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Synthesis and Characterization of Mononuclear and Binuclear Metal Complexes of a New Fluorescent Dye Derived from 2-Hydroxy-1-Naphthaldehyde and 7-Amino-4-Methylcoumarin

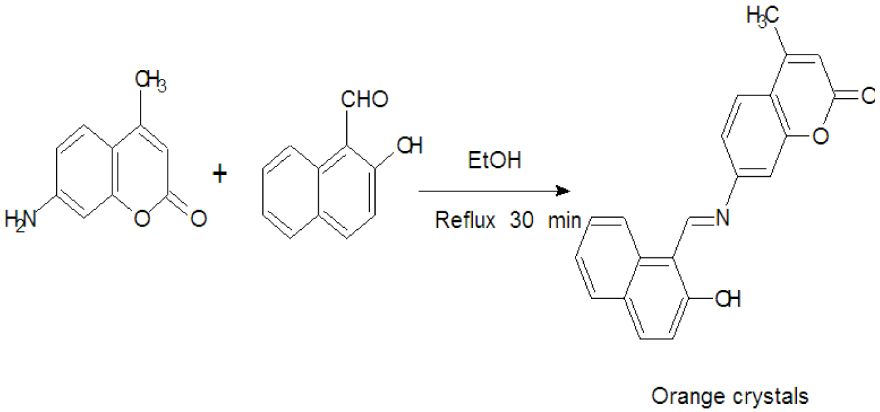
Elham S. Aazam
Department of Chemistry, Faculty of Science
King Abdulaziz University, Jeddah, Saudi Arabia
wayfield8@yahoo.com

Abstract: A mononuclear Cu(II), Zn(II) and binuclear Cu(II) complexes derived from the reactions of $Cu(acac)_2$, $Zn(OAc)_2.2H_2O$ and $Cu(OAc)_2.H_2O$ respectively with the monobasic, bidentate and fluorescent Schiff base ligand [7-{(2-hydroxynaphthalen-1-yl)methylidene]amino}-4-methyl-2*H*-chromen-2-one, HL] have been synthesized. The ligand and its metal complexes were characterized by microanalytical, mass, IR, UV-Vis, ESR, fluorescence, ^{1}H- and ^{13}C-NMR studies. The fluorescent HL consists of a methyl substituted coumarin group fused to a 2-hydroxynaphthaenyl ring *via* an azomethine linkage. The ligand acts as a bidentate, through NO in coordinating to the M(II) ions. The two bonding sites are the azomethine nitrogen and naphthanolic oxygen. Microanalytical and mass analyses are consistent with the formation of mono-and bi-nuclear complexes. Spectral studies indicate a square planar structure for the monnouclear [Cu(L)(acac)] complex, while the binuclear Cu(II) and mononuclear Zn(II) complexes exist as $[\{Cu(L)_2\}_2]$ and [Zn(L)(HL)(OAc)] respectively having penta-coordinate geometry. The ESR spectrum of $[\{Cu(L)_2\}_2]$ in DMSO further confirm that the ground state is dz^2 and the complex has a trigonal bipyramidal geometry around the Cu(II) centers.

