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Full Length Research Paper

Synthesis, Spectrophotometric and Biological Activity of Nickel (II) and Copper (II) Complexes with Schiff Base Derived from Acetylacetone and Histidine

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The reaction of the mixture of ethanolic solution of acetylacetone and aqueous solution of histidine yielded a Schiff base. The interaction of the Schiff base in hot aqueous-methanol mixture and a metal (II) chloride in ethanol gave the metal (II) Schiff base complex. The complexes were characterized by molar conductance measurement, infrared, potentiometry, decomposition temperatures, solubility and in vitro antimicrobial analysis. The Schiff base is yellow, has melting point of 244^{o}C and percentage yield of 66%. The nickel (II) and copper (II) complexes are green, have decomposition temperatures of 166 and 160^{o}C, and percentage yield of 64.65 and 71.78%, respectively. The Schiff base and the complexes are soluble in water, DMSO and DMF, but are slightly soluble in most organic solvents. Molar conductance measurement of the complexes showed that they are non-electrolyte. The infrared spectra of the Schiff base showed a band at 1550 cm^{-1} assigned to *v*(C=N) vibrational modes. Similar band appeared in the spectra of the complex, but in the lower frequency, confirming coordination of the Schiff base to the respective metal (II) ions. The bands in the spectra of the complex within 460 – 480 and at 625 - 630cm^{-1} are attributable to *v*(M-N) and *v*(M-O) stretching vibrations, respectively. The potentiometric analysis of nickel (II) and copper (II) complex compounds established 1:2, metal-ligand ratio. The stability constant of the complexes determined are 6.29x 10^{18} and 1.59x10^{20}. The Schiff base showed no activity against *Escheria coli* spp. *Staphylococcus aureus*, *Aspergillus niger* and *Candida Albican*, however, the complex compounds showed significant activity against the organisms.

Keywords: Acetylacetone, histidine, spectroscopy, conductance, nickel (II), copper (II), complex, stability constant, potentiometry and infrared.

INTRODUCTION

Schiff base compounds are formed by the condensation of primary amines with carbonyl compounds (Pierre, 1987). They act as ligands because they contain N and O donor atoms (Cotton and Wilkinson, 1972). Ben Saber *et al.,* 2005, reported the synthesis of a Schiff base derived from salicylaldeyde, and histidine and its complex compounds with divalent transition metal ions. The complexes were investigated by elemental analysis and were found to be of 1:1 metal to ligand ratio. In recent years, there has been enhanced interest in the synthesis and characterization of transition metal complexes containing Schiff bases due to

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their importance as catalyst in many reactions (Singh *et al*., 2006).

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.

The synthesis, characterization and antimicrobial activity of cobalt (II) and nickel (II) complexes of acetyl derivatives of urea and thiourea were reported by Joshua *et al* (1994). Urea and thiourea were readily acetylated with equimolar mixture of acetic anhydride and glacial acetic acid to form monoacytyl derivatives. All the ligands and their complexes were insoluble in petroleum ether and diethyl ether. Bis(acylthiourea) nickel (II) chloride was insoluble in acetone. The magnetic moment and the elemental analysis supported a tetrahedral structure of the complexes. The results of the inhibitory activity of the synthesized complexes on some organisms showed that apart from the organism, *Escherichia coli, Aspergillus flavus* and *Asperfillus niger* where there were full growth of the organism, the N-acylurea and N-acylothiourea complexes posses inhibitory activity which was comparable to that of their sulphathazole analogues which is a standard antimicrobial drug. Generally, the metal complexes of N-acylurea and N-acylthiourea had greater inhibitory activity on the organisms compared to their corresponding free ligands. The two metal salts ($NiCl_2.6H_2O$ and $CoCl_2.6H_2O$) possess absolutely no inhibitory activity in all the selected bacteria species while they have very slight effect on the growth of all the fungi except Aspergillus flavus with no effect.

