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Synthesis, Charectorization Of Mg^{+2}, Co^{+2} Metal Ion Chelate Of 2-(Cinnamyl) -4-Bromo-6-Methyl Benzothiazolyl Hydrazone.

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***Abstract*— Metal ion chelates of Mn and Co was synthesized 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.**

***Index Terms*—2- (cinnamyl)- 4-bromo-6-methyl benzothiazolyl hydrazones , Metal ion chelates.**

I. INTRODUCTION

Hydrazones are heterocyclic compound contain S,N atom. This is an important class of biologically active drug molecule which are anti-tubecular activity [1]. Hydrazones have the ability to form metal ion chelates. Literature survey indicate that there are many transition metal ion chelates with hydrazine [2-4]. There are many metal ion chelates acts as a catalyst[5]. There are many metal ion chelates which are found to active as antibactetial [6], antifungal,[7-9] antitumoral, antiviral activity[10].Some hydrazine derivative having antitubercular[11], anticonvulsant[12] and anti-inflametery[13] activity . Due to the wide importance of transition metal ion chelates increas the interest in the study of hydrazone metal ion chelates.

In the present study I have used the 2-(Cinnamyl)- 4-bromo- 6-methyl benzothiazolyl hydrazone as a ligend to synthesis of Mg^{+2} and Co^{+2} metal ion chelates. and these chelates are characterized by different methods.

Synthesis of ligand :-

i) Preparation of 2-bromo-4-methylanilin

95 ml acetic anhydride is added drop wise in a 500 ml round bottom flask containing 107 gm of p-toludine in ice cold condition and then it is refluxed for one hour. The reaction mixture is poured in ice cold water p-acetotoludine is obtained. This p-acetotoludine dissolve in 400 ml glacial acetic acid and then added 15 ml bromine in it drop by drop, temperature should be maintain near about 5º C. After complete addition of bromine the reaction mixture is poured in ice cold water in which 13 gm of NaHSO2. the 3-bromo-4-aceto-amino toluene is obtained. In this 3-bromo-4-aceto-amino toludine is refluxed with conc. HCl for three hour, it give hydrochloride of 3-bromo-4-amino toluene. the hydrochloride is filtered out . In this hydrochloride 70 gm of NaOH in 350 ml water is added., it gives oily product of 2-amino-4-bromo-methyl aniline.

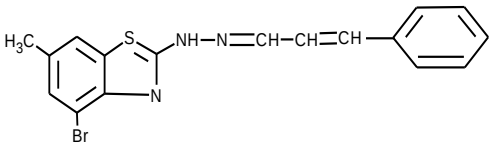
ii) Preparation of 2-amino-4-bromo-6-methyl benzothiazole.

18.6 gm of 2-bromo-4-methyl aniline and 16 gm of sodium thiocynate dissolved in 150 ml of glacial acetic acid. The solution is cooled in freezing mixture. 32 gm of bromine in 26 ml of glacial acetic acid is added with stirring below 25º C., the mixture is allow to stand an hour then to room temperature (overnight). The hydrobromide dissolved in hot water and base is precipitated with 10% NaOH. The amine thus is obtained is filtered and recrystlised in aqueous alcohol it will be 4-bromo-2-hydrazino-6-methyl benzothiazole

Preparation of 2- (cinnamyl)- 4-bromo-6-methyl benzothiazolyl hydrazones

To the ethanolic solutions of 4-bromo-2-hydrazino-6-methyl benzothiazole was added in cinnamaldehyde in ethanol. The mixture was refluxed on water bath for two hours. Yellow colored solid separated was allow to cool, filtered, washed with ethanol and recrystlised form hot benzene.

Structure of ligand.



2- (cinnamyl)- 4-bromo-6-methyl benzothiazolyl hydrazones

Physical parameter of the ligand,

Melting Point - 215 °C Empirical Formula -$C_{17}H_{13}N_3SBr$ Exact mass-371.18

Synthesis of metal ion chelates

i) Sythesis of Bis 2-(cinnamyl)-4-bromo-6-methyl benzothiazolyl hydrazones Mn(II) Chloride complex.

150 ml 0.1 M alcoholic solution of $MnCl_2$ $4H_2O$ were treated with 150 ml of alcoholic , 0.2M2-(cinnmyl)-4-bromo-6-methyl benzo- thiazolyl hydrazones in 500 ml flask. They were mixed in each other and pH of the reaction mixture were kept 6.8 by adding alcoholic solution of basic buffer solution drop by drop. The precipitate was obtained, this obtained precipitate digested and cooled and filtered through Buckner funnel, the precipitate was washed with alcohol and dried and stored in bottle.

ii) Synthesis of bis-2-(cinnamyl) -4-bromo-6-methyl benzothiazoly hydrazone Co(II) Chloride complex .

