Asian Journal of Chemistry Vol. 5, No. 3 (1993), 528–542

Synthesis and Characterisation of Lanthanide Nicotinates and Their Mixed Complexes Using Dimethylglyoxime, Salicylaldoxime and Pyridine-2-aldoxime as Secondary Ligands

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Simple complexes of the type $Ln(L)_3$ and mixed complexes of the type $Ln(L)_3(L')\cdot nH_2O$ where Ln = Y(III), La(III), Pr(III), Nd(III), Sm(III), Gd(III) and Dy(III), L = nicotinic acid, L′ = dimethylglyoxime, salicylaldoxime, pyridine-2-aldoxime and n = 2 or 3 have been prepared and characterised by a study of elemental analysis, electronic spectra, infra red spectra, thermoanalytical and conductivity measurements. The nmr spectra of La(III), Pr(III) and Dy(III) nicotinates and their mixed complexes have been recorded to elucidate the changes in chemical shift observed by these ions. A coordination number six and eight is suggested for the several lanthanide ions in simple and mixed complexes respectively.

INTRODUCTION

Rare earth chelates have received considerable attention because of their application to lasers[1]. The attractiveness of these materials lies in their relatively high efficiency of fluorescence, narrow emission lines and broad excitation bands. Hinckley[2] reported the influence of dipyridine adduct of europium-2,2,6,6-tetramethyl-3, 5-heptanedionato chelate [$Eu(thd)_3$] on the pmr spectra of cholesterol. Significant shifts were observed. Sanders and Williams[3] employed the chelate without the two molecules of pyridine and observed a four-fold increase in the magnitude of induced shifts owing to lack of composition with pyridine for coordination sites. It was reported[4] that nicotinic acid forms a series of salts with heavy metals but there is no information about its compounds with rare earths. Further it was stated that neodymium and samarium nicotinates appeared to have been used to prevent intravenous blood clots[4]. Chupakina and Serebrenikov[4] reported only a method of synthesis of rare earth nicotinates along

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with their analytical data. In view of the several uses of lanthanide chelates it was thought worthwhile to prepare and characterise lanthanide simple and mixed complexes with systems containing oxygen and nitrogen donors. This communication deals with the preparation and characterisation of simple lanthanide nicotinates and their mixed complexes using dimethyl glyoxime, salicylaldoxime and pyridine-2-aldoxime as secondary ligands.

EXPERIMENTAL

Spectrographically pure rare earth oxides used in this investigation were obtained from Bhaba Atomic Research Centre, Bombay. Solvents used were purified by standard methods. All the ligands, nicotinic acid (m.pt. 234–37°C) (BDH), dimethylglyoxime (m.pt. 239–240°C) (E. Merck), Salicylaldoxime (m.pt. 56°C) (BDH), pyridine-2-aldoxime (m.pt. 113°C) (Koch Light Lab Ltd.), employed in this investigation were recrystallized before use.

Preparation of Complexes

(i) *Lanthanide-nicotinates*: To a weighed amount of the rare earth chloride in ethanol a calculated amount of nicotinic acid in an ethanolic solution was added (keeping the metal to ligand ratio 1 : 3.5 approximately). The mixture was stirred and the pH of the solution was adjusted by alcoholic ammonia. The addition of alcoholic ammonia was stopped short of neutralization point. The pH of the solution was recorded and found to be 5.8. The solution was continuously stirred when the complex separated and was purified from ethanol and vacuum dried over calcium chloride for 48 hrs.

(ii) *Lanthanide-Nicotinic Acid Mixed Complexes using Dimethylglyoxime, Salicylaldoxime and Pyridine-2-aldoxime as Secondary Ligands*: The mixed complexes were prepared by mixing a weighed amount of lanthanide nicotinate in ethanol and a calculated amount of the second ligand (metal to ligand ratio 1 : 3.5 approximately). The mixture was stirred and alcoholic ammonia was added dropwise to short of neutralisation point. The resulting solution was concentrated on a steam bath when the solid separated. The complex was washed with ether or acetone as the case may be to remove excess ligand. The complexes were vacuum dried over fused calcium chloride for 48 hrs.

