Inorganica Chimica Acta 400 (2013) 184-190

Contents lists available at SciVerse ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica



Spectrophotometric determination of the formation constants of the cupric halogen complexes with 1,3-propanediamine and 1,4-butanediamine in methanol solution and their activity on the oxidative coupling of the 2,6-di-*tert*-butylphenol



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ARTICLE INFO

Article history: Received 9 August 2012 Received in revised form 24 December 2012 Accepted 13 February 2013 Available online 27 February 2013

Keywords: Copper(II) complexes Catalysis Oxidative coupling Speciation Solution equilibrium Non-aqueous solvents

ABSTRACT

In order to understand the effect that diamine ligands induce in the cupric complexes used as catalyst in the oxidative coupling of 2,6-di-*tert*-butylphenol, a spectrophotometric study of the speciation of copper(II) with 1,3-propanediamine and 1,4-butanediamine both with Cl⁻ or Br⁻ in methanol solution, was carried out at 303 K. The formation constants and the individual calculated electronic spectra of each species in methanol solution were obtained. The obtained formation constants for the copper(II)–1,3-propanediamine system are: log $\beta_{110} = 6.70 \pm 0.06$, log $\beta_{120} = 11.59 \pm 0.09$, while for the ternary-chloro or - bromo complexes are log $\beta_{111} = 10.23 \pm 0.06$ and log $\beta_{111} = 10.39 \pm 0.02$, respectively. On the other hand, for the copper(II)–1,4-butanediamine system are log $\beta_{110} = 7.44 \pm 0.04$, log $\beta_{210} = 11.07 \pm 0.04$, log $\beta_{120} = 11.86 \pm 0.05$, log $\beta_{230} = 22.53 \pm 0.09$, though for the ternary systems copper(II)–1,4-butanediamine-chloro or –bromo, the formation constants cannot be determined.

A comparative study of the kinetics for the oxidation reaction of 2,6-di-*tert*-butylphenol, catalyzed using the different cupric complexes with 1,3-propanediamine or 1,4-butanediamine and –chloro or – bromo, has been carried out. The catalytic activity of each complex on the oxidation of 2,6-di-*tert*-butylphenol was monitored in methanol solution, following the corresponding quinone formation, at 418 nm (ε = 3.95 × 10⁴ L mol⁻¹ cm⁻¹ at 303 K). These kinetic studies indicate that all the copper(II)–1,4-butanediamine complexes, show a remarkable high activity, while the complexes with 1,3-propanediamine are less active although much more active than 1,2-ethylenediamine complexes.

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1. Introduction

After the discovery of the oxidative coupling of 2,6-di-methylphenol by Hay [1], it was found that this reaction generate two products, the poly(2,6-dimethyl-1,4-phenylene oxide) as the main product and the 3,3',5,5'-tetra-methyl-4,4'-dibenzoquinone as a byproduct. The poly(2,6-dimethyl-1,4-phenylene oxide), has a very important industrial application, when blended with polystyrene the noryl resin is obtained [2]. This reaction can be carried out in several solvents such as methanol, benzene, 1,2-di-chloro-benzene and many others [1,3]. Several paths have been proposed to the oxidative coupling of 2,6-di-methylphenol, although the mechanism which drives this reaction is not well understood [2,4].

The copper complexes used as catalysts for the oxidative polymerization of 2,6-di-methylphenol were diverse; starting with the CuCl/pyridine system. Later, a wide variety of copper complexes, with diamines as ligands: diethylamine, di-*n*-butylamine, N,N,N',N'-tetramethylethylenediamine, N,N'-di-isopropyl-ethylendiamine, N,N'-di-*tert*-amylethylenediamine, and N,N'-di-*tert*-butylethylenediamine; were tested, being this last ligand, the one used for the synthesis of the patented copper catalyst [2,5].

The solution system containing the copper complex with this amine and bromide, is presumably the best catalytic system for this reaction [2,5]. Several studies postulate that the copper complex can be activated if binds a dioxygen species and create a peroxodicopper complex [6,7]; from this idea, some research groups have considered that the oxidative coupling is catalyzed by a biomimetic binuclear copper species (tyrosinase- or laccase-like active site) [4,6–8]. However, other groups, consider that a mononuclear copper complex is capable to form the active species for this reaction [4,9].

The ligand design of the copper catalyst for this reaction, has been extensively discussed, nevertheless, after 50 years of



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^{0020-1693/\$ -} see front matter © 2013 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.ica.2013.02.021

intensive research, the reasons why the *N*,*N*'-di-*tert*-butylethylenediamine is so active, remains unknown, and the catalytic copper active species for this reaction is not yet elucidated [4,9]. More studies are required in order to understand why *N*,*N*'-di-*tert*-butylethylenediamine presents higher activity.

