



SPECTROSCOPIC, THERMAL, AND CONDUCTOMETRIC STUDIES OF SOME (ARYLAZO) QUINOLIN-8-OL AND THEIR COMPLEXES WITH THE DIVALENT IONS OF MN, NI, CU, AND ZN

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Abstract

Elemental analysis, infrared (IR), proton nuclear magnetic resonance (1H NMR), and mass spectra were used to characterize (p-methylphenylazo)quinolin-8-ol (L1) and (p-methoxyphenylazo) quinolin-8-ol (L2). The important infrared (IR) spectral bands corresponding to the active groups in the two ligands and the solid complexes under investigation were studied. Also, the important fragments in the ligands and the complexes were determined using mass spectra, and the main peaks corresponded to the molecular weights of the ligands and complexes. The solid complexes have been synthesized and studied by elemental and thermal analyses (TG and DTA) as well as by IR, ¹HNMR, magnetic measurements, electronic transitions, and molar conductance. The proposed stereochemical structures for the investigated metal complexes suggest octahedral geometry with respect to Mn, Ni, Cu, and Zn metal ions with the investigated ligands 1:1 and 1:2 complexes, and all of the formed complexes contain coordinated water molecules and hydrated water. All of the prepared solid complexes behave as non-electrolytes in chloroform.

Keywords: quinolin-8-ol; Spectroscopic; Thermal analysis; conductivity; Electron spin resonance; Infrared; Absorption spectra; electronic transitions

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1. INTRODUCTION

Organic metal chelates have attracted more and more attention because of their high thermal stability, sufficient electron-transport, and luminescent properties in recent years [1]. In recent years, a great deal of attention has been drawn to the behaviors of amphoteric bifunctional molecules, which can serve as prototypes for structurally related subunits in many important biomolecules. In these bifunctional molecules, proton transfer from a hydroxyl or amino proton to an acceptor such as a carbonyl oxygen or a nitrogen atom is a fundamentally important reaction, playing a crucial role in many biological and photochemical processes [2], [3]. Hydroxyquinolines have been used at different times in organic, inorganic, and analytical [4] Among different types of dyes used for the purpose, azo dyes have a distinct advantage over others [5]. Furthermore, quinolin-8-ol derivatives may be used as chelate forming agents in chelate affinity chromatography [6]. These dyes are used as probes in protein chemistry to study the binding behavior of proteins [7], [8].

The present investigation is concerned with the use of some of these 8-HQ (8-hydroxyquinoline) azo dyes as chelating agents for the divalent Mn, Ni, Cu, and Zn metal ions. The 8-hydroxyquinoline azo dyes under investigation are represented in the experimental part. The solid chelates of the 8-hydroxyquinoline azo dye derivatives with Mn⁺², Ni⁺², Cu⁺² and Zn⁺² metal ions were prepared and subjected to many analytical studies, such as elemental analysis, infrared (IR), nuclear magnetic resonance (NMR), mass spectra (MS), thermal analysis (TG and DTA), magnetic susceptibility measurements, molar conductance and electronic absorption spectra.

EXPERIMENTAL

I.1. Chemicals

The purest chemicals available were employed in every application. These included manganese (II) chloride (MnCl₂·4H₂O), nickel(II) chloride (NiCl₂·6H₂O), copper (II) chloride (CuCl₂·2H₂O), zinc chloride (ZnCl₂), p-toluidine (p-methylaniline), p-ansidine (p-methoxyaniline),

potassium hydroxide, 8-hydroxyquinoline, ammonium hydroxide(30% NH_3), ammonium chloride, disodium salt of ethylenediamine tetraacetic acid dehydrate (EDTA), sodium chloride, silver nitrate (AgNO_3), sulphuric acid (H_2SO_4), hydrogen peroxide (H_2O_2) and hydrochloric acid (37% HCl). The solvents used were ethanol and dimethylsulfoxide (DMSO). Distillation was used to purify the solvents.

2.1 Preparation of ligands L1 and L2

An ice salt bath was used to chill a well-stirred solution of p-toluidine (p-methylaniline) (1.11mole in 40 ml ethanol) or p-ansidine (p-methoxy-aniline) (1.29 mmole in 40 ml ethanol)

and 20 ml of (2M, 2.68 ml, 32.19 mmol) HCl was cooled in an ice salt bath and diazotized with aqueous sodium nitrite solution (20 ml, 0.01mol). The cooled (0-5° C) diazonium solution was added slowly to a well-stirred solution of (1.55 g-10.73 mmole) quinolin-8-ol in (100 ml) ethanol containing potassium hydroxide (602 mg). The products were filtered off and recrystallized from absolute ethanol [9]. Elemental analyses for the prepared quinolin-8-ol azo dyes were done. The results obtained were in good agreement with the calculated values. The obtained data and the calculated values agreed well. The structural formulae of the made quinolin-8-ol azo dyes are as follows:

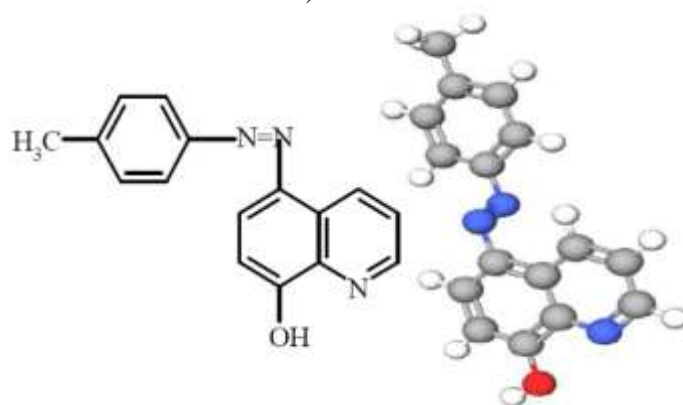


Figure 1 shows the ligand 5-(p-methylphenyl)quinolin-8-ol azo dyes

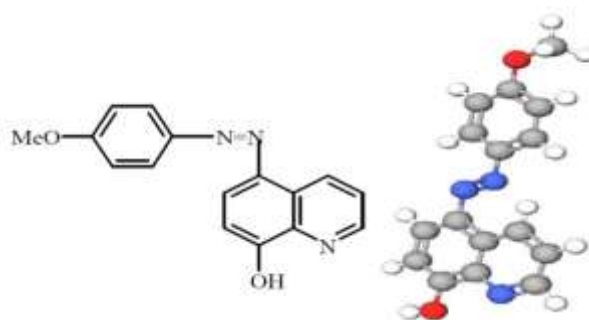


Figure 2 shows the ligand 5-(p-methoxyphenyl)quinolin-8-ol azo dyes

Table 1 shows the analytical data of the prepared quinolin-8-ol azo dyes

2.2. Preparation of the solid complexes

The solid complexes were prepared by mixing a hot alcoholic saturated solution of 0.001 M of metal salt solutions with the requisite amount of ligands under investigation (L1 and L2) sufficient to form 1:1 or 1:2 (M:L) complexes. The pH of the solution was then maintained at a value of 5-6 by addition of dilute (1:10) ammonia solution [10]. The reaction mixture was heated on a steam bath with occasional stirring for 4 hrs, and evaporated till dryness. The solid complexes were filtered off and washed several times with ethanol

until a colorless filtrate was obtained, suction, filtered and then finally kept in a vacuum desiccators. The metal content of the prepared solid complexes was determined [11].

3. Apparatus and techniques

The Micro-analytical Center at Cairo University in Giza, Egypt, did the elemental analysis as well as all other analyses. The IR spectra were captured using the KBr disc technique on a SHIMADZU FTIR-8201 PC spectrophotometer. Detracted DMSO was employed as the solvent and a VARIAN Gemini 200 MHz spectrophotometer was used to measure the NMR spectra (d^6 -DMSO). TMS was used as an internal standard to expand the spectra from (0–14) ppm. Thermal

analyzers of type TG-50 and DTA-50 from SHIMADZU were used to do the thermal analysis (TG and DTA).

The weight loss percentage for the tested solid complexes from room temperature up to 400°C with a heating rate of 10°C per minute was used to determine the TG curves. At the Micro Analytical Center, Cairo University, Giza, Egypt. Using a conductivity meter type device, the molar conductance of the solid complexes in chloroform was measured (Philips, PW 9526 digital conductivity meter). The magnetic susceptibility measurements [11] the most reliable technique for

measuring magnetic susceptibility, the Faraday method, was employed. Almost any solid sample, including alloys, single crystals, and polycrystalline solids, can be measured using a Faraday balance. Using a BECKMAN COULTER DU 800 spectrophotometer, matched 1 cm silica cells, chloroform as the solvent, and the studied quinolin-8-ol azo dyes and some of their complexes, the electronic spectra were determined.

4. RESULTS AND DISCUSSION

The examined ligands (L1 and L2) and the metal ions Mn^{2+} , Ni^{2+} , Cu^{2+} , and Zn^{2+} were synthesized as reported in the experimental section. Elemental analysis was used to determine the C, H, N, and metal compositions of the resulting complexes. IR spectrum investigations, 1H NMR nuclear magnetic resonance, magnetic susceptibility, thermogravimetric analysis, differential thermal analysis, electronic absorption spectra, molar conductance, and electron spin resonance (ESR) spectra are a few examples. As previously mentioned in the experimental phase, the solid chelates of the complexes under investigation were made. In all cases, 1:1 and 1:2 (M:L) solid complexes were isolated, which is in good agreement with those called for by the proposed formula. The above-mentioned free ligands and solid complexes' infrared spectra are recorded as KBr discs. The IR spectra of free ligands must first be studied in order to assign the significant bands in their spectra before making any comments on the structure of the solid complexes utilizing those spectra.

4.1. Infrared spectra of the free ligands and their metal complexes

L1 and L2, the ligands under investigation, were prepared. The experimental section contains reports on the preparation and elemental analysis.