RESULTS AND DISCUSSION

The analytical data suggest the general composition of all the complexes as ML_3 or $ML_3L'\cdot nH_2O$ (M = Y, La, Pr, Nd, Sm, Gd or Dy; L = nicotinic acid, L′ = dimethylglyoxime, salicylaldoxime or pyridine-2-aldoxime; n = 2 or 3). The ligand nicotinic acid has exhibited two band maxima in UV region at 214 and 216 nm ($\log \varepsilon = 4.16$ and 3.76 respectively). Both the bands of the ligand are observed in all the lanthanide complexes with slight variation in position and intensification of absorption. The log ε values are in the range 4.17–4.70 in the complexes. The ligands dimethylglyoxime and pyridine-2-aldoxime have exhibited only one band 220 nm (log ε = 4.40), 240 nm (log ε = 4.09) respectively. In the dimethylglyoxime and pyridine-2-aldoxime mixed complexes two bands are observed at 217, 260 nm (log ε range 4.15–4.75) and 210, 240 nm (log ε range 4.16–4.80) respectively. This evidently means that both the primary and secondary ligand bands have merged with each other because of overlapping regions. The intensification of absorption and merging of primary and secondary ligand bands indicates involvement of ligands in bond formation with the several lanthanide ions.

The secondary ligands salicylaldoxime has exhibited two band maxima at 260 nm (log ε = 4.22), 305 nm (log ε = 3.78). In the yttrium, lanthanum, praseodymium and samarium mixed complexes three band maxima are located at 215, 255–260 and 300–305 nm, whereas in Pr, Gd and Dy complexes only two band maxima at 210 and 255 nm are located. The log ε values are in the range 3.61–4.80. From these changes one could as a first approximation talk about the involvement of the ligands in bonding with the several lanthanide ions.

In the visible region a red shift is observed in the characteristic bands of Pr^{3+}, Nd^{3+} and Sm^{3+} ions on complexation. The phenomenon of red shift[5] was explained as an expansion on the lanthanide orbit due to covalent bonding and contraction in highly electrostatic bonding. Jørgensen[6] explained this as nephelauxetic effect and tried to give a quantitative picture of the same. Angelov[7] tried to compare the shifted lanthanide transitions in the complexes with those of Ln^{3+} aquo ions. Sinha[8] tried to explain the covalency of M–L bonding in Nd^{3+} complexes and calculated the percentage covalency (δ). In the investigation the maximum red shift of a particular band in Pr is 3 nm, Nd 7 nm and Sm 13 nm. The covalency parameter ($b^{1/2}$) is 0.12, 0.078 and 0.051 for 13, 7 and 3 nm shifts. The δ values calculated according to the formula of Sinha are positive indicating slight covalent character. The spectral data along with the covalency parameter are detailed in Table 1.

Lanthanide nicotinates

In the infrared region of free ligand, nicotinic acid has exhibited a broad band of low intensity around 3300–3500 cm^{-1}. Most probably the existence of this band may be due to the following reasons. The spectra have been recorded as KBr disc and most probably as reported by Taylor[9] it might have absorbed moisture and the acid in the undissociated form and hence this band. Bellamy[10] reports that normally carboxylic acids exhibit free OH str vibrations between 3560 and 3500 cm^{-1}. Hence the existence of the band in the free ligand around 3300–3500 cm^{-1} is due to the free OH str and also one can say that the acid is in the unionised form. However, there is a band in all the lanthanide complexes around 3100–3360 cm^{-1}. This indicates the presence of water molecules. But a study of

TABLE 1
VISIBLE ABSORPTION AND COVALENCY PARAMETER OF Pr, Nd AND Sm COMPLEXES

Praseodymium chloride (water)			Complex (DMSO)	Wavelength		log ε	$b^{1/2}$	δ%
nm	cm^{-1}	log ε		nm	cm^{-1}			
440	22727	1.17	$Pr(NA)_3$	442	22624	0.97	0.048	0.462
468	—	0.87		465	21505	0.67	—	—
476	21008	0.82		478	20920	0.52	0.046	0.421
577	17331	0.55		580	17241	0.44	0.051	0.522
			$Pr(NA)_3(DMG)3H_2O$	442	22624	1.15	0.048	0.462
				465	21505	0.88	—	—
				478	20920	0.83	0.046	0.421
				580	17241	0.88	0.051	0.522
			$Pr(NA)_3(SAox)3H_2O$	442	22624	1.52	0.048	0.462
				465	21505	1.32	—	—
				478	20920	1.24	0.046	0.421
				580	17241	0.94	0.051	0.522
			$Pr(NA)_3(PAox)2H_2O$	442	22624	1.12	0.048	0.462
				465	21505	0.93	—	—
				478	20920	0.86	0.046	0.421
				580	17241	0.71	0.051	0.522

TABLE 1 (contd.)

