Asian Journal of Chemistry Vol. 13, No. 3 (2001), 1142–1146

Studies on the Coordination Behaviour of a Polydentate Schiff Base in Presence of Dimethyl Sulphoxide on Rare Earth Metal Ions

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The present investigation is concerned with the studies on the coordination behaviour of Schiff base of pyridine-2-carboxaldehyde and 4-aminoantipyrine in presence of oxygen donor ligands such as dimethyl sulphoxide. Mixed ligand complexes of the lanthanide ions *viz.*, La^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Gd^{3+} and Dy^{3+} with Schiff base and dimethyl sulphoxide have been synthesised and characterized. The analytical data include elemental analysis, molecular weight determination, conductivity, magnetic moment, spectral, thermal and antimicrobial studies. The compositions of these complexes are found to be $[Ln(P_2CAAP)(DMSO)(NO_3)_3$ where Ln = La, Pr, Nd, Sm, Gd and Dy. In these complexes the primary ligand acts as a neutral bidentate ligand; the secondary ligands *viz.*, DMSO and the monovalent nitrate anion act as unidentate.

INTRODUCTION

A through search of the literature has shown that nitrate complexes of certain Ln^{3+} ions with the Schiff base derived from pyridine-2-carboxaldehyde and 4-aminoantipyrine were prepared and characterized. In all these complexes, the potential donor atoms were reported to be ring carbonyl oxygen, imino nitrogen and pyridne nitrogen.[1, 2] Hence it is most interesting to study the coordination behaviour of this ligand in presence of coordinating oxygen donor ligand such as dimethyl sulphoxide and monovalent nitrate ion. Thus a series of six mixed ligand complexes of lanthanide ion with this Schiff base (Fig. 1) and DMSO were prepared and characterized. It is observed that the Schiff base P_2CAAP acts as bidentate ligand coordinating with the ring carbonyl oxygen and the imino nitrogen and no coordination from pyridine nitrogen in all these complexes.

EXPERIMENTAL

The ligand 4 N-(pyridine-2′-carboxaldehyde) aminoantipyrine (P_2CAAP) was prepared by the literature method.[2] Equimolar quantities of pyridine-2-carboxaldehyde and 4-aminoantipyrine in ethanol were mixed together. The reaction

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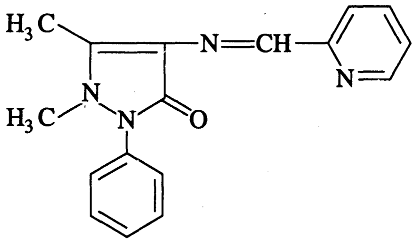

Fig. 1. 4N-(pyridine-2′-carboxalidene) amino antipyrine (P_2CAAP)

mixture was kept at 5–10°C for 2 h and then kept at room temperature (28 ± 2°C) for 30 min with vigorous stirring, whereupon crystals of P_2CAAP separated. The crystals were collected and washed with diethyl ether. The crude products were recrystallised from hot 50% (v/v) ethanol.

The following general procedure was employed for the preparation of lanthanide nitrate complexes with P_2CAAP and DMSO. Equimolar quantities of solutions of lanthanide nitrate, P_2CAAP and DMSO in methanol were mixed together and the reaction mixture was refluxed on a water bath for 2–3 h. Then the resulting solution was concentrated and extracted with diethyl ether. The complexes so prepared were collected, washed with hot benzene and dried in vacuo over phosphorus(V) oxide. All the six complexes are nonhygroscopic solids with yellow colour. These complexes are completely soluble in dimethyl formamide and DMSO, partially soluble in methanol, acetone, acetonitrile and nitrobenzene and insoluble in diethyl ether.

The TG and DTG curves of the complex were recorded on a thermal analyser from ambient to 700°C. The mass percentage *vs.* temperature curve obtained was redrawn on appropriate scale. Independent pyrolysis experiment in air was also carried out for each of the complexes studied, and loss of mass determined in each case was compared with that obtained from TG.

