**Article**

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# Preparation, Identification and Antimicrobial Activity of Silver (I) and Copper (II) Nano complexes with New Azo-Schiff ligand Derivative from Theophylline drug

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**Abstract:**

Silver (I) and Copper (II) complexes were prepared. The New complexes were characterized using elemental analysis (C .H .N) and Infrared spectroscopy (FT-IR), ultraviolet-visible spectroscopy (UV-Vis.), and flame atomic absorption spectroscopy (FAAS) to determine the percentages of metal ions in their complexes, in addition to molar conductivity using DMSO solvent at a concentration of ($1X10^{-3}$M) and at laboratory temperature. The infrared spectroscopy results showed clear changes in the stretching bands of the factional groups in the complexes spectra compared to the ligand spectrum, which confirms the occurrence of the coordination process between the selected metal ions and the donor atoms in the ligand. While the results of the ultraviolet-visible (UV-Vis.) spectrum of the metal complex solutions in (DMSO) showed clear charge transfer absorption peaks of the (M→L) type, evidence of the occurrence of the coordination process. It was also confirmed by the results of the flame atomic absorption spectrum and the results of the precise analysis of the elements carbon, hydrogen and nitrogen, in agreement between the practical values obtained and the theoretically calculated values for the compounds under study.

In addition to scanning electron microscopy (FESEM) spectroscopy of both copper (II) and silver (I) Nano complexes with the new ligand to measure the Nano size of each

of them, the measurements showed that the complexes were within the Nano scale range, i.e. less than 100 nm, with the crystalline nature of each of them being diagnosed.

The results of molar conductivity using DMSO solvent showed the presence of ionic character of Ag (I)complex, which is evidence that the complex was charged and have Electrolytic character with the presence of chloride ion outside the coordination sphere, and that the tridentate ligand is neutral while the copper (II) Nano complex showed Non-electrolytic behavior. their proposed geometrical shapes, where the octahedral structure was proposed for the copper(II) Nano complexes and the tetrahedral structure Nano silver (I) complexes. Their biological activity was studied against two specific types of pathogenic bacteria, one of which is Gram-positive (G +) ***Staph. aurous*** and the other is Gram-negative ***Escherichia coli*** (G -). The sensitivity of the bacteria was studied using the Well diffusion method, using three concentrations of (100, 1000, 500) ppm in DMSO solvent under the same conditions. The Nano complexes showed high positive results compared to the drug Theophylline. The complexes under study also showed inhibitory activity against Gram-positive bacteria that was greater than their activity against Gram-negative bacteria.

**Keywords: Characterization, Antimicrobial Activity , Silver (I) Nano complexes.**

## Introduction

Due to their superior physical, chemical and biological properties compared to bulk materials, nanoparticles are particularly necessary. As a result of their small size (1-100 nm), these Nano materials have a thicker surface-to-volume ratio, which leads to enhanced surface interaction [1]. Because of their unique properties, they can be used in various fields, including biotechnology and materials science. Three physical, chemical and biological methods can be used to formulate these nanoparticles [2]. Silver nanoparticles (AgNPs) are currently widely used in various fields, including agriculture, commerce, medicine, and industry. The unique properties of smaller dimensional AgNPs make them suitable for diverse applications. The application of nanomaterial's in biomedicine is becoming more widespread, resulting in the emergence of Nano biotechnology, AgNPs and silver-containing compounds are widely recognized in this field for their ability to eliminate conventional and advanced organisms, including present-day microorganisms[3]. AgNPs are primarily used in non-wound biomedical applications, drug delivery systems, tissue scaffolds, and protective coatings. As a

result, the use of AgNPs has expanded in the fields of nanotechnology, biomedical science, and ecological sustainability[4].

Azo-Schiff base compounds, known for their diverse biological activities, have garnered attention in Anti-Bacterial activity researches due to their potential properties, several azo-Schiff base compounds have shown promising Anti-Bacterial activity in various bacteria types[5-8]. The ligands of the Azo -Schiff include Azo groups as well as Azomethine, the azo group is excellent and important for coordination chemistry [9,10]. In the last few years huge amount of (N,N′)-donor ligands type azo- azomethine have synthesized [11-13].

Certain antibacterial activity azo Schiff base compounds and their complexes were found [14-17]. This class of compounds has an azo- imine, active (π-acidic), which functions as a stabilizer efficient in the low valiant oxidation of metals [11,12], as a result of the existence of azo-centered π*-molecular orbital. So, a quantity of these compounds have synthesized and their ability as poly chelating ligands was examined [18].

## Materials and Methods

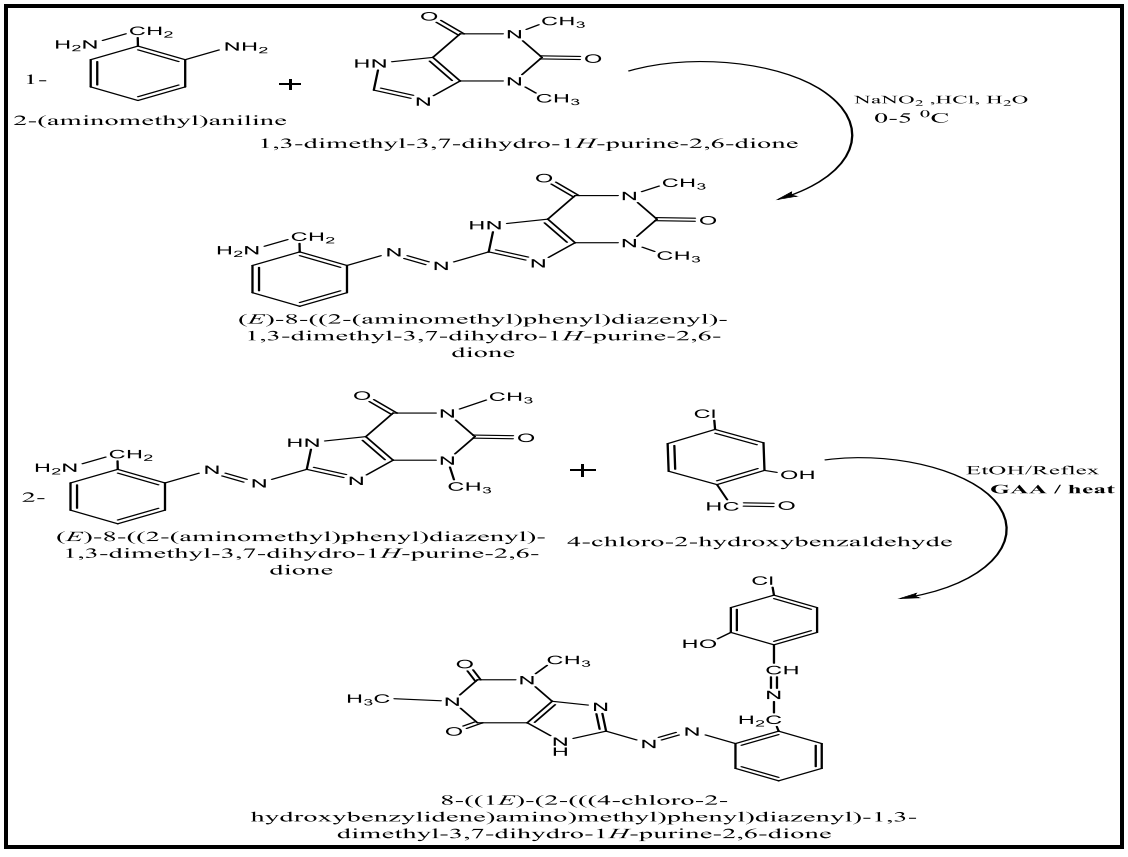
All chemicals were obtained from Merck, BDH and Sigma - Aldrich and used without further purification. Melting point were determined using model 9300 of ligand and its complexes. $^{1}$HNMR spectra were recorded as solution in DMSO-d6 as solvent using (varian 500MHZ Spectrophotometer) and Mass Spectra were recorded on Shimadzu Agilent Technologies 5975C. The UV-Visible spectra were recorded on Shimadzu spectrophotometer double band model 1700. Magnetic susceptibility measurements were carried out on a balance magnetic MSB-MKI using faraday method. The diamagnetic corrections were made by Pascal's constants. IR spectra were recorded on Shimadzu FTIR 8400 spectrometer using KBr pellet in the wavelength range 4000-400 cm-1. C.H.N Elemental analyses were performed by means of EURO 2012EA 300 C.H.N Elemental analysis. **Field Emission Scanning Electron Microscopes (FE-SEM) MIRA3 TESCAN, Czech** .

