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## SPECTRAL AND BIOLOGICAL STUDY OF SOME SCHIFF BASE COMPLEXES OF LANTHANIDES

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**Abstract:** *The studies of 12 new lanthanides (III) complexes are discussed. Schiff bases are obtained by the condensation of  $\alpha$  naphthylamine and 3 amino pyridine with different aldehydes eg.4 chloro benzaldehyde,4 hydroxy benzaldehyde,3 nitro benzaldehyde. Lanthanum (III) nitrate, dysprosium (III)nitrate, Neodymium(III) nitrate were chosen to synthesize new complexes. From the data it has been observed that the complexes has the composition of ML type. The complexes were characterized on the basis of physicochemical studies like IR,  $^1\text{HNMR}$ .All of the ligands and its complexes had been screened for their antibacterial activities against the bacteria (E.coli, Salmonella typhi .Bacillus subtilis, Staphylococcus aureus)and showed good antimicrobial activities against the tested Bacteria. Therefore possible use of the complexes as antibiotic can be suggested.*

**Key words:** *antimicrobial activity, metal complexes, Schiff bases, 3-amino pyridine,  $\alpha$  naphthylamine*

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## INTRODUCTION

Schiff bases, which are condensation products of primary amines and aldehydes or ketones ( $\text{RCH}=\text{NR}'$ , where R & R' represents alkyl and / or aryl substituents)[1]. Schiff bases have been subject of intense interest as a result of their synthetic accessibility and rich coordination chemistry. These compounds and their metal complexes have been reported to exhibit a wide spectrum of biological properties [2-3]. Schiff base complexes have remained an important and popular area of research due to their simple synthesis, versatility, and diverse range of applications [4,5]. Schiff bases and their transition and inner transition metal complexes, containing nitrogen and oxygen donor atoms play important role in biological and inorganic research and have been studied extensively due to their unique coordination and biological properties [6-7]. The chemistry of the lanthanide ions has been expanded rapidly in the past three decades. The interest in this chemistry is stimulated by their low toxicity, their potential uses as diagnostic tools in biology and their paramagnetic and luminescent properties [8]. The chemical behavior of Schiff base complexes with lanthanide has become increasingly significant in the last few years due to the wide variety of applications of lanthanide complexes in photochemistry, medicine [9]. Many biologically important Schiff bases have possessing antibacterial, antifungal, antihypertensive anticonvulsant, anti HIV, anti-inflammatory, antitumor and catalytic activities[10-16]. La (III) are of great importance for their industrial [17], chemical[18], biochemical and medicinal applications[19] due to their specific spectroscopic and magnetic properties.

## EXPERIMENTAL

### Material and Methods:

All the chemicals and solvents used were of A.R. grade. All chemicals used were of E-Merck and S.D. fine Ltd. Melting points were determined in an open capillary tube and are uncorrected. The IR spectra were recorded on a PERKIN ELMER spectrophotometer in the frequency range 4000-400  $\text{cm}^{-1}$  in Nujol mull and as KBr pellets.  $^1\text{H}$  NMR spectra were recorded on BRUKER AVANCE II 400 spectrometer with TMS as internal standard using DMSO as solvents.

### Synthesis of Schiff base:

The ligands were prepared by mixing equimolar solutions of 4-chloro benzaldehyde and 4-hydroxy benzaldehyde with the corresponding aromatic amine in ethanol and refluxing the



mixture for 4 hrs. After cooling, the product was crystallized from ethanol. The purity of the ligand was checked by M.P. ,TLC and elemental analysis. These are also characterized by IR,  $^1\text{H}$ NMR spectral studies.

### Synthesis of complexes:

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  $^1\text{H}$ NMR spectral analysis indicates that the complexes have 1:1 (lanthanide:ligand) stoichiometry. The lanthanide complexes are stable and colored. Ligands and their Lanthanide complexes are soluble in ethanol, DMSO, DMF and insoluble in water.

