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Article

Equilibria and Catalytic Properties of a Chloro-Bridged Diimine Copper(II) Complex in the *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine (TMPD) Oxidation

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Novos complexos de cobre(II) com uma imina tridentada, *bimpy* (ou 2-(benzimidazolil)metileno-2-amino-1-etilpiridina), foram preparados e tiveram sua atividade catalítica na oxidação da *N,N,N′,N′*-tetrametil-*p*-fenilenodiamina (TMPD) comparada. As espécies mononucleares, $[Cu(bimpy)(H_2O)_2](NO_3)_2$, (**1**) e $[Cu(bimpy)Cl_2]\cdot H_2O$, (**2**), assim como a espécie dinuclear contendo pontes cloreto, $[Cu_2(bimpy)_2Cl_2]X_2\cdot nH_2O$ preparada como sais perclorato **3**, nitrato **4** e cloreto **5**, respectivamente, foram isoladas e caracterizadas por técnicas espectroscópicas (UV/Vis, IV e EPR). O composto **2** teve sua estrutura determinada por cristalografia de raios-X. Em solventes não-aquosos predomina a espécie dinuclear, enquanto em solução aquosa, ou solventes contendo água, um equilíbrio entre a espécie dinuclear e a mononuclear **1** foi observado. Estudos cinéticos, em metanol, da oxidação catalisada de TMPD indicaram uma dependência de primeira-ordem da velocidade inicial com a concentração de catalisador e um efeito de saturação com aumento da concentração de substrato. O composto dinuclear é mais reativo que o mono-, e experimentos adicionais mostraram que o contra-íon cloreto afeta significativamente os parâmetros cinéticos, deslocando o equilíbrio envolvendo as espécies **2** e **5**, além de estabilizar um par iônico com o substrato.

Some new copper(II) complexes with a tridentate imine ligand, *bimpy* (or 2-(benzimidazolyl)methylene-2-amino-1-ethylpyridine), were prepared, and had their catalytic activity in the *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine (TMPD) oxidation compared. Mononuclear species, $[Cu(bimpy)(H_2O)_2](NO_3)_2$, (**1**) and $[Cu(bimpy)Cl_2]\cdot H_2O$, (**2**), as well as the dinuclear species containing chloro-bridges, $[Cu_2(bimpy)_2Cl_2]X_2\cdot nH_2O$ as perchlorate **3**, nitrate **4** and chloride **5** salts, respectively, were obtained and characterized by different techniques (UV/Vis, IR, EPR and X-ray crystallography). In non-aqueous solvents, the dinuclear species predominates; however, in aqueous solution or solvents containing water, equilibrium between dinuclear and correlated mononuclear species **1** was verified. Kinetic studies, in methanol solution, on the catalyzed TMPD oxidation indicated a first-order dependence of the initial rate with the catalyst concentration, and a saturation effect with increasing concentrations of the substrate. The dinuclear species was observed to be more reactive than the mononuclear one, and further experiments showed that the counter-ion chloride can significantly affect the kinetic parameters, mostly by shifting the mono-/dinuclear equilibrium, and stabilizing an ion-pair with the substrate.

Keywords: copper(II) complexes, dinuclear species, equilibria, kinetics, catalytic activity

Introduction

Copper complexes containing diimines have been extensively studied, and reported as good models for a variety of enzymes associated to the molecular oxygen metabolism.[1] Additionally some of them were used to construct exotic molecular architectures, sensitize photoelectrochemical cells, label biomaterials as the basis for selective sensors, and also to obtain new magnetic materials.[2]

Copper-containing active sites are responsible, in vivo, for the catalyzed oxidation of phenols, and amines, where two-electron transfer occurs between the substrate and two metal centres, as in tyrosinase and catechol oxidases,[3] or

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one metal centre and a radical forming co-factor, as in amine oxidases.[4] Many of the reported studies on mimics of these sites are focused on the simulation of their structural, and spectral properties,[5] as well as on O_2-activation mechanisms.[6] In both cases, imine ligands play an important role.

The interaction of imidazole and benzimidazole or their derivatives with transition-metal ions is believed to be essential in determining the activity of many biologically important molecules and metalloproteins.[7] One of the main reasons for the use of such ligands in mimetic studies was the identification of imidazol as an ubiquitous ligand in copper-containing proteins. Moreover, benzimidazoles have nitrogen donor atoms which are sterically hindered as a component of bulky imidazole groups, and such kind of rigidity in the ligand enforces peculiar geometric environments around the metal in their complexes, analogously to those imposed by protein backbone structure in biomolecules. Since it has been suggested that most of the unusual redox properties of some copper enzymes are due to an asymmetric metal environment, this is an additional reason to synthesize and study such complexes. Nishida and Takahashi[8] have determined the crystal structure of several 1:1 copper(II) complexes of bis(benzimidazol-2-ylmethyl)amine, and its homologues with alkyl substituents on the amine nitrogen atom, to elucidate the unusual changes verified in $A_{//}$ values. Palaniandavar and co-workers[9] have incorporated one more -NH group in this tridentate ligand, varying chelate ring size and alkyl substituents on the imidazole ring, in order to clarify the effect of bulky benzimidazole on the structure, spectra and redox behaviour of copper(II) complexes with bis-(benzimidazol-2-yl)diamines.

We have reported[10] an imidazole-bridged dinuclear copper(II) compound with a tridentade imine ligand that efficiently catalyzes the aerobic oxidation of 2,6-di-*tert*-butylphenol, in methanolic solution, and also of 3,4-dihydroxyphenylalanine (L-dopa) in aqueous solution, in the pH range of 7-11. This complex coexists in aqueous solution with the corresponding mono- and tetranuclear compounds, depending on the pH, and the catalytic activity increases from the mono- to the tetranuclear species. More recently, we have also reported the synthesis, and structural characterization of diverse dinuclear imine–copper(II) complexes containing imidazolate- or phenolate-bridges, and subsequently investigated them as models of tyrosinase and catecol oxidase enzymes, in comparison with previous related complexes.[11] In that work, it was shown that differences in the geometrical features of the ligands can bring about a varied reactivity of the metal centre, based on differences in the hydrophobicity of the complexes, accessibility of the substrate to the metal ion due to steric bulk of the ligand, and the extent of the steric match between the substrate and the complex.[10,11]

Another predominant factor on determining the catalytic activity of these complexes studied is the stability of the dinuclear moiety in solution. Further, since these complexes are frequently used as precursors of more elaborated polinuclear species, the distribution of the various complexes in solution is essential to obtain different desired frameworks. Therefore, herein we focused on distinguishing the various species present in solution, by investigating the chloride counter-ion influence on the equilibria, and also on the catalytic properties of copper(II) complexes containing both chloride and benzimidazole-derived ligands (shown in Figure 1). The oxidation of *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine (TMPD) was chosen as the discriminating reaction to be monitored, since it is a well-known monoelectronic process, catalyzed by all the species studied.

