

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

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Abstract: The present investigation is concerned with the studies on the coordination behaviour of schiff base of pyridine-2-carboxaldehyde and 4- amino antipyrine in presence of oxygen donor ligands such as dimethyl sulphoxide. Mixed ligand complexes of the lanthanide ions viz., La³⁺, Pr³⁺, Nd³⁺, Sm³⁺, Gd³⁺, and Dy³⁺ with schiff base and dimethyl sulphoxide have been synthesized and characterized. The analytical data include elemental analysis, molecular weight determination, conductivity, magnetic moment, spectral, thermal and antimicrobial studies. In these complexes the primary ligand acts as a neutral bidentate ligand, the secondary ligands viz., DMS and the monovalent nitrate anion act as unidentate.

Keywords: Antimicrobial studies, Dimethyl sulphoxide, Elemental analysis, Magnetic moment, Schiff base.

I. INTRODUCTION

A search through the literature has shown that nitrate complexes of certain Ln³⁺ ions with the schiff base derived from pyridine-2-carboxaldehyde and 4- amino antipyrine were prepared and characterized. In all these complexes, the potential donor atoms were reported to be ring carbonyl oxygen, imino nitrogen and pyridine 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 ions with this schiff base and DMS were prepared and characterized. It is observed that the schiff base P₂CAAP acts as bidentate ligand coordinating with the ring carbonyl oxygen and the imino nitrogen and no coordination from pyridine nitrogen in all these complexes. The structure of ligand can be represented as in Fig.1

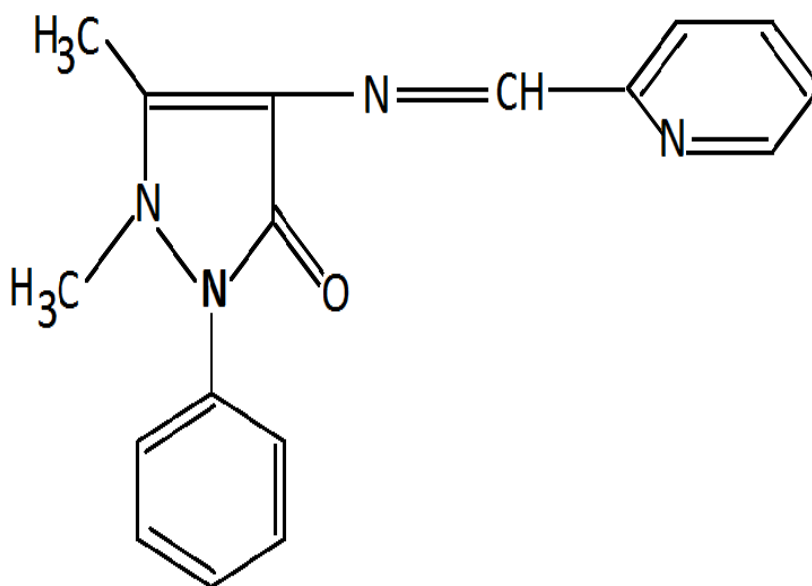


Fig.1 Structure of 4N-(pyridine-2'- carboxalidene) amino antipyrine (P₂CAAP)

II. MATERIALS AND METHODS

A. Chemicals and methods

All the chemicals used were of GR/AR grade quality obtained from Merck chemicals.

- 1) *Metal content and Molecular mass:* The metal contents of the complexes were obtained by oxalate- oxide method ^[3]. The nitrate content of the complexes was determined as nitron nitrate ^[4]. Molecular masses of the complexes were determined by Rast method using diphenyl as the solvent ^[4].
- 2) *Molar Conductivity:* The molar conductance values of the complexes in acetonitrile, methanol and nitrobenzene were measured at room temperature ($28 \pm 2^{\circ}\text{C}$) 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 .
- 3) *Electronic Spectra:* The electronic spectra of the ligand and the complexes were recorded in methanol ($\sim 10^{-3} \text{ M}$ solutions) in the range 185-900 nm.
- 4) *IR Spectra:* The IR spectra of the ligands and the complexes were recorded in KBr in the range $4000-400 \text{ cm}^{-1}$.
- 5) *Magnetic moment:* The magnetic moments of the complexes were obtained at room temperature ($28 \pm 2^{\circ}\text{C}$) using EG & G PARC MODEL 155 Vibrating Magnetometer. The diamagnetic corrections for the rest of the molecule and the completed shells of the lanthanide ions were computed from Pascal's constants ^[5].
- 6) *Antibacterial Study* The antibacterial study of the ligand and the complex $[\text{La}(\text{P}_2\text{CAAP})(\text{DMS})(\text{NO}_3)_3]$ were carried out turbidimetrically ^[6] on Staphylococcus Aureus ATCC 25923 at various concentrations.
- 7) *Thermal Analysis* The TG and DTG curves of the complex was recorded on a thermal analyser from ambient to 700°C . The mass percentage Vs. Temperature curve obtained was drawn in 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.

