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Studies on Mixed Ligand Complexes of Lanthanide(III) Ions

G. RAJENDRAN* and K.G. USHA DEVI†
Department of Chemistry, University College,Thiruvananthapuram-695 034, India

As part of our research programme, we have prepared and characterized a few nitrato, thiocyanato and perchlorato complexes of lanthanide(III) ions with ligands, *viz.*, a Schiff base derived from *p*-anisidine and vanillin and diphenyl sulphoxide. The complexes were characterized by the measurement of electrical conductances and magnetic susceptibilities, molecular mass and metal percentage and spectral analysis. The thermal decompositions were studied by TG and DTG techniques. The thiocyanato complexes were prepared by substitution method from nitrato complexes. *p*-Anisidine-vanillin (HDDA) and diphenyl sulphoxide (DPSO) are coordinated to the metal ion in unidentate fashion. All the anions were involved in coordination in these complexes. Thus they were found to have non-electrolytic behaviour with composition $[Ln(HDDA)_2(DPSO)X_3]$ where $X = NO_3^-$ or SCN^-. Perchlorato complexes were prepared from metal perchlorate as done in the case of nitrato complexes. They were found to have electrical conductance which corresponds to 1 : 1 electrolyte. Hence one of the perchlorate ions is outside the coordination sphere. The composition of this complex is found to be $[Ln(HDDA)_3(DPSO)(ClO_4)_2]ClO_4$.

Key Words: Mixed ligand complexes, Lanthanide(III), Schiff base, *p*-Anisidine-vanillin, Diphenyl sulphoxide.

INTRODUCTION

Literature study shows that 4′-hydroxy-4,3′-dimethoxy diphenyl azomethene (HDDA) complexes of some of the lanthanide(III) ions were prepared formerly[1]. But mixed HDDA-DPSO complexes of such metal ions were not prepared so far. Therefore we tried to prepare certain mixed ligand complexes of lanthanide metal ions with a Schiff base and diphenyl sulphoxide (DPSO) in presence of coordinating anions such as nitrate, perchlorate, thiocyanate etc. and they were studied by different analytical methods. The Schiff base HDDA was found to be monodentate even though it has four coordination sites, *viz.*, two methoxy-oxygen atoms, one imino nitrogen atom and one phenolic oxygen atom (Fig. 1). DPSO is also monodentate coordinating through oxygen atom.

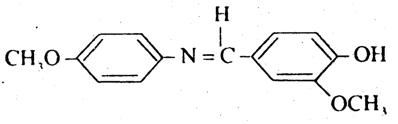

Fig. 1. 4′-Hydroxy-3′,4-Dimethoxy Diphenyl Azomethene (HDDA)

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†Selection Grade Lecturer, Department of Chemistry, S.N. College, Kollam, India

EXPERIMENTAL

The ligand HDDA was prepared by literature method[1]. Equimolar solutions of 4-methoxyaniline and 4-hydroxy-3-methoxy benzaldehyde in methanol were prepared, mixed together and refluxed for *ca.* 2 h. The resulting solution was concentrated and cooled to get the solid crystals of Schiff base. It was filtered, washed and dried *in vacuo* over P_2O_5 and recrystallized in ethanol. The melting point and yield of the product were noted. The nitrato complexes of the six lanthanide(III) ions, *viz.*, Pr^{3+}, Nd^{3+}, Sm^{3+}, Eu^{3+}, Gd^{3+} and Dy^{3+} were prepared by mixing the methanolic solutions of metal nitrate, HDDA and DPSO in the molar ratio 1 : 2 : 1 and refluxing the resulting mixture for *ca.* 6 h. The resulting solution was concentrated by evaporation on a water bath. It was then washed repeatedly with benzene and then extracted with petroleum ether to get the solid complex. The coloured complexes formed were filtered and dried *in vacuo* over P_2O_5. These complexes are soluble in methanol, partially soluble in acetone and acetonitrile and slightly soluble in nitrobenzene and insoluble in diethyl ether. The thiocyanato complexes were prepared by substitution method by refluxing methanolic solution of the nitrato complex with stoichiometric quantity of ammonium thiocyanate. The perchlorato complexes were prepared by the same method as nitrato complexes were prepared, *i.e.*, by refluxing a mixture of methanolic solution of metal perchlorate and ligands *p*-anisidine-vanillin and DPSO in the molar ratio 1 : 3 : 1.

