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Journal of Solid State Chemistry 171 (2003) 175–182

JOURNAL OF SOLID STATE CHEMISTRY

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An absorption spectral study of Nd (III) with glutathione (reduced), GSH in aqueous and aquated organic solvent in presence and absence of Zn (II)

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Received 1 May 2002; received in revised form 1 August 2002; accepted 17 November 2002

Abstract

The coordination chemistry of glutathione (reduced) GSH is of great importance as it acts as an excellent model system for the binding of metal ions. The GSH complexation with metal ions is involved in the toxicology of different metal ions. Its coordination behaviour for soft metal ions and hard metal ions is found different because of the structure of GSH and its different potential binding sites. We have studied two chemically dissimilar metal ions viz. Nd (III) being hard metal ion, which will prefer hard donor sites like carboxylic groups, and Zn (II) the soft metal ion more suited to peptide—NH and sulfhydryl groups. The absorption difference and comparative absorption spectroscopy involving $4f-4f$ transitions of the heterobimetallic complexation of GSH with Nd (III) and Zn (II) has been explored in aqueous and aquated organic solvents. The changes in the oscillator strengths of different $4f-4f$ bands and Judd–Ofelt intensity (T_λ) parameters determined experimentally is being used to investigate the complexation of GSH. The in vivo intracellular complexation of GSH with Ca (II) in presence of Zn (II) ion has been mimicked through Nd (III)–GSH–Zn (II) absorption spectral studies in vitro.

Keywords: *f–f* transition spectra; GSH; Nd (III) interaction

1. Introduction

The body fluid comprises of endogenous metal ions and physiological ligands, present as multi metal, multi ligand system, in which different metal ions may behave as *antagonist* and *stimulative* [1].

The tripeptide glutathione, γ-L-glutamyl-L-cysteinyl-glycine (GSH) contains a sulfhydryl group. GSH undergoes reversible oxidation to hexapeptide glutathione-oxidized (GSSG) by converting two sulfhydryl bonds to a disulphide bond.

$$2\,\mathrm{GSH} \rightleftharpoons \mathrm{GSSG} + 2\mathrm{H}^{+}.$$

GSH has several important functions in human metabolism, especially in Ca (II) ion homeostasis [2–4]. Zn (II) ion is occurred also intra-cellularly and is known to form very stable complex in vivo. Therefore, Ca (II) and Zn (II) ions (within the cell) may involve hetero-bimetallic simultaneous complexation with GSH. The coordination chemistry of GSH is of great importance as it acts as an excellent model system for the binding of metal ions. GSH complexation with metals is involved in the toxicology of different metals [5,6]. In its reaction with metal ions, GSH offers eight potential binding sites, two carboxylic oxygens, amino nitrogen, a sulfhydryl group, two amide groups and two peptide linkages. The structure of GSH is such that its all-potential binding sites cannot be simultaneously co-ordinated to the same metal ion [7].

Unfortunately, Ca (II) ion is a diamagnetic ion and hence does not give any spectroscopic signal in optical and magnetic spectral techniques. The isomorphous substitution of Ca (II) by Nd (III) [8] provides a very valuable aid to understand the interactions of GSH with Ca (II) because Nd (III) is paramagnetic, hence offers a number of signals in optical and magnetic spectroscopy, which can be utilized as an absorption spectral probe. Absorption difference and comparative absorption

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doi:10.1016/S0022-4596(02)00205-0

spectroscopy involving $4f-4f$ transitions are one of the most effective techniques to reveal the interaction of biomolecules with Nd (III) ion [9,10]. The interaction of GSH with Nd (III) in presence and absence of Zn (II) is followed by selecting different aquated organic solvents and the changes in the oscillator strengths of different $4f-4f$ bands and experimentally determined Judd–Ofelt intensity (T_λ) parameters are correlated with the binding of GSH.

2. Experimental

The solvents and chemicals used were of A.R/G.R grade from E. Merck. Neodymium chloride of 99.9% purity was supplied by M/S. Indian Rare Earths and GSH was procured from Aldrich Chemical Co. USA The stock solution of neodymium was standardized by EDTA method reported elsewhere [11]. The solutions were stored in an inert chamber at 5°C. GSH solution used for each experiment was freshly prepared.

The absorption spectral data were recorded on the model Lambda-2 UV–Visible Spectrophotometer of Perkin-Elmer, USA, equipped with a device for kinetic and high-resolution spectral analysis. The concentration of Nd (III) and Zn (II) was kept to 0.02 M and spectral analysis was carried out by taking different organic solvents in the region from 400 to 900 nm. Background correction was done to observe the actual effect of different conditions for each set of experiment.