Cobalt chloride and ligand 2-(cinnamyl) -4-bromo-6-methyl benzothiazolyl hydrazone were dissolve

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separately in ethanol so as to prepare solution of 0.1 molar with constant stirring. A clear solution of cobalt chloride was mixed to the ligand solution as 1:2 proportion. pH was adjusted to 6.5 with ammonia buffer solution and refluxed under water bath for one hour and allowed to cool . The contents were digested for one hour and filtered . pale pink coloured solid was washed with ethanol and dried.

Physical parameter and elemental analysis

M:L ratio was determined by heating known weight of complexes in platinum crucible. Metal ion percentages in a complex is determined by E.D.T.A. titration and melting point was determined with the help of melting point apparatus by open capillary method. Chloride was estimated by Mohr's method. molar conductivity of the complexes was measured on elico digital conductivity bridge model c-100 at room temperature from 1X10 -3 Molar solution in D. M .S. O. solvent.

Physical parameter and analytical data of the Mn(II), co(II) complexes and ligand CBMBTH are given in table 2.1 . metal ligand ratio and empirical formula were assigned on the basis of TG measurements and elemental analysis (table 1.2.)

Table. 1.1 physical and analytical data of CBMBTH metal complexes

Compound	color	D.P.°C	Yield (%)	%Cl
$[Mn(CBMBTH)_2(H_2O)_2]Cl_2$	cream	382-387	59	7.851
$[Co(CBMBTH)_2(H_2O)_2]Cl_2$	Pale pink	392-396	55	7.816

Characterization of complexes

Ultraviolet spectrum consist of electronic transition between ligand and the metal (Charge transfer) and also transition within the ligand itself which are usually π-π* and σ-σ* transition . the ligand transition in all cases are characteristic of the coordinated ligand and not the free ligand. However spectrum of the free ligand aids in classifying the transitions of the coordinated ligand. The intensities of the crystal field transition of the coordinated ligand. The electronic transition that are involved in ultrvolet and near visible regions are of the type σ-σ*,π-σ*.n-π*.π-π*. Compound that contain non bonding electrons on oxygen, nitrogen, sulphur and halogen atoms are capable of showing absorption n-σ* transition which are of lower energy than σ-σ* transition, π-π* transition are intermediate energy absorption to those transition which are usually between n-π* and n-σ*. The high energy transition n-π* occur at longer wavelength. Polar solvents generally shifts the n-π*and n-σ* bands of shorter wave length and the π-π* band to longer wavelength. The magnitude of the molar extinction coefficient for particular absorptions is directly proportional to probability of particular electronic transition.

In present investigation following observation are found

U.v. and visible spectra of ligand and complexes were recorded on U.V. SHIMADZU UV3600 spectrophotometer at range 200-700nm by using D.M.S.O. solvent. I.R. spectra of ligand and I.R. spectra of complexes were recorded at PERKIN ELMER spectrum-100/79720 by KBr platelate method. XRD patterns of the complexes recorded on PW3710/1710 Philips Holland spectrophotometer. E.S.R. spectra are

Result and discussion

The ligand 2-(cinnamyl)-4-bromo-6-methyl-benzothiazolyl hydrazones.(CBMBTH) is used to prepare metal complexes of Mn(II), Co(II). These complexes are coloured. Prepared complexes are insoluble in water, alcohol, chloroform , D.M.F. but it is soluble in D.M.S.O. Decomposition point of these complexes is very high in the range of 240-300C suggesting good thermal stability at room temperature . percentage of chlorine and molar conductivity suggest they are weak electrolytic in nature.

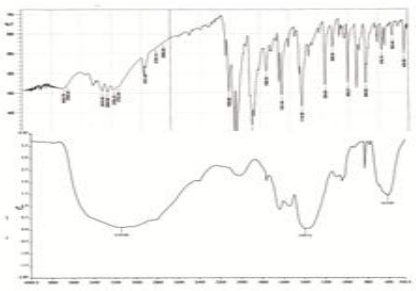
The electronic spectra 2-cinnamyl-4-bromo-6-methyl-benzothiazolyl hydrazones has exhibited one characteristic maxima in U.V. region at 358 nm. Where in [Mn(CBMBTH)2 (H2O)2] Cl2complexes it is shifted to lower region at 258 nm and in complex [Co(CBMBTH)2(H2O)2] Cl2 it is shifted at 300 nm . these two band observe blue shift .

Table no.1.2 Electronic spectral data of ligand CBMBTH and its complexes.