This paper reports synthesis, spectrophotometric and biological activity of nickel (II) and copper (II) complexes with schiff base derived from acetylacetone and histidine

MATERIALS AND METHODS

All reagents used in this work were of Analar Grade and were used without further purification. All glass wares were properly washed, rinsed with distilled water and dried in an oven. Electric balance, model AB 54 was used for weighing, pH measurements were done using Jenway pH meter model 3305. Molar conductance was done using Jenway conductivity meter model 4010. While the Infra red spectral analysis were recorded using Perkin Elmer spectrum 100 Fourier transformer IR spectrometer model within the range of 450-4000cm^{-1}. Melting point and decomposition temperature were obtained using a Gallenkamp melting apparatus. The in vitro anti-microbial screening was performed by disc diffusion method. Nutrient agar and Sabouraud $4^0/_0$ Glucose agar were used as culture medium. The fungi species used were *Candida albican and Aspergillus niger* while that of the bacteria were *Escherichia Coli specie* and *Staphyloccocus aureus*, all clinical isolates obtained from Aminu Kano teaching hospital.

Preparation of the Schiff base

1.03cm^3 acetylacetone (0.01mol) in ethanol (10cm^3) was added to 1.6 grams of stirred solution of the histidine (0.01mol) in water (20cm^3). The mixture was refluxed for four hours during which the colour of the solution turned to orange-yellow. This was cooled to produce a solid product which was filtered, washed with ethanol, then with ether and dried in phosphorus pentoxide. Crystallization from distilled water produced the desired ligand. The yield was 65.71% with the melting point of 244ºC and formular weight of 237.28g (Cholan *et al*., 2006).

Preparation of the nickel (II) and copper (II) complexes

For the preparation of the metal (II) Schiff base complexes, a solution (30cm^3) of the Schiff base in hot aqueous methanol (40:60) was added to a stirred solution of a metal (II) chloride in ethanol (25cm^3). The mixture was refluxed for three hours (3hrs) then cooled to room temperature which solidified on cooling. The product thus obtained was filtered, washed with methanol/ethanol mixture and finally dried in air (Chohan *et al*., 2006).

Determination of Dissociation constant of the Schiff base

To a 400cm^3 beaker, 90cm^3 of distilled water was added followed by 100cm^3 of 0.2mol dm^{-3} KNO_3, 10cm^3 of 0.4mol dm^{-3} solution of the Schiff base and a magnetic stirrer. 10cm^3 of standardized aqueous solution of NaOH (0.48mol dm^{-3}) was added gradually and the corresponding pH-value recorded after each addition. The dissociation constant pKa of the schiff base was calculated using the equation below by (Gregory *et al,* 1978).

Determination of stability constants of nickel (II) and copper (II) complexes

To a 400cm^3 beaker containing 100cm^3 of 0.2M KNO_3, 90cm^3 of water, 10cm^3 of 0.1mol dm^{-3} HNO_3 and 1mmole of a metal (II) chloride were added, followed by addition of 10cm^3 of 0.4M sodium salt of the Schiff base which was prepared by neutralizing weighed Schiff base with

Table1. Physical properties of the Schiff base and its nickel (II) and copper (II) complexes

Compound	% Yield	Colour	M. P. (^oC)	Decomposition Temp (^oC)
Schiff base (L)	63.32	Yellow	244	-
$[NiL_2(H_2O)_2]$	64.65	Green	-	166
$[CuL_2(H_2O)_2]$	72.78	Green	-	160

Table2. Solubility of the Schiff base and its nickel (II) and copper (II) complexes

Compound	Water	Ethanol	DMSO	Methanol	Chloroform	Ether	DMF
Schiff base (L)	S	SS	S	SS	SS	SS	S
$[NiL_2(H_2O)_2]$	S	SS	S	SS	SS	SS	S
$[CuL_2(H_2O)_2]$	S	SS	S	SS	SS	SS	S

Key
S = Soluble
SS = Slightly soluble
L = Ligand

Table3. Molar conductance of nickel (II) and copper (II) complexes in 10^{-3}M DMF solution

Compound	Electrical conductivity ($ohm^{-1}cm^{-1}$)	Molar conductivity ($ohm^{-1}cm^2mol^{-1}$)
$[NiL_2(H_2O)_2]$	34.0×10^{-6}	34.0
$[CuL_2(H_2O)_2]$	45.2×10^{-6}	45.2

calculated amount of standardized 0.48M NaOH solution. After each 0.2cm^3 aliquot addition, the corresponding pH was recorded and the average number of coordinated ligands per metal ion for each metal (II) complex was calculated using the expression below (Gregory *et al.,* 1978).

