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Synthesis, characterization and antimicrobial activity studies of some Schiff base complexes of Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) derived from 3-chloro-N'-[(1E,2E)-3-phenylprop-2-en-1-ylidene]-1-benzothiophene-2-carbohydrazide

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ABSTRACT

Complexes of Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) with the Schiff base derived from 3-chlorobenzob(b)thiophene-2-carbohydrazide and cinnamaldehyde has been synthesized and characterized on the basis of elemental analysis, electrical conductance, ESR, XRD, IR, FAB-MASS, TGA, ¹HNMR, electronic spectra and magnetic susceptibility measurements. The Schiff base behaves as bidentate ligand coordinating through ON donor site and forms the complexes of the types ML₂·(H₂O)_n·Cl₂ (where, L= Schiff base, M=Metal). The complexes are non electrolytes, monomers and octahedral in nature. The ligand and its complexes have been screened for their antimicrobial activity. © 2010 Trade Science Inc. - INDIA

KEYWORDS

Carbohydrazide;
Schiff base;
ESR;
XRD;
Antimicrobial activity.

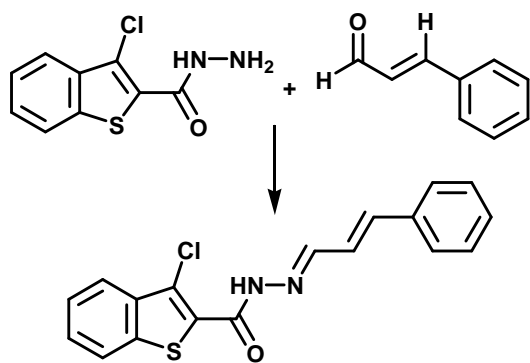
INTRODUCTION

The study of transition metal complexes of thiophene compounds is an area of current interest. This is due to the importance of thiophene compounds in hydrosulfurisation reaction in the petroleum industry^[1-3]. The industrial process is carried out heterogeneously over a CoMo/Al₂O₃ or CoW/Al₂O₃ catalyst. Increased activity of the catalyst has been observed when late transition metals are added as promoters to the catalyst^[1-3]. For these reasons thiophene and benzothiophene complexes of elements such as ruthenium^[4,5], rhodium^[6-8] and platinum^[9] and their catalytic reactions, have received considerable attention in recent years. Carbohy-

drazide compounds most directly associated with the foundation of organic chemistry are of special interest in view of their use in the synthesis of heterocyclic molecule, analytical chemistry, polymer and pharmaceutical applications. The chemistry of these compounds and some of their derivatives are reviewed by Kurzer and Wilkinson^[10]. The hydrazine group of these compounds display normal reactivity towards carbonyl compounds and give rise to a large variety of hydrazone or Schiff bases. It has been well established that these hydrazones are capable of exhibiting keto-enol tautomerism and one of the form is retained when they form complexes with the transition metal ions^[11].

In view of these findings and in continuation of our

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Scheme 1

research work on coordination chemistry^[12-14], we report here the synthesis, characterization and antimicrobial activity studies of Cu(II), Co(II), Ni(II), Zn(II), Cd(II) and Hg(II) complexes of Schiff base (Figure 1).

