

# RARE EARTH METAL CHELATES OF SCHIFF BASE LIGAND: SYNTHESIS, CHARACTERIZATION, CATALYSIS AND ANTIMICROBIAL STUDY.

Toral Yadav<sup>1\*</sup>, Manish P. Brahmhatt<sup>1</sup>, Jabali J. Vora<sup>2</sup>, Hitesh Patel<sup>1</sup>

1. Chemistry department, Sheth M. N. Science College, Patan-384265, Gujarat, India

2. Department of chemistry, Hemchandracharya North Gujarat University, Patan. Gujarat, India

## ABSTRACT

The rare earth metal perchlorates of trivalent lanthanum, cerium and samarium were used for the synthesis of metal chelates. The Schiff base (5BA) ligand was synthesized from 5-bromo salicylaldehyde and 2-amino benzoic acid (anthranilic acid) in ethanol. The synthesized ligand plays a significant role in biological applications due to the presence of halogen atom in its chemical structure. The Schiff base ligand acts as a chelating agent and it is able to form six membered ring by coordinating with metal ion through the oxygen and nitrogen donor atoms corresponding to the functional groups -OH, -COOH and -C=N groups. The synthesized metal chelates have been characterized by elemental analysis, FTIR, TGA, electronic spectra, magnetic and molar conductance. Activation energy of metal chelates was evaluated using TGA data by Broido method. The synthesized chelates were subjected to study of catalytic properties for various reactions. The catalytic study of all the chelates in organic synthesis reaction was carried out. The chemical kinetic reactions were also studied to check the effect of chelates on rate of reaction. All the chelates and Schiff base ligand were screened for antimicrobial study against gram positive (*B. subtilis*, *B. cereus*) and gram negative (*E. coli*, *P. aeruginosa*) bacterial species.

**Key words:** Rare earth metal chelates, catalysis, antimicrobial activity

## Introduction

The lanthanide elements are also termed as rare earth metals. The lanthanide chelates are interesting due to their reactivity, coordination property and their variety of applications. Lanthanide chelates have been shown to be applicable in the fields of catalysts, pharmaceutical, agriculture and electroluminescence [1,2]. Some Gd (III) chelates have been used in MRI medical imaging [3]. German chemist Hugo Schiff introduced imine compounds in 1864 [4]. They are prepared through alcohol condensation method. These ligands have been utilized in metal chelate formations due to their ease of synthesis and variety of applications. Schiff bases and their metal chelates have been studied for their applications as antibacterial agents, antifungal agents, antitumor drugs, catalysts in coordination chemistry. Metal chelation is very important to enhance biological activity of Schiff base ligand where the coordination can occur between a variety of metal ions and a wide range of ligands. Our interest in the chemistry of Lanthanide chelates of Schiff base ligand with O and N donor atoms comes from their structural importance as well as their interesting biological activities. Several metal chelates have been shown

to inhibit tumor growth [5-8]. Especially when Schiff base ligand exhibits halogen atom it enhances the biological property of Schiff base compound [9-11]. In this communication, we have reported a Schiff base ligand from 5-bromo salicylaldehyde and 2-amino benzoic acid (Fig 1.) and its rare earth metal chelates which were investigated by elemental analysis, FTIR, TGA, electronic spectra, magnetic and molar conductance. The synthesized rare earth metal chelates were investigated for their antimicrobial as well as catalytical studies.

## Experimental section

### Materials and Method

All reactants and solvents used were of analytical grade for experimental work. Spectroscopic grade solvents were used for recording the spectra. 5-Bromo salicylaldehyde and anthranilic acid were used for the synthesis of ligand. IR spectra of Schiff base and metal chelates were recorded in the range of  $4000 - 400\text{cm}^{-1}$  by using sample as KBr pallets on Shimadzu, IR Affinity 1 S IR spectrophotometer. C, H and N elemental analysis was carried out using CHN analyzer of Thermo Finnigan, FLASH EA 112 Series. UV visible absorbance spectra were recorded on Shimadzu UV 1800 Series UV Visible Spectrophotometer in 200.0 nm to 800.0 nm wavelength range. Thermogravimetric analysis was recorded by using a Perkin-Elmer Diamond Thermogravimetric/Differential Thermal Analyzer. Magnetic susceptibility measurements were recorded by using Goy's method at room temperature, using  $\text{Hg}[\text{Co}(\text{CNS})_4]$  as calibrant.

### Synthesis of ligand:

The Schiff base ligand was synthesized by adding 0.1 mol (4.02 gm) 50 ml ethanolic solution of 5-bromo salicylaldehyde to 0.1 mol (2.74 gm) 50 ml ethanolic solution of anthranilic acid and stirring the mixture for 3 hours. The concentrated solution contained orange color precipitates of Schiff base (IUPAC name 2-[(E)-(5-bromo-2-hydroxybenzylidene) amino] benzoic acid). The precipitates were filtered and recrystallized from hot ethanolic solution and dried. The melting point of this ligand was found to be  $250^\circ\text{C}$ .

