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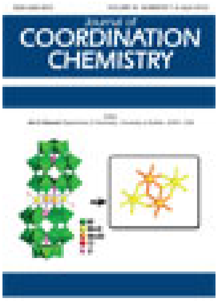

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Synthesis, characterization, and biological activities of zinc, cadmium, copper, and nickel complexes containing meta -aminophenyl benzimidazole

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Synthesis, characterization, and biological activities of zinc, cadmium, copper, and nickel complexes containing *meta*-aminophenyl benzimidazole

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ZnX_2, CdX_2, CuX_2, and NiX_2 ($X = Cl^-$, Br^-, ClO_4^-, or NO_3^-) react with *meta*-aminophenyl benzimidazole in 1 : 2 mole ratio at reflux in methanol to give $Zn_2Cl_4L_3 \cdot 2H_2O$, $ZnBr_2L_2(OH_2)$, $[Zn(OClO_3)L_3]ClO_4 \cdot 3H_2O$, $CdCl_2L(OH_2)$, $Cd_2Br_4L_3 \cdot 2H_2O$, $Cd(ONO_2)_2L_2 \cdot 2H_2O$, $[Cu_2Cl_4L_3] \cdot 2H_2O$, $Cu_2Br_4L_3$, $[Cu(OClO_3)L_2]_2(ClO_4)_2$, $[NiCl_2L(OH_2)] \cdot 2H_2O$, $[NiBrL_3]Br \cdot 3H_2O$, and $[Ni(OClO_3)L_3]ClO_4 \cdot H_2O$. These complexes were characterized by elemental analysis, melting point, TGA, conductivity, magnetic moment measurements, IR, far-IR, NMR, electronic, and mass spectral studies. Based on these studies, $Zn_2Cl_4L_3 \cdot 2H_2O$ and $Cd_2Br_4L_3 \cdot 2H_2O$ were assigned binuclear structures while $[Zn(OClO_3)L_3]ClO_4 \cdot 3H_2O$, $CdCl_2L(OH_2)$, $Cd(ONO_2)_2L_2 \cdot 2H_2O$, $[NiCl_2L(OH_2)] \cdot 2H_2O$, and $[NiBrL_3]Br \cdot 3H_2O$ were mononuclear with tetrahedral geometry. The copper complexes were binuclear and exhibit strong antiferromagnetic coupling at room temperature. Square pyramidal geometry was proposed for halo complexes of copper and $ZnBr_2L_2(OH_2)$ and square-planar geometry for perchlorato complexes of copper and nickel. All the synthesized compounds were screened for antimicrobial activities.

Keywords: *m*-APB; NMR spectra; Complexes; Biological activity

1. Introduction

Benzimidazoles are useful intermediates for the synthesis of compounds of pharmaceutical interest. Benzimidazole is structurally related to purine bases and is found in a variety of naturally occurring ring compounds such as vitamin B_{12} [1]. Benzimidazoles exhibit a wide variety of pharmacological properties such as antiinflammatory, antitumor, anticonvulsant, antifungal, antimalarial, antiparasitic, and antiviral [2–6] activities. The spectrum of pharmacological activity exhibited by benzimidazoles has been reviewed by several authors [7]. Optimization of benzimidazole-based structures has resulted in various drugs that are currently on the market.

Metal complexes of biologically important ligands are sometimes more effective than free ligand [8, 9]. Transition metal ions have a strong role in bioinorganic chemistry

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such as redox enzyme systems which may provide models for active sites of biological systems or act as catalysts. Recent efforts in our lab are towards the synthesis and characterization of biologically active coordination compounds containing various metals with substituted benzimidazoles.

The discovery of zinc in the active site of a variety of enzymes such as carbonic anhydrase, carboxypeptidase, thermolysin, and alcohol dehydrogenase has stimulated much effort to mimic the coordination environment of the active site [10]. In particular, the polypeptide backbone of zinc enzymes typically binds the metal *via* a combination of N, O, and S donors. NNN donors have been used to model the active site of carbonic anhydrase [11], while NNO donor ligands have been studied in attempt to provide a model for the coordination environment of enzymes that also incorporate oxygen donors such as carboxypeptidase and thermolysin [12]. Usually, d^{10} metal complexes display luminescence in the solid state [13]. There is growing interest in the construction of coordination polymers based on N-heterocyclic ligands such as triazole, tetrazole, and imidazole derivatives. Metal-organic polymers have the ability to affect the emission wavelength and intensity. The highly toxic Cd(II) is believed to operate in Zn(II) biological pathways causing toxicity [14]. Copper is an essential trace element required by all living organisms, playing a key role in many enzymes. While trace amounts of copper are required for normal metabolic processes, it can be extremely toxic in excess [15]. Some complexes of Cu(II) with 2-substituted benzimidazole have been prepared and examined for biological activities and binding behavior towards DNA [16, 17]. The bioinorganic chemistry of nickel(II) has become increasingly important as the active site of several important classes of metalloenzymes, including nickel(II) hydrogenases [18].

In this context, zinc, cadmium, copper, and nickel complexes of *meta*-aminophenyl benzimidazole have been prepared, characterized, and the probable structures have been assigned. All these synthesized compounds were screened for their biological activity.

2. Experimental

2.1. *Materials, methods, and equipment*

All reagents were of analytical grade. The solvents used were purified according to standard procedures. Metal halides were obtained from BDH. Hydrated perchlorates were prepared by dissolving metal carbonate in 1 : 2 aqueous perchloric acid, evaporating the resulting solution to almost dryness under reduced pressure. Standard drugs were obtained from Ranbaxy, India.

Microanalyses were obtained from ElementarVario EL III, STIC, Cochin and Carlo Erba 1108, SAIF, CDRI, Lucknow. IR (nujol mull) spectra were recorded on a Shimadzu FTIR 8400s spectrometer and far-IR spectra were recorded on a Thermo Nicolet model 6700 spectrometer. Electronic spectra were recorded in nujol on a Shimadzu UV 3101PC spectrophotometer. Electrospray mass spectra were recorded on a Micromass Quattro II triple quadrupole mass spectrometer and Thermo LCQ Deca XP MAX, Spectroscopy/analytical test facility, IISc, Bangalore. Thermogravimetric analysis (TGA) were recorded on Perkin Elmer, Diamond TG/DTA with a heating rate of 15°C min^{-1} in nitrogen atmosphere. Molar conductivity measurements were made on a Systronic conductivity meter 304 – cell type CD-10. Magnetic susceptibility measurements were recorded by Faraday's method. Variable temperature magnetic susceptibility was measured on a vibrating sample magnetometer, Lakeshore VSM 7410. NMR spectra were recorded on a Bruker DRX500 NMR spectrometer with TMS as the internal standard. Antimicrobial activities were carried out by agar diffusion method.

