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Phenoxide bridged tetranuclear Co(II), Ni(II), Cu(II) and Zn(II) complexes: Electrochemical, magnetic and antimicrobial studies

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ABSTRACT

Phenoxide bridged later first row transition metal(II) complexes have been prepared by the interaction of later 3d transition metal(II) chlorides with tetranucleating compartmental Schiff base ligand system derived from 2,6-diformyl-4-methylphenol, *p*-phenylenediamine and 2-hydrazinobenzothiazole. Ligand and complexes were characterized by analytical, spectral (IR, UV–visible, ESR, FAB-mass and fluorescence), magnetic and thermal studies. All complexes are found to have octahedral geometry. The mutual influence of metal centres in terms of cooperative effect on the electronic, magnetic, electrochemical and structural properties was investigated. The Schiff base and its complexes have been screened for their antibacterial (against *Escherichia coli*, *Staphylococcus aureus*, *Pseudomonas aeruginosa*) and antifungal activities (against *Aspergillus niger*, and *Candida albicans*).

1. Introduction

Schiff-base compounds have a great importance in coordination chemistry, due to their ability to form a range of complexes which have applications in different fields. One approach in the field of coordination chemistry has been to investigate the use of Schiff-base ligands to develop phenoxo-bridged transition metal complexes that have applications in biomedical [1–4], biomimetic and catalytic systems [5]. Planar ligands with amine or imine donor groups and bridging phenol oxygens are referred to as Robson-type ligands [6]. The donor groups of these compartmental ligands provide a significant diversification of the coordination sites making them good candidates for metal ion complexation and for mimicking biological systems. Recently, the design and synthesis of polynuclear metal complexes has been a topic of growing interest [7–9] for the reason that such supramolecular materials not only display interesting structures, but also occasionally exhibit novel properties such as porosity, magnetism and non-linear optical behaviour [10]. The chemistry of 2,6-diformyl-4-methylphenol and its derivatives is of a great interest in designing the compartmental ligands which can form polynuclear complex systems having magnetic communication between the metal centres. The study of their stereochemical, electronic, magnetic, catalytic spectroscopic and also biological properties have allowed the proposal of probes for some important applications [11,12]. Some compounds containing 2,6-diformyl-4-methylphenol and 2-substituted benzothiazole moiety do fluoresce and act as fluorescence sensor for zinc and can be used as zinc ion-selective luminescent probe for biological application under physiological conditions [13–15].

Benzothiazole finds use in research as a starting material for the synthesis of larger, usually bioactive structures. Its aromaticity makes it relatively stable. From the literature survey, it has been found that extensive work has been reported on 2-substituted benzothiazole derivatives in past and evaluated for different activities like antibacterial, anticancer, antiviral, antitumor [4], antifungal, anti-inflammatory, antioxidative, radioprotective, antidiabetic, anthelmintic, anti-leishmanial, anticonvulsant and neuroprotective [16–19].

In this paper we describe the preparation, characterization and antimicrobial activity of cobalt(II), nickel(II), copper(II) and zinc(II) complexes with a new Schiff base, LH_2 (Fig. 1), derived by condensing 2,6-diformyl-4-methylphenol, *p*-phenylene diamine and 2-hydrazinobenzothiazole. The complexes have the general composition $[M_4L(\mu\text{-}Cl_2)Cl_4(H_2O)_6]$.

2. Experimental

2.1. Materials and methods

Estimation of the metal(II) ions was done according to the standard methods. The molar conductivity measurements were made on ELICO-CM-82 conductivity bridge. The magnetic susceptibility measurements were made on Faraday balance at room temperature using $Hg[Co(SCN)_4]$ as calibrant. The ^1H NMR spectra were recorded

