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Hypersensitivity in the 4f–4f absorption spectra of tris (acetylacetonato) neodymium(III) complexes with imidazole and pyrazole in non-aqueous solutions. Effect of environment on hypersensitive transitions

Anees A. Ansari, Rashid Ilmi, K. Iftikhar*

Department of Chemistry, Jamia Millia Islamia, New Delhi 110025, India

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ABSTRACT

The optical absorption spectra of $[\text{Nd}(\text{acac})_3(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$, $[\text{Nd}(\text{acac})_3(\text{im})_2]$ and $[\text{Nd}(\text{acac})_3(\text{pz})_2]$ (where acac is the anion of acetylacetonate, im is imidazole and pz is pyrazole) complexes in the visible region have been analyzed. The transition ${}^4\text{G}_{5/2} \leftarrow {}^4\text{I}_{9/2}$ located near the middle of the visible region ($17,500 \text{ cm}^{-1}$) is hypersensitive. Its behavior is in sharp contrast to many other typically weak and consistently unvaried, normal 4f–4f transitions. It is overlapped by a less intense transition ${}^2\text{G}_{7/2} \leftarrow {}^4\text{I}_{9/2}$. The band shapes of the hypersensitive transition show remarkable changes on passing from aqueous solution to various non-aqueous solutions, which is the result of changes in the environment about the Nd(III) ion in the various solutions and suggests coordination of a solvent molecules. Pyridine has been found especially effective in promoting 4f–4f electric-dipole intensity. The DMSO invades the complexes and replaces the water molecules and heterocyclic amines from the coordination sphere. Two DMSO molecules coordinate and the complexes acquire similar structure, $[\text{Nd}(\text{acac})_3(\text{DMSO})_2]$ in solution. The oscillator strength and the band shape of the hypersensitive transition of all the complexes remains the same in this solvent. The IR spectra and the NMR spectra of the complexes have also discussed.

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1. Introduction

The lanthanide β -diketonate complexes have become of increasing significance in the last few years due to their specific spectroscopic and magnetic properties [1–3]. These are, therefore, increasingly used in lasers [4], labels for protein and amino acids [5,6], light emitting diodes and display devices [7,8], biological assays [9,10], magnetically addressable liquid crystals [11,12] and imaging applications [1–4]. The lanthanide tris(β -diketonates) [13–16] are known as efficient labels for immunoassay and their adducts with 1,10-phenanthroline (phen) and 2,2'-bipyridyl (bpy) [17–20] promise extensive photophysical applications [21–23]. The Ln^{3+} substituted materials for thin film generation has been introduced [24–27]. The majority of spectroscopic studies deal with Ln (III) compounds, which are characterized by electronic transitions within the 4f shell.

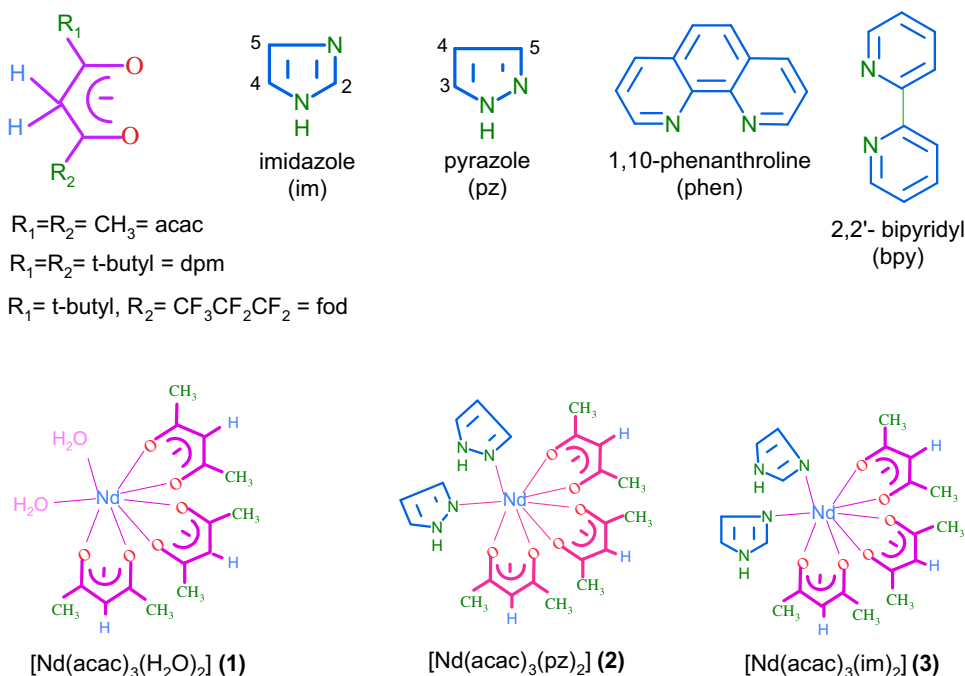
In our previous papers we have investigated the electronic spectra of 1,10-phenanthroline (phen) [20,28–32] and 2,2'-bipyridyl (bpy) [20,31–34] complexes of trivalent praseodymium, neodymium, holmium and erbium where the counter anions were

thiocyanate, chloride and diketonate, and have reported the effect of (i) the counter anions (monodentate or bidentate), (ii) the number of coordinated phen or bpy and (iii) the solvents on the oscillator strength and hypersensitivity of lanthanide spectra. In recent papers [30,35] the NMR and electronic spectra of $[\text{Nd}(\text{hfaa})_3\text{-phen}]$, $[\text{Nd}(\text{acac})_3\text{phen}]$ and $[\text{Nd}(\text{acac})_3\text{bpy}]$ where hfaa is the anion of 1,1,1,5,5,5-hexafluoro-2,4-pentanedione and acac is the anion of 2,4-pentanedione in a series of non-aqueous solvents have been reported. It has been found in the case of acetylacetonate complexes that phen is a stronger ligand for the lighter lanthanides (Pr and Nd) while bpy is a strongly coordinating ligand for heavier lanthanides [35–37]. It is interesting then, to compare the behavior of bidentate (bpy and phen) and monodentate (imidazole and pyrazole) heterocyclic amines and the influence of the solvents on the electronic spectra of the lanthanides. In the present paper we extend our investigations to the optical absorption results, in the visible region, obtained on the complexes $[\text{Nd}(\text{acac})_3(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$, $[\text{Nd}(\text{acac})_3(\text{im})_2]$ and $[\text{Nd}(\text{acac})_3(\text{pz})_2]$, where im is imidazole and pz is pyrazole, in a series of non-aqueous solvents (methanol, ethanol, isopropanol, chloroform, acetonitrile, pyridine, nitrobenzene and dimethylsulfoxide). All the complexes contain three acetylacetonate units. The chelate is triply hydrated eight-coordinate in which two of the water molecules are coordinated to the neodymium, while the third is lattice held whereas its complex with im and pz are anhydrous eight-coordinate (Scheme 1).

* Corresponding author. Tel.: +91 11 26837297;

fax: +91 11 26980229/26982489.

E-mail address: kiftikhar.ch@jmi.ac.in (K. Iftikhar).



Scheme 1. Structure of the compounds and the ligands with abbreviations.

2. Experimental

2.1. Materials

Neodymium oxide (Leico Chem., U.S.A.), imidazole and pyrazole (Fluka) and acetylacetone (E. Merck, England) were used as received. The solvents used were either AR or spectroscopic grade.

2.2. Synthesis

The chelate, $[Nd(acac)_3(H_2O)_2] \cdot H_2O$ was synthesized by the literature method [13], while the complexes of $[Nd(acac)_3(H_2O)_2] \cdot H_2O$ with im or pz were synthesized by mixing hot ethanol solutions of hydrated $[Nd(acac)_3(H_2O)_2] \cdot H_2O$ and the heterocyclic amine in 1:1 molar ratio on the hot plate. The reaction mixture was kept for half an hour on the hot plate with continuous stirring. It was removed from the hot plate and kept at room temperature for slow evaporation of the solvent. The crystals thus, obtained were washed with cold carbon tetrachloride and dried *in vacuo* over P_4O_{10} .

