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Synthesis, Characterization and Antimicrobial Activity of Cu(II), Co(II), Ni(II) and Zn(II) Complexes Derived from a New Mannich Base, N-(1-Morpholinobenzyl)benzamide and 1,2-Diaminobenzene

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This paper describes the synthesis of a new type of Mannich base, N-(1-morpholinobenzyl)benzamide (MBB), 1,2-diaminobenzene and its complexation behaviour with Cu(II), Co(II), Ni(II) and Zn(II) ions. The structural features of the complexes are characterized by microanalytical data, IR, UV-Vis, NMR and EPR technique. The electrolytic behaviour of the chelates was assessed from their molar conductance data. The monomeric nature of the chelates was confirmed from their magnetic susceptibility values. The X-band EPR spectra of the copper complex in DMSO at 300 and 77 K were recorded and their salient features are reported. The antimicrobial activity of the ligand and its complexes has been extensively studied on microorganisms such as *Staphylococcus aureus, Bacillus subtilis, Escherichia coli* and *Pseudomonas aeruginosa* and the fungi *Aspergillus niger* and *Rhizoctonia bataicola* by well-diffusion technique using DMF as solvent. The values of zone of inhibition were found out at 37 ºC for a period of 24 h. It has been found that all the complexes have higher activity than the free ligand and the standard.

Key Words: Mannich base, N-(1-Morpholinobenzyl)-benzamide, 1,2-Diaminobenzene, Antimicrobial activity.

INTRODUCTION

Organic chelating ligand containing amide moiety as a functional group have a strong ability to form metal complexes and exhibit a wide range of biological activities. Literature survey reveals that during the past decades, there has been a great deal of interest in the synthesis and structural elucidation of transition metal complexs containing amide moiety. A number of studies have been done on the Mannich base complexes formed by the condensation of morpholine with different aldehydes[1,2]. Similarly, a few works have been carried out on the Mannich base complexes formed by the condensation of benzamide with different amines[3,4]. Studies on metal

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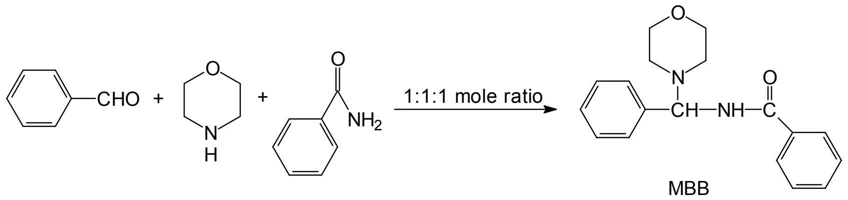
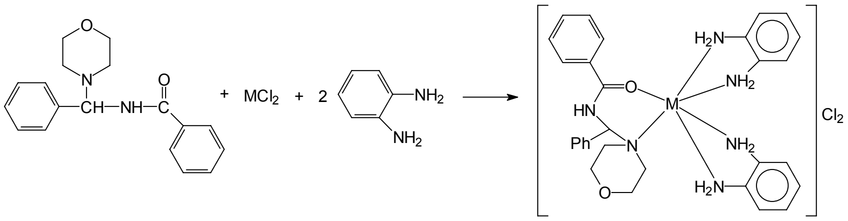
complexes of the benzaldehyde based Mannich base have been reported in literature[5-12]. However, there is no report on any metal complexes of N-(1-morpholinobenzyl)benzamide and 1,2-diaminobenzene. As a part of our continuing efforts to investigate the transition metal(II) complexes using Mannich bases, this paper describes the synthesis and characterization of Cu(II), Co(II), Ni(II) and Zn(II) complexes from the Mannich base, N-(1-morpholinobenzyl)benzamide and 1,2-diaminobenzene. The ligand coordinates with the metal ion in a bidentate manner through the oxygen atom of the carbonyl group and nitrogen atom of morpholine ring.

EXPERIMENTAL

Preparation of N-(1-morpholinobenzyl)benzamide: In the preparation of N-(1-morpholinobenzyl)benzamide (MBB) ligand, benzamide (12.1 g, 0.1 mol), morpholine (10 mL, 0.1 mol) and benzaldehyde (10 mL, 0.1 mol) were taken in 1:1:1 mole ratio in ice-cold condition. Benzamide was then added in drop wise and stirred in ice-bath. The resulting reaction mixture was kept at room temperature for *ca.* 5 d. The solid product formed was filtered, washed with water to remove the unreacted benzamide and morpholine followed by CCl_4 to remove any unreacted benzaldehyde. The ligand was then dried and recrystallized in methanol, yield *ca.* 64 %.



