

PHYSIOCHEMICAL CHARACTERIZATION AND EVALUATION OF ANTIMICROBIAL ACTIVITY OF SOME RARE EARTH METAL CHELATES DERIVED FROM 1-HYDROXYPROPAN-2-ONE

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Abstract : 1-hydroxypropan-2-one was used as a biologically active molecule to form lanthanide metal complexes. Three mononuclear lanthanide complexes of the type $[Ln(HA^-)_3(HA)(H_2O)_x] \cdot yH_2O$ Where, Ln = La(III), Sm(III) and Gd(III) were synthesized and their functional groups were elaborately demonstrated using UV-visible, IR spectroscopy, elemental analysis (CHNO analysis), mass spectroscopy, magnetic susceptibility and molar conductivity. Thermal properties of the complexes were studied using the thermo gravimetric analysis (TGA). IR spectral studies revealed that 1-hydroxypropan-2-one behaved as a bidentate ligand and it was structured with metal ion by the two oxygen atoms. The coordination number of three complexes was achieved by involving mono-dentate aqua groups in the coordination sphere. The catalytic activities have been investigated for the complexes. The synthesized metal complexes were elaborately performed for antimicrobial activity.

Index Terms - Antimicrobial activity, biologically active molecule, Catalytic activities, Lanthanide complexes, Mononuclear, Thermal Properties.

I. INTRODUCTION

1-hydroxypropan-2-one is a ketone compound which is also known as Acetol. 1-hydroxypropan-2-one contains both highly active hydroxyl and carbonyl functional groups [1]. Because of these two highly active functional groups 1-hydroxypropan-2-one act like bidentate chelating ligand in present study. 1-hydroxypropan-2-one is commercially available, but it also may be synthesized on a laboratory scale by a substitution reaction on bromoacetone[2]. 1-hydroxyacetone can be produced by degradation of various sugars. In foods, it is formed by the Maillard reaction [3]. Acetol is also used as main constituent of skin tanning agent in cosmetic industry [4]. 1-hydroxypropan-2-one is an anticonvulsant that is used to control seizures and trigeminal neuralgia in the form of 200mg tablet. 1-hydroxypropan-2-one exists in all living organisms, ranging from bacteria to humans. Outside of the human body, 1-hydroxypropan-2-one has been detected, but not quantified in, several different foods. This could make 1-hydroxypropan-2-one a potential biomarker for the consumption of these foods. 1-hydroxypropan-2-one is an intermediate in glycine, serine, and threonine metabolism[5,6]. The lanthanides have not been largely examined from biological point of view but it appears to possess some interesting pharmacological activities. It needs no discussion that the lanthanides have been investigated and widely described from the chemical viewpoint and they provide fascinating new possibilities for research in the coming decades[7]. Metal ions play an important role in the action of drugs. They are involved in specific interactions with antibiotics, proteins, membrane components, nucleic acids and other biomolecules. Many drugs possess modified toxicological and pharmacological properties in the form of metal complexes[8]. The metal which is probably the most widely studied in this respect is Gd(III) ion which has proved beneficial in many treatments such as Gd (III) compounds are components of MRI contrast agents. Lanthanide complexes are of increasing importance in cancer diagnosis and therapy, owing to the versatile chemical and magnetic properties of the lanthanide (III) ion. Lanthanides and lanthanide compounds have fascinated a great deal of significance in recent years because they have applications in medicinal inorganic chemistry and in materials science. In medicine, lanthanide complexes are utilized as contrast agents for magnetic resonance imaging(MRI) and are gaining importance in other diagnostic procedures and also as radio therapeutic drugs[9,10]. The redox stability of Lanthanide ions makes them extremely suitable for cellular applications in the presence of biological reducing agents like ascorbate and thiols, with the added advantage of favorable luminescent properties attributable to $4f \rightarrow 5d$, charge-transfer, and $f \rightarrow f$ transitions [11]. Due to the potential utility of lanthanides in the area of medicinal chemistry, investigators interested in the latest developments in this emerging field. These facts motivate us to explore the coordination behavior of 1-hydroxypropan-2-one with lanthanide metal ions. The present study reports on the synthesis, characterization and antibacterial activities of the ligand and its lanthanide metal complexes.

II. MATERIALS AND METHODS

All the chemicals and glass wares used all through the experimental work were of analytical grade. The metal carbonates of La (III), Sm (III) and Gd (III) and the ligand 1-hydroxypropan-2-one used were also of analytical grade. All the solvents used for recording spectra were of spectroscopic grade. For synthesis of metal-ligand complexes, perchlorates of lanthanum, samarium and gadolinium were prepared by adding metal carbonates in standardized 0.3 M perchloric acid solution. Aqueous solution of 0.1 M 1-hydroxypropan-2-one was used as a ligand solution[12]. The bacterial species used for antibacterial screening were *Escherichia coli* (*E. coli*), *Pseudomonas aeruginosa* (*P. aeruginosa*), *Staphylococcus aureus* (*S. aureus*), and *Staphylococcus pyogenus* (*S. pyogenus*). The bacterial species used for antifungal screening were *Candida albicans* (*C. albicans*), *Aspergillus niger* (*A. niger*), *Aspergillus clavatus* (*A. clavatus*). The bacterial species used in this study were obtained from Institute of Microbial Technology, Chandigarh.

Melting point and TLC (solvent: Toluene: methanol: water in 1: 1: 1 ml ratio) was carried out for the ligand and complexes. The melting points of ligand recorded was 145.5 °C, while the melting points for La-HA, Sm-HA and Gd-HA complexes recorded was higher than 360 °C. The conductance were recorded on a Zeal Tech conductometer (Cell constant $1 \pm 10\% \text{ cm}^{-1}$). The molar conductance was measured by using $1 \times 10^{-3} \text{ M}$ solutions of metal chelates prepared in DMF solvent. Microanalysis for carbon and hydrogen were measured by using THERMO FINNIGAN CHNS analyzer of Flash EA 112 series (Italy). The percentage proportions of La (III), Sm(III) and Gd (III) were determined by EDTA back titration method[13]. Complexes were decomposed with a mixture of concentrated perchloric acid ,sulphuric acid and nitric acid in 1:1:1 ml ratio. Metal content of complexes were obtained by complexometric titration against standard $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ solution using Eriochrome black T as an indicator at proper pH value. The pH of the solution was maintained by using ammonia ammonium chloride buffer solution. BRUKER ALPHA FT-IR ($4000\text{-}400 \text{ cm}^{-1}$) spectrophotometer was used to record Infrared spectra of La-HA and Sm-HA complexes as well as ligand and Shimadzu IR Affinity 1s spectrophotometer was used to record spectra of Gd-HA complex. The magnetic susceptibility measurements were carried out by using Gouy's method at 293 K temperature for solid metal ligand chelate complexes using $\text{Hg}[\text{Co}(\text{CNS})_4]$ as a calibrant[12,14,15]. Electronic spectra of complexes were obtained on UV-1800, Shimadzu (double beam) UV-Vis Spectrophotometer. Thermal measurements were performed using a NETZSCH STA F3 JUPITER, TGA/DSC system (room temperature to 1400°C) thermal analyzer. The mass spectra analysis was performed with water make MASS INSTRUMENT MODEL NO.ZQ 2000. Chemical kinetics study for redox reactions and catalytic study for reductive coupling reaction were carried out. The minimum inhibition concentrations for complexes were determined by Broth dilution methods to evaluate the antimicrobial activities of the synthesized complexes[16]. The kinetic parameters of thermal decomposition were calculated by broido method[17].

III. EXPERIMENTAL

Synthesis of metal chelates with 1-hydroxypropan-2-one: 0.3 M perchloric acid solution was prepared by diluting exact volume of 70% HClO_4 with de-ionized water. The exact strength of the solution was measured by pH metric titration method using 0.3 M NaOH solution which is formerly standardized with 0.3 M oxalic acid solution. 200 ml 0.3 M perchloric acid solution was taken and solid metal carbonate of La (III), Sm (III) and Gd (III) was added to it till the effervescences of CO_2 were observed. Slight excessive amount of metal carbonate was added to it. The solution was stirred for 30 minutes on a magnetic stirrer and filtered. Thus, 0.1 M metal perchlorate solution of La (III), Sm (III) and Gd (III) were obtained. The synthesis of metal complexes were carried out by mixing 100 ml, 0.1M metal perchlorate solution and 100 ml, 0.1M 1-hydroxypropan-2-onesolution prepared in water. The mole ratio of ligand and metal was (1:1). The reaction mixture was refluxed for 3 hours at 95°C temperature. After 3 hours the reaction mixture was cooled and stirred for about 1 hour. There was no immediate precipitation observed. The pH of the reaction mixture was raised up to 6.3 by using 0.1 M NaOH solution to obtained nearly neutral medium for precipitation of the complex[18]. Thus obtained precipitates of metal chelates were filtered, washed with alcohol to remove unreacted metal and ligand. The product was dried in an oven at 50°C . All the complexes were synthesized by same process. The ligand 1-hydroxypropan-2-one and its complexes with La (III), Sm (III) and Gd (III) are abbreviated as $\text{HA}[\text{CH}_3\text{COCH}_2\text{OH}]$, La-HA, Sm-HA and Gd-HA respectively. Reaction scheme for the synthesis of metal ligand chelates is shown in Fig. 1.

