IJARSCT
ISSN (Online) 2581-9429
International Journal of Advanced Research in Science, Communication and Technology (IJARSCT)
Volume 2, Issue 4, April 2022
Impact Factor: 6.252

Preparation and Characterization of Fe^{+3}, Co^{+2} First Transition Metal Ions Chelates with Heterocyclic Molecules

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Abstract: *The transition Metal ion chelates of Fe^{+3}, Co^{+2} is synthesized by using 2-(4′-dimethylamion 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

1.1 Chemistry of Ligands

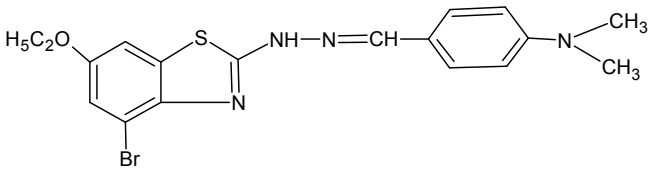
The coordination chemistry of hydrazones is an intensive area of study and numerous metal complexes of these ligand have been investigated[1]. The development of the field of bioinorganic chemistry has increased the interest in Schiff base complexes, since it has been recognized that many of these complexes may serve as models for bilogi8cally important species [2-4]. The hydrazones metal complexes have found application in various process like sensor, medicine, nonlinear optics etc. they are well known for their metal binding ability and exhibit interesting coordinating behavior with transition metal ion [5,6]. Coordination compound derived form aryl hydrazones have been reported because of their anti-tuberculosis, antimicrobial and corrosion inhibitor[7-9]. Hydrazones have been drawing much attention from coordination chemistry to transition metal[10]. In the context of the above application we have tried to the synthesis and characterization of transition metal complexes of 2-(4′-dimethyl amino phenyl)-4-bromo-6-ethoxy benzothiazolyl hydrazones. Prepared complexes were dried and the physical and chemical properties were recorded. analysis of the complexes and different spectral studies like I.R., Electronic spectra of the complex were used for find out the donor site of the ligand.

1.2 Synthesis of Ligand

Preparation of 2-(4′-dimethylamion phenyl)-4-bromo-6-ethoxy bemzothiazolyl hydrazones from 4-bromo-6-ethoxy bemzothiazolyl hydrazones.

To the ethanolic solution of 4-bromo-6-ethoxy bemzothiazol was added in ethanolic solution of 4-dimethylamino benzaldehyde. The mixture was refluxed on water bath for two hours. Obtained solid is cooled filtered, washed with ethanol and recrystlised from hot benzene.

A. Structure of ligand



2-(4′-dimethylamion phenyl)-4-bromo-6-ethoxy bemzothiazolyl hydrazones

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1.3 Physical Parameter

A. Synthesis of Complexes

i) Synthesis of 2-(4′-dimethylamion phenyl)-4-bromo-6-ethoxy bemzothiazolyl hydrazones Fe^{III} chloride complex

100 ml 0.1 M $FeCl_3.4H_2O$ were prepared in alcohol and 2-(4′-dimethylamion phenyl)-4-bromo-6-ethoxy bemzothiazolyl hydrazones 0.2 M solution were prepared in ethyl alcohol. These two solutions were mixed and transfer into 500 ml round bottom flask attached water condenser, the pH is of the reaction mixture were adjusted by adding basic buffer solution pH-10. Reaction mixture were fefluxed for one hour in water bath. The precipitate was obtained. it is digested, after cooling it is filtered through buckner funnel, the precipitate of complex were purified by washing with ethyl alcohol, the complex were dried by keeping it in oven. The product was packed into sample bottle.

ii) Synthesis of Cobalt Complex

Cobalt chloride and ligand 2-(4′-dimethylamion phenyl)-4-bromo-6-ethoxy bemzothiazolyl hydrazones were dissolved separately in ethanol so as to prepare 0.1 molar solution with constant stering . A clear solution of cobalt chloride was mixed in ligand solution in 1:2 proportion and pH is adjusted to 6.5 with buffer solution and refluxed on water bath for one hour and allowed to cool. the contents were digested for one hour and filtered. Pale pink colored solid is obtained it washed with ethanol and dried and stored in bottle.

1.4 Physical Parameter and Elemental Analysis.

Decomposition point was determined with the help of melting point apparatus by open capillary methos. M:L ratio was determined by heating known weight of complex in platinum crucible .Metal ion percentage in a complex is determined by E.D.T.A. titration method. Chloride is estimated by Mohr's method.

