



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



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A NEW Azo-Schiff base derivative (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 (HANPH) and its metal complexes which include Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Pt(II), and Au(III) metal ions were synthesized. The structure of these compounds has been investigated by using elemental analysis, FT-IR, UV-Vis spectrometric methods, ¹H-NMR, mass spectra, atomic absorption, molar conductivity and magnetic susceptibility of metal complexes. The spectroscopic data of the complexes suggest that their (1:1) (metal: ligand) is mole ratio. Also, the analytical studies for all new complexes have shown octahedral geometries, except for Pt (II) and Au (III) complexes which suggested square planar geometries also its conductivity measurements show electrical properties. These complexes show high conductance value supporting (1:1) electrolytic nature. Furthermore, the FTIR results show that the coordination site from the ligand to the metal ions were through the nitrogen of azomethine group and the nitrogen of the azo group for all new complexes, except for Pt (II) and Au (III) complexes which were through the nitrogen of imine groups only.

Keywords: N-(1-Naphthyl)ethylene diamine dihydrochloride, Azo-Schiff base, Transition metal complexes.

Introduction

Cobalt, Nickel, Copper and other transition metals complexes have bright colors and are often having a strange empirical formula [1], these compounds are called coordination complexes [2]. The presence of different chemical groups positioned geometrically around the metal ion is to give their major proposed feature, these groups are called coordinating groups. They change the chemical behavior of metal to make it have the electronic properties that the free metal or ion does not have and can adsorb visible light [3]. It is worth mentioning that large areas of biochemistry are applied in transitional metal chemistry [4]. Schiff base ligands and their metal complexes are widespread because of their miscellaneous

chelating capabilities. They show significant function in analytical structural studies such as a consequence of their fundamental miscellany and preparative convenience [5]. Concerning a variety of metal atoms, the metal complexes of Azo-Schiff bases are considered a result of flexibility, sensitivity, synthesis, and selectivity. They can be employed as dyes, intermediates in biological formation, catalysts and polymer stabilizers.

The chemistry of Schiff bases has played an important role as chelating ligands in main group and transition metal coordination chemistry due to their stability in a variety of oxidative and reductive conditions like imine ligands are borderline between hard and soft Lewis base [6,7]. The bases of Schiff are typified by the

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-N=CH- (azomethine group) which are typically created from the prime amines condensation and effective carbonyl group [8,9]. Schiff bases form some imperative kinds of biological compounds since they have different donor atoms and are capable of changing reaction based on the initial reagent. This category of compounds includes broad diversity of organic features [10-12].

Schiff base ligands which are derived from benzil could be a good class of organic compounds that are capable of binding to different metal ions through the azomethine nitrogen atom. The coordinating property of benzil is converted into easy ligand by condensation reaction with a variety of a primary amine. Benzil acts as diketones like acetyl acetone, acetoacetanilide, etc. [13]. Schiff base derived from benzil and its transition metal complexes investigated by many researchers. They are used as catalysts in medicine, such as in antibiotics and anti-inflammatory agents, analytical reagents for spectrophotometric metal analysis, and anticorrosive [14-16].

In this study, the synthesis and characterization of the 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 and its metal complexes with Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Pt(II), and Au(III) ions have been presented. The formation of these compounds was explained through spectroscopic techniques.

Experimental

Materials

All chemicals were of analytical grades and were used as received from suppliers without further purification.

Instruments

The melting point was determined using model 9300 of ligand and its complexes. Electronic

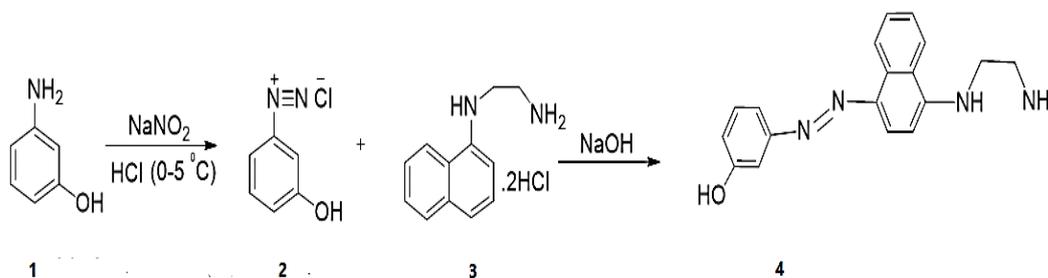
spectra for compounds in the (UV-Visible) region (200-1100) nm were recorded using Shimadzu spectrophotometer double beam model 1700. Fourier Transform Infrared (FTIR) spectra were recorded on Shimadzu FTIR 8400 spectrometer using KBr disc pellet in the wavelength range 400-4000 cm^{-1} . Magnetic susceptibility measurements were carried out on a balance magnetic MSB-MKI using faraday method. The diamagnetic corrections were made by Pascal's constants. Elemental analyses were performed by means of EURO 2012EA 300 C.H.N Elemental analysis. ^1H NMR spectra were recorded as solution in DMSO d_6 as solvent using (varian 500MHZ Spectrophotometer), and Mass Spectra were recorded on Shimadzu Agilent Technologies 5975C.

Results and Discussion

Chemistry

A diazonium solution **2** was prepared by dissolving (1.09g, 0.01mol) of 3-amino phenol (**1**) in (30 ml) of distilled water and 3 ml of HCl. The solution was treated with (5 ml) of aqueous (1 M) sodium nitrite dropwise, and stirred for 30 min at 0°C , N-(1-Naphthyl) ethylene diamine dihydrochloride (2.59 g, 0.01 mol) as coupling compound. It (**3**) was dissolved in 50 ml of ethanol and 10% NaOH was added. Then by dropwise addition, a diazonium chloride (**2**) solution was prepared in order to couple compound (**3**) with mixture stirred for (1h) at 0°C . The product (**4**) was filtered, air dried and recrystallized twice from hot ethanol and then dried in the oven at 60°C for 3 h. **Scheme 1**.

In an ethanolic solution (50ml) of product (**4**) (3.06g, 0.01mol) was added to (20ml) of Benzil (**5**) (2.10g, 0.01 mol) in the same solvent. Then a few drops of glacial acetic acid were added to the reaction solution and refluxed with stirring for (12h). The crystalline product (**6**) was filtered and recrystallized and dried over anhydrous CaCl_2 , yield= 83%, M.p= (102°C).



