

## Spectral study of the complexation of Nd(III) with glutathione reduced (GSH) in the presence and absence of Zn(II) in aquated organic solvents

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**Abstract.** Studies on the difference in energy parameters and comparative absorption spectrophotometry involving  $4f-4f$  transitions on Nd(III) and glutathione reduced (GSH) in the absence and presence of Zn(II) have been carried out in aquated organic solvents (50 : 50) like methanol, dioxane, acetonitrile and dimethylformamide. Variations in the spectral energy parameters – Slater–Condon ( $F_k$ ) factor, Lande spin-orbit coupling constant ( $x_{4f}$ ), nephelauxetic ratio ( $b$ ), bonding parameter ( $b^{1/2}$ ) and percent covalency ( $d$ ) – are calculated and correlated with binding of Nd(III) with GSH in presence and absence of Zn(II).

**Keywords.** Hypersensitive; pseudohypersensitive; glutathione reduced (GSH); absorption spectra; nephelauxetic effect.

### 1. Introduction

Lanthanide co-ordination chemistry in solution state is of great importance with the increasing use of lanthanides as probes in the exploration of the structural functions of biomolecular reactions.<sup>1–4</sup> This is particularly due to their ability to replace Ca(II) ions in specific manner.<sup>5,6</sup> Shah<sup>7</sup> studied comparative  $4f-4f$  transition spectra of Pr(III) with lysozyme by using energy interaction parameters to explain the behaviour of binding between them. Mehta<sup>8</sup> also studied the mode of binding between Pr(III) and Nd(III) with lysozyme in presence of Zn(II), a soft metal ion, by employing intensity parameters. The ligand we chose, glutathione reduced (GSH), is a naturally occurring tripeptide with  $\gamma$ -L-glutamyl-L-cysteinyl-glycine.<sup>9</sup> It has eight potential binding sites, viz. two carboxylic acid groups, an amino group, a sulphhydryl group and two peptide linkages.

Hard metal ions like Ca(II) and the soft metal ion Zn(II) are endogenous metal ions that have differing co-ordinating behaviour towards biological molecules. For binding, Ca(II) ions prefer hard donor sites like carboxylic and carbonyl group whereas Zn(II) prefers soft donor sites like the sulphhydryl (–SH) group found in GSH. Since Nd(III) resembles Ca(II), its

complexation can provide information about the co-ordination characteristics of diamagnetic Ca(II) with biomolecules during biochemical reactions. Hence, paramagnetic lanthanides are good spectral probes for exploring the biological roles of Ca(II) by isomorphous substitution.<sup>10</sup> The present work discusses the quantitative spectral energy interaction parameters of Nd(III) complexes with glutathione, reduced in presence and absence of Zn(II) in aquated organic solvents at pH 4 and 298 K. The present work reports the sensitivity of the hypersensitive transition  $^4I_{9/2} \rightarrow ^4G_{5/2}$  and ligand mediated pseudo hypersensitive transitions  $^4I_{9/2} \rightarrow ^4F_{3/2}$ ,  $^4I_{9/2} \rightarrow ^4F_{5/2}$ ,  $^4I_{9/2} \rightarrow ^4F_{7/2}$  and  $^4I_{9/2} \rightarrow ^4G_{7/2}$  of Nd(III) and uses the magnitude and variation of Slater–Condon factor ( $F_k$ ,  $K = 2, 4, 6$ ). Lande spin-orbit coupling ( $x_{4f}$ ), nephelauxetic ratio ( $b$ ), bonding ( $b^{1/2}$ ) and percent covalency ( $d$ ) parameters to discuss the bonding of Nd(III) with GSH in presence and absence of Zn(II).

### 2. Experimental

Neodymium(III) nitrate hexahydrate of 99.9% purity (CDH Analytical Reagents) and glutathione reduced (GSH) (Sisco Pvt Ltd, Mumbai), were used for the synthesis of the complex and for spectral analysis. Glutathione reduced (GSH) was kept below 4°C and a fresh solution (0.01M) prepared for spectral study.

