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# A chloro bridged Cu(II)–Cu(II) complex of a new aminophenol ligand: Magnetostructural, radical decay kinetic studies, highly efficient and aerial alcohol oxidation

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#### ABSTRACT

A new tripodal aminophenol-based ligand containing a pyridine unit was synthesized and characterized by IR and <sup>1</sup>H NMR spectroscopic techniques. A dimeric copper(II) complex of this ligand was prepared and characterized by X-ray crystallography, DFT calculations, spectroscopic techniques and magnetic susceptibility measurements. X-ray analysis revealed a complex in which one phenolate, and amine and imine nitrogens of the ligand are arranged in a distorted square pyramidal geometry (SP) around the copper ions. Two chloride bridges hold both copper atoms together to form the binuclear [L<sup>Aph</sup>CuCl]<sub>2</sub> complex. This complex exhibits nearly no superexchange coupling between the copper centers. The phenolate moieties of the copper complex were electrochemically oxidized to phenoxyl radical cations [L<sup>Aph</sup>CuCl]<sub>2</sub>·<sup>+</sup>. The decay kinetics of the mentioned radical were investigated using a simulation of the voltammogram data. In addition, highly efficient and eco-friendly oxidation of alcohols to aldehydes was achieved with molecular oxygen or air as the oxidant and the [L<sup>Aph</sup>CuCl]<sub>2</sub>-Cs<sub>2</sub>CO<sub>3</sub> system as a catalyst.

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### 1. Introduction

Many biological reactions are controlled by metalloenzymes containing one or more metal atoms and with their coordinated ligands, such as histidine and tyrosine, holding them. The Lewis acid properties of these metals allow them to complete a catalytic function that amino acids would not be able to catalyze [1]. Copper is one of these metal ions and serves as a cofactor in many fundamental reactions mediated by copper enzymes. These catalytic processing pathways include copper ions with two biological accessible oxidation states (Cu<sup>I</sup> and Cu<sup>II</sup>), mostly coordinated by amino acid residues and water [2,3]. Galactose oxidase (GOase), the best characterized member of the radical-copper oxidase family, has the ability to catalyze the oxidation of a wide range of primary alcohols to aldehydes. The active site of this enzyme contains a Cu(II) ion, cysteine, water and redox active tyrosine moieties [3]. Hemocyanines and tyrosinases are type III multicopper proteins and their active sites contain binuclear copper complexes. As well as GOase, these two enzymes are responsible for catalyzing some biological processes associated with redox reactions [4,5]. The chemistry of the enzyme's active site containing redox active transition-metal ions with pro-radical ligands is the basis of the synthetic analog approach. For that purpose, bioinorganic chemists

have synthesized Cu(II) complexes with tripodal aminophenol ligands involving [N,O] coordination spheres as synthetic analogs of tyrosine and histidine moieties of amino acids [6–12]. Copper model enzymes can be divided into mononuclear, binuclear and multinuclear complexes. Significant efforts have also been made to provide multinuclear copper complexes containing hydroxo, oxo and chloro bridged complexes as models for active sites of multi-copper enzymes and to evaluate their effective role in catalytic enzymatic reactions [13]. Mononuclear copper complexes are common as functional models in bioinorganic research, while binuclear complexes have received little attention. Chloro-bridged binuclear copper(II) complexes have received a special interest because of their diverse structural properties. On the other hand, the magneto chemistry of these complexes is a subject of current interest owing to their applications in molecular magnetism [14]. These complexes are classified into three types according to their copper(II)-copper(II) spin interaction: (a) non-interacting type, (b) strongly interacting type and (c) weakly (superexchange) type between copper ions with large separation distances (3–5 Å), which lead to antiferromagnetic or ferromagnetic properties of the complexes [15]. Although there are some reports about oxygen or chloro-bridged binuclear copper complexes as models for catechol oxidase [16–19], there is no report on any of these complexes for aerial alcohol oxidation. In this paper we report the synthesis, characterization, magnetic and redox properties of the [L<sup>Aph</sup>CuCl]<sub>2</sub> complex of the newly synthesized redox active [N,O]-donor





**Scheme 1.** The structure of the HL<sup>Aph</sup> ligand.

aminophenol ligand, 2,4-di-tert-butyl-6-(pyridine-2-ylmethylamino)phenol (HL<sup>Aph</sup>) (Scheme 1), which provides the coordination sphere around the copper centers. In addition, we describe a "green chemistry approach" with respect to the highly efficient, selective and eco-friendly oxidation of alcohols to aldehydes with molecular oxygen as the oxidant and the [L<sup>Aph</sup>CuCl]<sub>2</sub> complex as the catalyst.

#### 2. Materials and methods

Reagents and analytical grade materials were obtained from commercial suppliers and used without further purification, except those for electrochemical measurements. Elemental analyses (C,H,N) were performed by the Elementar, Vario EL III. Fourier transform infrared spectroscopy on KBr pellets was performed on a FT IR Bruker Vector 22 instrument. NMR measurements were done on a Bruker 400 instrument. UV-Vis absorbance digitized spectra were collected using a CARY 100 Bio spectrophotometer. Magnetic susceptibility data were measured from powder samples of the solid material in the temperature range 2-290 K using a SQUID susceptometer with a field of 1.0 T (MPMS-7, Quantum Design, calibrated with a standard palladium reference sample, error <2%). Multiple-field variable-temperature magnetization measurements were done at 1, 4 and 7 T, also in the temperature range 2-290 K with the magnetization equidistantly sampled on a 1/T temperature scale.

