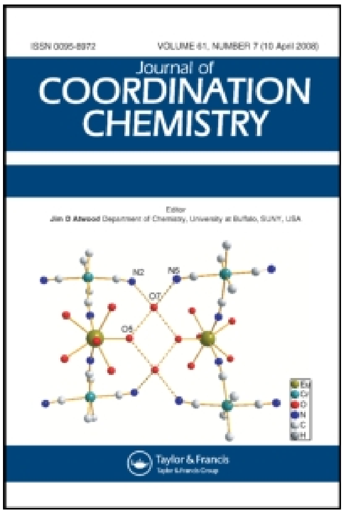

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Synthesis, spectral characterization and biological activity of benzofuran Schiff bases with Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) complexes

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Synthesis, spectral characterization and biological activity of benzofuran Schiff bases with Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) complexes

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New Schiff bases have been synthesized from benzofuran-2-carbohydrazide and benzaldehyde, [BPMC] or 3,4-dimethoxybenzaldehyde, [BDMeOPMC]; complexes of the type MLX_2, where M = Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II), L = BPMC or BDMeOPMC and X = Cl, have been prepared. Structures have been elucidated on the basis of elemental analysis, conductance measurements, magnetic properties, spectral studies i.e., ^{1}H NMR, electronic, ESR and IR studies show that the Schiff bases are bidentate through the azomethine nitrogen and oxygen of the carbonyl. We propose tentative structures for all of these complexes. The antifungal and antibacterial activities of the ligands and their metal complexes have been screened against fungi *Aspergillus niger* and *Aspergillus fumigatus* and against bacteria *Escherichia coli* and *S. aurious*.

Keywords: Benzofuran Schiff bases; Metal complexes; Spectral studies; Biological activity

1. Introduction

Benzofuran compounds are abundant in nature, particularly among plants; often natural products possessing benzofuran have useful pharmacological properties. Benzofuran compounds occur in nature in a variety of structural forms, the seed oil of plant ‘‘Egonoki’’ which contains a benzofuran derivative called ‘‘Egonal,’’ an effective synergist for rotenone pyrethrum against house flies, mosquitoes, aphids and many other insects [1]. Baker’s yeast contains a benzofuran derivative which acts as an antioxidant preventing haemorrhagine liver necrosis in rats and haemolysis of red cells in vitamin E deficiency [2]. Some benzofuran derivatives such as 2-acetylbenzofuran and 2-nitrobenzofuran are well known biodynamic agents possessing various pharmacological properties [3–5]. Schiff bases have wide applications in food industry, dye industry, analytical chemistry, catalysis, fungicidal, agrochemical and biological activities [6–8].

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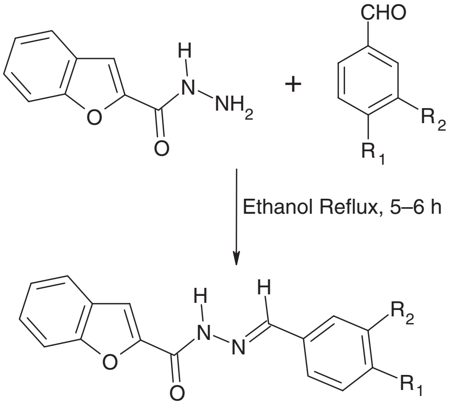
Many hydrazones and their complexes with metals have biological and pharmaceutical activities such as anticancer, antitumor and antioxidative activities as well as inhibition of lipid peroxidation etc. [9–11]. Drugs may possess modified toxicological and pharmacological properties when administered in the form of metal complexes. The most widely studied metal in this respect is copper(II) which proved beneficial in diseases such as tuberculosis, gastric ulcers and rheumatoid arthritis [12–14]. These results encouraged us to investigate coordination chemistry of Schiff-base compounds derived from the reaction between benzofuran-2-carbohydrazide and benzaldehyde [BPMC] or 3,4-dimethoxybenzaldehyde [BDMeOPMC] with transition and d^{10} metal ions such as Co(II), Cu(II), Ni(II), Zn(II), Cd(II) and Hg(II) [15, 16]. Synthesized complexes were characterized on the basis of elemental analyses, molar conductivity, IR, ^{1}H NMR, ESR, electronic spectral studies, and magnetic susceptibility measurements.

2. Experimental

All the chemicals were of analytical grade. Benzofuran-2-carbohydrazide was prepared by the literature method [17]. The metal and chloride contents are determined as per Vogel's procedure [18].

2.1. *Preparation of benzofuran[phenylmethine]carbohydrazone [BPMC] and benzofuran[3,4-dimethoxyphenylmethine]carbohydrazone [BDMeOPMC]*

A solution of benzofuran-2-carbohydrazide (2.2 g, 0.5 mol) in ethanol (25 mL) was added to benzaldehyde (1.4 g, 0.5 mol)/3,4-dimethoxy benzaldehyde (1.9 g, 0.5 mole) in ethanol (10 mL). The reaction mixture was refluxed on a water bath for 4–5 hrs. The Schiff base separated on removal of 50% of the solvent and cooling to room temperature. The light yellowish crystalline solid was filtered, washed with alcohol and crystallized from ethyl alcohol. The reaction is shown in figure 1.