Our interest is to understand how the copper complex works in the oxidative coupling of the 2,6-di-*tert*-butylphenol system. By using this system as a model of the polymerization of 2,6-di-methylphenol, we expect, it will allow us to understand the catalytic properties of the copper complex, and eventually, obtain a better knowledge of the role of the copper complex in the oxidative coupling formation of the polymer. Hopefully, this will let us find several ways to improve the activity. Finding better ligands with a lower cost represent a significant task with an immediate industrial application.

A review of equilibrium constants for the copper(II) complexes with 1,3-propanediamine and 1,4-butanediamine under several conditions in water is presented in Table 1. Apparently, the stability of the copper–1,3-propanediamine complexes increase as the ionic strength growths. Of course temperature plays an important role as well and as expected an increase in temperature decreases the stability of the complex. On the other hand, the copper–1,3propanediamine protonated complex, has a high stability value, this can be linked to the rich electron environment of the complex. At the opposite, the hydroxide complex has a very low stability value. Also, this last behavior is observed for the copper–1,4-butanediamine complexes.

In this work, we report the formation constants in methanol of the copper complexes with 1,3-propanediamine and 1,4-butanediamine, and their respective halogen ternary complexes, in order to determinate the predominant species of these systems and correlate these with their kinetic behavior in the coupling reaction. In this study, we suggest that the intermediary species of the oxidative coupling reaction is affected by the chain carbon size in the diamine. This is the second part of a study initiated to explore the nature of the copper complexes and their catalytic oxidation capabilities in the oxidative coupling reaction. In our first study, we explain how the copper(II)–1,2-ethylenediamine catalytic system was affected by the formation of the halide ternary complexes [10].

Table 1

Comparison of the stability constants of the copper(II) complexes with 1,3-propanediamine and 1,4-butanediamine under several conditions.

Complex	$\log \beta$	Ionic strength/ salt	Solvent	Reference
$[Cu(pn)]^{2+}$ $[Cu(pn)_2]^{2+}$	11.65, 0 °C 10.78, 25 °C 21.77, 0 °C 20.06, 25 °C	0.5 (KNO ₃)	Water/dioxane (1:1)	[27]
[Cu(pn)] ²⁺ [Cu(pn) ₂] ²⁺	10.58 19.66	0.5 (KNO ₃)	Water	[26]
$[Cu(pn)]^{2+}$ $[Cu(pn)_2]^{2+}$	9.85 17.18	0.15 (NaClO ₄)	Water	[25]
$\begin{array}{l} [{\rm CuH}({\rm pn})]^{3+} \\ [{\rm Cu}({\rm pn})]^{2+} \\ [{\rm Cu}({\rm pn})_2]^{2+} \\ [{\rm Cu}({\rm pn})_2({\rm OH})]^{1+} \\ [{\rm Cu}({\rm pn})_3]^{2+} \end{array}$	15.78 9.68 16.79 2.04 21.66	0.1 (NaClO ₄)	Water	[14]
$[CuH(bn)]^{3+}$ $[Cu(bn)]^{2+}$ $[Cu(bn)_2]^{2+}$ $[Cu(bn)_2(OH)]^{1+}$	15.83 8.62 13.40 0.065	0.1 (NaClO ₄)	Water	[13,15]

2. Experimental

2.1. Materials

Methanol spectrophotometric and HPLC grade (Tecsiquim, Mexico) were used as purchased as solvent for the formation constant determination and the kinetic studies, respectively. $Cu(NO_3)_2 \cdot 3H_2O$, sodium chloride and sodium bromide (J.T. Baker); 1,3-propanediamine, 1,4-butanediamine and 2,6-di-*tert*-butylphenol (Sigma–Aldrich), were analytical grade, and used without further purification. Due to problems with the solubility presented with several counterions, no ionic strength salt was employed.

2.2. Spectrophotometric equilibrium studies

An HP-8453 UV–Vis spectroscopy system, equipped with a HP-89090A Peltier temperature-controlled cell holder was employed in the spectral studies, with a standard quartz cell with 1 cm optical length and 3 mL volume at 303 K, each run was made by triplicate. The determination of the formation constants was performed refining the spectrophotometric data with the program HYPERQUAD [11]. The observed spectral region was from 450 to 950 nm for all the experiments.

2.3. Copper(II)-1,3-propanediamine equilibrium studies

Experiments were performed using two different stock solutions of 1,3-propanediamine (0.0478 and 0.0956 M). $Cu(NO_3)_2 \cdot 3H_2O$ was used to prepare copper stock solutions (0.0318 M and 0.0636 M). The 1,3-propanediamine concentrations were varied from 0.0005 to 0.0096 M and 0.0001 to 0.0191 M, respectively, in each experiment. The final copper concentration was set constant at 0.0032 and 0.0064 M, respectively. A total of 39 spectra were used for the refinement in HYPERQUAD.

