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# Synthesis, Characterization and Studying Thermal Analysis for Complexes of Some Metal Ions and Determining Their Activity as Antioxidants

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## Abstract

According to previous studies, a new azo ligand (N-(3-acetyl-2-hydroxy-5-methyl-phenyl)N-(4-carboxy-cyclohexylmethyl)-diazonium salt) was prepared and after verifying the proposed formula according to the results of the analyzes and after using Ligand to prepare a series of complexes using equal molar ratios (1:1) of the ligand and its reaction with each of the salts of manganese, cobalt, nickel, copper and zinc, and after verification according to spectroscopic (ultraviolet and infrared) and diagnostic analysis techniques, which gave tetrahedral shapes for all complexes in a neutral formula, and the ligand is tridentate (NOO) related to azo, ketonic and phenolic hydroxyl group, respectively .Then, the thermal decomposition of some compounds prepared using the TGA and DSC was studied and mass spectroscopy. The dye of the complexes prepared from it was used to determine their ability to inhibit free radicals by measuring their ability as antioxidants using DPPH as a free radical and ascorbic acid as a standard substance, and determining the IC50 value, as it was found that the ligand has a high ability to inhibit free radicals, and the complexes' ability to inhibit it varied according to the IC50 value. The results were as following (Ascorbic acid(0.022) < LH(0.124) < Zn-complex(0.186) < Mn-complex(0.316) < Co-complex(0.635) <Cu-complex(2.234) <Ni-complex(2.351)) and showed its ineffectiveness in inhibiting the growth of bacteria or fungi according to the concentrations prepared.

**Keywords:** Antioxidant, Azo complexes, 4-aminoethyl-cyclohexanecarboxylic, Mass spectra, Thermal analysis.

## Introduction

An important group of organic compounds known as azo dyes contains at least one azochromophore ($R_1$-N=N-$R_2$)[1,2].There are two separate kinds of azo compounds depending on whether the R1 and R2 are alkyl or aryl groups[2]. One of the first synthetic organic chemicals, azo compounds are still produced on a considerable scale in the dye industry today[1,2]. The type of substituents and their locations on the aromatic ring define the azo. The color of dyes is dependent on how well they can absorb electromagnetic energy inthe visible spectrum (400–700 nm)[3,4]. According to Witttheory, a colored dye requires both an auxochrome group and a chromophore group. Auxochromes intensify the color of a colored molecule when added, while chromophores provide color to the dye because they can absorb visible light (such as nitro, azo, and quinoid groups). Witt theory has been replaced by the present electronic theory. According to this theory, color originates from visible light excitation of the valance p electrons[3]. These compounds are defined by the functionalgroup (-N=N-) connecting two symmetric or asymmetric symmetric or nonsymmetric alkyl or aryl radicals[4]. Azo dyes today make up the majority of dye chemistry production, and in the future, their relative importance might increase[5]. Azolo dyes are colored by azo bonds and the chromophores and auxochromesto they are attached to[6]. Due to their several effective groups that can form coordination complexes with a variety of metal ions, which are distinguished by their hues, high molar absorbance, and high stability, azo compounds are very important in many different domains of chemical study[7].The prepared complexes were characterized by different analysis methods, FT-IR, mass spectrum, UV-Vis spectrum, $^1$H-NMR and $^{13}$C-NMR, Thermal analysis, molar conductance, magnetic susceptibility, Chloride content, FAA and CHN elemental analysis. The metal ions (Zn (II), Cu (II), Co (II), Mn (II), Ni (II)) reacted with the azo ligand (N-(3-Acetyl-2-hydroxy-5-methyl-phenyl)-N-(4-carboxy-cyclohexylmethyl)-diazenium a molar ratio of 1:1:, the formula of complexes [M (L)(Cl)] have been synthesized and the complexes showed tetrahedral geometries. There was synthesis of new ligand and its complexes and determine their ability to inhibit free radicals by measuring their ability as antioxidants using DPPH as a free radical and ascorbic acid as a standard substance, and determining the value of $IC_{50}$, as it was found that the ligand had a high ability to inhibit free radicals, and the ability to inhibit the complexes varied according to the value of $IC_{50}$, and the results of inhibition indicated as follows (Ascorbic acid >LH >Zn-complex >Mn-complex > Co-complex >Cu-complex >Ni-complex). This study aims to synthesize a novel azo ligand that can combine with Zn (II), Cu (II), Co (II), Mn (II), and Ni (II) metal ions. The antioxidant activity of these compounds was evaluated against the DPPH radical and compared to that of a reference natural antioxidant, ascorbic acid, in addition to their characterization through spectroscopic analysis, thermal stability, and thermal decomposition, which were investigated using DSC and TGA curves.

## Materials and Methods

All ingredients, including chemicals and reagents, were bought from suppliers including Sigma-Aldrich, Merck, and others. The elemental experiments (C, H, and N) used the single-V.3.O-single Euro vector model EA/3000. Using a gravimetric approach, metal ions were calculated as metal oxides. The molar conductance of the complexes was determined with a Conductometer WTW at room temperaturein $1\times10^{-3}$ M. All of the complexes were dissolved in di-methyl formamide (DMF). Mass spectra for a variety of compounds were logged on a mass spectrometry (MS) QP50A: DI Analysis ShimadzuQP-2010-Plus (E170Ev) spectrometer. The UV-Vis spectra were examined using the UV-1800 Shimadzu. The proton nuclear magneticresonance ($^1$H-NMR and $^{13}$C-NMR) spectra of the ligand in DMSO-$d_6$ were captured using a Brucker 300MHz. Thermo gravimetricanalysis studies were carried out using the Perkin-Elmer Pyris Diamond TGA and the IR Prestige-21 to study the Fouriertransform infrared FT-IRspectra.

### Synthesis of azo dye ligand: N-(3-Acetyl-2-hydroxy-5-methyl-phenyl)-N-(4-carboxy-cyclohexylmethyl)-diazenium

Melted in amixture of 10 mL EtOH and 3 mL HCl conc, 1 mmole of 4-aminoethyl-cyclohexanecarboxylic acid was diazotizedat 5 °C with a 10% $NaNO_2$ solution[5]. An ethanolic solution was chilled, then 0.15 g (1 mmole) of a diazotized solution was added while stirring for 6 houres. This created 1-(2-Hydroxy-5-methyl-phenyl)-ethanone. Following that, an azo ligand precipitation (%Yield=78%)and dark-colored mixture were seen. Thisdeposit was filtered, rinsed for a certain amount of ounces with a (1:1) ($C_2H_5OH$: $H_2O$) solution, and then dried. The solution is displayed in Scheme 1. The $^1$H-NMR and $^{13}$C-NMR spectra of the ligand LH in DMSO-$d_6$ Figs. 1, 2 , respectively show the signals of the azo ligand. The $^1$H-NMR & $^{13}$C-NMR revealed a peak at δ (3.66) ppm, which was ascribed to N=N–$CH_2$ chemical changes. The chemical shift of ($CH_2$-$CH_2$) protons on cyclohexane ring was ascribed to the peaks at δ (2.38, 2.45) ppm, the signals at (12.0) and (8.75) ppm were ascribed to the protons of (OH) carboxylic group and phenolic group respectively. The aromatic protons of benzene groups are attributed to the numerous peaks at δ (7.73–7.72) ppm, while in the $^{13}$C-NMR shows signals in C15= 19.55, C16= 25.24, C1,2,4,5= 34.12-34.14, C3,6 =44.28, C7= 53.75, C12= 127.64, C9=

128.47, C10= 133.97, C11= 140.88, C13= 155.27, C17= 173.45, C14 = 194.97, respectively[8-10].

