Spectroscopic, Thermal, Magnetic and conductimetric studies on some 7-hydroxy-4-methyl-8-(arylazo)coumarins and their complexes with some divalent transition metal ions

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Abstract: *7-hydroxy-4-methyl-8-(p-methylphenylazo)coumarin (L1) and 7-hydroxy-4-methyl-8-(p-methoxyphenylazo)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 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 characterized by elemental and thermal analyses (TG and DTA) as well as by IR, ^{1}H NMR, magnetic measurements, electronic transition, molar conductance, mass 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 divalent metal ions with the investigated ligands 1:1 and 1:2 complexes 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: Azocoumarins; Complexes; Spectroscopic; Thermal analysis; conductance

I.   Introduction

Coumarin (1,2-benzopyrone), 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 by using chromatography, elemental analysis, UV-Vis, fluorescence and ^{1}H NMR spectra [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 [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-methyl- coumarin dye groups on the periphery were prepared by cyclotetramerization of the novel 3-[(2-diethylamino)ethyl]-7-[(3,4-dicyanophenoxy)]-4-methylcoumarin [7]. The novel chromogenic compounds were characterized. A series of new fluorinated coumarins and 1-azacoumarins were synthesized and cha racterized[8]. 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 were synthesized and characterized. Their structures were determined by X-ray crystallography single crystal analysis. The fluorescence behaviors of the compounds in dichloromethane solutions were observed [10]. A novel ligand, 7-(2,3-dicyanophenoxy)-3-(2-chloro-4-fluorophenyl)coumarin was synthesized [11]. The structure of the compound was confirmed by elemental analysis, UV–Vis, IR, MALDI-TOF mass and ^{1}H NMR spectra.

The present investigation deals with the preparation of some arylazocoumarins and their complexes with divalent Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) metal ions. The solid complexes have been prepared and characterized by elemental and thermal analyses (TG and DTA) as well as by IR, ^{1}H NMR, magnetic measurements, electronic transition, molar conductance, mass and electron spin resonance (ESR) spectra to throw more light on the bonds formed and on their structures.

II.   Experimental

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 ($ZnCl_2$), p-toluidine (p-methylaniline), p-ansidine (p-methoxyaniline), sodium hydroxide, ammonium hydroxide (30% NH_3), ammonium chloride, disodium salt of ethylenediamine-tetraacetic 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.

2.1 Preparation of ligands L1 and L2

A well-stirred solution of p-toluidine (p-methylaniline) or p-ansidine (p-methoxy-aniline) (0.01mole in 40 ml ethanol) and 20 ml of 2 M 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 (0.01 mol) 7-hydroxy-4-methylcoumarin in (100 ml) ethanol containing sodium hydroxide (0.01 mol). The products were filtered off and recrystallized from absolute ethanol [12]. Elemental analyses for the prepared azocoumarin dyes were done. The results obtained were in good agreement with the calculated values. The structures of these ligands were established by ^{1}H NMR, mass and IR spectral analysis. The prepared azocoumarin dyes have the following structural formulae:
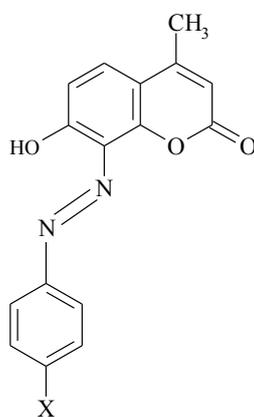
X = CH_3, 7-Hydroxy-4-methyl-8-(p-methylphenylazo)coumarin (L1)
X = OCH_3 7-Hydroxy-4-methyl-8-(p-methoxyphenylazo)coumarin (L2)

Table 1 shows the analytical data of the prepared azocoumarin 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 [13]. 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 desiccator. The metal content of the prepared solid complexes was determined [14].

III.   Apparatus and techniques

Elemental analysis and all of the other analyses were performed in the Micro-analytical center of Cairo University, Giza, Egypt. The IR spectra were recorded on Shimadzu FTIR-8201 PC spectrophotometer applying the KBr disc technique. The 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 coumarin azo dyes and some of their complexes were carried out using Q-1000 EX GC-MS Shimadzu spectrometer at 70 eV and MA energy using a direct insertion probe at temperature 90-110 ºC. Thermal analysis (TG and DTA) were obtained in a nitrogen atmosphere using a type TGA 50 Shimadzu derivatograph thermal analyzer. The heating rates were suitably controlled at 10 ºC min^{-1} under a nitrogen atmosphere and the weight loss was measured from ambient

temperature up to 400°C. The electron spin resonance (ESR) spectra of the copper complexes under study were recorded using EMS ESR spectrometer (Bruker) 1998 Y at Micro analytical center, Cairo University, Giza, Egypt. The molar conductance of the solid complexes in chloroform was measured using a conductivity meter type Philips, PW 9526 digital conductivity meter. The magnetic susceptibility measurements [15] 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. The electronic spectra of the investigated azocoumarin dyes and some of their complexes were measured by applying chloroform as solvent using Beckman Coulter DU 800 spectrophotometer using 1 cm matched silica cells.

