Pergamon

Polyhedron Vol. 16, No. 23, pp. 4143–4151, 1997

0277–5387/97 $17.00+0.00

PII: S0277–5387(97)00139–3

Mixed-ligand lanthanide complexes—X†. Interaction of trivalent lanthanides with 1,10-phenanthroline and thiocyanate in alcohol

Azad A. Khan, Arun K. Saxena and K. Iftikhar*

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

(Received 23 September 1996; accepted 10 April 1997)

Abstract—The interaction of trivalent lanthanide thiocyanates and phen in ethanol results in the formation of the complexes of the type $[Ln(phen)_3(SCN)_3]$, where Ln = La, Pr, Nd, Sm and Eu; and $[Ln(phen)_3(SCN)_3(H_2O)]$, where Ln = Dy, Ho, Er and Yb. The complexes have been characterized by elemental analyses, molar conductance, IR spectra and thermal analyses. The complexes behave as non-electrolytes in methanol. TGA showed the presence of coordinated water in the case of the heavier lanthanides making them ten-coordinate. The NMR spectra of the complexes of La, Pr, Nd, Sm, Eu and Yb have been studied in DMSO-d_6 and pyridine-d_5. The complexes do not dissociate in DMSO and retain their coordination number. The chemical shift ratios are constant for different phen protons which indicates dipolar nature of the shift. Pyridine coordinates without displacing any ligand and increases the coordination number of the lighter lanthanides from nine to ten. © 1997 Elsevier Science Ltd. All rights reserved

Keywords: mixed ligand; lanthanide complexes; 1,10-phenanthroline; thiocyanate NMR; paramagnetic shift.

The trivalent lanthanides, Ln^{III}, constituete a series of hard Lewis acids with similar chemical behaviour and their complexes with anionic ligands containing oxygen as donor atoms have been the most studied [1–3] as were also their complexes with synthetic ionophores, generally stabilized by the macrocyclic effect [4,5]. In the absence of strong stabilizing ligands, the complex formation is often precluded by the competition for the coordination sites from the solvent molecules and the counter anions. Non-aqueous solvents with weak basic properties offer a powerful means for the synthesis of Ln^{III} complexes with neutral ligands with N (or even S) as donor atoms [1,2,6,7]. The isolation of the first lanthanide complexes derived from the weakly basic nitrogen donor 1,10-phenanthroline (phen) was reported [8,9] as early as 1963. The number of phen ligands coordinated to the lanthanide ion depends primarily upon the coordinating ability of the anion present. When the anion is strongly chelating diketonate [10,11] or acetate [12] only one phen molecule coordinates, indicating the inability of the weakly basic amine to displace a strongly coordinated anion. With nitrate as the anion, complexes containing two phen units, $[Ln(NO_3)_3(phen)_2]$, are formed [13] and IR spectra have been interpreted in terms of all nitrate groups being coordinated making the lanthanide ions ten-coordinate which, in a recent report [14], has been verified by a crystal structure determination. Tris-phenanthroline complexes are obtained when the anion is thiocyanate [15] or selenocyanate [16]. The IR spectra of the $[Ln(phen)_3(NCSe)_3]$ species indicated coordinated selenocyanate groups (through N) only, suggesting a nine-coordinate complex. In a recent report [17] it has been shown that interaction of phen and thiocyanate with trivalent lanthanides in aqueous medium yield complex species of the type $[Ln(phen)_3(SCN)(H_2O)](SCN)_2$ in which both coordinated and non-coordinated isothiocyanate groups are present making the lanthanides eight-coordinate. The study of the $Ln(phen)_3(NCS)_3$ [15] species both in solution and in the solid phase are far from being complete and the complexes are likely to be nine-coordinate by analogy to $[Ln(phen)_3(NCSe)_3]$. In this paper we report syntheses of the complexes of trivalent lanthanides (Pr,

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* Author to whom all correspondence should be addressed
† Part—IX, See ref. 28.

Nd, Sm, Eu, Dy, Ho, Er and Yb) and La with thiocyanate and phen in ethanol under normal conditions.

EXPERIMENTAL

Materials

Lanthanide oxides (99.9%; Leico Chemicals, U.S.A.) were converted to the corresponding chlorides. 1,10-Phenanthroline monohydrate (E. Merck), potassium thiocyanate was AR grade. Ethyl alcohol (99.9%) was purchased from Fluka and was used as such.

