

Transition Metal-Containing Rotaxanes and Catenanes in Motion: Toward Molecular Machines and Motors

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Introduction: Recent Development of Functional Rotaxanes and Catenanes

The fascination exerted on molecular chemists by knots, catenanes and, to a lesser extent, by rotaxanes stems originally from their topology.¹

For instance, a simple² catenane (i.e., a compound consisting of two interlocking rings) is unique in the sense that any projection of the molecule on a plane will have to contain two crossing points, regardless of the distortion that might be imposed on bonds and angles: Its graph is nonplanar.² If the making of relatively simple catenanes and rotaxanes used to be a real synthetic challenge only 20 years ago,³ this is no more true today. Synthetic strategies based on various template effects have been proposed by several groups since the beginning of the 1980s, leading to efficient preparative procedures. The preassembled precursors, affording the desired ring-containing compounds after cyclization or blocking reactions, can be transition metal complexes,⁴ aromatic acceptor–donor complexes,⁵ and/or hydrogen-bonded⁶ species. Single-stranded DNA has also been used to construct interlocking rings of various complexity.⁷

The utilization of molecular fragments displaying specific properties and allowing the elaboration of the appropriate scaffolding used as catenane or rotaxane precursor leads to compounds displaying interesting properties originating both from those of the fragments incorporated and from the new topology obtained. As a consequence, the potential applications of catenanes are no longer restricted to polymers, displaying hypothetical mechanical or rheological properties of interest, but are now more general. For instance, new energy or electron transfer and photochemical features have been demonstrated in several systems.^{8,9}

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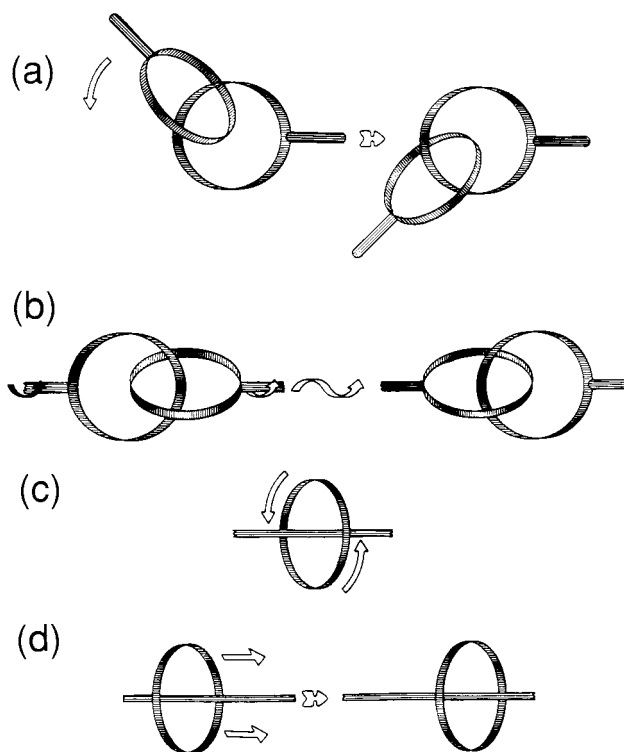


FIGURE 1. Interlocking rings and threaded systems can be considered as elemental working parts of future molecular machines. (a) Prototype molecular “ball and socket” joint. (b) Crude “universal joint”: the action of twisting the axle on the left clockwise is followed by the effect of rotating the right-hand axle due to the mechanical action of one ring onto the other. (c) Wheel and axle in action. (d) Translation of a ring on an axle.

Molecular Machines and Motors

Recently, a new dimension has been added by moving components of the molecular systems at will, under the action of a photochemical or electrochemical signal. In fact, compounds containing interlocking rings or rings threaded onto an acyclic fragment are the ideal precursors to molecular machines,¹⁰ i.e., multicomponent systems for which selected parts can be set in motion while the other fragments are motionless. As schematically represented in Figure 1, these topologies provide the working parts of the machines or motors to be elaborated.

Molecules whose shape is modified from the outside by sending a signal to the system are of course numerous. However, molecular machines tend to refer to *large-amplitude* motions leading to real translocation of some parts of the compound, reversibility being of course an essential feature of the system.

Photochemistry offers many examples of large motions, the *cis*–*trans* isomerization^{11,12} of an azo group being a very attractive process to modify the geometry and the properties of the compounds. Several other photochemical reactions can be utilized,^{13,14} including the photoisomerization of stilbene-like compounds.¹⁵

A chemical signal can also be used, as in the “molecular brake” recently described.¹⁶ In this case, it is rather the

