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Physicochemical Methods as Applied to Synthesis and Catalytic Studies of Selected Lanthanide Complexes

Haresh R. Patel [1*], H.D. Chaudhari[2] and J. J. Vora[3]

1. Smt. S.S.Patel Nootan Science and Commerce College, Visnagar, Gujarat, **INDIA**
2. Adarsh Science College, Radhanpur, Gujarat, **INDIA**
3. Department of Chemistry, Hemchandracharya North Gujarat University, Patan, Gujarat, **INDIA**

Email: hareshpatel6900@yahoo.com, jabali_vora@hotmail.com

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ABSTRACT

The combination of some rare metal ions with biologically important kynurenic acid ligand to form coordination compound is an important area of current research. Less explored biologically important, kynurenic acid ligand is allowed to react with solution of some rare metal perchlorates and attempt has been made to synthesize solid kynurenic acid complexes. These kynurenic acid complexes are subjected to U.V-Visible spectroscopy, IR spectroscopy, mass spectra, TGA analysis, elemental analysis etc. These complexes are used to study whether they possess catalytic activity in homogeneous or heterogeneous phase. Antimicrobial activity of these complexes has been evaluated by standard methods and attempts have been made to correlate structural characteristics with properties of these kynurenic acid complexes.

Keywords: Kynurenic acid, catalysis, antimicrobial activity, lanthanide complexes.

INTRODUCTION

The rare–earth metals are defined as the group III b elements Sc, Y, La and the 14 lanthanides Ce–Lu. The term ‘rare earth’ has often applied in the more restricted sense as synonym for the lanthanides [1] and this excludes Sc, Y and La. It is reasonable to consider the lanthanides as a group separate from the rest of the periodic table only if the principal interest in these elements is those properties that depend on the occupancy[2] of the 4f electron shell, from 0 (La) to 14 (Lu). An important example can be found in the magnetic properties of the lanthanide complexes, often exotic, magnetic structures observed in alloys and compounds containing these elements are intimately dependent on the lanthanide 4f electrons and are thus absent from Sc, Y and La.[3-4]. However, essential though the 4f electrons are in giving the lanthanides their character, the grouping together of the 17 rare–earth metals reminds that they have analogous electronic configurations — the outer three electrons are $(3d\ 4s)^3$ for Sc, $(4d\ 5s)^3$ for Y and $(5d\ 6s)^3$ for La and the trivalent lanthanides.[5] In the present work, complexes of lanthanides with kynurenic acid were prepared characterized for structure elucidation and subjected to biochemical study.

MATERIALS AND METHODS

Analytical grade chemicals were used throughout the course of experimental work. Spetroscopic grade solvents were employed for recording the spectra. The compound kynurenic acid (Sigma) was used as the ligand. All metal carbonates used were also A.R. grade. A definite volume of 70% $HClO_4$ was diluted with water to obtain 0.2M perchloric acid solution. The exact strength was determined by pH metric titration against standard 0.2M NaOH solution. 75 ml 0.2 M perchloric acid was taken and solid metal carbonate was added in it till effervescences observed (slight excess addition was done). The solution was stirred for 30 minutes and filtered and thus the metal perchlorate in aqueous solution was obtained.

The formation of complexes was carried out by mixing 75 mL (0.133 M) metal perchlorate solution and 50 mL(0.2M) ligand in DMSO solution. The mole ratio of ligand and metal was (1:1). The reaction mixture was refluxed for around 3.0 h at 95 ^{0}C temperature. After 3.0 h the reaction mixture was cooled. There was no immediate precipitation. The pH of the above solution was then raised up to 6.5 using 0.1M NaOH solution which resulted in the precipitation of the semi solid sticky material. This solid product was dissolved in methanol to remove stickiness, then into this solution, ice water was added and immediately precipitates were obtained. The complexes thus obtained were washed well with double distilled water to remove unreacted metal and ligand. All the complexes were dried in an oven at 40^o C to 50^{o}C. The ligand kynurenic acid, its complexes with La(III), Ce(III) and Pr(III) are abbreviated as KYNA, La-KYNA, Ce-KYNA and Pr-KYNA respectively.

Analyses and Physical Measurements: M.P. and TLC (solvent toluene: methanol is 7:3) were taken. TLC indicated single spot confirming complexes formation. Elemental analyses were performed with a Vario-MICRO CUBE C, H, N analyzer. There are two tubes (1) combustion tube 1150 ^{0}C and (2) reduction tube 850 ^{0}C. The gases used were helium and oxygen. The metal content was determined by titration with a solution of standardized disodium salt of EDTA after decomposing the complexes with a mixture of concentrated nitric acid, perchloric acid and sulfuric acid in 5:2:3 mL ratio, respectively [6]. Magnetic susceptibilities were measured by the Gouy's method [7] at room temperature, using Hg $[Co(CNS)_4]$ as calibrant. The IR spectra were recorded on a BRUKER ALPHA FT-IR 400 – 4000 cm^{-1} spectrophotometer. The UV – visible spectra were measured on a UV-1800 Shimadzu (Double beam) spectrophotometer. Thermal measurements were performed using a METTLER TOLEDO STAR^e system TGA/ DSC1(1150^{0}C) thermal analyzer. The mass spectra analyses were performed with a model QDA of Waters and Alliance 2690 analyzer. The results are given in table 1.

IR Spectra: The study of infrared spectral characteristics has proved to be a very useful tool in the structure elucidation and analysis of metal complexes. This is a method that identifies substances by the infrared wavelengths they can absorb[8].

Interpretation of spectra for structure elucidation: The band observed at 3420 cm^{-1} in the ligand are due to O-H stretching. Such strong bands occur at ~ 3413 cm^{-1} in the metal complexes. The frequencies 2944 cm^{-1} 3086cm-1 2975 cm^{-1} and 2914 cm^{-1} in the La-KYNA, Ce-KYNA and Pr-KYNA respectively indicate C-H stretching. The band at 1750 cm^{-1} of the ligand is due to the C=O stretching. In the La-KYNA, Ce-KYNA and Pr-KYNA, it is shifted to 20-25 cm^{-1} lower energy indicating coordination by the oxygen. >C=O group of –COO$^-$ of band loses a large fraction of intensity in Pr-BSPA which indicates the metal coordination with the Kynurenic acid. The frequencies observed at 650-700 cm^{-1} and 450-480 cm^{-1} in the metal Complexes due to (M-N)and (M-O) respectively (Table 2).

