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Synthesis and spectroscopic characterization of Ni(II) and Cu(II) Schiff base Transition Metal Complexes from a mix of drugs Sulfamethaxole with 2-aminopyridine and Benzaldehyde

Jibrin M Yelwa and Ahmad N Suleiman

Abstract
The Schiff base ligands were synthesized by condensation reaction of 2-Aminopyridine and Benzaldehyde. The mixed ligand Complexes were synthesized by reaction of Schiff base with Metals (II) salt and Sulfamethoxazole drug in a ratio of 1:1:1 {M: (L^1): (L^2)}. The metal(II) complexes were formed by refluxing the chloride salts of the metals with the Schiff base ligand. The Schiff base and its complexes were characterized by melting point/decomposition temperature, solubility test, molar conductance measurement, infrared and UV-visible spectral analysis. The ligand and the complexes were coloured, non-hygroscopic and air stable. The conductivity measurement data revealed that the complexes are non-electrolytes. The infrared data indicated the bidentate nature of the Schiff base ligand coordinated with the metal ions via the nitrogen atom of the azomethine(C=N) and oxygen atom of the hydroxyl group after deprotonation.

Keywords: Ligands, transition, imine, chelates

1. Introduction

Schiff bases are formed when any primary amine reacts with an aldehyde or a ketone under specific conditions. Structurally, a Schiff base (also known as imine or azomethine) is a nitrogen analogue of an aldehyde or ketone in which the carbonyl group (CO) has been replaced by an imine or azomethine group [7]. Schiff base were first reported by German Scientist Hugo Joseph Schiff in 1864 are obtained by condensing carbonyl compound such as aldehydes or ketones with primary amines resulting in the elimination of water molecule [7]. Schiff bases are of the general formula $R_3R_2C{=}N{-}R_3$, where R_3 is an aryl or alkyl group that makes the Schiff base a stable imine [4]. Schiff bases are generally excellent chelating agents, because of the relative easiness of preparation, synthetic flexibility, and the special property of C=N group which coordinated to five or six membered rings with the metal ion [3]. Metal-based drugs are a research area of increasing interest for inorganic, pharmaceutical and medicinal chemistry and have concentrated much attention as an approach to new drug development. Literature reveals that several inorganic complexes have been good source of medicine. This work aims at synthesizing and characterizing Ni(II) and Cu(II) Schiff base derived from Sulfamethaxole with 2-Aminopyridine and Benzaldehyde.

2. Experimental

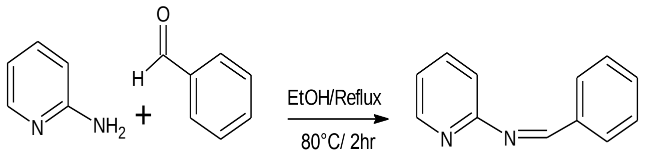
2.1 Materials/Reagents

The following Chemicals/Reagents were used. Nickel (II) chloride, Cobalt (II) chloride, Copper (II) sulphate, Manganese (II) Chloride, Iron (ll) chloride tetrahydrate, 2-Aminopyridine, Benzaldehyde, Sulfamethaxazole drugs, Phosphoru pentoxide, Sodium hydroxide, H_2SO_4 Methanol, Distilled water, Chloroform, Methanol, Acetone and Dimethylsulphoxide.

2.2 Preparation of the Schiff Base (L^1)

The Schiff Base was prepared with a slightly moderation as describe by Mahmud[5]. A solution of benzaldehyde (0.01mole) was slowly added to a solution of (0.01mole) 2-aminopyridine in 25cm^3 of ethanol in the present of HCl as catalyst.

The mixture was refluxed for 3hours. The mixture was allowed to cool at room temperature. The product obtained was filtered, washed in ethanol and dried in desiccators.

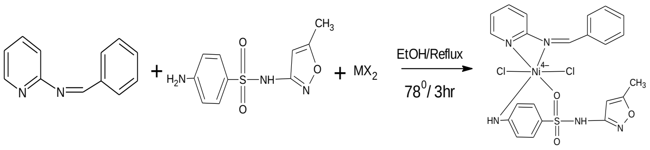


2-aminopyridine Benzaldehyde Schiff Base

Scheme 1: Schiff Base [(L^1)].

2.3 Preparation of [Ni(L^1)(L^2)]

A solution of $NiCl_2.6H_2O$ containing 0.202g (0.01mol) in 15cm^3 of ethanol was mixed with 1.82g(0.01mol) of Schiff Base and 2.53g(0.01mol) Sulfamethaxazole in 15cm^3 of ethanol in a ratio of 1:1:1. The mixture was refluxed for 3hours and the solution was allowed to cool at room temperature. The product obtained was filtered and dried in desiccators.

