Research Article

Complexing Behaviour and Antifungal Activity of N-[(1E)-1-(1H-Benzimidazol-2-yl)ethylidene]morpholine-4-carbothiohydrazide and Related Ligand with Metal Ions

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The coordination complexes of bivalent metal ions with N-[(1E)-1-(1H-Benzimidazol-2-yl)ethylidene]morpholine-4-carbothiohydrazide (H_2bmctz , H_2L-1) and N-[(1E)-1-(1H-Benzimidazol-2-yl)(phenyl)methylidene] morpholine-4-carbothiohydrazide ($H_2bpmctz$, H_2L-2) were prepared and their neutral, monoanionic, and dianionic forms of ligands of compositions $[M(H_2L)X_2]$ ($M=Co^{II}$, Ni^{II} , Cu^{II} , Zn^{II} , Cd^{II} , or Pd^{II} , $X=Cl^-$ or Br^- , and $H_2L=H_2L-1$ or H_2L-2), $[M(HL)_2]nH_2O$ where ($M=Co^{II}$, Cu^{II} , Mn^{II} , Ni^{II} , Zn^{II} , or Cd^{II} , $H_2L=H_2L-1$ or H_2L-2 , and $n=0$ or 2), and $[MLB]nB$ ($M=Cu^{II}$, Ni^{II} , Zn^{II} , Cd^{II} , or Pd^{II} , $B=H_2O$, Py , or $Y-pic$, $n=0$ and $n=1$ if $B=H_2O$ for $Ni(II)$ and $H_2L=H_2L-1$ or H_2L-2) have been characterised by magnetic susceptibility measurements, electrical conductance values and spectral properties. The magnetic moment value of $[M(HL_2)]$ ($M=Mn^{II}$, Ni^{II} , Fe^{II} or Cu^{II}) type complexes is consistent with high spin octahedral structure while those of $[M(H_2L)X_2]$ ($M=Co^{II}$, Ni^{II} , Cu^{II} , Zn^{II} , or Cd^{II} , $X=Cl^-$ or Br^-) possess five coordinated trigonal bipyramidal geometry. The adduct complexes $[MLB] \cdot nB$ ($M=Ni^{II}$ or Cu^{II} , $B=H_2O$, Py , or $Y-pic$) are four coordinated planar and those of Zn^{II} and Cd^{II} complexes $[MLB]$, ($H_2L=H_2L-1$ or H_2L-2 , $B=H_2O$, Py or $Y-pic$) are tetrahedral. These ligands have been suggested to coordinate as tridentate (N N S) donor molecule in complexes of type $[M(H_2L)X_2]$, $[M(HL)_2]$, and $[MLB]$. The antifungal activity of ligands and some of their metal complexes were studied and it was observed that metal complexes show higher activity than free ligand.

1. Introduction

Preparation and structural aspects of various metal ions with a number of benzimidazole derivatives have been reported by one of us and a number of chemists [1–10]. Medicinal properties of benzimidazole derivatives have established that benzimidazoles have privileged substructures for drug design [11, 12]. The most vital benzimidazole derivatives is N-ribosyl-5,6-dimethylbenzimidazole which is axial ligand in vitamin B_{12} possessing selective neuropeptide YY1 receptor antagonists [13], 5-lipo xyginase inhibitor [14] and poly (ADP-ribose) polymerase inhibitors [14]. Benzimidazole derivatives are of immense interest because of their wide

spectrum of biological activity such as anticancer [15], antiviral [16, 17], antihistaminic [18], antifungal [19], anti-HBV [20], antibacterial [21], antitumoral [22], antiparasitic [22], antihelminthic [23], anti-inflammatory, local analgesic, hypotensive [24], antiulcer [25], and neuroleptic cardiotoxic [26]. Extensive biochemical and pharmacological studies have confirmed that various benzimidazole derivatives are effective against various strains of microorganisms [25]. The wide ranging biological and industrial interest intrigued chemists to explore new benzimidazole derivatives and their metal complexes which might have novel mechanisms of action and drug activity [15–25]. The metal ions selected for present studies $Mn(II)$, $Co(II)$, $Cu(II)$, $Fe(II)$, $Ni(II)$, $Zn(II)$,

and Cd(II) are versatile essential micronutrients in biological systems [27–32]. Copper is crucial for biological function of several enzymes and proteins, in energy metabolism, antioxidant, and mitochondrial respiration [27]. Zinc(II) is essential for nucleic acid synthesis, cell growth division, and differentiation and its deficiency causes abnormalities in function of cell carboxypeptidase, amino peptidase, carbonic anhydrase, DNA and RNA polymerase. Zinc is also essential for life and it regulates the function of genes in the nuclei of the cell (Lipscomb and Starter, 1996). Iron is the most vital element for life and iron-sulphur proteins formation (Richardson, 2002). Manganese is a component of nucleic acid and it accelerates the synthesis of cholesterol. Manganese enzymes are involved in metabolic pathway of DNA synthesis, sugar metabolism and protein modification. Cobalt is a component of vitamin B₁₂ and enzyme nutritional cofactor necessary for the formation of red blood cell [31]. Nickel is remarkably useful metal in biological chemistry. It modifies antioxidant system and is associated with chromosomal aberrations and mutation [31]. In continuation of our work on coordinating behaviour of benzimidazole and imidazole derivatives with various metal ions [2–6], and biological significance of above metal ions, we report in present communication, the preparation, characterization, and antifungal activity of complexes of these metals with of N-[(1E)-1-(1H-benzimidazol-2-yl)ethylidene]morpholine-4-carbothiohydrazide (H₂L-1) and N-[(1E)-1-(1H-benzimidazol-2-yl)(phenyl)methylidene]morpholine-4-carbothiohydrazide (H₂L-2).

