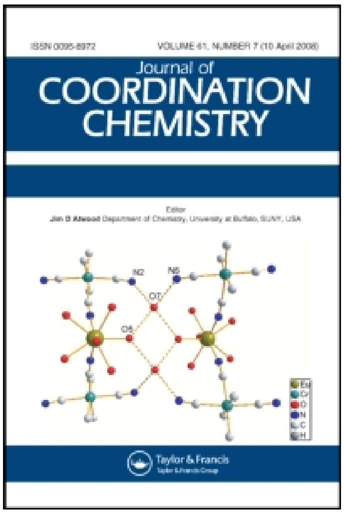

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Synthesis and spectral characterization of some binuclear complexes designed from N_4O and N_2O_3 donor Schiff-base ligands of 2,6-diformyl-4-methylphenol

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New pentadentate binucleating ligands containing phenoxide as an endogenous bridging group, 2,6-diformyl-4-methylphenol *bis*(carbohydrazone) (L^1H), and 2,6-diformyl-4-methylphenol *bis*(semicarbazone) (L^2H), and their binuclear Co(II), Ni(II), Cu(II) and Zn(II) complexes of general formula $[M_2LCl_3]\cdot nH_2O$ with chloride as an exogenous bridge have been synthesized. The complexes were characterized on the basis of elemental analysis, conductivity measurements, thermal analysis, IR, Far-IR, NMR, UV–Vis, EPR, FAB-mass and magnetic data. The coordination mode (N_4O, N_2O_3), as well as endogenous phenoxide bridge and an exogenous chloride bridge have been established on the basis of IR, Far-IR and ^{1}H-NMR spectral data. Electronic spectral data of the complexes indicate square-pyramidal geometry. EPR spectra show line broadening, which is further supported by weak antiferromagnetic interaction from the room temperature magnetic moment data. All compounds show appreciable antimicrobial activity.

Keywords: Binuclear; Schiff base; Coordination mode; Square pyramidal; Weak antiferromagnetic

1. Introduction

Carbohydrazide is a member of the structural sequence, urea, semicarbazide and carbohydrazide [1]. Both hydrazine groups of carbohydrazide display reactivity toward carbonyl compounds and give rise to a large number of crystalline mono- and dihydrazones. Carbohydrazone and semicarbohydrazones are among the most important nitrogen-oxygen donor ligands [2], capable of acting as neutral or charged ligands. During the past few years, a plethora of references describing transition metal complexes of these ligands appeared [3–10].

Applications of carbohydrazide, semicarbohydrazide (thiosemicarbohydrazone and semicarbohydrazone) in analysis of metals have been known for many years [11]. Biological activity associated with these hydrazones was first reported [12] in 1946; their action as antimicrobial and antiviral agents has been reviewed by Levinson [13], and Perrin and Stunzl [14]. In some cases, the highest *in vivo* activity is associated with metal complexes rather than the semicarbohydrazone itself [13]. Although hydrazones of the

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aldehyde have marked anti-tumor activity [15], their metal complexes have much more potential as determined by single-cell survival of Chinese hamster ovary cells [16]. The anti-tumor activity *in vivo* and the cytotoxicity *in vitro* depends on specific and unique properties of its metal(II) chelate, such as its basicity and its interactions with other ligands, rather than on the sequestering action of the ligand itself [17]. Metal complexes of such ligands have attracted much attention due to their biological activity against smallpox, viral diseases and certain kinds of tumors [9]. There is little information on binuclear transition-metal(II) complexes of these hydrazones and related ligands which can be related to their biological properties.

In view of the biological importance of such complexes, and desire to have two metal ions in close proximity, with different donor atoms (whether coordination to the metal ion occurs through the carbonyl oxygen or the available nitrogen donors to form a coordination sheath consisting of only bridging oxygen and nitrogen donor atoms) or cavities and to study their coordination properties, in this article we report the synthesis of Co(II), Ni(II), Cu(II) and Zn(II) complexes with L^1H and L^2H (figure 1) derived from condensation of 2,6-diformyl-4-methylphenol with carbohydrazide and semicarbazide. The compounds have been characterized on the basis of IR, Far-IR, NMR, UV–Vis, ESR and magnetic moment. Based on these studies, a general composition of $[M_2L(\mu\text{-Cl})Cl_2] \cdot nH_2O$ has been established.

