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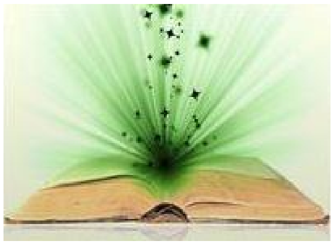

Synthesis and Structural analysis of N_4-donar ligands and their complexes with some bivalent transition metal ions

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ABSTRACT

N,N'-(propane-1,3-diyl)bis(2-aminobenzamide) [PBAB] and N,N'-(propane-1,3-diyl) bis(2-(pyrrolidin-1-yl)benzamide) [PPB] have been prepared and characterized using spectroscopic methods. The structure of the compound PPB was obtained by single crystal X-ray diffraction method. PPB crystallizes in monoclinic crystal system of space group P21/c with $a = 10..0035(12)$, $b = 13.6893(17)$, $c = 16.2941(22)$ Å, *and* $\alpha = 90^o$, $\beta = 91.388(12)^o$ *and* $\gamma = 90^o$; $Z=4$, $\rho = 1.25$ gcm^{-3} *and cell volume of 2230.67(8) Å. Bivalent transition metal complexes of PBAB and PPB have been prepared and characterized using elemental analyses, conductance and magnetic susceptibility measurements and spectral studies (mass, IR, electronic, ESR, and NMR). The complexes prepared are found to have formula* $[MLCl_2].H_2O$ {M = Co(II), Ni(II), Cu(II); L = PBAB or PPB} *and* $[M'L(CH_3COO)_2]$ {M' = Zn(II) or Cd(II); L = PBAB or PPB}.

Keywords: N_4-donors, X-ray structures, Transition metal complexes, Spectral properties of metal complexes, Characterization of complexes.

INTRODUCTION

The coordination chemistry of transition metal complexes has been the subject of interest, because of the complexities associated with variable oxidation states, variety of geometries around the metal ions, donating properties of ligands and their influence on spectral, catalytic and biological properties of metal ions [1]. The importance of transition metals in a number of biological systems [2-6] has motivated the study of the complexes of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II). Their effects provide a diversity of functions, including tunable redox potentials, activation of external substrates and small molecule transport [7, 8].

As part of our research we have developed a good number of polydentate ligands and investigated their reactions with different transition and inner-transition metal ions [9-11]. Further, the applications of the new complexes as catalysts in synthetic organic chemistry were also studied [12-14]. In this paper, we report the synthesis and characterization of two propane-1,3-diamine bridged diamine-diamide ligands: N,N'-(propane-1,3-diyl)bis(2-aminobenzamide) [11] (PBAB) and N,N'-(propane-1,3-diyl) bis(2-(pyrrolidin-1-yl)benzamide (PPB) and their Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes.

MATERIALS AND METHODS

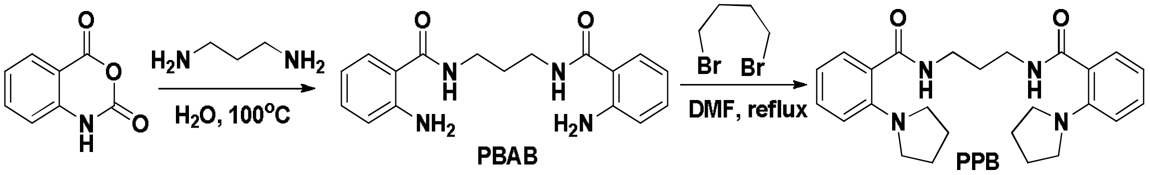
All reagents and solvents were used as obtained from the supplier and recrystallized/redistilled wherever necessary. Thin-layer chromatography (TLC) was performed for checking the purity of the compounds. Infrared spectra (KBr disc) were recorded with a PerkinElmer BX series-Fourier transform infrared spectrometer. ^{1}H and ^{13}C{^{1}H} NMR spectra were obtained on a Bruker AV500 MHz Spectrometer with chemical shifts referenced to internal standard, $Si(CH_3)_4$. Mass spectra were recorded by the HR-FAB and HR-EI techniques on JMS-700 double focusing mass spectrometer (JEOL, Tokyo, Japan) with a resolution of 8000(3000) (5% valley definition) at Mass Spectrometry facility in Indian Institute of Chemical Technology, Hyderabad. Thermo gravimetric analysis (TGA) was carried out using a Mettler–Toledo, TGA 822e series instrument at a heating rate of 10ºC per min. CHN analysis were carried out using Elemental Analyzer Flash EA 1112. Conductance of the metal complexes was measured on Digisun digital conductivity meter model DI-909. Magnetic susceptibility measurements of the metal complexes in the solid state were performed on the Gouy's balance at room temperature. Melting points were recorded on a Cintex apparatus. The electronic spectra were recorded in DMF solutions on a Shimadzu UV–Visible spectrophotometer model 2401 PC. ESR spectra of Cu(II) complexes were recorded at liquid nitrogen temperature on JEOL-JES-PE-3X ESR spectrometer using DPPH as the g-marker.