2.4. Copper(II)–1,3-propanediamine-chloride and copper(II)–1,3propanediamine–bromide equilibrium studies

In this case, two stock solutions of 1,3-propanediamine (0.0478 and 0.0956 M), Cu(NO₃)₂·3H₂O (0.0318 and 0.0636 M) and sodium chloride or sodium bromide (0.0154 and 0.0308 M) were prepared. For both experiments, the final copper concentration was set constant at 0.0032 and 0.0064 M and the 1,3-propanediamine at 0.0034 and 0.0067 M, respectively. The halide concentrations were varied from 0.0002 to 0.0031 M, and 0.0003 to 0.0062 M, respectively. The number of obtained spectra for the system copper(II)–1,3-propanediamine–chloride and –bromide were 30 and 39, respectively, and all were used for the refinement in HYPERQUAD.

2.5. Copper(II)–1,4-butanediamine equilibrium studies

Experiments were performed using three different stock solutions of 1,4-butanediamine (0.0397, 0.0793 and 0.1500 M). $Cu(NO_3)_2 \cdot 3H_2O$ was used to prepare copper stock solutions (0.0378, 0.0757 and 0.0753 M). The 1,4-butanediamine concentrations were varied from 0.0004 to 0.0079, 0.0008 to 0.0159 and 0.0015 to 0.0301 M, respectively, in each experiment. The final copper concentration was set constant at 0.0038, 0.0076 and 0.0075 M, respectively. Although several attempts were made to obtain the formation constants of the copper(II)–1,4-butanediamine–halogen complexes, however due to the very small absorbance changes observed in the spectrum when an halide is added, it was not possible to obtain a reliable value of these formation constants with this method and therefore is not possible to assure if the halide is coordinated to the copper center. The total

number of spectra obtained and employed for the HYPERQUAD refinement was 45.

2.6. Catalytic oxidation studies

All kinetic runs were performed at 303 K, in methanol solution, using pseudo-first-order conditions for the copper complex (1:255). The formation of 3,3',5,5'-tetra-*tert*-butyl-4,4'-dibenzoquinone, at 418 nm ($\epsilon = 3.95 \times 10^4$ L mol⁻¹ cm⁻¹) was followed spectrophotometrically. Stock solutions of Cu(NO₃)₂·3H₂O, 1,3-propanediamine or 1,4-butanediamine, sodium chloride or sodium bromide were prepared separately at the same concentration (0.0225 M); 2,6-di-*tert*-butylphenol was prepared at 0.0229 M. Aliquots of each reactive were used in order to obtain a final concentration of 0.00003 M for the corresponding catalyst and 0.0077 M for the substrate. At least three runs were averaged for each experiment. In order to compare these results with those published earlier [10,12], we have been employed the same concentrations.

3. Results and discussion

In this study, it is essential to avoid the use of ionic strength in all the equilibrium determinations, for if the ionic strength is adjusted with either PF_6^- , ClO_4^- or NO_3^- salts; early precipitation of the copper complexes occurs. This means of course, that the formation constants obtained here, should not be considered as thermodynamic stability constants. In order to compare the data obtained here with our last study [10] we have kept essentially the same conditions in these experiments.

The ligands **bn** (1,4-butanediamine) and **pn** (1,3-propanediamine) have been studied coordinated to copper(II), in water under several conditions and the stability constants reported [13–15]. The synthesis and some spectroscopic and crystallographic studies of several copper(II)–1,3-propanediamine complexes have been reported as well [16–24]. There are no reports about **pn** or **bn** as part of the copper(II) catalyst in the oxidative coupling of 2,6-di-*tert*butylphenol.

3.1. Formation constants of the copper(II)–1,3-propanediamine and copper(II)–1,3-propanediamine–halogen complexes

Copper(II)–1,3-propanediamine complexes have been studied in aqueous systems, at several ionic strengths. The existence of the complexes $[Cu(pn)_2]^{2+}$, $[Cu(pn)_2]^{2+}$ or $[Cu(pn)_3]^{2+}$ with their respective formation constants have been reported at ionic strength of 0.1 (NaClO₄) [14]; 0.15 (NaClO₄) [25]; 0.5 (KNO₃) [26]; and in a water/dioxane (1:1) system with ionic strength of 0.5 (KNO₃) [27]. However, in non-aqueous systems, these complexes have been less studied, and there are no reports concerning the formation constants of these complexes in methanol. On the other hand, several studies points out that in some alcoholic solutions, when the ligand to metal molar ratio is higher than 2, the $[Cu_2(pn)_5]^{4+}$ is generated [16,25,24].

The electronic spectra of the methanol solutions of copper(II)– 1,3-propanediamine are available as Supplementary material in Fig. S1. For this system, a maximum at 791 nm starts to appear at low ligand concentration, and as the 1,3-propanediamine concentration increases, a hyperchromic effect was observed with a hypsochromic change up to 559 nm.