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The Nd(III):GSH complex was synthesised by mixing Nd(III) nitrate (0.002M) with 0.004M GSH in ethylacetate–acetone mixture with constant stirring at pH 4. A pinkish crystalline complex was obtained after 8 to 10 days. The crystal obtained was washed with acetone and dried in a desiccator over P<sub>2</sub>O<sub>5</sub>. The purity of the complex was checked by elemental as well as spectral techniques and the stoichiometry of the complex was found to be [Nd(GSH)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>]. For preparation of the Nd(III)-GSH-Zn(II) complex, Zn(II) nitrate of the 0.001M was added to a mixture of Nd(III) nitrate (0.001M) and GSH (0.002M) in ethyl acetate and acetone mixture (50 : 50). The crystalline solid was highly hygroscopic in nature and the stoichiometry of the complex was [Nd<sub>2</sub>(GSH)<sub>2</sub>Zn(H<sub>2</sub>O)<sub>6</sub>]. Elemental analysis data of the two complexes are given in table 1. The metal contents in the complexes were estimated by complexometric titration with EDTA and estimation of water in the complex was done by the Karl Fisher method. The solvents used were CH<sub>3</sub>OH, CH<sub>3</sub>CN, DMF and dioxane of A/R grade from Qualigens. The absorption spectra were recorded on a Perkin–Elmer Lamda 35 UV-visible spectrophotometer with high resolution and expansion of scale in a water-jacketed cell holder in the region 300–1100 nm. The IR spectrum was taken on FTIR, Shimadzu model 8400/890. The temperature for all the observations was maintained at 298K by using water-circulating thermostat model-DS-G-HAAKE.

### 3. Theoretical

Nephelauxetic ratio has been regarded as a measure of covalency<sup>11–13</sup> and has been interpreted in terms of Slater–Condon and Racah parameters (inter electronic repulsion parameters) as well as by the ratio of the free ion and complex ion,<sup>14</sup>

$$\mathbf{b} = F_K^c / F_K \text{ or } E_C^K / E_f^K, \quad (1)$$

where  $F_k$  ( $K = 2, 4, 6$ ) is the Slater–Condon parameter and  $E^K$  is the Racah parameter for complex and free ions respectively. The bonding parameter ( $b^{1/2}$ ) is inter-related to nephelauxetic effect as,

$$b^{1/2} = [(1 - \mathbf{b})/2]^{1/2}. \quad (2)$$

The electrostatic term  $E_0$  is expressed in terms of the product of Slater radial integral known as Slater–Condon parameter  $F_k$  and is given by

$$E_0 = \sum_{k=0}^{k=6} K^k F_k. \quad (3)$$

The Slater–Condon parameters are also known as direct integrals and are a decreasing function of  $K$  as given by the relation,

$$F_1^K = \int_0^\infty \int_0^\infty \frac{r_<^K}{r_>^{K+1}} R_i^2(r_i) R_j^2(r_j) r_i^2 r_j^2 dr_i dr_j, \quad (4)$$

where  $R$  is the  $4f$ -radial wave function;  $r_<$  and  $r_>$  are the radii of near and more distant electrons; and  $i$  and  $j$  the  $i$ th and  $j$ th electrons under consideration. Condon and Shortley<sup>14</sup> redefined  $F^k$  integrals in terms of reduced integral  $F_k$  related to each other and the relation is

$$F_k = F^k / D_k. \quad (5)$$

Combining relations (4) and (5), the reduced Slater–Condon integral can be written as:

$$F_k = \frac{1}{D_k} \int_0^\infty \int_0^\infty r_<^k r_>^{k+1} R_i^2(r_i) R_j^2(r_j) r_i^2 r_j^2 dr_i dr_j. \quad (6)$$

Here  $D_K$  is the denominator and  $F_K$  are coefficients of linear combination and represent the angular part of the interaction. The energy  $E_{so}$  arising from the

**Table 1.** Analytical data of the complexes.

Complex	%Nd	%C	%H	%N	%S	%Zn
[Nd <sub>2</sub> (GSH) <sub>2</sub> 4H <sub>2</sub> O]	29.76 (28.87)	24.79 (24.12)	3.75 (2.98)	8.67 (8.36)	6.62 (6.07)	–
[Nd <sub>2</sub> (GSH) <sub>2</sub> Zn6H <sub>2</sub> O]	26.94 (26.14)	22.44 (22.13)	3.77 (3.17)	7.85 (7.24)	5.99 (5.02)	6.11 (5.38)

most important magnetic interactions, which are spin-orbit interactions, may be written as

