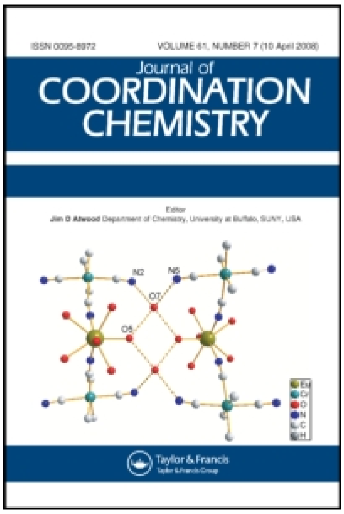

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Phenoxo-bridged symmetrical homobinuclear complexes derived from an "end-off" compartmental ligand, 2,6-*bis*[5′-chloro-3′-phenyl-*1H*-indole-2′-carboxamidyliminomethyl]-4-methylphenol

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A compartment ligand 2,6-*bis*[5′-chloro-3′-phenyl-*1H*-indole-2′-carboxamidyliminomethyl]-4-methylphenol was prepared and homobinuclear phenol-bridged Cu(II), Ni(II), Co(II), Zn(II), Cd(II), Hg(II), Fe(III), and Mn(II) complexes have been prepared by the template method using the precursors 2,6-diformyl-4-methylphenol, 5-chloro-3-phenylindole-2-carbohydrazide and metal chlorides in 1 : 2 : 2 ratio, respectively. The complexes were characterized by elemental analyses, conductivity measurements, magnetic susceptibility data, IR, NMR, FAB mass and ESR spectra, TGA, and powder XRD data. Cu(II), Co(II), Zn(II), Cd(II) and Hg(II) complexes exhibit square pyramidal geometry whereas Ni(II), Mn(II), and Fe(III) complexes are octahedral. Low magnetic moment values for Cu(II), Ni(II), Co(II), Fe(III), and Mn(II) complexes show antiferromagnetic spin-exchange interaction between two metal centers in binuclear complexes. The ligand and its complexes were tested for antibacterial activity against *Escherichia coli* and *Staphyloccocus aureus*, and antifungal activity against *Aspergillus niger* and *Candida albicans*.

Keywords: Binuclear complexes; "End-off" compartmental ligand; Phenoxo-bridged complexes

1. Introduction

Binuclear metal complexes have interest because of their unique physico-chemical properties, have contributed information on oxygen transport and activation by metalloenzymes such as heamocyanin (Cu_2) and cytochrome-C-oxidase (CuFe) [1], and have industrial catalytic applications [2]. Binuclear cores bridged by oxygen (oxo-, hydroxo-, or water) and one or two carboxylate groups are widely known in biosites such as herimeritryne [3], ribonucleotide reductase [4], and phospholipase C [5]; binuclear Zn(II) cores are often seen in biological systems, such as phosphotases [6] and aminopeptidases [7]. The utility of various cyclic and acyclic compartmental ligands in synthesis of mono-, di-, and poly-nuclear complexes has been recently reviewed for the role of bridging group in the metal–metal interaction and also in redox

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reactions [8]. Magnetic properties of homo- and hetero-binuclear complexes have significantly helped advance our understanding of spin-exchange mechanisms, relating them to geometries, ground-state electronic configurations of the constituting metal ions, and nature of the bridging groups [9]. The importance of binuclear complexes in bioinorganic chemistry is as synthetic analogs for bimetallic cores in metalloproteins [10–12]. The μ-phenoxodi(μ-carboxylato)dimanganese(II) [12] and μ-phenoxodi (μ-carboxylato)dizinc(II) [13] complexes of "end-off" ligands were investigated as the functional models of Mn-catalase and phosphatase. Urea adducts of binuclear nickel complexes derived from "end-off" ligands have relevance to urease-urea interaction and conversion of urea into cyanate [14, 15].

A literature survey revealed that most research has concentrated on synthesis and characterization of transition metal complexes using aliphatic diamines [16]. In the present study, an acyclic dinucleating ligand containing indole, 2,6-*bis*[5′-chloro-3′-phenyl-1H-indole-2′-carboxamidyliminomethyl]-4-methylphenol (HL) has been synthesized as a functional model containing a heterocyclic moiety and a bridging phenoxo, with a bimetallic core. We report synthesis, characterization, and antimicrobial activity of HL and its Cu(II), Ni(II), Co(II), Zn(II), Cd(II), Hg(II), Mn(II), and Fe(III) complexes.

