



Synthesis, characterization and antimicrobial activity studies of some transition metal complexes derived from 3-chloro-*N*-(*IE*)-[2-hydroxy quinoline-3-yl] methylene-1-benzo(b)thiophene carbohydrazide

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ABSTRACT

A series of new coordination complexes of Cu^{II}, Co^{II}, Ni^{II}, Zn^{II}, Cd^{II}, and Hg^{II} with the Schiff base 3-chloro-*N*-(*IE*)-(2-hydroxy quinoline-3-yl)methylene-1-benzo(b)thiophene-2-carbohydrazide have been synthesized and characterized by elemental analysis, electrical conductivity measurements, IR spectra, electronic spectra, ESR spectra, magnetic susceptibility, TGA and mass spectral data. The Schiff base behaves as tridentate ONO donor ligand and forms the complexes of the type ML stoichiometry. All the complexes are colored and non electrolytes. It is found that Cu^{II}, Co^{II}, Ni^{II}, Zn^{II}, Cd^{II}, and Hg^{II} complexes have exhibited octahedral geometry. The ligand and its metal complexes have been screened for their antibacterial activity against *E. coli*, *S. aureus* and antifungal activity against, *A. niger* and *C. albicans*.

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KEYWORDS

Benzothiophene;
Quinoline;
Schiff base complexes;
Antimicrobial activity.

INTRODUCTION

The study of transition metal compounds is an area of great current interest. Hydrosulphurisation reaction converts the organosulphur compound which contaminate crude oil in to alkanes, alkenes and hydrogen sulphide, which can then be easily removed. Although there are a wide range of organosulphur compounds found in crude oil, it is the thiophenes and benzo thiophenes which are the most difficult to desulphurise. In the industrial process it is carried out heterogeneously over a Co Mo/Al₂O₃ or CoW/Al₂O₃ catalyst. Increased activity of the catalyst has been observed when late transition metals are added as "promoters" to the catalyst^[1-4]. For these reasons

thiophene and benzothiophene derivatives of elements such as ruthenium^[5], rhodium^[6], platinum^[7] and their catalytic reaction 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^[8] where thiophene 2, 5-dicarboxylate anion (Tda⁻²) is monodentate. Mok et.al.^[9] have reported Cu^{II} complexes of thiophene-2, 5-dicarboxylic acid with a view of constructing diverse low dimensional coordination polymers and the model coordination compounds. Literature survey reveals that many benzothiophene^[10-12] and quinoline^[13-17] derivatives reported in the literature are known to possess good biological activity like antimicrobial, anti-inflamma-

tory, analgesic, diuretic and antiviral activities.

In view of these finding and in continuation of our research work on coordination chemistry^[18-23], we are reporting the synthesis, characterization and antimicrobial activity of Cu^{II}, Co^{II}, Ni^{II}, Zn^{II}, Cd^{II}, and Hg^{II} complexes of 3-chloro-*N*-(*IE*)-(2-hydroxyquinoline-3-yl)methylene)-1-benzo(b)thiophene-carbohydrazide (HL) (Figure 1) in this communication (H refers to phenolate).

RESULTS AND DISCUSSION

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

TABLE 1 : Physical, analytical, magnetic susceptibility and molar conductance data of ligand (HL) and its complexes.