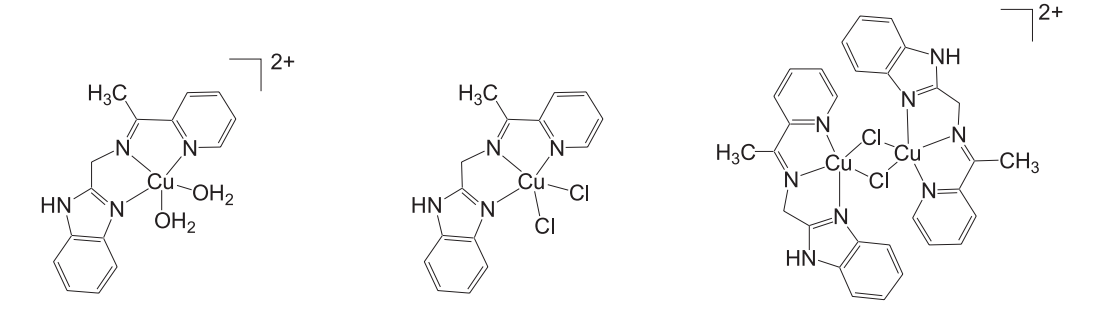


Figure 1. Schematic structures of the diimine-copper(II) complexes studied.

Experimental

Materials

All reagents were of analytical grade, purchased from different sources, and used without further purification. The following abbreviation was used: *bimpy* = ligand derived from 2-acetylpiridine and 2-(aminomethyl) benzimidazole dihydrochloride.

Preparation of the diimine copper(II) complexes

Warning: Although all the prepared compounds were shown to be very stable, perchlorate salts of metal complexes with organic ligands are potentially explosive, and should be handled very carefully, only in small amounts.

*[Cu(bimpy)(NO_3)(H_2O)](NO_3), (**1**)*

Initially, 224 mg (1 mmol) 2-(aminomethyl) benzimidazole dihydrochloride were dissolved in 15 mL methanol solution, followed by addition of 340 mg (2 mmol) $AgNO_3$ previously dissolved in 10 mL methanol/water (4:1, v/v) mixture. The formed precipitate of AgCl was separated by centrifugation, followed by filtration.

The desired mononuclear copper complex was obtained by dropping the previously described filtrated solution into 0.12 mL (1 mmol) of 2-acetylpiridine dissolved in 10 mL of methanol, under stirring, followed by the addition, after a few minutes, of 244 mg (1 mmol) copper(II) nitrate dissolved in 5 mL of methanol. The resulting solution was maintained under continuous stirring, at room temperature for 2 h, and after that the solution was kept in a refrigerator for 7 days, when dark blue crystals were separated. This precipitate was filtrated, washed with cold methanol and diethyl ether, and finally dried over P_4O_{10}, in a vacuum desiccator. Yield: 51%. Anal. Found: C, 39.76; H, 3.40; N, 18.16%. Calc. for $Cu(C_{15}H_{14}N_4)(H_2O)(NO_3)_2$: C, 39.52; H, 3.53; N, 18.43%. Λ_M: 275 S cm^2 mol^{-1} in water. IR ν_{max}/cm^{-1}: ν(O-H), 3395; ν(N-H), 3190; ν(C=N), 1665; ν(N-O), 1290-1418 and $\nu_1+\nu_3$ (NO_3), 1750.

*[Cu(bimpy)Cl_2]·H_2O, (**2**)*

449 mg (2 mmol) 2-(aminomethyl)benzimidazole dihydrochloride dissolved in methanol (20 mL) was carefully dropped to a solution of 2-acetylpiridine (0.23 mL, 2 mmol) in methanol (10 mL), and the mixture was stirred at 50 °C, for 1 h. During this time the solution turned yellow. A solution of $CuCl_2$ (340 mg, 2 mmol) in methanol (10 mL) was then added at once, under stirring at room temperature, when greenish colour solution was observed. The resulting solution was maintained under continuous stirring, at room temperature, for 1 h, and after that, it was kept in a refrigerator for 1 day, when dark green crystals were separated. This precipitate was filtrated, washed with cold methanol and diethyl ether, and finally dried over P_4O_{10}, in a vacuum desiccator. In this case, crystals suitable for X-ray structure determination were obtained by re-crystallization using acetonitrile and water as solvents. Yield: 74%. Anal. found: C, 45.48; H, 4.09; N, 13.99%. Calc. for $CuCl_2(C_{15}H_{14}N_4)(H_2O)$: C, 44.73; H, 4.00; N, 13.91%. Λ_M: 216 S cm^2 mol^{-1} in water. IR ν_{max}/cm^{-1}: ν(O-H), 3528; ν(N-H), 3234; ν(C=N), 1671.

*[Cu_2(bimpy)$_2Cl_2$](ClO_4)$_2$·H_2O, (**3**) and [Cu_2(bimpy)$_2Cl_2$](NO_3)$_2$·2H_2O, (**4**)*

These dinuclear species were prepared similarly by dissolving 449 mg (2 mmol) 2-(aminomethyl) benzimidazole dihydrochloride in 10 mL methanol and dropping this solution to 0.23 mL (2 mmol) acetylpiridine, dissolved in 10 mL methanol. Subsequently, 756 mg (2 mmol) $Cu(ClO_4)_2·6H_2O$ or 488 mg (2 mmol) $Cu(NO_3)_2·6H_2O$ previously dissolved in 10 mL methanol were added under stirring at room temperature, when a greenish colour solution was observed. The resulting solution was maintained under continuous stirring, at room temperature, for 1 h, and afterwards in an ice bath for 20 min. Deep blue crystals for both compounds were collected by filtration, washed with cooled methanol, acetonitrile, and finally dried over P_4O_{10}, in a vacuum desiccator. The obtained yield was 75% for **3**, and 82% for **4**. Anal. Found for **3**: C, 38.72; H, 3.39; N, 11.67%. Calc. for $Cu_2Cl_2(C_{15}H_{14}N_4)(H_2O)(ClO_4)_2$: C, 38.59; H, 3.45; N, 12.00%. Λ_M: 194 S cm^2 mol^{-1} in methanol. IR ν_{max}/cm^{-1}: ν(O-H), 3436; ν(N-H), 3113; ν(C=N), 1665; ν(Cl-O), 1094 and 624. Anal. Found for **4**: C, 41.90; H, 3.39; N, 16.25%. Calc. for $Cu_2Cl_2(C_{15}H_{14}N_4)(H_2O)_2(NO_3)_2$: C, 41.96; H, 3.75; N, 16.30 %. Λ_M: 186 S cm^2 mol^{-1} in methanol. IR (KBr ?): ν(O-H), 3457; ν(N-H), 3186, 3116; ν(C=N), 1666; ν(N-O), 1280-1420.

