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# Spectral and Biological Study of Some Schiff Bases and Their Lanthanide Complexes

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## ABSTRACT

The studies of 15 new lanthanides(III) complexes of Schiff bases are discussed, Schiff bases are obtained by condensation of 2-amino-4,6-dimethyl benzothiazole with 2,5-dihydroxy acetophenone, pyridine 2-aldehyde, lanthanide (III) chlorides viz. Lanthanum (III) chloride, Neodymium (III) chloride, Samarium (III) chloride, Gadolinium (III) chloride, Thorium (III) chloride were chosen to synthesize new complexes.
The complexes were characterized on the basis of physicochemical studies viz. elemental analysis, spectral studies like IR, $^1$H NMR studies, Molar conductivity of the representative complexes were also done.
All of the representative ligands and complexes were also screened for the antimicrobial activity, antibacterial activity against bacteria like *s-aureus, E-coli* and antifungal activity against *A-Niger and A-Flavus.*
**KEYWORDS:** Benzothiazole, Schiff bases, metal complexes, spectral study, antimicrobial activity.

## INTRODUCTION

Lanthanides or Lanthanones form a longest series of the periodic table. It is fourth inner transition series. Lanthanide (III) ions because of their size and charge are the best ions to form a stable complexes with high coordination number.

Schiff base metal complexes have played a major role in the development of coordination chemistry. Sulphur containing Schiff bases are well known for their anti carcinogenic, anti bacterial and antifungal activities, such ligands on complexation shows enhanced activity.

In recent past rare earth complexes have received considerable attention on account of their applications in Lasers[1-9]and as therapeutic agents especially as anticancer compounds[10]. In this work we wish to report Lanthanide (III) complexes with some Schiff base ligands.

## Experimental

All the melting points were determined in an open capillary tube and are uncorrected completion of the reaction was monitored by thin layer chromatography on precoated sheets of silica gel G. All the reagents used were chemically pure and are of AR grade. The ligand selected in the preparation of metal complexes are 2-N(2,5-dihydroxy acetophenyl diamine),-4,6-dimethyl benzothiazole ($SB_1$), 2-N(2-pyridyl amine)-4,6-dimethyl benzothiazole ($SB_2$) ,2-N-(2-pyrrolidimine)4,6 dimethyl benzothiazole($SB_3$).

Lanthanides (III) chlorides were obtained by dissolving dry rare earth oxide in minimum amount of dil.HCl, the solution was evaporated on water bath, 2-3 washings with distilled water were given & crystalline rare earth chloride $LnCl_3.3H_2O$ was collected .Requisite amount of respective rare earth chloride is dissolved in minimum amount of ethanol and the solution was used for precipitation complexes.

### Synthesis of ligands

Schiff bases were synthesized as follows.

1. Synthesis of Schiff bases derived from 2-amino 4-6 dimethyl benzothiazole and ketone ($SB_1$)
   2-amino, 4, 6-dimethyl benzothiazole and 2,5 dihydroxy acetophenone were dissolved in distilled ethanol in equimolar quantities. The reaction mixture was refluxed on water bath for about 4-5 hours; the progress of the reaction was monitored by TLC. The hot reaction mixture was then poured on ice cold water the solid thus separated was filtered washed with water and dried. The solid then recrystallised from ethanol.
2. Synthesis of Schiff bases derived from 2-amino,4-6 dimethyl benzothiazole and pyridine/pyrrole 2-carboxyaldehyde ($SB_1$/$SB_3$)
   Equimolar quantities of 2-amino, 4, 6-dimethyl benzothiazole and pyridine/ pyrrole 2-carboxyaldehyde were dissolved in ethanol and the mixture was refluxed on water bath for 4-5 hours .The progress of reaction was monitored by TLC .The hot mixture was poured on crushed ice[11], the mixture was kept overnight .The

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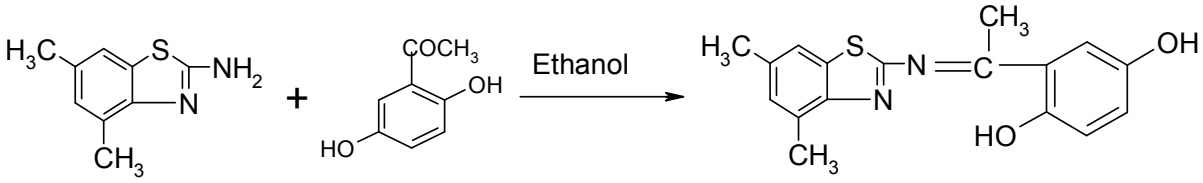
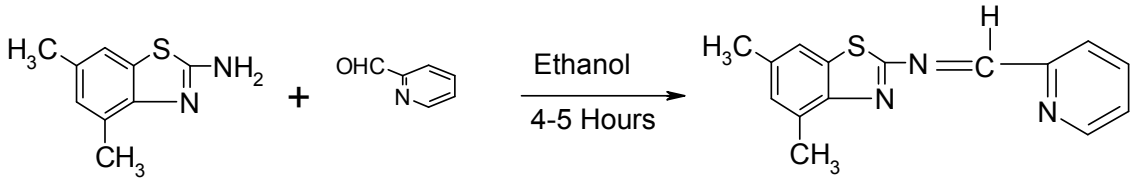
brown semi-solid and yellow semisolid were collected by filtration, air dried and used for preparation of complexes.