EXPERIMENTAL

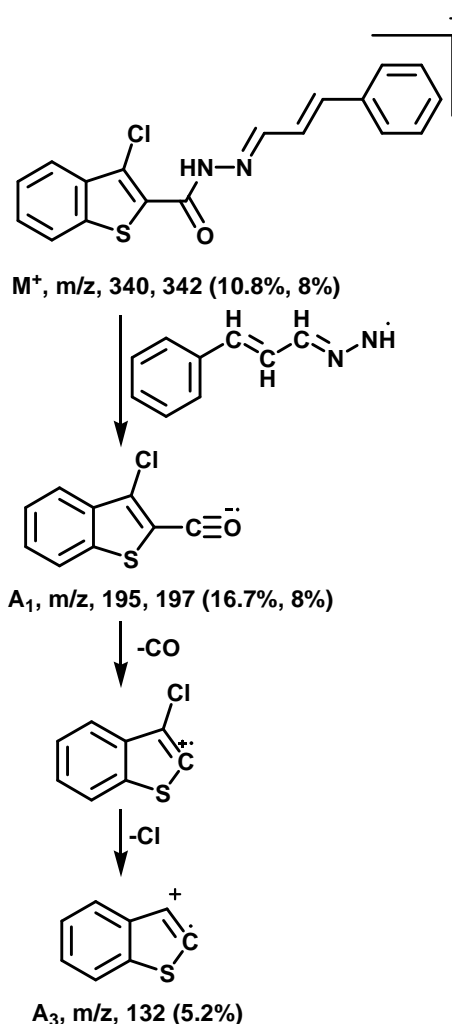
All the chemicals are of analytical grade. Solvents were dried and distilled before use according to standard procedures^[15]. Cinnamaldehyde used is of reagent grade and acetic acid were used is of an analytical grade.

Synthesis of 3-chloro-N'-[(1E,2E)-3-phenylprop-2-en-1-ylidene]-1-benzothio-2-carbohydrazide (Ligand L)

A mixture of 3-chlorobenzothio-2-carbohydrazide (0.001 mol) and cinnamaldehyde (0.001 mol) in ethanol (20 ml) containing few 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 (Scheme 1). (m.p.: 173-175°C).

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

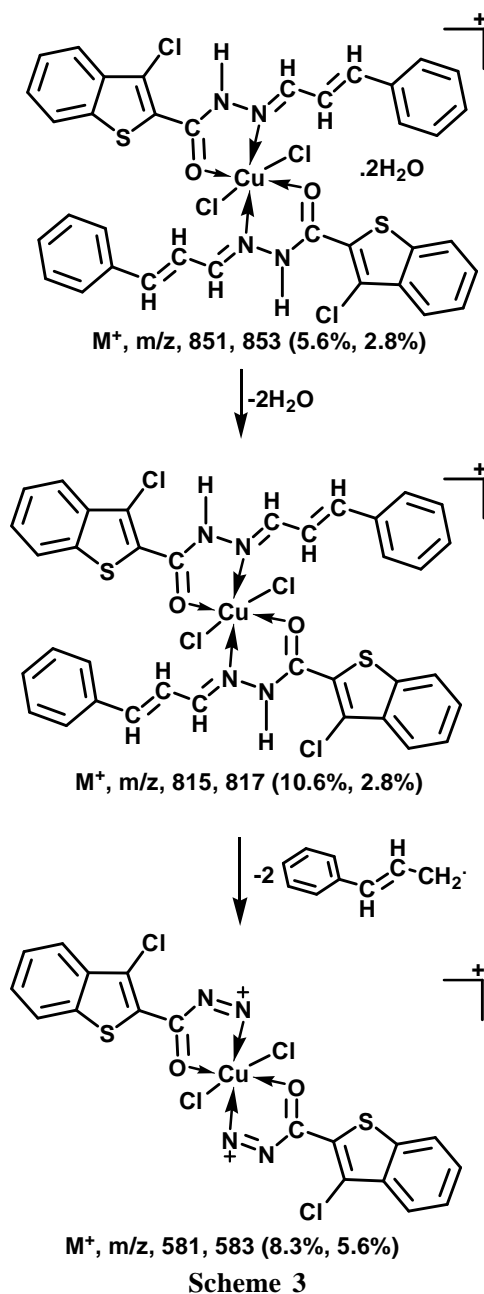
To a hot solution of 3-chloro-N'-[(1E,2E)-3-phenylprop-2-en-1-ylidene]-1-benzothio-2-carbohydrazide ligand L (0.001 mol) in ethanol (30 ml) was added a solution of the appropriate metal(II) chlorides (0.001 mol) in ethanol (10 ml) and the mixture was refluxed for 6-8 h. The resulting solid complex was collected by filtration and washed with hot ethanol and dried in a vacuum over anhydrous calcium chloride in desiccators. (Yield 65-75%).