### Synthesis of the new Azo- Schiff base ligand (2H-4Cl-DBAPD):

**The first step** included the preparation of azo dye where (0.02 mol, 2. 443 g) of ortho amino benzylamine was dissolved in (60 mL) of distilled water while maintaining the temperature of the reaction medium at a low temperature between (0-5℃). After that, (10 mL) of concentrated HCl acid was added with continuous shaking of the solution. (0.02 mol, 1.379g) of $NaNO_2$ was dissolved in (5 mL) of distilled water while cooling the solution to a temperature below zero Celsius. Then, the second cooled solution was added to the aromatic amine solution with shaking and stirring, and the solution was left for (30 min) to complete the Azotization process, after which the diazonium salt

solution was added drop by drop with continuous stirring to the solution of the pair compound consisting of (0.02 mol , 3.603g) theophylline and (20 mL) of sodium bicarbonate solution (40% NaHCO3) with the addition of (50 mL) of ethanol at a temperature of (0℃) with continuous stirring and at (pH ≈8) by monitoring with PH paper .A bright yellow precipitate was observed to form, and the reaction flask was left for two hours to complete the precipitation process. Then the azo formed in the form of yellow crystals was filtered and washed with distilled water several times, dried, and recrystallized using hot ethanol. Its melting point was measured and was (132 -134) ℃ [19].

**The Second step** included new azo-Schiff base ligand , was prepared by adding (0.0015 mol,0.2341g) of (2-hydroxy-4-chlorobenzaldehyde) to a round-bottomed flask with a capacity of (250 ml), then adding (2-3) drops of glacial acetic acid and leaving it for (5 min) at laboratory temperature, after which a solution prepared by dissolving (0.0015 mol, 0.5 g) of azo dye in (20 mL) of absolute ethanol alcohol was added, and the solution was sublimated for (16 hrs) At a temperature of (78℃), the new azo-Schiff base ligand (2H-4Cl-DBAPD) was obtained. The reaction was followed by TLC using (0.5mL Methanol: 4.5 ml benzen). The product was then cooled, dried, collected, and then recrystallized using hot absolute ethanol. Its physical properties are listed in Table (1). Scheme (1) shows the preparation steps of the new azo-Schiff base ligand (2H-4Cl-DBAPD) [20].



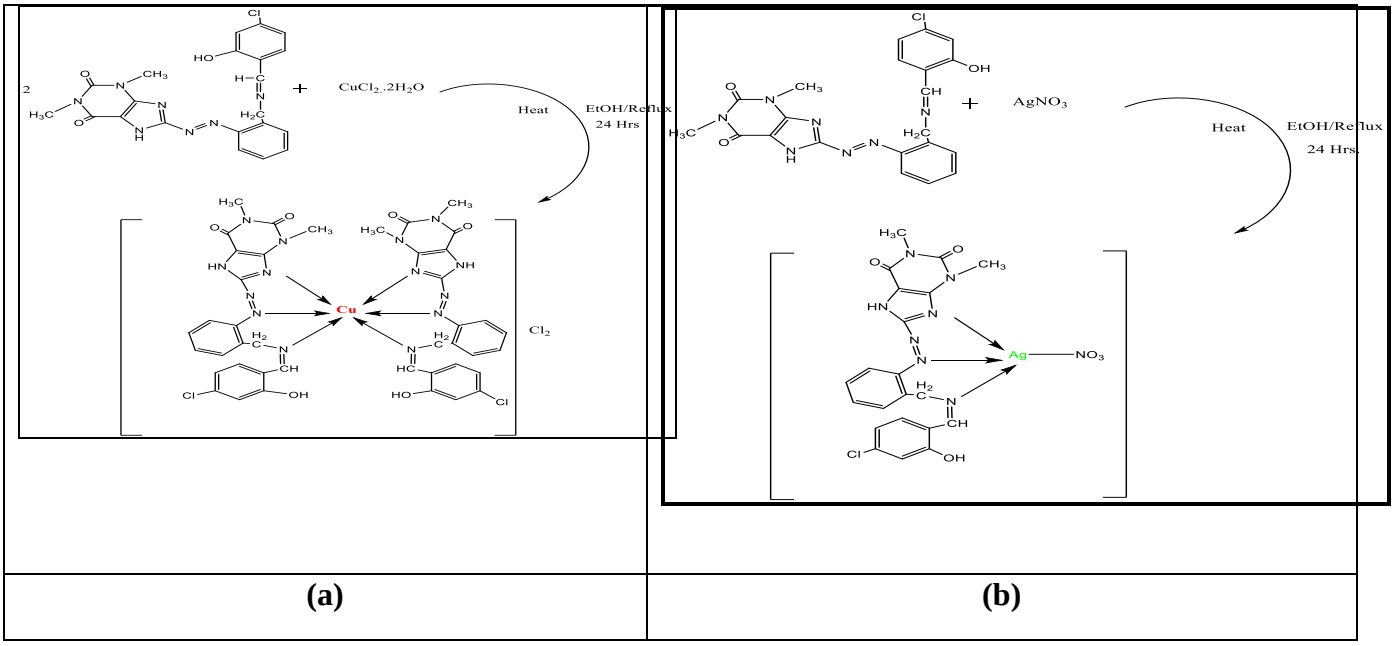

**Scheme-1: Synthesis of new azo-Schiff base ligand(2H-4Cl-DBAPD)**

## Synthesis of Ag(I) and Cu(II) Nano-metal complexes:

Nano Copper (II) complex was prepared by adding (0.0001mol ,0.0170 g) of aqueous $CuCl_2.2H_2O$ dissolved in (10 mL) of absolute ethanol to the ligand solution prepared by dissolving (0.0002mol, 0.0903g) in (10 mL) of absolute ethanol at a molar ratio of (2:1) (ligand: metal) with stirring and escalation for 25 hours at (78℃). The solid complex was observed to precipitate, then the solution was left to cool and dry, and the precipitate was collected and crystallized using hot ethanol, and its melting point was measured.[21].

Nano Silver (I) complex was prepared by adding (0.0169g, 0.0001mol) of silver nitrate dissolved in (10mL) of absolute ethanol to the ligand solution prepared by dissolving (0.0001mol, 0.0451g,) in (10mL) of absolute ethanol at a molar ratio of (1:1) (ligand: metal). With stirring and escalation for 25 hours at a temperature of (70℃), the solid complex was observed to precipitate. Then the solution was left to cool and dry, and the precipitate was collected and crystallized using hot ethanol. Its melting point was measured[22].

The physical properties of the complexes under study are listed in Table 1.Scheme 2(a and b) illustrates the steps of preparing the metal complexes with the ligand (2-H-4Cl-DBAPD).




