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Contributed Paper

Synthesis, Characterization and Antimicrobial Evaluation of Transition Metal Complexes of Monodentate 2-(Substituted Phenyl) -1*H*-benzo[d]imidazoles

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ABSTRACT

The synthesis, spectral characterization and antimicrobial activity of copper(II) chloride, nickel(II) chloride and cobalt(II) chloride complexes of the monodentate 2-(substituted phenyl)-1*H*-benzo[*d*]imidazole ligands are represented in this research article. The complex formation of metal(II) ions were taken with 2-substituted benzimidazole ligands in 1:2 mole ratio in ethanolic solution. Both benzimidazole ligands (BZa) and (BZb) were derived from o-phenylenediamine by the cyclocondensation with 4,5-dimethoxy-2-nitro benzaldehyde and 3-bromo-4-hydroxy-5-methoxy benzaldehyde respectively. The *in vitro* study of antimicrobial activity of benzimidazole ligands and their metal complexes was done on bacterial strains (*E. coli*, *P. aeruginosa*, *S. aureus*, *S. pyogenes*) and fungicidal strains (*C. albicans*, *A. niger* and *A. clavatus*). The antimicrobial results showed that the benzimidazole complexes were more active against bacterial and fungicidal strains than their corresponding ligands. Most benzimidazole complexes were active against the bacterial strains whereas only one benzimidazole complex was active against fungicidal strains.

Keywords: monodentate 1*H*-benzo[*d*]imidazole ligands, transition metal complexes, antimicrobial activity

1. INTRODUCTION

The pathogenic microbial (bacterial and fungicidal) infections are most common contagious disease worldwide. Many harmful bacteria may produce toxins in human body which is enough to damage the body and can result in many serious or life threatening complications, such as bacteremia (blood poisoning), kidney failure and toxic shock syndrome. Recently it is a challenge to surmount the infectious disease caused by micro organisms because the contagious disease originated by this kind of species recognised as a serious health problem world wide [1], therefore it is necessary for chemists and pharmacists to find out the new effective drug for contagious disease caused by micro organisms and it will be a big achievement for them, becasue no single drug found since last 60 years.

Azole motifs (*viz*., Imidazoles and Benzimidazoles) and their. derivatives are the key class of heterocyclic compounds with *N*-donor atom therefore they can be splendid organic ligands to generate various coordination compounds upon ligation to metal ion centres [2-5]. The coordination compounds of azole ligands having antibacterial, antifertile, antifungal and other biological properties have gathered lots of attention among scientific community over the past few decades [6-10].

After studying the facts of the *N*-donor azole type of ligands we had focused on benzimidazole molecules and synthesize novel monodentate benzimidazole ligands to prepare their transition metal complexes, because benzimidazole molecule itself is of greater significance due to its versatile biological and pharmacological activities.

In this direction 2-Substituted derivatives of benzimidazole moeity have found intersting application against fungal infectious diseases because of their great capability to control wide range of the fungicidal infections [11,12].Furthermore, 5,6-dimethyl derivative of benzimidazole molecule is the imperative part of the structure of vitamin B_{12} as well as of metalloproteins too. Most significantly 2-substituted benzimidazole derivatives are found to be the core structure of several therapeutic drugs which have been found applications as anticancers, antifungals, antivirals, antihypertensives, antiulcers, antihistaminics, anthelmintic and antibacterial [13-16].

Combination of these two facts about benzimidazole ligands and their metal complexes leads to an extensive study of the transition metal complexes containing 2-substituted benzimidazole molecules as ligands for their structural and various biological activities [17] as they are now renowned as more biologically active than those of free ligands because, when lone pair of electrons of ligands is entered into the *d*-orbital of transition metal ions to form new coordination compounds containing benzimidazole ligands and halide ions it makes chemical, physical and biological changes into the complexes [18].

In the present article we have reported the study on the spectral characterization and biological behavior of the new complexes in compare to their analogous monodentate benzimidazole ligands, which have empirical structural formula $[ML_2Cl_2].nH_2O$ suggested by elemental analysis [Where, M = Cu(II), Ni(II) and Co(II); L = BZa and BZb; n = 1, 1.5, 2, 2.5 and 3] and of ligands and their metal complexes.

2. MATERIALS AND METHODS

2.1 Reagents and Chemicals

All chemicals used in this study were supplied by Spectrochem. All solvents used were of analytical reagent grade and used without further purification.