2.3. Methods

The complexes were subjected to micro analyses for their carbon, hydrogen and nitrogen contents while metal content of the complexes were estimated by complexometric titrations using xylenol orange as the indicator. The results are in excellent agreement with the theoretically calculated values (% obs. C 43.00, H 5.03, N 9.61 and Nd 24.80; calcd. C 43.67, H 5.03, N 9.70, Nd 24.96 for $C_{21}H_{29}O_6N_4Nd$, $[Nd(acac)_3(im)_2]$ and % obs. C 43.42, H 5.30, N 9.61 and Nd 24.2 for $C_{21}H_{29}O_6N_4Nd$, $[Nd(acac)_3(pz)_2]$; the calculated values for the pz complex are equal to those of imidazole complex.) The molar conductance of 10^{-3} M methanol solution of the complexes was measured on the Orion conductivity meter model 122. The IR spectra were recorded on a Perkin-Elmer spectrum R X I FTIR Spectrophotometer as KBr disc in the range $4000\text{--}400\text{ cm}^{-1}$. The electronic spectra of the

complexes were recorded on a Perkin-Elmer Lambda-40 spectrophotometer, with the sample contained in 1 cm^3 stoppered quartz cell of 1 cm path length, in the range $200\text{--}1100\text{ nm}$, in the concentration range between 5×10^{-3} to 2×10^{-2} M. The solvents used, in this study, were methanol, ethanol, isopropanol, chloroform, acetonitrile, pyridine, nitrobenzene and dimethylsulfoxide (DMSO). The NMR spectra of the diamagnetic complexes were recorded on a Bruker DRX 300 MHz NMR machine in $CDCl_3$.

The intensity of the absorption band is measured by its oscillator strength P_{exp} , which is directly proportional to the area under the absorption band and can be evaluated from the expression [38].

$$P = 4.31 \times 10^{-9} \left[\frac{9\eta}{(\eta^2 + 2)^2} \right] \int \varepsilon(\nu) d\nu \quad (1)$$

Where ν is the energy of the transition in cm^{-1} , ε is the molar extinction coefficient and η is the refractive index of the medium. The oscillator strength of the transitions were determined by evaluating the area under the peak.

On complexation the radial integrals of the valence orbitals of a metal ion decrease. This phenomenon is known as nephelauxetic effect [39] and may be regarded as measure of covalency in a complex. The nephelauxetic ratio is generally measured as the ratio of the wave number of f-f transitions in the spectra of the complex and lanthanide aqua-ions [39] and is given by the following relation:

$$\bar{\beta} = \nu_{avg.(\text{complex})} / \nu_{avg.(\text{aqua-ion})} \quad (2)$$

where ν_{avg} is the average energy of the transitions are energies of the transition, in wave numbers, in the complexes and in the aqua-ion.

The bonding parameter, $b^{1/2}$, which measures the amount of 4f-ligand mixing can be calculated from the relation [40]

$$b^{1/2} = [1/2(1 - \bar{\beta})]^{1/2} \quad (3)$$

Sinha's covalency parameter, δ , which is also measure of degree of covalency, is calculated using the relation [41].

$$\delta = [(1 - \bar{\beta}) / \bar{\beta}] \times 100 \quad (4)$$

3. Results and discussion

The chelate $[\text{Nd}(\text{acac})_3(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ is soluble in all common organic solvents and imidazole is also soluble in common organic solvents (except CCl_4 , benzene and hexane). The adduct of imidazole, $[\text{Nd}(\text{acac})_3(\text{im})_2]$, with the chelate is soluble only in polar solvents. Both imidazole and the chelate dissolve in chloroform but the complex is insoluble in this solvent. This establishes the fact that imidazole has coordinated to $[\text{Nd}(\text{acac})_3(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ and maintain its integrity in the adduct. The pyrazole complex is soluble in all common solvents. The adducts $[\text{Nd}(\text{acac})_3(\text{im})_2]$ and $[\text{Nd}(\text{acac})_3(\text{pz})_2]$ synthesized, are eight-coordinated and are new and have not been reported so far. It should be pointed out that we wanted to synthesize seven-coordinate complexes of the type $[\text{Nd}(\text{acac})_3\text{im}]$ and $[\text{Nd}(\text{acac})_3\text{pz}]$ similar to the reported seven-coordinate complexes of $\text{Ln}(\text{dpm})_3$ [19,42] and $\text{Ln}(\text{fod})_3$ [43,44]. However, the reaction of $[\text{Nd}(\text{acac})_3(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ with imidazole and pyrazole yielded eight-coordinated complexes of the general composition $[\text{Ln}(\text{acac})_3(\text{L})_2]$ (where L is imidazole or pyrazole). The complexes, under study are crystalline solids with sharp melting points. The melting point of $[\text{Nd}(\text{acac})_3(\text{im})_2]$ (170 °C) is higher than the $[\text{Nd}(\text{acac})_3(\text{pz})_2]$ (125 °C). The melting points are generally lower than those of $[\text{Nd}(\text{acac})_3\text{phen}]$, $[\text{Nd}(\text{acac})_3\text{bpy}]$, $[\text{Nd}(\text{dpm})_3\text{im}]$, $[\text{Nd}(\text{fod})_3\text{im}]$, $[\text{Nd}(\text{dpm})_3\text{pz}]$ and $[\text{Nd}(\text{fod})_3\text{pz}]$ [19,43,44]. These are quite stable and can be handled without any effect of air or moisture. This behavior is quite similar to those reported for imidazole and pyrazole complexes of $\text{Ln}(\text{fod})_3$ and $\text{Ln}(\text{dpm})_3$. These complexes are non-electrolytes as revealed by their molar conductance in methanol ($2\text{--}4 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$).

3.1. IR spectra

The IR spectra of imidazole and pyrazole complexes show presence of coordinated heterocyclic amines. The N–H frequency appearing in free imidazole and pyrazole as a very broad band between $3150\text{--}2200$ and $3100\text{--}2800 \text{ cm}^{-1}$, respectively, because of intermolecular hydrogen bonding appears between $3150\text{--}3200 \text{ cm}^{-1}$ in the complex of imidazole and between $3400\text{--}3200 \text{ cm}^{-1}$ in the pyrazole complex. The observed shift of the N–H band suggests a decrease in hydrogen bonding and interaction of ring nitrogen with the neodymium. A weak and sharp band appearing in free pyrazole at 4035 cm^{-1} has disappeared in the adducts, upon coordination. Most of the imidazole and pyrazole absorptions could not be observed since these are obscured by the strong chelate absorptions. Several new bands are noted in the adducts, which are absent in the spectra of the chelate. This together with the shift in the N–H band has been taken as evidence that the heterocyclic amines have coordinated to the chelate. The absorption peaks, characteristics of acetylacetone, occurring in the chelate [45] are also present in the adducts with their positions shifted.

3.2. NMR spectra

The NMR spectrum of the lanthanum complex, $[\text{La}(\text{acac})_3(\text{im})_2]$ has been recorded in methanol- d_4 mixed with CDCl_3 . The complex was dissolved in minimum quantity of methanol- d_4 ($\sim 0.20 \text{ ml}$) and minimum volume required in the NMR tube was attained by adding CDCl_3 . Lanthanum(III) is diamagnetic and therefore the small chemical shifts observed is because of