The TG and DTG curves of the complexes were recorded on a thermal analyzer. Pyrolysis experiment in air was done for each complex and loss of mass thus obtained was compared with that obtained from TG. The metal contents of the complexes were obtained by oxalate-oxide method[2]. The nitrate content of the complexes was determined as nitron nitrate[3]. The molar conductances of the complexes were determined in methanol, acetonitrile and nitrobenzene at room temperature (about 30°C) using an ELICO conductivity bridge type CM82T with a dip type conductivity cell having platinum electrodes (cell constant = 0.94 cm^{-1}). 10^{-3} M solutions were used for conductivity measurements. The IR spectra of the ligands and complexes were recorded in the range 4000–400 cm^{-1}. Electronic spectra were also taken for ligand and complexes in the range 185–900 nm. Molecular mass was determined by Rast method using biphenyl as solvent. The magnetic moments of the complexes were determined at room temperature (about 30°C) using EG and G Parc Model 155 vibrating sample magnetometer. The diamagnetic correction for the rest of the molecule and the completed shells of lanthanide ions were computed from Pascal's constants. The antibacterial studies of the complexes at various concentrations were also done using four different bacteria[4]: *Staphylococcus aureus, Klebsiella pneumoniae, Escherichia coli, Pseudomonas aeruginosa.*

RESULTS AND DISCUSSION

From the analytical data (Table-1) the complexes have the general formulae $[Ln(HDDA)_2(DPSO)(NO_3)_3]$, $[Ln(HDDA)_2(DPSO)(NCS)_3]$ and $[Ln(HDDA)_3(DPSO)(ClO_4)_2]ClO_4$ where Ln = Pr, Nd, Sm, Eu, Gd or Dy.

TABLE-1
ANALYTICAL DATA OF LANTHANIDE(III) COMPLEXES

Complex (colour)	m.w. Calcd. (found)	% Analysis: Calcd. (found)					Yield (%)
		M	Anion	C	H	N	
$Pr(HDDA)_2(DPSO)(NO_3)_3$	1042.9	13.5	17.83	48.33	3.84	6.71	72
(Brown)	(1039)	(13.46)	(16.5)	(48.12)	(3.12)	(6.50)	
$Nd(HDDA)_2(DPSO)(NO_3)_3$	1046.24	13.78	17.77	48.33	3.82	6.69	69
(Chocolate brown)	(1040)	(12.07)	(17.00)	(48.02)	(2.89)	(5.98)	
$Dy(HDDA)_2(DPSO)(NO_3)_3$	1064.5	15.27	17.47	47.35	3.76	6.58	78
(Coffee brown)	(1052)	(14.29)	(17.40)	(47.5)	(3.40)	(6.50)	
$Sm(HDDA)_2(DPSO)(NCS)_3$	1040.35	14.45	16.73	51.91	3.84	6.72	72
(Yellowish brown)	(1030)	(13.9)	(15.99)	(51.80)	2.91	(5.45)	
$Gd(HDDA)_2(DPSO)(NCS)_3$	1047.25	15.02	16.61	51.56	3.82	6.68	76
(Brown)	(1038)	(14.90)	(16.12)	(51.0)	(2.99)	(5.18)	
$Pr(HDDA)_3(DPSO)(ClO_4)_3$	1418.4	9.9	21.04	48.43	3.89	2.97	71
(Chocolate brown)	(1414)	(11.2)	(21.6)	(48.13)	(4.00)	(3.10)	
$Eu(HDDA)_3(DPSO)(ClO_4)_3$	1429.5	10.63	20.88	48.05	3.85	2.94	72
(Light brown)	(1416.8)	(9.77)	(20.90)	(48.10)	(4.00)	(3.10)	
$Dy(HDDA)_3(DPSO)(ClO_4)_3$	1440	11.2	20.72	47.70	3.84	2.93	72
(Dirty brown)	(1436.2)	(11.81)	(20.80)	(48.00)	(4.01)	(3.01)	

Molar conductivity values of nitrato and thiocyanato complexes in three solvents, *viz.*, nitrobenzene, acetonitrile and methanol were determined and were found to be in the range corresponding to those of non-electrolytes. Perchlorato complexes show slightly higher values corresponding to 1 : 1 electrolytes in nitrobenzene showing that one of the perchlorate ions is outside the coordination sphere. In acetonitrile and methanol the perchlorato complexes show electrical conductance values corresponding to 1 : 2 electrolytes. The higher electrical conductance values in acetonitrile and methanol may be due to the replacement of the anions from the coordination sphere by the solvent molecules.

