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# Complexation, Spectroscopic, Thermal, Magnetic And Conductimetric Studies On Some 8-(Arylazo)Coumarins With Divalent Transition Metal Ions

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***Abstract:****7-hydroxy-4-methyl-8-(phenylazo) coumarin (L1)and 7-hydroxy-4-methyl-8-(o-carboxyphenylazo) coumarin (L2) have been prepared and characterized by elemental analysis, infrared (IR), proton nuclear magnetic resonance ($^1$H NMR) and Mass spectra. 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 done using mass spectra and the main peaks were corresponding 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, $^1$H NMR, magnetic measurements, electronic transition, molar conductance, mass spectra and electron spin resonance (ESR) spectra. The proposed steriochemical structures for the investigated metal complexes suggest octahedral geometry with respect to Mn, Co, Ni, Cu and Zn metal ions and all of the formed complexes contain coordinated and hydrated water molecules. All of the prepared solid complexes behave as non-electrolytes in chloroform.*

***Keywords:*** *Synthesis; Transition metal complexes; Spectroscopic; Thermal analysis; molar Conductance; Electron spin resonance; Electronic spectra*

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## I. Introduction

Coumarin (2H-1-benzopyran-2-one), the parent molecule of coumarin derivatives, is the simplest compound of a large class of naturally occurring phenolic substances made of fused benzene and α-pyrone rings [1]. The pharmacological and biochemical properties and therapeutic applications of simple coumarins depend upon the pattern of substitution [2].

Monohydroxy compounds containing coumarin nucleus have proved to be of great importance, introduction of azo group to such hydroxy coumarins increases its chelating tendency. From the structural point of view, these compounds were considered as metal indicators as they possess functional groups capable of chelate formation binding directly to the central metal ions. Synthesis of a series of 9 new azocoumarin dyes were reported. These dyes were obtained, confirmed and characterized [3]. The emission characteristics of some 8-(arylazo)-7-hydroxy-4-methylcoumarin have been studied [4]. The action of the coumarin-type drugs and related compounds is reviewed to their antagonistic effects. Twenty 3-pyridinyl, pyrimidinyl and pyrazolyl-4-hydroxycoumarin derivatives were synthesized. The most prospective compounds were the 3-pyrazolyl-4-hydroxy coumarin derivatives [5]. The cyclo addition reaction of unsymmetrically N-substituted and N-unsubstituted 1,3-oxazolium-5-olates with selected 3-substituted coumarins has been examined [6]. The synthesis of novel metal-free and zinc phthalocyanines with four 3-[(2-diethylamino)ethyl]-7-oxo-4-methylcoumarin dye groups on the periphery were prepared [7]. A series of new fluorinated coumarins and 1-azacoumarins were synthesized [8] and the effect of fluorine in the molecule on their anti-microbial, anti-inflammatory and analgesic activities is discussed. Structural study of supramolecular photochemical β-cyclodextrin (β-CD)–coumarin derivatives systems and the crystal structure of the β-CD–4,7-dimethylcoumarin complex has been determined [9]. Two new coumarin derivatives, 7-(diethylamino)-3-(pyridin-2-yl)coumarin (DAPC) and 3-(pyridin-2-yl)-benzo[5,6]coumarin (PBC) were synthesized [10]. A novel ligand, 7-(2,3-dicyanophenoxy)-3-(2-chloro-4-fluorophenyl)coumarin was synthesized by the reaction of 3-(2-chloro-4-fluorophenyl)-7-hydroxycoumarin with 1,2-dicyano-3-nitrobenzen in dry DMF as the solvent in the presence of $K_2CO_3$ as the base. The structures of the compounds were confirmed by elemental analysis, UV–vis, IR, MALDI-TOF mass and $^1$H NMR spectra [11].

The aim of this work is to synthesize and examine some arylazocoumarins and their complexes with Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) divalent transition metal ions. The solid complexes have been prepared and studied by elemental and thermal analyses (TG and DTA) as well as by IR, $^1$H NMR, magnetic measurements, electronic transition, molar conductance, mass spectra and electron spin resonance (ESR) spectra

to throw more light on the bonds formed and to elucidate the coordination properties of these ligands with these transition metal ions.

## II. Experimental

**Materials**

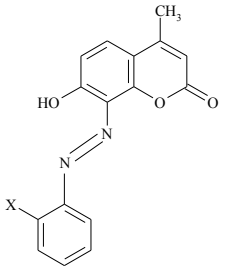
All chemicals used were of Analar or the highest purity grade from BDH used as received without further purification. These included manganese (II) chloride ($MnCl_2.4H_2O$), cobalt (II) chloride ($CoCl_2.6H_2O$), nickel (II) chloride ($NiCl_2.6H_2O$), copper (II) chloride ($CuCl_2.2H_2O$), zinc chloride ($ZnCl_2$), aniline, o-carboxyaniline (o-aminobenzoic acid), sodium hydroxide, ammonium hydroxide (30% $NH_3$), ammonium chloride, disodium salt of ethylenediaminetetraacetic acid dihydrate (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, chloroform and Dimethylsulphoxide (DMSO). The solvents were purified if needed by distillation.

**Synthesis of 7-Hydroxy-4-methylcoumarin**

7-Hydroxy-4-methylcoumarin was synthesized [12] by adding equal molar quantities of resorcinol and ethylacetoacetate in presence of concentrated $H_2SO_4$. 200 ml concentrated $H_2SO_4$ was placed in 500 ml beaker surrounded by ice salt bath. When the temperature falls below 10 °C, 20 g of resorcinol in 26.1 ml of ethylacetoacetate was added dropwisely with constant stirring. The temperature is kept below 10 °C by means of an ice salt bath during the addition (2 hours). The reaction mixture is kept at room temperature for about 18 hours, and then poured with vigorous stirring into a mixture of crushed ice and water. The precipitate was collected by suction filtration and washed with water. The solid was dissolved in 300 ml of 5% NaOH solution, filtered and dilute (1:10) $H_2SO_4$ (110 ml) was added with vigorous stirring until the solution is acid to litmus. The crude 7-hydroxy-4-methylcoumarin was collected by filtration at the pump, washed with cold water, dried at 100 °C, recrystallized form 25% ethanol. The structure was confirmed by its melting point 186 °C.