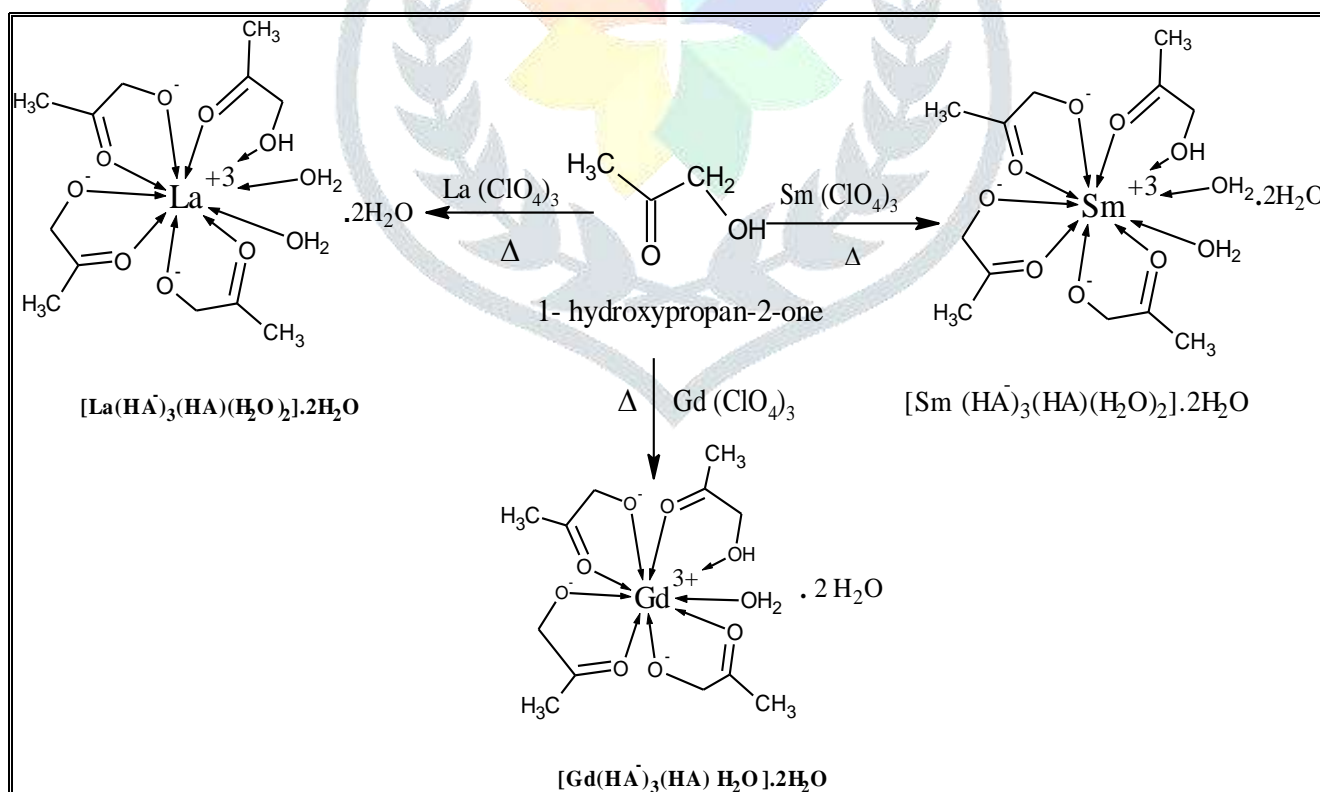


Fig. 1 : Reaction scheme for preparation of metal chelates

IV. RESULTS AND DISCUSSION

4.1 Characterization of ligand and its metal chelates

Analyses and Physical Measurements: Based on the present reports, complexes of the ligand 1-hydroxypropan-2-one [HA] with La(III), Sm(III) and Gd (III) metal ions were synthesized and characterized by various analytical methods. All the complexes are moderately soluble in DMSO and absolutely soluble in DMF but insoluble in methanol, ethanol, acetonitrile and ethyl acetate. Complexes of La(III), Sm(III) and Gd (III) possess somewhat hygroscopic properties consequently, it is desirable to preserve it in an

airtight containers. Melting point and TLC (solvent: Toluene: methanol: water in 5: 5: 5 ml ratio) was carried out for the ligand and complexes. The observed boiling point of 1-hydroxypropan-2-one is 145.5 °C and the melting points of all the complexes are more than 360 °C. The magnetic susceptibility measurements were carried out by using Gouy's method. It is observed that Gd(III) complex is highly paramagnetic. The magnetic moment of the lanthanide metal ions is essentially independent of the environment of the ligands bound to it, it cannot be distinguished between coordination geometries [9,19]. The molar conductance of metal complexes was found in the range of 0.259 to 1.428 $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ signifying that all the synthesized complexes are non-electrolytic in nature. This is reliable with the fact that molar conductance of non-electrolytes is below 60 $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ in DMF solution[20]. The percentage proportions of metal ions, carbon and hydrogen obtained are in aggregate with the calculated values. All the synthesized complexes proposed to have formula $[\text{Ln}(\text{HA})_n(\text{HA})(\text{H}_2\text{O})_x]_y \cdot \text{H}_2\text{O}$.

Table 1: Physical characterization of 1-hydroxypropan-2-one ligand and its complexes

4.2 Interpretation of IR spectra for structure elucidation

The binding mode of the ligand HA to Ln (III) ions in these complexes was studied by comparing the IR spectrum of the ligand HA with that of its Ln (III) complexes. The IR spectrum of the ligand shows two strong absorption bands at 1718 cm^{-1} and 1187 cm^{-1} , which are attributed to the (C=O) group and (C-O) of the hydroxyl substituent, respectively. The infrared spectra of all Ln (III) complexes displayed the ligand HA characteristic bands with various shifts due to complex formation, Table 2. The IR spectral shifts of different complexes are similar, indicating similar structures of the Ln(III) complexes. In the IR spectra of ligand, the band

Sr. No	Compound name	Mole. weight gm/mol	Colour and state	Molar cond. Mho/cm	Rf Value	Mag. Sus. BM	Elemental Analysis			
							% C	% H	% O	% M
							Cal. Fou.	Cal. Fou.	Cal. Fou.	Cal. Fou.
1	Ligand HA	74.07	Colour less (liquid)	0.728	0.83	---	$\frac{48.64}{48.06}$	$\frac{8.17}{7.89}$	$\frac{43.20}{----}$	$\frac{----}{----}$
2	La-HA	490.47	Brown	1.428	0.69	2.43	$\frac{29.39}{27.74}$	$\frac{6.16}{5.55}$	$\frac{35.88}{----}$	$\frac{28.56}{30.29}$
3	Sm-HA	491.26	Yellow	0.418	0.68	3.51	$\frac{27.07}{29.95}$	$\frac{5.51}{5.85}$	$\frac{33.80}{----}$	$\frac{35.32}{32.18}$
4	Gd-HA	458.56	Yellow	0.252	0.71	3.59	$\frac{31.43}{29.42}$	$\frac{5.75}{5.71}$	$\frac{31.40}{----}$	$\frac{31.45}{34.06}$

observed at 3425 cm^{-1} indicates O-H stretching. The frequencies 3565 cm^{-1} in La-HA, 3495 cm^{-1} in Sm-HA and 3332 cm^{-1} in Gd-HA metal ligand complexes. The frequencies 1718 cm^{-1} , 1633 cm^{-1} , 1626 cm^{-1} and 1550 cm^{-1} in ligand 1-hydroxypropan-2-one, La-HA, Sm-Ha and Gd-HA indicates C=O band stretching. The decrease in values indicates C=O: \rightarrow M bonding in complexes. The band at 1187 cm^{-1} in the ligand IR spectrum is due to -C-O band stretching. The decrease of frequencies from 1187 to 1071, 1062 and 1061 cm^{-1} in La-HA, Sm-Ha and Gd-Ha indicates C-O: \rightarrow M bonding. Important IR bands of ligand and its complexes listed in table 2 [21,22].

Table 2: Important Infrared spectrum of ligand and its metal chelates

Band	$\nu(\text{O-H})$ Stretch., cm^{-1}	$\nu(\text{C=O})$ Stretch., cm^{-1}	$\nu(\text{C-O})$ Stretch., cm^{-1}	$\nu(\text{H}_2\text{O})$ cm^{-1}	$\nu(\text{O-M})$ cm^{-1}
Ligand	3425	1718	1187	972	---
La-HA	3565	1633	1071	934	574, 622
Sm-HA	3495	1626	1062	932	565, 620
Gd-HA	3332	1550	1061	939	594, 626

