

SYNTHESIS AND PHARMACOLOGICAL STUDIES OF MIXED LIGAND COMPLEXES OF LANTHANIDE (III) IONS WITH SCHIFF'S BASE AND DIPHENYL SULPHOXIDE

Preethi P C

Department of Chemistry, Christian College Kattakada, India 695572

Abstract: The present research paper is concerned with synthesis and anti microbial studies of some mixed ligand complexes of certain lanthanide ions with a schiff's base and diphenyl sulphoxide. They are characterised on the basis of elemental analysis, molecular conductances, molecular mass and metal percentage, magnetic moments and special investigations which include electronic and IR spectra. Antimicrobial activity of the complexes was studied. The complexes confirm to the composition $[Ln (MDDA)_3 (DPSO)_X]_3$ where $X=NO_3^-$. The schiff's base is derived by the condensation of P-anisidine and P-dimethyl amino benzaldehyde. Both the Schiff's base and DPSO act as neutral monodentate ligands and the complexes appear to be seven-coordinated. The IR data suggests 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 & DTG techniques.

Keywords: Schiff's base, diphenyl sulphoxide, antimicrobial activity.

1. INTRODUCTION

The earlier studies on the complexing tendencies of P-anisidine - vanillin schiff base and diphenyl sulphoxide, which were known for their biological properties, we report here the synthesis and characterization of solid mixed ligand complexes of nitrates 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 MDDA was found to be monodentate eventhough 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

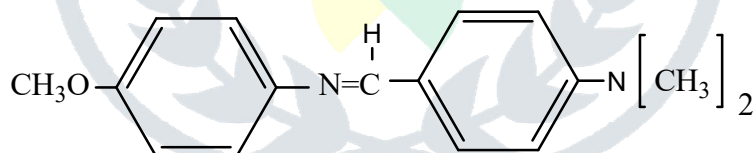


Fig.1. 4-Methoxy-4'-(N,N-Dimethylamino) Diphenyl Azomethine (MDDA)

2. EXPERIMENTAL DETAILS

The reagents and solvents were of analytical grade. The metal nitrates were prepared from their oxides purchased from BDH.

2.1 Synthesis of lanthanide nitrate

Nitrates of lanthanides were prepared from the respective oxides by dissolving a slight excess of the oxides in hot 50% (v/v) aqueous nitric acid. The undissolved oxides were filtered off and the lanthanide nitrates were crystallized by concentrating to 25% of the original volume and cooling. These lanthanide salts were dried in vacuum over phosphorus (v) oxide and stored in desiccators.

2.2 Synthesis of the ligand MDDA

The ligand MDDA was prepared by refluxing equimolar solutions of 4-methoxy aniline and 4-N, N- dimethyl amino benzaldehyde in methanol for 4h. The resulting solution was concentrated and cooled to get the solid crystals of Schiff base. It was filtered, washed and dried in vacuo over phosphorus (v) oxide and recrystallized in ethanol. The melting point and the yield of the products were noted¹.

2.3 Synthesis of the complex

Methanolic solutions of the ligand MDDA and DPSO were mixed with the metal nitrate solution in methanol in the ratio 3:1:1. This mixture was refluxed for about 6h. 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 vacuum over phosphorus (V) oxide. These complexes are soluble in methanol, partially soluble in acetone and acetonitrile and slightly soluble in nitrobenzene and insoluble in diethylether².

The nitrate contents of the complexes were determined gravimetrically by using nitron reagent.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 0.94cm^{-1}). 10^{-3} solutions were used for conductivity measurements. The infrared spectra of all the complexes and ligands were recorded in the range $4000 - 400\text{cm}^{-1}$. The electronic spectral bands were also taken for ligands and complexes in the range $185-900\text{nm}$. Molecular mass was determined by Rast Method using biphenyl as 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 pneumonia 3. Escherichia Coli and 4. Pseudomonas aeruginosa. The activity is reported by measuring the diameter of the inhibition zone in mm.

3. 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 nitrate complexes were found to be non-conducting in nitrobenzene as shown by the values of molar conductance which lie in the range $2-10\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$. However the values of nitrate 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. Based on these data, the present complex can be formulated as $[\text{Ln}(\text{MDDA})_3(\text{DPSO})(\text{NO}_3)]$,

IR values (cm^{-1})	Functional groups
1609	Stretching frequency of C=N
1240	OCH ₃ group
1030	Oxygen atom of sulphoxide of DPSO

Table1. IR spectral data of ligand and complex

Infrared spectrum of the ligand exhibits a strong band at 1609cm^{-1} which is assigned to stretching vibration of C=N. The band due to $\nu_{\text{C=N}}$ of the ligand undergoes a downward shift by $20-25\text{cm}^{-1}$ in the spectra of the complexes. This clearly indicates the coordination of azomethine nitrogen to metal atom. The band at 1240cm^{-1} in the spectra of the ligand is for ν_{OCH_3} which is retained in the spectra of the complexes without any change of position. This shows that OCH₃ group is not involved in bonding. The bands of phenyl ring, CH₃ group 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 70cm^{-1} found in the complex at 1030cm^{-1} is indicative of the bonding from the oxygen atom of the sulphoxide of DPSO. The nitrate complexes observed three bands at $1476, 1384$ and 1302 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 92cm^{-1} which supports the unidentate coordination of nitrate ions.