The infrared spectra of complexes were recorded on a Perkin-Elmer FT-IR spectrophotometer model no. 1600 series. The FT-IR were recorded between the range 4000–2000 cm^{-1}; 2000–800 cm^{-1} and 800–200 cm^{-1} (Fig. 3). The ^{1}H-NMR spectra of complexes were recorded on Brucker FT-NMR model no. DPX-200 in D_2O at 400 MHz and ^{13}C-NMR were recorded in D_2O at 220 MHz on same model.

3. Result and discussion

3.1. Result obtained from 4f–4f transition

The effect of pH is responsible for the degree of protonation and deprotonation of different coordinating sites of GSH. The bonding of GSH is affected significantly by degree of deprotonation of the coordinating sites and, therefore, pH of medium will have significant effect on Nd (III)–GSH binding, which is clearly reflected through significant intensity variation and interaction energy parameters.

The binding of Nd (III)–GSH brings about changes in the energies of various $f-f$ bands which cause the degree of lowering in the energy interaction, Slater–Condon inter-electronic repulsion, which leads to nephelauxetic effect and intensities of $4f-4f$ electronic transitions.

The Coulombic interaction includes both inter-electronic repulsion parameters, which are represented by different authors either as RACAH inter-electronic parameters E^k $(k = 2, 4, 6)$ or SLATER–CODON inter-electronic repulsion parameter F_k's $(k = 2, 4, 6)$. Needless to add both sets of parameters are inter-related to each other. The other factor which is also included in energy interaction parameters is spin–orbit coupling represented by Land's parameter (ξ_{4f}). This is because the energy of $4f-4f$ transitions comprises of two main components Coulombic F_k and spin–orbit coupling $_{4f}$ parameters, which can be given in the form of equation as follows.

$$E_{\mathrm{obs.}} = f^k F_k + A_{\mathrm{SO}\xi_{4f}},$$

where f^k and A_{SO} are the angular counterparts of Coulombic and spin–orbit interaction, while F_k (Slater–Condon inter-electronic repulsion parameter) and ξ_{4f} are the radial components.

Since interaction of Nd (III) with GSH is generally predominant with carboxylic groups of GSH, the bonding between Nd (III) ion and GSH is basically electrostatic in nature. Since lanthanides are hard metal ions their preference will be for hard donor sites like oxygen atoms. Therefore, the energy and nephelauxetic changes are not apparently significant. This phenomenon is clearly reflected in Tables 1 and 2. We have given more emphasis to quantitative $f-f$ transition intensity analysis because changes in intensities are more significant compared to energy changes. The absolute values of oscillator strengths and Judd–Ofelt intensity (T_λ) intensity parameters are determined under different experimental conditions for Nd (III) complexes with GSH (Table 3). This clearly suggests a significant change, when Nd (III) interacts with GSH in the solution. Comparative absorption spectra of Nd (III), Nd (III)–GSH in water or Nd (III)–GSH in aquated organic solvents clearly show that the addition of GSH to Nd (III) results in significant enhancement in the oscillator strengths of different $4f-4f$ transitions (Fig. 1) As a consequence, we have observed noticeable increase in the magnitude of Judd–Ofelt (T_λ) intensity parameters. These suggest the binding of the tripeptide GSH to Nd (III) in solution.

The absorption spectral study at pH 2.0 indicates the deprotonation of Glutamyl residue of GSH. Nd (III) being hard metal ion, has a tendency to coordinate, preferentially with –COOH group. Hence Nd (III) interacts with glutamyl residue in acidic medium, of GSH. One more carboxylic (Glycilic) group and sulfhydryl (–SH) group from glycine and cysteinyl residue gets deprotonated at pH 4.0 and 6.0, respectively. But the change in oscillator strengths and Judd–Ofelt (T_λ) intensity parameters is less significant in

Table 1
Computed value of energy interaction F_k (cm^{-1}), nephelauxatic effect (β), Bonding ($b^{1/2}$), and covalency (δ) parameters for Nd (III) complexes with GSH in different solvents

Sr.	Medium	F_2	F_4	F_6	β	$1-\beta$	$b^{1/2}$	δ
1	Water	335.13	46.42	5.17	0.9939	0.0060	0.055	0.612
2	DMF	332.55	48.35	5.17	0.9817	0.0183	0.096	0.864
3	MeOH	334.86	46.76	5.18	0.9903	0.0097	0.069	0.979
4	Dioxane	334.74	46.87	5.18	0.9899	0.0100	0.094	0.821
5	MeCN	334.95	46.62	5.17	0.9926	0.0074	0.061	0.746
6	DMF + MeOH	334.52	47.08	5.18	0.9879	0.0121	0.077	1.224
7	DMF + MeCN	334.54	47.06	5.15	0.9876	0.0124	0.079	1.256
8	DMF + Dioxane	334.56	47.06	5.19	0.9885	0.0115	0.076	1.163
9	MeOH + MeCN	334.87	46.73	5.18	0.9908	0.0092	0.067	0.928
10	MeOH + Dioxane	334.80	46.82	5.18	0.9901	0.0099	0.071	0.998
11	MeCN + Dioxane	334.80	46.80	5.17	0.9902	0.0098	0.070	0.997

