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Redox-Triggered Molecular Movement in a Multicomponent Metal Complex in Solution and in the Solid State

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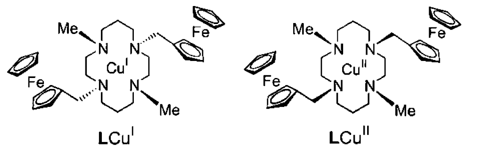
The Cu^I and Cu^{II} complexes of the new 1,8-diferro-cenylmethyl-4,11-dimethyl-1,4,8,11-tetraazacyclotetra-decane ligand (denoted **L**) have been isolated and characterized by X-ray structure determination and electrochemical studies. The Cu^I complex presents an unprecedented stability toward dioxygen. The two complexes adopt two energetically distinct and stable geometries, which differ mainly by the relative positioning of the substituents above or below the cyclam plane. Triggered by a copper-centered electron transfer, a fast and reversible motion of the noncoordinating subunits is obtained in homogeneous solution and in the solid state.

The design of functionalized 1,4,8,11-tetraazacyclo-tetradecane (cyclam) ligands and their corresponding metal complexes is still a subject of intense activity.[1,2] In particular, when cyclam derivatives coordinate to four equatorial sites of a metal cation, they can adopt five energetically distinct configurations (type I−V) depending on the relative orientation of the substituents on each nitrogen atom to the N4 coordination plane.[3] Several thermally and electrochemically induced topological reorganizations of cyclam complexes have already been reported, but the overall processes can be described as nonreversible conversions between species in the same redox state.[4−8] Of great interest would be to induce fast and reversible rearrangements between distinct geometries, signaled by a clear change in a physicochemical property, through the application of an external stimulus (e.g., a redox stimulus). Such systems, capable of controlled and readable movement at the molecular level, could indeed be considered as molecular switches, finding potential applications in the area of molecular electronics, multiredox reactivity, catalysis, and biomimetic chemistry.[9−15]

Chart 1



LCu^I
(Type V)

LCu^{II}
(Type I)

We described herein a molecular switch based on the copper complexes (Chart 1) of a bis(ferrocenyl)cyclam ligand, 1,8-dimethylferrocene-4,11-dimethyl-1,4,8,11-tetraazacyclotetradecane (**L**), capable of redox-triggered fast and reversible motion, in homogeneous solution and, better still, in the solid state.

Ligand **L** was prepared following a general and straightforward two-step procedure.[5,16] Mixing stoichiometric amounts of ligand **L** and Cu^{2+} or Cu^+ metal salts in CH_3CN readily formed the air-stable **L**Cu^{II} and **L**Cu^I complexes, respectively (Chart 1).

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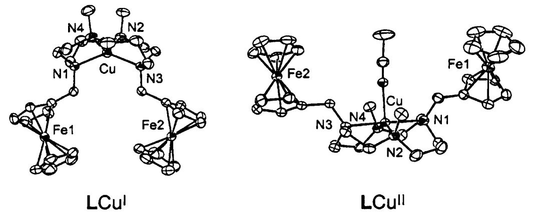

Figure 1. ORTEP views of V-[**L**Cu^{I}] and I-[**L**Cu^{II}(CH$_3$CN)]. (Anions, hydrogen atoms, and solvent molecules have been omitted for clarity.)

The X-ray structure determination of the purple **L**Cu^{II} complex ($[C_{34}H_{48}N_4Fe_2Cu(CH_3CN)](ClO_4)_2\cdot CH_3CN$) showed a type I arrangement with both ferrocenylmethyl and methyl substituents located on the same side of the N4 plane (Figure 1). This complex adopts a slightly distorted five-coordinate square-based pyramidal geometry around the Cu^{2+} center, described by the four macrocyclic nitrogen atoms and one CH$_3$CN nitrogen. The yellow **L**Cu^{I} complex ($[C_{34}H_{48}N_4Fe_2Cu]ClO_4$) adopts the type V geometry with both ferrocenyl groups on the same side of the N4 plane, the methyl groups being oriented toward the other side. A slightly distorted tetrahedral geometry is described about the Cu^{+} by the nitrogen donor atoms.[17]