coordination of imidazole to the lanthanum chelate. The NMR signals of acac moiety of the adduct appear at 1.87 ppm (δ) and 7.03 ppm (δ) for methyl and methine protons, respectively in the intensity ratio of 1: 6. The NMR spectrum of $[\text{La}(\text{acac})_3(\text{H}_2\text{O})]$ is reported [46] to display signals at 5.10 and 1.75 ppm (δ) for methine and methyl protons, respectively. Both the signals of methyl and methine proton have been deshielded and appear at lower fields, in the mixed-ligand complex, as compared to that of $[\text{La}(\text{acac})_3(\text{H}_2\text{O})]$ [46]. Other signals have been assigned to those of the imidazole coordinated to the chelate. Free imidazole gives [43] three signals in the intensity ratio of 1: 1: 2 at 12.53, 7.78, and 7.18 ppm (δ) for N–H, H-2 and (H-4 and H-5) protons, respectively. The signals of imidazole, in the complex, are found to shift to lower as well as higher fields. The H-2 proton appearing at 7.42 ppm (δ) is shielded whereas H-4 and H-5 protons show resonance at 7.62 ppm (δ) due to deshielding. This shielding and deshielding of imidazole protons obviously suggests that imidazole has coordinated to the chelate and does not dissociate in solution. The microanalysis result, which suggests formation of 1: 2, $\text{La}(\text{acac})_3$: im complex, is also supported by the NMR results. The area under the peak is in the following ratio: 2: 4: 3: 18 for H-2, (H-4 and H-5), methine and methyl protons, respectively. This supports the fact that only one species exists in solution and two imidazole molecules have coordinated to the lanthanum chelate. It is important to mention that the signal for N–H proton (H-3) is not seen in the spectrum of the complex, although $\nu_{\text{N-H}}$ frequency has been noted in the IR spectrum. Probably this proton is exchanged by D atom of the solvents, due to its labile nature. Report is available in the literature where this proton resonance was not observed [43]. The NMR spectrum of $[\text{La}(\text{acac})_3(\text{pz})_2]$ recorded in CDCl_3 also shows coordinated nature of two pyrazole molecules. Thus, on the basis of the results of microanalysis, metal estimation, molar conductance, IR and NMR spectra, the complexes have been assigned the formulae, $[\text{Nd}(\text{acac})_3(\text{im})_2]$ and $[\text{Nd}(\text{acac})_3(\text{pz})_2]$.

3.3. Electronic spectra

Practically all the lanthanide 4f–4f absorption bands are attributed to electric-dipole transitions, although in the strict sense such transitions are parity forbidden since these occur between the state within the same configuration. The intensities of the lanthanide transitions, which result in bands with $P \sim 10^{-6}$, indeed reflect highly forbidden character compared to allowed transitions (such as $f \rightarrow d$) where $P \sim 1$. The observed intensities could be accounted for by assuming a small mixing of the higher lying opposite parity configuration into the f^n states via the odd terms. The neodymium (III) is a useful ion for UV–vis absorption studies since it has a very peculiar transition $^4G_{5/2} \leftarrow ^4I_{9/2}$ around 585 nm in the absorption spectrum. The absorption spectra of the pyrazole complex were obtained over $25,000\text{--}10526 \text{ cm}^{-1}$ (400–950 nm) spectral region in methanol, ethanol, isopropanol, chloroform, acetonitrile, pyridine, nitrobenzene and dimethylsulfoxide while spectra of the imidazole complex were obtained in acetonitrile, isopropanol, pyridine and dimethylsulfoxide (since this complex has solubility in limited solvents). The absorption intensities, presented as oscillator strength, of the chelate, $[\text{Nd}(\text{acac})_3(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$, and hydrated NdCl_3 in water are presented in Table 1, and of the complexes are collected in Tables 2 and 3. The spectra of the complexes contain nine multiplet-to-multiplet transitions originating from ground state to the excited states. They are $^4F_{3/2}$ (Nd-I); $^2H_{9/2}$, $^4F_{5/2}$ (Nd-II); $^4S_{3/2}$, $^4F_{7/2}$ (Nd-III); $^4F_{9/2}$ (Nd-IV); $^2H_{11/2}$ (Nd-V); $^4G_{5/2}$, $^2G_{7/2}$ (Nd-VI); $^2K_{13/2}$, $^4G_{7/2}$, $^4G_{9/2}$ (Nd-VII); $^2K_{15/2}$, $^2G_{9/2}$, $^2(D,P)_{3/2}$, $^4G_{11/2}$ (Nd-VIII); and $^2P_{1/2}$, $^2D_{5/2}$ (Nd-IX) $\leftarrow ^4I_{9/2}$. These transitions are given in order of increasing frequency (energy). Of the above transitions $^4F_{9/2}$ and $^2H_{11/2}$ are

Table 1
Oscillator strengths of $[\text{Nd}(\text{acac})_3(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ in different solvents.

S'L'J' (ground state $^4I_{9/2}$)	Transitions ^a	Spectral range (cm^{-1})	Nd^{3+} aqua-ion 10^6 P	Solvents ^b							
				A	B	C	D	E	M	N	O
$^4F_{3/2}$	Nd-I	11,299–11,682	1.26	1.46	1.70	1.90	1.33	1.91	1.30	0.95	2.17
$^4F_{5/2}, ^2H_{9/2}$	Nd-II	12,048–12,820	7.84	6.74	6.21	7.26	7.85	6.61	6.61	4.05	6.07
$^4S_{3/2}, ^4F_{7/2}$	Nd-III	12,987–13,698	7.90	5.93	5.63	6.90	7.07	5.98	6.15	3.60	5.14
$^4F_{9/2}$	Nd-IV	14,204–14,836	0.36	0.50	0.32	0.43	0.48	0.13	0.50	0.30	–
$^2H_{11/2}$	Nd-V	15,286–16,129	0.16	0.17	0.18	0.06	0.15	–	0.07	–	–
$^4G_{5/2}, ^2G_{7/2}$	Nd-V I	16,556–17,667	8.60	51.66	46.01	31.47	41.53	43.67	47.45	21.62	41.50
$^4G_{9/2}, ^4G_{7/2}, ^2K_{13/2}$	Nd-VII	17,985–20,000	6.20	9.93	8.92	8.01	9.01	7.61	10.25	–	–
$^2G_{9/2}, ^4G_{11/2}, ^2K_{15/2}, ^2(D,P)_{3/2}$	Nd-VIII	20,661–22,075	1.09	1.26	0.83	1.20	1.11	0.10	0.20	–	–
$^2P_{1/2}, ^2D_{5/2}$	Nd-IX	22,988–23,640	0.35	0.16	0.15	0.14	0.20	–	0.15	–	–

^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 A=methanol; B=ethanol; C=isopropanol; D=chloroform; E=acetonitrile; M=pyridine; N = nitrobenzene; O=Dimethylsulfoxide.

Table 2
Oscillator strengths of $[\text{Nd}(\text{acac})_3(\text{im})_2]$ in different solvents.

S'L'J' (ground state $^4I_{9/2}$)	Transitions ^{a,b,c}	Solvents ^d			
		A	B	C	D
$^4F_{3/2}$	Nd-I	0.85	0.86	1.30	1.04
$^4F_{5/2}, ^2H_{9/2}$	Nd-II	5.95	5.97	5.60	5.35
$^2S_{3/2}, ^4F_{7/2}$	Nd-III	5.41	5.35	5.02	5.27
$^4F_{9/2}$	Nd-IV	1.35	0.30	0.32	0.70
$^2H_{11/2}$	Nd-V	0.10	0.12	–	0.11
$^4G_{5/2}, ^2G_{7/2}$	Nd-VI	19.41	22.94	43.90	42.01
$^4G_{9/2}, ^4G_{7/2}, ^2K_{13/2}$	Nd-VII	5.41	5.22	–	7.41
$^2G_{9/2}, ^4G_{11/2}, ^2(D,P)_{3/2}, ^2K_{15/2}$	Nd-VIII	1.30	0.40	–	1.21
$^2P_{1/2}, ^2D_{5/2}$	Nd-IX	0.10	0.20	–	0.16

^a For spectral ranges, see Table 1.

^b For transition region, see Table 1.

^c The oscillator strength of Nd^{3+} aqua-ion are given in Table 1.

^d A=acetonitrile; B=isopropanol; C=dimethylsulfoxide; D=pyridine.

very weak. Among these transitions the most intense is Nd-VI (8.60×10^{-6}) followed by $^4S_{3/2}, ^4F_{7/2}$ (7.96×10^{-6}); $^2H_{9/2}, ^4F_{5/2}$ (7.84×10^{-6}) and $^2K_{13/2}, ^4G_{7/2}, ^4G_{9/2}$ (6.20×10^{-6}), where the values in parentheses are the oscillator strength determined for hydrated NdCl_3 in aqueous solution.

