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Synthesis and Spectral Studies on Lanthanide Mixed Complexes

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A few mixed complexes of La(III), Pr(III), Nd(III), Sm(III), Gd(III) and Dy(III) using *ortho*phenylene-diamine and 2,2′-bipyridyl as primary ligands and N-phenylthiourea and N-N′-diphenylthiourea as secondary ligands have been prepared. They are characterised by a study of elemental, spectral, conductivity and thermal analysis. The nature of bonding has been established by a study of infra-red spectra and it was observed that while the primary ligands are coordinated through nitrogens, thus acting as bidentate ligands and the secondary ligands are coordinated through sulphur acting as a unidentate ligand.

INTRODUCTION

Rare earth complexes with systems containing both nitrogen and oxygen donors have been reported[1–4]. The interest centred around the preparation and characterisation of mixed rare earth complexes where the second ligand is basically a neutral one[5, 6]. This communication details the preparation and characterisation of several lanthanide mixed complexes where *ortho*phenylene-diamine (OPDA), 2,2′-bipyridyl (Bipy) have been used as primary ligands and N-phenylthiourea (NPTU) and N-N′-diphenylthiourea (DPTU) as secondary ligands.

EXPERIMENTAL

Spectrographically pure rare earth oxides used in this investigation were obtained from Indian Rare Earth Limited, Udyogmandal P.O., Kerala, India. Solvents used were purified by standard methods. Ligands: OPDA m.pt. 100–101°C and PTU m.pt. 153°C (Koch Light Lab, England), 2,2′-bipyridyl m.pt. 70–71°C (BDH), were recrystallised before use. N-N′diphenyl-thiourea m.pt 152–153°C was synthesised adopting the method described by Vogel[7].

Preparation of Complexes

The simple lanthanide OPDA and 2,2′-bipyridyl complexes were prepared by the method of Rao *et al.*[4] The mixed complexes were prepared by mixing a calculated amount of the first stage complex in ethanol with a calculated amount of the second ligand in ethanol (m : 1 as 1 : 3.5). The pH of the resulting

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*C-2 Kanchangeet, 57, Shivajinagar, Nagpur 440 010, India solution was found to be 5.8. The solution was evaporated to dryness on a steam bath when the solid complex separated. The solid was washed with ether or acetone as the case may be to remove the excess ligand. The complexes were further purified from ethanol and vacuum dried for 48 h over fused calcium chloride. The analytical data of the several lanthanide complexes along with their molar conductance values are detailed in Table 1.

All the physico-chemical measurements were performed as reported earlier[1–4].

RESULTS AND DISCUSSION

A study of the spectra in the UV region gave information regarding the shift in wavelength, changes in intensity and the splitting pattern of the ligand bands if any.

The primary ligands, *i.e.*, OPDA and bipyridyl have three band maxima around 210 nm ($\log \varepsilon = 4.33$), 230 nm ($\log \varepsilon = 3.86$), 287 nm ($\log \varepsilon = 3.60$) and 210 nm ($\log \varepsilon = 3.83$), 235 nm ($\log \varepsilon = 4.07$), 277 nm ($\log \varepsilon = 4.21$) respectively. Further the secondary ligands PTU and DPTU have two bands each at 210 nm, 262 nm ($\log \varepsilon = 4.18$) and 212, 270 nm ($\log \varepsilon = 4.33, 4.31$) respectively. In the OPDA-PTU and NPTU complexes only two bands are located around 210 and 265 nm and the $\log \varepsilon$ values are in the range 4.77–5.18. In the bipyridyl-PTU complexes three band maxima are located around 207, 235, 265 nm and the $\log \varepsilon$ values are in the range 4.47–4.74. While in the bipyridyl-DPTU complexes only two band maxima are located in the complexes at 210, 272 nm except in La and Dy complexes where three band maxima are located at 210, 235, 270 nm. The $\log \varepsilon$ values are in the range 4.33–5.16. In all these situations a change in position of maxima and also intensity was observed. From these changes it can be said that there is involvement of the ligands in bond formation with the several lanthanide ions.