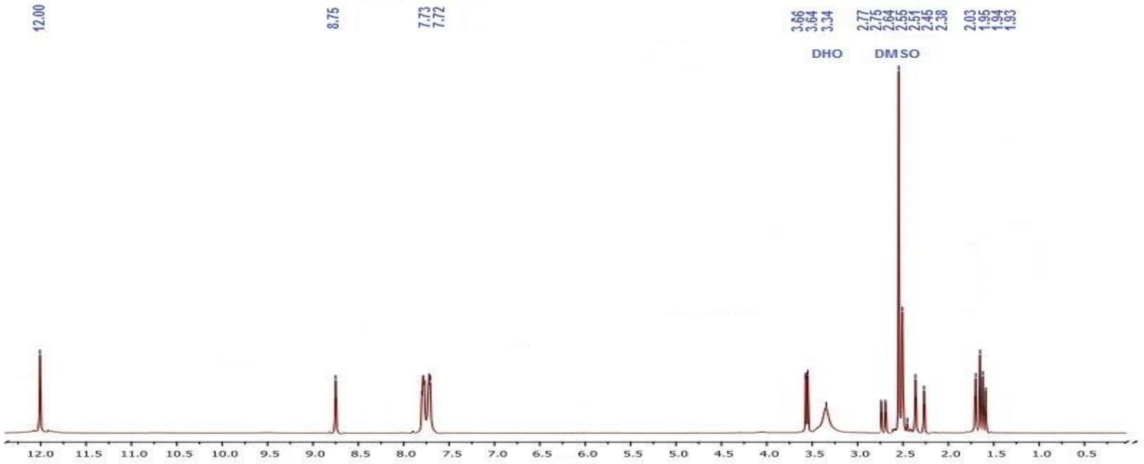


Figure 1. $^1$H-NMR spectrum of ligand

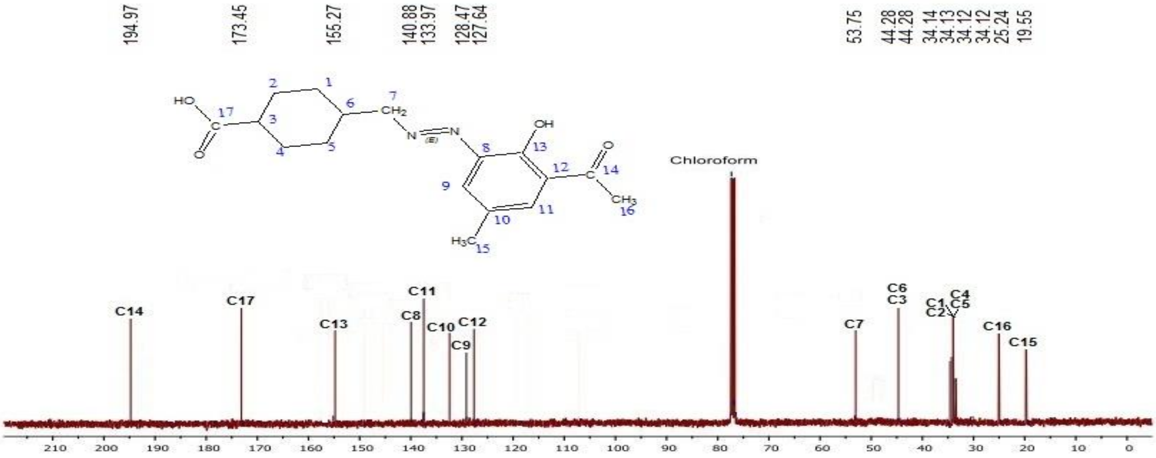
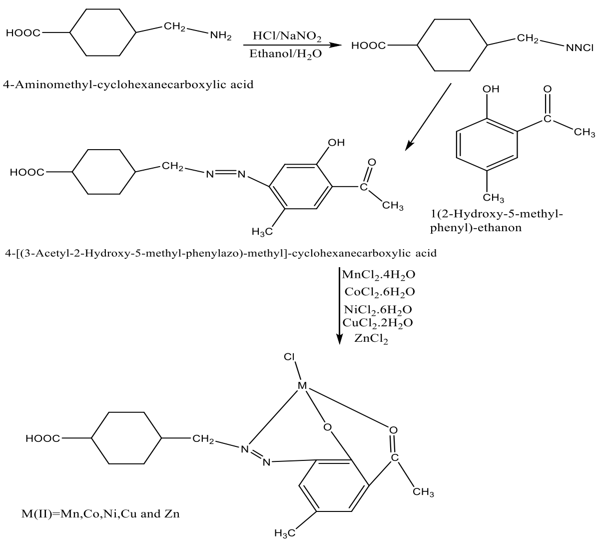


Figure 2. $^{13}$C-NMR spectrumof ligand(LH)

## Preparation of metallic Metal ions complexes

The metallic ions complexes for Mn (II), Co (II), Ni (II), Cu (II), and Zn (II) were made using metal chlorides. As a stoichiometric amount of [1:1] M:L for Mn (II) 0.1979g, Co (II) 0.357g, Ni (II) 0.358g,,Cu (II) 0.364g, and Zn (II) 0.136g chloride salts gradually added in dropwise additions, a stoichiometric amount of 0.319g (1m.mol) from azo ligand, dissolved in 10 mL pure ethanol, was stirred. The combination was brought to between (60 and 70)°C over the course of two hours, cooled in ice bath until precipitation started to form, and then permitted to stand overnight. To get rid of any unreacted components, the solid complexes were separated and washed with distilled water and a small amount of hot ethanol. Vacuum desiccators were then used to dry the compounds. The ligand and its metal complexes' analytic and physical characteristics are included in Table 1, Scheme 1. show the synthesis of compounds.



**Scheme 1. Synthesis of azo dye ligand and metal complexes**

## Results and discussion

The azo dye ligand (LH), which is a fine orange powder, stands out due to its amorphous nature. DMF and DMSO are both soluble in this synthesis ligand, but ethanol is by far the most user-friendly solvent. The resulting complexes of metallic ions and azo ligand were stable in the presence of air, and the analytic and physical characteristics are included in Table 1, the analysis results were compatible with theoretical calculated.

**Table 1. Pysical properties & analytical data of ligand & their complexes**

| Comp. | Chemical Formula M.$_{Wt}$ | Color | m.p °C | Elemental microanalysis% | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | C ( F.) | H (F.) | N (F.) | M (F.) | Cl(F.) |
| | | | | C (C.) | H (C.) | N (C.) | M (C.) | Cl(C.) |
| LH | $C_{14}H_{19}N_3O_3$ | orange | 188- | 65.07 | 7.11 | 7.77 | - | - |
| | 318.37 | | 190 | 64.13 | 6.97 | 8.80 | - | - |
| [MnLCl] | $C_{14}H_{20}ClN_3NiO_4$ | Light | 274- | 49.55 | 4.71 | 7.41 | 12.78 | 7.88 |
| | 407.75 | orange | 277d | 50.08 | 5.19 | 6.87 | 13.47 | 8.69 |
| [CoLCl] | $C_{28}H_{36}N_6PdO_6$ | | >300 | 50.11 | 4.89 | 7.55 | 13.79 | - |
| | 411.75 | brown | | 49.59 | 5.14 | 6.80 | 14.31 | - |
| [NiLCl] | $C_{28}H_{34}N_6PtO_6$ | brown | >300 | 48.99 | 4.59 | 7.74 | 13.27 | - |
| | 411.51 | | | 49.62 | 5.14 | 6.73 | 14.26 | - |
| [CuLCl] | $C_{14}H_{20}ClN_3NiO_4$ | brown | >300 | 50.01 | 4.59 | 7.41 | 16.17 | 8.79 |
| | 416.36 | | | 49.04 | 5.08 | 6.73 | 15.26 | 8.51 |
| [ZnLCl] | $C_{14}H_{20}ClN_3NiO_4$ | orange | >300 | 47.99 | 5.66 | 6.97 | 16.08 | 8.99 |
| | 418.20 | | | 48.82 | 5.06 | 6.70 | 15.64 | 8.48 |

**C.:Calculat, F.: Found**

### FT-IR spectroscopy

The infrared spectrum of the ligand LH gave multiple absorption bands ( 3459, 1451, 1671 and 3250 )cm$^{-1}$ Fig. 3 that could be attributed to the phenolic group, azo group, ketogenic and carboxylic carbonyl group, as well as other bands. Table 2 of IR spectra of all produced compounds revealed that the band of phenolic hydroxide disappeared in the complexes that means the ligand coordinated through this group in all complexes, and the ketonic carbonyl and azo groups shifted in the complex and showed new bands to (M-N, M-O and M-Cl) that means the azo-dye ligand connected to metal ions through three sites: the azo group's nitrogen site, oxygen of phenol group, and oxygen site of ketone group[11-14].As a result, the ligand behaved as an N,O,O tridentate ligand in all complexes.

