

Preparation and characterisation of lanthanide complexes using substituted ureas and thioureas as ligands

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Abstract

Simple complexes of the type $\text{LnL}_3\text{Cl}_3 \cdot n\text{H}_2\text{O}$, where $\text{Ln} = \text{Y(III)}, \text{La(III)}, \text{Pr(III)}, \text{Nd(III)}, \text{Sm(III)}, \text{Gd(III)}$ and Dy(III) , $\text{L} = \text{N-phenylurea}, \text{N-N' diphenylurea}, \text{N-phenylthiourea}, \text{N-N' diphenylthiourea}$ have been prepared and characterised by a study of elemental analysis, electronic spectra, infrared spectra, thermoanalytical and conductivity measurements. The presence of lattice-held and coordinated water molecules is inferred from thermal analysis. All the complexes behave as 1:1 electrolytes in methanol, dimethylformamide or dimethylsulphoxide. A coordination number of six or eight is postulated for several of the complexes reported.

Key words: Lanthanides, substituted ureas and thioureas, electronic and infrared spectra, covalency parameter, coordination number.

1. Introduction

Several transition metal complexes of N-phenylurea and N-N' diphenylurea have been reported. In most cases, the complexes were characterised by elemental analysis and spectral data¹. Complexes of $\text{Cu}^{2,3}$, $\text{Ni(II)}^{4,5}$, Pt(II) and $\text{Pd(II)}^{6,7}$, tellurium⁸, Ag(I)^9 , Ru(II)^{10} , Zn(II) , Cd(II) , Hg(II)^{11} with phenylthiourea and diphenylthiourea as ligands have been investigated by standard analytical and spectral methods and, in some cases, magnetic data have also been recorded. A spectrophotometric study of Cu(II) with orthohydroxyphenylthiourea¹² has been reported. Kinetics and mechanism of oxidation of thiourea and N-substituted thioureas by hexacyanoferrate(III) under acid conditions has

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been studied¹³. Recently, complexes of dichlorodicarbonylruthenium(II) of the formula $[\text{RuCl}_2(\text{CO})_2\text{L}_2]$, (L = tetramethylthiourea; monomethylthiourea) and $[\text{RuCl}_2(\text{CO})_2\text{L}']$, (L' = diaminomethane or tetramethylurea) have been reported¹⁴. The interaction of antimony(III) halides with amides and tetramethylurea in 1,2 dichloroethane solution has been reported¹⁵. Preparation of monosubstituted thiourea complexes of molybdenum carbonyl $[\text{Mo}(\text{CO})_5\text{L}]$ both by thermal and UV irradiation methods has been described¹⁶. The ligands used were N-N' dimethylthiourea (DMTU), N-N' diphenylthiourea (DPTU), tetramethylthiourea (TMTU) and tetraethylthiourea (TETU).

Lanthanide complexes with substituted ureas such as tetramethylurea¹⁷, acetylurea¹⁸, dimethyl and diethylureas¹⁹ as well as with substituted ureas²⁰ have been synthesised. The synthesis of mixed complexes of the europium ion with certain nitrogen-containing ligands such as 2 pyridyl-carbonyl-N-oxide, 2,2' bipyridyl and 1,10 phenanthroline has also been reported²¹.

In this paper, we report the preparation and characterisation of lanthanide complexes of phenyl and diphenylureas and thioureas as ligands.

2. Experimental

2.1. Materials

Spectroscopically pure rare earth oxides were obtained either from the Bhabha Atomic Research Centre, Bombay, or from the Indian Rare Earths Limited, Udyogmandal, Kerala, India. Solvents were purified by standard methods.

2.2. Ligands

The ligands, N-phenylurea (m.p. 147–148°C), N-N' diphenylurea (m.p. 241–242°C), N-N' diphenylthiourea (m.p. 152–153°C) were synthesised as described by Vogel²². N-phenylthiourea (m.p. 153–154°C) was synthesised by the method of Davis and Underwood²³.

2.3. Preparation of complexes

Rare earth chloride in ethanol was reacted with the ligand in an ethanolic solution (keeping the metal ligand ratio 1:3.5). The mixture was stirred and the solution was concentrated on a steam bath to obtain the solid complex. The complex was washed with acetone to remove the excess ligand and further purified by recrystallisation from ethanol. The pure complex was dried in vacuum over fused calcium chloride. The analytical data of the complexes and their molar conductance values are given in Table I.