The experimental data were corrected for underlying diamagnetism by use of tabulated Pascal's constants [20,21], as well as for temperature-independent paramagnetism. The susceptibility and magnetization data were simulated with our own package julX for exchange coupled systems [22]. The simulations are based on the usual spin-Hamiltonian operator (Eq. (1)) for binuclear complexes with two spins  $S_1 = S_2 = 1/2$ .

$$\hat{H} = -2J[\vec{S}_1 \cdot \vec{S}_2] + g\beta(\vec{S}_1 + \vec{S}_2) \cdot \vec{B}$$
<sup>(1)</sup>

where *J* is the spin coupling constant and *g* is the average of the electronic g-matrix components (kept equal for both Cu sites). Diagonalization of the Hamiltonian was performed with the routine ZHEEV from the LAPACK library [23] and the magnetic moments were obtained from the first-order numerical derivative dE/dB of the eigenvalues. The powder summations were done using a 16-point Lebedev grid [24,25]. Intermolecular interactions were considered by using a Weiss temperature,  $\Theta W$ , as the perturbation of the temperature scale,  $kT = k(T - \Theta W)$  for the calculation. Cyclic voltammetry was performed using an Autolab potentiostat/galvanostat 101. The working electrode was a glassy carbon disk (2.0 mm diameter) and a Pt wire was used as the counter electrode. The working electrode potentials were measured versus a quasi-reference electrode of silver wire (all electrodes from Azar Electrode). The Ag quasireference electrode was calibrated using a ferrocene/ferrocenium redox couple (0.41 V) as an external standard [26]. The ionic strength of all the experimental solutions were maintained at 0.1 M by adding tetrabutylammonium perchlorate solution. Prior to the measurement, the GC electrode was polished with 0.1 µm alumina powder and washed with distilled water. The voltage scan rate was set at 50 mV s<sup>-1</sup>. The solutions were deoxygenated by bubbling nitrogen gas through them for 10 min.

The X-ray data for the reported complexes were collected on a Bruker–Nonius Kappa CCD diffractometer at 100(2) K using graphite-monochromated Mo K $\alpha$  radiation ( $\lambda$  = 0.71073 Å). Final cell constants were obtained from a least-squares fit of integrated reflections. Intensity data were corrected for Lorentz and polarization effects. The data sets were corrected for absorption (sADABS, Bruker–Nonius 2004) [27]. The structures were solved by direct method and refined by full-matrix least-squares techniques based on  $F^2$  (SHELXTL software package) [28]. The GC analysis was carried out using a VARIAN CP 3800 with dihydrogen carrier gas.

#### 3. Experimental

# 3.1. Preparation of 3,5-di-tert-butylcyclohexa-3,5-diene-1,2-dione (3,5-DTBQ)

3,5-Di-tert-butylcyclohexa-3,5-diene-1,2-dione (3,5-DTBQ) was synthesized according to a modified literature procedure [29].

#### 3.2. Preparation of 2,4-di-tert-butyl-6-(pyridine-2-ylmethylamino)phenol (HL<sup>Aph</sup>)

To a solution of 3,5-DTBQ (1 mmol, 0.22 g) in *n*-heptane (9 ml) was added 2-(aminomethyl) pyridine (1 mmol, 0.108 ml), followed by stirring for 30 min at room temperature. A yellow precipitate was formed, collected by filtration and then washed with cold *n*-heptane. The solid material was air-dried and crystallized in a 1:1 dichloromethane/n-hexane mixture (0.2 g, 65%). *Anal.* Calc. (found) for C<sub>20</sub>H<sub>26</sub>N<sub>2</sub>O: C 77.38 (77.29), H 8.44 (8.26), N 9.02 (9.06). IR (KBr, cm<sup>-1</sup>): 688, 751, 793, 871, 915, 959, 1030, 1143, 1193, 1246, 1306, 1362, 1473, 1586, 1623, 2869, 2902, 2956, 3059, 3347. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si)  $\delta_{\rm H}$ : 1.359(s, 9H), 1.489(s, 9H), 7.292(s, 2H), 7.354(q, 1H), 7.853(q, 2H), 8.264(t, 1H), 8.746(t, 1H), 8.899(s, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si)  $\delta_c$ : 29.42, 31.59, 34.62, 34.99, 76.71, 77.03, 77.34, 110.38, 121.23, 124.55, 125.09, 135.51, 136.73, 141.69, 149.74, 154.58, 155.98. M.p.: 135–138 °C.

## 3.3. Synthesis of [L<sup>Aph</sup>CuCl]<sub>2</sub>

To a solution of HL<sup>Aph</sup> (1 mmol, 0.31 g) and triethylamine (2 mmol, 0.28 ml) in ethanol (30 ml) was added CuCl<sub>2</sub>·2H<sub>2</sub>O (1 mmol, 0.17 g), followed by stirring for 2 h at room temperature. A purple precipitate was formed, collected by filtration and then dried in a vacuum oven at 50 °C. Single-crystals suitable for X-ray crystallography were obtained by slow diffusion of ether into a solution of the complex in dichloromethane at room temperature (0.81 g, 90%). *Anal.* Calc. (found) for C<sub>40</sub>H<sub>50</sub>Cl<sub>2</sub>Cu<sub>2</sub>N<sub>4</sub>O<sub>2</sub>: C 58.81 (58.59), H 6.17 (6.19), N 6.86 (6.83). IR (KBr, cm<sup>-1</sup>): 762, 820, 864, 911, 1022, 1157, 1198, 1254, 1308, 1359, 1398, 1473, 1531, 1600, 2866, 2906, 2952, 3058, 3095. UV–Vis in CH<sub>2</sub>Cl<sub>2</sub>,  $\lambda_{max}$ , nm ( $\varepsilon$ , M<sup>-1</sup> cm<sup>-1</sup>): 240(892), 574(157).

# 3.4. Spectrophotometric investigation of mix ligand $HL^{Aph}$ -bipyridine and $Cu^{2*}$ complexation

In an experiment, 2 ml of a CuCl<sub>2</sub>·2H<sub>2</sub>O solution in CH<sub>3</sub>CN (4 × 10<sup>-6</sup> M) was transferred into a cuvette. UV–Vis spectra were recorded in the range 260–800 nm about 5 min after each addition of 10  $\mu$ L of a solution containing a 1:1:1 ratio (1.60 × 10<sup>-1</sup> M) of the ligands HL<sup>Aph</sup>/bipyridine/triethylamine. Changes in the absorbance of the copper chloride complex upon addition of the ligands in solution were monitored at the LMCT maximum wavelength of the complex.

