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Synthesis, spectral, thermal, powder x-ray diffraction and antimicrobial activity studies of some transition metal(II) complexes with schiff base derived from 3-chloro-N′-[(1E)-(3-methoxy phenyl)methylene]-1-benzothiophene-2-carbohydrazide

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ABSTRACT

A series of new coordination complexes of Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) with the Schiff base 3-chloro-N′-[(1E)-(3-methoxyphenyl) methylene]-1-benzothiophene-2-carbohydrazide have been synthesized and characterized by elemental analysis, electrical conductance, electronic spectra, ESR, XRD, IR, FAB-MASS, TGA, ^{1}HNMR and magnetic susceptibility measurements. The Schiff base behaves as bidentate ON donor ligand and forms the complexes of the types $ML_2 \cdot (H_2O)_n$ (Metal-Ligand ratio) stoichiometry and are non electrolytic in nature. It is found that, Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) complexes exhibit octahedral geometry. The ligand and its complexes have been tested for their antimicrobial activity.
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INTRODUCTION

In the field of coordination complexes, Schiff base metal complexes[1] have a curious history. Considerable interest attached with the chemistry of Schiff base[2] derived from heterocyclic aldehydes, glyoxals and primary amines. Various heterocyclic Schiff bases having O, N and S donor atoms, have been reported by several chemists[3-5]. In recent years application of Schiff bases and their metal complexes in pharmacological[6] and non-pharmacological[7] fields have been receiving increased attention.

Literature survey reveals that, the benzothiophene skeleton is found in various types of natural compounds and several synthetic heterocyclic compounds which exhibit good biological activities[8]. In view of these findings and in continuation of our research work on coordination chemistry[9-11], we hereby report the synthesis, characterization and antimicrobial activity of 3-chloro-N'-[(1E)-(3-methoxyphenyl)methylene]-1-benzothiophene-2-carbohydrazide and its Co(II),
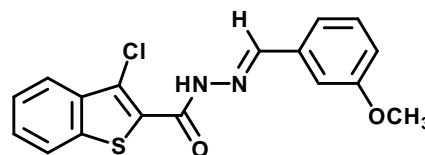

Figure 1

Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) complexes (Figure 1).

EXPERIMENTAL

Materials and methods

All the chemicals are of reagent grade. Solvents were dried and distilled before use according to standard procedures[12]. m-Anisaldehyde used is of reagent grade and glacial acetic acid of an analytical grade.

3-chloro-N'-[(1E)-(3-methoxyphenyl) methylene]-1-benzothiophene-2-carbohydrazide(Ligand L)

A mixture of 3-chlorobenzo(b)thiophene-2-carbohydrazide[13] (0.001 mol) and m-anisaldehyde (0.001 mol) in ethanol (20ml) containing one or two drops of glacial acetic acid was refluxed for about 5 hrs on water bath. The reaction mixture was cooled to room temperature; the separated compound was collected by filtration and recrystallized from absolute ethanol. (m.p.: 195-198C, yield 65%).

Synthesis of Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) complexes

To a hot solution of 3-chloro-N'-[(1E)-(3-methoxyphenyl)methylene]-1-benzothiophene-2-carbohydrazide ligand L (0.001 mol) in ethanol (30ml) was added a solution of the appropriate metal(II) chlorides (0.001 mol) in ethanol (10ml) and the mixture refluxed for 6-8 h. The resulting solid complex was collected by filtration, washed with 4-5 ml of hot ethanol and dried in a vacuum over anhydrous calcium chloride in a desiccator. (Yield 60-70%).

Physical measurements

IR spectra of the synthesized compounds were recorded as KBr pellets on PERKIN-ELMER Spectrum One FT-IR spectrometer. ^{1}H NMR spectra were recorded (d_6-DMSO as solvent) on a Bruker Avance 400 MHz spectrometer. UV-Vis spectra of the com-

plexes were recorded on Elico-SL 164 double beam spectrometer in the range 200-1200 nm in DMF solution (1×10^{-3}M). Molar conductance of the complexes were measured in DMF solution at room temperature using an Elico make, Equip-Tranics, Automatic conductivity meter Model No. EQ667 provided with Elico conductivity Bridge CC-01. FAB-mass spectra of the ligand and Cu(II) complex were obtained on JEOL SX 102/DA-6000 mass spectrometer using Argon/Xenon (6kv, 10mA) as the gas. The accelerating voltage was 10kV and the spectrum was recorded at room temperature using meta-nitrobenzyl alcohol (NBA) as a matrix. Elemental analyses were obtained from HERAEUS C, H, N-O rapid analyzer and metal analyses were carried out by following the standard methods. ESR measurements were carried out on a BRUKER BioSpin Gmbh spectrometer working at a microwave frequency of 9.157 GHz using DPPH as reference with the 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(SCN)$_4$][19]. Thermo gram (TGA) for the metal complex was taken on a Perkin Elmer TGA thermal analyzer at a heating rate of 10^0C per minute in dynamic nitrogen atmospheres.

