Catalytic and Biochemical Study of Novel Complexes of Some Lanthanides

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Abstract: - **Lanthanide ions are possessing typical characteristics for example, lanthanide contraction, unique magnetic properties etc. The product of lanthanide ions with 2-(1,3-benzoxazole -2-yl - sulfanyl)-N-phenyl acetamide ligand to form coordination compounds is an important area of current research. Less explored ,biologically important, 2-(1,3-benzoxazole -2-yl - sulfanyl)-N-phenyl acetamide (expressed as BSPA) ligand is allowed to react with solution of lanthanide perchlorates and attempt has been made to synthesize solid BSPA complexes. These complexes are subjected to U.V visible spectroscopy, IR spectroscopy, TGA analysis, mass spectroscopy, elemental analysis etc. For structure elucidation and then antimicrobial activity studies by standard methods. Catalytic effects of these complexes are studied for different types of chemical reactions. Attempts have been made to correlate structural characteristics with properties of these complexes.**

Keywords: ***lanthanide complexes, catalytic studies, antimicrobial activity.***

I. INTRODUCTION

Phenylacetamide which can be obtained by acetylation of aniline undergoes nitration at low temperature and yields para-nitro derivative. Acetyl group can then be removed by acid-catalyzed hydrolysis to yield para-nitroaniline. Although the activating affection of the amino group can be reduced, the acetyl derivative remains in ortho/para-orientation and activating substituent.[1-2]

Phenylacetamide is used as an inhibitor of peroxides and stabilizer for cellulose ester varnishes. It is used as an intermediate for the synthesis of rubber accelerators, dyes, dye intermediate and camphor. It is used as a precursor in penicillin synthesis and other pharmaceuticals including painkillers and intermediates. Phenylacetamide strucure shows analgesic and antipyretic effects. But phenylacetamide is not used directly for this application due to causing methemoglobinemia (the presence of excessive methemoglobin which does not function reversibly as an oxygen carrier in the blood). Acetaminophen (4'-hydroxy phenylacetamide) is the analogue widely used as a nonprescription drug with analgesic and antipyretic effects similar to aspirin.[3] Therefore, in the present study, one derivative of phenyl acetamide was selected as the ligand.

II. METHOD AND MATERIALS

All the chemicals used throughout the work were of analytical grade. Aniline, toluene, dichloromethane, TEA ((tri ethylamine), acetone and 1,3 benzoxazole -2-thiol and K_2CO_3 were used for the preparation of ligand. La(III), Ce(III), Pr(III) and Nd(III) perchlorates were prepared in the laboratory.

Preparation of Ligand

The organic compound was synthesized of 11 ml aniline in the 1000 ml conical flask. Drop wise addition of 300 ml of the dichloromethane was done and 25 gm of the potassium carbonate was added then after. The mixture was stirred well and constant stirring was maintained for five minutes. The solution became ready for the second part. Drop wise addition of 25 ml of chloracetyl chloride was followed by addition of 80 ml toluene and 2 - 3 drops of tri ethylamine in 1000 ml conical flask. The solution was kept in ice water bath with constant stirring for 3-4 hours.

The solution was transferred into a 500 ml beaker and extra ice was added in the solution for precipitation. The precipitates obtained were filtered. It was labeled as product -A.

This product -A (25 gm) was dissolved solution in 300 ml acetone and the compound -B (22.7 gm) (1,3 benzoxazole -2-thiol) was mixed with it and this mixture was stirred well with 25 gm K_2CO_3 in ice bath with constant stirring for 3-4 hours. The light white solid [compound C] was obtained by addition of approximate 40 ml cold water. The solid product was filtered, washed, dried and purified. In this way, the ligand BSPA was obtained.

III. PREPARATION OF COMPLEXES

A definite volume of 70% acid was diluted with water to obtain 0.2M perchloric acid solution in 500 ml flask. The exact strength was determined by pH metric titration against 0.2M NaOH solution (standardized with 0.2N oxalic acid previously prepared). 75 ml 0.2M perchloric acid was taken and solid metal carbonate was added. Initial effervescence were observed. Slight excess addition of carbonate was done.The solution was stirred for 30 minutes and filtered (this way 0.133 M lanthanide perchlorate was obtained).

The formation of complexes was carried out by mixing 75 ml 0.133 M metal perchlorate solution and 50ml 0.2 M ligand in DMSO solution. The mole ratio of ligand and metal was (1:1). The reaction mixture was refluxed for 2.5 to 3.0 hours at 95 ^{0}C temperature. After 3 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 sticky product was dissolved in methanol to remove stickiness. This mixture with methanol was slightly heated for total dissolution and after that cooled. Then after around 30 ml of cold water was added for precipitation of the complex in non sticky form. The complex thus obtained was washed well with double distilled water to remove unreacted metal perchlorate and ligand. All the complexes were dried in oven at 40^{O}C to 50^{O}C.

Table :- 1 BSPA ligand and its complexes

Sr. No.	Ligand or Complexes	Brief name
1	Ligand BSPA	BSPA
2	La(III)- BSPA	La- BSPA
3	Ce(III)- BSPA	Ce- BSPA
4	Pr(III)-BSPA	Pr-BSPA
5	Nd(III)-BSPA	Nd-BSPA

IV. ANALYSES AND PHYSICAL MEASUREMENTS

M.P. and TLC were taken with usual apparatus. TLC indicated single spot confirming complex formation. Elemental analyses were performed with a Vario-MICRO CUBE C, H, N, S analyzer. There were 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 [4].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 Waters and Alliance 2690 analyzer.

Sr. No.	Compound Name	M.P (^{0}C)	Rf value	Molar Cond. mho cm^{-1}	Mole. weight gm mol^{-1}	Color of complex	Uv- vis spectra λmax (nm)	Magn. Sus. (BM)	Elemental Analysis									
									% C		% H		% N		%Cl		% M	
									Cal.	Fou.	Cal.	Fou.	Cal.	Fou.	Cal.	Fou.	Cal.	Fou.
1	BSPA ligand	127	0.72	0.43	284.33	Creamy White	349.5, 286.5,279, 255.50, 226.5, 208.50	-----	63.01	63.30	4.09	4.22	9.94	9.85	---	---	---	---
2	La-BSPA	112	0.54	0.427	1304.41	Creamy White	339.5, 286.5, 279.50, 255.5, 209	Dia magnetic	63.97	41.27	4.38	3.02	9.82	6.42	8.14	---	12.23	10.61
3	Ce-BSPA	158	0.55	0.414	1061.22	Creamy White	253.5, 233, 227.50	2.53	30.29	34.50	3.10	3.01	3.21	5.36	10.20	---	35.06	13.43
4	Pr-BSPA	124	0.65	0.247	1310.4	light greenish	341, 286.5, 279.5, 256, 233.5,	3.14	58.01	41.21	3.88	3.02	3.94	6.41	8.12	---	9.00	10.75
5	Nd-BSPA	129	0.75	0.266	1295.73	Creamy White	286.5, 279.5, 256, 225.5	3.28	60.36	41.67	4.05	2.80	9.42	6.48	8.22	---	7.78	11.13

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

BSPA = 2-(1,3-Benzoxazole -2-yl - sulfanyl)-N-phenyl acetamide, Mole. = Molecular, Magn. Sus.= Magnetic susceptibility, Cal.= Calculated, Fou.= Found, Cond. = conductance, %M carried out by EDTA method , vis. = visible

V. INFRARED SPECTROSCOPY

Infrared spectroscopic technique [6-9] is of an immense importance to organic chemists for the identification of the presence of functional groups in the organic compounds. Furthermore, there is a finger print zone 650 cm-1 to 1400 cm-1 , in which any organic molecule will exhibit characteristic peaks of its own (like finger print). Therefore it can be used for the identification of the compounds. On complex formation, there will be addition of bands corresponding to M-N, M-O etc. This is usually accompanied by change in O-H, N-H etc wave numbers of stretching / bending vibrations. If metal ions replace H+, then vibrations corresponding to O-H, >N-H etc. will be absent in the spectra of complexes. Hence, IR spectra of metal- complexes also many times provide useful structural information.

Compound	**ν[Ar(C-H)] stre.**	**ν(C=N) stre.**	**ν(C=O) stre.**	**ν(N-H) stre.**	**ν(M-N) stre.**	**ν(M-O) stre.**	**ν(M-X) stre.**	**ν(C-O-C) stre.**	**ν(C-S) stre.**	**Bending Vibrations**	**Scissoring & Other bending Vibrations**
BSPA LIGAND	1082 1137 1148 1158	1440 1454	1598 1675	3529 3671	------	-----	-----	1236 1251	757 781 807 858	678, 690-OH out of plane 1508-CH, CH_2 and OH in plane	1454-Scissoring 1369- CH_2 Wagging and Twisting
La- BSPA	1099 1118 1137	1441 1454	1599 1635 1675	3333	678 690	500 488 460 453	500 756	1236 1251	781 807	678,690-OH out of plane 1508-CH, CH_2 and OH in plane	1454-Scissoring 1370- CH_2 Wagging and Twisting
Ce- BSPA	1108	1494 1420	1656	3335	622 692	490 479 462 452	756	1207	841	692- OH out of plane 1494-CH, CH_2 and OH in plane	1207- CH_2 Wagging and Twisting
Pr-BSPA	1002 1031 1082 1137	1382 1441 1454 1473	1599 1634 1675	3443 3510	624 654 665 678 690	449 463 479 510 537	585 596 702	1236 1251	781 807	654,665-OH out of plane 1509-CH, CH_2 and OH in plane	1454-Scissoring 1370- CH_2 Wagging and Twisting
Nd-BSPA	1031 1083 1137 1148	1370 1441 1454 1473	1599 1675	3334 3676	654 666 678 702	453 465 480 499 510	595 702	1236 1251	781 807	654,666-OH out of plane 1508-CH, CH_2 and OH in plane	1454-Scissoring 1370- CH_2 Wagging and Twisting

Table :-3 IR spectra of BSPA ligand and its complexes.*

(1)*Metal –Sulphur stretching (below 300 cm^{-1}) not measured by instrument. (2) All figures are in cm^{-1}

VI. MASS SPECTROMETRY

The most common use of mass spectrometry by the organic chemist is for the accurate determination of molecular formula. A second important use is to provide information about the structure of compounds by an examination of the fragmentation pattern.[10] Metal complexes may or may not be volatile but many times their mass spectra provide valuable information.