IV. 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) were prepared as described in the experimental section. The resulting complexes were subjected to elemental analysis for their C, H, N and metal content [14], infrared spectral studies (IR), nuclear magnetic resonance ^{1}H NMR, magnetic susceptibility, thermogravimetric analysis (TG and DTA), electronic absorption spectra, molar conductance and electron spin resonance (ESR) spectra. The results of elemental analysis which are listed in Tables 2 and 3 are in good agreement with those required by the proposed formula where in all cases 1:1 and 1:2 (M:L) solid complexes were isolated.

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

The infrared spectra of the free ligands and solid complexes are recoded as KBr discs. In order to give conclusive idea about the structure of the solid complexes, the main IR bands were compared with those of the free ligands (Table 4). The strong broad band observed at 3496 and 3498 cm^{-1} in the spectra of the free ligands is assigned to νOH. The OH stretching frequency appearing in the spectra of all complexes studies appeared as a broad band in the range 3114-3378 cm^{-1} is due to the presence of water of coordination and/or water of hydration. The bands in the 3122 and 3104 cm^{-1} region are due to Ar-H stretching vibration while those appeared in the 2821 and 2819 cm^{-1} region are due to aliphatic C-H stretching vibration. The band appearing at 1670 and 1675 cm^{-1} are assigned to the stretching vibration of C=O group. The IR spectra of the investigated ligands show the -C=C- bands at 1602-1606 cm^{-1}. The bands at 1488 and 1450 cm^{-1} are assigned to the stretching vibration of N=N [16]. Upon chelation a shift to lower wave number has been observed within the range 1380-1402 cm^{-1} indicating that it is a center of chelation. The bands appearing in the IR spectra of the ligands (L1 and L2) at 1267 cm^{-1} are assigned to the stretching vibration of νC-O. Upon chelation this band is shifted to lower wave number as shown in Tables 5 and 6 indicating that it may be considered as a center of chelation. The $γ_{CH}$ of the aromatic rings is observed at 846 and 844 cm^{-1}. In the infrared spectra of the ligands and complexes (Tables 3 and 4), the band observed in the range 1670-1695 cm^{-1} assigned to νC=O while those in the range 1592-1610 cm^{-1} assigned to νC=C. The new IR bands appearing at 518-539 and 428-468 cm^{-1} are assignd to (M←N) and (M-O) vibrations [17], respectively. In other words, these bands are possibly due to the formation of coordinated and covalent bonds between the donor atoms (N and O) and the central metal ion. The most significant conclusive drawn from the proceeding arguments is that ligands L1 and L2 acts as bidentate ligands towards the central metal ion to form six-coordinate chelates.

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

The ^{1}H NMR spectra of the investigated ligands (L1 and L2) and their Zn complexes (1:1 and 1:2) were recorded in DMSO as a solvent and tetramethylsilane (TMS) as an internal standard. The chemical shift values (δ) in ppm of the different types of protons in the investigated ligands (L1 and L2) are reported in Table 7. The ^{1}H NMR spectra of the investigated ligands L1 and L2 in DMSO exhibits a sharp signal at 10.52-10.51 ppm. This signal is assigned to the proton of the OH group. The aliphatic protons of the methyl groups of the pyrone ring appeared at 2.35-2.36 ppm while those observed at 2.19 and 3.87 ppm are for aliphatic protons of the methyl and methoxy groups of the aromatic ring. The signals observed at 6.69-8.00 ppm are assigned to the protons of the aromatic ring [18]. The signals observed at 6.12 ppm are assigned to the proton of the pyrone ring [18]. A further support for the results obtained from the IR spectra is gained by considering the changes for the NMR spectra of the Zn complexes under investigation in comparison with those of the free ligands (Table 7).

For Zn-L1 (1:1 and 1:2) complexes, the disappearance of the signal at 10.52 ppm indicates the involvement of the OH in chelation followed by a new signal at 3.75 and 3.74 ppm corresponding to H_2O of coordination and /or hydrated water in these complexes. These signals were not found in the spectra of the free ligands. The signal observed at 2.32 ppm corresponding to CH_3 in the pyrone ring for 1:1 and 1:2 complexes, while those observed at 2.15 and 2.49 ppm corresponding to the aliphatic protons of CH_3 group of the benzene ring for 1:1 and 1:2 complexes,

For Zn-L2 (1:1 and 1:2) complexes, the signal at 10.51 corresponding to OH proton disappeared due to complexation with the appearance of a new signal in the region 3.56 and 3.59 ppm due to coordinated water molecules. This signal was not obviously shown in the spectra of the free ligand. The singlet signal observed at 3.82 and 3.84 corresponding to the methoxy group for 1:1 and 1:2 complexes.

