IJRAR.ORG E-ISSN: 2348-1269, P-ISSN: 2349-5138

INTERNATIONAL JOURNAL OF RESEARCH AND ANALYTICAL REVIEWS (IJRAR) | IJRAR.ORG
An International Open Access, Peer-reviewed, Refereed Journal

Spectroscopic and Characterization studies of Sm^{3+}rare metal Complex with benzoxazole derivative ligand

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

[1]Department of Chemistry, Merchant Science College,Basna, Gujarat, India

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

Abstract: -

The mixture of some rare metal ions with an important 2-(1,3-benzoxazole -2-yl - sulfanyl)-N-phenyl acetamide (BSPA) ligand to form coordination complex is an important area of current research. Less explored biologically important 2-(1,3-benzoxazole -2-yl - sulfanyl)-N-phenyl acetamide ligand is allowed to react with solution of some rare metal perchlorate and attempt has been made to synthesize solid 2-(1,3-benzoxazole -2-yl- sulfanyl)-N-phenyl acetamide complexes. These 2-(1,3-benzoxazole-2-yl-sulfanyl)-N-phenyl acetamide complex are subjected to U.V Visible Spectroscopy, IR Spectroscopy, TGA Analysis, elemental analysis of Sm^{3+} complex has been evaluated by standard methods and attempts have been made to correlate structural characteristics with properties of these 2-(1,3-benzoxazole -2-yl - sulfanyl)-N-phenyl acetamide complex.

Keywords: -

Spectroscopic analysis, characterization, 2-(1,3-Benzoxazole-2-yl-sulfanyl)-N-phenyl acetamide(BSPA) complex,

1.0 Introduction

The rare–earth metals are by definition, the group IIIb elements Sc, Y, La and the 14 lanthanides Ce–Lu. [1,2]

2.0 Experimental

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 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 complexes was carried out by mixing 75 ml 0.133 M metal perchlorate solution and 50ml 0.2 M BSPA 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 Rare metal of the complexes

Sr. No.	Ligand or Complexes	Brief name
1	Ligand BSPA	BSPA
2	Sm(III)-BSPA	Sm-BSPA

2.1 Analyses and Physical Measurements

M.P. and TLC were taken with usual apparatus[solvent system for TLC 70% toluene + 30% 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.

Table -2 Physical characterization of BSPA ligand with Sm^{3+} Complexes

Sr. No.	**Compound Name**	**M.P (^{0}C)**	**Rf value**	**Molar Cond. mho cm^{-1}**	**Mole. weight gm mol^{-1}**	**Uv – vis spectral λmax (nm)**	**Color**	**Magn. Sus. (BM)**	**Elemental Analysis**											
									% C		**% H**		**% N**		**% S**		**%Cl**		**% M**	
									Cal.	**Fou.**	**Calc.**	**Fou.**	**Cal.**	**Fou.**	**Cal.**	**Fou.**	**Cal.**	**Fou.**	**Cal.**	**Fou.**
1	BSPA Ligand	127	0.72	0.43	284.33	349.5, 286.5, 279, 255.5, 240.5, 226.5, 208.5	Creamy White	-----	63.01	63.30	4.09	4.22	9.94	9.85	29.79	11.25	---	---	---	---
2	Sm-BSPA	148	0.39	0.258	1355.85	255.5, 236, 220, 206.5	light chocolate brown	0.979	52.15	40.82	4.55	3.122	7.41	6.20	35.67	7.08	7.85	---	18.87	11.09

BSPA = 2-(1,3-Benzoxazole -2-yl - sulfanyl)-N-phenyl acetamide, Mole. = molecular, Mag.Sus.=Magnetic susceptibility,

Cal. = calculated, Fou. = Found, Cond. = conductance, %M carried out by EDTA method,

*Solvent system for TLC = 70% toluene + 30% methanol

The physical data of the complexes and ligand are presented in the table no.2. The Sm(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) as the mobile phase. The Rf value of complex is different than ligand. Together, all these provide confirm formation of single complex in each case. The molar conductance of complex confirms that are quite low and these complex is nonionic.

