Synthesis and Spectral Studies of Lanthanide(III) Complexes with 4-Methoxy- 4'-N,N-dimethylaminodiphenyl Azomethine and Diphenyl Sulfoxide

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Twelve new complexes of Pr(III), Nd(III), Eu(III), Sm(III), Gd(III) and Dy(III) with the ligands 4-methoxy-4'-N,N-dimethylaminodiphenylazomethine (MDDA) and diphenylsulphoxide (DPSO) with the compositions $[Ln(MDDA)_3(DPSO)x_3]$ where $X = NO_3^-$ or NCS^- have been synthesized and characterized by metal estimation, elemental analysis, molar conductance and magnetic susceptibility measurements and IR and UV-Vis spectral studies and thermal analysis. Based on the data, appropriate structures are assigned for these complexes.

Key Words: Lanthanide(III) complexes, 4-Methoxy-4'-N,N-dimethylaminodiphenyl azomethine, Diphenyl sulfoxide.

INTRODUCTION

During the past decade the coordination chemistry of lanthanides has progressed enormously, where the ligands employed range from simple acyclic to complex macrocyclic ones[1-4]. As part of our study on coordination characteristics of Schiff base ligands on lanthanide ions, we have synthesized mixed ligand complexes of Pr(III), Nd(III), Sm(III), Eu(III), Gd(III) and Dy(III) ions with 4-methoxy-4'-N,N-dimethylaminodiphenylazomethine (MDDA) and diphenylsulphoxide (DPSO). They were characterized by various physicochemical methods. The Schiff base MDDA was found to be monodentate even though it has three coordination sites, *viz.*, one methoxy oxygen atom, one imino nitrogen atom, one tertiary nitrogen atom (Fig. 1). DPSO is also monodentate coordinating through oxygen atom.
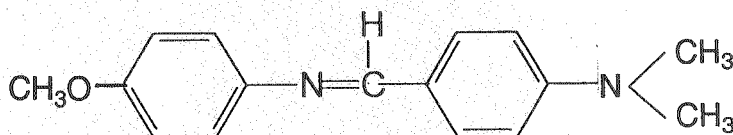

Fig. 1.   4-Methoxy-4'-N,N-dimethylaminodiphenylazomethine (MDDA)

EXPERIMENTAL

The Schiff base was prepared by refluxing equimolar methanolic solutions of 4-methoxy aniline and 4-N,N'-dimethylamino benzaldehyde for 3 h. The reaction

mixture was slowly cooled to get yellow crystals of the Schiff base. These crystals were filtered out, washed with ethanol and recrystallized from hot ethanol. The purity of the sample was checked by elemental analysis, IR spectral studies and the melting point (m.p. = 198°C). The yield was found to be 92%.

The following general procedure was employed for the preparation of lanthanide nitrato complexes with MDDA and DPSO. Lanthanide nitrate (2.06 mmol), MDDA (6.2 mmol) and DPSO (2.06 mmol) were dissolved separately in hot methanol (30 mL each). These solutions were mixed together and the reaction mixture was refluxed for 4 h on a water bath. The viscous mass was washed repeatedly with hot benzene (10 mL each) to remove excess ligand. The complex so obtained was then dissolved in minimum amount of methanol (3 mL) and to this solution, petroleum ether was added at a stretch with constant stirring, whereupon the solid complex separated out. The complex was then washed 3–4 times with petroleum ether (10 mL each) and dried *in vacuo* over P_4O_{10} (yield = 80–86%).

Thiocyanato complexes were prepared by substitution method. The nitrato complex was dissolved in 20 mL methanol. The solution was refluxed with the required quantity of ammonium thiocyanate for 3 h. The resulting solution was concentrated and was allowed to stand overnight when the solid material was obtained. This was then washed successively with benzene till the benzene washings became colourless. It was finally recrystallized from alcohol and washed with petroleum ether and dried *in vacuo* over P_4O_{10}.

The metal contents of the complexes were estimated by oxalate-oxide method. The CHN data of the complexes were taken from CDRI, Lucknow. The TG and DTG curves of the complexes were recorded using a thermal analyzer model TGA SDT-290 in an atmosphere of oxygen from room temperature to about 900°C. The nitrate content of the complexes was determined as nitronitrate[5, 6]. Thiocyanate was determined as AgSCN from alkali thiocyanate solution. The molar conductances of the complexes were determined in methanol, acetonitrile and nitrobenzene 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. IR spectra of the ligands and complexes were recorded in the range 4000–400 cm^{-1}. Electronic spectra were also taken for ligands and complexes in the range 185–900 nm using a Shimadzu UV-Vis spectrophotometer. Molecular mass was determined by Rast method using biphenyl as solvent. 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.

