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Ligand-Mediated Pseudohypersensitivity of Some 4f–4f Transitions in Neodymium(III) Interaction with Fluorinated Nucleic Acid Components

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Absorption difference and comparative absorption spectrophotometry of the systems containing Nd(III) and fluorinated nucleic bases (fluoroadenine, fluorocytosine, fluorothymine, and fluorouracil) and fluorinated nucleosides (fluoroadenosine, fluorocytidine, fluorothymidine, and fluorouridine) in ethyl acetate–water (90 : 10), have shown that certain 4f–4f transitions ($^4I_{9/2}\rightarrow{}^4G_{7/2}$, $^4F_{7/2}$, $^4F_{5/2}$, and $^4F_{3/2}$), which are generally considered to be insensitive, have been found to exhibit substantial sensitivity towards even minor changes in the coordination environment around neodymium(III). The observation has been referred to as "Ligand-Mediated Pseudohypersensitivity." The magnitude of various spectral parameters (energy interaction, Slater–Condon interelectronic repulsion F_k, spin–orbit interaction ξ_{4f}, nephelauxetic $\bar{\beta}$, b, δ, and Judd–Ofelt T_λ intensity and oscillator strength (P)), computed using regression analysis, has been used in exploring the degree of inner and outer sphere coordination, incidence of covalency and extent of involvement of metal 4f orbitals in bonding. The isolation of solid complexes and their characterization by elemental analysis, infrared spectral, and Karl Fischer titration suggested octa and nona coordinated environment around neodymium and some probable structures for these complexes have been proposed.

Complexation of lanthanoids brings about drastic changes in the intensity of certain transitions[1] which are characterized by the large values of $U^{(2)}$ matrix element and exhibit substantial increase and variation of Judd[2]–Ofelt[3] T_2 parameter while the intensities of other 4f–4f transitions are almost unaffected.[4–7] Such transitions called hypersensitive transitions and the shape, energy, and oscillator strength of these transitions have successfully been used to extract information about the degree of outer and inner sphere coordination and extent of involvement of metal 4f orbital,[9] in identifying binding sites of the biomolecules and in following the biochemical reactions involving calcium.[10,11]

During the course of our work on neodymium(III) with β-diketones, diols, and 1,10-phenanthroline, we have found unusual sensitivity of some nonhypersensitive transitions like $^4I_{9/2}\rightarrow{}^4G_{7/2}$, $^4F_{7/2}$, $^4F_{5/2}$, and $^4F_{3/2}$. These transitions were earlier considered to be almost insensitive[1–9] towards coordination changes but in this present investigation these transitions have been found to show substantial sensitivity towards even minor changes in the immediate coordination environment around neodymium(III). The name "Ligand-Mediated Pseudohypersensitivity" has been given for this observation because the coordinating ability, denticity, normalized bite, size of chelate ring of the different ligands affect the sensitivity of these nonhypersensitive transitions to different extent.[12]

The present communication describes the absorption difference, comparative absorption spectrophotometry along with the variation of various spectral parameters in exhibition of Ligand-Mediated Pseudohypersensitivity of $^4I_{9/2}\rightarrow{}^4G_{7/2}$, $^4F_{7/2}$, $^4F_{5/2}$, and $^4F_{3/2}$ using the interaction of Nd(III) with fluorinated nucleic bases like fluoroadenine, fluorocytosine, fluorouracil, and fluorothymine and fluorinated nucleosides, fluoroadenosine, fluorocytidine, fluorouridine, and fluorothymidine.

To support the absorption spectral studies, the neodymium(III) complexes with these fluorinated biomolecules have been isolated and characterized by analysis and IR. Peliminary ultrasonic studies have shown the ligating behavior of these biomolecules in aqueous as well as semi-nonaqueous (50 : 50 DMF–water) media. Probable structures have been proposed on the findings of the present study.

