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Lanthanoid Shift Reagents. Synthesis and Spectral Studies[†]

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The seven coordinate adducts of [Ln(fod)$_3$]chelates are described. The NMR spectra of diamagnetic and paramagnetic adducts have been discussed. The europium, praseodymium and ytterbium adducts have been scanned as potential shift reagents and these seven coordinate adducts produce large dipolar shifts in the proton magnetic resonances of organic moieties. The dipolar shift produced by [Eu(fod)$_3$(pz)] in the spectrum of benzyl alcohol is different from that reported. Some interelectronic and spectral parameters ($\bar{\beta}$, $b^{1/2}$, and δ) have been calculated. Ligand field parameter (T_λ) and oscillator strengths have been computed and discussed.

NMR spectra may usually be obtained from the complexes of paramagnetic lanthanoid ions with organic ligands.[1,2] Such spectra commonly show paramagnetic shifts, mainly of dipolar (pseudo-contact) origin. This principle has been applied by Hinckley[3] to weak association between tris(dipivaloylmethanato)-europium(III) and cholesterol (the complex being used as its bis(pyridine)adduct). Further investigations have established that (1) [Eu(dpm)$_3$], dpm=2,2,6,6-tetramethyl-3,5-heptanedione, itself (*i.e.*, without the pyridine molecules appended) is even better than the pyridine adduct[4] (pyridine tends to block coordination of substrate) (2) the analogous praseodymium compound, [Pr(dpm)$_3$], induces NMR shifts of opposite sign[5] and also much larger than those reported for [Eu(dpm)$_3$]. Selbin *et al.*[6] reported a series of analogous lanthanoid complexes with the same bulky β-keto enolate and their mixed ligand complexes with uni and bidentate ligands. Ahmad *et al.*[7] studied the temperature dependant shifts. It has been pointed[8] out that the mixed ligand adducts [Eu(dpm)$_3$-(bpy)] and [Eu(dpm)$_3$(phen)] (bpy=2,2′-bipyridyl and phen=1,10-phenanthroline) are inefficient in producing shifts. We have also shown[9] that our eight coordinate adduct, [Pr(fod)$_3$(phen)] (fod=6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato) does not produce dipolar shifts in the proton resonance of 1-butanol but it does not dissociate in solution as reported by Hinckley,[3] for eight coordinate complex. Recently[10–12] we have synthesized seven, eight and ten coordinate complexes of lanthanoid and studied their electronic spectra. During these investigations it has been found that as the coordination number increases the number of bands decrease and also the intensity of the hypersensitive bands increases.

The present paper deals with the synthesis and characterization of seven coordinate adducts of [Ln-(fod)$_3$] chelates with pyrazole (pz) and possible use of their europium, praseodymium, and ytterbium adducts as lanthanoid induced shift reagents. Covalency parameters[13–16] ($\bar{\beta}$ and δ), bonding parameter ($b^{1/2}$) have been calculated and discussed. Oscillator strength (P) have also been computed for some of the complexes[17–19]

Experimental

Rare earth oxides (Leico Chem., U.S.A.) were converted to corresponding chlorides. Hfod (Pierce Chem., U.S.A.), pyrazole, pz, (Fluka) and Xylenol Orange (BDH, England) were used in this study.

Synthesis. [Ln(fod)$_3$] chelates were synthesized by the method of Sievers *et al.*[20] with a slight modification. The adducts of all the lanthanoid with pyrazole were prepared as follows:

The pyrazole was refluxed in ethanol for 1 h; the solution of [Ln(fod)$_3$] chelates (in 1:1 ratio) was mixed with it. Finally the mixture was refluxed for 4 h on a water bath. The solvent of the resulting mixture was evaporated on a hot plate. The product thus, formed was crystallized from hexane by keeping it in the fridge for 30 d. Good crystals were obtained by recrystallization. Finally these were dried in vacuo over P_2O_5 for several days.

