

## Synthesis Characterisation and Derivatographic studies of 1-(1H-Benzimidazol-2-yl)ethanone and 1-(1H-benzimidazol-2-yl)phenone with Co(II), Ni(II) and Cu(II).

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**Abstract:** The solid complexes of 1-(1H-Benzimidazol-2-yl)ethanone [2-Acetylbenzimidazol = AcbzH], and 1-(1H-benzimidazol-2-yl)phenone [2-benzoylbenzimidazol = BnbzH] with Co(II), Ni(II) and Cu(II) of compositions  $M(LH)_2X_2 \cdot nH_2O$ . ( $M = Co^{II}, Ni^{II}$  or  $Cu^{II}$ ,  $LH = AcbzH$  or  $BnbzH$ ,  $X = Cl^-$  or  $NO_3^-$ ,  $\frac{1}{2} SO_4^{2-}$ ,  $n = 0$  or  $2$ ),  $Cu(LH)X_2$  ( $LH = AcbzH$  or  $BnbzH$  and  $X = Cl^-$  or  $Br^-$ ),  $ML_2 \cdot nH_2O$  ( $M = Co^{II}, Ni^{II}$  or  $Cu^{II}$ ,  $LH = AcbzH$  or  $BnbzH$  and  $n = 0$  or  $2$ ) and  $[ML_2Py_2]$  ( $M = Co^{II}$  or  $Ni^{II}$  and  $LH = AcbzH$  or  $BnbzH$ ) have been isolated and characterised from the studies of magnetic susceptibility electrical conductance and spectral studies. The derivatographic studies of some complexes have been performed to assess their stability.

**Keywords:** Benzimidazole derivatives, Characterisation, Derivatographic studies, Metal complexes, Synthesis.

### I. Introduction

The studies on coordination complexes of benzimidazole and benzothiazole derivatives have acquired immense prominence due their multidimensional utility in industry, analytical chemistry and bioactivity both with respect to their antibacterial and antifungal inhibitory action as well as their pharmacologically favourable nuclie for drug action<sup>1-4</sup>. Extensive biochemical studies have established that benzimidazole derivatives are effective against strains of pathogens and microorganism<sup>5,6</sup>. The wide spectrum of biological properties of benzimidazole derivatives<sup>7</sup> generated huge interest in studies of their metal complexes<sup>8-10</sup>. In pursuance of our interest towards studies of complexes of metal ions with benzimidazole derivatives<sup>15-19</sup>, the new coordination complexes of 1-(1H-Benzimidazole-2-yl)ethanone (AcbzH) and 1-(1H-benzimidazole-2-yl)phenone (BnbzH) are being reported in present communication. The TGA and DTA studies of dipyrindino adduct complexes  $[ML_2(Py)_2]$  ( $M = Ni^{II}$  or  $Co^{II}$  and  $LH = AcbzH$  or  $BnbzH$ ) in temperature range 40 – 650 °c have also been studied.

### II. Experimental

The ligands were prepared by reported method<sup>20-21</sup>. The metal salts chloride, sulphate or acetate used were E.Merck extra pure or BDH Anal-R grade reagent. The solvents and organic chemicals were obtained from E.Merck, Nice, Ranbaxy or Sd.Fine chemical work. The electrical conductance measurements were taken in DMF solution at room temperature (30-31 °c). Metal content of the sample were determined by standard method<sup>22</sup>. Magnetic susceptibility of complexes were recorded by Gouy balance at room temperature (301 – 302 K). The I.R.spectra were recorded in KBr disc on a Schimadzu 8201 Pc. FTIR and HNMR on a Bruker DRX – 300 in DMSO or  $CDCl_3$  at 300 MHz using TMS as a internal indicator. The results of C,H,N and S were obtained from CDRI Lucknow. In major cases the Nitrogen content were determined using nitrometer by Duma's method. Electronic absorption spectra were recorded in ethanol or DMF in the range 200- 550 nm range at IIT Patna. The results of elemental analysis are given in Table – I. The values of prominent and diagnostic I.R. bands are shown in Table II.

#### 2.1 Preparation of $ML_2 \cdot n H_2O$ ( $M = Co^{II}, Ni^{II}$ or $Cu^{II}$ , $LH = AcbzH$ or $BnbzH$ and $n = 0$ or $2$ )

About 0.02 mole of metal acetate dissolved in 30 – 40 ml aqueous methanol was added to hot methanolic solution of 0.04 mole of appropriate ligand reflexed on steam bath by adding 25 ml of 5% of aqueous sodium acetate solution drop wise. The bis- chelate separated gradually and the precipitate was digested for 1 hour and collected on a filter. The complexes washed with aqueous methanol and dried over  $CaCl_2$  yield 96 - 99%.