3.3.1. Hypersensitive transition

The transition $^4G_{5/2} \leftarrow ^4I_{9/2}$ (Nd-VI) located near the middle of the visible region ($17,500 \text{ cm}^{-1}$), which follows the selection rules, $|\Delta J| \leq 2$, $|\Delta L| \leq 2$ and $\Delta S=0$, is hypersensitive. It is overlapped by a less intense transition $^2G_{7/2} \leftarrow ^4I_{9/2}$. This transition has very peculiar feature with regard to its relative intensity and unusual sensitivity to the ligand environment about the neodymium ion. It has large $U^{(2)}$ and $U^{(4)}$ matrix elements [47], and conforms with previous studies, in which this has been classified as being hypersensitive [28–30,48,49]. Its behavior is in sharp contrast to many other typically weak and consistently unvaried, normal 4f–4f transitions. The oscillator strength of this transition for the $[\text{Nd}(\text{acac})_3(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ (Table 1) as well as its complexes with imidazole and pyrazole (Table 4) in any of the solvent employed is larger than the oscillator strength of Nd^{3+} aqua-ion. The larger value of the oscillator strength of the transition indicates considerable strong covalency of Nd-ligand bonds.

3.3.2. $[\text{Nd}(\text{acac})_3(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$

This complex is eight-coordinate and chloroform is non-coordinating solvent. Therefore, the band shape of the transitions of this complex in chloroform would be used as standard i.e. the band

shape of the eight-coordinate complex arising in a non-coordinating solvent. The band shape of the hypersensitive transition $^4G_{5/2}, ^2G_{7/2} \leftarrow ^4I_{9/2}$ of the complex in chloroform (Fig. 1) is similar to those of eight-coordinate complexes $[\text{Nd}(\text{acac})_3\text{phen}]$ and $[\text{Nd}(\text{acac})_3\text{bpy}]$ [35] and many eight-coordinate complexes investigated in this laboratory [30,50–52]. This transition is most intense in pyridine (Table 1) with the band shape similar to the typical eight-coordinate β -diketone complexes (Fig. 2). This conforms the previous studies from our laboratory [28,29,33,35] where it has been shown that pyridine is especially effective in promoting 4f–4f electric-dipole intensity. It is reasonable to associate this increase with ligand polarization effect such as those proposed by Mason, Peacock and Stewart in their theory of hypersensitivity [53]. It reflects that two pyridine molecules coordinate by replacing both water molecules present in $[\text{Nd}(\text{acac})_3(\text{H}_2\text{O})_2]$ giving the species $[\text{Nd}(\text{acac})_3(\text{py})_2]$ in solution. The spectra of the complex in chloroform, acetonitrile and nitrobenzene are identical in shape with similar pattern of crystal field splitting (Fig. 1). However, the oscillator strength in nitrobenzene (21.62×10^{-6}) is much lower than those in chloroform (41.53×10^{-6}) and acetonitrile (43.67×10^{-6}). It has been observed that the oscillator strength of the transition of many lanthanide complexes in aromatic solvents (benzene and nitrobenzene) decrease drastically [31,32]. The decreased intensity could be accounted for by assuming that the orientation of the ring current of the benzene ring makes the field around the neodymium(III) more symmetric. Similarity in the oscillator strength in acetonitrile and chloroform and identical shape of spectral bands in chloroform, nitrobenzene and acetonitrile favor that acetonitrile and nitrobenzene are non-coordinating for this system (Fig. 1).

The band shape of the hypersensitive transition (Fig. 3) in three alcohols (isopropanol, ethanol and methanol) are similar among themselves as well as with the band shape in chloroform and that of band shape of typical eight-coordinate β -diketone neodymium (III) complexes [30,35,50–52]. It indicates that species in alcohols is eight-coordinate. The three alcohols are coordinating by replacing both the water molecules present in $[\text{Nd}(\text{acac})_3(\text{H}_2\text{O})_2]$ to give the species $[\text{Nd}(\text{acac})_3(\text{alcohol})_2]$ in solution. The alcohols are stronger donor than water and could replace the water molecules from the inner-coordination sphere. The lower value of the oscillator strength in isopropanol indicates that the species $[\text{Nd}(\text{acac})_3(\text{isopropanol})_2]$ is more symmetric in solution resulting in less asymmetric field around Nd (III).

3.3.3. $[\text{Nd}(\text{acac})_3(\text{pz})_2]$

The bands shape of the hypersensitive transition of this complex in chloroform and nitrobenzene (Fig. 4) are similar to that of typical of eight-coordinate β -diketone complexes of neodymium

Table 3
Oscillator strengths of $[\text{Nd}(\text{acac})_3(\text{pz})_2]$ in different solvents.

S'L'J' (ground state ⁴ I _{9/2})	Transitions ^{a,b,c}	Solvents ^d							
		A	B	C	D	E	M	N	O
⁴ F _{3/2}	Nd-I	1.47	1.27	1.99	2.0	1.27	2.86	1.95	1.63
⁴ F _{5/2} , ² H _{9/2}	Nd-II	5.80	4.17	7.25	7.76	6.08	7.46	7.46	6.73
² S _{3/2} , ⁴ F _{7/2}	Nd-III	5.70	4.08	7.35	7.14	6.0	6.71	6.96	6.11
⁴ F _{9/2}	Nd-IV	0.36	0.50	0.48	0.61	0.25	1.37	0.57	0.32
² H _{11/2}	Nd-V	0.04	0.03	0.06	0.14	0.04	–	0.07	–
⁴ G _{5/2} , ² G _{7/2}	Nd-VI	23.46	21.30	20.30	36.62	17.80	47.68	37.20	43.63
⁴ G _{9/2} , ⁴ G _{7/2} , ² K _{13/2}	Nd-VII	5.4	4.27	5.76	8.50	5.40	7.25	–	–
² G _{9/2} , ⁴ G _{11/2} , ² (D,P) _{3/2} , ² K _{15/2}	Nd-VIII	0.48	0.40	1.60	0.18	–	–	–	–
² P _{1/2} , ² D _{5/2}	Nd-IX	0.12	0.10	0.15		–	–	–	–

^a For spectral ranges, see Table 1.

^b For transition region, see Table 1.

^c The oscillator strength of Nd^{3+} aqua-ion are given in Table 1.

^d A=methanol; B=ethanol; C=isopropanol; D=chloroform; E=acetonitrile; M=pyridine; N=nitrobenzene; O=Dimethylsulfoxide.

Table 4
Oscillator strengths of hypersensitive transitions of Nd(III) complexes in different solvents.

S'L'J' (ground state $^4I_{9/2}$)	Transitions ^a	Complexes	Solvents ^b							
			A	B	C	D	E	M	N	O
$^4G_{5/2}, ^2G_{7/2}$	Nd-VI	$[\text{Nd}(\text{acac})_3(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$	51.66	46.01	31.47	41.53	43.67	47.45	21.62	41.50
		$[\text{Nd}(\text{acac})_3\text{phen}]$	32.77	47.43	41.32	43.63	40.60	47.42	32.85	40.20
		$[\text{Nd}(\text{acac})_3\text{bpy}]$	25.16	39.68	28.95	32.80	13.50	39.57	25.27	41.00
		$[\text{Nd}(\text{acac})_3(\text{im})_2]$	–	–	22.94	–	19.41	42.01	–	43.89
		$[\text{Nd}(\text{acac})_3(\text{pz})_2]$	23.46	45.00	20.30	36.62	17.80	47.68	37.20	43.63
$^4G_{9/2}, ^4G_{7/2}, ^2K_{13/2}$	Nd-VII	$[\text{Nd}(\text{acac})_3(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$	9.93	8.92	8.01	9.01	7.61	10.25	–	–
		$[\text{Nd}(\text{acac})_3\text{phen}]$	–	9.71	8.01	8.72	9.15	9.25	–	–
		$[\text{Nd}(\text{acac})_3\text{bpy}]$	5.68	6.12	5.40	7.27	2.74	6.62	–	–
		$[\text{Nd}(\text{acac})_3(\text{im})_2]$	–	–	5.22	–	–	–	–	–
		$[\text{Nd}(\text{acac})_3(\text{pz})_2]$	5.40	7.98	5.08	8.50	4.80	6.40	–	–

^a For spectral ranges, transition regions and the oscillator strength of Nd^{3+} aqua-ion see Table 1.

