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Absorption spectra of ternary complexes of rare earths

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ABSTRACT

The absorption spectra of ternary complexes of Pr^{3+} and Nd^{3+} in different environments i.e. water, methanol, formamide and DMSO (dimethylsulphoxide) have been recorded in the visible region, using methionine as primary ligand and propane -1,2-diol as secondary ligand. The energies and intensities of various transitions calculated using the Judd-Ofelt relations are in good agreement with these obtained experimentally. This study reveals that the complexes are covalent in nature.

RESUMEN

El espectro de absorción de complejos ternarios Pr^{3+} y Nd^{3+} en diferentes solventes, esto es agua, metanol, formamida y DMSO (dimetil-sulfóxido) han sido registrados en la región visible, usando metionina como ligante primario y propano -1, 2-diol como ligante secundario. Las energías e intensidades de varias transiciones calculadas usando las relaciones de Judd-Ofelt concuerdan bastante bien con las obtenidas experimentalmente. Este estudio revela que los complejos son de naturaleza covalente.

INTRODUCTION

A great deal of spectroscopic work has been done on the rare earth complexes with oxygen donor ligands in last decade[1-10] as an important lasing material due to their narrow line width and weak crystal field interaction. The energy levels of Nd^{3+} ion in different lattice sites have been reported in the literature[11-15]. The present communication reports the study of various energy and intensity interaction parameter from the absorption spectra of complexes of Nd^{3+} and Pr^{3+} in different environments.

The values of spectral parameters like Slater-Condon (F_k), Lande (ζ_{4f}), Oscillator strength (P). Judd-Ofelt (T_λ), Nephelauxetic ratio (β) and Bonding ($b^{1/2}$) which give useful information regarding interelectronic repulsion and spin - orbit interaction in the complexes, have been computed by using partial regression method.

EXPERIMENTAL

The complexes were prepared by the method reported earlier by author[16]. Complexes synthesized were $NdM(P)_2$ and $PrM(P)_2$, where M stands for methionine and P stands for propane-1,2-diol and subscript 2 shows the number of moles used. The spectra have been recorded in the region 360-920 nm on Carl-Zeiss VSU-2 spectrophotometer in different solvents i.e. water, methanol, formamide and DMSO. The records were obtained between optical density and wave length.

RESULTS AND DISCUSSION

(a) ENERGY LEVELS : The energy levels of various transitions were evaluated theoretically[17] by using the relation

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

The observed and calculated values of energy levels using the above relation for the complexes of Nd^{3+} and Pr^{3+} in different solvents have been collected in Tables 1-2. Small r.m.s. deviations between theoretical and experimental values supports the validity of relation used in case of Nd^{3+} complex while high r.m.s. deviation for Pr^{3+} complex is due to the assumption of 4f - wave functions to be hydrogenic. The red shift of the energy levels from that of free ion in different solvents supports the complexation. The hypersensitive transition (${}^4G_{5/2} \leftarrow {}^4I_{9/2}$) in Nd^{3+}

complex and pseudohypersensitive transition ($^3P_2 \leftarrow {}^4H_3$) in Pr^{3+} complex show red shift as the solvents are changed in the order DMSO > Formamide > Methanol ≥ water. This may be attributed due to some participation of the oxigen atom orbitals of solvent with those of metals at different distances in solution.

(b) INTENSITY PARAMETERS : As we know that $P_{exp} = 4.6 \times 10^{-9} \times \varepsilon_m \times \Delta\nu_{1/2}$ ...(2) where ε_m and $\Delta\nu_{1/2}$ are the molecular extinction coefficient and band width for each transition respectively. The value of T_λ ($\lambda = 2,4,6$) parameters have been computed from Judd-Ofelt relation by using partial multiple and regression method. The values of reduced matrix elements have been taken from Carnall et al.[18]

The experimentally observed values of oscillator strength for Nd^{3+} complexes alongwith their calculated values usign the relation (2) have been collected in Tables 3 and 4 respectively.

The calculated values of intensity parameters T_2, T_4, T_6 have been collected in Tables 5 and 6. The value of the parameter T_2 which is sensitive to the environmental changes is found to be increased as the solvents are changed in the order of water-methanol-formamide-DMSO. The negative value of T_2 parameter has no physical significance.

It is observed that the ratio of (T_4/T_6) for a metal is fairly constant in all the four solvents. It is ∿ 0.25 in case of praseodymium while ∿ 0.80 in neodymium. This is due to the fact that coordinating environment around the metal-ion remains unaltered. Thus the ratio of (T_4/T_6) increases as the atomic number of metal ion increases. Oscillator strength for the hypersensitive transitions increases as the solvents are changed in the order of water < methanol < formamide < DMSO, which indicate that the coordinating affinity of the metal is largest for DMSO and smallest for water.

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Table 1. Observed and calculated values of energy levels (in cm^{-1}) for Nd(P)$_2$ complex in different environments.

