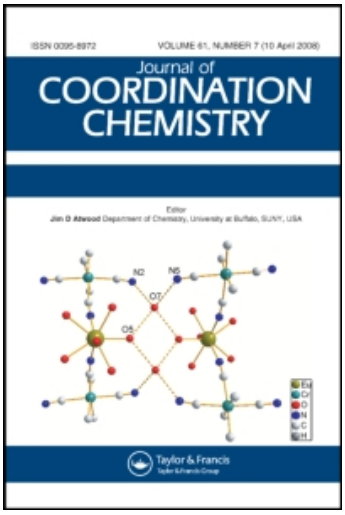


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# Synthesis, complex formation kinetics and thermodynamic study of some acyclic polyamine and $N_2O_2$ ligands with copper(II)

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The polydentate ligands, 3-(2-aminocyclohexylamino)-2-(2-aminocyclohexyl aminomethyl) propionic acid ($\mathbf{L^1}$), 4,7,10-triazatridecanedinitrile trihydrochloride ($\mathbf{L^2}$), and 2,2′-(ethane-1,2-diyl) *bis*(methylazanediyl) diethanol ($\mathbf{L^3}$) were prepared and their structures investigated by FT-IR, NMR, and MS. The kinetics of complex formation between Cu(II) and $L^1$, $L^2$, and $L^3$ were investigated in acidic aqueous solutions using the stopped-flow method. The stability constants of the complexes were determined by spectrophotometric titration ($T = 293\,K$, $\mu = 0.1\,mol\,L^{-1}$ $NaClO_4$), using a diode array UV-Vis spectrophotometer equipped with peristaltic pump and pH meter. The stability constants for the complexes were $CuL^1 > CuL^2 > CuL^3$. Activation enthalpies ($\Delta H\#$) of these complexes were $55\,kJ\,mol^{-1}$ for $CuL^1$, $61\,kJ\,mol^{-1}$ for $CuL^2$, and $36\,kJ\,mol^{-1}$ for $CuL^3$, respectively.

*Keywords*: Complexation; Polyamine; Kinetics; Stability constants; Stopped-flow; Spectrophotometric titration

## 1. Introduction

Polyamines form an important class of compounds due to the roles played by them as polyprotic bases [1], biologically important compounds [2, 3], and sensors for the detection of metal ions and metal ion complexation [4–8]. Metal complexes of polyamine ligands have applications in many areas from coordination chemistry to bioinorganic chemistry. Transition metal complexes of multidentate ligands are used as model systems for many metalloenzymes [9–11], in luminescence sensing, in light-emitting devices, in inter-metallic communication, as a catalyst, in molecular electronics [12, 13], and in coordination polymer chemistry [14].

Copper complexes play an important role in biological systems [15]. Catechol oxidase found in plants is a binuclear copper complex. This enzyme catalyzes the oxidation of catechols with molecular oxygen [16]. There is a deficiency in understanding the

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structures, oxygen activity, and functions in biological systems of many enzymes which contain different numbers of metal centers. Preparation of a synthetic model compound of an enzyme is one method to overcome this deficiency. Preparation of model compounds is important [17, 18] for a better understanding of the behavior of these enzymes.

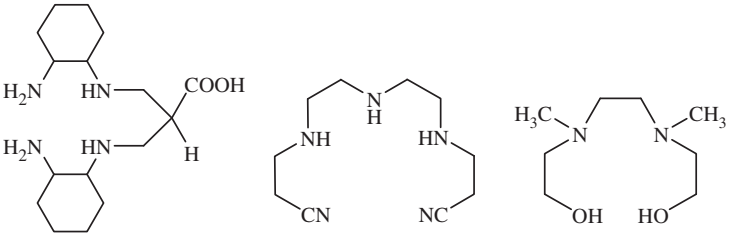
Here, we report the synthesis of $L^1$, $L^2$, and $L^3$ (figure 1) and the kinetics of the complex formation and stability of their copper(II) complexes. Kinetic inertness and thermodynamic stability are important properties of complexes with potential use in biological systems, as catalysts in organic reactions, or as sensors for metal ion recognition and magnetic resonance imaging (as a contrast agent) [15, 19–22]. Although there is a great deal of information available about the stability, kinetics of formation, decomposition, and hydrolysis of mononuclear complexes formed with polyaza ligands, we tried to add some contribution to this field. Therefore, Cu(II) complexes of $L^1$, $L^2$, and $L^3$ were studied, as they can be considered model compounds. In this article, the kinetic and thermodynamic properties of these complexes are reported.



