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Synthesis, Characterization and Antimicrobial Activities of Mixed Ligand Complexes of Fe (II), Co(II), Ni(II) and Cu (II) Ions Derived from Imine of Benzidine and *o*-phenylenediammine

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Abstract

Binuclear metal complexes of the metal ions Fe (II), Co (II), Ni (II) and Cu (II) were synthesized by the reaction of these metal ions with the imine of benzidine (H2L) as a primary ligand and o-phenylenediammine (OPD) as a secondary ligand in a molar ratio of 2:2:1. The prepared complexes were characterized using CHN elemental analysis, FT-IR, UV-visible, molar conductivity, magnetic susceptibility and TGA-DTA thermogravimetric analysis. All the prepared complexes showed apparent stability and could be stored for months without any appreciable change. According to the results obtained by elemental and spectral analyses, a tetrahedral structure is suggested for all the prepared complexes, except for the copper complex which showed a square planar structure. The antimicrobial activities of these complexes were evaluated against Bacillus spp. (Gram-negative bacteria), Proteus spp. (Gram-positive bacteria) and Aspergillus niger (A. niger, a fungal species). The results showed that all the prepared complexes have no apparent effects on Bacillus spp. viability, whereas Proteus spp. and A. niger were affected significantly.

Keywords: binuclear complexes, imine, benzidine, thermogravimetric analysis, antimicrobial activities

تحضير وتشخيص والفعاليات المضادة للميكروبات لمعقدات مختلطة الليكندات للأيونات ((Fe (II) و (Co (II)و Ni (II)) و (Cu (II) المشتقة من إيمين البنزيدين و اورثو فنلين ثنائي الامين)

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الخلاصة

تم تحضير معقدات فلزية ثنائية النواة من أيونات الفلزات Fe (II) و Co (II) و Ni (II) و(Cu (II من تفاعل الأيونات الفلزية المذكورة مع إيمين البنزيدين (H_2L) ليكند أولي وارثو فنلين ثنائي الامين (OPD) كليكند ثانوي بنسبة مولية [2: 1: 2]. شخصت المعقدات المحضرة باستخدام تحليل العناصر CHN و ^{1}H– NMR و FT–IR و الأشعة فوق البنفسجية المرئية و التوصيل المولاري و الحساسية المغناطيسية والتحليل

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الحراري TGA–DTA. أظهرت جميع المعقدات الاستقرار العالي ويمكن تخزينها لعدة أشهر دون أي تغيير ملموس بتركيبها. وفقا للنتائج التي تم الحصول عليها عن طريق التحليل العنصري والتحليل الطيفي، تم اقتراح الشكل الرباعي السطوح لجميع المعقدات المحضرة ما عدا الشكل المربع المستوي لمعقد النحاس. تم تقييم الفعالية المضادة للميكروبات من هذه المعقدات ضد بكتريا *Bacillus spp.* سالبة الجرام وبكتريا *Proteus spp.* موجبة الجرام و فطر Aspergillus niger (A. niger) . أظهرت النتائج أن جميع المعقدات المحضرة ليس لها تأثير واضح على بكتيريا *Bacillus spp.* ، بينما تأثرت ب *Proteus spp.* . و A.niger بشكل كبير.

INTRODUCTION

Transition ion complexes have a broad variety of industrial and technological applications, ranging from those as antibacterial, antifungal and anticancer drugs to those as catalysts [1-5]. In these complexes, the metal atom itself may have a number of roles, based on its oxidation state, coordination geometry, and, magnetic, electronic and photochemical behaviors. Schiff bases are an important class of ligands in coordination chemistry and their complex ability of containing different donor atoms is widely reported [6-8]. Compounds of Schiff bases are a class of organic compounds carrying the azomethine or imine (C=N–) functional group. These are the condensation products of carbonyl compounds with primary amines which were first prepared by Hugo Schiff [9]. Schiff bases form a remarkable class of the most widely used organic compounds and have a wide variety of applications in many fields, including inorganic, biological, and analytical chemistry. Schiff bases have acquired importance in pharmaceutical and medicinal fields due to a wide spectrum of biological activities, including their anti-inflammatory potential [10-12]. The nitrogen atom of azomethine may be responsible for the biological activity, as this atom is implicated in the formation of a hydrogen bond with the active centers of cell constituents and interferes in normal cell processes [13,14]. Schiff base metal complexes have been widely studied because they have industrial, antifungal, antibacterial, anticancer, antiviral and herbicidal applications [15]. Schiff base derivatives in different processes have driven the researchers to design novel aryl/heterocyclic Schiff bases for new environmental-friendly technologies [16]. Dioxomolybdenum (VI) complexes of tetradentate Schiff bases derived from benzidine with salicylaldehyde have been synthesized. These complexes were characterized by elemental analysis, molar conductance, IR, UV-Vis and HNMR spectroscopy, and cyclic voltammetry. The molybdenum(VI) six- coordinated complex of benzidine Schiff bases of binuclear complex, bridging through the azomethine nitrogen and represented as cis-$[Mo_2O_4(L^3)(OCH_3)_2(DMF)_2]$ $[L^3H_2]$ = salicylaldehyde-benzidine (sal-bzH_2), have been synthesized [17]. Mn(II), Co(II), Ni(II), Cu(II), and Hg(II) Schiff base complexes in the formula of $[M_2(L)_2(H_2O)_4]$ have been synthesized. The Schiff base ligand H_2L was prepared by the condensation of salicyladehyde with benzidine. Schiff base ligand and their metal complexes have been characterized by elemental analysis, ,molar conductance, , IR, UV-Vis, ^{1}HNMR,^{13}CNMR spectroscopy and magnetic moment measurements. All the complexes showed tetrahedral geometries. The ligand and its complexes exhibited biological activity against Bacillus (G+ve) and Pseudomonas (G-ve) strains [18]. In this paper, we report the synthesis of Fe (II),Co(II), Ni(II) and Cu (II) complexes by the reaction of these metal ions with the imine of benzidine (H_2L), as a primary ligand, and *o*-phenalinediammine(OPD), as a secondary ligand, in a molar ratio of 2:2:1. In addition, we evaluate the antimicrobial activities of the prepared complexes against pathogenic bacteria and fungi.

MATERIALS AND METHODS

All the chemicals and solvents for the prepared compounds were of analytical grade.

