Research Article

Synthesis, Characterization, and Antibacterial Activity of Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and Hg(II) Complexes of Schiff's Base Type Ligands Containing Benzofuran Moiety

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Six new complexes of Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and Hg(II) with substituted benzofuran derivatives have been synthesized and characterized by elemental analysis, magnetic moments, conductance measurements, spectral characterization, and so forth. Elemental data coincide with the general formula $MLCl_n$, where L = (E)-7-Methoxy-N1-(2,4,5-trimethoxybenzylidene) benzofuran-2-carbohydrazide (**L1**) or (E)-N1-(2,6-dichloro benzylidene)-7-methoxy benzofuran-2-carbohydrazide (**L2**), of the complexes. The ligands coordinate to the metal ions through the oxygen of the carbonyl group and the nitrogen of the hydrazine group. Electronic spectral data of the complexes suggests the probable geometry is octahedral in nature. All the complexes and ligands were screened for their antibacterial activity. Among them, Co, Ni, and Cu complexes of **L2** showed good activity against all microbes.

1. Introduction

Schiff's bases are the most widely studied chelating ligands in coordination chemistry [1]. They are useful in catalysis in organic synthesis and in medicine as antibiotics, antiallergic, and antitumor agents [2]. Recently metal complexes of Schiff's bases particularly derived from carbonyl compounds based on heterocyclic rings have been the centre of attraction in many areas [3–7]. Among them, benzofuran based fused heterocycles have been of great interest as they are abundant in nature and have wide pharmacological activities [8]. Benzofuran based compounds have been reported to show activities as anti-infective agents, like antifungal [9–12], antiprotozoal, and antitubercular [13–15], and also in the treatment of antiarrhythmic [16] and cardiovascular [17] diseases. According to the literature survey in the recent

years, there has been an increased interest investigation of anti-microbacterial activities on benzofuran derivatives, especially 2-substituted [18] or 2,3-disubstituted benzofurans derivatives [19]. It is due to the presence of benzofuran derivatives in natural compounds. For example, the seed oil of the Egonoki plant, which contains a benzofuran derivative called egonal (Figure 1(a)), is an effective synergist for rotenone and pyrethrum against house flies, mosquitoes, aphides, and many other insects [20]. Similarly, Baker's yeast contains a benzofuran derivative (Figure 1(b)) that acts as an antioxidant preventing hemorrhagic liver necrosis in rats and hemolysis of red cells in Vitamin-E deficient rats [21].

Therefore we thought it is worthwhile to synthesis and characterize the benzofuran based ligands and their transition metal complexes and investigate their antimicrobial properties.

FIGURE 1: Structures of the benzofuran derivatives in (a) Egonoki plant and (b) Baker's yeast.

SCHEME 1: Synthesis of ligands **L1** and **L2**.

As a part of our ongoing study on benzofuran derivatives [6, 7, 22–24], we report herein the synthesis, characterization, and antibacterial activity of (E)-7-Methoxy-N1-(2,4,5-trimethoxy benzylidene) benzofuran-2-carbohydrazide (**L1**) and (E)-N1-(2,6-dichloro benzylidene)-7-methoxy benzofuran-2-carbohydrazide (**L2**) and their metal complexes such as Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and Hg(II) as shown in Scheme 1.

2. Experimental

2,4,5-Trimethoxybenzaldehyde, 2,6-dichlorobenzaldehyde, and 2-hydroxy-3-methoxybenzaldehyde were of reagent grade purchased from Sigma-Aldrich. All other chemicals were of AR grade and used as supplied. The solvents were dried and distilled before use. The starting material, 7-methoxy-1-benzofuran-2-carbohydrazide, was prepared according to the literature method [25].

2.1. Preparation of (E)-7-Methoxy-N1-(2,4,5-trimethoxybenzylidene)benzofuran-2-carbohydrazide (L1**).** To a solution (25 mL) of 7-methoxy-1-benzofuran-2-carbohydrazide (2.5 g, 0.01 mol) dry ethanol (25 mL), a solution of 2,4,5-trimethoxybenzaldehyde (2.378 g, 0.01 mol) in dry ethanol (10 mL) was added. The reaction mixture was refluxed on

a water bath. A light yellow crystalline product formed during 7–8 hrs; the reaction mass was cooled and collected by filtration. The solid was washed several times with hot water (10 mL × 5) and then with diethyl ether (10 mL × 3) and finally dried *in vacuo*. The obtained ligand (**L1**) was recrystallized from dry ethanol. Mol. Formula, C₂₀H₂₀N₂O₆; Mol. Wt. 383.378, M.P. 252°C, Yield: 75%.