Methods. Carbon, hydrogen, and nitrogen contents of the complexes were estimated by microanalyses while the metals were estimated by complexometric titrations with edta using Xylenol Orange as the indicator. The IR spectra were recorded on a Perkin-Elmer model 621 spectrophotometer in the range 4000—200 cm^{-1}. A Beckman DU-2 spectrophotometer was used to obtain the optical spectra. The NMR spectra were recorded on a Varian A-60 NMR machine in carbon tetrachloride. The magnetic susceptibility was measured by Evans' NMR method[21] in methanol as well as in chloroform at the probe temperature. TGA and DTA studies were carried out at RRL Hyderabad, India.

Calculations

On complexation radial integrals of the valence orbital of the metal ion decrease. This phenomenon is known[13] as nephelauxetic effect and may be regarded as a measure of the covalency in a complex. Nephelauxetic ratio, $\bar{\beta}$, can be calculated from the relation

$$\bar{\beta} = \frac{1}{n}\sum_{n=1}^{n} \nu_{\text{comp}}/\nu_{\text{aq}}. \tag{1}$$

If the f orbitals are involved in covalent bond formation with the ligand the metal wave function can be expressed[14] as

$$<\phi_{4f}| = (1-b)^{1/2}<4f| - b^{1/2}<\phi_{\text{ligand}}|, \tag{2}$$

where $b^{1/2}$ measures the amount of 4f-ligand mixing and is calculated from the relation[15]

$$b^{1/2} = \left[\frac{1}{2}(1-\bar{\beta})\right]^{1/2}. \tag{3}$$

The positive and negative values of $b^{1/2}$ for a complex, correspond to covalent and ionic characters respectively.

[†] Abstracted in part from the thesis submitted by K. Iftikhar to the Aligarh Muslim University for the degree of Doctor of Philosophy.

Sinha's covalency parameter, δ, is calculated from the relation[16]

$$\delta = \left[\frac{1-\bar{\beta}}{\bar{\beta}}\right]100. \tag{4}$$

The experimental values of the oscillator strength (P_{exptl}) of the absorption bands are calculated by performing Gaussian curve analyses of the curves and using the equation[19]

$$P_{\text{exptl}} = 4.31 \times 10^{-9}\left[\frac{9\eta}{(\eta^2+2)^2}\right]\int \varepsilon(\nu)\mathrm{d}\nu, \tag{5}$$

where η is the refractive index of the medium, ε is the molar extinction coefficient and ν is the energy of the transition in wave number.

The oscillator strengths (P_{calcd}) can be computed from an equation[17,18] derived from a theory in which the ligand field interaction with central ion causes a mixing of higher configuration of opposite parity into the 4f^n configuration giving rise to induced electric dipole transions.

$$P = \sum_{\lambda=2,4,6} T_\lambda \nu (f^n\psi_J||U^{(\lambda)}||f^n\psi'_{J'})^2(2J+1)^{-1}, \tag{6}$$

where ν is the energy of the transition, $\psi_J \rightarrow \psi'_{J'}$ and $U^{(\lambda)}$ is the unit tensor operator connecting the initial and final states *via* three phenomenological parameters $T_\lambda(\lambda=2$, 4, and 6). The three T_λ parameters are related to the radial part of the 4f^n wave functions, the wave functions of the perturbing configurations, the refractive index of the medium and the ligand field parameters characterizing the environment of the ion. The three quantities, T_λ, can be treated as the parameters to be determined from the experimental oscillator strengths.

Results and Discussion

These adducts are well defined crystalline solids with sharp melting points. The melting points of pyrazole adducts are lower than those of imidazole adducts.[12] These are soluble in all organic solvents and are air stable. The molar conductances of these complexes in methanol (Table 1) showed their nonelectrolytic behaviour.[22]

IR Spectra. The IR spectra of these adducts show the presence of coordinated pyrazole. The N–H frequency in pyrazole ligand appears as a broad band (2300—3500 cm^{-1}) because of intermolecular hydrogen bonding. It appears as a sharp band in the region 3000—2940 cm^{-1} in the adducts. The weak band found between 305 and 290 cm^{-1} in these adducts has been assigned to metal-nitrogen frequency. We have found the metal-nitrogen frequency in the same region (282—290 cm^{-1}) for imidazole adducts[12]

