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# Mixed-ligand lanthanide complexes—XI.† Absorption spectra and Hypersensitivity in the complexes of $Pr^{III}$, $Nd^{III}$, $Ho^{III}$ and $Er^{III}$ in non-aqueous solutions

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**Abstract**—Absorption spectra are reported for the mixed-ligand complexes of $Pr^{III}$, $Nd^{III}$, $Ho^{III}$, and $Er^{III}$ containing ligands having nitrogen donors, in four different solvents (pyridine, DMSO, DMF and methanol). The solvents differ with respect to their donor atoms. The oscillator strengths for the hypersensitive and non-hypersensitive transitions have been determined and variations in the oscillator strengths and band shapes with respect to solvent type is rationalized in terms of ligand (solvent) structures and ligand coordination properties. Pyridine has been found most effective in promoting 4*f*–4*f* intensity and is the strongest ligand in a nephelauxetic sense among the solvents studied. © 1997 Elsevier Science Ltd.

*Keywords*: lanthanide complexes; absorption spectra; hypersensitivity; praseodymium(III); neodymium(III); holmium(III); erbium(III).

Some specific transitions in the lanthanide spectra are enhanced by an order of magnitude, in going from an aquated system to systems with larger, bulkier ligands. This intensity change is taking place while the remaining transitions in the spectrum are not drastically increased. For such enhanced transitions the selection rule $|\Delta J| \leqslant 2$, $|\Delta L| \leqslant 2$ and $|\Delta S| = 0$ is consistently obeyed [1] and these are called 'hypersensitive'. Much of the interest in the phenomenon of hypersensitivity has centred about an effort to implicate a particular intensity promoting mechanism. Apart from certain symmetry requirements (i.e., those concerning electric dipole selection rules) some of the effects which have been considered include covalency, ligand basicity, the nephelauxetic effect, solvent properties and ligand polarizability [2]. The intensity of the absorption band is measured by its oscillator strength. The oscillator strength defined [3] as:

$$P = 4.31 \times 10^{-9} \frac{9\eta}{(\eta^2+2)^2} \int \varepsilon(\nu)\,d\nu \qquad (1)$$

may be obtained by evaluating $\int \varepsilon(\nu)\,d\nu$ over the transition region of interest. $\eta$ is refractive index of the medium.

In a recent paper [4] we have reported syntheses of the trivalent lanthanide complexes of the type $[Ln(phen)_3(SCN)_3(H_2O)_x]$ where Ln = La, and all lanthanides (except Gd, Tb and Tm); $x = 0$ for La, Nd, Pr, Sm and Eu and $x = 1$ for Dy, Ho, Er and Yb. We have investigated NMR spectra of the paramagnetic complexes of Pr, Nd, Sm, Eu and Yb. In continuation of our research programme we report here results of the study of optical spectra, in the visible region, of the complexes: $[Pr(phen)_3(SCN)_3]$, $[Nd(phen)_3(SCN)_3]$, $[Ho(phen)_3(SCN)_3(H_2O)]$ and $[Er(phen)_3(SCN)_3(H_2O)]$, where phen = 1,10-phenanthroline, in different medium. The praseodymium and neodymium complexes are nine-coordinate; and holmium and erbium complexes are ten-coordinate. The solvents used include methanol, dimethylsulfoxide (DMSO), pyridine and dimethylformamide (DMF). Methanol is a very weak donor which in some cases does coordinate and otherwise does not. DMSO is a very strong oxygen donor. DMF and pyridine are strong nitrogen donors. Our interest is to see the solvent effect on the spectral intensity and shapes of the hypersensitive as well as non-hypersensitive bands in these complexes.

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† Part X, ref. [4].

## EXPERIMENTAL

The synthesis and characterization of the complexes has been reported elsewhere [4]. The electronic spectra of the complexes were recorded in methanol, DMSO, pyridine and DMF on a Perkin–Elmer Lambda 3B spectrophotometer in the concentration range of $10^{-3}$ to $2 \times 10^{-2}$ M using 1 $cm^3$ stoppered quartz cells of 1 cm path length. The complexes have a poor solubility in methanol, and are dissolved by warming the solution using a hot air blower. After dissolution the complexes do not reappear. The absorption spectra of the solid compounds, in the cases of neodymium and erbium, were recorded on mulls that were prepared by grinding the dry solid and then regrinding into a paste with paraffin oil. This paste was spread on one of the walls of the quartz absorption cell; the proper thickness was determined by trial and error. A thin layer of paraffin was spread on the other cell and was placed in the reference position. We have calculated covalency parameters ($\bar{\beta}$, $b^{1/2}$ and $\delta$) using previously reported methods [5]. The oscillator strengths were obtained using eq. (1). All measurements were made at room temperature ($\sim 30°C$).

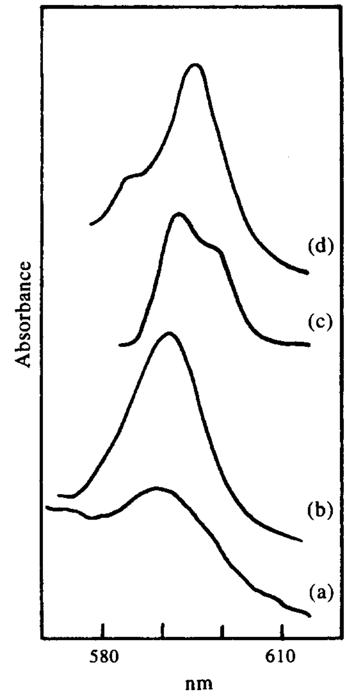

Fig. 1. $^3H_4 \rightarrow {}^1D_2$ transition of $[Pr(phen)_3(SCN)_3]$ in (a) methanol; (b) DMF; (c) pyridine and (d) DMSO.

