ISSN NO. 2320-5407

Journal homepage: http://www.journalijar.com

INTERNATIONAL JOURNAL OF ADVANCED RESEARCH

RESEARCH ARTICLE

La (III) complexes with Schiff base ligands: Synthesis, Characterization and Antimicrobial Studies.

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Manuscript Info

Manuscript History:

Received: 14 December 2015
Final Accepted: 22 January 2016
Published Online: February 2016

Key words:
La (III), antimicrobial activity, 3 amino pyridine, Schiff base.

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Abstract

Four novel lanthanum complexes with different Schiff bases were synthesized and characterized. Schiff bases were prepared by condensation 3 amino pyridine with different aldehydes.The prepared Schiff bases and their lanthanum complexes have been characterized by elemental analysis ,IR,^{1}H NMR spectral studies. The ligands and their lanthanum complexes have been screened for their biological activity against the bacteria, S.aureus, E.coli and the fungi Penicillium crysogenum and Aspergillus niger. The Schiff bases and their lanthanum complexes show variable activity of inhibition on the growth of bacteria.

Introduction:-

Coordination chemistry is an important branch of inorganic chemistry since the appearance of water on earth aqua complex ion of metal must have existed [1].The importance of Schiff bases in organic synthesis has increased over the past few decades because they are among the most versatile organic synthetic intermediates [2]. Schiff bases have also attracted much attention because of their ability to act as ligands for complexation of different metal ions in various oxidation states [3].They have been studied as a class of ligands and are known to coordinate with metal ions through the azomethine nitrogen atom. [4].Various metal complexes with bi and tridentate Schiff bases containing nitrogen and oxygen donor atoms play important role in biological system and represent interesting models for metalloenzymes, which efficiently catalyze the reduction of dinitrogen and dioxygen [5].In the recent years much interest has been focused on lanthanum complexes as they have found immense use as biological models and probes in material science and chemical process [6].Recently, the rare earth compounds have attracted a great deal of attention owing to their well-defined coordination geometries, distinctive electrochemical and photochemical properties[7].Schiff base metal complexes have been studied extensively because of their attractive chemical and physical properties and their wide range of applications such as catalysts, antimicrobials, corrosion inhibitors [8]. Schiff base derivatives and their transition metal complexes, known from the 19th century, have made considerable contributions to the advances in coordination chemistry [9].One of the most important applications is the use of Gd (III) complexes for magnetic resonance imaging(MRI)complexes are potentially useful as MRI contrast agents with low toxicity[10].Lanthanides (III) complexes show various biological activities antibacterial[11], antifungal[12], antitumor[13], antiHIV[14], anti-inflammatory[15].

Experimental:-

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.

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) (Fig. 1)
b. 1-(4-chloro benzylidene) amino pyridine(CBAP) (Fig. 2)
c. 1-(2-hydroxy benzylidene) amino pyridine(HBAP) (Fig. 3)
d. 1-(3-nitro benzylidene) amino pyridine(NBAP) (Fig. 4)

Synthesis of Lanthanum (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.

Results and discussion:-

It is well know that lanthanide ions have high affinity to hard donor atoms such as nitrogen and oxygen atoms. The result presented here show that, on the basis of IR and ^{1}HNMR spectral analysis indicates that the complexes have 1:1 (lanthanide: ligand) stoichiometry. The lanthanide complexes are stable and coloured. Ligands and their Lanthanide complexes are soluble in soluble in ethanol, DMSO, DMF.

Elemental analysis:-

The analytical data for the Complexes are given in Table 1. The data agree with the suggested molecular formula of the Complexes.

