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Mixed-Ligand Lanthanide Complexes.
Part VI*. Electronic Spectral Study of some Ln(fod)$_3$ Adducts with Heterocyclic Amines**

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Abstract

The electronic spectra of Ln(fod)$_3$pyz complexes (where Ln stands for Pr(III), Nd(III), and Er(III) and pyz is pyrazine) in the visible region have been analysed. The band shapes and oscillator strengths of the hypersensitive transitions display pronounced changes as compared to respective aqua-ions. The band shapes of the hypersensitive transitions show remarkable changes on passing from solid to solution states which are the result of changes in the environment about the lanthanide ion in the two states and suggest coordination of a solvent molecule. A comparative account of hypersensitivity in the present complexes with those of other adducts of Ln(fod)$_3$ with imidazole and pyrazole is discussed.

Introduction

The electronic spectra of lanthanide(III) complexes have been studied to give information regarding structure and bonding in these complexes. The oscillator strengths of certain 4f–4f transitions in lanthanide(III) complexes are especially sensitive to structural details and the chemical nature of the ligand environment. This phenomenon is generally referred to as hypersensitivity and it has been the subject of considerable experimental and theoretical investigations. The oscillator strengths and shapes of the hypersensitive transitions can be used to probe complex formation, coordination geometry, ligand structure and chelate solvent interactions [1–15].

Iftikhar *et al.* have previously investigated a number of mixed-ligand lanthanide(III) complexes containing oxygen and nitrogen donors, and interesting studies on the chemistry of these complexes, especially on their electronic spectra for ascertaining the dependence of the hypersensitive bands, have been reported [8, 9, 12]. In this paper electronic spectral studies of the complexes of the type Ln(fod)$_3$pyz (where Ln stands for Pr(III), Nd(III), and Er(III) and pyz is pyrazine) are reported.

Experimental

The complexes were synthesized by the literature method [16]. The electronic spectra were recorded on a Cary 17D spectrophotometer in ethanol (spectroscopic grade) in the concentration range 10^{-2} to 10^{-3} M and in the solid state. Covalency parameters were calculated using previously reported methods [8]. Oscillator strengths, defined by

$$P = 4.32 \times 10^{-9}\left[\frac{9\eta}{(\eta^2+2)^2}\right]\int \epsilon(\nu)\,\mathrm{d}\nu \qquad (1)$$

where η is the refractive index of the solvent, ϵ is the molar extinction coefficient and ν is the energy of the transition, were obtained by evaluating $\int\epsilon(\nu)\,\mathrm{d}\nu$ over the transition region of interest.

Results and Discussion

The observed spectra of the adducts reveal highly intense maxima ($\epsilon_{\max}$ 1700–45 000 l mol^{-1} cm^{-1}) in the 34 000–35 000 cm^{-1} region. These bands are broad, covering a spread of about 100 nm. The average position of the maxima varies slightly between the different adducts. The band is of metal–ligand charge-transfer origin [17].

The internal 4f–4f transitions of the lanthanide(III) ions are affected by the ligands on complex formation; shifts towards longer wavelength and splitting and enhancement of the intensity of certain bands are generally observed. These effects can provide useful information on the nature of the metal–ligand bonding and on the environment of the

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*Part V is ref. 27.

**(fod) = anion of the enol form of 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione.

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TABLE I. Oscillator Strengths[a, b]

Complexes	$[S'L'J']$	Energy (cm^{-1})	$P \times 10^6$
$Pr(fod)_3pyz$	$^3P_2$	22371 (22520)	3.42
	$^3P_1$	21276 (21300)	0.57
	$^3P_0$	20576 (20750)	0.48
$Nd(fod)_3pyz$	$^4G_{7/2}$	19120 (19160)	15.44
	$[^4G_{5/2}, ^2G_{7/2}]$	17240 (17300)	60.51
	$^4(F_{7/2}, S_{3/2})$	13421 (13500)	5.44
	$^4F_{5/2}$	12437 (12480)	7.25
	$^4F_{3/2}$	11415 (11460)	1.66
$Er(fod)_3pyz$	$(^2G, ^4F'\,^2H)_{9/2}$	24496 (24550)	0.40
	$^4F_{7/2}$	20408 (20450)	1.01
	$[^2H_{11/2}]$	19047 (19150)	16.44
	$^4I_{9/2}$	12300 (12400)	0.17

[a]Hypersensitive transitions are enclosed in square brackets. [b]The values in parentheses are for the aqua-ions.

