



## STUDIES OF Ni(II) AND Cu(II) COMPLEXES WITH SCHIFF BASE DERIVED FROM SALICYLALDEHYDE AND ANILINE

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### ABSTRACT

*The schiff base ligand and its complexes of divalent metal ions of Ni (II) and Cu (II) were synthesized. The ligand and the complexes were characterized by elemental analysis, potentiometry, molar conductance, melting point or decomposition temperatures and infrared analyses. The elemental analysis data show the formation of 1:2 metal-ligand ratio. The ligand and complexes were screened for antibacterial activity against Escherichia coli and Staphylococcus aureus, and antifungal activity against Aspergillums niger and Candida albican, using discs diffusion method. It has been found that the ligand and the complexes showed different activities against microorganisms. The complexes show higher activity than the free Schiff base ligand. The molar conductance of the complexes measured is low, indicating their non-electrolytic nature. The potentiometric studies of the complex compounds revealed 1:2 metal to ligand ratio.*

**Key words:** salicylaldehyde, aniline, ligand, potentiometry, antibacterial, antifungal.

### INTRODUCTION

Schiff base ligands are chemical compounds containing carbon-nitrogen double bond (C=N) functional group, called azomethine, Schiff bases are named after a German scientist, Hugo Schiff who had synthesized such compounds earlier (Hobday and Smith 1972, Holm 1966, John 2002). They are usually formed by the condensation reaction of a ketone or an aldehyde with a primary amine to generate an imine (Silver and Bassler 1967). The field of Schiff base complexes has been fast developing on account of the wide variety of possible structures for the ligands depending upon the aldehydes and amines. Schiff bases are considered as a very important class of organic compounds, which have wide application in many biological aspects. The properties of Schiff bases vary depending on the types of carbonyls and amines; they are mostly crystalline pale yellow with usually high melting points (Hassan, 1991). Schiff bases are known to form complexes with divalent or trivalent metal ions in different ratios depending on the Schiff bases that coordinate to the metal ion (Maihab *et al.*, 2005). The chemical investigation of the Schiff base metal complexes has been carried out by used of several techniques including elemental analysis, thermogravimetric analysis, magnetic moment, infrared (IR), conductivity measurement, electronic and mass spectrometry (Hassan, 1991). Schiff base metal complexes play an essential role in the different fields, such as medicine, Agriculture, Industries, and as catalysts in a chemical reaction. The present aim of the work is to synthesize a Schiff base derived from salicylaldehyde and aniline and to prepare its Ni(II) and Cu(II) complexes, characterize them and study their antibacterial and antifungal activities.

### MATERIAL AND METHODS

All the glass wares used in this research were well washed with detergent and clean water, then rinsed with distilled water and dried in an oven at 110°C, all the solid substances were weighed using electric mettler balance model AB 54. The IR spectra were recorded in the range of 4000-400cm<sup>-1</sup> with an FTIR Nicolet 100 in Nujol. pH measurement was carried using Jenway pH meter model 3320, while molar conductance was done on the cyber can 500 model, the melting point was determined using Gallemkerm melting point apparatus. The antimicrobial activities were carried out by disc diffusion method. All the reagents used in this work were of analytical reagent (AR) grade and were used without further purification.

#### Synthesis of Schiff Base

The Schiff base was prepared by mixing an ethanolic solution of 0.01mol of salicylaldehyde (1.22g) with 0.01mol aniline (0.93g) in the same solvent, after two hours refluxed yellow crystals appeared, the crystals were filtered and washed with ethanol and recrystallized from hot ethanol to give pure yellow crystals and dried over P<sub>2</sub>O<sub>5</sub> in a desiccator (Morad *et al.*, 2006).

#### Synthesis of the metal (II) Schiff Base complexes

The Schiff base complexes were synthesized by mixing 50cm<sup>3</sup> of ethanolic solution of the Schiff base (3.94g) with 25cm<sup>3</sup> of ethanolic solution of a metal (II) chloride and few drops of ammonia solution were added to adjust the pH, the obtained mixture was refluxed for two hours and final product were obtained and recrystallized from ethanol and dried over P<sub>2</sub>O<sub>5</sub> in a desiccator (Morad *et al.*, 2006).

