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Azza A. A. Abu-Hussen<sup>a</sup>; Wolfgang Linert<sup>b</sup>

<sup>a</sup> Chemistry Department, Ain Shams University, Women Faculty for Arts, Science and Education, Cairo, Egypt <sup>b</sup> Institute of Applied Synthetic Chemistry, Vienna University of Technology, Vienna, Austria

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## Synthesis, spectroscopic, thermal, and biological activities on solvatochromic mixed ligand copper(II) complexes

AZZA A. A. ABU-HUSSEN† and WOLFGANG LINERT\*‡

†Chemistry Department, Ain Shams University, Women Faculty for Arts,  
Science and Education, Cairo, Egypt

‡Institute of Applied Synthetic Chemistry, Vienna University of Technology,  
Vienna, Austria

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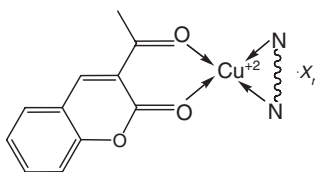
A series of solvatochromic copper(II) mixed ligand complexes of 3-acetylcoumarin (3-ACoum) and dinitrogen bases (L), with the general formula  $\text{Cu}(3\text{-ACoum})(\text{L})\text{X}_n$ ; where  $n=2$ ,  $\text{L} = N,N,N',N'$ -tetramethylethylenediamine (tmen), 1,10-phenanthroline (phen) and 2,2'-bipyridine (bipy) and  $\text{X} = \text{ClO}_4^-$ ,  $\text{BF}_4^-$  or  $\text{NO}_3^-$ , have been synthesized and characterized by elemental analysis, IR, UV-Vis, electron spin resonance spectra, magnetic susceptibility, and conductivity measurements. The d-d absorption bands of tmen-complexes in weak donor solvents show the formation of square planar or square pyramidal geometries, while strong donor solvents yield octahedral complexes. The observed solvatochromism is mainly due to the solute-solvent interaction between the chelate cation and the solvent molecules, and the spectra displayed the possibility of using these complexes as Lewis base indicators. Thermogravimetric analyses (TGA)/differential thermal analysis (DTA) as well as the kinetic parameters ( $\Delta H^\ddagger$ ,  $\Delta S^\ddagger$ , and  $\Delta G^\ddagger$ ) of thermal decomposition stages of nitrate complexes have been calculated. Furthermore, the antimicrobial activity of the ligand and its complexes as inhibiting agents have been screened *in vitro* against two kinds of pathogenic bacteria and plant pathogenic fungi.

**Keywords:** Solvatochromism; Lewis-base indicators; Mixed ligand complexes; Antimicrobial activity

### 1. Introduction

Copper(II) mixed-ligand complexes are of interest as Lewis acid-base indicators [1–5]. These compounds are chromotropic, exhibiting color change when exposed to solvent or environmental pollutant molecules [6–8]. Solvatochromism of metal complexes can be divided into two types [9, 10]; the first from direct attachment of solvent to the metal and the second due to the attachment of solvent onto ligands. Among the former, whose color changes are due to d-d transitions, copper(II) complexes with a strong Jahn-Teller effect can be anticipated to show simple and regular changes in their electronic spectra according to the strength of interactions with solvent

\*Corresponding author. Email: wlinert@mail.zserv.tuwien.ac.at



Scheme 1.  $\text{Cu}(3\text{-ACoum})(\text{L})\text{X}_n$ , where,  $\text{X} = \text{CClO}_4^-, \text{BF}_4^-, \text{NO}_3^-$ ,  $n=2$  and  $\text{N}\sim\text{N} = (\text{tmen}), (\text{phen})$  or  $(\text{bipy})$ .

molecules at the axial sites [11, 12]. In continuation of these studies, we have synthesized new mixed ligand complexes,  $\text{Cu}(3\text{-ACoum})(\text{L})\text{X}_n$ ; where  $n=2$ ,  $\text{L} = \text{N},\text{N},\text{N}',\text{N}'\text{-tetramethylethylenediamine (tmen), 1,10-phenanthroline (phen) and 2,2'-bipyridine (bipy) and } \text{X} = \text{ClO}_4^-, \text{BF}_4^- \text{ or } \text{NO}_3^-$  (scheme 1). The effect of the anion solvents on these chelates have been investigated. TGA-DTA analyses suggest good stability for most complexes followed by thermal decomposition in different steps. The kinetic parameters, namely enthalpy,  $\Delta H^\ddagger$ , entropy,  $\Delta S^\ddagger$ , and activation energy  $\Delta G^\ddagger$ , have been calculated using the Coats–Redfern method [13] (Supplementary Material). Furthermore 3-acetylcoumarin and its transition metal complexes are screened for antibacterial activity against *Escherichia coli* and *Azotobacter* as growth inhibitors by disc diffusion technique and for fungal activity against *Aspergillus niger* and *Fusarium oxysporum*.