2.2. *Preparation of* meta*-aminophenyl benzimidazole (*m*-APB)*

N-heterocycle, *meta*-aminophenyl benzimidazole (*m*-APB, figure 1) has been synthesized by the condensation of *o*-phenylene diamine and *meta*-aminobenzoic acid using polyphosphoric acid as condensing agent [19] at 235–240°C for 6 h. The melt was poured into ice cold water and neutralized with 15% sodium hydroxide. The product was filtered and recrystallized from alcohol to get white compound. Melting point 252°C, yield 80% [20–22].

2.3. *Synthesis of the complexes*

2.3.1. $[ZnCl_2L_{1.5}]_2 \cdot 2H_2O$, $ZnBr_2L_2(OH_2)$, and $[Zn(OClO_3)L_3]ClO_4 \cdot 3H_2O$. To 1 mmol of ZnX_2 ($X = Cl^-$, Br^-, or ClO_4^-) in 12 mL of methanol and triethyl orhoformate (teof) mixture (3 : 1), 10 mL of methanolic solution of *m*-APB (2 mmol) was added. The reaction mixture was refluxed for 6 h during which a light straw/white solid was separated. The solid was washed with methanol and dried in vacuum. Yield 50–75%.

2.3.2. $[CdCl_2L(OH_2)]$, $[CdBr_2L_{1.5}]_2 \cdot 2H_2O$, and $Cd(ONO_2)_2L_2 \cdot 2H_2O$. To 1 mmol of CdX_2 ($X = Cl^-$, Br^-, or NO_3^-) in 12 mL of methanol : teof mixture (1 : 3), 10 mL of methanolic solution of *m*-APB (2 mmol) was added. The reaction mixture was refluxed for 6–8 h on a steam bath when white/straw yellow solid was separated. The solids were washed with methanol and dried under vacuum. Yield 75–80%.

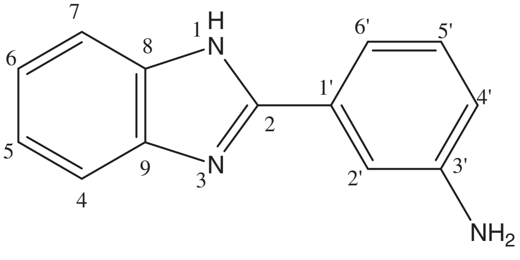

Figure 1. Structure of *m*-APB.

2.3.3. $[NiCl_2L(OH_2)] \cdot 2H_2O$, $[NiBrL_3]Br \cdot 3H_2O$, and $[Ni(OClO_3)L_3]ClO_4 \cdot H_2O$. To 1 mmol of NiX_2 ($X = Cl^-$, Br^-, or ClO_4^-) in 12 mL of methanol : teof mixture (3 : 1), 10 mL of methanolic solution of *m*-APB (2 mmol) was added. The reaction mixture was refluxed for 4–6 h on a steam bath during which green/orange complexes were separated. The solids were filtered and washed with acetone and dried under vacuum. Yield 55–70%.

2.3.4. $[CuCl_2L_{1.5}]_2 \cdot 2H_2O$, $[CuBr_2L_{1.5}]_2$, and $[Cu(OClO_3)L_2]_2(ClO_4)_2$. To 1 mmol of CuX_2 ($X = Cl^-$, Br^-, or ClO_4^-) in 12 mL of methanol : teof mixture (3 : 1), 10 mL of methanolic solution of *m*-APB (2 mmol) was added. The reaction mixture was refluxed for 4–6 h on a steam bath during which brown/green complexes were separated. The solids were filtered and washed with methanol and dried under vacuum. Yield 70–75%.

Caution: Perchlorates are potentially explosive. Care should be taken to prevent explosion.

3. Results and discussion

Zinc, cadmium, copper, and nickel halides/perchlorates/nitrates react with *m*-APB in 1 : 2 mole ratio in methanol–teof mixture to yield straw/white/green/orange/brown complexes of $[ZnCl_2L_{1.5}]_2 \cdot 2H_2O$, $ZnBr_2L_2(OH_2)$, $[Zn(OClO_3)L_3]ClO_4 \cdot 3H_2O$, $[CdCl_2L(OH_2)]$, $[CdBr_2L_{1.5}]_2 \cdot 2H_2O$, $Cd(ONO_2)_2L_2 \cdot 2H_2O$, $[NiCl_2L(OH_2)] \cdot 2H_2O$, $[NiBrL_3]Br \cdot 3H_2O$, $[Ni(OClO_3)L_3]ClO_4 \cdot H_2O$, $[CuCl_2L_{1.5}]_2 \cdot 2H_2O$, $[CuBr_2L_{1.5}]_2$, and $[Cu(OClO_3)L_2]_2(ClO_4)_2$. All the halo complexes were insoluble in common organic solvents, but soluble in DMF and DMSO in which they behaved as non-electrolytes except $[NiBrL_3]Br \cdot 3H_2O$ which exhibited 1 : 1 electrolytic behavior. All the zinc, copper, and nickel perchlorate complexes were soluble in DMF or DMSO with nickel and zinc complexes exhibiting 1 : 1 electrolytic behavior whereas the copper complex showed 1 : 2 electrolytic behavior. $Cd(ONO_2)_2L_2 \cdot 2H_2O$ was soluble in acetone in which it exhibited non-electrolytic behavior.

Since $ZnBr_2L_2(OH_2)$ and $[Ni(OClO_3)L_3]ClO_4 \cdot 3H_2O$ exploded during TGA, the TGA studies for all the complexes were restricted to 300°C to determine the nature of the water present in the complexes. $[ZnCl_2L_{1.5}]_2 \cdot 2H_2O$, $[Zn(OClO_3)L_3]ClO_4 \cdot 3H_2O$, $[CdBr_2L_{1.5}]_2 \cdot 2H_2O$, $Cd(ONO_2)_2L_2 \cdot 2H_2O$, $[NiBrL_3]Br \cdot 3H_2O$, $[Ni(OClO_3)L_3]ClO_4 \cdot H_2O$, and $[CuCl_2L_{1.5}]_2 \cdot 2H_2O$ lost water molecules before 150°C, indicating the presence of lattice water. The TGA of $ZnBr_2L_2(OH_2)$ and $[CdCl_2L(OH_2)]$ showed the loss of water above 200°C, indicating the presence of coordinated water. $[NiCl_2L(OH_2)] \cdot 2H_2O$ lost water in both regions, indicating the presence of lattice and coordinated water. The results are in accord with the composition of the complexes as determined by elemental analyses. The physical properties and analytical data of the compounds are listed in table 1.

3.1. *IR and far-IR spectral studies*

The spectra of *m*-APB and its complexes were recorded in nujol mulls and the assignments are listed in table 2. $\nu_{N\text{–}H}$ of NH_2 of *m*-APB occurs at 3350 cm^{-1} and the

Table 1. Physical properties and analytical data of the complexes.