4.3. Mass spectral studies of the investigated ligands and some of their complexes.

Mass spectrometry 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 [19]. The observed peak at m/z 294 (calculated 294) represents the molecular ion peak of 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 310 (calculated 310). From the data obtained we concluded that the molecular weights are in good agreement with the calculated values for the investigated ligands. The mass spectra of the some complexes were recorded and their molecular ion peaks confirm the suggested formula of these complexes. for Co-L1 (1:1), the main peak is observed at m/z 441 (calculated 441.4), Co-L1 (1:2) m/z 679 (calculated 680.9), Cu-L2 (1:1) m/z 461 (calculated 462.5), Cu-L2 (1:2) m/z 805 (calculated 807.5). The calculated values of the molecular weights of the investigated complexes are given with the corresponding elemental analysis in Tables 2 and 3.

4.4. 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-azocoumarin complexes, establish whether the water molecules are inner or outer sphere if present and suggest the thermal decomposition of these complexes [13]. The TG curves follows the decrease in sample mass with the linear increase in temperature. In the present investigation, heating rates were suitably controlled at 10 °C min^{-1} under nitrogen atmosphere and the mass loss followed up to 400 °C. From TG curves obtained, Figs. 1 and 2, the mass loss for each complex were calculated within the temperature range at which the loss occurs. The experimentally found and theoretically calculated mass losses are collected in Table 8.

For Cu-L1 (1:1) complex, two hydrated water molecules were expelled within the temperature range 60-120 °C corresponding to a loss of 7.25% (calculated 7.17%). In the temperature range 120-220 °C one coordinated water molecule is expelled corresponding to a loss of 4.66% (calculated 4.04%). In the temperature range 220-260 °C a weight loss of 8.79% (calculated 8.49%) is observed corresponding to the loss of two coordinated water molecules and in the temperature range 260-360 °C a weight loss of 22.38% (calculated 22.19%) is observed corresponding to the loss of one phenyl group. In the temperature range 360-380 °C a weight loss of 55.01% (calculated 55.33%) is observed corresponding to the loss of $C_9H_8O_3N_2$. At the end of the thermogram, the metal content was calculated from the residual metal oxide and found to be 17.45% (calculated 17.82%).

For Cu-L1 (1:2) complex, two hydrated water molecules were expelled within the temperature range 60-120 °C corresponding to the loss of 5.34% (calculated 5.99%). Two coordinated water molecules are expelled within the temperature range 120-240 °C corresponding to a loss of 5.62% (calculated 5.25%). In the temperature range 240-310 °C a weight loss of 16.50% (calculated 16.17%) is observed corresponding to the loss of $C_6H_5N_2$. In the temperature range 310-370 °C a weight loss of 47.57% (calculated 47.41) is observed corresponding to the loss of $C_{23}H_{21}N_2$. At the end of the thermogram the metal content was calculated from the residual metal oxide which was found to be 11.47% (calculated 11.59%).

For Mn-L2 (1:1) complex, one hydrated water molecule was expelled within the temperature range 80-130 °C corresponding to the loss of 3.94% (calculated 3.82%). Three coordinated water molecule is expelled within the temperature range 130-290 °C corresponding to a loss of 11.64% (calculated 11.61%). In the temperature range 290-370 °C a weight loss of 64.31% (calculated 64.35%) is observed corresponding to a loss of $C_{14}H_{13}N_2O_3$. At the end of the thermogram, the metal content was calculated from the residual metal oxide which was found to be 12.22% (calculated 12.11%).

For Mn-L2 (1:2) complex, one hydrated water molecule was expelled within the temperature range 80-140 corresponding to the loss of 2.66% (calculated 2.48). One coordinated water molecule was expelled within the temperature range 140-190 °C corresponding to a loss of 2.42% (calculated 2.54%). In the temperature range 190-290 °C a weight loss of 2.68% (calculated 2.61%) was observed corresponding to the loss of another one coordinated water molecule, while in the temperature range 290-320 °C a weight loss of 11.99% (calculated 11.44%) is observed corresponding to a loss of phenyl group and in the temperature range 320-360 °C a weight loss of 52.53% (calculated 53.60%) is observed corresponding to the loss of $C_{19}H_{16}N_4O$. At the end of the

thermogram the metal content was calculated from the residual metal oxide which was found to be 10.32% (calculated 10.00).