**Synthesis of Ligands L1 and L2**

A well-stirred solution of aniline or 2-carboxyaniline (o-aminobenzoic acid) (0.01mole in 40 ml ethanol) and 20 ml of 2M HCl was cooled in an ice salt bath and diazotized with aqueous sodium nitrite solution (20 ml, 0.01mole). The cooled (0-5° C) diazonium solution was added slowly to a well-stirred solution of (0.01 mole) 7-hydroxy-4-methylcoumarin in (100 ml) ethanol containing sodium hydroxide (0.01mole). The products were filtered off and recrystallized from absolute ethanol [13]. Elemental analyses for the prepared azocoumarin dyes were done. The results obtained were in good agreement with the calculated values. The prepared azocoumarin dyes have the following structural formulae:




X = H, 7-Hydroxy-4-methyl-8-phenylazocoumarin (L1)
X = COOH, 7-Hydroxy-4-methyl-8-(o-carboxyphenylazo)coumarin (L2)

Table I shows the analytical data of the prepared arylazocoumarin.

**Synthesis of Solid Complexes**

The solid complexes were synthesized by mixing a hot alcoholic saturated solution of (0.001 mole of metal ion dissolved in hot ethanol) with the required amount of the ligands under investigation sufficient to form 1:1 or 1:2 (M:L) complexes. The pH of the solution was then maintained at a value of 6-7 by addition of dilute (1:10) ammonia solution [14]. The reaction mixture was heated on a steam bath with occasional stirring for 4 hrs, and evaporated till dryness. The produced complexes were then dissolved in ethanol to remove unreacted species. It was then filtered off by suction and rewashed with ethanol till a colorless filtrate was obtained, suction, filtered and then finally kept in a vacuum desiccator. The metal content of the prepared solid complexes was determined [15].

**Apparatus**

**Elemental analysis** and all of the other analyses were performed in the micro-analytical center of Cairo University, Giza, Egypt.

**FTIR spectra** were recorded on SHIMADZU FTIR-8201 PC spectrophotometer applying the KBr disc technique.

**NMR spectra** were measured by using a VARIAN Gemini 200 MHz spectrophotometer and the solvent used was deutrated DMSO ($d^6$-DMSO). The spectra were extended from (0-14) ppm using TMS as internal standard.

**Mass spectra** of the arylazocoumarins and some of their complexes were carried out using Q-1000 EX GC-MS SCHIMADZU spectrometer at 70 eV and MA energy using a direct insertion probe at temperature 90-110 ºC.

**Thermal studies of the prepared metal complexes** were measured using SHIMADZU, Type TG-50 and DTA-50 derivatograph thermal analyzer (Japan). The TG curves were obtained by the weight loss percent for the investigated solid complexes from ambient temperature up to 400ºC with a heating rate of 10 ºC per minute.

**Electron spin resonance (ESR)** spectra of the arylazocoumarin copper complexes under study were recorded using EMS ESR spectrometer (Bruker) 1998 Y.

**Molar conductance** of the solid complexes in chloroform was measured using a conductivity meter type (PHILIPS, PW 9526 digital conductivity meter).

**Magnetic susceptibility measurements** [16] were done using Faraday's method which is the most suitable method for measuring the magnetic susceptibility. The Faraday balance is designed as for solid sample measurements which may be of almost any form, single crystal, and polycrystalline solid, alloys … etc.

**Electronic spectra** of the investigated arylazocoumarin ligands and some of their complexes were measured by applying chloroform as solvent using BECKMAN COULTER DU 800 spectrophotometer using 1 cm matched silica cells.

## III. Results And Discussion

The solid complexes of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) metal ions with the investigated ligands (L1 and L2) have been synthesized as described in the experimental section.

**Elemental analysis** data are shown in Tables (II and III) and metal content [15] were obtained, respectively.

**Magnetic moments** of the transition metal complexes show a high spin configuration as the ground state. The magnetic susceptibility of (1:1 and 1:2) (M:L) complexes of the investigated ligands (L1 and L2) with Manganese (II) are in the range 5.92-5.95 B.M. indicating the presence of 5 unpaired electrons in the d-orbital ($\mu_{eff}$ = 5.91 B.M.) and show a high spin $d^5$ configuration ($t_{2g}^3$ $e_g^2$) [17]. For Cobalt (II), (1:1 and 1:2) (M:L) complexes, the magnetic moments of the complexes are in the range 3.84-3.92 B.M. indicating the presence of three unpaired electrons per metal ion ($\mu_{eff}$ = 3.87 B.M.). For Nickel (II) (1:1 and 1:2) (M:L) complexes, the values show $\mu_{eff}$ in the range 2.83-2.84 B.M. denoting two unpaired electrons ($\mu_{eff}$=2.82 B.M.) and showing paramagnetic properties for all of the investigated ligands (L1 and L2). For Copper (1:1 and 1:2) (M:L) complexes, the magnetic moments of the complexes are in the range 1.72-1.75 B.M. indicating the presence of one unpaired electron per metal ion in its d-orbital ($\mu_{eff}$ = 1.73 B.M.). For Zinc (II) (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 Zinc complexes show a diamagnetic properties. All of the metal ions Mn(II), Co(II) , Ni(II) and Cu(II) 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 [18]. Zn(II) complexes show diamagnetic behavior since the d-orbitals are completely filled and thus Zn(II) considered as non-transition metal ion as shown in Tables (II and III).

**Electronic absorption spectra** of the investigated ligands (L1 and L2), exhibit two bands at 330 nm (30303 $cm^{-1}$) and 420 nm (20809 $cm^{-1}$), the first band may be assigned to the $\pi$-$\pi^*$ transition within the phenyl moiety and the second band may be ascribed to the n-$\pi^*$ transitions within the -N=N- followed by intramolecular charge (C.T.) or interligand transitions within the ligands. The electronic absorption spectra of Mn(II), Ni(II) and Cu(II) metal ions with the investigated ligands (L1 and L2) (1:1) and (1:2) complexes exhibit two absorption bands at 220 nm (45454 $cm^{-1}$), 330 nm (30303 $cm^{-1}$) and a shoulder at 470 nm (21276 $cm^{-1}$) may be attributed to charge transfer $^2A_{2g} \rightarrow {}^2T_{1g}$ transitions and an octahedral configuration was suggested around the central metal ion [19, 20]. For Co(II), these bands are typical for six-coordinate high-spin cobalt (II) complexes. The corresponding bands in the octahedral $[Co(H_2O)_6]^{2+}$ ion have been assigned to $^4T_{1g}$-$^4T_{2g}$(F), $^4T_{1g}$-$^2A_{1g}$(F), and $^4T_{1g}$-$^4T_{1g}$(P) transitions, respectively [21]

