

2025

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Al-Daffay, Rasha Khider Hussain; Al-Hamdani, Abbas Ali Salih; and Elluhaibi, Emran Abduljabbar Emran (2025) "Synthesis, Characterization and Studying Thermal Analysis for Complexes of Some Metal Ions and Determining Their Activity as Antioxidants," *Baghdad Science Journal*: Vol. 22: Iss. 3, Article 6.
DOI: <https://doi.org/10.21123/bsj.2024.9644>

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RESEARCH ARTICLE

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 in the visible spectrum (400–700 nm).^{3,4} According to Witt theory, 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 functional group (-N=N-) connecting

Received 24 September 2023; revised 18 March 2024; accepted 20 March 2024.
Available online 18 March 2025

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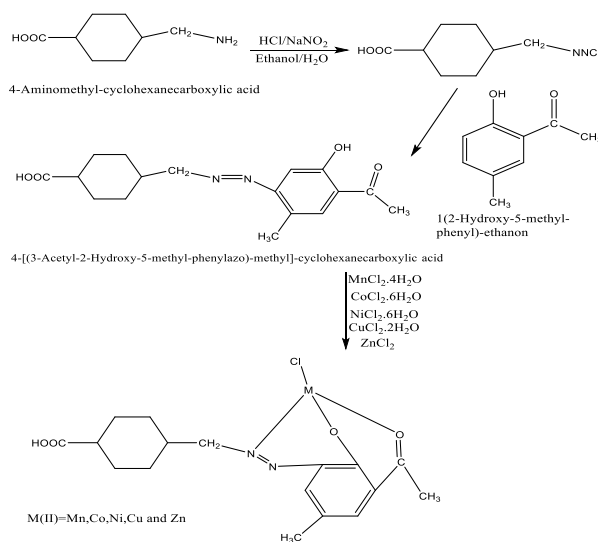
<https://doi.org/10.21123/bsj.2024.9644>

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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 Azo dyes are colored by azo bonds and the chromophores and auxochromes 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, ¹H-NMR and ¹³C-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)-diazonium 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 IC₅₀, 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 IC₅₀, 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.3.0-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 temperature in 1×10^{-3} M. All of the complexes were dissolved in



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

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 magnetic resonance (¹H-NMR and ¹³C-NMR) spectra of the ligand in DMSO-d₆ were captured using a Bruker 300 MHz. Thermo gravimetric analysis studies were carried out using the Perkin-Elmer Pyris Diamond TGA and the IR Prestige-21 to study the Fourier transform infrared FT-IR spectra.

Synthesis of azo dye ligand:

N-(3-Acetyl-2-hydroxy-5-methyl-phenyl)-*N*-(4-carboxy-cyclohexylmethyl)-diazonium

Melted in a mixture of 10 mL EtOH and 3 mL HCl conc, 1 mmole of 4-aminoethyl-cyclohexanecarboxylic acid was diazotized at 5 °C with a 10% NaNO₂ solution.⁵ An ethanolic solution was chilled, then 0.15 g (1 mmole) of a diazotized solution was added while stirring for 6 hours. This created 1-(2-Hydroxy-5-methyl-phenyl)-ethanone. Following that, an azo ligand precipitation (%Yield = 78%) and dark-colored mixture were seen. This deposit was filtered, rinsed for a certain amount of ounces with a (1:1) (C₂H₅OH: H₂O) solution, and then dried. The solution is displayed in Scheme 1. The ¹H-NMR and ¹³C-NMR spectra of the ligand LH in DMSO-d₆ Figs. 1 and 2, respectively show the signals of the azo ligand. The ¹H-NMR & ¹³C-NMR revealed a peak at δ (3.66) ppm, which was ascribed to N=N-CH₂ chemical changes. The chemical shift of (CH₂-CH₂) protons on cyclohexane ring was ascribed to the peaks at δ (2.38, 2.45) ppm,

