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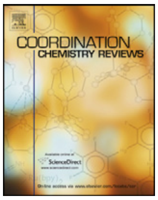

Review

The magic effect of endocyclic but non-sterically hindering biisoquinoline chelates: From fast-moving molecular shuttles to [3]rotaxanes

Fabien Durola[1], Jean-Pierre Sauvage*, Oliver S. Wenger[2]

Laboratoire de Chimie Organo-Minérale, Institut de Chimie, CNRS UMR 7177, Université de Strasbourg, 4 rue Blaise Pascal, 67070 Strasbourg Cedex, Alsace, France

Contents

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This review article is dedicated to Professor Daryle Busch, the founder of template effects, on the occasion of his 80th birthday.

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ABSTRACT

The use of 8,8′-diaryl-substituted 3,3′-biisoquinolines allows the construction of new multi-component assemblies that are inaccessible with the 2,9-diaryl-substituted 1,10-phenanthroline ligands previously developed by the Sauvage group. This is due to the sterically non-hindering nature of the new chelates, which makes three-component entanglements around octahedral metal centres such as iron(II), cobalt(II) and ruthenium(II) readily possible. Among the newly synthesized molecular assemblies are [3]rotaxanes and [3]pseudorotaxanes in which two molecular strings pass through a single macrocycle, as well as molecular shuttles that exhibit greatly improved shuttling kinetics when compared to previously investigated molecular machines that are based on copper(I)/copper(II) redox chemistry.

1. Formation of three-component entanglements from 3,3′-biisoquinoline-incorporating ligands and octahedral metal centres

Over the past few decades, chemists have learned to create molecular objects of very high complexity. Molecular Borromean rings [1], knots [2], and functional molecular flasks [3] are only three examples out of a long list that could be added here. Mechanically interlocked molecules such as catenanes and rotaxanes remain attractive research targets due to their unusual topologies and their potential to function as molecular machines. Successful approaches to obtain such multi-component assemblies often involve the use of template effects [4]. In our group, we focused on transition metal centres for gathering various organic building blocks and disposing them in a given spatial arrangement. Subsequently, covalently interlinking these fragments generates catenanes and rotaxanes.

Thanks to its well-defined tetrahedral coordination geometry, copper(I) has been particularly useful for the construction of many catenanes and rotaxanes [5]. This strategy involves the use of bidentate chelate ligands that can be enclosed in a ring in endocyclic fashion, typically 2,9-disubstituted 1,10-phenanthroline [6] or 6,6′-disubstituted 2,2′-bipyridine [7]. As illustrated in Scheme 1, only when substituted at the carbon atoms in α-position to the nitro-

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* Corresponding author. Tel.: +33 390 24 13 61; fax: +33 390 24 13 68.
E-mail address: sauvage@chimie.u-strasbg.fr (J.-P. Sauvage).

[1] Current address: The Scripps Research Institute, 10550 North Torrey Pines Road, La Jolla, CA 92037, United States.

[2] Current address: Georg-August-Universität Göttingen, Institut für Anorganische Chemie, Tammannstrasse 4, 37077 Göttingen, Germany.

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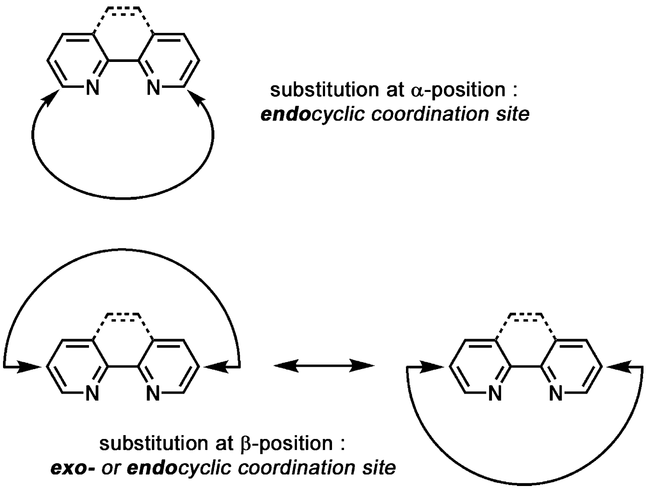


Scheme 1. Possible substitution patterns of 2,2′-bipyridine and 1,10-phenanthroline chelating agents and the resulting types of macrocyclic ligands.

gen atoms, the endocyclic coordination mode can be enforced. Any other substitution pattern of these chelates will either lead to a mixture of endocyclic and exocyclic species or to preferred exocyclic coordination.

