IJARSCT
ISSN (Online) 2581-9429
International Journal of Advanced Research in Science, Communication and Technology (IJARSCT)
Volume 2, Issue 3, March 2022
Impact Factor: 6.252

Synthesis, Characterization of Cu^{++}, Ni^{++} Metal Ion Chelates with Newly Synthesized Benzothiazolyl Hydrazone Derivatives

Bhagat S. M.
Department of Chemistry
I.C.S. College of Art's, Commerce and Science, Khed, Ratnagiri, Maharashtra, India

Abstract: *The transition Metal ion chelates of Cu^{+2} and Ni^{+2} is synthesized by using 2-(2´-hydroxy-3´-methyl phenyl)-4-bromo-6-ethoxy benzothiazolyl hydrazones and characterized by different analytical procedure and spectral study. These metal ion chelates are insoluble in common organic solvents. Infrared spectrum showed the bonding through azomethizine N and ring N.*

Keywords: Benzothiazolyl Hydrazones, Metal Ion Chelates.

I. INTRODUCTION

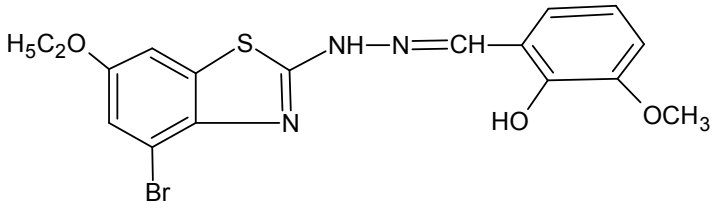
Hydrazones are organic compounds characterized by the presence of –NH-N-CH- group in their molecule. Hydrazone can acts as Schiff base due to the presence of strong donor sites, stability and fleidentacity[1,2]. Metal complexes of hydrazone derivative are wide application in various field. It can acts as anti-cancer, anti-neoplastic and anti-proliferative agent[3-6], anti-malarial[7], anti-fungal[8,9], anti-bacterial[10,11], anti-tumor[12,13]. It is also found that hydrazones metal complexes have number of pharmacological application[14,15]. Metal complexes of hydrazone play an important role in the fields of industries [16,17], it can acts as catalyst[18]. Hydrazone metal complexes can acts as corrosion inhibitor[19,20,21]. It is also found that metal complexes of hydrazone have some application in the fields of agriculture as insecticides and plant growth regulator 22. Here in presence work I have reported some metal ion chelates of hydrazone derivative.

II. EXPERIMENTAL

2.1 Synthesis of ligand

Synthesis of 2-(2´-hydroxy-3´-methyl phenyl)-4-bromo-6-ethoxy benzothiazolyl hydrazones. From 4- bromo-2-hydrazino-6-ethoxy benzothiazolyl hydrazones. 2.48 gm of 4- bromo-2-hydrazino-6-ethoxy benzothiazolyl hydrazones is dissolved in alcohol and alcoholic solution of 2-hydroxy-3-ethoxy benzaldehyde were refluxed for 1 hour using water condenser. The reaction solution were cooled and filtered, the product was recrystallized using alcohol in hot condition. The purity of compound is confirmed by TLC and decomposition point.

Structure and physical parameter of ligand.



Melting point-272°C Empirical formula- $C_{17}H_{16}N_3BrSO_3$ molecular weight- 422

2.2 Synthesis of Complexes

A. *Synthesis of Ni^{+2}metal complex with* 2-(2´-hydroxy-3´-methyl phenyl)-4-bromo-6-ethoxy benzothiazolyl hydrazones 0.2 M solution of *with* 2-(2´-hydroxy-3´-methyl phenyl)-4-bromo-6-ethoxy benzothiazolyl hydrazones and 100 ml of 0.1 M slolution of nickel chloride prepared in alcohol. These two solution were mixed in 500 ml flask .The pH of the reaction

IJARSCT
ISSN (Online) 2581-9429
International Journal of Advanced Research in Science, Communication and Technology (IJARSCT)
Volume 2, Issue 3, March 2022
Impact Factor: 6.252

mixture is adjusted up to 6.8 by adding dropwise basic buffer solution of pH-10. The reaction mixture were refluxed and the obtained precipitate is digested, after cooling it was filter and purified by washing with ether. It was dried and stored in bottle.