Table 1. Elemental analyses and some characterizing data

Complex	Found (Calcd) (%)				Mp θ_m/°C	Molar conductance Ω^{-1} cm^2	μ_{eff} BM	Colour
	Metal	C	H	N				
[Y(fod)$_3$(pz)]	8.52	38.20	3.18	2.70	—	—	Diamag.	White
	(8.54)	(38.00)	(3.26)	(2.68)				
[La(fod)$_3$(pz)]	13.33	35.87	3.33	2.58	209	6.8	Diamag.	White
	(12.73)	(36.26)	(3.12)	(2.57)				
[Pr(fod)$_3$(pz)]	12.69	36.88	3.05	2.73	105	16.3	3.67	Green
	(12.89)	(36.20)	(3.11)	(2.56)				
[Nd(fod)$_3$(pz)]	12.82	36.90	3.32	2.35	118	9.9	3.81	Violet
	(13.13)	(36.10)	(3.10)	(2.55)				
[Sm(fod)$_3$(pz)]	13.60	35.83	3.10	2.58	112	19.0	2.45	White
	(13.63)	(35.90)	(3.08)	(2.54)				
[Eu(fod)$_3$(pz)]	13.73	36.10	2.97	2.51	—	6.3	3.62	Light yellow
	(13.76)	(35.84)	(3.08)	(2.53)				
[Gd(fod)$_3$(pz)]	14.30	35.52	3.18	2.39	108	6.0	7.96	Light yellow
	(14.16)	(36.68)	(3.06)	(2.52)				
[Tb(fod)$_3$(pz)]	14.33	35.83	3.26	2.51	—	—	9.87	Light yellow
	(14.30)	(35.61)	(3.06)	(2.52)				
[Dy(fod)$_3$(pz)]	15.18	34.98	3.18	2.47	139	—	10.70	Light yellow
	(14.56)	(35.50)	(3.04)	(2.51)				
[Ho(fod)$_3$(pz)]	14.53	36.25	3.08	2.55	109	10.0	10.55	Pink
	(14.76)	(35.42)	(3.04)	(2.50)				
[Er(fod)$_3$(pz)]	14.90	35.30	3.21	2.58	—	—	9.51	White
	(14.92)	(35.36)	(3.03)	(2.50)				
[Tm(fod)$_3$(pz)]	15.21	35.75	2.95	2.43	—	7.6	7.39	White
	(15.06)	(35.30)	(3.03)	(2.50)				
[Yb(fod)$_3$(pz)]	15.35	35.10	3.15	2.46	90	—	4.50	White
	(15.36)	(35.10)	(3.02)	(2.49)				
[Lu(fod)$_3$(pz)]	15.30	35.29	2.98	2.50	—	—	Diamag.	White
	(15.50)	(35.12)	(3.01)	(2.48)				

of [Ln(fod)$_3$] chelates. The metal-oxygen frequency in [Pr(fod)$_3$] and [Sm(fod)$_3$] occurs at 390 cm^{-1}. These go up to 454 cm^{-1} and 450 cm^{-1} in the corresponding adducts. Thus the bands appearing between 445 and 460 cm^{-1} have been assigned to metal-oxygen frequency in these adducts. This is an observation in contrast to what is seen in imidazole[12] adducts.

The thermograms of the adducts of La, Eu, Gd, Tm, and Yb showed the same behaviour as reported for their respective chelates,[20] except in the temperature range of 200—220 °C in which pyrazole is eliminated. The total weight loss is consistent with the loss of pyrazole in this temperature range (Table 2). One sharp DTA peak is identified in all cases.

Thus, these adducts on the basis of their elemental analyses for carbon, hydrogen, nitrogen, and metals, molar conductance (Table 1), IR spectral and thermal studies have been assigned the general formula, [Ln(fod)$_3$(pz)].

The magnetic moments (Table 1) of these adducts, when plotted against their increasing atomic number, showed the characteristic unequal double humped curve.