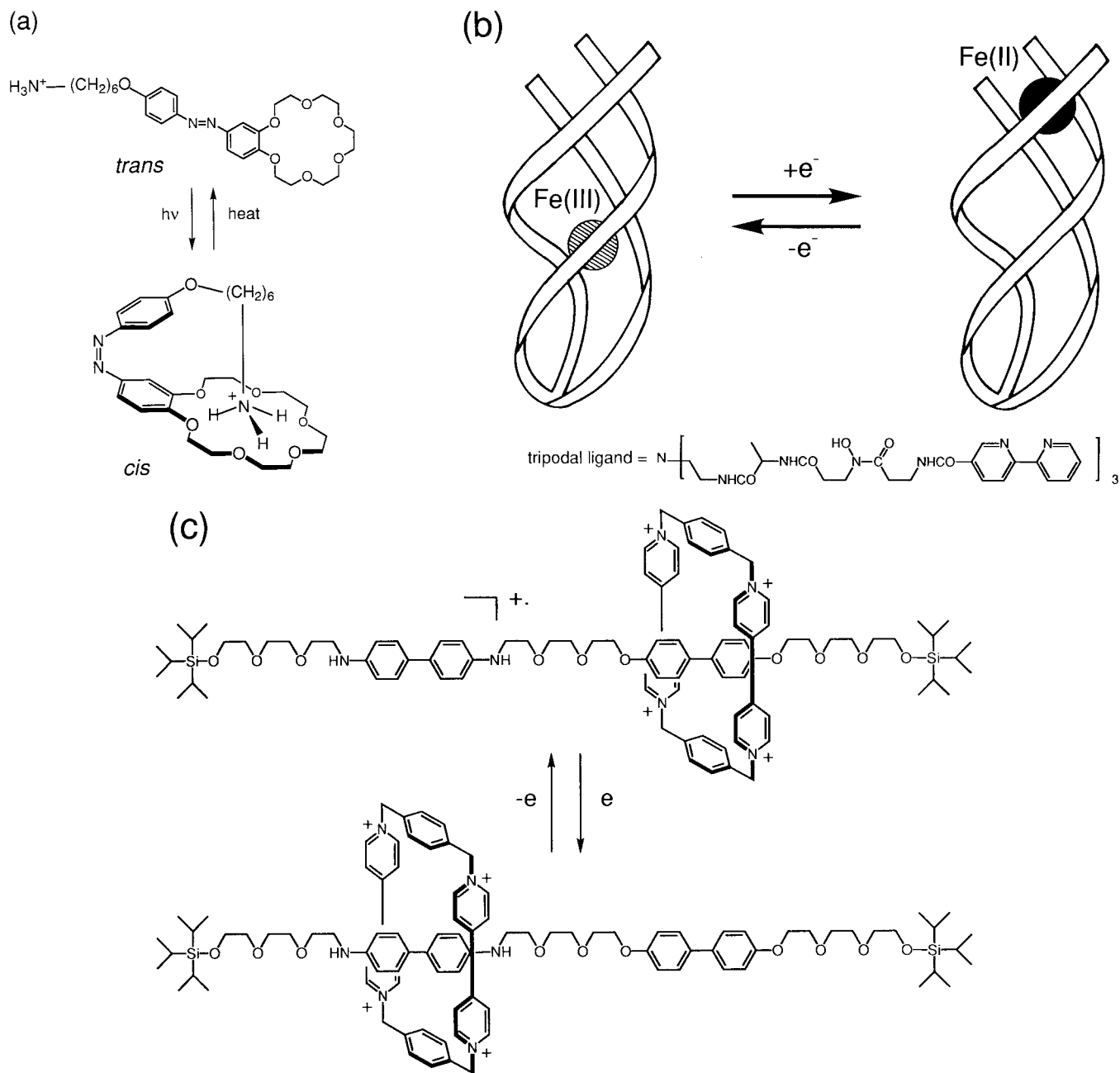


FIGURE 2. A few examples of machinelike compounds, able to undergo drastic geometrical changes under the action of an external signal. In some cases, this shape modification induces new properties and is followed by a subsequent reaction. (a) Photoresponsive crown ether^{11e} whose ammonium group can complex the coordination site ("tail-biting") in the cis form, thus partly masking the ability of the crown to bind and extract alkali cations. As expected, the trans isomer has much better complexation power. (b) Hopping of an iron center between the two complexation sites of a tripodal ligand. Fe(II) forms stable complexes with neutral ligands of the 2,2'-bipyridine type. After oxidation to Fe(III), the metal center moves to the anionic site.^{20a} (c) A switchable rotaxane based on acceptor–donor complexes.²³ Before oxidation, the electron acceptor (ring) interacts preferentially with the benzidine nucleus (donor). After electrochemical oxidation of the latter, the ring is shifted toward the biphenoxy group. The process is reversible.

motion properties (rotation of a group about a C–C bond) of the compound that are modified by adding a transition metal and not so much its shape.

Most of the systems described until now are based on redox signals. The most elaborate of these can thus be regarded as "electromechanical motors". Proteins¹⁷ form a very important class of such systems, able to undergo folding–unfolding processes by simply reducing or oxidizing a component of the protein (heme of a cytochrome,

amino acid, etc.). Inorganic systems based on linkage isomerism induced by changing the metal oxidation state are also known.^{18,19} For instance, a sulfoxide is O-bonded to ruthenium(III) in its stable form (Ru–OSR₂). By reducing the metal to the divalent state, the O-bonded species obtained at first rearranges to afford the stable S-bonded complex [Ru–S(O)R₂]. In an elegant study Taube and Sano have shown that this principle can lead to molecular hysteresis.¹⁹ Another pertinent example of redox-induced