## 2. Experimental

### 2.1. *Chemicals and methods*

All reagents were obtained commercially and used as received. Solvents were purified according to the standard methods prior to use. Mass spectra were measured with a VG Autospec-oa-TOF Mass Spectrometer (ESI). Nuclear magnetic resonance (NMR) spectra were measured with a Varian 300 MHz spectrometer. Elemental analyses were performed on a LECO, CHNO organic element analyzer. Reaction kinetics and spectrophotometric titration were measured with UV-Vis, HP 8453 Diode Array Spectrophotometer, and the Pro-K.2000 Stopped-Flow accessory with pneumatic drive system (Applied Photophysics) for rapid kinetics studies. For the spectrophotometric titration, acid or base solution was added to a 1-cm quartz cell with peristaltic pump (Cole Palmer, Masterflex) and the pH values of the solutions were measured with an Orion pH meter combined with a Metrohm semi-micro electrode. FT-IR spectra were measured with a Perkin Elmer BXII spectrometer.




$L^1$ $L^2$ $L^3$

Figure 1. Structures of ligands.

## 2.2. *Synthesis of ligands*

**2.2.1. Synthesis of 3-(2-aminocyclohexylamino)-2-(2-aminocyclohexylaminomethyl) propionic acid, $L^1 \cdot 4HCl \cdot 2H_2O$.** $L^1$ was prepared by template synthesis from *bis*(cyclohexane-1,2-diamine)copper(II), triethylamine, diethylmalonate, and formaldehyde in methanol. The synthetic pathway followed for $L^1$ is shown in figure 2. An aqueous solution of copper(II)perchlorate hexahydrate (11.28 g, 30.00 mmol) was added to a solution of 1,2-diaminocyclohexane (6.85 g, 60.00 mol) in deionized water (300 mL) on a magnetic stirrer. The reaction mixture was warmed to 50°C, stirred at this temperature for 2 h, and cooled to room temperature and *bis*(cyclohexane-1,2-diamine) copper(II)perchlorate (**1**) was separated by filtering.

Solution of *bis*(cyclohexane-1,2-diamine)copper(II)perchlorate (6.00 g, 12.00 mmol) in 250 mL methanol was heated to 50°C while stirring magnetically and to this solution, triethylamine (6 mL, 43.05 mmol) and diethylmalonate (1.90 mL, 12.00 mmol) were added. Then, a solution of formaldehyde (37% aqueous solution, 3 mL) in methanol (50 mL) was added dropwise to the reaction mixture and the reaction mixture was stirred for 16 h at 50°C. The color of the reaction mixture converted to purple-red during this time. After evaporation of the solvents, the purple-colored crude product was obtained. Five grams of crude product were dissolved in deionized water (250 mL) and the solution was diluted to 2 L with deionized water. Then the solution was passed through a column (35 × 3.5 cm) of SP Sephadex C-25 resin ($Na^+$ form) and the column was eluted with 0.2 mol $L^{-1}$ $NaClO_4$ solution. After a while, two bands, one narrow and one broad, were observed. Both bands were collected. A small amount of macrocyclic compound also formed. The solvent of the acyclic compound was evaporated and the compound was dried. Five milliliters of triethylamine were diluted to 25 mL with deionized water and added to the solution of acyclic compound (3.5 g) in