Table 2
Observed and calculated values of energy (cm^{-1}) for Nd (III)–GSH in different solvents. Ground state $^4I_{9/2}$

Sr.	Medium	$^4F_{3/2}$	$^4F_{5/2}$	$^4F_{7/2}$	$^4G_{5/2}$	$^4G_{7/2}$
1	Water	11565	12596	13515	17400	19190
		(11551)	(12641)	(13487)	(17395)	(19191)
2	DMF	11545	12514	13392	12277	19146
		(11502)	(12643)	(13371)	(12331)	(19147)
3	MeOH	11555	12582	13504	17328	19168
		(11539)	(12614)	(13405)	(17379)	(19169)
4	Dioxane	11554	12578	13505	17316	19166
		(11539)	(12613)	(13450)	(17376)	(19169)
5	MeCN	11556	12590	13510	17370	19183
		(11545)	(12696)	(13473)	(17386)	(19184)
6	DMF + MeOH	11550	12564	13495	17288	19157
		(11530)	(12595)	(13432)	(17396)	(19158)
7	DMF + MeCN	11551	12569	13497	17292	19161
		(11530)	(12598)	(13436)	(17368)	(19162)
8	DMF + Dioxane	11548	12566	13493	17283	19153
		(11529)	(12593)	(13430)	(17366)	(19169)
9	MeOH + MeCN	11557	12583	13506	17337	19172
		(11540)	(12617)	(13459)	(17381)	(19173)
10	MeOH + Dioxane	11554	12580	13504	17322	19168
		(11538)	(12612)	(13452)	(17377)	(19169)
11	MeCN + Dioxane	11554	12580	13504	17322	19168
		(11538)	(12612)	(13452)	(17377)	(19169)

Table 3
Observed oscillator strengths ($P \times 10^{-6}$) and Judd–Ofelt (T_λ) parameters for Nd (III)–GSH in different solvents

Sr.	Medium	$^4F_{3/2}$	$^4F_{5/2}$	$^4F_{7/2}$	$^4G_{5/2}$	$^4G_{7/2}$	T_2	T_4	T_6
1	Water	1.660	10.58	11.88	11.49	8.744	5.61	19.01	41.97
2	DMF	2.763	11.14	15.05	27.18	14.46	15.19	43.64	74.92
3	MeOH	2.155	9.320	11.80	16.25	7.675	9.08	24.45	48.37
4	Dioxane	2.736	11.33	13.79	19.55	17.01	9.04	38.04	63.73
5	MeCN	2.432	10.74	12.95	14.96	7.260	8.11	22.32	48.09
6	DMF + MeOH	2.200	9.633	12.69	19.67	9.160	11.21	29.69	55.81
7	DMF + MeCN	2.310	10.71	13.58	20.82	11.65	11.43	33.27	60.89
8	DMF + Dioxane	2.662	10.93	13.71	21.81	7.860	12.86	30.93	60.42
9	MeOH + MeCN	1.929	9.563	10.965	14.93	7.771	8.19	22.88	45.69
10	MeOH + Dioxane	2.010	8.920	11.04	15.51	9.420	8.19	25.54	47.46
11	MeCN + Dioxane	2.818	10.79	14.54	20.02	11.32	10.68	32.56	60.16