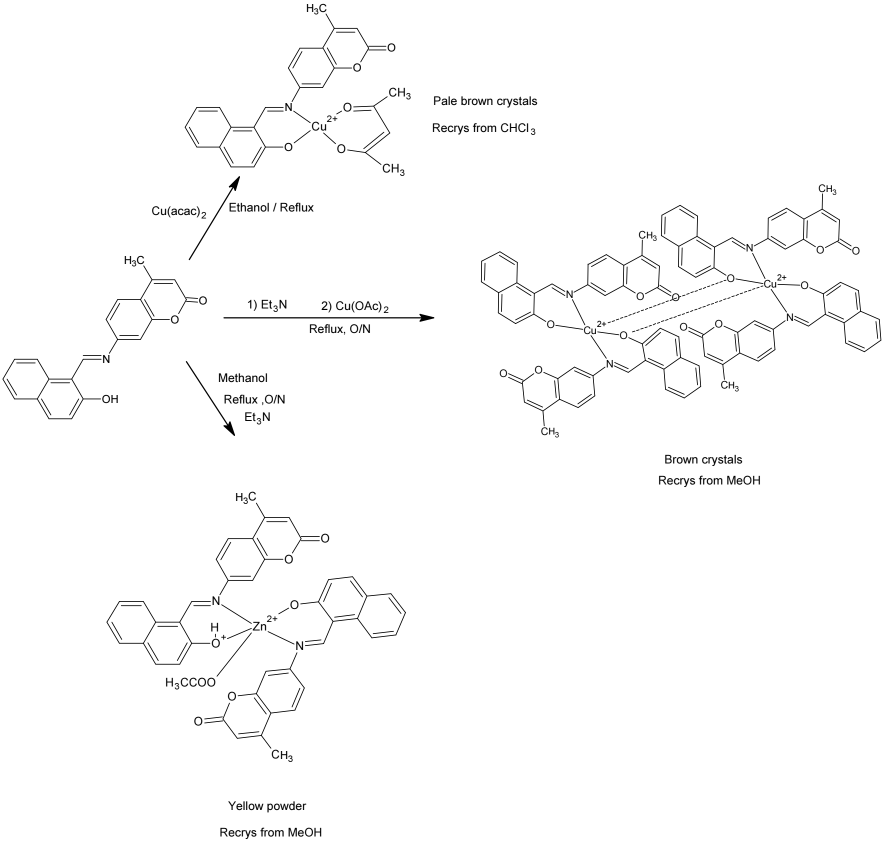
Keywords: Schiff base. Square planar. Trigonal bipyramidal. ESR. Coumarin. Fluorescence.

1. Introduction

Schiff base complexes play an important role in coordination chemistry[1,2]. Interest in metal–coumarin complexes is attributed to the attempts to discover novel lead compounds along with the desire to improve the efficiency and accelerates bioactivity[3,4]. We have recently reported synthesis, single crystal X-ray diffraction studies, characterization and antibacterial activity of a Schiff-base ligand incorporating coumarin moiety and their metal complexes[5-7]. Based on the research we found that the Schiff base ligand 4-methyl-7-(salicylidineamino) coumarin could be used as a potential Zn^{2+} sensor[8]. Biological activity screening proved the good antibacterial activity of the ligand, and its metal complexes. Zn(II) and Cu(II) complexes possessed high degree of inhibition and was attributed to the greater number of d-electrons, which increases the electrostatic field around metal ion[6]. The 4-methyl coumarin was chosen as the first flourophore since it acts as metal chelators and possesses a variety of biological activities[8,9]. We choose the naphthalene group as the second fluorophore due to its characteristic photophysical properties and the competitive stability in the environment. Accordingly, we combined 2-hydroxy-1-naphthaldehyde with 7-amino-4- methyl coumarin to form the fluorescent ligand (HL) (Scheme 1), In addition the precursor 2-hydroxy-1-naphthaldehyde is inexpensive, water-soluble, and is expected to provide the binding site for the target metal ion[10] .The structure of HL was confirmed by its spectroscopic data. The choice of copper(II) complexes have been the subject of a large number of research studies, since the role of Cu(II) complex in enhancing the pharmacological profile of the antimicrobial activities of some drugs and bioactive compounds is well-known[9,11,12]. Zinc ion, the second most abundant transition-metal ion in the human body, plays crucial roles in many important biological processes in acting as the structural and catalytic cofactors, neural signal transmitters or modulators, and regulators of gene expression[13]. Additionally, the effective role of azomethine linkage in certain biological reactions is well-documented[14]. In a continuation of our study of Schiff base ligands and their copper(II) and Zn(II) complexes, we report here the synthesis and characterization of HL and its metal complexes (Scheme 2).



Scheme 1: Synthesis of 7-{(2-hydroxynaphthalen-1-yl)methylidene]amino}-4-methyl-2*H*-chromen-2-one, HL.