## 2. Experimental

### 2.1. Materials

All chemicals were of analytical reagent grade and obtained from Merck or Aldrich and used without purification. Solvents used for spectral studies, nitromethane ( $\text{MeNO}_2$ ), acetonitrile ( $\text{MeCN}$ ), acetone ( $\text{Me}_2\text{CO}$ ), methanol ( $\text{MeOH}$ ), dimethyl formamide (DMF), and dimethyl sulfoxide (DMSO), were of Merck or BDH grade and further purified using standard methods [14].

### 2.2. Physical measurements

Carbon, hydrogen and nitrogen contents were analyzed using a Perkin–Elmer 2400 series II analyzer. Fourier transform infra red (FTIR) spectra ( $4000\text{--}400\text{ cm}^{-1}$ ) of the compounds in KBr pellets, in the  $4000\text{--}400\text{ cm}^{-1}$  range, were obtained with a Perkin–Elmer FTIR model 8101 spectrometer. Metal analysis was carried out on a Perkin–Elmer 238 atomic absorption spectrometer (AAS). Electronic spectra were recorded on a UV-3100 PC Perkin–Elmer spectrophotometer using 10 mm quartz cells at room temperature. Electron spin resonance (ESR) spectra were obtained on a Bruker EMX spectrometer working in the X band (9.78 GHz) with 100 kHz modulation frequency. The microwave power was set to 1 mW and the modulation amplitude was set to 4 G. Molar conductivities at  $25^\circ\text{C}$  were measured for solutions of the complexes in DMF with a Metrohm 660 conductivity bridge. Magnetic moments of the complexes were obtained using a magnetic susceptibility balance (Johnson Matthey Alfa product;

Model No. MKI). Thermal studies were carried out on a Shimadzu thermogravimetric analyzer at a heating rate of  $20^{\circ}\text{C min}^{-1}$  under nitrogen gas.

### 2.3. Syntheses of metal complexes

These complexes were prepared by adding a mixture of 0.700 g (3.719 mmol) of 3-acetylcoumarine (3-ACoum) and solid anhydrous  $\text{Na}_2\text{CO}_3$  (0.394 g, 3.719 mmol) in 25 mL absolute ethanol to a solution of 3.719 mmol of  $\text{CuX}_2 \cdot n\text{H}_2\text{O}$  in 25 mL ethanol ( $X = \text{ClO}_4^-$ ,  $\text{NO}_3^-$  or  $\text{BF}_4^-$ ). The mixture was continuously stirred for 30 min and the precipitate was filtered. Then a solution of 0.394 g, 3.719 mmol of diamine in 10 mL ethanol was added dropwise to the filtrate under continuous stirring for an additional 30 min. The resulting solution was filtered and left to stand overnight. The formed complexes were filtered off and recrystallized from dichloromethane. For  $\text{Cu}(3\text{-ACoum})(\text{L})\text{X}_n$  with  $\text{L} = 1,10\text{-phenanthroline (phen)}$  and  $2,2'\text{-bipyridine (bipy)}$  and  $X = \text{ClO}_4^-$ ,  $\text{BF}_4^-$  or  $\text{NO}_3^-$ , precipitates were formed during addition of  $\text{L}$ .

**2.3.1. Synthesis of  $[\text{Cu}(3\text{-ACoum})(\text{tmen})](\text{ClO}_4)_2$ .** The complex was prepared by adding a mixture of 0.700 g (3.719 mmol) of 3-acetylcoumarine (3-ACoum) and solid anhydrous  $\text{Na}_2\text{CO}_3$  (0.394 g, 3.719 mmol) in 20 mL ethyl alcohol solution to 1.378 g, 3.719 mmol of  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  in 25 mL ethanol. The mixture was continuously stirred for 30 min resulting in a green solution, which was then filtered to remove sodium carbonate. A solution (0.432 g, 3.719 mmol) of  $N,N,N',N'$ -tetramethylethylenediamine (tmen), in 10 mL ethanol was added dropwise to the filtrate with continuous stirring for an additional 30 min. The resulting solution was left to stand overnight. The complexes were recrystallized from dichloromethane. Violet crystals formed. The yield was 63.81% and the decomposition point was  $250^{\circ}\text{C}$ .