4.5. Differential thermal analysis (DTA)

For Cu-L1 (1:1), the DTA curve is characterized by the presence of two endothermic peaks at the temperatures 100 and 169 °C which are due to the elimination of water of hydration and coordinated water molecules. For Cu-L1 (1:2), the DTA curve is characterized by the presence of five endothermic peaks at the temperatures 25, 77, 103, 176 and 265 °C which are due to the elimination of water of hydration and coordinated water molecules. For Cu-L1 (1:1 and 1:2) an exothermic peak on the DTA curves at the temperatures 355 and 340 °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 these temperatures results in another decomposition and combustion followed by decarbonization of the organic material and at the end there would be the metallic residue as CuO.

For Mn-L2 (1:1), the DTA curve is characterized by the presence of four endothermic peaks at the temperatures 86, 108, 184 and 272 °C which are due to the elimination of water of hydration and coordinated water molecules. For Mn-L2 (1:2), the DTA curve is characterized by the presence of five endothermic peaks at the temperatures 35, 122, 175, 182 and 271 °C which are due to the elimination of water of hydration and coordinated water molecules. For Mn-L2 (1:1 and 1:2) An exothermic peak on the DTA curves at the temperature 390 °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 390 °C results in the combustion followed by decarbonization of the organic material and at the end there would be the metallic residue as MnO.

4.6. Magnetic susceptibility measurements.

The magnetic moment (μ) of a transition metal can give important information about the number of unpaired electrons in the metal ion, and in some special cases help to indicate the structure of the complex. Experimentally determined values of μ are in some cases higher than those calculated using 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 (μ_{eff} = 5.91 B.M.) and show a high spin d^5 configuration ($t_{2g}^3 \, e_g^2$). For Co^{2+}, (1:1 and 1:2) (M:L) complexes with the investigated ligands (L1 and L2), the calculated magnetic moments of the complexes are in the range 3.84-3.91 B.M. indicating the presence of three unpaired electrons per metal ion (μ_{eff} = 3.87 B.M.). For Ni^{2+} (1:1 and 1:2) (M:L), the complexes show μ_{eff} in the range 2.84-2.85 B.M. denoting two unpaired electrons (μ_{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 (μ_{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+}, Co^{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 [20]. Zn^{2+} complexes show diamagnetic behavior since the d-orbitals are completely filled and thus Zn^{2+} considered as non-transition metal ion.

4.7. Electron spin resonance (ESR).

The X-band ESR spectra of Cu^{2+}-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 9. Generally, the complexes are not magnetically dilute, therefore, exchanges [21] 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 [22] 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^{2+} 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 [23].

4.8. Molar conductivity measurements.

The molar conductivities of the solid complexes were measured for the 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 [24]. The conductivity values for all of the investigated complexes are listed in Tables 6 and 7.

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

The 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 π-π* transition within the phenyl moiety and the second band may be ascribed to the n-π* 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, Co, Ni and Cu 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 [25-27] and an octahedral configuration was suggested around the central metal ion.

Based on the results of elemental analysis, IR, ^1H NMR, thermal analysis, electron spin resonance (ESR), magnetic moments calculations, mass spectra and electron absorpation spectra for the investigated complexes, The 1:1 and 1:2 complexes are isolated. The proposed steriochemical structures for the investigated metal complexes suggest octahedral geometry for 1:1 and 1:2 complexes.
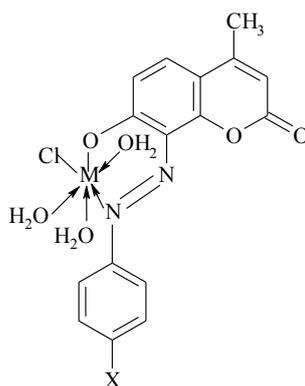
1:1 complexes

X = CH_3 (L1), OCH_3 (L2)

M = Mn, Co, Ni, Cu and Zn metal ions
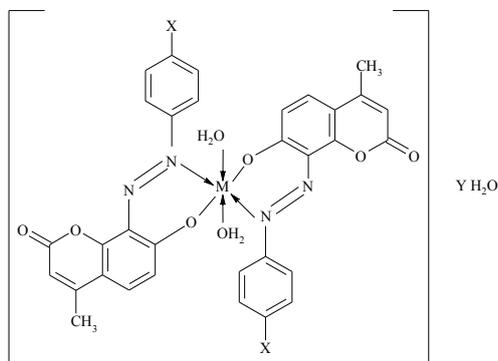
1:2 complexes

X = CH_3 (L1), OCH_3 (L2)

Y = 5 H_2O in case of Cu-L2 (1:2)

M = Mn, Co, Ni, Cu and Zn metal ions

V. Conclusion

Some 8-arylazo coumarins have been prepared and fully characterized using different analytical tools. The metal complexes of the investigated ligands L1 and L2 with Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} metal ions were prepared and subjected to elemental analysis, IR, ^{1}H NMR, mass spectra, Thermal analysis (TG and DTA), magnetic susceptibility, ESR spectra, molar conductance and electronic absorption spectra. The IR bands of the complexes were compared with those of the free ligands. The TG and DTA are documented. The weight losses for some complexes were calculated for the corresponding temperature ranges. The ^{1}H NMR spectra of the ligands and some of the prepared complexes are done and correlated. The magnetic susceptibility shows that all of the prepared complexes have high spin configuration. 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 prepared complexes have octahedral structures.