**Determination of dissociation constant of Schiff base**

To a 400cm<sup>3</sup> beaker, 90cm<sup>3</sup> of distilled water was added followed by 100cm<sup>3</sup> of 0.2moldm<sup>-3</sup> KNO<sub>3</sub>, 10cm<sup>3</sup> of a 0.4moldm<sup>-3</sup> solution of the Schiff base and

$$p^{Ka} = -\log [H^+] + \log \left[ A_{tot} - \frac{[Na^+] + [H^+] - [OH^-]}{[Na^+] + [H^+] - [OH^-]} \right]$$

where p<sup>Ka</sup> = Dissociation constant  
 [H<sup>+</sup>] = Hydrogen ion concentration  
 [OH<sup>-</sup>] = Hydroxyl ion concentration  
 [Na<sup>+</sup>] = Sodium ion concentration  
 A<sub>tot</sub> = A total

the solution of NaOH (0.48moldm<sup>-3</sup>) 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. (Gregory *et al.*, 1978)

**Determination of dissociation constant of the complexes**

Into a 400 cm<sup>3</sup> beaker 100cm<sup>3</sup> of 0.2 M KNO<sub>3</sub>, 1mmole of Ni(II) or Cu(II) chloride, 0.1 M HNO<sub>3</sub> and 90cm<sup>3</sup> of distilled water were added, respectively. A magnetic stirring bar and the sodium salt of the Schiff base prepared by neutralizing a known quantity of the

Schiff base with the calculated amount of standardized NaOH solution. After each 0.2cm<sup>3</sup> aliquot addition, the corresponding pH of the stirred reaction mixture was recorded. From the result obtained, the number of coordinated ligands per metal ion of each metal (II) schiff base complex was calculated using the expression below (Avar.*et. al.*, 1975).

$$n = \frac{A_{tot} - \left[ 1 + \frac{Ka}{[H^+]} \right] [(CH) + [OH^-] - [OH^+]}{M_{tot}}$$

Where n = Number of coordinated ligands  
 A<sub>tot</sub> = A total  
 [H<sup>+</sup>] = Hydrogen ion concentration  
 [OH<sup>-</sup>] = Hydroxyl ion concentration  
 M<sub>tot</sub> = M total

**Antibacterial and Antifungal activity**

The paper discs were impregnated with 1000, 2000 and 3000µg/ml of the Schiff base and its metal (II) complexes. Two loops 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 sterile syringe needle at 40mm

apart. For the bacteria, the plates were incubated at 37°C for one day (shamsuddeen *et al.*, 2008). For the fungal activity, it was incubated at room temperature for two days (Hassan, *et al.*, 2006). Each of the plates was examined for the clear zone of inhibitions. The diameters of the zone of inhibitions were measured with millimeter rule and the mean recorded in the nearest millimeter.

**RESULTS AND DISCUSSION**

**Table 1: Molecular weight, colour and percentage yield of the ligand and metal complexes**

Compound	Molecular weight	Colour	Melting point (°C)	Decomposition Temp. (°C)	Yield (%)
Ligand (C <sub>13</sub> H <sub>10</sub> NO)	197.00	Yellow	104	-	94.92
[NiL <sub>2</sub> ]. 2H <sub>2</sub> O	629.71	Yellow	-	132°C	54.88
[CuL <sub>2</sub> ]. 2H <sub>2</sub> O	562.48	Black	-	158°C	55.30

Where L =schiff base ligand

**Table 2: percentage compositions of metal ion, ligand, and water of crystallization.**

Complexes	Metal (%)	Ligand (%)	Water of crystallization (%)
[Ni (L) <sub>2</sub> ]2H <sub>2</sub> O	11.04	81.26	7.70
[Cu(L) <sub>2</sub> ]2H <sub>2</sub> O	12.10	78.05	9.85

**Table 3: Solubility of the ligand and its complexes in some common solvents**

Compound	DMSO	Meth	Water	Toluene	Ethanol	Acetone	Ether	Ben	Isopropanol	DE
Ligand(C <sub>13</sub> H <sub>10</sub> NO)	S	S	IS	SS	S	IS	IS	IS	IS	IS
[NiL <sub>2</sub> ]. 2H <sub>2</sub> O	S	S	IS	SS	IS	IS	IS	IS	IS	IS
[CuL <sub>2</sub> ]. 2H <sub>2</sub> O	S	S	IS	SS	S	S	IS	IS	IS	IS

**Key:** S = Soluble. SS = slightly soluble. IS = Insoluble, DE = diethyl ether, Meth = Methanol, Ben = Benzene

**Table 4: Conductivity measurement of the complex compounds**

Complexes	Concentration mol dm <sup>-3</sup>	Electrical conductivity ohm <sup>-1</sup> cm <sup>-1</sup>	Molar conductivity ohm <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup>
[NiL <sub>2</sub> ]. 2H <sub>2</sub> O	1 x 10 <sup>-3</sup>	9.40x10 <sup>-6</sup>	94.0
[CuL <sub>2</sub> ]. 2H <sub>2</sub> O	1 x 10 <sup>-3</sup>	6.85x10 <sup>-6</sup>	68.5

**Table 5: Infrared spectral data of the Schiff base and its metal complexes**

Compound	$\nu(\text{C} = \text{N})\text{cm}^{-1}$	$\nu(\text{C} - \text{O})\text{cm}^{-1}$	$\nu(\text{M} - \text{N})\text{cm}^{-1}$	$\nu(\text{M} - \text{O})\text{cm}^{-1}$	$\nu(\text{O} - \text{H})\text{cm}^{-1}$
Ligand(C <sub>13</sub> H <sub>10</sub> NO)	1620	1210	-	-	3460
[NiL <sub>2</sub> ]. 2H <sub>2</sub> O	1580	1240	680	550	-
[CuL <sub>2</sub> ]. 2H <sub>2</sub> O	1590	1270	560	440	-