Antibacterial and Antifungal bioassay

The paper discs were impregnated with 1000µg, 2000µ and 3000µg concerntrations of the Schiff base and its metal (II) complexes. Two loopfuls of the standard inoculums were evenly streaked on the plates in duplicates. Discs containing the impregnated quantities of the complexes as well as the control discs (with only DMSO) were placed firmly on the surface of the medium by means of a sterile syringe needle at about 40mm apart. For the bacteria, the plates were incubated at 37^{o}C for 24 hours (Shamsuddeen *et al.,* 2008). For the fungal activity, it was incubated at room temperature for 48 hours (Hassan, *et al.,* 2006). Each of the plates were examined for clear zones of inhibition. Diameters of the zone of inhibitions were measured with millimeter rule and the mean recorded in the nearest millimeter

RESULTS AND DISCUSSIONS

The Schiff base was prepared by refluxing a mixture of ethanolic solution of acetylacetone and aqueous solution of histidine. The Schiff base is yellow, has melting point of 244^{o}C and percentage yield of 66%. The nickel (II) and copper (II) Schiff base complexes synthesized are green, have decomposition temperatures of 166 and 160^{o}C, and percentage yield of 64.65 and 72.78%, respectively (Table 1). The Schiff base and its metal (II) complexes are soluble in water, DMSO and DMF, but are slightly soluble in most organic solvents (Table 2). Molar conductance measurement of nickel (II) and copper (II) complexes determine as reported by Geary (1971) are 34.0 and 45.2 $ohm^{-1}cm^2mol^{-1}$, which are very low, confirming that they are non-electrolytes (Table 3). The infrared spectra of the free Schiff base showed a band at 1550 cm^{-1} attributable to ν(C=N) stretching frequencies. Similar bands are observable in the spectra of nickel (II) and copper (II) Schiff base complexes, but in lower frequencies, indicating that the Schiff base has coordinated to the respective metal ions. Other bands in the spectra of the metal (II) complexes

Table4. The infrared spectral data of the Schiff base and its metal (II) complex

Compound	*v*(O-H)	*v*(C=N)	*v*(M-O)	*v*(M-N)
Schiff base	-	1550	-	-
$[NiL_2(H_2O)_2]$	3220	1500	630	480
$[CuL_2(H_2O)_2]$	3200	1521	625	460

Table5. Dissociation constant of the Schiff base

S/No.	Vol. of NaOH added (cm^3)	pH	$[H^+]$	$[OH^-]$	$[Na^+]$	A_{tot}	pKa
1	0.50	7.73	1.25E-8	5.80E-7	1.19E-3	2.00E-2	9.09
2	1.00	7.97	7.17E-9	1.01E-6	2.39E-3	1.99E-2	9.01
3	1.50	8.14	4.85E-9	1.49E-6	3.57E-3	1.99E-2	8.97
4	2.00	8.29	3.43E-9	2.11E-6	4.75E-3	1.98E-2	8.97
5	2.50	8.40	2.66E-9	2.72E-6	5.93E-3	1.98E-2	8.94
6	3.00	8.51	2.07E-9	3.49E-6	7.09E-3	1.97E-2	8.94
7	3.50	8.61	1.64E-9	4.40E-6	8.26E-3	1.97E-2	8.93
8	4.00	8.69	1.37E-9	5.29E-6	9.41E-3	1.96E-2	8.90
9	4.50	8.77	1.14E-9	6.36E-6	1.06E-2	1.96E-2	8.87
10	5.00	8.85	9.50E-9	7.65E-6	1.17E-2	1.95E-2	8.85
11	5.50	8.93	7.90E-9	9.1E-6	1.29E-2	1.95E-2	8.82
12	6.00	9.00	6.70E-9	1.08E-5	1.40E-2	1.94E-2	8.77
13	6.50	9.08	5.60E-9	1.30E-4	1.51E-2	1.94E-2	8.70
14	7.00	9.15	4.70E-9	1.53E-4	1.62E-2	1.93E-2	8.61
15	7.50	9.23	3.90E-9	1.84E-4	1.74E-2	1.93E-2	8.46
16	8.00	9.31	3.30E-9	2.21E-4	1.85E-2	1.92E-2	8.14