La-BSPA

Base peak (B.P.) - 285.2 (ES+), 284 (ES-) (Ligand peaks)

(B. P. +1) is 16 % of B.P. therefore 15 carbon atoms present in base peak

B.P. , B.P. + 2, B.P. + 4 (ratio 3:3:1) in fragment therefore 3 chlorine atoms may be present

Ligand - benzene + 2H (ES+) peak =211

Metal + Ligand – benzene = 344

Metal + Ligand peak = 423

Ce-BSPA

Base peak (B.P.) - 283.3 (ES+), 284 (ES-) (Ligand peaks)

(B. P. +1) is 16 % of B.P. therefore 15 carbon atoms present in base peak

B.P. , B.P. + 2, B.P. + 4 (ratio 3:3:1) in fragment therefore 3 chlorine atoms may be present

Ligand + Metal – Aniline peak = 332 (ES+)

Ligand + Metal – benzene + 1 (ES+) peak = 343.2

Pr-BSPA

Base peak (B.P.) - 285.2 (ES+), 283 (ES-) (Ligand peaks)

(B. P. +1) is 16 % of B.P. therefore 15 carbon atoms present in base peak

B.P. , B.P. + 2, B.P. + 4 (ratio 3:3:1) in fragment therefore 3 chlorine atoms may be present

Ligand + Metal + H_2O – benzene peak = 366

Ligand + Metal - H_2O peak = 425

Ligand + Metal + H_2O peak = 443

Nd-BSPA

Base peak (B.P.) - 285.2 (ES+), 283 (ES-) (Ligandd peaks)

(B. P. +1) is 16 % of B.P. therefore 15 carbon atoms present in base peak

B.P. , B.P. + 2, B.P. + 4 (ratio 3:3:1) in fragment therefore 3 chlorine atoms may be present

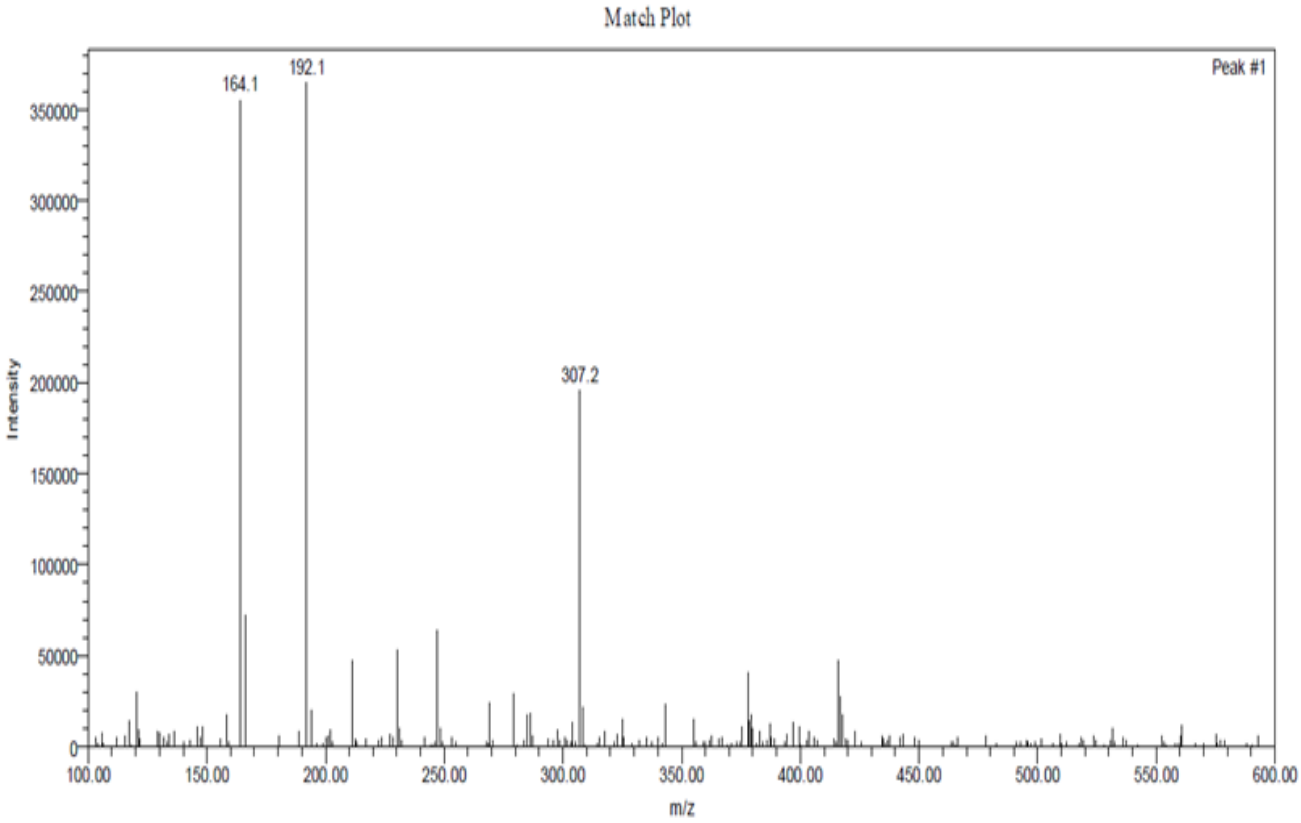
Ligand – Aniline peak = 192.1 (ES+)

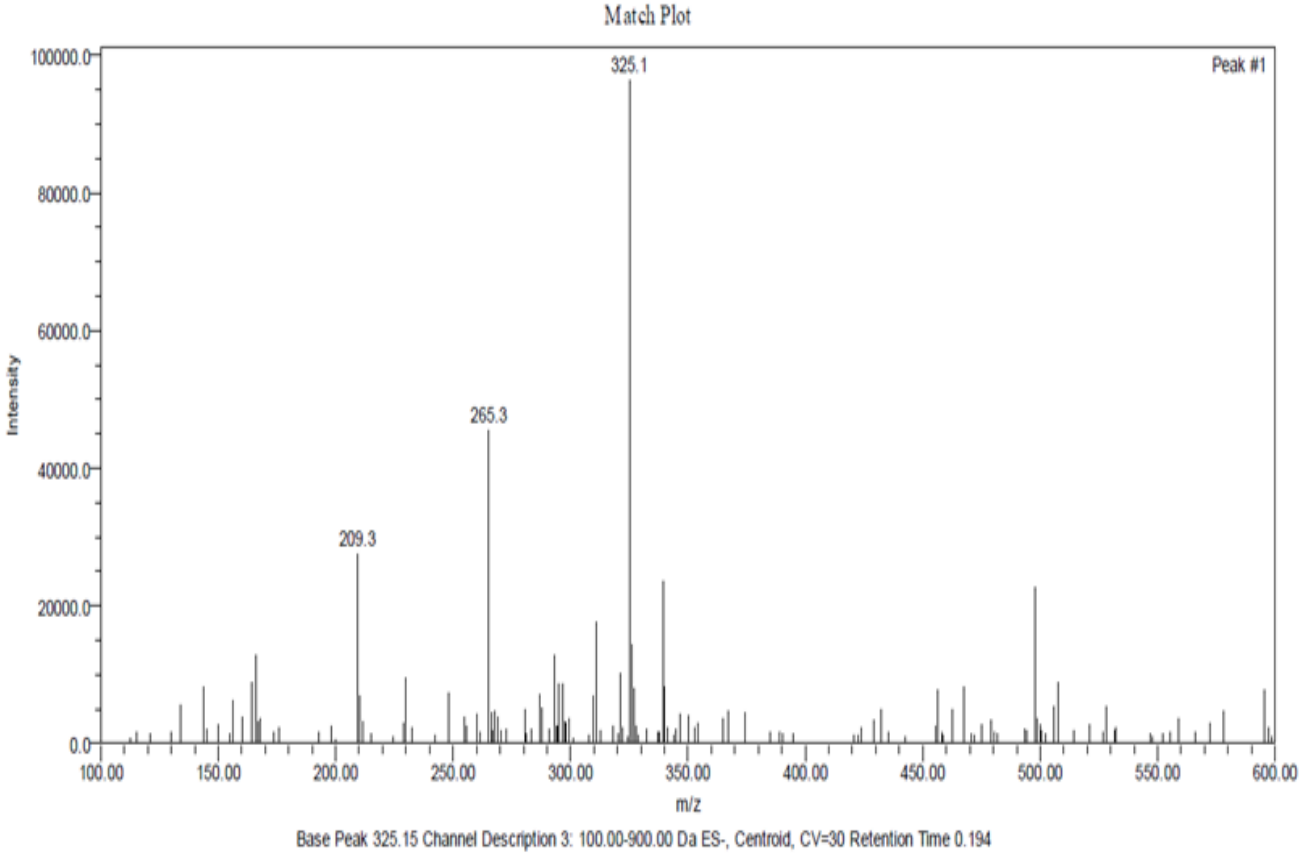
Metal + Lignad - N-Phenylformamide – 1 (ES-) peak = 307 (ES-)

Lignad - N-Phenylformamide peak = 164.1 (ES+)

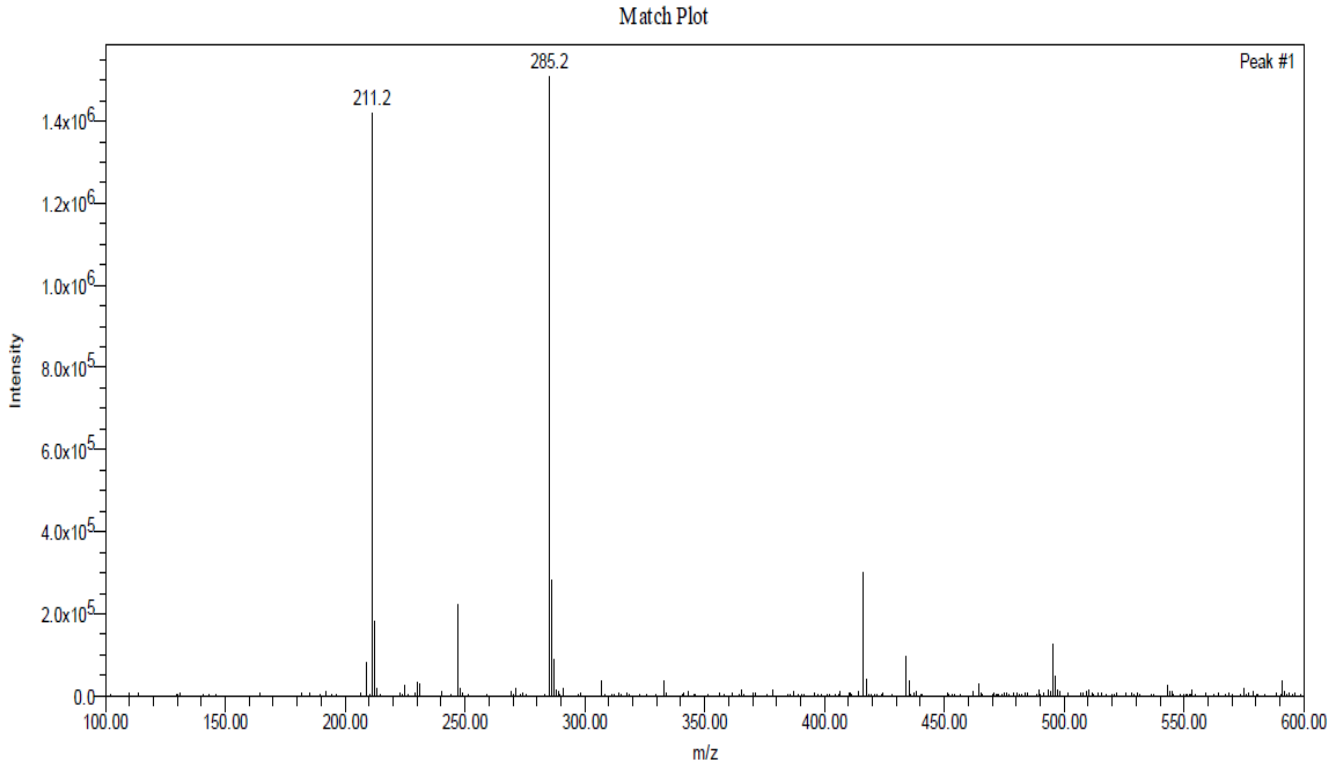
Metal + Ligand – 1,3- benzoxazole-2-thiol peak = 311.1 (ES-)

