

**Antioxidant of new Schiff base complexes (NO) derived
from (1-amino-2-naphthol-4-sulfonic acid and 4-methoxybenzaldehyde)**

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Abstract:

The research includes the preparation of a new Schiff base ligand condensation of (1-amino-2-naphthol-4-sulfonic acid with 4-methoxybenzaldehyde). And the reaction of the product with some binary metal salts (Pd, Cu, Ni, Co) The Schiff base ligand and the prepared complexes were identified using spectroscopic and analytical methods, including FT-IR, proton nuclear magnetic resonance ($^1\text{H-NMR}$), ultraviolet-visible (UV-Vis), thermogravimetric analysis (TGA), mass spectrometry (GC-Mass), as well as elemental decomposition (CHNS), measuring chlorine content, and atomic absorption of metallic elements. Molar conductivity and magnetic susceptibility Which showed the general formula of the complexes $[\text{M}(\text{L})_2(\text{H}_2\text{O})_2]$ while the general formula of the palladium complex is $[\text{M}(\text{L})_2]$ and indicated the geometric shapes of a distorted octahedron, while the shape of a planar square was suggested for the palladium complex. A study was conducted on the total antioxidant content of the ligand and the prepared complexes as free radical inhibitors or radical scavengers and showed activity as antioxidants compared to tannic acid and gallic acid.

Keywords: 1-Amino-2-naphthol-4-sulfonic acid, 4-methoxybenzaldehyde, Schiff base, ligand, antioxidant.

**تحضير وتشخيص معقدات جديدة لقاعدة شف نوع (NO) مشتقة
من (1-امينو-2-نافثول-4-حامض السلفونيك و 4-ميثوكسي بنزالديهايد)
ودراسة مضادات الاكسدة**

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مستخلص:

يتضمن البحث تحضير ليكاند قاعدة شف جديد مشتق من تكثيف (1-امينو-2-نافثول-4-حامض السلفونيك مع 4-ميثوكسي بنزالديهايد) ومفاعلة الناتج مع بعض الاملاح الفلزية الثنائية (Pd, Cu, Ni, Co) وشخص ليكاند قاعدة شف و المعقدات المحضرة بالطرق الطيفية والتحليلية منها طيف الاشعة تحت الحمراء (FT-IR) وطيف الرنين النووي المغناطيسي للبروتون ($^1\text{H-NMR}$) وطيف الاشعة فوق البنفسجية - المرئية (UV-Vis) والتحليل الحراري الوزني (TGA) واطياف الكتلة (GC-Mass) فضلاً عن التحلل الدقيق للعناصر (CHNS) وقياس محتوى الكلور والامتصاص الذري للعناصر الفلزية والتوصيلية المولارية والحساسية المغناطيسية والتي بينت الصيغة العامة للمعقدات $[\text{M}(\text{L})_2(\text{H}_2\text{O})_2]$ بينما الصيغة العامة لمعقد البلاديوم هي $[\text{M}(\text{L})_2]$ واقترحت الاشكال الهندسية ثمانية السطوح المشوهه، في حين اقترح لمعقد البلاديوم شكل المربع المستوي، وأجريت دراسة محتوى التضاد للأكسدة الكلي لليكاند والمعقدات المحضرة كمثبطات للجذور الحرة او كاسحات جذرية وظهرت نشاطاً كمضادات اكسدة مقارنةً بحامض التانك وحامض الكاليك. الكلمات المفتاحية: 1-امينو-2-نافثول-4-حامض السلفونيك، 4-ميثوكسي بنزالديهايد، قاعدة شف، الليكاند، مضادات الاكسدة.

Introduction

Schiff bases and their metal complexes are an important class of compounds due to their chemical activity, chelating capacity, physical properties, and numerous applications in several fields, most notably industry, due to their azomethine (CH=N--) group content. These compounds and their metal complexes have shown promising applications in fields such as biomedicine ⁽¹⁾, magnetism ⁽²⁾, solar cells ⁽³⁾ sensors, and biosensors ^(4,5). They are also used in the oxidation or reduction of organic compounds ⁽⁶⁾, as corrosion inhibitors, and in many other catalytic applications ⁽⁷⁾. They are also used as accelerators in rubber hardening ⁽⁸⁾ and as antioxidants. These properties make Schiff base complexes useful in various applications, particularly in the pharmaceutical and fine chemical industries ⁽⁹⁾

Schiff bases prepared from the reaction of aliphatic or aromatic amines with aromatic aldehydes are characterized by a relatively high thermal stability. Schiff bases form colored complexes with many transition metal ions, so they constitute one of the selective

and sensitive methods for the qualitative and quantitative determination of metals ⁽¹⁰⁾. They were also used as analytical reagents in diagnosis and quantitative determination, in the manufacture of selective electrodes for many metal ions and the separation of compounds containing carbonyl groups ⁽¹¹⁾, and in various chromatographic analysis methods for measuring selectivity and sensitivity ⁽¹²⁾. Schiff bases were used in the extraction of metals ⁽¹³⁾. Complexes of Schiff bases with Cr(III) were manufactured to be used as selective catalysts for opening the rings of heterocyclic compounds such as aziridine in organic reactions ⁽¹⁴⁾

Schiff bases and their metal complexes have attracted the attention of researchers because of their potential biological activity⁽¹⁵⁾. The main focus of their study is on identifying direct therapeutic agents for a wide range of bacterial infections, particularly for Schiff-base complexes, because many of these complexes can act as templates of practical biological importance ⁽¹⁶⁻¹⁷⁾. Although Schiff bases are useful antibacterial agents, their complexes have much higher antibacterial activity than free ligands ⁽¹⁸⁾

Materials and working methods

The chemicals and solvents used in the preparation were of high purity and from known sources, including (B.D.H, Merck, Fluka). The melting and dissociation points of the prepared complexes were measured, using the (Melting Point Advanced SMP30) device equipped by STUART Company. The infrared spectra of the ligands and prepared complexes were recorded using the (FT-IR-8400) device equipped by SHIMADZU Company in the region between (4000-400). The ultraviolet spectra were measured using the UV-6100PC DOUBLE BEAM Spectrophotometer (EMC LAB) UV at a temperature of Temperature (25°C) with a concentration of (10^{-3}) molar and using (DMSO) as a solvent within the range (190-1100nm), the ^1H -NMR spectra of the ligand dissolved in (DM-SO- d_6) were measured using a model ultra-shield device at 300 MHZ, Mass spectra of ligands and complexes were recorded using a GCMS-QP2010SE: Shimadzu Spectrometer. the (TGA) thermogravimetric decomposition curves were recorded using a STA device (LINSESS PT -1000) at a rate of 10 min-1 using an alumina bowl, the

precise analysis of the elements, the percentage of metal and the chlorine content were measured using EuroVector, model EA 3000 devices (single V.3.Osingle) Shimadzu Atomic Absorption / (Flame Emission spectrophotometer (A.A-160) ((Tritroprocessor (Metrohm) 686 In order, the molar electrical conductivity of the prepared complexes was measured using dimethyl sulfoxide (DMSO) solvent at laboratory temperature (25°C) with a concentration of (10^{-3}), using the device (P-SELECTA CONDUCTIVITY METER (CD-2005), the Gram magnetic susceptibility was measured at a temperature of (25°C) for the prepared complexes in the and using the Magnetic Susceptibility Balance Mode (MSB - MKI) device, as the Faraday method was relied upon.

Working methods

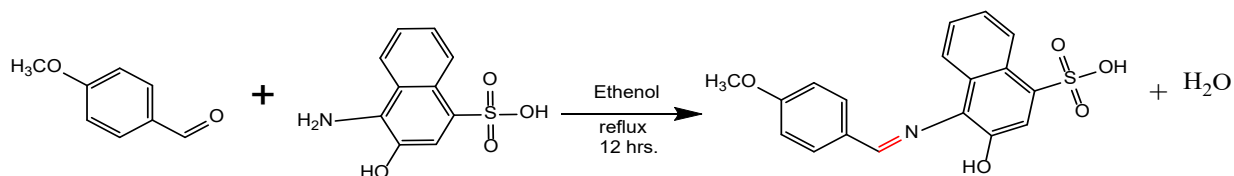
1) Preparation of ligand (L)^(20,19)

3-hydroxy-4-((4-methoxybenzylidene)amino)naphthalene-1-sulfonic acid

The ligand was prepared by dissolving (0.608mL, 5mmole) of (4-Methoxybenzaldehyde) in the smallest amount of absolute ethanol and adding

(5 drops) of glacial acetic acid (CH_3COOH) in a round flask with a capacity of (100 mL), and adding to it gradually with continuous stirring (1.196g, 5 mmole of 1-amino-2-naphthol-4-sulfonic acid dissolved in 30 mL of hot absolute ethanol, then leaving the mixture for the reflux process for 12 hours at

80°C in a water bath, then placing the reaction flask. In an ice bath for several minutes, then the precipitate was filtered and left to dry and washed with ethanol, which gave a brown precipitate weighing (1.45 g) and a percentage of (81%) and its melting point ($273\text{-}275^\circ\text{C}$) as shown in the diagram (1)



Scheme (1) Preparation of the ligand (L)

2) Preparation of the cobalt complex of the ligand L $[\text{Co}(\text{L})_2(\text{H}_2\text{O})_2]$ (21)

