International Journal of Advanced Science and Research
ISSN: 2455-4227
Impact Factor: RJIF 5.12
www.allsciencejournal.com
Volume 3; Issue 5; September 2018; Page No. 24-29

Synthesis, spectral and thermal study of some Trasition Metail ion chelates of hydrazone containing N, O, S, donor atoms

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Abstract
Metal complexes is one of the most important field due to its versatile application. Certain metal complexes are used in Industries, for synthesis, It work as catalyst, they have some application in Agriculture. Particularly hydrazine metal complexes are bio-active compound and can used as anti-tubercular, antimicrobial Antifungal, anticancer, Anti-convconvulasant and anti-inflammatory activity. Particularly, the antibacterial and antifungal properties of hydrazone and their complexes with some transition metal ion is reported in literature. The chelating agent like hydrazine contain C=N linkage is essential for biological activity. Several azomethazines were reported to possess remarkable antibacterial, antifungal, anticancer active.

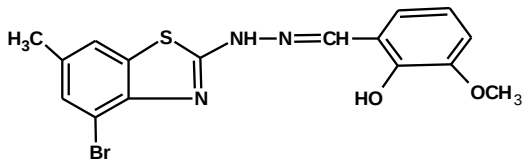
Keywords: metal, chelate, metal ion chelates

Introduction
Metal complexes is one of the most important field due to its versatile application. Certain metal complexes are used in Industries [1, 2], for synthesis, It work as catalyst [3], they have some application in Agriculture [4]. Particularly hydrazine metal complexes are bio-active compound and can used as anti-tubercular [5], antimicrobial [6] Antifungal [7], anticancer [8], Anti-convconvulasant [9] and antiinflamatori [10] activity. Particularly, the antibacterial and antifungal properties of hydrazone and their complexes with some transition metal ion is reported in literature. The chelating agent like hydrazine contain C=N linkage is essential for biological activity. Several azomethazines were reported to possess remarkable antibacterial, antifungal, anticancer active.
In present study I reported some transition metal ion complex and characterized them.

Chemistry of ligand
Hydrazones and derivatives of hydrazones containing N,O,S, donor atoms have chelating abilities with the transition metal ions. References indicate that $Ni^{+2,}$ Cu^{+2} and Zn^{+2} metal ions do produces the complexes with benzothiazoline hydrazones. Certain metal complexes are acting as antitumor and antifungal agents [1, 2]. Certain metal ion complexes of hydrazones have pharmacological importance [3, 4]. Literature is not available regarding use of 2-(2'-hydroxy-3'-methoxyphenyl)-4-bromo-6-methy lbenzothiazolyl hydrazones as chelating agent in the synthesis of Cr^{+2}, Mn^{+2}, Fe^{+3}, Co^{+2},Ni^{+2},Cu^{+2}, metal ion complexes.

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

Structure of ligand



2-(2'-hydroxy-3'methoxy phenyl)-4-bromo-6-methyl benzothiazolyl hydrazon.
Melting point-175 °C, Empiricalformula-$C_{16}H_{14}N_3BrSO_2$, Exact mass -392
This ligand is refered as HMPBMBTH

Synthesis of complexes
i) Synthesis of Ni^{+2} metal complex with 2(2'-hydroxy-3'-methoxy phenyl)-4-bromo-6-methyl benzothiazolyl hydrazone (HMPBMBTH)
150 ml of 0.2 M solution of 2(2'-hydroxy-3'-methoxy phenyl)-4-bromo-6-methyl benzothiazolyl hydrazone (HMPBMBTH) were prepared in alcohol and 100
ml of 0.1 M solution of $NiCl_2$ prepared in alcohol. These two solution were mixed in 500 ml flask, the pH is mainted up to 6.5 by addition of buffer solution. The reaction mixture is were refluxed for one hour. precipitate is obtained, it is digested after cooling it is filtered through Buckner funnel. The precipitate is purified by washing with ether, the complex were dried by keeping it in oven. The product was packed into sample bottle.

ii) Synthesis of cupper complex

Cupper chloride and ligand 2(2'-hydroxy-3'-methoxy phenyl)-4-bromo-6-methyl benzothiazolyl hydrazone (HMPBMBTH) were dissolved separately in ethanol so as to prepare 0.1 molar solution with constant stering. A clear solution of cupper 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 green colored solid is obtained it washed with ethanol and dried and stored in bottle.