## RESULTS AND DISCUSSION

### $[Pr(phen)_3(SCN)_3]$

The bands of praseodymium in the visible region are known to originate from symmetry-forbidden transitions from the ground state $^3H_4$ level to excited $J$ levels. The four transitions occur within the 400–600 nm spectral region. The oscillator strength of the four transitions ($^1D_2$, $^3P_0$, $^3P_1$, and $^3P_2$) of the complex in methanol, pyridine, dimethylsulfoxide (DMSO) and dimethylformamide (DMF) are given in Table 1. The oscillator strength of hydrated $PrCl_3$ in water are also collected in Table 1. Dissolving the complex in methanol, pyridine or DMF increases the oscillator strength of the $^3P_2$ transition (while there is no appreciable change in the oscillator strength in DMSO solution) relative to aqueous solution of hydrated $PrCl_3$ and decreases the oscillator strength of $^3P_1$ transition relative to the same standard. The pyridine solution of the complex shows a very marked intensification of $^3P_2$ peak. It is 42% more intense compared with praseodymium aqua-ion. This transition was found insensitive in the complex $[Pr(phen)_3(SCN)(H_2O)](SCN)_2$ [6]. The solution of the complex in any of the solvents fails to show any distinct spectral modifications for $^3P_2$, $^3P_1$ and $^3P_0$ transitions. Moreover, the $^1D_2$ transition gives distinctively different band shapes in different mediums (Fig. 1). The oscillator strength of this transition did not show appreciable variation going from one solvent system to the other. This transition was found [6] to be quite sensitive in the complex $[Pr(phen)_3(SCN)(H_2O)](SCN)_2$, both in respect to the value of the oscillator strength and band shape. The $^3P_2 \leftarrow {}^3H_4$ and $^1D_2 \leftarrow {}^3H_4$ transitions have been found to be sensitive to the change in the environment but since these do not obey the selection rules they are not considered hypersensitive. Some intensity enhancements are noted in a few praseodymium complexes but in most of the cases the oscillator strength is lower than for the aqua-ion [5,8–11].

### $[Nd(phen)_3(SCN)_3]$

The absorption spectra of the solutions of the neodymium complex were measured in the solvents mentioned (methanol, DMSO, pyridine and DMF). The absorption spectra of the solid compound was also measured. We also recorded the spectra of hydrated neodymium chloride in the four solvents. The absorption intensities, presented as oscillator strength, of the complex and hydrated chloride are collected in Table 2. The spectra of neodymium complex and neodymium chloride, in all solvents, have a very peculiar transition, ($^4G_{5/2}, {}^2G_{7/2} \leftarrow {}^4I_{9/2}$), near the middle of the visible region. The relatively high intensity of this transition and its unusual sensitivity to the chemical environment about the metal ion have lead to its classification as 'hypersensitive'; its behaviour is in sharp contrast to many other typically weak and consistently unvaried, normal *f–f* transitions [2,12]. The bands observed involved transitions from the $^4I_{9/2}$ ground state to the states $^4F_{3/2}$ (referred to hereafter as Nd–I); $^4F_{5/2}$, $^2H_{9/2}$, (Nd–II); $^4F_{7/2}$, $^4S_{3/2}$ (Nd–III); $^4F_{9/2}$ (Nd–IV); $^4G_{5/2}$, $^2G_{7/2}$ (Nd–V), $^2K_{13/2}$, $^4G_{7/2}$, $^4G_{9/2}$

Table 1. Oscillator strengths of [Pr(phen)$_3$(SCN)$_3$] in different solvents

| S′L′J′ | Spectral range[a] (cm$^{-1}$) | Pr$^{3+}$ Aqua-ion $10^6$P | P × $10^6$ | | | |
|---|---|---|---|---|---|---|
| | | | Methanol | DMSO | Pyridine | DMF |
| (ground state $^3H_4$) | | | | | | |
| $^1D_2$ | 16290–17180 | 3.12 | 3.22 | 2.57<br>(7.83)[b] | 2.92 | 4.36 |
| $^3P_0$ | 20200–21000 | 2.52 | 2.05 | 2.99<br>(3.40)[b] | 1.63 | 1.91 |
| $^3P_1$ | 21000–22100 | 6.60 | 3.40 | 4.25<br>(6.93)[b] | 5.65 | 5.55 |
| $^3P_2$ | 22100–23260 | 14.60 | 17.74 | 11.31<br>(11.35)[b] | 20.86 | 17.26 |

[a] The spectral ranges observed for the transitions vary from solvent to solvent, so the values listed here are only meant to indicate approximate location of the bands.

[b] The values given in parentheses are those for [Pr(phen)$_3$(SCN)(H$_2$O)](SCN)$_2$, ref. [6].

Table 2. Oscillator strengths of [Nd(phen)$_3$(SCN)$_3$] and NdCl$_3$ · 6H$_2$O in different solvents

| S′L′J′ | Spectral range[a] (cm$^{-1}$) | Nd$^{3+}$ Aqua-ion $10^6$P | $10^6$P Complex (NdCl$_3$ · 6H$_2$O)[b] | | | |
|---|---|---|---|---|---|---|
| | | | Methanol | DMSO | Pyridine | DMF |
| (ground state $^4I_{9/2}$) | | | | | | |
| $^4F_{3/2}$ | 11280–11770 | 1.26 | 1.32<br>(0.94) | 1.34<br>(1.09) | 2.20<br>(—) | 1.14<br>(1.52) |
| $^2H_{9/2}$, $^4F_{5/2}$ | 12060–12860 | 7.84 | 10.19<br>(7.28) | 9.27<br>(7.98)<br>[7.23][c] | 12.63<br>(2.46) | 11.71<br>(8.39) |
| $^4F_{7/2}$, $^4S_{3/2}$ | 12985–13815 | 7.90 | 11.43<br>(6.67) | 8.03<br>(7.52)<br>[8.38][c] | 13.47<br>(4.59) | 12.23<br>(7.80) |
| $^4F_{9/2}$ | 14370–15150 | 0.36 | 0.10<br>(0.43) | 0.57<br>(0.39) | 0.16<br>(—) | 0.86<br>(0.87) |
| $^4G_{5/2}$, $^2G_{7/2}$ | 16615–17850 | 8.60 | 24.82<br>(15.12) | 13.09<br>(13.59)<br>[40.39][c] | 29.28<br>(7.58) | 23.06<br>(19.17) |
| $^2K_{13/2}$, $^4G_{7/2}$, $^4G_{9/2}$ | 17590–20325 | 6.20 | 14.69<br>(4.81) | 9.68<br>(6.30)<br>[8.30][c] | 13.53<br>(—) | 10.30<br>(6.76) |
| $^2K_{15/2}$, $^2G_{9/2}$, $^2D_{3/2}$, $^2P_{3/2}$, $^4G_{11/2}$ | 20500–22220 | 1.09 | 3.51<br>(1.30) | 1.20<br>(1.79) | 2.52<br>(—) | 2.78<br>(1.34) |
| $^2D_{1/2}$, $^2D_{5/2}$ | 22750–23750 | 0.35 | 0.20<br>(—) | 0.42<br>(0.27) | 0.45<br>(—) | 0.99<br>(0.44) |