2.2. Preparation of (E)-N1-(2,6-Dichlorobenzylidene)-7-methoxybenzofuran-2-carbohydrazide (L2**).** To an ethanolic solution (25 mL) of 7-methoxy-1-benzofuran-2-carbohydrazide (2.5 g, 0.01 mol), 2,6-dichlorobenzaldehyde (2.122 g, 0.01 mol) in dry ethanol (10 mL) was added. The reaction mixture was refluxed on a water bath for 7–8 hrs. A light yellow crystalline solid formed. The reaction mixture was cooled and the solid was collected by filtration. This solid was washed with hot water (2 × 10 mL) and then with diethyl ether and then dried *in vacuo*. A crystalline solid was obtained by recrystallization from ethanol. Mol. Formula, C₁₇H₁₂N₂O₃; Mol. Wt. 363.198, M.P. 130°C, Yield: 80%.

2.3. Preparation of Complexes. Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and Hg(II) complexes, were prepared by mixing calculated quantity of **L1** and **L2** in ethanol and an aqueous solution of the corresponding metal chlorides in 2:1 molar

ratio. The reaction mixture was refluxed on a water bath for 3–4 hrs. The completion of the reaction was monitored by thin layer chromatography. Once the reaction was completed, the solvent was removed approximately 50%, from hot solution. Then the residue was cooled to room temperature. The solid complexes formed were filtered, washed with hot water (10 mL, 4–5 times) and ethyl alcohol (10 mL, 3–4 times), and finally dried in vacuum desiccators over anhydrous CaCl_2 . The formation of the complexes may be represented by the following equations:

3. Physical Measurements

Elemental analyses were carried out using Vario EL CHNS analyzer. Magnetic susceptibility measurements were carried out on a magnetic susceptibility balance (Sherwood scientific, Cambridge, England). Molar conductance measurements were made on an Elico CM-82 conductivity bridge in DMF (10^{-3} M) using a dip-type conductivity cell fitted with a platinum electrode having cell constant 0.1 Scm^{-1} . The ESR spectra of complexes were recorded on a Varian E-122 X-band spectrophotometer at liquid nitrogen temperature in DMSO. The FT-IR spectra of ligands and their complexes were recorded as KBr discs in the range $4000\text{--}350 \text{ cm}^{-1}$ on Shimadzu FT-IR spectrophotometer. ^1H NMR spectra were recorded in DMSO-d_6 on a Bruker 300 MHz spectrophotometer using TMS as an internal standard. The electronic spectra were recorded on an Elico-SL-159 single beam UV-Vis. spectrophotometer in the range of $200\text{--}1100 \text{ nm}$ in N, N-dimethyl formamide (DMF) (10^{-3} M) solution. FAB mass spectra were recorded on a JEOL SX 102/DA-6000 mass spectrophotometer from CDRI Lucknow, 6 KV, and 10 mA using argon as the FAB gas and m-nitro benzyl alcohol as the matrix.

4. Antibacterial Activity

In vitro antibacterial activity of the newly synthesized compounds were investigated against five Gram-positive bacteria species *Staphylococcus aureus*, *Staphylococcus citreus*, *Bacillus polymyx*, *Bacillus cereus*, and *Lactobacillus* and five Gram-negative species *Proteus mirabilis*, *Klebsiella pneumonia*, *E. coli*, *Salmonella typhi*, and *Pseudomonas aeruginosa* by the agar well diffusion method [26, 27]. Nutrient agar (Hi Media, India) was used as the bacteriological medium. The extracts were dissolved in 10% aqueous dimethylsulfoxide (DMSO) to a final concentration of $50 \mu\text{g}/\mu\text{L}$. Pure DMSO was taken as the control. $100 \mu\text{L}$ of inoculums was aseptically introduced on to the surface of sterile agar plates and sterilized cotton swabs were used for even distribution of the inoculums. Wells were prepared in the agar plates using a sterile cork borer of 6.0 mm diameter. $50 \mu\text{L}$ of test and control compound was introduced in the well. The same procedure was used for all the strains. The plates were incubated aerobically at 35°C and examined after 24 hours. The diameter of the zone of inhibition produced by each agent was measured with a ruler.