**Infrared spectral** data and band assignments of the investigated ligands (L1 and L2) are shown in Table IV. The IR spectra and the bands frequencies data shows the presence of a broad band at 3498-3496 $cm^{-1}$

which corresponds to the stretching vibration of the OH group of the ligands under investigation L1 and L2, respectively. The IR spectra of the investigated ligands show the –C=C-bands at 1606 $cm^{-1}$. The bands in the 3122-3104 $cm^{-1}$ region are due to Ar-H stretching vibration while those appeared in the 2821-2819 $cm^{-1}$ region is due to aliphatic C-H stretching vibration. The $\gamma_{CH}$ of the aromatic rings is observed at 846 $cm^{-1}$. The number and shape of these bands depends on the position and the type of substituent present. The bands appearing in the IR spectra of the ligands L1 and L2 at 1268 and 1267 $cm^{-1}$ are assigned to the stretching vibration of C-N and that at 1450 $cm^{-1}$ is assigned to the stretching vibration of N=N [22]. The band appearing at 1670 $cm^{-1}$ is assigned to the stretching vibration of C=O group.

**The infrared spectra** of the solid complexes display interesting changes which may give a reasonable idea about the structure of these complexes. However, if these changes are interpreted in relation to elemental analysis and the results of thermogravimetric analysis and mass spectra, the picture of the solid complexes may be clarified. In the infrared spectra of the complexes which are shown in Tables V and VI, the band observed at 1450 $cm^{-1}$ assigned to $\nu_{N=N}$ in the free ligands (L1 and L2) are shifted to the lower wave number on complex formation within the range 1382-1402 $cm^{-1}$ indicating that it is a center of complexation. In the complexes, the band observed within the range 3120-3426 assigned to $\nu_{O-H}$ of water of coordination and water of hydration, the band observed in the range 1670-1683 $cm^{-1}$ assigned to $\nu_{C=O}$, $\nu_{C=C}$ in the range 1592-1610 $cm^{-1}$ and the band observed in the range 1232-1270 $cm^{-1}$ corresponding to $\nu_{C-O}$ are shifted to lower wave number due to complexation. The spectra of metal complexes exhibit bands in the ranges 514-580 and 428-468 $cm^{-1}$ which may assigned to (M←N) and (M-O) stretching frequencies [23], respectively. In other words, these bands are possibly due to the formation of coordination and covalent bonds between the donor atoms ( N and O) and the central metal ion.

**$^1$H NMR spectra** of the investigated ligands (L1 and L2) and their Zn(II) complexes were recorded in DMSO as a solvent and tetramethylsilane (TMS) as an internal standard. The chemical shift (δ) values of the different types of protons in the investigated ligands (L1 and L2) are reported in Table VII. The $^1$H NMR spectra of the investigated ligand L1 in DMSO exhibits a sharp signal at 10.54 ppm. This signal is assigned to the protons of the OH group. The aliphatic protons of the methyl groups of the pyrone ring appeared at 2.35-2.33 ppm. The signals observed at 7.99-6.70 ppm are assigned to the protons of the aromatic ring [24] while that observed at 6.12-6.09 ppm are assigned to the proton of the pyrone ring [24]. The COOH and OH protons of the ligand L2 was not observed until 14.00 ppm indicating the involvement of these groups in hydrogen bonding and appeared downfield.

For Zn-L1, (1:1 and 1:2) complexes, the disappearance of the signal observed at 10.54 ppm in the free ligand indicates the deprotonation and involvement of the OH group in complexation. Coordinated water molecules were observed in the region 3.65 and 3.79 ppm for 1:1 and 1:2 complexes, respectively. All of the other signals observed in the free ligand still present with some upfield shift which may be due to complexation.

For Zn-L2, (1:1 and 1:2) complexes, coordinated water molecules were observed in the region 3.79 and 3.71 ppm for 1:1 and 1:2 complexes, respectively. All of the other signals observed in the free ligand still present with some upfield shift which may be due to complexation. The signal observed at 2.32 ppm corresponding to $CH_3$ in the pyrone ring for 1:1 and at 2.12 for 1:2 complexes.

**Mass spectral studies of the investigated ligands and some of their complexes** permits the elucidation of molecular weight. Mass spectroscopy has proved extremely valuable for the determination of accurate molecular weights, obtaining molecular formulae, ionization potentials and bond strengths [25]. The observed peak at m/z 280 (calculated 280) represents the molecular ion peak of ligand L1. The fragmentation pattern of this ligand can be regarded as general scheme showing the main fragmentation paths involved. The difference in the other ligand (L2) results from the effect of electronegativity of the substituent attached to the aromatic ring. For ligand L2, the main peak is observed at m/z 362 (calculated 360). From the data obtained we concluded that the molecular weights are in good agreement with the calculated values.

**The mass spectra** of some complexes were recorded and their molecular ion peaks confirm the suggested formulae of these complexes. For complexes of ligand L1 with Mn (1:1) m/z 423 (calculated 423.4) and (1:2) m/z 702 (calculated 702.9). For the complexes of ligand L2 with Mn (1:1) m/z 430 (calculated 430.9) and (1:2) m/z 698 (calculated 700.9). The calculated and found values of the molecular weights of some of these complexes are given in Tables II and III.

**Thermal analysis (TG and DTA)** of the complexes were carried out and the aim of this study is to obtain information concerning the thermal stability of the divalent transition metal-arylazocoumarin complexes, establish whether the water molecules are inner or outersphere if present and suggest the thermal decomposition of these complexes. In the present investigation, heating rates were suitably controlled at 10 °C $min^{-1}$ and the weight loss followed up to 400 °C. From the TG curves obtained, Figures (1 and 2) and Table VIII, the weight loss for each complex were calculated within the temperature range at which the loss occurs. The found and calculated mass loss (based on the suggested stoichiometry) were done. The TG curves show the decomposition of the organic moiety of the complexes and this continues till a constant weight is obtained where the metal

oxide (MO) residues are formed as the final product for the complexes. TG analysis of the complexes of the divalent Ni(II) and Zn(II) metal ions with the investigated ligands (L1 and L2) 1:1 and 1:2, were measured from ambient temperature up to 400 °C at rate of 10 °C $min^{-1}$ in presence of nitrogen atmosphere. The weight loss for each complex obtained from the thermographs was used to calculate the decomposed species of the organic material present.