Neodymium chloride (water)			Complex(DMSO)	Wavelength		log ε	$b^{1/2}$	δ%
nm	cm^{-1}	log ε		nm	cm^{-1}			
424	23584	0.73	$Nd(NA)_3$	505	19801	0.39	—	—
463	21598	0.64		517	19342	0.81	0.054	0.593
470	21276	0.64		572	17482	1.38	0.078	1.245
505	19801	0.77						
514	19455	1.01	$Nd(NA)_3(DMG)3H_2O$	505	19801	0.79	—	—
565	—	1.16		517	19342	0.99	0.054	0.593
665	15037	0.58		572	17482	1.39	0.078	1.245
725	13793	1.13						
			$Nd(NA)_3(SAox)3H_2O$	505	19801	0.94	—	—
				517	19342	1.08	0.054	0.593
				572	17482	1.42	0.078	1.245
				725	13793	1.11	—	—
			$Nd(NA)_3(PAox)2H_2O$	505	19801	0.74	—	—
				517	19342	0.94	0.054	0.593
				572	17482	1.36	0.078	1.245

TABLE 1 (contd)

Samarium chloride (water)			Complex(DMSO)	Wavelength		log	$b^{1/2}$	δ%
nm	cm^{-1}	log		nm	cm^{-1}			
400	25000	0.60	$Sm(NA)_3$	390	—	0.29	—	—
				398	—	0.78	—	—
				413	24213	0.22	0.125	3.25
			$Sm(NA)_3(DMG)3H_2O$	398	—	1.02	—	—
				413	24213	0.44	1.125	3.25
			$Sm(NA)_3(SAox)3H_2O$	398	—	1.58	—	—
			$Sm(NA)_3(PAox)2H_2O$	398	—	1.37	—	—

thermal analysis has indicated that the complexes are devoid of water. Hence one can say that the presence of these bands is due to the fact that KBr has absorbed moisture in which medium the spectra are recorded.

There is a band around 1700 cm^{-1} in the free ligand nicotinic acid which could be assigned to C=O str asymmetric mode and is shifted in all the complexes and observed between 1610–1650 cm^{-1}. This lowering is a clear indication of interaction of carbonyl oxygen with the lanthanide ions. Further the band observed around 1590 cm^{-1} which can be assigned to C=C and C=N str mode[12] practically remained unchanged in the complexes.

The band around 950 cm^{-1} in the free nicotinic acid which is due to characteristic pyridine ring vibration has undergone a significant positive shift in the lanthanide complexes now investigated and the shift is of the order of 20–30 cm^{-1}. This shift is almost similar to the shift postulated in a study of transition metal nicotinates[13] and hence one can say that the nitrogen of the pyridine ring is involved in coordination indicating that nicotinic acid has acted as a bidentate ligand. The i.r. spectral data is detailed in Table 2.

Lanthanide-Nicotinic Acid Mixed Complexes with Dimethyl Glyoxime and Salicylaldoxime

The primary ligand nicotinic acid has a broad band between 3300–3500 cm^{-1} and it can be attributed to the free OH str. The secondary ligands dimethyl glyoxime and salicylaldoxime have bands around 3400 and 3350 cm^{-1} respectively. These are due to OH of oxime and intramolecular hydrogen band in the ligands respectively. In the nicotinic acid-dimethyl glyoximates the maximum lowering is of the order of 300 cm^{-1}. From this lowering it can be said that the nitrogen of dimethyl glyoxime is involved in bond formation.

In a study of i.r. spectra of simple lanthanide salicylaldoximates[14] the band around 3350 cm^{-1} of the free ligand has been shifted to a lower frequency. From this observation it was postulated that the proton of the phenolic OH is eliminated. However the oxime porton was intact. In the mixed complexes now investigated the band around 3350 cm^{-1} of the lignd salicylaldoxime has been lowered and one can postulate an N–M bond from N–OH group and O–M bond from the phenolic group, with the elimination of phenolic proton.

The band around 1700 cm^{-1} in nicotinic acid due to C=O of the COO^- group is lowered in all the lanthanide mixed complexes and observed around 1600–1660 cm^{-1}. This lowering clearly indicates the involement of oxygen of the C=O group in bond formation with the several lanthanide ions. Both the secondary ligands have bands around 1620 cm^{-1} due to C=N str and these bands have merged with the lowered C=O str of the primary ligand.