**Table 6: The stability constant and Gibbs free energy ( $\Delta G$ ) of the metal complexes**

Complex	Stability constants	Gibb's Free energy DG (KJmol <sup>-1</sup> )
[NiL <sub>2</sub> ]. 2H <sub>2</sub> O	5.01 x 10 <sup>18</sup>	-106.6
[CuL <sub>2</sub> ]. 2H <sub>2</sub> O	8.32 x 10 <sup>21</sup>	-125.0

**Table 7: Antibacterial effect of Schiff base and complexes**

Compound	<i>Escherichia coli</i>			<i>Staphylococcus aureus</i>		
	1000ug/ml	2000ug/ml	3000ug/ml	1000ug/ml	2000ug/ml	3000ug/ml
Ligand (C <sub>13</sub> H <sub>10</sub> NO)	-	-	-	-	-	-
[NiL <sub>2</sub> ]. 2H <sub>2</sub> O	-	-	+	-	-	+
[CuL <sub>2</sub> ]. 2H <sub>2</sub> O	+	+	++	-	+	+

**Table 8: Antifungal effect of Schiff base and its metal complexes**

Compound	<i>Aspergillus niger</i>			<i>Candida albican</i>		
	1000 ug/ml	2000 ug/ml	3000ug/ml	1000ug/ml	2000ug/ml	3000ug/ml
Ligand (C <sub>13</sub> H <sub>10</sub> NO)	-	+	++	-	+	+++
[NiL <sub>2</sub> ]. 2H <sub>2</sub> O	+	+++	+++	-	-	-
[CuL <sub>2</sub> ]. 2H <sub>2</sub> O	-	-	+	+	++	++

**Key:** High active = +++ (Inhibition zone >12mm)  
 Moderate active = ++ (Inhibition zone 9 – 12mm)  
 Slightly active = + (Inhibition zone 7 – 9 mm)  
 Inactive = - (Inhibition zone ≤6mm)

**Table 9: Dissociation constant (pKa) of the Schiff base**

S/N	Vol. of NaOH (cm <sup>3</sup> )	pH	[H <sup>+</sup> ]	[OH <sup>-</sup> ]	[Na <sup>+</sup> ]	A <sub>tot</sub>	Pka
1	0.5	9.30	3.3535x10 <sup>-10</sup>	2.1577x10 <sup>-5</sup>	1.2070x10 <sup>-3</sup>	1.9950x10 <sup>-2</sup>	10.6730
2	1.0	10.33	3.1297x10 <sup>-11</sup>	2.3121x10 <sup>-4</sup>	2.4080x10 <sup>-3</sup>	1.9900x10 <sup>-2</sup>	11.4152
3	1.5	10.95	7.5076x10 <sup>-12</sup>	9.6382x10 <sup>-4</sup>	3.6030x10 <sup>-3</sup>	1.9851x10 <sup>-2</sup>	11.9389
4	2.0	11.21	4.1257x10 <sup>-12</sup>	1.7539x10 <sup>-3</sup>	4.7921x10 <sup>-3</sup>	1.9802x10 <sup>-2</sup>	12.1263