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Table 1

Analytical data of the prepared ligands L1 and L2

Ligand	X	Tentative formula	mp (°C)	Colour	Molecular weight	Yield %	C% calculated (found)	H% calculated (found)	N% calculated (found)
L1	p-CH$_3$	$C_{17}H_{14}N_2O_3$	150	Orange red	294	90	69.39 (69.37)	4.76 (4.73)	9.52 (9.26)
L2	p-OCH$_3$	$C_{17}H_{14}N_2O_4$	156	Orange red	310	80	65.80 (65.97)	4.51 (4.10)	9.03 (9.31)

Table 2

Elemental analysis, magnetic moments μ_{eff} and molar conductance Λ_m for the complexes of Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} metal ions with ligand L1.

Complex	Empirical formula	M:L	FW	C% (Calculated) found	H% (Calculated) found	N% (Calculated) found	M% (Calculated) found	μ_{eff}	Λ_m
[Mn(L1).Cl.3H$_2$O]	$C_{17}H_{19}MnN_2O_6Cl$	1:1	437.4	(46.63), 46.60	(4.34), 4.18	(6.40), 6.03	(12.55), 12.71	5.55	8.2
[Mn(L1)$_2$.2H$_2$O]	$C_{34}H_{30}MnN_4O_8$	1:2	676.9	(60.27), 60.80	(4.43), 4.70	(8.27), 8.57	(8.11), 8.31	5.95	24.6
[Co(L1).Cl.3H$_2$O]	$C_{17}H_{19}Co N_2O_6Cl$	1:1	441.4	(46.22), 46.55	(4.30), 4.66	(6.34), 6.08	(13.35), 13.66	3.84	8.2

[Co(L1)$_2$.2H$_2$O]	C$_{34}$H$_{30}$Co N$_4$O$_8$	1:2	680.9	(59.92), 58.00	(4.40), 4.30	(8.22), 8.22	(8.65), 8.77	3.91	16.4
[Ni(L1).Cl.3H$_2$O]	C$_{17}$H$_{19}$NiN$_2$O$_6$Cl	1:1	441.2	(46.24), 46.00	(4.31), 4.40	(6.34), 6.23	(13.30), 13.50	2.84	8.2
[Ni(L1)$_2$.2H$_2$O]	C$_{34}$H$_{30}$NiN$_4$O$_8$	1:2	676.7	(60.29), 60.88	(4.43), 4.22	(8.27), 8.37	(8.67), 8.51	2.85	16.4
[Cu(L1).Cl.3H$_2$O].2H$_2$O	C$_{17}$H$_{23}$CuN$_2$O$_8$Cl	1:1	482	(42.32), 42.61	(4.77), 4.39	(5.81), 6.51	(13.17), 14.55	1.74	8.2
[Cu(L1)$_2$.2H$_2$O]. 2H$_2$O	C$_{34}$H$_{34}$CuN$_4$O$_{10}$	1:2	721.5	(56.55), 56.32	(4.71), 4.67	(7.76), 7.47	(8.80), 8.22	1.76	16.4
[Zn(L1).Cl.3H$_2$O]	C$_{17}$H$_{19}$ZnN$_2$O$_6$Cl	1:1	447.8	(45.55), 45.05	(4.24), 4.49	(6.25), 6.71	(14.58), 14.45	0.06	8.2
[Zn(L1)$_2$.2H$_2$O)]	C$_{34}$H$_{30}$ ZnN$_4$O$_8$	1:2	687.3	(59.36), 59.09	(4.36), 4.89	(8.15), 8.09	(9.50), 9.44	0.08	16.4

Table 3

Elemental analysis, magnetic moments μ_{eff} and molar conductance Λ_m for the complexes of Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} metal ions with ligand L2