2. Material and Methods

The metal salts used were usually BDH Anal-R chemicals or E. Merk Extra pure reagent. Palladium(II) chloride was obtained from Johnson Matthey London. Solvents and organic reagent, hydrazine, morpholine, carbon disulphide, Chloroacetic acid were obtained from E. Merk, Nice, Sd. Fine and Ranbaxy. The metal contents of complexes were estimated by standard method sulphur content was determined as sulphate, and nitrogen content was estimated by Nitrometer (Duma's method) in the laboratory. The infrared spectra of complexes were recorded on Shimadzu-FTIR spectrometer at IIT Patna. The results of C, H, and N were obtained from CDRI Lucknow. The results of mass spectrum and U-V absorption spectrum of ligand and some complexes were obtained from IIT Patna. The ¹H NMR spectra were recorded at CDRI Lucknow. The magnetic susceptibilities of complexes were determined by Gouy method at room temperature. The electrical conductance values of complexes were determined in DMF on Systonic conductivity Meter Bridge at 30–31°C. The results of measurements are given in Tables 1 and 2.

Ligand molecules (H₂bmctz, H₂L-1 or H₂bpmctz, H₂L-2) were prepared by condensing 2-acetylbenzimidazole or 2-benzoylbenzimidazole [33] with morpholine-N-thiohydrazide [34] in aqueous ethanol containing a little amount of acetic acid. 2-Acetylbenzimidazole or 2-benzoylbenzimidazole in situ was prepared by oxidation of

1-(1H-benzimidazol-2-yl)ethanol and 1-(1H-benzimidazol-2-yl)phenylmethanol [35] with chromic acid [33]. The 0.1 mole of 2-acetylbenzimidazole in 100 mL aqueous ethanol containing 2 mL acetic acid was refluxed with 0.12 mole of aqueous ethanolic solution of morpholine-N-thiohydrazide (morpholine-4-carbothiohydrazide) on a steam bath for two hours. The ligand separated as cream of yellow product. The ligands were analysed. For H₂bmctz (H₂L-1) (C₁₄H₁₇N₅SO) nitrogen was found 23.06% calculated value is 23.11%. M.pt recorded, 197°C (uncorrected). The value of nitrogen found for H₂bpmctz (H₂L-2) is 19.01%, and that calculated for H₂L-2 (C₁₉H₁₉N₅SO) is 19.18%, M.pt recorded 242°C (uncorrected).

2.1. Preparation of Complexes [M(H₂L)X₂] (M=Cu^{II}, Co^{II}, Ni^{II}, Zn^{II} or Cd^{II} X=Cl⁻ or Br⁻ and H₂L=L-1 or L-2). About 0.01 mole of metal halide was dissolved in 40–50 mL ethanol and treated with 0.01 mole of appropriate ligand in dry ethanol (30–40 mL) slowly with constant stirring. The resulting solution was refluxed on a steam bath for half an hour and concentrated to 20–30 mL. The concentrated solution was chilled when crystalline precipitate separated. In case of Cu (II) the product were obtained immediately. The product was filtered, washed with cold dry ethanol, and dried over CaCl₂. Yield 80–85%.

2.2. Preparation of Bis Ligated Complexes [M(HL)₂], nH₂O (M=Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}, Cd^{II} or Pd^{II}, H₂L=H₂L-1 or H₂L-2 and n = 0 but 2 for Ni^{II} or Co^{II}). About 20 millimoles of ligand was dissolved in 80–90 mL hot methanol and treated slowly with aqueous methanolic solution of 10 millimoles of appropriate metal acetate {chloride in case of Pd(II) and sulphate in case of Fe(II)} and refluxed on steam bath for half an hour. In some cases a little aqueous solution of sodium acetate was added to adjust the pH 6–8. In most of the cases complexes were obtained immediately on diluting them with water. The products were digested on a steam bath and collected on a filter, washed with aqueous methanol, and dried over CaCl₂. Yield is 95–98%.

2.3. Preparation of [MLB]·nB (M=Cu^{II}, Pd^{II}, Ni^{II}, Zn^{II} or Cd^{II} B=H₂O, py or Y-pic and n = 0, H₂L=H₂L-1 or H₂L-2, if B=H₂O, n = 1 for Ni^{II} and H₂L-1 or H₂L-2). About 5 or 10 millimole of metal chloride was dissolved in 30–40 mL aqueous methanol and treated with 5–6 mL pyridine or Y-pic. The resulting solution was treated with 5 or 10 millimole of ligand dissolved in hot methanol (20–25 mL). The pH of the solution was raised by adding dilute ammonia when appropriate complexes separated. The aqua complexes were obtained on refluxing [MLPy] in hot water in presence of a little ammonia. The products were collected on a filter, washed with cold aqueous methanol, and dried over CaCl₂. The results of elemental analysis and physical data of complexes are presented in Tables 1 and 2.

TABLE 1: Analytical results and physical data of complexes.