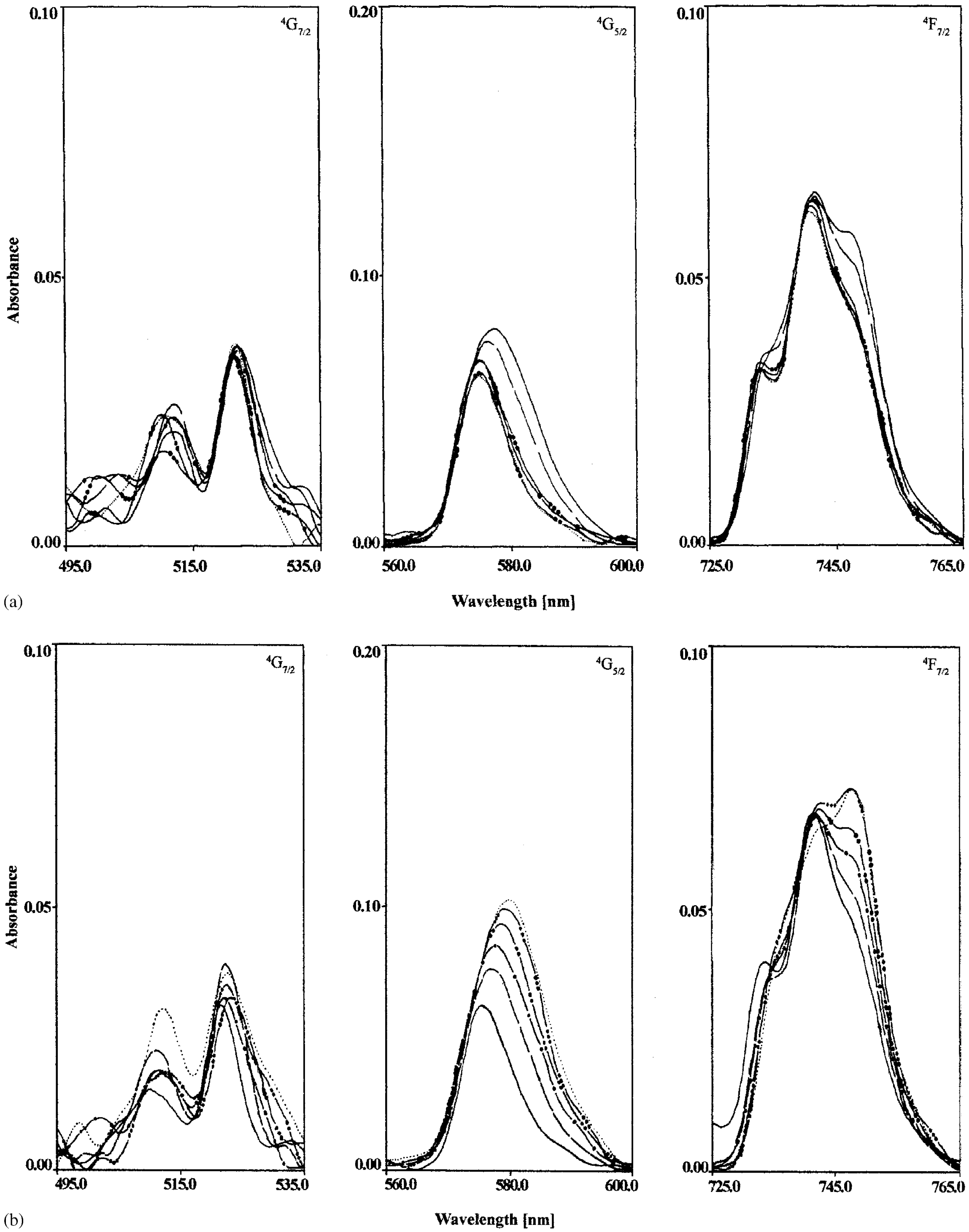


Fig. 1. Comparative absorption spectra of Nd (III)–GSH in different conditions like aquated organic solvents, water:DMF, water:MeOH, water:MeCN and water:Dioxane.

comparison with that observed for the Nd (III)-GSH species at pH 2.0. This is because of the fact that in weak acidic medium water has more affinity for coordination with Nd (III). The introduction of Zn (II) in the binary system of Nd (III)–GSH yields noticeable changes in the oscillator strengths and in the magnitude of Judd–Ofelt (T_λ) intensity parameters. This result obviously shows the enhancement in interaction of Nd (III)–GSH in the solution. The optimum pH for more stable species of Nd (III)–GSH in the presence of Zn (II) is at pH 6.0, because of the probable interaction of –SH group with Zn (II) in the solution (Fig. 2).

