

V. Callegari · C. Bucher · J.-C. Moutet · G. Royal
E. Saint-Aman · J. Pécaut

Electrochemically induced motion in copper complexes of tetraferrocene-cyclam

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Abstract The tetra(ferrocene)-cyclam macrocycle 1,4,8,11-tetra(ferrocenylmethyl)-1,4,8,11-tetraazacyclotetradecane (L) and two corresponding Cu^{I} and Cu^{II} complexes have been prepared and characterized from spectroscopic and electrochemical studies (cyclic voltammetry and rotating disk electrode experiments). Both complexes exist under two energetically distinct geometries which differ mainly from the relative positioning of the ferrocenylmethyl groups above or below the macrocyclic plane and it is shown that a reversible change from one geometry to the other can be electrochemically induced following a copper-centered electron transfer. The equilibrium constants, mechanisms and kinetic parameters of these rearrangements have been evaluated using electrochemical simulation.

Keywords Cyclic voltammetry · Cyclam · Copper complex · Redox-induced motion · Electrochemical simulation

Introduction

The design and the synthesis of functionalized polyazamacrocycles such as 1,4,8,11-tetraazacyclotetradecane

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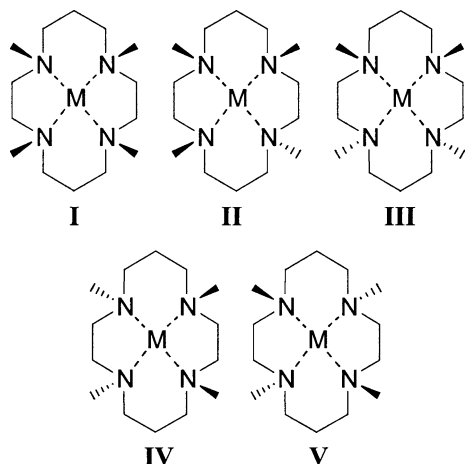
V. Callegari · C. Bucher · J.-C. Moutet (✉) · G. Royal
E. Saint-Aman
Laboratoire d'Electrochimie Organique et de Photochimie Rédox, (LEOPR, UMR CNRS 5630) Institut de Chimie Moléculaire de Grenoble (ICMG, FR CNRS 2607), Université Joseph Fourier Grenoble I, Grenoble Cedex 9, BP 53, 38041, France
E-mail: Jean-Claude.Moutet@ujf-grenoble.fr
Tel.: +33-04-76514682
Fax: +33-04-76514267

J. Pécaut
Laboratoire de Chimie de Coordination, DRMF/CEA/SCIB,
38054 Grenoble Cedex 9, France

(cyclam) remain a subject of intense activity [1, 2]. The cyclam framework allows the formation of strong complexes with d- and f-block metal and changes in the substitution pattern are most likely to act directly upon the properties and geometry of their metal complexes and thus be determining in regard to their potential applications [3–8]. In particular, functionalization of cyclam by substituents like ferrocene has led to a new class of redox-active ligands having wide applications [9–22]. One of the interests of these compounds stems from their electrochemical recognition ability, finding application in the development of new chemosensors [16]. Another interesting domain for these redox ligands deals with the possible electrochemically induced commutation of their metal complexes properties (redox-switching). Indeed, when cyclam derivatives coordinate to four equatorial sites of a metal cation, they can adopt five energetically distinct configurations (type I–V, see Scheme 1) depending on the relative orientation of the substituents on each nitrogen atom to the N4 coordination plane [4], the overall depending essentially on the size and electron density of this metal center.

Of great interest with these polyazamacrocyclic complexes would be to control fast and reversible rearrangements between distinct geometries through the application of an external stimulus (e.g., a redox stimulus), signaled by a clear change in a physico-chemical property (e.g., a spectroscopic property). Such systems, capable of induced and readable movement at the molecular level, could indeed be considered as molecular redox switches.