In accordance with a square pyramidal geometry,[18−20] the solid-state UV−vis spectrum (diffuse reflectance) of the I-**L**Cu^{II} crystals exhibits a broad asymmetrical band ($\lambda_{max} = 579$ nm, $\lambda_{sh} \sim 680$ nm). Upon dissolution of I-**L**Cu^{II} in CH$_3$CN, no significant change in the position of the d−d band was observed ($\lambda_{max} = 579$ nm, $\epsilon = 721$ M^{-1} cm^{-1}; $\lambda_{sh} \sim 680$ nm, $\epsilon = 609$ M^{-1} cm^{-1}). This result reasonably suggests that no significant modification in the coordination sphere around the copper center occurs upon dissolution of the complex in CH$_3$CN.[18,19] This coordination mode was confirmed from EPR measurements, which showed an anisotropic signal characteristic of an axial symmetry around Cu^{II} ($g_{\parallel} = 2.231$, $g_{\perp} = 2.045$, $A_{\parallel} = 15.8$ mT at 100 K).[19,21]

It should be noted that **L**Cu^{I} is totally inert toward dioxygen while, in comparison, the 1,4,8,11-tetramethylcyclam-Cu^{I} complex is highly air-sensitive. To our knowledge, **L**Cu^{I} is the first example of air-stable cyclam-Cu^{I} derivative.[17] This unprecedented stability can be attributed to the tetrahedral geometry of the metal center, which is kinetically protected against O$_2$ oxidation by the bulky ferrocenyl groups.

LCu^{II} and **L**Cu^{I} in the solid state differ mainly by the relative positioning of the ferrocenyl groups above or below the cyclam plane. The ability to trigger a movement in **L**Cu by a heterogeneous electron transfer was first judged from cyclic voltammetry experiments (CV, Figure 2). Measurements were performed in CH$_3$CN solutions of the complexes made from I-**L**Cu^{II} and V-**L**Cu^{I} crystals. It is important to note that no change was observed in the electrochemical and spectroscopic features in the 233−298 K temperature range, from $t = 0$ (dissolution of the complex) to several days, suggesting that no thermal isomerization occurs.[22]

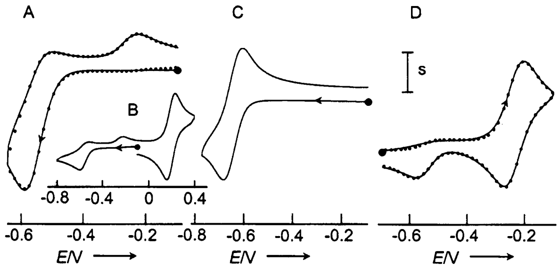

Figure 2. CV curves in CH$_3$CN + (n-Bu)$_4$NClO$_4$ 0.1 mol L^{-1} solutions of 1 mmol L^{-1} **L**Cu^{II} (A; $s = 2$ μA and B, $s = 10$ μA; 293 K), **L**Cu^{II} (C, $s = 2$ μA; 233 K), and **L**Cu^{I} (D, $s = 3$ μA; 293 K); Pt, $\phi = 2$ mm; E vs Ag/Ag^{+}; $v = 0.1$ V s^{-1}. Dotted curves: simulated CV curves.

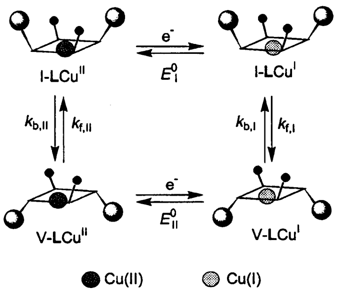

Figure 3. Redox-induced motion in **L**Cu complexes.

