

Redox Control of the Ring-Gliding Motion in a Cu-Complexed Catenane: A Process Involving Three Distinct Geometries

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Molecules whose shape and physical properties can be controlled and modified at will by using an external signal are fascinating. Electrochemical triggering of molecular motions between *two forms* has recently been reported for synthetic systems, either on transition metal complexes whose oxidation states are varied^{1–3} or using rotaxanes incorporating a controllable acceptor–donor complex.⁴ Proteins have also afforded interesting examples of redox-controlled molecular motions, the folding–unfolding process being switched by reducing or oxidizing the heme moiety of the enzyme.⁵

Multistage systems seem to be uncommon, although they are particularly challenging and promising in relation to photo- and electrochemical devices aimed at important electronic functions and information storage.⁶ We would like now to report that a Cu-complexed [2]-catenane represents an example of such a compound, with three distinct geometries, each stage corresponding to a different coordination number (CN) of the central complex (CN = 4, 5, or 6). The principle of the three-stage electrocontrollable catenane is represented in Figure 1.

It relies on the important differences of stereochemical requirements for coordination of Cu(I) and Cu(II). For the monovalent state the stability sequence is CN = 4 > CN = 5 > CN = 6. On the contrary, divalent Cu is known to form stable hexacoordinate complexes, with pentacoordinate systems being less stable and tetrahedral Cu(II) species being even more strongly disfavored.

The synthesis of the key catenane $\text{Cu(I)N}_4^+\text{PF}_6^-$ derives from the general three-dimensional template strategy which has been proposed by our group some time ago for making catenanes.⁷ In this case, a one-pot two-ring formation approach was employed. The starting fragments, the entwined Cu(I) complex precursor, and the catenane formation reaction are depicted in Figure 2. The reaction between complex $\text{Cu(1)}_2^+\text{BF}_4^-$ and 5,5''-di(3-bromo-1-propyl)-2,2':6',2''-terpyridine (**2**) in DMF in the presence of Cs_2CO_3 under high dilution conditions gave the

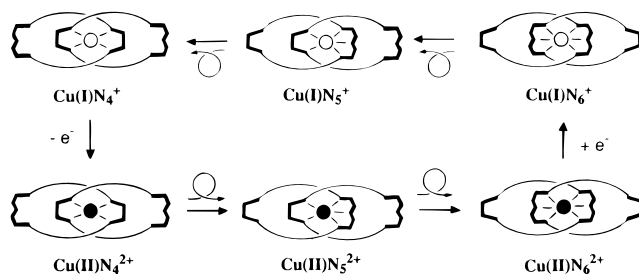
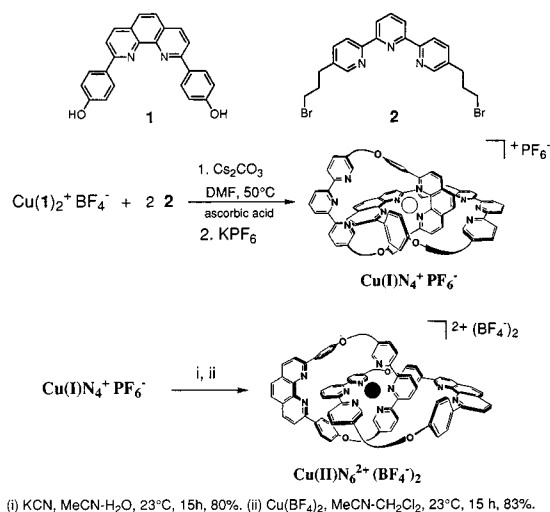


Figure 1. A three-configuration Cu(I) catenane whose general molecular shape can be dramatically modified by oxidizing the central metal (Cu(I) to Cu(II)) or reducing it back to the monovalent state. Each ring of the [2]-catenane incorporates two different coordinating units: the bidentate dpp unit (dpp = 2,9-diphenyl-1,10-phenanthroline) is symbolized by a U whereas the terpy fragment (2,2':6',2''-terpyridine) is indicated by a stylized W. Starting from the tetracoordinate monovalent Cu complex (Cu(I)N_4^+ ; top left) and oxidizing it to the divalent state (Cu(II)N_4^{2+}), a thermodynamically unstable species is obtained which should first rearrange to the pentacoordinate complex Cu(II)N_5^{2+} by gliding of one ring (left) within the other and, finally, to the hexacoordinate stage Cu(II)N_6^{2+} by rotation of the second cycle (right) within the first one. Cu(II)N_6^{2+} is expected to be the thermodynamically stable divalent complex. The double ring-gliding motion following oxidation of Cu(I)N_4^+ can be inverted by reducing Cu(II)N_6^{2+} to the monovalent state (Cu(I)N_6^+ ; top right), as represented on the top line of the Figure.



