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Synthesis and biochemically methods of some lanthanide complexes with Kynurenic acid

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Abstract:- *The compound of lanthanide ions with complexing or chelating 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 lanthanides perchlorates and attempt has been made to synthesize solid kynurenic acid complexes. These complexes are subjected to U.V visible spectroscopy, IR spectroscopy, TGA analysis, Mass Spectroscopy, Elemental analysis and antimicrobial activity of these compounds has been evaluated by standard methods and attempts have been made to correlate structural characteristic with properties of these complexes.*

Keyword:- *Spectroscopic characterization, lanthanide complexes, TGA analysis, mass spectroscopy, antimicrobial activity, elemental analysis*

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I. Introduction:-

The great amount of research work has been done on metal complexes. These constitute ordinary complexes, complexes and mixed ligand complexes[2]. There are large number of chelating and complexing agents known. The donor atoms which undergo combination with metals are restricted to the non metallic elements of group V and VI, of these N, O, and S are the common examples. During coordination, bond formation occurs between the metal ion and the ligand. In the formation of complexes one of these atoms, normally the ligand or the atom functions as an electron pair donor(Lewis base) and metal ion as electron pair accepter (Lewis acid).

The formation of complexes also depends on the relative position of the groups which are present in organic compounds or drug. When a group like –COOH, -OH, or $–SO_3H$ is suitably placed with groups like $–NH_2$, -OH, =S,>C=O, =N- the latter are found to coordinate with metal ion which is linked through a primary valency.[2]

II. Method And Materials:

Analytical grade chemicals were used throughout the course of experimental work. Spetroscopic grade solvents were employed for recording the spectra. Conductivity water was used throughout the work. Conductivity water was redistilled over alkaline potassium permanganate. The pH of this water was found to be ~ 6.9. This water was used for preparing solutions of metal perchlorates and reagents. Nd (III) perchlorate, Sm (III) perchlorate and Gd(III) perchlorate in DMSO solvent were prepared.The compound kynurenic acid was used as a ligand. It was obtained from Sigma and its purity was checked by noting its melting point and spectra. All metal carbonates used were also A.R. grade.[2]

Preparation of complexes:-

The formation of complexes was carried out by mixing 50 ml 0.2M metal perchlorate in DMSO solution and 75 ml 0.2M ligand in DMSO solution. The mole ratio of ligand and metal was (1:1)[1]

The reaction mixture was refluxed for 2.5 to 3.0 hours at 95^0 C temperature. After 3.0 hours 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 sodium hydroxide solution which resulted in the precipitation of the semi solid sticky material. Then, this solid product was dissolved in methanol to remove stickiness. The complex thus obtained was washed well with double distilled water to remove unreacted metal and ligand. All the complexes were dried in oven at 40^o C to 50^oC.[1]

Table :- 1 Abbreviations for the present purpose

Sr. No.	Chelate or Ligand	Formula	Brief name
1	Ligand Kynurenic acid	$[C_{10}H_7NO_3]$	KYNA
2	Nd- Kynurenic acid	$[Nd(C_{10}H_5NO_3)(H_2O)_2(ClO_4)].3H_2O$	Nd- KYNA
3	Sm- Kynurenic acid	$[Sm(C_{10}H_5NO_3)(H_2O)_2(ClO_4)].3H_2O$	Sm- KYNA
4	Gd- Kynurenic acid	$[Gd(C_{10}H_5NO_3)_3.(H_2O)]$	Gd- KYNA

Analyses and physical measurements:

M.P. and TLC weretaken. TLC indicated single spot confirming chelate formation. Elemental analyses were performed with a Vario-MICRO CUBE C, H, N analyzer. There are two tube (1) combution tube 1150 ^{0}C and (2) reduction tube 850 ^{0}C. The gas used helium and oxygen. The metal content was determined by titration with a solution of standardized disodium salt of EDTA[2].Magnetic susceptibilities were measured by the Gouy's method[5], 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 water and Alliance 2690 analyzer.[1]

Table: –2 Analytical Data and Some Physical Properties of the Ligand and Metal Chelates.

Sr. No.	Compound Name	M.P (°C)	Rf value	Molar Cond. mho cm^{-1}	Mole. weight gm mol^{-1}	Uv- vis spectra	Color	Magn. Sus. (BM)	Elemental Analysis							
									% C		% H		% N		% M	
									Cal.	Fou.	Calc.	Fou.	Cal.	Fou.	Cal.	Fou.
1	KYNA ligand	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	Nd-KYNA	>300	0.75	0.218	520.91	345.5, 331, 288.50, 246, 228	Brown black	3.32	23.03	21.43	3.00	3.40	2.68	1.45	27.69	36.04
3	Sm-KYNA	>300	0.84	0.22	473.03	332, 246.5, 229	Light brown yellow	1.779	22.76	19.09	3.01	3.24	2.65	1.12	28.53	41.56
4	Gd- KYNA	>300	0.71	0.23	736.76	345.5, 291, 255, 204	colourless	7.57	48.86	59.82	2.33	4.04	6.00	9.21	21.34	6.89

KYNA = Kynurenic acid , M.P = Melting point , Mole = Molecular , Magn. Sus. = Magnetic Susceptibility[3]
Cal. = calculated, Fou. = found, %M carried out by EDTA and TGA method.

Infrared Spectroscopy:-

The literature survey shows that there are 3n degrees of freedom for a molecule consisting of n atoms, in this, there are six rotational and translational motions. So, vibrational freedom has 3n-6 degree and if the molecule is linear it has 3n-5 degrees. Vibrational modes are often given the descriptive names, like stretching, bending, scissoring, rocking and twisting [2,6-7].

The band observed at 3420 cm^{-1} in the ligand are due to –OH 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 Nd-KYNA, Sm-KYNA and Gd-KYNA respectively indicate –CH stretching. The band at 1750 cm^{-1} of the ligand is due to the C=O stretching. In Nd-KYNA, Sm-KYNA and Gd-KYNA, it is shifted to 20-25 cm^{-1} lower energy indicating coordination by the oxygen. >C=O group of –COOH band loses a large fraction of intensity in Gd-KYNA which indicates the metal coordination with the KYNA. The frequencies observed at 650-700 cm^{-1} and 450-480 cm^{-1} in the metal chelates of (M-N) and (M-O) respectively indicates in IR spectra[3].

Table :- 3 infrared spectra

Compound	ν(O-H) stre.	ν[Ar(C-H)] stre.	ν(C=N) stre.	ν(C=O) stre.	ν(M-N) stre.	ν(M-O) stre.	ν(M-X) stre.	ν(C-O-C) stre.
KYNA Ligand	**3420**	**1070 1118**	**1591**	**1633 1658**	**-----**	**-----**	**------**	**1245 1265**
Nd-KYNA	**3422**	**1018 1088 1119 1143**	**1510 1600**	**1627**	**626**	**451 469 482**	**546**	**1245**
Sm-KYNA	**3409**	**1018 1088**	**1405**	**1599**	**627**	**451 457 478**	**494**	**1245**
Gd-KYNA	**3414**	**1118 1140**	**1329 1445 1471**	**1606 1735**	**636 664**	**457 472 519**	**519 750**	**1267**

X = Halogen , stre. = stretching

Infrared Spectroscopy of the Metal Chelates and ligand (cm^{-1})

