

Synthesis and characterization of Manganese (II) and Copper (II) complexes with a new Mannich base Ligand: Assessment of biological activity

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ABSTRACT

The new synthesis of Mannich base from nicotinamide derivative. The chemical structures of the Mannich base have been confirmed and elucidated by their physical and spectral data. The metal complexes of Nicotinamide containing Mannich base were synthesized and characterized by percentage of metal analysis, conductivity, FT-IR spectroscopy, UV-Vis spectroscopy and magnetic moment measurements. The molar conductivity of the complexes are much less than $54.0 \text{ } \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ showed the non-electrolyte nature of the complexes. The IR spectra showed that the organic ligand is neutral bidentate bonding through the dicyclohexylamino ring nitrogen and one of the carbonyl oxygen nicotinamide moiety. The magnetic susceptibility data showed that all the complexes were paramagnetic. The general formula of the Co(II) and Cu(II) chloro complexes MLX_2 are reported. The spectral analysis to ascertain mode of bonding and overall geometry of the complexes revealed square planer geometry. All the compounds synthesized were tested experimentally on their antibacterial activity against four Gram-positive and Two Gram-negative bacteria. The test outcomes revealed moderate to high antibacterial activity of metal complexes.

Keywords: Mannich base, Metal complexes, Thermal analysis, Nicotinamide, Biological activity

Introduction

The synthetic chemists have also taken interest in Mannich bases of heterocyclic molecules due to the various coordination modes it can have, and many antimicrobial properties (Adimule *et al.*, 2018), such as anti-inflammatory, anti-microbial, anti-oxidant, anti-influenza and anti-cancer properties (Balachandran *et al.*, 2015 and Ganga *et al.*, 2020). Nicotinamide is among the most significant

bioactive ligands that presents possible binding sites with the assistance of nitrogen and oxygen atoms (Kohanski *et al.*, 2010). The necessity to possess new and effective antimicrobial activity agents, having fewer side effects and better overall nature and safety profiles, is most obvious now, as the resistance of microbes to conventional antibiotics becomes more common. This has become a significant problem of the international research fraternity. Bacterial bioactive activity of the bioactive compound

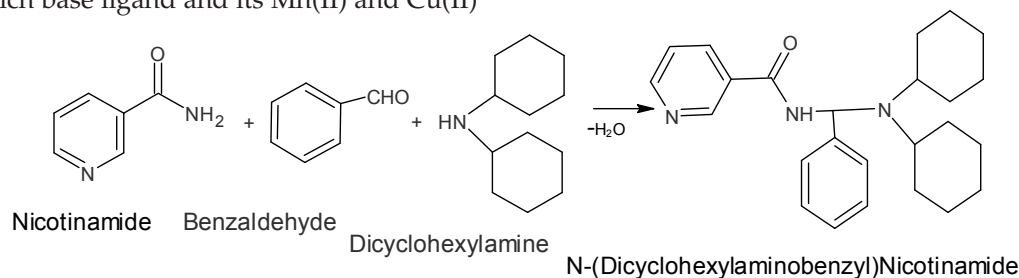
involves interaction of the compound and its corresponding target in the biochemical and molecular interaction *in vitro* studies (Kamat *et al.*, 1999). The ligand and few complexes were screened using Agar-well diffusion method on the basis of their antibacterial activity. The antimicrobial effects of the free organic ligand were positive and those of the complexes as compared to the normal drugs (Manjula *et al.*, 2016). The current research focuses on the synthesis, characterization, and antibacterial properties of nicotinamide, benzaldehyde, and dicyclohexylamine and their Mn(II) and Ni(II) mixed-ligand complexes. have been prepared in this study and well characterized using their physical, spectral, and analytical data. The synthesized compounds were further evaluated for their antimicrobial properties against various pathogens using the MIC method.

Materials and Methods

All reagents, Nicotinamide, benzaldehyde and dicyclohexylamine and various metal(II) chlorides, solvents: DMSO, DMF, methanol, ethanol were Merck products and used as supplied. Microanalyses (C, H and N) were carried out in Carlo Erba 1108 analyzer at Sophisticated Analytical Instrument Facility (SAIF), Molar conductivities in DMSO (10^{-2} M) at room temperature were measured using Systronic model-304 digital conductivity meter. TLC was used to determine the purities of the compounds. Using KBr pellets and a Spectrum One Perkin Elmer FT-IR spectrometer, infrared spectra were recorded. Using a Perkin Elmer EZ 301 spectrophotometer, UV-visible spectra were recorded. The samples ^1H and ^{13}C NMR spectra at 400 MHz were recorded using a Burcker topspin spectrometer.

