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### SPECTROSCOPIC STUDIES OF Nd<sup>3+</sup> TERNARY AMINO ACID COMPLEXES

#### ABSTRACT

The absorption spectra of six Nd<sup>3+</sup> ternary amino acid complexes have been recorded in water. Nine bands in the region 400-800 nm have been observed. Slater-Condon, Lande' spin-orbit interaction and Judd-Ofelt intensity parameters from the observed bands have been computed. Using these parameters energies and intensities of these bands have been calculated. The agreement between the calculated and observed values is good. The variation of all the parameters in the complexes from the corresponding Nd<sup>3+</sup> aquo ion parameters has been discussed. Using F<sub>2</sub> values, the nephelauxetic ratio and bonding parameter have been computed which indicate covalent character in these complexes.

#### RESUMEN

El espectro de absorción de seis complejos de ácido amino ternario Nd<sup>3+</sup> han sido registrados en el agua. Nueve bandas en la región 400-800 nm han sido observados y se computan. Interacción de "orbital-spin" Slater-Condon, Lande' y parámetros de intensidad Judd-Ofelt de las bandas observadas. Usando estos parámetros se han calculado las energías y las intensidades de estas bandas. Se nota una buena aproximación entre los valores calculados y los observados. Se discute la variación de todos los parámetros en los complejos correspondientes Nd<sup>3+</sup> se computan otros parámetros indicando el carácter covalente en estos complejos.

#### INTRODUCTION

Structural informations of lanthanide amino acid complexes are generally obtained through NMR<sup>1,2</sup> and I.R. studies [3,4]. Absorption studies in the visible region can also be helpful in determining structural informations [5] of lanthanide complexes specially the nature of bonding in terms of covalency and the contributions to it from different donors of different ligands [6-9]. From this point of view, Nd<sup>3+</sup> ternary amino acid complexes were studied in which amino acids have been used as primary ligand and 2,3-butandiol as secondary ligand. All the complexes were soluble in

water. The inter-electronic repulsion, spin-orbit interaction, nephelauxetic effect and bonding in various complexes have been discussed in the light of Slater-Condon (F<sub>k</sub>), Lande'(ζ<sub>4f</sub>), nephelauxetic ratio (β) and bonding (b<sup>1/2</sup>) parameters. The Judd-Ofelt intensity parameters (T<sub>λ</sub>) have also been calculated from the observed oscillator strengths of the various f-f transitions studied in the visible region. These have been further co-related with the co-ordination from different donors in the complexes. For the calculation of various parameters, partial regression method [10] has been used.

#### EXPERIMENTAL

The complexes of Nd<sup>3+</sup> with amino acid [Glycine (G) and Lucine (L)] as primary ligand and 2,3-butandiol (BD) as secondary ligand in the molecular ratio 1:1:1, 1:2:1 and 1:1:2 have been synthesized by the usual methods<sup>11</sup>. The reagents used were of AR grade. NdCl<sub>3</sub>·6H<sub>2</sub>O (99.99% pure) was supplied by Indian Rare-Earths limited. The complexes were crystallized under vacuum. The elemental analysis of the complexes was also carried out. The absorption spectra were recorded on 'Hitachi F-3000' Fluorescence spectrophotometer in the region 400 nm - 800 nm in triple distilled water with an accuracy of ± 0.1 nm.

#### PARAMETERS AND THEIR EVALUATION

(i) **Energy Parameters:** The initial set of parameters may be evaluated by expressing the energy as Taylor series expansion [12-15].

$$E_J(F_k, \zeta_{4f}) = E_{0j}(F_k^0, \zeta_{4f}^0) + \sum_{K=2,4,6} \left( \frac{\partial E_J}{\partial F_k} \right) \Delta F_k + \left( \frac{\partial E_J}{\partial \zeta_{4f}} \right) \Delta \zeta_{4f} \quad (1)$$

Table 1. Experimental and calculated energy values (in  $\text{cm}^{-1}$ ) of various transitions of neodymium ternary amino acid complexes.

Transition	NdG(BD)		NdG <sub>2</sub> (BD)		NdG(BD) <sub>2</sub>		NdL(BD)		NdL <sub>2</sub> (BD)		NdL(BD) <sub>2</sub>	
	$E_{\text{exp}}$	$E_{\text{cal}}$	$E_{\text{exp}}$	$E_{\text{cal}}$	$E_{\text{exp}}$	$E_{\text{cal}}$	$E_{\text{exp}}$	$E_{\text{cal}}$	$E_{\text{exp}}$	$E_{\text{cal}}$	$E_{\text{exp}}$	$E_{\text{cal}}$
$^4I_{9/2}$	0	0	0	0	0	0	0	0	0	0	0	0
$^4F_{7/2}$	13351	13291	13333	13285	13333	13288	13371	13307	13333	13292	13333	13293
$^4F_{9/2}$	14671	14726	14678	14723	14690	14723	14692	14742	14701	14713	14705	14713
$^2H_{11/2}$	16077	16075	16077	16075	16077	16047	16065	16053	16077	16074	16077	16074
$^4D_{5/2}$	17325	17263	17320	17266	17325	17275	17330	17291	17331	17298	17325	17277
$^4D_{7/2}$	19142	19228	19135	19218	19149	19226	19157	19231	19149	19225	19142	19221
$^4D_{9/2}$	19546	19561	19531	19553	19504	19559	19546	19574	19538	19545	19554	19511
$^2D_{9/2}$	21186	21168	21180	21165	21168	21169	21190	21172	21180	21178	21170	21172
$^4D_{11/2}$	21580	21518	21575	21511	21570	21515	21600	21547	21395	21522	21580	21527
$^2F_{3/2}$	23191	23197	23180	23169	23190	23176	23190	23198	23148	23165	23188	23185
r.m.s. deviation	47.34		45.89		40.68		44.41		44.60		41.18	