Compound/ Complex	Mol .Wt	M.P. ^o C (Yield)	Elemental analyses(%)found(cala)					μ_{eff} (BM)	λ_m (ohm ¹ cm ² Mol ⁻¹)
			M	C	H	N	Cl		
C ₁₉ H ₁₂ ClN ₃ O ₂ S	381.83	265 (75)	-	59.72 (59.84)	3.31 (3.15)	10.98 (11.02)	9.12 (9.18)	-	-
C ₁₉ H ₁₅ Cl ₂ CuN ₃ O ₄ S	514.54	280 (78)	12.30 (12.36)	44.21 (44.35)	2.84 (2.91)	8.11 (8.17)	13.59 (13.61)	1.80	24
C ₁₉ H ₁₅ Cl ₂ NiN ₃ O ₄ S	509.69	300 (71)	11.47 (11.51)	44.64 (44.73)	2.91 (2.94)	8.20 (8.24)	13.69 (13.73)	3.11	23
C ₁₉ H ₁₅ Cl ₂ CoN ₃ O ₄ S	509.93	325 (68)	11.51 (11.55)	44.63 (44.71)	2.86 (2.96)	8.22 (8.23)	13.84 (13.72)	4.99	22
C ₁₉ H ₁₅ Cl ₂ ZnN ₃ O ₄ S	516.39	285 (65)	12.60 (12.66)	43.98 (44.15)	2.80 (2.92)	8.10 (8.13)	13.68 (13.56)	Dia*	18
C ₁₉ H ₁₅ Cl ₂ CdN ₃ O ₄ S	563.41	300 (67)	19.90 (19.95)	40.40 (40.46)	2.61 (2.66)	7.42 (7.45)	12.58 (12.42)	Dia*	25
C ₁₉ H ₁₅ Cl ₂ HgN ₃ O ₄ S	651.59	302 (59)	30.60 (30.69)	34.92 (34.99)	2.23 (2.30)	6.42 (6.44)	10.67 (10.74)	Dia*	21

*Diamagnetic.

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 show a broad band at 3432 cm⁻¹ due to ν (OH) of the ligand which disappeared in all the complexes indicating its involvement in the coordination with the metal ion via deprotonation. The ligand showed medium intensity band at 3234 cm⁻¹ assigned to ν (NH) vibration which is observed in the region 3249–3158 cm⁻¹ in case of all the complexes indicating the non involvement of NH in coordination and no enolization of C=O bond during complexation. Strong intensity bands at 1650 cm⁻¹ and 1564 cm⁻¹ are assigned to ν (C=O) and ν (C=N) of the hydrazones function of the ligand respectively^[24,25]. The ligand showed an intense strong band at 1533 cm⁻¹ due to benzo(b)thiophene ring vibration^[26] and a strong band at 1270 cm⁻¹ due to phenolic ν (C-O) vibration respectively. In case of the complexes the band due to ν (C=O) was observed in the region 1645-1631 cm⁻¹, the shift

of this band towards lower wave number side by 5-19 cm⁻¹ indicates coordination of the ν (C=O) of the amide function to the metal ion^[27]. The band due to ν (C=N) which has been shifted to the region of lower wave number by 7-42 cm⁻¹ and observed in the range 1557-1522 cm⁻¹ in the case of all the complexes, which can be attributed to coordination of nitrogen of C=N bond to the metal ions^[18]. The band due to phenolic C-O observed at 1270 cm⁻¹ in the case of ligand has been shifted to higher wave number side by 67-39 cm⁻¹ and observed in the region 1337-1309 cm⁻¹ suggesting the coordination of the phenolate ion with the metal ions via deprotonation^[28]. The presence of broad stretching vibrations in the region 3468-3324 cm⁻¹ is due to presence of coordinated or lattice water in all the complexes. The new bands in the complexes at 516-530 cm⁻¹ and 469-487 cm⁻¹ have been assigned to ν (M-O) and ν (M-N), respectively. The bands in the region 316 cm⁻¹ have been assigned to (M-Cl) bands in the case of Hg^{II}, and Cd^{II} complexes (TABLE 2).

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TABLE 2 : IR spectra data (in cm^{-1}) ligand (HL) and its metal complexes.

Ligand/ Complex	OH/ H ₂ O	ν_{NH}	$\nu_{\text{C=O}}$	$\nu_{\text{C=N}}$	Phenolic		$\nu_{\text{C-S}}$	$\nu_{\text{M-O}}$	$\nu_{\text{M-N}}$	$\nu_{\text{M-Cl}}$
					$\nu_{\text{C-O}}$	$\nu_{\text{C-N}}$				
Ligand (L ₁)	3432	3234	1650	1564	1270	1533	-	-	-	-
Cu-Complex	3324	3183	1633	1543	1319	1516	517	483	-	-
Co-Complex	3398	3158	1644	1554	1336	1516	516	478	-	-
Ni-Complex	3370	3243	1631	1557	1337	1516	530	479	-	-
Zn-Complex	3436	3181	1645	1522	1328	1516	522	469	-	-
Hg-Complex	3432	3225	1642	1535	1309	1526	523	480	316	-
Cd-Complex	3468	3249	1642	1540	1314	1497	524	487	316	-

