

Copper (II) and Silver (I) Complexes with bis Schiff Base Ligand: Synthesis, Spectral Characterization and Thermal Studies

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Abstract

Metal complexes of the bis Schiff base (BSAA) ligand, synthesized via condensation 4-amino antipyrine with 4-(4-dimethylamino) benzaldehyde which has synthesized from condensation p-amino benzaldehyde and p-dimethyl amino benzaldehyde, are synthesized from nitrate salts of Cu(II) and Ag(I) with ligand in ethanol. The metal complexes and ligand are characterized on the basis of elemental analyses, melting point, molar conductance, UV -Visible, FTIR and thermo gravimetric analysis. The molar conductance data reveal that the metal chelates of the ligand with Cu (II) and Ag (I) are electrolytes. From the suggest that the concent sites were proven to be through oxygen of the ring and Nitrogen of the azomethine group.

Keywords: 4-aminoantipyrine, copper, Silver, TGA

Introduction

Schiff bases are the compounds containing azomethine group ($-\text{HC}=\text{N}-$) which coordinator from through it with metal ion [1]. These are formed by products by condensation of a primary amine and an aldehyde/ketone with acid, base catalysis or with heat [2, 3]. The presence of the ($-\text{HC}=\text{N}-$) group gives the color to Schiff bases and other colors of compounds are shown by introducing other oxochromic groups. When functional groups, such as $-\text{OH}$, $-\text{COOH}$, $-\text{SH}$ are present in these ligands in Sites suitable for linking with metal ions, So it enables them to be strong chelating used in analytical and biological reagents.

Schiff bases uses in many fields such as industry, medicine and biology. They have been used in dyes, photographic emulsions [4], heart resistant polymers [5], high temperature stabilizers [6], lubricating oils [7], anticorrosive agents [8], anti knocking agents [9] and liquid crystal display composition [10,11]. They have been used in biological activity as antibacterial [12], antiviral [13], antifungal [14], antitumor's [15], insecticides [16], antihelminthics [17] and antiemetics [18].

Several Schiff bases which are reported to be therapeutically active possess cytotoxic [19], anti-inflammatory [20], antipyretic [21], analgesics [22], diuretic [23], and antispasmodic activity [24].

Experimental

Measurements

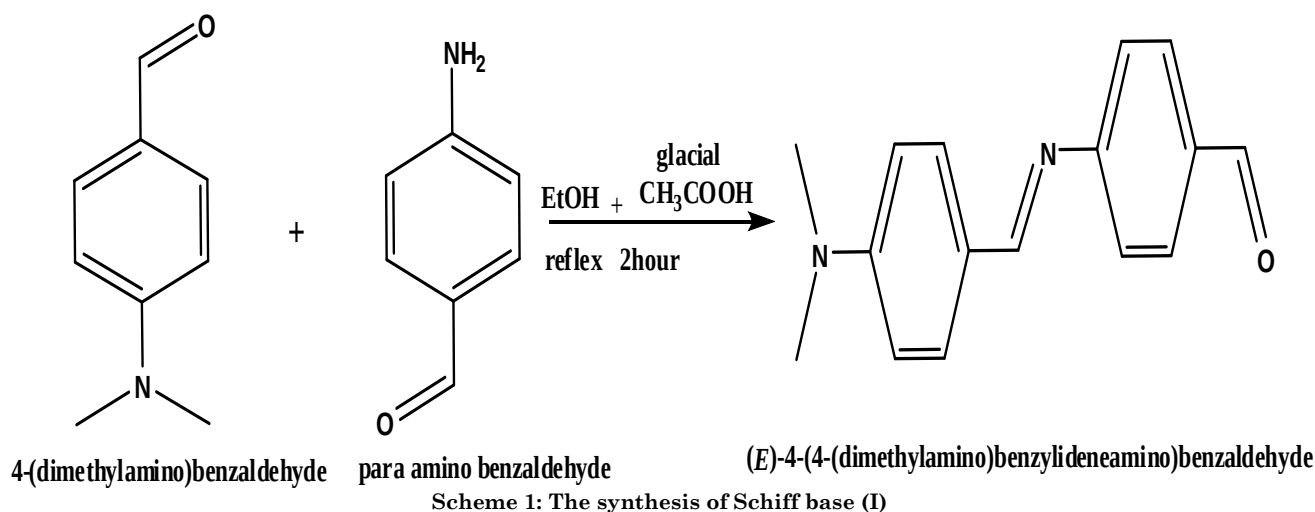
All chemicals used were of highest purity (BDH and Fluka). Microanalysis of carbon, hydrogen and nitrogen were obtained using by Perkin Elmer CHNS/O- analyzer 2400, The absorbance spectrum were recorded in the range of 250–900 nm using UV-Vis. Spectrophotometer model Shimadzu UV-Visible 1700 spectrophotometer.

The infrared spectra of the ligand and the obtained complexes were recorded using KBr discs on FT-IR 8000 Shimadzu, in the range of $(400-4000)\text{cm}^{-1}$. Thermal analysis (TGA) carried out by Perkin Elmer TGA-FTIR (USA). Electrical conductivity measured by digital conductivity meter Alpha-800 with the prepared complexes concentration of 10^{-3}M in ethanol at room temperature. pH measurements were carried out using (pH-meter), 720, WTW 82362.

