SYNTHESIS AND CHARACTERISATION OF Cu(II) AND Zn(II) SCHIFF BASE COMPLEXES

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Abstract

A bidentate Schiff base ligand (DBAP) was synthesized by a 1:1 molar condensation of 2-aminophenol and 4-(N,N-dimethylamino)benzaldehyde. The metal(II) complexes were synthesized by refluxing the ethanolic solutions of the Schiff base and the chloride salts of the metals. The Schiff base and the complexes were characterized by melting point, decomposition temperature, solubility, elemental analysis, infrared spectra, magnetic susceptibility and molar conductivity measurements. The Schiff base was cadmium orange and has a melting point of 119 ^{o}C. The decomposition temperature of the Cu(II) and Zn(II) complexes were 147 and 138 ^{o}C respectively. The elemental analysis of the complexes established the formation of 1:2 metal - ligand ratio. The molar conductivity values revealed the non-electrolytic nature of the complexes. The infrared data suggested bidentate behavior of the Schiff base ligand and its coordination with the metal ions via the azomethine nitrogen and hydroxyl oxygen after deprotonation. The magnetic moment values of the complexes suggested a four- coordinate square planar and tetrahedral geometries for the Cu(II) and Zn(II) complexes respectively.

Keywords: Schiff base ligand, infrared, magnetic moment

Introduction

A Schiff base is a compound formed from the condensation of primary amines with either a ketone or an aldehyde. The carbonyl group of the aldehyde gives aldimines while that of ketone gives ketimines (Aliyu and Zayyan, 2014). The common structural feature of these compounds is the azomethine group with a general formula RHC=N-R^{1}, where R and R^{1} are alkyl, aryl, cyclo alkyls or heterocyclic groups which may be variously substituted (Muhammad *et al.,* 2011). Chemists haveof Schiff base derived from 4-dimethylaminobenzaldehyde and cysteine. The reported on the chemical, structural and biological of Schiff bases (Gauri *et al.*, 2011).

El-ajaily *et al.* (2007) reported the preparation and physical investigation of complexes derived from 4-dimethylaminobenzaldehyde and 4-aminoantipyrine Schiff base with Ni(II), Cu(II), Rh(III), and Pt(IV) ions. The elemental analysis showed the formation of 1:1 M-L ratio. The molar conductivity measurements revealed that the complexes are non-electrolytes in nature. The magnetic moment results showed paramagnetic phenomena for Ni(II) and Cu(II) complexes and diamagnetic phenomena for Rh(III) and Pt(IV) complexes.

El-ajaily *et al.* (2006) synthesized Ni(II) chelate complexes were characterized by various techniques.

The aim of the present work is to synthesize and characterize Cu(II) and Zn(II) Schiff base complexes derived from 4-(N,N-dimethylamino)benzaldehyde and 2-aminophenol.

Materials and Methods

Materials

All chemicals used in this work were of analar grade and used as supplied without further purification. All weighing were observed on college B154 Metler Toledo electric balance. Melting point and decomposition temperatures were determined on Stuart SMP 10 melting point apparatus. IR spectra measurements were recorded using FTIR Nicolel IS10 Thermoscientific, in the region 4000-400 cm^{-1}. Electrical conductivity measurements were carried out using Siemens WPA CM35 Conductivity meter. Magnetic susceptibility measurements were carried out using Sherwood MK1Magnetic susceptibility balance, and Pascal's diamagnetic corrections constant were applied. The metal content was determined using Atomic Absorption spectrophotometer 210 VGP. The elemental analysis of CHN was carried out at OEA labs, Callington, United Kingdom using a CE instruments (thermo) EA1110 Elemental Analyser using Xperience software.

Methods

Preparation of the Schiff base ligand (DBAP)

75 cm^3 ethanolic solution of 2-aminophenol (5.46 g, 0.05 mol) was added to the same volume of ethanolic solution of 4-(N,N-dimethylamino)benzaldehyde (6.85 g, 0.05 mol). The mixture was refluxed with stirring for 3 hours. The resulting solution was evaporated to half its volume and the precipitated product was separated, washed twice with 15 cm^3ethanol and dried over anhydrous $CaCl_2$ in a desiccator (Muna, 2009).