TABLE II. Oscillator Strengths of the Hypersensitive Transitions of some Neodymium and Erbium Complexes

Complexes	Solvent	$P \times 10^6$
(a) Neodymium $^4I_{9/2} \rightarrow {}^4G_{5/2}, {}^2G_{7/2}$ (17 700–16 400 cm^{-1})		
$Nd(fod)_3phen$ [a]	hexane	54.00
$Nd(fod)_3pyz$ [b]	ethanol	60.51
$Nd(fod)_3pz$ [c]	ethanol	54.79
$Nd(fod)_3im$ [d]	ethanol	61.27
$Nd(fod)_3$ [e]	ethanol	53.00
(b) Erbium $^4I_{15/2} \rightarrow {}^2H_{11/2}$ (19 600–18 500 cm^{-1})		
$Er(fod)_3phen$ [a]	hexane	22.87
$Er(fod)_3pyz$ [b]	ethanol	16.44
$Er(fod)_3pz$ [c]	ethanol	24.86
$Er(fod)_3im$ [d]	ethanol	26.36
$Er(fod)_3$ [e]	ethanol	27.00

[a]Ref. 8. [b]This work. [c]Ref. 9. [d]Ref. 12. [e]Ref. 13.

lanthanide ion. The oscillator strengths evaluated using eqn. (1) for $Pr(fod)_3pyz$, $Nd(fod)_3pyz$ and $Er(fod)_3pyz$ are collected in Table I. The ^3P_j bands of the Pr(III) complex showed only a slight increase in intensity compared to the praseodymium aqua-ion. The oscillator strengths of $Pr(fod)_3pyz$, $Pr(fod)_3im$ [12] and $Pr(fod)_3pz$ [9] (where im is imidazole and pz is pyrazole) reveal larger P values for the imidazole system *versus* those observed for other systems (pz and pyz), indicating that imidazole is especially effective in promoting 4f–4f intensity.

For the $Nd(fod)_3pyz$ and $Er(fod)_3pyz$ systems, the largest intensity variations were observed in $^4I_{9/2} \rightarrow {}^4G_{5/2}, {}^4G_{7/2}$ (17700–16400 cm^{-1}) and $^4I_{15/2} \rightarrow {}^2H_{11/2}$ (19600–18500 cm^{-1}) transition regions, respectively, as compared to the corresponding aqua-ions (six times more intense than the corresponding neodymium and erbium aqua-ions [18]). Both the transitions $^4I_{9/2} \rightarrow {}^4G_{5/2}\ {}^4G_{7/2}$ (Nd^{3+}) and $^4I_{15/2} \rightarrow {}^2H_{11/2}$ (Er^{3+}) obey electric quadrupolar selection rules on $\Delta J \leqslant 2$, $\Delta L \leqslant 2$ and $\Delta S = 0$ and are classified as hypersensitive transitions [4, 5]. Only hypersensitive transitions show pronounced changes in the intensity and band shapes on a change in the environment of the ion.

Table II lists the oscillator strengths of the hypersensitive transition of $Nd(fod)_3pyz$ and $Er(fod)_3pyz$, along with some similar adducts of $Ln(fod)_3$ studied earlier [8, 9, 12, 13]. The oscillator strength of an ethanolic solution of $Nd(fod)_3pyz$ is equal to that of $Nd(fod)_3im$. These two are expected to have identical coordination geometry in solution. However, the oscillator strength is a little higher than for $Nd(fod)_3$, $Nd(fod)_3pz$ and $Nd(fod)_3phen$. The difference in P values may be attributed to a change in the nature of the ligands present; i.e. how the donor group interacts with the f-electrons of the lanthanide. The oscillator strength due to the hypersensitive transition of either $Nd(fod)_3$ or any of its adducts is surprisingly high compared to 20–40 $\times 10^{-6}$, the value found for other Nd(III) complexes [13, 19]. The relatively large value of the oscillator strength can, most likely, be attributed to the low molecular symmetries of these neodymium complexes in solution [12, 13].