Scheme 2

Physical measurements

IR spectra of the synthesized compounds were recorded as KBr pellets on PERKIN-ELMER Spectrum One FT-IR spectrometer. ¹H NMR spectra were recorded in *d*₆-DMSO as solvent on a Bruker Avance 400 MHz spectrometer. UV-Vis spectra of the complexes 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

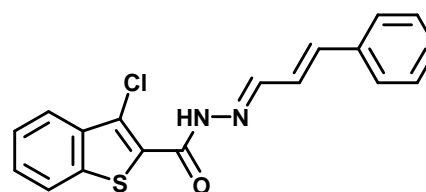
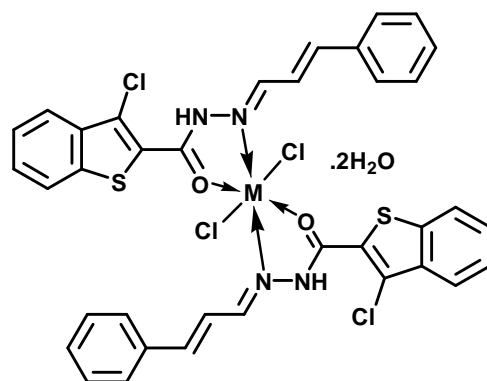


Figure 1 : 3-chloro-N'-[(1E, 2E)-3-phenylprop-2-en-1-ylidene]-1-benzothiophene-2-carbohydrazide



$M = \text{Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II)}$

Figure 2

$\text{Hg}[\text{Co}(\text{SCN})_4]^{[16]}$. Thermogram (TGA) for the Cu(II) complex of ligand L was taken on a Perkin Elmer TGA thermal analyzer at a heating rate of 10°C per minute in dynamic nitrogen atmospheres.

RESULT AND DISCUSSIONS

All the synthesized complexes are colored and amorphous in nature and stable in air. All these complexes found to be insoluble in common organic solvents but are soluble in solvent such as 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.

IR spectra

The IR spectra of the complexes are compared with that of the free ligand to determine the changes that might have taken place during the complexation (TABLE 2). The IR spectrum of ligand L showed a band at 3214 cm^{-1} attributable to $\nu(\text{NH})$ of amide group which is observed in the region $3071\text{-}3371 \text{ cm}^{-1}$ in case of complexes confirms that the carbonyl group has not undergone enolisation during complexation and thereby $\nu(\text{NH})$ remain intact in all the complexes. The band due to

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$\nu(\text{C}=\text{N})$ which was observed at 1583 cm^{-1} in case of ligand L has shown a negative shift of $6\text{--}20\text{ cm}^{-1}$ in case of all the complexes and appeared in the region $1577\text{--}1563\text{ cm}^{-1}$ indicating the involvement of azomethine nitrogen in the complexation with all the metal ions^[17]. The band due to $\nu(\text{C}=\text{O})$ observed in ligand L at 1642 cm^{-1} , suffers a negative shift of $20\text{--}32\text{ cm}^{-1}$ and appeared in the region $1610\text{--}1622\text{ cm}^{-1}$ in all the complexes, indicates the involvement of carbonyl oxygen in the complexation with the metal ion^[12]. The appearance of a new broad band in the region $3435\text{--}3363\text{ cm}^{-1}$ in all the complexes indicate the presence of lattice water^[18]. The characteristic vibration of the benzo(b)thiophene moiety observed at 1514 cm^{-1} in case of ligand L has appeared at about the same region $1497\text{--}1544\text{ cm}^{-1}$ in all the complexes which rules out the possibility of involvement of benzo(b)thiophene ring sulfur in the coordination with the metal ions^[19]. 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 $\nu(\text{M}-\text{O})$ and $\nu(\text{M}-\text{N})$ vibrations is the direct evidence for complexation. The bands observed in the region $488\text{--}516\text{ cm}^{-1}$ and $415\text{--}427\text{ cm}^{-1}$ are assigned to $\nu(\text{M}-\text{O})$ and $\nu(\text{M}-\text{N})$ respectively. The bands in the region $321\text{--}311\text{ cm}^{-1}$ have been assigned to $\nu(\text{M}-\text{Cl})$ bands in the all complexes^[19]. The presence of chloride in these complexes is further confirmed by quantitative chloride estimation.

