

# SYNTHESIS, CHARACTERIZATION, ANTIBACTERIAL AND ANTIFUNGAL STUDIES ON METAL COMPLEXES WITH BENZOTHAZOLYL HYDRAZONE

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## ABSTRACT

A series of Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) metal complexes containing the N, N, O donor tridentate Schiff base ligands have been synthesized and characterized. All the metal complexes (**1-3**) are [ML<sub>2</sub>] and (**4-5**) [MLCl] type. Where M= Fe(II), Co(II), Ni(II), Cu(II), Zn(II) and L=2-[(4,6-dimethyl-benzothiazol-2-yl)-hydrazonomethyl]-6-methoxy-phenol=(**DBYHMP**) act as tridentate ligand in all the complexes. The elemental analysis suggests the stoichiometry to be 1:2 (**1-3**) and 1:1 (**4-5**) (metal: ligand). Magnetic susceptibility data coupled with electronic spectra suggest octahedral (**1-3**) and tetrahedral structure (**4-5**). The Schiff base and its metal chelates were screened for their antibacterial *Escherichia coli*, *Salmonella typhi*, *Staphylococcus aureus*, *Bacillus subtilis*, *Erwinia*, *Xanthomonas* and antifungal activity *Aspergillus niger*, *Penicillium chrysogenum*, *Fusarium moneliforme*, *Aspergillus flavus* and the metal chelates were found to possess better activity than that of the respective Schiff base.  
**Keywords:** Schiff base, spectral analysis and antibacterial activity.

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## INTRODUCTION

The d-Block metal ions have tendency to form the complexes. A series of transition metal complexes with Schiff bases<sup>1</sup>, aromatic hydrazones<sup>2-5</sup> have been quite extensively investigated. The chemistry of hydrazone complexes involving O,N,S donor ligands has received special attention because of their coordination capability, their pharmacological activity<sup>6-10</sup> and their uses in analytical chemistry as metal extracting agents<sup>11-13</sup>. It has recently been shown that the metal complexes are more potent and less toxic in many cases as compared to the parent compound.

Considering these aspects, the present investigation deals with the synthesis of Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) metal complexes with 2-[(4,6-dimethyl-benzothiazol-2-yl)-hydrazonomethyl]-6-methoxy-phenol (Scheme-1) and their characterization by analytical, spectral and thermal studies.

## EXPERIMENTAL

### Preparation of hydrazone

#### 2-Hydrazino-4,6-dimethyl benzothiazole

Hydrazine hydrate (4 ml of 80%) was taken in round bottom flask and kept in freezing mixture. Concentrated hydrochloric acid (4ml) was added to it. On shaking and cooling the above mixture ethylene glycol (20ml), 2-amino-4,6-dimethyl benzothiazole (0.02 mole, 3.56 gms) was added. The mixture was refluxed for 2.5 hours at 150-160°C. The solution was cooled at room temperature. The crystalline product was obtained. (Yield 71%, m.p.175°C.)

#### 2-[(4,6-dimethyl-benzothiazol-2-yl)-hydrazonomethyl]-6-methoxy-phenol:(**DBYHMP**)

(4,6-dimethyl-benzothiazol-2-yl)-hydrazine (7 g, 0.005mole) was mixed with o-hydroxy-methoxybenzaldehyde (5.608 g, 0.005mol) in ethanol. The mixture was placed in round bottom flask and

refluxed on water bath for 1 h. and then allowed to cool at room temp. The resulting light brown colored precipitate was filtered, washed several times with ethanol (Scheme-2). (Yield 80%, m.p.= 200° C)

