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Der Chemica Sinica, 2012, 3(4):864-867

Pelagia Research Library
ISSN: 0976-8505
CODEN (USA) CSHIA5

Synthesis, characterization and antimicrobial studies of mannich base derived from benzohydrazide and its metal complexes

A. Abdul Jameel[a], M. Palanisamy[b*] and M. Syed Ali Padusha[a]

[a]*Department of Chemistry, Jamal Mohamed College, Tiruchirappalli-620 020,India*
[b]*Department of Chemistry, Poompuhar college, Melaiyur-609107, India*

ABSTRACT

The present study deals with the synthesis, characterization and antimicrobial properties of Mannich base and its metal [Co(II), Cu(II), Mn(II)] complexes. Analytical methods such as TLC, solubility test, melting point and spectral studies [UV, ^{1}H NMR, and ^{13}C NMR] were employed for the characterization. Both the ligand and its metal complexes were tested against some microorganisms for their antimicrobial activity.

Key words : Metal complexes, Mannich base of benzohydrazide, Antimicrobial study, Spectral studies.

INTRODUCTION

Studies on the chemistry of Mannich bases are of interest in various areas of application. Many researchers have studied the numerous applications of Mannich reactions [1]. The great interest in the chemistry of Mannich bases has been essentially inspired by two factors: The Mannich synthesis introduces a basic function which can render the molecule soluble in aqueous solvents when it is transformed into the aminium salt. Mannich bases are very reactive; infact, they can easily be transformed into numerous other compounds. Mannich reaction consists of the condensation of substrate possessing atleast one active hydrogen with an aldehyde/ketone and a primary/secondary amine. Many research articles are available in the literature for the synthesis of Mannich bases using formaldehyde, benzaldehyde and substituted benzaldehydes [2]. Hetero aldehydes have also been used in the Mannich base synthesis. A few reports are available on the mannich base synthesis using furan-2-carboxaldehyde [3]. Among the amines, diethyl amine, dimethyl amine, piperidine etc. have been employed extensively. A remarkable number of other amines such as morpholine, N-Methyl piperazine have also been employed [4]. In the recent years amides and hydrazine have been taken as a substrate for the Mannich base synthesis. Among the amides used acetamide, urea, thiourea are noteworthy [5]. Besides semi- and thiosemicarbazide have also been employed [6].

A probe into the literature reveals that no work has been carried out using pyridine-2-carboxaldehyde as an aldehyde and benzohydrazide as an active hydrogen compound for the synthesis of Mannich bases and hence an attempt has been made to synthesis and to characterize Mannich base using pyridine-2-carboxaldehyde, morpholine and benzohydrazide. Many reports are available in the literature over the synthesis and characterization of metal complexes of Mannich bases [1-5]. Organic chelating ligands containing amide moiety as a functional group have a strong ability to form metal complexes and exhibit wide range of biological activities [6-9]. In view of the above fact the metal complexes were synthesised using the first transition series metal ions.

The metals used were Mn(II) Co(II), and Cu(II) chlorides. The synthesized ligand and its metal complexes have been characterized through analytical methods [mp, TLC, C,H,N analysis] and spectral methods [UV, IR, ^{1}H NMR ^{13}C NMR]. Further the ligands and metal complexes have been subjected to biological studies.