**(a)** **(b)**

**Scheme- 2 (a and b ) Synthesis of the Nano-metal complexes**

**Table (1) Shows the physical properties of the new Azo Schiff base ligand and its complexes.**

| No | Chemical formula | Color | M.Wt g/Mole | M.P℃ | Yield% | Rf |
|---|---|---|---|---|---|---|
| 1 | 2H-4Cl-DBAPD= $C_{21}H_{18}ClN_7O_3$ | Yellow | 451.87 | 154-156 | 95 | 0.60 |
| 2 | $[Cu(C_{21}H_{18}ClN_7O_3)_2]Cl_2$ | Olive | 1038.19 | 200-202 | 86 | 0.65 |

| | | | | | | |
|---|---|---|---|---|---|---|
| 3 | $[Ag(C_{21}H_{18}ClN_7O_3)NO_3]$ | Brown | 621.74 | 170-172 | 93 | 0.79 |

## Antimicrobial Activity Test

### 1. Prepare the culture medium:

Mueller-Hinton agar was prepared according to the instructions of the Indian company (Hi media) by dissolving (38) g of the agar in one liter of distilled water in a glass flask and mixing well. Then the mixture was heated on a heater until the agar dissolved. This was followed by placing the agar in the sterilizer (Autoclave) equipped by the Japanese company (Hirayama) at a temperature of (121) C and under a pressure of 15 pounds/inch2 for (15) minutes. Then pour the medium into sterile Petri dishes at a rate of (15-20) ml per dish and leave it until solidification is complete. After that, place the dishes in a (Memmert) incubator equipped by the German company (Memmert) for (24) hours at a temperature of (37) C to ensure that there is no contamination in them [23].

### 2 -Preparation of solutions:

Solutions of the above-mentioned complexes, copper (II) and silver (I) nanoparticles with the ligand in under study, were prepared at concentrations of (1000, 500, 100) ppm by dissolving the appropriate weight of each compound in (10) ml of DMSO for the complexes, in addition to making a control plate containing 99% ethanol and a medical drug containing theophylline to test its biological effectiveness.

**3 -Source of bacteria:** Two isolates of pathogenic bacteria were used, isolated and laboratory diagnosed using biological and microscopic tests obtained from the Amin Laboratory for Advanced Biotechnology and Research / Holy Shrine of Imam Ali. These isolates are considered common pathogens of many diseases in humans, and they show high resistance to many antibiotics. It included Staphylococcus aureus, a representative of Gram Positive Bacteria, and Escherichia coli, a representative of Gram Negative Bacteria, the latter of which is highly resistant to many antibiotics.

**4- Method of inoculation and inhibition of bacterial isolates and calculation of inhibition zones:** The drilling method (74,73) was adopted, where sterile Petri dishes containing the solid culture medium Mueller-Hinton agar prepared in paragraph (12-2-2) were inoculated with the test bacteria mentioned in paragraph (12-2-3) by pouring a volume of (0.1) ml of the bacterial suspension (broth) onto the solid culture medium in different directions and then moving the dishes to ensure spreading the bacteria whose sensitivity is to be tested evenly in each dish. The dishes were left for (30) minutes at room temperature to ensure absorption of the nutrient broth liquid, and then holes were made using a cork drill with a diameter of 10 mm, at a rate of three holes for each dish, and to avoid overlapping between the inhibition areas, a distance of (2 cm) cm was left between one spot and another. Then, a volume of (10) microliters of metal complex

solutions at concentrations of (1000, 500, 100) ppm prepared in paragraph (8-2-2) was placed using a (Micropipette). The dishes were incubated after the holes dried in the incubator for (20) hours at a temperature of (37 $^{0}$C). After that, the inhibition zones of bacterial growth around each hole for the compounds under study were measured using a millimeter ruler, which appears as a halo free of bacterial growth surrounding the spot of the chemical compound. Each experiment was repeated three times and the average measurement for those experiments was taken.[24]

## Results and discussion:

All complexes are Freely soluble in THF, DMSO ,Methanol and Ethanol table 2 .Also They are stable in air .The ligand and its metal complexes were characterized by elemental analysis Table (2) ,molar conductivities, magnetic susceptibility, IR,UV-Vis,( Mass and $^{1}$H,MNR spectrum for the ligand) .The analytical data of the complexes are in agreement with the experimental data .The value reveal that the metal to ligand ratio was(1:2) (M:L) for Cu (II) complex and (1:1) for Ag(I) complex and were presented in table.2.The magnetic susceptibility of the chelate complexes at room temperature were consistent with octahedral geometry and showed higher conductivity value for Cu (II) complex and tetrahedral for Ag(I) complex and showed lower conductivity value, These proves that complexes have different electrolytic nature [20].

**Table (2) shows the Element Analysis** of **the new azo Schiff base ligand (2H-4Cl-DBAPD) and its Nano complexes.**

| Formula | M.Wt | (Found) Calc. % | | | |
|---|---|---|---|---|---|
| | | C% | H% | N% | M% |
| L1= $C_{21}H_{18}ClN_7O_3$ | 451.87 | 55.82 (55.94) | 4.02 (4.12) | 7.85 (7.95) | ---------- |
| $[Cu(L_1)_2]Cl_2$ | 1038.19 | 48.59 (48.68) | 3.50 (3.71) | 18.89 (19.11) | 6.12 (6.37) |
| $[Ag(L_1)NO_3]$ | 621.74 | 42.38 (42.52) | 3.05 (3.21) | 16.47 (16.81) | 18.12 (18.21) |

## Mass spectrum of the new ligand 2H-4Cl-DBAPD:

The mass spectra of the new azo Schiff base ligand(**2H-4Cl-DBAPD**) was recorded at room temperature .The obtained peaks confirm the proposed formulae for the compound .The mass spectrum of Ligand show the molecular ion peak at m/z+ 451 compound

($C_{21}H_{18}ClN_7O_3$) confirm the proposed formulae for compound . Due to the large molecular weight, high bombardment energy, and the large number of heterogeneous atoms in its chemical structure, which confirm the validity of the proposed formula for the compound. Figure 1 showed the mass spectrum of ligand [20].

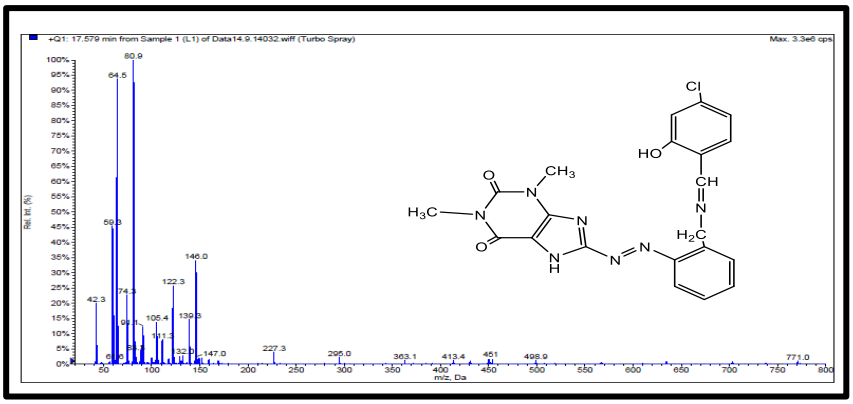
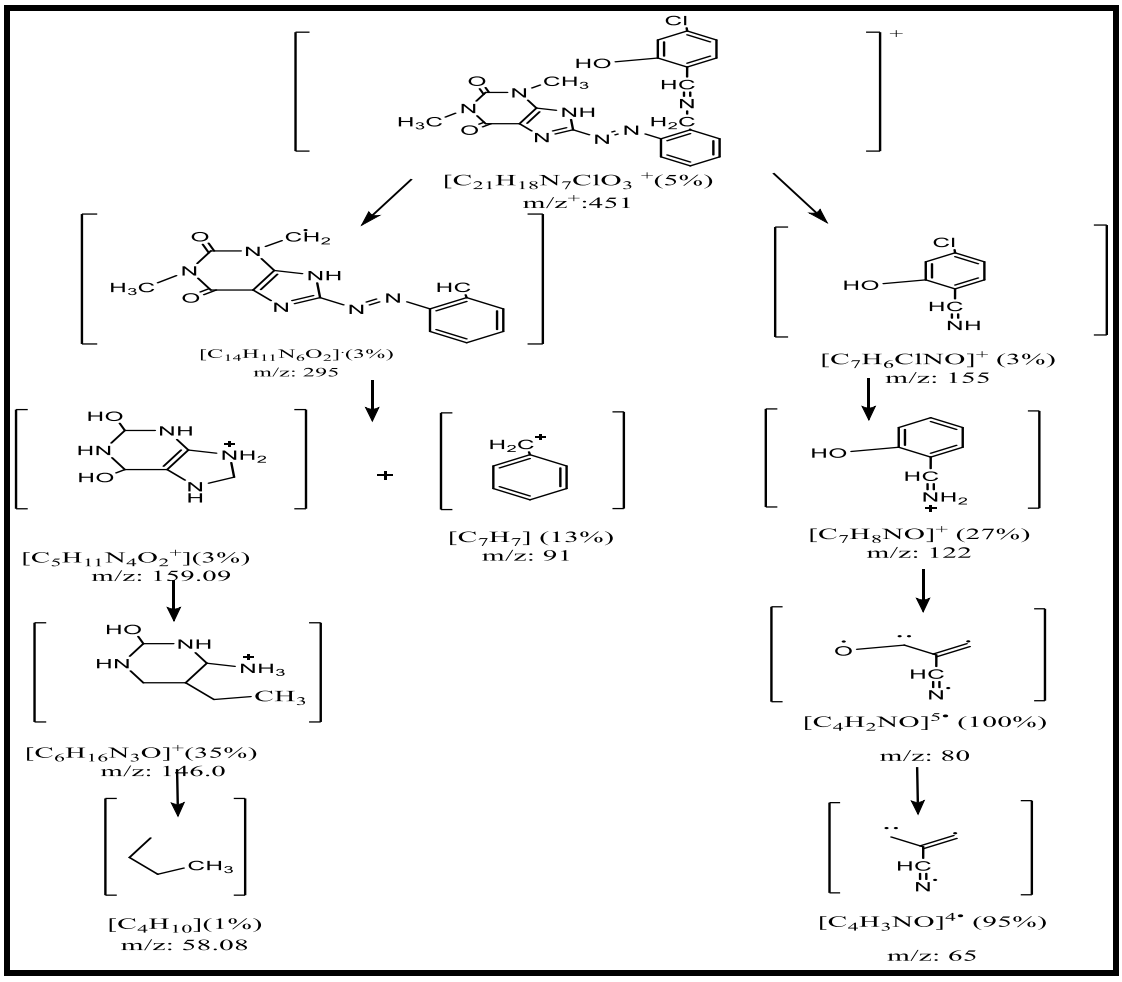


