

Synthesis, Characterization and Antimicrobial Studies of Some Mixed Ligand Complexes of Lanthanide(III) Ions

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The present investigation is concerned with the synthesis, characterization and antimicrobial studies of some mixed ligand complexes of lanthanide(III) ions, viz., La^{3+} , Pr^{3+} , Nd^{3+} , Sm^{3+} , Gd^{3+} and Dy^{3+} with the Schiff base pyridine-2-carboxaldehyde-4-aminoantipyrine and different anions such as acetate, chloride, nitrate and thiocyanate. The analytical data include elemental analysis, molecular mass determination, conductivity, magnetic moment, spectral, thermal and antimicrobial studies. The composition of these complexes is found to be $[\text{Ln}(\text{P}_2\text{CA4AAP})_2(\text{an})_3]$, where $\text{Ln} = \text{La, Pr, Nd, Sm, Gd and Dy}$ and $\text{an} = \text{acetate, chloride, nitrate and thiocyanate}$. In these complexes the primary ligand acts as a neutral tridentate ligand, the secondary ligands, viz., the monovalent acetate, chloride, nitrate and thiocyanate anions act as unidentate.

Key Words: Mixed ligand complexes, Lanthanides, Synthesis, Characterization, Antimicrobial.

INTRODUCTION

A search through 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 characterized¹. In all these complexes, the potential donor atoms were reported to be the ring carbonyl oxygen, imino nitrogen and pyridine nitrogen^{1,2}. Hence it is most interesting to investigate the coordination behaviour of this ligand in presence of coordinating anions and their antimicrobial activities. Thus a series of 24 mixed ligand complexes of lanthanide ions with this Schiff base and four different anions were prepared and characterized. It is observed that the Schiff base $\text{P}_2\text{CA4AAP}$ acts as a neutral tridentate ligand coordinating with the ring carbonyl oxygen, imino nitrogen and pyridine nitrogen in all these complexes.

EXPERIMENTAL

The ligand $\text{P}_2\text{CA4AAP}$ was prepared by the literature method¹. Equimolar quantities of pyridine-2-carboxaldehyde and 4-aminoantipyrine in ethanol were

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mixed together. The reaction mixture was kept at 5–10°C for 2 h and then kept at room temperature ($28 \pm 2^\circ\text{C}$) for 30 min with vigorous stirring, where upon crystals of $\text{P}_2\text{CA4AAP}$ separated. The crystals were collected and washed with diethyl ether. The crude products were recrystallized from hot 50% (v/v) ethanol.

Preparation of complexes

The lanthanide nitrate complexes with $\text{P}_2\text{CA4AAP}$ were prepared by the reported method¹. Lanthanide nitrate (2.0 mmole) and $\text{P}_2\text{CA4AAP}$ (4.1 mmole) were dissolved separately in hot methanol. These solutions were mixed together and the reaction mixture was stirred well so that the complex was separated out. The reaction mixture was kept on a steam bath for 20 minutes and the complex separated was filtered, washed with benzene to remove excess ligand and dried *in vacuo* over P_4O_{10} .

Lanthanide chloride (2.0 mmole) and $\text{P}_2\text{CA4AAP}$ (4.1 mmole) in hot methanol were mixed together and the reaction mixture was refluxed on a water bath for 2 h. Then the resulting solution was concentrated to 15 mL and petroleum ether was added to it with vigorous stirring to separate the solid chloro complex. The complexes so prepared were collected, washed with hot benzene and dried *in vacuo* over P_4O_{10} .

The acetato and thiocyanato complexes were prepared by substitution method. Each of the lanthanide nitrate complexes with $\text{P}_2\text{CA4AAP}$ (1 mmole) was dissolved in methanol, which was mixed with an aqueous-methanol (50% v/v) of each of the different anionic salts such as sodium acetate (3.0 mmole) and ammonium thiocyanate (3 mmole). Each of the reaction mixtures was refluxed on a water bath for 3 h in order to replace the nitrate ions with the respective anions. The resulting solution was then concentrated to 10 mL by evaporation on the water bath, and the concentrate was cooled to get the complex precipitated. The solid complex so obtained in each case was collected, washed repeatedly with hot 50% (v/v) aqueous-methanol and dried *in vacuo* over P_4O_{10} .