2.3 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^{-1} range using KBr pellet.[5] IR spectral analysis confirms the presence of characteristic groups in the compound. In the ligand bands at~3344 and 3333 cm^{-1}is assigned to the ν(N-H)stretching of the amine group. The sharp band at 1598cm^{-1} can be attributed to the ν(C=N) stretching mode in the ligand. This band shifted in the complexes. This indicates participation in coordinate bond. The band at 1675cm^{-1}of the ligand is due to the C=O stretching. In the Sm-BSPA, it is shifted to 15-40 cm^{-1} either at lower energy or at higher energy indicating the coordination by the carbonyl-oxygen atom.

Table -3 IR spectra of BSPA ligand with Sm^{3+} complex

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-Cl) stre.	ν(C-O-C) stre.	ν(C-S) stre.	ClO_4^- vibrations	Scissoring and other bending Vibrations
BSPA ligand	2912 2978	1440 1454	1598 1675	3529 3671	-------	--------	------	1236 1251	757 781 807 858	------	1454- CH_2 Scissoring 1369- wagging and twisting
Sm-BSPA	2906 2957	1416 1145 1498	1559 1600 1647 1682	3520 3607	691 755	451 463 479	503 534	1240	835	(s) 1111 (b) 691	1445- CH_2 Scissoring 1332- wagging and twisting

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

2.4 Electronic Spectra and Magnetic Studies

The Sm-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 complex along with metal to ligand charge transfer band.[6,7]

The room temperature magnetic moment of the solid Sm-BSPA was found to be 0.98 BM. [8] This indicates five unpaired electrons per Sm (III) ion in CaF_2 type environment. [8,9]

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

Ion/ Configuration	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
Sm^{III}/f^{9}	yellow	$^6H_{5/2}$	$^6F_{1/2}$, $^6H_{3/2}$, $^4H_{7/2}$	0.84	5	5

Reference: - [10,11]

Table :-5 Electronic spectra of Sm^{3+} complex

Complexes	Cm^{-1}	Assignment
Sm-BSPA	39138.9	$^6H_{5/2} \rightarrow {}^4G_{7/2}$ (C_1)
	42372.8	$^6H_{5/2} \rightarrow {}^4I_{13/2}$ (F_1)
	45454.5	$^6H_{5/2} \rightarrow {}^4G_{9/2}$ (H_3)
	48426.1	$^6H_{5/2} \rightarrow {}^4L_{13/2}$ (K_3)

2.5 Thermal analysis

Thermal analysis of metal complexes 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 ^{0}C minute^{-1}. The temperature range wise % weight loss data of metal complexes are shown in table.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^{0}C to 250^{0}C correspond to loss in weight due to water of coordination. After approximately 800 ^{0}C, almost constant weight is observed.

This is due to oxide of corresponding metal hence from this constant weight, percentage of metal can be obtained.

Table :- 6 TGA data of Sm^{3+} Complexes of BSPA

RT = Room temperature

Compound	**RT-150 ^{0}C**			**150 ^{0}C - 250 ^{0}C**		
	% 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**
Sm-BSPA	**0.33**	**1.76**	**0**	**9.8**	**52.35**	**3**

Table :-7 Complex and Coordination number

Complexes	**Coordination number of metal in the probable structures**	**Usual coordination number * of metal ion**
Sm-BSPA	**9**	**6, 7, 8, 9**