Figure-1 Infrared Spectrum of KYNA Ligand

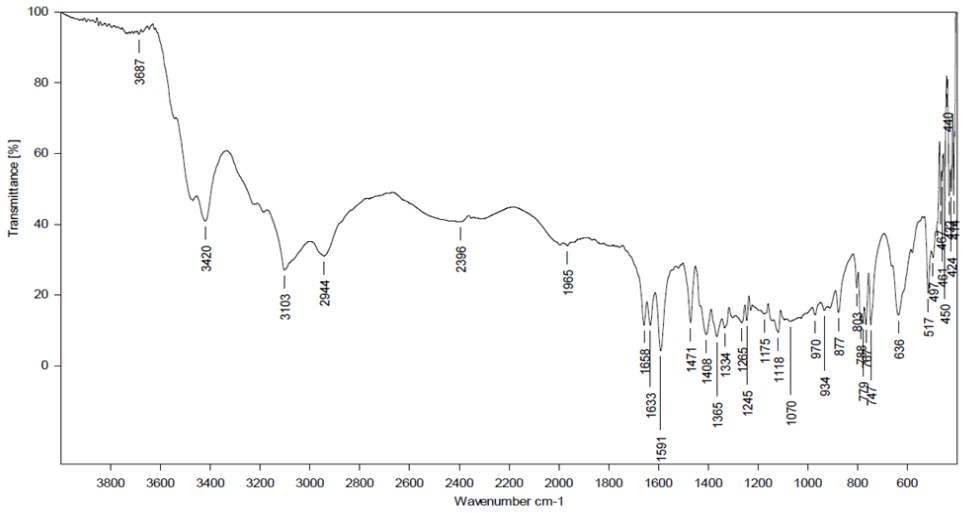


Figure-2 Infrared Spectrum of Nd-KYNA

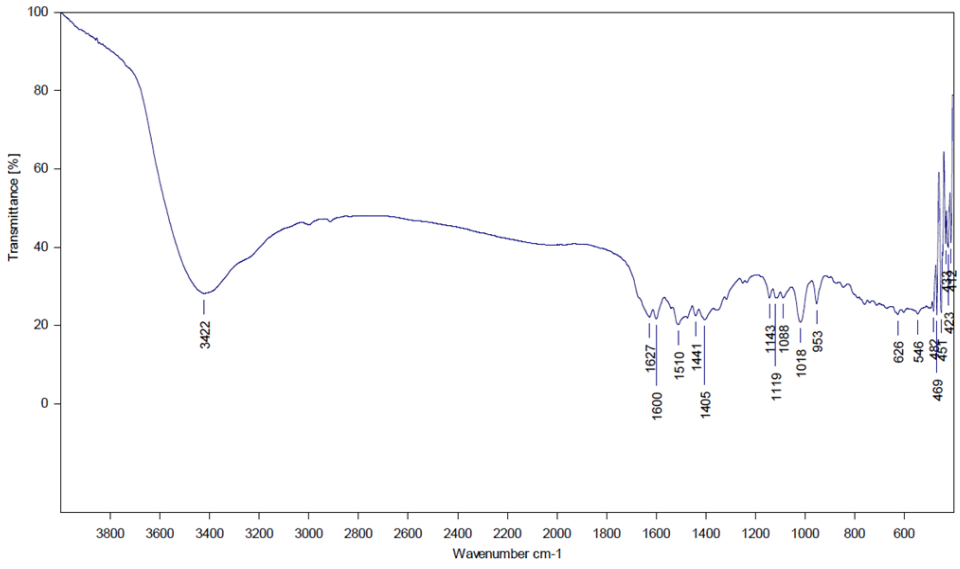


Figure-3 Infrared Spectrum of Sm-KYNA

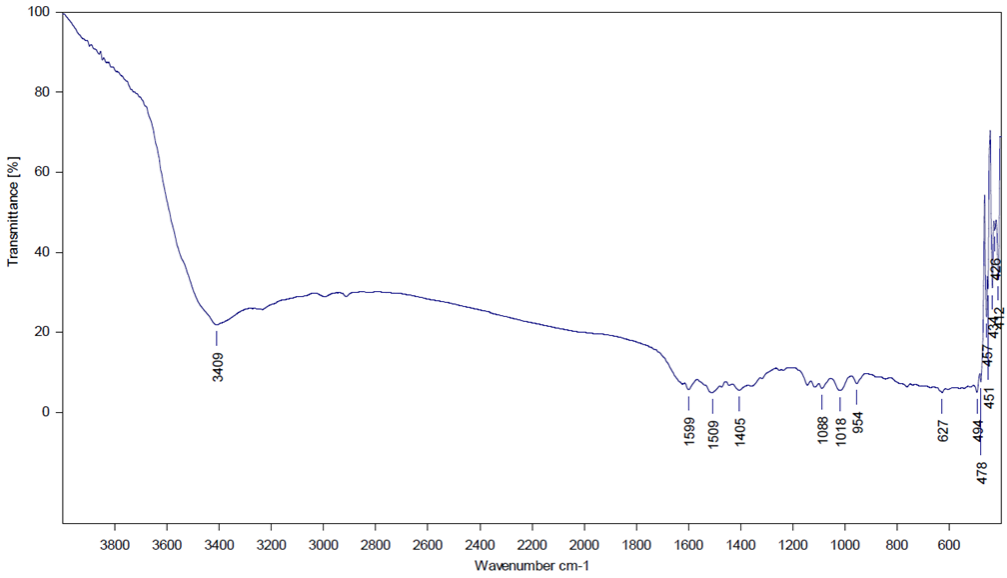
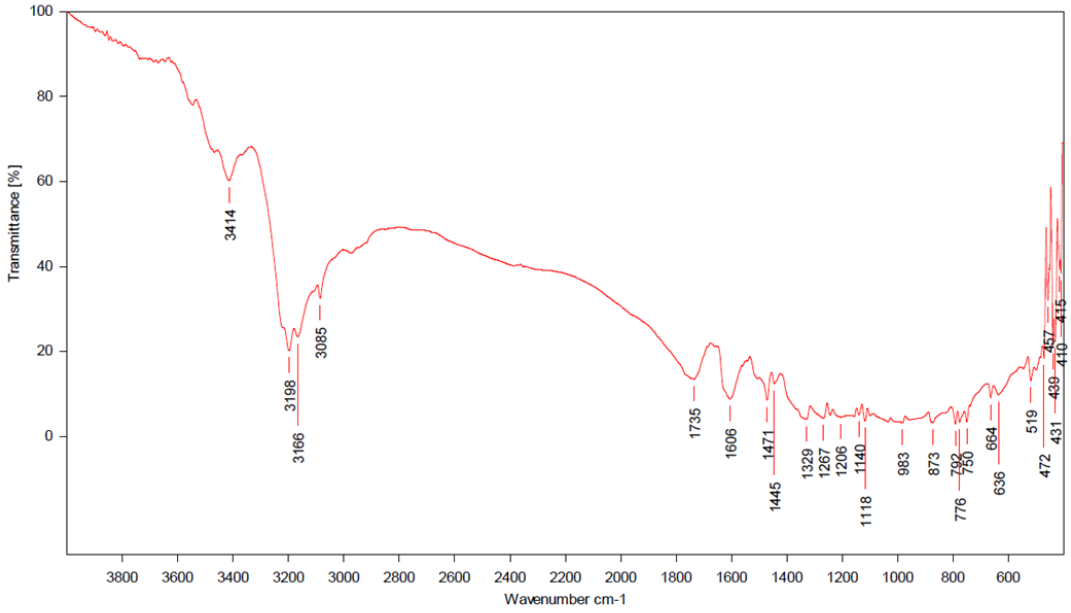


Figure-4 Infrared Spectrum of Gd-KYNA



Mass Spectroscopy:-

Nd-KYNA

Probable molecular peak – 290 (M+L – COOH group),,Base peak - 303.2 (ES+), 302 (ES-)

M+1 = 11.25% ,,M+ 2 peak is observed therefore Cl atom is present in molecule peak = 264 (ES+) , 321(ES-), Ligand – COOH group + H peak = 146.1 (ES+), Metal peak = 144 (ES+ , ES-) , Ligand – O_2 + 1 peak = 159 (ES+), Ligand + Metal –COOH – Cl atom – 1 peak = 321.5 (ES-), Ligand + 2H_2O atom – 1 peak = 222.8