RESULTS AND DISCUSSION

All the synthesized complexes are colored, amorphous in nature and stable in air. All these complexes were found to be insoluble in common organic solvents but are soluble in solvents such as DMF and DMSO. The analytical data of all the complexes are given in the TABLE 1. Molar conductivity data obtained in DMF suggest that all the complexes are of non-electrolyte type.

I.R spectra

The important IR frequencies exhibited by the ligand and its Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II)
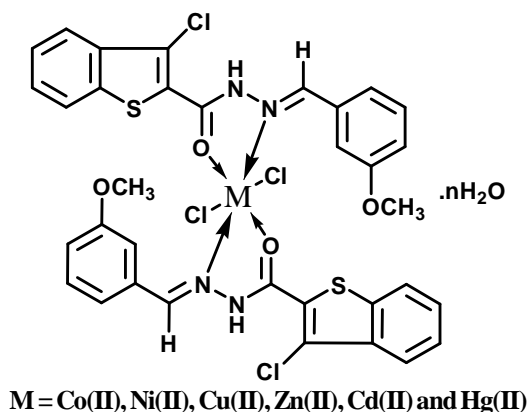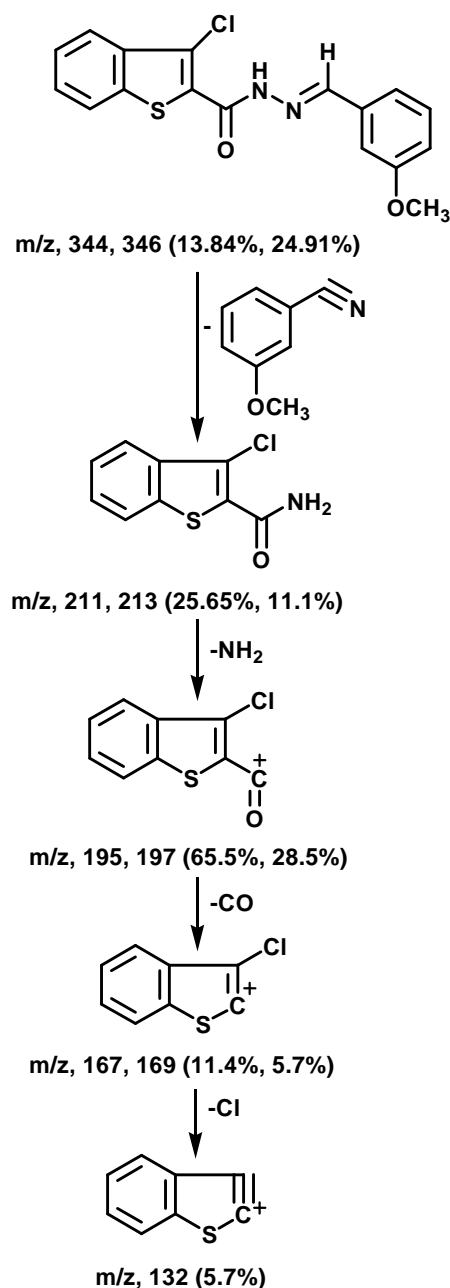

Scheme 1

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M = Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II)
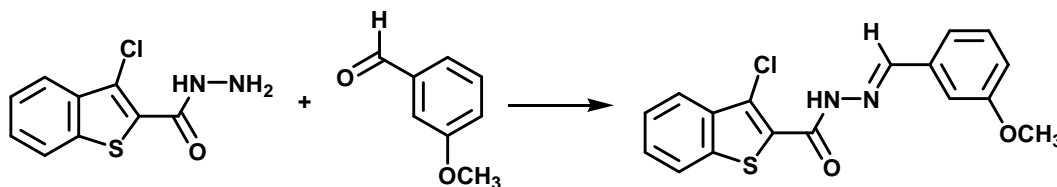
Figure 2