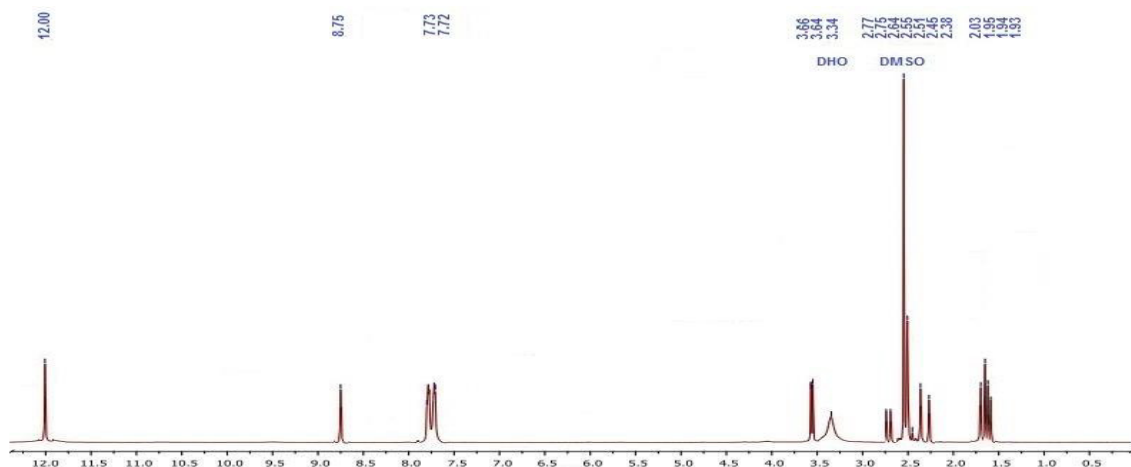


Fig. 1. ^1H -NMR spectrum of ligand.

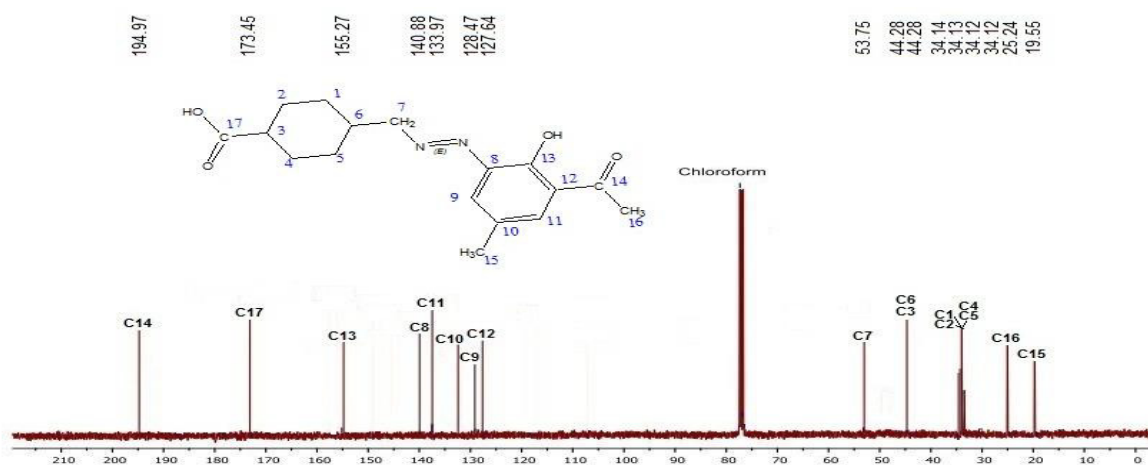


Fig. 2. ^{13}C -NMR spectrum of ligand(LH).

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}

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) 0.1979 g, Co (II) 0.357 g, Ni (II) 0.358 g, Cu (II) 0.364 g, and Zn (II) 0.136 g chloride salts

gradually added in dropwise additions, a stoichiometric amount of 0.319 g (1 m.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.