**2.3.2. Synthesis of  $[\text{Cu}(3\text{-ACoum})(\text{phen})](\text{BF}_4)_2$ .** The complex was prepared by adding a mixture of 0.700 g, 3.719 mmol of 3-acetylcoumarine, (3-ACoum) in 20 mL absolute ethanol and solid anhydrous  $\text{Na}_2\text{CO}_3$ , (0.502 g, 3.719 mmol) to 0.949 g, 3.719 mmol, of  $\text{Cu}(\text{BF}_4)_2 \cdot \text{H}_2\text{O}$  in 25 mL ethanol. The mixture was continuously stirred for 30 min resulting in a green solution which was then filtered to remove sodium carbonate and a solution of 0.737 g (3.719 mmol) of 1,10-phenanthroline (phen), in 10 mL ethanol was added dropwise to the filtrate with continuous stirring for an additional 30 min. The resulting solution was filtered and left to stand overnight. A bluish violet precipitate formed, was filtered off and left to stand overnight. Violet crystals were formed in 74.16%; the decomposition point was  $250^{\circ}\text{C}$ .

### 2.4. Spectral measurements

Electronic spectra of the complexes were recorded at room temperature with a two-beam UV-3100 PC Perkin-Elmer spectrophotometer using 10 mm quartz cells at room temperature in the range of 250–900 nm using 1,2-dichloroethane as solvent. The sample solutions were prepared by mixing 2 mL of 1,2-dichloroethane solution of the chelate (5 mmol) and 1 mL of donor solvent; the measurements were carried out in such mixed solvent systems [15].

### 3. Results and discussion

The analytical and physicochemical data are given in table 1. Elemental analyses confirm the proposed formula,  $\text{Cu}(3\text{-ACoum})(\text{L})\text{X}_n$ ; where  $n=2$ ,  $\text{L} = N,N,N',N'$ -tetramethylethylenediamine (tmen), 1,10-phenanthroline (phen) and 2,2'-bipyridine (bipy) and  $\text{X} = \text{ClO}_4^-$ ,  $\text{BF}_4^-$ , or  $\text{NO}_3^-$ . The obtained complexes are either violet, green, or blue crystals. The molar conductivity values in DMF are in the expected range for 1:2 electrolytes. Magnetic moment data are found in the range corresponding to four- or five-coordinate Cu(II) complexes.

#### 3.1. Infrared spectra

The absorption frequencies and their assignments are listed in table 2. The free ligand showed two strong bands at 1727 and  $1686\text{ cm}^{-1}$  which are assigned to overlap the stretching frequencies of the  $\nu(\text{C}=\text{C})$  and the two carbonyl groups. These bands shift to lower frequencies compared to the free ligand on coordination, suggesting involvement of the carbonyl group in coordination. The coordination behaviors of  $\text{BF}_4^-$ ,  $\text{ClO}_4^-$ , and  $\text{NO}_3^-$  have been investigated from the infrared spectra. Perchlorate complexes **1**, **2**, and **3** show two sharp stretching vibrational bands in the range  $1125\text{--}1100\text{ cm}^{-1}$  and  $620\text{--}633\text{ cm}^{-1}$ , corresponding to antisymmetric stretching and bending vibrations of perchlorate, indicating that it is not coordinated [16, 17]. Tetrafluoroborate complexes show similar behavior with  $\text{BF}_4^-$  not coordinated to the metal [18, 19]. The absence of splitting for tetrafluoroborate around  $1100\text{ cm}^{-1}$  for all the complexes [20] and the presence of stretching vibrations in the range  $1044\text{--}1023\text{ cm}^{-1}$  indicates uncoordinated  $\text{BF}_4^-$  [21]. The  $\text{NO}_3^-$  ions are coordinated to the metal in **7**,  $[\text{Cu}(3\text{-ACoum})(\text{tmen})(\text{NO}_3)](\text{NO}_3)$ , as unidentate with  $\text{C}_{2v}$  symmetry. Each unidentate nitrate possesses three non-degenerate modes of vibrations ( $\nu_s$ ,  $\nu'_s$ , and  $\nu_{\text{as}}$ ) at 1430, 1234, and  $1064\text{ cm}^{-1}$ , respectively [22]. The non-coordinated nitrates show a very strong band around  $1385\text{ cm}^{-1}$ , similar to other complexes [20, 23–25]. Nitrate complexes, **8**  $[\text{Cu}(3\text{-ACoum})(\text{phen})](\text{NO}_3)_2$  and **9**  $[\text{Cu}(3\text{-ACoum})(\text{bipy})](\text{NO}_3)_2$ , display strong stretching vibrations at 1386 and  $1380\text{ cm}^{-1}$ , respectively, for ionic  $\text{NO}_3^-$  [26]. New bands in all complexes located at  $498\text{--}565\text{ cm}^{-1}$  and  $434\text{--}458\text{ cm}^{-1}$  can be assigned to  $\nu(\text{M}\text{--}\text{O})$  and  $\nu(\text{M}\text{--}\text{N})$ , respectively, which are absent in the IR spectra of the free ligands [22].