Physical parameter and elemental analysis

Melting point of complexes are determined with the help of melting point apparatus by open capillary method. Chlorine is estimated by Mohr's method. Metal ion percentage in a complexes is determined by E.D.T.A. titration. M:L ratio is determined by heating known weight of complexes in platinum crucible. Physical parameter and analytical data of the Ni(II) Cu(II) complexes and ligand CBMBTH are given in table 1. metal ligand ratio and empirical formula were assigned on the basis of TGA measurements and elemental analysis (table 2.)

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.

Result and Discussion

The complexes of Ni(II), Cu(II), are prepared with the ligand HMPBMBTH. 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 HMPBMBTH metal complexes.

Complex	color	D.P.	Yield%	%Cl
[Ni(HMPBMBTH) H_2O] Cl_2	Pale green	223-227	59	11.989
[Cu(HMPBMBTH) Cl] Cl.H_2O	Sky blue	232-235	73	13.034

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

Compound	M. wt	Empirical formula	%C	%H	%N	%M
HMPBMBTH	392.17	$C_{16}H_{14}N_3BrSO_2$	49.005	3.569	10.714	-
[Ni(HMPBMBTH) H_2O] Cl_2	539.88	$C_{16}H_{16}$ Cl_2 NiN_3SBrO_3	32.45	2.701	7.092	9.914
[Cu(HMPBMBTH) Cl] Cl.H_2O	544.71	$C_{16}H_{16}Cl_2NiN_3SBrO_3$	35.281	2.937	7.710	11.66

Electronic spectra

The ligand 2-(2′-hydroxy-3′-methoxyphenyl)-4-bromo-6-methyl benzo-thiazolyl hydrazones (HMPBMBTH) has exhibited one characteristic maxima in U.V. region at 344 nm while in [Ni(HMPBMBTH) H_2O] Cl_2 complex it is shifted towards blue shift i.e. lower region and observed at 324nm. While in [Cu(HMPBMBTH) Cl] Cl.H_2O complex the band is shifted towards red shift and observed at 352 nm. This shifting of bands indicate that there is complexetion in metal and ligand.

Table 3: Electronic data of ligand HMPBMBTH metal complexes.

Compound	Wavelength	Log E
Ligand HMPBMBTH	344	2.942
[Ni(HMPBMBTH) H_2O] Cl_2	324	1.936
[Cu(HMPBMBTH) Cl] Cl.H_2O	352	2.009

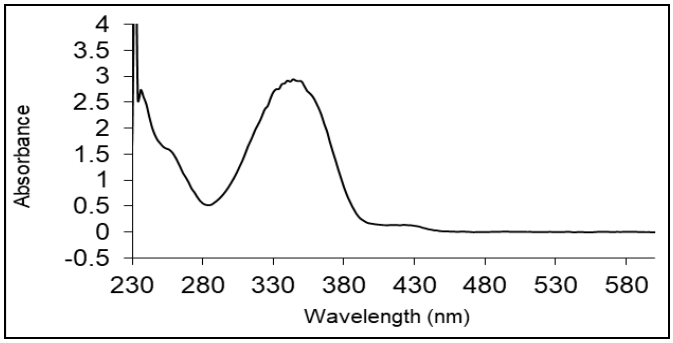


Fig 1: U.V. of Ni complex with HMPBMBTH

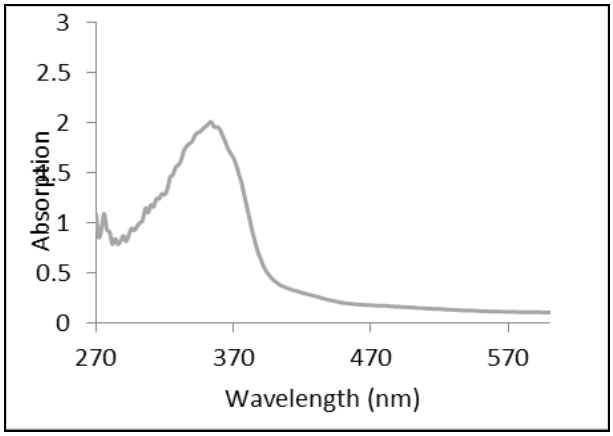


Fig 2: Cu complex with (HMPBMBTH)

