International Journal of ChemTech Research
CODEN(USA): IJCRGG ISSN : 0974-4290
Vol.4, No.3, pp 925-927, July-Sept 2012

Studies on Ni(II) and Cu(II) Metal ion Chelates with 2-(Cinnamyl)-4-Brom-6-Methyl Benzothiazolyl Hydrazone.

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Abstract: Metal ion chelates of Ni(II) and Cu(II) with 2-(cinnamyl)-4-brom-6-methyl benzothiazolyl hydrazone have been synthesized and charecterised by elemental analysis , I.R. Spectra, DGA/DTA. , I.R. Spectra suggest that ligand acts as bidentate ligand. E.S.R. spectra suggest compounds are covalent coumpound.
Key words: metal ion chelates. 2-(cinnamyl)-4-brom-6-methyl benzothiazolyl hydrazone, I.R. E.S.R.

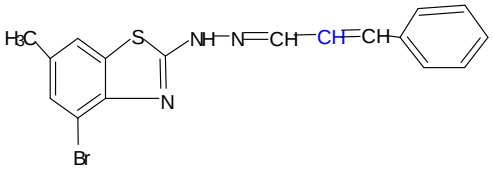
Introduction.

The study of the complexes formed with hydrazones is very interesting because of their pharmacological activity, attributed to their ability to form stable chelates with transition metal. It has been also observed that the biological activity of the hydrazones increases by complexation to metal ions like cobalt, nickel copper, iron. There are many hydrazones and their metal ion chelates have been reported as antitumor [1,2] antibacterial and antifungal [3-5], tuberculostatic [6,7],agent . The thiazole and benzothiazole hydrazones which have sulphyr, nitrogen doner sites have been reported to shows various pharmacological importance [8-11]. A series of hydrazones obtained by the condensation of benzothiazole with aromatic aldehyde have been demonstrated to posses tuberculostatic and anticonvulsant. In this proposed work we used the 2-(cinnamy)-4-brom-6-methyl benzothiazolyl hydrazone as a chelating agent to prepare Ni(II) and Cu(II) metal ion chelates.

Material and Method.

All chemical used for the synthesis of ligand and metal ion chelates were of reagent grade. we were adopted standard method for preparation of ligand and metal ion chelates.

Synthesis of ligand.
We used the standard method for the preparation of ligand 2-(cinnamy)-4-brom-6-methyl benzothiazolyl hydrazones and purity is checked by TLC. This prepared ligand is used to synthesise the metal ion chelates.



2-(cinnamyl)-4-brom-6-methyl benzothiazolyl hydrazones.(CBMBTH)

Synthesis of metal ion chelates.

1) ***Synthesis of Ni^{+2} metal complex with 2-(cinnamyl) -4- bromo-6-methyl benzothiazolyl hydrazone***

0.2 M solution of 2-(cinnamyl) -4-bromo-6-methyl benzothiazolyl hydrazones were prepared in alcohol 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 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.

ii) Synthesis of copper complex with 2-(cinnamyl) -4- bromo-6-methyl benzothiazolyl hydrazones

Weighed quantities of $CuCl_2$ $2H_2O$ and 2-(cinnamyl) -4-bromo-6-methyl benzothiazolyl hydrazones were separately dissolved in ethanol to prepare 0.1 molar solution and mixed into each other in 1:3 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 precipitat is obtained at the end was digested, separated by filtration, washed with ethanol for 3-4 times and dried in vacuum at room temperature.

Result and Discussion

Elemental analysis.

Compound	M.wt	%C	%H	%N	%M
CBMBTH	372	55.01(55.25)	3.50(3.45)	11.32(11.37)	-
$[Ni(CBMBTH)_2]$ Cl_2 H_2O	719.71	45.78(45.69)	3.13(3.15)	9.46(9.42)	6.58(6.55)
[Cu(CBMBTH)l H_2O] Cl	524.54	38.98(38.40)	3.05(3.08)	8.01(8.05)	12.32(12.3)

Compound	N-H cm^{-1}	O-H cm^{-1}	C=N cm^{-1} (thiazolring)	C=N cm^{-1} (azomethine)	M-N cm^{-1}
CBMBTH	3145	-	1642	1608	-
$[Ni(CBMBTH)_2]Cl_2H_2O$	3145	-	1620	1580	612
[Cu(CBMBTH) Cl H_2O]Cl	-	3445	1600	1500	595

Infrared spectra.