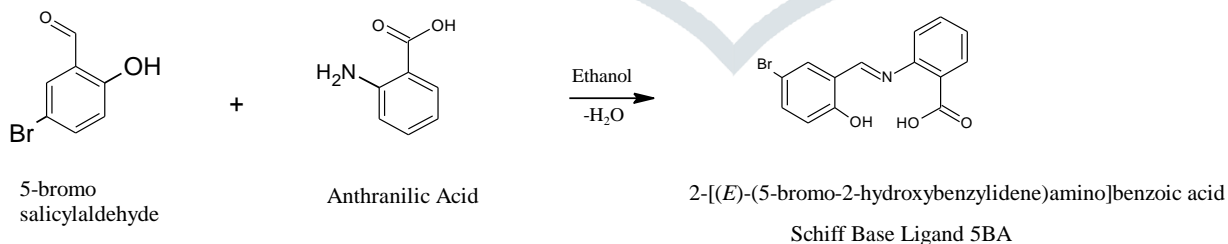


Figure 1: synthesis of Schiff base ligand 5BA

### Synthesis of metal Chelates

The synthesis of metal chelates was carried out by mixing 100ml 0.1M metal perchlorate solution and 100ml 0.1M ligand alcoholic solution. The reaction mixture was refluxed for 5 to 6 hours at  $\sim 100^\circ\text{C}$  temperature. After five hours the reaction mixture was cooled. After 10 hours chelates slowly precipitated, the chelate, thus obtained, was washed well with absolute hot solution of alcohol and distilled water to remove unreacted metal salt and ligand. All the chelates were dried in oven at  $60$  to  $70^\circ\text{C}$  temperature.

## RESULTS AND DISCUSSION

### Physical Measurements

**Table 1: Analytical data and physical measurements of the ligand and metal chelates**

compound	Colour	Formula Weight gm/ mol	Solvent	M.P. °C	Magnetic Susceptibility (B.M.)	R.F. Value	Molar Conductance S cm <sup>2</sup> mol <sup>-1</sup>
Ligand 5-BA	Orange	320.13	Ethanol	250	-	0.71	-
La-5BA	Orange	829.18	DMF	285	Diamagnetic	0.63	22.57
Ce-5BA	Light Orange	812.39	DMF	288	2.01	0.68	26.35
Sm-5BA	Orange	840.63	DMF	290	1.24	0.61	18.66

### Elemental Analysis

**Table 2: Elemental analysis of the ligand and metal chelates**

compound	Elemental Analysis. Experimental (Calc) %			
	C	H	N	M
5BA	52.52 (51.13)	3.15 (2.8)	4.38 (4.03)	-
La-5BA	41.46 (40.73)	2.49 (3.04)	3.45 (3.3)	16.80 (17.12)
Ce-5BA	41.40 (40.25)	2.48 (2.8)	3.45 (3.2)	16.24 (17.25)
Sm-5BA	39.47(40.88)	2.71 (2.45)	3.07 (3.41)	17.89 (18.28)

Metal contents of rare earth metal chelates were determined by complex-metric titration against standardized EDTA solution at proper pH value using appropriate indicator.

### IR Spectra

The spectra of ligand and metal chelates are obtained in the range of 4000 – 400cm<sup>-1</sup> in the form of KBr pellets. The important infrared absorption bands of ligand and its metal chelates are shown in table 3. All the spectra are characterized by vibrational bands mainly due to C=N, COOH and OH functional groups. The schiff base ligand 5-BA contains functional groups such as azomethine, carboxyl acid and hydroxyl. The  $\nu$  (O-H) for ligand appears at 3076 cm<sup>-1</sup> and this peak in chelates shifts to 3058-3060 cm<sup>-1</sup>, which indicates the coordination of O-H bond to the metal ion. The  $\nu$  (C=O) vibration of carboxylic acid group in the free ligand is at 1640 cm<sup>-1</sup>; for the chelates the peak shifts to 1595-1599 cm<sup>-1</sup> indicating the coordination of O atom of C=O group to the metal ion. The O-H stretching frequency of carboxylic acid group in Schiff base ligand is observed at 2748 cm<sup>-1</sup>, whereas in the metal chelates this frequency disappears. This gives the assurance that the oxygen atom of OH bond of carboxylic acid group is coordinated to the metal ion in the formation of its chelates. The IR band 1606 cm<sup>-1</sup>, for the free ligand, is assigned to the  $\nu$  (C=N) stretch. It shifts to 1572-1573 cm<sup>-1</sup> for its chelates [12-14].

IR Spectra (cm<sup>-1</sup>) Analysis for Ligand 5-BA and its metal chelates

**Table 3: IR spectral data of the ligand and metal chelates**

Compounds	$\nu$ (C=N)	Phenolic		$\nu$ (O-H) (H <sub>2</sub> O)	COOH				$\nu$ (M-N)	$\nu$ (M-O)
		$\nu$ (O-H)	$\nu$ (C-O)		$\nu$ (C=O)	$\nu$ (O-H)	$\nu$ (COO <sup>-</sup> )			
							(Asym- metric)	(Symm- etric)		
5-BSAA	1606	3076	1244	---	1640	2748	---	---	--	--
La-5BA	1572	3060	1232	3405	1595	---	1510	1477	471	522
Ce-5BA	1572	3059	1232	3386	1595	---	1511	1470	474	522
Sm-5BA	1573	3054	1234	3396	1599	---	1514	1472	470	522

All of these IR stretching frequencies are observed in both the compounds, chelates as well as Schiff base ligand

with noticeable differences due to the coordination of metal ion to the donor atoms of the ligand but some IR frequencies are only observed in metal chelates and not in the ligand. The IR band between 3384-3405 cm<sup>-1</sup> are only observed in metal chelates and not in Schiff base, which is assigned for -OH stretching frequency of water molecule. This gives the confirmation of coordination of H<sub>2</sub>O molecule in the formation of metal chelates which is further also confirmed from TGA data. The  $\nu$  (M-O) and  $\nu$  (M-N) vibrational frequencies are at 522 and 470-474 cm<sup>-1</sup> respectively [15]. From the above discussed IR stretching frequencies it can be concluded that the nitrogen atom from azomethine group, oxygen atom from phenolic -OH group, ketone group, carboxylic group and carboxylate ion act as donor atoms in metal chelates formation. So, the Schiff base ligand 5-BA acts as multidentate ligand.

