

Preparation, Characterisation and Anti-fungal activity of 1E-1-(1H-Benzimidazol-2-yl)-N-hydroxy ethanimine and 1E-1-(1H-Benzimidazol-2-yl)-N-hydroxy-1-phenyl methanimine with Co(II), Ni(II), Cu(II), Zn(II) and Cd(II).

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Abstract: The complexes of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) with 1E-1-(1H-Benzimidazol-2-yl)-N-hydroxy-ethanimine (Hbhe) and 1E-1-(1H-Benzimidazol-2-yl)-N-hydroxy-1-phenylmethanimine (Hbhpm) of compositions $[M(HL)_2Cl_2]$, ($M=Co^{II}$, or Ni^{II} and $HL=Hbhe$ or $Hbhpm$), $[M(HL)X_2]$, ($M=Cu^{II}$, Zn^{II} or Cd^{II} , $HL=Hbhe$ or $Hbhpm$ and $X=Cl$ or Br) and $ML_2.nH_2O$, ($M=Co^{II}$, Ni^{II} , Cu^{II} , Zn^{II} or Cd^{II} , $HL=Hbhe$ or $Hbhpm$ and $n=0$ or 2) have been prepared and characterised by electrical conductance value, magnetic susceptibility and spectral studies. The anti-fungal activity of ligands and neutral bis-chelates $ML_2.nH_2O$ was investigated by growth inhibition method. The complexes exhibited enhanced activity than free ligands.

Key Words: Anti-fungal activity, Benzimidazoloxime, Characterisation, Metal complexes, Synthesis.

I. Introduction

In previous communication, we have reported the spectral and structural aspects of metal complexes of benzimidazole and substituted benzimidazoles in solid state¹⁻⁴. The analytical uses, industrial characteristics and wide spectrum of pharmacological activity of benzimidazole derivatives created huge interest during last few decades to investigate microbial activity of new benzimidazole derivatives⁵⁻¹⁰. Extensive biochemical studies have confirmed that various benzimidazole derivatives are effective against strains of microorganisms⁵⁻⁶. Certain derivatives exhibit the biosynthesis of Ergosterol in the cell membrane of Fungi⁷. In addition to potential use of benzimidazole derivatives for treatment of bacterial, viral, fungal, HBV and parasitic diseases as effective and selective medicines⁷⁻¹⁹. A number of its derivatives produce temperature resistant electrical conducting polymer²⁰. In present communication we report synthesis characterisation and anti-fungal activity of Hbhe and Hbhpm and their complexes with Co^{II} , Ni^{II} , Cu^{II} , Zn^{II} and Cd^{II} .

II. Method and Materials

Metal halide and acetate used were E. Merck Extra pure or BDH Anal R grade chemicals. Ortho-phenylenediamine, lactic acid, Mandelic acid, DMF, organic solvents were either obtained from E. Merck or Nice and Sd. Fine chemicals. The ligands, Hbhe and Hbhpm were prepared by condensing 2-Acetylbenzimidazole [1-(1H-benzimidazol-2-yl)ethanone] and 2-Benzoylbenzimidazole [1-(1H-benzimidazol-2-yl)phenone] with hydroxylamine hydrochloride in aqueous ethanol in basic medium using K_2CO_3 . 2-Acetylbenzimidazole and 2-Benzoylbenzimidazole were synthesized by reported method^{21, 22}. The ligands separated as white crystalline precipitate by neutralising the reactants with dilute hydrochloric acid. The ligands were analysed. For Hbhe, Nitrogen found 23.73% required for $C_9H_9N_3O$, 24% for Hbhpm, Nitrogen found 17.68%, required for $C_{14}H_{11}N_3O$, 17.72% m.pt of Hbhe-243^oc and that of Hbhpm-195^oc.

Metal and halogen of complexes were determined by standard procedure²³. Results of C, H and N analysis were obtained from CDRI Lucknow by Gouy method at room temperature (304-305K). Infrared spectra of compounds as KBr disc in the range of 4000-400 cm^{-1} on SHIMADZU- FTIR spectrophotometer at IIT Patna. The U-V spectra in ethanol or DMF solution of ligands and complexes were recorded in the range 200-550 nm or 200-850 nm at IIT Patna. The NMR spectra were recorded on Bruker DRX FT-NMR spectrometer (300MHz) in DMSO or $CDCl_3$. Mass spectra of ligands were recorded at IIT Patna. The molar electrical conductance values were measured at room temperature (30-31^oc) by Digital conductivity meter of model 611E having cell constant- 1, using 10^{-3} molar solution of complexes in DMF solution.

2.1 Preparation of complexes $ML_2.nH_2O$ ($M=Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}$ or Cd^{II} , $HL=Hbhe$ or $Hbhpm$ and $n=0$ or 2)
About 5 millimole of metal acetate or chloride was dissolved in 25-30 ml hot aqueous ethanol and added with constant stirring to hot ethanol solution of 10 millimole of appropriate ligand (30 ml). The mixed solution was heated on steam bath by adding 20-25 ml (5%) aqueous solution of potassium acetate. The neutral bis-chelates

separated gradually. The products were digested on steam bath by adding 50-60ml distilled water. The products were cooled at room temperature, filtered, washed with aqueous ethanol and dried over CaCl₂. Yield 96-98 %.