Scheme 2

complexes are given in the TABLE 2. In the IR spectra of all the complexes, medium intensity bands observed in the region 3248-3059cm^{-1} were due to amide -NH stretching vibrations. These bands have been found to appear at about the same region in all the complexes when compared to that of ligand L which appeared at 3244cm^{-1}, thereby indicating the non-involvement of amide -NH in coordination with the metal ions.
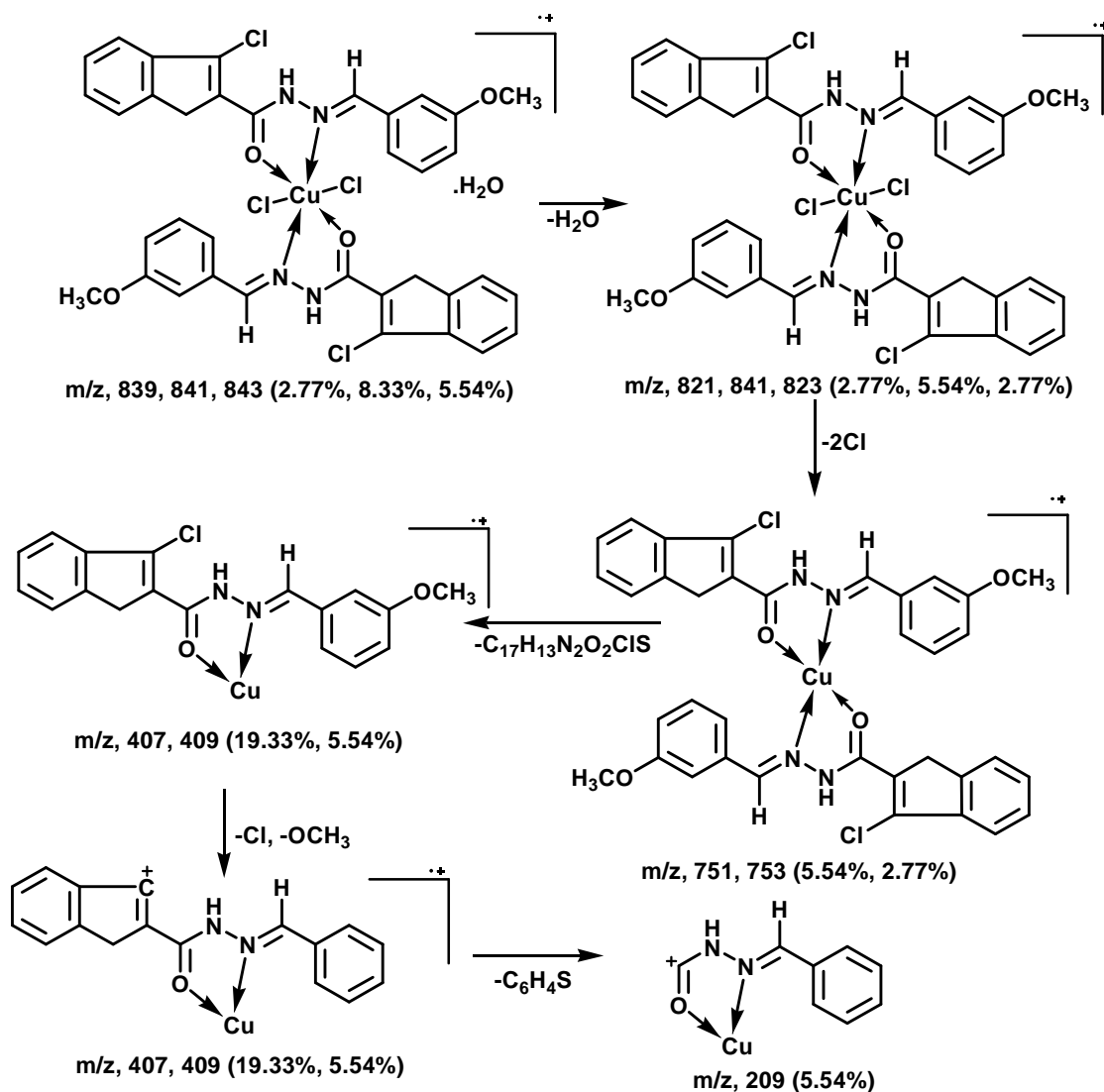
The sharp band at 1603cm^{-1} which was assigned to $\nu(C = N)$ in the ligand L has been shifted to lower energy by 62-6cm^{-1} and appeared in the region 1597-1541cm^{-1} suggesting the coordination of N-atom of azomethine group to metal ions. A sharp band observed at 1641cm^{-1} in case of ligand L due to the $\nu(C = O)$ function was found to be shifted to lower frequency side by 45-6cm^{-1} appeared in the region 1635-1596cm^{-1} in all the complexes. The shift of $\nu(C = O)$ vibrations towards lower frequency side in these complexes when compared to that of ligand indicates the involvement of O-atom of the carbonyl function in the coordination with the metal ions, without enolisation of CONH functional group[10]. In all the complexes, the appearance of broad absorption band in region 3448-3424cm^{-1} is assigned to $\nu(OH)$ vibrations of H$_2$O molecule (lattice)[15]. The C-S-C vibration of the benzothiophene moiety observed at about the same region 1538-1510cm^{-1} in all the complexes when compared to that of ligand L which appeared at 1542 cm^{-1} rule out the possibility of involvement of benzothiophene ring sulphur in the coordination with the metal ions.