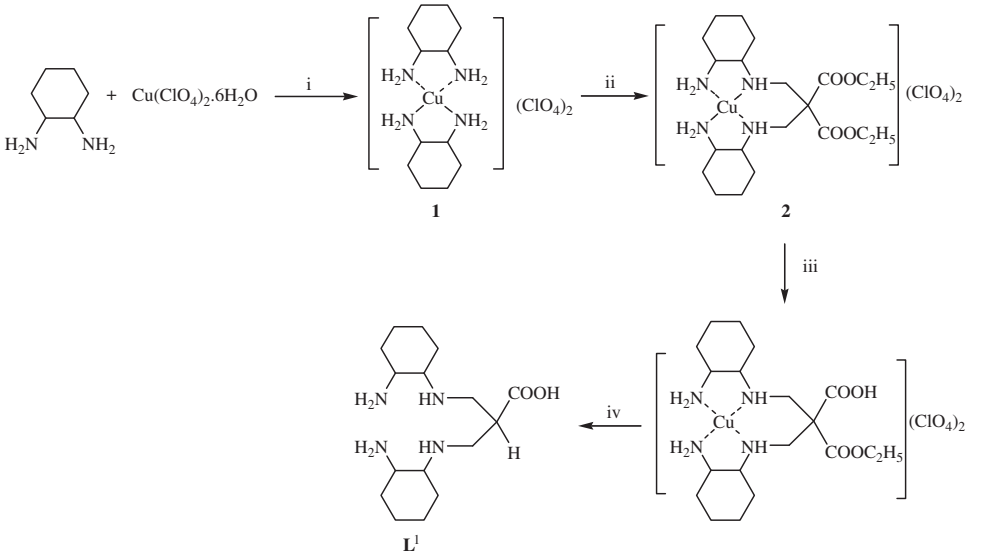



Figure 2. Preparation of $L^1$. Reagents and conditions: (i) $H_2O$, 50°C, 2 h; (ii) $N(C_2H_5)_3$, $CH_2(COOC_2H_5)_2$, $CH_2O$, $CH_3OH$, 50°C, 14 h; (iii) $N(C_2H_5)_3$, $CH_3OH$, 60°C, 12 h; and (iv) Zn, HCl.

methanol (200 mL). The reaction mixture was stirred on a magnetic stirrer at 60°C for 12 h. At the end of this time, the mixture was cooled to room temperature and was diluted to 2 L with deionized water. The diluted solution was passed through a column (35 × 4 cm) of SP Sephadex C-25 resin ($Na^+$ form) and the column was eluted with 0.2 mol $L^{-1}$ $NaClO_4$ solution. The band observed in the column was collected and the solution was concentrated to 300 mL by rotary evaporation. This solution and 3 mol $L^{-1}$ HCl solution were simultaneously added dropwise from dropping funnels over 2 h to Zn powder while stirring on a magnetic stirrer at room temperature. Then, the solution was heated to 50°C and stirred for 30 min. The solution was cooled to room temperature and was filtered on Celite to remove Cu and residual Zn. The clear solution was diluted to 2 L with deionized water and the solution was passed through a column (35 × 3 cm) of Dowex 50 W × 2 resin ($H^+$ form); the column was eluted for a while with deionized water and afterward with 1 mol $L^{-1}$ HCl solution to remove $Zn^{+2}$. Elution continued until no further $Zn^{+2}$ was present (checked by the addition of NaOH solution to the eluant in order to observe $Zn(OH)_2$). After the formation of gelatinous $Zn(OH)_2$, the column was eluted with 3 mol $L^{-1}$ HCl. Evaporation of the solvent by rotary evaporator gave a white crude product and this product was twice recrystallized with hot methanol and $L^1$ was obtained as a white powder ($C_{16}H_{32}N_4O_2 \cdot 4HCl \cdot H_2O$), $L^1$. Yield: 2.1 g, 52%. $C_{16}H_{35}Cl_4N_4O_2 \cdot 4HCl \cdot 2H_2O$ (Calcd C, 38.95; H, 7.97; and N, 11.36) found %: C, 38.79; H, 7.81; and N, 11.44). $^{13}$C-NMR ($D_2O$) 19.26(2C); 19.37(2C); 22.87; 23.09; 26.05(2C);33.67;40.63;41.57;47.44(2C);54.61;56.38;and173.34;*m*/*z*:314($M^+$),FTIR(ATR, $cm^{-1}$): $\nu$(COOH): 2911 vs (br), 2017 m, 1612 s, and 1514 s.

