

# Infinite zig-zag and cyclic-tetranuclear isomeric imidazolate-bridged polynuclear copper(II) complexes: Magnetic properties, catalytic activity and electrospray mass and tandem mass spectrometry characterization

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## Abstract

Two mononuclear copper(II) complexes **1** and **2** with the unsymmetrical tridentate ligands 2- and 4-[(imidazol-2-ylmethylidene)amino]ethylpyridine have been prepared. In alkaline solution, deprotonation of the imidazole moiety in **1** and **2** promotes self-assembly, which yielded two structurally different species. Depending on the binding site in the imidazole ring, a polymeric complex with an infinite zig-zag-chain **3**, or a cyclic-tetranuclear complex **4** is formed, as shown by spectroscopic and spectrometric analysis. Herein, structural characterization of these isomeric polynuclear complexes was performed by electrospray mass (ESI-MS) and tandem mass spectrometric experiments (ESI-MS/MS). Each isomer was shown to be stable in methanolic solutions and to display unique mass spectra with characteristic multiply charged molecular and fragment ions, corroborating previous data by EPR measurements. Magnetic data in the solid state fit a typical curve for an one-dimensional infinite regular chain system, with  $J = -(32.4 \pm 1.2) \text{ cm}^{-1}$  and  $g = 2.03$  for **3**, and that of a cyclic-tetranuclear structure with  $J = -(55.5 \pm 0.4) \text{ cm}^{-1}$  and  $g = 2.29$  for **4**. In the oxidation of 3,5-di-*tert*-butylcatechol (3,5-DTBC) by molecular oxygen, both complexes were shown to act as efficient catalysts, exhibiting very similar ratios:  $k_{\text{cat}}/K_{\text{M}} = 9.12 \times 10^6 \text{ mol}^{-1} \text{ dm}^3 \text{ min}^{-1}$  for **3** and  $8.73 \times 10^6 \text{ mol}^{-1} \text{ dm}^3 \text{ min}^{-1}$  for **4**. These similar ratios indicate that interactions between the metal centres in **3** or **4** and the substrate in solution occur predominantly at the outside of the catalyst framework.

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**Keywords:** Copper(II) complexes; ESI mass spectrometry; Magnetic properties; Catalytic activity

## 1. Introduction

Continuing interest in the synthesis and characterization of polynuclear copper(II) complexes derives from the efforts to understand their many varied physico-

chemical properties such as electrochemical, optical, magnetic, mechanical, and catalytic activity, which constitute important characteristics for its potential applications [1]. On the other hand, multicopper proteins such as laccase, ascorbate oxidase and ceruloplasmin show a trinuclear copper cluster in addition to other metal domains, in which interactions between the metal centres are important factors for its peculiar reactivity, promoting very rapid electron transfers [2]. Therefore,

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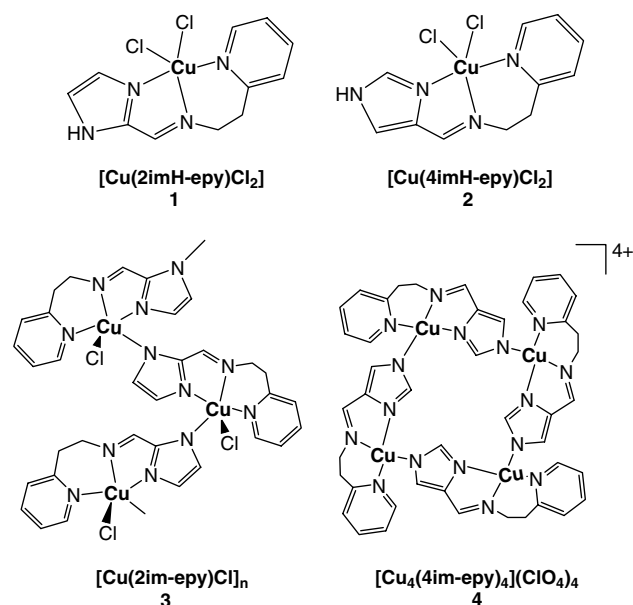
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polynuclear copper(II) complexes could also be helpful for better elucidation of the cooperative action between metal centres in the active sites of such enzymes [3].

Copper(II) complexes with imine ligands containing imidazolate-bridging groups have been used as precursors of assemblies based on supramolecular coordination chemistry, leading to highly ordered, symmetrical molecular or supramolecular structures [4]. Matsumoto and coworkers, for instance, verified the influence of substituents in the imidazole ring on the deprotonation and interconversion between monomer and assembled oligomers by inputting external information, specifically a change of pH [4,5]. Substituents in the imidazole ring apparently have a marked effect on ring size and in the structural orientation of these complexes, since different architectures were realized, for example: cyclic tetramers [5,6] and hexamers [5], as well as 1D chains [6,7].

Although the syntheses and characterization of polynuclear coordination complexes have been extensively investigated in the last years, mainly in solid state [4–8], the stability and reactivity of these oligomeric species in solution are relatively unknown, generally due to problems of solubility in specific solvents. MS characterization of such complexes has also been a difficult task. Electrospray mass spectrometry (ESI-MS) [9] using the soft electrospray ionization technique, which is able to gently transfer pre-formed ions [10] directly from solution to the gas phase, has become a major technique for mass and structural analysis of a large variety of both neutral and ionic metallic complexes [11], and we have been using extensively such technique for fine structural analysis of metallo-organic species [12]. ESI-MS has also been used to characterize polynuclear complexes. As a typical example, Stoeckli-Evans and coworkers self-assembled two new tetranuclear copper(II) and nickel(II) complexes from the ligand pyrazin-2,3-dicarboxylic acid bis[(pyridine-2-ylmethyl)-amide] with multiple anion encapsulation, and used ESI-MS to estimate their stability in methanol and water solvents [13]. ESI-MS shows that anions are not essential for the formation of the macrocyclic complexes as proposed previously [14], suggesting that the formation of the tetranuclear species is ruled primarily by the design of suitable ligands and the choice of appropriate metal ions.

We have previously reported the synthesis and characterization of some new copper(II) complexes containing imidazolate group incorporated in the imine ligand, as precursors of dinuclear and polynuclear species, designed to act as oxidation catalysts in homogeneous solution [15]. In this work, we wish to investigate the stability and reactivity of these polynuclear complexes in solution, and have therefore prepared **3** and **4** (Scheme 1), two species with different structural orientations about the binding position of the imidazole ring. These two complexes are particularly interesting, since



Scheme 1.

they show a sterical influence of the heterocyclic ligand in the building of the final molecular architecture.

## 2. Experimental

*Caution!* Perchlorate salts of metal complexes with organic ligands are potentially explosive and should be handled very carefully, only in small amounts.