#### 3.2. Solvatochromism of the mixed chelates

Absorption spectra of complexes were measured in organic solvents with different donor numbers (DN) [27] which can be related to the Lewis basicity of the solvent molecules. Complexes **1**, **4**, and **7** are soluble in most organic solvents. The high solubility of these complexes in various solvents and the change in color yields solvatochromism of their solutions. Complexes **2**, **3**, **5**, **6**, **8**, and **9** are sparingly soluble in most organic solvents. The absorption spectra in DMF show only one broad band in the visible region (table 1).

Figure 1 shows the visible absorption spectra of  $[\text{Cu}(3\text{-ACoum})(\text{tmen})]\text{ClO}_4$  in a number of solvents. The complex exhibits violet solutions in solvents of low DN (Guatman's donor number) [28, 29] and change from blue to green as the solvent donor

Table 1. Physicochemical properties of Cu(3-A-Coum)(L)<sub>n</sub>.

	Complex	Molecular formula	M. Wt.	Yield	Color	$(\Delta^a)$	$\mu_{\text{eff}}^b$	$\nu_{\text{max}}/10^3$ (cm <sup>-1</sup> )	Elemental analysis; Calcd (Found)		
									% C	% H	% N
(1)	[Cu(3-A-Coum)(tmen)](ClO <sub>4</sub> ) <sub>2</sub>	C <sub>17</sub> H <sub>24</sub> N <sub>2</sub> O <sub>11</sub> Cl <sub>2</sub> Cu	566.836	(63.81)	Violet	159	1.57	16.02	36.02 (35.60)	4.26 (4.17)	4.94 (4.96)
(2)	[Cu(3-A-Coum)(phen)](ClO <sub>4</sub> ) <sub>2</sub>	C <sub>23</sub> H <sub>16</sub> N <sub>2</sub> O <sub>11</sub> Cl <sub>2</sub> Cu	630.838	(59.30)	Violet	131	1.72	15.12	43.79 (43.12)	2.55 (2.68)	4.44 (4.62)
(3)	[Cu(3-A-Coum)(bipy)](ClO <sub>4</sub> ) <sub>2</sub>	C <sub>21</sub> H <sub>16</sub> N <sub>2</sub> O <sub>11</sub> Cl <sub>2</sub> Cu	606.816	(54.35)	Violet	145	1.62	15.56	41.56 (42.12)	2.65 (2.89)	4.61 (4.53)
(4)	[Cu(3-A-Coum)(tmen)](BF <sub>4</sub> ) <sub>2</sub>	C <sub>17</sub> H <sub>24</sub> N <sub>2</sub> O <sub>3</sub> B <sub>2</sub> F <sub>8</sub> Cu	541.542	(66.34)	Violet	156	1.63	16.18	37.70 (38.12)	4.46 (4.04)	5.17 (5.53)
(5)	[Cu(3-A-Coum)(phen)](BF <sub>4</sub> ) <sub>2</sub>	C <sub>23</sub> H <sub>16</sub> N <sub>2</sub> O <sub>3</sub> B <sub>2</sub> F <sub>8</sub> Cu	605.544	(74.12)	Violet	179	1.97	15.87	45.62 (44.92)	2.66 (2.73)	4.62 (4.55)
(6)	[Cu(3-A-Coum)(bipy)](BF <sub>4</sub> ) <sub>2</sub>	C <sub>21</sub> H <sub>16</sub> N <sub>2</sub> O <sub>3</sub> B <sub>2</sub> F <sub>8</sub> Cu	581.522	(81.81)	Violet	164	1.68	16.27	43.37 (43.48)	2.77 (2.63)	4.81 (4.93)
(7)	[Cu(3-A-Coum)(tmen)(NO <sub>3</sub> )]	C <sub>17</sub> H <sub>24</sub> N <sub>4</sub> O <sub>9</sub> Cu	491.900	(63.45)	Reddish -blue	143	1.85	15.79	41.50 (41.82)	4.91 (4.25)	11.38 (11.29)
(8)	[Cu(3-A-Coum)(phen)](NO <sub>3</sub> ) <sub>2</sub>	C <sub>23</sub> H <sub>16</sub> N <sub>4</sub> O <sub>9</sub> Cu	555.948	(52.63)	Dark blue	136	1.69	15.83	49.69 (50.42)	2.90 (2.71)	10.07 (10.15)
(9)	[Cu(3-A-Coum)(bipy)](NO <sub>3</sub> ) <sub>2</sub>	C <sub>21</sub> H <sub>16</sub> N <sub>4</sub> O <sub>9</sub> Cu	531.926	(62.24)	Dark blue	115	1.81	15.09	47.41 (46.81)	3.03 (2.82)	10.53 (9.89)

Notes: <sup>a</sup>Molar conductance ( $\Delta$ ), (cm<sup>2</sup>mol<sup>-1</sup>) was measured in 10<sup>-4</sup> mol<sup>-1</sup> cm<sup>-1</sup> in DMF solvent.<sup>b</sup>Magnetic moment,  $\mu_{\text{comp}}$  (B.M.).