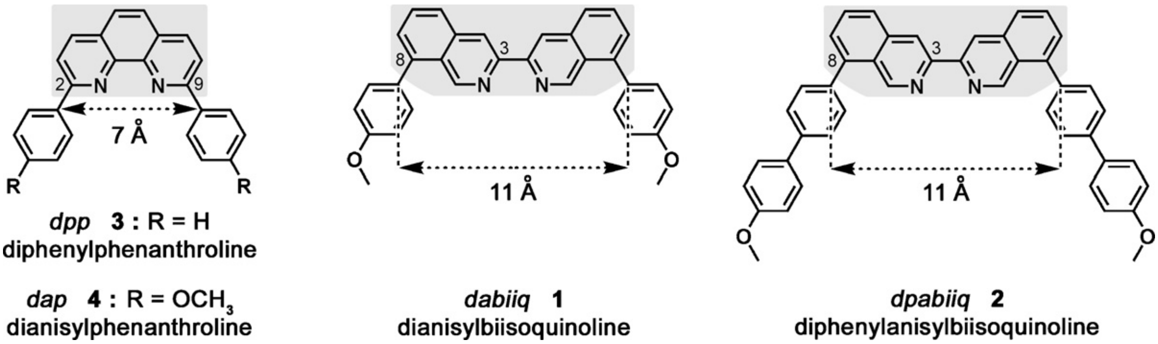
The 2,9-diphenyl-1,10-phenanthroline (dpp) fragment (Scheme 2, left) has played a particularly prominent role due to its extended rigid backbone. This chelating agent is sterically strongly hindering, leading to very stable $[Cu(dpp)_2]^+$ complexes with endocyclic coordination. Mechanically interlocked molecules are then obtained by macrocyclisation via flexible polyethylene glycol chains attached to the dpp-phenyls and subsequent removal of the metal [8]. While this approach to obtain molecules with unusual topologies has been very successful, it also has its limitations. In particular, steric constraints impede the formation of complexes in which three dpp fragments gather around a single octahedral metal centre. Clearly such octahedral complexes are an attractive synthetic target as they might pave the way to molecular species with new and more sophisticated topologies. This has been an important impetus for the search of macrocyclic ligands incorporating non-sterically hindering chelates. Additional motivation for this research comes from the fact that non-sterically hindering chelating agents might lead to molecular machines that display more rapid mechanical motions than previously investigated systems [9]. In the $[Cu(dpp)_2]^+$ fragment, the metal centre is very well shielded from the solvent, and consequently the complex is not labile. However, in molecular machines a certain degree of lability is desirable in view of obtaining reasonably rapid shuttling or pirouetting motions. In short, the two main perspectives for the use of sterically non-hindering endocyclic chelates are: (i) to access new chemical topologies and (ii) to construct fast-moving molecular machines.

We have identified 8,8′-disubstituted 3,3′-biisoquinolines **1** and **2** (Scheme 2) as promising chelates that fulfil all the necessary requirements: first, they have no substituents at the α-positions to the chelating nitrogen atoms. Second, they are rigid and crescent-shaped, thereby allowing incorporation of the ligand in a ring with an endocyclic coordination site. As seen from Scheme 2, the 8,8′-diphenyl substituted 3,3′-biisoquinoline fragment (dpbiiq) offers a much more open coordination site than the dpp ligand (**3**); the distance between the phenyl-rings attached to the 3,3′-biisoquinoline backbone is ∼11 Å, whereas for the 1,10-phenanthroline backbone it is only ∼7 Å [10]. Indeed, in the biisoquinoline ligand the coordinated metal centre will be rather remote from the phenyl-rings used to ensure the endocyclic coordination mode.

Obtaining the 8,8′-disubstituted biisoquinolines from Scheme 2 is a synthetically non-trivial matter. In our efforts, we explored both the synthesis of phenyl and biphenyl substituted ligands **1** and **2** [10,11], but encountered serious solubility problems with the latter. However, as anticipated, complexation of these ligands to octahedral metal centres such as Fe(II), Ru(II) and Re(I) proceeds smoothly and with excellent yields [10,12,13]. The homoleptic complexes $[\mathrm{Ru^{II}}(\mathbf{1})_3]^{2+}$ ($\mathbf{5}^{2+}$) and $[\mathrm{Fe^{II}}(\mathbf{2})_3]^{2+}$ ($\mathbf{6}^{2+}$) are particularly interesting: X-ray structure analyses of crystals containing these molecules provide the proof of concept, namely the successful three-component entanglement consisting of three crescent-shaped chelates coordinated to a single octahedral metal centre (Fig. 1). In both cases a more or less symmetrical helical pseudo-D_3 structure is obtained. The endotopic cleft distances, i.e., the distances between the oxygen atoms attached to two different anisyls on a given 3,3′-biisoquinoline, range from 15.6 to 16.4 Å in the case of $[\mathrm{Ru}(\mathbf{1})_3]^{2+}$ ($\mathbf{5}^{2+}$) and from 18.7 to 20.9 Å for the $[\mathrm{Fe}(\mathbf{2})_3]^{2+}$ complex ($\mathbf{6}^{2+}$) [12]. These structures are not only aesthetically pleasing, but they also form the basis for new chemical topologies and molecular machines, thereby illustrating the usefulness of coordination chemistry for the creation of multi-component assemblies with precisely designed geometries.

2. A fast-moving copper-based molecular shuttle with a 3,3′-biisoquinoline-based ring

Molecular shuttles constitute a promising class of molecular machines [14]. A ring can glide in a controlled fashion along an axis on which it has been threaded. This motion can even be realised over large distances by playing with the length of the various fragments incorporated in the thread and the number of "stations" with which a given part of the ring is able to interact. The approach of our group is based on transition metals and, in particular, on Cu(I) and Cu(II). The principle of a two-station molecular shuttle whose motions are driven by changing the metal centre oxidation state



Scheme 2. Old (left) and new (middle, right) endocyclic ligands explored in the Sauvage group [10,11]. Only the new 3,3′-biisoquinoline chelates **1** and **2** are sterically non-hindering.