**Table 2. The IR spectra bands (cm$^{-1}$) of compounds**

| Comp. | υOH carboxylic | υCO ketonic | υ(N=N) | Other bands |
|---|---|---|---|---|
| LH | 3250 | 1671 | 1451 | υOH phenolic(3459) |
| [MnLCl] | 3255 | 1644 | 1462 | υ M-N(510,462), υ M-O(424) υ M-Cl(380) |
| [CoLCl] | 3248 | 1637 | 1466 | υ M-N(480,468), υ M-O(429) υ M-Cl(385) |
| [NiLCl] | 3249 | 1642 | 1443 | υ M-(460,441), υ M-O(420) υ M-Cl(375) |
| [CuLCl] | 3250 | 1655 | 1469 | υ M-N(477,469), υ M-O(433) υ M-Cl(387) |
| [ZnLCl] | 3251 | 1653 | 1441 | υ M-(463,447), υ M-O(418) υ M-Cl(391) |

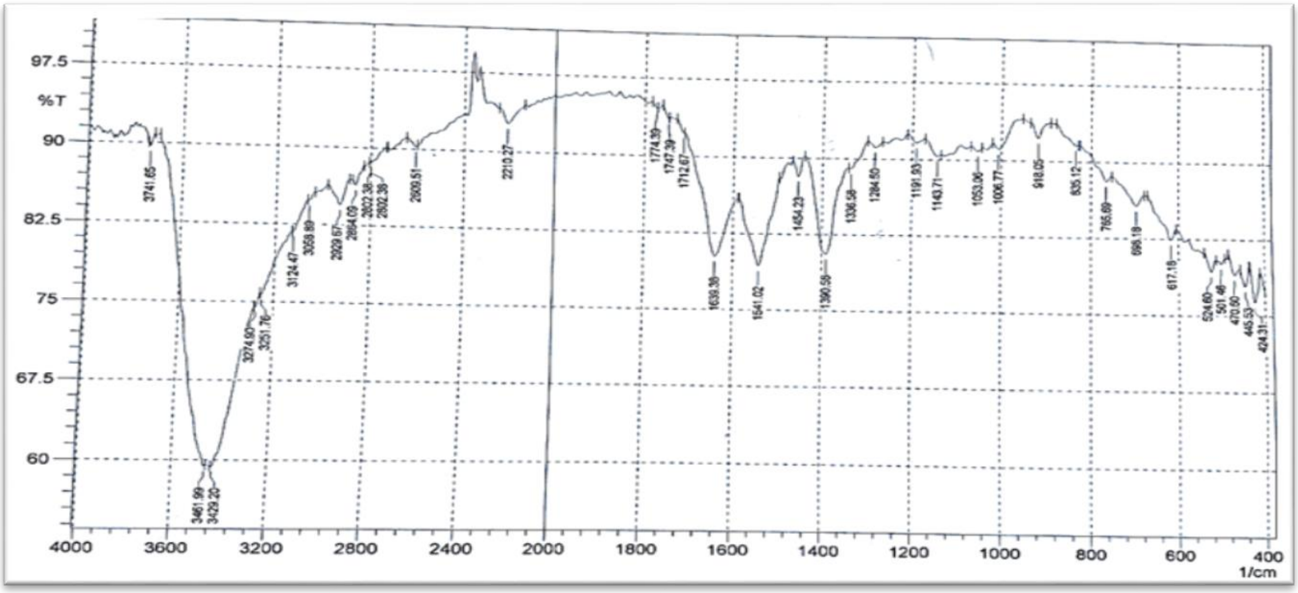


**Figure 3. FT.IR Spectrum of Ligand**

## UV-Vis spectra, mass Spectrum,molar conductivity and magnetic susceptibility

The UV–vis spectrum of the ligand gave multiple absorption peaks 269, 310 and 350 nm that could be attributed to $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$. The UV-Vis spectra of the Mn(II) complex are shown in Table 3 and Fig. 4, with peaks at 696 and 850 nm, 14368 and 11765 cm$^{-1}$, $^6A_1 \rightarrow {}^4T_{1G}$ , and , $^6A_1 \rightarrow {}^4A_{1G} + {}^4E_{(G)}$, and absorption maxima at 265 nm, 313 nm, and 345 nm attributable to the inter ligand and the C.T. M→L, respectively. The Co(II) complex's electronic spectra contained five absorption peaks[15,16]. The peak at 677 is assigned to the (d-d) electronic transitions types $^4A_2 \rightarrow {}^4T_{1(P)}$, whereas the peaks at 266, 312 and 357nm are attributed to the ligand, Fig. 5. The Ni(II) complex's electronicspectra showed six peaksat 266, 312 nm, 348 nm, and 357 nm that correspond to the inter ligand, as well as a peak at 410 nm that was assigned to the C.T( M→L), the peak at 797 nm is assigned to the (d-d) electronic transitions types $^3T_1 \rightarrow {}^3T_{1(P)}$, The peaks at 269, 316, and 360 nm in the Cu(II) complex were attributed to the inter ligand, with the peak at 405 nm correlating to the C.T (M→L)[17,18]. electronic transitions and the peak at 953 nm being assigned to the $^2T_2 \rightarrow {}^2E$ transition, implying a Td shape. Electronic spectra were useless due to the impossibility of d-d transitions, but the magnetic susceptibility of the Zn(II) complex revealed the presence of diamagnetic moments. This conclusion really agrees well with other studies on tetrahedral geometry [19,20].The measured molar conductivity are (11.6, 13.76, 9.21, 14.8 and 11.42) Λm (S.cm$^2$.mol$^{-1}$) nonelectrolyt for all complexes[20]. The magnetic measured was of the prepared Mn, Co, Ni, Cu-complexes shown in Table 3, the magnetic value 5.45,4.10,3.9 and 1.73 B.M. respactivly. This agrees with tetrahedral geometry for all complexes. The Zn-complex have diamagnetic properties[20].

