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## Synthesis spectral, thermal and antimicrobial activity studies of some transition metal complexes derived from 3-chloro-N (1E) [2-hydroxy-6-methylquinoline-3yl] methylene)-1-benzo(b)thiophene-2-carbohydrazide

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### ABSTRACT

A series of new coordination complexes of Cu<sup>II</sup>, Co<sup>II</sup>, Ni<sup>II</sup>, Mn<sup>II</sup> Zn<sup>II</sup> and. Cd<sup>II</sup> with the Schiff base 3-chloro-N(1E)[2-hydroxy-6-methylquinoline-3-yl]methylene)-1-benzo(b)thiophene-2-carbohydrazide have been synthesized and characterized by elemental analysis, electrical conductivity measurement, IR spectra, NMR, TGA, XRD data, electronic spectra and magnetic susceptibility measurements. The schiff base behaves as tridentate ONO donor ligand and forms the complexes of the type ML<sub>2</sub> stoichiometry. All the complexes are colored and non-electrolytes. It is found that Cu<sup>II</sup>, Co<sup>II</sup>, Ni<sup>II</sup>, Cd<sup>II</sup>, Mn<sup>II</sup>, and Zn<sup>II</sup> complex under the present investigation showed octahedral geometry. The ligand and their metal complex have been screened for their antibacterial activity against *E.coli*, *S.aureus* and antifungal activity against, *A. niger* & *C. albicans*. © 2011 Trade Science Inc. - INDIA

### KEYWORDS

Benzothiophene;  
Carbohydrazide;  
Schiff base;  
TGA;  
XRD;  
Antimicrobial activity.

### INTRODUCTION

The study of metal complexes with potentially tridentate and polydentate ligands have evoked much interest in coordination chemistry.<sup>[1]</sup> The schiff base complexes of transition metals have played an important role in the development of coordination chemistry.<sup>[2]</sup> The study of transition metal thiophene compounds is an area of great current interest. This is due to the importance of thiophene compounds in hydrodesulphurization reaction in the petroleum industry<sup>[3-5]</sup>.

The industrial process is carried out heterogeneously over a CoMo/Al<sub>2</sub>O<sub>3</sub>, Ni MoS catalyst. Increased activity of the catalyst has been observed when late transition metals are added as promoters to the catalyst<sup>[3-5]</sup>.

For these reasons thiophene and benzothiophene complexes of elements such as ruthenium<sup>[6]</sup>, rhodium<sup>[7]</sup> and platinum<sup>[8]</sup> and their catalytic reactions have received considerable attention in recent years. There are also reports on coordination behavior of thiophene-2, 5-dicarboxylic acid copper (II) with 1, 10 – phenanthroline<sup>[9]</sup> where thiophene 2, 5-dicarboxylate anion (Tda<sup>2-</sup>) is monodentate as reported by Mok et.al<sup>[10]</sup>. The literature survey reveals that many benzothiophene<sup>[11-13]</sup> and quinoline<sup>[14-17]</sup> possess good biological activity like antimicrobial anti-inflammatory, analgesic, and antiviral activities.<sup>[18]</sup>

In view of these finding and in continuation of our research work on coordination chemistry<sup>[19-23]</sup>, we are reporting the synthesis, characterization and antimicro-

bial activity studies of some transition metal complexes of 3-chloro-N-(*IE*)-(2-hydroxyquinoline-3-yl)methylene-1-benzo(b)thiophene-2-carbohydrazide. ( $H_2L$ ). Figure 1 in this communication. (H refers to phenolate).

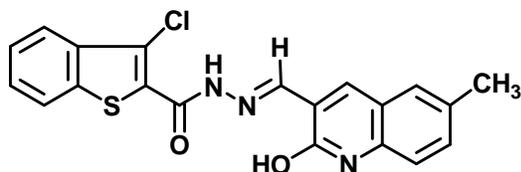


Figure 1

## RESULT AND DISCUSSION

The analytical data of the synthesized ligand  $H_2L$  and its  $Cu^{II}$ ,  $Co^{II}$ ,  $Ni^{II}$ ,  $Zn^{II}$ ,  $Cd^{II}$ ,  $Fe^{III}$ , and  $Mn^{II}$  complexes are given in the TABLE 1. The molar conductance of the complexes was measured in DMF at  $10^{-3}M$  concentration. Measured conductance values of these complexes are too low to account for their electrolytic behavior.