Synthesis of the metal (II) complexes

0.015 mol (3.6 g) of the Schiff base ligand (DBAP) dissolved in 75 cm^3 hot ethanol was added with stirring to 75 cm^{-1} ethanolic solution of 0.0075 mol of the metal(II) chlorides separately refluxed for 1 hour. On cooling to room temperature, the coloured complexes precipitated out, were separated, washed with 15cm^3ethanol and dried over anhydrous $CaCl_2$ in a desiccator (Muna, 2009)

Results

Table 1: Physical Properties of the Schiff base Ligand and its Metal(II) Complexes

Compound	M. wt. (g/mol)	Colour	% yield	M.P.(^oC)	D. Temp. (^oC)	Molar conductivity ($ohm^{-1}cm^2mol^{-1}$)	μ_{eff} (B.M)
DBAP	240.15	Cadmium Orange	64.72	119	-	-	-
$[Cu(DBAP)_2].8H_2O$	685.84	Black	61.22	-	147	11.72	1.51
$[Zn(DBAP)_2].3H_2O$	597.67	Crimson	71.05	-	138	15.58	0

Where; DBAP is $C_{15}H_{15}N_2O$, M.P= Melting point, D. Temp.= Decomposition temperature, M. wt.= molecular weight.

Table 2: Solubility Test of the Schiff base and its Metal(II) Complexes

Compounds	Solvents								
	Acetone	CCl_4	Chloroform	DMF	DMSO	Ethanol	Methanol	Nitro benzene	water
DBAP	S	SS	S	S	S	S	S	S	IS
$[Cu(DBAP)_2].8H_2O$	SS	SS	SS	S	S	SS	SS	SS	IS
$[Zn(DBAP)_2].3H_2O$	SS	IS	IS	S	S	SS	S	S	IS

KEY: IS=Insoluble, S=Soluble, SS= Slightly soluble

Table 3: Elemental Analysis Data of the Schiff base and its Metal(II) Complexes.

	M. wt. (g/mol)	% Found (Calculated)			
Compound		C	H	N	M
DBAP	240.15	74.68 (74.97)	6.81 (6.71)	11.52(11.66)	-
$[Cu(DBAP)_2].8H_2O$	685.84	51.97 (52.53)	3.63 (6.71)	7.93 (8.17)	9.19 (9.27)
$[Zn(DBAP)_2].3H_2O$	597.67	60.70 (60.28)	5.59(6.02)	9.32 (9.37)	10.76 (10.94)

Where DBAP is $C_{15}H_{15}N_2O$, M. Wt. = Molecular Weight

Table 4: Relevant Infra-red Frequencies (cm^{-1}) of the Schiff base Ligand and its Metal(II) Complexes.

Compounds	ν(OH) cm^{-1} Phenolic	$\nu(H_2O)$ cm^{-1}	ν(C=N) cm^{-1}	ν(C-O) cm^{-1}	ν(M-N) cm^{-1}	ν(M-O) cm^{-1}
DBAP	3335.14	-	1615.10	1374.16	-	-
$[Cu(DBAP)_2].8H_2O$	-	3446.93	1593.74	1339.48	472.08	445.99
$[Zn(DBAP)_2].3H_2O$	-	3386.86	1576.37	1363.00	472.73	458.22

Discussion

The Schiff base and its metal (II) complexes were prepared in good yield, ranging from 48.21-64.72%. The Schiff base was cadmium orange solid while the Cu(II) and Zn(II) complexes are respectively black and lemon yellow non-hygroscopic crystals. The molar conductance of the complexes was determined. It was found to be 12.64 and 18.53 $ohm^{-1}cm^2mol^{-1}$ for the Cu(II) and Zn(II) complexes respectively. These low values suggested their non-electrolytic nature (Eman, 2015).