#### 2.2 Complexes $Cu(LH)X_2$ ( $LH = AcbzH$ or $BnbzH$ , $X = Cl^-$ or $Br^-$ )

About 0.02 mole of copper (II) halide was dissolved in 20ml dry methanol and treated with 0.02 mole of appropriate ligand dissolved in 20 ml hot methanol. The reaction mixture was stirred for 10 – 15 minute when crystalline product separated on cooling. The product were collected on a filter, washed with ice cold methanol and dried over  $CaCl_2$ .

**2.3 Complexes M ((LH) X<sub>2</sub>.nH<sub>2</sub>O (M = Co<sup>II</sup> or Ni<sup>II</sup>, LH = AcbzH or BnbzH, n = 0 or 2 and X = Cl<sup>-</sup> or Br<sup>-</sup> )**

About 0.02 mole of appropriate metal halide was dissolved in hot dry methanol (20ml) and added with stirring to 0.04 mole of ligand dissolved in methanol (20ml). The resulting solution were concentrated on steam bath to 10 – 15 ml and chilled with stirring when dihalo complexes separated slowly. The products were collected on a filter washed with cold methanol and dried in air and finally in a desiccator over CaCl<sub>2</sub>. The yield 80 – 90%.

**2.4 [M (LH) <sub>2</sub>(H<sub>2</sub>O) <sub>2</sub>] SO<sub>4</sub> (M = Co<sup>II</sup> Cu<sup>II</sup> and Ni<sup>II</sup>, LH = AcbnzH or BnbzH)**

The complex sulphates were prepared as above by using aqueous solution of metal sulphate and ligand in 1:2 molar ratio in hot methanol. The mixed solution on refluxing, yielded complex sulphate on gentle warming. The product were filtered, washed and dried over CaCl<sub>2</sub>.

**2.5 [ML<sub>2</sub>Py<sub>2</sub>] (LH = AcbzH or BnbzH and M = Co<sup>II</sup> or Ni<sup>II</sup>)**

About 0.02 mole of aqueous methanol solution of metal chloride was added with constant stirring to methanol solution of 0.4 mole of ligand (40ml) containing 5 – 6 ml pyridine. The resulting solution was heated on steam bath and treated with dilute ammonia (5 – 10 ml) when crystalline pyridine adducts separated gradually. The product collected on filtered, washed with methanol containing pyridine. The complexes were dried in a desiccator over KOH in pyridine atmosphere. The complexes were analysed and results of elemental analysis are given in Table I.

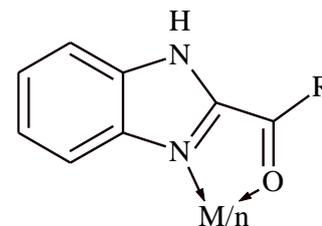
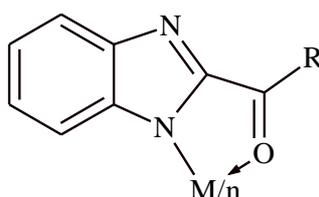
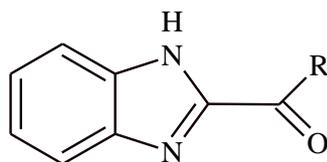
**Table - I**  
Analytical results and physical data of complexes