$R_1 = R_2 =$ H, [BPMC]
–OCH_3, [BDMeOPMC]

Figure 1. Synthesis of Schiff bases.

$C_{16}H_{12}O_2N_2$ [BPMC]: Mol. wt. 264, m.p. 215°C, yield 75%
$C_{18}H_{16}O_4N_2$ [BDMeOPMC]: Mol. wt. 324, m.p. 228°C, yield 80%

2.2. *Preparation of complexes*

Metal complexes were prepared by adding (0.1 mol, 20 mL) of aqueous solution of metal(II) chloride to 0.1 mol (1.55/1.78 g) of [BPMC]/[BDMeOPMC] in 30 mL alcohol. The reaction mixture was refluxed on a water bath for 3–4 hrs; removal of 50% of the solvent and cooling to room temperature gave solid colored complexes which were filtered, washed with ethyl alcohol and recrystallized from ethyl alcohol. All the complexes were dried in air and kept in a vacuum desiccator. Formation of complexes may be represented by the following equations.

$$\underset{\text{(L=BPMC/BDMeOPMC)}}{n\,\mathrm{NiCl_2\cdot 6H_2O} + n\mathrm{L}} \xrightarrow[\text{reflux, 3 h}]{\text{ethanol}} [\mathrm{NiLCl_2}]_n + 6\mathrm{H_2O} \tag{1}$$

$$\underset{\text{(L=BPMC/BDMeOPMC)}}{n\,\mathrm{CoCl_2\cdot 6H_2O} + n\mathrm{L}} \xrightarrow[\text{reflux, 3 h}]{\text{ethanol}} [\mathrm{CoLCl_2}]_n + 6\mathrm{H_2O} \tag{2}$$

$$\underset{\text{(L=BPMC/BDMeOPMC)}}{n\,\mathrm{CuCl_2\cdot 2H_2O} + n\mathrm{L}} \xrightarrow[\text{reflux, 3 h}]{\text{ethanol}} [\mathrm{CuLCl_2}]_n + 2\mathrm{H_2O} \tag{3}$$

$$\underset{\text{(L=BPMC/BDMeOPMC, M=Cd, Zn or Hg)}}{\mathrm{MCl_2} + n\mathrm{L}} \xrightarrow[\text{reflux, 3 h}]{\text{ethanol}} [\mathrm{MLCl_2}] \tag{4}$$

2.3. *Physical measurements*

All the complexes were analyzed for metal content by standard procedure [18]. CHN analyses were carried out microanalytically on a Perkin Elmer 240C at the Central Drug Research Institute (CDRI), Lucknow. Chloride was determined as AgCl. Magnetic susceptibility measurements were made at room temperature on a Gouy balance using $Hg[Co(NCS)_4]$ as the calibrant, with diamagnetic corrections made using PASCAL's constants. 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 s cm^{-1}. The ESR spectra of complexes in polycrystalline state (powder) were recorded on a Varian E-4X band spectrophotometer using (TCNE) as "g" marker ($g = 2.0027$) at room temperature. The IR spectra of ligands and their complexes were recorded in KBr discs in the 4000–350 cm^{-1} range on a Perkin Elmer 783 FT-IR spectrophotometer. ^{1}H NMR spectra were recorded in DMSO-d_6 on a Bruker 300 MHz spectrophotometer using TMS as internal standard. The electronic spectra were recorded on an Elico-SL-164 double beam UV-visible spectrophotometer in the 200–1100 nm range in DMF (10^{-3} M) solution. FAB mass spectra were recorded on a JEOL SX 102/DA-6000 mass spectrophotometer from CDRI LUCKNOW, 6 KV, 10 mA using argon as the FAB gas and *m*-nitro benzyl alcohol as the matrix.

2.4. *Biological activities*

All the ligands and complexes were screened for their antibacterial and antifungal activity by agar cup plate zone of inhibition technique [19] against two bacteria *E. Coli* and *S. aurious* and two fungal species *Aspergillus niger* and *Aspergillus fumigatus*.

2.5. *Antibacterial screening using agar cup-plate method*

Peptone 10 g, NaCl 5 g, Beef extract 3 g, Nutrient agar 15 g, was used as the medium.

The sterile molten medium held at 55°C was poured aseptically into sterile petri dishes and allowed to solidify. After solidification, 24 h culture (incubated at 37°C) of each of the bacterial cultures was spread on the agar medium with the help of a glass spreader. Then with a sterile cork borer (8 mm dia.), cups were punched and scooped out from the agar at suitable distances from each other. The cups were filled with 0.1 mL of the test solutions ($10\,\mathrm{mg\,mL^{-1}}$ in DMF); streptomycin ($10\,\mathrm{mg\,mL^{-1}}$) was used as the standard antibiotic and DMF as the control. The plates were incubated upright at 37°C for 24 h before reading the inhibition zones around each cup.

2.6. *Antifungal screening using cup-plate method*

Sabouraud Dextrose Agar (SDA) was used for the screening of test compounds for their antifungal activity. The test compound was screened by the agar cup plate diffusion method using SDA ($10\,\mathrm{mg\,mL^{-1}}$) as the medium against *A. niger* and *A. fumigatus*. The fungal inoculates were prepared in SDA broth and incubated at room temperature for 3 days; the fungal spores were harvested in sterile DW and used as inoculate.