Intensity values of X, X+2, X+4, X+6…etc. indicate possibility of presence of three chlorine atoms in that fragment consequently the presence of at least three chlorine atoms in the molecule is indicated. Likewise, presence of fifteen carbons in the base peak indicates presence of minimum fifteen carbon atoms in the molecule.

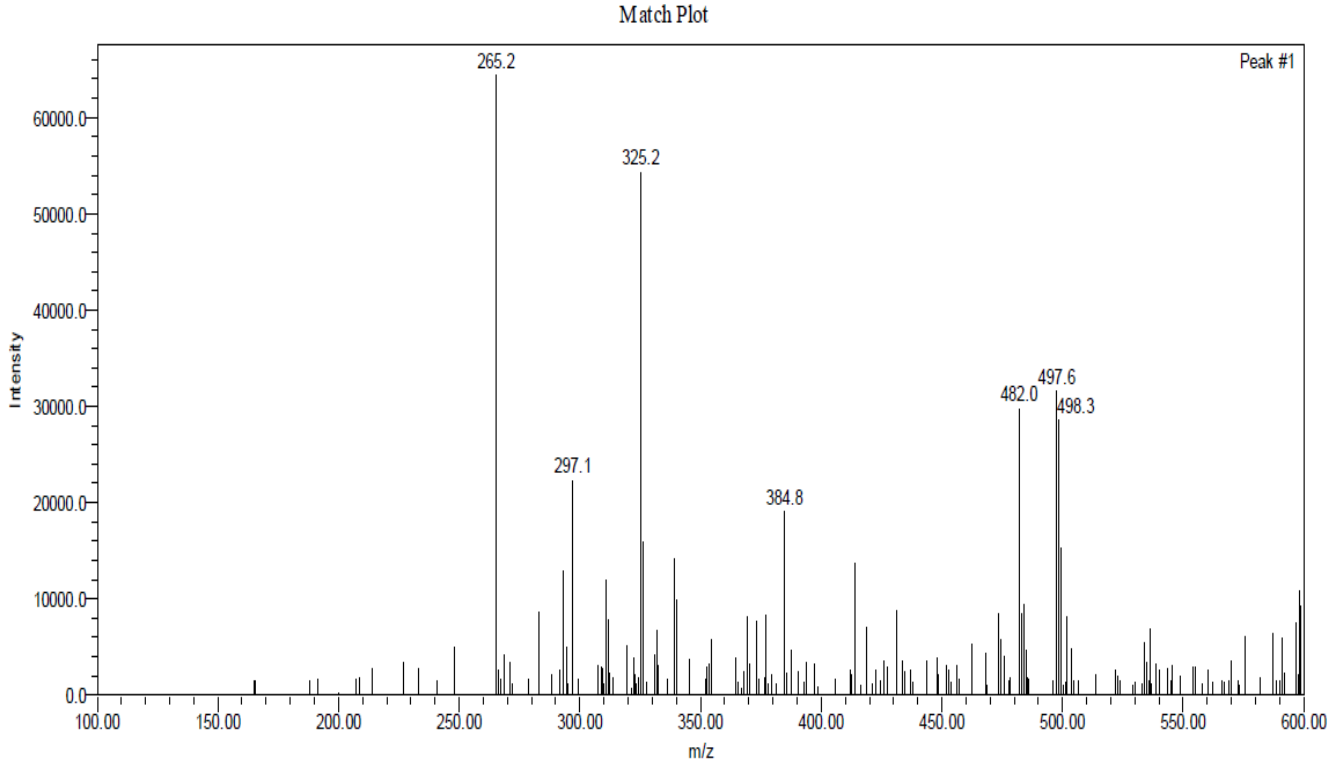




MASS SPECTRA LIGAND BSPA

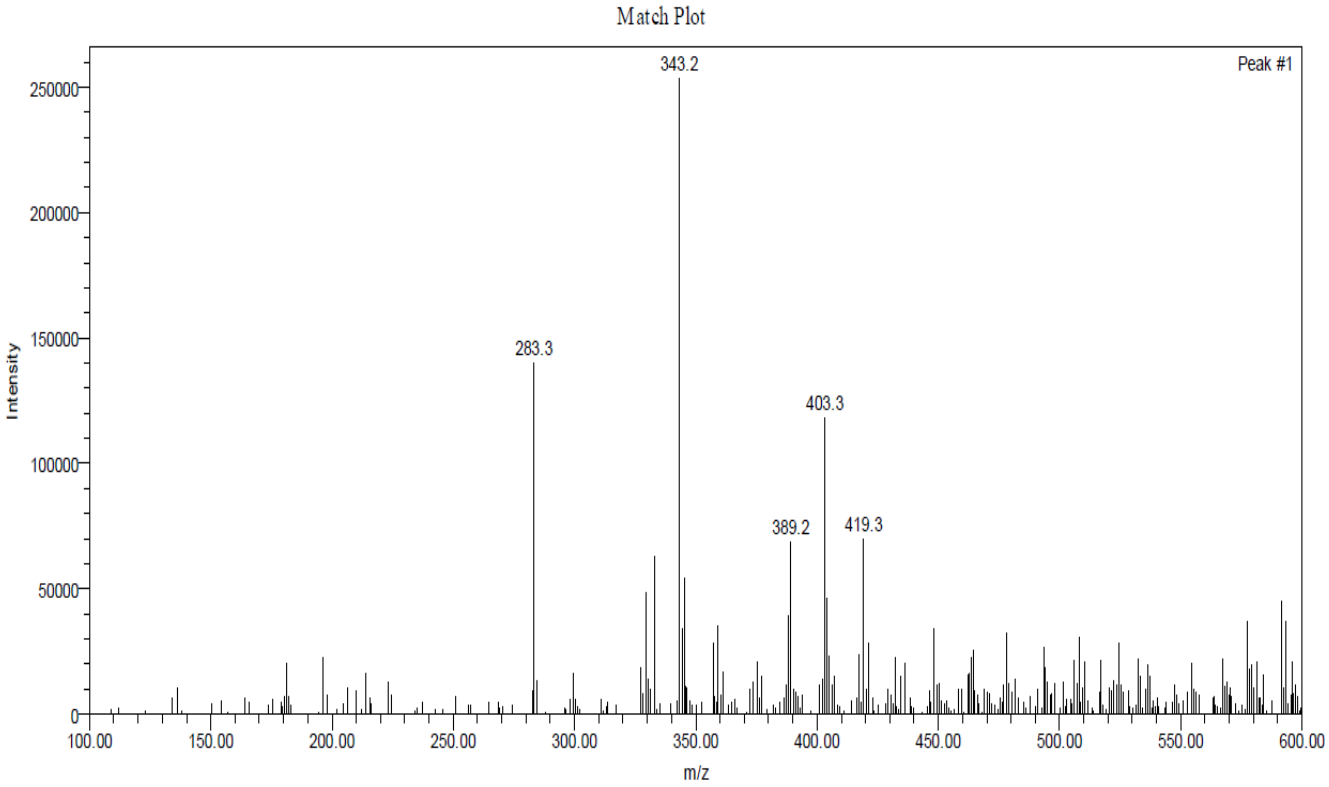


Base Peak 285.17 Channel Description 2: 100.00-900.00 Da ES+, Centroid, CV=10 Retention Time 0.191

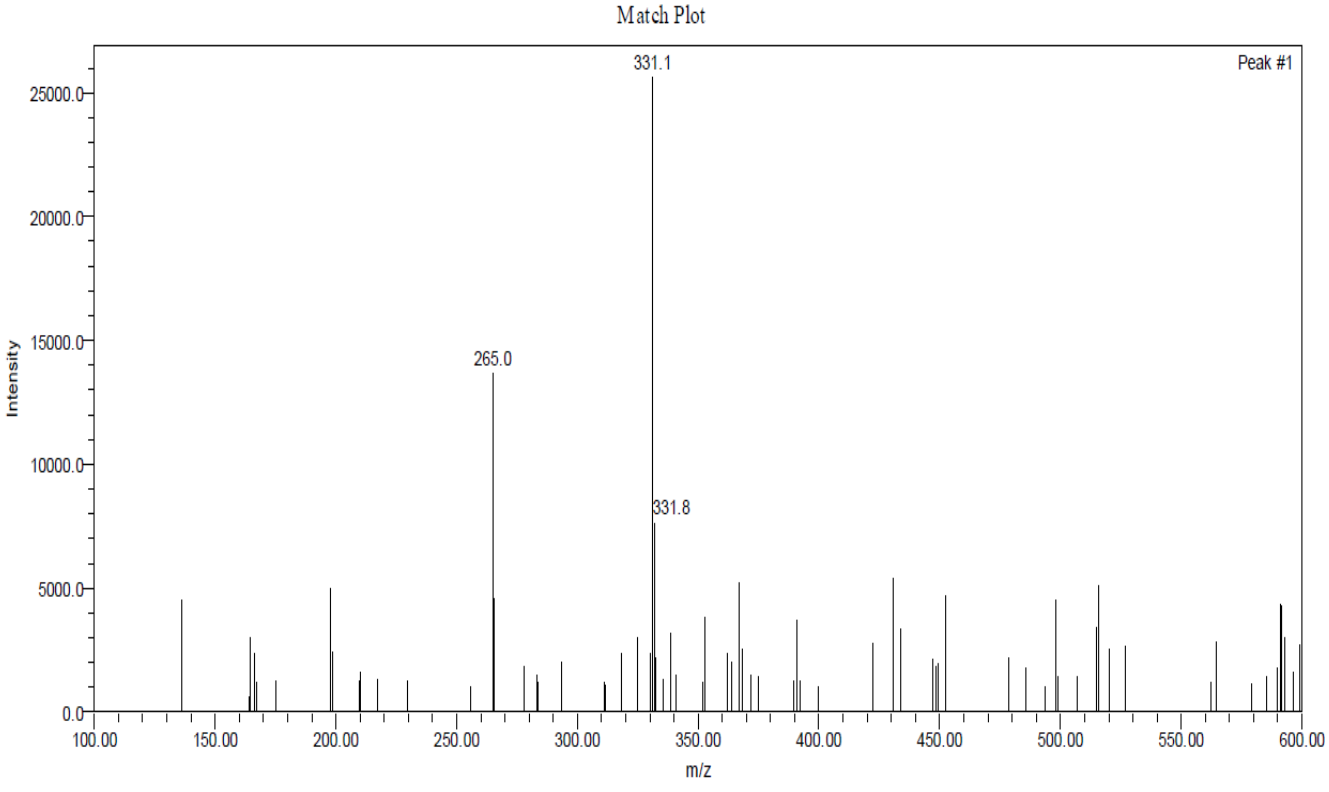


Base Peak 265.18 Channel Description 4: 100.00-900.00 Da ES-, Centroid, CV=10 Retention Time 0.187