2. Experimental

2.1. *Physical measurements*

Co(II), Ni(II), Cu(II) and Zn(II) ions were determined volumetrically using EDTA. Carbon, hydrogen and nitrogen analyses were carried out on a Thermoquest elemental analyzer. Molar conductance measurements were made on an ELICO–CM–82 conductivity bridge with a cell having cell constant of $0.51\,\text{cm}^{-1}$. Magnetic measurements were made on a Gouy balance at room temperature using $Hg[Co(SCN)_4]$ as calibrant. The electronic spectra of the complexes were recorded on a Hitachi 150-20

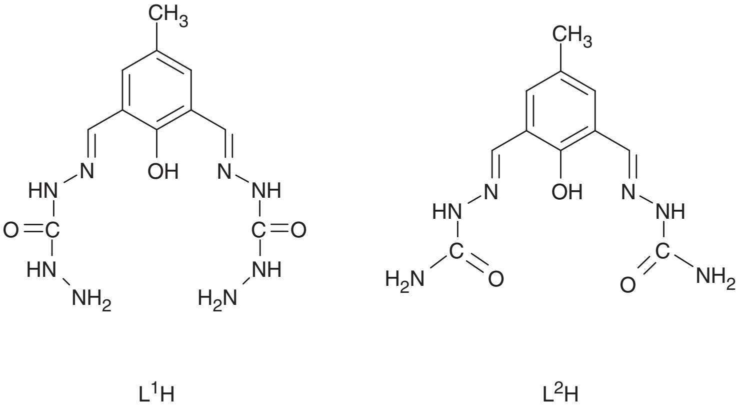

Figure 1. Schiff-base ligands L^1H and L^2H.

spectrophotometer from 200–1100 nm. IR spectra were recorded in KBr using an Impact 410 Nicolet (USA) FT-IR spectrometer in the range 4000–400 cm^{-1}. Far infrared spectra (600–100 cm^{-1}) of the ligands and complexes were recorded on a Bruker IFS66V using polyethylene pellets. ESR spectra of the complexes were recorded on a Varian E–4X-band EPR spectrometer using TCNE as the g-marker. TG and DTG measurements were carried out in nitrogen on a Rigaku thermoflex instrument to 800°C with a heating rate of 10°C min^{-1}. The FAB mass spectra were recorded on a JEOL EX 102/DA-6000 mass spectrometer/data system using Argon/Xenon (6 kV, 10 mA) as the FAB gas. The ^{1}H-NMR spectra were recorded in the range 0–15 ppm in DMSO on a Varian 300 MHz spectrometer at room temperature using TMS as internal reference.

2.2. *Materials*

All chemicals were of reagent grade. Solvents were dried and distilled before use according to standard procedures. The preparation of 2,6-diformyl-4-methylphenol by the method of Denton and Suschitzky [18], with slight modification. Carbohydrazide and semicarbazide, as hydrochlorides, were purchased from S D Fine Chemicals (Mumbai, India) and used directly for the preparation of Schiff bases. Metal salts were in the hydrated form, i.e. $CoCl_2 \cdot 5H_2O$, $NiCl_2 \cdot 5H_2O$, $CuCl_2 \cdot 2H_2O$ and $ZnCl_2 \cdot 2H_2O$.

2.3. *Synthesis of 2,6-diformyl-4-methylphenol bis(carbohydrazone) (L^1H)*

Ethanolic solution of 2,6-diformylphenol (0.04 mol) was added dropwise to an aqueous ethanolic solution of carbohydrazide (0.08 mol). The reaction mixture was stirred for one hour. Then a small amount of aqueous NaOH was added dropwise, refluxed for 4–6 h on a hot water bath and kept overnight. The product (yellow amorphous) was filtered off, air dried, and recrystallized from ethanol. Yield: 68%; m.p. > 250°C.

2.4. *Synthesis of 2,6-diformyl-4-methylphenol bis(semicarbazone) (L^2H)*

This ligand was prepared by condensation of 2,6-diformyl-4-methylphenol with semicarbohydrazide in 1 : 2 molar ratio. The procedure was exactly as discussed for L^1H. In this case colorless amorphous product was obtained. Yield: 75%; m.p. > 250°C.

2.5. *Synthesis of complexes with L^1H and L^2H*

The following general method was used for the preparation of metal complexes. The cobalt(II), nickel(II), copper(II) and zinc(II) complexes were prepared by refluxing respective hydrated metal chloride (0.02 mol) in ethanol (30 mL) with the ligands (L^1H and L^2H) (0.01 mol) in ethanol (25 mL). The reaction mixtures were refluxed for 8–10 h, the colored complexes so obtained were filtered off, the product was washed with hot ethanol repeatedly to remove excess metal ions, then thoroughly washed with dichloromethane to remove impurities of ligands and dried under vacuum over $CaCl_2$. Yield: 50–60%.

2.6. *Evaluation of antibacterial and antifungal activities*

2.6.1. Antibacterial activity. Antibacterial activity of test compounds was assessed against *Pseudomonas auregenosa* and *Bacillus cirroflgellosus* by the cup-plate method [19].

