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# Thermal, spectroscopic, and solvent influence studies on mixed-ligand copper(II) complexes containing the bulky ligand: Bis[N-(p-tolyl)imino]acenaphthene

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# Abstract

Four mixed-ligand copper(II) complexes containing the rigid bidentate nitrogen ligand bis[*N*-(*p*-tolyl)imino]acenaphthene (abb. *p*-Tol-BIAN) ligand are reported. These complexes, namely [Cu(*p*-Tol-BIAN)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> **1**, [Cu(*p*-Tol-BIAN)(acac)](ClO<sub>4</sub>) **2**, [Cu(*p*-Tol-BIAN)Cl<sub>2</sub>] **3** and [Cu(*p*-Tol-BIAN)(AcOH)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> **4** (where acac, acetylacetonate and AcOH, acetic acid) have been prepared and characterized by elemental analysis, spectroscopic, magnetic and molar conductance measurements. ESR spectra suggest a square planar geometry for complexes **1** and **2**. In complexes **3** and **4**, a distorted tetrahedral arrangement around copper(II) centre was suggested. Solvatochromic behavior of all studied complexes indicates strong solvatochromism of their solutions. The observed solvatochromism is mainly due to the solute–solvent interaction between the chelate cation and the solvent molecules. Thermal properties and decomposition kinetics of all complexes are investigated. The kinetic parameters (*E*, *A*,  $\Delta H$ ,  $\Delta S$  and  $\Delta G$ ) of all thermal decomposition stages have been calculated using the Coats–Redfern and other standard equations. (© 2006 Elsevier B.V. All rights reserved.

Keywords: Mixed-ligand copper(II) complexes; Thermal analysis; Spectroscopic

# 1. Introduction

Mixed-ligand complexes are observed in biological systems or in the intermediate chemical reactions with metal ions, which is important to understand the respective chemistry. Investigations concerning diimine mixed-ligand chelate systems have a great help toward understanding the driving forces that led to the formation of such mixed-ligand complexes [1-3].

Solvatochromism in the mixed-ligand metal complexes has received great attention because they may be used as a Lewis acid–base color indicators [4] and also utilizes to develop optical sensor materials to monitor pollutant levels in the environment [5]. Extensive studies have been focused on mixed-ligand copper(II) complexes containing  $\beta$ -diketonates (dike) and *N*-alkylated diamines (diam) of the general formula [Cu(dike)(diam)]X (X is an univalent anion, such as ClO<sub>4</sub><sup>-</sup>,

 $NO_3^-$  or a halogen) [6–10]. Solvatatochromism depends mainly on the: (i) the more or less pronounced coordination of solvent molecules to the complex and (ii) the more or less pronounced coordination of anions (X<sup>-</sup>) to the complex. Both forms of coordination lead to significant changes in the d–d transitions and to a strong change in the color of the complexes in solution. The former effect is governed by the donor strength of the respective solvent molecules and, in fact, the observed solvatochromism can be used to visualize and to measure donor properties of solvents and even solvent mixtures.

In the present work, we report the syntheses, spectral, thermal and solvatochromic behavior of four mixed-ligand copper(II) complexes containing the bidentate nitrogen ligand bis[*N*-(*p*-tolyl)imino]acenaphthene (Fig. 1). These complexes, namely [Cu(*p*-Tol-BIAN)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> **1**, [Cu(*p*-Tol-BIAN)(acac)](ClO<sub>4</sub>) **2**, [Cu(*p*-Tol-BIAN)Cl<sub>2</sub>] **3** and [Cu(*p*-Tol-BIAN)(AcOH)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> **4**. The kinetic parameters, such as the reaction order, *n*, the activation energy, *E* and the pre-exponential factor, *A* have been determined using Coats–Redfern method [11]. The other kinetic parameters, namely enthalpy,  $\Delta H$ , entropy,  $\Delta S$ , and activation energy,  $\Delta G$ , have been calculated using the standard equations.

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Fig. 1. Bis[N-(p-tolyl)imino]acenaphthene (p-Tol-BIAN).