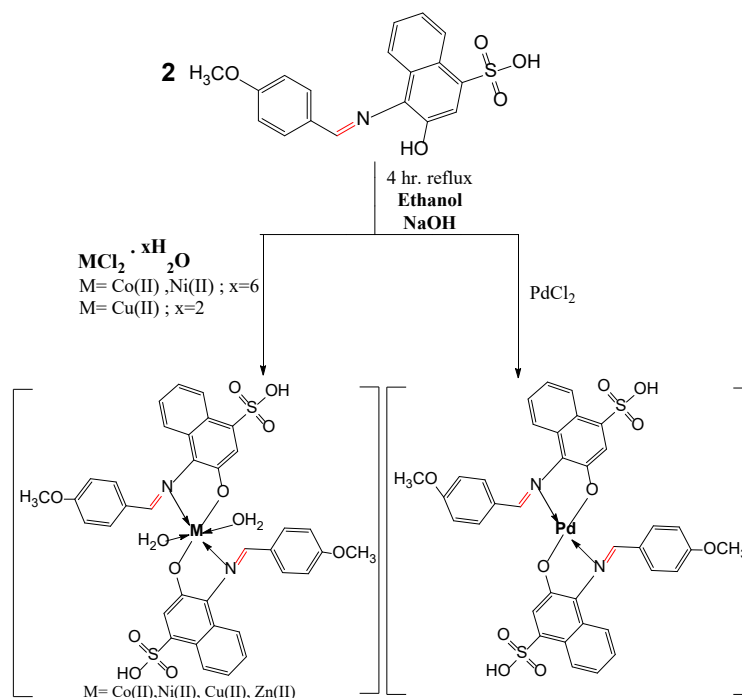
The complex was prepared by dissolving (0.2g, 0.56mmole) of the ligand (L) in (10mL) of absolute ethanol, then adding (0.023g) of sodium hydroxide (NaOH) dissolved in (10mL) of distilled water. Then (0.066g, 0.28mmole) of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ dissolved in (10mL) of ethanol was gradually added with continuous stirring in a round-bottomed flask with a capacity of (100mL). The mixture was left to reflux for

(4 hrs) at (80°C). The solution was then filtered after cooling by placing it in an ice bath. The precipitate was

then dried and washed with ethanol. Its weight was (0.25g) at a percentage of (55%) and a melting point of (317°C) as shown in the diagram (2)..

3) Preparation of complexes for ligand (L) of metal (II) ions (Pd, Cu, Ni):

These complexes for ligand (L) were prepared using the method mentioned in the same paragraph (2). Table (1) shows the quantities of metals used in preparing the complexes, the molecular formulas of the prepared complexes, their weights, the percentage of the resulting complex, their colors, and some of their physical properties.



Scheme (2) Preparation of ligand (L) complexes with binary metal salts

4). Total Antioxidant Capacity ⁽²²⁾

The effectiveness of the prepared complexes was estimated (ex vivo), showing that the increased absorbance of the resulting color indicates the total antioxidant capacity of the complex, which is measured spectrophotometrically at 695 nm. The following method was used:

o Sample preparation:- The sample was prepared at a concentration of 100 $\mu\text{g/mL}$ for all prepared compounds.

o Solutions used

1) **Working solution:** Consisting of a 4 mmol ammonium molybdate solu-

tion and a 28 mmol sodium phosphate solution dissolved in a 600 mmol sulfuric acid solution.

2) Working method:

- 3 cm^3 of the working solution was taken and mixed with 1 cm^3 of the sample.

- The tubes were covered with aluminum foil and incubated in a water bath at 95°C for 90 minutes.

- The tubes were cooled to laboratory temperature, and the absorbance was measured at 695 nm after zeroing on the equivalent representing the solvent used.

Table (1) Some physical properties, weight of raw materials, and percentage of prepared complexes

No.	Compound	Weight (g)	Empirical formula	Color	M.PC °	Yield %
	L	0.2	C ₁₈ H ₁₅ NO ₅ S	brown	273–275	81
	CoCl ₂ .6H ₂ O	0.066	[CoL ₂ (H ₂ O) ₂]	Dark brown	317 dec	55
	NiCl ₂ .6H ₂ O	0.066	[NiL ₂ (H ₂ O) ₂]	Dark green	298-301	62
	CuCl ₂ .2H ₂ O	0.047	[CuL ₂ (H ₂ O) ₂]	Light orange	< 390	65
	PdCl ₂	0.049	[Pd(L) ₂]	brown	349-351	62

dec. = decomposition Results and Discussion

1. Infrared Spectra of the Ligand and Schiff Base Complexes (L)

The infrared spectrum of the prepared ligand showed a new band, attributed to the azomethine group (C=N), with a strong intensity at position (1639 cm⁻¹)⁽²³⁾. This is evidence of the formation of Schiff base⁽²⁴⁾ as a result of the disappearance of the aldehyde (C=O)^ν⁽²⁵⁾ group and the amino ^ν(NH₂) group. A sharp, strong band appeared at wavenumber (3225 cm⁻¹) due to the stretching frequency of the ^ν(OH) group. The remaining bands retained their normal positions with a slight change in their ranges, as shown in Table (2) and Figure (1) The prepared complexes were characterized by

comparing them with the spectrum of the prepared ligand (L), as some bands were shifted with a change in their shape and intensity and the appearance of other new bands. The infrared spectra of the prepared complexes showed a strongly intense absorption band within the range (1651-1612) cm⁻¹ due to the stretching frequency of the azomethine group ^ν(C=N) which was shifted to lower or higher frequencies and with greater intensity for the complexes of Pd(II), Cu(II), Ni(II), Co(II)) compared to the same band in the spectrum of the ligand and appeared at position (1639 cm⁻¹). The shift of the stretching frequency of the ^ν(C=N) group and the change in the shape and intensity of the

band confirms the occurrence of coordination between the metal ion and the ligand through the nitrogen atom N between the metal ion and the ligand through the nitrogen atom N⁽²⁶⁾

The stretching frequency of the C-O group (ν) also suffered a shift towards lower frequencies for all complexes within the range 1145-1126 cm^{-1} when compared to the location of the same band in the ligand spectrum at 1188 cm^{-1} , with a change in the shape and intensity of the band in the complex spectra. This supports the occurrence of coordination between the metal ion and the ligand via the phenoxide oxygen atom⁽²⁷⁾. The prepared complexes Pd(II), Cu(II), Ni(II), Co(II)) showed two new

bands, the first in the range 540-505 cm^{-1}) attributed to the stretching frequency of the M-N bond (ν), while the other band appeared in the range 466-432 cm^{-1} attributed to the stretching frequency of the M-O bond (ν), which confirms the coordination between the metal ion and the nitrogen and oxygen atoms, respectively⁽²⁸⁾. As for the bands that appeared in the range 810-833 cm^{-1} and 910-952 cm^{-1} ⁽²⁹⁾, they are due to the coordination water, except for the palladium complex. The table shows: (2) Figures (2) and (3) show the positions of the main absorption bands of the infrared spectrum of the ligand and some of the prepared complexes.

