Synthesis and Pharmacological Studies of Mixed Ligand Complexes of Lanthanide(III) Ions with Schiff Base and Diphenyl Sulphoxide

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The present research paper is concerned with the synthesis and antimicrobial studies of some mixed ligand complexes of certain lanthanide(III) ions with a Schiff base and diphenyl sulphoxide. They are characterized on the basis of elemental analysis, molar conductances, molecular mass and metal percentage, magnetic moments and spectral investigations (electronic and infrared spectra). Antimicrobial activity of the complexes was studied. The complexes conform to the composition $[Ln(MDDA)_3(DPSO)X_3]$ where $X = NO_3^-$ or NCS^- $[Ln(MDDA)_4(DPSO)X_2]X$ where $X = ClO_4^-$. The Schiff base 4-methoxy-4′(N,N-dimethylamino) diphenyl azomethine (MDDA) is derived by the condensation of *p*-anisidine and *p*-dimethyl amino benzaldehyde. Both the Schiff base and DPSO act as neutral monodentate ligands and the complexes appear to be seven-coordinated. The infrared data suggest coordination of the ligand to the metal ions in a unidentate fashion through the nitrogen atom of the azomethine group and oxygen atom of the diphenyl sulphoxide molecule. The antimicrobial screening of the ligands and their complexes has been carried out. Thermal decompositions were studied by TG and DTG techniques.

Key Words: Lanthanide(III), Schiff base, Diphenyl sulphoxide, Mixed ligand complexes.

INTRODUCTION

In continuation of our early studies on the complexing tendencies of *p*-anisidine-vanillin Schiff base and diphenyl sulphoxide, which were known for their biological properties.[1] We report here the synthesis and characterization of solid mixed ligand complexes of nitrates, perchlorates and thiocyanates of lanthanide ions with a Schiff base of *p*-anisidine and *p*-dimethyl amino benzaldehyde as the primary ligand and diphenyl sulphoxide molecule as secondary ligand. The Schiff base 4-methoxy-4′(N,N-dimethylamino) diphenyl azomethine (MDDA) was found to be monodentate even though it has three coordinating sites, *viz.*, one imino nitrogen atom, methoxy oxygen atom and amino nitrogen atom (Fig. 1). DPSO is monodentate ligand coordinating through oxygen atom

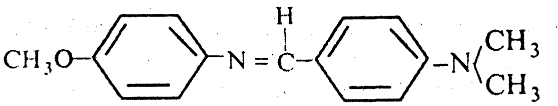

Fig. 1. 4-Methoxy-4′-(N,N-dimethylamino) diphenyl azomethine (MDDA).

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EXPERIMENTAL

The reagents and solvents were of analytical grade. The lanthanide(III) nitrates and perchlorates were prepared from their oxides purchased from BDH. Perchlorates and nitrates of these six lanthanides were prepared from the respective oxides by dissolving a slight excess of the oxides in hot 50% (v/v) in aqueous nitric acid or perchloric acid. The undissolved oxids were filtered off and the lathanide nitrates or perchlorates were crystallized by concentrating to 25% of the original volume and cooling. These lanthanide salts were dried *in vacuo* over phosphorus(V) oxide and stored in a desiccator. The ligand MDDA was prepared by refluxing equimolar solutions of 4-methoxy aniline and 4-N,N-dimethyl amino benzaldehyde in methanol for 4 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 phospourus(V) oxide and recrystallized in ethanol. The melting point and the yield of the products were noted.

The complexes were prepared as follows: Methanolic solutions of the ligands MDDA and DPSO were mixed with the lanthanide(III) nitrate solution in methanol in the ratio 3 : 1 : 1. This mixture was refluxed for about 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 phosphorus(V) oxide. 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 from the nitrato complex by substitution method.[1] The methanolic solution of nitrato complex was refluxed with stoichiometric quantity of ammonium thiocyanate. The perchlorato complexes were prepared by the same method that was used for nitrato complexes. But the molar ratio of the ligands DPSO, MDDA and metal perchlorate was 1 : 4 : 1.

The metal contents of the complexes were estimated by oxalate-oxide method.[2] The nitrate contents of the complexes were determined gravimetrically by using nitron reagent.[3] The thiocyanate contents of the complexes were determined gravimetrically as AgSCN.[3] The molar conductances of the complexes in methanol, acetonitrile and nitrobenzene were determined at room temperature 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 infrared spectra of all the complexes and ligands were recorded in the range 4000–400 cm^{-1}. The electronic spectral bands were also taken for ligands and complexes in the range 185–900 nm. Molecular mass was determined by Rast method using biphenyl and solvent[4]. The magnetic moments of the complexes were determined at room temperature 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.[5] The antimicrobial studies of the complexes at various concentrations were also done using four different bacteria, *viz.*, (1) *Staphylococcus aureus* (2) *Klebsiella pneumoniae* (3) *Eschrichia Coli and* (4) *Pseudomonas aeruginosa.* The activity is reported by measuring the diameter of the inhibition zone in mm.