Single crystal X-ray diffraction data of the compound, PPB, was collected on CrysAlis CCD Xcalibur, Eos(Nova), Oxford Diffractometer with X-ray generator operating at 50 kV and 1 mA, using Mo Kα radiation (λ=0.7107 Å). The structure was solved and refined using SHELX97 module in the program suite WinGX[15-17]. The molecular diagrams were generated using ORTEP-3 and the packing diagrams were generated using Mercury 2.3 [18]. The geometric calculations were carried out by PARST95 and PLATON [19]. Preliminary lattice parameters and orientation matrices were obtained from four sets of frames. Unit cell dimensions were determined from 2240 reflections for PPB. Anisotropic displacement parameters were included for all non-hydrogen atoms. The hydrogen atoms attached to nitrogen atoms were located in a difference density map and refined isotopically. All other H atoms were positioned geometrically and treated as riding on their parent C atoms. The crystal data for PPB are listed in table **1**. Further, details of X-ray structure determination are deposited at the CCDC (deposition number CCDC 886544).

Preparation of Ligands

The ligand PBAB was prepared using the reported procedure from this laboratory [11] and purity was checked by TLC and comparing the spectral properties.

Synthesis of N,N'-(propane-1,3-diyl)bis(2-(pyrrolidin-1-yl)benzamide : The ligand PPB was prepared by the reaction as shown in the Scheme 1. A solution of N,N'-propane-1,3-diyl-*bis*-(2-aminobenzamide) (7.80 g, 25 mmol) in 10 mL of anhydrous DMF was added under nitrogen, to a solution containing K_2CO_3. After the mixture was stirred at room temperature for 15 min. , it was cooled to 0^oC, solution of 1,4–dibromobutane (10.8 g, 50 mmol) in 10 ml DMF was added slowly. The resulting mixture was refluxed for 6 h. The suspension was poured into ice-cold water and extracted with ethyl acetate and washed with saturated NaCl solution. After removal of the solvent the crude product was obtained, which was further purified by column chromatography using chloroform : methanol mixture (9:1) as the eluent, yielding colorless crystals of N,N'-(propane-1,3-diyl)bis(2-(pyrrolidin-1-yl)benzamide [PPB] (6.3 g, 60%). M.P (uncorrected): 256–258°C. ^{1}H-NMR (400 MHz, d_6-DMSO), ∂ (ppm): 8.26 (t, J = 14.8 Hz, 2H), 7.22-7.14 (m, 4H), 6.76 – 6.58 (m, 4H), 3.24 (m, 4H) 3.19 – 3.13 (m, 8H) 1.94–1.88 (m, 8H) and 1.65 (q, 2H); ^{13}C-NMR (100 MHz, d_6-DMSO) ∂ 171.23, 146.54, 131.16, 130.89, 125.54, 116.38, 114.34, 50.72, 37.92, 29.56, 26.48. HRMS (FAB+, m/z) 421.2 $(M+1)^{\rceil\ +}$; calculated for $C_{25}H_{32}N_4O_2$: 420.2.



Scheme 1 Preparation of PBAB and PPB

Preparation of Complexes*:* To 2.0 mmol of methanolic solution of ligands PBAB or PPB a solution of the metal salt (2.0 mmol) [chlorides in the case of (Co(II), Ni(II), Cu(II); acetates in the case of Zn(II) and Cd(II)] in 10 ml methanol was added at room temperature while stirring continuously. The mixture was refluxed for 5 – 8 h. On cooling the solution to room temperature fine powder of the corresponding complex started separating. The reaction mixture was cooled in a refrigerator overnight. The solid complexes precipitated were filtered, washed with cold methanol and dry acetone, dried under vacuum.

RESULTS AND DISCUSSION

Molecular structure of PPB

The spectral properties of the PPB give an idea of the tentative structure of the compound. In order to establish the solid state structure of PPB, single crystal X-ray diffraction study was performed. Crystals suitable for X-ray diffraction were grown from chloroform-methanol solution at room temperature. The compound crystallizes in the monoclinic crystal system of space group $P2_1/c$. The selected hydrogen bonding parameters are listed in table **2**. The molecular structure and the packing diagram are presented in figures **1** and **2**. The packing diagram shows that the molecules are held together by strong intermolecular hydrogen bonds between O1–H4N' and O2–H3N".