RESULTS AND DISCUSSION

From the analytical data (Tables 1 and 2) the complexes have the general formula [Ln(MDDA)$_3$(DPSO)X$_3$] where Ln = Pr, Nd, Sm, Eu, Gd or Dy and X = NO$_3^-$ or NCS$^-$. Molar conductivity values of all complexes in three solvents, *viz.*, nitrobenzene, acetonitrile and methanol were determined and they gave very

TABLE-1

ANALYTICAL DATA OF LANTHANIDE(III) NITRATO COMPLEXES WITH MDDA AND DPSO

Complex	Colour	m.w. Found (Calcd.)	% Analysis: Found (Calcd.)					Yield (%)
			Ln	Anion	C	H	N	
[Nd(MDDA)$_3$(DPSO)(NO$_3$)$_3$]	Brown	1289.5 (1290.9)	10.66 (10.92)	14.30 (14.40)	56.12 (55.77)	4.92 (4.96)	9.75 (9.76)	86
[(MDDA)$_3$(DPSO)(NO$_3$)$_3$]	Brown	1292.0 (1294.2)	11.02 (11.10)	14.30 (14.37)	55.61 (55.63)	4.90 (4.95)	9.71 (9.74)	82
[(MDDA)$_3$(DPSO)(NO$_3$)$_3$]	Dark Brown	1299.9 (1300.35)	11.46 (11.50)	14.20 (14.30)	55.29 (55.37)	4.89 (4.92)	9.68 (9.69)	86
[(MDDA)$_3$(DPSO)(NO$_3$)$_3$]	Brown	1301.8 (1302.0)	11.59 (11.60)	14.20 (14.29)	55.29 (55.30)	4.89 (4.92)	9.67 (9.68)	80
[(MDDA)$_3$(DPSO)(NO$_3$)$_3$]	Light Brown	1306.8 (1307.25)	11.98 (12.02)	14.11 (14.22)	55.01 (55.08)	4.82 (4.90)	9.62 (9.64)	81
[(MDDA)$_3$(DPSO)(NO$_3$)$_3$]	Reddish Brown	1310.2 (1312.5)	12.12 (12.30)	14.10 (14.17)	54.24 (54.86)	4.79 (4.88)	9.51 (9.60)	82

TABLE-2

ANALYTICAL DATA OF LANTHANIDE(III) THIOCYANATO COMPLEXES WITH MDDA AND DPSO

Complex	Colour	m.w. Found (Calcd.)	% Analysis: Found (Calcd.)					Yield (%)
			Ln	Anion	C	H	N	
[(MDDA)$_3$(DPSO)(NCS)$_3$]	Light Brown	1277.5 (1278.9)	10.90 (11.02)	13.45 (13.61)	58.90 (59.11)	4.99 (5.00)	9.80 (9.85)	72
[(MDDA)$_3$(DPSO)(NCS)$_3$]	Brown	1280.0 (1282.24)	10.99 (11.25)	13.40 (13.57)	58.70 (58.96)	4.98 (4.99)	9.80 (9.83)	74
[n(MDDA)$_3$(DPSO)(NCS)$_3$]	Yellowish Brown	1285.5 (1288.35)	11.50 (11.67)	13.30 (13.51)	58.60 (58.68)	4.95 (4.97)	9.76 (9.78)	68
[(MDDA)$_3$(DPSO)(NCS)$_3$]	Brown	1289.0 (1290.0)	11.69 (11.78)	13.29 (13.49)	58.58 (58.60)	4.95 (4.96)	9.73 (9.77)	62
[(MDDA)$_3$(DPSO)(NCS)$_3$]	Dark Brown	1293.5 (1295.25)	11.90 (12.14)	13.28 (13.43)	58.25 (58.37)	4.92 (4.94)	9.70 (9.73)	70
[y(MDDA)$_3$(DPSO)(NCS)$_3$]	Brown	1299.0 (1300.5)	12.49 (12.50)	13.20 (13.37)	58.10 (58.13)	4.90 (4.92)	9.60 (9.69)	72

low values showing the non-electrolytic character of molecules. The ligand MDDA exhibits a strong band at 1610 cm^{-1} which is attributed to $\nu(C=N)$ of azomethine group in the ligand. This band appears at a lower wavenumber region appearing at 1585 cm^{-1} in the spectra of the complexes. The lower shift (*ca.* 25 cm^{-1}) of $\nu(C=N)$ suggests that the azomethine nitrogen is coordinated to the lanthanide ions in the present complexes.