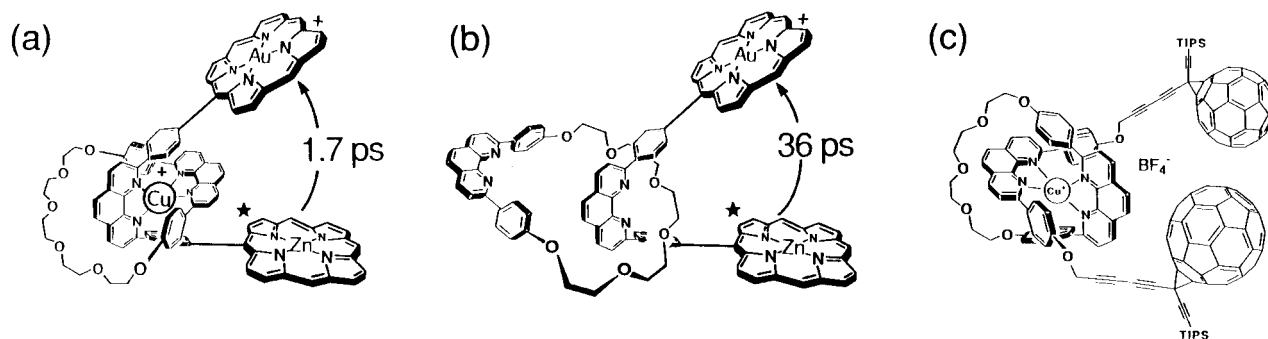


FIGURE 3. Rotaxanes with photo- and electroactive stoppers. (a) The “zinc–copper–gold” compound²⁶ is able to undergo ultrafast electron transfer between the zinc porphyrin component in its singlet excited state (donor) and the gold(III) porphyrin (acceptor), mediated by the central copper(I) complex (the substituents borne by the porphyrins have been omitted). (b) Removal of the copper(I) atom was shown to have a strong influence on the photochemical behavior of the compound, by slowing down electron transfer. (c) A fullerene-stoppered rotaxane²⁷; TIPS is triisopropylsilyl.

movement is based on a multifunctional system incorporating sets of ligands forming two distinct coordination sites, adapted to either Fe(II) or Fe(III).²⁰ By changing the iron oxidation state, translocation of the metal is observed. Another interesting case²¹ is that of a bis-porphyrin in which the two tetrapyrrolic nuclei are linked by an ethene group ($-\text{CH}_2=\text{CH}_2-$) and undergo redox-induced cis–trans isomerization. After reduction of the porphyrins in the cis isomer, isomerization to the trans species takes place.

The group of Stoddart has recently created a vast and new family of interlocking and threaded compounds constructed on acceptor–donor aromatic complexes.⁵ This remarkable synthetic work has been sustained by very elegant photochemical and electrochemical studies carried out by the groups of Balzani²² and Kaifer,²³ respectively. These demonstrated that molecular movements can be induced in such systems, either by irradiating the compounds with visible light in the presence of other additional reagents or by using electrochemical reactions. A few recent examples of molecules undergoing large-amplitude photo- or electrochemically piloted conformational changes are indicated in Figure 2.

Transition Metal Containing Rotaxanes: From Electronic to Molecular Motion

Our interest in photosynthesis and its models²⁴ combined with our ability to thread molecular fragments (“strings”) into macrocycles (“rings”)^{4a,25} has naturally prompted us to make electro- and photoactive rotaxanes with porphyrins as stoppers²⁶ or, more recently, C₆₀ moieties.²⁷ In Figure 3 are represented a few examples from our group.

The synthetic strategy developed in our group for making rotaxanes relies on the ability of copper(I) to gather the two constitutive organic fragments (a ring incorporating a bidentate chelate and an open chain component) and to force the string to thread through the ring. This threading step is generally quantitative provided the stoichiometry of the reaction is carefully respected, due to the selective formation of very stable tetrahedral copper(I) complexes (Figure 4a). It can be extended to strings containing two identical coordination sites, thus permitting the threading of two identical rings

(Figure 4b).^{25,28} It can also be generalized to molecular strings containing two *different* sites, such as *bidentate* and *terdentate* coordinating units (Figure 4c). In this case, again because of the very strong preference of copper(I) for 4-coordinate complexes (tetrahedral or distorted tetrahedral), the threading process will be very selective and lead to a situation in which the ring is exclusively associated with the bidentate chelate fragment of the string, in its coordination to copper(I), as indicated in Figure 4c.²⁹

It is of course this latter compound that will be prompted to undergo motions by changing the redox state. This particular system and all the other “molecular machines” elaborated and studied in our group function on the same principle. Among the first-row transition metal ions, copper displays unusual features related to the geometrical properties of its complexes: The stereo-electronic requirements of copper(I) and copper(II) are markedly different. This characteristic will provide the driving force for setting our systems into motion. Whereas a coordination number (CN) of 4, usually with a roughly tetrahedral arrangement of ligands, corresponds to stable monovalent systems, copper(II) requires higher coordination numbers. The most commonly encountered copper(II) complexes have a CN of 5 (square pyramidal or trigonal bipyramidal geometries) or 6 (octahedral arrangement, with Jahn–Teller distortion). Thus, by switching alternatively from copper(I) to copper(II), one should be able to induce changes in the molecule so as to afford a coordination situation favorable to the corresponding oxidation state. The principle is illustrated in Figure 5,²⁹ using the threaded system of Figure 4c.

Of course, if the acyclic molecular fragment that threads the ring does not bear blocking groups at its ends, dethreading may occur. This is indeed observed in polar solvents (CH₃CN), mostly at the 2+ stage, to afford a bis-terpy-like (terpy = 2,2',6',2''-terpyridine) complex obtained when two strings are taken up by the same copper(II) center. The obvious improvement is to attach one or, better, two bulky groups at the extremities of the string in order to prevent unthreading.³⁰ These new systems are represented in Figure 6.

