## Synthesis and Bio-chemically Characterization studies on Ho<sup>3+</sup> Complex with banzoxazole derivative ligand

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Abstract: - The combination of some rare metal ion with an important 2-(1,3-benzoxazole -2-yl - sulfanyl )-Nphenyl acetamide (BSPA) ligand to form coordination compound is an important area of current research. Less explored and biologically important BSPA ligand is allowed to react with solution of some rare metal perchlorate and attempt have been made to synthesize solid Ho-BSPA complex. These 2-(1,3-benzoxazole-2-ylsulfanyl)-N-phenyl acetamide complex is subjected to U.V visible spectroscopy, IR spectroscopy, TGA analysis and elemental analysis. Antimicrobial activity of these complex has been evaluated by standard methods and attempts have been made to correlate structural characteristics with properties of these BSPA complex.

Keywords: - 2-(1,3-Benzoxazole-2-yl-sulfanyl)-N-phenyl acetamide complex, catalysis, antimicrobial activity.

#### INTRODUCTION

The rare-earth metals are, by definition, the Group IIIb elements Sc, Y, La and the 14 lanthanides Ce-Lu. [1,2] The term 'rare earth' has often been applied in the more restricted sense as synonym for the lanthanides, thus excluding Sc, Y and La. An important example can be found in the magnetic properties of the lanthanides the complex, [1,2] 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.[1,2] The structure of rareearth metal surfaces however, the same can not be said of the 5f electrons in the actinides due to the greater spatial extent of their wave functions. In this respect, the actinides bear more resemblance to the d-block transition metals than they do to the lanthanides. Thus, treating the rare-earth elements as a group distinct from the rest of the periodic table is a reasonable practice. [1,2]

#### EXPERIMENTAL

A definite volume of 70% acid was diluted with water to obtain 0.2M perchloric acid solution. The exact strength was determined by pH metric titration against previously standardized 0.2M NaOH solution. 75 ml 0.2M perchloric acid was taken and excess solid metal carbonate was added. The solution was stirred for 30 minutes and filtered (this way 0.133 M lanthanide was obtained). The formation of complex was carried out by mixing 75 ml 0.133 M metal perchlorate solution and 50 ml 0.2 M ligand in DMSO solution. The mole ratio of ligand and metal was (1:1).

The reaction mixture was refluxed for 3.0 hours at 95 <sup>0</sup>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. The complex was dried in oven at 40°C to 50°C.

## ANALYSES AND PHYSICAL MEASUREMENTS

M.P. and TLC were taken with usual apparatus [solvent system for TLC 70% V/V toluene + 30% V/V methanol]. TLC indicated single spot confirming complex formation. Elemental analyses were performed with a Vario-MICRO CUBE C, H, N, S analyzer. The metal content was determined by titration with a solution of standardized disodium salt

of EDTA [3]. Magnetic susceptibilities were measured by the Gouy's method. [4], at room temperature using Hg[Co(CNS)<sub>4</sub>]as calibrant. The IR spectra were recorded on a BRUKER ALPHA FT-IR 400 – 4000 cm<sup>-1</sup> spectrophotometer. The UV – visible spectra were measured on a UV-1800 Shimadzu (Double beam) spectrophotometer. Thermal measurements were performed using a METTLER TOLEDO STAR<sup>e</sup> system TGA/DSC1(1150<sup>o</sup>C) thermal analyzer. The mass spectra analyses were performed with a model QDA of Waters and Alliance 2690 analyzer. The physical data of the complex and ligand are presented in the table no.2. The Ho(III) complex is colored while BSPA is colorless. The melting point of ligand is different than the complex. The TLC of solid was carried out using silica gel as the stationary phase and toluene: methanol (7:3 V/V) as the mobile phase. The Rf value of complex is different than ligand. Together, all these provide confirm formation of single complex in the present case. The molar conductance of the complex is quite low and this complex is nonionic.

Sr				Molar	Mole.	Uv – vis		Magn		Elemental Analysis				
	Compound	M.P	Rf	Cond.	weight	spectral	Color	Volor Sus	% C	% H	% N	%Cl	% M	
Ν	Name	(0C)	value	mho	gm	λmax		(PM)	Cal.	Calc.	Cal.	Cal.	Cal.	
0.				cm-1	mol-1	(nm)		(BM)	(Fou.)	(Fou.)	(Fou.)	(Fou.)	(Fou.)	
1	BSPA	127	0.72	0.43	284.33	349.5, 286.5, 279, 255.5, 240.5, 226.5,	Creamy White		63.01 (63.30)	4.09 (4.22)	9.94 (9.85)			
						208.5								
2	Ho-BSPA	118	0.59	0.388	1352.42	336.5, 299, 252, 234.5, 215.5	light orange	10.37	44.73 (40.02)	3.63 (3.00)	6.18 (6.21)	 (7.87)	18.35 (12.19)	