Table 1: elemental analysis of schiff base and lanthanum (iii) complexes

Compound	**Molecular Formula**	**Molecular weight**	**Cal.(Exp.)%**		
			C	**H**	**N**
HBAP	$C_{12}H_{10}N_2O$	198	72.72(72.76)	5.05(5.07)	14.14(14.17)
[La (L1)(NO_3)(H_2O)]NO_3	$C_{12}H_{12}N_3O_8La$	454	31.71(31.73)	2.64(2.68)	9.25(9.27)
CBAP	$C_{12}H_9NCl$	217	66.35(66.38)	4.14(4.17)	6.45(6.47)
[La(L2)(NO_3)$_2$(H_2O)]NO_3	$C_{12}H_{11}N_3O_7La$	473	30.44(30.46)	2.32(2.34)	8.87(8.90)
HBAP	$C_{12}H_{10}N_2O$	198	72.72(72.75)	5.00(5.5)	14.15(14.17)
La (L3)(NO_3)(H_2O)]NO_3	$C_{12}H_{12}N_3O_8La$	454	31.70(31.74)	2.65(2.67)	9.24(9.26)
NBAP	$C_{12}H_9N_3O_2$	227	63.43(63.41)	3.96(3.97)	18.50(18.55)
La (L4)(NO_3)(H_2O)]NO_3	$C_{12}H_{12}N_5O_9La$	483	29.89(29.81)	2.48(2.51)	14.49(14.52)

IR spectral studies:-

The IR spectra of the complexes were compared with those of the free ligand in order to determine the coordination sites that may be involved in coordination. Upon comparison it was determined that the v(C=N) stretching vibration is found in the Schiff base at 1570-163 cm1.This band shifted to lower wave numbers in the complexes indicating the participation of nitrogen in coordination. The new band at v M-O and M-N stretching vibrations were appeared at 550-450 and 510-560 cm-1in the spectra of metal complexes.

Table 2: ir spectral data of schiff baseand lanthanum (iii) complexes

Compound	**(Ar-H)**	**(CH=N)**)	**(-NO_3)**	**(M-N)**	**(M-O)**
SB_1	1580	3059	-		
[La(L1)(NO_3)(H_2O)]NO_3	1572	3039	1373	510	467
SB_2	1624	3035	-		
La (L2)(NO_3)(H_2O)]NO_3	1621	3048	1374	516	463
SB_3	1615	3050	-		
La (L3)(NO_3)(H_2O)]NO_3	1614	3054	1341	520	444
SB_4	1616	3055	-		
La (L4)(NO_3)(H_2O)]NO_3	1614	3097	1355	562	536

^{1}HNMR spectral data:-

^{1}H–NMR spectral studies of ligands and their lanthanum complexes were recorded in DMSO d6. The data are summarized in Table 3.The formation of Schiff bases and their lanthanum complexes were confirmed by the sharp singlet between 8.3-8.6 due to the azomethine proton. The sharp multiplet signals of the aromatic protons are found in the region 7.2-7.8.

Table 3: ^{1}hnmr spectra data of schiff baseand lanthanum (iii) complexes.

Compound	Aromatic H	C-H azomethine
SB_1	7.28	8.35
[La(L1)(NO_3)(H_2O)]NO_3	7.5-7.7	8.18
SB_2	7.93	8.49
La (L2)(NO_3)(H_2O)]NO_3	7.4-7.6	8.66
SB_3	7.66	8.60
La (L3)(NO_3)(H_2O)]NO_3	7.3-7.6	8.94
SB_4	7.69	8.45
La (L4)(NO_3)(H_2O)]NO_3	7.7-7.8	8.88