Physical parameter and analytical data of the Fe(II), Co(II), complexes and ligand 2-(4′-dimethylamion phenyl)-4-bromo-6-ethoxy bemzothiazolyl hydrazones (MAPBEBTH). Are given in table no. 5.1. metal ligand ratio and empirical formula were assigned on the basis of T.G.A. measurement and elemental analysis is given in table no.5.2.

1.5 Characterization of Complexes

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. I.R. spectra of ligand were recorded at Yeshwant Mahavidyala Nanded and I.R. spectra of complexes are recorded at PERKIN ELMER spectrum-100/79720 by KBr platelate method at Shivaji University Kolhapur. Thermo gravimetric analysis (T.G./D.T.A.) measurement are recorded on thermo gravimetric analyzer on TA model S.T.D-2960 at Shivaji University Kolhapur in Nitrogen atmosphere .XRD 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.

II. Result and Discussion

The complexes of Fe(III), Co(II), are prepared with the ligand 2-(4′-dimethylamion phenyl)-4-bromo-6-ethoxy bemzothiazolyl hydrazones (MAPBEBTH). This complexes are coloured. These complexes are soluble in D.M.S.O. but insoluble in water, alcohol, chloroform, and D.M.F. 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: physical property of (MAPBEBTH) metal complexes.

Complex	color	D.P.	Yield%	%Cl
$[Fe(MAPBEBTH)_2Cl_2]$ Cl H_2O	Faint brown	272-280	59	10.453
$[Co(MAPBEBTH)_2(H_2O)_2]Cl_2$.	Pale pink	284-289	64	7.069

Table 2: Percent C, H, N and metal ion in HMPBMBTH metal *complex*

Compound	M. wt	Empirical formula	%C	%H	%N	%M
MAPBEBTH	419.20	$C_{18}H_{19}N_4BrSO$	51.576	4.532	13.365	-
$[Fe(MAPBEBTH)_2Cl_2]$ Cl H_2O	1018.75	$C_{36}H_{40}Cl_3FeN_8S_2Br_2O_3$	42.445	3.926	10.993	5.482
$[Co(MAPBEBTH)_2(H_2O)_2]Cl_2$.	1004.34	$C_{36}H_{42}Cl_2CoN_8S_2Br_2O_4$	43.054	4.181	11.156	5.868

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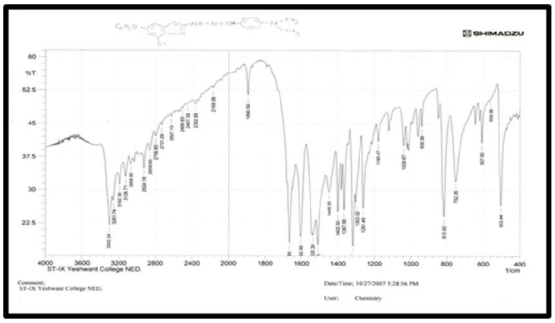
2.1 U.V.

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.

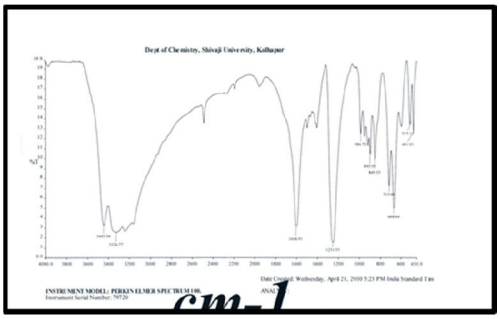
Theligand 2-(4′-dimethylamion phenyl)-4-bromo-6-ethoxy bemzothiazolyl hydrazones has exhibited one characteristic maxima in U.V. region at 246 nm where in $[Fe(MAPBEBTH)_2Cl_2]$ Cl H_2O complex it is shifted at 258 nm and in complex $[Co(MAPBEBTH)_2(H_2O)_2]Cl_2$. Band is observed at 266 nm this shifteing of band is due the complex formation.

