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SYNTHESIS, CHARACTERIZATION AND BIOCHEMICAL STUDIES OF CERIUM(III), PRASEODYMIUM(III) AND NEODYMIUM(III) CHELATES WITH 1-HYDROXY-2-PROPANONE

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ABSTRACT

The combination of selective rare earth metal ions with biologically active molecule to form metal-ligand complex is an important area of current research. Lanthanide ions are having typical chemical and physical properties. For example, Lanthanide contraction, magnetic properties etc. On complexation of bio-active molecule capable of forming chelate ring with three lanthanide metals ion Ce (III), Pr (III), and Nd (III), there is a drastic change in chemical and biological properties have been observed. Less explored and biologically active 1-Hydroxy-2-propanone ligand is used to form complexes. Thus obtained complexes are subjected to characterization by laboratory methods and instrumental methods including spectroscopic methods. Antimicrobial studies were carried out by standard methods and then catalytic activities of Ce-HA, Pr-HA and Nd-HA complexes are studied by using standard chemical reaction. The difference in properties of metal ions, ligand and chelates is becoming a very important study area.

Keywords: Antimicrobial activity, Biologically active molecule, Catalysis, Lanthanide complexes.

1. INTRODUCTION

Up to now, a vast experience has been accumulated in the field of synthesis and study of lanthanide complexes. In present paper we describe the synthesis of several lanthanide complexes (Ce, Pr and Nd) with 1- hydroxy 2- propanone ligand (Fig. 1). Hydroxyacetone (acetol) contains both hydroxyl and carbonyl functional groups therefore it is an extremely reactive compound. It is water soluble and miscible with ethanol and ethyl ether [1]. Hydroxyacetone was first prepared by reaction between bromoacetone and potassium or sodium acetate or formate followed by the hydrolysis by methyl alcohol [2]. Hydroxyacetone undergoes rapid polymerization. It rapidly undergoes aldol condensation under alkaline medium. It can form hemiacetal cyclic diamer. Hydryoxyacetone can be prepared by degradation of various sugars. It is formed by the Maillard reaction in foods [3]. Acetol 200 mg tablet is used for epilepsy and as an anticonvulsant drug which controls seizures and trigeminal neuralgia. Trivalent lanthanide ions form more stable complexes with oxygen-donor ligands in comparison with nitrogen-donor ligands. They form complexes with 8, 9 or 10-12 coordination numbers [4].

Lanthanides can form stronger complexes by complexation with chelating ligands than monodanted ligands because of the chelate effect. Lanthanides elements have numerous applications in combination with other elements. Approximately 16,000 metric tonnes lanthanides are consumed yearly. Every year a large amount of lanthanide complexes, including lanthanide oxides, are used as a catalysts in various industries. Because of their particular electronic configuration, lanthanide complexes have leads to many efforts on the design and synthesis as potential anticancer and antibacterial agents [5-8]. Due to their biological effectiveness, lanthanide complexes can be used as MRI contrast agents [8, 9]. Thus, lanthanide complexes can be used as biological probes in the areas of clinical chemistry and molecular biology.



Fig. 1: 1-Hydroxy-2-propanone

2. EXPERIMENTAL

2.1. Materials and methods

All the chemicals and glass wares used throughout the experimental work were of analytical grade .The metal carbonates of Ce (III), Pr (III) and Nd (III) and the ligand hydroxyacetone 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, cerium and praseodymium were prepared by adding metal carbonates in standardized 0.3 M perchloric acid solution. Aqueous solution of 0.1 M hydroxyacetone was used as a ligand solution. The bacterial species used in this study were obtained from Institute of Microbial Technology, Chandigarh. 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). Microanalysis for carbon and hydrogen were carried out using Thermo Finnigan CHNS analyzer of Flash EA 112 series (Italy). Bruker

Alpha FT-IR (4000-400 cm⁻¹) spectrophotometer was used to record Infrared spectra of La-HA and Pr-HA complexes as well as ligand and Shimadzu IR Affinity 1s spectrophotometer was used to record spectra of Ce-HA complex. 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 1000°C) thermal analyzer. The mass spectra analyses were performed with water make Mass Instrument Model NO.ZQ 2000. The magnetic susceptibility measurements were carried out by using Gouy's method at 293 K temperature for solid metal ligand chelate complexes using $Hg[Co(CNS)_4]$ as a calibrant [10-12]. Chemical kinetics study for redox reactions and catalytic study for benzopinacol formation reaction were carried out. The minimum inhibition concentrations for complexes were determined by Broth dilution method to evaluate the antimicrobial activities of the synthesized complexes [13, 14]. The kinetic parameters of thermal decomposition were calculated by broido method [15].