Complexes	Colour	Molecular mass Cal(exp)	%of analysis		CHN data			% of yield
			Metal Cal(exp)	Anion Cal(exp)	C cal (exp)	H cal(exp)	N cal(exp)	
$[\text{Pr}(\text{MDDA})_3(\text{DPSO})(\text{NO}_3)_3]$	Brown	1290.9 (1288)	10.9 (10.16)	14.4 (15)	55.75 (54.12)	4.96 (3.98)	9.76 (8.98)	72
$[\text{Sm}(\text{MDDA})_3(\text{DPSO})(\text{NO}_3)_3]$	Dark brown	1300.35 (1299)	11.5 (11.06)	14.3 (14.5)	55.37 (54.54)	4.92 (3.99)	9.69 (9.10)	74
$[\text{Gd}(\text{MDDA})_3(\text{DPSO})(\text{NO}_3)_3]$	Sand brown	1307.25 (1305)	12.02 (10.68)	14.22 (14)	55.08 (54.98)	4.9 (4.8)	9.64 (9.3)	58

Table 2. Analytical Data of MDDA, DPSO, Lanthanide (III) Complexes

The structure and bonding of metal complexes of weakly coordinating perchlorate ion have been reviewed by Rosenthal. The perchlorato complexes show a strong band around 1177cm^{-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 1023cm^{-1} is assigned to ν_1 vibration. The bands at 624cm^{-1} and 525cm^{-1} can be assigned respectively to ν_3 and ν_5 of monodentately coordinated perchlorate ions. ν_2 is observed at 938cm^{-1} as a medium intensity absorption band. All these observations 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 $\mu = 2.84\sqrt{X_m}$ where X_m = molar susceptibility corrected for diamagnetism.

The TGA curves for the representative nitrate complexes of lanthanide (III) have been recorded. The nitrate complex of Gd^{3+} undergoes two stage decomposition at $328^{\circ}C$ and $988^{\circ}C$. The thermogravimetric results indicate that the nitrate complexes are stable upto $250^{\circ}C$ 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 $328 - 423^{\circ}C$. The second stage consists of the decomposition of nitrate at $424 - 988^{\circ}C$ to form lanthanide (III) oxide. The weight loss becomes constant at $988^{\circ}C$. The DTA curves show exothermic behaviour in both the stages of decomposition.

The thiocyanato complex, viz; $[Dy(MDDA)_3(DPSO)(NSC)_3]$ undergoes two stage decomposition at $305^{\circ}C$ and $814^{\circ}C$. The thiocyanato complexes are stable upto $260^{\circ}C$ showing the absence of water and other solvent molecules. The decomposition at $305^{\circ}C$ is due to the dissociation of the organic moiety i.e. the ligands MDDA and DPSO are removed from the parent molecule and making the mass loss by 74%. At $814^{\circ}C$ 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 3.

Complex	Temperature of the peak ($^{\circ}C$)	Mass loss calculated (Experimental)
$[Gd(MDDA)_3(DPSO)(NO_3)_3]$	328	73.4(74)
	988	86.09(87)
$[Dy(MDDA)_3(DPSO)(NCS)_3]$	305	74.1(71.5)
	814	14.34(15.9)

Table 3. Data of thermal studies

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 3h. 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 nitrate, 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.

ANTIBACTERIAL STUDY

The ligand and the complexes were tested for their antimicrobial activities by plate diffusion method as given in Indian pharmacopoeia. 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 indicates that the antimicrobial activity increases with the increase in concentration. The complex $[Sm(MDDA)_4(DPSO)(ClO_4)_2]ClO_4$ 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 were placed in table 4.

Compound	E.Coli			S.aures			K.Pneumoniae			P.aeruginosa		
	5mg	10mg	15mg	5mg	10mg	15mg	5mg	10mg	15mg	5mg	10mg	15mg
Ligand	No Inh.	No Inh.	No Inh.	No Inh.	No Inh.	No Inh.	No Inh.	No Inh.	No Inh.	No Inh.	No Inh.	No Inh.
$[Sm(MDDA)_3(DPSO)(NO_3)_3]$	No Inh.	No Inh.	No Inh.	2	4	5	No Inh.	No Inh.	No Inh.	No Inh.	No Inh.	No Inh.
$[Sm(MDDA)_4(DPSO)(ClO_4)_2]ClO_4$	2	2	3	2	3	3	No Inh.	No Inh.	No Inh.	No Inh.	No Inh.	No Inh.

Table 4. Data of antimicrobial activity studies

On the basis of these investigations it is concluded that three molecules of MDDA and one molecule of DPSO and three molecules of anions are bound to lanthanide ion with a coordination number of seven in nitrate and thiocyanato complexes. Perchlorato complexes have four molecules of primary ligand and 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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