5	2.5	11.37	2.8543x10 <sup>-12</sup>	2.5351x10 <sup>-3</sup>	5.9753x10 <sup>-3</sup>	1.9753x10 <sup>-2</sup>	12.2205
6	3.0	11.47	2.2673x10 <sup>-12</sup>	3.1915x10 <sup>-3</sup>	7.1577x10 <sup>-3</sup>	1.9764x10 <sup>-2</sup>	12.2438
7	3.5	11.54	1.9297x10 <sup>-12</sup>	3.7497x10 <sup>-3</sup>	8.3243x10 <sup>-3</sup>	1.9656x10 <sup>-2</sup>	12.2326
8	4.0	11.61	1.6425x10 <sup>-12</sup>	4.4055x10 <sup>-3</sup>	9.4902x10 <sup>-3</sup>	1.9608x10 <sup>-2</sup>	12.2403
9	4.5	11.68	1.3980x10 <sup>-12</sup>	5.1761x10 <sup>-3</sup>	1.0650x10 <sup>-2</sup>	1.9560x10 <sup>-2</sup>	12.2650
10	5.0	11.72	1.2750x10 <sup>-12</sup>	5.6754x10 <sup>-3</sup>	1.1805x10 <sup>-2</sup>	1.9512x10 <sup>-2</sup>	12.2336
11	5.5	11.75	1.1899x10 <sup>-12</sup>	6.0814x10 <sup>-3</sup>	1.2954x10 <sup>-2</sup>	1.9465x10 <sup>-2</sup>	12.1875
12	6.0	11.80	1.0605x10 <sup>-12</sup>	6.8234x10 <sup>-3</sup>	1.4097x10 <sup>-2</sup>	1.9417x10 <sup>-2</sup>	12.1971
13	6.5	11.84	9.6716x10 <sup>-13</sup>	7.4817x10 <sup>-3</sup>	1.5235x10 <sup>-2</sup>	1.9370x10 <sup>-2</sup>	12.1727
14	7.0	11.87	9.0261x10 <sup>-13</sup>	8.0168x10 <sup>-3</sup>	1.6367x10 <sup>-2</sup>	1.9324x10 <sup>-2</sup>	12.1632
15	7.5	11.90	8.4236x10 <sup>-13</sup>	8.5901x10 <sup>-3</sup>	1.7493x10 <sup>-2</sup>	1.9277x10 <sup>-2</sup>	12.1409
16	8.0	11.92	8.0445x10 <sup>-13</sup>	8.9950x10 <sup>-3</sup>	1.8615x10 <sup>-2</sup>	1.9231x10 <sup>-2</sup>	12.0941
17	8.5	11.93	7.8614x10 <sup>-13</sup>	9.2045x10 <sup>-3</sup>	1.9731x10 <sup>-2</sup>	1.9185x10 <sup>-2</sup>	12.0196
18	9.0	11.95	7.5076x10 <sup>-13</sup>	9.6383x10 <sup>-3</sup>	2.0842x10 <sup>-2</sup>	1.9139x10 <sup>-2</sup>	11.9747
19	9.5	11.97	7.1697x10 <sup>-13</sup>	1.0093x10 <sup>-2</sup>	2.1947x10 <sup>-2</sup>	1.9093x10 <sup>-2</sup>	11.9303
20	10	11.99	6.8470x10 <sup>-13</sup>	1.0568x10 <sup>-2</sup>	2.3048x10 <sup>-2</sup>	1.9048x10 <sup>-2</sup>	11.8857