Electronic spectra

The electronic spectra of Co^{II}, Ni^{II} and Cu^{II} complexes of the ligand (HL) were recorded in DMF solution at 10⁻³ molar concentration. The light green colored Cu^{II} complex exhibited a broad asymmetric band in the region 16400 cm^{-1} with the maxima at 13485 cm^{-1} in a distorted octahedral geometry^[29]. The broadness of the band may be due to dynamic Jahn-Teller distortion and it is assigned to ${}^2T_{2g} \rightarrow {}^2E_g$ transition. In the electronic spectra of Co^{II} complex the three absorption bands observed at 10312 cm^{-1} , 15898 and 20741 cm^{-1} are due to ${}^4T_{1g}(F) (v_1) \rightarrow {}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F) (F) (V_2)$ and ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(p) (v_3)$ transition respectively. These transitions suggest octahedral geometry for the Co^{II} complex. The assignments are in good agreement with the reported values^[30,31]. The ligand field parameter such as Dq B β_1 and $\beta\%$ have been calculated by using fitting equation given by Underhill and Billing^[32]. The crystal field splitting energy (Dq) values are well within the range reported for most of octahedral Co^{II} complexes. The Co^{II} complex under present investigation possess interelectronic repulsion parameter β at 932 cm^{-1} , the Raeha parameter β_1 is 971 cm^{-1} which is less than free ion. Nephelauxetic reaction (β) for the present Co^{II} complexes is 0.91 which is less than one, suggesting partial covalency in the metal ligand band. The values Dq $\beta\%$ LFSE and V_2/V_1 (TABLE 3) suggest the octahedral geometry for Co^{II} complex^[33]. The electronic spectra of Ni^{II} complex under present investigation exhibited three bands at 9865, 15024 and 25152 cm^{-1} respectively in DMF solution. These bands are assigned to ${}^3A_{2g}(F) \rightarrow T_{2g}(F) (V_1)$ and ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F) (v_2)$ and ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F) (V_3)$ transition respectively. More over the ratio V_2/V_1 was found to be

1.522 which is well within the range 1.56-1.61 which indicates octahedral stereochemistry for Ni^{II} complex which is indicating octahedral geometry. Further the ratio V_2/V_1 (1.522) and $\beta\%$ (5.39) supports the octahedral geometry around the Ni^{II} ion (TABLE 3).

TABLE 3 : Electronic spectral data and ligand field parameters of CuII, NiII & CoII complexes of ligand (HL).

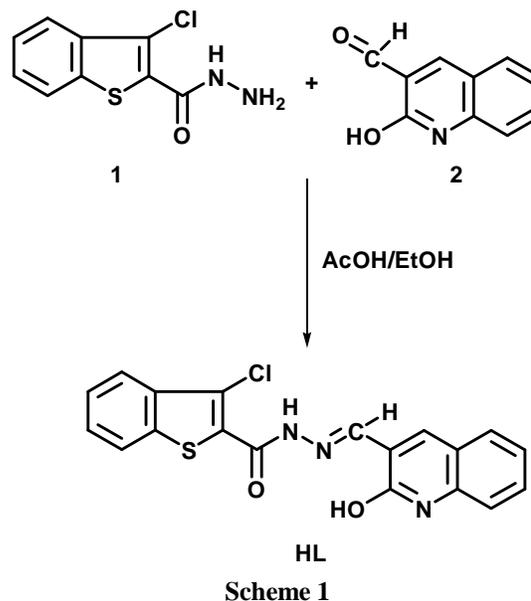
Complex	V_1	V_2	V_3	Dq (cm^{-1})	B^1	β	$\beta\%$	V_2/V_1	LFSE Kcal mol ⁻¹
Cu-complex	163100	13485	--	1494	--	--	--	--	25.62
Co-complex	10312	15898	20741	832	971	0.91	12.07	1.542	19.02
Ni-Complex	9865	15024	25152	937	835	0.86	5.39	1.522	32.13

¹H NMR spectrum of the ligand HL

In the ¹H NMR spectrum of the ligand HL, the three singlets observed at 8.65, 12.00 and 12.30 ppm due to a proton of azomethine function, a proton of amide NH and a proton of OH function attached to quinoline moiety respectively. A multiplet due to nine aromatic protons has resonated in the region 7.15-8.55. ppm.