The sterile molten medium held at 55°C was poured aseptically into sterile petri dishes and allowed to solidify. After solidification, 3 days culture (incubated at 37°C) of each of the bacterial cultures was spread on the agar medium with the help of a glass spreader. Then with a sterile cork borer (4 mm dia.), cups were punched and scooped out from the agar at suitable distances from each other. The cups were filled with 0.1 mL of the test solutions ($10\,\mathrm{mg\,mL^{-1}}$ in DMF). Nystatine ($10\,\mathrm{mg\,mL^{-1}}$) was used as the standard fungicidal and DMF as the control. The plates were incubated upright at 37°C for 3 days before reading the inhibition zones around each cup [20, 21].

3. Results and discussion

The physical appearance and analytical results show that all of the complexes have the stoichiometry MLX_2 (table 1). The molar conductance values of the complexes in DMF (10^{-3} M) are in the range 10.6–20.8 $\mathrm{Ohm^{-1}\,cm^2\,mol^{-1}}$ suggesting non electrolytes. All the complexes possess high melting points (decomposition), are stable in air, are partially or insoluble in common organic solvents and soluble in DMF, DMSO and pyridine.

3.1. *Magnetic properties*

Magnetic susceptibility measurements at room temperature exhibit paramagnetism for Co, Cu, and Ni complexes. The six-coordinate Co(II) complexes exhibit magnetic moments of 4.88 and 4.93 B.M. (table 1), suggesting octahedral geometry for Co(II) [22, 23]. The Ni(II) complexes show magnetic moment values of 2.87 and 2.98 B.M., slightly higher than the spin only (2.83 B.M.) value, indicating an octahedral environment around Ni(II) [24]. The observed magnetic moments for the Cu(II) complexes are 1.70 and 1.77 B.M., suggesting a distorted octahedral geometry around Cu(II).

3.2. *Electronic spectral studies*

The electronic spectra of the Cu(II), Co(II) and Ni(II) complexes were taken in DMF (10^{-3} M) solution (table 2). The light green Cu(II) complexes exhibit a single broad asymmetric band in the region 18678–12345 cm^{-1}. The broadness of the band indicates the three transitions, $^2B_{1g} \rightarrow {}^2A_{1g}$ (ν_1), $^2B_{1g} \rightarrow {}^2B_{2g}$ (ν_2) and $^2B_{1g} \rightarrow {}^2E_g$ (ν_3), which are similar in energy and give rise to only one broad band. The high intensity band observed in the region 30 000–28 000 cm^{-1} was assigned to charge transfer. 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).

The six coordinate Ni(II) complexes exhibit bands at 15 267 cm^{-1}, 16 110 and 26 881 cm^{-1}, 25 575 cm^{-1} assignable to $^3A_{2g} \rightarrow {}^3T_{1g}$ (F) (ν_2) and $^3A_{2g} \rightarrow {}^3T_{1g}$ (P) (ν_3) transition, respectively, in an octahedral environment. The lowest band ν_1 (10 Dq) could not be observed due to limited range of the instrument used. However, it is calculated by using an equation suggested by Underhill and Billing [25].

The electronic spectra of Co(II) complexes show bands at 16 949, 16 956, 20 167, and 20 491 cm^{-1} for [BPMC] and [BDMeOPMC], respectively. These two bands are assignable to $^4T_{1g}$ (F) $\rightarrow {}^4A_{2g}$ (F) (ν_2) and $^4T_{1g}$ (F) $\rightarrow {}^4T_{2g}$ (p) (ν_3) transitions, respectively, in an octahedral environment [26]. The ν_1 could not be observed, however, ν_1 would be calculated using band fitting producer [25]. The octahedral geometry [27] is further supported by the values of ligand field parameters such as Racah inter-electronic repulsion parameter (B'), ligand field splitting energy ($10D_q$), covalency factor (β) and ligand field stabilization energy (LFSE) (table 2) [28].

For the Co(II) complex the Racah inter-electronic repulsion parameter (B') is calculated using the following equation,

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

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

$$D_q = \frac{18(\nu_2 + \nu_3) + \sqrt{[18(\nu_2 + \nu_3)]^2 - 4x340x\nu_2\,x\nu_3}}{2x340}$$

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

Table 1. Elemental analysis, molar conductance and magnetic susceptibility data for [BPMC] and [BDMeOPMC] and their metal complexes.