Synthesis of Mannich base ligand

The Mannich base ligand and its Mn(II) and Cu(II)



Scheme 1. Synthesis of Mannich base ligand (DBN)

complexes were synthesized as follows: An ethanolic solution of benzamide (6.10 g, 0.05 mol), benzaldehyde (2.65 ml, 0.05 mol), and dicyclohexylamine (4.53 ml, 0.05 mol). The mixture was refluxed with constant stirring for one hour; The precipitate formed was filtered, washed several times with a cold ethanol/water mixture, and recrystallized from methanol to give the title compound as colorless single-crystalline solids (Scheme 1).

Synthesis of Metal complexes

The hot ethanolic solution of the metal complexes (0.05 mol) in 100 mL beaker was stirred with an ethanolic solution of the Mannich base ligand N-(dicyclohexylaminobenzyl) benzamide (0.05 mol) to make the mixture. 1 hours were spent on a water bath in which the content of the beaker was digested. The coloration variant is burst into the color of the salt product, the product throughout was filtered out in each instance, washed and dried up using ethanol and vacuum in desiccators. Metal complexes thus obtained were stored in a vacuum desiccators (Pohontu *et al.*, 2015).

Biological Assay

The compound was obtained after a few weeks of synthesis, which is N-(dicyclohexylaminobenzyl) nicotinamide. This crystal compound was ground to obtain powdered form. The powdered form were then dissolved using 25% mixture of ethanol and methanol and then were used in the bacterial assay.

Result and Discussion

The synthetic pathways for nicotinamide derivatives are shown in Schemes 1. Nicotinamide was first reacted with the amine (dicyclohexylamine) in the presence of benzaldehyde and Metal Chloride to yield the target compounds (Scheme 1). The molecular formulae of the complexes were deduced

from the elemental analysis data. The preparation of the ligand (HL) is shown in Scheme 1. The molecular structure of (HL) was established by the appearance of characteristic absorption bands in the IR region. The percentage composition of each element in the complexes, as shown in Table 1, may be used to establish the identity of the complex based on the analytical data (Sakthikumar *et al.*, 2018). The molar conductance of the metal complexes was determined at 25 %C.

FT-IR Spectroscopy

This topic will deal with the infrared spectra of the ligand (DBN) and DBN-Mn(II) and DBN-Cu(II) complexes, as shown in Figure 4. The prominent carbonyl band of the Mannichbase ligand was observed at 1681 cm^{-1} , ν_{NN} Stretching at 3405 cm^{-1} and ν_{CNC} stretching at 1269 cm^{-1} . The participation of the Mannich base ligand in the coordination of the metal complexes was evident from the shift of the band to lower wave numbers. The carbonyl stretching vibration of DBN showed a band at 1624 cm^{-1} for Mn(II) complexes and 1613 cm^{-1} for Cu(II) complexes, indicating the ligand entry into the coordination sphere via an oxygen atom in a carbonyl group. The N-H Stretching frequency bands are at 3401 and 3447 cm^{-1} and the ν_{CNC} Stretching bands are at 1252 and 1179 cm^{-1} . These bands also indicate that the Mannich base acts as a bidentate ligand that coordinates via the N atom containing the dicyclohexylamine moiety. Other bands in the complexes were greatly affected at the lower or higher level, such as $\nu_{\text{C-N}}$ (stretching) 1311 and 1320 cm^{-1} ,

$\nu_{\text{C-H}}$ (aromatic)2934 and 2933 cm^{-1} , $\nu_{\text{C=C}}$ (stretching)1594 and 1571 cm^{-1} , $\nu_{\text{M-O}}$ stretching 547 and 549 cm^{-1} [18], $\nu_{\text{M-N}}$ 478 and 479 cm^{-1} and $\nu_{\text{M-X}}$ 415 and 446 cm^{-1} , confirming the ligand coordination via the bidentative model oxygen and nitrogen atoms in these complexes (Sankar Ganesh *et al.*, 2018).