Scheme 1: Reaction scheme for synthesis of metal ligand chelates

2.2.Synthesis of complexes with 1-hydroxy 2propanone ligand

A definite volume of 70% HClO₄ was diluted with water to obtain 0.3 M perchloric acid solution. The exact strength of the solution was determined by pH metric titration method using 0.3 M NaOH solution which was previously standardized with 0.3 M oxalic acid solution. 200 ml 0.3 M perchloric acid solution was taken and

solid metal carbonate was added to it till the effervescences of CO₂ 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 Ce (III), Pr (III) and Nd (III) were obtained. The formations of complexes were carried out by mixing 100 ml, 0.1M metal perchlorate solution and 100 ml, 0.1M ligand solution prepared in water. The molar ratio of ligand and metal was 1:1. The reaction mixture was refluxed for 3 hours at 95°C temperature [16]. After 3 hours, reaction mixture was cooled and stirred for about 1 hour. There was no immediate precipitation observed. The pH of the above 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. 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 hydroxyacetone and its complexes with Ce (III), Pr (III) and Nd (III) are abbreviated as HA, Ce-HA, Pr-HA and Nd-HA respectively. Reaction scheme for the synthesis of metal ligand chelates is given in scheme 1.

2.3. Antimicrobial Screening

2.3.1. Preparation of cultures for antimicrobial screening

Bacterial and fungal species were grown in 5mL aliquots of Muller-Hinton broth medium for 24 hours at 37°C. The inoculum size for Test Strain was adjusted to 10⁸ Cfu per mL by comparing the turbidity [13].

2.3.2. Minimum Inhibition Concentration (MIC) by Micro Broth Dilution Method

Antibacterial and antifungal activities of the synthesized complexes were studied by the determination of minimum inhibition concentration (μ g/mL) using micro broth dilution method [13]. 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 μ g/ml, 500 μ g/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 μ g/ml 100 μ g/ml, 50 μ g/ml, 25 μ g/ml, 12.5 μ g/ml, and 6.250 μ g/ml concentrations and used for secondary screening [17]. Standard drugs were also

prepared in serial dilutions. Common standard strains were used for screening of antibacterial and antifungal activities. The control tubes were sub cultered immediately before inoculation over a quarter of medium suitable plate for the growth of the test organism and put for incubation at 37°C overnight. The MIC of the control organism were read and the lowest concentration inhibiting growth of the organism was recorded as MIC [18].

3. RESULTS AND DISCUSSION

3.1.Physical Measurements and characterization of complexes

In the present studies, new lanthanide metal complexes hydroxyacetone 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 Pr (III) and Ce (III) posses somewhat hygroscopic properties consequently, it is desirable to preserve it in an airtight containers while complex of Nd (III) is non-hygroscopic in nature. Melting point and TLC (solvent: Toluene: methanol: water in 1: 1: 1 ml ratio) was recorded for the ligand and complexes. The melting points of ligand recorded was 145.5°C, while the melting points for Ce-HA, Pr-HA and Nd-HA complexes recorded was higher than 360°C. The magnetic susceptibility measurements were carried out by using Gouy's method. 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.

3.1.1. Molar conductance of metal chelates

The conductance was recorded on a Zeal Tech conductometer (Cell constant $1\pm10\%$ cm⁻¹). The molar conductance was determined by using 1×10^{-3} M solutions of metal ligand chelates in DMF solvent. The molar conductance of metal complexes was found in the range of 0.252 to 1.428 Ω^{-1} cm² mol⁻¹ suggesting 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 Ω^{-1} cm² mol⁻¹ in DMF solution [19].

3.1.2. Elemental analysis of metal chelates

The percentage proportions of metal ions were determined by EDTA back titration method. Complexes were decomposed with a mixture of concentrated

analyzer of Flash EA 112 series (Italy). The percentage proportions of metal ions, carbon and hydrogen obtained are in aggregate with the theoretical values. All the synthesized complexes proposed to have formula $[Ln(HA)_4 (H_2O)_x]$. yH₂O. The results are shown in table 1.