### IR spectra

The important bands in the IR spectra of the ligand as well as complexes together with their assignments are listed in the TABLE 2. The free ligand showed a broad

band at  $3442\text{ cm}^{-1}$  due to  $\nu(\text{OH})$  of the ligand which has disappeared in all the complexes indicating its involvement in the coordination with the metal ion via deprotonation. This is further evidenced by the shift of phenolic  $\nu(\text{C-O})$  band observed in ligand at  $1281\text{ cm}^{-1}$  to higher frequency number and appeared in the range  $1311\text{--}1343\text{ cm}^{-1}$  in all the complexes. In  $Ni^{II}$ ,  $Co^{II}$ ,  $Zn^{II}$  and  $Cd^{II}$  complexes a broad band has appeared at  $3391\text{--}3456\text{ cm}^{-1}$  due to the presence of water of crystallization. The ligand showed medium intensity band at  $3207\text{ cm}^{-1}$  assigned to  $\nu(\text{NH})$  vibration of carboxamide function. Strong intensity bands at  $1660\text{ cm}^{-1}$  is assigned due to  $\nu(\text{C=O})$  of carboxamide function which has disappeared in all the complexes indicating its involvement in coordination with metal ions via its enolization followed by deprotonation during complexation. This is further confirmed by appearance of a new band in all the complexes in the region  $1595\text{--}1613\text{ cm}^{-1}$  due to  $-\text{C}=\text{N}-\text{N}=\text{C}-$ . A band at  $1564\text{ cm}^{-1}$  is assigned to  $\nu(\text{C}=\text{N})$  of the hydrazone functions of the ligand which has been shifted to the region of lower wave number and observed in the range  $1531\text{--}1555\text{ cm}^{-1}$  in all the complexes. The ligand showed a band at  $1643\text{ cm}^{-1}$  which corresponds to quinoline ( $\text{C}=\text{C}+\text{C}=\text{N}$ ) and observed at about the same re-

TABLE 1: Physical and analytical, magnetic susceptibility and molar conductance data of ligand  $H_2L$  and its complexes

Empirical formula	Mol. Wt.	M.P. $^{\circ}\text{C}$	Elemental Analysis (%) Calcd. ( Found)					$\mu_{\text{eff}}$ (BM)	$\lambda_m$ $\frac{\text{ohm}^2}{\text{cm}^2 \text{ mol}^{-1}}$	Colour
			M	C	H	N	Cl			
$C_{20}H_{14}N_3O_2S_2Cl$	395	263	--	60.00 (60.06)	3.54 (3.58)	10.63 (10.69)	8.86 (8.91)	-	-	Yellow
$Cu[C_{40}H_{24}Cl_2N_6O_4S_2]$	849.5	285	7.47 (7.49)	56.50 (56.47)	2.82 (2.86)	9.88 (9.92)	8.24 (8.19)	1.80	24	Light Green
$Ni[C_{40}H_{28}Cl_2N_6O_6S_2]$	880.69	267	6.66 (6.70)	54.50 (54.51)	3.17 (3.20)	9.53 (9.59)	7.94 (8.00)	3.29	23	Dark yellow
$Mn[C_{40}H_{24}Cl_2N_6O_4S_2]$	840.93	>300	6.53 (6.59)	57.07 (57.01)	2.85 (3.49)	9.98 (9.29)	8.32 (8.46)	5.45	21	Light yellow
$Co[C_{40}H_{28}Cl_2N_6O_6S_2]$	880.93	>301	6.68 (6.71)	54.48 (54.46)	3.17 (3.22)	9.53 (9.55)	7.94 (7.99)	4.99	22	Brown
$Zn[C_{40}H_{28}Cl_2N_6O_6S_2]$	887.39	287	7.36 (7.45)	54.09 (54.11)	3.15 (3.18)	9.46 (9.48)	7.88 (7.91)	Dia*	18	Yellow
$Cd[C_{40}H_{28}Cl_2N_6O_6S_2]$	934.41	300	12.03 (12.07)	51.36 (51.39)	2.99 (3.02)	8.98 (9.01)	7.49 (7.53)	Dia*	19	Yellow