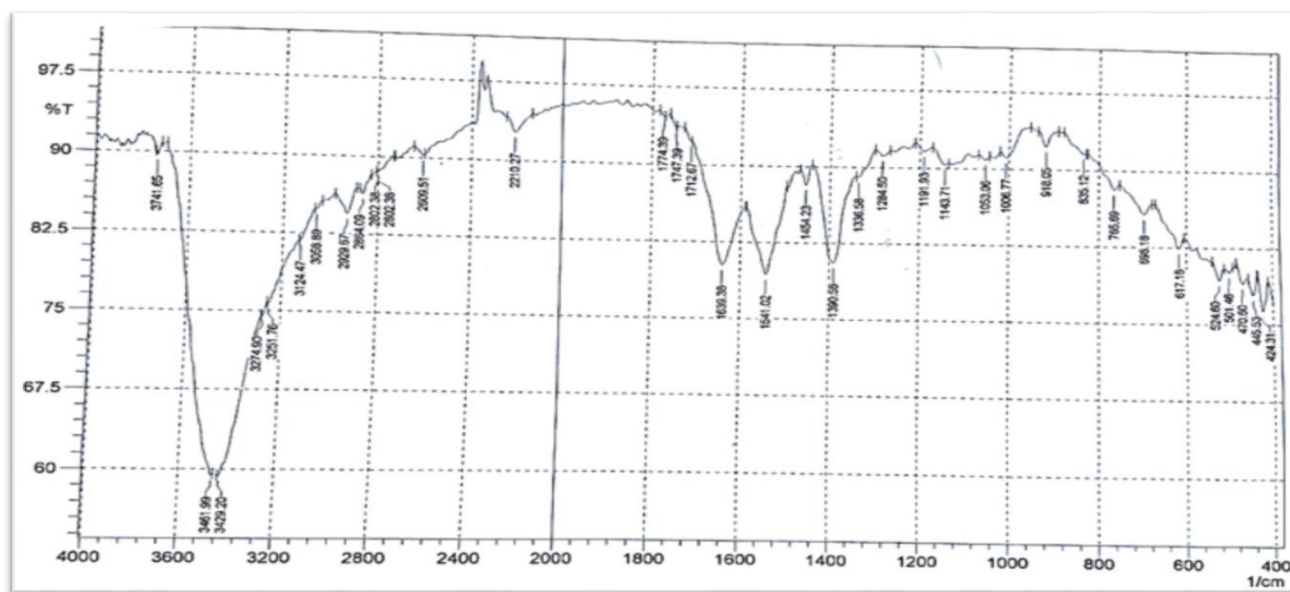
Results and discussion

The azo dye ligand (LH), which is a fine orange powder, stands out due to its amorphous nature.

Table 1. Physical 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 ₃ O ₃	318.37	orange	188–190	65.07	7.11	7.77	-	-
					64.13	6.97	8.80	-	-
[MnLCl]	C ₁₄ H ₂₀ ClN ₃ NiO ₄	407.75	Light orange	274–277d	49.55	4.71	7.41	12.78	7.88
					50.08	5.19	6.87	13.47	8.69
[CoLCl]	C ₂₈ H ₃₆ N ₆ PdO ₆	411.75	brown	> 300	50.11	4.89	7.55	13.79	-
					49.59	5.14	6.80	14.31	-
[NiLCl]	C ₂₈ H ₃₄ N ₆ PtO ₆	411.51	brown	> 300	48.99	4.59	7.74	13.27	-
					49.62	5.14	6.73	14.26	-
[CuLCl]	C ₁₄ H ₂₀ ClN ₃ NiO ₄	416.36	brown	> 300	50.01	4.59	7.41	16.17	8.79
					49.04	5.08	6.73	15.26	8.51
[ZnLCl]	C ₁₄ H ₂₀ ClN ₃ NiO ₄	418.20	orange	> 300	47.99	5.66	6.97	16.08	8.99
					48.82	5.06	6.70	15.64	8.48

C.:Calculated, F.: Found.

**Fig. 3.** FT-IR spectrum of ligand.

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.

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.

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

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

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

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

Comp.	λ nm	ν cm^{-1}	ABS	$\epsilon\text{L.}$ $\text{mol}^{-1}\text{cm}^{-1}$	Assignment	Λ S.cm^2 mol^{-1}	μ_{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	${}^6\text{A}_1 \rightarrow {}^4\text{A}_1 + {}^4\text{E}_{(\text{G})}$		
[CoLCl]	850	11764.7	0.068	68	${}^6\text{A}_1 \rightarrow {}^4\text{T}_{1\text{G}}$	13.76	4.10
	266	37593	1.327	1327	Inter ligand		
	312	32051.2	1.851	1851	Inter ligand		
	357	28011.2	1.423	1423	Inter ligand		
	485	20618.5	2.167	2167	C.T		
[NiLCl]	677	14771.0	0.306	306	${}^4\text{A}_2 \rightarrow {}^4\text{T}_{1(\text{P})}$	9.21	3.9
	266	37593.9	1.368	1368	Inter ligand		
	312	32051.2	1.866	1866	Inter ligand		
	348	28735.6	1.788	1788	Inter ligand		
	357	28011.2	1.411	1411	Inter ligand		
[CuLCl]	410	24390.2	0.186	186	C.T	14.8	1.73
	797	12547.0	0.102	102	${}^3\text{T}_1 \rightarrow {}^3\text{T}_{1(\text{P})}$		
	269	37174.7	1.760	1760	Inter ligand		
	316	31645.5	1.587	1587	Inter ligand		
	360	27777.7	1.508	1508	Inter ligand		
[ZnLCl]	405	24691.3	2.016	2016	C.T	11.42	diamagnetic
	953	10493.1	0.528	528	${}^2\text{T}_2 \rightarrow {}^2\text{E}$		
	269	37174.7	1.744	1744	Inter ligand		
	325	30769.2	1.482	1482	Inter ligand		
	337	29673.5	1.507	1507	Inter ligand		
[ZnLCl]	390	25461.0	2.216	2216	Inter ligand		
	465	21505.3	2.462	2462	C.T		