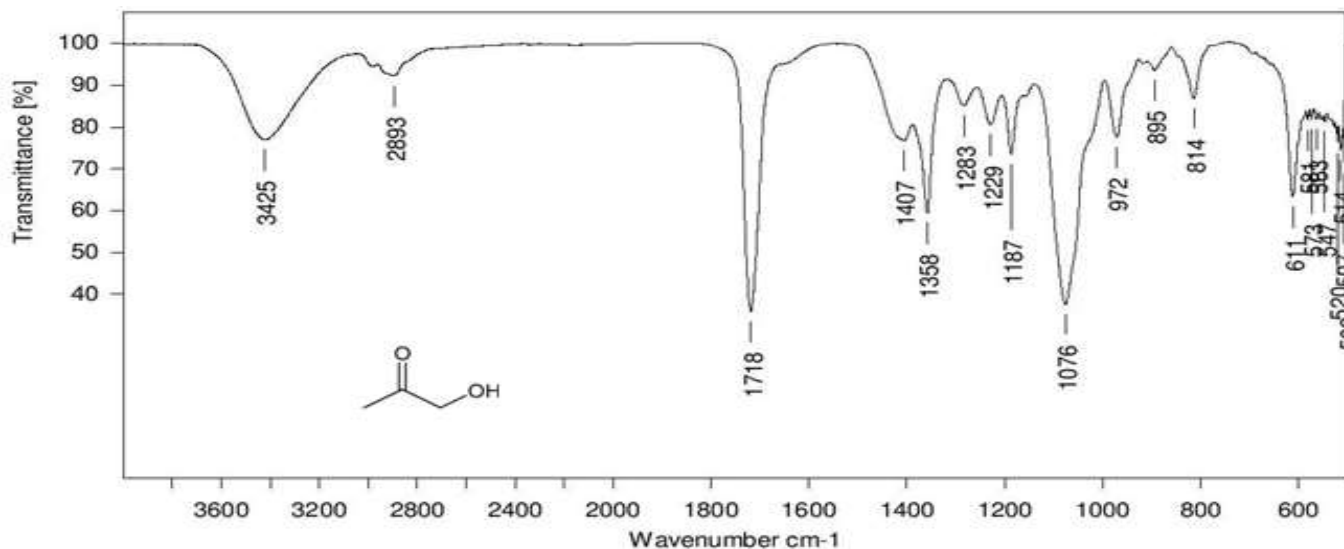


Fig. 2 : Infrared spectrum of ligand 1-hydroxypropan-2-one

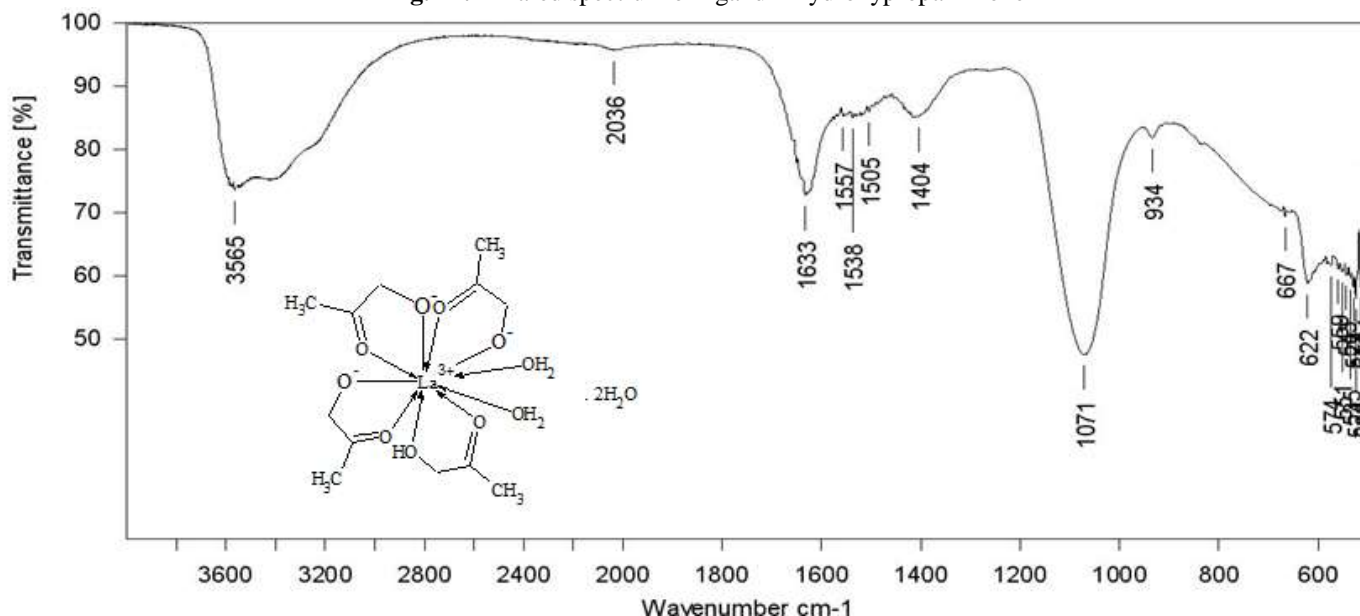


Fig. 3: Infrared spectrum of chelate of La(III) complex with 1-hydroxypropan-2-one

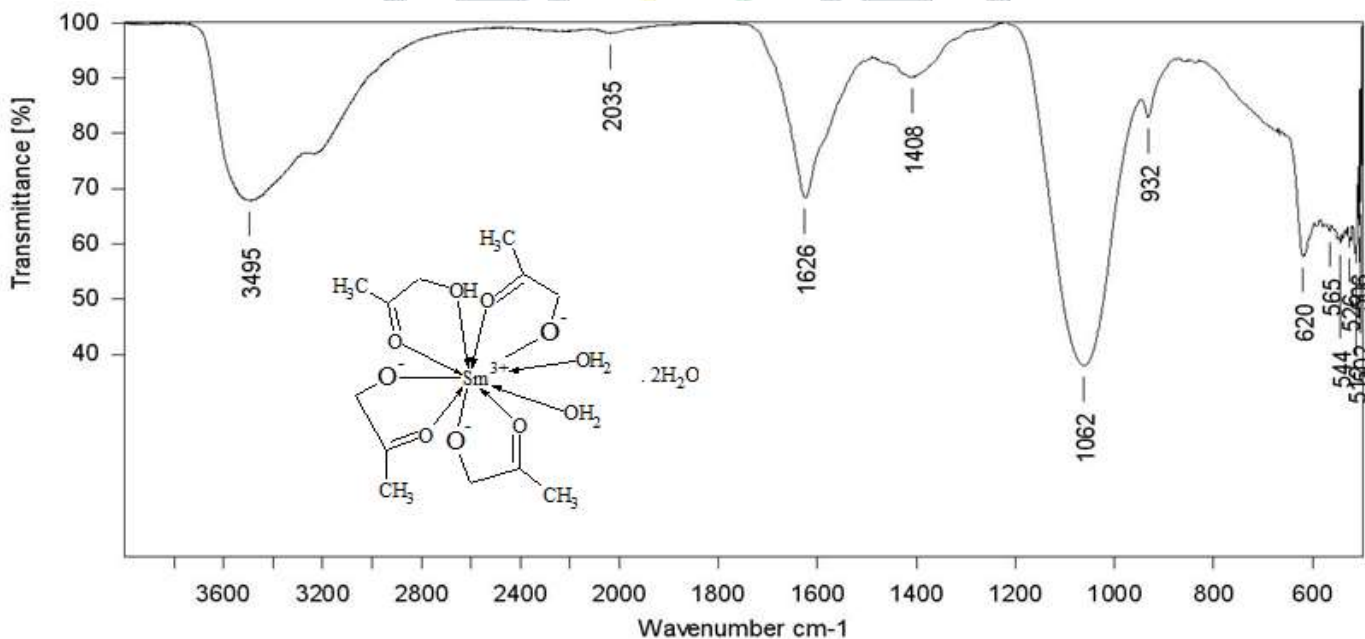


Fig. 4: Infrared spectrum of chelate of Sm(III) complex with 1-hydroxypropan-2-one

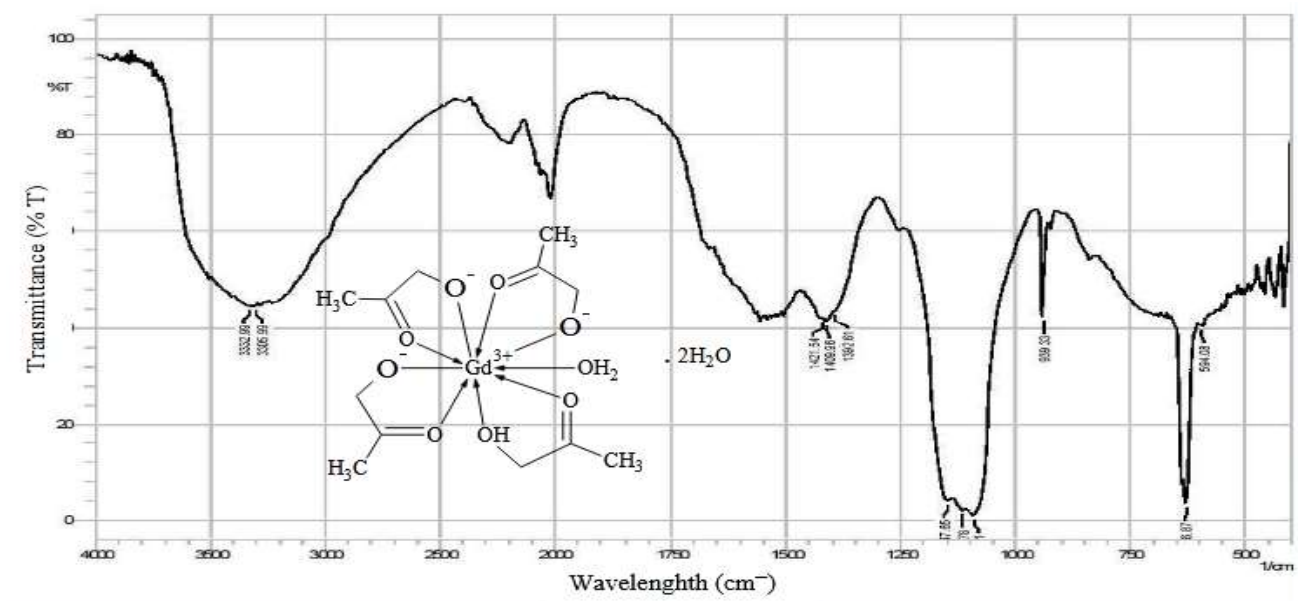


Fig. 5: Infrared spectrum of chelate of Gd (III) complex with 1-hydroxypropan-2-one

4.3 Electronic Spectral study

The UV- visible absorption spectral data of the maximum absorption wavelength λ_{\max} and the corresponding band assignment for the ligand and its complexes are shown in Fig. 6. The concentration of the samples prepared was (1.0×10^{-6} M) by using DMF as a solvent and the spectrum was recorded at room temperature. The ligand (HA) shows two absorption bands with maxima at 261 and 401 nm. The bands are assigned to $n \rightarrow \pi^*$ transitions of conjugation between the lone pair of electrons of O atoms and π electrons of $>C=O$ group. In case of La (III) complex, Broad but weak intensity absorption bands were obtained on the visible region at 402.50 and 463 nm, associated with charge transfer (CT) transition of the type $L \rightarrow M$ and $M \rightarrow L$ between La (III) and the ligand. Meanwhile, other weak bands appeared in the range of 569.50 and 690 nm showed the d-d transition of La (III) ($2B_{1g} \rightarrow 2E_g$) [23]. On the other hand, the bands observed for Sm (III) complex corresponded to the 4f-4f transition from the ground state $^6H_{5/2}$ to the excited states of $^4F_{3/2}$, $^4F_{9/2}$, $^6F_{11/2}$, and $^4G_{5/2}$ [24]. Gd (III) complex shows f-f transition bands at 687.50 and 448.50 nm range, corresponds to the 4f-4f transition from the ground state $^8S_{7/2}$ to the excited states of $^6D_{5/2}$ [25]. The electronic spectrum of the complexes showed a general red-shift associated with covalent bonding. The UV-vis spectroscopic parameters showed that the covalent character occurred between hard lanthanide(III) ion and the soft ligands. Altogether, based on absorption spectra, magnetic properties and elemental analysis, the stoichiometry of the complexes can be shown as $[Ln (HA^-)_n (HA) (H_2O)_x] yH_2O$ (where, $HA = CH_3COCH_2OH$).