In both **L**Cu^{II} and **L**Cu^{I} complexes, oxidation of the chemically and electrochemically equivalent ferrocenyl groups is characterized (Figure 2B) by a single reversible two-electron transfer at $E_{1/2} = 0.20$ V (0.125 V in the free ligand). In contrast, the copper-localized redox features turned out markedly different for the two complexes. At room temperature and for moderate scan rates, the CV curve for I-**L**Cu^{II} (Figure 2A,B) is characterized by an irreversible reduction process at $E_{pc} = -0.58$ V leading to the Cu^{I} complex that is reoxidized on the reverse scan at $E_{pa} = -0.22$ V, indicating that the electron transfer is followed by a chemical reaction. Similarly, the copper-centered oxidation process in V-**L**Cu^{I} ($E_{1/2} = -0.24$ V) is not fully reversible ($I_{pa}/I_{pc} > 1$), an irreversible reduction peak being observed at $E_{pc} = -0.58$ V on the reverse scan (Figure 2D). These results show that a chemical reaction, i.e., a reversible type I to type V rearrangement, follows the electron transfer.

The overall electrochemically driven process can be modeled as a classic square scheme (Figure 3). The best fit of the experimental data performed starting from I-**L**Cu^{II} and V-**L**Cu^{I} over the sweep rate range 0.02−3 V s^{-1} allowed the determination of the characteristic constants of the

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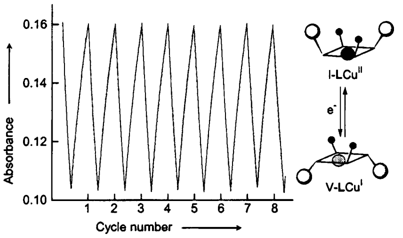

Figure 4. Absorbance (λ = 600 nm) vs time (one cycle = 400 s under our experimental conditions) recorded using a UV−vis dip probe (1 cm), in a conventional electrochemical cell (V = 5 mL) with a platinum grid working electrode. Between each cycle, the applied potential was switched between −0.8 and +0 V when 75% of the complex was reduced or oxidized in CH_3CN.

system: $k_{f,I} = 2.0 \pm 0.5\ s^{-1}$, $k_{f,II} = 0.11 \pm 0.02\ s^{-1}$, $E^0{}_I = -0.563 \pm 0.004$ V, and $E^0{}_{II} = -0.237 \pm 0.001$ V (293 K). I-**L**Cu^{I} and V-**L**Cu^{II} have apparent half-lives of ca. 0.35 and 6.30 s, respectively. The stabilization of the Cu^{II} redox state in the 5-coordinate type I isomer compared to the 4-coordinate type V isomer is in agreement with the stability sequence of copper complexes according to their redox state.[10]

Moreover, at high scan rates (e.g., 293 K, $v = 3\ V\ s^{-1}$) or at lower temperature (e.g., 233 K at 0.1 V s^{-1}), the CV signals at $E_{pc} = -0.58$ V (I-**L**Cu^{II}; Figure 2C) or $E_{pa} = -0.22$ V (V-**L**Cu^{I}) become reversible ($E_{1/2} = -0.56$ V for the 5-coordinate **L**Cu^{II}/**L**Cu^{I} redox couple and −0.24 V for the 4-coordinate one) indicating that the chemical rearrangements are not apparent on the CV time scale.

Because these complexes have different spectroscopic features, the reversibility and stability of the electrochemically driven motion were further examined by potentiostatic exhaustive electrolysis coupled with UV−vis spectroscopy. At first, exhaustive reduction of a I-**L**Cu^{II} solution led to the quantitative generation of V-**L**Cu^{I}. Further exhaustive reoxidation of the latter fully restored the starting I-**L**Cu^{II} complex as judged from electrochemical and UV−vis measurements. To assess the ability of **L**Cu^{II}/**L**Cu^{I} to behave as a reversible switch, redox cycling studies were then conducted in solution and monitored by UV−vis spectroscopy (Figure 4).