RESULTS AND DISCUSSION

The results of analysis data of the complexes are presented in Table-1. All these complexes are insoluble in ether and partially soluble in nitrobenzene. The nitrato and thiocyanato complexes were found to be non-conducting in nitrobenzene as shown by the values of molar conductance which lie in the range 2–10 ohm^{-1} cm^{2} mol^{-1}.[6] However, the values of nitrato and thiocyanato complexes in methanol are slightly higher than those of non- electrolytes. The higher value in methanol can be attributed to partial displacement of the weakly coordinated nitrate ions by methanol molecules. Electrical conductance values of lanthanide perchlorato complexes in nitrobenzene correspond to those of 1 : 1 electrolytes suggesting that only two of the perchlorate ions are coordinated to the lanthanide ions in these complexes. The higher values corresponding to those of 1 : 3 electrolytes in acetonitrile and methanol are attributed to possible substitution of the solvent molecules for the coordinated perchlorate ions. Based on these data, the present complexes can be formulated as $[Ln(MDDA)_3(DPSO)(NO_3)_3]$, $[Ln(MDDA)_3(DPSO)(NCS)_3]$ and $[Ln(MDDA)_4(DPSO)(ClO_4)_2]ClO_4$.

TABLE-1
ANALYTICAL DATA OF LANTHANIDE(III) COMPLEXES DERIVED FROM MDDA AND DPSO

Complexes (Colour)	m.w. Found (Calcd.)	% Analysis: Foun (Calcd.)				
		Ln	Anion	C	H	N
$[Pr(MDDA)_3(DPSO)(NO_3)_3]$ (Brown)	1288 (1290.9)	10.16 (10.90)	15.00 (14.40)	54.12 (55.75)	3.98 (4.96)	8.98 (9.76)
$[Sm(MDDA)_3(DPSO)(NO_3)_3]$ (Dark brown)	1299 (1300.35)	11.06 (11.50)	14.50 (14.30)	54.54 (55.37)	3.99 (4.92)	9.10 (9.69)
$[Gd(MDDA)_3(DPSO)(NO_3)_3]$ (Sand brown)	1305 (1307.25)	10.68 (12.02)	14.00 (14.22)	54.98 (55.08)	4.80 (4.90)	9.30 (9.64)
$[Nd(MDDA)_3(DPSO)(NCS)_3]$ (Brown)	1280 (1282.24)	10.89 (11.25)	12.00 (13.57)	58.60 (58.96)	4.98 (4.99)	9.80 (9.83)
$[Dy(MDDA)_3(DPSO)(NCS)_3]$ (Brown)	1299 (1306.50)	11.49 (12.50)	13.20 (13.37)	58.20 (58.13)	4.90 (4.92)	9.70 (9.69)
$[Sm(MDDA)_4(DPSO)(ClO_4)_2]ClO_4$ (Bluish brown)	1665 (1666.85)	8.65 (9.02)	17.61 (17.90)	53.99 (54.71)	4.89 (4.92)	6.69 (6.72)
$[Dy(MDDA)_4(DPSO)(ClO_4)_2]ClO_4$ (Orange yellow)	1675 (1679)	9.50 (9.68)	17.50 (17.78)	54.01 (54.32)	4.80 (4.88)	6.60 (6.67)

Infrared spectrum of the ligand exhibits a strong band at 1609 cm^{-1} which is assigned to stretching vibration of C=N. The band due to ν(C=N) of the ligand undergoes a downward shift by 20–25 cm^{-1} in the spectra of the complexes. This clearly indicates the coordination of azomethine nitrogen to metal atom. The band at 1240 cm^{-1} in the spectra of the ligand is for $\nu(OCH_3)$ which is retained in the spectra of the complexes without any change of position. This shows that OCH_3 group is not involved in bonding. The bands of phenyl ring, CH_3 are present at the same region in the spectra of complexes. Thus MDDA is acting as a neutral monodentate ligand in all these complexes. The lowering in the 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 of DPSO. The nitrato complexes observed three bands at 1476, 1384 and 1302 cm^{-1} due to ν_4, ν_1 and ν_2 modes of coordinated nitrate ion which is absent in the spectra of ligand and other anionic complexes. The difference between ν_4 and ν_1 is 92 cm^{-1} which supports the unidentate coordination of nitrate ions.[7]

The thiocyanato complexes exhibit two bands at 2056 and 834 cm^{-1} which are assigned to $\nu(CN)$ and $\nu(CS)$ modes of coordinated thiocyanate which are not present in the spectra of ligand and 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.[8]

The structure and bonding of metal complexes of weakly coordinating perchlorate ion have been reviewed by Rosenthal.[9] The perchlorato complexes show a strong band around 1177 cm^{-1} which is not in ligand or in other anionic complexes. This is due to the ν_4 vibration of monodentate perchlorate. The second band occurring around 1023 cm^{-1} is assigned to ν_1 vibration. The bands at 624 and 525 cm^{-1} can be assigned respectively to ν_3 and ν_5 of monodentately coordinated perchlorate ions. ν_2 is observed at 938 cm^{-1} as a medium intensity absorption band. All these obeservations confirm that the perchlorate ions are monodentately coordinated to metal ions in the complexes.