Average pka Value = 12.0178

**Table 10: Estimation of number of coordinated Schiff base per Nickel (II) complex**

S/N	Volume of sodium ligandate (cm <sup>3</sup> )	p <sup>H</sup>	[H <sup>+</sup> ]	[OH <sup>-</sup> ]	Log [A]	M <sub>total</sub>	N
1	2.2	4.76	1.16 x 10 <sup>-5</sup>	6.22 x 10 <sup>-10</sup>	-10.09	4.95 x 10 <sup>-3</sup>	0.6801
2	2.4	4.86	9.24 x 10 <sup>-6</sup>	7.83 x 10 <sup>-10</sup>	-9.99	4.94 x 10 <sup>-3</sup>	0.7595
3	2.6	5.06	5.83 x 10 <sup>-6</sup>	1.24 x 10 <sup>-9</sup>	-9.79	4.94 x 10 <sup>-3</sup>	0.8385
4	2.8	5.27	3.59 x 10 <sup>-6</sup>	2.01 x 10 <sup>-9</sup>	-9.57	4.93 x 10 <sup>-3</sup>	0.9179
5	3.0	5.49	2.17 x 10 <sup>-6</sup>	3.34 x 10 <sup>-9</sup>	-9.36	4.93 x 10 <sup>-3</sup>	0.9973
6	3.2	5.75	1.19 x 10 <sup>-6</sup>	6.08 x 10 <sup>-9</sup>	-8.92	4.92 x 10 <sup>-3</sup>	1.0769
7	3.4	5.93	7.86 x 10 <sup>-7</sup>	9.20 x 10 <sup>-9</sup>	-8.91	4.92 x 10 <sup>-3</sup>	1.1567
8	3.6	6.11	5.19 x 10 <sup>-7</sup>	1.39 x 10 <sup>-8</sup>	-8.73	4.91 x 10 <sup>-3</sup>	1.2366
9	3.8	6.24	3.85 x 10 <sup>-7</sup>	1.88 x 10 <sup>-8</sup>	-8.60	4.91 x 10 <sup>-3</sup>	1.3162
10	4.0	6.37	2.85 x 10 <sup>-7</sup>	2.53 x 10 <sup>-8</sup>	-8.47	4.90 x 10 <sup>-3</sup>	1.3960
11	4.2	6.48	2.22 x 10 <sup>-7</sup>	3.27 x 10 <sup>-8</sup>	-8.36	4.90 x 10 <sup>-3</sup>	1.4758
12	4.4	6.57	1.80 x 10 <sup>-7</sup>	4.02 x 10 <sup>-8</sup>	-8.27	4.89 x 10 <sup>-3</sup>	1.5557
13	4.6	6.63	1.57 x 10 <sup>-7</sup>	4.61 x 10 <sup>-8</sup>	-8.21	4.89 x 10 <sup>-3</sup>	1.6362
14	4.8	6.69	1.37 x 10 <sup>-7</sup>	5.30 x 10 <sup>-8</sup>	-8.15	4.88 x 10 <sup>-3</sup>	1.7152
15	5.0	6.73	1.25 x 10 <sup>-7</sup>	5.81 x 10 <sup>-8</sup>	-8.11	4.88 x 10 <sup>-3</sup>	1.7950
16	5.2	6.79	1.09 x 10 <sup>-7</sup>	6.67 x 10 <sup>-8</sup>	-8.06	4.87 x 10 <sup>-3</sup>	1.8747
17	5.4	6.85	9.45 x 10 <sup>-8</sup>	7.66 x 10 <sup>-8</sup>	-7.99	4.87 x 10 <sup>-3</sup>	1.9546
18	5.6	6.90	8.42 x 10 <sup>-8</sup>	8.59 x 10 <sup>-8</sup>	-7.95	4.86 x 10 <sup>-3</sup>	2.0344
19	5.8	6.94	7.68 x 10 <sup>-8</sup>	9.42 x 10 <sup>-8</sup>	-7.90	4.86 x 10 <sup>-3</sup>	2.1142
20	6.0	6.98	7.01 x 10 <sup>-8</sup>	1.03 x 10 <sup>-7</sup>	-7.86	4.85 x 10 <sup>-3</sup>	2.1918
21	6.2	7.04	6.10 x 10 <sup>-8</sup>	1.19 x 10 <sup>-7</sup>	-7.80	4.85 x 10 <sup>-3</sup>	2.2737
22	6.4	7.11	5.19 x 10 <sup>-8</sup>	1.39 x 10 <sup>-7</sup>	-7.73	4.85 x 10 <sup>-3</sup>	2.3536
23	6.6	7.14	4.85 x 10 <sup>-8</sup>	1.49 x 10 <sup>-7</sup>	-7.68	4.84 x 10 <sup>-3</sup>	2.4333
24	6.8	7.17	4.52 x 10 <sup>-8</sup>	1.60 x 10 <sup>-7</sup>	-7.67	4.84 x 10 <sup>-3</sup>	2.5152
25	7.0	7.22	4.03 x 10 <sup>-8</sup>	1.79 x 10 <sup>-7</sup>	-7.62	4.83 x 10 <sup>-3</sup>	2.5931
26	7.2	7.26	3.68 x 10 <sup>-8</sup>	1.97 x 10 <sup>-7</sup>	-7.58	4.83 x 10 <sup>-3</sup>	2.6726
27	7.4	7.32	3.20 x 10 <sup>-8</sup>	2.26 x 10 <sup>-7</sup>	-7.52	4.82 x 10 <sup>-3</sup>	2.7526
28	7.6	7.37	2.85 x 10 <sup>-8</sup>	2.54 x 10 <sup>-7</sup>	-7.47	4.82 x 10 <sup>-3</sup>	2.8324
29	7.8	7.47	2.54 x 10 <sup>-8</sup>	2.84 x 10 <sup>-7</sup>	-7.42	4.81 x 10 <sup>-3</sup>	2.9121
30	8.0	7.52	2.32 x 10 <sup>-8</sup>	3.12 x 10 <sup>-7</sup>	-7.38	4.81 x 10 <sup>-3</sup>	2.9495