Scheme 1. Synthesis of the compound 4.

The new ligand (**8**) was prepared by the condensation of product (**6**) and 3,4-diamino benzophenone (**7**) in equimolar (2:1) ratio in ethanol absolute presence drops of glacial acetic acid, the reaction mixture was refluxed with stirring for (35h). The product (**8**) was recrystallized from the ethanol solvent and dried in vacuum. The physico-chemical properties and analytical data for the product (**8**) are given in (Table 1), yield= 80%, M.p= (132-134°C). **Scheme. 2**.

General procedure for preparation of Azo-Schiff base Metal complexes

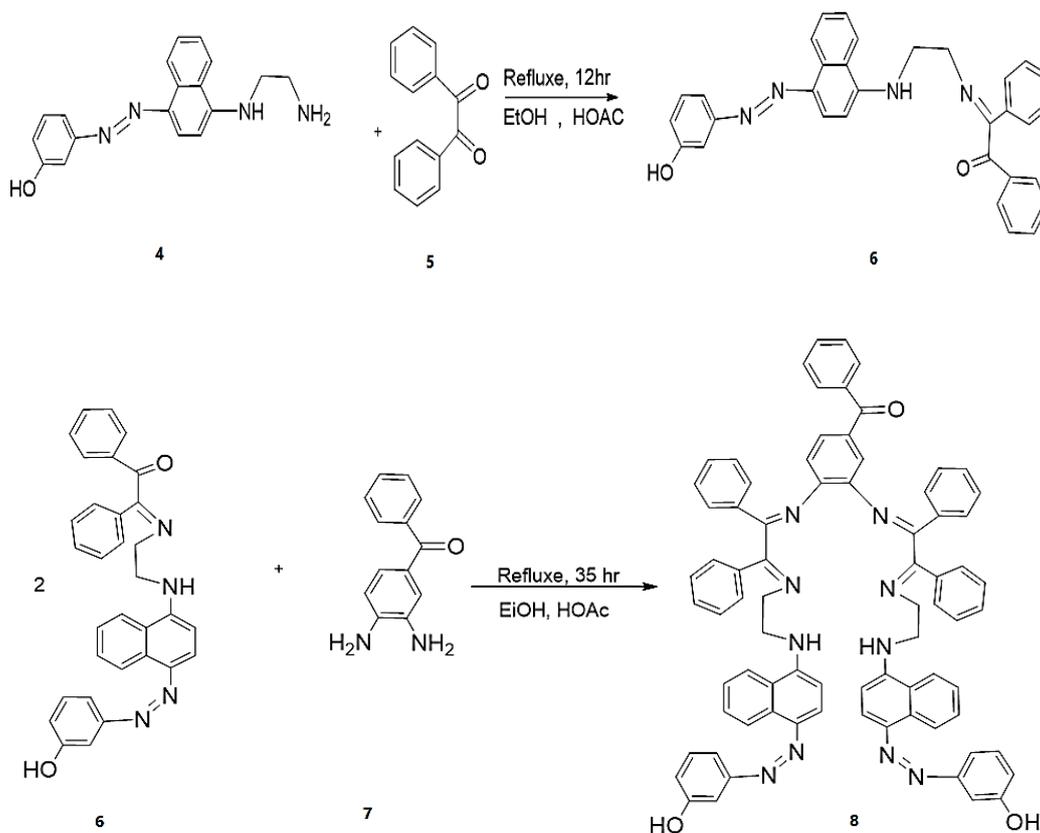
The metal complexes were prepared from hot ethanol solution of the ligand 3,4-bis(((1E,2E)-2-((2-((4-((Z)-(3-hydroxyphenyl)diazenyl)naphthalen-1-yl)amino)ethyl)imino)-1,2-diphenylethylidene) amino) phenyl) (phenyl) Methanone (**8**) (1.172g, 001mole) in (25ml) ethanol absolute with (0.001 mole) of metal ions Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Pt(II), and Au(III). The reaction mixture was refluxed at 70°C for (2 h). The formed precipitate was filtered off and washed with ethanol then it was dried.

Physical Properties and Elemental Analyses

The new Azo-Schiff base ligand (**8**) and its metal complexes were isolated, purified and gave very good yields. All complexes were colored, stable to air and temperature, and insoluble in water, but they were soluble in common organic solvents (DMSO, DMF, Methanol and ethanol). The metal complexes were characterized by (C.H.N) Micro elemental analysis, FT-IR, UV-Vis, ¹HNMR, molar conductivities and magnetic moment. The analytical data of the complexes were consistent with the experimental data. The molar conductivity values show that all the complexes have been electrolytic and their magnetic moment values were in agreement with geometry structure. Some physical properties and data of elemental analyses for the new azo-Schiff base ligand (**8**) and its chelate complexes were recorded in Table (1).

Mass spectroscopy

The fragmentation pattern of the new azo-Schiff base ligand (**8**) (Fig 2) and its complex with Cu (II) (Fig 3) were studied by Mass spectroscopy which showed peaks clearly corresponding to the calculated formula mass of each one [11].



Scheme 2: Synthesis of the compounds 6 and 8.

TABLE 1. Some Physical properties and analytical data of the azo – Schiff base ligand **8** and its complexes

No.	Compound	weight formulae	Colour	M.p. °C	Yield %	R _f	Found, (Calc.)%			
							%C	%H	%N	%M
1	*L=C ₇₇ H ₆₀ N ₁₀ O ₃	1172	Deep red	132-134	80	0.97	(78.83) 78.34	(5.11) 5.62	(11.94) 11.43	-----
2	[Co L] Cl ₂	1301.9	Green	150-152	75	0.90	(70.97) 70.14	(4.60) 4.45	(10.75) 10.64	(4.52) 4.28
3	[Ni L] Cl ₂ .H ₂ O	1319.6	Green	157-159	78	0.87	(70.02) 70.98	(4.54) 5.11	(10.60) 10.21	(4.44) 4.15
4	[Cu L] Cl ₂	1306.5	Purple	158-160	82	0.64	(70.72) 70.21	(4.59) 4.24	(10.71) 10.25	(4.86) 4.96
5	[Zn L] Cl ₂	1308.3	red	162-164	72	0.58	(70.62) 69.83	(4.58) 4.23	(10.70) 10.20	(4.99) 4.10
6	[Cd L] Cl ₂	1355.4	Green	160-161	74	0.71	(68.17) 68.00	(4.42) 4.87	(10.32) 10.12	(8.29) 8.22
7	[Pt L] Cl ₂	1438	Deep Purple	310>	70	0.94	(64.25) 64.02	(4.17) 4.54	(9.73) 10.21	(13.56) 13.55
8	[Au L] Cl ₃	1475.4	Deep Green	310>	80	0.88	(62.62) 63.01	(4.06) 3.43	(9.48) 8.27	(13.34) 13.51