NMR Spectra. The NMR spectral data are summarized in Table 3. NMR signals of fod moiety of the adducts appear at 1.05—1.15 ppm for *t*-butyl protons and at 5.95—6.11 ppm for methine protons as sharp singlet (for diamagnetic adducts). It has been found that the signals due to *t*-butyl and methine protons have been shifted to higher fields as compared to their respective chelates.[20] Perhaps it is due to withdrawal of electron density from pyrazole, that the Ln^{3+} ions become more polarized and transfer some charge to diketonate ring, which can be very conveniently accommodated by the highly electronegative fluorine. Other signals can be assigned to those of the coordinated pyrazole.

Table 2. TGA data for some of the complexes

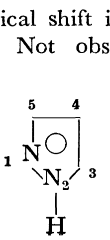
Complex	Temperature °C	% Weight loss for pyrazole[a)]
[La(fod)$_3$(pz)]	220	7.00 (6.22)
[Eu(fod)$_3$(pz)]	200	6.25 (6.15)
[Gd(fod)$_3$(pz)]	220	6.25 (6.12)
[Tm(fod)$_3$(pz)]	200	6.00 (6.06)
[Yb(fod)$_3$(pz)]	200	5.75 (6.04)

a) Theoretical weight loss is in parenthesis.

Table 3. NMR spectral data[a)]

Complex	Signals due to pyrazole			Signals due to β-keto enolate	
	H-2	H-3 and H-5	H-4	CH	Bu^t
Pyrazole	13.73	7.57	6.26	—	—
[Y(fod)$_3$(pz)]	b)	7.61	6.36	6.11	1.13
[La(fod)$_3$(pz)]	b)	7.42	6.24	5.95	1.05
[Lu(fod)$_3$(pz)]	b)	7.73	6.45	6.08	1.15
[Pr(fod)$_3$(pz)]	b)	12.11	1.30	b)	−0.48[c)]
[Yb(fod)$_3$(pz)]	b)	34.92	3.18	b)	3.72

a) Obtained in carbon tetrachloride at the probe temperature. chemical shift in ppm downfield from internal Me$_4$Si. b) Not observed. c) In ppm upfield w.r.t. Me$_4$Si.



Pyrazole is reported[23] to give two signals (one for H-4 and another for H-3 and H-5) with relative areas of 1:2. But we found all the three signals (for H-2, H-4, and H-3 and H-5) with relative areas of 1:1:2. The signals of the coordinated pyrazole are found to shift to the lower fields, except in the case of lanthanum in which the signals are slightly shifted to higher fields. This deshielding effect of pyrazole protons obviously suggests the coordination of pyrazole to metal ion.

Information concerning electron delocalization in lanthanoid complexes may be obtained from NMR studies of paramagnetic species, provided nuclear relaxation times are long enough to allow well-resolved spectra to be obtained. Paramagnetic lanthanoid complexes whose spectra have been recorded are few.[1,8] In the spectra of [Pr(fod)$_3$(pz)] and [Yb(fod)$_3$(pz)] the methine signal is not seen but the proton resonances of pyrazole show large chemical shifts as compared to their diamagnetic analogue. These shifts are due to pseudo-contact (dipolar) interaction as $\boldsymbol{g}$ tensor is anisotropic. If $\boldsymbol{g}$ is isotropic this interaction goes to zero. The dipolar shift is limited by the geometry of the complex species, as given by the expression[24]

$$\left(\frac{\Delta\nu}{\nu_0}\right) = -K_p f(\theta, r) f(g_{\parallel}, g_{\perp}),$$

or simply

$$\left(\frac{\Delta\nu}{\nu_0}\right) = -D\left(\frac{3\cos^2\theta-1}{r^3}\right),$$

where all notations have their usual connotations.

One of the intents of this study was to examine praseodymium, europium and ytterbium adducts as potential shift reagents. [Eu(fod)$_3$(pz)] added to a solution of 1-butanol show large chemical shifts (Fig. 1). The two methylene protons which resonate as a singlet get resolved into two individual signals. The substrate associates with the complex at the hydroxyl group and the induced shifts decrease rapidly with increasing distance of the protons from the hydroxyl group. When [Pr(fod)$_3$(pz)] was used, it induced the 1-butanol spectrum to become first order and all peaks greatly shifted to high field (Fig. 3). On addition of [Yb(fod)$_3$(pz)] the spectrum is amenable to a first order analysis and the magnitude of the induced shift is larger than the europium adduct, but with a little broadening and the coupling interactions of the nuclei having disappeared. This little broadening is due to long electron relaxation time of Yb(III) ion as compared to europium(III). In the above examples, the shifts of the hydroxyl protons are of course extremely large and have not been recorded, (See Tables 4—6).