Experimental

Neodymium(III) oxide of 99.99% purity from Indian Rare Earths Ltd., India, was converted into nitrate and then was used for synthesis and spectral studies. Fluorocytosine, fluorouridine, and fluorocytidine were prepared by the methods described.[13] Fluoroadenosine and fluorothymidine were prepared by selective fluorination of adenosine and thymidine by xenon difluoride in genetron.

Absorption spectra in the visible region was recorded on Shimadzu FS 260 and Beckman DU-7 spectrophotometer. The hypersensitive $^4I_{9/2}\rightarrow{}^4G_{5/2}$ and pseudohypersensitive $^4I_{9/2}\rightarrow{}^4G_{7/2}$, $^4F_{7/2}$, $^4F_{5/2}$, $^4F_{3/2}$ were resolved and recorded on expanded scale and were used as Marker bands.

Preparation Complexes of Fluorouracil Fluorocytosine, and Fluorothymine with Neodymium(III). The reactions of neodymium(III) nitrate (0.001 M, 1M=1 mol dm^{-3}) and fluorinated nucleic base (0.005 M) in ethyl acetate and acetone (50 : 50) mixture with constant stirring in inert atmosphere for several hours, resulted in the separation of pinkish microcrystalline solids corresponding to the formula; $[Nd(base)_4\cdot(H_2O)_4]^{3+}$ established after elemental analysis, and analysis of water by Karl Fischer titration.

Preparation of Complexes of Fluorouridine, Fluorocytidine, Fluorothymidine, and Fluoroadenosine. The solution of neodymium(III) nitrate (0.002 M) was added to the ethyl acetate–acetone mixture containing 0.005 M nucleoside and was stirred for 6 h at 20 °C. The reaction mixture was then

placed in a vacuum desiccator and after four days, the crystalline complex slowly separated out from the liquor. These crystals were washed with ethyl acetate and dried in desiccator. The analysis of the product suggested the stoichiometry: $[Nd(nucleoside)_2 \cdot (H_2O)_3]^{3+}$. The amount of coordinated water was estimated in the complex by Karl Fischer titration. The reaction involving fluoroadenosine yielded a mixture of 1:2 and 1:3 products. These could not be separated effectively in pure state. The analytical data showed that observed and calculated percentage of Nd, C, N, H_2O of the neodymium(III) complexes with the fluorinated nucleic bases and fluorinated nucleosides tally within ±2%. The analytical data can be provided by the author on request.

Results and Discussion

The $^4I_{9/2} \rightarrow {}^4G_{5/2}$ transition of Nd(III) is universally accepted as hypersensitive transition as it obeys selection rules for quadrupole transitions and undergoes very high intensification on complexation.[1,8,9,12,14,15] Small changes in the immediate coordination environment around Nd(III) bring about wide variation of oscillator strength. Contrary to this the intensities of nonhypersensitive transitions are reported either vary slightly or not changed at all or sometimes decrease.[4–6] Iftikar[15] has reported a marginal increase (ca. 15%) in the oscillator strength of the nonhypersensitive transition, contrary to the several fold increase shown by hypersensitive $^4I_{9/2} \rightarrow {}^4G_{5/2}$ transition.

Table 2 clearly shows that the percentage variation of the oscillator strength of $^4I_{9/2} \rightarrow {}^4G_{7/2}, {}^4F_{7/2}$, $^4F_{5/2}$, $^4F_{3/2}$ which does not obey selection rule, yet these show significant sensitivity evidenced by large percentage variation of oscillator strength which is almost same as shown by the hypersensitive $^4I_{9/2} \rightarrow {}^4G_{5/2}$ transition. We are reporting the high sensitivity of these nonhypersensitive transitions for the first time. The name "Ligand-Mediated Pseudohypersensitivity" has been suggested for such observation. It appears that the nature of the ligand (denticity, number and coordinating power of ligating sites, degree of chelation, normalized bite of the ligand) and the nature, lability, and geometry of complex species, induce the unusual sensitivity to these nonhypersensitive transitions, Other factors may also be attributed to the enhancement and sensitivity of these transitions.

i) The second-order interactions which are two order magnitude less than the Coulombic interaction (generally ignored) may become prominent by the ligating characteristics of the coordinating molecule. This may lower the excited state of these pseudohypersensitive transitions and in consequence their transition possibility enhances.

ii) The nephelauxetic effect may induce some broadening of the bands and hence may contribute to the intensification of the bands.

iii) These transitions may be borrowing intensities from the neighboring transitions.

