Synthesis, Characterization and Biological Activity of Mixed Ligand Metal Salts Complexes with Various Ligands

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Abstract. Metal (III) and (II) coordination compounds of o- phenylenediamine, oxalic acid dihydrate and 8-hydroxyquinoline were synthesized for mixed ligand complexes and characterized using FT-IR, UV-Vis and mass spectra, atomic absorption, elemental analysis, electric conductance and magnetic susceptibility measurements. In addition, thermal behavior (TGA) of the metal complexes (1-6) showed good agreement with the formula suggested from the analytical data. The stoichiometric reaction between the metal (III) and (II) ions with three various ligands in molar ratio at aqueous ethyl alcohol for (1:1:1:1) (M: O-PDA: OA: 8-HQ) [where M = Cr+3, Mn+2, Co+2, Ni+2. Cu+2 and Zn+2; O-PDA = O-Phenylenediamine; OA = Oxalic acid and 8-HQ = 8-Hydroxyquinoline]. Resulted in the formation of six – coordinate octahedral geometry was suggested for metal complexes (1-6). The ligands and complexes were tested for antibacterial and antifungal activity against Staphylococcus aureus, Staphylococcus epidermidis, Escherichia coli, Klebsiella sp., Psedomonas aeruginosa and Candida albicans by the agar well diffusion method. Mostly, the results shown a significant increase in antibacterial and antifungal activity of the metal complexes (1-6) compared to ligands.

Keywords. O-Phenylenediamine; oxalic acid dehydrate; 8-hydroxyquinoline; mixed ligand complexes; spectral studies; thermal analysis and bioactivities.

1. Introduction
Many research papers have been published on preparing of metal complexes with mixed ligand and characterization [1, 2, 3]. Mixed ligand also play an important role in the biological field as exemplified by many ways in which enzymes are known to be activated by metal ions [4, 5]. O-Phenylenediamine (O-PDA) is used in the copper catalyzed synthesis of quinoxalines [6]. (O-PDA) is also suitable for removing memental sulfur in mining ores and removing aldehyde color formers in polymers [7]. (O-PDA) has been used in many Schiff base interactions because it contains two groups amine [8, 9, 10].Oxalic acid dihydrate (OA), the history from oxalates chemistry in long-term coordination and regeneration feature can be seen in the recent years. (OA) acts as a bidentate ligand in the form of dianion, functions as a involving the two-ions have been extensively studied, the consequence of their
use as model systems in the investigation of physic-chemical property [11, 12]. Synthesis and properties from transition metals compounds for carboxylates is widely studied. The cause is the bis-chelating capacity from the oxalates at combination through current efforts in the preparation molecular based on materials through higher dimensions. Synthesis and properties from transitions metals compounds for carboxylates is widely studied [13, 14].

8-Hydroxyquinoline (Oxine) (8-HQ) behaves as bidentate through (N and O) and will-characterizes organic chelating ligand. It has been found that a majority of the metal complexes with (8-HQ) posses biological activity [15]. Compounds containing quinolone moiety are great interest to synthetic and medicinal chemists due to their unique chemical and biological properties [16]. However its derivatives have long been used for their antibacterial and antifungal activity [17]. (8-HQ) is ability to get bonded with metal ion with its phenolic stable chelates with metals results in forming stable chelates with metals the producing stable mixed ligand complexes [18]. The current implementation is to prepare mixed ligand complexes derived of various three ligand (o-phenylenediamine, oxalic acid dihydrate and 8-hydroxyquinoline with metal (III) and (II) salts such as Cr+3, Mn+2, Co+2, Ni+2, Cu+2 and Zn+2, the prepared complexes were performed using different physic-chemical methods as well as spectra studies, thermal analysis also antibacterial and antifungal efficacy studies from various three ligands and novel mixed ligand metal complexes (1-6).