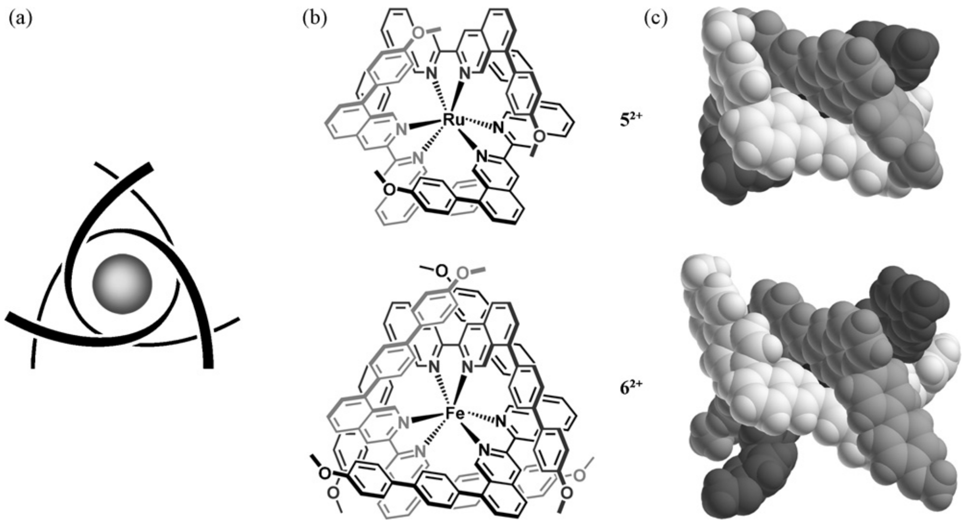


Fig. 1. (a) Schematic representation of the three-component entanglement; (b) chemical structures of the $[Ru(dabiiq)_3]^{2+}$ and $[Fe(dpabiiq)_3]^{2+}$ cations (**5**$^{2+}$ and **6**$^{2+}$); (c) X-ray crystal structure of these species [12].

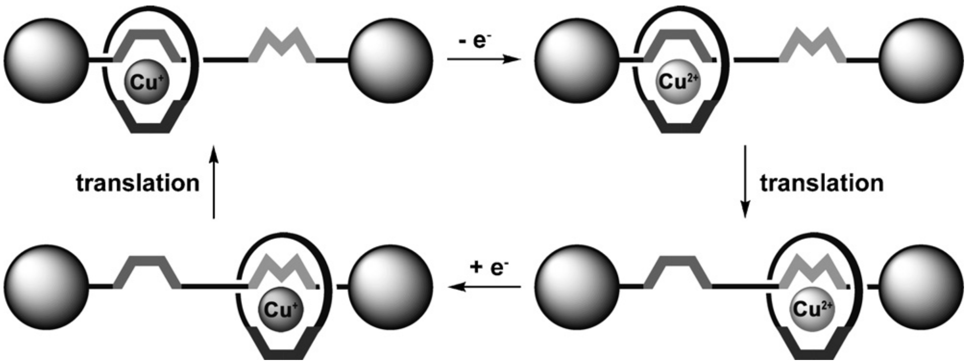
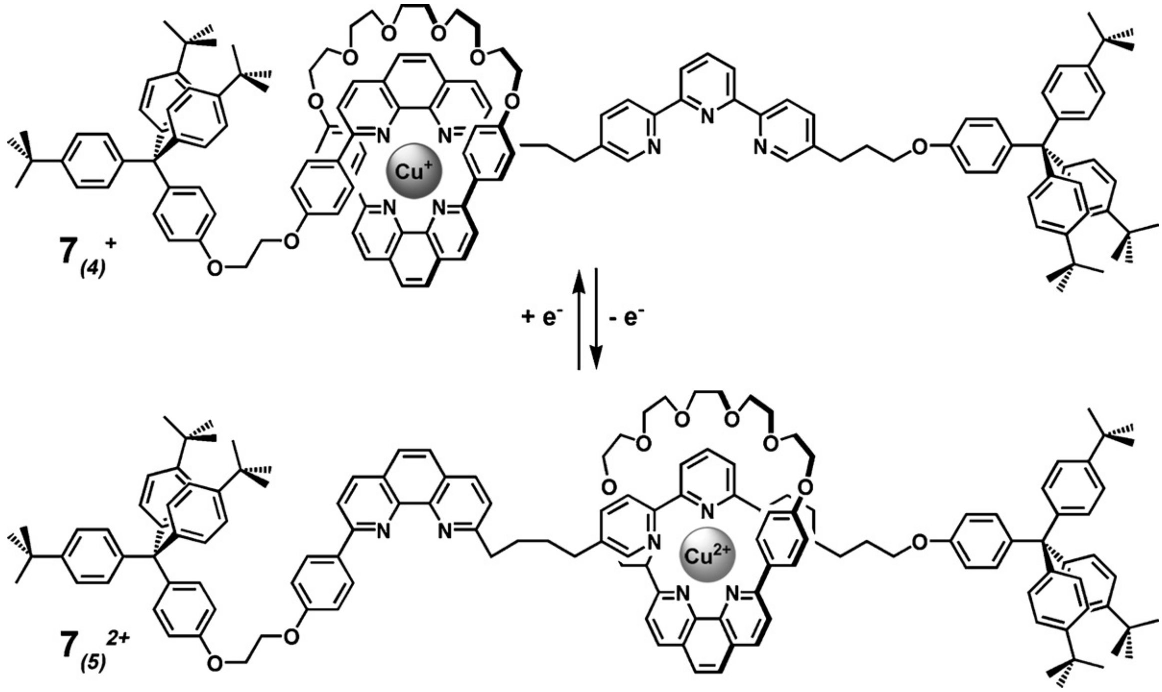


Fig. 2. Schematic representation of a metal-complexed [2]rotaxane acting as an electrochemically driven molecular shuttle. The ring contains a bidentate coordinating unit interacting with the metal centre in both states. The axis incorporates two chelating units: a bidentate one and a tridentate chelate.



Scheme 3. The two stable states of a previously reported copper-complexed bistable rotaxane **7**$^{n+}$: a slow moving shuttle. The mobile ring **8** is a 30-membered ring which incorporates a dpp chelate. The coordinating “stations” on the thread are a 2,9-disubstituted-1,10-phenanthroline unit and a 2,2′,6′,2″-terpyridine (terpy).