# 2. Experimental

#### 2.1. Instrumentation and materials

All starting materials were purchased from Wako Pure Chemical Industries Ltd., and used without further purification. Elemental analyses (C, H, N) were performed on a Perkin-Elmer 2400 Series II Analyzer. Electronic spectra were recorded on a UV-UNICAM 2001 spectrophotometer using 10 mm pass length quartz cells at room temperature. Magnetic susceptibility was measured with a Sherwood Scientific magnetic susceptibility balance at 297 K. Infrared spectra were recorded on a Perkin-Elmer FT-IR Spectrometer 2000 as KBr pellets and as Nujol mulls in the 4000–370 cm<sup>-1</sup> spectral range. <sup>1</sup>H and <sup>13</sup>C NMR measurements at room temperature were obtained on a Jeol JNM LA 300 WB spectrometer at 400 MHz, using a 5 mm probe head in CDCl<sub>3</sub>. Chemical shifts are given in ppm relative to internal TMS (tetramethylsilane).

ESR spectrum was obtained on a Bruker EMX spectrometer working in the X-band (9.78 GHz) with 100 kHz modulation frequency. The microwave power was set at 1 mW and modulation amplitude was set at 4 G. The low field signal was obtained after four scans with a 10-fold increase in the receiver gain. A powder spectrum was obtained in a 2 mm quartz capillary at room temperature.

# 2.2. Synthesis of bis[N-(p-tolyl)imino]acenaphthene (p-Tol-BIAN)

Preparation of the ligand was carried out in two steps (Fig. 2) similarly as reported earlier [12] with the very similar bis[*N*-(2,4,6-trimethylphenyl)imino]acenaphthene.

Yield: 3.50 g (72%) of (*p*-Tol-BIAN) (360.45). Found: C, 86.60; H, 5.50; N, 7.66. Calcd. for  $C_{26}H_{20}N_2$  (360.45): C, 86.64; H, 5.59; N, 7.77%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, recorded at 400 MHz at 23.6 °C)  $\delta$  = 2.44 (s, *p*-Me), 6.92 (d, H3), 7.03 (d, H9), 7.26 (d, H10), 7.37 (pst, H4), 7.86 (d, H5). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 400 MHz, 24.5 °C):  $\delta$  = 21.06 (*p*-Me), 161.06 (C1), 128.49 (C2), 123.68 (C3), 127.38 (C4), 128.62 (C5), 131.0 (C6), 141.49 (C7), 149.0 (C8), 118.04 (C9, C13), 129.77 (C10, C12), 133.68 (C11).

#### 2.3. Synthesis of metal complexes

Mixed-ligand copper complexes were prepared by adding the appropriate amount of copper perchlorate or copper chloride (in case of 3) to an ethanolic solution of the *p*-Tol-BIAN ligand. To this mixture acac (in case of 2) or AcOH (in case of 4) was added. The mixtures were stirred (while heating) for 1-3 h. The resulting green solid product was filtered, washed with ethanol and dried in air.

Yield: 0.20 g (80.0%) of  $[Cu(p-Tol-BIAN)_2](ClO_4)_2$  (1, C<sub>52</sub>H<sub>40</sub>Cl<sub>2</sub>CuN<sub>4</sub>O<sub>8</sub>) (983.35): calcd. C 63.51, H 4.10, N 5.69%; found C 62.28%, H 4.15%, N 5.44%. Magnetic moment  $\mu_{eff}/\mu_{BM} = 1.39$  at 297 K.

0.25 g (74.0%) of [Cu(*p*-Tol-BIAN)(acac)](ClO<sub>4</sub>) (**2**,C<sub>31</sub>H<sub>28</sub>ClCuN<sub>2</sub>O<sub>6</sub>) (623.56): calcd. C 59.71%, H 4.53%, N 4.49%; found C 60.07%, H 4.54%, N 4.27%. Magnetic moment  $\mu_{eff}/\mu_{BM} = 1.56$  at 297 K.