TABLE 2: The IR data of ligand HL and its complexes

Ligand complex	$\nu$ (OH)	$\nu$ (NH)	$\nu$ (C=O)	$\nu$ (C=N)	-C=N-N=C-	Quinoline C=C+C=N	Thiophene Ring vib.	$\nu$ (M-O)	$\nu$ (M-N)	$\nu$ (M-Cl)
$C_{20}H_{14}N_3O_2S_2Cl$	3442	3207	1660	1564	--	1643	1514	--	--	--
$Cu[C_{40}H_{24}Cl_2N_6O_4S_2]$	--	--	--	1541	1605	1635	1517	542	402	--
$Ni[C_{40}H_{28}Cl_2N_6O_6S_2]$	3390	--	--	1555	1613	1646	1517	513	402	--
$Mn[C_{40}H_{24}Cl_2N_6O_4S_2]$	--	--	--	1531	1595	1644	1517	604	498	--
$Co[C_{40}H_{28}Cl_2N_6O_6S_2]$	3379	--	--	1541	1602	1649	1514	566	410	--
$Zn[C_{40}H_{28}Cl_2N_6O_6S_2]$	3391	--	--	1555	1611	1650	1513	567	436	--
$Cd[C_{40}H_{28}Cl_2N_6O_6S_2]$	3456	--	--	1534	1606	1646	1511	517	422	--

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gion 1635-1650  $\text{cm}^{-1}$  in all the complexes. The ligand showed an intense strong band at 1514  $\text{cm}^{-1}$  due to benzo(b)thiophene ring vibration<sup>[24]</sup> and observed at about the same region 1511-1517  $\text{cm}^{-1}$  in all complexes confirming the noninvolvement of benzo(b)thiophene ring sulfur in coordination. The new bands observed in the complexes at 513-604  $\text{cm}^{-1}$  and 402-498  $\text{cm}^{-1}$  have been assigned to  $\nu(\text{M-O})$  and  $\nu(\text{M-N})$  respectively.

### Electronic spectra

Electronic spectral data of the  $\text{Co}^{\text{II}}$ ,  $\text{Cu}^{\text{II}}$ ,  $\text{Ni}^{\text{II}}$ , complexes of the ligand HL were carried out in DMF at  $10^{-3}$  molar concentration. The electronic spectrum of  $\text{Co}^{\text{II}}$  complex showed three bands observed at 10756  $\text{cm}^{-1}$ , 15946  $\text{cm}^{-1}$  and 20245  $\text{cm}^{-1}$ . due to the  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F}) (\nu_1)$ ,  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F}) (\nu_2)$  and  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{P}) (\nu_3)$  transitions respectively. These transitions suggests octahedral geometry for  $\text{Co}^{\text{II}}$  complex, These assignment are in good agreement with the reported value.<sup>[26]</sup> The electronic spectra of  $\text{Ni}^{\text{II}}$  complex under the present investigation exhibited three bands at 10524  $\text{cm}^{-1}$ , 15954  $\text{cm}^{-1}$  and 25121  $\text{cm}^{-1}$  respectively in DMF solution. These bands are assigned to  ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F}) (\nu_1)$ ,  ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F}) (\nu_2)$  and  ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P}) (\nu_3)$  transition respectively. The band around 10516  $\text{cm}^{-1}$  is attributed to a d-d component of  $\text{Ni}^{\text{II}}$  complex<sup>[27]</sup> there by suggesting the octahedral geometry for the  $\text{Ni}^{\text{II}}$  complex. The light green colored  $\text{Cu}^{\text{II}}$  complex exhibits asymmetric band in the region 16321 – 13459  $\text{cm}^{-1}$  with maxima at 14486  $\text{cm}^{-1}$  in a distorted octahedral geometry<sup>[27]</sup>. The broadness of the band may be due to dynamic John-Teller distortion and assigned to  ${}^2\text{T}_{2g} \rightarrow {}^2\text{E}_g$  transition.