Compound	Colour	% Analysis Found / (Cal)				$\mu_{\text{eff}}$ BM 304 K	$\wedge\alpha$ ohm <sup>-1</sup> mol <sup>-1</sup> cm <sup>2</sup>
		M	C	H	N		
Cu(LH)Cl <sub>2</sub>	Greenish	21.31(21.54)	36.42(36.67)	2.68(2.71)	9.31(9.53)	1.82	12
Cu(L H)Cl <sub>2</sub>	Greenish yellow	17.76(17.80)	47.41(47.12)	2.91(2.81)	7.91(7.85)	1.87	10
Cu(LH)Br <sub>2</sub>	Brown	16.32(16.54)	28.01(28.16)	1.91(2.08)	7.10(7.36)	1.86	15
Cu(L H)Br <sub>2</sub>	Brown	14.01(14.24)	37.48(37.71)	2.41(2.24)	6.10(6.28)	1.82	12
[Cu(LH) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]SO <sub>4</sub>	Bluish green	12.11(12.30)	41.71(41.90)	3.55(3.88)	10.48(10.86)	1.87	135
[Cu(LH) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ]	Yellowish green	12.28(12.50)	42.31(42.56)	3.73(3.94)	16.41(16.55)	1.88	15
[Cu(LH) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ](NO <sub>3</sub> ) <sub>2</sub>	Bluish green	9.61(9.50)	50.11(50.33)	3.41(3.59)	12.46(12.58)	1.86	190
[Cu(L H) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]SO <sub>4</sub>	Bluish green	9.71(9.92)	52.42(52.52)	3.91(3.75)	8.91(8.75)	1.85	140
Co(LH) <sub>2</sub> Cl <sub>2</sub>	Pink	13.21(13.08)	47.71(48.00)	3.68(3.55)	12.31(12.44)	5.01	15
Co(L H) <sub>2</sub> Cl <sub>2</sub>	Pink	9.81(10.26)	58.41(58.53)	3.71(3.48)	9.58(9.75)	4.98	13
[Co(LH) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]SO <sub>4</sub>	Pink	11.36(11.52)	42.01(42.27)	4.01(3.91)	10.69(10.95)	4.96	138
[Co(L H) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]SO <sub>4</sub>	Pink	9.11(9.27)	52.81(52.91)	3.67(3.78)	9.31(9.45)	4.97	140
Ni(LH) <sub>2</sub> Cl <sub>2</sub>	Light blue	12.91(13.04)	47.81(48.00)	3.91(3.55)	12.21(12.44)	3.10	12
Ni(L H) <sub>2</sub> Cl <sub>2</sub>	Light blue	10.11(10.22)	58.28(58.54)	3.60(3.48)	9.81(9.75)	2.98	10
CuL <sub>2</sub> 2H <sub>2</sub> O	Ash	14.92(15.19)	45.31(45.97)	4.51(4.31)	13.61(13.41)	1.87	8
CuL <sub>2</sub> 2H <sub>2</sub> O	Ash	11.63(11.71)	62.11(62.05)	3.91(4.06)	10.18(10.34)	1.89	10
CoL <sub>2</sub> 2H <sub>2</sub> O	Buff	14.29(14.19)	51.84(52.06)	4.63(4.34)	13.41(13.48)	5.02	8
CoL <sub>2</sub> 2H <sub>2</sub> O	Buff	10.80(10.92)	62.44(62.33)	4.21(4.01)	10.41(10.38)	4.98	10
NiL <sub>2</sub> 2H <sub>2</sub> O	Cream yellow	10.91(10.89)	62.41(62.43)	4.23(4.02)	10.48(10.38)	2.87	11

NiL <sub>2</sub> 2H <sub>2</sub> O	Cream yellow	14.21(14.15)	51.69(52.08)	4.51(4.34)	13.71(13.50)	2.93	9
NiL <sub>2</sub> (Py) <sub>2</sub>	Bluish green	10.68(10.93)	62.69(62.59)	4.71(4.41)	15.48(15.65)	3.12	8
CoL <sub>2</sub> (Py) <sub>2</sub>	Orange yellow	11.01(10.92)	62.81(62.58)	4.61(4.47)	15.41(15.65)	4.89	10
NiL <sub>2</sub> (Py) <sub>2</sub>	Bluish green	8.68(8.91)	69.46(69.23)	4.35(4.25)	12.81(12.75)	3.01	9
CoL <sub>2</sub> (Py) <sub>2</sub>	Orange yellow	9.01(8.93)	69.41(69.22)	4.31(4.26)	12.88(12.75)	5.01	10

### III. Result and Discussion

The ligand 1-(1H-Benzimidazol-2-yl) ethanone (AcbzH LH) and 1-(1H-benzimidazole-2-yl)phenone (BnbzH LH)



R = CH<sub>3</sub>, LH = AcbzH R = C<sub>6</sub>H<sub>5</sub>, LH = BnbzH

Coordinate as neutral chelating molecule in dry ethanol or methanol in weakly acidic medium forming complexes [Cu(LH)X<sub>2</sub>] (X = Cl<sup>-</sup> or Br<sup>-</sup> and LH = AcbzH or BnbzH), [M(LH)<sub>2</sub>X<sub>2</sub>].nH<sub>2</sub>O (M = Co<sup>II</sup>, Cu<sup>II</sup> or Ni<sup>II</sup>, X = Cl<sup>-</sup> or NO<sub>3</sub><sup>-</sup> or 1/2 SO<sub>4</sub><sup>2-</sup> and n = 0 or 2, LH = AcbzH or BnbzH). In basic medium the benzimidazole ring (NH) proton is deprotonated forming neutral bis-chelates ML<sub>2</sub>nH<sub>2</sub>O (M = Co<sup>II</sup>, Ni<sup>II</sup> or Cu<sup>II</sup>, LH = AcbzH or BnbzH and n = 0 or 2). The neutral bis chelate form adduct complex [ML<sub>2</sub>B<sub>2</sub>] in presence of pyridine at basic medium. The complexes are fairly stable at room temperature and insoluble in water. The dihalo complexes are slightly soluble in ethanol or methanol but dissolve fairly in DMF and DMSO. The other complexes are partially soluble in ethanol and methanol but dissolve appreciably in mixed solvent system. The DMF solution of complexes (Table I) indicated that complex sulphates [ML<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]SO<sub>4</sub> are ionic while others are non-ionic.