0.25 g (74.0%) of [Cu(*p*-Tol-BIAN)Cl<sub>2</sub>], (3, C<sub>26</sub>H<sub>20</sub> Cl<sub>2</sub>CuN<sub>2</sub>) (494.9): calcd. C 63.10, H 4.10, N 5.66%; found C 62.47%, H 4.24%, N 5.27%. Magnetic moment  $\mu_{eff}/\mu_{BM}$  = 1.88 at 297 K.

0.25 g (74.0 of  $[Cu(p-Tol-BIAN)(AcOH)_2](ClO_4)_2$  (4, C<sub>30</sub>H<sub>28</sub>Cl<sub>2</sub>Cu N<sub>2</sub>O<sub>12</sub>) (743.0): calcd. C 48.5, H 3.8, N 3.77%; found C 48.1%, H 3.66%, N 3.6%. Magnetic moment  $\mu_{eff}/\mu_{BM} = 1.98$  at 297 K.

#### 3. Results and discussion

#### 3.1. IR spectra of ligand and the complexes

Infrared spectral data for the free *p*-Tol-BIAN ligand and complexes **1–4** are listed in Table 1. Formation of the free *p*-Tol-BIAN ligand can be concluded from the IR spectroscopy where only C=N stretching vibrations were observed in the 1630–1675 cm<sup>-1</sup> range and no C=O stretching vibrations of



Fig. 2. Preparation of (p-Tol-BIAN) ligand.

Table 1	
Electrical conductivity data $(\Lambda_m)$ and infrared data $(cm^{-1})$	of complexes 1-4

Compound		$\Lambda_{\rm m}~(\Omega^{-1})$	$\Lambda_{\rm m}  (\Omega^{-1} {\rm cm}^2  {\rm mol}^{-1})$			$IR (cm^{-1})$	
Empirical formula	F Wt	AN	NM	ν (C=N)	v (ClO <sub>4</sub> <sup>-</sup> )	$\nu$ (AcOH)	
p-Tol-BIAN	360.45			1675, 1657, 1630			
$[Cu(p-Tol-BIAN)_2](ClO_4)_2$ (1)		330	192	1652, 1622	1090, 623		
$C_{52}H_{40}Cl_2Cu N_4O_8$	983.35						
$[Cu(p-Tol-BIAN)(acac)](ClO_4)$ (2)		180	100	1652, 1635	1102, 623		
$C_{31}H_{28}ClCuN_2O_6$	623.56						
$[Cu(p-Tol-BIAN)Cl_2]$ (3)		25	5	1667, 1624		1751, 1719	
$C_{26}H_{20}$ $Cl_2CuN_2$	494.9						
$[Cu(p-Tol-BIAN)(AcOH)_2](ClO_4)_2$ (4)		320	188	1675, 1652	1123, 624		
$C_{30}H_{28}Cl_2Cu N_2O_{12}$	743.0						

the starting diketones in the 1700–1800 cm<sup>-1</sup> region. Bands assigned to  $\nu$  (C=N) are shifted to lower wavenumbers in complex spectra indicating the coordination of both diimine nitrogen atoms of *p*-Tol-BIAN ligand to the copper ion.

Strong band observed at  $\sim 1100 \text{ cm}^{-1}$  (antisymmetric stretch) and the sharp band at  $\sim 620 \text{ cm}^{-1}$  (antisymmetric bend), suggest uncoordinated perchlorate anion [13] in complexes 1, 2 and 4 (Table 1).

Infrared spectroscopic data (Table 2) suggest the coordination of (acac) ligand to the copper(II) centre in **2** [14].

Generally, it is known that the aromatic rings with three adjacent carbon-hydrogen bonds show strong bands in the  $810-750 \text{ cm}^{-1}$  region due to out-of-plane CH deformation vibrations [15]. Their position is determined almost wholly by their location on the ring rather than by the nature of the substituent and, with certain limitations, they provide an excellent method for recognition of the type of substitution. The very high intensity and sensitivity of these characteristic bands in this region make them particularly well suited for quantitative work, too. The splitting of these out-of-plane CH deformation vibrations bands in the  $850-750 \text{ cm}^{-1}$  region of the complex 1 can be considered as a sign of the coordination of two *p*-Tol-BIAN ligands to the copper(II) ion [16].