The effective magnetic moments of the complexes were calculated. Although the value is found to be a bit lower than expected, the magnetic moment of 1.51 B.M observed for Cu(II) complex is suggestive of square planar geometry, indicating one unpaired electron (De *et al.,* 2008; Eman, 2015). The magnetic moment for Zn(II) complex is zero as expected for a d^{10} configuration and was found to be diamagnetic suggesting a tetrahedral geometry (Iqbal *et al*., 2007; Muna, 2009). The physical properties are presented in Table 1. The solubility of the Schiff base and its metal (II) complexes were determined in water and some common organic solvents. The Schiff base was found to be soluble in all the solvents used except carbontetrachloride and water. The complexes were soluble in DMSO, DMF and methanol but insoluble in water and slightly soluble in the other solvents. The result is presented in Table 2.

The elemental analysis of the Schiff base and its metal(II) complexes were determined. The observed and calculated values were in good agreement. The elemental analysis data of the Schiff base suggested the formation of $C_{15}H_{15}N_2O$ while that of the complexes revealed the formation of $[Cu(DBAP)_2].8H_2O$ and $[Zn(DBAP)_2].3H_2O$. The complexes are formed in 1:2 metal-ligand ratio. This is in agreement with similar works done and suggested the relative purity of the compounds (Muna, 2009; El-ajaily *et al.,* 2007). The results are presented in Table 3.

The infrared spectrum of the Schiff base showed a band due to the phenolic ν(OH) stretching vibration at ~ 3335 cm^{-1}. This band disappeared in the spectra of the complexes suggesting deprotonation and involvement of the oxygen atom in

complexation (Abdullahi and Gareth, 2013). The broad band at ~3447 and 3387 cm^{-1} in the spectra of the complexes are attributed to water of hydration (El-ajaily *et al.,* 2007). The band at ~1615 cm^{-1} in the free ligand is assigned to the *v*(C=N) stretching vibration. This band shifted towards lower frequencies of ~1594 and 1576 cm^{-1} in the complexes suggesting the participation of the nitrogen atom of the azomethine in coordination (Usharani *et al.,* 2012; Suresh and Prakash, 2010). The *v*(C-O) phenolic stretching of the Schiff base is observed at ~ 1374 cm^{-1} which got shifted to lower frequencies of ~1340 and 1363 cm^{-1} in the complexes. This is indicative of coordination through the phenolic oxygen (Mounika *et al*., 2010). The coordination of the Schiff base with the metals is further evidenced by the appearance of weak low frequency non-ligand bands at ~ 472 and 473 cm^{-1} due to *v*(M-N) stretching vibration, and at ~ 446 and 458 cm^{-1} due to *v*(M-O) stretching vibration (Zahid *et al.,* 2001; Rasha and Farah, 2012). The IR spectra are shown in Fig. 4, 5 and 6. The results are presented in Table 4.

Conclusion

The Schiff base and its metal (II) complexes were synthesized and characterized. The conductivity measurement data revealed that the complexes are non-electrolytes. The elemental analysis data confirmed 1:2 metal to ligand ratio. The infrared data indicated that the Schiff base ligand acted as bidentate ligand coordinated to the metal ions through the imine nitrogen and oxygen atom of the hydroxyl group after deprotonation. The magnetic moment suggested a four-coordinate square planar and tetrahedral geometries for the Cu(II) and Zn(II) complexes respectively.

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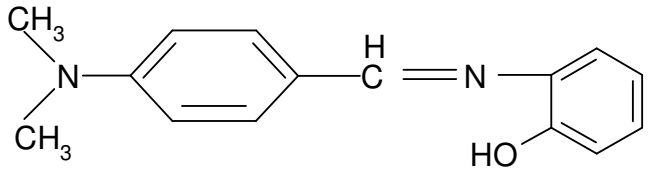