# 3.5. Synthesis of [L<sup>Aph</sup>Cu(bpy)]

A solution of CuSO<sub>4</sub> (1 mmol, 0.16 g) in 3 ml H<sub>2</sub>O was added to a solution of HL<sup>Aph</sup> (1 mmol, 0.22 g) and bipyridine (1 mmol, 0.156 g) in 5 ml 50% ethanol. A purple precipitate was formed immediately. The suspension was diluted with water, collected by filtration and dried in a vacuum oven at 70 °C over 12 h (0.401 g, 80%). All efforts to get crystals from the complex were unsuccessful. *Anal.* Calc. (found) for C<sub>28</sub>H<sub>31</sub>CuN<sub>4</sub>O: C 66.84 (66.16), H 6.21 (6.13), N 11.14 (10.80). IR (KBr, cm<sup>-1</sup>): 704, 755, 798, 827, 867, 912, 1035, 1087, 1153, 1202, 1258, 1358, 1469, 1553, 1595, 2868, 2906, 2955, 3065, 3411. UV–Vis in CH<sub>2</sub>Cl<sub>2</sub>,  $\lambda_{max}$ , nm ( $\varepsilon$ , M<sup>-1</sup> cm<sup>-1</sup>): 238(714), 287(713), 553(153).

# 3.6. Catalytic activity of the $[L^{Aph}CuCl]_2$ complex for the oxidation of alcohols

The oxidation was carried out in an oxygen atmosphere at room temperature. In a typical experiment, alcohol (1 mmol),  $[L^{Aph}CuCl]_2$ (0.024 g, 5 mol%) and  $Cs_2CO_3$  (0.650 g, 2 mmol) in 5 ml of air (oxygen) saturated toluene were taken in a 15-ml two-necked roundbottom flask which was equipped with an air or oxygen balloon. The solution was magnetically stirred for some hours and the mixture was filtered through a plug of silica, then diluted with toluene (2 ml). The progress of the reaction was monitored by gas chromatography. In a separate blank test, a 15-ml two-necked roundbottom flask was charged with a solution of copper(II) chloride or the ligand in a mixed medium of  $Cs_2CO_3$  (0.650 g, 2 mmol) in 5 ml of air (oxygen) saturated toluene. Then the flask was equipped with an oxygen balloon. The progress of the reaction was monitored by gas chromatography.

### 4. Discussion

The ligand HL<sup>Aph</sup> was synthesized based on a simple condensation of 2-(aminomethyl) pyridine with 3,5-DTBQ to give the iminophenol ligand. NMR and IR results show that an aminophenol ligand has been produced. The reason for this criterion can be seen clearly in Scheme 2. This reaction involves a [1,5] hydrogen sigmatropic shift between the carbon  $C^1$  and oxygen  $O^5$  atoms of the iminophenol ligand (Scheme 2).

The binuclear copper complex was easily formed in good yield by the reaction of a methanolic solution of the ligand with copper chloride and triethylamine in a suitable ratio at room temperature (Scheme 3).

In the IR spectrum of the ligand (HL<sup>Aph</sup>), the  $v_{OH}$  stretch is observed in the range 2900–3000 cm<sup>-1</sup>. The occurrence of this band at such a relatively low wavenumber is characteristic of aminophenol ligands and is an indication of extensive hydrogen bonding. A strong band in the 1620–1640 cm<sup>-1</sup> region was assigned to v(C=N). In the IR spectrum of the complex, the strong and sharp band at a frequency around 3000 cm<sup>-1</sup> for the  $v_{OH}$  stretch of the ligand disappeared, proving the coordination of the phenol group to

HL<sup>Aph</sup> 
$$\xrightarrow{\text{CuCl}_2. 2H_2O}$$
  $[L^{Aph}CuCl]_2$   
Ethanol, NEt<sub>3</sub>

Scheme 3. Synthesis of the binuclear copper complex.

the metal. The v(C=N) band of the copper complex, compared with the corresponding ligand, is shifted to lower energy (1600–1630 cm<sup>-1</sup>) by 10–20 cm<sup>-1</sup> which indicates coordination of the imine nitrogen to the metal. The electronic spectrum of the [L<sup>Aph-</sup>CuCl]<sub>2</sub> complex recorded in CH<sub>2</sub>Cl<sub>2</sub> is presented in Fig. 1.

The intra-ligand absorption for the higher energy band (<400 nm) is assigned to  $\pi - \pi^*$  and  $n - \pi^*$  transitions (ILCT). The lower energy band (274 nm) is assigned to a phenolate-to-Cu(II) charge transfer transition (LMCT). In order to explore the effects of a secondary  $\pi$ -acceptor bipyridine (bpy) ligand on the electronic spectrum of complex, we decided to investigate the electronic spectrum of the mixed ligand complex of [L<sup>Aph</sup>Cu(bpy)]. The mentioned complex was prepared in situ from a titration of the copper salt with a mixture of HL<sup>Aph</sup>, triethylamine and bipyridine in suitable ratio. The formation of [L<sup>Aph</sup>Cu(bpy)] was monitored by following the increase of the band at 553 nm, corresponding to the LMCT maximum wavelength of the above mentioned complex. The effect of bipyridine on the electronic spectrum of the complex was observed by a blue shift compared to the transition band of [L<sup>Aph</sup>CuCl]<sub>2</sub> at 574 nm (Fig. 1). This shift can be attributed to the electron-withdrawing effect of bipyridine, stabilizing the phenolate  $\pi$  (HOMO) orbitals.