For [Zn-L1 (1:1)] complex, one coordinated water molecule is expelled within the temperature range 160–195 °C corresponding to a loss of 4.24% (calculated 4.14%). In the temperature range 195–280 °C a weight loss of 8.29% (calculated 8.29%) is observed corresponding to the loss of two coordinated water molecules and in temperature range 280–325 °C a weight loss of 13.50% (calculated 13.43%) is observed corresponding to the loss of two nitrogen atoms, two oxygen atoms and methyl group and in the temperature range 325–400 °C weight loss of 36.60% (calculated 37.22%) is observed corresponding to the loss of methylene group and phenyl group. At the end of the thermogram there will be a metallic oxide residue from which the metal content was calculated and found to be 17.28 (calculated 17.22%)

For [Zn-L1 (1:2)] complex, three hydrated water molecules are expelled within the temperature rang 35–120 °C corresponding to a loss of 8.42% (calcd. 7.66) in the temperature range 120–280 °C, a weight loss of 5.39% (calculated 5.46%) is observed corresponding to the loss of two coordinated water molecules. In the temperature range 280–340 °C a weight loss of 19.66% (calculated 19.24%) is observed corresponding to the loss of phenyl group, two nitrogen atoms and methyl group and in the temperature range 340–400 °C a weight loss of 36.87% (calculated 36.59%) is observed corresponding to the loss of phenyl group, two nitrogen atoms, two methyl groups and two oxygen atoms. The metal content was calculated from the metallic residual which is 9.55% (calculated 9.17%)

For [Ni-L2 (1:1)] complex, one hydrated water molecule is expelled within the temperature range 65-100 °C corresponding to a loss of 3.91 (calculated 3.68). In the temperature range 100–155 °C a weight loss of 7.89% (calculated 7.65%) is observed corresponding to the loss of two hydrated water molecules. One coordinated water molecule is expelled within the temperature range 155–190 °C corresponding to a loss of 4.13% (calculated 4.14%). In the temperature range 190–290 °C a weight loss of 8.00% (calculated 8.64%) is observed corresponding to the loss of two coordinated water molecules, and in the temperature range 290–400 °C a weight loss of 47.81% (calculated 47.54%) is observed corresponding to the loss of phenyl group, two nitrogen atoms, methyl group, oxygen atom and carboxyl group. At the end of the thermogram the metal content was calculated from the residual metal oxide and was found to be 17.22% (calcd. 17.18%).

For [Ni-L2 (1:2)] complex, three hydrated water molecules are expelled within the temperature range 65–150 °C corresponding to a loss of 6.24% (calculated 6.79%). In the temperature range 150–187 °C a weight loss of 4.23% (calculated 4.86%) is observed corresponding to the loss of two coordinated water molecules and in the temperature range 187–400 °C a weight loss of 36.50% (calculated 36.60%) is observed corresponding to the loss of phenyl group, four nitrogen atoms, four carbon atoms, two methyl groups and one carboxyl group. At the end of the thermogram the metal content was calculated from the residual metal oxide and was found to be 9.79% (calculated 9.34%).

**DTA** for Zn-L1 (1:1) complex, the differential thermal analysis curve (DTA) is characterized by the presence of a two endothermic peaks at the temperatures 178 and 264 °C due to elimination of coordinated water molecules. Since the coordinated water molecules occupy some positions in the coordination sphere of the central metal ion, they are more strongly bonded to the central metal ion than the water of hydration and hence are eliminated at higher temperature than those of hydrated water molecules.

For Zn-L1 (1:2), the DTA curve is characterized by the presence of a two endothermic peaks at the temperatures 60, 174 which are due to the elimination of water of hydration and at 260 °C due to the elimination of coordinated water molecules. For Zn-L1 (1:1 and 1:2) A sharp exothermic peak on the DTA curve at the temperature 290 °C is due to the decomposition of the organic moiety of the complex followed by the formation of an intermediate species, at this temperature a phase change is liable to occur due to the change in crystal structure of the complex. Raising the temperature than 300 °C results in the rearrangement of the decomposed species and combustion followed by decarbonization of the organic material and at the end there would be the metallic residue as ZnO.

For Ni-L2 (1:1), the DTA curve is characterized by the presence of four endothermic peaks at the temperatures 83, 152, 176 and 254 °C which are due to the elimination of water of hydration and coordinated water molecules.

For Ni-L2 (1:2), the DTA curve is characterized by the presence of five endothermic peaks at the temperatures 51, 87, 107, 187 and 257 °C which are due to the elimination of water of hydration and coordinated water molecules. For Ni-L2 (1:1 and 1:2) an exothermic peak on the DTA curve at the temperature 370 °C is 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 370 °C results in the combustion followed by decarbonization of the organic material and at the end there would be the metallic residue as NiO.

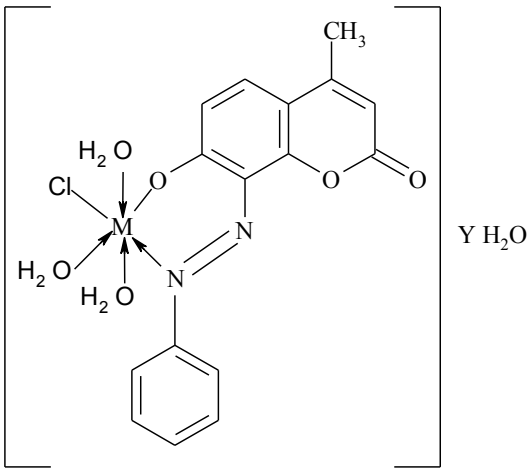
**Electron spin resonance (ESR),** The X-band ESR spectra of Cu(II)-azocoumarin complexes at room temperature generally show one, two or three broad signals depending on the nature of the ligands used and the type of the complexes formed, Table IX. Generally, the complexes are not magnetically dilute, therefore, exchanges [26] and/or dipolar forces are expected to operate in such a case, the g anisotropy is likely to be reduced. The absence of hyperfine is taken as evidence of exchange as is the fact that