#### Molar conductivity measurements

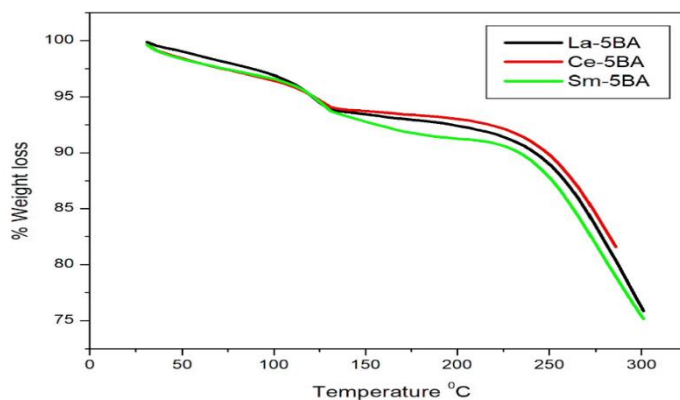
The molar conductance of metal chelates using 10<sup>-3</sup> M solutions in DMF were recorded which is illustrated in Table 1. The molar conductance measurements of metal chelate were observed in the range of 18.66 to 26.35 S cm<sup>2</sup> mol<sup>-1</sup> which indicates the non-electrolytic nature of all the chelates.

#### Thermo Gravimetric Analysis

It is observed that in TGA analysis for one mole La-5BA chelate at 150 °C temperature, 52.23 gm/mole weight loss occurred, which indicates that two H<sub>2</sub>O molecules of crystallization are present and at 250 °C temperature 32.08 gm/mole weight loss occurred for one mole La-5BA chelate which indicates that one H<sub>2</sub>O molecule is coordinated with La<sup>3+</sup> metal ion in its chelate. In TGA analysis for one mole of Ce-5BA at 150 °C temperature, 48.66 gm/mole weight loss occurred which indicates that there are two H<sub>2</sub>O molecules of crystallization, present and at 250 °C temperature 27.23 gm/mole weight loss occurred for one mole Ce-5BA chelate which indicates that one H<sub>2</sub>O molecule is coordinated with Ce<sup>3+</sup> metal ion in Ce-5BA. For Sm-5BA chelate, at 150 °C temperature 52.11 gm weight loss per molecule occurred, which indicates two H<sub>2</sub>O molecules of crystallization are present and at 250 °C temperature 31.69 gm/mole weight loss occurred for one mole Sm-5BA chelate which indicates that one coordinated H<sub>2</sub>O molecule is present in Sm-5BA chelate. The possible water molecules in the structure of metal chelates are shown in table 5. From the table it can be concluded that each of the metal chelates contains three water molecules in their structures two of them are water molecules for crystallization and one is for coordination [16,17].

**Table 4: Thermo Gravimetric Analysis of metal chelates**

Metal chelate	RT to 150°C			150°C to 250°C		
	% Weight loss	Loss of weight (Gm/mole)	No. of water molecule per metal chelate molecule (water of crystallization)	% Weight loss	Loss of weight (Gm/mole)	No. of water molecule per metal chelate molecule (water of coordination)
5BA	-	-	-	-	-	-
La-5BA	6.03	52.23	2	3.87	32.08	1
Ce-5BA	5.86	48.66	2	3.28	27.23	1
Sm-5BA	6.2	52.11	2	3.77	31.69	1

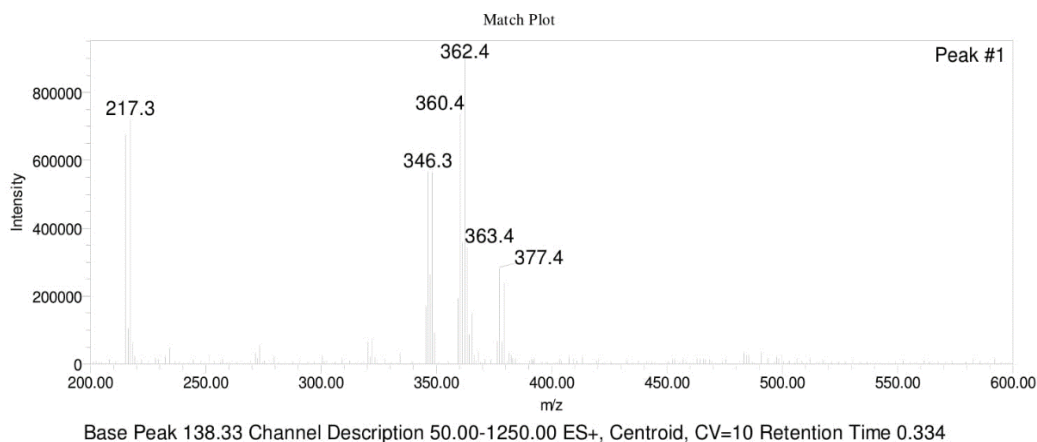
**Figure 2: TGA of Chelate****Mass Spectra**

From elemental analysis the molecular formula of Schiff base ligand is suggested  $C_{14}H_{10}O_3NBr$ . The molecular ion peak at  $m/z = 217.3(M)$  amu corresponds to the fragment  $[C_7H_5NBr]^+$  in ligand moiety. In the mass spectrum of the ligand 5-BA, the base peaks at 138.33 amu ascribable to the fragment  $[C_7H_5NO_2]^+$ . The  $m/z$  value of each fragment agree with the calculated value in Schiff base ligand and its metal chelates.

