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# Synthesis, Characterization and Evaluation of fungal Activity of Copper(II) and Cobalt(II) Complexes with Imine Glutaraldehyde Derivatives.

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**Abstract.** Two metal complexes have been prepared throughout the reaction of copper(II) and cobalt(II) salts with the bidentate Schiff base synthesized from the reaction of two moles of *o*-toluidine and one mole of glutaraldehyde. These metal complexes have been characterized using physico-chemical techniques such as <sup>1</sup>H-NMR, FTIR, Atomic Absorption A.A, CHN, UV-Vis spectra, magnetic susceptibility and conductivity measurements. The obtained results showed good agreement with theoretical data and the geometry of both metal complexes was octagonal geometry. The biological activity have been tested using two types of fungus *Aspergillus niger* and *Aspergillus parasiticus*. Both metal complexes showed good activity against these two types of fungus. Furthermore, antifungal activity of the synthesized metal complexes was better than antifungal drugs, Nystatin and Griseofulvin, which are used to treat both types of fungus.

## 1. Introduction

Imine compounds played an important role in the development of coordination chemistry, because they contain azomethine group (-C=N-) which is considered as an important class of compounds due to their ability to form a series of stable complexes with ionic metal in general and with transition metal in particular[1] which were applied in many applications such as biological, medical and environmental sciences[2,3]. Furthermore, the Schiff-base ligands are a very important compounds for synthesizing inorganic compounds as they are widely used to design compounds and test their biological modelling applications[4]. These metal complexes showed significant activity against many types of germs, fungus and bacteria. These ligands were also used to remove mercury and cesium from natural water. Nickel(II) complexes with substituted benzylidene benzoic acid were synthesized by Gouin Aqvaig and his colleagues showed efficient biological activity against many types of bacteria, fungus and cancer cells[5-7]. In the recent research, we have been synthesized and characterised novel imine glutaraldehyde compounds and their metal complexes with Co(II) and Cu(II) ions. In addition, biological experiments using two types of fungus were also carried out and compared with two types of anti-fungus drug which are commercially available.

## 2. Material and Methods

### 2.1. Materials

All reagents were commercially available and used without further purification.

### 2.2. Instruments



Melting points were obtained on a DMP-500 capillary melting point apparatus and are uncorrected. IR spectra were recorded as KBr discs using a Bruker FT spectrophotometer. Metals were determined using a EA 300, Euro Vector Shimadzu (A.A) 620 atomic absorption spectrophotometer. Conductivity measurements were made with DMSO solutions using a BC3020 Professional Bench top conductivity meter. Using Euro Vector 3000, the elemental analysis (C, H, N, and S) for the compounds were obtained. Finally, the electronic spectra is measured by using a Shimadzu UV-Visible 160A Spectrophotometer by dissolving synthesised compounds in DMSO at concentration of ( $10^{-3}$  M).

### 2.3. Synthesis

#### 2.3.1 Imine Compound

Imine Schiff base have been synthesized using the well known procedure[7]. Before the preparation process, glutaraldehyde was extracted using dichloromethane as a solvent from its aqueous solution using separatory funnel. In a 50 ml round flask with (0.25 g, 2.49 mmole) from Glutaraldehyde dissolved in (20 ml) 95% ethanol acidified with hydrogen bromide. Then, (0.53 g, 4.99 mmole) of ortho-toluidine was dissolved in (25ml) of 95% ethanol and added slowly to the mixture. The mixture was refluxed for 4 hours and the solution was left overnight for cooling in room temperature. The yielded precipitate was filtered using filter paper and washed with the cooled absolute ethanol(5 ml), left to dry and then it was recrystallized from the solvent. Dark red precipitate was collected ( yield 79%, melting point 140-142°C). Exact Mass m/e: 278.18 and Elemental Analysis: C, 81.97; H, 7.97; N, 10.06