Really we are not in a position to give some concrete explanation for this unusual sensitivity of these nonhypersensitive f–f transitions.

Judd[2]–Ofelt[3] theory predicts that the intensity of 4f–4f transition arises principally from forced electric dipole mechanism. Thus the electric dipole oscillator strength (P) is expressed as the product of T_λ parameters and appropriate transition matrix element $U^{(\lambda)}$ at frequency of transition ν, of the transition J→J′

$$P_{e.d} = \sum_{\lambda=2,4,6} T_\lambda \nu (f^n \psi_J || U^{(\lambda)} || f^n \psi'_{J'})^2$$

The Judd–Ofelt intensity parameters are empirical, yet these show high sensitivity towards even minor changes in the coordination environment (T_2) and symmetry of the molecule (T_4, T_6).[16] These parameters have been widely used in the structure elucidation of lanthanoid coordination compounds both in the solid as well as in solution. The T_λ and P have also been computed by regression analysis and are summarized in Table 2.

The energy of a 4f–4f transition comprises of two major components: the Coulombic (represented by inter-electronic repulsion F_k Slater Condon parameter) and spin orbit (Lande-ξ_{4f}) components (Table 1). The complexation of lanthanoids brings about lowering of these components resulting in the phenomenon of nephelauxetic effect represented by nephelauxetic ratio ($\bar{\beta}$):

$$\beta_1 = \frac{F_k{}^c}{F_k{}^f};\ \beta_2 = \frac{\xi_{4f}{}^c}{\xi_{4f}{}^f};\ \bar{\beta} = \frac{\beta_1 + \beta_2}{2}$$

$$b^{1/2} = \left[\frac{1-\bar{\beta}}{2}\right]^{1/2};\ \delta = \left[\frac{1-\bar{\beta}}{\bar{\beta}}\right] \times 100$$

Bonding (b) and percentage covalency parameter (δ) which are related to nephelauxtic ratio ($\bar{\beta}$) are also used to describe the structural features of a lanthanoid complex. The significance and evaluation of these (F_k, $\bar{\beta}$, δ, ξ_{4f}, and b) parameters have been discussed in earlier publications.[12,14]

Peacock[4] has shown that the inclusion of covalency can affect the angular part of the 4f wave function and thus can affect preferentially T_2 parameter. Writing ligand wave function, as the sum of the renormalized radial wave function, multiplied with spherical harmonics with the origin at central metal ion,

$$\Phi_{Ligand} = \sum_k \bar{\alpha}_{km} \sum_m Y_{km} \text{ with } k, \text{ odd},$$

while metal wave function can be written as the sum of the original 4f wave function and ligand wave function weighted by mixing coefficient (b) also known as bonding parameter and related to nephelauxetic effect.

$$\Phi_{Metal} = (1-b)^{1/2} |4f> b^{1/2} |\Phi_{Ligand}>$$

Hence the relevant term which can affect T_λ parameter is b. Generally covalency increase is accompanied by increase in T_λ parameter. Nephelauxetic effect which is caused by the lowering of the excited state, of the metal ion by surrounding ligand field, is influenced by the asymmetric part of the crystal field. The significant

Table 1. Computed Energy Interaction (F_K/cm^{-1}), Spin Orbit Interaction (ξ_{4f}), Nephelauxatic ($\overline{\beta}$), Bonding (b), and Covalency (δ) Parameters Derived from Energy Level Data of Nd(III) Complexes with Metabolites