5. Results and Discussion

5.1. Characterization of Ligands L1 and L2. The ligands **L1** and **L2** are air stable crystalline solids. The analytical data are given in Table 1. The FT-IR spectrum of ligands **L1** and **L2** showed strong bands at 3354 and 3185 cm^{-1} due to $\nu_{\text{asy}}(\text{NH})$ and $\nu_{\text{sy}}(\text{NH})$ stretching vibrations, respectively, of secondary amide. Strong bands observed at 1670 and 1702 cm^{-1} in free ligands are assigned to $\nu(\text{C=O})$ of $-\text{CONH}$ group which matches with the literature reports [22]. Medium to strong intense bands at 1606 and 1596 cm^{-1} in **L1** and **L2** were assigned to $\nu(\text{C=N})$ of the azomethine group [28]. The medium bands at 942 and 958 cm^{-1} were assigned to $\nu(\text{N-N})$ stretching vibrations of hydrazine and $\nu(\text{C-O-C})$ stretching vibrations of furan was observed in the region of $1029\text{--}1125 \text{ cm}^{-1}$ [29, 30]. ^1H NMR spectra of ligands **L1** and **L2** were recorded in DMSO-d_6 . The singlet at δ , $12.00\text{--}12.10 \text{ ppm}$ was assigned to amide proton ($-\text{CONH}-$). The singlet at δ , $8.30\text{--}8.65 \text{ ppm}$ were assigned to azomethine ($-\text{HC=N}-$) proton in both ligands. The aromatic ring protons were appeared as multiplet at δ , $7.0\text{--}7.7 \text{ ppm}$ in the ^1H NMR spectra. The ^1H NMR spectrum of **L1** is shown in Figure 2.

The mass spectrometric studies of **L1** and **L2** were performed. The mass spectra of the ligands showed molecular ion peaks (M^+) at 383 and 363 , respectively, are the corresponding molecular weights of both **L1** and **L2**.

5.2. Characterization of the Metal Complexes. The analytical data (Table 1) of the complexes, **1–6** indicated that all the complexes were of stoichiometry, $[\text{M}(\text{L1/L2})\text{Cl}_n]$, where $\text{M} = \text{Co(II)}$ [**1**], Ni(II) [**2**], Cu(II) [**3**], Zn(II) [**4**], Cd(II) [**5**], and Hg(II) [**6**]. The molar conductivity values of the complexes in DMF (10^{-3} M) are in the range $13.8\text{--}20.3 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ suggested non-electrolytic nature of the complexes [31]. All the complexes are partially or almost insoluble in common organic solvents, but soluble in DMF, DMSO, and pyridine.

TABLE 1: Analytical data of ligands and their metal complexes.

