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Synthesis and Characterization of N-(Pyrrolidinobenzyl)-benzamide and its Complexes with Cobalt(II), Nickel(II), Copper(II) and Zinc(II)

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A new Mannich base, N-(pyrrolidinobenzyl)benzamide, derived from pryrrolidine, benzamide and benzaldehyde and its complexes with cobalt(II), nickel(II), copper(II) and zinc(II) have been synthesized and characterized. Their chemical composition have been established from microanalytical, magnetic, molar conductance, spectral, thermal and X-ray powder diffraction studies. In these complexes, N-(pyrrolidinobenzyl)benzamide acts as a bidentate ligand and all the complexes exhibit square planar geometry. The monomeric and non-electrolytic nature of the complexes are evidenced by their conductance and magnetic susceptibility data. The antimicrobial activity of the ligand and the complexes are also studied. The complexes have higher activity than that of the ligand.

Key Words: Synthesis, N-(Pyrrolidinobenzyl)benzamide, Co(II), Ni(II), Cu(II), Zn(II), Complexes.

INTRODUCTION

Literature survey shows that the compounds containing amide moiety have a strong ability to form metal complexes and show a wide range of biological activities[1-5]. An amide group has two potential binding sites, *i.e.*, oxygen and nitrogen for complexation. It is a generally accepted fact that for neutral amide groups both protonation and metal ion binding will be at the amide oxygen[6]. On deprotonation the binding shifts to the amide nitrogen[7]. But, the coordination may also take place at amide nitrogen due to factors such as steric hindrance. The present communication reports the synthesis of the mannich base, N-(pyrrolidinobenzyl)benzamide (PBB) which also contains an amide moiety. The synthesis of PBB, its complexation characteristics with cobalt(II), nickel(II), copper(II) and zinc(II) salts and the antibacterial activity of the ligand and the complexes are described in this work. The structure of the ligand may be represented as in Fig. 1.

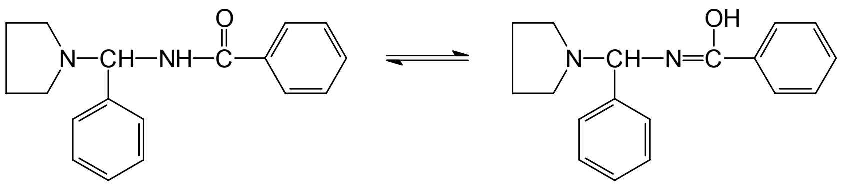


Fig. 1

EXPERIMENTAL

All the chemicals used were of AnalaR or G.R (Merck) grade. Organic solvents were purified by standard methods.

Synthesis of Mannich base, PBB: Benzamide (1.21 g, 10 mmol) in 20 mL of ethanol was mixed with pyrrolidine (0.7 ml, 10 mmol) with stirring to get a clear solution at 100 ºC. To this solution, benzaldehyde (1 mL, 10 mmol) was added in drops with stirring for about 10-15 min. The reaction mixture is kept at room temperature for 2 d. The colourless crystals were filtered and recrystallized from ethanol (yield 69.5 %; m.p. 89 ºC).

Synthesis of metal complexes: A solution of 5 m mol of MCl_2 [M = Co(II), Ni(II), Cu(II) and Zn(II)] and the Mannich base (10 m mol, 2.8 g) in 50 mL of ethanol and chloroform mixture (1:6, v/v) was boiled under reflux at 58 ºC (b.p. of azeotropic mixture) for about 4 h. The resulting solution was concentrated and then cooled. The precipitated complexes were filtered, washed with ethanol and dried *in vacuo*.