Synthesis of Schiff Base (I)

20mL absolute ethanol solution of p-amino benzaldehyde (1.06g /0.01mol) was added to 20mL absolute ethanol solution of p-dimethyl amino benzaldehyde (1.34 g/ 0. 01 mol) in the presence of 5 drops of glacial acetic acid as a

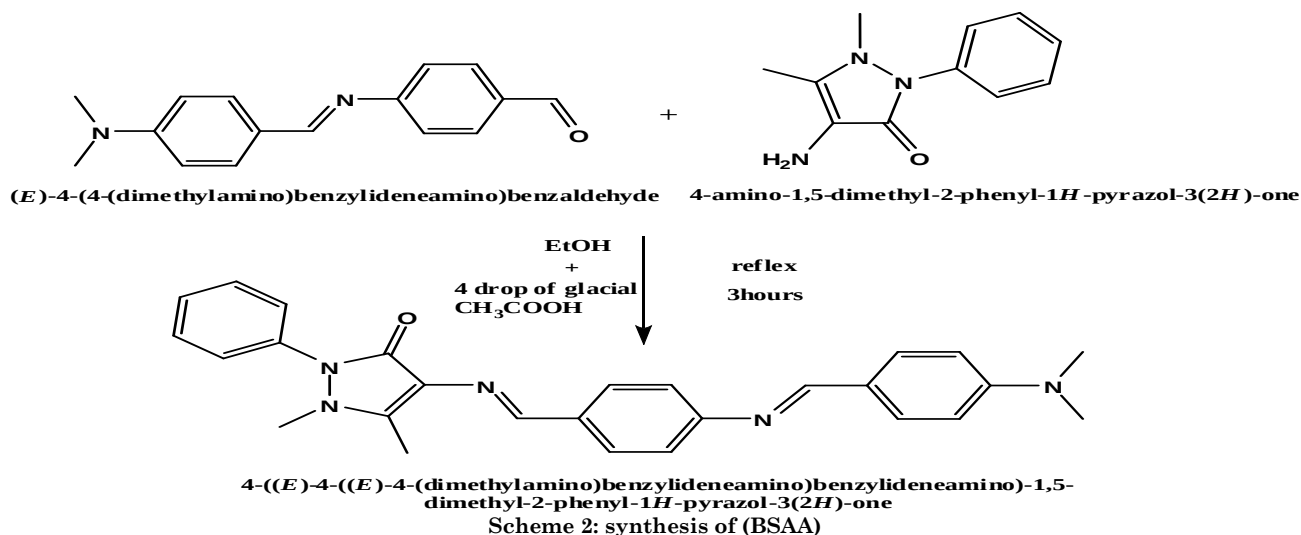
catalyst. The reaction mixture was refluxed for 3 hours. The resultant solution was cooled to room temperature. The yellow precipitate of 1- (4- (4- hydroxy- 3- methoxy benzylidene amino) phenyl) ethanone was formed which was filtered and recrystallized in absolute ethanol (Scheme 1).



Synthesis of Schiff base ligand (BSAA) [25]

In ethanol solution of 4-aminoantipyrine (2.03 g, 0.01mole, 20 ml) was taken in a burette and added drop wise to the ethanolic solution of 4-(4-dimethylamino) benzalidene

amino) benzaldehyde (2.5 g, 0.01 mol, 20 ml), Add 6 drops of glacial (CH_3COOH) with constant stirring for 4 hours. The dark yellow precipitate compound (II) was the obtained by filtration and recrystallized from hot ethanol, and dried over CaCl_2 (Scheme 2).



Synthesis of Schiff base Complexes

The mixtures of the (BSAA) under investigation (0.01 mole; 4.37 g) in 30 ml ethanol and metal salts [0.01mole, AgNO_3 (1.69g), (0.005mole) $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1.47g)] in the same amount of the same solvent were refluxed for two hours. The complexes were collected by filtration and then washed several times with hot ethanol. The resulted products were dried in air and stored in a desiccator over CaCl_2 under vacuum.

Results and Discussion

In Table (1) shows the analytical results of all prepared compounds with some measured physical properties. Two complexes show the conductivity measurement values ranging between (16 – 17.7) $\text{S.cm}^2 \cdot \text{mol}^{-1}$ in ethanol solution at 25°C , these values shown that the prepared complexes is non-ionic structure.

Table 1: Physical characterization, analytical and molar conductance of the Schiff bases and their complexes

No.	Molecular formula	Found (Calc.) (%)			Δm S.cm ² .mol ⁻¹	m.p C°	Yield (%)
		C	H	N			
1	C ₁₆ H ₁₆ N ₂ O	76.11 (76.16)	6.36 (6.39)	11.12 (11.10)	-----	201	85
2	C ₂₇ H ₂₇ N ₅ O	74.02 (74.12)	6.18 (6.22)	16.13 (16.01)	-----	295	76
3	[Cu(C ₂₇ H ₂₇ N ₅ O) ₂] (NO ₃) ₂	61.01 (61.04)	5.03 (5.12)	15.89 (15.82)	16	293	71
4	[Ag(C ₂₇ H ₂₇ N ₅ O) (NO ₃) ₂	57.56 (57.63)	4.87 (4.94)	15.03 (14.94)	17.7	<301	79

Effect of pH

To evaluate optimum pH values on the absorbance for the compounds solution were

studied in the 50% (V/V) ethanolic solution in the range of (5-10) as shown in Fig.1. (BSAA) ligand formed a very stable complex with metal ions Ag (I) and Cu (II) wide pH range.