The low conductance value of [Cu(LH)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>] (LH = AcbzH) indicated the nitrate to be bonded with metal atom. The magnetic moment value of Co<sup>II</sup>, Cu<sup>II</sup> and Ni<sup>II</sup> complexes (Table – I) occur in the normal range of spin free octahedral complexes<sup>23</sup>. The di-pyridine bis ligated complexes [ML<sub>2</sub>(Py)<sub>2</sub>] (LH = AcbzH or BnbzH and M = Co<sup>II</sup> or Ni<sup>II</sup>) are fairly soluble in ethanol, methanol, acetone and DMF. These complexes can be extracted in cyclohexane and benzene in presence of pyridine quantitatively.

The electronic absorption spectra of complexes in ethanol were recorded in the range 200 – 850 nm and those of ligand in the range 200 – 500 nm. The ligand AcbzH displays three electronic absorption bands located at 205, 240 and 280 nm attributed from σ→σ\*, σ→π\* and π→π\* transitions. The n→π\* transition is located as weak shoulder at 320 nm. The ligand BnbzH in ethanol shows absorption bands at 210 nm (σ→σ\*) and 246 nm (π→π\*) phenyl ring and 285 nm {(π→π\*) (C=O)} group of ligand molecule. The complexes display d-d transitions in the range 400 – 850 nm as medium to weak band. The electronic absorption band positions of complexes in ethanol or DMF are recorded in Table II. The electronic transition of Ni(II) complexes in the range 24800 – 24200 cm<sup>-1</sup> is assigned to <sup>3</sup>A<sub>2g</sub>→<sup>3</sup>T<sub>1g</sub> (p) and absorption between 16500 – 15800 cm<sup>-1</sup> has been attributed to <sup>3</sup>A<sub>2g</sub>→<sup>3</sup>T<sub>1g</sub> (F) transition<sup>25</sup>. The medium weak bands located for cobalt (II) complexes in the range 19400 – 20750, and 22500 – 22750 cm<sup>-1</sup> are assigned to <sup>4</sup>T<sub>1g</sub>→<sup>4</sup>T<sub>1g</sub> (p) and <sup>4</sup>T<sub>1g</sub>→<sup>4</sup>A<sub>2g</sub> transition in octahedral field<sup>25</sup>. The prominent band of complex sulphate [Co(LH)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]SO<sub>4</sub>, (LH = AcbzH or BnbzH) at 19400 cm<sup>-1</sup> is attributed to <sup>4</sup>T<sub>1g</sub>→<sup>4</sup>T<sub>2g</sub> transition acquired intensely due to tetragonal distortion (d<sub>π</sub>-p<sub>π</sub> mixing) copper (II) complexes show strong absorption below 420nm (23,810 cm<sup>-1</sup>) attributed to charge transfer transition while a broad asymmetric absorption band between 14500 – 14300 cm<sup>-1</sup> is assigned to <sup>2</sup>B<sub>1g</sub>→<sup>2</sup>A<sub>2g</sub>, → <sup>2</sup>B<sub>1g</sub> transition in tetragonal distorted field<sup>26</sup>.