Ligand/complex	Molecular weight	Yield (%)	Colour	M.P °C	Elemental analysis found (cal)			μ_{eff} (BM)	A_M ($\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$)
					C	H	N		
L1 [$\text{C}_{20}\text{H}_{20}\text{O}_6\text{N}_2$]	383.378	75	Yellow	252	62.62 (62.65)	5.2 (5.3)	7.45 (7.306)	—	—
[Cu($\text{C}_{20}\text{H}_{20}\text{O}_6\text{N}_2$)Cl ₂]	517.858	80	Green	244	46.53 (46.39)	3.95 (3.89)	5.98 (5.41)	1.74	18.452
[Co($\text{C}_{20}\text{H}_{20}\text{O}_6\text{N}_2$)Cl ₂]	513.211	78	Dark brown	238	46.95 (46.81)	3.84 (3.93)	5.81 (5.46)	4.68	15.951
[Ni($\text{C}_{20}\text{H}_{20}\text{O}_6\text{N}_2$)Cl ₂]	512.968	72	Light brown	262	46.54 (46.83)	3.68 (3.93)	5.63 (5.46)	2.85	14.274
[Cd($\text{C}_{20}\text{H}_{20}\text{O}_6\text{N}_2$)Cl ₂]	566.689	75	Yellow	>300	42.45 (42.39)	3.68 (3.55)	4.85 (4.94)	—	20.361
[Hg($\text{C}_{20}\text{H}_{20}\text{O}_6\text{N}_2$)Cl ₂]	654.868	75	Light yellow	>300	36.67 (36.68)	3.75 (3.08)	4.58 (4.27)	—	13.853
[Zn($\text{C}_{20}\text{H}_{20}\text{O}_6\text{N}_2$)Cl ₂]	519.67	72	Yellow	265	46.25 (46.23)	3.63 (3.88)	5.52 (5.39)	—	18.593
L2 [$\text{C}_{17}\text{H}_{12}\text{N}_2\text{O}_3$]	363.198	80	Brown	130	56.26 (56.22)	3.43 (3.33)	7.6 (7.7)	—	—
[Cu($\text{C}_{17}\text{H}_{12}\text{N}_2\text{O}_3$)Cl ₂]	497.637	75	Green	>300	41.58 (41.03)	3.56 (3.44)	5.85 (5.63)	1.79	16.653
[Co($\text{C}_{17}\text{H}_{12}\text{N}_2\text{O}_3$)Cl ₂]	493.030	70	Light brown	123	41.65 (41.41)	2.55 (2.45)	5.75 (5.68)	4.87	15.032
[Ni($\text{C}_{17}\text{H}_{12}\text{N}_2\text{O}_3$)Cl ₂]	492.788	73	Light brown	>276	41.57 (41.44)	2.82 (2.45)	5.69 (5.68)	2.92	15.965
[Cd($\text{C}_{17}\text{H}_{12}\text{N}_2\text{O}_3$)Cl ₂]	546.508	72	Yellow	>300	37.46 (37.36)	2.35 (2.21)	5.25 (5.12)	—	19.942
[Hg($\text{C}_{17}\text{H}_{12}\text{N}_2\text{O}_3$)Cl ₂]	634.687	75	Yellow	162	32.25 (32.17)	1.95 (1.91)	4.25 (4.42)	—	14.093
[Zn($\text{C}_{17}\text{H}_{12}\text{N}_2\text{O}_3$)Cl ₂]	499.488	73	Yellow	168	41.08 (40.88)	2.81 (2.42)	5.74 (5.61)	—	19.573

FIGURE 2: ^1H NMR spectrum of the ligand L1.

Room temperature magnetic susceptibility measurements indicated paramagnetic nature for Co, Cu, and Ni complexes. The six-coordinate Co(II) complexes exhibit magnetic moments of 4.68 and 4.87 B.M., suggesting octahedral geometry for Co(II) [32]. Ni(II) complexes showed magnetic moment values of 2.85 and 2.92 B.M., slightly higher than the spin only (2.83 B.M.) value, indicating an octahedral environment around Ni(II) ion [33]. The observed magnetic

moments for Cu(II) complexes are 1.74 and 1.79 B.M., suggesting a distorted octahedral geometry around Cu(II). FT-IR spectra of ligands and their metal complexes are presented in Table 2. The FT-IR stretching frequencies of free ligands were compared with that of their metal complexes. The FT-IR spectrum of ligands showing a strong band at 3354 cm^{-1} and 3185 cm^{-1} , respectively, is due to $\nu_{\text{asy}}(\text{NH})$ and $\nu_{\text{sy}}(\text{NH})$ stretching vibrations of secondary amide. According to

TABLE 2: Important IR spectral bands (cm^{-1}) of ligands and their metal complexes.