2. Results and discussion

The analytical data of the synthesized ligand and its Cu(II), Ni(II), Co(II), Zn(II), Cd(II), Hg(II), Mn(II), and Fe(III) complexes are given in table 1. All complexes were binuclear with formula $[M_2(L)(\mu\text{-Cl})Cl_n(H_2O)n]\cdot nH_2O$. The molar conductance of the complexes measured in DMF at 10^{-3} M concentrations are low (table 1), indicating that the chlorides are inside the coordination sphere of the complexes. The molecular structures are given in figure 1.

2.1. *IR spectra*

The important IR frequencies exhibited by HL and complexes are given in table 2 along with their assignments. In the IR spectra of the complexes, medium intensity sharp bands at 3300–3202 and 3072–3045 cm^{-1} were due to indole–NH and amide-NH stretching vibrations, respectively, at about the same region in all the complexes as for HL (3274 and 3050 cm^{-1}), indicating non-involvement of indole-NH and amide-NH in coordination. A broad band at 3440 cm^{-1} of free ligand assigned to ν(OH) vibrations [17] was absent in all the complexes suggesting phenolic oxygen coordinating with metal ions via deprotonation [18, 19]. A sharp band at 1661 cm^{-1} of HL due to C=O shifted to lower frequency by 4–75 cm^{-1} to 1657–1586 cm^{-1}, indicating coordination with the metal ions, without enolization. The absorption band at 1631 cm^{-1} for HL due to azomethine ν(C=N) [20] shows a negative shift of 15–103 cm^{-1} (1616–1528 cm^{-1}) suggesting coordination of oxygen and nitrogen of the carbonyl and azomethine. In all complexes except Co(II), Fe(III), and Hg(II), broad absorption bands in the region 3451–3406 cm^{-1} are assigned to ν(OH) of H_2O.

Table 1. Analytical, magnetic susceptibility and molar conductance data of HL and its complexes.

Compound	Mol. Wt.	Calcd/(found) (%) M	C	H	N	Cl	Magnetic moment μ_{eff} (BM)	λ_m ($cm^2\ \Omega^{-1}\ mol^{-1}$)	m.p./yield (°C)/(%)
$C_{39}H_{28}N_6O_3Cl_2$	699.58	–	66.96 (66.01)	4.03 (3.76)	12.01 (11.40)	10.14 (10.02)	–	–	285/88
$[Cu_2(L)(\mu\text{-}Cl)Cl_2]\cdot 2H_2O$ $Cu_2(C_{39}H_{31}N_6O_5Cl_5)$	968.06	13.13 (13.01)	48.39 (48.20)	3.23 (3.19)	8.68 (8.52)	18.31 (18.22)	1.49	51	275^b/77
$[Ni_2(L)(\mu\text{-}Cl)Cl_2(H_2O)_2]$ $Ni_2(C_{39}H_{31}N_6O_5Cl_5)$	958.35	12.25 (12.15)	48.88 (48.74)	3.26 (3.21)	8.77 (8.62)	18.50 (18.41)	2.65	57	>320^b/72
$[Co_2(L)(\mu\text{-}Cl)Cl_2]$ $Co_2(C_{39}H_{27}N_6O_3Cl_5)$	922.80	12.77 (12.65)	50.76 (50.62)	2.95 (2.91)	9.11 (9.04)	19.21 (19.14)	4.33	61	>330/69
$[Zn_2(L)(\mu\text{-}Cl)Cl_2]$ $Zn_2(C_{39}H_{27}N_6O_3Cl_5)$	935.75	13.98 (13.88)	50.06 (49.07)	2.91 (2.88)	8.98 (8.91)	18.94 (18.85)	^{a}Dia.	55	300^b/68
$[Cd_2(L)(\mu\text{-}Cl)Cl_2]\cdot 2H_2O$ $Cd_2(C_{39}H_{31}N_6O_5Cl_5$	1065.79	21.09 (21.00)	43.95 (43.85)	2.93 (2.89)	7.89 (7.81)	16.63 (16.53)	^{a}Dia.	56	295/75
$[Hg_2(L)(\mu\text{-}Cl)Cl_2]$ $Hg_2(C_{39}H_{27}N_6O_3Cl_5)$	1206.12	33.26 (33.16)	38.84 (38.76)	2.26 (2.21)	6.97 (6.90)	14.70 (14.62)	^{a}Dia.	49	285/68
$[Mn_2(L)(\mu Cl)Cl_2(H_2O)_2]$ $Mn_2(C_{39}H_{31}N_6O_5Cl_5)$	950.84	11.56 (11.48)	49.26 (49.18)	3.29 (3.26)	8.84 (8.78)	18.64 (18.57)	5.68	61	>330/69
$[Fe_2(L)(\mu\text{-}Cl)Cl_4]$ $Fe_2(C_{39}H_{29}N_6O_4Cl_7)$	1005.55	11.11 (11.00)	46.58 (46.51)	2.91 (2.88)	8.36 (8.26)	24.68 (24.57)	5.72	60	300/78