Table -2 Physical characterization of BSPA ligand and its Complex

Mole. = molecular, Mag. Sus.= Magnetic susceptibility, Cal. = calculated, Fou. = Found, Cond. = conductance, %M carried out by EDTA titration method, \*Solvent system for TLC = 70% V/V toluene + 30% V/V methanol,

### INFRARED SPECTRA STUDY

IR bands corresponding to BSPA and its complexes are shown in table no.3. The IR spectra of ligand and metal complexes were recorded in the 4000-400cm<sup>-1</sup>

<sup>range</sup> using KBr pellet. IR spectral analysis confirms the presence of characteristic groups in the compound. In the ligand bands, at~3344 and 3333 cm<sup>-1</sup> is assigned to the

v(N-H) stretching of the amine group. The sharp band at 1598cm<sup>-1</sup> can be attributed to the v(C=N)stretching mode in the ligand. This band is shifted in the complex. This indicates participation in coordinate bond. The band at 1675cm<sup>-1</sup> of the ligand is due to the C=O stretching. In the Ho-BSPA, it is shifted to indicating the coordination by the carbonyl-oxygen atom.

Further conclusive evidence of coordination of this ligand with metal ion was shown by the appearance of weak low frequencies new bands at 650-750cm<sup>-1</sup> and 450-510cm<sup>-1</sup>. These were assigned to the metal nitrogen (M-N) and metal oxygen (M-O) vibration respectively, and were observed in the spectra of the metal complexes and not in the spectra of the ligand. [5].

Thus it confirms that 'N' and 'O' atoms of heterocyclic ring and oxygen of carbonyl participate in coordination.

Compound	v[Ar(C-H)] stre.	v(C=N ) stre.	v(C=O ) stre.	v(N-H) stre.	v(M- N) stre.	v(M- O) stre.	v(M-Cl) stre.	v(C-O-C) stre.	v(C- S) stre.	ClO <sub>4</sub> Bending vibrations	Scissoring and other bending Vibrations
BSPA	2912 2978	1440 1454	1598 1675	3529 3671				1236 1251	757 781 807 858		1454- CH <sub>2</sub> Scissoring 1369- wagging and twisting
Ho-BSPA	3048	1497	1547 1600 1635 1660	3586	691 754	451 457 465 479 510	510	1250	838	Stre 1111 bend - 691	1547- CH <sub>2</sub> Scissoring 1330- wagging and twisting

Table -3 IR spectra of BSPA and its complex

(1) \*Metal –Sulphur stretching (below 300 cm<sup>-1</sup>) could not be measured by the instrument

(2) All figures are in cm<sup>-1</sup>

(3) bend = bending and stre.= stretching

# ELECTRONIC SPECTRA AND MAGNETIC STUDIES

The Ho-BSPA is analyzed for UV- Visible spectra and magnetic moments. These f-block metals have 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 paramagnetic nature of the complexes along with metal to ligand charge transfer band. [6,7] The room temperature magnetic moment of the solid Ho-BSPA was found to be 10.37 BM. This indicates four unpaired electrons per Ho (III) ion in possibly distorted trigonal prism [8] environment.

 $\text{Ho}^{3+}$  is the only one of the rare earths for which resolved nuclear hyperfine structure has been observed in the optical spectra. The separation of the eight components is of the order of magnitude 0.2 cm<sup>-1</sup> and varies slightly from line to line showing that the lower and upper states are both involved. [9]

 Table :-4
 Literature information: Electronic structure and Magnetic properties

Ion/ Configurati on	Colour of common salts	Ground State term Excited state levels of hypersensitive transitions		Usual Magnetic moment values (B.M)	Number of unpaired electrons	Total orbital angular momentum
HoIII/ f $^{\rm 10}$	yellow	<sup>5</sup> I8	<sup>5</sup> G <sub>6</sub> , <sup>3</sup> H <sub>6</sub>	10.60	4	6

Reference: - [10]

 Table :-5
 Electronic spectra of complex

Complex	Cm <sup>-1</sup>	Assignment
	29717.6	${}^{5}I_{8} \rightarrow {}^{3}K_{6}$ (P <sub>1</sub> )
	33444.8	
Ho-BSPA	39682.5	${}^{5}I_{8} \rightarrow {}^{3}D_{3}$ (Q <sub>5</sub> ), ${}^{3}L_{8}$
	42643.9	${}^{5}\mathrm{I}_{8} \rightarrow {}^{3}\mathrm{I}_{6}$ (W <sub>0</sub> )
	46403.7	${}^{5}I_{8} \rightarrow {}^{5}G_{5}$ (J <sub>0</sub> )

## THERMAL ANALYSIS

Thermal analysis of metal complex is carried out by thermo gravimetric analyzer. The heating was carried out until there was no further loss in weight (up to ~1000  $^{0}$ C). Change in weight was recorded with time. A regular temperature change makes possible to plot a

graph of weight as a function of temperature Thermo grams were analyzed by increasing the temperature at a uniform rate of 10 <sup>0</sup>C minute<sup>-1</sup>. The temperature range wise percentage weight loss data of metal complexes are shown in table no-6.