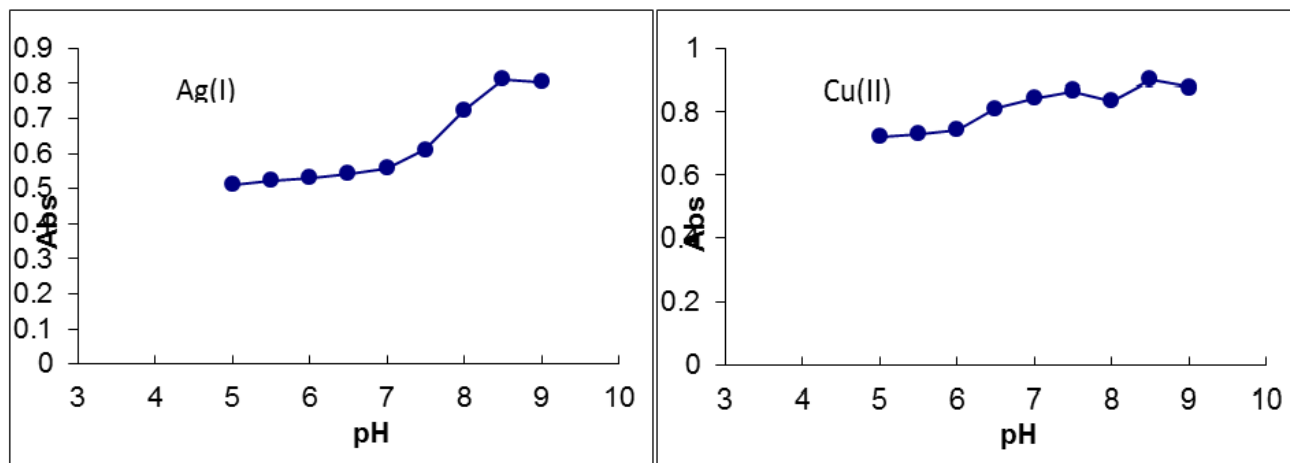


Figure 1: The effect of pH on the absorbance of Cu (II) and Ag (I) complexes

Absorption Spectra

The absorption spectra of (BSAA) ligand and its complexes were studied [26]. The wavelength for the maximum absorption (λ_{max}) of the compound (I) was found at 341nm while the (λ_{max}) of (BSAA) ligand was found at 360nm. The spectra of metal complexes were recorded within wavelength range (245– 360) nm. The absorption maximum (λ_{max}) of the each complex. Two absorption bands appeared for the Schiff base(I) at 243 nm which referred to the

($\pi \rightarrow \pi^*$) transitions of benzene ring while the band at 341nm assigned to ($n \rightarrow \pi^*$). The UV-visible spectra of the (BSAA) ligand showed two bands at 242nm and 360nm assigned to ($\pi \rightarrow \pi^*$) and ($n \rightarrow \pi^*$) transitions within the molecule. The UV-Vissible spectra of the complexes Cu(II) and Ag(I) showed absorption peaks at(250, 295,360nm) and (245,300nm) which were assign to ligand field and charge transfer transition respectively The spectrum of the complexes shows relative change in the bands position compared to that of the ligand ,as showed in Figures(2-5).