**2.2.2. Synthesis of 4,7,10-triazatridecanedinitrile trihydrochloride, $L^2 \cdot 3HCl$.** 4,7,10-Triazatridecanedinitrile trihydrochloride was synthesized by the condensation of diethylenetriamine (dien) and acrylonitrile according to the literature [23]. Acrylonitrile (3.19 g, 60.00 mmol) was added dropwise to the dien (2.58 g, 25 mmol) while stirring magnetically, and the mixture was stirred for 20 h at room temperature. The crude product was purified as trihydrochloride by recrystallization from methanol/water/HCl and $L^2 \cdot 3HCl$ was obtained as a white powder. Yield: 3.20 g, 40%. $C_{10}H_{19}N_5 \cdot 3HCl$ (Calcd C, 37.69; H, 6.96; and N, 21.98) found %: C, 37.43; H, 7.11; and N, 21.84). $^{13}$C-NMR ($D_2O$) 120.25(2C); 46.87(2C); 46.51(2C); 46.28(2C); and 17.96(2C); *m*/*z*: 210 ($M^+$), FTIR (ATR, $cm^{-1}$): $\nu(NH_3^+)$: 2667, 2435; $\nu$(CN): 2661.

**2.2.3. Synthesis of 2,2′-(ethane-1,2-diyl) bis(methylazanediyl))diethanol, $L^3$.** Ethylene oxide (3.02 g, 60.00 mmol) was added dropwise to a solution of *N*,*N*′-dimethylethylenediamine (2.00 g, 22.68 mmol) in methanol (50 mL) at 0°C, stirred at 0°C for 12 h, and warmed to room temperature; the solvent volume was reduced by a rotary evaporator. The solution was left for crystallization and $L^3$ was obtained as a viscous oil. Yield: 2.7 g, 76%. $C_8H_{20}N_2O_2$ (Calcd C, 38.88; H, 8.16; N, and 11.33) found %: C, 38.79; H, 7.88; N, and 11.28). $^{13}$C-NMR ($D_2O$) 58.58(2C); 58.09(2C); 53.63(2C); and 41.72(2C); *m*/*z*: 176.99 ($M^+$), FTIR (ATR, $cm^{-1}$): $\nu$(OH): 3270.

**2.2.4. Synthesis of copper(II)- $L^1$ complex.** $L^1 \cdot 4HCl$ (0.82 g, 1.35 mmol) and $Cu(ClO_4)_2 \cdot 6H_2O$ (0.5 g, 1.35 mmol) were dissolved in 50 mL water. The pH of the solution was adjusted to 8 with aqueous NaOH (2.5 mol $L^{-1}$) and the solution was

allowed to stir at room temperature overnight. The solution was then diluted to 2 L with water and loaded onto a column of SP-Sephadex (C-25) cation exchange resin ($4 \times 30$ cm). The column was then washed with 1 L of water. Elution with 0.32 mol $L^{-1}$ $NaClO_4$ resulted in two bands. Both bands proved to be stable in acidic solution and were thus identified as being acyclic products. Both solutions were reduced in volume to ~50 mL and then left to stand. Within 24 h, the first solution precipitated a purple solid, which was shown (IR spectrum: 1641 $cm^{-1}$, $COO^-$) to be the deprotonated form. A few days later, the second solution precipitated a pink solid which was shown (IR spectrum: 1711 $cm^{-1}$, COOH) to be the protonated form of the complex. Visible spectra, measured at pH ~10 and then pH ~3, showed identical $\lambda_{max}$, confirming that both products were of the same ligand in different protonation states. The protonated complex was characterized by microanalysis (Found %C, 31.18; %H, 5.4; and %N, 9.5. $C_{16}H_{28}N_4O_8Cl_2Cu \cdot 2H_2O$ requires %C, 31.66; %H, 5.31; and %N, 9.23). Electronic spectrum $\lambda_{max}$ ($H_2O$, pH 7) 260, 530 nm.

### 2.3. *Kinetics*



Complex formation kinetics of Cu(II) complexes with $L^1$, $L^2$, and $L^3$ were followed under second-order conditions (1.2 mmol ligand and metal concentrations) at four different temperatures with the combination of an Agilent HP 8453 Diode Array UV-Vis spectrophotometer and Pro-K.2000 rapid kinetics system with pneumatic drive system. The kinetics mode of the HP was used with activated external trigger. Global kinetic analysis and simulation software were used for kinetic data analysis. A 1-cm quartz cell was used in the kinetic measurements, thermostated ±0.1°C using an external circulating water bath. Measurements were made at multiple wavelengths and kinetics traces were acquired at all wavelengths. Argon-saturated deionized water was used in the kinetic study. Each kinetic run was repeated at least three times. Ionic strength of the solutions was adjusted with 0.1 mol $L^{-1}$ $NaClO_4$. All the kinetic measurements were followed by a UV-Vis spectrophotometer with stopped-flow accessory in the $\lambda_{max}$ of the absorption peak (table 1). Figure 3 shows the typical 3-D spectral changes and 3-D residue at a pH of 4.00 and 0.1 mol $L^{-1}$ ionic strength for the formation of $CuL^1$.