The determination of the formation constants β_{jkl} , corresponding to the successive equilibrium between Cu²⁺ and 1,3-propanediamine, was made by processing all the obtained spectra of the two experiments at high and low concentrations simultaneously and takes into account a large array of data. The observed absorbance values at different wavelengths were recorded at 303 K. Considering that only two colored species plus Cu²⁺ were found, the formation constants calculation was achieved using this model:

$$\operatorname{Cu}^{2+} + \operatorname{pn} \rightleftharpoons \left[\operatorname{Cu}(\operatorname{pn})\right]^{2+} \quad \log \beta_{110} \tag{1}$$

$$\operatorname{Cu}^{2+} + 2pn \rightleftharpoons \left[\operatorname{Cu}(pn)_2\right]^{2+} \quad \log \beta_{120} \tag{2}$$

The logarithmic values of the formation constants and the summary of the experimental parameters are reported in Table 2, according to the format suggested by the IUPAC Tuck [29].

The reported values for the stability constants in aqueous systems [14] are usually higher than those reported in pure methanol, in addition, the formation of the tris-1, 3-propanediamine-cupric complex is not observed in methanol under the conditions employed in this study, probably due to the fact that methanol is

Table 2

Summary of experimental parameters for the system: copper(II)-1,3-propanediamine and copper(II)-1,3-propanediamine-halogen complexes in methanol.

Solution com	position	$ \begin{bmatrix} T_L \end{bmatrix} \text{ range from 0.0} \\ 0.0096 \text{ mol } L^{-1} \text{ and} \\ 0.0001 \text{ to } 0.0191 \text{ m} \\ \begin{bmatrix} T_M \end{bmatrix} \text{ constant at} \\ 0.0032 \text{ mol } L^{-1} \text{ and} \\ 0.0064 \text{ mol } L^{-1} \\ \text{ lonic strength,} \\ electrolyte \\ pH \text{ range} \\ \end{bmatrix} $	005 to l from nol L ⁻¹ Not used Not used
Experimental method		Spectrophotometric titration. Spectrophotometer calibrated with holmium oxide glass filters [36]	
Temperature	of data acieta	30 °C	20
Nothed of col		solution spectra	
		HYPERQUAD [11]	_
species	Equilibrium	LOg β	σ
[Cu(pn)] ²⁺ [Cu(pn) ₂] ²⁺	$Cu^{2*} + pn \rightleftharpoons [Cu(pn)]^{2*}$ $Cu^{2*} + 2 pn \rightleftharpoons [Cu(pn)_2]^{2*}$	Log $\beta_{110} = 6.70 \pm 0.06$ Log $\beta_{120} = 11.59 \pm 0.09$	0.0399
Solution com	position	$ \begin{array}{l} [T_{\rm X}] \mbox{ range from 0.0} \\ 0.0031 \mbox{ mol } L^{-1} \mbox{ and } 0.00031 \mbox{ mol } L^{-1} \mbox{ and } 100032 \mbox{ mol } L^{-1} \mbox{ mol } L^$	002 to l from lol L ⁻¹ Not used Not used
Experimental method		Spectrophotometric titration. Spectrophotometer calibrated with holmium oxide glass filters [36]	
Temperature Total number of data points		30 °C Cu-ligand to halide complexation: 30 solution spectra for chloride ion and 39 solution spectra for bromide ion	
Method of ca	culation	hyperquad [11]	
[Cu(pn)Cl] ⁺	$\mathrm{Cu}^{2+} + \mathrm{pn} + \mathrm{Cl}^- \rightleftharpoons [\mathrm{Cu}(\mathrm{pn})\mathrm{Cl}]^{1+}$	Log $\beta_{111} = 10.23 \pm 0.06$	0.0274
[Cu(pn)Br] ⁺	$Cu^{2*} + pn + Br^{-} \rightleftharpoons [Cu(pn)Br]^{1+}$	Log $\beta_{111} = 10.39 \pm 0.02$	0.2618

better nucleophile than water [30,31], the formation of the superior complexes is less favored.

When an equimolar solution of cupric nitrate and 1,3-propanediamine in methanol is made, the $[Cu(pn)]^{2+}$ complex has about 80% formation relative to copper, as can be seen below. In order to study the ternary system of copper(II)–1,3-propanediamine–halide, we employed the equimolar Cu:pn concentrations, where the $[Cu(pn)]^{2+}$ complex has the highest formation percentage, varying the halide concentration.

The observed electronic spectra of the copper(II)–1,3-propanediamine–chloride and –bromide solutions are also available as Supplementary material in Figs. S2 and S3, respectively. For the copper(II)–1,3-propanediamine–chloride system, a maximum at 643 nm appears at low chloride ion concentration, as the chloride ion concentration increases, a hyperchromic/bathochromic effect is observed in the region near to 665 nm. For the copper(II)–1,3propanediamine–bromide system, a maximum at 665 nm appears at low bromide ion concentration, when bromide ion concentration increases, the hyperchromic and bathochromic effect also appears at 665 nm.

The determination of the formation constants β_{jkl} , corresponding to the successive equilibriums between copper, 1,3-propanediamine and each halide were made using the same methodology as described above.