2.2 [Cu (HL)X₂], (HL = Hbhe or Hbhpm and X = Cl or Br) and [M(HL)Cl₂], (M = Zn^{II} or Cd^{II} and HL = Hbhe or Hbhpm)

About 0.02 mole of appropriate ligand was dissolved in 10 ml hot absolute ethanol and treated with ethanolic solution of 0.01 mole of metal halide in 15 – 20 ml ethanol. The resulting solutions were heated on steam bath with stirring. In most of the cases the dihalo complexes separated gradually. In some cases the solutions were concentrated and chilled, when dihalo products were obtained. The bis ligated dichloro complexes [M (HL)₂Cl₂] were obtained as above by using M:L in 1:2 molar proportion and concentrating the refluxate to 10 – 15 ml. The products were dried over CaCl₂.

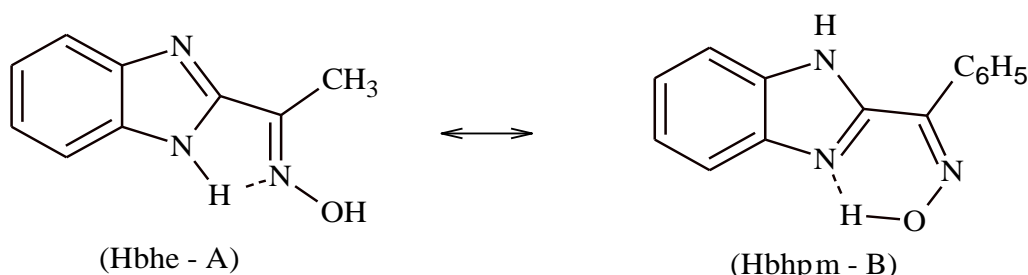
The analytical results, molar conductance value and magnetic susceptibility data are recorded in Table I.

2.3 Table-I

Compound	Colour	Analysis% found (Calc.)				μ_{eff} BM 304 K	χ_m ohm ⁻¹ mol ⁻¹ cm ²
		M	N	C	H		
Hbhe = HL	Cream	--	23.73(24.01)	61.51(61.71)	5.31(5.14)	--	--
Hbhpm = HL	Cream	--	17.93(71.18)	17.68(17.72)	4.91(4.64)	--	--
Cu(HL)Cl ₂	Bright Green	20.31(20.50)	13.32(13.57)	34.71(34.49)	3.06(2.90)	1.84	12
Cu(HL)Cl ₂	Bright Green	17.07(16.91)	11.10(11.30)	45.09(45.21)	3.16(2.96)	1.86	10
Cu(HL)Br ₂	Brown	15.92(15.81)	10.28(10.54)	26.91(27.10)	2.42(2.25)	1.81	8
Cu(HL)Br ₂	Brown	13.61(13.77)	8.91(9.14)	36.21(36.49)	2.46(2.38)	1.83	10
CuL ₂ 2H ₂ O	Ash	13.91(14.17)	18.51(18.77)	48.16(48.32)	4.68(4.46)	1.89	6
CuL ₂ 2H ₂ O	Ash	11.01(11.11)	14.47(14.71)	58.45(58.84)	4.21(4.20)	1.86	7
Zn(HL)Cl ₂	Cream white	20.92 (21.10)	13.31(13.48)	34.46(34.68)	3.01(2.89)	Dia	6
Zn(HL)Cl ₂	Cream white	17.35(17.51)	11.31(11.25)	45.12(44.99)	3.11(2.94)	Dia	8
Cd(HL)Cl ₂	Cream white	31.01(31.36)	11.82(11.71)	30.31(30.13)	2.68(2.51)	Dia	6
Cd(HL)Cl ₂	Cream white	29.41(29.49)	10.11(9.99)	40.02(39.96)	2.92(2.61)	Dia	5
ZnL ₂	Cream	15.71(15.82)	20.12(20.31)	52.31(52.25)	4.01(3.87)	Dia	6
ZnL ₂	Cream	12.09(12.16)	15.78(15.63)	62.63(62.52)	3.86(3.72)	Dia	5
CdL ₂	Cream yellow	24.61(24.41)	18.31(18.24)	47.01(46.91)	3.61(3.47)	Dia	7
CdL ₂	Cream yellow	19.02(19.29)	14.16(14.37)	57.55(57.49)	3.61(3.42)	Dia	7
Co(HL) ₂ Cl ₂	Pink	12.41(12.32)	17.37(17.57)	45.31(45.18)	3.93(3.76)	4.92	6
Co(HL) ₂ Cl ₂	Pink	9.83(9.78)	14.06(13.95)	55.96(55.81)	3.81(3.65)	5.01	9
CoL ₂ (H ₂ O) ₂	Buff	13.31(13.29)	19.21(18.96)	48.87(48.75)	4.63(4.51)	4.88	7
CoL ₂ (H ₂ O) ₂	Buff	10.41(10.38)	14.76(14.81)	59.41(59.25)	4.36(4.23)	4.94	5
Ni(LH) ₂ Cl ₂	Greenish yellow	12.21(12.38)	17.63(17.53)	45.41(45.57)	3.91(3.75)	2.98	15
Ni(LH) ₂ Cl ₂	Greenish yellow	9.51(9.75)	13.71(13.95)	58.61(58.84)	3.46(3.65)	3.11	18
[NiL ₂]2H ₂ O	Cream Yellow	13.10(13.24)	18.69(18.93)	48.48(48.75)	4.31(4.50)	Dia	7
[NiL ₂]2H ₂ O	Cream Yellow	10.18(10.37)	14.69(14.84)	59.48(59.25)	4.18(4.23)	Dia	6

III. Result and discussion

1E-1-(1H-Benzimidazol-2-yl)-N-hydroxy ethanimine (Hbhe – A) and 1E-1-(1H-Benzimidazol-2-yl)-N-hydroxy-1-phenyl methanimine (Hbhpm – B) have similar donor atoms and they are expected to exist in different orientation of N-hydroxy group as shown in fig (A, B)



The existence of different orientation of ligands has been reflected in proton NMR spectrum. The orientation A is suitable for formation of stable five membered chelate rings either as neutral or mono-anionic (N-N) donor ligand molecules. The complexes of bivalent metal with neutral ligands are formed in absolute ethanol in acidic medium (p^H 4-5) but complexes with anionic ligand of composition $ML_2 \cdot 2H_2O$ are formed in basic or neutral aqueous ethanol.