Methanol, ethanol, glacial acetic acid, DMSO, DMF and other solvents were of high purity and supplied by BDH. Benzidine, salicyaldehyde, *o*-penylenediamine and metal salts [$FeCl_2 \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$, and $CuCl_2 \cdot 2H_2O$] were supplied by BDH and Sigma-Aldrich. Elemental analysis (CHN) was performed for the ligand and complexes by EuroEA Elemental Analyzer. Infrared spectra for the ligand and complexes were recorded by Fourier transform-infrared (FT-IR). The measurements were carried out by the KBr method in the frequency range of 4000–400 cm^{-1}using a Shimadzu corporation 8000S FTIR spectrometer. All electronic spectra of the prepared compounds were recorded in the region of 200–1100 nm using ShimadZu Uv-240 Uv–visible recorder spectrometer, with dimethylformamide (DMF) as a solvent in the concentration of 1×10^{-3}M. Magnetic susceptibility measurements for the complexes were carried out at room temperature by utilizing

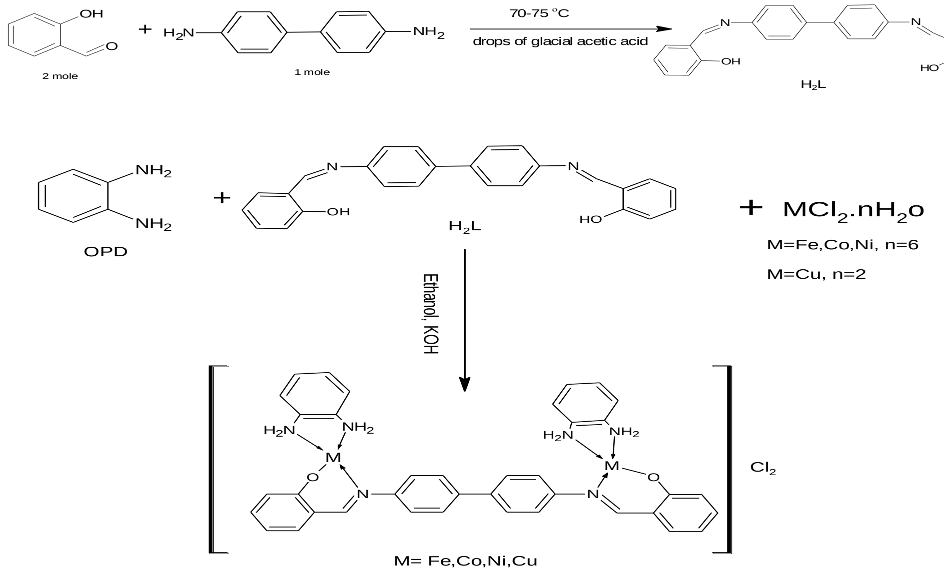
Magnetic Susceptibility Balance-MSBMKI. Molar conductivity was measured using Jen way Ltd-4071 Digital conductivity meter, with DMF as a solvent in the concentration of 3×10^{-3} M. Melting point was measured using Stuart melting point apparatus.

Preparation of Schiff base ligand

The ligand H_2L was prepared according to a previously published procedure [17] from the reaction of 0.032 mol salicyldehyde with 0.016 mol benzidine in 25 mL absolute ethanol, into which 1-2 drops of glacial acetic acid were added. The mixture was refluxed in water bath at 70 ºC for 3 hrs. The reaction was then allowed to cool. A bright yellow precipitate was obtained and then recrystallized by a hot mixture of acetone, ethanol and distilled water. Results of elemental analysis and physical properties for the H_2L ligand and its complexes are listed in Table-1. H_2L was synthesized by the reaction sequence outlined in Scheme (1).

Synthesis of binuclear complexes

In a round bottomed flask, 0.5g of H_2L (0.00058mmol) was added to an ethanol solution of potassium hydroxide and 0.2g of *o*-phenylenediammine (0.00116mmol). Next, a suitable volume of ethanol solution of some metal salts ($FeCl_2.6H_2O$, $NiCl_2.6H_2O$, $CoCl_2.6H_2O$ and $CuCl_2.2H_2O$) was added in a ratio of 1:2:2 (H_2L: *o*-phenylenediammine : Metal salt). The reaction mixture was refluxed with heating at about 60 ºC for 3hrs . The solid product was filtered, washed with ethanol, and dried for 24 h. The steps of the synthesis of these compounds are illustrated in Scheme (1).



Scheme (1): The reaction sequences and the possible structures of prepared complexes. The catalyst, solvent and temperature were shown.

Antimicrobial activity test

In this study, the biological activities of the prepared complexes were tested in DMF, as a solvent, against the growth of *Proteus sp.* and *Bacillus sp*., which represent Gram-negative and positive bacteria, respectively, and the fungi *Aspergillus niger*. The isolates were obtained from the laboratories of Biology Department, College of Science, and University of Kerbala. The isolated microorganisms were first activated by the development of bacteria on the nutrient agar medium and the fungus on the Sabouraud Dextrose Agar (SDA). 250 mg/ L of the antibiotic chloramphenicol was then added to prevent the growth of bacteria [19]. The well diffusion assay was used to determine the antimicrobial activities of the prepared complexes.

To determine the biological activities against the studied bacteria, a stock of the young bacteria (at 24h age) was prepared by transferring a colony to physiological saline solution and controlling its turbidity with the first tube of the 0.5 McFarland standard. Then, the bacterial solution was spread out on Muller Hinton agar in petri dishes, which were left for 15 minute to infuse the medium with bacterial growth. Holes with 6 diameter were then made in the center of each dish by a sterile cork borer and a volume of 0.1 ml of complex solution was added to the cultures using micropipette. in the treated cultures were then incubated at 37 ºC for 24 h., followed by measurement of the growth inhibition zone of the tested bacteria[20]. and the results were compared with those for Ciprofloxacin (CIP) (10mg disc) following the standard method of Bauer *et al.*[21]. The effects of the prepared complexes on the bacterial growth were tested in duplicates.

As for the determination of the biological activities of the complexes against the fungus *A. niger*, the well diffusion assay was also employed [22]. The fungal colony was activated using a sterile needle in a tube containing 5mL of physiological saline solution and shaken well [23]. The solution was left at room temperature for 30 min before being used. Using a sterile glass diffuser, a part of the developing fungal colony was transferred to the center of Sabouraud Dextrose Agar and the dishes were left for 15 min. Holes were made onto the agar medium as described above, then 0.1 ml of each compound was added and the dishes were incubated at 28 ºC for 3 days. The diameter of the growth inhibition zone after treatment with each compound was measured [24] and compared with that caused by the antifungal Clotrimazole (10 mg/mL) [23]. The effects of the prepared complexes on the fungal growth were tested in duplicates.

RESULTS and DISCUSSION

Binuclear complexes were prepared by the reaction of H_2L with *o*-phenylenediammine and metal salts ($FeCl_2.6H_2O$, $NiCl_2.6H_2O$, $CoCl_2.6H_2O$, or $CuCl_2.2H_2O$) added in the ratio of 1:2:2. The complexes were characterized by means of elemental analysis, infrared, UV-Vis spectra ,^{1}H-NMR, magnetic susceptibility and thermal analysis.

Elemental analysis and physical properties of the ligand and binuclear complexes

Table-1 shows the data of element analysis (CHN) of the ligand and its complexes. The results obtained are in good agreement with those calculated for the suggested formula. Some physical features (color and melting points) for H_2L and its complexes are also shown in Table-1, which shows that the complexes have different colors from that of the ligand color, with high melting degrees that indicate a high stability towards air and light.