The observed absorbance values at different wavelengths were recorded at 303 K, considering that one additional colored species was found plus Cu^{2+} , $[\text{Cu}(\text{pn})]^{2+}$ and $[\text{Cu}(\text{pn})_2]^{2+}$ the determination of the formation constants was achieved using the next model:

$$\operatorname{Cu}^{2+} + \operatorname{pn} + \operatorname{Cl}^{-} \rightleftharpoons [\operatorname{Cu}(\operatorname{pn})\operatorname{Cl}]^{+} \quad \log \beta_{111} \tag{1}$$

$$Cu^{2+} + pn + Br^{-} \rightleftharpoons [Cu(pn)Br]^{+} \quad \log \beta_{111}$$
(2)

The logarithmic values of the formation constants are presented in Table 2. The calculated electronic spectra for the $[Cu(pn)]^{2+}$ display an absorption maximum at 658 nm with $\varepsilon = 67.29 \text{ L mol}^{-1}$ cm⁻¹, while the complex $[Cu(pn)Cl]^+$ exhibit a maximum at 672 nm with $\varepsilon = 91.79 \text{ L mol}^{-1} \text{ cm}^{-1}$, and the complex $[Cu(pn)Br]^+$ at 677 nm with $\varepsilon = 207.56 \text{ L mol}^{-1} \text{ cm}^{-1}$. The $[Cu(pn)Br]^+$ has a greater extinction coefficient than the complex $[Cu(pn)Cl]^+$, probably due to the fact that bromide ion is a softer base than chloride ion, this is consistent with the expected higher charge transfer from the bromide ion coordinated to the copper. Finally, $[Cu(pn)_2]^{2+}$ reveal an absorption maximum at 569 nm with $\varepsilon = 123.05 \text{ L mol}^{-1}$ cm⁻¹. The calculated electronic spectra of the copper(II)–1,3-propanediamine complexes are presented in Fig. S4 and the –chloro and –bromo complexes, in Fig. S5, respectively.

3.2. Distribution curves of the copper(II)–1,3-propanediamine and copper(II)–1,3-propanediamine–halogen complexes

The speciation diagrams of the copper(II)–1,3-propanediamine, copper(II)–1,3-propanediamine–chloride and the copper(II)–1,3-propanediamine–bromide systems are shown in Fig. 1, Fig. 2 and Fig. 3, respectively. A solution with equimolar concentration of copper(II) and 1,3-propanediamine (at 0.0032 M or 0.0064 M, for low and high concentration experiments, respectively), roughly yields 80% of the copper(II)–1,3-propanediamine complex and less than 20% of the mixture of free copper and the *bis* complex. Yet having two molar equivalents of 1,3-propanediamine per copper generates virtually 100% of the *bis* complex.

According to Fig. 2 and Fig. 3, solutions with equimolar concentrations of copper(II), 1,3-propanediamine and sodium chloride or copper(II), 1,3-propanediamine and sodium bromide (at 0.0032 M or 0.0064 M, for low and high concentrations, respectively), generates around 71% and 78% of the copper-1-3-propanediamine-



Fig. 1. Formation curves of the copper(II)–1,3-propanediamine complexes in methanol. $[Cu]^{2+} = 0.0064 \text{ M}$ and 1,3-propanediamine range from 0.0010 to 0.0191 M.



Fig. 2. Formation curves of the copper(II)–1,3-propanediamine–chloro complexes in methanol, $[Cu]^{2+} = 0.0064 \text{ M}$, [1,3-propanediamine] = 0.0067 M and sodium chloride range from 0.0003 to 0.0061 M.

chloro and copper-1-3-propanediamine-bromo complex, respectively. In both systems, when the halide concentration is increased more than one molar equivalent per copper, both systems become insoluble, suggesting that when the second halide gets into the coordination sphere a neutral species is formed. This neutral complex precipitates immediately, the same behavior was observed in the copper(II)-1,2-ethylenediamine-halide system reported before [10].

3.3. Formation constants of the copper(II)–1,4-butanediamine complexes

The copper(II)–1,4-butanediamine system has been scarcely studied, and there are just a few examples reported of copper(II)–1,4-butanediamine complexes in aqueous systems, where the existence of the complexes $[Cu(bn)]^{2+}$ and $[Cu(bn)_2]^{2+}$ with



Fig. 3. Formation curves of the copper(II)–1,3-propanediamine–bromo complexes in methanol. $[Cu]^{2+} = 0.0064 \text{ M}$, [1,3-propanediamine] = 0.0067 M and sodium bromide range from 0.0003 to 0.0061 M.

their respective formation constants of log β_{110} = 8.62 and log β_{120} = 13.40, had been established [13–15]. Even so, in non-aqueous solvents, the copper–1,4-butanediamine system has been even less studied, and to our knowledge, there are no reports concerning the formation constants of copper(II)–1,4-butanediamine complexes in methanol.