Loss in weight of the sample between room temperature and approximately, upto 150  $^0\!C$  –

correspond to water of crystallization. Loss in weight of the sample between approximately 150 °C to 250 °C corresponds to loss in weight due to water of coordination. After approximately 800 °C, almost constant weight is observed. This is due to oxide of corresponding metal hence (provided that oxide is not volatile) from this constant weight, percentage of metal can be obtained.

Table :- 6 TGA data of BSPA and Ho-BSPA

Complex	Coordination number	Usual coordination number * of		
Complex	of metal in the probable structure	metal ion		
Ho-BSPA	8	8		
DT D				

RT = Room temperature

Table :-7 Complex and Coordination numbers

		RT-150 °C		150 °C - 250 °C			
Compound	% Loss	Loss of weight(gm) for 1 mole complex	Corresponding water molecules	% Loss	Loss of weight(gm) for 1 mole complex	Corresponding water molecules	
BSPA ligand	0.15	0.42	0	1.50	4.28	0	
Ho-BSPA	1.70	9.33	0	8.03	44.06	2	

Reference: - [11]



TGA spectrum of BSPA Ligand



TGA spectrum of Ho-BSPA

It has been observed that Ho-BSPA shows loss in weight

corresponding to two water molecules in range 150 C-

250 °C. This indicates that two water molecules coordinate with the Ho-BSPA respectively but there are no water molecules of crystallization.

When thermal analysis was carried out, the sample, because of its hygroscopic nature, absorbed water molecules from air and all the corresponding result was uniformly lower than anticipated. Therefore, the results have been expressed for the complex on dried basis. This hygroscopic complex was dried at 50 <sup>o</sup>C for 90 minutes in oven to remove absorbed water.

#### Mass spectroscopy

The most common use of mass spectrometry by the organic chemist is for the accurate determination of molecular weight and from that molecular formula so is the case for the inorganic chemist. A second important use is to provide information about the structure of compound by an examination of the

fragmentation pattern and also from the relative intensities of M+1, M+2, M+4 peaks.[12,13] The information and interpretation of mass spectra is shown below.

### Ho- BSPA

Probable (Metal + Ligand) peak – 449 amu

Base peak (B. P. ) - 211.2 amu (ES+) , 331.1 amu (ES-)

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

Peak., peak. +2, peak. +4 (ratio 3:3:1) in certain fragments therefore 3 chlorine atoms may be present in the fragment and the molecule.

Metal + Ligand - Ph - (ES-) peak = 370.0 amu

Ligand - Ph + (ES+) peak = 211.2 amu

Metal + Ligand - 1,3-benzoxazole peak = 331.1 amu Molecular weight of the complex is higher than 1000 amu, the mass spectra are taken upto 600 amu only. The fragments present in the spectra largely confirm the probable structures proposed.



Mass Spectrum of Ho-BSPA

Based upon all the experimental data of physico chemical analyses, the most structures of the metal complexes can be shown as below.



Ho-BSPA structure

Usual laboratory tests (M.P., U.V-visible spectra, TLC, Colour, molar conductance etc.) confirmed formation of coordination compound which was finally characterized by (IR, Mass, TGA etc.). Electronic spectra and magnetic moment values gave information regarding number of unpaired electrons, spin –orbit coupling, charge transfer bands, probable geometry etc. Combining all this information, the tentative structure was assigned to the new complex.

#### CONCLUSION

Rare metals and their compound own a wide variety of properties. With a view to discovering them, holmium ion and the ligand BSPA were chosen. The selection of the BSPA ligand was based upon the possibility of complex formation through contribution of electron pair by any two/ three/ more atoms out of two nitrogen atoms, two oxygen atoms and one Sulphur atom of the ligand. There exists a option of isomerism also and difference in structures can make possible a huge variation in bio- chemical properties. The complex exhibited highly promising catalytic effects which can very easily be applied upon suitable industrial reactions. Likewise, some antimicrobial activities values showed better performance that could be further explored.

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