Compounds	$\nu(\text{NH})$	$\nu(\text{C}=\text{N})$	$\nu(\text{C}=\text{O})$	$\nu(\text{N}-\text{N})$	$\nu(\text{M}-\text{O})$	$\nu(\text{M}-\text{N})$	$\nu(\text{M}-\text{Cl})\text{t}$	$\nu(\text{M}-\text{Cl})\text{b}$	$\nu(\text{M}-\text{Cl})$
L1 [$\text{C}_{20}\text{H}_{20}\text{O}_6\text{N}_2$]	3264	1606	1696	942	—	—	—	—	—
[$\text{Cu}(\text{C}_{20}\text{H}_{20}\text{O}_6\text{N}_2)\text{Cl}_2$]	3265	1586	1659	961	546	475	354	342	—
[$\text{Co}(\text{C}_{20}\text{H}_{20}\text{O}_6\text{N}_2)\text{Cl}_2$]	3267	1584	1653	978	532	462	372	368	—
[$\text{Ni}(\text{C}_{20}\text{H}_{20}\text{O}_6\text{N}_2)\text{Cl}_2$]	3269	1568	1656	969	567	465	361	372	—
[$\text{Cd}(\text{C}_{20}\text{H}_{20}\text{O}_6\text{N}_2)\text{Cl}_2$]	3265	1578	1650	985	575	463	—	—	345
[$\text{Hg}(\text{C}_{20}\text{H}_{20}\text{O}_6\text{N}_2)\text{Cl}_2$]	3266	1581	1655	968	525	473	—	—	356
[$\text{Zn}(\text{C}_{20}\text{H}_{20}\text{O}_6\text{N}_2)\text{Cl}_2$]	3268	1575	1662	972	549	461	—	—	330
L2 [$\text{C}_{17}\text{H}_{12}\text{N}_2\text{O}_3$]	3267	1596	1702	958	—	—	—	—	—
[$\text{Cu}(\text{C}_{17}\text{H}_{12}\text{N}_2\text{O}_3)\text{Cl}_2$]	3269	1581	1655	974	515	448	358	355	—
[$\text{Co}(\text{C}_{17}\text{H}_{12}\text{N}_2\text{O}_3)\text{Cl}_2$]	3268	1573	1672	968	545	453	375	361	—
[$\text{Ni}(\text{C}_{17}\text{H}_{12}\text{N}_2\text{O}_3)\text{Cl}_2$]	3269	1568	1662	971	562	458	391	368	—
[$\text{Cd}(\text{C}_{17}\text{H}_{12}\text{N}_2\text{O}_3)\text{Cl}_2$]	3269	1582	1669	973	573	425	—	—	347
[$\text{Hg}(\text{C}_{17}\text{H}_{12}\text{N}_2\text{O}_3)\text{Cl}_2$]	3267	1583	1670	965	542	469	—	—	359
[$\text{Zn}(\text{C}_{17}\text{H}_{12}\text{N}_2\text{O}_3)\text{Cl}_2$]	3272	1578	1668	969	564	459	—	—	330

TABLE 3: Electronic spectral bands and ligand field parameters of the Cu(II), Co(II), and Ni(II) complexes in DMF (10^{-3}) solution.

Ligand	Complexes	Transition in cm^{-1}			Dq (cm^{-1})	B (cm^{-1})	β	β (%)	ν_2/ν_1	LFSE (k.cal)
		ν_1^a	ν_2^b	ν_3^b						
L1 [$\text{C}_{20}\text{H}_{20}\text{O}_6\text{N}_2$]	[$\text{Co}(\text{C}_{20}\text{H}_{20}\text{O}_6\text{N}_2)\text{Cl}_2$]	7535	16628	21154	815.14	972.15	0.9606	1.42	2.206	14.88
	[$\text{Ni}(\text{C}_{20}\text{H}_{20}\text{O}_6\text{N}_2)\text{Cl}_2$]	9372	15342	25810	1237.5	869.06	0.6889	12.23	1.6370	31.33
	[$\text{Cu}(\text{C}_{20}\text{H}_{20}\text{O}_6\text{N}_2)\text{Cl}_2$]		16194							
L2 [$\text{C}_{17}\text{H}_{12}\text{N}_2\text{O}_3$]	[$\text{Co}(\text{C}_{17}\text{H}_{12}\text{N}_2\text{O}_3)\text{Cl}_2$]	7340	15902	20752	799.39	975.60	0.9505	1.35	2.1665	14.92
	[$\text{Ni}(\text{C}_{17}\text{H}_{12}\text{N}_2\text{O}_3)\text{Cl}_2$]	9415	15530	25637	1218.05	975.33	0.9513	17.11	1.649	32.11
	[$\text{Cu}(\text{C}_{17}\text{H}_{12}\text{N}_2\text{O}_3)\text{Cl}_2$]		16205							

^aCalculated values. ^bMolar extension coefficient values are given in parenthesis (in units of $\text{L mol}^{-1} \text{cm}^{-1}$).