(i) KCN, MeCN-H₂O, 23°C, 15h, 80%. (ii) Cu(BF₄)₂, MeCN-CH₂Cl₂, 23°C, 15h, 83%.

Figure 2. Synthesis of the catenates $\text{Cu(I)N}_4^+\text{PF}_6^-$ and $\text{Cu(II)N}_6^{2+}(\text{BF}_4)_2$.

desired complex which was isolated as the PF_6^- salt in 21% yield after chromatographic purification.⁹ The visible spectrum of this deep red complex shows a metal-to-ligand charge transfer (MLCT) absorption band $\lambda_{\text{max}} = 439 \text{ nm}$ ($\epsilon = 2570 \text{ mol}^{-1} \text{ L cm}^{-1}$, MeCN). Cyclic voltammetry (CV) of a MeCN solution shows a reversible redox process at +0.63 V (vs SCE). Both the CV data and the UV-vis spectrum are similar to those of other related species.^{2,7} The reaction of $\text{Cu(I)N}_4^+\text{PF}_6^-$ with KCN in MeCN/H₂O afforded the free catenane, which was subsequently reacted with $\text{Cu(BF}_4)_2$ to give $\text{Cu(II)N}_6^{2+}(\text{BF}_4)_2$ as a very pale green complex (Figure 2). The hexacoordinate structure of this species was evidenced by UV-vis spectroscopy and electrochemistry. A weak absorption appears at $\lambda_{\text{max}} = 687 \text{ nm}$ ($\epsilon = 100 \text{ mol}^{-1} \text{ L cm}^{-1}$, MeCN). The cyclic voltammogram shows an irreversible reduction at -0.43 V (vs SCE, MeCN). These data are similar to the ones obtained for

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(8) $\text{Cu(1)}_2^+\text{BF}_4^-$ was prepared in quantitative yield by reaction of $\text{Cu(MeCN)}_4\text{BF}_4$ with **1** (2 equiv) in MeCN/CH₂Cl₂ at 23 °C.

(9) Experimental data for $\text{Cu(II)N}_6^{2+}(\text{PF}_6)_2$: MS (FAB, *m/z*) 1418.4 (M – PF₆). Anal. Calcd: C, 69.12; H, 4.52; N, 8.96. Found: C, 69.13; H, 4.59; N, 9.21. See text for CV and UV-vis data.

the complex $\text{Cu}(\text{diMe-tpy})_2(\text{BF}_4)_2$ (diMe-tpy = 5,5''-dimethyl-2,2':6',2''-terpyridine).¹⁰

When a MeCN dark red solution of $\text{Cu}(\text{I})\text{N}_4^+\text{PF}_6^-$ was oxidized by an excess of NO^+BF_4^- , a green solution of $\text{Cu}(\text{II})\text{N}_6^{2+}$ was obtained. The CV is the same as for the starting complex, and the visible absorption spectrum shows a band at $\lambda_{\text{max}} = 670 \text{ nm}$ ($\epsilon = 810 \text{ mol}^{-1} \text{ L cm}^{-1}$, MeCN) typical of these tetrahedral $\text{Cu}(\text{II})$ complexes.² A decrease of the intensity of this band was observed when monitoring it as a function of time. This fact is due to the gliding motion of the rings to give the penta- and hexacoordinate $\text{Cu}(\text{II})$ complexes, whose extinction coefficients are lower as compared to the one for $\text{Cu}(\text{II})\text{N}_6^{2+}$ (ca. 125² and 100, respectively). The rate of this process is strongly dependent on the presence of water and other cosolvents. Water seems to retard the process whereas DMF accelerates the ring-gliding motion. The rate of the rearrangement is roughly twice as large as that for the monoterpy-related catenate,² which is in accordance with the presence of two terpy moieties. The final product is $\text{Cu}(\text{II})\text{N}_6^{2+}$ as indicated by the final spectro- and electrochemical data. A similar behavior was observed when a solution of $\text{Cu}(\text{I})\text{N}_4^+$ was electrochemically oxidized.