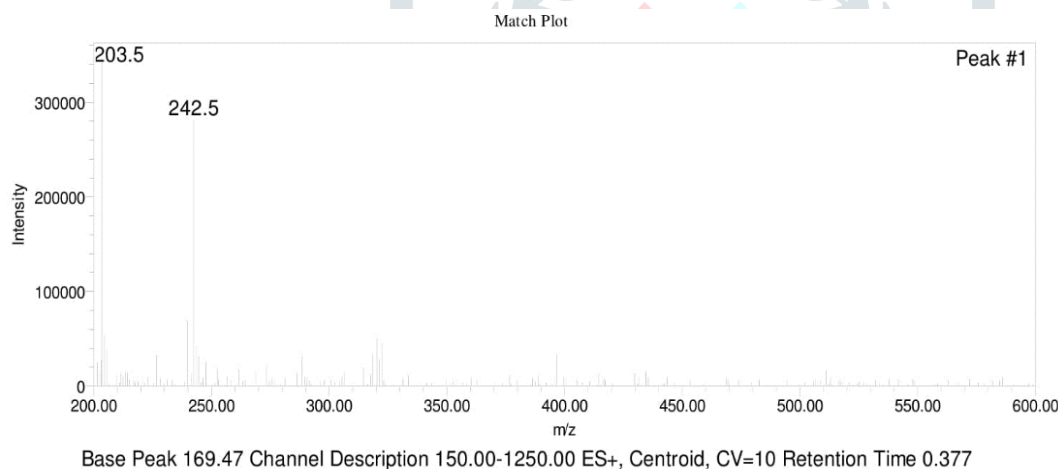
**Table 5: Mass fragmentation of metal chelates and Schiff base ligand**

Compound	Possible Fragments	m/z value	
		Calculated	Found
5-BA	$[C_7H_5O_3Br]^+$	217.02	217.3
	$[C_7H_5O_3]^+$	137.11	138.33
La-5BA	$[C_7H_5OBrLa]^+$	321.91	320.34
	$[C_7HBrLa]^+$	303.89	302.3
Ce-5BA	$[C_{14}H_{10}O_3NBr]^+$	320.14	320.34
	$[C_{14}H_8O_2NBr]^+$	303.0	302.3
	$[C_6H_4OBr]^+$	172.00	173.42
Sm-5BA	$[C_6H_6NSm]^+$	242.0	242
	$[C_4H_4Sm]^+$	202.3	203.5

The Schiff base ligand is structurally confirmed by IR, CHN analysis and also by mass spectra. The mass spectrum of Schiff base is shown in the figure 03. The base peak is observed at  $m/z$  138.33 corresponds to the molecular ion of the ligand. The observed possible fragmentations are identified in the mass spectrum of Sm chelate (figure 04). In the mass spectrum of Sm-5-BA chelate the molecular peak at 242.0 ( $m/z$ ) corresponds to the ligand moiety. The possible fragments for all the metal chelates and ligand are shown in table 5 [18].



**Fig. 3: Mass spectra of Schiff base ligand 5-BA**



**Fig 4: Mass spectrum of Sm-BA Chelate**

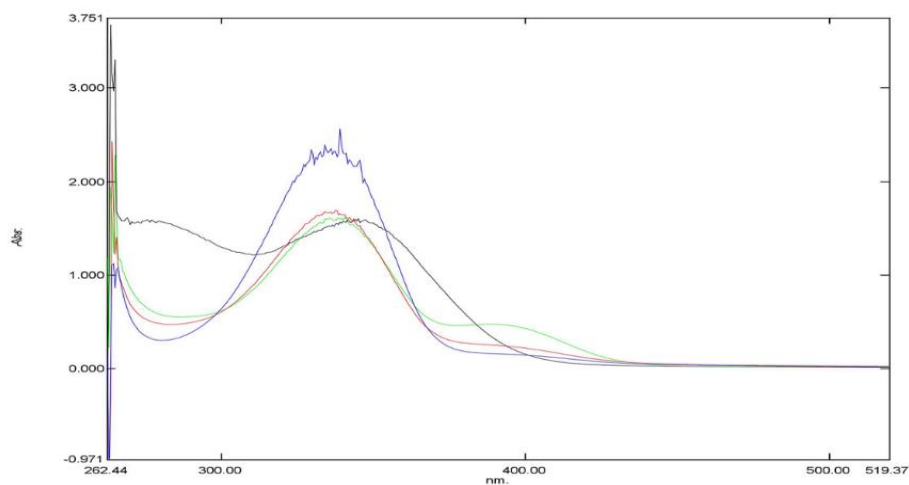
### Electronic Spectral Study and Magnetic properties

The lanthanide metal ions are found primarily in trivalent state. Their magnetic property is determined by 4f electrons, which are well shielded by the outer shells of 6s and 5d electrons. The magnetic moment of solid metal chelates of  $\text{La}^{3+}$ ,  $\text{Ce}^{3+}$  and  $\text{Sm}^{3+}$  measured by Gouy's method [19] at room temperature is illustrated in table 4. Lanthanide trivalent ions, in the form of their metal chelates have no or very weak absorption in the visible range. The very important characteristics of rare earth ions in absorption spectra are their linear-like behavior. This comes from Laporte forbidden f-f transitions where 4f electrons exchange between different 4f energy levels. The 4f orbitals are not so exposed to coordinated ligand molecules as they are inner shell orbitals. Their absorption spectra are very different from d-block compounds. The electronic spectra of Schiff base ligand and metal chelates are illustrated in table 7. The Sm chelate shows absorption in visible region. The UV-visible spectra of Schiff base ligand and its metal chelates were recorded at room temperature