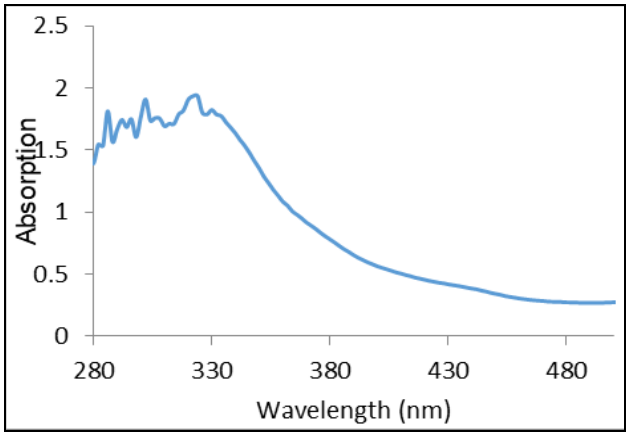


Fig 3: U.V. of HMPBMBTH

I.R. Spectra

The ligand 2(2′-hydroxy-3′-methoxy phenyl)-4-bromo-6-methyl benzothiazolyl hydrazones exhibit a sharp strong band at 3533 cm-1in I.R. spectra which may be assign to phenolic hydroxyl group In [Ni(HMPBMBTH) H_2O] Cl_2 complex borad strong is observed at 3435 and in [Cu(HMPBMBTH) Cl] Cl.H_2O complex broad band is observed at 3456 cm-1. The shifting of band indicate that the coordination of metal ion through 'O' of phenolic OH group. In I.R. spectra of one band is observed at 1616 cm-1 it is due to C=N (ring) but in but in [Ni(HMPBMBTH) H_2O] Cl_2 it is observed at 1600 cm-1 this shifting of band in complex clearly indicate that Nitrogen of benzothiazine ring is involved in the complex formation. The band is observed at 1605 cm-1 in [Cu(HMPBMBTH) Cl] Cl.H_2O this shifting of band is indicate that 'N' of thiazol ring is involved in the complex formation. One band is observed at 1580 cm-1 in ligand it may be due to the C=N (azomethine) group this band is shifted to lower region in [Ni(HMPBMBTH)H_2O] Cl_2 and observed at 1560cm-1 it indicate that azomethine nitrogen is involve in the formation of coordinate bond with Ni+2. In [Cu(HMPBMBTH) Cl] Cl.H_2O complex band is observed at lower region and it appear at 1530 cm-1 is indicate that the azomethine nitrogen is involved in the complex formation. Another band is observed at 3163 in I.R. spectra of ligand which may assign N-H stretching but in [Ni(HMPBMBTH) H_2O] Cl_2 and [Cu(HMPBMBTH) Cl] Cl.H_2O it is not observe because it may merged in the broad peak of OH group and water molecule this indicate that N-H is not involve in the complex formation. Another band is 595 in [Ni(HMPBMBTH) H_2O] Cl_2 and [Cu(HMPBMBTH) Cl] Cl.H_2O complexes but not observed in ligand it indicate that there is formation of M-O bond in both complexes. One band is observed at 515 cm-1 in both complex which is absent in ligand this indicate that the formation of M-N coordinate band. Thus 2-(2'-hydroxy-3'-methoxy phenyl)-4-bromo-6-methyl benzothiazolyl hydrazones act as tridentate in both complexes and coordinate through ring nitrogen, azomethine nitrogen and oxygen of phenolic OH. I.R. spectral data with probable is given in the table 4