*L= compound **8**

The mass spectrum of compound (**8**) and its complex with Cu (II) showed peak at m/z values of 304.7 as a base peak for each of them. The mass spectrum of the compound (**8**), displays a peak at m/z 1172.4 (2.8%) due to the original molecular weight. The peak at the mass spectrum of Cu (II) complex displays a peak at m/z 1306.8 (3.5%) which corresponds to the exact molecular weight of the Cu (II) complex [15,16].

The suggested molecular ion in the mass spectrum of the compound (**8**) is formed by ionization at the (C=N) and (N=N) linkages to display a peak at m/z 1172.4 (2.8%) is attributed to the original molecular weight. The Fission of this ionized bond afforded a fragment at m/z 684.8. This ion can split in the two possible tracks to afford a molar ion at m/z 565.9 (Scheme 3), and by losing a phenyl amine moiety could afford an ion at m/z 360.8, while phenyl moiety loses could afford an ion at m/z 360.8. Later cation loses ethyl amine moieties to afford an ion at m/z 304.7 as the base peak of the spectrum.

The MS fragmentation pattern of the Cu (II) complex (Fig. 3) is formed by ionization of the complex by losing an electron to display a peak at m/z 1306.8 (3.5%) which corresponds to the exact molecular weight of the Cu (II) complex then by losing two chloride ions to form a cation at m/z 1235.9. Then a molecular ion is suggested to be formed by ionization of azo group (N=N) linkage at m/z 1067.8. Later this cation losing azo moieties to afford an ion at m/z 831.5 and

by losing a phenyl moiety could afford an ion at m/z 360.8. Finally, it followed exactly the same mechanism employed in the fragmentation of compound (**8**) to afford an ion at m/z 304.7 as the base peak of the spectrum. The mass fragmentation patterns of the Compound (**8**) and its chelate complex with Cu (II) were shown in schemes **3** and **4**.

¹H NMR spectra

The confluence of spectral data from these spectra highlights deep features about the structure of organic compounds. Thus, in the ¹H NMR spectra of free ligand (**8**) and Zn(II) complex were recorded in DMSO-d₆ as a solvent with TMS as internal standard. The amine proton of Naphthyl ring moiety appeared as singlet signal at δ ~ 4.7 ppm [17]. It was shifted to δ = 5.1 ppm in the complex of Zn(II) on moving from the down-field to the up-field region of the ¹H NMR spectrum [18]. The multiple signals in the region between δ = 7.1- 8.0 ppm belong to the aromatic protons [19], while the methylene group (-CH₂) appeared at 1.89 ppm. Finally, the position of phenolic hydroxide (-OH) appeared at δ = 9.8 ppm in the spectrum of ligand (**8**) and Zn(II) complex. This indicates that (-OH) group is not involved in the coordination [20]. The ¹H NMR spectra of the new azo-Schiff base ligand **8** and Zn (II) complex are shown in (Figure 4 and 5).

Infrared Spectra

All the infrared frequencies of the azo-Schiff base ligand (**8**) and their complexes are given in Table 2 and IR spectra of the free ligand and