# 3.2. ESR spectroscopy

To obtain further information about the stereochemistry and the site of the metal ligand bonding and to determine the magnetic interaction in the metal complexes, ESR spectra of the complexes were recorded in the solid state. The spin Hamiltonian

Table 2								
Infrared l	band	positions	and	band	assignn	ients of	f comple	x 2

Band position (cm <sup>-1</sup> )	Assignment
464	$\nu$ (Cu–O) + $\nu$ (C–CH <sub>3</sub> )
555	Ring def. + $\nu$ (Cu–O)
660	$\nu$ (C–CH <sub>3</sub> ) + ring def. + $\nu$ (Cu–O)
933	$\nu(C=C) + \nu(C=O)$
1281	$\nu$ (C–CH <sub>3</sub> ) + $\nu$ (C=C)
1520	$\nu$ (C=C) + $\nu$ (C=O) combination
1583	

parameters of the complexes were calculated and are summarized in Table 3.

The room temperature solid state ESR spectra of all complexes (Fig. 3) are quite similar and exhibit an axially symmetric *g*-tensor parameters with  $g_{||} > g_{\perp} > 2.0023$  indicating that the copper site has a  $d_{x^2-y^2}$  ground-state characteristic of square planar, square base pyramidal, tetrahedral or octahedral geometry [17].

No band corresponding to the forbidden magnetic dipolar transition for the complexes are observed at half-field (ca. 1500 G, g = 4.0), ruling out any Cu–Cu interaction and indicating that the complexes are mono nuclear copper(II) complexes.



Fig. 3. Solid state X-band ESR spectra of complexes 1-4.

Complex	$g_{  }$	$G_{\perp}$	$A_{  } \times 10^{-4} \ (\mathrm{cm}^{-1})$	$g_{  }/A_{  }$	G	$\alpha^2$	$\beta^2$
$[Cu(p-Tol-BIAN)_2](ClO_4)_2$ (1)	2.25	2.04	178	126	6.25	0.78	0.73
$Cu(p-Tol-BIAN)(acac)](ClO_4)$ (2)	2.27	2.05	175	129	5.4	0.81	0.82
$Cu(p-Tol-BIAN)Cl_2$ ] (3)	2.38	2.08	170	140	4.75	0.92	0.99
$[Cu(p-Tol-BIAN)(AcOH)_2](ClO_4)_2$ (4)	2.35	2.06	165	142	5.8	0.87	0.99

Table 3ESR data of complexes at room temperature

In axial symmetry, the *g*-values are related by the expression,  $G = (g_{||} - 2)/(g_{\perp} - 2) = 4$ , which measures the exchange interaction between copper centers in the solid.

According to Hathaway [18,19], if the value of G is greater than four, the exchange interaction between copper(II) centers in the solid state is negligible, whereas when is less than four, a considerable exchange interaction is indicated in the solid complex. The calculated G values are given in Table 3. The G values are greater than four suggesting that there are no copper–copper exchange interactions.

The tendency of  $A_{||}$  to decrease with an increase of  $g_{||}$  is an index of an increase of the tetrahedral distortion in the coordination sphere of copper [20,21]. In order to quantify the degree of distortion of the copper(II) complexes, we selected the  $\mathbf{f}$  factor  $g_{\parallel}/A_{\parallel}$  obtained from the ESR spectra. Although the **f** factor, which is considered an empirical index of tetrahedral distortion [22]. Its value ranges between 105 and 135 for square planar complexes, depending on the nature of the coordinated atoms. In the presence of a tetrahedrally distorted structure, the values can be much larger. For complexes 1 and 2, the  $g_{\parallel}/A_{\parallel}$  quotient are 126 and 129, evidence in support of the square planar geometry with no appreciable tetrahedral distortion. The ratio  $g_{\parallel}/A_{\parallel}$ for complexes 3 and 4 are 140 and 142 demonstrating the presence of significant dihedral angle distortion in the xy-plane and indicating a tetrahedral distortion from square planar geometry [23].