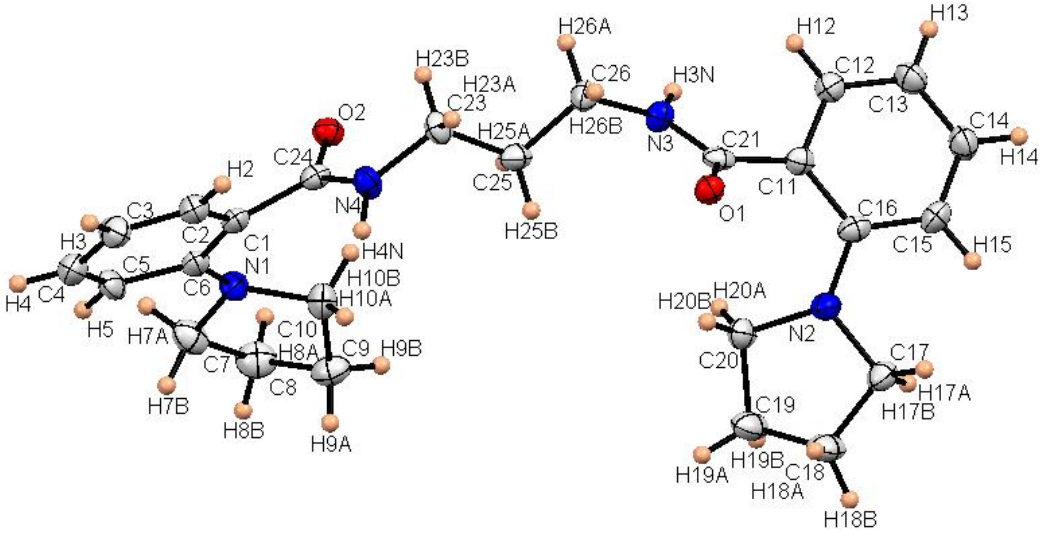
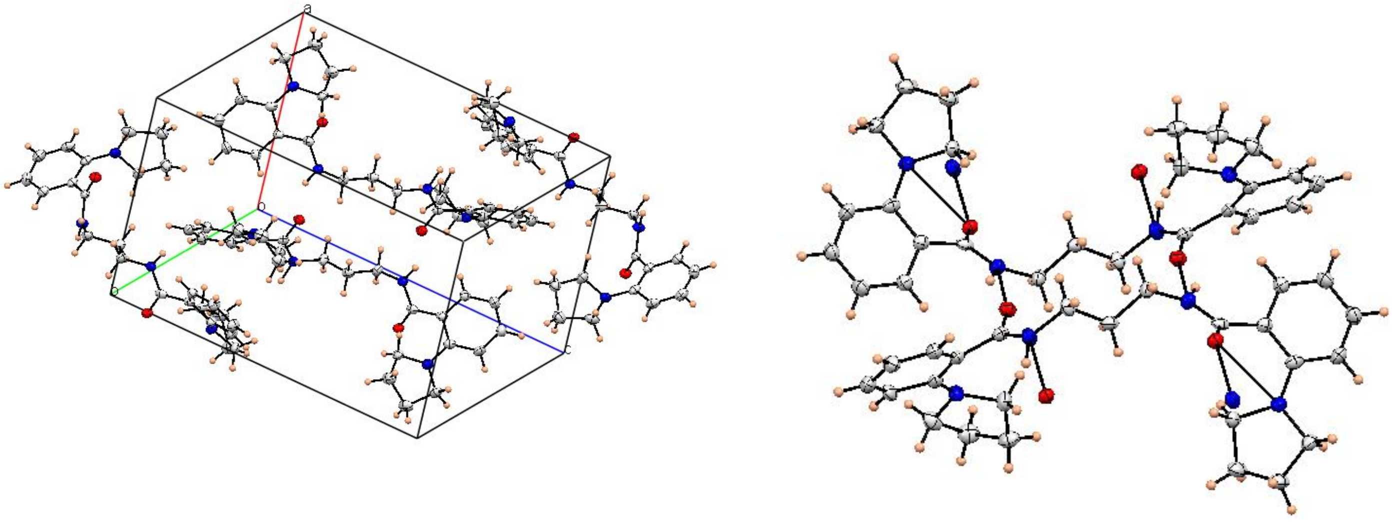


Figure 1: ORTEP structure of PPB with 50% ellipsoid probability level



A **B**

Figure 2: (A) Packing diagram of PPB; (B) H-Bonded dimeric structure

Table 1: Crystal data for PPB

Formula	$C_{24}H_{32}N_4O_2$
Formula weight	420.6
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	10.0035(12)
b (Å)	13.6893(17)
c (Å)	16.2941(22)
α (°)	90
β (°)	91.388(12)
γ (°)	90
Volume (Å^3)	2230.67(8)
Z	4
Density (gcm^{-3})	1.25
μ (mm^{-1})	0.081
F (000)	903.8
$h_{min, max}$	-11, 11
$k_{min, max}$	-16, 8
$l_{min, max}$	-13, 19
No. of measured reflections	8439
No. of unique reflections	3924
No. of reflections used Parareflnparameters	2240
$R_{\_all}$, $R_{\_obs}$	0.147, 0.095
wR_{2_all}, wR_{2_obs}	0.264, 0.235
$\Delta\rho_{min,max}$ (e Å^{-3})	-0.355,0.418
GOOF	1.089

Table 2: Selected bond lengths, bond angles and possible hydrogen bonds in PPB and their bond lengths