[a] The spectral ranges observed for the transitions vary from solvent to solvent, so the values listed here are only meant to indicate approximate location of the bands.

[b] The values given in parentheses are those observed for NdCl$_3$ · 6H$_2$O in the respective solvents.

[c] The values given in square brackets in the case of DMSO, are those for [Nd(phen)$_3$(SCN)(H$_2$O)](SCN)$_2$, ref. [6].

(Nd–VI); $^2K_{15/2}$, $^2G_{9/2}$, $^2D_{3/2}$, $^2P_{3/2}$, $^4G_{11/12}$ (Nd–VII) and $^2P_{1/2}$, $^2D_{5/2}$ (Nd–VIII). The changes in band shapes of the transitions Nd–I, Nd–II, Nd–III, Nd–V and Nd–VI as the solvent is changed are shown in Figs 2–5. In all five bands there is a distinct change in shape as the environment (solvent) around the neodymium ion is varied. The band shapes in the solid complex (Figs 2–5) do not resemble those of the bands in the complex in any of the four solvents. Despite variation in the appearance of the band shapes as solvent is changed, the oscillator strength of Nd–I and Nd–II transitions are nearly constant. The variation in the oscillator strengths of Nd–III, Nd–V and Nd–VI bands identifies them as resulting from hypersensitive transitions. The latter two transitions has been classified as hypersensitive [12].

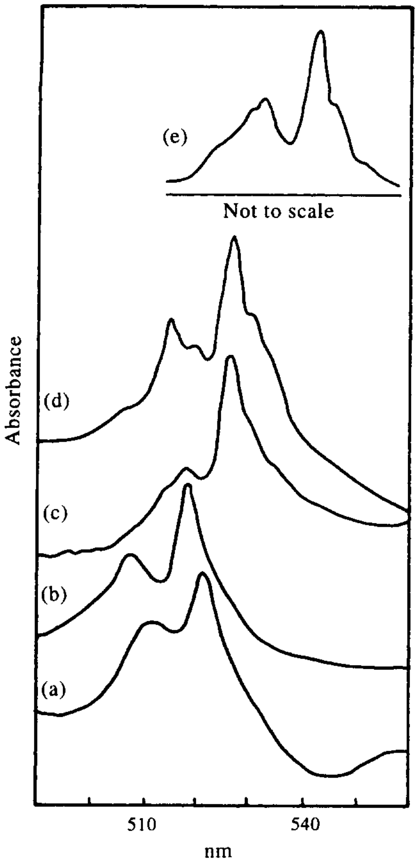

Fig. 2. $^4I_{9/2} \rightarrow {}^2K_{13/2}, {}^4G_{7/2}, {}^4G_{9/2}$ transitions of [Nd(phen)$_3$(SCN)$_3$] in (a) methanol; (b) DMF; (c) pyridine and (d) DMSO (e) solid complex.

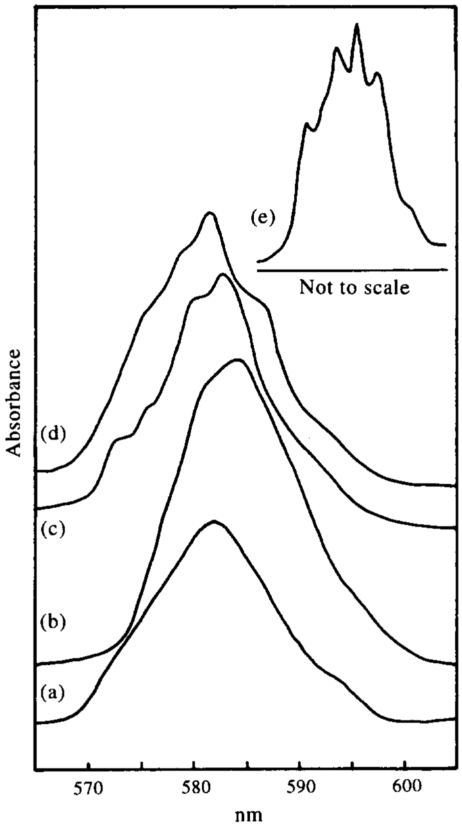

Fig. 3. $^4I_{9/2} \rightarrow {}^4G_{5/2}, {}^2G_{7/2}$ transition of [Nd(phen)$_3$(SCN)$_3$] in (a) methanol; (b) DMF; (c) DMSO (d) pyridine and (e) solid complex.