Compound	Colour	% analysis found (Calc)			μ_{eff} B.M (305°K)	$\Omega\alpha$ mol ⁻¹ ohm ⁻¹ cm ² , 30° C
		M	N	Halogen		
Cu(H ₂ L-1)Cl ₂	Green ash	14.31 (14.52)	15.73 (16.00)	16.01 (16.25)	1.81	12
Cu(H ₂ L-1)Br ₂	Brown	11.91 (12.07)	13.31 (13.48)	30.11 (30.44)	1.84	8
Zn(H ₂ L-1)Cl ₂	White	14.61 (14.88)	15.91 (16.18)	15.01 (15.12)	Dia	10
Zn(H ₂ L-1)Br ₂	White	12.31 (12.52)	13.01 (13.25)	30.11 (30.25)	Dia	8
Cd(H ₂ L-1)Cl ₂	Cream	22.86 (23.13)	14.11 (14.29)	14.36 (14.53)	Dia	11
Cd(H ₂ L-1)Br ₂	Cream	19.46 (19.54)	12.11 (12.32)	27.38 (27.67)	Dia	10
Ni(H ₂ L-1)Cl ₂	Greenish yellow	13.32 (13.54)	16.31 (16.48)	16.57 (16.70)	3.18	10
Co(H ₂ L-1)Cl ₂	Brown	13.41 (13.58)	16.28 (16.49)	16.51 (16.71)	3.25	11
Ni(H ₂ L-1)Br ₂	Bottle green	11.10 (11.21)	13.50 (13.61)	30.17 (30.64)	3.21	8
Cu(H ₂ L-2)Cl ₂	Ash green	12.53 (12.71)	14.21 (14.02)	13.87 (14.19)	1.81	11
Cu(H ₂ L-2)Br ₂	Brown	10.61 (10.79)	11.63 (11.81)	26.93 (27.13)	1.83	8
Cd(H ₂ L-2)Cl ₂	Cream	20.49 (21.67)	12.76 (13.54)	12.69 (12.93)	Dia	11
Zn(H ₂ L-2)Cl ₂	Cream	13.31 (13.45)	13.21 (13.96)	14.00 (14.15)	Dia	10
Cd(H ₂ L-2)Br ₂	Cream	17.38 (17.64)	10.71 (10.98)	23.01 (23.30)	Dia	9
Zn(H ₂ L-2)Br ₂	Cream	10.91 (11.08)	11.61 (11.84)	26.81 (27.06)	Dia	11
Ni(H ₂ L-2)Cl ₂	Greenish yellow	11.61 (11.86)	13.96 (14.15)	14.16 (14.35)	3.20	12
Co(H ₂ L-2)Cl ₂	Brown	11.68 (11.89)	13.89 (14.16)	14.23 (14.36)	3.32	13
Ni(H ₂ L-2)Br ₂	Bottle green	9.92 (10.05)	11.71 (11.99)	27.01 (27.38)	3.18	14

(H₂L-1)=H₂bmctz and (H₂L-2)=H₂bpmctz.

3. Results and Discussion

The ligands N-[(1E)-1-(1H-benzimidazol-2-yl)ethylidene]morpholine-4-carbothiohydrazide (H₂L-1) and N-[(1E)-1-(1H-benzimidazol-2-yl)phenyl(methylidene)]morpholine-4-carbothiohydrazide (H₂L-2) are potential N N S donor coordinating molecule capable of forming five membered strong chelates with The elemental analysis of complexes of Ni^{II}, Co^{II}, Cu^{II}, Zn^{II}, Cd^{II} and halide formed in dry ethanol corresponds to compositions [M(H₂L)X₂], and (H₂L=H₂L-1 or H₂L-2, X=Cl or Br) metal ions. Depending on pH of medium, these ligands coordinate as neutral, monoanionic, and dianionic donor molecules. The elemental analysis of complexes of Mn^{II}, Fe^{II}, Ni^{II}, Co^{II}, Cu^{II}, Zn^{II}, Cd^{II}, and Pd^{II} corresponds to compositions [M(H₂L)X₂] (M=Cu^{II}, Ni^{II}, Zn^{II} or Cd^{II} and X=Cl⁻ or Br⁻) [M(HL)₂]*n*H₂O (M=Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}, Cd^{II} or Pd^{II}, H₂L=H₂L-1 or H₂L-2, *n* = 0 but 2 for Co^{II} and Ni^{II}) and [MLB]*n*B (M=Ni^{II}, Cu^{II}, Pd^{II}, Zn^{II} or Cd^{II} and H₂L=H₂L-1 or H₂L-2, B=Py, Y-pic or H₂O and *n* = 0 or 1). These complexes are quite stable at room temperature and do not lose texture in desiccator. On heating the complexes [M(HL)₂]*n*H₂O (M=Co^{II}, or Ni^{II}, and HL=HL-1 or HL-2) in air oven between 60 and 80°C for one hour, is loss H₂O and loss in weight incurred in complexes correspond to loss of required for 2H₂O, and no change in colour of the complexes that was noticed which indicated that H₂O molecules are not coordinated to metal atom rather they are held up in crystal lattices. The weight loss incurred in complexes Ni(L-1)2H₂O and Ni(L-2)2H₂O at 120°C corresponds to loss of only one H₂O, indicating that one H₂O is coordinated to nickel (II) in complex [NiL(H₂O)]H₂O and the second H₂O is held up in crystal lattices. The dihalo