Bond lengths, (Å)		Bond angles, °			
O1 – C21	1.2347(5)	C1 – C24 – N4	116.72(3)	N3 – C21 – C11	123.23(4)
O2 – C24	1.2347(5)	C24 – N4 – C23	120.76(3)	N3 – C26 – C25	114.71(4)
N1 – C6	1.3687(5)	C1 – C6 – N1	123.23(4)	O1 – C21 – N3	122.51(3)
N1 – C7	1.4769(6)	C7 – N1 – C10	109.68(3)	O1 – C21 – C11	121.26(4)
N1 – C10	1.4609(6)	C6 – N1 – C7	119.83(3)	O2 – C24 – N4	122.08(3)
N2 – C16	1.3923(5)	C16 – N2 – C20	122.79(3)	O2 – C24 – C1	120.93(3)
N2 – C20	1.4632(6)	C16 – N2 – C17	119.96(3)		
N2 – C17	1.4571(6)	C17 – N2 – C20	110.44(3)		
N3 – C21	1.3338(5)	N2 – C16 – C11	120.61(4)		
N3 – C26	1.4393(5)	N2 – C16 – C15	120.61(5)		
N4 – C23	1.4622(6)	C26 – N3 – C21	121.58(3)		
N4 – C24	1.3258(5)	N3 – C21 – O1	122.51(3)		

D-H...A	D...H/Å	D...A/Å	H...A/Å	∠D-H...A	Symmetry
N3–H3N ···O2	0.967(.004)	2.779(.005)	1.893(.003)	151.04(0.23)	-x+1,-y+2,-z
N4–H4N ···O1	1.036(.004)	2.840(.005)	1.885(.003)	151.67(0.21)	-x,-y+2,-z

Characterization of Complexes

The complexes of PBAB and PPB with Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) are prepared by the method described and their characterization using physicochemical and spectral methods is presented in the following sections.

Elemental Analyses : The physicochemical and analytical data of all the metal(II) complexes with the ligands PBAB and PPB are given in table **3**. The experimentally determined contents of elements: C, H, N, Cl and metal are in agreement with the values calculated for the formulae $[MLCl_2].H_2O$ for M = Co(II), Ni(II) or Cu(II) and $[M(L)(OAc)_2]$ for Zn(II) or Cd(II) and L= PBAB or PPB. These formulae support the data acquired from thermal studies and molar conductivities of all complexes [20,21].

Conductivity Studies : The molar conductance values of all complexes were precise in dimethylformamide at 10^{-3} *M* concentration. The results are presented in table **1**. The molar conductance values are in the range of 8.96 to 11.21 ohm^{-1} cm^{2} mol^{-1} signifying that all the complexes are non-electrolytes [21]. The conductance values remained constant even after 48 hours substantiating that, there is no noticeable ionization and also strong interactions between the metal ions, ligands and the chloride or acetate ions. As a result, these complexes may be formulated as $[MLX_2].H_2O$, where M = Co(II), Ni(II) or Cu(II) X = Cl^- and for metal ions Zn(II) or Cd(II), X = CH_3COO^- and L = PBAB or PPB.

Mass spectral studies : The mass spectra of all complexes were recorded by using HRMS technique and reveals that the high mass peak can be assigned to $[(MLX_2).H_2O]^{\rceil+}$ in the case of Co(II), Ni(II) and Cu(II) complexes. Another heavier peak that verifies the coordination of the ligand to the metal ion is that of $ML^{\rceil+}$ fragment. Other fragment peaks appeared in the mass spectra of the complexes correspond to those of the ligands. Similarly, the mass spectra of Zn(II) and Cd(II) complexes of PBAB and PPB were recorded. The high mass peak in the spectra of these complexes is that of $[ML(OAc)_2]$ {L = PBAB or PPB, M= Zn(II), Cd(II)}. Other conspicuous peaks are those of the ligands. The results of the EI-mass spectra of complexes are in conformity with the proposed formula [22,23].

	Compound	m/z (calcd)	% Yield	Dc. Comp. °C	%C	%H	%N	%Cl	%M	μ_{eff} B.M.	$\Lambda_\circ$ ohm^{-1} cm^{2} mol^{-1}
1	$[Co(PBAB)Cl_2].H_2O$	460.2 (459.0)	70	336.81	44.29 (44.37)	4.78 (4.82)	12.09 (12.17)	15.33 (15.41)	12.74 (12.81)	4.81	10.15
2	$[Ni(PBAB)Cl_2].H_2O$	459.1 (458.0)	67	381.36	44.31 (44.39)	4.77 (4.82)	12.63 (12.76)	15.31 (15.41)	12.66 (12.76)	3.05	9.56
3	$[Cu(PBAB)Cl_2].H_2O$	463.9 (463.0)	78	349.25	43.88 (43.93)	4.70 (4.77)	11.96 (12.05)	15.16 (15.25)	13.59 (13.67)	1.90	10.25
4	$[Zn(PBAB)(OAc)_2]$	495.1 (494.1)	63	399.25	50.80 (50.87)	5.22 (5.29)	11.19 (11.30)	--	13.11 (13.19)	---	9.23
5	$[Cd(PBAB)(OAc)_2]$	545.0 (544.1)	58	458.79	46.39 (46.46)	4.76 (4.83)	10.25 (10.32)	--	20.58 (20.71)	--	9.99
6	$[Co(PPB)Cl_2].H_2O$	569.4 (568.4)	58	352.12	52.72 (52.83)	5.97 (6.03)	9.83 (9.86)	12.39 (12.47)	10.09 (10.37)	4.73	10.37
7	$[Ni(PPB)Cl_2].H_2O$	569.3 (568.2)	61	347.62	52.79 (52.85)	5.98 (6.03)	9.79 (9.86)	12.41 (12.48)	10.18 (10.33)	3.17	9.91
8	$[Cu(PPB)Cl_2].H_2O$	574.1 (573.0)	65	361.04	52.33 (52.40)	5.92 (5.98)	9.71 (9.78)	12.43 (12.48)	10.96 (11.09)	1.92	11.21
9	$[Zn(PPB)(OAc)_2]$	605.0 (604.0)	49	453.28	57.58 (57.66)	6.29 (6.34)	9.21 (9.28)	--	10.67 (10.83)	---	9.43
10	$[Cd(PPB)(OAc)_2]$	652.2 (651.0)	52	467.98	53.43 (53.50)	5.83 (5.88)	8.57 (8.61)	--	17.13 (17.27)	--	10.97

