

# Synthesis and characterization of mixed ligand metal(II) complexes with Schiff base and 8-hydroxyquinoline as ligands

Abubakar Abdullahi Ahmed\*, Joy Oleka Peter, Fatima Alhaji Bala Ngaramu

Department of Pure and Applied Chemistry, Faculty of Science, P.M.B. 1069, Maiduguri, Borno State, Nigeria

## ARTICLE INFO

### Article history:

Received  
Received in revised form  
Accepted  
Available online

### Keywords:

Complexation  
Non-electrolyte  
Bidentate  
Uncoordinated water

## ABSTRACT

Co(II), Ni(II) and Cu(II) mixed ligand complexes have been synthesized from a Schiff base (L) obtained by the condensation reaction of acetophenone and 2-aminophenol, as primary ligand and 8-hydroxyquinoline (HQ) as secondary ligand. The Schiff base and metal(II) mixed ligand complexes were accordingly investigated using some physicochemical techniques. The Schiff base ligand was shiny brown crystalline solid obtained in low yield of 36.21 % with melting point of 240 °C. The metal(II) complexes were obtained as brown to deep brown coloured solids, air stable with decomposition temperatures of 310 – 340 °C. The molar conductivity values of the complexes in dimethylformamide (DMF) was found to be 2.13 - 3.77  $\text{Ohm}^{-1}\text{cm}^2\text{mol}^{-1}$  indicating their non-electrolytic nature. The determination of water of crystallization showed presence of  $1\frac{1}{2}$  uncoordinated water molecules in the Co(II) and Cu(II) complexes while 2 was estimated for Ni(II) complex. The infrared spectral data allude that, on complexation, the Schiff base ligand loses its phenolic hydrogen and coordinated bidentately to the metal(II) ions through deprotonated phenolic oxygen and imine nitrogen ( $\text{HC}=\text{N}-$ ) as monobasic ligand. Similarly, HQ coordinated *via* deprotonated phenolic oxygen and quinoline nitrogen. The resultant data showed that the mixed ligand might formulated as  $[\text{ML}(\text{HQ})]\cdot n\text{H}_2\text{O}$  exhibiting four-coordinate square planar geometry.

## 1. Introduction

Schiff bases are compounds containing the carbon-nitrogen double bond ( $-\text{HC}=\text{N}-$ ), obtainable by condensation of primary amines with carbonyl compounds. They are also called imines, anils or azomethines. The presence of imine group in these compounds have contributed to their chemical and biological importance [1].

Schiff bases are generally excellent chelating agents especially when a functional group like  $-\text{OH}$  or  $-\text{SH}$  is present close to the azomethine group so as to form a five or six membered ring with the metal ion [2].

8-Hydroxyquinoline is a chelating agent which has been used for the quantitative determination of metal ions. It reacts with metal ions, losing the proton and forming 8-hydroxyquinolinato-chelate complexes [3]. The structure of 8-hydroxyquinoline is shown in Fig. 1.

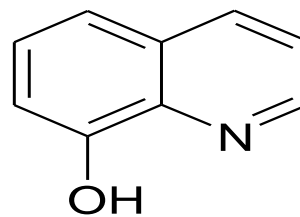


Fig.1. Structure of 8- hydroxyquinoline

The literature survey revealed that the strategy of designing metal complexes with mixed ligands is a promising approach for developing new compounds bearing better biological activity [4-7].

The objective of the present investigation is to prepare Schiff base derivable from acetophenone and 2-aminophenol and then coordinate it to Co(II), Ni(II) and

\* Corresponding author. Tel.: +2348034568942; e-mail: abubakarabdullahiahmed28@gmail.com

Cu(II) ions using 8-hydroxyquinoline as a co-ligand and to elucidate their geometric structures.