Synthesis of complexes: An ethanolic solution of N-(1-morpholinobenzyl)benzamide (5 mM), 1,2-diaminobenzene (5 mM) were mixed with corresponding chlorides (5 mM) in ethanol (20 mL) solution keeping ligand: 1,2-diaminobenzene:metal salt in 1:1:1 ratio. The reaction mixture was then warmed for 1 h on water bath till the complex precipitated out. The solid complex obtained was removed by filteration, successively washed with water, dried at room temperature and recrystallized from ethanol and dried *in vacuo*.



RESULTS AND DISCUSSION

The analytical data of the complexes correspond well with the formation of 1:1 (metal:ligand) complex (Table-1). Molar conductance values of the complexes in DMSO lie in the range 238 to 357 mho cm^2 mol^{-1} which is quite high for an electrolyte and reveal their electrolytic nature. The magnetic susceptibility measurement values show that octahedral geometry for copper, nickel and cobalt complexes.

TABLE-1
PHYSICAL CHARACTERIZATION, ANALYTICAL, MOLAR CONDUCTANCE, MAGNETIC SUSCEPTIBILITY DATA

Complex	Found/ (Calcd.) %					m.w.	Yield (%)	λ_m mho cm^2 mol^{-1}	μ_{eff} BM
	M	C	H	N	Cl				
MBB	–	(72.70)	(7.12)	(9.42)	–	297.38	63.9	–	–
Cu(II)		54.71	5.18	12.09	–	647.08	63.4	238	1.9
	(9.82)	(55.68)	(5.61)	(12.98)	(10.96)				
Co(II)		54.97	5.21	12.76	–	642.47	62.3	337	3.9
	(9.17)	(56.09)	(5.65)	(13.08)	(11.04)				
Ni(II)		55.12	5.11	12.26	–	642.23	60.7	353	2.8
	(9.14)	(56.10)	(5.65)	(13.08)	(11.04)				
Zn(II)		54.30	5.01	12.19	–	648.90	57.0	292	–
	(10.08)	(55.50)	(5.59)	(12.95)	(10.93)				

Infrared spectrum of the ligand, N-(1-morpholinobenzyl)benzamide and its metal complexes were recorded in KBr medium. IR spectrum of the ligand shows bands at 3367, 1636 and 1140 cm^{-1} is due to amide NH_2, amide C=O and C–N–C of morpholine group, respectivey. Up on complexation with metal salts, the amide C=O and C–N–C of morpholine bands are shifted to lower frequencie *viz.*, 1627-1604 and 1114-1101 cm^{-1}, respectively. The lowering in frequencies observed in all the complexes shows the involvement of carbonyl oxygen and tertiary morpholine nitrogen atom in coordination to the metal ion. Several evidences on the coordination of substituted benzamide through carbonyl oxygen have been reported[13,14]. Further, the IR spectra of the metal complexes show the band attributed to NH_2 of the coordinated amino groups are shifted to lower frequencies >50 cm^{-1} than in the spectrum of 1,2-diaminobenzene wherein the nitrogen coordination is observed by tracing a medium intensity band around 1524-1523 cm^{-1}. These results are comparable to the data reported elsewhere[14].

The electronic absorption spectrum of Cu(II) complex of MBB shows a broad band at 16638 cm^{-1} assignable to $^2E_g \rightarrow {}^2T_{2g}$, transition, suggests an octahedral geometry[15] for the complex. The magnetic movement value of Cu(II) complex is 1.9 BM which suggests a distorted octahedral geometry[16,17] around the metal ion. The Co(II) complex of MBB exhibits a band with maxima at *ca.* 18657 cm^{-1} which is assigned to $^4A_2 \rightarrow {}^4T_1(P)$ for octahedral geometry[18] for the complex and the magnetic movement values fall in 3.9 BM, which conforms the octahedral arrangement of cobalt complex. The Ni(II) complex of MBB showed band at *ca.* 22883 cm^{-1} which is assigned as $^1A_{1g} \rightarrow {}^1A_{2g}$ transition confirming a octahedral geometry for the complex. This is further supported by its magnetic movement value, which is 2.8 BM[19,20]. The absence of any band below 10000 cm^{-1} eliminates the possibility of a tetrahedral environment in this complex. The electronic spectrum of the Zn(II) complex shows an absorption band at 23364 cm^{-1} attributed to the LMCT transition, which is compatible with the complex having an octahedral structure[21,22].