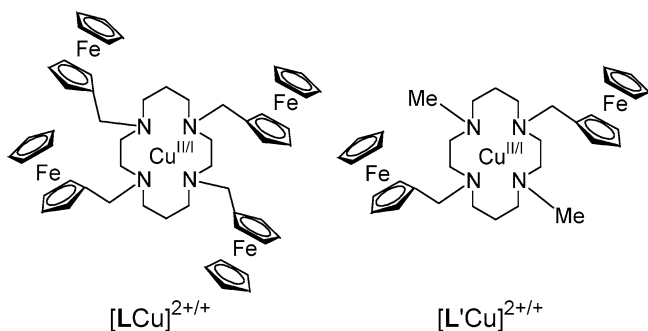
In this context, we have recently designed and characterized a true air-stable molecular redox switch that operates through the $\text{Cu}^{\text{II/I}}$ couple of a novel bis-ferrocenyl-bis-methyl-appended cyclam copper complex denoted $[\text{L}'\text{Cu}]^{2+/+}$ [23]. In this multicomponent complex, the metal center behaves as a switch which can be operated through an external electrochemical input. The conversion of one redox state of the copper center to the other induces drastic changes in the system topology: a fast and fully reversible, electrochemically induced mo-



Scheme 1 Stereochemistry of metal complexes of cyclam

tion of noncoordinating subunits was observed between two distinct and stable configurations. This molecular reorganization was observed in solution and also in the solid phase through adsorption of the complex onto the electrode surface and cavity microelectrode techniques.

In order to get an insight into the influence of the nature of the substituents appended to the macrocycle on the electrochemically induced motion, we present here the electrochemical properties of the copper (I) and (II) complexes of the 1,4,8,11-tetra(ferrocenylmethyl)-1,4,8,11-tetraazacyclotetradecane ligand ($[\text{LCu}]^+$ and $[\text{LCu}]^{2+}$).



Experimental

Chemicals, instrumentation and procedures

Acetonitrile (Rathburn, HPLC grade) was used as received. Tetra-*n*-butylammonium perchlorate (TBAP) was purchased from Fluka. All other compounds were of reagent grade and used without further purification. Electrochemical experiments were performed with a CHI 600 instrument (CH Instrument, USA) and a conventional three-electrode cell under an argon atmosphere at 20 °C. A coiled Pt wire was used as the counter electrode and the reference electrode was Ag/AgNO_3

(10 mM in CH_3CN containing 0.1 M TBAP). The potential of the regular ferrocene/ferrocenium (Fc/Fc^+) redox couple in acetonitrile is 0.07 V under our experimental conditions. The electrochemical behavior of the isolated $[\text{LCu}]^{2+}$ and $[\text{LCu}]^+$ complexes was studied by rotating disc electrode (RDE) voltammetry and cyclic voltammetry (CV). The working electrode was a Pt disc (5 mm in diameter for CV or 2 mm for RDE voltammetry) polished with 1 μm diamond paste before each record. The characteristic constants of the square scheme describing the electrochemical behavior of the system (see the text) have been determined by simulating and best fitting of the experimental data (CV and RDE voltammetry) using the Digisim (V 3.0) software distributed by the Bioanalytical Systems Corporation. Each CV (scan rate between 20 mV s^{-1} and 3 V s^{-1}) and RDE (rotation rate between 50 rpm and 5,000 rpm) voltammograms were fitted independently. An average value of the characteristic parameters of the mechanism was then used to simulate the whole set of experimental voltammograms obtained starting from isolated $[\text{LCu}]^{2+}$ and $[\text{LCu}]^+$. All the electro-kinetic parameters were fitted and we found: $\alpha_1 = \alpha_2 = 0.45 \pm 0.15$, $k_1^0 = 0.04 \pm 0.01 \text{ cm s}^{-1}$, $k_2^0 = 0.4 \pm 0.1 \text{ cm s}^{-1}$, $D_{[\text{LCu}],\text{typeA}}^{2+} = (0.8 \pm 0.1) 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, $D_{[\text{LCu}],\text{typeB}}^{2+} = (0.9 \pm 0.1) 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, $D_{[\text{LCu}],\text{typeA}}^+ = (1.7 \pm 0.2) 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, $D_{[\text{LCu}],\text{typeB}}^+ = (1.8 \pm 0.1) 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ where $\alpha_1, \alpha_2, k_1^0, k_2^0$ are the transfer coefficients (α) and the heterogeneous transfer constants (k^0) of electrochemical steps (1) and (2) of the mechanism depicted on Scheme 2 and D_i the diffusion coefficient of the species *i*. A value of double layer capacity equal to 1.2 μF has been used for the simulations. Electrolysis were performed at controlled potential using a Pt plate and were followed by UV-vis spectroscopy. FAB (positive mode) mass spectra were recorded with an AEI Kratos MS 50 spectrometer fitted with an Ion Tech Ltd gun and using *m*-nitrobenzyl alcohol as matrix. UV-vis spectra were recorded on a Varian Cary 100 spectrophotometer using quartz cells ($l = 1 \text{ cm}$). For X-ray structure determination, single crystal of L was used for data collection on a SMART CCD diffractometer using $\text{Mo-K}\alpha$ graphite-monochromated radiation ($\lambda = 0.71073 \text{ \AA}$). Intensity data were corrected for Lorentz, polarization effects and absorption. Structure solution and refinement were performed with the SHELXTL package. CCDC 242656 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at <http://www.ccdc.cam.ac.uk/conts/retrieving.html> [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk]. Elemental analysis were performed by the Service Central d'Analyses, CNRS, Lyon, France.