La-BSPA

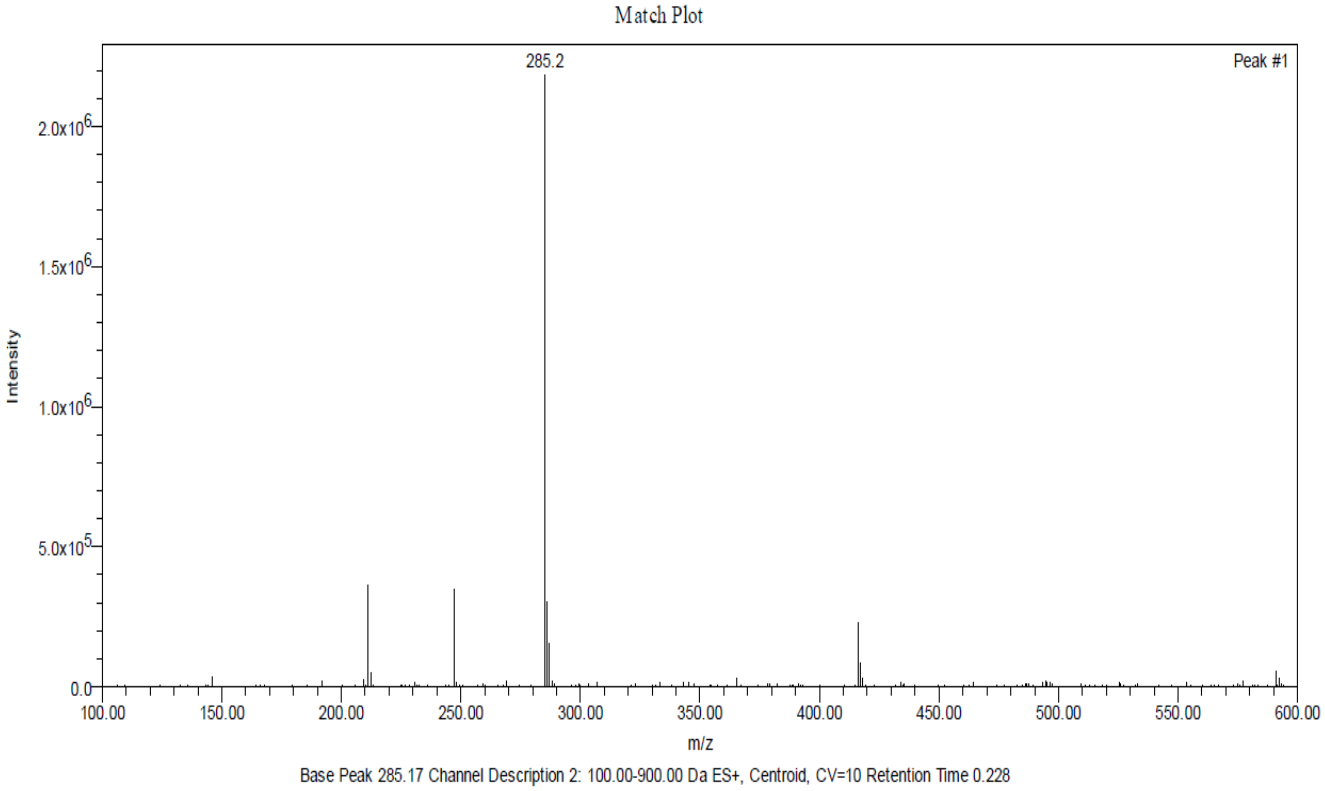


Base Peak 343.21 Channel Description 2: 100.00-900.00 Da ES+, Centroid, CV=10 Retention Time 0.190

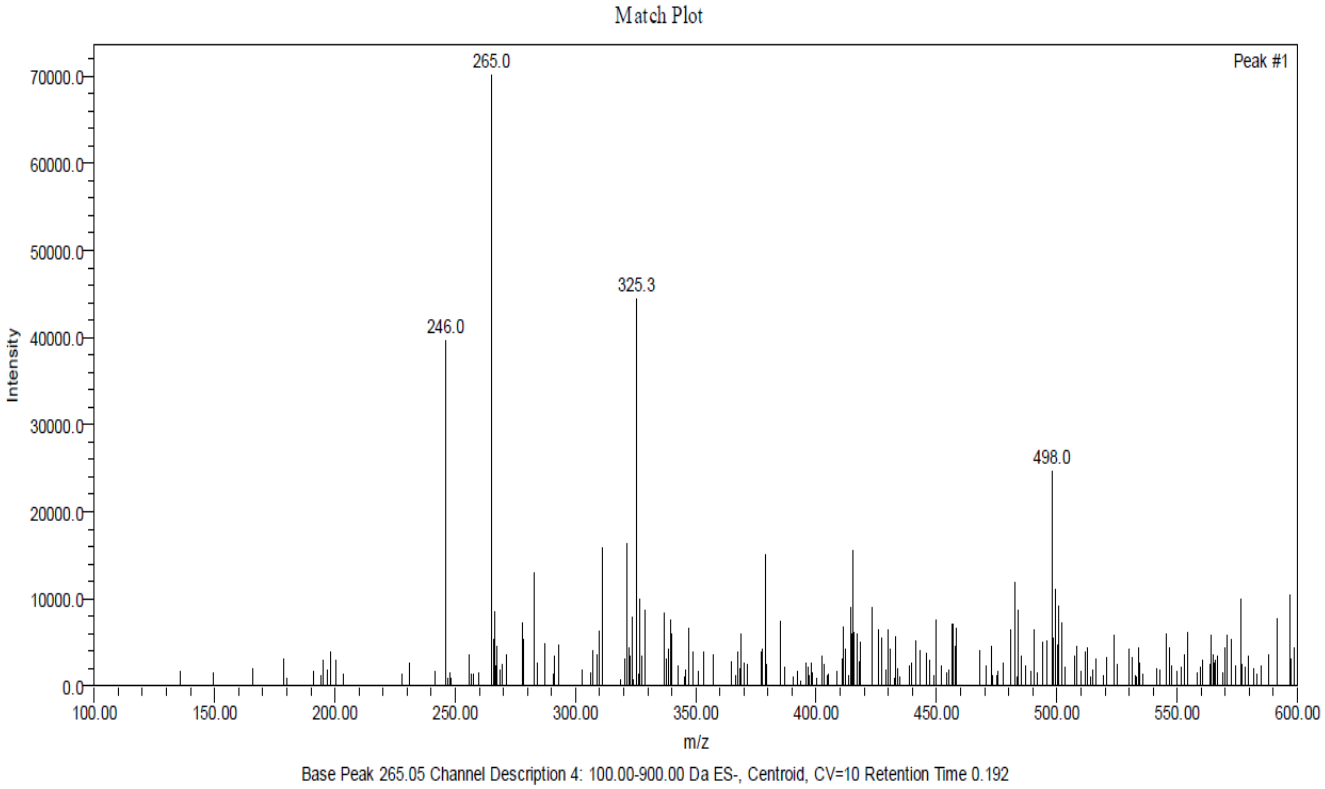


Base Peak 331.13 Channel Description 4: 100.00-900.00 Da ES-, Centroid, CV=10 Retention Time 0.192

Ce-BSPA



Base Peak 285.17 Channel Description 2: 100.00-900.00 Da ES+, Centroid, CV=10 Retention Time 0.228