### 2.4. *Spectrophotometric titrations*

Stability constants of the complexes were measured with an automatic titration setup, consisting of a computer interfaced to the Agilent HP 8453 Diode Array

Table 1. Maximum absorbance peaks for the complex formation reactions of $CuL^1$, $L^2$, and $L^3$ studied at 25°C and $I = 0.1$ mol $L^{-1}$ $NaClO_4$ in water.

| Complex | pH | UV-Vis ($\lambda_{max}$, nm) |
|---|---|---|
| $L^1$ | 4.00 | 260 |
| $L^2$ | 3.22 | 265 |
| $L^3$ | 3.63 | 263 |

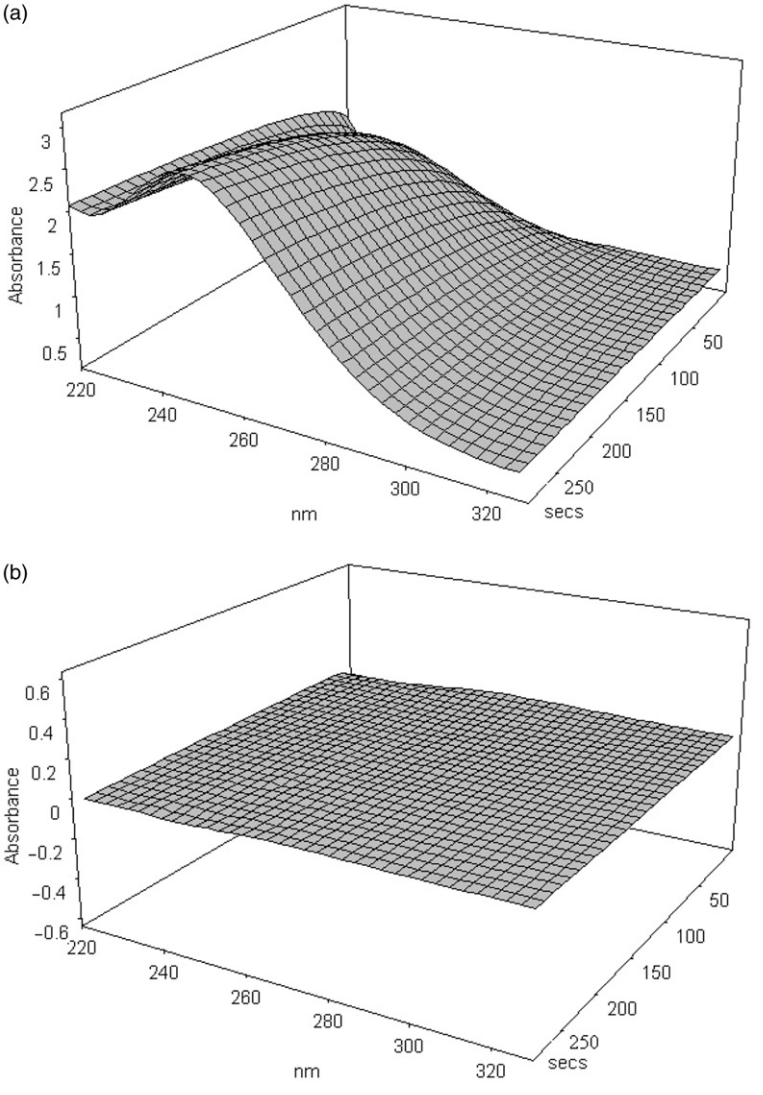



Figure 3. (a) 3-D spectral changes during complex formation of $CuL^1$ pH = 4.00, I = 0.1 mol $L^{-1}$ $NaClO_4$ and (b) 3-D display of residuals to kinetic fit of $CuL^1$ formation reaction, [M] = [L] = 1.20 m mol $L^{-1}$.