Average n = 1.8336

**Table 11: Estimation of number of coordinated Schiff base per Copper (II) complex**

S/N	Volume of sodium ligandate (cm <sup>3</sup> )	p <sup>H</sup>	[H <sup>+</sup> ]	[OH <sup>-</sup> ]	Log [A]	M <sub>total</sub>	N
1	2.2	3.57	1.80 x 10 <sup>-4</sup>	4.02 x 10 <sup>-11</sup>	-11.35	4.95 x 10 <sup>-3</sup>	0.7142
2	2.4	3.72	1.28 x 10 <sup>-4</sup>	5.68 x 10 <sup>-11</sup>	-11.18	4.94 x 10 <sup>-3</sup>	0.7834
3	2.6	3.83	9.90 x 10 <sup>-5</sup>	7.31 x 10 <sup>-11</sup>	-11.06	4.94 x 10 <sup>-3</sup>	0.8587
4	2.8	3.88	8.82 x 10 <sup>-5</sup>	8.20 x 10 <sup>-11</sup>	-11.00	4.93 x 10 <sup>-3</sup>	0.9351
5	3.0	3.94	7.68 x 10 <sup>-5</sup>	9.42 x 10 <sup>-11</sup>	-10.94	4.93 x 10 <sup>-3</sup>	1.0125
6	3.2	3.99	6.85 x 10 <sup>-5</sup>	1.06 x 10 <sup>-10</sup>	-10.88	4.92 x 10 <sup>-3</sup>	1.0907
7	3.4	4.03	6.24 x 10 <sup>-5</sup>	1.16 x 10 <sup>-10</sup>	-10.84	4.92 x 10 <sup>-3</sup>	1.1692
8	3.6	4.06	5.83 x 10 <sup>-5</sup>	1.24 x 10 <sup>-10</sup>	-10.81	4.91 x 10 <sup>-3</sup>	1.2483
9	3.8	4.09	5.44 x 10 <sup>-5</sup>	1.33 x 10 <sup>-10</sup>	-10.78	4.91 x 10 <sup>-3</sup>	1.3272
10	4.0	4.12	5.08 x 10 <sup>-5</sup>	1.43 x 10 <sup>-10</sup>	-10.75	4.90 x 10 <sup>-3</sup>	1.4063
11	4.2	4.13	4.96 x 10 <sup>-5</sup>	1.46 x 10 <sup>-10</sup>	-10.74	4.90 x 10 <sup>-3</sup>	1.4859
12	4.4	4.14	4.85 x 10 <sup>-5</sup>	1.49 x 10 <sup>-10</sup>	-10.73	4.89 x 10 <sup>-3</sup>	1.5656
13	4.6	4.17	4.52 x 10 <sup>-5</sup>	1.60 x 10 <sup>-10</sup>	-10.69	4.89 x 10 <sup>-3</sup>	1.6446
14	4.8	4.19	4.32 x 10 <sup>-5</sup>	1.67 x 10 <sup>-10</sup>	-10.67	4.88 x 10 <sup>-3</sup>	1.7141
15	5.0	4.20	4.22 x 10 <sup>-5</sup>	1.71 x 10 <sup>-10</sup>	-10.66	4.88 x 10 <sup>-3</sup>	1.8037
16	5.2	4.24	3.85 x 10 <sup>-5</sup>	1.88 x 10 <sup>-10</sup>	-10.62	4.87 x 10 <sup>-3</sup>	1.8826
17	5.4	4.26	3.68 x 10 <sup>-5</sup>	1.97 x 10 <sup>-10</sup>	-10.60	4.87 x 10 <sup>-3</sup>	1.9621
18	5.6	4.28	3.51 x 10 <sup>-5</sup>	2.06 x 10 <sup>-10</sup>	-10.58	4.86 x 10 <sup>-3</sup>	2.0416
19	5.8	4.30	3.35 x 10 <sup>-5</sup>	2.16 x 10 <sup>-10</sup>	-10.56	4.86 x 10 <sup>-3</sup>	2.1211
20	6.0	4.34	3.06 x 10 <sup>-5</sup>	2.37 x 10 <sup>-10</sup>	-10.52	4.85 x 10 <sup>-3</sup>	2.2002
21	6.2	4.35	2.99 x 10 <sup>-5</sup>	2.42 x 10 <sup>-10</sup>	-10.51	4.85 x 10 <sup>-3</sup>	2.2799
22	6.4	4.36	2.92 x 10 <sup>-5</sup>	2.48 x 10 <sup>-10</sup>	-10.50	4.85 x 10 <sup>-3</sup>	2.3596
23	6.6	4.37	2.85 x 10 <sup>-5</sup>	2.54 x 10 <sup>-10</sup>	-10.49	4.84 x 10 <sup>-3</sup>	2.4392
24	6.8	4.39	2.73 x 10 <sup>-5</sup>	2.65 x 10 <sup>-10</sup>	-10.47	4.84 x 10 <sup>-3</sup>	2.5189
25	7.0	4.41	2.60 x 10 <sup>-5</sup>	2.78 x 10 <sup>-10</sup>	-10.44	4.83 x 10 <sup>-3</sup>	2.5985
26	7.2	4.42	2.54 x 10 <sup>-5</sup>	2.84 x 10 <sup>-10</sup>	-10.43	4.83 x 10 <sup>-3</sup>	2.6779
27	7.4	4.43	2.48 x 10 <sup>-5</sup>	2.91 x 10 <sup>-10</sup>	-10.42	4.82 x 10 <sup>-3</sup>	2.7576
28	7.6	4.46	2.32 x 10 <sup>-5</sup>	3.12 x 10 <sup>-10</sup>	-10.39	4.82 x 10 <sup>-3</sup>	2.8373
29	7.8	4.47	2.27 x 10 <sup>-5</sup>	3.19 x 10 <sup>-10</sup>	-10.38	4.81 x 10 <sup>-3</sup>	2.9168
30	8.0	4.49	2.17 x 10 <sup>-5</sup>	3.34 x 10 <sup>-10</sup>	-10.36	4.81 x 10 <sup>-3</sup>	2.9966

