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Synthesis and Physicochemical Properties of Copper (II) Complex with a Schiff base Derived from 2 – Hydroxy – 1 – naphthaldehyde and Ethylenediammine

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ABSTRACT

Synthesis of Copper (II) complex with a Schiff base derived from the condensation of 2 ï hydroxyl-1-naphthaldehyde and ethylenediammine was carried out. Solubility, melting/decomposition temperature, molar conductance, potentiometric 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. Jobôs 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. Gibbôs free energy determination showed that the complex is very stable as shown by the high decomposition temperature measurements.

Keywords: Complex, Potentiometry, Schiff base, Stability constant

INTRODUCTION

A metal surrounded by a cluster of ions or molecules (ligand), is used for preparation of complex compounds named as Schiff bases (Dhar and Taploo, 1982) which are condensation products of primary amines and aldehydes or ketones (RCH = NR`, where R and R` represents akyl and/or aryl substituents). Schiff bases and their complexes have been extensively studied due to synthetic flexibility, selectivity and sensitivity towards a variety of metal atoms (Osowale, 2008). This is because Schiff bases and their metal complexes are found to have various applications. They can act as catalysts (Nashinaga *et al*., 1988; Xi *et al*., 1987), antimicrobial agents (Dholakiya and Patel, 2002), plant growth regulators (Wang *et al*., 2002), polymers and dyes (George *et al*., 1993 and Levitin *et al*., 2005), besides some are used as antifertility agents (Singh *et al*., 1999). The earliest systematic synthetic study of Schiff bases was initiated by Pfeiffer et at (1931). They prepared a variety of complexes derived from salicyldehyde and pyrrole -2- aldehyde. Much work has been reported on transition metal complexes of Schiff bases derived from suitably substituted aromatic carbonyl compounds and a number of amines (Alev et al., 2004, Jeon-Geun and Yong-Koo, 1999). However, exhaustive literature search revealed paucity of information on transition metal complexes of aromatic Schiff bases derived from aliphatic diamines and aromatic compounds such as 2 ï hydroxyl-1-naphthaldehyde. One of the available works suggested the formation of N,N`-bis(2-hydroxy-1-naphthyl) ethylenediiminato copper (II) complex during attempted preparation of copper (II) mixed chelates from dibasic Schiff base (Ahmed and Akhtar, 1986). This paper reports the synthesis and physiochemical properties of copper (II) complex with a Schiff base derived from 2 ï hydroxyl ï 1- naphthaldehyde and ethylenediamine.

MATERIALS AND METHOD

All the chemicals used were of analytical (AR) 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 ï 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. For metal (II) complex, 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 ligands coordinated to a metal ion.

Preparation of the Ligand

A solution of 0.1mole diamine in 50cm^3 ethanol was slowly added to a solution of 0.2 mole 2-hydroxy-1-naphtahldehyde in 50cm^3 ethanol and the mixture was refluxed for an hour. The ligand formed was then filtered, washed with ethanol and dried over phosphorus pentoxide in a dessicator for a week (Ahmed and Akhtar, 1986; Beong-Goo *et al.*, 1996).

Preparation of Complex

The complex was prepared as described by Ahmed and Akhtar (1986), Boeng-Goo *et al*. (1995). It was then washed with ethanol and dried over phosphorus pentoxide for a week.

Determination of Number of Coordinated Ligands

The ligand to metal ratio in the complex was determined using continuous variations method (Jobôs method) (Angelici, 1971). A 0.003moldm^{-3} solution of copper (II) salt was prepared and absorbance was measured from the UV-Visible spectrophometer of each of 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, 0.6, 0.8, 0.9 and 1.0 were prepared. The absorbance of each of these solutions mixture was measured at a ə̃$_{max}$ of 301nm.

Determination of Ionization Constant (pKa) of the Schiff Base

A magnetic stirrer bar was placed in a 400cm^3 beaker containing 90cm^3 distilled water, 100cm^3 0.2moldm^{-3} potassium nitrate and 10cm^3 0.4moldm^{-3} of the Schiff base was then added to the solution mixture. Using a burette, 10 cm^3 standardized sodium hydroxide (0.45 moldm^{-3}) was continuously 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

10cm^3 of 0.4moldm^{-3} Sodium-liganate was added to a stirred mixture of 90cm^3 distilled water, 10cm^3 of 0.1moldm^{-3} nitric acid, 100cm^3 of 0.2moldm^{-3} potassium nitrate and 0.1mmole of copper (II) salt 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 using the pH meter.