Spectrophotometer with a stirred thermostated cell holder, a peristaltic pump (Cole Palmer, Masterflex), and an Orion pH meter combined with a Metrohm semi-micro electrode. The electrode was calibrated with a pH of 4.0 and 7.0 buffers for measurements in aqueous solutions. An argon-saturated acidic mixture of the ligand (1.2 mmol) and the metal ion (1.2 mmol) containing 0.1 mol $L^{-1}$ $NaClO_4$ for adjustment of ionic strength was titrated with a base (0.1 mol $L^{-1}$ NaOH) in a 1-cm quartz cell. The cell compartment was thermostated to $20 \pm 0.1^{\circ}C$ during titration. The cell was closed with a Teflon cap containing a pH electrode and a capillary tip from the peristaltic pump. The UV-Vis spectrum was determined during the titration at 60 s intervals over the wavelength range 350–1100 nm. Figure 4 shows typical absorption spectra of $CuL^1$

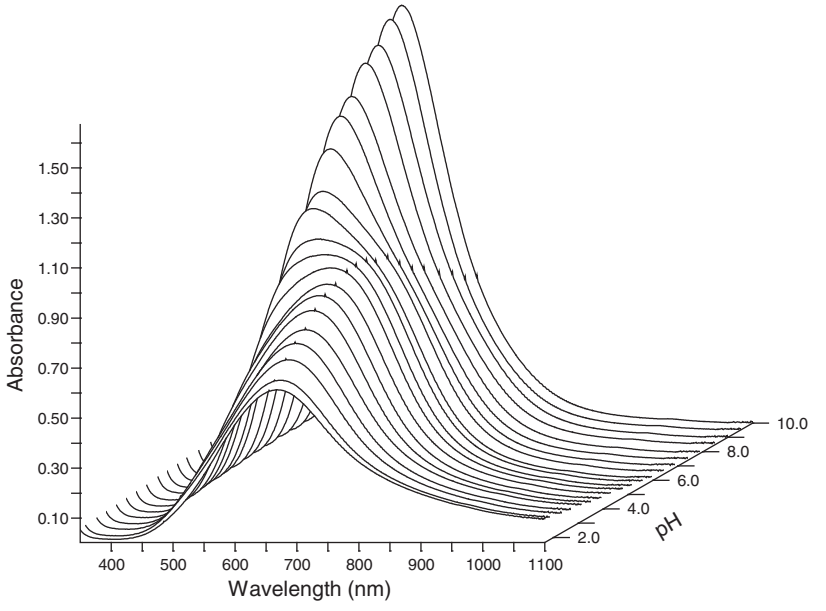



Figure 4. 3-D absorption spectra of $CuL^1$ ($\lambda = 675$ nm) during spectrophotometric titration as a function of pH at 293 K, $I = 0.1 mol\,L^{-1}$ $NaClO_4$.



during spectrophotometric titration as a function of pH at $0.1\,mol\,L^{-1}$ ionic strength at 20°C. The measurements were made from pH 2.0 to 11.0. Triplicate data analyses were performed for each complex. Data analysis was carried out using the nonlinear least-square fitting program Specfit/32. An initial guess for the equilibrium constant was entered and iteratively refined until the best fit indicated by least squares was achieved.

## 3. Results and discussion

### 3.1. *Kinetics*

Kinetic experiments were carried out under second-order conditions, in the pH range 3–4. In the investigated range of pH, many species with different protonation numbers may occur, but these species have low concentrations which may not affect the reaction rate. The kinetic behavior was modeled by the Eigen–Wilkins mechanism. The solvated metal ion reacts with the ligand rapidly forming an outer sphere complex. The ligand then enters the inner sphere where the ligand replaces a coordinated solvent molecule. The rate of this interchange controls the rate of complex formation. For the polydentate ligand, there is another step during which ring closure occurs and determines the rate of reaction. Kinetic experiments show that formation of CuL complexes occurs in a single kinetic step and values derived from second-order rate constants includes all species in solutions. The values are $392.1 \pm 0.3$ for $CuL^1$, $82.7 \pm 0.3$ for $CuL^2$, and $818.7 \pm 0.3$ for