Visible Region

In this 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[8] was explained as expansion of the lanthanide orbit due to covalent bonding and contraction in highly electrostatic bonding. Jørgensen[9] explained this as nephelauxetic effect and tried to give a quantitative picture of the same. Angelov[10] tried to compare the shifted lanthanide transitions in the complexes with those of Ln^{3+} aquo ions. Sinha[11] tried to explain the covalency of M–L bonding in Nd^{3+} complexes and calculated the percentage covalency (δ).

As a first approximation if one tries to compare the red shift in the lanthanide complexes, now investigated, in the solvent dimethylsulphoxide the maximum red shift of a particular band in Pr is 10 nm, Nd is also about 9 nm and Sm 2–4 nm. The covalency parameter is around 0.08–0.1 where there is 9 nm–10 nm red shift and 0.043 to 0.06 where there is 2–4 nm red shift. Hence it can be said that the highest covalency parameter is shown in Pr.

TABLE 1
ANALYTICAL AND MOLAR CONDUCATANCE DATA OF REPRESENTATIVE LANTHANIDE MIXED COMPLEXES

Complex	% Found (Calc.)						Molar conductance ohm^{-1}mole^{-1}cm^{2}	
	C	H	M	N	Cl	S	DMSO	DMF
Nd(OPDA)$_3$(PTU)$_3$Cl$_3$H$_2$O	44.10 (44.67)	4.58 (4.77)	13.45 (13.75)	16.00 (16.03)	9.86 (10.16)	8.89 (9.16)	83.28	74.03
Sm(OPDA)$_3$(PTU)$_3$Cl$_3$H$_2$O	43.90 (44.37)	4.55 (4.74)	13.67 (14.25)	15.50 (15.90)	9.52 (10.10)	9.00 (9.10)	96.70	75.31
Nd(OPDA)$_3$(DPTU)$_3$Cl$_3$2H$_2$O	52.40 (52.86)	4.60 (4.94)	11.01 (11.15)	12.90 (12.98)	8.30 (8.23)	7.48 (7.41)	88.80	81.72
Sm(OPDA)$_3$(DPTU)$_3$Cl$_3$H$_2$O	53.10 (53.32)	4.69 (4.83)	11.60 (11.72)	12.95 (13.10)	7.97 (8.30)	7.46 (7.48)	91.60	92.71
Nd(Bipy)$_2$(PTU)$_3$Cl$_3$H$_2$O	47.41 (47.50)	3.86 (4.05)	13.24 (13.92)	13.30 (13.51)	9.84 (10.28)	9.10 (9.27)	88.30	89.20
Sm(Bipy)$_2$(PTU)$_3$Cl$_3$H$_2$O	47.30 (47.20)	3.85 (4.02)	14.04 (14.42)	13.12 (13.42)	9.80 (10.22)	9.14 (9.20)	96.40	92.57
Nd(Bipy)$_2$(DPTU)$_3$Cl$_3$H$_2$O	52.90 (56.01)	4.00 (4.27)	11.20 (11.41)	11.00 (11.07)	8.12 (8.40)	7.51 (7.55)	91.00	99.00
Sm(Bipy)$_2$(DPTU)$_3$Cl$_3$H$_2$O	55.00 (55.80)	4.07 (4.25)	11.65 (11.83)	10.97 (11.01)	8.21 (8.38)	7.41 (7.50)	97.30	97.80

OPDA = *Ortho*phenylene diamine; Bipy = 2,2′-Bipyridine; NPTU = N-Phenylthiourea;
DPTU = N-N′-Diphenylthiourea DMSO = Dimethyl sulphoxide; DMF = Dimethylformamide
Calculated values are given in parentheses.