Among the Nd$^{III}$ transitions examined, the absorption intensity of the $^2G_{7/2}, {}^4G_{5/2} \leftarrow {}^4I_{9/2}$ (Nd–V) pair exhibits the greatest sensitivity to the solvent environment. These transitions centred around 580 nm have large $U^{(2)}$ and $U^{(4)}$ matrix elements [13]. These observations conform with previous studies in which this region has been classified as being hypersensitive [2,5,12]. This transition is most intense in pyridine followed by DMF and methanol and least intense in DMSO. The oscillator strengths of this transition in any of the solvents studied is larger than the oscillator strength of neodymium hydrated chloride in the respective solvent, except DMSO where the complex and the chloride both have same intensity. The results given in Table 2 show that the $^4S_{3/2}, {}^4F_{7/2} \leftarrow {}^4I_{9/2}$ (Nd–III) transition intensities also exhibit significant change in going from Nd$^{3+}$ (aqua) system to neodymium complex in pyridine, DMF and methanol. DMSO is again the exception where there is no change within experimental error. These transitions have small $U^{(2)}$ and $U^{(4)}$ matrix elements but a very large $U^{(6)}$ matrix element [13]. We note that the transitions $^2K_{13/2}, {}^4G_{9/2}, {}^4G_{7/2} \leftarrow {}^4I_{9/2}$ (Nd–VI) centred around 530 nm show significant intensity enhancement in going from Nd$^{3+}$ (aqua) system to certain neodymium complex/solvent systems (especially for methanol and pyridine). These transitions have small $U^{(2)}$ matrix element but significantly larger $U^{(4)}$ and $U^{(6)}$ matrix elements [13].

We note generally higher oscillator strength for the pyridine system *vs* those observed for other solvent systems indicating that pyridine is especially effective in promoting 4*f*–4*f* electric dipole intensity. This indicates association of pyridine with neodymium which changes the nature of the chemical environment around of the metal ion. To propose that solvent polarizability is contributing to an enhanced oscillator strength requires evidence of at least some degree of solvent coordination to establish this. We have sufficient evidences of pyridine coordination to neodymium without displacing any end of phen ligand. These include appearance of a resonance in the NMR spectra of pyridine solution of europium and ytterbium analogues of this complex for coordinated pyridine and inducement of large paramagnetic shifts in the resonance frequencies of phen without displaying any signal for free phen [4], and appearance of different band shapes in the solid state and in pyridine solution of the neodymium complex (Figs 2–5). Thus, the pyridine enters the coordination sphere of the metal ion and enhances its coordination number from

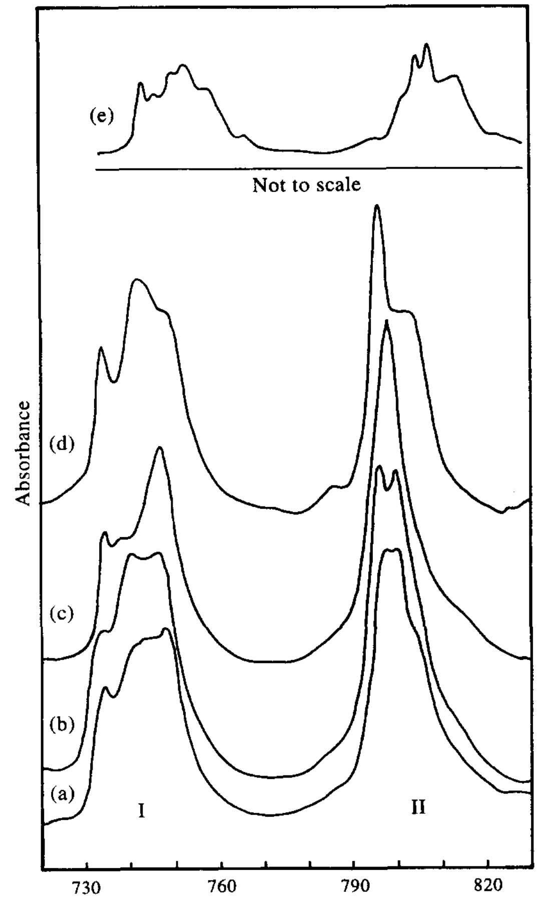

Fig. 4. $^4I_{9/2} \rightarrow$ (i) $^4F_{3/2}$, $^4F_{7/2}$ and (ii) $^2H_{9/2}$, $^4F_{5/2}$ transitions of $[Nd(phen)_3(SCN)_3]$ in (a) methanol; (b) DMF; (c) DMSO; (d) pyridine and (e) solid complex.

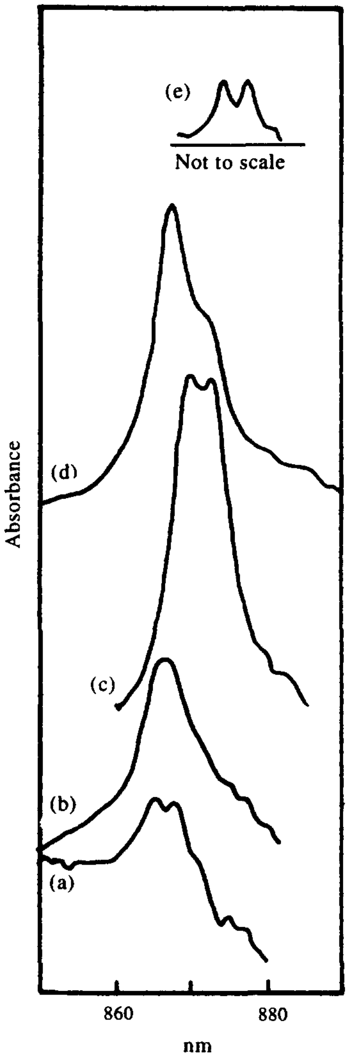

Fig. 5. $^4I_{9/2} \rightarrow {}^4F_{3/2}$ transition of $[Nd(phen)_3(SCN)_3]$ in (a) methanol; (b) DMF; (c) pyridine; (d) DMSO and (e) solid complex.

