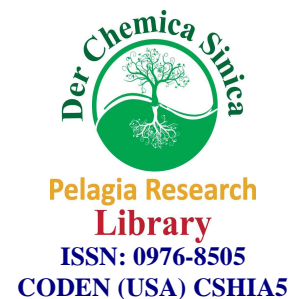




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### Synthesis, characterization and antimicrobial studies of metal complexes of Mannich Base derived from pyridine-2-Carboxaldehyde

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#### ABSTRACT

*In the present study, a new Mannich base was synthesized by the condensation reaction of pyridine-2-carboxaldehyde, morpholine and semicarbazide. The complexation behaviour of Cu(II), Cd(II), Mn(II) and Ni(II) ions with the newly synthesised Mannich base has been studied. The Mannich base and the complexes were characterized by spectroscopic methods [UV, IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR] and analytical methods [C, H and N analysis, mp, TLC and conductometry]. Antimicrobial activities of the ligand and its complexes were tested against some selected bacteria.*

**Key words :** Mannich base, metal complexes of Pyridine -2-carboxaldehyde, spectral study, antimicrobial study.

#### INTRODUCTION

Mannich reaction is a three component condensation reaction consisting of an aldehyde, an amine and a compound containing an active hydrogen atom [1]. From the literature, it has been observed that the compounds such as acetone, substituted acetone, acetamide and substituted amides and phenols have been extensively studied as compounds containing active hydrogen atom [2]. Only a little work is available with semicarbazide as an active hydrogen compound for the synthesis of Mannich bases [2]. Many reports are available for the synthesis of Mannich bases using aliphatic, aromatic and hetero aldehydes [3-6]. Among the hetero aldehydes, a few reports are available using furan-2-aldehyde as a reactant for the synthesis of Mannich bases [7]. A probe into the literature clearly reveals that no work has been carried out on the synthesis of Mannich bases using pyridine-2-carboxaldehyde. Generally primary and secondary amines have been used as one of the reactants for the synthesis of Mannich bases. Among the amines, piperidine, diethylamine, N-methyl piperazine have been extensively used [8].

Hence, an attempt has been made to synthesize Mannich bases using pyridine-2-carboxaldehyde, morpholine as fixed components and varying the compounds containing active hydrogen atom. Mannich base complexes have remained an important area of research due to their diverse range of applications. From the survey of literature, it appears that metal complexes of Mannich bases play a vital role in the development of coordination chemistry [8-11]. Literature studies reveal that there has been a great deal of interest in the synthesis and structural elucidation of transition metal complexes containing amide moiety [2]. In the present work, Mannich base derived from the condensation of pyridine-2-carboxaldehyde, morpholine and semicarbazide and its metal complexes with Cu(II), Cd(II), Mn(II) and Ni(II) are synthesized and characterized using different physico-chemical and spectral

techniques. The ligand and its metal complexes have been subjected to various microbes such as *E. coli*, *S. aureus*, *A. nigar*, and *C. albicans*.