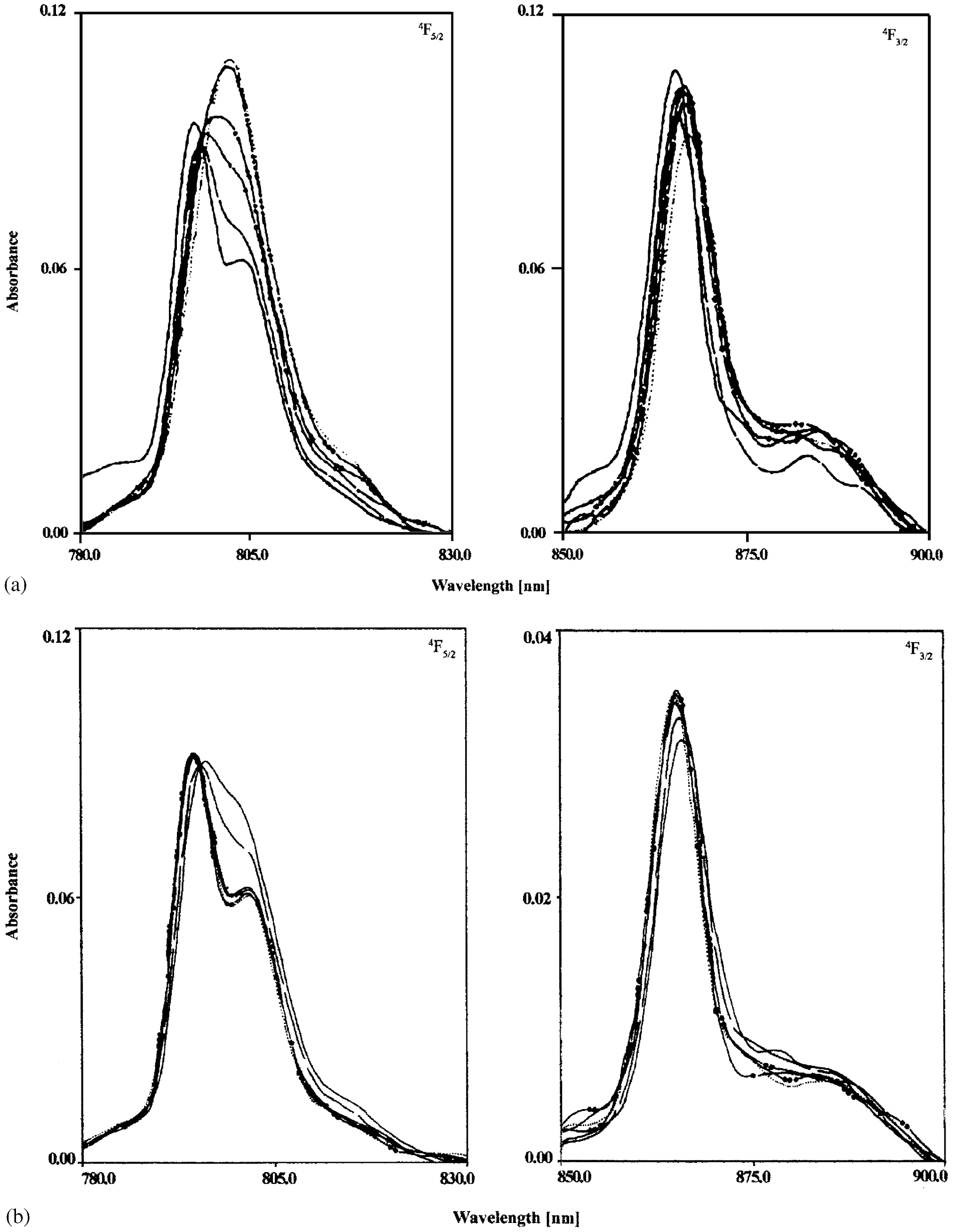


Fig. 2. Comparative absorption spectra of Nd (III)–GSH in presence of Zn (II) in different Conditions like water:DMF, water:MeOH, water:MeCN and water:Dioxane.

The effect of solvent on complexation is quite significant. DMF appears to induce the strongest complexation influence on Nd (III)–GSH complex. The red shift is observed in the energies of all five bands (including combined bands), which are considered as marker for quantitative analysis in Nd (III) ion i.e., $^4I_{9/2} \rightarrow ^4G_{5/2}$ ($^4I_{9/2}$ is ground state for Nd (III) ion and $^4G_{7/2}$, $^4G_{5/2}$, $^4F_{7/2}$, $^4F_{5/2}$, $^4F_{3/2}$ are internal excited state for Nd (III) ion) the hypersensitive transition and other transitions like $^4I_{9/2} \rightarrow ^4G_{7/2}$, $^4I_{9/2} \rightarrow ^4F_{3/2}$, $^4I_{9/2} \rightarrow ^4F_{5/2}$, $^4I_{9/2} \rightarrow ^4F_{7/2}$. These transitions, other than hypersensitive, do not obey $|\Delta J|$ selection rules and hence can only be considered as pseudo-hypersensitive (this word was for the first time published in our previous publication and quoted in Hand book of Physics and Chemistry of Rare Earths in 1998). The relative sensitivity of all the five transitions can be best explained through the plot of oscillator strengths as a function of T_2^c/T_2^a ("c" for complex ion and "a" for aqua ion). This shows the following order of relative sensitivity for all the five bands of Nd (III) ion; $^4G_{5/2} > ^4G_{7/2} > ^4F_{7/2} > ^4F_{5/2} > ^4F_{3/2}$ as highest value of slope is found for hypersensitive transition i.e., $^4G_{5/2}$ and lowest value for pseudo-hypersensitive transition $^4F_{3/2}$ (Figs. 3 and 4).