Cobalt (II) complexes $Co(HL)_2(H_2O)_2$ and $Co(HL)_2Cl_2$ ($HL = Hbhe$ and $Hbhpm$), display magnetic moment value (4.88 – 5.01 BM) similar to high spin octahedral $Co(II)$ complexes²⁵. The dichloro Ni (II) complexes $[Ni(HL)_2Cl_2]$, ($HL = Hbhe$ or $Hbhpm$) are paramagnetic at room temperature and their magnetic moment value (2.98 or 3.11 BM) suggested octahedral structure²⁵. The magnetic moment value of copper (II) complexes $Cu(HL)X_2$, ($X = Cl^-$ or Br^- and $HL = Hbhe$ or $Hbhpm$) and $CuL_2(H_2O)_2$ show magnetic moment values between 1.81 and 1.89 BM similar to magnetically dilute copper (II) complexes^{26, 27}. The aqua bis chelate of $Co(II)$ and $Cu(II)$ on heating do not loss water below 90 - 100^oc suggesting coordinated nature of H_2O in aqua complexes.

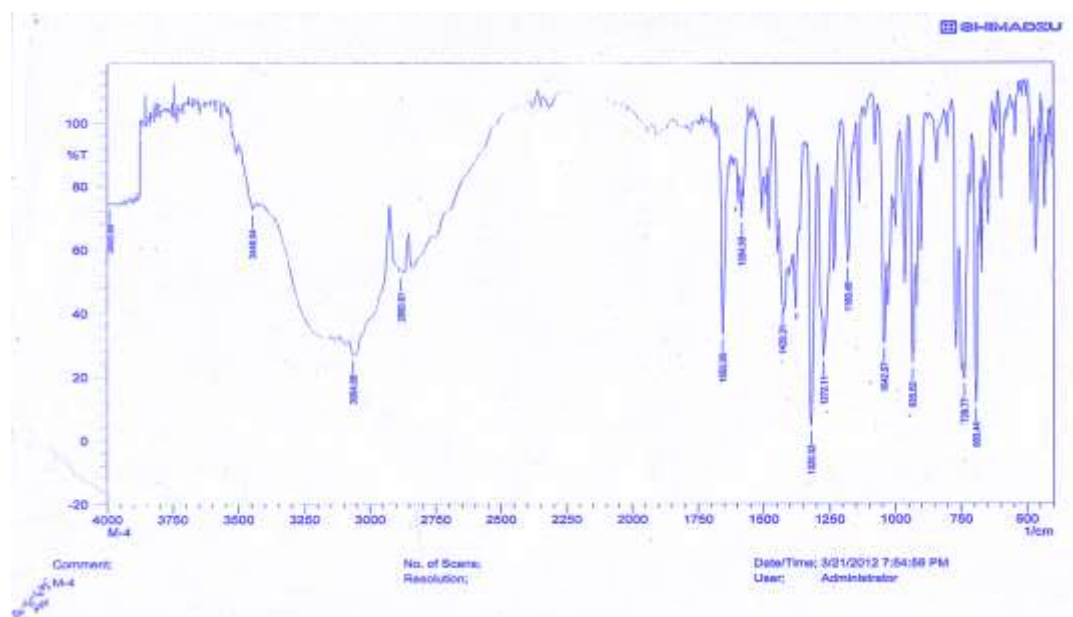
The dihalo complexes $M(HL)_2X_2$, ($M = Cu^{II}$, Zn^{II} or Cd^{II} and $X = Cl^-$ or Br^-) and $M(HL)_2Cl_2$, ($M = Co^{II}$ or Ni^{II} and $HL = Hbhe$ or $Hbhpm$) dissolves slightly in ethanol and their DMF solution show negligible molar electrical conductance value (6 – 15 $\text{ohm}^{-1} \text{mol}^{-1} \text{cm}^2$) suggesting coordinated natures of halogens²⁴. The complex solution on long standing become conducting due to solvolysis by coordinating nature of DMF. The neutral bis chelates $ML_2 \cdot nH_2O$ are also non – conducting (Table – I) supporting their non-ionic character²⁴. Zinc (II), Cadmium (II) complexes as expected are diamagnetic. The diamagnetism of $[NiL_2]2H_2O$ ($HL = Hbhe$ or $Hbhpm$) suggested their square planar structure²⁵. The $Co(II)$ and $Cu(II)$ complexes show magnetic moment value consistent with octahedral or distorted octahedral geometry of $Co(II)$ and $Cu(II)$ complexes²⁵⁻²⁷. Neutral Nickel (II) bis chelate $[NiL_2]2H_2O$ on heating above 50^oc gradually losses H_2O and become anhydrous without change in colour by 80^oc indicating presence of H_2O in lattice or weakly hydrogen bonded.