2.2 Physico-chemical Studies

The elemental microanalysis of synthesized compounds were satisfactorily performed on EURO EA Elemental Analyzer, EA-3000, RS-232. IR spectra as KBr discs were recorded on Shimadzu FT-IR 8400 spectrophotometer. The ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were measured in DMSO-d_6 solutions on a Bruker AV spectrophotometer using TMS as an internal reference (Chemical shifts are in δ ppm). The mass spectra were recorded on Shimadzu GC-MS-QP-2010 Gas Chromatography. UV-visible spectra were recorded in methanol on a Shimadzu UV mini-1700 spectrophotometer. The ESI mass spectra were recorded on Micromass Q-Tof Micro having mass Range of 4000 amu in quadruple and 20000 amu in ToF. The TGA of all metal complexes were taken of the Diamond Thermogravimetric/ Differential Thermal Analyzer (TG/DTA) from the room temperature to 1000 °C under the heating

rate of 20 °C. The magnetic susceptibility measurements of all the complexes were carried out by Gouy balance at room temperature. The Conductivity values of all the complexes were measured on an Elico conductivity bridge (type CM82T) by using methanol as a solvent. TLC was performed on silica gel-G using ethyl acetate: hexane (1:4) solvent system.

2.3 Pathogens

The pathogenic bacterial and fungal MTCC strains were acquired from Institute of Microbial Technology, Chandigarh.

2.4 Synthesis of Aryl Aldehydes

Both aldehydes used for the synthesis of ligands were prepared by previously published methods [19,20].

2.5 General Synthesis of 2-(Substituted Phenyl)-1*H*-benzo[*d*]imidazoles

The 2-(substituted phenyl)-1*H*-benzo[*d*] imidazoles were prepared by mixing substituted aldehydes (0.005 mol) with *o*-phenylenediamine (0.005 mol) using ceric ammonium nitrate (Catalytic amount) in presence of hydrogen peroxide in 50 mL methanol and allowed to reflux for 6-8 hours. The progress of reaction was monitored by TLC. After completion of reaction, the reaction mixture was allowed to cool to room temperature and poured in to crushed ice, formed product was separated by filtration and was recrystallized from hot methanol to give brown crystals.

2.5.12-(3′,4′-Dimethoxy-6′-nitro-phenyl)-1*H*-benzo[*d*]imidazole (BZa)

Yield: 79 %, m.p. 170 °C, IR (KBr) ν cm^{-1}: 3300, 3254, 3189, 3156 (N-H), 3066 (C-H), 1661 (C=N), 1263, 1039 (C-O-C), 818 (C-N). ^{1}H NMR (DMSO-d_6+400 MHz) δ in ppm: 3.91-3.95 (s, 6H, 2′-OCH_3), 7.23-7.26 (m, 2H, Ar-H of benzimidazole ring), 7.43 (s, 1H, Ar-H), 7.59-7.62 (m, 2H, Ar-H of benzimidazole ring), 7.68 (s, 1H, Ar-H), 11.30 (s, 1H, benzimidazole).^{13}C NMR (DMSO-d_6+100 MHz)δ in ppm: 56.54, 107.58, 108.68, 109.92, 123.06, 138.04, 141.37, 149.46, 152.77, 178.19 and 188.44. Mass *m*/z: 299 (M). Anal.Cacld. for $C_{15}H_{13}N_3O_4$; Cacld.: C, 60.20; H, 4.38; N, 14.04; Found: C, 60.01; H, 4.22; N, 13.93 %.

2.5.2 2-(3′-Methoxy-4′-hydroxy-5′-bromophenyl)-1*H*-benzo[*d*]imida-zole (BZb)

Yield: 70 %, m.p. 205 °C, IR (KBr) $\nu$$cm^{-1}$: 3450, 3435 (O-H), 3320, 3292, 3217, 3153 (N-H), 3084, 3018 (C-H), 1647 (C=N), 1228, 1099 (C-O-C), 682 (C-Br). ^{1}H NMR (DMSO-d_6 + 400 MHz) δ in ppm: 3.91 (s, 3H, -OCH_3), 5.47 (s, 1H, -OH), 6.77-6.81 (t, 1H, Ar-H of benzimidazole), 6.93-6.95 (d, 1H, Ar-H), 7.14-7.17 (m, 2H, Ar-H of benzimidazole), 7.19-7.23 (t, 1H, Ar-H of benzimidazole), 7.73 (s, 1H, Ar-H), 12.68 (s, 1H, Ar-H of benzimidazole).^{13}C NMR (DMSO-d_6 + 100 MHz) *d* in ppm: 56.40, 109.29, 124.26, 126.49, 141.25, 145.44, 148.52, 177.64 and 190.31. Mass *m*/z: 318 (M). Anal. Cacld. for $C_{14}H_{11}BrN_2O_2$; Cacld.: C, 52.69; H, 3.47; N, 8.78; Found: C, 52.52; H, 3.34; N, 8.58 %.