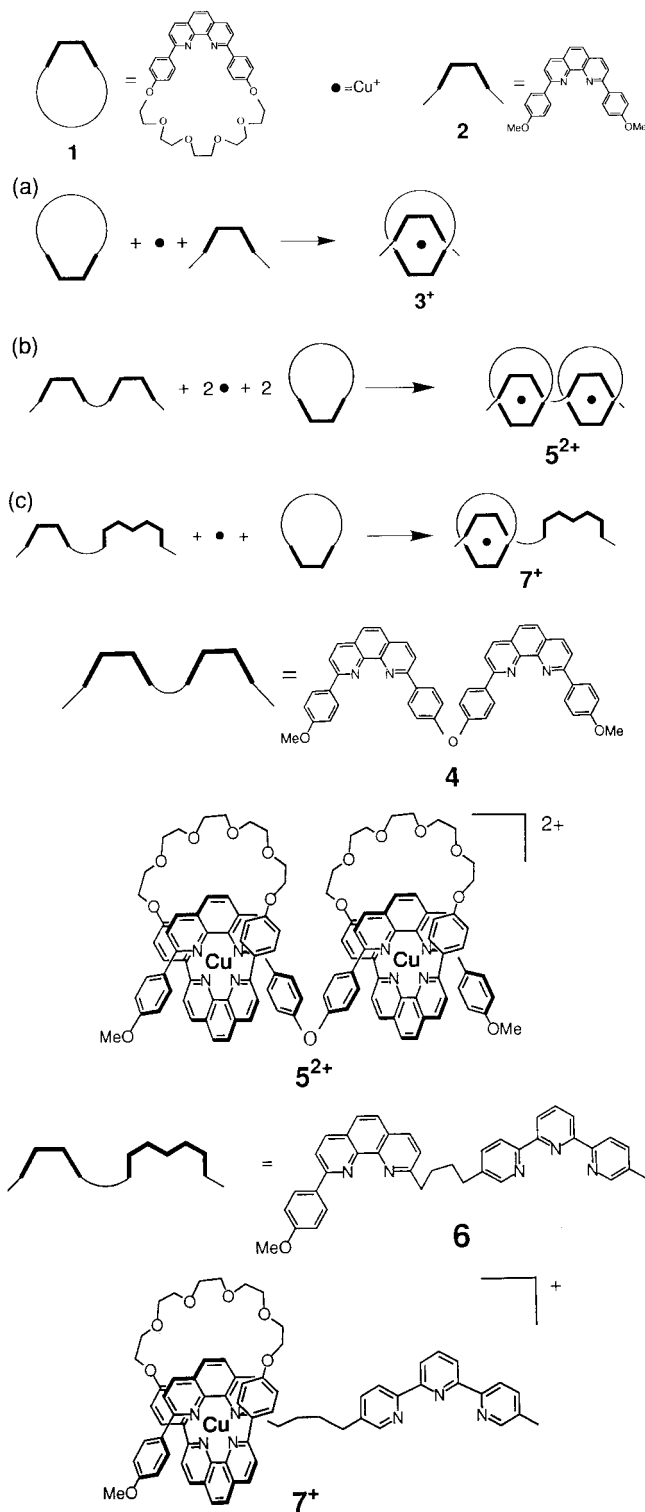


FIGURE 4. Copper(I)-induced threading of one or two rings on a molecular string. **1** is a 30-membered ring, containing a bidentate ligand. (a) The acyclic fragment **2** is a simple phenanthroline derivative. This threading process has been used in our group since the early 1980s to make catenanes.^{4a} (b) The string **4** now incorporates two identical bidentate units; as in panel a, the process is quantitative.²⁸ (c) A slightly more complex case: the acyclic component contains both a *bidentate* ligand and a *terdentate* coordinating unit (2,2',6',2''-terpyridine). With copper(I) as gathering metal, exclusive formation of the 4-coordinate complex **7**⁺ is observed.

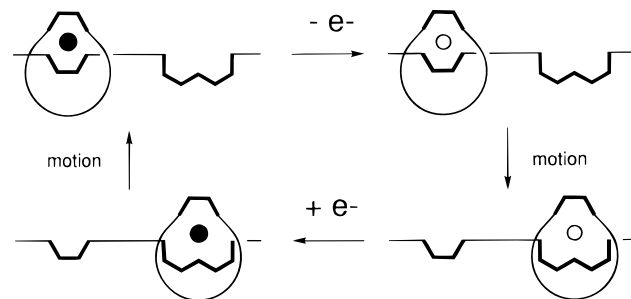


FIGURE 5. Principle of the electrochemically induced molecular motions in a copper(I) complex pseudorotaxane. The stable four-coordinate monovalent complex is oxidized to an intermediate tetrahedral divalent species. This compound undergoes a rearrangement to afford the stable five-coordinate copper(II) complex. Upon reduction, the five-coordinate monovalent state is formed as transient. Finally, the latter undergoes the reorganization process that regenerates the starting complex (the black circle represents Cu^I and the white circle represents Cu^{II}).