Table 2. Infrared frequencies of the characteristic bands of Cu(II) complexes.

	Complex	$\nu(\text{C}=\text{O})$ & $\nu(\text{C}=\text{C})$	Stretching vibration of the anions				$\nu(\text{M}-\text{O})$	$\nu(\text{M}-\text{N})$
			$\nu(\text{ClO}_4^-)$	$\nu(\text{BF}_4^-)$	$\nu(\text{NO}_3^-)$			
1	[Cu(3-A Coum)(tmen)](ClO <sub>4</sub> ) <sub>2</sub>	1717 s 1677 s	1100 s, 620 s	—	—	518 m	457 w	
2	[Cu(3-A Coum)(Phen)](ClO <sub>4</sub> ) <sub>2</sub>	1711 s 1629 s	1114 s, 633 s	—	—	525 m	435 w	
3	[Cu(3-A Coum)(bipy)](ClO <sub>4</sub> ) <sub>2</sub>	1621 s 1603 s	1125 s, 625 s	—	—	545 w	458 w	
4	[Cu(3-A Coum)(tmen)](BF <sub>4</sub> ) <sub>2</sub>	1619 s 1600 s	—	1034 s	—	498 w	446 w	
5	[Cu(3-A Coum)(phen)](BF <sub>4</sub> ) <sub>2</sub>	1611 s 1596 s	—	1023 s	—	565 m	452 w	
6	[Cu(3-A Coum)(bipy)](BF <sub>4</sub> ) <sub>2</sub>	1614 s 1600 s	—	1044 s	—	510 m	445 w	
7	[Cu(3-A Coum)(tmen)(NO <sub>3</sub> )](NO <sub>3</sub> )	1620 s	—	—	1430 s, 1234 m, 1064 m, 1385 s	513 w	448 w	
8	[Cu(3-A Coum)(phen)](NO <sub>3</sub> ) <sub>2</sub>	1631 s	—	—	1386 s	505 m	474 w	
9	[Cu(3-A Coum)(bipy)](NO <sub>3</sub> ) <sub>2</sub>	1626 s	—	—	1380 s	487 w	434 w	

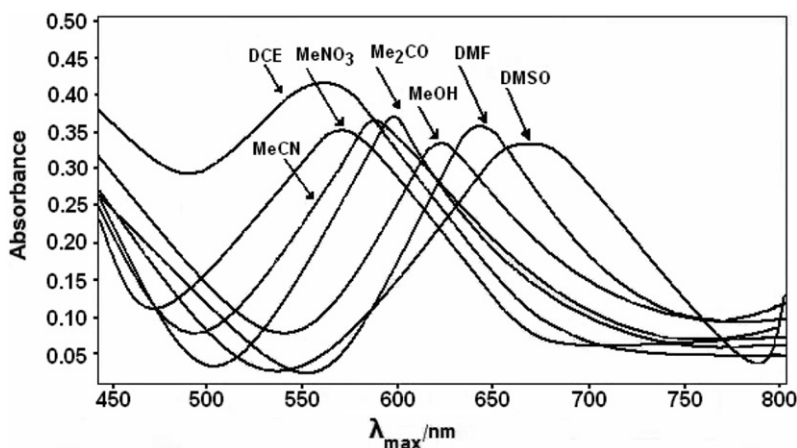


Figure 1. Electronic absorption spectra of (1)  $[\text{Cu}(3\text{-ACoum})(\text{tmen})](\text{ClO}_4)_2$ , ( $4 \times 10^{-3} \text{ mol dm}^{-3}$ ) in DCE, MeCN, MeNO<sub>3</sub>, Me<sub>2</sub>CO, MeOH, DMF and DMSO.

Table 3. Absorption maxima of **1**, **4**, and **7** in various solvents.