The electronic spectra of copper(II)–1,4-butanediamine solutions are available as Supplementary material in Fig. S6. For this system, a maximum at 776 nm appears at low ligand concentration. As the 1,4-butanediamine concentration increases, also a hyperchromic effect was observed with a hypsochromic change to 589 nm. The determination of the stepwise formation constants β_{jkl} , corresponding to the successive equilibriums between Cu²⁺ and 1,4-butanediamine, takes into account a large array of data and was made using all spectra at low an high concentrations simultaneously, the observed absorbance values at different wavelengths were recorded at 303 K. Four additional colored species plus Cu²⁺ were identified and the evaluation of the formation constants was achieved using the next model:

$$\mathbf{C}\mathbf{u}^{2+} + \mathbf{b}\mathbf{n} \rightleftharpoons \left[\mathbf{C}\mathbf{u}(\mathbf{b}\mathbf{n})\right]^{2+} \quad \log \beta_{110} \tag{1}$$

$$\mathbf{Cu}^{2+} + 2\mathbf{bn} \rightleftharpoons \left[\mathbf{Cu}(\mathbf{bn})_2\right]^{2+} \quad \log \beta_{120} \tag{2}$$

$$2Cu^{2+} + bn \rightleftharpoons [Cu_2(bn)]^{4+} \quad \log \beta_{210} \tag{3}$$

$$2\mathrm{Cu}^{2+} + 3\mathrm{bn} \rightleftharpoons [\mathrm{Cu}_2(\mathrm{bn})_3]^{4+} \quad \log \beta_{230} \tag{4}$$

The logarithmic values of the formation constants and the summary of the experimental parameters are reported in Table 3. The reported values for the stability constants are higher in aqueous systems [13–15] than in pure methanol. This can be explained in terms of the nucleophilic character of the methanol [28,30,31]. Low values for the formation constants in methanol denote that the ligand has to compete with stronger bonded solvent molecules.

The calculated electronic spectra for the $[Cu(bn)]^{2+}$ has an absorption maximum at 655 nm with $\varepsilon = 51.84 \text{ L mol}^{-1} \text{ cm}^{-1}$, while the complex $[Cu_2(bn)]^{4+}$ has a maximum at 722 nm with $\varepsilon = 91.09 \text{ L mol}^{-1} \text{ cm}^{-1}$, and the complex $[Cu(bn)_2]^+$ at 584 nm with $\varepsilon = 86.31 \text{ L mol}^{-1} \text{ cm}^{-1}$. Finally, the $[Cu_2(bn)_3]^{4+}$ has the absorption maximum at 595 nm with $\varepsilon = 150.45 \text{ L mol}^{-1} \text{ cm}^{-1}$. The $[Cu_2(bn)_3]^{4+}$ has a greater extinction coefficient because the amount

Table 3

Summary of experimental parameters for the system copper(II)-1,4-butanediamine complexes in methanol.

Solution composition		$[T_{L}]$ range from 0.0004 to 0.0079, 0.0008 to 0.0159 and 0.0015 to 0.0301 mol L ⁻¹ $[T_{M}]$ constant at 0.0038, 0.0076 and 0.0075 mol L ⁻¹	
		electrolyte	used
		pH range	Not
		1 0	used
Experimental method		Spectrophotometric titration. Spectrophotometer calibrated with holmium oxide glass filters [36]	
Temperature		30 °C	
Total number	of data points	Cu complexation: 45 s spectra	olution
Method of ca	lculation	HYPERQUAD [11]	
Species	Equilibrium	Log β	σ
$[Cu(bn)]^{2+}$ $[Cu(bn)_2]^{2+}$	$Cu^{2^{+}} + bn \Rightarrow [Cu(bn)]^{2^{+}}$ $Cu^{2^{+}} + 2bn \Rightarrow [Cu(bn)_2]^{2^{+}}$	$\begin{array}{l} \text{Log } \beta_{110} = 7.44 \pm 0.04 \\ \text{Log} \\ \beta_{120} = 11.86 \pm 0.05 \end{array}$	0.0423
$[Cu_2 (bn)]^{4+}$	$2\mathrm{Cu}^{2^{+}} + \mathrm{bn} \rightleftharpoons [\mathrm{Cu}_2(\mathrm{bn})]^{4^{+}}$	Log $\beta_{210} = 11.07 \pm 0.04$	
$[Cu_2(bn)_3]^{4+}$	$2Cu^{2*} + 3bn \rightleftharpoons [Cu_2(bn)_3]^{2*}$	Log $\beta_{230} = 22.53 \pm 0.09$	

of copper atoms per molecule. The calculated spectra are shown in Fig. S7.