### 2.1. Syntheses of complexes

#### 2.1.1. [Cu(2imH-epy)Cl<sub>2</sub>] (**1**) and [Cu(4imH-epy)Cl<sub>2</sub>] (**2**)

2-(aminoethyl)pyridine (0.13 ml, 1 mmol) in methanol (10 ml) was added dropwise to a solution of 2-imidazole-carboxaldehyde (96 mg, 1 mmol) or 4-imidazole-carboxaldehyde (0.19 g, 2 mmol) in methanol (15 ml), and the mixture was stirred at 55 °C, for 1 h. A methanolic solution (10 ml) of CuCl<sub>2</sub> · 2H<sub>2</sub>O (170 mg, 1 mmol) was then added at once. After several hours of standing, a green powder precipitate was observed for **1** or a blue one for **2**, which was collected by filtration, washed with small amounts of methanol and diethyl ether, and finally dried in vacuum under P<sub>2</sub>O<sub>5</sub>. The obtained yield was 78% for [Cu(2imH-epy)Cl<sub>2</sub>] and 47% for [Cu(4imH-epy)Cl<sub>2</sub>]. *Anal. Calc.* for compound **1**, C<sub>11</sub>H<sub>12</sub>N<sub>4</sub>CuCl<sub>2</sub>: C, 39.47; H, 3.61; N, 16.73; Cl, 21.18. Found: C, 39.69; H, 3.64; N, 16.68; Cl, 20.93%. *A<sub>M</sub>* = 212 S cm<sup>2</sup> mol<sup>-1</sup> in water, and *A<sub>M</sub>* = 42 S cm<sup>2</sup> mol<sup>-1</sup> in DMF. UV-Vis, λ<sub>max</sub>/nm, (ε/l mol<sup>-1</sup> cm<sup>-1</sup>) in water: 256 (8060), 304 (9280), 670 (47). UV-Vis, λ<sub>max</sub>/nm, in solid: 692. FTIR (KBr, cm<sup>-1</sup>): 3142–3125 (ν<sub>N-H</sub>); 1628 (ν<sub>C=N</sub>); 1607, 1482, 1439 (ν<sub>C=C</sub>, ν<sub>C=N</sub> (pyridine ring)). *Anal. Calc.* for compound **2**, C<sub>11</sub>H<sub>12</sub>N<sub>4</sub>CuCl<sub>2</sub> · H<sub>2</sub>O: C, 37.45; H, 4.00; N, 15.88.

Found: C, 37.10; H, 3.87; N, 15.56%.  $A_M = 241 \text{ S cm}^2 \text{ mol}^{-1}$  in water, and  $A_M = 52 \text{ S cm}^2 \text{ mol}^{-1}$  in DMF. UV–Vis,  $\lambda_{\text{max}}/\text{nm}$ , ( $\epsilon/\text{l mol}^{-1} \text{ cm}^{-1}$ ) in water: 264 (13 700), 661 (46). UV–Vis,  $\lambda_{\text{max}}/\text{nm}$ , in solid: 680 (d–d). FTIR (KBr,  $\text{cm}^{-1}$ ): 3252 ( $\nu_{\text{N–H}}$ ); 1625 ( $\nu_{\text{C=N}}$ ); 1606, 1481, 1443 ( $\nu_{\text{C=C}}$ ,  $\nu_{\text{C=N}}$ (py ring)).

### 2.1.2. $[\text{Cu}(2\text{im-epy})\text{Cl}]_n$ (**3**) and $[\text{Cu}_4(4\text{im-epy})_4](\text{ClO}_4)_4$ (**4**)

To a solution of **1** (266 mg, 0.8 mmol) or **2** (252 mg, 0.7 mmol), in a MeOH/H<sub>2</sub>O mixture (4:1, v/v), triethylamine (181  $\mu\text{l}$ , 1.3 mmol) was added and subsequently NaClO<sub>4</sub> (120 mg, 1 mmol), in the case of the mixture containing **2**. The resulting solution was maintained under continuous stirring, at room temperature for 30 min. After that, the solution was filtered and the obtained precipitate was washed with small amounts of methanol and diethyl ether, and finally dried in vacuum under P<sub>2</sub>O<sub>5</sub>. A green microcrystalline precipitate for **3** or a dark blue coloured one for **4** was observed. The obtained yield was 82% for  $[\text{Cu}(2\text{im-epy})\text{Cl}]_n$  and 77% for  $[\text{Cu}_4(4\text{im-epy})_4](\text{ClO}_4)_4$ . Anal. Calc. for compound **3**, C<sub>11</sub>H<sub>11</sub>N<sub>4</sub>CuCl · 1.5H<sub>2</sub>O: C, 40.62; H, 4.34; N, 17.22; Cl, 10.90. Found: C, 40.82; H, 4.69; N, 16.60; Cl, 11.09%.  $A_{\text{Cu}} = 103 \text{ S cm}^2 \text{ mol}^{-1}$  in water. UV–Vis,  $\lambda_{\text{max}}/\text{nm}$ , ( $\epsilon/\text{l mol}^{-1} \text{ cm}^{-1}$ ) in water: 255 (9393), 313 (7538), 632 (63). FTIR (KBr,  $\text{cm}^{-1}$ ): 3413 ( $\nu_{\text{O–H}}$ ); 1610 ( $\nu_{\text{C=N}}$ ); 1571, 1486, 1451, 1422 ( $\nu_{\text{C=C}}$ ,  $\nu_{\text{C=N}}$  (pyridine ring)). Anal. Calc. for compound **4**, C<sub>11</sub>H<sub>11</sub>N<sub>4</sub>Cu(ClO<sub>4</sub>) · 0.25H<sub>2</sub>O: C, 36.02; H, 3.16; N, 15.27. Found: C, 36.55; H, 3.38; N, 14.75%.  $A_{\text{Cu}} = 43 \text{ S cm}^2 \text{ mol}^{-1}$  in DMF. UV–Vis,  $\lambda_{\text{max}}/\text{nm}$ , ( $\epsilon/\text{l mol}^{-1} \text{ cm}^{-1}$ ) in DMF: 267 (12 420), 291 (12 050), 632 (104). FTIR (KBr,  $\text{cm}^{-1}$ ): 3423 ( $\nu_{\text{O–H}}$ ); 1613 ( $\nu_{\text{C=N}}$ ); 1550, 1478, 1444 ( $\nu_{\text{C=C}}$ ,  $\nu_{\text{C=N}}$ (py ring)); 1089 and 627 ( $\nu_{\text{Cl–O}}$ ).

### 2.2. Materials and physical measurement

All reagents were of analytical grade, purchased from different sources, and used without further purification. The following abbreviations were used: *2imH-epy* or *4imH-epy* = 2(4)-[[(imidazol-2-ylmethylidene)amino]ethyl]pyridine, diimine ligands derived from the condensation of 2- or 4-imidazolecarboxaldehyde with 2-(aminoethyl)pyridine. Elemental analyses were performed at the *Central Analítica* of our Institution, using a Perkin–Elmer 2400 CHN Elemental Analyzer. Optical absorbance spectra were recorded with a Shimadzu UV-1601PC spectrophotometer, with thermostated 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 (9.35 GHz), using standard Wilmad quartz tubes, at room temperature or at 77 K. DPPH ( $\alpha, \alpha'$ -diphenyl- $\beta$ -

picrylhydrazyl) was used as frequency calibrant ( $g = 2.0036$ ) for powder samples and  $[\text{Cu}(\text{edta})]^{2+}$  solutions (1.00 mmol dm<sup>-3</sup>) were used as standard for frozen solutions. Infrared spectra of the complexes obtained were recorded in a BOMEM 3.0 instrument, in the range 4000–400 cm<sup>-1</sup>, using KBr pellets. The temperature dependence of the magnetic susceptibility of polycrystalline samples was measured between 1.8 and 290 K at a field of 500 Oe using computer-controlled SQUID magnetometer. Diamagnetic correlations were made using Pascal's constants. The mass spectrometric measurements were performed using a high resolution hybrid quadrupole (Q) and orthogonal time-of-flight (ToF) mass spectrometer (QqToF from Micromass, UK) operating in the positive ion electrospray ionization mode. Sample solutions were introduced into the electrospray source using the syringe pump of the instrument at a flow rate of 8  $\mu\text{L min}^{-1}$ ; the ESI source operates at 3.5 kV, the temperature of the nebulizer was set at 200 °C and cone voltage at 20 V. The He pressure inside the trap was kept constant. The tandem mass (MS/MS) spectra were acquired using the product ion scan mode via Q1 mass-selection of the singly charged complex. Those collision-induced dissociations (CID) were performed with N<sub>2</sub>, at 15 eV energy in Q2, and high-resolution orthogonal ToF mass analysis of the corresponding CID ionic fragments.

