SYNTHESIS AND CHARACTERIZATION OF COBALT(II) AND NICKEL(II) COMPLEXES WITH A SCHIFF BASE DERIVED FROM 2-AMINOPHENOL AND 4-(N,N-DIMETHYLAMINO)BENZALDEHYDE

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Abstract

The Schiff base ligand (DBAP) was synthesized in ethanol by condensation reaction of 2-aminophenol and 4-(N,N-dimethylamino)benzaldehyde in 1:1 molar ratio. The metal(II) complexes were formed by refluxing the chloride salts of the metals with the Schiff base ligand. The Schiff base ligand and its complexes were characterized on the basis of melting point/decomposition temperature, solubility, elemental analysis, molar conductivity measurement, infrared spectra and magnetic susceptibility. The ligand and the complexes were variously coloured, non-hygroscopic crystalline solids. The ligand has a melting point of 119 $^{\circ}$C while the decomposition temperature of the Co(II) and Ni(II) complexes are 146 and 140 $^{\circ}$C respectively. The elemental analysis data of the complexes showed the formation of 1:2 metal - ligand ratio. The molar conductivity measurements 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 value of the Co(II) complex suggested a distorted square planar structure and a four- coordinate tetrahedral geometry for the Ni(II) complex.

Keywords: Synthesis, Characterization, Schiff base ligand

Introduction

Schiff bases are compounds containing a carbon-nitrogen double bond (C=N) with the nitrogen atom connected to an aryl or alkyl group but not hydrogen (Ndahi e*t al*, 2012). They result from the condensation of primary amines with ketones or aldehydes to give imines containing a C=N (Rizwan and Santha, 2012). The common structural feature of these compounds is the azomethine group with a general formula RHC=N-R1, where R and R1 are alkyl, aryl, cyclo alkyls or heterocyclic groups which may be variously substituted (Muhammad *et al*, 2011). Chemists have reported on the chemical, structural and biological of Schiff bases (Gauri *et al*, 2011).

The preparation and physical investigation of complexes derived from 4-dimethylamino benzaldehyde and 4-aminoantipyrine Schiff base with Ni(II), Cu(II), Rh(III), and Pt(IV) ions has been reported (El-ajaily *et al,* 2007). 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.

Cu(II), Zn(II) and Cd(II) metal complexes of Schiff base derived from 2-

aminobenzoic acid and 4-(N,N-dimethylamino)benzaldehyde were synthesized. The complexes were investigated by several physicochemical techniques such as elemental analysis, IR and electronic spectra, molar conductance and magnetic moment measurements (Muna, 2009). Ni(II) chelate of Schiff base derived from 4-dimethylaminobenzaldehyde and cysteine was synthesized. The complexes were characterized by various techniques (El-ajaily *et al,* 2006). Due to paucity of information, the present work aims at synthesizing and characterizing Ni(II) and Co(II) Schiff base complexes derived from 2-aminophenol and 4-(N,N-dimethylamino) benzaldehyde .

Materials and Methods

All chemicals used in this work were of analar grade and used as supplied without further purification. All weighing were carried out 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 4000-400cm^{-1}. 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. The metal contents were determined using Atomic Absorption spectrophotometer 210 VGP. 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 correction constants were applied.

Preparation of the Schiff base (DBAP)

The Schiff base was prepared by adopting a procedure in the literature (Muna, 2009). 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^{3}ethanol and dried over anhydrous $CaCl_2$ in a desiccator.

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^3 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 15 cm^3 ethanol and dried over anhydrous $CaCl_2$ in a desiccators (Muna, 2009).