complexes are formed in dry ethanol by interacting solutions of ligand with metal halides. The bis ligated complexes [M(HL)₂]*n*H₂O were formed in neutral or weakly basic medium (pH 6–8) by interacting aqueous methanolic or ethanolic solutions of metal acetate or metal chloride and appropriate ligand in 1:2 molar proportion. The ligands coordinate as dianionic tridentate molecule in much basic medium (pH 9–12) and form complexes of stoichiometry, [MLB]*n*B (M=Cu^{II}, Ni^{II}, Zn^{II}, Cd^{II} or Pd^{II} and H₂L=H₂L-1 or H₂L-2, B=H₂O, py or Y-pic and *n* = 0 or 1). The complexes are all insoluble in water but aqueous ethanolic suspension of [M(H₂L)X₂] gradually dissociates into M(HL)₂ and MX₂ giving conducting solution. Freshly prepared DMF solution of complexes, however shows negligible electric conductance value indicating them to be nonionic and even halogens are coordinated to metal atom [36]. Zinc(II), cadmium(II), and nickel(II) complexes [NiLB]*n*B are diamagnetic. At room temperature all copper(II) complexes show normal magnetic moment value (1.81–1.89 B.M) and magnetic moment value of Mn(II) complexes [Mn(HL)₂] (5.88–5.92 B.M), Ni(II) complexes [Ni(HL)₂] (2.93–3.01 B.M), and Fe(II) complexes Fe(HL)₂ (4.89–4.91 B.M) corresponds to spin free octahedral geometry of metal ions [37]. The moment value of cobalt(II) complexes [Co(HL)₂] (3.26–3.68 B.M) is lower than spin free octahedral geometry and anomalous probably due to spin-exchange interactions [38]. The dihalo complexes [Co(HL)X₂] show magnetic moment value (4.54–4.71 B.M) similar to five coordinated TBP structure [37, 38]. As expected zinc(II) or Cd(II) complexes M(HL)₂ and [M(H₂L)X₂] (X=Cl⁻ or Br⁻) are diamagnetic. The electronic absorption spectra of ligand (H₂L-1 or H₂L-2) and their complexes were determined in ethanol or ethanol

TABLE 2: Analytical results and physical data of complexes.

Compound H ₂ L=H ₂ bmctz H ₂ L'=H ₂ bpmctz	Colour	% analysis found/(Calc)			μ_{eff} B.M 305°K	$\chi \times 10^3$ mol ⁻¹ Ohm ⁻¹ cm ² , 30° C
		M	N	Sulphur		
[Co(HL-1) ₂]2H ₂ O	Brown	8.61 (8.88)	21.01 (21.12)	9.50 (9.65)	3.26	8
[Cu(HL-1) ₂]	Ash colour	9.31 (9.52)	20.87 (21.09)	9.31 (9.59)	1.86	7
[Mn(HL-1) ₂]	Dull cream	8.14 (8.33)	21.22 (21.24)	9.41 (9.78)	5.88	8
[Fe(HL-1) ₂]	Light brown	8.31 (8.47)	21.01 (21.20)	9.48 (9.64)	4.91	6
[Cu(HL-2) ₂]	Ash green	7.91 (8.01)	17.61 (17.79)	8.00 (8.08)	1.88	8
[Mn(HL-2) ₂]	Dull cream	6.88 (7.01)	17.61 (17.88)	9.11 (9.26)	5.92	8
[Fe(HL-2) ₂]	Light brown	7.01 (7.12)	17.15 (17.86)	9.11 (9.24)	4.86	6
[Co(HL-2) ₂]2H ₂ O	Brown	7.02 (7.16)	17.00 (17.01)	7.61 (7.77)	3.68	10
[Ni(HL-1) ₂]2H ₂ O	Reddish brown	8.37 (8.40)	19.81 (20.02)	9.00 (9.22)	3.13	8
[Ni(HL-2) ₂]2H ₂ O	Reddish brown	7.10 (7.13)	16.81 (17.01)	7.57 (7.78)	2.98	7
[Zn(HL-1) ₂]	Yellow	9.82 (9.76)	20.73 (20.90)	9.09 (9.10)	Dia	10
[Zn(HL-2) ₂]	Yellow	8.01 (8.29)	17.51 (17.65)	8.01 (8.06)	Dia	8
[Pd(HL-1) ₂]	Reddish brown	14.61 (14.98)	19.56 (19.71)	8.90 (9.01)	Dia	9
[Pd(HL-2) ₂]	Reddish brown	12.61 (12.75)	16.66 (16.87)	7.51 (7.67)	Dia	7
[Pd(L-1)Py]	Orange	21.63 (21.75)	17.01 (17.27)	6.51 (6.58)	Dia	6
[Pd(L-2)Py]	Orange	19.31 (19.40)	15.01 (15.32)	5.69 (5.83)	Dia	8
[Pd(L-1)(Y-pic)]	Orange	21.11 (21.27)	16.68 (16.86)	6.30 (6.39)	Dia	8
[Pd(L-2)(Y-pic)]	Orange	18.68 (18.98)	14.91 (15.01)	5.68 (5.73)	Dia	7
[Ni(L-1)Py]	Yellowish red	13.31 (13.38)	19.11 (19.21)	7.10 (7.29)	Dia	8
[Ni(L-1)(Y-pic)]	Yellowish red	12.78 (12.99)	18.48 (18.59)	6.87 (7.08)	Dia	7
[Ni(L-1)(H ₂ O)]H ₂ O	Yellowish orange	14.63 (14.83)	17.51 (17.69)	8.11 (8.06)	Dia	9
[Ni(L-2)Py]	Orange yellow	11.43 (11.72)	16.71 (16.77)	6.11 (6.39)	Dia	10
[Ni(L-2)(Y-pic)]	Orange yellow	11.14 (11.42)	16.21 (16.32)	6.01 (6.23)	Dia	8
[Ni(L-2)(H ₂ O)]H ₂ O	Orange yellow	12.78 (12.82)	15.11 (15.29)	6.81 (6.99)	Dia	7
[Cd(L-1)(Y-pic)]	Orange yellow	22.01 (22.22)	16.51 (16.62)	6.11 (6.33)	Dia	10
[Cd(L-1)(H ₂ O)]	Orange yellow	26.15 (26.05)	16.02 (16.23)	7.31 (7.42)	Dia	8
[Cd(L-1)Py]	Orange yellow	22.61 (22.81)	17.34 (17.51)	6.41 (6.49)	Dia	9
[Cd(L-2)Py]	Orange yellow	20.11 (20.21)	15.01 (15.15)	5.70 (5.77)	Dia	11
[Cd(L-2)(Y-pic)]	Orange yellow	19.61 (19.88)	14.92 (14.88)	5.41 (5.64)	Dia	10
[Cd(L-2)(H ₂ O)]	Yellow	22.48 (22.78)	14.21 (14.19)	6.51 (6.48)	Dia	9
[Zn(L-2)Py]	Orange yellow	14.51 (14.62)	18.76 (18.86)	7.00 (7.18)	Dia	10
[Zn(L-1)(H ₂ O)]	Yellow	17.14 (17.01)	18.41 (18.23)	8.10 (8.32)	Dia	8
[Zn(L-2)Py]	Yellow	12.81 (12.88)	16.47 (16.55)	6.03 (6.36)	Dia	6
[Zn(L-2)(Y-pic)]	Orange yellow	12.41 (12.54)	15.91 (16.11)	5.91 (6.14)	Dia	9
[Zn(L-2)(H ₂ O)]	Yellow	14.61 (14.72)	15.58 (15.78)	6.91 (7.17)	Dia	8
[Zn(L-1)(Y-pic)]	Yellow	14.21 (14.23)	18.41 (18.59)	6.91 (7.08)	Dia	11
[Cu(L-1)Py]	Bottle green	14.01 (14.32)	18.32 (18.54)	7.03 (7.21)	1.86	8
[Cu(L-2)Py]	Bottle green	13.81 (13.95)	18.71 (18.93)	7.11 (7.21)	1.84	9
[Cu(L-1)(Y-pic)]	Ash colour	13.61 (13.88)	18.17 (18.36)	6.81 (6.99)	1.89	6
[Cu(L-2)(Y-pic)]	Ash colour	12.31 (12.25)	16.01 (16.20)	6.01 (6.16)	1.84	5
[Cu(L-2)(H ₂ O)]	Brown	13.61 (13.73)	15.00 (15.14)	6.71 (6.91)	1.79	8
[Cu(L-1)(H ₂ O)]	Brown	15.48 (15.74)	17.13 (17.35)	7.76 (7.93)	1.78	10