Sm-KYNA

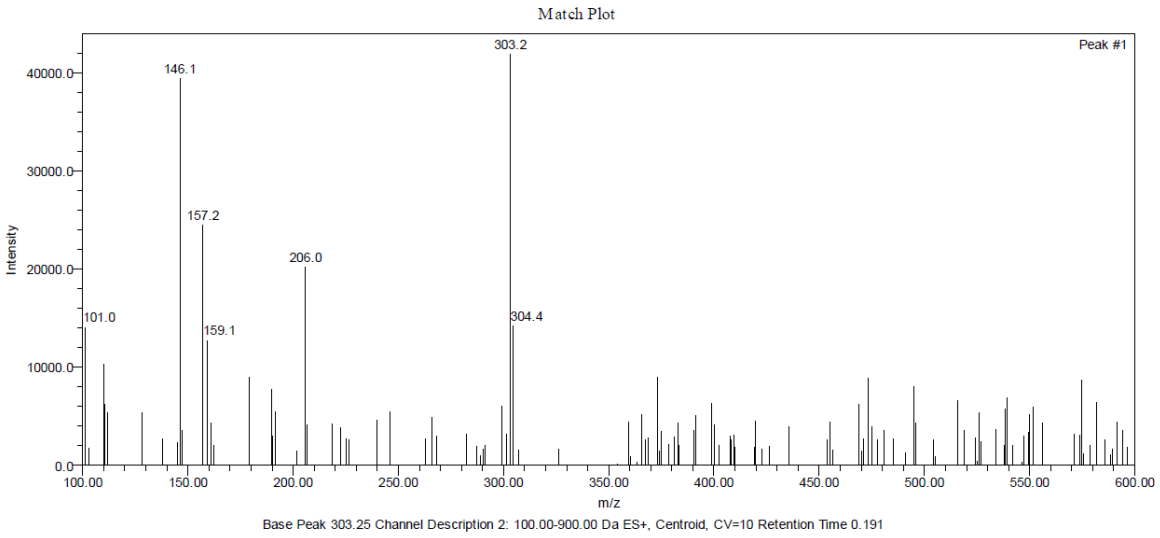
Probable molecular peak – 296 (M+L – COOH group), Base peak - 247.3 (ES+), 549.8 (ES-)

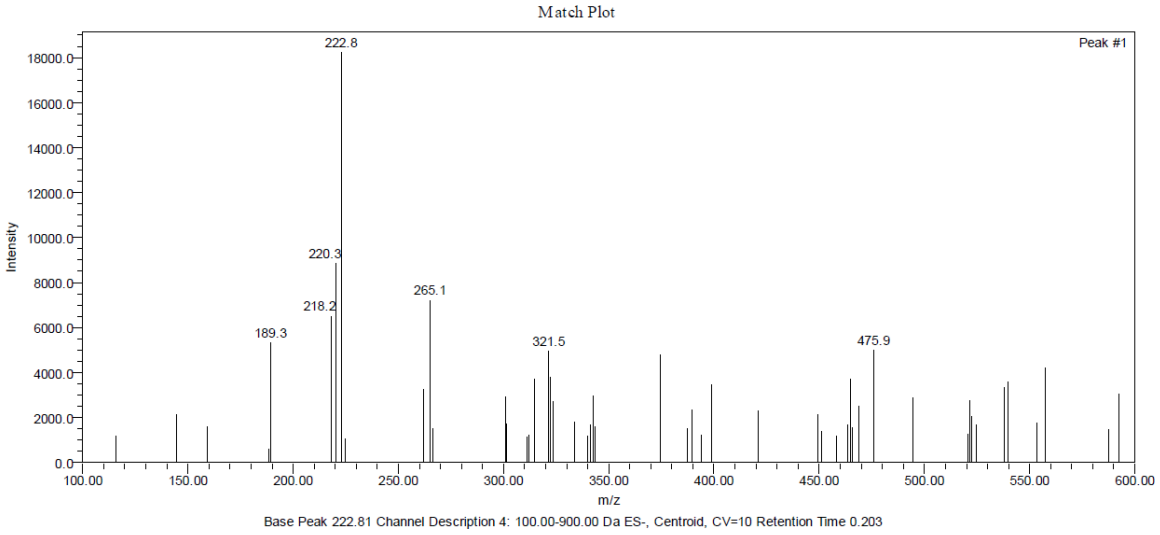
M+1 = 8.01% = (Ligand –COOH group) , M+ 2 peak is observed therefore Cl atom is present in molecule peak = 200 (ES-), Ligand –COOH group peak = 146.1 (ES+), Metal +1 peak = 157 (ES+), Ligand –COOH group -1 peak = 144.3 (ES-)

Gd-KYNA

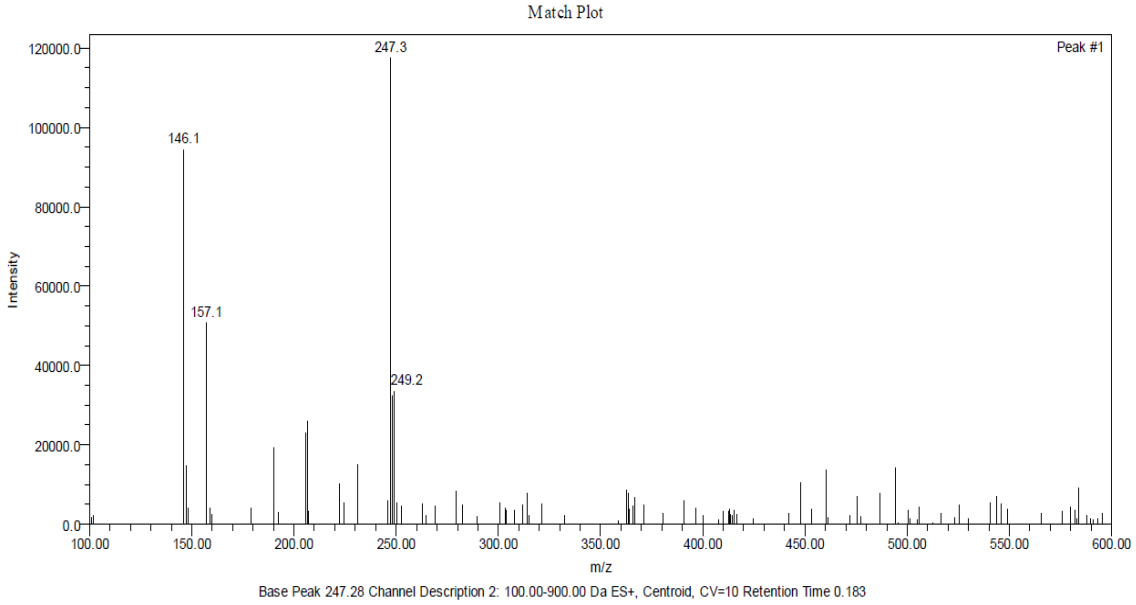
Probable molecular peak – 344 (M+L) (ES+), Base peak - 144.1 (ES+), 144.0 (ES-), M+1 = 8.01% = (Ligand –COOH group), M+ 2 peak are not observed therefore Cl, Br and S atom are not present in molecule., Metal peak = 157 (ES+, ES-), Ligand – O atom – C atom +1 peak = 162.2 (ES+)

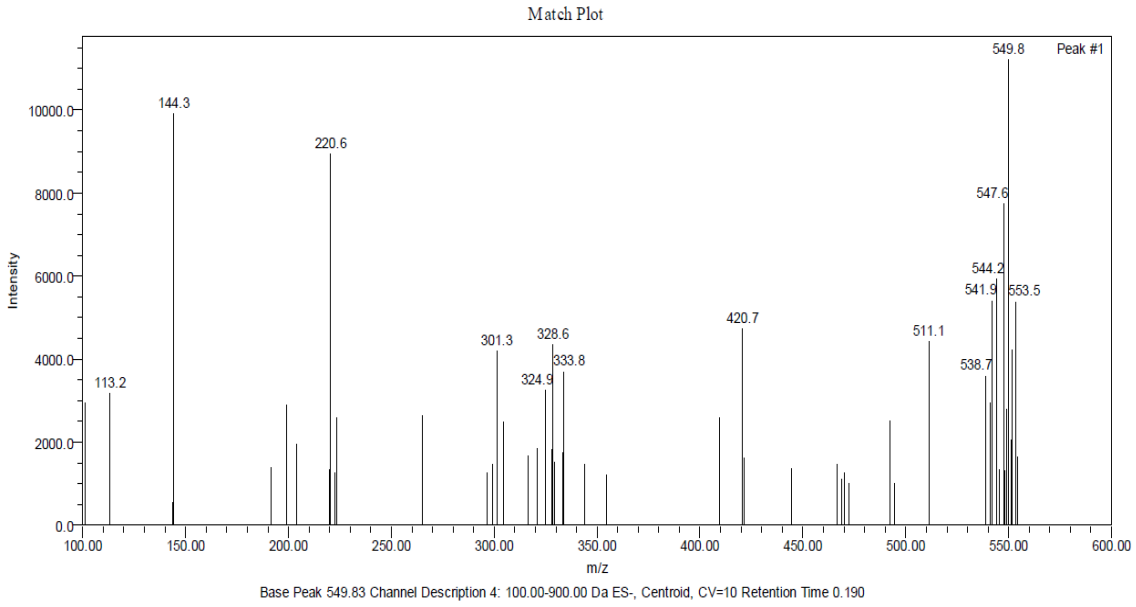
Mass spectrum of the metal chelate
Nd-KYNA