Compound		Colour and				E	Element	al Analys	sis
Compound	Mole. weight		Molar cond.	Rf	Mag. Sus.	% C	% H	% O	% M
Hame	gm/mol	state	Ω -1 cm ² mol- ¹	Value	BM	Cal.	<u>Cal.</u>	<u>Cal.</u>	<u>Cal.</u>
						Fou.	Fou.	Fou.	Fou.
Ligand UA	74.07	Colourless	rless 0.729			48.64	8.17	43.20	
	74.07	liquid	0.720	0.05		48.06	7.89		
Co HA	490 47	Brown	1 4 2 8	0.69	2 4 3	<u>29.39</u>	<u>6.16</u>	<u>35.88</u>	<u>28.56</u>
CC-11/1	т70.т7	BIOWII	1.720	0.07	2.75	27.74	5.55		30.29
Pr-HA	101 26	Creen	0.418	0.68	2 5 1	<u>27.07</u>	<u>5.51</u>	<u>33.80</u>	<u>35.32</u>
	+91.20	Green			5.51	29.95	5.85		32.18
Nd-HA	158 56	· 1	0.252	0.71	2 50	<u>31.43</u>	5.75	<u>31.40</u>	<u>31.45</u>
	T30.30	ршк	0.252	0.71	5.59	29.42	5.71		34.06

Table 1: Physical characterization of hydroxyacetone ligand and its complexes

3.2. Interpretation of IR spectra for structure elucidation

solution using appropriate indicator at proper pH value.

The percentage proportions of C and H elements were

measured by using THERMO FINNIGAN CHNS

Infrared spectral characteristics study is of immense help to organic chemists because it can be directly related to the molecular structure. It can also provide a variety of information on structure, symmetry, purity, structural and geometrical isomers and hydrogen bonding. The important infrared absorption bands of ligand and its metal complexes are obtained in the range of 4000-400 cm⁻¹ using compound in the form of KBr pallets. In the IR spectra of ligand, the band observed at 3425 cm⁻¹ indicates O-H stretching. The frequencies 3502 cm⁻¹ in Ce-HA, 3585 cm⁻¹ in Pr-HA and 3522 cm⁻¹ in Nd-HA respectively indicates hydrogen bonding occurs in metal ligand complexes. The frequencies 1718 cm⁻¹, 1633 cm⁻¹, and 1622 cm⁻¹ and 1623 cm⁻¹ in ligand hydroxyacetone, Ce-HA, Pr-HA and Nd-HA indicates C=O stretching. The decrease in values indicates C=O \rightarrow M bonding in complexes. The band at 1187 cm⁻¹ and 1076 cm⁻¹ of the ligand is due to -C-O- band stretching. The decrease of frequencies to 1091, 1032 and 1055 cm⁻¹ in Ce-HA, Pr-HA and Nd-HA indicates C-O \rightarrow M bonding occurred. Frequency observed at 459 cm⁻¹ in Ce-HA indicates formation of $-O \rightarrow$ M bond. Important IR bands of ligand and its complexes are shown in fig. 2 -5 [20].



Fig. 2: Infrared spectrum of ligand Hydroxyacetone



Fig. 3: Infrared spectrum of chelate of Ce (III) complex with Hydroxyacetone



Fig. 4: Infrared spectrum of chelate of Pr (III) complex with Hydroxyacetone



Fig. 5: Infrared spectrum of chelate of Nd (III) complex with Hydroxyacetone

3.3. Electronic Spectral study

Electronic spectra of complexes and ligand were recorded on a UV-1800, Shimadzu (double beam) UV-Vis Spectrophotometer in the range of 200-800 nm. The concentration of the samples prepared was 1.0×10^{-6} M by using DMF as a solvent and the spectra were recorded at room temperature [21]. The results are shown in table 2 (fig. 6).