Synthesis

The complexes were synthesized by the method reported by Hart and Laming [15]. All the complexes were prepared by similar methods, we are reporting synthesis of lanthanum complex as an example. Hydrated lanthanum chloride (0.501 g; 1.35×10^{-3} mol) dissolved in 25 cm^3 ethanol was treated with a solution of potassium thiocyanate (0.525 gm; 5.40×10^{-3} mol) in 75 cm^3 ethanol in 1 : 4 molar ratio. The two solutions were mixed thoroughly and the precipitate of potassium chloride removed by filtration. The filtrate was added slowly with vigorous stirring, to a solution of 1,10-phenanthroline (1.07 g; 5.40×10^{-3} mol) in 50 cm^3 ethanol (1 : 4 molar ratio). A precipitate appeared immediately after mixing the two solutions. This crude product was collected by filtration and dried *in vacuo* over P_4O_{10}. The dry crude product was washed several times with chloroform/carbon tetrachloride to remove excess of unreacted phen. It was further washed three times with warm ethanol to remove any unreacted lanthanum chloride or thiocyanate. The yield of the pure product was 75% (literature yield 95%).

Methods

The complexes were subjected to microanalyses for carbon, hydrogen and nitrogen while the metals were estimated by complexometric titration with EDTA using xylenol orange as the indicator. Molar conductances of 10^{-3} M solutions of the complexes were measured on the Orion conductivity meter model 122 in methanol, dimethyl sulfoxide and dimethylformamide. IR spectra of the complexes were taken on a Perkin–Elmer model 782 IR spectrophotometer as KBr disc in the range 4000–400 cm^{-1}. The Thermograms were recorded on duPont TA 2000 and on a Metler 3000, TGA machine. The NMR spectra of the complexes were taken on a Varian 200 MHz NMR machine at the Indian Institute of Chemical Technology, Hyderabad and in few cases on a Bruker 300 MHz NMR machine at the National Institute of Immunology, New Delhi, in DMSO-d_6, and pyridine-d_5.

RESULTS AND DISCUSSION

The reaction of lanthanide thiocyanates with phenanthroline resulted in the isolation of the complexes listed in Table 1. These complexes are amorphous solids which do not have sharp melting points and decompose over the temperature range 175–328°C (Table 1). They are air stable and can be handled without effect of air or moisture. The synthesis was carried out in air and no precaution was taken to exclude moisture. Hart and Laming reported [15] the synthesis by mixing metal and phen in 1 : 4 ratio for lighter lanthanides and 1 : 6 ratio for heavier lanthanides. We found that 1 : 4 ratio for the entire series serve the purpose and use of excess phen does not increase the yield. The complexes are highly soluble in DMSO and DMF. These have poor solubility in methanol and pyridine. However a 10^{-3} M solution may be prepared in these solvents. The molar conductances of the complexes in methanol (10^{-3} M solution) is in the range 49–58 ohm^{-1} cm^2 mol^{-1} (Table 1). The molar conductance range for 1 : 1 electrolytes in this solvent [18] is 80–115 ohm^{-1} cm^2 mol^{-1}. Thus, the complexes behave as non-electrolytes and the three thiocyanate ions present are inside the coordination sphere. The molar conductances were also measured in DMSO (10^{-3} M solutions) and are in the range 50–76 ohm^{-1} cm^2 mol^{-1} which is compatible with a 1 : 1 electrolyte type [18]. Because of the strong donor capacity of DMSO which leads to displacement of anionic ligand and change of electrolyte type, it is proposed that one thiocyanate group (SCN) is displaced by a molecule of DMSO: $[Ln(phen)_3(SCN)_3] + DMSO \rightarrow [Ln(phen)_3(SCN)_2(DMSO)](SCN)$. No change in molar conductance was recorded on keeping the solutions for two days. We have also recorded, in a few cases, the molar conductance in DMF (Table 1) and note that like DMSO, the complexes behave at 1 : 1 electrolyte [18] in this solvent too.