### ${}^1\text{H}$ NMR spectrum of the ligand $\text{H}_2\text{L}$

In the  ${}^1\text{H}$  NMR spectrum (in  $\delta$  ppm) of the ligand  $\text{H}_2\text{L}$ , two singlets observed at 12.02 (s, 1H, NH) and 12.19 (s 1H, OH) are assigned to NH of amide group and proton of OH group attached to quinoline moiety respectively. Protons of benzo(b)thiophene and quinoline rings have resonated in the region 7.25-8.40 ppm (m, 8H, ArH) as multiplet. A singlet observed at 8.67 (s, 1H, CH) is due to proton of azomethine group. Three protons of a methyl group attached to quinoline nucleus have resonated as a singlet at 2.10. These data confirms the structure of ligand.

### ${}^1\text{H}$ NMR spectrum of $\text{Zn}^{\text{II}}$ complex of the ligand HL

In the  ${}^1\text{H}$  NMR spectrum of the  $\text{Zn}^{\text{II}}$  complex of the ligand  $\text{H}_2\text{L}$ , showed a distinct singlet at 8.75 due to two protons of azomethine (s, 1H, CH). A multiplet appeared at 7.21-8.40 is due to sixteen aromatic protons. The disappearances of the singlets due to protons of OH and CONH groups which were observed at 12.02 and 12.30 respectively in the  ${}^1\text{H}$  NMR spectrum of the ligand proves beyond doubt the deprotonation of phenolic OH group and enolized carboxamide proton during complexation. A singlet observed at 2.10 is due to six protons of a two methyl groups attached to two quinoline moieties. These data confirms the structure  $\text{Zn}^{\text{II}}$  complex of the ligand  $\text{H}_2\text{L}$ .

### Magnetic susceptibility data

Magnetic susceptibility measurements of the complexes were performed at room temperature. The magnetic moment for  $\text{Cu}^{\text{II}}$  complex of the ligand  $\text{H}_2\text{L}$  is 1.80 BM. The reported values for the mononuclear  $\text{Cu}^{\text{II}}$  having no major spin interaction is 1.75 - 2.20 BM<sup>[27,28]</sup>. Thus the present  $\text{Cu}^{\text{II}}$  complex is devoid of any spin interaction with distorted octahedral geometry. In octahedral  $\text{Co}^{\text{II}}$  complex the ground state is  $4\text{T}_{1g}$  and a large orbital contribution to the magnetic moment is expected. The mixing of singlet state lowers the magnetic moment. The reported magnetic moment values for the various  $\text{Co}^{\text{II}}$  complexes are in the range 4.7- 5.2 BM for octahedral complexes. In the present investigation, the observed magnetic moment value for  $\text{Co}^{\text{II}}$  complex is 4.99 B.M indicates octahedral geometry for this  $\text{Co}^{\text{II}}$  complex. For  $\text{Ni}^{\text{II}}$  complex the observed magnetic moment value is 3.89 BM which is well within the expected range of 2.86- 3.98 BM<sup>[29,30]</sup> for  $\text{Ni}^{\text{II}}$  complex with octahedral stereochemistry. The observed magnetic moment value of  $\text{Mn}^{\text{II}}$  complex of the present study was found to be 5.79 B.M. which is well within the expected range 5.65-6.10 B.M reported to octahedral geometry<sup>[31]</sup>.

### ESR spectral studies of the $\text{Cu}^{\text{II}}$ complex of the ligand $\text{H}_2\text{L}$

The X- Band ESR spectrum of the powder  $\text{Cu}^{\text{II}}$  complex was recorded at room temperature using DPPH as reference standard. One unpaired electron in  $\text{Cu}^{\text{II}}$  complex with  ${}^2\text{B}_{1g}$  as ground state lies in  $dx^2-y^2$  orbital and follows the trends  $g_{\parallel} > g_{\perp} > g_e$

( $g_{\parallel} = 2.0036$  free ion value).