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 10567 cm^{-1} , 15610 cm^{-1} and 20215 cm^{-1} due to the ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$ (ν_1), ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})$ (ν_2) and ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$ (ν_3) transitions respectively. These transitions suggest octahedral geometry for the Co(II) complex. These assignments are in good agreement with the reported values^[20,21]. These values are well within the range reported for most of the octahedral Co(II) complexes. 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

to ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})$ (ν_1), ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})$ (ν_2) and ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})$ (ν_3) transitions respectively. The band around $\sim 10516\text{ cm}^{-1}$ is attributable to a d-d component of the Ni(II) complex as reported by earlier workers^[22]. The light green colored Cu(II) complex exhibits a broad asymmetric band in the region $16341\text{--}13142\text{ cm}^{-1}$ with maxima at 14495 cm^{-1} in a distorted octahedral geometry^[23]. The broadness of the band may be due to dynamic Jahn-Teller distortion and is assigned to ${}^2\text{T}_{2g} \rightarrow {}^2\text{E}_g$ transitions.

${}^1\text{H}$ NMR spectral studies

(a) ${}^1\text{H}$ NMR spectrum of the ligand L

${}^1\text{H}$ NMR spectrum of ligand L showed a fine singlet due to amide proton of CONH function at $\delta 10.49$ ppm (1H, s). The nine aromatic protons of benzothiophene and phenyl ring have appeared in the region $\delta 6.91\text{--}7.45$ ppm (m, 9H) as a multiplet. The Azomethine proton has appeared as a doublet at $\delta 8.05$ ppm (d, 1H). The two vinyl protons have resonated as two distinct doublets at $\delta 6.91$ ppm (d, 1H) and $\delta 6.98$ ppm (d, 1H).

(b) ${}^1\text{H}$ NMR spectrum of Zn(II) complex of the ligand L

In the ${}^1\text{H}$ NMR spectra of Zn(II) complex the nine aromatic protons were observed in the region $\delta 6.92\text{--}7.49$ ppm (m, 9H) as a multiplet. The azomethine proton that was resonated at $\delta 8.05$ ppm (s, 1H) in the ligand L, has resonated at $\delta 8.39$ ppm (s, 1H). Proton of the amide NH function which was resonated at $\delta 10.49$ ppm (s, 1H) in ligand appeared at $\delta 10.72$ ppm (s, 1H). Signal due to a proton on vinyl carbon attached to the azomethine carbon atom has resonated as a doublet at $\delta 6.92$ ppm (d, 1H, $\text{N}=\text{CH}-$). Another vinyl proton on carbon atom attached to benzene ring has appeared as doublet at $\delta 7.12$ ppm (d, 1H, $=\text{CH}-\text{Ar}$). When the ${}^1\text{H}$ NMR spectra of the ligand and the complex are compared, it was observed that the signals of the protons of different functionalities of the ligand have been shifted towards the downfield region confirming the coordination of the ligand to the Zn(II) ion.

FAB-mass spectral analysis

FAB-Mass spectrum of ligand L showed M+1 & M+3 peaks at m/z 341, 343 respectively which on loss