In the normal ^{1}H NMR spectrum of benzyl alcohol

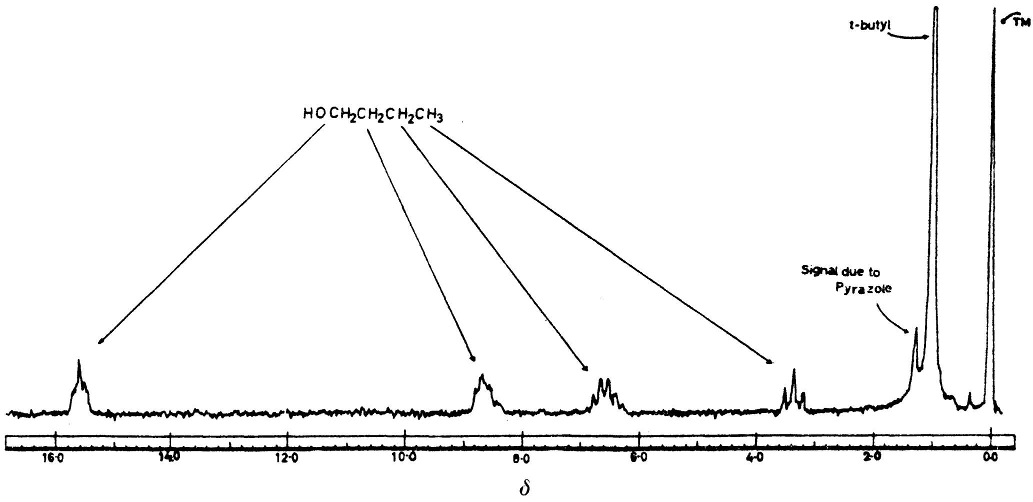


Fig. 1. 60 MHz ^{1}H NMR spectrum of 1-butanol (0.2 M, 1 M = 1 mol dm^{-3}) and [Eu(fod)$_3$(pz)] (0.2 M) in CCl$_4$. Chemical shifts relative to internal Me$_4$Si.

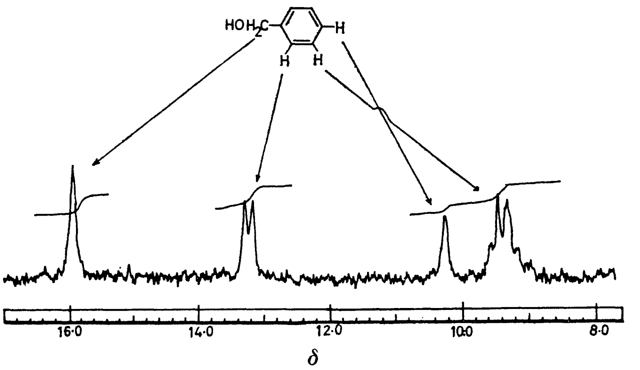


Fig. 2. 60 MHz ^{1}H NMR spectrum of benzyl alcohol (0.2 M) and [Eu(fod)$_3$(pz)] in CCl$_4$. Chemical shifts relative to internal Me$_4$Si.

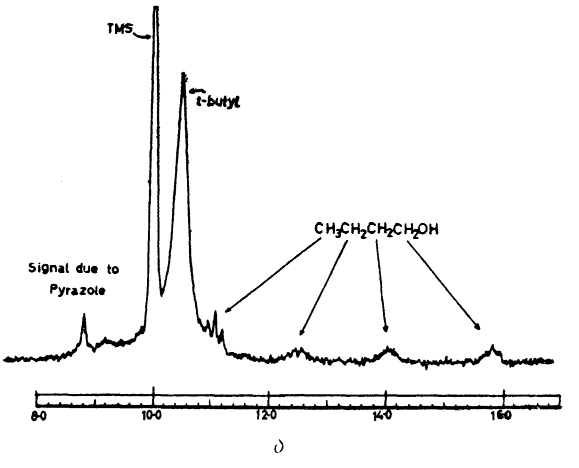


Fig. 3. 60 MHz ^{1}H NMR spectrum of 1-butanol (0.2 M) and [Pr(fod)$_3$(pz)] (0.2 M) in CCl$_4$. Chemical shifts relative to internal Me$_4$Si.