4.1. X-ray data collection and crystal structure determination of  $[L^{Aph}CuCl]_2$ 

## 4.1.1. Crystal structure of [L<sup>Aph</sup>CuCl]<sub>2</sub>

Crystals of  $[L^{Aph}CuCl]_2$ , appropriate for X-ray analysis, were obtained by slow diffusion of ether into a solution of the complex in dichloromethane at 298 K. Dark purple crystals of  $[L^{Aph}CuCl]_2$  in the monoclinic crystalline system, space group  $P2_1/c$  (a =16.253(2), b = 9.1951(11), c = 13.4351(17) Å) were formed. Crystal data for the  $[L^{Aph}CuCl]_2$  complex are given in Table 1. An ORTEP view of the complex is shown in Fig. 2. Selected bond distances and bond angles are listed in Table 2. All the bond lengths and angles for  $[L^{Aph}CuCl]_2$  are presented in the supplementary material. The symmetrical parts of the structure is formed by a binuclear complex of the formula  $[L^{Aph}CuCl]_2$  and the two symmetrical parts are linked by two chloride bridges (Fig. 2).

The distortion parameter  $\tau([(\Phi_1 - \Phi_2)/60])$ , in which  $\Phi_1$  and  $\Phi_2$  are the two largest L–M–L angles of the coordination sphere [30], for this complex is 0.196 for each copper center (Table 2). Comparing these  $\tau$  values with the corresponding values for an ideal trigonal bipyramid ( $\tau = 1$ ) and square pyramid ( $\tau = 0$ ) indicate that this complex has a distorted square based pyramidal (SP) structure. In this geometry for [L<sup>Aph</sup>CuCl]<sub>2</sub>, the nitrogens N(1) and N(8), chloro



Scheme 2. [1,5] Hydrogen shift between the C(7) carbon and O(15) oxygen atoms in HL<sup>Aph</sup>.



**Fig. 1.** UV–Vis spectra of [L<sup>Aph</sup>CuCl]<sub>2</sub> and [L<sup>Aph</sup>Cu<sup>II</sup>(bpy)].

Table 1

Crystal data and structure refinement for  $[L^{Aph}CuCl]_2$ .

Identification code	[CuL <sup>Aph</sup> Cl] <sub>2</sub>
Empirical formula	$C_{40}H_{50}Cl_2Cu_2N_4O_2$
Formula weight	816.82
Temperature (K)	100(2)
Wavelength (Å)	0.71073
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	16.253(2)
b (Å)	9.1951(11)
c (Å)	13.4351(17)
α (°)	90
β (°)	107.422(2)
γ (°)	90
Volume (Å <sup>3</sup> )	1915.8
Ζ	2
Calculated density (Mg/m <sup>3</sup> )	2, 1.416
Absorption coefficient (mm <sup>-1</sup> )	1.289
F(000)	852
Crystal size (mm)	$0.16 \times 0.14 \times 0.02$
Theta range for data collection (°)	2.58-30.82
Limiting indices	$-23 \leqslant h \leqslant 23$
	$-13 \leqslant k \leqslant 13$
	$-19 \leqslant l \leqslant 19$
Reflections collected/unique	$52862/6004 (R_{int} = 0.0590)$
Completeness	99.9% ( <i>θ</i> = 30.82)
Refinement method	Full-matrix least-squares on $F^2$
Data/restraints/parameters	6004/7/248
Goodness-of-fit (GOF) on $F^2$	1.161
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0597, wR_2 = 0.1306$
R indices (all data)	$R_1 = 0.0821, wR_2 = 0.1415$
Largest difference in peak and hole (e $Å^{-3}$ )	1.036 and -0.939

bridging ligand Cl(1) and O(15) phenolate atoms of the ligand are nearly coplanar, occupying the basal positions of the pyramid, whereas the other chloro bridging ligand #Cl(1) occupies the apical position. Consequently, the geometry of the complex consists of two square pyramids (Scheme 4) sharing a base-to-apex edge with parallel basal planes (SP II type) [31,32].

There are two other kinds of pyramidal arrangements [31]: SP I type, square pyramids sharing a basal edge with the two bases nearly perpendicular to one another, and SP III type, two square pyramids that share a base-to apex edge, but with coplanar basal planes (Scheme 5). The Cu–Cu distance of 3.495 Å is in agreement

with the average value (3.499 Å) for chloro-bridged copper(II) dimers [32]. Regarding the Cu( $\mu$ -Cl<sub>2</sub>)Cu core, the distance " $R_0$ " between the copper center and the apical chloro ligand Cu–Cl of 2.555(8) Å is larger than that value for the copper and basal chloro ligand Cu–Cl of 2.320(9) Å. These two distances are in good agreement with the reported range (2.2–2.554 Å) of Cu–Cl bond lengths for five-coordinate copper(II) complexes [32]. The basal Cu–Cl–Cu and apical Cu–Cl–Cu core angles are the same, 91.50(3)°, and both Cl–Cu–Cl bond angles have a value of 88.51(3)°. Consequently, the Cu( $\mu$ -Cl<sub>2</sub>)Cu core has a symmetric geometry. The Cu–N distance of 2.044(2) Å and Cu–N(8) distance of 1.959(3) Å are relatively similar. The C(7)–N(8) bond length of 1.293 Å is shorter than a normal C–N bond. According to the literature, C(7)–N(8) seems to be a double bond, which confirms the sigmatropic shift during the ligand synthesis process [33].

#### 4.2. Magnetic susceptibility measurements

Magnetic susceptibility data for polycrystalline samples of  $[L^{Aph}CuCl]_2$  complex were collected in the temperature range 2–290 K with an applied magnetic field of 1 T. The effective magnetic moment per molecule ( $\mu_{eff}$ ) for the  $[L^{Aph}CuCl]_2$  complex remains nearly constant, 2.55  $\mu_B$ , in the temperature range 290–30 K (Fig. 3), which is close to the value of the magnetic moment for two uncoupled spins of *S* = 1/2. Below 30 K, this value starts to decrease smoothly with decreasing temperature and reaches a value of  $\mu_{eff}$  = 2.06  $\mu_B$  at 1.88 K (Fig. 3), which is slightly lower than the expected value for two uncoupled spin-only Cu(II) ions (*S* = 1/2, *g* = 2.0).