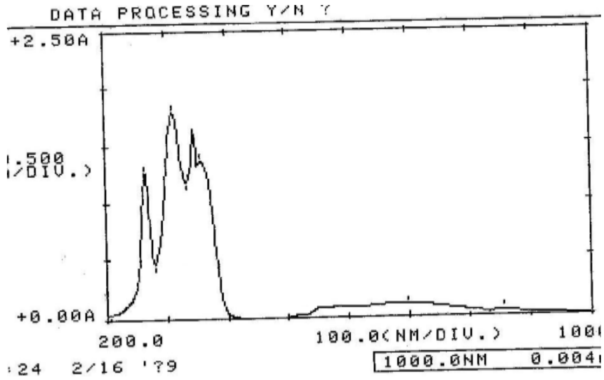


**Figure. 4 UV-Vis spectra of Mn-complex**

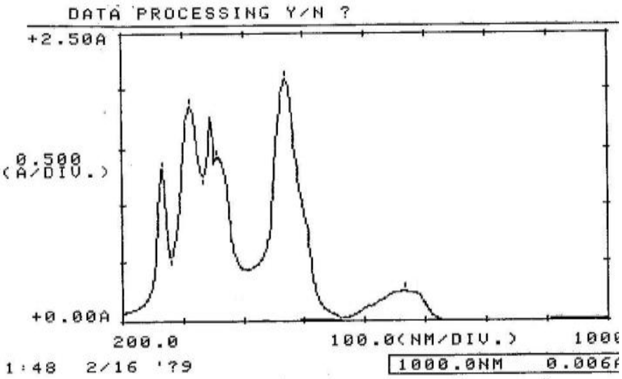


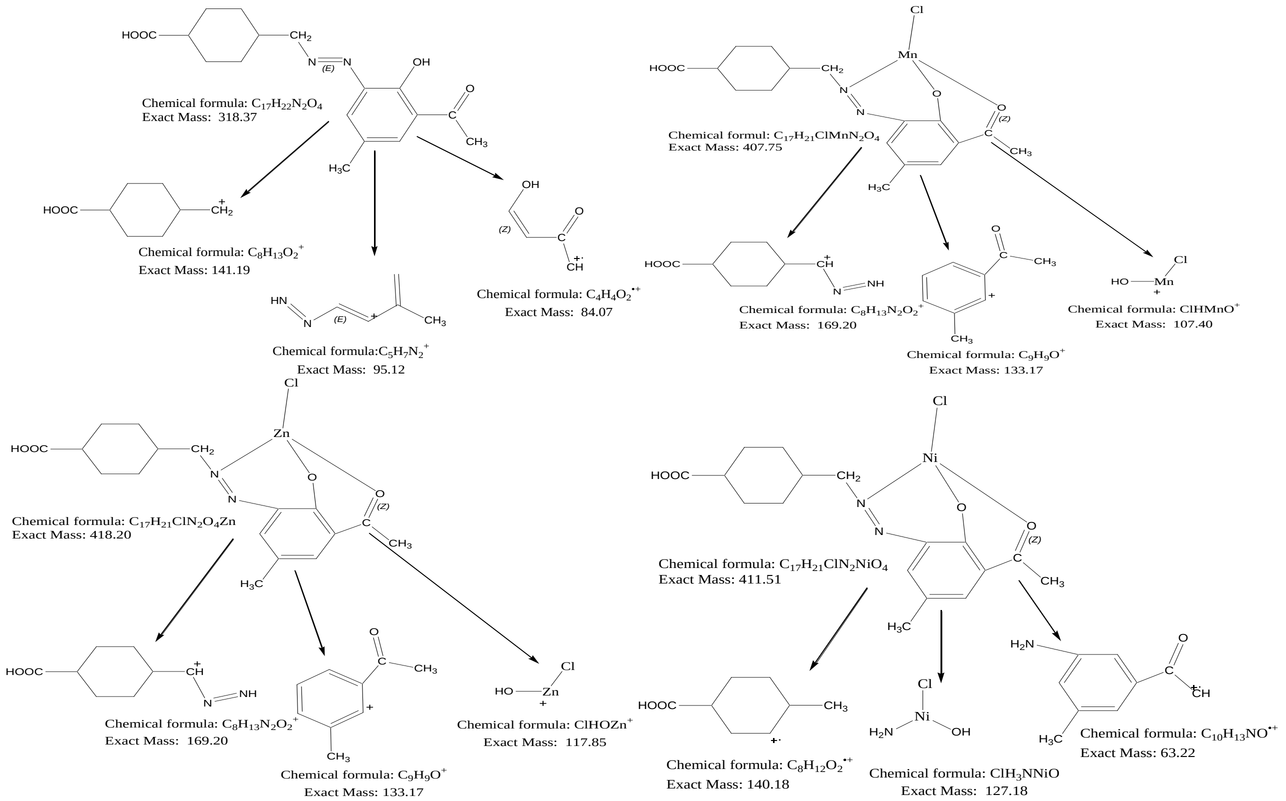
**Figure. 5 UV-Vis spectra of Co-complex**

**Table 3. Electronic spectral dataof the compounds and molar conductivity in DMF (1 × 10$^{-3}$ M)**

| Comp. | λ nm | ύ cm$^{-1}$ | ABS | ε L. mol$^{-1}$cm$^{-1}$ | Assignment | Λ S.cm$^{2}$ mol$^{-1}$ | $\mu_{eff}$ B.M |
|---|---|---|---|---|---|---|---|
| [MnLCl] | 265 | 37735.8 | 1.266 | 1266 | Inter ligand | 11.6 | 5.45 |
| | 313 | 31948.8 | 1.781 | 1781 | Inter ligand | | |
| | 345 | 28985.5 | 1.610 | 1610 | Inter ligand | | |
| | 357 | 28011.2 | 1.368 | 1368 | C.T | | |
| | 696 | 14367.8 | 0.216 | 216 | $^{6}A_{1} \rightarrow {}^{4}A_{1}+{}^{4}E_{(G)}$ | | |
| | 850 | 11764.7 | 0.068 | 68 | $^{6}A_{1} \rightarrow {}^{4}T_{1G}$ | | |
| [CoLCl] | 266 | 37593 | 1.327 | 1327 | Inter ligand | 13.76 | 4.10 |
| | 312 | 32051.2 | 1.851 | 1851 | Inter ligand | | |
| | 357 | 28011.2 | 1.423 | 1423 | Inter ligand | | |
| | 485 | 20618.5 | 2.167 | 2167 | C.T | | |
| | 677 | 14771.0 | 0.306 | 306 | $^{4}A_{2} \rightarrow {}^{4}T_{1(P)}$ | | |
| [NiLCl] | 266 | 37593.9 | 1.368 | 1368 | Inter ligand | 9.21 | 3.9 |
| | 312 | 32051.2 | 1.866 | 1866 | Inter ligand | | |
| | 348 | 28735.6 | 1.788 | 1788 | Inter ligand | | |
| | 357 | 28011.2 | 1.411 | 1411 | Inter ligand | | |
| | 410 | 24390.2 | 0.186 | 186 | C.T | | |
| | 797 | 12547.0 | 0.102 | 102 | $^{3}T_{1} \rightarrow {}^{3}T_{1(P)}$ | | |
| [CuLCl] | 269 | 37174.7 | 1.760 | 1760 | Inter ligand | 14.8 | 1.73 |
| | 316 | 31645.5 | 1.587 | 1587 | Inter ligand | | |
| | 360 | 27777.7 | 1.508 | 1508 | Inter ligand | | |
| | 405 | 24691.3 | 2.016 | 2016 | C.T | | |
| | 953 | 10493.1 | 0.528 | 528 | $^{2}T_{2} \rightarrow {}^{2}E$ | | |
| [ZnLCl] | 269 | 37174.7 | 1.744 | 1744 | Inter ligand | 11.42 | diamagnatic |
| | 325 | 30769.2 | 1.482 | 1482 | Inter ligand | | |
| | 337 | 29673.5 | 1.507 | 1507 | Inter ligand | | |
| | 390 | 25461.0 | 2.216 | 2216 | Inter ligand | | |
| | 465 | 21505.3 | 2.462 | 2462 | C.T | | |

### LC-Mass measurements

The electron impact of fragmentation was used to get the mass spectra of the novel ligand and metal complexes. High-resolution MS was generally used to recover significant fragments linked to breakdown products as well as the free azo ligand and its complexes[21]. In Fig. 6, you can see the ligand LH electron impact mass spectrum. The computed molecular weight of this ligand is 318.27 g/mol. A peak at 141.19 m/z in the spectrum was attributed to $C_8H_{13}O_2^+$, while additional notable peaks at 95.12 and 84.07 m/z may have been caused by other components. Their brilliance denotes the stability of the parts, Fig.7 shows the Mn(II) complex's electron impact mass spectrum. A peak at 407.75 m/z in the spectra allowed researchers to pinpoint the complexmoiety $C_{17}H_{21}ClN_2MnO_4$. The peaks at 169.20, 133.17, and 107.40 m/z, which are all distinctive, possibly belong to different parts. The mass spectrum of the Ni(II) complex displays a peak at 411.51 m/z that matched the $C_{17}H_{21}ClN_2NiO_4$ complexmoiety. The odd peaks at 140.18, 127.18, and 63.22 m/z could be the result of other fragments. Fig. 8 illustrates the Zn(II) complex's mass spectrum. The signal at 418.20 m/z in the spectra allowed the identification of the chemical moiety $C_{17}H_{21}ClN_2O_4Zn$.The components maybe responsible for the peculiar peaks at 196.20, 133.17, and 117.85 m/z. The structural assignments of the pieces and possible fragmentation routes are provided in Scheme 2 [22,23].