Solvent	DN <sup>a</sup>	$(\lambda_{\text{max}}, \text{nm})^b, (\nu_{\text{max}}/10^3 \text{ (cm}^{-1}\text{)})^c$		
		(1) $[\text{Cu}(3\text{-ACoum})(\text{tmen})](\text{ClO}_4)_2$	(4) $[\text{Cu}(3\text{-ACoum})(\text{tmen})](\text{BF}_4)_2$	(7) $[\text{Cu}(3\text{-ACoum})(\text{tmen})(\text{NO}_3)](\text{NO}_3)$
<b>1</b> 1,2-Dichloromethane	0.00	554(18.05)	537(18.62)	605(16.26)
<b>2</b> Nitromethane	2.70	568(17.60)	548(18.24)	596(16.77)
<b>3</b> Acetonitrile	14.10	573(17.45)	563(17.76)	604(16.50)
<b>4</b> Acetone	17.00	578(17.30)	557(17.95)	611(16.66)
<b>5</b> Methyl alcohol	19.10	618(16.18)	600(16.66)	621(16.26)
<b>6</b> Dimethylformamide	26.60	622(16.02)	618(16.18)	633(15.79)
<b>7</b> Dimethylsulfoxide	29.80	658(15.19)	645(15.50)	641(15.60)

Notes: <sup>a</sup>Donor number of the solvent.

<sup>b</sup>Maximum absorption in nm.

<sup>c</sup>Referring to the wave number of the d-d transition bands of the complexes in reflectance spectrum.

number increases. The absorption spectra of **1** and **4** display only one broad band in methylene chloride at 568 and 537 nm, respectively, assigned to the  ${}^2B_{1g} \rightarrow {}^2B_{2g}$  transition of square-planar geometry. This band is shifted to longer wavenumber as the Lewis basicity of the solvent increases (table 3). The red shift is attributed to strong repulsion of the electron in  $d_{z^2}$  orbital by the lone pair electrons of the solvent axially coordinated to copper, decreasing the energy required to transfer the electrons to  $d_{x^2-y^2}$  [30]. Magnetic susceptibility measurements are 1.67 and 1.63 B.M., confirming the proposed geometry. The absorption spectra of **7** in weak donor solvents show  $\lambda_{\text{max}}$  at 615 nm, attributed to  ${}^2B_1 \rightarrow {}^2E_g, d_{x^2-y^2} \rightarrow d_{z^2}$ , corresponding to square-pyramidal structure. The values of the magnetic moment are in accord with previous results (1.68 B.M.) [31].

Absorption spectra of tetrafluoroborate complexes in different solvent solutions have lower  $\lambda_{\text{max}}$  than the corresponding perchlorate and nitrate complexes, attributed to gradual increase of the donor strength of the anion.



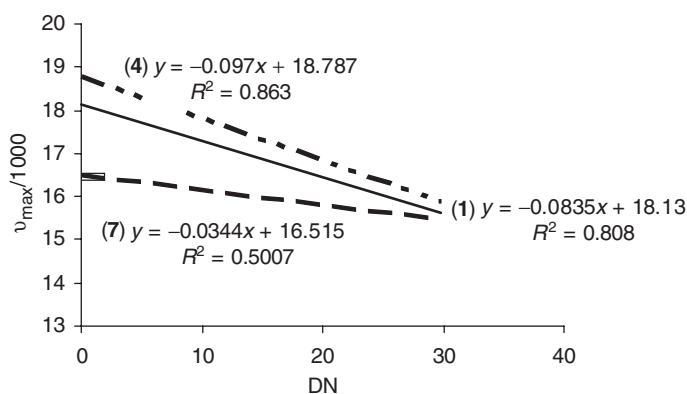


Figure 2. Solvation free energy relationship between the donor number (DN) and the maximum absorption  $\nu_{\max}/1000$ .

The solvatochromic behaviors for **1**, **4**, and **7** are studied by applying the linear solvation free energy relationship,  $\nu_{\max}/10^3 = \nu^{\circ} + a(\text{DN})$ ; where  $\nu_{\max}$  is the measured  $d-d$  absorption frequency,  $\nu^{\circ}$ , the extrapolated frequency, and  $a$ , the slope, representing the sensitivity of the complex towards solvent [27]. The  $\nu_{\max}$  decreases nearly linearly with increasing solvent ability. Linearity of the  $\nu_{\max}$  versus DN confirms the solvatochromic behavior and stabilization of the reactive complexes with Lewis bases (figure 2). The negative slope indicates that the strength of the Cu–O bond decreases as the donor strength of the coordinated anion increases. The slope value ( $a$ ) is in the order **4** =  $-0.097 < \text{(1)} = -0.083 < \text{(7)} = -0.034$ . Complex **4** has the lowest slope due to dinitrogen ligand causing a large steric hindrance to the axial coordination of the entering solvent, leading to less solvatochromism [8, 11]. From the conductivity values (table 1), it can be concluded that  $\text{ClO}_4^-$  and  $\text{BF}_4^-$  are counterions and do not interact with complex cation, and the structure only depends on the donor properties of the solvent; only solute–solvent interactions need be considered. The values of the nitrate complexes are higher than expected due to replacement of nitrate ions by dimethyl formamide. Conductivity measurements for all the complexes in DMF suggest ionic mixed chelates [32].