$$G = g_{//} - 2/g_{(\perp-2)}$$

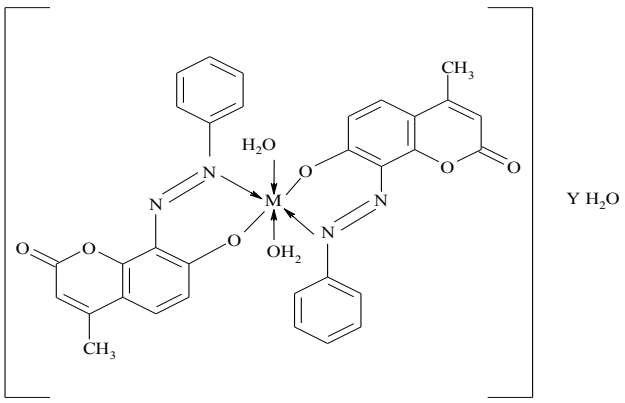
is lower than four [27] which could be attributed to octahedral symmetry around the $Cu^{2+}$ ions. Moreover, the apparent broadening of the ESR signals may be due to an interaction between Cu(II) ions which are probably present in nonequivalent lattice position, the positive shift of g values from that of the free electron (2.0023) indicates a high covalent character of the bonding between the $Cu^{2+}$ ions and the azocoumarin ligands [28].

**The molar conductivities** of the solid complexes were measured for 1:1 and 1:2 complexes in chloroform and are found in the range of 8.2-16.4 $ohm^{-1}$ $cm^2$ $mol^{-1}$. These values were measurably small for the ionic complexes of the divalent metal ions. These low conductivity values may be attributed to the presence of chloride ions in the coordination sphere rather than ionic association to the metal ions during complex formation and also no white precipitate is formed by the addition of $AgNO_3$. This directly supports the fact that all of the investigated complexes are non-ionic or non electrolytes in nature [29]. The conductivity values for all of the investigated complexes are listed in Tables II and III.

Based on the results of elemental analysis, IR, $^1H$ NMR, mass spectra, thermal analysis, Electron spin resonance (ESR), magnetic moments calculations and electronic transitions for the investigated ligands L1 and L2, the 1:1 and 1:2 complexes are isolated as shown in Figures 3 and 4. The proposed steriochemical structures for the investigated metal complexes suggest octahedral geometry for 1:1 and 1:2 complexes.

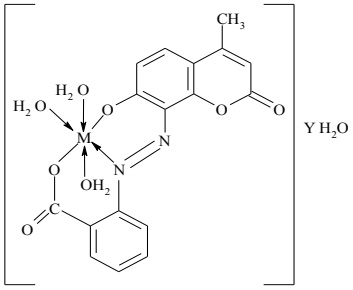



Y = 3 $H_2O$ in case of Mn-L1 (1:1)

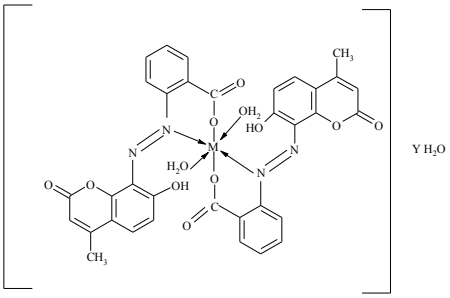



Y = 3 $H_2O$ in case of Zn -L1 (1:2)
M = Mn, Co, Ni, Cu and Zn metal ions

FIGURE 3 The proposed structures of the metal (II)-L1 complexes




Y = 3 $H_2O$ in case of Ni-L2 (1:1)




Y = 3 $H_2O$ in case of Ni -L2 (1:2)
M = Mn, Co, Ni, Cu and Zn metal ions

FIGURE 4 The proposed structures of the metal (II)-L2 complexes

## IV. Conclusion

From elemental analysis, FTIR spectral data, $^1$H NMR, mass spectral data, thermal analysis (TG and DTA), Electron spin resonance (ESR), magnetic moments calculations and electronic transitions for the investigated ligands L1 and L2, the 1:1 and 1:2 complexes are isolated and one can conclude that:

(A) The synthesized 8-arylazocoumarin complexes show that the structure of the complexes are formed through the deprotonation of the OH group in the aromatic ring and coordination of the nitrogen atom of the azo group in ligand L1 (1:1 and 1:2); through the deprotonation of OH and COOH groups in ligand L2 (1:1) while for 1:2 the complexes are formed through the two carboxylate oxygen of the two ligands followed by coordination of nitrogen atom of the azo groups. All these changes are reflected by FTIR spectra. The spectra show that the absorption band $\nu_{OH}$ at (3120-3426 $cm^{-1}$) arises from water of coordination and water of hydration in some complexes.

(B) The TG and DTA data show that these complexes have high thermal stability. The weight losses for some complexes were calculated for the corresponding temperature ranges. When the hydrated water molecules are lost, a strong endothermic peaks appears for coordinated water molecules followed by an exothermic peaks due to the decomposition of the organic moiety.

(C) The $^1$H NMR spectra of the ligands and their Zn(II) complexes are obtained and correlated, The proton of the OH group disappeared upon complexation.

(D) All complexes show high spin magnetic moments. Peaks due to the bound $M^{2+}$ at 470 nm can be attributed to d-d transitions of octahedral symmetry.

(E) The molar conductance shows that all of the complexes are neutral or non-electrolytes in nature. ESR and electronic absorption spectra show that all of the Cu(II) complexes have octahedral geometry.

(F) The analytical and spectral data suggest an octahedral coordination as formulated in Figures 3 and 4. M(II) coordinate with ligand L1 and L2 as a bidentate ligands.