The metal contents of the complexes were determined gravimetrically by oxalate-oxide method³. The nitrate contents of the nitrate complexes were determined gravimetrically using the nitron reagent⁴. The chloride contents of chloro compounds were determined gravimetrically by Volhard's method⁴. The thiocyanate contents of the thiocyanato complexes were determined gravimetrically as AgSCN from alkali thiocyanate solution using AgNO_3 solution in presence of nitric acid⁴. The CHN data of the acetato complexes were obtained from Regional Research Laboratory, Thiruvananthapuram. Molecular mass of the complexes were determined by the Rast method⁵ using biphenyl as the solvent. The molar conductance 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 of 10^{-3} M . The electronic spectra of the ligand and the complexes were recorded in methanol ($\text{Ca.} 10^{-3} \text{ M}$ solutions) in the range 185–900 nm. The IR spectra of the ligand and the complexes were recorded in KBr in the range $4000\text{--}400 \text{ cm}^{-1}$. The magnetic moments of the complexes were

obtained at room temperature $28 \pm 2^\circ\text{C}$ using EG and 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 constants⁶.

The antibacterial activity of the ligand and its complexes was evaluated by the agar plate diffusion technique⁷ at 500 $\mu\text{g}/\text{disc}$ concentration of each compound in DMSO. Filter paper (Whatman no. 4) discs (6 mm dia) were soaked in solutions of the test compounds and placed after drying off the solvent on Muller Hinton agar plate containing lawn culture of different bacteria. The plates were incubated at an optimum growth temperature of 37°C . The zones of inhibition around the discs were measured after 24 h. The test bacteria included (a) *Staphylococcus aureus*, (b) *Escherichia coli*, (c) *Klebsiella* and (d) *Pseudomonas aeruginosa*. Streptomycin was used as a standard drug. The activity is reported by measuring the diameter of the inhibition zone in mm. The results are presented in Table-2.

The TG and DTG curves of the complex were recorded on a thermal analyser from ambient to 700°C . 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.

TABLE-1
CHARACTERIZATION DATA OF COMPLEXES

Complex	m.w. Found (Calcd.)	% Analysis, Found (Calcd.)			
		M	Anion		
[LaL ₂ (NO ₃) ₃]	900 (909.62)	15.01 (15.27)	20.39 (20.45)		
[NdL ₂ (NO ₃) ₃]	920 (914.95)	15.50 (15.77)	20.19 (20.33)		
[LaL ₂ Cl ₃]	821 (829.94)	16.53 (16.74)	12.79 (12.81)		
[DyL ₂ Cl ₃]	850 (853.53)	18.99 (19.04)	12.38 (12.46)		
[SmL ₂ (NCS) ₃]	905 (909.27)	16.44 (16.54)	19.01 (19.16)		
[GdL ₂ (NCS) ₃]	910 (916.17)	17.01 (17.16)	18.87 (19.02)		
[LaL ₂ (OAc) ₃]	891 (900.72)	15.34 (15.42)	C 53.29 (53.34)	H 4.63 (4.59)	N 12.47 (12.44)
[PrL ₂ (OAc) ₃]	905 (902.72)	15.55 (15.61)	53.10 (53.22)	4.48 (4.58)	12.39 (12.42)