Notes: ^{a}Diamagnetic.
^{b}Melted with decomposition.

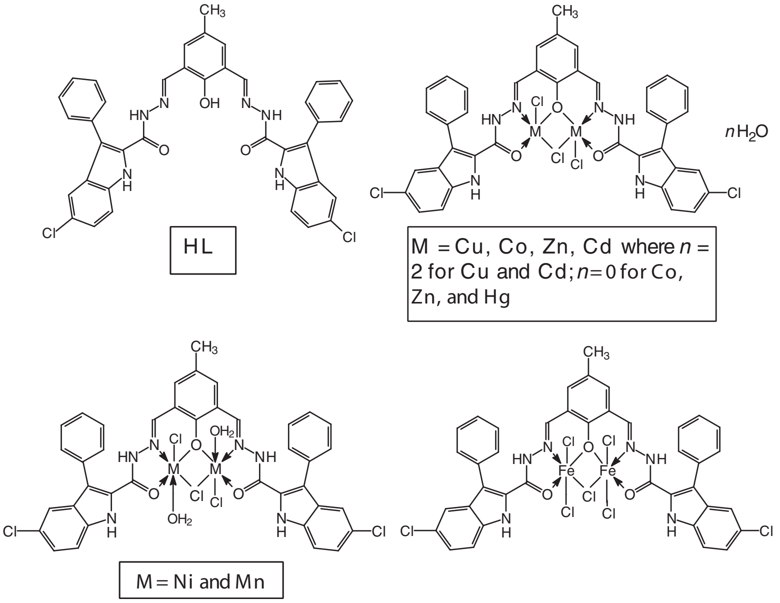

Figure 1. Molecular structures of HL and its metal complexes.

Table 2. IR spectral data (cm^{-1}) of HL and its complexes.

Compound	ν(OH)/ $\nu(H_2O)$	$\nu(CH_3)$	ν(NH) (amide/indole)	ν(C=O)	ν(C=N)	ν(C–O) (bridged-phenolic)	ν(M–O)	ν(M–N)	ν(M–Cl)
HL-ligand	3440	2924	3274/3050	1661	1631	–	–	–	–
Cu-complex	3420	2925	3259/3057	1620	1528	1512	568	429	320
Co-complex	–	2923	3300/3055	1599	1561	1524	578	471	311
Ni-complex	3406	2925	3239/3072	1620	1598	1530	579	479	311
Zn-complex	3422	2922	3202/3055	1620	1562	1515	573	475	317
Cd-complex	3421	2922	3263/3045	1650	1533	1510	575	472	314
Hg-complex	–	2923	3270/3055	1657	1616	1533	574	453	318
Mn-complex	3451	2917	3272/3060	1586	1548	1524	575	440	308
Fe-complex	–	2924	3300/3052	1592	1550	1530	556	441	320

IR data indicate HL coordinates pentadentate through carbonyl oxygen, azomethine nitrogen, and phenolic-oxygen via deprotonation. Medium intensity bands from 1533 to 1512 cm^{-1} are assigned to bridged phenolic-oxygen vibrations [21, 22], additional evidence for coordination of phenolic-oxygen [21].

Skeletal metal–oxygen and metal–nitrogen vibrations can be assigned from the far IR, 579–556 and 479–429 cm^{-1} to ν(M–O) and ν(M–N), respectively [23, 24].