*Crystallographic data collection and structure determination of complex **2***

A single crystal of the complex [Cu(bimpy)Cl_2] was mounted in the Enraf-Nonius turbo CAD4 diffractometer, at room temperature, and using 20 (θ from 11.25 to 17.99°) automatically centered reflections, the cell parameters were

obtained and refined. Table 1 shows the data collection and the refinement conditions. The data were corrected by absorption factors [$\mu(MoK_\alpha)$ = 1.552 mm^{-1}] using the PSISCAN method.[12] Due to the poor quality of the crystal the crystal data were taken in the range 3.1< θ< 21.1. The structure was solved using the WinGX system[13] by SIR92,[14] and refined by full matrix least squares and difference Fourier synthesis.[15] The hydrogen atoms were located in their ideal positions, except those for the water molecule that were located using CALC-OH,[16] and not refined. The thermal displacement for the hydrogen atoms were set equal to 1.3 times the isotropic equivalent B of the attached atom. All non-hydrogen atoms were refined anisotropically. The structural analysis was performed by PLATON system.[16]

In the determined [Cu(bimpy)Cl_2] asymmetric unit (Figure 2a) the Cu atom has coordination number equal to 5, in a distorted tetragonal pyramidal environment, with two Cl^- ions in apical and equatorial positions and the bimpy ligand in equatorial position. The atoms of the water molecules are disordered each one (Figure 2b) with occupation factor equal to 0.65.

Table 1. Crystal data and structural parameters for **2**

Formula	$C_{15}H_{14}Cl_2Cu\ N_4.1.25\ H_2O$
Formula Weight	408.17
Crystal System	Orthorhombic
Space group	Pbca
a [Å]	12.420(3)
b [Å]	13.253(3)
c [Å]	21.414(6)
V [$Å^3$]	3525(2)
Z	8
D(calc) [Mg/m^3]	1.538
μ(MoKα) [mm^{-1}]	1.552
F(000)	1664
Crystal Size [mm]	0.10 x 0.15 x 0.20
Temperature (K)	293
Radiation MoKα [Å]	0.71073
θ min-max [°]	3.6, 21.1
hk*l* max : min	$\bar{1}2$: 0 ; 0 : 13 ; 0 : 21
Tot., Uniq. Data, R(int)	1926, 1925, 0.073
Observed data [I > 2.0 sigma(I)]	948
Nref, Npar	1925, 221
R, wR2, S	0.0584, 0.2047, 0.94
Max. and Av. Shift/Error	0.21, 0.03
min. and max. Resd. Dens. [e/$Å^3$]	-0.34, 0.54

Physical measurements

Elemental analyses were performed at the *Central Analítica* of our Institution, using a Perkin-Elmer 2400 CHN Elemental Analyzer. Electronic spectra were registered in a Beckman DU-70 spectrophotometer, or an Olis modernized-Aminco DW 2000 instrument, with termostated cell compartment. Ligand field spectra of the solids (300-1000 nm, diffuse reflectance) were taken on a Perkin-Elmer 330 spectrophotometer equipped with a data station, using MgO as a reference. EPR spectra were recorded in a Bruker EMX instrument, operating at X-band frequency, using standard Wilmad quartz tubes, at 77 K. DPPH (α,α'-diphenyl-β-picrylhydrazyl) was used as frequency calibrant (g = 2.0036) for powder samples, and $[Cu(edta)]^{2+}$ solutions (1.00 mmol L^{-1}) as standard for frozen solutions. Infrared spectra of the complexes isolated were recorded in a BOMEM 3.0 instrument, in the range 4000-400 cm^{-1}, using KBr pellets. The temperature dependence of the magnetic susceptibility of polycrystalline samples was measured between 2 and 300 K at field of 500 Oe, using computer-controlled SQUID magnetometer. Diamagnetic correlations were made using Pascal's constants.[17] Conductivity experiments with the complexes studied (in 1 mmol L^{-1} aqueous solution) were carried out in a Digimed DM-31 instrument, using a 10.0 mmol L^{-1} KCl solution as standard (specific conductivity = 1412.0 μS cm^{-1}, at 25 °C).[18]

Kinetic studies

The catalyzed oxidation of *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD) was performed under pseudo-first order conditions, in a standard quartz cell with 10 mm optical length, and 3.00 mL volume, at (25.0 ± 0.5)°C, in methanol solution. The reaction was monitored by the formation of the corresponding radical cation $TMPD^{\bullet+}$ at 565 nm, with ε = 12 000 mol^{-1} L cm^{-1}.[19] Experimental curves of increases in absorbance as a function of time were analyzed by initial rate method. Deviations in values of rate constants were ≤ 5% as indicated, estimated by repeated experiments.

Results and Discussion

Recently, we have reported the synthesis and structural characterization of a mononuclear complex, and the corresponding dinuclear species containing a diimine ligand, derived from the condensation of 2-acetylpyridine and histamine.[20] This dinuclear complex coexists in solution with the corresponding mononuclear species, in an equilibrium very dependent on the solvent. Analogous behaviour was now observed for a similar compound derived from 2-acetylpyridine and 2-(aminomethyl)benzimidazole, and is discussed in this paper.

*Structural description of [Cu(bimpy)Cl_2] · 2H_2O, (**2**)*

The determined structure for this complex **2** consists of discrete $[CuCl_2(C_{15}H_{14}N_4)]\cdot 2H_2O$ molecules. The Cu^{II}

atom is coordinated by two chloride ions and three N atoms from the imine ligand [$C_{15}H_{14}N_4$] in a distorted tetragonal pyramidal environment. An ORTEP view of the complex is shown in Figure 2a, and selected bond distances and angles are given in Table 2.

Table 2. Selected bond lengths (Å) and angles (°) for **2**

Cu	Cl1	2.256(4)	Cu	Cl2	2.588(3)
Cu	N1	2.057(9)	Cu	N2	1.99(1)
Cu	N3	2.00(1)			
Cl1	Cu N1	96.9(3)	Cl2	Cu N1	95.6(3)
Cl1	Cu N2	167.3(3)	Cl2	Cu N2	93.0(3)
Cl1	Cu N3	99.6(3)	Cl2	Cu N3	96.5(3)
N1	Cu N2	79.6(4)	N1	Cu N3	157.6(4)
N2	Cu N3	81.0(4)	Cl1	Cu Cl2	99.5(1)

The verified axial Cu-Cl distance (2.588(3) Å) is considerably longer than the basal distance (2.256(4) Å) in the tetragonal pyramidal structure, as ascertained by Reedijk's τ factor of 0.1 ($\tau = 0$ for a square pyramid, and $\tau = 1$ for a trigonal bipyramid).[21] However, the two Cu-Cl distances in this title compound are comparable to those found in [$CuCl_2(C_{12}H_{14}N_4)(H_2O)$] complex (2.538(1) and 2.302(1) Å), in which the Cu^{II} ion adopts similar geometry.[22]

In the basal plane, the Cu-N1 distance in bz (bz = benzimidazole), 2.057(9) Å is slightly longer than the two others (1.99(1) Cu-N2, and 2.00(1) Å Cu-N3). Both the N-C and C-C bond lengths in the pyridine and benzimidazole groups are in the expected ranges. The bond angles at the Cu central atom, between 79.6(4) and 167.3(3)°, are also very close to those found in a similar [$CuCl_2(C_{12}H_{14}N_4)(H_2O)$] complex, 80.32(7) to 167.18(7)°.[22]

The supramolecular arrangement in the solid is completed by hydrogen bonds between the N_4-H**…**Cl_2 in an infinite one-dimensional chain along the [100] direction as the base vector (dCl**…**N = 3.14(1)Å and angle = 164°), as shown in Figure 2b.