### IV. TG and DTA studies

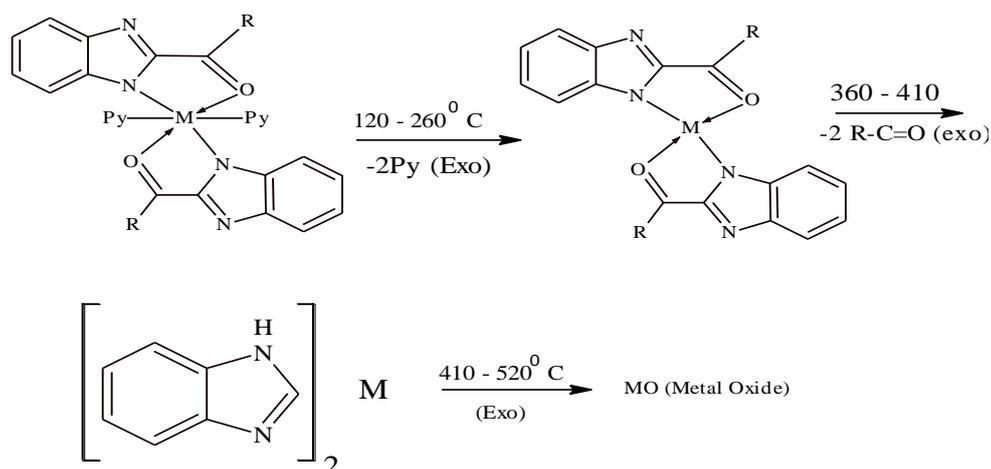
Derivatographic studies of dipyridine complexes of Co (II) and Ni (II), [ML<sub>2</sub>Py<sub>2</sub>] were performed on thermogravimetric balance with heating rate 10<sup>0</sup> per minute. All most all di pyridine complexes were stable in dry up to 90<sup>0</sup>c in static air. The complexes Ni(Acbz)<sub>2</sub>Py<sub>2</sub> was stable upto 105<sup>0</sup>c and started loss in weight at 105<sup>0</sup>c giving DTG maxima at 180<sup>0</sup>c and DTA at 180<sup>0</sup>c was exothermic in nature. The TG loss continues upto

230<sup>0</sup>c giving stable product Ni(Acbz)<sub>2</sub> with weight loss of 30.5% which corresponds to loss of 2Py molecules (calculated value 29.5%). The product Ni(Acbz)<sub>2</sub> was stable between 230<sup>0</sup>c and 340<sup>0</sup>c. After 340<sup>0</sup>c, the product started second stage of weight loss slowly, probably with decomposition and it is rapid with exothermic DTA maxima at 385<sup>0</sup>c. The loss continues slowly upto 410 - 420<sup>0</sup>c with 46.5% of total weight loss which corresponds to 2CH<sub>3</sub>CO group from coordinated ligand. The loss calculated at this stage is 45.6%. The product further decomposes rapidly at 430 - 480<sup>0</sup>c forming stable product. The residual weight of product was 13.2% which corresponds to weight of metal oxide (13.9%). The last step of decomposition was also exothermic with DTA maxima at 470<sup>0</sup> c. The thermogram of complexes [Ni (Bnbz)<sub>2</sub>Py<sub>2</sub>] and [Co (L<sub>2</sub>) Py<sub>2</sub>] (HL = HAcbz or Hbnbz) were recorded and were found to show similar pattern of thermogram. The results of the thermogram is presented in Table II. It is observed that Cobalt (II) complexes are more stable than Nickel (II) product. The stability of di pyridine adduct is thermally less stable those of acetyl substituted benzimidazole probably due to steric factor.