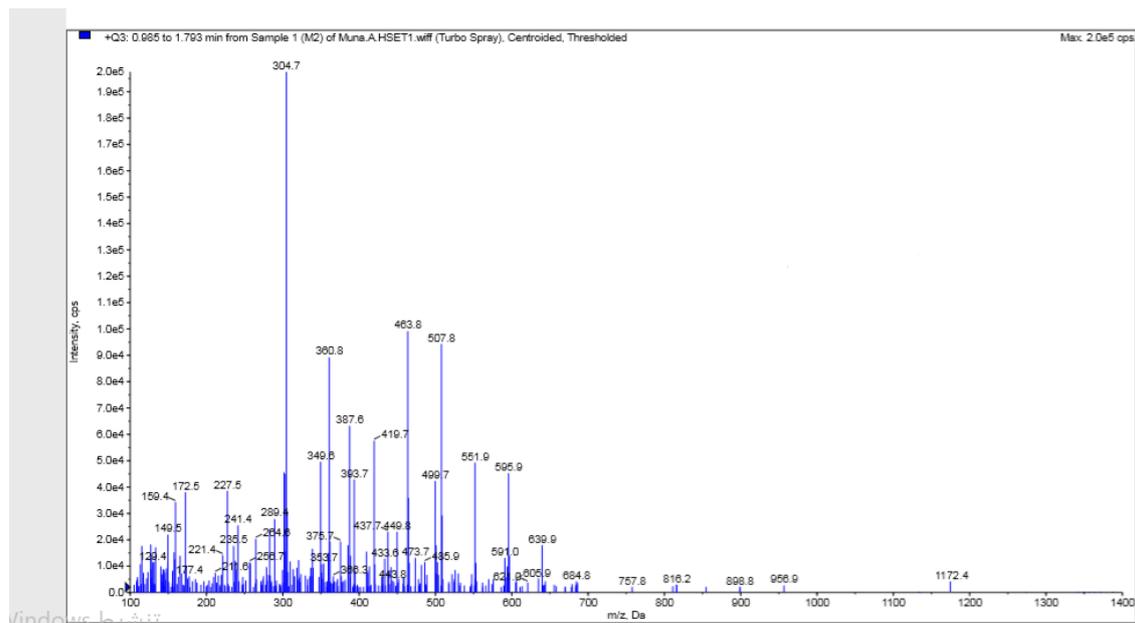
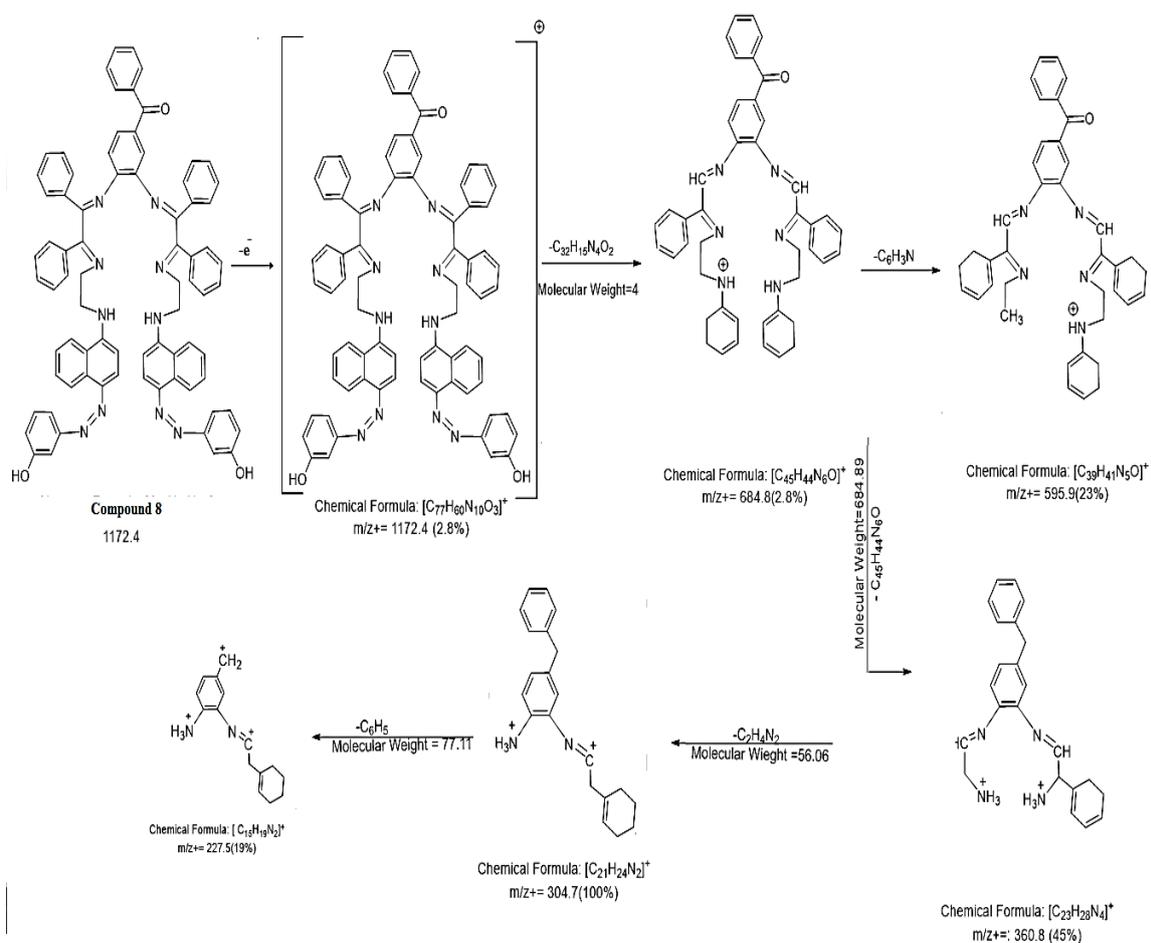


Fig. 2: the mass spectrum of the compound 8 .



Scheme 3. Suggested fragmentation pathways of the compound 8 .

