Bayero Journal of Pure and Applied Sciences, 3(2): 138 - 141
Received: October, 2010
Accepted: November, 2010
ISSN 2006 - 6996

SYNTHESIS AND CHARACTERIZATION OF DIAQUO BIS(N – 2 – AMINOPROPYL ACETYLACETONATO) COPPER (II) COMPLEX

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ABSTRACT
N – 2 – aminopropyl acetylacetone Schiff base was prepared from the reaction of 2 – aminopropanoic acid and acetylacetone. The reaction of the Schiff base with copper (II) chloride formed diaquo bis(N – 2 – aminopropyl acetylacetonato) copper (II) complex. The Schiff base is crystalline orange yellow, has a yield of 53% and melting point of 160^{o}C. The prepared diaquo bis(N – 2 – aminopropyl acetylacetonato) copper (II) complex is crystalline blue, has a yield of 70% and decomposition temperature of 245^{o}C. The N – 2 – aminopropyl acetylacetone Schiff base is soluble in most solvents including water, but insoluble in ether. Its copper (II) complex is soluble in water, DMSO and DMF, but insoluble in most common organic solvents. The molar conductance of copper (II) Schiff base complex determined is 26 ohm^{-1} cm^{2} mol^{-1}. The infra-red spectral data of the Schiff base and its copper (II) complex showed bands in the range 1607 – 1641 and 1589 - 1624cm^{-1}, respectively, assignable to v(C=N) stretching vibrations. The broad bands in the range 3294 - 3428 and 3342 - 3402cm^{-1} are attributable to v(O-H) stretching frequencies in the Schiff base and its complex compound, respectively. The weak bands at 534 and 376 cm^{-1} are attributable to v(Cu-O) and v(Cu-N) stretching vibrations, respectively in the copper (II) Schiff base complex. The dissociation constant (pKa) of N – 2 – aminopropyl acetylacetone schiff base determined is 4.17. The stability constant and Gibb's free energy of copper (II) Schiff base complex determined are 4.5x10^{9} and -5.50x10^{4} Jmol^{-1}, respectively. The ratio of copper (II) ion to N – 2 – aminopropyl acetylacetone schiff base determined is 1:1.

Keywords: Alanine (2-aminopropanoic acid), Complex compound, acetylacetone, stability constant, potentiometry, N – 2 – aminopropyl acetylacetone

INTRODUCTION

Alanine (2-aminopropanoic acid) belongs to chemical compounds known as amino acids, which are chemical compounds containing an amino group (-NH_2), a carboxylic group (-COOH), a hydrogen atom (H) and a distinctive R – group bonded to the α – amino carbon atom. The carbon atom to which these groups are attached is called α – amino because it is adjacent to the carbonyl acidic group. Amino acids were earlier discovered as constituents of natural products even before they were recognized as components of proteins; asparagine was discovered in 1806 in juice of asparagus plant and cystine in 1810 in urinary stones. In deed, their names are based on the sources from which they were isolated (Akpurieme, 2001). The first amino acid isolated from hydrolysis of protein was glycine, obtained in 1820 from gelatin by Braconnot as reported by Lehninger (1975). He also reported threonine an amino acid, isolated from hydrolyzates of fibrin by Rose in 1935 (Lehninger, 1975). Hofmeister and Fischer (1902) have explained the mode of combination of the amino acids in proteins (Akpurieme, 2001). Their development of the peptide hypothesis of protein structure is regarded as one of the most important events in the history of protein chemistry. Amino acids are the essential constituents of plants and animal tissues (Holmes and Hazel, 1993). They also occur in plants cells both as free acid or amides (Evans *et al.*, 1986). Over 200 different amino acids have been found in higher plants and twenty (20) are known to be the building blocks of protein found in cytoplasm. Amino acids are reactive, for example they react with aldehydes and ketones to form Schiff bases, which belong to a class of compounds that contain an imine or azomethine group (-C=N-), and are formed by the condensation of an amine with an aldehyde or ketone. The aldehyde forms aldimines and ketone forms ketoimines (Cotton and Willkinson 1994). Schiff bases have been used extensively as ligands in the field of coordination chemistry, these are either neutral or charged species possessing at least a lone pair of electrons, which can be coordinated to transition metals, forming complexes (Shriver *et al.*, 1994). Schiff bases and their complex compounds have been studied for their important properties, for example, thiazole and benzothiazole Schiff bases show effective antifungal activity (Dash et al., 1984). Some Schiff bases derived from quinazolinones show antifungal activity against *Candida albicans, Trichophyton rubrum, T. mentagrophytes, A. niger and Microsporum gypseum* (Rao et al., 1987). metal complexes of molybdenum (IV) and manganese (II) with Schiff base ligands derived from hydrazine carboxamide and hydrazine carbothiaamide show antibacterial activity against *S. aureus and xanthomonas compestris* (Singn *et al.*, 1999). In another report, Guar (2003) explained that Schiff base complexes of copper (II) and nickel (II) show antibacterial activities to *Colibacillus and pseudomonas aeruginosa*.