3.4. Distribution curves of the copper(II)–1,4-butanediamine complexes

The distribution diagram of copper(II)-1,4-butanediamine complexes is exhibited in Fig. 4. A solution with a molar equivalent of copper and a half molar equivalent of 1.4-butanediamine (at 0.0038 and 0.0019 M or 0.0075 and 0.0038 M or 0.0076 and 0.0038 M. respectively, for low, medium and high concentration) yields about 80% of the [Cu₂(bn)]⁴⁺ complex and 10% of a mixture of free copper and $[Cu(bn)]^{2+}$. An equimolar solution of copper(II) and 1,4-butanediamine (at 0.0038, 0.0075 or 0.0076 M, for low, medium and high concentrations, respectively), roughly yields 45% of the copper(II)–1,4-butanediamine complex and about 25% of $[Cu_2(bn)]^{4+}$ and $[Cu_2(bn)_3]^{4+}$ each, the remaining 5% of copper is a mixture of Cu^{2+} and $[Cu(bn)_2]^{2+}$. Having two molar equivalents of 1,4-butanediamine per copper (at 0.0038 and 0.0076 M, 0.0075 and 0.01507 M or 0.0076 and 0.0152 M, respectively, for low, medium and high concentration) generates almost 70% of the [Cu₂ $(bn)_3$ ⁴⁺ complex and about 15% of a mixture of $[Cu(bn)]^{2+}$ and $[Cu(bn)_2]^{2+}$ each. Yet having three molar equivalents of 1,4-butanediamine per copper generates virtually 100% of the bis complex.

The formation of binuclear copper(II)–1,4-butanediamine complexes in methanol has been not reported yet. In the studies of this system in water [13–15], the binuclear complex was not detected. This can be explained considering that a solvent with a low dielectric constant, such as methanol, stabilizes the ionic pairs required for the binuclear complex, while in water, with a high dielectric constant, the necessary ionic pairs are not formed and this may prevent that the second copper coordinate to the 1,4-butanediamine ligand. Further studies should be completed in order to corroborate this hypothesis and explain the type of solvent environment that requires the binuclear complexes to be generated. From the ligands employed in this work and the previous study, it is clear that increasing the diamine chain up to increase the affinity of the ligand for the copper. As the ligand chain increases, the formation constants increase, for the monocomplexes



Fig. 4. Formation curves of the copper(II)–1,4-butanediamine complexes in methanol. $Cu^{2+} = 0.0076$ M and 1,4-butanediamine range from 0.0015 to 0.0301 M.

 $[Cu(en)]^{2+}$ (6.13), $[Cu(pn)]^{2+}$ (6.7) and $[Cu(bn)]^{2+}$ (7.44). For the *bis*-complexes, same behavior can be observed for $[Cu(en)_2]^{2+}$ (10.54), $[Cu(pn)_2]^{2+}$ (11.59) and $[Cu(bn)_2]^{2+}$ (11.86).

The observed tendency in the formation constants for the three copper(II)-diamine complexes, is not what should be expected in terms of the chelate effect for a ring size. However a possible explanation can be suggested considering first that methanol is better nucleophile than water, and on the other hand, bearing in mind that increasing the ligand chain from two to three and to four carbons increases the conformational flexibility of the ligands [17–19].

Then taking into account both phenomena together, this is, that the rate of solvent exchange (k_{exch}) of Cu in water is at least two orders of magnitude faster than that of methanol (water $k_{exch} \approx$ 10^{10} s⁻¹; methanol $k_{exch} = 10^7$ s⁻¹ [28,31]), and at the same time conformational flexibility increases from 1,2-ethanodiamine to 1,3-propanediamine to 1,4-butanediamine, is possible to suggest that both effects contribute to compensate the changes in the geometry and have in consequence increasing the stability of the copper(II)-1,4-butanediamine complex. The first having more stable conformations for the larger ring, and the second allowing the best conformational arrangement to take place.

3.5. Catalytic oxidation studies

The catalytic activity of the copper(II)–1,3-propanediamine, copper(II)–1,3-propanediamine-halogen and copper(II)–1,4-butanediamine systems in the oxidative coupling of 2,6-di-*tert*-butylphenol to 3,3',5,5'-tetra-*tert*-butyl-4,4'-dibenzoquinone was measured at 418 nm (a typical run is available as Supplementary material in Fig. S8). All kinetic runs were stopped at approximately 2.3 of absorbance, values higher than this, the Lambert–Beer law fail, and the molar absorbance of the 3,3',5,5'-tetra-*tert*-butyl-4,4'-dibenzoquinone is no longer linear. At this absorbance value the converted quinone has a concentration of about 1.75 × 10⁻⁷ M and the oxygen solubility in methanol is roughly 10.3 × 10⁻³ M [32], showing that the oxygen is not depleted.

Several solutions were tested: a equimolar mixture of copper(II) and 1,3-propanediamine (at 0.00003 M) generate $[Cu(pn)]^{2^+}$ with 80% abundance, $[Cu(pn)_2]^{2^+}$ and free Cu²⁺, each with 10% abundance; a solution with an equimolar mixture of copper(II), 1,3-propanediamine and sodium chloride (at 0.00003 M), with 71% of $[Cu(pn)Cl]^+$, 17% of $[Cu(pn)]^{2^+}$ and less than 10% of $[Cu(pn)_2]^{2^+}$

and copper(II)-halogen complexes; a solution with an equimolar mixture of copper(II), 1,3-propanediamine and sodium bromide (at 0.00003 M), with 78% of $[Cu(pn)Br]^+$, 15% of $[Cu(pn)]^{2+}$ and less than 10% of $[Cu(pn)_2]^{2+}$ and copper(II)-halogen complexes.