2. Materials and Methods

All ligands, metal (III) and (II) salts and solvents used were of analytical grade. Melting points (M.P.) were measured using Stuart Melting Point Apparatus. The UV-Vis spectra were obtained using Shimadzu-U.V-160 of the metal complexes (1-6). The magnetic susceptibility measurement were obtained at room values of the prepared metal complexes (1-6) were estimated using AutoMagnetic Susceptibility Balance Sherwood Scientific. The infrared spectra (KBr) were recorded for the three various ligand and metal complexes (1-6) were recorded in the range 4000-400 cm⁻¹ on FT-IR-600 FT-IR Spectrophotometer. Electric conductivity measurments were recorded at 25°C for 10⁻³M solutions of the ligands and metal complexes (1-6) in DMSO using CON 510 Conductivity. Elemental C.H.N microanalysis have been accomplished on the metal complexes (1-6) were nominated through the micro analytical unit at Euro EA Elemental Analyzer. Mass spectra was recorded for metal complexes (1-6) base by MS Model 5973 Network Mass Selection Technology (HP) with Triple –Axis Detector by the analyzer Quadrupole at 230°C. When metal (III) and (II) contents of the complexes have been identified from before Atomic Absorption (A.A) Technique / Flame Emission Spectrophotometer using AA – 680 Shimadzu. Thermal analysis was Differential Scanning Calorimetry carried out on a STAPT- 1000 Lineseis (TGA) with a heating rate of 10 °C/min using Ar atmosphere for the Cr(III) and Cu(II) complexes.

2.1. Synthesis of the Metal Complexes

The metal complexes (1-6) were prepared according in (Scheme 1), through the addition of the three ligands:

1. O-Phenylenediamine solution (0.108g /1mmol), in 15cm³ of ethyl alchol.
2. Sodium oxalate dehydrate solution (0.126g / 1mmol) in 15cm³ of ethyl alchol with adding (0.04g / 1mmol) of sodium hydroxide with distilled water
3. Sodium 8-oxyquinolinate solution (0.145g / 1mmol) in 15 cm³ of ethyl alchol with [0.04g / 1mmol] solution of sodium hydroxide in distilled water.

All three ligands have been added with stirring to aqueous solution of CrCl₃.6H₂O (0.267g / 1mmol), MnCl₂.4H₂O (0.197g / 1mmol), CoCl₂.6H₂O (0.237g /1 mmol), NiCl₂.6H₂O (0.237g /1mmol), CuCl₂.2H₂O (0.170g /1mmol) and ZnCl₂ (0.136/1mmol). The resulted homogeneous solution were refluxed for 2hr. at 10°C during this period the products formed, then they were filtered, washed with diethylether dried in vacuo anhydrous CaCl₂.
2.2. Antimicrobial Activity

The biological activities of various three ligands and metal complexes (1-6) have been studied for their antibacterial against six species of bacteria three strain of a gram positive and three strain of a gram negative as well antifugal of Candida albicans by well diffusion method. The screened compounds were dissolved individually in DMSO solvent in order to make up a solution of 10^{-3}M concentration for each of the compounds. The discs were placed on the surface of solidified Nutrient agar dishes seeded by the tested bacteria and fungi. The diameters of inhibition zones (mm) were measured at the end of an incubation period, which was 24 hr. at 37°C for bacteria and fungi.

3. Result and Discussion

Characterization of Metal Complexes (1-6): All the metal complexes (1-6) are coloured, non-hygroscopic and thermally stable solids, indicating a strong metal – ligand bond. The all complexes insoluble in water except the Cr^{3+} complex and also insoluble in common organic solvent such as diethyl ether, benzene, carbon tetrachloride and petroleum ether, but are soluble in ethanol, methanol, acetone, DMSO and DMF. The metal complexes (1-6) were prepared in a molar ratio [metal:O-PDA:OA:8-HQ (1:1:1:1)]. Cr(III), Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) were used as chloride salts. The composition of which is consistent with their micro-analytical, thermal analysis and spectral data. Physical measurements and analytical data of the ligands and the complexes (1-6) are given in (Table 1). The flame atomic absorption technique as well as elemental analysis of the complexes (1-6) gave approximated values for theoretical values according to the (Table 1). The molar conductivity of mixed ligand complexes (1-6) with the mentioned metal ions, the obtained data indicate that the synthesized mix ligand complexes according in (Table 2) have electrolytic nature except the Cr^{3+} complex have non-electrolytic nature [19].
### Table 1. Show Some Physical Properties and Analytical Data for Prepared Various Three Ligands as well metal Complexes.