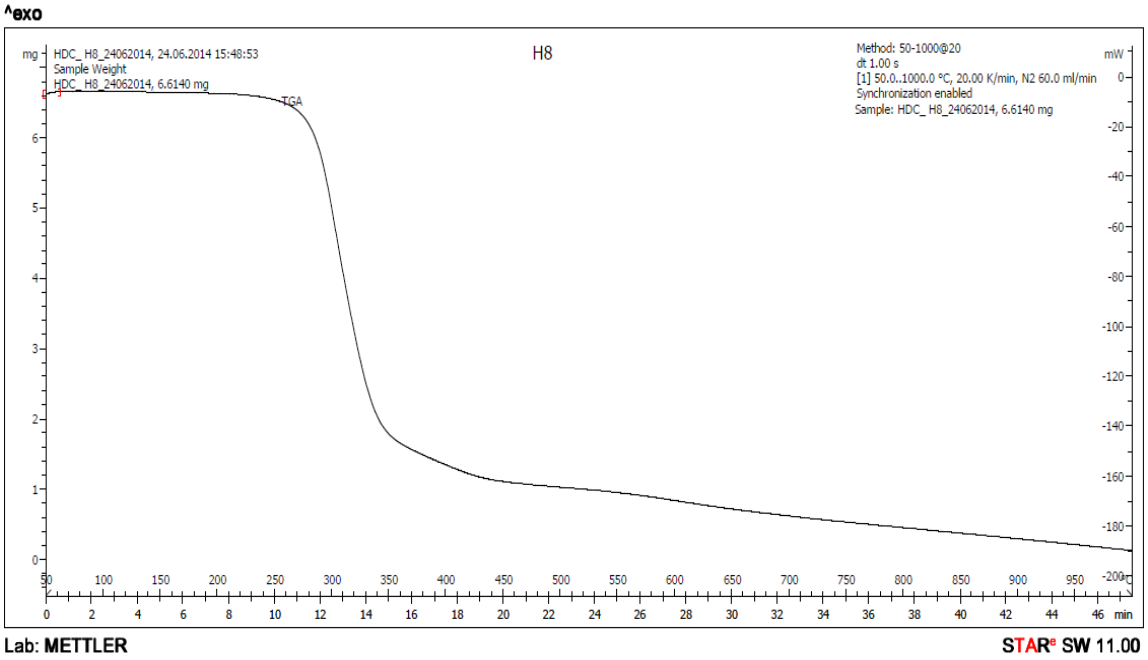


Figure: - 1 TGA spectrum of BSPA Ligand

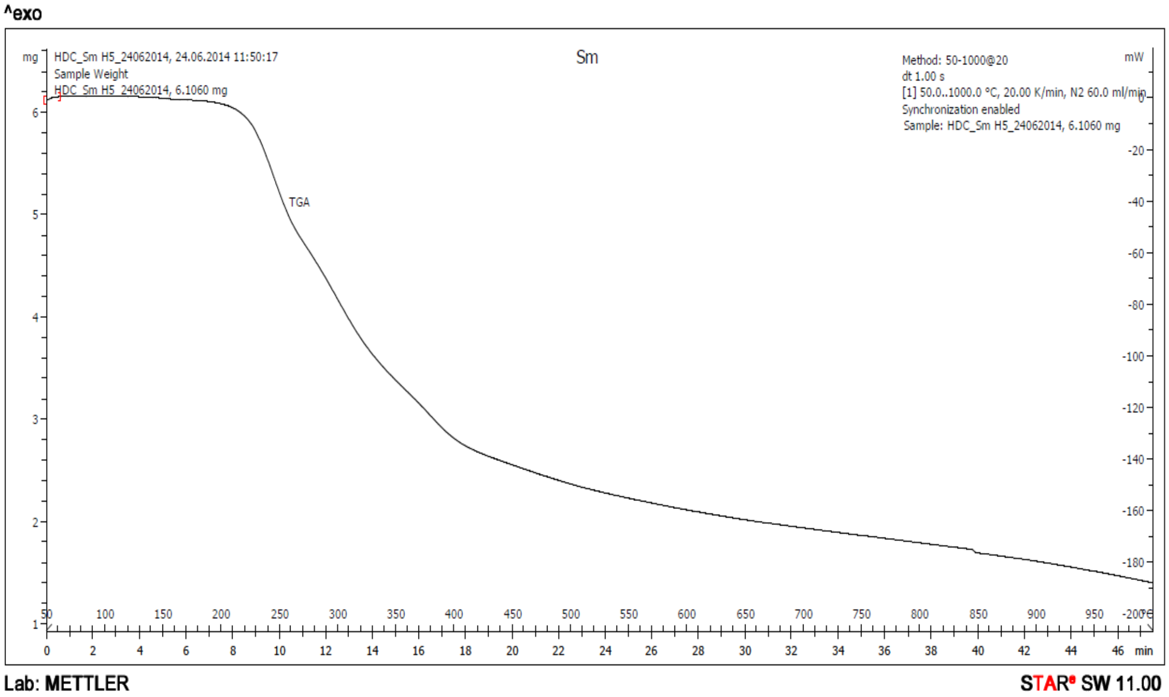


Figure:- 2 TGA spectrum of Sm-BSPA

It has been observed that Sm-BSPA show loss in weight corresponding to three water molecules in range 150 ^{0}C-250 ^{0}C This indicates that three and two water molecules coordinate with the Sm-BSPA respectively. It has been also observed that Sm-BSPA lose weight corresponding to no water molecules up to 150 ^{0}C hence, no water molecules are there for water of crystallization.

The reported values for Gd-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 water molecules from air and all the corresponding results were uniformly lower than anticipated. Therefore, the results have been