Uv-Visible Spectroscopy

The UV-Vis spectra of the N (dicyclohexylaminobenzyl) nicotinamide ligand and its complexes are given in Table 3. Figure 2 illustrates The UV-Vis spectra of the ligand and its metal complexes recorded in the wavelength range (200–800 nm) using a DMSO solution at room temperature. The first sharp peak is due to the DMSO peaks. The carbonyl group in N-(dicyclohexylaminobenzyl) nicotinamide undergoes $\pi-\pi^*$ and $n-\pi^*$ transitions at 202–327 nm, which undergo red and blue shifts during metal complexation. The bathochromic and hypsochromic effects confirmed the formation of the metal complexes compared to the free ligand. The electronic spectrum of the complex Mn(II) band at 269 and 219 nm appears at $\pi-\pi^*$, $n-\pi^*$ and due to the square planar geometry, respectively, and the effective magnetic moment value at 5.90 BM also indicates the square planar arrangement. The Cu(II) complex band at 216, 323, and 715 nm corresponds to the $\pi-\pi^*$, $n-\pi^*$ and ligand-to-metal charge transfer (LMCT) transitions, respectively. This could serve as an additional confirmation for the participation of the ligand in complex formation (Raman *et al.*, 2003).

Table 1. Physico-chemical and Analytical data of Mannich base and its metal complexes

Molecular Formula	Colour	Yield	M.P°C	Mol. Wt	μ_{eff} B.M	m ohm ⁻¹ cm ² mol ⁻¹	Calc.(Found)%				
							'C	H	N	O	M
DBN	Pale brown	84	184	391	77.69 (77.54)	8.50 (8.42)	10.73 (10.70)	4.09 (4.04)	-
MnCl ₂ -DBN	Gray color	72	178	516	1.83	54	67.25 (67.03)	7.45 (7.30)	9.41 (9.22)	3.58 (3.44)	12.30 (13.03)
CuCl ₂ -DBN	green color	81	197	524	1.91	51	65.98 (66.33)	7.31 (7.30)	9.23 (9.25)	3.52 (3.12)	13.96 (12.87)

Table 2. IR spectral data of Ligand DBN and their complexes

Assignment	$\nu_{\text{N-H}}$	$\nu_{\text{C-H}}$ (Ar)	$\nu_{\text{C=O}}$	$\nu_{\text{C=C}}$ (Ar)	$\nu_{\text{C-N}}$ (Ar)	$\nu_{\text{C-N-C}}$	$\nu_{\text{M-O}}$	$\nu_{\text{M-N}}$	$\nu_{\text{M-X}}$
DBN	3405	2936	1681	1564	1386	1269	-	-	-
MnCl ₂ .DBN	3401	2934	1624	1594	1311	1252	547	478	415
CuCl ₂ .DBN	3447	2933	1613	1571	1320	1179	549	479	446

NMR Spectroscopy

^1H -NMR Spectra

The proton positions were confirmed using the ^1H NMR spectrum. The protons of the aromatic ring are the cause of the multiple signal at the range of 7.91 - 7.89 ppm. The chemical shift at δ 2.92- 2.50 ppm represents the protons of the N(CH) groups of the dicyclohexylamino moiety. The different CH_2 protons of the cyclohexyl rings gave rise to the multiplet signals that occurred at δ 1.94-1.05 ppm. The chemical shift at δ 3.06 ppm corresponds to protons of the methyl group that is bridged between nicotinamide and dicyclohexylamine (NCHN). In DBN, the title compound, signals at δ 7.67 ppm in nicotinamide and δ 0.78 ppm in dicyclohexylamine were attributed to the corresponding NH protons. The ^1H NMR spectrum of DBN proved the existence of an aromatic ring, a dicyclohexylamino and a new formed methyl bridge in the DBN molecule. The correlation between the intensity ratio of the obtained signals and the number of protons in each chemically equivalent category is good. The protons on the methyl bridge were in the chemical environment that was in agreement with the fact that they are between the two nitrogen atoms. Besides, no other unanticipated peaks suggest high purity of the synthesized compounds. All these spectral characteristics testify to the successful creation of the desired DBN structure (Syed Abuthahir *et al.*, 2014).