**Scheme 2. Fragmentation pattern of ligand and its complexes**

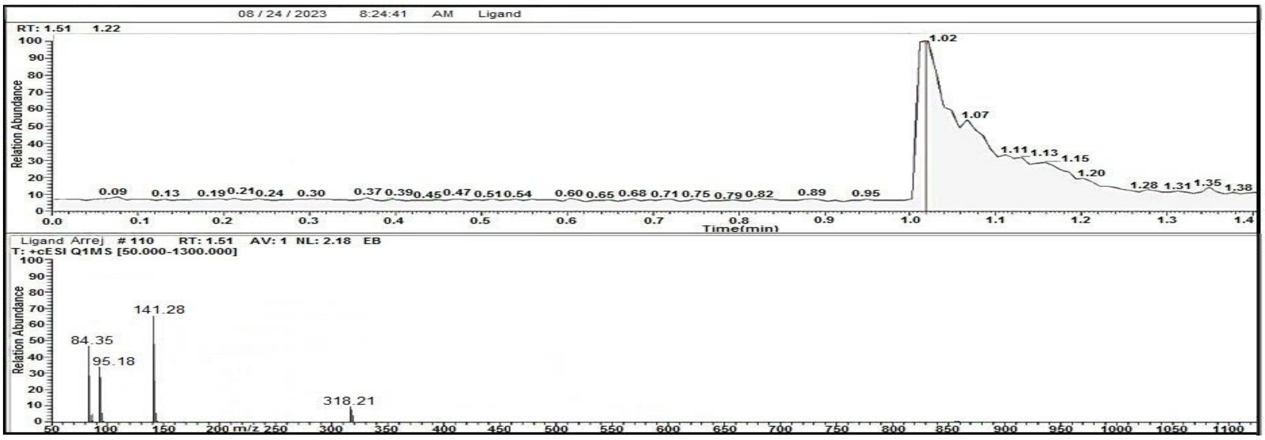


Figure 6. LCMass spectrum of ligand

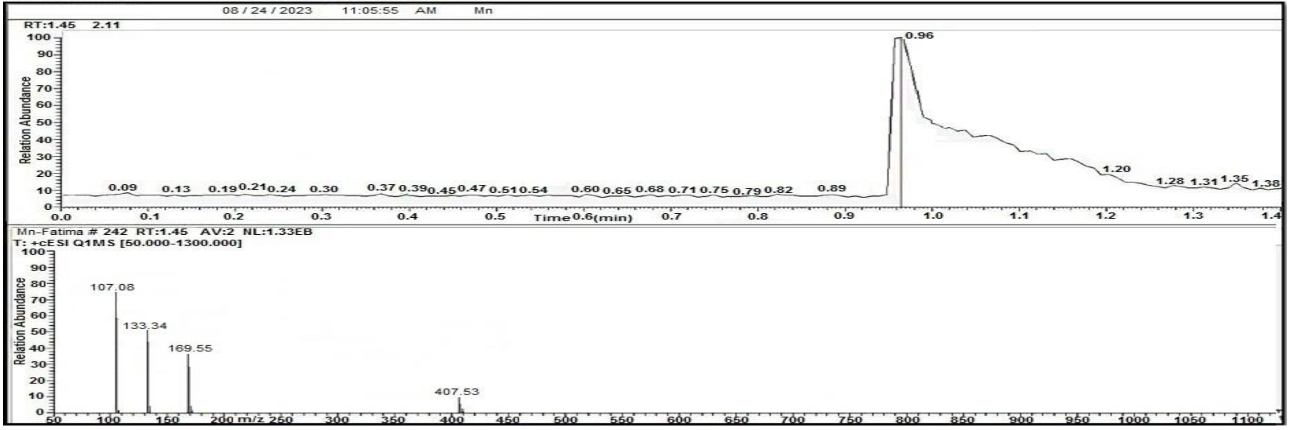


Figure 7. LCMass spectrum of Mn-Complex

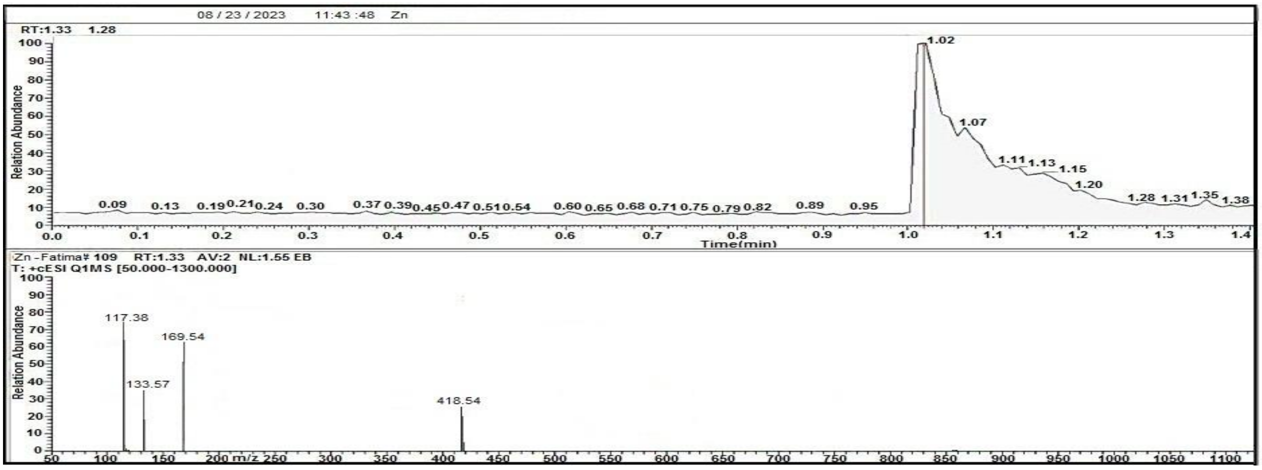


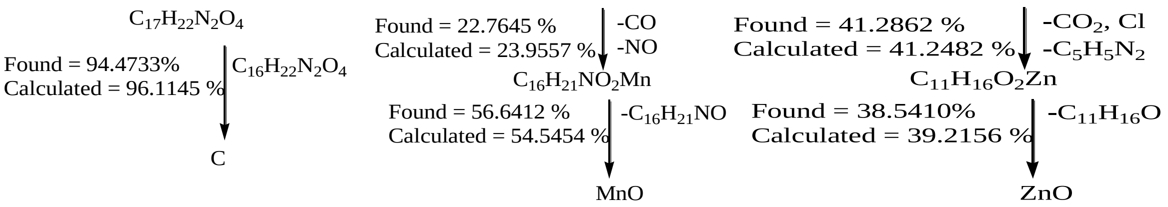
Figure 8. LCMass spectrum of Zn-Complex

**Thermal measurements**

The thermal breakdown of the ligand LH and their metal complexes was observed by DSC and TGA, as shown in Figs. 9 -11. Information on the thermal deterioration process can be found in table 4. The produced substances showed a decomposition in the thermogravimetric decomposition curve, with the ligand displaying minimal thermal stability at 111°C and the complexes exhibiting minimal stability at 129°C for Mn complexes and 99°C for Zn complexes. The information in Scheme 3 and Table 4 shows that the ligand decomposes in one degree while leaving a portion intact and that Mn decomposes in two ranges while leaving a residue intact. However, the Zn combination disintegrates with a complete residue in two step. This corresponds with both the calculated valuesand the proposed formula[24-26]. The DSC curve values for the ligand gave three phases that were endothermic (Δ H =-14.2, -6.3 and 11.0) and Mn complex gave three phases that were endothermic (ΔH =-12.5, -6.8 and 11.5) and Zn complex gave three phases that were endothermic (ΔH =-14.2, -4.0 and 4.1)[26,27].