Complex	F_2	F_4	F_6	ξ_{4f}	$\overline{\beta}_e$	$(1-\overline{\beta}_e)$	$b_e^{1/2}$	δ
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	
Nd-fluoroadenine								
1:1	332.94	47.957	4.960	884.00	0.958	0.042	0.107	3.143
1:2	332.94	47.957	4.960	884.00	0.958	0.042	0.107	3.242
1:3	329.167	48.132	5.630	889.00	0.988	0.012	0.107	1.052
Nd-fluorouracil								
1:1	330.867	47.957	4.96	884.0	0.958	0.042	0.107	3.280
1:2	330.942	47.957	4.96	884.0	0.958	0.042	0.108	3.258
1:3	330.942	47.957	4.96	884.0	0.958	0.042	0.107	3.242
Nd-fluorocytosine								
1:1	330.867	47.957	4.96	884.4	0.958	0.042	0.108	3.242
1:2	330.867	47.957	4.96	884.0	0.958	0.042	0.108	3.249
1:3	330.667	47.957	4.97	884.00	0.956	0.044	0.112	3.428
Nd-fluorothymine								
1:1	330.87	47.96	4.96	884.00	0.958	0.042	0.108	3.242
1:2	330.95	47.96	4.96	884.00	0.958	0.042	0.108	3.242
1:3	328.56	46.35	5.07	866.0	0.990	0.010	0.070	1.052
Nd-fluoroadenosine								
1:1	330.94	47.95	4.96	884.00	0.970	0.030	0.110	2.857
1:2	329.91	48.50	5.04	887.00	0.958	0.042	0.112	3.012
1:3	329.56	48.06	5.02	897.00	0.970	0.030	0.112	2.894
Nd-fluorouridine								
1:1	330.94	47.96	4.96	884.00	0.958	0.442	0.108	3.249
1:2	330.31	47.15	5.02	884.00	0.957	0.043	0.112	3.489
1:3	329.117	48.05	5.02	895.0	0.962	0.038	0.111	2.965
Nd-fluorocytidine								
1:1	330.91	47.55	4.97	884.0	0.963	0.037	0.109	3.472
1:2	330.94	47.95	4.96	884.00	0.964	0.036	0.107	3.242
1:3	329.56	48.05	5.02	890.0	0.968	0.032	0.108	2.894
Nd-fluorothymidine								
1:1	328.56	48.06	5.02	896.0	0.970	0.030	0.110	2.857
1:2	328.86	48.00	5.01	897.00	0.958	0.042	0.112	3.012
1:3	328.91	47.98	5.02	896.50	0.978	0.030	0.112	2.894

changes in the T_λ parameters in absence of significant nephelauxetic effect (as observed in our system) show that the unsymmetrical part of the field has major influence on these (T_λ) parameters. The chromophore present in these complexes is identical, while changes are due to the attachment of functional groups which are not directly involved in the metal ligand bonding. These appear to be most probably responsible for the distortion of the oxygen around neodymium lowering the site symmetry and thus increasing the probability of 4f–4f transition. Using Judd–Ofelt theory, above assumption can be explained where the expression for T_λ parameters is

$$T_\lambda = \chi\left[\frac{8\pi^2 m}{3h}\right](2\lambda+1)\sum_{t,p} A_{t,p}|\,^2\xi^2(t,\lambda)>$$

In the above equation $A_{t,p}$ (t, odd) are odd parity term in crystal field expansion depending upon the site symmetry of the complex. The quantity $\xi^2(t, \lambda)$ contains integral involving radial part of the wave function and excited parity electronic wave function measuring the symmetric part of the ligand field (amount of covalency) and does not vary appreciably in Nd(III) complexes with these fluorinated biomolecules. However, T_λ prameters vary substantially with the change and stoichiometry of the ligands. Hence the quantity $\xi^2(t, \lambda)$ which is not dependent on the nature and stoichiometry of the ligand is not the factor causing change in T_λ. Thus the remaining part of the equation ($A_{t,p}$) the asymmetric part of the ligand field expansion appears to be responsible for the variation of T_λ parameter. These remaining quantities arise therefore from the distortion of the geometry around neodymium.