## 2. Results and Discussion

The physical characteristics of the Schiff base ligand, 8-hydroxyquinone and mixed ligand metal(II) complexes are presented in Table 1. The Schiff base ligand was produced from condensation reaction between acetophenone and 2-aminophenol. It is a shiny brown crystalline solid obtained in low yield of 36.21 % with melting point of 240 °C. The metal(II) mixed ligand complexes were obtained as brown to deep brown solids, air stable with excellent percentage yield of 83.16 % and 79.42 % for Cu(II) and Ni(II) complexes respectively but low yield of 25.79 % for Co(II) complex. The complexes have decomposition temperatures of 310 °C – 340 °C. The change in colour and increase in the melting point of the

ligand after interaction with metal salts revealed that reaction has occurred resulting in complex formation. The melting point of the Schiff base ligand is basically lower than that of metal(II) complexes because of intra-molecular interaction [8]. It could be deduced from the melting points/decomposition temperatures that these compounds are thermostable and relatively free from impurities [8,9]. The molar conductivity values of the complexes in DMF solvent were found to be 2.13 - 3.77  $\text{Ohm}^{-1}\text{cm}^2\text{mol}^{-1}$  indicating their non-electrolytic nature [7]. These values reveal that there is no anion outside the co-ordination sphere. This is apparent as no precipitate was formed on addition of  $\text{AgNO}_3$  solution to the solution of the complexes; Thus, the complexes may be formulated as  $[\text{ML}(\text{HQ})].n\text{H}_2\text{O}$  where  $\text{M}=\text{Co(II)}$ ,  $\text{Cu(II)}$  or  $\text{Ni(II)}$  and  $n=1\frac{1}{2}$  or 2 [10].

**Table 2.** Colour, melting point, conductivity and percentage yield of the schiff base and Mixed ligand metal complexes

Compound	F. weight ( $\text{gmol}^{-1}$ )	Colour	% Yield	M.P/D.T ( $^{\circ}\text{C}$ )	Molar Conductivity ( $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ )
Schiff base	211.28	Light brown	36.21	240	-
8-Hydroxyquinoline	145.16	Yellow	-	-	-
$[\text{Cu}(\text{L})(\text{HQ})].1\frac{1}{2}\text{H}_2\text{O}$	445.44	Deep brown	83.16	310	3.77
$[\text{Co}(\text{L})(\text{HQ})].2\text{H}_2\text{O}$	441.39	Brown	25.79	340	2.13
$[\text{Ni}(\text{L})(\text{HQ})].1\frac{1}{2}\text{H}_2\text{O}$	450.37	Dark brown	79.42	315	2.44

The solubility of the Schiff base ligand and its metal(II) mixed ligand complexes were tested in distilled water and some polar and non-polar solvents. The Schiff base was soluble in all the polar solvents (water, acetone, ethanol and DMF) used but insoluble in the non-polar solvents. This could be ascribed to the polar nature of the Schiff base ligand [11]. Moreover, the metal(II) mixed ligand complexes were found insoluble in all solvents used except DMF, in which complete solubility was observed. This could be attributed to the strong coordinating nature of DMF [12,13].