**Table 4. TGA data of the ligand HLand some complexes**

| Complexes | Step | $T_i$/°C | $T_f$/°C | Tmax | Weight mass loss% Calc | Weight mass loss% Found | Reaction |
|---|---|---|---|---|---|---|---|
| Ligand | 1 | 111.351 | 594.515 | 247.362 | 96.1145 | 94.4733 | $-C_{16}H_{22}N_2O_4$<br>C |
| Calculated: 96.1145 %final=3.8855 %; Estimated 94.4733 %final=5.5267 % | | | | | | | |
| Mn-complex | 1 | 129.265 | 309.688 | 192.431 | 23.9557 | 22.7645 | -CO, -NO |
| | 2 | 309.688 | 593.931 | 401.830 | 54.5454 | 56.6412 | $-C_{16}H_{21}NO$<br>MnO |
| Calculated:78.5011 % final =21.4989 %;Estimated 79.4057% final =20.5943% | | | | | | | |
| Zn-complex | 1 | 99.435 | 330.148 | 201.820 | 41.2482 | 41.2862 | $-Cl, -CO_2, -C_5H_5O$ |
| | 2 | 330.148 | 594.902 | 413.951 | 39.2156 | 38.5410 | $-C_{11}H_{16}O$<br>ZnO |
| Calculated:80.4638 % final =19.5362 %;Estimated 79.8272 % final =20.1728% | | | | | | | |



Scheme 3. TG decomposition of Ligand and Mn , Zn Complexes

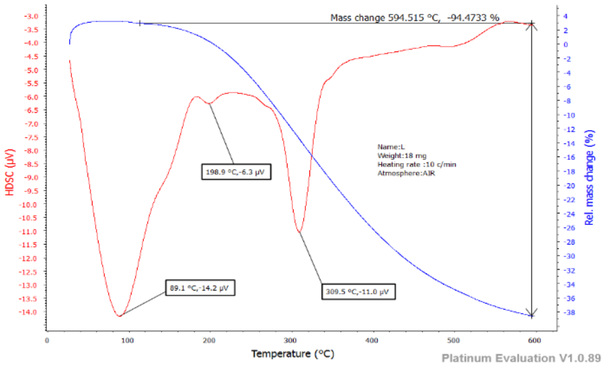


Figure 9. TGA &DSCof Ligand

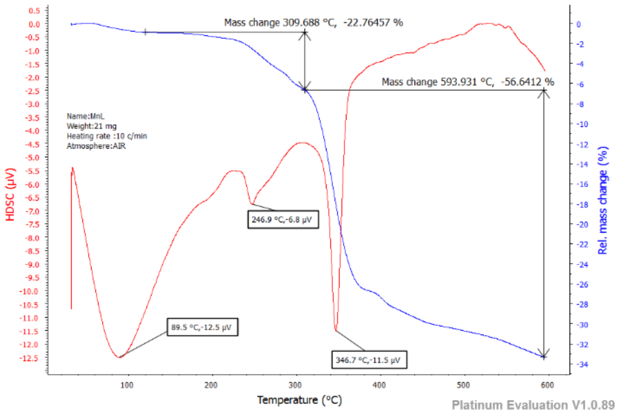


Figure 10. TGA &DSCof Mn-complex

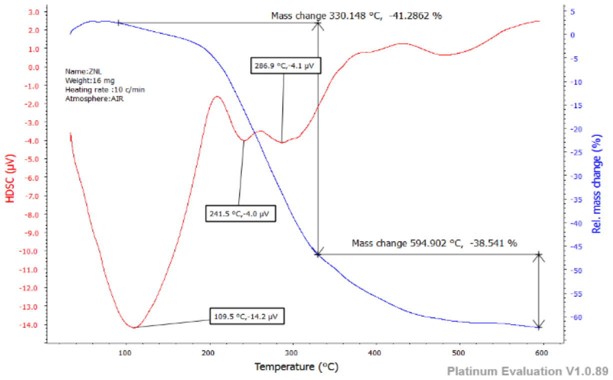


Figure 11. TGA &DSC of Zn-complex

### Spector photometric determination of DPPH radical scavenging efficiency

Because of its straightforward procedure accuracy, DPPH tests are typically used to evaluate the anti-oxidant effectiveness of its objectives. According to Table 5, the results of the compounds' efficiency at scavenging DPPH radicals are shown. Better DPPH radical-scavenging effectiveness is indicated by a lower Depress $IC_{50}$ value[28,29]. The table clearly shows that almost all of the compounds have effective radical scavenging properties when tested using the DPPH method. It is important to keep in mind that the Schiff base of the complex was more effective as an antioxidant than azo day was see Table 5. The efficiency of DPPH radical scavenging is also impacted by the presence of azo and -OH groups. Additionally, the antioxidant's capabilities are unaffected by the ethylene spacer[30,31]. As a result, while a check the sample solution is added, the free radical is equalized through the exam sample, which either contributes hydrogen or an electron to result in free radical neutralization[32,33]. Due to the neutralization of the free radical, the screening sample will produce fewer radicals. The results are as follows (Ascorbic acid >LH >Zn-complex >Mn-complex > Co-complex >Cu-complex >Ni-complex) showed its ineffectiveness in inhibiting the growth of bacteria or fungi according to the concentrations prepared. [34,35].

Table 5.The antioxidant results of ligand and their metal complexes

| Comp. | Conc. Mg/mL | PI | RSA | $IC_{50}$ mg/mL |
|---|---|---|---|---|
| Ligand | 0.260 | 39.26 | 60.74 | 0.124 |
| | 0.130 | 43.12 | 56.88 | |
| | 0.065 | 56.88 | 43.12 | |
| | 0.033 | 65.76 | 34.24 | |
| [MnLCl] | 0.260 | 56.45 | 43.55 | 0.316 |
| | 0.130 | 61.60 | 38.40 | |
| | 0.065 | 71.06 | 28.94 | |
| | 0.033 | 82.66 | 17.34 | |
| [CoLCl] | 0.326 | 70.49 | 29.51 | 0.635 |
| | 0.163 | 89.54 | 10.46 | |
| | 0.081 | 93.98 | 6.02 | |

| | | | | |
|---|---|---|---|---|
| | 0.041 | 98.14 | 1.86 | |
| [ZnLCl] | 0.113 | 67.48 | 32.52 | 0.186 |
| | 0.057 | 82.38 | 17.62 | |
| | 0.028 | 97.28 | 2.72 | |
| | 0.014 | 99.14 | 0.86 | |
| [CuLCl] | 2.083 | 52.87 | 47.13 | 2.234 |
| | 1.042 | 60.03 | 39.97 | |
| | 0.521 | 68.34 | 31.66 | |
| | 0.260 | 77.65 | 22.35 | |
| Ascorbic acid | 0.062 | 15.27 | 85.19 | 0.022 |
| | 0.031 | 39.08 | 62.07 | |
| | 0.016 | 61.07 | 40.74 | |
| | 0.008 | 74.81 | 27.41 | |

## Conclusion

A new azo ligand was synthesized in this work, and it was used to prepare a series of complexes using equal molar ratios (1:1) of the Ligand: Metal. After verification through spectroscopic (ultraviolet and infrared) and diagnostic analysis techniques, all of the complexes in the neutral formula showed tetrahedral shapes, and the ligand is tridentate (NOO) related to azo, keton, and phenolic hydroxyl group, respectively. Azo compounds are a family of chemicals with clear pharmacological applications and are well-known in the literature.These substances and their metal complexes exhibited potent antioxidant qualities. Even though combining antioxidant functional groups increases their antioxidant potential, it is still necessary to investigate the antioxidant characteristics of those that have already been created and to create new antioxidant functional group complexes with additional qualities.

