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Synthesis, Characterization and Antibacterial activities of some Transition metal complexes with a new Mannich base (1-(3-furan-2-yl)-3-oxo-1-phenyl propyl)urea

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Abstract

A new Mannich base(1-(3-(furan-2-yl)-3-oxo-1-phenyl propyl)urea and its metal complexes with Co(II), Ni(II), Cu(II), Zn(II) ions have been synthesised and characterized. Their structural features have been established on the basis of analytical magnetic, conductance, IR, UV-Visible, Mass, ^{1}H and ^{13}C NMR spectra. The non electrolytic nature of the complexes was inferred from their low molar conductance values. On the basis of colour, magnetic moments and electronic spectal data, the geometries of Co(II), Ni(II), Cu(II), Zn(II) complexes were assigned. Cyclic voltammetric analysis of a Cu(II) complexes was discussed to understand the redox behaviour. The antibacterial activities of the ligand and a selected few complexes have been studied with the microorganisms such as Bacillus substillis, Staphylococcus aureus Escherichia Coli, Pseudomonas aeruginosa, Candida albicans, Aspergillus niger, employing disc diffusion method. The ligand and the complexes possess significant antibacterial activity comparable to that of the standard drugs.

***Keywords**: Mannich base; metal complexes; geometry; antibacterial activity.*

1 INTRODUCTION

Mannich bases and their coordination compounds have been reported to show a broad spectrum of biological properties and pharmacutical applications[1]. Metal ion complexes of mannich bases have been studied extensively in the recent years due to their selectivity and sensitivity towards biologocally important metal ions(Jujatha et al. 2000). To our knowledge, Mannich reaction is a three- component condensation reaction consisting of active hydrogen containing compound aldehyde and secondary amine. Much work has been done so far on isolation of solid complexes of different aromatic aldehydes or ketones and semicarbazones with transition metals[8-10]. A search through the literature reveals that no work has been done on the condensation of 2-Furyl methyl ketone, benzaldehyde and Urea. It is interesting to note that NH- amides also behave as an amine reactant and several reports are available to support this reference[11]. Literature survey reveals that 2-Furyl methyl ketone derivatives and amide moieties have widely been used for various biological activities [12-14]. In the present work, a new mannich base derived from the condensation of 2-furyl methyl ketone, benzaldehyde and urea and its metal complexes with Co(II), Ni(II), Cu(II), Zn(II) were synthesised and characterized using different physiochemical techniques. The ligand and its metal complexes have biological activities.

2 MATERIALS AND METHODS

2.1 Chemicals

Reagents such as 2-Furyl methyl ketone , benzaldehyde, urea and various Metal(II) chlorides were of Merk product. Spectroscopic grade solvents were used for the spectral and cyclic voltammetric measurements. The carbon, hydrogen and nitrogen contents in each samples were done at the Regional Sophisticated Instrumentation Centre, Central Drug

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Research Institute, Lucknow. The ^{1}H NMR and ^{13}C NMR spectra of the samples were measured in Bruker 300 MHz Instrument using DMSO as solvent. Mass spectra were recorded on a JEOL-8X102. The IR spectra were recorded with KBr pellets using FT-IR Shimadzu Instrument. Molar conductivity was measured using 10^{-3}M solution of complexes in DMSO on Systronic Conductivity Bridge. UV-Visible spectra of the complexes were recorded on Perkin Elmer Lambda EZ 301 spectrometer in DMSO solutions. Electrochemical measurements were carried out with electrochemical analyzer mode BAS-27 voltammogram. Magnetic susceptibility was measured with Gouy balance at room temperature. $Hg[Co(SCN)_4]$ was used as a standard. Nutrient agar was used for testing the susceptibility of microorganisms to antimicrobial agents using the *Disc-diffusion* technique. *Ciprofloxacin* was used as standard for antibacterial activity and *Nystatin* for antifungal activity.

2.2 Synthesis of Mannich base

The FBU was synthesised by mannich condensation reaction[15] between 2-furyl methyl ketone, benzaldehyde, urea in 1:1:1 mol ratio(Figure-1). Urea 1.5 mL (0.025mol) was dissolved in water. To this solution, 2-Furylmethyl ketone 2.75 mL (0.025 mol) was added dropwise with constant stirring. After 10 minutes benzaldehyde 2.65 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 half 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 was uncorrected. Yield: 78%, M.P :92 °C.