B. *Synthesis of copper complex with with* 2-(2′-hydroxy-3′-methylphenyl)-4-bromo-6-ethoxybenzothiazolyl hydrazones

Weighed quantities of $CuCl_2$ $2H_2O$ and *with* 2-(2′-hydroxy-3′-methyl phenyl)-4-bromo-6-ethoxy benzothiazolyl hydrazones were separately dissolved in ethanol to prepare 0.1 molar solution and mixed into each other in 1:2 ratio and stirred well , pH of the mixture was adjusted to 6.0 and refluxed for two to two and half hour . The light blue solid complex precipitated at the end was digested, separated by filtration, washed with ethanol for 3-4 times and dried in vaccume at room temperature.

2.3 Physical Parameter and Elemental Analysis

M:L ratio is determined by the heating weight of complex in platinum crucible. Chloride is estimated by Mohr's method. Metal ion percentage is determined by E.D.T.A. titration method. Decomposition point is determined by open capillary method. Physical parameter and analytical data of the Ni(II), Cu(II), and ligand 2-(2′-hydroxy-3′-methyl phenyl) 4-bromo-6-ethoxy benzothiazolyl hydrazones are given in table no.4.1, metal ligand ratio and empirical formula were assigned on the basis of T.G.A. measurement and elemental analysis is given in table no. 4.2

2.4 Characterization of Complexes

I.R. spectra of ligand were recorded at Yeshwant mahavidyalaya Nanded and I.R. spectra of complexes are recorded at PERKIN ELMER spectrum-100/79720 by KBr platelet method at Shivaji University Kolhapur. Thermo gravimetric analysis are recorded at Shivaji University, Kolhapur. On TA model S.T.D-2960, in nitrogen atmosphere. U.V. and visible spectra of complexes and ligand recorded on U.V. SHIMADZU U.V.-3600 spectrophotometer at range 200-800 nm at P.G. Department of chemistry, Shivaji University, Kolhapur. X.R.D. pattern of the complexes recorded on PW-3719/1710 Philips Holland spectrometer at Shivaji University Kolhapur and E.S.R. is recorded at IIT, Pawai, Mumbai.

III. Result and Discussion

The 2-(2′-hydroxy-3′-methyl phenyl)-4-bromo-6-ethoxy benzothiazolyl hydrazones is used to prepare complexes of Ni(II), Cu(II). prepared complexes are coloured These complexes are insoluble in water , alcohol, chloroform, carbon tetrachloride and D.M.F. but soluble in D.M.S.O. Decomposition point of complexes are in the range of 240-300°C. It suggest that they have good thermal stability at room temperature.

Table 1.1: Physical property of HMPBEBTH metal complexes.

Complex	color	D.P.	Yield%	%Cl
[Ni(HMPBEBTH) H_2O] Cl_2	Pale green	223-227	63	12.458
[Cu(HMPBEBTH) Cl] Cl.H_2O	Sky blue	232-235	68	12.353

Compound	M.wt	Empirical formula	%C	%H	%N	%M
HMPBEBTH	422.18	$C_{17}H_{16}N_3BrSO_3$	48.366	3.789	9.952	-
[Ni(HMPBEBTH) H_2O] Cl_2	569.89	$C_{17}H_{18}$ Cl_2 NiN_3SBrO_4	35.829	3.158	7.369	10.301
[Cu(HMPBEBTH) Cl] Cl.H_2O	574.72	$C_{17}H_{18}Cl_2NiN_3SBrO_4$	35.528	3.131	7.307	11.055

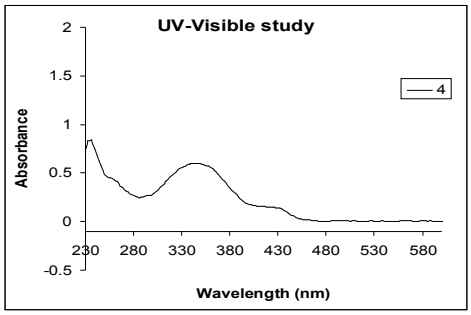
Electronic Spectra

U.V. and visible spectra of complexes and ligand recorded on U.V. SHIMADZU UV3600 spectrophotometer at range 200-800 nm by using D.M.S.O. solvent at P.G. department of chemistry Shivaji University Kolhapur.