					Elemental analysis (%) found/(calculated)						
Molecular formula	Color	Formula weight	m.p. (°C)	Yield (%)	C	H	N	M	Cl	μ_{eff} (B.M.)	Λ (Ohm^{-1} cm^2 mol^{-1})
$[C_{16}H_{12}O_2N_2]$	Light yellow	264	215	75	72.812 (72.727)	4.330 (4.544)	9.903 (10.606)	–	–	–	–
$[Co(C_{16}H_{12}O_2N_2)Cl_2]_n$	Yellow	394.93	268	70	48.584 (48.616)	3.145 (3.038)	7.056 (7.086)	16.120 (16.078)	18.361 (18.231)	4.88	13.059
$[Ni(C_{16}H_{12}O_2N_2)Cl_2]_n$	Light brown	394.71	>300	75	48.567 (48.643)	3.124 (3.040)	7.102 (7.093)	14.802 (14.874)	18.345 (18.240)	2.87	14.679
$[Cu(C_{16}H_{12}O_2N_2)Cl_2]_n$	Brown	399.50	284	70	48.212 (48.060)	3.161 (3.003)	7.308 (7.008)	15.624 (15.894)	18.106 (18.022)	1.70	20.825
$[Zn(C_{16}H_{12}O_2N_2)Cl_2]$	Yellow	401.38	263	65	47.834 (47.683)	2.902 (2.988)	6.823 (6.975)	16.280 (16.288)	17.861 (17.938)	–	19.825
$[Cd(C_{16}H_{12}O_2N_2)Cl_2]$	Light yellow	448.41	290	65	42.852 (42.817)	2.721 (2.676)	6.356 (6.244)	25.092 (25.068)	16.234 (16.124)	–	20.795
$[Hg(C_{16}H_{12}O_2N_2)Cl_2]$	Light yellow	536.59	>300	75	35.852 (35.781)	2.246 (2.336)	5.349 (5.218)	37.356 (37.386)	13.621 (13.418)	–	12.655
$[C_{18}H_{16}O_4N_2]$	Light yellow	324	228	80	66.000 (66.666)	4.800 (4.938)	8.521 (8.641)	–	–	–	–
$[Co(C_{18}H_{16}O_4N_2)Cl_2]_n$	Yellow	454.93	>300	65	47.689 (47.478)	3.687 (3.517)	6.387 (6.154)	12.857 (12.953)	15.664 (15.824)	4.93	14.725
$[Ni(C_{18}H_{16}O_4N_2)Cl_2]_n$	Light brown	454.71	286	70	47.525 (47.502)	3.698 (3.518)	6.354 (6.154)	12.857 (12.911)	15.748 (15.834)	2.98	17.685
$[Cu(C_{18}H_{16}O_4N_2)Cl_2]_n$	Brown	459.50	294	75	47.087 (47.007)	3.784 (3.482)	6.125 (6.093)	13.755 (13.819)	15.556 (15.669)	1.77	10.635
$[Zn(C_{18}H_{16}O_4N_2)Cl_2]$	Yellow	461.38	280	65	42.568 (42.485)	3.382 (3.147)	6.147 (6.068)	14.269 (14.170)	15.450 (15.605)	–	15.038
$[Cd(C_{18}H_{16}O_4N_2)Cl_2]$	Light yellow	508.41	>300	65	42.568 (42.485)	3.382 (3.47)	5.247 (5.507)	22.325 (22.110)	14.542 (14.161)	–	18.341
$[Hg(C_{18}H_{16}O_4N_2)Cl_2]$	Light yellow	596.59	298	80	36.487 (36.205)	2.254 (2.681)	4.982 (4.693)	33.856 (33.622)	12.354 (12.068)	–	10.918

Table 2. Electronic spectral bands and ligand field parameters of the Cu(II), Co(II) and Ni(II) complexes in DMF (10^{-3} M) solution.

		Transition in cm^{-1}								
Ligand	Complexes	ν_1[a]	$\nu_2(\varepsilon)$[b]	$\nu_3(\varepsilon)$	$D_q\,(\mathrm{cm}^{-1})$	$B'\,(\mathrm{cm}^{-1})$	β	β (%)	ν_2/ν_1	L.F.S.E. (k.cal)
[BPMC]	$[Co(C_{16}H_{12}O_2N_2)Cl_2]_n$	7909	16949 (280)	20167 (440)	904	893	0.9196	8.033	2.1430	15.497
$[C_{16}H_{12}O_2N_2]$	$[Ni(C_{16}H_{12}O_2N_2)Cl_2]_n$	9680	15267 (250)	26881 (580)	968	874	0.8404	15.961	1.5772	33.188
	$[Cu(C_{16}H_{12}O_2N_2)Cl_2]_n$		12345–16393 (320)		1436	–	–	–	–	24.617
[BDMeOPMC]	$[Co(C_{18}H_{16}O_4N_2)Cl_2]_n$	8396	16956 (360)	20491 (480)	856	819	0.8435	15.654	2.0195	14.674
$[C_{18}H_{16}O_4N_2]$	$[Ni(C_{18}H_{16}O_4N_2)Cl_2]_n$	8340	16110 (280)	25575 (520)	834	885	0.8509	14.900	1.9316	28.594
	$[Cu(C_{18}H_{16}O_4N_2)Cl_2]_n$		13513–18678 (350)		1540	–	–	–	–	26.40

[a] Calculated values.

[b] Molar extinction coefficient values are given in parenthesis in units of $\mathrm{L\,mol^{-1}\,cm^{-1}}$.

Table 3. ^{1}H NMR spectral data of [BPMC] and [BDMeOPMC] and their Zn(II) and Cd(II) [chemical shifts in δ(ppm)].