Table – 3 : Analytical and Physicochemical data of M(II) complexes

Thermo Gravimetric Analyses : The thermal decomposition characteristics of all the complexes with PBAB and PPB were studied to find out their relative thermal stability and decomposition features. The TGA data of all the complexes were obtained under N_2 atmosphere between 50 and 1000°C at a heating rate of 10°C min^{-1}and given in the table **4**.

The Co(II), Ni(II) and Cu(II) complexes of PBAB and PPB, undergo decomposition in two stages while the complexes of Zn(II) and Cd(II) undergo decomposition in a single stage. The observed TG curves reveal that Co(II), Ni(II) and Cu(II) complexes 1ose the water molecules between 80^o and 175^oC and the weight loss was found to be around 4% which is close to the calculated values in all the complexes. The weight loss in this temperature range indicates that the water molecule is outside the coordination sphere [24]. The TG curves of these complexes show a plateau from 240^o to 665^oC, and then the second stage decomposition starts between 220^o and 305^oC and ends around 800^oC. The experimental values coincide with the calculated values for the decomposed portion of the complex, i.e. one water molecule (wherever present) and the organic part (ligand) of the complex. The final part or residual mass left accounts for the anhydrous metal oxide, Co_3O_4, NiO, CuO [25] as the final products. In the case of the Zn(II) and Cd(II) complexes the decomposition takes place in only one step between 320^o and 900^oC and the residual mass left in the crucible is equivalent to that of ZnO or CdO [26,27].

Table – 4: Thermal data of M(II) complexes

S. No.	Complex	Thermal Process	Temperature Range, ^0C	Pyrolysis product, %	
				Found	Calcd
1	$[CoL_1Cl_2].H_2O$	$[CoL_1Cl_2].H_2O \rightarrow [CoL_1Cl_2]$ $[CoL_1Cl_2]\rightarrow[CoCl_2]\rightarrow[Co_3O_4]$	78.9-156.2 260.3-801.5	3.68 64.79	3.79 64.94
2	$[NiL_1Cl_2].H_2O$	$[NiL_1Cl_2].H_2O \rightarrow [NiL_1Cl_2]$ $[NiL_1Cl_2]\rightarrow [NiCl_2]\rightarrow[\ [NiO]$	75.8-156.7 226.4-835.5	3.86 82.99	3.92 83.58
3	$[CuL_1Cl_2].H_2O$	$[CuL_1Cl_2].H_2O\rightarrow [CuL_1Cl_2]$ $[CuL_1Cl_2]\rightarrow[CuCl_2]\rightarrow[\ [CuO]$	69.9-160.6 288.4-796.7	3.81 82.11	3.88 82.16
4	$[ZnL_1(OAc)_2$	$[ZnL_1(OAc)_2] \rightarrow [ZnO]$	338.9-901.6	83.50	83.56
5	$[CdL_1Cl_2]$	$[CdL_1(OAc)_2] \rightarrow [CdO]$	321.2-899.5	76.35	76.44
6	$[CoL_2Cl_2].H_2O$	$CoL_2Cl_2].H_2O \rightarrow [CoL_2Cl_2]$ $[CoL_2Cl_2]\rightarrow[CoCl_2]\rightarrow[Co_3O_4]$	92.4 – 173.6 305 – 866.8	3.13 69.12	3.18 69.84
7	$[NiL_2Cl_2].H_2O$	$[NiL_2Cl_2].H_2O \rightarrow [NiL_2Cl_2]$ $[NiL_2Cl_2]\rightarrow [NiCl_2]\rightarrow[\ [NiO]$	84.6 – 168.4 286.4 – 794.2	3.09 85.92	3.17 86.40
8	$[CuL_2Cl_2].H_2O$	$[CuL_2Cl_2].H_2O\rightarrow [CuL_2Cl_2]$ $[CuL_2Cl_2]\rightarrow[CuCl_2]\rightarrow[\ [CuO]$	74.6 – 154.8 272 – 865.8	3.04 85.03	3.15 85.64
9	$[ZnL_2(OAc)_2]$	$[ZnL_2(OAc)_2] \rightarrow [ZnO]$	356.2 – 882.4	85.92	86.50
10	$[CdL_2(OAc)_2]$	$[CdL_2(OAc)_2] \rightarrow [CdO]$	326.8 – 912.4	79.46	80.24