| Compounds | Empirical Formula | Molecular Weight (g/mol) | Color       | M.P.°C | Analysis Calc (%) | Found (%) |
|-----------|------------------|--------------------------|-------------|--------|-------------------|-----------|
|           |                  |                          |             |        |                   | M%        |
|           |                  |                          |             |        |                   | C%        |
|           |                  |                          |             |        |                   | H%        |
|           |                  |                          |             |        |                   | N%        |
| O-PDA    | C₆H₈N₂           | 108.14                   | Brown (102-104) | 12.67 | 49.76             | 3.44      |
| OA       | C₂H₂O₄.2H₂O      | 126.07                   | White (101-102) | 11.69 | 46.10             | 3.62      |
| 8-HQ     | HCO₄H₂NO         | 145.16                   | Pale-yellow (70-73) | 14.28 | 45.89             | 3.17      |
| [Cr(OPDA)(OA)(8HQ)].H₂O | C₁₇H₁₄N₃O₅Cr.H₂O | 410.32                  | Brown >350 | 12.59 | 46.80             | 3.23      |
| Na[Mn(O-PDA)(OA)(8-HQ)].H₂O | NaC₁₇H₁₄N₃O₅Mn.H₂O | 436.26                  | Reddish brown >350 | 13.39 | 46.38             | 3.21      |
| Na[Co(O-PDA)(OA)(8-HQ)].H₂O | NaC₁₇H₁₄N₃O₅Co.H₂O | 440.26                  | Green >350 | 13.34 | 46.37             | 3.21      |
| Na[Ni(O-PDA)(OA)(8-HQ)].H₂O | NaC₁₇H₁₄N₃O₅Ni.H₂O | 440.02                  | Deep brown >350 | 13.34 | 46.37             | 3.21      |
| Na[Cu(O-PDA)(OA)(8-HQ)].H₂O | NaC₁₇H₁₄N₃O₅Cu.H₂O | 444.86                  | Deep yellow >350 | 14.28 | 45.89             | 3.17      |
| Na[Zn(O-PDA)(OA)(8-HQ)].H₂O | NaC₁₇H₁₄N₃O₅Zn.H₂O | 446.70                  | Pale brown >350 | 14.64 | 45.71             | 3.15      |

#### 3.1. UV-Vis Spectra as well as Magnetic Properties for metal Complexes

Electronic spectra of the prepared metal complexes are recorded in DMSO. The assignments for the electronic spectra are given in (Table 2). UV-Vis spectroscopy into ligand (O-PDA) displays three peaks, the first and second in 270 and 323 nm whom were appointed into (π–π*), the third peak in 417 nm consequent into (n–π*) electronic transitions [20]. The electronic spectrum from ligand (OA) exhibit two peaks in 266 and 393 nm were qualified into (π–π*) and (n–π*) [21]. Spectrum of ligand (8-HQ) shows peaks at 271 and 329 nm were qualified into (π–π*) [22]. The spectrum of Cr(III) complex displays peaks in 270, 326, 345nm were assigned to ligand field, peak in 419nm was specified into charge transfer. three peaks at 639, 730 and 951 nm whom were referred into electronic transition type 4A2g(F) → 4T1g(P), 4A2g(F) → 4T1g(G) as well 4A2g(F) → 4T2g(F) respectively, also the value from magnetic moment on 3.73 B.M may be possessed as extra confirmation to octahedral geometry [23].

The electronic spectrum for the Mn+2 complex displays peaks in 271, 326 and 423 nm whom was qualified into ligand field and charge transfer. Else peak at 561 and 680 nm referred into electronic transition type 6A1g → 4T2g(G) and 6A1g → 4T1g(G). The magnetic moment for complex has been discovered in 5.90 B.M whom was much close to the octahedral perimeter [24].