using DMF as solvent. The absorption of the ligand is characterized by four main absorption bands in the regions 200-400 nm. The band at the 219 nm and 239 nm corresponds to  $\Pi \rightarrow \Pi^*$  transition state. The band at 345 nm corresponds to the  $\Pi \rightarrow \Pi^*$  transition state of the azomethine group. The UV spectra of metal chelates show some noticeable changes. These modifications of the shifts and intensity of the absorption band provide confirmation of the coordination of the ligand to the metal ion. The absorption bands around 219 and 345 nm are slightly shifted to the lower frequencies due to chelation. The absorption band around  $\lambda_{\max} = 340$  nm assigned to the  $\Pi \rightarrow \Pi^*$  transition state of the azomethine group coupled with charge transfer from ligand to central metal ion [20,21].

**Table 6: Electronic spectra and Magnetic moment data of metal chelates and Schiff base ligand**

Chelate	$\lambda$ (nm)	$\text{cm}^{-1}$	Band Assignments	Metal ion	$\mu$ (Expt)	Possible number of unpaired electrons
Ligand 5BA	345.00 263.50 239.50 228.50 219.00	28985.5 38022.8 41841.0 43859.6 45662.1	$\Pi \rightarrow \Pi^*$ $n \rightarrow \Pi^*$	-	-	-
La-5BA	339.00 261.00 227.50 218.00	29498.52 38314.17 44052.86 45871.55	Ligand and C.T. transitions	$\text{La}^{3+}$	Diamagnetic	0
Ce-5BA	337.50 237.00 215.00	29673.59 42194.09	${}^2F_{5/2} \rightarrow {}^2D_{3/2}$ ${}^2F_{5/2} \rightarrow {}^5D_{5/2}$	$\text{Ce}^{3+}$	2.02	1
Sm-5BA	340.50 389.00 214.00	29411.7 25706.9	${}^4H_{5/2} \rightarrow {}^6P_{7/2}$ ${}^4H_{5/2} \rightarrow {}^4P_{9/2}$	$\text{Sm}^{3+}$	1.24	5



**Fig 5 : Electronic spectra of Metal chelates and Ligand**

**5 BA, La-5 BA, Ce-5BA, Sm-5BA**

#### Possible coordination number of metal chelates

From elemental analysis (C, H, O and metal content), IR, UV and TGA data of Schiff base ligand and their metal chelates of rare earth metals La(III), Ce(III) and Sm(III) it is concluded that the stoichiometry of metal to ligand in metal chelates is found to be 1:2 which

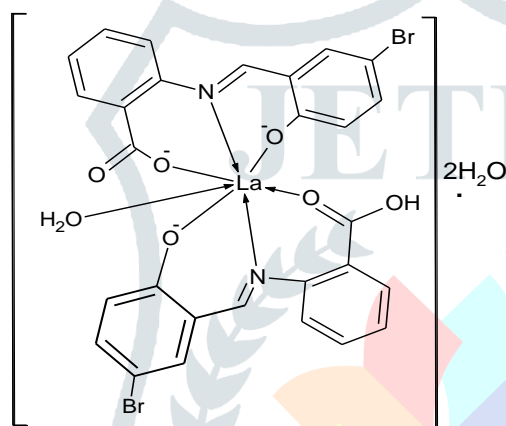
indicates the  $ML_2 \cdot 2 H_2O$  (M=La(III), Ce(III) and Sm(III)) type structure of all the three metal chelates. From these discussions the coordination number of metal chelates are shown in table 6.

**Table 10: Coordination numbers and Possible Structures of metal Chelates**

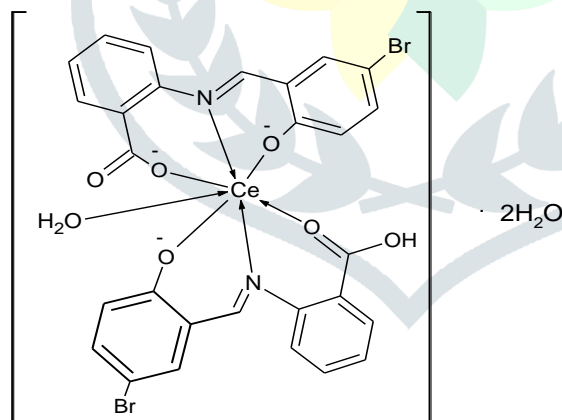
Metal chelate	Coordination number of metal chelates in the proposed structure	Usual coordination number of rare earth metal ion*
La-5BA	7	4-8-10
Ce-5BA	7	6-12
Sm-5BA	7	6-12

\* See the reference no [22,23]

Based upon the physicochemical analysis, the probable structures of the three chelates can be shown as below



**Fig 6: La-chelate  $[La(5BA)_2(H_2O)] 2 H_2O$**



**Fig 7: Ce-chelate  $[Ce(5BA)_2(H_2O)] 2 H_2O$**



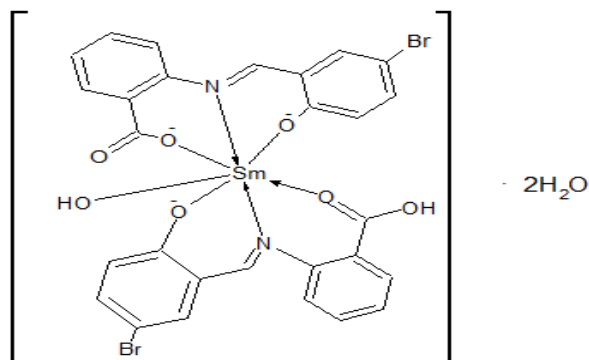


Fig 8: Sm-chelate  $[Sm(5BA)_2(H_2O)] \cdot 2 H_2O$

### Activation energy of metal chelates by Broido method

Activation energy ( $E_a$ ) is related to the thermal stability of the metal chelates. Using kinetic parameters from the TGA curves the Broido method was applied to evaluate the activation energy. The formula to calculate activation energy of degradation reaction and form Broido method is given below:

$$\ln \ln \left( \frac{1}{y} \right) = - \left( \frac{E_a}{R} \right) \left( \frac{1}{T} \right) + \text{constant}$$