Skeletal vibrations of metal-oxygen and metal-nitrogen bonds of the complexes can be precisely assigned in the Far IR region. Appearance of a new set of bands in case of all the complexes under study, due to $\nu(M-O)$ and $\nu(M-N)$ vibrations is the direct evidence for complexation. The bands observed in the region 531-528cm^{-1} and 427-408cm^{-1} are assigned to $\nu(M-O)$ and (M-N) respectively. The bands in the region 321-311 cm^{-1} have been assigned to $\nu(M-Cl)$ bands in all the complexes[14]. The presence of chlorine atoms in these complexes is further confirmed by quantitative chloride estimation. From the IR spectral data, it is found that the ligand L has coordinated to the metal ions in a bidentate fashion through the carbonyl oxygen atom and azomethine nitrogen atom.

m/z, 839, 841, 843 (2.77%, 8.33%, 5.54%)   **m/z, 821, 841, 823 (2.77%, 5.54%, 2.77%)**

m/z, 407, 409 (19.33%, 5.54%)

m/z, 751, 753 (5.54%, 2.77%)

m/z, 407, 409 (19.33%, 5.54%)

m/z, 209 (5.54%)

Scheme 3

Electronic spectra

The electronic spectra of Co(II), Ni(II) and Cu(II) complexes of the ligand L were recorded in DMF solution at 10^{-3} molar concentration. In the electronic spectra of Co(II) complex, the three absorption bands observed at 10567cm^{-1}, 15610cm^{-1} and 20215cm^{-1} due to the $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)(\nu_1)$, $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ (ν_2) and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)(\nu_3)$ transitions respectively. These transitions suggest octahedral geometry for the Co(II) complex. These assignments are in good agreement with the reported values[17,18]. The electronic spectra of Ni(II) complex under the present investigation exhibited three bands at 10511 cm^{-1}, 16114 cm^{-1} and 24373 cm^{-1} respectively in DMF solution. These bands are assigned $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)(\nu_1)$,

$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)(\nu_2)$ and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)(\nu_3)$ transitions respectively. The band around 10516cm^{-1} is attributable to a d-d component of the Ni(II) complex[19] for octahedral geometry, thereby suggesting the octahedral geometry for the nickel(II) complex. The light green colored Cu(II) complex exhibits a broad asymmetric band in the region 16341-13142cm^{-1} with maxima at 14495cm^{-1} in an distorted octahedral geometry[19]. The broadness of the band may be due to dynamic John-Teller distortion and is assigned to $^2T_{2g} \rightarrow {}^2E_g$ transitions.

¹H NMR spectral studies

¹H NMR spectrum of the ligand L

¹H NMR spectrum of ligand L showed a fine singlet due to amide proton CONH function at δ 10.33

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TABLE 1 : Analytical, magnetic susceptibility and molar conductance data of ligand L and its complex