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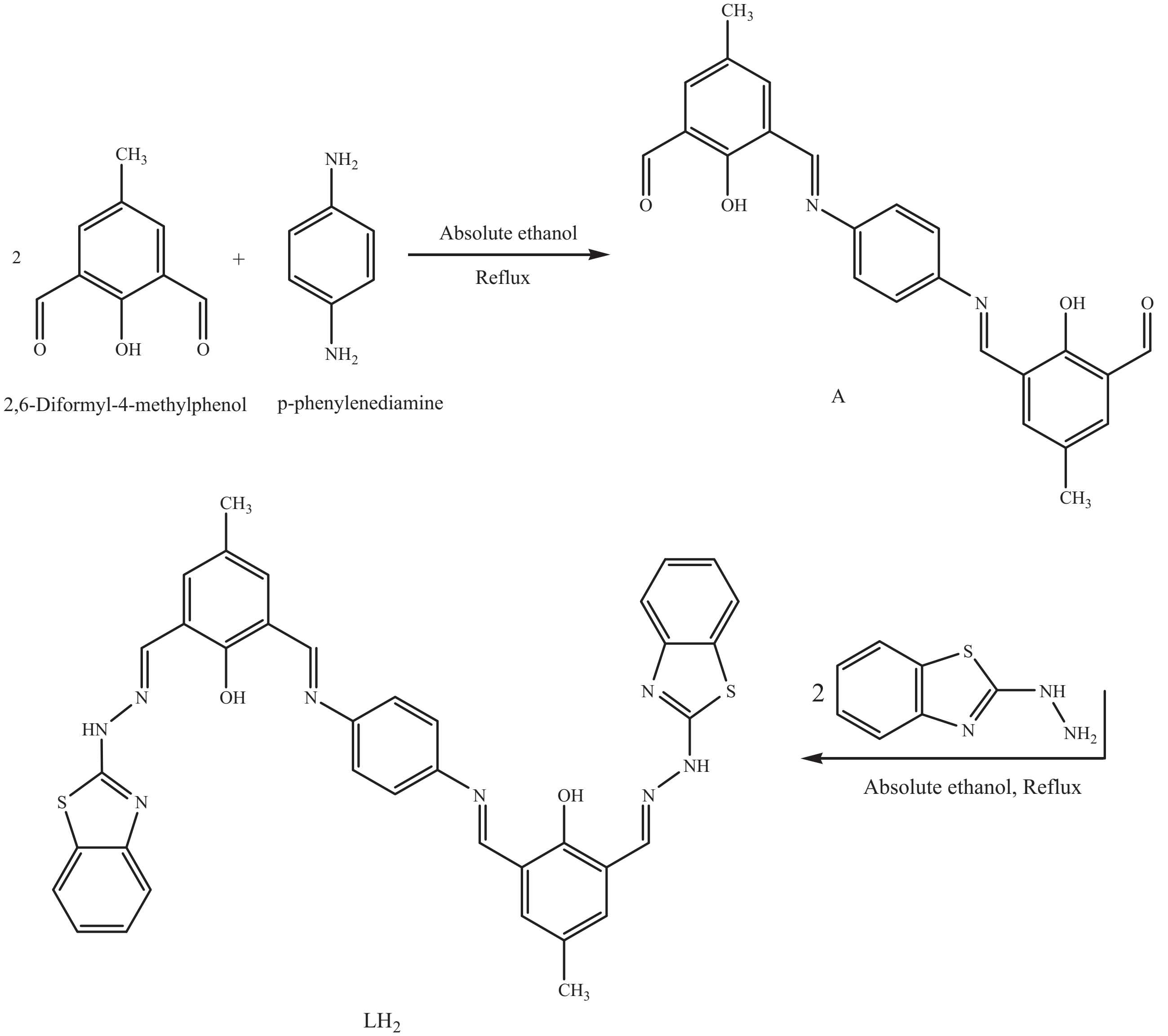

Fig. 1. Preparation of the ligand LH_2.

in $CDCl_3$ and DMSO-d_6 solvent on Bruker-300 MHz spectrometer at room temperature using TMS as internal reference. IR spectra were recorded in a KBr matrix using an Impact-410 Nicolet (USA) FT-IR spectrometer in 4000–400 cm^{-1} range. The electronic spectra of the complexes were recorded on a Hitachi 150-20 spectrophotometer in the range of 1000–200 nm. The cyclic voltametric studies were performed at room temperature in DMSO under O_2 free condition using CH instruments Electrochemical analyzer, CHI-1110A (USA). The ESR spectra of the copper complexes were scanned (at room temperature and liquid nitrogen temperature) on a Varian E-4X-band EPR spectrometer, using TCNE as the g-marker. TG and DTA measurements of the complexes were recorded in nitrogen atmosphere on Universal V2.4F TA instrument keeping final temperature at 800 °C and heating rate 10 °C/min. The FAB mass spectra were drawn from JEOL SX 102/DA-6000 mass spectrometer using Argon/Xenon (6 kV, 10 mA) as the FAB gas.

2.2. Synthesis

All chemicals used were of reagent grade. Solvents were dried and distilled before use according to standard procedures [20]. 2,6-Diformyl-4-methylphenol was prepared according to the method reported by Denton and Suschitzky [21] but with slight modification. 2-Mercaptobenzothiazole was purchased from SD Fine Chemicals. The zinc chloride used was anhydrous whereas the other metal salts were in their hydrated form, i.e., $CoCl_2{\cdot}6H_2O$, $NiCl_2{\cdot}6H_2O$ and $CuCl_2{\cdot}2H_2O$.

2.2.1. 2-Hydrazinobenzothiazole

A mixture of hydrazinehydrate (0.01 mol), 2-mercaptobenzothiazole (0.01 mol) and EtOH (ca. 50 cm^3) was placed in a round-bottomed flask and boiled under reflux for 8–10 h, i.e., until H_2S evolution had ceased. The reaction mixture was then left overnight and, on cooling, a white crystalline solid mass separated. This was filtered off, air dried and recrystallized from EtOH [4]. m.p.: 193–194 °C (Lit. 197–199 °C), yield: 80%.

2.2.2. Synthesis of ligand LH_2

2,6-Diformyl-4-methylphenol (0.1 mol) was taken in 50 ml of absolute ethanol, to which *p*-phenylenediamine (0.05 mol) in absolute alcohol was added dropwise with constant stirring. Further the mixture was stirred at room temperature for 30 min. The reaction

Table 1
Analytical and conductance data of complexes.