(CCl$_4$ solution) the aromatic protons resonate as a sharp singlet. Sanders and Williams[4] studied NMR spectrum of benzyl alcohol using [Eu(dpm)$_3$] and reported that the signals appear in order CH$_2$, *o*-protons, *m*-protons, and then *p*-proton (all lower field to TMS). Our studies gave a different result. [Eu(fod)$_3$(pz)] when added to a CCl$_4$ solution of benzyl alcohol resolved all the ring protons (Fig. 2) but in a different manner as reported.[4] The CH$_2$ protons appear at the lowest field as a sharp singlet, the next resonance is due to *o*-protons after this appear signal for *p*-proton and the *m*-protons appear at the last (all lower field to TMS). When [Pr(fod)$_3$(pz)] is used only CH$_2$ signal appears at higher field to TMS the other signals lie within the TMS envelope. The CH$_2$ proton resonance shows that the angle between the principal axis and line joining the paramagnetic ion and the proton inquestion is greater than 54.7° or 125.3°.

Table 4. [Eu(fod)$_3$(pz)] shifts in ppm downfield

	H_α	H_β	H_γ	H_δ
1-Butanol	12.04	7.23	5.22	2.37
	CH_2	H_o	H_p	H_m
Benzyl alcohol	11.33	5.89	2.89	2.04

Table 5. [Pr(fod)$_3$(pz)] shifts in ppm

	H_α	H_β	H_γ	H_δ
1-Butanol	−9.40	−5.90	−3.90	−2.06
	CH_2	H_o	H_p	H_m
Benzyl alcohol	−6.77	3.14	1.09	0.78

Negative sign indicate shifts upfield w.r.t. Me$_4$Si and positive shifts are downfield w.r.t. Me$_4$Si.

Table 6. [Yb(fod)$_3$(pz)] shifts in ppm downfield

	H_α	H_β	H_γ	H_δ
1-Butanol	28.67	27.82	17.82	8.92

The NMR spectra of these adducts show no resonance for free pyrazole. Even on keeping the solutions for several days no change in signal line width or position is seen. This shows that coordinated pyrazole does not dissociate in solution as suggested by Hinckley[3] for pyridine.

Electronic Spectra. The electronic spectra of the complexes are recorded in ethanol. The intraligand

TABLE 7. COVALENCY PARAMTERS

Complex	$\bar{\beta}$	$b^{1/2}$	δ
$[Pr(fod)_3(pz)]$	0.98284	0.09263	1.74596
$[Nd(fod)_3(pz)]$	0.99598	0.04483	0.40362
$[Er(fod)_3(pz)]$	0.99225	0.06225	0.78105

TABLE 8. T_λ PARAMETERS ($T_\lambda \times 10^8$)

Complex	T_2	T_4	T_6
$[Pr(fod)_3(pz)]$	23.53370	0.11519	1.31464
$[Nd(fod)_3(pz)]$	75.40279	−195.39910	280.95548
$[Er(fod)_3(pz)]$	2.01493	0.30832	0.03987

TABLE 9. OSCILLATOR STRENGTH ($P \times 10^6$)

Complex	S′L′J′	P_{exptl}	P_{calcd}
$[Pr(fod)_3(pz)]$	${}^1D_2$	4.57982	4.36339
	${}^3P_0$	1.66622	3.90265
	${}^3P_1$	2.20341	1.39446
	${}^3P_2$	0.19348	8.19343
$[Nd(fod)_3(pz)]$	${}^4F_{9/2}$	3.98525	16.10470
	${}^2H_{11/2}$	32.38545	32.38533
	$\left[{}^4G_{5/2}\right.$ $\left.{}^2G_{7/2}\right]$	54.78670	54.78660
	$\left.{}^2K_{13/2}\right\}$ ${}^4G_{7/2}$ ${}^4G_{9/2}$	9.34646	9.34695
$[Er(fod)_3(pz)]$	${}^4F_{9/2}$	2.77998	2.78000
	$[{}^2H_{11/2}]$	24.86433	24.86433
	${}^4F_{7/2}$	1.81117	1.81079