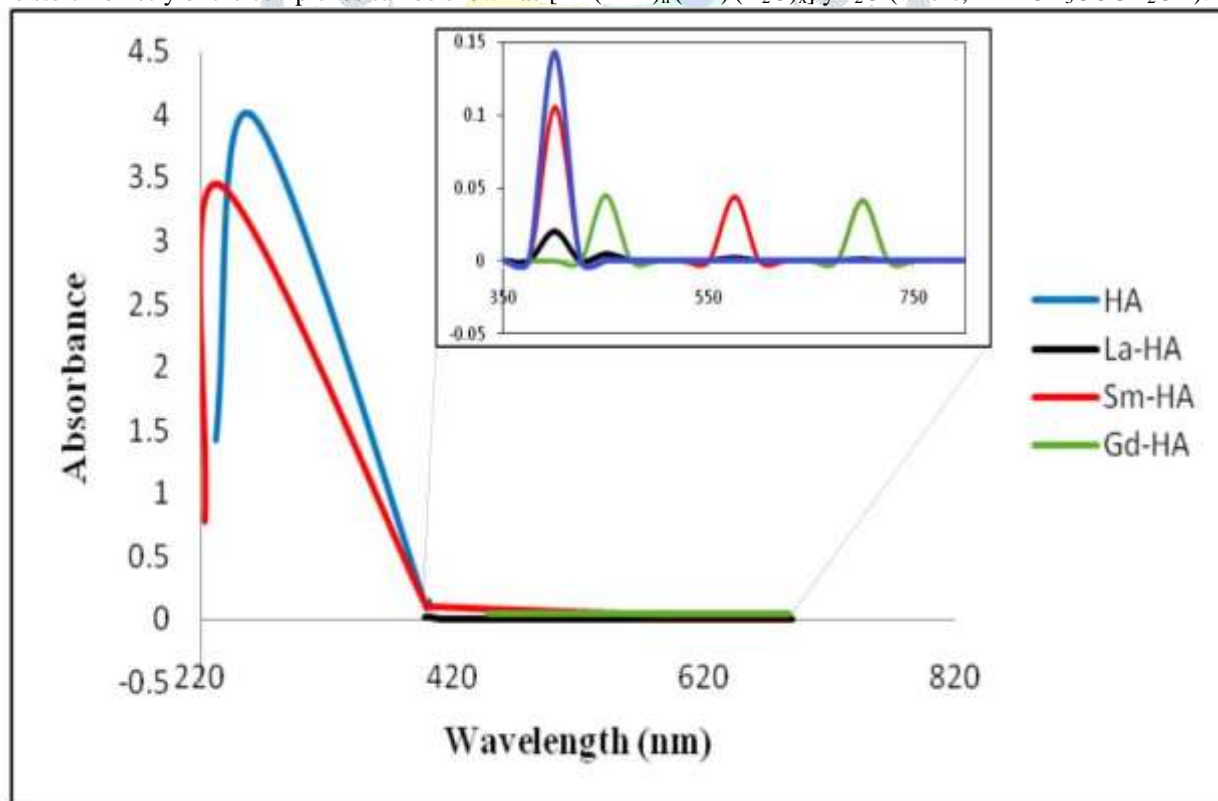


Fig. 6 : Comparative UV-Vis Spectra of the ligand and the complexes
(Inset figure showing the weak absorbance bands of complexes in larger scale.)

Table 3: UV-Vis spectral data λ_{\max} . (nm) for the ligand and its complexes

Complex	Uv-Vis spectral λ_{\max} (nm)	Frequency Cm^{-1}	Energy Kcal/mole	Assignment
Ligand	261	38314	109.5500	$\eta \rightarrow \pi$ transition
La- HA	690	14493	41.4370	M→L charge transfer $\eta \rightarrow \pi$ Transition
	569.5	17559	50.2040	
	463	21598	61.7520	
	402.5	24845	71.0340	
Sm-HA	687	14556	41.6180	${}^6\text{H}_{5/2} \rightarrow {}^6\text{F}_{11/2}$
	568	17606	50.3370	${}^6\text{H}_{5/2} \rightarrow {}^4\text{G}_{5/2}$
	402.5	24645	71.0340	${}^6\text{H}_{5/2} \rightarrow {}^4\text{F}_{3/2}$
	235	42554	121.670	${}^6\text{H}_{5/2} \rightarrow {}^4\text{F}_{9/2}$
Gd-HA	687.5	14546	41.5870	${}^8\text{S}_{7/2} \rightarrow {}^6\text{P}_{7/2}$
	448.5	22297	63.7490	${}^6\text{P}_{5/2}, {}^6\text{P}_{3/2}$ ${}^8\text{S}_{7/2} \rightarrow {}^6\text{D}_{5/2}$

4.4 Thermo gravimetric analysis of Complexes

Thermo gravimetric analysis was carried out for Ln (III) chelates within the temperature range from ambient temperature to 900° C. The correlation between the different decomposition steps of Ln (III) complexes with corresponding weight losses are discussed in terms of proposed formula of the Ln (III) complexes[26]. The number of water molecules present in the outer sphere and the number of water molecules present in the coordination sphere was determined by thermo gravimetric analysis (TGA). The thermal behavior studies of La (III), Sm(III) complexes are almost same. The No. of molecules of lattice water and Coordination sphere are shown in table 3 (Fig. 7-9). As trivalent gadolinium prefers a coordination number of 9, this one available coordination site free for an inner sphere water molecule, allowing its relaxation rate to be enhance, and high relaxivities are indicative of more effective MRI agents[27]. On the basis of present study, the coordination number of La(III), Sm (III) and Gd (III) can be assigned as 10, 8 and 9, respectively [28].