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} , ${}^6\text{A}_1 \rightarrow {}^4\text{T}_{1\text{G}}$, and, ${}^6\text{A}_1 \rightarrow {}^4\text{A}_{1\text{G}} + {}^4\text{E}_{(\text{G})}$, and absorption maxima at 265 nm, 313 nm, and 345 nm attributable to the inter ligand and the C.T. M \rightarrow 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 ${}^4\text{A}_2 \rightarrow {}^4\text{T}_{1(\text{P})}$, whereas the peaks at 266, 312 and 357 nm are attributed to the ligand,

Fig. 5. The Ni(II) complex's electronic spectra showed six peaks at 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 \rightarrow L), the peak at 797 nm is assigned to the (d-d) electronic transitions types ${}^3\text{T}_1 \rightarrow {}^3\text{T}_{1(\text{P})}$. 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 \rightarrow L).^{17,18} electronic transitions and the peak at 953 nm being assigned to the ${}^2\text{T}_2 \rightarrow {}^2\text{E}$ transition, implying a Td shape. Electronic

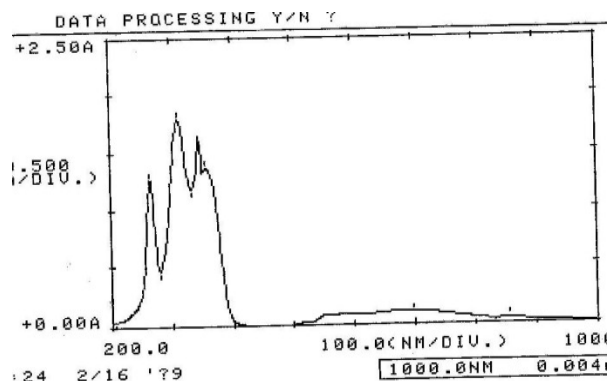


Fig. 4. UV-Vis spectra of Mn-complex.

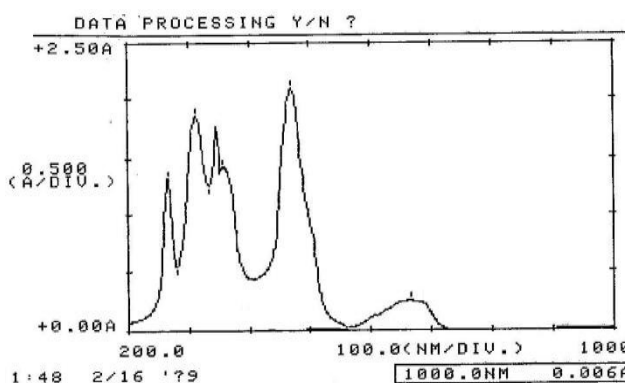


Fig. 5. UV-Vis spectra of Co-complex.

