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Synthesis and Characterisation of Lanthanide Thiourea Simple and Mixed Complexes using Urea, N-Phenylurea and N, N′-Diphenyl-Urea as Secondary Ligands

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Simple lanthanide complexes of the type $[Ln(L)_5(Cl)Cl_2.2H_2O$ and mixed complexes of the type $[Ln(L)_5(L')_3Cl]Cl_2.nH_2O$ where Ln = Y(III), La(III), Pr(III), Nd(III), Sm(III), Gd(III), Dy(III), L = thiourea, L′ = urea, N-phenylurea or N, N′-diphenylurea have been prepared and characterised by a study of u.v., visible and i.r. spectra, thermal analysis and conductivity measurements.

INTRODUCTION

Thiourea is potentially capable of forming bonds through both sulphur and nitrogen. In the study of Ti(IV) coordination complexes with thiourea, Rivest[1] postulated bonding through one of the nitrogens, while bonding through sulphur is reported in a study of bivalent transition metal thiocyanates[2]. Khan[3] in a study of Cr(III) simple and mixed complexes using thiourea, reported bonding through sulphur in simple complexes and through nitrogen in mixed complexes. In a study of Pt(II) and Pd(II) urea complexes,[4] coordination through nitrogen is postulated. While in a study of Cr(III), Zn(II), Cu(II) urea complexes, coordination occurs through oxygen. Literature survey revealed that in urea, thiourea and substituted ureas, the bonding is either through oxygen or nitrogen or sulphur. In view of this a systematic study of the several lanthanide complexes using thiourea as primary ligand and urea, N-phenylurea and N, N′-diphenylurea as secondary ligands is undertaken to understand nature of bonding in all the ligands stated above.

EXPERIMENTAL

Spectroscopically pure oxides of the rare earth elements were obtained from Indian Rare Earths Ltd., Kerala. Urea (m. pt. 132–133°C) and thiourea (m. pt. 179–180°C) of E. Merck quality were used after recrystallisation. The ligands N-phenylurea (m. pt. 147–148°C) and N, N′-diphenylurea (m. pt. 241–242°C) were synthesized adopting the procedure described by Vogel[5]. The visible and u.v. spectra were recorded on a Beckman D B Spectrophotometer as KBr disc. All conductance measure-

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ments were carried out on a systronic direct reading conductivity meter type 303. The thermal analysis of the complexes were carried out using MOM Budapest derivatograph.

Synthesis of complexes

The method adopted for the preparation of lanthanide complexes is basically the one reported by Rao *et al*[6]. The simple thiourea complexes were prepared by adding a calculated amount of thiourea (metal to ligand ratio *ca.* 1 : 5.5) in an ethanolic solution to a weighed amount of rare earth chloride in ethanol. The mixture was stirred and pH was found to be around 5.8. The solution was concentrated on a steam bath, when the solid complex separated. The excess ligand was washed with ether.

The mixed complexes were prepared by mixing a weighed amount of the corresponding lanthanide thiourea simple complex in an ethanolic solution with a calculated amount of (metal to ligand ratio 1 : 3.5) the secondary ligand, either urea, N-phenylurea or diphenylurea. The solution was stirred vigorously and the pH of the solution was recorded and found as 5.8. The resulting solution was concentrated on a steam bath, when the solid complex separated. The excess ligand was washed with a mixture of acetone and ether (1 : 1) ratio. The simple and mixed complexes were purified from ethanol and vacuum dried over fused calcium chloride for 48 hrs.

RESULTS AND DISCUSSION

The analytical data of the simple and mixed complexes suggest the general composition $M(TU)_5Cl_3{\cdot}2H_2O$ and $M(TU)_5(L')_3Cl_3{\cdot}3H_2O$ respectively, (where M = Y, La, Pr, Nd, Sm, Gd or Dy; TU = thiourea and L' = urea, N-phenylurea or N,N'-diphenylurea).