The elemental analyses in Table 1, 1H NMR, mass, and IR spectrum analysis were used to determine the structures of these ligands. It was done to analyze the L1 and L2 ligands' infrared absorption spectra. Table 2 provides a summary of the most important IR bands that have an impact on the structures. The stretching vibration of the OH group of the ligands under study, L1 and L2, is indicated by the existence of a broad band at 3348–3432 cm^{-1} when the IR spectra and band frequencies data are examined. The $C=C$ bands are shown in the ligands under investigation IR spectra at 1606 cm^{-1} . Ar-H stretching vibration is responsible for the bands in the 3104–3122 cm^{-1} region, whereas aliphatic C-H stretching vibration is responsible for the bands in the 2819–2821 cm^{-1} region. At 828 cm^{-1} , the aromatic rings' \odot_{CH} is observed. These bands' number and shape are determined by the position and kind of substituents present. The results are listed in Table 2. The stretching vibration of C-N is attributed to the bands in the IR spectra of the ligands (L1 and L2) at 1280 and 1325 cm^{-1} , while the band at 1404 cm^{-1} is thought to be responsible for the N=N stretching vibration. The stretching vibration of the C=O group is responsible for the band that appears at 1673 cm^{-1} . Interesting variations can be seen in the infrared spectra of solid complexes, which may provide a good indication of their structural makeup. The picture of the solid complexes may be clarified, though, if these modifications are understood in relation to elemental analysis, the outcomes of thermogravimetric analysis, and mass spectra. The band found at 1404 cm^{-1} ascribed to $\nu N=N$ in the free ligands (L1 and L2) is shifted to a lower wave number on complex formation within the range of 3133–3448 cm^{-1} , indicating that it is a center of chelation, according to the infrared spectra of the complexes (Tables 3 and 4). The band observed in the range 3114–3378 cm^{-1} assigned to $\nu O-H$ of water of coordination and/or hydration, the band observed in the range 1670–1695 cm^{-1} assigned to $\nu C=O$, and the band observed in the range 1592–1610 cm^{-1} assigned to $C=C$ were all found in the examined complexes. The new IR bands that emerge at 518–539 cm^{-1} and 428–468 cm^{-1} have been ascribed to (M-N) and (M-O), respectively, vibrations. In other words, the creation of coordinated and covalent bonds between the donor atoms (N and O) and the main metal ion may be the cause of these bands.

4.2. 1H NMR spectra of the investigated ligands and their Zn complexes

In DMSO as the solvent and tetramethylsilane (TMS) as the internal standard, the ^1H NMR spectra of the examined ligands (L1 and L2) and their Zn complexes (1:1 and 1:2) were obtained. Table 5 lists the chemical shift values (δ) of the various proton types found in the ligands (L1 and L2) under investigation in Table 5. The ^1H NMR spectra of the investigated ligands L1 and L2 in DMSO displays a sharp signal at 10.51-10.52 ppm. This signal belongs to the OH group's proton. The ligands ^1H NMR spectra show a signal around 3.37 ppm that is attributed to the solvent's CH_3 protons. also the aliphatic protons of the methyl groups of the pyridine ring appeared at 2.35 ppm for the investigated ligands. The signals observed at 8.15 -8.75 ppm are assigned to the protons of the aromatic ring. By taking into account the differences between the NMR spectra of the investigated Zn complexes and those of the ligands, one can further support the conclusions drawn from the IR spectra (Table 4).

For Zn-L1 (1:1 and 1:2) complexes, a new signal at 3.47 and 3.49 ppm corresponding to H_2O of coordination in these complexes appears after the signal at 10.51 ppm vanishes, indicating the participation of the OH in chelation. The spectra of the unbound ligands did not contain these signals. For 1:1 and 1:2 compounds, the signal measured at 2.32 ppm is CH_3 in the pyridine ring. For 1:1 and 1:2 complexes, the singlet signal at 2.37 and 2.36 ppm that corresponds to the CH_3 group in the benzene ring, For Zn-L2 (1:1 and 1:2) complexes, the signal at 9.41 corresponding to OH disappeared due to complexation with the appearance of a new signal in the region 3.49-3.47 ppm due to coordinated water molecules. This signal was not obviously shown in the spectra of the free ligand. The singlet signal observed at 3.57 and 3.85 corresponding to the methoxy group for 1:1 and 1:2 complexes.

4.3. Thermogravimetric analysis (TG).

The aim of the thermal analysis is to open up new possibilities for the investigation of metal complexes and to obtain information concerning the thermal stability of the divalent transition metal-azoquinolin-8-ol complexes, establish whether the water molecules are inner or outer sphere if present and suggest the thermal decomposition of these complexes [10]. The TG curves exhibit a linear relationship between sample mass loss and temperature increase. In the current experiment, mass loss was monitored up to 400°C while heating rates were properly controlled at $10^\circ\text{C min}^{-1}$. The mass loss for each complex within the temperature range at which

the loss occurs was computed using the TG curves obtained in Figs. 1 and 2.