Table 1-Elemental analysis and physical properties for the ligand H_2L and its complexes

Compound	**Elemental analysis Found(Cal.)%**			**Color**	**M. P. (ºC)**	**Yield %**
	C	**H**	**N**			
H_2L	79.25 (79.57)	5.14 (4.89)	7.14 (6.95)	Bright Yellow	209	75
$[Co_2(OPD)_2(L)]Cl_2$	64.27 (64.79)	5.96 (5.58)	10.79 (10.49)	Brownish orange	296	75
$[Fe_2(OPD)_2(L)]Cl_2$	64.02 (64.28)	5.91 (5.83)	10.71 (10.61)	Dark orange	234	55
$[Ni_2(OPD)_2(L)]Cl_2$	63.99 (64.32)	5.91 (5.56)	10.72 (10.45)	Green	242	79
$[Cu_2(OPD)_2(L)]Cl_2$	63.22 (63.54)	5.84 (5.63)	10.59 (10.43)	Brown	293	66

IR spectroscopy

IR absorption spectra of the Schiff base for the ligand H_2L showed the absence of absorption bands for the stretching vibrations (symmetrical and asymmetrical) for secondary amine (NH_2), benzidine, carbonyl (C=O), and salcylialdehyde (Figure-1). The spectra also demonstrated the appearance of stretching vibrations for azomethine group (-C=N) at 1618 cm^{-1} [25].Moreover, the FT-IR spectra for H_2L was revealed a broad band at 3465cm^{-1} which belongs to the hydroxyl group [15]. The stretching of the hydroxyl band was absent in the FT-IR spectra of the complexes Figures-(2 -5). A confirmation comes from the absence of OH bending band for H_2L in the complexes of the mixed ligand. While, a band appeared in the range 3294-3465 cm^{-1} which indicated a NH_2 group for OPD. The band of azomethine group (-C=N) was shifted in the coordination process to lower frequencies in some complexes or to higher frequencies in others . In addition, new bands appeared in the regions of 536–

623 and 445–538 cm^{-1}, which are probably due to the formation of M-O and M-N bands, respectively [15].

Table 2-The characteristic FT-IR frequencies of H_2L and its complexes

Compounds	ν(C-H) aliphatic	ν(C-H) aromatic	ν(C=N)	(O-H)υ	υ(N – H_2)	(M-N)υ	υ(M-O)
H_2L	29876	3053.42	1618.61	3465	—	—	—
$[Co_2(OPD)_2(L)]Cl_2$	2989.77	3067.77	1608.69	–	3412.19 3294.53	468.72	542.02
$[Fe_2(OPD)_2(L)]Cl_2$	2987.88	3069.61		—	3421.83 3375.65	538.16	609.53
$[Ni_2(OPD)_2(L)]Cl_2$	29941	31097	1608.69	—	3433.33 3389.76	445.57	623.03
$[Cu_2(OPD)_2(L)]Cl_2$	3338.89	3448.84	1610.61	—	3465.33 3338.84	465.00	536.23

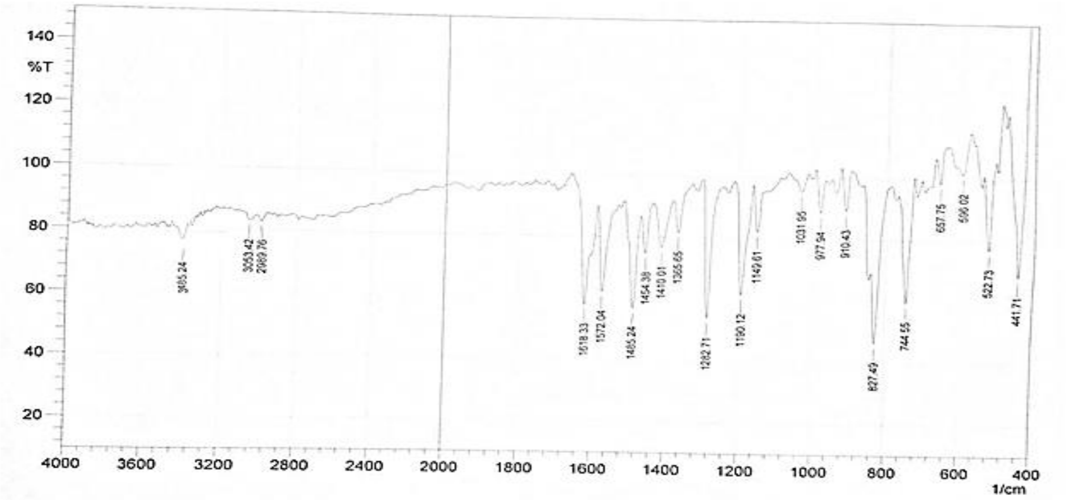


Figure 1-The FT-IR spectrum of Schiff base H_2L

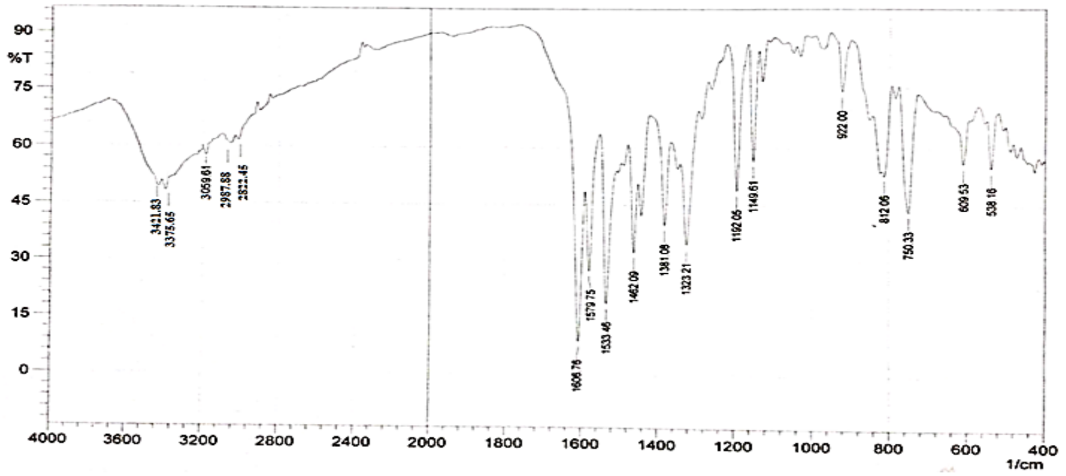


Figure 2-The FT-IR spectrum of $[Fe_2(OPD)_2(L)]Cl_2$.