**Table – II**  
Result of TG analysis

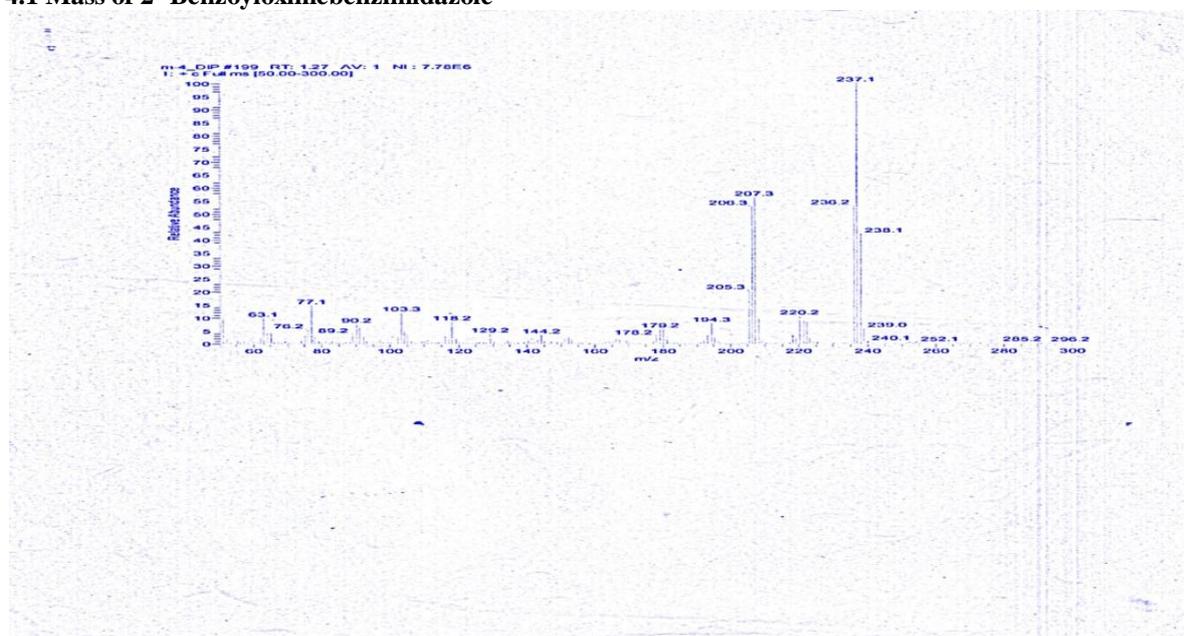
Compound and TG step	Temperature of TG loss (0c)	Molecule lost	Expected product	% loss found (calculated)	Nature and temperature DTA maxima
Ni(Acbz) <sub>2</sub> Py <sub>2</sub> Ist Step IIInd Step IIIrd Step	105 – 230 340 – 410 420 – 480	2Py 2CH <sub>3</sub> CO Decomposes	[Ni(Acbz) <sub>2</sub> Ni(Bz) <sub>2</sub> NiO	30.05(29.5) 46.5(45.5) 86.8(86.1)	1800C Exothermic 3850C Exothermic 4700C Exothermic
Ni(Bnbz) <sub>2</sub> Py <sub>2</sub> Ist Step IIInd Step IIIrd Step	95 – 200 330 – 415 420 – 480	2Py 2C <sub>6</sub> H <sub>5</sub> CO Decomposes	Ni(B <sub>2</sub> bz) <sub>2</sub> Ni(Bz) <sub>2</sub> NiO	23.61(23.96) 56.40(55.90) 89.10(88.70)	1600C 3800C Exothermic 4750C
Co(Acbz) <sub>2</sub> Py <sub>2</sub> Ist Step IIInd Step IIIrd Step	110 – 220 350 – 425 410 – 485	2Py 2CH <sub>3</sub> CO Decomposes to form oxide	Co(Acbz) Co(Bz) <sub>2</sub> CoO + Co <sub>2</sub> O <sub>3</sub>	31.2(29.4) 46.2(45.4) 85.9(86.1)	1820C 3900C Exothermic 4800C Exothermic
Co(B <sub>2</sub> bz) <sub>2</sub> Py <sub>2</sub> Ist Step IIInd Step IIIrd Step	90 – 210 335 – 425 430 – 485	2Py 2C <sub>6</sub> H <sub>5</sub> CO Decomposes	Co(B <sub>2</sub> bz) <sub>2</sub> Co(Bz) <sub>2</sub> CoO	24.3(23.9) 56.2(55.9) 88.8(88.7)	1600C Exothermic 3850C Exothermic 4700C Exothermic

The scheme for derivatographic loss and products formed are shown below.



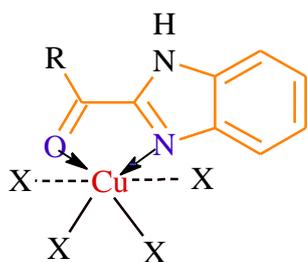
The I.R spectra of ligands and their complexes were recorded as KBr disc in the range 4000–400  $\text{cm}^{-1}$ . AcbzH (CH<sub>2</sub>), (CH), (NH) and phenyl ring (C-H) stretches 2880, 2940, 3060 and 3305  $\text{cm}^{-1}$  and  $\nu$  (C=O) and at 1655  $\text{cm}^{-1}$ . The  $\nu$  (C=N),  $\delta$  (NH) and  $\nu$  (C=C) vibrations are 1595, 1512 and 1414  $\text{cm}^{-1}$ . The  $\nu$  (NH),  $\nu$  (CH) phenyl ring in BnbzH was located at 3300 and 3040  $\text{cm}^{-1}$ . The broad weak band at 3260 – 3150  $\text{cm}^{-1}$  can be attributed to hydrogen bonded (NH-O=C-) vibration<sup>27</sup>. The  $\nu$  (CO) of BnbzH is observed at 1704  $\text{cm}^{-1}$  as very strong and sharp band. The I.R band located 1612, 1590, 1530, 1485 and 1430  $\text{cm}^{-1}$  can be assigned to  $\nu$  (C=N),  $\nu$  (C=N),  $\delta$  (NH) and  $\nu$  (C=C) and phenyl ring skeletal vibrations. The AcbzH and BnbzH complexes  $\nu$  (C=O) band between 1653 – 1626  $\text{cm}^{-1}$  suggesting the involvement of carbonyl oxygen to metal atoms. The complexes containing neutral ligand display  $\delta$  (NH) as prominent band near 1510  $\pm$  5 for AcbzH complexes while near 1525  $\pm$  5 in case of complexes with BnbzH. The absence of  $\nu$  (NH) and  $\delta$  (NH) in complexes with deprotonated ligand suggested deprotonation of (NH) proton in bis chelated neutral complexes. The diagnostic IR bands of some complexes are recorded in Table III. The complex sulphate [NiL<sub>2</sub> (H<sub>2</sub>O)<sub>2</sub>] SO<sub>4</sub> and [CuL<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]SO<sub>4</sub> display SO<sub>4</sub>  $\nu_1$  and  $\nu_4$  stretch as strong and broad band at 1105 – 1115 and 615 - 618  $\text{cm}^{-1}$  conforming ionic nature of sulphate<sup>27</sup>. The dinitro copper (II) complex [CuL<sub>2</sub> (H<sub>2</sub>O)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub> display a strong band at 1381  $\text{cm}^{-1}$  ionic nitrate group<sup>27</sup>. The  $\nu_3$  (NO<sub>3</sub>) of complex [Cu (AcbzH)<sub>2</sub> (NO<sub>3</sub>)<sub>2</sub>] splits into two band located at 1438 and 1282  $\text{cm}^{-1}$  suggesting coordinated nature of NO<sub>3</sub> group. The bis pyridino complexes exhibit strong  $\nu$  (C=N) band at 1590  $\pm$  5 and pyridine ring breathing mode of vibrations at 1020  $\pm$  5  $\text{cm}^{-1}$  for coordinated pyridine molecule. In finger print region, the ligand and complexes display a number of i.r bands for skeletal and plane as well as out of plane (C-H) and (N-H), (C=N), (C-C) and (C=O) bending mode of vibrations<sup>27-30</sup>.