Table 8 compiles the experimentally discovered and theoretically predicted mass losses. One hydrated water molecule is released from the [Ni-L1(1:1)] chelate between 55 and 90°C , which corresponds to a loss of 4.73% (calculated as 4.42%). A weight loss of 13.04% (calculated 13.21%) is observed in the temperature range (110 - 258°C), corresponding to the loss of three coordinated water molecules, and a loss of 66.03% (calculated 65.08%) is observed in the temperature range (258 - 610°C), corresponding to the loss of two phenyl groups, a pyridine ring, three nitrogen atoms, and one oxygen atom. The metal content was determined from the remaining metal oxide at the conclusion of the thermogram and was discovered to be 17.98% (calcd. 18.28%). For the [Ni-L1(1:2)] chelate, two coordinated water molecules are expelled within the temperature range (249 - 280°C) corresponding to a loss of 6.12% (calcd. 5.87%). In the temperature range (280 - 559°C) a weight loss of 80.18% (calcd. 80.23%) is observed corresponding to the loss of four phenyl groups and four nitrogen atoms and two pyridine rings and one oxygen atom. At the end of the thermogram the metal content was calculated from the residual metal oxide which was found to be 13.24% (calcd. 12.11%). Two hydrated water molecules are ejected from the [Zn-L2 (1:1)] chelate between (49 and 147°C), resulting in a loss of 7.33% (calculated at 7.97%). Three coordinated water molecules are lost in the temperature range (147 - 275°C) at a weight loss of 11.50% (calculated as 11.96%), and two phenyl groups, two nitrogen atoms, a methoxy group, and two oxygen atoms are lost in the temperature range (275 - 615°C) at a weight loss of 67.67% (calculated as 68.37%). The leftover metal oxide at the end of the thermogram was used to compute the metal content, which was discovered to be 18.43% (calcd. 18.03%). Two hydrated water molecules are released from the [Zn-L2 (1:2)] chelate between 74 and 155°C , which corresponds to a loss of 5.25% (calculated at 5.19%). A weight loss of 13.63% (calculated 13.26%) is observed in the temperature range (155 - 283°C), corresponding to the loss of two coordinated water molecules and four nitrogen atoms, and a weight loss of 69.32% (calculated 69.51%) is observed in the temperature range (283 - 636°C), corresponding to the loss of four phenyl groups and two methoxy groups and two pyridine rings. The leftover metal oxide at the end of the thermogram was used to determine the

metal content, which was discovered to be 13.11% (calcd. 12.74%).

4.4. Differential thermal analysis (DTA)

The DTA curve for Ni-L1 (1:1) is distinguished by the existence of one exothermic peak at 390 °C, which is brought on by the destruction of coordinated water molecules. At 404°C, the DTA curve exhibits an exothermic peak, and at this temperature, the organic moiety begins to degrade. This is followed by the creation of an intermediate species and the rearrangement of the decomposed species. Overheating causes more decomposition and combustion, followed by the decarbonization of the organic material and, finally, the formation of NiO, a metallic byproduct.

For Ni-L1 (1:2), the DTA curve is characterized by the presence of one exothermic peak at the temperature 439°C which are due to the elimination of coordinated water molecules, followed by the decomposition of the organic moiety and formation of an intermediate species due to rearrangement of the decomposed species. Raising the temperature than 450°C results in the decomposition and combustion followed by decarbonization of the organic material and at the end there would be the metallic residue as NiO.

For Zn-L2 (1:1), the DTA curve is characterized by the presence of two endothermic peaks at the temperatures 97°C which is due to the elimination of water of hydration. Two exothermic peaks on the DTA curve at the temperature 453 °C due to elimination of coordinated water and 550°C are observed due to the decomposition of the organic moiety followed by the formation of an intermediate species and rearrangement of the decomposed species. Raising the temperature than 550°C results in the combustion followed by decarbonization of the organic material and at the end there would be the metallic residue as ZnO.

The DTA curve for Zn-L2(1:2) is distinguished by the existence of one endothermic peak at 111°C, which is caused by the removal of water from hydration. The elimination of coordinated water and the organic moiety's subsequent disintegration, production of an intermediate species, and rearrangement of the decomposed species cause an exothermic peak to appear on the DTA curve at a temperature of 421°C. More than 516°C results in combustion, which is followed by the decarbonization of the organic material and, finally, the presence of metallic residue in the form of ZnO.

4.5. Magnetic susceptibility measurements.

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A transition metal's magnetic moment (μ) can reveal significant details about the number of unpaired electrons in the metal ion and, in some rare circumstances, can aid to reveal the complex's structural details. In some instances, experimentally determined values of are higher than those determined by utilizing the spin-only approximation. Such is the case for some complexes, in which case orbital contribution cannot be neglected. The calculated magnetic moments of (1:1 and 1:2) (M:L) complexes of the investigated ligands (L1 and L2) with Mn^{2+} metal ion are in the range 5.55-5.95 B.M. indicating the presence of 5 unpaired electrons in the d-orbital ($\mu_{\text{eff}} = 5.91$ B.M.) and show a high spin d^5 configuration ($t_{2g}^3 e_g^2$).

For Ni^{2+} (1:1 and 1:2) (M:L) complexes show μ_{eff} in the range 2.84-2.85 B.M. denoting two unpaired electrons ($\mu_{\text{eff}}=2.82$ B.M.) and showing paramagnetic properties for all of the investigated ligands (L1, L2). For Cu^{2+} complexes (1:1 and 1:2) (M:L) complexes, the calculated magnetic moments of the complexes are in the range 1.74-1.76 B.M. indicating the presence of one unpaired electron per metal ion in its d-orbital ($\mu_{\text{eff}} = 1.73$ B.M.).

For Zn^{2+} (1:1 and 1:2) (M:L) complexes with the investigated ligands (L1 and L2), the calculated magnetic moments are in the range 0.06-0.08 B.M. indicating the absence of unpaired electrons and Zn^{2+} complexes show a diamagnetic properties.

All of the metal ions (Mn^{2+} , Ni^{2+} and Cu^{2+}) complexes show paramagnetism, which means that the ligands have little effects on the metal ions field i.e. the ligands exhibit a weak field effect [12]. Zn^{2+} complexes show diamagnetic behavior since the d-orbitals are completely filled and thus Zn^{2+} considered as non-transition metal ion.