## MATERIALS AND METHODS

### Experimental

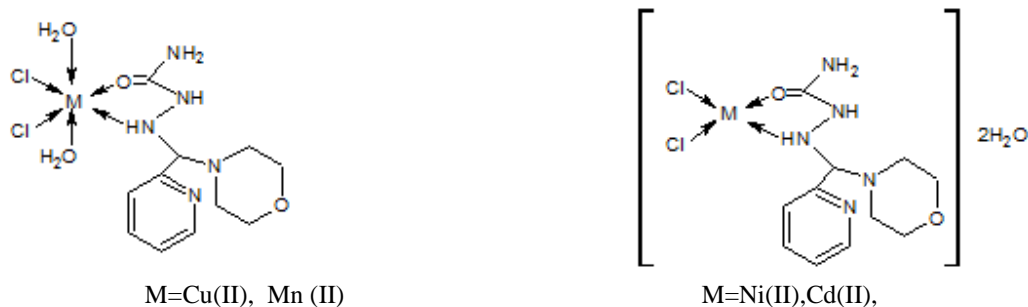
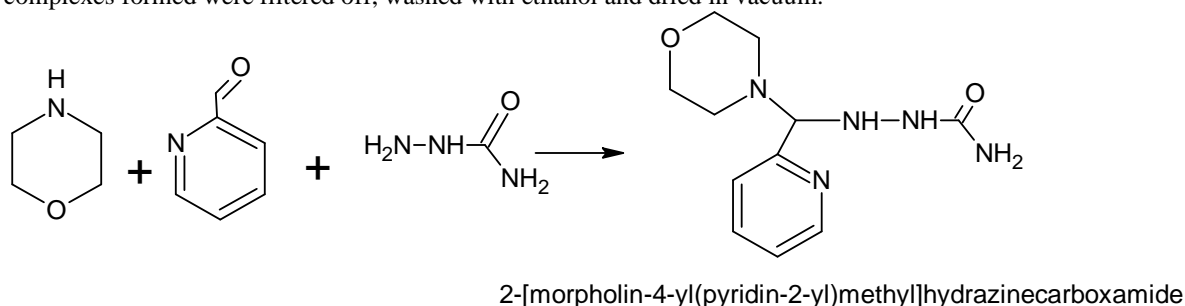
The reagents morpholine, pyridine-2-carboxaldehyde and semicarbazide were of Merck products and were used as such. The IR spectra were recorded with KBr pellets using FT-IR Shimadzu instrument.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded using Bruker 300 MHz instrument using DMSO as solvent. Elemental analysis was carried out using varion EL III instrument. Molar conductivities of the complexes were measured using  $10^{-3}$  M solution in DMSO on systronic bridge. Muller-Hinton Agar (MHA) was used for the study of antimicrobial activity of the ligand and the complexes using well-diffusion technique. Gentamycin and amphotracin-B were used as standards for antibacterial and antifungal activities respectively.

### 1. Synthesis of Mannich base

Semicarbazide hydrochloride (2.786 g, 0.025 mol) dissolved in water was taken in a beaker. To this morpholine (2.2 mL, 0.025 mol) was added in drops with constant stirring. With this mixture, pyridine-2-carboxaldehyde (2.7 mL, 0.025 mol) was added dropwise and the beaker was placed in an ice bath that was kept over magnetic stirrer. The stirring was continued for 45 minutes. The colourless compound obtained was filtered and recrystallised using 1,4-Dioxan. The purity of the compound was checked through melting point and TLC.

### 2. Synthesis of metal complexes

The Mannich base was dissolved in a mixture of methanol and chloroform(1:1). The metal chlorides,  $\text{MCl}_2$  [where M = Cu(II), Ni(II), Mn (II) and Cd(II)] were dissolved in methanol. The metal chloride solution was added to ligand solution in 1:1 molar ratio. The mixed solution was stirred for an hour under ice cold condition. The metal complexes formed were filtered off, washed with ethanol and dried in vacuum.



### 3. Antimicrobial activity

The biological activity of the ligand and the synthesised metal complexes have been studied for their antibacterial and antifungal activities by well-diffusion test. The antibacterial activities were done with bacteria (*S. aureus* and *E. coli*) and antifungal activities were measured with fungi (*C. albicans* and *A. niger*). The zone of inhibition values were taken 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 Mannich base and its metal [Cu (II), Ni (II), Mn (II) and Cd (II)] complexes were characterised by elemental [C, H and N] analysis. The analytical data of ligand and complexes are presented in Table 1. Molar conductance data show that all the complexes are non-electrolytes.

**Infrared Spectra**

In order to study the binding mode of the ligand to the metal ion, the IR spectrum of the ligand was compared with those of the complexes. The bands at 3407 and 3355  $\text{cm}^{-1}$  for the ligand are assigned to  $\nu_{\text{N-H}}$  asymmetric and  $\nu_{\text{N-H}}$  symmetric stretching respectively. The band at 1689  $\text{cm}^{-1}$  is assigned to  $\nu_{\text{C=O}}$  of the ligand. The nitrogen coordination of the ligand to the metal ion is known from the decrease in  $\nu_{\text{N-H}}$  stretching from 3355  $\text{cm}^{-1}$  to 3304  $\text{cm}^{-1}$ . The reduction in  $\nu_{\text{C=O}}$  stretching from 1689 to 1672  $\text{cm}^{-1}$  reflects to oxygen coordination. From these observations, it has been concluded that the ligand acts as a neutral bidentate ligand. The bands at 1589 and 1513  $\text{cm}^{-1}$  are assigned to  $\nu_{\text{N-H}}$  in-plane bending. The frequency assigned at 1428  $\text{cm}^{-1}$  refers to  $\nu_{\text{C-N}}$  stretching. The band at 3054  $\text{cm}^{-1}$  signifies  $\nu_{\text{C-H}}$  stretching of the pyridine nucleus. The bands due to  $\nu_{\text{C-H}}$  out-of-plane bending of the pyridine nucleus are located in the regions 732 and 765  $\text{cm}^{-1}$ . Isolated C-H stretching appears at 2923  $\text{cm}^{-1}$ . In the far infrared region, all the complexes exhibit bands in the regions 414-472  $\text{cm}^{-1}$  and 472-543  $\text{cm}^{-1}$  which are assigned to  $\nu_{\text{(M-N)}}$  and  $\nu_{\text{(M-O)}}$  modes respectively. The band due to  $\nu_{\text{(M-O)}}$  usually occurs in higher frequency region because the dipole moment of the M-O bond is usually larger than those of the M-N bond. Moreover the peaks of M-O bond is stronger than M-N bond.

