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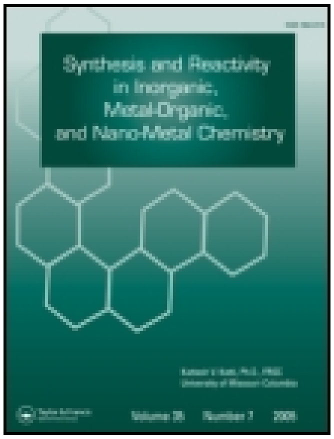

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Cu(II) and Ni(II) Complexes of Novel Three 2-{1′-Phenyl-3′-(4″-Halophenyl)-1H-Pyrazole-4-yl}-1H-Benzimidazoles: Synthesis and Structural Depiction

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Cu(II) and Ni(II) Complexes of Novel Three 2-{1′-Phenyl-3′-(4″-Halophenyl)-1*H*-Pyrazole-4-yl}-1*H*-Benzimidazoles: Synthesis and Structural Depiction

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Novel three 2-{1′-Phenyl-3′-(4″-halophenyl)-1*H*-pyrazole-4-yl}-1*H*-benzimidazoles ($HB_{a–c}$) synthesized by the condensation of *o*-phenylenediamine and substituted-1*H*-pyrazole aldehydes in the presence of H_2O_2 through Ceric ammonium nitrate in catalytic amount and the nonchelated monodentate benzimidazoles complexes of 2-{1′-Phenyl-3′-(4″-halophenyl)-1*H*-pyrazole-4-yl}-1*H*-benzimidazoles were synthesized with a choice of metal salts in 2:1 mole ratio of ligand and metal salts, respectively, in ethanolic solution. The confirmed structures and characteristics of complexes were in good agreement with various physicochemical studies. The monodentate behavior of the ligands was proposed on the basis of spectral studies. The newly synthesized complexes possess octahedral and tetrahedral, square pyramidal and square planar geometry.

Keywords Cu(II) and Ni(II) complexes, monodentate 1*H*-benzimidazole ligands, physicochemical studies, pyrazole aldehydes

INTRODUCTION

The coordination ability of a number of monodentate benzimidazole derivatives has been reported in past literature.[1–6] Numerous complexes involving d-block metals and imidazole derivatives are well known[7–13] and there is enormous interest in the transition metal complexes of imidazole and its derivatives as ligands.[14–18] Parasitic and antiviral activities of benzimidazoles and some substituted benzimidazole compounds have been widely investigated in medicinal fields. In medicine, drugs based on benzimidazoles and benzimidazole derivatives have been patented, due to their antiviral and antihelmintic activity.[19] In metallurgy, benzimidazole has been used as a corrosion inhibitor.[20]

Benzimidazole as its 5,6-dimethyl derivative is present in vitamin B_{12} and related biomolecules. Coordination complexes of benzimidazole derivatives with transition metals have been used in attempts to prepare structural and spectroscopic models of the active sites of some metalloenzymes.[21] Reaction of the benzimidazoles with transition metal salts, $MCl_2.nH_2O$ (M = Cu and Ni; $n = 2$ & 6, respectively) in ethyl alcohol led to the formation of monodentate benzimidazole complexes $M(HB_{a–c})_2Cl_2$ (HB = benzimidazole ligands). 2-{1′-Phenyl-3′-(4″-halophenyl)-1*H*-pyrazole-4-yl}-1*H*-benzimidazoles compounds are an *N*-monodentate ligands that contains one donor group of relevance to the coordination of metal centers. In the present article, we reported the synthesis and structural characterization of the dichloro-bis[2-{1′-Phenyl-3′-(4″-halophenyl)-1*H*-pyrazole-4-yl}-1*H*-benzimidazoles]metal(II)complexes $[M(HB_{a–c})_2Cl_2].nH_2O$.

EXPERIMENTAL

Reagents and Material

All procedures were carried out by using standard solvents and chemicals without further purification which were commercially available and used as purchased. IR spectra as KBr discs were recorded on Shimadzu FT-IR 8400 spectrophotometer. The ^1H NMR spectra were measured in DMSO-d^6 solutions on a Bruker Av spectrophotometer (400 MHz) using TMS as an internal reference (Chemical shifts in δ ppm). The mass spectra were recorded on Shimadzu GC-MS QP2010 Gas Chromatograph. 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 ESR spectral measurement of all Cu(II) complexes was carried out on a Varian E-112 X-band spectrophotometer at room temperature using TCNE as *g* marker. The TGA graphs of all metal complexes were taken by the Diamond Thermogravimetric/Differential Thermal Analyzer (TG/DTA) at room temperature of 1000°C under heating rate of 20°C min^{-1}. The electronic spectra were recorded on Shimadzu UV-1700, UV-Visible spectrophotometer. The magnetic moment of all the complexes was measured by Gouy balance at room temperature. Molar Conductance of all the complexes was performed on an Elico conductivity bridge (type CM82T).

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All the synthesized compounds were micro analyzed satisfactorily for C, H, and N (EURO EA Elemental Analyzer, EA-3000, RS-232).