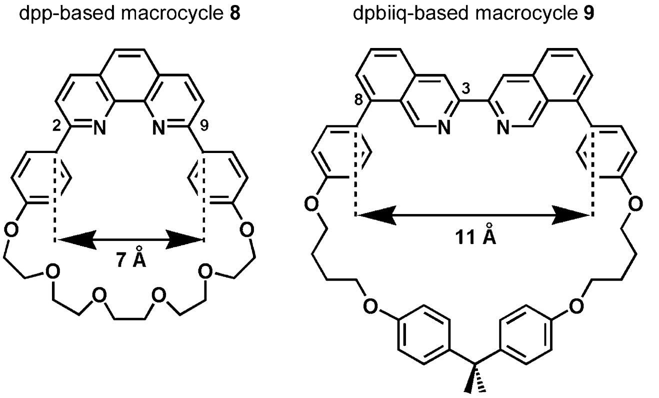
is indicated in Fig. 2. The stable 4-coordinate monovalent complex (top left) is first oxidised to an intermediate tetrahedral divalent species (top right). This compound undergoes a complete reorganisation process by translating the ring along the thread to afford the stable 5-coordinate Cu(II) complex (bottom right). Upon reduction, an unstable Cu(I) 5-coordinate complex is formed (bottom left), and finally undergoes the inverse conformational change that regenerates the starting complex.

The coordination properties of the two ligands on the axis are markedly different. In this way, by oxidising or reducing the metal centre, the system will be strongly destabilised. In order for the system to relax, the ring and the metal will have to glide along the axis. The driving force for the rearrangement of the rotaxane (i.e., for the shuttling motion of the metal-coordinated ring between the two "stations") will be determined by the energy difference between one of the two stable states and the corresponding unstable one generated by metal oxidation or reduction.

The first copper-complexed shuttle $\mathbf{7}^{n+}$ prepared and studied in our group [15] is represented in Scheme 3. In this compound, the thread is flexible which makes it difficult to have a clear view of the geometry with, in particular, an accurate knowledge of the distance between the two stations of the shuttle. In addition, and more important in terms of function, the coordination site is highly congested in the 4-coordinate situation due to the presence of a 2,9-diphenyl-1,10-phenanthroline (dpp) motif in the mobile ring **8** (Scheme 4). This structural feature is detrimental to fast ligand exchange and thus to fast motions. As a matter of fact, the rearrangements of the unstable species $\mathrm{Cu}_{(5)}(\mathrm{I})$ and $\mathrm{Cu}_{(4)}(\mathrm{II})$, described by Eqs. (1) and (2) take place on the minute to hour timescale (the subscripts (4) and (5) indicate the coordination number of the copper atom).

$$\mathbf{7}_{(5)}{}^{+} \rightarrow \mathbf{7}_{(4)}{}^{+} \qquad (1)$$

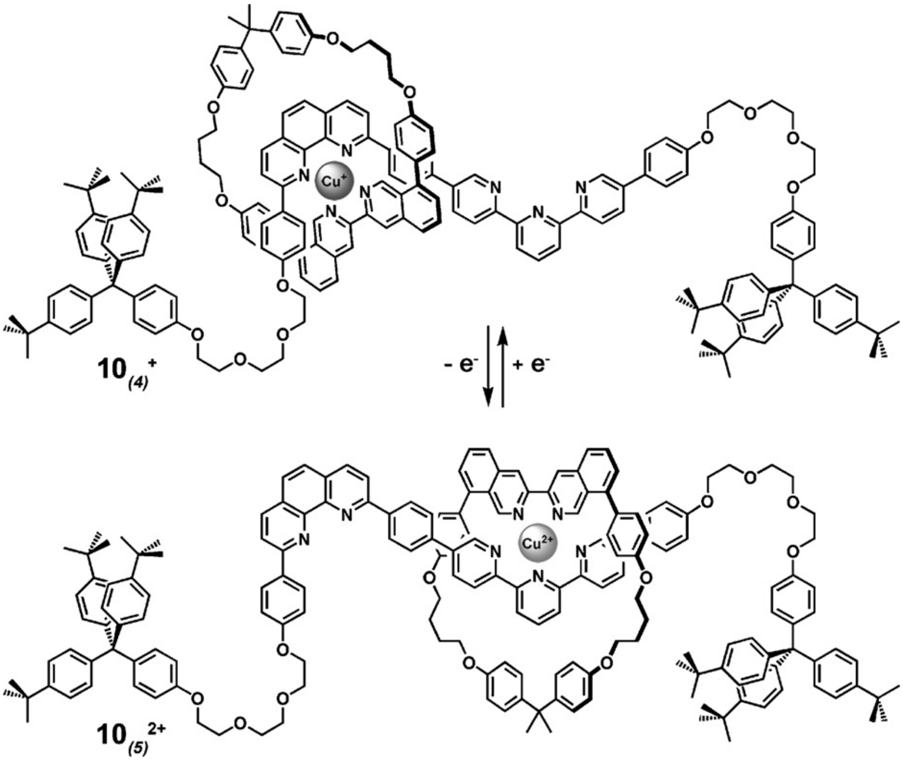
$$\mathbf{7}_{(4)}{}^{2+} \rightarrow \mathbf{7}_{(5)}{}^{2+} \qquad (2)$$



Scheme 4. Two different macrocycles containing a diimine chelating unit. The dpp-based macrocycle **8** leads to pronounced steric hindrance once a metal centre is coordinated. On the other hand, by using a dpbiiq chelate, a sterically non-hindering macrocycle **9** is obtained.

As shown recently for "pirouetting" copper-complexed rotaxanes, decreasing the steric congestion around the copper centre has a strong effect on the rearrangement rates of the complexes [9]. In order to resolve the slowness problem of the previous molecular shuttle, a new larger macrocycle **9**, incorporating a 8,8′-diphenyl-3,3′-biisoquinoline (dpbiiq) fragment has been designed and synthesized (Scheme 4) [16].