#### 4.1 Mass of 2- Benzoyloximebenzimidazole

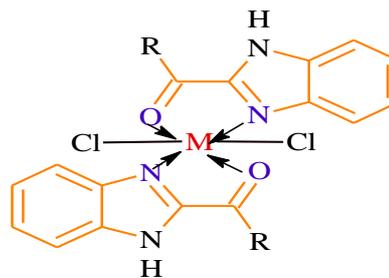


The NMR and mass spectra of ligand molecules were recorded at IIT Patna and CDRI Lucknow. The mass spectra (m/z) of AcbzH gave M<sup>+</sup> 160(30%), 145(10%), 118(100%), 91, 90, 63 and 43(100% base peak). The C<sup>13</sup> spectra displayed CH<sub>3</sub> signal at 26.07 ppm and phenyl plus imidazole ring carbon atom signals at  $\delta$  = 112.3, 121.97, 123.93, 126.63, 133.78, 143.46 and 147.76. The (C=O) carbon signal was located at 192 ppm. The <sup>1</sup>HNMR spectrum of AcbzH showed CH<sub>3</sub> at  $\delta$  = 2.78 (3H, S) and  $\delta$  = 7.28 – 7.80 (4H multiplet for benzene protons). The NH proton signal was observed at  $\delta$  = 13.42 ppm.

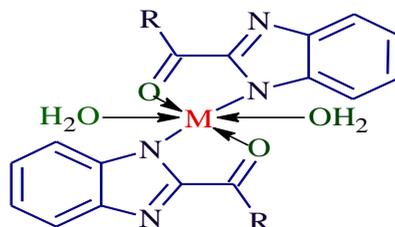
The mass spectral M/z value of BnbzH (M = 222) gave M<sup>+</sup> signal at 222(57%), 221(12%), 194(100%), 145(12%), 118(45%), 77(60%) and 56(15%). The base peak is formed due to formation of 2-Phenylbenzimidazole. The <sup>13</sup>CNMR of ligand BnbzH shows  $\delta$  at 111.96, 122.29, 123.75, 126.45 128.51, 131.33, 133.19, 133.88, 135.39, 143.98 and 147.76 for phenyl ring <sup>13</sup>C signals and  $\delta$  = 184.05 for C=O Carbon. The <sup>1</sup>HNMR signals of phenyl proton were observed between  $\delta$  = 7.257 and 7.990 as multiplets. The NH proton were observed at  $\delta$  = 8.693 and 8.717 ppm (for 1H). The splitted (NH) signals indicated that free ligand (CO) exists in cis and trans to (NH) part of benzimidazole nucleus. The mass spectrum of Zinc (II), BnbzH complexes [Zn(Bnbz)<sub>2</sub>] displayed absence of (NH) proton signals of ligand form  $\delta$  = 8.693 and 8.717 ppm supporting the deprotonation of NH proton in bond formation. The phenyl ring proton signals get down field shifted and observed at 7.215 to 8.105 ppm as multiplets. The down field shifting supported delocalisation of CH proton in chelate ring formation on complexation. The probable structures of complexes are shown below:-