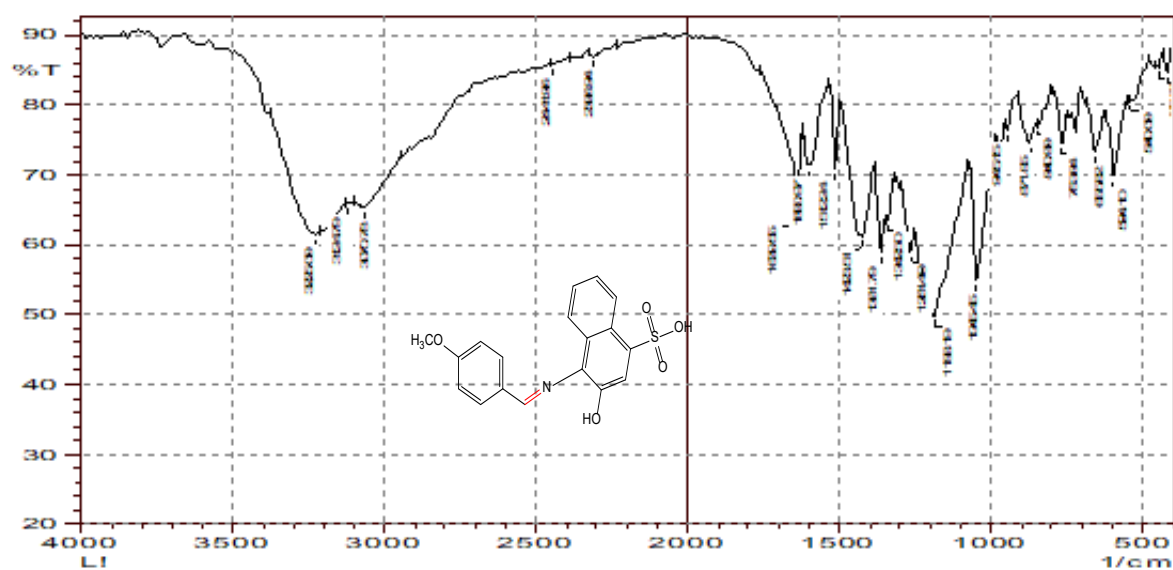


Figure (1) Infrared spectrum of the Schiff ligand L

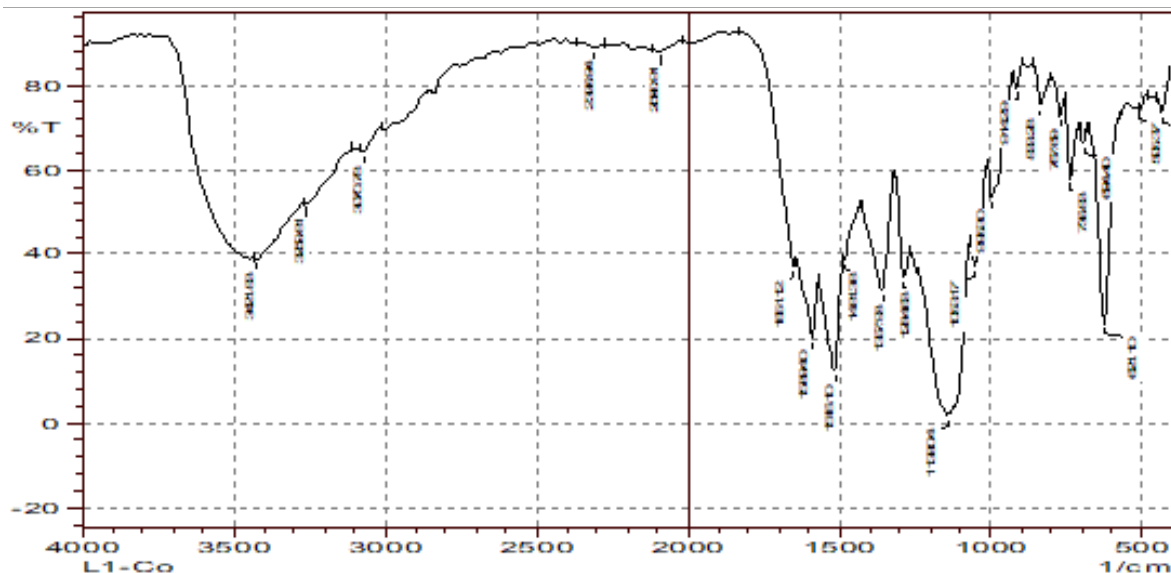


Figure (2) Infrared spectrum of the complex $[Co(L)_2(H_2O)_2]$

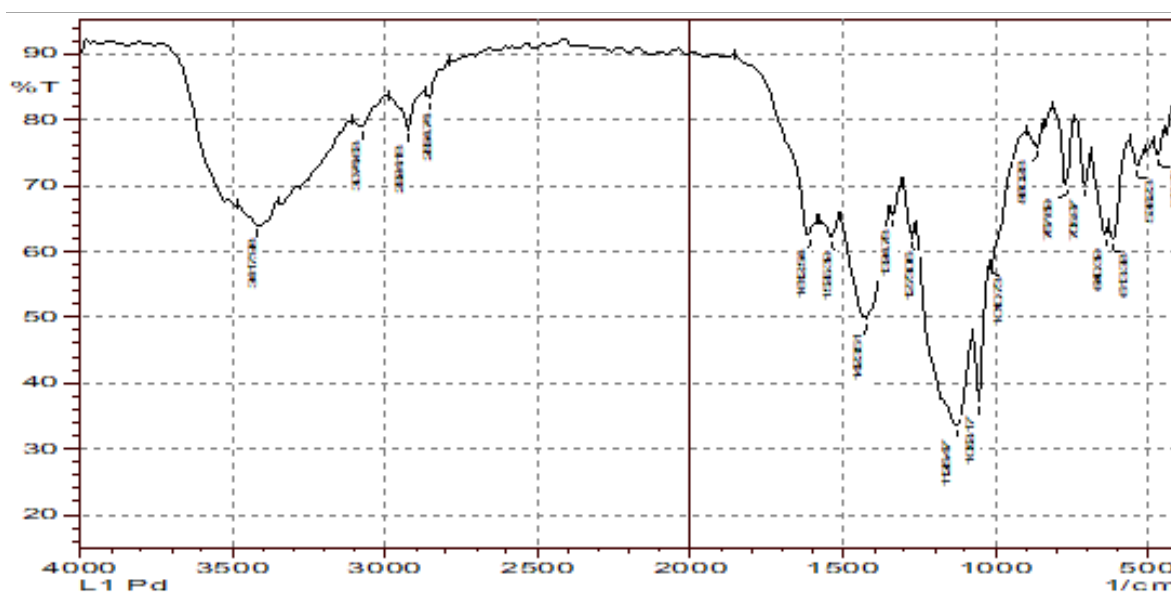


Figure (3) Infrared spectrum of the complex $[Pd(L)_2]$

2. ^1H NMR spectrum of the prepared ligand (L)

The ^1H NMR spectrum of the ligand (L) in the deuterium-substituted DM-SO- d_6 solvent (Figure (4)) showed a signal at position (δ 2.5 ppm) attributed to the protons of the solvent (DMSO), and five single signals at positions $\delta\text{H} = (9.87, 9.37, 8.61, 7.71, 3.86)$ ppm. The first is attributed to the proton of the methyl carbon atom (CH_3), the second is attributed to the proton of the carbon atom of the naphthalene ring, the third is attributed to the proton of the carbon atom of the isomethene group ($\text{N}=\text{C}-\text{H}$), the fourth is attributed to the proton of the sulfonate (OH) group, and the fifth is attributed to the proton of the (OH) group of the naphthalene. The spectrum showed two double signals at positions 6.80 and 7.05 attributed to the protons of the ring. Vinyl, and the spectrum showed two binary signals at positions 7.32 and 7.99 and two triple signals at positions 7.77 and 7.91, which are due to the protons of the second naphthalene ring ⁽³⁰⁾

Table (2) Infrared spectrum values of the prepared ligand and complexes

Compound	$\nu(\text{OH})$	$\nu(\text{C}=\text{N})$	$\nu(\text{C}=\text{C})$ aromatic	$\nu(\text{CO})$	H_2O Coord $\rho, \omega (\text{OH})$	$\nu(\text{CN})$	(MN)	(MO)
L	3225(s) 3124(m)	1639 (s)	1600(m) 1512(m)	1188(m)	---	1045(s)	---	---
$[\text{Co}(\text{L})_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$	3441	1651(w)	1589(m) 1516(m)	1138(s)	3259(m) 914(m), 833(m)	1053 (m)	505(w)	432(w)
$[\text{Ni}(\text{L})_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$	3414	1620(w)	1585(m) 1550(m)	1145(s)	3414(br) 952(w), 833(w)	1049(m)	513(m)	447(w)
$[\text{CuL}_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$	3433	1631(m)	1589(s)	1132(m)	3433(br) 910(m), 810(m)	1049(w)	540(m)	460(w)
$[\text{Pd}(\text{L})_2] \cdot \text{H}_2\text{O}$	3417	1612(m)	1535(m)	1126(s)	----	1053(m)	536(m)	466(w)

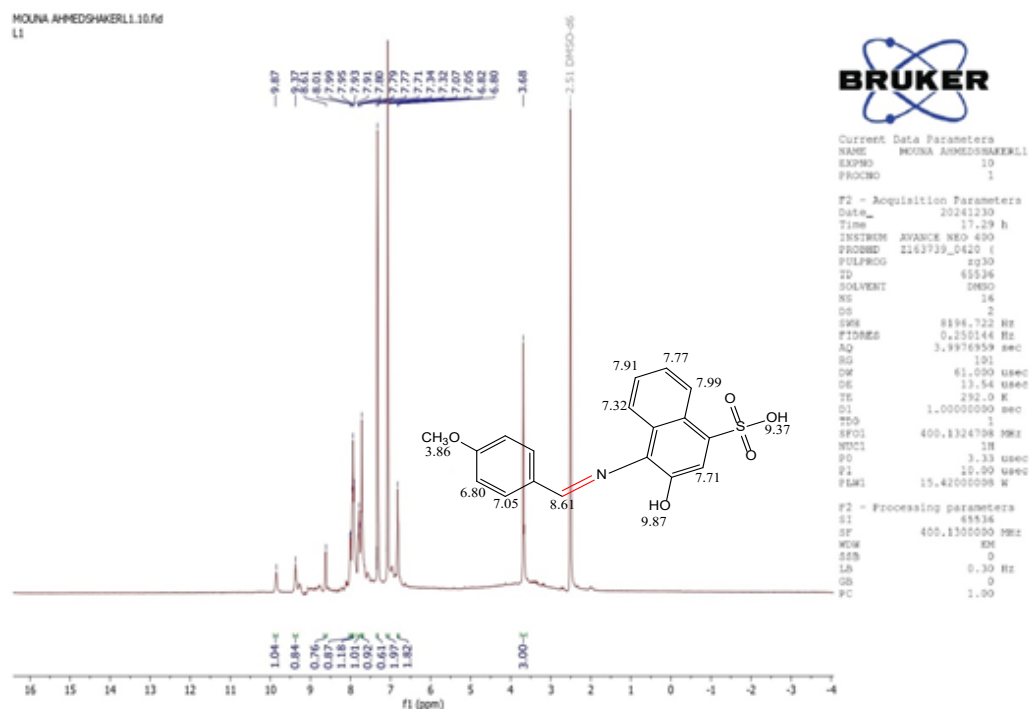


Figure (4) ¹H-NMR spectrum of the prepared Schiff base ligand L

3. UV-Vis Spectra of the Ligand and Schiff Base Complexes (L)

The UV-Vis spectrum of the prepared ligand (L) in Figure (5) showed two absorption peaks. The first peak was highly intense at 209 nm, resulting from the ($\pi \rightarrow \pi^*$) electronic transition. The second peak was of medium intensity at 257 nm, resulting from the ($n \rightarrow \pi^*$) electronic transition ⁽³¹⁾, as shown in Table 3. The complex spectra were as follows:

- The electronic spectrum of the Co-balt(II) complex showed three absorption peaks at wavelengths (228, 248,

and 349 nm), attributed to the intra-ligand electronic transition. The spectrum showed two absorption peaks at wavelengths (740 and 812 nm), attributed to the (d-d) electronic transitions of the type. ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ and (${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$) respectively, which is consistent with what is stated in the literature ⁽³²⁾

- The electronic spectrum of the nickel (II) complex Ni showed three absorption peaks at wavelengths of (482, 349, and 236 nm) which are attributed to intra-ligand transitions, and the spectrum showed absorption peaks

at wavelengths of (855, 834 nm) which are attributed to electronic transitions (d-d) type ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ respectively, which is consistent with what is stated in the literature for the spectra of octahedral nickel (II) complexes ⁽³³⁾.