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

Compounds/ complexes	Mol wt	Calcd./ (Found)(%)						Magnetic moment μ_{eff} B.M.	Molar conductance(λ_m) ($\text{cm}^2 \text{?}^{-1} \text{mol}^{-1}$)	M.P. °C yield (%)
		M	C	H	N	S	Cl			
$\text{C}_{18}\text{H}_{13}\text{N}_2\text{OCIS}$	340	--	63.50 (63.42)	6.01 (5.99)	8.23 (8.18)	9.41 (7.38)	10.29 (10.39)	--	30	173 (67)
$[\text{Cu}(\text{C}_{18}\text{H}_{13}\text{N}_2\text{OCIS})_2] \cdot \text{Cl}_2 \cdot 2\text{H}_2\text{O}$	851	7.40 (7.42)	50.76 (50.69)	3.52 (3.50)	6.58 (6.54)	7.52 (7.48)	16.68 (16.59)	2.11	32	257 (73)
$[\text{Co}(\text{C}_{18}\text{H}_{13}\text{N}_2\text{OCIS})_2] \cdot \text{Cl}_2 \cdot 2\text{H}_2\text{O}$	847	6.96 (6.90)	51.00 (50.98)	3.54 (3.51)	6.61 (6.58)	7.55 (7.52)	16.76 (16.69)	5.08	35	293 (69)
$[\text{Ni}(\text{C}_{18}\text{H}_{13}\text{N}_2\text{OCIS})_2] \cdot \text{Cl}_2 \cdot 2\text{H}_2\text{O}$	847	6.96 (6.87)	51.00 (50.99)	3.54 (3.57)	6.61 (6.57)	7.55 (7.53)	16.76 (16.72)	2.91	20	298 (71)
$[\text{Zn}(\text{C}_{18}\text{H}_{13}\text{N}_2\text{OCIS})_2] \cdot \text{Cl}_2 \cdot 2\text{H}_2\text{O}$	853	7.62 (7.60)	50.64 (50.61)	3.51 (3.54)	6.56 (6.53)	7.50 (7.46)	16.64 (16.58)	Diamag.	26	296 (74)
$[\text{Cd}(\text{C}_{18}\text{H}_{13}\text{N}_2\text{OCIS})_2] \cdot \text{Cl}_2 \cdot 2\text{H}_2\text{O}$	900	12.44 (12.41)	48.00 (47.94)	3.33 (3.30)	6.22 (6.18)	7.11 (7.09)	15.77 (15.70)	Diamag.	24	289 (65)
$[\text{Hg}(\text{C}_{18}\text{H}_{13}\text{N}_2\text{OCIS})_2] \cdot \text{Cl}_2 \cdot 2\text{H}_2\text{O}$	988	20.24 (20.23)	43.72 (43.67)	3.03 (3.01)	5.66 (5.63)	6.47 (6.44)	14.37 (14.32)	Diamag.	25	286 (75)

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

Compounds/complexes	$\nu(\text{OH})$	$\nu(\text{NH})$	$\nu(\text{C}=\text{O})$	$\nu(\text{C}=\text{N})$	Thiophene Ring vib.	$\nu(\text{M}-\text{O})$	$\nu(\text{M}-\text{N})$	$\nu(\text{M}-\text{Cl})$
$\text{C}_{18}\text{H}_{13}\text{N}_2\text{OCIS}$	--	3214	1642	1583	1514	--	--	--
$[\text{Cu}(\text{C}_{18}\text{H}_{13}\text{N}_2\text{OCIS})_2] \cdot \text{Cl}_2 \cdot 2\text{H}_2\text{O}$	3435	3071	1610	1577	1497	516	415	311
$[\text{Co}(\text{C}_{18}\text{H}_{13}\text{N}_2\text{OCIS})_2] \cdot \text{Cl}_2 \cdot 2\text{H}_2\text{O}$	3412	3209	1617	1568	1499	511	422	315
$[\text{Ni}(\text{C}_{18}\text{H}_{13}\text{N}_2\text{OCIS})_2] \cdot \text{Cl}_2 \cdot 2\text{H}_2\text{O}$	3405	3260	1622	1576	1544	504	417	315
$[\text{Zn}(\text{C}_{18}\text{H}_{13}\text{N}_2\text{OCIS})_2] \cdot \text{Cl}_2 \cdot 2\text{H}_2\text{O}$	3435	3363	1611	1563	1511	488	416	318
$[\text{Cd}(\text{C}_{18}\text{H}_{13}\text{N}_2\text{OCIS})_2] \cdot \text{Cl}_2 \cdot 2\text{H}_2\text{O}$	3363	3157	1612	1564	1511	508	427	320
$[\text{Hg}(\text{C}_{18}\text{H}_{13}\text{N}_2\text{OCIS})_2] \cdot \text{Cl}_2 \cdot 2\text{H}_2\text{O}$	3434	3371	1612	1564	1511	509	409	321