I.R. spectra of [Ni(CBMBTH)Cl]Cl H_2O complex.

A sharp strong band is observed at 1608 cm-1 in the ligand CBMBTH it assigned to C=N (azomethine) group. In Ni^{+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 Ni-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 nickel complex it indicate that Nitrogen of N-H group is not involve in the complex formation. One band is observed in Ni-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 [Cu (CBMBTH) Cl H_2O] Cl complex

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 band is 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 in ligand it indicate the formation of M-N coordinate bond which is absent in ligand. Thus 2-cinnamyl-4-bromo-6-methyl-benzothiazolyl hydrazones act as bidented and coordinate through azomethine nitrogen and thiazole ring nitrogen. I.R. spectral data with probable assignment is detailed in the table

The X-band E.S.R. spectrum of the powder Ni(II) and Cu(II) complexes was recorded at room temperature. The calculated values of Ni(II) and Cu(II) calculated $g_{\|}$, $g_{\perp}$, $g_{avg,}$ and G are 2.1597,2.0175, 2.0649, 4.1773 and2.2347, 2.017157, 2.0899, 4.2523 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.

T.G.A./D.T.A plot of $[Ni(CBMBTH)_2]Cl_2H_2O$

T.G.A./D.T.A plot of $[Ni(CBMBTH)_2]Cl_2H_2O$ has decomposed in five step. 9.978% mass is burn in the first step at temperature range 85-110 °C. This loss of mass due to the elimination of lattice chloride and water molecule from the complex molecule. Observed value is coincide with the calculated value. In second step 21.279 % mass is lost in the temperature range 110-260°C. This loss of mass is due to the elimination of methyl group and bromide atom from the molecule. Third peak is observed at the temperature range 260-390°C and loss of mass is 25.98% is observed . This loss in mass is due to the elimination of 2 CH-CH=CH and benzene ring .In fourth peak 16.351% loss is observed in the temperature range 390-570°C This losss of mass is due the elimination of benzene ring. Fifth step observed at the temperature range 570-760°C and loss of mass 19.509% is observed . this loss of mass is due to the elimination of thiazole ring part and its substituted chain.The graph shows constant curve above 760°C . It indicate that the residue of metal oxide. Observed mass of metal is approximately equal to the calculated mass of metal.

T.G.A. /D.T.A. plot of [Cu(CBMBTH) Cl H_2O]Cl

T.G.A. /D.T.A. plot of [Cu(CBMBTH) Cl H_2O]Cl shows six peak . In first peak 6.76% mass is lost in the temperature range 70-120°C . This loss of mass is due to the elimination of lattice chloride from the molecule. Second peak is observed in the temperature range 120-260°C and 10.195% mass is lost. This loss of mass is due to the elimination of co-ordinate chloride and water molecule from the complex. Third peak is observed at the temperature tange 260-380°C and loss of mass 18.104% is observed . this loss of mass is due to the elimination of of CH_3 and Br from the molecule . Fourth peak is observed in the temperature range 380-530°C and 22.106% loss of mass is observed. This loss is due the the elimination of benzene ring and substituted propyl chain from the molecule. In fifth peak loss of 14.102% mass is lost in the temperature range 530-640°C . this loss of mass is due to the elimination of benzene ring from complex molecule . six peak is observed in the temperature range 610-760°C and loss of mass is 16.579% is observed . this loss of mass is due to the elimination of thiazole ring part and its substituent's chain. From the temperature 760°C graph shows constant curve , it indicate that the mass is remaining is metal oxide. Calculated values are coincide with observed values.

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