Scheme 2: Synthesis of HL metal complexes.

2. Experimental

2.1. Chemicals

7-amino-4-methyl coumarin was obtained from Fluka. 2-hydroxy-1-naphthaldehyde was purchased from Aldrich. Copper(II) acetate monohydrate, zinc(II) acetate dihydrate, was procured from BDH. Acetonitrile, Methanol, ethanol, dimethyl sulphoxide and diethyl ether were of pure grade and used as submitted from BDH.

2.2. Physical Measurements

Infrared spectra of solids were recorded in the region 4000-650 cm^{-1} on a Perkin Elmer Spectrum 100 FT- IR Spectrometer. Electronic absorption spectra were recorded in the 200-900 nm region in a JASCO V-530 UV/ Vis Spectrophotometer. Fluorescence spectra were recorded on a Perkin Elmer LS-55 Spectrometer at room temperature (298 K) in DMSO solution with a 1cm path length quartz cell. Elemental analysis of carbon, hydrogen, and nitrogen were determined in the Micro Analytical Unit using Perkin Elmer 2400. Melting points were carried out on a melting point apparatus, Gallenkamp, England. Solution NMR spectra were recorded using AM-400 Bruker spectrometer with $CDCl_3$ was used as an internal standard and the chemical shifts are given in ppm. ESR spectra were recorded on Bruker ESP-300 and JEOL JESRE - IX with variable temperature unit.

2.3. Synthesis of the Ligand and its Metal Complexes

2.3.1. Synthesis of HL

2-hydroxy-1-naphthaldehyde (0.49g, 2.85mmol) dissolved in 20ml of ethanol was added to a warm stirred solution of 7-amino-4-methylcoumarin (0.5g, 2.85mmol) in absolute ethanol (30 ml), an immediate change in color was observed from yellow to orange and an orange precipitate was formed . The mixture was left to stir for 10 min. The resulting orange precipitate was removed, washed with ethanol followed by diethyl ether and then dried in *vacuo*. HL was recrystallised by slow evaporation from dichloromethane. Yield (0.7g, 2.127mmol, 75%), m.p207°C. Elemental analysis calculated for $C_{21}H_{15}NO_3$: C(76.58%) H(4.59%) N(4.25%); found: C(76.%), H(4.49%) , N(4.34%). EI MS: $M^{+\cdot}$ *m/z* 329 (100%).^{1}H NMR (399 MHz, $CDCl_3$, 298 K, ppm) δ: 15.05 (s, 1H, OH), 9.41 (s, 1H, CH=N), [8.13 (d, *J* = 8.3, 1H), 7.86 (d, *J* = 9.1, 1H), 7.75 (d, *J* = 8.1, 1H), 7.67 (d, *J* = 8.0, 1H), 7.57 (t, *J* = 7.7, 1H), 7.39 (t, *J* = 7.4, 1H), 7.31 (d, *J* = 4.0, 2H), 7.12 (d, *J* = 8.8, 1H), aromatic H], 6.29 (s, 1H, C<u>H</u>=C-CH$_3$), 2.47 (s, 3H, CH$_3$). ^{13}C NMR (399 MHz, CDCl$_3$, 298 K, ppm) δ: 18.88 (CH$_3$), 108.24–149.82 (aromatic C), 152.40 (C-OH), 156.83 (CH=N), 169.79 (C=O).

2.3.2. Synthesis of [{Cu(L)$_2$}$_2$]

A solution of (0.06g, 0.30mmol) Cu(II) acetate monohydrate in chlorform (15ml) was added to a solution of HL ligand (0.1g, 0.30mmol) in the same solvent (20ml), the resulting mixture turned olive green immediately and a green precipitate was formed. The resulting precipitate was removed, washed with ethanol followed by diethyl ether and then dried in *vacuo*. [{Cu(L)$_2$}$_2$] was recrystallised by slow evaporation from methanol. Yield (0.7g, 2.127mmol, 75%), 309°C. Yield (0.13g, 0.067mmol, 90%). Elemental analysis calculated for $C_{42}H_{28}CuN_2O_6$: C(70.04%) H(3.92%) N(3.89%); found: C(69.61%), H(3.37%), (3.48%).