Cor	nplex	Uv-Vis specral λmax (nm)	Frequency Cm ⁻¹	Energy Kcal/mole	Assignment
Liş	gand	261	38314	109.5500	$\eta \rightarrow \pi$ transition
		685	17422	49.8110	$^{2}\mathbf{E} \qquad \mathbf{\lambda}^{2}\mathbf{D}$
Ce	- HA	266	37594	107.4900	$F_{5/2} \rightarrow D_{5/2}$
		239	41,841	119.6300	$^{2}\mathrm{F}_{5/2} \rightarrow ^{2}\mathrm{D}_{3/2}$
		590.50	16935	48.4190	${}^{3}\mathrm{H}_{4} \rightarrow {}^{1}\mathrm{D}_{2}$
Dre	r-HA 482.50 469.50		20726	59.2570	${}^{3}H_{4} \rightarrow {}^{3}P_{0}$
FF			21299	60.8980	$^{3}H_{4} \rightarrow ^{3}P_{1}$
		444.50	22497	64.3230	${}^{3}H_{4} \rightarrow {}^{3}P_{2}$
		796.5	12555	35.8960	${}^{4}I_{9/2} \rightarrow {}^{2}F_{5/2}, {}^{2}H_{9/2}$
NJ	Nd-HA	681.5	14674	41.9540	${}^{4}I_{9/2} \rightarrow {}^{2}S_{3/2} {}^{4}F_{7/2}$
ING		579.5	17256	49.3380	${}^{4}I_{9/2} \rightarrow {}^{4}G_{5/2} {}^{4}F_{7/2}$
		523	19570	55.9520	${}^{4}I_{9/2} \rightarrow {}^{2}G_{9/2}$

Table 2: UV-Vis spectral data λ max. (nm) for the ligand and its complexes



Fig. 6: Comparative UV-Vis Spectra of the ligand and the complexes

3.4. Thermo gravimetric analysis of Complexes

Thermo gravimetric analysis was carried out for Ce(III), Pr(III) and Nd(III) complexes within the temperature range from ambient temperature to 1000°C. The correlation between the different decomposition steps of complexes with corresponding weight losses are discussed in terms of proposed formula of the complexes. The number of water molecules present in the outer sphere and the number of water molecules present in the coordination state was determined by thermo gravimetric analysis (table 3). Weight loss below 150°C is due to lattice water and above 150°C to 250°C is due to coordinated water present in the metal chelates. Complexes of Ce(III) and Pr(III) undergo three stage decomposition process while Nd(III) undergoes two stage decomposition process. At the temperature range of 1000° C, the formation of Ce₂O₃ Pr₂O₃ and Nd₂O₃ were take place. The thermal behavior studies of Ce (III), Pr (III) and Nd (III) complexes are almost same [20].

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

		R.T. – 1	150°C	150°C – 250°C				
	Weight loss	gm/mole	No. of H ₂ O molecule	Weight loss	gm/mole	No. of H ₂ O molecule		
Complex	in %	-	(water of crystallization)	in %		(water of coordination)		
Ce- HA	3.2000	15.69	1	8.0327	39.39	2		
Pr-HA	4.8256	23.70	1	8.3192	40.86	2		
Nd-HA	1.3353	6.123	0	3.7859	17.36	1		



Fig. 7: Thermogravimetric spectra of complexes

3.5. Mass Spectroscopy

A mass spectrum of hydroxyacetone ligand and newly synthesized metal ligand complexes confirms the proposed formula by detecting the molecular fragments. 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 [22]. The m/z values of every fragment observed for complexes are aggregately similar to the corresponding values that are calculated.





Fig. 10: Mass spectra of chelate of Pr (III) with Hydroxyacetone ligand

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Fig. 11: Mass spectra of chelate of Nd (III) with Hydroxyacetone ligand

Table 4: Mass fragmentation of metal chelates

Compound	Possible	m/z v	alue
Compound	Fragments	Calculated	Found
	$[C_3H_6O_2]$	74.0784	74
НА	$[C_2H_3O]^+$	43.0357	43
11/1	$[CH_3O]^+$	31.0337	31
	$[CH_3]^+$	15.0347	15
	$[C_{11}H_{22}O_{6}Ce]^{+}$	390.408	390.6
$[Ce (HA)_4 (H_2O)_2] . H_2O$	$[C_{11}H_{23}O_{6}Ce]^{+}$	391.416	391.6
	$[C_{12}H_{21}O_7Ce]^+$	417.410	417
	$[C_4H_{11}O_2Pr]^+$	248.037	249.4
[Pr(HA), (H,O), 1, H,O]	$[C_9H_{17}O_6Pr]^+$	362.112	362.7
	$[C_{12}H_{24}O_{9}Pr]^{+}$	453.220	453.7
	$[C_{12}H_{30}O_{10}Pr]^+$	475.269	475.7
	$[C_6H_{12}O_5Nd]^+$	308.396	308.2
	$[C_7H_{14}O_5Nd]^+$	322.422	322.2
	$[C_8H_{13}O_5Nd]^+$	333.427	333.4
$[Nd (HA)_4 (H_2O)]$	$[C_9H_{15}O_5Nd]^+$	347.452	347.3
	$[C_9H_{16}O_5Nd]^+$	348.459	348.3
	$[C_{10}H_{20}O_7Nd]^+$	396.491	396.3
	$[C_9H_{21}O_8Nd]^+$	417.49	418.4