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TABLE I Analytical data and yield % for the investigated ligands (L1 and L2)

| | | | | | | | Elemental Analysis | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | Calcd. / Found | | |
| Ligand | X | Tentative formula | mp (°C) | Color | M. wt | Yield % | C% | H% | N% |
| L1 | H | $C_{16}H_{12}N_2O_3$ | 172 | Orange red | 280 | 75 | 68.57 /68.17 | 4.28 /4.08 | 10.00 /10.28 |
| L2 | COOH | $C_{17}H_{16}N_2O_7$ | 122 | Orange red | 360 | 80 | 56.67 /56.97 | 4.72 /4.40 | 7.78 /7.31 |

TABLE II Analytical data, magnetic moments $\mu_{eff}$ and molar conductance $\Lambda_m$ for the divalent metal complexes with ligand L1

| | | | Elemental Analysis | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | Calcd./ Found | | | | | |
| Complex | Empirical formula | M:L | C% | H% | N% | M% | $\mu_{eff}$ (B.M.) | $\Lambda_m$ |
| $[Mn(L1) . Cl . (H_2O)_3]$ Mol. wt. = 423.4 | $C_{16}O_6N_2H_{17}ClMn$ | 1:1 | 45.35 /45.30 | 4.02 /4.20 | 5.67 /5.88 | 12.98 /12.40 | 5.92 | 8.2 |
| $[Mn(L1) . (H_2O)_2] . 3H_2O$ Mol. wt. = 702.9 | $C_{32}O_{11}H_{32}N_4Mn$ | 1:2 | 54.63 /54.27 | 4.57 /4.40 | 7.99 /7.70 | 7.44 /7.23 | 5.93 | 16.4 |
| $[Co(L1)_2 . (H_2O)_2]$ Mol. wt. = 652.9 | $C_{32}O_8H_{26}N_4Co$ | 1:2 | 58.81 /58.40 | 3.98 /3.90 | 8.58 /8.41 | 9.03 /9.11 | 3.91 | 16.4 |
| $[Ni(L1) . Cl . (H_2O)_3]$ Mol. wt. = 427.2 | $C_{16}O_6N_2H_{17}ClNi$ | 1:1 | 44.94 /44.40 | 3.98 /3.70 | 5.85 /5.52 | 13.74 /13.41 | 2.83 | 8.2 |
| $[Ni(L1)_2 . (H_2O)_2]$ Mol. wt = 652.7 | $C_{32}O_8H26_6N_4Ni$ | 1:2 | 58.83 /58.50 | 4.16 /4.39 | 3.58 /3.28 | 8.99 /8.50 | 2.84 | 16.4 |
| $[Cu(L1) . Cl . (H_2O)_3]$ Mol. wt. = 432.1 | $C_{16}O_6N_2H_{17}ClCu$ | 1:1 | 44.43 /44.50 | 3.93 /3.90 | 6.48 /6.88 | 14.71 /14.99 | 1.72 | 16.4 |
| $[Cu(L1)_2 . (H_2O)_2]$ Mol. wt. = 657.6 | $C_{32}O_8H_{26}N_4Cu$ | 1:2 | 58.39 /58.90 | 3.95 /3.90 | 8.52 /8.76 | 9.66 /9.74 | 1.74 | 8.2 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $[Zn(L1) . Cl . (H_2O)_3]$<br>Mol. wt . = 433.9 | $C_{16}O_6N_2H_{17}ClZn$ | 1:1 | 44.25<br>/44.05 | 3.92<br>/4.06 | 6.45<br>/6.08 | 15.07<br>/15.11 | 0.73 | 8.2 |
| $[Zn(L1)_2 . (H_2O)_2] . 3H_2O$<br>Mol. wt. 713.4 | $C_{32}O_{11}H_{32}N_4Zn$ | 1:2 | 53.82<br>/53.32 | 4.49<br>/4.69 | 7.85<br>/7.73 | 9.17<br>/9.60 | 0.56 | 16.4 |

TABLE III Analytical data, magnetic moments $\mu_{eff}$ and molar conductance $\Lambda_m$ for the divalent metal complexes with ligand L2

| | | | *Elemental Analysis* | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | *Calcd. / Found* | | | | | |
| *Complex* | *Empirical formula* | *M:L* | *C%* | *H%* | *N%* | *M%* | *μeff (B.M.)* | *Λm* |
| $[Mn(L2) . (H_2O)_3]$<br>Mol. wt. = 430.9 | $C_{17}H_{16}O_8N_2Mn$ | 1:1 | 47.34<br>/47.43 | 3.71<br>/3.89 | 6.49<br>/6.40 | 12.75<br>/12.41 | 5.92 | 8.2 |
| $[Mn(L2)_2 . (H_2O)_2]$<br>Mol. wt. = 736.9 | $C_{34}H_{26}N_4O_{12}Mn$ | 1:2 | 52.11<br>/52.59 | 3.53<br>/3.08 | 7.99<br>/7.87 | 7.60<br>/7.99 | 5.95 | 8.2 |
| $[Co(L2) . (H_2O)_3]$<br>Mol. wt. = 434.9 | $C_{17}H_{16}O_8N_2Co$ | 1:1 | 46.91<br>/46.99 | 3.68<br>/4.05 | 6.44<br>/6.56 | 13.55<br>/13.66 | 3.86 | 8.2 |
| $Co(L2)_2 . (H_2O)_2]$<br>Mol. wt. = 740.9 | $C_{34}H_{26}N_4O_{12}Co$ | 1:2 | 55.07<br>/55.40 | 3.51<br>/3.49 | 7.56<br>/7.43 | 7.96<br>/8.22 | 3.92 | 8.2 |
| $[Ni(L2) . (H_2O)_3]. 3H_2O$<br>Mol. wt. = 488.7 | $C_{17}H_{22}O_{11}N_2Ni$ | 1:1 | 41.74<br>/41.98 | 4.50<br>/4.21 | 5.73<br>/5.98 | 12.01<br>/12.58 | 2.83 | 8.2 |
| $Ni(L2)_2 . (H_2O)_2]. 3H_2O$<br>Mol. wt. = 794.7 | $C_{34}H_{32}N_4O_{15}Ni$ | 1:2 | 51.34<br>/51.26 | 4.03<br>/4.06 | 7.05<br>/7.64 | 7.38<br>/7.22 | 2.84 | 16.4 |
| $[Cu(L2) . (H_2O)_3]$<br>Mol. wt. = 439.5 | $C_{17}H_{16}O_8N_2Cu$ | 1:1 | 47.42<br>/47.26 | 3.64<br>/3.17 | 6.37<br>/6.52 | 14.46<br>/14.55 | 1.73 | 16.4 |
| $Cu(L2)_2 . (H_2O)_2]$<br>Mol. wt. = 745.5 | $C_{34}H_{26}N_4O_{12}Cu$ | 1:2 | 54.73<br>/54.41 | 3.49<br>/3.01 | 7.51<br>/7.24 | 8.52<br>/8.79 | 1.75 | 8.2 |
| $[Zn(L2) . (H_2O)_3]$<br>Mol. wt. = 441.4 | $C_{17}H_{16}O_8N_2Zn$ | 1:1 | 46.22<br>/46.71 | 3.63<br>/3.95 | 6.34<br>/6.93 | 14.81<br>/14.82 | 0.76 | 8.2 |
| $Zn(L2)_2 . (H_2O)_2]$<br>Mol. wt. = 747.4 | $C_{34}H_{26}N_4O_{12}Zn$ | 1:2 | 54.59<br>/54.07 | 3.48<br>/3.22 | 7.39<br>/7.12 | 8.75<br>/8.55 | 0.60 | 16.4 |