TABLE 3: Prominent I.R. bands of ligands and their complexes in cm^{-1} .

Compound	$\nu(\text{NH})$, $\nu(\text{OH})$, $\nu(\text{CH}_2)$, + $\nu(\text{C-H})$	$\nu(\text{C=N})$ imidazole, $\nu(\text{C=N})$ azomethene	Ring breathing mode	$\nu(\text{C=S})$	$\nu(\text{M-N})$ $\nu(\text{M-S})$
H ₂ L-1	3350, 3240, 3120, 3040, 2949, 2860	1653, 1610, 1585	1040	912	435, 415
H ₂ L-2	3238, 3190, 3060, 2950, 2832	1628, 1605, 1585	1035	938	431, 418
[Cu(H ₂ L-1)Cl ₂]	3280, 3235, 3125, 3040, 2950, 2850	1622, 1590, 1580	1055	892	427
[Zn(H ₂ L-1)Cl ₂]	3320, 3235, 3140, 3035, 2960, 2845	1615, 1595, 1580	1024	896	429
[Cu(H ₂ L-2)Cl ₂]	3340, 3230, 3145, 3045, 2960, 2840	1621, 1610, 1590	1025	908	436, 413
[Ni(H ₂ L-2)Cl ₂]	3340, 3240, 3140, 3045, 2950, 2840	1618, 1595, 1584	1040	912	428, 410
[Co(HL-1) ₂]2H ₂ O	3320, 3245, 3140, 3050, 2960, 2840	1618, 1602, 1595	1035	768	441, 418
[Zn(HL-2) ₂]	3340–3140, 3050, 2960, 2850	1622, 1605, 1592	1030	772	438, 416
[Ni(HL-2) ₂]2H ₂ O	3380–3100br, 2960, 2840	1615, 1600, 1595	1040	782	435, 418
[Cd(HL-2) ₂]	3320, 3240, 3130, 2960, 2850	1612, 1595, 1580	1038	788	436, 417
[Co(HL-2) ₂]2H ₂ O	3400–3120br, 2960, 2840	1618, 1605, 1585	1028	792	438, 422
[Ni(L-1)Py]	3320–3180, 3040, 2980, 2845	1612, 1595, 1575	1024	760	443, 418
[Cu(L-2)]Y-pic	3340, 3260, 3140, 3050, 2840	1620, 1590, 1580	1025	772	434, 415
[Cu(L-2)]2H ₂ O	3350–3060, 2950, 2840	1620, 1600, 1580	1025	781	438, 410
[Zn(L-1)Py]	3320, 3270, 3130, 3040, 2955, 2845	1615, 1600 1590	1030	776	436, 413