Complex	Color	m.p./d.p. (°C)	Λ^a	Found (Calcd) (%)			TGA data	
				C	H	N	Temperature (°C)	Species lost
m-APB	White	267	–	74.47 (74.62)	5.27 (5.29)	20.34 (20.08)	–	–
$[ZnCl_2L_{1.5}]_2 \cdot 2H_2O$	Light straw	> 280	9	49.77 (50.02)	3.79 (3.98)	13.19 (13.46)	98	Lattice H_2O
$ZnBr_2L_2(OH_2)$	Buff	232	20	47.09 (47.30)	3.97 (3.63)	12.71 (12.74)	240	Coordinated H_2O
$[Zn(OClO_3)L_3]ClO_4 \cdot 3H_2O$	White	> 280	45^b	49.50 (49.51)	3.90 (4.16)	13.30 (13.32)	85	Lattice H_2O
$CdCl_2L(OH_2)$	Half white	> 280	21	38.34 (38.03)	2.98 (3.19)	10.21 (10.23)	300	Coordinated H_2O
$[CdBr_2L_{1.5}]_2 \cdot 2H_2O$	Half white	240	42	38.58 (38.90)	3.23 (3.09)	10.55 (10.46)	88	Lattice H_2O
$Cd(ONO_2)_2L_2 \cdot 2H_2O$	Light straw	185	12^c	44.04 (44.05)	3.66 (3.41)	15.71 (15.81)	83	Lattice H_2O
$[CuCl_2L_{1.5}]_2 \cdot 2H_2O$	Brown	285	26^b	51.24 (50.22)	3.50 (4.00)	12.50 (13.5)	88	Lattice H_2O
$Cu_2Br_4L_3$	Brown	290	57	44.46 (43.76)	3.10 (3.10)	11.77 (11.77)	–	–
$[Cu(OClO_3)L_2]_2(ClO_4)_2$	Green	> 300	172	45.64 (45.86)	3.28 (3.26)	12.05 (12.34)	–	–
$[NiCl_2L(OH_2)] \cdot 2H_2O$	Green	180	59	40.74 (39.54)	5.36 (4.36)	10.69 (10.69)	103,275	Lattice H_2O Coordinated H_2O
$[NiBrL_3]Br \cdot 3H_2O$	Green	190	78	52.14 (52.14)	3.34 (4.34)	13.03 (14.03)	<137	Lattice H_2O & $2Br^-$
$[Ni(OClO_3)L_3]ClO_4 \cdot H_2O$	Yellow	> 300	76	51.85 (51.85)	3.30 (3.90)	13.50 (13.90)	97	Lattice H_2O

Λ in $\Omega^{-1}\,cm^2\,mol^{-1}$, a in DMF, b in DMSO, and c in acetone.

Table 2. IR and far-IR spectral data (cm^{-1}).

	ν_{N-H} of NH_2	ν_{N-H} of benzimidazole	$\nu_{C=N}$	ν_{C-N} and δ_{N-H}	$\nu_{M-X(b)}$ $X = Cl/Br$	$\nu_{M-X(t)}$ $X = Cl/Br$	νClO_4	νNO_3
m-APB	3350	3174	1614	1311				
$[ZnCl_2L_{1.5}]_2 \cdot 2H_2O$	3300	3174	1651	1317	262	303		
$ZnBr_2L_2(OH_2)$	3269	3180	1674	1323				
$[Zn(OClO_3)_2L_3]ClO_4 \cdot 3H_2O$	3400	3217	1650	1321			1101, 1126, 1033 1006, 622	
$CdCl_2L(OH_2)$	3388	3286	1695	1326				
$[CdBr_2L_{1.5}]_2 \cdot 2H_2O$	3300	3205	1658	1320	154	193		
$Cd(ONO_2)_2L_2 \cdot 2H_2O$	3257	3245	1676	1310				1448, 1303, 1008
$[CuCl_2L_{1.5}]_2 \cdot 2H_2O$	3329	3167	1608	1366	209	286	–	
$[CuBr_2L_{1.5}]_2$	3200	3175	1608	1366	183	261	–	
$[Cu(OClO_3)L_2]_2(ClO_4)_2$	3329	3167	1620	1305	–	–	1090, 1084, 621	
$[NiCl_2L(OH_2)] \cdot 2H_2O$	3363	3150	1631	1311	–	–	–	
$[NiBrL_3]Br \cdot 3H_2O$	3200	3150	1634	1317	–	–	–	
$[Ni(OClO_3)L_3]ClO_4 \cdot H_2O$	3300	3050	1632	1319	–	–	1074, 1082, 620	

peak at 3209 cm^{-1} is assigned to $\nu_{\text{N–H}}$ of benzimidazole. $\nu_{\text{C=N}}$ and $\nu_{\text{C=C}}$(ring) vibrations are at 1684 cm^{-1}. The peak at 1312 cm^{-1} is assigned to $\nu_{\text{C–N}}$ and $\delta_{\text{N–H}}$. Peaks at 1585 and 787 cm^{-1} are assigned to N–H in-plane deformation and N–H out-of-plane bending, respectively. Benzimidazole ring vibrations are at 619, 743, 1007, and 1406 cm^{-1}. C–H out-of-plane deformation of *meta* substituted benzene is at 1146 cm^{-1}.

In general, IR spectra of the complexes were similar to ligand with minor shifts in the positions of peaks. In all the complexes $\nu_{\text{C=N}}$ is shifted in relation to free ligand, indicative of coordination through benzimidazole nitrogen. Benzimidazole ligand coordinates to metal ions through the pyridine like nitrogen of the imidazole ring. $\nu_{\text{N–H}}$ for the complexes are in the region 3300–2900 cm^{-1} and $\nu_{\text{C–N}}$, $\delta_{\text{N–H}}$ are in the range 1300–1380 cm^{-1} [8].

Perchlorato complexes, in addition to ligand peaks, exhibited peaks at 1100 and 620 cm^{-1}, indicative of the presence of both coordinated and ionic perchlorate [23]; this is supported from the conductivity data. Nitrato complex of cadmium exhibited peaks due to the presence of nitrate at 1028 cm^{-1} which is assigned for N–O symmetrical stretch and peaks at 1151 and 933 cm^{-1} indicate the presence of monodentate nitrato. The absence of peak near 1360 cm^{-1} confirms that only coordinated nitrato groups are present.

The far-IR spectrum of the chloro complex of zinc displayed peaks at 262 and 303 cm^{-1} and copper at 209 and 286 cm^{-1} with the former peak assigned to $\nu_{\text{M–Cl}}$ bridging and the latter to $\nu_{\text{M–Cl}}$ terminal [24]. The far-IR spectra of bromo complexes of cadmium and copper also indicate both $\nu_{\text{M–Br}}$ bridging and $\nu_{\text{M–Br}}$ terminal.