On an examination of covalency parameter and percent covalency one can say that it is in the following decreasing order:

Pr > Nd > Sm

Infrared Region

Lanthanide-orthophenylene diamine-N-phenylthiourea mixed complexes: The primary ligand *ortho*phenylene diamine has two bands around 3340 and 3170 cm^{-1}. The 3340 cm^{-1} band is not observed in the complexes indicating that nitrogen is involved in bond formation. The 3170 cm^{-1} band is split into two inflections in La, Nd, Sm and Dy complexes. There are three bands in the secondary ligand N-phenylthiourea, around 3420, 3260 and 3180 cm^{-1}. The 3420 and 3260 cm^{-1} bands appear to have shifted to a higher frequency and 3180 cm^{-1} band might have merged with the 3170 cm^{-1} band of the primary ligand. From these changes of N-H str. frequency one can postulate that the primary ligand is bonded through nitrogen, whereas the nitrogen of the secondary ligand is not involved in bonding.

There is a band of low intensity between 3540 and 3570 cm^{-1} in La, Pr, Nd and Gd complexes due to OH str of water molecules[12].

Since both the ligands contain $-NH_2$ groups both of them exhibit bands in the 1580–1620 cm^{-1} region. The primary ligand band at 1620 cm^{-1} due to NH_2 deformation is lowered in the complexes and merged with the second ligand bands in this region. However the band around 1580–70 cm^{-1} in the primary ligand which is due to N–H bending could not be located in the complexes. One can say that it might have merged with the second ligand band around 1585 cm^{-1}.

The second ligand has bands at 1515, 1485 (sh), 1460 and 1445 cm^{-1}. The band around 1515 cm^{-1} (N–C–N str) is split into two inflections in La, Sm and Gd complexes. The band around 1485 cm^{-1} (NH_2 rocking) is shifted to higher frequency. Further the 1460 cm^{-1} band remained unchanged in the complexes. The one at 1445 cm^{-1} which is due to the coupled vibration NH_2 rocking, N–C–N bending and ν(C–S) str has exhibited slight change in position in all the lanthanide complexes.

Hence one can, as a first approximation, say that the secondary ligand is bonded through sulphur. There is also indirect proof of sulphur bonding from the changes of NH_2 str of the secondary ligand. The bands observed in the secondary ligand at 1075 and 1060 cm^{-1} which are due to the coupled vibration of N–C–N and ν(C–S) str have exhibited change in position and intensity indicating the presence of S–M bond. Further the bands in the region 815–700 cm^{-1} which are due to a coupled vibration of C–S and N–C–N str have either been lowered or could not be located in the complexes. From the above changes it can be said that *ortho*phenylene-diamine has acted as a bidentate ligand, indicating that the bonding is through nitrogens and N-phenylthiourea has bonded through sulphur exhibiting unidentate nature (Table 2).

Lanthanide orthophenylene diamine-N-N′ diphenyl thiourea mixed complexes: The primary ligand OPDA has a band around 3340 cm^{-1} which is due

TABLE 2

INFRARED ABSORPTION BANDS (cm^{-1}) OF LANTHANIDE *ORTHO*PHENYLENE DIAMINE-N-PHENYLTHIOUREA MIXED COMPLEXES

OPDA	PTU	La(III) complex	Pr(III) complex	Nd(III) complex	Sm(III) complex	Gd(III) complex	Dy(III) complex	Assignment
		3570–50 bm	3550 bm	3570–50 bm		3540 sm		O–H str
3340 bm	3420 bm 3260 bm	3430 ss	3430 ss	3410 ss	3440 ss	3415 ss	3440 ss	N–H str
3170 bm	3180 bm	3200 3180 bm	3180 bs	3180 3160 bs	3200 3180 bm	3170 bm	3200 3180 bm	N–H str
1620 low	1610 ss 1585 sm	1610 ss 1590 sm	1610 ss 1590 ss	1605 ss 1590 ss	1610 ss 1595 sm	1610 ss 1590 ss	1615 ss 1595 sm	NH_2 deformation
1580 1570 bm								NH_2 bending
	1515 bs 1485 sh	1510 1490 bm	1510 bm	1495 ss	1520 1500 sm	1515 1495 bm	1520 bs	N–C–N str
	1460 sl 1445 sm	1460 sm 1440 ss	1460 sm 1445 ss	1445 sm 1440 ss	1460 sl 1450 ss	1460 sm 1445 ss	1465 sm 1450 ss	N–C–N bending and ν(C–S) str
	1075 sh	1055 sm	1055 sl	1055 ss	1060 sl	1060 sm	1060 sl	N–C–N bending
	1060 sm							C–S str
	815 sm	806 sm		800 bl		810 sl		C–S str
	755 sm 700 ss	740 ss 695 bm	740 bm 690 bl	740 ss 690 sm	750 bm 695 bl	745 sm	745 sm 690 sm	N–C–N bending