Binding of Fluorinated Nucleic Bases with Neodymium(III). These fluorinated nucleic bases possess both nitrogen and oxygen as potential donor sites except fluoroadenine, which has only nitrogen as coordinating sites. The complexes isolated with fluorocytosine, fluorouracil, and fluorothymine corresponded to the composition $[Nd(Base)_4\cdot(H_2O)_4]^{3+}$. The pure compound with fluoroadenine could not be isolated, however, some ill defined complexes appear to be formed with fluoroadenine. A look at the Table 2 shows that the oscillator strength (P) of neodymium(III) fluoroadenine system was almost similar to that neodymium(III) fluorouracil system suggesting that fluoroadenine inter-

Table 2. Computed and Observed Oscillator Strengths (P) of Important 4f—4f Transition and T_λ Parameters of Nd(III) Complexes with Fluorinated Metabolites

Complex	$^4I_{9/2}\rightarrow{}^4G_{7/2}$		$^4I_{9/2}\rightarrow{}^4G_{5/2}$		$^4I_{9/2}\rightarrow{}^4F_{7/2}$		$^4I_{9/2}\rightarrow{}^4F_{5/2}$		$^4I_{9/2}\rightarrow{}^4F_{3/2}$		T_2	T_4	T_6
	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd			
Nd-fluoroadenine													
1:1	1.942	1.292	4.798	4.798	5.013	5.319	5.376	5.466	0.964	0.874	179.27	251.78	327.1
1:2	1.352	1.620	6.053	6.005	5.002	5.015	4.965	5.314	0.831	1.096	224.77	315.70	410.1
1:3	1.550	1.988	7.923	7.638	3.201	3.090	4.018	3.668	0.874	1.447	300.25	418.00	543.0
Nd-fluorouracil													
1:1	1.362	1.258	4.668	4.668	4.545	3.806	3.348	4.040	0.791	0.882	175.61	245.81	319.22
1:2	2.616	1.554	5.758	5.758	4.994	4.896	5.087	5.170	0.869	1.052	215.50	302.3	393.16
1:3	2.437	1.644	7.170	7.170	5.216	4.898	5.032	5.327	1.331	1.310	268.42	377.0	489.63
Nd-fluorocytosine													
1:1	2.477	1.344	4.983	4.985	5.72	5.565	5.57	5.715	1.198	0.909	186.55	262.10	340.29
1:2	2.649	1.668	6.179	6.173	5.419	5.722	6.271	5.985	1.064	1.126	231.07	324.55	421.52
1:3	2.210	2.216	8.210	8.208	6.000	5.254	5.074	5.768	0.894	1.498	307.96	431.81	560.79
Nd-fluorothymine													
1:1	2.940	1.842	4.080	4.080	3.652	4.060	4.35	4.218	0.804	0.749	152.72	214.52	279.57
1:2	2.788	1.688	6.187	6.187	5.084	5.373	5.563	5.563	0.948	1.130	231.61	325.27	422.46
1:3	2.067	1.930	7.160	7.160	7.160	6.665	6.062	6.224	0.850	1.305	268.70	376.68	489.28
Nd-fluorodenosine													
1:1	3.348	2.378	5.110	5.110	5.484	5.620	5.603	5.780	0.990	0.932	191.28	268.70	348.93
1:2	2.456	2.221	8.221	8.221	5.442	4.970	4.970	5.518	0.658	1.532	310.78	433.48	562.98
1:3	2.081	2.994	11.124	11.124	4.968	5.111	5.384	5.938	0.686	1.031	420.6	586.00	761.76
Nd-fluorouridine													
1:1	2.248	1.426	5.294	5.292	5.389	5.598	5.78	5.776	0.911	0.966	198.11	278.26	361.37
1:2	2.265	2.523	9.379	9.377	6.368	6.124	6.124	6.514	0.804	1.718	356.21	495.16	643.05
1:3	2.758	3.010	11.274	11.274	6.342	5.343	5.343	6.588	0.962	2.053	427.20	594.82	772.50
Nd-fluorocytidine													
1:1	1.610	1.908	7.088	7.084	7.350	6.692	5.939	6.986	1.107	1.294	285.81	372.71	484.04
1:2	3.627	2.698	10.013	10.013	7.021	5.994	5.090	6.646	1.456	1.827	374.78	526.40	683.64
1:3	2.952	3.409	13.586	13.584	6.478	5.214	5.596	6.312	1.195	2.307	478.65	666.49	865.56
Nd-fluorothymidine													
1:1	1.550	2.329	8.868	8.886	5.425	5.38	5.376	5.960	0.870	1.616	336.86	468.20	607.99
1:2	1.842	3.130	11.629	11.622	6.018	5.669	5.478	6.526	0.928	2.126	440.40	613.20	796.40
1:3	2.628	3.763	14.995	13.943	6.420	5.525	4.926	6.750	2.065	2.160	528.40	735.72	955.54