$$E_{\text{so}} = A_{\text{so}} \hat{l}_{4f}, \quad (7)$$

where  $A_{\text{so}}$  is the angular part of spin-orbit interaction and  $\hat{l}_{4f}$  is the radial integral and is known as Lande's parameter. By first order approximation, the energy  $E_j$  of the  $j$ th level is given by Wong<sup>15</sup> as

$$E_j(F_K, \mathbf{x}_{4f}) = E_{\text{oj}}(F_K^0, \mathbf{x}_{4f}^0) + \frac{\partial E_j}{\partial F_K} \Delta F_K + \frac{\partial E_j}{\partial \mathbf{x}_{4f}} \Delta \mathbf{x}_{4f}, \quad (8)$$

where  $E_{\text{oj}}$  is the zero order energy of the  $j$ th level. The value of  $F_K$  and  $\mathbf{x}_{4f}$  are given by

$$F_K = F_K^0 + \Delta F_K, \\ \mathbf{x}_{4f} = \mathbf{x}_{4f}^0 + \Delta \mathbf{x}_{4f}. \quad (9)$$

The difference between the observed  $E_j$  value and the zero order value,  $\Delta E_j$ , is evaluated by

$$\Delta E_j = \sum_{K=2,4,6} \frac{\partial E_j}{\partial F_K} \Delta F_K + \frac{\partial E_j}{\partial \mathbf{x}_{4f}} \Delta \mathbf{x}_{4f}. \quad (10)$$

By using the zero order energy and partial derivatives of Nd(III) ions given by Wong,<sup>15</sup> the above equation can be solved by least square technique and the value of  $\Delta F_2$ ,  $\Delta F_4$ ,  $\Delta F_6$  and  $\Delta \mathbf{x}_{4f}$  can be determined. The percent covalency parameter ( $\mathbf{d}$ ) representing the nephelauxetic effect was calculated from the relation

$$\mathbf{d} = ((1 - \mathbf{b})/\mathbf{b}) \times 100. \quad (11)$$

#### 4. Results and discussion

From figure 1 we can see that there is a red shift as GSH is added to Nd(III) and further longer wavelengths are observed on addition of Zn(II) in DMF. Table 1 shows the variation of the magnitude of energy interaction parameters like Slater–Condon ( $F_K$ ), Lande factor ( $\mathbf{x}_{4f}$ ), Racah energy ( $E^k$ ), nephelauxetic ratio ( $\mathbf{b}$ ), bonding ( $b^{1/2}$ ) and percentage covalency ( $\mathbf{d}$ ) for Nd(III), Nd(III):GSH and Nd(III):GSH:Zn(II) in aqueous and different aquated organic solvents. Table 2 gives the computed and observed values of energies for the various transition bands and root

mean square (RMS) deviation showing the correctness of the various energy parameters. There is a slight decrease in the values of  $F_K$  and  $\mathbf{x}_{4f}$  as the complexation goes on which leads to increase in the values of nephelauxetic ratio ( $\mathbf{b}$ ) and percentage covalency ( $\mathbf{d}$ ). The IR spectrum of the glutathione reduced (GSH) shows a stretching frequency due to sulphhydryl (–SH) group occurring as sharp intense band around 2523  $\text{cm}^{-1}$ . The IR spectra of GSH, Nd(III):GSH and Nd(III):GSH:Zn are given in figures 2 and 3. The addition of Nd(III) to GSH clearly leads to its deprotonation; the addition of Zn(II) to the Nd(III):GSH complex enhances the deprotonation tendency. Zn(II)-S band absorptions can be expected in the region 800–200  $\text{cm}^{-1}$ . This confirms the binding of Zn(II) with the thiol group.