The influence of solvents like acetonitrile and dioxane are less on complexation of Nd (III)–GSH. Although we have found red shift in energies of all transitions, the effect is found pronounced in DMF. The red shift is due to the expansion of the metal orbital radius resulting in the decrease of inter-electronic repulsion, which leads to the phenomenon of nephelauxetic effect and thus can lead to the lowering of coordination number [12,13]. The nephelauxetic effect also sometimes induces band broadness and hence some band intensification is observed. The analysis of the oscillator strengths and Judd–Ofelt (T_λ) intensity parameters are used in the investigation of formation and nature of Nd (III)–GSH complexes. T_2 parameter changes significantly as a function of ligand concentration. The value of T_2 parameter which increased in the presence of organic solvents suggest that solvents have a better coordinating power in comparison with water as a result of solvation. T_4 and T_6 are slightly affected in comparison with T_2 parameter. Both parameters are related to changes in symmetry properties of the complex species [14]. At the same time the extent of mixing of $4f^n$ and $5d$ orbital will also influence T_6 parameter predominantly, while some influence on T_4 can also be extended. Table 3 clearly reflect, that T_4 and T_6 are affected significantly in the presence of different solvents, suggest that not only immediate coordination environment of Nd (III) but symmetry of the complex species is also changed dramatically. These changes are considered to be good evidence for the involvement of GSH in the inner-sphere coordination of Nd (III) ion. Though the ligand environment has only weak influence on the electronic cloud of the Nd (III), the 4*f* shell is efficiently shielded by the closed 5*s* and 5*p* shells. This clearly shows without doubt that the complexation of Nd (III)–GSH in presence and in absence of Zn (II), is affected significantly by changes in the nature of solvent (Table 4). All the results obtained clearly suggest that minor coordination changes in the Nd (III) complexes are caused by different coordinating sites of GSH, normalized bite, denticity, solvent nature, coordination number, nature of Nd (III)–GSH bond, which do induce significant variation in the intensity of $f-f$ transitions.

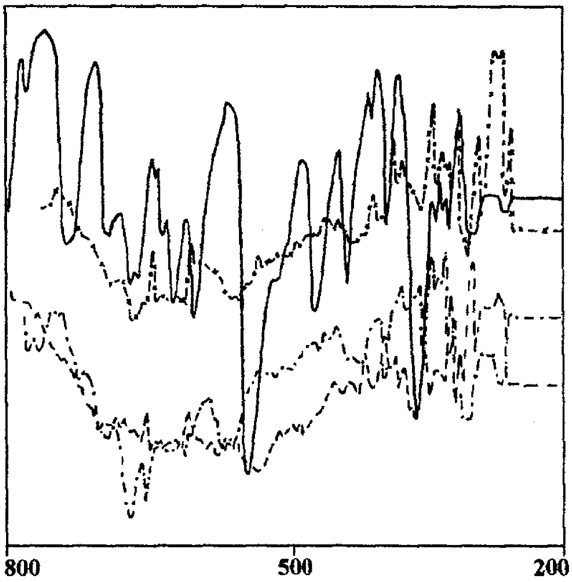
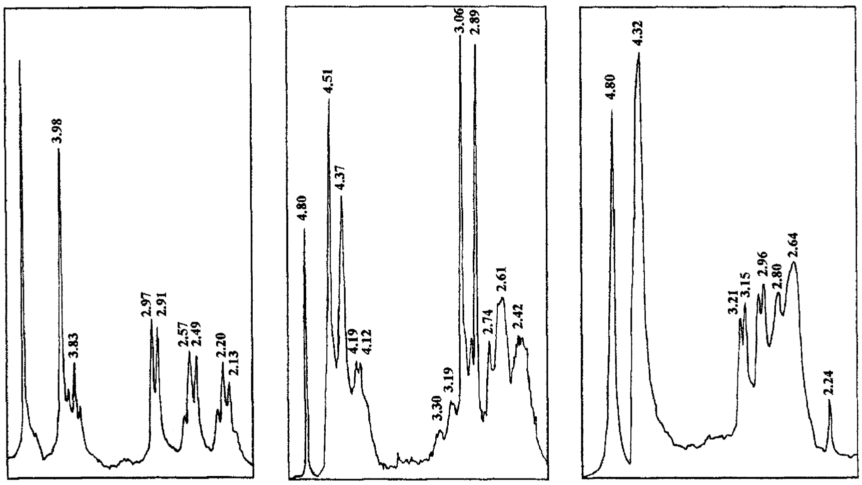


Fig. 3. Comparative IR spectra of Nd (III) complexes in the region from 800 to 200 cm^{-1} for the observation of new bands.

3.2. *The infrared spectral analysis of Nd (III)–GSH–Zn (II) (1:1:1)*

Infrared spectral studies have been made to find out the important structural features of Nd (III)–GSH complexes. The FT-IR was recorded in the range 4000–200 cm^{-1}. The figure in the range 800–200 cm^{-1}



^{1}H NMR Spectrum of GSH ^{1}H NMR Spectrum of Nd(III):GSH: ^{1}H NMR Spectrum of Nd(III):GSH:Zn

Fig. 4. ^{1}H-NMR of Nd–GSH and Nd–GSH in the presence of Zn (II).