Infrared Spectral Studies : The bonding modes of the ligands were elucidated by comparing IR spectra of the ligands, PBAB or PPB, and their metal complexes. The IR spectral absorptions of M(II) complexes along with assignments are presented in Table **5**. The strong bands observed at 1627 and 3479 cm^{-1} in the spectrum of PBAB are attributed to the stretching vibrations of the amide –(N-$\underline{C=O}$) and amine (NH_2) groups respectively [28]. In the spectra of all the complexes the amide carbonyl group has exhibited a shift to high frequency side by 5–10 cm^{-1} indicating the non-coordination of carbonyl oxygen. While the amide –NH group and primary amine (–NH_2) group stretching frequencies shifted to low frequency side, table **3**. These low frequency shifts indicate coordination of amide and amine nitrogen atoms [29-31]. Similarly, in the case of complexes of PPB, the amide and tertiary amine bands have shifted to lower frequencies as compared to those in the free ligand.

The two new absorptions, one between 418 and 431 cm^{-1} and the other between 249 and 271 cm^{-1}, in the far-IR spectra of Co(II), Ni(II) and Cu(II) complexes are observed. These may be attributed to ν(M-N) [32] and ν(M-Cl) [33] respectively. But, in the case of the spectra of the complexes of Zn(II) and Cd(II) one absorption was same as found in the case of other metals while the other one is between 501 and 543 cm^{-1}. This absorption is due to ν(M-O) [32]. The assignment of this to the M–O group frequency is further supported by the presence of asymmetric and symmetric stretching frequencies around 1600 and 1300 cm^{-1} [34] in the complexes of Zn(II) and Cd(II). These absorptions in the infrared spectra of complexes indicating that Co(II), Ni(II) and Cu(II) ions are coordinated through the four nitrogen atoms of the ligands PBAB or PPB and to two chloride ions. While Zn(II) and Cd(II) ions coordinate to the ligands through four nitrogen atoms and the oxygen atom of the monodentate acetate ions. Further, the presence of two chlorides or acetate ions confirms that the ligands are neutral and the low molar conductivities of the complexes reveal that the anions chloride/acetate groups are in the coordination sphere.

Table – 5: Infrared spectral data (cm^{-1}) of M(II) complexes

S. No.	Complex	ν (*NH-CO*)	ν (Ar-NH$_2$)	ν(C=O) amide-I	ν(O-H)$_{br}$	ν(M-O)	ν(M-Cl)	ν(M-N)
1	PBAB							
2	[Co(PBAB)Cl$_2$].H$_2$O	3254	3456	1632	3500 - 3200	---	270	418
3	[Ni(PBAB)Cl$_2$].H$_2$O	3263	3449	1630	3500 - 3200	---	259	422
4	[Cu(PBAB)Cl$_2$].H$_2$O	3254	3460	1636	3500 - 3200	---	267	431
5	[Zn(PBAB)(OAc)$_2$]	3268	3455	1642	---	543	---	426
6	[Cd(PBAB)(OAc)$_2$]	3272	3462	1634	---	501	---	419
7	PPB	3380	3367	1629				
8	[Co(PPB)Cl$_2$].H$_2$O	3265	3405	1638	3500 - 3200	---	263	434
9	[Ni(PPB)Cl$_2$].H$_2$O	3269	3411	1629	3500 - 3200	----	276	428
10	[Cu(PPB)Cl$_2$].H$_2$O	3258	3429	1632	3500 - 3200	---	249	431
11	[Zn(PPB)(OAc)$_2$]	3266	3426	1636	---	532	--	429
12	[Cd(PPB)(OAc)$_2$]	3273	3416	1644	--	518	--	419

Magnetic moment : The magnetic moment values of Co(II), Ni(II) and Cu(II) complexes obtained at room temperature are presented in table **3**. The Co(II) complexes of ligands PBAB and PPB exhibit the magnetic moment values of 4.68 and 4.73 B.M respectively, which correspond to three unpaired electrons. These high spin values of Co(II) complexes confirm that they have octahedral geometry [35]. The magnetic moment values of the Ni(II) complexes are found to be 2.90 and 3.17 B.M. respectively. These values are in tune with a high spin configuration and indicate octahedral environment around the Ni(II) ion in the complexes [36]. The Cu(II) complexes of PBAB and PPB exhibit magnetic moment values of 1.89 and 1.92 B.M. respectively. These values indicate that there is one unpaired electron. The observed magnetic moment values are higher than the spin-only value of 1.73 B.M. for one unpaired electron. This reveals that these complexes are monomeric in nature and that there are no metal–metal interactions. The higher values confirm distorted octahedral geometry due to John-Teller distortions [35-37], with considerable orbital contribution.