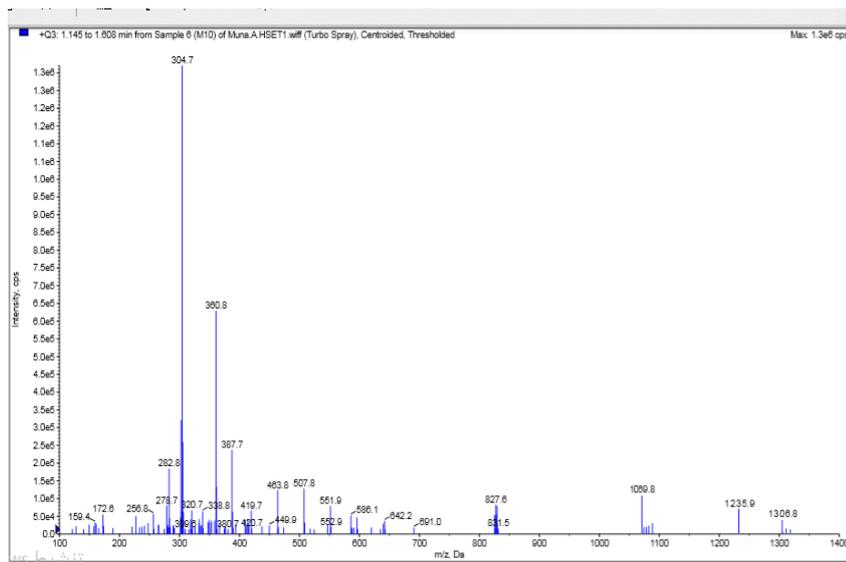
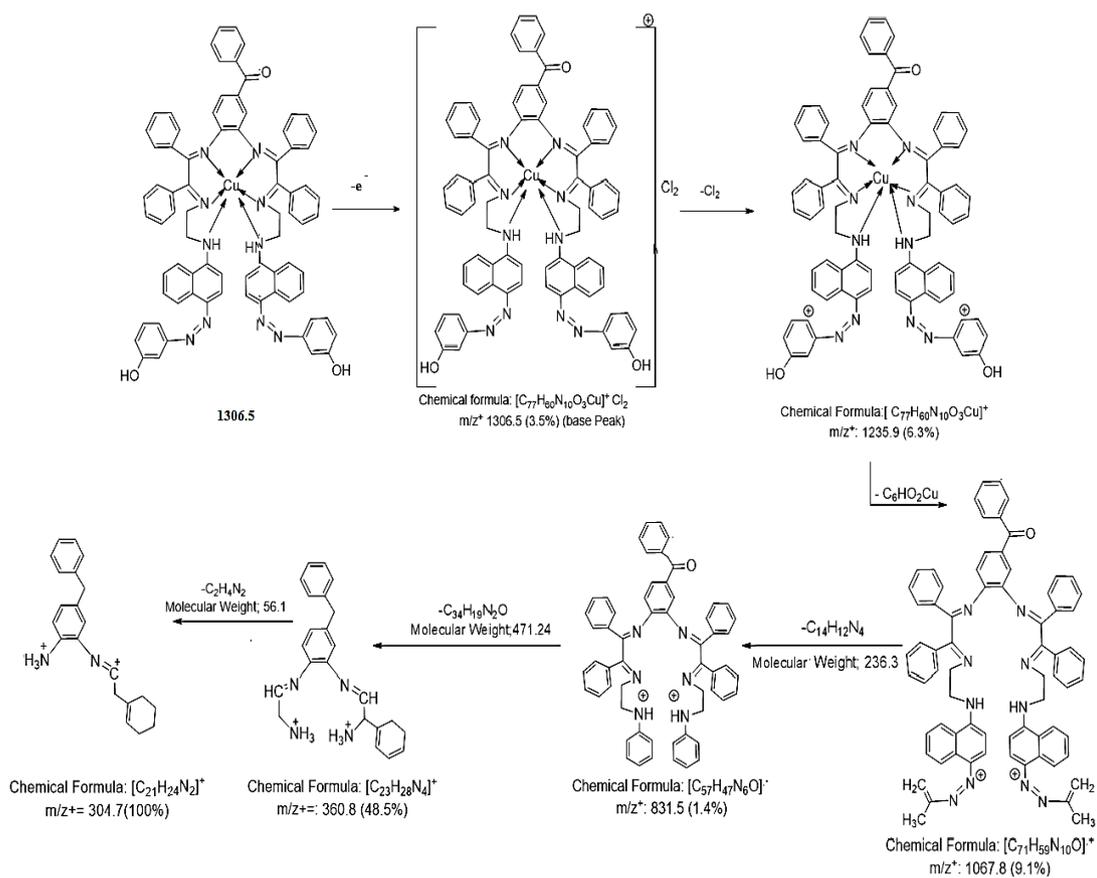
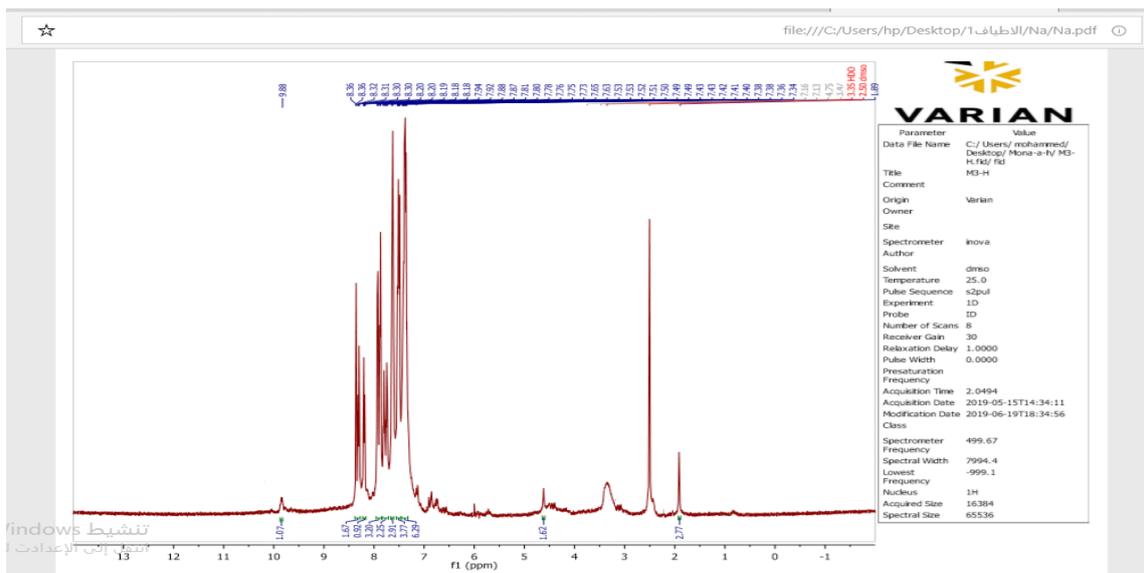
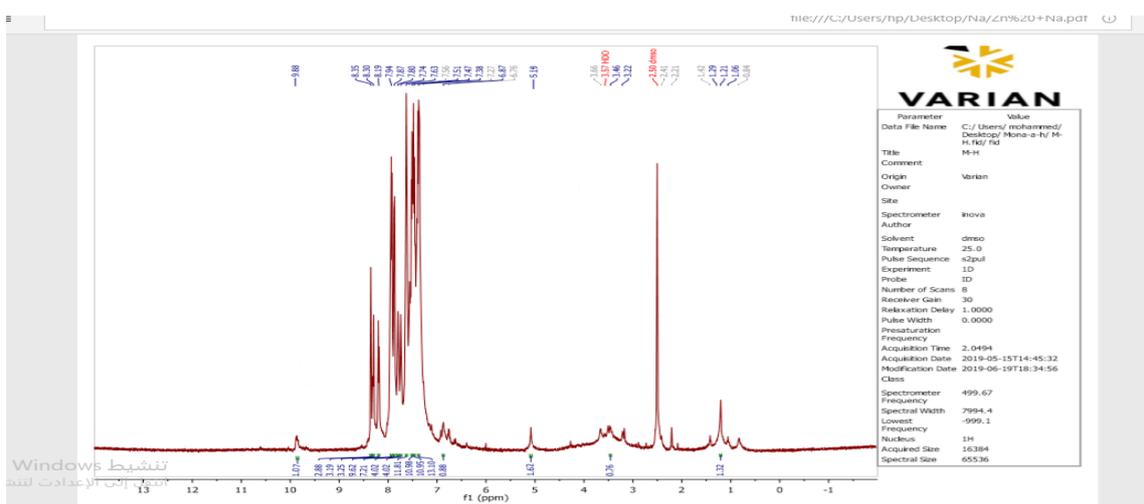


Fig. 3: the mass spectrum of the Cu (II) complex.



