IJCRT.ORG ISSN : 2320-2882

INTERNATIONAL JOURNAL OF CREATIVE RESEARCH THOUGHTS (IJCRT)

An International Open Access, Peer-reviewed, Refereed Journal

Antimicrobial and Kinetic studies of Ho^{3+} Complex with banzoxazole derivative ligand

Dr. Haresh R. Patel[1], H. D. Chaudhari[2]

[1]Department of Chemistry, Merchant B.Sc. & M.Sc. College, Basna, Gujarat, India

[2] Department of Chemistry, Adarsh Science College, Patan, Gujarat, India

Email:- [1]hareshpatel6900@yahoo.com ,[2]haresh09032007@gmail.com

Abstract: -

The combination of some rare metal ion with an important 2-(1,3-benzoxazole -2-yl - sulfanyl)-N-phenyl 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-yl-sulfanyl)-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.

1. Introduction: -

The rare–earth metals are, by definition, the Group IIIb elements Sc, Y, La and the 14 lanthanides Ce–Lu. The term ‘rare earth’ has often been applied in the more restricted sense as synonym for the lanthanides, [1,2] 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]

2.0 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 ^{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. The complex was dried in oven at 40^{0}C to 50^{0}C.

2.1 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 $Hg[Co(CNS)_4]$as calibrant. The IR spectra were recorded on a BRUKER ALPHA FT-IR 400 – 4000 cm^{-1} spectrophotometers. 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.

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

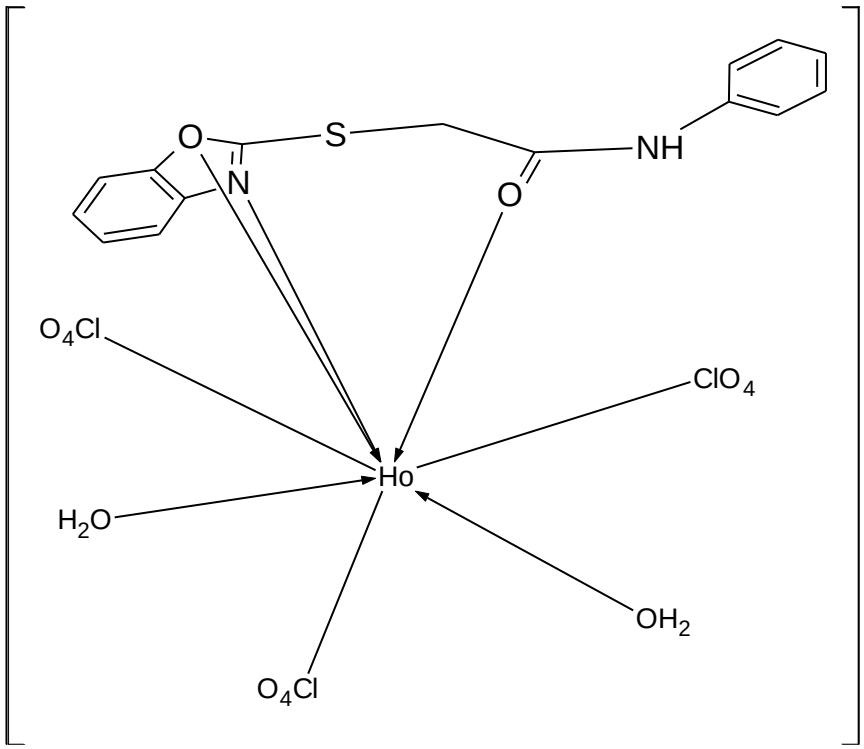


Figure: -1 Ho-BSPA structure

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.

2.3 Chemical Kinetics

Based upon the results of kinetic experiments carried out earlier, it was thought worthwhile to employ Ho-BSPA as probable catalyst. [5]

Reaction 1:-

The experiment was carried out with two reacting species $K_2S_2O_8$ and KI using their equal concentrations. This reaction is carried out as under gives the kinetic data without addition of any catalyst.