MATERIALS AND METHODS

All glass wares used were well washed with a detergent, rinsed with distilled water and dried in an oven before use. Weightings were carried out on digital balance model, AB 54 to four decimal places. Infrared spectral analyses were recorded using a Nicolade IR 100 model in Nujol in the range 400 – 4000cm^{-1}. pH measurements were also carried out using Jenway pH Meter model 3320 and electrical conductance using conductivity meter, model 4010-Jenway.

Preparation of the Schiff Base

Exactly 0.2g of acetylacetone in 10cm^3 ethanol was added into a stirred solution of 20mmol 2 – aminopropanoic acid solution in 30cm^3 water. The mixture was refluxed for 6hrs during which yellow orange precipitate was observed to form on cooling. The residue was filtered and recrystallized from ethanol-propanol (60:40) mixture and dried in a desiccator over phosphorus pentoxide.

Preparation of the Copper (II) Schiff Base Complex

To ethanolic solution of copper (II) dihydrate (0.01mol; 1.705g) in a round bottom flask was added hot methanolic solution of the Schiff base (0.02mole). The resulting mixture was refluxed for 3hrs and greenish blue precipitate was observed to form on cooled, which was separated, washed with ethanol/methanol mixture and ether before recrystallized from water/ethanol (40:60) mixture and then dried over a desiccator.

Determination of Dissociation Constant (pKa) of the Schiff Base

Into a 400cm^3 beaker containing a magnetic stirrer were added 90cm^3 of water, 100cm^3 of 0.2M KNO_3 and 10cm^3 of 0.4M Schiff base solution. A 0.47M standardized solution of sodium hydroxide was added drop wise to a total volume of 10cm^3, the corresponding pH of the mixture was recorded after each addition (Angelici, 1977).

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

Into a 400cm^3 beaker containing a magnetic stirrer were added 90cm^3 of water,10cm^3 of 0.1M HNO_3, 100cm^3 of 0.2M KNO_3 and 1mmol of copper (II) chloride dihydrate. A solution of 0.4M sodium salt of the Schiff base was gradually introduced into the reaction mixture to total volume of 10cm^3. After each addition of the 0.4M sodium salt of the Schiff base, the corresponding pH of the reaction mixture was recorded (Angelici, 1977).

RESULT AND DISCUSSION

The reaction of 2 – aminopropanoic acid and acetylacetone formed N - 2 – aminopropyl – acetylacetone Schiff base, which is a crystalline orange-yellow solid, has high melting temperature of 160^oC and percentage yield 53%. The reaction of the Schiff base with copper (II) chloride dihydrate gave diaquo bis(N - 2 – aminopropyl acetylacetonato) copper (II) complex, which is a crystalline blue complex compound of 245^oC decomposition temperature and percent yield of 70% (Table 1). The Schiff base is soluble in water and most organic solvents except ether, however, the diaquo bis(N - 2 – aminopropyl acetylacetonato) copper (II) complex is soluble in water, DMSO and DMF but insoluble in most common organic solvents (Table 2). Molar conductance measurement of 10^{-3}M complex in DMSO determined is 26 ohm^{-1} cm^2 mol^{-1} (Table 3), revealing that the compound is non electrolyte (Geary, 1971). The empirical formula of the complex compound determined suggested the molecular formula $[Cu(L)_2(H_2O)_2]$. The infrared spectral band of the free Schiff base exhibits two bands in the region 1607-1641 and 3294 – 3428cm^{-1}, which were assigned to ν(C=N) and ν(O-H) stretching vibrations, respectively. Similarly, the infrared spectra of the complex, diaquo bis(N - 2 – aminopropyl acetylacetonato) copper (II) complex showed bands in the region 1589 – 1624 and 3342 - 3402cm^{-1} that are attributed to ν(C=N) and ν(O-H) stretching vibrations, respectively. The second band in the spectra revealed the presence of water in the complex, as the acidic hydrogen in the Schiff base has been deprotonated on coordination to the copper (II) ion (Bellamy, 1971; Arif *et al.,* 2006). The bands at 534 and 376 cm^{-1} are observed in the complex, which are attributed to ν(Cu-O) and ν(Cu-N) stretching vibrations, respectively (Ferrero,1971; Nakamoto,1970). The infrared spectral results are shown in Table 5. The average dissociation constant (pKa) of N - 2 – Aminopropyl acetylacetone Schiff base determined is 4.17, indicating a weak acid. This value is in agreement with literarture value (Katzin *et al.*,1971). The stability constant K_f of diaquo bis(N - 2 – Aminopropyl acetylacetonato) copper (II) complex determined is $4.5x10^9$, which is high, revealing good stability for the complex compound. The Gibb's free energy of the complex compound determined is very low (-5.50 $x10^4$ $Jmol^{-1}$), suggesting a stable complex, which is in agreement with the high stability constant and large decomposition temperature shown by the complex (Table 6). The ratio of copper (II) ion to N - 2 – Aminopropyl acetylacetone Schiff base is 1:2, which agrees with the empirical formula calculation.

From the analytical results of the complex compound and available literature, the molecular structure below is proposed.