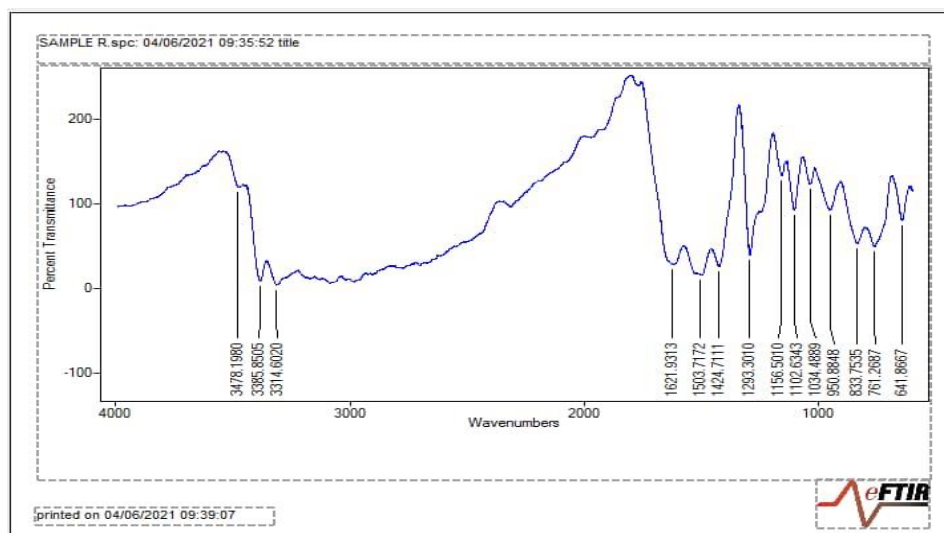
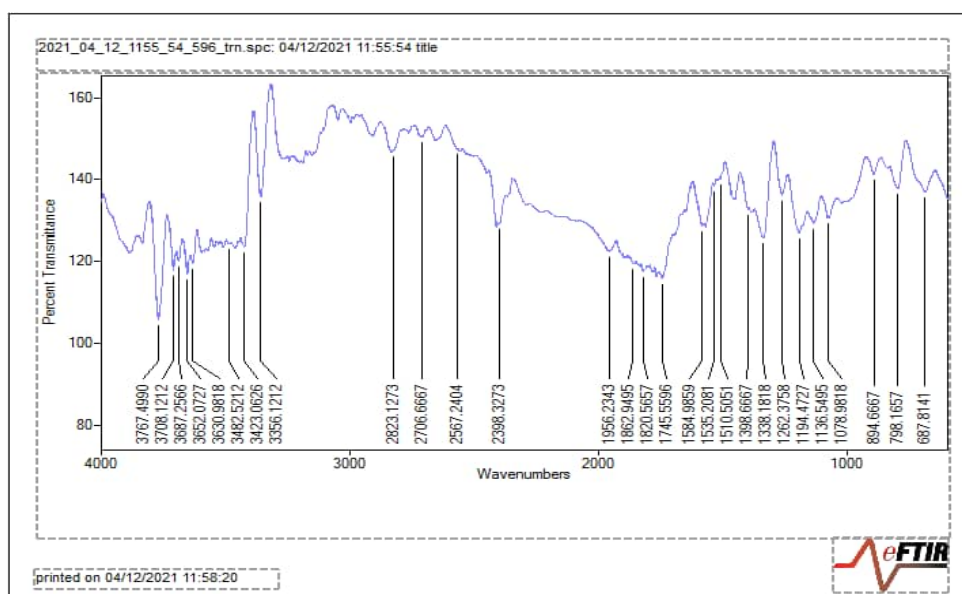
The Infrared spectroscopic data of the Schiff base, and its mixed ligand metal(II) complexes with 8-hydroxyquinoline are summarized in Table 2 and the spectra shown in figures 2 - 5. The comparison of the spectrum of the schiff base ligand, 8-hydroxyquinoline and mixed ligand metal(II) complexes have revealed certain characteristics difference in some of these spectra either by disappearance or shifting of peaks. The spectrum of the free Schiff base ligand shows a spiky broad band at 3385.85 and 3314.60  $\text{cm}^{-1}$  due to phenolic

$\nu(\text{OH})$  [14]. The spectra of the metal(II) mixed ligand complexes show broad bands at 3356.12 - 3412.77  $\text{cm}^{-1}$  which is due to the presence of water of hydration [10,15]. The band due to azomethine ( $\text{C}=\text{N}$ ) observed at 1621.93  $\text{cm}^{-1}$  in the free schiff base ligand shifted to lower frequencies (1584.98 and 1587.43  $\text{cm}^{-1}$ ) and upper frequency of 1640.53  $\text{cm}^{-1}$  suggesting linkage of the metal ions with nitrogen atom of the azomethine [5]. New weak bands at 794.34 - 821.26  $\text{cm}^{-1}$  and 687.81 - 715.38  $\text{cm}^{-1}$  may be due to  $\nu(\text{M}-\text{N})$  and  $\nu(\text{M}-\text{O})$  respectively supportive of the formation of the complexes under study [16].