TABLE-2
ANTIBACTERIAL ACTIVITY DATA OF THE LIGAND AND COMPLEXES

L/Complex	Inhibition Zone (in mm) against			
	<i>Staphylococcus aureus</i>	<i>Escherichia coli</i>	<i>Klebsiella</i>	<i>Pseudomonas aeruginosa</i>
L	R	R	8	8
[LaL ₂ (NO ₃) ₃]	R	8	9	R
[NdL ₂ (NO ₃) ₃]	R	R	8	9
[LaL ₂ Cl ₃]	12	10	12	10
[DyL ₂ Cl ₃]	12	11	12	10
[SmL ₂ (NCS) ₃]	R	R	R	R
[GdL ₂ (NCS) ₃]	R	8	8	10
[LaL ₂ (OAc) ₃]	9	R	R	R
[PrL ₂ (OAc) ₃]	8	10	8	R

RESULTS AND DISCUSSION

From the analytical data (Table-1) the complexes have the general formula [Ln(P₂CA4AAP)₂(an)₃], where Ln = La, Pr, Nd, Sm, Gd and Dy; an = acetate, chloride, nitrate and thiocyanate.

Molar conductivity values of the complexes in acetonitrile, methanol and nitrobenzene were in the ranges corresponding to those of non-electrolytes in these solvents⁸. The conductance values support that the anions like acetate, chloride, nitrate and thiocyanate ions are coordinated to the metal ion and hence the anions act as additional ligands.

The IR spectral studies of the complexes, when compared with those of the ligand, show a considerable shift in $\nu(\text{C}=\text{O})$ of ring carbonyl from 1644 cm^{-1} to ca. 1620 cm^{-1} and in the $\nu(\text{C}=\text{N})$ of azomethine absorptin from 1565 cm^{-1} to ca. 1507 cm^{-1} indicating a decrease in stretching force constant of C=O and C=N groups. As a consequence of the coordination from the ring carbonyl oxygen and the azomethine nitrogen, bond order is reduced⁹. The bands appearing at 1488 and 701 cm^{-1} in the spectrum of the ligand which are assigned respectively to the stretching and out-of-plane bending vibrations of the pyridine ring are shifted to ca. 1473 and 676 cm^{-1} respectively. Hence P₂CA4AAP acts as a neutral tridentate ligands towards the lanthanide ions in presence of acetate, chloride, nitrate and thiocyanate ions, the donor atoms being the ring carbonyl oxygen, azomethine nitrogen and pyridine nitrogen.

The nitrate complexes show three additional bands at 1473, 1376 and 1024 cm^{-1} which are not present in the spectra of P₂CA4AAP and other anionic complexes. These bands are due to ν_4 , ν_1 and ν_2 modes of the coordinated nitrate ion. The separation between ν_4 and ν_1 bands is 97 cm^{-1} in the present complexes indicating that nitrate ions are coordinated unidentately¹⁰. In the spectra of complexes there are three additional bands at 516, 476 and 425 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 ion¹¹. The band at 476 cm^{-1} indicates the covalently bonded nitrogen atom¹² $\nu(\text{Ln}-\text{N})$ and the band at 425 cm^{-1} indicates the covalently bonded oxygen atom¹³ $\nu(\text{Ln}-\text{O})$ of the ligand.

The spectra of the chloro complexes with $\text{P}_2\text{CA4AAP}$ show an additional weak band in the far infrared region at 290 cm^{-1} assignable to $\nu(\text{M}-\text{Cl})$ vibration¹⁴.

The spectra of the acetato complexes with $\text{P}_2\text{CA4AAP}$ show two bands at 1589 and 1344 cm^{-1} which are absent in the spectra of the ligand and other complexes. These bands are assigned respectively to asymmetric and symmetric stretching vibrations of carboxylate ion¹⁵. It is also observed that ν_{asym} and ν_{sym} bands of the carboxylate ion in the free acid (acetic acid) occur at 1560 and 1416 cm^{-1} respectively¹⁶. In the spectra of the complexes the $\nu_{\text{asym}}(\text{OCO})$ mode is shifted to higher region (1589 cm^{-1}) whereas $\nu_{\text{sym}}(\text{OCO})$ mode is shifted to lower frequency (1344 cm^{-1}). These shifts indicate that acetate ion is coordinated to the lanthanide ions in these complexes.