Ultraviolet

In this region, band shifts and intensity alterations of the ligands alone indicate the involvement of ligands in complexation with the lanthanide ions. U.V. spectra is recorded in methanol. Primary ligand, thiourea exhibits two bands at 204 nm (log ϵ 3.75) and nm 238 (log ϵ 4.07). In all lanthanide thiourea simple complexes, two bands are observed around 204–206 nm (log ϵ 4.44–4.53) and 240–242 nm (log ϵ 4.70–4.84). Of the secondary ligands urea exhibits a band at 207 nm (log ϵ 0.9). N-phenylurea exhibits two bands at 203 nm (log ϵ 4.06), 234 nm (log ϵ 4.18) and N-N' diphenylurea exhibits two bands at 203 nm (log ϵ 4.32) and 250 nm (log ϵ 4.45). In all the mixed complexes only two bands are located. In thiourea—urea mixed complexes the bands are observed at 202–204 nm (log ϵ 4.27–4.61) and 240 nm (log ϵ 4.60–4.82), in thiourea

N-phenylurea complexes around 203–208 nm (log ϵ 4.77–4.89) and 236–237 nm (log ϵ 4.97–5.12) and in thiourea-N-N'-diphenylurea complexes around 202–206 nm (log ϵ 5–5.6) and 244–248 nm (log 5.14–5.20). The shift in the band maxima and intensification of absorption indicate the involvement of ligands in complexation with lanthanide ions.

Visible Region

Visible spectra of Pr(III), Nd(III) and Sm(III) simple and mixed complexes are recorded in DMSO solution where a red shift has been observed in some of the characteristic bands of lanthanides. The covalency parameter $b^{1/2}$ and the % covalency[7,8] δ have been calculated where there is a red shift. In this investigation in Pr, Nd and Sm complexes it was observed that the red shift of a particular band observed is almost the same in the above lanthanide ions. This is a very interesting observation since hitherto reported results indicate[9] that always a maximum red shift of a particular band is observed either in the case of Nd or Pr. The red shift observed in this investigation of a particular band in all the above lanthanides is around 6 nm i.e. Pr (6 nm) = Nd (6 nm) = Sm (6 nm). The covalency $b^{1/2}$ is around .071–.08 in all the cases. The values calculated according to Sinha's formula are positive indicating a slight covalent character. Since the extent of red shift is almost equal in all these lanthanide ions, it can be said that the extent of coordination for the ligand is almost the same.

Infra-red

The details of i.r. data are summarized in Table 1. The primary ligand thiourea has exhibited three bands in the region 3375–3340, 3245 and 3160–3140 cm^{-1} due to NH stretch. In all the lanthanide simple complexes reported these bands have remained unchanged. This suggests that nitrogen is not involved in complexation.

The secondary ligands urea, N-phenylurea and N-N'-diphenylurea have bands around bands 3400–3340 cm^{-1} which are due to NH stretch. All these are observed without any change in urea and DPU complexes in position indicating the non-involvement of nitrogen in complexation. However in N-phenylurea complexes there is considerable lowering in the N-H stretch indicating involvement of nitrogen in complexation. The secondary ligand urea has two bands at 1670, 1610 cm^{-1} which are due to C=O stretch and coupled C=O and NH$_2$ bending vibration. Similarly N-phenylurea and diphenylurea do have bands in the C=O stretch region. From the changes observed in this region the nature of bonding is postulated. In the urea mixed complexes C=O stretch has completely disappeared while in diphenylurea complexes it is lowered by about 20 cm^{-1}. In the N-phenylurea complexes the C=O stretch around 1660 cm^{-1} remained

TABLE I

INFRARED ABSORPTION BANDS (cm^{-1}) OF LANTHANIDE THIOUREA SIMPLE AND MIXED COMPLEX

TU	U/NPU/ DPU	Y(III) Complex	La(III) Complex	Pr(III) Complex	Nd(III) Complex	Sm(III) Complex	Gd(III) Complex	Dy(III) Complex	Assignments
3375 3340 bm		3365 3340 bm	3340 3250 bs	3350 bs	3360 3340 bm	3360 3340 bm	3340 4230 bs	3370 bs	NH stretch
3245 bl		3240 bl		3260 3240 bm	3245 3240 bm	3140 3120 bl	3160 3140 bm	3280 3260 bm	
3160 3140 bl		3150 bl	3150 bl	3145 sl	3145 sl			3170 sm	
1585 ss		1575 sm	1575 ss	1580 ss	1580 ss	1580 ss	1575 ss	1585 ss	NH_2 deformation
1460 sm		1455 sl	1455 sl	1460 ss	1455 sm	1455 sm	1450 sl	1460 ss	N—C—N assy. stretch
1425 sm		1420 bl	1425 1410 bm	1425 sl	1420 sl	1420 l	1420 bm	1430 sl 1395 l	C—S symm. stretch
1380 sl			1375 l	1380 l			1380 l	1385 l	
1090 sm		1085 bl	1085 sm	1090 sm	1085 sl	—	1085 sm	1090 sm	NH_2 Rocking
735 730 lbl 720 sl		725 720 sl	720 sm	730 720 lbl	725 715 ldl	710 l	720 sm	730 725 ldl	νC—S+N—C—N stretch
	Urea								
	3400 ss 3340 ss	3480 3120 bl	3460 3120 bm	3020 3280 bm	3400 3100 bm	3410 3100 bm	3300 3000 bm	3420 3120 bm	NH frequency
	1670 sm								C=O str. of urea
	1610 bm	1570 bm	1610 l 1580 bm	1580 sl	1620 1560 bm	1620 1600 bm 1590 1570 bm	1580 1550 bm	1610 1580 bm	Coupled C=O and NH_2 bedning vibration NH_2 deformation