The broad band at 3259.49  $\text{cm}^{-1}$  due to OH in the spectrum of 8-hydroxyquinoline disappeared in the spectra of the complexes indicating coordination via the deprotonated OH group of the quinolone ring [5,15]. The IR data suggest that both ligands behave as uninegative bidentate ligand coordinated through N and O atoms of the azomethine and deprotonated phenolic OH in the case of the Schiff base and oxygen and nitrogen of quinolone ring [20-22].

**Table 1.** Relevant IR Bands ( $\text{cm}^{-1}$ ) of the Schiff Base and Metal(II) Mixed Ligand Complexes

Compound	IR Bands ( $\text{cm}^{-1}$ )				
	$\nu\text{OH}$	$\nu\text{H}_2\text{O}$	$\nu\text{C}=\text{N}$	$\nu\text{M}-\text{N}$	$\nu\text{M}-\text{O}$
Schiff base	3385.85 3314.60	-	1621.93	-	-
8-Hydroxyquinoline	3259.49	-	1616.48	-	-
[Cu(L)(HQ)].1½ H <sub>2</sub> O	-	3356.12	1584.98	798.16	687.81
[Co(L)(HQ)].2H <sub>2</sub> O	-	3357.57	1587.43	794.34	694.44
[Ni(L)(HQ)].1½ H <sub>2</sub> O	-	3412.77	1640.53	821.26	725.38