2.4. Physical measurements

The ultraviolet spectra (in methanol) and visible spectra (in DMSO) were recorded using a

Table I
Analytical and molar conductance data of lanthanide phenylurea and N-N' diphenylurea complexes

Complex	Percentage of			Molar conductance					
	Carbon	Hydrogen	Metal	Nitrogen	Chloride	Sulphur	Methanol	DMF	DMSO
Y(NPU) ₃ Cl ₃ ·3H ₂ O	38.20 (38.33)	4.40 (4.54)	13.40 (13.52)	12.6 (12.77)	16.10 (16.20)		85.1	79.14	82.59
La(NPU) ₃ Cl ₃ ·3H ₂ O	35.46 (35.62)	4.18 (4.24)	19.50 (19.63)	11.13 (11.87)	14.71 (15.05)				
Pr(NPU) ₃ Cl ₃ ·3H ₂ O	35.40 (35.52)	4.17 (4.22)	19.56 (19.86)	11.52 (11.84)	14.92 (15.01)				
Nd(NPU) ₃ Cl ₃ ·3H ₂ O	35.00 (35.35)	4.04 (4.20)	19.10 (20.23)	11.56 (11.78)	14.54 (14.94)				
Sm(NPU) ₃ Cl ₃ ·3H ₂ O	34.94 (35.05)	3.95 (4.17)	20.50 (20.91)	11.10 (11.68)	14.11 (14.81)		97.20	78.90	68.36
Gd(NPU) ₃ Cl ₃ ·3H ₂ O	34.57 (34.73)	4.01 (4.13)	20.83 (21.66)	11.03 (11.57)	14.2 (14.67)				
Dy(NPU) ₃ Cl ₃ ·3H ₂ O	34.25 (34.47)	4.02 (4.10)	22.18 (22.22)	11.04 (11.49)	14.14 (14.56)		103.12	86.20	74.76
Y(DPU) ₃ Cl ₃ ·2H ₂ O	53.55 (53.95)	4.50 (4.61)	10.10 (10.25)	9.67 (9.68)	3.11 (3.28)		106.2	85.60	93.72
La(DPU) ₃ Cl ₃ ·2H ₂ O	50.95 (51.01)	4.25 (4.36)	14.9 (15.15)	9.12 (9.15)	11.37 (11.61)				
Pr(DPU) ₃ Cl ₃ ·2H ₂ O	50.50 (50.90)	4.29 (4.35)	15.21 (15.32)	8.95 (9.13)	11.10 (11.58)				
Nd(DPU) ₃ Cl ₃ ·2H ₂ O	50.55 (50.72)	4.11 (4.33)	15.47 (15.63)	8.91 (9.10)	11.50 (11.54)				

(continued)

Table 1 (continued)