Table 1. Physical characterization of KYNA ligand and complexes

Sr. No.	Compound Name & Formula	M.P . (^{0}C)	Rf value *	Molar Cond. Mho /cm	Mole. Weight gm / mol	Uv – vis spectral λmax (nm)	Color of complex	Magn . Sus. (BM)	Elemental Analysis									
									% C		% H		% N		%Cl		% M	
									Cal.	Fou.	Calc.	Fou.	Cal.	Fou.	Cal.	Fou.	Cal.	Fou.
1	KYNA Ligand $[C_{10}H_7NO_3]$	282-283	0.9	1.096	189.17	346.5, 291.5, 259.5	Creamy White	-----	63.43	62.30	2.64	2.36	7.40	7.25	--	---	---	---
2	La-KYNA $[La(C_{10}H_5NO_3)_4]$	>300	0.67	0.436	895.7	347, 291, 260, 234	Creamy White	Dia-magnetic	54.07	58.10	2.27	3.875	6.30	6.55	--	----	15.5	7.8
3	Ce-KYNA $[Ce(C_{10}H_5NO_3)_3]$	>300	0.63	0.27	707.63	346, 291, 257, 226	Creamy White	2.33	51.31	54.13	2.15	3.73	6.10	6.65	----	----	19.9	10.5
4	Pr-KYNA $[Pr(C_{10}H_5NO_3).(H_2O)_3(ClO_4)_2]\ 6H_2O$	>300	0.76	0.214	692.0	333, 246.5, 225.5	light greenish	3.449	17.41	10.38	3.36	3.5	2.03	0.0	10.3	----	20.4	42.7

KYNA = kynurenic acid , Mole. = molecular, Mag. Sus. = magnetic susceptibility, Cond. = conductance,%M carried out by EDTA method, Uv = ultra violet, *Solvent system for TLC = Toluene : Methanol (7:3)

Table 2. IR spectral band (cm^{-1}) of KYNA ligand and its complexes*

Compound	ν(O-H) stre.	N[Ar(C-H)] stre.	N(C=N) stre.	N(C=O) stre.	N(M-N) stre.	N(M-O) stre.	N(M-Cl) stre.	N(C-O-C) stre.	Bending vibrations	Scissoring& Other bending vibrations
KYNA ligand	3420	2944	1591	1633 1658	----	----	----	1245 1265	747-OH out of plane	1365- wagging and twisting
La-KYNA	3413	3084	1471	1766	664	450 469	-----	1267	752- OH out of plane 1209-CH, CH_2 ,OH in plane	1446- CH_2 scissoring and Asymmetric
Ce-KYNA	3413	2975	1446, 1472	1768	625 664	457 468	------	1267	754-OH out of plane 1213-CH, CH_2 ,OH in plane	1446- CH_2 scissoring and Asymmetric
Pr-KYNA	3408	2914 2997	1436, 1489	1636	699	459 479	724	1121	724-OH out of plane	1436- CH_2 scissoring and Asymmetric

***(1)** All the figures are in cm^{-1}

Electronic Spectral study: The kynurenic acid, La-KYNA, Ce-KYNA and Pr-KYNA are analyzed for UV- Visible spectra and magnetic moments. These metals belong to f block elements. This group has a usual characteristic of absence of d-d transition because no space for excited electron is present in the d orbital which is completely filled in these ions. The results indicate diamagnetic nature of the complexes with ligand to metal charge transfer bands [9].The electronic spectra and magnetic moment values are shown table1. In the table 4, the spectral bands are assigned to the transitions and hence presence of coordinated ligand and lanthanide coordination is confirmed. The table 3 gives usual properties of ions.

Magnetic studies: The magnetic moments of the complexes were measured by the Gouy's method. The room temperature magnetic moment of the solid La-KYNA was found to be 0.0 BM. This indicates zero unpaired electrons per La (III) ion in cubic [10] environment. The room temperature magnetic moment of the solid Ce-KYNA was found to be 2.33 BM. This indicates one unpaired electron per Ce (III) ion in probably, square antiprism [10] environment. The room temperature magnetic moment of the solid Pr-KYNA was found to be 3.45 BM. This indicates two unpaired electrons per Pr (III) ion in perhaps, distorted trigonal prism [10] environment. The magnitude of the spin- orbit coupling for a particular ion is usually given in terms of one of two different so called spin – orbit coupling constants, **ζ** (zeta) and **λ**. The former is the one electron spin –orbit coupling constant and useful when comparing the relative magnitudes of spin- orbit coupling for different ions. In practice, for many electron ions, what is measured is a resultant spin-orbit coupling between the resultar spin magnetic moment and the resultant orbital moment. It is this latter spin- orbit coupling constant which is called λ. For ground states the two constants are simply related:

$$\lambda = \pm \quad \zeta /2S$$

Where 'S' is the spin multiplicity of the ion and the plus sign refers to $d^1 – d^4$ ions and the minus sign $d^6 – d^9$. For these latter, it is simplest to think of holes circulating, the holes having the opposite charge to electron. Values for λ (and thence ζ) are obtained for free ions from atomic spectral data and for complex ions from magnetic measurements of the type discussed in the magnetic moment[11].

Table 3. Normal electronic Configuration and Magnetic properties of lanthanide ions

Ion/ Configuration	**Colour of common salts**	**Ground state term**	**Excited state levels of Hypersensitive transition**	**Usual Magnetic moment values (B.M) ***	**Number of unpaired electrons**	**Total orbital angular momentum**
La^{III}/ f^0	Colorless	$^1S_0$	none	Dia magnetic	0	0
Ce^{III}/ f^1	Colorless	$^2F_{5/2}$	none	2.33	1	3
Pr^{III}/ f^2	Yellow-greenish	$^3H_4$	$^3H_5$, $^3F_2$	3.45	2	5

*Reference:-[11]

There is symmetry in the colours of the ions in aqueous solution, a symmetry which seems to be accidental. For the electronic spectra of aqueous Ce^{III} , $4f^1$ and Pr^{III}, $4f^2$, only in the latter are f → f transition evident; this is because for the Ce^{III} the only transition is between the two spin-orbit components of the ^2F term. When a lanthanide ion is at a center of symmetry, in the hydrated perchlorates where the lanthanide is octahedrally surround by water molecules, for intense, the f→f transitions are an order of magnitude weaker than in low symmetry complexes. The fact that the ground state, $^3H_4$, mixes with $^1G_4$ ensures that all of the f→f electronic transitions of an f^2 ion such as praseodymium(III) are of mixed spin character, emphasizing the fact that because of spin-orbit coupling it is not useful to attempt to consider spin on its own.[11]

Table 4. Electronic Spectra of Complexes and Assignment

Complex	**Cm $^{-1}$**	**Assignment**
La- KYNA	28818.8 34364.2 38461.5 42735	Ligand and charge – transfer transitions

Ce- KYNA	28901.7 34364.2 38910.5 44247.7	$^2F_{5/2} \rightarrow {}^2D_{5/2}$ $^2F_{5/2} \rightarrow {}^2D_{3/2}$
Pr- KYNA	30030 40567.95 44345.8	$^3H_4 \rightarrow {}^1D_2$ $^3H_4 \rightarrow {}^3P_0$ $^3H_4 \rightarrow {}^1S_0$ ($^3P_1$)

TGA of Complexes: The result of thermal analyses of complexes is presented in table 5 (Fig 1-4). It has been observed that La and Ce complexes show loss in weight corresponding to no water molecules of crystallization as well as coordination [13].