MATERIALS AND METHODS

Experimental

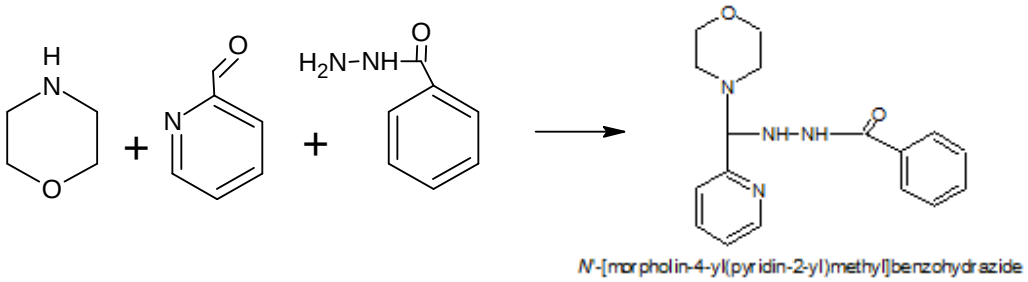
The reagents pyridine-2-carboxaldehyde, morpholine, benzohydrazide and metal chlorides were of Merck Products and were used as such. The IR spectra were recorded with KBr pellets using FT-IR Shimadzu Instrument. ^{1}H NMR and ^{13}C NMR Spectra were recorded in Bruker 300 MHz Instrument using DMSO as solvent. Molar conductivity was measured using 10^{-3} M solution of complexes in DMSO on systronic conductivity bridge. Muller-Hinton agar was used for the study of antimicrobial activity of ligand and the complexes by employing well-diffusion technique. Gentamycin and Amphotracin-B were used as standards for antibacterial and antifungal studies respectively.

2.1 Synthesis of Mannich base

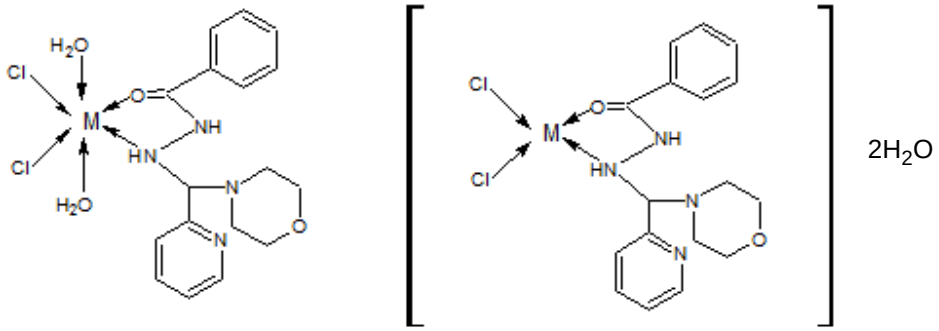
Benzohydrazide (3.4 g, 0.025 mol) was dissolved in water. To this solution, morpholine (2.2 mL, 0.025 mol) was added dropwsie with constant stirring. After 10 minutes, pyridine-2-carboxaldehyde (2.7 mL, 0.025 mol) was added in drops and the reaction mixture was kept in an ice bath that was placed over a magnetic stirrer and stirred for an hour. Compound formed was filtered and then recrystallised from ethanol. Purity of the compound was checked by TLC and the melting point of the compound was determined in an open capillary tube and were uncorrected.

2.2 General Synthesis of metal complexes

The Mannich base dissolved in methanol and methylene chloride(1:1) and the metal chlorides, MCl_2 [where M = Cu(II), Mn(II), and Co(II)] dissolved in methanol were mixed in 1:1 molar ratio. The reaction mixture was warmed gently on a water bath for an hour. The metal complexes formed were filtered, washed with ethanol and dried in vacuum.



N-[morpholin-4-yl(pyridin-2-yl)methyl]benzohydrazide



M= Mn(II) M= Cu (II), Co(II)

2.3 Antimicrobial activity

The antimicrobial activities of the synthesised compounds and metal complexes have been studied by well-diffusion test against the selected organisms such as *S. aureus, E. Coli C. albicans* and *A.niger***.** The zone of inhibition values were found out at the end of 24 h at 37°C for the bacterial stains and 48 h at 37°C for the fungal stains. The values are presented in Table 2.

RESULTS AND DISCUSSION

The ligand and its Metal [M = Cu(II), Mn (II) and Co (II)] complexes were characterised by elemental analysis and the results are presented in Table 1. Molar conductivity results show that all the complexes are non-electrolytes in nature. The complexes are very stable at room temperature in air.