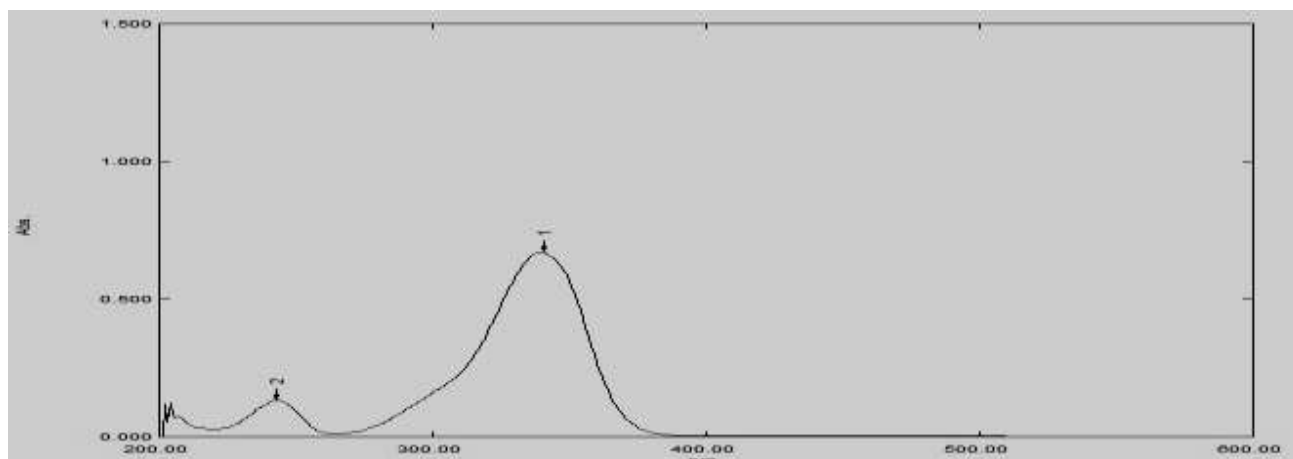


Figure 2: Absorbance spectrum of Schiff base

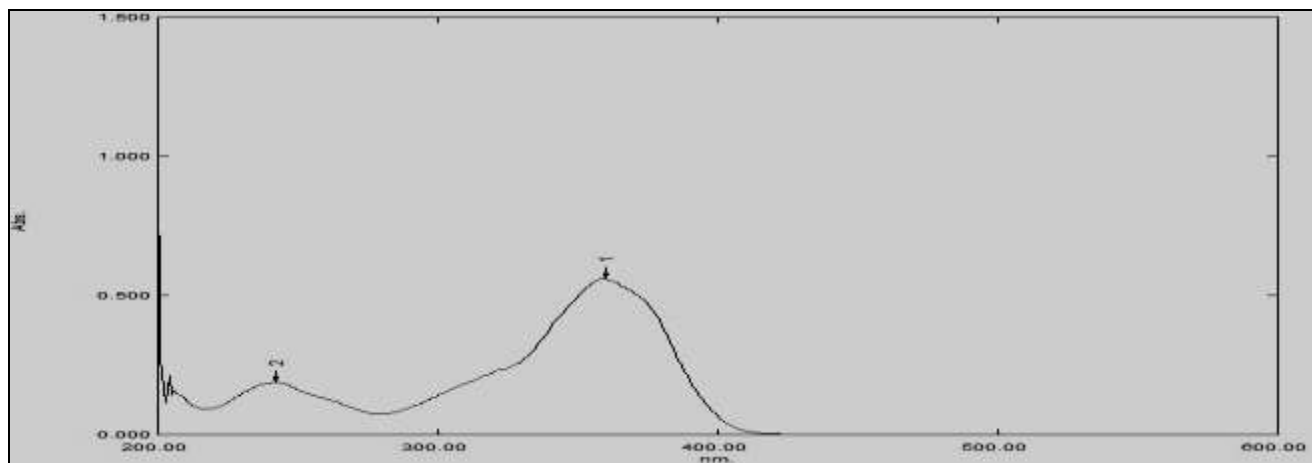


Figure 3: Absorbance spectrum of (BSAA) ligand

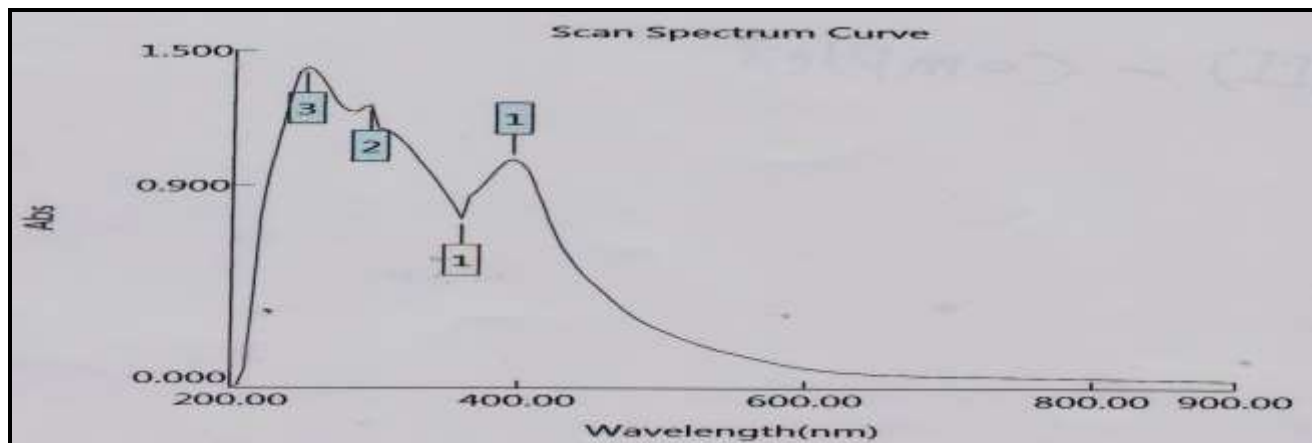


Figure 4: Absorbance spectrum of Cu (II) Complex

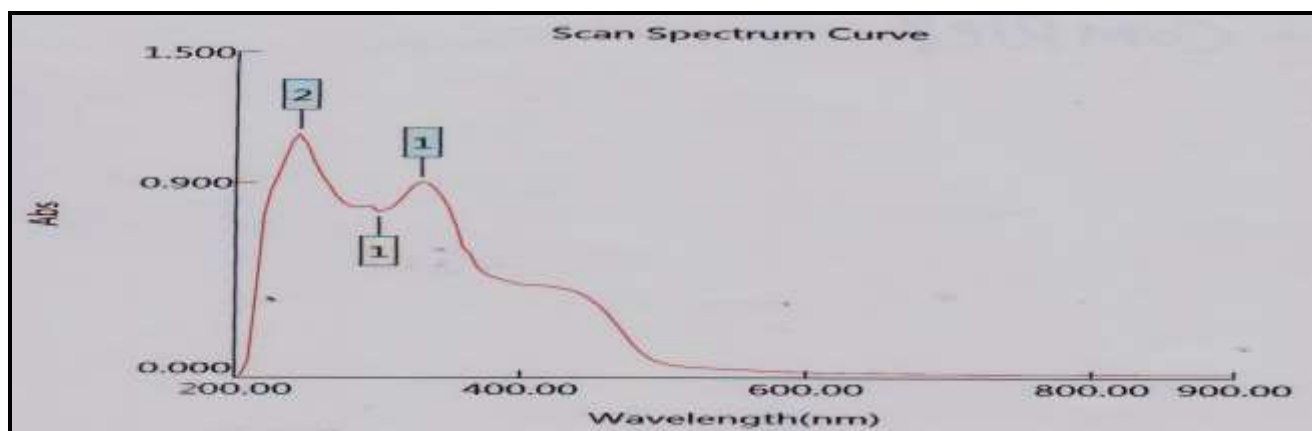


Figure 5: Absorbance spectrum of Ag (I) Complex

Infrared Spectral Studies of the Ligand and its Complexes

After the infrared measurements of the Schiff base and its complexes, The data of the IR spectra were compared with each other in

order to determine the participation of the coordinate sites and detect the changes that may have occurred. The obtained data are summarized in Table 2 with some assignments of the important characteristic bands.

Table 2: Some IR frequencies in (cm⁻¹) of the ligand and its metal complexes

No.	Compounds	ν (C-H) _{ar.}	ν (C-H) _{alip.}	ν (C=N)	ν (C=O)	ν (M-N)	ν (M-O)
1	C ₁₆ H ₁₆ N ₂ O	3071 3011	2902 2823	1596	1658	----	----
2	C ₂₇ H ₂₇ N ₅ O	3049 3019	2894 2804	1610	1647	----	----
3	[Cu(C ₂₇ H ₂₇ N ₅ O) ₂ (NO ₃) ₂]	3163 3039	2908 2823	1596	1650	509	594
4	[Ag(C ₂₇ H ₂₇ N ₅ O) (NO ₃) (H ₂ O)]	3182 3062	2947 2893	1597	1651	509	594

The absorption bands recorded within the range of (1596-1610 cm^{-1}) back to the existence of the azomethine ν ($\text{HC}=\text{N}-$) group. It refers to change the frequency of this group to a higher frequency to the affected complexation [27]. The other coordination site that can participate in consistency is a ($\text{C}=\text{O}$) group, The strong evidence for the participation of this group can be seen from the location of the band at (1647 cm^{-1}) in the spectrum of the (BSAA) . The displacement of beams to a higher frequency in the spectra of

the complexes indicates the participation of the group ($\text{C}=\text{O}$) in the bond with the metal. New bands have appeared within the range of (509-594 cm^{-1}) Which did not appear in the free (BSAA) are due to $\nu(\text{M}-\text{N})$ and $\nu(\text{M}-\text{O})$ vibrations and the appearance of these vibrations support the involvement of nitrogen atom and oxygen atom of ($\text{HC}=\text{N}-$) and ($\text{C}=\text{O}$) groups of the (BSAA) ligand when formed complexation with the metal ions under investigation(Figures 6-9).