The IR spectra of the thiocyanato complexes with $\text{P}_2\text{CA4AAP}$ exhibit three additional bands at 2064 , 777 and 511 cm^{-1} , which are assigned respectively to $\nu(\text{CN})$, $\nu(\text{CS})$ and $\delta(\text{NCS})$ modes of the coordinated thiocyanate ion¹⁶. It has been ascertained that $\nu(\text{CN})$ occurs at a lower wavenumber around 2050 cm^{-1} in N-bonded complexes as compared to the position in the case of S-bonded complexes appearing above 2100 cm^{-1} . Moreover, $\nu(\text{CS})$ mode appears in the range $860-780\text{ cm}^{-1}$ for N-bonded complexes while it appears in the range $720-690\text{ cm}^{-1}$ for S-bonded complexes. N-bonded complexes also exhibit a single sharp $\delta(\text{NCS})$ band near 480 cm^{-1} , whereas the S-bonded complexes show several bands of low intensity¹⁷ near 420 cm^{-1} . In the present thiocyanato complexes, $\nu(\text{CN})$ appears at 2064 cm^{-1} , $\nu(\text{CS})$ at 777 cm^{-1} and $\delta(\text{NCS})$ at 511 cm^{-1} . In view of these observations thiocyanate ions of the present complexes are coordinated unidentately to the lanthanide ions through the nitrogen atom and not through the sulphur atom¹⁷. Coordination of the thiocyanate ion is also supported by the non-electrolytic behaviour of the complexes as evident from the molar conductivity values of the complexes in different solvents.

The magnetic moments of the complexes at room temperature are in good agreement with the theoretical values calculated from Van Vleck formula¹⁸. 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 values which are in agreement with Van Vleck values.

The electronic spectrum of the ligand exhibits three bands at 42 , 39 and 29 kK . The spectra of the complexes also exhibit these three bands more or less at the same regions. Therefore 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.

The stability of these complexes has been studied in their thermal behaviour. All these complexes are stable up to *ca.* 200°C and undergo decomposition in two stages except the acetato complex which decomposes in a single stage. These two decomposition stages are parts of a continuous process of decomposition and,

hence, there is no separation between these stages. Therefore, isolation of intermediate products could not be possible. The decomposition is over by *ca.* 650 °C. As far as the final products are concerned, all the complexes gave La_2O_3 irrespective of the ligand. The mass loss data obtained from TG curve and independent pyrolysis along with theoretical value agree well with the final residue.

From the thermal decomposition studies it is evident that these complexes do not contain any water of hydration and they can be very well dried at a temperature below 200°C.

All these investigations confirm the structure of the complexes as $[\text{Ln}(\text{P}_2\text{CA4AAP})_2(\text{an})_3]$ where $\text{Ln} = \text{La, Pr, Nd, Sm, Gd}$ and Dy and $\text{an} = \text{acetate, chloride, nitrate and thiocyanate}$. Thus the coordination number 9 is assigned to the metal ions in all the twenty four complexes.

Biological activity: There are reports¹⁹ that metal chelates of lanthanides possess considerable biocidal properties. The screening data of the complexes have been presented in Table-2. It was observed that the Schiff base was physiologically active against *Klebsiella* and *Pseudomonas aeruginosa*. In certain cases chelation enhanced their activity. The increased activity of the complexes is probably due to a comparatively faster diffusion of the metal complexes as a whole through the cell membrane of the bacteria. It was also observed that the presence of chloride ion in the coordination sphere further increased the activity when compared to the nitrate complex²⁰. The low activities of some complexes can be explained on the basis of low lipid solubility. Therefore, the metal ion cannot reach the desirable site of action of the cell wall to interfere with the normal cell activity. The nature of metal ion also plays a decisive role in determining antibacterial properties²¹. Nitrate complexes exhibited less inhibition. The bonding capacity of nitrate ion towards central metal ion is greater than that of the chloride ion. As a result of this the extent of metal ion available is lessened for the display of antibacterial activity. A possible mode of toxicity may be speculated in the light of chelation theory²².

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