The non-hindering 39-membered macrocycle **9** has then been used as the mobile ring in the formation of a new molecular shuttle **10** (Scheme 5) [17]. The linear part contains, as in the previous molecular shuttle, one bidentate 1,10-phenanthroline-based chelate and one tridentate terpy unit. An important difference is the phenylene group introduced as a linker between the two "stations", which makes this thread more rigid than that of $\mathbf{7}^{n+}$ (Scheme 3).



Scheme 5. New copper-based molecular shuttle $\mathbf{10}^{n+}$, containing the non-sterically hindering biisoquinoline-based macrocycle **9** and a more rigid axis than shuttle **7** in Scheme 3.

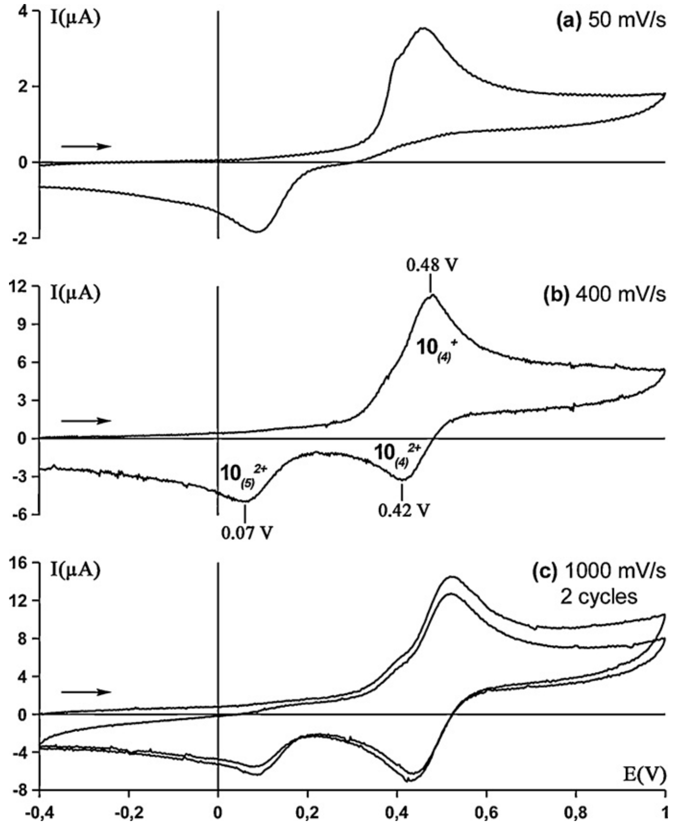


Fig. 3. Cyclic voltammetry study of bistable rotaxane $\mathbf{10}^{n+}$ [17]. The electrochemical experiments have been performed at room temperature, in a 0.1 M solution of Bu_4NBF_4 in CH_3CN/CH_2Cl_2 (9:1), with a Pt working electrode, Ag wire as a pseudo-reference electrode and Pt wire as a counter-electrode.

The electrochemically triggered translation of the copper-complexed ring between the dpp "station" and the terpy unit was investigated by cyclic voltammetry, by analogy with previously described copper-containing bistable catenanes and rotaxanes [18]. By modifying the potential scan rate, one can estimate the rate of the gliding motion undergone by the copper-complexed ring between the dpp and terpy units. A few representative cyclic voltammograms (CVs) are represented in Fig. 3.

In a similar way to previous studies [18], the rearrangement rate was estimated from the shape of the CVs obtained at different potential scan rates. In agreement with the other copper-based molecular machines made and investigated previously in our group, the unstable 5-coordinate copper(I) complex $\mathbf{10}_{(5)}{}^{+}$ moves much faster than the other unstable species, namely the 4-coordinate copper(II) complex $\mathbf{10}_{(4)}{}^{2+}$. This can easily be explained by considering that ligand substitution reactions are likely to be more facile around the singly charged metal centre Cu(I) than around Cu(II). Whereas rearrangement of the Cu(II)-complexed rotaxane is sufficiently slow to allow the gliding rate constant to be determined by the present technique, the opposite gliding motion experienced by the 5-coordinate Cu(I) rotaxane is too fast to permit estimation of its rate constant. In this case, more sophisticated techniques would be required to afford a relatively precise value. We thus indicate the lower limit of this rate constant only. The back-and-forth motion can be described by the following equations:

$$\mathbf{10}_{(4)}{}^{+} - e^{-} \rightarrow \mathbf{10}_{(4)}{}^{2+} \quad \text{Cu(I) oxidation}$$

$$\mathbf{10}_{(4)}{}^{2+} \rightarrow \mathbf{10}_{(5)}{}^{2+} \quad \text{gliding} \quad k = 2\,s^{-1}$$

$$\mathbf{10}_{(5)}{}^{2+} + e^{-} \rightarrow \mathbf{10}_{(5)}{}^{+} \quad \text{Cu(II) reduction}$$

$$\mathbf{10}_{(5)}{}^{+} \rightarrow \mathbf{10}_{(4)}{}^{+} \quad \text{gliding} \quad k > 50\,s^{-1}$$

In the shuttle with the sterically hindered chelate from Scheme 3 ($\mathbf{7}^{(4)+}$), the rate constants for the two gliding motions are at least two orders of magnitude lower. Thus, it is obvious that there exists a pronounced kinetic biisoquinoline effect. This ligand leads to a markedly more mobile electrochemically driven machine than the previous copper-based shuttle. The endocyclic but non-sterically protecting nor hindering nature of dpbiiq is with no doubt responsible for this spectacular improvement. Besides this non-hindering character, another important structural difference is the less rigid nature of the dpbiiq chelate. Whereas dpp contains a rigid 1,10-phenanthroline nucleus, the biisoquinoline part is able to complex a metal centre or dissociate from it in a stepwise manner. Indeed, easy rotation between the C–C bond connecting the two isoquinoline fragments (C_3–$C_{3'}$) can take place, which is likely to lower the activation barrier for both complexation and decomplexation reactions compared to the identical processes with a highly rigid molecule such as dpp.