2.6 Preparation of Metal Complexes

The solution of metal salts (0.001 mol in 10 mL ethanol) was added drop wise to the 2-(substituted phenyl)-1*H*-benzo[*d*]imidazole ligands solution (0.002 mol in 25 mL ethanol) with continuous stirring. After completion of addition, the reaction was stirred and refluxed for 48 hours at 50 °C on stirring device. The colored solid product was separate out in the flask which was filtered off and wash with alcohol. The conductivity measurement (10^{-3} M dimethyl formamide solution) and elemental analysis of all metal complexes tabulated in table 1.

2.7 Biological Activity

Antibacterial and antifungal activity of

Table 1. Elemental and analytical data of monodentate benzimidazole metal complexes.

No.	Complex	% Analysis, Found (Calcd.)				Λ^b
		C	H	N	M	
1	$[Cu(BZa)_2Cl_2]2.5H_2O$	49.16 (48.74)	3.58 (3.21)	11.47 (11.07)	8.67 (8.26)	12.43
2	$[Ni(BZa)_2Cl_2].H_2O$	49.48 (49.06)	3.60 (3.15)	11.54 (11.13)	8.06 (7.57)	14.50
3	$[Co(BZa)_2Cl_2].1.5H_2O$	49.47 (49.02)	3.60 (3.18)	11.54 (11.11)	8.09 (7.51)	20.00
4	$[Cu(BZb)_2Cl_2].H_2O$	43.52 (43.17)	2.87 (2.45)	7.25 (6.85)	8.22 (7.81)	8.40
5	$[Ni(BZb)_2Cl_2].3H_2O$	43.79 (43.36)	2.89 (2.49)	7.30 (6.12)	7.64 (7.18)	19.17
6	$[Co(BZb)_2Cl_2].3H_2O$	43.78 (43.38)	2.89 (2.50)	7.29 (6.89)	7.67 (7.32)	20.00

[b]Conductance at room temperature in 10^{-3} M DMF solution ($cm^2W^{-1}mol^{-1}$)

the ligands and their metal complexes were evaluated by the cup palate method and MIC values of synthesized compounds were determined by previously published method [21,22]. Seven microbial strains were selected for antimicrobial activity on the basis of their clinical consequence of causing diseases in humans for newly synthesized 2-(substituted phenyl)-1*H*-benzo[*d*] imidazoles and their transition metal complexes as MIC *in vitro* by broth dilution method with two Gram positive bacteria *S. aureus* MTCC 96 and *S. pyogenes* MTCC 443 and two Gram negative bacteria *E. coli* MTCC 442 and *P. aeruginosa* MTCC 441 and three fungi (*C. albicans* MTCC 227, *A. niger* MTCC 282 and *A. clavatus* MTCC 1323), taking ampicillin, ciprofloxacin, norfloxacin, nystatin and griseofulvin as standard drugs. The bacterial and fungal cultures were procured from Institute of Microbial Technology, Chandigarh.

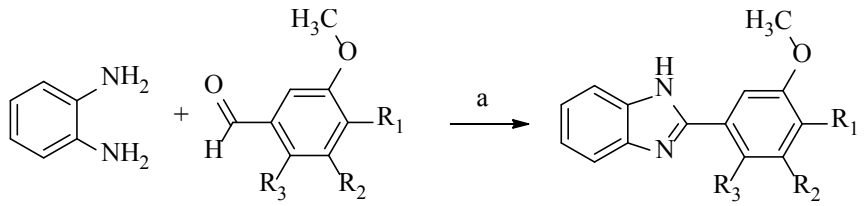
The bacteria were sub-cultured on Nutrient agar and fungi were sub-cultured on Sabouraud's dextrose agar (SDA) and incubated aerobically at 37 °C.