^{13}C NMR Spectra

The ^{13}C NMR spectrum of DBN shows very weak absorptions at 152.36 ppm which is due to the two

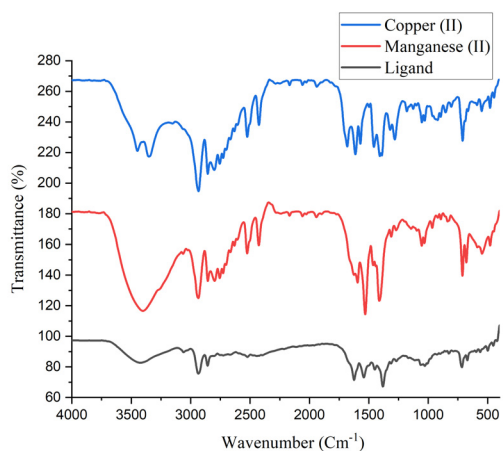


Fig. 1. FT-IR spectra of DBP and its Mn (II) and Cu (II) Complexes

carbonyl carbons [3]. atoms in DBN. The bridgehead carbons of the aromatic ring contribute to chemical shifts at 129.58 ppm, as indicated on Figure 4. There are chemical shifts of other aromatic carbons at the 128.27 ppm multiplet. N(CH) carbons in the dicyclohexyl moiety are found at 40.60 ppm. Others of the NH_2 carbons of the cyclohexyl rings are shown to have a multiplet at between -24.63 40.39 ppm. The CH signaling group to which the nicotinamide and dicyclohexylamine fragments (NCHN) are attached is given a signal of 52.41 ppm. The ^{13}C NMR signals of the DBN, as well as the identification of various carbon atoms in the molecule are congruent with the structure of DBN. The article details the findings of a ^{13}C nuclear magnetic resonance (NMR) experiment on a compound with dicyclohexyl and nicotinamide components: The nitrogen in the dicyclohexyl component of the compound was found to have a signal at 40.60 ppm. The other carbon atoms in the cyclohexyl rings to the NH_2 groups gave the signal between 40.39 and 24.63 ppm. - The signal at 52.41 ppm is that of the carbon atom linking the nicotinamide moiety to the dicyclohexylamine moiety. The total ^{13}C NMR signals were in agreement with the anticipated structure of the compound thus, confirming its identity. This shows that the NMR data validates the chemical structure of the molecule which was proposed Vinoth Kumar *et al.*, (2018).

Mass Spectroscopy

The mass spectrometry was calculated to determine the fragmentation of the compounds studied and the molecular weight of the compounds made. The mass Spectrum of the ligand prepared was in agreement with the proposed structural formula of $\text{C}_{25}\text{H}_{33}\text{N}_3\text{O}$. The mannich base ligand molecular mass m/z of 391.4. Peptides of molecular ions in the metal complexes were found at $m/z = 516$ [MnCl_2].DBN and $m/z = 524$ [CuCl_2].DBN.