of hydrogen radical gave a molecular ion peak M^+ at m/z 340, 342 (10.8%, 37.5%), which is equivalent to its molecular weight. The molecular ion M^+ by the expulsion of $\text{C}_9\text{H}_9\text{N}_2$ species gave fragment ion A_1 at m/z 195, 197 ($M^+ - \text{C}_9\text{H}_9\text{N}_2 = A_1$, 16.7%, 6.9%). The fragment ion A_1 by the loss of carbon monoxide molecule gave fragment ion A_2 at m/z 167, 169 ($A_1 - \text{CO} = A_2$, 10.6%, 2.7%). Fragment ion A_2 underwent further fragmentation by the loss of chloride radical and gave fragment ion A_3 at m/z 132 ($A_2 - \text{Cl} = A_3$, 5.6%) (Scheme 2). The IR, ^1H NMR and Mass spectral data of the ligand L are in conformity with its structure.

FAB-Mass spectrum of Cu(II) complex showed a molecular ion peak M^+ at m/z 851, 853 (5.6%, 2.8%), which is equivalent to its molecular weight. The molecular ion M^+ by the expulsion of $2\text{H}_2\text{O}$ molecules gave fragment ion A_1 at m/z 815, 817 ($M^+ - 2\text{H}_2\text{O} = A_1$, 10.6%, 2.8%). The fragment ion A_1 by the loss of two C_9H_9 radicals simultaneously gave fragment ion A_2 at m/z 581, 583 ($A_1 - \text{C}_9\text{H}_9 = A_2$, 10.6%, 2.8%) (Scheme 3). The IR, ^1H NMR and Mass spectral data of the

Cu(II) complex is in conformity with its structure.

Magnetic susceptibility data

The magnetic susceptibility measurements of the complexes were performed at room temperature (TABLE 1). In octahedral Co(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 moments. The reported magnetic moment values for various Co(II) complexes are in the range 4.7-5.2 B.M. for octahedral complexes^[24]. In the present investigation the observed magnetic moment value for Co(II) complex is 5.08 B.M. indicates octahedral geometry for the Co(II) complex. For Ni(II) complex the observed magnetic moment is 2.91 B.M. which is well within the expected range for Ni(II) complexes with octahedral stereochemistry 2.83-4.0 B.M.^[25,26]. The present Cu(II) complex has a magnetic moment value 2.11 B.M. The reported values for the mononuclear Cu(II) complexes having no major spin interactions is in the range 1.75-2.20 B.M.^[27,28]. Thus

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TABLE 3 : Powder x-ray diffraction data of the ligand L

Peak	2θ	θ	sinθ	sin ² θ	h k l	Relative intensity (%)	d		h ² +k ² +l ²	a in Å
							Calc.	Obs.		
1	5.69162	2.84581	0.04965	0.00247	100	50.04	15.5146	15.51472	1	15.52
2	7.75203	3.87601	0.0676	0.00457	110	88.54	11.39497	11.39508	2	15.52
3	13.20088	6.60044	0.11495	0.01321	210	19.96	6.70117	6.70130	5	15.52
4	15.58743	7.79371	0.13561	0.01839	---	24.55	5.68026	65.68024	7	15.52
5	17.43713	8.71856	0.15158	0.02298	221	28.89	5.0818	5.08164	9	15.52
6	19.24725	9.62363	0.16717	0.02795	311	17.98	4.60788	4.60762	11	15.52
7	20.28494	10.14247	0.1761	0.03101	320	100.00	4.37422	4.37419	13	15.52
8	24.38225	12.19113	0.21117	0.04459	330	73.80	3.64777	3.64762	18	15.52
9	25.09102	12.54551	0.21567	0.04652	331	41.33	3.57166	3.54616	19	15.52
10	27.72675	13.86338	0.23961	0.05741	---	28.99	3.21481	3.21476	23	15.52
11	31.50587	15.75294	0.27149	0.07371	521	33.47	2.83731	2.83723	30	15.52
12	33.49744	16.74872	0.28817	0.08304	530	35.87	2.67307	2.67296	34	15.52
13	35.06628	17.53314	0.30126	0.09076	610	13.55	2.55693	2.55688	37	15.52
14	40.11582	20.05791	0.34297	0.11763	444	19.66	2.24597	2.24591	48	15.52
15	43.7579	21.87895	0.37265	0.13887	642	22.06	2.06709	2.06705	56	15.52
16	53.86194	26.93097	0.45292	0.20514	911		8.90	1.70074	83	15.52