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) $\Delta\text{m (S.cm}^2\text{mol}^{-1})$ 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. respectively. This agrees with tetrahedral geometry for all complexes. The Zn-complex have diamagnetic properties.²⁰

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 $\text{C}_8\text{H}_{13}\text{O}_2^+$, 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 complex moiety $\text{C}_{17}\text{H}_{21}\text{ClN}_2\text{MnO}_4$. 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 $\text{C}_{17}\text{H}_{21}\text{ClN}_2\text{NiO}_4$ complex moiety. 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 $\text{C}_{17}\text{H}_{21}\text{ClN}_2\text{O}_4\text{Zn}$. 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}

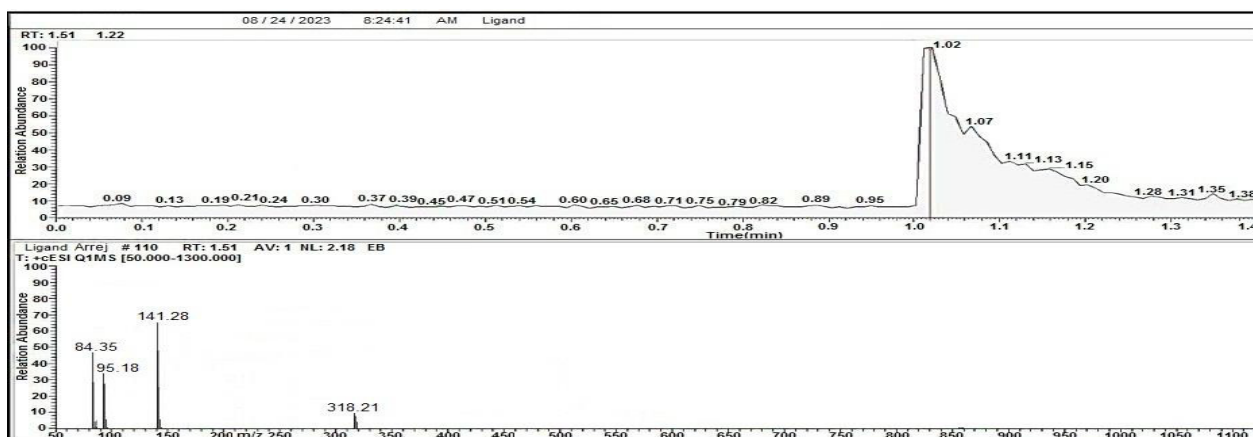
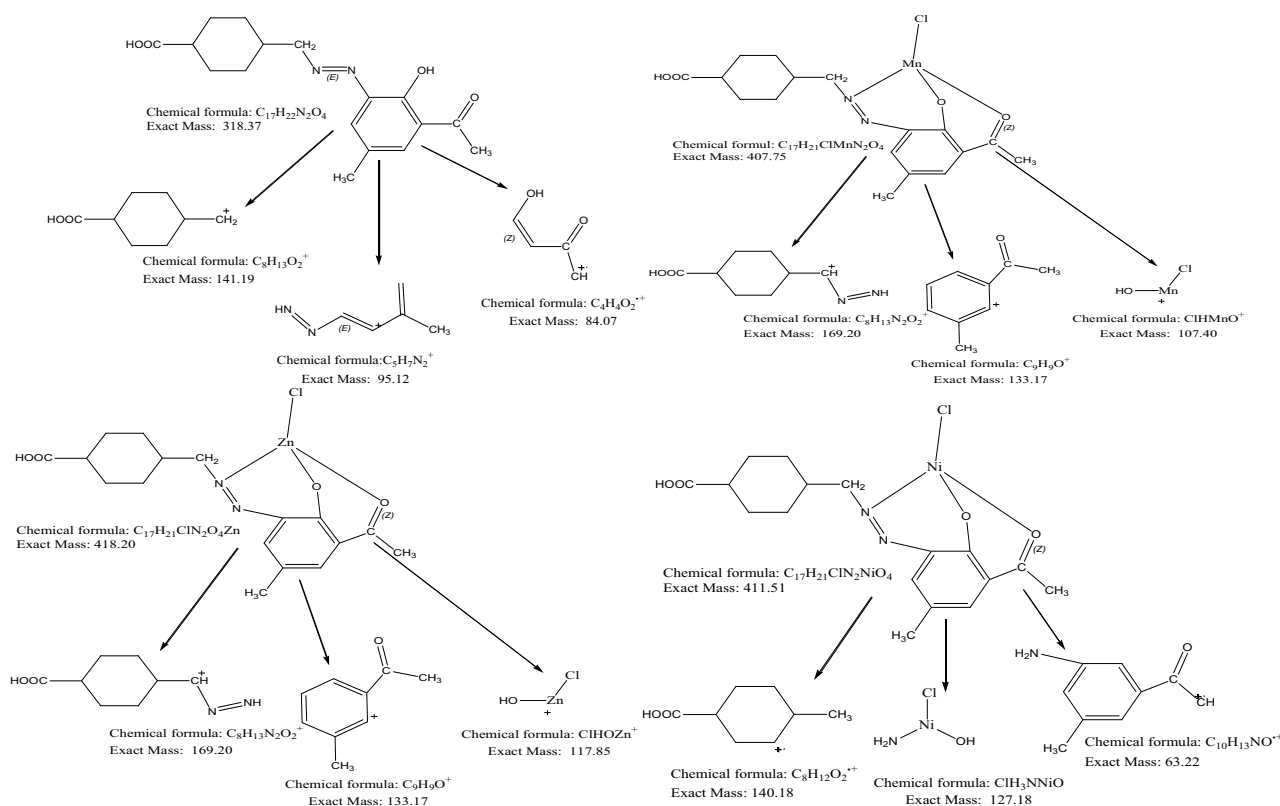