### 2.3. Catalytic oxygenation studies

The catalyzed oxidation of 3,5-di-*tert*-butylcatechol 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  $\pm$  0.5) °C, in a mixture of methanol/aqueous carbonate buffer (50 mM, pH 9.61), following the formation of the corresponding quinone at 390 nm. Kinetic experiments were carried out using the polynuclear complexes **3** and **4** as catalyst in the same concentration of copper centres. The sequential additions of reagents in quartz cell were: carbonate buffer solution (2.0 ml); methanolic solution of the catalyst (0.12 ml,  $4.98 \times 10^{-5} \text{ mol dm}^{-3}$ ), followed by the addition of 3,5-di-*tert*-butylcatechol (0.38 ml;  $7.60 \times 10^{-4} \text{ mol dm}^{-3}$ ) in methanolic solution.

## 3. Results and discussion

### 3.1. Syntheses

The mono- and polynuclear copper(II) complexes with unsymmetrical tridentate ligand 2- or 4-[[[(imidazol-2-ylmethylidene)amino]ethyl]pyridine were prepared by standard methods with minor suitable modifications [5a]. When the precursor mononuclear complexes **1** and **2** are treated with an excess of triethylamine, the deprotonation of the imidazole moiety promotes self-assembly by

coordination of the imidazolate nitrogen atom to a Cu(II) centre in an adjacent unit, leading therefore to two isomeric species with different structural orientations around the binding site of the imidazole ring, that is, a polymeric complex with an infinite zig-zag-chain **3** or a cyclic-tetranuclear complex **4** (Scheme 1). IR and Raman spectroscopy have been used to verify the deprotonation of the NH group in the imidazole ring on forming these polynuclear species, by monitoring the characteristic band around  $3150\text{ cm}^{-1}$  [15]. Characteristic absorptions of aliphatic  $\text{NH}_2$  and  $\text{C}=\text{O}$  groups were not observed in the IR spectra of **3** and **4**, as expected. A strong band around  $1620\text{ cm}^{-1}$  was assigned to the characteristic  $\nu(\text{C}=\text{N})$ . IR spectra exhibited also medium-to-strong bands around  $1600$  and  $1440\text{ cm}^{-1}$  as expected for the pyridine-ring vibrations. For **4**, the IR spectrum shows additional bands at  $1089$  and  $627\text{ cm}^{-1}$ , characteristic of non-coordinated perchlorate ions [16].

The measured molar conductivities of **1** and **2** were  $212$  and  $241\text{ S cm}^2\text{ mol}^{-1}$  in water, and  $42$  and  $52\text{ S cm}^2\text{ mol}^{-1}$  in DMF, respectively, indicating that these complexes behave as 1:2 electrolytes in water and as neutral species in DMF [17]. In the solid-state, two  $\text{Cl}^-$  anions are bonded to the Cu(II) ion as confirmed by the X-ray analyses of **1**, previously described by Colacio et al. [18], and our results attested the lability of  $\text{Cl}^-$  ligands in aqueous solution for both complexes.

For the polymeric species, the molar conductivity for compound **3**,  $A_{\text{Cu}} = 103\text{ S cm}^2\text{ mol}^{-1}$  in water, indicated that the dissociation into the corresponding cationic 1:1 compound,  $[\text{CuL}(\text{H}_2\text{O})]_n\text{Cl}_n$ , occurred. For the cyclic compound, the corresponding value  $A_{\text{Cu}} = 43\text{ S cm}^2\text{ mol}^{-1}$  was measured in DMF, owing to its low solubility in water, and also confirmed a 1:1 ratio of perchlorate to copper ions,  $[\text{Cu}_4\text{L}_4](\text{ClO}_4)_4$ .

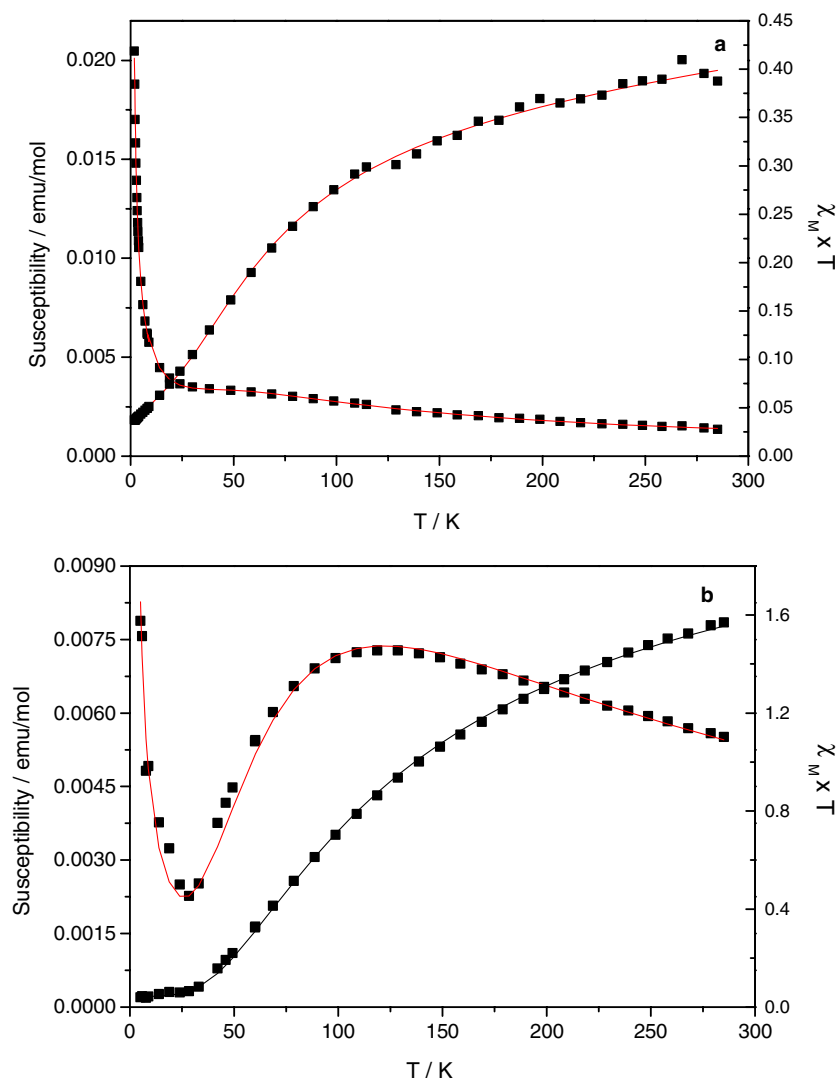


Fig. 1. Temperature dependence of the magnetic susceptibility,  $\chi_M$ , for the polynuclear compounds **3** (a) and **4** (b), in the range 1.80–290 K.