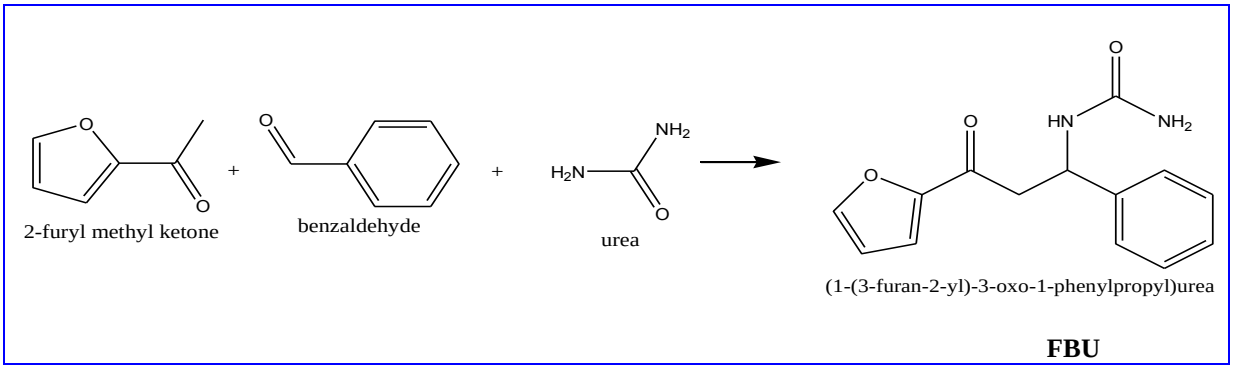

Figure-1: Formation of Mannich base

2.3 General synthesis of metal complexes

All the complexes of FBU were isolated from non aqueous media using methanol, and ethanol[16] in each case the methonolic solution of metal salt was added slowly with constant stirring to the ethonolic solution of the ligand 1:1 mol ratio. The reaction mixture was stirred under ice bath maintained at 5-10^{0}C for an hour. The solid product was filtered, washed with ethonal and dried under vacuum desiccator. The proposed structure of the complexes is given in **Figure 2.**

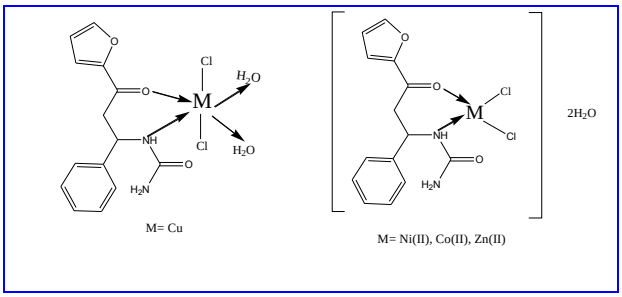

Fig. 2: Proposed structure of metal complexes

3. *IN VITRO* ANTIBACTERIAL AND ANTIFUNGAL ASSAY

The biological activities of synthesized Mannich base and its Co(II), Ni(II), Cu(II) and Zn(II) complexes have been studied for their antibacterial and antifungal activities by *Disc diffusion* test using Nutrient agar (NA) and Sabouraud Dextrose Agar(SDA). The antibacterial and antifungal activities were done at 10 µg/mL concentrations in DMSO solvent using bacteria (*S aureus, B substillis, E.coli and P.aeruginosa*) and fungi

(*C.albicans,A.niger*) at the minimum inhibitory concentration (MIC) method. These bacterial strains were incubated for 24 h at 37 ^{0}C and fungi strains were incubated for 48 h at 37 ^{0}C. Standard antibacterial (*ciprofloxacin*) and antifungal drug (*Nystatin)* were used for comparison under similar conditions. Activity was determined by measuring the diameter of the zone showing complete inhibition (mm).

4 RESULTS AND DISCUSSION

4.1 Structural Characterization of the Mannich base

Based on analytical and spectral data, the structure of the ligand has been conformed. The analytical and spectral data obtained for the ligand are summerized in Table1.

The spectral data obtained for the ligand are furnished below:

FT-IR (KBr, υ_{max}cm^{-1}): 3469(NH str), 2820(Ar CH), 1650(C=O), 1250 (C-N-C), 1605(C-C), 1119(C-O-C).

^{1}H NMR (DMSO-d_6, δppm): 2.1(s,2H,NH_2), 7.46(d,1H,NH), 6.6(H,1H,CH), 3.17(d,2H,CH_2) 7.42-7.50(m,Ar), 7.67-7.86(m,5H,Ar).

^{13}C NMR*(DMSO-d_6, δppm)*:176(C=O, 2-furyl methyl ketone), 152(amide C=O), 134(Ar-CH) 121(Ar CH).

Mass(m/z): 258(M^+ peak).

4.2 Characterization of metal complexes

The analytical and molar conductance data of the complexes are provided in **Table-1**. The conductance data[17] indicates that all the metal complexes suggest that the anions of the salts have coordinated to the metal ions in the formation of metal complexes.