- The electronic spectrum of the copper (II) complex Cu showed three absorption peaks at wavelengths of (369, 223 nm), which are attributed to the intra-ligand electron transition. The spectrum also showed three absorption peaks at wavelengths of 811, 740 nm, which are attributed to the (d-d) electron transitions of type $({}^2B_{1g} \rightarrow {}^2E_g)$, $({}^2B_{1g} \rightarrow {}^2A_{1g})$, respectively. This is consistent with what was reported in the

literature ⁽³³⁾.

- The electronic spectrum of the Pd(II) complex showed three absorption peaks at wavelengths of (346, 289, and 223 nm), which are attributed to the intra-ligand electron transition. The peak at wavelength (420 nm) is attributed to the C.T.M $\rightarrow$ L charge transfer spectrum. The spectrum also showed an absorption peak At a wavelength of (729 nm), which is due to electronic transitions (d-d) of type $({}^1A_{1g} \rightarrow {}^1A_{2g})$, and this is consistent with what was stated in the literature for the spectra of square-planar palladium (II) complexes ⁽³²⁾. Figures (5-7) show the ultraviolet-visible spectra of the ligand and some complexes.

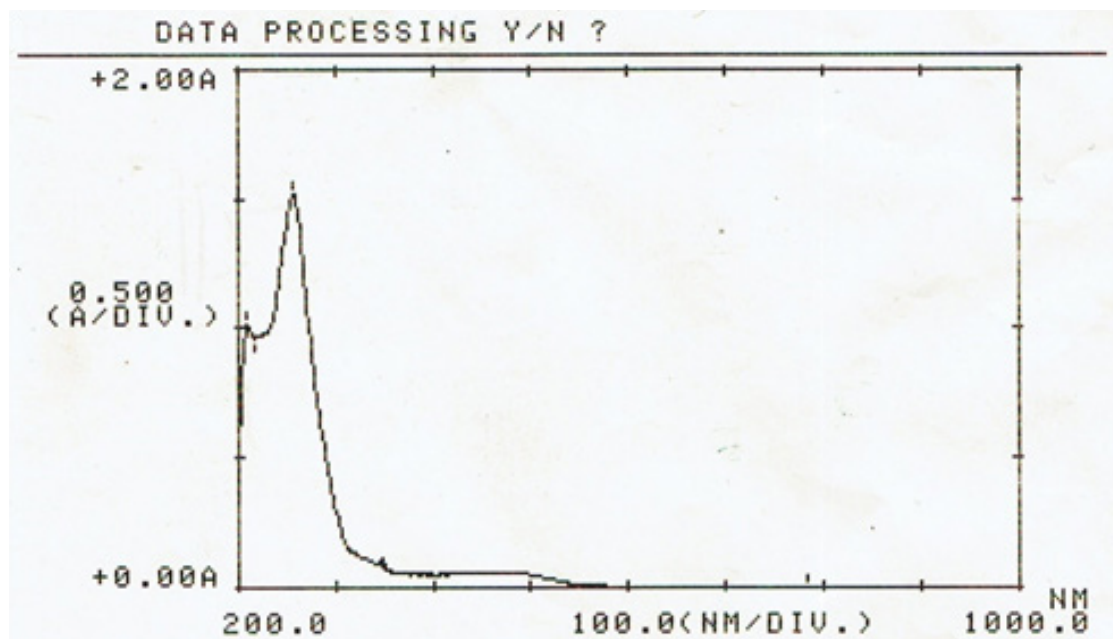


Figure (5) UV-vis spectrum of the Schiff base ligand (L

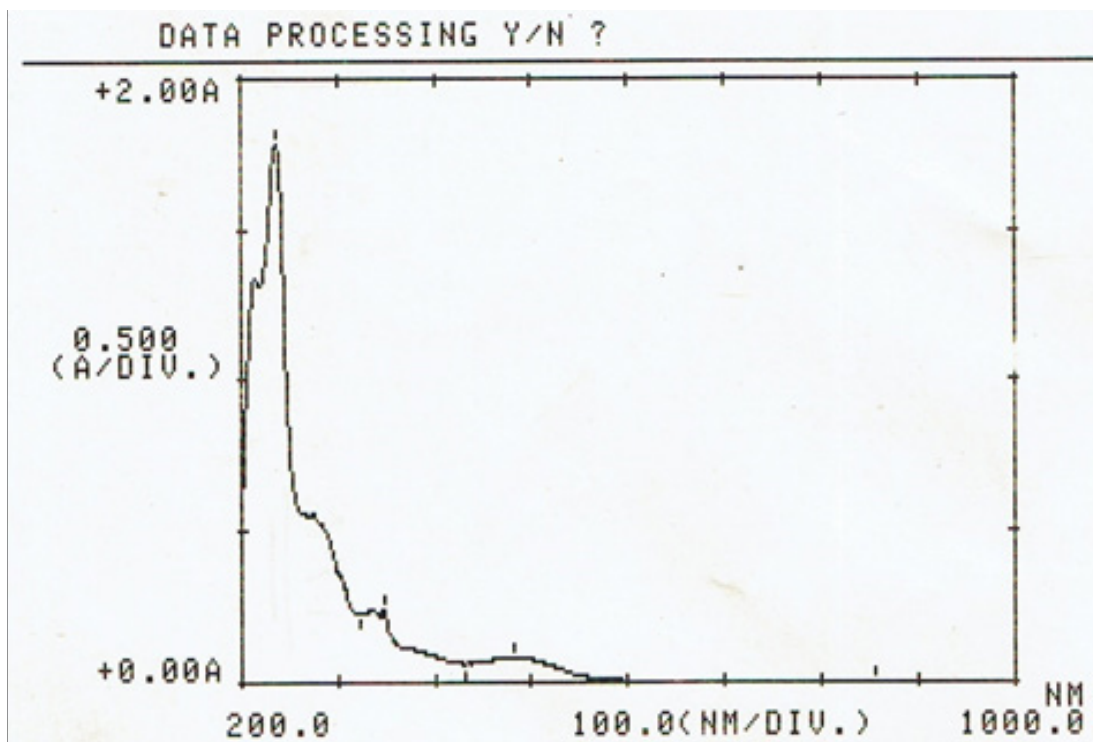


Figure (6) UV-vis spectrum of the complex $[\text{Ni}(\text{L})_2(\text{H}_2\text{O})_2]$

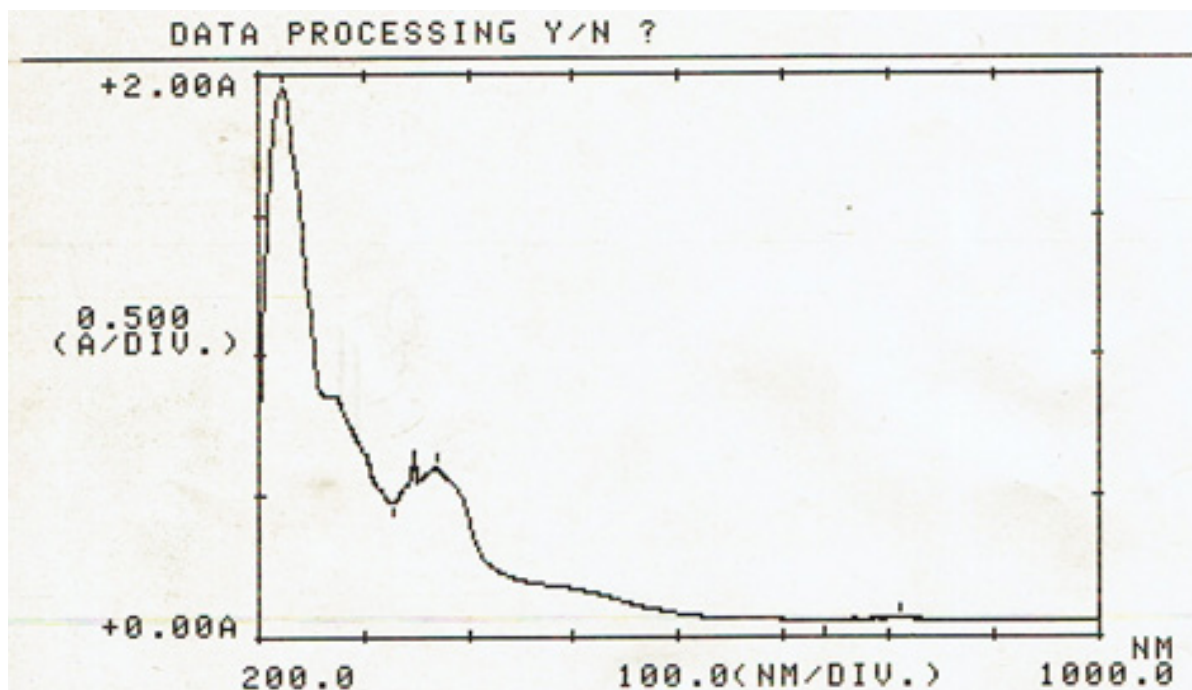


Figure7 UV- - vis spectrum of the compl $[\text{Cu}(\text{L})_2(\text{H}_2\text{O})_2]$

4. Thermogravimetric Analysis of the Prepared Ligand and Complexes:

The thermogravimetric analysis technique is a unique technique used to study the thermal behavior and stability of the compound. It is characterized by its unaffected by air, indicating its thermal stability ⁽³⁴⁾.