Table – 1 Reaction kinetics (without catalyst):

Reaction of	:	$K_2S_2O_8$	+ KI +	Methanol
Concentration	:	(0.0227M)	(0.0227M)	--
Volume	:	50ml	50ml	10ml

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

t_∞ =113.5 ml

Reaction:-

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

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

Table – 2 Reaction kinetics table without catalyst

Reaction of : $KBrO_3$ + KI + HCl + Methanol

Concentration : (0.0096M) (0.0096M) --

Volume : 25ml 25ml 10ml 10ml

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 = 25 ml

t∞ = 25ml

Reaction :-

$KBrO_3 + HCl \longrightarrow KCl + HBrO_3$

$KI + HCl \longrightarrow KCl + HI$

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

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

Table – 3 Reaction kinetics table without catalyst

Reaction of : H_2O_2 + KI + H_2SO_4 + Methanol

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

Volume : 10ml 10ml 10ml

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 = 50 ml

t∞ =50ml

Reaction:-

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

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

Table :- 4 Overall Results of catalytic activity for the addition of Ho-BSPA

Reactions	k without Complex	k with Ho-BSPA (1%)	% Increase reaction rate at T = 300 K Ho-BSPA
$K_2S_2O_8$ + KI	2.085×10^{-5}	5.10×10^{-5}	145
$KBrO_3$ + HI	1.44×10^{-3}	10.82×10^{-3}	651
H_2O_2 + HI	6.78×10^{-5}	3.13×10^{-4}	362

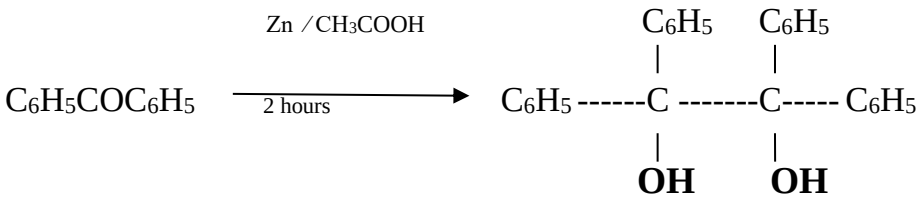
k = reaction rate constant for the second order reaction, 1% complex = 1 % molecular weight of the complex

1 % MW of Ho-BSPA = 0.0135 gm Ho-BSPA ≡ 0.043 % of mole of $K_2S_2O_8$ ≡ 0.104 % of mole of $KBrO_3$ ≡ 0.11 % of mole of H_2O_2.

2.3.1 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 [5].

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 crystallized from glacial acetic acid. [6] The yield is 4.5 gm (30%). (M.P. 188-189 ^{o}C)[6]



Benzophenone **Benzpinacol**

Table:- 5 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	55.55%	30.00 %

Table :-6 Percentage yield with catalyst metal complex (for 2 hours reaction time)

Temperature = 368 K (yield without catalyst is 30%)

Complex	% yield for 1%catalyst addition	% yield for 5%catalyst addition	% yield for 10%catalyst addition
Ho-BSPA	23.77	42.66	68.44

1%MW of complex (catalyst) ≡ 0.0243 % of mole of benzophenone

5%MW of complex (catalyst) ≡ 0.121 % of mole of benzophenone

10%MW of complex (catalyst) ≡ 0.243 % of mole of benzophenone

2.3.2 Results and Discussion of Catalysis Experiment: -

The benzpinacol formation reaction was carried out with identical conditions. Here, Ho-BSPA also successfully acted as homogeneous catalysts. It was observed that addition of the complex in catalytic amounts increased the yield. The most possible cause of lower yield on addition of 1% catalyst in each case

seems to be due to the solvent methanol. When complex was added in the reaction system, the yield increased significantly and hence there is a great chance that some of this complex can increase the yield of an industrially important reaction by saving time, energy and consequently money.

2.4 Antibacterial activity:

This part deals with the in-vitro screening of the complex 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 carried out for the in-vitro screening for antibacterial activity.[7,8] The results of the compound employed for antibacterial screening are mentioned in following Table.

Table:-7 Antimicrobial activity of Standard drugs

Standard Drugs				
Minimum Inhibition Concentration (µg/ml)				
Drugs	***E.coli***	***P.aeruginosa***	***S.aureus***	***S.pyogenes***
µg/ml	**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:-8 Antibacterial activity of BSPA Ligand and its Complex

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	BSPA	200	200	100	125
2	Ho-BSPA	200	250	500	250

Comparison of antimicrobial activity of produced compounds with that of standard antimicrobial drugs reveals that the synthesized compound show moderate to good activity against all four bacterial strains.