#### 2.3.2 Metals Complexes

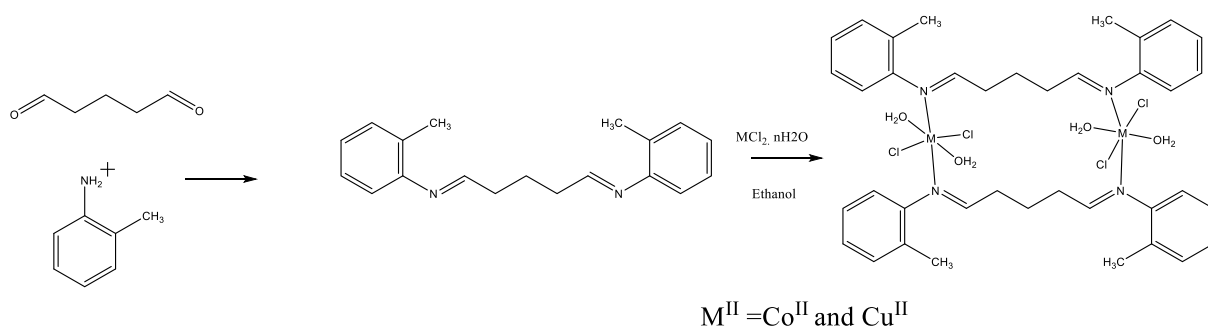
(0.06 g, 0.25mmole) of cobalt (II) chloride hexahydrate dissolved in absolute ethanol was added gradually to a warm mixture of (0.15 g, 0.53mmole) of the synthesized ligand which was dissolved in absolute ethanol (10 ml), reaction mixture was allowed to reflux for 2 hours, and the yielded crude precipitate was filtered off, left overnight to evaporate the solvent slowly at room temperature. Dark green precipitate was formed as a powder and filtered (yield 93.33%, melting point 208-210°C). Molecular weight m/z: 888.52

Elemental Analysis: C, 50.84; H, 5.84; N, 6.24; and the Atomic absorption for Co Ione due to 14.16 in Co-complex

Same procedure was used copper(II) complex by adding (0.04 g, 0.16 mmole) of ( $\text{CuCl}_2 \cdot 6\text{H}_2\text{O}$ ) to give dark purple powder (yield 94.4%, melting point 333-335°C). Molecular weight m/z: 897.75, Elemental Analysis: C, 51.37; H, 5.90; N, 6.31, and the Atomic absorption for Cu ion due to 13.27 in Cu-complex.

## 3. Results and discussion

The imine ligand was prepared by the reaction of the extracted Glutaraldehyde from water solution with orthotoluidine. Then the resulting organic ligand was coordinate to Co (II) and Cu (II) to give hexagonal complexes as shown in scheme (1):

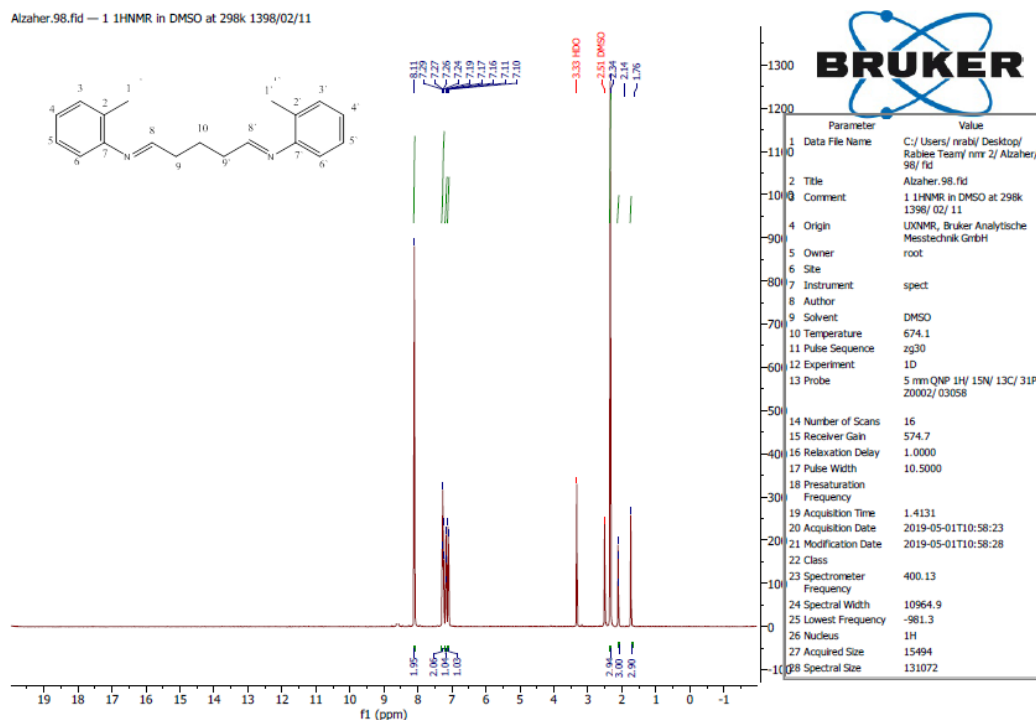


**Scheme1:** synthesis of glutaraldehyde with o-toluidine to yield Schiff base and its cobalt(II) and copper(II) complexes

The prepared compounds were analyzed by spectroscopic techniques to demonstrate the identification of compounds and studying their characteristics.