IR spectrum of DPSO exhibits a strong band at 1090 cm^{-1}. In the spectra of the complexes it is red shifted to 1025 cm^{-1} indicates that the oxygen atom of the sulfoxide of DPSO is coordinated to the lanthanide ions. The stretching frequency of (S=O) in the ligand is lowered by 65 cm^{-1}. Thus the primary and secondary ligands are coordinated in a monodentate fashion.

Infrared spectra of lanthanide nitrato complexes show bands at 1475 cm^{-1} and 1334 cm^{-1}. These bands are assigned to ν_4 and ν_1 of monodentate nitrate groups and the separation between the bands is 141 cm^{-1}. This is in support of the unidentate character of nitrate groups. These complexes show a vibrational mode at 1060 cm^{-1} (ν_2). Two medium intensity bands are seen at 1720 cm^{-1} and 1706 cm^{-1} which are the combination bands. Since the difference is only 14 cm^{-1} it can be inferred that the nitrate group is coordinated monodentately to the metal ion[7-9].

In the thiocyanato complexes, the very strong band observed at 2050 cm^{-1} can be assigned to $\nu(C-N)$ of the coordinated thiocyanate group. The medium intensity band found at 820 cm^{-1} is assigned to $\nu(C-S)$ vibration of N-coordinated NCS group. The spectrum shows a medium intensity band at 470 cm^{-1} which is attributed to $\delta(NCS)$ bending vibration of nitrogen coordinated thiocyanate group. Thus it can be inferred that the thiocyanate groups is coordinated to metal through its nitrogen atom[10-12].

Two complexes of MDDA and DPSO, *viz.*, [Gd(MDDA)$_3$(DPSO)(NO$_3$)$_3$] and [Dy(MDDA)$_3$(DPSO)(NCS)$_3$] were subjected to thermal analysis in oxygen atmosphere. The details are given in Table-3

TABLE-3

Complex	DTG (K)				Final residue	% mass of final product	
	First stage	Peak temp.	Second stage	Peak temp.		Indpendent pyrolysis	Theor.
[Gd(MDDA)$_3$(DPSO)(NO$_3$)$_3$]	403–573	522	613–773	676	Gd$_2$O$_3$	13.82	13.85
[Dy(MDDA)$_3$(DPSO)(NCS)$_3$]	423–583	533	633–753	683	Dy$_2$O$_3$	14.31	14.34

Both have two stages of decomposition. The first one corresponds to the decomposition of one mole of DPSO per mole of the complex followed by the formation of metal oxide.

The spectrum of the ligand exhibits two bands in the UV region at 237 nm and 362 nm. These bands are assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions respectively of the ligand. These two bands are present in the same region in the spectra of all the complexes. An additional band is present at 300 nm in the spectra of the complexes. This band is due to L $\rightarrow$ M charge transfer transition. There is no band corresponding to *f-f* transitions in the spectra of the complexes indicating that the *f-f* transitions are too weak to be observed.

The observed magnetic moments of all the complexes except those of Sm and Eu agree well with the Hund values[13]. The experimental magnetic moments of all the complexes including Sm and Eu agree well with the Van Vleck theoretical values. The disagreement of the observed magnetic moments of Sm and Eu complexes with that of the Hund theoretical value is due to the fact that the first excited state of these metal ions is close to the ground states and hence mixing up of these states is possible. However, in the Van Vleck theoretical value the first excited state of Sm and Eu is taken into consideration and hence there is agreement with the observed and theoretical values. The magnetic moment values of these complexes are in agreement with the values reported for the free lanthanide ions. This shows that the $4f$ electrons are not disturbed by the ligand field and that they are not involved in bonding in the present complexes.

Analytical, molar conductance and theromogravimetric data suggest the following general formula for these complexes: $[Ln(MDDA)_3(DPSO)X_3]$ where $Ln = Pr$, Nd, Sm, Eu, Gd and Dy and $X = NO_3^-$ or NCS^-. Thus a coordination number 7 is assigned to all these complexes.

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