IR spectra

The IR spectra of the complexes are consistent with the presence of coordinated phen [19], since changes in the spectra of the ligand are observed, particularly the strong bands in the region 1400–1650 cm^{-1} (C=C and C=N ring stretching vibrations) and out-of-plane hydrogen deformation vibrations of free phen at 735 and 845 cm^{-1} are modified on coordination [20]. A band in free phen at ca 413 ± 2 cm^{-1} is shifted to higher frequencies on complexation suggesting that both the nitrogens are coordinated to the lanthanides [20,21]. The C—N stretching frequency of thiocyanates are generally lower in the N-bonded complexes (near and below 2050 cm^{-1}), than the S-bonded

Table 1. Characterizing data of the complexes

	M.P./ Decomposition °C	% Observed (Calculated)				Λ_M (Ohm^{-1} cm^{-2} mol^{-1})			
Complexes		Metal	Carbon	Hydrogen	Nitrogen	MeOH	DMSO	DMF	Colour
$[La(phen)_3(SCN)_3]$	320–328	16.4 (16.3)	53.5 (54.8)	2.7 (2.8)	14.7 (14.8)	50.0	70.0	105.9	White
$[Pr(phen)_3(SCN)_3]$	305–309	16.2 (16.5)	54.4 (54.7)	2.8 (2.8)	(15.0) (14.7)	53.0	51.0	82.2	Light green
$[Nd(phen)_3(SCN)_3]$	300–306	16.6 (16.8)	54.0 (54.5)	2.8 (2.8)	14.9 (14.7)	58.0	72.0	96.7	Light violet
$[Sm(phen)_3(SCN)_3]$	275–280	17.4 (17.4)	54.3 (54.1)	2.8 (2.8)	14.4 (14.6)	51.7	67.5	—	Dirty white
$[Eu(phen)_3(SCN)_3]$	260–265	17.6 (17.5)	53.8 (54.0)	2.8 (2.8)	14.3 (14.6)	50.0	73.5	—	Light yellow
$[Dy(phen)_3(SCN)_3(H_2O)]$	240–242	18.2 (18.2)	52.3 (52.3)	3.0 (2.9)	14.2 (14.1)	49.1	72.4	—	Dirty white
$[Ho(phen)_3(SCN)_3(H_2O)]$	175–180	18.3 (18.4)	52.0 (52.2)	3.0 (2.9)	14.1 (14.0)	51.0	71.0	—	Light yellow
$[Er(phen)_3(SCN)_3(H_2O)]$	260–262	18.6 (18.6)	52.5 (52.0)	3.0 (2.9)	14.2 (14.0)	51.0	71.0	105.5	Pink
$[Yb(phen)_3(SCN)_3(H_2O)]$	240–260	19.0 (19.1)	51.5 (51.7)	2.9 (2.9)	14.2 (13.9)	29.0	68.0	—	White

complexes (near 2100 cm^{-1}) [22]. A single very strong band in these complexes in the region 2030–2050 cm^{-1} has been assigned as νC—N of thiocyanate, bonded through nitrogen. This corroborates the result of molar conductance which showed non-electrolyte behaviour of these complexes in methanol. These bands are in accord with the literature [15] value where these had been assigned to show the presence of thiocyanate of ionic type only. But in presence of molar conductance data we can safely argue for coordinated thiocyanate groups. Although it is difficult to assign νC—S in these complexes since phen has absorptions in the region of νC—S, however a careful comparison of IR spectra of the ligand and the complexes reveals that a sharp band, in the region 850–870 cm^{-1}, is present in all the complexes. This band does not have its equal in the spectrum of phen and could be assigned to νC—S since known N-bonded thiocyanates absorb in 780–860 cm^{-1} (νC—S) frequency range [23–25]. The spectral data support M—NCS bonding assignment for all the complexes.

Satori *et al.* [26] have calculated frequencies of coordinated water and found the rocking, wagging and metal–oxygen frequencies at 900, 768 and 643 cm^{-1}, respectively. Nakagawa and Shimanouchi [27] suggested the frequency range 900–600 cm^{-1} for rocking mode of coordinated water. We have observed bands for coordinated water at 950 and 930 cm^{-1} in the complexes of phen and 2,2′-bipyridyl, respectively [11,17]. A new band of low intensity observed in the spectra of Dy, Ho, Er and Yb in the range 980–950 cm^{-1} has been assigned as the rocking mode of water activated by coordination to metal. This band does not have an analogue in the ligand and in the complexes of the lighter lanthanides. This is supported by TGA studies.