Compounds/complexes	Mol. Wt.	Calcd. / (Found)(%)					Magnetic Moment(B.M.)	λ_m ($cm^2\Omega^{-1}$ mol^{-1})	M.P.(°C) Yield (%)
		M	C	H	N	Cl			
$C_{17}H_{13}ClN_2O_2S$	344	--	59.30(59.18)	3.77(3.78)	8.13(8.09)	10.17(10.25)	--	28	195
$[Cu(C_{17}H_{13}ClN_2O_2S)_2]Cl_2. H_2O$	839	7.39(7.36)	48.62(47.45)	3.33(3.51)	6.67(6.48)	16.68(16.46)	1.97	31	286
$[Co(C_{17}H_{13}ClN_2O_2S)_2]Cl_2.2H_2O$	852	6.89(6.86)	47.88(47.69)	3.52(3.51)	6.57(6.53)	16.43(16.55)	4.98	34	269
$[Ni(C_{17}H_{13}ClN_2O_2S)_2]Cl_2.2H_2O$	852	6.86(6.84)	47.88(47.43)	3.52(3.52)	6.57(6.53)	16.43(16.55)	2.99	23	288
$[Zn(C_{17}H_{13}ClN_2O_2S)_2]Cl_2.2H_2O$	859	7.59(7.56)	47.49(47.34)	3.49(3.48)	6.51(6.48)	16.29(16.42)	Diamag.	25	273
$[Cd(C_{17}H_{13}ClN_2O_2S)_2]Cl_2.2H_2O$	906	12.37(12.35)	44.03(44.90)	3.31(3.30)	6.18(6.13)	15.45(15.56)	Diamag.	26	278
$[Hg(C_{17}H_{13}ClN_2O_2S)_2]Cl_2.2H_2O$	994	20.12(20.09)	41.04(40.92)	3.02(3.01)	5.63(5.59)	14.08(14.18)	Diamag.	25	285

TABLE 2 : IR spectral data (cm^{-1}) of ligand L and its complexes

Compounds/complexes	ν(OH)	ν (NH)	ν (OCH₃)	ν (C=O)	ν (C=N)	Thiophene Ring vib.	ν (M-O)	ν (M-N)	ν (M-Cl)
$C_{17}H_{13}ClN_2O_2S$	--	3244	2923	1641	1603	1542	--	--	--
$[Cu(C_{17}H_{13}ClN_2O_2S)_2]Cl_2.H_2O$	3456	3158	2926	1596	1541	1522	530	427	311
$[Co(C_{17}H_{13}ClN_2O_2S)_2]Cl_2.2H_2O$	3424	3248	2925	1635	1594	1538	529	408	315
$[Ni(C_{17}H_{13}ClN_2O_2S)_2]Cl_2.2H_2O$	3442	3248	2930	1635	1597	1537	531	409	315
$[Zn(C_{17}H_{13}ClN_2O_2S)_2]Cl_2.2H_2O$	3448	3247	2925	1635	1594	1510	528	423	318
$[Cd(C_{17}H_{13}ClN_2O_2S)_2]Cl_2.2H_2O$	3446	3248	2925	1631	1594	1511	530	416	320
$[Hg(C_{17}H_{13}ClN_2O_2S)_2]Cl_2.2H_2O$	3446	3159	2925	1571	1596	1512	530	422	321

TABLE 3 : Thermal decomposition of Cu(II) complex of the ligand L

Complex	Stage	PeakTemp. TG (°C)	Loss of Mass (%)		Probable assignments
			Practical	Theoretical	
	-	-	-	-	$Cu(C_{34}H_{28}Cl_4O_5N_4S_2)$
	I	97	2.17	2.14	
	II	264	4.42	4.38	↓ $-H_2O$
					$Cu(C_{34}H_{26}Cl_4O_5N_4S_2)$
					↓ $-HCl$
					$Cu(C_{34}H_{25}Cl_3O_4N_4S_2)$
					↓ $-C_{17}H_{12}N_2O_2ClS$
$[Cu(C_{17}H_{13}ClN_2O_2S)_2]Cl_2. H_2O$	III	415	51.89	51.87	$Cu(C_{17}H_{13}Cl_2O_2N_2S)$
					↓ $-HCl$ ↓ $-N_2$
					$Cu(C_{17}H_{12}ClO_2S)$
					↓
					CuO

(1H, s). The eight aromatic protons of benzothiophene and phenyl ring have appeared in the region δ 6.84-7.97 (m, 8H) as a multiplet. The Azomethine proton has appeared as a singlet at δ 8.29 (s, 1H). Another fine singlet due to methoxy group appeared as singlet at δ 3.77 (s, 3H).