Synthesis of Aldehydes

1-Phenyl-3-(4′-halophenyl)-1*H*-pyrazole-4-carbaldehydes ($Pyl_{a–c}$) were synthesized as previously published method.[22–25]

Synthesis of Ligands ($HB_{a–c}$)

In 50 mL round bottom flask a mixture of *o*-phenylenediamine (OPD) (0.01 mole), pyrazole aldehyde ($Pyl_{a–c}$) (0.01 mole), Ceric Ammonium Nitrate (CAN) (0.001 mole) hydrogen peroxide (30%, 10 ml) and sufficient amount of methanol were allow to reflux with continuous stirring on preheated oil bath. Reaction was monitored by TLC (Solvent system, Hexane : Ethyl acetate- 4:1). After completion of the reaction, the reaction mass was poured into ice water and filtered with suction to get the benzimidazole ligands in 76–82% yield.

2-(3′-(4-Chlorophenyl)-1′phenyl-1*H*-pyrazol-4-yl)-1*H*-benzimidazole (HB_a)

Yield: 72%, m.p.: 250°C, IR (ν cm^{-1}, KBr): 3423, 3392, 3236 (N–H stretching), 3128, 3076, 3036 (C–H stretching of Ar), 1724, 1689 (C=N stretching of benzimidazole), 1602, 1560 (C=N stretching of pyrazole), and 793 (C–Cl stretching). ^1H NMR (400 MHz + DMSO-d_6) δ in ppm: 7.24–7.26 (m, 2H, Ar-H of benzimidazole), 7.41–7.47 (t, 3H, Ar-H of pyrazole), 7.51–7.53 (d, 2H, Ar H of pyrazole, $J = 8.4\ Hz$), 7.59–7.62 (t, 4H, Ar-H of pyrazole), 7.96–8.02 (d, 2H, Ar-H of benzimidazole, $J = 8.4\ Hz$), 9.12 (s, 1H, pyrazole H), and 13.02 (s, 1H, benzimidazole H). Mass *m*/*z*: 369. Anal. Cacld. for $C_{22}H_{15}ClN_4$; Cacld.: C, 71.25; H, 4.08; Cl, 9.56; N, 15.11; Found: C, 70.66; H, 3.90; Cl, 9.40; N, 15.00%.

2-(3′-(4-Bromophenyl)-1′phenyl-1*H*-pyrazol-4-yl)-1*H*-benzimidazole (HB_b)

Yield: 67%, m.p.: 230°C, IR (ν cm^{-1}, KBr): 3248, 3227 (N–H stretching), 3142, 3099, 2995 (C–H stretching of Ar), 1591 (C=N stretching of benzimidazole), 1537 (C=N stretching of pyrazole), and 667 (C-Br stretching). ^1H NMR (400 MHz + DMSO-d_6) δ in ppm: 7.26–7.31 (m, 2H, Ar-H of benzimidazole), 7.34–7.36 (d, 2H, Ar-H of benzimidazole, $J = 8.4$ Hz), 7.40–7.44 (m, 3H, Ar-H of pyrazole), 7.55–7.61 (m, 4H, Ar-H of pyrazole), 7.94–8.03 (dd, 2H, Ar-H of pyrazole), 9.11 (s, 1H, pyrazole H), and 13.15 (s, 1H, benzimidazole H). Mass *m*/*z*: 415. Anal. Cacld. for $C_{22}H_{15}BrN_4$; Cacld.: C, 63.63; H, 3.64; Br, 19.24; N, 13.49; Found: C, 63.51; H, 3.44; Br, 19.10; N, 13.46%.

2-(3′-(4-Fluorophenyl)-1′phenyl-1*H*-pyrazol-4-yl)-1*H*-benzimidazole (HB_c)

Yield: 62%, m.p.: 190°C, IR (ν cm^{-1}, KBr): 3354, 3304, 3282 (N–H stretching), 3111, 3055 (C–H stretching of Ar), 1597 (C=N stretching of benzimidazole), 1533, 1502 (C=N stretching of pyrazole), and 960 (C—F stretching). ^1H NMR (400 MHz + DMSO-d_6) δ in ppm: 7.19–7.21 (m, 1H, Ar-H of pyrazole), 7.41–7.42 (d, 2H, Ar-H of pyrazole, $J = 7.6$ Hz), 7.55–7.60 (m, 2H, Ar-H of pyrazole), 7.62–7.64 (d, 2H, Ar-H of pyrazole, $J = 8.8$ Hz), 7.69–7.71 (d, 2H, Ar-H of pyrazole, $J = 8.4$ Hz), 7.89–7.91 (d, 2H, Ar-H of benzimidazole, $J = 10.0$ Hz), 7.93–7.99 (m, 2H, Ar-H of benzimidazole), 9.09 (s, 1H, pyrazole H), and 12.70 (s, 1H, benzimidazole H). Mass *m*/*z*: 354. Anal. Cacld. for $C_{22}H_{15}FN_4$; Cacld.: C, 74.56; H, 4.27; F, 5.36; N, 15.81; Found: C, 74.38; H, 4.03; F, 5.12; N, 15.61%.