9 to 10. The higher values of the oscillator strength of the bands in pyridine is due to polarizability of this solvent which is contributing to an enhanced oscillator strength [2]. The oscillator strength of the transition are nearly similar in methanol and DMF. The band shapes of this transition are also similar in shape. This is attributed to the coordination of DMF through its oxygen. DMF generally binds *via* oxygen, not nitrogen, when it coordinates to hard acids like the lanthanides. Most interesting is the comparison between values obtained in DMF and DMSO since both enter the coordination sphere by replacing one thiocyanate group and the complex in both the solvents behaves as 1 : 1 electrolyte [4]. This may be attributed to the different structure of the two, presence of nitrogen in DMF and how the donor groups interact with the electrons of the lanthanide ion. We compare the oscillator strengths of the transitions of the present neodymium complex with those observed for $[Nd(phen)_3(SCN)(H_2O)](SCN)_2$ [6] in DMSO. The oscillator strength of the non-hypersensitive transitions do not show appreciable change. Moreover, the hypersensitive transitions have lower values in the present complex. The oscillator strength of the Nd–V transition is much lower than the complex reported earlier [6] (Table 2). The $[Nd(phen)_3(SCN)(H_2O)](SCN)_2$ in DMSO was argued to be nine-coordinated by accepting one solvent molecule. The present complex is also nine-coordinated and one DMSO molecule enters the coordination sphere by replacing one SCN unit [4]. This large difference in the oscillator strength may be explained by invoking the difference in symmetry of the two complexes. The low molecular symmetry is responsible for unusually higher oscillator strength in $[Nd(phen)_3(SCN)(H_2O)](SCN)_2$. Both the complexes give distinctively different band shapes in the solid state and in DMSO solution. Given a symmetry effect [1,14] on the hypersensitive transitions, the occurrence of different spectra for different symmetry is a predictable result. Finally we compare the values of the oscillator strength of the present complex and hydrated neodymium chloride in meth-

anol with those reported [15] for the neodymium perchlorate and; neodymium perchlorate and phen in different mole ratios in methanol. The values observed for hydrated $NdCl_3$ in methanol for Nd–III Nd–V and Nd–VI transitions are lower than those reported for anhydrous or hydrated $Nd(ClO_4)_3$ in methanol [15]. The higher values in case of perchlorate is because of coordination of bidentate perchlorate ion to the neodymium ion. The coordination of $ClO_4^-$ has been shown by Bunzli *et al.* [16,17] for lanthanide perchlorates in solution. However, the oscillator strength of these transitions, in the complex, are higher than for the 1 : 4 neodymium perchlorate (hydrated or anhydrous) phen ratios in this solvent. The higher values are due to the presence of thiocyanate ion in the inner coordination sphere, in addition to phen, which would lead us to expect a greater deal of covalency in its bonding compared with $[Nd(phen)_4(solvent)_{x-2}]$ [15] and a corresponding increase in the oscillator strength.

### $[Ho(phen)_3(SCN)_3(H_2O)]$

Transitions were observed from $^5I_8$ ground state to the $^5F_5$ (Ho–I), $^5S_2$, $^5F_4$ (Ho–II), $^5F_3$ (Ho–III), $^5F_2$, (Ho–IV), $^3K_8$ (Ho–V), $^5G_6$ (Ho–VI) and $^5G_5$, $^3G_5$ (Ho–VII) excited states. The oscillator strengths of the transitions are listed in Table 3. Of special note are the significantly larger values of the oscillator strength observed within the 22,500–22,800 $cm^{-1}$ region *vs* those observed within the other six regions. This reflects the strongly hypersensitive behaviour of the $^5G_6 \leftarrow {}^5I_8$ transition in holmium(III) systems [2,12]. We also note the generally higher *P* values observed for the pyridine system *vs* those observed for the other solvent systems, indicating that the pyridine solvent is especially effective in promoting 4*f*–4*f* intensity. Among the $Ho^{III}$ transitions examined in this study the absorption intensity of $^5G_6 \leftarrow {}^5I_8$ exhibits the greatest sensitivity to the ligand (solvent) environment. This transition has a very large $U^{(2)}$ matrix element as well as a relatively large $U^{(4)}$ matrix element [13]. The oscillator strength of this transition increases almost 7-, 4- and 3-fold on going from $Ho^{3+}$ aqua system to the complex in pyridine, DMF and methanol systems, respectively. Previous studies have also shown the intensity of this transition to be hypersensitive [2,5,12]. The pyridine *vs* DMF and DMSO *vs* methanol comparisons for holmium complex are qualitatively identical with those discussed for neodymium complex. The comparison of oscillator strength for Ho–VI transition in the present complex with that of the $[Ho(phen)_4]$ [8] (Ho perchlorate and phen in 1 : 4 ratio) in methanol reveals that the values are similar in magnitude ($P = 17.5 \times 10^6$ for $[Ho(phen)_4]$ in methanol). We believe this species is 10-coordinate in solution, if one $ClO_4^-$ ion enters the coordination sphere of $Ho^{3+}$. The tetrakis(phen) complexes of the lanthanide perchlorates, $Ln(phen)_4(ClO_4)_3$, have been isolated [19,20]. The oscillator strength of Ho–VI transition in the present complex in DMSO is much lower than that reported for $[Ho(phen)_3(SCN)(H_2O)](SCN)_2$ [6] in this solvent. The lower value of the oscillator strength, as discussed for the neodymium complex, is due to different symmetry of the complexes accepting the premise that oscillator strength of the hypersensitive transitions depend on the symmetry of the field around the ion [1,14].