When either the $\text{Cu}(\text{II})\text{N}_6^{2+}$ solution resulting from this process or a solution prepared from a sample of isolated solid $\text{Cu}(\text{II})\text{N}_6^{2+}(\text{BF}_4^-)_2$ were electrochemically reduced at -1 V , the tetracoordinate catenate was quantitatively obtained. The cycle depicted in Figure 1 was thus completed. The changeover process for the monovalent species is faster than the rearrangement of the $\text{Cu}(\text{II})$ complexes, as previously observed for the above-mentioned related catenate.² In fact, the rate is comparable to the CV time scale and three Cu species are detected when a CV of a MeCN solution of $\text{Cu}(\text{II})\text{N}_6^{2+}(\text{BF}_4^-)_2$ is performed (Figure 3). The waves at $+0.63 \text{ V}$ and -0.41 V correspond, respectively, to the tetra- and hexacoordinate complexes mentioned above. Given that the topological constraint reduces the number of possible species that may be formed, and by analogy with the value found for the *isolated* and previously reported structurally related catenate (-0.07 V),² the wave at -0.05 V was assigned to the pentacoordinate couple. The relative heights of the oxidation waves for the three complexes depend on the scan rate and vary from 1:1:4 for CN = 4, 5, and 6, respectively, at 100 mV s^{-1} to 1:4:1.5 at 2 V s^{-1} . Therefore, at high scan rates the pentacoordinate species $\text{Cu}(\text{I})\text{N}_5^+$ becomes the major one. Both $\text{Cu}(\text{I})$ and $\text{Cu}(\text{II})$ pentacoordinate complexes are intermediates which could be

(10) This compound was prepared by reacting $\text{Cu}(\text{BF}_4)_2$ with an excess of 5,5''-dimethyl-2,2':6',2''-terpyridine in MeCN: $\lambda_{\text{max}} = 693 \text{ nm}$ ($\epsilon = 70 \text{ mol}^{-1} \text{ L cm}^{-1}$, MeCN); $E_{\text{red}} = -0.41 \text{ V}$ (vs SCE, MeCN).

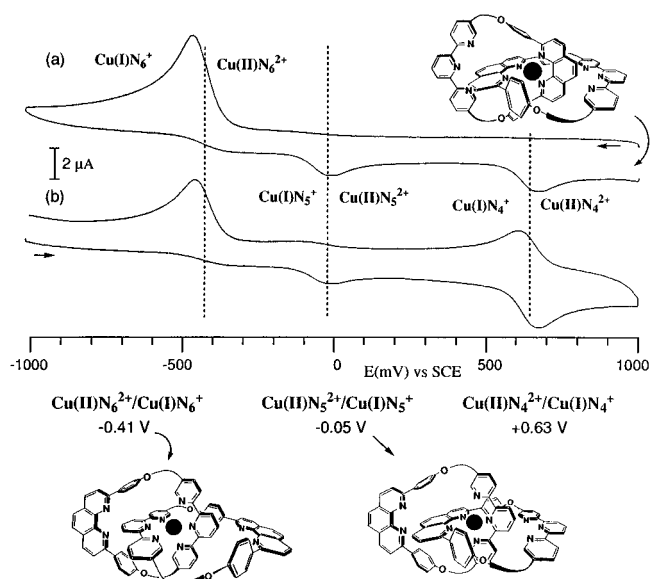


Figure 3. Cyclic voltammogram of a solution of $\text{Cu}(\text{II})\text{N}_6^{2+}(\text{BF}_4^-)_2$ (MeCN; Bu_4NBF_4 , 0.1 M; 200 mV s^{-1} ; reference electrode: SCE). (a) Starting from $+1 \text{ V}$, only one reduction wave is observed ($\text{Cu}(\text{II})\text{N}_6^{2+}$ to $\text{Cu}(\text{I})\text{N}_6^+$). When coming back to positive potential, the three possible species (CN = 4, 5, and 6) formed by ring gliding are detected. In the time scale of the experiment, the tetracoordinate $\text{Cu}(\text{I})$ complex becomes the major one. (b) The same solution but starting from -1 V . The reversible signal at $+0.63 \text{ V}$ corresponds to the $\text{Cu}(\text{II})\text{N}_4^{2+}/\text{Cu}(\text{I})\text{N}_4^+$ couple. The tetrahedral $\text{Cu}(\text{I})$ complex is formed during the experiment from the reduced hexacoordinate species. The reduction wave of $\text{Cu}(\text{II})\text{N}_6^{2+}$ is not due to the complex formed by ring rotation (which is too slow) but to the starting species already existing in the bulk solution.

characterized by various techniques as transient species, but in principle, the present system does not allow to stop motions at this stage. Only three complexes of the six species of Figure 1 have been spectroscopically identified.

The overall cyclic process depicted in Figure 1 does not consume or produce electrons; it describes the interconversion between three molecular topographies (CN = 4, 5, or 6), the topological properties of the backbone being of course unmodified in the whole process.

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