2.8 Determination of MIC

The minimum inhibitory concentration (MIC) of the compounds was determined by the micro broth dilution technique using Muller Hinton broth. Serial threefold dilution ranged from 1000 to 1.56 μgmL^{-1} for compounds. The inoculums was prepared in broth which had been kept overnight at 37 °C and which had been diluted with Muller Hinton broth to give a final concentration of 10^8 cfu mL^{-1} (where cfu = Colony forming unit) in the test tray. The trays were covered and placed in plastic bags to prevent drying. After incubation at 37 °C for 24 hours, the MIC value was defined as the lowest concentration of the compound giving complete inhibition of visible growth [22].

3. Results and Discussions

The synthetic course used for novel monodentate 2-(substituted phenyl)-1*H*-benzo[*d*] imidazole ligands is portrayed in scheme 1. Synthesis of the titled ligands (**BZa**) and (**BZb**) was accomplished by cyclocondensation reaction of *o*-phenylenediamine and substituted phenyl aldehydes by adding hydrogen peroxide and ceric ammonium nitrate (CAN) in catalytic amount in alcoholic media. The figure 2 shows the proposed structure of benzimidazole metal complexes which were synthesized by using metal salt and benzimidazole ligands in hot ethanol. All the synthesized benzimidazole complexes have been found stable at room temperature and soluble in DMF, THF and DMSO and less soluble in methanol, benzene and chloroform.



[a]**Reagents and conditions: Methanol; Ceric ammonium nitrare; Hydrogenperoxide; Reflux 6-8 hr**

Scheme 1. Synthetic route for the synthesis of benzimidazole ligands

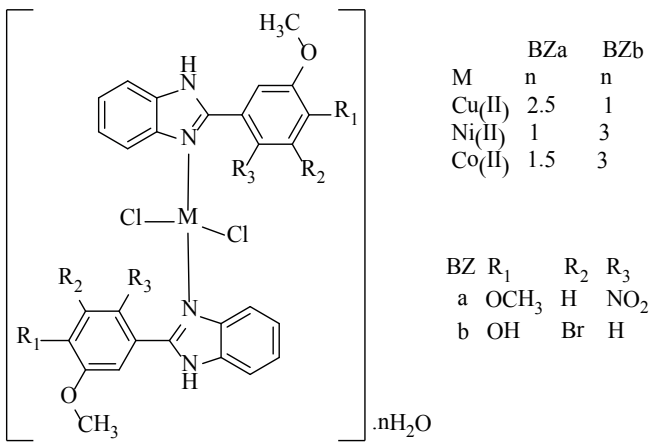


Figure 2. Proposed structure of monodentate benzimidazole metal complexes.

3.1 IR Spectral Studies

The IR spectra of ligands shows characteristic bands at 3320-3153 cm^{-1} and 3084-3018 cm^{-1} corresponds to the N-H stretching of benzimidazole ring and C-H stretching of aromatic ring respectively. Asymmetric and symmetric C-H stretching of methyl group was observed at 2970-2923 cm^{-1} and 2885-2865 cm^{-1} respectively. Asymmetric and symmetric stretching of C-O-C methoxy group were observed at 1263-1228 and 1099-1039 cm^{-1}. The stretching frequencies of C=N of free ligands were obtained at 1661-1647 cm^{-1} which have been shifted by 35 to 40 cm^{-1} in metal complexes corresponding to their ligands which clearly indicates that the tertiary nitrogen of benzimidazole ring coordinative covalently bonded to the metal ions via the lone pair of electron of nitrogen atom (Table 2). The medium intensity bands of metal-nitrogen and metal-chloride were observed in far IR for the metal complexes at 460-435 cm^{-1} and 424-399 cm^{-1} assignable to M-N [23] and M-Cl stretching vibrations respectively.

3.2 Electronic Spectra and Magnetic Moment Studies

All metal complexes shows the sharp hump in their electronic spectra near about at 395-410 nm (25316.4-24390.2 cm^{-1}) due to the ligand to metal charge transfer transition which is the best evidence of the complex formation (Figure 1). The electronic spectra of both copper complexes gives $^2E_g \rightarrow {}^2A_{1g}$, $^2E_g \rightarrow {}^2B_{2g}$ and