4.6. Molar conductivity measurements

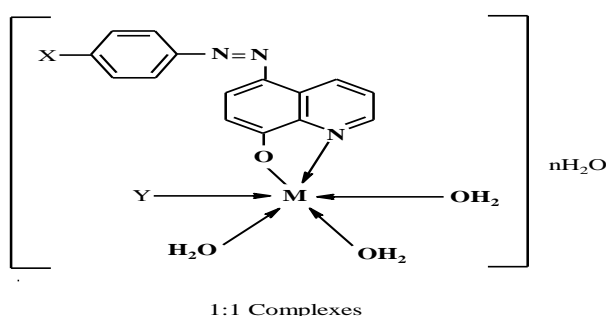
For the 1:1 and 1:2 complexes in chloroform, the molar conductivities of the solid complexes were tested, and they were found to be in the range of 6.2-21.5 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$. These values for the ionic complexes of the divalent metal ions were noticeably tiny. The presence of chloride ions in the coordination sphere rather than ionic connection with the metal ions during complex formation may be the cause of these low conductivity values. Additionally, adding $AgNO_3$ does not result in the production of a white precipitate. This demonstrates unequivocally that none of the complexes under investigation are ionic or electrolytes by nature [13].

4.7. Electronic absorption spectra of the ligands and some of their complexes

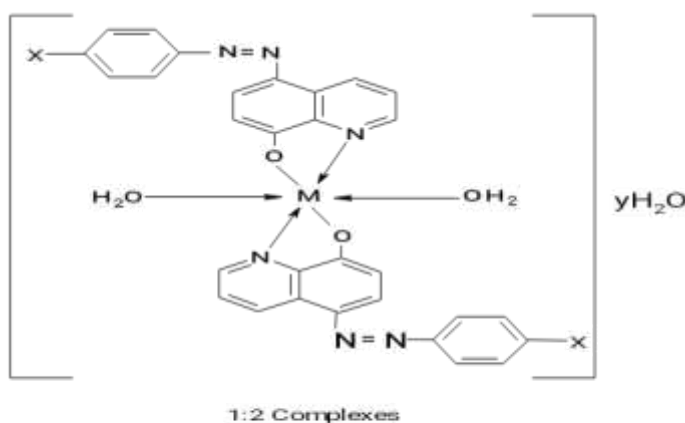
The electronic absorption spectra of the investigated ligands (L1-L2), exhibit two bands at 380 nm (26316 cm^{-1}) and 390 nm (25641 cm^{-1}), the first band may be assigned to the $\pi\text{-}\pi^*$ transition within the phenyl moiety and the second band may be ascribed to the $n\text{-}\pi^*$ transitions within the -N=N- followed by intramolecular charge (C.T.) or interligand transitions within the ligands.

The electronic absorption spectra of the divalent Mn, Ni and Cu metal ions with the investigated ligands (L1-L2) (1:1) and (1:2) complexes are

shown in Figures (36-37) and exhibit two absorption bands at 220 nm (45454 cm^{-1}), 380 nm (26316 cm^{-1}) and a shoulder at 470 nm (21276 cm^{-1}) may be attributed to charge transfer ${}^2A_{2g}\text{-}{}^2T_{1g}$ transitions and an octahedral configuration was suggested around the central metal ion. [12], [14] The 1:1 and 1:2 complexes are isolated based on the results of elemental analysis, IR, ${}^1\text{H}$ NMR, thermal analysis, magnetic moments calculations, mass spectra, and electron absorption spectra for the examined complexes. Octahedral geometry for 1:1 and 1:2 complexes is suggested by the predicted stereochemical structures for the metal complexes under investigation.



X= CH_3 (L1), OCH_3 (L2)
M= Mn, Ni, Cu and Zn metal ions
Y= OH in cases of all complexes of Cu, Mn and Zn (1:1).
Y= Cl in case of all complexes of Ni (1:1).



X= CH_3 (L1), OCH_3 (L2)
M= Mn, Ni, Cu and Zn metal ions.
 H_2O y=3-5

5. CONCLUSION

Utilizing various analytical techniques, some 8-arylazo quinolin-8-ol has been synthesized and completely described. Prepared and subjected to elemental analysis, IR, ${}^1\text{H}$ NMR, thermal analysis (TG and DTA), magnetic susceptibility, molar conductance, and electronic absorption spectra were the metal complexes of the examined ligands L1 and L2. The IR bands of the complexes and the free ligands were contrasted. There are records of the TG and DTA. For a few complexes, the

weight losses for the respective temperature ranges were computed. The ligands' ${}^1\text{H}$ NMR spectra as well as some of the produced complexes' spectra are completed and correlated. The magnetic susceptibility demonstrates the high spin configuration of each produced compound. All of the complexes are neutral or non-electrolytes, according to the molar conductance. The octahedral structures of all the produced compounds is visible in electronic absorption spectra.