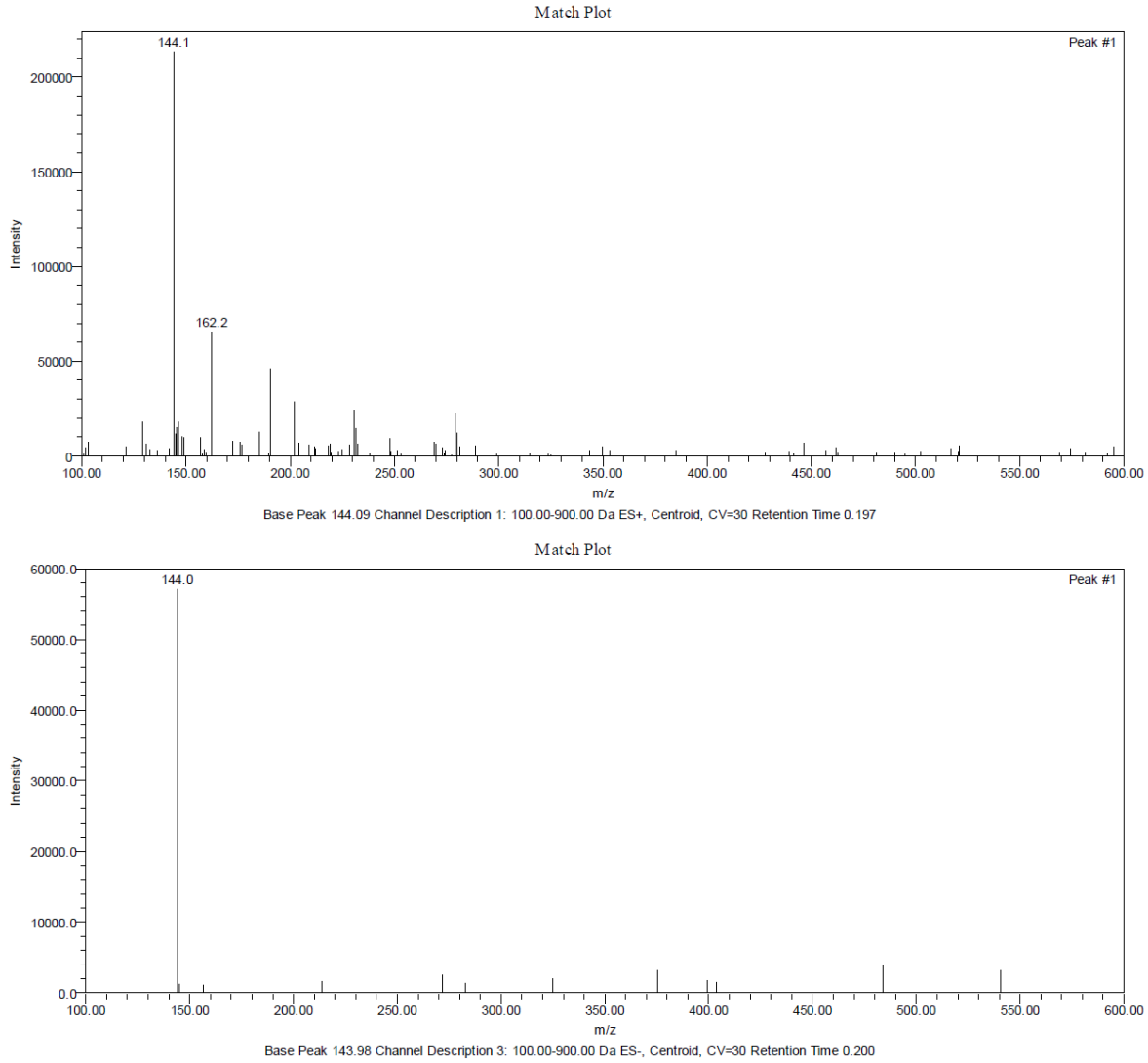


Sm-KYNA


Match Plot
Peak #1
247.3
146.1
157.1
249.2
Intensity
m/z
Base Peak 247.28 Channel Description 2: 100.00-900.00 Da ES+, Centroid, CV=10 Retention Time 0.183


Match Plot
Peak #1
549.8
144.3
220.6
547.6
544.2
541.9
553.5
420.7
511.1
301.3
328.6
333.8
324.9
538.7
113.2
Intensity
m/z
Base Peak 549.83 Channel Description 4: 100.00-900.00 Da ES-, Centroid, CV=10 Retention Time 0.190

Gd-KYNA



Electronic Spectral study:-

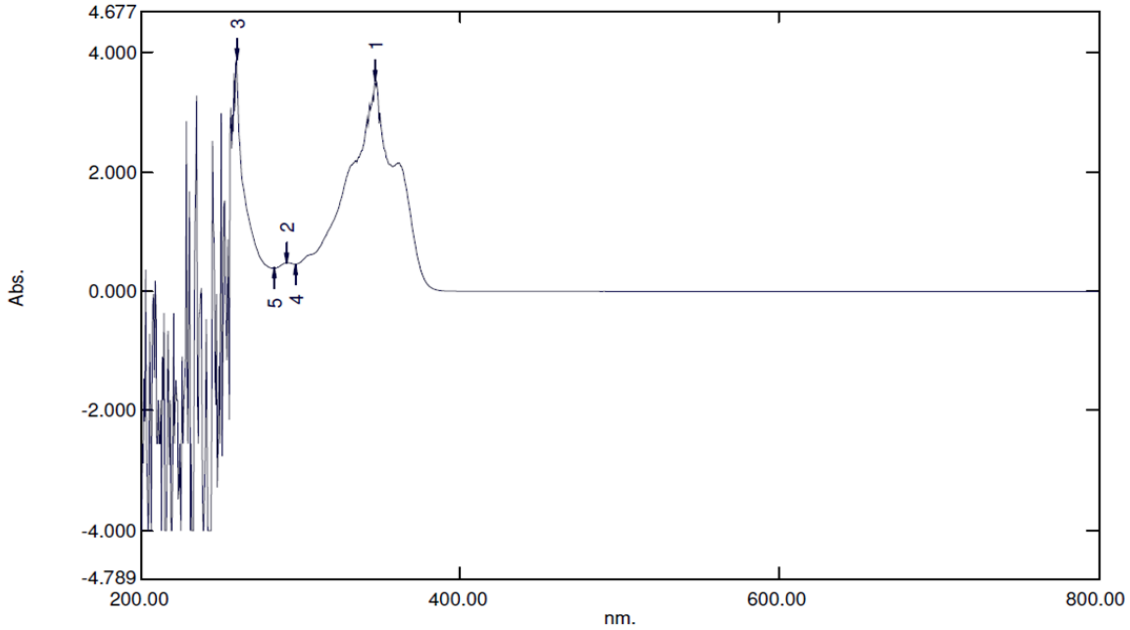
The La-KYNA, Ce-KYNA and Pr-KYNA are analyzed for UV- Visible spectra and magnetic moments. These metals belong to f block elements. This group has a usual characteristic of absence of d-d transition[3] and f-f transition because no space for excited electron is present in the d orbital which is completely filled in these ions. The results indicate paramagnetic nature of the chelates with ligand to metal charge transfer bands [2-3,8].