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## Author’s Declaration

- Conflicts of Interest: None.
- We hereby confirm that all the Figures and Tables in the manuscript are ours. Furthermore, any Figures and images, that are not ours, have been included with the necessary permission for re-publication, which is attached to the manuscript.
- No animal studies are present in the manuscript.
- No human studies are present in the manuscript.
- No potentially identified images or data are present in the manuscript.
- Ethical Clearance: The project was approved by the local ethical committee at University of Baghdad.

## Author's Contributions Statements

R.K.H.: conducted part of the practical side of the research, analysis of the results, writing the manuscript and correspondent the journal. A.A.S.: conceived the idea of the research, contributed to the analysis of the results, conducted part of the practical side of the research, and did the revision and the proofreading of the manuscript. E.A.E.: conducted part of the practical side of the research and analysis of the results.

## References

1. Mohammed HS, Al-Hasan HA, Chaieb Z, Zizi Z, Abed HN. Synthesis, characterization, DFT calculations and biological evaluation of azo dye ligand containing 1, 3-dimethylxanthine and its Co (II), Cu (II) and Zn (II) complexe. Bull Chem Soc Ethiop. 2023; 37(2): 347-56. https://dx.doi.org/10.4314/bcse.v37i2.8.

2. Kareem IK, Hadi MA. Synthesis and characterization of some transition metal complexes with new azo-schiff base ligand 3, 4-bis [((1E, 2E)-2-((2-((4-((Z)-(3-Hydroxyphenyl) Diazenyl) Naphthalen-1-yl) amino) ethyl) imino)-1, 2-Diphenylethylidene) Amino) Phenyl)(phenyl] Methanone. Egypt J Chem. 2020 Jan 1; 63(1): 301-13. https://doi.org/10.21608/ejchem.2019.18924.2166
3. Hassan AS. Problems and solutions in colors, dyes and pigments chemistry: A Review, Chem Int. 2017; 3(2): 97-105. https://doi.org/10.31221/osf.io/4hmsw
4. Abdulrazzaq AG, Al-Hamdani AA. Ni$^{2+}$, Pt$^{4+}$, Pd$^{2+}$, and Mn$^{2+}$ Metal ions Complexes with Azo Derived from Quinolin-2-ol and 3-amino-N-(5-methylisoxazol-3-yl) Benzenesulfonamide: Synthesis, Characterization, Thermal Study, and Antioxidant Activity. Baghdad Sci J. 2023; 20(6): 2207-2223. https://doi.org/10.21123/bsj.2023.7708
5. Hamza IS, Mahmmoud WA, Al-Hamdani AA, Ahmed SD, Allaf AW, Al Zoubi W. Synthesis, characterization, and bioactivity of several metal complexes of (4-Amino-N-(5-methyl-isaxazol-3-yl)-benzenesulfonamide). Inorg Chem Commun. 2022 Oct 1; 144: 109776. https://doi.org/10.1016/j.inoche.2022.109776
6. Parveen S. Recent advances in anticancer ruthenium Schiff base complexes. Appl Organomet Chem. 2020 Aug; 34(8): e5687. https://doi.org/10.1002/aoc.5687
7. El-Habeeb AA , Refat MS. Synthesis, structure interpretation, antimicrobial and anticancer studies of tranexamic acid complexes towards Ga (III), W(VI), Y(III) and Si (IV) metal ions. J Mol Struct. 2019; 2019(1175): 65-72.https://doi.org/10.1016/j.molstruc.2018.07.099
8. Al-Daffaay RKH. Preparation-and Spectroscopic Characterization of Transition Metal Complexes with Schiff base 2-[1-(1H-indol-3-yl)ethylimino) methyl]naphthalene-1-ol, Baghdad Sci J. 2022; 19(5): 1036-1044. https://doi.org/10.21123/bsj.2022.6162
9. .Reda SM, Al-Hamdani AAS. Mn (II), Fe (III), Co (II) and Rh (III) complexes with azo ligand: Synthesis, characterization, thermal analysis and bioactivity, Baghdad Sci J. 2022; 91(5): 890–896. https://doi.org/10.21123/bsj.2022.7289
10. Nakamoto K. Infrared and Raman Spectra of Inorganic and Coordination Compounds, Wiley-Inter Science: New York. 1997.ed$^{3}$: 197-210. https://doi.org/10.1002/97804704058
11. Reem GD, Walaa HM, Gehad GM. Metal complexes of tetradentateazo-dye ligand derived from 4,4-oxydianiline: Preparation, structural investigation, biological evaluation and MOE studies, App Org Chem.2020; 34(10): 1-20.https://doi.org/10.1002/aoc.5883
12. Ibraheem IH, Mubder NS, Abdullah MM, Al-Neshmi H. Synthesis, characterization and bioactivity Study from azo-ligand derived frommethyl-2-amino benzoate with some metal ions, Baghdad Sci J. 2023; 20(1): 0114-0114.. https://doi.org/10.21123/bsj.2022.6584
13. Mihsen HH, Abass SK,Abed –Alhasan MT, Hassan ZM, Abbas AK. 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, Iraqi J Sci. 2020; 61(11): 2762-2775. https://doi.org/10.24996/ijs.2020.61.11.2
14. Nagasundaram N, Govindhan C, Sumitha S, Sedhu N, Raguvaran K, Santhosh S, et. al. Synthesis, characterization and biological evaluation of novel azo fused 2, 3-dihydro-1H-perimidine derivatives: In vitro antibacterial, antibiofilm, anti-quorum sensing, DFT, in silico ADME and Molecular docking studies, J Mol Struct. 2022; 1248: 131437. https://doi.org/10.1016/j.molstruc.2021.131437
15. Greay WJ. The use of conductivity measurements in organic solvents for the characterisation of coordination compounds, Cood Chem Rev. 1971; 7(1): 81-122. https://dx.doi.org/10.1016/S0010-8545(00)80009-0
16. Al-Hamdani AAS, Al-Alwany TAM, Mseer MA, Fadhel AM, Al-Khafaji YF. Synthesis, Characterization, Spectroscopic, Thermal and Biological Studies for New Complexes with N1, N2-bis (3-hydroxyphenyl) Oxalamide. Egy J. Chem. 2023; 66(4) : 223-235. https://doi.org/10.21608/EJCHEM.2022.144403.6297
17. Shaalan N. Preparation, Spectroscopy, Biological Activities and Thermodynamic Studies of New Complexes of Some Metal Ions with 2-[5-(2-Hydroxy-Phenyl)-1, 3, 4-Thiadiazol-2-Ylimino]-Methyl-Naphthalen-1-Ol] . Baghdad Sci J. 2022; 19(4): 0829. https://doi.org/10.21123/bsj.2022.19.4.0829
18. Gajanan D, Anand A. Show moreSynthesis, spectral characterization, thermo-kinetic and biological studies of some complexes derived from tridentate hydrazone Schiff base, J Saudi Chem Soc. 2021; 25(10): 1-18. https://doi.org/10.1016/j.jscs.2021.101325
19. Kundalkesha D G, Rahul M K, Sachin A D, Panchsheela A U, Pratibha CD, Rekha MO, et. al., Chemical synthesis, spectral characterization and biological activities of new diphenylsulphone derived Schiff base ligand and their Ni(II) complexes. Results Chem. 2022; 4(24): 100617. https://doi.org/10.1016/j.rechem.2022.100617
20. Geary WJ. The use of conductivity measurements in organic solvents for the characterisation of coordination compounds. Coord Chem Rev. 1971; 7(1): 81–122. http://dx.doi.org/10.1016/S0010-8545(00)80009-0
21. Refatab MS., Alghoola S., Robson FF. Synthesis, spectral, and thermal studies of Cu(II), Ni(II), Fe(III), and Sn(II) complexes with captopril drug. Synth

