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Synthesis and spectral analysis of some new lanthanide complexes derived from 2,4 and 2,5-dihydroxy acetophenones and screened their antimicrobial activity

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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 comparision 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 co-ordination chemistry for the preparation of metal complexes [5-6]. Schiff bases and their co-ordination 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

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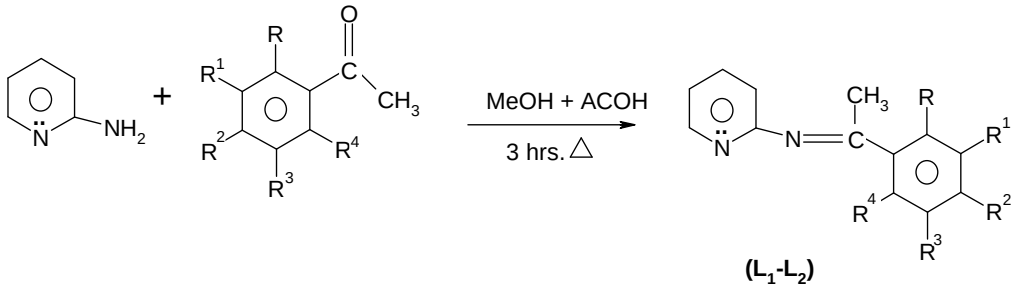
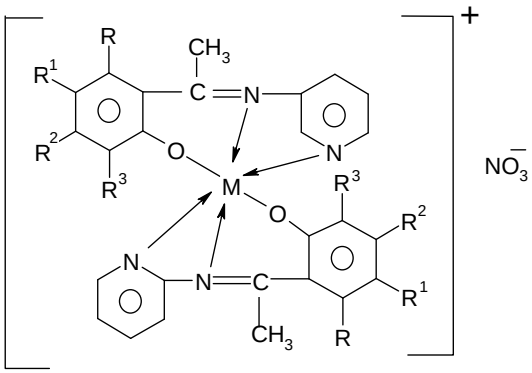
them have been used as complexing agent [11-12] and powerful corrosion inhibitors [13]. A Schiff base of hydroxy acteophenone and its complex have a variety of applications in biological, clinical, analytical and pharmacological areas [14-16]. Earlier work has shown that some drugs showed increased activity when administered as metal chelates rather than as organic compounds [17-18] and that the co-ordinating 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, we 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 compounds 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.



(L_1-L_2)

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-1**



(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.

Scheme-2

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 ^{1}HNMR spectra were recorded in DMSO on varian Inova 300 FTMHz spectrophotometer using TMS as a internal standard. (δ, 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^{o}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^{o}C. The solid colored complex formed was filtered, washed with ethanol and dried in vaccum (Comp. L_1La,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 ^{1}H NMR data and antimicrobial activity of synthesized compounds are given below.

Spectroscopic data of selected compounds
(L_1): 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), cm-^{1} ; ^{1}H NMR(DMSO,300 FTMHz): δ 2.5 (s, 3H, CH_3), δ 6.2-7.3 (m, 7H, Ar-H), δ 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_1(La): IR (KBr): 1622 (C=C Ar str.), 1384 (C=N str.), 1240 (C-O Ar-OH str.), 770-740 (C-H bending), cm^{-1}; ^{1}H NMR (DMSO, 300 FTMHz): δ 2.5 (s, 3H, CH_3), 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_1(Sm): IR (KBr): 1622 (C=C Ar str.), 1386 (C=N str.), 1223 (C-O Ar-OH str.), 780-755 (C-H bending), cm^{-1}; ^{1}H NMR (DMSO, 300 FTMHz): δ 2.5 (s, 3H, CH_3), 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_2(Th): IR (KBr): 1620 (C=C Ar str.), 1330 (C=N str.), 1242 (C=O Ar-OH str.), 780-743 (C-H bending), cm^{-1}; ^{1}H NMR (DMSO, 300 FTMHz): δ 2.3 (s, 3H, CH_3), 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_2(UO_2^{+2}): IR (KBr): 1619 (C=C Ar str.), 1332 (C=N str.), 1240 (C=O Ar-OH str.), 770-739 (C-H bending), cm^{-1}; ^{1}H NMR (DMSO, 300 FTMHz): δ 2.4 (s, 3H, CH_3), 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. (^oC)	Colour	Yield (%)
L_1	$C_{13}H_{12}O_2N_2$	228	230	Radish	78
L_2	$C_{13}H_{12}O_2N_2$	228	210	Greenish	80

Table 2: Physical data and yields of synthesized metal complexes

Comp. Code	Molecular Formula	Colour	Decomposion temp (^oC)	Yield (%)
L_1 (La)	$C_{26}H_{22}O_7N_5$	Pink	>273	68
L_1(Sm)	$C_{26}H_{22}O_4N_4$	Ash	>250	60
L_1(Th)	$C_{26}H_{22}O_{10}N_6$	Faint pink	>250	52
L_1(U)	$C_{26}H_{22}O_6N_4$	Black	>248	58
L_2(La)	$C_{26}H_{22}O_7N_5$	Greenish	>252	52
L_2(Sm)	$C_{26}H_{22}O_4N_4Cl$	Muddy	>250	60
L_2(Th)	$C_{26}H_{22}O_{10}N_6$	Greenish	>250	62
L_2(U)	$C_{26}H_{22}O_6N_4$	black	>250	C6

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^{o}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^{o}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 ±28^{o}C for 6 days. After the completion of recommended period, the zones of inhibition were measured (Tabel-3).

Table 3: Antimicrobial activity of ligands and their complexes

Comp. Code	Antibacterial Activity. Zone of inhibition (mm)		Antifungal activity Zone of inhibition (mm)
	Bs	*E.coli*	*Af*
L_1	12	13	10
L_1 (La)	17	16	12
L_1(Sm)	20	18	14
L_1(Th)	16	20	13
L_1(U)	16	14	12
L_2	13	12	10
L_2(La)	21	16	21
L_2(Sm)	15	16	10
L_2(Th)	18	15	13
L_2(U)	22	13	20
DMSO (200ppm)	10	10	11

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

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