Compound	Yield in %	Elemental analysis (%)			Found (calculated)			Molar cond. $\Lambda M\ \Omega^{-1}\ cm^2\ mol^{-1}$
		C	H	N	S	M	Cl	
A	90	71.83 (72.00)	5.02 (4.96)	7.06 (6.99)	–	–	–	–
LH_2	78	65.43(65.76)	4.55 (4.34)	16.70 (16.14)	9.14 (9.22)	–	–	–
$[Co_4L(\mu\text{-}Cl_2)Cl_4(H_2O)_6].H_2O$	74	36.70 (36.02)	3.48 (3.31)	8.45 (8.84)	5.25 (5.06)	18.87 (18.66)	16.97 (16.78)	38.7
$[Ni_4L(\mu\text{-}Cl_2)Cl_4(H_2O)_6].2H_2O$	73	35.73 (35.45)	3.48 (3.42)	8.86 (8.72)	4.76 (4.99)	18.40 (18.28)	16.75 (16.56)	23.8
$[Cu_4L(\mu\text{-}Cl_2)Cl_4(H_2O)_6].4H_2O$	76	34.08 (34.00)	3.07 (3.57)	8.96 (8.35)	4.55 (4.77)	18.96 (18.93)	15.92 (15.84)	34.2
$[Zn_4L(\mu\text{-}Cl_2)Cl_4(H_2O)_6]$	72	35.86 (35.79)	3.25 (3.13)	8.88 (8.79)	5.50 (5.02)	20.60(20.51)	16.76 (16.68)	15.9

mixture was refluxed on water bath temperature for 4 h. The reddish solid that formed (precursor A) was filtered off and washed with hot ethanol (m.p.: 260 °C, yield: 90%).

The ethanolic solution of 2-hydrazinobenzothiazole (0.2 mol) is added slowly to the above obtained compound (0.1 mol) in 70 ml of ethanol with constant stirring. After completion of the addition the mixture was stirred at room temperature for 15 min and refluxed on water bath temperature for 4 h. Catalytical amount of acetic acid is added while refluxing. The dirty-yellow solid that formed was filtered off and washed with hot ethanol (m.p.: 340 °C, yield: 78%). The reaction pathway is given in Fig. 1.

2.2.3. *Preparation of complexes*

The Co^{II}, Ni^{II}, Cu^{II} and Zn^{II} complexes were prepared by refluxing the respective hydrated metal chloride (0.04 mol) in EtOH (30 cm^3) with ligand (0.01 mol) for 4 h, during this little ammonia was added to separate the complexes in solid form. So obtained solids were filtered off, washed with hot ethanol and dried over fused $CaCl_2$.

3. Results and discussion

The phenoxo bridged binuclear complexes obtained in the present investigation were non-hygroscopic and in the form of amorphous solids. They are insoluble in ethanol, water and chloro-hydrocarbons, but partially soluble in DMF and DMSO. The analytical and physicochemical data of the complexes are summarized in Table 1.

3.1. *Infrared spectral studies*

The key IR absorption bands are summarized in Table 2. The FT-IR spectrum of free ligand shows a band in the region 3395–3407 cm^{-1}, assigned to the phenolic ν(OH) group. The peaks at 1676 and 1619 cm^{-1} in precursor A are due to aldehydic ν(C=O) and azomethine ν(>C=N) respectively [3]. The azomethine ν(>C=N), which is observed at 1619 cm^{-1} in ligand has shifted to higher frequency in all complexes due to its participation in the coordination. ν(C=N) of benzothiazole ring is observed at 1570 cm^{-1} in ligand and has shifted to lower frequency region in all complexes indicating the coordination of nitrogen [4]. Phenolic ν(C–O) in ligand observed at 1274 cm^{-1} shifted to higher frequency in all complexes due to coordination of oxygen upon deprotonation [22]. The appearance of bands in the region of 1530–1545 cm^{-1} in all the complexes suggests phenoxide bridging with the metal ions [3]. Further, the bands in the region 520–570 cm^{-1} and 400–480 cm^{-1}, are probably due to the formation of M–O and M–N bonds respectively [23]. Also, the presence of coordinated water molecules in the complexes is supported by the two bands in the ranges 820–850 and 737–756 cm^{-1} which are due to (–OH) rocking and wagging mode of vibrations, respectively [24].

3.2. *^1H NMR studies*

NMR studies provide significant conclusion regarding the nature of bonding and coordination. Precursor A, ligand LH_2 and zinc complex were scanned in the region of 0–16 ppm for proton NMR studies. The spectrum of precursor A show signals at 13.98, 10.56 and 8.73 ppm corresponding to phenolic, azomethine and aldehydic protons respectively. Aromatic protons resonate in the range 6.75–7.78 ppm. NMR spectrum of ligand LH_2 showed broad peak at 12.31 ppm due to phenolic –OH protons and are exchangeable with D_2O. Absence of this peak in the spectrum of zinc complex indicates the coordination of phenolic oxygen after deprotonation. The signal at 8.49 ppm is due to azomethine protons attached to hydrazide part, 7.78 ppm is due to azomethine protons attached to *p*-phenylenediamine and are shifted to little downfield in zinc complex, i.e., to 8.71, 8.24 ppm respectively owing to the coordination through nitrogen. The –NH– of hydrazide resonated at 6.65 and 6.41 ppm in ligand and complex respectively. The aromatic protons resonated in the region 7.12–7.61 ppm and 6.87–7.50 ppm in ligand and complexes respectively. Ar–CH_3 protons resonated around 2.33 ppm for all above compounds. The absence of OH protons (coordinated H_2O) may be due to their replacement by DMSO-*d*6 molecules [25].

3.3. *Magnetic susceptibility and absorption spectral studies*

The magnetic susceptibility of metal ions, encapsulated by the organic ligand field, is one of the most important properties of coordination compounds, which focuses the electronic structure [26]. The magnetic moments of the complexes were recorded at room temperature and the observed magnetic moment value for the Co(II), Ni(II) and Cu(II) complexes are 5.33, 3.49 and 1.68 BM respectively. The magnetic moment value for copper complex is less than the spin only value of free metal ion. Hence the antiferromagnetic exchange interaction exists through endogenous phenoxide bridge. The common entity measured for these ions from the magnetism

Table 2
Infrared spectral data in cm^{-1}.