### 3.2. Magnetic properties and EPR spectra studies

The magnetic susceptibilities of **3** and **4** were measured under a 500 Oe applied magnetic field, in the temperature range of 1.80–290 K, as shown in a plot  $\chi_M$  vs. absolute temperature  $T$  (Fig. 1), where  $\chi_M$  is the magnetic susceptibility per copper. These  $\chi_M$  vs.  $T$  plots show maxima at 68 and 118 K for **3** and **4**, respectively, clearly indicating some antiferromagnetic interaction between the metal centres for both species.

For **3**, the magnetic susceptibility data were analyzed according to Eq. (2), based on the Bonner and Fisher model for a one-dimensional infinite-chain structure for which  $J < 0$ , and where the spin Hamiltonian is defined as  $H = -2\sum J_{ij}S_iS_j$  and  $K = J/kT$  [7].

$$\chi_0 = (N\beta^2g^2/12kT)(\exp(4K) + (2 + K^{-1})\exp(2K) - K^{-1}\exp(-2K) + 5)/(\exp(2K) + \exp(-2K) + 2). \quad (1)$$

Usually, a temperature independent contribution to the magnetic susceptibility is also present. This contribution includes a paramagnetic and a diamagnetic constant contribution of the ligands and anions, and the introduction of a temperature independent term  $N\alpha$ . The small temperature dependent paramagnetic contribution of free monomers, proportional to  $1/T$  (with concentration  $p \ll 1$ ), that may also be present in the sample has to be included in the expression of  $\chi_0$ . Therefore, the susceptibility after correction with these two terms is expressed by

$$\chi_M = \chi_0(1 - p) + [N\beta^2g^2/2kT]p + N\alpha. \quad (2)$$

The magnetic parameters which gave the best fit were  $J = -(32.4 \pm 1.2) \text{ cm}^{-1}$ ,  $g = 2.03$ ,  $\rho = 0.03$  and  $N\alpha = 165 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ . Similar results have been reported previously for the same linear polynuclear complex **3** [18].

For the novel complex **4**, the magnetic susceptibility data were interpreted quantitatively by Eq. (3) considering a cyclic-tetranuclear structure [6], where the spin Hamiltonian is defined as  $H = -2J(S_1S_2 + S_2S_3 + S_3S_4 + S_4S_1)$  and  $K = J/kT$ .

$$\chi_M = (N\beta^2g^2/kT)((0.25 + 0.14995K + 0.30094K^2)/(1 + 1.9862K + 0.68854K^2 + 6.0626K^3))(1 - \rho) + \rho(N\beta^2g^2/2kT) + N\alpha. \quad (3)$$

In this case, the best fit parameters were  $J = -(55.5 \pm 0.4) \text{ cm}^{-1}$ ,  $g = 2.29$ ,  $\rho = 0.02$  and  $N\alpha = 432 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ . The magnitude of the  $J$  exchange integral is compatible with similar tetra- and hexanuclear cyclic complexes described by Matsumoto et al. [5a], containing 4-[(2-substituted-imidazol-ylmethylidene)amino]ethylpyridine tridentate ligands, where the 2-substituent is a methyl ( $J = -54.7 \text{ cm}^{-1}$ ) or a phenyl

group ( $J = -45.7 \text{ cm}^{-1}$ ), respectively. As expected, the moderate antiferromagnetic coupling obtained for **4** can be explained by the nature of the 2-imidazole substituent at this specific position, where steric hindrance is minimum when compared with similar species, included in a Schiff base ligand at 4-position [5a]. This magnetic behaviour for the different tetra- and hexanuclear imine-copper(II) complexes shows the importance of the bonding angle between Cu–N (imidazole) and N–N (imidazole) vectors, that are affected by dihedral angles between the copper coordination plane and the imidazole plane, as a function of the least steric hindrance around the ligand acting as a bridge. In addition, the difference verified between the species **3** ( $J = -32.4 \text{ cm}^{-1}$ ) and **4** ( $J = -55.5 \text{ cm}^{-1}$ ) for the amplitude of the antiferromagnetic interaction can also be ascribed to the diversity in the bonding angle, since these  $J$  values suggest that an imidazolate group bridges two copper ions at their equatorial positions in a square pyramidal geometry, in both compounds.

To further investigate the nature of the magnetic coupling, EPR measurements of the corresponding

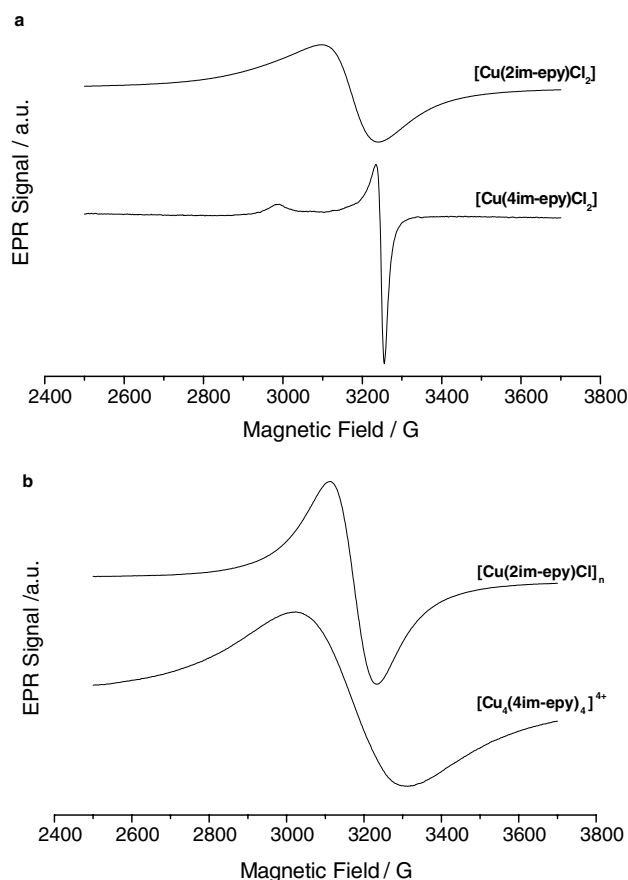


Fig. 2. EPR spectra of the mono- and polynuclear species in solid state, at 77 K. (a)  $[\text{Cu}(2\text{imH-epy})\text{Cl}_2]$  (**1**) (gain =  $2.00 \times 10^2$ ) and  $[\text{Cu}(4\text{imH-epy})\text{Cl}_2]$  (**2**) (gain =  $6.32 \times 10^3$ ); (b)  $[\text{Cu}(2\text{im-epy})\text{Cl}]_n$  (**3**) (gain =  $4.48 \times 10^3$ ) and  $[\text{Cu}_4(4\text{im-epy})_4](\text{ClO}_4)_4$  (**4**) (gain =  $4.48 \times 10^3$ ).