Thermal analyses

The thermograms were recorded for all the complexes (except Pr) in the temperature range 35–800°C and in few cases in the range 35–1000°C. The thermal data are given in Table 2. The thermograms of the complexes show stepwise decomposition. The thermograms of lighter lanthanides do not show the presence of water molecules. The lanthanum complex is stable up to 310°C and does not show any weight loss below this temperature. The weight loss starts from 310°C and an inflexion point in the TGA curve is observed at 377°C which represents expulsion of two thiocyanate groups (obs. 13.2%; calc. for two thiocyanate groups is 13.6%). The corresponding DTG plot shows a strong peak at this temperature. Another

Table 2. Thermal data of the complexes[a]

Complexes	DTG Peak (Temp. °C)	% wt loss obs. (calc.)	Constituents lost
La	377	13.2 (13.6)	two thiocyanate groups
	424	19.8 (21.1)	one phen molecule
	639	44.3 (42.2)	two phen molecules
Nd	345	22.1 (21.0)	one phen molecule
	452	17.2 (21.0)	one phen molecule
	646	34.2 (34.5)	two thiocyanate groups and one phen molecule
Sm	287	13.2 (13.2)	two thiocyanate groups
	509	19.4 (20.4)	one phen molecule
	648	39.6 (40.8)	two phen molecules
Eu	394	34.8 (34.2)	two thiocyanate and one phen molecule
	620	36.1 (41.6)	two phen molecules
Dy	73	1.5 (—)	residual moisture
	162	2.2 (2.0)	one water molecule
	236 326	12.6 (12.9)	two thiocyanate groups
	422 621	60.4 (60.4)	three phen molecules
Ho	159	2.2 (2.0)	one water molecule
	358	14.6 (13.0)	two thiocyanate groups
	396	20.5 (20.1)	one phen molecule
	604	35.2 (40.1)	two phen molecules
Er	167	2.2 (2.0)	one water molecule
	272	7.7 (6.5)	one thiocyanate group
	423	26.3 (26.5)	one thiocyanate group and one phen molecule
	623	39.6 (40.0)	two phen molecules
Yb	159	2.1 (2.0)	one water molecule
	405	34.3 (32.7)	two thiocyanate groups and one phen molecule
	614	37.0 (39.8)	two phen molecules

[a] The formulae for the complexes are those listed in Table 1.

inflexion point is observed at 424°C with a weight loss of 19.8% representing elimination of phen molecule (calculated weight loss for one phen molecule is 21.1%). A corresponding peak in the DTG curve is present at this temperature. In the third step of decomposition two phen molecules are eliminated in the temperature range 545–750°C. An inflexion point at 639°C in the TGA curve and a corresponding peak in the DTG plot is observed. No weight loss is observed further up to 1000°C. The europium complex is stable up to 250°C and loses its constituents in two steps. In the first step (start temp. 253°C, end temp. 512°C) two thiocyanate groups and one phen unit are eliminated together and in the second step of decomposition the remaining two phen units are expelled in the temperature range 529–664°C (for wt loses see Table 2).

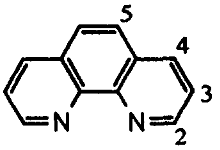
The complexes of Dy, Ho, Er, and Yb show the presence of one coordinated water molecule. These complexes show an inflexion point in the temperature range 155–160°C with a weight loss of 2.00–2.22% (calc. wt loss for one water molecule is between 1.99 and 2.05%). The DTG curve shows a peak in this temperature range. The removal of water molecule above 155°C is indicative of the fact that it is present inside the coordination sphere of the metal ion. This corroborates the results of the IR spectra which displayed a band for coordinated water molecule. We note that the water molecule is more strongly held in the present complexes compared with the complexes of phen reported earlier [17]. The further steps of decomposition are removal of thiocyanate and phen units (for wt loss see Table 2). The decomposition pattern of all the complexes reveal that the third thiocyanate group is not eliminated up to 1000°C.

Thus, on the basis of the results of elemental analyses (Table 1), molar conductances, IR spectra and thermal analyses (Table 2) the complexes fall in two categories and have been assigned the general formulae $[Ln(phen)_3(SCN)_3]$ where Ln = La, Pr, Nd. Sm and Eu and $[Ln(phen)_3(SCN)_3(H_2O)]$ where Ln = Dy, Ho, Er, and Yb. The lighter lanthanides are thus nine-coordinate and the heavier lanthanides are ten-coordinate. This is in contrast to the general observation that the coordination number of the larger lanthanides is greater than for the smaller lanthanides. Moreover, all the evidences are in favour of proposed formulae. The reason for this trend is, at present, not clear.