The spectrum of Co+2 complex shows peaks in 270, 345 and 427 nm whom were qualified into ligand field and charge transfer. Else three peaks at 540, 635 and 710 nm whom were referred into electronic transition type 4T1g(F) → 4T1g(P), 4T1g(F) → 4A2g(F) as well 4T1g(F) → 4T2g(F) respectively, also the value from magnetic moment on 4.63 B.M may be possessed as extra confirmation to octahedral geometry [25]. Electronic spectrum from Ni(II) complex do show peaks in 290, 324 and 416 nm consequent into ligand field. Another three peaks in 517, 653 and 764 nm whom were appointed into electronic transition style 3A2g(F) → 3T1g(F), 3A2g(F) → 3T1g(G) and 3A2g(F) → 3T2g(F) continuity, the magnetic moment for complex has been discovered in 2.82 B.M whom was much close to the octahedral perimeter [26]. Cu(II) complex spectrum appears peaks in 270, 325 as well 433 nm
attributed to ligand field and charge transfer, peak in 692 nm whom was qualified into electronic transition style 2Eg → 2T2g. The magnetic moment for this complex was found on 1.77 B.M whom was much close environment of the octahedral [27]. Electronic spectral from Zn(II) complex do offer charge transfer and magnetic susceptibility seemed the complex has diamagnetic moments, result to (d-d) transition are not likely hence electronic spectrum did not confer any productive datum, on fact outcome is a good agreement for former work from geometry of octahedral [28].

Table 2. Electronic Spectral Data of the Various Three Ligands also Metal Complexes Magnetic Moment (BM) as well Conductance (Am).

| Compounds | λ_max (nm) | ABS | Wave number (cm-1) | ε_max (L.mol. cm-1) | Remarks | μeff (B.M) | Am(S. cm2.mol-1) In DMSO |
|-----------|----------|-----|------------------|--------------------|---------|------------|----------------------|
| O-PDA     |          |     |                  |                    |         |            |                      |
| 270       | 1.449    | 37037 | 1449              | (π – π*)           |         | -          | 1.27                 |
| 323       | 1.684    | 30959 | 1684              | (π – π*)           |         | -          | 5.44                 |
| 417       | 0.057    | 23980 | 57                | (n – π*)           |         | -          | 2.35                 |
| 266       | 0.749    | 37593 | 749               | (π – π*)           |         | 3.73       | 26.82                |
| 393       | 0.080    | 25445 | 80                | (n – π*)           |         | 5.90       | 39.72                |
| 271       | 1.590    | 36900 | 1590              | (π – π*)           |         | 3.82       | 4.63                 |
| 329       | 2.182    | 30395 | 2182              | (π – π*)           |         | 5.17       | 30.70                |
| 270       | 1.594    | 37037 | 1594              | L.F                |         | 4.63       | 30.70                |
| 326       | 1.746    | 30674 | 1746              | L.F                |         | 4.63       | 30.70                |
| 345       | 1.789    | 28985 | 1789              | L.F                |         | 4.63       | 30.70                |
| 419       | 2.131    | 23866 | 2131              | C.T                |         | 4.63       | 30.70                |
| 580       | 0.180    | 17241 | 180               | 4A2g(F) → 4T1g(P)  |         | 4.63       | 30.70                |
| 633       | 0.040    | 15797 | 40                | 4A2g(F) → 4T1g(F)  |         | 4.63       | 30.70                |
| 703       | 0.003    | 14224 | 3                 | 4A2g(F) → 4T2g(F)  |         | 4.63       | 30.70                |
| 271       | 1.613    | 36900 | 1613              | L.F                |         | 4.63       | 30.70                |
| 326       | 1.935    | 30674 | 1935              | L.F                |         | 4.63       | 30.70                |
| 432       | 1.827    | 23640 | 1827              | C.T                |         | 4.63       | 30.70                |
| 561       | 0.236    | 17825 | 236               | 6A1g → 4T2g(G)     |         | 4.63       | 30.70                |
| 680       | 0.118    | 14705 | 118               | 6A1g → 4T1g(G)     |         | 4.63       | 30.70                |
| 270       | 1.466    | 37037 | 1466              | L.F                |         | 4.63       | 30.70                |
| 345       | 1.514    | 28985 | 1514              | L.F                |         | 4.63       | 30.70                |
| 427       | 2.362    | 23419 | 2362              | C.T                |         | 4.63       | 30.70                |
| 540       | 0.273    | 18518 | 273               | 4T1g(F) → 4T1g(P)  |         | 4.63       | 30.70                |
| 635       | 0.132    | 15748 | 132               | 4T1g(F) → 4A2g(f)  |         | 4.63       | 30.70                |
| 710       | 0.021    | 14084 | 21                | 4T1g(F) → 4T2g(F)  |         | 4.63       | 30.70                |
| 270       | 1.574    | 37037 | 1574              | L.F                |         | 4.63       | 30.70                |
| 324       | 1.766    | 30959 | 1766              | L.F                |         | 4.63       | 30.70                |
| 416       | 0.854    | 24038 | 854               | L.F                |         | 4.63       | 30.70                |
| 517       | 0.281    | 19342 | 281               | C.T, 3A2g(F) → 4T1g(P) |         | 4.63       | 30.70                |
| 653       | 0.117    | 15313 | 117               | 3A2g(F) → 4T1g(P)  |         | 4.63       | 30.70                |
| 764       | 0.007    | 13089 | 7                 | 3A2g(F) → 3T2g(F)  |         | 4.63       | 30.70                |
| 270       | 1.447    | 37037 | 1447              | L.F                |         | 4.63       | 30.70                |
| 325       | 1.099    | 30769 | 1099              | L.F                |         | 4.63       | 30.70                |
| 433       | 2.375    | 23094 | 2375              | C.T                |         | 4.63       | 30.70                |
| 692       | 0.07    | 14450 | 7                 | 2Eg → 2T2g         |         | 4.63       | 30.70                |
| 271       | 1.590    | 36900 | 1590              | L.F                |         | 4.63       | 30.70                |
| 325       | 1.870    | 30769 | 1870              | L.F                |         | 4.63       | 30.70                |
| 416       | 1.249    | 24038 | 1249              | L.F                |         | 4.63       | 30.70                |
| 626       | 0.027    | 15974 | 27                | C.T                |         | 4.63       | 30.70                |
3.2. IR Spectral Studies of the Various Ligands as well Metal Complexes