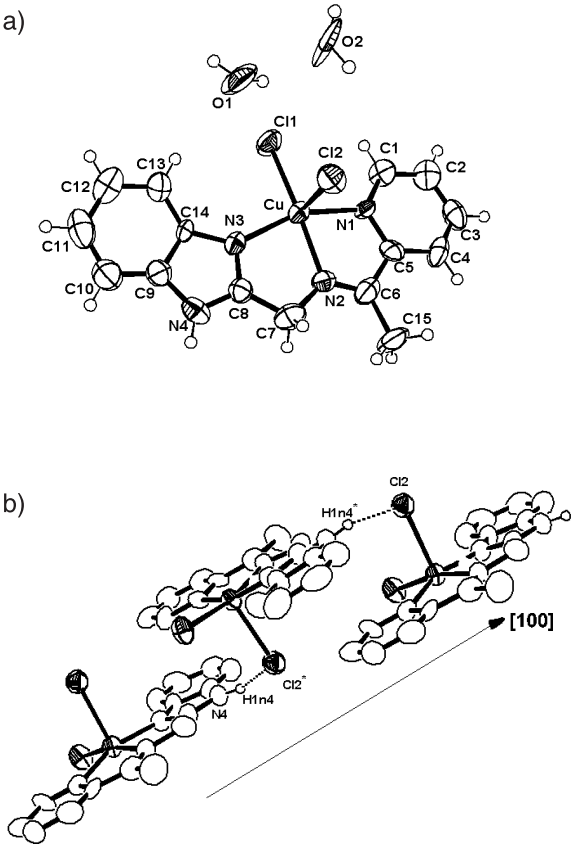


Figure 2. ORTEP plot of the (a) [Cu(bimpy)Cl_2] unit; (b) infinite chain along [100].

IR spectroscopy

All the studied complexes showed bands attributed to ν(O-H) and ν(N-H) around 3400 and 3200 cm^{-1}, respectively. Absorption characteristics of NH_2 aliphatic and C=O groups were not observed in their spectra, as expected. A strong band around 1660 cm^{-1} was assigned to the characteristic ν(C=N), and a further band at 1600 cm^{-1} to the ν(C=N) of the benzimidazole-ring. Comparison of these values to that for free benzimidazole-ring indicated coordination of the benzimidazole nitrogen to the copper atom. The IR spectra exhibited further medium-to-strong bands around 1570 and 1460 cm^{-1} as expected for the pyridine-ring vibrations. The low frequencies observed at 630 and 425 cm^{-1} also suggested coordination of the pyridine nitrogen to the copper(II) atom.[23]

The inspection of the spectra for those complexes containing the nitrate anion, measured in the 1800 - 1200 cm^{-1} region, allowed us to verify the coordination modes of this anion. Lever and Montovani studied the IR absorptions of the NO_3^- group in this region for diverse coordination modes.[24] The analyzed complexes showed a complicated spectrum in this region, which was consistent with the presence of both ionic and coordinated NO_3^- groups, confirmed by X-ray diffraction.[24-27] In our case, both compounds **1** and **4** showed bands in the 1280 – 1420 cm^{-1} region, characteristic of ionic or non-coordinated nitrate groups. However, only the mononuclear compound **1** exhibited a weak-to-medium band at 1750 cm^{-1}, characteristic of coordinated nitrate,[25] and therefore attesting the presence of both types NO_3^- groups.

On the other hand, for the complex **3** containing perchlorate anion bands at 1094 and 624 cm^{-1}, characteristic of non-coordinated perchlorate ions, were observed.[28]

Conductivity measurements

The estimated molar electrical conductivity of compounds **1** and **2** are 275 and 216 S cm^2 mol^{-1} in water, respectively, indicating that these complexes behave as 2:1 electrolytes. These results attested the lability of Cl^- and NO_3^- anions in aqueous solution. In the solid-state, NO_3^- and Cl^- anions are bonded to the Cu(II) ion as confirmed by IR and X-ray analyses described previously. These data also indicated that there are no Cu-NO_3 or Cu-Cl bonds in aqueous solution, since water molecules easily replaced the coordinated NO_3^- or Cl^- ions.

For all the dinuclear complexes, results from conductivity measurements in methanol were consistent with the corresponding proposed formulae, as 2:1 electrolytes, as shown in the Experimental section. Therefore, most of the dinuclear species predominate in this solvent. On the contrary, in aqueous solution all these complexes dissociated completely, almost certainly as the mononuclear aqua-complex **1**.

Electronic spectra

The electronic spectra of complexes **1** to **4** were registered both in solid state and in solution. The reflectance spectra in the solid do not agree with that determined in solution, indicating that dissociation or structural changes of the title complex occurs under influence of the solvent, as shown in Table 3.

Table 3. d-d band of the copper(II) complexes prepared, in solid and in different solvents

Compounds	λ_{max}/nm (d-d band)		
	In H_2O	In CH_3OH	F(R)
$[Cu(bimpy)(H_2O)_2](NO_3)_2$, (**1**)	665	—	648
$[Cu(bimpy)Cl_2]\cdot H_2O$, (**2**)	667	689	694
$[Cu_2(bimpy)_2Cl_2](ClO_4)_2\cdot H_2O$, (**3**)	667	689	684
$[Cu_2(bimpy)_2Cl_2](NO_3)_2\cdot 2H_2O$, (**4**)	667	689	660

Hathaway and Tomlinson[29] pointed out that it is possible to infer the stereochemistry of the local copper(II) ion environment in penta-coordinated complexes from the positions and intensities of d-d transition bands in CuX_5 chromophores. In general, trigonal-bipyramidal copper(II) complexes with $^2A'_1$ ground states exhibit a single, relatively intense band at 481 ± 58 nm. On the other hand, the electronic spectra of square-pyramidal complexes consist of a single broad band in the range 578 ± 77 nm.