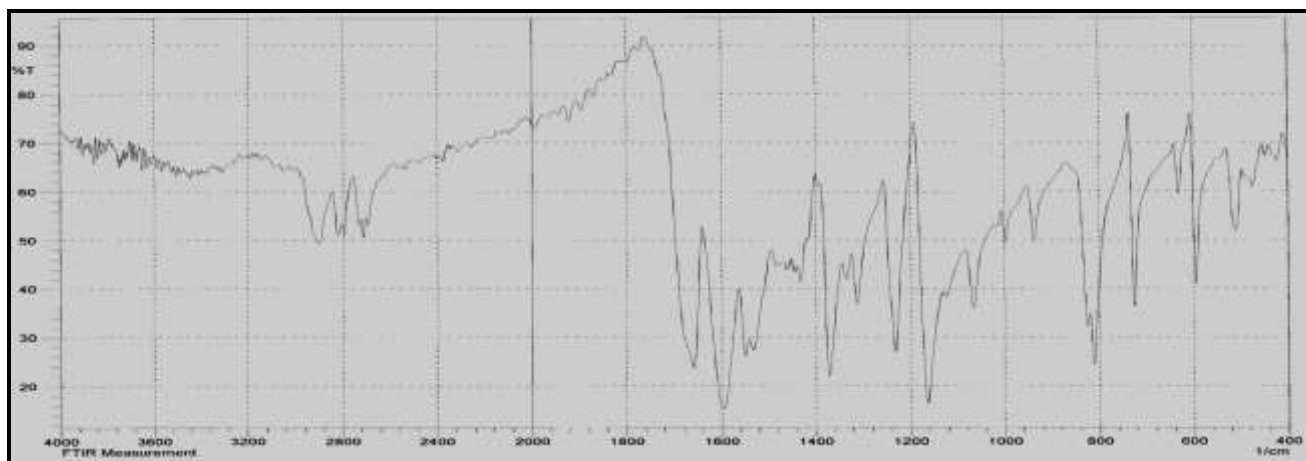


Figure 6: FT-IR spectrum of Schiff base (I)