**Fig. 2.** FT-IR Spectrum of the Schiff base Ligand**Fig. 3.** FT-IR Spectrum of Cu(II) Mixed Ligand Complex

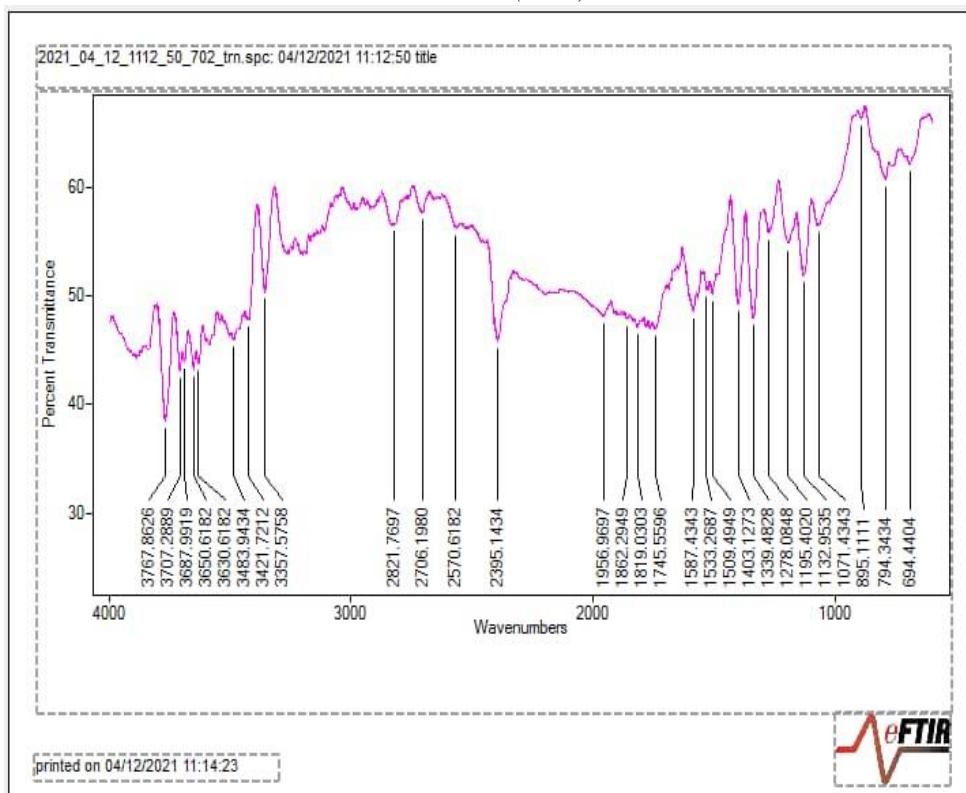


Fig. 4. FT-IR Spectra of Co(II) Mixed Ligand Complex

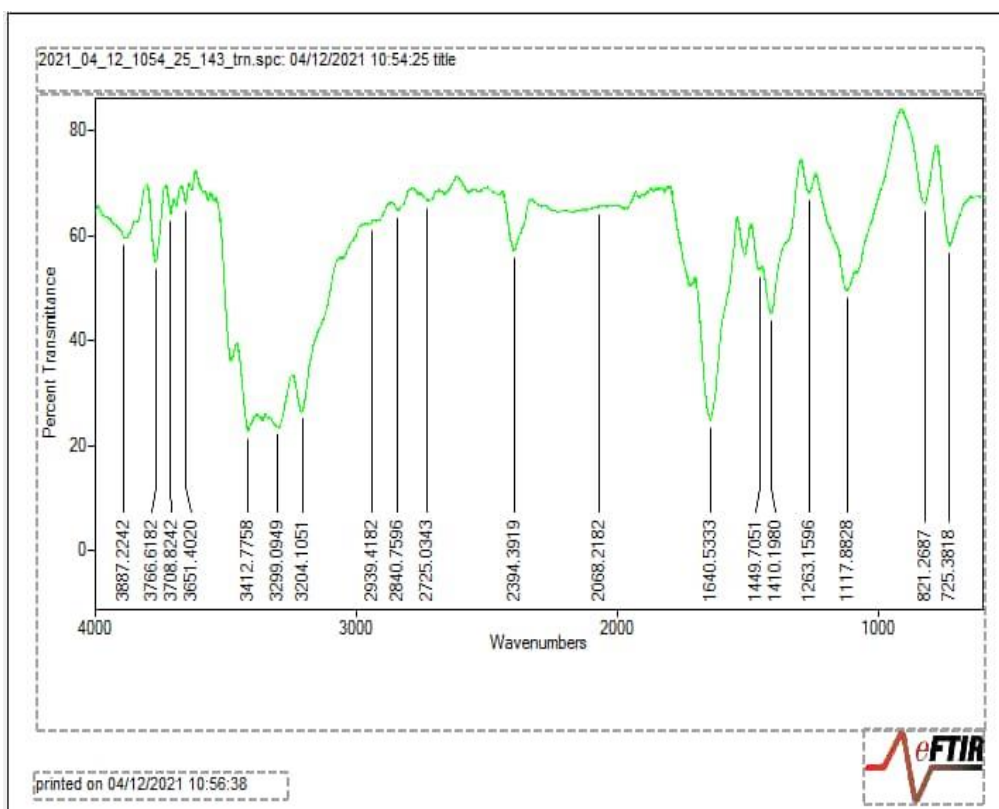


Fig. 5. FT-IR Spectra of Ni(II) Mixed Ligand Complex

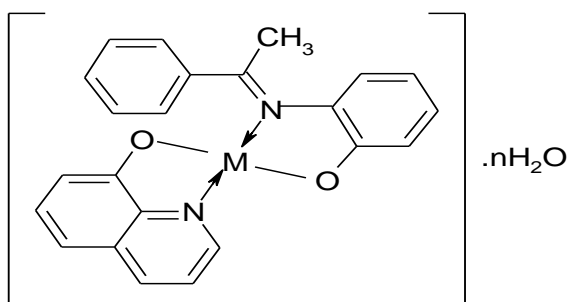
The observed and calculated percentage metal composition in the complexes are in good agreement. The water of crystallization in the mixed ligand metal complexes were determined and estimated as 2 for Ni(II)

complex and 1½ for Co(II) and Cu(II) complexes. This implies that the complexes under study are hydrated. The results are presented in Table 3.