**Table 1: Analytical data of newly synthesized Schiff bases**

Sr.No.	Compound	Molecular formula	Colour	Melting point
1.	SB <sub>1</sub>	C <sub>17</sub> H <sub>12</sub> NCl	Brown	155
2.	SB <sub>2</sub>	C <sub>17</sub> H <sub>13</sub> NO	White	112
3.	SB <sub>3</sub>	C <sub>12</sub> H <sub>9</sub> NCl	Red	121
4.	SB <sub>4</sub>	C <sub>12</sub> H <sub>10</sub> No	Gray	115

**Table 2: Analytical data of newly synthesized metal complexes**

Sr.No.	Complex	Molecular Formula	Colour	Melting Point
1	La (SB <sub>1</sub> )	La(C <sub>17</sub> H <sub>12</sub> NCl)	Red	>280
2	Nd (SB <sub>1</sub> )	Nd(C <sub>17</sub> H <sub>12</sub> NCl)	White	>270
3	Dy (SB <sub>1</sub> )	Dy(C <sub>17</sub> H <sub>12</sub> NCl)	Yellow	>278
4	La (SB <sub>2</sub> )	La(C <sub>17</sub> H <sub>13</sub> NO)	Light Pink	>265
5	Nd (SB <sub>2</sub> )	Nd(C <sub>17</sub> H <sub>13</sub> NO)	White	>279
6	Dy (SB <sub>2</sub> )	Dy(C <sub>17</sub> H <sub>13</sub> NO)	Faint Yellow	>272
7	La (SB <sub>3</sub> )	La(C <sub>12</sub> H <sub>9</sub> NCl)	Light Red	>275
8	Nd (SB <sub>3</sub> )	Nd(C <sub>12</sub> H <sub>9</sub> NCl)	Cream	>268
9	Dy (SB <sub>3</sub> )	Dy(C <sub>12</sub> H <sub>9</sub> NCl)	White	>280
10	La (SB <sub>4</sub> )	La(C <sub>12</sub> H <sub>10</sub> NO)	Brown	>279
11	Nd (SB <sub>4</sub> )	Nd(C <sub>12</sub> H <sub>10</sub> NO)	Gray	>269
12	Dy (SB <sub>4</sub> )	Dy(C <sub>12</sub> H <sub>10</sub> NO)	Faint Yellow	>278



### 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  $\nu(\text{C}=\text{N})$  stretching vibration is found in the Schiff base at  $1633\text{ cm}^{-1}$ . This band shifted to lower wave numbers in the complexes indicating the participation of nitrogen in coordination<sup>13</sup>. The new band at  $\nu$  M-O and M-N stretching vibrations were appeared at  $550\text{-}495$  and  $435\text{-}425\text{ cm}^{-1}$  in the spectra of metal complexes.

**Table 3: IR Spectral data of Lanthanide (III) Complexes**

Sr.No.	Complex	$\nu(\text{C}=\text{N})$	$\nu(\text{C}=\text{O})$	$\nu(\text{Ln}-\text{N})$	$\nu(\text{Ln}-\text{o})$
1	SB <sub>1</sub>	1635	1398	-	-
2	La(SB <sub>1</sub> )	1620	1345	573	498
3	Nd(SB <sub>1</sub> )	1621	1298	771	499
4	Dy(SB <sub>1</sub> )	1526	1350	775	501
5	(SB <sub>2</sub> )	1630	1370	-	-
6	La(SB <sub>2</sub> )	1602	1326	677	510
7	Nd(SB <sub>2</sub> )	1615	1350	774	518
8	Dy(SB <sub>2</sub> )	1624	1288	769	518
9	(SB <sub>3</sub> )	1645	1375	-	-
10	La(SB <sub>3</sub> )	1575	1343	715	463
11	Nd(SB <sub>3</sub> )	1613	1345	751	463
12	Dy(SB <sub>3</sub> )	1615	1369	746	520
13	(SB <sub>4</sub> )	1635	1367	-	-
14	La(SB <sub>4</sub> )	1574	1345	704	467
15	Nd(SB <sub>4</sub> )	1618	1286	717	550
16	Dy(SB <sub>4</sub> )	1613	1316	715	478