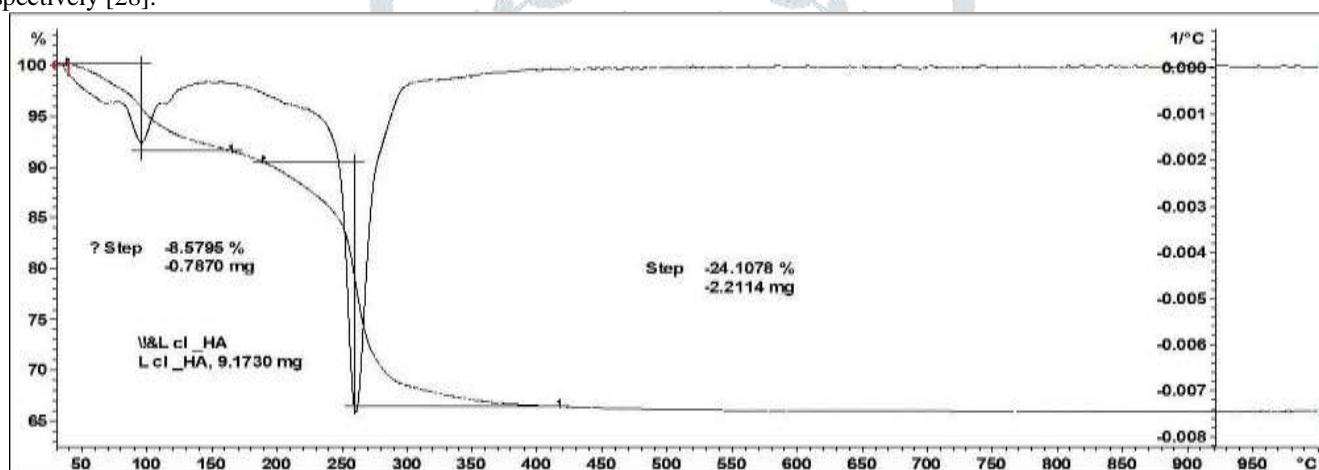


Fig. 7 : TGA Graph of chelate of La(III) with 1-hydroxypropan-2-one

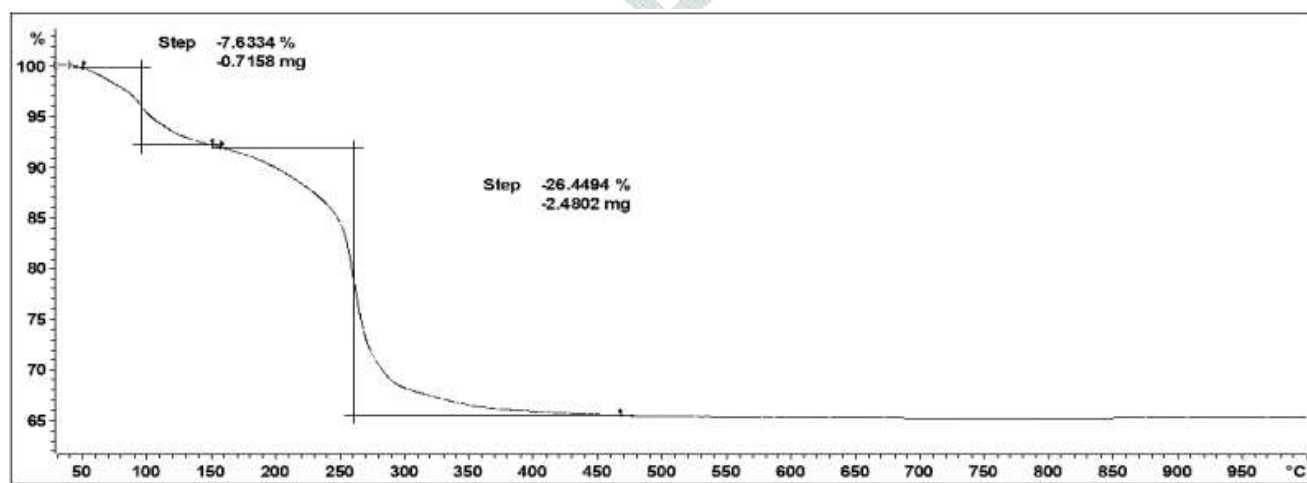


Fig. 8 : TGA Graph of chelate of Sm(III) with 1-hydroxypropan-2-one

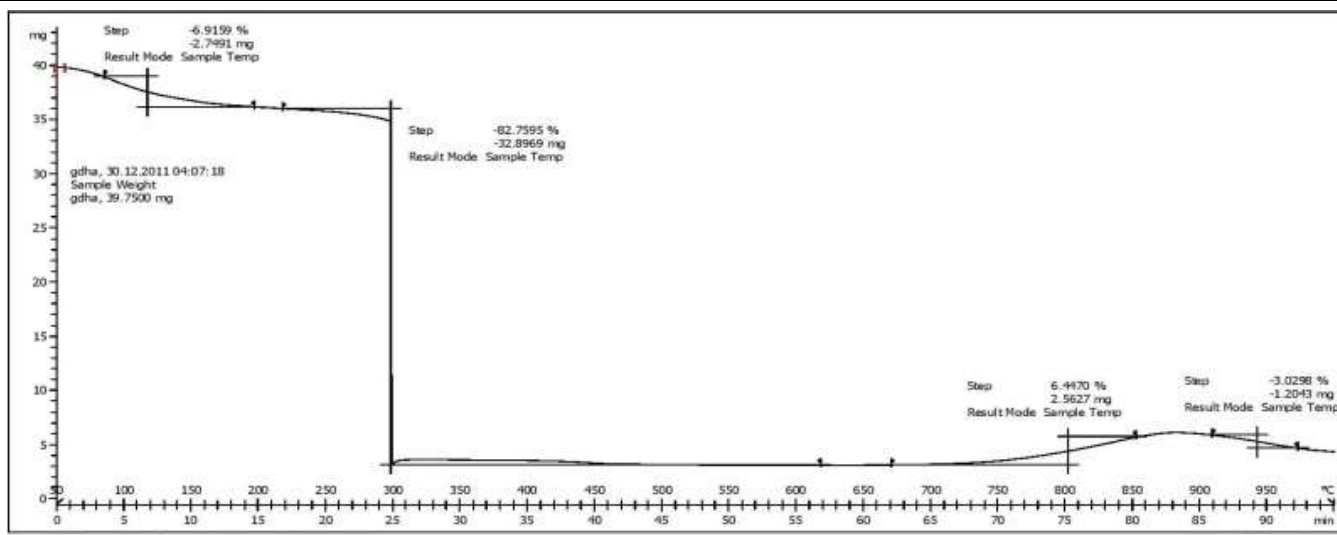


Fig. 9 : TGA Graph of chelate of Gd (III) with 1-hydroxypropan-2-one

Table 3 : Water content and weight loss data of metal chelates

Chelate	R.T. – 150 °C			150 °C – 250 °C		
	Weight loss in %	Weight loss gm/mole	No. of H ₂ O molecule (lattice water)	Weight loss in %	Weight loss gm/mole	No. of H ₂ O molecule (water of coordination)
La-HA	8.5795	43.2630	2	7.293	36.77577	2
Sm-HA	7.6334	39.3666	2	8.011	41.31403	2
Gd-HA	6.9159	34.89704	2	3.398	17.14601	1

4.5 Mass Spectroscopy

A mass spectrum of 1-hydroxypropan-2-one ligand and newly synthesized lanthanide metal ligand complexes confirms the proposed formula by detecting the molecular fragments. The mass spectrum of 1-hydroxypropan-2-one ligand showed the formation of a molecular ion peak at m/z : 74 corresponding to the total molecular weight of the ligand. The molecular ion peak is not detected in the recorded mass spectra of the synthesized Ln(III) complexes. The obtained mass spectra exhibited a large number of peaks possibly due to extensive fragmentation[29]. With the help of Mass spectrometry abundant molecular ions can be shown by the chemical ionization of the ligand and the lanthanide complexes at various m/z values. The m/z values of every fragments observed for complexes are aggregately similar to the corresponding values that are calculated (shown in the bracket). The molecular ion peaks are shown in Fig. 10-13.

Mass spectrum of ligand HA : $ES^+ = 43$ amu is a base peak corresponding to $[C_2H_3O]^+$, which is aggregate to the calculated value 43.035. and it is present due to removal of $-CH_2OH$ fragment from the molecule of 1-hydroxypropan-2-one. $m/z = 74$ (74.07) corresponds to $[C_3H_6O_2]^+$, $m/z = 31$ (31.0337) corresponds to $[CH_2OH]^+$, $m/z = 15$ (15.0347) for $[CH_3]^+$.

Mass spectrum of $[La(HA^-)_3(HA)(H_2O)_2] \cdot 2H_2O$ complex: $ES^+ = 55.08$ amu is a base peak reliable with $[C_3H_3O]^+$ that is aggregate to the theoretically calculated m/z value 55.0552 and it is observed due to the formation of $[C_3H_3O]^+$ fragment. $m/z = 475.7$ (474.23) corresponds to $[C_{11}H_{27}O_{11}La]^+$, $m/z = 341.7$ (341.066) corresponds to $[C_8H_{10}O_6La]^+$, $m/z = 55.08$ (55.055) reliable with $[C_3H_3O]^+$.

Mass spectrum of $[Sm(HA^-)_3(HA)(H_2O)_2] \cdot 2H_2O$ complex: $ES^+ = 245.27$ amu base peak corresponding to $[C_2H_7O_4Sm]^+$ is aggregate with the calculated m/z value 245.4343 and observed due to removal of 2 ligand molecule and a methyl group from the chelate molecule. $m/z = 245.7$ (245.43) corresponds to $[C_2H_7O_4Sm]^+$, $m/z = 373.2$ (373.55) corresponds to $[C_8H_{15}O_7Sm]^+$, $m/z = 371.2$ (371.54) corresponds to $[C_8H_{13}O_7Sm]^+$, $m/z = 335.2$ (335.51) corresponds to $[C_5H_{13}O_7Sm]^+$, $m/z = 317.3$ (317.49) corresponds to $[C_5H_{11}O_6Sm]^+$.

Mass spectrum of $[Gd(HA^-)_3(HA)(H_2O)] \cdot 2H_2O$ complex: $ES^+ = m/z = 471.2$ (471.5355) corresponds to $[C_{11}H_{22}O_{10}Gd]^+$, $m/z = 440.6$ (440.5017) corresponds to $[C_{10}H_{19}O_9Gd]^+$, $m/z = 398.3$ (398.4651) corresponds to $[C_8H_{17}O_8Gd]^+$, $m/z = 380.6$ (380.4499) corresponds to $[C_8H_{15}O_7Gd]^+$, $m/z = 338.2$ (337.4054) corresponds to $[C_6H_{12}O_6Gd]^+$, $m/z = 325.4$ (325.3947) corresponds to $[C_5H_{12}O_6Gd]^+$.