The carbon, hydrogen and nitrogen contents in each complex were determined by micro analytical method at RRL, pappanamcode, Trivandrum. The metal contents of the complexes were determined by quantitative methods[8]. The molar conductances of the complexes in ethanol were mesured at room temperature (about 30 ºC) using an Elico conductivity bridge type CM82T with a dip type conductivity cell having platinum electrodes (cell constant = 0.94 cm^{-1}). 10^{-3} M solutions were used for conductivity measurements. The magnetic moments of the complexes were determined at room temperature using EG and G PARC Model 155 vibrating sample magnetometer at RSIC, IIT, Madras. IR spectra of the ligand and the complexes were recorded in KBr pellets using a Bruker IFS 66 V FT-IR spectrophotometer at RSIC, IIT, Madras. The X-ray powder pattern of the complexes were recorded on a Rigaku (Japan) PW 1710 X-ray powder diffractometer on chart recorder at RRL, Trivandrum. The mass spectra were recorded on a finnigan mat 8230 mass spectrometer at RSIC, IIT, Madras. The UV-visible spectra of the complexes were recorded on a Varian Cary 2390 UV-Vis-NIR spectrophotometer at RSIC, Chennai, India. The X band ESR spectrum of the copper (II) complex was recorded by using a Varian E-112 esr spectrometer RSIC, Madras. The antimicrobial studies of the complexes at various concentrations were also done using four different bacteria, *viz.*, *Staphylococcus aureus, Klebsiella pneumoniae, Escherichia coli* and *Pseudomonas aerugionosa* by Well diffusion method[9] using agar nutrient as the medium at Sree Chithra Tirunal Institute for Medical Sciences and Technology, Trivandrum.

RESULTS AND DISCUSSION

The analytical results indicate a 1:2 (M:L) stoichiometry for all the complexes (Table-1). All the complexes are coloured except the Zn(II) complex and stable at room temperature. The complexes are soluble in DMSO, nitrobenzene and DMF. The molar conductance values of the complexes show them to be non-electrolytes[10]. The magnetic susceptibility values of the complexes at room temperature show that they are mononuclear.

TABLE-1
ANALYTICAL DATA OF THE COMPLEXES

Compd./ (colour)	Elemental Analysis Calcd. (Found) %					λ_M (mho cm^2 mol^{-1})	μ_{eff} (BM)
	M	C	H	N	m.w.		
$C_{18}H_{20}N_2O$	–	77.30	6.89	9.88	280	–	–
Colourless		(77.14)	(7.14)	(10.00)			
$C_{36}H_{38}N_4O_2Cu$	9.68	69.78	6.26	8.89	634.26	16.2	1.78
Green	(9.71)	(69.50)	(6.11)	(9.00)	(621.54)		
$C_{36}H_{38}N_4O_2Zn$	9.88	68.71	5.89	8.73	636.10	12.1	–
Colourless	(9.96)	(69.30)	(6.09)	(8.98)	(623.35)		
$C_{36}H_{38}N_4O_2Co$	9.61	69.81	6.37	9.18	638.60	13.2	3.28
Pink	(9.55)	(70.02)	(6.16)	(9.07)	(616.93)		
$C_{36}H_{38}N_4O_2Ni$	9.10	69.72	6.38	9.12	629.40	7.6	–
Green	(9.03)	(70.05)	(6.15)	(9.08)	(616.69)		

The mass spectra of the ligand and its cobalt complex were recorded. The base peak observed at m/z 122 shows the presence of benzamide moiety. The molecular ion peak for the ligand is observed at m/z = 280 ($C_{18}H_{20}N_2O$). Other important peaks at m/z 120 and 105 correspond to the presence of C_6H_5–CONH and C_6H_5–CO, respectively. The molecular ion peak for the cobalt complex is observed at m/z = 617 ($C_{36}H_{38}N_4O_2Co$) and the other peaks at m/z 407, 484 and 540 correspond to the release of $C_6H_5CONHCHC_6H_5$, $C_6H_5CONHCH$ and C_6H_5, respectively. The data indicates the stoichiometry of the metal complexes being ML_2 type.

In the infrared spectrum of N-(pyrrolidinobenzyl)benzamide, the ν(NH) modes appear at 3460 (asymmetric) and 3360 cm^{-1} (symmetric). The carbonyl and C–N–C stretching frequencies of PBB appear at 1650 and 1160 cm^{-1}, respectively. The ν(NH) bands appearing at 3460 and 3360 cm^{-1} remain unaltered in the spectra of the complexes showing the non-participation of nitrogen of NH_2 in coordination. The band at 1160 cm^{-1} in the ligand[11], which is due to C–N–C stretching frequency shifts to 1140-1135 cm^{-1}, in the spectra of the complexes. This indicates the coordination through the tertiary nitrogen of pyrrolidine ring. The spectra of the complexes show negative shifts of the carbonyl band at 1650 to 1630-1620 cm^{-1} showing the coordination through the carbonyl oxygen. The additional bands in the region 430-410 and 530-510 cm^{-1} are assigned to ν(M–O) and ν(M–N), respectively.