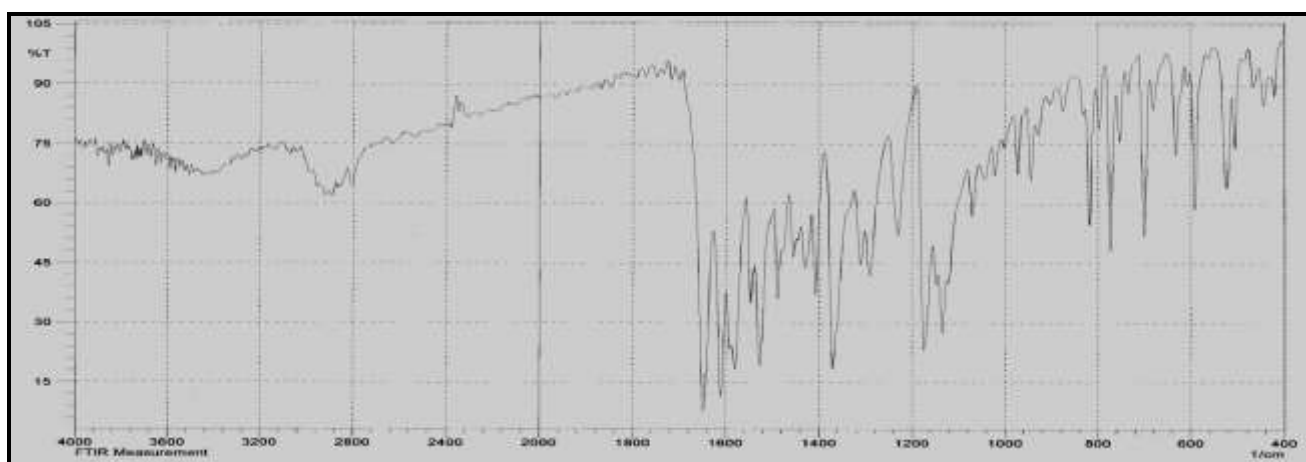


Figure 7: FT-IR spectrum of (BSAA) ligand

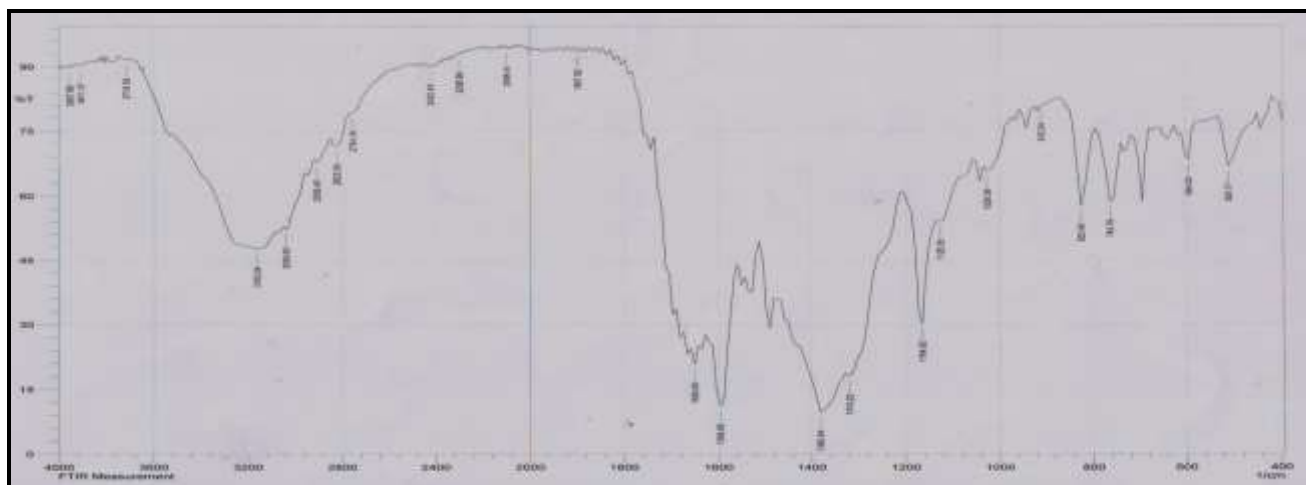


Figure 8: FT-IR spectrum of Cu (II)-complex

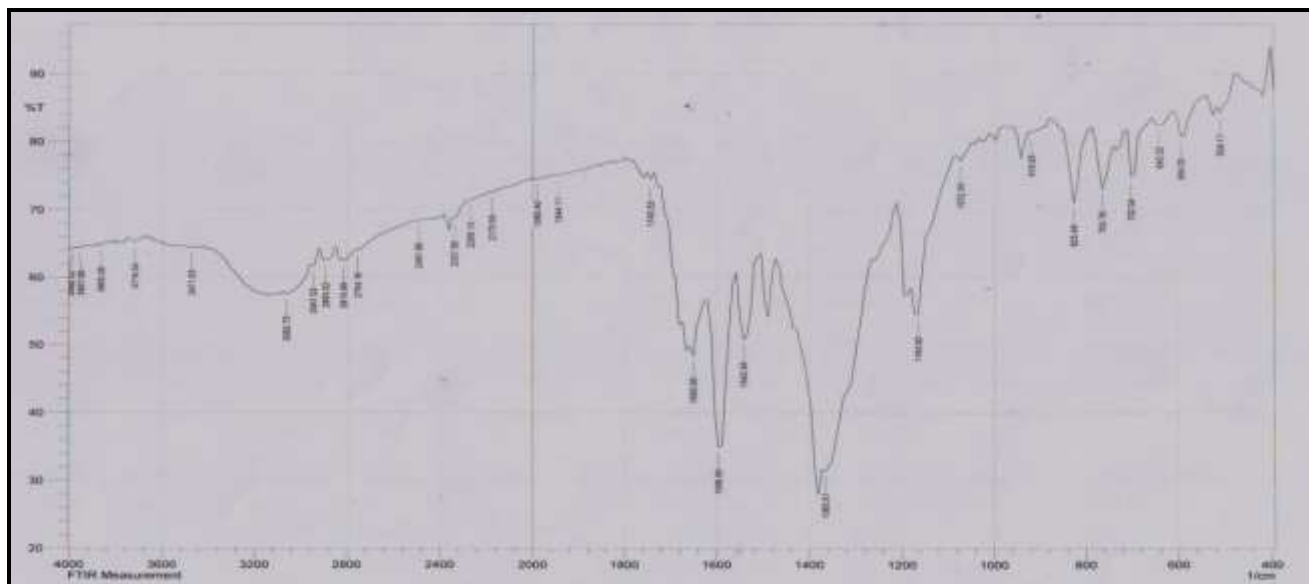


Figure 9: FT-IR spectrum of Ag (I) – Complex

Thermogravimetric Analysis

TGA was carried out for solid (BSAA) ligand and Cu (II), Ag (I) metal complexes under N_2 flow. The heating rate was suitably controlled at $40^\circ C \text{ min}^{-1}$ and the weight loss was measured from the ambient temperature up to $803^\circ C$ [28]. The results of analysis of have been abridged in Table (3) indicating a good correlation between calculated and found weight loss values.

The thermogram of bis Schiff ligand (Figure 10) exhibited three decomposition steps in the temperature range of $40\text{--}803^\circ C$. The first decomposition step in the temperature range of $40\text{--}297^\circ C$ with % mass loss of 48.32% is assignable to the loss of $(C_{11}H_{11}N_3O)$ molecules from the ligand. The second and third decomposition steps with mass loss of 35.85% and 10.73% in the temperature range of $297\text{--}425^\circ C$ and $425\text{--}803^\circ C$ have considered the loss of remain organic ligand moiety. The TGA and DTG curve of Cu(II) complex was shown in Figure (11), the curve indicated that the complex was decomposed into three main steps. The first step involves the removal of

Molecule $(C_{11}H_{11}N_3O)$ (calculated 38.44%, experimental 39.09%) at temperature range $40\text{--}288^\circ C$. The part of ligand $(C_9H_{11}N_2)$ was decomposed between temperature range ($288\text{--}480^\circ C$) (calculated 22.50%, experimental 19.21%) This represents the second step. The third step was occurred at temperature range $480\text{--}803^\circ C$ that suggested the completely decomposed and removed as Cu/Cu₂O and carbon residue. From the TGA and DTG curve of silver complex Figure (12) indicated that the complex was stable up to $358^\circ C$ and decomposition was taken place into three main steps [29].

In the first step of decomposition the part of ligand $(C_{11}H_{11}N_3O)$ (calculated 26.21%, experimental 24.85%) between $40\text{--}358^\circ C$ were decomposed. At temperature range $358\text{--}452^\circ C$ the rest part of ligand $(C_9H_{11}N_2)$ (calculated 22.45%, Experimental 22.38%) was removed. At above $452^\circ C$ temperature the complex was decomposed completely and removed as Ag/AgO and Carbon residue. All the possible degradation pathways is shown in Figure (13).

Table 3: Thermal analysis of ligand and its complexes by TGA and DTG

Compounds	DTG peak ($^\circ C$)	TG range ($^\circ C$)	step	TG mass		Remain mass	Metallic residue
				Found%	Calc. %		
$C_{27}H_{27}N_5O$	260.63	40-297	1 st	48.32	46.01	51.68	$C_{11}H_{11}N_3O$
	329.78	297-425	2 nd	35.85	34.32	15.82	$C_9H_{11}N_2$
	463.24	425-803	3 rd	10.73	-	5.10	carbonation
$[Cu(C_{27}H_{27}N_5O)_2(NO_3)_2]$	200.02	40-288	1 st	39.09	38.44	60.91	$C_{11}H_{11}N_3O$
	271.07	288-480	2 nd	19.21	22.50	41.70	$C_9H_{11}N_2$
	333.86	480-803	3 rd	8.95	-	32.75	Cu/Cu ₂ O /Carbon residue
$[Ag(C_{27}H_{27}N_5O)(NO_3)_2]$	225.67	40-358	1 st	24.85	26.21	75.15	$C_{11}H_{11}N_3O$
	437.65	358-452	2 nd	22.38	22.45	52.77	$C_9H_{11}N_2$
	---	452-803	3 rd	11.55	11.84	41.22	Ag/AgO /Carbon residue