2-Amino 4,6-dimethyl benzothiazole

2,5-dihydroxy acetophenone

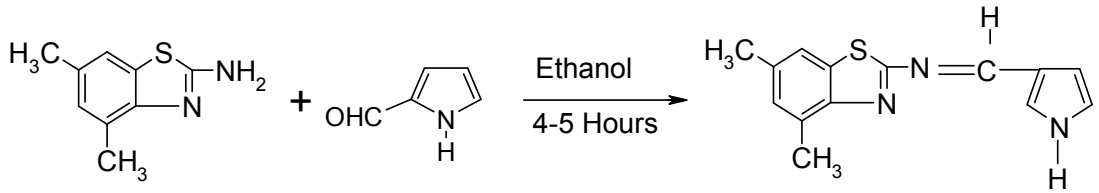
SB1




2-Amino 4,6-dimethyl benzothiazole

pyridine 2-aldehyde

SB2




2-Amino 4,6-dimethyl benzothiazole

pyrrole 2-aldehyde

SB3

**Preparation of complexes**

The ligand (0.02 moles) and the metal salt (0.01 moles) in 50 ml ethanol were mixed. The $p^H$ of the mixture solution was raised up to 5 using alcoholic ammonia .The solution was then concentrated on steam bath in a china bowl. Solid complex thereafter separate out washed with acetone to remove excess of ligand and dried over $CaCl_2$ overnight.

**RESULT AND DISCUSSION**

All the complexes at room temperature are insoluble in water and the most of the common organic solvent but soluble in DMF and DMSO. The analytical data of the complexes (Table-1) indicate that their stoichiometry may be represented as 1:2 metal to ligand ratio. The magnetic moment values i.e $\mu_{eff}$ values at room temperature for the prepared complexes shows the octahedral geometry for the complexes.
The molar conductance values of the complexes suggested their non electrolytic nature[12].

**Spectroscopic data of selected compounds**

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 1633 $cm^{-1}$. This band shifted to lower wave numbers in the complexes indicating the participation of nitrogen in coordination[13]. The new band at *v* M-O and M-N stretching vibrations were appeared at 540-525 and 435-425 $cm^{-1}$ in the spectra of metal complexes[14].

$^1H$ NMR spectra of the lanthanide complexes were recorded, unfortunately, however due to the presence of a metal ion, proton resonance was not affected and one could observe only broad peaks indicating the formation of the complex.

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

| Sr. no | Compound | Molecular Formula | Colour | Melting point °C |
|---|---|---|---|---|
| 1 | $SB_1$ | $C_{17}H_{16}SN_2O_2$ | Green | 155 |
| 2 | $SB_2$ | $C_{15}H_{13}SN_3$ | Brown | 110 |
| 3 | $SB_3$ | $C_{12}H_{13}SN_3$ | Yellow | 98 |