Hypersensitive transitions are enclosed in parentheses.

transitions occur in UV region and have not been discussed. The sharp line like f-f transitions originating within the $4f^n$ configuration of lanthanoid(III) ions are affected by the influence of the ligands on complexation. The shift of absorption bands to lower wave numbers (nephelauxetic effect) is usually of the order of a few percent[13] and is caused by a decrease in interelectronic repulsion parameter in the complexes.[25] A general red shift of the f-f transitions would be observed for these complexes as compared to the corresponding aqua ions. The $\bar{\beta}$ values for these complexes are presented in Table 7. The $\bar{\beta}$ values which are less than one show covalent nature of bonding between the metal and the ligand. The $\bar{\beta}$ value of Nd(III) complex is higher than the Pr(III) complex but it is lower for Er(III) complex as compared to Nd(III) complex. This is in contrast to the general observation that the nephelauxetic effect is more pronounced in the beginning of the 4f group than in the later members. The bonding parameter, $b^{1/2}$ and Sinha's covalency parameter, δ are positive for these complexes indicating covalent bonding (Table 7). The greater the values of $b^{1/2}$ and δ the greater will be the degree of covalency. The $b^{1/2}$ and δ values of Nd(III) complex are less than those for Pr(III) complex showing decrease of covalency with increase of atomic number. The higher values of $b^{1/2}$ and δ for Er(III) complex than for Nd(III) complex are surprising in view of the general observation and trend observed in case of $[Ln(fod)_3(im)]$ (im=imidazole) complexes.[12] The $[Ln(fod)_3(pz)]$ complexes are less covalent as compared to the corresponding $[Ln(fod)_3(im)]$[12] complexes since values of $b^{1/2}$ and δ are lower in the former case than in the later.

Another point of interest in these spectra are the intensities of the f-f transitions. Experimentally hypersensitivity refers to transitions having oscillator strengths which show a relatively large variability in oscillator strengths as the environment about the lanthanoid ion is changed. The large variability in oscillator strengths for the hypersensitive transitions is due to eigen perturbation.[26] Hypersensitivity can also be disccused from the theoretical point of view of Judd-Ofelt. According to this theory hypersensitivity is intimately associated with T_2 parameter of Eq. 6. Consequently only those transitions having relatively large values of $U^{(2)}$ matrix element should be called hypersensitive. Judd[27] has suggested that hypersensitivity may be due to symmetry of the crystal fields. Henrie[28] has shown that T_4 and T_6 appear to be primarily influenced by the symmetry of the complexes whereas T_2 seems to be correlated with the basicity of the ligand.

The oscillator strengths are listed in Table 9 and hypersensitive transitions classified by previous workers[28] are enclosed in parentheses. There is a good correlation between P_{exptl} and P_{calcd} showing that the intensity theory of Judd-Ofelt is applicable but poor correlation between P_{exptl} and P_{calcd} in case of Pr(III) complex strengthens the conclusion of the earlier workers[29,30] that this theory is not applicable to the complexes of Pr(III).

The transitions in Pr(III) and Er(III) complexes have values of $U^{(2)}$ which are significantly larger than either the $U^{(4)}$ or $U^{(6)}$ values and thus have oscillator strengths which are affected primarily by T_2 parameter.

In Nd(III) complex the magnitude of $U^{(2)}$ is not large enough to permic the effect of T_2 parameter to dominate instead T_4 and T_6 are more sensitive than T_2 and hence the observed oscillator strength is governed by these parameters. The oscillator strength of ${}^2H_{11/2}$ in Nd(III) complex shows a very large change as compared to the aqua ion. This change is larger than the change shown by hypersensitive transition (enclosed in parenthesis).