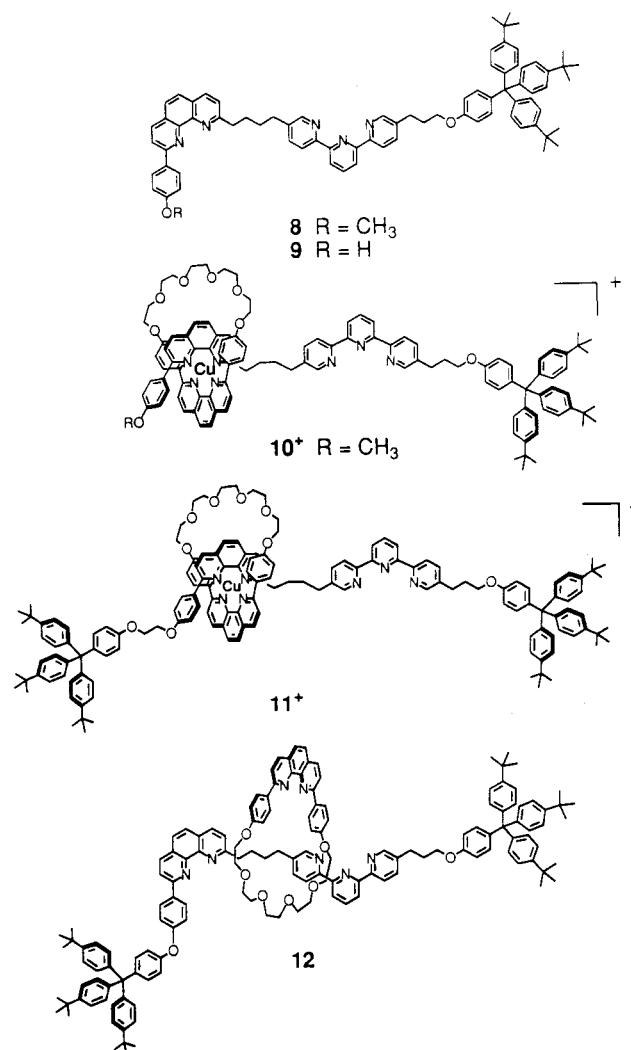


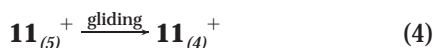
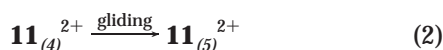
FIGURE 6. Semirotaxane **10**⁺, real copper-containing rotaxane **11**⁺, and demetalated rotaxane **12**.

The semirotaxane was simply obtained by mixing stoichiometric amounts of **8**, which is an improved version of **6** (Figure 4), Cu(CH₃CN)₄⁺, and **1** (Figure 5). If, in **9**, the OCH₃ group borne by the phen unit of the string (phen

= 1,10-phenanthroline) is replaced by a phenolic function (**9**), threading will lead to a 10^+ -type compound with a reactive end. Activation of the $-OH$ function and covalent attachment of the blocking group affords the real rotaxane **11**⁺. It is real in the sense that demetalation furnishes a copper-free system (**12**) whose acyclic component will not dethread from the 30-membered ring.

The electrochemical behavior of **11**⁺ is particularly clean and interesting since only the 4- and the 5-coordinate geometries can be obtained by translating the metal-complexed ring from the phen site to the terpy site.³⁰ The electrochemically induced molecular motions (square scheme³¹) similar to those represented in Figure 5 but now involving stoppered compounds can be monitored by cyclic voltammetry.³⁰

It is noteworthy that oxidation of **11**⁺ to the divalent copper(II) state affords exclusively the 5-coordinate species after rearrangement of the system. The bis-terpy complex, which would be formed by decomplexation of the copper(II) center and recoordination to the terpy fragments of two different molecules of **12**, is not detected. This observation is important in relation to the general mechanism of the changeover step converting a 4-coordinate Cu(II) species [Cu(II)₍₄₎] into the corresponding stable 5-coordinate complex [Cu(II)₍₅₎] (the subscripts 4 and 5 indicate the coordination number of the copper center). It tends to indicate that the conversion does not involve full demetalation of Cu(II)₍₄₎ followed by recomplexation but is rather an intramolecular reaction, probably consisting of several elemental dissociation–association steps involving the phen and terpy fragments of the string as well as solvent molecules and, possibly, counterions. The square scheme involving the fully blocked rotaxanes **11**ⁿ⁺ ($n = 1$ or 2) corresponds to the following sequence of reactions:



For the reaction shown in eq 1, $E^{\circ} = +0.68$ V (vs SCE in CH₃CN); for eq 3, $E^{\circ} = -0.03$. It is noteworthy that the redox couples of eq 1–3 are perfectly reversible provided the scan rate is sufficient (>100 mV s⁻¹). The gliding motions, either for the divalent or the monovalent complex, are slow on the time scale of the voltammetry measurements (eqs 2 and 4).

Electrochemically Induced Ring-Gliding Motions in Copper-Complexed Catenanes

The first molecular motor elaborated and studied in our group was a catenane containing two different interlocking rings. Its principle is explained in Figure 7.³² The actual system and the full-square scheme are indicated

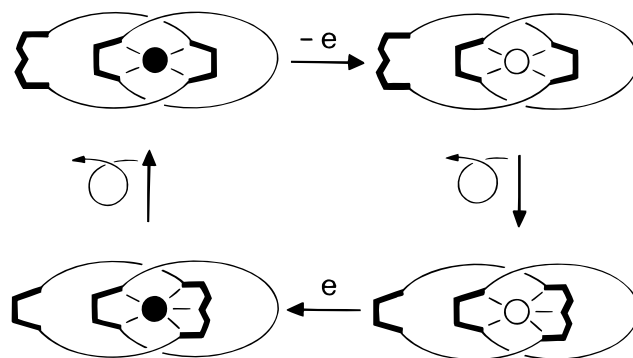


FIGURE 7. Electrochemically triggered rearrangement of a [2]-catenane containing two different rings. The stable 4-coordinate monovalent complex [top left; the black circle represents Cu(I)] is oxidized to an intermediate tetrahedral divalent species [top right; the white circle represents Cu(II)]. This compound undergoes a complete reorganization process to afford the stable 5-coordinate Cu(II) complex (bottom right). Upon reduction, the 5-coordinate monovalent state is formed as a transient (bottom left). Finally, the latter undergoes the conformational change that regenerates the starting complex.

in Figure 8. The starting copper(I) complex **13**₍₄₎⁺ is a 4-coordinate species, whose high redox potential (+0.63 V vs SCE in CH₃CN) clearly indicates that the geometry of the system (tetrahedral or distorted tetrahedral) is well adapted to copper(I). This redox state being very stable with the environment provided by **13**₍₄₎⁺, a relatively high redox potential will have to be applied for the monovalent copper center to be oxidized to the divalent state. Interestingly, the 4-coordinate Cu(II) complex **13**₍₄₎²⁺ is an intense green species, with a d–d absorption band at 670 nm ($\epsilon = 800$) in CH₃CN. This compound can be generated by either chemical (Br₂ or NOBF₄) or electrochemical oxidation.