The ligand has exhibited one characteristic maxima in U.V. region at 348 nm where in [Ni(HMPBEBTH) H_2O] Cl_2 complex it is shifted at 344 nm this shifteing of band is due the complex formation.

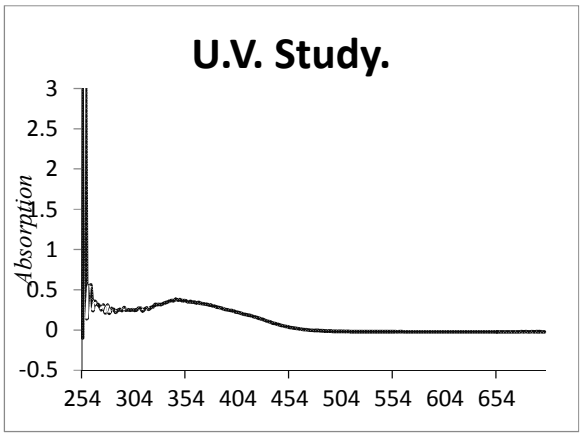
IJARSCT
ISSN (Online) 2581-9429
International Journal of Advanced Research in Science, Communication and Technology (IJARSCT)
Volume 2, Issue 3, March 2022
Impact Factor: 6.252

Dept. of chemistry, Shivaji university, Kolhapur

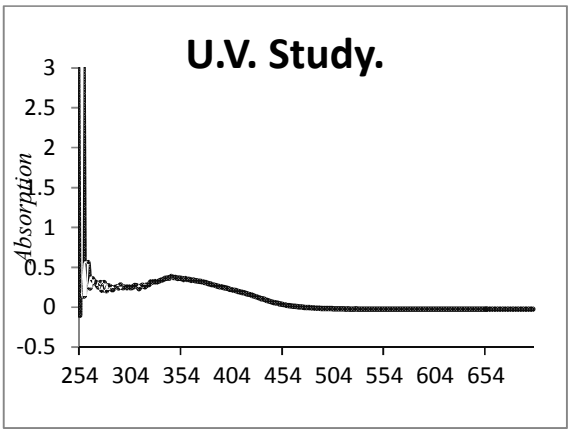


U.V. of HMPBEBTH

Dept. of chemistry, Shivaji university, Kolhapur.



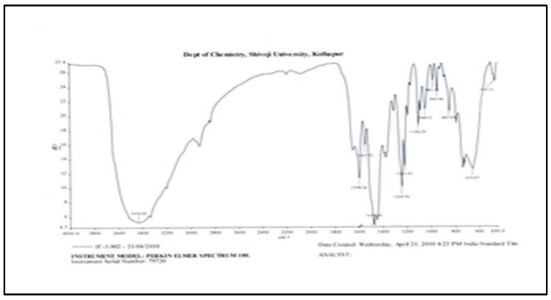
[Ni(HMPBEBTH) H_2O] Cl_2



[Cu(HMPBEBTH) Cl] Cl.H_2O

I.R. Spectra

The ligand 2-(2'-hydroxy-3'-methoxy phenyl)-4-bromo-6-ethoxy benzothiazolyl hydrazones exhibit a strong band at 3423 Cm in I.R. spectrum which is due to phenolic OH group is present in the ligand. This band is shifted in [Cu(HMPBEBTH) Cl] Cl.H_2O complex and observed at 3335 Cm it indicate that phenolic OH group involve in complex formation. Another co-ordinate site is azomethine Nitrogen. A strong band is found in lagan at 1745 while in complex it is shifted to 1598 this is evidence that the azomethine Nitrogen is involved in the bond formation. In I.R. spectra of ligand one band is observed at 1618 it is due to the thaizole ring Nitrogen, this band is shifted at 1547 in complex.