For spectral studies on the structures of co-ordination compounds of lanthanides in solution, any evidence of the relationship between the nephelauxetic band shift and the structure is of special interest. Jorgensen and Ryan<sup>16</sup> noticed the dependence of the nephelauxetic effect on the co-ordination number and suggested that shortening in the metal–ligand distance occurs with decrease in the co-ordination number. To interpret the correlation, analyses of the relationships between nephelauxetic effect, geometry and 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,

$$n = [(1 - \mathbf{b}^{1/2})/\mathbf{b}^{1/2}]. \quad (12)$$

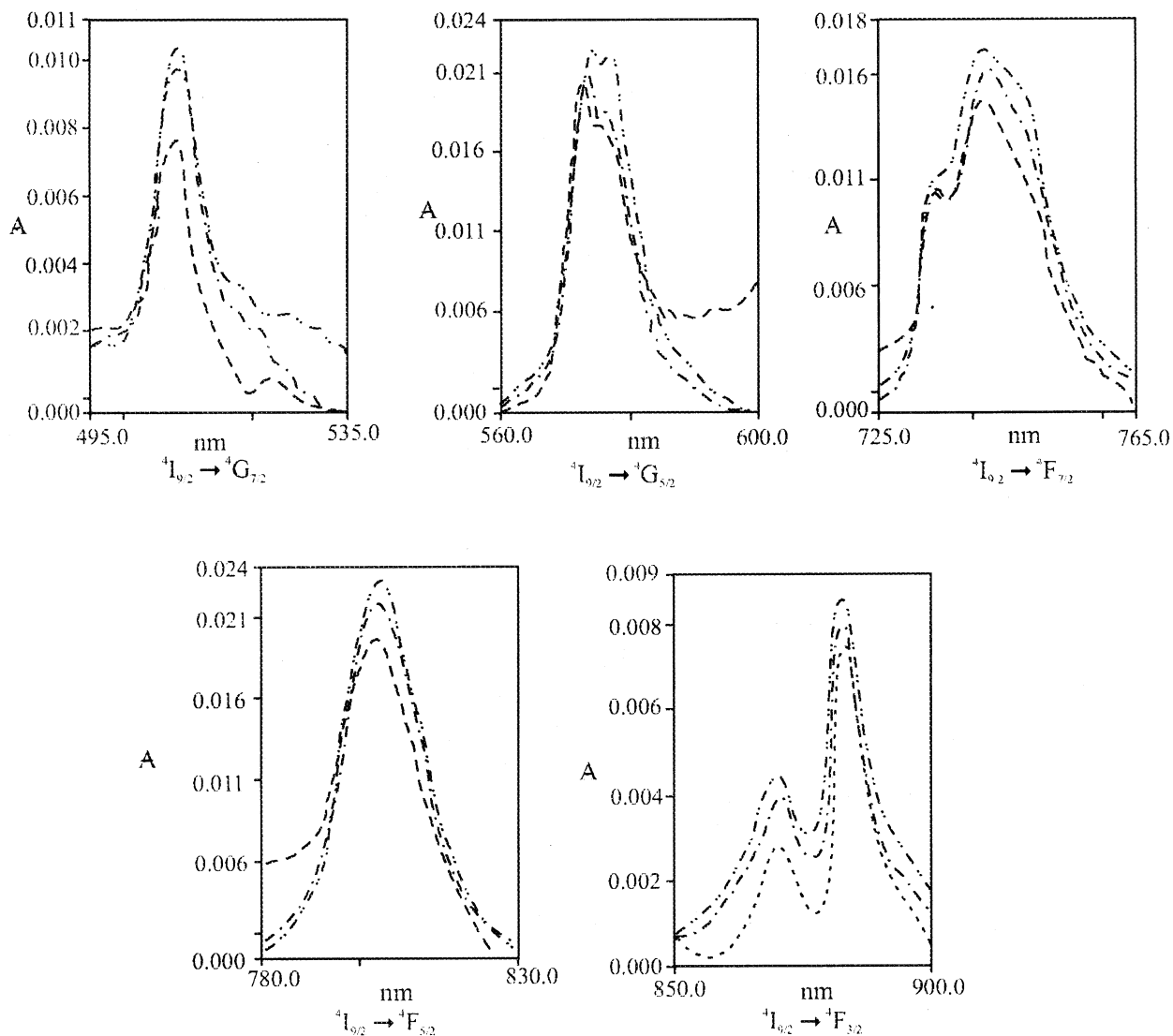
It may be expressed as

$$n = \{H^2L/(H_M - H_L)^2\} (S^*R)^2 N, \quad (13)$$

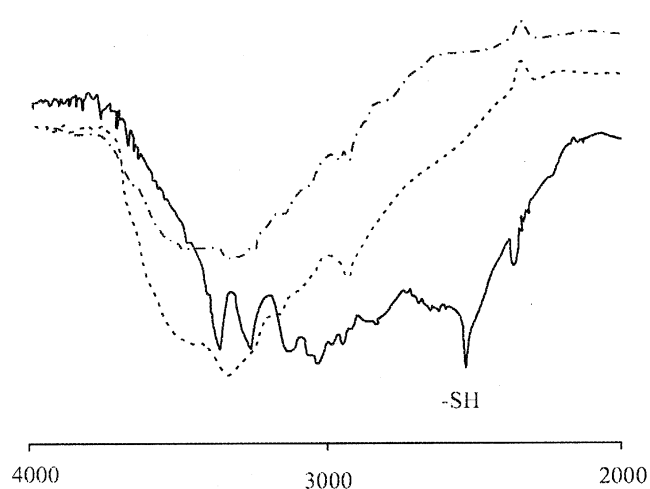
where  $N$  is the co-ordination number,  $H_M$  and  $H_L$  are coulomb integrals of the atomic orbital,  $S$  is the overlap integral,  $R$  is the radius of the orbit. For compounds with ligands coordinated through identical donor atoms, the first term of the RHS of (13) is a constant and (13) then becomes