3.2. *Electronic spectra and magnetic studies*

The electronic spectrum of *m*-APB in DMF exhibits absorptions at 300 and 309 nm which have been assigned to π–π^* transitions and a band at 332 nm to n–π^* transition. The electronic spectra of copper and nickel complexes are recorded in nujol mull. $[\text{NiCl}_2\text{L(OH}_2)]\cdot 2\text{H}_2\text{O}$ and $[\text{NiBrL}_3]\text{Br}\cdot 3\text{H}_2\text{O}$ exhibit absorptions at 700, 1150, and 1500 nm assigned for ${}^3T_1(F) \rightarrow {}^3T_1(P)$, ${}^3T_1(F) \rightarrow {}^3A_2(F)$, and ${}^3T_1(F) \rightarrow {}^3T_2(F)$ transitions arising out of tetrahedral stereochemistry [25]. D_q values of these complexes are 455 and 476, respectively. The magnetic moment values of chloro and bromo complexes of nickel are 2.76 and 4.01 BM, respectively. The magnetic moment value 2.76 BM of $[\text{NiCl}_2\text{L(OH}_2)]\cdot 2\text{H}_2\text{O}$ is low for high-spin tetrahedral complex and this may be attributed to spin equilibrium between low- and high-spin states [26–28]. The magnetic moment of 4.01 BM of $[\text{NiBrL}_3]\text{Br}\cdot 3\text{H}_2\text{O}$ indicated tetrahedral geometry of the complex. Perchlorato complex of nickel is diamagnetic in nature and the electronic spectrum showed absorption bands at 368 and 570 nm which are assigned for ${}^1A_{1g} \rightarrow {}^1B_{1g}$ and ${}^1A_{1g} \rightarrow {}^1A_{2g}$ transitions, typical for nickel complexes of square planar geometry [29–32].

All the copper complexes were binuclear and diamagnetic at room temperature. Variable-temperature magnetic susceptibility for $[\text{Cu}_2\text{Cl}_4\text{L}_3]\cdot 2\text{H}_2\text{O}$ was carried out from 20 to 300 K. Magnetic moment of Cu^{2+} in $[\text{Cu}_2\text{Cl}_4\text{L}_3]\cdot 2\text{H}_2\text{O}$ was 0.8 BM at 20 K and decreased to zero at 170–300 K. The unusual magnetic behavior of binuclear copper complexes is attributed to strong antiferromagnetic coupling between the two Cu(II) ions *via* Cu–X–Cu (X = Cl/Br) in halo complexes and Cu–L–Cu in perchlorato complex [30, 33]. The variable temperature magnetic moment result for

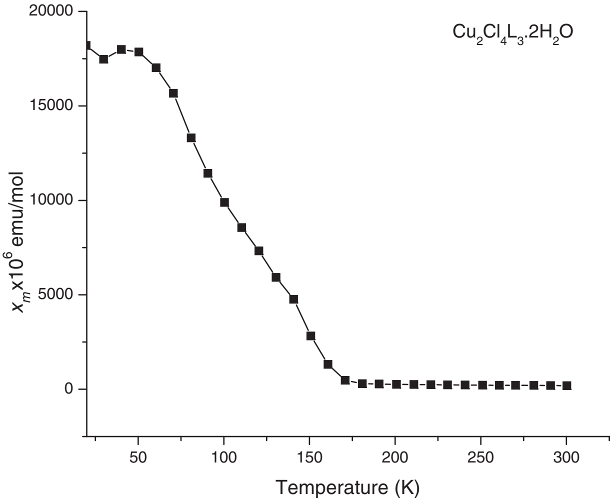

Figure 2. Plot of χ_M *vs.* temperature for $[CuCl_2L_{1.5}]_2 \cdot 2H_2O$.

$[Cu_2Cl_4L_3] \cdot 2H_2O$ is plotted in figure 2. Electronic spectra of $[Cu_2Cl_4L_3] \cdot 2H_2O$ and $Cu_2Br_4L_3$ exhibit absorptions around 700 and 950 nm which are assigned for $^2B_1 \rightarrow {}^2E_2$ and $^2B_1 \rightarrow {}^2B_2$ transitions arising out of distorted square pyramidal geometry [34]. $[Cu(OClO_3)L_2]_2(ClO_4)_2$ displayed absorption at 630 nm which is attributed to d–d transition arising out of square planar geometry [35].

3.3. *NMR spectral studies*

^1H NMR and ^{13}C NMR of *m*-APB was recorded in DMSO-d_6. The structural and spectroscopic assignments were made through combined use of 1-D and 2-D NMR experiments such as COSY, HSQC, and HMBC experiments carried out for the ligand.

The HSQC spectrum of the ligand exhibits cross peaks corresponding to single-bond proton carbon links, thus cross peaks are observed for the 2′, 4′, 5, 6, 5′, and 6′ protons with the corresponding carbon atoms. HMBC experiment gives information about long-range carbon–proton coupling and also helps in assignment of the quaternary carbons.

The ^1H NMR spectrum of *m*-APB exhibits a singlet at 12.69 ppm due to imine proton. A resonance at 5.31 ppm is assigned to NH_2 protons. 5′, 5, and 6 protons of benzimidazole appear as multiplet at 7.18 ppm, and doublet at 6.66 ppm is assigned to the 4′ proton. Phenyl ring exhibits a broad resonance at 7.54 ppm, which is assigned to 4 and 7 protons. A triplet at 7.42 ppm and a doublet at 7.27 ppm are due to 2′ and 6′ protons of phenyl, respectively.

The ^{13}C NMR spectrum of *m*-APB exhibits signals from 152.1 to 111.9 ppm. Quaternary carbons 3′, 8, and 9 exhibit signal at 149.1 ppm and carbon 2 exhibits signal at 152.1 ppm. Benzimidazole ring carbons 4, 7, and 5′ of phenyl exhibit signals at 121.8 ppm, 5 and 6 at 129.4 ppm. Phenyl ring carbons exhibit signals at 111.9, 114.0, 115.6, and 130.7 ppm which are assigned to 2′, 4′, 6′, and 1′ carbons, respectively.

^{1}H NMR spectral data of the ligand and the complexes of zinc and cadmium along with coordination induced shifts (c.i.s.) are given in table 3. ^{1}H and ^{13}C NMR spectra for *m*-APB and complexes have been taken in DMSO-d$_6$. The resonance due to NH_2 for *m*-APB is at δ 5.30 and undergoes up-field shift on complexation except for $ZnBr_2L_2(OH_2)$. The peak for NH of benzimidazole at δ 12.69 shift down-field on complexation, except for $CdCl_2L(OH_2)$. Resonances due to benzimidazole and phenyl rings are δ 6.70–7.54 with slight shifts on complexation. The c.i.s. for various protons of *m*-APB are in the range δ 0.02–2.91.

On complexation, ^{13}C NMR peaks undergo slight shifts (table 4). The assignments are made with the aid of off-resonance decoupled spectrum of the heterocycle and the literature reports [36–38]. The c.i.s. for various carbons of the coordinated N-heterocycles are in the range δ 0.1–30.4. The negative c.i.s. may be attributed to greater metal-to-ligand π back donation whereas positive c.i.s. to ligand-to-metal σ donation.