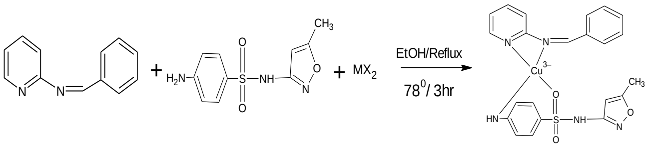


Schiff Base Sulfamethaxazole Metal Salt Metal (II) Complex

Scheme 2: [Ni(L^1)(L^2)]

2.4 Preparation of [Cu(L^1)(L^2)]

A solution of $CuSO_4.5H_2O$ containing 0.248g (0.01mol) in 15cm^3 of ethanol was mixed with 1.82g(0.01mol) of Schiff Base and 2.53g(0.01mol) Sulfamethaxazole in 15cm^3 of ethanol in a ratio of 1:1:1. The mixture was refluxed for 3hours and the solution was allowed to cool at room temperature. The product obtained was filtered and dried in desiccators.



Schiff Base Sulfamethaxazole Metal Salt Metal (II) Complex

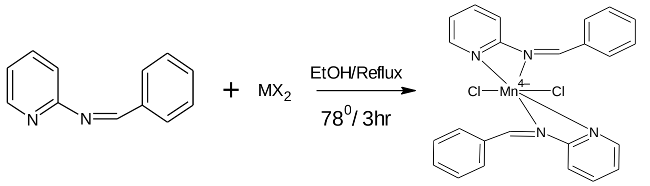
Scheme 3. [Cu(L^1)(L^2)]

2.5 Preparation of Schiff Base with Metal (II) Salt [M(L^1)$_2$]

The Schiff base with Metal (II) complexes were prepared with a slightly moderation as describe by Raman [7].

2.5.1 Preparation of [Ni {M(L^1)$_2$}]

A solution of $NiCl_2.6H_2O$ containing (0.01mol) were dissolve in 25cm^3 of hot ethanol and (0.01mol) of the Schiff base was added to the solution, 1:2 molar ratio of metal-ligand. The mixture was heated at 80^{O}c while stirring under refluxed for 3hrs. The product was filtered, washed in distilled in ethanol, dried in desiccator over calcium chloride for 1 day

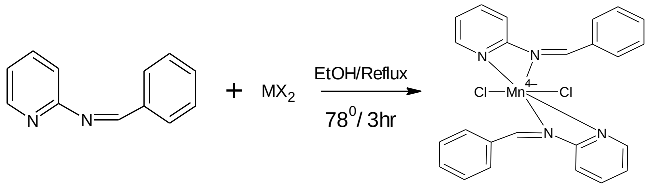


Schiff Base Metal Salt Metal (II) Complex

Scheme 4. [Ni(L^1)$_2$]

2.5.2 Preparation of Cu {M(L^1)$_2$}

A solution of $CuSO_4.5H_2O$ containing (0.01mol) were dissolve in 25cm^3 of hot ethanol and (0.01mol) of the Schiff base was added to the solution, 1:2 molar ratio of metal-ligand. The mixture was heated at 80^{O}c while stirring under refluxed for 3hrs. The product was filtered, washed in distilled in ethanol, dried in desiccator over calcium chloride for 1 day.



Schiff Base Metal Salt Metal (II) Complex

Scheme 5: [Cu(L^1)$_2$]

2.6 Physicochemical analysis of the Schiff Base and Metal (II) complexes

2.6.1 Solubility Test

The solubility test was carried out at using some solvent such as Dimethylsulphoxiden (DMSO), Chloroform, Acetone, Methanol and Distilled water. 6mg of the Schiff Base and the Metal (II) complexes were dissolves in 2ml of different solvent at room temperature and at elevated temperature.

2.6.2 Color and Texture

The color and texture of the synthesized Schiff base and its Metal (II) complexes were determine by it physical appearance after bringing out from desiccator.

2.6.3 Melting Point Determination

The melting points were determined on electro thermal melting point apparatus.

2.6.4 Conductivity Test

The molar conductivity was carried out using Conductivity meter model HI9835 of Hanna with a cell constant of at 2× $10^{-1}\Omega^{-1}cm^{-2}mol^{-1}$ at a concentration of 10^2M solution in DMSO as a solvent^4.

2.6.4 Percentage Yield

The percentage yield was determind by the formula.

$$percentageyield = \frac{experimentalyield}{theoriticalyield} \times 100 \quad (1)$$

2.7 Characterizations

2.7.1 FT-IR Analysis

Buck scientific infrared spectrophotometer, Model 530 Buck Sci. USA, within the range of (4000-400cm^{-1}).