mono- and polynuclear complexes were carried out in solid and frozen methanol/water (4:1, v/v) solutions, at 77 K, to further investigate the nature of the magnetic coupling. In the solid state, a  $g_{\text{iso}} = 2.106$  was calculated

for complex **3**, exhibiting a zig-zag structure. Preliminary data in solution indicated [15a] a very similar  $g_{\text{iso}}$  value (2.110) for **3**, but for the cyclic tetranuclear complex **4** a hyperfine structure was observed (see Fig. 1 in [15a]),

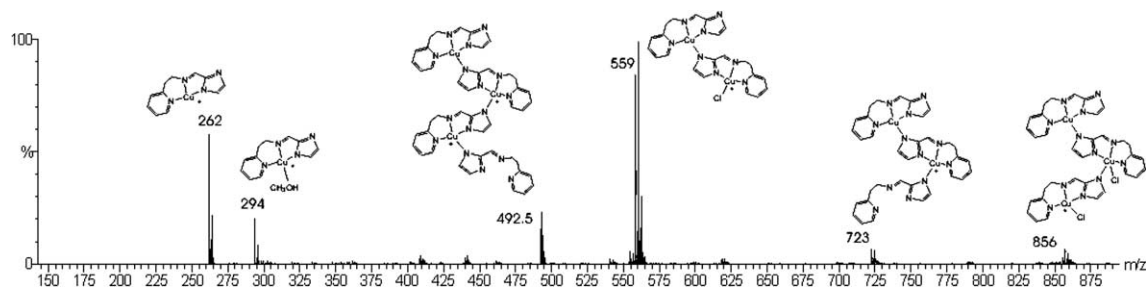
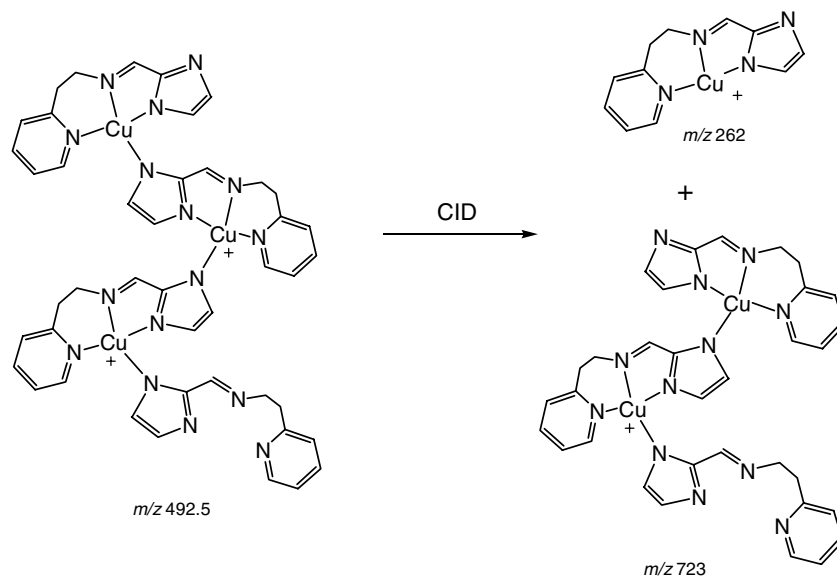


Fig. 3. ESI mass spectrum in the positive ion mode of a methanolic solution of  $[\text{Cu}(\text{2im-epy})\text{Cl}]_2$  (**3**).



Scheme 2. Dissociation patterns for the doubly charged ion of  $m/z$  492.5 from ESI of **3**.

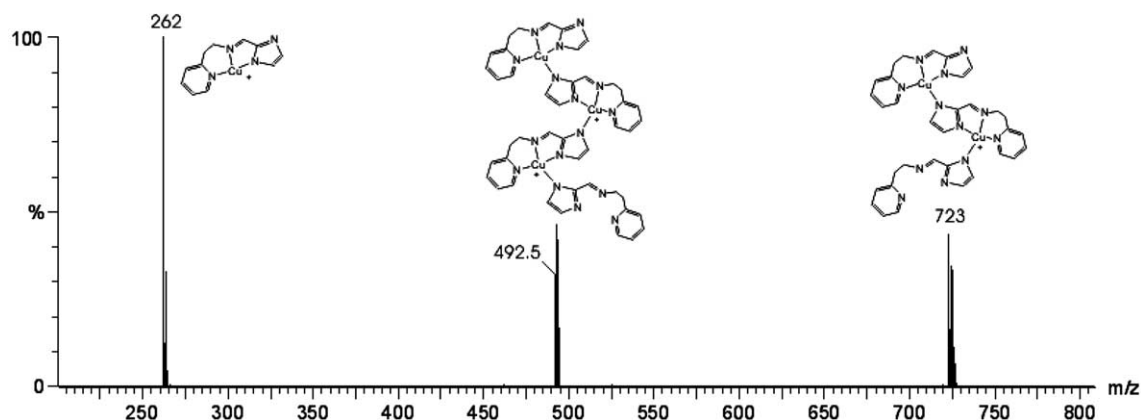
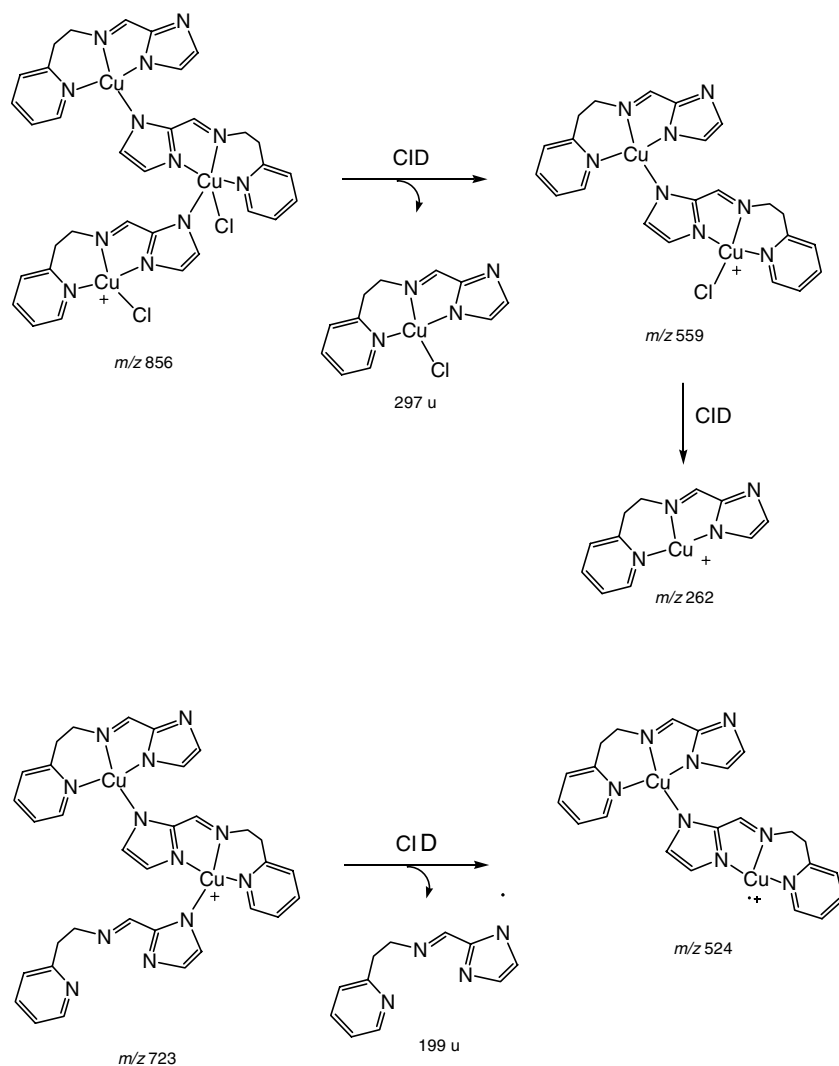