Compound	M.wt	Empirical formula	%C	%H	%N	%M
CBMBTH	372	$C_{17}H_{14}N_3BrS$	55.01	3.50	11.32	-
$[Mn(CBMBTH)_2(H_2O)_2]Cl_2$	905.9	$C_{34}H_{32}Cl_2MnN_6S_2Br_2O_2$	45.16	3.53	9.27	6.06
$[Co(CBMBTH)_2(H_2O)_2]Cl_2$	891.94	$C_{34}H_{32}Cl_2CoN_6S_2Br_2O_2$	44.96	3.52	9.25	6.48

In $[Co(CBMBTH)_2(H_2O)_2]\ Cl_2$complex

Compound	N-H cm^{-1}	OHcm^{-1}	C=N cm^{-1} (thiazolring)	C=N cm^{-1} (azomethine)	M-Ncm^{-1}
CBMBTH	3145	--	1642	1608	--
$[Mn(CBMBTH)_2(H_2O)_2]\ Cl_2$	3145	--	1620	1580	612
$[Co(CBMBTH)_2(H_2O)_2]\ Cl_2$	--	3445	1600	1500	595



IR Spectra

	compound	Wavelength (nm)	Log E
1	CBMBTH	358	2.678
2	$[Mn(CBMBTH)_2(H_2O)_2]\ Cl_2$	258	2.682
3	$[Co(CBMBTH)_2(H_2O)_2]\ Cl_2$	300	2.097

Table. 1.4 I.R. spectral data of ligand CBMBTH and its complexes.

Determination of coordinating atom in the complex is made on the basis of comparision of I.R. spectra of ligand and complex. Significant shift are observed in the complex which summarized in table no.2.4.

I.R. spectra of $[Mn(CBMBTH)_2(H_2O)_2]\ Cl_2$complex.

A sharp strong band is observed at 1608 cm-1 in the ligand CBMBTH it assigned to C=N (azomethine) group. In Mn^{+2} complex this band is observed at 1580 . this shifting of band indicate that the N of azomethine coordinate with metal. Another strong sharp band is observed at 1842 in the I. R. of ligand which may be due to the C=N (thiazole ring) while this band is shifted at 1620 in the Mn-complex , this clearly indicate that the nitrogen atom of thiazole ring participate in complex formation .In I.R. spectra of ligand , one band is observed at 3145 cm it may be the presence of N-H group. The same band is observed in the Mn complex it indicate that Nitrogen of N-H group is not involve in the complex formation . One band is observed in Mn- complex at 612 but it is not present in ligand , it indicate that there is a formation of M-N bond. Thus 2-cinnamyl-4-bromo-6-methyl-benzothiazolyl hydrazones acts as bidentate ligand and coordinate through the azomethazine Nitrogen, and 'N' of thiazole ring to transition metal ion.

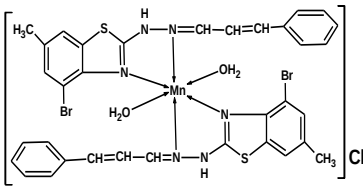
In the ligand sharp band is observed at 1608 it is assigned to C=N (azomethine) group . In the complex investigated the band 1608 is shifted to the 1500 it indicate the N of azomethiane involve in the complex formation. Another sharp band is observed at 1642 in ligand . In complex this band is observed at 1600 shifting of this band is indicate that 'N' of thiazole ring is involved in the complex formation. One band is observed at 3445 in complex it may be due to the coordinate water molecule which is absent in ligand .In I.R. spectra one band is is observed at 3145 it is due to N-H group. This ba mearged in the broad peak of water molecule and it is not participate in coordination. One band is observed at 595 in complex but absent inligand it indicate the formation of M-N coordinate bond which is absent in ligand. Thus 2-cinnamyl-4-bromo-6-methyl-benzothiazolyl

Electron spin Resonance Spectroscopy

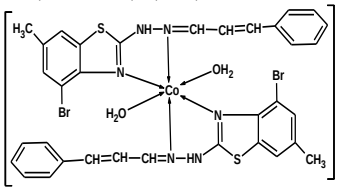
The X-band E.S.R. spectrum of the powder Mn(II) and Co(II) complexes was recorded at room temperature. The calculated values of Mn(II) is g‖ , g1 , g avg, and G are 2.15975, 2.01757, 2. 0649633, 4.17732 respectively. And Co(II) is g‖ , g1 , g avg, and G are 2.23474, 2.017157, 2.08996, 4.25231 respectively. The values are typical for one unpaired electron in an orbital of mostly dxy 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.

CONCLUSION

From above study it concluded that the ligand2-(cinnamyl)-4-bromo-6-methyl benzothiazolyl hydrazones is found to coordinate with Mn^{+2} and Co^{+2} metal ion through Azomethazine N and Ring N. and proposed structures of metal ion chelets are as follows



Proposed structure of [$Mn(CBMBTH)_2(H_2O)_2]\ Cl_2$



Proposed structure of [$Mn(CBMBTH)_2(H_2O)_2]$ C

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