All the copper complexes and perchlorato complex of nickel are diamagnetic at room temperature. ^{1}H NMR for $[CuCl_2L_{1.5}]_2 \cdot 2H_2O$, $[CuBr_2L_{1.5}]_2$, and $[Ni(OClO_3)L_3]ClO_4 \cdot H_2O$ are recorded in DMSO-d$_6$ and assignments are listed in table 3. The proton signals of these complexes undergo down-field shift on complexation with respect to *m*-APB, except for the resonances due to 5 and 6 protons of $[Ni(OClO_3)L_3]ClO_4 \cdot H_2O$. The spectra of halo complexes of copper exhibit two signals for proton 4 around 8.4 and 10.5 ppm which are assigned to proton 4 of the bridging and terminal ligand, respectively.

3.4. *Mass spectral studies*

Mass spectra of $Zn_2Cl_4L_3 \cdot 2H_2O$, $Cd_2Br_4L_3 \cdot 2H_2O$, $[CuCl_2L_{1.5}]_2 \cdot 2H_2O$, and $[CuBr_2L_{1.5}]_2$ have supported the binuclear nature of the complexes [39]. These compounds exhibit molecular ion peaks at 900, 1167, 896, and 1070 due to $Zn_2Cl_4L_3$, $Cd_2Br_4L_3$, $Cu_2Cl_4L_3$, and $Cu_2Br_4L_3$, respectively, supporting the binuclear nature of the complexes. The various fragments and their *m*/*z* peaks of these complexes are listed in table 5. The mass spectra of $Zn_2Cl_4L_3 \cdot 2H_2O$, $Cd_2Br_4L_3 \cdot 2H_2O$, and $[CuCl_2L_{1.5}]_2 \cdot 2H_2O$ are given in figure 3. The intensity ratios of these complexes were consistent with the isotope pattern calculated using isopro 3.0.

4. Stereochemistry

Elemental analyses, IR, far-IR, and NMR spectral studies have indicated that *m*-APB is coordinated to the metal ions (figure 4). Mass spectral studies supported the binuclear nature of $Zn_2Cl_4L_3 \cdot 2H_2O$, $Cd_2Br_4L_3 \cdot 2H_2O$, $[CuCl_2L_{1.5}]_2 \cdot 2H_2O$, and $[CuBr_2L_{1.5}]_2$. For binuclear halo complexes, L is both monodentate and bridging bidentate. Far-IR spectra of binuclear complexes indicate the presence of both bridging and terminal halides. Thermogravimetric analytical data indicate the presence of lattice water in $[ZnCl_2L_{1.5}]_2 \cdot 2H_2O$, $[Zn(OClO_3)L_3]ClO_4 \cdot 3H_2O$, $[CdBr_2L_{1.5}]_2 \cdot 2H_2O$, $Cd(ONO_2)_2L_2 \cdot 2H_2O$, $[NiBrL_3]Br \cdot 3H_2O$, $[Ni(OClO_3)L_3]ClO_4 \cdot H_2O$, and $[CuCl_2L_{1.5}]_2 \cdot 2H_2O$ and the presence of coordinated water in $[CdCl_2L(OH_2)]$ and $ZnBr_2L_2(OH_2)$; both lattice

Table 3. ^{1}H NMR spectral data in DMSO-d_6 (δ in ppm).[a]

	N–H	NH_2	4	5	6	7	2′	4′	5′	6′
m-APB	12.69s	5.30s	7.54b	7.18m	7.18m	7.54 b	7.42t	6.70d	7.18m	7.27d
$[ZnCl_2L_{1.5}]_2 \cdot 2H_2O$	12.90s (0.21)	4.35s (−0.95)	10.45s (2.91)	7.30m (0.12)	7.30m (0.12)	8.40d (0.86)	7.80m (0.38)	7.30m (0.60)	7.60d (0.42)	7.80m (0.53)
$ZnBr_2L_2(OH_2)$	12.80s (0.11)	5.30s –	10.40s (2.86)	7.20m (0.02)	7.20m (0.02)	8.40d (0.86)	7.60m (0.18)	6.69b –	7.20m (0.02)	7.60m (0.33)
$[Zn(OClO_3)_2L_3]ClO_4 \cdot 3H_2O$	12.8s (0.11)	5.26s (−0.04)	7.51m (−0.03)	7.20m (0.02)	7.20m (0.02)	7.86b (0.32)	7.51m (0.09)	7.20m (0.50)	7.20m (0.02)	7.51m (0.24)
$CdCl_2L(OH_2)$	12.69s –	5.25s (0.05)	7.41s (−0.13)	7.18m –	7.18m –	7.61d (0.07)	7.48t (0.06)	6.68d (0.02)	7.18m –	7.27d –
$[CdBr_2L_{1.5}]_2 \cdot 2H_2O$	12.89s (0.2)	5.27s (−0.03)	10.35s (2.81)	7.19m (0.01)	7.19m (0.01)	7.83d (0.29)	7.50m (0.08)	7.19m (0.49)	7.50m (0.32)	7.67d (0.4)
$Cd(ONO_2)_2L_2 \cdot 2H_2O$	12.89s (0.20)	5.27s (−0.03)	10.38s (2.84)	7.18m –	7.18m –	7.84d (0.34)	7.54m (−0.12)	7.18m (0.48)	7.54m (0.36)	7.67d (0.4)
$[CuCl_2L_{1.5}]_2 \cdot 2H_2O$	12.0s (0.69)	6.91s (1.61)	8.37s (0.83) 10.52s (2.98)	7.51m (0.33)	7.51m (0.33)	7.84b (0.30)	7.84b (0.42)	7.46m (0.76)	7.65m (0.47)	7.71d (0.44)
$[CuBr_2L_{1.5}]_2$	13.3s (0.61)	6.6s (1.30)	8.34s (0.80) 10.36s (2.82)	7.19m (0.01)	7.19m (0.01)	7.93b (0.39)	7.67b (0.25)	7.19m (0.49)	7.38m (0.20)	7.53m (0.26)
$[Ni(OClO_3)L_3]ClO_4 \cdot H_2O$	16.0s (3.31)	5.78s (0.48)	7.66m (0.12)	7.18m –	7.18m –	7.66m (0.12)	7.43m (0.01)	6.98d (0.28)	7.30m (0.12)	7.43m (0.16)

[a] Values in parentheses are coordination induced shifts (c.i.s. = δ complex–δ ligand). s = singlet, d = doublet, t = triplet, m = multiplet, b = broad.