**Fig1: Mass spectrum of the new azo Schiff base ligand .**

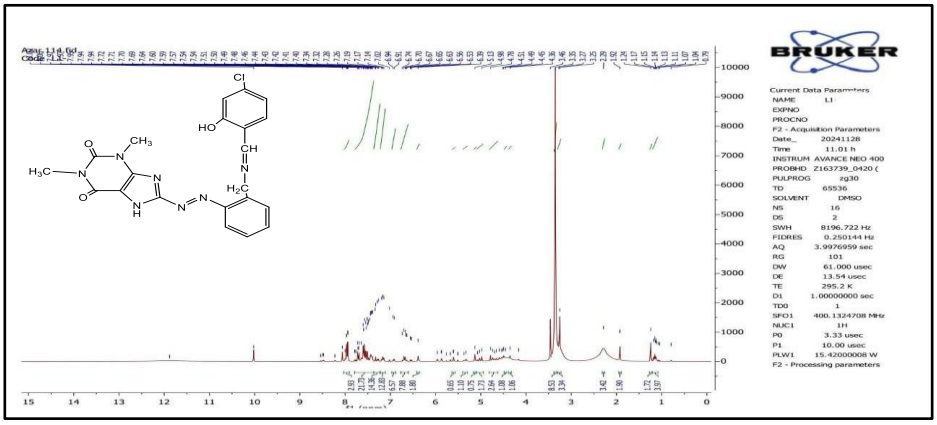



Scheme (3-1) Mass fractionation of the ligand (2H-4Cl-DBAPD)

## $^1$H-NMR Spectra

The spectrum of newly synthesized ligand gave a satisfactory data and the molecular structure was assigned on the basic of $^1$H - NMR chemical shift by using DMSO-d$^6$ as a solvent with TMS as an internal reference.

The $^{1}$HNMR spectra of the newly prepared ligand showed all signals in its expected ranges similar to those reported in the literature and using a solvent (DMSO-d6). The ligand (2H-4Cl-DBAPD) showed a single signal at a chemical shift of δ = 3.37 ppm attributed to the protons of water molecules due to the presence of moisture, and the ligand showed a separate single signal at a chemical shift of δ = 2.29 ppm attributed to the protons of the ($CH_2$) group (104). The ligand showed a single discrete signal at chemical shift δ = 1.24, 1.29 ppm due to the protons of the (CH3) group. The ligand also showed multiple signals at chemical shift δ = (6.39, 8.1) ppm due to the protons of the aromatic benzene rings (105). The ligand showed a single signal at the chemical shift of 8.5 ppm = δ attributed to the proton of the azomethine group (N=CH) (106). The spectrum of the ligand also showed a single, non-sharp signal at the chemical shift of 12 ppm = δ attributed to the proton of the (N-H) group of the imidazole ring (107). as shown in Fig.(2).




**Fig(2): $^{1}$H-NMR spectrum of the ligand (2H-4Cl-DBAPD)**

## Infrared Spectra studies

The IR spectra of the complexes are compared with that of the free ligand to determine the changes that might have taken place during the Complexation [18,25] all data are listed in table (3).

**Table (3) FTIR spectra frequencies for the new azo Schiff base ligand and its Nano metal complexes in $cm^{-1}$**

| Compound | OH | N-H Imid. | C-$H_{Aro}$ | C-$H_{alph}$ | N=C-H Schiff | C=O | C=N Schiff | C=N Endo | N=N | C=C | M-N |
|---|---|---|---|---|---|---|---|---|---|---|---|
| L1: $C_{21}H_{18}ClN_7O_3$ | 3427 | 3390 | 3043 | 2885<br>2833 | ----- | 1705 | 1622 | 1590 | 1440 | 1498 | ----- |
| $[Cu(L1)_2]Cl_2$ | 3471 | 3383 | 3051 | 2981<br>2831 | 3230 | 1707 | 1624 | 1600 | 1388 | 1624<br>1492 | 538<br>495 |
| $[Ag(L1)NO_3]$ | 3475 | 3363 | 3061 | 2885<br>2831 | 3250 | 1693 | 1624 | 1589 | 1382 | 1624<br>1494 | 551<br>511 |

