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SYNTHESIS AND CHARACTERIZATION OF N, N'-BIS-(3-METHOXYSALICYL)-*p*-PHENYLENEDIIMINATO COPPER (II) COMPLEX COMPOUND

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ABSTRACT

N,N'-bis(3-methoxysalicyl)-p-phenylenediimine Schiff base was prepared from the interaction of ethanolic solution of 3-methoxysalicylaldehyde and p-phenylenediamine. The Cu (II) Schiff base complex was synthesized from aqueous solutions of $CuCl_2.2H_2O$ and ethanolic solution of N, N'-bis(3-methoxysalicyl)-p-phenylenediimine. The Cu (II) Schiff base complex decomposed at 280^oC. The ligand is soluble in most common organic solvents except nitro benzene. The Cu (II) Schiff base complex is insoluble in most solvents except DMF and DMSO. The molar conductance value of Cu (II) Schiff base complex is 7.8 ohm^{-} cm^2mol^{-1}. The empirical formula of the metal Schiff base compound determined is $[CuL].2H_2O$. The spectral data of the ligand and its Cu (II) complex compound were used to characterize the complex. The dissociation constant of the Schiff base (pKa) determined is 10.23. The stability constant of Cu (II) Schiff base complex was found to be 3.55 x 10^6.

Keywords: Schiff base, 3-methoxysalicylaldehyde, *p*-phenylenediamine, Stability constant.

INTRODUCTION

Schiff bases are of the general formula $R_1R_2C=N-R_3$ (where R_3 is an alkyl or aryl group) and can be synthesized from an aromatic amine and a carbonyl compound in a nucleophilic addition reaction to a hemiaminal followed by the elimination of water from the imine (Patai., 1970). The condensation of primary amine with an aldehyde gives the aldimines while that of the ketones produces the ketoimines (Cotton, 1972).

The design and synthesis of Schiff base ligands and their complexes has been the subject of interest in the recent past (Maurya *et al.,*2008) which is due to their possession of excellent characteristics, structural similarities with natural biological substances, relatively simple preparation procedures and a synthetic flexibility that enables design of suitable structural properties (Patai, 1970).

Schiff bases are used as substrates in the preparation of a number of industrial and biologically active compounds via ring closure, cycloaddition and replacement reactions. They have a wide variety of applications in many fields e.g.; biological, inorganic, and analytical chemistry (Cimerman *et al., 2000*).

Medicinally, the microbial resistance to antibiotics in use nowadays necessitates the search for new compounds with potential effects against pathogenic bacteria. Thus, extensive investigations in the field of Schiff bases have been reported and a range of these compounds have been synthesized, their chemical, physical and complexation behavior studied (Jigna *et al.*, 2005). For example, El-ajaily *et al* (2005) reported the antibacterial activity of some Schiff base complexes derived from Salicylaldehyde and histidine with some divalent transition metal ions. Furthermore, Syed (1993) reported the synthesis, characterization and biological evaluation of some Schiff base metal complexes derived from Anthranilic acid-sugar and naturally occurring amino acid-sugar.

Schiff bases are also widely applicable in analytical determination. Applications of many new analytical devices require the presence of organic reagents as essential compounds of the measuring systems. For example, they are used in optical and electrochemical sensors, as well as in various chromatographic methods to enable detection of enhance selectivity and sensitivity (Khan *et al.*, 2002). Mohamed *et al* (2007) reported the reaction of some aromatic amines with aromatic aldehyde and their use as fluorimetric analytical reagents. Schiff bases are used as rubber accelerators, dyes, reaction intermediates and also as liquid crystals in electronic display systems (Peter, 1990).

Transition metal Schiff base complexes are applicable in areas such as electrochemistry, catalysis, bioinorganic, metallic deactivators, separation techniques and environmental chemistry (Trevin *et al.*, 1997). Perla *et al.* (2006) reported the synthesis of Ni (II) and Co(II) complexes with N,N'-Bis(2-benzyl)ethylenediimine as modifying agents to produce chemically modified electrodes used to facilitate the detection of organic pollutants in water. This paper reports the synthesis and characterization of the complex: N,N'-bis(3-methoxysalicyl)-*p*-phenylenediiminato copper (II) complex.