acts in some way with neodymium(III), most probably involving pyrimidine or imidazole nitrogen in semi-nonaqueous 80:20 DMF: water.

The infrared spectra of the ligands in the carbonyl region show considerable changes on complexation. For fluorouracil and fluorocytosine complexes, the carbonyl absorption in the infrared region appears as a broad band, with its center of gravity shifted to lower energy as compared to corresponding ligand. Susi and Ard[17] considered the band in the 1540—1800 cm^{-1} region to $\nu(^2C{=}O)$ in phase $\nu(^4C{=}O)+\nu(C{=}O)$ and out phase $\nu(C{=}O)+\nu(C{=}O)$. In case of fluorothymine complex the bands at 1735 cm^{-1} (m), 1677 cm^{-1} (s) of fluorothymine shifted to the lower energy side indicating the participation of carbonyl oxygen in complexation with neodymium(III). Susi and Ard[17] suggested, that highest band in the region 1540—1800 cm^{-1} can be ascribed to $\nu(^2C{=}O)$, on the basis of the bond length reported for thymine hydrate by Gerdil.[18] Though the complexation can also be expected through ($^4C{=}O$), the donor capability of ($^2C{=}O$) will be more than that of ($^4C{=}O$). In fluorothymine the presence of electron-releasing CH_3 group on the fifth carbon atom will make ($^4C{=}O$) a less attractive donor. This points out clearly that the pyrimidinone oxygen atom can effectively act as donor. The weakness of the field is in accordance with the high π-electron density calculated for both oxygen in fluorouracil and fluorothymine. These atoms would be expected to act as moderate donor with ligand field at this low end of the oxygen donor range. The metal-ligand bond may well be fairly strong with very low crystal field stabilization energy. This situation in neodymium(III) complexes will make them very labile. The lability of neodymium(III) complexes with fluorinated nucleic bases will impart only weak intensities to the intra 4f–4f bands as is observed in the present study.

Preliminary ultrasonic studies of fluorouracil, fluorocytosine, fluorothymine in aqueous medium in presence of neodymium(III), have clearly shown that these fluorinated nucleic bases weaken water structures, while the same metabolite strengthen water structure in presence of aprotic solvent.[19]

(i) In water, fluorouracil, fluorocytosine, fluoroadenine, and fluorothymine gave positive values for partial metal compressibility (Φ_k°). This appears to be due to the displacement of net water molecules into the interstices, with the result these fluorinated bases in aqueous medium become highly hydrated and hence are not

readily available for coordination with neodymium.

(ii) The high dielectric constant of water induces significant ionization of metal-ligand bond hence the energies of various 4f–4f transition vary very little while the shape of the intra 4f–4f bands, specially $^4I_{9/2} \rightarrow {}^4G_{5/2}$ and $^4I_{9/2} \rightarrow {}^4F_{5/2}$ hypersensitive and pseudohypersensitive bands respectively change significantly.

(iii) The addition of aprotic solvent (DMF/DMSO) lowers the dielectric constant of the solvent mixture and decreasing the ionization of metal ligand bond. Secondly in the DMSO–water mixture these nucleic bases strengthen water structure (shown by negative values of partial molal compressibility Φ_k°),[19] hence these metabolites behave as better ligands. Thirdly the addition of DMSO also removes partly the water molecules from the coordination shell around Nd(III) and hence create different immediate coordination environment around neodymium(III).