^b A=methanol; B=ethanol; C=isopropanol; D=chloroform; E=acetonitrile; M=pyridine; N=nitrobenzene; O=Dimethylsulfoxide.

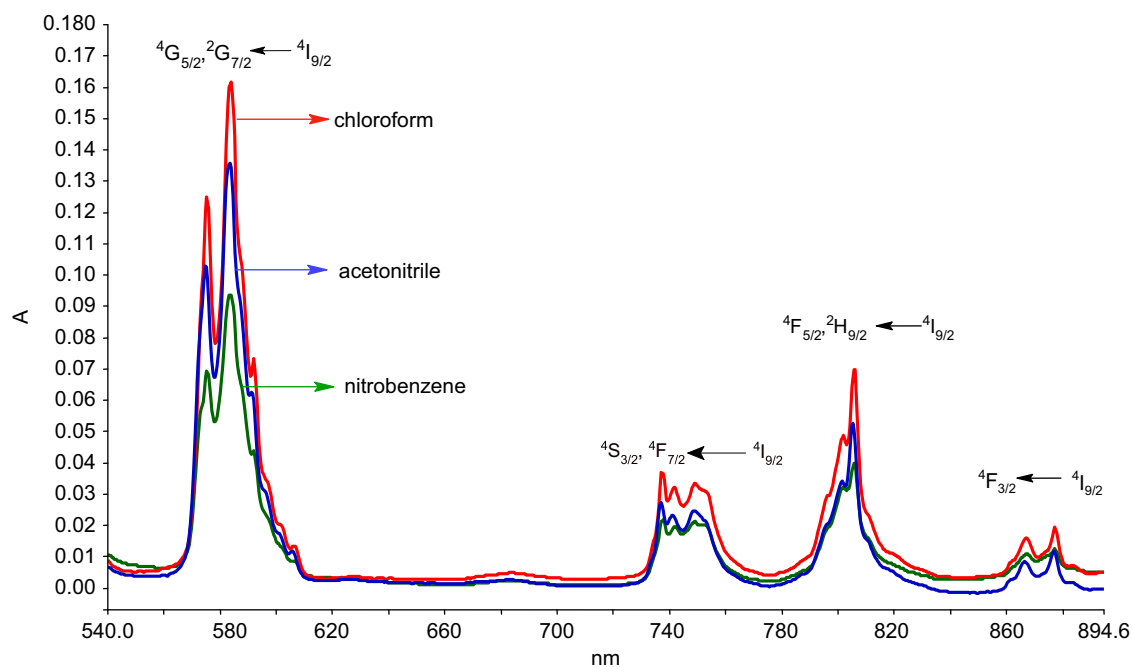


Fig. 1. 4f–4f absorption spectra of $[\text{Nd}(\text{acac})_3(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ in chloroform (red), nitrobenzene (green) and acetonitrile (blue). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

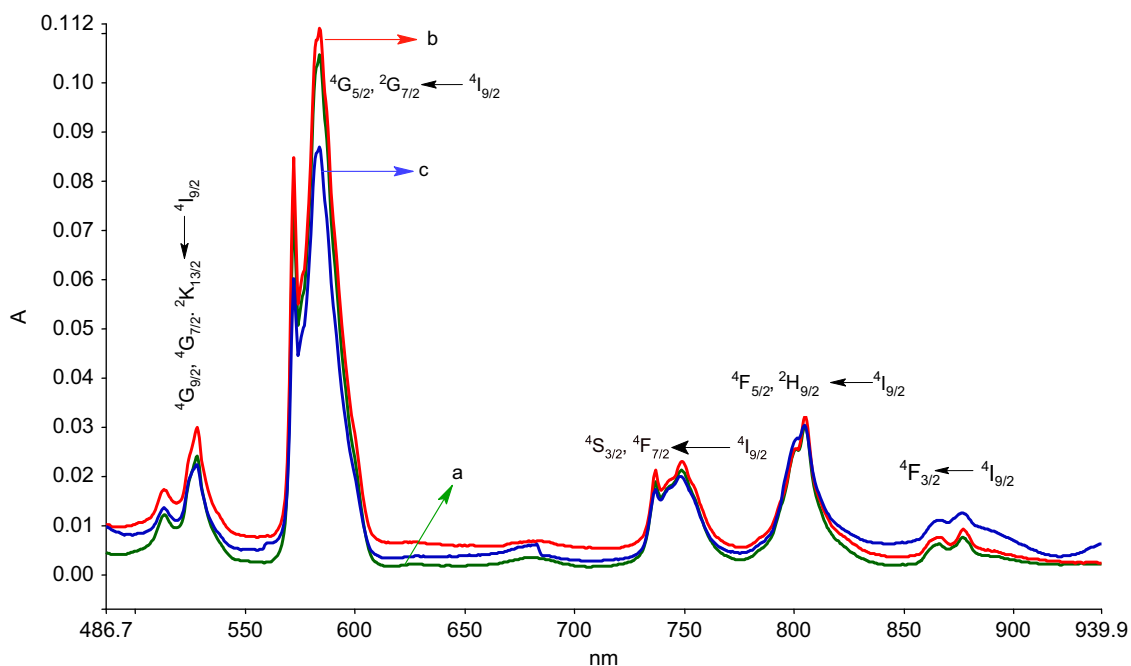


Fig. 2. 4f–4f absorption spectra of (a) $[\text{Nd}(\text{acac})_3(\text{im})_2]$ (green), (b) $[\text{Nd}(\text{acac})_3(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ (red), and (c) $[\text{Nd}(\text{acac})_3(\text{pz})_2]$ (blue) in pyridine. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

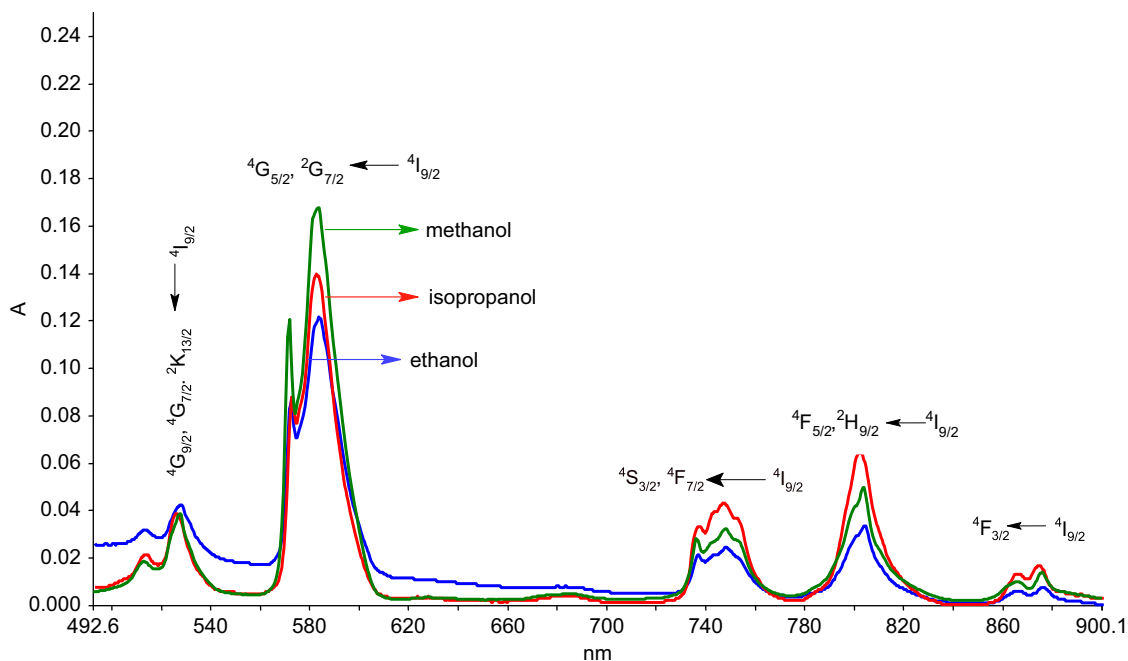


Fig. 3. 4f–4f absorption spectra of $[\text{Nd}(\text{acac})_3(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ in methanol (green), isopropanol (red) and ethanol (blue). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