MATERIALS AND METHODS

The solvents and reagents used in this research work are of Analar grade purity and were used without further purification. Distilled water was used in the preparation of reagents and the glass wares used were washed with detergent, rinsed with distilled water, soaked in (1:4) HNO_3, rinsed again with distilled water and then dried in an oven at 110^oC. Samples were weighed using an electric Metler Balance Model AB 54. pH and electrical conductivity measurements were carried out using Jenway pH meter Model 3320 and a conductivity meter Model 4010 respectively.

IR spectra analysis was recorded using a Fourier transformed spectrophotometer model IR Genesis series using KBr pellets in the range 4000 – 400cm^{-1}. The melting point of the ligand and the decomposition temperature of the complex were determined using Gallenkemp melting point apparatus.

Preparation of Schiff base

An ethanolic solution (50cm^3) of 3-Methoxysalicylaldehyde (3.043g, 20mmol) was added to an ethanolic solution (50cm^3) of *p*-Phenylenediamine, (1.081g, 10mmol), in a 500cm^3 round bottom flask. The mixture was refluxed for 5hours. A solid mass separated out on cooling and was suction-filtered, washed several times with ethanol, recrystallised and subsequently dried over P_2O_5 in a dessicator (Joshi *et al.,* 1984).

Synthesis of the metal complex

The copper (II) Schiff base metal complex was synthesized by mixing an ethanolic solution (50cm^3) of the Schiff base (3.744g, 0.01mol) with an ethanolic solution (50cm^3) of copper (II) chloride (1.7048g, 0.01mol). The resulting mixture was refluxed for 4hours. On cooling, a coloured complex precipitated out which was suction - filtered, washed several times with ethanol and finally with ether and was dried over P_2O_5 in a dessicator (Joshi *et al.*, 1984).

RESULTS AND DISCUSSION

The interaction of 3-Methoxysalicylaldehyde with *p*-phenylenediamine yielded N, N'- bis(3-methoxysalicyl)-*p*-phenylenediimine. The Schiff base is a green crystalline solid with sharp melting point (188^{0}C) with a percentage yield of 69% (Table 1). Further interaction of this Schiff base with copper (II) ion produced an intense coloured Schiff base complex compound with an appreciable percentage yield (Table 1).

The Schiff base is soluble in most organic solvents except nitro benzene. However, the copper (II) Schiff base complex is insoluble in organic solvents except DMF and DMSO (Table 2).

The observed molar conductance (Table 3) of the complex in 10^{-3}M DMSO solution is 7.8 ohm^{-1}cm^{2}mol^{-1} which is low, revealing the non-electrolytic nature of the complex compound.

The empirical formula calculated from the quantitative analysis results of the ligand, metal and water determined, suggested the molecular formula; [CuL].2H_2O for the complex (Table 4).

The IR spectra of the Schiff base ligand showed a sharp band at 1593cm^{-1} attributed to the *v*(C=N) stretching vibration mode which confirmed the condensation reaction between 3-Methoxysalicylaldehyde and *p*-Phenylenediamine. The slight change in this wave number (1596cm^{-1}) in the complex suggested the coordination of the azomethine nitrogen to the metal center. This is further substantiated by the presence of new bands in the regions 599cm^{-1} and 488cm^{-1} assignable to *v*(Cu-O) and *v*(Cu-N) stretching vibrations (Table 5). The characteristic phenolic group *v*(O-H) mode due to the presence of a hydroxyl group at the "ortho-" position in the ligand was observed in the region 3409cm^{-1}. A broad band in the region 3430 - 3500cm^{-1} in the complex provides evidence for the presence of water of crystallization.