2.6.1.1. Materials. Materials used were nutrient agar, sterilized Petri dishes and pipettes, 20–24 h old subcultures in nutrient agar medium, and sterilized test tubes containing solution of the test compounds in desired concentration.

2.6.1.2. Preparation of inoculation medium. Definite volumes of peptone (0.5%), yeast extract (0.15%), beef extract (0.15%), sodium chloride (0.35%), dipotassium phosphate (0.36%), and potassium dihydrogen phosphate (0.13%) were dissolved in distilled water and the pH adjusted to 7.2. This solution was sterilized by autoclaving at 15 p.s.i. for 20 min.

2.6.1.3. Preparation of subcultures. One day prior to the tests, inoculation of above bacterial cultures was made in the inoculation medium, as described above, and incubated at 37°C for 18–24 h.

2.6.1.4. Preparation of base-layer medium. Base-layer medium was prepared by dissolving definite volumes of peptone (0.6%), yeast extract (0.3%), beef extract (0.13%), and agar (2.5%) in distilled water. The pH of this medium was also adjusted to 7.2 and sterilized by autoclaving at 15 p.s.i. for 20 min.

2.6.1.5. Preparation of test compounds. Each test compound (5 mg) was dissolved in dimethylformamide (5 mL) to give a solution of 1000 $\mu g\,mL^{-1}$. This solution (0.1 mL) was used for antimicrobial testing.

2.6.1.6. Testing method. Base-layer was obtained by pouring about 10–15 mL of base-layer medium into sterilized Petri dishes which were allowed to attain room temperature. This solid layer after attaining room temperature is called the base layer. Overnight grown sub-cultures of bacteria were mixed with seed layer medium and immediately poured into Petri dishes containing the base layer and then allowed to attain room temperature. The cups were made by scooping out nutrient agar with a sterile cork borer. To these cups, solutions of test compounds (0.1 mL) were added using sterile pipettes, and these plates were subsequently incubated at 37°C for 36 h. The zone of inhibition, if any, was measured in mm for the particular compound. Norfloxacin was used as positive-control and activity of the solvent was also examined.

2.6.2. Antifungal activity. Fungicidal activity of test compounds was assessed against *Aspergillus niger* and *Candida albicans* by the cup-plate method.

2.6.2.1. Materials. Materials used were nutrient agar, sterilized Petri dishes and pipettes, 16–18 h old sub-cultures in nutrient agar medium supplemented with 1% glucose, and sterilized test tubes containing solutions of the compounds in desired concentration.

2.6.2.2. Preparation of inoculation medium. Inoculation medium was prepared by dissolving peptone (1.0%), yeast extract (0.6%), sodium chloride (0.5%), potassium dihydrogen phosphate (0.3%), and glucose (1.0%) in distilled water. The pH of the medium was adjusted to 6.0 and sterilized at 15 p.s.i. for 20 min.

2.6.2.3. Preparation of sub-cultures. One day before testing, fungi were inoculated in the inoculation medium and incubated at 37°C for 18–24 h.

2.6.2.4. Preparation of base-layer medium. Definite volumes of peptone (4.0%), yeast extract (0.6%), sodium chloride (0.5%), potassium dihydrogen phosphate (0.3%), glucose (1.0%), and agar (2.5%) were dissolved in distilled water. The pH of the medium was adjusted to 6.0 and sterilized by autoclaving at 15 p.s.i. for 20 min.

2.6.2.5. Preparation of seed layer medium. Peptone (4.0%), yeast extract (0.6%), sodium chloride (0.5%), potassium dihydrogen phosphate (0.3%), glucose (1.0%) and agar (2.5%) were dissolved in distilled water, the pH adjusted to 6.0 and sterilized separately by autoclaving at 15 p.s.i. for 20 min.

2.6.2.6. Testing method. The method of testing for antifungal activity is the same as for assessing antibacterial activity. Grisofulvin was used as a positive control and activity of the solvent was also a control.

3. Results and discussion

3.1. *Characterization*

Condensation of 2,6-diformyl-4-methylphenol with carbohydrazide and semicarbazide in ethanol (1 : 2 molar ratio) in the presence of a small amount of aqueous sodium hydroxide gives open chain products. The ligands react with metal(II) chlorides in ethanol

$$2\mathrm{M(II)Cl_2} + \mathrm{L^1H} \rightarrow \left[\mathrm{M_2L^1}(\mu\text{-Cl})\mathrm{Cl_2}\right] \cdot 5\mathrm{H_2O}$$

$$2\mathrm{M(II)Cl_2} + \mathrm{L^2H} \rightarrow \left[\mathrm{M_2L^2}(\mu\text{-Cl})\mathrm{Cl_2}\right] \cdot 6\mathrm{H_2O}$$

where M(II) = Co, Ni, Cu and Zn.