1.4 Thermal Decomposition of the Schiff Base Ligand (L)

The thermal study of the prepared ligand (L) ($C_{18}H_{15}NO_5S$) was conducted by thermogravimetric analysis (TGA) in an oxygen-containing atmosphere at a temperature of $10^\circ\text{C min}^{-1}$ and a sample weight of 13.51 mg, as shown

in Figure (8). The TGA curve of the ligand showed that it undergoes two stages of weight loss:

- The first stage: in the temperature range $395-199^\circ\text{C}$, resulting in the loss of the $C_{10}H_4SO_3$ segment at a rate of 57.18%, i.e. (obs. = 7.71 mg, calc. = 7.73 mg).

- The second stage: At temperatures between 571 and 402°C , the ($C_6H_{10}NO_2$) segment is lost by 35.94% (Obs. = 4.83 mg, Calc. = 4.85 mg).

The remaining ligand, observed at temperatures above 571°C , reverts to the (C_2H_2O) segment (Obs. = 0.94 mg, Calc. = 0.95 mg)

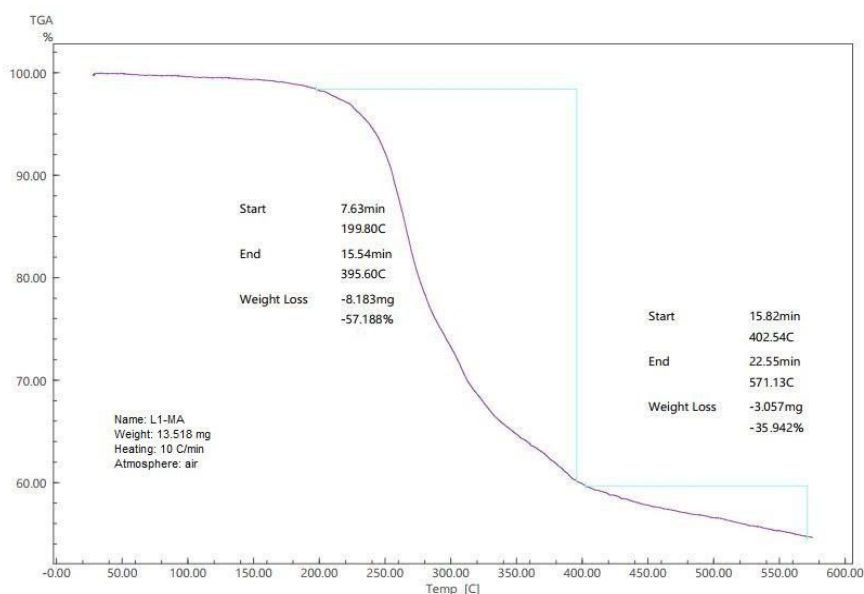


Figure (8) Thermal breakdown of the Schiff base ligand L

4. Thermogravimetric decomposition of the complex $[\text{Cu}(\text{L})_2(\text{H}_2\text{O})_2]$

The thermal study of the complex $\text{CuC}_{36}\text{H}_{32}\text{N}_2\text{O}_{12}\text{S}_2$ was carried out at a temperature of $(10^\circ\text{C min}^{-1})$ with a weight of (15.97 mg) of the sample, as shown in Figure (9). The TGA curve of the complex showed that it went through three stages of weight loss:

- Stage 1: In the temperature range $228.6\text{--}73.4^\circ\text{C}$, the loss of the $(\text{C}_{10}\text{H}_5\text{SO}_3, \text{CN})$ segment was 28.7% (obs. = 4.58 mg, calc. = 4.59 mg)

- Stage 2: In the temperature range

$348.8\text{--}236.8^\circ\text{C}$, the loss of the $(\text{C}_7\text{H}_8\text{O}, \text{OH}, 2\text{H}_2\text{O}, \text{SO}, \text{H}_2\text{C}_2\text{O})$ segment was 30.9% (obs. = 4.93 mg, calc. = 4.94 mg)

- Stage 3: In the temperature range 506°C , the loss of the $(\text{C}_6\text{H}_7\text{N}, \text{C}_4\text{H}_6\text{O}_2)$ segment was 30.9% (obs. = 4.93 mg, calc. = 4.94 mg) At a rate of 22.1%, i.e. (obs. = 3.53 mg, calc. = 3.54 mg).

The remaining part of the complex is the (C_6CuO) segment, at a rate of 18.6%, i.e. (obs. = 2.97 mg, calc. = 2.98 mg).

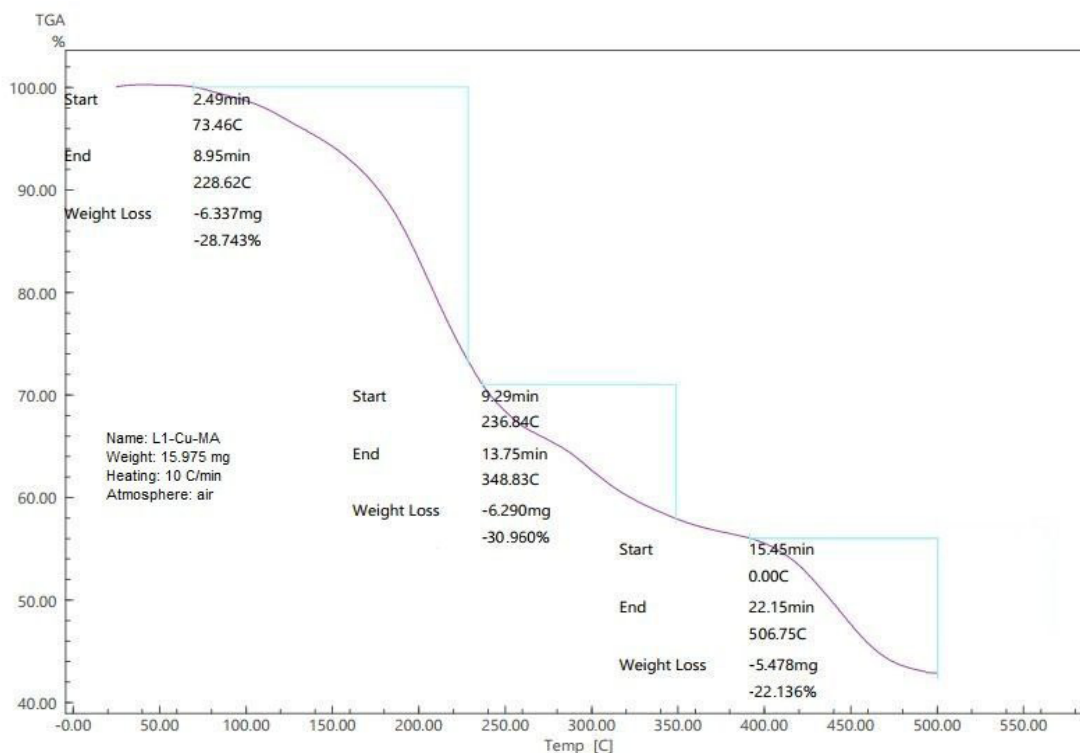


Figure (9) Thermal breakdown spectrum of the complex $[\text{Cu}(\text{L})_2(\text{H}_2\text{O})_2]$

5-Mass spectra of the ligand and some of the prepared complexes:

The mass spectrum of the prepared ligand (L), shown in Figure (10), showed a signal at $m/z = 357$, corresponding to the formula ($C_{18}H_{15}NO_5S$), which indicates the molecular weight of the ligand. This was achieved by

identifying the molecular ion peak of the prepared compound and the main peak, in addition to some fragment peaks generated from the fission of the molecule after its ionization. Diagram (3) illustrates the mechanism of the mass fragmentation of the prepared ligand.

