



Synthesis and characterization of transition metal complexes with newly synthesized substituted benzothiazole

T. M. Bhagat¹ D.K.Swamy², M. N. Deshpande³

¹P.G. Dept. of Chemistry, G. S. Gawande College, Umarched, Dist. Yavatmal. (M.S.) India

²Dept. of Chemistry, P. N. College, Nanded. (M. S.) India

³P. G. Dept. of Chemistry, N.E.S. Science College, Nanded. (M.S.) India

ABSTRACT

Heterocyclic compounds with different functional group have a chelating inheritance. It is also proved that the metal chelates have drugs activities and some metal chelates acts as plant growth promoter. Hence we have synthesized heterocyclic compound, 4-bromo-2-hydrazino-6-methyl benzothiazole and different experiments were conducted to see the chelating tendency of newly synthesized heterocyclic compound. When 4-bromo-2-hydrazino-6-methyl benzothiazole were treated with metal ions like Fe^{++} , Co^{++} , Ni^{++} at different P^H and different laboratory conditions, the metal chelates are formed. The synthesized complexes were purified and characterized by analytical, thermal and spectral parameters.

Key words: Metal- chelates, characterization.

INTRODUCTION

d-Block metal ion have a tendency to form the complexes. A series of transition metal ions forms complexes with Schiff bases[1], aromatic hydrazones [2-5] like o-hydroxy 5-methyl salicylidine hydrazone, 2-hydroxy-4-methyl acetophenone phenyl hydrazone, o-hydroxy 5-methyl acetophenone phenyl hydrazone, o-hydroxy 4-methoxy salicylidine phenyl hydrazone, o-hydroxy 5-methyl salicylidine phenyl hydrazone, hydroxamic acid, α -mercapto-2-amino phenyl acetohydroxamic acid [6].

The benzothiazole compounds containing different heteroatom, substituent have a tendency to form a good metal complex [7]. Substituted benzothiazole are antifungal [8], antibacterial [9] intramural depressant [10], antituberculosis agents [11], showing antitumor activity [12], anticancer [13] used for treatment of cardiovascular disorder [14] and controlling horticultural viral infection [15]. Activity of the substituted benzothiazole enhances on complex formation with suitable metal [16]. These reports encourage the study the metal chelates of substituted benzothiazole with transition metal. No references are found regarding the use of 2-hydrazino-4-bromo-6-methyl benzothiazole used as a chelating agent.

In this paper, we have synthesized, 2-hydrazino-4-bromo-6-methyl benzothiazole chelating agent and used to synthesis of metal chelates with Fe (II), Co (II) and Ni (II) transition metal. These metal chelates were characterized by analytical, thermal, Infrared and electronic spectroscopy.

EXPERIMENTAL SECTION

Preparation of 4-bromo-2-hydrazino-6-methyl benzothiazole Iron (II) chloride (Fe-BHMB):

All chemicals were used A. R. grade. Hydrated ferrous chloride (A.R. BDH make) 0.3gm were accurately weighed and it is transferred into 25ml distilled alcohol. The brown coloured solution was formed. 0.9gm of 4-bromo-2-hydrazino-6-methyl benzothiazole (BHMB) was accurately weighed and dissolves in 35 ml distilled alcohol. These two solutions were transferred into R.B. flask. The P^H of the solution was adjusted 6.5 by adding drop by drop alcoholic ammonia solution. The reaction mixture was refluxed for three hours. Black coloured ppt. appeared. It is cooled and filtered through whatmann's filter paper. The precipitate was washed three times with warm ethyl alcohol, the black ppt. of Fe⁺⁺ complex is dried under sunlight and fine black crystal of Fe-BHMB complex is stored in test tube having glass cork. The prepared complex is characterized by determining decomposition point and other physical properties, spectral studies and X-ray diffraction method.

4-bromo-2-hydrazino-6-methyl benzothiazole Cobalt (II) chloride complex (Co-BHMB):-

A.R. grade BDH make CoCl₂.6H₂O were used to synthesis the metal chelate. 0.32gm of CoCl₂.6H₂O was weighed and it is dissolved in 30 ml of redistilled ethyl alcohol. 4-Bromo-2-hydrazino-6-methyl benzothiazole solution was prepared by dissolving 0.9gm of BHMB in distilled alcohol. The metal ion solution and ligand solution were mixed in R.B. flask. The 6.7 P^H was maintained by adding alcoholic ammonia. The reaction mixture was refluxed by keeping the round bottom flask in water bath maintaining the temp.70 °C. Water condenser was used while refluxing the reaction mix, after two hour refluxing brownish coloured precipitate appeared and it is further refluxed for half an hour. It is filter through whatmann's filter paper and the complex is dried in oven by keeping temp. 75 °C. The complex was stored in glass sample bottle having a cork.