Table 4. ^{13}C NMR spectral data in DMSO-d_6 (δ in ppm).[a]

	Quaternary carbon atoms					4	5	6	7	2′	4′	5′	6′
	2	8	9	3′	1′	Benzimidazole moiety				Phenyl ring			
m-APB	152.1	149.1	149.1	149.1	130.7	121.8	129.4	129.4	121.8	111.9	114.0	121.8	115.6
$[ZnCl_2L_{1.5}]_2 \cdot 2H_2O$	159.8	138.8	148.7	148.7	130.8	120.9	129.7	129.7	120.9	111.6	119.1	120.9	120.6
	(7.7)	(−10.3)	(−0.4)	(−0.4)	(0.1)	(−0.9)	(0.3)	(0.3)	(−0.9)	(0.3)	(5.1)	(−0.9)	(5.0)
$ZnBr_2L_2(OH_2)$	159.8	151.1	152.2	152.2	130.6	119.0	129.3	129.3	119.0	112.1	117.5	119.0	120.6
	(7.7)	(2.0)	(3.1)	(3.1)	(−0.1)	(−2.8)	(−0.1)	(−0.1)	(−2.8)	(0.2)	(3.5)	(−2.8)	(5.0)
$[Zn(OClO_3)_2L_3]ClO_4 \cdot 3H_2O$	151.3	143.8	148.5	148.5	131.0	120.5	129.7	129.7	120.5	111.3	118.8	120.5	121.6
	(−0.8)	(−5.3)	(−0.6)	(−0.6)	(0.3)	(−1.3)	(0.3)	(0.3)	(−1.3)	(−0.6)	(4.8)	(−1.3)	(6.0)
$CdCl_2L(OH_2)$	152.0	134.9	143.7	143.7	130.7	121.3	129.2	129.2	121.3	111.1	115.4	121.3	118.6
	(−0.1)	(−14.2)	(−5.4)	(−5.4)	(0.0)	(−0.5)	(−0.2)	(−0.2)	(−0.5)	(−0.8)	(1.4)	(−0.5)	(3.0)
$[CdBr_2L_{1.5}]_2 \cdot 2H_2O$	159.8	150.9	152.0	152.0	130.8	118.9	129.6	129.6	118.9	111.9	117.4	118.9	120.5
	(7.7)	(1.8)	(2.9)	(2.9)	(0.1)	(−2.9)	(0.2)	(0.2)	(−2.9)	(0.0)	(3.4)	(−2.9)	(4.9)
$Cd(ONO_2)_2L_2 \cdot 2H_2O$	159.8	150.9	152.0	152.0	130.6	118.9	129.4	129.4	118.9	111.9	117.4	118.9	121.8
	(7.7)	(1.8)	(2.9)	(2.9)	(0.1)	(−2.9)	(0.0)	(0.0)	(−2.9)	(0.0)	(3.4)	(–2.9)	(6.2)

[a] Values in parentheses indicate coordination induced shifts (c.i.s. $= \delta$ complex – δ ligand).

Table 5. Mass spectral data.

$[CdBr_2L_{1.5}]_2 \cdot 2H_2O$		$[ZnCl_2L_{1.5}]_2 \cdot 2H_2O$		$[CuCl_2L_{1.5}]_2 \cdot 2H_2O$		$[CuBr_2L_{1.5}]_2$	
Fragments	*m*/*z*	Fragments	*m*/*z*	Fragments	*m*/*z*	Fragments	*m*/*z*
$Cd_2Br_4L_3$	1167	$Zn_2Cl_4L_3$	900	$Cu_2Cl_4L_3$	896	$Cu_2Br_4L_3$	1070
$CdBr_4L_2$	852	$Zn_2Cl_4L_2(L\text{–}NH_2)$	882	$Cu_2Cl_3L_3$	860	$Cu_2Br_4L_2$	860
$CdBr_3L_2$	772	$Zn_2Cl_2L_1(L\text{–}NH_2)$	605	$CuCl_2L_2(C_7H_5N_2)$	666	$Cu_2Br_2L_2$	640
$CdBr_3L(C_7H_5N_2)$	680	$Zn_2L(C_7H_5N_2)Cl_3$	566	$Cu_2L_2(C_6H_6N)$	639	$CuBrL_2$	560
$CdBr_4L$	639	$Zn_2L(C_7H_5N_2)Cl_2$	527	$CuCl_2L_2$	552	$Cu_2Br\ L_2(C_7H_5N_2)$	738
$CdBr_3L$	611	$Zn_2L(C_7H_5N_2)Cl$	491	$Cu_2L(C_7H_5N_2)$	452	$Cu_2L_2(C_6H_6N)$	639
$CdBr_2L$	482	$Zn_2L(C_6H_6N)$	431	CuL_2	481	$CuBr_2L$	430
Cd_2L	433	Zn_2L	339	$Cu_2L(C_6H_6N)$	429	$Cu_2L(C_6H_6N)$	429
$CdBrL$	402	L	210	L	210	Cu_2Br_3	368
L	210					L	210

and coordinated water molecules are present in $[NiCl_2L(OH_2)] \cdot 2H_2O$. $[ZnCl_2L_{1.5}]_2 \cdot 2H_2O$ and $ZnBr_2L_2(OH_2)$ are assigned square pyramidal geometry, while $[Zn(OClO_3)L_3]ClO_4 \cdot 3H_2O$ is assigned tetrahedral geometry. $[CdCl_2L(OH_2)]$ and $[CdBr_2L_{1.5}]_2 \cdot 2H_2O$ are assigned square pyramidal geometry, while tetrahedral geometry is proposed for $Cd(ONO_2)_2L_2 \cdot 2H_2O$. Electronic spectral studies and magnetic moment measurements of complexes of nickel suggest tetrahedral geometry for halo complexes and square planar geometry for $[Ni(OClO_3)L_3]ClO_4 \cdot H_2O$. Halo complexes of copper have square pyramidal geometry while perchlorato complex of copper is assigned square planar geometry.

5. Biological activity

The ligand *m*-APB, its complexes and a standard drug were dissolved in DMSO (50 µg/0.1 mL) and used for testing biological activity. Nutrient agar medium was prepared by dissolving peptone (0.6%), beef extract (0.15%), sodium chloride, dextrose, and agar (2%) in 1000 cm^3 of distilled water by heating at 7.4 pH. The medium was sterilized by autoclaving at 121°C for 15 min at 15 lb pressure/sq. inch. The mixture was cooled to 45°C. Fresh culture (6 g of peptone, 1.5 g of beef extract, 1 g of dextrose, 15 g of agar, and 5 g of sodium chloride in 1000 mL of distilled water) was added, mixed well, and the medium was allowed to solidify. In each petri dish, five wells were made using a sterile borer. 0.1 mL of test solution (50 µg/0.1 mL), standard solution, and DMSO control were poured into separate wells in each plate. The petri dish was covered and incubated at 37°C for 24 h. Zones of inhibition were observed and the average of three readings were recorded. The antibacterial activities of the synthesized compounds were compared with *Ampicillin*. The percentage activity index data for the ligand and metal complexes were calculated as follows:

$$\text{Activity index (\%)} = \frac{\text{Zone of inhibition by test compound (diameter)}}{\text{Zone of inhibition by standard (diameter)}} \times 100$$

