ChemSearch Journal 5(1): 12 – 20, June, 2014
Publication of Chemical Society of Nigeria, Kano Chapter

Received: 17/12/2013 Accepted: 04/03/2014

Characterization of Schiff base derived from 2-hydroxo-1-naphthaldehyde and Ethylenediammine and its Copper (II) Complex by Potentiometric and Spectrophotometric Methods

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ABSTRACT

Synthesis of Copper (II) complex with a Schiff base derived from the reaction of 2 – hydroxyl-1-naphthaldehyde and ethylenediammine was carried out. Solubility, melting/decomposition temperature, molar conductance, potentiometric, elemental analysis as well as uv-visible spectrophotometric studies were carried out. The pKa of the Schiff base was determined potentiometrically and checked using ORIGIN 50 method. Potentiometric studies revealed 1:1 metal to ligand ratio. Job's method of continuous variation also revealed 1:1 metal to ligand ratio. Molar conductance measurements showed that the complex is non electrolyte with very high stability constant value. Gibb's free energy determination showed that the complex is very stable as shown in the high decomposition temperature measurements.

Keywords: Potentiometry, Schiff base, Spectrophotometry, Stability constant

INTRODUCTION

A Schiff base (or azomethine), is a nitrogen analogue of an aldehyde or ketone in which the C= O group is replaced by a C = N carbon – nitrogen double bond with the nitrogen atom connected to an aryl or alkyl group, but not hydrogen. They are usually obtained by the condensation of an aldehyde or ketone with primary amine (Holm *et al*., 1966). Schiff bases are of the general formula $R_1R_2C = NR_3$, where R_3 is an aryl or alkyl group that makes the Schiff base a stable imine (Henry and Lange, 1977). Transition metal Schiff base complex compounds are well known, for example, Ettling (1840) isolated a dark green crystalline product from the reaction of cupric acetate, salicyladehyde and aqueous ammonia (Holm *et al*., 1966). However, there was no comprehensive and systematic study until the preparative work of Pfeiffer and associates (1931), who reported a series of complexes derived from Schiff bases of salicylaldehyde and its substitution products. Gupta *et al*. (2002) reported the synthesis and characterization of cobalt (II) N, N' - bis(acetylacetone)ethylenediiminato complex from the interaction of cobalt (II) salt and N, N'-bis(acetylacetone)ethylenediimine Schiff base ligand. In another report, Xishi *et al.* (2003) described the synthesis and spectroscopic properties of manganese (II), cobalt (II) and copper (II) complexes with novel Schiff base ligand derived from 2, 2' bis(p-methoxylphenylamine) and salicylic aldehyde.

Transition metal Schiff base complexes show properties such as antitumor, anti fertility, bioactivity and catalytic activity. For example, some Schiff bases and their metal complexes containing Co(II), Ni(II), Cu(II) and Zn(II) synthesized from salicyldehyde, 2, 4 – dihydroxybezaldehyde, glycine and L-alanine possess antitumor activity (Gaowen *et al*., 1995). Schiff bases derived from hydrazine carboxyamide and hydrazine with dioxo Mo(IV) and Mn(II) have been reported to alter reproductive physiology (Singh *et al*., 1999). Schiff base derived from furylglyoxal and p-toluidene shows antibacterial activity against *Escherichia coli, staphylococcus aureus, bacillus subtilis and proteus vulgaris* (Bhardwaj and Singh, 1994). They can also be used as catalysts, iron (II) schiff base complex exhibits catalytic activities towards electro-reduction of oxygen (Chakraborty *et al.*, 1994).

This paper reports potentiometric and spectrosphotometric studies of Copper (II) complex with a schiff base base derived from 2 – Hydroxy – 1 – naphthaldehyde and Ethylenediammine.