### 3.1 <sup>1</sup>H-NMR for organic ligand (di-o-tolylpentane-1,5-dimine)

The <sup>1</sup>H-NMR spectrum for [Schiff base (L)] scheme (1), displays chemical shift at  $\delta = 1.76$  ppm (2H, p, JHH=7.33Hz) assigned to (C<sub>10</sub>-H). The signal at  $\delta = 2.14$  ppm (4H, m) assigned to (C<sub>9</sub>, 9'-H) protons, the chemical shift at 2.34 ppm (6H, S,) assigned to (C<sub>1,1'</sub>-CH<sub>3</sub> groupe) the chemical shift at  $\delta = 7.10$ - 8.11 ppm (8H, m) attributed to (C<sub>3&3'</sub>, C<sub>4&4'</sub>, C<sub>5,5'</sub>, C<sub>6&6'</sub>-H) due to Aromatic protons. The spectrum displays chemical shift at  $\delta = 8.61$  ppm (2H, t, JHH=7.34 Hz) assigned to (C<sub>8&8'</sub>-H) imine protons.



**Fig. 1.** <sup>1</sup>H NMR spectra of Schiff base.

3.2 The electronic spectra of the ligand and its metal complexes:

The prepared ligand and its metal complexes was characterized by the UV-Vis spectroscopy using (DMSO) as a solvent and a reference as explained in figures (2-4), It became clear that the UV spectrum for the Ligand has shown absorption at (313nm) which belongs to (n-π\*) and (291, 275nm) to (π-π\*). As for the prepared complexes, the ultraviolet spectrum showed absorption bands ranging from (300-370 nm) And these bands are due to the charge transfer of a type (M-L) between the metal and the ligand which confirm the complexes formation. The d-d transitions of copper ions at 750 nm are belonging to  $^2B_{1g} \rightarrow ^2A_{1g}$ . While the cobalt ions exected band at 660 nm are belonging to  $^4T_{1g} \rightarrow ^4T_{2g}$  which confirms the formation of the distorted octahedral structure around the central atoms [14,15]. These suggested was agreement with the magnetic susceptibility and conductivityt measurements as shown bellow

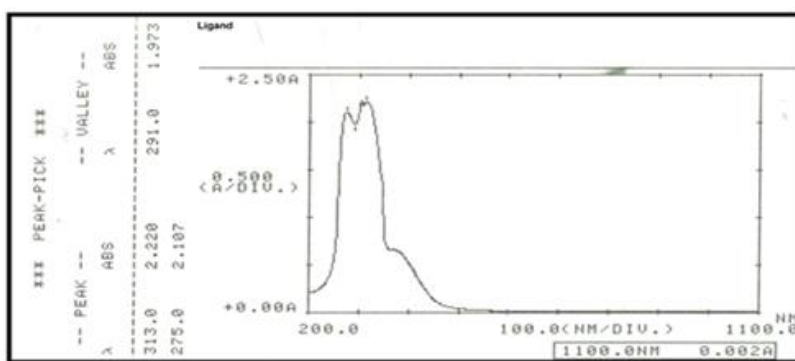


Fig. 2. UV-Vis spectra of ligand (Schiff base).