### 3.3. ESR spectroscopy

ESR spectra were recorded in the solid state at room temperature (25°C) with ‘ $g$ ’ values and spin Hamiltonian parameters. Kivelson and Neiman [33] reported  $g_{\parallel} < 2.3$  for covalent character of the metal–ligand bond and  $>2.3$  for ionic character. Applying this criterion the covalent character of the metal–ligand bond in the complexes under study can be predicted. The trend  $g_{\parallel} > g_{\perp} > 2.0023$  observed for **1** and **7** show that the unpaired electron is localized in  $d_{x^2-y^2}$  ground state characteristic of square planar, square pyramidal or octahedral geometry [34]. No band corresponding to  $\Delta m_s = \pm 2$  forbidden transition was observed in the spectra, ruling out Cu–Cu interaction and revealing that the complexes are mononuclear. In addition, exchange coupling interaction is explained by the Hathaway expression [35]; if the value of  $G$  is greater than 4, the exchange interaction in the solid state is negligible, whereas when it is less

Table 4. Thermal decomposition stages for **7**, **8**, and **9**.

Complex	Decomposition transitions	M.Wt	Temperature (°C)		Weight loss (%)	
			TGA	DrTGA	Calcd	Found
<b>(7)</b>	(I) [Cu(3-ACoum)(tmen)(NO <sub>3</sub> )] · (NO <sub>3</sub> ) → (-N <sub>2</sub> O <sub>5</sub> )	491.946	53–287	179	21.96	20.82
	(II)[Cu(3-ACoum)(tmen)] → (-2CH <sub>3</sub> + N <sub>2</sub> )		287–411	335	17.92	19.31
	(III)[Cu(3-ACoum)(C <sub>2</sub> H <sub>4</sub> )] → (-C <sub>2</sub> H <sub>4</sub> )		411–482	464	5.69	6.18
	(IV)[Cu(3-ACoum)] → (-3-ACoum) + [-CuO]		482–700	586	54.43	53.69
<b>(8)</b>	(I)[Cu(3-ACoum)(phen)] · (NO <sub>3</sub> ) <sub>2</sub> → (-N <sub>2</sub> O <sub>5</sub> )	555.948	38–245	228	19.43	20.21
	(II)[Cu(3-ACoum)(phen)] → (-C <sub>12</sub> H <sub>8</sub> N <sub>2</sub> )		245–428	410	32.42	32.89
	(III)[Cu(3-ACoum)] → (-3-ACoum)		238–560	–	33.84	31.21
	(IV)[CuO]		560–700	–	14.31	15.68
<b>(9)</b>	(I)[Cu(3-ACoum)(bipy)] · (NO <sub>3</sub> ) <sub>2</sub> → (-N <sub>2</sub> O <sub>5</sub> )	531.926	46–266	234	20.31	21.75
	(II)[Cu(3-ACoum)(C <sub>10</sub> H <sub>8</sub> N <sub>2</sub> )] → (-C <sub>5</sub> H <sub>4</sub> N)		266–423	410	29.36	28.70
	(IV)[Cu(3-ACoum)] → (-3-ACoum)		423–572	526	35.37	34.35
	(V)[CuO]		572–700	–	14.96	15.14

than 4, considerable exchange interaction is present, [ $G = (g_{\parallel} - 2)/(g_{\perp} - 2)$ ]. ESR spectra are typical for square planar **1**, ( $g_{\parallel} = 2.28$ ,  $g_{\perp} = 2.06$ , and  $G = 4.66$ ) [36] (Supplemental Material), and square pyramidal for **7**, ( $g_{\parallel} = 2.14$ ,  $g = 2.04$ , and  $G = 3.5$ ) [37, 20] (Supplemental Material).

### 3.4. Thermogravimetric study

All the nitrate complexes **7**, **8**, and **9** are thermally investigated by TGA-DTA analysis and their degradation schemes presented in table 4. The thermograms show complete decomposition at 700°C. TGA displays mainly three features (Supplemental Material). The first assigned to the loss of N<sub>2</sub>O<sub>5</sub> gas is due to loss of nitrate. The second stage can be ascribed to loss of the dibasic amine as endothermic peaks. The last feature of the TGA is the removal of 3-acetylcoumarin followed by complete decomposition of the complex and formation of the metal oxide as a residue.