The changeover reaction converting **13**₍₄₎²⁺ to the stable 5-coordinate species **13**₍₅₎²⁺ is quantitative. It is easily monitored by visible absorption spectroscopy since the product of the rearrangement reaction is only slightly colored (pale olive green; $\lambda_{\text{max}} = 640$ nm; $\epsilon = 125$). Both copper(II) complexes **13**₍₄₎²⁺ and **13**₍₅₎²⁺ have electronic spectra typical for 4- and 5-coordinate species, respectively, in accordance with previously reported complexes having analogous ligand sets³³. The same conversion process can also be monitored by electron paramagnetic resonance spectroscopy (EPR).³⁴ It was demonstrated in an unambiguous fashion that **13**₍₄₎²⁺ is a distorted tetrahedral complex and that the product of the changeover, **13**₍₅₎²⁺, is a square pyramidal compound.

An interesting question is dealing with the rate of the ring gliding motion that transforms **13**₍₄₎²⁺ into **13**₍₅₎²⁺ or, after reduction of the latter, **13**₍₅₎⁺ into **13**₍₄₎⁺. It was observed that this last process, involving Cu(I), is fast (a few seconds at room temperature, regardless of the solvent) whereas the copper(II) complex rearrangement **13**₍₄₎²⁺ → **13**₍₅₎²⁺ is slow and depends enormously on experimental conditions. This linkage isomerization reaction was shown to take place in a few minutes in anhydrous acetonitrile but it requires hours or even days to go to completion in noncoordinating solvents or in the

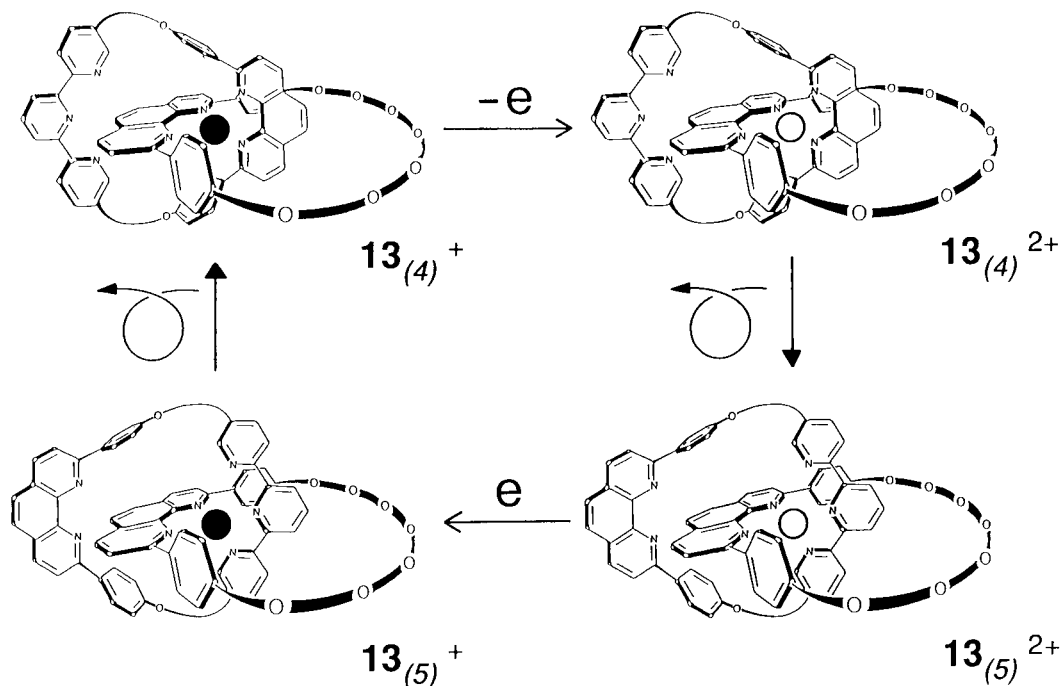


FIGURE 8. Electrochemically induced molecular rearrangements undergone by the copper catenane $\mathbf{13}^{2+/+}$. In the text, the subscript 4 or 5 indicates the number of nitrogen atoms coordinated to the metal. This number is explicitly shown on the figure.

absence of coordinating counterions. The strong accelerating influence of CH_3CN (over CH_2Cl_2) or Cl^- (over PF_6^-) may give indications regarding the rearrangement mechanism. In the course of the changeover process, removal of a dpp unit (dpp = 2,9-diphenyl-1,10-phenanthroline) from the copper(II) coordination sphere has to proceed before any interaction between the metal center and the entering terpy ligand is possible. This implies that the copper(II) atom is “half-naked” at some stage. If coordinating ions or solvent molecules are present in the medium, they could interact with the metal in this coordinatively unsaturated complex, in a transitory fashion, and thus lower the activation barrier of the rearrangement by stabilizing intermediate states.

The last system we will discuss is based on a[2]-catenane that can adopt three distinct geometries³⁵ and contains two identical interlocking rings. 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. In particular, if molecules or molecular assemblies are to be utilized one day as information storage devices, it is obvious that the use of three-state systems will produce a great increase in information density as compared to bistable systems. For instance, an assembly of 10 distinct molecules whose each individual molecular component can occupy two states (say, + or -) will lead to 2^{10} different states (i.e., 1024 states), whereas if the same collection of 10 distinct molecules is such that each compound can now occupy three states (+, 0, and -), the overall number of states is now 3^{10} (i.e., 59 049).