2.3.3. Synthesis of [Cu(L)(acac)]

A solution of (0.16g, 0.61mmol) Cu(II) acetyl acetonate in methanol (15ml) was added to a solution of HL ligand (0.2 g, 0.61 mmol) in the same solvent (20ml), the resulting mixture was refluxed overnight upon which a precipitate was formed. The resulting pale-brown precipitate was removed, washed with ethanol followed by diethyl ether and then dried in *vacuo*. [Cu(L)(acac)] was recrystallised by slow evaporation from dichloromethane. Yield (0.24g, 0.48mmol, 80 %), m.p 365°C. Elemental analysis calculated for $C_{26}H_{21}CuNO_5$: C(63.60%) H(4.31%) N(2.85%); found: C(63.67%), H(4.25%), (2.91%). *m/z* 490 (10%), 391 (100%).

2.3.4. Synthesis of [Zn(L)(HL)(OAc)]

A clear solution of (0.094g, 0.43mmol) Zinc(II) acetate dihydrate in chlorform (15ml) was added to a solution of HL ligand (0.14gm, 0.43mmol) in the same solvent (30ml), the resulting mixture was refluxed for 1 hour and few drops of triethylamine was added. The mixture was left to reflux for 2 hrs upon which a change in color of solution from orange to yellow was observed. The solvent was pumped off; this was followed by Recrystallisation from methanol affording yellow powder. (Yield based on HL (0.1g, 0.13mmol, 47%), m.p Decomp >400°C, Elemental analysis calculated for $C_{44}H_{32}N_2O_8Zn$: C(67.57%) H(4.12%) N(3.58%); found: C(67.55%), H(3.50%), (3.64%). EI MS: $[\{ZnL(OAc)\}.\ 0.5\ H_2O]^{+\cdot}$ *m/z* 462 (75 %). ^{1}H NMR (399 MHz, CDCl$_3$, 298 K, ppm) δ: 15.05 (s, 1H, OH), 9.38 (s, 2H, CH=N), [8.11 (d, *J* = 8.0, 2H), 7.82 (d,

J = 9.2, 2H), 7.82 (d, J = 9.2, 2H), 7.64 (d, J = 8.0, 2H), 7.53 (s, J = 7.7, 2H), 7.2 (d, J = 22.4, 4H), 7.06(s, 2H), aromatic H], 6.24 (s, 2H, C<u>H</u>=C-CH_3), 2.44 (s, 6H, CH_3), 1.21 (s, 3H, OAC). ^{13}C NMR (399 MHz, $CDCl_3$, 298 K, ppm) δ: 18.78 (CH_3), 30 (OAc), 107.84–137.58 (aromatic C), 152.40 (C-OH), 156.32 (CH=N), 160 (OAC) 169.39 (C=O).

3. Results and Discussion

3.1. Electronic and Fluorescence Spectral Studies

The electronic absorption spectra of the Schiff base and its metal complexes were recorded in 10^{-5} M at room temperature using DMSO as the solvent. The electronic spectrum of the free ligand HL shows maxima at 250 nm and 355nm due to π-π* transitions[15]. The ligand also shows a broad band at 478 nm due to the n–π* transition associated with the azomethine linkage[16]. This band in the zinc complex has shown a bathochromic shift due to the donation of a lone pair of electrons to the metal and hence the coordination of azomethine[17]. The [Cu(L)(acac)] complex shows a d–d band in the region 481 nm due to $^2B_{1g} \rightarrow {}^2A_{1g}$ transition which supports square-planar geometry [18]. The $[\{Cu(L)_2\}_2]$ shows an absorption band due to d–d transition of Cu^{2+} ions at 650-700 nm consistent with penta coordinate symmetry[19].