The oscillator strength due to the hypersensitive transition of $Er(fod)_3pyz$ is lower than for $Er(fod)_3$ [13] and for $Er(fod)_3pz$ [9] and $Er(fod)_3im$ [12]. It is much lower compared to 30–52 $\times 10^{-6}$, the value found for other erbium β-diketonates [20]. However, the lower value is not peculiar since it compares well with 17.1 $\times 10^{-6}$, the value found for an erbium complex with a hexadentate ligand in aqueous solution [21]. It is generally believed that low molecular symmetry of the complex is responsible for the higher oscillator strength. However, this theory fails to account for the intensity of the hypersensitive transition in $Er(fod)_3pyz$, as well as its imidazole and pyrazole analogues. The variation in the oscillator strength among imidazole, pyrazole and pyrazine adducts of $Er(fod)_3$ may be explained by the pK_a of the ligands [5]. Imidazole ($pK_a = 7.1$) being more basic than pyrazole ($pK_a = 2.54$) and pyrazine ($pK_a = 0.65$) leads one to expect more covalency in its bonding and hence an increase in the oscillator strength.

Attempts have been made to relate the intensity and band shape of the hypersensitive transitions to the coordination environment of the lanthanide ion [13, 22]. The complexes give distinctively different band shapes in the solid and solution spectra (Fig. 1). This possibly reflects that the solvent molecule is entering the coordination sphere [13, 23] which changes the coordination geometry. One can also think that the change in the band shape in the two

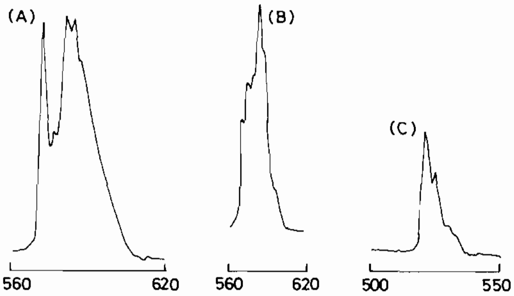

Fig. 1. (A) Spectra of the Nd^{3+} $^4I_{9/2} \rightarrow {}^4G_{5/2}$, $^2G_{7/2}$ transition of an ethanolic solution of $Nd(fod)_3pyz$. (B) Solid $Nd(fod)_3pyz$. (C) Spectrum of the Er^{3+} $^4I_{15/2} \rightarrow {}^2H_{11/2}$ transition of an ethanolic solution of $Er(fod)_3pyz$.

TABLE III. Covalency Parameters

Complexes	$\bar{\beta}$	$b^{1/2}$	δ
$Pr(fod)_3im$ [a]	0.978	0.101	2.083
$Pr(fod)_3pz$ [b]	0.983	0.093	1.746
$Pr(fod)_3pyz$ [c]	0.995 (0.996)[d]	0.050 (0.045)[d]	0.503 (0.402)[d]
$Nd(fod)_3im$ [a]	0.982	0.094	1.801
$Nd(fod)_3pz$ [b]	0.996	0.045	0.404
$Nd(fod)_3pyz$ [c]	0.996 (0.998) [d]	0.045 (0.032)[d]	0.404 (0.200)[d]
$Ho(fod)_3im$ [a]	0.987	0.080	1.280
$Ho(fod)_3pyz$ [e]	0.998 (0.999)[d]	0.032 (0.022)[d]	0.200 (0.100)[d]
$Er(fod)_3im$ [a]	0.991	0.068	0.929
$Er(fod)_3pz$ [b]	0.992	0.062	0.781
$Er(fod)_3pyz$ [c]	0.998	0.032	0.200

[a]Ref. 12. [b]Ref. 9. [c]This work. [d]Values in parentheses are those calculated from solid state spectra. [e]Ref. 23.

states could be due to replacement of pyrazine by ethanol. However, it has been found in NMR experiments that pyrazine does not dissociate in solution even in the presence of a strong donor like DMSO [16]. The band shapes of the hypersensitive transition of $Nd(fod)_3pyz$, $Nd(fod)_3im$ and $Nd(fod)_3pz$ in the solid state are not identical, indicating different geometrical arrangements about neodymium in the three complexes in the solid state. However, the band shapes in the three complexes are similar in solution. The appearance of similar band shapes is indicative of a similar coordination number. Thus, it is concluded that in solution these complexes take one solvent molecule and become eight-coordinate [13].