The metal contents of the complexes were obtained by oxalate-oxide method.[3] The nitrate contents of the complexes were determined as nitron nitrate.[4] the molar conductances of the complexes in acetonitrile, methanol and nitrobenzene were measured at room temperature (28 ± 2°C) using an ELICO conductivity bridge type CM82T with a dip type conductivity cell having platinum electrodes (cell constant = 0.94 cm^{-1}). The solutions used for conductivity measurements had concentrations in the range 10^{-3} M. The electronic spectra of the ligand and the complexes were recorded in methanol (*ca.* 10^{-3} M solutions) in the range 185–900 nm. The IR spectra of the ligands and the complexes were recorded in KBr in the range 4000–400 cm^{-1}. Molecular masses of the complexes were determined by Rast method using biphenyl as the solvent.[5] The magnetic moments of the complexes were obtained at room temperature (28 ± 2°C) using EG&G Parc Model 155 Vibrating Sample Magnetometer. The diamagnetic corrections for the rest of the molecule and the completed shells of the lanthanide ions were computed from Pascal's constants.[6] The antibacterial study of the ligand

and the complex [La(P_2CAAP)(DMSO)(NO_3)$_3$] were carried out trubidimetrically[7] on *Staphylococcus aureus* ATCC 28923 at various concentrations.

RESULTS AND DISCUSSION

From the analytical data (Tables 1) the complexes have the general formula [Ln(P_2CAAP)(DMS)(NO_3)$_3$], where Ln = La, Pr, Nd, Sm, Gd and Dy.

TABLE-1
ANALYTICAL DATA OF LANTHANIDE(III) COMPLEXES

Complex (colour)	m.w. found (calcd.)	% Analysis, found (calcd.)		
		M	Anion	S
[La(P_2CAAP)(DMSO)(NO_3)$_3$] (yellow)	686 (695)	19.71 (19.97)	26.42 (26.75)	4.41 (4.60)
[Pr(P_2CAAP)(DMSO)(NO_3)$_3$] (yellow)	689 (697)	20.03 (20.20)	26.25 (26.67)	4.42 (4.59)
[Nd(P_2CAAP)(DMSO)(NO_3)$_3$] (yellow)	690 (701)	20.36 (20.58)	26.43 (26.55)	4.30 (4.57)
[Sm(P_2CAAP)(DMSO)(NO_3)$_3$] (yellow)	695 (707)	21.10 (21.27)	26.07 (26.32)	4.25 (4.53)
[Gd(P_2CAAP)(DMSO)(NO_3)$_3$] (yellow)	705 (714)	21.19 (22.03)	25.89 (26.06)	4.12 (4.48)
[Dy(P_2CAAP)(DMSO)(NO_3)$_3$] (yellow)	707 (719)	22.45 (22.60)	25.66 (25.87)	4.08 (4.45)

TABLE-2
MOLAR CONDUCTANCE DATA OF LANTHANIDE(III) COMPLEXES

Complexes	Molar conductance in ohm^{-1} cm^2 mol^{-1}		
	Acetonitrile	Methanol	Nitrobenzene
[La(P_2CAAP)(DMSO)(NO_3)$_3$]	48	52	2.7
[Pr(P_2CAAP)(DMSO)(NO_3)$_3$]	44	63	2.5
[Nd(P_2CAAP)(DMSO)(NO_3)$_3$]	45	71	3.1
[Sm(P_2CAAP)(DMSO)(NO_3)$_3$]	43	64	3.2
[Gd(P_2CAAP)(DMSO)(NO_3)$_3$]	38	63	3.5
[Dy(P_2CAAP)(DMSO)(NO_3)$_3$]	40	62	3.4

Molar conductivity values of the complexes in acetonitrile, methanol and nitrobenzene were in the ranges corresponding to those of non-electrolytes in these solvents.[8] The conductance values support that the nitrate ion is coordinated to the metal and hence the anions act as additional ligand.