to N–H str and is not observed in any of the complexes indicating that it is bonded through nitrogens. The one at 3170 cm^{-1} is split into two inflections in all the complexes except in praseodymium confirming the nitrogen bonding of the primary ligand.

The 3220 cm^{-1} band of the secondary ligand is not isolated distinctly since it might have merged with the primary ligand bands in this region. A band around 1610–1620 cm^{-1} is observed in La, Pr, Sm and Gd complexes and this can be assigned to the H–O–H bending mode of water molecules.

The bands around 1600–1590 cm^{-1} in the secondary ligand which are due to aromatic vibration and N–H bending mode have been observed without much variation and one can say that the nitrogen of the second ligand is not involved in bond formation.

The bands observed around 1620 cm^{-1} and 1580–70 cm^{-1} in the ligand orthophenylene diamine have been lowered and could not be located distinctly in the complexes suggesting nitrogen bonding from primary ligand *ortho*phenylene diamine.

The second ligand has exhibited three bands at 1545, 1495 and 1450 cm^{-1} which are due to N–H deformation, N–C–N str and N–H rocking, N–C–N bending respectively. All these bands have been shifted to higher frequency in all the lanthanide complexes indicating the non-involvement of nitrogen in the complexes. Such a phenomenon was observed in a study of copper[13] and lanthanide[14] complexes reported.

The bands around 1345 and 1315 cm^{-1} in the ligand N–N′ diphenylthiourea are mainly due to C–S str and part of C–N str. It was reported[14, 15] that these bands have been lowered or split into inflections in a study of its complexes. In this investigation also these bands have either been split into two inflections or lowered with change in intensity indicating sulphur coordination from this ligand.

The second ligand bands at 1070 and 1005 cm^{-1} which are due to N–C–N and asy C–N, N–H rocking respectively have practically remained unchanged or shifted to a higher frequency in some cases indicates the absence of N → M bond from the second ligand.

In this investigation the second ligand has exhibited four sharp bands at 765, 760, 700 and 690 cm^{-1}. Of these the 765 and 760 cm^{-1} which are due to 50% or more C–S str bands have been lowered and observed between 760 and 750 cm^{-1} in the complexes. The 700 cm^{-1} band is observed without any change while the 690 cm^{-1} band could not be located. From the above changes one can postulate S → M bond formation contributed from the second ligand.

Hence it can be said that the bonding to the lanthanide ions from the primary ligand is through nitrogen and the second ligand is bonded through sulphur. (Table 3).

Lanthanide 2–2′ bipyridyl–N–phenylthiourea mixed complexes: The ligand NPTU has three bands at 3420, 3260, 3180 cm^{-1} due to N–H str. In a study of simple lanthanide-N-phenylthiourea complexes[15], it was observed that the three bands in this region have exhibited a positive shift in the complexes indicating