Elemental analyses of these complexes reveal 1 : 2 ligand to metal stoichiometry (table 1). The complexes are soluble in DMF, DMSO, and acetonitrile and sparingly soluble in ethanol and chloroform. The composition and coordination geometry of these complexes has been established by the following experimental observations. (i) The molar conductance values in DMF fall in the expected range ($10–32\,\mathrm{cm^2\,\Omega^{-1}\,mol^{-1}}$) of non-electrolytes, indicating that chlorides are coordinated with general formula $[\mathrm{M_2L}(\mu\text{-Cl})\mathrm{Cl_2}]$. (ii) The presence of a bridging chloride for each complex was confirmed by two peaks between $240–270\,\mathrm{cm^{-1}}$ in the far-IR spectrum. (iii) FAB-mass spectra of the Cu(II) complexes of $\mathrm{L^1H}$ and $\mathrm{L^2H}$ show the molecular ion peaks at $\mathrm{M^+}$ 635 and 613, respectively, indicating monomeric complexes. (iv) The coordination of terminal amine $\mathrm{NH_2}$ to the central metal is supported by the

Table 1. Elemental analyses of the compounds.

Sl. no.	Compound	Color	M	C	H	N	Cl
L1	L^1H	Yellow		42.46 (42.85)	5.09 (5.23)	36.14 (36.35)	
L2	L^2H	Colorless		47.22 (47.48)	4.97 (5.07)	30.01 (30.02)	
C-1	$[Co_2L(\mu\text{-}Cl)Cl_2)]\cdot 5H_2O$	Green	18.75 (18.96)	21.09 (21.26)	3.98 (4.05)	17.88 (18.03)	17.02 (17.11)
C-2	$[Ni_2L(\mu\text{-}Cl)Cl_2)]\cdot 5H_2O$	Yellow	18.37 (18.23)	20.45 (20.67)	4.11 (4.26)	17.24 (17.53)	16.34 (16.64)
C-3	$[Cu_2L(\mu\text{-}Cl)Cl_2)]\cdot 5H_2O$	Green	20.01 (20.15)	20.69 (220.94)	3.71 (3.99)	17.46 (17.76)	16.69 (16.86)
C-4	$[Zn_2L(\mu\text{-}Cl)Cl_2)]\cdot 5H_2O$	Yellow	20.29 (20.61)	20.72 (20.82)	3.74 (3.97)	17.46 (17.66)	16.44 (16.76)
C-5	$[Co_2L(\mu\text{-}Cl)Cl_2)]\cdot 6H_2O$	Orange	19.12 (19.34)	21.45 (21.67)	4.02 (4.13)	13.45 (13.79)	17.22 (17.45)
C-6	$[Ni_2L(\mu\text{-}Cl)Cl_2)]\cdot 6H_2O$	Red	19.08 (19.27)	21.45 (21.69)	4.03 (4.14)	13.64 (13.80)	17.22 (17.46)
C-7	$[Cu_2L(\mu\text{-}Cl)Cl_2)]\cdot 6H_2O$	Green	20.22 (20.54)	21.09 (21.35)	3.97 (4.07)	13.32 (13.58)	17.02 (17.19)
C-8	$[Zn_2L(\mu\text{-}Cl)Cl_2)]\cdot 6H_2O$	Yellow	20.84 (21.01)	21.02 (21.22)	3.87 (4.05)	13.27 (13.5)	16.91 (17.08)

Table 2. IR spectral data (cm^{-1}) of the ligands and their complexes.

Compd.	ν(C=N)	ν(C=O)	ν(O–H)/(H_2O)	ν(C–O) (Phenolic)	ν(NH_2)	ν(N–H)	ν(M–N)	ν(M–O)	ν(M–Cl–M)	
L^1H	1622	1684	2650	1250	3280	3170	–	–	–	
L^2H	1653	1690	2780	1225	3260	3180	–	–	–	
C-1	1616	1678	3444	1295	3140	3150	420	470	300	320
C-2	1622	1680	3462	1320	3162	3180	415	529	340	325
C-3	1616	1681	3450	1345	3112	3125	419	524	325	315
C-4	1622	1679	3475	1290	3200	3130	425	490	328	310
C-5	1625	1642	3420	1278	3245	3150	421	525	335	326
C-6	1630	1650	3455	1300	3250	3145	429	534	338	321
C-7	1635	1648	3462	1324	3248	3130	426	541	335	326
C-8	1640	1655	3444	1329	3260	3154	430	521	340	328

shift in the resonance of NH_2 protons in L^1H. (v) The analytical data (C, H, and N) for the complexes support the structures. (vi) The presence of water in the complexes was inferred from thermogravimetric analysis.