2.2. *Electronic spectra*

The electronic spectra of HL and complexes were recorded in DMF at 10^{-3} molar concentration. The ligand showed a strong band at 37,672 cm^{-1} and a broad peak at

27,853 cm^{-1}, assigned to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions, respectively, of azomethine [25]. In electronic spectra of the Cu(II) complex, bands at 10,189, 14,585, and 18,035 cm^{-1} are assigned to $^2B_1 \rightarrow {}^2A_1$, $^2B_1 \rightarrow {}^2B_2$, and $^2B_1 \rightarrow {}^2E$ transitions, respectively, well within the range of 9000–10,000 cm^{-1} (v_1), 11,500–16,000 cm^{-1} (v_2), and 15,000–19,000 cm^{-1} (v_3) for Cu(II) complexes with square pyramidal geometry [26, 27]. For the Co(II) complex, the three absorption bands at 11,096, 17,079, and 20,187 cm^{-1} representing the $^4A_2 + {}^4E \rightarrow {}^4B_1$ (v_1), $^4A_2 + {}^4E \rightarrow {}^4E$ $(p)(v_2)$, and $^4A_2 + {}^4E \rightarrow {}^4A_2$ $(p)(v_3)$ transitions, respectively, indicate square pyramidal geometry [28]. The Ni(II) complex showed bands at 10,329, 16,395, and 25,626 cm^{-1} which correspond to $^3A_{2g} \rightarrow {}^3T_{2g}$ (v_1), $^3A_{2g} \rightarrow {}^3T_{1g}$ $(E)(v_2)$ and $^3A_{2g} \rightarrow {}^3T_{1g}$ $(P)(v_3)$, respectively, well within the range of 8,000–13,000 cm^{-1} (v_1), 15,000–19,000 cm^{-1} (v_2), and 25,000–30,000 cm^{-1} (v_3) transitions reported for distorted octahedral geometry [29]. The Mn(II) and Fe(III) complexes showed weak absorptions in the visible region, probably due to spin-forbidden transitions [30]. The Mn(II) complex exhibited four weak absorption bands at 18,025, 24,090, 29,015, and 31,958 cm^{-1}, attributed to $^6A_{1g} \rightarrow {}^4T_{1g}$ $({}^4G)(v_1)$, $^6A_{1g} \rightarrow {}^4E_g$ $({}^4G)(v_2)$, $^6A_{1g} \rightarrow {}^4E_g$ $({}^4D)(v_3)$, and $^6A_{1g} \rightarrow {}^4T_{1g}$ $({}^4P)(v_4)$ [27]. The Fe(III) complex has three weak transitions at 16,820, 20,561, and 25,961 cm^{-1}, corresponding to v_1, v_2, and v_3 transitions, suggesting octahedral geometry [31].

2.3. *^{1}H NMR spectra*

2.3.1. ^{1}H NMR spectra of HL. In the ^{1}H NMR spectrum of the ligand, a singlet due to phenolic-OH was observed at 12.20 ppm (s, 1H, –OH). Two protons of the symmetrical azomethine resonated together as a singlet at 8.37 ppm (s, 2H, $2 \times \mathrm{CH}=\mathrm{N}$) [24]. Singlets at 11.80 ppm (s, 2H, 2 × CONH) and 12.10 ppm (s, 2H, 2 × indole-NH) have been assigned to the protons of two symmetrical amide-NH and indole-NH moieties. Methyl protons of the phenol ring are at 2.25 ppm (s, 3H, $\mathrm{CH_3}$) [18]. Sixteen aromatic protons of two 3-phenylindole rings and two protons of phenol ring resonated in the region 7.30–7.60 ppm.

2.3.2. ^{1}H NMR spectrum of Zn(II) complex of HL. The ^{1}H NMR spectrum of the Zn(II) complex displayed singlets at 11.78 ppm (s, 2H, 2 × CONH) and 12.07 ppm (s, 2H, 2 × indole-NH) due to the symmetrical amide-NH and indole-NH protons, respectively. The singlet at 12.20 ppm assigned to phenolic-OH was absent in the Zn(II) complex, indicating coordination of phenolic-oxygen with the metal ions through deprotonation. Small downfield/upfield shifts of methyl, amide-NH, azomethine, and/or indole-NH protons could be attributed to the interaction of the ligand with the metal ions as a result of complexation.

2.4. *FAB mass spectral data*

2.4.1. FAB mass spectra of HL. The FAB mass spectrum of HL and its fragmentation pattern are provided in Supplementary Material. The molecular ion peak, M^+ was observed at m/z 698, 700, 702 (40%, 65%, 30%), which is equivalent to its molecular weight of A_4 at *m*/*z* 190 (A_3–$C_{14}H_9NCl^{\cdot} = A_4$, 20%). The fragmentation pattern of the ligand HL is in conformity with its structure.