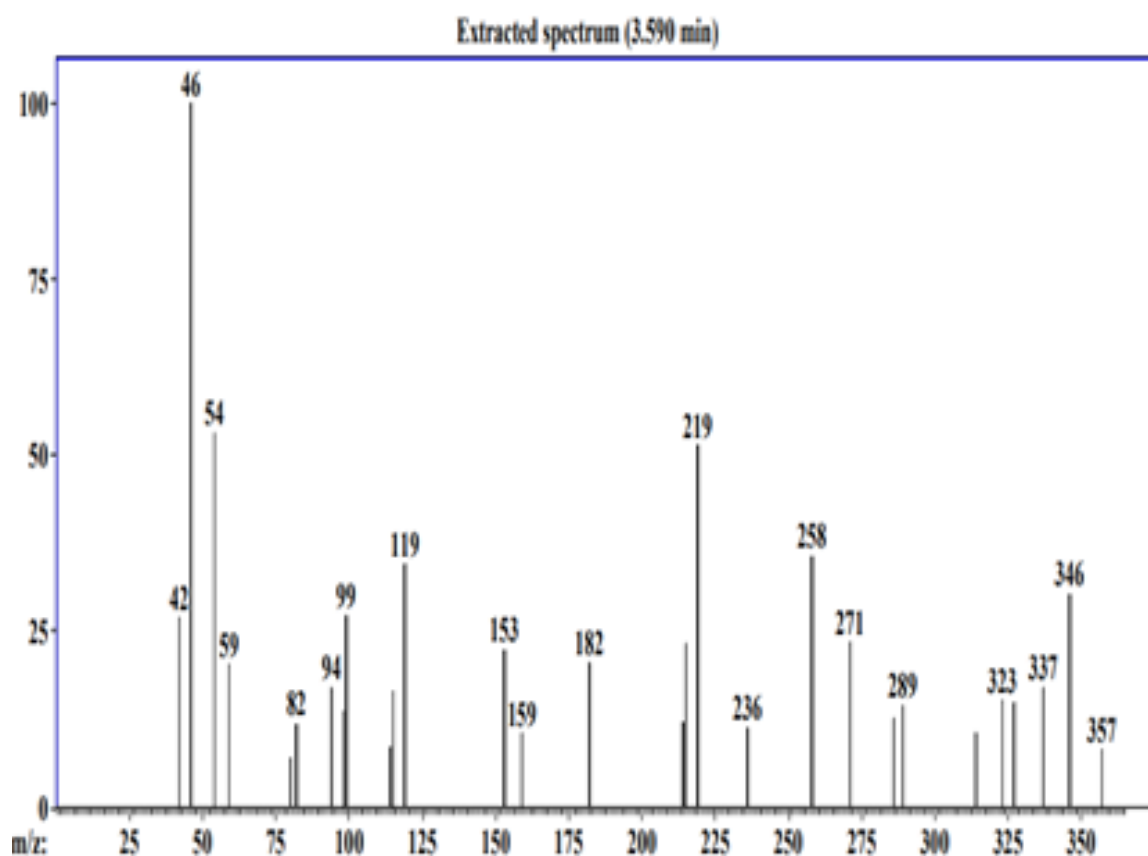
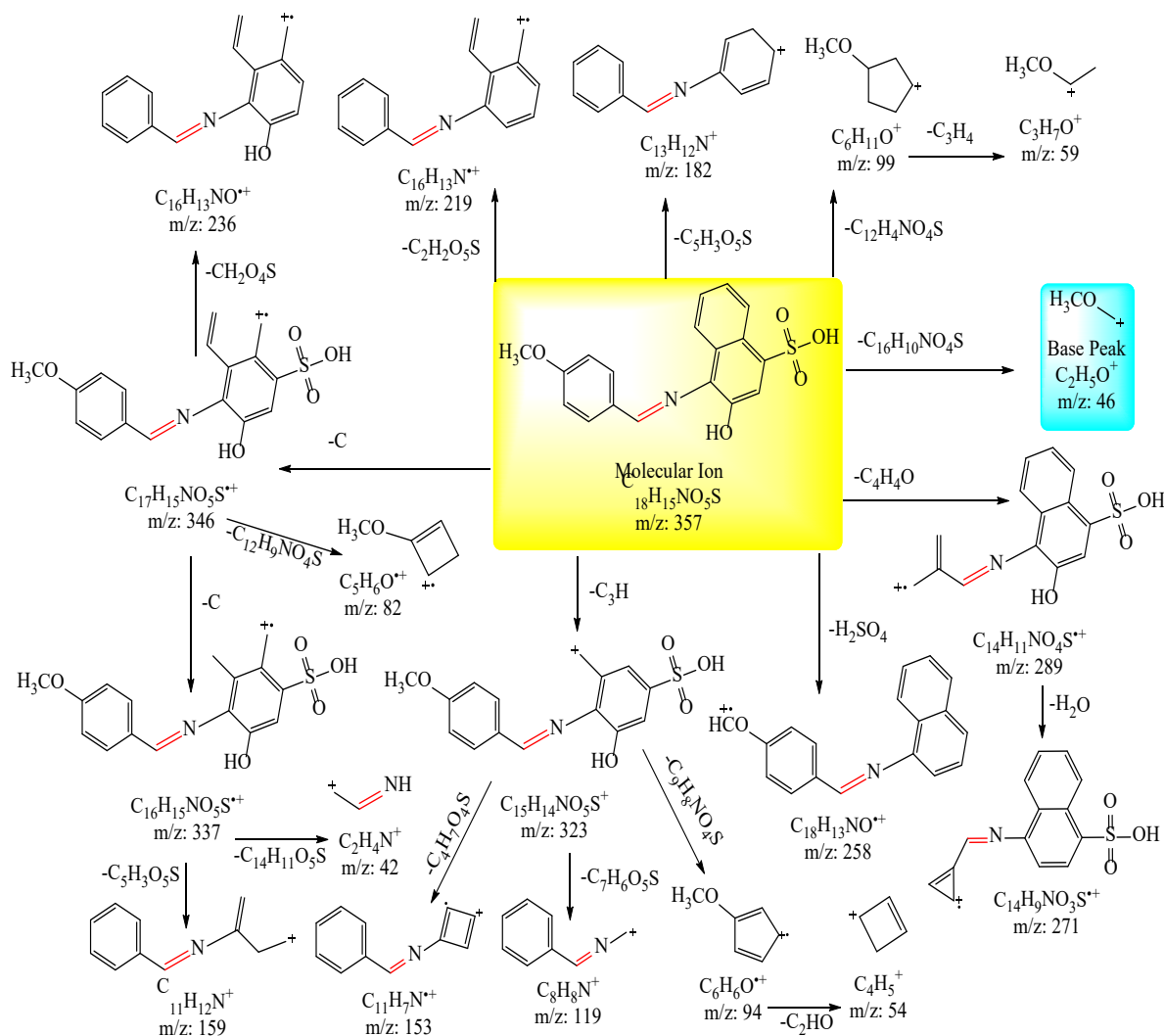


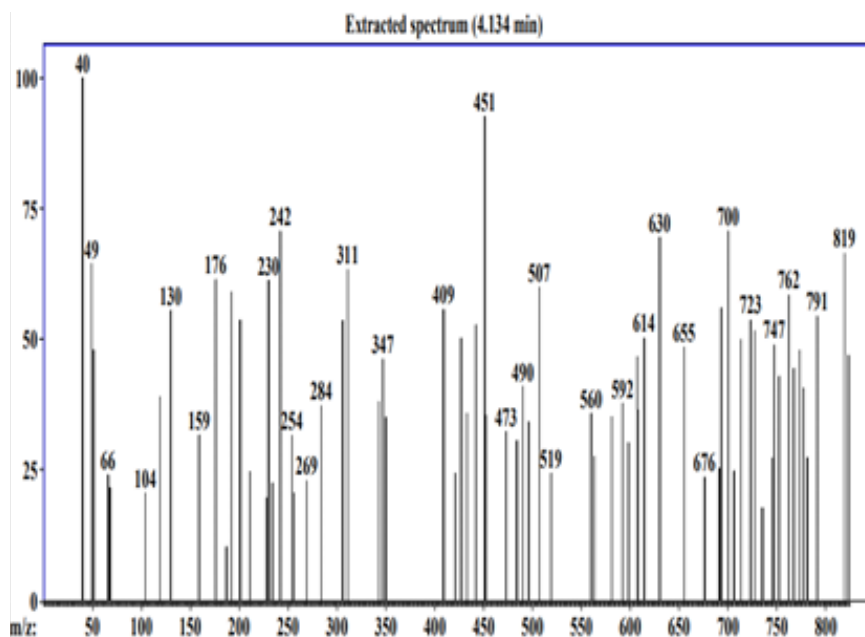
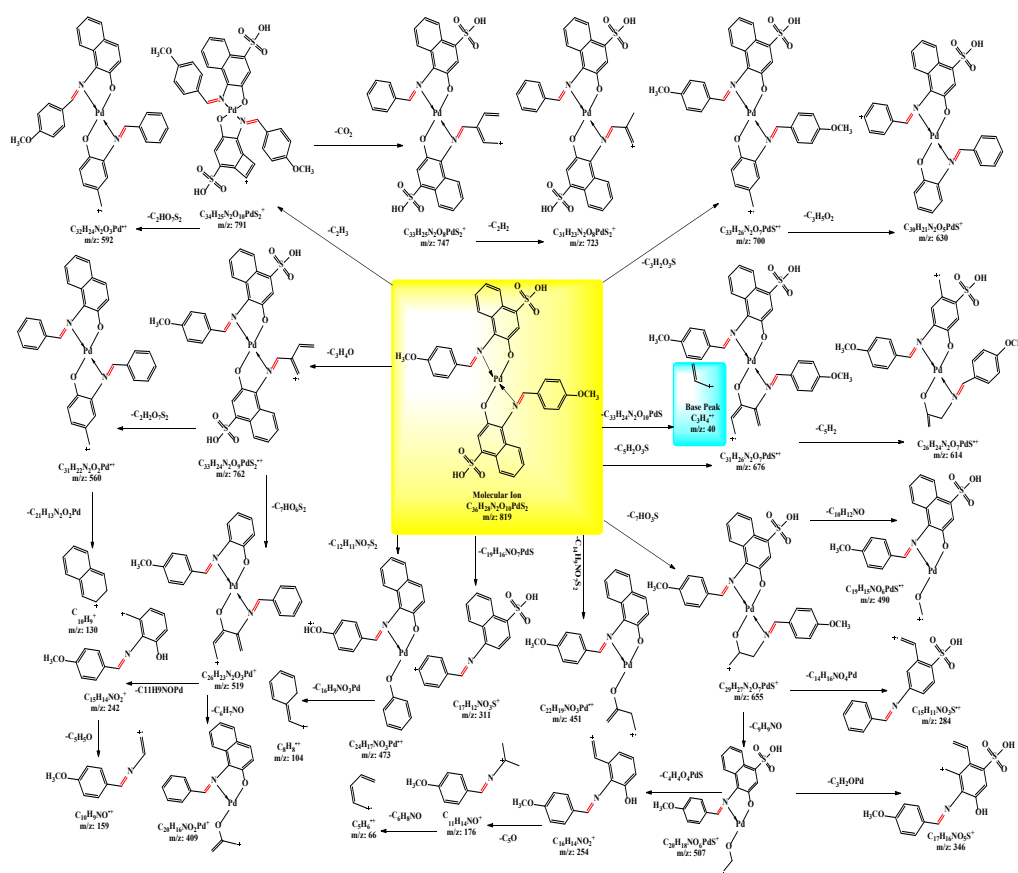
Figure (10) Mass spectrum of the Schiff base ligand (L1)