3.2. *IR spectra (table 2)*

L^1H and L^2H exhibit characteristic IR bands for amide ketonic group at 1684 and 1690 cm^{-1} and a weak shoulder at ca. 1622 and 1653 cm^{-1}, which can be assigned to the ν(C=N) azomethine linkage. A broad band at 3250 and 3280 cm^{-1}, along with two shoulders at 3300, 3230 cm^{-1} and 3300, 3260 cm^{-1}, may be assigned to ν_{asym}(N–H) and ν_{sym}(N–H) vibrations, respectively.

In complexes of L^1H, there is no significant change in the amide ketonic band, indicating that amide oxygen does not coordinate to the metal [20–24]. The band due to ν(C=N) appears at slightly lower wavenumber (~1620–1610 cm^{-1}) in the complexes, suggesting [25, 26] that nitrogens of the azomethine are coordinated to the metal. The high intensity band of the ligand around 1250 cm^{-1} due to phenolic vibration appears at 1320–1340 cm^{-1} in the complexes, emphasizing that the –OH of the ligand reacts with metal(II) via deprotonation [27, 28]. In the complexes, a shoulder (ca. 3230 cm^{-1}) corresponding to ν(N–H) disappears, indicating the coordination of the terminal amino to the metal. The spectra also show broad bands at 3480–3420 cm^{-1}, assigned to ν(O–H) of uncoordinated water. From the far IR spectra, bands in the region 540–520 cm^{-1} and 435–420 cm^{-1} in the complexes are assigned to ν(M–N) and ν(M–O), respectively [29]. The presence of chloride bridge is evident from IR peaks at 270 and 240 cm^{-1}, characteristic of chloro-bridged binuclear complexes [30].

In complexes of L^2H, the band due to amide ketonic group shifts downward (~20–40 cm^{-1}), indicating [22] coordination of oxygen (ketonic) to the metal(II). The band due to ν(C=N) shifts to lower frequency (ca. 20–30 cm^{-1}), suggesting nitrogens of the azomethine coordinate to the metal. This is further supported by appearances of weak far-IR bands at 540–520 cm^{-1} and 435–420 cm^{-1} assigned [27] to ν(M–N) and ν(M–O), respectively. Bands assigned to ν_{asym}(N–H) and ν_{sym}(N–H) vibrations persist, indicating non-coordination of the terminal amino group to the metal [31]. The spectra of metal complexes show broad bands at ca. 3480–3420 cm^{-1}, assigned to ν(O–H) vibrations of the uncoordinated water molecules.

Table 3. Electronic spectral and magnetic moment data for the complexes.

Sl. no		$\lambda_{\max}$ in nm	($\nu_{\max}$ in cm^{-1})		Magnetic moment μ_{eff} (BM)
C-1	570 (17543)	428 (23364)	375 (26666)	266 (37593)	3.70
	840 (11904) 790				
C-2	(12658) 625 (16000)	340 (294110)	328 (30487)	258 (38759)	2.70
	380 (26315)				
C-3	609 (164200)	350 (28571)	287 (34843)	250 (40000)	1.80
C-4	–	421 (23752)	380 (26315)	256 (39062)	–
C-5	565 (17699)815 (12269) 780	415 (24096)	360 (2777)	280 (37142)	3.75
C-6	(12820) 610 (16393)	350 (28571)	330 (30303)	270 (37037)	2.68
	375 (26666)				
C-7	649 (15408)	360 (27777)	330 (30303)	265 (37738)	1.72
C-8	–	410 (24390)	365 (27397)	256 (39062)	–

3.3. *Electronic spectra*

Electronic absorption spectra of the ligands and their binuclear complexes were recorded in DMF from 200–1100 nm. The distinguishable absorption bands of electronic spectra of the complexes are listed in table 3. The strong absorptions between 260 and 380 nm can be assigned to π–π transitions of the ligand. The medium absorption bands at ca. 415 nm are charge-transfer transitions from the phenoxide of the ligand to metal ions (LMCT). The d-d transitions are observed (except for zinc(II) complexes) in the visible region. The $\lambda_{\max}$ values are observed at lower energies compared to analogous symmetrical binuclear complexes [32–37].