Table 5. Thermo Gravimetric Analysis of KYNA and its complexes

	% Loss	**Loss of weight(gm) for 1 mole complex**	**water molecules**	**% Loss**	**Loss of weight(gm) for 1 mole complex**	**water molecules**
KYNA ligand	----	-----	-----	----	-----	-----
La-KYNA	0.72	3.07	0	1.3	5.56	0
Ce-KYNA	0.59	2.53	0	0.74	3.17	0
Pr-KYNA	23.85	102.45	6	13.3	57.13	3

RT = Room temperature

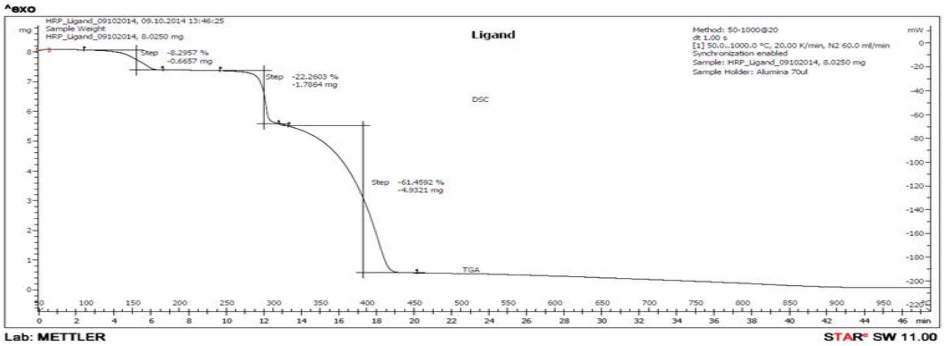


Fig 1. TGA spectrum of KYNA Ligand

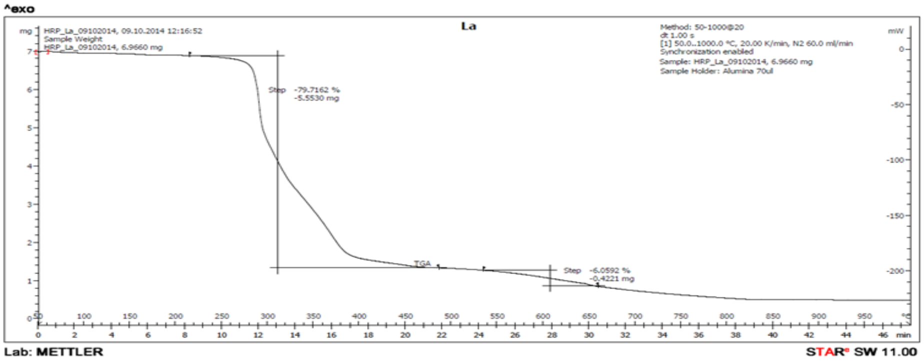


Fig 2. TGA spectrum of La-KYNA

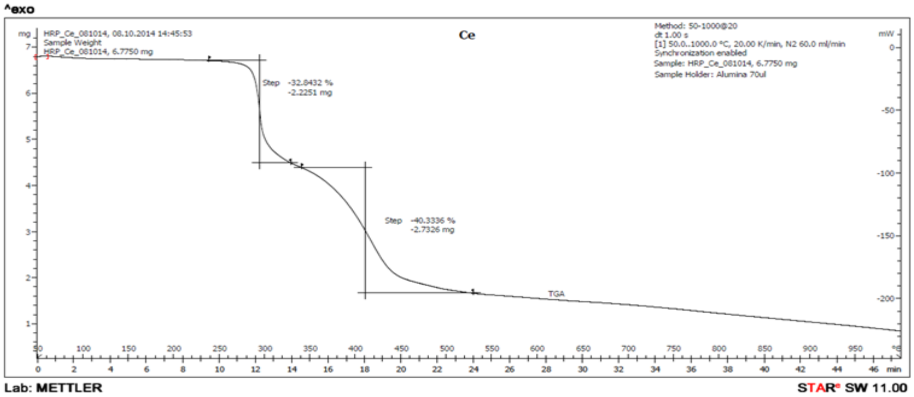


Fig 3 TGA spectrum of Ce-KYNA

It has been observed that at 150 ^{0}C temperature 3.07 gm weight loss per mole of complex occurred by Lanthanum complex which indicates that no H_2O molecule of crystallization with La- KYNA and at the 250 ^{0}C temperature 5.56 g weight loss occurred for one mole complex which indicates that no water molecule coordinated with La- KYNA.

Thermo gravimetric analysis for one mole of Ce-KYNA at 150 ^{0}C temperature the 2.53 g weight loss occurred which indicated that there are no water molecules of crystallization. At 250 ^{0}C temperature 3.17g weight loss occurred by one mole complex which indicates that no coordinated water molecules is present in Ce-KYNA.

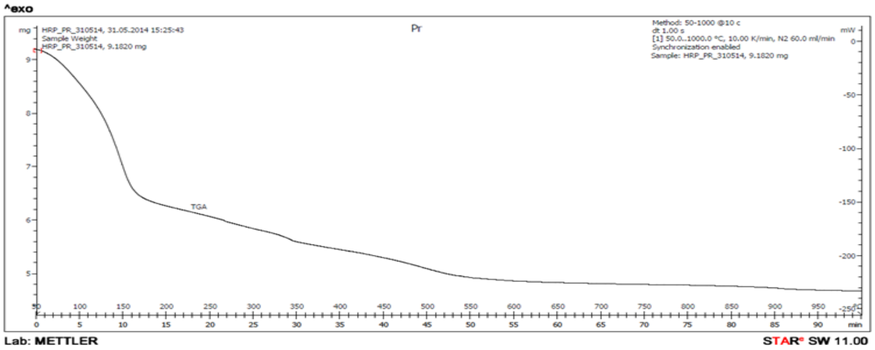


Fig 4. TGA spectrum of Pr-KYNA

In the Pr-KYNA at150 ^{0}C 102.45g weight loss occurred which indicates that 6 water molecules are present as water of crystallization and at 250 ^{0}C temperature 57.13 g weight loss occurred for one mole complex which indicates that three water molecules coordinate with Pr^{3+}metal ion.