The observed temperature dependent magnetic moment for  $[L^{Aph}CuCl]_2$  confirms the dimeric nature of this complex. The fitting of these data shows exchange coupling parameters of  $J = -1 \text{ cm}^{-1}$  and g = 2.10. It is observed that J is nearly zero, suggesting that super-exchange coupling does not happen in  $[L^{Aph}CuCl]_2$ . It is well known that in binuclear copper(II) complexes, the singlet-triplet (S–T) energy gap J correlates (Eqs. (2) and (3)) with the structural factors of the bridge angle ( $\alpha$ ) and Cu...Cu distance (d) [12,28,30–32,34,35].

$$2J = E_{\rm T} - E_{\rm S} \tag{2}$$

$$J = 2\kappa - (\varepsilon_{\rm s} - \varepsilon_{\rm a})^2 / U \tag{3}$$

where  $2\kappa$  and  $(\varepsilon_s - \varepsilon_a)^2/U$  terms describe the ferro- and antiferromagnetic contributions, respectively.

The variation of  $\alpha$ , *d* and the ratio of  $\alpha/R_0$  affects the overlap of the Cu(3d<sub>x2-v2</sub>)/Cl(3p) orbitals and therefore changes  $\varepsilon_s - \varepsilon_a$ (the energy difference between the  $Cu(3d_{x2-y2})/Cl(3p_x)$  and  $Cu(3d_{x2-v2})/Cl(3p_v)$ ) SOMO orbitals (Scheme 6). Based on the Hatfield [36] theory, if  $\alpha/R_0$  is in the range of 32.6 to 34.8 Å<sup>-1</sup>, the exchange interaction is ferromagnetic, and for values lower than 32.6 and higher than 34.8 Å<sup>-1</sup> the exchange interaction is antiferromagnetic [37,38]. In the case of our chloro-bridged dimer, [L<sup>Aph</sup>Cu Cl]<sub>2</sub>, the value of the  $\alpha/R_0$  is 35.8 Å<sup>-1</sup> close to the border value of 34.8  $Å^{-1}$ . It demonstrates that in this complex, the ferromagnetic term  $2\kappa$  is nearly equal to the antiferromagnetic term  $(\varepsilon_s - \varepsilon_a)^2/2$ U. Indeed this ratio  $(\alpha/R_0)$  is the crossover point between ferromagnetic and antiferromagnetic properties. In other word, our complex shows no superexchange interaction between the copper centers. This corresponds to the results for chloro-bridged binuclear copper(II) complexes (SP II type) which usually show very small ferromagnetic [39-45] or antiferromagnetic coupling constants [46,47]. This behavior is attributed to the distortion around the copper ions, resulting in the orthogonality between the magnetic orbitals  $(d_{x2-v2})$  positioned on the basal plane of each unit [31].



Fig. 2. The structure of [L<sup>Aph</sup>CuCl]<sub>2</sub>. Ellipsoids are plotted at the 40% probability level. Hydrogen atoms are omitted for clarity.

 Table 2

 Selected bond lengths (Å) and angles (°) for  $[L^{Aph}CuCl]_2$ .

Cu <sup>23</sup> -O(15)	1.947(2)
$Cu^{23} - N(8)$	1.959(3)
Cu <sup>23</sup> –N <sup>23</sup>	2.044(2)
Cu <sup>23</sup> -Cl <sup>23</sup>	2.3197(9)
Cu <sup>23</sup> -Cl <sup>23</sup> #1	2.5548(8)
Cl <sup>23</sup> -Cu <sup>23</sup> #1	2.5548(8)
$N^{23}-C(2)$	1.331(5)
N <sup>23</sup> -C <sup>23</sup>	1.350 <sup>23</sup>
C(2)-C(3)	1.397 <sup>23</sup>
$C(3)-C^{23}$	1.385(5)
$C^{23}-C(5)$	1.382(5)
$C(5)-C^{23}$	1.395 <sup>23</sup>
$C^{23}-C(7)$	1.444(5)
C(7)-N(8)	1.292(3)
N(8)-C(9)	1.388 <sup>23</sup>
$O(15)-Cu^{23}-N(8)$	82.45(10)
$O(15)-Cu^{23}-N^{23}$	162.50(11)
$N(8)-Cu^{23}-N^{23}$	80.07(11)
$O(15)-Cu^{23}-Cl^{23}$	99.55(8)
$N(8)-Cu^{23}-Cl^{23}$	150.76(7)
N <sup>23</sup> -Cu <sup>23</sup> -Cl <sup>23</sup>	96.10(9)
$O(15)-Cu^{23}-Cl^{23}#1$	98.08 <sup>23</sup>
$N(8)-Cu^{23}-Cl^{23}\#1$	120.28(7)
$N^{23}-Cu^{23}-Cl^{23}\#1$	90.08(7)
$Cl^{23}-Cu^{23}-Cl^{23}#1$	88.51(3)
Cu <sup>23</sup> -Cl <sup>23</sup> -Cu <sup>23</sup> #1	91.49(3)

#### 4.3. Computational structural study

Complementary to the X-ray structure determination of the current synthesized dichloro-bridged Cu(II)–Cu(II) complex and in order to gain more insight into the correlation between molecular structure and spin multiplicity (2s + 1) of the complex, calculations based density functional theory (DFT) have been carried out



**Scheme 4.** Geometry of the binuclear dichloro-bridged  $[L^{Aph}CuCl]_2$  complex (SP II type).



**Scheme 5.** SP I and SP III geometries of binuclear dihalo-bridged Cu(II) complexes [32].



Fig. 3. variation of magnetic susceptibility (  $\chi$  ) with variation in temperature for the complex  $[L^{Aph}CuCl]_2$ .

using the GAUSSIAN 09 suite of programs [48]. We used the X-ray crystallographic information file (cif) as the initial molecular geometry for all computations. Two separate molecular structural optimization calculations have been performed at the B3LYP/6-31G(d) level, one with multiplicity 1 and another with multiplicity 3. The calculated structural parameters of the optimized structures are summarized in Table 3 and compared with the X-ray data for



Scheme 6. The two SOMO orbitals of the complex [L<sup>Aph</sup>CuCl]<sub>2</sub> [31].