Magnetic moments:-

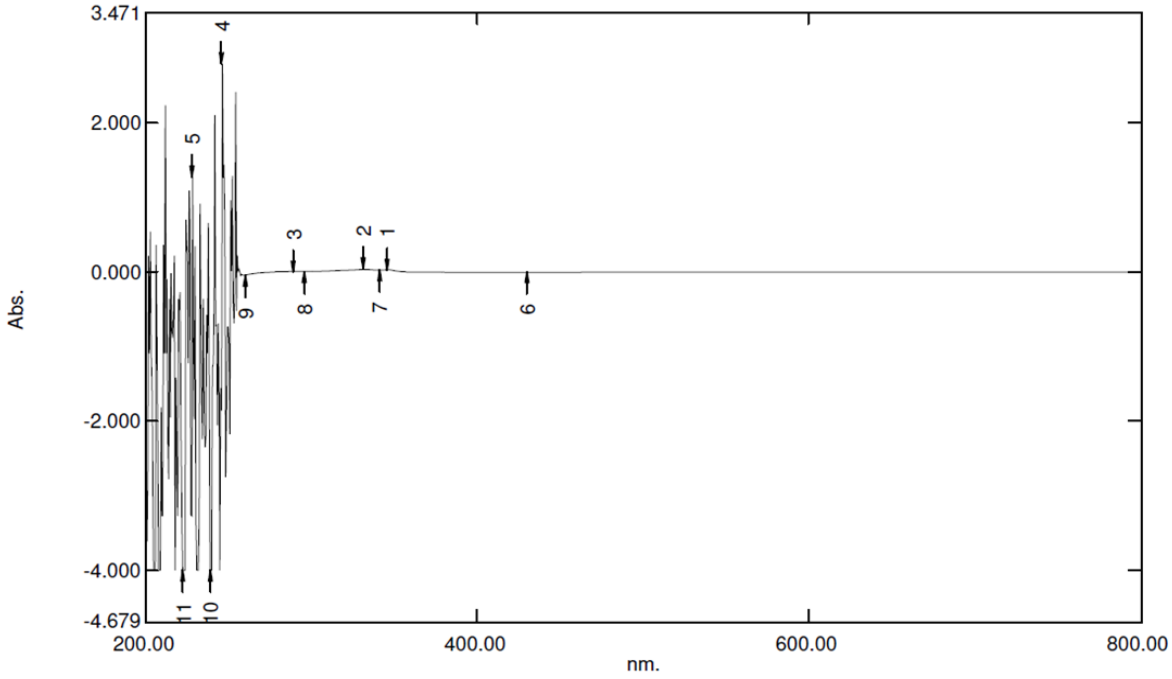
The magnetic moments of the chelates were meausured by the Gouy's method. The room temperature magnetic moment of the solid complexes was found to be 3.32 BM, 1.78 BM, 7.57 BM.[1] This indicates 3, 3 and 5 unpaired electrons per Nd(III), Sm(III), Gd(III) ion in monocapped trigonal prism, pent. bipyramide and Bicapped trigonal prism [9] environment.

Ion	**Ground state term**	**Excited state levels of**
		Hypersensitive transitions
Nd^{III}	$^4I_{9/2}$	$^4G_{5/2}$, $^4G_{7/2}$, $^2G_{7/2}$, $^2K_{13/2}$
Sm^{III}	$^6H_{5/2}$	$^6F_{1/2}$, $^6F_{3/2}$, $^4H_{7/2}$
Gd^{III}	$^8S_{7/2}$	none