Table 2. Rate constants and activation parameters for the formation of Cu(II) complexes at 25°C and $I = 0.1\,mol\,L^{-1}$ $NaClO_4$ in water.

| Complex | $k$ $((mol\,L^{-1})^{-1}\,s^{-1})$ | $\Delta H^{\#}$ $(kJ\,mol^{-1})$ | $\Delta S^{\#}$ $(J\,mol^{-1}\,K)$ |
|---|---|---|---|
| $L^1$ | $392.1 \pm 0.3$ | 55 | 34 |
| $L^2$ | $82.7 \pm 0.2$ | 61 | 39 |
| $L^3$ | $818.7 \pm 0.2$ | 36 | 67 |

$L^3$ (table 2). Enthalpies of activation of these complexes are 55, 61, and $36\,kJ\,mol^{-1}$, respectively. The positive entropy of activation indicates that the reaction proceeds in a dissociative pathway.

### 3.2. *Stability of the complexes*

Accurate determination of the stability constants is required in various chemical and biochemical fields. Spectrophotometric titrations have often been employed and they consist of recording and evaluating spectra derived from the titration system as a function of variables, such as pH. The range of techniques available through spectrometry has been covered extensively [24]. Spectrophotometric methods are, in general, highly sensitive and suitable for studying protonation equilibria in solutions [25].

The $L^1$ and $L^2$ polyamines were prepared as described in the experimental section. $L^3$ was prepared using a procedure similar to that previously described for the related diamine compounds. The stability constant values of the Cu(II) complexes were obtained from analysis of spectrophotometric titrations (table 3). These values were derived from the analysis of a solution containing 1 : 1 molar ratios at 20°C in the presence of $0.1\,mol\,L^{-1}$ $NaClO_4$. The equilibrium model for Cu(II) complexes of these ligands is simple and includes only formation of CuL and HCuL. The stability of $CuL^1$ is about two orders of magnitude higher than $CuL^2$ and six orders higher than $CuL^3$. These observations can be explained from the higher basicity of $L^1$. The same trend can be observed for the HCuL species. For the open-chain polyamine complexes, the protonation pattern is such that electrostatic repulsion is minimized. Protons attach first to the terminal primary amine, and then to the secondary amines. $L^1$ is potentially a pentadentate ligand with carboxylate pendant. N-alkylation, changing the basicity of the nitrogen donor, could change the stability of $CuL^3$. The methyl groups, apart from causing a decrease in basicity of the secondary amine donor, may introduce steric crowding which can cause a low stability constant.

## 4. Conclusion

As a whole, the stability constants and kinetic data used in this article indicate that changes in the donor for the open-chain tetradentate ligand lead to a change in the properties of their Cu(II) complexes. For $L^1$, the single metal ion is tightly coordinated to four amines to yield a very stable complex. N-alkylation and two oxygen donors in

Table 3. Stability constants of the complexes at 20°C, $I = 0.1\,mol\,L^{-1}$ $NaClO_4$.

| Ligand | Metal | M, L, H | Log $\beta_{MLH}$ | Equilibrium, $K$ | Log $K_{MLH}$ |
|---|---|---|---|---|---|
| $L^1$ | $Cu^{2+}$ | 110 | 17.11 | $M + L \leftrightarrows ML$ | $17.1 \pm 0.1$ |
| | | 111 | 23.42 | $ML + H \leftrightarrows MLH$ | $6.3 \pm 0.1$ |
| $L^2$ | $Cu^{2+}$ | 110 | 15.43 | $M + L \leftrightarrows ML$ | $15.4 \pm 0.2$ |
| | | 111 | 19.51 | $ML + H \leftrightarrows MLH$ | $4.1 \pm 0.1$ |
| $L^3$ | $Cu^{2+}$ | 110 | 11.44 | $M + L \leftrightarrows ML$ | $11.4 \pm 0.3$ |
| | | 111 | 15.31 | $ML + H \leftrightarrows MLH$ | $3.9 \pm 0.1$ |

$L^3$ decrease the stability of the mononuclear complex by several orders of magnitude. By contrast, $L^3$ reacts faster with Cu(II) than $L^1$. These results demonstrate that the kinetics and stability of the complexes can be finetuned by introducing minor modifications in the ligand structures.



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