Complex	Percentage of				Molar conductivity ohm ⁻¹ mole ⁻¹ cm ²				
	Carbon	Hydrogen	Metal	Nitrogen	Chloride	Sulphur	Methanol	DMF	DMSO
Sm(DPU) ₃ Cl ₃ ·2H ₂ O	50.12 (50.39)	4.12 (4.30)	16.00 (16.19)	8.71 (9.04)	11.20 (11.57)		118.5	91.47	83.53
Gd(DPU) ₃ Cl ₃ ·2H ₂ O	50.01 (50.03)	4.15 (4.27)	16.80 (16.81)	8.90 (8.98)	11.10 (11.39)				
Dy(DPU) ₃ Cl ₃ ·2H ₂ O	49.50 (49.73)	4.17 (4.25)	17.15 (17.27)	8.89 (8.92)	11.21 (11.32)		110.25	86.66	80.58
Y(NPTU) ₃ Cl ₃ ·3H ₂ O	35.40 (35.72)	4.01 (4.25)	12.21 (12.60)	11.52 (11.90)	15.01 (15.09)	13.35 (13.51)	83.42	88.48	107.01
La(NPTU) ₃ Cl ₃ ·3H ₂ O	33.10 (33.35)	3.50 (3.97)	18.08 (18.39)	10.90 (11.11)	13.90 (14.09)	12.35 (12.70)			
Pr(NPTU) ₃ Cl ₃ ·3H ₂ O	33.17 (33.27)	3.52 (3.96)	18.51 (18.60)	10.93 (11.09)	13.91 (14.06)	12.13 (12.67)			
Nd(NPTU) ₃ Cl ₃ ·3H ₂ O	33.00 (33.12)	3.71 (3.94)	18.89 (18.95)	10.69 (11.04)	13.94 (13.99)	12.43 (12.61)			
Sm(NPTU) ₃ Cl ₃ ·3H ₂ O	32.50 (32.86)	3.80 (3.91)	19.50 (19.61)	10.05 (10.95)	13.21 (13.81)	12.30 (12.51)	78.51	77.60	88.11
Gd(NPTU) ₃ Cl ₃ ·3H ₂ O	32.30 (32.58)	3.63 (3.87)	20.14 (20.32)	10.51 (10.86)	13.58 (13.76)	12.12 (12.40)			
Dy(NPTU) ₃ Cl ₃ ·3H ₂ O	32.10 (32.35)	3.67 (3.85)	20.10 (20.86)	10.22 (10.78)	13.16 (13.67)	11.96 (12.30)	114.02	90.33	96.99
Y(DPTU) ₃ Cl ₃ ·3H ₂ O	49.60 (50.17)	4.20 (4.29)	9.07 (9.57)	8.91 (8.99)	11.29 (11.40)	10.16 (10.28)	98.17	70.14	86.30
La(DPTU) ₃ Cl ₃ ·3H ₂ O	47.20 (47.58)	4.15	13.90	8.39	10.50	9.58			
Pr(DPTU) ₃ Cl ₃ ·3H ₂ O	47.15 (47.49)	4.15 (4.26)	14.17 (14.29)	8.28 (8.52)	10.50 (10.80)	9.53 (9.79)			

Nd(DPTU) ₃ Cl ₃ ·3H ₂ O	47.10	4.00	14.22	8.16	10.02	9.44	76.39
	(47.33)	(4.24)	(14.58)	(8.49)	(10.77)	(9.70)	
Sm(DPTU) ₃ Cl ₃ ·3H ₂ O	46.90	4.13	14.35	8.10	10.54	9.40	101.8
	(47.03)	(4.22)	(14.11)	(8.44)	(10.70)	(9.64)	
Gd(DPTU) ₃ Cl ₃ ·3H ₂ O	46.50	4.09	15.50	8.03	10.45	9.38	100.70
	(46.73)	(4.19)	(15.69)	(8.39)	(10.63)	(9.58)	
Dy(DPTU) ₃ Cl ₃ ·3H ₂ O	46.25	4.00	15.70	7.99	10.22	9.35	82.39
	(46.47)	(4.70)	(16.13)	(8.34)	(10.57)	(9.53)	

Conductivity measurements are given in representative cases, and calculated values in parenthesis. NPU = N-phenylurea; DPU = N-N' Diphenylurea; NPTU = N-phenylthiourea; DPTU = N-N' Diphenylthiourea.

Perkin-Elmer model 350 spectrophotometer. IR spectra were recorded in nujol mulls using Perkin-Elmer model 237 spectrophotometer. Thermal analysis of the complexes was carried out using MOM Budapest derivatograph at a heating rate of 10° per minute in an air flow at atmospheric pressure. All the conductance measurements were carried out in methanol, dimethylsulphoxide or dimethylformamide on a Systronics direct-recording conductivity meter Type 303. Carbon and hydrogen determination was carried out at the Regional Sophisticated Instrumentation Centre, CDRI, Lucknow. The complexes were analysed for metal, nitrogen, sulphur and anion by standard methods.

3. Results and discussion

3.1. Electronic spectra

The spectra of the ligands in methanol exhibit only one band in the region 235–272 nm ($\log \epsilon = 4.12$ –4.72). In the complexes also, only one band is observed in the region 235–272 nm ($\log \epsilon = 3.87$ –5.62). However, there is an intensification of absorption in all the complexes except in the dysprosium phenylurea complex.