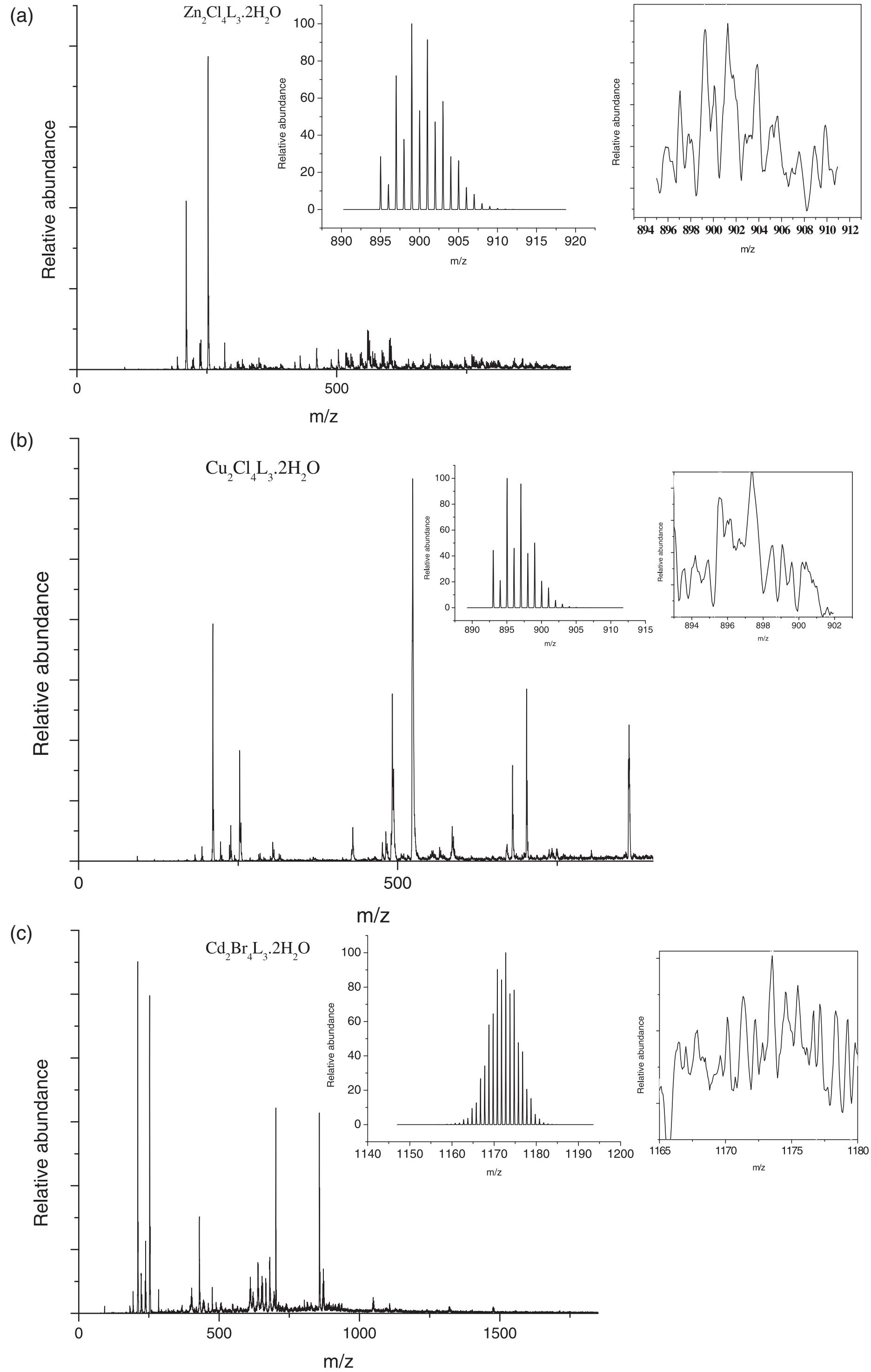

Figure 3. (a) ESI mass spectrum of $Zn_2Cl_4L_3\cdot 2H_2O$; (b) ESI mass spectrum of $Cu_2Cl_4L_3\cdot 2H_2O$; (c) ESI mass spectrum of $Cd_2Br_4L_3\cdot 2H_2O$.

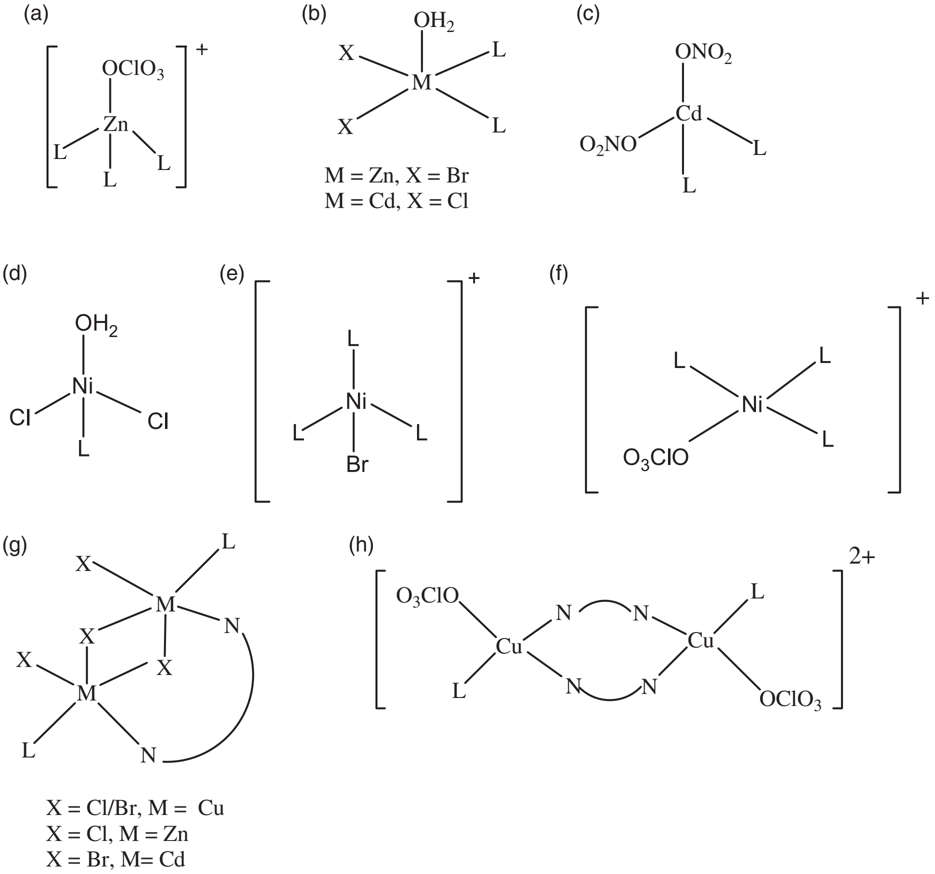

Figure 4. Proposed structures for the complexes.