¹H NMR spectrum of Zn (II) complex of the ligand HL

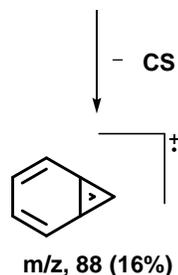
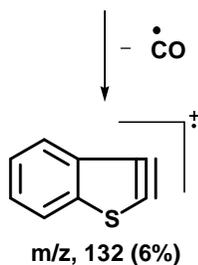
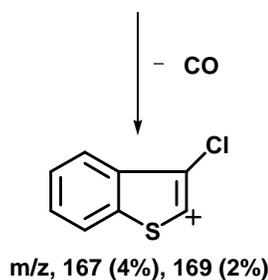
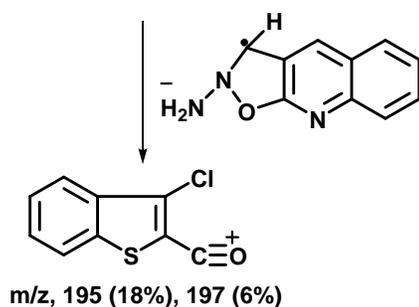
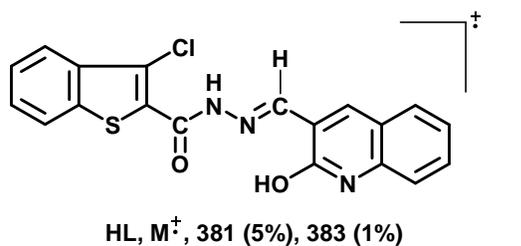
In the ¹H NMR spectrum of the Zn^{II} complex of the ligand HL, the disappearance of peak at 12.30 ppm due to phenolic proton when compared to that of ligand, clearly confirms the deprotonation of the phenolic OH during complexation, A fine singlet appeared at 12.05ppm is due to NH proton of amide function. The aromatic protons have appeared in the region 7.10 – 8.70 ppm.



Mass spectral analysis

Mass spectrum of the ligand HL

In the mass spectrum of the ligand HL the molecular ion M^+ peak observed at 381 (5%), 383 (1%) which corresponds to its molecular weight. This molecular ion due to sequential loss of $C_{10}H_8N_3O$ radical,



Scheme 2

$C=O$ molecule, chloride radical and $C=S$ fragments gave fragment ions recorded at m/z 195, 197 (18%, 6%), m/z 167, 169 (4%, 1%), m/z 132 (6%) and m/z 88 (16%) respectively (Scheme 2).

Mass spectrum of Cu^{II} complex of the ligand HL

In the mass spectrum of Cu^{II} complex of the ligand HL the molecular ion M^+ peak observed at 516, 518, 520 (4%, 2%, 1%) which corresponds to its molecular weight. This molecular ion gave fragmented ions at m/z 480, 482, 484 (5%, 2%, 1%), m/z 443, 445 (55%, 17%), m/z 276 (5%) and 107 (51%) due to sequential loss of two water molecules, simultaneous loss of hydrochloric acid and hydrogen radical, C_6H_4SCl radical and $C_{10}H_5N_2O$ radical fragments respectively (Scheme 3).