Complex	Empirical formula	M:L	M. wt.	C% (Calculated) found	H% (Calculated) found	N% (Calculated.) found	M% (Calculated) Found	μ_{eff}	Λ_m
[Mn(L2).Cl.3H$_2$O].H$_2$O	C$_{17}$H$_{21}$MnN$_2$O$_8$Cl	1:1	471.4	(43.28), 43.84	(4.46), 4.59	(5.94), 6.33	(11.66), 12.15	5.57	8.2
[Mn(L2)$_2$.2H$_2$O].H$_2$O	C$_{34}$H$_{32}$MnN$_4$O$_{11}$	1:2	726.9	(56.13), 56.76	(4.4), 4.32	(7.70), 7.68	(7.58), 7.77	5.93	8.2
[Co(L2).Cl.3H$_2$O]	C$_{17}$H$_{19}$CoN$_2$O$_7$Cl	1:1	457.4	(44.60), 44.22	(4.15), 4.26	(6.12), 6.29	(12.88), 12.49	3.90	8.2
[Co(L2)$_2$.2H$_2$O]	C$_{34}$H$_{30}$CoN$_4$O$_{10}$	1:2	712.9	(57.45), 57.23	(4.21), 4.33	(7.85), 7.53	(8.26), 8.13	3.84	8.2
[Ni(L2).Cl.3H$_2$O]	C$_{17}$H$_{19}$NiN$_2$O$_7$Cl	1:1	457.2	(44.61), 44.71	(4.15), 4.52	(6.12), 6.38	(12.83), 12.71	2.84	8.2
[Ni(L2)$_2$.2H$_2$O]	C$_{34}$H$_{30}$ NiN$_4$O$_{10}$	1:2	712.6	(57.25), 57.33	(4.21), 4.02	(7.86), 7.82	(8.22), 8.35	2.84	16.4
[Cu(L2).Cl.3H$_2$O]	C$_{17}$H$_{19}$Cu N$_2$O$_7$Cl	1:1	462.5	(44.11), 44.13	(4.11), 4.55	(6.05), 5.55	(13.73), 13.66	1.76	8.2
[Cu(L2)$_2$.2H$_2$O].5H$_2$O	C$_{34}$H$_{40}$ CuN$_4$O$_{15}$	1:2	807.5	(50.52), 50.56	(4.95), 5.33	(4.80), 4.44	(6.93), 6.86	1.74	16.4
[Zn(L2).Cl.3H$_2$O]	C$_{17}$H$_{19}$ZnN$_2$O$_7$Cl	1:1	463.8	(43.98), 43.69	(4.10), 4.01	(6.04), 6.13	(14.08), 14.33	0.06	8.2
[Zn(L2)$_2$.2H$_2$O)]	C$_{34}$H$_{30}$ ZnN$_4$O$_{10}$	1:2	719.3	(56.72), 56.91	(4.17), 4.62	(7.78), 7.98	(9.08), 9.22	0.08	8.2

Table 4

IR band assignments of the investigated free ligands L1 and L2

L1	L2	Band Assignment
3498	3496	ν_{OH}
3122	3104	ν_{C-H} aromatic
2821	2819	ν_{C-H} aliphatic
1675	1670	$\nu_{C=O}$
1606	1606	$\nu_{C=C}$
1450	1450	$\nu_{N=N}$
1350	1350	ν_{C-H}
1267	1267	ν_{C-O}
1168	1267	ν_{C-H}
1066	1066	δ_{OH}
846	846	γ_{C-H}

Table 5

IR band assignment of Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} complexes with the investigated ligand L1

Complex	M:L	ν(OH)	ν(C=O)	ν(C=C)	ν(N=N)	ν(C-O)	ν(M-N)	ν(M-O)
[Mn(L1).Cl.3H$_2$O]	1:1	3166	1681	1598	1382	1226	526	445
[Mn(L1)$_2$.2H$_2$O]	1:2	3338	1685	1600	1382	1216	518	428
[Co(L1).Cl.3H$_2$O]	1:1	3143	1681	1594	1382	1234	528	443
[Co(L1)$_2$.2H$_2$O]	1:2	3143	1681	1592	1382	1234	534	443
[Ni(L1).Cl.3H$_2$O]	1:1	3160	1681	1594	1384	1226	532	445
[Ni(L1)$_2$.2H$_2$O]	1:2	3168	1681	1598	1390	1224	524	447
[Cu(L1).Cl.3H$_2$O].2H$_2$O	1:1	3160	1677	1594	1402	1260	538	445
[Cu(L1)$_2$.2H$_2$O].2H$_2$O	1:2	3158	1681	1592	1382	1234	534	445
[Zn(L1).Cl.3H$_2$O]	1:1	3176	1677	1608	1392	1260	526	468
[Zn(L1)$_2$.2H$_2$O)]	1:2	3114	1670	1606	1384	1260	539	466

Table 6

IR band assignment of Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} complexes with the investigated ligand L2