¹HNMR spectrum of Cd(II) complex of the ligand L

In the ¹H NMR spectra of Cd(II) complex the eight aromatic protons were observed in the region δ

TABLE 4 : Powder x-ray diffraction data of the ligand L

Peak	2θ	θ	$\sin\theta$	$\sin^2\theta$	h k l	d Calc.	d Obser.	$h^2+k^2+l^2$	a in Å
1	5.70297	2.85148	0.04975	0.00248	111	15.48342	15.48388	3	15.49
2	11.58844	5.79422	0.10095	0.01019	200	7.63051	7.62986	4	15.49
3	13.61674	6.80837	0.11855	0.01405	211	6.49768	6.49757	6	15.49
4	21.04039	10.52019	0.18258	0.03334	320	4.21897	4.21881	13	15.49
5	22.29656	11.14828	0.19339	0.0374	--	3.98314	3.98389	15	15.49
6	26.15454	13.07727	0.22626	0.05119	421	3.40449	3.40433	21	15.49
7	27.46553	13.73277	0.23739	0.05635	--	3.24487	3.24474	23	15.49
8	34.76621	17.38311	0.29875	0.08925	442	2.57841	2.57826	36	15.49
9	60.64842	30.32421	0.50489	0.25491	--	1.52568	1.52563	103	15.49

CONVERSION FACTOR = 2.47506

TABLE : 5 Powder x-ray diffraction data of Cu(II) complexes of the ligand L

Peak	2θ	θ	$\sin\theta$	$\sin^2\theta$	h k l	d Calc.	d Obser.	$h^2+k^2+l^2$	a in Å
1	10.02751	5.01375	0.08739	0.00764	100	8.81451	8.81379	1	8.81
2	22.41828	11.20914	0.19439	0.03779	210	3.96265	3.96253	5	8.81
3	26.22895	13.11448	0.22515	0.05069	--	3.42127	3.39484	7	8.81
4	29.91344	14.95672	0.25809	0.06661	221	2.98462	2.98455	9	8.81
5	69.15095	34.57547	0.56749	0.32204	541	1.35738	1.35734	42	8.81

CONVERSION FACTOR = 7.63701

TABLE 6 : Antimicrobial screening data of the ligand L and its complexes

Test Compound	Antibacterial Activity (Zone of Inhibition in mm)		Antifungal Activity (Zone of Inhibition in mm)	
	E. coli	S. aureus	A. niger	C. albicans
$C_{17}H_{13}ClN_2O_2S$	13	11	14	16
$[Cu(C_{17}H_{13}ClN_2O_2S)_2]Cl_2 \cdot H_2O$	15	14	18	17
$[Co(C_{17}H_{13}ClN_2O_2S)_2]Cl_2 \cdot 2H_2O$	14	10	18	19
$[Ni(C_{17}H_{13}ClN_2O_2S)_2]Cl_2 \cdot 2H_2O$	15	14	20	21
$[Zn(C_{17}H_{13}ClN_2O_2S)_2]Cl_2 \cdot 2H_2O$	13	12	15	14
$[Cd(C_{17}H_{13}ClN_2O_2S)_2]Cl_2 \cdot 2H_2O$	10	10	16	15
$[Hg(C_{17}H_{13}ClN_2O_2S)_2]Cl_2 \cdot 2H_2O$	18	19	16	14
Standard-I (Streptomycin)	20	22	--	--
Standard-II (Grisofulvin)	--	--	24	23
DMF (Control)	0	0	0	0
(Bore size)	08	08	08	08

6.91-8.29 (m, 8H) as a multiplet. The azomethine proton which was resonated at δ 8.29 (s, 1H) in the ligand L, has resonated at δ 8.59 (s, 1H) in its Cd(II) complex. Proton of the amide NH function which was resonated at δ 10.33 (s, 1H) in ligand L has appeared at δ 10.42 (s, 1H) in the case of its Cd(II) complex suggesting that the ligand L had coordinated to the metal ion. A broad peak observed at δ 3.84 is appeared due to the presence of lattice water molecule. Protons of OCH₃ group have resonated as a singlet at δ3.84(s, 3H).

When the ¹HNMR spectra of the ligand L and the complex are compared, it was observed that the signals of the protons of different functionalities of the ligand L have been shifted towards the downfield region indicating the coordination of the ligand L to the Cd(II) ion.

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FAB-mass spectral analysis

FAB-Mass spectrum of ligand L showed a molecular ion peak M^+ at m/z 344,346 (13.84%, 24.91%), which is equivalent to its molecular weight. The molecular ion M^+ by the expulsion of C_8H_7NO species gave fragment ion A_1 at m/z 211, 213 ($M^+ - C_8H_7NO = A_1$, 25.65%, 11.4%). The fragment ion A_1 by the loss of NH_2 radical gave a fragment ion A_2 at m/z 195, 197 ($A_1 - NH_2 = A_2$, 65.5%, 28.5%). Fragment ion A_2 underwent further fragmentation by the loss of CO molecule and gave fragment ion A_3 at m/z 167, 169 ($A_2 - CO = A_3$, 11.4%, 5.7%). Fragment ion A_3 underwent further fragmentation by the loss of chloride radical and gave fragment ion A_4 at m/z 132 ($A_3 - Cl = A_4$, 5.7%) (Scheme 2). The IR, ^{1}HNMR and Mass spectral data of the ligand L are in conformity with its structure.

