

STUDIES ON TRANSITION METAL (II) COMPLEXES DERIVED FROM MANNICH BASE

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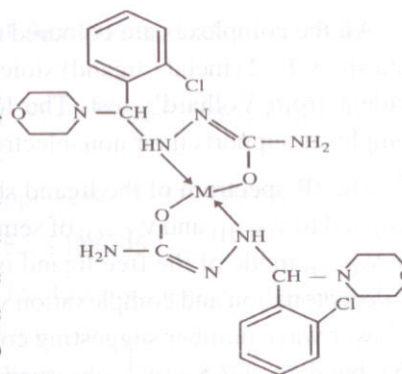
ABSTRACT

A new Mannich base ligand, N-[1-morpholino(2-chlorobenzyl)semicarbazide], formed by the condensation of morpholine, semicarbazide and 2-chlorobenzaldehyde and its complexes with Cu (II), Ni (II), Co (II) and Zn (II) have been synthesized. Their structures have been confirmed on the basis of analytical, magnetic and spectral studies. The complexes exhibit square-planar geometry. The ligand and its complexes have also been screened for their antibacterial activity against, *Staphylococcus aureus*, *Bacillus subtilis*, *Escherichia coli* and *Pseudomonas aeruginosa*. All the complexes have higher activity than that of the free Mannich base and the standard.

Key words : Mannich base, complexes.

INTRODUCTION

From the survey of existing literature, it appears that transition metal complexes have evolved great interest due to their biological properties¹⁻³. Studies of metal complexes of the benzaldehyde based Mannich bases have been reported in literature⁴⁻⁷. Metal complexes of Mannich bases containing azomethines have been studied⁸⁻¹⁰ extensively in recent years due to the selectivity and sensitivity of the ligands towards various metal ions. Azomethines constitute one of the most important classes of biologically active ligands providing potential binding sites through nitrogen and oxygen donor atoms. Keeping the above facts in mind and in continuation of our research work¹¹⁻¹³ on transition metal complexes with Mannich base, the present communication reports the synthesis of N-[1-morpholino(2-chlorobenzyl)semicarbazide] by reacting semicarbazide, morpholine and 2-chlorobenzaldehyde in 1:1:1 mole ratio and its complexation characteristics with Cu (II), Co (II), Ni (II) and Zn (II) salts. The ligand system coordinates with the metal ion in a bidentate manner through the oxygen atom of the carbonyl group and nitrogen atom of semicarbazide group. The proposed structure of the complexes is given as :



Where

M = Cu (II), Co (II), Ni (II) and Zn (II)

EXPERIMENTAL

All the reagents used for the preparation of the ligand and the complexes were Merck products. The elemental analysis was done at RSIC, CDRI, Lucknow. ^1H -NMR spectra of the samples were measured in $\text{DMSO}-d_6$ at Madurai Kamaraj University, Madurai. The IR spectra were recorded in KBr pellet using Perkin-Elmer 783 spectrophotometer. The UV-Visible spectra of the complexes were recorded on a Shimadzu UV-1601 spectrophotometer. Magnetic susceptibility measurements of the complexes were carried out using Gouy balance. Copper sulphate was used as the calibrant. The molar conductivity was measured on a Systronic conductivity bridge with a dip type cell, using 10^{-3} M solution of complexes in DMSO. The biological screening effects of the investigated compounds were tested by the well diffusion method, using Muller Hinton agar as the nutrient medium.

Synthesis of Mannich base, MBSC

Semicarbazide hydrochloride (1.11 g, 10 mmol) in 20 mL of ethanol was neutralised with ammonia. To this solution, morpholine (0.9 mL, 10 mmol) was added dropwise with constant stirring under ice-cold condition. Then, 2-chlorobenzaldehyde (1.3 mL, 10 mmol) was added dropwise under the same condition. After 5 min. the colourless solid obtained was filtered and recrystallised from ethanol. Yield: 90 % ; m.p. 225°C .

Synthesis of metal complexes

A solution of 5 mmol of MCl_2 [where M = Cu (II), Ni (II), Co (II) and Zn (II)] and the Mannich base (2.8 g, 10 mmol) in ethanol and chloroform mixture was boiled under reflux for about 3h. The pH of the resulting solution was adjusted to optimum pH 7.0 by dropwise addition of NH_3 solution. The precipitated complexes were filtered, washed with water and dried *in vacuo*.