Synthesis of Metal Complexes $[M(HB_{a–c})_2Cl_2].nH_2O$

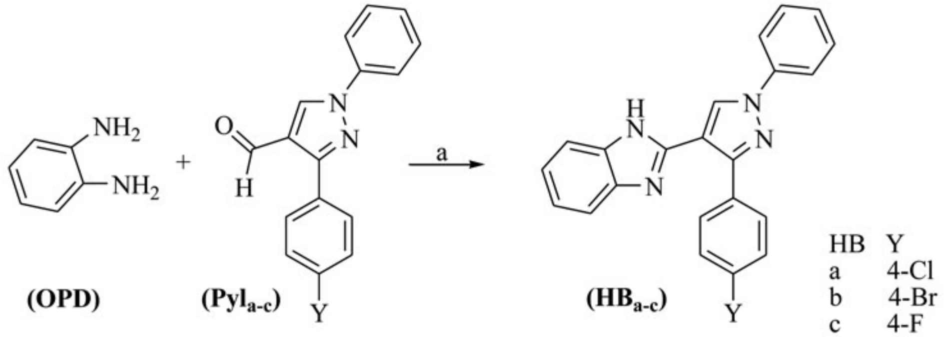
Hot solution of hydrated metal chloride (0.01 mol) in absolute ethanol was added to the hot solution of the benzimidazole ligand (0.02 mol) in the same solvent (25 mL). The resulting mixture was stirred under reflux for several days whereupon the complex precipitate. Dark-colored crystals were collected by filtration, washed with a distilled water and methanol.

RESULT AND DISCUSSION

Newly synthesized 1*H*-benzimidazoles ($HB_{a–c}$) were prepared by the cyclocondensation of *o*-phenylenediamine and 1-phenyl-3-(4′-halophenyl)-1*H*-pyrazole-4-carbaldehydes in the presence of hydrogen peroxide by using ceric ammonium nitrate as catalyst, the use of ceric ammonium nitrate in favor of increase the rate of reaction and the formation of product in good yield percentage because ceric ammonium nitrate has been widely used in many organic reactions as an efficient catalyst, especially for the synthesis of 2-substituted azoles.

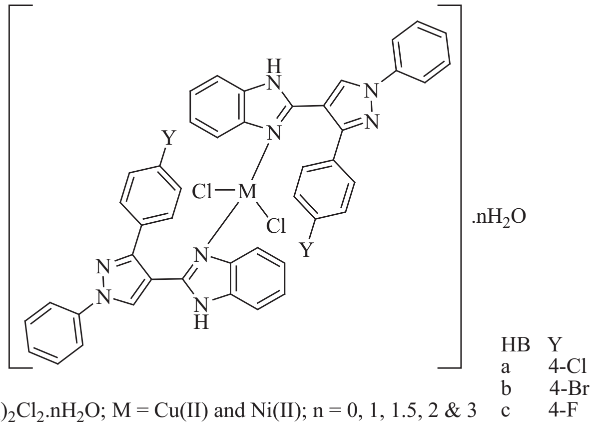
Six novel complexes were obtained using metal chloride salts of Cu(II) and Ni(II) ions with benzimidazole ligands ($HB_{a–c}$) by a one pot method. The monodentate benzimidazole ligands ($HB_{a–c}$) linked directly to metal ion through tertiary nitrogen atom of imidazole ring, which have a lone pair of electron to form a coordinate covalent bond. In forming of the coordination bond, the metal ion attracts the electrons of the imidazole ring of tertiary nitrogen. The solubility of all complexes with the attached benzimidazole ligands is much less than that of the free benzimidazole ligands ($HB_{a–c}$) in common organic solvents such as alcohols and ketones but highly soluble in DMF and DMSO (Scheme 1).

All complexes were synthesized in the warm ethanolic solution of the metal chloride salts with benzimidazole ligands ($HB_{a–c}$) in 1:2 mole ratios, respectively. It should be noticed that the reaction of all the metal ions with ligands yielded $[M(HB_{a–c})_2Cl_2].nH_2O$ complexes (where M=Cu(II) and Ni(II); $n = 0, 1, 1.5, 2, \& 3$). The proposed structure of metal complexes



^{a}Reaction and conditions: Ceric ammonium nitrate, Hydrogen peroxide, Methanol, Reflux

SCH. 1. Reaction scheme for the synthesis of 2-{1′-phenyl-3′-(4″-halophenyl)-1H-pyrazole-4-yl}-1H-benzimidazoles ($HB_{a–c}$).



$M(HB_{a\text{-}c})_2Cl_2.nH_2O$; M = Cu(II) and Ni(II); n = 0, 1, 1.5, 2 & 3

SCH. 2. Proposed structure of dichloro-bis[($HB_{a–c}$)]metal(II) complexes.

forms the all physicochemical characteristics given in Scheme 2. The molar conductance values suggest that all complexes are nonelectrolyte in 10^{-3} M DMF solution.[26] The elemental analysis data recommend the 1:2—metal:ligand stoichiometry for all complexes as expected.[27] The elemental analysis, and molar conductivity data of complexes are summarized in Table 1.