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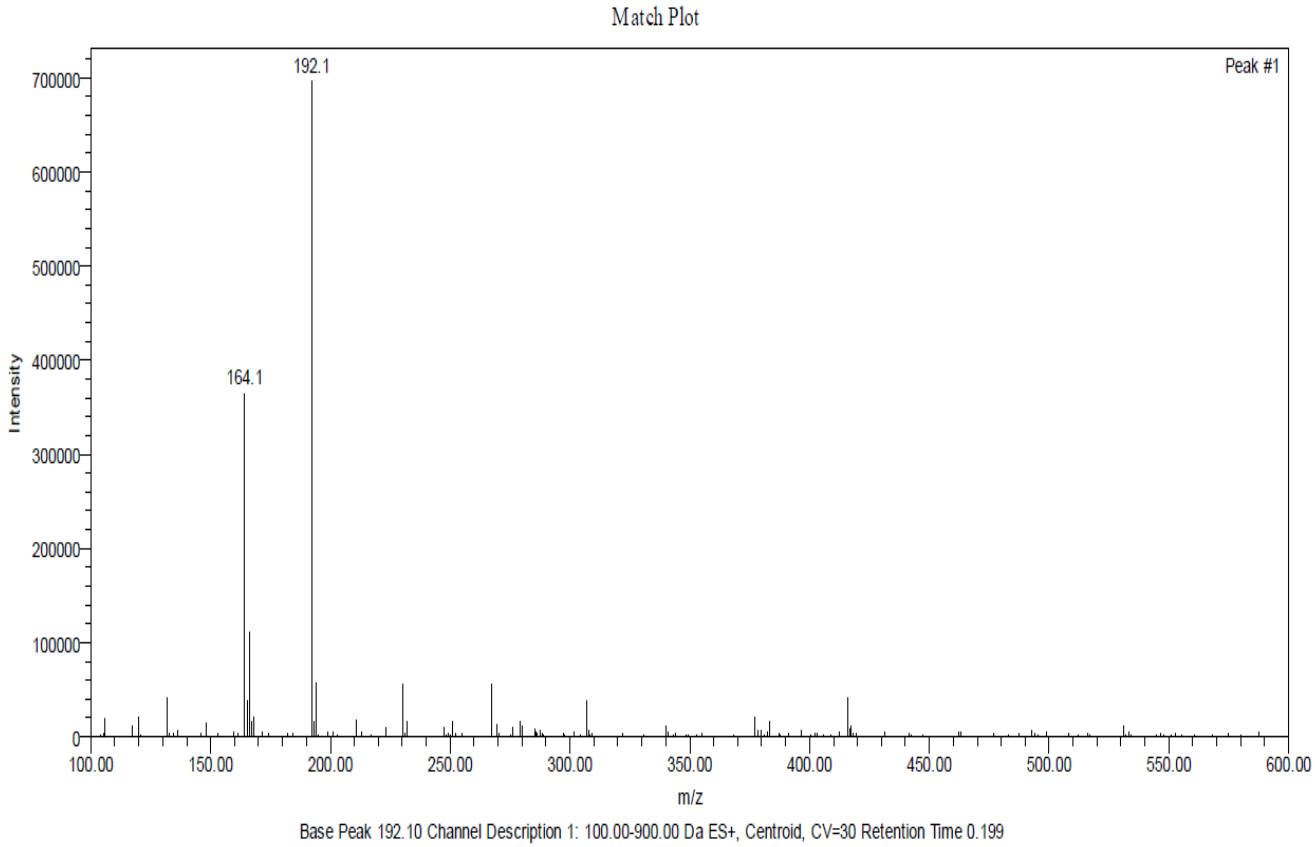
Pr-BSPA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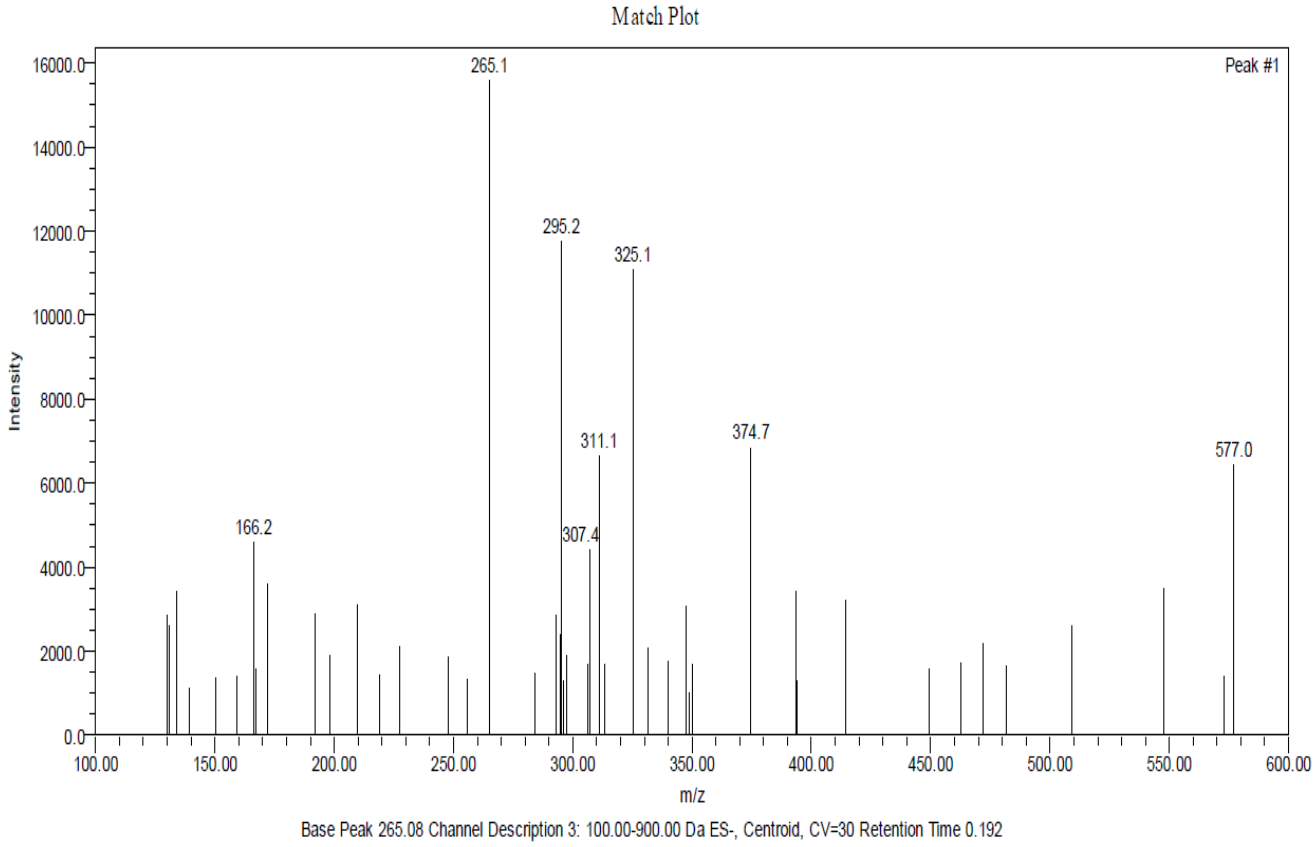
164.1
Intensity
m/z
Base Peak 192.10 Channel Description 1: 100.00-900.00 Da ES+, Centroid, CV=30 Retention Time 0.199


Match Plot
Peak #1
265.1
295.2
325.1
311.1
374.7
577.0
166.2
307.4
Intensity
m/z
Base Peak 265.08 Channel Description 3: 100.00-900.00 Da ES-, Centroid, CV=30 Retention Time 0.192

Nd-BSPA

VII. MAGNETIC MOMENTS

The magnetic moments of the complexes were measured by the Gouy's method. The room temperature magnetic moment of the solid complexes was found to be 0 BM, 2.53 BM, 3.14 BM, 3.28 BM. This indicates 0, 1, 2, 3 unpaired electrons for La(III), Ce(III), Pr(III), Nd(III) ion respectively in probably mono capped square antiprismatic [11] environment.

Spin orbit coupling is similar orbital- solenoid like magnets coupling with electron spin, bar like magnet. Furthermore, angular momentum is a characteristic of both, orbital and spin magnets. For lanthanides, spin-orbit coupling is significant. The judgment of number of unpaired electrons only from the data of magnetic susceptibility (without considering spin-orbit coupling) is not possible – table no.4 mentions usual magnetic moments ground state terms and other information of lanthanides.

VIII. ELECTRONIC SPECTRAL STUDY

Table :- 4 Orbital splitting of lanthanide and Typical colours of lanthanide [12]

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 angular momentum
La^{III}/ f^0	colorless	$^1S_0$	none	Dia magnetic	0	0
Ce^{III}/ f^1	Colorless	$^2F_{5/2}$	none	2.54	1	3
Pr^{III}/ f^2	Yellow-greenish	$^3H_4$	$^3H_5$, $^3F_2$	3.58	2	5
Nd^{III}/ f^3	Red -blue	$^4I_{9/2}$	$^4G_{5/2}$, $^4G_{7/2}$, $^2G_{7/2}$, $^2K_{13/2}$	3.62	3	6

Lanthanum (III) ion has no significant absorption in the visible region, due to the absence of 4f orbital electrons. Visible spectral bands of the lanthanide (III) complexes are hypersensitive to stereochemistry. The absorption bands of praseodymium(III), neodymiun(III) complexes in the UV and visible regions appear due to the transitions within 4f levels which are normally forbidden but may become allowed after the removal of degeneracy of 4f orbitals by an external crystal field. For other lanthanide(III) complexes, no absorption bands due to f–f transitions could be located in the visible region probably due to the fact that the f–f bands are very weak and are obscured by the intense charge transfer bands that appear in this spectral region.[13, 14] The adsorption spectra of lanthanide (III) complexes are shown in table -5 and are in conformity with the above mentioned description.

Table :- 5 Electronic spectra of complexes

Complex	Cm^{-1}	Assignment
La-BSPA	29498 34965 35842 39215 47846	Ligand and C.T. transitions
Ce-BSPA	39525.69 42918.45 44052.86	$^2F_{5/2} \rightarrow {}^2D_{5/2}$ $^2F_{5/2} \rightarrow {}^2D_{3/2}$
Pr-BSPA	29325.5 34843.2 35778.17	$^3H_4 \rightarrow {}^1L_8$ $^3H_4 \rightarrow {}^1D_2$ $^3H_4 \rightarrow {}^3P_0$

	39062.5 42826.5	$^3H_4 \rightarrow {}^1I_6$ ($^3P_1$)
Nd-BSPA	34843.2 35842.29 39062.5 44444.4	$^4I_{9/2} \rightarrow {}^2G_{7/2}$ (D_5) $^4I_{9/2} \rightarrow {}^2G_{9/2}$ (F_1) $^4I_{9/2} \rightarrow {}^2P_{1/2}$ (I_1)

IX. THERMAL ANALYSIS

Thermogravimetric 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. TGA can also provide information about chemical phenomena including chemisorptions, desolvation (especially dehydration), decomposition, and solid-gas reactions (e.g., oxidation or reduction).[15]