Fig. 1: proposed structure of the Schiff base

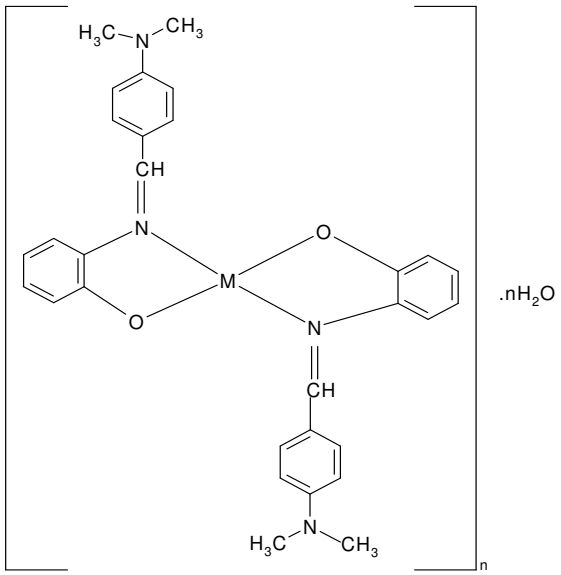


Fig. 2: proposed structure of Cu(II) complex

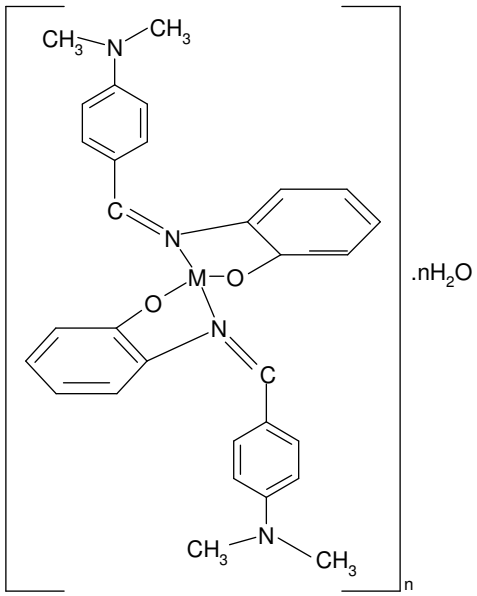
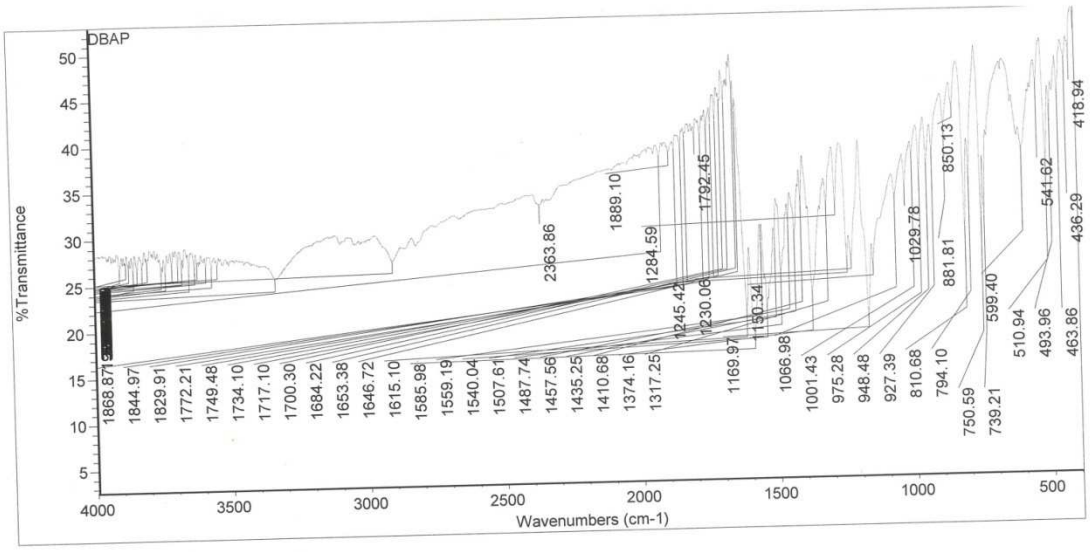