MATERIALS AND METHODS

All the chemicals used are of analytical grade (AnalaR, BDH) while 2-hydroxy-1-naphthaldehyde and ethylenediamine (AR) were obtained from Sigma-Aldrich and used without further purification. Melting and decomposition temperatures were determined using Galenkemp apparatus. UV-visible spectrophotometric analysis was carried out using UV-visible spectrophotometer model 3310 and infrared analysis was carried out on the Schiff base as well as the complex using Fourier Transform IR Genesis series Model in Nujol in the range 400 – 4000 cm^{-1}. Elemental analyses for carbon, nitrogen and hydrogen were carried out at the Microanalytical Laboratory in the School of Chemistry, University of Bristol, United Kingdom. Conductivity measurement was carried out using Jenway Conductivity Meter Model 4010 while pH measurements were carried out using pH meter Model 3320.

Preparation of the Schiff Base

A solution of 0.1 mole ethylenediamine in $50cm^3$ ethanol was slowly added to a solution of 0.2 mole 2 – hydroxy – 1 – naphthaldehyde in $50cm^3$ ethanol and the mixture was refluxed for an hour. The Schiff base that formed was filtered, washed with ethanol and dried over Phosphorus pentoxide for a week (Ahmed and Akhtar, 1983; Byeong-Goo *et al*., 1996).

Preparation of the complex

N, N' bis(2 – hydroxy - 1-naphthaly)ethylenediiminato Copper (II) complex was prepared by addition of Schiff base (0.01 mole) in hot ethanol ($100cm^3$) into an aqueous solution of Copper (II) chloride (0.01 mole) and the mixture was refluxed for 2 hours. The Copper (II) Schiff base complex formed was separated, washed with ethanol and dried over Phosphorus pentoxide for a week (Ahmed and Akhtar, 1983; Byeong-Goo *et al*., 1996).

Determination of Ionization Constant (pKa) of the Schiff Base

A magnetic stirrer bar was put in a $400cm^3$ beaker containing $90cm^3$ distilled water, $100cm^3$ $0.2moldm^{-3}$ Potassium nitrate and $10cm^3$ $0.4moldm^{-3}$ Schiff base was introduced into the solution mixture. From a burette, 10 cm^3 standardized sodium hydroxide was added. After each aliquot ($0.50cm^3$) addition, the corresponding pH meter reading was recorded (Angelici, 1971).

Determination of Stability Constant of the Schiff Base Copper (II) Complex

$0.4moldm^{-3}$ Sodium-liganate was added to a stirred mixture of $90cm^3$ distilled water, $10cm^3$ $0.1moldm^{-3}$ nitric acid, $100cm^3$ $0.2moldm^{-3}$ Potassium nitrate and 0.1mmole of Copper (II) chloride contained in a $400cm^3$ beaker. After each addition of an aliquot ($0.20cm^3$) of the sodium-liganate solution, the pH value was recorded from the pH meter (Angelici, 1971).

Determination of Number of Coordinated Ligands

The ligand to metal ratio in the complex was determined using continuous variations method (Job's method) (Angelici, 1976). $0.003moldm^{-3}$ solution of Copper (II) chloride was prepared and its absorbance was measured and the wavelength at maximum absorbance (λ_{max}) was recorded from the UV-Visible spectrophometer. Eight solution mixtures each having a total volume of $16cm^3$, in which the mole fraction of each Schiff base, X is 0.1, 0.4, 0.5, 0.6, 0.8, 0.9 and 1.0 were prepared. The absorbance of each of these solutions mixture was measured at the λmax of each of Copper (II) solutions. A plot of absorbance against mole fraction was prepared from mole fraction χ at maximum absorbance was recorded for the mixture containing a stoichiometric amount of Copper (II) and Ligand. The number of coordinated ligand ($\bar{n}$) to Copper (II) was calculated.

RESULTS AND DISCUSSION

Equimolar ratio of 2-hydroxy-1-naphthaldehyde and the diamine produced the ligand as yellow crystalline solid. The percentage yield recorded was 78.50 %. The complex was produced by mixing 2:1 ligand to Copper (II) chloride ethanolic solution and also recorded a good yield. Moreover, the melting and decomposition temperatures recorded were 215°C and 297°C respectively as shown in Table 1 (Byeong-Goo *et al*., 1996).