Fig. 6. LCMass spectrum of ligand.



Scheme 2. Fragmentation pattern of ligand and its complexes.

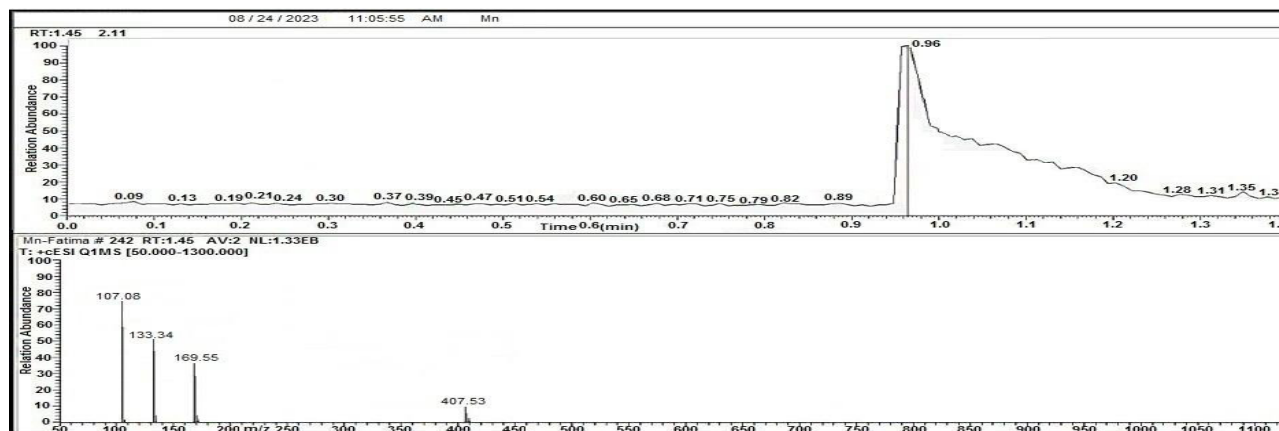


Fig. 7. LCMass spectrum of Mn-complex.

Thermal measurements

The thermal breakdown of the ligand LH and their metal complexes was observed by DSC and TGA, as shown in Figs. 9 to 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 values and the proposed formula.^{24–26} The DSC curve values for the ligand gave three phases that were endothermic ($\Delta H = -14.2$, -6.3 and 11.0) and Mn

