Ligands and complexes to perform controlled movements and translocations at the molecular scale

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A new series of ligands suitable for double cation translocation (L2-L3) or helicate complexes assembling-disassembling (L5-L7) has been synthesized. Macrocycles L2-L3 contain two couples of polydentate coordinative compartments: two bis-amino bis-amido and two pyridine-diamino donor sets. The coordination chemistry of these ligands towards Cu\textsuperscript{2+} has been characterized: both systems are capable of double Cu\textsuperscript{2+} translocation. L2 bears a propargyl group, suitable for ligand grafting on Si surfaces and shows a peculiar molecular rearrangement associated to the translocation process. L3 bears an electrochemical signalling unit, which allows to monitor the molecular movement in a novel way. Ligands L5-L7 are based on the same binding set used for L4, bearing simple –OR substituents in the 8-position of the quinoline rings. These ligands confirm the ability of performing assembling and disassembling of double helical complexes in presence of the Cu\textsuperscript{II}/Cu\textsuperscript{I} couple. The new ligands show a particular kinetic intertness in the disassembling process.

1 Introduction

Transition metals are versatile components for molecular machines. The metal cation can modify various properties in a molecular machine and it can induce drastic changes in system topology [1]. We focused our attention on two different kind of molecular devices: a) macrocyclic ligands able to bind two metal cations. In this complexes the transition metal can be bound in two different ways, switching on and off the binding ability of the receptor towards an anionic substrate (Figure 1a) b) tetradentate bis(imino-quinoline) ligands able to bind both Cu\textsuperscript{I} and Cu\textsuperscript{II} cations (Figure 1b). With a simple redox switching between the two oxidation states a double helical dinuclear complex can be reversibly assembled and disassembled.

![Fig. 1: Ligands L1 and L4 have already been studied and are used for reference in this work.](image)

1.1 Double cation translocation

Recently, our group synthesized and studied a macrocyclic ligand (L1) containing two dioxo232 and two diaminopyridine binding sites[2]. At slightly acidic or neutral pH values, the two Cu\textsuperscript{2+} cations are bound
in the diaminopyridine compartments, but at higher pH values the two dioxo232 compartments lose their amido protons and the metal cations move into this stronger binding set, with a square planar coordination. In the dioxo232 donor set, copper is coordinatively saturated, and it’s been proven that it cannot interact with other ligands. On the other hand, when copper is in the tridentate diamino-pyridine framework, water or hydroxide molecules complete the coordination sphere. Water and hydroxide ions can easily be substituted by other substrates as anions. In this coordinatively “open” form the system can uptake bidentate anionic substrates. Through a malonic synthesis, various R groups can be introduced on the dioxo232 framework: we studied ligands bearing a propargyl group (L2) and a ferrocene group (L3). Propargyl can be exploited to graft molecules on Si surfaces [3], while Fc in this kind of systems behaves as a particular signalling unit for copper complexation [4].

1.2 Electrochemical assembling/disassembling of helicates

In the area of controlled molecular movements, but shifting to overall molecular rearrangements, in the last year our group developed some ligands like L4 and similar ones [5], designed to work as molecular “memories”. L4 can bind both CuI and CuII forming, respectively, a double helical dinuclear complex and a distorted square planar monometallic complex. In an appropriate range in the redox potential scale, complexes of L4 with Cu can exist in the two different states, depending on the “history” of the system. This hysteresis cycle can be exploited to store informations in the supramolecular system. In this paper we describe ligands similar to L4, bearing substituents on the quinoline ring. This simple functionalization on the quinoline rings gives rise to interesting modifications in the electrochemical behaviour and opens new routes for further modification (e.g. attaching functional groups for grafting on surfaces, signalling units, etc.).

Fig. 2: a) Pictorial representation of the electrochemically controlled self-assembling and disassembling cycle of bis-imine-heterocycle copper helicates. Reduction and oxidation (electrochemical processes) are followed by rearrangements (chemical processes). b) An ORTEP view of the [L52Cu2][22c5](ClO4)2 salt (thermal ellipsoids are drawn at the 20% probability level; H atoms and perchlorate counterions were omitted for clarity).
2 Results and Discussion