The bands around 1590 and 1570 cm^{-1} of the primary ligand which are due to C=C and C=N str have been located in both the mixed complexes without

TABLE 2
INFRARED ABSORPTION BANDS (cm^{-1}) OF LANTHANIDE-NICOTINATES

Nicotinic acid	Y(III) complex	La(III) complex	Pr(III) complex	Nd(III) complex	Sm(III) complex	Gd(III) complex	Dy(III) complex	Assignment
3500 3300 bl	3300 3100 bm	3300 3100 bm	3300 3100 bm	3350 3200 bm	3300 3200 bm	3300 3100 bm	3360 3200 bm	OH str.
1700 ss	1650ss	1615 ss	1610 ss	1620 bs	1630 ss	1635 ss	1640 bs	C=O str.
1590 sm 1570 sh	1585 ss	1585 sm	1580 sm	1580 sm	1585 sm	1585 ss	1585 sm	C=C/C=N str.
950 l	975 sm	980 d 975 low	970 bl	970 bl	975 sl	975 sl	975 sl	Pyridine ring vibration

much variation. Of the secondary ligands only salicylaldoxime has a band around 1570 cm^{-1}.

The secondary ligand salicylaldoxime has a band around 1500 cm^{-1} which is due to *o*-substituted benzene ring vibration. There is no band in the primary ligand in this region. This band of the secondary ligand is lowered in the mixed complexes and also split into two inflections, 1495 and 1475 cm^{-1}.

In the nicotinic acid-dimethylglyoxime mixed complexes now reported the 950 cm^{-1} (pyridine ring vibration), 987 cm^{-1} (N–OH of oxime) respectively have suffered a positive shift. Such a positive shift of the pyridine ring vibration in transition metal nicotinates was observed[13] and hence one can say that the nitrogen of the pyridine ring and also nitrogen of the oxime are involved in bond formation. In the nicotinic acid-salicylaldoxime complexes also such a positive shift was observed in pyridine ring vibration of the primary ligand. The N–O str of oxime group of the secondary ligand salicylaldoxime at 965 cm^{-1} has not shown much vibration in the complexes. From the above observations it can be said that nicotinic acid and the secondary ligands have acted in a bidentate manner. The i.r. spectral data is detailed in Tables 3 and 4.

Lanthanide Nicotinic Acid-Pyridine-2-Aldoxime Mixed Complexes

The primary ligand nicotinic acid has a band around 3300–3500 cm^{-1} due to the moisture absorbed by the KBr disc in which medium the spectra are recorded.

Oximes normally exhibit bands between 3150–3300 cm^{-1} due to OH str 1620–1690 cm^{-1} due to C=N str and around 930 cm^{-1} due to N–O str. The secondary ligand PAo has an absorption band at 3350 cm^{-1} due to OH str of oxime. However Krause[15] in a study of i.r. spectra of pyridine-2-aldoxime observed that it differs from conventional oximes and the band around 3250 cm^{-1} is replaced by multiple bands between 3194–2791 cm^{-1}. This implies much stronger hydrogen bonding than in other oximes. In the PAo now investigated four bands are located in the region 2850–3150 cm^{-1} and these bands have been lowered, with a change in intensity in the lanthanide mixed complexes. This indicates that nitrogen of the oxime group is involved in bond formation. The band around 1700 cm^{-1} in the primary ligand nicotinic acid due to C=O of the COO^- group is lowered in all the mixed complexes and the lowering is of the order of 80 cm^{-1} indicating involvement of C=O group in bond formation.

In the ligand PAo in the region 1460–1600 cm^{-1}, there are four bands which are due to ring stretching vibration and the one at 1625 cm^{-1} is due to C=N str.