Mass Spectroscopy: Mass spectrometry is an analytical tool used for measuring the molecular mass of a sample. For large samples such as biomolecules, molecular masses can be measured to within an accuracy of 0.01% of the total molecular mass of the sample i.e. within a 4 Daltons (Da) or atomic mass units (amu) error for a sample of 40,000 Da. This is sufficient to allow minor mass changes to be detected, e.g. the substitution of one amino acid for another or a post-translational modification. For small organic molecules the molecular mass can be measured to within an accuracy of 5 ppm or less, which is often sufficient to confirm the molecular formula of a compound, and is also a standard requirement for structure elucidation [14].

La-KYNA: Base peak (B.P.) –188.1 (ES-) ; for ES+ 247.2, B. P. +1 peak of second highest intensity 190.1 (ES+) is 11 % of B.P. therefore 10 carbon atoms present in base peak (ES-), peak + 2 are not observed having 3:1 intensity ratio in ES+ as well as ES- spectra hence Cl absent in the molecule (ligand – COOH group) x 3 = 432 amu, Ligand – CO_2 = 146 amu (ES+) 144 amu (ES-).

Ce-KYNA: Base peak (B.P.) = 144.1 (ES+) and 144.0 (ES-) = (ligand – COOH group),In B.P.+1 is 10 % of B.P. therefore 9 carbon atoms present in base peak, peak + 2 are not observed having 3:1 intensity ratio in ES+ as well as ES- spectra hence Cl absent in the molecule.Metal + 2ligand = 518.34 (ES+)

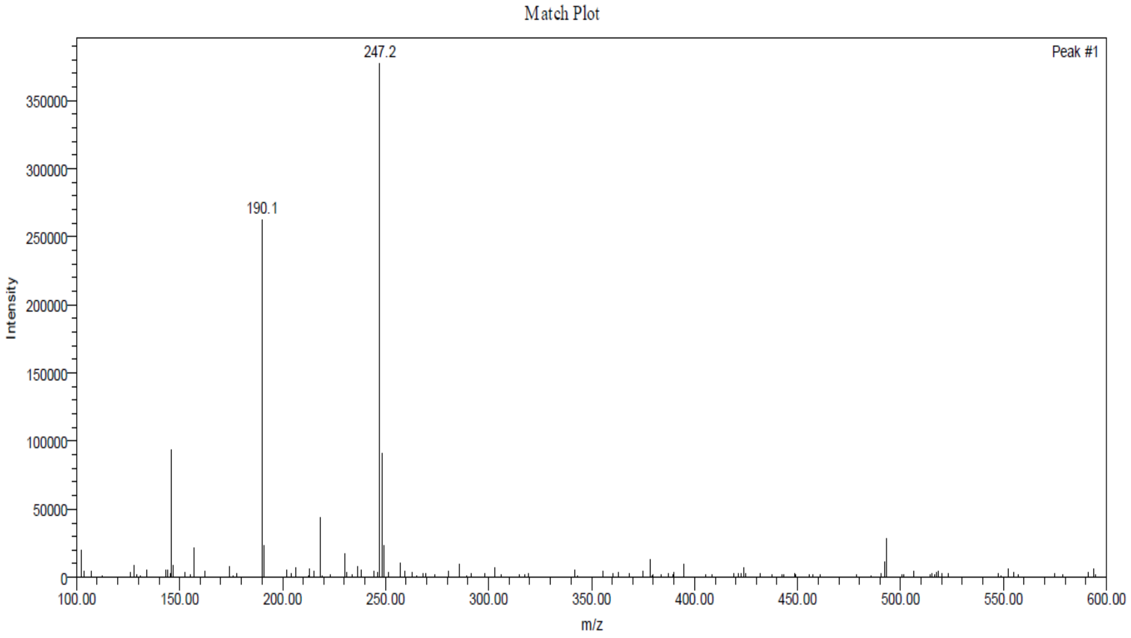
Pr-KYNA: Ligand base peak (B.P.)= 188.1 (ES-) Base Peak for (ES+) = 247 amu, Ligand – COOH group + (ES+) = 146.2, Ligand – COOH group – (ES-) = 143.9, Metal + ligand = 330 (ES- 325, 326 amu). Ligand – O_2 = 157.2 amu (ES+), In B.P.+1 is 10 % of B. therefore 10 carbon atoms present in base peak, B.P., B.P.+ 2, (ratio 9:6:1) in fragment therefore 2 chlorine atoms present, Ligand + Metal + $ClO_4 – C_6H_4$ = 356 amu (ES+)

Intensity values of X, X+2, indicate possibility of Pr- KYNA presence of two chlorine atoms in that fragment consequently the presence of at least two chlorine atoms in the molecule is indicated. Likewise, presence of ten carbons in the base peak indicates presence of minimum ten carbon atoms in the molecule. Instrument did not record molecular peak as all molecular masses are more than 690 amu and spectra had been recorded only upto 600 amu.

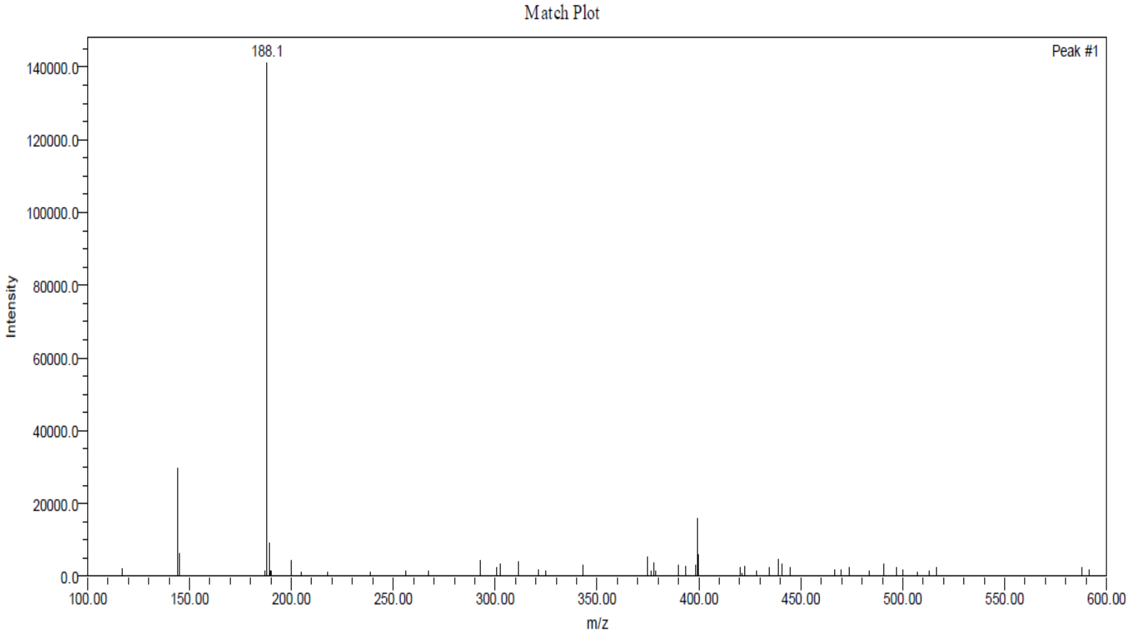
The coordination numbers of lanthanide ions as shown in the proposed structures of La-KYNA, Ce-KYNA and Pr-KYNA are 8, 9 and 8 respectively. The usual coordination numbers of La, Ce, Pr are 8 to 11, 10&12, 6 and12 respectively [10].