1460 sm	1455 bl 1380 bl	1460 sm 1425 l	1460 l 1430 sl	1460 l 1405 bm	1455 sm	1450 bl 1420 l	1455 sm 1425 l	N—C—N assy. stretch
							1390 bl 1380	C—S Symm. stretch
1150 sm	1150 bm 1085 bl	1155 sm 1085 sl	1150 sl 1080 bl	1150 sm 1080 sm	1150 bm 1080 sl	1145 bm 1085 bl	1150 sm 1080 sm	NH_2—rocking
	720 sl	720 sm	690 ss	725 sm	720 sm	720 sm	725 sm	νC—S)+N—C—N str.
N—PU								
	3480 sm	3460 sm	3460 sm	3460 sm	3460 sm	3460 sm	3460 sm	OH str. of water
3400 sm 3300 sm	3320 bm 3360 sl 3160 sl	3320 bm 3360 bm 3165 sl	3340 3320 bm 3260 3165 bm	3340 3320 bm 3260 sh 3170 bm	3340 3320 bm 3160 sl	3340 3300 bm 3260 bm 3165 sl	3340 3240 bm 3160 sl	N—H stretch
1660 ss 1620 ss	1655 sm	1660 sm	1665 sm	1660 sm	1655 sm	1660 sm	1655 bm	C=0, NH_2 bending mixed vibr.
1590 sm	1600 sm	1600 sm	1600 sm	1605 sm	1600 bm	1600 sm	1600 bm	NH_2 bending
	1880 sm	1580 sl	1580 sm	1580 sm	1580 sm	1580 sm	1575 bm	C=O+NH_2 mixed vibration NH_2 deformation
N—PU								
1445	1435 sm	1435 sm	1440 sm	1440 sm	1435 sm	1440 sm	1435 sm	N—C—N assy stretch
	1390 sm 1345 sm	1390 sm 1345 sm	1390 bm 1345 bm	1390 bm 1345 sm	1390 sm 1345 sm	1390 sm 1345 sm	1390 sm 1345 sm	C—S symm. str.
1120 sl	1150 sl 1090 sl	1150 sl 1090 sl	1150 sl 1090 sl	1150 sl 1090 sl	1150 sl 1095 sl	1150 sl 1095 sl	1150 sl 1090 sl	NH_2 rocking
	725 sm 695 sm	720 sm 695 sm	725 sm 695 sm	730 sm 700 sm	725 sm 695 sm	725 sm 695 sm	725 sm 695 sm	ν(C—S)+N—C—N stretch

TABLE 1 (contd.)

TU	U/NPU/ DPU	Y(III) Complex	La(III) Complex	Pr(III) Complex	Nd(III) Complex	Sm(III) Complex	Gd(III) Complex	Dy(III) Complex	Assignments
	NN'DPU								
	3340 sm	3340] bm	3320 bm	3310 sm	3320 sm	3310 sm	3320 bm	3320 bm]	NH stretch
	3320] bm	3240]	3260 bm	3250 sm	3260 sm	3260] bm	3280 bm	3260 bm]	
	3300]	3160 bm	3160 bm	3160] bm	3180] bm	3240]	3170 sm	3160 bm]	
				3140]	3140]	3140 bm			
	1655 ss	1630 bm	1635 bm	1640 ss	1635 sm	1635 sm	1645 sm	1640 bm	C=O stretch
		1580 sm	1590 sm	1585 sm	1585 ss	1585 sm	1590 sm	1585 sm	NH_2 deformation
	1455 ss	1460 sm	1460 sl	1460 sl	1460 sl	1460 bm	1460 sm	1460 sl	N—C—N str.
	1445 sm	1430 sm	1435 sm	1430 sm	1440 sh	1440] sm	1445] m	1445] m	
					1430 sm	1430] dl	1430] dl	1435] dl	
		1380 sh	1380 sh	1390] l	1380 bl	1380 l	1385 l	1390 bl	C—S sym. stretch
				1380] dl					
		1305 sm	1310 sm	1305 sm	1305 sm	1310 sm	1310 sm	1310 sm	
	1160 sl	1150 sm	1155 sl	1150 sl	1150 sm	1150 sm	1155 sm	1155 sl	NH_2 rocking
		1085 bl	1080 sm	1090 bm	1080] bm	1080 sl	1090 l	1090 bm	
					1075]				
		735 sh	736 sl	730 sl	735 sh	735 sl	735 sl	735 sl	ν(C—S)+N—C—N stretch
		720 l	725 l		720 l		720 l	725 l	
		690 ss	690 ss	690 ss	690 ss	695 ss	695 sm	695 sm	