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Table 1 Analytical data of the prepared ligands L1 and L2

Ligand	X	Tentative formula	Colour	Molecular weight	Yield%	C% calculated (found)	H% calculated (found)	N% calculated (found)
L1	p-CH ₃	C ₁₇ H ₁₄ N ₂ O ₃	Orange	294	90	73.00 (72.37)	4.42 (4.38)	16.86 (16.09)
L2	p-OCH ₃	C ₁₇ H ₁₄ N ₂ O ₄	Orange	310	80	61.80 (61.97)	4.51 (4.10)	15.05 (15.15)

Table 2 IR band assignments of the investigated free ligands L1 and L2

L1	L2	Band Assignment
3431	3366	ν_{OH}
2921	2921	ν_{C-H} aliphatic
1470	1461	$\nu_{C=C}$
1404	1404	$\nu_{N=N}$
1287	1318	ν_{C-H}
1576	1577	ν_{C-N}
819	828	γ_{C-H}

Table 3 IR band assignment of Mn²⁺, Ni²⁺, Cu²⁺ and Zn²⁺ complexes with the investigated ligand L1

Complex	M:L	$\nu(OH)$	$\nu(C=C)$	$\nu(N=N)$	$\nu(C-O)$	$\nu(M-N)$	$\nu(M-O)$
[Mn(L1).Cl.3H ₂ O]	1:1	3410	1464	1400	1251	519	464
[Mn(L1) ₂ .2H ₂ O]	1:2	3448	1465	1402	1246	554	457
[Ni(L1).Cl.3H ₂ O]	1:1	3433	1463	1400	1245	518	477
[Ni(L1) ₂ .2H ₂ O]	1:2	3417	1464	1400	1247	518	480
[Cu(L1).Cl.3H ₂ O]	1:1	3352	1464	1402	1248	505	472
[Cu(L1) ₂ .2H ₂ O]	1:2	3433	1463	1382	1248	505	472
[Zn(L1).Cl.3H ₂ O]	1:1	3428	1465	1400	1253	521	463
[Zn(L1) ₂ .2H ₂ O]	1:2	3421	1465	1403	1255	517	463

Table 4 ¹H NMR spectral data of the investigated ligands (L1, L2) and their Zn complexes

Ligands and complexes	Chemical Shift (τ^m)	Assignment
L1	9.29	OH
	9.02-7.78	Aromatic C-H protons
	7.43-7.24	Pyrdine ring C-H
	3.41	H ₂ O solvent protons
	2.51	DMSO protons
	2.37	CH ₃ benzene ring
L2	9.41	OH
	9.30-7.80	Aromatic C-H protons
	7.43-7.27	Pyrdine ring C-H
	3.86	OCH ₃ benzene ring
	3.75	H ₂ O solvent protons
	2.50	DMSO protons
Zn-L1 (1:1)	8.75-7.33	Aromatic C-H protons
	6.89-6.87	Pyrdine ring C-H
	3.47	H ₂ O of coordination
	2.51	DMSO protons
	2.37	CH ₃ benzene ring
Zn-L1 (1:2)	8.15-7.32	Aromatic C-H protons
	6.95-6.87	Pyrdine ring C-H
	3.33	H ₂ O of coordination
	2.51	DMSO protons
	2.36	CH ₃ benzene ring
Zn-L2 (1:1)	8.76-7.32	Aromatic C-H protons
	6.91-6.87	Pyrdine ring C-H
	3.31	H ₂ O of coordination
	3.57	OCH ₃ benzene ring
	2.51	DMSO protons

Zn-L2 (1:2)	8.92 -7.07	Aromatic C-H protons
	6.82-6.67	Pyrdine ring C-H
	3.31	H ₂ O of coordination
	3.85	OCH ₃ benzene ring
	2.51	DMSO protons

Table 5 Elemental analysis, magnetic moments μ_{eff} and molar conductance ζ_m for the complexes of Mn²⁺, Ni²⁺, Cu²⁺ and Zn²⁺ metal ions with ligand L1.

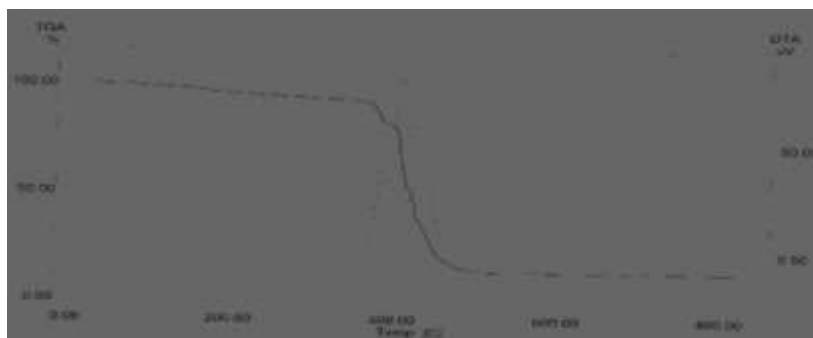
Complex	M:L	FW	C% (Calculated) found	H% (Calculated) found	N% (Calculated) found	M% (Calculated) found	μ_{eff}	ζ_m	color
[Mn(L1).Cl.3H ₂ O]	1:1	406.5	(47.24) 48.60	(4.43) 4.43	(10.33) 10.41	(13.52) 13.46	5.63	6.2	yellow
[Mn(L1) ₂ .2H ₂ O]	1:2	614.9	(62.44) 62.40	(4.43) 4.70	(13.65) 13.57	(8.93) 8.70	5.04	21.5	yellow
[Ni(L1).Cl.3H ₂ O]	1:1	392.7	(48.89) 48.60	(5.09) 4.98	(10.69) 10.47	(14.95) 14.71	2.51	6.2	brown
[Ni(L1) ₂ .2H ₂ O]	1:2	618.7	(62.06) 62.12	(4.52) 4.80	(13.57) 13.43	(9.48) 9.63	2.62	12.4	brown
[Cu(L1).Cl.3H ₂ O]	1:1	396	(46.26) 46.01	(4.34) 4.39	(10.12) 10.51	(15.30) 15.23	1.54	6.2	brown
[Cu(L1) ₂ .2H ₂ O]	1:2	623.5	(61.58) 61.32	(4.49) 4.67	(13.47) 13.43	(10.19) 10.34	1.67	12.4	pink
[Zn(L1).2Cl.2H ₂ O]	1:1	394.4	(48.68) 48.68	(5.07) 5.28	(10.64) 10.87	(16.58) 16.43	0.00	6.2	orange
[Zn(L1) ₂ .2Cl]	1:2	625.4	(59.36) 59.09	(4.48) 4.99	(13.43) 13.11	(10.45) 10.33	0.00	12.4	orange

