parameter ($b^{1/2}$), which is related[11] to nephelauxetic ratio, has also been calculated (Table 3). It is interesting to point out that the covalency increases as the primary ligand is changed in order of increasing molecular weight viz. glycine < valine < leucine < tryptophan.

INTENSITY PARAMETERS: The observed intensity may be interpreted in terms of Judd-Ofelt theory[12]. According to which the oscillator strength may be expressed in terms of T_λ (λ= 2,4,6) parameters as[13],

$$P_{ed} = \sum_{\lambda=2,4,6} \tau_\lambda \nu < f^n \psi_J || U^{(\lambda)} || f^n \psi'_{J'} >^2 / (2J+1) \qquad \ldots(8)$$

where symbols have usual meaning τ_λ is related to T_λ parameter by the relation,

$$\tau_\lambda = (2J + 1) T_\lambda \qquad \ldots(9)$$

The T_λ values computed by replacing P_{ed} by P_{obs} are given in Table 4.

The ratio of T_4/T_6 (∿0.20-0.218) suggests that the coordination in the complexes is predominently through oxygen atom. The calculated P_{cal} values may be obtained by using the computed values of T_λ parameters. These values have been includede in Table 2. The low values of r.m.s. deviation (0.46×10^{-6} - 0.61×10^{-6}) indicate the applicability of Judd-Ofelt theory.

The $^3P_2 \leftarrow {}^4H_3$ transition, known to be pseudohypersensitive transition, is sensitive to ligands and the intensity increases in the order of increasing molecular weight of the primary ligand viz. glycine < valine < leucine < tryptophan. It is further interesting to note that this pseudohypersensitive transition shows a red shift as the primary ligand is changed in the order of increasing molecular weight viz. glycine < valine < leucine < tryptophan.

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Table 1. Observed and calculated values of energies (cm^{-1}) of peaks in different Pr^{3+} complexes.

Complex	Levels	Water		
		$\bar{\nu}_{obs}$	$\bar{\nu}_{cal}$	$\Delta\bar{\nu}$
$Pr^{3+}G_2$(ED)	$^3P_2$	22421	22450	-29
	$^3P_1$	21276	21288	-12
	$^3P_0$	20703	20759	-56
	$^1D_2$	17035	17120	-85
r.m.s. dev.(σ)			53.26	
$Pr^{3+}V_2$(ED)	$^3P_2$	22371	22426	-55
	$^3P_1$	21244	21260	-16
	$^3P_0$	20661	20724	-63
	$^1D_2$	17008	17097	-91
r.m.s. dev.(σ)			62.31	
$Pr^{3+}L_2$(ED)	$^3P_2$	22321	22403	-82
	$^3P_1$	21231	21232	-1
	$^3P_0$	20618	20687	-69
	$^1D_2$	17006	17074	-68
r.m.s. dev.(σ)			63.46	
$Pr^{3+}T_2$(ED)	$^3P_2$	22271	22416	-145
	$^3P_1$	21231	21216	15
	$^3P_0$	20533	20629	-96
	$^1D_2$	17006	17057	-51
r.m.s. dev.(σ)			90.92	

Table 2. Observed and calculated values of oxillator strengths of different peaks in different Pr^{3+} complexes.

Complex	Transition	$P_{obs} \times 10^6$	$P_{cal} \times 10^6$	$\Delta P \times 10^6$
$Pr^{3+}G_2$(ED)	$^3P_2$	9.016	9.0158	0
	$^3P_1$	2.903	2.2046	0.69
	$^3P_0$	1.484	2.1716	-0.68
	$^1D_2$	2.145	2.1447	0
r.m.s. dev.(σ)			0.49×10^{-6}	
$Pr^{3+}V_2$(ED)	$^3P_2$	10.091	10.091	0
	$^3P_1$	3.152	2.4183	0.73
	$^3P_0$	1.614	2.377	-0.76
	$^1D_2$	2.202	2.202	0
r.m.s. dev.(σ)			0.53×10^{-6}	
$Pr^{3+}L_2$(ED)	$^3P_2$	11.141	11.1407	0
	$^3P_1$	3.420	2.7583	0.66
	$^3P_0$	2.061	2.7116	-0.65
	$^1D_2$	2.362	2.3616	0
r.m.s. dev.(σ)			0.46×10^{-6}	
$Pr^{3+}T_2$(ED)	$^3P_2$	12.912	12.9122	0
	$^3P_1$	3.941	3.0624	0.85
	$^3P_0$	2.138	2.9982	-0.86
	$^1D_2$	2.383	2.3828	0
r.m.s. dev.(σ)			0.61×10^{-6}	

Table 3. Computed values of different interaction parameters (cm^{-1}) for different Pr^{3+} complexes.

Complex	Parameters	Free ion	Water
	F_2	322.09	310.147
	F_4	44.46	42.831
	F_6	4.867	4.686
	ζ_{4f}	741	694.35
$Pr^{3+}G_2$(ED)	E_1	4729	4553.96
	E_2	24.74	23.828
	E_3	478.14	460.43
	β	-	0.9629
	$b^{1/2}$	-	0.1361
	F_2	322.09	309.494
	F_4	44.46	42.742
	F_6	4.867	4.676
	ζ_{4f}	741	697.47
$Pr^{3+}V_2$(ED)	E^1	4729	4544.39
	E^2	24.74	23.778
	E^3	478.14	459.47
	β	-	0.9609
	$b^{1/2}$	-	0.1398
	F_2	322.09	308.783
	F_4	44.46	[illegible]
	F_6	4.867	4.666
	ζ_{4f}	741	701.46
$Pr^{3+}L_2$(ED)	E^1	4729	455[illegible]
	E^2	24.74	23.724
	E^3	478.14	458.39
	β	-	0.9586
	$b^{1/2}$	-	0.1437
	F_2	322.09	306.948
	F_4	44.46	42.389
	F_6	4.867	4.638
	ζ_{4f}	741	726.22
$Pr^{3+}T_2$(ED)	E^1	4729	4507.05
	E^2	24.74	23.583
	E^3	478.14	455.67
	β	-	0.9529
	$b^{1/2}$	-	0.1533

Table 4. Computed values of T_λ parameters for different Pr^{3+}-complexes.

Complex	$T_\lambda \times 10^9$			
	T_2	T_4	T_6	T_4/T_6
$Pr^{3+}G_2$(ED)	-11.6557	0.607	2.8055	0.216
$Pr^{3+}V_2$(ED)	-17.5736	0.6658	3.1511	0.211
$Pr^{3+}L_2$(ED)	-21.168	0.7611	3.4802	0.218
$Pr^{3+}T_2$(ED)	-32.6952	0.845	4.053	0.208

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