The cobalt(II) complexes (C-1 and C-5) show an intense band at ~375 nm, a shoulder at 380–428 nm and a distinct band at ~570 nm. The intense band can be assigned to π–π^* transition associated with the azomethine group [38]; the last two bands with an absorption coefficient of ca. $1 \times 10^3\,\mathrm{M^{-1}\,cm^{-1}}$ can be assigned to charge-transfer bands from the filled pπ orbital of the phenolic oxygen to the vacant orbitals of Co(II).

The nickel(II) complexes (C-2 and C-6) exhibit four d–d bands around 840, 790, 625 and 380 nm. The bands observed for complexes at about 11800, 12700, 16000 and 26500 cm^{-1} have energies similar to those of well characterized square-pyramidal nickel(II) complexes [39].

The copper(II) complexes (C-3 and C-7) exhibit three main bands at 609–649 nm ($\varepsilon = 103$–$141\,\mathrm{l\,mol^{-1}\,cm^{-1}}$), 350–360 nm ($\varepsilon = 8450$–$12840\,\mathrm{l\,mol^{-1}\,cm^{-1}}$) and 259–270 nm ($\varepsilon = 34900$–$50000\,\mathrm{l\,mol^{-1}\,cm^{-1}}$). The lowest energy asymmetric band, which does not occur in the corresponding zinc(II) complexes, is assigned to d–d transition. Broad asymmetric peaks at approximately 600 nm, with a low energy shoulder, have been observed for related cyclic and acyclic Schiff-base binuclear copper(II) complexes with square-planar and square-pyramidal geometries [40–42]. The intense bands observed in the range 350–360 nm are associated with intraligand and ligand to metal charge-transfer transitions, while the higher energy, very intense bands are π–π^*. Alkoxo [43] and phenolate-bridged [44] dicopper complexes generally show a LMCT band in the near-UV region. Handa *et al.* have reported that the LMCT band is characteristic of a di-μ-hydroxo- or di-μ-alkoxo-dicopper bivalent core with a significant electrostatic interaction between the bridging oxygens [45]. The spectral features of the copper(II) complex is similar to that of the Cl^- adduct of half-met haemocyanin, which exhibits no charge-transfer transition in the visible region [46].

The zinc(II) complexes (C-4 and C-8) show strong absorption spectra at 380 and 421 nm, due to ligand to metal charge-transfer transition.

3.4. *EPR spectra*

The X-band EPR spectra of polycrystalline Cu(II) complexes are recorded at room temperature. The EPR spectra (Supplementary Material) of the binuclear complexes are characteristic of square-pyramidal coordination, slightly broadened with $g_\parallel$ and $g_\perp$ values in the range of 2.22–2.43 and 2.08–2.19. In general, chloride-bridged binuclear copper(II) complexes give broad ESR signals [47] providing further evidence for bridging chloride structures. The broadening is assigned to a dipolar interaction. The trend $g_\parallel > g_\perp > g$ suggests (table 3) that $d_{x^2-y^2}$ is the ground state for Cu^{+2} [48]. The g values are related to the axial symmetry parameter, *G*, by the expression $G = (g_\parallel - 2)/(g_\perp - 2)$. The *G* values, a measure of exchange interaction between copper centers in the polycrystalline solid, are 2.62 and 2.26, indicating considerable exchange interaction in the complex.

3.5. *Magnetic data*

The magnetic susceptibilities of the complexes were recorded at room temperature showing comparatively high magnetic moments, indicating the presence of weak antiferromagnetic interactions. The magnetic properties can be explained from their core structures [49]. Some dinuclear complexes with phenoxo and chloro bridges are known [50]; complexes of Schiff bases derived from 2,6-diformyl-4-methylphenol and glycine or alanine a weak antiferromagnetic interaction is observed. For the $[Cu_2Cl_6]^{2-}$ with large cations, a significant ferromagnetic interaction is observed [51]. Analysis of the magnetic results shows that the antiferromagnetic interaction of cobalt, nickel and copper complexes is very weak, in keeping with the magnitude of change observed by Lambert and Hendrickson [52] and Glick and Lintvedt [53]. Smaller antiferromagnetic coupling of chloride-bridged complexes has been observed for phenoxide-bridged complexes of the LM_2X_2 series. As shown by Cairns and Busch [54] and Mallah *et al.* [55], electronegativity predicts more efficient overlap integral for phenoxide when phenoxide and chloride are in equivalent bridging configurations.

These complexes are examples of counter-complimentarity of the bridging groups in doubly-bridged dinuclear(II) complexes, and the overall magnetic interaction of these complexes is very weakly antiferromagnetic.

3.6. *Mass spectral studies*

The FAB mass spectra of copper(II) complexes of L^1H and L^2H show the molecular ion peaks (M^+) at *m*/*z* 635 and 613, respectively, thus supporting the monomeric nature of the complexes. The spectra show various fragments of the complexes isotopic patterns from copper and chloride.