#### Table 3

The structural parameters from the X-ray data and molecular geometry optimizations by B3LYP method using 6-31G(d) basis sets for all atoms with two different multiplicities.

Method; multiplicity	Cu-Cu distance (Å)	Cu-Cl bond, (Å) in-plane, out-of-plane	Cu-Cl-Cu α angle (°)	Cl-Cu-Cl angle (°)	$\frac{\alpha/R_0}{(\circ \text{\AA}^{-1})}$	τ
X-ray data, (cif file)	3.495	2.320, 2.555	91.50	88.51	35.81	0.196
DFT-based 2s + 1 = 1	3.514	2.514, 2.448	90.15	89.85	35.86	0.441
DFT-based $2s + 1 = 3$	3.587	2.508, 2.455	92.56	87.44	36.91	0.410

#### Table 4

The total energy (in Hartree) and the energy gap (in eV) between the HOMO and LUMO orbitals of the complex calculated by B3LYP method using 6-31G(d) basis sets for two different multiplicities. In these calculations, all of the non-hydrogen atomic sites are frozen.

Calculation type (frozen non-hydrogen sites)	Energy (a.u.)	HOMO-LUMO gap (eV)	
B3LYP/6-31G(d) 2s + 1 = 1	-6124.96830267	0.02787	
B3LYP/6-31G(d) 2s + 1 = 3	-6125.03784889	α 0.09392	β 0.09381

the current Cu(II) complex. The differences between the structural parameters of the chloro-bridged Cu(II)–Cu(II) complex for ferroand antiferromagnetic conditions can be investigated. The achieved parameters of both X-ray data (with  $J_{exptl.} = -1 \text{ cm}^{-1}$ ) and DFT calculations with multiplicity 1 correspond to an antiferromagnetic property for the complex, while the obtained parameters of DFT calculations with multiplicity 3 match a ferromagnetic property for the respected optimized structure of the complex. Changing the spin multiplicity from 1 to 3, increased both the Cu–Cu distance and the Cu–Cl–Cu ( $\alpha$ ) angle of the main core of the chloro-bridged complex.

In the next stage, keeping the distortions of real structure of the complex, all atomic sites of the complex were frozen, except for the

#### 4.4. Electrochemistry

The electrochemical behaviors of the ligand  $(L^{Aph})$ , metal ion  $(Cu(acac)_2)$  and  $[L^{Aph}CuCl]_2$  and  $[L^{Aph}Cu(bpy)]$  complexes were studied using cyclic voltammetry. The cyclic voltammogram (CV) of the ligand  $(HL^{Aph})$  revealed two anodic peaks  $(A_1 \text{ and } A_2)$  in the positive direction scan (Fig. 4). These oxidation peaks are attributed to ligand centered redox processes in which the phenol moiety of the ligand converts into related phenoxyl radicals.

In order to explore the effects of the secondary  $\pi$ -acceptor bipyridine ligand on the stability of the radical species, the electrochemical oxidation of the [L<sup>Aph</sup>Cu(bpy)] complex was investigated. As seen in Fig. 4, comparing the oxidation potentials of [L<sup>Aph</sup>CuCl]<sub>2</sub> and [L<sup>Aph</sup>Cu(bpy)] with the ligand (756 mV), reveals a positive shift in the peak potentials of the complexes of 110 and 403 mV for [Cu- $L^{Aph}Cl_{2}$  and  $[L^{Aph}Cu(bpy)]$  respectively. It may be related to the lower amount of negative charge on the phenolate group of the complexes due to coordination to the copper center. [L<sup>Aph</sup>Cu(bpy)] shows a positive shift compared to [L<sup>Aph</sup>CuCl]<sub>2</sub>, which is attributed to the hard oxidation of phenolate to the phenoxyl radical  $[L^{Aph}CuCl]_2$ .<sup>+</sup> due to the  $\pi$ -acceptor character of the bipyridine ligand. A UV-Vis study of the phenolate-to-Cu(II) charge transfer band of the [L<sup>Aph</sup>Cu(bpy)] complex showed a blue shift of the LMCT band (Fig. 1). The higher energy of the phenolate-to-Cu(II) chargetransfer band of this complex indicates that the Cu(II)bpy moiety has a high tendency to pull electrons from the phenolate group towards itself. Based on these results, one can say that the stability constant of [L<sup>Aph</sup>Cu(bpy)] is more than the stability constant of [L<sup>Aph</sup>CuCl]<sub>2</sub>. The metal-centered voltammograms, which have been observed in the negative potential range, reveal the Cu<sup>II</sup>/Cu<sup>I</sup> reduction of the complexes.

Fig. 5 shows that the reduction peak of the complexes shifts to less negative potentials comparing to  $Cu(acac)_2$  due to the electron donating ability of the ligands. The shift of the cathodic peak potential for  $[L^{Aph}Cu(bpy)]$  is considerably more than that for  $[L^{Aph}CuCl]_2$ . For all of the complexes, the first anodic peak  $(A_1)$  is considered as the oxidation of the phenolate ligand to its radical cation and its cathodic counterpart  $(C_1)$  is considered as the reduction of this electrochemically generated radical.

It is shown in Fig. 6 that the CV of the ligand does not show a considerable cathodic peak. This fact is indicative that the oxidized intermediate formed at the surface of electrode is removed by a chemical reaction in the timescale of the voltammetric experiment. On the other hand, the CV of  $[L^{Aph}Cu(bpy)]$  shows a cathodic peak with a cathodic to anodic peak ratio nearly equal to but less than unity. It is a good criteria for the stability of the electrogenerated species on the timescale of the voltammetric experiments. The timescale of a voltammetric experiment is determined by the variation of the scan rate [49]. More detailed studies of the complexes were performed at various scan rates (Fig. 6).