Table 4
Computed value of energy interaction F_k (cm^{-1}), nephelauxatic effect (β), Bonding ($b^{1/2}$), and covalency (δ) parameters for Nd (III) complexes with GSH–Zn (II) in different solvents

Sr.	Medium	F_2	F_4	F_6	β	$1-\beta$	$b^{1/2}$	δ
1	Water	335.06	46.47	5.17	0.9944	0.0058	0.053	0.614
2	DMF	334.67	46.97	5.17	0.9888	0.0112	0.075	0.864
3	MeOH	335.01	46.56	5.18	0.9928	0.0072	0.060	0.976
4	Dioxane	334.94	46.65	5.18	0.9925	0.0075	0.061	0.921
5	MeCN	335.05	46.52	5.17	0.9928	0.0072	0.060	0.745
6	DMF + MeOH	334.61	46.97	5.18	0.9906	0.0094	0.068	1.224
7	DMF + MeCN	334.69	46.90	5.15	0.9908	0.0092	0.067	1.225
8	DMF + Dioxane	334.72	46.91	5.19	0.9895	0.0101	0.071	1.163
9	MeOH + MeCN	335.41	46.29	5.18	0.9938	0.0062	0.055	0.928
10	MeOH + Dioxane	334.89	46.66	5.18	0.9925	0.0075	0.061	0.998
11	MeCN + Dioxane	335.00	46.57	5.18	0.9927	0.0073	0.060	0.997

clearly shows appearances of few new bands. These bands are due to metal-oxygen and metal sulphur bands.

The IR spectrum of GSH shows a stretching frequency of sulfhydryl group occurring around 2535 cm^{-1} as sharp intense band. The addition of Nd (III) and Zn (II) to GSH clearly leads to its deprotonation. It induces the formation of Zn (II)–sulphur bond and very weak bond with Nd (III) ion. The IR spectra given shows without doubt that deprotonation of sulfhydryl group occur around pH 6.0 at which complex is being synthesized.

The carboxylic group frequencies and carbonyl group frequencies are highly sensitive to introduction of metal ions like Nd (III). The carbonyl stretching frequency occurring at 1715 cm^{-1} in GSH is shifted to lower frequency at around 1630 cm^{-1} indicating involvement of CO group in binding with Nd (III). The IR spectra in the range 800–200 cm^{-1} indicate the appearance of new band corresponding to Zn–S ($\sim$650 cm^{-1}). In this region few new bands also appeared corresponding to Nd (III)–oxygen bond ($\sim$550 cm^{-1}).

3.3. ^{1}H-NMR and ^{13}C-NMR spectral analysis of GSH and Nd–GSH–Zn

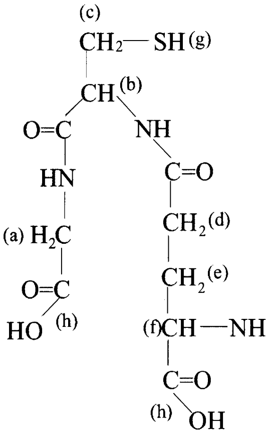


Table 5
^{1}H-NMR shifts for selective protons of GSH and its complex

Sr.	Compound	*a*	*b*	*c*	*d*	*e*	*f*	*g*	*h*
1	GSH	3.98	3.77 3.83 3.90	2.97 2.91	2.64 2.47	2.26	2.27	7.50 8.00	1.50 1.70
2	Nd–GSH–Zn	4.66	4.19	3.10 3.15	2.80 2.49	2.42	2.42	—	—

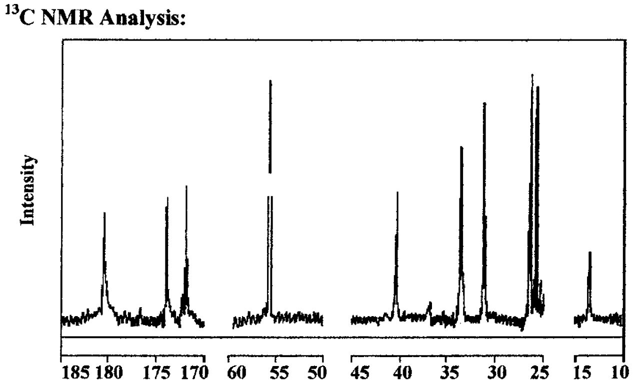
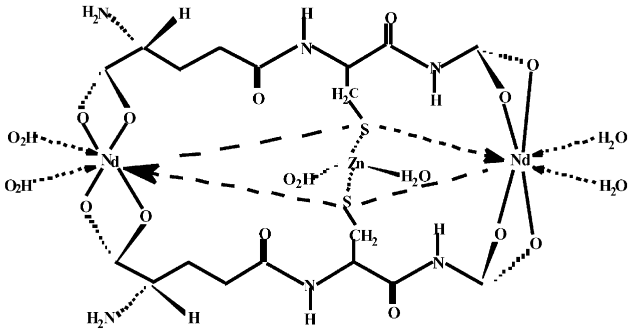


Fig. 5. ^{13}C-NMR of Nd–GSH in the presence of Zn (II).