The band shapes of the Ho–VI transition of the complex in different solvents are shown in Fig. 6. The band shapes of this transition in methanol and pyridine are similar in shape which is due to association of solvent molecules. This has been shown for $[Yb(phen)_3(SCN)_3(H_2O)]$ that pyridine enters the

Table 3. Oscillator strengths of $[Ho(phen)_3(SCN)_3(H_2O)]$ in different solvents]

| S′L′J′ | Spectral range[a] ($cm^{-1}$) | $Ho^{3+}$ Aqua-ion $10^6P$ | $P \times 10^6$ | | | |
|---|---|---|---|---|---|---|
| | | | Methanol | DMSO | Pyridine | DMF |
| (ground state $^5I_8$) | | | | | | |
| $^5F_5$ | 15050–15850 | 3.35 | 0.59 | 3.54<br>(5.20)[b] | 3.48 | 3.02 |
| $^5S_2$, $^5F_4$ | 18050–19050 | 5.11 | 2.69 | 4.82<br>(6.80)[b] | 6.88 | 6.36 |
| $^5F_3$ | 20100–21000 | 3.09 | 1.19 | 1.04 | 2.15 | 1.49 |
| $^5F_2$ | 20800–21450 | 0.24 | 0.50 | 0.22 | 1.20 | 0.42 |
| $^3K_8$ | 21200–21750 | 0.15 | 0.19 | 0.19 | 1.10 | 0.26 |
| $^5G_6$ | 21500–22800 | 5.64 | 14.27 | 11.52<br>(38.38)[b] | 32.20 | 19.84 |
| $^5G_5$, $^3G_5$ | 23400–24510 | 2.93 | 1.72 | 3.51<br>(3.43)[b] | 3.63 | 3.73 |

[a] The spectral ranges observed for the transitions vary from solvent to solvent, so the values listed here are only meant to indicate approximate locations of the bands.

[b] The values given in parentheses in the case of DMSO, are those for $[Ho(phen)_3(SCN)(H_2O)](SCN)_2$, ref. [6].

Table 4. Oscillator strengths of $[Er(phen)_3(SCN)_3(H_2O)]$ in different solvents

| S′L′J′ | Spectral range[a] ($cm^{-1}$) | $Er^{3+}$ Aqua-ion $10^6P$ | $P \times 10^6$ Methanol | DMSO | Pyridine | DMF |
|---|---|---|---|---|---|---|
| (ground state $^4I_{15/2}$) | | | | | | |
| $^4I_{9/2}$ | 12300–12660 | 0.13 | — | 1.23<br>(1.08)* | — | 1.13 |
| $^4F_{9/2}$ | 14700–15625 | 1.94 | 0.92 | 2.70<br>(4.05)[b] | 1.34 | 2.86 |
| $^4S_{3/2}$ | 17790–18700 | 0.41 | 0.19 | 0.42<br>(3.86)[b] | 0.77 | 0.77 |
| $^2H_{11/12}$ | 18700–19770 | 2.91 | 9.14 | 3.74<br>(46.00)[b] | 12.98 | 8.27 |
| $^4F_{7/2}$ | 19840–21100 | 2.22 | 2.16 | 2.03<br>(3.59)[b] | 3.03 | 2.96 |
| $^4F_{5/2}$, $^4F_{3/2}$ | 21550–22730 | 1.10 | 1.09 | 0.89 | 1.44 | 1.74 |
| $(^2G, ^4F)_{9/2}$ | 23800–25660 | 0.51 | 0.47 | — | 1.23 | 1.00 |
| $^4G_{11/2}$ | 25640–27550 | 5.90 | 17.65 | 6.44<br>(31.85)[b] | 16.01 | 15.26 |
| $^4G_{9/2}$ | 27770–28330 | 0.94 | — | 0.58 | — | — |

[a] The spectral ranges observed for the transitions vary from solvent to solvent, so the values listed here are only meant to indicate approximate location of the bands.

[b] The values given in parentheses in the case of DMSO are those for $[Er(phen)_3(SCN)(H_2O)](SCN)_2$, ref. [6].

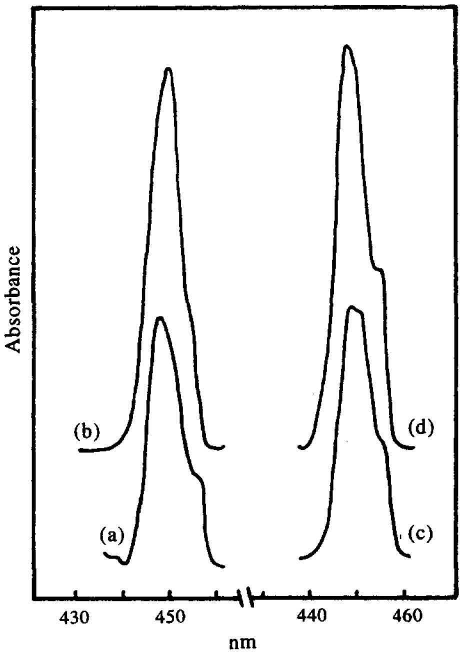

Fig. 6. $^5I_8 \rightarrow {}^5G_6$ transition of $[Ho(phen)_3(SCN)_3(H_2O)]$ in (a) methanol; (b) DMSO; (c) DMF and (d) pyridine.

coordination sphere by replacing water molecule [4]. Methanol may also enter in the first coordination sphere since it is a stronger donor compared with water [21]. Small differences in the band shapes between methanol, pyridine and DMF as solvents may be attributed to differences in how DMF *vs* pyridine or methanol groups interact with the *f*-electrons of the holmium ion.