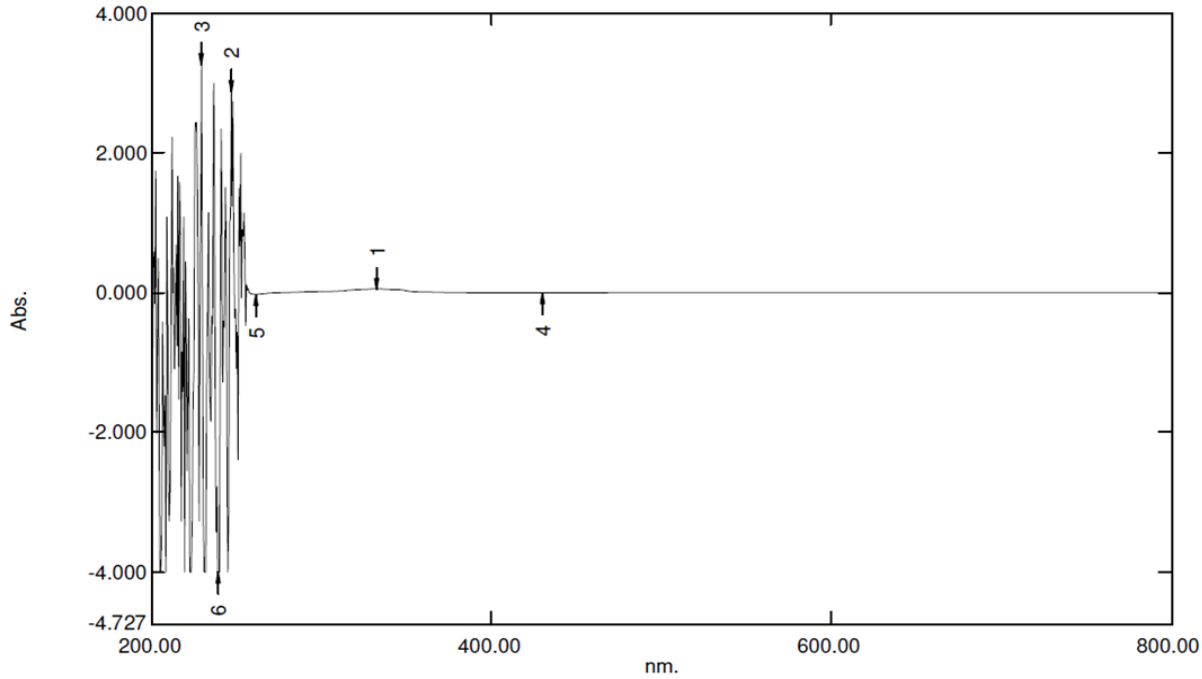
Electronic Spectrum of KYNA Ligand



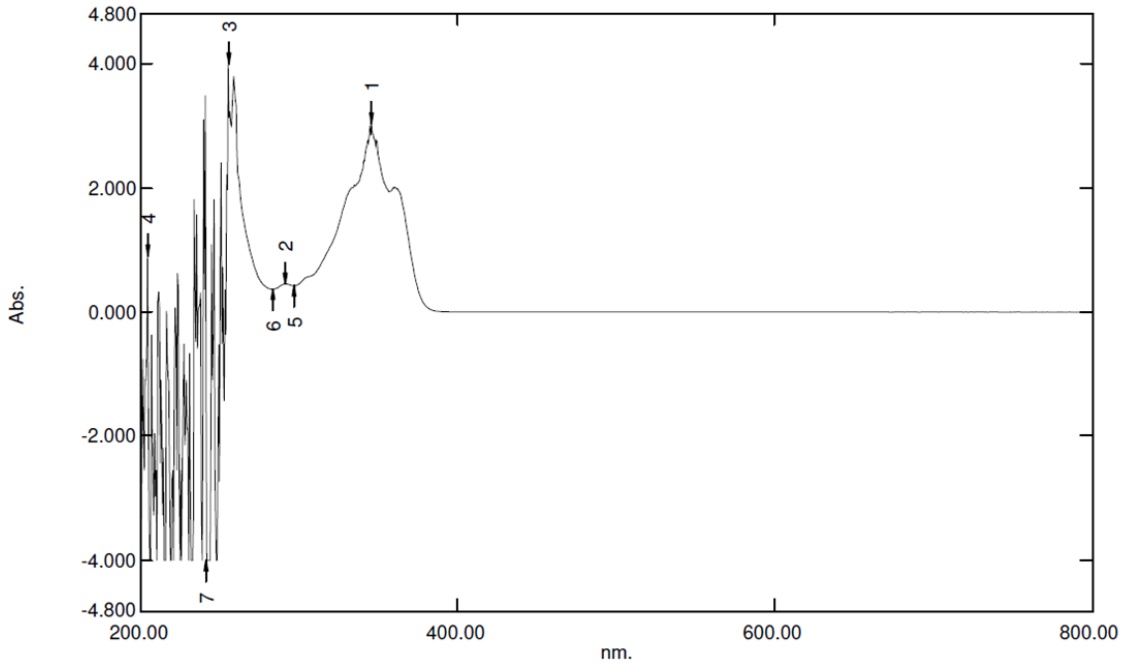
Electronic Spectrum of Nd- KYNA



Electronic Spectrum of Sm- KYNA



Electronic Spectrum of Gd- KYNA



Thermal Analysis:-

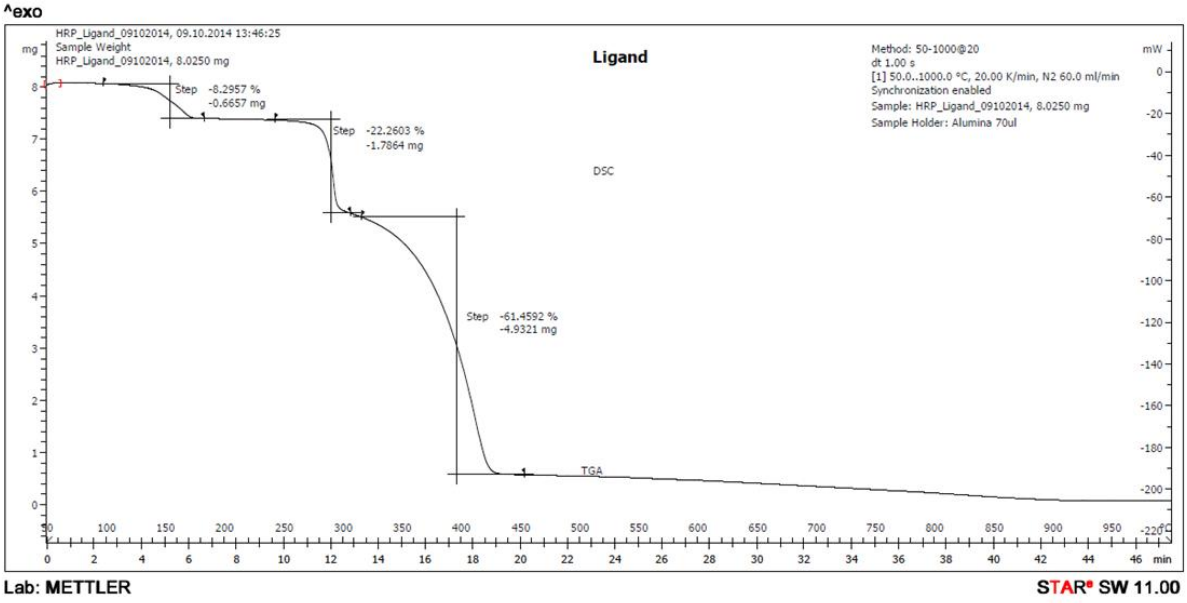
Thermogravimetric analysis or thermal gravimetric analysis (TGA) is a method of thermal analysis in which changes in physical and chemical properties of materials are measured as a function of increasing temperature (with constant heating rate), or as a function of time (with constant temperature and/or constant mass loss). TGA can provide information about physical phenomena, such as second-order phase transitions, including vaporization, sublimation, absorption, adsorption, and desorption. Likewise, TGA can provide information about chemical phenomena including chemisorptions, desolvation (especially dehydration), decomposition, and solid-gas reactions[5] (e.g., oxidation or reduction).[5,10]

Table :- 4 Thermo gravimetric analysis

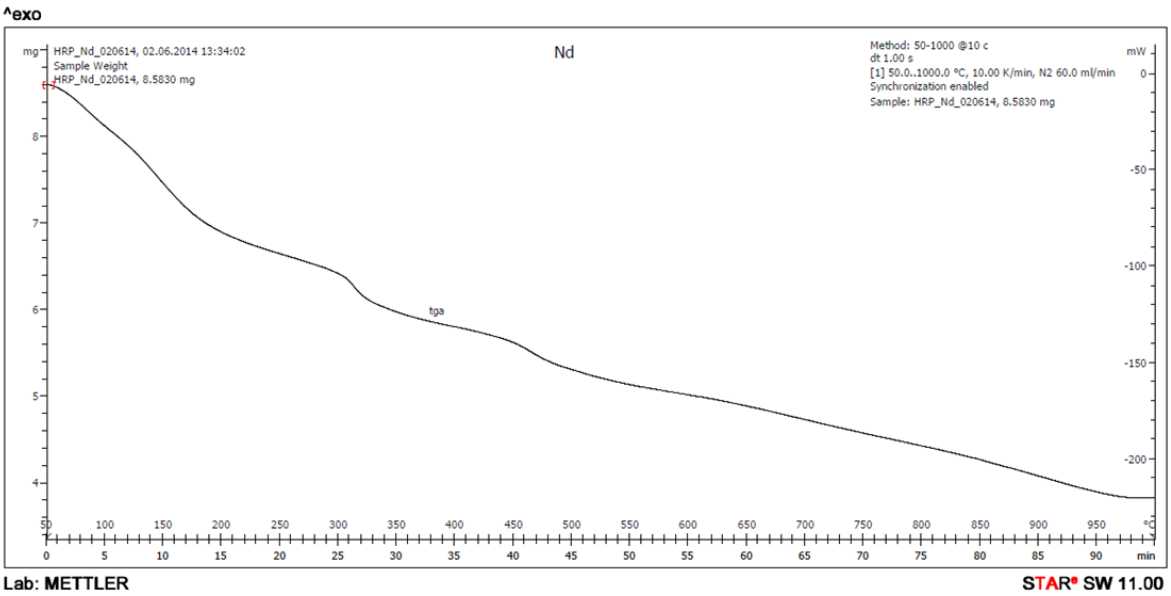
Compound	RT-150 C			150 C - 250C		
	%	Loss of weight(gm)	water	%	Loss of weight(gm)	water
	Loss	for 1 mole complex	molecules	Loss	for 1 mole complex	molecules
Nd-KYNA	13.17	57.82	3	10.33	45.36	2
Sm-KYNA	10.34	46.11	3	9.59	42.76	2
Gd-KYNA	2.95	13.15	0	2.9	12.93	1