2.7.2 UV-VISIBLE

The UV-visible spectrophotometer was used to determine the wavelength of absorption.

3. Results and Discussion

3.1 Physical properties of the Schiff base and metals complexes

From the results of the physicochemical analysis of the mixed ligand [M(L^1)(L^2)] and the Metal (II) [M$(L^1)_2$] complexes, it showed that the melting point of the Schiff Base (L^1) was lowest which may be due to the different structural arrangements and bond strengths within the M(L^1)(L^2) and M$(L^1)_2$ Complexes [3]. The color of Ni(L^1)(L^2) complex was found to be Black, Cu(L^1)(L^2) complex was found to be Light Brown, Ni$(L^1)_2$ was found to be brown and Cu$(L^1)_2$ was found to be dark blue. These colors may be due to either d-d transition, charge transfer transition or imperfection in the crystal structure of the compound [1]. In the test for texture, only the Schiff base was found to be crystal while all the other complexes were found to be powders [4]. The percentage yield of the Schiff base was 52%, Ni$(L^1)_2$ was 59%, Cu$(L^1)_2$ was 70%, Ni(L^1)(L^2) 78% and Cu(L^1)(L^2) 82%. The lowest yield may be due to incomplete reaction of the complex during the synthesis. The conductivity value for the Schiff base and the complexes ranges between 21×10^{-2} to 16×10^{-2} $\Omega^{-1}cm^{-2}mol^{-1}$. Indicated that they all have low conductivity value showing that they are non-electrolyte [6].

Table 1: Physical properties of the Schiff Base (L^1) and Metals (II) Complexes [M $(L^1)_2$ and M(L^1)(L^2)]

Compounds	**Melting P. (°C)**	**Conductivity $\Omega^{-1}cm^{-2}mol^{-1}$**	**Colors**	**Texture**	**Yield (%)**
SB	200	21×10^{-2}	White	Crystal	52
Ni$(L^1)_2$	260	8 10^{-2}	Brown	Powder	59
Cu$(L^1)_2$	210	4 10^{-2}	Dark blue	Powder	70
Ni(L^1)(L^2)	270	15×10^{-2}	Light Brown	Powder	78
Cu(L^1)(L^2)	240	16×10^{-2}	Black	Powder	82

3.1 Solubility test

The synthesized Schiff base and its Metal (II) complexes are all soluble in water, Acetone and Dimethylsulphoxide (DMSO), insoluble in Chloroform but slightly soluble in methanol.

Table 2: Solubility test for Schiff base and the Metal (II) complexes

Compound	**H_2O R E**	**MeOH R E**	**Acetone R E**	**Cloroform R E**	**DMSO R E**
SB	S S	SS SS	S S	IS IS	S S
Ni$(L^1)_2$	S S	SS SS	S S	IS IS	S S
Cu$(L^1)_2$	S S	SS SS	S S	IS IS	S S
Cu(L^1)(L^2)	S S	SS SS	S S	IS IS	S S
Ni(L^1)(L^2)	S S	SS SS	S S	IS IS	S S

R= Room Temperature, E=Elevated Temperature, S=Soluble, SS = Slightly Soluble and IS = Insoluble

3.2 FT-IR Analysis

Table III. shows the FT-IR spectral data of the mixed Ligand M(L^1)(L^2) Complexes. The FT-IR spectra predicted all the absorption bands of the Schiff base ligand and some new bands at specific frequency confirmed the modes of absorption and the completion of the ligand with the metal ions through nitrogen and oxygen [10]. The stretch vibration due to hydroxyl of the Schiff base was observed as a broad and weak at 3307 cm^{-1}- 3632 cm^{-1}. This is a consequence of strong intramolecular hydrogen bonding between the hydroxyl proton and imine nitrogen OH-NH [3]. The strong band at 1603 cm^{-1}-1651 cm^{-1}was assigned to the imine v(C=N) band of the ligand, the increase in the v(C=N) values for the 2-aminopyridine and benzaldehyde(Schiff base) may be understood to be due to the presence of the methylene bridge that isolated the pyridine ring from the π conjugation of the rest of the molecule [1]. The Imine stretch vibration was, however observed at higher frequency in the Cu (II) chelates than in the Schiff base (1603 cm^{-1} and 1651 cm^{-1}) indicating coordination of the Schiff base via the imine Nitrogen. Further evidence of the coordination of the Schiff base and the metal ions was shown by the appearance of weak frequency new bands of M-N and M-O vibration (595cm^{-1} - 760cm^{-1}) and (482 cm^{-1} - 618 cm^{-1}) respectively, These band are absent in the spectra of the Schiff base [1, 3].