NMR spectra

The NMR spectra of the complexes of lanthanum, praseodymium, neodymium, samarium, europium and ytterbium have been recorded in DMSO-d_6; and in the cases of europium and ytterbium the spectra have also been recorded in pyridine-d_5. The chemical shifts and the paramagnetic shifts are collected in Table 3. The signals of phen, in the case of diamagnetic lanthanum complex, have been found to shift to lower fields compared with free phen. The shifts are comparable to other diamagnetic lanthanum complexes [17,28] of phen in DMSO-d_6 and $CDCl_3$. No signal for free phen is observed in the spectrum. The lower field shifts of phen resonances is strong evidence that the aromatic amine remains coordinated to the lanthanum metal even in DMSO solution. The spectra of paramagnetic complexes are more interesting where the phen resonances have been shifted to lower fields as well as higher fields compared with the diamagnetic analogue. We note that the magnitude of the paramagnetic shift is small compared with those observed for other phen complexes of the paramagnetic lanthanides [17,28]. In all the complexes changes produced in the chemical shifts of phen resonances are approximately equal. The magnitude and direction of such changes are a function of the central atom. In the praseodymium complex all resonances of phen are shifted to higher fields relative to the lanthanum complex. The paramagnetic shifts are given in Table 3. These protons have been shifted to higher fields but lie within the TMS envelope. The shifts decreases with increasing distance of the proton from the metal ion and it is largest for H(2) protons ($\delta = -0.70$). The neodymium complex displayed a higher fields shift of H(2) protons and other resonances have been shifted to lower fields. We note an upfield shift of phen protons (except H(4) which has moved to downfield) in the case of the europium complex, relative to its diamagnetic analogue. The ytterbium is known to

Table 3. NMR spectral data



1,10-phenanthroline

Compounds[f]	Solvents	Chemical shifts[a] (paramagnetic shift)[b]			
		H(2)	H(3)	H(4)	H(5)
phen	$CDCl_3$	9.19	7.63	8.24	7.83
La	DMSO	9.25[d]	7.76(q)	8.40(q)	7.92(s)
Pr	DMSO	8.55	7.39	8.17	7.67
		(−0.70)	(−0.37)	(−0.23)	(−0.25)
Nd	DMSO	9.11	7.78	8.50	8.03
		(−0.14)	(0.02)	(0.10)	(0.11)
Sm	DMSO	9.27(s)	7.78	8.44	7.93
		(0.02)	(0.02)	(0.04)	(0.01)
Eu	DMSO	8.91	7.61	8.49(d)	7.91
		(−0.34)	(−0.15)	(0.09)	(−0.01)
	Pyridine-d_5	8.02	[c]	9.62(d)	[c]
		(−1.23)		(1.22)	
Yb	DMSO	9.14	7.80	8.50	8.03
		(−0.11)	(0.04)	(0.10)	(0.11)
	Pyridine-d_5	12.84	[c]	10.73	[c]
		(3.59)		(2.33)	

[a] Chemical shifts and paramagnetic shifts are expressed in ppm (δ). Paramagnetic shifts are relative to the diamagnetic lanthanum complex.

[b] The negative sign indicates an upfield shift.

[c] Could not observe since obscured by strong pyridine signals.

[f] The formulae of the complexes are listed in Table 1.

(d) = doublet.

(q) = quartet.

(s) = singlet.

induce very large downfield shifts of ligands in its complexes or organic substrate associated to a shift reagent. These larger shifts appear at the expense of resolution since the Yb^{3+} ion has a long electron relaxation time. In the present ytterbium complex the aromatic amine resonances are very broad and fine structures have disappeared from the spectrum (Fig. 1). These observations together with the fact that praseodymium and europium complexes display broad resonances for H(2) protons show that both the ends of the aromatic amine remain coordinated in this solvent.

The dipolar (pseudocontact) interactions of the paramagnetic centres with the magnetically active nuclei is given by the relationship [29],

$$\left(\frac{\Delta H}{H}\right) = K(3\cos^2\theta - 1)/R^3$$

in which the upfield shift is predicted for $\sim 55 < \theta < \sim 125°$, independent of Ln–proton distance [30]. A possible explanation for the upfield shifts of phen resonances in the europium complex would be substantial alternation of geometry after the interaction of DMSO with this compound (molar conductance has shown that DMSO enters the coordination sphere of the metal ions in the present complexes). With such an alternation the dependence of shift on angle could become important enough to change the sign of the shift. A proton residing at an angle Eu–N–H angle of *ca* 55° is predicted to experience neither shielding nor deshielding from the paramagnetic centre [30]. A corresponding sign variation has been found for alkyl substituted bipyridyl europium complex [31].