TABLE 3

INFRARED ABSORPTION BANDS (cm^{-1}) OF LANTHANIDE *ORTHO*PHENYL DIAMINE N-N'-DIPHENYLTHIOUREA MIXED COMPLEXES

OPDA	DPTU	La(III) complex	Pr(III) complex	Nd(III) complex	Sm(III) complex	Gd(III) complex	Dy(III) complex	Assignment
3340 bm								N–H str
3170 bm	3220 bs	3200 3180 } bm	3200 bm	3180 3160 } bm	3180 3145 } bl	3180 3145 } bl	3180 3145 } bm	N–H str
1620 low		1615 sm	1620 sm		1610 sm	1610 sm	1610 bm	H–OH bending
	1600 ss 1590 ss		1600 1595 } cl	1600 sl 1595 sl	1590 1585 } dl	1590 1580 } dl	1585 sm	NH_2 bending
1580 1570 } bm	1545 bs	1550 ss	1530 ss	1535 1530 } bm	1540 bw	1540 sm	1555 sh	N–H deformation
	1495 sm	1495 ss	1500 ss	1500 sm	1490 ss	1500 ss	1490 sm	N–C–N str
	1450 ss	1470 sm 1450 ss	1455 ss	1470 sm 1455 ss	1460 sm 1450 ss	1445 ss	1450 sm	N–N rocking and N–C–N bending
	1345 ss	1350 1340 } sdl	1350 ss 1320 ss	1345 bs 1320 bm	1340 sm		1335 ss	Mainly from C–S str + part of C–N
	1315 ss	1320 bs	1300 ss		1310 ss	1310 dl	1315 sm	
	1070 sm 1005 ss	1075 bm 1010 sm	1080 sm 1010 sl	1080 sl 1015 low	1070 sm 1000 sm	1070 sm 1005 sm	1070 sm 1000 sm	N–C–N bend Sym C–N + N–H rocking
	765 ss 760 ss	760 bm 750 sh	760 ss	760 sm 750 sh	750 ss	755 ss	750 ss	50% or more C–S str + C–N str
	700 ss 690 ss	700 ss	705 ss	705 ss	700 ss	700 ss	700 ss	

non-involvement of nitrogen in bond formation. In the mixed complexes now reported these bands have been observed without any shift. This observation also indicates the non-involvement of nitrogen in bond formation.

All the complexes have water molecules and normally one would expect a band around 3200–3550 cm^{-1} due to OH str[12]. However the OH str of water molecules could not be isolated as they might have merged with the N–H str frequency of the secondary ligand.

The secondary ligand has exhibited two bands at 1610 and 1585 cm^{-1}, which are due to N–H bending and are observed without much change in the several lanthanide complexes. This observation not only gives information about the non-involvement of nitrogen but also gives indirect evidence for $S \rightarrow M$ bonding in the complexes contributed from the second ligand.

The primary ligand 2,2′-bipyridyl has exhibited two bands at 1580 and 1550 cm^{-1} which are the characteristic bipyridyl bands and could not be located in the lanthanide complexes.

In this investigation, there are four bands in the second ligand in the region 1515–1445 cm^{-1}. These bands are mainly due to N–C–N str and NH_2 rocking and practically remained unchanged in the complexes indicating the absence of N–M bond, giving thereby an indirect evidence for the presence of S–M bond from the second ligand.

The primary ligand 2,2′-bipyridyl has two bands at 1450 and 1415 cm^{-1}, which are characteristic bipyridyl bands. These bands could not be isolated distinctly, giving an indication that these bands have disappeared or merged with the bands of the secondary ligand in this region.

The primary ligand has exhibited two bands at 1270 and 1250 cm^{-1}, which are the characteristic vibrations of *ortho*-substituted pyridine ring system. These bands have been effected in the complexes exhibiting variation both in position and intensity.

The *ortho*-substituted pyridine ring vibration located around 1090–85 cm^{-1} in the free ligand is absent in all the lanthanide complexes except in lanthanum where it is located around 1090 cm^{-1}. The bands around 1075 and 1060 cm^{-1} of the second ligand which are due to the presence of N–C–N bending plus C–S str have exhibited a varied situation in the complexes. Nabar[16] reported that the band observed at 1062 cm^{-1} in N-phenylthiourea is very much weakened and observed with broadening and reduction in intensity in Cu(I) complexes. He postulated that there is a contribution of C–S stretch at this frequency and from the changes observed sulphur co-ordination was thought of. In the lanthanide complexes now reported, such a situation was observed and one can postulate sulphur coordination from N-phenylthiourea.