The observed  $g_{\parallel} = 2.295$ ,  $g_{\perp} = 2.061$  values of the  $\text{Cu}^{\text{II}}$  complex under the present study followed the same trend  $g_{\parallel} > g_{\perp} > g_e$  which suggest the presence of unpaired electron in  $d_{x^2-y^2}$  orbital giving octahedral geometry<sup>[29]</sup>. The observed  $G = 4.463$  for the complex under present study evidenced the monomeric nature of the complexes<sup>[32]</sup>. This fact is further supported by the absence of a band corresponding to  $\Delta M_s = \pm 2$  transition<sup>[33]</sup> in the observed ESR spectrum which is characteristic of monomeric complex.

$$G = (g_{\parallel} - 2)/(g_{\perp} - 2) = 4.89$$

### X-ray diffraction studies

The ligand L and its  $\text{Zn}^{\text{II}}$  complex have characterized by powder XRD studies with a view to find type of the crystal system. The ligand L and its  $\text{Zn}^{\text{II}}$  complex are chosen for powder XRD study. The XRD data of the ligand and its  $\text{Zn}^{\text{II}}$  complex are chosen for powder XRD

study. The XRD data of the ligand L and its  $\text{Zn}^{\text{II}}$  given in the (TABLE 3 and 4) respectively. There are 10 reflections ( $2\theta$ ) between 5.69771 and 23.11163 with maximum at  $2\theta = 10.03695$  and  $d = 4.4178\text{\AA}$  in case of ligand L whereas  $\text{Zn}^{\text{II}}$  complex consist 10 reflections  $2\theta$  between 5.69883 and 27.31791 with maxima at  $2\theta = 8.38022$  corresponding to the value of  $d = 5.28334\text{\AA}$ . The inter planar spacing ( $d$ ) has been calculated from the position of intense peaks using Braggs relation  $n\lambda = 2d \sin \theta$  (where  $\lambda =$  wave length of X-ray used  $\text{Cu K}\alpha = 1.5406\text{\AA}$ ) The observed and calculated values of  $d$  are quite consistent (TABLE 3 and 4) The unit cell calculations have been carried out for the cubic system<sup>[35,37]</sup>. The cell parameter have been calculated by using the equation for the cubic system  $\sin^2\theta = \lambda^2/4a^2 (h^2 + k^2 + l^2)$ , where  $\lambda^2/4a^2$  common factor. In the present case ligand L and its  $\text{Zn}^{\text{II}}$  complex have  $\lambda^2/4a^2 = 0.0024712$  and  $0.0024703$  respectively. The  $h^2 + k^2 + l^2$  values given in the (TABLE 3 and 4). The absence of forbidden num-

TABLE 3 : Powder x-ray diffraction data of ligand (HL)

Peak No.	$2\theta$	$\theta$	$\sin\theta$	$\sin^2\theta$	$h^2+k^2+l^2$	hkl	d		a in $\text{\AA}^0$
							Calc	Obser	
1.	5.69771	2.8488	0.049670	0.00247023	1	100	15.492	15.49816	15.71
2.	10.23056	5.11528	0.08915	0.0079494	3	111	8.6337	8.63931	15.00
3.	13.41815	6.70907	0.116828	0.013648	5	210	6.5908	6.5932	15.00
4.	13.85859	6.92929	0.120644	0.014555	6	211	6.3826	6.3847	15.63
5.	15.81666	7.90833	0.137588	0.018930	8	220	5.5963	5.5984	15.89
6.	18.06460	9.0323	0.156991	0.024646	10	310	4.9047	4.9065	15.51
7.	20.07391	10.03695	0.174283	0.030374	12	222	4.41810	4.41970	15.30
8.	20.44706	10.22353	0.177488	0.031502	12	222	4.3393	4.3398	15.64
9.	22.28983	11.14491	0.193291	0.037361	15	- - -	3.9851	3.98508	15.42
10.	23.11163	11.55581	0.200322	0.040129	16	400	3.8438	3.8452	15.37