The IR spectrum of the ligand exhibits a strong band at 1621 cm^{-1} which is assigned to the stretching vibration of $\nu(C{=}N)$. In all complexes this band is red-shifted to about 1596 cm^{-1}. This indicates the coordination through azomethene nitrogen[5]. A broad band observed in the region 3300–3100 cm^{-1} of the complex is assigned to $\nu(OH)$ vibration. The band at 1250 cm^{-1} in the spectrum of the ligand is for $\nu(OCH_3)$ which is retained in the spectrum of the complex without any change of position. This shows that —OCH_3 group of the ligand is not involved in bonding. The bands of phenyl ring, CH_3 group are present at the same region in the spectra of complexes. Thus HDDA is acting as a neutral monodentate ligand in all these complexes. The lowering in stretching frequency of 70 cm^{-1} found in the complex at 1030 cm^{-1} is indicative of the bonding from the oxygen atom of the sulphoxide[6]. The nitrato complexes observed three bands at 1464, 1384 and 1302 due to ν_4, ν_1 and ν_2 modes of coordinated nitrate ion which are absent in spectra of ligands and other anionic complexes. The difference between ν_4 and ν_1 is 80 cm^{-1} which supports the unidentate coordination of nitrate ions[7].

The thiocyanato complexes exhibit two bands at 2052 and 826 cm^{-1} which are assigned to $\nu(CN)$ and $\nu(CS)$ modes of coordinated thiocyanate which are not in spectra of ligand and spectra of other anionic complexes. Since $\nu(CN)$ mode is lower than 2100 cm^{-1} and $\nu(CS)$ vibration is greater than 774 cm^{-1}, the thiocyanate ions are coordinated to metal through nitrogen atom in a unidentate fashion[5, 8].

The perchlorato complexes show a strong band around 1135 cm^{-1} which is not in ligand or in other anionic complexes. This is attributed to ν_4 vibration of monodentate perchlorate. The second band occurring around 1013 cm^{-1} is assigned to its ν_1 vibration. The bands at 624 cm^{-1} and 512 cm^{-1} can be assigned respectively to ν_3 and ν_5 of monodentately coordinated perchlorate ions. ν_2 is observed at 774 cm^{-1} as a medium intensity absorption band. All these observations confirm that the perchlorate ions are monodentately coordinated to metal ions in the complexes[10].

The magnetic moments of the complexes[9, 10] at room temperature are in good agreement with the theoretical values calculated from Van Vleck formula (Table-2).

TABLE-2
MAGNETIC MOMENTS OF LANTHANIDE(III) COMPLEXES

Complex	Magnetic moments (BM)	
	μ_{eff} found	μ_{eff} calculated from formula
$Pr(HDDA)_2(DPSO)(NO_3)_3$	3.40	3.58
$Nd(HDDA)_2(DPSO)(NO_3)_3$	3.59	3.62
$Sm(HDDA)_2(DPSO)(NO_3)_3$	1.81	1.60
$Eu(HDDA)_2(DPSO)(NO_3)_3$	3.90	3.61
$Gd(HDDA)_2(DPSO)(NO_3)_3$	8.01	7.94
$Dy(HDDA)_2(DPSO)(NO_3)_3$	10.17	10.63

Thermal studies were conducted on certain representative complexes, *viz.*, nitrato complexes of Dy^{3+}, thiocyanato complexes of Gd^{3+} and perchlorato complexes of Eu^{3+}. The nitrato complex of Dy^{3+} undergoes two stage decomposition at 336 and 544°C. The decomposition at 336°C is due to the dissociation of the organic moiety, *i.e.*, the ligands HDDA and DPSO are removed from the parent molecule and the mass loss by 48.2%. At 544°C the metal oxide Dy_2O_3 is formed with a mass loss of 82.5%.

Pyrolysis experiments in air were conducted on all complexes separately and the metal percentage was determined for each complex. For this a known mass of the complex was heated on a weighed silica crucible to a high temperature for 2 h. From the mass of the residue (metal oxide) the metal percentage of the complex was determined. The mass percentage thus determined was found to agree with the one obtained from thermal analysis. Thus the proposed formula of the nitrato complex is $[Ln(HDDA)_2(DPSO)(NO_3)_3]$. This complex undergoes two stage decomposition during thermal analysis (Table-3).