Pathogenic fungi were isolated by inoculating infected sample into corn meal agar. The inoculated plates were incubated at 28°C for 2 days. Colonies thus formed were selected for further screening. The *Sabouraud's agar* medium was prepared for *Candida albicans* and *Aspergillus niger*. The medium was sterilized, fresh culture of fungi and *Ampicillin* were added to prevent bacterial growth at a concentration 25 µg/30 mL of the culture medium and the plates were prepared. In each petri dish, five wells were made using a sterile borer. 0.1 mL of test solution, standard solution, and DMSO control were poured into separate wells in each plate. The petri dishes were covered and incubated at 28°C for 48 h. Zones of inhibition were observed and the average of three readings were recorded.

5.1. *Antibacterial activity*

Investigation of antibacterial activity was carried out by the agar diffusion method. Metal complexes, ligand, standard drug *Ampicillin,* and DMSO control were screened separately for their antibacterial activities. All the synthesized compounds were tested

Table 6. Antibacterial activity of the ligand, complexes and standard drug.

	Zone of inhibition (mm)				Activity index (%)			
Compound	*St. aureus*	*B. subtilus*	*E. coli*	*K. pneumoniae*	*St. aureus*	*B. subtilus*	*E. coli*	*K. pneumoniae*
$Zn_2Cl_4L_3 \cdot 2H_2O$	05	04	05	05	45	31	31	42
$ZnBr_2L_2(OH_2)$	05	04	05	06	45	31	31	50
$[Zn(OClO_3)L_3]ClO_4 \cdot 3H_2O$	07	07	08	06	64	54	50	50
$CdCl_2L(OH_2)$	06	07	07	NA	55	54	44	NA
$Cd_2Br_4L_3 \cdot 2H_2O$	07	08	09	07	64	62	56	58
$Cd(ONO_2)_2L_2 \cdot 2H_2O$	04	02	NA	03	36	15	NA	25
$[Cu_2Cl_4L_3] \cdot 2H_2O$	07	08	05	08	64	62	31	67
$Cu_2Br_4L_3$	08	04	11	06	73	31	69	50
$[Cu(OClO_3)L_2]_2(ClO_4)_2$	08	09	11	08	73	69	69	67
$[NiCl_2L(OH_2)] \cdot 2H_2O$	05	06	07	05	45	46	44	42
$[NiBrL_3]Br \cdot 3H_2O$	09	05	08	07	82	38	50	58
$[Ni(OClO_3)L_3]ClO_4 \cdot H_2O$	06	07	06	09	55	54	38	75
m-APB	04	05	06	04	36	38	38	33
Ampicillin	11	13	16	12	100	100	100	100

Zone of inhibition excludes bore size and zone of inhibition of control; NA = not active: Error $-2 \le 0 \le +2$.

against two Gram-negative (*Escherichia coli* and *Klebsiella pneumoniae*) and two Gram-positive (*Staphylococcus aureus* and *Bacillus subtilus*) bacterial strains, exhibiting varying degrees of inhibitory effect on the growth of tested strains. Antibacterial studies were carried out in triplicate and the zone of inhibition was obtained by the average of three readings. Antibacterial activity data are listed in table 6. The data indicate that the ligand was less sensitive toward antibacterial activity, but enhanced upon complexation [40], except for $Cd(ONO_2)_2L_2 \cdot 2H_2O$. Halo complexes of zinc exhibited low antibacterial activities. All the copper complexes and $[NiBrL_3]Br \cdot 3H_2O$ show relatively higher antibacterial activity at 500 ppm. $CdCl_2L(OH_2)$ was not sensitive to *K. pneumoniae* and $Cd(ONO_2)_2L_2 \cdot 2H_2O$ was found to be insensitive to *E. coli*. Increase in activity upon complexation may be attributed to increased lipophilicity and inertness of metal–ligand linkages and the molecule is protected against enzymatic degradation [41]. The % activity index data indicate that $[NiBrL_3]Br \cdot 3H_2O$ shows higher activity against *St. aureus*, $[Cu(OClO_3)L_2]_2(ClO_4)_2$ higher against *B. subtilus* and *E. coli* while $[Ni(OClO_3)L_3]ClO_4 \cdot H_2O$ exhibits higher activity against *K. pneumoniae*. On comparing the antibacterial activity data of different metal complexes with the same ligand, the toxicity varied in the order Cu > Ni > Cd > Zn.

5.2. *Antifungal activity*

All the synthesized compounds, ligand, and standard drug were screened against *A. niger* and *C. albicans* against DMSO control with a dose concentration of 500 ppm. The antifungal activity data of the synthesized compounds and the standard drug *Miconazole* are listed in table 7. The ligand exhibited moderate activity; the copper complexes exhibited higher activity compared to the other metal complexes and the ligand. Halo complexes of zinc and chloro complex of cadmium showed less activity

Table 7. Antifungal activity of the ligand, their complexes, and standard drug.

	Zone of inhibition (mm)	
Compound	*A. niger*	*C. albicans*
$Zn_2Cl_4L_3 \cdot 2H_2O$	09	10
$ZnBr_2L_2(OH_2)$	09	09
$[Zn(OClO_3)L_3]ClO_4 \cdot 3H_2O$	11	12
$CdCl_2L(OH_2)$	10	11
$Cd_2Br_4L_3 \cdot 2H_2O$	18	13
$Cd(ONO_2)_2L_2 \cdot 2H_2O$	08	08
$[Cu_2Cl_4L_3] \cdot 2H_2O$	19	18
$Cu_2Br_4L_3$	18	13
$[Cu(OClO_3)L_2]_2(ClO_4)_2$	17	18
$[NiCl_2L(OH_2)] \cdot 2H_2O$	17	14
$[NiBrL_3]Br \cdot 3H_2O$	14	14
$[Ni(OClO_3)L_3]ClO_4 \cdot H_2O$	16	15
m-APB	15	12
Miconazole nitrate	25	23

compared to that of the ligand; $Cd(ONO_2)_2L_2 \cdot 2H_2O$ exhibited lowest activity against both the organisms.

Tavman *et al.* [42] reported biological activities of zinc, cadmium, and mercury complexes against a wide range of microorganisms like *St. aureus*, *Staphylococcus epidermidis*, *E. coli*, *K. pneumoniae*, *Salmonella typhi*, *Shigella flesneri*, *Proteus mirabilis*, and *C. albicans* and found that zinc complexes were effective against *St. aureus* and *S. epidermidis* while cadmium complexes were effective only on *S. epidermidis*. Kalanithi *et al.* [43] reported biological activities of substituted imidazole ligand and its zinc, cadmium, copper, nickel, and cobalt complexes against *St. aureus*, *E. coli*, *Pseudomonas aeruginosa*, and *C. albicans*. Zinc and cadmium complexes were more potent than copper, nickel, and cobalt complexes. Naveen and Revankar [44] screened zinc, cobalt, copper, and nickel complexes of pyrazole-based ligand at 250 and 500 ppm concentrations, finding that percentage inhibition increased at higher concentration and biological activity increased upon complexation, which was attributed to the combined effect of the ligand and the metal. These results were comparable to the biological activity of the *m*-APB complexes.

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