Scheme 4. Suggested fragmentation pathways of Cu-complex

Fig. 4: ¹H-NMR. Spectrum of the Compound 8Fig.5: ¹H-NMR. Spectrum of Zn(II) complex

their complex with Au(III) are given in figures 6 and 7. The complex of Ni(II) exhibits broad band in the 3000-3600 cm^{-1} range and this may be attributed to the presence of water molecular outside the coordination sphere [21,22]. A strong IR absorption band observed in the free ligand 1620 cm^{-1} assignable to the absorption of the imine groups ($>\text{C}=\text{N}$ -) in the free azo-Schiff base ligand (8) was shifted and changing in the range of 1531-1630 cm^{-1} and this visualizes the coordination by the nitrogen atoms of imine groups to the metal ions [23]. Also, spectrum of the new ligand 8 displays the azo group ($-\text{N}=\text{N}-$). This band did not show any frequency shifting in infrared spectra

of the chelates complexes [24] while in the low frequency regions, bands were detected around 542-596 cm^{-1} ranges assigned to $\nu(\text{M}-\text{N})$ [25].

Thus, the above infrared spectral data lead to the suggestion that the coordination sites of the new ligand (8) were by the nitrogen atom of imine group ($-\text{C}=\text{N}$) and the nitrogen atom (NH) of Naphthyl ring. The stretching of NH group of this ligand is displayed in the region (3379 cm^{-1}), which were shifted in the infrared spectra of the chelates complexes. This is an evident that it was a coordination to the metal atoms [22], except the Pt (II) and Au (III) complexes which were through the nitrogen of imine groups only.

TABLE 2: FT-IR spectral data (cm⁻¹) of azo-Schiff base ligand 8 and its complexes.

Compound	<i>v</i> (OH) Phenolic H ₂ O	<i>v</i> (NH)	<i>v</i> (C=N)	<i>v</i> (N=N)	<i>v</i> (M-N)
Ligand 8 C ₇₇ H ₆₀ N ₁₀ O ₃	3545	3379	1595, 1577, 1535	1446, 1398	-----
[Co L] Cl ₂	3483	3423	1600, 1548	1448, 1402	596
[Ni L] Cl ₂ .H ₂ O	3402	3383	1630, 1600, 1575	1446, 1396	509
[Cu L] Cl ₂	3545	3401	1597, 1579, 1544	1446, 1396	584
[Zn L] Cl ₂	3545	3408	1589, 1570, 1542	1448, 1396	596
[Cd L] Cl ₂	3545	3367	1593, 1531	1446, 1396	574
[Pt L] Cl ₂	3545	3415	1600	1446, 1406	501
[Au L] Cl ₃	3542	3486	1612, 1558, 1537	1446, 1402	574

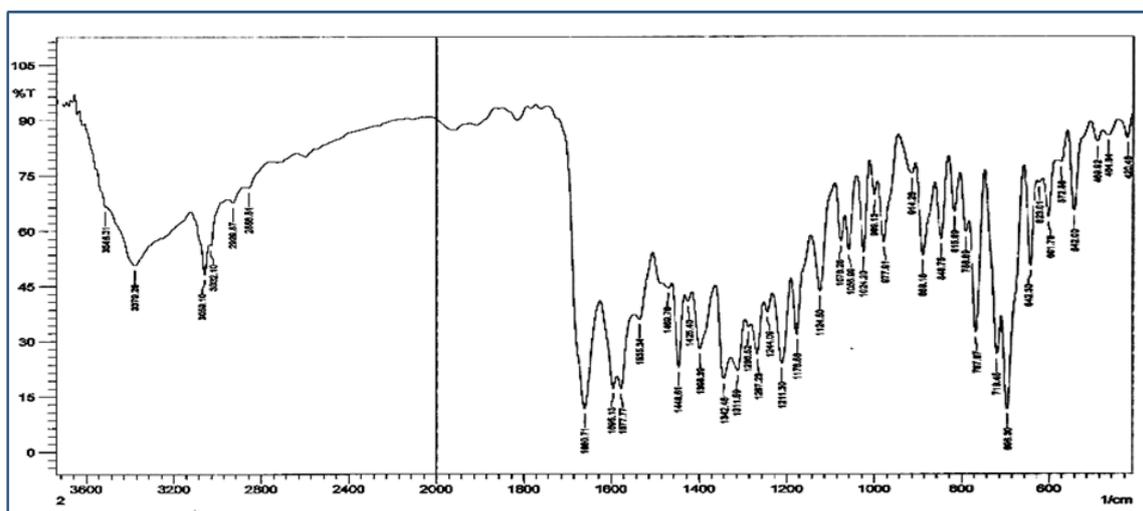


Fig. 6: FT-IR bands of the compound 8 .

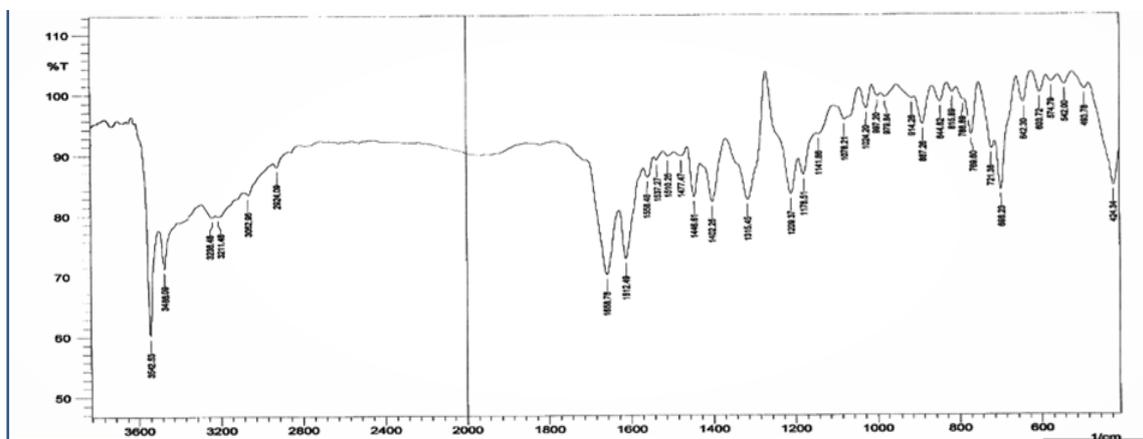


Fig. 7: FT-IR bands of Au(III) complex

Molar conductivity measurements

All complexes showed the conductivity measurement values ranging between (72.51 – 138) S.cm².mol⁻¹ in DMSO at room temperature. These values indicate the ionic structure of these complexes. These results explain molar conductance and suggest that the complexes were electrolyte indicating that the chloride ions were outside the coordination sphere [26]. The conductivity values are listed in **Table (3)**.