(R = CH<sub>3</sub> or C<sub>6</sub>H<sub>5</sub>, X = Cl<sup>-</sup> or Br<sup>-</sup>)  
Distorted octahedral



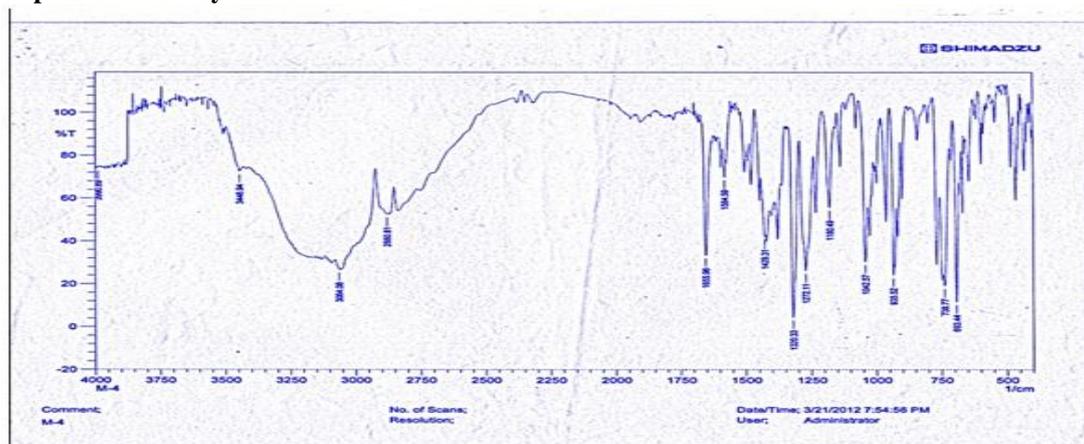
(M = Co<sup>II</sup> or Ni<sup>II</sup>, R = CH<sub>3</sub> or C<sub>6</sub>H<sub>5</sub>)  
Structure of [ML<sub>2</sub>Cl<sub>2</sub>]



(M = Co<sup>II</sup>, Cu<sup>II</sup> or Ni<sup>II</sup>)

Structure of [ML<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] type of complexes, octahedral

#### 4.2 IR spectra of Benzoyloxime benzimidazole



#### 4.3 Diagnostic IR bands of ligands and some metal complexes.

Compound	v(NH)	v(C=O)	v(C=N)	δ(NH)	Py ring breathing mode	Out of plane substituted phenyl (C-H)
AcbzH = L H	3305sb 3045	1672sb	1612	1515	1026	748
BnbzH = L H	3280m 3060	1655	1605	1540	1032	745
Cu(L H)Cl <sub>2</sub>	3280 3050	1653	1597	1518	1020	745
Cu(L H)Cl <sub>2</sub>	3250 3040	1648	1597	1532	1052	740
Cd(L H)Cl <sub>2</sub>	3300 3040	1652	1586	1518	1020	746
Cd(L H)Cl <sub>2</sub>	3280 3050	1662	1588	1530	1030	748
Co(L H) <sub>2</sub> Cl <sub>2</sub>	3300 3040	1642	1602	1515	1015m	752

Ni(L <sup>''</sup> H) <sub>2</sub> Cl <sub>2</sub>	3270 3060	1656	1608	1528	1055	750
NiL <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub>	3360br 3040	1646	1585	----	1030	747
CoL <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub>	3350br 3040	1652	1670	---	1035	748
[ZnL <sub>2</sub> ]	3050	1648	1596	----	1030	743
[ZnL <sub>2</sub> ]	3060	1655	1594	----	1035	746
[NiL <sub>2</sub> Py <sub>2</sub> ]	3060	1645	1595	1495	1015	740
[CoL <sub>2</sub> Py <sub>2</sub> ]	3045	1650	1590	1490	1018	---
[NiL <sub>2</sub> Py <sub>2</sub> ]	3045	1665	1590	1485	1028	742
[CoL <sub>2</sub> Py <sub>2</sub> ]	3040	1660	1595	1480	1025	748

### V. Conclusion

Both AcbzH and BnbzH coordinate as bidentate neutral or monoanionic chelating molecule, forming octahedral complexes with Co<sup>II</sup>, Ni<sup>II</sup> and Cu<sup>II</sup>. The pyridine adduct of Cobalt (II) are more stable than Nickle (II) adduct NiL<sub>2</sub>Py<sub>2</sub>.

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