Ligands/Complexes	–CONH–	–N=CH–	Aromatic protons	Methoxy protons
[BPMC]	11.73 (s, 1H)	8.74 (s, 1H)	8.62–6.89 (m, 10H)	–
Zn(II)	11.80 (s, 1H)	8.89 (s, 1H)	8.60–6.90 (m, 10H)	–
Cd(II)	12.24 (s, 1H)	8.94 (s, 1H)	8.70–6.80 (m, 10H)	–
[BDMeOPMC]	11.98 (s, 1H)	8.81 (s, 1H)	7.94–6.89 (m, 8H)	3.84 (s, 6H)
Zn(II)	12.04 (s, 1H)	8.94 (s, 1H)	8.20–6.80 (m, 8H)	3.90 (s, 6H)
Cd(II)	12.00 (s, 1H)	8.96 (s, 1H)	8.40–7.00 (m, 8H)	3.92 (s, 6H)

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

$$\beta = \frac{B'}{B} \text{(where } B \text{ is free ion value)}$$

The B' values for complexes were lower than free ion values (table 2), which is an indication of orbital overlap and delocalization of d-orbitals. The β values obtained are less than unity suggesting a considerable amount of covalent character for the metal-ligand bonds. The β values for Ni(II) complexes are less than the Co(II) complex, indicating more covalency of M–L. The high energy band in the region 29,000–30,000 cm^{-1} is assigned to charge transfer in the case of Co(II) and Ni(II) complexes.

3.3. *^{1}H NMR spectra*

^{1}H NMR spectra of [BPMC] and [BDMeOPMC] and their Zn(II) and Cd(II) complexes were recorded in DMSO-d$_6$. The signals at δ(11.73, 11.98) (s, 1H) are assigned to amide proton (–CONH–) of [BPMC] and [BDMeOPMC] ligands, respectively. The signals at δ(8.74, 8.81) (s, 1H) are assigned to azomethine (N=CH–) groups in both ligands. The signals due to (–CONH–) are downfield in the spectra of Zn(II) and Cd(II) complexes in the region δ(11.80–12.04) (s, 1H), indicating coordination of oxygen of '–CONH–' with metal ions. The azomethine proton shifts downfield in the region δ(8.89–8.94) (s, 1H) supporting coordination of 'N' of the –N=CH– group with the metal ions. The aromatic protons at δ(8.62–6.89) shift downfield in the complexes. Thus, ^{1}H NMR spectral observations supplement the assigned geometry.

3.4. *Mass spectral studies*

The FAB mass spectrum of the Co(II) complex of BPMC is recorded at room temperature by using *m*-nitro benzyl alcohol as the matrix. The complex has a molecular ion peak at *m*/*z* 393, which is a proton less than the molecular weight of the metal complex; this is confirmed with the presence of chloride cluster. The metal along with the halogen eliminated the molecular ion peak of the ligand at *m*/*z*, 263, a proton less. This species lost benzyl to give a fragment ion at *m*/*z*, 176, which on further loss of N$_2$ along with CO radical gave a fragment corresponding to *m*/*z*, 119. This fragmentation pattern is in agreement with the structure.

The FAB mass spectrum of the Ni complex of BDMeOPMC is also recorded using NBA as the matrix. The molecular ion of the complex could not be identified; however, the ion due to BDMeOPMC was recorded at *m*/*z*, 326, with two mass units more. This on loss of two CH_2 radicals yielded an ion at *m*/*z*, 297. The corresponding di-ion peak was observed as expected at *m*/*z*, 149, which on further loss of benzyl radical gave a fragment ion at *m*/*z*, 177. Further elimination of N_2CO radical gave fragment ion peak at *m*/*z*, 120. This fragmentation is consistent with the assigned structure.

3.5. *IR spectra*

The main stretching frequencies of the IR spectra of the ligands and their complexes are presented in table 4. These bands give valuable information regarding bonding modes of ligands to metal ions in the complexes. The IR spectrum of the free ligand was compared with the spectra of the metal complexes. The IR spectrum of [BPMC] and [BDMeOPMC] show strong bands at 3150 cm^{-1} and 3262 cm^{-1} assigned to ν(NH). The shifting of these bands to higher wavenumber in the complexes by 8–14 cm^{-1} indicates non-involvement of 'N' of the hydrazine residue in bonding [29].

The strong bands observed at 1702 cm^{-1} and 1617 cm^{-1} in free ligands are assigned to ν(C=O) of CONH group [30]. These bands shift to lower wavenumber in all the complexes by about 90–30 cm^{-1}, indicating participation of the carbonyl oxygen in coordination [31]. Medium to strong intensity bands at 1607 cm^{-1} and 1574 cm^{-1} in the free ligands are assigned to ν(C=N) of the azomethine group based on earlier reports [32]. This ν(C=N) shift to lower wavenumber in all the complexes by about 20–52 cm^{-1} indicates involvement of the azomethine nitrogen in bonding [33]. The medium bands at 989 and 982 cm^{-1} are assigned to ν(N–N) stretching vibrations of hydrazine. These bands in the complexes shift slightly to higher wavenumber confirming involvement of one nitrogen of ν(N–N). Many workers [34, 35] have reported ν(C–O–C) stretching vibrations of furan in the region 1020–1250 cm^{-1}. In the present case, the ν(C–O–C) stretch is in the region 1100–1220 cm^{-1}, remaining unaltered in the metal complexes, indicating non-participation of the furan ring oxygen atom in bonding with metal. 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 complexes in the regions 546–516 cm^{-1} and 475–448 cm^{-1} are assigned to ν(M–O) and ν(M–N) stretching vibrations, respectively [36].

