

## Synthesis, Characterization, Spectral & Antimicrobial studies of some new lanthanide complexes derived from 2,4 and 2,5-dihydroxy acetophenones.

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### ABSTRACT

*La (III), Sm (III), Th (IV) and  $UO_2^{+2}$  (IV) complexes were synthesized from 2-aminopyridine with 2,4 and 2,5 dihydroxy acetophenones. The Schiff bases and complexes were characterized by elemental analysis and spectral data. The Schiff bases as well as metal complexes of La (III), Sm (III), Th (IV) and  $UO_2^{+2}$  (IV) have been screened for their antimicrobial activity against *Bacillus Subtilis*, *Escherichia coli*, and *Aspergillus flavis* respectively. The comparison of antimicrobial activities of the ligands and metal complexes shows that the presence of metal causes more inhibition ie more activity.*

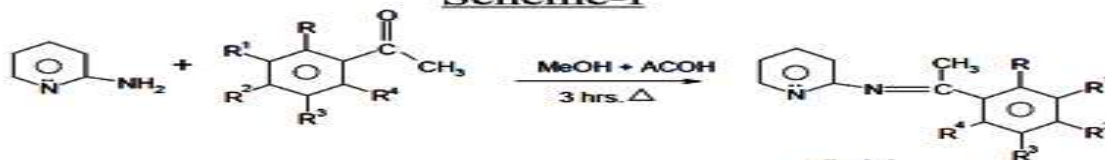
**Key words:** 2-Amino pyridine, Acetophenones, Ligands, Complexes and Antimicrobial activity.

### INTRODUCTION

Hydroxy acetophenones were used as starting material for the synthesis of chalcones [1] flavones[2] and Schiff bases [3-4] etc. Schiff bases of hydroxy aldehydes and ketones were widely used in coordination chemistry for the preparation of metal complexes [5-6]. Schiff bases and their coordination compounds have been gained importance now-a-days as they are useful in biochemical [7], anti-cancer [8], anti-inflammatory [9], antipyretic [10], among others. Some of them have been used as complexing agent [11-12] and powerful corrosion inhibitors [13]. A Schiff base of hydroxy acetophenone and its complex have a variety of applications in biological, clinical, analytical and pharmacological areas [14-16]. Earlier work has shown that some drugs showed increased activity when administered as metal chelates rather than as organic compounds [17-18] and that the coordinating possibility of hydroxy acetophenone has been improved by condensing with a variety of carbonyl compounds. A search through literature [19-25] reveals that no work has been done on inner transition metal complexes of the Schiff bases derived from 2-amino pyridine and hydroxy acetophenones.

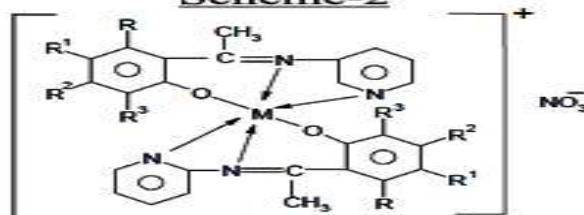
In this paper, I report the synthesis of new type of ligands and their metal complexes with La(III), Sm (III), Th (IV),  $UO_2^{+2}$ (IV) and screening their antimicrobial activity. Further the structure of synthesized complexes were confirmed by elemental analysis and spectral studies. The structure of the ligands are shown in scheme-1 and complexes are shown in scheme-2.

Scheme-1



$L_1$ : R=H,  $R^1$ =H,  $R^2$ =OH,  $R^3$ =H,  $R^4$ =OH,  $L_2$ : R=H,  $R^1$ =OH,  $R^2$ =H,  $R^3$ =H,  $R^4$ =OH

Scheme-2



( $L_1$  La, Sm, Th,  $UO_2^{+2}$  -  $L_2$  La, Sm, Th,  $UO_2^{+2}$ )  
 Complexes with  $L_1$  (La, Sm, Th,  $UO_2^{+2}$ ): R=H,  $R^1$ =H,  $R^2$ =OH,  $R^3$ =H.  
 Complexes with  $L_2$  (La, Sm, Th,  $UO_2^{+2}$ ): R=H,  $R^1$ =OH,  $R^2$ =H,  $R^3$ =H.

## EXPERIMENTAL SECTION

All melting points were taken in open glass capillaries and were uncorrected. The purity of compounds has been checked by T.L.C. on silica gel G. The IR spectra in KBr were recorded on shimazu spectrophotometer and  $^1H$ NMR spectra were recorded in DMSO on varian Inova 300 FTMHz spectrophotometer using TMS as a internal standard. ( $\delta$ , ppm)

### General procedure for the synthesis of ligands derived from 2-amino pyridine (scheme-1)

2-amino pyridine (0.01 mole) was dissolved in methyl alcohol (50 ml) to which was added ketone (0.01 mole) and the mixture was refluxed for 3-4 hr at 80-100°C. The reaction mixture was then poured over crushed ice or cold water. The solid separated was filtered, washed with water and recrystallized from ethyl alcohol. (Comp.  $L_1$ - $L_2$ ) Table-1.