Table :-6 Thermo gravimetric Analysis

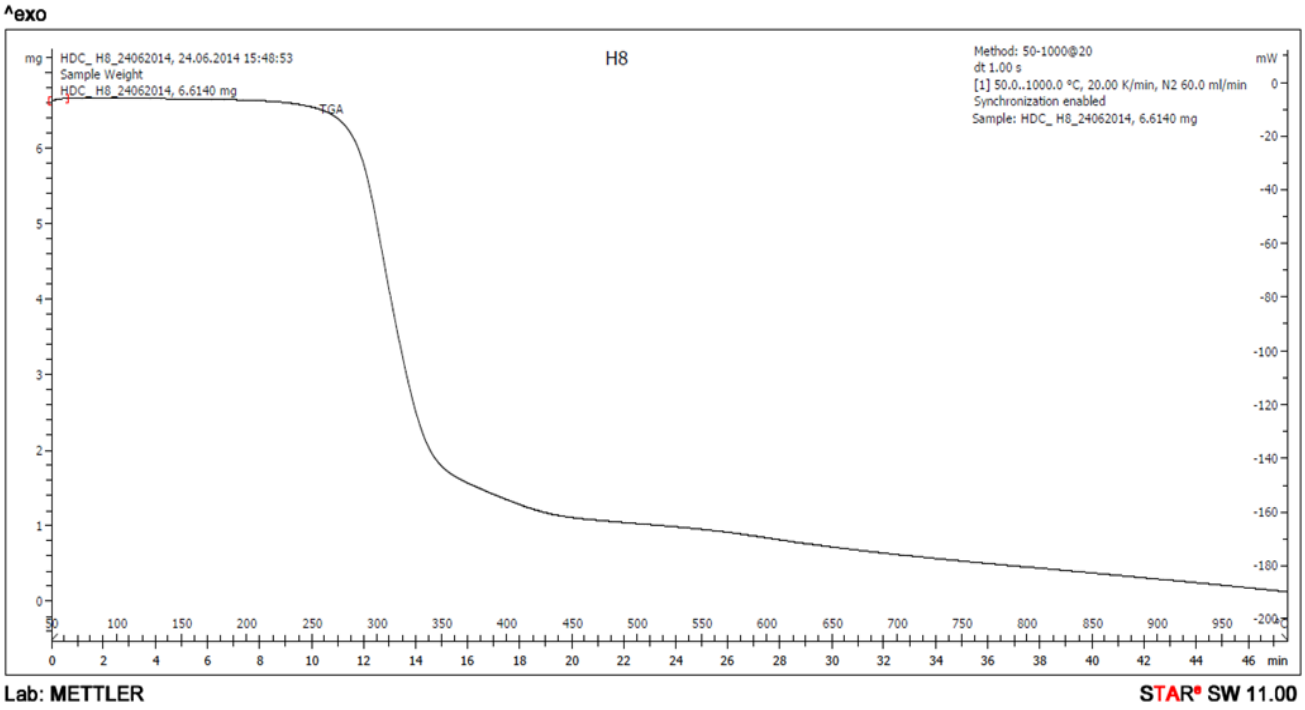
Complex	**RT-150 ^{0}C**			**150 ^{0}C – 250 ^{0}C**		
	% Loss	**Loss of weight(gm) for 1 mole complex**	**water molecules**	**% Loss**	**Loss of weight(gm) for 1 mole complex**	**water molecules**
La-BSPA	**0**	**0.00**	**0**	**2.5**	**13.07**	**1**
Ce-BSPA	**3.11**	**16.29**	**1**	**5.94**	**31.12**	**2**
Pr-BSPA	**0.33**	**1.73**	**0**	**2.67**	**14.01**	**1**
Nd-BSPA	**0.43**	**2.27**	**0**	**0.87**	**4.59**	**0**

RT = Room temperature

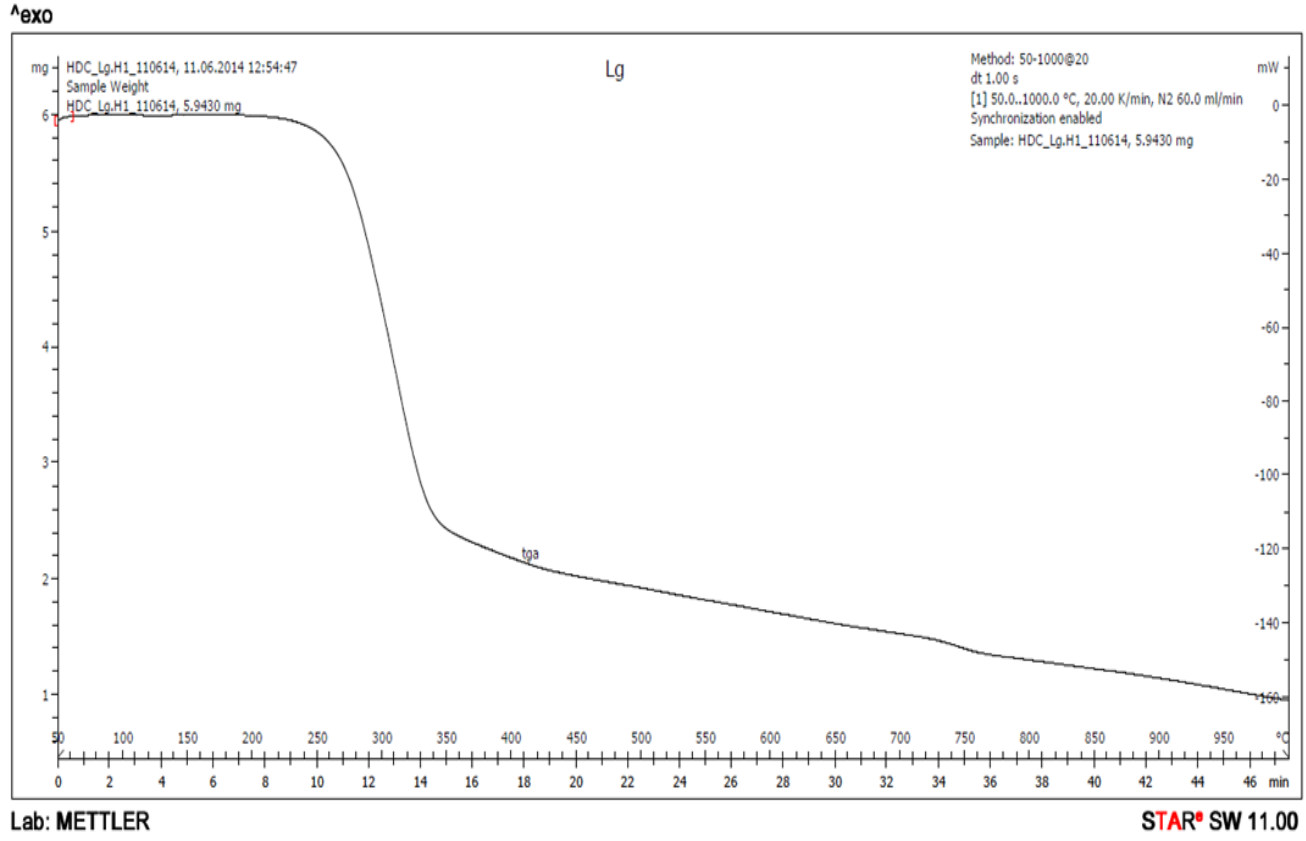
Table :- 7 Complexes and Coordination Numbers

Complexes	**Coordination number of metal in the probable structures**	**Usual coordination number * of metal ion**
La- BSPA	**9**	**4, 8-11**
Ce- BSPA	**10**	**10, 12**
Pr-BSPA	**12**	**6, 12**
Nd-BSPA	**9**	**6 - 9, 11**

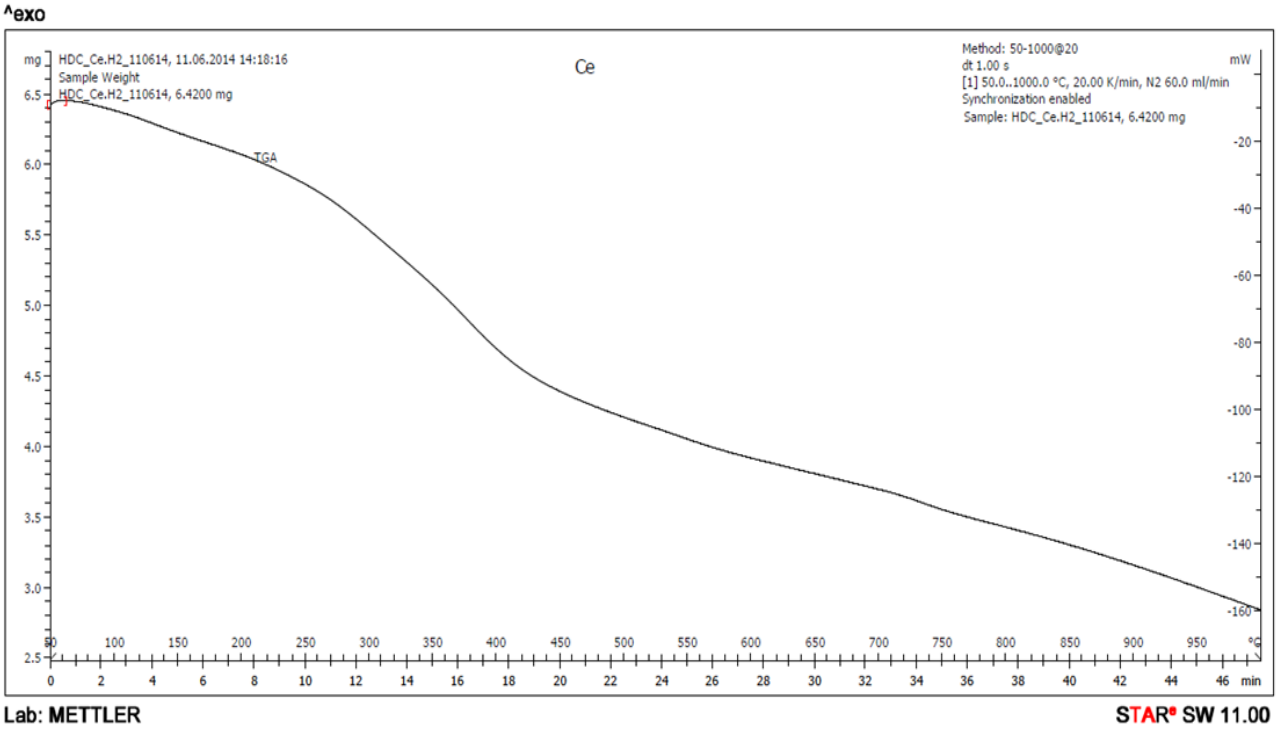
*References: - [11]