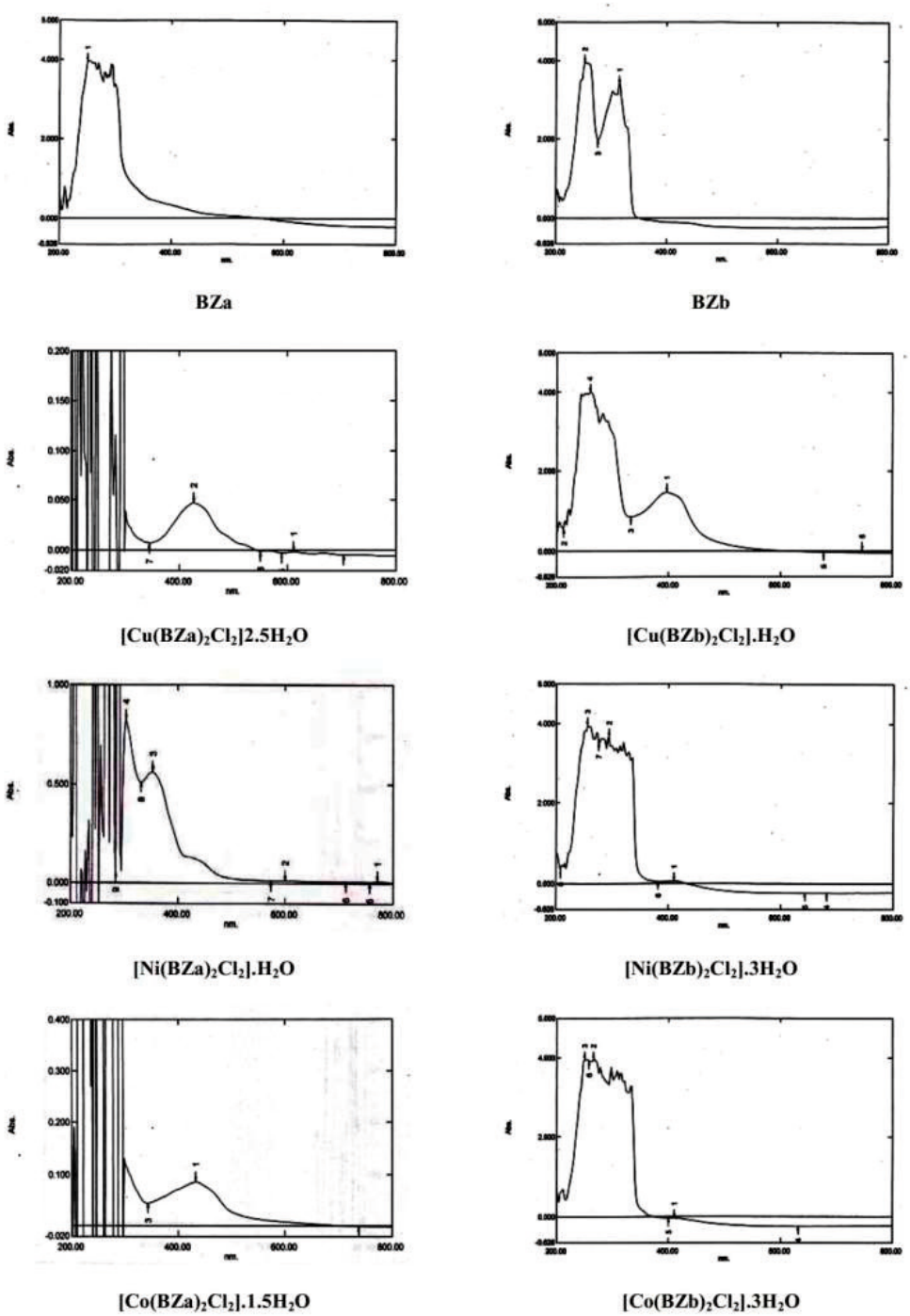


Figure 1. UV-Visible spectrums of benzimidazole ligands and their metal complexes.

Table 2. Confirmative IR frequencies (cm^{-1}) of benzimidazole ligands and their metal(II) complexes.