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

| Sr.no | Complex | Molecular formula | Colour | M.P °C |
|---|---|---|---|---|
| 1 | $La(SB_1)_2$ | $La(C_{17}H_{16}N_2O_2S)_2Cl_3.3H_2O$ | Green | >280 |
| 2 | $Nd(SB_1)_2$ | $Nd(C_{17}H_{16}N_2O_2S)_2Cl_3.3H_2O$ | Greenish Brown | >280 |
| 3 | $Sm(SB_1)_2$ | $Sm(C_{17}H_{16}N_2O_2S)_2Cl_3.3H_2O$ | Faint Green | 278 |
| 4 | $Gd(SB_1)_2$ | $Gd(C_{17}H_{16}N_2O_2S)_2Cl_3.3H_2O$ | Light Green | >280 |
| 5 | $Th(SB_1)_2$ | $Th(C_{17}H_{16}N_2O_2S)_2(NO_3)_4.6H_2O$ | Yellow Green | 265 |
| 6 | $La(SB_2)_2$ | $La(C_{15}H_{13}N_3S)_3Cl_3.3H_2O$ | Green | 279 |
| 7 | $Nd(SB_2)_2$ | $Nd(C_{15}H_{13}N_3S)_3Cl_3.3H_2O$ | Green | 272 |
| 8 | $Sm(SB_2)_2$ | $Sm(C_{15}H_{13}N_3S)_3Cl_3.3H_2O$ | Dull Green | >280 |
| 9 | $Gd(SB_2)_2$ | $Gd(C_{15}H_{13}N_3S)_3Cl_3.3H_2O$ | Greenish | >280 |
| 10 | $Th(SB_2)_2$ | $Th(C_{15}H_{13}N_3S)_2(NO_3)_4.6H_2O$ | Yellow Green | >280 |
| 11 | $La(SB_3)_2$ | $La(C_{14}H_{13}N_3S)_2Cl_3.3H_2O$ | Faint Green | >280 |
| 12 | $Nd(SB_3)_2$ | $Nd(C_{14}H_{13}N_3S)_2Cl_3.3H_2O$ | Green | >280 |
| 13 | $Sm(SB_3)_2$ | $Sm(C_{14}H_{13}N_3S)_2Cl_3.3H_2O$ | Faint Green | >280 |
| 14 | $Gd(SB_3)_2$ | $Gd(C_{14}H_{13}N_3S)_2Cl_3.3H_2O$ | Faint Green | >280 |
| 15 | $Th(SB_3)_2$ | $Th(C_{14}H_{13}N_3S)(NO_3)_4.6H_2O$ | Green | >280 |

### *Antimicrobial activity*

The antibacterial activity of the compounds was determined by agar diffusion method against various bacteria like *E.coli*, *and S. aureus* at various concentrations such as 20, 50and 100 µg /ml. The zone of inhibition was measured in mm and DMSO was used as solvent. Sterile nutrient agar was seeded with test organism and layered in sterile petri plate. After solidification, agar cups were borered with cork borer 0.1 ml of the compound solution was added to the cup with the help of micropipettes, one cup in the plates was filled with solvent. Standard penicillin (10v/ml) was used as reference drug. The plates were kept at low temperature (4 °C) for 20minute to allow diffusion of the compound. Then the plates were incubated at 37 °C for 24 hr. After proper incubation the plates were observed for zone of no growth (zone of inhibition of growth) around the cup. Similarly the same compounds were screened for the antifungal activity against different organisms like *A. niger, A. flavus* by using poison plate method. The compound was mixed with sterile potato dextrose agar medium so as to get final concentration 2%. It was then poured in sterile petri plate and allowed to solidify. Spots of test organisms were placed on the agar surface. A plate without compound was prepared for control. The plates were incubated at room temperature for 48 hr. After proper incubation plates were observed for growth of the test organisms. The growth indicates that the compound is not antifungal while inhibition of growth of test organism indicates antifungal activity. The antifungal activities of the compounds were compared with standard grysofulvin.

**Table- In vitro Antimicrobial activity of ligand and their complexes**

| Sr.no | ligand | Complex | *S-aureus* | *E-coli* | *A.Niger* | *A.flavus* |
|---|---|---|---|---|---|---|
| **1** | $SB_1$ | $SB_1$ | 8 | 11 | +Ve | -Ve |
| | | La(III) $SB_1$ | 6 | 8 | -Ve | -Ve |
| | | Nd(III) $SB_1$ | 6 | 10 | -Ve | -Ve |
| | | Sm(III) $SB_1$ | 12 | 8 | -Ve | +Ve |
| | | Gd(III) $SB_1$ | 7 | 8 | +Ve | +Ve |
| **2** | $SB_2$ | SB2 | 10 | 10 | +Ve | -Ve |
| | | La(III) $SB_2$ | 9 | 9 | -Ve | +Ve |
| | | Nd(III) $SB_2$ | 8 | 7 | +Ve | +Ve |
| | | Sm(III) $SB_2$ | 12 | 10 | +Ve | -Ve |
| | | Gd(III) $SB_2$ | 7 | 7 | +Ve | RG |
| **3** | $SB_3$ | $SB_3$ | 9 | 8 | -Ve | +Ve |
| | | La(III) $SB_3$ | 10 | 8 | -Ve | -Ve |
| | | Nd(III) SB3 | 12 | 7 | -Ve | +Ve |
| | | Sm(III) SB3 | 10 | 8 | +Ve | -Ve |
| | | Gd(III) SB3 | 8 | 7 | RG | +Ve |
| **4** | | Penicillin | 32 | 28 | NA | NA |
| **5** | | Grysofulvin | NA | NA | -Ve | -Ve |

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**Conclusion**

It is clear from the present result that preliminary studies showed their good inhibitory properties. In general the Pr(III), Nd(III), Sm(III) and Gd(III) complexes of $SB_1$, $SB_2$ and $SB_3$ are more active than their parent ligand and hence may serve as vehical for activation of the ligand as principle cytotoxic species.

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