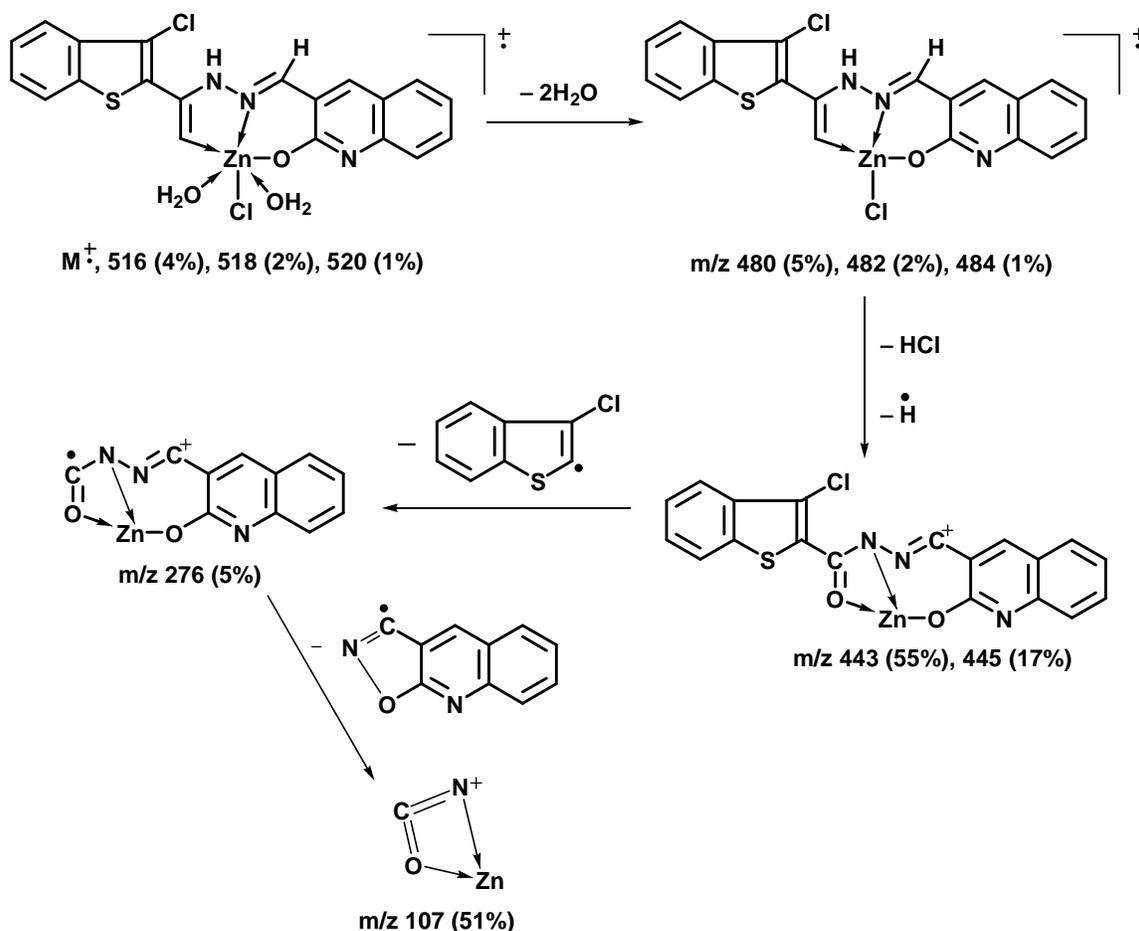
Magnetic susceptibility data

Magnetic susceptibility measurements of the complexes were performed at room temperature. The magnetic moment for Cu^{II} complex of the ligand HL is 1.80 BM. The reported values for the mononuclear Cu^{II} having no major spin interaction is 1.75 - 2.20 BM^[34,35]. Thus the present Cu^{II} complex is devoid of any spin interaction with distorted octahedral geometry. In octahedral Co^{II} complex the ground state is $4T_{1g}$ and a large orbital contribution to the magnetic moment is expected. The mixing of the singlet states lowers the magnetic moment. The reported magnetic moment values for the various Co^{II} complexes is in the range 4.7-5.2 BM for octahedral complexes. In the present investigation the observed magnetic moment value for Co^{II} complex is 4.99 BM indicates octahedral geometry for this Co^{II} complex. For Ni^{II} complex the observed magnetic moment value is 3.11 BM which is well within the expected range 2.83-4.0 BM^[36,37] for Ni^{II} complex with octahedral stereochemistry.