2.4.2. FAB mass spectrum of Co(II) complex.

The FAB mass spectrum of the Co(II) complex [$Co_2(L)(\mu\text{-}Cl)Cl_2$] and its fragmentation pattern are given in Supplementary Material. Molecular ion peak, M^+ of the complex was observed at *m*/*z* 922, 924, 926, which is equivalent to the molecular weight of the Co(II) complex. The FAB mass fragmentation pattern suggests binuclear Co(II) complex.

2.5. *Magnetic susceptibility data*

The magnetic susceptibility measurements of the complexes were performed at room temperature (table 1). The magnetic moment for the Cu(II) complex is 1.49 B.M. per copper ion, less than the normal value, due to antiferromagnetic spin exchange interaction between two Cu(II) ions [32]. The binuclear Co(II) complex has a magnetic moment value of 4.33 B.M. per Co(II) ion. Pilkington and Robson [33] reported lowered magnetic moment values in the range 4.3–4.6 B.M. for five coordinate, square pyramidal binuclear Co(II) complexes. The observed low magnetic moment for the present Co(II) complex could be due to weak spin-exchange interaction between Co(II) ions. The observed magnetic moment values for Ni(II), Mn(II) and Fe(III) complexes in the present study were 2.65, 5.68, and 5.72 B.M., respectively, which are less than their normal values, indicating weak antiferromagnetic coupling interactions [34, 35].

2.6. *ESR spectrum of Cu(II) complex*

An ESR spectrum of the Cu(II) complex at room temperature using diphenylpicrylhydrazyl (DPPH) as a standard gave "*g*" values, $g_{\parallel} = 2.236$, $g_{\perp} = 2.0653$ following the decreased trend $g_{\parallel} > g_{\perp} > g_e$ (2.0023), suggesting the presence of an unpaired electron in the $d_{x^2-y^2}$ orbital [36]. The '*g*' values are related to axial symmetry and $g_{\parallel} > g_{\perp}$ suggests square pyramidal geometry [28, 29], in agreement with the electronic spectral data. The spectrum was broad with no hyperfine splitting, consistent with chloro-bridged binuclear copper(II) complexes [29]. The broadening is assigned to spin-exchange interaction between two Cu-centers [35]. The *G* value is a measure of the extent of spin-exchange interaction between two metal centers. In the present Cu(II) complex, *G* was 3.64, less than 4 which is characteristic of mononuclear complexes devoid of spin-interactions, suggesting weak antiferromagnetic spin-exchange interaction between the two copper centers [36].

2.7. *Thermogravimetric analysis*

The thermogram of the Fe(III) complex, is shown in Supplementary Material, showed a first inflection point at 274°C with a weight loss of 2.903%, consistent with loss of carbon monoxide. The thermal decomposition of the Fe(III) complex with probable molecular species at each inflexion is given in table 3.

Table 3. Thermal decomposition of Fe(III)-complex of HL.

Complex	Stage	TG Peak temp. (°C)	Loss of mass (%)		Probable assignments
			Practical	Theoretical	
$[Fe_2(L)(\mu\text{-}Cl)Cl_4]$	–	–	–		$Fe_2(C_{39}H_{27}N_6O_3Cl_7)$ $\downarrow -CO$ $Fe_2(C_{38}H_{27}N_6O_2Cl_7)$ $\downarrow -CO, -Cl_2$ $Fe_2(C_{37}H_{27}N_6OCl_5)$ $\downarrow -C_{14}H_{11}N_2Cl$ $Fe_2(C_{23}H_{16}N_4OCl_4)$ $\downarrow$ Fe_2O_3
	I	274	2.903	2.837	
	II	354	9.734	10.22	
	III	490	36.59	36.24	