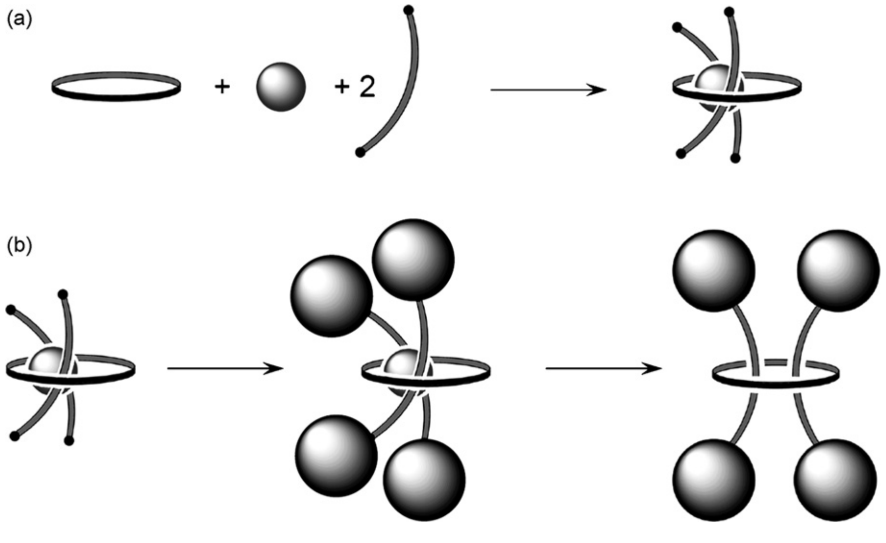
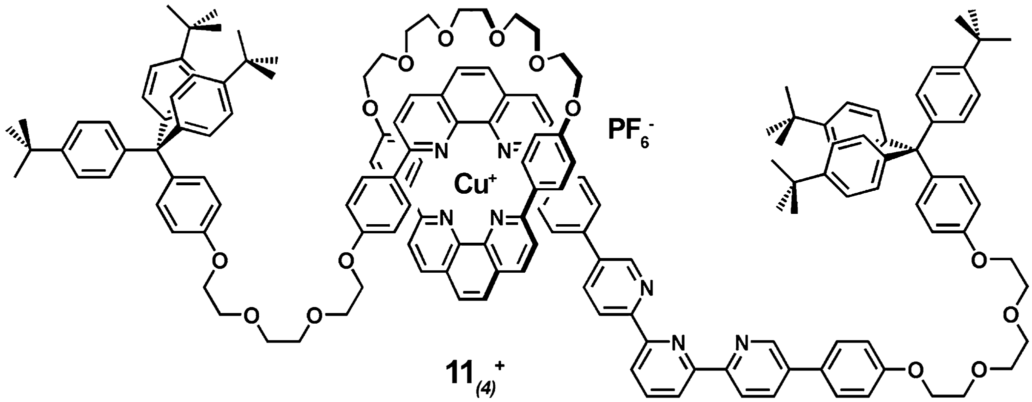


Fig. 4. (a) Principle of the double-threading reaction driven by coordination of the macrocyclic and non-cyclic ligands to an octahedral metal centre; (b) the stoppering reaction leads to a metal-complexed rotaxane which, after demetalation, yields the metal-free [3]rotaxane. The ring R and each string-like fragment, L, incorporate a bidentate chelate.



Scheme 6. Chemical structure of rotaxane [$\mathbf{11}_{(4)}^+$][PF_6^-], containing a sterically hindering dpp-based macrocycle and the same rigid axis as in rotaxane [$\mathbf{10}^+$][PF_6^-] from Scheme 5.

In order to compare the dynamic properties of $\mathbf{10}_{(4)}^+$ and $\mathbf{10}_{(5)}^{2+}$ to those of a molecule displaying as much similarity as possible in terms of chemical function, we also prepared and studied the rotaxane $\mathbf{11}_{(4)}^+$, depicted in Scheme 6. $\mathbf{11}_{(4)}^+$ contains exactly the same axis and stoppers as $\mathbf{10}_{(4)}^+$ but the mobile ring is now the former strongly shielding macrocycle **8**. This allows to assess the effect of replacing this dpp-containing ring **8** by the recently prepared dpbiiq-based macrocycle **9**. The difference in shuttling kinetics is remarkable. As discussed above, the unstable 4-coordinate copper(II) complex in the shuttle from Scheme 5 rearranges within less than 1 s. By contrast, after oxidation of $\mathbf{11}_{(4)}^+$ to $\mathbf{11}_{(4)}^{2+}$, the thermodynamically unstable form of the complex seems to be stable for several hours.

To confirm the coordination number of copper(II) both in thermodynamically stable (5-coordinated) and unstable (4-coordinated) states, electronic absorption spectroscopy measurements were performed on $\mathbf{10}^{2+}$ and $\mathbf{11}^{2+}$. First the dark red solution of [$\mathbf{10}_{(4)}^+$][PF_6^-] (2×10^{-4} M) in CH_3CN/CH_2Cl_2 (9:1) was oxidised with $NO^+BF_4^-$, in a similar way to previous studies [19], which resulted in an immediate colour change to give a very pale yellow solution. The electronic spectrum shows a band maximum at $\lambda_{max} \approx 640$ nm ($\varepsilon \approx 150\,M^{-1}\,cm^{-1}$), which is a clear indication of a 5-coordinate copper(II) [20]. This form of the complex was obtained within seconds, as expected from the electrochemical study. By contrast, a similar experiment done with [$\mathbf{11}_{(4)}^+$][PF_6^-] under the same conditions gave a relatively intense green solution ($\lambda_{max} \approx 670$ nm, $\varepsilon \approx 750$), indicative of a 4-coordinate copper(II) complex, as expected for this kinetically inert complex.