Scheme (3) Proposed pathways for the fragmentation of the Schiff base ligand L

While the mass spectrum of the complex $[\text{Pd}(\text{L})_2]$ shown in Figure (11) showed a signal at ($m/z=819$) that belongs to the formula $\text{PdC}_{36}\text{H}_{28}\text{N}_2\text{O}_{10}\text{S}_2$)

which shows the molecular weight of the complex and the diagrams(4) illustrate the mechanism of the mass fragmentation of the palladium complex.

Figure (11) Mass spectrum of the complex $[Pd(L)_2]$ Scheme (4) Proposed pathways for the fragmentation of the complex $[Pd(L)_2]$

6. Molar Conductivity, Magnetic Susceptibility, and Elemental Micro-analysis

Molar conductivity measurements determine the ionic character of complexes in solution to determine whether they are neutral, ionic conductivity, or weak conductivity ⁽³⁵⁾. Determining the value of the molar conductivity of a complex depends on the number of ions it releases. The greater the number of ions released by the complex into the solution, the greater the electrical conductivity value. If the conductivity is low, it means that the complex released few ions ⁽³⁶⁾. The molar conductivity of complexes was measured by preparing solutions with a concentration of (10^{-3} M) in DMSO at 298 K. Comparing the molar conductivity values in the literature ⁽³⁷⁾ reveals that the prepared complexes were non-electrolytic (neutral).

Magnetic measurements, however, focus on the effects resulting from partially filled outer shells ⁽³⁸⁾. This represents the most important indicator in providing information about the compound, its electronic arrangement, and its state. The oxidation state of transition metal atoms. Determining the number of unpaired electrons of the metal ion indicates whether the complex under study has a high spin

state or a low spin state. This then determines the hybridization type of the central atom and determines the geometric shape of the complex⁽³⁹⁾

Table 4 Magnetic susceptibility, molar conductivity (Δm), and elemental microanalysis

Complexes	Chemical Formula	A_m	μ_{eff} (BM)	M.wt.	Analysis . Calc (Found)				
					M	C	H	N	S
L	$C_{18}H_{15}NO_5S$	--	--	433.48	--	60.49 (60.47)	4.23 (4.20)	3.92 (3.96)	8.97 (8.95)
$[Co(L)_2(H_2O)_2]$	$C_{36}H_{32}CoN_2O_{12}S_2$	10.3	4.97	923.87	7.30 (7.26)	53.53 (53.49)	3.99 (3.97)	3.47 (3.51)	7.94 (7.91)
$[Ni(L)_2(H_2O)_2]$	$C_{36}H_{32}NiN_2O_{12}S_2$	8.6	2.79	923.63	7.27 (7.23)	53.55 (53.51)	3.99 (3.96)	3.47 (3.49)	7.94 (7.90)
$[Cu(L)_2(H_2O)_2]$	$C_{36}H_{32}CuN_2O_{12}S_2$	12.8	1.77	928.48	7.82 (7.78)	53.23 (53.20)	3.97 (3.95)	3.45 (3.48)	7.89 (7.86)
$[Pd(L)_2]$	$C_{36}H_{28}PdN_2O_{10}S_2$	14.6	0.00	971.36	12.99 (12.96)	52.78 (52.76)	3.45 (3.42)	3.42 (3.47)	7.83 (7.81)

Total antioxidant content

Free radicals play an important role in the treatment of inflammatory diseases. Many complexes have been used as free radical inhibitors or radical scavengers. The ligand and its metal complexes exhibit antioxidant activity, and the prepared compounds have been used to treat diseases resulting from oxidative stress ⁽⁴⁰⁾.

The antioxidant activity of the ligand and the prepared complexes was evaluated by studying radical scavenging compared to tannic acid and gallic acid. The results obtained show that the absorbance increases with increasing concentration, which gives them antioxidant activity, as shown in Table and Figure (12), which illustrates the behavior of the prepared complexes as antioxidants.

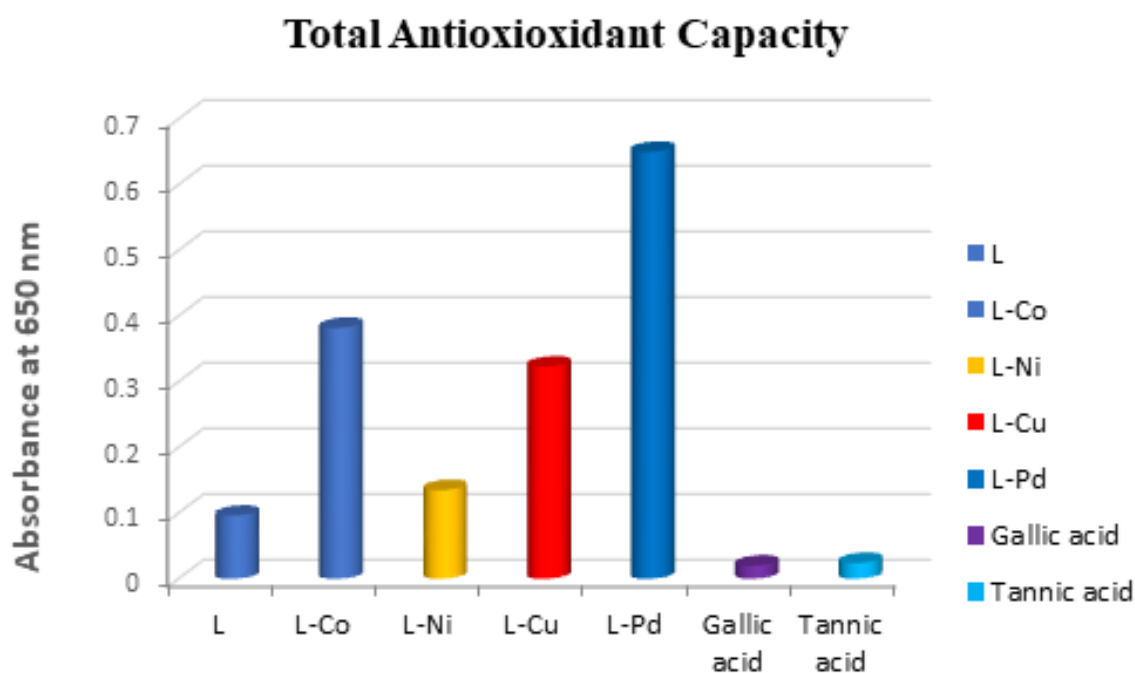


Figure (12) Behavior of the ligand (L) and its prepared complexes as antioxidants compared to tannic acid and gallic acid..

Conclusions

In this research, a Schiff base ligand was prepared and reacted with some binary metal salts (Pd, Cu, Ni, Co). High stability of the ligand and its metal complexes was observed through their identification with analytical and spectroscopic data (C.H.N.S) GC-Mass, TGA, $^1\text{H-NMR}$, UV-Vis, FT-IR), which confirmed the proposed structures. The general formula for the complexes was suggested as $[\text{M}(\text{L})_2(\text{H}_2\text{O})_2]$, while the general formula for the palladium complex was $[\text{M}(\text{L})_2]$, and it gave a distorted octahedral geometric shape, while the palladium complex was suggested as a square-planar shape, which was confirmed by magnetic susceptibility results as well as measurements. Molar conductivity showed the lack of ionic character of the prepared complexes through its low values, and measuring the chlorine content showed the absence of chlorine inside the coordination sphere as an electron-donating ligand or outside it, and the antioxidant results of the prepared complexes showed that the absorbance increases with increasing concentration, which makes them have antioxidant activity.