The paramagnetic shift in the case of lanthanides are predominantly from dipolar mechanism. This may be verified if the ratio R_{ij} of the shift of the nucleus i to another j in the same molecule remains the same for all lanthanides [32]. The ration of the chemical shifts of the protons H(5) and H(4) are 0.94, 0.94, 0.94 and 0.93; of the H(3) and H(5) are 0.96, 0.96, 0.98 and 0.96 for the complexes of praseodymium, neodymium, samarium and europium, respectively. The ratios are similar, for a given set of protons, and therefore, the shifts owe their origin to dipolar interaction. We note that ratios of the chemical shifts induced by different metal ions in the complexes, for phen protons, are similar. The ratios for Eu/Pr are 1.04, 1.03, 1.04 and 1.03; for the Eu/Nd are 0.98, 0.98, 0.99 and 0.98 and for the Pr/Nd are 0.94, 0.95, 0.96 and 0.95 for the H(2), H(3), H(4) and H(5), respectively. Thus, we conclude that the paramagnetic shift, though small in magnitude, in these complexes, are exclusively due to dipolar interactions [33]. The ytterbium complex is not taken into account since it has different stoichiometry in the solid state (Table 1).

The paramagnetic shifts induced by europium and

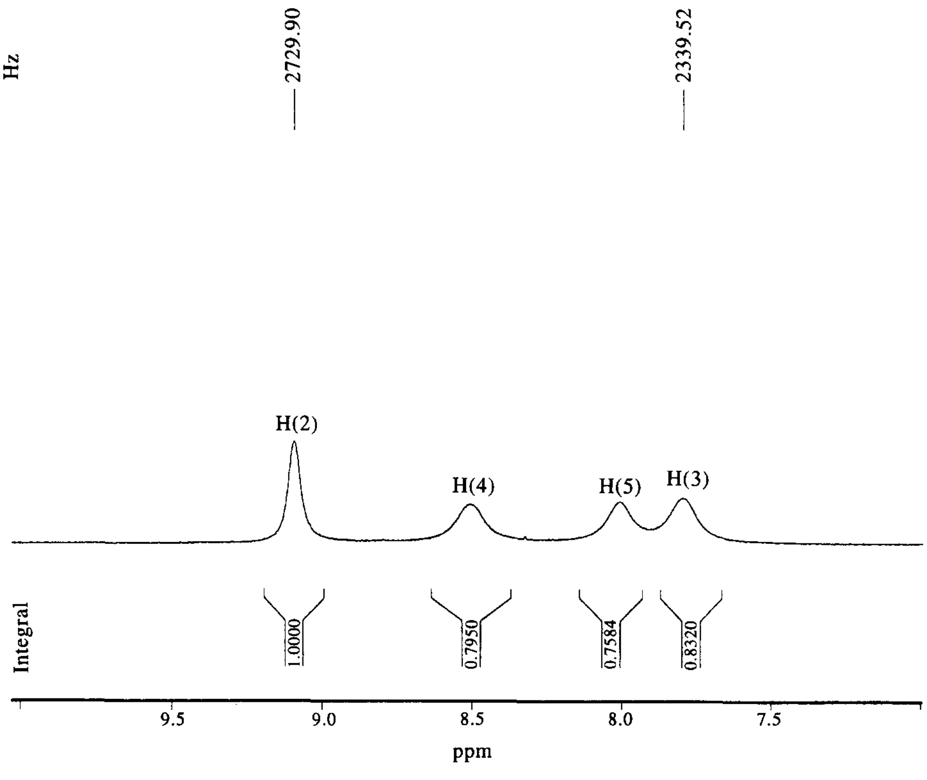


Fig. 1. The 300 MHz ^1H NMR spectra of $[Yb(phen)_3(SCN)_3(H_2O)]$ in DMSO-d_6. Chemical shifts are expressed in ppm (δ) downfield from internal Me_4Si.