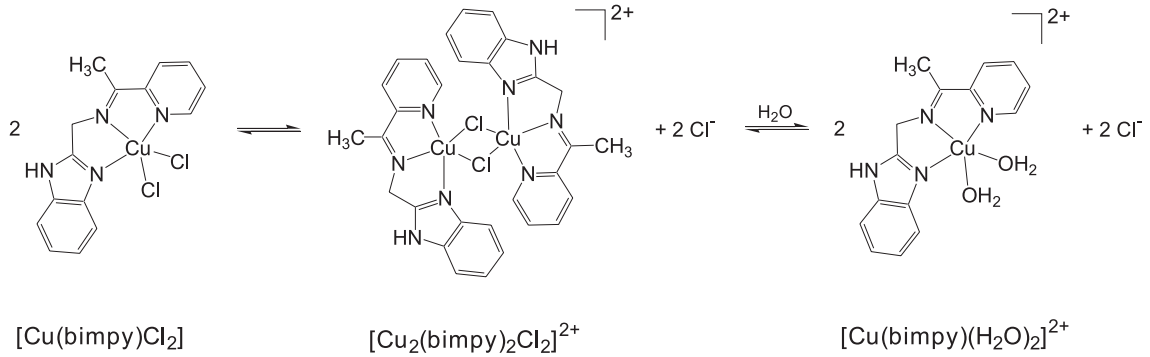
For all the complexes studied the d-d bands observed in solid-state (diffuse reflectance) spectra are much broader than those observed in solution. In this case, a square-pyramidal geometry is more feasible, since such geometry may lead to two well separated transitions.[29,30] These data are consistent with a Cl^- apically coordinated to the Cu^{II} ion, as revealed in the X-ray crystal structure of compound $[Cu(bimpy)Cl_2]$, (**2**). However, when these complexes were dissolved in methanol or water only one relatively sharp d-d band was observed in all cases, at 667 nm in water, or 689 nm in methanol, suggesting a distorted tetragonal pyramidal structure. Analogous spectral change was observed for the mononuclear complex $[Cu(bimpy)(NO_3)(H_2O)]^+$, (**1**), when dissolved in aqueous solution, leading to the dissociation of the nitrate ligand. Therefore, in aqueous solution all the compounds dissociate most likely into the same mononuclear aqua-complex.

In the near-UV region, the spectra of these complexes in methanol solution were almost identical, with intense pyridine and benzimidazole internal absorptions, at 210 nm (ε = 50-75 x 10^3 mol^{-1} L cm^{-1}), 272 nm (ε = 15-20 x 10^3 mol^{-1} L cm^{-1}), and 278 nm (ε = 12-22 x 10^3 mol^{-1} L cm^{-1}), and another intense band around 350 nm (ε = 1.0-2.5 x 10^3 mol^{-1} L cm^{-1}), assigned to a charge transfer from the amino and benzimidazole groups to the Cu^{II} centres.[31]

EPR spectra and equilibria studies

With the aim of comparing the structural environment around copper ions in those complexes, spectroscopic studies by EPR were then carried out. Spectra in frozen methanol / water solution (4:1, v/v), at 77 K, are shown in Figure 3, illustrating both the signals at g~2, around 3100 G, and at g~4, around 1500 G. As expected, the additional peak at 1500 G (near half-field) was observed in the EPR spectra of compounds **3** and **4**, attesting the dimeric structure of these complexes, due to a triplet forbidden transition ($\Delta M_S = \pm 2$).[32] However, this signal was also observed for the mononuclear compound $[Cu(bimpy)Cl_2]$, (**2**), indicating clearly an equilibrium with the corresponding dinuclear species **5** in solution, as shown in Scheme 1 and Figure 3A. On the contrary, the corresponding aqua mononuclear complex $[Cu(bimpy)(H_2O)_2]^{2+}$ or $[Cu(bimpy)(NO_3)(H_2O)]^+$, (**1**) does not exhibit this signal at g~4 (Figure 3D). Analogous behaviour has been observed for similar compounds derived from 2-acetylpiridine and histamine.[20]

The EPR spectra of those dinuclear complexes in frozen methanol / water solution (4:1, v/v) exhibit a resolved hyperfine structure in the $g_{//}$ region, around 3100 G, with several detectable lines as shown in Figure 4. This feature, observed in mixtures containing water, arises from the



Scheme 1.

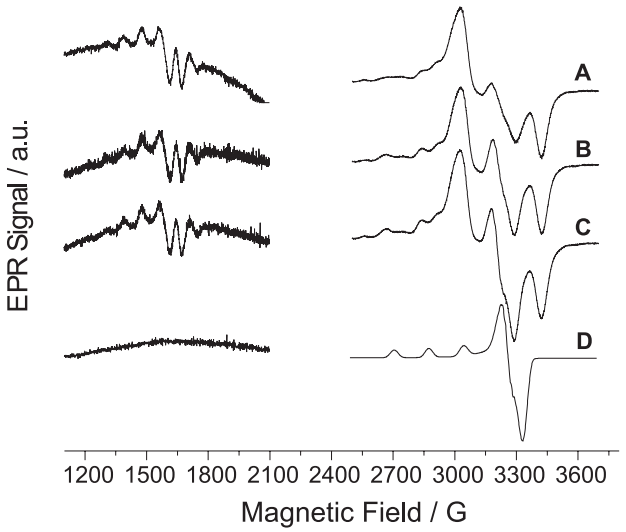


Figure 3. EPR spectra of the copper(II) complexes studied (~ 3 mmol L^{-1}) in frozen methanol/water (4:1, v/v) solutions, at g ~ 2, and g ~ 4 regions (~10X). **A**, $[Cu(bimpy)Cl_2]$, (**2**), gain = 1.00 x 10^4, 4.48 x 10^5; **B**, $[Cu_2(bimpy)_2Cl_2](NO_3)_2$, (**4**), gain = 1.42 x 10^4, 3.56 x 10^5; **C**, $[Cu_2(bimpy)_2Cl_2](ClO_4)_2$, (**3**), gain = 1.26 x 10^4, 2.24 x 10^5; **D**, $[Cu(bimpy)(NO_3)(H_2O)](NO_3)$, (**1**), gain = 1.59 x 10^3, 2.24 x 10^5.

overlap of two sets of peaks, corresponding to two different copper(II) complexes in tetragonal environments, probably due to the equilibrium between the dinuclear μ-chloro bridged species $[Cu_2(bimpy)_2Cl_2]^{2+}$, and the related mononuclear aqua-compound $[Cu_2(bimpy)_2(H_2O)_2]^{2+}$. This equilibrium has been also confirmed by molar conductivity, UV-Vis spectra in solution and reflectance measurements, previously described. The corresponding EPR parameters for all the dinuclear complexes containing different counter-ions (perchorate, nitrate or chloride), in methanol/water solution, were determined by comparison to the corresponding spectrum of the mononuclear species **1**, as indicated (in bold types) in Table 4.

Further, EPR spectra obtained in different solvents corroborated this mono-/dinuclear species equilibrium, as shown in Figure 5. In aqueous solution the mononuclear complex $[Cu(bimpy)(H_2O)_2]^{2+}$ is predominantly formed, while in methanol the dinuclear species $[Cu_2(bimpy)_2Cl_2]^{2+}$ is favoured. In methanol / water (4:1, v/v) solutions both species can be equally observed, as a result of μ-chloro-bridges dissociation.