$$n = \text{constant} (S^*R)^2 N. \quad (14)$$

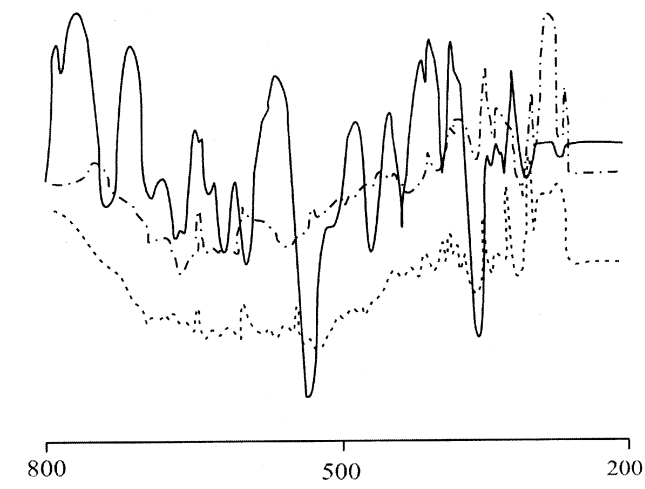
Equation (14) represents the nephelauxetic effect as a function of two variables.  $S^*R$  and  $N$ , which vary with changes in lanthanide–ligand distance in opposite directions. However, any variation in the value of  $R$  leads to a larger change in  $(S^*R)^2$  compared to



**Figure 1.** Comparative absorption spectra of Nd(III) - - -, Nd(III):GSH - · - · and Nd(III):GSH:Zn(III) · · · in DMF: water (50 : 50).



**Figure 2.** Comparative IR spectra of GSH —, Nd(III):GSH - - - and Nd(III):GSH:Zn · · · in the range 4000–2000  $\text{cm}^{-1}$ .



**Figure 3.** Comparative IR spectra of GSH —, Nd(III):GSH - - - and Nd(III):GSH:Zn · · · in the range 800–200  $\text{cm}^{-1}$ .

**Table 2.** Computed values of energy interaction: Slater–Condon  $F_K$  ( $\text{cm}^{-1}$ ), spin-orbit interaction  $\chi_{4f}$  ( $\text{cm}^{-1}$ ), nephelauxetic ratio ( $\mathbf{b}$ ), bonding ( $b^{1/2}$ ), covalency ( $\mathbf{d}$ ) parameters for Nd(III), Nd(III):GSH and Nd(III):GSH:Zn(II) systems in different aquated organic solvents at pH 4.