The IR spectrum of the various ligands showed in (Table 3) and (Figure 1) for the metal complexes (1-6) have been registered into KBr at area 4000-400 cm⁻¹. The spectrum for(O-PDA) offer bands on 3394 cm⁻¹ as well 3325 cm⁻¹ have been specified into ν(NH₂) stretching frequency [29], on complexation a shifting for alteration into from were noticed of these bands, whereas growing into density were observe, specified can be an outcome from coordination for metal ion. Band into IR spectrum to the (OA) ligand in 3431 cm⁻¹ whom was qualified into stretching vibration for υ(OH) carboxyl, this band has been remove into spectra for every generated complexes, whom referred coordination this band for metal ion [30]. A change at the density and at position into reduce wave number has been noticed in metal chelates spectra for band to the(OA) ligand in 1587 cm⁻¹, that shows consequent into υ(OH) phenol, this band has been remove into spectra for every generated complexes, whom referred coordination this band for metal ion. Band at 3431 cm⁻¹ at the spectrum into the (OA), related into υ(C=O) asymmetric vibration, afforded a large change into lower wave number in metal chelates spectra [31]. The IR spectrum for the (8-HQ) offer broad band in 3324 cm⁻¹, whom was qualified into stretching vibration for υ(OH) phenol, this band has been remove into spectra for every generated complexes, whom referred coordination this band for metal ion. Band at 1624 cm⁻¹ has been specified into ν(C=O) stretching frequency [32, 33], on complexation a shifting for alteration into from were noticed of these bands, whereas growing into density were observe, specified can be an outcome from coordination for metal ion. New bands watched in (561-449) cm⁻¹ are temporarily appointed into ν(M-N) and ν(M-O) (Metal-Ligands) stretching bands [34, 35]. Depending on the consequences gained and spectral analysis an octahedral geometry has been proposed of produced compounds.

Table 3. The Most Characteristic Bands of the Various Ligands as well the Metal Complexes (1-6) (cm⁻¹).