### General experimental procedure for the synthesis of metal complexes (Scheme-2)

An ethanolic solution of Schiff base and metal ion solution ( $Cl^-/NO_3^-$ ) in molar amount was refluxed for 4hr. After refluxing, the volume of solution was reduced to one third and concentrated, cooled at 0°C. The solid colored complex formed was filtered, washed with ethanol and dried in vaccum (Comp.  $L_1$ La,Sm,Th, $UO_2^{+2}$  -  $L_2$  La,Sm,Th, $UO_2^{+2}$ ). Table-2.

## RESULTS AND DISCUSSION

Characterization of compounds ( $L_1$ - $L_2$ ) and ( $L_1$  La, Sm, Th,  $UO_2^{+2}$  -  $L_2$  La, Sm, Th,  $UO_2^{+2}$ ) Table 1 and 2 shows the molecular formula, molecular weight, melting point, percentage yield of all newly synthesized compounds. The IR and  $^1H$  NMR data and antimicrobial activity of synthesized compounds are given below.

**Spectroscopic data of selected compounds**

**(L<sub>1</sub>):** IR (KBr): 3000-3200 (b), (-OH), 1620(C=C Ar-str.), 1360 (C=N str.), 1250 (C-O Ar-OH str.), 781-742 (C-H bending),  $\text{cm}^{-1}$ ; <sup>1</sup>H NMR(DMSO,300 FTMHz):  $\delta$  2.5 (s, 3H,CH<sub>3</sub>),  $\delta$  6.2-7.3 (m, 7H, Ar-H),  $\delta$  12.50 (s, 2H, Ar-OH)ppm; Anal. Found (Calcd.):C, 68.22 (68.42); H, 52.21(52.63); N, 12.00 (12.28) %

**L<sub>1</sub>(La):** IR (KBr): 1622 (C=C Ar str.), 1384 (C=N str.), 1240 (C-O Ar-OH str.), 770-740 (C-H bending),  $\text{cm}^{-1}$ ; <sup>1</sup>H NMR (DMSO, 300 FTMHz):  $\delta$  2.5 (s, 3H, CH<sub>3</sub>), 6.4-7.5 (m, 7H, Ar-H), 1253 (s, 1H, -OH str.) ppm; Anal. Found (Calcd.): C, 52.53 (52.70); H, 3.57 (3.70); N, 11.42 (11.80)%

**L<sub>1</sub>(Sm):** IR (KBr): 1622 (C=C Ar str.), 1386 (C=N str.), 1223 (C-O Ar-OH str.), 780-755 (C-H bending),  $\text{cm}^{-1}$ ; <sup>1</sup>H NMR (DMSO, 300 FTMHz):  $\delta$  2.5 (s, 3H, CH<sub>3</sub>), 7.0-7.8 (m, 7H, Ar-H), 1252 (s, 1H, -OH str.) ppm; Anal. Found (Calcd.): C, 48.58 (48.75); H, 3.09 (3.43); N, 8.64 (8.75)%

**L<sub>2</sub>(Th):** IR (KBr): 1620 (C=C Ar str.), 1330 (C=N str.), 1242 (C=O Ar-OH str.), 780-743 (C-H bending),  $\text{cm}^{-1}$ ; <sup>1</sup>H NMR (DMSO, 300 FTMHz):  $\delta$  2.3 (s, 3H, CH<sub>3</sub>), 6.28-7.5 (m, 7H, Ar-H), 1242 (s, 1H, -OH str.) ppm; Found (Calcd.): C, 45.40 (45.48); H, 2.98 (3.20); N,11.99 (12.24)%

**L<sub>2</sub>(UO<sub>2</sub><sup>+2</sup>):** IR (KBr): 1619 (C=C Ar str.), 1332 (C=N str.), 1240 (C=O Ar-OH str.), 770-739 (C-H bending),  $\text{cm}^{-1}$ ; <sup>1</sup>H NMR (DMSO, 300 FTMHz):  $\delta$  2.4 (s, 3H, CH<sub>3</sub>), 6.5-7.3 (m, 7H, Ar-H), 1266 (s, 1H, -OH str.) ppm; Found (Calcd): C, 42.92 (43.09); H, 2.80 (3.03); N,7.61 (7.75)%

