

Physico chemical and biocidal studies of metal complexes of Bidentate schiff base derived from 2-hydroxy-1-Naphthaldehyde and p-anisidine

Raj Kamal Sahu* and Basanti Singh

*University Department of Chemistry, T.M. Bhagalpur University, Bhagalpur-812007

Email. Id: sahurajkamal60@gmail.com

Manuscript received online 02 November 2017, accepted on 04 December 2017

Abstract: Synthesis of Schiff base derived from 2-hydroxy-1-naphthaldehyde and p-anisidine, and its (1:2) Cu^{2+} , Ni^{2+} , Zn^{2+} , and Mn^{2+} derivatives, have been described. The analytical, IR and magnetic studies have been carried out to suggest tentative structure for the complexes. The biocidal studies have also been undertaken.

(Keywords : Schiff base, 2-hydroxy-1-naphthaldehyde and p-anisidine)

Introduction

Metal complexes of Schiff bases¹⁻⁴ have played a central role in the development of coordination chemistry and are known over a century for their increasing uses as biochemical and antimicrobial agents. Pfeiffer et al⁵, carried out a systematic study of Schiff base complexes. Thereafter a lot of work has been done on the complexes of Schiff bases⁶⁻⁹. The survey of literature reveals that much work has been done on the synthesis and physio-chemical studies of first row transition metal complexes¹⁰⁻¹² of a number of Schiff bases. In this communication the results of the physio-chemical and biocidal studies of the Cu(II) , Ni(II) , Zn(II) and Mn(II) complexes of Schiff base obtained by the condensation of 2-hydroxy-1-naphthaldehyde and p-anisidine have been reported.

Experimental:

The metal chlorides and other chemicals used were of AR grade unless stated otherwise.

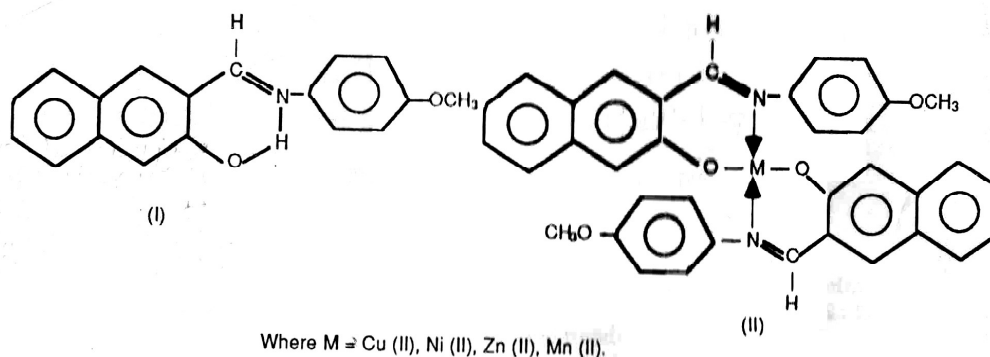
(a) Synthesis of ligand:

The title Schiff base was synthesized¹³ by mixing the recrystallised 2-hydroxy-1-naphthaldehyde (0.1 M, 17.2 gm) and p-anisidine (0.1 M, 12.3 gm) in equimolar ratio in an ethanolic medium and refluxing this mixture for about two hours on a water bath in presence of few drops of piperidine as condensing agent. The reaction mixture on ice-cooling gave the Schiff base in the form of needle shaped golden yellow crystals in good yield. The product was filtered, dried and recrystallised from ethanol.

(b) Synthesis of metal complexes:

The ethanolic solution of crystallized ligand (0.02 M, 5.54 gm) was mixed with (0.01M) metal chloride ($\text{M}^{2+} = \text{Cu}^{2+}$, Ni^{2+} , Zn^{2+}) and Mn^{2+} solution keeping ligand metal ratio 2: 1. The mixture was then refluxed for 3 hours on a water bath. The refluxed material was concentrated and ice-cooled. On adjusting the pH of the concentrate between 4-5 in the case of copper complex and at 8 in the case of other metal complexes under study, the solid derivatives were obtained. The complexes were filtered under suction and washed with ethanol and air-dried.

The Schiff base and the metal complexes were analyzed and characterized by its elemental analysis (table-1) and IR spectral studies. On the basis of the results of these studies the following tentative structure for the Schiff base (I) and its metal derivatives (II) may be proposed.