Compound	ν(C=N) (azomethine)	ν(C=N) (benzothiazole)	ν(C–O) (phenolic)	ν(M–N)	ν(M–O)
LH_2	1619	1570	1274	–	–
$[Co_4L(\mu\text{-}Cl_2)Cl_4(H_2O)_6]\cdot H_2O$	1626	1542	1280	468	551
$[Ni_4L(\mu\text{-}Cl_2)Cl_4(H_2O)_6]\cdot 2H_2O$	1632	1556	1276	471	530
$[Cu_4L(\mu\text{-}Cl_2)Cl_4(H_2O)_6]\cdot 4H_2O$	1627	1562	1282	474	512
$[Zn_4L(\mu\text{-}Cl_2)Cl_4(H_2O)_6]$	1621	1543	1278	473	520

Table 3
The electronic spectra and magnetic moment data.

Compound	λ_{max} (nm)	μ_{eff} (BM)
LH_2	340, 387	–
$[Co_4L(\mu\text{-}Cl_2)Cl_4(H_2O)_6]\cdot H_2O$	268, 419, 450, 583, 678	5.33
$[Ni_4L(\mu\text{-}Cl_2)Cl_4(H_2O)_6]\cdot 2H_2O$	266, 399, 440, 617, 679	3.49
$[Cu_4L(\mu\text{-}Cl_2)Cl_4(H_2O)_6]\cdot 4H_2O$	268, 415, 430, 605	1.68
$[Zn_4L(\mu\text{-}Cl_2)Cl_4(H_2O)_6]$	265, 386, 440	Diamagnetic

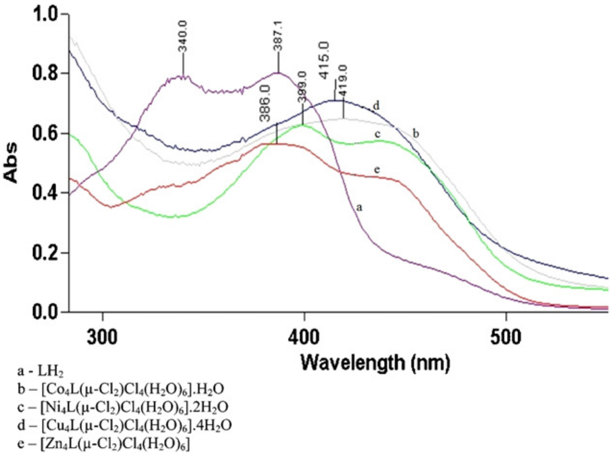

Fig. 2. UV–visible spectra of ligand and complexes in the range 275–500 nm.

point of view is that, they have surrounded by the octahedral ligand field.

The electronic absorption spectra of the complexes were recorded in DMF solution over the range 200–1000 nm and the spectral data are listed in Table 3. Ligand exhibits absorption bands at 340 and 387 nm, which are due to the intra ligand $\pi \rightarrow \pi^*$ transition and $n \rightarrow \pi^*$ transitions respectively. In all complexes $\pi \rightarrow \pi^*$ transition has suffered blue shift (Fig. 2) which internally supports the enough stability of bonding molecular orbitals and indicates the coordination of nitrogen of benzothiazole unit. The $n \rightarrow \pi^*$ transition associated with azomethine linkage. This band in complex has shown bathochromic shift due to the donation of a lone pair of electrons to the metal and hence the coordination of azomethine [27]. The medium absorption bands at 415–440 nm range in all complexes are charge transfer transitions from the ligand phenoxide to metal ions (LMCT). The d–d transitions have observed for all complexes in the visible region except for zinc(II) complex. Copper complex exhibits the broad band at 605 nm corresponding to the $^2E_g \rightarrow {}^2T_{2g}$ transition which is in agreement with the copper complexes of octahedral geometry [28]. Co^{II} complex shows two bands at 583 and 678 nm, because of the $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ and $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ transitions concordant with octahedral structure. Ni^{II} complex exhibit bands at 617 and 679 nm due to $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ and $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ transitions which shows its octahedral nature [29].

3.4. Fluorescence studies

Fluorescence studies have been performed by using a Spectrofluorimeter model F-7000 (Hitachi, Japan) equipped with 150 W Xenon lamp and a slit width of 3 nm. Schiff-base systems exhibit fluorescence due to intraligand $\pi \rightarrow \pi^*$ transitions. Fluorescence spectra of the ligand and complexes show (Fig. 3) an emission band at 519 nm when excited with 440 nm radiation, at room temperature with sample concentration of 0.1 mmol in DMF. Almost double enhancement in fluorescence intensity was observed in zinc complex. The emission is neither MLCT (metal-to-ligand charge transfer) nor LMCT in nature, since a similar emission is also observed for the free ligand with reduced intensity. Hence we tentatively assign it to the intraligand ($\pi \rightarrow \pi^*$) fluorescence. After complexation with zinc, the free rotation of the flexible bonds of the ligand is reduced and energy dissipation through non-radiative channels is reduced [30]. As ligand LH_2 acts as fluorescence sensor for Zn and can be used as zinc ion-selective luminescent probe for biological application under physiological conditions [13,14]. The fluorescence property of ligand was quenched with copper and vanished completely with cobalt and nickel after complexation.