IR Spectra and Mode of Bonding

The infrared spectra of the all ligands exhibit the bands at 3423 to 3227 cm^{-1} which assigned to ν(N–H) stretching vibration. Substituted phenyl groups of pyrazole moiety in all ligands shows the ring skeletal ν(C–H) stretching vibrations at 3142 to 2995 cm^{-1}. The band emerging at 1724 to 1519 cm^{-1} about to ν(C=N) stretching vibrations.[28,29] The investigated complexes are similar to those of the corresponding ligands with all frequencies except ν(C=N) stretching, there are some significant changes between the metal complexes and their free ligand. The co-ordination mode and sites of the ligand to the metal ion were investigated by comparing the infrared spectra of the free ligand with its metal complexes. Upon co-ordination, it is noteworthy that the peak at about 1724 to 1519 cm^{-1} attributed to ν(C=N) stretching vibration originating from *N*-3-Imidazole ring, is shifted by 10 to 40 cm^{-1} on complexation, indicating co-ordination of *N*-3-atom of imidazole ring toward metal ions.[30] The stretching of ν(N–M) observed near about at 461 to 432 cm^{-1} and the stretching of ν(N–Cl) were obtained at 412 to 399 cm^{-1}.

^{1}H NMR spectra

The ^{1}H NMR spectrums of 2-{1′-Phenyl-3′-(4″-halophenyl)-1*H*-pyrazole-4-yl}-1*H*-benzimidazoles ($HB_{a–c}$) in DMSO-d_6 conform its preparation and displays a singlet peaks in between 12.70 and 13.15 δ ppm[31] for secondary amine hydrogen of imidazole ring, which conforms the formation of imidazole ring. Also the doublet, double doublet, triplet, and multiplet signals observed at 7.19–8.03 δ ppm are assignable to aromatic and benzimidazole ring protons.

Mass Spectra

GC-MS spectra of Ligands

The mass spectra of all three halo benzimidazole compounds show total molecular ion peaks and fragmented molecular ion peaks with respect to their molecular weight in form of cations or anions. The fragmentation in all compounds at 116 to 118 *m*/*z* is prediction of the formation of the benzimidazole ring ion.

ESI-MS Spectra of Complexes

The structures of all metal complexes can be confirmed by the molecular ion peaks obtained in ESI-MS spectra. The ESI mass spectrums of the represented metal complexes show that all complexes are thermodynamically and kinetically stable during the ESI process. The electron spray ionization spectrum of all metal complexes of benzimidazole ligands show molecular ion peak corresponding to a 2:1 species of ligands and metals respectively, the presence of metal ions in all species has been shown based on the isotopic peak pattern observed with all peaks.[32,33] The ESI spectra of all complexes show the molecular ion peaks with respect to their total molecular weight in the form of $M(HB_{a–c})_2Cl_2$ and fragmented molecular ion peaks of their corresponding ligands ($HB_{a–c}$), and complexed ions as $M(HB_{a–c})_2Cl$, $M(HB_{a–c})Cl_2$, $M(HB_{a–c})$, and $M(HB_{a–c})_2$.

TABLE 1
Physical characteristics and analytical data of the metal complexes

Complex	Yield%	Λ^a	Analytical% Cacld.(Found) C	H	N	M
$Cu(HB_a)_2Cl_2(H_2O)_{1.5}$	77	15.31	60.32 (60.18)	3.45 (3.32)	12.79 (12.68)	7.25 (7.12)
$Ni(HB_a)_2Cl_2(H_2O)_2$	80	8.68	60.66 (60.57)	3.47 (3.38)	12.86 (12.76)	6.74 (6.61)
$[Cu(HB_b)_2Cl_2].3H_2O$	68	18.99	54.76 (54.61)	3.13 (3.00)	11.61 (11.50)	6.58 (6.47)
$Ni(HB_b)_2Cl_2$	72	12.65	55.04 (54.88)	3.15 (3.02)	11.67 (11.56)	6.11 (6.00)
$Cu(HB_c)_2Cl_2$	83	19.91	62.67 (62.52)	3.59 (3.45)	13.29 (13.18)	7.54 (7.43)
$[Ni(HB_c)_2Cl_2].H_2O$	82	13.95	63.04 (62.93)	3.61 (3.49)	13.37 (13.24)	7.00 (6.86)

[a] Molar conductance in 1×10^{-3} M DMF solution at r.t. ($\Omega^{-1}cm^2mol^{-1}$).

Electronic Spectra

The UV-Visible graphs of all ligands and their Cu(II) and Ni(II) complexes are given in Figure 1. The electronic spectra of the free ligands show two adsorption bands in the range of 250 to 288 nm due to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$. The visible spectrum of all complexes in DMF displays clear bands in the range of 565 to 785 nm and the broad low laying shoulder at 380 to 420 nm due to the red shift shows $\pi \rightarrow d_{x^2-y^2}$ and/or $(\pi, \sigma) \rightarrow d_{x^2-y^2}$ LMCT transition in all complexes. The Cu(II) complexes shows $^2B_{1g} \rightarrow {}^2E_g$, $^2B_{1g} \rightarrow {}^2A_{1g}$, and $^2B_{1g} \rightarrow {}^2B_{2g}$ d–d transitions at 565 to 785 nm suggesting the square planar configuration of Cu(II) complexes of HB_b and HB_c ligands, whereas $^2B_1 \rightarrow {}^2E$, $^2B_1 \rightarrow {}^2B_2$, and $^2B_1 \rightarrow {}^2A_1$ transitions suggests the square pyramidal configuration of Cu(II) complex of HB_a ligand.[34,35]