The IR spectral studies of the complexes when compared with those of the ligand show a considerable shift in ν(C═N) azomethine absorption and ν(C=O) of ring carbonyl absorption to lower frequency indicating a decrease in stretching force constant of C=N and C=O groups. As a consequence of the coordination from azomethine nitrogen and ring carbonyl oxygen, the double bond character is reduced.[1,2] The strong bands observed at 1717 and 1587 cm^{-1} in the spectra of complexes are tentatively assigned to combination bands of ν(C=C) and ν(C=N) of pyridine ring which remain practically unchanged, revealing the non-involvement of the coordination of pyridine nitrogen.[9] The lowering in stretching frequency of the order of 80 cm^{-1} observed in the complexes at 1020 cm^{-1} is indicative of the bonding from the oxygen atom of sulphoxide.[10]

TABLE-3
MAGNETIC SUSCEPTIBILITIES OF LANTHANIDE(III) COMPLEXES

Complexes	Magnetic moment in B.M.		
	μ_{eff} found	μ_{eff} Calcd.*	μ_{eff} Calcd.†
$[Ln(P_2CAAP)(DMSO)(NO_3)_3]$	0	0	0
$[Pr(P_2CAAP)(DMSO)(NO_3)_3]$	3.71	3.58	3.62
$[Nd(P_2CAAP)(DMSO)(NO_3)_3]$	3.76	3.62	3.69
$[Sm(P_2CAAP)(DMSO)(NO_3)_3]$	1.83	0.84	1.69
$[Gd(P_2CAAP)(DMSO)(NO_3)_3]$	7.86	7.94	7.94
$[Dy(P_2CAAP)(DMSO)(NO_3)_3]$	10.52	10.61	10.61

*The Hund values; †The Van Vleck values.

The complexes show three additional bands at 1470, 1378 and 1026 cm^{-1} which are absent in the spectra of ligand. These bands are due to ν_4, ν_1 and ν_2 of the coordinated nitrate ion. The magnitude of the splitting of the ν_3 band (*i.e.*, $\Delta\nu = \nu_4 - \nu_1$) is 92 cm^{-1}. Therefore, the nitrate ions are coordinated unidentately in these complexes, This is further confirmed by observing conductivity.

In the spectra of complexes, there are three additional bands at 516, 460 and 410 cm^{-1} which have no corresponding bands in the spectrum of the ligand. The band at 516 cm^{-1} may be attributed to ν(Ln—O) mode of the covalently bonded oxygen atom of the nitrate ion. The band at 460 cm^{-1} indicates the covalently bonded nitrogen atom ν(Ln—N) and the band at 410 cm^{-1} indicates the covalently bonded oxygen atom ν(Ln—O) of the ligand.

The magnetic moments of the complexes at room temperature are in good agreement with the theoretical values calcuataed from Van Vleck formula.[11] The lanthanide complex is diamagnetic as expected for the noble gas configuration of La^{3+} ion with $4f^0$ state and others are paramagnetic with $4f^n$ state. The complex of Dy^{3+} exhibits higher magnetic moment and that of Sm^{3+} has lower value which are in agreement with Van Vleck values.

The electronic spectra of the complexes exhibit only the electronic transitions within the ligand moiety and they do not give much structural information of the complexes.

Thermal behaviour of one of the representative complexes, *i.e.*, [Ln(P_2CAAP) (DMSO)(NO_3)$_3$] has been studied. The TG plateau up to 280°C shows that it is stable up to this temperature. There are two decomposition stages as indicated by DTG peaks at 290°C and at 530°C. The TG curve exhibits a second plateau after 600°C. This shows the completion of decomposition. The independent pyrolysis experiment shows that the final decomposition product is La_2O_3 (23.43%) in conformity with the mass loss data obtained from TG (24%).

All these investigations confirm the structure of the complexes at [Ln(P_2CAAP)(DMSO)(NO_3)$_3$] where Ln = La, Pr, Nd, Sm, Gd and Dy. Thus the coordination number 6 is assigned to the metal in all the six complexes.

Anti-Bacterial Study: From literature it is found that the Schiff bases derived from heterocyclic aldehydes such as furan-2-aldehyde, thiophene-2-aldehyde and pyridine-2-aldehyde have been found to act as potential ligands and show considerable antibacterial activity.[12–14] The antibacterial property of the ligand P_2CAAP and the complex [Ln(P_2CAAP)(DMSO)(NO_3)$_3$] were studied at different concentrations (0.01, 0.02, 0.03, 0.04 and 0.05 mg/mL). The bacterial strain used for the study was *Staphylococcus aureus* ATCC 25923. But the observation revealed that the present ligand and the complex are not showing antibacterial property.

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(*Received:* 2 March 2001; *Accepted:* 28 April 2001) AJC-2332