Synthesis

1,4,8,11-tetra(ferrocenylmethyl)-1,4,8,11-tetraaza cyclotetradecane

L was prepared following literature procedures by the reaction of 1,4,8,11-tetraazacyclotetradecane (cyclam) with (ferrocenylmethyl)-trimethylammonium iodide [9].

[LCu]²⁺ complex

The [LCu]²⁺ complex was prepared upon adding dropwise a stoichiometric amount of Cu(ClO₄)₂·6H₂O (37.32 mg in 2 mL of degassed MeOH) to a suspension of L (100 mg in 30 mL of degassed MeOH). The solution was stirred under an inert atmosphere for 12 h and the blue solid complex was precipitated upon addition of diethyl ether and collected by suction filtration (105 mg, yield: 83%). [LCu](ClO₄)₂: UV/vis (CH₃CN): λ_{max}, nm (ε, M⁻¹ cm⁻¹) = 618 br (665), 720 sh (516); FAB⁺-MS, *m/z*: 1,055 (100%, [M-2ClO₄]⁺), 1,154 (40%, [M-ClO₄]⁺). Anal. Calcd. for C₅₄H₆₄N₄Fe₄CuCl₂O₈ (M_w = 1254.94): C, 51.68, H, 5.14, N, 4.46; found: C, 51.77, H, 5.23, N, 4.54 (%).

[LCu]⁺ complex

To a suspension of 40 mg of L in 20 mL of CH₃CN was added a stoichiometric amount of Cu(CH₃CN)₄ClO₄ (13.18 mg) dissolved in 10 mL of CH₃CN. A 5 mL of CH₂Cl₂ were then added and the solution was refluxed for 24 h. The solvent was then partially evaporated under vacuum and the yellow solid complex was finally precipitated upon addition of diethyl ether (150 mL) and collected by suction filtration (34 mg, yield: 72%). Due to its relative unstability toward dioxygen, this complex was kept under inert atmosphere. [LCu](ClO₄): FAB⁺-MS, *m/z*: 1,055 (100%, [M-ClO₄]⁺). Anal. Calcd. for C₅₄H₆₄N₄Fe₄CuClO₄ (M_w = 1155.89): C, 56.13, H, 5.58, N, 4.85; found: C, 55.78, H, 5.72, N, 4.78 (%).

Warning! Perchlorate salts are hazardous because of the possibility of explosion.

Results and discussion

Preparation of the complexes

The preparation of L was performed according a literature procedure through the reaction of 1,4,8,11-tetraazacyclotetradecane (cyclam) with (ferrocenylmethyl)-trimethylammonium iodide [9]. Due to the very low solubility of this compound in usual solvents, NMR studies could not be achieved and this ligand was characterized by X-ray structure determination (Fig. 1). Under its crystallized form, this ligand adopts a Type IV geometry [24] in which the four nitrogen atoms define a plane with two ferrocenylmethyl groups disposed on each side of this plane. The corresponding [LCu]⁺ and [LCu]²⁺ complexes were prepared by reacting stoichiometric amounts of ligand and Cu(CH₃CN)₄ClO₄ or Cu(ClO₄)₂·6H₂O, respectively. These complexes were characterized using conventional physico-chemical techniques. Assignment of the geometry of these complexes will be discussed in the following sections.