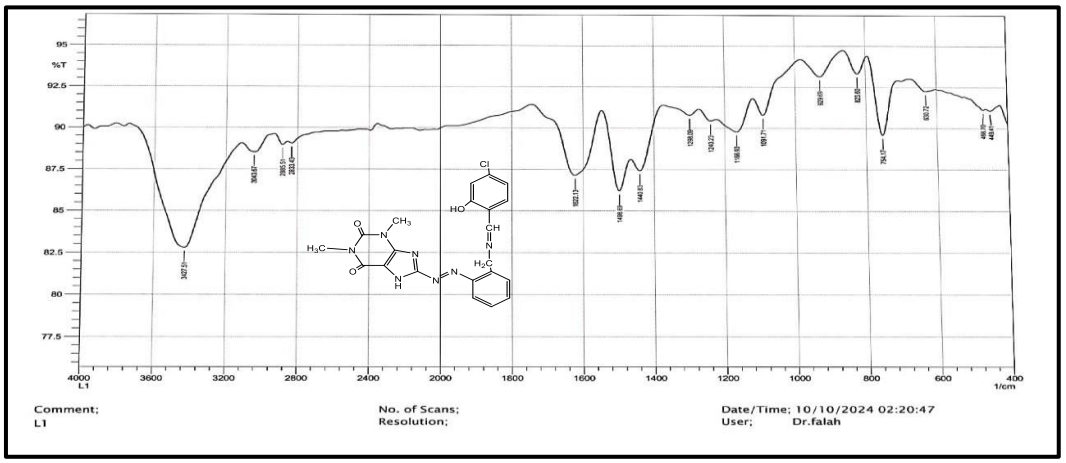



**Fig (3): IR-spectra of the ligand**

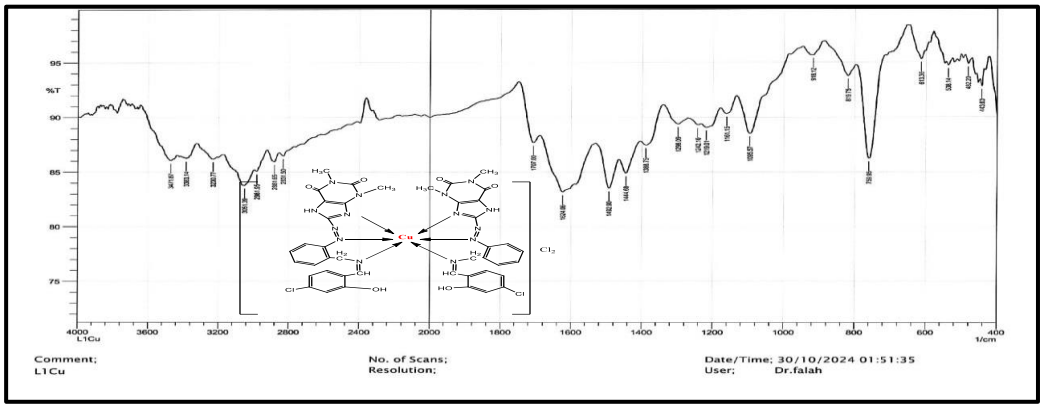



**Fig (4): IR-spectra of Cu (II) complex**

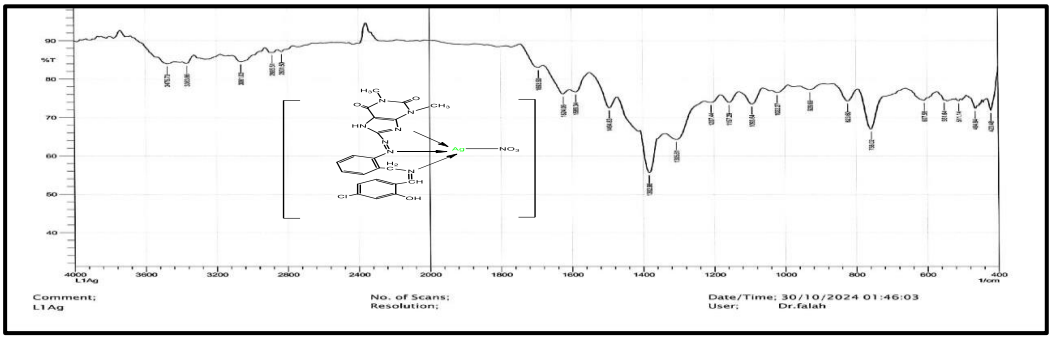



**Fig (5): IR-spectra of Ag(I) complex**

## Magnetic susceptibility:

The results of the magnetic susceptibility measurements are listed in the table (4) where the magnetic moment value of the magnetic moment of Cu(II) Complex reach ( 1.78) B.M , which indicates the presence of the paramagnetic characteristic [25]. As for the complexes of Ag(I), it has shown Di magnetic properties due to Electron cover saturation (nd) in the electrons [26].

## Measurement of molar conductivity:

From the results obtained, it is clear that the molar electrical conductivity measurements for solutions of Chelate complexes of ions under study with the new ligand and with

concentration of ($1\times10^{-3}$) molar per complex at the laboratory temperature and using DMSO as solvent , were listed in table (4), We find the ionic properties of Cu(II) complex only. These results are identical to what was stated in the literature for metallic complexes with ionic properties [26].

**Table (4) Molar conductivity and Magnetic susceptibility values for the Complexes**

| compounds | $\mu_{eff}$ (B.M) | Geometrical | Hybridization | $\Lambda_M$(S.cm$^2$ . mol$^{-1}$) | Solvent | Electrolyte Type |
|---|---|---|---|---|---|---|
| $[Cu(L_1)_2]Cl_2$ | 1.76 | Oh. | $Sp^3d^2$ | 78.41 | DMSO | 1:2 |
| $[Ag(L_1)\ NO_3]$ | Dia | Th. | $Sp^3$ | 6.71 | DMSO | 1:1 |

## Electronic spectra:

The electronic absorption spectra are very useful in the estimation of effects equipped thru out her approaches of structural exploration.

The spectrum of the new ligand (2H-4Cl-DBAPD) in DMSO solvent showed three absorption peaks, two absorption peaks at (276 and 269 nm) were attributed to the ($\pi \rightarrow \pi^*$) electronic transition, while the third peak at (306 nm) was attributed to the ($n \rightarrow \pi^*$) electronic transition; as a result of the ligand having double bonds with atoms that have unshared electron pairs [27].

The spectrum of the ligand (2H-4Cl-DBAPD) was compared with the UV-vis. spectrum of the copper (II) complex solution. An absorption peak at (474nm) was attributed to the internal charge transfer in the ligand (IL.CT) and a broad absorption peak at (734nm) was attributed to the electronic transition $^2Eg \longrightarrow {}^2T_2g$. This is consistent with what was reported in the literature .[20,27]

As for electronic spectrum of the Ag(I) complex with new ligand, it does not possess type (d-d) electronic transmissions because of the fullness of the five (d) orbitals. As new peak appeared in the metal ion complex that was not visible in the ligand spectrum, this indicates the consistency of the metal ion with the new ligand due to the charge transfer (C.T)(41). the spectrum of the free ligand is red-shifted in complexes due to ligand to metal charge transfer (LMCT) transition , suggesting an octahedral geometry around Cu(II)complex and tetrahedral geometry around Ag (I) complex as showed in Fig.(6) ,(7)and (8) and Table (5) Electronic transitions for the new azo Schiff base ligand and its Nano metal complexes in cm$^{-1}$.