Average n = 1.7825

The interaction between Salicylaldehyde and aniline gave a yellow crystalline schiff base. The percentage yield and melting point of the schiff base are 94.92% and 104°C, respectively. The reaction of schiff base with Ni (II) and Cu (II) chlorides gave metal (II) complexes with the following percentage yields 54.88% and 55.30%, respectively. Cu (II) and Ni (II) schiff base complexes are yellow and black crystals with the decomposition temperature of 132°C and 158°C, respectively (Table 1). The colour of complexes is due to the electronic excitation from low  $t_{2g}$  to higher  $e_g$  by absorption of visible light. (Nazeeruddin and Gratzel, 2007)

The percentage composition of the metal ion, ligand and water content of each metal (II) schiff base complex determined, revealed the general formula  $[ML_2] \cdot nH_2O$ . (Table 2). The solubility test of the schiff base and its complex compounds (Table 3) generally showed good solubility in DMSO and methanol. Cu (II) complex is soluble in ethanol and acetone. However, the schiff base ligand and its complexes recorded poor solubility in water and some organic solvent such as Toluene, ether, benzene, diethyl ether, and isopropanol. The molar conductance of synthesized complexes (Table 4) were measured using  $10^{-3}M$  methanol and DMSO and the values are 94.0 and 68.5  $\text{Ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$  respectively. These values are too low to account for any dissociation of the complexes and the obtained values were taken as a good evidence of the existence of a non-electrolytic nature of the complexes (Geary, 1972).

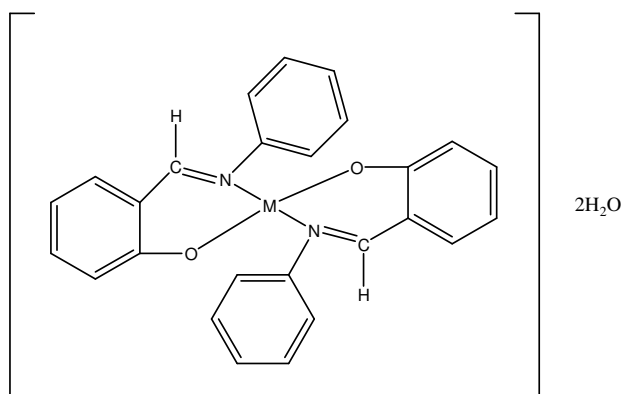
The FT-IR frequencies exhibited by the schiff base ligand and their complexes are tabulated in Table 5. The free schiff base absorbs in the region  $3460 \text{cm}^{-1}$  which is assigned to  $\nu(\text{O-H})$  stretching vibration which did not appeared in the complexes, indicating the coordination through the metal atom. The bands at  $1620 \text{cm}^{-1}$  shown by ligand are attributed to  $\nu(\text{C=N})$  which has been shifted toward lower region at  $1580$  and  $1590 \text{cm}^{-1}$  in the respective complexes, indicating the participation of the azomethine group in the

complexation, this corroborate with what Makodeand Aswa,(2004) reported. The band at  $1210 \text{cm}^{-1}$  are due to  $\nu(\text{C-O})$  stretching frequencies, however, a Shift to higher frequency was observed in the complexes. Ni(II) and Cu(II) complexes showed bands at lower frequency region of  $560 \text{cm}^{-1}$  and  $680 \text{cm}^{-1}$  assigned to  $\nu(\text{M-N})$  respectively while  $440 \text{cm}^{-1}$  and  $550 \text{cm}^{-1}$  are also assigned to respective  $\nu(\text{M-O})$  stretching vibration (Saleen *et al.*, 2003), confirming coordination of the ligands to the respective metals. (Table 5).

The dissociation constant (pKa) of the schiff base is 12.0178 suggesting weak base (Table 9). The stability constants of Ni (II) and Cu (II) schiff base complexes determined are  $5.01 \times 10^{18}$  and  $8.32 \times 10^{21}$  respectively, indicating good stability of the complexes, supported by high decomposition temperature shown in Table 1. The Gibbs free energy ( $\Delta G$ ) of the schiff base complexes fall in the range of -106.6 and -125.0  $\text{KJmol}^{-1}$  are relatively low suggesting good stability for the complex compounds. The magnitude of  $\Delta G$  indicates the extent to which reaction goes toward the formation of the product before equilibrium is reached (Table 6). The potentiometric studies also revealed 1:2 metal-ligand ratio for the respective nickel (II) and copper (II) complexes (Table 10 and 11).

Antibacterial activity test of the schiff base and its metal (II) complexes has been determined at different concentrations. The diameter of inhibition zone (mm) was measured for each treatment. schiff base and its complexes displayed different activities against the tested bacteria, *Escherichia coli* and *Staphylococcus aureus* (Table 7). The sensitivity of fungal isolate *Aspergillus niger* and *Candida albican* show that Ni(II) schiff base complex is more active against *Aspergillus niger*, while Cu(II) schiff base complex is more active against *Candida albican* at higher concentration. (Table 8)

From the analyses of the schiff base metal (II) complex compounds carried out the general molecular structure is proposed.