Fig. 4. Product ion ESI tandem mass spectrum for CID of the ion of  $m/z$  492.5.

probably due to a little monomeric fraction also present in solution. However, an analogous hyperfine structure could not be observed for the polymeric **3**, in spite of

the presence of a small amount of the corresponding mononuclear species **1** as a paramagnetic impurity, probably due to the broadened signals from both



Scheme 3. Dissociation patterns for the singly charged ions of  $m/z$  856 and 723 from ESI of **3**.

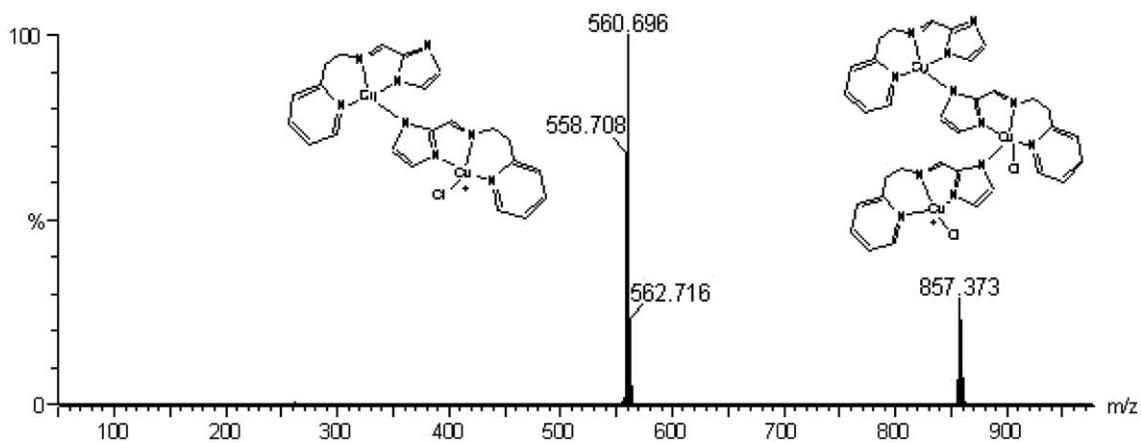


Fig. 5. Product ion ESI tandem mass spectrum for CID of the ion of  $m/z$  856.

dipolar and exchange interactions [19]. This dipolar interaction is easily verified when comparing the spectra in the solid state of both **1** and **3** (Fig. 2). For **1**, the line shape is more consistent with a dipolar interaction ( $g_{\text{iso}} = 2.109$ , and line width = 140 G), whereas for **3** the line width (123 G) lies between the exchange-narrowed and the dipolar broadened limits.

EPR spectra for **2** in the solid state are very similar both at room temperature and at 77 K, and are characteristic of a copper(II) mononuclear complex with axial symmetry, exhibiting  $g_{\perp} = 2.059$  and  $g_{\parallel} = 2.236$ . In frozen methanol/water solution, this complex exhibits a further hyperfine structure, with  $g_{\perp} = 2.065$ ,  $g_{\parallel} = 2.274$ , and  $A_{\parallel} = 180 \times 10^{-4} \text{ cm}^{-1}$  [15a]. The absence of hyperfine structure in the solid state is due to intermolecular interactions, provided by the  $\text{ClO}_4^-$  ions. However, for both mononuclear complexes **1** and **2**,  $\Delta M_S = 2$  transitions characteristic of the dimeric intermolecular association in solid state due to triplet state splitting were not observed. The very broad signal for tetranu-

clear complex **4** in the solid state ( $g_{\text{iso}} = 2.103$  and line width = 284 G) is, however, a result of higher  $J$  value and zero-field splitting, since the last interaction is responsible for the increasing in the anisotropy as a function of the magnetic field applied, and the decreasing of the relaxation time [20].

### 3.3. Mass spectrometry analysis

Population of gas phase ions generated by ESI often closely reflects that in solution. Hence, we used ESI-MS to verify the solution and gas phase stability of the polynuclear complexes **3** and **4**, and to structurally characterize such isomeric thermally labile complexes via ESI-MS and collision-induced dissociation (CID) in tandem mass spectrometry (ESI-MS/MS) experiments.

The ESI mass spectrum of a methanolic solution of **3** (Fig. 3) in the positive ion mode is structurally enlightening, since it displays a series of characteristic singly

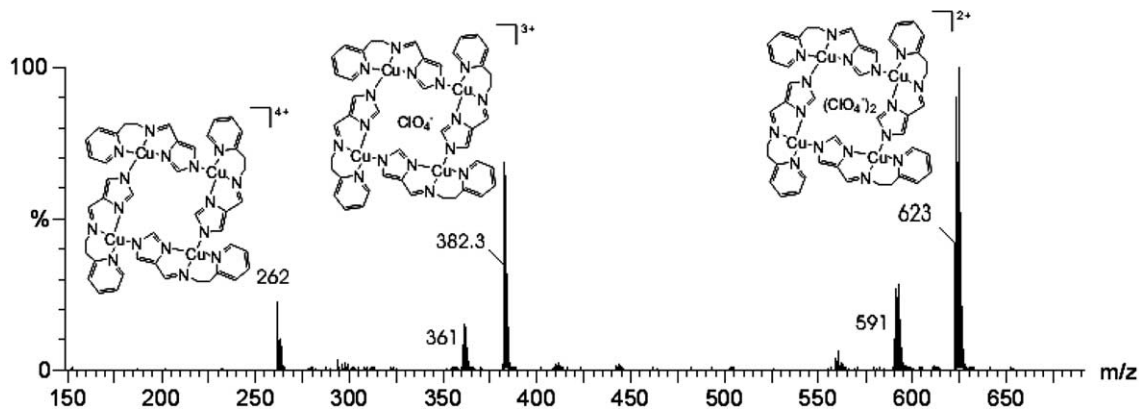


Fig. 6. ESI mass spectrum in the positive ion mode of a methanol solution of  $[\text{Cu}_4(4\text{im-epy})_4](\text{ClO}_4)_4$  (**4**).