(iv) Preliminary stability constant measurements of neodymium(III) fluorinated base systems have indicated significant stacking,[19] which also contributes towards weak intensities of intra 4f–4f bands.

Thus one can infer from infrared, absorption spectral and solution studies that these fluorinated nucleic bases act as better ligands in DMSO–water than in H_2O and their binding to neodymium is through carbonyl oxygen preferably through $\nu(^2C{=}O)$ carbonyl oxygen as unidentate manner as the bands due ν(N–H) do not appear to show any appreciable change. The presence of four water molecules of coordination and four base molecule coordinated in neutral unidentate manner through carbonyl oxygen and thus providing an octacoordinated environment around Nd(III) in these complexes.

Binding of Fluorocytidine, Fluorothymidine, Fluorouridine, and Fluoroadenosine with Neodymium(III). Significant shifts have been observed in ν(C=O) vibration which occurs around 1660—1680 cm^{-1} in fluorocytidine, fluorouridine, and fluorothymidine shifts to ca. 1700 cm^{-1} as asymmetric shaped broad band, whose center of gravity is around ca. 1700 cm^{-1} probably indicative of the participation of oxygen of the carbonyl group in bonding to neodymium(III). The presence of three water molecules have been indicated by Karl Fischer titration. The ν(OH) bands of the ligand change into broad band, suggesting the participation of ribose hydroxyl group in complexation to neodymium. These informations suggest the probable structure for $[Nd(nucleoside)_2(H_2O)_3]^{3+}$ complexes, involving nona coordinated Nd(III). Similar structure has been proposed by Brittain[20] and Richardson[21] earlier for $[Nd(uridine)_2(H_2O)_2]$ complexes. The terdentate attachment of the nucleoside to metal involves two cis hydroxyl oxygen of ribose and participation of carbonyl oxygen.

The proposed structures for Nd–adenosine complexes are given on our observations in Nd–fluorouridine/fluorothymidine/fluorocytidine systems. Since the pure 1 : 2 and 1 : 3 complexes could not be separated and hence the structure proposed are only on analytical data (C, H, N, H_2O, and Nd) and the conclusion derived from other Nd(nucleoside) complexes.

Absorption spectra of the solution containing neodymium(III) and fluoroadenosine, fluorouridine, fluorocytidine, fluorothymidine, and fluoroadenine, fluorouracil, fluorocytosine, and fluorothymine in 1 : 1, 1 : 2, and 1 : 3 stoichiometry have shown that the intensities increase with the ligand stoichiometry. However, the spectra recorded in 1 : 4 stoichiometry did not show change from that observed in 1 : 3 stoichiometry hence the data has not been included. There has been significant variation in intensity parameters while the variation in the energy interaction parameters has been insignificant. No doubt the energy interaction parameters are quite different from that of neodymium(III) aquo and more so from neodymium(III) free ion. Comparing the magnitude of spectral parameters like P and T_λ for fluorinated nucleic bases and their nucleosides, the parameters have higher values for fluorinated nucleosides as compared to these observed for corresponding to non-fluorinated nucleic base which is understandable in view of the better complexing power shown by the former biomolecule.

Conclusion

The interaction of fluorouracil, fluorocytosine, and 1fluorothymine and their nucleosides with neodymium involves participation of oxygen donor sites of the ligand. The attachment of the ligand is as neutral species. The presence of water molecules complete the nona- or octa-coordination around neodymium in presence of fluoronucleosides and fluoronucleic bases respectively. The magnitude and variation of spectral parameter shows significant changes in the intensities and intensity parameters but less prominent changes in the coulombic and spin orbit interaction parameters. These point to the fact that the changes in the symmetry of the complex play dominant role. The unusual intensification and wide variation of oscillator strength of some nonhypersensitive 4f–4f transitions was observed which was given the name 'LIGAND-MEDIATED PSEUDOHYPERSENSITIVITY'.

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