Electronic spectral properties : The electronic spectra of Co(II), Ni(II) and Cu(II) complexes were recorded in DMF. The spectral absorptions are given in table **6**. The electronic spectra of Co(II) high-spin octahedral complexes exhibit two to three absorptions. The electronic spectra of Co(II) octahedral complexes are fairly complex and often pose problems in correct assignment due to the admixture of spin forbidden transitions to doublet states from ^{2}G and ^{2}H, spin-orbit coupling and vibrations of low symmetry components [38]. The electronic spectra of the Co(II) complexes with ligands PBAB and PPB, exhibit absorptions at 8792, 13586, 22342, 29069 and 8636, 14212, 24012, 30428 cm^{-1} respectively, characteristic for an octahedral geometry. The bands may be assigned to the transitions: $^4T_{2g}(F) \leftarrow {}^4T_{1g}(F)$ (ν_1); $^4A_{2g}$ (F) $\leftarrow$ $^4T_{1g}$ (F) (ν_2); $^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$ (ν_3) respectively. The fourth high frequency absorption may be ascribed to the charge transfer transition [39]. The absorption spectra of the Ni(II) complexes of the ligands PBAB and PPB display three absorption bands at 9178, 14662, 22342 and 8932, 14686, 23582 cm^{-1} respectively. An examination of these bands indicates that the complexes have an octahedral geometry and might possess O_h or D_{4h} symmetry. The ground state of Ni(II) in octahedral environment is $^3A_{2g}$. Thus, the observed bands may be assigned to the three spin allowed transitions $^3T_{2g}(F) \leftarrow {}^3A_{2g}(F)$ (ν_1); $^3T_{1g}(F) \leftarrow {}^3A_{2g}(F)$ (ν_2) and $^3T_{1g}(P) \leftarrow {}^3A_{2g}(F)$ (ν_3) respectively [35]. The ligand field parameters like B and □ are evaluated for the Co(II) and Ni(II) complexes and are presented in table **6**. These values indicate that the metal-ligand bond is essentially covalent. Electronic spectra of six-coordinate Cu(II) complexes have either D_{4h} or C_{4v} symmetry, and the e_g and t_{2g} levels of the ^{2}D free ion term will further split into $^2B_{1g}$, $^2A_{1g}$ and $^2B_{2g}$, ^2E_g levels respectively. Thus the three spin allowed transitions are predictable in the visible and near IR region. But only a very few complexes are known in which such bands are resolved either by Gaussian Analysis or single crystal polarization studies. The electronic spectra of the complexes [Cu(PBAB)Cl_2] and [Cu(PPB)Cl_2] display two absorptions at 16694, 20202 and 16486, 21126 cm^{-1} respectively. The low energy absorption is assigned to $^2B_{1g} \rightarrow {}^2A_{1g}$ [38] and the higher energy absorption is assigned to the charge transfer transition. The broad absorption in *d-d* transition region of d^9 system of [Cu(II)] advises a distorted octahedral geometry for the complexes studied and sustains the conclusion from the magnetic moment data.

Table – 6: Electronic spectral absorptions of M(II) complexes

S. No.	Complex	λ_{max}, cm^{-1}	ν_2/ν_1	ν_3/ν_1	B (cm^{-1})	β	μ_{Cal}
1	[Co(PBAB)Cl_2].H_2O	8792, 13586, 22342,	1.55	2.54	636.8	0.65	
2	[Ni(PBAB)Cl_2].H_2O	9178, 14662, 24569	1.59	2.68	779.8	0.75	3.22
3	[Cu(PBAB)Cl_2].H_2O	16694, 20202	--	--	--	--	
4	[Co(PPB)Cl_2].H_2O	8636, 14212, 24012	1.65	2.69	821.1	0.85	
5	[Ni(PPB)Cl_2].H_2O	8932, 14686, 23582	1.64	2.64	764.8	0.73	3.23
6	[Cu(PPB)Cl_2].H_2O	16486, 21126	--	--	--	--	

ESR Spectral Studies of Cu(II) complexes : The EPR spectra of the complexes were recorded as polycrystalline samples in DMF solution, both at room temperature and at liquid nitrogen temperature. Spectra of the complexes in solution exhibit absorptions typical for the mononuclear species with axial symmetry. The EPR spectra of the polycrystalline sample and in DMF solution have comparable features. This hyperfine interaction observed for all the complexes is attributable to interaction with the four nitrogen nuclei adjacent to the copper ion.

The $g_{||}$ and $g_{\perp}$ values were computed from the spectrum using DPPH free radical as 'g' marker and are given in table **7** along with spin Hamiltonian parameters and calculated and observed magnetic moment values. Kivelson and Neiman have attributed the $g_{||}$ value <2.3 for covalent character of the metal–ligand bond and >2.3 for ionic character. Applying this criterion the nature of the metal–ligand bond in the complexes under study has been predicted to be covalent. The trend $g_{||} > g_{\perp} > g_e$ (g_e = 2.0023) observed for these complexes shows that the unpaired electron is localized in d_{x2-y2} orbital of the Cu(II) ions and the spectral features are characteristics of axial symmetry. The complexes under study have six coordinated tetragonal geometry [40,41].