The principle of the three-situation electromediated catenane is represented in Figure 9. Again, it relies on the

drastic differences of stereochemical requirements for coordination of Cu(I) and Cu(II), the sequence of preferred coordination numbers (CN) being $\text{CN} = 4 > \text{CN} = 5 > \text{CN} = 6$ for Cu(I) and $\text{CN} = 6 > \text{CN} = 5 > \text{CN} = 4$ for Cu(II). The compound is made in modest yield but following a very straightforward approach. The entwined complex $\mathbf{14}^+$, used in many syntheses by our group,^{4a} is reacted with the difunctionalized terpy $\mathbf{15}$, in the presence of Cs_2CO_3 under high dilution conditions. This one-pot two-ring-forming reaction (Figure 10) affords $\mathbf{16}_{(4)}^+$ in 21% yield, as a deep red 4-coordinate complex ($\lambda_{\text{max}} = 439 \text{ nm}$; $\epsilon = 2570 \text{ mol}^{-1} \text{ L cm}^{-1}$ in CH_3CN).³⁵

The free catenane $\mathbf{17}$ is easily obtained from $\mathbf{16}_{(4)}^+$ by removing the metal with KCN. Interestingly, remetallation of $\mathbf{17}$ by the divalent copper salt $\text{Cu}(\text{BF}_4)_2$ affords the hexacoordinate species $\mathbf{16}_{(6)}^{2+}$ (see Figure 11) as a very pale green complex ($\lambda_{\text{max}} = 687 \text{ nm}$; $\epsilon = 100 \text{ mol}^{-1} \text{ L cm}^{-1}$).

Detailed electrochemical studies have been carried out on $\mathbf{16}_{(4)}^+$. Although we will not discuss them in the present review, they afford very conclusive data and, in particular, they demonstrate unambiguously that the compound undergoes the rearrangement reactions schematically represented in Figure 9.

The sequence of electron-transfer steps and ring-gliding motions corresponding to the cyclic process of Figure 9 can also be induced by using chemical reagents. For instance, when a dark red solution of $\mathbf{16}_{(4)}^+$ is oxidized by $\text{NO}^+ \text{BF}_4^-$ in CH_3CN , an intense green solution of $\mathbf{16}_{(4)}^{2+}$ is first obtained. As expected, the cyclic voltammogram (CV) of this species is the same as for the starting complex, which is in accordance with the 4-coordinate situation for both oxidized and reduced forms. The visible absorption spectrum shows a band at $\lambda_{\text{max}} = 670 \text{ nm}$ with

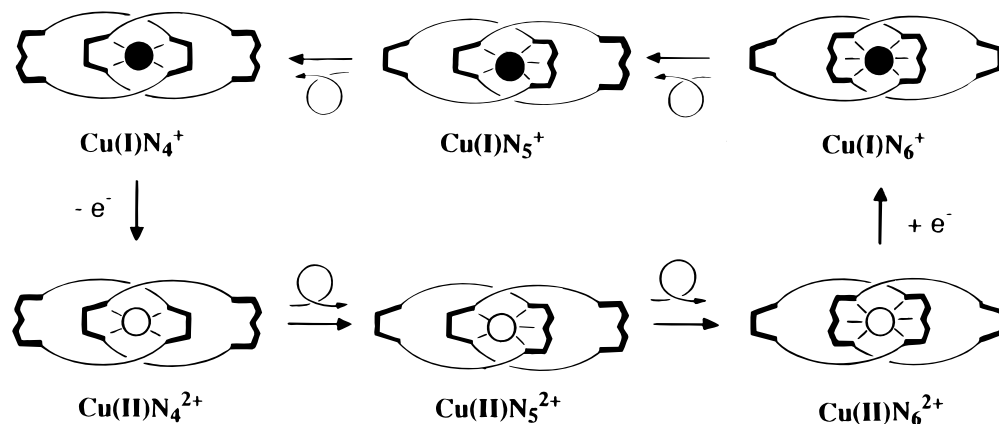


FIGURE 9. A three-configuration Cu(I) catenate whose general molecular shape can be dramatically modified by oxidizing the central metal [Cu(I) to Cu(II)] or reducing it back to the monovalent state. Each ring of the [2]-catenate now incorporates two different coordinating units: a bidentate unit and a terdentate fragment. Starting from the tetra-coordinate monovalent Cu complex [Cu(I)N₄⁺; top left] and oxidizing it to the divalent state [Cu(II)N₄²⁺], a thermodynamically unstable species is obtained that should first rearrange to the 5-coordinate complex Cu(II)N₅²⁺ by gliding of one ring (left) within the other and, finally, to the hexacoordinate stage Cu(II)N₆²⁺ by rotation of the second cycle (right) within the first one. Cu(II)N₆²⁺ is expected to be the thermodynamically stable divalent complex. The double ring-gliding motion following oxidation of Cu(I)N₄⁺ can be inverted by reducing Cu(II)N₆²⁺ to the monovalent state [Cu(I)N₆⁺; top right], as represented on the top line of the figure.