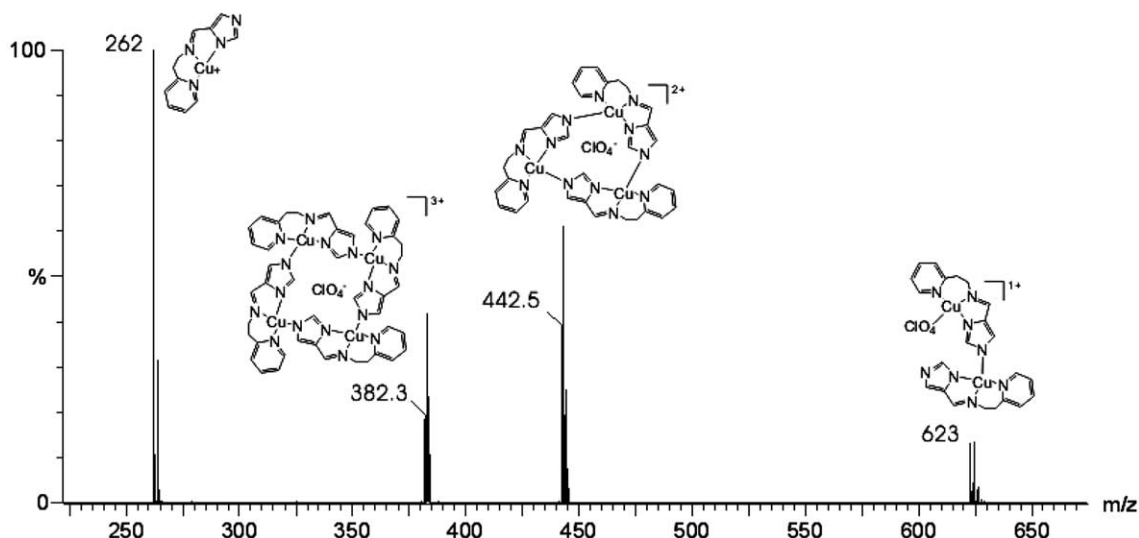


Fig. 7. Product ion ESI tandem mass spectrum for CID of the ion of  $m/z$  382.3.



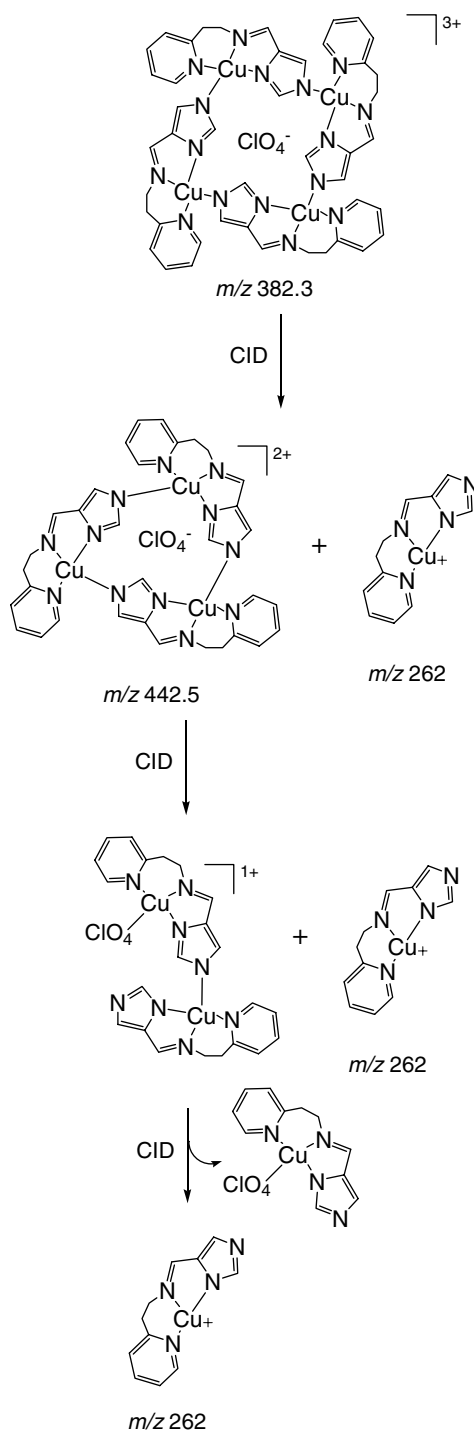
charged ions of  $m/z$  262, 294, 559, 723, and 856 ( $m/z$  ratios refer to the lightest isotopologue ions containing for instance  $^{63}\text{Cu}$  and  $^{35}\text{Cl}$  lightest isotopes) and a doubly charged ion of  $m/z$  492.5 (with characteristic peak separation of  $1/2m/z$  units) that can directly relate to ions formed upon ionization in the methanolic solution of the neutral polymeric structure **3**. The structural assignments for such ions, shown as insets in Fig. 3, are supported both by their characteristic isotopic distributions particularly affected by the presence of copper ( $^{63}\text{Cu}$ : $^{65}\text{Cu}$  of 1:0.44) and chlorine atoms ( $^{35}\text{Cl}$ : $^{37}\text{Cl}$  of 1:0.33), by accurate mass measurements (not shown), and by ESI-MS/MS experiments. For instance, the doubly charged ion of  $m/z$  492.5 dissociates, as easily rationalized, by a “charge-partitioning” route [21] to form two ionic fragments of  $m/z$  262 and 723 (Scheme 2) following heterolytic breaking of the labile Cu–N bond (Fig. 4). The singly charged ion of  $m/z$  856 dissociates nearly exclusively by the loss of a neutral species of 297 u (Scheme 3) to form the ion of  $m/z$  559 (Fig. 5). The ion of  $m/z$  723 dissociates then mainly by the loss of a neutral species of 199 u to form the ion of  $m/z$  524, whereas that of  $m/z$  559 dissociates to yield mainly the ion of  $m/z$  262 (Scheme 3).

The ESI mass spectra for the tetranuclear isomer **4** (Fig. 6) are also unique and structurally enlightening. The quadruply charged ion of  $m/z$  262 is observed as a very minor ion. Owing to the high charge state of **4**, gaseous species are formed mainly by association with the  $\text{ClO}_4^-$  counter-ion, that is:  $[\mathbf{4} + \text{ClO}_4]^{3+}$  of  $m/z$  382.3 and  $[\mathbf{4} + (\text{ClO}_4)_2]^{2+}$  of  $m/z$  623. The minor ions of  $m/z$  361,  $[\mathbf{4} + \text{Cl}]^{3+}$ , and  $m/z$  591  $[\mathbf{4} + \text{Cl} + \text{ClO}_4]^{2+}$  are formed by association with residual  $\text{Cl}^-$ . The structural assignments for such ions, shown as insets in Fig. 6, are also supported both by their characteristic isotopic distributions particularly affected by the presence of copper ( $^{63}\text{Cu}$ : $^{65}\text{Cu}$  of 1:0.44) and chlorine atoms ( $^{35}\text{Cl}$ : $^{37}\text{Cl}$  of 1:0.33), by accurate mass measurements, and by ESI-MS/MS experiments. For instance, the tetramer triply charged ion of  $m/z$  382.3 (Fig. 7) dissociates, as easily rationalized, by two sequential “charge-partitioning” processes [10c] that form the singly charged monomer of  $m/z$  262 and the doubly charged trimer of  $m/z$  442.5, which then dissociates in turn to the same singly charged monomer of  $m/z$  262 and the dimer of  $m/z$  623 (associated with the counter-ion). The ion of  $m/z$  623 dissociates in turn by neutral loss (Scheme 4) to also form the monomer of  $m/z$  262. This dissociation pattern is corroborated by the ESI tandem mass spectra (not shown) of the ions of  $m/z$  442.5 and 623.