DMF (50%) mixed solvent in the range 200–850 nm. The ligand H₂L-1 displays strong bands at 214, 252, and 268 and a medium band at 295 nm attributed from $\sigma \rightarrow \sigma^*$, $\sigma \rightarrow \pi^*$, $\pi \rightarrow \pi^*$, and $n \rightarrow \pi^*$ transitions of ligand molecule [39]. The electronic absorption bands of H₂L-2 are observed as strong band at 212, 245, 270, and 290 nm attributed from $\sigma \rightarrow \sigma^*$, $\sigma \rightarrow \pi^*$, $\pi \rightarrow \pi^*$, and $n \rightarrow \pi^*$ (C=S) of ligand. In complexes these transition are mostly enveloped by strong charge transfer from M $\rightarrow$ L and L $\rightarrow$ M electronic transitions. The metal complexes form very deep coloured solutions in DMF-ethanol mixture and distinct d–d electronic transitions could not be located below 380–390 nm. The Zn(II) and Cd(II) complexes as expected do not have d–d electronic transition but due to charge transfer band show strong absorption near 420–400 nm. The medium band at 460–480 nm for [NiLB].*n*B (H₂L=H₂L-1 or H₂L-2, B=py or Y-pic) is attributed to $^1A_{1g} \rightarrow ^1B_{1g}$ transition in planar field [39]. In DMF-ethanol mixture the complexes [Ni(HL)₂] as well as [Ni(H₂L)Cl₂] have same colour and similar electronic absorption band near 460–480 nm. The complexes probably acquire planar structure in basic DMF medium. The cobalt (II) complexes display weak electronic absorption near 430–440 nm and 560–580 nm assignable to $^4T_{1g} \rightarrow ^4T_{2g}$ and $^4T_{1g} \rightarrow ^4A_{2g}$, $^4T_{1g}(P)$ transitions in octahedral field [39]. The Cu(II) complexes

[Cu(HL)₂] show strong absorption below 420 assignable to charge transfer transition. The complexes display d–d transitions at 450 nm (medium) and 650–680 nm as broad weak band assignable to $^2B_{1g} \rightarrow ^2B_{2g}$, 2E_g , and $^2B_{1g} \rightarrow ^2A_{1g}$ transition in distorted octahedral field [39]. In case of Mn(II) no distinct d–d transitions could be located definitely, since all d–d transitions of Mn(II) complexes are of spin forbidden type. Iron (II) complexes display a shoulder near 440 and 450 nm attributable to $^5T_{2g} \rightarrow ^5E_g$ transitions in octahedral field [37–39] (See Figures 1 and 2).

The IR spectra of ligands and their complexes were recorded as KBr optics in range 4000–400 cm^{-1} . The diagnostic I.R. bands of ligands and some of their complexes are recorded in Table 3. The ligand H₂L-1 displays medium I.R. bands at 3350, 3240, 3120, 3040, 2949, 2860, and 2840 cm^{-1} attributed from $\nu(\text{NH})$, phenyl (C–H) stretches, and morpholine ring $\nu(\text{CH}_2)$ vibrations and most of them are retained in complexes. The $\nu(\text{C=N})$, $\nu(\text{N-N})$ of imidazole ring and azomethene part of ligand were observed at 1653, 1610 and 1585 cm^{-1} . The $\delta(\text{NH})$ of ligand was located at 1515 and 1485 cm^{-1} . The IR spectrum of Cu(H₂L-1)Cl₂ displays azomethene $\nu(\text{C=N})$ at 1622 cm^{-1} and imidazole ring $\nu(\text{C=N})$ at 1590 which is lower than free ligand molecule that indicated

TABLE 4: Results of fungal activity (conc. of compound in ppm).

Compound	Conc. in ppm	<i>A. niger</i>	<i>A. flavus</i>	<i>F. oxysporum</i>	<i>R. bataticola</i>	<i>R. phaseoli</i>
$H_2bmctz=H_2L-1$	100	40	35	30	45	50
	200	55	50	52	68	75
$H_2bpmctz=H_2L-2$	100	46	36	40	48	55
	200	68	52	65	72	80
$Cu(H_2L-1)Cl_2$	100	48	55	32	50	55
	200	65	70	55	75	85
$Cu(H_2L-2)Cl_2$	100	50	60	42	52	56
	200	70	78	70	78	86
$Cu(H_2L-1)Br_2$	100	50	56	42	52	57
	200	68	72	68	76	87
$Cu(HL-1)_2$	100	48	50	35	50	54
	200	62	65	60	70	80
$Zn(H_2L-1)_2 Cl_2$	100	48	42	40	48	54
	200	64	60	60	70	80
$Zn(H_2L-2)_2 Br_2$	100	50	45	42	50	55
	200	68	62	65	74	82
$Zn(H_2L-2)Br_2$	100	52	42	45	52	60
	200	72	60	70	76	85
$Mn(HL-1)_2$	100	42	40	35	46	50
	200	58	53	55	70	75
$Fe(HL-2)_2$	100	41	42	36	48	52
	200	57	55	55	74	78
$Pd(L-1)Py$	100	52	45	40	50	52
	200	68	68	62	72	78
$Ni(H_2L-1)Cl_2$	100	48	42	45	48	54
	200	56	56	55	72	80
$Ni(L-1)Py$	100	46	40	32	45	52
	200	56	52	55	70	76
$Cd(HL-1)_2$	100	46	43	35	48	54
	200	60	58	60	72	80
$Cd(HL-2)_2$	100	48	42	43	50	60
	200	66	60	65	74	85
Ref. Mancozeb	100	75	80	78	81	82
	200	99	98	97	99	100