Halli et al. [23] coordination of NH results in splitting or shifting of bands to lower frequency side or decrease in intensity. In the present study no such changes were observed, instead $\nu(\text{NH})$ bands were observed at higher wave number indicating non-participation of the coordination of NH with metal ion. The shift of about $15\text{--}40 \text{ cm}^{-1}$ of $\nu(\text{C}=\text{O})$ band to lower region in complexes was observed indicating participation of the carbonyl oxygen in coordination [34]. In free ligands at $\nu(\text{C}=\text{N})$ of the azomethine group is observed at 1606 cm^{-1} and 1596 cm^{-1} , which was shifted to lower region by $20\text{--}52 \text{ cm}^{-1}$ which indicated the involvement of the azomethine N in dative bonding with metal ions [35]. The medium bands in ligands due to $\nu(\text{N}-\text{N})$ stretching vibrations are shifted to higher wave number region confirming the involvement of one of the nitrogens of $-\text{N}-\text{N}-$ in bonding with metal ions. The stretching vibration due to $\nu(\text{C}-\text{O}-\text{C})$ of furan remains unaltered in the metal complexes, indicating non-participation of the O-furan ring in bonding with metal ions.

Metal-ligand vibrations are generally observed in the far-IR region and usually give valuable information regarding the bonding of ligands to the metal ions. The weak non-ligand bands observed in the spectrum in the regions $515\text{--}575 \text{ cm}^{-1}$, $425\text{--}475 \text{ cm}^{-1}$, and $376\text{--}410 \text{ cm}^{-1}$ are assigned to $\nu(\text{M}-\text{O})$, $\nu(\text{M}-\text{N})$, and $\nu(\text{M}-\text{Cl})$ stretching vibrations, respectively [36]. The electronic spectra of the Cu(II), Co(II), and Ni(II)

complexes were recorded in DMF (10^{-3} M) solution at room temperature and spectral data are shown in Table 3.

In electronic spectra of Co(II) complexes appeared two absorption bands at 16628 , 21154 cm^{-1} due to **L1** and 15902 , 20752 cm^{-1} due to **L2** respectively. These bands are assigned to $^4\text{T}_{1g}(\text{F}) \rightarrow ^4\text{A}_{2g}(\text{F})(\nu_2)$ and $^4\text{T}_{1g}(\text{F}) \rightarrow ^4\text{T}_{2g}(\text{F})(\nu_3)$ transitions, respectively, in an octahedral environment. The band ν_1 could not be observed; however, ν_1 would be calculated using band fitting procedure [37]. The octahedral geometry is further supported by the values of ligand field parameters such as Racah inter-electronic repulsion parameter (B^1), ligand field splitting energy ($10Dq$), covalency factor (β), and ligand field stabilization energy (LFSE).

The six coordinate Ni(II) complexes exhibit bands at 15342 , 25810 cm^{-1} and 15530 , 25637 cm^{-1} assignable to $^3\text{A}_{2g} \rightarrow ^3\text{T}_{1g}(\text{F})(\nu_2)$ and $^3\text{A}_{2g} \rightarrow ^3\text{T}_{1g}(\text{P})(\nu_3)$ transition, respectively. The high energy band in the region $29000\text{--}30000 \text{ cm}^{-1}$ is assigned to charge transfer in the case of Co(II) and Ni(II) complexes. The octahedral geometry is further supported by ligand field parameters like Dq , B^1 , β , $\beta\%$, ν_2/ν_1 ratio, and LFSE value. The B^1 values for the complexes were lower than the free ion values, which is an indication of the orbital overlap and delocalization of d-orbitals. The β values obtained were less than unity, suggesting a considerable amount of covalency for the metal-ligand bonds. The β value

TABLE 4: ESR-Spectral data of Cu(II) complexes of MBMePC and MBDPC bonding coefficient parameters.

Complex	$g_{\parallel}$	$g_{\perp}$	g_{av}	$A_{\parallel} \times 10^{-4} \text{ (cm}^{-1}\text{)}$	$A_{\perp} \times 10^{-4} \text{ (cm}^{-1}\text{)}$	$A_{av} \times 10^{-4}$	$g_{\parallel}/A_{\parallel}$	G	α^2
$[\text{Cu}(\text{C}_{20}\text{H}_{20}\text{O}_6\text{N}_2)\text{Cl}_2]$	2.4596	2.0623	2.1947	144.19	27.91	66.672	170.57	7.62	0.1225
$[\text{Cu}(\text{C}_{17}\text{H}_{12}\text{O}_3\text{N}_2)\text{Cl}_2]$	2.4675	2.0515	2.1901	147.91	37.67	74.42	166.82	9.45	0.1154

for the Ni(II) complex was less than that of the Co(II) complex, indicating the greater covalency of the M–L bond [24].