ESR spectral studies of the Cu^{II} complex of the ligand HL

The X-Band ESR spectrum of the powder Cu^{II} complex was recorded at room temperature using DPPH as reference standard. One unpaired electron in Cu^{II} complex with $^2B_{1g}$ as ground state lies in dx^2-y^2 orbital and follows the trends $g_{||} > g_{\perp} > g_e$ ($g_e = 2.0036$ free ion value).

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Scheme 3

The observed $g_{\parallel}=2.2787$, $g_{\perp}=2.0570$ values of the Cu^{II} complex under the present study followed the same trend $g_{\parallel} > g_{\perp} > g_e$ which suggest the presence of unpaired electron in dx^2-y^2 orbital giving octahedral geometry^[36]. The observed $G=4.49$ for the complexes under present study evidenced the monomeric nature of the complexes^[38]. This fact is further supported by the absence of a band corresponding to $\Delta M_s = \pm 2$ transition^[39] in the observed ESR spectrum which is characteristic of monomeric complex.

Thermo gravimetric analysis

The decomposition studies of the Ni^{II} complex has been carried out in the thermogram of the $[Ni(C_{19}H_{15}N_3O_4)]$ loss of $2H_2O$ was observed at $128^\circ C$ indicated by inflexion in the curve at $118^\circ C$ with 7.03% weight loss which is in accordance with the theoretical weight loss 7.07%. The resultant intermediate complex under went further degradation and gave another break at $409^\circ C$ with weight loss of 6.83%

which corresponds to the expulsion of HCl molecule from the intermediate complex. The theoretical weight loss for this decomposition was 6.82% agreeing well with the observed value. Third inflection occurred at $460^\circ C$ with weight loss of 47.72% which accounts for the loss of C_9H_4NOSCl species. This practical weight loss 47.72% of the third stage decomposition is in accordance with the theoretical weight loss of 47.75%. Thereafter the complex showed a gradual decomposition up to $822^\circ C$ and onwards. The weight of residue corresponds to the formation of NiO (TABLE 4).

Antimicrobial activity

Antimicrobial activity was carried out by the cup-plate method^[19,20]. The ligand HL and its Cu^{II} , Ni^{II} , Co^{II} , Zn^{II} , Cd^{II} and Hg^{II} , complexes have been tested for their antimicrobial and antifungal activity at 1mg/mL concentration. The results of the antimicrobial activity have been presented in TABLE 5. The antimicrobial activity ligand HL and its Cu^{II} , Ni^{II} , Co^{II} , Zn^{II} , Cd^{II} and Hg^{II} complexes

TABLE 4 : Thermal decomposition of NiII complex of ligand HL.

Complex	Stage	Peak temp TG (°C)	Loss of mass (in %)		Probable assignments
			Practical	Theoretical	
Ni(C ₁₉ H ₁₅ Cl ₂ NiN ₃ O ₄ S)	-	-	-	-	Ni (C ₁₉ H ₁₅ Cl ₂ NiN ₃ O ₄ S) ↓ -2H ₂ O
	I	128	7.03	7.07	Ni(C ₁₉ H ₁₁ Cl ₂ NiN ₃ O ₂ S) ↓ -HCl
	II	409	6.83	7.59	Ni(C ₁₉ H ₁₀ ClN ₃ O ₂ S) ↓ -C ₉ H ₄ NOSCl
	III	460	47.72	47.75	Ni(C ₁₀ H ₆ N ₂ O) ↓ NiO

TABLE 5 : Antimicrobial activity screening data of the ligand HL and its complexes.