Table 4. EPR parameters of the mononuclear and dinuclear copper(II) complexes studied

Compounds	EPR parameters			
	$g_\perp$	$g_\parallel$	$A_\parallel$, 10^{-4} cm^{-1}	$g_\parallel / A_\parallel$, cm
$[Cu(bimpy)(H_2O)_2](NO_3)_2$, (**1**)	**2.066**	**2.278**	**180**	**127**
$[Cu(bimpy)Cl_2]\cdot H_2O$, (**2**)	2.151	2.346	193	121
	2.069	**2.278**	**179**	**127**
$[Cu_2(bimpy)_2Cl_2](ClO_4)_2\cdot H_2O$, (**3**)	2.151	2.349	193	121
	2.066	**2.278**	**180**	**127**
$[Cu_2(bimpy)_2Cl_2](NO_3)_2\cdot 2H_2O$, (**4**)	2.153	2.344	193	121
	2.064	**2.277**	**179**	**127**

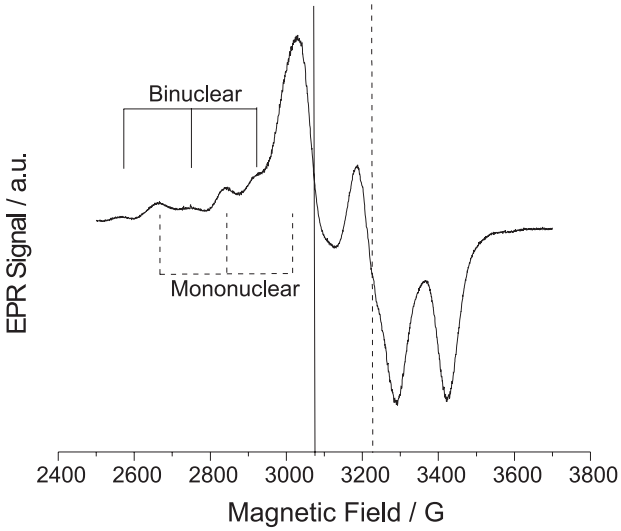


Figure 4. EPR spectrum of the copper(II) complex $[Cu_2(bimpy)_2Cl_2](NO_3)_2$, (**4**) registered (~ 3 mmol L^{-1}), in frozen methanol/water (4:1, v/v) solutions, at g ~ 2, gain = 1.42 x 10^4.

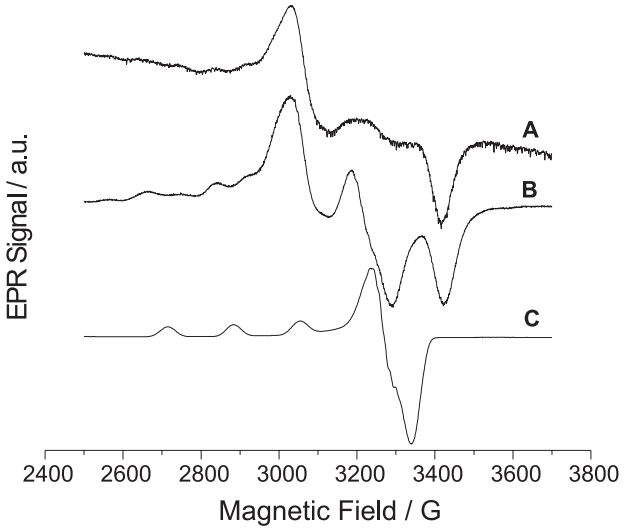


Figure 5. EPR spectra in different solvents, indicating an equilibrium between the mononuclear complex $[Cu(bimpy)(H_2O)_2]^{2+}$, and the corresponding dinuclear species $[Cu_2(bimpy)_2Cl_2]^{2+}$. Modulation amplitude = 12G; Gain = 1.42 x 10^4. **A**, $[Cu_2(bimpy)_2Cl_2](NO_3)_2$, (**4**) dissolved in methanol; **B**, $[Cu_2(bimpy)_2Cl_2](NO_3)_2$, (**4**) dissolved in methanol/water (4:1, v/v); **C**, $[Cu(bimpy)(NO_3)(H_2O)](NO_3)$, (**1**) dissolved in methanol/water (4:1, v/v).

The verified EPR spectral features for the dinuclear $[Cu_2(bimpy)_2Cl_2]^{2+}$ species with different counter-ions (perchlorate, nitrate or chloride), and of mononuclear $[Cu(bimpy)(H_2O)_2]^{2+}$ species in solution are characteristics of axial symmetry, with the unpaired electron in the $d_{x^2-y^2}$ orbital, since $g_{//} > g_{\perp}$. Also, by comparing the empirical ratio $g_{//}/A_{//}$ (see Table 4), frequently used to evaluate tetrahedral distortions in tetragonal structures of copper(II) compounds,[33] some distortion in the tetragonal pyramidal coordination geometry is expected for all these penta-coordinated mono- and dinuclear complexes, similarly to that observed in other diimine-copper complexes.[34]

Additional experiments, with increasing amounts of chloride added to the methanol/water solution, indicated only minor modifications in the EPR spectrum (curve B in Figure 5), with slight decreasing in the dinuclear signal as a consequence of equilibrium shift.

Magnetic properties

A plot of χ_M versus T (Figure 6) shows the temperature dependence of molar magnetic susceptibility for a powder sample of $[Cu_2(bimpy)_2Cl_2](ClO_4)_2$, (**3**), in the 2 to 300 K temperature range.

The major magnetic interaction in this kind of system has a dimeric character, and can be calculated within the framework of the known Bleaney-Bowers equation.[35] The two copper ions interact, with an exchange interaction $H = -2JS_1S_2$. In this isotropic Heisenberg Hamiltonian, a negative value of J refers to an antiferromagnetic interaction within the dimer, while a positive J refers to a ferromagnetic one. Usually a temperature-independent contribution to the susceptibility is also present, including the Van Vleck paramagnetic contribution, and the diamagnetic contribution of the ligands and anions, indicated by the term Nα. Finally, the small temperature-dependent paramagnetic contribution of free monomers (with concentration $p << 1$) that may be present in the samples was included in the final expression for the susceptibility. The singlet – triplet energy gap is expressed in terms of $2J$; and in this expression other symbols have their usual meanings.

$$\chi = 2N\beta^2g^2/kT\,[3 + \exp(-2J/kT)]^{-1}\,(1-p) + [N\beta^2g^2/2kT]p + N\alpha \quad (1)$$

Good least-square fits to the experimental data for compound **3** were obtained with this equation (1), as shown in Figure 6. The magnetic parameters were obtained as: $2J = +(0.57 \pm 0.06)$ cm^{-1}, $g = 2.1 \pm 0.07$, $p = 0.03$ and $N\alpha = 0.007$. The singlet-triplet energy separation ($\Delta E = 2J$) is equal to +0.57 cm^{-1}. This result points to a weak intramolecular ferromagnetic interaction between the two Cu^{II} centres, and also indicates that the interaction between the two unpaired electrons through the chloro-ligand-bridges is not very strong. This result can be justified on the basis of the structural distortion around the copper ions.[36-38]