The electronic spectra of the ligand and the Ni(II), Co(II) and Cu(II) complexes were recorded in DMSO solution. The green coloured Ni(II) complex showed a band at 16235 cm^{-1} which is assigned to $^1A_{1g} \rightarrow {}^1B_{1g}$ transition indicating square planar geometry for the complex[12,13]. Pink coloured Co(II) complex exhibited a band at 19286 cm^{-1} which is assigned to $^1A_{1g} \rightarrow {}^1B_{1g}$ indicating square planar structure of the complex. The green coloured Cu(II) complex showed a band at 17080 cm^{-1} which is assigned to $^2B_{1g} \rightarrow {}^2A_g$ transition indicating square planar geometry for the complex. These facts are supported by the magnetic measurements. The magnetic moments of Co(II) [3.28 BM] and Cu(II) [1.78 BM] complexes confirm the square planar structure of them. The Ni(II) complex is diamagnetic in nature showing its square planar configuration.

The X-band ESR spectrum of Cu(II) complex with PBB gave $g_{\parallel}$ and g values 2.3034 and 2.146, respectively. The trend $g_{\parallel} > g_{\perp} > g_e$ (free ion value) shows that the unpaired electron is localized in the $d_{x^2-y^2}$ orbital of the Cu(II) ion and the spectrum is of axial symmetry[14]. The X-ray powder patterns were recorded for the Cu(II) and Ni(II) complexes. The diffraction patterns were indexed by the method developed by Hesse[15] and Lipson and Steeple[16]. Both the complexes were found to be rhombic. The cell parameters have been calculated by using the equation, $\sin^2\theta(hkl) = Ah^2 + Bk^2 + Cl^2$ where, $A = \frac{\lambda^2}{4a^2}$, $B = \frac{\lambda^2}{4b^2}$ and $C = \frac{\lambda^2}{4c^2}$. For Cu(II) complex, the lattice constants are: A = 0.0023, B = 0.0041 and C = 0.0071 and the unit cell dimensions are: a = 18.6653, b = 13.9789 and c = 10.4765Å. The cell volume is 2.733×10^{-21} c.c. and density is 0.7719. These gave n = 2.043 ≈ 2. Thus, the number of molecules per unit cell is two. For the Ni(II) complex, the lattice constants are: A = 0.0023, B = 0.0044 and C = 0.0073 with the edge lengths a = 18.6642 Å, b = 13.4939 Å and c = 10.4753 Å, respectively. The cell volume is 2.638×10^{-21} c.c. and the density of the complex is 0.7798. This gave n = 2.008 ≈ 2. Thus, the number of molecules per unit cell of the complex is two.

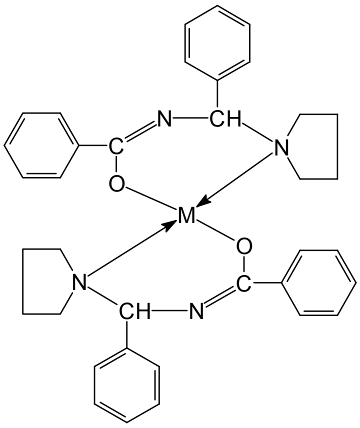
All the metal complexes were tested for their antibacterial activity against four bacteria: *Staphylococcous aureus, Klebsiella pneumoniae, Pseudomonas aeurginosa* and *Escherichia coli* by the well diffusion method. The zone of inhibition values of the compounds against the growth of microorganisms were summarized in Table-2. It was observed that the metal chelates show higher activity than that of the free ligand and control (ampicillin). The order of activity towards these bacteria was found to be

Cu > Co > Zn > Ni. The increase in antimicrobial activity is due to faster diffusion of metal complexes through the cell membrane or because of the combined effect of the activities of the metal and ligand.

TABLE-2
ANTIBACTERIAL ACTIVITY OF THE LIGAND AND THEIR COMPLEXES
(Zone of inhibition in mm)

Compd.	*S. aureus*	*E. coli*	*P. aeruginosa*	*K. pneumoniae*
Ampicillin	10	12	15	12
PBB	8	9	7	6
$Cu(PBB)_2$	18	20	22	16
$Co(PBB)_2$	15	17	16	14
$Zn(PBB)_2$	13	15	14	13
$Ni(PBB)_2$	12	13	10	12

On the basis of the above studies, the structures of the present complexes may be represented as in Fig. 2



M = Co, Cu, Ni or Zn

Fig. 2

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