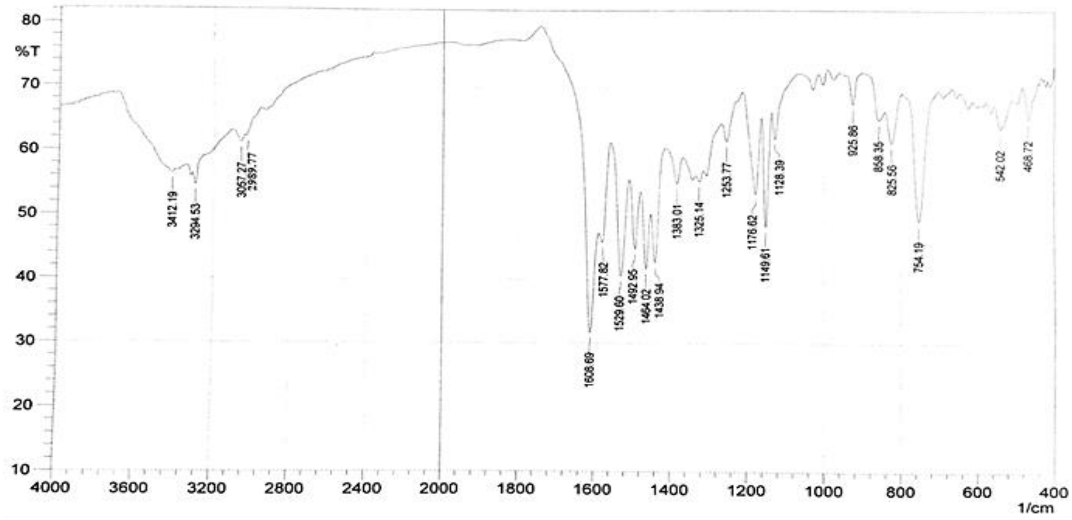


Figure 3-The FT-IR spectrum of $[Co_2(OPD)_2(L)]Cl_2$

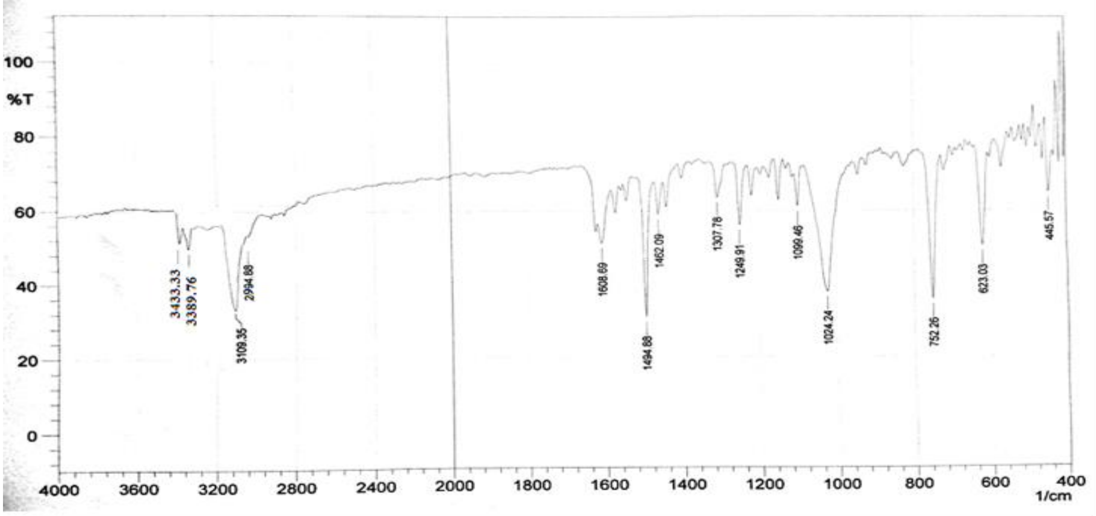


Figure 4-The FT-IR spectrum of $[Ni_2(OPD)_2(L)]Cl_2$

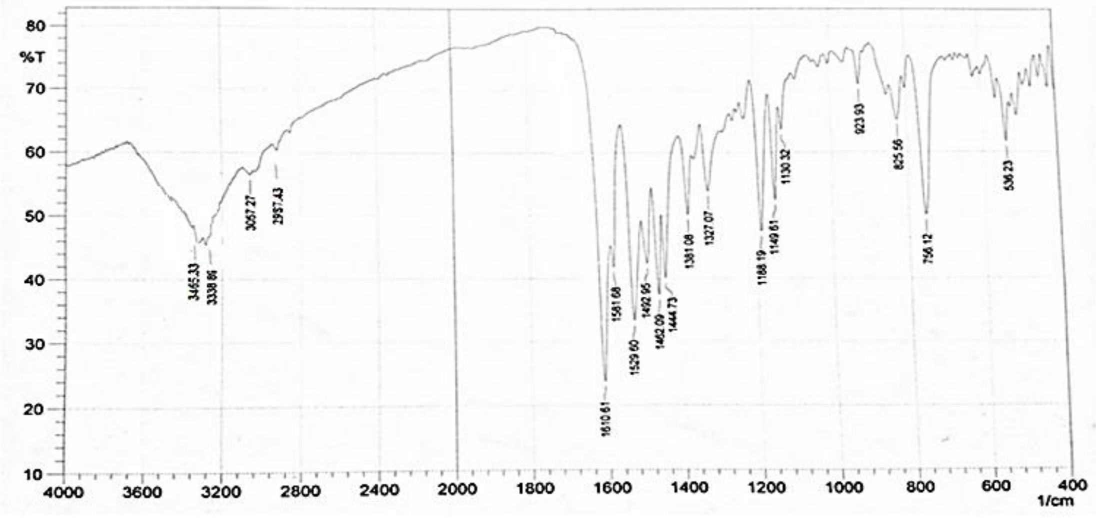


Figure 5-The FT-IR spectrum of $[Cu_2(OPD)_2(L)]Cl_2$

Electronic spectra, molar conductivity, and magnetic susceptibility

The electronic spectra of the prepared compounds were measured in DMF solvent (1×10^{-3} M) at room temperature. The UV-Vis spectra of the primary ligand (H_2L) displayed two absorption bands (Figure-6). The first band was at 222 nm (45045 cm^{-1}) which is assigned to π–π^* electronic transition.

The second band was at 356 nm (28089 cm^{-1}) and attributed to n–π* electronic transition. The electronic spectrum of the $[Fe_2(OPD)_2(L)]Cl_2$ (Fig.7), d-d transitions were not observed due to their disappearance under the charge transfer bands that were observed in the range 400-500 nm. The value of conductivity of $[Fe_2(OPD)_2(L)]Cl_2$ complex was 132.7 µS/cm ,which indicating their 1:2 electrolytic behaviour, while the magnetic moment for this complex was 5.363 B.M., which refers to four single electrons in a tetrahedral environment. The electronic spectrum of $[Co_2(OPD)_2(L)]Cl_2$ complex (Fig. 8) showed broad bands at 600 nm (16666 cm^{-1}) and 750 nm (13333 cm^{-1}) due to two transitions at υ_3 $^4A_2 \rightarrow ^4T_2$ and υ_2 $^3A_2 \rightarrow ^3T_{1(p)}$, respectively. These bands refer to tetrahedral geometry around the cobalt(II) ion [26]. The magnetic susceptibility (5.089 B.M.) and molar conductivity (160.5 µS/cm) measurements indicated that the complex is paramagnetic and electrolyte in a ratio of 1:2. The electronic spectrum of the complex $[Ni_2(OPD)_2(L)]Cl_2$ (Fig. 9) in the visible region showed a charge transfer band at 435nm (22988cm^{-1}) and d-d transition band at 790nm (12658cm^{-1}) belonging to the υ_2 ($^3T_{1(F)} \rightarrow ^3T_2$) in the tetrahedral geometry of Ni(II) complexes [27]. The magnetic susceptibility was 3.7 B.M indicated that the complex is paramagnetic. The molar conductivity in DMF was 158 µs/cm indicated a strong 1:2 electrolyte [28]. From these results, a tetrahedral geometry around Ni(II) can be suggested. The spectrum of $[Cu_2(OPD)_2(L)]Cl_2$ (Fig. 10) have a broad band at 500nm (20000 cm^{-1}) due to a combination of two transitions, $^2B_1g \rightarrow ^2Eg$ and $^2B_1g \rightarrow ^2A_1g$, respectively. These transitions refer to a square planar geometry around Cu (II) ion [26]. The value of magnetic moment at room temperature was 2.1 B.M. This value came within the range of square planar [26]. The molar conductivity value was 166 µs/cm, show that the complex was an electrolyte. According to these data, a square planar geometry around Cu (II) ion can be suggested.