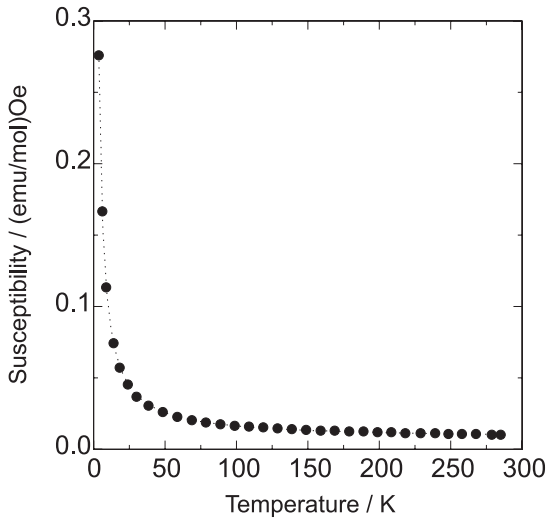


Figure 6. Temperature dependence of the magnetic susceptibility χ_M, for the compound $[Cu_2(bimpy)_2Cl_2](ClO_4)_2$, (**3**).

For the present complex $[Cu_2(bimpy)_2Cl_2](ClO_4)_2$, (**3**), a distorted pyramidal coordination geometry is expected in each mononuclear unit that comprises the dimer. In both units, $d_{x^2-y^2}$ orbitals are the partially occupied or

magnetically active orbitals, and a small intramolecular coupling between these monomer units is expected, since the $d_{x^2-y^2}$ orbitals lie in the basal plane of each monomer, and it is clear that the magnetic orbital of a copper that is involved in one half of a bridge is orthogonal to the d_{z^2} orbital that is involved in the other half of the bridge. Therefore, according to this simple bonding description, a very little coupling between the copper atoms is expected. Other complexes of type II (with parallel square bases) have shown similar behaviour.[36,38]

For compound **2**, the usual Curie-Weiss equation fitted the experimental data.

Catalytic activity in the oxidation of TMPD

The catalytic activity of these studied complexes in the oxidation of an aromatic amine was then verified. Kinetic experiments, using [TMPD] = 2.5 x 10^{-4} mol L^{-1}, and [catalyst] = 2.5 x 10^{-5} mol L^{-1}, except for complex **1**, $[Cu(bimpy)(NO_3)(H_2O)]^+$ = 5.0 x 10^{-5} mol L^{-1}, were performed in methanol solutions at (25.0 ± 0.3)°C, monitoring the generation of the corresponding radical cation $TMPD^{\bullet+}$, at 565 nm (see Figure 7).

In methanol solution, those dinuclear compounds containing μ-chloro bridges efficiently catalyze the oxidation of TMPD, a hindered aromatic amine that favoured the formation of the corresponding radical $TMPD^{\bullet+}$.[19,39] The dinuclear species $[Cu_2(bimpy)_2Cl_2]^{2+}$ were more catalytically active than the mononuclear ones. All the dinuclear complexes **3**, **4** and **5**, with different counter-ions, had approximately the same behaviour. These experiments indicated that the dimer structure of these copper(II) species is an important factor in determining the reactivity toward the amine oxidation, while variation of counter-ion is much less significant.

Nishida and co-workers have discussed the importance of structural factors in the catalytic activity of copper(II) complexes towards aerobic oxidation of TMPD.[40] They concluded that dinuclear copper(II) complexes have good catalytic activity, while square planar mononuclear complexes are either poor catalysts, or are inactive. It is believed that two proximate metal atoms are needed for the formation of an intermediate complex involving two molecules of TMPD, a dinuclear copper(II) complex and dioxygen.[41,42] The formation of this intermediate is necessary to transfer two electrons simultaneously from two molecules of TMPD to a dioxygen molecule, in a concerted mechanism, since a two-electron transfer process is more favourable for reduction of dioxygen than two one-electron steps, from the thermodynamic point of view.[43]

The rate law determined for the TMPD oxidation

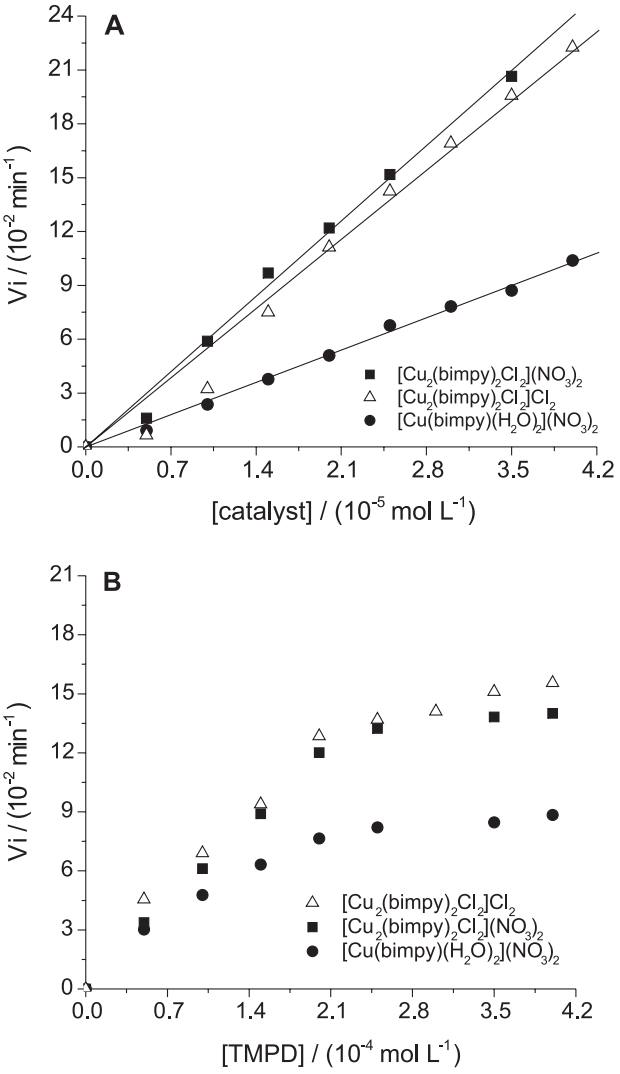


Figure 7. Dependence of the initial oxidation rate of TMPD on the catalyst and substrate concentrations, at (25.0 ± 0.5)°C. (A) [TMPD] = 2.50 x 10^{-4} mol L^{-1} and (B) [catalyst] = 2.50 x 10^{-5} mol L^{-1}.

