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Synthesis, characterization and biological evaluation of Schiff base derived from 3 amino pyridine and its lanthanides (III) complexes

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Abstract- The synthesis of lanthanide complexes derived from Schiff base ligands obtained by the condensation of 3 amino pyridine with different aldehydes viz. 4 hydroxy benzaldehyde, 4 chloro benzaldehyde were synthesized in alcoholic medium. The prepared Schiff bases and their complexes were characterized on the basis of elemental analysis, IR, 1HNMR, Mass spectral studies. The compounds have been screened for Antimicrobial activity against the organisms Escherichia coli, Salmonella typhi, Staphylococcus aureus, and Basillus subtilis. The antifungal Activities of complexes were tested using fungal species such as Aspergillus Niger and Pencillium Crysogenum. Some complexes showed good antibacterial activities.

Keywords- *3 amino pyridine , Schiff base ,antimicrobial activity, Lanthanide*

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I. INTRODUCTION

Metal complexes have been receiving considerable attention for many years, due to their interesting characteristics in the field of material science and biological systems. A large number of Schiff bases and their complexes have possessed important properties. Example ,their ability to reversibly bind oxygen, transfer of an amino group and complexing ability towards some metals[1-4] One of the major applications of lanthanide complexes in medicine is their use as water proton relaxation agents for NMR imaging [5, 6]. The research in this field is directed towards the synthesis of stable, nontoxic, highly paramagnetic molecules with the ability to improve efficiently the contrast of the magnetic resonance image. There is lots of variety in Schiff-base metal complexes with wide number of ligands and coordination environments have prompted researchers to take interest in this research area [7]. The development of the field of bioinorganic chemistry has increased the interest in Schiff base complexes, since it has been recognized that many of these complexes may serve as models for biologically important species and were investigated for antifungal, antimicrobial, anti- bacterial ,anti-inflammatory, anti-convulsant ,anticancer activities[8-12]. The chemistry of lanthanide complexes with Schiff bases has received little attention compared with the *d* block metal complexes. Recently, there has been a growing interest in the lanthanide–Schiff base complexes owing to the important applications of both metals and ligands [13].

II. EXPERIMENTAL

A. Material and Methods

All the chemicals and solvents used were of A.R. grade. All chemicals used were of Merck and S.D. fine Ltd. The IR spectra were recorded on a PERKIN ELMER spectrophotometer in the frequency range 4000-400 cm-1 in Nujol mull and as KBr pellets. 1HNMR spectra were recorded on BRUKER AVANCE II 400 spectrometer with TMS as internal standard using DMSO as solvents. Mass Spectra were recorded on Q-TOF MICROMASS spectrometer. The reactions were followed up and purity of compounds was monitored on TLC plates using different solvent system and visualizing the spots in iodine chamber.

B. Step I:

Synthesis of Schiff base ligands:

The Schiff base ligands were prepared by equimolar mixture of aldehyde derivatives (0.01mol) and 3amino pyridine (0.01mol) in ethanol for 4-5 hr. The reaction mixture was poured in ice cold water, on cooling the obtained crystalline precipitates were filtered, washed with ethanol and recrystallized from absolute ethanol and dried. They are light coloured crystalline solids, stable at normal condition and soluble in DMSO, DMF; partially soluble in benzene and water.

The following Schiff base ligands obtained and characterized.

a. 3-(4 hydroxy- benzylidene) amino pyridine(HBAP) (Figure. 1)
b. 1-(4-chloro benzylidene) amino pyridine(CBAP) (Figure. 2)

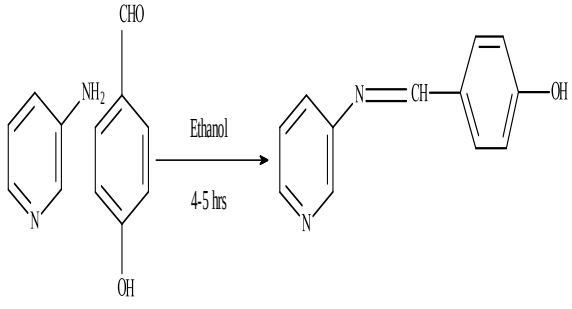

Figure 1: 3- (4-hydroxy benzylidene) amino pyridine (HBAP)

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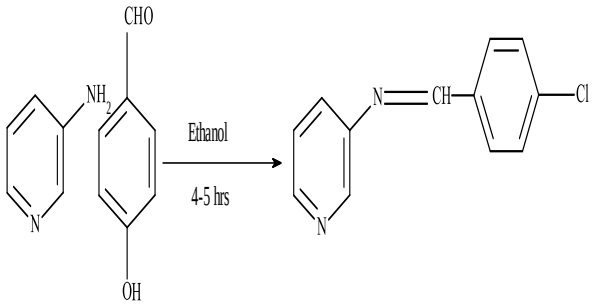

Figure 2: 3- (4-chloro benzylidene) amino pyridine (CBAP)

C. *Step II :*

Synthesis of Lanthanide (III) complexes:

Lanthanum (III) complexes were prepared by the following method**:**

To a hot solution of ligand (0.01) moles in 40ml of ethanol 0.01 moles of metal salt dissolved in 25ml of ethanol was added drop wise. The contents were refluxed for four hours. The precipitated complex was further digested for one hour. The complex formed was filtered and washed with alcohol and followed by petroleum ether. It was dried in vacuum desiccators over calcium chloride.