Applications: In the present work, two different applications of KYNA complexes have been studied [a] catalysis/ chemical kinetics [b] antimicrobial studies.

Chemical kinetics: Three reactions (i)$K_2S_2O_8$ + KI (ii) $KBrO_3$ + KI and (iii) H_2O_2 + KI were selected. These reactions are usually carried out in neutral or acidic medium. The reactions are such that they proceed with moderate velocity $K= 10^{-2}$ to 10^{-5} per min. The product of all these three reactions is iodine which is titrated with standard aqueous sodium thiosulphate using starch solution as indicator. The rates of all these reactions can easily be measured by simple kinetic methods therefore one of the important applications of coordination compounds, as catalysts is being investigated. In present work, the set up of experiments and measurement of all the second order reactions has been carried out by standard procedures [15]. These reactions were carried out at room temperatures. Solutions of three complexes were prepared in methanol and in the blank sets; equal volume of methanol was added to equate the effect of solvent on the reaction. Catalytic amounts of complexes were added to the reaction systems.

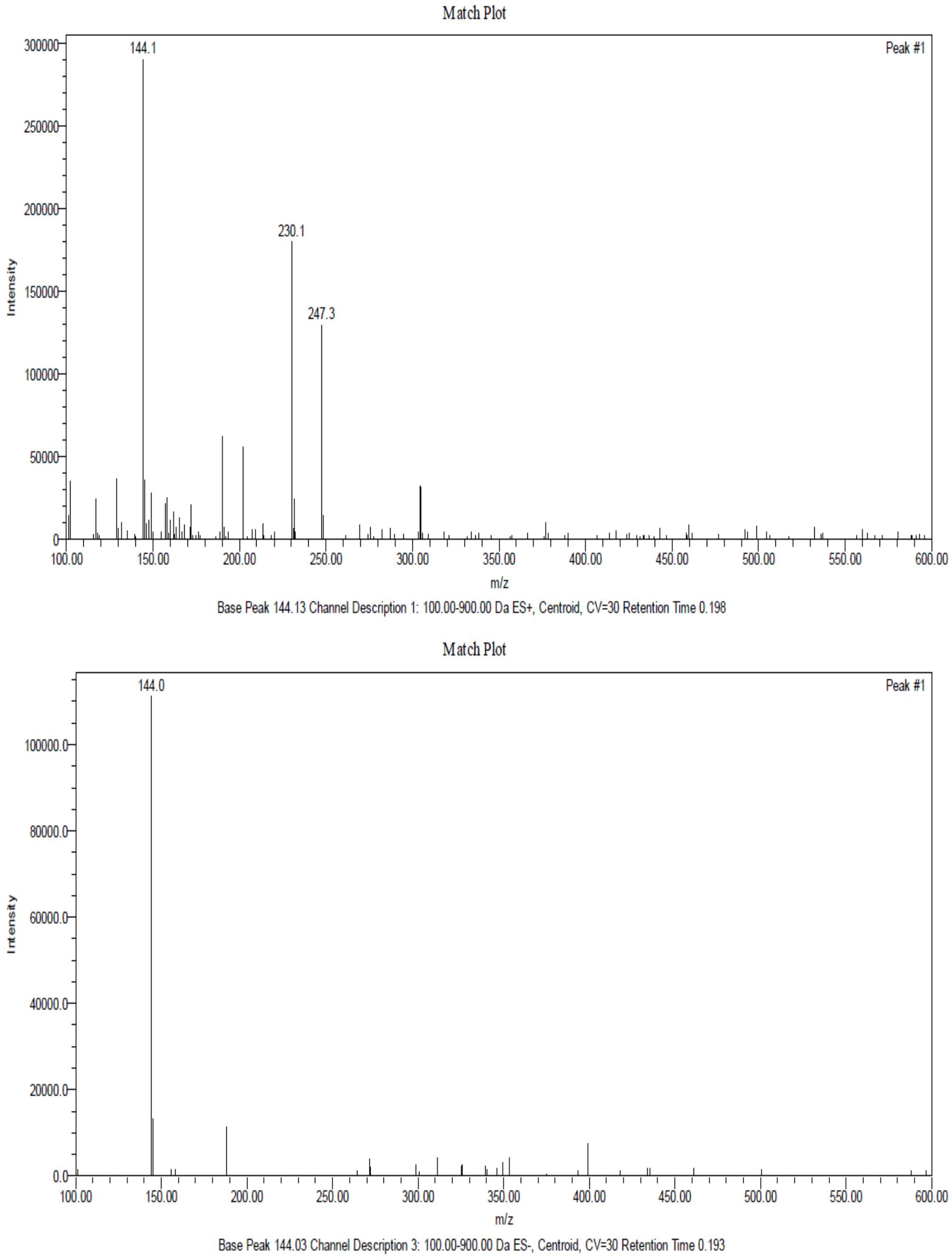


Base Peak 247.24 Channel Description 2: 100.00-900.00 Da ES+, Centroid, CV=10 Retention Time 0.182



Base Peak 188.15 Channel Description 4: 100.00-900.00 Da ES-, Centroid, CV=10 Retention Time 0.198