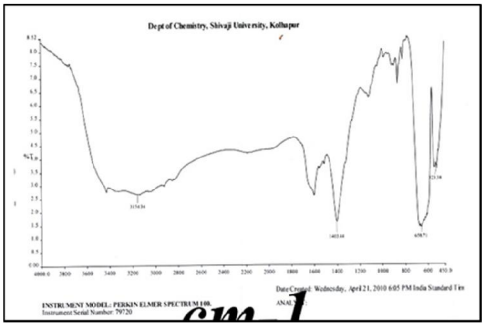


It is supported evidence to that the Nitrogen of thiazole ring co-ordinate with metal ion. One band is observed at 3200 in ligand which is due to the presence of N-H group, this band is also observed in complex it indicate that N-H group is not involved in the complex formation. One band is observed at 655 in complex. Thus 2-(2'-hydroxy-3'-methoxy

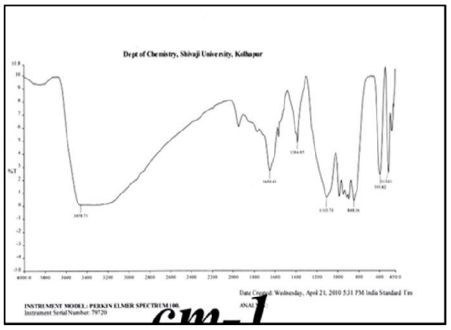
IJARSCT
ISSN (Online) 2581-9429
International Journal of Advanced Research in Science, Communication and Technology (IJARSCT)
Volume 2, Issue 3, March 2022
Impact Factor: 6.252

phenyl)-4-bromo-6-ethoxy benzothiazolyl hydrazones co-ordinate with transition metal through phenolic OH group, Nitrogen of azomethazine and Nitrogen of thaizole ring and it act as tridentate ligand.

I.R. Spectra of ligand HMPBEBTH



[Ni(HMPBEB2 TH) H2O] Cl



[Cu(HMPBEBTH) Cl] $Cl.H_2O$

Electron Spin Resonance Spectroscopy

The X-band E.S.R. spectrum of the powder Cu(II) complexes was recorded at room temperature. The calculated values of Cu(II) is $g_{\|}$, $g_{\perp}$, g_{avg}, and G are 2.21932, 2.06947, 2.11942, 4.288792 respectively. The values are typical for one unpaired electron in an orbital of mostly d_{xy} character. If $g_{\|}$ value is less than 2.3 the compound is covalent and $g_{\|}$ value is greater than 2.3 then it is ionic. Present values indicate that the complexes are covalent. G value is greater than 4 it indicate that the ligand is weak field ligand.

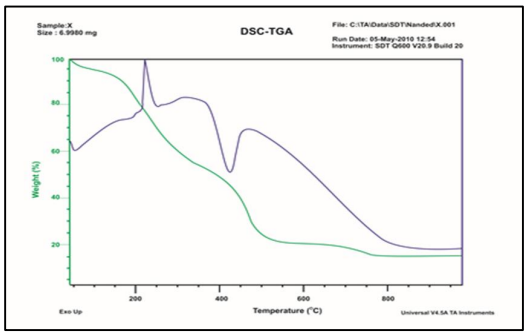
Thermal Analysis

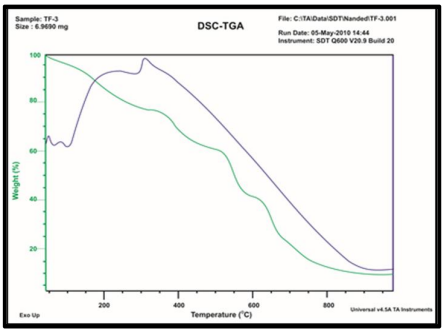
Results of TG analysis were used to determine the nature of water molecules present and decomposition pattern of the complexes. Lattice water molecules were lost in the 70-110 °C temperature range while coordinate water molecules were eliminated at relatively high temperature range of 150-240 °C. complete decomposition of ligand occur at about 800 °C and observed residue corresponds to respective metal oxide.