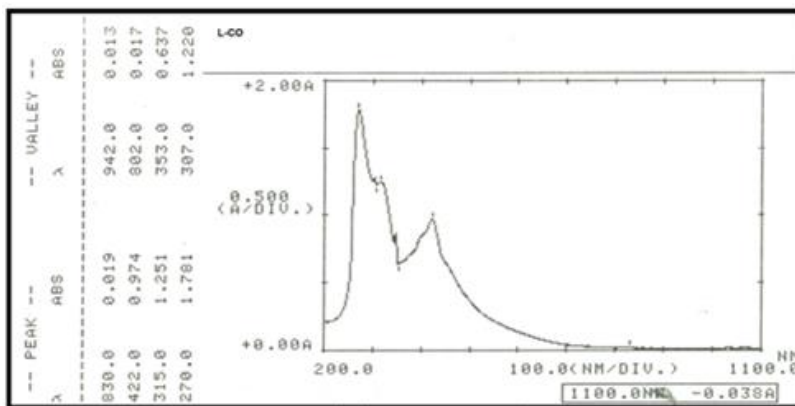
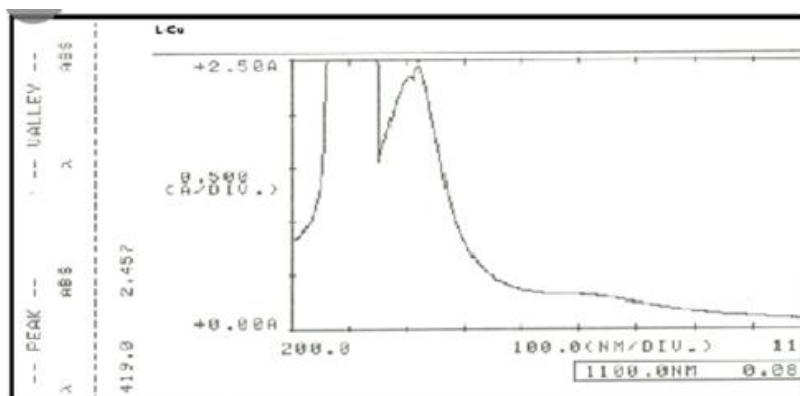


Fig. 3. UV-Vis spectra of cobalt(II) complex.



**Fig. 4.** UV-Vis spectra of copper(II) complex.

### 3.3. Infrared spectrum (FTIR) mm

#### 3.3.1 Infrared radiation spectrum for ligand (imine compound)

Ligand infrared spectrum (IR) was described depending on available information in literature review about the molecules of the ligand. Besides, the absorption bands of the free ligand were characterized, also It was noticed changing in shape, intensity and location when the ligand coordinate with the metallic ions to form the complexes.

Table (1) and Fig. (5 and 6) represent the location of the absorption of the prepared Schiff base, in fact it has a special absorption bands at the infrared spectra within the range (1580-1637 $\text{cm}^{-1}$ ) due to the stretching vibration of (C=N) bond[8]. Also, it has a band within the range of (1482-1525 $\text{cm}^{-1}$ ) due to the stretching vibration of (C=C) bond[9] which belongs to the aromatic rings. It was found that the prepared Schiff base also has a band at (3006- $\text{cm}^{-1}$ ) which belongs to the vibration of aromatic (C-H) group[10]. IR contains a band at (2857-2931 $\text{cm}^{-1}$ )[11] which belongs to the stretching vibration of the non-aromatic (C-H) group,

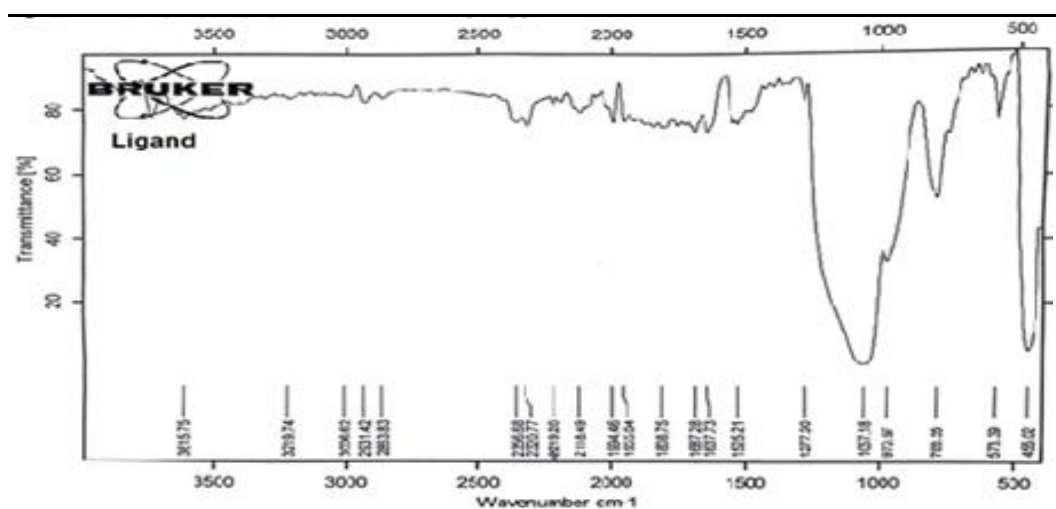
#### 3.3.2 Infrared spectra of the synthesized complexes

Table (1) and the Fig. (5-7) illustrate the most important bands positions of the prepared Schiff base complexes. FTIR has been distinguished by getting displacement in the spectral range for each band which was prominent in spectral Schiff base that complexes had prepared from. where as the appearance of bands from 3213 to 3235  $\text{cm}^{-1}$  [12,13] which refers to the water molecules existence.