Superhyperfine structures for these complexes are not seen at higher fields excluding any interaction of the nuclear spins of the nitrogen (I=1) with the unpaired electron density on Cu(II) centre [24].

Molecular orbital coefficients,  $\alpha^2$  (a measure of the covalency of the in-plane  $\sigma$ -bonding between a copper 3d orbital and the ligand orbitals) and  $\beta^2$  (covalent in-plane  $\pi$ -bonding), were calculated by using the following equations [25–28], where  $\alpha^2 = 1$ indicates complete ionic character, whereas  $\alpha^2 = 0.5$  denotes 100% covalent bonding, with the assumption of negligibly small values of the overlap integral.

$$\alpha^{2} = \left(\frac{A_{\parallel}}{0.036}\right) + (g_{\parallel} - 2.0023) + \frac{3}{7(g_{\perp} - 2.0023)} + 0.04$$
$$\beta^{2} = -\frac{(g_{\parallel} - 2.0023)E}{8\lambda\alpha^{2}},$$

where  $\lambda = -828 \text{ cm}^{-1}$  for the free copper ion and *E* is the electronic transition energy. From Table 3, the  $\alpha^2$  and  $\beta^2$  values indicate that there is a substantial interaction in the inplane  $\sigma$ -bonding whereas the in-plane  $\pi$ -bonding is almost ionic.

The lower value of  $\alpha^2$  compared to  $\beta^2$  indicates that the inplane  $\sigma$ -bonding is more covalent than the in-plane  $\pi$ -bonding. In complexes **3** and **4**, the  $\alpha^2$  values are (0.92 and 0.87) indicate the slight ionic nature of the metal–ligand  $\sigma$ -bonding, and the values of  $\beta^2$  are 0.99 indicates the presence of considerable inplane  $\pi$ -bonding contribution in metal–ligand  $\pi$ -bonding. These data are well in accordance with other reported values [29].

# 3.3. Solvatochromism

The absorption spectra of complexes 1-4 were measured in different organic solvents with different donor numbers (DN). The donor number proposed by Gutmann [30,31] is a measure of the donor ability or Lewis basicity of a solvent molecule measured on the basis of the amount of heat evolved when the same solvent is added to a solution of SbCl<sub>5</sub> in DCE.

The absorption spectra show one broad band attributed to the promotions of the electron in the lower energy orbitals to the hole in  $d_{x^2-y^2}$  orbital of the copper(II) ion (d<sup>9</sup>). The position of this band is shifted to longer wavelength (red shift) as the donor number of solvent increases (Table 4). Assuming that the approach of the solvent occurs along with *z*-axis, the solvent molecules are repelled by the two electrons in the  $d_z^2$  orbital of copper(II) and only the more species can force their way in to form relatively strong bonds. Upon coordination, they exert a *z*-component field proportional to their position in the spectrochemical series. Thus, while a solvent of low donor number (basicity) have less effect in the band maxima, others with higher values induce larger red shift.

Conductivity data (Table 1) of studied complexes suggest that  $ClO_4^-$  acts only as a counter ion and do not interact with any solute (complex cation) [32]. Therefore, the complex structure depends only on the donor properties of the solvent used (Gutmann's donor number DN) [33], and only solute–solvent interactions can be considered.

Table 4				
Absorption maxima $\lambda_{max}$	(nm) of complexes,	1–4, in	different so	vents

Solvent	DN	$\lambda_{\max} \ (\varepsilon \ l \ mol^{-1} \ cm^{-1})^a$					
		1	2	3	4		
CH <sub>2</sub> Cl <sub>2</sub>	0	656 (429)	610 (338)	620 (215)	607 (429)		
CH <sub>3</sub> NO <sub>2</sub>	2.7	661 (387)	630 (255)	n.d.	n.d.		
CH <sub>3</sub> CN	14.1	693 (195)	n.d.	720 (200)	n.d.		
CH <sub>3</sub> OH	19.1	714 (150)	720 (209)	750 (153)	745 (272)		
HCON(CH <sub>3</sub> ) <sub>2</sub>	26.6	740 (272)	763 (331)	769 (206)	763 (472)		
CH <sub>3</sub> SOCH <sub>3</sub>	29.8	763 (65)	830 (44)	868 (56)	845 (67)		

n.d. Not detected.