B. Synthesis of Ligand

The ligand P₂CAAP was prepared by the literature method ^[2]. Equimolar quantities of pyridine-2- carboxaldehyde and 4- amino antipyrine in ethanol were mixed together. The reaction mixture was kept at $5-10^{\circ}\text{C}$ for 2 hours and then kept at room temperature ($28 \pm 2^{\circ}\text{C}$) for 30 minutes with vigorous stirring, whereupon crystals of P₂CAAP separated. The crystals were collected and washed with diethyl ether. The crude products were crystallized from hot 50%(v/v) ethanol.

C. Synthesis of Complexes

Equimolar quantities of solutions of lanthanide nitrate, P₂CAAP and DMS in methanol were mixed together and the reaction mixture was refluxed on a water bath for 2-3 hr. Then the resulting solution was concentrated and extracted with diethyl ether. The complex so prepared were collected, washed with hot benzene and dried in vacuo over phosphorus (V) oxide.

III. RESULTS AND DISCUSSION

All these complexes are non- hygroscopic solids with yellow colour. These complexes are completely soluble in dimethyl formamide and DMS, partially soluble in methanol, acetone, acetonitrile and nitrobenzene and insoluble in diethyl ether.

A. Elemental Analysis

The formulae of complexes computed from analytical data is given in Table 1.

Table.1 Analytical data of Lanthanide Complexes

Complex	Colour	Mol. mass Calcd. (Found)	Percentage Analysis Calcd. (found)		
			Metal	Anion	Sulphur
$[\text{La}(\text{P}_2\text{CAAP})(\text{DMS})(\text{NO}_3)_3]$	Yellow	695 (686)	19.97 (19.71)	26.75 (26.42)	4.60 (4.41)

[Pr(P ₂ CAAP) (DMS)(NO ₃) ₃]	Yellow	697 (689)	20.20 (20.03)	26.67 (26.25)	4.59 (4.24)
[Nd(P ₂ CAAP) (DMS)(NO ₃) ₃]	Yellow	701 (690)	20.58 (20.36)	26.55 (26.43)	4.57 (4.30)
[Sm(P ₂ CAAP) (DMS)(NO ₃) ₃]	Yellow	707 (695)	21.27 (21.10)	26.32 (26.07)	4.53 (4.25)
[Gd(P ₂ CAAP) (DMS)(NO ₃) ₃]	Yellow	714 (705)	22.03 (21.91)	26.06 (25.89)	4.48 (4.12)
[Dy(P ₂ CAAP) (DMS)(NO ₃) ₃]	Yellow	719 (707)	22.60 (22.45)	25.87 (25.66)	4.08 (4.45)

B. Molar Conductivity

Molar conductivity values of the complexes in acetonitrile, methanol and nitrobenzene were in the ranges corresponding to those of non- electrolytes in these solvents ^[7]. The conductance values support that the nitrate ion is coordinated to the metal and hence the anion act as additional ligand.

Table 2. Molar Conductance data of Lanthanide complexes

Complex	Molar conductance in (Ohm ⁻¹ cm ² mol ⁻¹)		
	Acetonitril e	Methanol	Nitrobenzene
[La(P ₂ CAAP) (DMS)(NO ₃) ₃]	48	52	2.7
[Pr(P ₂ CAAP) (DMS)(NO ₃) ₃]	44	63	2.5
[Nd(P ₂ CAAP) (DMS)(NO ₃) ₃]	45	71	3.1
[Sm(P ₂ CAAP) (DMS)(NO ₃) ₃]	43	64	3.2
[Gd(P ₂ CAAP) (DMS)(NO ₃) ₃]	38	63	3.5
[Dy(P ₂ CAAP) (DMS)(NO ₃) ₃]	40	62	3.4

C. Magnetic moment

The magnetic moments of the complexes at room temperature are in good agreement with the theoretical values calculated from Van Vleck formula ^[10]. The lanthanide complex is diamagnetic as expected for the noble gas configuration of La³⁺ ion with 4f⁰ state and others are paramagnetic with 4fⁿ state. The complex of Dy³⁺ exhibits higher magnetic moment and that of Sm³⁺ has lower value which are in agreement with Van Vleck values.