the coordination of both (C=N) nitrogen to metal atom. The thione $\nu(C=S)$ of ligand shifted from 912 cm^{-1} to 892 cm^{-1} in complex $[Cu(H_2L-1)Cl_2]$ indicated the involvement of thiol sulphur in coordination. Thus the ligand is bonded as tridentate N, N, S donor molecule in complexes. The $\delta(NH)$ at 1515 and $\nu(N-H)$ at 3240 cm^{-1} of ligand were absent in complexes with dianionic ligand $[M(L-1)B]$. The complexes containing pyridine or *Y*-picoline molecule display a prominent band at $1590\text{--}1595$ and $1015\text{--}1025\text{ cm}^{-1}$ due to $\nu(C=N)$ of coordinated pyridine ring and pyridine ring breathing mode of vibration [40]. The imidazole part $\nu(C=N)$ and azomethene part $\nu(C=N)$ stretches of ligand shift to lower frequency in complexes by $10\text{--}15\text{ cm}^{-1}$ that suggested the coordination of both (CN) nitrogen. The thioamide $\nu(C=S)$ of ligand was observed at 912 cm^{-1} , which is shifted by $20\text{--}25\text{ cm}^{-1}$ in complexes of type $[M(H_2L-1)X_2]$ indicating that (C=S) is

bonded through thione sulphur. The $\nu(C=S)$ of ligand shifts to $760\text{--}780\text{ cm}^{-1}$ in complexes $[M(HL-1)_2]$ and $[M(L-1)B]$ type of complexes indicating the coordination of thioamide (C=S) through deprotonated thiol sulphur. The ligand H_2L-2 shows $\nu(N-H)$, $\nu(C-H)$ phenyl ring and (CH_2) ring vibration morpholine at 3238 , 3190 , 3060 , 2950 , and 2832 cm^{-1} . These are retained with some change in intensity and band position in complexes. The complexes $[M(HL)_2]2H_2O$, (HL=HL-2 or HL-1) show broad IR band near $3180\text{--}3450\text{ cm}^{-1}$ attributed to hydrogen bonded $\nu(OH)$ of H_2O . The $\nu(C=N)$ of azomethene part and benzimidazole located at 1628 , 1605 , and 1585 of (H_2L-1) shift to lower frequencies that indicated their bonding to metal atom. The thioamide $\nu(C=S)$ of H_2L-2 located at 938 cm^{-1} shifted by $20\text{--}30\text{ cm}^{-1}$ in complexes of types $[M(H_2L-2)X_2]$ indicating bonding of thione sulphur (Table 3). The $\nu(C=S)$ shifts to $770\text{--}790\text{ cm}^{-1}$ in complexes

FIGURE 1: Figure of thione where $R=CH_3=H_2bmctz$ and $R=C_6H_5=H_2bpmctz$.

of types $[M(HL-2)_2]$ and $[M(L-2)B]$ supporting bonding through deprotonated thiol sulphur of thioamide group [40, 41]. The I.R. spectral band of both H_2L-1 and H_2L-2 shows similar trend of bonding of donor atoms. In far I.R. range, the I.R. spectra of complexes were recorded above 400 cm^{-1} , therefore $\nu(M-S)$ and $\nu(M-N)$ stretches could not be located definitely. However, the new I.R. bands in complexes at $420-435\text{ cm}^{-1}$ are tentatively suggested to $\nu(M-N)$ and $\nu(M-S)$ vibrations (Table 3). In Finger print region H_2L-1 , H_2L-2 , and their complexes display a number of I.R. bands due to phenyl ring skeletal vibrations and $\delta(CH_2)$, $\delta(CH_3)$, $\nu(N-N)$, $\nu(C-N)$, and $\nu(C-C)$ vibrations as well as ring deformation vibrations [40, 41]. In general, almost all complexes display very strong band near $735-745\text{ cm}^{-1}$ attributed to phenyl ring out of plane bending of substituted phenyl ring. The Finger print region, I.R. stretches of H_2L-1 are located at 1545 , 1515 , 1480 , 1441 , 1363 , 1271 , 1235 , 1155 , 1110 , 1004 , and 744 cm^{-1} . These are retained in complexes with slight change in intensity and slight change in position [40-42]. The I.R. bands of H_2L-2 were observed at 1540 , 1505 , 1482 , 1442 , 1336 , 1280 , 1240 , 1150 , 1105 , 1030 , 845 and 742 cm^{-1} . From the I.R. studies, it is concluded that the ligands are tridentate and dianionic in [MLB] type of complexes.

1H NMR spectra of ligands H_2L-1 and H_2L-2 were recorded in DMSO at field strength 300 MHz . The ligand H_2L-1 shows (CH_2) proton. Signals of morpholine ring as two triplets for $8H$ at $\delta = 4.016$, 4.030 , 4.047 and 4.154 , 4.170 , 4.184 ppm , the CH_3 , proton signals at $\delta = 1.787\text{ ppm}$ (Singlet), the phenyl ring signal at $\delta = 6.843-6.914\text{ ppm}$ as multiplet ($4H$). The benzimidazole ring $N-H$ and hydrazone part NH signals are located at $\delta = 7.262$ and $\delta = 8.6\text{ ppm}$. The ligand H_2L-2 displays (CH_2) proton signal of morpholine ring at $3.781-4.145\text{ ppm}$ as two triplets ($8H$, t) and phenyl ring ($C-H$) proton signal at $\delta = 6.93-7.28$ as multiplet ($9H$). The benzimidazole ring (NH) and hydrazone ($N-H$) proton signals were located at $\delta = 7.415$ and 8.215 ppm . The mass spectrum of H_2L-1 gave M^+/z at $303(3\%)$, $288(3.8\%)$, $217(40\%)$, $117(100\%)$, and $86(30\%)$. The calculated value of mass was 303 . The mass spectral results of H_2L-2 indicated M^+/z values $365(5\%)$, $288(3\%)$, $279(8\%)$, $86(30\%)$, and $117(100\%)$ as base peak. The mass calculated for H_2L-2 was 365 . The 1HNMR spectra of complexes could not be recorded due to their poor solubility (See Figure 3).