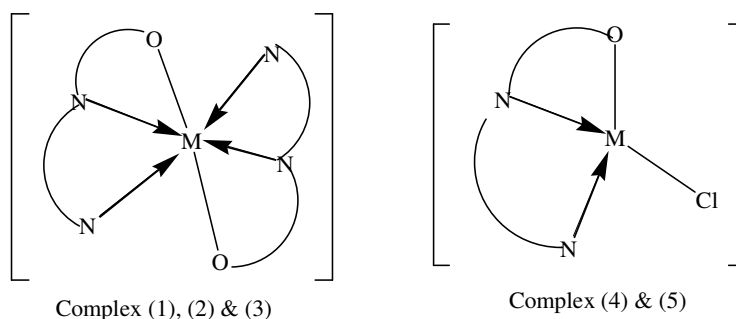
### Preparation of the complex

**[Fe(DBYHMP)<sub>2</sub>]:** The complex was prepared by refluxing 1:2 molar mixture of ethanolic solutions of the ligand and ferrous sulphate for 1 h, maintaining pH (~8) by adding alcoholic ammonia. The sparingly soluble, pale brown product was separated and washed with ethanol and the complex was dried over anhydrous calcium chloride in vacuum and tested with TLC (yield=69%). Chemical analysis. Found: Fe 7.82; C 57.65; H 4.57; N 11.90; O 9.08; S 9.15 %. FeC<sub>34</sub>H<sub>32</sub>N<sub>6</sub>O<sub>4</sub>S<sub>2</sub> requires: Fe 7.88; C 57.63; H 4.55; N 11.86; O 9.03; S 9.05 %.

**[Co(DBYHMP)<sub>2</sub>]:** The complex was prepared by refluxing for 1 h, the ethanolic solution of the ligand with cobalt sulphate in ethanol in 1:2 molar ratio, maintaining pH (~8) by adding alcoholic ammonia. The sparingly soluble, dark brown colored product was filtered and washed with ethanol and the complex was dried over anhydrous calcium chloride in vacuum and tested with TLC (yield=65%). Chemical analysis. Found: Co 8.21; C 57.30; H 4.65; N 11.92; O 8.87; S 9.13 %. CoC<sub>34</sub>H<sub>32</sub>N<sub>6</sub>O<sub>4</sub>S<sub>2</sub> requires: Co 8.28; C 57.38; H 4.53; N 11.81; O 8.99; S 9.01.

**[Ni(DBYHMP)<sub>2</sub>]:** The complex was prepared by refluxing for 1 h, the ethanolic solution of the ligand with nickel chloride in ethanol in 1:2 molar ratio, maintaining pH (~8) by adding alcoholic ammonia. The sparingly soluble, reddish brown colored product was separated and washed with ethanol and the complex was dried over anhydrous calcium chloride in vacuum and tested with TLC (yield=73%). Chemical analysis. Found: Ni 8.26; C 57.48; H 4.50; N 11.87; O 9.09; S 9.14 %. NiC<sub>34</sub>H<sub>32</sub>N<sub>6</sub>O<sub>4</sub>S<sub>2</sub> requires: Ni 7.98; C 57.63; H 4.55; N 11.86; O 9.03; S 9.05 %.

**[Cu(DBYHMP)Cl]:** The complex was prepared by refluxing for 1 h, the ethanolic solution of the ligand with copper chloride in ethanol in 1:2 molar ratio, maintaining pH (~8) by adding alcoholic ammonia. The sparingly soluble, yellowish brown colored product was separated and washed with ethanol and the complex was dried over anhydrous calcium chloride in vacuum and tested with TLC (yield=67%). Chemical analysis. Found: Cu 14.90; C 47.90; H 3.74; N 9.83; O 7.64; S 7.67; Cl 8.20 %. CuC<sub>17</sub>H<sub>16</sub>N<sub>3</sub>O<sub>2</sub>SCl requires: Cu 14.94; C 48.00; H 3.79; N 9.88; O 7.52; S 7.54; Cl 8.33%.



Scheme 1 - Proposed structures for the Fe(II), Co(II), Ni(II), Cu(II) & Zn(II) complexes

**[Zn(DBYHMP)Cl]:** The complex was prepared by refluxing for 1 h, the ethanolic solution of the ligand with zinc chloride in ethanol in 1:2 molar ratio, maintaining pH (~8) by adding alcoholic ammonia. The sparingly soluble, pale yellow colored product was separated and washed with ethanol and the complex was dried over anhydrous calcium chloride in vacuum and tested with TLC (yield=74%). Chemical analysis. Found: Zn 15.27; C 47.66; H 3.58; N 9.76; O 7.36; S 7.71; Cl 8.42 %. ZnC<sub>17</sub>H<sub>16</sub>N<sub>3</sub>O<sub>2</sub>SCl requires: Zn 15.31; C 47.79; H 3.77; N 9.84; O 7.49; S 7.51; Cl 8.30 %.