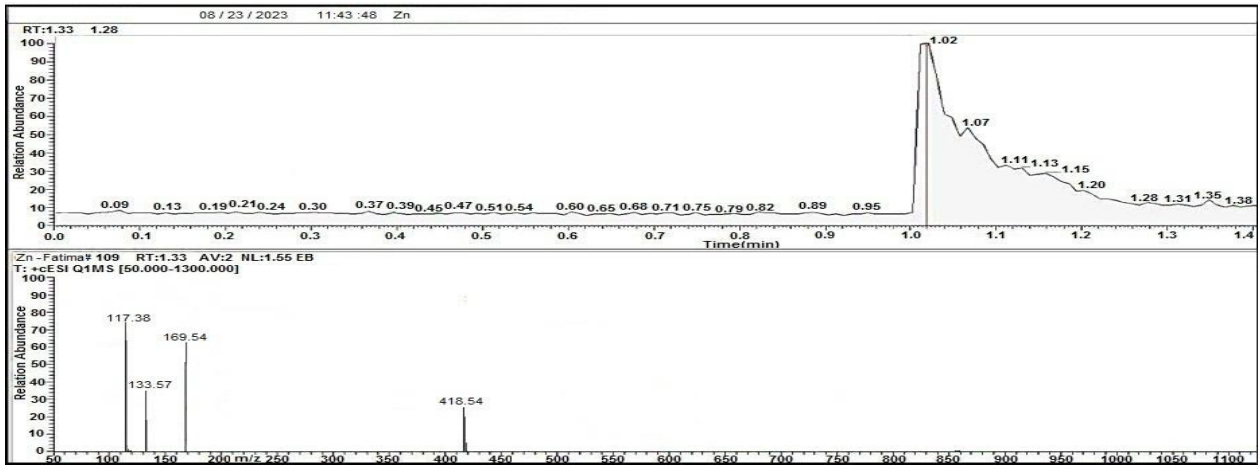


Fig. 8. LCMass spectrum of Zn-complex.

Table 4. TGA data of the ligand HL and some complexes.

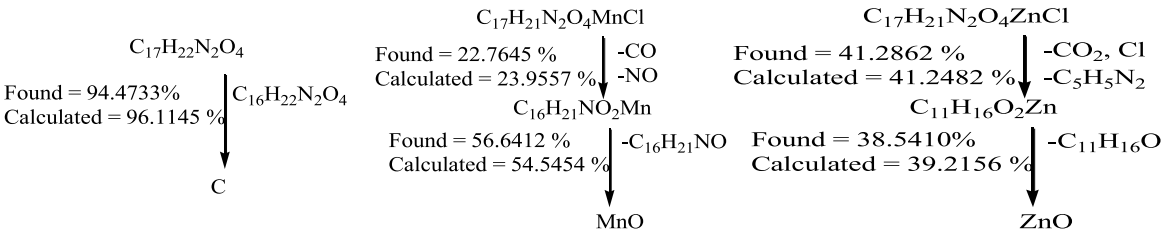
Complexes	Step	T _i /°C	T _f /°C	Tmax	Weight mass loss%		Reaction
					Calc	Found	
Ligand	1	111.351	594.515	247.362	96.1145	94.4733	-C ₁₆ H ₂₂ N ₂ O ₄ C
Calculated: 96.1145 %final = 3.8855 %; Estimated 94.4733 %final = 5.5267 %							
Mn-complex	1	129.265	309.688	192.431	23.9557	22.7645	-CO, -NO
	2	309.688	593.931	401.830	54.5454	56.6412	- C ₁₆ H ₂₁ NO 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 ₅ H ₅ O
	2	330.148	594.902	413.951	39.2156	38.5410	-C ₁₁ H ₁₆ O ZnO
Calculated: 80.4638 % final = 19.5362 %; Estimated 79.8272 % final = 20.1728%							

complex gave three phases that were endothermic ($\Delta H = -12.5, -6.8$ and 11.5) and Zn complex gave three phases that were endothermic ($\Delta H = -14.2, -4.0$ and 4.1).^{26,27}

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 IC₅₀ 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.



Scheme 3. TG decomposition of ligand and Mn, Zn complexes.

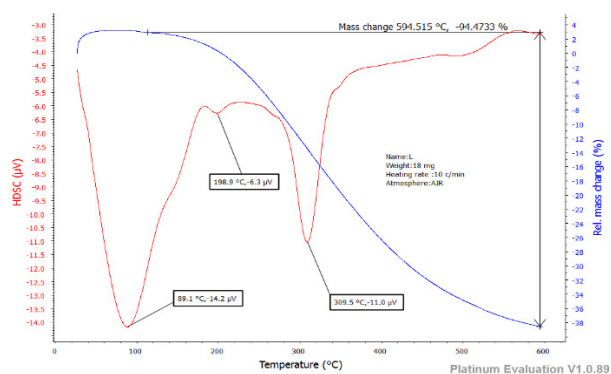


Fig. 9. TGA & DSC of ligand.

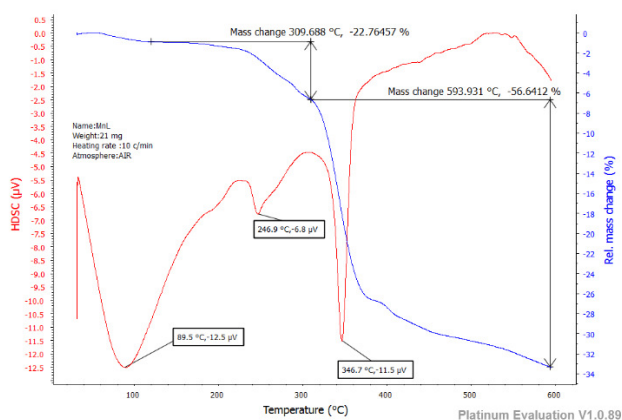


Fig. 10. TGA & DSC of Mn-complex.