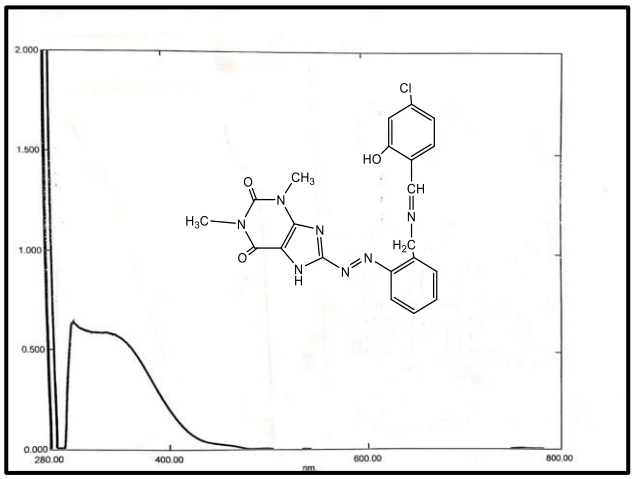


Fig (6): UV-Vis spectra of new Ligand

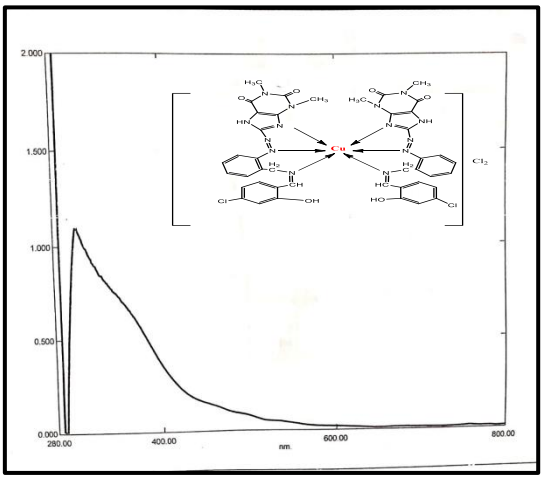


Fig (7): UV-Vis spectra of Cu (II) complex

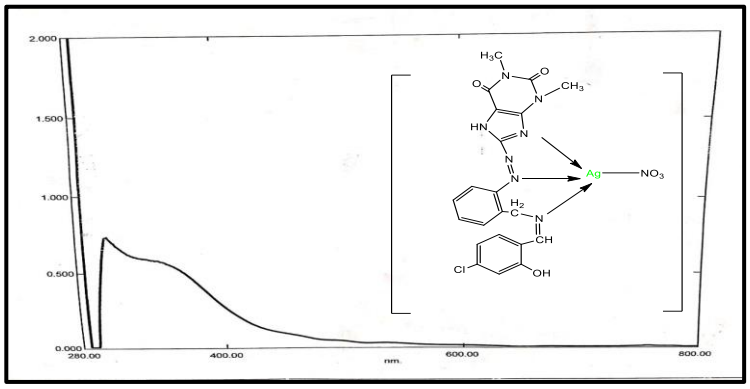


Fig (8): UV-Vis spectra of Ag (I) complex

**Table (5) Electronic transitions for the new azo Schiff base ligand and its Nano metal complexes in $cm^{-1}$**

| Compounds | Λmax (nm) | Transitions | Geometry | Hybridization |
|---|---|---|---|---|
| **L1=$C_{21}H18ClN_7O_3$** | 306<br>276<br>269 | n →π*<br>π →π*<br>π →π* | ---- | ---- |
| **[Cu(L1) $_2$]$Cl_2$** | 474 | IL. CT<br>v3= $^4T1g$ ⟶ $^4T1g(p)$ | Octahedral | $Sp^3d^2$ |
| **[Ag(L1) $NO_3$]** | 534 | ML.CT | Tetrahedral | $Sp^3$ |

## Proposed Structural:

Based on the previously mentioned analytical and spectroscopic measurements of the metal complexes and the diagnosis of the coordination sites available in the organic molecule and how these sites bind to the metal ions, we can conclude that the new azo-azomethine ligand behaves as a neutrally charged Tri chelate ligand with the metal ions selected in this study, as the ligand binds via a nitrogen atom present in the imidazole molecule. And through the nitrogen atom of the azo group that is far from the heterogeneous ring and through the nitrogen atom of the azomethine group, since the connection of the two molecules of the trichelate ligand with the copper ion provides six coordination bonds with the presence of two negatively charged chloride ions outside the coordination sphere to balance the positive charge of the central metal ion to form the octahedral shape. While a single trichelate ligand molecule is bound to an Ag(I) ion providing three coordination bonds with a fourth bond via a negatively charged (mono-negatively charged) chloride ion to exchange the positive charge of the central metal ion. To form the tetrahedral shape so the complex of Ag(I) did not contain the chloride ion outside the coordination sphere.

Figures (9) and (10) show the proposed geometrical shapes of Cu(II) and Ag(I) complexes.

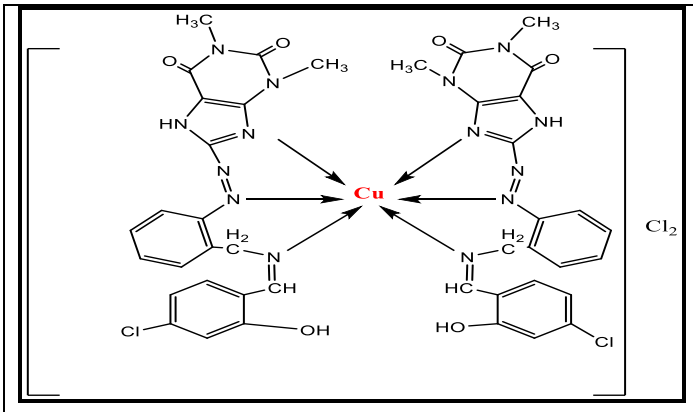



**Fig.(9): Proposed Structural of the Cu(II)complex**

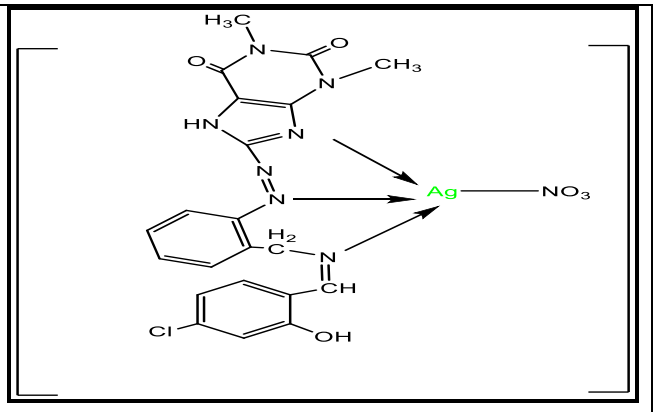



**Fig.(10): Proposed Structural of the Ag(I)complex**

## Field Emission Scanning Electron Microscopy (FESEM) analyses of Cu(II) and Ag(I) Nano-complexes with the new ligand (2H-4Cl-DBAPD).

The surface properties of the nanoparticles of copper (II) and silver (I) complexes with the new azo-Schiff base ligand (2H-4Cl-DBAPD) were studied in terms of the crystalline shape of the particles and aggregates by scanning electron microscopy (SEM) technique with a cross-sectional area of 4.61 mμ and a magnification power of Mag = 30.00 K X and through the FESEM analysis image of the noncomplex of copper

(II) with the ligand. Where it became clear to us that its shape is in the form of homogeneous, needle-shaped, regular crystals, and its average size reached 68.9 nanometers, while the FESEM analysis image of the silver (I) noncomplex appeared in the form of heterogeneous spherical crystals, and the average particle size reached 26 nanometers. As noted from the results obtained through the FESEM images shown in Figure (11) below, it is clear that the two complexes were within the Nano scale range[28,29].