FAB-Mass spectrum of the Cu(II) complex with ligand L showed a molecular ion peak M^+ at m/z 839, 841, 843 (2.77%, 8.33%, 5.54%), which is equivalent to its molecular weight. The molecular ion M^+ by the expulsion of H_2O species gave fragment ion A_1 at m/z 821, 823, 825 ($M^+ - H_2O = A_1$, 2.77%, 5.54%, 2.77%). The fragment ion A_1 by the loss of two Cl· radical gave fragment ion A_2 at m/z 751, 753 ($A_1 - 2Cl· = A_2$, 5.54%, 2.77%). Fragment ion A_2 underwent further fragmentation by the loss of $C_{17}H_{13}N_2O_2ClS$ species and gave fragment ion A_3 at m/z 407, 409 ($A_2 - C_{17}H_{13}N_2O_2ClS = A_3$, 19.33%, 5.54%). Fragment ion A_3 underwent further fragmentation by the loss of chloride radical and OCH_3 radical and gave fragment ion A_4 at m/z 341 ($A_3 - Cl - OCH_3 = A_4$, 13.85%). Fragment ion A_4 underwent further fragmentation by the loss of C_8H_4S and gave fragment A_5 at m/z 209 ($A_4 - C_8H_4S = A_5$) (Scheme 3). The IR, ^{1}HNMR and Mass spectral data of the Cu(II) complex with ligand L are in conformity with its structure.

Magnetic susceptibility data

The magnetic susceptibility measurements of the complexes were performed at room temperature (TABLE 1). The reported values for the mononuclear Cu(II) complexes having no major spin interactions are in the range 1.75-2.20B.M.[20,21]. The present Cu(II) complex has a magnetic moment value 1.97B.M. Thus, the present Cu(II) complex is devoid of any spin inter-

actions with distorted octahedral geometry. In octahedral Cu(II) complexes 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 various Co(II) complexes are in the range 4.7-5.2B.M. for octahedral complexes[22]. In the present investigation the observed magnetic moment value for Co(II) complex is 4.98 B.M. indicates octahedral geometry for the Co(II) complex. For Ni(II) complex the observed magnetic moment is 2.99B.M which is well within the expected range for Ni(II) complexes with octahedral stereochemistry 2.83-4.0B.M[22,23]. The Zn(II), Cd(II) and Hg(II) complexes showed a diamagnetic behavior having a d^{10} system which is as per expectation.

ESR spectrum

The X-band ESR spectrum of the powder Cu(II) complex was recorded at room temperature using DPPH as a reference standard. One unpaired electron in Cu(II) complex with $^2B_{1g}$ as ground state lies in d_{x2-y2} orbital and follows the trend $g_Ô > g\perp > g_e$ ($g_e = 2.0036$-free ion value). The observed $g_Ô = 2.36$ and $g\perp = 2.07$ values of the Cu(II) complex under the present study followed the same trend $g_Ô > g\perp > g_e$ which suggest that the presence of unpaired electron in d_{x2-y2} orbital giving octahedral geometry[24]. This fact is in agreement with its electronic spectral data for octahedral geometry. The observed $G = 4.428$ for the complex under present study evidenced the monomeric nature of the complex[25]. This fact is further supported by the absence of a band corresponding to $\Delta Ms = \pm 2$ transition[26] in the observed ESR spectrum which is characteristic of monomeric complex.

Thermal study of $[Cu(L)_2(Cl)_2.H_2O]$

In the thermogram of the $[Cu(L)_2(Cl)_2.H_2O]$[27]. The first stage decomposition represents the weight loss of H_2O molecule at 97°C, with weight loss of 2.17%. The theoretical weight loss for this decomposition was 2.14%, agreeing with the observed value 2.17%. The complex underwent further degradation and gave a break at 264°C with a weight loss of 4.42%, which corresponds to the decomposition of the HCl molecule. This practical weight loss 4.42% is in accordance with

theoretical weight loss of 4.38%. The third stage decomposition at 415⁰C, with weight loss of 51.89%, which corresponds to the decomposition of $C_{17}H_{12}N_2O_2SCl$ species and one molecule of hydrogen chloride and one molecule of N_2. This practical weight loss 51.89% is in accordance with theoretical weight loss of 51.87%. Thereafter the compound showed a gradual decomposition up to 1100°C and onwards. The weight of the residue corresponds to copper oxide. The thermal decomposition of $[Cu(L)_2$ $(Cl)_2 H_2O]$ with probable assignments are given in the[28] TABLE 3.