Solubility test carried out on the ligand in some common solvents showed that, it is soluble in methanol, ethanol and DMSO but insoluble in water, ether and carbon tetrachloromethane while in nitrobenzene and acetonitrile slightly soluble as shown in Table 2. The solubility of the complex shows that all the complexes are soluble in DMSO, insoluble in methanol, ethanol, distilled water and other common organic solvents as shown in Table 1. Molar conductance measurement of the Copper (II) complex was 10 ohm^{-1} cm^2 mol^{-1} indicating non electrolytic compound. The melting point temperature of the ligands recorded 215°C while the decomposition temperature of the complex 297°C suggests that the ligand and the complexes are stable (Byeong-Goo *et al*, 1996; Ahmed and Akhtar, 1983).

Table 1: Colour, Percentage Yield, Melting / decomposition temperature of the ligand and complex

Ligand/Complex	Colour	% Yield	Melting Point (^{o}C)	Decomposition Temp. (^{o}C)
L`	Yellow	78.50	215	-
[CuL`]	Blue	68.99	-	297

L` = N, N` - bis (2-hydroxy-1-naphthyl) ethylenediiminato

Table 2: Solubility of the Ligand and Copper (II) Complex in Water and Some Common Organic Solvents

Solvents	L`	[CuL`]
Water	IS	IS
Methanol	S	S
Ethanol	S	S
Ether	IS	IS
Acetone	S	SS
Nitrobenzene	SS	SS
Acetonitrile	SS	SS
Carbon tetrachloride	IS	IS
DMSO	S	S

KEY: S – Soluble
IS – Insoluble
SS – Slightly Soluble

IR spectra of the ligand (Table 30) show broad bands around 3400 - 3200cm^{-1} attributed to ν(O-H) stretching vibrations. The strong peaks observed in the 1631 – 1642 cm^{-1} region are due to the azomethine ν (C = N) group (Byeong-Goo *et al*, 1996). This band in the complex is shifted to the lower frequencies relative to those of the corresponding free ligand. These relative shifts observed for ν (C = N) bonds in the complex clearly showed the participation of azomethine nitrogen in coordination to the metal ions (Ahmed and Akhtar, 1983). Two absorption bands at 742 – 749 cm^{-1} and 575 – 594cm^{-1} in the Copper (II) chelates, respectively, were indicating the formation M – N and M – O bonds confirming coordination of the ligands to the metal (II) ions.

Table 3: IR for the ligands and the Complex

Ligand/Complex	ν (O – H)cm^{-1}	ν C = N (cm^{-1})	ν M - O (cm^{-1})	ν M - N (cm^{-1})
L`	3250	1623	-	-
[CuL`]	-	1621	508	751

The elemental analyses (Tables 4) of the metal (II) chelates for H, C and N showed that the observed and the calculated percentages of the elements are in good agreement and support 1:1 metal-ligand ratio in the complex.

Table 4: Elemental Analysis Results

	Calculated(Found)		
Ligand / Complex	% C	% H	% N
L`	78.33(78.15)	5.48(5.40)	7.61(7.33)
[CuL`]	67.87 (66.64)	4.27 (4.25)	6.60 6.59)

The number of coordinated ligand to metal ion was also determined using continuous variation method. A plot of absorbance versus mole fraction of the ligand was made. The mole fraction of the ligand at maximum absorbance was used in calculating the number of ligand coordinated to Copper (II) ion. The result obtained established 1:1 metal to ligand ratio as shown Fig. 1.