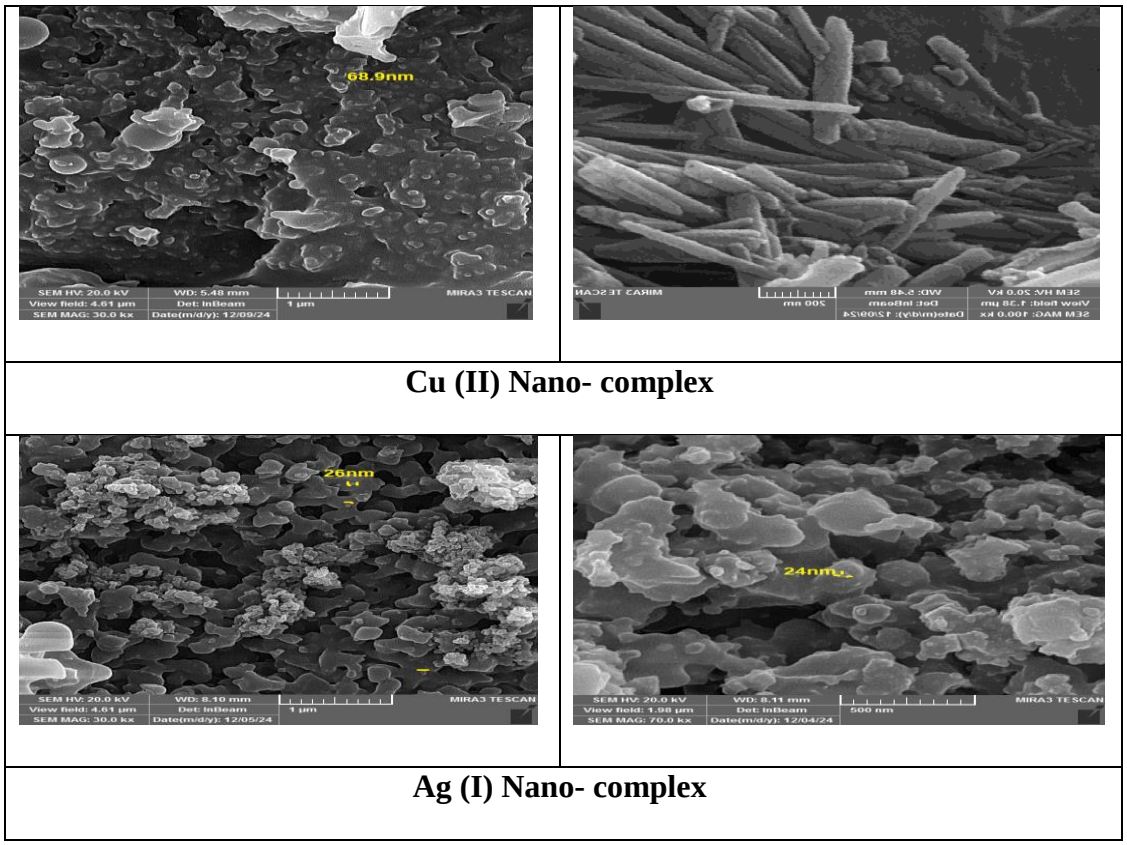



**Figure (11): - FESEM images of copper and silver Nano complexes with the ligand (2H-4Cl -DBAPD))**

## Efficacy of copper and silver Nano complexes as antibacterial against Gram-positive bacteria *Staph. aureus*:

The complex **[Ag(2H-4Cl-DBAPD)Cl ]** showed the greatest inhibitory effect at the highest concentration (1000 ppm) where the inhibition diameter reached (24 mm) and the average diameter for the concentration of (500 ppm) was (22 mm) while the lowest average inhibition diameter was recorded for the concentration of (100 ppm) which reached (18 mm). As for the complex **$[Cu\ (2H\text{-}4Cl\text{-}DBAPD)_2]Cl_2$**, its inhibition diameter reached (20mm) for a concentration of (1000 ppm), and the average diameter for a concentration of (500 ppm) was (18mm), while the lowest average inhibition diameter was recorded for a concentration of (100 ppm), which reached (12mm).

## Efficacy of copper and silver Nano complexes as antibacterial agents against Gram-negative bacteria E.coli:

The complex **[Ag (2H-4Cl-DBAPD)Cl ]** showed the greatest inhibitory effect at the highest concentration of (1000 ppm) as its inhibition diameter reached (22 mm), while at a concentration of (500 ppm) a difference in the rate of the complex inhibition diameter was observed as it was (20 mm), while the lowest rate of the inhibition diameter was recorded for the concentrations of (100 ppm) which reached (16 mm). As for the complex **[Cu (2H-4Cl-DBAPD)$_2$]Cl$_2$**, it showed the greatest inhibitory effect at the highest concentration of (1000 ppm) as its inhibition diameter reached (18 mm), while at a concentration of (500 ppm) it recorded a diameter of (16) mm, while the lowest rate of the inhibition diameter was recorded for the concentrations of (100 ppm) which reached (11 mm).

It can be said that the metal Nano complexes at a concentration of (1000) ppm can act as strong antibiotics that have the same effect on other types of bacteria that have not been tested. The Nano complexes under study may not show a similar effect in the living body, despite the sensitivity of bacteria to them, as what happens in the living body sometimes differs from the picture we observe on plates because the therapeutic process usually goes through a series of complex metabolic and physiological reactions[28].

The highest results were from Gram+ positive bacteria , while Gram-negative bacteria that recorded a lower success rate of distillation lines for all nodes and in all tracers[29]. The reason for this is due to the presence of a double generation in each bacterial cell wall. Gram-negative bacteria are characterized by having an integrated membrane for editing that consists of two experiences. Two layers, one of which is made of protein fats and the other of fats combined with polysaccharides. This makes the negative bacterial cell have a unique cell wall that excludes the antibiotic or the therapeutic chemical from penetrating the bacterial cell. As for the Gram-positive bacteria, their cell wall consists of a thick layer of Mucopeptides composed of amino acids with monosaccharides, so they are less resistant to drugs and antibiotics[29]. The behavior of the metal nanocomplexes is explained by the lipophilic nature of these metal complexes, and chelation will facilitate the process of crossing the cell membrane of the complexes [31]. It is also shown that the complexes have antimicrobial activity that can inhibit these microorganisms and stop their growth by blocking their active sites [32,33]. as listed in Table (6) Inhibition zones of Nano complexes with ligand at a concentration of (1000,500,100) ppm for the bacteria under study.

**Table (6) Inhibition zones of Nano complexes with ligand at a concentration of (1000,500,100) ppm for the bacteria under study.**

| Compound / Bacteria | (+) G *Staph.aureus* | (-) G *E.coli* |
|---|---|---|
| | At 1000 ppm | |
| **[Cu(L$_1$)$_2$]Cl$_2$** | 20 | 18 |
| **[Ag (L$_1$)Cl]** | 24 | 22 |

| | At 500 ppm | |
|---|---|---|
| $[Cu(L_1)_2]Cl_2$ | 18 | 16 |
| $[Ag\ (L_1)Cl]$ | 22 | 20 |
| | **At 100 ppm** | |
| $[Cu(L_1)_2]Cl_2$ | 12 | 11 |
| $[Ag\ (L_1)Cl]$ | 18 | 16 |

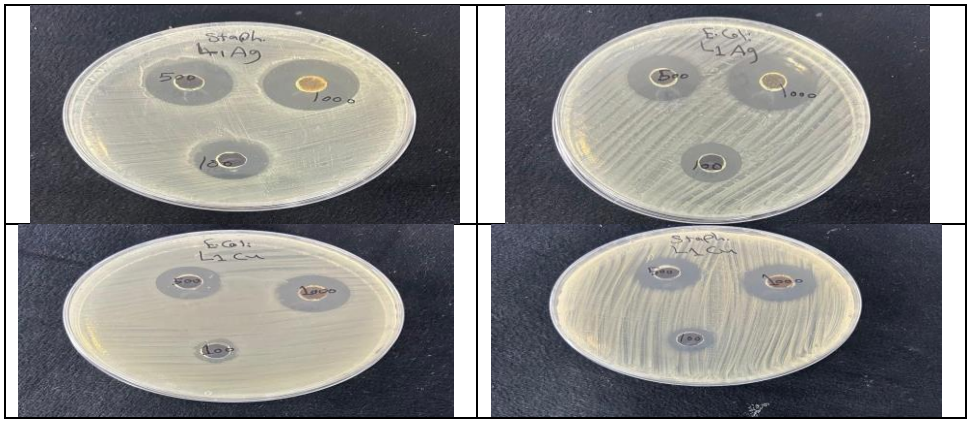


**Figure (12) Biological activity of copper (II) and silver (I) Nano complexes against Gram- and Gram+bacteria.**

## References


[1] Chen, Y., Bagnall, D. M., Koh, H. J., Park, K. T., Hiraga, K., Zhu, Z., & Yao, T. (1998). Plasma assisted molecular beam epitaxy of ZnO on c-plane sapphire: Growth and characterization. Journal of Applied Physics, 84(7), 3912-3918.

[2] Abdelbaky A. S., Mohamed A. M., Sharaky M., Mohamed N. A., and Diab Y. M., (2023) Green approach for the synthesis of ZnO nanoparticles using Cymbopogon citratus aqueous leaf extract: characterization and evaluation of their biological activities, Chemical and Biological Technologies in Agriculture., 10(1), 63

[3]. Sathiyapriya, R., Hariharan, V., Prabakaran, K., Durairaj, M., & Aroulmoji, V. (2019). Nanotechnology in materials and medical sciences. *International journal of advanced Science and Engineering*

[4] Yadav, B. C., & Kumar, R. (2008). Structure, properties and applications of fullerenes. International Journal of Nanotechnology and Applications, 2(1), 15-24.