The magnitude of the cathodic currents and cathodic to anodic peak current ratio increases with increasing scan rate. Such behaviors are good criteria for the *EC* mechanism to consist of an electron transfer reaction (*E*) followed by a chemical reaction (*C*). According to these results, electrochemical oxidation of  $[L^{Aph}CuCl]_2$  causes the formation of a related radical that undergoes a degradation reaction under these conditions [50]. The rate constant of the phenolate



**Fig. 4.** Cyclic voltammograms of 1.0 mM (a)  $\text{HL}^{\text{Aph}}$ , (b)  $[\text{L}^{\text{Aph}}\text{CuCl}]_2$  and (c)  $[\text{L}^{\text{Aph}}\text{Cu}^{\text{II}}(\text{bpy})]$  in dichloromethane solution containing 0.1 M tetrabutylammonium perchlorate at a glassy carbon electrode, scan rate 100 mV s<sup>-1</sup>.



**Fig. 5.** Cyclic voltammograms of 1.0 mM (a)  $[L^{Aph}Cu^{II}(bpy)]$ , (b)  $[L^{Aph}CuCI]_2$  and (c) (Cu(acac)<sub>2</sub>) in dichloromethane, the other conditions are the same as for Fig. 4.

group was estimated at various scan rates. The simulation was carried out based on the proposed EC mechanism and assuming semiinfinite one-dimensional diffusion on a planar electrode. The experimental parameters entered for the digital simulation consist of the following: starting potential ( $E_{\text{start}}$ ), switching potential ( $E_{switch}$ ), scan rate (v), half wave potential ( $E_{1/2}$ ) and analytical concentration of the species. The formal potentials were obtained experimentally as the midpoint potential between the anodic and cathodic peaks  $(E_{mid})$ . All of these parameters were kept constant and the observed rate constant of the chemical reaction,  $k_{obs}$ , was allowed to change during the fitting processes. The fitting consists of finding a rate constant for which the differences between the digitally simulated and the experimental data reach a minimum [51]. Fig. 6 shows that there is good agreement between the simulated and experimental cyclic voltammograms. The obtained rate constant of radical degradation was 0.6 s<sup>-1</sup> for [L<sup>Aph-</sup> CuCl]<sub>2</sub>, from the average of four independent simulations at



**Fig. 6.** Experimental (curves a and c) and simulated (curves b and d) cyclic voltammograms of 1.0 mM  $[L^{Aph}CuCl]_2$  scan rates are: 400 mV s<sup>-1</sup> for (a) and (b) and 200 mV s<sup>-1</sup> for (c) and (d).

Table 5

Alcohol oxidation results in toluene, catalyzed by copper  $[L^{Aph}CuCl]_2$  in the presence of  $Cs_2CO_3$  as a base and  $O_2$  as the oxidant.

Entry	Substrate	Time (h)		Conver	Conversion (%)	
		02	Air	02	Air	
1	ОН	8	12	89	81	
2	OH	8	12	96	86	
3	ОН	6	24	83	82	
4	ОН	8	8	96	82	
5	ОН	14	24	90	85	
6	ОН	14	16	87	84	
7	СІ СІ	10	20	98	85	
8	ОН	6	10	96	92	
9		8	12	95	91	
10	Он Он	8	8	99	97	
11		24	24	5	3	
12	MeS	12	12	92	87	



**Scheme 7.** Catalytic activity of [L<sup>Aph</sup>CuCl]<sub>2</sub> in the aerobic oxidation of alcohols.

Table 6The effect of base and solvent on catalytic activity.

Entry	Base	Solvent	Time (h)	Conversion (%)
1	K <sub>2</sub> PO <sub>3</sub>	Toluene	24	26
2	$K_2CO_3$	Toluene	24	20
3	Et <sub>3</sub> N	Toluene	24	3
4	Cs <sub>2</sub> CO <sub>3</sub>	CH <sub>3</sub> CN	8	57
5	Cs <sub>2</sub> CO <sub>3</sub>	THF	8	54
6	Cs <sub>2</sub> CO <sub>3</sub>	1,2-Dichloroethane	8	62
7	Cs <sub>2</sub> CO <sub>3</sub>	n-Hexane	8	84
8	1 eq Cs <sub>2</sub> CO <sub>3</sub>	Toluene	8	76
9	2 eq Cs <sub>2</sub> CO <sub>3</sub>	Toluene	8	89
10	3 eq Cs <sub>2</sub> CO <sub>3</sub>	Toluene	8	90

various scan rates. The obtained rate constant of degradation is a good criteria for the relative stability of the phenoxyl radical which was obtained by electrochemical oxidation of the complex.

# 4.5. The catalytic activity of the $[L^{Aph}CuCl]_2$ complex in the aerobic oxidation of alcohols

In continuation of our studies on the application of  $[L^{Aph}CuCl]_2$ , we were interested in using this complex for the oxidation of benzyl alcohols to the corresponding aldehydes. With optimized conditions, we studied the efficiency of this complex for the oxidation of various alcohols in toluene using cesium carbonate as a base and air or oxygen as the oxidant at room temperature. The results for the oxidation of a variety of benzyl alcohols are summarized in Table 5. The catalytic activity of the  $[L^{Aph}CuCl]_2$  complex in the aerobic oxidation of alcohols is shown in Scheme 7.

#### Table 7

The result of blank tests with L<sup>Aph</sup> and copper salt.

Entry	Catalytic system	Solvent	Time (h)	Conversion (%)
1	Copper(II) chloride/Cs <sub>2</sub> CO <sub>3</sub>	Toluene	24	28
2	Copper(II) acetate/Cs <sub>2</sub> CO <sub>3</sub>	Toluene	24	24
3	Copper(II) chloride/Cs <sub>2</sub> CO <sub>3</sub> /L <sup>Aph</sup>	Toluene	8	66
4	$L^{Aph}/Cs_2CO_3$	Toluene	24	17
5	Copper(II) chloride/Cs <sub>2</sub> CO <sub>3</sub> / pyridine	Toluene	8	63



Fig. 7. Screening the reaction of benzyl alcohol under optimized conditions.