### 3.4. Catalytic oxygenation

Our previous studies involving dinuclear complexes with imidazole-bridged ligands have shown that they can act as good mimics of tyrosinase [15b]. Those

complexes, as well as their corresponding tetranuclear species were able to efficiently oxidize phenol and catechol substrates to the analogous quinones. In this context, the catalytic activity of the polynuclear complexes **3** and **4** in the oxidation of 3,5-DTBC by molecular oxygen was carried out in methanol-aqueous solutions containing carbonate buffer (50 mM,



Scheme 4. Fragmentation patterns for the gaseous  $[\mathbf{4} + \text{ClO}_4]^{3+}$  triply charged ion of  $m/z$  382.3.

pH 9.61), monitored by the absorption band of the corresponding quinone formed, at 390 nm. This substrate is the most widely used in the literature, owing to its low redox potential, and its bulky substituents with difficult ring opening via oxidation [22]. An alkaline buffered solution was used, since polynuclear species containing imidazolate-bridged ligands are very stable in these conditions [5a,15c]. Preliminary studies have shown, however, a pH dependence of the non-catalytic oxidation of the 3,5-DTBC, when the rate of quinone formation is increased by the facilitated coordination of the substrate to the Cu(II) centres [21]. However, in our experiments the non-catalyzed substrate autoxidation in basic solution is negligible, in comparison with the catalyzed steps by the polynuclear complexes studied.

The experimental rate law indicates a first order dependence on the catalyst, and a first order dependence followed by a saturation effect on the substrate concentration, for both the complexes, as shown in Fig. 8.

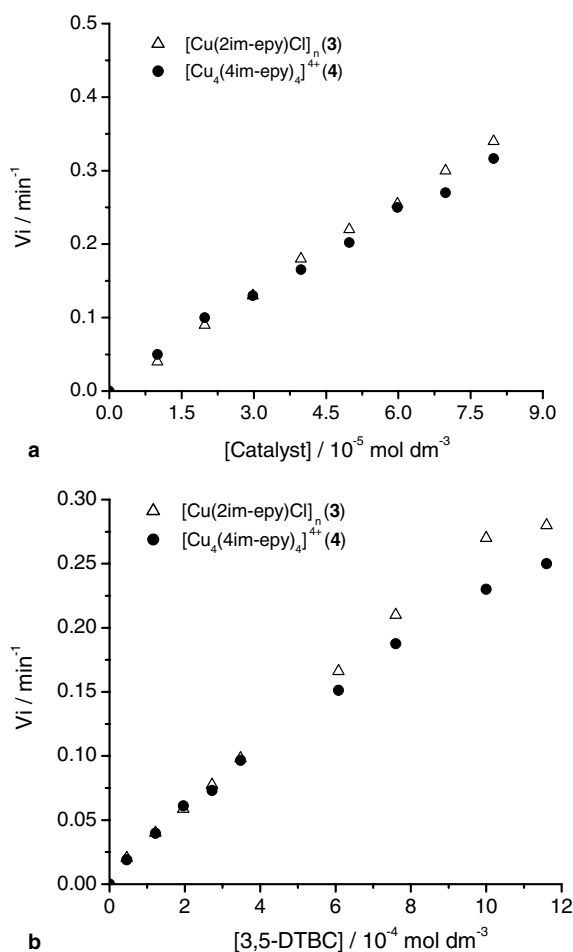


Fig. 8. Initial reaction rate versus catalyst and substrate concentrations, for the catalyzed oxidation of 3,5-DTBC by complexes **3** and **4**, at  $(25.0 \pm 0.5)^\circ\text{C}$ . (a)  $[\text{catalyst}] = 4.98 \times 10^{-5} \text{ mol dm}^{-3}$ , and (b)  $[\text{3,5-DTBC}] = 7.60 \times 10^{-4} \text{ mol dm}^{-3}$ .

Table 1

Kinetic parameters determined in the 3,5-DTBC oxidation catalysed by polynuclear copper(II) complexes

Compounds	$k_{\text{cat}}$ , $\text{min}^{-1}$	$K_{\text{M}}$ , $\text{mol dm}^{-3}$	$k_{\text{cat}}/K_{\text{M}}$ , $\text{mol}^{-1} \text{ dm}^3 \text{ min}^{-1}$
$[\text{Cu}(\text{2im-epy})\text{Cl}]_n$ ( <b>3</b> )	$5.81 \times 10^3$	$6.37 \times 10^{-4}$	$9.12 \times 10^6$
$[\text{Cu}_4(\text{4im-epy})_4]^{4+}$ ( <b>4</b> )	$5.80 \times 10^3$	$6.65 \times 10^{-4}$	$8.73 \times 10^6$

Applying the Michaelis–Menten approach, the kinetic behaviour was characterized using the parameters  $k_{\text{cat}}$ ,  $K_{\text{M}}$ , and  $k_{\text{cat}}/K_{\text{M}}$  (see Table 1). The obtained values for the complexes **3** and **4** do not differ significantly, showing that the zig-zag species ( $k_{\text{cat}}/K_{\text{M}} = 9.12 \times 10^6 \text{ mol}^{-1} \text{ dm}^3 \text{ min}^{-1}$ ) is a little better catalyst than the cyclic one ( $k_{\text{cat}}/K_{\text{M}} = 8.73 \times 10^6 \text{ mol}^{-1} \text{ dm}^3 \text{ min}^{-1}$ ). A steric match between the substrate and the copper centres seems to be a determining factor in the reactivity, since the coordination of catechol as a bridging ligand between two copper atoms is an essential condition for a fast two-electron transfer. In this case, the tetranuclear complex has a geometry with difficult interactions with the substrate inside the cavity, as supported by minimized structures obtained using MM<sup>+</sup> module within the HyperChem program, version 5.1. A gradient of  $1 \times 10^{-5} \text{ kcal \AA}^{-1} \text{ mol}^{-1}$  was used as a convergence criterion in a conjugate gradient algorithm. So, these interactions seem to occur predominantly at the outside of the catalyst framework. In fact, the  $K_{\text{M}}$  values show a differentiation in the substrate binding interaction to form an adduct with the metal complex. A larger value indicates that formation of a bridged catecholate for **4** is more difficult than for **3** [23]. However, the very similar  $k_{\text{cat}}$  values verified suggest the same efficiency in the electron transfer from bound catechol substrate to the copper ions, probably due to quite similar redox potentials.

#### 4. Conclusions

Two different polynuclear imine-copper(II) complexes were prepared by a self-assembly process, with very different structural orientations. Depending on the binding site in the imidazole ring, a polymeric complex with an infinite zig-zag-chain **3** or a cyclic-tetranuclear complex **4** was isolated. These species were obtained as chloride and perchlorate salts, respectively, and characterized in the solid state by their magnetic properties, in the range 1.8–290 K, as well as in frozen solution by EPR spectroscopy, in addition to UV/Vis and IR spectra.

Unique and structurally enlightening ESI mass and tandem mass spectra were acquired for each compound, in which singly and multiply charged gaseous ions that are characteristic for both **3** and **4** were clearly detected and characterized. Further, catalytic data in the

oxidation of 3,5-di-*tert*-butylcatechol showed that both compounds **3** and **4** are efficient catalysts, with kinetic parameters quite similar, although having very different sterical characteristics, indicating that probably the interactions in **4** between the metal centres and the substrate occur outside the molecular framework.

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