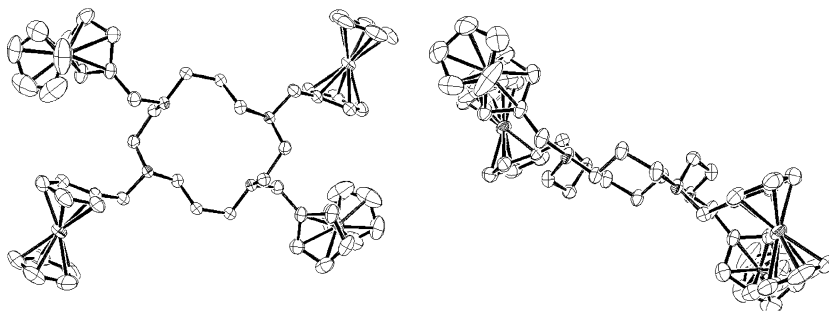
Electrochemical measurements

The electrochemical behavior of the isolated [LCu]²⁺ and [LCu]⁺ complexes in CH₃CN solutions (from 0.4 mM to 1 mM) was investigated at room temperature (23 °C) using CV and RDE voltamperometry.

As expected, in the positive region of potentials, the CV curves for both complexes present a single four-independent electron, reversible wave at *E*_{1/2} = 225 mV vs Ag/Ag⁺ (10⁻² M) with Δ*E*_p ~ 60 mV (Fig. 2a, b). This signal corresponds to the reversible oxidation of the four metallocene groups in the complexes. The observation of a unique wave and the Δ*E*_p value close to 60 mV strongly suggest that the four chemically equivalent ferrocenyl groups in L are electrochemically independent, without intramolecular communication [25].

The cathodic RDE behavior of [LCu]²⁺ is characterized by a single wave at *E*_{1/2} = -0.44 V, attributed to the one-electron reduction of the Cu^{II} center in the complex (Fig. 2C, curve b). From CV experiments, this one-electron reduction appears to be fully reversible at high scan rates (*E*_{1/2} = -0.44 V and Δ*E*_p = 95 mV at 3 V/s⁻¹; Fig. 3C). At lower scan rates (e.g., 0.1 V/s⁻¹;

Fig. 1 ORTEP views of L. Hydrogen atoms have been omitted for clarity. Ellipsoids are drawn at a 40% probability