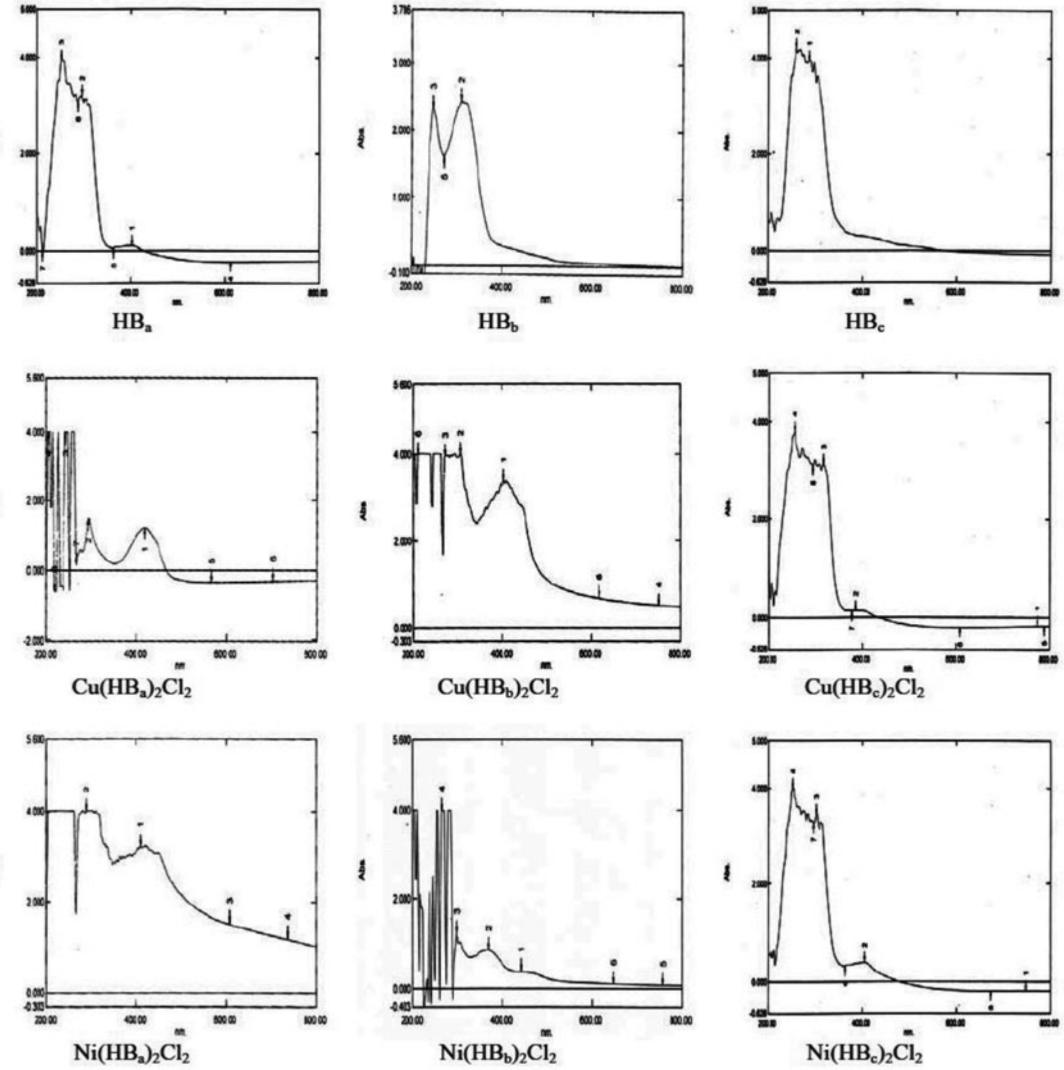
The Ni(II) complexes of HB_b and HB_c ligands show $^3T_1(F) \rightarrow {}^3T_2$, $^3T_1(F) \rightarrow {}^3A_2$, and $^3T_1(F) \rightarrow {}^3T_1(P)$ transitions between 615 and 768 nm and these transitions are probably an indication of four coordinate tetrahedral geometry around Ni(II) ions.[30] The Ni(II) complex of ligand HB_a displays $^3A_{2g} \rightarrow {}^3T_{2g}$, $^3A_{2g} \rightarrow {}^3T_{1g}(F)$, and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ transitions at 610 and 750 nm, the last two transitions that merged with each other suggested octahedral geometry for $Ni(HB_a)_2Cl_2(H_2O)_2$ complex.[36]

Suggested geometries of all benzimidazole metal complexes with the help of the electronic transitions are also confirmed by magnetic susceptibility values of all metal complexes given in Table 2.

TABLE 2
UV-visible spectral and magnetic moment data of complexes

Complex	LMCT	d–d bands	Excited state	Ground state	μ_{eff} (BM)^b	Geometry
$Cu(HB_a)_2Cl_2(H_2O)_{1.5}$	24096	19608	^2E	$^2B_1$	1.73	Square pyramidal
		17544	$^2B_2$			
		14085	$^2A_1$			
$Ni(HB_a)_2Cl_2(H_2O)_2$	24390	22222	$^3T_{2g}$	$^3A_{2g}$	3.43	Octahedral
		16529	$^3T_{1g}(F)$			
		13699	$^3T_{1g}(P)$			
$[Cu(HB_b)_2Cl_2].3H_2O$	24691	22472	^2E_g	$^2B_{1g}$	1.71	Square planar
		16129	$^2A_{1g}$			
		12987	$^2B_{2g}$			
$Ni(HB_b)_2Cl_2$	26316	23256	$^3T_2$	$^3T_1(F)$	3.27	Tetrahedral
		15625	$^3A_2$			
		13158	$^3T_1(P)$			
$Cu(HB_c)_2Cl_2$	25907	16393	^2E_g	$^2B_{1g}$	1.68	Square planar
		13072	$^2A_{1g}$			
		12821	$^2B_{2g}$			
$[Ni(HB_c)_2Cl_2].H_2O$	24752	14837	$^3T_2$	$^3T_1(F)$	3.94	Tetrahedral
		13369	$^3A_2$			

[b] Measurement were performed at r.t.