Fig. 3: proposed structure of Zn(II) complex



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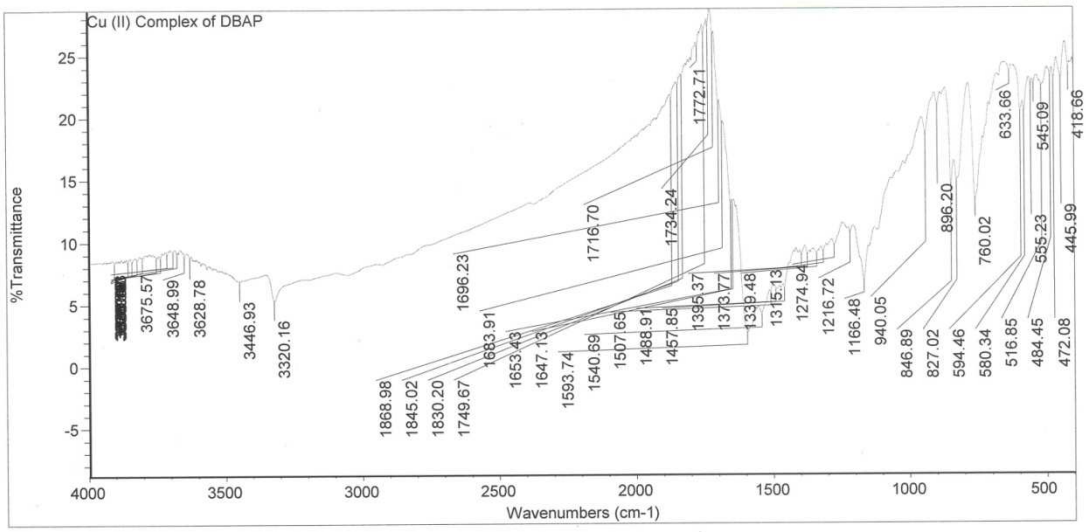
Region: 4000.00 400.00
Absolute threshold: 51.876
Sensitivity: 56

Fig. 4: IR Spectrum of the Schiff Base



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Sensitivity: 74

Fig. 5: IR Spectrum of Cu(II) Complex

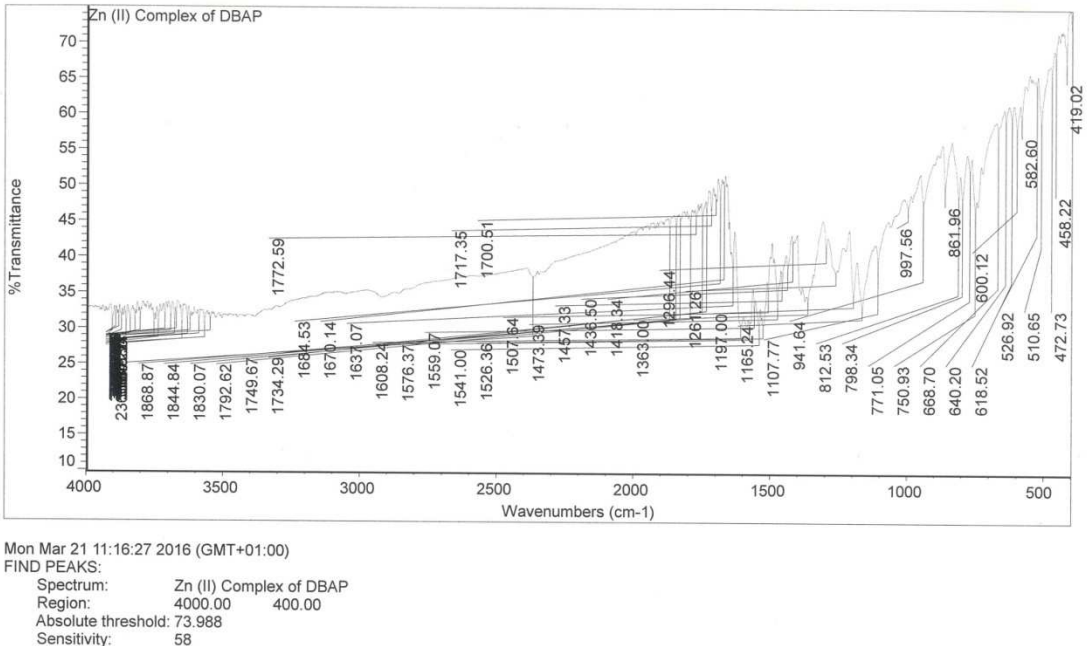

Fig. 6: IR Spectrum of Zn(II) Complex

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