The pyridine ring bending mode of the primary ligand at 995 cm^{-1} is shifted to a higher frequency in the lanthanide complexes now reported. Such a situation was also observed by Sinha[17] in a study of rare earth 2,2′-bipyridyl simple complexes.

The bands observed in the secondary ligand NPTU at 815, 755 and 700 cm^{-1} are a contribution of C–S str and N–C–N bending. All these bands are effected on complexation both in position and intensity. Most of these bands have a contribution of 50% or more of C–S character and from these changes one can postulate S→M bonding from the secondary ligand.

The two bands of 2,2′-bipyridyl at 760 and 740 cm^{-1}, which are due to the out-of-plane ring hydrogens of bipyridyl, have also exhibited changes. From the above changes one can conclude that the primary ligand is bonded through nitrogens, while the secondary ligand is bonded through sulphur (Table 4).

Lanthanide 2-2′-bipyridyl N-N′-diphenylthiourea mixed complexes: The secondary ligand N-N′-diphenylthiourea has exhibited a broad band around 3220 cm^{-1} which is due to N–H st. This band remained unaltered in position in all the complexes indicating the non-involvement of nitrogen in bond formation.

Further the bands around 1600 and 1590 cm^{-1} which are due to aromatic vibration and N–H stretch have also been observed in the complexes. This fact also confirms that the nitrogen of the second ligand is not involved in bond formation.

The compounds do contain water molecules. The OH str and the H–OH bending mode in the respective regions have merged with N–H str and N–H bending respectively.

The primary ligand has two bands at 1580 and 1550 cm^{-1}, which are due to the characteristic bipyridyl bands, could not be isolated distinctly in the complexes, may be they have shifted in position and merged with the N–H deformation bands.

There are three bands at 1545, 1495 and 1450 cm^{-1} in the second ligand which are mainly due to N–H deformation, N–C–N str and NH rocking. These bands have been observed without much variation, clearly indicating that nitrogen of the ligand is not involved in bond formation.

The bands at 1345 and 1315 cm^{-1} which are mainly due to C–S str and part of C–N str have exhibited slight variation in position and intensity in the lanthanide mixed complexes now reported. However Deshpande[15] in a study of simple lanthanide diphenylthiourea complexes observed that the bands in this region have been considerably lowered in position and also split into two inflections, indicating the contribution S–M bonding as these bands are mainly due to ν (C–S).

The behaviour of these bands in the mixed complexes now reported in non-uniform; may be due to the partial C–N character. The changes in the N–H str indicate about the non-involvement of nitrogen in bonding and hence one can unhesitatingly say that there is S → M bonding from the second ligand.

The primary ligand 2-2′-bipyridyl has exhibited two bands at 1090, 1085 cm^{-1} due to the *ortho*-substituted pyridine ring system. The bands have been lowered, indicating the involvement of nitrogen of the primary ligand in bond formation. Most probably they have merged with the second ligand bands at 1070 cm^{-1} which are due to N–C–N band, and which have not exhibited any change in the complexes.