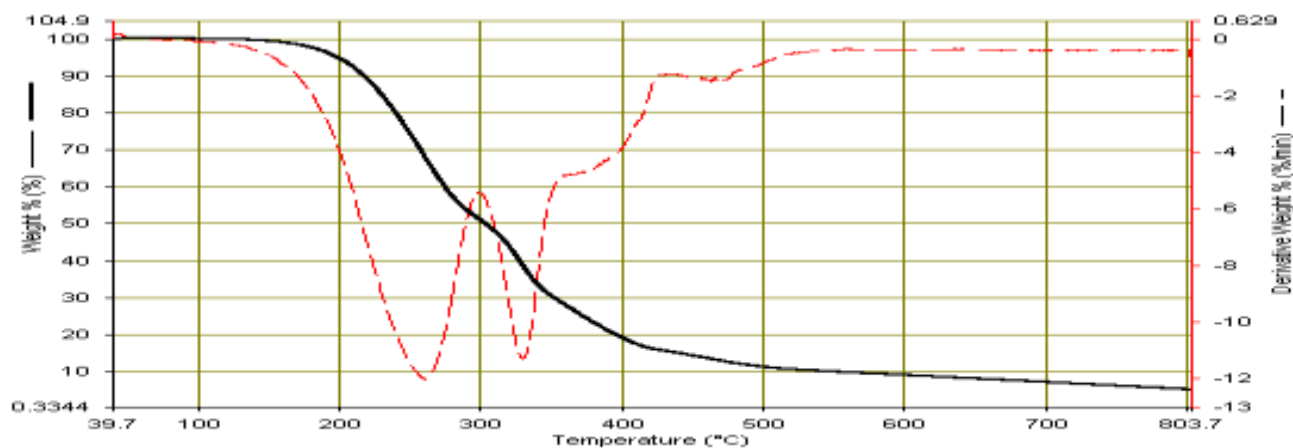


Figure 10: TGA of (BSAA)