Compound	*n(C=N)*	*n (M-N)*	*n (M-Cl)*
BZa	1661	-	-
$[Cu(BZa)_2Cl_2]2.5H_2O$	1629	435	401
$[Ni(Bza)_2Cl_2].H_2O$	1629	441	399
$[Co(Bza)_2Cl_2].1.5H_2O$	1629	459	424
BZb	1631	-	-
$[Cu(BZb)_2Cl_2].H_2O$	1620	435	406
$[Ni(BZb)_2Cl_2].3H_2O$	1622	447	418
$[Co(BZb)_2Cl_2].3H_2O$	1620	445	400

$^2E_g \rightarrow {}^2B_{1g}$ transitions at 540-570 nm (18518.5-17543.8 cm^{-1}), 617-670 nm (16207.4-14925.3 cm^{-1}) and 705-755 nm (14184.3-13245.0 cm^{-1}) suggesting the square planar environment around Cu(II) metal ion. The magnetic moment values were found at 1.75 BM and 1.71 BM which is also agree with the known value of Cu(II) complex in square planar geometry. Ni(II) complexes of (**BZa**) and (**BZb**) ligands shows $^3T_1(F) \rightarrow {}^3T_2$, $^3T_1(F) \rightarrow {}^3A_2$ and $^3T_1(F) \rightarrow {}^3T_1(P)$ transitions at 580(17241.3 cm^{-1}), 650-725 (15384.6-13793.1 cm^{-1})and 700-775(14285.7-12903.2 cm^{-1}), suggesting tetrahedral stereochemistry and by the measurement of magneticmoment both complexes gave 4.02 BM and 3.53 BM values, signifying the typical tetrahedral configuration around Ni(II) ion.

The Co(II) complexes of benzimidazole ligands (**BZa**) and (**BZb**) displays only a merged broad and weak band at 632 nm (15822.7 cm^{-1}) and 733 nm (13642.5 cm^{-1}) respectively for the $^4A_2(F) \rightarrow {}^4T_2$, $^4A_2(F) \rightarrow {}^4T_1(F)$ and $^4A_2(F) \rightarrow {}^4T_1(P)$ transitions, confirmed the tetrahedral geometry for both cobalt(II) complexes respectively, the magnetic moment of both cobalt(II) complex are in agreement with known value of cobalt(II) complexes in tetrahedral geometry which were 4.51 BM and 4.79 BM [24-28].

3.3 TGA Study

The $[Cu(BZa)_2Cl_2]$ complexes starts from 30 °C and end at 860 °C temperature showing gradual weight loss in only one step of decomposition by the loss of two and half molecule of latice water molecules (Found: 5.99 %, 46.48 gm; Calcd.: 5.80 %, 45.02 gm) and majority part of ligands (Found: 59.49 %, 461.67 gm; Calcd.: 60.32 %, 468.15 gm) from the complex. The Ni(II) complex of ligand (**BZa**) decomposes in to two steps, first step of decomposition at 80-170 °C temperature probably due to the loss of one lattice water molecule (Found: 2.708 %, 20.14 gm; Cacld.: 2.42 %, 18.01 gm) and the second step of decomposition at 170-1000 °C temperature (Found: 70.168 %, 522.08 gm; Cacld.: 72.31 %, 538.09 gm) suggesting the loss of ligand parts from the complex. The $[Co(Bza)_2Cl_2]$ complex also decomposes in to two stepsat 20-130 °C temperature (Found: 3.852 %, 27.967 gm; Cacld.: 3.58 %, 29.025 gm) and 130-1000 °C temperature (Found: 65.385 %, 493.01gm; Cacld.: 66.72 %, 503.12 gm) showing loss of one and half water and ligand molecules respectively. The Cu(II) complex of (**BZb**) ligand shows first step of decomposition at 55-160 °C temperature suggesting the loss of one mole of lattice water molecule (Found: 2.592 %, 20.39 gm; Cacld.: 2.29 %, 18.025 gm) and

second step of decomposition at 160-945 °C temperature suggesting the loss of ligand molecules (Found: 90.766 %,714.18 gm; Cacld.: 89.71 %, 705.94 gm).The $[Ni(BZb)_2Cl_2]$ complex decomposes at 45-180 °C and 180-1000 °C temperature showing 3 lattice water molecules(Found: 7.170 %, 58.64 gm; Cacld.: 6.60 %, 54.03 gm) and ligand molecules (Found: 83.041 %, 679.19 gm; Cacld.: 82.035 %, 670.97 gm) respectively. The Co(II) complex of ligand (**BZb**) also shows two step of decomposition at 30-150 °C and 150-1000 °C temperature suggesting the loss of 3 lattice water molecule (Found: 6.857 %, 56.152 gm; Cacld.: 6.605 %, 54.03 gm) and ligand molecules (Found: 89.726 %, 734.76 gm; Cacld.: 86.205 %, 705.94 gm) respectively.