2.5 Antifungal activity:

This part deals with the in-vitro screening of newly prepared compound for antifungal 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.[8] The results of the compound for antifungal screening are mentioned in following table.

Table:-9 Antifungal Activity of Standard Drugs

Minimal Inhibition Concentration (Standard drugs)			
DRUGS	***C.albicans*** **MTCC 227**	***A.niger*** **MTCC 282**	***A.clavatus*** **MTCC 1323**
mg/ml			
NYSTSTIN	100	100	100
GRESEOFULVIN	500	100	100

Table:-10 Antifungal activity of BSPA ligand and its Complex

Antifungal Activity Table				
Minimum Fungicidal Concentration µg/ml				
Sr. No.	**Code No.**	***C.albicans*** **MTCC 227**	***A.niger*** **MTCC 282**	***A.clavatus*** **MTCC 1323**
1	BSPA	500	1000	>1000
2	Ho-BSPA	250	1000	>1000

Comparison of antimicrobial activity of produced compounds with that of standard antimicrobial drugs reveals that the prepared complex show moderate to good activity against all three fungal strains.

2.5.1 Result and Discussion: -

The selected antibiotics exhibited greater activities compared to the antibacterial performance of the holmium complex. The antifungal activities of the complex were found to be less than that of standard antifungal antibiotic drugs.

2.6 Conclusion: -

Rare metals and their compound possess a wide variety of properties. With a view to exploring them, holmium ion and the ligand BSPA were chosen. The selection of the BSPA ligand was based upon the possibility of complex formation through donation 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 possibility 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.

2.7 Acknowledgements

Authors thank the Department of Chemistry, Hemchandracharya North Gujarat University, Patan, Gujarat, India, for Laboratory facilities and spectral analyses. We are also thankful to Microcare Laboratory, Dr. D.P. Rajani, Surat, India, for the antimicrobial activity.

References: -

1. Heiserman, David L. "Piezoelectric polymer micromanipulator." U.S. Patent No. 4 (1986) 610,475.
2. Greenwood, N. N. “Ludwig Mond Lecture. Taking stock: the astonishing development of boron hydride cluster chemistry”. Chem. Soc. Rev., 21(1), (1992) 49-57.
3. Satyendra, R. V., Vishnumurthy, K. A., Vagdevi, H. M., Rajesh, K. P., Manjunatha, H., and Shruthi, A. “Synthesis, in vitro antioxidant, anthelmintic and molecular docking studies of novel dichloro substituted benzoxazole-triazolo-thione derivatives. European journal of medicinal chemistry, 46(7),. (2011) 3078-3084.
4. Paramashivappa, R., Kumar, P. P., Rao, P. S., and Rao, A. S. “Design, synthesis and biological evaluation of benzimidazole/benzothiazole and benzoxazole derivatives as cyclooxygenase inhibitors”. Bioorganic and medicinal chemistry letters, 13(4),. (2003) 657-660.
5. Hattori, H.. “Heterogeneous basic catalysis. Chemical Reviews, 95(3), (1995) 537-558.
6. Ahluwalia, V. K., Bhagat, P., Aggarwal, R., and Chandra, R. “Intermediates for Organic Synthesis”, IK International Pvt. LTd, New Delhi, (2005) 336.
7. Fiore, C., Eisenhut, M., Krausse, R., Ragazzi, E., Pellati, D., Armanini, D., and Bielenberg, J. “Antiviral effects of Glycyrrhiza species”. Phytotherapy research, 22(2), (2008).141-148.
8. Abbracchio, M. P., Abou-Donia, M. B., Accomazzo, M. R., Adams, A. D., Agyeman, A. S., Aird, R., and Alvesalo, J. available at www. sciencedirect. com. biochemical pharmacology, 71, (2006).1765-1769.
9. Doshi, A., Zaheer, A., and Stiller, M. J. “Methods for assessing erythema: a critique of parametric and nonparametric techniques”. International journal of dermatology, 36(5), (1997).334-337.