TABLE 4 : Powder x-ray diffraction data of Zn complex

Peak No.	$2\theta$	$\theta$	$\sin\theta$	$\sin^2\theta$	$h^2+k^2+l^2$	hkl	d		a in $\text{\AA}^0$
							Calc	Obser	
1	5.69883	2.849415	0.0497111	0.0024712	1	100	15.4895	15.4951	15.49
2	8.03626	4.01813	0.070072	0.0049101	2	110	10.9886	10.9926	15.54
3	12.0356	6.01793	0.104839	0.0109913	4	200	7.3445	7.34722	14.68
4	12.84131	6.422065	0.1118271	0.0125053	5	210	6.8860	6.88813	15.39
5	16.76044	8.38022	0.1457414	0.0212405	8	220	5.28334	5.28525	15.00
6	18.24113	9.120565	0.1585124	0.0251262	10	310	4.85766	4.85943	15.36
7	21.9890	10.99495	0.1907224	0.0363750	14	321	4.0372	4.03875	15.10
8	24.33592	12.16796	0.2107781	0.044427	17	410	3.53566	3.65446	15.06
9	26.65254	13.32627	0.2304959	0.0531283	21	421	3.34115	3.34184	15.30
10	27.31791	13.65895	0.236142	0.0557563	22	332	3.26074	3.26193	15.29

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bers 7,13 in case of ligand and Zn<sup>II</sup> complex indicate that they may belong to cubic system respectively.

### Thermo gravimetric analysis

Thermo gravimetric data is given in the TABLE 5. The decomposition studies of the compound Ni<sup>II</sup> complex has been carried out. In the thermogram of [Ni(L<sub>2</sub>)], The loss of CH<sub>9</sub>Cl<sub>2</sub>O<sub>2</sub> was observed at 118 C° indicated by inflexion in the curve at up to 359 C° with loss of 13.81%. This practical weight loss is 13.81% is in accordance with theoretical weight loss of 13.96%. The resultant intermediate complex underwent further degradation and gave another break at 370 C° with weight loss 43.16% by the expulsion of C<sub>20</sub>H<sub>12</sub>NO<sub>2</sub>S species from the above intermediate complex. The theoretical weight loss for this decomposition was 43.51% is in accordance of practical weight loss is 43.16%. The third inflection occurred at 450 C° with weight loss of 57.03% which amounts for the weight loss C<sub>12</sub>H<sub>7</sub>N<sub>3</sub>OS species. This practical weight loss of 57.03% of third stage decomposition is in accordance with the theoretical weight loss 56.11%. There after the compound showed a gradual decomposition up to 1000 C° and onwards. The weight of the residue corresponds to the formation of NiO. The thermal decomposition of [Ni(L<sub>2</sub>)] with probable assignment are gives in the TABLE 5.

**TABLE 5 : Thermal decomposition of Ni (II) complex of the ligand L**

Complex	Stage	Peak Temp TG(C°)	Loss of mass (%)		Probable assignment
			Practical	Theoretical	
Ni(L <sub>2</sub> )	---	---	-----	----	Ni(C <sub>40</sub> H <sub>28</sub> N <sub>6</sub> O <sub>6</sub> Cl <sub>2</sub> S <sub>2</sub> )
	I	118 C°	13.81%	13.96%	↓ -CH <sub>9</sub> Cl <sub>2</sub> O <sub>2</sub> Ni(C <sub>39</sub> H <sub>19</sub> N <sub>6</sub> O <sub>4</sub> S <sub>2</sub> )
	II	370 C°	43.16%	43.51%	↓ -C <sub>20</sub> H <sub>12</sub> NO <sub>2</sub> S Ni(C <sub>19</sub> H <sub>7</sub> N <sub>3</sub> O <sub>2</sub> S <sub>2</sub> )
	III	450 C°	57.03%	56.11 %	↓ -C <sub>12</sub> H <sub>7</sub> N <sub>3</sub> OS NiO

### Antimicrobial activity

Antimicrobial activity was carried out by the cup-plate method<sup>[37]</sup>. The ligand H<sub>2</sub>L and its Cu<sup>II</sup>, Ni<sup>II</sup>, Mn<sup>II</sup>, Co<sup>II</sup>, Zn<sup>II</sup> and Cd<sup>II</sup>, complexes have been tested for their antibacterial and antifungal activity at 1mg/ml concentration. The results of the antimicrobial activity have