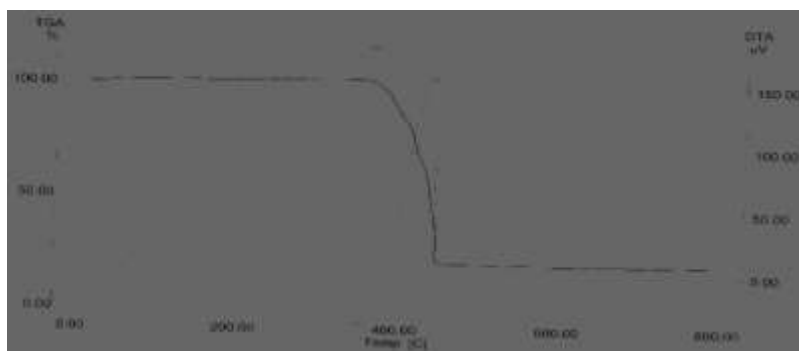
Table 6: Elemental analysis, magnetic moments μ_{eff} and molar conductance ζ_m for the complexes of Mn²⁺, Ni²⁺, Cu²⁺ and Zn²⁺ metal ions with ligand L2.

Complex	M:L	FW	C% (Calculated) found	H% (Calculated) found	N% (Calculated) found	M% (Calculated) found	μ_{eff}	ζ_m	color
[Mn(L1).Cl.3H ₂ O]	1:1	404.9	(47.41) 47.54	(4.94) 4.59	(10.37) 10.44	(13.56) 13.36	5.91	6.2	brown
[Mn(L1) ₂ .2H ₂ O]	1:2	664.4	(59.36) 59.76	(4.33) 4.32	(12.98) 13.08	(8.29) 8.44	5.65	12.4	orange
[Ni(L1).Cl.3H ₂ O]	1:1	408.6	(46.99) 47.07	(4.50) 4.52	(10.29) 10.36	(14.36) 14.65	2.49	6.2	orange
[Ni(L1) ₂ .2H ₂ O]	1:2	650.6	(59.01) 59.33	(4.30) 4.02	(12.91) 12.23	(9.02) 9.33	2.82	12.4	brown
[Cu(L1).Cl.3H ₂ O]	1:1	396.5	(48.27) 48.13	(4.79) 4.55	(10.59) 10.45	(16.02) 16.13	1.95	6.2	brown
[Cu(L1) ₂ .2H ₂ O]	1:2	655.5	(58.58) 58.56	(4.18) 4.33	(12.81) 12.92	(9.69) 9.43	1.58	12.4	brown
[Zn(L1).2Cl.2H ₂ O]	1:1	451.4	(42.53) 42.32	(4.43) 4.19	(9.30) 9.63	(14.49) 14.56	0.00	6.2	orange
[Zn(L1) ₂ .2Cl]	1:2	657.4	(55.37) 55.49	(3.74) 3.62	(12.11) 12.53	(9.43) 9.36	0.00	12.4	orange

Table 7: Thermogravimetric results of Ni²⁺ and Zn²⁺ complexes with the investigated ligands L1 and L2

Complex	Molecular weight	Temperature (°C)	Calculated loss %	Found loss %	Assignment
i-L1(1:1)	408.7	55-90	4.42	4.73	H ₂ O
		110-258	13.21	13.04	3H ₂ O
		258-610	65.08	66.03	C ₁₆ H ₁₂ -O-N ₃
		610-802	18.28	17.98	NiO
Ni-L1 (1:2)	616.7	249-280	5.87	6.12	2H ₂ O
		280-559	82.23	80.18	C ₃₂ H ₂₄ -N ₆ -O
		560-780	12.11	13.24	NiO
Zn-L2 (1:1)	451.4	49-147	7.97	7.33	2H ₂ O
		147-275	11.96	11.50	3H ₂ O
		275-615	68.37	67.67	C ₁₆ H ₁₄ -N ₃ -O ₂
		615-948	18.03	18.43	ZnO
Zn-L2 (1:2)	693.4	74-155	5.19	5.25	2H ₂ O
		155-283	13.26	13.63	2H ₂ O-4N
		283-636	69.51	69.32	C ₃₂ H ₂₂ -N ₂ -O ₃
		636-1074	12.74	13.11	ZnO

**Ni-L1(1:1)**



Ni-L1(1:2)