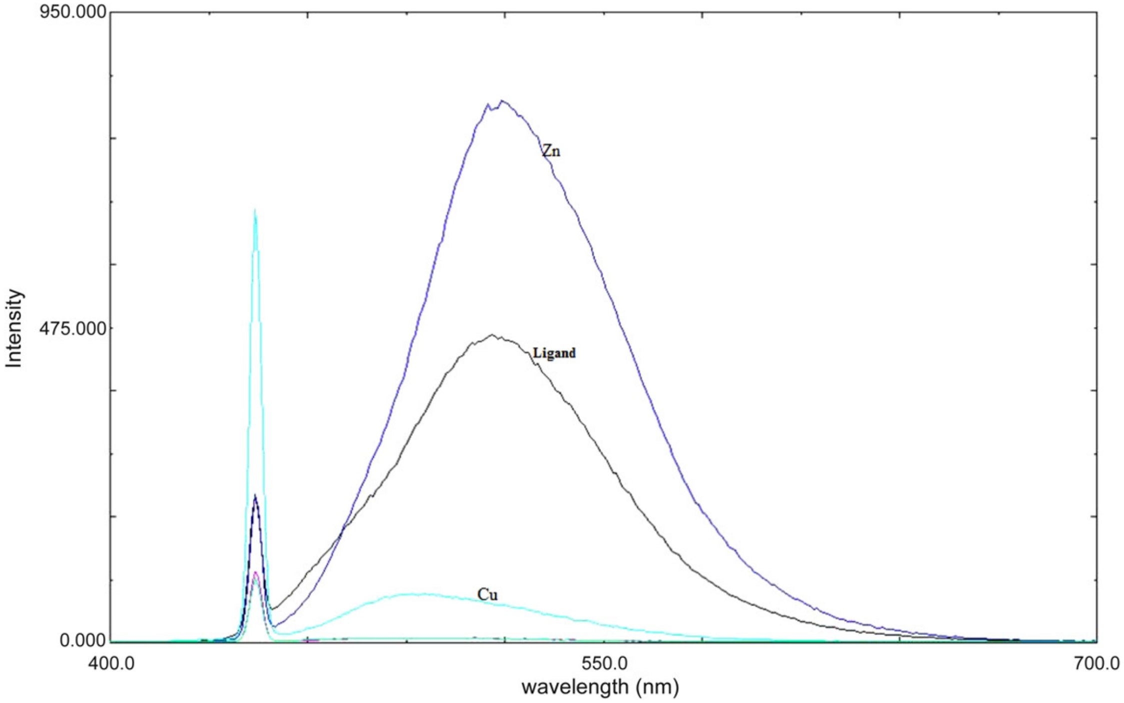

Fig. 3. Emission spectra of ligand and complexes.

Table 4
Antimicrobial data of ligand and metal complexes.

Compound	Concentration (μg ml^{-1})	% inhibition against bacteria		% inhibition against fungi	
		Pseudomonas aeruginosa	*Staphylococcus aureus*	*Aspergillus niger*	*Candida albicans*
Ligand (LH_2)	5	36.15	5.71	0	0.36
	10	36.15	6.67	7.55	1.35
	25	41.54	8.10	37.74	6.76
	50	48.46	8.57	39.62	17.57
	100	51.54	42.86	50.94	29.73
$[Co_4L(\mu\text{-}Cl_2)Cl_4(H_2O)_6]\cdot H_2O$	5	15.38	3.81	16.98	0
	10	40.00	6.19	33.96	4.05
	25	46.15	6.67	39.62	8.11
	50	50.77	8.57	50.94	24.32
	100	52.31	9.52	64.15	44.89
$[Ni_4L(\mu\text{-}Cl_2)Cl_4(H_2O)_6]\cdot 2H_2O$	5	36.92	4.29	16.98	1.35
	10	40.00	5.71	20.75	4.05
	25	48.46	7.62	32.08	8.11
	50	56.15	19.52	37.74	16.22
	100	63.08	24.29	39.62	21.62
$[Cu_4L(\mu\text{-}Cl_2)Cl_4(H_2O)_6]\cdot 4H_2O$	5	36.92	2.86	20.75	2.70
	10	38.46	8.10	33.96	10.81
	25	44.62	10.48	35.85	21.62
	50	55.38	17.62	43.40	44.59
	100	64.62	18.10	73.58	55.41
$[Zn_4L(\mu\text{-}Cl_2)Cl_4(H_2O)_6]$	5	38.46	1.43	0	0
	10	39.23	7.62	0	0
	25	46.15	8.10	0	12.16
	50	54.62	10.95	16.98	21.32
	100	57.69	11.90	28.30	29.73
Gentamycin	5	60.00	27.62	–	–
	10	68.46	54.29		
	25	80.00	76.67		
	50	86.15	95.71		
	100	90.77	100		
Amphotericin	5	–	–	41.51	19.57
	10			53.49	27.38
	25			67.93	44.60
	50			100	78.38
	100			100	100

3.5. *Molar conductivity measurements*

The molar conductance values of all the complexes measured at room temperature in DMF solution with 10^{-3} mol dm^{-3} concentration fall in the range 15.9–38.7 Ω^{-1} cm^2 mol^{-1}, which indicates the non-electrolytic nature of the complexes [31].