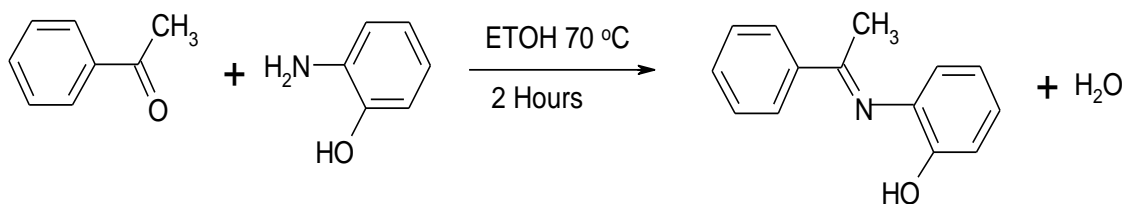
**Table 3.** % water of crystallization and metal content in the complexes

Compound	weight loss(g)	% Found(Calculated)	
		H <sub>2</sub> O	Metal
[Cu(L)(HQ)].1½ H <sub>2</sub> O	0.012	6.00	14.04
		(6.06)	(14.27)
[Co(L)(HQ)].2H <sub>2</sub> O	0.014	7.00	12.86
		(7.49)	(13.08)
[Ni(L)(HQ)].1½ H <sub>2</sub> O	0.012	6.00	13.53
		(6.11)	(13.29)

From the analytical and spectroscopic data, a square planar geometry is suggested for the metal(II) mixed ligand complexes under study. The proposed structure is shown in Fig. 6 below.



Where M= Co<sup>2+</sup>, Ni<sup>2+</sup> or Cu<sup>2+</sup>, n= 1½ or 2

**Fig.6.** Proposed structure of metal(II) mixed ligand complexes**Fig. 1.** Schematic synthesis pathway of Schiff base

### 3.3. General Procedure for Synthesis of Mixed Ligand Metal(II) Complexes

The complexes were synthesized in equimolar ratio of M: L: HQ (1: 1: 1). An ethanolic solution (30 ml) of 0.003 mol of appropriate metal salt (NiCl<sub>2</sub>.6H<sub>2</sub>O, 1.4262 g); (CoCl<sub>2</sub>. 6H<sub>2</sub>O, 0.7138 g), CuCl<sub>2</sub>.2H<sub>2</sub>O, 1.71 g) was added to hot ethanolic solution (30 ml) of Schiff base ligand (0.003 mol, 0.6879 g). To the resultant mixture, 30 ml ethanolic solution of 8-hydroxyquinoline (0.003 mol, 0.4355 g) was added. The mixture heated, with constant stirring for 3 hours in the presence of 10 % NaOH (2 ml) to maintain the pH of the solution. The solid complex obtained was filtered and washed with ethanol to remove

## 3. Experimental

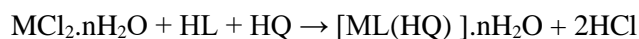
### 3.1. General

All reagents and solvents used in the work were of analytical grade and used without further purification. These include acetophenone, 2-aminophenol, ethanol, 8-hydroxyquinoline, acetone, benzene, ethanol, dichloromethane, diethyl ether, dimethyl formamide, and chloroform. Melting point was determined using an electro-chemical melting point apparatus. It was fitted with the thermometer and one side opened capillary tube with powdered prepared compounds. The electro-thermal melting point apparatus was switched on and the temperature was noted when the compound first or just began to melt to clear liquid. The IR spectra were determined on BUCK Scientific Fourier transform IR model M 530 spectrophotometer. Conductance was recorded using LIDA instrument model DDS-307 conductivity meter at 32 °C. The colours of the synthesized compounds were identified physically.