**Table 1: Physical data and yields of synthesized Schiff bases**

Comp. Code	Molecular Formula	Molecular Weight	M.P. (°C)	Colour	Yield (%)
L <sub>1</sub>	C <sub>13</sub> H <sub>12</sub> O <sub>2</sub> N <sub>2</sub>	228	230	Radish	78
L <sub>2</sub>	C <sub>13</sub> H <sub>12</sub> O <sub>2</sub> N <sub>2</sub>	228	210	Greenish	80

**Table 2: Physical data and yields of synthesized metal complexes**

Comp. Code	Molecular Formula	Colour	Decomposition temp (°C)	Yield (%)
L <sub>1</sub> (La)	C <sub>26</sub> H <sub>22</sub> O <sub>7</sub> N <sub>5</sub>	Pink	>273	68
L <sub>1</sub> (Sm)	C <sub>26</sub> H <sub>22</sub> O <sub>4</sub> N <sub>4</sub>	Ash	>250	60
L <sub>1</sub> (Th)	C <sub>26</sub> H <sub>22</sub> O <sub>10</sub> N <sub>6</sub>	Faint pink	>250	52
L <sub>1</sub> (U)	C <sub>26</sub> H <sub>22</sub> O <sub>6</sub> N <sub>4</sub>	Black	>248	58
L <sub>2</sub> (La)	C <sub>26</sub> H <sub>22</sub> O <sub>7</sub> N <sub>5</sub>	Greenish	>252	52
L <sub>2</sub> (Sm)	C <sub>26</sub> H <sub>22</sub> O <sub>4</sub> N <sub>4</sub> Cl	Muddy	>250	60
L <sub>2</sub> (Th)	C <sub>26</sub> H <sub>22</sub> O <sub>10</sub> N <sub>6</sub>	Greenish	>250	62
L <sub>2</sub> (U)	C <sub>26</sub> H <sub>22</sub> O <sub>6</sub> N <sub>4</sub>	black	>250	66

## Antimicrobial activity

### Preparation of plates and microbiological assays

The *in vitro* antibacterial activity of synthesized ligands as well as complexes was tested against some clinically important bacteria by the disc diffusion method [26] using Mueller-Hinton agar No. 2 as the nutrient medium. The solutions of ligands as well as their complexes were prepared in DMSO (200 ppm). Inoculation of test bacteria (*E.coli* and *Bs*) was prepared by inoculating a loopful of organism in a 10 ml nutrient broth and incubated at 37°C for 24 hrs each till a moderate turbidity was developed. 0.1 ml of this suspension was thoroughly mixed with 25 ml of nutrient agar medium in each. Pre-sterilized Petri plates and was set aside. After the cooling, the seeded agar plate was used for testing compounds by disc diffusion method. The sterilized paper discs were dipped in each compound solution. These discs were placed in the plates at equidistant. The central disc without any compound was taken as control. The Petri-plates then incubated at 37°C for 24 hrs. After the recommended period, zones of inhibition were measured.

For testing fungal activity the monoculture (*As*) was used to prepare spore suspension in distilled water. The medium Mortins Rose Bengal streptomycin in Agar (MRBSA) was poured in pre-sterilized Petri-plates. After solidification of medium, 0.1 ml of spore suspension was spread by sterilized spreader in a specific zone.

The compounds were dissolved in DMSO solvent in 200 ppm concentration. The paper discs were deeped in each compound solution for 5 min. Then these paper discs were placed equidistant in the plates. The central disc was deeped in DMSO solvent without compound was used as control. These

Petri plates were kept for incubation period at  $\pm 28^{\circ}\text{C}$  for 6 days. After the completion of recommended period, the zones of inhibition were measured (Table-3).

**Table 3: Antimicrobial activity of ligands and their complexes**

Comp. Code	Antibacterial Activity.		Antifungal activity
	Zone of inhibition (mm)		Zone of inhibition (mm)
	<i>Bs</i>	<i>E.coli</i>	<i>Af</i>
L <sub>1</sub>	12	13	10
L <sub>1</sub> (La)	17	16	12
L <sub>1</sub> (Sm)	20	18	14
L <sub>1</sub> (Th)	16	20	13
L <sub>1</sub> (U)	16	14	12
L <sub>2</sub>	13	12	10
L <sub>2</sub> (La)	21	16	21
L <sub>2</sub> (Sm)	15	16	10
L <sub>2</sub> (Th)	18	15	13
L <sub>2</sub> (U)	22	13	20
DMSO (200ppm)	10	10	11

\* *Bs* = *Bacillus Subtilis* \**Ecoli* = *Escherichia coli* \**Af* = *Aspergillus flavis*

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