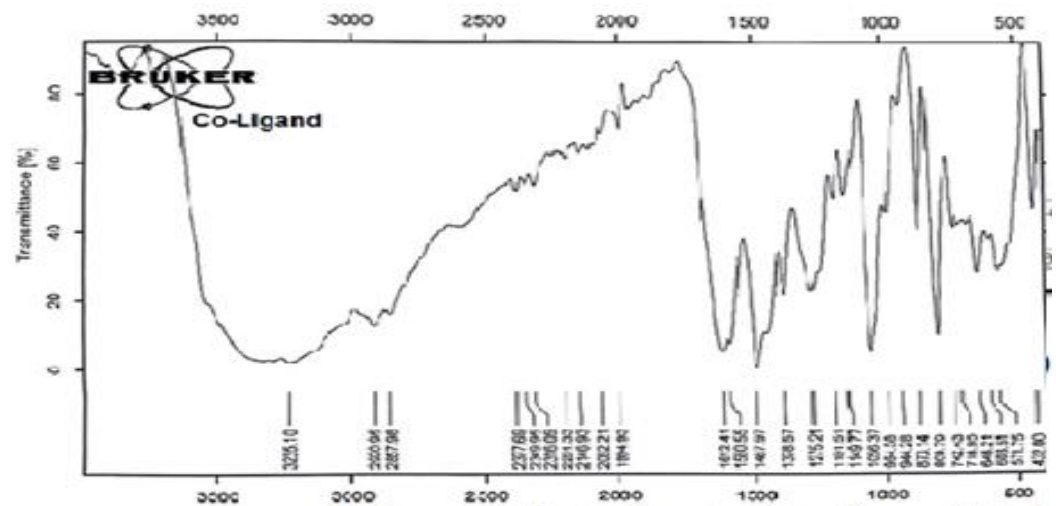
The stretching vibration of (C=N) group <sup>(6)</sup> shows displacement from the range (1687 and 1637 $\text{cm}^{-1}$ ) to (1612 and 1580 $\text{cm}^{-1}$ ), (1599 $\text{cm}^{-1}$ ) for copper and cobalt complexes in sequence, which means that the range was reduced. The spectrum of the prepared complexes has been distinguished by the appearance of the new bands that has not been exist in the ligand spectrum. These bands belong to the stretching vibration of (M-N), (M-OH<sub>2</sub>). These bands appeared in the location (514-751 $\text{cm}^{-1}$ ) and (432-444 $\text{cm}^{-1}$ ) which belong to stretching vibration of (Co-N) and (Cu-N) sequentially and this confirms the complex formation, the reason behind the appearance of these bands in low frequency zone is related to the heavy mass of the central atom [12,13].

**Table 1.** FTIR bands for the ligand and its complexes

Compound	$\nu(\text{H}_2\text{O})$	$\nu(\text{C}=\text{N})$	$\nu(\text{C}=\text{C})$	C- $\nu(\text{H})$ Ar	C- $\nu(\text{H})$ Alph	M- $\nu(\text{N})$	M- $\nu(\text{OH}_2)$
Ligand	-----	1637 1637	1525	3006	2931 2863	-----	-----
$[\text{Co}_2(\text{L})(\text{H}_2\text{O})_2\text{Cl}_2]$	3235	1580	1487	3050	2920 2857	571	<b>432</b>
$[\text{Cu}_2(\text{L})(\text{H}_2\text{O})_2\text{Cl}_2]$	3213	1599	1482	3045	2923	571	<b>444</b>