The perfect regularity of at least 20 successive cycles demonstrates the high reversibility and reproducibility of the switching process.

The remarkable features of this novel molecular material prompted us to investigate its ability to undergo redox-triggered molecular motion in the solid state. At first, I-**L**Cu^{II} was adsorbed onto a carbon electrode surface by slow evaporation of a CH_2Cl_2 drop of the complex. The resulting modified electrode was then transferred into a 0.1 M KNO_3 aqueous solution, in which **L**Cu^{II} is totally insoluble. Its electrochemical features (Figure 5) are similar to those observed in homogeneous CH_3CN solution: at room temperature and at a moderate scan rate (0.1 V s^{-1}; Figure 5A), the CV curve is characterized by an irreversible copper-centered electron transfer at $E_{pc} = -0.37$ V (vs Ag/AgCl) leading to the Cu^{I} complex which is reoxidized at $E_{pa} = -0.04$ V. At higher scan rate (e.g., 0.5 V s^{-1}; Figure 5B) the CV signal becomes reversible ($E_{1/2} = -0.36$ V).

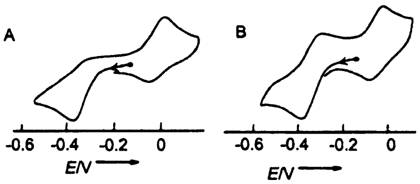

Figure 5. CV curves of **L**Cu^{II} adsorbed onto a carbon electrode (ϕ = 5 mm) in $H_2O + KNO_3$ 0.1 mol L^{-1}, at $v = 0.1\ V\ s^{-1}$ (A) and 0.5 V s^{-1} (B). E vs Ag/AgCl/KCl (3 mol L^{-1}).

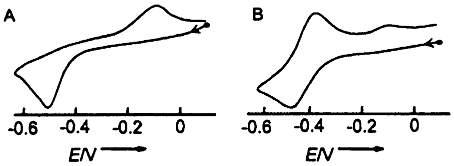

Figure 6. CV curves of solid **L**Cu^{II} inserted into a gold CME (ϕ = 32 μm) in $H_2O + KNO_3$ 0.1 mol L^{-1}, at v = 0.02 (A), 0.5 (B) V s^{-1}. E vs Ag/AgCl/KCl (3 mol L^{-1}).

CV experiments were then carried out on an isolated, structurally characterized I-**L**Cu^{II} powder material, using a cavity microelectrode (CME; Au wire, $V = 10^{-8}$ cm^3).[23,24] Once again, the CV behavior of the powder material (Figure 6) was found to be similar to that observed in the homogeneous or adsorbed phases, with $E_{pc} = -0.46$ V (reduction of I-**L**Cu^{II}) and $E_{pa} = -0.08$ V (oxidation of electrogenerated **L**Cu^{I} in the reverse scan), and with the reversibility of the processes depending on the sweep rate. Moreover, after microelectrolysis of I-**L**Cu^{II} at −0.6 V, the CV features of the electrogenerated **L**Cu^{I} were similar to the results obtained in homogeneous solution starting from V-**L**Cu^{I}.

Thus, the electrochemically induced motion is retained in the solid state. A precise determination of the kinetic parameters could not be achieved as there is no appropriate model that allows these to be extracted from CME experiments. However, since the chemical coupled reaction was observed at the same CV time scale in solution and in the solid state it can be anticipated that in both cases the kinetics of the redox-induced movement is of the same order of magnitude for these first-order reactions.

In summary, we have designed and characterized a true air-stable molecular redox switch that operates through the Cu$^{II/I}$ couple of a novel ferrocenyl-appended cyclam copper complex. A fast and fully reversible, electrochemically induced motion of noncoordinating subunits is observed between two distinct and stable configurations. This molecular reorganization was observed in solution but also in the solid phase using adsorption or cavity microelectrode techniques.

Supporting Information Available: Experimental, synthesis, UV−vis data, and X-ray data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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