Present losses of material as obtained from TGA curve are good agreement with calculated percent loss in mass. Thermo gravimetric results coincide well with DTA peaks. TGA/DTA scans are depicted in fig.

TGA/DTA plot of [Cu(HMPBEBTH) Cl] $Cl.H_2O$ shows five peak first peak is observed at temperature range 50-120°C and loss of mass is observed 9.308% . this loss of mass is due to the elimination of lattice chloride and water molecule . In second step 13.223% loss of mass is observed in the temperature range 120-340°c. this loss of mass is due to the elimination of ethoxy group and methoxy group form the compound molecule. Third peak is observed at the temperature range 340-480°C and loss of mass is observed 23.054% , this loss of mass is due to the burning of chloride , bromide and hydroxyl group from the complex molecule. In the fourth step 25.925% mass is loss in the temperature range 480-590°C . this loss of mass is due to the elimination of two benzene ring form the compound molecule. The last peak is observed at the temperature range 590-760°C and 17.399% mass is lost. This loss in mass is due to the elimination of thaizole ring part and and it's substituent chain NH-N=CH form the temperature 760°C the curve of graph is constant it indicate that the remaining mass is of metal oxide.

IJARSCT
ISSN (Online) 2581-9429
International Journal of Advanced Research in Science, Communication and Technology (IJARSCT)
Volume 2, Issue 3, March 2022
Impact Factor: 6.252





Thermal decomposition of [Ni(HMPBEBTH) H_2O] Cl_2 Thermal decomposition of [Cu(HMPBEBTH) Cl] Cl.H2O

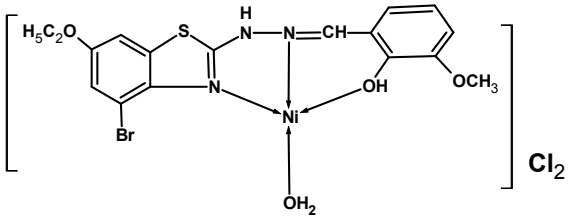
Table: Thermal decomposition value of [Ni(HMPBEBTH) H_2O] Cl_2metal complex

Temp. range °C	% loss	Nature of decomposition
50-120	9.308(9.87)	Lattice chloride water
120-340	13.223(13.113)	OCH_3 & OC_2H_5
340-480	23.054(23.165)	Cl, -OH & -Br
480-590	25.959(25.385)	Two Benzen ring
590-760	17.399 (17.301)	Thiazole ring part and substituted chain-NH-N=CH

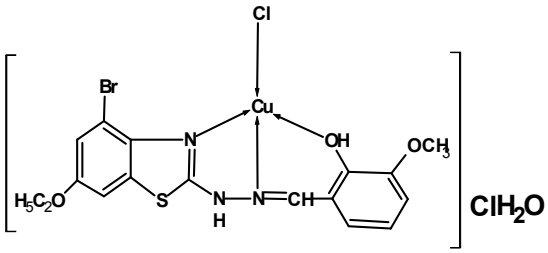
Table: Thermal decomposition value of [Cu(HMPBEBTH) Cl] Cl.H_2O metal complex

Temp. range°C	% loss	Nature of decomposition
50-110	9.821(9.569)	Lattice water and chloride
110-225	6.517(6.625)	Coordinated Cl
225-450	23.13(22.895)	-CH_3, -OCH_3 & -Br
450-580	27.35(27.269)	Two Benzen ring
580-790	21.47(21.40)	Thiazole ring and substituted chain.