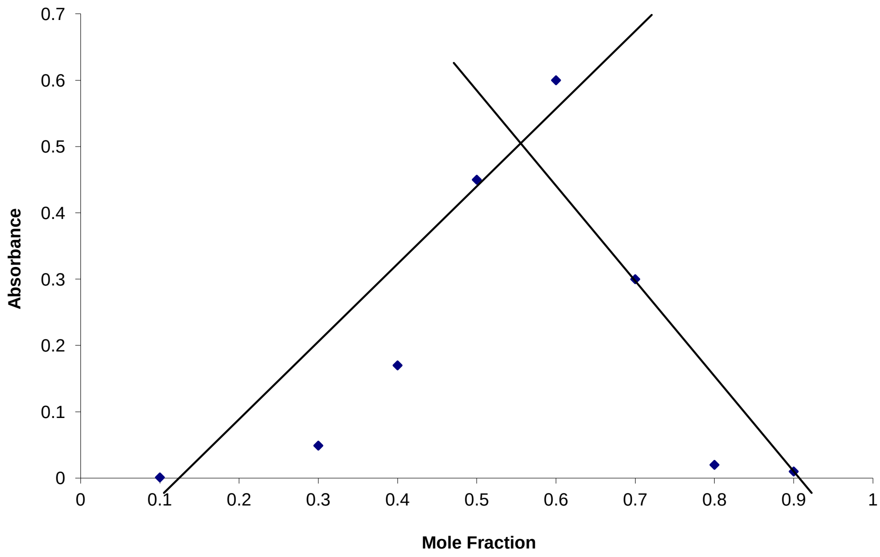

Fig. 1: Plot of Absorbance Copper (II) chloride solution with L` against mole fraction

The dissociation constant (pKa) of the ligand is as shown in Table 5. The value obtained is 12.55. It can be seen that the Schiff base has very low dissociation constants indication of weak acid. Exhaustive literature search revealed no dissociation constant value of this Schiff base ever reported to compare with. Nevertheless, ORIGIN 50 method (Aliyu and Na'aliya, 2010) was used. From that method, L` recorded dissociation constant values of 13.199 (Fig. 2) indicating slight variation in dissociation constant value determined from the two methods employed, suggesting that the values are reliable.

Table 5: Determination of Dissociation Constant (pKa) of L`

Vol	pH	[H$^+$]	[OH-]	[Na$^+$]	Atot	pKa
0.50	10.61	1.64E-11	0.98E-4	1.07E-3	0.02	10.87
1.00	11.49	2.17E-12	0.75E-3	1.06E-3	0.02	11.75
1.50	11.82	1.01E-12	0.16E-3	1.06E-3	0.02	12.08
2.00	11.98	7.01E-13	2.31E-2	1.06E-3	0.02	12.24
2.50	12.12	5.08E-13	3.18E-2	1.06E-3	0.02	12.38
3.00	12.22	4.03E-13	4.00E-2	1.06E-3	0.02	12.48
3.50	12.31	3.28E-13	4.93E-2	1.06E-3	0.02	12.57
4.00	12.38	2.79E-13	5.79E-2	1.05E-3	0.02	12.64
4.50	12.44	2.43E-13	6.65E-2	1.05E-3	0.02	12.70
5.00	12.49	2.17E-13	7.46E-2	1.05E-3	0.02	12.67
5.50	12.54	1.93E-13	8.38E-2	1.05E-3	0.02	12.72
6.00	12.57	1.8E-13	8.97E-2	1.04E-3	0.02	12.75
6.50	12.62	1.61E-13	0.10	1.04E-3	0.02	12.80
7.00	12.65	1.5E-13	0.10	1.04E-3	0.02	12.83
7.50	12.68	1.4E-13	0.11	1.04E-3	0.02	12.86
8.00	12.7	1.34E-13	0.12	1.03E-3	0.02	12.88
8.50	12.73	1.25E-13	0.13	1.03E-3	0.02	12.91
9.00	12.75	1.19E-13	0.14	1.03E-3	0.02	12.93
9.50	12.78	1.11E-13	0.15	1.03E-3	0.02	12.96
10.00	12.81	1.04E-13	0.16	1.02E-3	0.02	12.99