The average dissociation constant (pKa) = 8.81

Table6. Stability Constant and Gibb's free energy of nickel (II) and copper (II) complexes

Compound	Stability constant (K)	Gibb's free energy, ΔG ($KJmol^{-1}$)
$[NiL_2(H_2O)_2]$	$6.29x10^{18}$	107.20
$[CuL_2(H_2O)_2]$	$1.589x10^{20}$	115.19

in the ranges 460 – 480 and 630 - 625 cm^{-1}, respectively, are assigned to *v*(M-N) and *v*(M-O) vibrational modes, confirming the combination of the Schiff base to the respective metal ions (Table 4). The strong bands at 3220 and 3200 $cm^{-1}$are attributable *v*(O-H) stretching frequencies for coordinated water in nickel (II) and copper (II) Schiff base complexes, respectively (Byeong-Goo *et al*,. 1996; Ahmed and Akhtar, 1983; Zhang *et al*., 2009; and Guo *et al*., 2009).

The dissociation constant of the Schiff base determined as reported by Gregory (1978) is 8.81, indicating that it is a weak acid (Table 5). The potentiometric analytical result of nickel (II) and copper (II) Schiff base complex compounds established 1:2, metal-schiff base ratio, while the stability constants of the complexes determined are $6.29x10^{18}$ and $1.589x10^{20}$, and the corresponding change in Gibb's free energy are 107.20 and 115.19 $KJmol^{-1}$, respectively (Table 6). The empirical formula calculation of the metal (II) ion, water content and the Schiff base from their known percentage compositions in the complexes, suggested the general formula $[ML_2(H_2O)_2]$.

The antibacterial activity tested for the Schiff base and the metal (II) complexes have been determined. The diameter of inhibition zone (mm) was measured for each treatment. All the organisms are found to be resistant to the Schiff base at all concentrations. The two metal (II) complexes showed strong activity on the isolates at

Table7. Bacterial activity against the Schiff base and its nickel (II) and copper (II) complexes

Test organism	Compound	Zone of inhibition			
		3000µg	2000µg	1000µg	Control (DMSO)
Escheria coli spp	$[NiL_2(H_2O)_2]$	13mm	8mm	000	000
	$[CuL_2(H_2O)_2]$	16mm	11mm	000	000
	Schiff base	000	000	000	000
Staphylococcus aureus	$[NiL_2(H_2O)_2]$	14mm	11mm	000	000
	$[CuL_2(H_2O)_2]$	14mm	11mm	000	000
	Schiff base	000	000	000	000

Table 8. Fungal activity against the Schiff base and its nickel (II) and copper (II) complexes

Test organism	Compound	Zone of inhibition			
		3000µg	2000µg	1000µg	Control (DMSO)
Aspergillus niger	$[NiL_2(H_2O)_2]$	13mm	9mm	000	000
	$[CuL_2(H_2O)_2]$	12mm	8mm	000	000
	Schiff base	000	000	000	000
Candida Albican	$[NiL_2(H_2O)_2]$	15mm	12mm	000	000
	$[CuL_2(H_2O)_2]$	16mm	9mm	000	000
	Schiff base	000	000	000	000

medium and high concentrations (Table 7). Sensitivity of fungal isolates (*Mucor sp. and Rhizopus sp.*) showed that the Schiff base is not active on both the isolates at all concentrations. The result for *Mucor sp. and Rhizopus sp.* showed strong activity against the organism at high concentrations for both the complexes (Table 8).

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