2.8. *Powder X-ray diffraction (XRD) studies*

Although the compounds were soluble in polar organic solvents (DMSO and DMF) we did not obtain crystals suitable for single-crystal studies. In order to test the degree of crystallinity of the synthesized complexes, we obtained the powder XRD patterns Cu(II) and Fe(III) complexes. The powder XRD patterns of Cu(II) and Fe(III) complexes are provided in Supplementary Material. Both complexes show some crystalline behavior and preliminary calculations were performed for the cubic symmetry of the complexes [37]. The Cu(II) complex showed nine reflections in the range of 3–30° (2θ), arising from the diffractions of X-rays by the planes of the complex. All important peaks have been indexed and observed values of inter-planar distances (d) have been compared with the calculated ones (Supplementary Material). The unit cell calculations were performed for cubic system and the $(h^2+k^2+l^2)$ values were determined. The absence of forbidden numbers (7, 15, and 23) indicate that the Cu(II) complex has cubic symmetry. The calculated lattice parameters were $a=b=c=22.93$ Å. Similar calculations were performed for Fe(III) complex, and this complex showed eight reflections in the range of 3–30° (2θ). The calculations revealed cubic symmetry for Fe(III) complex with the lattice parameters: $a=b=c=22.95$ Å (Supplementary Material).

2.9. *Antimicrobial activity*

To evaluate the antimicrobial properties of indole derivatives, we have tested HL and its complexes for their antimicrobial properties against selected bacteria (*Escherichia coil* and *Staphyloccocus aureus*) and fungi (*Aspergillus niger* and *Candida albicans*). The antimicrobial activities of the tested compounds are given in table 4. 3-Phenylindoles possess antimicrobial properties [38] and substituted indole derivatives [39] also exhibited good antitubercular activity against *Mycobacterium tuberculosis*. 3-Phenyl-5-substituted indole-2-carbohydrazones and their Cu(II), Co(II) and Ni(II) complexes

Table 4. Antimicrobial screening data of HL and its complexes.

	Antibacterial activity zone of inhibition (in mm)		Antifungal activity zone of inhibition (in mm)	
Compound	*E. coli*	*S. aureus*	*A. niger*	*C. albicans*
Ligand (HL)	11	12	16	13
Cu-complex	12	14	15	14
Co-complex	12	12	14	14
Ni-complex	11	15	11	13
Zn-complex	13	11	13	14
Cd-complex	11	12	16	13
Hg-complex	13	14	15	16
Mn-complex	11	13	11	15
Fe-complex	14	12	12	13
Streptomycin	22	20	–	–
Griseofulvin	–	–	24	23
DMF (control)	0	0	0	0
Bore size	08	08	08	08

were active against the bacteria *E. coli* and *S. aureus* and the fungus *A. niger* [40]. Recently, we reported [28] a new series of macroacyclic metal complexes derived from an "end-off" binucleating ligand containing a benzindole moiety active against *E. coli* and *S. aureus* and the fungi *A. niger* and *Fusarium oxysporum*. Mahboobi *et al.* [41] reported some substituted 2-phenylindole derivatives active against *S. aureus* but inactive against *E. coli* and *C. albicans*. In the present study, HL has weak antibacterial activity with zones of inhibition of 11 and 12 mm against *E. coli* and *S. aureus* when compared to the standard drug streptomycin with zones of inhibition of 22 and 20 mm, respectively. The metal complexes also showed less activity with zones of inhibition in the range 11–13 and 11–14 mm against *E. coli* and *S. aureus*. Substitution at the 1- or 2-position in the indole in active compounds such as 3-phenylindole, results in the cancellation of their activity almost completely [38]. This could be a reason for the reduced or weak antibacterial activity of the ligand and its complexes in the present study. The weak activity against the bacteria *E. coli* is in line with the observations made by Mahboobi *et al.* [41]. However, the ligand showed moderate activity against the fungi *A. niger* and *C. albicans* with zones of inhibition of 16 and 13 mm, respectively, compared to the standard drug griseofulvin with zones of inhibition of 24 and 23 mm against *A. niger* and *C. albicans*, respectively. The complexes of HL showed weak to moderate activity with zones of inhibition in the range of 11–16 mm against *A. niger* and 13–16 mm against *C. albicans*.

3. Experimental

All the chemicals were of reagent grade. Solvents were dried and distilled before use, according to standard procedures [42]. 2,6-Diformyl-4-methylphenol was prepared according to the method reported by Denton and Suschitzky [43]. The precursor indole-2-carbohydrazide was prepared by the literature method [44]. The metal salts used were in their hydrated form except $HgCl_2$.

3.1. *Synthesis of HL*

HL was synthesized by "1 + 2" condensation of 2,6-diformyl-4-methylphenol (0.001 mol) and 5-chloro-3-phenylindole-2-carbohydrazide (0.002 mol) by refluxing in the presence of catalytic amounts of glacial acetic acid (1–2 drops) in methanol for 4 h. The pale yellow solid separated was collected by filtration and washed with 5 mL of hot methanol, dried, and recrystallized from dioxane.