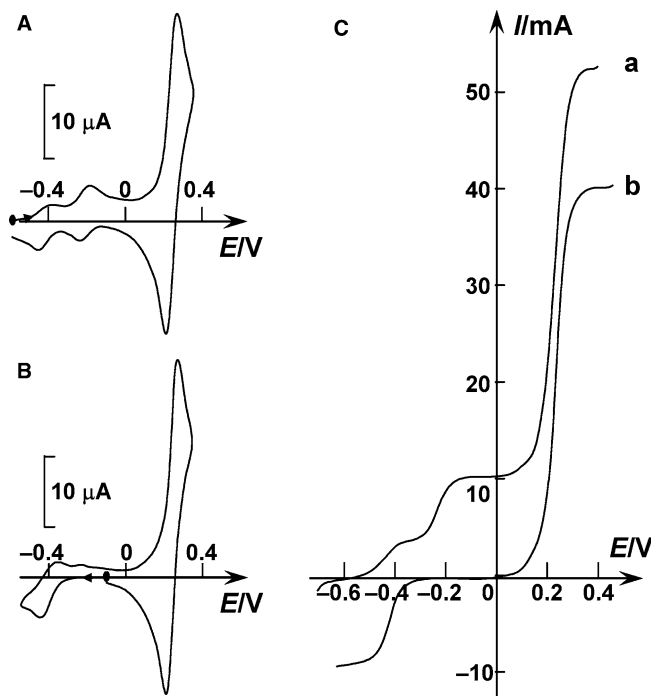


Fig. 2 Representative cyclic voltammetry (CV) curves (scan rate 0.1 V s^{-1}) of (A) $[\text{LCu}]^+$ and (B) $[\text{LCu}]^{2+}$ and (C) rotating disk electrode experiments (RDE) curves (600 rpm, scan rate: 10 mV s^{-1}) of a $[\text{LCu}]^+$ and b $[\text{LCu}]^{2+}$. E vs. Ag/Ag^+ $10 \text{ mM} + \text{TBAP } 0.1 \text{ M}$ in CH_3CN ; $[\text{LCu}]^+$: 0.45 mM ; $[\text{LCu}]^{2+}$: 0.4 mM

Fig. 3A), this system becomes less reversible ($I_{\text{pa}}/I_{\text{pc}} < 1$) and an additional anodic peak is seen at $E_{\text{pa}} = -0.22 \text{ V}$. However, on the reverse scan, the anodic peak corresponding to the initial system at $E_{1/2} = -0.44 \text{ V}$ remains still observable at very low scan rate ($< 50 \text{ mVs}^{-1}$).

The electrochemical behavior of $[\text{LCu}]^+$ appears to be more complicated. The RDE curve (Fig. 2C, curve a) is characterized by two anodic waves at $E_{1/2} = -0.44$ and -0.23 V . Interestingly, the relative height of these two waves depends on the rotation rate of the electrode (see Fig. 4B,C). However, the sum of the intensities of these two systems is $I = 1$ compared to the intensity $I = 4$ found for the anodic wave corresponding to the oxidation of the four metallocene groups at $+0.225 \text{ V}$. From CV experiments, two non fully reversible ($I_{\text{pa}}/I_{\text{pc}} \neq 1$) copper-centered waves are observed at $E_{1/2} = -0.44 \text{ V}$ and $E_{1/2} = -0.23 \text{ V}$ respectively (Figs. 2A, 4A), and the relative intensity of these two

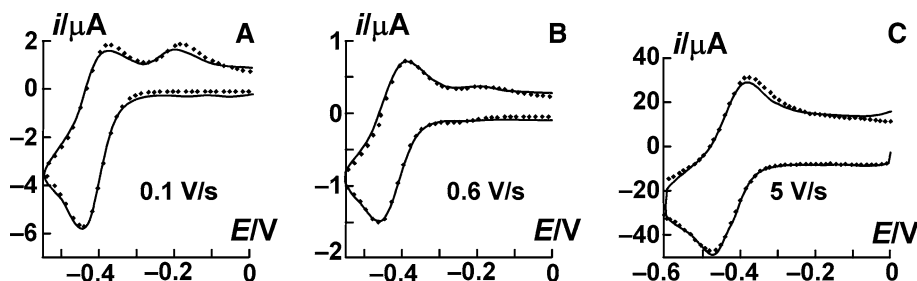
systems and their respective $I_{\text{pa}}/I_{\text{pc}}$ ratio appeared to be dependent on the scan rate.

Moreover, upon exhaustive electrolysis at -0.7 V ($n = 1.0$ exchanged electron) of a $[\text{LCu}]^{2+}$ solution, the resulting solution presents the same electrochemical characteristics than those obtained with a solution of the isolated copper(I) complex. In the same way, the exhaustive electrolysis of a $[\text{LCu}]^+$ solution at 0 V ($n = 1.0$ exchanged electron) leads to the formation of the copper(II) complex presenting the same electrochemical behavior than that of the isolated $[\text{LCu}]^{2+}$ complex.

The irreversibility of the $[\text{LCu}]^{2+/+}$ system shows that the homogeneous chemical reactions are coupled to the electron transfer undergone by the complexes at the electrode surface; these complexes being in electrochemical interconversion. Such behavior is similar to what has been observed with the copper complexes of the bis-ferrocenyl-bis-methyl-appended cyclam ligand ($[\text{L}'\text{Cu}]$) [23]. It was unambiguously demonstrated that it is due to topological rearrangements undergone by the copper complexes upon electron transfer, i.e., to a change in the configuration adopted by the complex according to its redox state, the complex oscillating between two distinct geometries under the effect of an electron transfer [23].