The electronic absorption spectra of ligands and some of their complexes were recorded in ethanol or DMF in the range 200 – 850 nm. The ligand Hbhe in ethanol displays strong absorption bands at 208, 210, 232 and 293 nm attributed to $\sigma \rightarrow \sigma^*$, $\sigma \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions. The electronic absorption spectrum of Hbhpm displays $\sigma \rightarrow \sigma^*$, $\pi \rightarrow \pi^*$ phenyl and imidazole ring as well as $C=N-OH$ group were observed at 210, 236, 272 and 308 nm. In complexes some ligand absorptions are eclipsed in charge transfer transition with metal ions. In very dilute solution these transitions are observed at higher wavelength. In addition to ligand transition the electronic absorption bands of $Cu(HL)X_2$ located as weak broad bands at 620 – 640 and 690 – 720 nm are assigned to ${}^2B_{1g} \rightarrow {}^2A_{2g}$, ${}^2B_{1g} \rightarrow {}^2E_g$ transition in distorted octahedral field²⁷⁻²⁸. The electronic transition of $CuL_2(H_2O)_2$, ($HL = Hbhe$ or $Hbhpm$) at 670 or 680 nm is assigned to ${}^2B_{1g} \rightarrow {}^2B_{2g}$, 2E_g transition. The U-V band of $Co(bhe)_2(H_2O)_2$ at 440 and 520 nm can be attributed to ${}^4T_{1g} \rightarrow {}^4T_{2g}$ and ${}^4T_{1g} \rightarrow {}^4A_{2g}$ transitions in octahedral field²⁸. The electronic transition at 480 nm for $[Ni(bhpm)_2]2H_2O$ can be attributed to ${}^1B_{1g} \rightarrow {}^1A_{2g}$ transition in square planar field²⁵. The dichloro complex $[Ni(bhe)_2Cl_2]$ shows medium band at 385 and 470 nm assignable to ${}^3A_{2g} \rightarrow {}^3T_{1g}$ and ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$ transition in distorted octahedral field²⁸. Due to limitation of range of U-V instrument the expected third ligand field transition of octahedral $Co(II)$ and $Ni(II)$ complexes could not be observed. The u-v spectra of neutral bis chelates of nickel (II), $Ni(bhe)_2 \cdot 2H_2O$ a medium absorption band at 470 nm and strong absorption below 390 nm. The electronic band at 470 nm is assigned to ${}^1A_{1g} \rightarrow {}^1B_{1g}$ transition in planar field and strong absorption below 390 nm as charge transfer transition²⁸.

3.1 The infra - red spectra

The IR spectra of ligand and some of their metal complexes were recorded in KBr disc. The IR spectrum of Hbhe displays $\nu(OH)$, NH and CH vibrations 3340, 3195, 3060, 2880 cm^{-1} and these vibrations are retained in complexes with neutral ligand with slight change in band position and intensity³⁰. The IR band of

Hbhpmm displays $\nu(\text{OH})$, $\nu(\text{CH})$ phenyl ring at 3440, 3190 and 3064 cm^{-1} . The $\nu(\text{C}=\text{N})$ of imidazole ring and azomethine ($\text{C}=\text{N}$) are observed at 1600 and 1665 cm^{-1} for Hbhe and at 1655 and 1595 cm^{-1} for Hbhpmm. These vibrations are shifted to lower frequency on coordination Table – II.