3.4 Molar Conductivity

The molar conductivity of all the metal complexes were taken in dimethyl formamide 10^{-3} M solution. The conductance values indicate that all benzimidazole metal complexes are non-electrolytes (Table 1) [29,30].

3.5 Antimicrobial Activity

The benzimidazole (**BZa**) and (**BZb**) ligands and their metal complexes were evaluated for *in vitro* antibacterial activity against *E. coli* MTCC 442, *P. aeruginosa* MTCC 441, *S. aureus* MTCC 96 and *S. pyogenes*MTCC 443 and also evaluated for antifungal activity against *C. albicans* MTCC 227, *A. niger* MTCC 282 and *A. clavatus* MTCC 1323.

Compounds (**BZa**)and (**BZb**)shows zones of inhibition ranging between 7 to 22 mm. On the basis of the zones of inhibition produced against the tested bacteria, compounds (**BZa**) and (**BZb**) were found to be most effective against *S. aureus* and *S. pyogenes* showing the maximum zones of inhibition at 7-20 mm, compound (**BZb**) was found to be effective against *S. pyogenes* and compound (**BZa**) was found to be effective against *S. aureus*. All the benzimidazole metal complexes show comparatively fair activity against gram-positive bacterial strains than gram-negative (Table 3). The nickel complex $[Ni(BZa)_2Cl_2]$ of (**BZa**) shows MIC value at 62.5 μgmL^{-1} (13 mm

Table 3. TG analysis data of benzimidazole metal complexes.

Complex	Temp. range °C	Wt. loss %		Total wt.loss %		Assignment of wt. loss	Residue
		Found	Calcd.	Found	Calcd.		
$[Cu(BZa)_2Cl_2]2.5H_2O$	30-130	5.99	5.80	65.48	64.04	$2.5H_2O$	$C_{10}H_{12}Cl_2CuN_4$
	130-860	59.49	60.32			$C_{24}H_{24}N_2O_8$	
$[Ni(Bza)_2Cl_2].H_2O$	80-170	2.708	2.42	72.876	74.73	H_2O	$C_{10}H_{12}N_4Ni$
	170-1000	70.168	72.31			$C_{24}H_{24}N_2O_8$	
$[Co(Bza)_2Cl_2].1.5H_2O$	20-130	3.852	3.58	69.237	70.30	$1.5H_2O$	$C_{10}H_{12}ClCoN_4$
	130-1000	65.385	66.72			$C_{24}H_{24}ClN_2O_8$	
$[Cu(BZb)_2Cl_2].H_2O$	55-160	2.592	2.29	93.358	92.293	H_2O	CuO
	160-945	90.766	89.71			$C_{28}H_{22}Br_2Cl_2N_4O_4$	
$[Ni(BZb)_2Cl_2].3H_2O$	45-180	7.170	6.60	90.211	88.635	$3H_2O$	NiCl
	180-1000	83.041	82.035			$C_{28}H_{22}Br_2N_4O_4$	
$[Co(BZb)_2Cl_2].3H_2O$	30-150	6.857	6.605	96.583	92.81	$3H_2O$	CoO
	150-1000	89.726	86.205			$C_{28}H_{22}Br_2Cl_2N_4O_4$	

ZOI) against *P. aeruginosa* whereasthe cobalt complex $[Co(BZa)_2Cl_2]$ of (**BZa**) ligand gives zone of inhibition of 9 mm (10 μgmL^{-1}) against *S. aureus* and 11 mm (12.5 μgmL^{-1}) against *S. pyogenes*. Copper(II), nickel(II) and cobalt(II) complexes of ligand (**BZa**) were found very much effective against *S. aureus* and *S. pyogenes* with MIC values 10 μgmL^{-1} (8-20 mm inhibition zones). The nickel complex $[Ni(BZb)_2Cl_2]$ of (**BZb**) ligand have minimum inhibition concentration in compare to all complexes was 6.25 μgmL^{-1}against *S. pyogenes* with zone of inhibition of 22 mm. Only cobalt(II) complex $[Co(BZb)_2Cl_2]$ of ligand (**BZb**) showed zone of inhibition at 18 mm against gram negative bacteria *E. coli* with 10 μgmL^{-1} MIC value. The MIC (minimum inhibitory concentration) values of all tested benzimidazole ligands and their metal complexes were in ranged between 10 and 50 μgmL^{-1} against gram-positive bacteria and more than two complexes and (**BZb**) ligand were inactive or needs more than 1000 μgmL^{-1} complex and (**BZb**) ligand against gram-negative bacteria.