The fluorescence spectrum of the Schiff base ligand HL containing coumarin moiety was studied in DMSO at room temperature. The fluorescence quantum yield was determined using 7-amino-4-methylcoumarin (Coumarin 120) laser dye as a reference with a known Φ_f of 0.63in MeCN. The ligand and the reference dye were excited at 370 nm, maintaining nearly equal absorbance (~0.1), and the emission spectra were recorded from 200 to 600 nm[20]. The Stokes shift parameter indicates the difference in the properties and structure of the compounds between the ground state S_0 and the first exited state S_1[21], and has been estimated according to Eq. (1)[22]:

$$\Delta\acute{\upsilon} = \acute{\upsilon}_{abs} - \acute{\upsilon}_{em} = (1/\lambda_{abs} - 1/\lambda_{em}) \times 10^7\ cm^{-1} \qquad (1)$$

where:

λ_{abs}, λ_{em} = Absorbance and emission wavelength (nm)

$\acute{\upsilon}_{abs}$, $\acute{\upsilon}_{em}$ = Wavenumbers for the absorption and emission maxima (cm^{-1})

As in 7-amino-4-methylcoumarin (Figure 1), the emission spectrum of the fluorescent HL showed a maximum at 420 nm having Stokes shift of 4359.5 cm^{-1}, however, a lower quantum yield of 0.40 was observed (Φ_f = 0.66 for coumarin 120in DMSO), possibly due to the non-planarity of the Schiff base and the presence of hydroxyl group which play a more important role in enhancing the intersystem crossing. Moreover, recently it has been reported that the C=N isomerization was the predominant decay process of the excited states for compounds with an unbridged C=N structure so that these compounds were often non fluorescent[23, 24] .

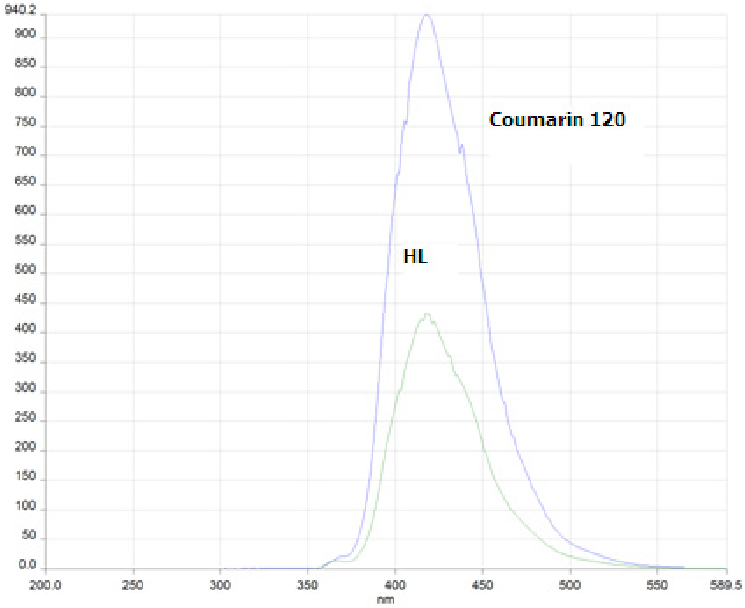


Fig. 1: Fluorescence emission spectrrum of Coumarin 120 and HL (excitation at 370 nm) in DMSO.

3.2. ^{1}H and ^{13}C NMR Studies

The ^{1}H NMR of HL showed a peak at $\delta = 15.05$ ppm for the naphthanolic –OH, which is different than that observed for its precursor 2-hydroxy-1-naphthaldehyde ($\delta = 13.13$), thus confirming Schiff base formation. A peak for the coumarin methyl was observed at $\delta = 2.44$ ppm.