Table 4: I.R. data of ligand HMPBMBTH metal complex

compound	O-H cm^{-1}	N –H cm^{-1}	C=N cm^{-1} ring	C=N cm^{-1} azomethine	M-O cm^{-1}	M-N cm^{-1}
HMPBMBTH	3533	3163	1515	1580	--	--
[Ni(HMPBMBTH) H_2O] Cl_2	3435	-	1600	1560	595	515
[Cu(HMPBMBTH) Cl] Cl.H_2O	3458	-	1605	1530	658	523

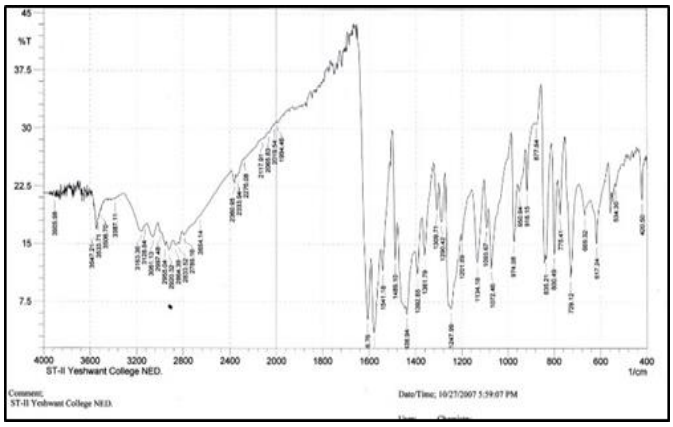


Fig 4: I.R. spectra of ligand HMPBMBTH

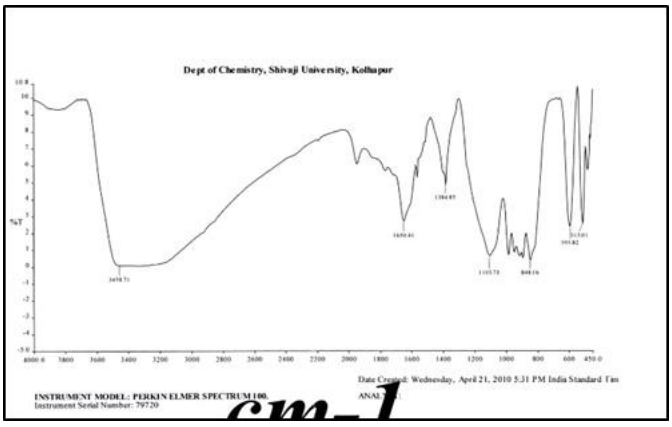


Fig 5: I.R. spectra of [Ni(HMPBMBTH) H_2O] Cl_2

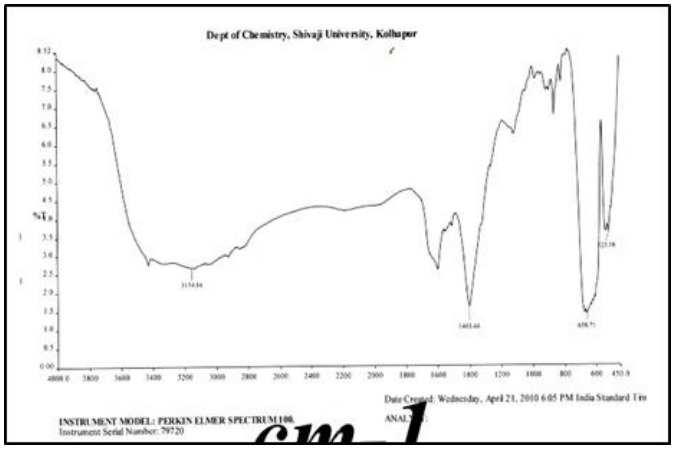


Fig 6: I.R. spectra of [Cu(HMPBMBTH) Cl] Cl.H_2O

Electron spin resonance spectroscopy

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) is $g_{\|}$, $g_{\perp}$, g $_{avg,}$ and G are 2.227, 2.03674, 2.10016, 4.26374 respectively. And Cu(II) is $g_{\|}$, $g_{\perp}$, g $_{avg,}$ and G are 2.23474, 2.01126, 2. 0857533, 4.246 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 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.