been presented in TABLE 6. The ligand Cu<sup>II</sup>, Ni<sup>II</sup>, Mn<sup>II</sup> and Co<sup>II</sup> complexes showed moderate activity against *S.aureas* with 13-15 mm inhibition whereas Zn<sup>II</sup> and Cd<sup>II</sup> complexes showed good activity with 16 and 17 mm inhibition respectively against the same microorganism. Ligand H<sub>2</sub>L was found to be weakly active against *E.coli* with only 10 mm inhibition, its Cu<sup>II</sup>, Ni<sup>II</sup>, Co<sup>II</sup> and Cd<sup>II</sup> complexes showed moderate activity with 14-15 mm inhibition. Mn<sup>II</sup> complex showed very good activity with 23 mm inhibition against *E.coli*. This activity of Mn<sup>II</sup> complex was found to be equal to that of standard drug streptomycin, which showed 24 mm inhibition against *S.aureas* and 22 mm inhibition against *E.coli* at the same concentration as that of the test drug.

**TABLE 6 : Antimicrobial activity screening data of the ligand HL and its complexes**

Compound and complexes	Antimicrobial activity (zone of inhibition in mm)*			
	Antibacterial activity		Antifungal activity	
	<i>S.aureus</i>	<i>E.coli</i>	<i>A.niger</i>	<i>c</i>
S	13	10	12	16
C <sub>20</sub> H <sub>14</sub> N <sub>3</sub> O <sub>2</sub> SCl	15	14	14	14
Cu[C <sub>40</sub> H <sub>24</sub> Cl <sub>2</sub> N <sub>6</sub> O <sub>4</sub> S <sub>2</sub> ]	14	15	11	15
Ni[C <sub>40</sub> H <sub>28</sub> Cl <sub>2</sub> N <sub>6</sub> O <sub>6</sub> S <sub>2</sub> ]	15	23	12	15
Mn[C <sub>40</sub> H <sub>24</sub> Cl <sub>2</sub> N <sub>6</sub> O <sub>4</sub> S <sub>2</sub> ]	14	15	10	14
Co[C <sub>40</sub> H <sub>28</sub> Cl <sub>2</sub> N <sub>6</sub> O <sub>6</sub> S <sub>2</sub> ]	16	16	10	18
Zn[C <sub>40</sub> H <sub>28</sub> Cl <sub>2</sub> N <sub>6</sub> O <sub>6</sub> S <sub>2</sub> ]	17	14	14	21
Streptomycin	24	22	-	-
Fluconazole	---	----	20	23
DMF(control)			---	---

### Bore size-06 mm

Ligand and its Ni<sup>II</sup>, Co<sup>II</sup> and Zn<sup>II</sup> complexes showed weak activity with 10-12 mm inhibition against *A.niger* whereas Cu<sup>II</sup> and Cd<sup>II</sup> complexes showed good activity with 14 mm inhibition against the same microorganism. But the standard drug fluconazole showed 20 mm inhibition against *E.coli* at the same concentration as that of the standard drug.

Ligand and its Cd<sup>II</sup> complex showed good activity with 16 and 18 mm inhibition respectively against *C.albican*. Ni<sup>II</sup>, Mn<sup>II</sup> and Co<sup>II</sup> complexes showed moderate activity with 14-15 mm inhibition and Cd<sup>II</sup> complex showed very good activity with 21 mm inhibition against *C.albican* respectively. Standard drug fluconazole showed 23 mm inhibition against the same microorganism.

ism at the same concentration as that of the test drugs. Under these conditions DMF solvent did not show any activity against any of the above microorganisms.

## EXPERIMENTAL

### Material and method

All the chemicals are of reagent grade. Solvents were dried and distilled before use according to standard procedures<sup>[38]</sup>. The precursor, 3-chloro-1-benzothiophene-2-carbohydrazide and 2-hydroxy-3-formyl quinoline<sup>[17]</sup> were prepared by literature methods. The metal chlorides used were in their hydrated form.

### Synthesis of the ligand H<sub>2</sub>L

An equimolar mixture of 3-chloro-1-benzothiophene-2-carbohydrazide (0.001 mol) and 3-formyl-2-hydroxy quinoline (0.001 mol) in ethanol (30 mL) were refluxed in presence of catalytic amount of glacial acetic acid (1-2 drops) for about 6 h on water bath. The reaction mixture was cooled to room temperature, the separated Schiff base (H<sub>2</sub>L) was collected by filtration, washed with ethanol, dried and recrystallized from absolute ethanol.