For polymeric complexes where both terminal and bridging metal-halogen linkages are present, ν(M–Cl) for terminal halide is observed at higher wavenumber than for bridging halide [37, 38]. In the present study we assign the broad and weak intensity non-ligand bands to ν(M–Cl) in the region 353–390 cm^{-1} and ν(M–Cl) bridging in the region 302–360 cm^{-1} in the case of Co(II), Ni(II) and Cu(II) complexes in support of their chloride bridged polymeric structures. Medium intensity bands in the region 324–365 cm^{-1} are assigned to ν(M–Cl) in Zn(II), Cd(II) and Hg(II) complexes.

Table 4. Important IR spectral bands (cm^{-1}) for [BPMC] and [BDMeOPMC] and their metal complexes.

Compound	ν(NH)	ν(C=O)	ν(C=N)	ν(N–N)	ν(M–O)	ν(M–N)	ν(M–Cl)t	ν(M–Cl)b	ν(M–Cl)
$[C_{16}H_{12}O_2N_2]$	3150	1702	1607	989	–	–	–	–	–
$[Co(C_{16}H_{12}O_2N_2)Cl_2]_n$	3159	1611	1541	990	541	475	372	352	–
$[Ni(C_{16}H_{12}O_2N_2)Cl_2]_n$	3158	1625	1575	1001	516	448	360	348	–
$[Cu(C_{16}H_{12}O_2N_2)Cl_2]_n$	3163	1611	1546	998	533	460	353	302	–
$[Zn(C_{16}H_{12}O_2N_2)Cl_2]$	3159	1612	1555	990	546	461	–	–	340
$[Cd(C_{16}H_{12}O_2N_2)Cl_2]$	3159	1614	1542	998	529	456	–	–	365
$[Hg(C_{16}H_{12}O_2N_2)Cl_2]$	3163	1623	1560	996	521	462	–	–	324
$[C_{18}H_{16}O_4N_2]$	3262	1617	1574	982	–	–	–	–	–
$[Co(C_{18}H_{16}O_4N_2)Cl_2]_n$	3271	1583	1552	990	519	470	378	360	–
$[Ni(C_{18}H_{16}O_4N_2)Cl_2]_n$	3270	1570	1553	998	519	459	390	352	–
$[Cu(C_{18}H_{16}O_4N_2)Cl_2]_n$	3274	1587	1554	985	533	470	353	309	–
$[Zn(C_{18}H_{16}O_4N_2)Cl_2]$	3276	1574	1550	988	542	469	–	–	345
$[Cd(C_{18}H_{16}O_4N_2)Cl_2]$	3270	1567	1548	995	536	456	–	–	358
$[Hg(C_{18}H_{16}O_4N_2)Cl_2]$	3275	1582	1544	990	516	451	–	–	329

3.6. *ESR spectra*

ESR spectra of powdered (polycrystalline state) samples of $[Cu(C_{16}H_{12}O_2N_2)Cl_2]$ and $[Cu(C_{18}H_{16}H_{16}O_4N_2)Cl_2]$ were recorded at room temperature. The spectra have asymmetric bands (table 5) with $g_{\|} > g_{\perp} > 2.00277$ observed, indicating the unpaired electrons lie predominantly in the $d_{x^2-y^2}$ orbital with possibly some mixing of d_{z^2} because of low symmetry [39].

The ESR parameters g_{iso}, $A_{\|}$, $A_{\perp}$ and $A_{\mathrm{a}\nu}$ were calculated and the energies of d–d transition used to evaluate bonding parameters. The axial symmetry parameter 'G' is defined as $G = (g_{\|} - 2.00277)/(g_{\perp} - 2.00277)$ as a measure of the exchange interaction between copper centers [40]. The molecular-orbital coefficient parameters, α^2, a measure of the covalency of the in-plane σ bonding between the 3d and ligand orbitals and β^2, the covalency in plane π-bonding, were calculated employing the equations,

$$\alpha^2 = -\left(\frac{\mathrm{A}_{\|}}{0.036}\right) + (g_{\|} - 2.00277) + \frac{3}{7}(g_{\perp} - 2.00277) + 0.04$$

$$\beta^2 = \frac{(g_{\|} - 2.00277)\mathrm{E}}{-8\lambda\alpha^2}$$

where $\alpha = -828\,\mathrm{cm}^{-1}$ for free Cu(II) and E is the electronic transition energy. Lower values of α^2 compared to β^2 indicate that the σ-bonding in plane is more covalent than the in-plane π bonding. These data are in good agreement with reported data [41, 42]. The α^2 values 0.612 and 0.693 in $[Cu(BPMC)Cl_2]_n$ and $[Cu(BDMeOPMC)Cl_2]_n$ indicate existence of slight ionic character for the metal ligand σ bonding where the β^2 values 0.832 and 0.781 indicate considerable metal ligand π-bonding in the plane. The orbital reduction parameters $K_{\perp}$, $K_{\|}$ and degree of covalency K_0^2 are compiled in table 5. Hathway [43] pointed out that for pure σ bonding $K_{\|} \approx K_{\perp} \approx 0.77$ and for

Table 5. ESR-spectral data of Cu(II) complexes of BPMC and BDMeOPMC and bonding coefficient parameters.