<sup>a</sup> The extinction coefficient values are given in parenthesis.



Fig. 4. Solvation free energy relationship (DN vs.  $\nu_{max}/10^3$ ) secondary axis is the ordinate of complex 1.

Solvatochromic behavior was studied quantitatively by applying the linear solvation free energy relationship [17],  $v_{max}/10^3 = v^\circ + a$  (DN); where  $v_{max}$  the measured d–d absorption frequency,  $v^\circ$  the extrapolated frequency and *a* is the slope, represents the sensitivity of the complex toward solvent. Linearity of the  $v_{max}$  versus DN, (Fig. 4) confirms the solvatochromic behavior in perchlorate complexes. The slope value (*a*) is the smallest in case of **1**, in which two diimine ligand are coordinated to the copper(II) centre imposing a large steric hindrance to the axial coordination of incoming solvent leading to less solvatochromic behavior.

# 3.4. Thermal analysis

Thermogravimetric (TG) and differential thermogravimetric (DTG) analysis were carried out for *p*-Tol-BIAN free ligand and complexes 1-4 (Figs. 5–9). The stages of decomposition, temperature ranges, decomposition product loss as well as the found and calculated weight loss percentages of free ligand and the complexes are given in Table 5.

The TG, DTG curves of *p*-Tol-BIAN free ligand indicate that the ligand is thermally stable in the temperature range 25-226 °C. Decomposition of the ligand started at 227 °C and



Fig. 5. TG and DTG of (p-Tol-BIAN) free ligand.



Fig. 6. TG and DTG of [Cu(p-Tol-BIAN)2](ClO<sub>4</sub>)2.



Fig. 7. TG and DTG of [Cu(p-Tol-BIAN)(acac)](ClO<sub>4</sub>).

finished at 694 °C with to stages (Fig. 5). The first stage of decomposition occurs in the 227–356 °C temperature range, corresponding to the loss of two toluene ( $C_6H_5CH_3$ ) molecules. The second stage of decomposition involves the cleavage of the naphthalene backbone in the 580–787 °C temperature range, and is accompanied by a weight loss of 27.8%, corresponding to the loss of  $C_8H_6$ .



Fig. 8. TG and DTG of [Cu(p-Tol-BIAN)Cl<sub>2</sub>].

Table 5
Thermal behavior of p-Tol-BIAN free ligand and complexes 1-4

Compound (molecular weight)	DTG peak (°C)	Temperature range (°C)	Decomposition product lost (formula wt.)	Wt. (%) found (calculated)
<i>p</i> -Tol-BIAN (360.45)	289.0	227–356	2 (184.3)	50.0 (51.0)
	694.0	580–786	C <sub>8</sub> H <sub>6</sub> (102.13)	27.8 (28.3)
[Cu( <i>p</i> -Tol-BIAN) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub> (983.35)	294.0	249–367	2 (184.3)	17.6 (18.7)
	445	367–532	ClO <sub>4</sub> (99.45)	10.6 (10.1)
	626	533-707	2 + ClO <sub>4</sub> (283.75)	28.1 (28.8)
[Cu( <i>p</i> -Tol-BIAN)(acac)](ClO <sub>4</sub> ) (623.56)	280	241–348	$ + 2 (CH_3) + C_2H_4 (150.26) $	23.5 (24.1)
	661	546–759	$+ ClO_4 + 2CO_2 (279.6)$	45.7 (44.8)
[Cu( <i>p</i> -Tol-BIAN)Cl <sub>2</sub> ] (494.9)	246	216–290	Cl <sub>2</sub> (70.9)	13.4 (14.3)
	586	461–647	2 (184.3)	37.2 (37.2)
	686	647–759	C <sub>8</sub> H <sub>6</sub> (102.1)	21.0 (20.6)
[Cu( <i>p</i> -Tol-BIAN)(AcOH) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub> (743.0)	267	225-329	2 (CH <sub>3</sub> COOH) (120.1)	16.2 (16.1)
	574	493–657	2 + 2 ClO <sub>4</sub> (383.18)	51.57(51.57)