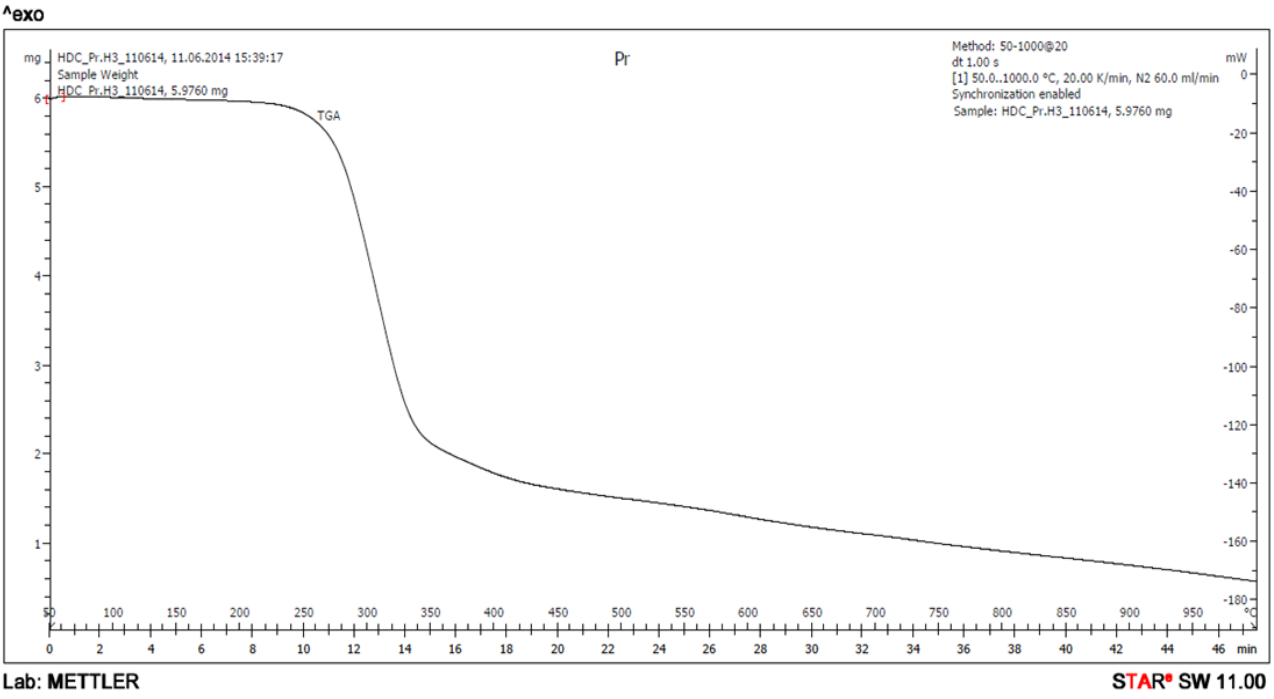
TGA of BSPA Ligand



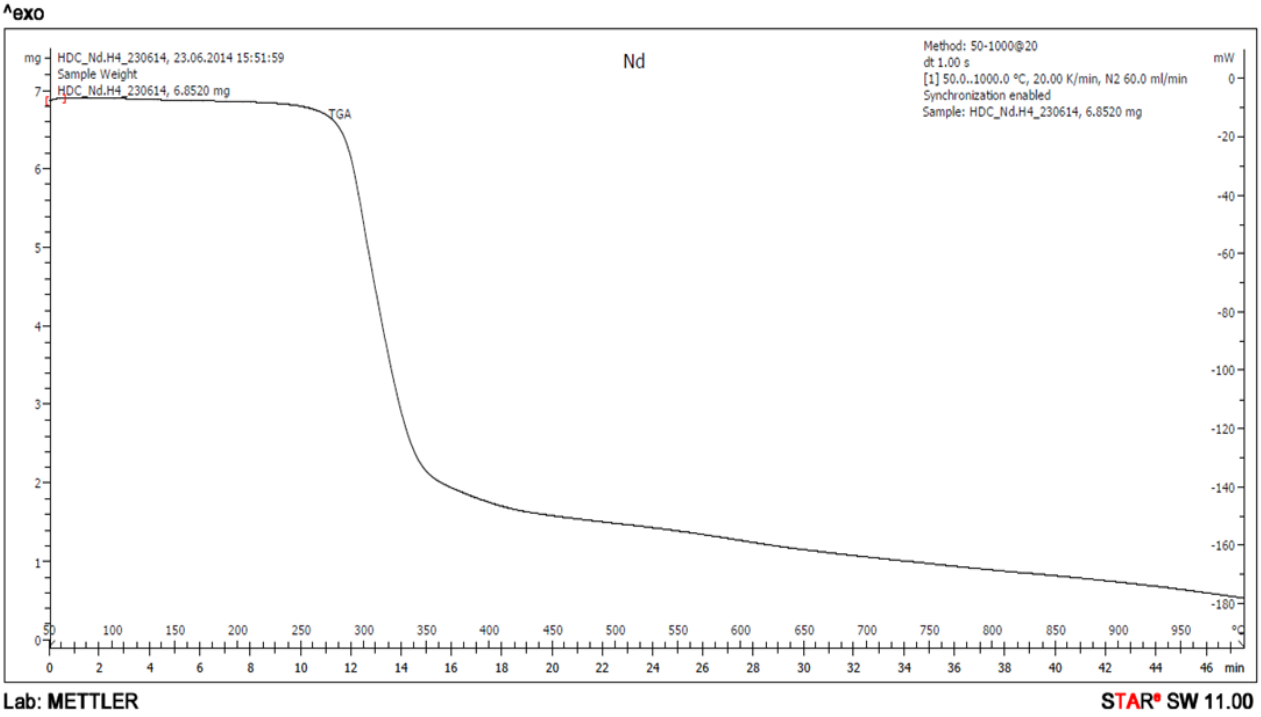
TGA of La-BSPA



TGA of Ce-BSPA



TGA of Pr-BSPA



TGA of Nd-BSPA

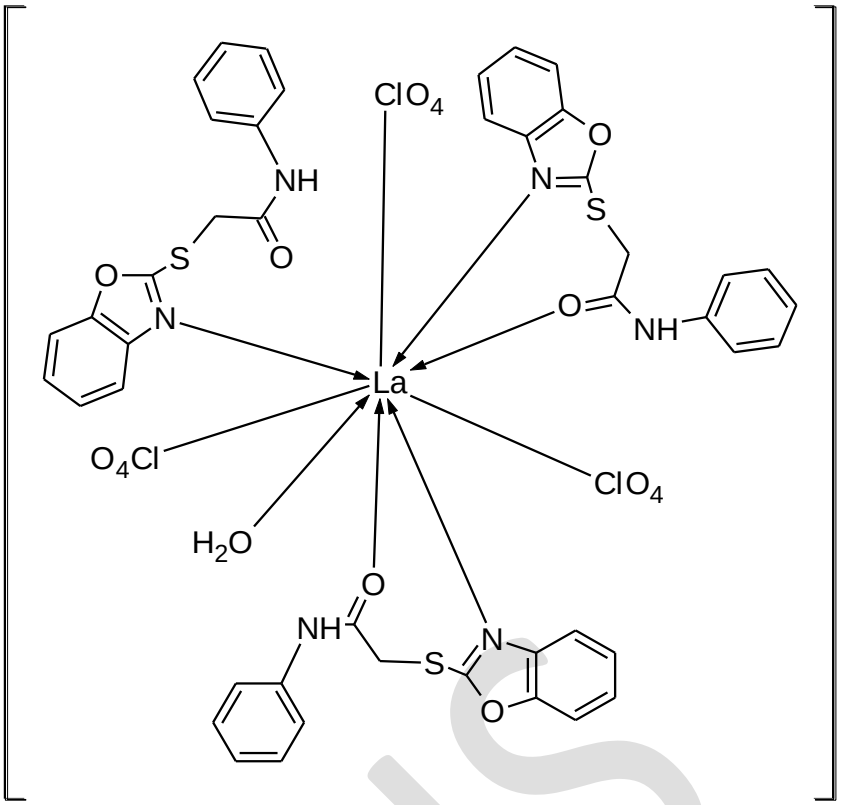
X. TGA OF COMPLEXES

It has been observed that La-BSPA, Ce-BSPA and Pr-BSPA show loss in weight corresponding to one, two and one water molecules respectively in range150 ^{0}C - 250 ^{0}C. Nd-BSPA does not show any loss in weight in the range150 ^{0}C -250 ^{0}C. This indicates that one, two and one water molecules coordinate with the La-BSPA, Ce-BSPA and Pr-BSPA but there are no water molecules that coordinate with Nd-BSPA.

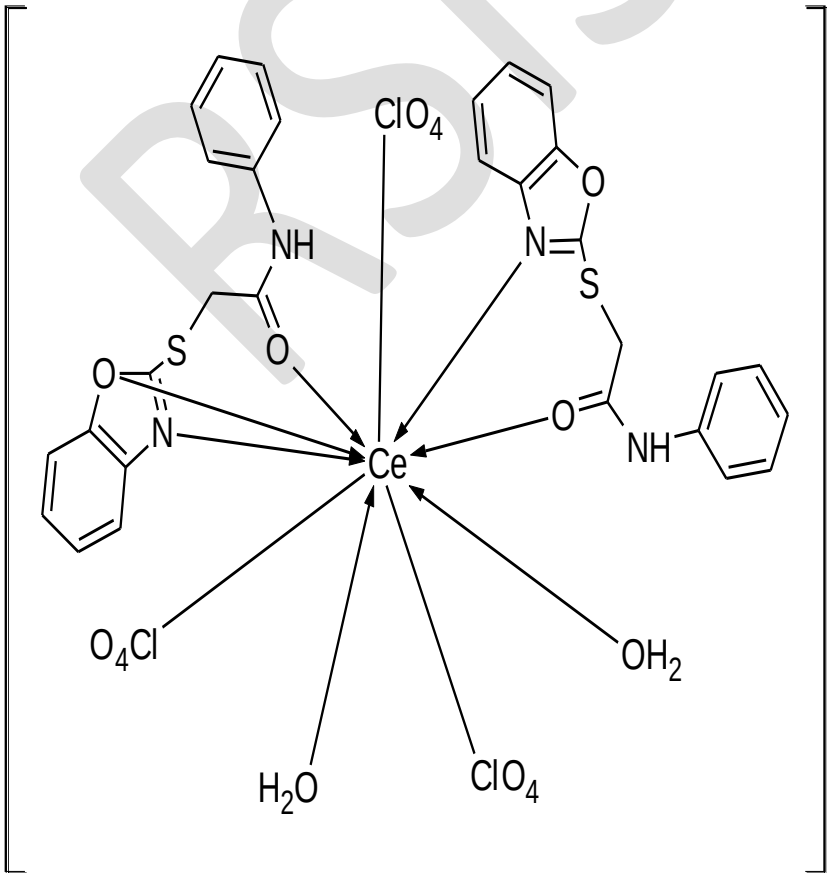
It has been also observed that Ce-BSPA lose weight corresponding to one water molecule in range of room temperature to 150 ^{0}C temperature so Ce-BSPA has one water of crystallization or water of hydration.

The values reported in this communication for Ce-BSPA are based upon the results of complexes without water of crystallization. When thermal analysis was carried out, the sample, because of its hygroscopic nature, absorbed three molecules of water from air and all the corresponding results were uniformly lower than anticipated. Therefore, the results have been expressed for the complex on dried basis which match uniformly better.