Average pKa = **12.55**

Ka = **2.81E-13**

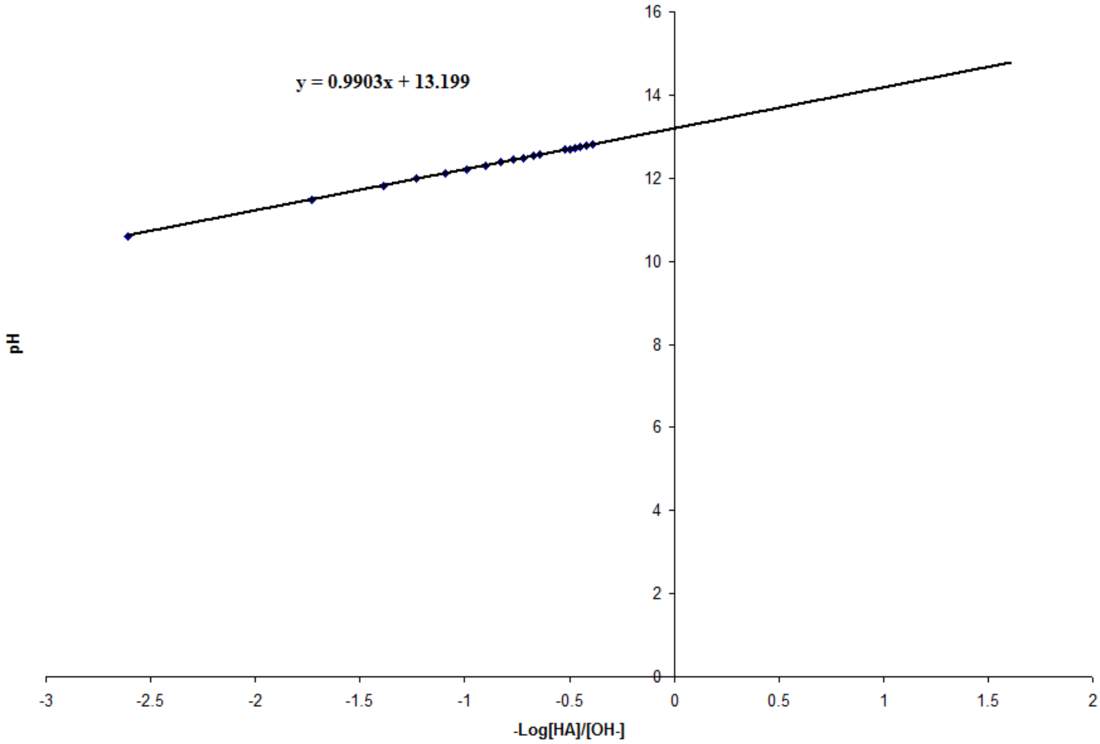

Fig.2: Graphical Method to Determine pKa of L`

The average number of coordinated ligand to the metal ions was determined potentiometrically. For Cu with L`, the average number of coordinated ligand fall in the range 1.08 (Table 6). Therefore, from these results, the ratio of number of coordinated ligand to Copper (II) ions is 1:1.

Table 6: Determination of Log [A^{2-}] and $\bar{n}$ in [CuL`]