Results

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

Compound	M. wt (g/mol)	Colour	% yield	M.P.(°C)	D. Temp. (°C)	Molar conductivity	μ_{eff} (B.M)
DBAP	240.15	Cadmium Orange	64.72	119	-	-	-
$[Co(DBAP)_2].4H_2O$	609.23	Black	53.14	-	146	10.49	3.59
$[Ni(DBAP)_2].15H_2O$	843.01	Lemon Yellow	48.21	-	140	16.36	4.10

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	Chloro form	DMF	DMSO	Ethanol	Methanol	Nitro benzene	water
DBAP	S	SS	S	S	S	S	S	S	IS
$[Co(DBAP)_2].4H_2O$	SS	SS	SS	S	S	SS	S	SS	IS
$[Ni(DBAP)_2].15H_2O$	SS	IS	SS	S	S	SS	S	IS	IS

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

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

Compound	M. wt. (g/mol)	% Found (Calculated)			
		C	H	N	M
DBAP	240.15	74.68 (74.97)	6.81 (6.71)	11.52(11.66)	-
$[Co(DBAP)_2].4H_2O$	609.23	58.80 (59.14)	4.70 (6.24)	9.55 (9.19)	9.46 (9.67)
$[Ni(DBAP)_2].15H_2O$	843.01	41.79 (42.73)	5.22 (7.11)	6.04 (6.64)	6.78 (6.96)

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 and its Metal(II) Complexes.

Compounds	ν(OH) cm^{-1} Phenolic	νOH(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	-	-
$[Co(DBAP)_2].4H_2O$	-	3275.46	1590.21	1368.90	538.02	472.27
$[Ni(DBAP)_2].15H_2O$	-	3359.01	1592.94	1339.39	548.13	439.17

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 Co(II) and Ni(II) complexes are black and lemon yellow non-hygroscopic crystals respectively. The molar conductance of the complexes was determined in dimethylformamide (DMF). It was found to be 12.64 and 18.53 $ohm^{-1}cm^2mol^{-1}$ for the Co(II) and Ni(II) complexes respectively. These low values suggested their non-electrolytic nature (Eman, 2015).

The effective magnetic moments of the complexes were calculated. The observed magnetic moment of 3.59 B.M for Co(II) complex suggested a distorted square planar structure while 4.10 B.M for Ni(II) complex is complimentary to tetrahedral geometry (De, 2008).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 dimethylsulphoxide (DMSO), DMF and methanol but insoluble in water and slightly soluble in the other solvents. The results are presented in Table 2. The elemental analysis of the Schiff base and its metal(II) complexes were determined. The found and calculated values were fairly in good agreement thus suggesting the purity of the compounds (Abdullahi and Gareth, 2013). 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 $[Co(DBAP)_2].4H_2O$ and $[Ni(DBAP)_2].15H_2O$. The complexes are formed in 1:2 M-L ratio. 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 $\simeq$ 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 $\simeq$3276 and 3359 cm^{-1} in the spectra of the complexes are attributable to water of hydration (El-ajaily *et al,* 2007). The band at $\simeq$1615 cm^{-1} in the free ligand is assigned to the ν(C=N) stretching vibration. This band shifted towards lower frequencies of $\simeq$1590 and 1593 cm^{-1} in the complexes suggesting the participation of the nitrogen atom of the azomethine in coordination (Usharani *et al*, 2012; Suresh and Prakash, 2012). The ν(C-O) phenolic stretching of the Schiff base is observed at $\simeq$ 1374 cm^{-1} which got shifted to lower frequencies of $\simeq$1369 and 1339 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 ≃ 538 and 548 cm^{-1} due to *v*(M-N) stretching vibration, and at ≃ 472 and 479 cm^{-1} due to *v*(M-O) stretching vibration (Zahid *et al*, 2001; Rasha and Farah, 2012). The results are presented in Table 4 and the IR spectra are shown in figs. 4, 5 and 6.

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 moments suggested a four-coordinate distorted square planar for Co(II) and tetrahedral geometry for Ni(II) complexes.