[5] Hadi, F. H., & Jamel, H. O. (2025). Preparation and characterization of a new ligand derived from the compounds 2-hydrazinobenzothiazole and 2-amino-6-methoxy benzothiazole and its complexes with some metal ions, evaluating its antibacterial activity, and studying its nanoscale properties. Journal of Kufa for Chemical Sciences, 4(1), 133-152.

[6] Maryam Methaq Najm, & Hanan Faleh Mohsein. (2024). Synthesis, Antibacterial Evaluation and Study Molecular Docking of New derivatives from sulfapyridine. *Journal of Kufa for Chemical Sciences*, *3*(3), 134-149.

[7] Sadeek, S. A., El-Shwiniy, W. H., Zordok, W. A., and El-Didamony, A. M. (2011). Spectroscopic, structure and antimicrobial activity of new Y(III) and Zr (IV) ciprofloxacin. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy,78(2),854-867.

[8] Imran, M., Iqbal, J., Iqbal, S., and Ijaz, N. (2007). In vitro antibacterial studies of ciprofloxacin-imines and their complexes with Cu (II), Ni (II), Co (II), and Zn (II). Turkish journal of biology, 31(2), 67-72.

[9] Abebe, A., & Hailemariam, T. (2016). Synthesis and assessment of antibacterial activities of ruthenium (III) mixed ligand complexes containing 1, 10-phenanthroline and guanide. Bioinorganic chemistry and applications.

[10] [Oforka. N.C. and Mkpenie V.N. "A new method of synthesis of azo Schiff base ligands with azo and azomethine donors: Synthesis of N-4-methoxy-benzylidene-2- (3-hydroxyphenylazo)-8-hydroxyaniline and its nickel (II) complex". Chin. J. Chem., 28, 561–511. 2111 .

[11] Layla. A. M., Muna. A. H., and allham. A. m., "Preparation and Characterization of Some Metal Ions Complexes with Heterocyclic Azo Ligand (Bbai)", Journal of kerbala university, 11,.3. 2012.

[12] Kapil B and Shipra B., "Acoustical Studies of Some Derivatives of Azomethines in Methanol and N, N-Dimethyl form amide at 313318 K", Physics and Materials Chemistry, 1, 1, 1- 4, 2013 .

[13] Sudhir K.P, Ghosh .G, Rout S. K. and Paul D, "Synthisis and antimicrobial Evalution of Some novel 4-hydroxy coumarin derivatives bearing azomoity", RJC, 6, 2, 141-182, 2113..

[14] Debnath, T. et al. (2022). "Molecular docking studies and in vitro evaluation of novel azo-bridged Schiff bases as potential anticancer agents." Journal of Molecular Structure, 1252, 133538.

[15] Hamdy, N. A. et al. (2021). "Synthesis, characterization, anticancer activity, and molecular docking studies of novel azo compounds derived from chloroquine as dual inhibitors of HDAC and topoisomerase II enzymes." Journal of Molecular Structure, 1240, 130672

[16] Ghoneim, A. I. et al. (2022). "Synthesis, biological evaluation, and molecular docking studies of some novel azo compounds containing piperazine moiety as potential anticancer agents." Research on Chemical Intermediates, 48(2), 1413-1429.

[17] El-Shehawy, A. A. et al. (2021). "Synthesis, anticancer evaluation, and molecular docking studies of novel azo compounds derived from phenothiazine." Journal of Molecular Structure, 1240, 130634.

[18] Rham Najeh Kurdy, & Ibtihal Kadhim Kareem. (2024). Synthesis, Characterization and study of molecular docking of a new Azo-Schiff base ligand with its metal complexes. *Journal of Kufa for Chemical Sciences*, *3*(3), 68-85.

[19] Muna Abass Hadi, Ibtihal Kadhim Kareem and Ammar Kshash Atban,[2021]: Synthesis And Characterization Of Novel Metal Complexes With New Schiff Base Ligand Derived From 6-Amino Pencillic Acid And Toxicological Studies Of Its Complex With Au(Iii) On Human Cells For Colon Cancer Ls-174, Biochem. Cell. Arch. Vol. 21, Supplement 1, pp. 2477-2488.

[20] Siham Sami Noor and Ibtihal Kadhim Kareem.(2024): Exploring the Anticancer Activity of Gold Complex with Newly Ligand (DDIBM): Synthesis, Spectral Identification and Magnetic Susceptibility of Its Metallic Complexes, Indones. J. Chem., 2024, 24 (3), 822 - 834

[21] Abdalla M. Khedr [a], Ayman A. Gouda [b], Hoda A. El-Ghamry ,(2022), Nano-synthesis approach, elaborated spectral, biological activity and in silico assessment of novel nano-metal complexes based on sulfamerazine azo dye Journal of Molecular Liquids,Volume 352, 15 April 2022, 118737.

[22] Kaushal Kumar , SatyeshRaj Anand , Mithun Kori , Neha Mishra , S.P. Shrivastava ,(2023): A study on the synthesis and characterization of Schiff base stabilized silver nanoparticles against propionic bacteria, Journal of the Indian Chemical Society,Volume 100, Issue 4, 100965.

[23] Ali, A.M.and Hassani,Z.R. 2020, Preparation and Characterization of New Azo Ligand and Some of Its Chelate Complexes ,J. of Kufa for Chem. Sci. ,2 (6) ,13-23.

[24] Mbarkia,F. and Ammari,F. ,2021, Chemical Modification Of Commercial And Recovered Poly(Vinyl Chloride) With Amino Groups - Adsorption Of Heavy Metals (Cr(III), Pb(II), Cd(II), Or Co(II)) By Modified Pvc Polymers ,J. Mar. Chim. Heterocycl., 20(2), 80-94.

[25] Siham Sami Noor, & Ibtihal Kadhim Kareem. (2024). A bio scientific study of the new gold complex as an anti-breast cancer agent, as well as its preparation , Molar Conductivity and Spectral identification of some other metal complexes. Journal of Kufa for Chemical Sciences, 3(3), 201-222.

[26] Mohammed,L.A., Hadi, M.A. and Basim,N. A.,2020, Preparation and Characterization of some Complexes with New (Azo-Schiff base) Ligand and Study of Complex as Anticancer Indian Journal of Forensic Medicine & Toxicology, Vol. 14, No. 2.,1298-1305.

[27] Nassar, M. Y., Ahmed, I. S., Dessouki, H. A., and Ali, S. S. ,2018, Synthesis and characterization of some Schiff base complexes derived from 2, 5-dihydroxyacetophenone with transition metal ions and their biological activity. Journal of Basic and Environmental Sciences, 5, 60-71.

[28] El-Sonbati, A. Z., et al. "Geometrical structures, thermal stability and antimicrobial activity of Schiff base supramolecular and its metal complexes." Journal of Molecular Liquids 215 (2016): 423-442.

[29] Afanou KA, Straumfors A, Skogstad A, Skaar I, Hjeljord L, Skare Ø, et al. Profile and morphology of fungal aerosols characterized by field emission scanning electron microscopy (FESEM). Aerosol Science and Technology. 2015;49(6):423-35.

[30] Joseyphus, R. S., and Nair, M. S. (2008). Antibacterial and antifungal studies on some schiff base complexes of zinc (II). Mycobiology, 36(2), 93-98.

[31] Tweedy, B. G. (1964). Plant extracts with metal ions as potential antimicrobial agents. Phytopathology, 55, 910-914.

[32] Raman, N., Joseph, J., Senthil, A., Kumara, V., Pothiraj, V., (2006). Antifungal Activities of Biorelevant Complexes of Copper(II) with biosensitive macrocyclic ligands. Mycobiology, 34 (4): 214-218.

[33] La, M., Wang, P. P., and Xue, L. W. (2020). Syntheses, characterization, crystal structures, and antimicrobial activity of oxidovanadium (V) complexes with hydrazone and pyrone ligands. Inorganic and Nano-Metal Chemistry, 50(3), 151-155.