expressed for the complex on dried basis. This hygroscopic complex was dried at 50 ^{0}C for 90 minutes in oven to remove absorbed water.

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

Sm-BSPA

Probable (Metal + Ligand) peak – 436.3 amu (weak)

Base peak (B. P.) - 333.2 (ES+) , 331.1 (ES-)

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

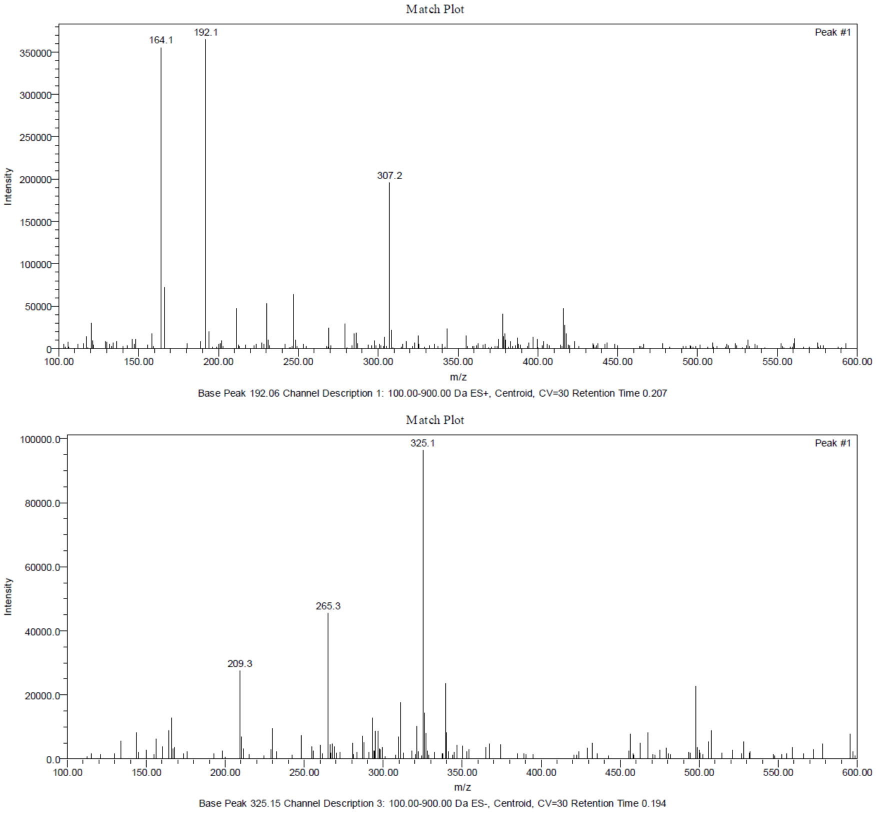
Peak , peak +2, peak + 4 (ratio 3:3:1) in certain fragments therefore 3 chlorine atoms may be present

Metal +1,3-benzoxazol – S- CH_2 - CO + (ES+) = 333.2 amu

Metal + 1,3-benzoxazol – S- CH_2 - CO - (ES-) = 331.1 amu

Metal + Ligand – Ph-NH_2 –(ES-) = 341 amu

Molecular weight of all complexes are 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.