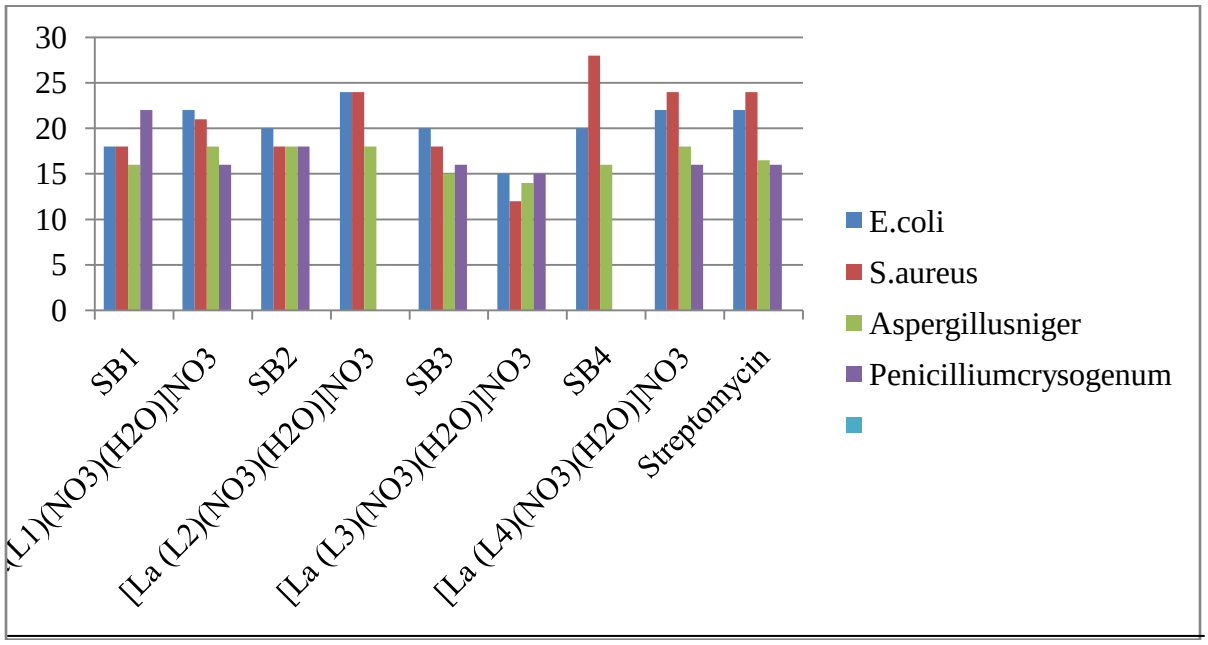
Antimicrobial activity:-

The ligand and some of their corresponding metal complexes were screened invitro for their antibacterial and antifungal activity against bacterial strains S.aureus, E.coli and the fungi Penicillium crysogenum and Aspergillus niger using agar well diffusion method using Streptomycin as standard. The results of antibacterial studies are presented in Table 5 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 and the control. Hence complexation increases antimicrobial activity.

Table 5: antimicrobial activity tests of schiff bases and their lanthanum (iii) complexes.

Compound	Antibacterial		Antifungal	
	E.coli	S.aureus	Aspergillusniger	Penicilliumcrysogenum
SB_1	18	18	16	22
[La(L1)(NO_3)(H_2O)]NO_3	22	21	18	16
SB_2	20	18	18	18
[La (L2)(NO_3)(H_2O)]NO_3	24	24	18	R
SB_3	20	18	15	16
[La (L3)(NO_3)(H_2O)]NO_3	15	12	14	15
SB_4	20	28	16	R
[La (L4)(NO_3)(H_2O)]NO_3	22	24	18	16
Streptomycin	22	24	16.5	16

(Diameter of inhibition zone in mm)



In Table 5-

R	: Resistant (10.0 mm and below)
S	: Sensitive (10.0 mm and above)
Slightly sensitive	: (10.0 mm above to 15.0 mm)
Moderately sensitive	: (15.0 mm above to 20.0 mm)
Highly sensitive	: (20.0 mm above)

Conclusion:-

In this paper, the synthesis of novel Schiff base ligand and its lanthanum metal complexes derived from condensation of 3-amino pyridine with different aldehydes have been described.. The complexes are in ML composition, non electrolytes and paramagnetic in nature. The biological activity of ligand is lower than the metal complexes. This means that metal chelation is significantly effective than the antimicrobial activity of Schiff base.

Acknowledgments:-

We are grateful to Dr. R.E. Khadsan, Principal the D.M. Burungle Science and Arts college, Shegaon, District: Buldhana (MS) for providing instrumental facilities and also thankful to Head of Department of Chemistry Dr. G. D. Tambatkar for their valuable guidance. We are also thankful to the Sophisticated Analytical Instrument Facility (SAIF), Chandigarh for providing IR, ^{1}H NMR Spectra of synthesised compounds.

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