The visible region is more informative and the red shift attributed to Nephelauxetic effect by Jorgensen²⁴ is observed. The maximum red shift of a particular band observed is in the case of Nd^{3+} ion. The covalency parameter $b^{1/2}$, calculated according to the formula of Angelov²⁵, turns out to be 0.08 when the shift is 8–11 nm and is between 0.04 and 0.07 when the shift is 2–4 nm. The covalency parameter decreases in the order $\text{Nd} > \text{Pr} > \text{Sm}$.

3.2. Infrared spectra

3.2.1. Lanthanide *N*-phenylurea (NPU) and *N*-*N'* diphenylurea complexes (DPU)

The spectra of both the ligands exhibit bands characteristic of N–H, C–O and N–H rocking vibrations. The N–H stretching frequency of NPU at 3410, 3300, 3190 cm^{-1} is observed in all the complexes with a reduction in intensity and a shift to lower wave numbers. The decrease is of the order of 70 cm^{-1} indicating that the nitrogen of the ligand is involved in coordination to the metal.

Two bands at 3310 and 3270 cm^{-1} are observed in the spectra of DPU and these do not show any significant changes in the complexes indicating that the nitrogen atom of DPU is not involved in bond formation. This inference is supported by the fact that $\nu(\text{C}=\text{O})$ of the free ligand at 1655 cm^{-1} is lowered for all the complexes.

The bands in the region 3340–3580 cm^{-1} observed in the spectra of the complexes arise from water molecules.

3.2.2. Lanthanide *N*-phenylthiourea and *N*-*N'* diphenylthiourea complexes

The IR spectra of ligands NPTU and DPTU exhibit bands in the region 3140–3410 cm^{-1} , which are due to $\nu(\text{N}-\text{H})$ vibrations. These bands undergo a slight positive shift in all the

lanthanide complexes. The shift to a higher frequency indicates the non-involvement of the nitrogen of the ligands in bond formation.

The N-H bending vibration of NPTU (1625 cm^{-1}) DPTU (1610 cm^{-1}) either remains unchanged in position or shifts to a higher frequency in the lanthanide complexes again indicating the non-involvement of nitrogen in bonding.

All the lanthanide complexes contain water molecules. This fact is supported by thermal analysis and IR spectra. However, the OH; N-H stretching vibrations have merged in the spectra of NPTU complexes, whereas OH-stretching vibrations are observed distinctly in the Sm, Gd and Dy DPTU complexes.

Venkappayya and Brown²⁶ observed, in a study of Co(II), Zn(II), Hg(II) complexes with DPTU, that the $\nu(\text{C-S})$ bands around $1350, 1310\text{ cm}^{-1}$ are observed with a change in intensity and position also.

In the DPTU lanthanide complexes band at $1350, 1310\text{ cm}^{-1}$ attributable to $\nu(\text{C-S})$ are lowered in position and also there is a reduction in their intensities compared to the free ligand. Nabar² reports that the 1062 cm^{-1} band of NPTU which is due to C-S stretching has been weakened and broadened in its Cu(I) complex. A similar effect is observed for the 1062 cm^{-1} band of the lanthanide NPTU complexes.

Furthermore, the bands in the region $690-807\text{ cm}^{-1}$ of both the ligands which are mainly due to C-S character are observed with (1) reduction in intensity, and (2) lowering in position in the lanthanide complexes. One can, therefore, conclude that both the ligands have acted as unidentate ligands and the bonding is through sulphur.

3.3. Thermal analysis

Thermogravimetric analysis of several lanthanide complexes was carried out. It was reported²⁷ that on the basis of thermal analysis, one could consider that water molecules eliminated below 150°C as lattice water, while around 200°C and above as coordinated water. Based on these observations, water molecules are present as lattice water in DPU, NPTU and DPTU complexes as they are eliminated below 150°C and as coordinated water in NPU complexes as they are eliminated around 200°C .

3.4. Conductivity measurements

The molar conductance values of several lanthanide complexes in methanol, dimethylsulphoxide, dimethylformamide are in the range 83-118, 70-91, 68-107 $\text{ohm}^{-1}\text{ mole}^{-1}\text{ cm}^2$, respectively (Table I). These values correspond to 1:1 electrolyte in these solvent²⁸⁻³⁰.

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