The average dissociation constant (pKa) of the ligand is 10.228. This value revealed that the ligand is a weak acid. A plot of Log [A$^-$] against number of coordinated ligand (n) was made and from the graph, the stability constant of the corresponding complex compound was evaluated. The stability constant of the Schiff base complex was found to be 3.55 X 10^6 (Table 6). This good thermodynamic stability of the complex may be due to the chelation effect of the ligand which is almost like a cage i.e the metal is almost caged within an envelope of the ligand, hence the higher stability. The high stability constant value is supported by relative high decomposition temperature of the complex compound (280^{0}C). The number of coordinated ligand to copper (II) ion determined is 1, this is in agreement with the result obtained from the empirical formula calculation.

From the analytical results obtained for the complex formed by N,N' –bis(3-methoxy salicyl)-*p*-phenylenediimine with the divalent metal ion, the following structure was proposed:

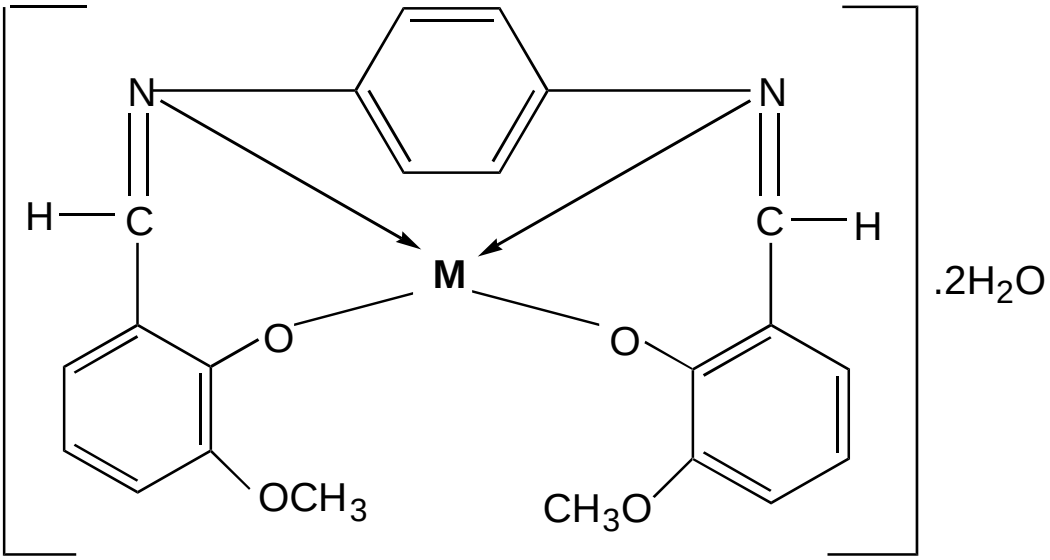

Figure 1: the proposed molecular structure of the copper (II) Schiff base complex.
M = Cu (II) or Mn (II)

Table 1: Physical Data of the Schiff base and its complex

Compound	Appearance	Melting point	Decomposition temperature	Percentage yield(%)
Ligand	Greenish yellow	188	_____	69
[CuL].2H_2O	Black	_____	265	65

KEY: L = N,N'-bis(3-methoxysalicyl)-*p*-phenylenediimine.

Table 2: Solubility of the Schiff base and its copper (II) complex

Compound	Water	Ethanol	Metanol	Acetone	DMF	DMSO	Nitro benzene
L	IS	S	S	S	S	S	IS
[CuL].2H_2O	SS	SS	SS	SS	S	S	SS

Where S = Soluble, SS = Slightly soluble., IS = Insoluble
DMF = dimethylformamide, DMSO = dimethylsulphoxide

Table 3: Molar conductivity measurement of the complex in 1 X10^{-3} DMSO solution

Complex	Electrical conductivity ($ohm^{-1}cm^{-1}$)	Molar conductivity ($ohm^{-1}cm^{2}mol^{-1}$)
[CuL].2H_2O	7.80 X 10^{-6}	7.80

Table 4: Determination of chemical composition of the complex

Parameters	Composition(%)
Cu^{2+}	14.50
Ligand	77
Water of crystallization	8.50
Molar ratio (Cu^{2+}: Ligand: H_2O)	1:1:2