In the same way, it seems that $[\text{LCu}]^{2+}$ and $[\text{LCu}]^+$ complexes exist under two energetically different geometries, denoted type A and type B, respectively. Unfortunately, all attempts to obtain crystals of $[\text{LCu}]^{2+}$ and $[\text{LCu}]^+$ suitable for X-ray structure determination were unsuccessful, preventing the definitive determination of the configuration adopted by these complexes in the solid state. Nevertheless, the UV-visible data of $[\text{LCu}]^{2+}$ in solution are indicative of a pentacoordinated species, with a broad band at 618 nm ($\epsilon = 665 \text{ M}^{-1} \text{ cm}^{-1}$) and a shoulder at 720 nm ($\epsilon = 516 \text{ M}^{-1} \text{ cm}^{-1}$). Pentacoordinated transition metal complexes are common with tetrasubstituted cyclam derivatives and generally correspond to a Type I geometry (see Scheme 1), where the metal center is located above the four nitrogen plane in a pyramidal geometry, with a solvent molecule playing the role of the fifth ligand [23, 26, 27]. This configuration was found to be adopted by the bis-ferrocenyl-bis-methyl-appended cyclam copper(II) complex, $[\text{L}'\text{Cu}]^{2+}$, with $\lambda_{\text{max}} = 579 \text{ nm}$ ($\epsilon = 721 \text{ M}^{-1} \text{ cm}^{-1}$) and $\lambda_{\text{sh}} = 680$ ($\epsilon = 609 \text{ M}^{-1} \text{ cm}^{-1}$). Concerning the structure of $[\text{LCu}]^+$, recent results indicate that a very

Fig. 3 Continuous lines: experimental CV curves in $\text{CH}_3\text{CN} + \text{TBAP } 0.1 \text{ M}$ solutions of 0.4 mmol L^{-1} $[\text{LCu}]^{2+}$ at (A) 0.1 V s^{-1} , (B) 0.6 V s^{-1} and (C) 5 V s^{-1} . E vs Ag/Ag^+ ; $v = 0.1 \text{ V s}^{-1}$. Dotted lines: simulated CV curves



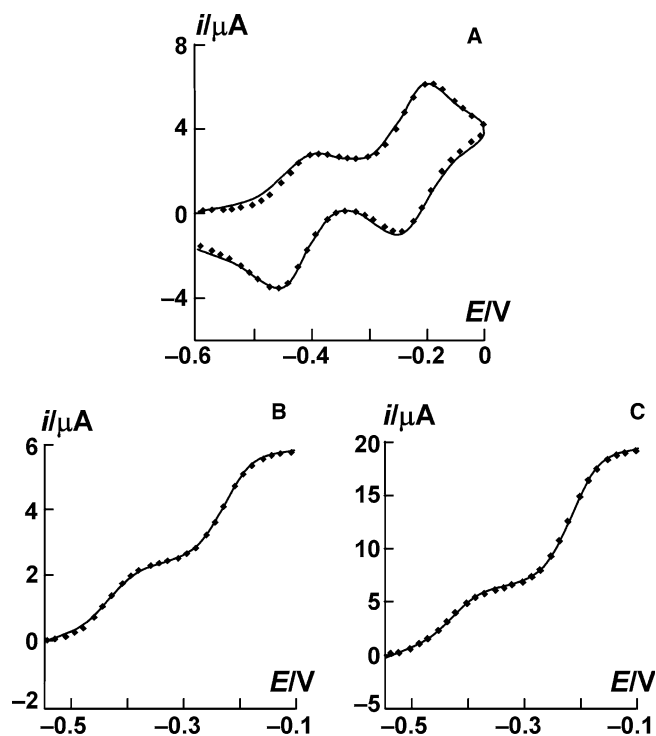


Fig. 4 Continuous lines: experimental CV (A: scan rate: 0.1 V s^{-1}) and RDE curves (B: 100 rpm, scan rate: 10 mV s^{-1} and C: 1,500 rpm, scan rate: 10 mV s^{-1}) in $\text{CH}_3\text{CN} + \text{TBAP}$ 0.1 M solutions of 0.45 mmol L^{-1} $[\text{LCu}]^+$. E vs Ag/Ag^+ ; $v = 0.1 \text{ V s}^{-1}$. Dotted lines: simulated curves