HB_a HB_b HB_c

$Cu(HB_a)_2Cl_2$ $Cu(HB_b)_2Cl_2$ $Cu(HB_c)_2Cl_2$

$Ni(HB_a)_2Cl_2$ $Ni(HB_b)_2Cl_2$ $Ni(HB_c)_2Cl_2$

FIG. 1. UV-visible spectrums of ($HB_{a–c}$) ligands and their Cu(II) & Ni(II) complexes.

Magnetic properties

A suggestion of the most probable stereochemistry of the synthesized Cu(II) and Ni(II) complexes is given by its magnetic moments. The effective magnetic moments of all complexes were measured in DMF solution at 27°C temperatures. The μ_{eff} value for Cu(II) complexes of benzimidazole ligands HB_b and HB_c ($\mu_{eff} = 1.71$ and 1.68 BM) suggests square planar geometry and the Cu(II) complex of ligand HB_a ($\mu_{eff} = 1.73$) suggests the square pyramidal geometry and these values are closely related to those of electronic. All the Ni(II) complexes have $\mu_{eff} = 3.27$ to 3.94 BM magnetic moments suggesting the octahedral geometry for Ni(II) complex of HB_a ligand and tetrahedral geometry for rest of two Ni(II) complexes of HB_b and HB_c ligands, respectively.[37] The magnetic properties of all the complexes are given in Table 2.

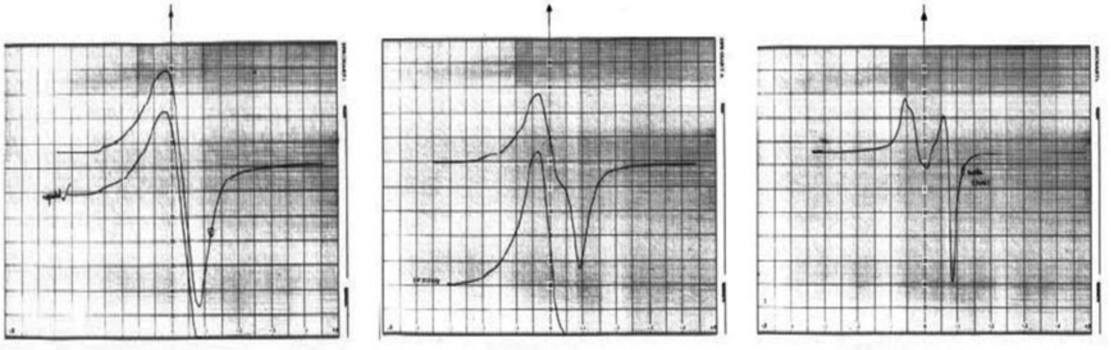
ESR spectra

The ESR spectral measurement of all Cu(II) complexes were carried out on a Varian E-112 X-band spectrophotometer at room temperature using TCNE as g marker. The EPR spectrum of Cu(II) complexes at room temperature (Figure 2) exhibits an axial pattern with no obvious hyperfine structure. The absence