3.2. *Preparation of Cu(II), Ni(II), Co(II), Zn(II), Cd(II), Hg(II), Mn(II), and Fe(III) complexes of HL*

The complexes were synthesized by template method due to insolubility of the ligand in common organic solvents. To a hot methanolic solution (10 mL) of 2,6-diformyl-4-methylphenol (0.001 mol) was added a methanolic solution (20 mL) of 3-phenyl-5-chloroindole-2-carbohydrazide (0.002 mol) and refluxed for 2 h. To the resulting mixture, a hot solution of metal(II) chloride (0.002 mol) in methanol (10 mL) was added and further refluxed for 4–6 h with occasional shaking, on a water bath. It was then allowed to cool to room temperature, which yielded metal complex. The solid complexes obtained were collected by filtration, washed with 4–5 ml of hot methanol and dried in vacuum over anhydrous calcium chloride. The yields and melting points of all the compounds are reported in table 1.

3.3. *Physical measurements*

IR spectra of the synthesized compounds were recorded as KBr pellets on a Perkin–Elmer FT-IR spectrometer. ^{1}H NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer. UV–Vis spectra of the ligand and its complexes were recorded on an Elico-SL 164 spectrometer from 200–1000 nm in DMF (1×10^{-3} M). FAB mass spectra were obtained on a Jeol SX 102/DA-6000 mass spectrometer using Argon/Xenon as the FAB gas. The accelerating voltage was 10 kV and the spectra were recorded at room temperature using *m*-dinitrobenzyl alcohol as a matrix. Elemental analyses were obtained on a Heraeus CHN–O rapid analyzer and metal analysis was carried out by standard methods. ESR measurements were carried out on a Bruker Biospin Gmbh spectrometer working at a microwave frequency of 9.903 GHz using DPPH as a reference with the field set at 3200 Gauss. XRD spectra were recorded on a Philips PW 3710 diffractometer attached to a digital computer along with graphical assembly using Cu-Kα radiation (1.54 Å). The X-ray tube was operated at 25 kV/20 mA and samples scanned in the range of 3–100° at a scanning speed of 0.010°/0.2 s at 25°C. Magnetic susceptibility measurements were performed by Faraday method using a model 300 Lewis Coil Force magnetometer at room temperature using $HgCo(SCN)_4$ as calibrant [45].

3.4. *Antimicrobial activity*

The antibacterial and antifungal activities were performed by the cup–plate method, as reported earlier [18]. In a typical procedure, molten nutrient agar kept at 45°C was then poured into petri dishes and allowed to solidify. Holes of 8 mm diameter were punched using a sterile cork borer and these were completely filled with test solutions (1 mg mL^{-1} in DMF). The plates were incubated for 24 h at 37°C. The diameter of the zones of inhibition for all the test compounds were measured and the results compared with streptomycin of the same concentration as that of the test compound under identical conditions.

Antifungal activity of the compounds was evaluated against the *A. niger* and *F. oxysporum* by the cup–plate method, cultured on potato-dextrose agar medium adapting similar procedure as described above. The plates were incubated at 37°C for 48 h. The diameters of the zone of inhibition for all the test compounds were measured and the results compared with the standard drug griseofulvin of the same concentration under identical conditions.

All test compounds and standard drugs were prepared in freshly distilled DMF for which the zone of inhibition was negligible.

4. Conclusion

The end-off compartmental ligand HL coordinates to the metal ions are mononegative, hexadentate. The ligand was designed to secure two metal ions in proximity. The metal ions are bonded to a phenoxo-bridge which endogenously coordinates to the metal ions. The other coordinating sites of the ligand are the azomethine nitrogens and amide carbonyl oxygens. The phenoxide ion, azomethine, and amide carbonyl groups surround two metal ions which are in close proximity within the ligand compartment to form a square and a chloride ion/s and/or water molecule coordinates to each metal, giving a square pyramidal or octahedral configuration to the metal ions. The Cu(II), Co(II), Zn(II), Cd(II), and Hg(II) complexes exhibited square pyramidal geometry whereas Ni(II), Mn(II), and Fe(III) complexes exhibited octahedral geometry. The ligand and its complexes were tested for antimicrobial activity; the compounds were less active against the bacteria *E. coli* and *S. aureus*, but showed moderate activity against the fungi *A. niger* and *C. albicans*.

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