Complex	$g_{\parallel}$	$g_{\perp}$	g_{av}	g_{iso}	$A_{\parallel} \times 10^{-4}\,cm^{-1}$	$A_{\perp} \times 10^{-4}\,cm^{-1}$	$A_{av} \times 10^{-4}\,cm^{-1}$	G	$K_{\parallel}$	$K_{\perp}$	α^2	β^2	K_0^2
$[Cu(BPMC)Cl_2]_n$	2.2841	2.1026	2.2267	2.3356	172.67	26.07	82.70	2.818	0.610	0.866	0.612	0.832	0.735
$[Cu(BDMeoPMC)Cl_2]_n$	2.2912	2.0903	2.1903	2.2859	166.41	19.75	95.30	3.295	0.670	0.815	0.693	0.781	0.696

Table 6. Antimicrobial activity results of ligands and their metal complexes.

	Zone of inhibition (mm)			
	Bacteria		Fungi	
Ligands/complexes	*E. coli*	*S. aurious*	*A. niger*	*A. fumigatus*
BPMC	12	12	15	13
$[Cu(BPMC)Cl_2]_n$	10	16	14	15
$[Co(BPMC)Cl_2]_n$	12	11	11	13
$[Ni(BPMC)Cl_2]_n$	11	14	13	14
$[Zn(BPMC)Cl_2]$	10	12	12	10
$[Cd(BPMC)Cl_2]$	12	11	12	13
BDMeOPMC	13	11	17	10
$[Cu(BDMeOPMC)Cl_2]_n$	11	14	12	13
$[Co(BDMeOPMC)Cl_2]_n$	11	11	17	10
$[Ni(BDMeOPMC)Cl_2]_n$	10	11	13	13
$[Zn(BDMeOPMC)Cl_2]$	11	12	13	12
$[Cd(BDMeOPMC)Cl_2]$	11	11	14	14
Streptomycin	22	20	–	–
Nystatine	–	–	21	20
Control (DMF)	08	08	04	04

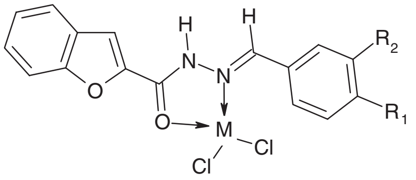
in-plane π bonding $K_\perp > K_\parallel$, while for out-of-plane $K_\parallel > K_\perp$. In all the complexes $K_\perp > K_\parallel$, indicating significant in-plane π bonding in the present complexes.

3.7. *Biological activities*

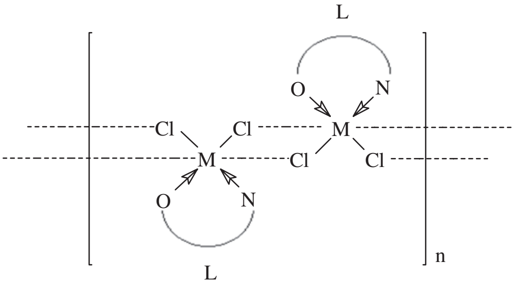
From table 6, it is clear that Co(II) and Cd(II) complexes of [BPMC] are moderately active toward *E. Coli*, whereas Cu(II), Zn(II) and Ni(II) complexes of [BPMC] and Cu(II) and Zn(II) complexes of [BDMeOPMC] are more active against *S. aurious* as compared to free ligands. None of the complexes are active against *A. niger*, but in the case of *A. fumigatus*, Cu(II), Co(II), Ni(II) and Cd(II) complexes of [BPMC] and Cu(II), Ni(II), Zn(II) and Cd(II) complexes of [BDMeOPMC] are more active than the parent ligands [44, 45]. The results of antibacterial and antifungal activity (table 6) reveal that some complexes have good activity compared to free ligands.

4. Conclusion

Based on stoichiometries and spectro-chemical studies the ligands [BPMC] and [BDMeOPMC] are neutral bidentate, coordinating through the amide "O" and "N" of the azomethine group. All the complexes possess 1 : 1 (M : L) stoichiometry and we suggest chloride-bridged polymeric octahedral structures based on high melting points, insolubility in common organic solvents, analytical and spectral data to Cu(II), Co(II) and Ni(II) complexes and monomeric/dimeric tetrahedral structures to Zn(II), Cd(II) and Hg(II) complexes (figure 2).



$R_1 = R_2 = H$ or $-OCH_3$
M = Zn, Cd or Hg



L = [BPMC] or [BDMeOPMC]
M = Co, Cu or Ni

Figure 2. Suggested structures of the complexes.