**Figure 1 Proposed structure of Complexes**  
Where M = Ni (II) or Cu (II).

## CONCLUSION

The schiff base and its complexes of Ni(II) and Cu(II) have been synthesized and characterized. The analytical data show that the metal-ligand stoichiometry in all the complexes is 1:2. The

synthesized complexes are non-electrolyte using DMSO solvents. The spectral data show that the schiff base act as bidentate ligand coordinating through the nitrogen atoms of the azomethine and oxygen atoms of the hydroxyl group of salicylaldehyde.

Base on analytical data the complexes are assigned to be in tetrahedral geometry. Antimicrobial studies of the schiff base ligand and complexes revealed that, the complexes are more active than schiff base.

#### Contribution of Authors

The work was carried out in collaboration between all the reported authors. S. Y. Hussaini designed the

experiment and performed the laboratory work. A. Ahmad contributed to the literature search and S. Sani partook in the results interpretation. All authors accepted the final version of the manuscript.

#### Conflict of interest

Authors declare that, no conflict of interest.

#### REFERENCES

- Avar B. Lajos T. Hoter, N and Kurt, R. (1975). "Schiff base complexes of transition metals as highest stabilizers for plastics and Fibres" *Chemical Abstract* 84 1849.
- Geary WJ, *Coord.chem. Rev*, 1972, 1, 81.
- Gregory S, Thomas BR, Robert JA (1978). *Synthesis and techniques in inorganic chemistry* 3rd edition, Longman publishers, London. 119-126.
- Hassan A. M., (1991), "Co (II) and Fe (III) Schiff base chelates derived from Isatin and some amino acids" *Journal of Islamic Academy of Science*, 4 (4), 271-274.
- Hassan S. W, Umar R. A, Lawal M, Bilbis L S, Muhammad B. Y (2006). "Evaluation of antifungal Activity of ficus sycomores L. (Moraceae)". *Best Journal* 3 (2), 18-25.
- Hobday M.D and Smith T.D, (1972). *Coordination Chemistry Rev.* 9, 311 – 337.
- Holm R.H (1966). "Metal Complexes of Schiff base and B. Ketamines". *Inorg. Chem.* 7, 83 – 214.
- Janes D. and Kreft S (2008), "Salicylaldehyde is a characteristic aroma component of buckwheat groats". *Food chemistry*. 109, 293-298.
- John, N.C (2002). *Organic Transition metal and inorganic chemistry*. Cheuron Science Centre, Pittsburg. Pg 1 –2
- Makode J. T, Aswa A. S (2004) "Synthesis, characterization, biological and thermal properties of some new Schiff base complexes derived from 2-hydroxy-5-chloroacetophenone and S-methyldithiocarbamate" *Indian Journal of Chem.* 43A. 2120-2125.
- Maihab A.A., El-ajaily M.M., & El-tajoury A.N., (2005). "Preparation and Physical Characterization of some Schiffbase Ligands derived from Salicylaldehyde and tyrosine with divalent metal ions". *The Egyptian Sciences Magazine*, 2 (4). 83-87.
- Muhammad Basheer Ummathur, P. Sayudevi and K. Krishnan kutty(2008). "Metal complexes of Schiff bases derived from dicinnamoylmethane and aromatic amines". *Journal of the Argentine chemical society*, 96, 13-21.
- Morad F. M, A.N. El – Tajoury and M.M. El-ajaily, (2006). "Chelation behaviour and biological, the activity of divalent metal ions towards Schiff base". *Basic Science and its application J.* 1 (1) 196 – 210.
- Nazeeruddin M.K., Gratzel M. (2007) "Transition Metal Complexes for Photovoltaic and Light Emitting Applications". *Photofunctional Transition Metal Complexes. Structure and Bonding*, 123. 113-175. Springer, Berlin, Heidelberg
- Neelakandan, M. A., Raman N. And Dhaveethuraja J, (2008), "DNA Cleavage and Antimicrobial Activity Studies on Transition Metal (II) Complexes". *Journal of the Chilean chemical society*. 41, 399-410.
- Saleem, H. S., El-Shetary, B. A. and Khalil S. M. (2003) "Potentiometric and Spectrophotometric Studies of Complexation of Schiff base Hydrazine containing the pyrimidine moiety" *J. Serb. Chem. Soc.*, 68(10) 729 –748.
- Shamsudden U, Mukhtar MD, Salisu M (2008). "Comparative in-vitro study of Activity of Methanolic and Ethanolic extracts of onion seeds on gram-negative and gram-positive bacteria". *Best journals*. 5(3)17-20.
- Sharma R.C and Mohan G, (1990), the biological activity of some Schiff bases and its complexes, *Chemical Abstract*. 113, 165240.
- Silver S. S.M and Bassler G.C (1967) *Spectrophotometric identification of organic compounds*, Wiley, New York 12-23.
- Vogel A.I (1972). *Quantitative inorganic analysis including elementary instrumental analysis* 3<sup>rd</sup> Edition Longman co. London Pg. 526-535.