We also test an equimolar mixture of copper(II) and 1,4-butanediamine (at 0.00003 M), with 45% of the complex $[Cu(bn)]^{2+}$, about 26% of $[Cu_2(bn)]^{4+}$ and $[Cu_2(bn)_3]^{4+}$ each, and about 2% of Cu^{2+} and $[Cu(bn)_2]^{2+}$; a mixture of 1 M equivalent of Cu(II) and two molar equivalent of 1,4-butanediamine (at 0.00003 and 0.00006 M, respectively), with 67% of $[Cu_2(bn)_3]^{4+}$, 16.5% of $[Cu(bn)]^{2+}$ and $[Cu(bn)_2]^{2+}$ each; a mixture of 1 M equivalent of 1,4-butanediamine and 2 M equivalent of Cu(II) (at 0.00003 and 0.00006 M, respectively), with 78% of $[Cu_2(bn)]^{4+}$, 11% of free copper and 11% of $[Cu(bn)]^{2+}$; and finally a mixture of 3 M equivalent of 1,4butanediamine and 1 M equivalent of Cu(II) (at 0.00009 and 0.00003 M, respectively), with 94% of $[Cu(bn)_2]^{2+}$, and 6% of $[Cu_2(bn)_3]^{4+}$.

Fig. 5 presents the kinetics runs of each of the mixtures of this work and those obtained in our previous work. From these experiments, it is clear that increasing the length of the carbon chain of the amine from 2 to 4 carbons increase the rate of the coupling reaction. Addition of the halide also increases the rate of the reaction. On the other hand, as the amount of the amine is increased (this is, as the concentration of the *bis* complex increase) decrease the activity. This means that the *bis* complex is less active that the corresponding mono complex. This effect is possibly related to the steric hindrance in these complexes. Then the presence of the second ligand, may prevent the substrate molecule approach close to the copper catalytic site, weakening the interaction with the phenol molecule, decreasing the activity. This effect is not quite clear in the case of the 1,4-butanediamine probably due to the fact that the mono complex is less abundant than in the other two amines.

Then, it is clear that the 1,2-ethylenediamine complexes have a very slow catalytic rate, while the 1,3-propanediamine is four times faster; the 1,4-butanediamine is 11 times faster. The tendency observed on the activity growth may be related to an increase in the conformational flexibility of the complex, this also can be observed in those complexes containing halogen. Apparently, conformational flexibility has been evaluated only in the case of the *bis*-1,3-propanediamine cupric complexes [17–19].

However, conformational flexibility is a parameter dependant on the size of the ligand and is correlated with a steric control in several catalysts [33–35]. If this is the case then, probably the 1,4-butanediamine ligand may have a greater potential for



Fig. 5. Kinetic curves of the catalyzed oxidation of 2,6-di-*tert*-butylphenol (0.00763 M) at 303 K, in methanol solution, monitored at 418 nm [complex] = 0.00003 M.

processes where significant changes in coordination number and geometry are desired.

The binuclear complex $[Cu_2(bn)]^{4+}$ show a less activity compared with the mononuclear complex, probably due to the mass of the complex, this may reduce the conformational flexibility of the complex. The complex $[Cu_2(bn)_3]^{4+}$ is not so active, this is probably due to an analogous reason to the activity of the binuclear copper(II)-1,4-butanediamine complex.

4. Conclusions

Because no ionic strength was used, the formation constants determined here can only be used when compared to systems measured in similar conditions. The results presented indicate that the catalytic activity is enhanced when the diamine chain is longer, and also when a halide is coordinated. This may be associated with two facts: the size of the chain may induce and help to conserve the active geometry maintaining a better steric control over the substrate and the presence of the halide may help to conserve this active geometry, also may help to charge transference over the mechanism of the catalyst reaction.

While copper (II)–1,3-propanediamine complexes behave in a very similar way to the copper(II)–1,2-ethylenediamine, we find that copper(II)–1,4-butanediamine complexes have very interesting catalytic properties and deserve more studies in order to understand this system. Although, several aspects of the complexes with pn and bn ligands have been covered, some properties remain to be studied. A very important task is to establish how long the ligand chain can be increased before the complexes with di-*tert*-butylethylenediamine and their respective halides as catalyst in oxidative coupling of 2,6-di-*tert*-butylphenol, and compare this activity with the observations made here.

Acknowledgments

The authors thank DGAPA-UNAM for the Postdoctoral grant for J.J.N.S.G. and Facultad de Química-UNAM for financial support on this work.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2013.02.021.

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