In short, a non-hindering dpbiiq-based macrocycle (**9**) has been synthesized and used for the formation of a new rigid copper-based molecular shuttle $\mathbf{10}_{(4)}^+$ which can move on the milliseconds to seconds timescale. These shuttling kinetics are roughly 4 orders of

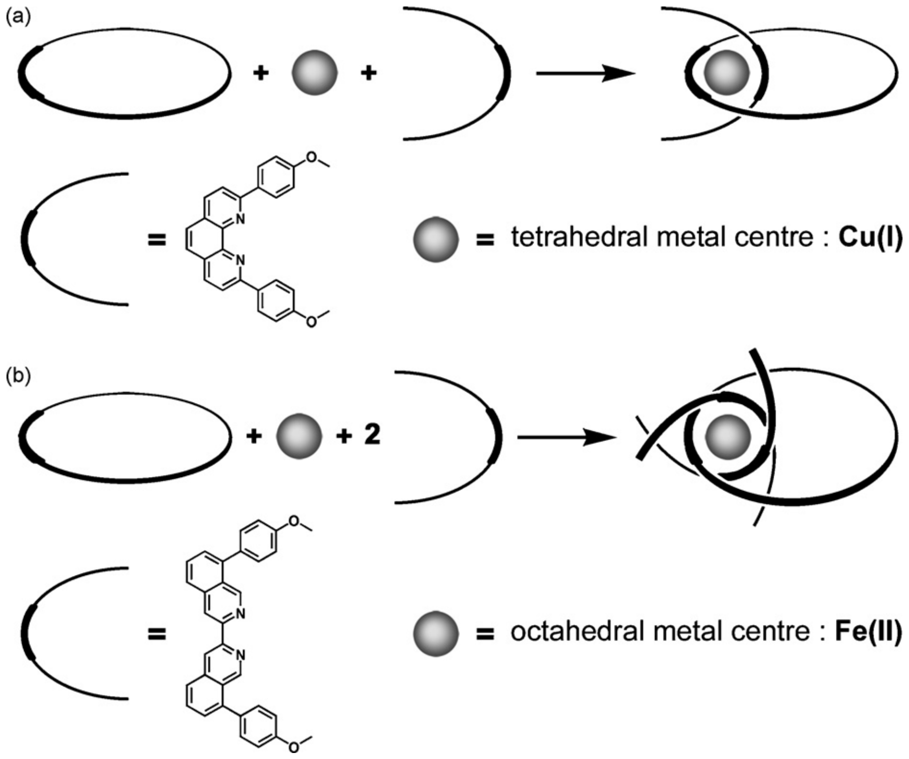


Fig. 5. The single- and double-threading reactions: (a) copper(I)-induced threading reaction leading to a [2]prerotaxane and (b) double-threading reaction driven by coordination of the ligands to an octahedral metal centre such as Fe(II), yielding a [3]pseudorotaxane.

magnitude more rapid than those observed for a molecular shuttle ($\mathbf{11}_{(4)}{}^{+}$) comprised of a sterically hindered (phenanthroline-based) macrocycle (**8**) and the exact same molecular axle.

3. [3]Rotaxanes and [3]pseudorotaxane: passing two strings through the same ring using an octahedral metal centre as template

3.1. Principle of the double-threading reaction and of the [3]rotaxane synthesis

In the course of the last 2 decades, the templated synthesis of [2]catenanes and [2]rotaxanes (the number 2 into brackets indicates the number of components) has been remarkably successful. The most efficient strategies are based on transition metals [21] or on organic templates [22]. Several examples of topologically more complex molecules have also been reported. These compounds have generally been prepared in an efficient way from several precursor fragments [23]. As already mentioned, among the most spectacular examples of topologically novel synthetic molecules, molecular knots, such as the trefoil knot [24] or its derivatives [25], as well as the Borromean rings [1], are particularly representative. Even if rotaxanes are not, strictly speaking, topologically significant compounds due the planarity of their molecular graphs, rotaxanes have often been considered as topologically non-trivial due to their analogy to catenanes [26], at least in terms of synthetic approaches. This is the case for [*n*]rotaxanes (*n*: number of cyclic or thread-like components; $n > 2$) which are certainly challenging compounds. [*n*]Rotaxanes generally consist of $n - 1$ rings threaded on the same thread [27], as in the case of cyclodextrin-based rotaxanes [28]. Most of the systems with more than one thread passing through the ring(s) are restricted to non-stoppered inclusion complexes [29], whereas very few real [3]rotaxanes have been reported [30].

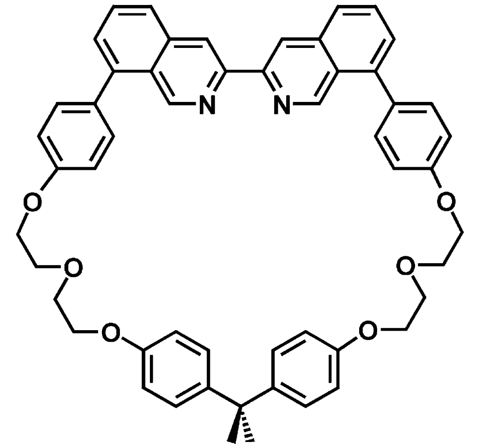
Recently, our group proposed a transition metal-based approach for preparing such threaded species. The principle of the double-threading process is represented in Fig. 4a. This reaction leads to an entanglement consisting of three components: a ring and two acyclic fragments. Stoppering and removing the templating metal affords the free [3]rotaxane, as depicted in Fig. 4b. The double-threading reaction is expected to be quantitative provided the reaction stoichiometry is rigorously respected. Mixing one equivalent of ring (R), one equivalent of metal centre (M) and two equivalents of acyclic ligand (L) will lead to the threaded species if the complexation reaction is done under thermodynamic control. With this 1:1:2 stoichiometry for R, M and L, the doubly threaded complex depicted in Fig. 4a represents the only situation in which neither ligands nor metal centres are “frustrated”. In other words, any other state will involve uncoordinated ligands and/or coordinatively unsaturated metal centres. This principle has been applied very long ago by our group for making singly threaded species from a 1,10-phenanthroline-containing ring, copper(I) and another 1,10-phenanthroline-type ligand [6,21,31]. These [2]pseudorotaxanes were the precursors to various catenanes and rotaxanes. As demonstrated by our recent studies, the coordination chemistry-driven formation of threaded species turned out to be virtually as efficient for making doubly threaded species as it used to be for generating copper(I)-complexed singly threaded compounds.