La-KYNA


Match Plot
Peak #1
144.1
230.1
247.3
Intensity
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250000
200000
150000
100000
50000
0
100.00
150.00
200.00
250.00
300.00
350.00
400.00
450.00
500.00
550.00
600.00
m/z
Base Peak 144.13 Channel Description 1: 100.00-900.00 Da ES+, Centroid, CV=30 Retention Time 0.198
Match Plot
Peak #1
144.0
Intensity
100000.0
80000.0
60000.0
40000.0
20000.0
0.0
100.00
150.00
200.00
250.00
300.00
350.00
400.00
450.00
500.00
550.00
600.00
m/z
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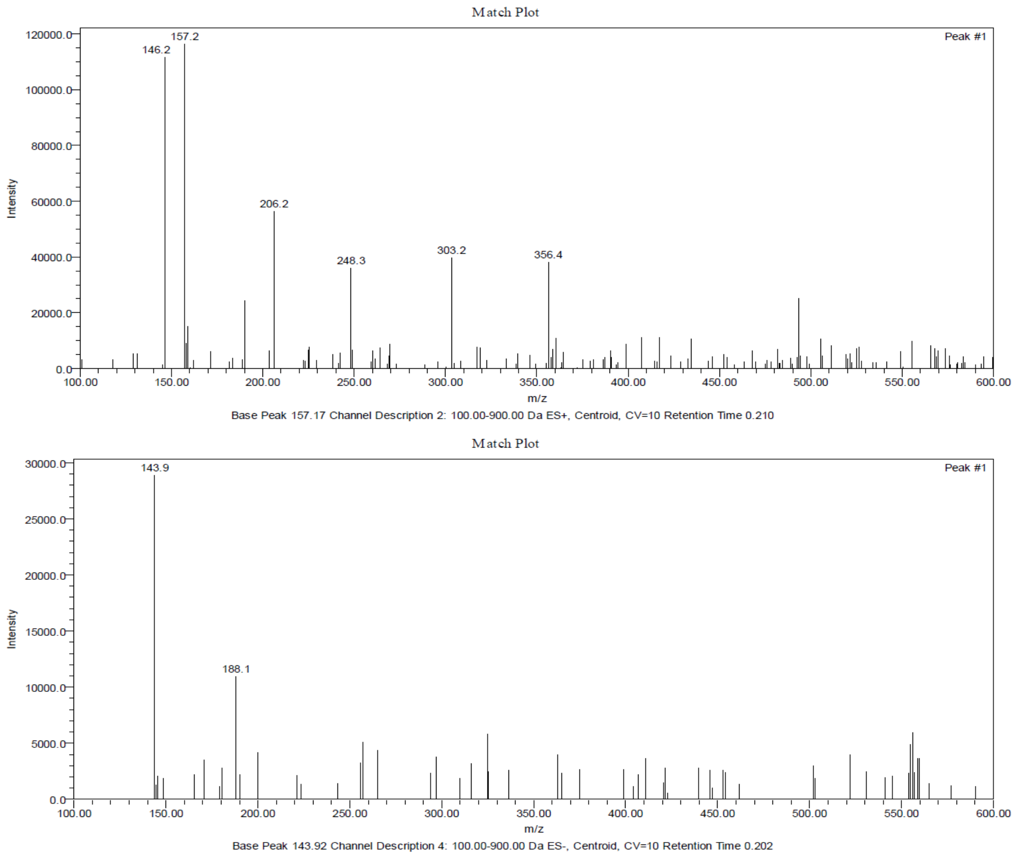
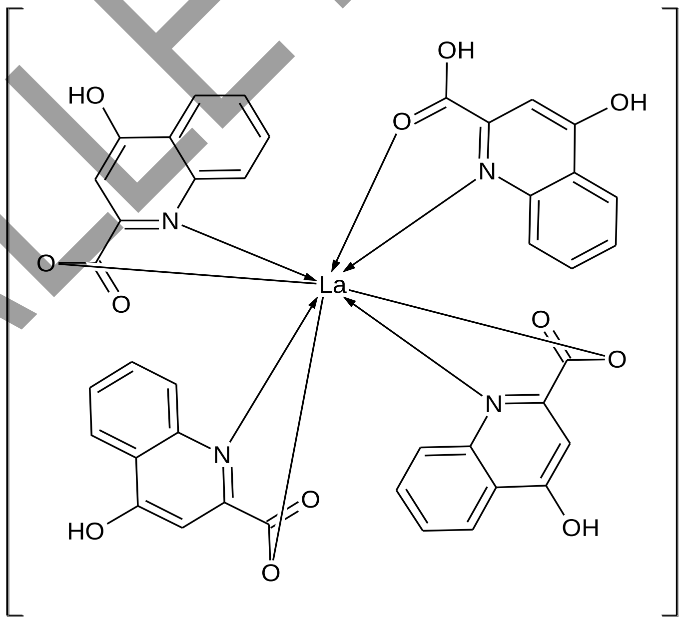
Ce-KYNA

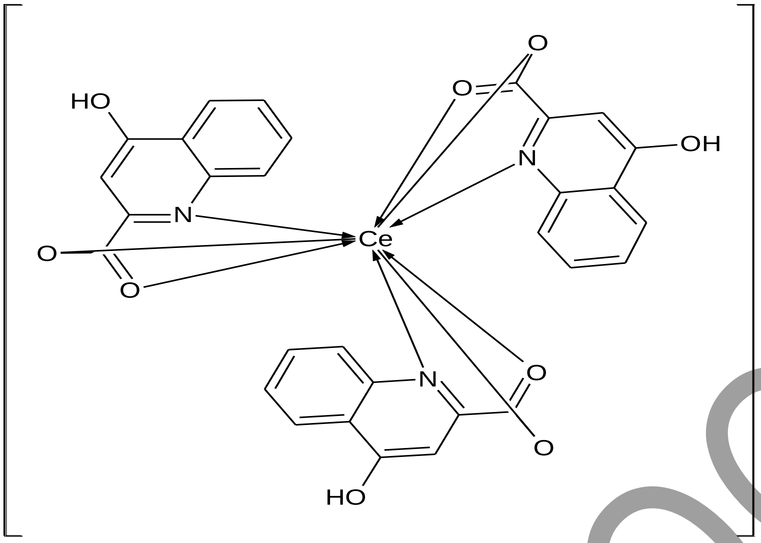


Pr-KYNA

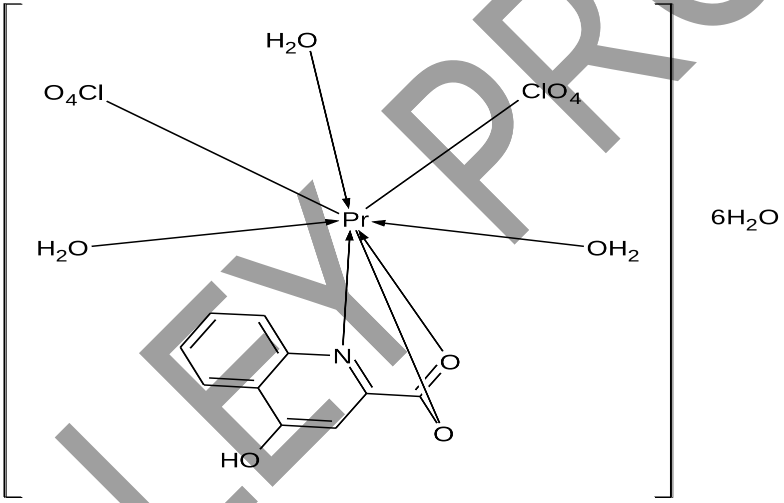
Structures: From the physicochemical analyses data, the most probable structures of three complexes can be represented as below.