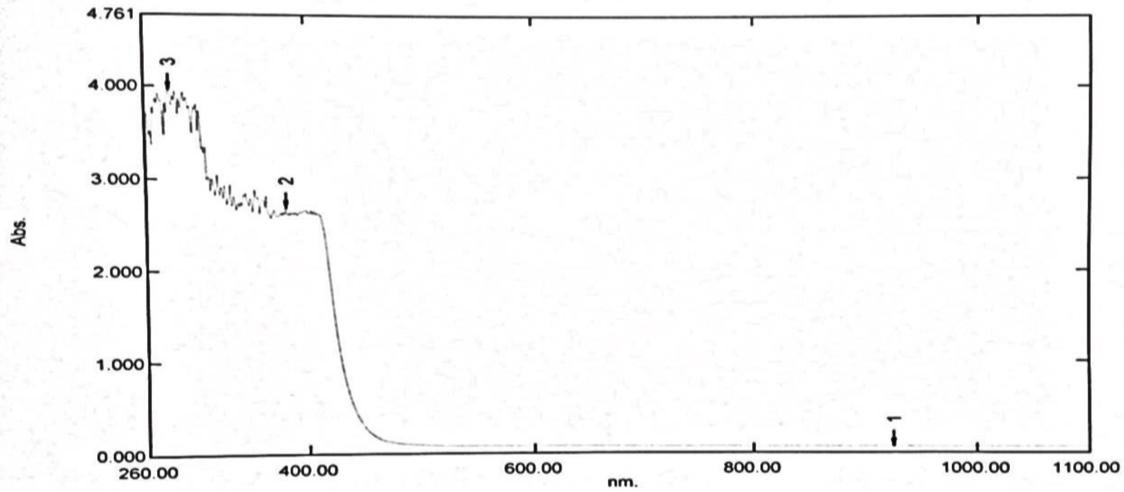


Figure 6-The electronic spectrum of $[H2L]_2$.