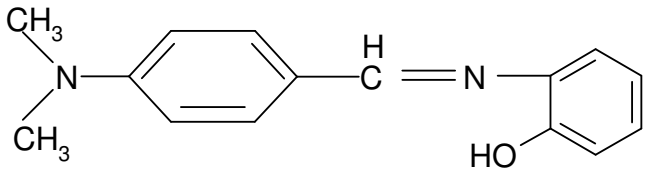


Fig. 1: proposed structure of the Schiff base

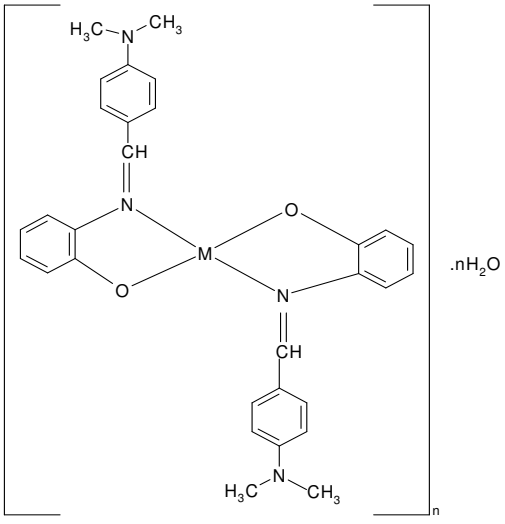


Fig. 2: proposed structure of Co(II) complex

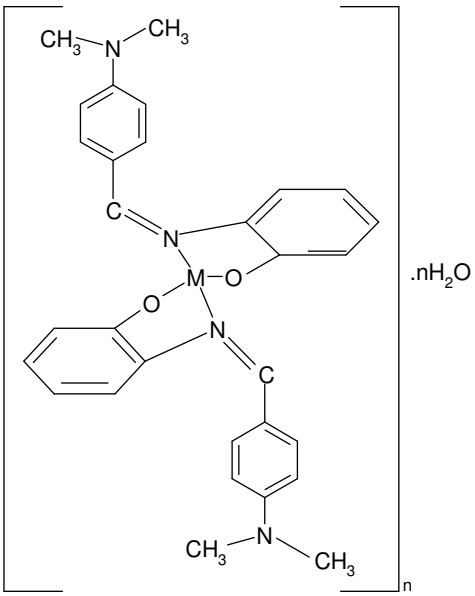
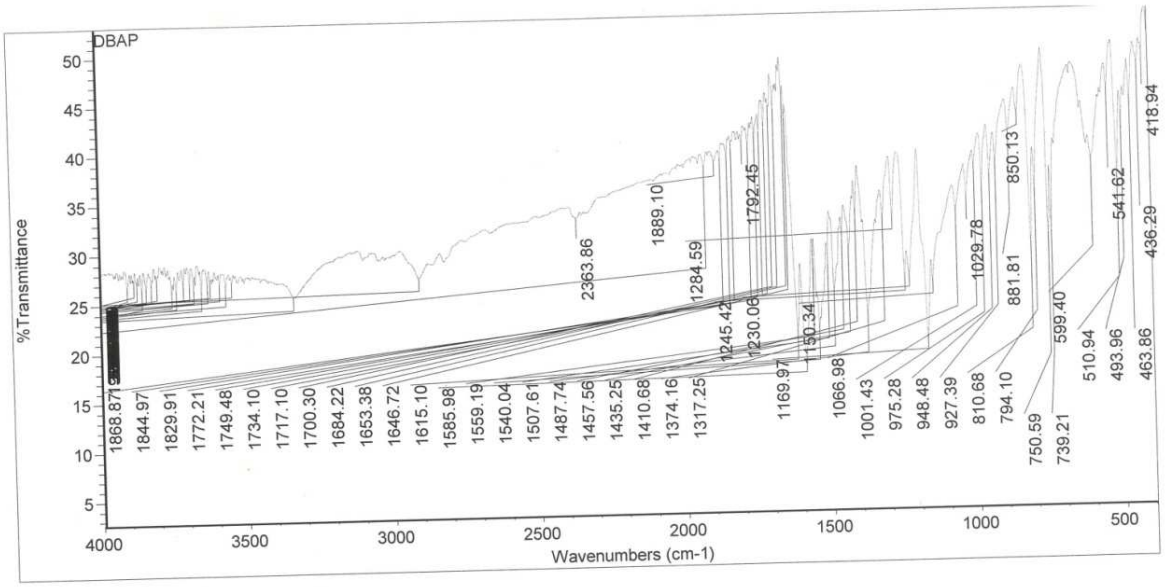