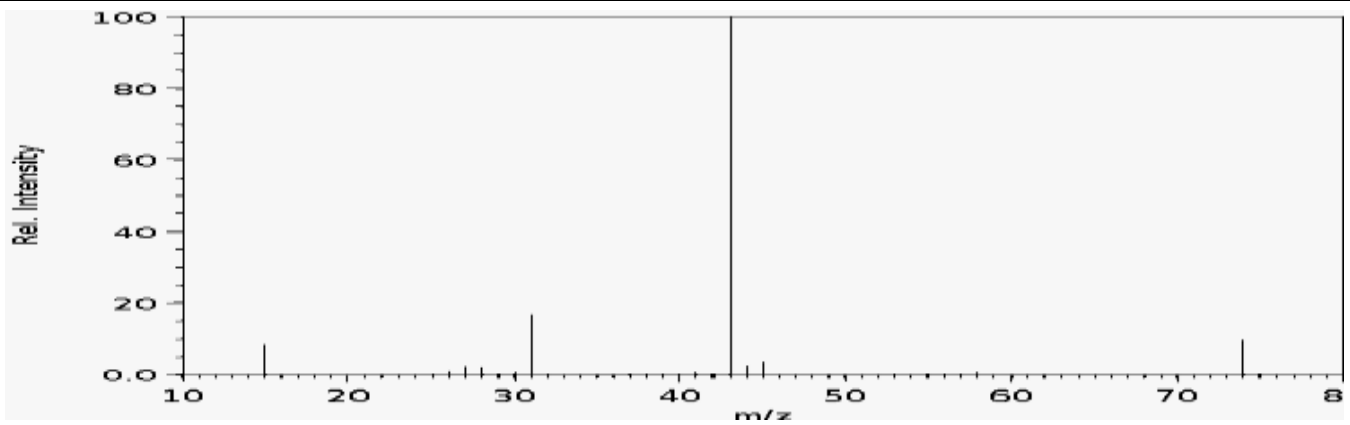


Fig. 10 : Mass spectra of 1-hydroxypropan-2-one ligand

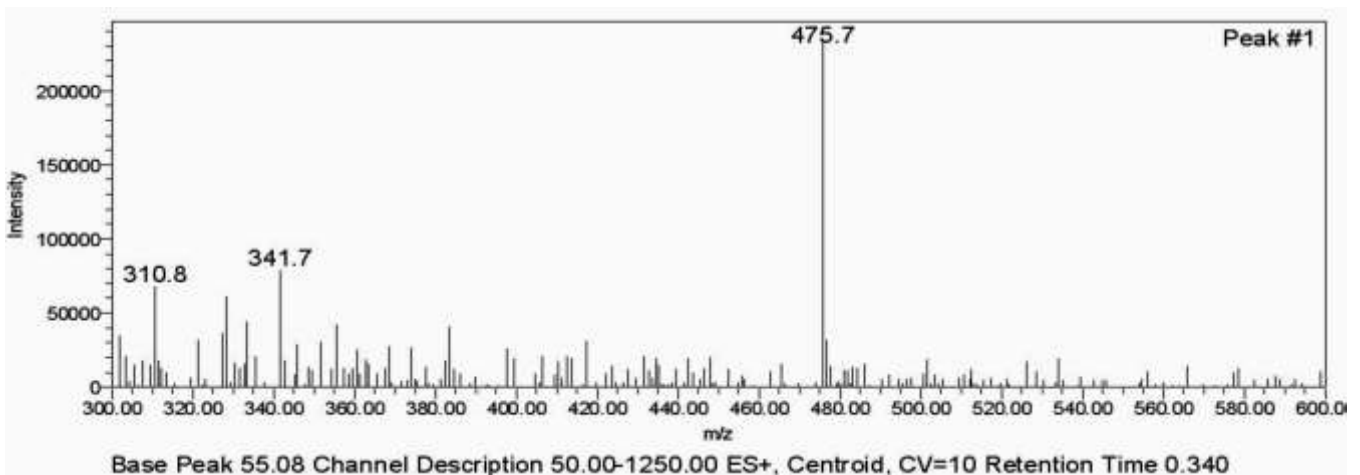


Fig. 11: Mass spectra of chelate of La(III) with 1-hydroxypropan-2-one ligand

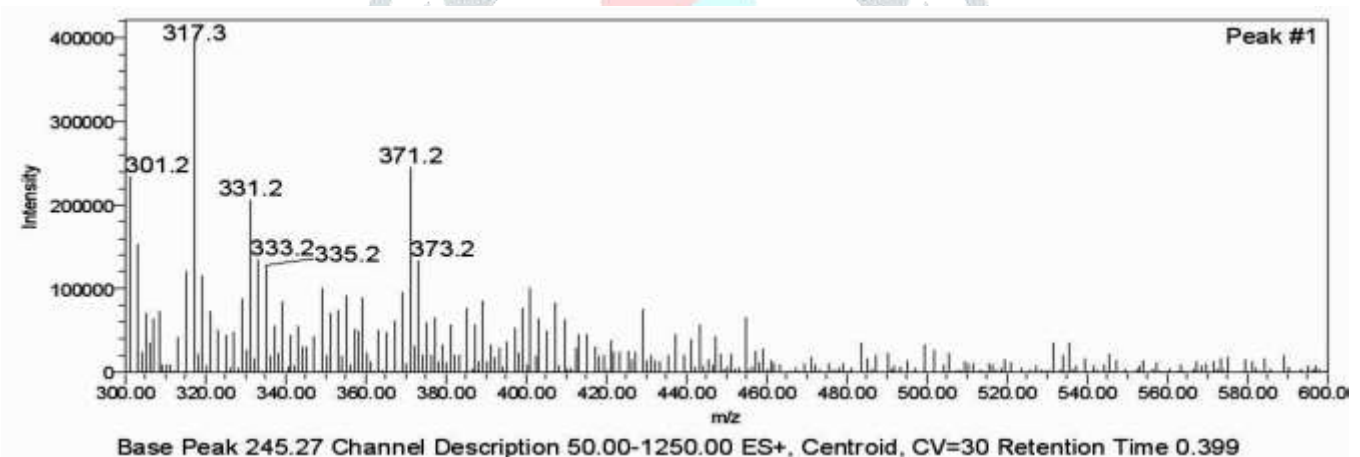


Fig. 12: Mass spectra of chelate of Pr(III) with 1-hydroxypropan-2-one ligand

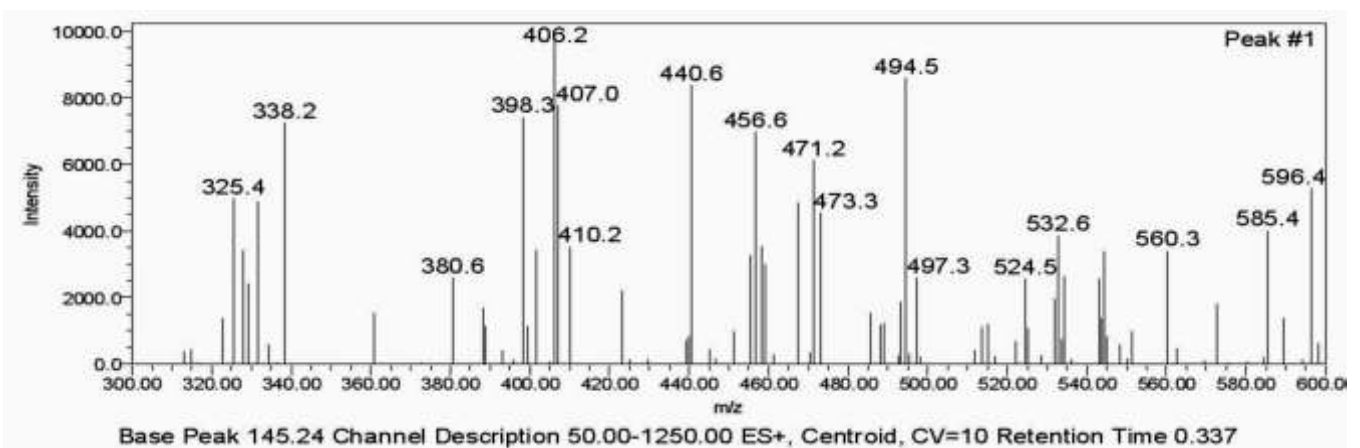


Fig. 13: Mass spectra of chelate of Nd(III) with 1-hydroxypropan-2-one ligand

Structures: From the physicochemical data analysis, the most probable structures of the complexes $[\text{La}(\text{HA}^-)_3(\text{HA}(\text{H}_2\text{O})_2)] \cdot 2\text{H}_2\text{O}$, $[\text{Sm}(\text{HA}^-)_3(\text{HA}(\text{H}_2\text{O})_2)] \cdot 2\text{H}_2\text{O}$, $[\text{Gd}(\text{HA}^-)_3(\text{HA}(\text{H}_2\text{O})_2)] \cdot 2\text{H}_2\text{O}$ can be represented as below.

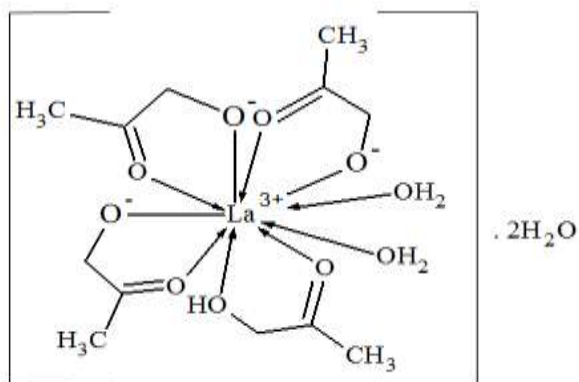


Fig.14 : structure of $[La(HA^-)_3(HA)(H_2O)_2] \cdot 2H_2O$

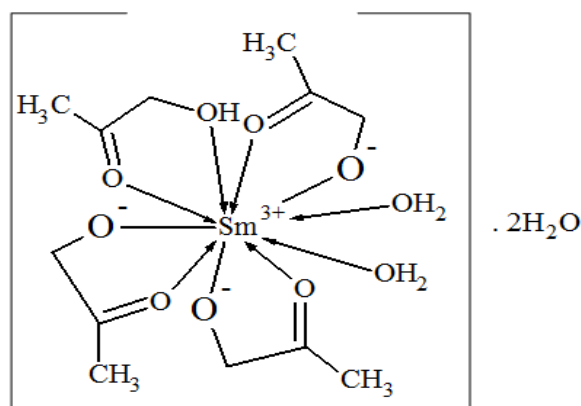


Fig.15 : structure of $[Sm(HA^-)_3(HA)(H_2O)_2] \cdot 2H_2O$

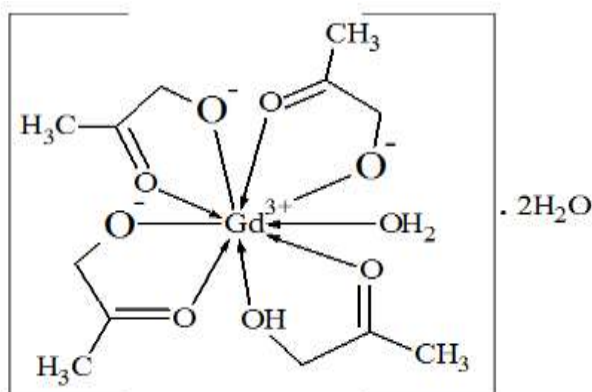


Fig. 16 : structure of $[Gd(HA^-)_3(HA)(H_2O)] \cdot 2H_2O$

4.6 Conclusion

In the present studies, new lanthanide metal complexes of the ligand 1-hydroxypropan-2-one were synthesized and characterized by various analytical methods. All the complexes were synthesized by given experimental procedure, in which carbonates of metals were used as the source of metal and the complexes obtained with the corresponding formula $[Ln(HA^-)_3(HA)(H_2O)_x] \cdot yH_2O$. All the complexes are moderately soluble in DMSO and absolutely soluble in DMF but insoluble in methanol, ethanol, acetonitrile and ethyl acetate. Complexes of La(III), Sm(III) and Gd(III) possess somewhat hygroscopic properties consequently, it is desirable to preserve it in an airtight containers.

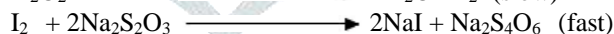
5. APPLICATION

In the present work, three different applications of 1-hydroxypropan-2-one complexes have been studied. [a] chemical kinetics [b] catalysis [c] antimicrobial studies

5.1 Chemical kinetics

To find out the catalytic activities of the synthesized complexes, reaction between hydrogen peroxide and hydrogen iodide, potassium bromate with potassium iodide and potassium persulphate with potassium iodide has been carried out. In the entire reaction first step is the rate determining step and all the reactions are of second order reactions [30,31].