X-ray diffraction studies

The ligand L and its Cu(II) complex have characterized by powder XRD studies with a view to find the type of the crystal system. The ligand L and its Cu(II) complex are chosen for powder XRD study. The XRD data of ligand L and its Cu(II) complex are given in the TABLE 4 and 5 respectively. There are 9 reflections (2θ) between 5.70297 and 60.64842° with maximum at 2θ = 5.70297° and d = 15.48388 Å in case of ligand L whereas its Cu(II) complex consists of 9 reflections with maxima at 2θ = 29.91344° corresponding to the value of d = 2.98455 Å. The interplanar spacing (d) has been calculated from the positions of intense peaks using Braggs relation nλ = 2d Sinθ (where λ = wavelength of X-ray used CuKα = 1.5406 Å). The observed and calculated values of d are quite consistent (TABLE 4 and 5). The unit cell calculations have been carried out for the cubic system[29,30]. The cell parameters have been calculated by using the equation for cubic system, $\sin^2 \theta = \lambda^2/4a^2 (h^2+k^2+l^2)$, where $\lambda^2/4a^2$ is common factor. In the present case ligand L and Cu(II) complex have $\lambda^2/4a^2 = 0.00248$ and 0.00764 respectively. The $h^2+k^2+l^2$ values are given in the TABLE 4 and 5. The presence of forbidden number 15, 23 and 103 in case of ligand L and 7 in case Cu(II) complex indicates the ligand L and Cu(II) complex may belong to hexagonal or tetragonal system[31,32].

Antimicrobial activity

Antimicrobial activity was carried out by the cup-plate method[30]. The ligand L and its Cu(II), Co(II), Ni(II), Zn(II), Cd(II) and Hg(II) complexes have been tested for their antibacterial and antifungal activities at

1mg/mL concentration. The results of the antimicrobial activity with zone of inhibition have been presented in TABLE 6. The antibacterial activity of the ligand L and its Cu(II), Ni(II), Co(II), Zn(II) and Cd(II) complexes found to be weakly active with 10-15 mm inhibition against *E.coli* and *S. aureus,* whereas Hg(II) complex showed moderate activity with 18 mm and 19 mm inhibition against the same organisms, when compared to the standard drug Streptomycin which showed 20 mm and 22 mm inhibition against *E. coli* and *S. aureus* respectively at the same concentrations as that of the test compounds. The antifungal activity results of the ligand L and its above complexes revealed that the ligand L showed moderate activity against *A. niger* and *Candida albicans* with 14 mm and 16 mm inhibition respectively. The Cu(II), Co(II) and Ni(II) complexes showed good antifungal activity with 17-21 mm inhibition against both *A. niger* and *Candida albicans* whereas Cd(II), Zn(II) and Hg(II) complexes showed moderate activity against both *A. niger* and *Candida albicans* with 14-17 mm inhibition compared to the standard drug Grisofulvin which showed 24 mm and 23 mm inhibition against *A. niger* and *Candida albicans* respectively at the same concentrations as that of the test compounds.

CONCLUSIONS

In the present investigation the ligand L acts as bidentate ligand coordinating through oxygen of amide carbonyl and azomethine-N. The analytical data of complexes suggested the 1:2 type stoichiometry for all the complexes $[ML_2].Cl_2.(H_2O)_n$. Ligand as well as its complexes were found to be less active against the bacteria *E.coli* and *S.aureus* where as moderately active against the fungi *A.niger* and *C. albicans*. All the complexes showed enhanced antimicrobial activity compared to their ligand L. On the basis of elemental analysis, UV-Vis, magnetic susceptibility data, IR, NMR, FAB mass and ESR the following structures proposed for the present complexes (Figure 2).

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providing laboratory facilities. Central University, Hyderabad, STIC Kochi and CDRI Lucknow for ^{1}HNMR, ESR, Mass, FAB-Mass, XRD and elemental data.

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