For the Co(II) complex the Racah inter-electronic repulsion parameter (B^1) is calculated using the following equation:

$$B^1 = \frac{1}{510} \left[7(\nu_3 - 2\nu_2) + 3\{81\nu_3^2 - 16\nu_2(\nu_2 - \nu_3)\}^{1/2} \right], \quad (2)$$

while for Ni(II) complexes Dq and B are calculated from

$$Dq = \frac{18(\nu_2 + \nu_3) + \sqrt{[18(\nu_2 + \nu_3)]^2 - 4 \times 340 \times \nu_2 \times \nu_3}}{2 \times 340},$$

$$B = \frac{\nu_2 + \nu_3 - 3\nu_1}{15}. \quad (3)$$

The covalency factor (β) was obtained in the following manner:

$$\beta = \frac{B^1}{B}, \text{ (where } B \text{ is free ion value)}. \quad (4)$$

The light green Cu(II) complexes exhibit a single broad asymmetric band in the region $18678\text{--}12345 \text{ cm}^{-1}$. The broadness of the band indicates the three transitions, $^2B_{1g} \rightarrow ^2A_{1g}(\nu_1)$, $^2B_{1g} \rightarrow ^2B_{2g}(\nu_2)$, and $^2B_{1g} \rightarrow ^2E_g(\nu_3)$, which are similar in energy and give rise to only one broad band. The high intensity band observed in the region $33,000\text{--}28,000 \text{ cm}^{-1}$ was assigned to charge transfer [38]. The broadness of the band may be due to dynamic John-Teller distortion. All of these data suggest a distorted octahedral geometry around Cu(II). Typical electronic spectrum of Cu(II) complex of **L1** is shown in the Figure 3.

ESR spectra of the copper (II) complexes were recorded at liquid nitrogen temperature in DMSO. The $g_{\parallel}$ and $g_{\perp}$ values were calculated from the spectrum using the tetracyanoethylene (TCNE) free radical as the “ g ” marker. Typical ESR spectrum of $[\text{Cu}(\text{L1})\text{Cl}_2]$ is given in Figure 4. Neiman and Kivelson [39] have reported that $g_{\parallel}$ is less than 2.3 for covalent character and greater than 2.3 for ionic character of the metal-ligand bond in complexes. As seen in Table 4, $g_{\parallel}$ values for the present complexes are slightly higher than 2.3 suggesting a small amount of ionic character of the metal-ligand bond. The trend $g_{\parallel} > g_{\perp} > 2.0023$ suggests that the unpaired electron lies predominantly in the $d_{x^2-y^2}$ orbital [40] characteristic of square planar or octahedral geometry in copper(II) complexes [41]. The g_{av} value for these complexes is greater than 2 indicating the presence of covalent character [42]. The axial symmetry parameter (G)

FIGURE 3: A typical electronic spectrum of copper complex of **L1**. FIGURE 4: X-Band ESR spectra of $[\text{Cu}(\text{L1})\text{Cl}_2]$ at liquid nitrogen temperature (LNT) in DMSO.

values of the complexes (greater than 4) suggest that there are no interactions between the copper centres in DMSO medium. The empirical factor $f (= g_{\parallel}/A_{\parallel}) \text{ cm}^{-1}$ is a measure of deviation from idealized geometry [43]. Values from 165 to 171 cm^{-1} for the present complexes suggest a moderate to considerable distortion in the geometry.

Based on the analytical data and spectral characterization of the compounds tentative structures of the complexes are shown in Figures 5(a) and 5(b).

6. Antibacterial Activities

Antibacterial activity of substituted benzofuran derivatives and their metal complexes were tested *in vitro* against representative Gram-positive bacteria species like “*Staphylococcus*

TABLE 5: Antibacterial activity of ligands and their metal complexes.