3.6. The possible Structures of synthesized metal chelates

From the physicochemical data analysis , the probable structures of the complexes [Ce $(HA)_4 (H_2O)_2$] $.H_2O$, [Pr $(HA)_4 (H_2O)_2$] $.H_2O$, [Nd $(HA)_4 (H_2O)$] can be represented as below.







Fig. 12 : [a] structure of $[Ce(HA)_4(H_2O)_2].H_2O$ [b] structure of $[Pr(HA)_4(H_2O)_2].H_2O$ [c] structure of $[Nd(HA)_4(H_2O)]$

4. APPLICATIONS

In the present work, three different applications of hydroxyacetone complexes *viz*. [a] chemical kinetics [b] catalysis [c] antimicrobial studies have been studied.

4.1. 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 [23, 24].



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 Pr (III) and Nd (III) were able to raise the rate of reaction between hydrogen peroxide and hydrogen iodide while the reaction rates of the reactions between potassium persulphate and potassium iodide were decreased with cerium chelate complex. The reaction rate of the reaction between potassium bromate and hydrogen peroxide with potassium iodide correspondingly, chelates of praseodymium and neodymium were found to decrease the reaction rate. Overall, increase in the rate of the reaction of hydrogen peroxide and hydrogen iodide in the presence of Pr(III) and Nd(III) chelates, the values 178 % and 104.14 % respectively, indicates that the Pr(III) and Nd(III) complexes are highly effective as redox catalysts.

	Та	bl	e 6	:	Rate	0	f rea	ctions	with	ı and	withou	t com	plexes	of h	vdrox	vaceton
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Reactions	K without Complexes	k with Ce-HA (1 %) MW	k with Pr-HA (1 %) MW	k with Nd-HA (1 %) MW	% Increase Reaction rate at T = 300 K Ce-HA	% Increase Reaction rate at T = 300 K Pr-HA	% Increase Reaction rate at T = 300 K Nd-HA
$K_2S_2O_8 + KI$	1.47 X 10 ⁻⁵	1.3 X 10 ⁻⁵	1.55 X 10 ⁻⁵	1.54 X 10 ⁻⁵	-11.56 %	5.44 %	4.76 %
$H_2O_2 + HI$	2.41 X 10 ⁻⁵	2.6 X 10 ⁻⁵	6.70 X 10 ⁻⁵	4.92 X 10 ⁻⁵	7.88~%	178 %	104.14 %
$KBrO_3 + HI$	3.53 X 10 ⁻⁴	3.9 X 10 ⁻⁴	2.15 X 10 ⁻⁴	3.12 X 10 ⁻⁴	10.48 %	-39.93 %	-11.61 %

4.2. Catalysis of Organic Reaction

Reductive coupling reaction was selected to examine the catalytic nature of the metal chelate complexes of Ce (III), Pr (III), and Nd (III). 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 [25]. 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 $188-190^{\circ}$ C. (Room Temperature: 316 K).



Name of the	Yield (gms)	% yield	% Increase	Yield (gms)	% yield	% Increase	
compound	for 2 hours	With catalyst for 2	/Decrease	For 3 hours	with Catalyst for	/decrease	
	reaction	hours reaction	of yield	reaction	3 hours reaction	of yield	
Without	1 607	27 710/		2 030	AE 210/0/		
complex	1.097	37.7170		2.039	T3.3 17070		
Ce-HA	1.806	40.14 %	2.43%	2.037	45.35 %	0.04%	
Pr-HA	2.250	50%	12.29%	2.259	50.2 %	4.89%	
Nd-HA	1.803	40.066 %	2.365%	2.257	50.16 %	4.85%	

Table 8: Percentage yield without and with catalyst metal complexes

The data displayed in the table showed that from 2 hours reaction with Ce (III), Pr (III) and Nd (III) complexes the yield of product is increased to about 2.36 % to 12.29 %. With Pr (III) the yield of product has been expanded up to 12.29%. On the contrary, 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.