4-bromo-2-hydrazino-6-methyl benzothiazole Nickel (II) chloride complex (Ni-BHMB):

Metal salt NiCl₂.6H₂O 0.32gm was weighed on analytical balance. Its solution was prepared in distilled alcohol. The solution is warmed on steam bath. The ligand solution (solution of BHMB) was also prepared by dissolving 0.95gm of BHMB in 50 ml of distilled alcohol. The green coloured NiCl₂ solution and colourless solution of ligand were mixed in round bottom flask. The water condenser is attached to the R.B. flask and contents were refluxed on water bath for three and half hours at 65 °C temperatures. The product was faint green colour and it is isolated by filtering through whatmann's filter paper. The product was purified by washing with distilled alcohol. The product was dried and it is stored in corked bottle.

RESULTS AND DISCUSSION

The newly synthesized metal chelates were characterized by Colour, decomposition point, elemental analysis, M/L ratio and magnetic susceptibility. The values are shown in table No.1. The elemental analysis of the products was obtained from Sophisticated Analytical Instrument Facility, Madras. The M/L ratios of metal complexes were determined by decomposing the known weight of metal complex in platinum crucible at high temp.

Spectral studies of complexes:

The electronic spectra of chelating agent BHMB and prepared complexes of Fe⁺⁺, Co⁺⁺, Ni⁺⁺ were obtained from UDCT, Mumbai. The range of spectrum is from 220 nm. to 700 nm. The electronic spectra of chelating agent and metal chelate are different due to different electronic transition. The absorbance peaks of ligands are obtained in U. V. region while the absorbance peaks are obtained in visible region for metal complexes. The absorbance in case of ligand may be due to n - π* and π - π* transition in U. V. region. Such transitions are not found in case of metal complexes. In spectrum of BHMB chelating agent, three bands at 270 nm, 294 nm and 327 were obtained. The maximum absorbance is at 294 nm. These may be due to n - π* and π - π* transition in the chelating agent.

The new absorbance peak at 400 nm, 450 nm, 480 nm and 550 nm are observed in Fe-BHMB complex. These new peaks may be due to ligand to metal electronic transition. These peaks proved the involvement of electron of donor atom to the metal ion. While in Co-BHMB metal chelates bands are observed at 400 nm, 460 nm, 475nm and 510 nm. These bands are not found in the electronic spectra of chelating agent BHMB. These new peaks are in the visible region indicates, there is an electronic charge transfer from donor atom of chelate to central metal ion.

The I.R. spectra of prepared complexes and chelating agents are brought from I.I.C.T. Hyderabad by using thermo Nicolet nexus 670 spectrometer. DTGS. KBr detector is used for detection. By comparing the I.R. spectra of chelating agent 4-bromo-2-hydrazino-6-methyl benzothiazole and metal chelates are different. Some peaks are disappeared and some new peaks are obtained in the I. R. of metal complexes. The broadening of peaks and the formation of new peaks in the IR of metal complexes assures that there is a formation of metal-Nitrogen bond. The chelating agent contains secondary nitrogen in ring and primary nitrogen of amine. The bonding takes place with

these nitrogen of ligand. Therefore ligand acts as tridentate ligand. The band is obtained at 3400 cm^{-1} indicates that there is presence of lattice water. The band at 3100 cm^{-1} and 3000 cm^{-1} indicates that the compound has free $-\text{NH}_2$ and $-\text{NH}$ group. The broadening of peaks assures that bonding with three nitrogen atom with metal ion. New sharp peaks are obtained at 679 cm^{-1} , 549 cm^{-1} , 459 cm^{-1} indicates the bonding to metal ion with different nitrogen of chelating agent.(table 2)

TABLE: 1 Analytical data and physical properties of complexes

Sr. No.	Ligand / Metal Complex	Colour	Mol. Wt.	% Yield	M.P/ D.P.	M/L ratio	M.B. μ_{eff}	Elemental analysis % Found (calculated)			
								M	C	H	N
1	4-Bromo-2-hydrazino-6-methyl benzothiazole	White	258	90	248	--	--	--	36.9 (37.2)	2.9 (3.1)	16.0 (16.2)
2.	Bis-4-bromo-2-hydrazino-6-methyl benzothiazole Iron (II) chloride	Black	678	76	257	M : L ₂	5.40	8.08 (8.23)	28.16 (28.28)	2.28 (2.35)	12.29 (12.37)
3.	Bis-4-bromo-2-hydrazino-6-methyl benzothiazole Cobalt (II) chloride	Brown	681.9	56	254	M : L ₂	5.10	8.56 (8.63)	27.98 (28.15)	2.26 (2.34)	12.27 (12.31)
4.	Bis-4-bromo-2-hydrazino-6-methyl benzothiazole Nickel (II) chloride	Yellowish green	681.7	64	346	M : L ₂	3.11	8.64 (8.61)	27.82 (28.16)	2.27 (2.34)	12.19 (12.32)