RESULTS AND DISCUSSION

All the complexes are coloured except zinc and stable at room temperature. The elemental data show 1 : 2 (metal : ligand) stoichiometry for all the complexes. The absence of chloride is evident from Volhard's test. The low conductance values ($1.8\text{--}5.4\text{ mho cm}^2\text{ mol}^{-1}$) of the complexes supports their non-electrolytic nature.¹⁴

The IR spectrum of the ligand shows bands in the regions 3465 and 1690 cm^{-1} , which are assigned to $\nu_{(\text{N-H})}$ and $\nu_{(\text{C=O})}$ of semicarbazone, respectively^{15,16}. In the spectra of complexes, the $\nu_{(\text{C=O})}$ mode of the free ligand is not observed indicating the enolisation of C=O followed by deprotonation and complexation with metal ions. The $\nu_{(\text{C=N})}$ mode of ligand is found to shift to lower wave number suggesting coordination of azomethine nitrogen to the central metal ion. The band at 3465 cm^{-1} observed in the ligand, is absent in the complexes, suggesting deprotonation of $-\text{NH}$ of the ligand prior to the coordination to the metal.

The UV-Vis spectrum of copper complex in CH_3COOH solution displays a broad band at 14598 cm^{-1} attributable to ${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g}$ transition which strongly favour the square-planar geometry around the central metal ion¹⁷⁻¹⁹. This is further supported by the magnetic susceptibility value (1.7 BM). The cobalt complex shows a d-d band at 16420 cm^{-1} assigned as transition, which conforms square-planar geometry. This is further confirmed by its magnetic susceptibility value (4.8 BM). The nickel complex is diamagnetic suggesting the square-planar geometry. The nickel complex shows a d-d band at 25125 cm^{-1} assigned as transition¹⁸, which also indicates the square-planar geometry. Absence of any band below $10,000\text{ cm}^{-1}$ rules out the possibility of tetrahedral structure for nickel complex.

The ${}^1\text{H}$ -NMR spectra of the ligand shows a multiplet between 7.1 and 7.9 δ , which is due to aromatic protons. It shows a signal at 6.9 δ assigned to the -CH group. A broad absorption around 6.2 δ is due to the NH proton; morpholine -N-CH₂ at 2.5-2.6 δ and morpholine O-CH₂ at 3.3-3.4 δ . The singlet corresponding to one proton at 10.0 is assigned to -N=C-OH group. In the complex, shifting of -CH and -NH protons to the downfield confirms the involvement of azomethine nitrogen in coordination to the metal ion. The peak observed at 10.0 δ in the ligand was absent in the complex suggesting that the ligand is in enol form followed by coordination of carbonyl oxygen to the metal ion *via* deprotonation.

The ligand PBSC and complexes were tested for antibacterial activity. Mueller-Hinton agar was used for testing the susceptibility of microorganism by well diffusion method²⁰ using DMSO as solvent, at a concentration of 0.1M against Gram-positive (*S.aureus*, *B.subtilis*) and Gram-negative (*E.coli*, *P.aeruginosa*) bacteria. The zones of inhibition against the growth of microorganisms were determined at the end of an incubation period of 24 h at 37⁰ C and the results are presented in Table 1. It was found that the metal complexes are more active than the free ligand. 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^{21,22}.

Table 1. Antibacterial activity of ligand and its metal complexes

Compound	Zone of inhibition (in mm)			
	<i>S. aureus</i>	<i>B. subtilis</i>	<i>E. coli</i>	<i>P. aeruginosa</i>
MBSC	7.0	7.0	6.0	5.0
Cu(MBSC) ₂	14.0	10.0	13.0	14.0
Co(MBSC) ₂	10.0	9.0	11.0	7.0
Ni(MBSC) ₂	11.0	12.0	10.0	11.0
Zn(MBSC) ₂	9.0	14.0	12.0	13.0
Ampicillin	8.0	5.0	7.0	9.0

CONCLUSIONS

Transition metal (II) complexes have been synthesised from the Mannich base, N-[1-morpholino(2-chlorobenzyl)semicarbazide] and characterized by elemental data, magnetic and spectral analyses. The metal complexes exhibit higher activity than the free ligand and the standard, ampicillin.

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