2.1 Double cation translocation and molecular rearrangement

Potentiometric titrations carried out with standard base, first on solution containing \( \text{L}_2H_4 \) or \( \text{L}_3H_4 \), then on a solution containing the ligand in presence of two equivalents of \( \text{Cu}^{2+} \) followed by nonlinear least-squares treatment of the obtained electrode potential versus added base data, allowed us to calculate the protonation constants and formation constants of the copper-containing complexes of both \( \text{L}_2H_4 \) and \( \text{L}_3H_4 \). From these data, distribution diagrams for \( \text{L}_2/2\text{Cu}^{2+} \) and \( \text{L}_3/2\text{Cu}^{2+} \) systems are drawn, as shown in Fig. 3. Subsequently, coupled pH-metric and spectrophotometric titrations were carried out and two distinct colors and types of absorption band are observed changing pH values in the 2-12 range. A band centered around 650 nm, responsible of a blue color in solution, predominates at acidic pH, when \( [\text{Cu}_2(\text{L}_4)]^{4+} \) complexes are formed. At higher pH \( \text{Cu}^{2+} \) ions move to the deprotonated diamino-diamidic framework forming the neutral, coordinatively closed, \( [\text{Cu}_2(\text{L}_4)] \) complex and translocation is clearly signalled with a change in the spectra. \( \text{L}_2H_4 \) and \( \text{L}_3H_4 \) show a different behaviour in their \( [\text{Cu}_2(\text{L}_4)] \) complexes. The spectra of \( [\text{Cu}_2(\text{L}_3)] \) show the formation of a band around 510 nm (visible as a shoulder of the stronger Fc absorption). This UV-Vis band is typical of square planar \( \text{Cu}^{2+} \) complexes, as shown in similar systems [2]. On the other hand, \( [\text{Cu}_2(\text{L}_2)] \) show an absorption band shifted at higher wavelengths (570 nm): this is due to a molecular rearrangement with formation of a pentacoordinate, square pyramidal copper complex [5]. We obtained a crystal structure from \( [\text{Cu}_2(\text{L}_2)] \) complex, confirming that the slim propargyl groups allows a molecular rearrangement in which each pyridine ring is folded on the apical position of the metal ion. This folding is impossible with bulkier substituents, as benzyl and ferrocenyl groups.

Fig. 3: Distribution diagrams and absorbance vs pH plots for \( \text{L}_2H_4/2\text{Cu}^{2+} \) (a) and \( \text{L}_3H_4/2\text{Cu}^{2+} \) systems (b). Solvent is water for \( \text{L}_2H_4/2\text{Cu}^{2+} \), dioxane/water 4:1 for \( \text{L}_3H_4/2\text{Cu}^{2+} \).

2.2 Electrochemical signalling of \( \text{Cu}^{2+} \) translocation

In most molecular systems using ferrocene as an electrochemical signalling unit, the presence of a metal cation makes the oxidation potential of Fc increase due to the electrostatic repulsion between the cation and ferricinium [7]. We studied the electrochemical behaviour of \( \text{L}_3H_4 \), both in the presence and in the absence of copper ions, by means of CV measurements at different pH values. Redox potential for the Fc/Fc couple remains unchanged in the whole pH range (2-12) when no metal ion is present. On the other hand, studying the \( \text{Cu}^{2+} \)-complexes of \( \text{L}_3H_4 \) we measured a significant negative shift in the redox potential when metal ions move from the diamino-pyridine to the dioxo232 binding set. When copper is bound in the diamino pyridine sets (4<pH<10) the \( E_{1/2} \) remains constant at -180 mV vs Ag⁺/Ag. The same value is observed for both the free and the protonated ligand. This indicates that when copper ions are in the diamino-pyridine moiety they are too far from Fc to interact. On the other hand, when pH is raised
enough (<9.8) to translocate the two cations inside the deprotonated dioxo[232] framework, a significant
shift in the redox potential is observed, with \( E_{1/2} \) decreasing to a final value of -230 mV vs Ag\(^+\)/Ag. The
lowering of the the oxidation potential of ferrocene due to the presence of a nearby metal cation is unusual
but not new, as it was already reported in a ferrocene containing dioxo[232] ligand [8]. The complex is
neutral, but the positive charge on the cation and the negative deprotonated amido groups form a dipole
pointing its negative end towards the ferrocene moiety.

2.3 Kinetic inertness in disassembling of Cu(I) double helical complexes

In the chemical/electrochemical cycle studied for \( \text{L}_4 \) with the Cu\(^{1}\)/Cu\(^{II}\) couple, both the chemical steps
(assembling and disassembling) were fast and the electrochemical signals were reversible. Studying the
novel \( \text{L}_5 - \text{L}_7 \) functionalized bis(imino-quinoline) ligands we noticed a peculiar behaviour: disassembling
of double helical Cu\(^{I}\) complexes (whose stoichiometry and structure has been confirmed by spectropho-
tometric titrations, \(^1\)H-NMR and X-ray diffraction on crystals, as shown in Fig.2b) is kinetically inert.
CV measurements made on \([\text{Cu}^{1}\text{L}_2]^2+\) complexes show a reversible two-waves signal. On changing
the sweep rate between 50 mV/s and 2000 mV/s, the same profile is obtained, due to the reversible sin-
gle electron oxidation of each Cu\(^{I}\) center. Reversibility of the CV profile indicates that the system does
not undergo a chemical rearrangement on the time scale of the electrochemical measurement. Examina-
tion of the CV behaviour of \([\text{Cu}^{II}\text{L}]^{2+}\) complexes discloses a different type of profile. An irreversible
reduction peak is observed, that does not feature a return wave. However, returning to positive potential
values, the two reversible waves observed for the \([\text{Cu}^{1}\text{L}_2]^2+\) helicate are found again. In this case, the
self assembling process following the reduction of \([\text{Cu}^{II}\text{L}]^{2+}\) to \([\text{Cu}^{I}\text{L}]^+\) is fast on the time scale of the
electrochemical measurement, while the disassembling process pertaining to the \([\text{Cu}^{II}\text{L}_2]^4+\) oxidized
species is confirmed to be slow.

References

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