The nephelauxetic ratio has long been regarded as a measure of covalency [24] and this ratio has been correlated with the intensity of the hypersensitive transition [25]. The nephelauxetic effect in the spectra of these complexes is revealed by the expected red-shift of the spectral bands as compared to those of the respective aqua-ions. The nephelauxetic parameter ($\bar{\beta}$) [24], bonding parameter ($b^{1/2}$) [25] and covalency parameter (δ) [26] for the complexes of Pr(III), Nd(III), Ho(III) and Er(III) are given in Table III. Less than one value of $\bar{\beta}$ and positive values of $b^{1/2}$ and δ for these complexes show the covalent nature of the bonding between the metal and the ligands. The covalency parameters of the complexes show the following decreasing order of covalency: $Ln(fod)_3im > Ln(fod)_3pz > Ln(fod)_3pyz$. It follows that imidazole complexes are more covalent than pyrazole and pyrazine complexes. The higher values of the covalency parameters in solution for pyrazine complexes show that covalency is greater in solution than in the solid state.

References

1 C. K. Jorgensen and B. R. Judd, *Mol. Phys., 8,* 281 (1964).
2 S. F. Mason, R. D. Peacock and B. Stewart, *Mol. Phys., 30,* 1829 (1975).
3 W. F. Krupke, *Phys. Rev., 145,* 325 (1966).
4 R. D. Peacock, *Struct. Bonding (Berlin), 22,* 83 (1975).
5 D. F. Henrie, R. L. Fellows and G. R. Choppin, *Coord. Chem. Rev., 18,* 199 (1976).
6 S. F. Mason, *Struct. Bonding (Berlin), 39,* 43 (1980).
7 A. F. Kirby and R. A. Palmer, *Inorg. Chem., 20,* 1030, 4219 (1981).
8 K. Iftikhar, M. Sayeed and N. Ahmad, *Inorg. Chem., 21,* 80 (1982).
9 K. Iftikhar, M. Sayeed and N. Ahmad, *Bull. Chem. Soc. Jpn., 55,* 2258 (1982).
10 C. K. Jorgensen and R. Reisfeld, *J. Less-Common Met., 93,* 107 (1983).
11 E. M. Stephens, M. F. Reid and F. S. Richardson, *Inorg. Chem., 23,* 4611 (1984).
12 K. Iftikhar and N. Ahmad, *Polyhedron, 4,* 333 (1985).
13 D. G. Karraker, *Inorg. Chem., 6,* 1863 (1967); *7,* 473 (1968); *J. Inorg. Nucl. Chem., 33,* 3713 (1971).
14 A. Kothari and S. N. Misra, *Can. J. Chem., 61,* 1778 (1983).
15 K. B. Yatsimirskii and N. N. Davidenko, *Coord. Chem. Rev., 27,* 223 (1979).
16 K. Iftikhar, A. U. Malik and N. Ahmad, *J. Chem. Soc., Dalton Trans.,* 2547 (1985).
17 E. A. Boudreaux and W. Chen, *J. Inorg. Nucl. Chem., 39,* 595 (1977).
18 W. T. Camall, P. R. Fields and K. Rajnak, *J. Chem. Phys., 49,* 4412 (1968).
19 K. Nag and M. Chaudhery, *Inorg. Chem., 15,* 2291 (1976).
20 T. Isobe and S. Misumi, *Bull. Chem. Soc. Jpn., 47,* 281 (1974).
21 S. A. Davis and F. S. Richardson, *Inorg. Chem., 23,* 184 (1984).
22 G. R. Choppin, D. E. Henrie and K. Baijs, *Inorg. Chem., 5,* 1743 (1966).
23 K. Iftikhar and N. Ahmad, *Aust. J. Chem., 36,* 695 (1983).
24 C. K. Jorgensen, 'Modern Aspects of Ligand Field Theory', North-Holland, Amsterdam, 1971.
25 D. E. Henrie and G. R. Choppin, *J. Chem. Phys., 49,* 477 (1968).
26 S. P. Sinha, *Spectrochim. Acta, 22,* 57 (1966).
27 K. Iftikhar, *Inorg. Chim. Acta, 118,* L53 (1986).