Table 4. ^{1}H-NMR spectral data (ppm) of the free ligands L^1H and L^2H and their zinc complexes.

Compound	Methyl (–CH_3)	Aromatic proton (H)	Azomethine (–CH=N)	Phenolic OH	Amide-NH	Hydrazine NH_2
L^1H	2.33	7.43	8.32	10.14	12.15	5.81
L^2H	2.35	7.82	8.23	10.65	12.35	6.45
C-4	2.34	7.44	8.39	–	12.45	5.98
C-8	2.36	7.83	8.40	–	12.48	6.46

3.7. *^{1}H-NMR spectral studies (table 4)*

The ^{1}H-NMR spectra of the ligands show peaks at 8.32 ppm (L^1H) and 8.23 ppm (L^2H) assigned to –CH=N–. In zinc complexes these peaks shift downfield, suggesting coordination of azomethine. The singlet of phenolic-OH that appeared at 10.14 ppm (L^1H) and 10.65 ppm (L^2H) in ligands disappears in the complexes, suggesting deprotonation. The resonance due to NH_2 in L^1H at 5.81 ppm shifts to 5.98 ppm in the complex, suggesting that terminal amino nitrogens are involved in coordination; there is no difference in intensity or position for L^2H and its complex (6.45 ppm in ligand and 6.47 ppm in complex).

The information clearly indicates that L^1H coordinates to metal through phenolic oxygen via deprotonation, azomethine nitrogens and terminal NH_2, while L^2H coordinates through phenolic oxygen, azomethine nitrogen and both carbonyl oxygens.

3.8. *Thermal studies*

TG and DTG of the complexes have been carried out in nitrogen with a heating rate of 10°C min^{-1}; these complexes are stable at room temperature. The thermal decomposition data are presented in table 5. The TG curves of complexes of L^1H (Supplementary Material) show the initial weight loss in the temperature range 30–70°C, due to elimination of water; axially-coordinated chloride was lost in the temperature range 100–270°C. On increasing the temperature, further weight loss was observed up to 550°C, attributed to loss of bridging chloride and whole ligand moiety. No weight loss was observed beyond 550°C, due to formation of metal oxide. In complexes of L^2H the initial decomposition is accompanied by combined loss of lattice water and axially-coordinated chloride; further weight loss is due to decomposition of ligand and the bridging chloride. The final residue was found to be the corresponding oxides Co_2O_3, NiO, CuO and ZnO.

Based on chemical composition and physico-chemical studies, the following structure (figure 2) is proposed for these complexes.

4. Antibacterial and antifungal activity

The ligands and their corresponding complexes were screened for antifungal and antibacterial activity against *Aspergillus niger*, *Candida albicans*, *Pseudomonas auregenosa* and *Bacillus cirroflagellosus* by the cup plate method using Nutrient agar. The radial growth of the colony was recorded on completion of the incubation and the

Table 5. Thermal analysis of the binuclear complexes.

					Wt. loss (%)			Residue (%)	
Compound	Process (Decomposition)	Decomposition Temp. range (K)	Peak Temp. (K)	Decomposition Product	Obs.	Calcd	No. of moles	Obs.	Calcd
C-1	Water	313–433	343	H_2O	13.71	14.29	5	–	–
	Chloride	433–543	503	Cl	10.86	11.30	2	–	–
	Ligand + Chloride	543–803	673	L + Cl	58.14	54.37	2	27.57	26.13
C-2	Water	303–413	363	H_2O	13.88	14.49	5		
	Chloride	413–523	483	Cl	10.61	11.43	2		
	Ligand + Chloride	523–833	653	L + Cl	57.13	55.15	2	11.33	12.01
C-3	Water	327–443	383	H_2O	13.47	14.29	5		
	Chloride	443–533	503	Cl	10.62	11.27	2		
	Ligand + Chloride	533–823	693	L + Cl	57.82	54.37	2	11.39	12.65
C-4	Water	303–383	353	H_2O	14.18	13.52	5		
	Chloride	383–533	463	Cl	11.19	10.23	2		
	Ligand + Chloride	533–783	623	L + Cl	53.98	53.98	2	12.77	10.98
C-5	Water	313–413	373	H_2O	17.72	16.23	6	–	–
	Ligand + Bridging Cl	413–793	603	L + 3Cl	62.91	58.78	4	27.23	28.45
C-6	Water	303–423	383	H_2O	17.73	16.43	6	–	–
	Ligand + Bridging Cl	423–813	683	L + 3Cl	62.96	59.34	4	12.25	13.01
C-7	Water	303–403	353	H_2O	17.45	15.98	6	–	–
	Ligand + Bridging Cl	403–813	633	L + 3Cl	61.98	64.03	4	12.88	14.13
C-8	Water	303–433	393	H_2O	17.35	18.67	6	–	–
	Ligand + Bridging Cl	433–803	563	L + 3Cl	61.61	64.49	4	13.01	14.63