**Table 1 : Physical characterisation, Analytical and Molar conductance data**

Compound/ Complex	Found (Calculated)				Mol. Wt.	$\lambda_m$ mho $\text{cm}^2 \text{mol}^{-1}$
	M	C	H	N		
Ligand (L) $\text{C}_{11}\text{H}_{17}\text{N}_5\text{O}_2$	-	51.54 (52.58)	6.76 (6.82)	27.78 (27.86)	251.26	-
[Cu (L)(H <sub>2</sub> O) <sub>2</sub> Cl <sub>2</sub> ]	14.89 (15.07)	31.10 (31.33)	4.90 (5.02)	16.58 (16.61)	421.73	48.4
[Ni(L) Cl <sub>2</sub> ]2H <sub>2</sub> O	14.44 (14.67)	32.90 (33.02)	5.13 (5.29)	17.45 (17.51)	400.09	49.5
[Cd(L) Cl <sub>2</sub> ]2H <sub>2</sub> O	24.65 (24.77)	28.99 (29.12)	4.55 (4.67)	15.39 (15.43)	453.78	51.3
[Mn(L) (H <sub>2</sub> O) <sub>2</sub> Cl <sub>2</sub> ]	13.21 (13.30)	31.83 (31.98)	5.01 (5.12)	16.86 (16.94)	413.13	50.4

**<sup>1</sup>H NMR and <sup>13</sup>C NMR Spectra**

The ligand displays the following <sup>1</sup>H NMR signals: a multiplet at 7.5 – 7.6  $\delta$  (Py – H), 2.5  $\delta$  (t, morpholine N-CH<sub>2</sub>), 3.38  $\delta$  (t, morpholine O-CH<sub>2</sub>), 11.8  $\delta$  (s, NH<sub>2</sub>), 6.9  $\delta$  (s, -CONH), 6.6  $\delta$  (d, -NH). In <sup>13</sup>C NMR, a peak at 163 ppm is assigned to C=O carbon, a peak at 112 ppm is assigned to -CH carbon and a multiplet at 127-137 ppm is assigned aromatic carbons.

**Table 2 : Antimicrobial Activities of Mannich base and its Metal(II) complexes.**

Compound/ Complex	<i>S. aureus</i>	<i>E. coli</i>	<i>A. niger</i>	<i>C. albicans</i>	Control	DMSO
Ligand	-	11	-	-	Sensitive	-
Cu (II) Complex	17	24	17	36	Sensitive	-
Ni (II) Complex	16	21	-	29	Sensitive	-
Cd(II) Complex	22	22	-	32	Sensitive	-

**Electronic Spectra**

The Electronic spectrum of the Mn(II) complex exhibits three absorption bands at 10929, 16949 and 26373  $\text{cm}^{-1}$  which are assigned to  ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g} ({}^4\text{G})$ ,  ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g} ({}^4\text{G})$  and  ${}^6\text{A}_{1g} \rightarrow {}^4\text{E}_g.{}^4\text{A}_{1g} ({}^4\text{G})$  transitions respectively, confirming an octahedral geometry [13]. The Electronic spectrum of Nickel displays a band at 26121  $\text{cm}^{-1}$  and this suggests the square planar geometry for nickel chelate. Absence of any band below 10,000  $\text{cm}^{-1}$  rules out the possibility of tetrahedral structure for the nickel complex.

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