Copper(II), nickel(II) and cobalt(II) complexes of (**BZb**) ligand displayed good antibacterial activity with the lowest MIC value at 10 μgmL^{-1} against *S. aureus*.Only two complexes, $[Ni(BZb)_2Cl_2]$ and $[Co(BZb)_2Cl_2]$ of ligand (**BZb**) possessed antibacterial activity with MIC value of 6.25 μgmL^{-1} against *S. pyogenes* (Gram positive) and 10 μgmL^{-1} against *E. coli* (Gram negative) (Table 4).

Amongst the synthesized compounds, benzimidazole ligand (**BZa**)shows more mycelia growth inhibition against *C. albicans*, very less growth against *A. niger* and *A. clavatus* whereas compound (**BZb**) was found to be

Table 4. Antibacterial activity of monodentate benzimidazole ligands and their metal complexes (μgmL^{-1}).

No.	Compound	*E. coli*	*P. aeruginosa*	*S. aureus*	*S. pyogenes*
		MTCC 442	**MTCC 441**	**MTCC 96**	**MTCC 443**
1	BZa	25	250	1000	500
2	BZb	1000	1000	>1000	500
3	$[Cu(BZa)_2Cl_2]2.5H_2O$	500	1000	250	500
4	$[Ni(Bza)_2Cl_2].H_2O$	100	>1000	1000	1000
5	$[Co(Bza)_2Cl_2].1.5H_2O$	12.5	500	>1000	1000
6	$[Cu(BZb)_2Cl_2].H_2O$	500	500	1000	500
7	$[Ni(BZb)_2Cl_2].3H_2O$	6.25	250	50	1000
8	$[Co(BZb)_2Cl_2].3H_2O$	250	500	500	25
	Standard drugs				
1	Ampicillin	100	100	250	100
2	Ciprofloxacin	25	25	50	50
3	Norfloxacin	10	10	10	10

Table 5. Antifungal activity of monodentate benzimidazole ligands and their metal complexes (μgmL^{-1}).

No.	Compound	*C. albicans*	*A. niger*	*A. clavatus*
		MTCC 227	**MTCC 282**	**MTCC 1323**
1	BZa	>1000	>1000	100
2	BZb	500	1000	500
3	$[Cu(BZa)_2Cl_2]2.5H_2O$	250	500	250
4	$[Ni(BZa)_2Cl_2].H_2O$	1000	1000	500
5	$[Co(BZa)_2Cl_2].1.5H_2O$	500	500	500
6	$Cu(BZb)_2Cl_2].H_2O$	500	500	>1000
7	$Ni(BZb)_2Cl_2].3H_2O$	500	250	500
8	$Co(BZb)_2Cl_2].3H_2O$	>1000	500	500
	Standard drugs			
1	Nystatin	100	100	100
2	Griseofulvin	500	100	100

sufficient active against *A. niger* and *A. clavatus* and inactive or required compound solution more than 1000 μgmL^{-1} against *C. albicans* (Table 5). All the metal complexes formed from (**BZa**) and (**BZb**) benzimidazole ligands have enough growth against *C. albicans*, *A. niger* and *A. clavatus*. Copper complexes of both ligands $[Cu(BZa)_2Cl_2]$ and $[Cu(BZb)_2Cl_2]$ found to be active more than its corresponding ligands were 200 μgmL^{-1} against *A. clavatus* and more active than comparative standard drug griseofulvin (Table 5).

From the overall result it is conspicuous that all metal complexes could be predictable as the more biologically active compounds with good antifungal and antibacterial profile in compare to their corresponding ligands.

4. Conclusion

The studies on antimicrobial activity of newly synthesized ligands and their metal complexes have been tested on seven microorganisms. The antimicrobial study of the metal complexes gives good results in compare to corresponding ligands. The square planar geometry of both copper(II) complexes is confirmed by the measurement of magnetic moment, whereas, the value of magnetic monent suggest the tetrahedral geometry for both nickel(II) and cobalt(II) complexes. The TGA studies of all metal complexes gives the information about the water molecules attached with metal complexes (Figure 2) and it is clear from the TG graphs that every complex have lattice water molecules and not coordinated water molecule. The conductivity measurement in DMF solution shows that all complexes are non-electrolytes.

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