The band around 995 cm^{-1} of the primary ligand could not be located in the

TABLE 4

INFRARED ABSORPTION BANDS (cm^{-1}) OF LANTHANIDE-2-2′ BIPYRIDYL-N-PHYNYLTHIOUREA MIXED COMPLEXES

2-2′-bipyridyl	NPTU	La(III) complex	Pr(III) complex	Nd(III) complex	Sm(III) complex	Gd(III) complex	Dy(III) complex	Assignment
	3420 ss	3420 sm	3430 bm	3420 sm	3420 ss	3410 sm	3420 ss	
	3260 bm	3280–60 b	3280 dl	3280 dl		3260 bm	3260 low	N–H str
	3180 bm	3160 bl	3180 bm	3180 bl	3180 sm			
					3080 low	3170 low	3180 broad	
	1610 ss	1610 sm	1610 sm	1610 sm	1610 ss	1605 } sdl	1605 sm	N–H bending
	1585 sm	1590 sm	1585 sh	1590 dl	1595 sh	1595	1590 sh	
1580 sm								Bipyridyl bands
1550 sh								
	1515 bs	1530 } bdl	1515 bs	1515 sm	1515 sm	1510 bs	1515 bm	
		1515						N–C–N str
	1485 sh	1485 sh	1485 sh		1485–80 dl	1480 bm	1480 low	
	1460 sl	1460 sl	1460 sl	1465 sl	1460 sl		1460 low	
1450 sm	1445 sm	1445 sm	1445 sm	1440 sm	1450 } dl	1440 bm	1435 bm	NH_2 rocking
		1420 sl			1440			
1415 sm								N–C–N bending and ν(C–S) str
1270 sl		1245 sl	1275 sm	1275 } dl	1275 sm	1275 sm	1270 } dl	o-substituted pyridine ring
1250 sm			1265 sh	1260		1260 sh	1260	
		1230 sm	1230 sm	1230 sm	1230 sm	1230 sm	1230 sm	

2-2′-bipyridyl	NPTU	La(III) complex	Pr(III) complex	Nd(III) complex	Sm(III) complex	Gd(III) complex	Dy(III) complex	Assignment
1090 1085 } dl		1090 sl						*Ortho*-substituted pyridine ring
	1075 sh	1075 sl	1075 sh	1075 sh				N–C–N bending + C–S str
	1060 sm	1065 sm	1060 sm	1060 sm	1060 sm	1065 sh	1060 sm	
995 sm			1010 sl	1015 sm	1015 sm	1020 sm	1015 sm	Pyridine ring bending mode
			1000 sm					
	815 sm	815 sm	815 sm	815 ss	815 sm	815 sm	810 sm	C–S str + N–C–N bending
760 ss		765 755 } dl			770 sm	770 ss	770 ss	C–S str + N–C–N bending
	755 ss		755 ss	750 sm	755 sm	755 sm	750 sm	
					740 sm	740 sm	740 sm	Out of plane bending of hydrogen
740 sh								
	700 ss	700 sm	700 sm	695 sm	695 sm	695 sm	695 sm	

complexes indicating nitrogen involvement in bond formation. The other bands at 760 and 740 cm^{-1} which are due to out of plane bending of hydrogen are lowered and merged with the secondary ligand bands in this region.

The second ligand has bands in the region 765–690 cm^{-1} which are due to 50% C–S str and partially C–N character. Because of this even if there is an S → M bond the changes are not expected to be pronounced. However in the mixed complexes now investigated at least 5 bands are located in Nd, Sm, Gd and Dy complexes. Whereas in lanthanum and praseodymium complexes three and two bands respectively are observed. Hence the C–S character has effect on these bands upon complexation and hence S → M bond can be postulated from the second ligand (Table 5).

Thermal Analysis

A study of thermal analysis of neodymium *ortho*-phenylene diamine mixed complex with phenylthiourea and diphenylthiourea indicated that the water molecules in both the complexes are lost below 120°C indicating that they are present in both the complexes as lattice water. The reaction is as follows.

$$Nd(OPDA)_3(NPTU)_3Cl_3 \cdot H_2O \xrightarrow{120°C} Nd(OPDA)_3(NPTU)_3Cl_3$$

$$Nd(OPDA)_3(DPTU)_3Cl_3 \cdot 2H_2O \xrightarrow{120°C} Nd(OPDA)_3(DPTU)_3Cl_3$$