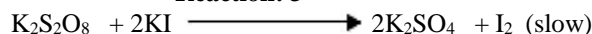
Reaction: 1



Reaction: 2



Reaction: 3



All these second order reactions were performed with and without catalysts. (1 mol %) amount of synthesized metal chelates were used as a catalyst. From the catalytic study, chelate of La(III) and Gd(III) were able to raise the rate of reaction between hydrogen peroxide and hydrogen iodide while the reaction rate of the reactions between hydrogen peroxide and hydrogen iodide decreased with Sm(III) chelate. The reaction rate of the reaction between potassium bromate with potassium iodide correspondingly, chelates of Gadolinium was found to decrease the reaction rate. Overall, increase in the rate of the reaction of hydrogen peroxide and hydrogen iodide in the presence of La(III) and Gd(III) chelates, the values 39 % and 91.28 % respectively, indicates that the La(III) and Gd(III) complexes are highly effective as redox catalysts.

Table 6: Rate of reactions with and without complexes of 1-hydroxypropan-2-one

Reactions	K without Complexes	k with La-HA (1 %) MW	k with Sm-HA (1 %) MW	k with Gd-HA (1 %) MW	% Increase reaction rate at T = 300 K La-HA	% Increase reaction rate at T = 300 K Sm-HA	% Increase reaction rate at T = 300 K Gd-HA
K ₂ S ₂ O ₈ + KI	1.47 × 10 ⁻⁵	1.93×10 ⁻⁵	1.60× 10 ⁻⁵	1.60× 10 ⁻⁵	31.26%	25.85%	8.84%
H ₂ O ₂ + HI	2.41× 10 ⁻⁵	3.35×10 ⁻⁵	1.66× 10 ⁻⁵	4.61× 10 ⁻⁵	39%	-31.12%	91.28%
KBrO ₃ + HI	3.53 ×10 ⁻⁴	4.13×10 ⁻⁴	4.02× 10 ⁻⁴	3.11× 10 ⁻⁴	16.99%	13.88%	-11.89%

5.2 Evaluation of thermal parameters by Broido method

Broido is the well known method to calculate the activation energy associated with each stage of decomposition of a complex. The lanthanide chelate Complexes undergoes three step degradation processes. In which first step is associated with removal of one molecule of water of crystallization, the second step is in order to removal of water of coordination and the third step is related to decomposition of the complexes [32]. The energy of activation (Ea) can be calculated by the equation,

$$\ln(\ln(\frac{1}{y})) = \frac{-E_a}{RT} + K(\text{constant})$$

Where, $y = \frac{W_t - W_\infty}{W_0 - W_\infty}$

Where, y is small proportion of initial molecules that are not yet decomposed, W₀ is the initial weight of the complex and W_∞ is the weight of the remaining complex at the end of the degradation reaction. A plot of ln(ln 1/y) → 1/T yields a straight line. The slope of the plot is measured which is equal to -E_a/2.303R. (R= 8.314J/ mol. K) [17,33-35].

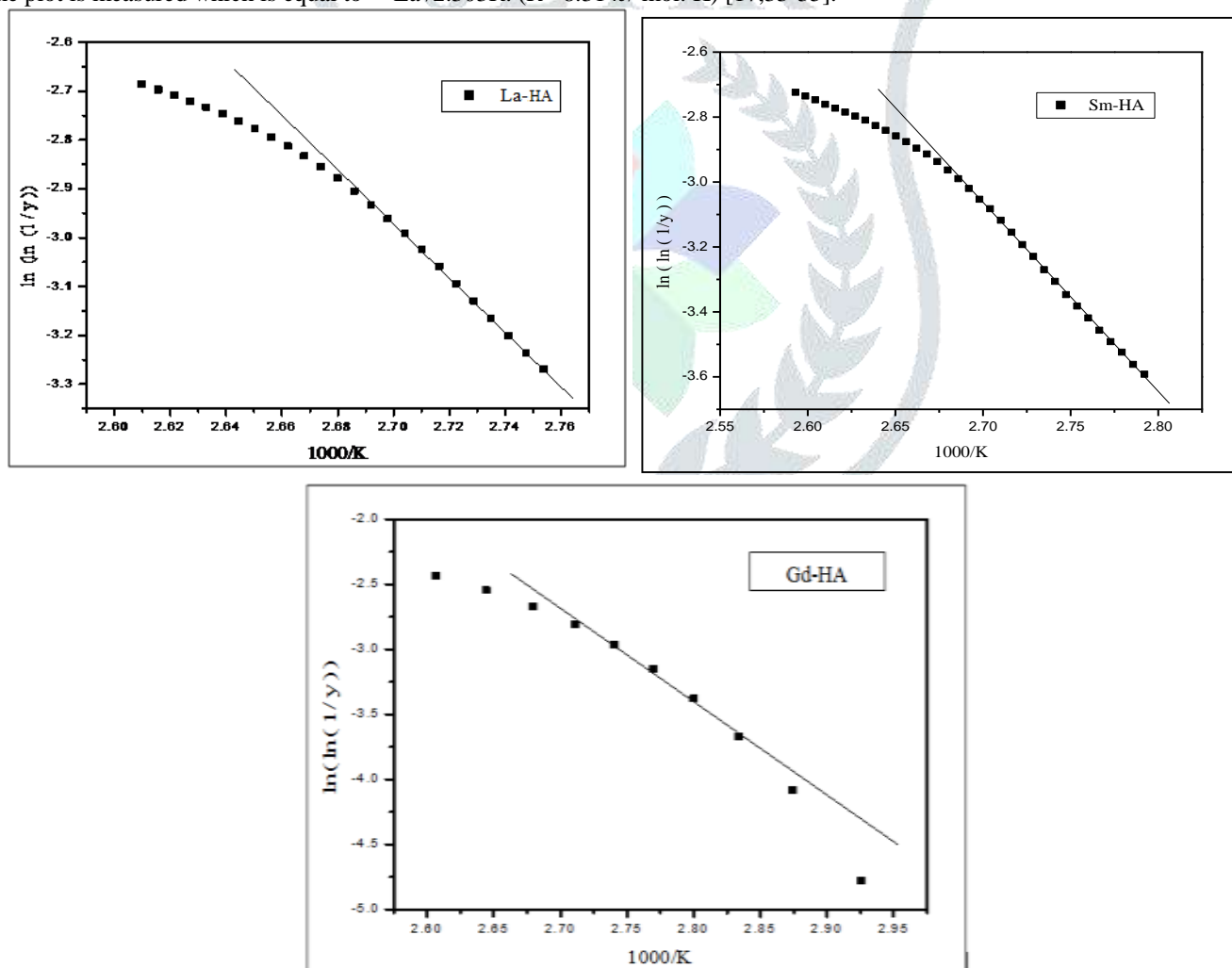


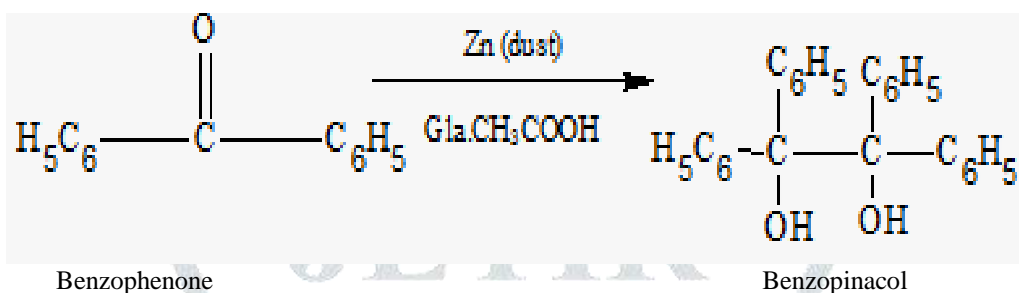
Fig. 17: Plot of ln(ln(1/y)) → 1000/K for [La(HA⁻)₃(HA) (H₂O)₂].2H₂O, [Sm(HA⁻)₃(HA) (H₂O)₂].2H₂O, [Gd(HA⁻)₃(HA) (H₂O)].2H₂O

Table 7: Activation energy of metal chelates

Metal chelates	Temperature range (°C)	Activation energy (Ea) (kJmol ⁻¹)
La-HA [La(CH ₃ COCH ₂ O ⁻) ₃ (CH ₃ COCH ₂ OH) (H ₂ O) ₂].2H ₂ O	92.5 °C -99.5 °C	106.19
Sm-HA [Sm(CH ₃ COCH ₂ O ⁻) ₃ (CH ₃ COCH ₂ OH) (H ₂ O) ₂].2H ₂ O	86.66 °C -95.16 °C	109.88
Gd-HA [Gd(CH ₃ COCH ₂ O ⁻) ₃ (CH ₃ COCH ₂ OH) (H ₂ O) ₂].2H ₂ O	79.81 °C- 131.93 °C	144.142

5.3 Catalysis of Organic Reaction

Reductive coupling reaction was selected to examine the catalytic nature of the metal chelate complexes of La (III), Sm(III), and Gd (III).



Reaction Scheme: Benzopinacol from Benzophenone (Reductive Coupling)

In a 100 ml round bottom flask, Benzophenone (7.5 gm, 0.041 moles), zinc dust (4 gm), deionized water (22 ml) and glacial acetic acid (110 ml) were taken and the reaction mixture was refluxed for 2 hours [36,37]. The reaction mixture was filtered and cooled at room temperature. The separated benzopinacol is filtered and recrystallized from glacial CH₃COOH and the yield of product found was 1.697 gms (37.71%). This reaction was carried out with the synthesized metal chelate complexes with same conditions and parameters. This C-C coupling reaction is also carried out with and without complexes for 3 hours. The yield of product obtained without complex is 2.039gms (45.31%). The results are shown in Table: 8. The melting point of product is 188-190°C. (Room Temperature: 316 K)

Table 8: Percentage yield without and with catalyst metal complexes

Name of the Chelate	Yield in Gms for 2 hours	% Yield for 2 hours	% Increase / Decrease of yield for 2 hours	Yield in Gms for 3 hours	% Yield for 3 hours	% Increase / Decrease of yield for 3 hours
Without complex	1.697	37.71	-----	2.039	45.31%	----
La-HA	1.723	39.24 %	1.53 %	2.112	48.91 %	3.60 %
Sm-HA	1.839	40.87 %	3.16%	2.296	51.02 %	5.71%
Gd-HA	1.804	40.88 %	2.38%	2.003	44.41%	-0.9%

(negative sign indicates decrease in yield)

5.4 Result and discussion

For the catalytic assessment of metal chelates one significant organic synthesis reaction was selected. The reaction was carried out with the same conditions in two sets; for added catalysts and without catalysts. The data displayed in the table showed that from 2 hours and for 3 hours reaction, no drastic change is observed. From the results shown in the table, all the complexes are very less likely to be useful as a catalyst for the reaction.