TABLE IV IR Frequencies and band assignments of the investigated ligands (L1 and L2).

| L1 | L2 | Band Assignment |
|---|---|---|
| 3498 | 3496 | $\nu_{OH}$ |
| 3122 | 3104 | $\nu_{C\text{-}H\ aromatic}$ |
| 2821 | 2819 | $\nu_{C\text{-}H\ aliphatic}$ |
| 1670 | 1670 | $\nu_{C=O}$ |
| 1606 | 1606 | $\nu_{C=C}$ |
| 1450 | 1450 | $\nu_{N=N}$ |
| 1350 | 1350 | $\nu_{C\text{-}H}$ |
| 1268 | 1267 | $\nu_{C\text{-}N}$ |
| 1168 | 1167 | $\nu_{C\text{-}H}$ |
| 1066 | 1066 | $\delta_{OH}$ |
| 846 | 846 | $\gamma_{C\text{-}H}$ |

TABLE V Frequencies and band assignment of ligand L1 and its metal complexes ($cm^{-1}$)

| | Band Assignment | | | | | | |
|---|---|---|---|---|---|---|---|
| Complex | $\nu_{OH}$ | $\nu_{C=O}$ | $\nu_{C=C}$ | $\nu_{N=N}$ | $\nu_{C\text{-}O}$ | $\nu_{M\text{-}N}$ | $\nu_{M\text{-}O}$ |
| Mn-L1 (1:1) | 3158 | 1677 | 1594 | 1386 | 1236 | 530 | 433 |
| Mn-L1 (1:2) | 3168 | 1679 | 1596 | 1384 | 1234 | 534 | 445 |
| Co-L1 (1:1) | 3203 | 1683 | 1606 | 1386 | 1267 | 538 | 443 |
| Co-L1 (1:2) | 3156 | 1679 | 1592 | 1384 | 1234 | 534 | 431 |
| Ni-L1(1:1) | 3376 | 1673 | 1610 | 1398 | 1236 | 580 | 445 |
| Ni-L1 (1:2) | 3158 | 1679 | 1594 | 1392 | 1236 | 536 | 447 |
| Cu-L1 (1:1) | 3340 | 1679 | 1592 | 1382 | 1232 | 514 | 447 |
| Cu-L1 (1:2) | 3345 | 1679 | 1594 | 1402 | 1270 | 514 | 453 |
| Zn-L1 (1:1) | 3156 | 1681 | 1592 | 1382 | 1236 | 532 | 445 |
| Zn-L1(1:2) | 3162 | 1675 | 1608 | 1390 | 1267 | 536 | 445 |

TABLE VI Frequencies and band assignment of ligand L2 and its metal complexes ($cm^{-1}$)

| Complex | Band Assignment | | | | | | |
|---|---|---|---|---|---|---|---|
| | $\nu_{OH}$ | $\nu_{C=O}$ | $\nu_{C=C}$ | $\nu_{N=N}$ | $\nu_{C-O}$ | $\nu_{M-N}$ | $\nu_{M-O}$ |
| Mn-L2 (1:1) | 3156 | 1681 | 1594 | 1382 | 1234 | 532 | 428 |
| Mn-L2 (1:2) | 3145 | 1681 | 1592 | 1382 | 1234 | 534 | 428 |
| Co-L2 (1:1) | 3120 | 1670 | 1606 | 1384 | 1268 | 534 | 428 |
| Co-L2 (1:2) | 3397 | 1683 | 1602 | 1392 | 1267 | 543 | 430 |
| Ni-L2 (1:1) | 3160 | 1677 | 1598 | 1402 | 1268 | 524 | 445 |
| Ni-L2 (1:2) | 3426 | 1670 | 1606 | 1394 | 1267 | 541 | 466 |
| Cu-L2 (1:1) | 3160 | 1681 | 1598 | 1384 | 1234 | 526 | 445 |
| Cu-L2 (1:2) | 3328 | 1681 | 1598 | 1384 | 1247 | 534 | 443 |
| Zn-L2 (1:1) | 3158 | 1673 | 1602 | 1388 | 1268 | 528 | 468 |
| Zn-L2(1:2) | 3185 | 1683 | 1594 | 1386 | 1267 | 534 | 447 |

TABLE VII $^{1}H$ NMR spectral data of the investigated ligands (L1 and L2) and their Zn complexes

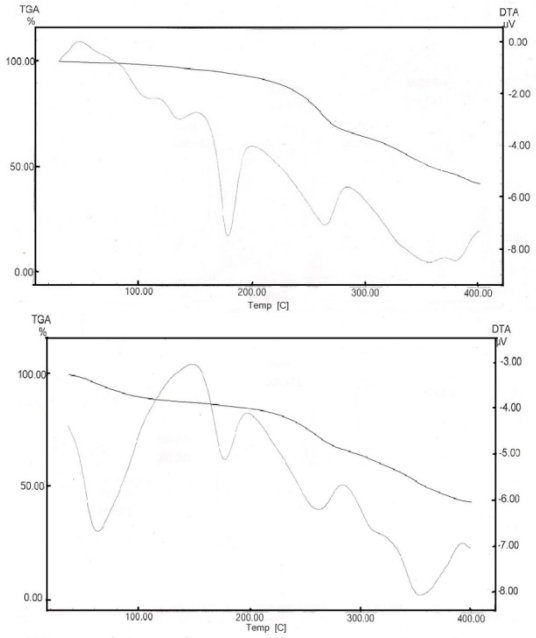
| Ligands and complexes | Chemical Shift (δ) | Assignment |
|---|---|---|
| L1 | 10.54 | OH proton |
| | 7.60-6.70 | Aromatic C-H protons |
| | 6.12 | Pyrone ring C-H |
| | 2.35 | $CH_3$pyrone ring |
| L2 | 7.99-6.68 | Aromatic C-H protons |
| | 6.09 | Pyrone ring C-H |
| | 2.33 | $CH_3$pyrone ring |
| Zn-L1 (1:1) | 7.53-6.63 | Aromatic C-H protons |
| | 6.01 | Pyrone ring C-H |
| | 3.65 | $H_2O$ of coordination |
| | 2.32 | $CH_3$pyrone ring |
| Zn-L1 (1:2) | 7.55-6.66 | Aromatic C-H protons |
| | 6.05 | Pyrone ring C-H |
| | 3.79 | $H_2O$ of coordination |
| | 2.32 | $CH_3$pyrone ring |
| | 2.12 | $CH_3$pyrone ring |
| Zn-L2 (1:1) | 7.55-6.66 | Aromatic C-H protons |
| | 6.06 | Pyrone ring C-H |
| | 3.79 | $H_2O$ of coordination |
| | 2.32 | $CH_3$pyrone ring |
| Zn-L2 (1:2) | 7.51-6.62 | Aromatic C-H protons |
| | 6.00 | Pyrone ring C-H |
| | 3.71 | $H_2O$ of coordination |
| | 2.31 | $CH_3$pyrone ring |
| | 2.12 | $CH_3$pyrone ring |