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References

[1] H. Mastubara. *Botyk Kogaku*, **19**, 15 (1954).
[2] M. Forbes, F. Zilliikan, G. Robert, P. Gyorgy. *J. Am. Chem. Soc.*, **80**, 385 (1985).
[3] A.H. Rahama, E.M. Khandel. *J. Indian Chem. Soc.*, **58**, 404 (1981).
[4] R.A. Scherrer. *US Patent*, **3**, 37, 927 (1975).
[5] S.B. Kadin. *J. Med. Chem.*, **15**, 551 (1972).
[6] S. Gaur. *Asian J. Chem.*, **15**(1), 250 (2003).
[7] M.J. Geni, C. Biles, B.J. Keiser, S.M. Poppe, S.M. Swaney, W.G. Tarapley, D.L. Romeso, Y. Yage. *J. Med. Chem.*, **43**(5), 1034 (2000).
[8] R. Uma, M. Palanindavar, R.J. Butcher. *J. Chem. Soc., Dalton Trans.*, 2061 (1996).
[9] L.F. Wang, Y. Zhu, Z.Y. Yang, J.G. Wu, Q. Wang. *Polyhedron*, **10**, 2477 (1991).
[10] J.G. Wu, R.W. Deng, Z.N. Chen. *Transition Met. Chem.*, **18**, 23 (1993).
[11] Z.Y. Yang. *Synth. React. Inorg. Met.-Org. Chem.*, **30**, 1265 (2000).
[12] D.R. Williams. *The Metals of Life*, Van Nostrand Reinhold, London (1971).
[13] J.R.J. Sorenson. *J. Med. Chem.*, **19**, 135 (1976).
[14] D.H. Brown, W.E. Smith, J.W. Teape. *J. Med. Chem.*, **23**, 729 (1980).
[15] A. Bravo, J.R. Anacona. *J. Coord. Chem.*, **44**, 173 (1988).
[16] J.R. Anacona, E.M. Figueroa. *J. Coord. Chem.*, **48**, 181 (1999).

[17] Y. Kawas, M. Nakayma, P. Tamatskuri. *Bull. Chem. Soc.* (*Japan*), **35**, 149 (1962); *Chem. Abstr.*, **57**, 2204 (1962).

[18] A.I. Vogel. *A Text Book of Quantitative Inorganic Analysis*, 3rd Edn, Longman ELBS, London (1968).

[19] C.H. Collins, P.M. Cyne. *Microbiological Methods*, 4th Edn, Butterworth, London (1976).

[20] K.M. Mahadevan, V.P. Vaidya. *J. Indian Council Chem.*, **18**(2), 78 (2001).

[21] S.P. Tripati, R. Kumar, G.K. Chaturvedi, R.C. Sharma. *J. Indian Chem. Soc.*, **61**, 847 (1984).

[22] B.N. Figgis, J. Lewis. In *Progress in Inorganic Chemistry*, F.A. Cotton (Ed.), Interscience, New York (1964).

[23] B.P. Baranwal, T. Gupta. *Synth. React. Inorg. Met.-Org. Chem.*, **34**(10), 1737 (2004).

[24] N.N. Jha, I. Prasad Ray. *Asian J. Chem.*, **12**, 703 (2000).

[25] A.E. Underhill, D.E. Billing. *Nature*, **210**, 834 (1966).

[26] H. Temel. *J. Coord. Chem.*, **57**(a), 723 (2004).

[27] A.P. Mishra, S.K. Gsutams. *J. Indian Chem. Soc.*, **81**, 324 (2004).

[28] D.N. Sathyanarayana. *Electronic Absorption Spectroscopy and Related Techniques*, Universities Press India Limited, New Delhi (2001).

[29] L.J. Bellamy. *Infrared Spectra of Complex Molecules*, 2nd Edn, Mathuen, London (1958).

[30] D.H. Sutaria, J.R. Patel, M.N. Patel. *J. Indian Chem. Soc.*, **73**(7), 309 (1996).

[31] C.N.R. Rao, R. Venkatraghavan. *Spectrochim. Acta.*, **18**, 541 (1962).

[32] H.H. Reddy, P.S. Reddy. *J. Indian Chem. Soc.*, **79**, 132 (2002).

[33] Z.Y. Yang. *Synth. React., Inorg. Met.-Org. Chem.*, **32**, 903 (2002).

[34] B. Singh, P. Shahi, P.K. Singh. *Indian J. Chem.*, **35A**, 494 (1996).

[35] I.S. Ahuja, R. Singh. *J. Indian Chem. Soc.*, **78**, 39 (2001).

[36] K. Nakamoto. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th Edn, John Wiley and Sons, New York (1986).

[37] A.C. Hiremath, K.M. Reddy, K.M. Patel, M.B. Halli. *Proc. Natl. Acad. Sci. India*, **63A**(11), 341 (1993).

[38] D.N. Sathyanarayana. *Vibrational Spectroscopy*, pp. 406–408, New Age International Pub., New Delhi (2004).

[39] D. Kivelson, R. Neiman. *J. Chem. Phys.*, **35**, 149 (1961).

[40] B. Prabhakar, K. Laxma Reddy, P. Lignhaih. *Proc. Indian Acad. Sci.*, **101**(2), 121 (1989).

[41] P. Bindu, M.R. Prathachandra Kurup, T.R. Stayakerty. *Polyhedron*, **18**, 321 (1999).

[42] B.J. Hathway. *Struct. Bonding (Berlin)*, **57**, 55 (1984).

[43] B.J. Hathway. *Structure and Bonding*, Vol. 14, pp. 60–80, Springer-Verlag, Heidelberg (1973).

[44] J.A. Bakir, Jeragh, A. El-Dissouky. *J. Coord. Chem.*, **58**(12), 1029 (2005).