Where,  $y = \left( \frac{W_t - W_\infty}{W_0 - W_\infty} \right)$ ,

= Fraction of the number of initial molecules not yet decomposed.

$W_0$  = initial weight of sample.

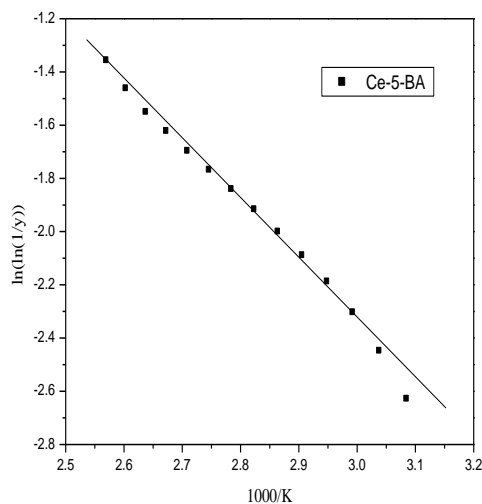
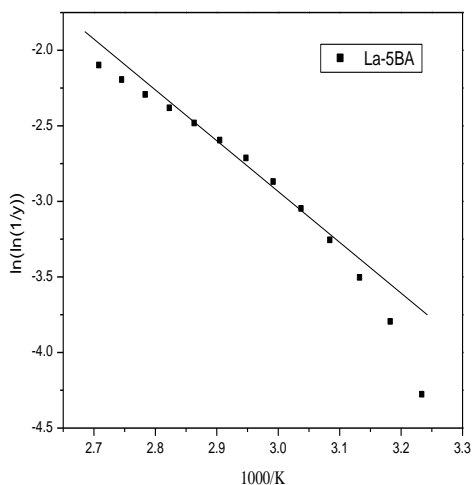
$W_t$  = residual weight of sample at any time  $t$

$W_\infty$  = weight of sample at infinite time

$R$  = gas constant

From the slope of the plot  $\ln(\ln(1/y)) \rightarrow 1000/T$ , activation energy ( $E_a$ ) can be calculated as,

$$E_a = -2.303 \times R \times \text{slope}$$



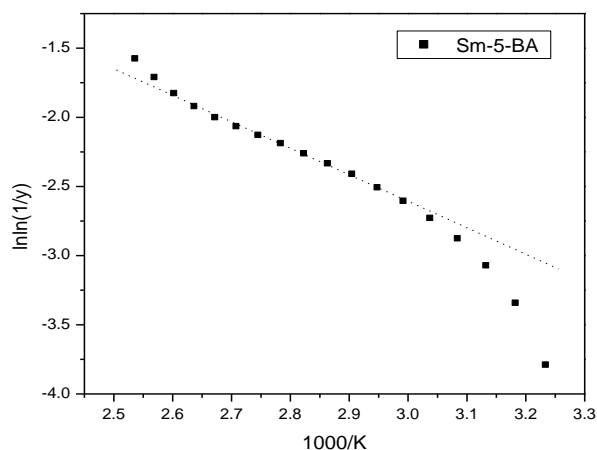


Fig. 9 : Plot of  $\ln(\ln(1/y)) \rightarrow 1000/K$  for La, Ce and Sm Chelates

The calculated activation energies corresponding to temperature, of thermal degradation of rare earth metal chelates are shown in table 4.

Table 7: Activation energy of metal chelates

Metal chelates	Temperature range	Activation energy ( $E_a$ ) in $\text{kJmol}^{-1}$
La-5BA	51°C to 81°C	82.34
Ce-5BA	51°C to 61°C	82.25
Sm-5BA	56°C to 141°C	41.02

The activation energy of thermal degradation of lanthanum, cerium and samarium chelates were found to be  $82.34 \text{ kJmol}^{-1}$ ,  $82.25 \text{ kJmol}^{-1}$  and  $50.61 \text{ kJmol}^{-1}$ . The higher value of activation energy reflects the thermal stability of the metal chelates [24,25].

### Kinetic study

Metal chelates have been utilized in many chemical kinetic reactions as they play significant role as catalysts in these reactions. Three second order redox reactions, potassium bromate with potassium iodide, potassium persulphate with potassium iodide and hydrogen peroxide with potassium iodide were selected to study catalytic effect of rare earth metal chelates.



To study the catalytic effect of metal chelates all of the above reactions were carried out in two ways, with and without addition of metal chelates of La, Ce and Sm. Out of three metal chelates, cerium and samarium chelates were able to increase the rate of reaction between  $\text{K}_2\text{S}_2\text{O}_8$  and KI while the lanthanum chelate shows no effect on rate of reaction. In the reaction between potassium bromate and potassium iodide the lanthanum chelate increases rate of reaction. In the last reaction all the chelates decreases the rate of reaction except samarium chelate [26,27].



structure. It was observed that metal chelates of this Schiff base are more biologically active than that of ligand due to chelation. Ce-5BA was found to have increased antibacterial activity than free ligand against all the bacterial species. Sm-5BA showed higher antibacterial activity against E. coli and P. aeruginosa. La-5BA showed lower antibacterial activity than schiff base ligand and also compared to Ce-5BA and Sm-5BA.