Table 2. Computed values of interaction parameter (in  $\text{cm}^{-1}$ ),  $\beta$  and  $b^{1/2}$  for neodymium ternary amino acid complexes.

Complex	$F_2$	$F_4$	$F_6$	$F_{2f}$	$F_0/F_2$	$F_4/F_2$	$\beta$	$b^{1/2}$
Free ion	331.15	50.71	5.15	884.00	0.015	0.153	-	-
NdG(BD)	330.64	51.60	5.29	856.23	0.016	0.155	0.998	0.028
NdG <sub>2</sub> (BD)	330.44	51.53	5.29	857.94	0.016	0.155	0.998	0.033
NdG(BD) <sub>2</sub>	330.03	51.60	5.27	856.75	0.015	0.156	0.997	0.042
NdL(BD)	330.96	51.30	5.28	860.86	0.016	0.155	0.999	0.017
NdL <sub>2</sub> (BD)	329.75	51.57	5.26	860.80	0.015	0.156	0.996	0.046
NdL(BD) <sub>2</sub>	330.38	51.42	5.28	861.04	0.016	0.155	0.998	0.035

\* No units.

Table 3. Experimental and calculated oscillator strength of various transitions in neodymium ternary amino acid complexes.

Transition	NdG(BD)		NdG <sub>2</sub> (BD)		NdG(BD) <sub>2</sub>		NdL(BD)		NdL <sub>2</sub> (BD)		NdL(BD) <sub>2</sub>	
	$f_{\text{exp}}$	$f_{\text{cal}}$	$f_{\text{exp}}$	$f_{\text{cal}}$	$f_{\text{exp}}$	$f_{\text{cal}}$	$f_{\text{exp}}$	$f_{\text{cal}}$	$f_{\text{exp}}$	$f_{\text{cal}}$	$f_{\text{exp}}$	$f_{\text{cal}}$
$^4F_{7/2}$	4.88	4.92	4.95	4.99	5.02	5.05	4.82	4.83	4.97	4.98	5.09	5.06
$^4F_{9/2}$	0.89	1.04	0.90	1.06	0.90	1.07	0.90	1.01	0.91	1.05	0.95	1.06
$^2H_{11/2}$	0.24	0.29	0.29	0.30	0.30	0.30	0.28	0.28	0.29	0.29	0.30	0.29
$^4D_{5/2}$	9.46	9.53	9.75	9.83	9.95	10.03	11.18	11.20	11.60	11.63	11.41	11.39
$^4D_{7/2}$	3.67	3.75	3.77	3.85	3.84	3.92	3.56	3.59	3.70	3.70	3.70	3.74
$^4D_{9/2}$	1.87	1.98	1.94	2.01	1.97	2.04	1.82	1.85	1.81	1.92	2.12	1.95
$^2D_{9/2}$	0.45	0.65	0.46	0.66	0.49	0.68	0.47	0.62	0.49	0.64	0.54	0.65
$^4D_{11/2}$	0.36	0.34	0.36	0.34	0.37	0.35	0.44	0.32	0.49	0.33	0.53	0.34
$^2F_{3/2}$	0.49	0.51	0.50	0.53	0.50	0.54	0.43	0.43	0.45	0.44	0.48	0.45
r.m.s. deviation	$0.10 \times 10^{-6}$		$0.10 \times 10^{-6}$		$0.10 \times 10^{-6}$		$0.07 \times 10^{-6}$		$0.09 \times 10^{-6}$		$0.10 \times 10^{-6}$	

Table 4. Computed values of intensity parameters  $F_A$  for neodymium ternary amino acid complexes.

Complex	$F_A \times 10^3$			$F_4/F_2$
	$F_2$	$F_4$	$F_6$	
NdG(BD)	0.275	0.602	1.56	0.386
NdG <sub>2</sub> (BD)	0.285	0.622	1.56	0.393
NdG(BD) <sub>2</sub>	0.291	0.635	1.60	0.395
NdL(BD)	0.429	0.503	1.52	0.329
NdL <sub>2</sub> (BD)	0.446	0.517	1.58	0.327
NdL(BD) <sub>2</sub>	0.426	0.529	1.60	0.329

Table 5. Comparative study of hyperparametric band observed in complexes having ligands in different ratios.