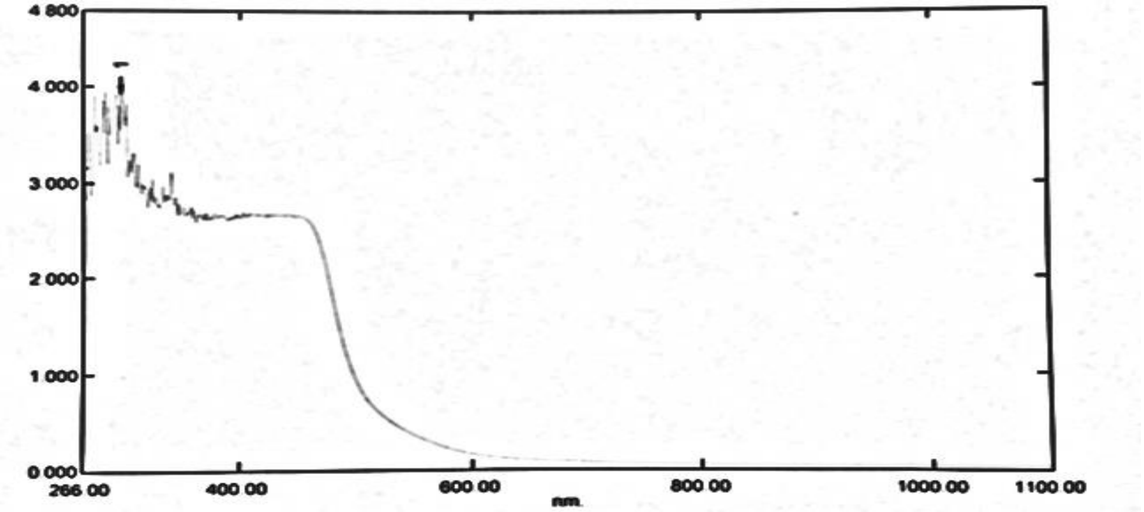


Figure 7-The electronic spectrum of $[Fe_2(OPD)_2(L)]Cl_2$

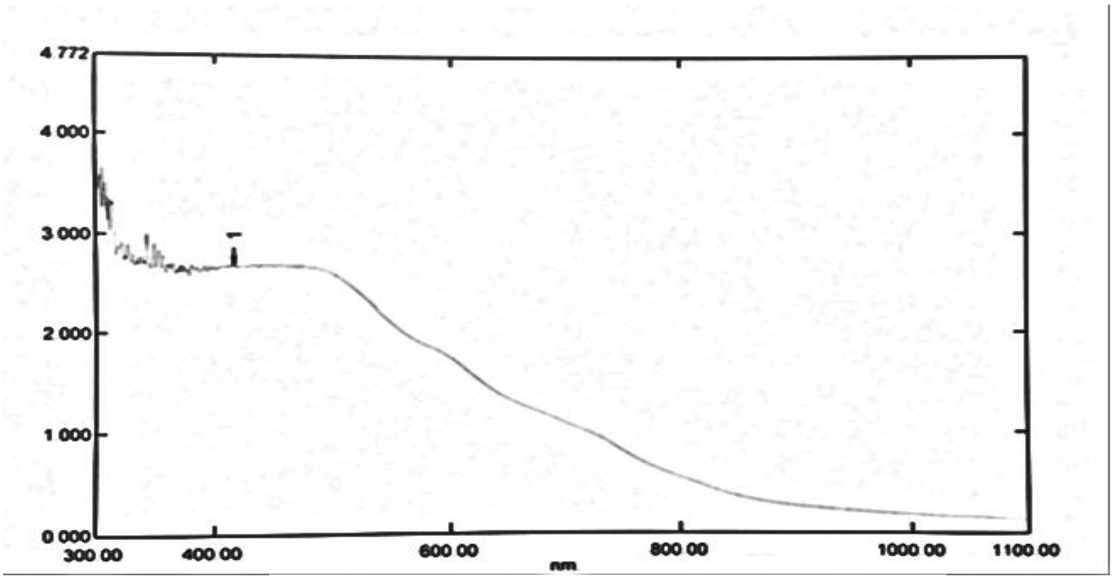


Figure 8-The electronic spectrum of $[Co_2(OPD)_2(L)]Cl_2$

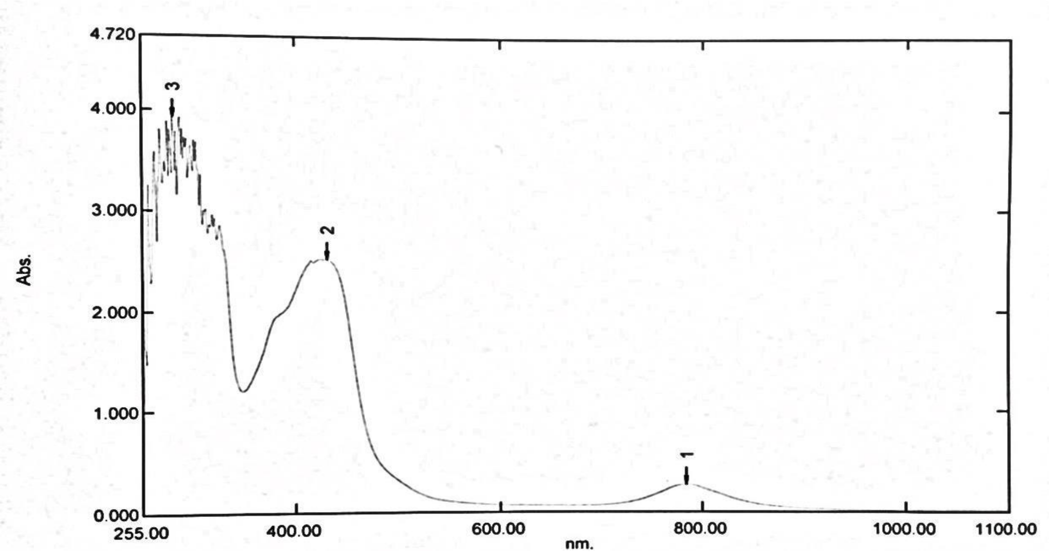


Figure 9-The electronic spectrum of $[Ni_2(OPD)_2(L)]Cl_2$

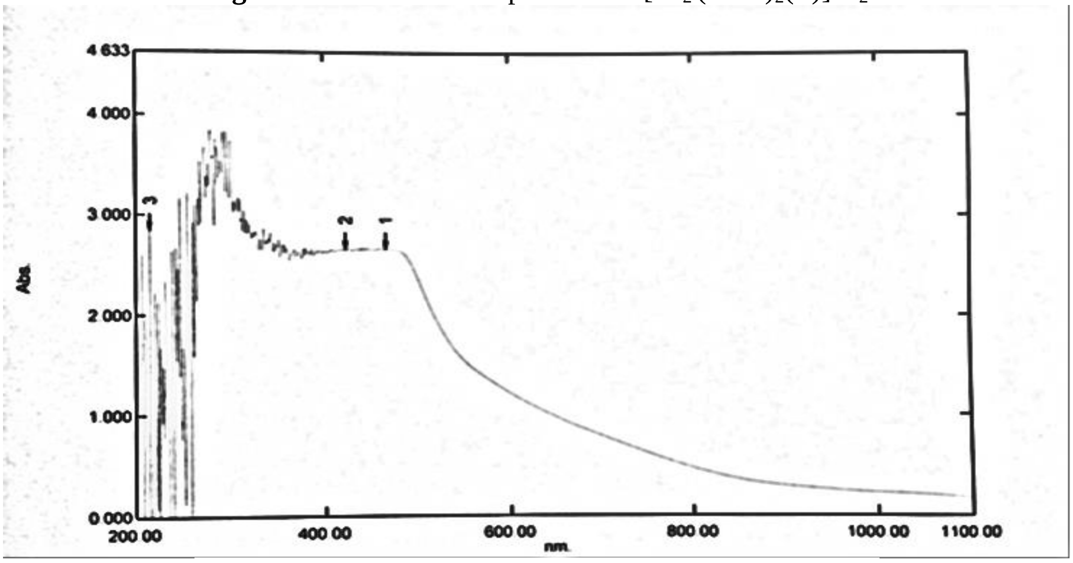


Figure 10-The electronic spectrum of $[Cu_2(OPD)_2(L)]Cl_2$

Thermogravimetric analyses (TGA/DTA)

The results obtained from the thermal analysis of the ligand H_2L and its metal complexes by TG and DTA techniques, within the range of 30-900 ºC, a heating rate of 20 ºC /min, and under nitrogen atmosphere, are described in Table-3, while their thermographs are shown in Figs (11-15). Chlorine molecules, in most of the complexes that were not directly coordinated to the metal ion, were found to be lost at lower temperatures. Stages of decomposition reflect the nature of binding between the metal and ligand atoms and the stability of the complexes [28]. Final steps of decomposition appeared left the metal ion with oxygen or alone, which reflects the affinity of metal atoms towards oxygen according to Pearson's law [29]. Finally, a general trend in thermolysis steps was observed in the earlier stages, where the small molecules were lost first, followed by the large groups.

Table 3-Data of thermal decomposition of the ligand H_2L and its metal complexes

Compound	M.Wt	Weight loss %		Thermal Range ºC	Decomposed Compounds	Produce Compounds
		Fou.	Calc.			
H_2L	392	78	76.959	70-455	↓ $2(C_7H_6O)$, (C_6H_4N)	C_6H_4N
		24	22.959	455-700	↓ C_6H_4N	0
$[Fe_2(OPD)_2(L)]Cl_2$	789.311	8	8.108	30-230	↓ Cl_2	$C_{38}H_{34}Fe_2N_6O_2$
		12	11.402	230-380	↓ C_6H_4N	$C_{32}H_{30}Fe_2N_5O_2$
		14	13.303	380-580	↓ C_7H_5O	$C_{25}H_{25}N_5$ FeO,Fe
$[Co_2(OPD)_2(L)]Cl_2$	795.487	12	11.56	40-260	↓ C_6H_6N	$C_{32}H_{28}Cl_2Co_2N_5O_2$
		8	8.04	260-360	↓ Cl_2	$C_{38}H_{28}Co_2N_5O_2$
		26	25.142	360-550	↓ $C_{12}H_{12}N_2O$	$C_{20}H_{16}N_3$, CoO, Co
$[Ni_2(OPD)_2(L)]Cl_2$	795.008	40	40	30-310	↓ $C_{20}H_{18}N_2O_2$	$C_{18}H_{16}Cl_2Ni_2N_4$
		22	22.5	310-360	↓ $C_6H_8N_2Cl_2$	$C_{12}H_8N_2$, 2Ni
$[Cu_2(OPD)_2(L)]Cl_2$	804.713	8	8.82	55-240	↓ Cl_2	$C_{38}H_{34}Cu_2N_6O_2$
		12	12.7	240-370	↓ C_7H_5N	$C_{31}H_{29}Cu_2N_5O_2$
		22	22.86	370-730	↓ $C_{12}H_{12}N_2$	$C_{19}H_{17}N_3$, 2CuO