In the mixed complexes several bands are observed in this region (at least 4 to 5 bands). If one expects $C{=}N{-}O^{(-)}$ group[15], in the several lanthanide complexes, a fall in C=N str should be observed and the bands should be located aroud 1519–1505 cm^{-1}. In the lanthanide mixed complexes now investigated there is

TABLE 3

INFRARED ABSORPTION BANDS (cm^{-1}) OF LANTHANIDE-NICOTINIC ACID-DIMETHYL GLYOXIME MIXED COMPLEXES

Nicotinic acid	Dimethyl glyoxime	Y(III) complex	La(III) complex	Pr(III) complex	Nd(III) complex	Sm(III) complex	Gd(III) complex	Dy(III) complex	Assignment
3500 3300 bl	3400 b	3300 ss	3200 bm	3175 bm	3300 3100 bl	3200 bm	3200 bm	3200 bm	OH str.
1700 ss		1650sh					1650 ss	1695 sh 1650 ss	C=O of COO^-
	1620 bl	1600 ss	1620 ss	1620 ss	1620 ss	1625 ss	1600 ss		C=N str.
1590 sm			1590 sm	1590 sm				1595ss	C=C & C=N str. of pyridine ring
1570 sh		1570 ss		1575 ss	1580 ss				
950 l	978 ss	985 ss	985 ss	985 ss	985 ss	985 ss	985 ss	985 ss	N–O of oxime and pyridine ring vibration

TABLE 4

INFRARED ABSORPTION BANDS (cm^{-1}) OF LANTHANIDE NICOTINIC ACID SALICYLALDOXIME MIXED COMPLEXES

NA	SAox	Y(III) complex	La(III) complex	Pr(III) complex	Nd(III) complex	Sm(III) complex	Gd(III) complex	Dy(III) complex	Assignment
3500 3300 bm	3350 ss	3400 3300 bm	3100 3000 bm	3100 3040 bm	3100 3040 bm	3340 ss 3050 bl	3400 3000 bm	3380 3300 bm	OH str.
1700 ss		1655 ss				1635 ss	1660 sh 1640 ss	1645 ss	C=O of COO$^-$ group
	1620 ss		1620 ss	1625 ss	1625 ss	1615 sh			C=N str. of oxime
1590 sm		1595 ss	1595 ss	1595 dbl 1585 ss	1595 dbl 1585 ss	1590 ss	1590 ss	1590 ss	C=C & C=N str. of pyridine ring
1570 sh	1570 ss	1585 ss 1570 sm	1585 ss 1570 sm	1570 sm	1570 sl				
	1500 ss	1495 sh 1480 sm	1490 sl 1475 sl	1485 sl 1475 sl	1490 sh 1475 sl	1490 sh 1480 sm	1495 sh 1480 sl	1495 l 1480 l	*Ortho*-substituted benzene ring
950 l	965 sm	960 l	950 l	975 sl 950 l	975 sl 955 l	960 l	975 l 960 sl	965 sl	Pyridine ring vibration & N–O str. of oxime

TABLE 5

INFRARED ABSORPTION BANDS (cm^{-1}) OF LANTHANIDE NICOTINIC ACID-PYRIDINE-2-ALDOXIME MIXED COMPLEXES

NA	PAox	Y(III) complex	La(III) complex	Pr(III) complex	Nd(III) complex	Sm(III) complex	Gd(III) complex	Dy(III) complex	Assignments
3500 3300 } bl	3350 sm	3280 ss				3400 3000 } bl		3400 3000 } bl	OH str
	3150 sm	3180 bl	3180 bl	3190 sm	3180 sm		3180 sl		Multiple bands due to hydrogen banding in PAox
	3100sm	3120 l	3120 l						
		3065 l	3060 bl	3060 bl	3060 bl		3080 bl		
		3050 l	3000 sl	3000 sl	3000 sl		3000 sl		
	3000 sm	3000 sm					2910 bl	2920 l	
	2850 bm	2880 bm	2900 bm	2920 sl	2920 sl	2920 l			
		2800 sl	2800 l	2800 l	2800 l		2800 l		
1700 ss									
		1650 sm							
					1630 sm	1635 sm	1645 ss	1645 ss	C=O of COO^- group
	1625 ss			1625 ss					C=N str. of oxime
			1620 ss						
	1600 ss	1600 ss							Pyridine ring vib. of PAox
1590 sm		1590 sm	1595 dl	1595 dl	1595 dl	1595 dl	1595 dl	1595 ss	
			1585 ss	1585 ss	1585 ss	1585 ss	1580 ss	1580 ss	

TABLE 5 (*Contd.*)