The IR spectra of the Schiff base and the metal derivatives were recorded on perkinelmer spectrophotometer (IR 4250) in KBr/CsI matrix in the region $4000\text{--}200\text{cm}^{-1}$. The magnetic susceptibilities were measured on a Gouy balance at room temperature.

Results and Discussion

The analysis and magnetic moment data of the complexes are given in table-I. The calculated and the experimental values for the

analysis of C, H, N and the metal in the complexes are in agreement, within the limits of experimental error.

The structure and coordination of Schiff base and its metal derivatives can be explained on the basis of their IR spectra. The title Schiff base having imino nitrogen atom and hydroxyl oxygen as the principal bonding sites behaves as a bidentate ligand. The IR bands of the ligands and the complexes can be explained on the basis of earlier studies¹⁵.

Table-1 : Analytical and Magnetic Moment Data

Compd. (Mol. Wt.)	M.P.	Colour	% Found (Calculated)				μ eff. B.M.
			M	C	H	N	
Schiff base (Hydroxy-PA) 277	120	Yellow	- (77.97)	77.99 (5.41)	5.31 (5.05)	5.26	
[Cu(Hydroxy-PA) ₂] (615.54)	233	Brown	10.66 (10.32)	69.80 (70.18)	4.33 (4.54)	4.31 (4.25)	1.80
[Ni(Hydroxy-PA) ₂ 2H ₂ O] 646.71	235	Green	9.20 (9.07)	67.02 (66.79)	5.11 (4.94)	3.96 (4.23)	3.22
[Zn(Hydroxy-PA) ₂] 617.38	200	Light Yellow	10.61 (10.58)	70.07 (69.97)	4.54 (4.53)	5.00 (4.63)	0.90
[Mn(Hydroxy-PA) ₂ 2H ₂ O] 642.94	208	Orange Yellow	8.44 (8.54)	66.92 (67.19)	5.25 (4.97)	4.54 (4.35)	5.88

The ligand shows a band at 2750 cm^{-1} which is assigned to the intramolecular hydrogen bonding¹⁶ v OH. In the corresponding complexes this band is absent which indicates the cleavage of H-bonding, leading to the deprotonation during coordination to the metal ion resulting in the formation of the O-M bond¹⁷. A strong band due to C=N stretching (azomethine) in ligand appears around 1610 cm^{-1} which upon complexation suffers a downward frequency shift suggesting the involvement of azomethine nitrogen atom in coordination with the metal ion.

Strong to medium intensity bands observed in the region $580\text{-}260\text{ cm}^{-1}$ are assigned to M-N and M-O stretches¹⁸⁻²⁰.

The magnetic susceptibilities data evidenced that the complexes of Cu^{2+} , Ni^{2+} , Mn^{2+} were paramagnetic in nature except the complex of Zn^{2+} which was found to be diamagnetic. The data recorded in table-1 showed the high spin octahedral geometry²¹ in the case of Ni^{2+} and Mn^{2+} complexes, whereas in the case of Cu^{2+} , values of Bohr magneton (1-80) was found to be normal²²

corresponding to one unpaired electron, which is well within the range reported for most of the distorted octahedral Cu^{2+} complexes.

The antimicrobial activities of the prepared Schiff base and its metal derivatives were tested on some bacteria viz *Salmonella typhi*, *Escherichia coli*, *Pseudomonas fluorescens*, *Proteus vulgaris* and *Staphylococcus aureus* employing filter paper disc diffusion plate method²³⁻²⁴ (zone inhibition technique). Almost all the prepared metal complexes exhibit appreciable anti-bacterial activity. The antifungal activities of these complexes were also investigated against *Fusarium oxysporum* and *Penicillium citrinum* employing Agar plate technique²⁵⁻²⁶. The metal complexes of the prepared Schiff base and *Penicillium citrinum* showed better biocidal activity in comparison to that of parent Schiff base. The activities were increased with increasing concentration. Most of the metal complexes were found to inhibit the total growth at 300 ppm concentration. The studies were made at different concentration lower than 300 ppm.

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Abstracted / Indexed in : Chemical Abstract U.S.A.

JC- 1270/2K18 (ISSN:0973-239X), INDIA

Journal Chemtracks Vol. 20 (1&2), 19-22, January to December 2018