The thermal decomposition process of  $[Cu(p-Tol-BIAN)_2](CIO_4)_2$  involves three decomposition steps (Fig. 6). The first decomposition step (within the temperature range 249–366 °C) corresponds to the loss of two terminal toluene molecules attached to nitrogen atoms. The second decomposition step accompanied by a weight loss of 10.6% in the 367–532 °C temperature range, corresponding to the elimination of one perchlorate molecule. The third decomposition step centered at 626 °C DTG-peaks, involving weight loss of 27% corresponding to the elimination of another two toluene molecules and one perchlorate molecule.



Fig. 9. TG and DTG of [Cu(p-Tol-BIAN)(AcOH)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>.

The thermal decomposition curves of the complex [Cu(*p*-Tol-BIAN)(acac)](ClO<sub>4</sub>) show two decomposition steps (Fig. 7). The first one corresponding to the loss of two methyl groups, one ethylene and one toluene molecules, in the 241–280 °C temperature range. The second decomposition step occurs in the 546–759 °C temperature range and is accompanied by a weight loss of 45.7%, corresponding to the loss of  $2CO_2 + ClO_4 + C_6H_5CH_3$ . The residue of 0.071 mg (22.1%) exactly corresponding to the fragment C<sub>4</sub>N<sub>2</sub>Cu.

The TG, DTG curves of  $[Cu(p-Tol-BIAN)Cl_2]$  (Fig. 8) show three steps of decomposition. The first step involves the elimination of chlorine molecule in the 216–290 °C temperature range. The second decomposition step brings a weight loss of 37.25% due to the loss of two toluene molecules in the 461–647 °C temperature range. In the third decomposition step (647–759 °C), a weight loss of 21.9% corresponding to the loss of (C<sub>8</sub>H<sub>6</sub>) fragment resulting from breaking of naphthalene moiety. There is no further mass loss beyond 760 °C and a plateau is obtained exactly corresponding to C<sub>4</sub>N<sub>2</sub>Cu.

The thermal decomposition curves of the complex [Cu(*p*-Tol-BIAN)(AcOH)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> show two decomposition steps (Fig. 9). The first one corresponding to the loss of two acetic acid molecules in the 225–329 °C temperature range. In the second decomposition step, a weight loss corresponding to two toluene and two perchlorate molecules was obtained. The residue of 0.066 mg (23%) exactly corresponding to C<sub>7</sub>N<sub>2</sub>Cu.

In order to access the influence of the structural properties of the ligand and the type of the metal on the thermal behavior of the complexes, the order n, and the heat of activation E of



Fig. 10. Coats–Redfern plots for *p*-Tol-BIAN free ligand, where  $Y = -\ln(1 - \alpha)/T^2$ .

the various decomposition stages were determined from the TG and DTG thermograms using the Coats–Redfern equations in the following forms:

$$\ln\left[\frac{1 - (1 - \alpha)^{1 - n}}{(1 - n)T^2}\right] = \frac{M}{T} + B \quad \text{for} \quad n \neq 1$$
(1)

$$\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right] = \frac{M}{T} + B \quad \text{for} \quad n = 1$$
(2)

where M = -E/R and  $B = \ln AR/\Phi E$ ; *E*, *R*, *A* and  $\Phi$  are the heat of activation, the universal gas constant, pre-exponential factor and heating rate, respectively.

The correlation coefficient, r, was computed using the least square method for different values of n by plotting the left-hand side of Eq. (1) or (2) versus 1000/T, Figs. 10–14. The n value which gave the best fit ( $r \cong 1$ ) was chosen as the order parameter for the decomposition stage of interest. From the intercept and linear slope of such stage, the A and E values were determined. The other kinetic parameters,  $\Delta H$ ,  $\Delta S$  and  $\Delta G$  were computed



Fig. 11. Coats–Redfern plots for  $[Cu(p-Tol-BIAN)_2](ClO_4)_2$ , where  $Y = -\ln(1-\alpha)/T^2$ .