### Preparation of Cu<sup>II</sup>, Co<sup>II</sup>, Ni<sup>II</sup>, Zn<sup>II</sup>, Cd<sup>II</sup> and Mn<sup>II</sup> complexes of ligand H<sub>2</sub>L

To the hot solution of 3-chloro-*N*-1*E*-(2-hydroxyquinoline-3-yl)methylene)-1-benzo(b)thiophene-2-carbohydrazide (H<sub>2</sub>L) (0.002 mol) in ethanol (30 mL) was added a hot ethanolic solution (10 mL) of respective metal (II) chloride (0.001 mol), the reaction mixture was refluxed on a steam bath for 4 h, then sodium acetate (0.5 g) was added to it and refluxed for further 2 h. It was then poured in to distilled water. The resulting solid complexes were collected by filtration, washed with sufficient quantity of distilled water, then with hot ethanol to apparent dryness and dried in a vacuum over anhydrous calcium chloride in a desiccators (yield 60-70 %).

### Physical measurements

IR Spectra of the synthesized ligand and its complexes were recorded as KBr pellets on Perkins-Elmer Spectrum One FT-IR spectrometer. <sup>1</sup>H NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer in d<sub>6</sub>-DMSO as solvent and with TMS internal standard. Elemental analysis was obtained from

HERAEUS C, H, N, O rapid analyzer and metal analyses were carried out by following the standard methods. ESR measurement was carried out on a BRUKER BioSpin GmbH spectrometer working at microwave frequency of 9.903 GHz. The experiment was carried out by using diphenylpicrylhydrozyl (DPPH) as reference with field set at 3200 gauss. Magnetic susceptibilities were determined by the Faraday method using a model 300 Lewis coil force magnetometer of tesla field strength at room temperature and the instrument was calibrated with [HgCo(SNC)<sub>4</sub>]<sup>[39]</sup>.

## CONCLUSION

In the light of above discussion, we have proposed octahedral geometry for Co<sup>II</sup>, Cu<sup>II</sup>, Ni<sup>II</sup>, Zn<sup>II</sup>, Cd<sup>II</sup> and Mn<sup>II</sup> complexes. The ligand behaves as ONO tridentate chelating agent coordinating through the deprotonation of hydroxyl group, enolized amide carbonyl group and azomethine nitrogen. The analytical data, electronic spectral, magnetic susceptibility, IR, <sup>1</sup>H NMR, of the ligand as well as its metal complexes were found to be less active against the bacteria whereas moderately active against the fungi *A.niger*. All the com-

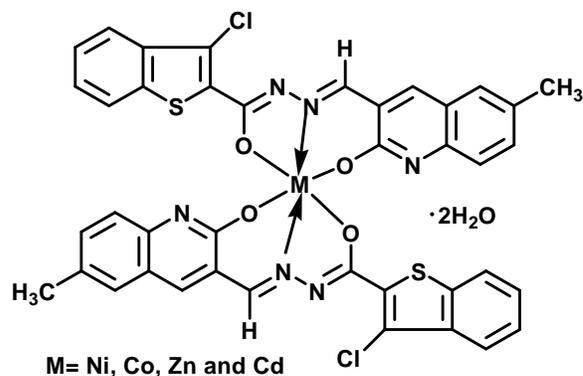


Figure 2

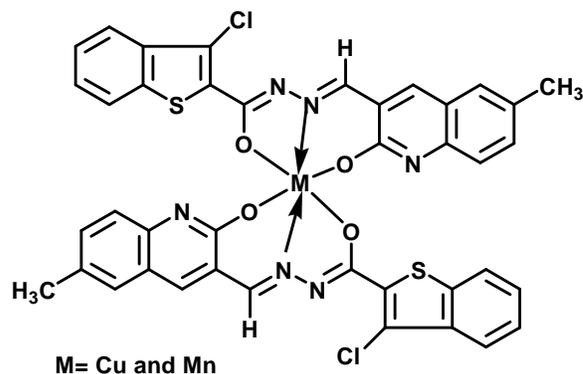


Figure 3

## Full Paper

plexes showed good activity as compared with the ligand. On the basis of spectral evidences, following structures have been assigned for synthesized complexes.

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