### 3.2. Synthesis of Schiff Base Ligand (L)

The Schiff base was prepared by mixing 50 ml hot ethanolic solution of 2-aminophenol (0.1 mol; 10.91 g) and acetophenone (0.1 mol; 11.6 g). The resultant mixture was heated under reflux for 2 hours with continuous stirring on a hot plate magnetic stirrer. Consequently, a brown solution formed was allowed to cool to ambient temperature, the product precipitated out, filtered, washed with 20 ml ethanol followed by drying in desiccator containing moisture absorbent [17]. The reaction is depicted in Fig. 1.

unreacted metal chloride or ligand and was dried under vacuum in desiccator [5].



### 3.4 Gravimetric estimation of metal content in the complexes

0.04 g of each complex was placed in 100 cm<sup>3</sup> beaker containing 25 cm<sup>3</sup> of distilled water, which 5 cm<sup>3</sup> of concentrated HNO<sub>3</sub> was added and then heated to about dryness. The contents in the beaker was allowed to cool to room temperature and 25 cm<sup>3</sup> of distilled water was added, and the mixture was stirred before the filtrate

which contains the metal ions was collected [18]. Nickel, cobalt and copper were precipitated as nickel(II) dimethylglyoxime, dipyridine cobalt(II) thiocyanate and dipyridine copper(II) thiocyanate respectively. The percentage composition by mass of the metals in the complexes were calculated using equations 1-3 [19].

$$\frac{\text{Gravimetric factor (G. F)}}{\text{Relative atomic mass of the metal}} = \frac{\text{Molecular weight of the precipitated Compound}}{\text{Molecular weight of the metal}} \quad (1)$$

$$\text{Average weight dried ppt} = \text{G. F} \times \text{weight of ppt} \quad (2)$$

$$\% \text{ Metal} = \frac{\text{Average weight of dried precipitate}}{\text{original weight of metal complex used}} \times 100 \% \quad (3)$$

### 3.5 Gravimetric estimation of water of crystallization

Exactly 0.2 g of the complex was weighed into a watch glass of known weight and placed in a thermostat oven at a temperature of 110 °C, the complex was left in the oven for 2 hours. It was weighed and placed again in the oven until constant weight was obtained [12]. The % was calculated using equations 4 and 5.

$$\% \text{ water crystallization} = \frac{\text{Weight loss}}{\text{original weight}} \times 100 \% \quad (4)$$

Equation (4) could be expressed as:

$$\% \text{ water of crystallization} = \frac{W_3 - W_2}{W_1} \times 100 \% \quad (5)$$

Where  $W_1$  = Original weight of complex (g),  $W_2$  = Watch glass + Original weight of complex before heating in oven (g),  $W_3$  = Watch glass + Complex after heating to constant weight (g)

## 4. Conclusion

The Schiff bases ligand, L, derived from acetophenone and 2-aminophenol and its metal(II) mixed ligand complexes with 8-hydroxyquinoline were successfully synthesized and characterized by physico-chemical techniques and FT-IR spectroscopy. The molar conductance measurement envisaged the non-electrolytic nature of the complex. Based on the FT-IR results, the Schiff base existed as monobasic bidentate ligand (ON) bonded to the metal(II) ions via the deprotonated phenolic oxygen and azomethine nitrogen whereas HQ ligand existed as monobasic bidentate ligand with the deprotonated oxygen of the hydroxyl group and nitrogen of the quinoline ring being the donor sites. From the data obtained, a square planar have been proposed for the complexes under study.

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## How to Cite This Article

Abubakar Abdullahi Ahmed; Joy Oleka Peter; Fatima Alhaji Bala Ngaramu. "Synthesis and characterization of mixed ligand metal(II) complexes with Schiff base and 8-hydroxyquinoline as ligands". *Journal of Chemistry Letters*, 2, 1, 2021, 43-49. doi: 10.22034/jchemlett.2021.292242.1034