Base Peak 192.06 Channel Description 1: 100.00-900.00 Da ES+, Centroid, CV=30 Retention Time 0.207

Base Peak 325.15 Channel Description 3: 100.00-900.00 Da ES-, Centroid, CV=30 Retention Time 0.194

Figure:- 4 Mass Spectra Ligand BSPA

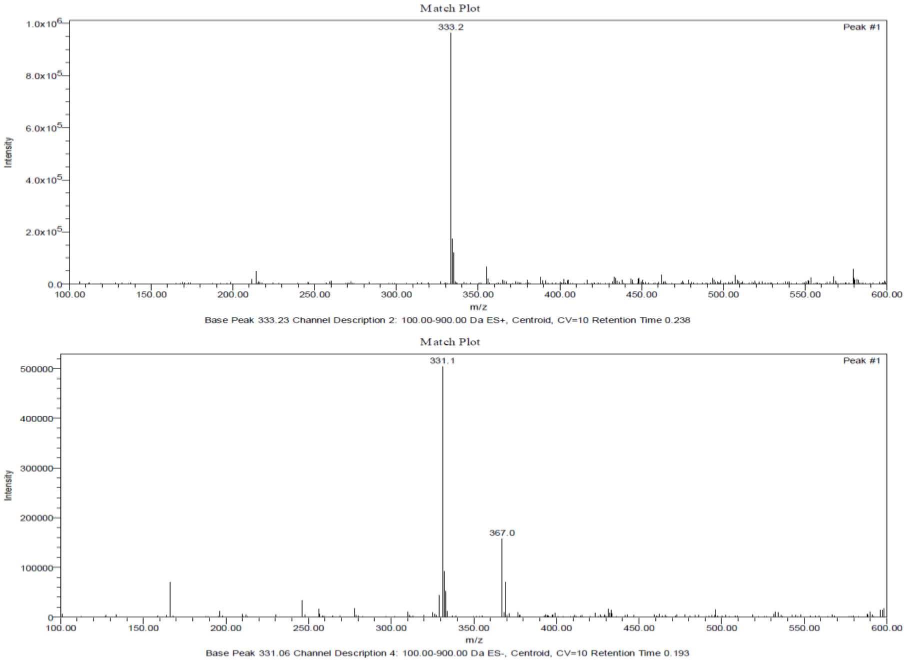


Figure:- 5 Mass Spectrum of Sm-BSPA

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

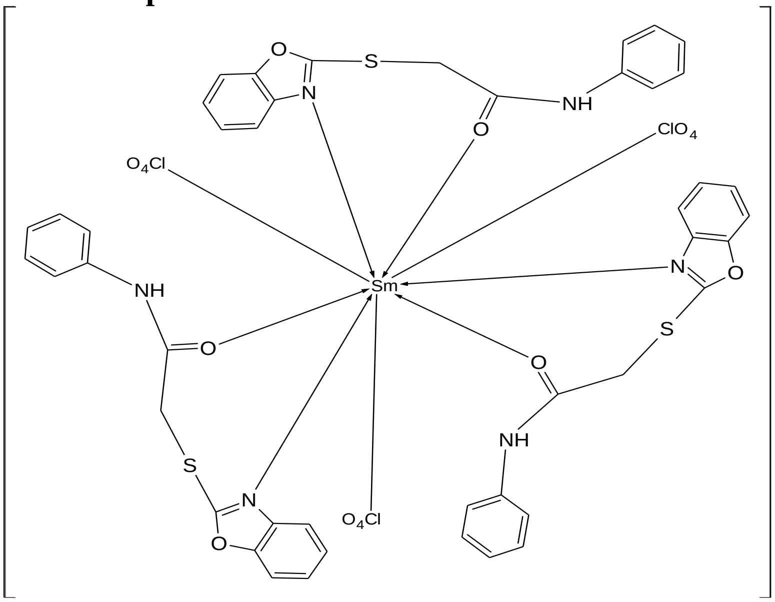


Figure:- 6 Sm-BSPA probable structure

2.7 Conclusion

This portion describes preparation of the ligand BSPA and its complexes with three lanthanide ions. Usual laboratory tests (M.P., U.V-visible spectra, TLC, colour etc.) confirmed formation of coordination compounds which were 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 these information, the tentative structures were assigned to the new complexes. Electronic spectra and magnetic moment values gave information regarding number of unpaired electrons, spin –orbit coupling, charge transfer bands, probable geometry etc.

3.0 Acknowledgement

Authors thank to Hemchandracharya North Gujarat University, Patan, India for supply chemical, A grade glass were and wonderful laboratory provide. we are thankful to Central Instrumental Maintenance Facilities (CIMF) Laboratory Hemchandracharya North Gujarat University, Patan, India to facilities of Spectral analysis.

References:-

1. Heiserman, David L. "Piezoelectric polymer micromanipulator." U.S. Patent No. 4 (1986) p-610,475.
2. Greatrex, R., Greenwood, N. N., Lal, M., and Fernandez, I. A study of the ruthenium (V) perovskites M 2 LnRuO 6 (M= Ca, Ln= Y, La, or Eu; M= Sr, Ln= Y; M= Ba, Ln= La or Eu) by 99 Ru Mössbauer spectroscopy and other techniques. Journal of Solid State Chemistry, 30(2),**(1979)** p-137-148.
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)**. p- 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)**. p-657-660