ytterbium are more pronounced when pyridine-d_5 was used as solvent. This is due to ring current effect [34] of the pyridine ring. Moreover, some of the phen resonances are obscured by strong pyridine signals. In the case of the europium complex the H(2) proton resonance has shifted to higher field relative to the position of this proton in the DMSO-d_6 solution of the complex. It appears at 8.02 ppm (δ), as a relatively broad single resonance. The paramagnetic shift is -1.23 ppm (δ) as compared with its diamagnetic analogue in DMSO-d_6. The H(4) proton resonates as a doublet ($J = 6$ cps) at 9.62 ppm (δ) (Fig. 2). The H(2) and H(4) protons of the aromatic amine, in case of the ytterbium complex in pyridine have moved more downfield and appear as broad resonances at 12.84 ppm (δ) and 10.73 ppm (δ), respectively (Fig. 3). The H(3) and H(5) signals, in both the complexes are obscured by strong pyridine resonances. It is worth mentioning that spectra of both the complexes show resonances for coordinated solvent molecule (pyridine). The signal of coordinated pyridine is found to shift to higher field compared with free pyridine and appears as a relatively sharp single resonance, at 6.75 ppm (δ) in the case of the europium complex (Fig. 2); and at 3.45 ppm (δ), in the case of the ytterbium complex, as a broad single resonance (Fig. 3). The paramagnetic shifts of pyridine protons have, with the exception of H(2) protons in the europium complex, their signs opposed to that of phen protons. Although the pyridine protons (α, β and γ) are not separate, it seems not unlikely that the solvent protons shifts are dominated by dipolar interactions. This suggestion is strongly supported by the observation on Ln(fod)$_3$ phen [28] complexes (where fod = anion of 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione),according to which shift values of t-butyl and methine protons of the diketonate have their signs opposed to that of phen protons. The higher field shift of the H(2) proton in the pyridine solution of the europium complex suggests that the possibility of contact interactions cannot be ruled out for this nucleus. The area under the peak of the signal of coordinated pyridine indicates that only one solvent molecule enters the coordination sphere of the lanthanide. Thus, the europium complex, by accepting one pyridine, becomes ten-coordinate and in the case of ytterbium complex probably pyridine replaces the water molecule and the complex remains ten-coor-

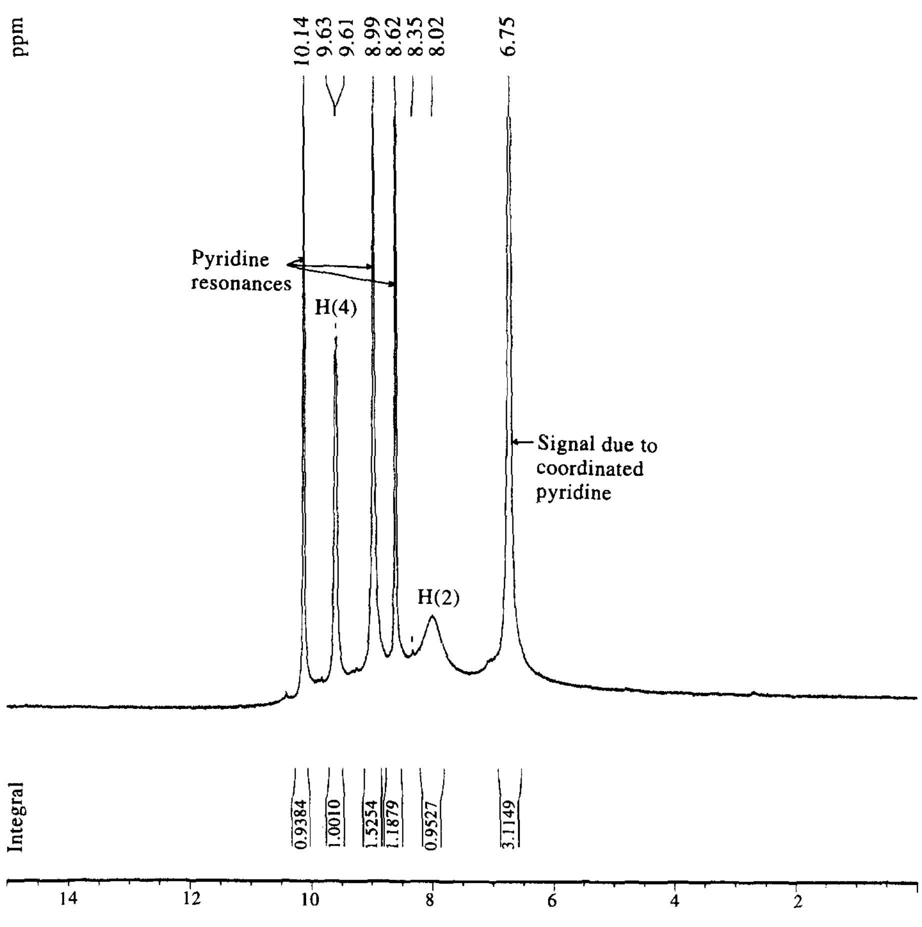


Fig. 2. The 300 MHz ^{1}H NMR spectra of [Eu(phen)$_3$(SCN)$_3$] in pyridine-d_5. Chemical shifts are expressed in ppm (δ) downfield from internal Me$_4$Si.