TGA/DTA plot of [Ni(HMPBMBTH)H_2O] Cl_2 has reflected five step. In first step 13.1510% loss is found in the temperature range 50-120°C it is due to the elimination of lattice chloride. Observed value is coincide with the calculated value. In second step loss in mass is observed at the range of temp 120-225°C it is due to the loss of coordinated water molecule. The third step is observed at the temperature range 225-460°C and loss of mass observed 23.33%. This loss of is due to the elilmination of methyl group, methoxy group, and bromide from the molecule. In the temperature range 460-525°C loss of mass is observed 27.59%. this loss in weight is due to the elimination of two benzene rings. In the fifth step 21.62% loss of mass in the temperature range 525-760°C. this loss of mass is due to the elimination of thiazole ring part, co-ordinated OH group and NH-N=CH 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.

In complex [Cu(HMPBMBTH)Cl]Cl.H_2O five step of decomposition were observed. Form table (table no.) In first step compound is lost 9.82 % at the temperature range 50-110 °C which corresponds to the calculated weight of water molecule and chloride it indicate that water molecule chloride is present in complex. Second peak is observed at the 110-225°C and loss of mass is 6.517% is observed. This loss of mass is due to the elimination of chloride atom which is co-ordinate with metal. In the third step 23.13 % loss of mass is observed in the temperature range 225-450°C. this loss of mass is due to the elimination of methyl group, methoxy group and bromide from the molecule. In the fourth step temperature range 450-580°C, 27.35% loss is observed. It may be due to the elimination of two benzene ring from the molecule. Last step is observed in the temperature range 580-790°C and loss of mass is observed 21.47%. This loss of mass is due to the thiazole ring part, OH group, and CH-NH=N part. Observed values and calculated values are approximately matches with each other, TGA/DTA graph curve show constant value from temperature 790°C and 11.66% mass is constant in the sample. this mass is residue of metal oxide.

Table 5: Thermal decomposition value of [Ni(HMPBMBTH)H_2O] Cl_2 *metal complex*

Temp. range °C	% loss	Nature of decomposition
50-120	13.1510(13.87)	Lattice chloride
120-225	3.334(3.232)	Coordinated water molecule
225-460	23.33(22.901)	-CH_3, -OCH_3 & -Br
460-525	27.59(27.385)	Two Benzen ring
525-760	21.63 (21.26)	Thiazole ring part and substituted chain.

Table 6: Thermal decomposition value of [Cu(HMPBMBTH)H2O]Cl 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.