### $[Er(phen)_3(SCN)_3(H_2O)]$

Transitions were observed from the $^4I_{15/2}$ ground state to the states $^4I_{9/2}$ (Er–I), $^4F_{9/2}$ (Er–II), $^4S_{3/2}$ (Er–III), $^2H_{11/12}$ (Er–IV), $^4F_{7/2}$ (Er–V), ($^4F_{5/2}$,$^4F_{3/2}$) (Er–VI), $(^2G, ^4F)_{9/2}$ (Er–VII), $^4G_{11/12}$ (Er–VIII), $^4G_{9/2}$ (Er–IX). The absorption intensities, presented as the oscillator strength are given in Table 4. From the results given in Table 4 the drastic increase in the oscillator strengths of the two transitions namely $^2H_{11/2} \leftarrow {}^4I_{15/2}$ (Er–IV) and $^4G_{11/12} \leftarrow {}^4I_{15/2}$ (Er–VIII) centred at 520 nm and 380 nm, respectively from the values found for the aquated $Er^{3+}$ ion, are very evident. This reflects their strongly hypersensitive behaviour and conforms to previous studies [2,12] where these have been classified as hypersensitive. Of the two transitions the Er–VIII band is more intense. This transition is nearly twice as intense as the Er–IV band (except in pyridine where the Er–VIII band is partially obscured by strong solvent absorption). Both the transitions have large $U^{(2)}$ and $U^{(4)}$ matrix elements. Moreover, the values are larger for Er–VIII transition. Besides intensification we also note considerable splitting of the two levels (Figs 7 and 8) in different solvents. As noticed in the case of the neodymium complex, the band shapes of the hypersensitive transition (Er–IV) of this complex are similar in methanol and DMF. The oscillator strengths are also not much different in magnitude (Methanol, 9.14; DMF 8.27) in the two solvents. From Table 4 we see that the oscillator strength of the hypersensitive transitions is largest in pyridine as compared to other solvent systems. The reason is similar to that discussed for $Nd^{III}$ and $Ho^{III}$ complexes.

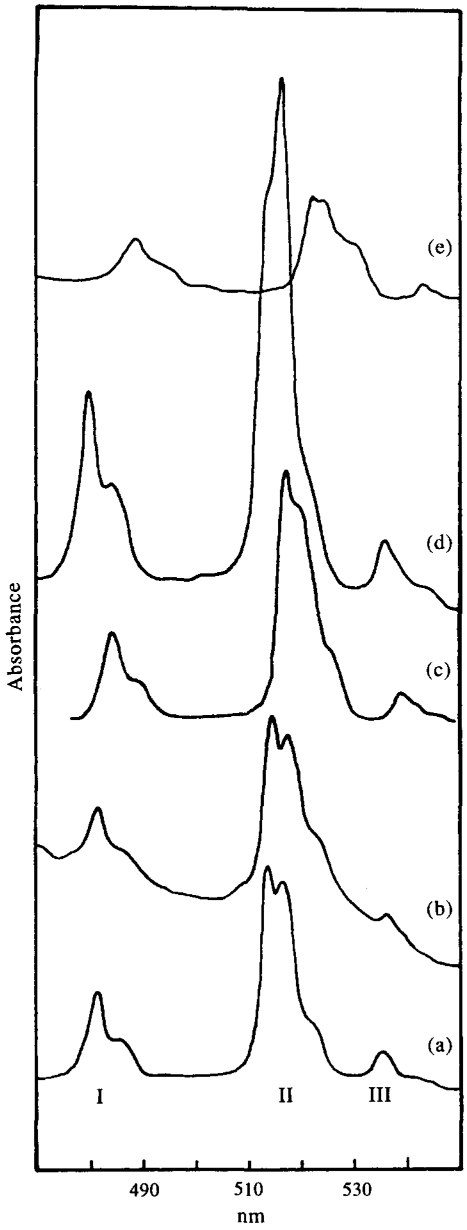

Fig. 7. $^4I_{15/2} \rightarrow$ (i) $^4F_{7/2}$, (ii) $^2H_{11/12}$ and (iii) $^4S_{3/2}$ transitions of [Er(phen)$_3$(SCN)$_3$(H$_2$O)] in (a) DMF; (b) methanol; (c) pyridine; (d) DMSO and (e) solid complex.

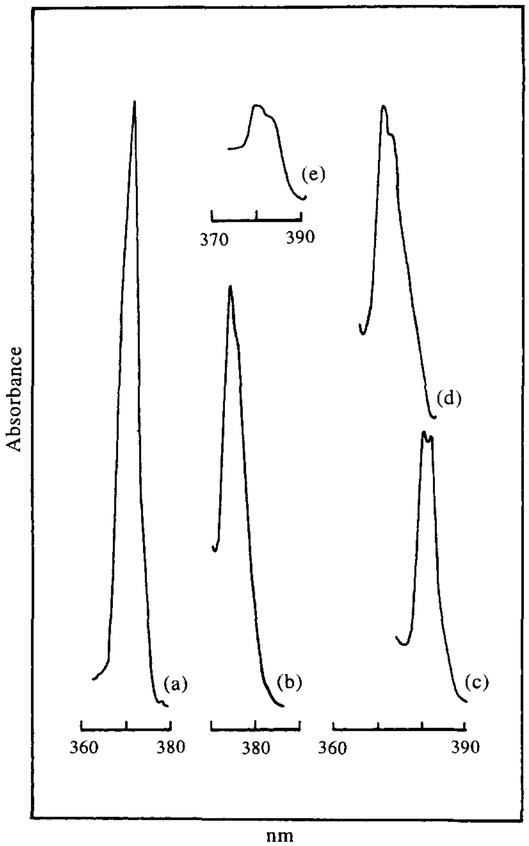

Fig. 8. $^4I_{15/2} \rightarrow {}^4G_{11/2}$ transition of [Er(phen)$_3$(SCN)$_3$(H$_2$O)] in (a) DMSO; (b) pyridine; (c) DMF; (d) methanol and (e) solid complex.

Another point of interest in the spectra of these complexes is the shift of spectral bands towards lower energy as compared to the position in the respective aqua-ions. These red shifts have been called the nephelauxetic effect and have long been regarded as a measure of covalency [22]. The nephelauxetic effect in the spectra of lanthanide complexes is analogous to that observed in the spectra of *d*-transition element complexes. This is of course, a smaller effect than that observed for *d*-orbitals in transition metals, because of *d*-orbitals are about the same distance from the nucleus as the orbitals used for bond formation, where as the *f*-orbitals lie closer to the nucleus. Moreover, it cannot be quantitatively interpreted by neglecting the covalent interaction of the lanthanide ions with the neighbouring ligands [22]. The nephelauxetic parameter ($\bar{\beta}$), bonding parameter ($b^{1/2}$) [23] and covalency parameter ($\delta$) [24] for the complexes have been calculated from the spectra and are collected in Table 5. The nephelauxetic parameter is less than one and bonding and covalency parameters are positive for these complexes, showing some covalent nature in the bonding between the metal and the ligands. The values of $b^{1/2}$ and $\delta$ are highest for pyridine followed by DMSO. It follows that pyridine is the strongest ligand in a nephelauxetic sense and the complexes in this solvent show largest covalency.