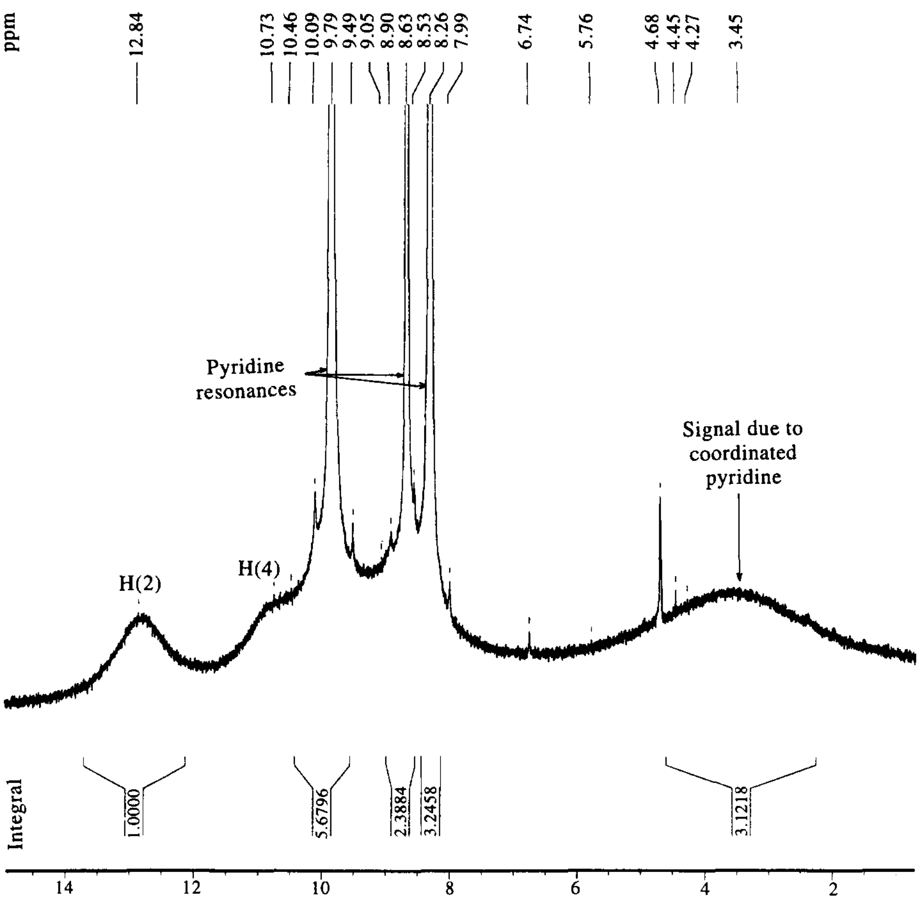


Fig. 3. The 300 MHz ^{1}H NMR spectra of [Yb(phen)$_3$(SCN)$_3$(H$_2$O)] in pyridine-d_5. Chemical shifts are expressed in ppm (δ) downfield from internal Me$_4$Si.

dinate. Both the complexes acquire similar geometries in this solvent. This suggestion is strongly supported by the observation that the ratios of the chemical shifts induced by europium and ytterbium metal ions are similar in magnitude. The Eu/Yb ratios are 0.88 and 0.89 for H(2) and H(4), respectively.

It would be interesting to obtain information about the structure of these complexes and the role played by thiocyanate ion, the molecule of the ligand and solvent molecule in the first coordination sphere of the lanthanide ion. Electronic spectroscopy appears quite sensitive method for investigating the coordination process in solution for lanthanide complexes. The next step in the study of these complexes, examined in this report, is to consider the influence of other ligands in the mixed-first coordination sphere of the lanthanides by investigating electronic spectra in different solvents and in the solid state. We pursue these matters in the following paper [35].

Acknowledgements—We express our thanks to Dr R. A. Vishkarma of the National Institute of Immunology, New Delhi and Dr Imtiyaz A. Ansari of the Indian Institute of Chemical Technology, Hyderabad, for their help in getting NMR spectra of the complexes. Thanks are also due to Dr B. T. Thaker of South Gujrat University, Surat and Dr Sharif Ahmad of this department for very kindly running the thermograms. This research was supported by University Grants Commission through a grant to K.I. which is gratefully acknowledged. One of us (A.K.S) thanks UGC for financial assistance in the form of research associateship. A.A.K. thanks Jamia Millia Islamia, for the grant of study leave to pursue this research.

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