Vol Na Salt	pH	[H+]	[OH-]	Ka/[H+]	Log[A2-]	Atot	CH+[OH-]-[H+]	n
2.00	5.48	4.9488E-06	7.29E-09	7.68E-08	-1.81	8.00E-04	9.95E-04	0.10
2.20	5.65	3.3458E-06	1.08E-08	1.14E-07	-6.94	8.80E-04	9.97E-04	0.11
2.40	5.81	2.3147E-06	1.56E-08	1.64E-07	-6.78	9.60E-04	9.98E-04	1.00
2.60	5.88	1.9702E-06	1.83E-08	1.93E-07	-6.71	1.04E-03	9.98E-04	1.00
2.80	5.91	1.8387E-06	1.96E-08	2.07E-07	-6.68	1.12E-03	9.98E-04	1.00
3.00	6.02	1.4272E-06	2.53E-08	2.66E-07	-6.57	1.20E-03	9.99E-04	0.20
3.20	5.99	1.5293E-06	2.36E-08	2.48E-07	-6.60	1.28E-03	9.98E-04	0.28
3.40	6.00	1.4945E-06	2.42E-08	2.54E-07	-6.59	1.36E-03	9.99E-04	0.36
3.60	6.02	1.4272E-06	2.53E-08	2.66E-07	-6.57	1.44E-03	9.99E-04	0.44
3.80	6.05	1.332E-06	2.71E-08	2.85E-07	-6.54	1.52E-03	9.99E-04	0.52
4.00	6.09	1.2148E-06	2.97E-08	3.13E-07	-6.50	1.60E-03	9.99E-04	0.60
4.20	6.12	1.1337E-06	3.18E-08	3.35E-07	-6.47	1.68E-03	9.99E-04	0.68
4.40	6.14	1.0827E-06	3.33E-08	3.51E-07	-6.45	1.76E-03	9.99E-04	0.76
4.60	6.18	9.8742E-07	3.66E-08	3.85E-07	-6.41	1.84E-03	9.99E-04	0.84
4.80	6.20	9.4297E-07	3.83E-08	4.03E-07	-6.39	1.92E-03	9.99E-04	0.92
5.00	6.23	8.8004E-07	4.1E-08	4.32E-07	-6.36	2.00E-03	9.99E-04	1.00
5.20	6.25	8.4043E-07	4.3E-08	4.52E-07	-6.34	2.00E-03	9.99E-04	1.08
5.40	6.30	7.4903E-07	4.82E-08	5.07E-07	-6.29	2.16E-03	9.99E-04	1.16
5.60	6.37	6.3753E-07	5.66E-08	5.96E-07	-6.22	2.24E-03	9.99E-04	1.24
5.80	6.44	5.4263E-07	6.65E-08	7.00E-07	-6.15	2.32E-03	9.99E-04	1.32
6.00	6.62	3.5851E-07	1.01E-07	1.06E-06	-5.97	2.40E-03	1.00E-03	1.40
6.20	6.78	2.4803E-07	1.46E-07	1.53E-06	-5.81	2.56E-03	1.00E-03	1.48
6.40	7.48	4.9488E-08	7.29E-07	7.68E-06	-5.11	2.64E-03	1.00E-03	1.56
6.80	7.98	1.5649E-08	2.31E-06	2.43E-05	-4.61	2.72E-03	1.00E-03	1.64
7.00	8.49	4.8362E-09	7.46E-06	7.86E-05	-4.10	2.80E-03	1.00E-03	1.80
7.20	8.74	2.7196E-09	1.33E-05	1.40E-04	-3.85	2.88E-03	1.00E-03	1.88
7.40	8.85	2.1111E-09	1.71E-05	1.80E-04	-3.74	2.96E-03	1.00E-03	1.96
7.60	8.93	1.7559E-09	2.06E-05	2.16E-04	-3.66	3.04E-03	1.00E-03	2.04
7.80	9.01	1.4605E-09	2.47E-05	2.60E-04	-3.58	3.12E-03	1.00E-03	2.03
8.00	9.04	1.363E-09	2.65E-05	2.79E-04	-3.55	3.20E-03	1.00E-03	2.03
								1.08

Stability constant for the Copper (II) complex is determined from a plot of n versus log[A^{2-}] as shown in Fig.3. For Copper (II) ions with L`, the value is 2.78 x $10^{12}$. From this result, it can be seen that the complex has high stability constant (Choon-pyo *et al.*, 1999). Gibb's free energy for the Copper (II) with L` was determined. The value obtained is -70.99KJmol^{-1}. This result showed very low values for Gibb's free energy suggesting good stability for the Copper (II) complex and this agrees with the results obtained from stability constant of the complex studied (Choon-pyo *et al.*, 1999).