NA	PAox	Y(III) complex	La(III) complex	Pr(III) complex	Nd(III) complex	Sm(III) complex	Gd(III) complex	Dy(III) complex	Assignments
1570 sh	1550 ss	1565 ss	1565 sm	1570 sl	1570 sl 1555 sh	1570 sl	1570 sl	1575 sh	C=C and C=N of pyridine ring
	1500 ss	1510 sl	1535 sm	1535 sm	1535 sm	1540 ss	1545 ss	1545 sm	
	1460 ss 1060 sl	1470 sl	1470 sl	1470 sl	1470 sl	1475 sl	1470 sl	1475 sm	
	1055 sh	1040 sm	1040 sm	1040 sm	1040 sl	1040 sl	1045 sl	1045 sl	N–O str. of C=N–OH
	975 ss	960 sl	975 sm 960 sl	975 sm 960 sl	975 sm 960 sl	975 sl	975 sm 960 sl	975 1	N–O of oxime
950 1	955 ss								Pyridine ring vibration

no absorption in the region 1519–1505 cm^{-1} except in yttrium complex where there is a band around 1510 cm^{-1} of very low intensity. This fact indicates that the oxime group in PAo is in the unionized form i.e. as C=N–OH(R) indicating that the OH of oxime is intact and the bonding is through nitrogen of the oxime group.

The bands around 1590 and 1570 cm^{-1} of the primary ligand due to C=C and C=N str of pyridine ring have merged with the ring vibrations of the secondary ligand and observed in all the mixed complexes with slight variation. The N–O str contributed by the presence of C=N–OH(R) group is located in the complexes around 1040 cm^{-1} indicating its presence in this group.

The band around 975 cm^{-1} of N–O str oxime is observed in all the complexes. Further the characteristic pyridine ring vibration around 950 cm^{-1} of the primary ligand has undergone a positive shift in the mixed complexes and observed around 960 cm^{-1} in the complexes.

From the above observations, it can be concluded that both the ligands have acted in a bidentate manner; further the oxime proton is not eliminated during complexation. The i.r. spectral data is detailed in Table 5.

A study of the thermal analysis of the complexes has shown that the simple lanthanide nicotinates are devoid of water molecules. However the dimethyl glyoxime, salicylaldoxime and pyridine-2-aldoxime mixed complexes do contain water molecules and are eliminated below a temperature of 170°C indicating that all of them are present as lattice water. The analysis further indicated the loss of the ligand in stages leading to the formation of the oxide.

In nmr spectra, both in La and Pr nicotinates the phenyl proton signals of the free ligand at 6.4, 6.85, 6.90, 7.2 (δ) ppm have exhibited a downfield shift and observed at 7.2, 8.0, 8.25 (δ) ppm for La and 8.3, 9.4, 9.45 (δ) ppm for Pr. These shifts indicate the stretching of nitrogen of pyridine ring and also the change in π electron density and indirectly prove the oxygen coordination from COO^- group. In the dysprosium-nicotinic acid complex no signal is observed.

In the lanthanum-nicotinic acid-dimethylglyoxime mixed complex a signal around 2.1 (δ) ppm is observed which could be assigned to the methyl groups. There are signals around 5.85, 6.7, 7.0, 7.45 (δ) ppm which are due to phenyl protons. There is a sharp signal at 9.65 (δ) ppm which is due to the oxime proton.

In the praseodymium-nicotinic acid-dimethyl glyoxime mixed complex signals are observed at 8.32, 9.4, 9.45 (δ) ppm. The 8.32 (δ) ppm signals could be assigned to the presence of phenyl protons. The 9.4 and 9.45 (δ) ppm signals could either be due to the downfield shift of the phenyl protons or the upfield shift of the oxime protons.

No signals were obtained in the dysprosium-nicotinic acid-dimethyl glyoxime mixed complex. The changes observed in the signals of phenyl protons and oxime protons in the complexes, when compared with those of the free ligand signals, indicate the nature of bonding of the ligands with the lanthanide ions.

The conductivity measurements of a few representative samples are recorded in the solvents methanol and DMF. The molar conductances of the several lanthanide complexes in these solvents are in the range 21.02–66.82, 5.48–12.12 ohm^{-1} $mole^{-1}$ cm^2 respectively suggesting the non-electrolytic nature of these complexes.[16, 17]

In conclusion a coordination number six and eight for the lanthanide ions in simple and mixed complexes respectively is suggested.

ACKNOWLEDGEMENTS

One of the authors (MVP) is grateful to Shri V.B. Pathak, Principal, Dharampeth Arts, Commerce and M.P. Deo Memorial Science College, Nagpur for the necessary permission to carry out research work and to Dr. G.N. Garud, Principal, VRCE, Nagpur, for the necessary facilities to carry out research work.

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(*Received*: 25 October 1991; *Accepted*: 10 October 1992) AJC-481.