Table 3: FTIR data of Mixed Ligand M(L^1)(L^2) Complexes

COMPOUND	**V(NH)**	**V(C=N)**	**V(M-N)**	**V(M-O)**
SB	3307	1603	----	------
Cu(L^1)(L^2)	3443	1614	746	618
Ni(L^1)(L^2)	3500	1651	760	499
*cm^{-1}				

Table 4. shows the FT-IR of of Schiff Base $(L^1)_2$ and Metal (II) Complexes. The lattice and coordinated water were observed at (3307 cm^{-1}-3435 cm^{-1}). The spectra of the first ligand (L1) showed a strong band at 3300 cm^{-1} due to stretching vibration of O-H group, this band was shifted to the lower frequency in the spectrum of Metal (II) complexes 3435 cm^{-1} as a result of complexation [2]. The band appeared at 3300 cm^{-1} was attributed to stretching vibration of N-H group for Schiff base (L^1) and which absent in spectra of Metal (II) complexes because of coordinate through the N atom [2]. The spectra of L^1 and Metal (II) Complexes showed bands at 2200 cm^{-1}, 2256 cm^{-1},2267 cm^{-1}, 2366 cm^{-1}, 2366 cm^{-1} and 2363 cm^{-1} respectively, these bands assigned to vibrational mode of C=H. The spectrum of L^1 exhibited the moderate band at 1603 cm^{-1} belong to C=N, while this band was shifted to lower frequency at 1635 cm^{-1}, 1620 cm^{-1}, 1527 cm^{-1}, 1635 cm^{-1} and 1627 cm^{-1} for Metal (II) Complexes respectively (Mohammed *et al.*, 2016). The strong band at 845 cm^{-1}, 725 cm^{-1}, 798 cm^{-1}, 845 cm^{-1} and 749 cm^{-1}is due to M-N, this band is absented in the spectra of the L^1 (Schiff base) as a result of coordinate N atom of M=N with metal ions. The bands appeared at 698 cm^{-1}, 578 cm^{-1}, 667 cm^{-1}, 689 cm^{-1} and 564 cm^{-1} is due to stretching vibration of M-Cl [1].

Table 4: FTIR Data of Schiff Base $(L^1)_2$ and Metal (II) Complexes

Compound	V(O-H)	V(C-N)	V(C=H)	V(M-N)	V(M-Cl)
SB	3307	1603	200	----	------
$Cu(L^1)_2$	3435	1526	2366	798	667
$Ni(L^1)_2$	3435	1635	2366	845	689
*cm^{-1}					

3.3 UV–visible spectra of $M(L^1)(L^2)$ complexes

The ultraviolet visible electronic spectrum of the Schiff base (L^1) complexes is shown in figure 5 above. The Schiff base showed three weak bands at 500, 600 and700nm attributed to π→ p*, π→ p* and n → p* electronic transitions respectively. For all complexes it showed the similar electronic transition as observed in the Schiff base and it also showed the electronic transitions of the metal d orbital (d-d electronic transition) observed located in the visible region as extra information [1].

The $Cu(L^1)(L^2)$ complexes showed three major absorption bands between 10 Dq band for a distorted octahedral geometry corresponding σ'σ to the transitions ^2Eg -+^2T_2g. The bands at 400-500 and 700nm may be due to intra-ligand charge transfer transitions. The electronic spectrum of the $Cu(L^1)(L^2)$ complex suggests an octahedral geometry [1].

The electronic spectrum of the $Ni(L^1)(L^2)$ complexes exhibited three spin-allowed bands at 500, 600 and 700 nm, assigned to $^3A_2g(F) \rightarrow {}^3T_2g(F)$, $^3T_1g(F)$ and $^3T_1g(P)$ transitions, respectively, which indicate octahedral geometry of the $Ni(L^1)(L^2)$ complex [9].

3.4 UV–visible spectra of $M(L^1)$ complexes

The Ultraviolet Spectrum of $Ni(L^1)_2$ Schiff base Complex in Figure above designated the maximum peak around 630nm, indicating n→π* Electronic Transition Which fall within the Visible Region, which indicate octahedral geometry of the $Ni(L^1)_2$ complex [1].

In the other hand, the UV-Spectrum of $Cu(L^1)_2$ Complex of was observed a λ-max at 313 as presented in figure above, this assigned to π→π* Electronic Transition Which fall within the UV Region which indicate octahedral geometry of the $Cu(L^1)_2$ complex [9].

4. Conclusion

Sulfamethaxole and their derivatives can be good chelating ligands when condensed with 2-Aminopyridine and Benzaldehyde 1:1:1 ratio to form bi, tri and tetra dentate Schiff base ligands suitable to form complexes with Transition Metals. These Metal-Schiff base complexes exhibited broad range of biological activities, such as antibacterial properties.

5. Conflict of Interest: No conflict of interest declared

6. References

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