Table-1: Physical characterization, Analytical, Molar conductance, Magnetic susceptibility data

Compound	Colour	Found/Calculated					M.Wt	Yield %	Λ-m Mho cm^2 mol^{-1}	μ-eff B.M
		M%	C%	H%	N%	Cl%				
FBU $C_{14}H_{14}N_2O_3$	Colourless	-	65.11 (65.27)	5.42 (5.48)	5.42 (4.47)	-	258	78	-	-
Cu(II) Complex	green	14.75 (14.90)	39.14 (39.19)	4.20 (4.38)	6.55 (6.67)	16.39 (16.48)	427	60	2.8	1.9
Co(II) Complex	pink	15.24 (15.40)	43.41 (43.52)	3.61 (3.48)	7.23 (7.38)	18.18 (18.27)	387	72	4.2	3.6
Ni(II) Complex	pale green	15.02 (15.22)	43.52 (43.68)	3.62 (3.74)	7.25 (7.39)	18.14 (18.27)	386	58	3.4	_
Zn(II) Complex	Colourless	16.53 (16.64)	42.74 (42.84)	3.56 (3.67)	7.12 (7.27)	16.53 (16.67)	393	62	2.4	_

4.3 Infrared spectra

The characteristic IR absorpsion bands of the complexes have been compared with the ligand L in order to get meaningful information regarding the binding sites. It is observed that the band appearing at 1658cm^{-1} due to $\nu_{(C=O)}$ in the ligand spectrum is shifted to a lower side by 10-20 cm^{-1} in the spectra of the complexes indicating the involvement of carbonyl oxygen in coordination. The IR specra of free ligands exist in $\nu_{(N-H)}$ absorption band at 3469 $\nu_{(C=N)}$ band and at 1644cm^{-1}, indicating that the ligand probably exist in equilibrium with tautomeric enol form. By the loss of proton the enolic form may act as a slightly charged ligand. The bands appearing in the spectra of the ligands 1658,1644 cm^{-1} are attributed to $\nu_{(C=O)}$, $\nu_{(C=N)}$ and modes respectively. The two strong bands observed at 656 and 677 are assigned to furan ring deformation modes. In the case of $[M(L)Cl_2]$ complexes [whereM=Ni(II), L=FBU] the amide band shifts to lower frequency in the spectra of these complexes The $\nu_{(C=N)}$ shifts to lower frequency (Δ=10cm^{-1}) . The non-ligand bands[18]occurring at 577 and 460 are assigned to $\nu_{(M-O)}$ and $\nu_{(M-N)}$ modes respectively. The presence of coordinated water molecules in Cu(II) complex is determined by the

appearance of bands at 3200-3600 and a peak at 926cm^{-1} assignable to the –OH stretching and rocking of water molecules.

4.4 Mangnetic moment and uv-visible spectra

Electronic spectra and magnetic measurements were recorded in order to obtain information about the geometry of the complexes. The μ_{eff}(1.9BM)value of the Cu(II) represents distorted octahedral geometry of the ligand around the central metal ion. The four coordinated Co(II)complexes shows μ_{eff} value of 3.6BM which indicates the presence of three unpaired electrons, supporting tetrahedral geometry. The observed zero magnetic moment value confirms the square planar environment for the Ni(II). The Zn(II) complexes are found to be diamagnetic as expected for d^{10} configuration.

The electronic spectra of the ligand and its complexes were recorded in DMSO solution. The Cu(II) ion with d^9 coordination in a complex can be either octahedral or tetrahedral or rarely square planar. The octahedral coordinated Cu(II) ion has the ground state ^2E_g $(t_{2g})^6$ $(e_g)^3$. The only exited state should then be $^2T_{2g}$ $(t_{2g})^5$ $(e_g)^4$, the energy difference being 10Dq. The Cu(II) complex under the present study exhibits a broad band in the region 12790cm^{-1}. The broadness of the band may be due to Jahn-Teller distortion[19,20]. These observations indicate that the complexes have distorted octahedral structure. Co(II) complex displays a band at 15655cm^{-1} which is assigned to $^4A_2 \rightarrow {}^4T_1$ for tetrahedral geometry[21]. The Ni(II) complex is diamagnetic suggesting a square planar geometry[22]. It shows a broad band at 14588cm^{-1} which is assigned to $^1A_{1g} \rightarrow {}^1B_{1g}$. No transition was observed in the visible region for the Zn(II) complex consistent with the d^{10} configuration of the Zn^{2+} ion. This complex is also found to be diamagnetic as expected for the d^{10} configuration.

4.5 ESR spectra

The ESR spectrum of the Cu(II)chloro complex have been recorded in solid state at room temperature. The measure of symmetry of these complexes is in terms of g values, that is g>2.04 indicates that the ground state of copper (II) ion is predominantly the d_{x2-y2} orbital. The g value of these complexes is found to be less than 2.3 indicating the covalent nature of the complexes. This has been further supported by the spin-orbit coupling constant (λ) value of -485 cm-1. The elongated octahedral geometry of the complexes have been established from the relation $g_{\parallel} > g_{\perp} > 2.04$.