React Inorg M. 2010; 40(9).Pages? https://doi.org/10.1080/15533174.2010.509295

22. Asim N, Amin MH, Alghoul MA, Sulaiman SN, Razali H, Akhtaruzzaman M, et. al. Developing of chemically treated waste biomass adsorbent for dye removal. J Nat Fibers. 2021; 8(7), 968-977. https://doi.org/10.1080/15440478.2019.1675214
23. Sudhakar C, Saravanabhavan M, Ramesh KS, Badavath VN, Chandrasekar S , Babu B, et. al. Pharmacological and quantum chemical studies of 2-aminobenzo[d]thiazol-3-ium 4-chlorobenzenesulphonate: Synthesis, spectral, thermal analysis and structural elucidation. Results Chem. 2022; 4 (100442): 1-11. https://doi.org/10.1016/j.rechem.2022.100442
24. Manika R , Chavan VL. Thermal and Antimicrobial studies of Synthesized and Characterized Rhodium, Platinum and Gold Metal Complexes Derived from (2E) N-(naphthalen-2yl)-3 phenyl prop-2en-1 imine Schiff Base. J Sci Res. 2021**;** 65(2): 30-38. https://doi.org/10.37398/JSR.2021.650206
25. Sahar YJ, Mohammed H, Al-Abady ZN. Synthesis and characterization of new metal complexes containing azo-indole moiety and anti-leukemia human (HL-60) study of its palladium (II) complex. Results Chem. 2023; 1(1): 100847. https://doi.org/10.1016/j.rechem.2023.100847
26. Subhash, Chaudhary A , Jyoti M. Synthesis, structural characterization, thermal analysis, DFT, biocidal evaluation and molecular docking studies of amide-based Co(II) complexes. ChemPap. 2023; 77: 5059–5078. https://doi.org/10.1007/s11696-023-02843-y
27. Ashrafzzaman MD, Camellia FK, Al-Mahmud A, Pramanik JMD, Nahar K., Haque MDM et al. Bioactive Mixed Ligand Metal Complexes Of Cu(II), Ni(II), And Zn(II) Ions: Synthesis, Characterization, Antimicrobial And Antioxidant Properties. J Chil Chem Soc. 2021; 66(3): 5295-5299. http://dx.doi.org/10.4067/S0717-97072021000305295
28. Mohamd GG, Mahmoud WH, Refaat AM, Nano-Azo Ligand and Its Superhydrophobic Complexes: Synthesis, Characterization, DFT, Contact Angle, Molecular Docking, and Antimicrobial Studies. J Chem. 2020; 2020: 1-9. https://doi.org/10.1155/2020/6382037
29. Keshavayya J, Pushpavathi I, Keerthikumar CT, Maliyappa MR, Ravi BN. Synthesis, characterization, computational and biological studies of nitrothiazole incorporated heterocyclic azo dyes.Str Chem. 2020; 31 (4): 1317-1329. https://doi.org/10.1007/s11224-020-01493-0
30. Abd SS, Alkam HH, Al-Shemary RKR, Composition, depiction, antibacterial, antioxidant, and cytotoxicity activities studies of a new nano-sized binuclear metal (II) Schiff base complexes, AIP Conf. Proc. 2023; 2414(1). https://doi.org/10.1063/5.0121776
31. Norma FS, Raúl SC, Claudia VC and Beatriz HC. Antioxidant Compounds and Their Antioxidant Mechanism , 2019.ed[1]: 26-35. https://doi.org/10.5772/intechopen.85270
32. Vhanale B, Kadam D, Shinde A. Synthesis, spectral studies, antioxidant and antibacterial evaluation of aromatic nitro and halogenated tetradentate Schiff bases. Heliyon. 2022; 8(e09650): 1-7. https://doi.org/10.1016/j.heliyon.2022.e09650
33. Saleh TA, Al-Samarrai RRH, Abdul-Razzaq NE. The antioxidant and antimicrobial activity for some new synthesized Schiff bases derived from Ascorbic acid. Int J Res Pharm Sci. 2019; 10(2): 1510-1515. https://doi.org/10.26452/ijrps.v10i2.730
34. Mohammed HS. Synthesis and Characterization of Some Complexes of Azo-Chalcone Ligand and Assessment of their Biological Activity. Mater Plast. 2021; 58(3): 23-31. https://doi.org/10.37358/MP.21.3.5500
35. Ozdemir O. Bis-azo-linkage Schiff bases—Part (II): Synthesis, characterization, photoluminescence and DPPH radical scavenging properties of their novel luminescent mononuclear Zn (II) complexes. J Photochem Photobiol A: Chem. 2020; 392: 112356. https://doi.org/10.1016/j.jphotochem.2020.112356

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# تحضير وتشخيص ودراسة تحلل حراري لمعقدات بعض ايونات المعادن وتقييم فعاليتها كمضادات اكسدة

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## الخلاصة

وفقاً للدراسات السابقة تم تحضير ليكاند آزو جديد (ن-(3-اسيتايل-2-هيدروكسي-5-مثيل-فنيل)ن-(4-كاربوكسي-سايكلوهكسيل مثيل)-ملح الدايازونيوم) وبعد التحقق من الصيغة المقترحة وفق نتائج التحاليل وبعد استخدام الليكاند لتحضير سلسلة ن المعقدات باستخدام نسب مولية متساوية (1:1) من الليكاند وتفاعلها مع كل من املاح المنغنيز والكوبلت والنيكل والنحاس والخارصين وبعد التحقق وفق تقنيات التحاليل الطيفية والتشخيصية(الاشعة فوق البنفسية والاشعة تحت الحمراء) التي اعطت اشكال رباعية السطوح لكل المعقدات بصيغة متعادلة والليكاند ثلاثي السن من نوع (نيتروجين- اوكسجين- اوكسجين) ثم دراسة التحلل الحراري لبعض المركبات المحضرة بتقنية التحليل الوزني الحراري و المسعر التفاضلي مطيافية الكتلة . استخدم الصبغة المعقدات المحضرة منها لتحدد قابليتها على كبح الجذور الحرة من خلال قياس قابليتها كمضادات اكسدة باستخدام مادة DPPH كجذر حر وحامض الاسكوربك كمادة قياسية وتحديد قيمة $IC_{50}$ حيث وجد ان الليكاند يمتلك قابلية عالية على كبح الجذور الحرة والمعقدات تفاوتت قابليتها على الكبح حسب قيمة $IC_{50}$ وكانت النتائج كما يلي
(Ascorbic acid >LH >Zn-complex >Mn-complex > Co-complex >Cu-complex)

**الكلمات المفتاحية:** مضادات اكسدة، معقدات الازو، 4-امينو مثيل-سايكلوهكسان كاربوكسيلك، اطياف الكتلة، التحاليل الحرارية.