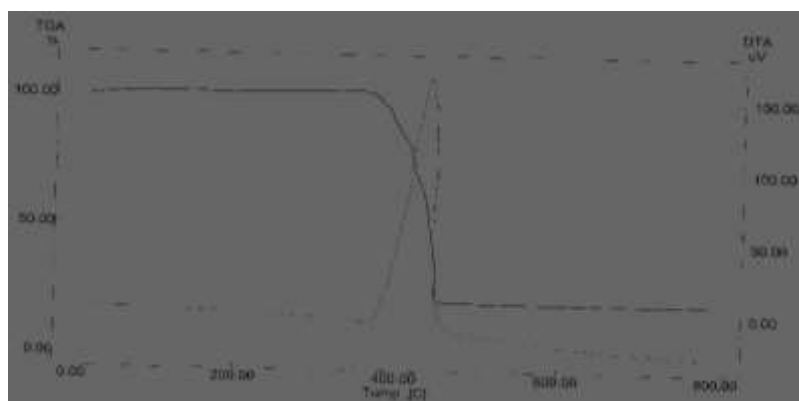
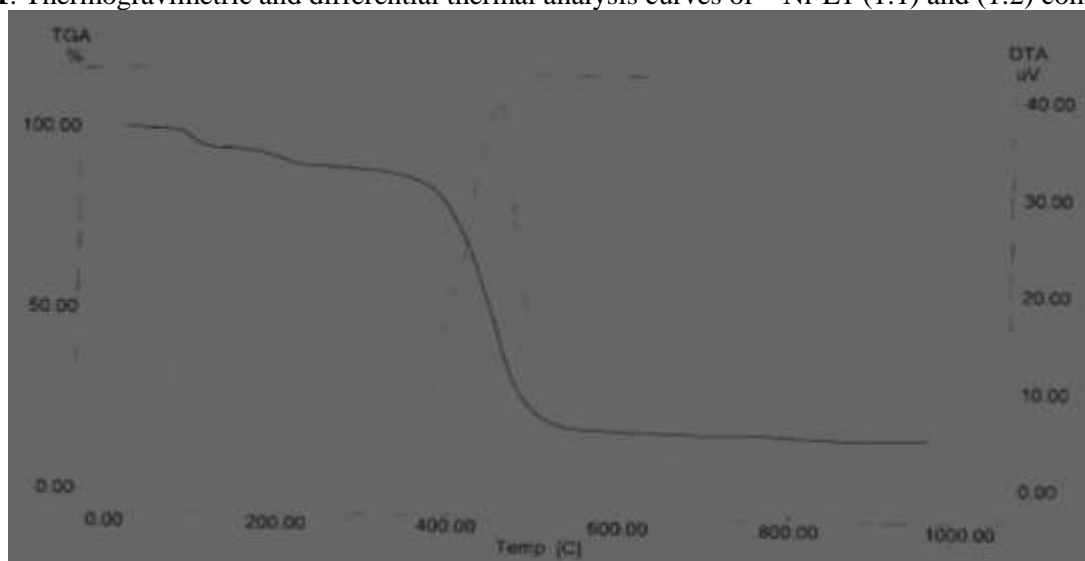
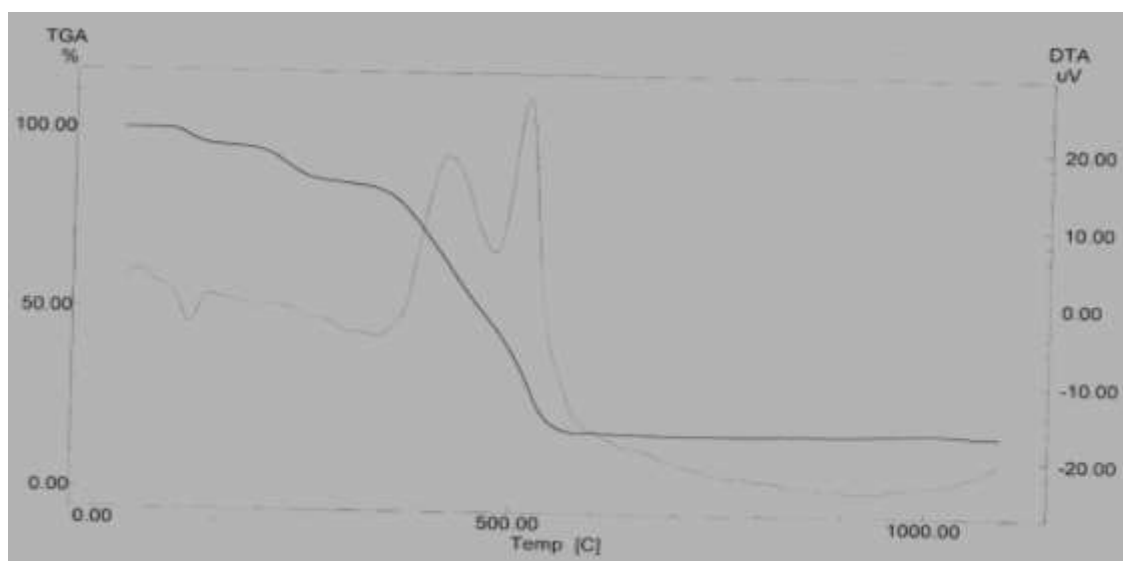


Fig. 1. Thermogravimetric and differential thermal analysis curves of Ni-L1 (1:1) and (1:2) complexes



Zn-L2 (1:1)



Zn-L2 (1:2)

Fig. 2. Thermogravimetric and differential thermal analysis curves of Zn-L2 (1:1) and (1:2) complexes

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