**Table 9: Results of comparison of antibacterial activity of ligand and metal chelates with Ciprofloxacin**

Culture	Concentration µg/ml	Zone of inhibition (mm)				
		Ligand 5-BA	La-5BA	Ce-5BA	Sm-5BA	Ciprofloxacin
Bacillus Subtilis (Gram Positive)	100	-	-	+	-	+++
	200	+	-	+	-	+++
	300	+	-	+++	+	+++
	400	++	+	+++	+	+++
Staphylococcus aureus (Gram Positive)	100	-	-	-	-	+++
	200	+	-	+	-	+++
	300	++	+	++	+	+++
	400	++	+	+++	+	+++
Escherichiaoli (Gram Negative)	100	-	-	+	-	+++
	200	+	-	+	+	+++
	300	+	+	++	++	+++
	400	++	+	++	++	+++
Pseudomonas aeruginosa (Gram Negative)	100	-	-	+	-	+++
	200	+	+	++	+	+++
	300	++	+	++	++	+++
	400	++	++	++	+++	+++

**Inhibition zone diameter in mm: - = <6 (inactive); + = 6-10 (less active); ++ = 10-14 (moderately active); +++ = 14> (highly active).**

### Conclusion

From elemental analysis (C, H, O and metal content), IR, UV, molar conductance, mass spectra, magnetic susceptibility and TGA data, the structures of Schiff base ligand and its metal chelates of rare earth metals La(III), Ce(III) and Sm(III) have been determined. The Schiff base was synthesized from 5-bromosalicylaldehyde and anthranilic acid. It is observed that the stoichiometry of metal to ligand in metal chelates is found to be 1:2 indicates the  $ML_2 \cdot 2 H_2O$  (M=La(III), Ce(III) and Sm(III)) type structure of all the three metal chelates. For catalytic study of metal chelates, three well known second order reactions have been studied. Chelates of samarium and cerium showed increased rate of reaction between potassium persulphate and potassium iodide. In organic synthesis reaction of glycine, the metal chelates significantly increased the percentage yield by 1.2% to 9.8%. From thermal degradation of metal chelates the activation energy was also evaluated using Broido method which indicates good thermal stabilities. The antibacterial property of Schiff base was compared with its metal chelates. The comparative study indicates that the chelates are biologically more active than the parent Schiff base compound. The Sm-5BA showed good antibacterial activity compared with the other compounds.

### REFERENCES

1. Pang, Xin, Decheng Li, and An Peng. 2002. Application of Rare-Earth Elements in the Agriculture of China and Its Environmental Behavior in Soil. *Environmental Science and Pollution Research* 9 (2): 143.
2. Wei, Peng-Hui, Ling Xu, Li-Cheng Song, Wen-Xiong Zhang, and Zhenfeng Xi. 2014. Cyclopentadienyl-Like Ligand as a Reactive Site

- in Half-Sandwich Bis (Amidinato) Rare-Earth-Metal Complexes: An Efficient Application in Catalytic Addition of Amines to Carbodiimides. *Organometallics* 33 (11): 2784–89.
- Aime, Silvio, S. Geninatti Crich, Eliana Gianolio, G. B. Giovenzana, Lorenzo Tei, and Enzo Terreno. 2006. High Sensitivity Lanthanide (III) Based Probes for MR-Medical Imaging. *Coordination Chemistry Reviews* 250 (11–12): 1562–79.
  - Adabiardakani, Amir, H. H. K. Mohammad, and Hadi Kargar. 2012. Cinnamaldehyde Schiff Base Derivatives: A Short Review. *World Appl Program* 2: 472–76.
  - Premkumar, T., and S. Govindarajan. 2006. Antimicrobial Study on Trivalent Lighter Rare-Earth Complexes of 2-Pyrazinecarboxylate with Hydrazinium Cation. *World Journal of Microbiology and Biotechnology* 22 (10): 1105–8.
  - Mohamed, Gehad G., M. M. Omar, and Ahmed MM Hindy. 2005. Synthesis, Characterization and Biological Activity of Some Transition Metals with Schiff Base Derived from 2-Thiophene Carboxaldehyde and Aminobenzoic Acid. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* 62 (4–5): 1140–50.
  - Liu, Hai-Bin, Mei Wang, Ying Wang, Lin Wang, and Li-Cheng Sun. 2010. Synthesis of Tri- and Disalicylaldehydes and Their Chiral Schiff Base Compounds. *Synthetic Communications* 40 (7): 1074–81.
  - Prakash A, Adhikari D. 2011. Application of Schiff Bases and Their Metal Complexes-A Review. *Int. J. Chem. Tech. Res.* 3 (4): 1891–96.
  - Chohan, Zahid H., Asifa Munawar, and Claudiu T. Supuran. 2001. Transition Metal Ion Complexes of Schiff-Bases. Synthesis, Characterization and Antibacterial Properties. *Metal-Based Drug* 8 (3): 137–43.
  - El-Sherif, Ahmed A., and Taha MA Eldebss. 2011. Synthesis, Spectral Characterization, Solution Equilibria, in Vitro Antibacterial and Cytotoxic Activities of Cu (II), Ni (II), Mn (II), Co (II) and Zn (II) Complexes with Schiff Base Derived from 5-Bromosalicylaldehyde and 2-Aminomethylthiophene. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* 79 (5): 1803–14.
  - Kursunlu, Ahmed Nuri, Ersin Guler, Fatih Sevgi, and Birol Ozkalp. 2013. Synthesis, Spectroscopic Characterization and Antimicrobial Studies of Co (II), Ni (II), Cu (II) and Zn (II) Complexes with Schiff Bases Derived from 5-Bromo-Salicylaldehyde. *Journal of Molecular Structure* 1048: 476–81.
  - Robert M. silverstien, Francis X, webster DJK.n.d. *Spectrometric Identification of Organic Compounds*. 7<sup>th</sup> ed. John Wiley and Sons, Inc. 88,96 p.
  - Li TR, Yang ZY, Wang BD, Qin DD. 2008. Synthesis, Characterization, Antioxidant Activity and DNA-Binding Studies of Two Rare Earth (III) Complexes with Naringenin-2-Hydroxy Benzoyl Hydrazone Ligand. *European Journal of Medicinal Chemistry*. 43 (8): 1688–95.
  - Pettinari C, Marchetti F, Pettinari R, Drozdov A, Troyanov S, Voloshin AI, Shavaleev NM. 2002. Synthesis, Structure and Luminescence Properties of New Rare Earth Metal Complexes with 1-Phenyl-3-Methyl-4-Acylpyrazol-5-Ones. *Journal of the Chemical Society, Dalton Transactions*. (7): 1409-15.