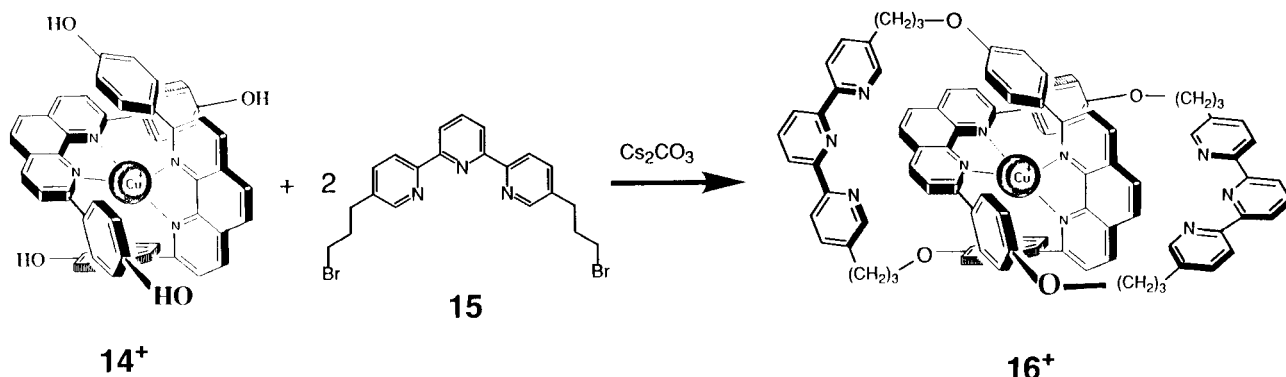


FIGURE 10. Synthesis of the symmetrical catenate $16_{(4)}^+$ ($16^+ = [\text{Cu}(17)]^+$).

a high extinction coefficient ($\epsilon = 810 \text{ mol}^{-1} \text{ L cm}^{-1}$ in $\text{CH}_3\text{-CN}$), typical of tetrahedral complexes with nitrogen ligands. The ring-gliding step will subsequently lead to a hexacoordinate complex, the 5-coordinate compound being characterized as a transient species by electrochemistry only. As for the changeover reaction of the disymmetrical catenate ($13_{(4)}^{2+} \rightarrow 13_{(5)}^{2+}$), the rearrangement $16_{(4)}^{2+} \rightarrow [16_{(5)}^{2+}] \rightarrow 16_{(6)}^{2+}$ depends critically on the experimental conditions used and can be performed in minutes or hours.

Reversing the process, reduction of the stable species $16_{(6)}^{2+}$ will afford $16_{(6)}^+$, which rapidly rearranges to the stable monovalent complex $16_{(4)}^+$. The intermediate $16_{(5)}^+$ has not been isolated nor spectroscopically characterized, but its formation was clearly evidenced by cyclic voltammetry, due to its analogy with $13_{(5)}^+$. The three forms of the catenate are represented in Figure 11.

The redox potentials for the three situations (CN = 4, 5, or 6) are in perfect agreement with those of similar systems with identical CNs. The pentacoordinate complexes were characterized as transient species, but in principle, the present system does not allow us to stop motions at this stage.

Conclusion and Prospects

The first templated synthesis of a catenane^{4a} was published almost 15 years ago, making these molecules accessible from a preparative viewpoint, although highly elegant but less practical work had previously been reported, based on pure organic chemistry.³ Since these early days, more and more functionality has been introduced into the molecules, either in relation to electron and energy transfer processes or with regard to controlled molecular motions. The use of transition metals as templates and of their complexes as electroactive and mobile components turned out to be particularly useful in the construction of *electromechanical molecular machines* based on coordination compounds. It would of course be unwise to predict that nanoscopic motors and related machines will have any practical application in the future as molecular information storage devices or as nanoscale components in electronics, but the search for such molecules or molecular assemblies is important in itself.

Molecular machines constitute an emerging field of research, at the interface with many areas of molecular

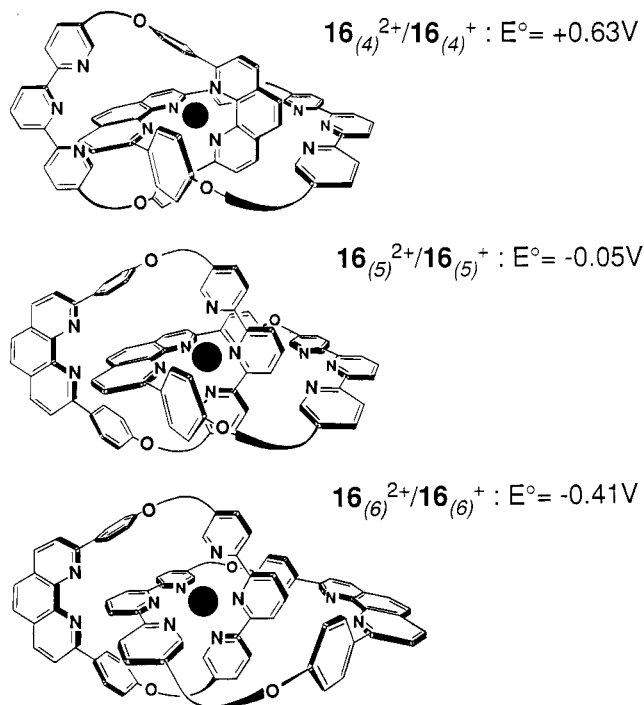


FIGURE 11. The 4-, 5-, and 6- coordinate copper complexes involved. The corresponding Cu(II)/Cu(I) redox potentials are also indicated. They clearly show the sequence of preferred stabilities for copper(II) versus copper(I), the hexacoordinate complex leading to the most stable divalent complex.

sciences. For instance, the concepts discussed in the present paper can certainly be generalized to organized assemblies of molecules (liquid crystals) or to molecular components attached to an electrode surface. The overall properties of the system (now, a “device”) such as liquid crystal character, ability to carry electrons or transport molecules, etc., could be switched by just applying a given signal. The variety of impulses to be used is immense: redox (as in the present examples), photonic, heat or pressure change, magnetic field variation, pH change, chemical signal (recognition of a molecule), electric field, etc. The effect obtained is also multifarious and could lead to dramatic modifications of the bulk properties of the system. Since a simple signal can change the shape and the volume of a compound and of its assemblies, fascinating features related to mechanics (contraction or stretching) could be imagined, reminiscent of biological systems such as muscles or other biological molecular machines.

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