(III) and confirms its eight-coordinate geometry in non-coordinating chloroform and nitrobenzene. It is interesting to note that the oscillator strength is also similar in the two solvents, which is in contrast to the observation noted in the case of $[\text{Nd}(\text{acac})_3(\text{H}_2\text{O})_2]$. The largest intensification of the hypersensitive band of this complex is noted in pyridine, which is in agreement with the observation noted for the $[\text{Nd}(\text{acac})_3(\text{H}_2\text{O})_2]$. The reason for the largest intensification and consequently higher oscillator strength in pyridine is due to the greater polarizability of this solvent. Furthermore the band shape (Fig. 2) is similar to the

eight-coordinate complex in non-coordinating solvent. This indicates that pyridine being more basic ($\text{p}K_a=5.21$) and stronger donor than the pyrazole ($\text{p}K_a=2.52$) replaces the two pyrazole units from the complex and forms $[\text{Nd}(\text{acac})_3(\text{py})_2]$ species in solution. Pyridine coordination has been demonstrated in many lanthanide complexes [28,29,31,32,35,54]. Dissolving the $[\text{Nd}(\text{acac})_3(\text{pz})_2]$ in any of the alcohols (methanol, ethanol or isopropanol) results in striking changes in the shape of the absorption band due to hypersensitive transition (Fig. 5). The band shape in alcohols is distinctly different from the band shape in non-coordinating

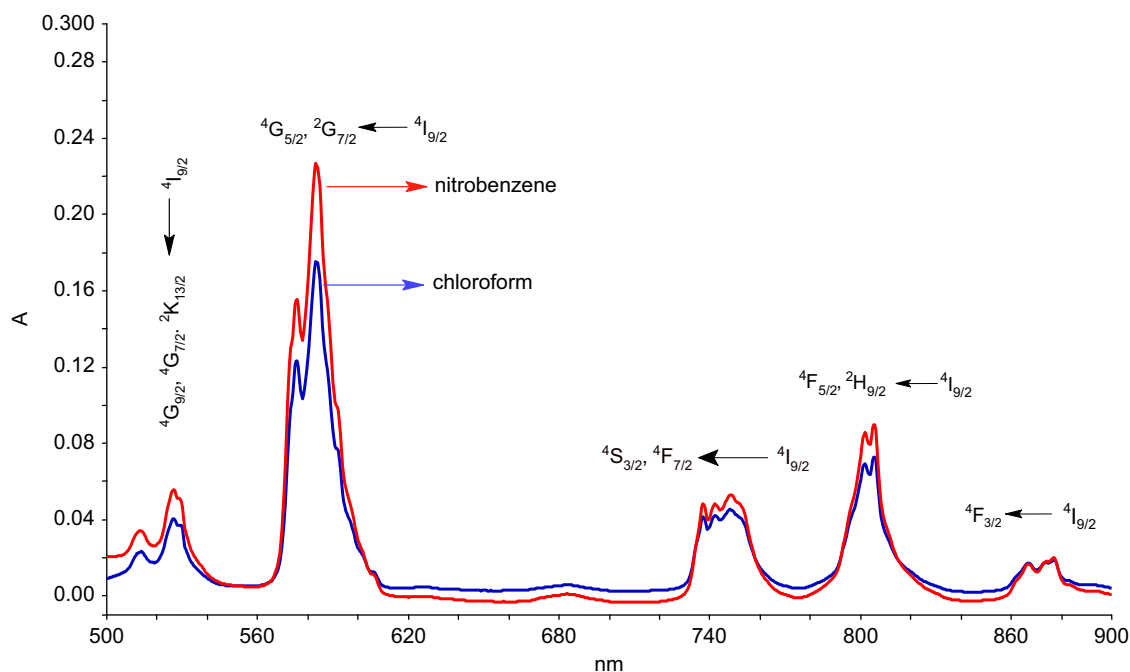


Fig. 4. 4f–4f absorption spectra of $[\text{Nd}(\text{acac})_3(\text{pz})_2]$ in nitrobenzene (red) and chloroform (blue). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

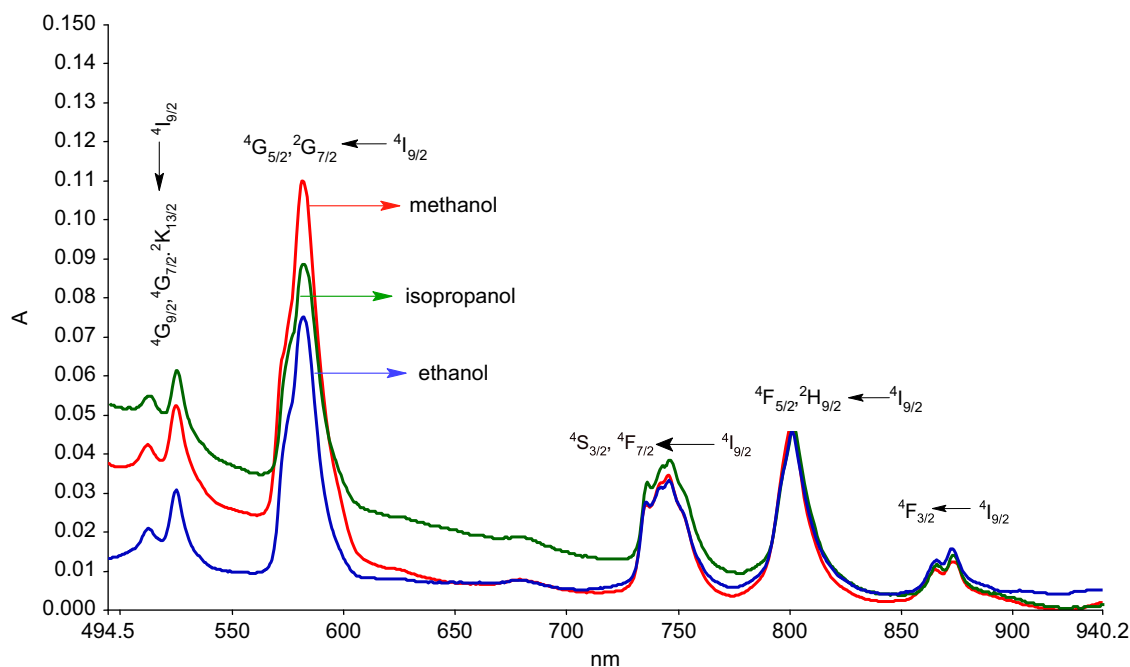


Fig. 5. 4f–4f absorption spectra of $[\text{Nd}(\text{acac})_3(\text{pz})_2]$ in methanol (red), isopropanol (green) and acetonitrile (blue). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

(chloroform and nitrobenzene) and coordinating (pyridine) solvents. However, the band shape is similar to that of ten-coordinate $[\text{Nd}(\text{hfaa})_3(\text{phen})_2]$ [30] in non-coordinating solvent. It is a strong evidence that two alcohol molecules coordinate with neodymium without displacing any of the pyrazole units and transform the eight-coordinate complex into ten-coordinate species in solution. Drastic reduction in the oscillator strength is noted in these solvents relative to the value observed in chloroform. The lower value of the oscillator strength is due to the transformation of the eight-coordinate complex into more symmetric ten-coordinate

structure, which results in lowering of the asymmetry of the field around Nd (III). This suggests the premise that the oscillator strength of the hypersensitive transition depends upon symmetry of the field around Ln (III) ion in solution. Similar effect of the acetonitrile is observed on the spectrum of the complex. Acetonitrile also coordinates without replacing any of the pyrazole units. The band shape is similar to the band shape in methanol and isopropanol (Fig. 5). The lower oscillator strength of the hypersensitive transition in this solvent also favors the formation of highly symmetric ten-coordinate species in solution.