Further decomposition indicated that OPDA is eliminated > 375°C in NPTU and > 380°C in DPTU complex. Such an elimination of OPDA around and > 385°C was also observed in the thermal analysis of dysprosium simple complex[18]. The reactions are indicated as follows:

$$Nd(OPDA)_3(NPTU)_3Cl_3 \xrightarrow{220°C} Nd(OPDA)_2(NPTU)_2Cl_3 \xrightarrow{375°C} Nd(NPTU)_2Cl_3 \xrightarrow{565°C} NdCl_3 \xrightarrow{650°C} Nd_2O_3,$$

$$Nd(OPDA)_3(DPTU)_3Cl_3 \xrightarrow{280°C} Nd(OPDA)_1(DPTU)_2Cl_3 \xrightarrow{>380°C} Nd(DPTU)_1Cl_3 \xrightarrow{>550°C} NdCl_3 \xrightarrow{740°C} Nd_2O_3,$$

$$Dy(OPDA)_3Cl_32H_2O \xrightarrow{170°C} Dy(OPDA)_3Cl_3 \xrightarrow{230°C} Dy(OPDA)_2Cl_3 \xrightarrow{>385°C} DyCl_3 \xrightarrow{580°C} Dy_2O_3.$$

The elimination of OPDA in its simple and mixed complexes is around 380°C indicating that the ligand has exhibited the same thermal stability. Further in a thermal study of NPTU and DPTU simple lanthanide complexes it was observed[19] that NPTU and DPTU are eliminated around 600°C and >500°C

TABLE 5

INFRARED ABSORPTION BANDS (cm^{-1}) OF LANTHANIDE 2-2′-BIPYRIDYL N-N′-DIPHENYLTHIOUREA MIXED COMPLEXES

2-2′-bipyridyl	DPTU	La(III) complex	Pr(III) complex	Nd(III) complex	Sm(III) complex	Gd(III) complex	Dy(III) complex	Assignment
	3220 bs	3210 bs	3220 b	3220 bs	3220 sm	3210 bs 1625 low	3220 bs	N–H str
	1600 ss			1600 ss	1600 sm	1605 ss	1600 ss	N–H bending + aromatic
1580 sm	1590 ss	1590 sh	1585 sm	1595 sh	1590 sh	1595 sm	1590 sh	ring vibration
1550 sh	1545 bs	1540 1530 } bm	1550 sm	1550 sm	1550 sm	1550 bs	1550 ss	N–H deformation + C–N asy. str
	1495 ss	1495 1490 } sm	1495 ss	1495 sm	1495 m	1500 sm	1495 ss	N–C–N str
	1450 ss	1450 sm	1450 ss	1450 ss	1450 ss	1455 ss	1450 ss	NH rocking + N–C–N bending + C–S str
	1345 ss	1345 sm	1340 bs	1345 ss	1345 ss	1350 ss	1345 ss	mainly C–S str
1090 1085 } m. dl	1315 ss	1315 sm	1320bm	1320 sm	1315 sm	1320 sm	1315 sm	and part of C–N
	1070 sm	1070 sm	1070 sm	1075 sm	1070 sm	1075 sm	1070 sm	N–C–N bend + (C–S)
	1005 ss	1005 ss	1005 ss	1010 sm	1015 sm	1010 sm	1005 ss	str + sym. C–N + NH rocking
996 sm								
				770 sh	770 sh	770 sm	770 ss }	
760 ss	765 ss	760 ss	760 ss	765 ss	760 ss	760 ss	760 ss }	
	760 ss							50% or more
740 sh				740 sl	740 l	740 l	740 l }	C–S str + C–N str
	700 ss	700 ss	700 ss	705 ss	700 ss	700 ss	700 ss }	
	690 ss	690 sh		700 sh	695 ss	695 ss	695 ss }	

respectively. Such a thermal stability is exhibited in their lanthanide mixed complexes now reported.

Hence it can be concluded that irrespective of the fact that a particular ligand is present, either primary or secondary, the same thermal stability is exhibited.

The conductivity measurements of some representative lanthanide complexes have been measured in the solvents dimethylsulphoxide and dimethylformamide and the values are in the range 83.28 to 97.3, 74.03 to 99.0 $ohm^{-1}mole^{-1}\ cm^{-2}$ respectively. The values in both the solvents are in the range of 1 : 1 electrolyte system and agree with the values reported[20, 21].

From the above observations one can conclude that the lanthanides have exhibited a coordination number greater than six in the complexes reported.

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