Table 3. Magnetic Moment values of Lanthanide complexes

Complex	Magnetic moment in B. M		
	μ_{eff} (found)	μ_{eff} (Calcd)*	μ_{eff} (Calcd)**
[La(P ₂ CAAP) (DMS)(NO ₃) ₃]	0	0	0
[Pr(P ₂ CAAP) (DMS)(NO ₃) ₃]	3.71	3.58	3.62
[Nd(P ₂ CAAP) (DMS)(NO ₃) ₃]	3.76	3.62	3.69
[Sm(P ₂ CAAP) (DMS)(NO ₃) ₃]	1.83	0.84	1.65
[Gd(P ₂ CAAP) (DMS)(NO ₃) ₃]	7.86	7.94	7.94
[Dy(P ₂ CAAP) (DMS)(NO ₃) ₃]	10.52	10.61	10.61

* The Hund Values

** The Van Vleck values

Based on these investigations, the present complexes can be formulated as

[Ln(P₂CAAP) (DMS)(NO₃)₃], Where Ln = La, Pr, Nd, Sm, Gd and Dy.

D. IR Spectra

The IR spectral studies of the complexes when compared with those of the ligand, show a considerable shift in $\nu_{\text{C}=\text{N}}$ azomethine absorption and $\nu_{\text{C}=\text{O}}$ 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 coordination from azomethine nitrogen and ring carbonyl oxygen, the double bond character is reduced [1,2]. The strong band observed at 1717 and 1587 cm⁻¹ in the spectra of complexes are tentatively assigned to combination bands of $\nu_{\text{C}=\text{C}}$ and $\nu_{\text{C}=\text{N}}$ of pyridine ring which remain practically unchanged, revealing the non- involvement of the coordination of pyridine nitrogen [8]. 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 oxygen atom of sulphoxide [9].

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 $\nu_{\text{Ln}-\text{O}}$ mode of the covalently bonded oxygen atom of the nitrate ion. The band at 460 cm⁻¹ indicates the covalently bonded nitrogen atom ($\nu_{\text{Ln}-\text{N}}$) and the band at 410cm⁻¹ indicates the covalently bonded oxygen atom ($\nu_{\text{Ln}-\text{O}}$) of the ligand.

E. Electronic Spectra

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.

F. Thermal Analysis

Thermal behaviour of one of the representative complex i.e., [La(P₂CAAP) (DMS)(NO₃)₃] has been studied. The TG plateau upto 280⁰C shows that it is stable upto this temperature. There are two decomposition stages as indicated by DTG peaks at 290⁰C and 530⁰C. The TG curve exhibits a second plateau after 600⁰C. this shows the completion of decomposition. The independent pyrolysis experiment shows that the final decomposition product is La₂O₃(23.43%) in conformity with the mass loss data obtained from TG (24%)

G. Antibacterial Study

From literature, it is found that the schiff bases derived from heterocyclic aldehydes such as furan-2- aldehyde, thiophene and pyridine-2- aldehyde can act as potential ligands and show considerable antibacterial activity [10-13]. The antibacterial property of the ligand P₂CAAP and the complex [Ln(P₂CAAP) (DMS)(NO₃)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.

IV. CONCLUSION

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 synthesized and characterized by analytical and spectral data. Analytical and spectral data confirmed the structure of complexes as $[\text{Ln}(\text{P}_2\text{CAAP})(\text{DMS})(\text{NO}_3)_3]$, Where Ln = La, Pr, Nd, Sm, Gd and Dy. Thus the coordination number 6 is assigned to the metal in all the complexes. According to conductivity measurements all the complexes are non-electrolytes. The ligand and its complexes do not show any antibacterial activity.

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