4.6 ^{1}H NMR and ^{13}C NMR spectra

Evidence for the bonding mode of ligand is also provided by the ^{1}H-NMR spectra of the Mannich base and the diamagnetic Zn(II) complex, which were recorded in $CDCl_3$. The ^{1}H NMR spectrum of the ligand shows the following resonance signals: Signals due to aromatic protons appear at 7.42-7.50 δ . The N-H proton chemical shift occurs at 7.46 δ which gives rise to weak doublet. The ^{1}HNMR spectrum of Zinc (II)chloro complexes of FBSC has been recorded in DMSO-d_6 and compared with the free ligand . Upon coordination the downfield shifting of the amide N-H proton signal in the complex has been observed which may be due to the deshilding of N-H proton adjacent to C=O group. This further confirms the participation of C=O group in coordination. The signals due to the protons of furan ring and free-NH_2 of the ligand remain unchanged in the complex indicating the non-involvement of oxygen and nitrogen atom in coordination.

4.7 Cyclic voltammetry

The CV is the most versatile electroanalytical technique for the study of electroactive species. The redox properties of copper(II) complex have been studied by cyclic voltammetry experiments using glass carbon working electrode in DMSO solvent at scan rate 100 mVs^{-1}. The Cyclic voltammogram of the copper complex in DMSO solution recorded over a potential range -0.4V to -1.1V shows two quasi-reversible peaks, one at cathodic direction and another at anodic direction. The quasi-reversible reduction peak at -0.92V due to the formation of Cu(II)/Cu(I) while the other quasi-reversible oxidation peak at -0.56V is due to formation of Cu(I)/Cu(II).

4.8 *In vitro* antibacterial assay

For in vitro antimicrobial activity, the synthesized compounds were tested against the **bacteria** *Bacillus Subtillis, Staphylococcus aureus, Escherichia coli and Pseudomonas aeruginosa and* **fungi** *Candidaalbicans and Aspergillus niger*[23,24]. The minimum inhibitory concentration (MIC) values of the investigated compounds with the standard drugs are presented in Table 2. Antimicrobial activity of metal chelates can be explained on the basis of coordination theory [25]. On chelation, the polarity of the metal ion will be reduced to a greater extent due to the overlap of the ligand orbital and partial sharing of the positive charge of the metal ion with donor groups. Further, it increases the delocalization of π electrons over the whole chelate ring and enhances the presentation of the complexes into lipid membranes and blocking of

the metal binding sites in the enzymes of microorganism. These complexes also disturb the respiration process of the cell and thus block the synthesis of proteins, which restricts further growth of the organism.

Table:2 Antimicrobial Activities of Metal Complexes of FBU

Compound	*Bacillus substillis*	*Staphylococcus Aureus*	*Escherichia Coli*	*Pseudomonas aeruginosa*	*Candida albicans*	*Aspergillus niger*
FBU	23	19	21	20	11	23
Cu(II) complex	20	17	22	19	12	17
Co(II) complex	19	22	20	23	15	18
Ni(II) complex	19	20	19	25	12	19
Zn(II) complex	20	19	28	18	18	20
Standard	30*	23*	31*	30*	33**	32**
Solvent(DMSO)	NI	NI	NI	NI	NI	NI

NI=No Inhibition,*Ciprofloxacin, * *Nystatin

5.0 CONCUSION

A new mannich base, (1-(3-(furan-2-yl)-3-oxo-1-phenyl propyl)urea and its metal complexes have been synthesized and characterized by elemental analysis and spectral studies.

REFERENCES

Sujatha, S., Rajendran, T. M., Kannappan, R. Venkatesan R. and Sambasiva Rao., P., Proc.Ind.Acad. Sci.,(Chem Sci), 112, 559(2000). doi:10.1007/BF02704363

Clearee, M., The use of conductivity measurements in organic solvents for the characterisation of coordination compounds, Crood. Chem. Rev., 7, 81-122 (1971). doi:10.1016/S0010-8545(00)80009-0

Kamalakanan, P. and Vengappayya., D., Spectral, Thermal, and Antimicrobial Studies on the Copper(II), Zinc(II), Cadmium(II), and Mercury(II) Chelates of a New Antimetabolite–5-Dimethylaminomethyl-2-Thiouracil, Russian J. Coord. Chem., 28, 423-433 (2002). doi:10.1023/A:1016032928816

Mcauliffe, C. A. and Perry, W. D., Hydrated and anhydrous nickel(II) complexes with amino-acids: bidentate and terdentate ligands, J. Chem.Soc., 1, 634-636 (1969). doi:10.1039/j19690000634

Narang, K. K., and Agarwal, A., Salicylaldehyde salicylhydrazone complexes of some transition metal ions, Inorg. Chem.Acta., 9,137-142 (1974). doi:10.1016/S0020-1693(00)89895-3