TABLE 3

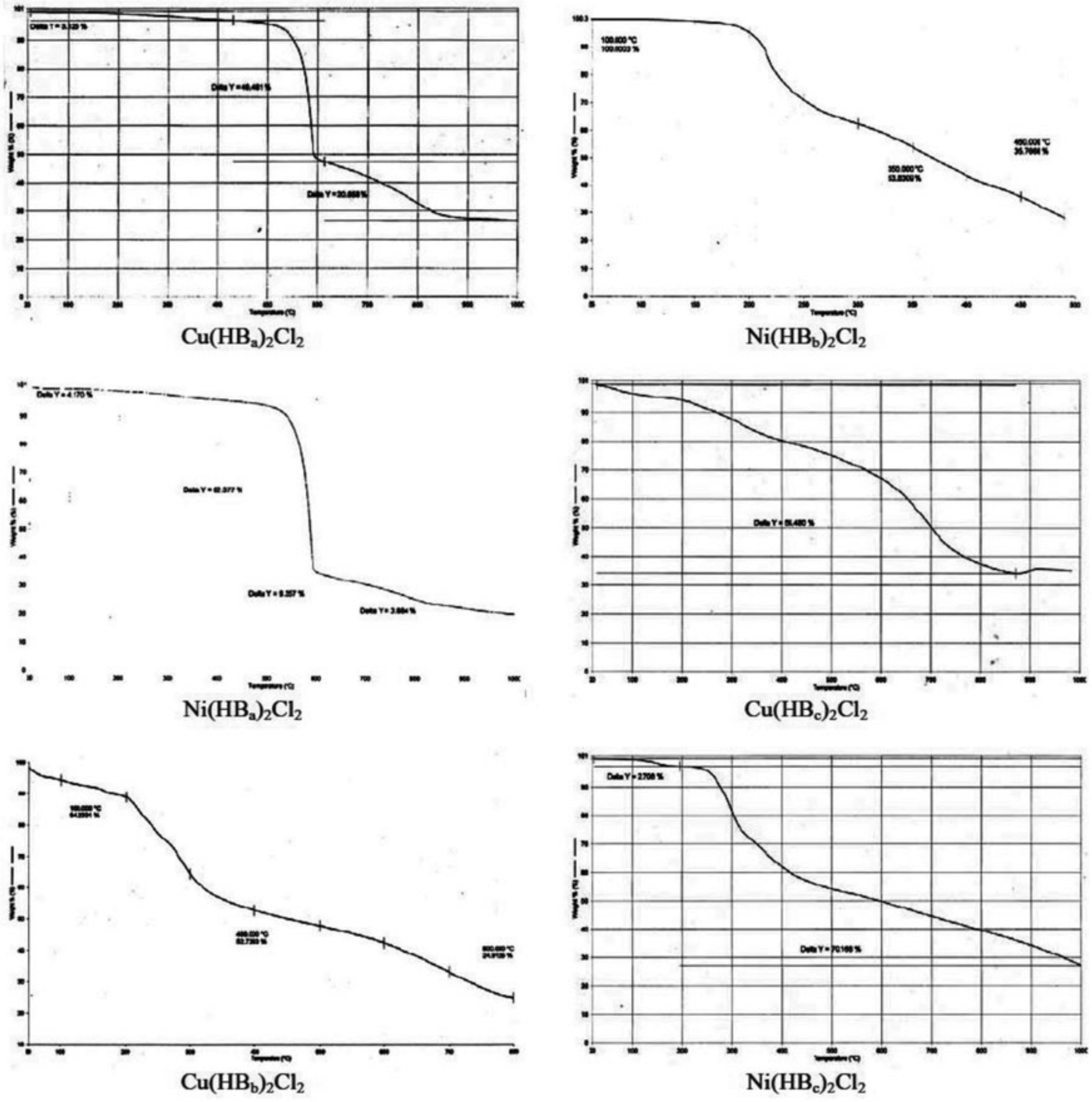
Electron spin resonance data of Cu(II) complexes

Compound	$g_{\parallel}$	$g_{\perp}$	g_{ave}	μ_{eff}
$Cu(HB_a)_2Cl_2(H_2O)_{1.5}$	2.484	2.121	2.239	1.66
$[Cu(HB_b)_2Cl_2].3H_2O$	2.524	2.101	2.242	1.67
$Cu(HB_c)_2Cl_2$	2.477	2.108	2.231	1.65



$Cu(HB_a)_2Cl_2$ $Cu(HB_b)_2Cl_2$ $Cu(HB_c)_2Cl_2$

FIG. 2. ESR graphs of Cu(II) complexes of (HB_{a-c}) ligands.



$Cu(HB_a)_2Cl_2$ $Ni(HB_b)_2Cl_2$

$Ni(HB_a)_2Cl_2$ $Cu(HB_c)_2Cl_2$

$Cu(HB_b)_2Cl_2$ $Ni(HB_c)_2Cl_2$

FIG. 3. TGA graphs of Cu(II) & Ni(II) complexes of (HB_{a-c}) ligands.

TABLE 4
TGA data of $[M(Hb_{a\text{–}c})_2Cl_2].nH_2O$ complexes

		Weight loss%		Total weight loss%			
Compound	Temp. Range (°C)	Found	*Calcd.*	Found	*Calcd.*	Assignment of weight loss	Residue
$Cu(HB_a)_2Cl_2(H_2O)_{1.5}$	30–400	3.125	3.092			$1.5H_2O$	
	400–615	54.50	55.39	78.27	78.81	$C_{24}H_{18}Cl_4$	$C_{10}H_7CuN_4$
	615–850	20.65	20.33			$C_{10}H_7N_4$	
$Ni(HB_a)_2Cl_2(H_2O)_2$	30–380	4.170	4.147			$2H_2O$	
	380–590	62.37	62.55	79.78	80.68	$C_{32}H_{20}Cl_3N_4$	$C_6H_5N_3Ni$
	590–800	9.357	10.06			C_6H_5N	
	800–1000	3.884	3.926			Loss of Cl	
$[Cu(HB_b)_2Cl_2].3H_2O$	30–100	5.77	5.32			$3H_2O$	
	100–400	41.51	41.42	75.09	74.57	$C_{18}H_{13}Br_2Cl$	$C_9H_{13}CuN_6$
	440–800	27.81	27.83			$C_{17}H_{15}ClN_2$	
$Ni(HB_b)_2Cl_2$	30–350	46.17	47.17	64.15	65.84	$C_{21}H_{14}Br_2N_2$	$C_{14}H_{12}ClN_4Ni$
	350–500	17.98	18.67			$C_9H_7ClN_2$	
$Cu(HB_c)_2Cl_2$	30–880	65.480	64.651	65.480	64.651	$C_{30}H_{20}Cl_2F_2N_4$	$C_{14}H_{12}CuN_4$
$[Ni(HB_c)_2Cl_2].H_2O$	30–170	2.708	2.147	72.876	73.759	H_2O	$C_6H_{12}ClN_4Ni$
	170–1000	70.168	71.612			$C_{38}H_{28}ClF_2N_4$	

of hyperfine structure at room temperature may be attributed as the strong dipolar and exchange interactions between the Cu(II) ions.[38]