Ligand	Energy $\ln(\text{cm}^{-1})$	Intensity $F_{\text{exp}} \times 10^3$	Hyperparametric Ratio ( $\beta$ )	Covalency $(b^{1/2})$
G(BD)	17325	9.456	0.9984	0.0288
G <sub>2</sub> (BD)	17320	9.757	0.9978	0.0331
G(BD) <sub>2</sub>	17325	9.941	0.9965	0.0418
L(BD)	17330	11.175	0.9994	0.0173
L <sub>2</sub> (BD)	17331	11.601	0.9957	0.0463
L(BD) <sub>2</sub>	17325	11.406	0.9976	0.0346

where  $E_{0j}$  is the zero-order energy of the  $j^{\text{th}}$  level. Putting the observed energy value  $E_j$ , zero order energy value and the partial derivatives  $F_2, F_4, F_6$ , and  $\zeta_{4f}$  have been computed by using the partial regression method [10].

(ii) **Bonding parameters:** The nephelauxetic ratio ( $\beta$ ) and bonding parameter ( $b^{1/2}$ ) along with the ratios  $F_4/F_2$  and  $F_6/F_2$  which infer covalency due to complexation have also been reported in table 2.

(iii) **Intensity parameters:** The experimental oscillator strength is obtained from

$$P_{\text{exp}} = 4.318 \times 10^{-9} \int \epsilon(\nu) d\nu$$

where  $\epsilon(\nu)$  is the molar extinction coefficient corresponding to energy  $\nu$ . Theoretically the oscillator strength  $P_{\text{cal}}$  of the induced-dipole transition  $\psi_j - \psi'_j$ , of energy  $\nu$  ( $\text{cm}^{-1}$ ) in accordance with Judd-Ofelt relation [16] can be expressed as

$$P_{\text{cal}} = \sum_{\lambda=2,4,6} T_{\lambda} (f^{\text{n}} \psi_j | U^{(\lambda)} | f^{\text{n}} \psi'_j)^2 \quad (3)$$

The values of  $T_{\lambda}$  parameters have been computed from Judd-Ofelt expression by using partial regression method where the values of reduced matrix elements have been taken from Carnall et al. [17]. The values of  $T_{\lambda}$  parameters are considered to be characteristic of particular lanthanide complex. The computed values of  $T_{\lambda}$  parameters have been given in Table 4.

## RESULTS AND DISCUSSION ENERGY LEVELS AND INTERACTION PARAMETERS

The close agreement between experimental and calculated values of the energy levels (Table 1) indicates the suitability of the relation used which takes into account the electrostatic and magnetic interactions. Red shift of all the energy levels from that of the free ion supports the formation of complexes.

In general the parameters  $F_k$  and  $\zeta_{4f}$  of  $\text{Nd}^{3+}$  ternary amino acid complexes exhibit a decrease from the corresponding values of the parameters for  $\text{Nd}^{3+}$  aquo ion. The decrease in the interelectronic repulsion and spin-orbit interaction indicates the expansion of the central metal ion orbital on complexation and is in accordance with the theory of f-f transitions reported earlier. [18]

Positive  $b^{1/2}$  and  $\beta$  values less than one indicate [13] the covalent bonding in complexes. The small value of  $b^{1/2}$  and small variation in it suggests that the co-ordinating environment around the neodymium ion does not change significantly when the ligands are changed. The amino acids co-ordinate through carboxylic oxygen only while nitrogen remains unaffected. Thus amino acids behave as typical oxygen donor ligands. This conclusion has been supported by infra-red studies [19] which clearly shows a very weak bonding of metal ion with the nitrogen.

In Table 2, the average value of  $F_4/F_2$  for  $\text{Nd}^{3+}$  ternary amino acid complexes is larger than those calculated by using Hartree-Fock method [20], but they are nearer to the value for the aquo ion. The same trend has been observed for the ratio  $F_6/F_2$ .

## SPECTRAL INTENSITIES

The experimental and calculated oscillator strengths for the various transitions in the complexes in water are collected in Table 3. The small r.m.s. deviations between the observed and the calculated values of oscillator strength indicates the suitability of Judd-Ofelt relation [11] in these complexes. There is small variation in the value of  $T_2$  (Table 4) for the complexes under study. The ratio of  $T_4/T_6 \sim 0.32$  agrees well [6, 7, 21-22] with that for other  $\text{Nd}^{3+}$  amino acid ternary complexes. This shows that the coordination in these complexes is predominantly through oxygen.

It is important to note that the hypersensitive transition (which is sensitive to environmental changes),  $4G_{5/2} - 4I_{9/2}$ , exhibits (Table 5) the increase in the intensity with the increase in covalency of the complexes. The hypersensitivity has been found to be proportional to nephelauxetic ratio ( $\beta$ ). It also decreases with decreasing frequency of the transition. This is in conformation of the earlier observation reported by Peacock [5].

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