Fig. 12. Coats–Redfern plots for [Cu(p-Tol-BIAN)(acac)](ClO<sub>4</sub>), where  $Y = -\ln(1 - \alpha)/T^2$ .

using the relationships;  $\Delta H = E - RT$ ,  $\Delta S = R[\ln(Ah/kT) - 1]$ and  $\Delta G = \Delta H - T\Delta S$ , where *k* is the Boltzmann's constant and *h* is the Planck's constant. The kinetic parameters are listed in Table 6. The following remarks can be pointed out: (i) all complexes decomposition stages show a best fit for (*n* = 1) indicating a first order decomposition in all cases. Other *n* values (e.g. 0, 0.33 and 0.66) did not lead to better correlations. (ii) The value of  $\Delta G$  increases significantly for the subsequently decomposition stages of a given complex. This is due to increasing the values of  $T\Delta S$  significantly from one stage to another which override the values of  $\Delta H$ . Increasing the values of  $\Delta G$  of a given complex as going from one decomposition step subsequently to another reflects that the rate of removal of the subsequent ligand will be lower than that of the precedent ligand [34,35]. This may be attributed to the structural rigidity of the remaining complex after the expulsion of one and more ligands, as compared with the precedent complex, which require more energy,  $T\Delta S$ , for its rearrangement before undergoing any compositional change. (iii) The negative values of activation entropies  $\Delta S$  indicate a more ordered activated complex than the reactants and/or the reactions are slow [36]. (iv) The positive values of  $\Delta H$  mean that the decomposition processes are endothermic.



Fig. 13. Coats–Redfern plots for [Cu(*p*-Tol-BIAN)Cl<sub>2</sub>], where  $Y = -\ln(1 - \alpha)/T^2$ .



Fig. 14. Coats–Redfern plots for  $[Cu(p-Tol-BIAN)(AcOH)_2](ClO_4)_2$ , where  $Y = -\ln(1-\alpha)/T^2$ .

Table 6		
Temperature of decomposition, and the	kinetic parameters of p-Tol-BIAN	free ligand and complexes 1–4

Compound	Step	$T(\mathbf{K})$	$A(S^{-1})$	$E (\mathrm{kJ}\mathrm{mol}^{-1})$	$\Delta H (\mathrm{kJ}\mathrm{mol}^{-1})$	$\Delta S (\mathrm{kJ}\mathrm{mol}^{-1}\mathrm{K}^{-1})$	$\Delta G (\mathrm{kJ}\mathrm{mol}^{-1})$
p-Tol-BIAN	First	562	11318.8	135.7	131.0	-0.181	232.7
	Second	967	5021.2	139.7	131.7	-0.192	317.5
$[Cu(p-Tol-BIAN)_2](ClO_4)_2$	First	567	337	56.0	51.3	-0.210	170.5
	Second	718	5553.4	115.0	109.0	-0.189	244.6
	Third	899	4757.5	130.4	123.0	-0.192	295.6
[Cu(p-Tol-BIAN)(acac)](ClO <sub>4</sub> )	First	553	1399.6	67.2	62.6	-0.198	172.1
· · · · · · ·	Second	933	8833.7	157.6	150.0	-0.187	324.6
[Cu(p-Tol-BIAN)Cl <sub>2</sub> ]	First	519	12285.5	138.0	133.7	-0.180	226.8
	Second	859	3921	96.6	89.5	-0.190	255.5
	Third	959	13562.9	194.4	186.4	-0.184	362.7
[Cu(p-Tol-BIAN)(AcOH) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	First	540	15354.6	162.3	157.8	-0.178	254.0
L	Second	847	9079.0	150.2	143.2	-0.186	300.9

# 4. Conclusion

In solid state, the ESR spectra gave good evidence for the proposed structure and the bonding for all studied complexes. Thermal analyses are investigated and allow calculating the kinetic parameters of all thermal decomposition stages of all complexes.

In solution, these mixed-ligand copper complexes showed a good correlation between their d–d absorption maxima and the donor strength of the solvent used (positive solvatochromism). This behavior is further confirmed by applying the linear solvation free energy relationship.

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