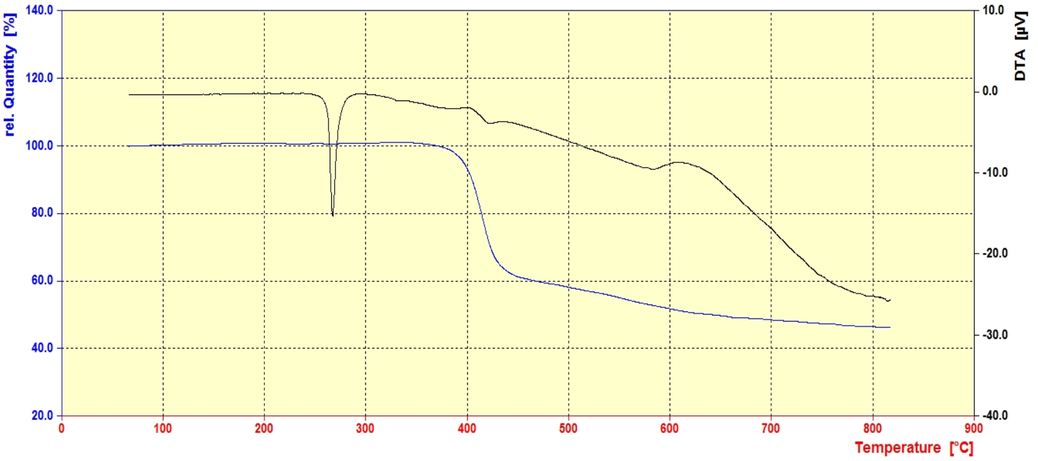


Figure 11-TGA- DTA thermographs of H_2L

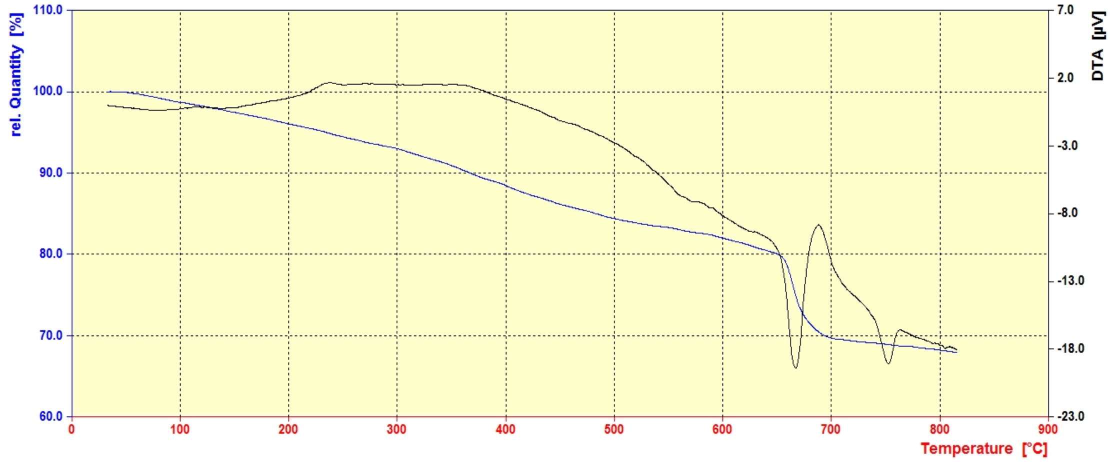


Figure 12-TGA- DTA Thermographs of [$Fe_2(OPD)_2(L)]Cl_2$

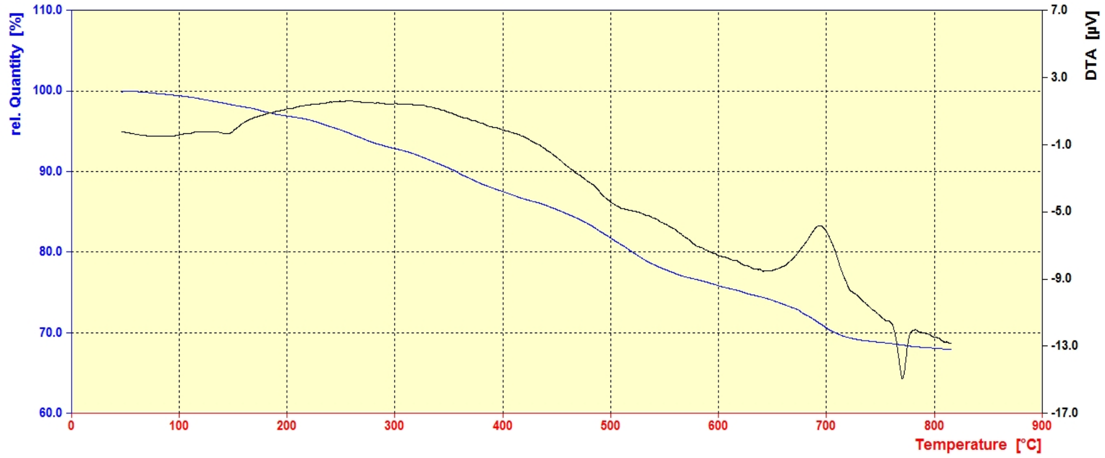


Figure 13-TGA- DTA thermographs of [$Co_2(OPD)_2(L)]Cl_2$

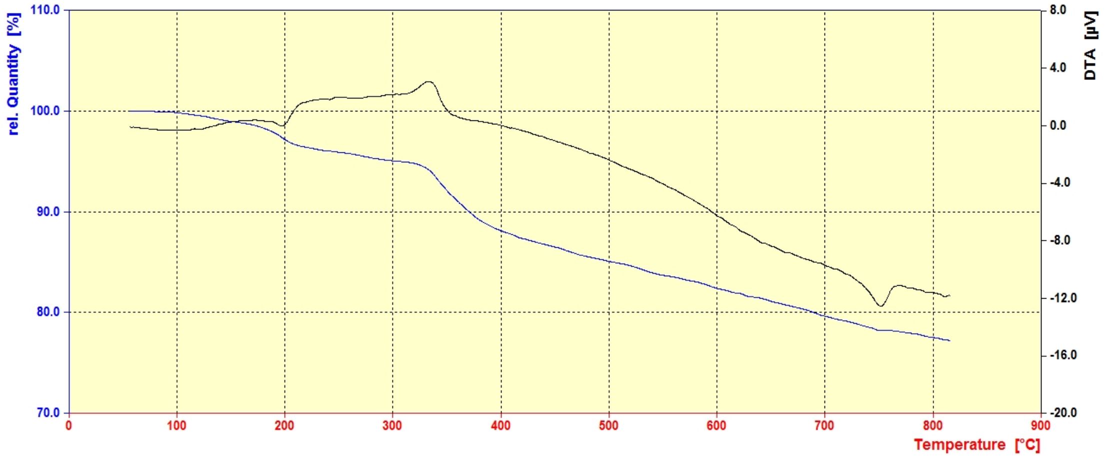


Figure 15-TGA- DTA Thermographs of [$Cu_2(OPD)_2(L)]Cl_2$

Antimicrobial Activities

The antimicrobial activities of the complex compounds were studied and the results are presented in Table-4.

Table 4-Biological activity of the complexes against certain genera of bacteria and fungi .

Compounds	**Antibacterial activity (mm)**		**Antifungal activity (mm)**
	Bacillus sp.	*Proteus sp.*	*A.niger*
$[Fe_2(OPD)_2(L)]Cl_2$	0	16	21
$[Co_2(OPD)_2(L)]Cl_2$	0	18	0
$[Ni_2(OPD)_2(L)]Cl_2$	0	17	16
$[Cu_2(OPD)_2(L)]Cl_2$	0	17	30
DMF	0	15	0
CIP	28	22	-
Clotrimazole	-	-	25

From the results presented in Table- 4, it can be noted that all the compounds have no effects on the biological activity of *Bacillus sp.*, as compared to the effects of the bacterial antibiotics which were clear in terms of the diameter of the growth inhibition zone (reaching 28 mm) as shown in Figure-16. Nevertheless, the majority of the complexes showed high antibacterial activities against *Proteus sp.* (Figure-17). The complexes of $[Co_2(OPD)_2(L)]Cl_2$, $[Ni_2(OPD)_2(L)]Cl_2$, and $[Cu_2(OPD)_2(L)]Cl_2$ caused remarkably high antimicrobial activities (inhibition zone diameters of 18, 17, 17 mm, respectively). This effect approximates that of the used antibiotic, which reached 22 mm. However, MDF showed the lower activity of 15 mm. It has been suggested that organic ligands with oxygen and nitrogen donor atoms inhibit the enzymatic activity. Polarity of metal ions is reduced as a result of coordination with organic ligands, due to the partial sharing of its positive charge with the donor groups within the chelate ring system. Hence, the produced metal complexes can be used as antibacterial agents[13].