RT = Room Temperature

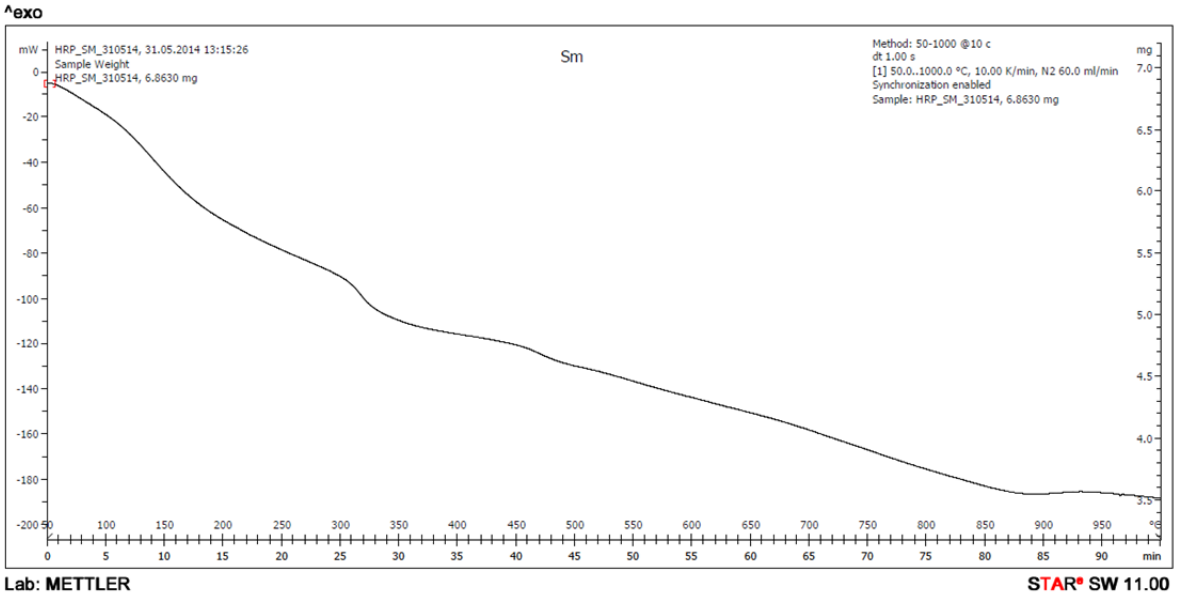
TGA spectrum of KYNA Ligand



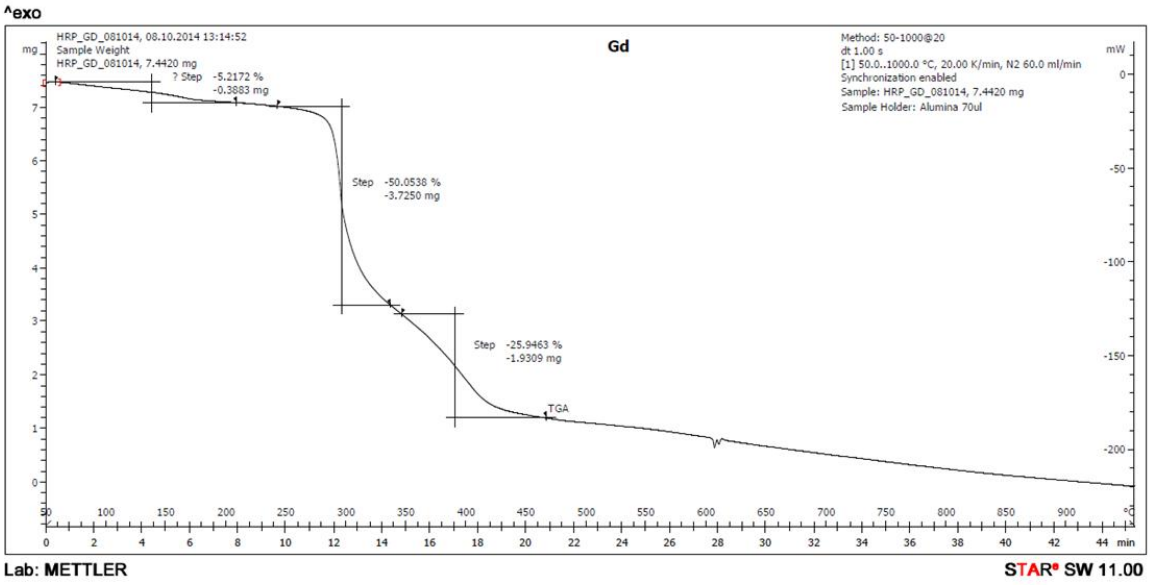
TGA spectrum of Nd-KYNA



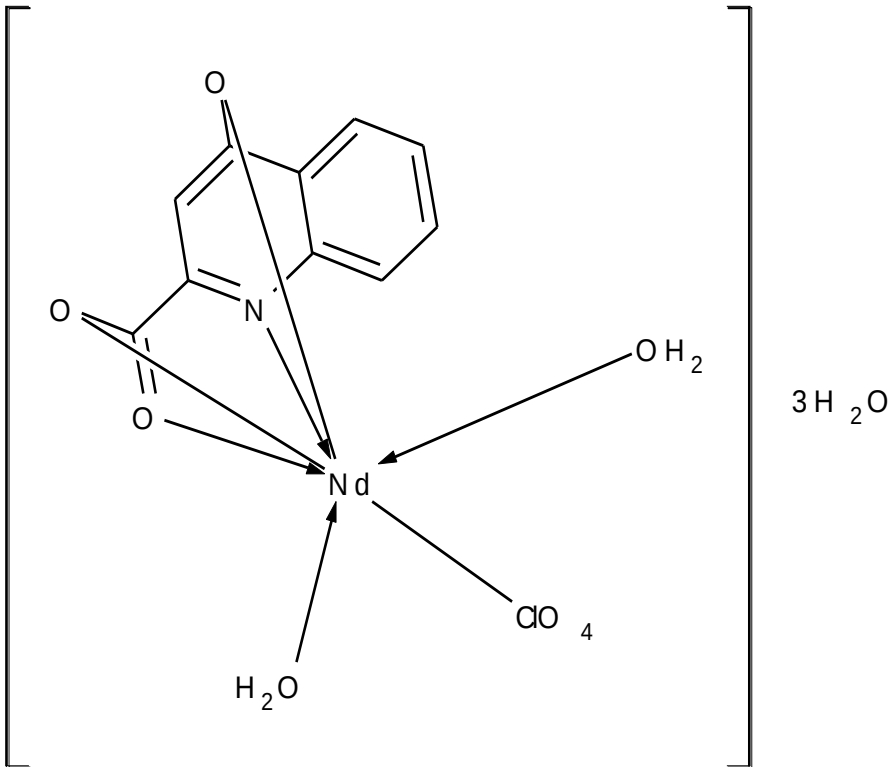
TGA spectrum of Sm-KYNA



TGA spectrum of Gd-KYNA

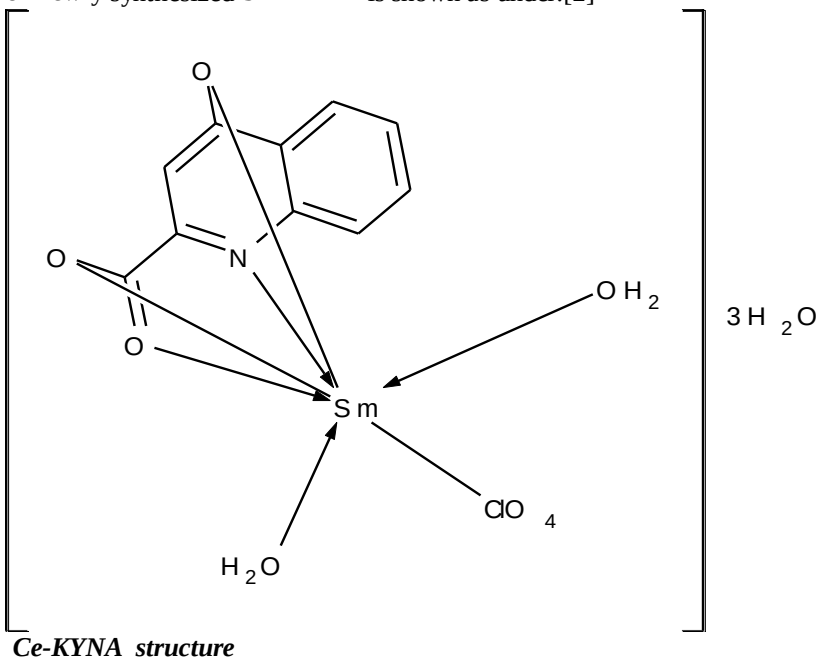


It has been observed that at 150^0C temperature 57.82 gm weight loss occurred by neodymium complex which indicates that three H_2O molecule (mw 18.0gm/mole) coordinated with Nd- KYNA and at the 250 ^{0}C temperature 45.36 gm weight loss occurred which indicates that two water molecules of crystallization with Nd- KYNA. So the probable structure of the newly synthesized Nd- KYNA may be shown as under.[2]