3.6. *Electron spin resonance spectral study*

The X-band ESR spectrum of copper(II) complex in solid form was scanned in the region of 9000 MHz with corresponding field intensity at ~3000 Gauss, at room temperature as well as liquid nitrogen temperature. The spectrum is characteristically a tetragonally distorted octahedral, which shows slight broadened features with $g\perp$ and $g_{||}$ values of 2.079 and 2.253. The spectrum at liquid nitrogen temperature is slightly broadened. In general, chloro-bridged binuclear copper(II) complexes give broad ESR signals [4] in which the broadening is assigned to a dipolar interaction. The existences of $g_{||} > g\perp$ suggests that $dx^2 - y^2$ is in the ground state with the d^9 (Cu^{II}) configuration [32]. The g values are related to the axial symmetry parameter, G, by the expression $G = (g_{||} - 2)/(g\perp - 2)$. The G values measure the extent of the exchange interaction between copper centres in the polycrystalline solid. In the present case, $G = 3.19$, which indicates the presence of a weak exchange interaction in the complex. The ESR spectra at room temperature and liquid nitrogen temperature have similar nature, which shows no considerable change in the geometry of ligand field around the metal ion when temperature is lowered.

3.7. *FAB mass spectral studies*

In the mass spectrum of the copper complex shows m/z ion peak at 1342 corresponding to molecular weight of the complex. The molecular ion observed in the spectrum corresponds to the mass of

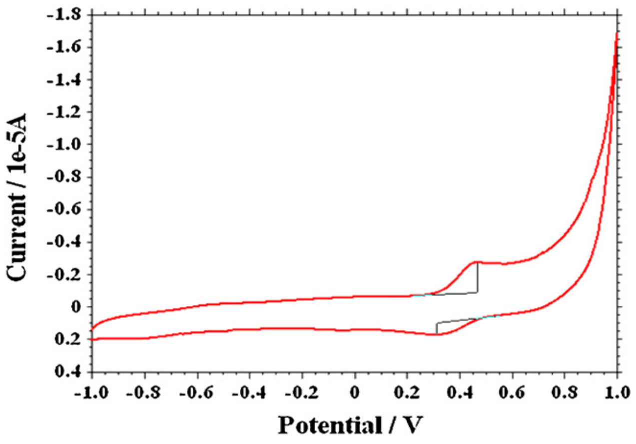

Fig. 4. Cyclic voltammogram of Cu^{II} complex at the scan rate of 0.05 V/s.

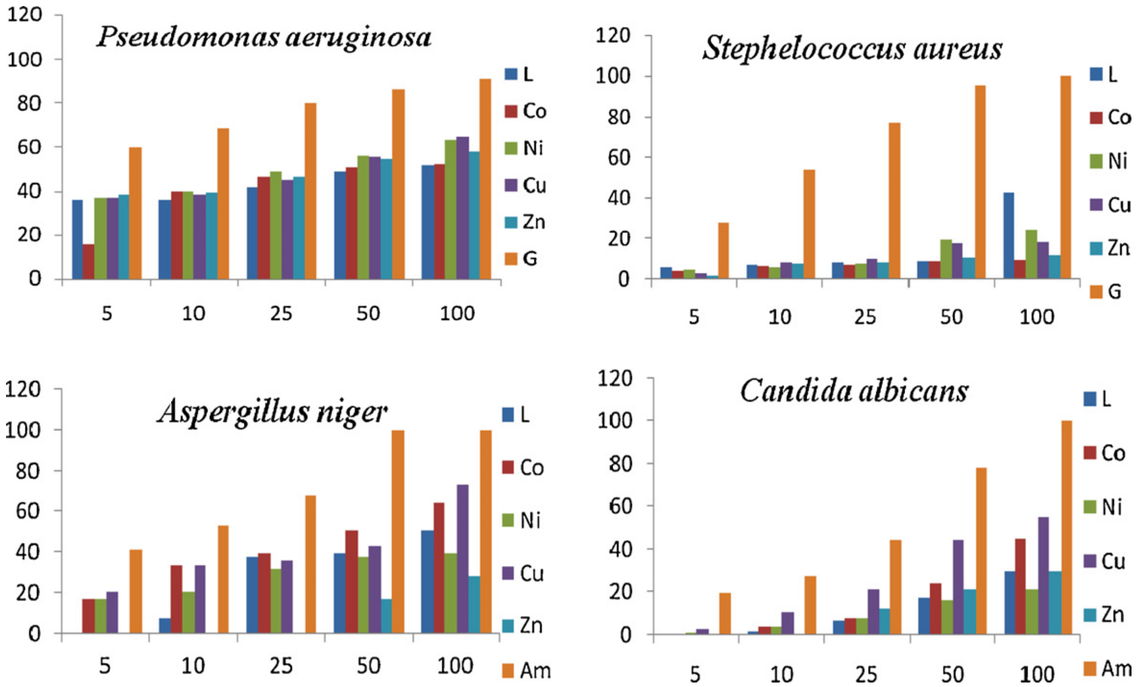

Fig. 5. Graphical representation of antimicrobial studies (% inhibition V/s µg ml^{-1}).

entire complex including bridging chloride, lattice held and coordinated water molecules. The spectrum also contains peaks due to molecular cations of the various fragments of the complex. The information gathered from FAB mass data agrees well with elemental analysis data. The tentative structures of complexes are given in Fig. 6.