Thermal spectra of metal complexes

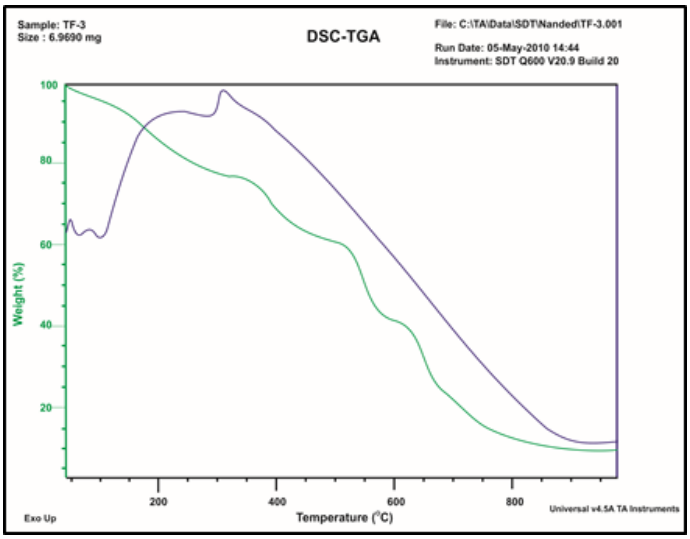


Fig 7

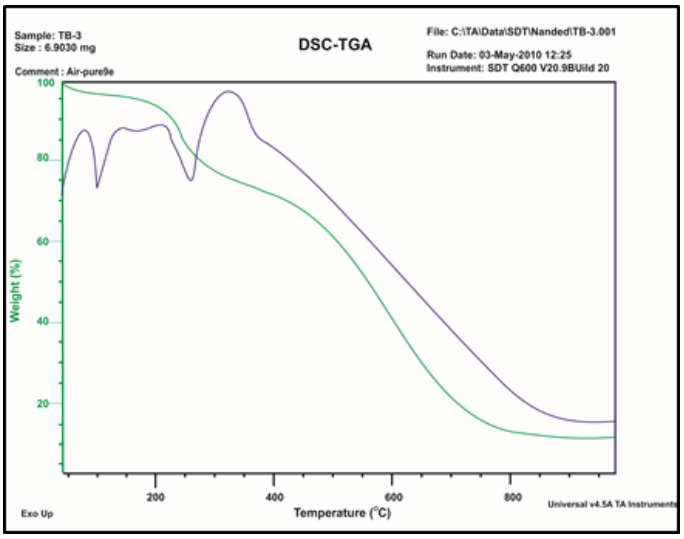
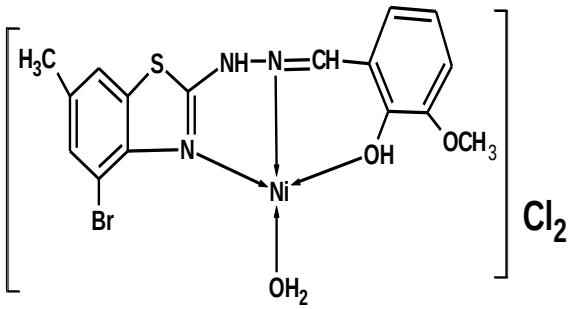
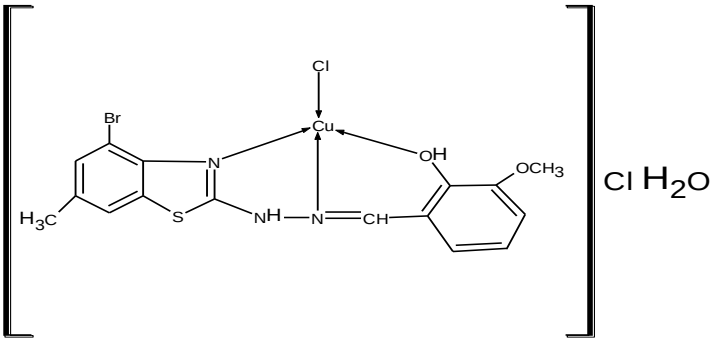


Fig 8

A) Proposed structure of [Ni(HMPBMBTH) H2O] Cl2
B) Proposed structure of [Cu(HMPBMBTH) Cl] Cl H2O

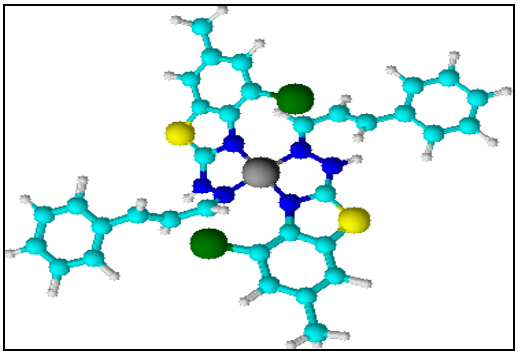


(A)

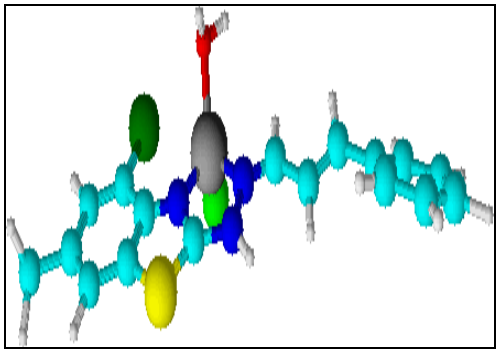


(B)

Proposed 3D structure metal complexes



$[Ni(CBMBTH)_2]\ Cl_2 2H_2O$



$[Cu(CBMBTH)_2]\ Cl_2\ 2H_2O$

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