TABLE 4 : Powder x-ray diffraction data of Cu (II) complex of the ligand L

Peak	2θ	θ	sinθ	sin ² θ	h k l	Relative intensity (%)	d		h ² +k ² +l ²	'a' in Å
							Calc.	Obs.		
1	5.67716	2.83858	0.04982	0.00248	100	100	15.46166	15.55421	1	15.47
2	13.49337	6.74669	0.11748	0.0138	---	25.52	6.55686	6.55669	7	15.47
3	18.25154	9.12577	0.1586	0.02515	310	28.88	4.85687	4.85668	10	15.47
4	21.18097	10.59048	0.18379	0.03378	321	15.04	4.1912	4.19113	14	15.47
5	24.71907	12.35953	0.21405	0.04582	330	30.78	3.59869	3.59867	18	15.47
6	27.78230	13.89115	0.24008	0.05764	---	56.85	3.20851	3.20846	23	15.47
7	29.09720	14.5486	0.2512	0.0631	500	24.92	3.06648	3.06639	25	15.47
8	52.14024	26.07012	0.43947	0.19313	752	24.53	1.75279	1.75274	78	15.47
9	69.29800	34.649	0.56855	0.32325	970	11.78	1.35485	1.35482	130	15.47

the present Cu(II) complex is devoid of any spin interactions with distorted octahedral geometry. The Zn(II), Cd(II) and Hg(II) complexes showed a diamagnetic behavior having a d¹⁰ system which is as expected.

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_{||} > g_⊥ > g_e (g_e = 2.0036-free ion value). The observed g_{||} = 2.36 and g_⊥ = 2.07 values of the Cu(II) complex under the present study followed the same trend g_{||} > g_⊥ > g_e which suggest that

the presence of unpaired electron in d_{x²-y²} orbital giving octahedral geometry^[29]. This is also in agreement with its electronic spectral data for octahedral geometry. The observed G = 5.143 for the complex under present study evidenced the monomeric nature of the complex^[30]. This fact is further supported by the absence of a band corresponding to ΔMs = ±2 transition^[31] in the observed ESR spectrum which is characteristic of monomeric complex.

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)

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

Complex	Stage	Peak temp. TG (°C)	Loss of mass (%)		Probable assignments
			Practical	Theoretical	
[Cu(C ₁₈ H ₁₃ N ₂ OCIS) ₂].Cl ₂ .2H ₂ O	--	--	--	--	Cu(C ₃₆ H ₃₀ Cl ₄ O ₄ N ₄ S ₂)
	I	78	4.13	4.22	↓ -2H ₂ O Cu(C ₃₆ H ₂₆ Cl ₄ O ₂ N ₄ S ₂)
	II	276	3.37	3.43	↓ -N ₂ Cu(C ₃₆ H ₂₆ Cl ₄ O ₂ N ₂ S ₂)
	III	493	62.17	61.80	↓ -C ₂₆ H ₁₆ ClOS ↓ -2HCl Cu(C ₁₀ H ₈ ClON ₂ S) ↓ CuO