The $g_{\|}$ and $g_{\perp}$ values were found at 2.477 to 2.524 and 2.101 to 2.121, respectively (Table 3) and suggest that $d_{x^2-y^2}$ may be the ground state as $g_{\|} > g_{\perp} > 2$, which is consistent with square planar Cu(II) complexes.[39] The trend $g_{\|} > g_{\perp} > 2$ observed for this complexes indicated that the unpaired electron is most likely in the $d_{x^2-y^2}$ orbital and the spectral features are of axial symmetry.[40,41]

$g_{\|}$, $g_{\perp}$, and g_{ave} values for each and every Cu(II) complexes can be calculated using the following expressions.[33]

$$g_{II} = g - \frac{8\lambda}{\Delta E}, \quad g_{\perp} = g - \frac{2\lambda}{\Delta E}, \quad \text{and} \quad g_{ave} = \frac{1}{3}\left(g_{II} + 2g_{\perp}\right).$$

The magnetic moment of the complexes can also be calculated from the following equation from the values of $g_{\|}$ and $g_{\perp}$.

$$\mu_{eff} = \sqrt{\frac{g_{II}^2}{4} + \frac{g_{\perp}^2}{4} + \frac{3kT}{\lambda}(g-2)}\,\text{BM}.$$

The values of magnetic moment obtained from the above equation are most similar with the measured values of magnetic susceptibilities of all Cu(II) complexes, which is evidence for the square planar and square pyramidal geometry of Cu(II) complexes.

Thermal analysis

The TGA graphs of all complexes are given in Figure 3. Thermal analysis of all complexes shows decomposition into one, two, or three steps at different temperature ranges. The TG analysis graphs of Cu(II) complexes of HB_a and HB_b ligands show elimination of water molecules, starts from 30°C and end at 400 and 100°C, respectively, which, indicates the loss of most probably coordinated water molecules and lattice water molecules binding to the complexes $Cu(HB_a)_2Cl_2(H_2O)_{1.5}$ and $[Cu(HB_b)_2Cl_2].3H_2O$, respectively. Further heating of the complexes may lead to elimination of major part of ligand as well as chloride ions in the rest of two steps of decomposition with 704.43 gm, 78.27% weight loss (calculated 709.29 gm, 78.81% weight loss) of $Cu(HB_a)_2Cl_2(H_2O)_{1.5}$ and 726.16 gm, 75.09% weight loss (calculated 756.88 gm, 74.57% weight loss) of $[Cu(HB_b)_2Cl_2].3H_2O$. The Cu(II) complex of HB_c ligand shows only one step of decomposition losing ligand parts and chloride atoms from 30°C to 880°C temperature displaying 550.58 gm, 65.480% weight loss (calculated 545 gm, 64.651% weight loss). The Ni(II) complex $Ni(HB_b)_2Cl_2$ of HB_b ligand shows two step of decomposition without losing any lattice or coordinated water molecules showing total 613.26 gm, 64.15% weight loss (calculated weight loss 629.5 gm, 65.84%), whereas another Ni(II) complexes of HB_a and HB_c ligands display elimination of coordinated and lattice water molecules indicating 721.21 gm, 79.78% weight loss (calculated weight loss 729.34 gm, 80.68%) and 622.30 gm, 72.876% weight loss (calculated weight loss 629.82 gm, 73.759%), respectively, from the TGA graphs (Figure 3) of $Ni(HB_a)_2Cl_2(H_2O)_2$ and $[Ni(HB_c)_2Cl_2].H_2O$ (Table 4). The residue observed after all decompositions from the TGA graphs of all metal complexes are tabulated in Table 4. All complexes may undergo complete decomposition convert into their corresponding metal oxides (CuO and NiO).

CONCLUSION

The ligands 2-{1′-Phenyl-3′-(4″-halophenyl)-1*H*-pyrazole-4-yl}-1*H*-benzimidazoles ($HB_{a–c}$) were formed with Cu(II) and Ni(II) in the $[M(HB_{a–c})_2Cl_2].nH_2O$ formula (where, M = Cu and Ni; $n = 0, 1, 1.5, 2, \& 3$). The complexes were synthesized and characterized by elemental analysis of the C, H N & metal, molar conductivity, magnetic susceptibility, TG analysis, ESR and IR spectra. All Cu(II) and Ni(II) complexes behave as nonelectrolytes, $Cu(HB_a)_2Cl_2(H_2O)_{1.5}$ complex have square pyramidal stereochemistry, whereas complexes $[Cu(HB_b)_2Cl_2].3H_2O$ and $Cu(HB_b)_2Cl_2$ have square planar geometry. The $Ni(HB_a)_2Cl_2(H_2O)_2$ complex have octahedral configuration around metal ions and complexes $Ni(HB_b)_2Cl_2$ and $[Ni(HB_c)_2Cl_2].H_2O$ posses tetrahedral geometry. The configuration of all complexes is realized by coordination of tertiary nitrogen of imidazole ring or benzimidazole molecule.

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