RESULTS AND DISCUSSION

Equimolar ratio of 2-hydroxy-1-naphthaldehyde and the diamines produced the ligands as yellow crystalline solids. The percentage yield recorded was 78.50 %. The complex was produced by mixing 2:1 ligand to metal (II) chlorides ethanolic solution and also recorded a good yield (Byeong-Goo *et al*., 1996). Molar conductance of the copper (II) complex was found to be 10 ohm^{-1} cm^{-2} mol^{-1} indicating non electrolytic compound (Eman *et al*., 2008). The melting point temperature of the ligand was also found to be 215^{o}C while the decomposition temperature of the complex is found as 297^{o}C. This suggests that the ligand and the complex are stable (Byeong-Goo *et al*, 1996; Ahmed and Akhtar, 1986) with stability constant and Gibbôs free energy values of 2.78 x 10^{12} and -70.99KJmol^{-1} respectively indicating low Gibbôs free energy suggesting good stability for the metal complex which agrees with the results of stability constant of the complex (Choon-pyo *et al.*, 1999).

Solubility tests carried out on the ligand in some solvents showed that, it is soluble in methanol, ethanol and DMSO but insoluble in water, ether and carbon tetrachloromethane while slightly soluble in nitrobenzene and acetonitrile. The solubility of the complex follows a similar pattern as shown in Table 1. The IR spectra of the free ligands showed broad bands around 3400 - 3200cm^{-1} and were assigned to з(O-H) stretching vibrations. The strong peaks observed in the 1631 ï 1642 cm^{-1} region were attributable to the azomethine з (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 з (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 ï 749 cm^{-1} and 575 ï 594cm^{-1} in the metal (II) chelates, respectively, indicating the formation M ï N and M ï O bonds confirming coordination of the ligand to the metal (II) ions.

The elemental analyses of the metal (II) chelates for H, C and N (Table 2) showed that the observed and the calculated percentages of the elements are in good agreement and support 1:1 metal-ligand ratio in all the complexes. The number of coordinated ligands per metal ion was also determined using continuous variation method and was established to be 1:1.

The dissociation constant (pKa) of the ligand (N, N`- bis(2-hydroxy-1-

naphthyl)ethylenediimine) is as shown in Tables 3. The value is 12.55. It can be seen that the Schiff base has very low dissociation constant indicating weak acidity. Exhaustive literature search revealed no dissociation constant values of this Schiff base ever reported to compare with. Nevertheless, ORIGIN 50 method (Aliyu and Naôaliya, 2010) was used. From that method, L` recorded dissociation constant value of 13.199 as shown in Fig. 2 indicating slight variation in dissociation constant value determined from the two methods employed, suggesting that the value is reliable.

The average number of coordinated ligand to the metal ion was determined potentiometrically. The average number of coordinated ligand is 1.08 as shown in Table 4. Generally, from these results, the ratio of number of ligand to the metal ion is 1:1. From these analyses, the proposed molecular formula of the ligand and complex is presented in Fig. 3 and 4 respectively.

Conclusion

A Schiff base ligand derived from condensation of 2 ï hydroxyl -1- naphthaldehyde and ethylenediamine was synthesized. It was characterized by melting point, potentiometric studies. Its Copper (II) complex was also synthesized. The complex was subjected to uv-visible spectrophotometric studies, molar conductance as well as Gibbôs free energy determination.

Table 1: Solubility Test for L` and [CuL`]

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

IS = Soluble, SS = Slightly Soluble, S = Soluble

Table 2: Elemental Analysis of L` and [CuL`]

Compound	% Calculated (Found)		
	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)

Table 3 : Determination of Dissociation Constant (pKa) of L`

Vol	pH	Atot	pKa
0.50	10.61	0.02	10.87
1.00	11.49	0.02	11.75
1.50	11.82	0.02	12.08
2.00	11.98	0.02	12.24
2.50	12.12	0.02	12.38
3.00	12.22	0.02	12.48
3.50	12.31	0.02	12.57
4.00	12.38	0.02	12.64
4.50	12.44	0.02	12.70
5.00	12.49	0.02	12.67
5.50	12.54	0.02	12.72
6.00	12.57	0.02	12.75
6.50	12.62	0.02	12.80
7.00	12.65	0.02	12.83
7.50	12.68	0.02	12.86
8.00	12.7	0.02	12.88
8.50	12.73	0.02	12.91
9.00	12.75	0.02	12.93
9.50	12.78	0.02	12.96
10.00	12.81	0.02	12.99

Average pKa = **12.55**

Ka = **2.81E-13**

Table 4: Determination of Average number of Coordinated Ligand (□) 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