La-KYNA structure



Ce- KYNA structure



Pr-KYNA structure

The experimental results are as follows:

Reactions:

(i) Reaction-1

$K_2S_2O_8 + 2KI \longrightarrow 2K_2SO_4 + I_2$

$2Na_2S_2O_3 + I_2 \longrightarrow 2NaI + Na_2S_4O_6$

(ii) Reaction-2

$KBrO_3 + HCl \longrightarrow KCl + HBrO_3$

$I_2 + 2Na_2S_2O_3 \longrightarrow 2NaI + Na_2S_4O_6$

TableA. **Reaction-3**

$H_2O_2 + 2HI \longrightarrow 2H_2O + I_2$

$I_2 + 2Na_2S_2O_3 \longrightarrow 2NaI + Na_2S_4O_6$

Table 6. Reaction kinetics (without catalyst)

Reaction of : $K_2S_2O_8$ + KI + Methanol
Concentration : (0.0227M) (0.0227M) --
Volume : 50mL 50mL 10mL (t_∞ =113.5 mL)

Time t (min.)	Burette reading x (ml)	k = 1/at * x/(a-x) (lit.mol^{-1} min^{-1})
5	**3.2**	**4.20 X 10^{-5}**
10	**3.7**	**2.44 X 10^{-5}**
15	**4.1**	**1.80 X 10^{-5}**
20	**4.6**	**1.52 X 10^{-5}**
25	**5.0**	**1.33 X 10^{-5}**
30	**5.5**	**1.22 X 10^{-5}**

average k = 2.085 x 10^{-5}
a=b=initial concentrations of reactants =113.5 ml (in terms of hypo solution)

Table7. Reaction kinetics table without catalyst

Reaction of : $KBrO_3$ + KI + HCl + Methanol
Concentration : (0.0096M) (0.0096M) --
Volume : 25ml 25ml 10ml (t_∞ =25ml)

Time t (min.)	Burette reading x (ml)	k= 1/at * x/(a-x) (lit.mol^{-1} min^{-1})
5	**6.9**	**3.04 X 10^{-3}**
10	**7.4**	**1.68 X 10^{-3}**
15	**7.7**	**1.18 X 10^{-3}**
20	**8.6**	**1.04 X 10^{-3}**
25	**9.0**	**0.9 X 10^{-3}**
30	**9.5**	**0.81 X 10^{-3}**

average k = 1.44 X 10^{-3}
a=b=initial concentrations of reactants=25ml

Table 8. Reaction kinetics table without catalyst

Reaction of : H_2O_2 + KI + H_2SO_4 + Methanol
Concentration : (0.0091M) (0.0091M) --
Volume : 10ml 10ml 10ml (t_∞ =50ml)

Time t (min.)	Burette reading x (ml)	k = 1/at * x/(a-x) (lit.mol^{-1} min^{-1})
5	**1.2**	**9.8 X 10^{-5}**
10	**1.7**	**7.03 X 10^{-5}**
15	**2.3**	**6.42 X 10^{-5}**
20	**2.9**	**6.15 X 10^{-5}**

25	**3.4**	**5.83×10^{-5}**
30	**3.8**	**5.48×10^{-5}**

average k = 6.78×10^{-5}
a=b=initial concentrations of reactants =50 ml

Table 9. Common Reaction Kinetics- experimental Set ups with Catalysts

Reactions (I)	**$K_2S_2O_8$ (0.0227M) + KI (0.0227M) + M-KYNA in 10 ml methanol (1 % MW)**	**t∞ = 113.5 ml a=b=113.5ml**
Reactions (II)	**$KBrO_3$ (0.0091M) + HI (0.0091M) + M-KYNA in 10 ml methanol (1 % MW)**	**t∞ = 25 ml a=b=25 ml**
Reactions (III)	**H_2O_2 (0.0091M) + HI (0.0091M) + M-KYNA in 10 ml methanol (1 % MW)**	**t∞ = 50 ml a=b=25 ml**

M = La^{3+}, Ce^{3+}, and Pr^{3+} one by one.

The results of all the twelve kinetic – experiments are shown in table 10

Table 10. Kinetic experiments with complexes of lanthanide metal ions.

reaction rate constant for the second order reaction, 1% complex = 1 % molecular weight of the complex

1 % MW of La-KYNA = 0.0896 gm La-KYNA ≡ 0.0435 % of mole of $K_2S_2O_8$ ≡ 0.104 % of mole of $KBrO_3$ ≡ 0.11 % of mole of H_2O_2

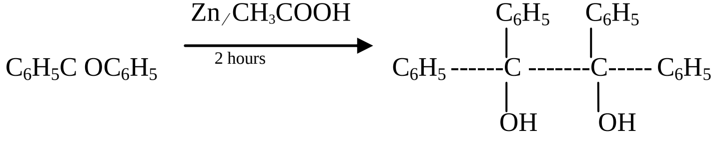
Reactions	**K without Complexes**	**k with La-KYNA (1 %) MW**	**k with Ce-KYNA (1 %) MW**	**k with Pr-KYNA (1 %) MW**	**% Increase reaction rate at T = 300 K La-KYNA**	**% Increase reaction rate at T = 300 K Ce-KYNA**	**% Increase reaction rate at T = 300 K Pr-KYNA**
$K_2S_2O_8$ + KI	**2.085×10^{-5}**	**3.41×10^{-5}**	**3.86×10^{-5}**	**3.59×10^{-5}**	**64 %**	**85 %**	**72 %**
$KBrO_3$ + HI	**1.44×10^{-3}**	**9.35×10^{-3}**	**6.68×10^{-2}**	**9.63×10^{-3}**	**549 %**	**364%**	**569 %**
H_2O_2 + HI	**6.78×10^{-5}**	**3.64×10^{-4}**	**4.11×10^{-4}**	**4.38×10^{-4}**	**437 %**	**506 %**	**546 %**

1 % MW of Ce-KYNA= 0.0708 gm Ce-KYNA ≡ 0.0435 % of mole of $K_2S_2O_8$≡ 0.104 % of mole of $KBrO_3$≡ 0.11 % of mole of H_2O_2

1 % MW of Pr-KYNA = 0.0692 gm Pr-KYNA ≡ 0.0435% of mole of $K_2S_2O_8$ ≡ 0.104 % of mole of $KBrO_3$ ≡ 0.11 % of mole of H_2O_2

Catalysis of Organic Reaction: A mixture of benzophenone (7.5 g, 0.041 mol) zinc dust (4 g) glacial acetic acid (110 mL) and water (22 mL) is refluxed for 2 h. The solution is filtered (if necessary) and cooled. The separated benzpinacol is filtered and crystalline from glacial acetic acid. The yield was found to be 4.5 g (30%).