The main objectives of this study were to (1) obtain intensity parameters of the complexes of Nd$^{III}$ and the structurally similar Ho$^{III}$ and Er$^{III}$ complexes in different solvents and (2) demonstrate the sensitivity of the oscillator strength and band shape between the complexes in different environment. The results obtained for the complexes of Nd$^{III}$, Ho$^{III}$ and Er$^{III}$ clearly show that among the solvents studied pyridine is most effective in promoting 4*f*–4*f* intensity. This is related to the higher covalency of pyridine which would lead us to expect a greater deal of covalency in its bonding since it could result in some changes in

Table 5. Covalency Parameters

| Complexes/ | | Parameters | |
|---|---|---|---|
| solvents | $\bar{\beta}$ | $b^{1/2}$ | $\delta$ |
| $[\mathrm{Pr(phen)_3(SCN)_3}]$ | | | |
| Pyridine | 0.9856 | 0.08 | 1.46 |
| DMSO | 0.9903 | 0.07 | 0.98 |
| DMF | 0.9948 | 0.05 | 0.52 |
| Methanol | 0.9960 | 0.04 | 0.40 |
| $[\mathrm{Nd(phen)_3(SCN)_3}]$ | | | |
| Pyridine | 0.9849 | 0.09 | 1.53 |
| DMSO | 0.9863 | 0.08 | 1.39 |
| DMF | 0.9879 | 0.08 | 1.23 |
| Methanol | 0.9879 | 0.08 | 1.22 |
| $[\mathrm{Ho(phen)_3(SCN)_3(H_2O)}]$ | | | |
| Pyridine | 0.9904 | 0.07 | 0.97 |
| DMSO | 0.9965 | 0.04 | 0.35 |
| DMF | 0.9981 | 0.03 | 0.19 |
| Methanol | 0.9969 | 0.04 | 0.31 |
| $[\mathrm{Er(phen)_3(SCN)_3(H_2O)}]$ | | | |
| Pyridine | 0.9885 | 0.08 | 1.16 |
| DMSO | 0.9916 | 0.06 | 0.85 |
| DMF | 0.9958 | 0.05 | 0.42 |
| Methanol | 0.9971 | 0.04 | 0.29 |

the extent of overlap. This is in accordance with the mechanism proposed by Choppin *et al.* [12] and receive support from the observation that the hypersensitivity depends upon the polarizability of the ligand [2].

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## REFERENCES

1. Jorgensen, C. K. and Judd, B. R., *Molec. Phys.*, 1964, **8,** 281.
2. Peacock, R. D., *Struct. Bonding*, 1975, **22,** 83.
3. Carnall, W. T., Fields, P. R. and Wybowrne, B. G., *J. Chem. Phys.*, 1965, **42,** 3797.
4. Khan, A. A., Saxena, A. K. and Iftikhar, K., *Polyhedron*, 1997, **16,** 4143.
5. Iftikhar, K., Sayeed, M. and Ahmad, N., *Inorg. Chem.*, 1982, **21,** 80.
6. Khan, A. A. and Iftikhar, K., *Polyhedron*, 1994, **23,** 3199.
7. Peacock, R. D., *J. Chem. Soc.* (*A*), 1971, 2028; *Chem. Phys. Letters*, 1970, **7,** 187.
8. Tandon, S. P. and Mehta, P. C., *J. Chem. Phys.*, 1970, **52,** 4313.
9. Iftikhar, K., Sayeed, M. and Ahmad, N., *Bull. Chem. Soc. Jpn*, 1982, **55,** 2258.
10. Iftikhar, K., *Inorg. Chim. Acta*, 1987, **128,** 273.
11. Iftikhar, K., *Inorg. Chim. Acta*, 1987, **129,** 261.
12. Henrie, D. E., Fellows, R. L. and Choppin, G. R., *Coord. Chem. Rev.*, 1976, **18,** 199.
13. Carnall, W. T., Fields, P. R. and Rajnak, K., *J. Chem. Phys.*, 1968, **49,** 4424.
14. Judd, B. R., *J. Chem. Phys.*, 1966, **4,** 839.
15. Bukietynska, K. and Thuy, P. N., *Inorg. Chim. Acta*, 1987, **132,** 21.
16. Bunzli, J. C. G., Yersin, J. R. and Mabillard, C., *Inorg. Chem.*, 1982, **21,** 1471; Bunzli, J. C. G. and Mabillard, C., *Inorg. Chem.*, 1986, **25,** 2750.
17. Bunzli, J. C. G. and Kasparek, V., *Inorg. Chim. Acta*, 1991, **182,** 101.
18. Bukietynska, K. and Thuy, P. N., *Polyhedron*, 1988, **7,** 641.
19. Krishnamurthy, S. S. and Soundararajan, S., *Z. Anorg. Allg. Chem.*, 1966, **348,** 309.
20. Grandey, R. C. and Moeller, T., *J. Inorg. Nucl. Chem.*, 1970, **32** 333.
21. Karaker, D. G., *J. Inorg. Nucl. Chem.*, 1971, **33,** 3713.
22. Jorgensen, C. K., *Modern Aspects of Ligand Field Theory*, North-Holland, Amsterdam (1971).
23. Henrie, D. E. and Choppin, G. R., *J. Chem. Phys.*, 1968, **49,** 477.
24. Sinha, S. P., *Spectrochim. Acta.*, 1966, **22,** 57.