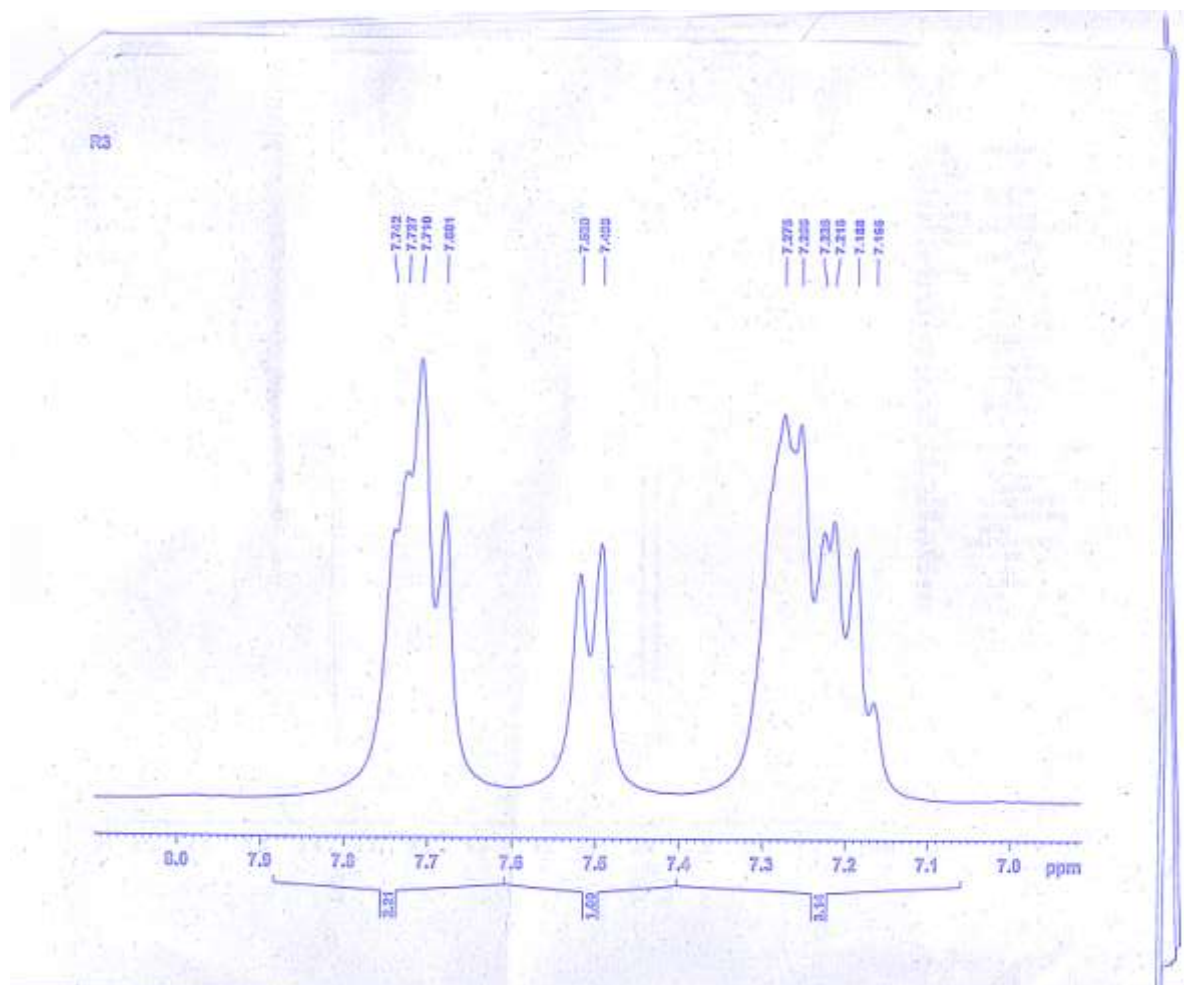


3.2 Prominent IR and u-v spectral band of ligands and their complexes

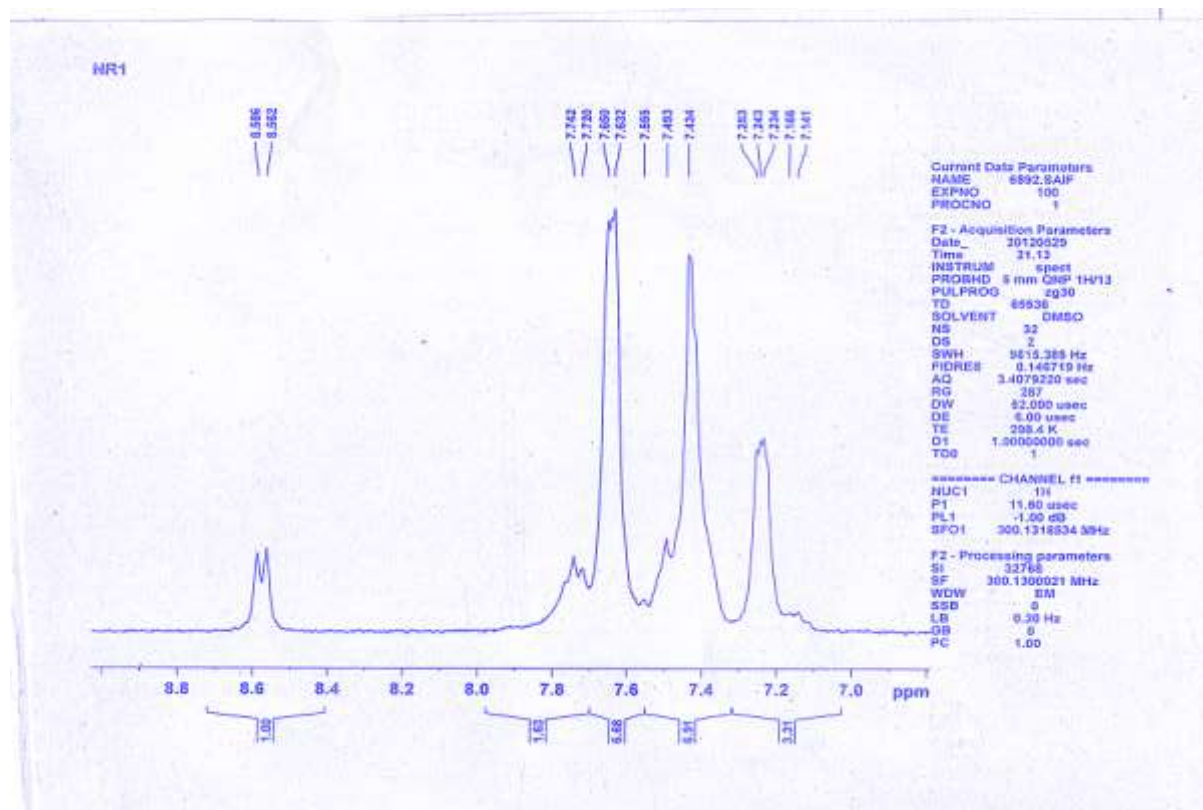
Compound	U-V band positions in (nm)	IR band positions in cm^{-1}				
		$\nu(\text{OH}), +\nu(\text{NH})$	$\nu(\text{C}=\text{N})$	$\nu(\text{C}=\text{N})$ ring	$\delta(\text{NH})$	$\nu(\text{NO})$
Hbhe = HL	208, 210, 232, 293	3340, 3195, 3060, 2880	1665	1600	1492	1035
Hbhpmm = HL	210, 236, 272, 308	3440, 3190, 3064	1655	1595	1485	1042
$\text{Cu}(\text{HL})\text{Cl}_2$	210, 236, 300 – 620, 720	3430, 3055, 2890	1653	1595	1490	1040
$\text{Cu}(\text{HL})\text{Br}_2$	212, 240, 275, 315, 640br, 690	3380, 3165, 3060	1642	1590	1480	1046
$\text{Zn}(\text{HL})\text{Cl}_2$	240, 290,	3400, 3190, 2980	1652	1590	1485	1060
$\text{Ni}(\text{HL})_2\text{Cl}_2$	210, 290, 385, 570br	3400, 3180, 3050, 2890	1652	1590	1472	1070
ZnL_2	212, 235, 300	3360, 3060, 2980	1656	1585	1480	1340
CdL_2	----	3340, 3050, 2980	1635	1590	1475	1320
CdL_2	---	3380, 3060, 2900	1645	1585	1480	1335
$\text{NiL}_2 \cdot 2\text{H}_2\text{O}$	208, 235, 380, 480	3350 – 3100br, 3050, 2890	1646	1600	1470	1320
$\text{CuL}_2 \cdot 2\text{H}_2\text{O}$	212, 240, 308, 440, 680br	3420 – 3120, 3040	1638	1590	1472	1320
$\text{CoL}_2 \cdot 2\text{H}_2\text{O}$	210, 270, 385br, 440, 520	3360 – 3100br, 3040, 2890	1655	1595		1380
$\text{CuL}_2 \cdot 2\text{H}_2\text{O}$	210, 235, 380, 670	3400 – 3010br, 3045	1630	1595	1480	1325