2.2 I.R. Spectra

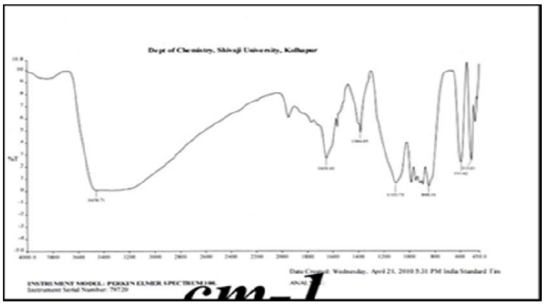
A sharp strong band is observed in I.R. spectra of ligand at 1665 in ligand it is due to the C=N of thiazole ring nitrogen. This band is shifted in Fe^{+2} complex as well as in Co^{+3} complex. In Fe^{+3} complex it is observed at 1645 and in Co^{+2} complex it is observed at 1606 this shifting of band in both complexes it indicate that the Nitrogen of thiazole ring is involve in the complex formation. Another band is observed at 1602 in ligand. This band is support to the presence of C=N (azomethazine) group in ligand. This band is shifted in Fe^{+3} and Co^{+2} complexes. The band is observed in Fe^{+3} complex at 1590 wherein Co^{+2} complex it is observed at 1510. This shifting of band indicate that the azomethazine nitrogen involve in the complex formation. One band is observed at 3302 in ligand it may be due to the presence of N-H group. This band is also observed in Fe^{+3} and Co^{+2} complexes it is evidence that the N-H group is not involve in the complex formation. In Co^{+2} complex one band is observed at 3606 which is absent in ligand and in Fe^{+3} complex. it indicate that the water molecule is coordinate with metal. Another one band is observed in both complexes but absent in ligand. In Fe^{+3} complex it is observed at 481 where as in Co^{+2} complex it is observed at 468 it indicate that there is a formation of M-L bond. Thus the ligand act as a bidentate. It coordinate through azomethazine, Nitrogen of thiazole ring.



I.R. Of MAPBEBTH



I.R. Of $[Fe(MAPBEBTH)_2Cl_2]$ Cl H_2O



I.R. Of $[Co(MAPBEBTH)_2(H_2O)_2]Cl_2$

2.3 Electron spin Resonance Spectroscopy

The X-band E.S.R. spectrum of the powder Fe(II) and Co(II) complexes was recorded at room temperature. The calculated values of Fe(II) is $g_{\|}$, $g_{\perp}$, $g_{avg.}$ and G are 2.18171, 2. 08286, 2.11581, 4.26457 respectively. And Co(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.

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2.4 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 metaloxide.

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.

2.5 TGA/DTA of $[Fe(MAPBEBTH)_2Cl_2]$ Cl H_2O

TGA/DTA plot of $[Fe(MAPBEBTH)_2Cl_2]$ Cl H_2O shows five peak of decomposition. The first peak is observed at the temperature range 50-130°C and 9.023% loss of mass is observed. This loss of mass is due to the elimination of lattice chloride and water molecule from the compound. In second peak 18.047% loss is observed in the temperature range 130-280°C. The loss of mass is due to the elimination of two molecule of $N(CH_3)$ and ethoxy group form the complex. Third peak is observed in the temperature range 280-430°C and 15.411% mass is lost. This loss in mass is due to the elimination of two benzene ring from the molecule. In the fourth peak 31.228% mass is lost in the temperature range 430-570°C.The loss of mass is due to the elimination of two bromobenzene rings from the complex. Last peak is observed in the temperature range 570-760°C. In this peak 20.277% mass is lost. This loss in weight is due to the elimination of thiazole ring part and its substituent chain NH-N=CH. From the temperature 760°C curve of graph show constant value. It indicate that remaining mass is of metal oxide. Calculated value are coincide with observed value.

2.6 TGA/DTA $[Co(MAPBEBTH)_2(H_2O)_2]Cl_2$ Complex

TGA/DTA plot of $[Co(MAPBEBTH)_2(H_2O)_2]Cl_2$. Complex Shows five peaks of decomposition. First peak is observed at temperature range 50-110°C and 6.208% mass is lost. This loss in mass is due to the elimination of lattice chloride from the complex. In second peak 9.356% mass is lost in the temperature range110-260°C. This loss in weight is due to the burning of coordinate chloride and water molecule. Observed values are in good agreement with calculated values. Third peak is observed at the temperature range 260-490°C. In this temperature range 15.564% weight is lost form the complex compound. this loss of mass is due to the elimination of $N(CH_3)_2$ and OC_2H_5 group from complex. Fourth peak is observed at temperature range 490-620°C and 40.622% weight is lost. This loss in weight is due to the elimination of bromobenzen ring. In last fifth peak 17.488% mass is lost in the temperature range 620-770°C this loss in mass is due to the elimination of thiazole ring part and its substituent chain NH-N=CH. Form the temperature range 770°C curve of the graph show constant value of weight of complex it indicate that remaining mass is of metal oxide. Observed figures and calculated figures are approximately equal.