The proton-NMR of GSH and its complexes are recorded at 400 MHz in D_2O. GSH contains three different amino acid residues and eight different types of protons are found in the structure. All the peaks show a lower field shift in the Nd–GSH–Zn complex. The proton (a) peak observed at $\delta_{3.98}$ in the GSH spectrum is shifted to $\delta_{4.66}$ in the complex. The triplet (b) proton peaks centred at $\delta_{3.83}$ in the ligand are shifted to $\delta_{4.19}$. The peak due to –SH proton $\delta_{1.5-1.7}$ and –COOH protons $\delta_{7.5-8.0}$ is found disappeared in the complex. Similarly other protons peaks of the complexes are showing lower field shift with slightly broad peak in nature due to the paramagnetic nature of the complex.

Table 6
^{13}C-NMR shifts for selective carbons of GSH and its complex

Sr.	Compound	Cys-C	Gly-C	Glu-C	Glu-C	Glu-C	Cys-C	Gly-COOH	Cys-CONH	Glu-CONH	Glu-COOH
1.	GSH	28.4	28.9	34.1	41.2	55.5	56.5	174.0	175.2	175.4	176.4
2.	Nd–GSH–Zn	25.7	26.2	33.9	40.3	55.6	—	171.0	173.7	173.7	180.3



Scheme 1. Probable structure for Nd–GSH–Zn complex (carried out by S.O. Sommerer).

The results clearly suggest involvement of –SH and –COOH groups in the coordination of GSH with Nd (III) and Zn (II) ions (Table 5).

^{13}C-NMR of GSH and its complex is recorded at 220 MHz (Fig. 5). The structure of GSH shows 10 carbon atoms is evidence of complexation with Nd (III) and Zn (II). The chemical shift of cysteinyl-carbon (Cys-C$_\alpha$) which shows a down-field shift by 3.00 ppm indicates that Zn (II) or Zn (II)/Nd (III) are bound to the sulfhydryl group, but Nd (III) being hard metal ion, possibility of its coordination is less preferable with –SH group. It means Zn (II) may coordinate to –SH of GSH. The shift in Glu-COOH and Glu-C$_\alpha$ of glutamyl residue is about 4.00 ppm in lower field, indicate that the Nd (III) is bind to these groups of GSH. The overall results also suggest that Nd (III) and Zn (II) bind to some extent to peptide linkage of cysteinyl and glycine residue (Table 6). All the results from $4f-4f$ transition, IR and NMR suggest the following probable structure for hetero bimetallic complex of Nd–GSH–Zn (Scheme 1).

References

[1] G. Bellomo, S. Orrenius, Hepatology 5 (1985) 876.
[2] S. Orrenius, G. Bellomo, Glutathione, calcium metabolism, in: D.D. Poulson, D. Avramovic (Eds.), Glutathione: Chemical, Biochemical and Medical Aspect, Part-B, Wiley Interscience, New York, 1989, p. 384 (Chapter 11).
[3] C.P. Agata, B.K. Anna, Acta Biochim. Pol. 47 (1) (2000) 223.
[4] R. Sharma, S. Awasthi, P. Zimniak, Y. Awasthi, Acta Biochim. Pol. 47 (3) (2000) 751–762.
[5] S. Orrenius, G. Bellomo, in: W.Y. Cheung (Ed.), Toxicology Implications of Perturbation of Calcium Homeostasis in Hepatocytes in Calcium and Cell Functions, Vol. VI, Academic Press, New York, 1986, p. 185.
[6] D.L. Rabenstein, Metal complexes of glutathione and their biological significance, in: D.D. Poulson, D. Avramovic (Eds.), Glutathione: Chemical, Biochemical and Medical Aspect, Part-A. Wiley Interscience, New York, 1989, pp. 147 (Chapter 5).
[7] D.L. Rabenstein, J. Am. Chem. Soc. 93 (1973) 2797.
[8] C.A. Evans, Biochemistry of Lanthanide, Pennulam Press, New York, 1990 Chapter-2,3.
[9] J.P. Mehta, P.N. Bhatt, S.N. Misra, Bull. Pure Appl. Sci. C 20-C (2) (2001) 93.
[10] J.P. Mehta, P.N. Bhatt, S.N. Misra, Ind. J. Biochem. Biophys. 39 (2002) 66.
[11] S.N. Misra, M. Indiradevi, C.M. Suveerkumar, J. Pure Appl. Phys. 35 (1997) 17.
[12] C. Gorller-Walrand, K. Binnemans, in: K.A. Gscheidner, L. Eyring (Eds.), Hand Book of the Physics and Chemistry of Rare Earths, Vol. 23, 1996, pp. 163–164 (Chapter 155).
[13] S.N. Misra, S.O. Sommerer, Appl. Spectrosc. Rev. 26 (1991) 150–201.
[14] S.N. Misra, J. Sci. Ind. Res. 44 (1985) 344.