The $\delta(\text{NH})$ of benzimidazole was assigned to a band at 1492 cm^{-1} for Hbhe and at 1495 for Hbhpm, are not affected indicating NH nitrogen is not the bonding site of ligand molecules. The $\nu(\text{NO})$ of oxime ($=\text{N-OH}$) was assigned to air band at 1035 in case of Hbhe and at 1042 for Hbhpm²⁹⁻³⁰. The $\nu(\text{NO})$ vibration is raised to higher wave number in complexes with neutral and deprotonated ligands. In case of deprotonated ligand the $\nu(\text{NO})$ was observed at $1320 - 1340\text{ cm}^{-1}$ suggesting the coordination of oxime ($=\text{NOH}$) through nitrogen on deprotonation. The aqua complexes $[\text{CoL}_2(\text{H}_2\text{O})_2]$ as well as complex hydrate display broad $\nu(\text{H}_2\text{O})$ of coordinated or hydrated hydrogen bonded water molecule between $3360 - 3050\text{ cm}^{-1}$. The complexes $[\text{CoL}_2(\text{H}_2\text{O})]$ (Hbhe or Hbhpm) display new medium band at $670 - 680\text{ cm}^{-1}$ for rocking vibration of coordinated water molecule²⁹.

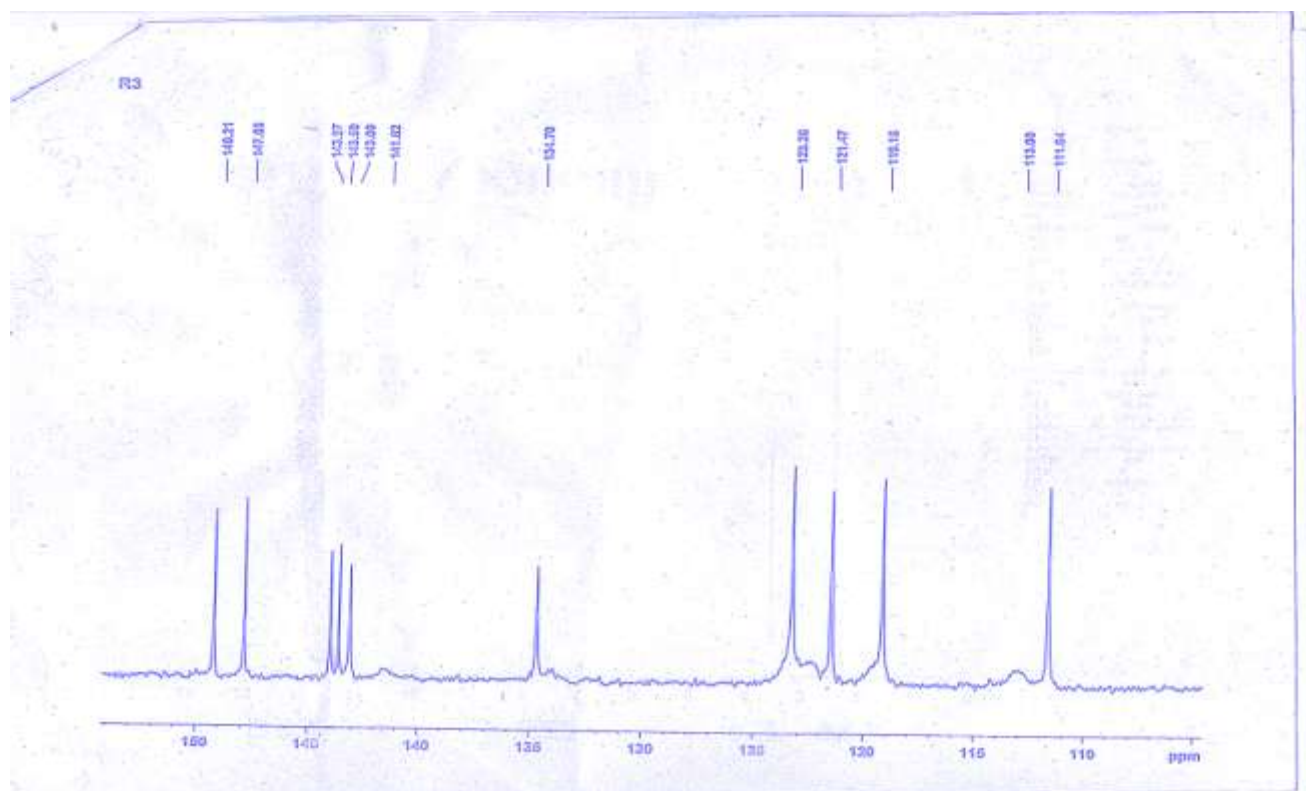
3.3 NMR and Mass spectra:

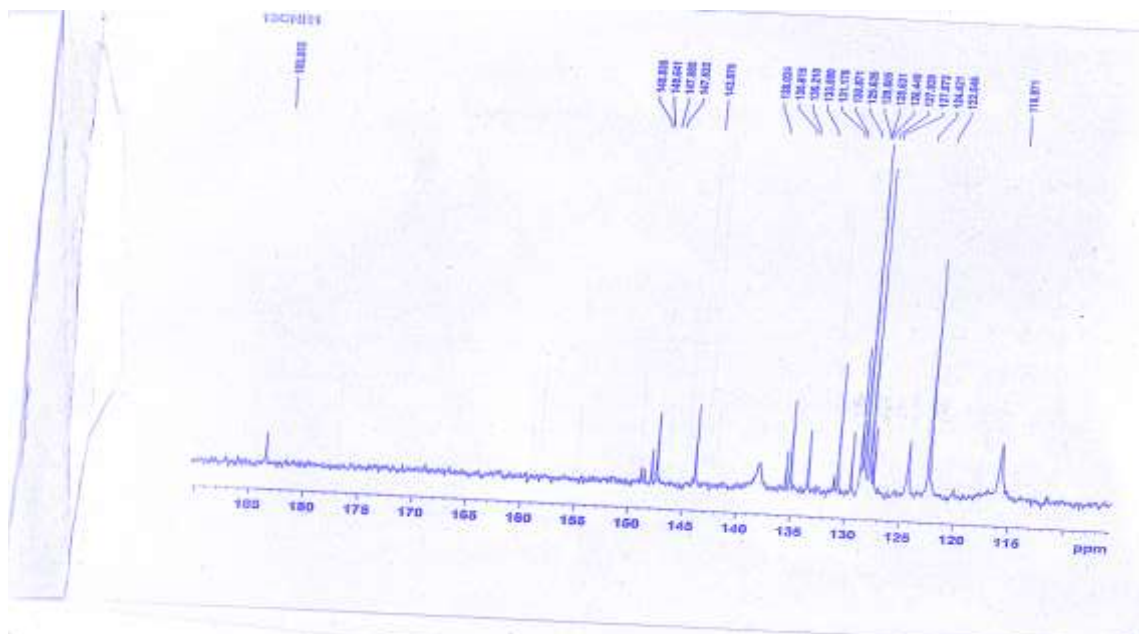


The ^1H NMR and ^{13}C NMR of ligands and their Zn (II) complexes were recorded to ascertain the nature of bonding in complexes. The ^1H NMR spectrum of Hbhe displays ($-\text{C}=\text{N}-\text{CH}_3$) proton signal at $\delta = 3.523$ ppm and phenyl ring proton signals as multiplets between $\delta = 7.165 - 7.742$ ppm (fig R3). The (N-OH) proton signals of N -hydroxyethanimine group was absorbed at $\delta = 11.823, 12.541$ ppm as prominent signals. The splitting is attributed to cis – trans orientations of phenyl and N-OH group with respect to benzimidazole nuclei. The NMR spectrum of $\text{Zn}(\text{bhe})_2$ in DMSO shows the absence of (NOH) proton signals at $\delta = 11.823, 12.541$ ppm. The phenyl ring and CH_3 proton signals of complexes get down field shifted observed between $6.985 - 7.865$ ppm and 3.845 ppm respectively. The absence of (N-OH) NMR proton signal supported coordination of deprotonated NOH nitrogen in complexes. The ^{13}C NMR of Hbhe phenyl and imidazole ring carbon signals were observed between $\delta = 111.64$ and 148.21 ppm (Fig-¹³ CNR1). The CH_3 carbon band was observed at 18.29 ppm. The DMSO carbon signal in spectrum was located at $38.67 - 40.34$ ppm. The ^1H NMR of Hbhpm shows phenyl ring proton signals as multiplets between $\delta = 7.141$ and 7.742 ppm. The proton signal at 8.562 and 8.586 is attributed to imidazole ring NH proton (fig NR1).



The N-OH proton signals were located at $\delta = 12.612$ and 12.629 ppm. The ^{13}C NMR of Hbhpms shows phenyl and imidazole ring carbon signals between $\delta = 115.971$ and 148.935 ppm and C=NOH carbon signal was observed at 183.568 as singlet (Fig- ^{13}C NMR1). The C=NOH carbon signal shifted to 210.331 ppm in Cd(II) complex supporting the coordination of C=NOH nitrogen to metal atom.





The mass spectrum of Hbhpm gave m/z value at M^+ = 237.23 (63%), 221.2 (42%), 222.3 (31%), 160.21 (35%), 120.2 (20%), 118, (100% base peak), 77 (48%). The mass spectrum of Hbhpm is consistent with its molecular mass 237.