Temp. range °C	% loss	Nature of decomposition
50-130	9.023(9.087)	Lattice chloride &water molecule
130-280	18.047(18.022)	$N(CH_3)_2$ & OC_2H_5
280-430	15.411(15.241)	Two benzene ring
430-570	31.228(31.385)	Two bromo Benzene ring
5570-760	20.277(20.262)	Thiazole ring part and substituted chain.

Temp. range °C	% loss	Nature of decomposition
50-110	6.208(6.069)	Lattice chloride
110-260	9.356 (6.325)	Coordinated chloride & water molecule
2260-490	15.564(15.495)	$N(CH_3)_2$ & OC_2H_5
490-620	40.223(40.269)	Two Benzen ring & Br.
620-770	17.488(17.40)	Thiazole ring and substituted chain.

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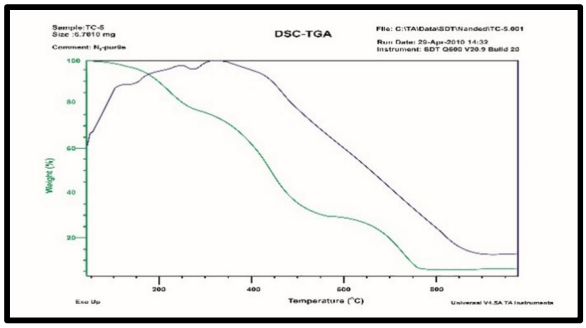
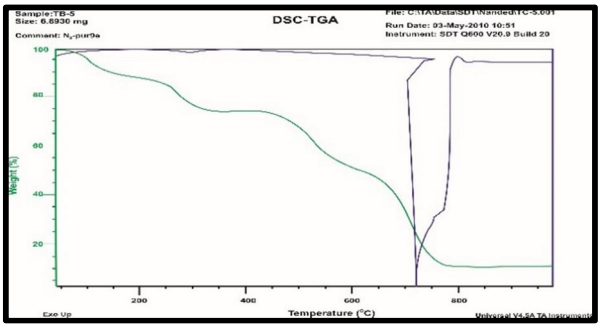
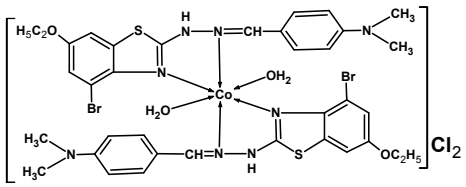


Thermal decomposition value of
$[Fe(MAPBEBTH)_2Cl_2]$ Cl H_2O metal complex

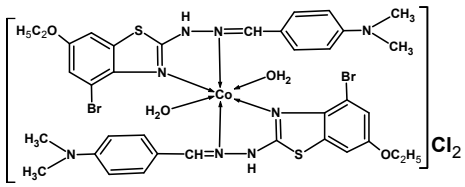


Thermal decomposition value of
$[Co(MAPBEBTH)_2(H_2O)_2]Cl_2$ metal complex

Proposed Structure of Complexes

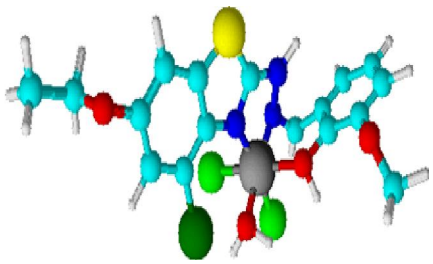


$[Fe(MAPBEBTH)_2Cl_2]$ Cl H_2O *metal complex*

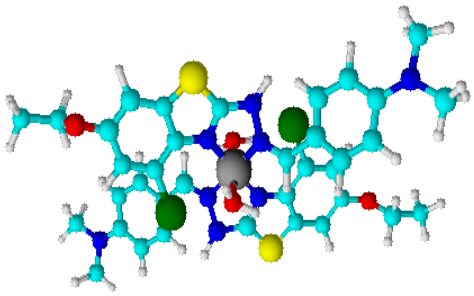


$[Co(MAPBEBTH)_2(H_2O)_2]Cl_2$ *metal complex*

Proposed 3D Structure Metal Complexes



$[Fe(MAPBEBTH)_2Cl_2]$ Cl H_2O



$[Co(MAPBEBTH)_2(H_2O)_2]Cl_2$

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