3.8. Thermogravimetric analysis

The thermal stability and decomposition pattern of the complexes was analyzed by TG and DTA studies. Thermo gravimetric analysis of the complexes has been carried out in nitrogen atmosphere over the temperature range of 30–800 °C with heating rate of 10 °C/min. All complexes show similar decomposition pattern with weight losses in three stages. In the first stage 9.9%, 10.9%, 12.5% and 7.8% in the temperature range 40–180 °C is attributed to the weight loss of coordinated water molecules along with lattice held water for Co^{II}, Ni^{II}, Cu^{II} and Zn^{II} complexes respectively. The corresponding DTA curve indicates the endothermic nature of the process. In the next stage the weight loss around 16% in all complexes correspond to coordinated chlorides in the temperature range 180–400 °C. In the third stage weight loss is due to the decomposition of ligand part. The final decomposition products were found to be stable metal oxides. The weights of the

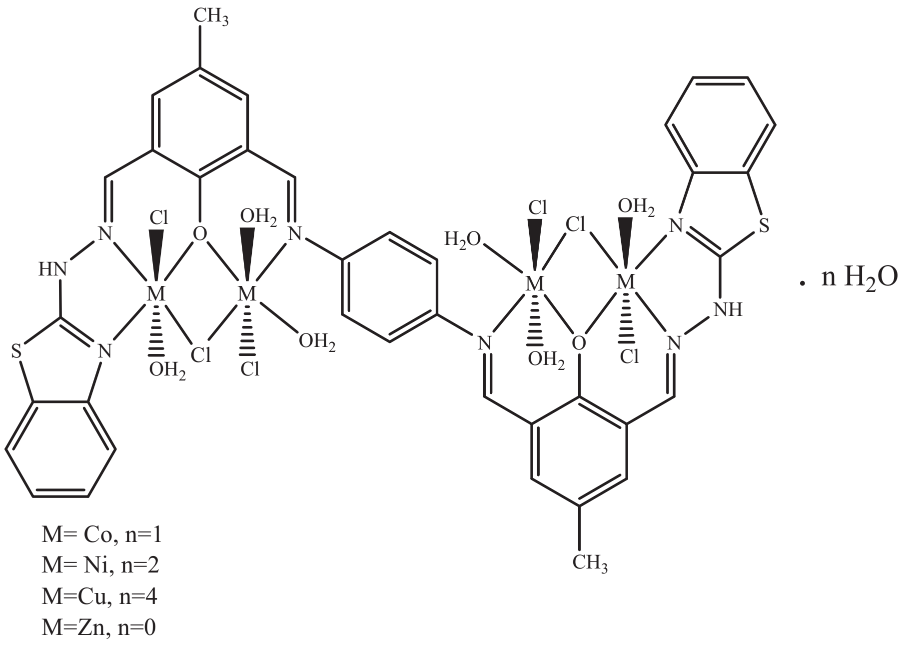

Fig. 6. Proposed structures of the complexes.

final decomposition products left are 32%, 31%, 40% and 41% for cobalt, nickel, copper and zinc complexes respectively. The fragmentation patterns of the thermograms agree well with theoretical calculations and support the stereochemical and stoichiometrical assignments.

3.9. Electrochemistry

The redox behaviour of ligands and their complexes were scanned at room temperature in DMF solution using cyclic voltammeter in the working potential range of −1 to +1 V at three different scan rates viz., 0.05, 0.1 and 0.15 V/s under the nitrogen atmosphere. The voltammograms of the copper complex is shown in Fig. 4. In the electrochemical investigation, the anodic peak (E_{pa}) observed in the voltammogram at 0.467, 0.482, 0.481 V represents oxidation ($Cu^{II} \rightarrow Cu^{III}$) at varying scan rates of 0.05, 0.1, and 0.15 V/s, respectively. The corresponding cathodic potential scans give peaks (E_{pc}) at 0.311, 0.342, 0.339 V representing reduction ($Cu^{III} \rightarrow Cu^{II}$). The high value of ΔE_p, separation between the cathodic and anodic peak potentials ($E_{pa} - E_{pc} > 60$ mV), indicates quasi-reversible nature of the redox process [33]. I_{pc}/I_{pa} is almost constant but not unity which further supports the quasireversible nature of electron transfer process [34]. Ligand and other complexes are found to be electrochemically innocent.

3.10. Antimicrobial analysis

The ligand and its complexes were screened for antibacterial activity against *Staphylococcus aureus*, *Escherichea coli*, *Pseudomonas aeruginosa* and antifungal activity against *Aspergillus niger*, *Candida albicans* by turbidity method at 100 μg ml^{-1} using Gentamycin (for bacteria) and Amphotericin (for fungi) as standards. The minimum inhibitory concentration (MIC) is fixed to be 5–50 μg ml^{-1} accordingly. Schiff base is highly active against *P. aeruginosa* and the activity increased on complexation. Increase in activity is may be due to the metal chelation which makes complexes, more powerful and potent bactereostatic agents [35,36]. Ligand showed good activity against *C. albicans* and *A. niger*, which has been increased on complexation with cobalt and copper. Ligand is moderately active against *S. aureus* whereas complexes have not shown any activity against *E. coli*. The data is summarized in Table 4 and the same is represented graphically in Fig. 5.

4. Conclusion

Ligand reported in this article is tetranucleating towards the later first row transition metal ions. All synthesized complexes have $[M_4L(\mu\text{-}Cl_2)Cl_4(H_2O)_6]\cdot nH_2O$ composition and octahedral geometry. All complexes are monomers and non-electrolytic in nature. Antiferromagnetic interaction is present between the metal ions in copper complex via phenoxide bridge. Ligand is fluorescence active and can act as fluorescence sensor for zinc. The copper complex has shown quasireversible redox responses over the applied potential range, whereas ligand and other complexes are found to be electrochemically innocent. All compounds have shown good antimicrobial activity.

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References

[1] N.A. Illan-Cabeza, F. Hueso-Urena, M.N. Moreno-Carretero, J.M. Martinez-Martos, M.J. Ramirez-Exposito, J. Inorg. Biochem. 102 (2008) 647–655.