Table 5: IR Spectra data of the Ligand and its complex

Name	*v*(O-H) cm^{-1}	*v*(C=N) cm^{-1}	*v*(C-O) cm^{-1}	*v*(M-O) cm^{-1}	*v*(M-N) cm^{-1}
L	3540	1593	1429	_____	_____
[CuL].2H_2O	3438	1592	1410	599	488

Table 6: Stability Constant of the Complex

Complex	Stability constatnt k_1
[CuL].2H_2O	3.55 X 10^{6}

CONCLUSION

A Schiff base was prepared by the condensation of 3 – methoxysalicylaldehyde with *p* – phenylenediamine. The corresponding Copper (II) complex was also prepared. The Schiff base and its corresponding complex were characterized through various analytical procedures, such as; gravimetric, conductivity, potentiometry and infrared spectral, analysis.

The formation of the Schiff base ligand was inferred by the appearance of a strong band in the IR spectra (1590-1603)cm^{-1} due to azomethine group. The Infrared spectra of the complex agree with the coordination to the central metal ion through the nitrogen of the azomethine (-HC=N-) group and the phenolic oxygen after deprotonation. Elemental analysis of the chelate suggested a 1:1 metal-ligand ratio. From the physical studies discussed above, the ligand have been shown to act as a tetradentate ligand which coordinate to the central metal atom to form mononuclear complexe in a 1:1 stoichiometry. The complexe under study may be formulated as: [**M**L].2H_2O.

Where **M** = Cu(II).

L = N,N'-bis(3-methoxysalicyl)-*p*-phenylenediimine.

The physical and analytical measurements carried out in this work were used in proposing the general molecular structure of the complex. However, further analysis such as crystallography, thermogravimetry, and bioactivity should be carried out to fully establish the proposed structure and its applications.

REFERENCES

Cimerman Z., Miljani S., and Galic N. (2000) "Schiff bases derived from Aminopyridines as Spectrofluorimetric analytical reagents". Croatia chemica acta **73**(1): 81-95.

Cotton F.A. and Wilkinson G. (1972). "Advanced Inorganic Chemistry" Interscience pub. New York, 3rd Edition. Pp 625.

El-ajaily, M. M., Ben-Gweirif, S., Maihub, A. A. and El-tajoury, A. N. (2005) "Chelation behaviour and biological activity of divalent metal ions towards Schiff base derived from salicylaldehyde and histidine". *Science and its application journal,* **1**: 196-210.

Jigna .P., Paranav I. and Radish .N.(2005) *Journal Serb. Chem. Soc.***70**(10): 1155-1161.

Joshi G.K., Megh S. and Sudhindra N. M. (1984). "Spectrophotometric study of some praseodymium(III) Schiff base complexes" *Indian journal of chemistry,***23A**: 329-331.

Khan S. A., Siddiqui A.A., Bhatt S., (2000) *Asian Journal, Chem.***14**: 1117.

Maurya R. C., Chourasia J. and Sharma P. (2008) "Bis (*o*-Vanillin) bemzidine(o-$V_2b_zH_2$) as a binucleating ligand with some transition metal complexes" *Ind. J. Chem*, **47**: 517.

Mohammed N. and Salah A. (2007) "Synthesis, characterization and use of Schiff bases as flourimetric analytical reagents". Journal. Chem. **4**(4): 531-535.

Patai S. (Ed,) (1970), "The Chemistry of the Carbon – Nitrogen Double bond" Wiley J. and Sons London.

Perla E. M.,, Blanca N. M. and Cecilia R. de Barbarin. (2006). "A Schiff base Nickel Complex. A new material as modifier for selective electrodes".*The Azo J. of material online,* **2**

Peter M. B. W., (1990); Academic Press Dictionary of Science and Technology, 3rd Edition, U. K. Academic Press Limited, Pp:125-129

Syed J. K. (1993) "Studies of novel Schiff base transition metal complexes" A thesis submitted to University of Punjab, Lahore.

Trevin, S., Bedioui, F., Gomez, M. G. and Charreton, C. B. (1997) "Electro polymerized nickel Micro cyclic complex – base films design and elctro catalytic application" *Journal of material chemistry,* **7**(6): 923-928.