TABLE VIII Thermal Data of the dehydration and decomposition processes of some metal complexes in nitrogen atmosphere

| Complex | M. wt. | Temp. range °C | Loss of wt. % Caltd. | Loss of wt. % Found | Assignment |
|---|---|---|---|---|---|
| [Zn(L1) . Cl . $(H_2O)_3$] | 433.9 | 160-195 | 4.14 | 4.24 | $H_2O$ |
| [Zn(L1) . Cl . $(H_2O)_2$] | 415.9 | 195-280 | 8.29 | 8.29 | $2H_2O$ |
| [Zn(L1) . Cl] | 479.9 | 280-325 | 13.43 | 13.50 | $CH_3$, $N_2$, $O_2$ |
| | 388.9 | 325-400 | 37.22 | 36.60 | $C_6H_5$, $CH_2$ |
| | | | 17.22 | 17.28 | ZnO |
| [$Zn(L1)_2$ . $(H_2O)_2$] . $3H_2O$ | 713.4 | 35-120 | 7.66 | 8.42 | $3H_2O$ |
| [$Zn(L1)_2$ . $(H_2O)_2$] | 659.4 | 120-280 | 5.46 | 5.39 | $2H_2O$ |
| [$Zn(L1)_2$] | 623.4 | 280-340 | 19.24 | 19.66 | $C_6H_5$, $N_2$, $CH_3$ |
| | 456.4 | 340-400 | 36.59 | 36.87 | $C_6H_5$, $N_2$, $2CH_3$-$O_2$ |
| | | | 9.17 | 9.55 | ZnO |
| [Ni(L2) . $(H_2O)_3$]. $3H_2O$ | 488.7 | 65-100 | 3.68 | 3.91 | $H_2O$ |
| [Ni(L2) . $(H_2O)_2$]. $2H_2O$ | 470.7 | 100-155 | 7.65 | 7.89 | $2H_2O$ |
| [Ni(L2)] | 434.7 | 155-190 | 4.14 | 4.13 | $H_2O$ |
| | 416.7 | 190-290 | 8.64 | 8.00 | $2H_2O$ |
| | 380.7 | 290-400 | 47.54 | 47.81 | $C_6H_5$, $N_2$, $CH_3$, COOH, O |
| | | | 17.18 | 17.22 | NiO |
| $Ni(L2)_2$ . $(H_2O)_2$] . $3H_2O$ | 794.7 | 65-150 | 6.79 | 6.24 | $3H_2O$ |
| $Ni(L2)_2$ . $(H_2O)_2$] | 740.7 | 150-187 | 4.86 | 4.23 | $2H_2O$ |
| $Ni(L2)_2$] | 704.7 | 187-400 | 36.60 | 36.50 | $C_6H_5$, COOH, $2CH_3$. $N_4$, 4C |
| | | | 9.34 | 9.79 | NiO |

TABLE IX ESR spectral data of Cu (II) complexes with the investigated ligands L1 and L2.

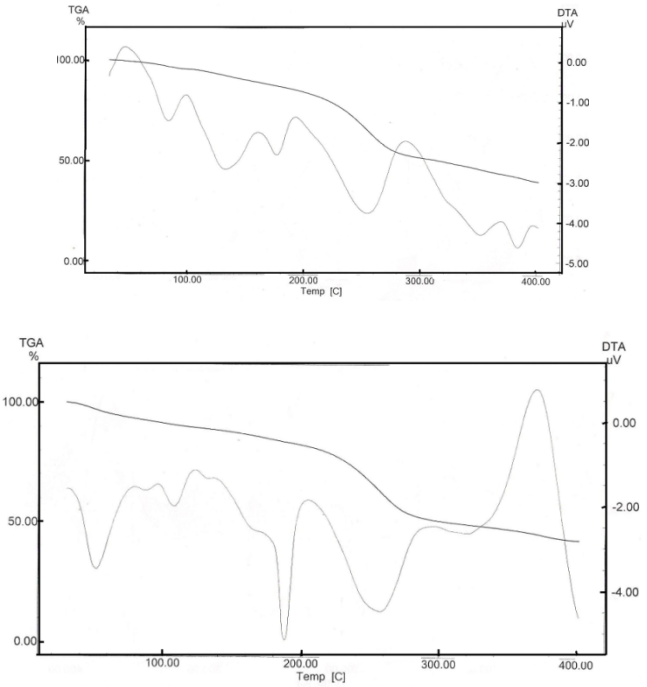
| Complex | $g_z = g_{//}$ | $g_x = g_{\perp}$ |
|---|---|---|
| $[Cu(L1) . Cl . (H_2O)_3]$ | 2.0563, 2.1486 | 2.2411 |
| $[Cu(L1)_2 . (H_2O)_2]$ | 2.0478, 2.0981 | 2.2270 |
| $[Cu(L2) . (H_2O)_3]$ | 2.0545 | 2.2350 |
| $Cu(L2)_2]$ | 2.1168 | 2.1899 |




(a)

(b)

FIGURE 1 Thermogravimetric and differential thermal analysis curves of Zn-L1 (1:1) (a) and (1:2) (b) complexes.




(a)

(b)

FIGURE 2 Thermogravimetric and differential thermal analysis curvesof Ni-L2 (1:1) (a) and (1:2) (b) complexes