### 3.5. Biological activities

Several studies report the inhibitory activity of ligands and their complexes against pathogenic bacteria and plant pathogenic fungi [38–40]. 3-Acetylcoumarin and complexes have been screened for antibacterial activity against *E. coli* and *Azotobacter*, and for fungal activity against *A. niger* and *F. oxysporium* [41–45], using standard methods [46, 47]. The results are summarized in table 5. Mixed complexes have higher inhibition capacity than the ligand, [figure 3(a) and (b)]. This enhancement can be rationalized on the basis of their structures possessing an addition C=N bond. Coordination reduces the polarity of the metal ion by partial sharing of its positive charge with donor groups and possibly the  $\pi$ -electron delocalization within the whole chelate ring system [48]. Thus, chelation increases the lipophilic nature of the central metal atom, which in turn favors its permeation through the lipid layer of the membrane of the microorganisms cell wall, raising the activity of the drug [49].

Table 5. Antibacterial activity and antifungal activity of the ligand and complexes.

Item	Compound	% Zone diameter showing complete growth inhibition			
		Antibacterial activity		Antifungal activity	
		<i>Escherichia coli</i>	<i>Azotobacter</i>	<i>Aspergillus niger</i>	<i>Fusarium oxysporium</i>
(1)	3-Acetylcoumarine, (3-ACoum)	64	34	47	56
(2)	[Cu(3-ACoum)(tmen)](ClO <sub>4</sub> ) <sub>2</sub>	68	54	57	76
(3)	[Cu(3-ACoum)(phen)](ClO <sub>4</sub> ) <sub>2</sub>	74	47	80	60
(4)	[Cu(3-ACoum)(bipy)](ClO <sub>4</sub> ) <sub>2</sub>	82	53	65	87
(5)	[Cu(3-ACoum)(tmen)](BF <sub>4</sub> ) <sub>2</sub>	73	41	55	64
(6)	Cu(3-ACoum)(phen)](BF <sub>4</sub> ) <sub>2</sub>	75	42	49	74
(7)	[Cu(3-ACoum)(bipy)](BF <sub>4</sub> ) <sub>2</sub>	68	39	56	64
(8)	[Cu(3-ACoum)(tmen)(NO <sub>3</sub> )](NO <sub>3</sub> )	73	57	86	61
(9)	[Cu(3-ACoum)(phen)](NO <sub>3</sub> ) <sub>2</sub>	77	58	65	76
(10)	[Cu(3-ACoum)(bipy)](NO <sub>3</sub> ) <sub>2</sub>	74	54	57	78

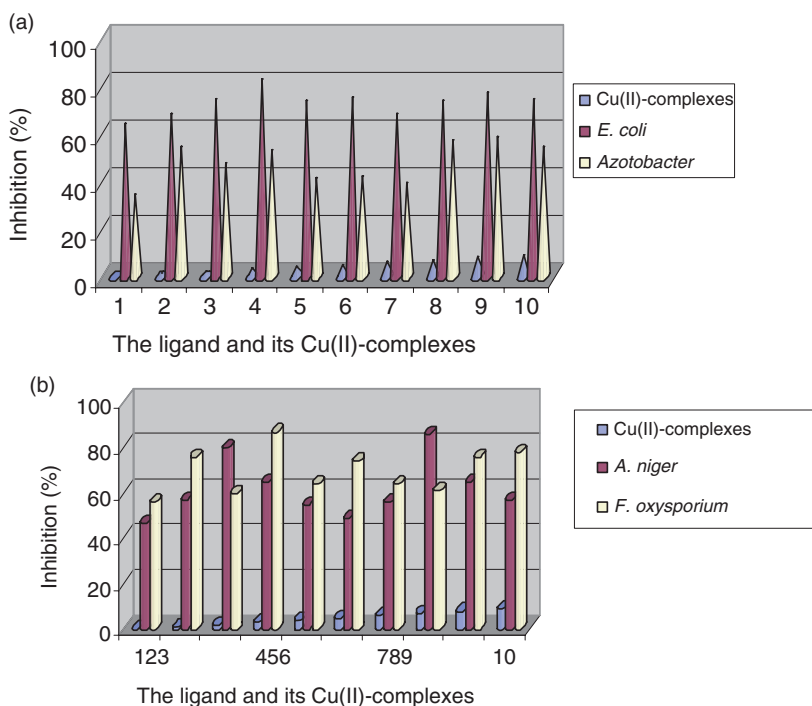


Figure 3. Biological screening of the ligand and its Cu(II) complexes against (a) bacteria and (b) fungi.

#### 4. Conclusion

This study prepared new 3-acetylcoumarin-tmen-copper(II) complexes with solvatochromism due to the donor property of various solvents. The absorption bands in weak donor solvents show the formation of square planar or square pyramidal geometries, while strong donor solvents yield octahedral complexes. TGA-DTA analyses suggest

high stability for the complexes. 3-Acetylcoumarin and their transition metal complexes show inhibitory activity against pathogenic bacteria (*E. coli* and *Azotobacter*) and plant pathogenic fungi (*A. niger* and *F. oxysporium*).

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