Levels	Water		Methanol		Formamide		DMSO	
	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.
$^{2}P_{1/2}$	23148	23142	23148	23141	23148	23143	23095	23127
$^{4}G_{11/2}$	21692	21574	21692	21578	21645	21563	21598	21515
$^{4}G_{9/2}$	21186	21175	21142	21139	21142	21140	21097	21104
$^{2}G_{9/2}$	19606	19593	19606	19582	19606	19570	19569	19531
$^{4}G_{7/2}$	19231	19243	19231	19226	19231	19213	19194	19178
$^{4}G_{5/2}$	17301	17308	17301	17315	17271	17290	17241	17256
$^{4}F_{9/2}$	14706	14749	14706	14743	14706	14741	14684	14712
$^{4}F_{7/2}$	13369	13321	13369	13325	13369	13315	13351	13287
$^{4}F_{5/2}$	12392	12499	11392	12503	12392	12491	12361	12464
$^{4}F_{3/2}$	11521	11483	11521	11488	11507	11473	11494	11452
r.m.s. dev.	56.16		55.79		52.35		52.09	

Table 2. Observed and calculated values of energy levels (in cm^{-1}) for Pr(P)$_2$ complex in different environments.

Levels	Water		Methanol		Formamide		DMSO	
	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.
$^{3}P_{2}$	22548	22446	22548	22436	22523	22411	22472	22379
$^{3}P_{1}$	21368	21315	21345	21302	21322	21279	21299	21245
$^{3}P_{0}$	20812	20845	20790	20825	20768	20806	20725	20771
$^{1}D_{2}$	16949	17149	16935	17136	16920	17121	16892	17093
r.m.s. dev.	118.51		119.19		118.57		116.28	

Table 3. Observed and calculated values of oscillator strength for Nd(P)$_2$ complex in different environments.

Levels	Water		Methanol		Formamide		DMSO	
	Obs. $x10^{6}$	Cal. $x10^{6}$	Obs. $x10^{6}$	Cal. $x10^{6}$	Obs. $x10^{6}$	Cal. $x10^{6}$	Obs. $x10^{6}$	Cal. $x10^{6}$
$^{2}P_{1/2}$	1.15	0.58	1.30	0.69	1.42	0.73	1.54	0.70
$^{4}G_{11/2}$	1.25	0.25	1.25	0.27	1.25	0.25	1.44	0.28
$^{4}G_{9/2}$	0.89	1.91	0.98	1.99	1.08	2.11	1.18	2.10
$^{2}G_{9/2}$	1.53	0.50	1.70	0.53	1.70	0.56	1.87	0.56
$^{4}G_{7/2}$	4.08	4.26	4.41	4.42	4.74	4.91	5.03	4.90
$^{4}G_{5/2}$	18.28	18.53	19.47	19.69	24.00	24.30	24.80	24.96
$^{4}F_{9/2}$	0.38	0.69	0.43	0.74	0.43	0.77	0.47	0.83
$^{4}F_{7/2}$	5.21	5.75	5.53	6.16	5.66	6.41	6.00	6.63
$^{4}F_{5/2}$	7.33	6.95	7.86	7.33	8.15	7.66	8.35	7.76
$^{4}F_{3/2}$	2.21	2.72	2.12	2.78	2.18	2.93	2.18	2.86
r.m.s. dev.	$0.65x10^{-6}$		$0.71x10^{-6}$		$0.73x10^{-6}$		$0.77x10^{-6}$	

Table 4. Observed and calculated values of oscillator strength for Pr(P)$_2$ complex in different environments.

Levels	Water		Methanol		Formamide		DMSO	
	Obs. $x10^{6}$	Cal. $x10^{6}$	Obs. $x10^{6}$	Cal. $x10^{6}$	Obs. $x10^{6}$	Cal. $x10^{6}$	Obs. $x10^{6}$	Cal. $x10^{6}$
$^{3}P_{2}$	16.82	16.82	17.70	17.70	20.92	20.92	23.90	23.90
$^{3}P_{1}$	4.54	3.68	6.53	4.70	8.77	7.80	7.66	6.73
$^{3}P_{0}$	2.79	3.63	2.86	4.63	6.11	7.39	5.70	6.63
$^{1}D_{2}$	1.27	1.27	1.59	1.59	3.39	3.39	2.83	2.83
r.m.s. dev.	$0.60x10^{-6}$		$1.27x10^{-6}$		$0.90x10^{-6}$		$0.66x10^{-6}$	

Table 5. Computed values of energy and intensity parameters for Nd(P)$_2$ complex in different environments.

Parameters	Solvents			
	Water	Methanol	Formamide	DMSO
F_2	329.847	330.727	330.617	330.487
F_4	51.337	50.587	50.527	50.777
F_6	5.213	5.227	5.245	5.265
ζ_{4f}	862.56	862.71	864.94	862.00
β	0.999	0.999	0.998	0.997
$b^{1/2}$	0.0224	0.0224	0.0316	0.0387
$T_2 \times 10^{10}$	7.58	8.58	11.33	11.93
$T_4 \times 10^{10}$	8.06	8.11	8.61	8.25
$T_6 \times 10^{10}$	9.30	10.03	10.41	10.85
T_4/T_6	0.8667	0.8085	0.8271	0.7604

Table 6. Computed values of energy and intensity parameters for Pr(P)$_2$ complex in different environments.

Parameters	Solvents			
	Water	Methanol	Formamide	DMSO
F_2	312.37	311.96	311.75	311.14
F_4	43.12	43.07	43.04	42.95
F_6	4.720	4.714	4.711	4.701
ζ_{4f}	668.92	669.96	667.49	668.21
β	0.970	0.969	0.968	0.966
$b^{1/2}$	0.1225	0.1254	0.1267	0.1304
$T_2 \times 10^{9}$	-82.00	-81.32	-82.39	-94.87
$T_4 \times 10^{9}$	1.01	1.29	2.06	1.85
$T_6 \times 10^{9}$	5.24	5.48	6.30	7.36
T_4/T_6	0.19	0.24	0.33	0.25