15. Zhou J, Wang LF, Wang JY, Tang N. 2001. Synthesis, Characterization, Antioxidative and Antitumor Activities of Solid Quercetin Rare Earth (III) Complexes. *Journal of Inorganic Biochemistry*. 83 (1): 41-8.
16. Shelke VA, Jadhav SM, Patharkar VR, Shankarwar SG, Munde AS, Chondhekar TK. 2012. Synthesis, Spectroscopic Characterization and Thermal Studies of Some Rare Earth Metal Complexes of Unsymmetrical Tetradentate Schiff Base Ligand. *Arabian Journal of Chemistry*. 5 (4): 501-7.
17. Zhao G, Feng Y, Wen Y. 2006. Syntheses, Crystal Structures and Kinetic Mechanisms of Thermal Decomposition of Rare Earth Complexes with Schiff Base Derived from o-Vanillin and p-Toluidine. *Journal of Rare Earths*. 24 (3): 268-75.
18. Mohanan K, Aswathy R, Nitha LP, Mathews NE, Kumari BS. 2014. Synthesis, Spectroscopic Characterization, DNA Cleavage and Antibacterial Studies of a Novel Tridentate Schiff Base and Some Lanthanide (III) Complexes. *Journal of Rare Earths*. 32 (4): 379-88.
19. Huheey JE, Keiter EA, Keiter RL, Medhi OK. 2006. *Inorganic Chemistry: Principles of Structure and Reactivity*. 4th ed. Pearson education. 488 p.
20. Lekha L, Raja KK, Rajagopal G, Easwaramoorthy D. 2014. Schiff Base Complexes of Rare Earth Metal Ions: Synthesis, Characterization and Catalytic Activity for the Oxidation of Aniline and Substituted Anilines. *Journal of Organometallic Chemistry*. 753: 72-80.
21. Lekha, L, K Kanmani Raja, G Rajagopal, and D Easwaramoorthy. 2014. Synthesis , Spectroscopic Characterization and Antibacterial Studies of Lanthanide ( III ) Schiff Base Complexes Containing N , O Donor Atoms. *Journal of Molecular Structure* 1056: 307-13.
22. El-Sonbati AZ, Issa RM, El-Gawad AA. 2007. Supramolecular Structures and Stereochemical Versatility of Azoquinoline Containing Novel Rare Earth Metal Complexes. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*. 68 (1): 134-38.
23. CH Huang. 2011. *Rare Earth Coordination Chemistry: Fundamentals and Applications*. John Wiley & Sons. 10,15 p.
24. A. Broido. 1969. A Simple, Sensitive Graphical Method of Treating Thermogravimetric Analysis Data. *Journal of Polymer Science Part A-2: Polymer Physics*. 7 (10): 1761-73.
25. K.R. Patel, Dhara Patel and V D Patel. 2018. Characterization, Activation Energy and Thermodynamic Parameter of Crystals Synthesized from Solvent Evaporation Method. *In J Res Biosci Agric Technol*. 2 (2): 746-53.
26. JB. Yadav. 2006. *Advanced Practical Physical Chemistry*. Krishna Prakashan Media. 63-85 p.
27. Haresh R. Patel, H. D. Chaudhari and J. J. Vora. 2015. Physicochemical Methods as Applied to Synthesis and Catalytic Studies of Selected Lanthanide Complexes. *Journal of Applicable Chemistry*. 4 (6): 1774-90.
28. Gnanaprakasam B, Balaraman E, Ben-David Y, Milstein D. 2011. Gnanaprakasam B, Balaraman E, Ben-David Y, Milstein D. Synthesis of Peptides and Pyrazines from B-Amino Alcohols through Extrusion of H<sub>2</sub> Catalyzed by Ruthenium Pincer Complexes: Ligand-Controlled Selectivity. *Angewandte Chemie International Edition*. 50 (51): 12240-44.
29. Martins MB, Carvalho I. 2007. Diketopiperazines: Biological Activity and Synthesis. *Tetrahedron* 63 (40): 9923-32.
30. Ahluwalia V K, Aggarwal R. 2001. *Comprehensive Practical Organic Chemistry: Preparation and Quantitative Analysis* No Title. Universities press. 123-24 p.