Ligands/complexes	Gram Positive			Gram Negative						
	<i>Staphylococcus aureus</i>	<i>Staphylococcus citreus</i>	<i>Bacillus polymyxa</i>	<i>Bacillus cereus</i>	<i>Lactobacillus</i>	<i>Pseudomonas aeruginosa</i>	<i>Klebsiella pneumonia</i>	<i>Salmonella typhi</i>	<i>E. coli</i>	<i>Proteus mirabilis</i>
L1 (C₂₀H₂₀O₆N₂)	23	20	22	21	21	18	20	22	21	18
[Cu(C ₂₀ H ₂₀ O ₆ N ₂)Cl ₂]	20	15	18	19	16	13	19	17	14	16
[Ni(C ₂₀ H ₂₀ O ₆ N ₂)Cl ₂]	17	15	12	12	12	12	10	12	20	14
[Co(C ₂₀ H ₂₀ O ₆ N ₂)Cl ₂]	18	12	16	10	14	18	12	16	12	15
[Hg(C ₂₀ H ₂₀ O ₆ N ₂)Cl ₂]	08	11	09	10	11	12	07	10	08	08
[Zn(C ₂₀ H ₂₀ O ₆ N ₂)Cl ₂]	16	14	14	14	14	14	16	16	12	16
[Cd(C ₂₀ H ₂₀ O ₆ N ₂)Cl ₂]	12	14	12	07	10	14	12	14	18	12
L2 (C₁₇H₁₂O₃N₂)	24	22	19	25	22	22	24	25	22	20
[Cu(C ₁₇ H ₁₂ O ₃ N ₂)Cl ₂]	20	17	22	19	17	18	15	18	22	18
[Ni(C ₁₇ H ₁₂ O ₃ N ₂)Cl ₂]	18	14	18	14	16	12	18	16	12	14
[Co(C ₁₇ H ₁₂ O ₃ N ₂)Cl ₂]	16	17	14	10	18	15	19	16	20	19
[Hg(C ₁₇ H ₁₂ O ₃ N ₂)Cl ₂]	10	12	11	10	11	08	13	09	13	08
[Cd(C ₁₇ H ₁₂ O ₃ N ₂)Cl ₂]	14	12	13	16	14	14	14	12	11	14
[Zn(C ₁₇ H ₁₂ O ₃ N ₂)Cl ₂]	15	16	14	14	15	15	17	17	13	17
Streptomycin	27	25	24	26	26	24	26	27	23	25

(a) Suggested structure of Co(II), Ni(II) and Cu(II) complexes of Schiff bases

Where M = Zn(II), Cd(II) and Hg(II)

(b) Suggested structure of Zn(II), Cd(II) and Hg(II) complexes of Schiff bases

FIGURE 5

aureus," *Staphylococcus citreus*," *Bacillus polymyx*," *Bacillus cereus*," and *Lactobacillus*" and Gram-negative bacteria species such as "*Proteus mirabilis*," "*Klebsiella pneumonia*," "*E. coli*," "*Salmonella typhi*," and "*Pseudomonas aeruginosa*" by agar well diffusion method. Compounds inhibiting growth of one or both microorganisms were further tested for their minimum inhibitory concentration (MIC) of the compound. Benzofuran ligands are more active against all most all microbes. Among all the complexes [Cu(L2)Cl₂], [Ni(L2)Cl₂], and [Co(L2)Cl₂] complexes showed very good activity against all organisms (MIC = 25 µg/mL), whereas zinc and cadmium complexes are moderately active, but mercury complexes are least active. Least activity of mercury may be due to its toxic nature towards microbes. However,

the synthesized compounds showed relatively higher or lower activity than the standard drug Streptomycin. It may be due to the nature of the metal ion, the nature of the ligand, and orientation of the ligand around the metal ion. The results are summarized in Table 5.

7. Conclusion

Based on stoichiometries and analytical data of the ligands, (E)-7-Methoxy-N1-(2,4,5-trimethoxy benzylidene) benzofuran-2-carbohydrazide (L1) or (E)-N1-(2,6-dichloro benzylidene)-7-methoxy benzofuran-2-carbohydrazide (L2) are neutral, bidentate ligands coordinating through the "O" and "N" of the amide and azomethine group, respectively.

All the complexes possess 1:1 (M:L) stoichiometry based on analytical and spectral data to chloride bridged polymeric octahedral structures of Cu(II), Co(II), and Ni(II) complexes (Figure 5(a)) and monomer/dimeric tetrahedral structures to Zn(II), Cd(II), and Hg(II) complexes (Figure 5(b)). Benzofuran ligands are more active against almost all microbes. Hg complexes are less active; Zn and Cd complexes are moderately active. Cu, Co, and Ni complexes showed very good activity against all bacteria.

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