Complex	M:L	ν(OH)	ν(C=O)	ν(C=C)	ν(N=N)	ν(C-O)	ν(M-N)	ν(M-O)
[Mn(L2).Cl.3H$_2$O].H$_2$O	1:1	3158	1683	1594	1382	1236	532	430
[Mn(L2)$_2$.2H$_2$O].H$_2$O	1:2	3282	1695	1610	1380	1259	530	428
[Co(L2).Cl.3H$_2$O]	1:1	3156	1683	1596	1382	1236	532	428
[Co(L2)$_2$.2H$_2$O]	1:2	3154	1683	1600	1384	1261	532	428
[Ni(L2).Cl.3H$_2$O]	1:1	3378	1681	1610	1388	1261	534	445
[Ni(L2)$_2$.2H$_2$O]	1:2	3162	1681	1598	1382	1247	534	430
[Cu(L2).Cl.3H$_2$O]	1:1	3160	1683	1602	1384	1259	534	443
[Cu(L2)$_2$.2H$_2$O].5H$_2$O	1:2	3328	1677	1606	1388	1251	536	466
[Zn(L2).Cl.3H$_2$O]	1:1	3147	1677	1600	1400	1261	520	447
[Zn(L2)$_2$.2H$_2$O)]	1:2	3160	1683	1600	1396	1261	528	445

Table 7

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

Ligands and complexes	Chemical Shift (δ)	Assignment
	10.52	OH
	8.00-6.69	Aromatic C-H protons
	6.12	Pyrone ring C-H
L1	3.36	H$_2$O solvent protons
	2.50	DMSO protons
	2.35	CH$_3$ pyrone ring
	2.19	CH$_3$ benzene ring
	10.51	OH
	7.60-6.69	Aromatic C-H protons
	6.12	Pyrone ring C-H
L2	3.87	OCH$_3$ benzen ring
	3.37	H$_2$O solvent protons
	2.51	DMSO protons
	2.36	CH$_3$ pyrone ring
Zn-L1 (1:1)	7.53-6.62	Aromatic C-H protons
	6.01	Pyrone ring C-H
	3.75	H$_2$O of coordination DMSO protons

	2.50	CH$_3$ pyrone ring
	2.32	CH$_3$ benzene ring
	2.15	
Zn-L1 (1:2)	7.55-6.65	Aromatic C-H protons
	6.05	Pyrone ring C-H
	3.74	H$_2$O of coordination
	2.50	DMSO protons
	2.32	CH$_3$ pyrone ring
	2.49	CH$_3$ benzene ring
Zn-L2 (1:1)	7.47-6.56	Aromatic C-H protons
	5.94	Pyrone ring C-H
	3.56	H$_2$O of coordination
	3.82	OCH$_3$ benzene ring
	2.50	DMSO protons
	2.31	CH$_3$ pyrone ring
Zn-L2 (1:2)	7.53-6.62	Aromatic C-H protons
	6.00	Pyrone ring C-H
	3.59	H$_2$O of coordination
	3.84	OCH$_3$ benzene ring
	2.50	DMSO protons
	2.38	CH$_3$pyrone ring
	2.33	CH$_3$pyrone ring

Table 8

Thermogravimetric results of Mn^{2+} and Cu^{2+} complexes with the investigated ligands L1 and L2

Complex	Molecular weight	Temperature (ºC)	Calculated loss %	Found loss %	Assignment
[Cu(L1).Cl.3H$_2$O].2H$_2$O	482	60-120	7.17	7.25	2H$_2$O
[Cu(L1).Cl.3H$_2$O]	446	120-220	4.04	4.66	H$_2$O
[Cu(L1).Cl.2H$_2$O]	424	220-260	8.49	8.79	2H$_2$O
[Cu(L1).Cl]	347	260-360	22.19	22.38	C$_6$H$_5$
	155	360-380	55.33	55.01	C$_9$H$_8$O$_3$N$_2$
		380-400	17.82	17.45	CuO
[Cu(L1)$_2$]2H$_2$O].2H$_2$O	721.5	60-120	4.99	5.34	2H$_2$O
[Cu(L1)$_2$]2H$_2$O]	685.5	120-240	5.25	5.62	2H$_2$O
[Cu(L1)]$_2$	649.5	240-310	16.17	16.50	C$_6$H$_5$N$_2$
	544.5	310-370	47.41	47.57	C$_{23}$H$_{21}$N$_2$
		370-400	11.59	11.47	CuO
[Mn(L2).Cl.3H$_2$O].H$_2$O	471.4	80-130	3.82	3.94	H$_2$O
[Mn(L2).Cl.3H$_2$O]	453.4	130-290	11.91	11.64	3H$_2$O
[Mn(L2).Cl]	399.4	290-370	64.35	64.31	C$_{14}$H$_{13}$N$_2$O$_3$
		370-400	12.11	12.22	MnO
Mn(L2)$_2$. 2H$_2$O].H$_2$O	726.9	80-140	2.48	2.66	H$_2$O
Mn(L2)$_2$. 2H$_2$O]	708.9	140-190	2.54	2.42	H$_2$O
Mn(L2)$_2$.H$_2$O]	690.9	190-290	2.61	2.68	H$_2$O
Mn(L2)$_2$]	672.9	290-320	11.44	11.99	C$_6$H$_5$
	356.9	320-360	53.60	53.53	C$_{19}$H$_{16}$N$_4$O
		360-400	10.00	10.32	MnO