III. RESULTS AND DISCUSSION

A. *Physical Properties*

All the complexes are stable at room temperature and are non-hygroscopic. On heating, They decompose at high temperatures. The complexes are insoluble in water but are soluble in DMSO.

Table 1. Physical Properties of Schiff Base Dy (III) Complexes

Compound	Molecular Formula	Colour	Yield
HBAP(L_1)	$C_{12}H_{10}N_2O$	White	76%
CBAP(L_2)	$C_{12}H_9NCl$	White	79%
$[Dy(L_1)(NO_3)(H_2O)]NO_3$	$C_{12}H_{12}N_3O_8Dy$	Light Red	68%
$[Dy(L_2)(NO_3)(H_2O)]NO_3$	$C_{12}H_{11}N_3O_7Dy$	Pale Yellow	78%

B. *IR Spectra*

The relevant infrared data are given in Table 2. The assignments of the bands were made by comparison of spectral data of analogous compounds The presence of a strong, sharp peak at 1626cm–1 in the ligand spectrum corresponds to C=N vibrations and confirms the formation of the Schiff base. In complexes, this band suffers a bathochromic shift to 1570–1590cm–1 region indicating the involvement of imine nitrogen atom in coordination to the metal ion.

Sr. No.	Compound	(Ar-H)	(CH=N)	(-NO_3)	(M–N)	(M–O)
1	L1	3059	1622	-	-	-
2	$[Dy(L1)(NO_3)(H_2O)]NO_3$	2923	1604	1356	598	494
3	L2	3035	1621	-	-	-
4	$[Dy(L2)(NO_3)(H_2O)]NO_3$	3080	1620	1306	573	413

Table 2. IR Spectral Data Of Schiff Base and Dysprosium (III) Complexes

Sr. No.	Compound	(CH=N)	(Ar-H)	(-OH)
1	L1	8.35	7.28	10.17
2	$[Dy(L1)(NO_3)(H_2O)]NO_3$	8.60	7.5-7.8	-
3	L2	8.49	7.93	-
4	$[Dy(L2)(NO_3)(H_2O)]NO_3$	8.46	7.1-7.6	-

Table 3. ^{1}HNMR Spectra Data Of Schiff Base and Dysprosium (III) Complexes

Sr. No.	Compound	Obtained mass m/Z	Peak assigned
1	L1	198	M+
2	$[Dy(L1)(NO_3)(H_2O)]NO_3$	472	M+
3	L2	217	M+
4	$[Dy(L2)(NO_3)(H_2O)]NO_3$	491	M+

Table 4: Mass Spectra Data Of Schiff Base and Dysprosum (III) Complexes

C. *Antimicrobial activity*

The Schiff base and their corresponding metal complexes were screened in vitro for their antibacterial activity against two Gram-negative (Escherichia coli and Salmonella typhi) and two Gram-positive (Bacillus subtilis and Staphylococcus aureus) bacterial strains and antifungal activity against organisms *A.niger* and *P.Crysogenum* using agar well diffusion method using Streptomycin as standard. The results of antibacterial studies are presented in Table 4. A comparative study of the ligand and their metal complexes indicates that most of the metal complexes exhibit higher antimicrobial activity than that of the free ligand. Hence Complexation increases antimicrobial activity.

Compound	Antibacterial				Antifungal	
	E. coli	*S. aureus*	*B. subtilis*	*S. typhi*	*A. niger*	*P.Crysogenum*
HBAP	19	20	R	20	18	14
$[Dy(L_1)(NO_3)(H_2O)]NO_3$	20	20	R	20	18	18
CBAP	16	20	15	10	14	16
$[Dy(L_2)(NO_3)(H_2O)]NO_3$	22	20	R	22	18	16

Table 5. Antimicrobial Activity Tests of Schiff Bases and Their Dysprosium (III) Complexes

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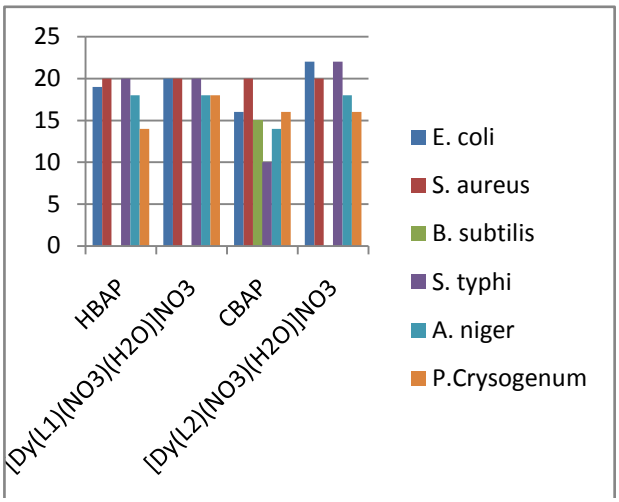

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