Having optimized the reaction conditions, we investigated the effect of bases on the oxidation of benzyl alcohol. Using bases such as  $K_3PO_4$ , triethylamine and CaCO<sub>3</sub>, the alcohol conversions were lower than that in Cs<sub>2</sub>CO<sub>3</sub> (Table 6, entries 1, 2, 3 and 9). The number of equivalents of Cs<sub>2</sub>CO<sub>3</sub> was optimized (Table 6, entries) and



Scheme 8. The possible reaction pathway in the catalytic cycle of alcohol oxidation using the [L<sup>Aph</sup>CuCl]<sub>2</sub>/Cs<sub>2</sub>CO<sub>3</sub> catalyst.

the best results (89% conversion) was achieved when 2 equivalents of Cs<sub>2</sub>CO<sub>3</sub> were used. The solvent effect was also investigated and the results are summarized in Table 6. Employment of polar solvents, such as acetonitrile and THF, yielded low conversions of benzyl alcohol (>60%, Table 6, entries 4 and 5) compared to non-polar solvents, such as *n*-hexane, 1,2-dichloroethane and toluene (<60%, Table 6, entries 6, 7 and 9). According to the literature [40,41,44], for the "copper complex-Cs<sub>2</sub>CO<sub>3</sub>" the higher activity in toluene can be attributed to possible adduct formation between copper and/or cesium cations and the aromatic solvent, as well as polarity effects. These results lead us to suggest that Cs<sub>2</sub>CO<sub>3</sub> acts not only as a strong base for deprotonation of alcohol, but also as a heterogeneous support for copper to produce an stable [L<sup>Aph</sup>CuCl]<sub>2</sub>-Cs<sub>2</sub>CO<sub>3</sub> catalytic species [52]. Comparing the alcohol oxidation results in the presence of Cs<sub>2</sub>CO<sub>3</sub> with triethyl amine as a base, confirm this claim. In this system, [L<sup>Aph</sup>CuCl]<sub>2</sub> is soluble in toluene while Cs<sub>2</sub>CO<sub>3</sub> is not soluble. Therefore, the [L<sup>Aph</sup>CuCl]<sub>2</sub>-Cs<sub>2</sub>CO<sub>3</sub> catalyst can possibly be considered as an intermediate between a homogenous and heterogeneous catalyst (Scheme 8).

All the alcohols could be oxidized to the corresponding aldehydes with good conversions (>80%, Table 5, entries 1-12), and the formation of over-oxidized carboxylic acids was not observed. The blank tests verified copper(II) chloride/Cs<sub>2</sub>CO<sub>3</sub> and copper(II) acetate/Cs<sub>2</sub>CO<sub>3</sub> affords the aldehydes in low yield (Table 7). In other words, this "ligand-free" copper catalyst does not show good efficiency for the aerobic oxidation of alcohols. On the other hand, the blank test with copper(II) chloride/Cs<sub>2</sub>CO<sub>3</sub> and copper(II) acetate/Cs<sub>2</sub>CO<sub>3</sub> and free ligand improved the aldehyde yield (Table 7). Supposing the solubility effect of the ligand increased the alcohol conversion, the above test was repeated in the presence of pyridine. According to the literature [11], pyridine causes increasing solubility of the CuCl<sub>2</sub> salt in a non-polar solvent by the formation of the  $[Cu(py)_2Cl_2]$  coordinated complex. The result shows that increasing the solubility of the copper salt in a non-polar solvent causes an increased alcohol conversion (Table 7, entry 5). Comparing these results with those for  $[L^{Aph}CuCl]_2$ -Cs<sub>2</sub>CO<sub>3</sub>] as a catalyst system led us to the fact that the structure of this coordination copper complex has an important role in the oxidation of alcohols. in which not only the copper but also the ligand is oxidized and reduced during the catalytic cycle.

Alternatively, time screening of the reaction showed an initiation time of 2 h (Fig. 7). It suggests the production of a catalytically active species due to the possible electrostatic interaction between the Cl anions of the  $[L^{Aph}CuCl]_2$  complex and the Cs cations, based on literature reports [53]. The similarity of the results for alcohol oxidation in the presence of  $O_2$  or air as the oxidant led us to the consideration that the alcohol oxidation yield was independent of the oxidant concentration. In other words, the oxidation rate is zero order related to the oxidant concentration.

#### 5. Conclusions

In summary, we have prepared and characterized a novel symmetric chloride bridge dimeric copper(II) complex with a pyridine based aminophenol ligand. Magnetostructural studies of this complex shows no exchange interaction between the copper centers through the chloride bridges due to the structural distortion in the square pyramidal geometry around the copper(II) centers in the dimeric form. This complex can be presented as a candidate for magneto-structural correlation of the halide bridged copper complexes with an aminophenol based ligand including a pyridine unit. Electrochemical oxidation of this complex yielded the corresponding Cu(II)–phenoxyl radical species. The kinetics of radical decay was investigated by the voltammetry technique. In this way, the role of  $\pi$ -acceptor ligands, such as bipyridine, in the

stabilization of the phenoxyl radicals was investigated. In addition, a highly efficient and eco-friendly oxidation of alcohols to aldehydes was achieved with air or molecular oxygen as the oxidant and the  $[L^{Aph}CuCl]_2-Cs_2CO_3$  system as a catalyst. This is the first report on the aerial oxidation of alcohols using chloro bridged binuclear copper complexes.

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### Appendix A. Supplementary data

CCDC 835103 contains the supplementary crystallographic data for [L<sup>Aph</sup>CuCl]<sub>2</sub>. These data can be obtained free of charge via http:// www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.poly.2012.07.096.

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