### Antibacterial activity

The antibacterial activity of the hydrazone and its complexes were studied against bacterial species. The antibacterial results are given in the (Table-1). Antibacterial activity was carried out by agar cup method. The Schiff bases and all its complexes individually varying degrees of inhibitory effects on the growth of the tested bacterial species. The metal complex (3) showed good antibacterial activity against *Escherishia coli* and *Salmonella typhi*. The maximum activity shown by Compound (5) against *Bacillus subtilis*. The metal complex (6) also displayed good antibacterial activity against *Staphylococcus aureus*, *Erwinia* and *Xanthomonas*. Metal complexes (4) and (6) showed similar activity against *Xanthomonas*. Most of the metal complexes showed better activity than ligand.

### Antifungal activity

The newly prepared complexes were screened for antifungal activity against *Aspergillus niger*, *Fusarium moneliforme*, *Penicillium chrysogenum* and *Aspergillus flavus* by Poison plate method. Grysofulvin (antifungal) was used as a reference drug. This experiment indicates that chelating agent do not show antifungal property. The metal chelates of this chelating agent acquire some moderate activity. Results are given in (Table-2).

### Analysis and physical measurements

All the chemicals and solvents used to carry out experimental works were of AR (Sd, E-Merk) grade. The electronic spectra of metal ion complexes were recorded on UV- visible DMR – 21 spectrophotometer. Molar conductance measurements were made on Systronics digital conductivity meter at room temperature using conductivity cell. The magnetic measurements were carried out using Gouy's balance at room temperature. Infrared spectra of metal complexes were taken on Perkin Elmer recording IR Spectrophotometer. TG analysis were carried out in 25-850 °C range using thermal analysis with heating rate 10 °C min<sup>-1</sup> using alumina as a standard. The purity of hydrazone Schiff base and its complexes was confirmed by C, H and N analysis, using a Carlo Erba 1180 analyzer. MO and Cl were determined by standard procedures. The metal contents were determined by atomic spectra on Perkin Elmer atomic absorption spectrophotometer (model 2380).

## RESULTS AND DISCUSSION

The formation of the complex occurs by the reaction of ethanolic solution of the ligand (DBYHMP) with ethanolic solution of metal salt FeSO<sub>4</sub>, CoSO<sub>4</sub>, NiCl<sub>2</sub>, CuCl<sub>2</sub> and ZnCl<sub>2</sub>. The results of elemental analysis, the molar conductance values in DMF and the spectral data are in agreement with the proposed formulas [FeL<sub>2</sub>] (1), [CoL<sub>2</sub>] (2), [NiL<sub>2</sub>] (3), [CuLCl] (4) and [ZnLCl] (5). The molar conductance values (10<sup>-4</sup> M), lie in the range of nonelectrolytes for all the complexes (1), (2), (3), (4) and (5) (42, 55, 50, 48 and 56 Ω<sup>-1</sup>cm<sup>2</sup> mol<sup>-1</sup> respectively).