3.4 Anti-fungal activity

The anti-fungal activity of ligands Hbhe, Hbhpm and their metal complexes were screened using radial growth method³¹. The Fungi used were *A.niger*, *C.albicans*, *R.phaseoli* and *R.aryzae*. Czapek agar medium was prepared by dissolving 20g starch and 20g glucose in one litre water, was used as basal medium to evaluate the efficiency of these synthesised products³². The medium containing 100 and 200 ppm compounds were poured into petri plate and spores of fungi were placed on medium. The chemical Mancozeb fungicides were used as standard for this process. The inoculated plates were incubated at $30 \pm 0.5^{\circ}\text{C}$ for 120 hours. The growth inhibition of fungi over control was calculated using % inhibition = $[(C-T)/C] \times 100$ where C = growth of fungus diameter in mm for control and T = growth of fungus in (mm) on treatment. The zone of inhibition was evaluated in mm and percentage inhibition was presented in Table-III. It has been observed that the metal complexes display larger anti-fungal activity than free ligand and anti-fungal activity for metal was largest for Cu(II) and Zinc (II) complexes of Hbhpm. The compounds were tested at 100 and 200 $\mu\text{g/ml}$ concentration in DMF. The inhibition was maximum for *Candida albicans*. The larger fungal activity of metal complexes may be due to large electron delocalisation which enhanced lipophilicity of central metal ion causing permeation through the lipid layer of fungi cell membrane.

3.5 Table-III

Anti-fungal screening results of ligands and their complexes

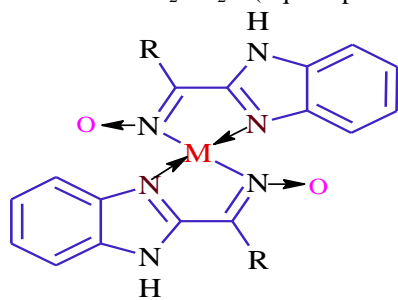
Compound	Fungi and the concentration of product in ppm								
	A.	Niger		C.albicans		R.aryze		R. phaseoli	
		100	200	100	200	100	200	100	200
Hbhe =HL	-	35		18	40	15	36	18	35
Cu(HL)Cl ₂		58	80	60	82	38	62	30	55
CuL'' ₂ 2H ₂ O		55	82	60	83	36	58	35	60
NiL'' ₂ 2H ₂ O		48	68	35	58	25	42	22	40
ZnL'' ₂		52	75	36	63	45	62	30	45
CdL'' ₂		50	70	41	62	42	60	28	42
CoL'' ₂ (H ₂ O) ₂		52	72	44	65	35	56	30	45
Hbhpm =HL''		36	45	26	42	20	42	-	-
Cu(HL)Br ₂		60	82	35	55	30	48	20	48
CuL'' ₂ 2H ₂ O		62	84	36	55	32	50	22	40
Ni(HL'') ₂		42	68	30	48	28	48	20	38
NiL'' ₂		45	70	32	55	22	44	22	40

[CdL ⁺] ₂	40	65	42	65	26	48	28	48
ZnL ⁺ ₂	52	76	45	70	30	65	35	65
Ref Mancozeb	72	98	76	99	75	100	76	99

IV. Conclusion

From IR, electrical conductance, magnetic susceptibility and other spectral studies it is inferred that both Hbhe and Hbhpm coordinates as neutral, monoanionic chelating group. Nickel (II) bis chelates are square planar, Zn (II), Cd (II) complexes are tetrahedral, Cobalt (II) and Copper (II) complexes are distorted octahedral. The probable structures of complexes are shown below:

Structure of NiL₂ 2H₂O (Square planar) and ML₂ (M= Zn^{II} or Cd^{II} and HL= Hbhe or Hbhpm) tetrahedral Fig-A



Tetrahedral or Planar structure

or Hbhpm)

Fig - A

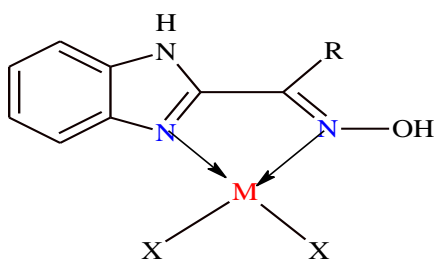
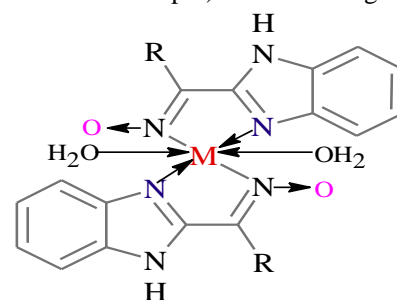


Fig - C

Tetrahedral Zn^{II} or Cd^{II} and tetragonal for Cu^{II}
M=Co^{II}, Ni^{II}, and



Octahedral structure

[ML₂(H₂O)₂, (M = Co^{II} or Cu^{II} and HL = Hbhe

Fig - B

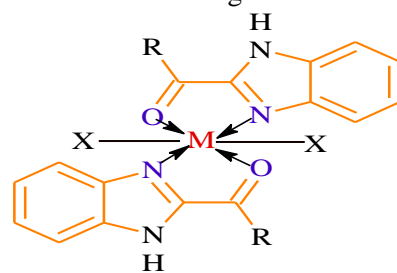


Fig - D

Octahedral M(HL)₂X₂

Cu^{II}

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