Complex [Zn(L)(HL)OAc)] presents a signal at 1.21 ppm in the ^{1}H NMR spectrum, in agreement with the coordination of the acetate ligand to the metal center in solution. This point was further confirmed by the ^{13}C NMR spectrum that shows two peaks at 30 and 160 ppm, typical of acetate groups [25]. The EI mass spectrum show the existence of mononuclear units in the solid state, with peaks at *m*/*z* *ca*. 462, due to $[\{ZnL(OAc)\}.\ 0.5\ H_2O]^{+\cdot}$ fragment, although no peaks related to Zn(L)(HL)OAc species could be observed. Supported by elemental analysis it can be concluded that the penta-coordinated zinc atoms are in square pyramidal environment (Scheme 2, Table 1 and 2).

Table 1: ^{1}H NMR δ of HL and its Zinc complex.

Compound	CH_3	OH	CH=N	CH=C	H-arom	$C=O(OCH_3)$
HL	2.47 s	15.05 s	9.41 s	6.29 s	7.12-8.13	__
[Zn(L)(HL)(OAc)]	2.44 s	15.03 s	9.38 s	6.24 s	7.06-8.11	1.21

Table 2: ^{13}C-NMR of HL and its Zinc complex.

Compound	CH_3	CH=N	C-OH	C-arom	$C=O(OCH_3)$
HL	18.88	156.83	152.40	108.24-149.82	__
[Zn(L)(HL)(OAc)]	18.78	156.32	152.40	107.84-137.58	30 and 160

3.3. IR Spectral Studies

The infrared spectrum of the Schiff base ligand [7-{(2-hydroxynaphthalen-1-yl)methylidene]amino}-4-methyl-2*H*-chromen-2-one, HL, displayed very strong ν(C=N) band at 1595 cm^{-1} and ν(C=O) lactone at 1714 cm^{-1}[26,27]. The variable bands at 3432-3243 cm^{-1} was attributed to strong intramolecular hydrogen bonding (O-H…N) between the hydroxyl-hydrogen and azomethine nitrogen atoms and the electrostatic (C-H…O) intermolecular interactions[5]. The strong bands at 1542, 1396 cm^{-1} were assigned to in plane ring, C=C and C=N vibrations respectively. The band at 1214 cm^{-1} was assigned to ν(C-O) phenolic group[9]. The band observed at 1133 cm^{-1} is characteristic for ν_{asym} (C-O-C) of the pyran ring[28]. The most significant changes in the absorption frequencies between free and metal (II) coordinated ligand is collected in Table 3.

In all the metal complexes, the azomethine group is shifted to lower frequency in the region 1576–1571 cm^{-1} which indicates that chelation takes place through the azomethine group, the position of the νC=O band remained largely unchanged, suggesting that the lactone carbonyl oxygen is not involved in coordination to the metal[29]. The [Zn(L)(HL)(OAc)] complex showed ν(OH) broad band around 3037, indicating deprotonation of only one phenolic oxygen of the $(L)_2$ unit on coordination to the Zn(II) metal centre. The spectrum showed ν_{as} (COO-) and ν_{sy} (COO-) at 1424 and 1460 cm^{-1} respectively indicating the binding of the acetate to the metal in a monodentate fashion[30].

Table 3: Characteristic *v* IR (cm^{-1}) bands of HL and its metal complexes.

Compound	O-H,OH--- N and C-H---O	C=O	C=N	=C-O	C-O-C=O
HL	3432-3243	1714	1595	1214	1133
[Cu(L)(acac)]	305 and 2923	1713	1576	1254	1133
[{Cu(L)$_2$}$_2$]	3432-3245	1713	1574	1253	1133
[Zn(L)(HL)(OAc)]	3037	1716	1571	1263	1138

3.4. ESR Studies

The ESR spectrum of [{Cu(L)$_2$}$_2$] in DMSO at 273 K in Fig. 2, showed parameters which indicates the electric field symmetry around Cu^{2+} centers to be anisotropic in nature with rhombic symmetry having g_x=2.031, g_y=2.090 and g_z=2.143. As the temperature is lowered to 130 K (Figure 3), an anisotropic nature with axial pattern was observed, having two g-values ($g_{\|}$ =2.037, $g_{\perp}$= 2.136) where $g_{\perp} > g_{\|}$ indicating that the ground state is dz^2 and that the complex has a trigonal bipyramidal geometry around the Cu(II) centers[31]. The g_{av} value was calculated from Eq. (2) and found to be equal to 2.103.