**Fig. 5.** FTIR spectrum of ligand (Schiff base).



**Fig. 6.** FTIR spectrum of cobalt(II) complex.

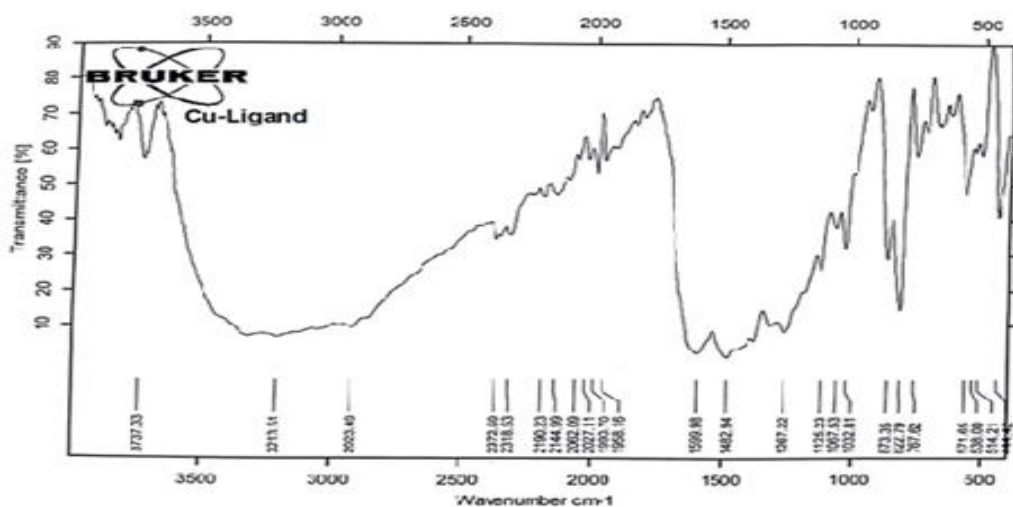


Fig. 7. FTIR spectrum of copper(II) complex.

### 3.4. Molar Conductivity

Molar conductivity was measured for the prepared complexes solution in (DMSO) as a solvent at the concentration of  $10^{-3}$  M at 25°C in order to determine the non electrolyte property. It has been shown from the measurements of the molar electrical conductivity that the cobalt(II) complex has a molar conductivity of  $7.00 \text{ S.cm}^2.\text{mol}^{-1}$  and for copper(II) complex  $15.00 \text{ S.cm}^2.\text{mol}^{-1}$  which means that the complexes charged with a ratio of (1:1) if it compared to the standard tables for solvent conductivity (DMSO).

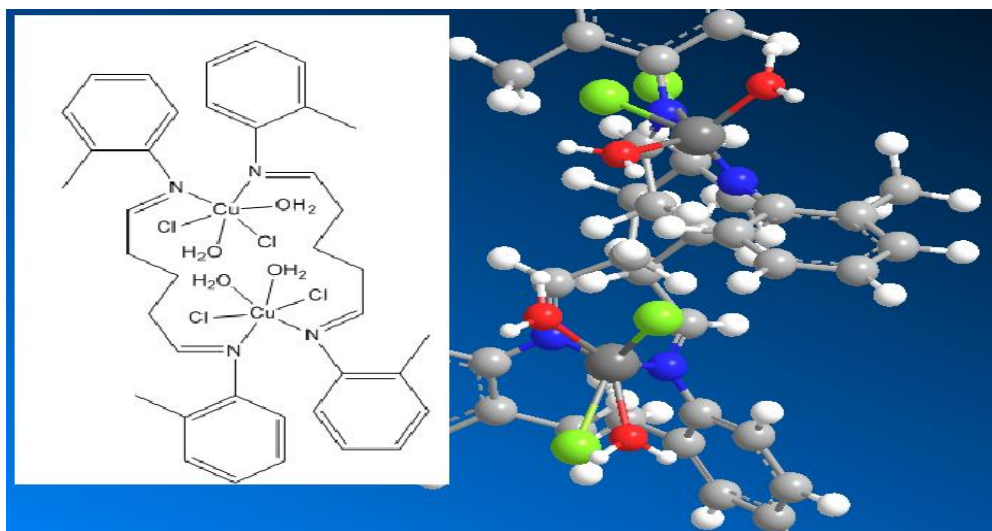
### 3.5. Magnetic susceptibility

the magnetic susceptibility is important technique because it is described and fixe the number of unber electron in external Schell. The measurement obtains duplication magnetic moment value for ( $\text{Co}^{\text{II}}$  and  $\text{Cu}^{\text{II}}$ ) ions (10.55 B.M and 3.4 B.M) respctifilly, that is indicated to the molecules are binuclear [16] and paramagnetic (high spin) look table (2).

Table 2. Magnetic susceptibility for Co(II) and Cu(II) complexes.