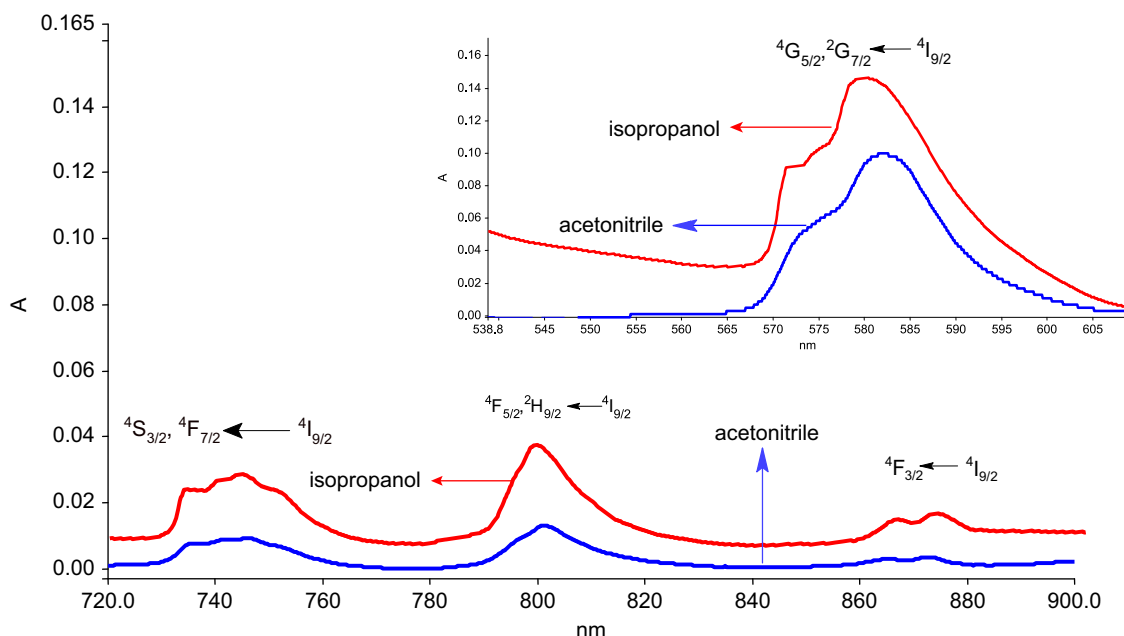


Fig. 6. ${}^4G_{5/2}, {}^2G_{7/2} \leftarrow {}^4I_{9/2}$ transition of $[\text{Nd}(\text{acac})_3(\text{im})_2]$ in isopropanol (red) and acetonitrile (blue). Inset shows the ${}^4G_{5/2}, {}^2G_{7/2} \leftarrow {}^4I_{9/2}$ hypersensitive transition. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

3.3.4. $[\text{Nd}(\text{acac})_3(\text{im})_2]$

Due to insolubility of this complex the optical absorption properties could not be investigated beyond acetonitrile, isopropanol, pyridine and DMSO. The effect of acetonitrile and isopropanol are similar to that noted for the pyrazole complex. Two molecules of both the solvents coordinate in solution to the neodymium without displacing any of the imidazole units and resulting band shape of the hypersensitive transition (Fig. 6) is similar to the band shape of the transition of pyrazole complex in these solvents. The effect of pyridine is similar to those noted on the $[\text{Nd}(\text{acac})_3(\text{H}_2\text{O})_2]$ and its pyrazole complex. The oscillator strength of the three complexes are 47.45×10^{-6} , 42.01×10^{-6} and 47.68×10^{-6} in this solvent. These values are similar in magnitude. The band shape of the hypersensitive transition of the three complexes are identical (Fig. 2) and are similar to the band shape of typical eight-coordinate $\text{Nd}(\beta\text{-diketonate})_3$ complexes [30,35,50,51]. This proves that pyridine being more basic and strong donor replaces both the molecules of water, imidazole or pyrazole from the complexes and two pyridine molecules coordinate to the neodymium giving $[\text{Nd}(\text{acac})_3(\text{py})_2]$ species in solution. These complexes, which may have different structures in the solid state acquire similar structure in this solvent. The oscillator strength of the hypersensitive transition of the imidazole complex in acetonitrile and isopropanol is higher than the values obtained for the pyrazole complex. The higher oscillator strength could be related to higher basicity of the imidazole ($\text{p}K_a=7.1$) than the pyrazole ($\text{p}K_a=2.52$), which leads to greater degree of covalency of Nd–N bonds. These results clearly indicate, that pyrazole is weaker bonding ligand for neodymium ion than imidazole.

3.3.5. Absorption properties in DMSO.

The hypersensitive transition is peculiarly sensitive to the changes in the coordination structures around neodymium and yields important information on the symmetry of the species in solution. The oscillator strength increase with increasing asymmetry of the field around the lanthanide [55,56] while increases in the symmetry of the field lowers the oscillator strength. It is

important to mention that the oscillator strengths of the hypersensitive transition of $[\text{Nd}(\text{acac})_3(\text{H}_2\text{O})_2]$, $[\text{Nd}(\text{acac})_3(\text{im})_2]$ and $[\text{Nd}(\text{acac})_3(\text{pz})_2]$ in DMSO, are 41.5×10^{-6} , 43.89×10^{-6} and 43.63×10^{-6} , respectively (Table 4). These oscillator strength values are similar in magnitude. The oscillator strength of this transition for the complexes $[\text{Nd}(\text{acac})_3\text{phen}]$ and $[\text{Nd}(\text{acac})_3\text{bpy}]$ has been reported [35] as 39×10^{-6} and 37×10^{-6} in DMSO. We have re-investigated the spectra of the complexes reported in Ref. [35] and found the oscillator strength of the hypersensitive transition ${}^4G_{5/2}, {}^2G_{7/2} \leftarrow {}^4I_{9/2}$ as 40.20×10^{-6} and 41.00×10^{-6} for eight-coordinate $[\text{Nd}(\text{acac})_3\text{phen}]$ and $[\text{Nd}(\text{acac})_3\text{bpy}]$. The oscillator strength of the complexes under study and of $[\text{Nd}(\text{acac})_3\text{phen}]$ and $[\text{Nd}(\text{acac})_3\text{bpy}]$ are similar in magnitude. Moreover, the band shape of this transition for all the complexes in DMSO are identical (Fig. 7) and are quite similar to band shape of the eight-coordinate tris(β -diketonate)neodymium(III) complexes in non-coordinating solvents [30,35,50,51]. It indicates that these complexes have similar structure in solution. This is only possible if the complexes dissociate in this solvent and acquire similar structure (geometry) and similar symmetry of the ligand field around Nd^{3+} ion. The DMSO, which has a very high Gutmann donor number (29.8), invade the coordination environment and may easily enters the inner-coordination sphere of Nd^{3+} by replacing water molecules, in the case of $[\text{Nd}(\text{acac})_3(\text{H}_2\text{O})_2]$ and the heterocyclic amines in the cases of the imidazole and pyrazole complexes. The NMR spectra of the imidazole and pyrazole complexes in DMSO- d_6 show signals for free imidazole and pyrazole while no signal due to free acetylacetonate is observed. The dissociation of the $[\text{Nd}(\text{fod})_3\text{phen}]$ or $[\text{Nd}(\text{fod})_3\text{bpy}]$ in DMSO solution has been observed in this laboratory [52]. It is, therefore, believed that in the case of adducts it (DMSO) enters the coordination sphere by replacing the heterocyclic amines. It is certain that DMSO could not displace any of the chelate acetylacetonate units since molar conductance shows that it is a non-electrolyte in this solvent (molar conductance found for $[\text{Nd}(\text{acac})_3(\text{H}_2\text{O})_2]$ is $2 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$). Therefore, the neodymium ion, in DMSO solution of the complexes ($[\text{Nd}(\text{acac})_3(\text{H}_2\text{O})_2]$, $[\text{Nd}(\text{acac})_3(\text{im})_2]$ or $[\text{Nd}(\text{acac})_3(\text{pz})_2]$), has similar environment around it. Therefore, we believe that two