System	$F_2$	$F_4$	$F_6$	$\chi_{4f}$	$\mathbf{b}$	$b^{1/2}$	$\mathbf{d}$
Solvent – CH <sub>3</sub> OH							
Nd(III)	329.9268	48.1191	5.1316	630.3109	0.9988	0.0247	0.1217
Nd(III):GSH	329.9122	48.1233	5.1313	930.4989	0.9989	0.0236	0.1117
Nd(III):GSH:Zn(II)	329.8822	48.1217	5.1310	930.8920	0.9990	0.0225	0.1009
Solvent – DMF							
Nd(III)	329.7506	48.0432	5.1632	936.9598	1.0121	0.0779	1.1977
Nd(III):GSH	329.6665	48.0692	5.1631	939.3620	1.0139	0.0833	1.3689
Nd(III):GSH:Zn(II)	329.6118	48.0690	5.1629	940.3386	1.0145	0.0851	1.4274
Solvent – dioxane							
Nd(III)	330.0494	48.1105	5.1288	929.1102	1.0074	0.0610	0.7391
Nd(III):GSH	329.9625	48.1026	5.1220	929.1096	1.0082	0.0601	0.8147
Nd(III):GSH:Zn(II)	339.0654	48.0939	5.1208	929.0977	1.0084	0.0607	0.7305
Solvent – CH <sub>3</sub> CN							
Nd(III)	329.9409	48.1148	5.1349	931.0499	1.0087	0.0659	0.8600
Nd(III):GSH	329.9155	48.1052	5.1306	929.8215	1.0089	0.0627	0.7872
Nd(III):GSH:Zn(II)	329.1208	48.1046	5.1213	926.8599	1.0091	0.0550	0.6018
Solvent – CH <sub>3</sub> CN:dioxane							
Nd(III)	329.9739	48.1417	5.1329	929.9167	1.0081	0.0636	0.8027
Nd(III):GSH	329.9562	48.1376	5.1308	929.4261	1.0088	0.0623	0.7692
Nd(III):GSH:Zn(II)	329.1288	48.0941	5.1249	928.0430	1.0091	0.0580	0.6672
Solvent – CH <sub>3</sub> CN:CH <sub>3</sub> OH							
Nd(III)	329.9846	48.0825	5.1305	930.4892	1.0081	0.0638	0.8070
Nd(III):GSH	329.9819	48.0752	5.1304	930.6191	1.0082	0.0639	0.8112
Nd(III):GSH:Zn(II)	329.1447	48.0696	5.1227	927.7653	1.0085	0.0568	0.6409
Solvent – CH <sub>3</sub> CN:DMF							
Nd(III)	329.9221	48.1222	5.1359	931.2720	1.0088	0.0665	0.8772
Nd(III):GSH	329.8899	48.1075	5.1324	935.5252	1.0118	0.0768	1.1619
Nd(III):GSH:Zn(II)	329.8611	48.0820	5.1581	936.5738	1.0123	0.0785	1.2170

that in  $N$ . As a result, the nephelauxetic effect increases when the co-ordination number decreases. The Ln–O distance shortens in spite of the additive nature of  $\mathbf{b}$  and decrease in the number of co-ordinating ligands. Variation in the value of  $E^K$  ( $K = 2, 4, 6$ ); corresponds to that in the value of  $F^K$ , since they are inter-related. Misra *et al*<sup>17,18</sup> observed a general decrease in the values of  $F_K$  and  $\chi_{4f}$  parameters as compared to the corresponding parameters of the free ion.

The hypersensitive transition,  ${}^4I_{9/2} \rightarrow {}^4G_{5/2}$  obeys the selection rule, while the ligand mediated pseudohypersensitive transitions,  ${}^4I_{9/2} \rightarrow {}^4F_{3/2}$ ,  ${}^4I_{9/2} \rightarrow {}^4F_{5/2}$ ,  ${}^4I_{9/2} \rightarrow {}^4F_{7/2}$  and  ${}^4I_{9/2} \rightarrow {}^4G_{7/2}$  of Nd(III) do not.

The latter however exhibit substantial sensitivity, reflected through the wide variation of oscillator strengths and energies with even minor changes in the immediate coordination environment around then even in the presence of a structurally related ligand.<sup>19–21</sup> Due to extremely fast water-exchange rate and very low crystal field stabilization energy, conversion from one geometry to another is very convenient and facile. Karraker<sup>21</sup> showed that the shape, energy and oscillator strength of hypersensitive or pseudohypersensitive transitions can be correlated with coordination number and are diagnostic of the immediate coordination environment around the lanthanide ions.

Computed and observed values of energies ( $\text{cm}^{-1}$ ) and RMS values for Nd(III), Nd(III):GSH (1:1), Pr(III):GSH:Zn(II) (1 : 1 : 1) in aqueous and diffuse :50) at pH 4.