The ^{1}H NMR spectra of the ligand and its zinc complex were recorded in DMSO-d_6 solution. The ligand shows a multiplet between 7.2-7.7 δ, which is due to aromatic protons. The N–H proton chemical shift occurs at 5.5 δ which gives rise to a weak doublet. The morpholine ring proton signals occur at 2.5 δ due to morpholine N–CH_2 and 3.6 δ due to morpholine O–CH_2, respectively. In Zn(II) complex, the doublet of N–H proton shifted slightly downfield to which reveals the coordination of carbonyl oxygen to Zn(II) ion. Due to the coordination of carbonyl oxygen, the electron pair on amide nitrogen drifts towards C=O group and consequently the N–H protons of the amide group will be less shielded. Hence, the N–H proton signal appears at slightly downfield in the complex compared to that of free ligand. In addition, the signal due to morpholine N–CH_2 protons also shifted slightly downfield and appeared at 2.7 δ in the complex. This is an indication of the coordination of morpholine nitrogen to the metal ion. Other proton signals in the complex do not differ much from those of the ligand. A broad absorption around 6.2 δ is due to the NH_2 proton of 1,2-diaminobenzene which is slightly shifted to downfield at 6.4 δ in Zn(II) complex. This is an indication of coordination of nitrogen of 1,2-diaminobenzene to the metal. Thus, ^{1}H NMR and IR results confirm the bidentate nature of MBB ligand.

The X-band EPR spectra of the Cu(II) complex, recorded in DMSO both at liquid nitrogen temperature (77 K) and room temperature (300 K). The copper complex exhibited the $g_{\parallel}$ value of 2.36 and $g_{\perp}$ value of 2.06. The observed order ($g_{\parallel}$ =2.36 > $g_{\perp}$ = 2.06) indicates that the complex is akin to axially elongated octahedral geometry. Further, it is also supported from the fact that the unpaired electron lies predominantly in the $d_{x^2-y^2}$ orbital[23-25].

Antimicrobial study: Antibacterial activity of the ligand MBB and its complexes have been carried out against the gram positive bacteria like *S. aureus, B. subtilis* and gram negative bacteria such as *E. coli, P. auroginosa* using Mueller Hinton agar by well-diffusion method using

DMSO as solvent (Table-2). Ampicillin was used as the standard for comparing the results. The zone of inhibition values was determined at the end of an incubation period of 24 h at 37 ºC. It has been observed from the results that the metal complexes have a higher activity than that of the free ligand and the standard. The increase in antibacterial activity is due to faster diffusion of metal complexes as a whole through the cell membrane or due to the combined activity effect of the metal and ligand. Such increased activity of the metal chelates can be explained on the basis of Overtone's concept and Tweedy's chelation theory. According to Overtone's concept of cell permeability the lipid membrane that surrounds the cell favours the passage of only lipid soluble materials due to which liposolubility has imortant factor which controls the antimicrobial activity. On chelation, the polarity of the metal ion will be reduced to a greater extent due to the overlap of the ligand orbital partial sharing of positive charge of metal ion with donor groups. Further, it increases the delocalization of π-electrons over the whole chelate ring and enhances the lipophilicity of the complex. This increased lipophilicity leads to break-down of the permeability barrier of the cell and thus retards the normal cell processes.

TABLE-2
ANTIBACTERIAL ACTIVITIES OF METAL(II) COMPLEXES

Complex	*S. aureus* (mm)	*E. coli* (mm)	*P. auroginosa* (mm)	*B. subtilis* (mm)
Ampicillin	11	11	11	10
MBB	11	11	12	10
Cu(II)	15	15	14	16
Co(II)	15	14	13	13
Ni(II)	17	19	15	16
Zn(II)	19	20	20	24

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