stable geometry adopted for tetrasubstituted cyclam copper(I) complexes, as in $[\text{L}'\text{Cu}]^+$ [23, 28], corresponds to a type V arrangement (Scheme 1) in which the four nitrogen atoms of the cyclam macrocycle define a tetrahedral geometry around the copper(I) center. Under this assumption, the stabilization of the Cu^{I} redox state in the 4-coordinate complex (type B, $E_{1/2} = -0.23 \text{ V}$) compared to the 5-coordinate isomer (type A, $E_{1/2} = -0.44 \text{ V}$), and the contrary for the Cu^{II} redox state,

Scheme 2 Electrochemical mechanism for the $[\text{LCu}]^{2+}/[\text{LCu}]^+$ system

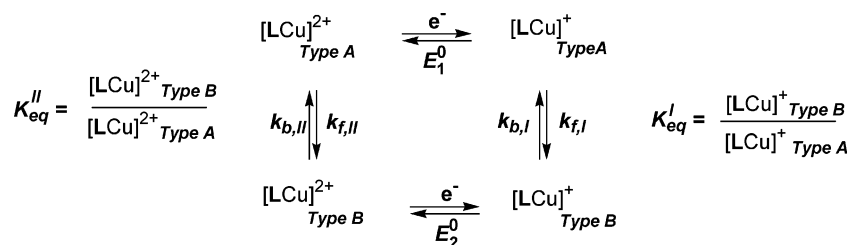


Table 1 Characteristic parameters (see Scheme 2) of the electrochemical mechanism for the $[\text{LCu}]^+ / [\text{LCu}]^{2+}$ and $[\text{L}'\text{Cu}]^+ / [\text{L}'\text{Cu}]^{2+}$ systems (taken from ref. [23])

	E_1^0 (V)	$K_{\text{eq}}^{\text{I,a}}$	$k_{f,I}$ (s^{-1})	$k_{b,I}$ (s^{-1})	E_2^0 (V)	$K_{\text{eq}}^{\text{II,a}}$	$k_{f,II}$ (s^{-1})	$k_{b,II}$ (s^{-1})
$[\text{LCu}]^{2+}/+$	-0.44 ± 0.01	2.51	0.6 ± 0.1	0.23 ± 0.05	-0.23 ± 0.01	$5.6 \cdot 10^{-4}$	$(1.0 \pm 0.1) \cdot 10^{-4}$	0.18 ± 0.02
$[\text{L}'\text{Cu}]^{2+}/+$	-0.56 ± 0.01	$> 2 \cdot 10^3$	2.0 ± 0.5	$< 10^{-3}$	-0.24 ± 0.01	$< 10^{-2}$	$< 10^{-3}$	0.11 ± 0.02

^a : $K_{\text{eq}}^{\text{II}}/K_{\text{eq}}^{\text{I}} = 3.1 \cdot 10^{-4}$ ($[\text{LCu}]^+ / [\text{LCu}]^{2+}$) and $4.6 \cdot 10^{-6}$ ($[\text{L}'\text{Cu}]^+ / [\text{L}'\text{Cu}]^{2+}$)

is in full agreement with the stability sequence of copper complexes according to their redox state [29].

The overall electrochemical behavior of $[\text{LCu}]^{2+}/+$ was modeled as a classical square scheme with two redox reactions corresponding to the copper-centered electron transfer in the complexes and two chemical reactions corresponding to the topological rearrangements between the type A and type B geometries of the complexes (Scheme 2). In order to confirm the proposed mechanism and to determine the associated kinetic parameters, we have used electrochemical simulation and best fitting of the experimental CV and RDE data. Studies were performed starting from solutions prepared using pure isolated $[\text{LCu}]^+$ and $[\text{LCu}]^{2+}$ complexes.