Table – 7: ESR parameters of Cu^{II} complexes

Complex	$g_{\|\|}$	$g_{\perp}$	g_{ave}	G	μ_{cal}	μ_{expt}
$[Cu(PBAB)Cl_2].H_2O$	2.21	2.08	2.12	2.60	1.84	1.90
$[Cu(PPB)Cl_2].H_2O$	2.23	2.091	2.14	2.53	1.85	1.92

The $g_{||}$ and $g_{\perp}$ values calculated using the spectra are used to evaluate g_{ave} values using the equation: $g_{ave} = 1/3(g_{||} + 2g_{\perp})$. The electronic spectral absorptions and the ESR spectral data have been used to calculate the spin-orbit coupling constant of Cu(II) in the complexes. The magnetic moment values of Cu(II) complexes have been evaluated using the equation: $\mu = 0.866 \times g_{ave}$. From the *g*-values presented in the table **7**, it may be proposed that the Cu(II) ions are in crystallographically equivalent sites and there are covalent interactions between Cu(II) and the ligands PBAB and PPB [42].

^{1}H-NMR Studies: The ^{1}H-NMR spectra of diamagnetic Zn(II) and Cd(II) complexes were recorded in DMSO-d_6 at room temperature. The characteristic signals are presented in table **8**. The amine ($-N\underline{H_2}$) protons resonance signal observed at 2.90 ppm in the spectrum of ligand PBAB is found to have shifted to down field side by 0.25 - 0.32 ppm, and indicate that the nitrogen atoms are coordinated to the metal ions [43]. The aromatic protons, the methylene and methyl protons ($-H_2C-CH_2-$ and $-N-CH_3$) resonance signals are shifted very small towards downfield side in the ^{1}H-NMR spectra of complexes as compared to those in the spectra of ligands. The spectra of Zn(II) complexes exhibit one new signal observed at 2.26 ppm, that is attributable to the methyl protons of the coordinated acetate ion [22].

The amide ($-C=O-N\underline{H}$) protons of Zn(II) complex of ligand PPB, resonance signal observed at 8.26 ppm in the spectrum of ligand is found to have shifted to down field side by 0.37 ppm [22]. The pyrrolidine ring, CH_2 group protons resonance signals observed at 3.19 – 3.13 ppm in the spectrum of the ligand is found to have shifted to down field side by 0.1- 0.15 ppm, indicating the coordination of pyrrolidine nitrogen atom.

^{13}C-NMR Studies : The ^{13}C NMR spectra of Zn(II) and Cd(II) complexes are recorded in d_6-DMSO. The carbons atoms bonded to amide-N atom, ($H_2\underline{C}-N-\underline{C}=O$), show resonance signals at 45.32 and 175.82 ppm in the spectrum of the ligand PBAB. These signals are found to have altered to down field side by 1.42 and 2.1 ppm, indicating that amide group nitrogen atoms are coordinated to the metal ions [43]. The aromatic and aliphatic carbon atoms' resonance signals have exhibited very small shifts towards downfield side in the ^{13}C-NMR spectra of the complexes as compared to those in the spectra of the ligand. The spectra of metal complexes exhibit two new signals one at 183.48 ppm, and another at 23.27 ppm which are characteristic of the coordinated acetate ion.

The amide (–$\underline{C}$=O-NH) and N-$\underline{C}H_2$ carbons of Zn(II) complex of ligand PPB, resonance signal observed at 171.23 and 50.72 ppm in the spectrum of ligand are found to have shifted down field side by 2.3 and 1.31 ppm respectively. The pyrrolidine ring, CH_2 group resonance signals observed at 37.92 and 29.56 ppm in the spectrum of the ligand are found to be shifted down field side by 0.51 and 0.25 ppm. The new signals observed at 184.74 and 23.30 ppm that are characteristic of the coordinated acetate ion.

Based on the data obtained from physicochemical and spectral studies of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes, the tentative structures proposed are presented in figure **4**.

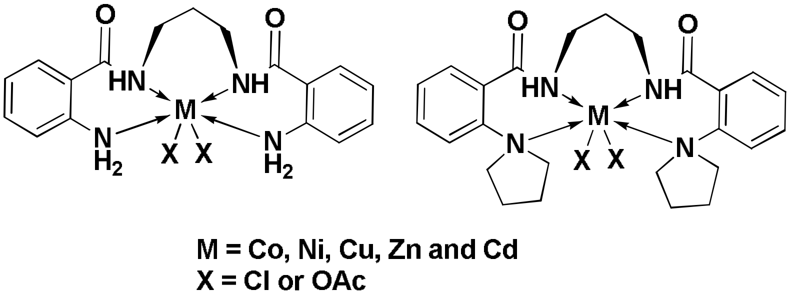


Figure 4: Tentative structures of the prepared metal complexes

APPLICATIONS

The coordinated ligands modify the properties of the metal ions and the same has been exploited in tuning the catalytic properties of different metal complexes. The application of Co(II), Ni(II) and Cu(II) complexes of PBAB and PPB in the above synthetic reactions have been studied. Not much interesting results were obtained. The work on application of the complexes in other reactions is being carried out and the results will be published seperately.

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