Fig. 3: proposed structure of Ni(II) complex



Mon Mar 21 11:19:27 2016 (GMT+01:00)
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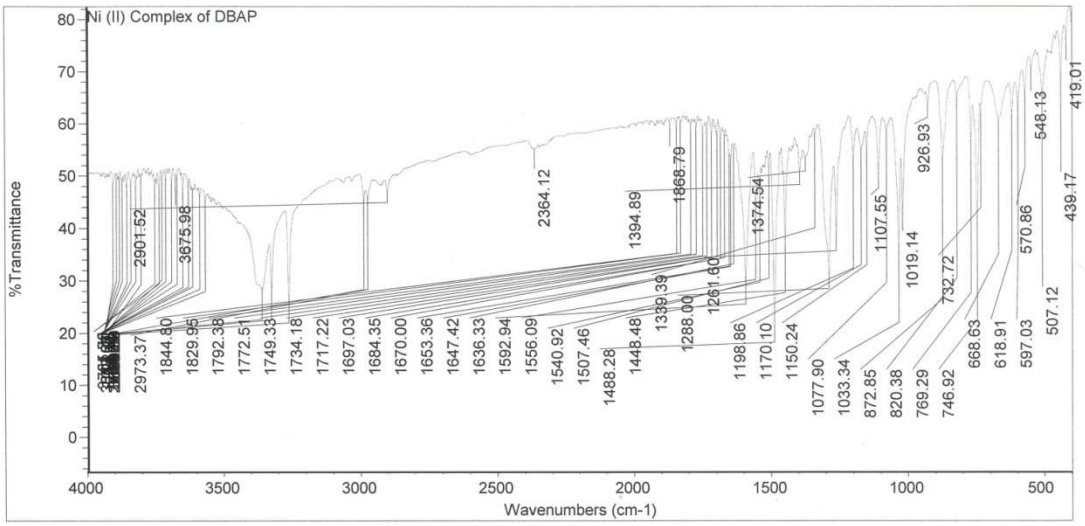
Region: 4000.00 400.00
Absolute threshold: 51.876
Sensitivity: 56

Fig. 4: IR Spectrum of Schiff Base



Mon Mar 21 11:26:33 2016 (GMT+01:00)
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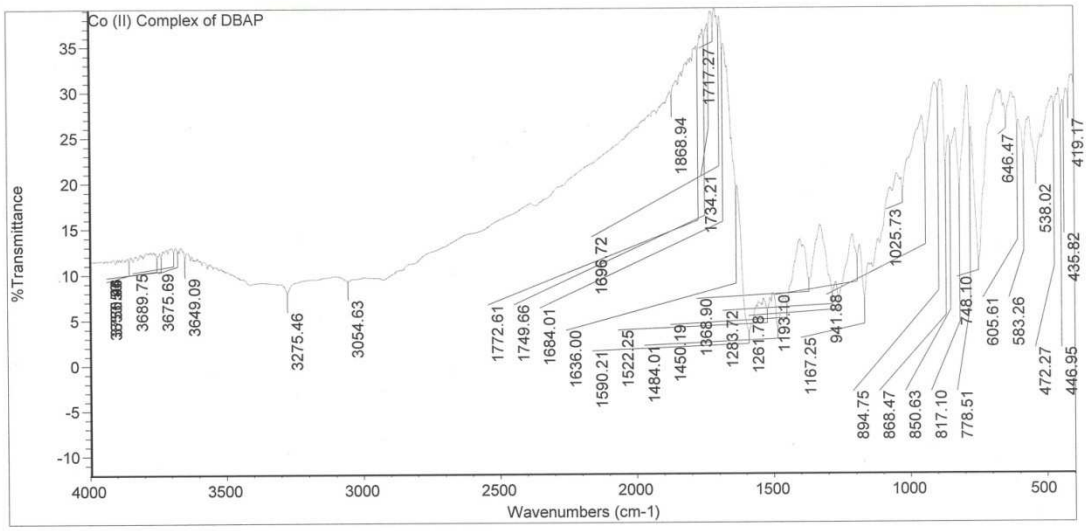
Region: 4000.00 400.00
Absolute threshold: 81.717
Sensitivity: 62

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



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Region: 4000.00 400.00
Absolute threshold: 38.342
Sensitivity: 67

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

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