**Table 4: <sup>1</sup>HNMR spectra data of Lanthanide complexes**

Sr.No.	Complex	-CH	-NH	Aryl
1	SB <sub>1</sub>	3.9	8.91	7.69
2	La(SB <sub>1</sub> )	3.2	8.27	7.51.
3	Nd(SB <sub>1</sub> )	3.32	8.53	7.42
4	Dy(SB <sub>1</sub> )	3.22	8.34	7.51
5	(SB <sub>2</sub> )	3.86	8.82	7.74
6	La(SB <sub>2</sub> )	3.43	8.66	7.52
7	Nd(SB <sub>2</sub> )	3.40	8.0	7.50
8	Dy(SB <sub>2</sub> )	3.38	8.37	7.63
9	(SB <sub>3</sub> )	3.69	8.69	7.73
10	La(SB <sub>3</sub> )	3.38	8.37	7.60
11	Nd(SB <sub>3</sub> )	3.42	8.67	7.51
12	Dy(SB <sub>3</sub> )	3.48	8.38	7.53



Sr.No.	Complex	-CH	-NH	Aryl
13	(SB <sub>4</sub> )	3.75	8.89	7.70
14	La(SB <sub>4</sub> )	3.32	8.46	7.35
15	Nd(SB <sub>4</sub> )	3.34	8.35	7.36
16	Dy(SB <sub>4</sub> )	3.46	8.37	7.42

### Antimicrobial activity

The ligand and some of their corresponding metal complexes were screened invitro for their antibacterial activity against two Gram-negative (Escherichia coli and Salmonella typhi) and two Gram-positive (Bacillus subtilis and Staphylococcus aureus) bacterial strains using agar well diffusion method using Penicillin as standard. The results of antibacterial studies are presented in Table 5. 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 and the control. Hence complexation increases antimicrobial activity.

**Table 5 : Results of Antibacterial Assay (concentration used 1mg/mL of DMSO). <10: weak, Between 10 and 16: Moderate, >16: Significant**

Compound	Gram -ve Bacteria		Gram + ve Bacteria	
	E.Coli	S.Typhi	B.Subtilis	S.Aureus
SB <sub>1</sub>	11	14	13	12
La(SB <sub>1</sub> )	18	16	12	13
Nd(SB <sub>1</sub> )	14	18	17	17
Dy(SB <sub>1</sub> )	20	19	18	20
(SB <sub>2</sub> )	12	13	11	12
La(SB <sub>2</sub> )	22	21	19	20
Nd(SB <sub>2</sub> )	12	18	17	15
Dy(SB <sub>2</sub> )	20	19	18	20
(SB <sub>3</sub> )	10	12	11	12
La(SB <sub>3</sub> )	20	22	24	21
Nd(SB <sub>3</sub> )	18	20	22	19
Dy(SB <sub>3</sub> )	20	18	21	18
(SB <sub>4</sub> )	13	11	10	09
La(SB <sub>4</sub> )	19	22	18	19
Nd(SB <sub>4</sub> )	20	21	18	20
Dy(SB <sub>4</sub> )	21	18	19	19
SD*	17	16	13	12

\* Penicillin as a standard



## CONCLUSION

It is clear from the present result that preliminary studies showed their good inhibitory properties. In general the La (III), Nd (III), Dy (III) and complexes of SB<sub>1</sub>, SB<sub>2</sub>, SB<sub>3</sub> and SB<sub>4</sub> are more active than their parent ligand and hence may serve as vehicle for activation of the ligand as principle cytotoxic species.

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