Table 9

ESR spectral data of Cu^{2+} complexes with the investigated ligands L1 and L2.

| Complex	M:L	g$_z$ = g$_{//}$	g$_x$ = g$_\perp$
[Cu(L1).Cl.3H$_2$O].2H$_2$O	1:1	2.0549, 2.113	2.2438
[Cu(L1)$_2$.2H$_2$O].2H$_2$O	1:2	2.0663, 2.1634	2.2446
[Cu(L2).Cl.3H$_2$O]	1:1	2.0477, 2.1129	2.2228
[Cu(L2)$_2$.2H$_2$O].5H$_2$O	1:2	2.0558, 2.1129	2.2281

(a)

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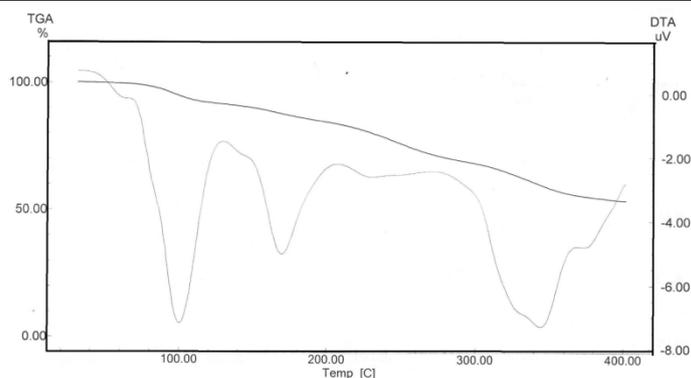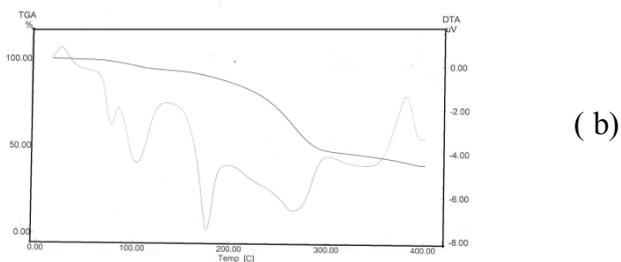
Fig. 1. Thermogravimetric and differential thermal analysis curves of   Cu-L1 (1:1) (a) and (1:2) (b) complexes


(a)

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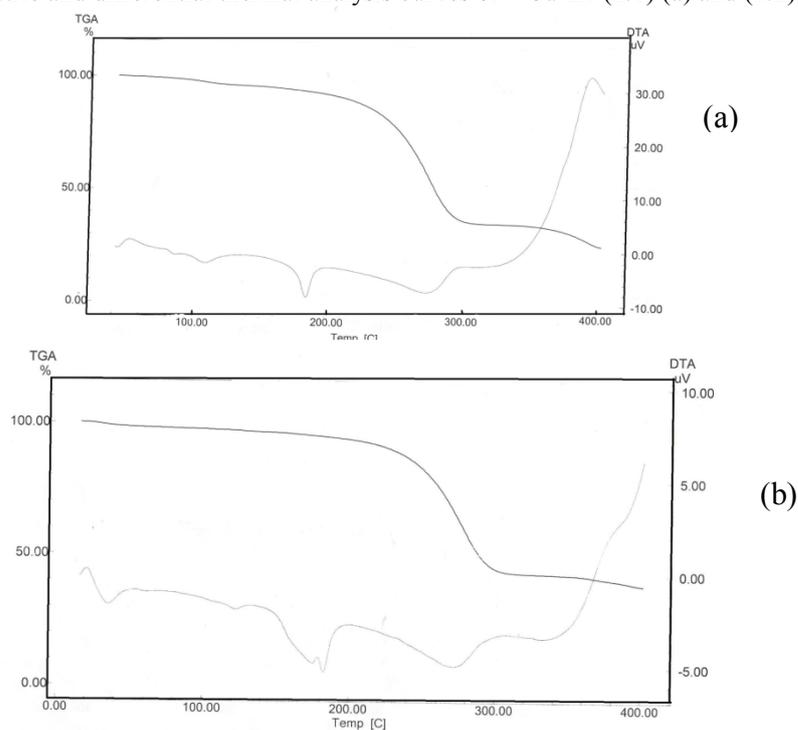
Fig. 2. Thermogravimetric and differential thermal analysis curves of Mn-L2 (1:1) (a) and (1:2) (b) complexes