5.5 Antibacterial activity

All the Synthesized complexes were subjected to Antibacterial test procedures. Minimal Inhibition concentrations (MIC) determination has been carried out by micro 'Broth Dilution Method'. The common standard strains were used for screening of antibacterial activities. Gram negative bacteria E. coli and P.aeruginosa and Gram Positive bacteria S.aureus and S.pyogenus are used for testing of antibacterial studies [12,15]. 2000 microgram/ml concentrations of each complex were diluted to obtain the stock solution. DMSO was used as the diluent to get desired concentration of complexes to test upon Standard bacterial strains. 1000 micro/ml, 500 micro/ml, and 250 micro/ml concentrations of the synthesized drugs were used for primary screening and the

complexes found active in primary screening were similarly diluted to obtain 200 micro/ml, 100 micro/ml, 50 micro/ml, 25 micro/ml, 12.5 micro/ml, 6.250 micro/ml, and concentrations and used for secondary screening [36]. The results of the compounds synthesized for antibacterial screening are mentioned in following table 9.

Table 9: Comparison of antibacterial activities (MIC) of ligand and the chelates of 1-hydroxypropan-2-one ligand with standard drugs.

Compound	S. aureus MTCC 96	S. pyogenus MTCC 442	E. coli. MTCC 443	P. aeruginosa MTCC 441
Ligand HA	50	25	12.5	12.5
La-HA	250	125	50	100
Sm-HA	62.5	125	250	500
Gd-HA	125	125	100	250
Gentamycin	0.25	0.5	0.05	1
Ampicillin	250	100	100	--
Chloramphenicol	50	50	50	50
Ciprofloxacin	50	50	25	25
Norfloxacin	10	10	10	10

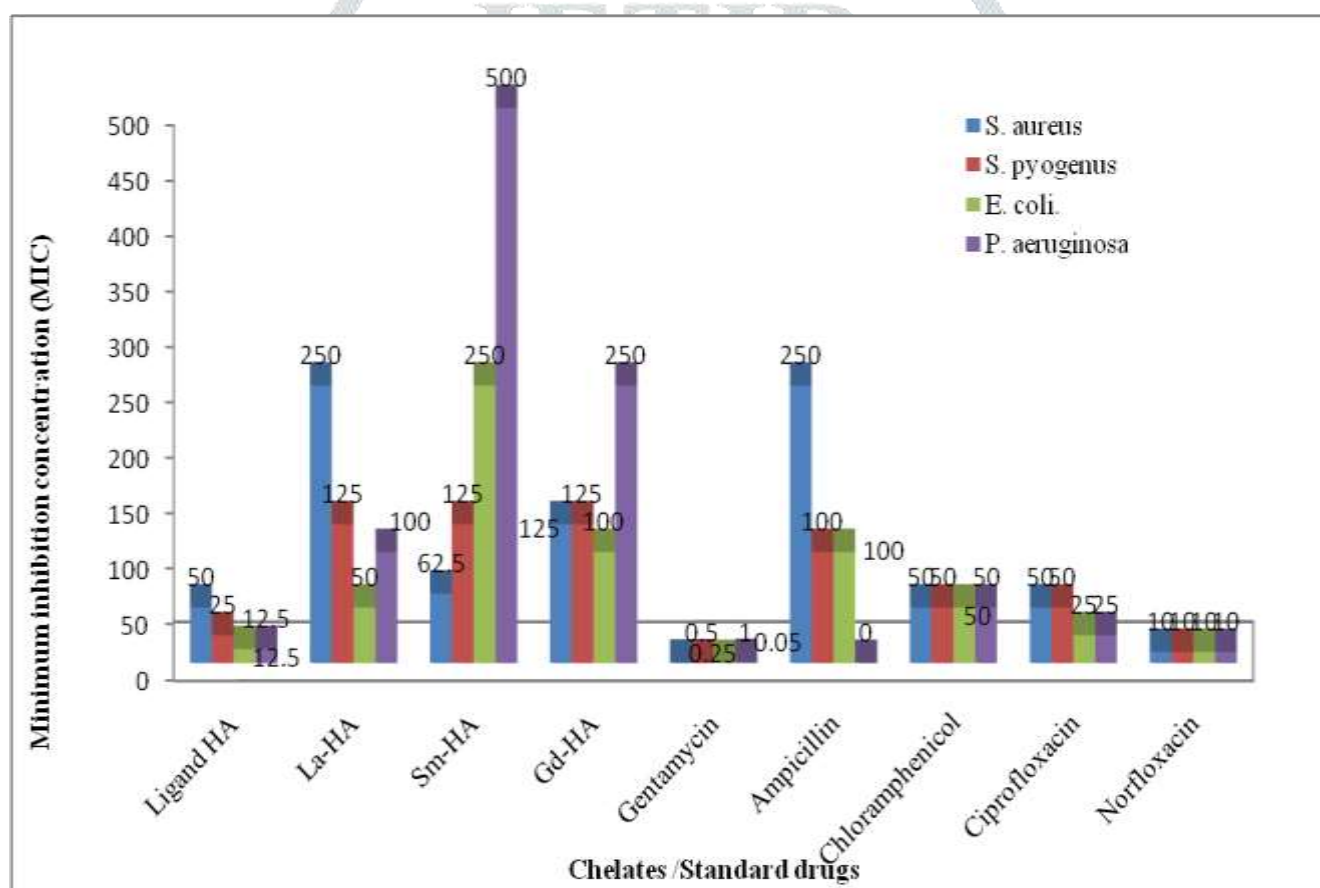


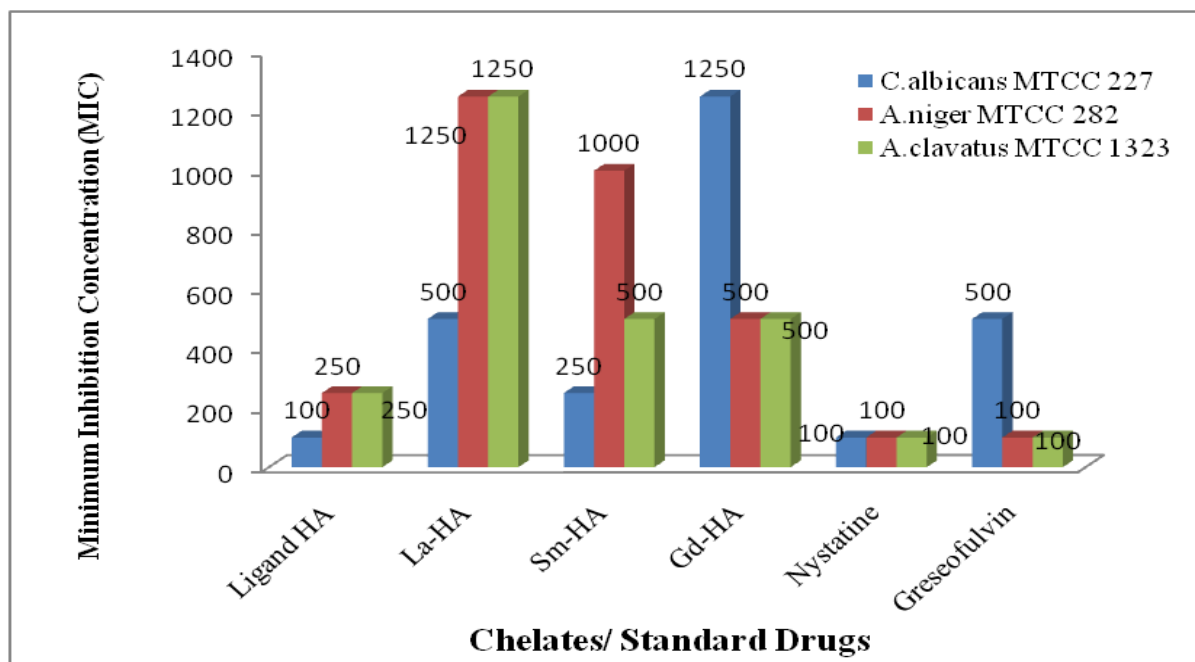
Fig. 18: Comparison of antibacterial activities of metal chelates and standard drugs

5.6 Antifungal activity

The newly prepared complexes were subjected to the in-vitro screening for antibacterial activity. *C. albicans*, *A. Niger*, *A. clavatus* have been used for testing the antifungal activities of complexes. Agar-cup method was used for the in-vitro screening for antifungal activity [18]. The result for antifungal screening is mentioned in as under table 10.

Table 10: Comparison of antifungal activities (MIC) of ligand and the chelates of 1-hydroxypropan-2-one ligand with standard drugs.

Compound	C.albicans MTCC 227	A.niger MTCC 282	A.clavatus MTCC 1323
Ligand HA	100	250	250
La- HA	500	>1000	>1000
Sm-HA	250	1000	500
Gd-HA	>1000	500	500
Nystatin	100	100	100
Greseofulvin	500	100	100

**Fig. 19:** Comparison of antifungal activities of metal chelates and standard drugs

VI. CONCLUSIONS

The novel series of rare earth metal complexes were synthesized, analyzed and characterized for their possible structure. Expected structural formula was been supported by spectral data and chemical analyses. These complexes were subjected to antibacterial and antifungal screening. The antimicrobial activities of the complexes observed, were not as expected. However, the complex of La-HA was found more effective compared to standard drug Ampicillin against *E. coli* and *S.Pyogenus*. The complex Sm-HA was found more active against *S. aureus* compared to Ampicillin. The antifungal activities of all complexes were less compared to the standard drugs. Overall, the synthesized complexes showed less antimicrobial activities. However, proper structure modification may lead to increased antifungal activity.

CONFLICT OF INTEREST

The author has declared that there is no conflict of interest.

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