| Compounds | υ(OH) + υ(H₂O) | υ(NH₂) | υ(C=O) | υ as,s(COO) | υ(M-N) | υ(M-O) |
|-----------|----------------|--------|--------|-------------|--------|--------|
| O-PDA     | -              | 3394 sh.| -      | -           | -      | -      |
| OA        | 3431 br.       | -      | -      | 1587 sho.   | -      | 1350 sho.|
| 8-HQ      | 3324 br.       | -      | -      | 1587 sho.   | -      | 1350 sho.|
| [Cr(O-PDA)(OA)(8-HQ)].H₂O | -              | 3367 br. | 1579 | 1498 sh. | 530 w. | 478 w. |
| Na[Mn(OPDA)(OA)(8HQ)].H₂O | -              | 3332 br. | 1576 sh. | 1522 sho. | 511 w. | 449 w. |
| Na[Co(OPDA)(OA)(8HQ)].H₂O | -              | 3281 sho. | 1576 | 1527 s. | 517 w. | 494 w. |
| Na[Ni(O-PDA)(OA)(8-HQ)].H₂O | -              | 3344 s. | 1570 | 1502 sh. | 546 w. | 490 w. |
| Na[Cu(OPDA)(OA)(8HQ)].H₂O | -              | 3357 sho. | 1572 sh. | 1525 sh. | 561 w. | 498 w. |
| Na[Zn(O-PDA)(OA)(8-HQ)].H₂O | -              | 3348 br. | 1572 | 1498 sho. | 499 w. | 451 w. |

s = strong, br. = broad, w= weak, sho =shoulder. sh= sharp

**Thermal Studies:** The results of thermo gravimetric analyses of Cr³⁺ and Cu²⁺ complexes are given in (Figure 2 and 3), Table- 4. The thermograms have been carried out in the range of up to 600 °C at a heating rate of 10 °C/min in nitrogen atmosphere, they show an agreement in weight loss between their results obtained from the thermal decomposition and the calculated values, which supports the results of elemental analysis and confirms the suggested formula. The complexes show in (Scheme. 2) showed a common behavior as in the following four and five steps to the Cr³⁺ and Cu²⁺ complexes, respectively [36-37]. The first step (C₁₇H₁₆N₃O₆Cr) and (C₁₇H₁₆N₃O₆CuNa) of the Cr³⁺ and Cu²⁺ complexes were loss of H₂O and (H₂O, CO₂, Na), respectively moity followed by the other parts of the Cr³⁺ and Cu²⁺
complexes. Furthermore, the final step of the thermolysis reactions of the complexes were found to give the metal oxide.

![Figure 1. FT-IR Spectrum of Metal Complexes](image)

### Table 4. Characterization Parameters of Thermal Decomposition (10°C/ min) of the Cr(III) and Cu(II) Complexes.

| Compounds                      | Step | Ti/°C | Td/°C | TDTG max/°C | Weight mass loss (calc) found% | Reaction          | Total mass loss % |
|-------------------------------|------|-------|-------|-------------|-------------------------------|-------------------|------------------|
| [Cr(O-PDA)(OA)(8-HQ)].H2O     | 1    | 48    | 184   | 127         | (4.386) 4.26                 | -H2O              | 85.222 (83.348)  |
|                               | 2    | 218   | 335   | 267         | (25.833) 25.681              | -C6H4NO           |                  |
|                               | 3    | 335   | 441   | 389         | (16.085) 16.001              | -C12H2O           |                  |
|                               | 4    | 441   | 593   | 527         | (37.044) 39.280              | -C11H11N2O2C2O+   |                  |
|                               |      |       |       |             | (37.5) 36.48                 |                   |                  |
| Na[Cu(OPDA)(OA)(8HQ)].H2O     | 1    | 64    | 282   | 211         | (19.107) 21.036              | -(H2O, CO2, Na)   |                  |
|                               | 2    | 284   | 349   | 314         | (11.689) 10.161              | -(C3H2N)          | (82.047 79.044) |
|                               | 3    | 351   | 401   | 378         | (17.983) 15.481              | -(C4H4ON)         |                  |
|                               | 4    | 404   | 461   | 437         | (12.138) 11.118              | -(C3H2N)          |                  |
|                               | 5    | 461   | 596   | 538         | (9.441) 11.068               | -(C3H2O)          |                  |
|                               |      |       |       |             | (11.689) 10.018              | CuO               |                  |

Wight experimental loss(85.222)% , final (14.778)% , weight theoretical loss (83.348)% and final(16.652)%
3.3. Mass Spectra of the Metal Complexes
The recorded mass spectra and the molecular ion peaks for the metal complexes (1-6) have been used to confirm the molecular formula. The mass spectrum of the complexes (Figure 4) is in a good agreement with the suggested structure (Scheme 1). The mass spectrum for the complexes displayed molecular peak at m/z 410.32, 436.26, 440.02, 444.86 and 446.70 M+ ions into Cr+3, Mn+2, Co+2, Ni+2, Cu+2 and Zn+2 complexes suggesting that the molecular weight of the assigned product matching with elemental analysis calculated (Table 1). The suggested molecular formula of the metal complexes (1-6) were prevented through resembling their molecular formula weights with m/z values. Structural probability models with the types been been built on chem.3D of Cr+3 complex according of (Figure 5).