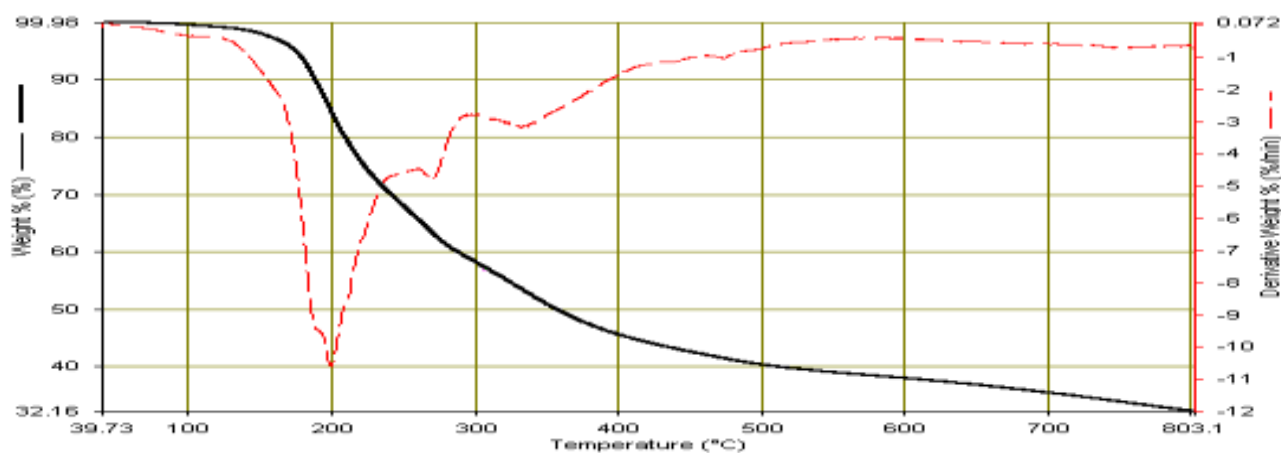


Figure 11: TGA of Cu (II)-complex

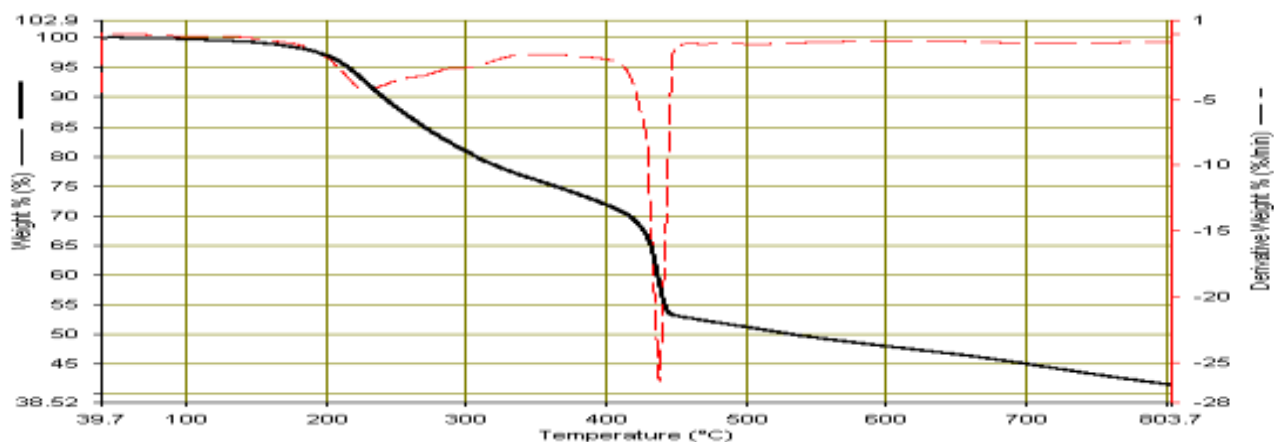


Figure 12: TGA of Ag (I)-complex

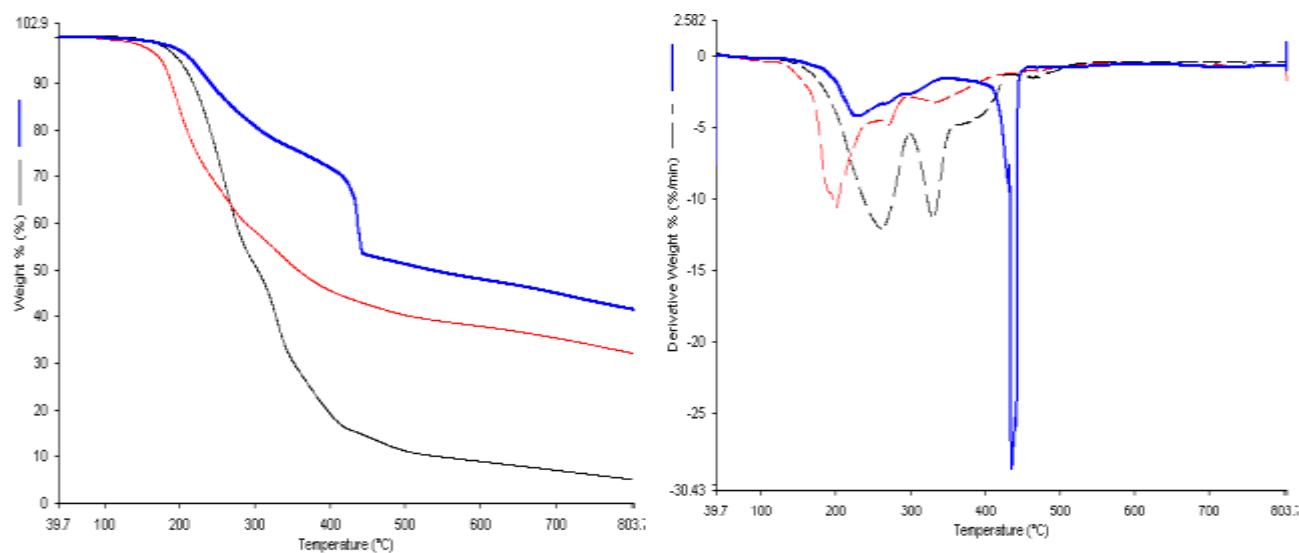


Figure 13: TGA of ligand and complexes

Conclusion

The proposed geometry of the Cu (II) complex is octahedral while Ag (I) complex is

tetrahedral. According to these results the structural formulas of these complexes may be proposed in Figures (14, 15).

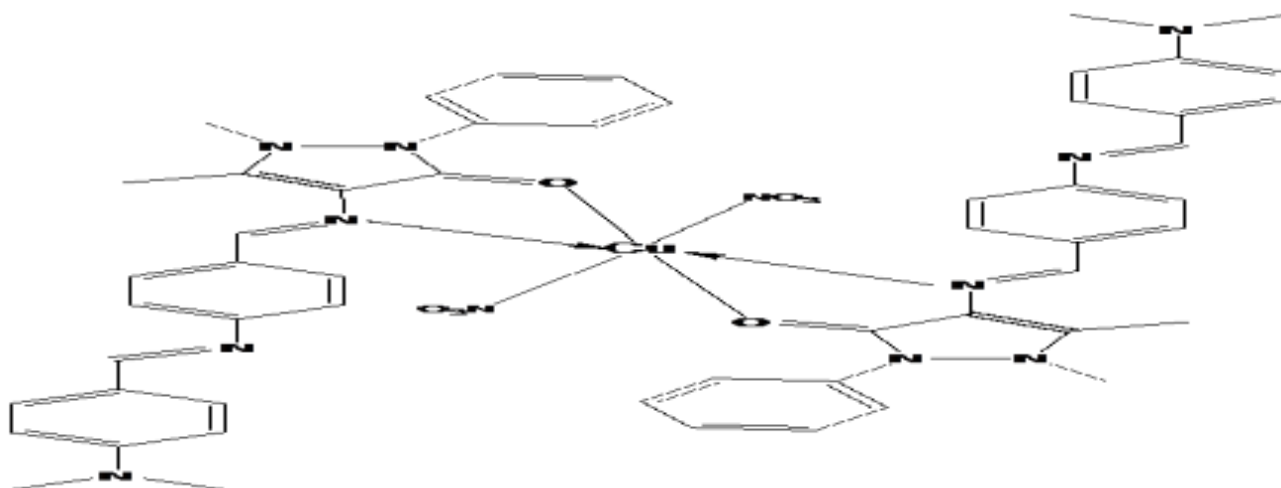


Figure 14: The proposed structural formula of Cu (II) with Schiff base (II) ligand

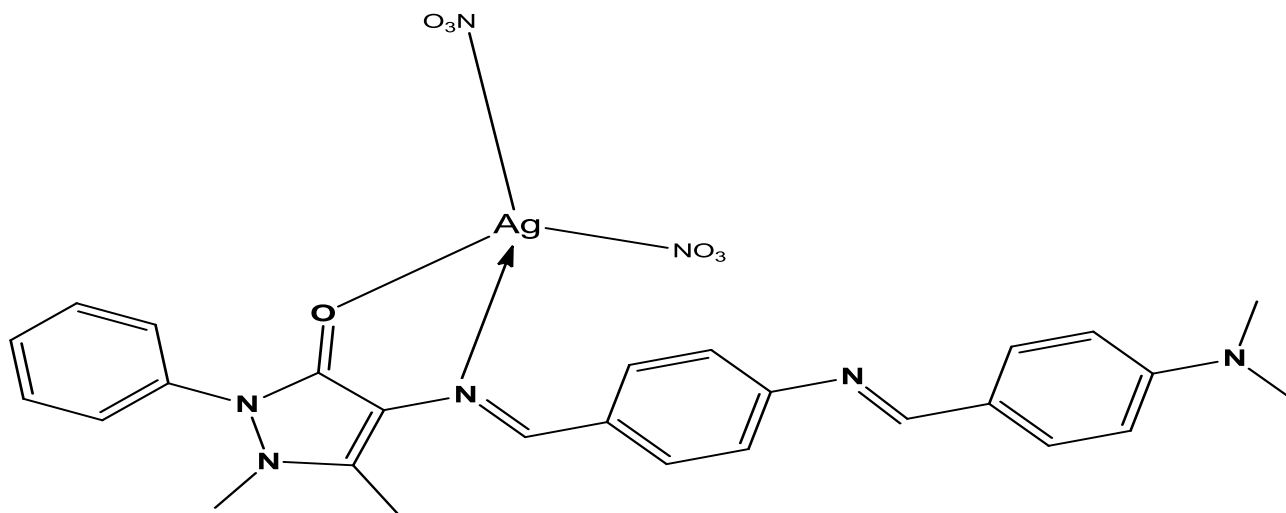


Figure 15: The proposed structural formula of Ag (I) with Schiff base (II) ligand

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