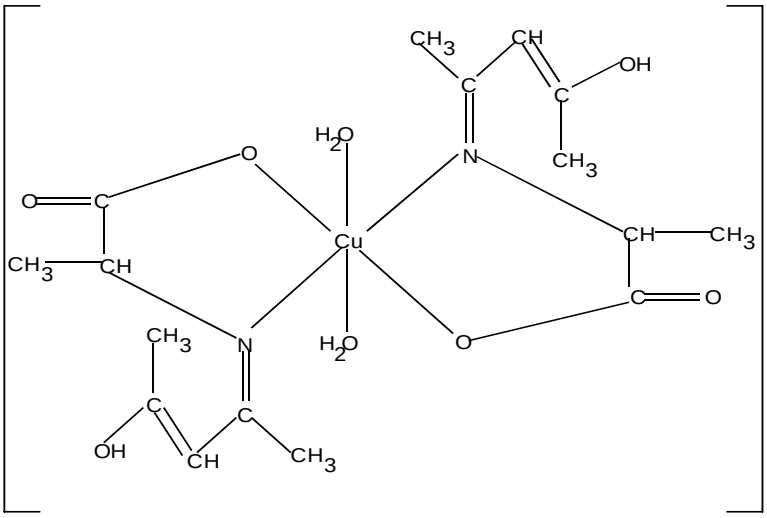

Fig.1: Proposed molecular structure of diaquo bis(N - 2 – Aminopropyl acetylacetonato) copper (II) complex

Table 1:Physical properties of the Schiff base and its copper (II) complex

Compound	Colour	Melting Point (°C)	Decomposition Temp. (°C)	Per cent Yield (%)
Schiff base	Orange yellow	210	-	53
$[CuL_2(H_2O)_2]$	Greenish blue	-	231	73

Key: L = N - 2 – Aminopropyl acetylacetonato ligand

Table 2: Solubility of the Schiff base and **its copper (II) complex**

Compound	Water	Methanol	Ethanol	Acetone	DMF	Chloroform	DMSO	Ether
Schiff base	S	S	S	S	S	S	S	IS
$[CuL_2(H_2O)_2]$	S	IS	IS	IS	S	IS	S	IS

Key: L = N - 2 – Aminopropyl acetylacetonato ligand, S = Soluble, IS = Insoluble, SS = Slightly soluble

Table 3: Conductivity of the Schiff base and its copper (II) complex

Compound	Molar Conductance (Ohm^{-1} cm^2 mol^{-1})
$[CuL_2(H_2O)_2]$	31

Key: L = N - 2 – Aminopropyl acetylacetonato ligand

Table 4: Infra red spectral data of the Schiff base and its copper (II) complex

Compound	ν(C=N) (cm^{-1})	ν(O-H) (cm^{-1})	ν(M-O) (cm^{-1})	ν(M-N) (cm^{-1})
Schiff base	1612 – 1636	3278 – 3423	-	-
$[CuL_2(H_2O)_2]$	1592 - 1624	3314 - 3397	514	387

Key: L = N - 2 – Aminopropyl acetylacetonato ligand

Table 5: Determination of pKa of the Schiff base

S/No.	Value of NaOH (cm^3)	pH	$[H^+]$ x 10^{-5}	$[Na^+]$ x 10^{-3}	[A-]	pKa
1	0.5	3.80	9.97	1.15	2.00	5.15
2	1.0	3.92	8.04	2.29	1.20	5.11
3	1.5	4.20	4.22	3.42	1.90	5.05
4	2.0	4.24	3.85	5.66	1.90	4.93
5	2.5	4.31	3.28	6.80	1.98	4.87
6	3.0	4.33	3.13	7.90	1.98	4.78
7	3.5	4.36	2.92	9.01	1.97	4.70
8	4.0	4.39	2.73	10.10	1.97	4.63
9	4.5	4.44	2.43	11.20	1.96	4.57
10	5.0	4.47	2.27	12.30	1.96	4.52
11	5.5	4.50	2.12	13.40	1.96	4.47
12	6.0	4.52	2.02	14.50	1.95	4.43
13	6.5	4.54	1.93	15.60	1.95	4.39
14	7.0	4.61	1.64	16.60	1.94	4.35
15	7.5	4.63	1.57	17.70	1.94	4.28
16	8.0	4.63	1.56	18.80	1.93	4.22
17	8.5	4.64	1.53	19.20	1.93	4.19
18	9.0	4.64	1.53	19.50	1.92	4.14
19	9.5	4.64	1.49	19.90	1.92	4.09
20	10.0	4.65	1.47	19.90	1.91	4.06

Average dissociation constant of N - 2 – Aminopropyl acetylacetone Pka = 4.55

Table 6: Stability constant of the Schiff base and its copper (II) complex

Compound	Stability constant (K_f)	Gibb's free energy $\Delta G\ (J\ Mol^{-1})$
$[CuL_2(H_2O)_2]$	$3.8x10^9$	-5.47

Key: L = N - 2 – Aminopropyl acetylacetonato ligand

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