Each CV (scan rate between 20 mV s^{-1} and 3 V s^{-1}) and RDE (rotation rate between 50 rpm and 5,000 rpm) voltammogram was fitted independently and an average value of the characteristic parameters of the mechanism was then used to simulate the whole set of experimental voltammograms. Examples of calculated curves are represented on Figs. 3 and 4. The data, compared to those obtained with the $[\text{L}'\text{Cu}]^{2+}/+$ system [23], are given in Table 1.

From the value of the equilibrium constant $K_{\text{eq}}^{\text{II}} = 5.6 \cdot 10^{-4}$ corresponding to the $[\text{LCu}]^{2+}$ complex, it is seen that $[\text{LCu}]^{2+}$ exists under one stable configuration in solution (type A in Scheme 2), as for the close copper(II) complex derived from the bis-ferrocenyl-bis-methyl-appended cyclam, $[\text{L}'\text{Cu}]^{2+}$, presenting also a very weak equilibrium constant. Moreover, the order of magnitude of the kinetics associated with the rearrangement in the +2 redox state is the same for both complexes, $[\text{LCu}]^{2+}$ and $[\text{L}'\text{Cu}]^{2+}$.

This result contrasts with the behavior of the copper (I) complex. Indeed, when only one configuration of $[\text{L}'\text{Cu}]^+$ is detectable in solution, it clearly appears that the $[\text{LCu}]^+$ complex in CH_3CN exists under the two configurations A and B at equilibrium ($K_{\text{eq}}^{\text{I}} = 2.51$). Moreover, the electrochemically induced rearrangement in $[\text{LCu}]^+$ from the less stable form (type A) to the most

stable form (type B) proceeds slower than in $[L'Cu]^+$ and when the back reaction is kinetically negligible in $[L'Cu]^+$, it proceeds at an appreciable rate (0.23 s^{-1}) in $[LCu]^+$. As a consequence, two RDE waves are observable from a solution containing $[LCu]^+$ and their relative intensities depends on the rotation rate of the electrode. This RDE behavior was confirmed by experimental and simulation results (Fig. 4).

From these results, it appears that if the replacement of the two methyl groups in L' by two ferrocenylmethyl in L has no marked effects on the configurational stability of the corresponding copper (II) complexes. In contrast, deep changes are observed with the copper (I) derivatives. Indeed, the solution chemistry of $[LCu]^+$ differs from that of $[L'Cu]^+$ since $[LCu]^+$ exists under two geometrical forms in equilibrium when only one form predominates with $[L'Cu]^+$. This can be due to different steric hindrance and electronic effects between the methyl and the ferrocenylmethyl groups which induce modifications on the ligand field and change in the reactivity of the complexes.

Conclusion

The copper complexes of the 1,4,8,11-tetra(ferrocenylmethyl)-1,4,8,11-tetraazacyclotetradecane ligand L exist under two distinct configurations in solution. The application of a redox stimulus allows a conversion of one configuration to another, and thus induces a movement of the substituents on both sides of the plane defined by the nitrogen atoms of the cyclam platform. This conclusion generalizes previous results [23, 28] obtained with copper complexes of tetrasubstituted cyclam, and in particular with a close copper complex from the 1,8-diferrocenylmethyl-4,11-dimethyl-1,4,8,11-tetraazacyclotetradecane ligand, L' , which differs from L by the replacement of two methyl substituents in L' by two ferrocenylmethyl groups in L . However, changes in the electrodonating character and in the steric hindrance of the substituents, from L' to L , influence markedly the +1 redox state behavior when the behavior of both copper(II) complexes is close. Indeed, the kinetics of the electrochemically induced reorganization is of the same order of magnitude in the +2 redox state for both complexes when the movement in the +1 redox state of the complexes proceeds slower in $[LCu]^+$ than in $[L'Cu]^+$. Moreover, in solution, the two configurations of $[LCu]^+$ coexists ($K_{eq} = 2.51$) when only one isomer is detectable for $[LCu]^{2+}$, $[L'Cu]^+$ and $[L'Cu]^{2+}$. Of interest with $[LCu]^+/[LCu]^{2+}$ system would deal with its immobilization onto an electrode surface, e.g., in a solid matrix, in order to transfer the movement observed in homogeneous solution toward a solid phase.

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