$$g_{av} = 1/3\ (g_{\|} + 2\ g_{\perp}) \qquad (2)$$

The deviation of the g_{av} from that of the free electron (2.0023) is due to the covalence property. In axial symmetry the g-values are related by the expression in Eq. (3) where the G value is less than 4 suggesting exchange interaction of Cu-Cu in the complex[31,32].

$$G = g_{\|} -2\ /\ g_{\perp} -2 = 0.272 \qquad (3)$$

The additional peak observed at 1500 G in the ESR spectrum yields a g value of 4.16, which is due to a singlet-triplet transition, being coincident with a dimeric structure of the Cu(II) complex[19]. The hyperfine splitting signal of the parallel component of [{Cu(L)$_2$}$_2$] is broad due to the equilibrium between the mononuclear and binuclear complexes in solution[33].

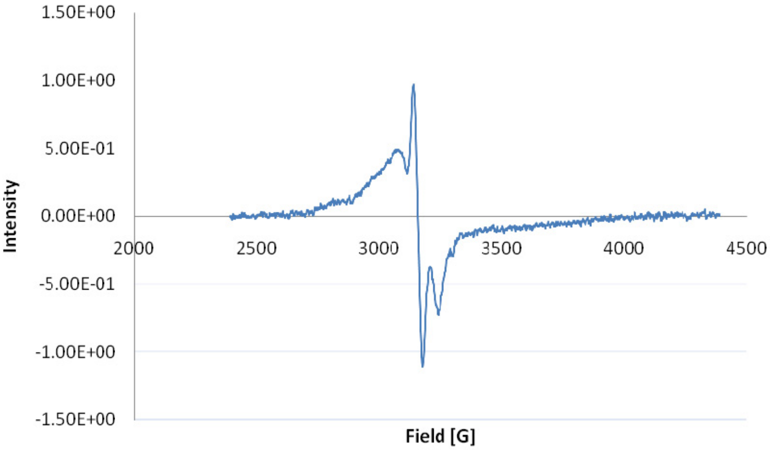


Fig. 2: ESR spectrum of [$\{Cu(L)_2\}_2$] complex: in DMSO solution at room temperature. Conditions are as follows: *V*= 9.237 GHz.

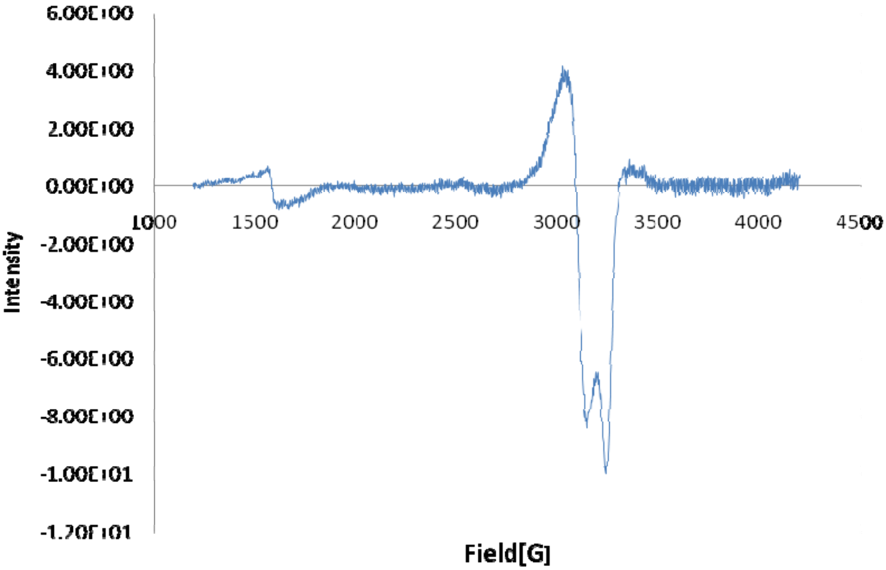


Fig. 3: ESR spectrum of [$\{Cu(L)_2\}_2$] complex in DMSO solution at 130 K Conditions are as follows: *V*= 9.387 GHz.