Table 5. Kinetics parameters determined in the TMPD oxidation catalyzed by diimine-copper(II) complexes

Compounds	k_{cat} / (10^3 min^{-1})	K_M / (10^{-4} mol L^{-1})	k_{cat}/K_M / (10^6 mol^{-1} L min^{-1})
$[Cu(bimpy)(H_2O)_2](NO_3)_2$, (**1**)	0.53	1.71	3.09
$[Cu_2(bimpy)_2Cl_2](NO_3)_2$, (**4**)	1.44	4.66	3.09
[a]$[Cu_2(bimpy)_2Cl_2]Cl_2$, (**5**)	1.41	2.81	5.02

[a] In equilibrium with the respective mononuclear complex **2** in methanol solvent.

indicated a first order dependence on the catalyst concentration, and a first order dependence followed by a saturation effect on the substrate concentration, for the complexes studied, as shown in Figure 7B. Those data fit to the Michaelis-Menten approach, and values for the V_{max} and K_M kinetic parameters were obtained from the corresponding $1/V_i$ *versus* 1/[TMPD] curves, shown on Table 5. In this approach, V_{max} is the maximum rate at saturating concentrations of the substrate, $k_{cat} = V_{max}/[\text{catalyst}]$ (turnover rate) and K_M is the dissociation constant of the substrate from the catalyst-substrate complex.[44] In this case, the mononuclear complex $[Cu(bimpy)(H_2O)_2](NO_3)_2$, (**1**), showed the lowest catalytic activity in the series as a result of a low turnover rate; in spite of showing a K_M value characteristic of a high affinity for the substrate. Additionally, the determined value for the second-order rate constant k_{cat}/K_M is the same as that for the dinuclear complex $[Cu_2(bimpy)_2Cl_2](NO_3)_2$, (**4**).

The dinuclear complexes $[Cu_2(bimpy)_2Cl_2]Cl_2$, (**5**), and $[Cu_2(bimpy)_2Cl_2](NO_3)_2$, (**4**), show the same turnover rate, but high differences in the K_M values which result in significant differences on the second-order rate constant k_{cat}/K_M, probably due to the higher affinity of the dinuclear complex containing chloride as counter-ion for the substrate.

We also investigated the dependence of the reaction rate with the variation of chloride concentration, in the oxidation of TMPD. For these experiments, the standard concentrations used were $[Cu_2(bimpy)_2Cl_2](NO_3)_2 = 2.5 \times 10^{-5}$ mol L^{-1}, and [TMPD] = 2.5×10^{-4} mol L^{-1} in a methanol solution containing different concentrations of added KCl.

Experimental kinetic curves in Figure 8 show clearly two stages in this oxidation reaction: a fast initial step, followed by a slow one. In the presence of different concentrations of KCl, from 3.0 to 263×10^{-5} mol L^{-1}, the initial rate of TMPD oxidation is nearly not altered. On the contrary, a noteworthy decrease on the second step rate was verified with increasing KCl concentrations, followed by a saturation at [KCl] > 25×10^{-5} mol L^{-1}, that is, when the ratio $[Cl^-]/[\text{TMPD}] \geq 1$. A possible explanation for these results is mainly the shift of the dinuclear/mononuclear equilibrium favouring species **2**, and additionally the formation of a stable ion-pair $[TMPD^{\bullet+}Cl^-]$ in solution, with increasing chloride concentration, which would difficult the subsequent formation of other oxidation products, absorbing at the same region of spectrum.[45] Indeed, a similar ion-pair but containing perchlorate anion, $[TMPD^{\bullet+}ClO_4^-]$, has been already prepared and isolated by oxidizing TMPD with 2,2,6,6-tetramethyl-4-acetoxypiperidine oxoammonium perchlorate, in anhydrous acetonitrile.[46]

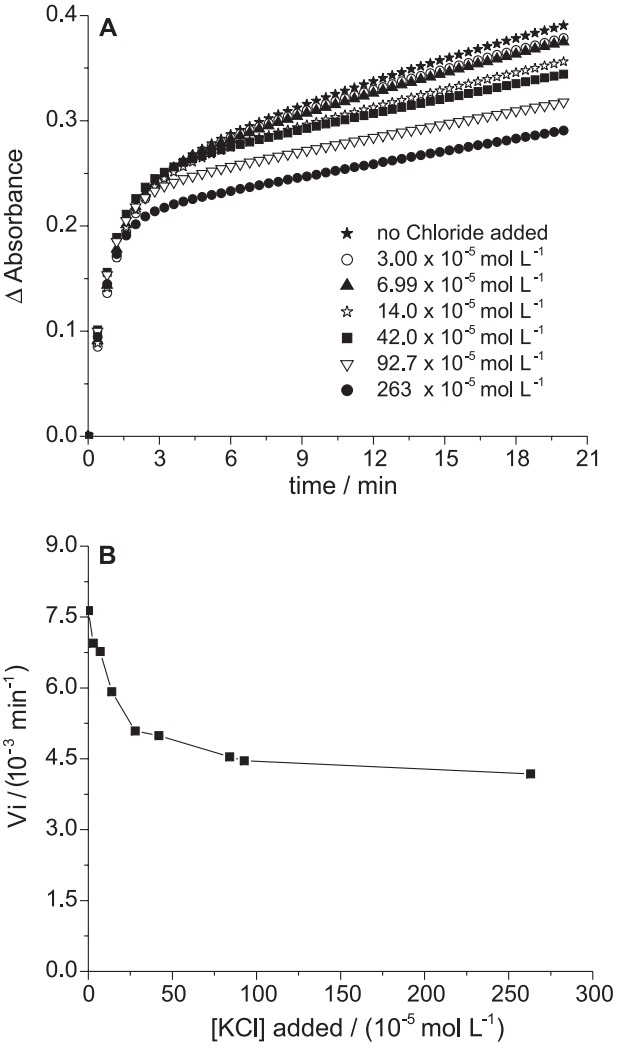


Figure 8. (A) Kinetic curves of TMPD oxidation catalyzed by the complex $[Cu_2(bimpy)_2Cl_2](NO_3)_2$ **4**. The reactions were performed in methanol solution, at (30.0 ± 0.5)°C, in the presence of different concentrations of KCl, [catalyst] = 2.50×10^{-5} mol L^{-1} and [TMPD] = 2.50×10^{-4} mol L^{-1}. (B) Influence of the chloride concentration on the reaction rate of TMPD catalyzed oxidation.

Conclusions

Different mononuclear and dinuclear copper(II) complexes were isolated containing *bimpy* = 2-(benzimidazolyl)methylene-2-amino-1-ethylpyridine as ligand, and were characterized both in solid state and in solution. Equilibria involving mono- and dinuclear species containing chloro-bridges were monitored in solution, indicating a significant dependence on the solvent, and on the presence of excess chloride.

The dinuclear species was observed to be more reactive than mononuclear ones in the oxidation of TMPD by molecular oxygen, in a concerted two-electron transfer mechanism. Further experiments showed that the counter-

ion chloride can significantly affect the kinetic parameters, inhibiting the reaction, mostly by shifting the di-/ mononuclear equilibrium involving species **5** and **2**, and stabilizing an ion-pair with the substrate.

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Supplementary Material

Crystallographic data (excluding structure factors) for the structure(s) reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 214271 copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code + 44(1223)336-033; E-mail: deposit@ccdc.cam.ac.uk].

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