Reference

- More MS, Joshi PG, Mishra YK, Khanna PK. Metal complexes driven from Schiff bases and semicarbazones for biomedical and allied applications: a review. *Materials Today Chemistry* . 20 20100195 , 14 ;
- Long J, Luminescent Schiff-base lanthanide single-molecule magnets: The association between optical and magnetic properties, *Front. Chem* . 2019; 7:63 .
- Zhang J, Xu L, Wong WY. Energy materials based on metal Schiff base complexes. *Coordination Chemistry Reviews* , 2018; 355 : 180-198.
- Li Y, Zhong H, Huang Y, Zhao R. Recent advances in AIEgens for metal ion biosensing and bioimaging . *Molecules* , 20 204593 :(24) 24 ;
- Berhanu AL, Mohiuddin I, Malik AK, Aulakh JS, Kumar V. A review of the applications of Schiff bases as optical chemical sensors. *TrAC Trends in Analytical Chemistry* , 2019; 116 , 74-91.
- Ourari A, Khelafi M, Aggoun D, Jutand A, Amatore C. Electrocatalytic oxidation of organic substrates with molecular oxygen using tetradentate

ruthenium (III)-Schiff base complexes as catalysts. *Electrochimica Acta* , 2012; 75 , 366-370.

Kaur M, Kumar S, Younis SA, Yusuf M, Lee J. Post-Synthesis modification of metal-organic frameworks using Schiff base complexes for various catalytic applications. *Chem. Engine. J* , 2021; 423 , 130230

George RS, Joseph RA, George KE. Study of poly schiff's base as a protective agent in natural rubber. *Inter. J. Poly. Mater.* , 1993; 23 (1-2), 17-26.

Uddin MN, Ahmed SS, Alam SR. Biomedical applications of Schiff base metal complexes. *J. Coordi. Chem.* , 2020; 73 (23), 3109-3149.

BlackDSC. Markham E. Effect of chelation on synthesis of organic macrocycles . *Rev. Pure Appl. Chem.* 1965; 15: 109.

Clark P.J. Treble IE, Uden PC. Adsorption HPLC of tetradentate β - keto-imine copper, nickel and palladium chelates. *Polyhedron*, 1982; 1 (11): 785. 57

Fan J, Liu Z, Li J, Zhou W, Gao H, Zhang S. PEG-modified magnetic Schiff base network-1 materials for the magnetic solid phase extraction of benzoylurea pesticides from environ-

mental water samples. *J. Chromato. A* , 2020; 1619 , 460950 .

Zhou Y, Luan L, Tang B, Niu Y, Qu R, Liu Y. Fabrication of Schiff base decorated PAMAM dendrimer /magnetic Fe_3O_4 for selective removal of aqueous Hg(II) . *Chem. Engineer. J.* 2020; 398 , 125651 .

Castro AS, Rodrigues CHP, de Menezes MMT., da Silva ABD, Bruni AT. Fe (II), Ni (II), Cu (II), and Co (II) salen Schiff base complexes: Proposal for a voltammetric sensor to analyze cocaine hydrochloride and its interfering elements . *Forensic Chemistry* , 2021: 25 , 100347 .

Kargar H, Fallah-Mehrjardi M, Behjatmanesh-Ardakani R., Rudbari HA, Ardakani AA, Sedighi-Khavidak S, Tahir MN. Synthesis, spectral characterization, crystal structures, biological activities, theoretical calculations and substitution effect of salicylidene ligand on the nature of mono and dinuclear Zn(II) Schiff base complexes. *Polyhedron* . 2022; 213 , 115636 .

Kargar H, Adabi Ardakani A, Munawar KS, Ashfaq M, Tahir MN. Nickel (II), copper (II) and zinc (II) complexes containing symmetrical Tetradentate Schiff base ligand derived from

3, 5-diiodosalicylaldehyde: Synthesis, characterization, crystal structure and antimicrobial activity. *J. Iran. Chem. Soc.* , 2021; 18 , 2493-2503.

Kargar H, Aghaei-Meybodi F, Behjatmanesh-Ardakani R, Elahifard MR, Torabi V, Fallah-Mehrjardi M. Synthesis, crystal structure, theoretical calculation, spectroscopic and antibacterial activity studies of copper (II) complexes bearing bidentate Schiff base ligands derived from 4-aminoantipyrine: Influence of substitutions on antibacterial activity. *J. Mole. Structure* . , 2021; 1230 , 129908.

Kargar H, Fallah-Mehrjardi M, Behjatmanesh-Ardakani R, Rudbari HA, Ardakani AA, Sedighi-Khavidak S, Tahir MN. Binuclear Zn(II) Schiff base complexes: Synthesis, spectral characterization, theoretical studies and antimicrobial investigations. *Inorganica Chimica Acta* , 2022; 530 , 120677 .

Farhan MA, Ali WB, Nief OA. Synthesis, Characterization, and Biological Activity of Schiff Bases Derived from Heterocyclic Compounds. *Synthesis* , 2022; 45 (01): 4781-4790.

Yassen TM, AL- Azzawi, AM Synthesis and Characterization of New Bis-Schiff Bases Linked to Various Imide

Cycles. *Iraqi Journal of Science*, 2023; 64 (3): 1062 1070 .

Abed RR, Ismail HA. Synthesis, characterization, and biological activity assessment of new metal complexes of Schiff bases produced from benzoin. *Al- Kitab J. Pure Sci.* 2023; 7 (1): 27-41.

Prieto , P.; Pineda, M.; Aguilar, M. Spectrophotometric quantitation of antioxidant capacity through the formation of a phosphomolybdenum complex: specific application to the determination of vitamin E. *Anal. Biochem* . 1999; 269(2):337-341.

Mahdi SH. Spectroscopic, structural and antibacterial activity of mixed ligand complexes from Schiff base with anthranilic acid. *J.Phy . Confer. Seri.* 2019; 1234 (1):012089.

Abdulhadi SL, Abdulkadir MQ, Al- Mudhafar MM. The Importance of 2-AminoThiazole Schiff Bases as Antimicrobial and Anticancer Agents. *Al- Mustansiriyah Journal of Science* . 2020; 31 (3): 46-64.

Patel, NH, Parekh, HM, Patel, MN Synthesis, characterization and biological evaluation of manganese (II), cobalt (II), nickel (II), copper (II), and cadmium (II) complexes with monoba-

sis (NO) and neutral (NN) Schiff bases. *Transition metal chemistry*. 2005; 30 : 13-17.

Uddin, MN, Ahmed, SS, Alam , SR Biomedical applications of Schiff base metal complexes. *J. Coordi. Chem* . 2020; 73 (23), 3109-3149.

AL- nama, KS, AL Nidaa , EM Preparation and Characterization of Co(II), Ni(II), Cu(II) and Zn(II) Complexes with Unsymmetrical Tetradentate Schiff Bases Ligands. *Journal of Education & Science* , 2019; 28 (2): 233-248.

Yusuf, T. L., Oladipo, S. D., Zamisa , S., Kumalo , H. M., Lawal, I. A., Lawal , M. M., & Mabuba, N. Design of new Schiff-Base Copper (II) complexes: Synthesis, crystal structures, DFT study, and binding potency toward cytochrome P450 3A4. *ACS Omega* , 2021; 6 (21), 13704-13718.

Al- Mafrgy, MM, Mohammed, HA, Alzahwi , HM Synthesis and Characterization of Some Copper (II) Complexes with New Schiff Bases Ligands. *Kirkuk University Journal-Scientific Studies*, 2021; 16 (1), 28-47.

Pathan HK, Fatima A, Garg P, Muthu S, Yadav A, et al. Spectroscopic, Computational, Molecular Docking, and Dy-

namics Simulations Studies of 4-Amino-3-hydroxyNaphthalene-1-Sulfonic Acid (ANSA). *Polycyclic Aromatic Compounds*, 2023; 1-20.

Tunçel M, Serin S. Synthesis and characterization of new azo-linked Schiff bases and their cobalt (II), copper (II) and nickel (II) complexes. *Transition metal chemistry*. 2006; 31 (6), 805-812.

Ibraheem , I. H., Sadiq , A. S., Al-Tameemi , M., Alias, M. F. Synthesis, Spectral Identification, Antibacterial Evaluation and Theoretical Study of Co, Fe, Rh and Pd Complexes for 2-benzoylthiobenzimidazole. *Baghdad Sci. J.* 2022; 19 (6): 1326-1326.

J Althaher , L. Synthesis and Characterization of Mn (II), Co(II), Ni(II), Cu(II), Zn(II), and Hg(II) Complexes with [(N-(N- benzylidene) aminoethyl) Iodomethylene Dithiocarbamate]. *Raf. J.Sci.* 2013; 24 (7), 25-33.

Refat MS. Synthesis and characterization of ligation behavior of curcumin drug towards some transition metal ions: Chelation effect on their thermal stability and biological activity. *Spectro . Acta Part A: Mole. Bio. Spectro.* 2013; 105 , 326-337.

Al- Zaidi BH, Hasson MM, Ismail

AH. New complexes of chelating Schiff base: Synthesis, spectral investigation, antimicrobial, and thermal behavior studies. *J. Appl. Pharma . Sci.* , 2020; 9 (4), 045-057.

Suleman VT, Al- Hamdani AAS, Ahmed SD, Jirjees VY, Khan ME, et al. Phosphorus Schiff base ligand and its complexes: Experimental and theoretical investigations. *Appl. Organomet . Chem.* , 2020; 34 (4): 1–16.

Moor WJ, Physical Chemistry. 5th ed. Longman, London;1972; P.425.

Hikmat YR, Thesis, Ph.D. Mousl. University.1999.

Al-Mukhtar SE, Mustafa IA “Inorganic and Coordination Chemistry” Mosul University, Iraq. 1988.

Shah, S.S., Shah, D., Khan, I., Ahmad, S., Ali, U., Rahman, A. Synthesis and antioxidant activities of Schiff bases and their complexes: An updated review. *Biointerface Res. Appl. Chem*, 2020; 10 (6): 6936-6963.