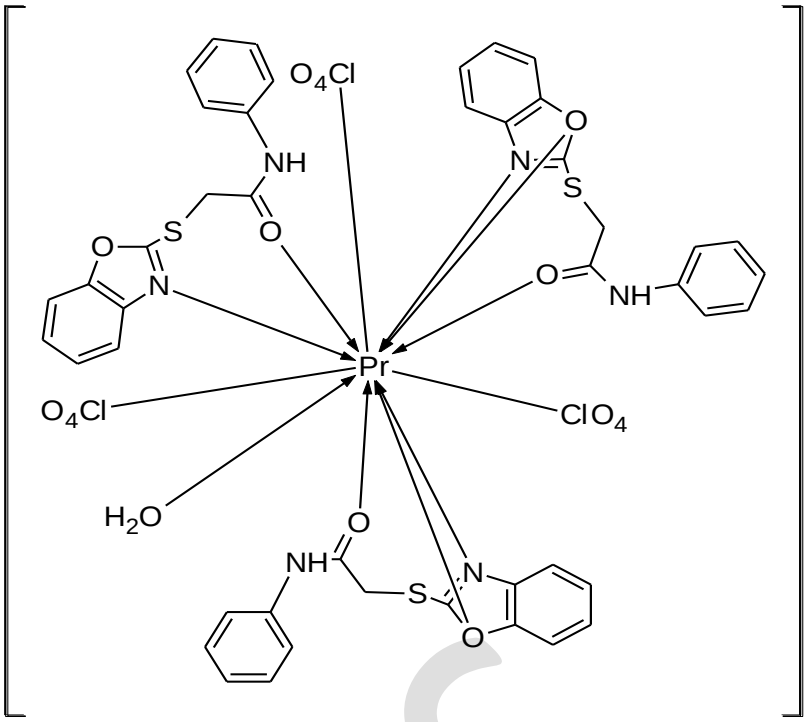
Based upon the results of physicochemical analyses their probable structures are shown in figures below.



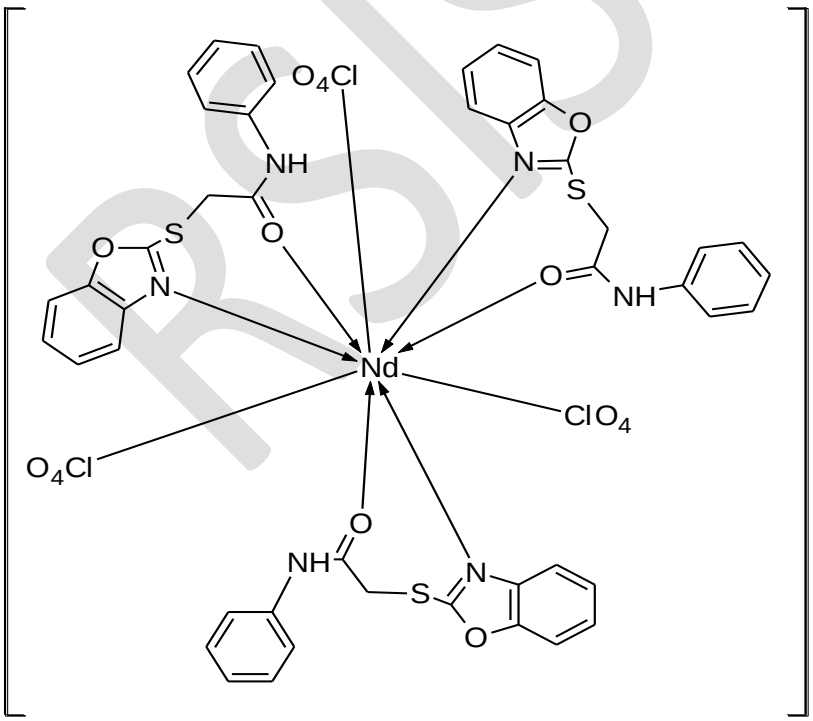
La-BSPA structure



Ce-BSPA structure



Pr-BSPA structure



Nd-BSPA structure

XI. CATALYTIC ACTIVITY

Coordination compounds are known to catalyze some reactions by heterogeneous or homogeneous processes. The complex compounds of the ligand selected showed promising performance earlier and hence in the present work they were subjected to catalytic studies for the following reactions. In these reaction 1 %(mole/mole) amount of catalyst was added

.

Reaction :- $K_2S_2O_8$ + KI

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

Reaction :- $KBrO_3$ + KI

$$KBrO_3 + HCl \longrightarrow KCl + HBrO_3$$

$$KI + HCl \longrightarrow KCl + HI$$

$$HBrO_3 + 6HI \longrightarrow HBr + 3H_2O + 3I_2$$

Reaction :- H_2O_2 + KI

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

In all the three cases, the liberated iodine was titrated with thiosulphate solution to give colourless end point from blue starch iodide complex.

Table – 8

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 – 9

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	3.04×10^{-3}
10	7.4	1.68×10^{-3}
15	7.7	1.18×10^{-3}
20	8.6	1.04×10^{-3}
25	9.0	0.9×10^{-3}
30	9.5	0.81×10^{-3}

average k = 1.44×10^{-3}

a=b=initial concentrations of reactants =0.0227M

Table – 10

Reaction kinetics table (without catalyst)

Reaction of : H_2O_2 + KI + H_2SO_4 + Methanol

Concentration : (0.0091M) (0.0091M) --

Volume : 10ml 10ml 10ml ($t\infty$ =50ml)

.

Time t (min.)	Burette reading x (ml)	k = 1/at * x/(a-x) ($lit.mol^{-1} min^{-1}$)
5	1.2	9.8×10^{-5}
10	1.7	7.03×10^{-5}
15	2.3	6.42×10^{-5}
20	2.9	6.15×10^{-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 =0.0227M

Table – 11 Overall results of catalytic activity for the lanthanoide complexes.

Reactions	k without complexes	k with La-BSPA (1 %)	k with Ce-BSPA' (1 %)	k with Pr-BSPA (1 %)	k with Nd-BSPA (1 %)	% Increase in reaction rate at T = 300 K La-BSPA	% Increase in reaction rate at T = 300 K Ce-BSPA	% Increase in reaction rate at T = 300 K Pr-BSPA	% Increase in reaction rate at T = 300 K Nd-BSPA
$K_2S_2O_8$ +KI	2.085 x10^{-5}	3.46 x10^{-5}	5.003 x10^{-5}	5.91 x10^{5}	8.85 x10^{-5}	**66**	**140**	**183**	**324**
$KBrO_3$ + HI	1.44 x10^{-3}	6.20x10^{-3}	6.665 x10^{-3}	12.125 x10^{-3}	19.17 x10^{-3}	**330**	**363**	**742**	**1231**
H_2O_2 + HI	6.78 x10^{-5}	3.49 x10^{-4}	4.06 x10^{-4}	4.045 x10^{-4}	4.68 X 10^{-4}	**415**	**499**	**497**	**590**

k = reaction rate constant for the second order reaction,

1% complex = 1 % molecular weight of the complex

1 % MW of complex = 0.043 % of mole of $K_2S_2O_8$,

1 % MW of complex = 0.10 % of mole of $KBrO_3$

1 % MW of complex = 0.11 % of mole of H_2O_2

XII. RESULTS

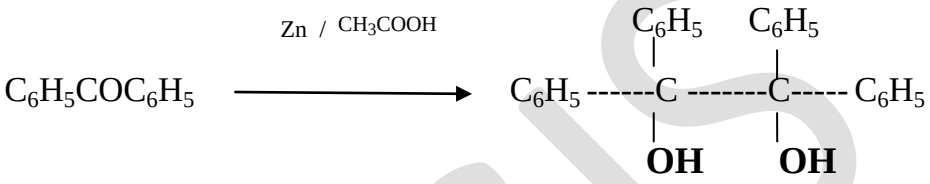
1 % addition of lanthanide complexes produced wonderful results in increasing the reaction rates up to 1231% of the un catalyzed reaction. This and other reaction accelerations are phenomenal and these complexes can be explored for industrially important redox reactions in bulk.

XIII. CATALYSIS OF ORGANIC REACTION

The catalyst is one type of molecule which facilitates the reaction. In homogeneous catalysis, the reactant (s) coordinate to the catalyst (or vice versa), are transformed to product, which are then released from the catalyst [16].

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 and cooled. The separated benzpinacol is filtered and crystallized from glacial acetic acid. The yield normally obtained would be around 4.5 gm (30%).

The product melting point is 188-189 ^{0}C.



Benzophenone **Benzpinacol**

Table:- 11 Percentage yield without catalyst for different reaction times

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: - 12 Percentage yield with catalyst metal complexes for 2 hours

Temperature = 368 K

Complexes	For 1 % catalyst, yield obtained	For 5 % catalyst, yield obtained	For 10 % catalyst, yield obtained
La-BSPA	33 %	45 %	64 %
Ce-BSPA	30 %	47 %	72 %
Pr-BSPA	28 %	53 %	77 %
Nd-BSPA	26 %	42 %	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

XIV. RESULTS AND DISCUSSION

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] Accurately weighed amount of catalyst, was added in solid form into the reaction mixture. The reaction was carried out with identical conditions for added and without catalyst. La-BSPA, Ce-BSPA , Pr-BSPA and Nd-BSPA acted as homogeneous catalysts in the above reaction. It was observed that addition of all the complexes in catalytic amounts drastically reduced the time requirement as well as increased reaction rate and percentage yield within the same duration. Order of effectiveness as catalyst found was Pr-BSPA > Ce-BSPA > Nd-BSPA > La-BSPA.

Antimicrobial activity

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

Table :13 - 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

Table :-14 Antibacterial activity of BSPA Ligand d and its complexes

ANTIBACTERIAL ACTIVITY TABLE					
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	BSPA	200	200	100	125
2	La- BSPA	200	250	200	250
3	Ce- BSPA	250	500	100	125
4	Pr- BSPA	250	250	250	250
5	Nd- BSPA	125	250	125	200

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. Ligand,

Ce-BSPA and Nd-BSPA complexes show antibacterial activity higher than ampicillin against *S.aureus.*

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. The results of the compounds synthesized taken for antifungal screening are mentioned as under.

Table:-15 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 BSPA ligand 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	BSPA	500	1000	>1000
2	La- BSPA	250	1000	1000
3	Ce- BSPA	250	1000	1000
4	Pr- BSPA	500	500	1000
5	Nd- BSPA	500	1000	1000

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. La-BSPA and Ce-BSPA complexes show better activity against *C.albicans* compared to greseofulvin. The actyivity of these complexes is even better than the ligand itself.

XV. CONCLUSION

In an attempt to prepare new materials in the form of coordination compounds, BSPA ligand was synthesized, purified and it was allowed to react with perchlorates of La $^{3+}$ and three other lanthanide ions. These new complexes were characterized by spectroscopic methods. These were subjected to catalytic studies and were found to be excellent catalysts that increased the reaction rates very efficiently. As far as antimicrobial activities are concerned, some of them showed better anti bacterial and anti fungal activities. In all, the new complexes bear great potential as industrially useful technology material.

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