5. De Andrade Martins, Roberto. "The rise of magnetochemistry from Ritter to Hurmuzescu." Foundations of Chemistry 14.2 **(2012)**: p-157-182.
6. Kovala-Demertzi, D., Domopoulou, A., Demertzis, M. A., Valdés-Martínez, J., Hernández-Ortega, S., Espinosa-Pérez, G., and Bloom, P. D. “Structures and spectral properties of palladium (II) complexes of 2-acetylpyridine N (4)-dimethylthiosemicarbazone.” Polyhedron, 15(15), **(1996).** p- 2587-2596.

7. Kovala-Demertzi, D., Domopoulou, A., Demertzis, M. A., Valdés-Martínez, J., Hernández-Ortega, S., Espinosa-Pérez, G., and Bloom, P. D. “Structures and spectral properties of palladium (II) complexes of 2-acetylpyridine N (4)-dimethylthiosemicarbazone.” Polyhedron, 15(15), **(1996).** p-2587-2596.

8. Nakamoto, Kazuo, Marvin Margoshes, and R. E. Rundle. "Stretching frequencies as a function of distances in hydrogen bonds." Journal of the American Chemical Society 77.24 **(1955)**: p-6480-6486.
9. Lever, A. B. P. "The electronic spectra of tetragonal metal complexes analysis and significance." Coordination Chemistry Reviews 3.2 **(1968)**: p-119-140.
10. Jotham, R. W., S. F. A. Kettle, and J. A. Marks. "Antiferromagnetism in transition-metal complexes. Part IV. Lowlying excited states of binuclear copper (II) carboxylate complexes." Journal of the Chemical Society, Dalton Transactions 3 **(1972)**: p-428-438.
11. Osborn, J. A., Jardine, F. H., Young, J. F., and Wilkinson, G. “The preparation and properties of tris (triphenylphosphine) halogenorhodium (I) and some reactions thereof including catalytic homogeneous hydrogenation of olefins and acetylenes and their derivatives.” Journal of the Chemical Society A: Inorganic, Physical, Theoretical,**(1966)** p-1711-1732.
12. Dieke, Gerhard Heinrich, and John Joseph Hopfield. "The structure of the ultra-violet spectrum of the hydrogen molecule." Physical Review 30.4 **(1927)**: p-400.