	${}^4I_{9/2} \rightarrow {}^4F_{3/2}$		${}^4I_{9/2} \rightarrow {}^4F_{5/2}$		${}^4I_{9/2} \rightarrow {}^4F_{7/2}$		${}^4I_{9/2} \rightarrow {}^4G_{5/2}$		${}^4I_{9/2} \rightarrow {}^4G_{7/2}$		RMS
	$E_{\text{obs}}$	$E_{\text{cal}}$	$E_{\text{obs}}$	$E_{\text{cal}}$	$E_{\text{obs}}$	$E_{\text{cal}}$	$E_{\text{obs}}$	$E_{\text{cal}}$	$E_{\text{obs}}$	$E_{\text{cal}}$	
-CH <sub>3</sub> OH	11542.68	11476.47	12569.60	12600.19	13484.18	13460.33	17324.42	17278.75	19144.25	19249.67	100.9700
	11542.41	11475.86	12568.97	12599.84	13483.81	13460.13	17324.12	17277.68	19143.89	19249.78	101.6940
	11542.15	11474.78	12568.34	12599.36	13483.27	13459.93	17323.52	17275.84	19142.42	19249.61	103.0389
-DMF	11538.95	11461.89	12559.66	12595.18	13490.54	13460.17	17290.57	17252.41	19134.73	19249.22	110.4541
	11538.28	11455.36	12559.34	12591.91	13485.63	13458.86	17273.25	17240.66	19134.36	19250.82	111.6868
	11538.15	11452.77	12558.71	12590.74	13483.99	13458.41	17268.77	17236.13	19132.17	19250.81	113.3604
-dioxane	11544.81	11480.28	12570.71	12602.16	13488.54	13461.46	17323.52	17285.16	19149.38	19250.08	96.8813
	11541.08	11476.70	12570.71	12600.46	13485.27	13460.68	17322.98	17278.97	19146.09	19249.91	98.5990
	11545.34	11480.78	12570.87	12602.68	13490.18	13461.91	17322.92	17285.99	19149.02	19249.65	96.7888
-CH <sub>3</sub> CN	11539.75	11474.99	12569.76	12599.67	13485.09	13460.42	17320.22	17275.89	19145.72	19250.18	99.2197
d(III)	11541.88	11478.52	12570.24	12601.44	13488.18	13461.25	17323.82	17282.06	19147.92	19249.92	97.6620
	11550.68	11485.54	12574.66	12604.21	13486.72	13461.83	17328.62	17294.61	19152.32	19250.07	93.8272
-CH <sub>3</sub> CN:dioxane	11542.28	11477.24	12569.45	12600.22	13484.54	13460.22	17323.22	17325.32	19148.29	19148.65	75.9795
	11543.35	11478.60	12568.97	12600.90	13485.99	13460.50	17325.32	17282.33	19148.65	19250.65	98.9487
	11547.48	11483.62	12572.45	12603.98	13491.27	13462.44	17324.42	17290.95	19151.58	19249.74	94.6086
-CH <sub>3</sub> CN:CH <sub>3</sub> OH	11541.08	11477.27	12568.02	12601.25	13490.36	13461.45	17323.82	17279.88	19144.98	19249.13	100.5584
	11539.88	11477.09	12569.60	12601.28	13489.63	13461.55	17324.12	17279.56	19144.62	19248.89	99.4722
	11546.11	11484.65	12573.24	12604.67	13492.36	13462.85	17327.42	17292.78	19151.22	19249.19	94.0320
-CH <sub>3</sub> CN:DMF	11544.94	11474.25	12568.34	12599.25	13484.54	13460.19	17313.02	17274.60	19144.98	19250.44	101.2220
	11542.55	11464.783	12566.44	12595.64	13485.81	13459.91	17280.11	17257.13	19146.45	19252.45	101.6806
	11544.68	11462.84	12562.66	12595.18	13489.27	13460.19	17273.54	17253.54	19143.52	19251.89	106.5208

## 5. Conclusion

From the present investigation it has been observed that there is possibility of the involvement of Zn(II) in the complexation of Nd(III) and GSH, revealed by the comparative absorption spectra, which is further supported by the decreased value of the inter-electronic repulsion parameter (Slator–Condon parameter,  $F_k$ ) and increased values of the nephelauxetic ratio. Further work on the evaluation of intensity parameters is going on.

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