4. Conclusion

We have synthesized divalent Cu and Zn complexes using the new bidentate Schiff base ligand formed by the condensation of 2-hydroxy-1-naphthaldehyde and 7-amino-4-methylcoumarin. The emission spectral studies for the ligand revealed its fluorescent nature. The coordination ability of HL towards M(II) complexes were examined by different spectroscopic methods that unequivocally determine the two coordination sites of L, naphthanolic oxygen and azomethine nitrogen. Emphasis has been given to the examination of the structural geometry of the M(II) chelated complexes. Spectral data confirm the 1:2, 1:2 and 1:1 metal to ligand stoichiometry for $[\{Cu(L)_2\}_2]$, [Zn(L)(HL)(OAc)] and [Cu(L)(acac)] respectively. The existence of dimeric copper complex [{Cu(L)2}2] was further investigated by ESR studies.

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تحضير ودراسة خصائص متراكبات أحادية وثنائية النواة لصبغة جديدة ذات خصائص تألقية مشتقة من ٢-هيدروكسي-١- نفثالدهيد، و٧- أمينو -٤-ميثيل كومارين

إلهام شفيق أعظم

أستاذ مساعد- قسم الكيمياء- كلية العلوم

جامعة الملك عبدالعزيز- جدة - المملكة العربية السعودية

المستخلص. تم في هذا البحث تحضير متراكبات النحاس والخارصين (II) وحيدي الفلز، ومتراكب النحاس (II) ثنائي الفلز، بتفاعل كل من $Zn(OAc)_2.2H_2O$,$Cu(acac)$ و $Cu(OAc)_2.H_2O$ على التوالي مع المتصل قاعدة شيف, أحادي القاعدية, ثنائي المخلب ذو انبعاث تألقي [7-{(2-hydroxynaphthalen-1yl)methylidene]amino} -4-methyl-2*H*-chromen-2-one, HL]. كما درست خصائص المتصل ومتراكباته اعتمادا على التحليل العنصري, ومطياف الكتلة, وطيف الأشعة تحت الحمراء, وطيف امتصاص الأشعة المرئية وفوق البنفسجية, والرنين البارامغنطيسي

الإلكتروني, وطيف التألق ودراسات طيف الرنين النووي المغنطيسي للبروتون ^{1}H، والكربون ^{13}C. يتكون المتصل المتألق من مجموعة ميثيل كومارين متصلة مع حلقة ٢-هيدروكسي نفثالين، بواسطة رابطة الآزوميثين. وقد أوضحت الدراسات أن المتصل ثنائي المخلب، يرتبط بالفلز ثنائي التكافؤ بواسطة NO أي بواسطة ذرة النيتروجين في الآزوميثين، وذرة الأكسجين في النفثالين. تؤيد دراسات التحليل العنصري ومطياف الكتلة تكون المتراكبات أحادية أو ثنائية الأنوية. كما تم التوصل بمساندة دراسة أطياف الامتصاص الإلكترونية من اتخاذ المتراكب أحادي النواة [Cu(L)(acac)] شكل مربع مستو، بينما يتخذ متراكبي النحاس ثنائي النواة والخارصين أحادي النواة $[\{Cu(L)_2\}_2]$ و[Zn(L)(HL)(OAc)] التناسق الخماسي. كما تساند نتائج الرنين البارامغنطيسي الإلكتروني من أن الحالة الأرضية للمتراكب $[\{Cu(L)_2\}_2]$ هي dz^2، وأن المتراكب يتخذ الشكل الهندسي المكون من هرمين بقاعدة مثلثة واحدة.