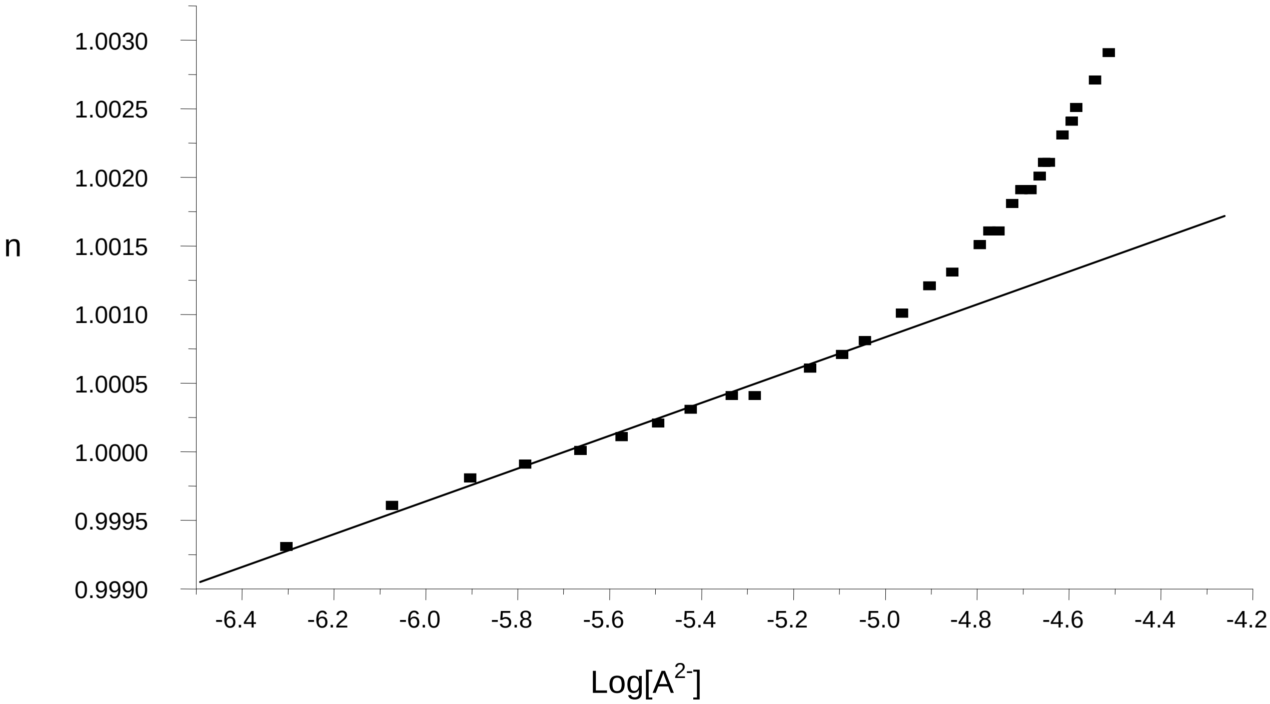

Fig.3: Plot of $\overline{n}$ against Log[A^{2-}] for [CuL`]

From the results of the analyses carried out on the complex compounds and the earlier report on similar work, the general molecular structure is suggested below:

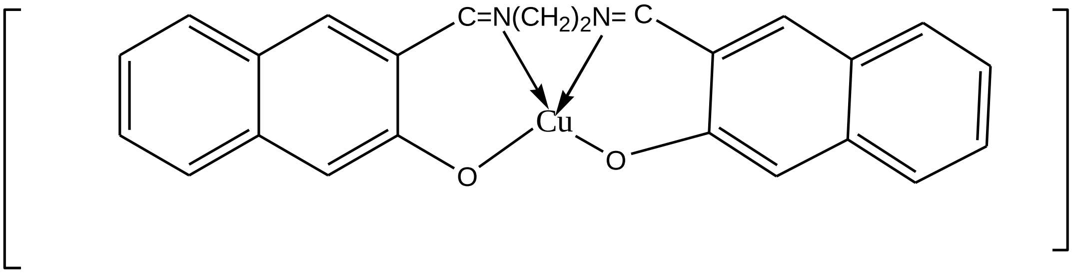

Figure 4: Proposed Molecular Structure of the Cu (II) Schiff Base Complex

CONCLUSION

Schiff base complex of Cu (II) was successfully synthesized from the reactions of schiff base ligand derived from 2-hydroxy-1-naphthaldehyde and ethylenediamine. Characterization studies showed that the complex is nonionic, with variable degree of solubility in water and common organic solvents. The ratio of metal to ligand and the results of spectroscopic studies fitted the complex to have tetragonal coordination via the N and O atoms.

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