As for the biological activity of the compounds against *A. niger*, the results shown in Table-4 reveal that the complexes of $[Fe_2(OPD)_2(L)]Cl_2$, $[Ni_2(OPD)_2(L)]Cl_2$, and $[Cu_2(OPD)_2(L)]Cl_2$ were effective against this fungus (inhibition zone diameters of 21, 16 and 30 mm, respectively). In addition, the compounds $[Co_2(OPD)_2(L)]Cl_2$ and DMF showed no efficiency. When comparing the activity of the complex $[Ni_2(OPD)_2(L)]Cl_2$ with that of the antifungal drug (clotrimazole), we observe that $[Ni_2(OPD)_2(L)]Cl_2$ had a higher efficacy , as shown in Figure-18. The biological activity of the metal complexes may be attributed to the effect of metal ions on the normal cell membrane. Consequently, the difference in the activity of metal complexes against different organisms depends either on the impermeability of cells of the microbes or variations in the their ribosomes cells [30] .

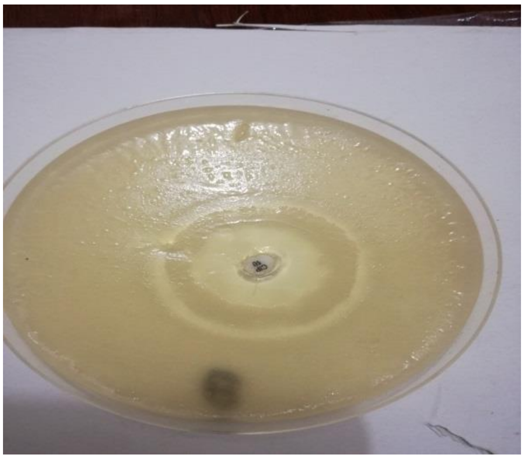


Figure 16-Sensitivity of the bacteria *Bacillus sp.* towards Ciprofloxacin .

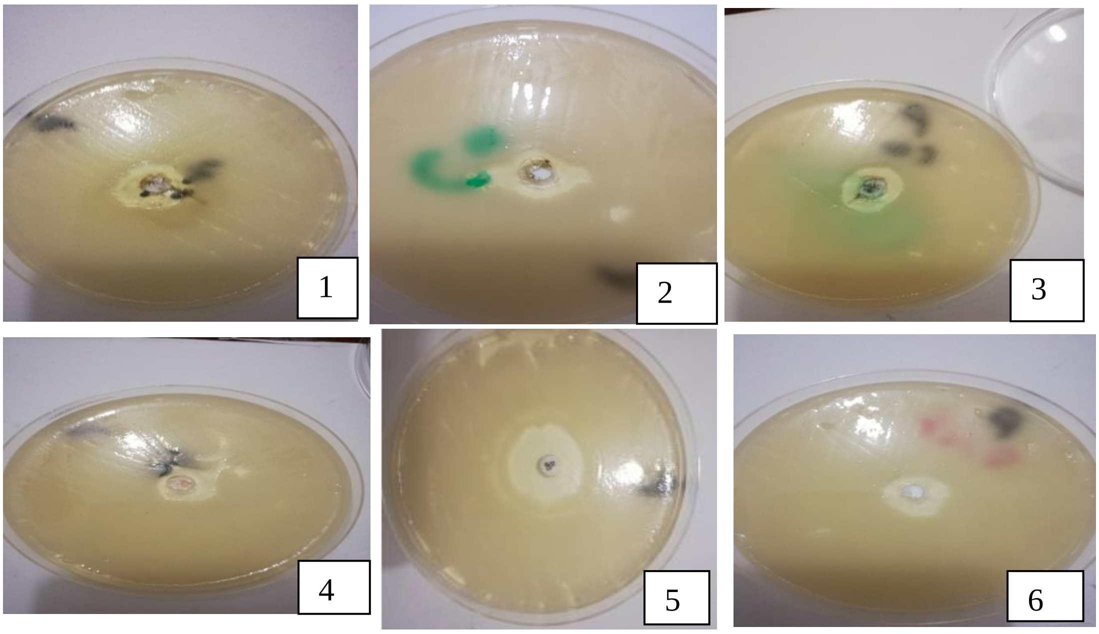


Figure 17-Sensitivity of the bacteria *Proteus sp*. towards:1- Fe complex,2- Co complex,3- Ni complex,4- Cu complex, 5- Ciprofloxacin, and 6- DMF.

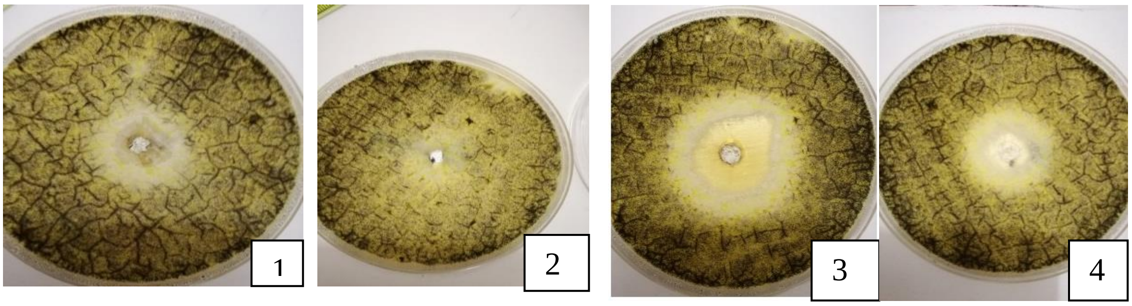


Figure 18-Sensitivity of the fungus *A. niger* towards:1- Fe complex, 2- Ni complex, 3- Cu complex, and 4- Clotrimazol.

CONCLUSIONS

Fe(II), Co(II), Ni(II) and Cu (II) complexes of the mixed ligands OPD and Schiff base H_2L were synthesized and characterized. Conductivity measurements indicated that the complexes are 1:2 electrolytes. The results of infrared spectroscopy clearly elucidated that the Schiff base ligand coordinates with metal ions as bidentate via nitrogen and oxygen atoms and by the two nitrogen atoms of OPD molecule. Fe (II), Co(II), and Ni(II) complexes have tetrahedral geometry, while the Cu(II) complex has a square planar geometry. Thermogravemetric analysis indicated that the chlorine molecules in most complexes that are not directly coordinated with the metal ion were lost at lower temperatures and final steps of decomposition appeared left the metal ion with oxygen or alone which reflects the affinity of metals atoms towards oxygen. The antimicrobial activity of the metal complexes indicated that all the prepared metal complexes have no effects on *Bacillus* bacteria but, however, they largely affected the growth of *Proteus* bacteria and *A. niger* fungus.

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