The oscillator strength of the hypersensitive transitions is related to the degree of covalency. As the covalency in the complex increases the oscillator strength of the hypersensitive transitions exhibits a corresponding increases. The oscillator strengths of the hypersensitive transitions of pyrazole complexes have lower values as compared to the corresponding imidazole complexes[12] since imidazole is more basic than pyrazole.

In the last we can say that pyrazole complexes, though less covalent, have superiority over imidazole complexes[12] since they can be used as potential shift reagents.

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References

1) D. R. Eaton, *J. Am. Chem. Soc.*, **87**, 3097 (1965).

2) F. A. Hart, J. E. Newbery, and D. Shaw, *J. Chem. Soc., Chem. Commun.*, **1967**, 45; *J. Inorg. Nucl. Chem.*, **32**, 3585 (1970).

3) C. C. Hinckley, *J. Am. Chem. Soc.*, **91**, 5160 (1969); *J. Org. Chem.*, **35**, 2834 (1970).

4) J. K. M. Sanders and D. H. Williams, *J. Chem. Soc., Chem. Commun.*, **1970**, 422.

5) J. Briggs, G. H. Frost, F. A. Hart, G. P. Moss, and M. L. Staniforth, *J. Chem. Soc., Chem. Commun.*, **1970**, 749.

6) J. Selbin, N. Ahmad, and N. Bhacca, *Inorg. Chem.*, **10**, 1383 (1971).

7) N. Ahmad, N. S. Bhacca, J. Selbin, and J. D. Wander, *J. Am. Chem., Soc.*, **93**, 2564 (1971).

8) N. S. Bhacca, J. Selbin, and J. D. Wander, *J. Am. Chem. Soc.*, **94**, 8719 (1972).

9) K. Iftikhar, M. Sayeed, and N. Ahmad, *Inorg. Chem.*, **21**, 80 (1982).

10) M. Sayeed and N. Ahmad, *J. Inorg. Nucl. Chem.*, **43**, 3197 (1981).

11) K. Iftikhar, M. Sayeed, and N. Ahmad, *Indian J. Chem.*, **20A**, 1028 (1981).

12) K. Iftikhar and N. Ahmad, submitted for publication.

13) C. K. Jørgensen, *Prog. Inorg. Chem.*, **4**, 73 (1962).

14) S. P. Tandon and P. C. Mehta, *J. Chem. Phys.*, **52**, 4896, 5417 (1970).

15) D. E. Henrie and G. R. Choppin, *J. Chem. Phys.*, **49**, 477 (1968).

16) S. P. Sinha, *Spectrochim. Acta*, **22**, 57 (1966).

17) B. R. Judd, *Phys. Rev.*, **127**, 750 (1962).

18) G. S. Ofelt, *J. Chem. Phys.*, **37**, 511 (1962).

19) J. Hooschagen, *Physica*, **11**, 513 (1946).

20) C. S. Springer, D. W. Meek, and R. E. Sievers, *Inorg. Chem.*, **6**, 1105 (1967).

21) D. F. Evans, *J. Chem. Soc.*, **1959**, 2003.

22) W. J. Geary, *Coord. Chem. Rev.*, **7**, 81 (1971).

23) J. H. Ridd and R. F. M. White, *Biochem. J.*, **77**, 546 (1960).

24) H. M. McConnel and R. E. Robertson, *J. Chem. Phys.*, **29**, 1361 (1958).

25) S. P. Sinha and S. S. Schmidtke, *Mol. Phys.*, **10**, 7 (1965).

26) W. Pricke, *Z. Phys.*, **B 33**, 261 (1979).

27) B. R. Judd., *J. Chem. Phys.*, **44**, 839 (1966).

28) D. E. Henrie, R. L. Fellows, and G. R. Choopin, *Coord. Chem. Rev.*, **18**, 199 (1976).

29) W. T. Carnall, P. R. Fields, and B. G. Wybourne, *J. Chem. Phys.*, **42**, 3797 (1965).

30) W. T. Carnall, P. R. Fields, and K. Rajnak, *J. Chem. Phys.*, **49**, 4412 (1968).