Electronic spectra and Magnetic Moments

The UV-Visible spectrum of Azo-Schiff base ligand (**8**) showed two bands at 352 nm (28409 cm⁻¹) and 435 nm (22988 cm⁻¹). These two bands are observed due to (π - π^*), (n- π^*) transition respectively, which were shifted in the electronic spectra of complexes [27].

The electronic spectrum of the Co(II) complex exhibited three well defined bands at 744 nm (13440 cm⁻¹), 675 nm (14814 cm⁻¹), and 553 nm (18083 cm⁻²). These bands were assigned to ${}^4T_{1g} \rightarrow {}^4T_{2g(F)}$ (ν_1), ${}^4T_{1g} \rightarrow {}^4A_{2g(F)}$ (ν_2), and ${}^4T_{1g} \rightarrow {}^4T_{2g(P)}$ (ν_3) transitions respectively. The magnetic moment is 3.87 B.M. Thus, the octahedral geometry has been assigned for this complex [28,29].

The electronic spectrum of the Ni(II) complex exhibited bands at 810 nm (12345 cm⁻¹), 718 nm (13927 cm⁻¹), and 567nm (17636 cm⁻¹). These bands were assigned to ${}^3A_{2g} \rightarrow {}^3T_{1g(F)}$

(ν_1), ${}^3A_{2g} \rightarrow {}^3T_{1g(F)}$ (ν_2), and ${}^3A_{2g} \rightarrow {}^3T_{1g(P)}$ (ν_3) transitions respectively. Its magnetic moment is 2.97 B.M the octahedral geometry has been assigned for this Ni (II) complex [30,31].

The electronic spectrum of The Cu(II) complex exhibited two bands at 574 nm (17421 cm⁻¹). These bands were assigned to ${}^2E_g \rightarrow {}^2T_{2g}$ transition. The magnetic moment is 1.71 B.M, an octahedral geometry around Cu (II) ions [32,33].

The spectra of Zn(II), and Cd(II) complexes showed bands at 594 nm, (16835 cm⁻¹), and 678 nm (14749 cm⁻¹) transitions respectively, assigned to charge transfer transitions. The Zn (II), and Cd(II) complexes are diamagnetic moment; based on these data, an octahedral geometry is proposed to the complexes [34-36].

The spectra of Pt(II), and Au(III) complexes were diamagnetic and their spectra showed one band at 632 nm (15822 cm⁻¹), 599nm (16694 cm⁻¹) transitions respectively. These bands were assigned to ${}^1A_{1g} \rightarrow {}^1T_{1g}$, and ${}^1A_{1g} \rightarrow {}^1B_{1g}$ transitions respectively. According to these data, we suggest a square planar geometry around Pt(II), and Au(III) ions[37,38]. The UV-Vis spectra of the new azo-Schiff base ligand and Au(III) complex are shown in (**Figure 8 and 9**). The electronic spectra of the new Azo-Schiff base ligand (**8**) and its complexes in freshly ethanol solvent, and magnetic moments are given in **Table 3**.

TABLE 3. Electronic spectra (nm, cm⁻¹) magnetic moments, geometry, hybridization and conductivity.

Compounds	λ_{max} (nm)	Absorption bands(cm ⁻¹)	Transitions	μ_{eff} (B.M)	Geometry	Hybridization	Conductivity S.mol ⁻¹ . cm ²
Ligand	352	28409	$\pi \rightarrow \pi^*$				
C ₇₇ H ₆₀ N ₁₀ O ₃	435	22988	n \rightarrow π^*	----	----	----	----
[Co L] Cl ₂	744 675 553	13440 14814 18083	$\nu_1 = {}^4T_{1g} \rightarrow {}^4T_{2g(F)}$ $\nu_2 = {}^4T_{1g} \rightarrow {}^4A_{2g(F)}$ ${}^4T_{1g} \rightarrow {}^4T_{2g(P)}$ $\nu_3 =$	5.07	Octahedral	Sp ³ d ²	77
[Ni L] Cl ₂ .	810 718	12345 13927	$\nu_1 = {}^3A_{2g} \rightarrow {}^3T_{1g(F)}$ $\nu_2 = {}^3A_{2g} \rightarrow {}^3T_{1g(F)}$	2.97	Octahedral	Sp ³ d ²	72
H ₂ O	567	17636	$\nu_3 = {}^3A_{2g} \rightarrow {}^3T_{1g(P)}$				
[Cu L] Cl ₂	574	17421	${}^2E_g \rightarrow {}^2T_{2g}$	1.71	Octahedral	Sp ³ d ²	76
[Zn L] Cl ₂	594	16835	$d\pi(Zn)^{2-} \rightarrow \pi^*(L)$	Dia	Octahedral	Sp ³ d ²	78
[Cd L] Cl ₂	678	14749	$d\pi(Cd)^{2-} \rightarrow \pi^*(L)$	Dia	Octahedral	Sp ³ d ²	78
[Pt L] Cl ₂	632	15822	${}^1A_{1g} \rightarrow {}^1T_{1g}$	Dia	Square planer	dsp ²	80
[Au L] Cl ₃	599	16694	${}^1A_{1g} \rightarrow {}^1B_{1g}$	Dia	Square planer	dsp ²	138