3.1 Infrared Spectra

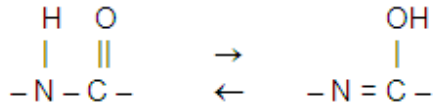
The IR spectrum of the free ligand was compared with those of the metal complexes to determine the coordination sites involved in coordination. The IR spectrum provides valuable information regarding the nature of the functional group attached to the metal ion. The infrared bands of the ligand observed at 3462, 1659 and 1283 cm^{-1} have been assigned to ν_{N-H} stretching, benzohydrazide $\nu_{C=0}$ and ν_{C-O-C} of morpholine respectively. The band at 1469 cm^{-1} indicates C-N stretching. The decrease in ν_{N-H} stretching of the ligand from 3462 to 3453 cm^{-1} in the complex indicates Nitrogen Coordination. The reduction in $\nu_{C=0}$ stretching of the ligand from 1659 to 1602 cm^{-1} in the complex denotes the oxygen coordination of the ligand. From these observations, it has been concluded that the ligand acts as a neutral bidentate ligand.

Table 1 : Physical characterisation, Analytical, Molar conductance data

Compound/ Complex	Found (Calculated)				Mol. Wt.	λ_m mho cm^2 mol^{-1}
	M	C	H	N		
Ligand (L) $C_{17}H_{20}N_4O_2$	-	65.26 (65.37)	6.33 (6.45)	17.81 (17.94)	312.37	—
[Cu (L) Cl_2] $2H_2O$	13.08 (13.16)	42.15 (42.29)	4.98 (5.06)	11.46 (11.60)	482.84	50.1
[Mn (L) $(H_2O)_2$ Cl_2]	11.49 (11.58)	42.98 (43.06)	5.03 (5.10)	11.67 (11.81)	474.24	48.2
[Co (L) Cl_2] $2H_2O$	12.21 (12.32)	42.57 (42.70)	5.01 (5.06)	11.60 (11.72)	478.23	47.8

^{1}H NMR and ^{13}C NMR Spectra

The Ligand displays the following ^{1}H NMR signals : 7.4 – 7.7 δ (m, Ar-H), 2.5 δ (t, morpholine N-CH_2), 3.4 δ (t, morpholine O-CH_2) 11.8 δ (s, -N=C-OH). The –NH proton nearer to C=0 undergoes tautomerisation.



7.9 δ (d, for –NH coupled with –CH). In ^{13}C NMR, a peak at 163 ppm is for C=0 carbon, a peak at 147 ppm is for –CH carbon. peaks at 127-134 ppm signifies aromatic carbon. When nitrogen coordinates with the metal, the charge density on nitrogen decreases. This leads to the shifting of equilibrium towards the keto form in the complex. This is confirmed with the absence of C-OH NMR peaks in ^{1}H NMR and ^{13}C NMR spectra.

Table 2 : Antimicrobial Activities of Mannich base and its Metal complexes

Compound/ Complex	*S. aureus*	*E. coli*	*A. nigar*	*C. albicans*	*Control*	*DMSO*
Ligand	23	25	-	17	Sensitive	-
Cu (II) Complex	22	22	30	31	Sensitive	-
Mn(II) Complex	26	25	-	21	Sensitive	-
Co(II) Complex	28	26	39	29	Sensitive	-

Electronic Spectra

For Cu (II) complex, the bands at 24390-26316 cm^{-1} is assigned to $^2B_{1g} \rightarrow {}^2A_{1g}$ transitions which is in the range generally observed for planar Cu(II) complexes [13]. The band at 24390-26316 cm^{-1} is due to ligand to metal charge-transfer transition [11]. Hence, square planar geometry is assigned to Cu(II) complex. The Co(II) complex shows two bands at 14837 and 25053 cm^{-1} which are assigned to $^4A_2 \rightarrow {}^4T_1$ (P) and charge transfer transitions respectively, considering, a tetrahedral geometry [12].

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