Compound	M.wt/m/z	$6 \cdot 10^4 \cdot X_g$	$X_p$	$\mu = 2.83(X_p T)^{1/2}$	$\mu(\text{B.M}) / 2$
$[\text{Co}_2(\text{L})(\text{H}_2\text{O})_2\text{Cl}_2]$	888.52	1.8511	0.051	10.55	5.275
$[\text{Cu}_2(\text{L})(\text{H}_2\text{O})_2\text{Cl}_2]$	897.75	0.9326	0.005	3.45	1.725



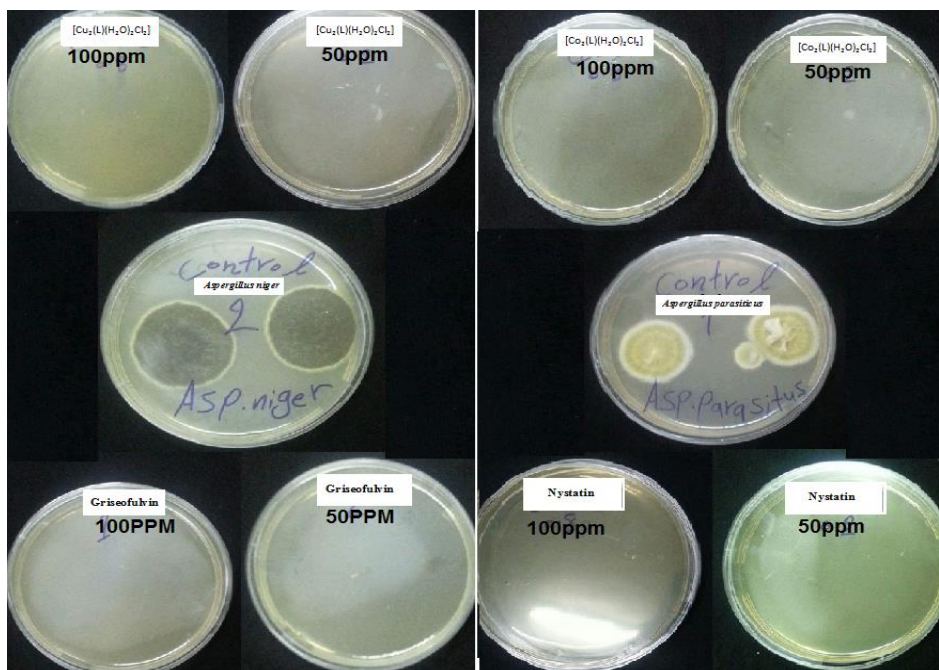


**Fig. 8.** Octahedral geometry for complexes

3.6. Evaluation of biological activity of complexes

The main aim of production of any antimicrobial compound is to fight against microbes without affecting the patients and the antimicrobial factors works in selective mode on the function of the important microbes without any effects on the other functions[17,18].

In this research, there was a use of the spread of Agar to test the prepared complexes against two types of fungus and these two types were tested because of its importance in the medial field [19].



**Fig. 9.** The effect of complexes on two type fungicides with two concentrations

**Table 3.** Dimeter fungi growth compared with control dimeter

Compound	Concentration	<i>Aspergillus niger</i>	<i>Aspergillus parasiticus</i>
		Control = 45 mm	Control = 43 mm
[Co <sub>2</sub> (L)(H <sub>2</sub> O) <sub>2</sub> Cl <sub>2</sub> ]	50	--	--
	200	--	--
[Cu <sub>2</sub> (L)(H <sub>2</sub> O) <sub>2</sub> Cl <sub>2</sub> ]	50	--	--
	200	--	--

-- nongrowth

**Table 4.** The activity of commercial drag (Nystatin and Griseofulvin) on the same fungus

Comp	Names of Standard drugs	Conc	<i>Aspergillus niger</i>	<i>Aspergillus parasiticus</i>
1	Nystatin	50	10	17
		200	5	10
2	Griseofulvin	50	5	26
		200	2.5	10

#### 4. Conclusion

Through the previous phesco- chemical techniques 1H-NMR, FTIR, AA, CHNM, UV-Vis, Magnetic moments, and conductivity measurement. From these processes we can suggest molecular formula and molecular structure shape hexa coordination (Octahedral) look Fig. (8). On the other side the effective antimicrobial compound to fight against microbes is very good when we compare with the some drugs mentioned in berodic (3&4)

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