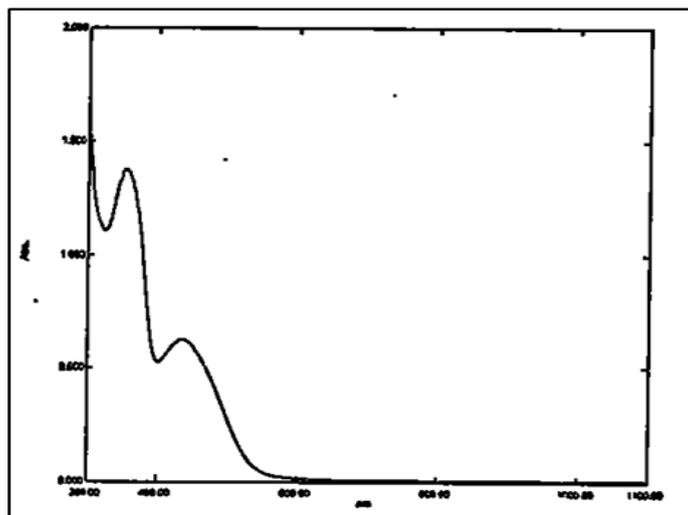


Fig. 8: UV-Vis. Spectrum of the compound 8

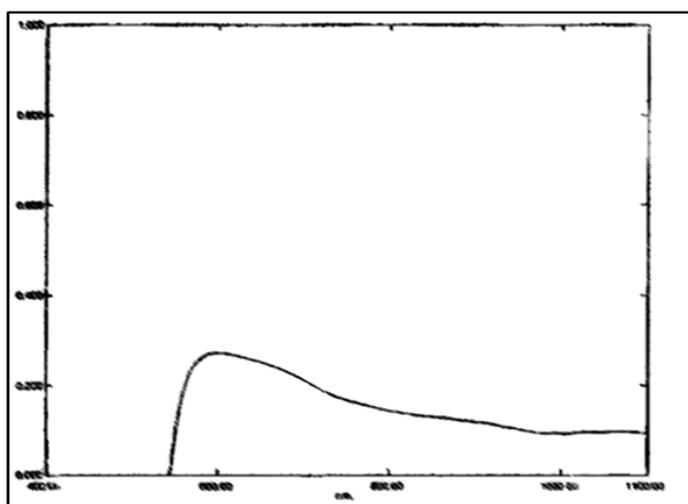


Fig. 9: UV-Vis. Spectrum of Au(III) complex.

Conclusion

1. The preparation of the New azo-Schiff base ligand (**8**) included two steps: the first step included diazotization reaction giving an azo compound (**4**), while the second step included two condensation reactions : between azo compound (**4**) with α, β diketon (**5**) and between the azo-schiff base compound (**6**) with carbonyl compound (**7**).
2. All the prepared compounds were colored, stable towards air and temperature, and insoluble in water.
3. The fragmentation pattern of the new azo-Schiff base ligand (**8**) and its complex with Cu(II) were studied by mass spectroscopy, which showed peaks clearly corresponding

to the calculated formula mass of each one. These results validate the expected structures of the prepared complexes.

4. The micro elemental analysis gives conclusive evidence on the validity of the mole ratio (1:1) (M:L) for all the prepared complexes.
5. The spectroscopic data of all complexes: FT-IR, UV-Vis spectrometric methods, and $^1\text{H-NMR}$ as well as Atomic absorption were suggested octahedral geometries, except for Pt(II) and Au(III) complexes suggesting square planar geometries.
6. The conductivity measurements show electrical properties. These complexes show high conductance value supporting (1:1) electrolytic nature.

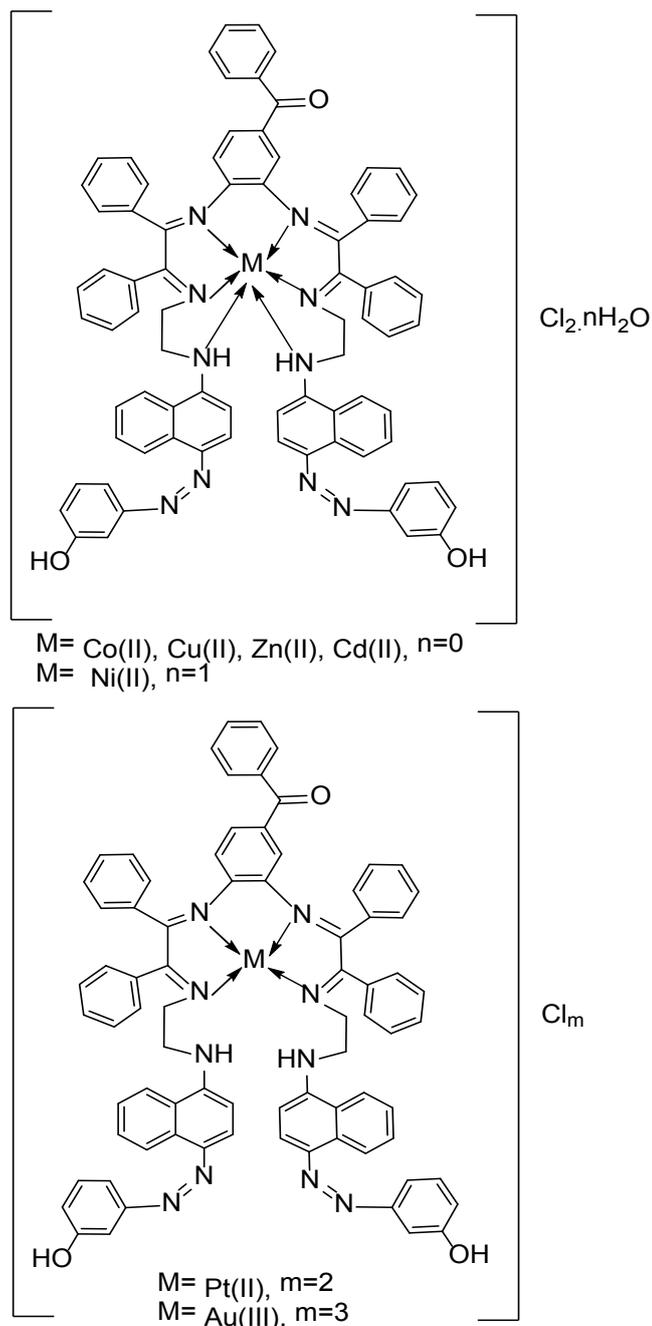


Fig .10. The proposed structural formula of the complexes.

7. According to the above results, the coordination sites from the ligand to the metal ions Co(II), Ni(II), Cu(II), Zn(II) and Cd(II), were through the nitrogen of imine group and the nitrogen of azo group, except for Pt(II) and Au(III) complexes which were through the nitrogen of imine groups only, as shown in Figure 10.

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