[2] S. Sreedaran, K. Shanmuga Bharathi, A. Kalilur Rahiman, L. Jagadish, V. Kaviyarasan, V. Narayanan, J. Incl. Phenom. Macrocycl. Chem. 66 (2010) 297–306.

[3] S. Sreedaran, K.S. Bharathi, A.K. Rahiman, R. Prabu, R. Jagadesh, N. Raaman, V. Narayanan, Trans. Met. Chem. 34 (2009) 33–41.

[4] S.M. Annigeri, A.D. Naik, U.B. Gangadharmath, V.K. Revankar, V.B. Mahale, Trans. Met. Chem. 27 (2002) 316–320.

[5] S.J. Smith, C.J. Noble, R.C. Palmer, G.R. Hanson, G. Schenk, L.R. Gahan, M.J. Riley, J. Biol. Inorg. Chem. 13 (2008) 499–510.

[6] N.H. Pilkington, R. Robson, Aust. J. Chem. 23 (1970) 2225–2236.

[7] L.K. Thompson, C.J. Matthews, L. Zhao, Z.Q. Xu, D.O. Miller, C. Wilson, M.A. Leech, J.A.K. Howard, S.L. Heath, A.G. Whittaker, R.E.P. Winpenny, J. Solid State Chem. 159 (2001) 308–320.

[8] P. Gamez, P. de Hoog, M. Lutz, W.L. Driessen, A.L. Spek, J. Reedijk, Polyhedron 22 (2003) 205–210.

[9] A. Maspero, S. Brenna, S. Galli, A. Penoni, J. Organomet. Chem. 672 (2003) 123–129.

[10] M.T. Bujaci, X.T. Wang, S.J. Li, C. Zheng, Inorg. Chim. Acta 333 (2002) 152–154.

[11] P.A. Vigato, S. Tamburini, Coord. Chem. Rev. 248 (2004) 1717–2128.

[12] S. Khanra, T. Weyhermüller, E. Bill, P. Chaudhuri, Inorg. Chem. 45 (2006) 5911–5923.

[13] P. Jiang, Z. Guo, Coord. Chem. Rev. 248 (2004) 205–229.

[14] P. Roy, K. Dhara, M. Manassero, J. Ratha, P. Banerjee, Inorg. Chem. 46 (2007) 6405–6412.

[15] T. Chattopadhyay, M. Mukherjee, K.S. Banu, A. Banerjee, E. Suresh, E. Zangrando, D. Das, J. Coord. Chem. 62 (2009) 967–979.

[16] G. Alang, R. Kaur, A. Singh, P. Budhlakoti, A. Singh, R. Sanwal, Int. J. Pharm. Biol. Arch. 1 (2010) 56–61.

[17] H. Ucar, K. Van derpoorten, S. Cacciaguerra, S. Spampinato, J.P. Stables, P. Depovere, M. Isa, B. Masereel, J. Delarge, J.H. Poupaert, J. Med. Chem. 41 (1998) 1138–1145.

[18] A.R. Barde, H.K. Barsu, A.S. Bobade, Indian Drugs 35 (1998) 554–557.

[19] C.D. Prouillac, P. Hernandez, C. Amourette, M. Diserbo, C. Lion, G. Rima, Bioorg. Med. Chem. 17 (2009) 5275–5284.

[20] A.I. Vogel, Text Book of Practical Organic Chemistry, 5th ed., Longman, London, 1989.

[21] D.A. Denton, H. Suschitzky, J. Chem. Soc. (1963) 4741–4743.

[22] A.M. El-Hendawy, A.H. Alkubaisi, A.G. El-Ghany El-Kourashy, M.M. Shanab, Polyhedron 12 (1993) 2343–2350.

[23] K. Nakamato, Infrared and Raman Spectra of Inorganic and Coordination Compounds, Wiley Interscience, New York, 1971.

[24] S.M.E. Khalil, J. Chem. Pap. 54 (2000) 12–18.

[25] M. Shebl, H.S. Seleem, B.A. El-Shetary, Spectrochim. Acta A 75 (2010) 428–436.

[26] I.B. Bersuker, Electronic Structure and Properties of Transition Metal Compounds, Wiley, New York, 1996.

[27] E.W. Ainssough, A.M. Brodie, J. Rangford, J.M. Waters, J. Chem. Soc. Dalton Trans. (1997) 279–282.

[28] A.B.P. Lever, Inorganic Electronic Spectroscopy, Elsevier, New York, 1968.

[29] S.A. Sallam, A.S. Orabi, Trans. Met. Chem. 27 (2002) 447–453.

[30] A.D. Naik, V.K. Revankar, Proc. Indian Acad. Sci. (Chem. Sci.) 113 (2001) 285–290.

[31] W.J. Geary, Coord. Chem. Rev. 81 (1971) 81–122.

[32] M. Shakir, S.P. Varkey, I.S. Hameed, Polyhedron 13 (1994) 1355–1361.

[33] C.L. Bailey, R.D. Bereman, D.P. Rillema, Inorg. Chem. 25 (1986) 3149–3153.

[34] S. Budagumpi, U.N. Shetti, N.V. Kulkarni, V.K. Revankar, J. Coord. Chem. 62 (2009) 3961–3968.

[35] Z.H. Chohan, A. Scozzafava, C.T. Supuran, J. Enzyme Inhib. Med. Chem. 18 (2003) 259–263.

[36] N. Dharamraj, P. Viswanathamurthi, K. Natrajan, Trans. Met. Chem. 26 (2001) 105–109.