3.1. Antifungal Studies. The antifungal activity of ligands and some of their complexes have been evaluated by radial growth

FIGURE 2: Figure of thiol where $R=CH_3=H_2bmctz$ and $R=C_6H_5=H_2bpmctz$.

method [43, 44]. Czapek agar medium was prepared by dissolving 20 g starch, 20 g agar agar and 20 g glucose in one litre distilled water. The resulting medium was added requisite amount of test compound to get 100 and 200 ppm of solution. The resulting medium was then poured into Petri plates and the spores of fungi were placed on medium with the help of inoculum needle. The petri plates were wrapped in polythene bags containing two to three drops of ethanol and then placed in incubator at $30 \pm 0.5^\circ\text{C}$. The linear growth of fungus was evaluated by measuring the fungal zone diameter after five days. The percentage inhibition was calculated from the relation $100 \times (C - T/C)$ where C and T are the diameter of the fungus colony and control test plate, respectively. The fungi used in present investigation for screening against the fungi, *Aspergillus niger*, *Aspergillus flavus*, *F. oxysporum*, *Rhizoctonia bataticola*, and *R. phaseoli*. The control solution was mycostatin. The result of activity is shown in Table 4. It has been found that the ligand containing phenyl substituent is more active than methyl substituent. The $Cu(II)$ and $Zn(II)$ complexes in general show larger activity than $Mn(II)$ and $Fe(II)$ complexes. The bromo complexes show larger activity than that of chloro or pyridine or Y -picoline adduct. The chemical Mancozeb fungicides were used as standard for this process. In general the antifungal activities observed for $Cu(II)$ and $Zn(II)$ halo complexes were much larger than other metal complexes and ligand. The antifungal activity observed for *R. phaseoli* is larger compared to other fungi, indicating selectivity of complexes for particular fungi. The enlarged activity of complexes may be attributed to increased delocalisation of π -electrons of ligand over the whole chelate ring which enhances the lipophilicity of the complexes. The increase lipophilicity enhances the penetration of complexes into fungi membrane and blocking the active binding sites in the microorganism. In addition the complexes disturb the respiration process of the fungi cell thus blocking the synthesis of proteins essential for fungi growth and restrict the further growth of the organism. The activity of complexes of phenyl substituted ligand is larger than methyl derivatives due to larger π -delocalised electron in phenyl substituted ligand than that of methyl derivatives and free ligand as well.

In addition to above facts, the chelate formation reduces the polarity of metal ions, increases the lipophilic character of the chelate, and increases the interaction between metal ion and fungi cell membrane. Consequently it blocks the cell growth of microorganism. According to overtone's concept the lipophilicity of complexes is major factor which favours

FIGURE 3: Graph of I.R. spectra of morpholine-N-carbothiohydrazide of 2-acetylbenzimidazole (H_2bmctz).

FIGURE 4: Proposed structure of $[M(HL)_2]$ where $M = (Co^{II}, Ni^{II})$ and $HL = Hbmctz$ or $HL = Hbpmctz$.

FIGURE 5: Proposed structure of $[M(H_2L)X_2]$ type of complexes where $M = Zn^{II}, Cu^{II}, Ni^{II}, Cd^{II}$, and $X = Cl^-$ or Br^- .

FIGURE 6: Tetrahedral structure for Zn^{II} or Cd^{II} , square planar for Ni^{II} or Pd^{II} .

FIGURE 7: Structure of $[MLB]$ where $M = Ni^{II}, Cu^{II}$ are planar but tetrahedral for Zn^{II}, Cd^{II} $H_2L = H_2bmctz$ or $H_2bpmctz$, $B = Py, H_2O$ and $Y = Pic$.

antimicrobial activity [45, 46]. The hydrogen bond formation between fungi and complex molecule through azomethene ($C=N$) and heteroatoms S and O and halogens of complexes interacts with cell constituents resulting in interference with the normal cell process. These factors are tentatively suggested for enhanced antimicrobial activities of metal chelates complexes of N and S donor.

From the results of I.R. and physical data, the probable structures of complexes are shown in Figures 4, 5, 6, and 7.

4. Conclusion

The physicochemical data suggested octahedral structure for $[M(HL)_2]$ type of complexes of $Ni(II)$, $Co(II)$, and $Cu(II)$ while four coordinated planar to $Pd(II)$ complexes. The monoligated $Ni(II)$ and $Pd(II)$ complexes $[M(L-1)/(1-2)B]$ show characteristics of planar geometry. The complexes of $[M(H_2L)Cl_2]$, ($M = Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}$ or Cd^{II}) have been suggested to possess trigonal bipyramidal structures. The ligand H_2L-1 and H_2L-2 coordinate as neutral, monoanionics or dianionic tridentate (N, N, S) donor molecules. The biological activity of phenyl substituted ligand and its complexes are larger than those of methyl substituted products probably due

to excessive delocalized π -electron system present in phenyl ring.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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