### Infrared spectral studies

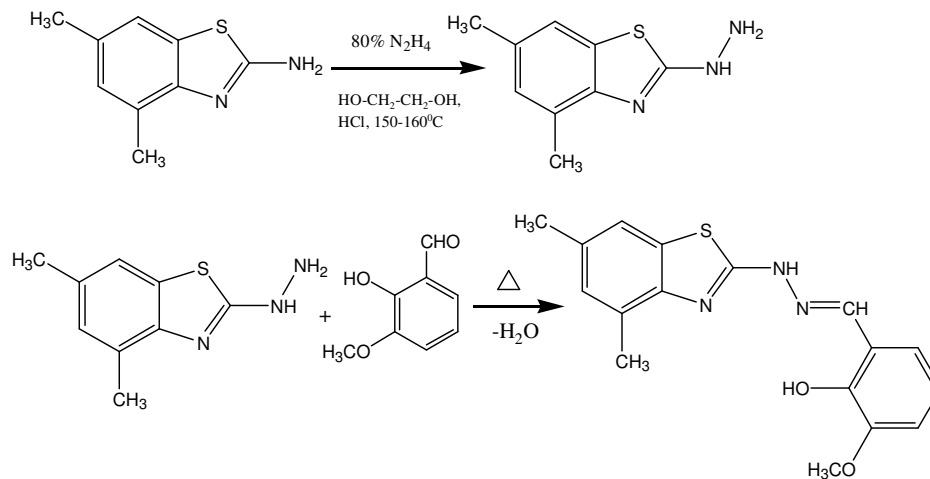
The important frequencies exhibited by the ligand and its complexes are listed in Table-3. The spectra of the complexes show a downward shift C=N, N-N and C-O of these bands, accompanied by a significant decrease of intensity, in accordance with the coordination of the ligands through the azomethine, benzothiazole nitrogen and phenolic oxygen atoms. On the basis of IR spectra we can conclude that the ligand coordinates to the metal ion through the azomethine, benzothiazole nitrogen and phenolic oxygen atom.

Table-1: Report for antimicrobial testing

Medium- Nutrient Agar		Method- Agar Cup method					
Dose of compound – 1%		Cup size – 10 mm					
S. No.	Compound	<i>Escherishia coli</i>	<i>Salmonella typhi</i>	<i>Staphylococcus aureus</i>	<i>Bacillus subtilis</i>	<i>Erwinia</i>	<i>Xanthomonas</i>
1	[Fe(DBYHMP) <sub>2</sub> ]	-ve	-ve	13	14	10	11
2	[Co(DBYHMP) <sub>2</sub> ]	14	13	13	20	11	15
3	[Ni(DBYHMP) <sub>2</sub> ]	11	12	12	15	12	16

4	[Cu(DBYHMP)Cl]	12	11	18	23	12	11
5	[Zn(DBYHMP)Cl]	-ve	11	21	22	15	16
6	(DBYHMP)	5	8	10	15	9	10
7	DMSO	-ve	-ve	-ve	-ve	-ve	-ve
8	Penicillin	13	25	24	23	16	18

Legends -ve - No antibacterial activity



**Scheme-2**

2-[(4,6-Dimethyl-benzothiazol-2-yl)-hydrazonomethyl]-6-methoxy-phenol

Table-2: Report for antifungal testing

S. No.	Compound	<i>Aspergillus niger</i>	<i>Penicillium chrysogenum</i>	<i>Fusarium moneliforme</i>	<i>Aspergillus flavus</i>
1	[Fe(DBYHMP) <sub>2</sub> ]	+ve	RG	+ve	+ve
2	[Co(DBYHMP) <sub>2</sub> ]	RG	RG	+ve	RG
3	[Ni(DBYHMP) <sub>2</sub> ]	RG	RG	+ve	+ve
4	[Cu(DBYHMP)Cl]	RG	RG	+ve	RG
5	[Zn(DBYHMP)Cl]	+ve	RG	RG	RG
6	(DBYHMP)	+ve	+ve	+ve	+ve
7	Grysofulvin	-ve	-ve	-ve	-ve
8	Blank	+ve	+ve	+ve	+ve

Legends +ve - Growth (No antifungal activity)  
-ve - Growth (antifungal activity observed)  
RG -Reduced Growth (moderate activity)

### Electronic spectra

The information referring to the geometry of these compounds was obtained from the electronic spectra (Table-4) and from the values of the magnetic moments.

The electronic spectrum of iron (II) complex consisted of a pair of low intensity bands at 12500 and 10200 cm<sup>-1</sup>, arising from <sup>5</sup>T<sub>2g</sub> → E<sub>g</sub> transitions, similar to those found for distorted octahedral complexes. The doublet is attributed to a Jahn-Teller distortion in the excited state<sup>14</sup>. The room temperature magnetic moment (4.98 μB) corresponded to octahedral symmetry.