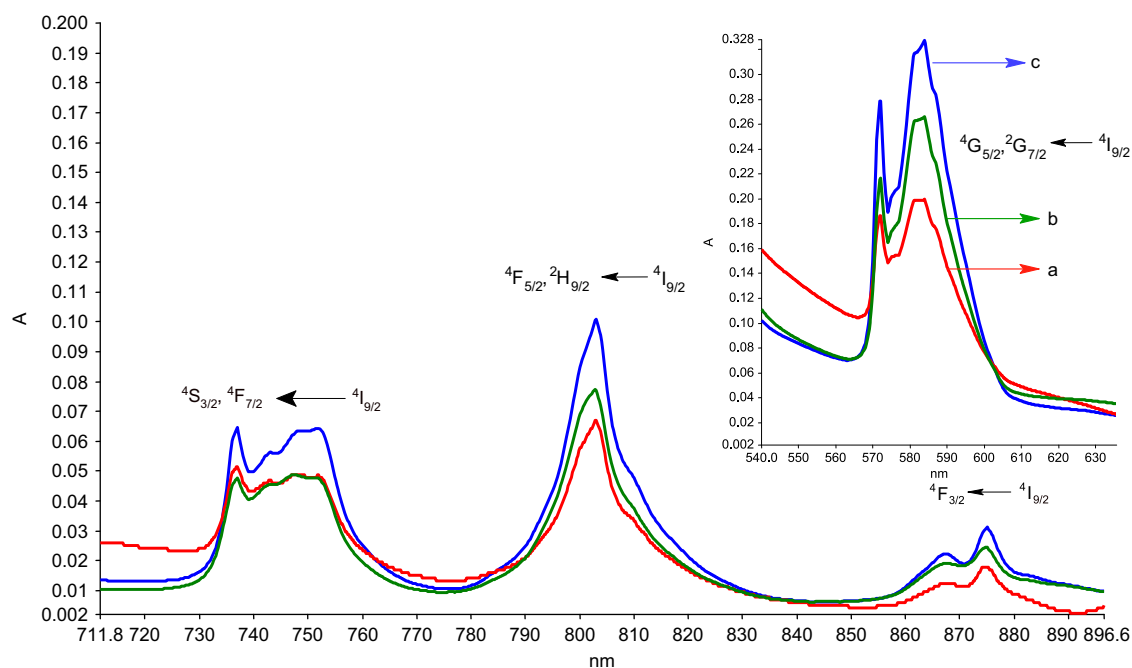


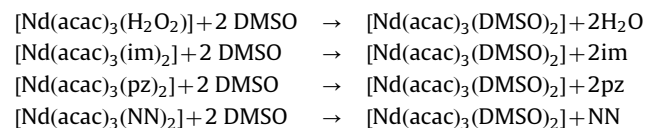
Fig. 7. $^4F_{3/2}$, $^4F_{5/2}$, $^2H_{9/2}$ and $^4F_{7/2}$, $^4S_{3/2} \leftarrow ^4I_{9/2}$ transitions of (a) $[\text{Nd}(\text{acac})_3(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ (red), (b) $[\text{Nd}(\text{acac})_3(\text{pz})_2]$ (green) and (c) $[\text{Nd}(\text{acac})_3(\text{im})_2]$ (blue) in DMSO. Inset shows the $^4G_{5/2}$, $^2G_{7/2} \leftarrow ^4I_{9/2}$ hypersensitive transition. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

Table 5
Covalency parameters of neodymium (III) complexes in different solvents.

Complexes	Solvents ^a							
	A	B	C	D	E	M	N	O
$[\text{Nd}(\text{acac})_3(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$								
β	0.9882	0.9860	0.9895	0.9881	0.9811	0.9866	0.9859	0.9841
$b^{1/2}$	0.0768	0.0836	0.072	0.077	0.0972	0.0818	0.084	0.089
δ	1.1941	1.4198	1.061	1.204	1.926	1.358	1.43	1.61
$[\text{Nd}(\text{acac})_3(\text{pz})_2]$								
β	0.991	0.9889	0.9900	0.9856	0.9898	0.9859	0.9855	0.9845
$b^{1/2}$	0.067	0.074	0.071	0.0848	0.071	0.083	0.085	0.088
δ	0.910	1.12	1.01	1.46	1.022	1.42	1.47	1.57
$[\text{Nd}(\text{acac})_3(\text{im})_2]$								
β		–	0.9849	–	0.9888	–	–	0.9843
$b^{1/2}$			0.087		0.074			0.089
δ			1.530		1.120			1.60

^a A = methanol; B = ethanol; C = isopropanol; D = chloroform; E = acetonitrile; M = pyridine; N = nitrobenzene; O = Dimethylsulfoxide.

DMSO molecules have coordinated making the Nd (III) ion eight-coordinate as shown below:



where (NN) is phen or bpy

Report of eight-coordinate $[\text{Ln}(\beta\text{-diketonate})_3(\text{DMSO})_2]$ is available in the literature [57].

Due to presence of similar species, for the systems studied, the oscillator strength is also similar in magnitude. Both changes in band shape and intensity of hypersensitive transition can be used as qualitative indication of symmetry and coordination number around the lanthanide ion. Fig. 7 shows the band shapes of the hypersensitive (Nd–VI) transitions of the complexes in DMSO, which are quite similar in shape. Occurrence of similar spectra is indicative of similar symmetry (i.e., similar geometry and similar coordination number).

Thus, these complexes, which may have different geometries (coordination number) in the solid state acquire similar structure and symmetry in solution and are eight-coordinate in DMSO. Similar results have been obtained for closely related Pr, Ho and Er complexes [31,32,58]. The number of coordinated DMSO further gets support from a recent report on the crystal structure of a closely related compound containing three β -diketonate like ligands and two DMSO molecules [59]. The band shape of the non-hypersensitive transitions Nd–I, Nd–II and Nd–III are also similar (Fig. 7).

A general feature in the spectra of these complexes is a shift of absorption bands towards lower energy (longer wave length) as compared to those of the Nd^{3+} aqua-ion. These red shifts are called the nephelauxetic effect [39] and is due to lowering of inter electronic repulsion parameters in the complex. This effect is, of course, smaller effect than that observed for d-orbitals in transition metals because of d-orbitals are about of the same distance from the nucleus as the orbitals used for bond formation, whereas the f-orbitals lies closer to the nucleus. The values of nephelauxetic effect and covalency parameters are given in Table 5.

The values of nephelauxetic effect (β), which are less than unity, and positive values of ($b^{1/2}$) and (δ) for the complexes support the existence of covalent bonding between the metal and the ligand.

4. Conclusion

The principal objectives of this study were to (i) obtain intensity of the hypersensitive as well as non-hypersensitive transitions of structurally related Nd(III) complexes in various non-aqueous solvents, (ii) demonstrate the sensitivity of the hypersensitive transition (oscillator strength and changes in the band shape) to structural differences between ligand in the various complexes and (iii) demonstrate the effect of various coordinating and non-coordinating non-aqueous solvent. The results obtained clearly show that the multiplet-to-multiplet transitions exhibiting largest intensity variations among the complexes is $^4G_{5/2} \leftarrow ^4I_{9/2}$ (centered at 571 nm) transition. It is noted that this transition obeys the electric-quadrupolar selection rules and is hypersensitive. These results clearly show that among the solvent studied pyridine is most effective in promoting the 4f–4f intensity. The solvents nitrobenzene and acetonitrile are non-coordinating while the alcohols coordinate by replacing the water molecules for the $[\text{Nd}(\text{acac})_3(\text{H}_2\text{O})_2]$ system. The acetonitrile and alcohols are coordinating for imidazole and pyrazole systems giving distinctively different band shape of the hypersensitive transition, which resemble with the band shape of the ten-coordinate complexes. It clearly indicates that the two solvent molecules coordinate. The DMSO due to its strong coordinating ability coordinates the complexes by replacing the water molecules and heterocyclic amines giving $[\text{Nd}(\text{acac})_3(\text{DMSO})_2]$ species in this solution. The oscillator strength and band shape are similar for the three complexes in this solvent. Imidazole has been found stronger coordinating ligand for the neodymium system than pyrazole. The work is still in progress and praseodymium, holmium and erbium complexes are being investigated.

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