Where *n* average number of coordinated ligand to complex

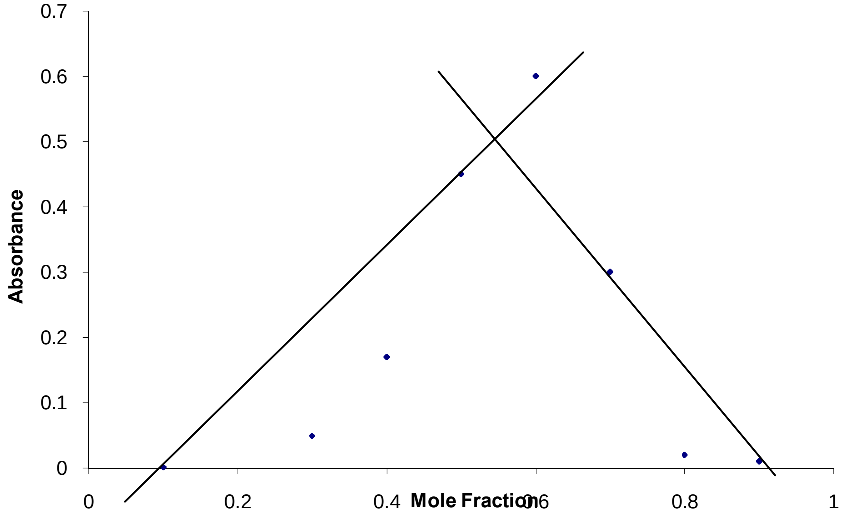


Fig.1 : Plot of Absorbance Copper (II) chloride solution with L` against mole fraction

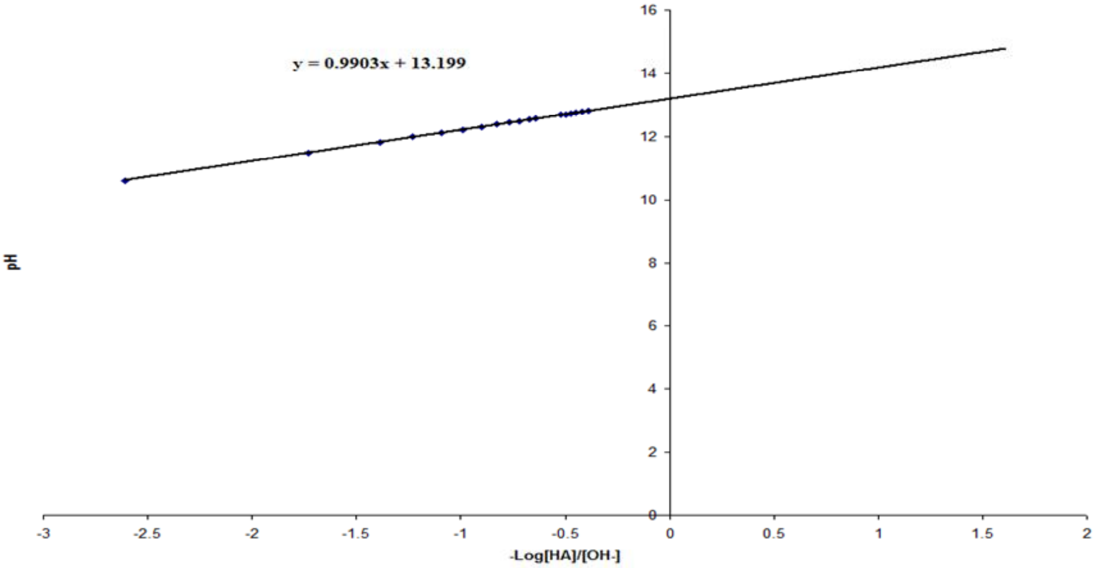


Fig. 2: pKa of L` using the graphical method

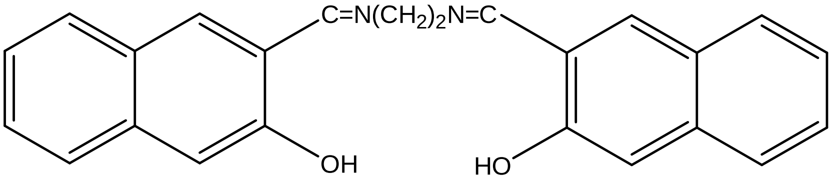
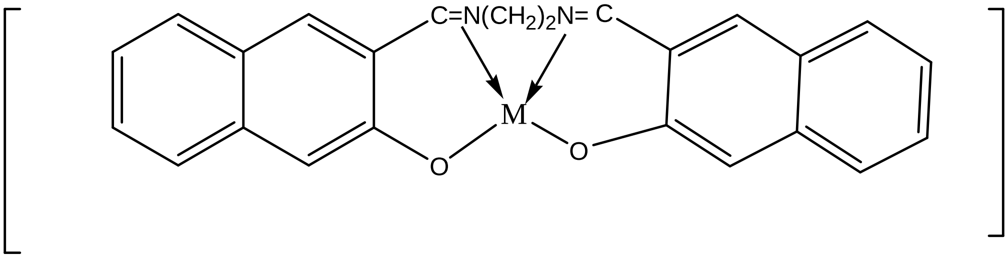


Fig. 3: Proposed General Structure of the Schiff base



M = Cu(II)

Fig. 4: Proposed General Structure of the Metal Complex

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