The electronic spectrum of Co (II) compound exhibited three bands (Table-4). The bands at 19500 and 18200 cm<sup>-1</sup> arise from the <sup>4</sup>T<sub>1g</sub> → <sup>4</sup>T<sub>1g</sub> (P) transition, which is split in complexes of D<sub>4h</sub> symmetry. That at 15250 cm<sup>-1</sup> arises from <sup>4</sup>T<sub>1g</sub> → <sup>4</sup>A<sub>2g</sub> transition and that at 10100 cm<sup>-1</sup> from <sup>4</sup>T<sub>1g</sub> → <sup>4</sup>T<sub>2g</sub> transition<sup>15</sup>. These transitions correspond to a distorted octahedral geometry, which was also supported by the magnetic moment (3.90 μB).

The electronic spectrum of Ni (II) the following electronic transitions from  $^3A_{2g}(F)$  ground state to the  $^3T_{2g}(F)$  ( $\nu_1$ ),  $^3T_{1g}(F)$  ( $\nu_2$ ) and  $^3T_{1g}(P)$  ( $\nu_3$ ) excited states for nickel (II). The low energy band of this complex is broad and split into two components at (at 10100 and 9300  $\text{cm}^{-1}$ ). The magnetic moment (3.02  $\mu_B$ ) lies in the region expected for octahedral complexes.

The Cu complex displays electronic spectral bands in the region 18200 and 15500  $\text{cm}^{-1}$  which may be assigned to  $^2B_{1g} \rightarrow ^2E_g$  and  $^2B_{1g} \rightarrow ^2A_{1g}$  transitions. The magnetic moment (1.89  $\mu_B$ ) lies in the region expected for tetrahedral complexes.

The electronic spectra of Zn (II) complex exhibit a sharp band of high intensity at 26500  $\text{cm}^{-1}$ , which may be due to ligand metal charge transfer.

In the light of the above discussion, octahedral structures for the Fe(II), Co(II) and Ni(II) complexes and tetrahedral for Cu(II) and Zn(II) complexes is proposed. It is tentatively proposed that the Schiff base ligands coordinate through the nitrogen of the azomethine group and nitrogen of benzothiazole and phenolic oxygen, forming a stable chelate ring structure.

Table-3: Characteristic bands in the IR spectra of the ligand and its complexes. ( $\nu$  max.,  $\text{cm}^{-1}$ )

Assignments	(DBYHMP)	1	2	3	4	5
$\hat{\nu}$ (OH)	3125	-----	-----	-----	-----	-----
$\hat{\nu}$ (NH)	3279	3246	2922	2918	3180	3178
$\hat{\nu}$ (C=N) <sub>exo</sub>	1600	1610	1613	1625	1609	1608
$\hat{\nu}$ (C=N) <sub>endo</sub>	1605	1608	1612	1630	1617	1600
$\hat{\nu}$ (C <sub>arom</sub> -N)	1286	1308	1312	1310	1320	1322
$\hat{\nu}$ (C-O <sub>phen</sub> )	1246	1278	1280	1288	1285	1302
$\hat{\nu}$ (N-N)	1066	1101	1098	1093	1095	1104
$\hat{\nu}$ (M-N)	-----	556	518	563	550	570
$\hat{\nu}$ (M-O)	-----	615	612	657	630	642

Table-4: Electronic spectra of the complexes

Compound	Absorption maxima, $\text{cm}^{-1}$
[Fe(DBYHMP) <sub>2</sub> ]	12500; 10200
[Co(DBYHMP) <sub>2</sub> ]	19500; 18200; 15250; 10100
[Ni(DBYHMP) <sub>2</sub> ]	25900; 15100; 10100; 9300
[Cu(DBYHMP)Cl]	18200; 15500
[Zn(DBYHMP)Cl]	24600

### Thermogravimetric analysis

The TG curves of the compounds (4) and (5) shows the removal of anionic chloride of the complex takes place in an endothermic process with maximum at 250°C and 227°C. All the complexes lose their organic ligand in a large exothermic process in the range of 350 -700°C.

The analytical and thermogravimetric data, correlated with the observations from IR spectra permitted to conclude that the metal ion is six co-ordinated in the complex (1), (2) & (3) and four co-ordinated in the complex (5) and (6).

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