The thiocyanato complex of Gd^{3+} decomposes at two different stages. At first the organic moiety is evaporated from the complex at a temperature of 222°C and the remaining part changes to metal oxide Gd_2O_3 at higher temperature of 820°C. The mass loss at the two stages confirms the structure of the thiocyanato complex as $[Gd(HDDA)_2(DPSO)(NCS)_3]$. There are two DTG curves for perchlorato complex of Eu^{3+}. The first one at 257°C is due to the dissociation of organic moiety and the second peak is at 960°C where it forms the metal oxide Eu_2O_3. The two decomposition stages confirm the structure of the perchlorate complex as $[Eu(HDDA)_3(DPSO)(ClO_4)_2]ClO_4$. Thus coordination number six is assigned to all these complexes.

TABLE-3
DATA OF THERMAL STUDY

Complex	Temperature of the peak (°C)	Mass loss calculated (found) %
$[Dy(HDDA)_2(DPSO)(NO_3)_3]$	335.9	48.28 (50.00)
	543.9	82.48 (82.50)
$[Gd(HDDA)_2(DPSO)(NCS)_3]$	222	49.08 (50.00)
	820	82.70 (82.50)
$[Eu(HDDA)_3DPSO(ClO_4)_2]ClO_4$	257	53.93 (52.00)
	960	87.56 (85.12)

The antimicrobial activities of compounds were tested by plate diffusion method as given in Indian Pharmacopoeia[4]. It was observed that some of the complexes show antimicrobial activities towards certain bacteria.

A few representative complexes were used for these studies. Complexes were dissolved in absolute methanol and impregnated in Whatman no. 1 filter paper to get a concentration of 1 mg, 5 mg and 10 mg per disc. The methanol in the discs was evaporated and the discs were sterilized by autoclaving.

Mueller Hinton agar plates were inoculated with the test bacterial strains, *Escherichia coli, Staphylococcus aureus, Klebsiella pneumoniae* and *Pseudomonas aeruginosa.* The test and control samples were placed on the media surface and incubated at 37°C for 24 h. The positive control used was Gentamicin disc. The negative control used was Whatman no. 1 filter paper discs impregnated with 150 μL of absolute methanol. The methanol in the discs was evaporated and the discs were sterilized by autoclaving.

TABLE-4
BACTERIAL ACTIVITY OF $Ln(HDDA)_2(DPSO)X_3$ COMPLEXES

Bacteria	$[Nd(HDDA)_2(DPSO)(NO_3)_3]$	$[Dy(HDDA)_2(DPSO)(NCS)_3]$	$[Eu(HDDA)_3(DPSO)(ClO_4)_2)]ClO_4$
Pseudomonas aeruginosa	No inhibition	No inhibition	No inhibition
Staphylococcus aureus	1 mm	1 mm	1 mm
Escherichia coli	No inhibition	No inhibition	No inhibition
Klebsiella pneumoniae	No inhibition	No inhibition	1 mm

The perchlorato complex of Eu^{3+} was found to be more active than the nitrato complex of Nd^{3+} and thiocyanato complex of Dy^{3+}. All the complexes were found to be active towards *S. aureus*. The perchlorato complex was found to be active towards *Klebsiella pneumoniae* in addition to *Staphylococcus aureus (Table-4).* Bacterial activity of perchlorato complex of Pr^{3+} in different concentrations was studied. It was observed that the activity is increased with concentration of the solution. In the case of $[Pr(HDDA)_3(DPSO)(ClO_4)_2]ClO_4$, it was found to be active towards *Escherichia coli* when the concentration of the solution was increased. Activity towards *Klebsiella pneumoniae* was found to increase when the concentration of the solution was increased. (Table-5).

TABLE-5
BACTERIAL ACTIVITY OF $[Pr(HDDA)_3(DPSO)(ClO_4)_2]ClO_4$ IN DIFFERENT CONCENTRATIONS

Concentration	*E. coli*	*S. aureus*	*Ps. aeruginosa*	*K. pneumoniae*
1 mg	No inhibition	2 mm	No inhibition	1 mm
5 mg	No inhibition	2 mm	No inhibition	2 mm
10 mg	1 mm	2 mm	No inhibition	2 mm

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