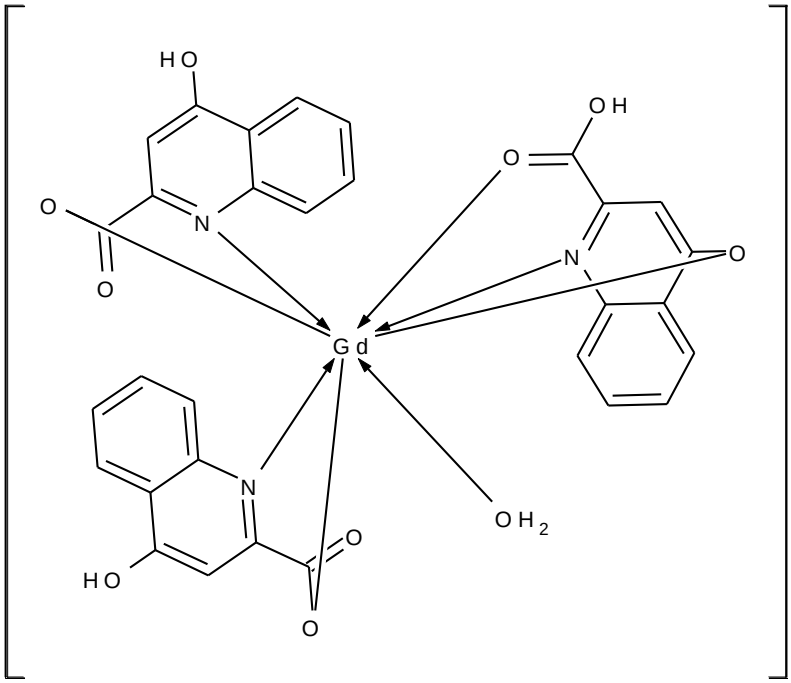
Nd-KYNA structure

Thermogravimetric analysis for Sm-KYNA at 150^0C temperature the 46.11 gm weight loss occur which indicated that three water molecules coordinated with Sm-KYNA and at 250^0C temperature 42.76 gm weight loss occurred which indicates that two water molecules of crystallization are present in Sm-KYNA. So the probable structure of newly synthesized Sm-KYNA is shown as under.[2]



Ce-KYNA structure

In the Gd-KYNA at 150^0 C 13.15 gm weight loss occurred which indicates that no water molecule is present as water of crystallization and at 250^0C temperature 12.93 gm weight loss occurred which indicates that one water molecules coordinates with Gd^{3+} metal ion. The reason for assigning 12.93 gm as one water molecule from room temperature to 250 ^{0}C a total loss of ~ 26 gm water molecule occurred which can not be considerd to be zero. So the probable structure of Gd -KYNA is as under.[2]



Gd-KYNA structure

Catalytic activity:-
Table – 5

Reaction kinetics (without catalyst):

Reaction of : $K_2S_2O_8$ + KI + Methanol

Concentration : (0.0227M) (0.0227M) --

Volume : 50ml 50ml 10ml (t_∞ =125ml)

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

average k = 2.085×10^{-5}

a=b=initial concentrations of reactants= 0.0227M
Table – 6

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

Table – 7

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	$5.83 X 10^{-5}$
30	3.8	$5.48 X 10^{-5}$

average k = $6.78 X 10^{-5}$

a=b=initial concentrations of reactants

Table :- 8 overall results of catalytic activity for complexes of lanthanide metal ions. (Nd-KYNA, Sm-KYNA, Gd-KYNA)

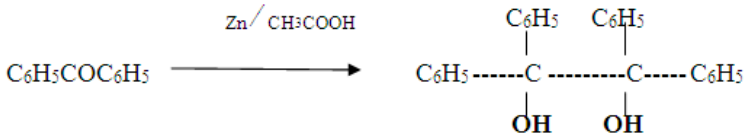
Reactions	k without complexes	k with Nd-KYNA	k with Sm-KYNA	k with Gd-KYNA	% Increase in reaction rate at T = 300 K Nd-KYNA	% Increase in reaction rate at T = 300 K Sm-KYNA	% Increase in reaction rate at T = 300 K Gd-KYNA
$K_2S_2O_8$ +KI	$2.085 x10^{-5}$	$4.248 x10^{-5}$	$4.52 x10^{-5}$	$5.09 x10^{5}$	104	117	144
$KBrO_3$ + KI + HCl	$1.44 x10^{-3}$	$2.267 x10^{-2}$	$3.98 x10^{-2}$	$2.25 x10^{-2}$	1474	2664	1462
H_2O_2 + KI + H_2SO_4	$6.78 x10^{-5}$	$4.42 x10^{-4}$	$5.105 x10^{-4}$	$3.83 x10^{-4}$	552	653	465

Uncatalyzed Organic Reaction:-

The catalyst is a one type of molecule. It facilitates the reaction in homogeneous catalysis[2], the reactant (s) coordinate to the catalyst (or vice versa), are transformed to product, which are then released from the catalyst [11].

A mixture of benzophenone (7.5 gm , 0.041 mole) zinc dust (4 gm) glacial acetic acid (110 ml) and water (22 ml) is refluxed for 2 hours. The solution is filtered (if necessary) and cooled. The separated benzpinacol is filtered and crystalline from glacial acetic acid. The yield is 4.5 gm (30%).[1]
The product melting point is 188-189 ^{0}C[1].

Figure:- product of bezpinacol



Benzophenone **Benzpinacol**

Table:- 9 % yield without catalyst for 2 and 3 hours

Sr. No	Temperature	% yield without catalyst (for 3 hours reaction)	% yield without catalyst (for 2 hours reaction)
1	368 K	32.70%	30.00 %

Table:- 10 % yield with catalyst metal complexes for 2 hours

Compound	1% yield	5% yield	10 % yield
Nd-KYNA	28.88	31.11	57.77
Sm-KYNA	22.26	34.33	63.75
Gd-KYNA	22.00	42.22	62.66

Antimicrobial activity:-

This part deals with the in-vitro screening of newly prepared compounds for antibacterial activity. The species *S.aureus, E.coli, S.Phyogenus* and *P.Aeruginosa* have been taken for the antibacterial activities. Agar-cup method was employed for the in-vitro screening for antibacterial activity.[12] The results of the compounds synthesized given for antibacterial screening are mentioned in following Table.[1]

Table :-11 Antibacterial activity of standard drugs:

STANDARD DRUGS				
MINIMUM INHIBITION CONCENTRATION (µg/ml)				
DRUG	***E.COLI***	***P.AERUGINOSA***	***S.AUREUS***	***S.PYOGENUS***
	MTCC 443	**MTCC 1688**	**MTCC 96**	**MTCC 442**
GENTAMYCIN	0.05	1	0.25	0.5
AMPICILLIN	100	0	250	100

CHLORAMPHENICOL	50	50	50	50
CIPROFLOXACIN	25	25	50	50
NORFLOXACIN	10	10	10	10

Table :-12 Antibacterial activity of KYNA Ligand d and its complexes

ANTIBACTERIAL ACTIVITY TABLE					
MINIMUM INHIBITION CONCENTRATION (µg/ml)					
SR NO	**CODE NO**	**E.COLI MTCC 443**	**P.AERUGINOSA MTCC 1688**	**S.AUREUS MTCC 96**	**S.PYOGENUS MTCC 442**
1	KYNA ligand	100	250	250	200
2	Nd-KYNA	50	100	250	500
3	Sm-KYNA	200	200	100	250
4	Gd-KYNA	62.5	200	100	125

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.[3]

Antifungal activity:

This part deals with the in-vitro screening of newly prepared compexes 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.[3,13] The results of the compounds synthesized taken for antifungal screening are mentioned in as under.

Table:-12 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 :- 13 Antifungal activity of KYNA ligand and its complexes

ANTIFUNGAL ACTIVITY TABLE				
MINIMAL FUNGICIDAL CONCENTRATION (µg/ml)				
SR NO	**CODE NO**	**C.ALBICANS MTCC 227**	**A.NIGER MTCC 282**	**A.CLAVATUS MTCC 1323**
1	KYNA ligand	1000	500	500
2	Nd-KYNA	1000	250	250
3	Sm-KYNA	500	1000	1000
4	Gd-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.[3]

III. Conclusion:-

In several cases, it has been observed that complexation with KYNA or BSPA leads to increase in antimicrobial activity compared to the original ligand. If one compares the results with those of standard antibiotics, Nd and Gd complexes with KYNA leads to better antimicrobial activity against *E.coli* as well as Sm and Gd complexs exhibit better antimicrobial activity, against *S.aureus.* In the case of antifungal activity, the ligand BSPA and its complexes with Pr^{3+} and Nd^{3+} exhibit equal activity as compared to greseofulvin. The La^{3+} and Ce^{3+}complexes exhibit better antifungal activities compared to greseofulvin. Remaining all activities was moderate. Thus selected complexes exhibited better antimicrobial activity in comparison with standard antibiotic drug molecules and their further exploring can give promising out come in future.

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