The product melting point was 188-189 ^{0}C [16].



$$C_6H_5COC_6H_5 \xrightarrow[\text{2 hours}]{Zn/CH_3COOH} C_6H_5\text{------}\underset{OH}{\overset{C_6H_5}{C}}\text{-------}\underset{OH}{\overset{C_6H_5}{C}}\text{-----}C_6H_5$$

Benzophenone Benzpinacol

Table 11. Yield of C-C coupling reaction without catalyst for different reaction times

Sr. No	Temperature	% yield without catalyst (for 4 hours reaction)	% yield without catalyst (for 3 hours reaction)	% yield without catalyst (for 2 hours reaction)
1	368 K	64.44%	55.55%	30.00 %

Table 12. Percentage yield with catalyst metal complexes for 2 h duration
Temperature = 368 K

Complexes	For 1 % catalyst, yield obtained	For 5 % catalyst, yield obtained	For 10 % catalyst, yield obtained
La-KYNA	**27%**	**32%**	**53%**
Ce-KYNA	**28%**	**36%**	**64%**
Pr-KYNA	**23%**	**38%**	**67%**

1% MW of complex = 0.0243 % of mole of benzophenone
5% MW of complex = 0.121 % of mole of benzophenone
10% MW of complex = 0.243 % of mole of benzophenone

RESULTS AND DISCUSSION

It was apparent that rates of all the redox reactions selected were increased by the addition of catalytic amounts of individual complexes. An increase of 63 % to 85% was possible for reaction (i) $K_2S_2O_8$ + KI and for reactions (ii) $KBrO_3$ + KI + HI and (iii) H_2O_2 + HI, a profound increase from 360% to 568% was possible. Thus a significant increase in reaction rates could be achieved with help of two complexes and hence application of these complexes as catalyst is certainly of immense significance.

The preparation of benzpinacol from benzophenone is an example of reductive coupling. The carbonyl group is reduced with zinc dust. Simultaneously, two units couple to form a new carbon-carbon bond in the center of the product molecule. Because this reaction is an example of two processes (reduction and new C-C bond formation) therefore it was chosen for possible application of lanthanide complexes as homogeneous catalysts. [16] The reaction was carried out with identical conditions for added catalysts and without catalyst. La-KYNA, Ce-KYNA and Pr-KYNA acted as homogeneous catalyst for the above reaction. It was observed that addition of all the complexes in catalytic amounts drastically reduced the time requirement and increased the reaction yield. The highest increase was 67% and the lowest increase was 23%. Order of effectiveness as catalyst found was Pr-KYNA > Ce-KYNA > La-KYNA.

Antibacterial activity: This part deals with the in-vitro screening of newly prepared compounds for antibacterial activity. The species *S.aureus*, *E.coli*, *S.Pyogenes* and *P.Aeruginosa* have been taken for the antibacterial activities. Agar-cup method was employed for the in-vitro screening for antibacterial activity.[17] The results of the compounds synthesized for antibacterial screening are mentioned in following table.13.

Table13. Antibacterial activity of standard drugs

STANDARD DRUGS				
MINIMUM INHIBITION CONCENTRATION (µg/ml)				
DRUG	***E.coli***	***P.aeruginosa***	***S.aureus***	***S.pyogenes***
	MTCC 443	**MTCC 1688**	**MTCC 96**	**MTCC 442**
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

Table14. Antibacterial activity of kynurenic acid and its complexes

ANTIBACTERIAL ACTIVITY					
MINIMUM INHIBITION CONCENTRATION (µg/ml)					
SR	**CODE**	***E.coli***	***P.aeruginosa***	***S.aureus***	***S.pyogenes***
NO	**NO**	**MTCC 443**	**MTCC 1688**	**MTCC 96**	**MTCC 442**
1	KYNA ligand	100	250	250	200
2	La-KYNA	100	200	250	200
3	Ce-KYNA	250	250	500	250
4	Pr-KYNA	200	100	500	500

Comparison of antimicrobial activity of synthesized compounds with that of standard antimicrobial drugs reveals that the complexes show moderate to good activity against all four bacterial strains, however by and large lower than the standard.

Antifungal activity: This part deals with the in-vitro screening of newly prepared complexes for antibacterial activity. The species *C. albicans,A. niger*, *A. clavatus* have been taken for the antifungal activities. Agar-cup method was used for the in-vitro screening for antifungal activity. [18] The results of the compounds synthesized and taken for antifungal screening are mentioned in as under table 15.

Table15. Antifungal activity of standard drugs

MINIMAL INHIBITION CONCENTRATION (µg/ml)			
DRUGS	***C.albicans***	***A.niger***	***A.clavatus***
	MTCC 227	**MTCC 282**	**MTCC 1323**
NYSTATIN	100	100	100
GRESEOFULVIN	500	100	100

Table:- 16 Antifungal activity of kynurenic acid and its complexes

ANTIFUNGAL ACTIVITY TABLE				
MINIMAL FUNGICIDAL CONCENTRATION (µg/ml)				
SR	**CODE**	***C.albicans***	***A.niger***	***A.clavatus***
NO	**NO**	**MTCC 227**	**MTCC 282**	**MTCC 1323**

1	KYNA ligand	1000	500	500
2	La-KYNA	500	1000	1000
3	Ce-KYNA	500	1000	1000
4	Pr-KYNA	1000	500	500

Comparison of antimicrobial activity of complexes with that of standard antimicrobial drugs reveals that the synthesized complexes show moderate to good activity against all three fungal strains; however they are in no way better for the purpose in comparison with standard.

CONCLUSIONS

Kynurenic acid is an important biological molecule with important physiological functions. In order to peep into its biological role and also to understand its complexing tendency and to explore some biochemical properties of its complexes, in the present work, three complexes of kynurenic acid with lanthanide ions were prepared, characterized for structure and studied for catalytic as well as antimicrobial activities. These results were encouraging as this bio active kynurenic acid molecule has good tendency of complex formation, as well as excellent catalysis and has moderate antibacterial activities. At many places, they were found to be excellent catalysts that can enhance reaction rates for selected redox and C-C coupling type organic chemical reactions.

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AUTHORS’ ADDRESSES

1. **Haresh R. Patel**
   Smt. S.S.Patel Nootan Science and Commerce College,
   Visnagar, Gujarat, India
   Email – hareshpatel6900@yahoo.com
2. **H.D. Chaudhari**
   Adarsh Science College,
   Radhanpur, Gujarat, India
3. **J. J. Vora**
   Department of Chemistry,
   Hemchandracharya North Gujarat University,
   Patan, Gujarat, India
   Email- jabali_vora@hotmail.com