Compound/ complexes	Antimicrobial activity (Zone of inhibition in mm)*			
	Antibacterial activity		Antifungal activity	
	E.coli	S.aureus	A.niger	C.albicans
HL	13	16	15	18
Cu – complex	13	15	16	15
Co – complex	12	14	17	18
Ni - complex	13	12	10	09
Zn - complex	14	16	09	11
Cd – complex	16	17	15	17
Hg – complex	15	12	20	22
Streptomycin	21	22	-	-
Fluconazole	-	-	22	24
DMF (Control)	0	0	0	0

*Bore size-6mm

were found to show weak activity with 12-15 mm inhibition against *E. coli* and *S. aureus* whereas Cd^{II} complex showed moderate activity with 16 mm and 17 mm inhibition against the same organisms when compared to the standard drug streptomycin which showed 21 mm and 22 mm inhibition against *E. coli* and *S. aureus*, respectively at the same concentration as that of the test compound. The antifungal activity result of the ligand and its above complex revealed that the ligand HL

showed moderate activity against *A. Niger* and *C. albicans* with 15 mm and 18 mm inhibitions respectively. The Cu^{II} Co^{II}, Cd^{II}, Ni^{II}, and Hg^{II} complexes showed good antifungal activity with 18 mm - 22 mm inhibition against both *A. Niger* and *C. albicans* whereas Ni^{II} - Zn^{II} complex showed moderate activity against both *A. niger* and *C. albicans* with 09 mm - 11 mm inhibition compared to the standard drug Fluconazole which showed 22 mm and 24 mm inhibition against *A. niger* and *albicans* respectively at the same concentration as that of test compounds.

EXPERIMENTAL

Material and method

All the chemicals are of reagent grade. Solvents were dried and distilled before use according to standard procedure^[40]. The precursor 3-chloro-1-benzothiophene-2-carbohydrazide^[41] and 2-hydroxy-3-formyl quinoline were prepared by literature method^[17]. The metal chlorides used were in their hydrated form.

Synthesis of the ligand HL

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

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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 (HL) was collected by filtration, washed with ethanol, dried and recrystallized from absolute ethanol.

Preparation of Cu^{II}, Co^{II}, Ni^{II}, Zn^{II}, Cd^{II} and Hg^{II} complexes of ligand HL

To the hot solution of 3-chloro-*N*-1*E*-(2-hydroxyquinoline-3-yl) methylene)-1-benzo(b)thiophene-2-carbohydrazide (HL) (0.002 mol) in ethanol (30mL) was added a hot ethanolic solution (10mL) of respective metal(II) chloride (0.002 mol), the reaction mixture was refluxed on a steam bath for 4h, 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 desiccator (yield 60-70 %) (TABLE 1).

Physical measurements

IR Spectra of the synthesized ligand and its complexes were recorded as KBr pellets on Perkins-Elmer Spectrum One FT-IR spectrometer. ¹H NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer. UV-vis spectra of the complexes were recorded on Elico-SL 164 spectrometer in the range 200-1000 nm in DMF solution (1x10⁻³M). Mass spectrum of ligand acquired on MASPEC system and FAB-mass spectrum of Cu^{II} complexes at using Argon Xenon as the gas, accelerating voltage was recorded at room temperature using meta-dinitrobenzyl alcohol as a matrix. 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 Bio Spin GmbH spectrometer working at microwave frequency of 9.903 GHz. The experiment was carried out by using diphenylpicrylhydrazyl (DPPH) as reference with field set at 3200 gauss. Magnetic susceptibility were determined by the Faraday method using a model 300 Lewis coil force magnetometer of tesla field strength at room temperature. The instrument was calibrated with Hg [Co(SNC)₄]^[42].

CONCLUSION

In the light of above discussion we have proposed octahedral geometry for Ni^{II} Co^{II}, Cu^{II}, Zn^{II}, Cd^{II} and Hg^{II} complexes. The ligand behaves as ONO tridentate chelating agent coordinating through the deprotonation of hydroxyl group, carbonyl group and azomethine nitrogen. The analytical data, electronic, spectral, magnetic susceptibility, IR, ¹H NMR, ESR and mass spectral data revealed mononuclear nature of the complexes. The ligand as well as its metal complexes was found to be less active against the bacteria whereas moderately active against the fungi *A niger*. All the complexes showed good activity as compared with their ligand. On the basis of spectral evidence following structures have been assigned for synthesized complexes.

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