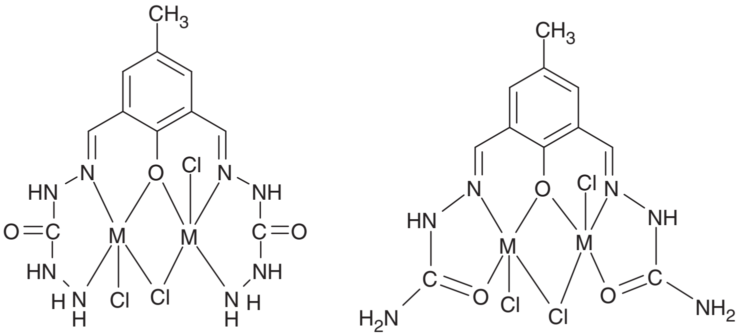

Figure 2. Proposed structures for the complexes of L^1H(C1–C4) and L^2H(C5–C8). M = Co(II), Ni(II), Cu(II) and Zn(II).

Table 6. Screening data of ligands and complexes.

		Representation zone of inhibition			
		Antibacterial		Antifungal	
Sl. no	Compound	P.a	B.c	A.n	C.a
	L^1H	++	++	+	+
	L^2H	++	++	++	++
C-1	$[Co_2L(\mu\text{-}Cl)Cl_2)]\cdot 5H_2O$	++	++	++++	+++
C-2	$[Ni_2L(\mu\text{-}Cl)Cl_2)]\cdot 5H_2O$	+	++	+++	+++
C-3	$[Cu_2L(\mu\text{-}Cl)Cl_2)]\cdot 5H_2O$	+	++	++++	++++
C-4	$[Zn_2L(\mu\text{-}Cl)Cl_2)]\cdot 5H_2O$	+	–	++	+++
C-5	$[Co_2L(\mu\text{-}Cl)Cl_2)]\cdot 6H_2O$	++	+	+++	+++
C-6	$[Ni_2L(\mu\text{-}Cl)Cl_2)]\cdot 6H_2O$	+	++	+++	+++
C-7	$[Cu_2L(\mu\text{-}Cl)Cl_2)]\cdot 6H_2O$	++	++	++++	+++
C-8	$[Zn_2L(\mu\text{-}Cl)Cl_2)]\cdot 6H_2O$	+	++	+++	+++

Pseudomonas auregenosa = P.a; *Bacillus Cirroflagellosus* = B.c; *Aspergillus niger* = A.n; *Candida albicans* = C.a
10 mm = −(inactive); 10–20 mm = +(weakly active); 21–25 mm = ++(moderately active); 26–35 mm = +++(highly active); 36–40 mm = ++++ (most active); DMF = 12 mm; Norfloxacin = 29 P.a and 31 B.c, Grisofulvin = 20 A.n and 23 C.a

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1) Concentration of the compound : 1 mg mL^{-1} in dimethyl formamide
2) Quantity in each cup : 0.1 mL
3) Diameter of the cup : 10 mm
4) Control of the antibacterial activity : Norfloxaicn
5) Control of the anti-fungal activity : Grisofulvin
6) Solvent used : Dimethyl formamide

mean diameter for each complex at a single concentration was recorded. The average percentage inhibition of the fungicidal growth medium was compared using the Vincent [56] equation: $I = 100\ (C\text{-}T)/C$, where I = percentage inhibition, T = average diameter of the fungal and bacterial growth on the tested plates and C = average diameter of the growth on the control plates. Data of the inhibition of the fungi and bacteria are given in table 6. The free ligands of carbohydrazone and semicarbohydrazone are inactive against *P. auregenosa*, weakly active against *B. cirroflagellosus* and moderately active against fungi *A. niger* and *C. albicans*. The fungi tested are more susceptible to the metal complexes than the bacteria and highly sensitive to copper(II) chelates of both ligands.

5. Conclusion

Reaction of metal(II) chloride with symmetric Schiff-bases L^1H and L^2H gave binuclear complexes. IR, Far-IR, and NMR studies indicate open-chain compounds with chloride as exogenous bridge. Electronic spectra suggest square-pyramidal coordination geometry for the complexes. Line broadening in the ESR spectra of copper(II) complexes is generally observed in chloro-bridged complexes due to dipolar interaction between the metal ions. This is further confirmed by weak antiferromagnetic interaction between the metal ions.

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