complex are chosen for powder XRD study. The XRD data of ligand L and its Cu(II) complex are given in the TABLE 3 and 4 respectively. There are 16 reflections (2θ) between 5.69162 and 53.86194° with maximum at $2\theta = 20.285^\circ$ and $d = 4.37419 \text{ \AA}$ whereas Cu(II) complex consists of 9 reflections with maxima at $2\theta = 5.67716^\circ$ corresponding to the value of $d = 15.55421 \text{ \AA}$. The interplanar spacing (d) has been calculated from the positions of intense peaks using Braggs relation $n\lambda = 2d \sin\theta$ (where $\lambda =$ wavelength of X-ray used $\text{CuK}\alpha = 1.5406 \text{ \AA}$). 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^[32,33]. 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 $\lambda^2/4a^2 = 0.00247$ and 0.00248 respectively. The $h^2+k^2+l^2$ values are given in the TABLE 3 and 4. The presence of forbidden number 7 and 23 in case of the ligand L and Cu(II) complex respectively indicate that they may belong to hexagonal or tetragonal system^[34,35].

Thermal study of [Cu(L)₂(Cl)₂.2H₂O]

The decomposition studies of the compound copper(II) complex has been carried out. In the thermogram of the [Cu(L)₂(Cl)₂.2H₂O], the first stage decomposition represents the weight loss of 2H₂O mol-

ecule at 78°C , with weight loss of 4.13% agreeing well with the theoretical weight loss of 4.22%. The complex further underwent degradation and gave a break at 276°C with a weight loss of 3.37%, which corresponds to the decomposition of the N₂ molecule. This practical weight loss 3.37% is in accordance with theoretical weight loss of 3.43%. The complex further underwent degradation and gave a break at 493°C with a weight loss of 62.17% agreeing well with the theoretical weight loss of 61.80% which corresponds to the decomposition of C₂₆H₁₈OCl₃S molecule. There after the compound showed a gradual decomposition up to 800°C and onwards. The weight of the residue corresponds to copper oxide. The thermal decomposition of [Cu(L)₂(Cl)₂.2H₂O] with probable assignments are given in the TABLE 5.

Antimicrobial activity

Antimicrobial activity was carried out by the cup-plate method^[36]. The ligand L and its Co(II), Ni(II), Cu(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

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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)	
	<i>E. coli</i>	<i>S. aureus</i>	<i>A. niger</i>	<i>C. albicans</i>
C ₁₈ H ₁₃ N ₂ OCIS	13	11	14	16
[Cu(C ₁₈ H ₁₃ N ₂ OCIS) ₂].Cl ₂ .2H ₂ O	15	14	18	17
[Ni(C ₁₈ H ₁₃ N ₂ OCIS) ₂].Cl ₂ .2H ₂ O	14	10	18	19
[Co(C ₁₈ H ₁₃ N ₂ OCIS) ₂].Cl ₂ .2H ₂ O	15	14	20	21
[Zn(C ₁₈ H ₁₃ N ₂ OCIS) ₂].Cl ₂ .2H ₂ O	13	12	15	14
[Cd(C ₁₈ H ₁₃ N ₂ OCIS) ₂].Cl ₂ .2H ₂ O	10	10	16	15
[Hg(C ₁₈ H ₁₃ N ₂ OCIS) ₂].Cl ₂ .2H ₂ O	18	19	16	14
Standard-I (Streptomycin)	20	22	--	--
Standard-II (Grisofulvin)	--	--	24	23
	00	00	00	00
DMF (Control) (Bore size)	08	08	08	08

showed moderate activity with 18 mm and 19 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 concentrations as that of the test compounds. The antifungal activity results of the ligand 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), Ni(II) and Co(II) complexes showed good antifungal activity with 17-21 mm inhibition against both *A. niger* and *Candida albicans* whereas Zn(II), Cd(II) and Hg(II) complexes showed moderate activity against both *A. niger* and *Candida albicans* with 14-16 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 amide-O, azomethine-N. The analytical data of complexes suggested the 1:2 type stoichiometry for all the complexes [ML₂].Cl₂.(H₂O)_n. Ligands as well as its complexes were found to be less active against bacteria *E. coli* and *S. aureus* where as moderately active against fungi

A. niger and *C. albicans*. All the complexes showed enhanced antimicrobial activity compared to their ligand. 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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