4.3.Evaluation of kinetic parameters of the thermal decomposition 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 [15]. The energy of activation (Ea) can be calculated by the equation,

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

Where, $y = \frac{Wt - W\infty}{Wa - W\infty}$

Where, y is small proportion of initial molecules that are not yet decomposed, Wo 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) $\rightarrow 1/T$ yields a straight line. The slope of the plot is measured which is equal to -Ea / 2.303R. (R= 8.314J/mol. K) [26-29].





Fig. 13: Plot of $\ln(\ln(1/y)) \rightarrow 1000/K$ for [Ce (HA)₄ (H₂O)₂] .H₂O, [Pr (HA)₄ (H₂O)₂].H₂O and [Nd (HA)₄ (H₂O)]

 Table 7: Activation energy of metal chelates

Metal Chelate	Temperature range	Activation
	(°C)	Energy
$\overline{[Ce (HA)_4 (H_2O)_2]}.H_2O$	262.45°C -305°C	74.122
$[Pr (HA)_4 (H_2O)_2] .H_2O$	128.33°C -187.33°C	25.965
$[\mathrm{Nd}(\mathrm{HA})_4(\mathrm{H}_2\mathrm{O})]$	197.167 °C - 236.5 °C	33.114

4.4. Antimicrobial study

4.4.1. 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 [30]. 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 [11, 12]. Antibacterial activity of Nd-HA complex against E.coli, S. aureus and S. pyogenus showed less effectiveness with MIC value of 250 µg/mL, whereas, Ce-HA complex shows more effectiveness in compare to ampicillin against all bacterial strains. Pr-HA complex shows equal inhibition activities to ampicillin against E. coli bacterial strain. The antibacterial activities of the all complexes were compared to standard drugs. The comparative result of metal complexes and standard drugs for antibacterial demonstrated in fig.14 screening is and the determination of minimum inhibition concentration (MIC) is listed in table 8.

4.4.2. Antifungal activity

The newly prepared complexes were subjected to the invitro screening for antifungal activity. *C. albicans, A. niger, A. clavatus* have been used for testing the antifungal activities of complexes. All the three complexes showed very less effectiveness against all strains compared to Nystatin and Greseofulvin. The result suggested that the chelation reduce the polarity of the complexes, which in turns enables the permeation through the lipoid layer of the microorganism [31]. The comparative result of metal complexes and standard drugs for antifungal screening is demonstrated in fig.15 and table 9.





Compound	E. coli	P. aeruginosa	S. aureus	S. pyogenus
Compound	MTCC 443	MTCC 441	MTCC 96	MTCC 442
Ce-HA	25	50	100	50
Pr-HA	100	125	250	500
Nd-HA	250	100	250	250
Gentamycin	0.05	1	0.25	0.5
Ampicillin	100		250	100
Chloramphenicol	50	50	50	50
Ciprofloxacin	25	25	50	50
Norfloxacin	10	10	10	10

Table 8: Minimum inhibition concentration (μ g/mL) for metal complexes and standard drugs for bacterial strains

Table 9: Minimum inhibition concentration (μ g/mL) for metal complexes and standard drugs for fungal strains

Strain	Ce-HA	Pr-Ha	Nd-Ha	Nystatin	Greseofulvin
C.albicans (MTCC 227)	500	1000	250	100	500
A.niger (MTCC 282)	1000	1250	500	100	100
A.clavatus (MTCC 1323)	500	1250	500	100	100



Fig. 15: Comparison of Antifungal activities of the complexes and standard drugs

5. 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. The complexes were studied for catalytic effect on three well known redox reactions. Catalytic study for metal chelates was also carried out for the synthesis of benzopinacol from benzophenone. By using broido method, activation energy of thermal degradation These complexes were reaction was measured. subjected to antibacterial and antifungal screening. The antimicrobial activities of the complexes observed, were not as expected. However, the complex of Ce-HA was found more effective compared to standard drug Ampicillin against E. coli, P. aeruginosa, S. aureus and S.pyogenus. The complex Nd-HA was found more active against С. albicans compared to Greseofulvin.

The antifungal activities of other 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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