without any change in most of the complexes. These observations indicate that urea and NN'DPU are coordinated through oxygen while in N-phenylurea the bonding is through nitrogen. Further this is supported by the changes observed in N-H stretching frequency. The NH_2 bending vibrations in N-phenylurea around 1620 cm^{-1} is lowered in all the complexes which also confirms nitrogen bonding.

The NH_2 deformation at 1585 cm^{-1} of thiourea has remained stationnary in all the simple and mixed complexes indicating the none involvement of nitrogen of primary ligand in bond formation.

$N\text{-}C\text{-}N_{assym.}$ stretching is observed around 1460 cm^{-1} in thioureas. This is observed with lowering in all simple complexes. Such a lowering has been attributed by Manas and Bhatia[10] to sulphur coordination. The secondary ligands urea and N-phenylurea exhibit N-C-N stretch at 1460 and 1445 cm^{-1} respectively and there are two bands around 1455, 1445 cm^{-1} in diphenylurea. The 1460 cm^{-1} band of urea is lowered while in diphenylurea complexes the 1455 cm^{-1} band is slightly shifted to higher frequency and is observed around 1460 cm^{-1} and the 1445 cm^{-1} band is lowered in Y, La, Pr, Nd complexes and in the other complexes it is split into two inflections. All these observations support that oxygen of $C=O$ is involved in bonding. In the N-phenylurea complexes there is not much change in this N—C—N stretch which supports nitrogen bonding.

$C\text{-}S_{sym.}$ stretching of thiourea at 1425–1380 cm^{-1} is observed with variation i.e., they are reduced in intensity, lowered and split into inflections, indicating involvement of sulphur in coordination both in simple and mixed complexes.

The NH_2 rocking of primary ligand thiourea at 1099 cm^{-1} has been observed without any change in position or intensity giving conclusive evidence of non-involvement of nitrogen in coordination indicating sulphur coordination.

NH_2 rocking observed in urea around 1150 cm^{-1} is observed without any change indicating non-involvement of nitrogen in bond formation. However NH_2 rocking in N-phenylurea at 1120 cm^{-1} is shifted to higher frequency at 1150 cm^{-1}. This change can be taken as an indication of nitrogen bonding. NH_2 rocking of diphenylurea at 1160 cm^{-1} is observed without much change.

The ν(C–S) and N–C–N coupled vibration of the primary ligand has exhibited a doublet around 725–730 cm^{-1} and a sharp band at 720 cm^{-1} in the free ligand. The doublet is lowered and merged with 720 cm^{-1} band in the simple complexes while in mixed complexes two bands are observed in this region with variation in intensity and position, suggesting the involvement of sulphur of the primary ligand in bond formation.

Thermal analysis

The study of elemental analysis has shown that the complexes contain water molecules. To confirm whether they are present at lattice or coordinated water the thermal analysis of neodymium simple and mixed complexes has been carried out. From the analysis it is observed that the water molecules are lost below 150°C indicating their presence as lattice water. Further analyses indicate the loss of both primary and secondary ligands in stages leading to the formation of sesquioxide.

Conductivity

The molar conductances of Pr(III) and Dy(III) simple and mixed complexes have been measured in the solvent methanol. The molar conductances are in the range of 167–208 ohm^{-1} mol^{-1} cm^{2}. In a study of conductivity in methanol of some lanthanide nitrates Vicentini *et al*[11] reported conductance values in the range of 189-220 ohm^{-1} mol^{-1} cm^{2} for 1 : 2 electrolyte systems. Hence it can be concluded that all simple and mixed complexes exhibit 1 : 2 electrolyte systems in methanol. Lanthanides exhibit coordination number six in the simple complexes and nine in all mixed complexes.

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