Table: 2- I. R. and electronic spectral data

Sr. No.	Compound /Complex	N-H Stret.	C=N Stret.	N-N Stret.	M-N Stretching.	U.V.- Visible nm (cm^{-1})
1	BHMB	3452	1636	1074	--	270 (37037)
						294 (34013)
						327 (30581)
2	Fe-BHMB	3413	1623	1033	459	275 (63363)
						370 (27027)
						484 (20661)
3	Co-BHMB	3428	1628	1068	406	294 (34013)
						370 (27027)
						484 (20661)
4	Ni-BHMB	3437	3437	1073	420	--
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						--

Table: 3-TGA-DTA

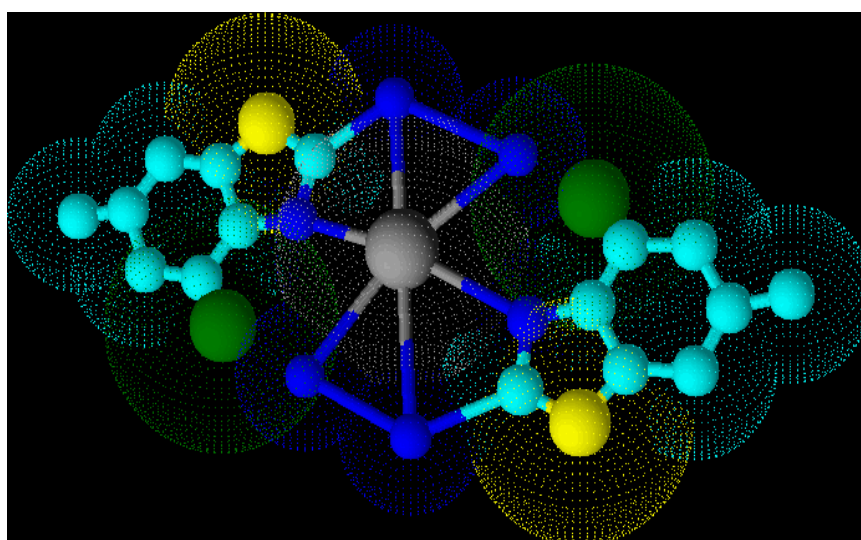
Sr. No.	Complex	Total mass loss		Temp. °C	% loss
		Theo. %	Exp. %		
1.	Bis-4-bromo-2-hydrazino-6-methyl benzothiazole iron (II) Chloride	91.78	91.73	50 – 130	4.95
				130 – 285	12.40
				285 – 370	33.06
				370 – 385	22.04
				385 – 678	19.28
				678 – 800	8.26 exp./res. Cal./res.
2.	Bis-4-bromo-2-hydrazino-6-methyl benzothiazole cobalt (II) Chloride	91.38	91.12	50 – 115	5.75
				115 – 200	23.56
				200 – 360	19.40
				360 – 555	42.4
				555 – 800	8.87 exp./res. 8.62 cal./res.
				3.	Bis-4-bromo-2-hydrazino-6-methyl benzothiazole nickel (II) Chloride
125 – 240	27.77				
240 – 430	22.22				
430 – 610	24.99				
610 – 675	11.11				
675 – 800	8.33 exp./res. 8.59 cal./res.				

The ESR spectra of prepared complexes were obtained from SAIF, Madras. The scan range is 500 gauss, mode of amplitude 4G, mode of frequency 100 KHz and number of scan-6. The g value of iron complex, Cobalt complex and Nickel complex is 2.07, 2.01 and 2.02 respectively. These g values were less than 2.3, which indicate covalent nature of bonding between co-ordinating donar atoms of ligand with the central metal ion.

The X-ray spectra of metal complexes were obtained from Tata Institute of Fundamental Research, Mumbai. The crystalline structure of Iron complex, Cobalt complex and Nickel complex is confirmed by using X-ray diffraction. To determine the effect of temperature during the decomposition of prepared metal complexes, TGA-DTA study was undertaken. The TGA-DTA of prepared complexes was obtained from C-MET laboratory Pune. The instrument used to determine TGA-DTA was STAR[®] SW 9.01 The temperature range is from room temperature to 1000 °C. Method used for TGA-DTA analysis is TG-RT-900 @ 10 °C. The values are given in table no.3.

CONCLUSION

On the basis of physical, chemical and spectral studies, the prepared complexes may have following structures.



- I) Central metal ion Fe^{++} , Co^{++} , Ni^{++} .
- II) The nature of ligand is basic and tridentate.
- III) The Co-ordination number of metal ion is six
- IV) The Co-ordination number carries two positive charge.
- V) All complexes are paramagnetic.
- VI) Geometry of complexes is octahedral.
- VII) Donar sites are tertiary, secondary and primary nitrogen.

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