Proposed structure of metal complexes

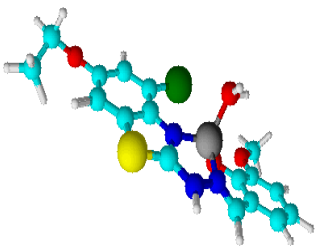


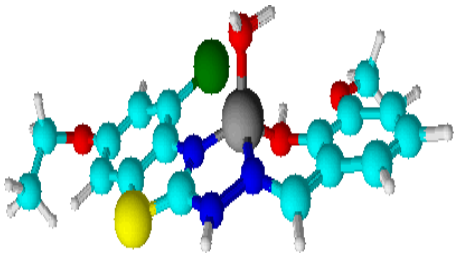
[Ni (HMPBEBTH) H_2O] Cl_2



[Cu (HMPBEBTH) Cl] Cl H_2O

Proposed 3D structure metal complexes





IJARSCT
ISSN (Online) 2581-9429
International Journal of Advanced Research in Science, Communication and Technology (IJARSCT)
Volume 2, Issue 3, March 2022
Impact Factor: 6.252

[Ni (HMPBEBTH) H_2O] Cl_2 [Cu (HMPBEBTH) Cl] Cl H_2O

REFERENCES

[1]. Kajal,A., Bala, S., Sharma N., Kamboj S. and Saini V. International Journal of medicinal Chemistry 1,11 (2014).
[2]. A Vaji p. G., Vinodkumar C.H., Patil S.A., Shivananda K.N. and Nagaraju C. European Journal of medicinal Chemistry (2009)
[3]. J. easmon, G. Puerstinger, T. Roth, H.H. Fiebig, M. Jenny, G. Helnish and J. Hofmann Int. J. Cancer, 94,88-96 (2001)
[4]. M.Hong, H. Yin., X. Zhang, C.Li. C. Yue and S. Cheng J. Organomet, Chem. 724, 23-31, (2013).
[5]. A. Datta, P.H. Liu, J. H. Huang, E. Garribba, Turnabull, B. Machura, C.L. Hsu, W.T. Chang and A Pevec.Polyhedron, 44, 77-87,(2012)
[6]. A.S. Abu-Surrah, K.A. Abu Safieh, I.M. Ahmad, M.Y. abdalla, M.T. Ayoub, A.K. Qaroush and A.M. Abu-Mahtheieh. Eur. J. Med. Chem. 45, 471-475, (2010).
[7]. Melnk p., Leroux V., Sergheraert C. and Greuier p. Bioorg.Med.Chem., Lett, 16(1) 31-35, (2006)
[8]. Fontes, A.P.S., Guerra, W. Machado , F.C. Transition Met. Chem. 29, 382 (2004)
[9]. Sharma V.K., Shrivastava S. Met.Org. Chem. 35, 311,(2005).
[10]. Iskandar M.F. , El-Sayed, L. Salem, N.M.H.Waner., R. Haase W.J. Coord. Chem. 58, 125,(2005)
[11]. Martsinko E.E. , Seitullia I.I. Ya, Zub. V Russ. J. Coord. Chem. 31, 795, (2005)
[12]. M. Mohan, M.P. Gupta, L. Chandra and N.K. Jha Inorg. Chem. Acta. 15, 61-68, (1988)
[13]. M. Mohan, A Kumara and M. Kumar Inorg. Chem. Acta, 136,65-74, (1987).
[14]. M.S. Nair, D. Arish, R.S. Joseyphus Journal of Saudi Chemical Society, 16, 83-88 (2012).
[15]. K.S. Abou-Melha Spectrochemica Acta. Part A, 70, 162-170 (2008).
[16]. Katsuki. T. Coord. Chem. Rev., 140, 189, (1995).
[17]. Di. Bella S. Chem. Soc. Rev 30, 355 (2001).
[18]. Cogan D.A., Liu G.C., Kim K.J. and Co. Am. Chem. Soc. 120, 8011, (1998).
[19]. Pouda A.S. G.E. Badr and M.N. El. Haddad J. Korean Chem. Soc. 2, 124, (2008).
[20]. Ali M.A., M.H. Kabir, M. Nazimuddin, S.M. H. Mujumdar, M.T.H. Tarafder and M.A. Khair. Indian J. Chem. 27A, 1064, (1988).
[21]. Ferrari M.B., S. S. Capacchi, G. Pelosi, G. Reffo, P. Tarasconi, R. Alberlini, S. Pinelli and P. Lunghi. Inorg.Chim, Acta 286, 134, (1999).
[22]. Sanjeev R. Dudhal, Shrikant Kulkarni IJETSR volume 5, Issue 3 (2018)