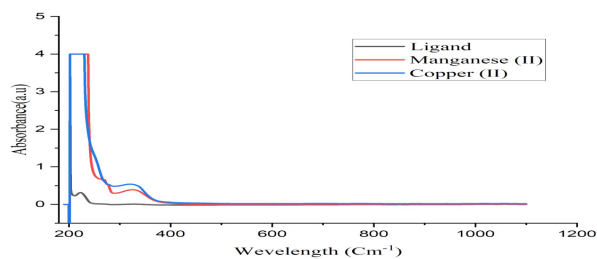


Fig. 2. UV-Vis Spectrum of DBP and its Mn^{II} and Cu^{II}Complexes

Biological Assay

The inhibition zone (mm) of the synthesised N-(dicyclohexylaminobenzyl) nicotinamide Mannich base ligand (L) and its metal complexes towards the actions of the bacteria shown in Table 3a and 3b, Figure 4a and 4b depict the widths of inhibition zones of all the compounds against the microbes. Base ligand compounds of Mannich were of moderate, good, and satisfactory activity against bacteria. Co(II) complex had moderate antibacterial activity against all but the *E. coli* strains. Good antibacterial activity was seen. Ni (II) complex was found to be of good antibacterial activity against *S. aureus* and *E. coli* strains than Co (II) complex which was found to be of good antimicrobial activity when compared with the ligand and Ni (II) complex. $MnCl_2 \cdot DBN > DBN > CuCl_2 \cdot DBN$ were in that order of antimicrobial activity. The Ni (II) complex had good antifungal effects on both *A. niger* and *C. albicans* strains (Vijay *et al.*, 2011). The Co (II) complex was also found to have moderate antifungal activity except against the *C. albicans* strain. Ni (II) complex had the greatest antifungal activity than the other metal ions and the Mannich base ligand. $CuCl_2 \cdot DBN > MnCl_2 \cdot DBN > DBN$ (Yosuva Suvaikin *et al.*, 2012). The antifungal and antibacterial properties of the newly synthesized compounds are summarized in Tables 3a and 3b.

ligand and its metal complexes ligand and its metal complexes

Conclusion

In conclusion, a new series of nicotinamide derivatives were designed, and the first step was to investigate the reactivity of nicotinamide molecules as ligands. A number of physical, chemical, and spectroscopic methods were employed to design and synthesize a new mannich base ligand N-(dicyclohexylaminobenzyl) nicotinamide and Mn(II) and Ni(II) metal complexes. such as ¹H NMR, ¹³C NMR, MS, FT-IR, Uv-Visible, C,H,N, and O analyses, and magnetic susceptibility. Based on the molar conductance results, the complexes were found to be non-electrolytes. The electronic absorption spectral results of the complexes indicate a square planar geometry around the central metal ion. Having established that the nicotinamide molecule has two potential coordination sites, the oxygen atom and the nitrogen atom of the amide group and dicyclohexylamine, we have, based on geometrical parameters, atomic charges, and electrostatic potentials at atoms, and established that the coordination of the ligand with a metal ion is preferably done through the oxygen atom. Biological activity screen-

Table 3a. Mannich base Ligand and its Mn (II) and Cu (II) complexes antibacterial properties

Compound	Zone of Inhibition (mm)							
	E.Coli				S.aureus			
	Conc. of compound(µg/ml)				Conc. of compound(µg/ml)			
	25	50	75	100	25	50	75	100
DBN	11	13	16	19	10	15	16	17
MnCl ₂ .DBN	14	17	21	22	14	16	17	18
CuCl ₂ .DBN	13	16	20	21	14	16	17	18
Kanamycin	10	-	-	-	-	-	-	-
Tetracyclin	-	-	-	-	9	-	-	-

Table 3b. Mannich base Ligand and its Mn (II) and Cu (II) complexes antifungal properties

Compound	Zone of Inhibition (mm)							
	<i>A.niger</i>				<i>C.albicans</i>			
	Conc. of compound(µg/ml)				Conc. of compound(µg/ml)			
	25	50	75	100	25	50	75	100
DBN	8	13	14	18	8	14	15	17
MnCl ₂ .DBN	11	16	17	19	12	15	18	20
CuCl ₂ .DBN	12	18	19	22	13	16	19	23
Nystatin	8	-	-	-	-	-	-	-

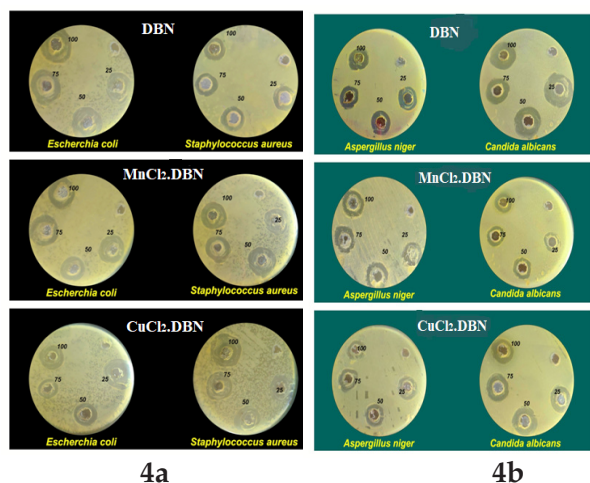


Fig. 4a. Antimicrobial activity of mannichbase
Fig. 4b. Antifungal activity of mannich base

ing revealed that the metal complexes had higher activity than the ligands against the tested bacteria and fungi.

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Conflict of Interest - None

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