![Figure 2. Curve (TGA) for the Cr(III) Complex](image1)

![Figure 3. Curve (TGA) for the Cu(II) Complex](image2)

![Scheme 2. The Tentative Decomposition Reactions of the Cr(III) and Cu(II) Complexes](image3)
3.4. Antimicrobial activity

The free ligands (O-PDA, OA and 8-HQ) and their mix ligand complexes were screened in vitro for their ability to inhibit the growth of representative [(Staphylococcus aureus, Staphylococcus epidermidis and Steptococcus sp.) as gram positive] and [(Escherichia coli, Klebsiella sp. and Psedomonas aeruginosa) as gram negative] are shown in (Table 5) and (Figure 6). Also, the study was done against (Candida albicans fungi), in DMSO as a solvent, (Table5). According to the results from the above mentioned studies, the following points were concluded:

1. (OA, 8-HQ and O-PDA) were non active against Staphylococcus aureus, Staphylococcus epidermidis and Psedomonas aeruginosa (Table 5).
2. Ni(II), Cu(II) and Zn(II) complexes were more effective against the all types of bacteria, in comparison to the ligands and the Cr(III), Mn+3 and Co+2 complexes.
3. The Cu(II) complex was highly active against Steptococcus sp., Escherichia coli and Klebsiella sp. in comparison to the ligands and the rest of the other complexes, was more toxic in comparison to their parent ligands (OA, 8-HQ and O-PDA) toward the same micro-organisms and under the identical experimental conditions.
4. Results of the antifungal activity such as Candida albicans, which shows that were active in (Table 5) of the ligands and the metal complexes except the Co(II) complex. It was more effective for the Mn(II) complex. The increase in the antibacterial activity of the Cu(II) complex and antifungal activity of the Mn(II) complex may be due to the effect of the metal ion on the normal cell process. These activities may be explained by Tweedy’s Chelation theory [38] according to which chelation reduces the polarity of the metal atom mainly, because of the
partial sharing of its positive charge with the donor groups of the ligand, which favours permeation of the complexes through the lipid layer of cell membrane [39].

### Table 5. Antimicrobial Results of Various Ligands and Metal Complexes

| Compounds                        | Staphylococcus aureus | Staphylococcus epidermidis | Streptococcus sp. | Escherichia coli | Klebsiella sp. | Pseudomonas aeruginosa | Candida albicans |
|----------------------------------|-----------------------|----------------------------|-------------------|------------------|----------------|------------------------|-----------------|
| Control (DMSO)                   | -                     | -                          | -                 | -                | -              | -                      | -               |
| OA                               | -                     | -                          | 15                | 12               | 11             | -                      | 29              |
| 8-HQ                             | -                     | -                          | 14                | 9                | 9              | -                      | 13              |
| O-PDA                            | -                     | -                          | 13                | 9                | -              | -                      | -               |
| [Cr(OPDA)(OA)(8HQ)].H2O          | 13                    | -                          | 14                | -                | -              | -                      | -               |
| Na[Mn(OPDA)(OA)(8HQ)].H2O        | 13                    | -                          | 13                | 13               | 10             | -                      | -               |
| Na[Co(O-PDA)(OA)(8HQ)].H2O       | -                     | -                          | 13                | -                | -              | -                      | -               |
| Na[Ni(O-PDA)(OA)(8HQ)].H2O       | 13                    | 12                         | -                 | 19               | 19             | 11                     | 15              |
| Na[Cu(O-PDA)(OA)(8HQ)].H2O       | 22                    | 22                         | 50                | 50               | 50             | 30                     | 17              |
| Na[Zn(O-PDA)(OA)(8HQ)].H2O       | 19                    | 20                         | 19                | 19               | 19             | 19                     | 19              |

### Figure 6. Biological efficacy for the Various Ligands as well Metal Complexes

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