The magnetic moment values of complexes at room temperature are in good agreement with the theoretical values calculated from Van Vleck formula.[10] The effective magnetic moment was calculated using the formula $\mu_{eff} = 2.84\sqrt{\chi_m^i T}$ where χ_m^i = molar susceptibility corrected for diamagnetism.

The TGA curves for the representative nitrato complexes of lanthanide(III) have been recorded. The nitrato complex of Gd^{3+} undergoes two state decomposition at 328 and 988°C. The thermogravimetric results indicate that the nitrato complexes are stable up to 250°C showing the absence of water and other coordinated solvent molecules. The decomposition of complexes occurs in two steps. The first step involves the decomposition of organic moiety in the temperature range 328–423°C. The second stage consists of the decomposition of nitrate at 424–988°C to form lanthanide(III) oxide. The weight loss becomes constant at 988°C. The DTA curves show exothermic behaviour in both the stages of decomposition.[11]

The thiocyanato complex, *viz.*; $[Dy(MDDA)_3(DPSO)(NCS)_3]$ undergoes two stage decomposition at 305 and 814°C. The thiocyanato complexes are stable up to 260°C showing the absence of water and other solvent molecules. The decomposition at 305°C is due to the dissociation of the organic moiety, *i.e.*, the ligands MDDA and DPSO are removed from the parent molecule, making the mass loss 74%. At 814°C the metal oxide Dy_2O_3 is formed with a mass loss of 71.4%. The DTA studies show that both the decomposition stages are exothermic. The data of the thermal studies were recorded in Table-2.

TABLE-2

Complex	Temp. of the Peak (°C)	Mass loss calculated (Experimental)
$[Gd(MDDA)_3(DPSO)(NO_3)_3]$	328	74.00 (73.70)
	988	87.00 (86.09)
$[Dy(MDDA)_3(DPSO)(NCS)_3]$	305	71.50 (74.10)
	814	15.90 (14.34)

Pyrolysis experiments in air were conducted on all the 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 3 h. From the mass of the residual 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 formulae of the nitrato, thiocyanato and perchlorato complexes are $[Ln(MDDA)_3(DPSO)(NO_3)_3]$, $[Ln(MDDA)_3(DPSO)(NCS)_3]$ and $[Ln(MDDA)_4(DPSO)(ClO_4)_2]ClO_4$. Thus coordination number seven is assigned to all these complexes.

The ligand and the complexes were tested for their antimicrobial activities by plate diffusion method as given in Indian pharmacopoecia.[12] The bacterial strains for the study are (1) ***Staphylococcus aureus*** (2) ***Escherichia Coli*** (3) ***Klebsiella Pneumoniae*** and (4) ***Pseudomonas aeruginosa***. It was observed that the ligand has no antimicrobial activity. The representative complexes used for the antimicrobial study were $[Gd(MDDA)_3(DPSO)(NO_3)_3]$ and $[Sm(MDDA)_4(DPSO)(ClO_4)_2]ClO_4$. The complex $[Gd(MDDA)_3(DPSO)(NO_3)_3]$ was found to be active towards only one bacteria, *viz*; ***S. aureus***. The data indicate that the antimicrobial activity increases with the increase in concentration. The complex $[Sm(HDDA)_4(DPSO)(ClO_4)_2]ClO_4$ was found to be active towards ***E .Coli*** and ***S. aureus*** and the activity was found to increase with increase in concentration. The data of the bacterial study of these complexes are shown in Table-3.

TABLE-3

Compound	*E. coli*			*S. aureus*			*K. pneumoniae*			*P. aeruginosa*		
	5 mg	10 mg	15 mg	5 mg	10 mg	15 mg	5 mg	10 mg	15 mg	5 mg	10 mg	15 mg
Ligand (MDDA)	No Inh.	No Inh.	No Inh.	No Inh.	No Inh.	No Inh.	No Inh.	No Inh.	No Inh.	No Inh.	No Inh.	No Inh.
$[Gd(MDDA)_3(DPSO)(NO_3)_3]$	No Inh.	No Inh.	No Inh.	2	4	5	No Inh.	No Inh.	No Inh.	No Inh.	No Inh.	No Inh.
$[Sm(MDDA)_3(DPSO)(ClO_4)_2]ClO_4$	2	2	3	2	3	3	No Inh.	No Inh.	No Inh.	No Inh.	No Inh.	No Inh.

On the basis of these investigations it is concluded that three molecules of MDDA, one molecule of DPSO and three molecules of anions are coordinated to lanthanide ion with a coordination number of seven in nitrato and thiocyanato complexes. Perchlorato complexes have four molecules of primary ligand, one molecule of secondary ligand and two molecules of perchlorate ions in the coordination sphere which constitute a coordination number of seven.

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