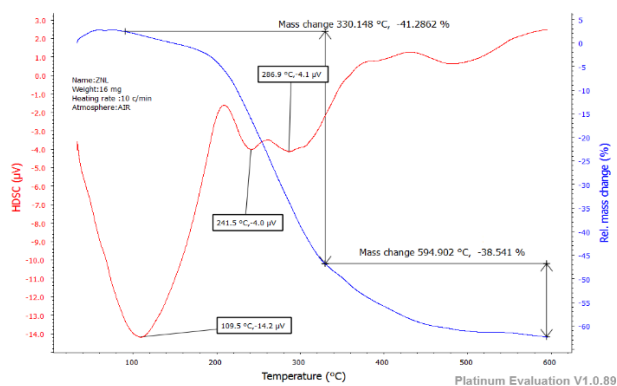


Fig. 11. TGA & DSC of Zn-complex.

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

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	

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}

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.

Acknowledgment

The authors would like to thank everyone who contributed to the success of this article: Department of Chemistry, College of Science for Women, College of Science, University of Baghdad.

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 republication, 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

- 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) complexes. *Bull Chem Soc Ethiop.* 2023;37(2):347–56. <https://dx.doi.org/10.4314/bcse.v37i2.8>.
- Kareem IK, Hadi MA. Synthesis and characterization of some transition metal complexes with new azo-schiff base ligand 3, 4-bis [((1E, 2E)-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>.
- 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>.
- Abdulrazzaq AG, Al-Hamdani AA. Ni²⁺, Pt⁴⁺, Pd²⁺, and Mn²⁺ 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>.
- 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-methylisoxazol-3-yl)-benzenesulfonamide). *Inorg Chem Commun.* 2022 Oct 1;144:109776. <https://doi.org/10.1016/j.inoche.2022.109776>.
- 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>.
- 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>.
- 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>.
- 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>.
- Nakamoto K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Wiley-Inter Science: New York. 1997.ed3: 197–210. <https://doi.org/10.1002/97804704058>.
- Reem GD, Walaa HM, Gehad GM. Metal complexes of tetradentate azo-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>.
- Ibraheem IH, Mubder NS, Abdullah MM, Al-Neshmi H. Synthesis, characterization and bioactivity Study from azo-ligand derived from methyl-2-amino benzoate with some metal ions, *Baghdad Sci J.* 2023;20(1):0114–0114. <https://doi.org/10.21123/bsj.2022.6584>.
- 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-phenylenediamine. *Iraqi J Sci.* 2020;61(11):2762–2775. <https://doi.org/10.24996/ij.s.2020.61.11.2>.
- Nagasundaram N, Govindhan C, Sumitha S, Sedhu N, Raguraman 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>.
- 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](https://dx.doi.org/10.1016/S0010-8545(00)80009-0).
- 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>.
- Shalan 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 more Synthesis, 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](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-2-en-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. Ashrafzaman 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, Beatriz HC. Antioxidant compounds and their antioxidant mechanism, 2019.ed1:26–35. <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>.

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

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الخلاصة

وفقاً للدراسات السابقة تم تحضير ليكاند أزو جديد (ن- (3-اسيتايل-2-هيدروكسي-5-مثيل-فنيول)-ن- (4-كاربوكسي-سايلوهكسيل مثيل)-ملح الدايازونيوم) وبعد التحقق من الصيغة المقترحة وفق نتائج التحاليل وبعد استخدام الليكاند لتحضير سلسلة من المعقدات باستخدام نسب مولية متساوية (1:1) من الليكاند وتفاعلها مع كل من املاح المنغنيز والكوبلت والنيكل والنحاس والخاصين وبعد التحقق وفق تقنيات التحاليل الطيفية والتشخيصية (الاشعة فوق البنفسجية 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 لتحديد 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 والمعادن 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-سايلوهكسان كاربوكسيلك، اطياف الكتلة ، التحاليل الحرارية.