For comparison, the formation of singly threaded and doubly threaded species with appropriate rings and two dramatically different chelates is indicated in Fig. 5. The main structural difference holds to the steric hindrance of the chelate used. It should be noted that the first reaction leads to a two-component entanglement, one of the components being macrocyclic (a). In contrast, the second reaction leads to an entanglement consisting of three components: a ring and two acyclic fragments (b). Whereas 2,9-diaryl-1,10-phenanthroline chelates similar to the compound represented in Fig. 5a are sterically highly congested and are thus unable to afford a three-chelate octahedral complex, the ligand represented in Fig. 5b, in agreement with the results discussed in the first part of this review article, forms very easily three-chelate octahedral complexes in the presence of an appropriate metal centre. Again, the key feature of these 3,3′-biisoquinoline-based ligands is their endotopic or endocyclic nature combined with their non-sterically hindering nature [10–12]. The 3,3′-biisoquinoline (biiq) backbone is such that the two aromatic groups introduced at the 8 and 8′ positions (8,8′-diphenyl-3,3′-biisoquinoline = dpbiiq) are sufficiently remote from the coordination site so as not to sterically interfere with it or, at most, in a very minor fashion only.

In the present section, we will discuss the use of octahedral transition metal centres such as Fe(II), Co(II) or Co(III) as templates. These metals allow for high yield synthesis of two-string [3]pseudorotaxanes and, subsequently, [3]rotaxanes. The metal is used in a novel “gathering and threading” strategy, leading to a doubly threaded structure, which represents a generalization of the previously reported principle based on copper(I) and leading to a singly threaded complex consisting of one ring and one “string” [6,31]. A few examples of this new approach have recently been published in which the template was Fe(II), Co(II) or Co(III) [32]. With Fe(II), demetalation seemed to be highly problematic under classical conditions. This is one of the reasons why we undertook similar studies with cobalt as template since cobalt(III) is inert and will thus allow the synthesis of the rotaxanes even under relatively aggressive conditions whereas the corresponding cobalt(II) complexes is labile and can thus be easily removed to afford the corresponding free ligands.

The synthesis of [3]pseudorotaxanes similar to those represented in Fig. 4a as well as that of the corresponding stoppered compounds and metal-free rotaxanes (Fig. 4b) is a multistep procedure involving the following reactions: (i) the double-threading reaction, (ii) the stoppering reaction and (iii) the demetalation reaction. In principle, any inert octahedral metal centre is adapted to the two first steps, provided the stoppering reaction conditions are compatible with the threaded complex. The success of the last step will largely depend on the lability of the final metal-complexed [3]rotaxane. Fe(II) complexes are normally reasonably labile although the $3d^6$ electronic configuration is expected to stabilise them. However, we were surprised by the high kinetic inertness of the iron complexes, which prompted us to use cobalt. As already demonstrated by other groups [33], cobalt(III) is sufficiently inert to stabilise precursors in the course of a template reaction. By contrast, after reduction to the divalent state, a labile complex is obtained. The strategy is thus straightforward: the formation of the doubly threaded species will be performed using the kinetically labile cobalt(II) centre; subsequently, in order to “freeze” the complex in the desired geometry, the threaded precursor will be oxidised to yield a Co(III) complex able to resist the reaction conditions of the stoppering step. The [3]rotaxane will be prepared on the Co(III) precursor complex. After reduction of the cobalt(III)-complexed [3]rotaxane, the labile Co(II) species will be decomplexed thus producing the free rotaxane.

The macrocyclic compound used for the preparation of the [3]rotaxanes is depicted in Scheme 7. As opposed to macrocycle **9** (Scheme 4) which is only a 39-membered ring, molecule **12** is a 41-membered ring [16]. The size of the macrocyclic cavity has been adjusted to allow threading of two 3,3′-biisoquinoline-based chelates in the presence of the templating metal. It was also hoped that the ring would not be too large so as to prevent fast unthreading of the “strings” once the stoppers are attached on both ends of the threaded chelates.



dpbiiq-based 41-membered ring **12**

Scheme 7. The macrocyclic ligands **12** used for the threading reactions illustrated in Figs. 4 and 5 [16].

*3.2. Iron(II)-driven double-threading of two 3,3′-biisoquinoline derivatives through ring **12** and [3]rotaxane synthesis*

The various organic fragments used in the double-threading reaction and in the rotaxane synthesis are depicted in Scheme 8. **1** is a model compound with the same chelating unit as the fragment used for synthesizing the target rotaxanes, namely **13**. The stopper precursor **14** is attached to a terminal acetylene function in view of using click chemistry for stoppering the system.

As represented in Scheme 9, the first step of the [3]rotaxanes synthesis was the complexation reaction of the macrocycle (**12**) with stoichiometric amounts of a metal salt (e.g. $Fe(BF_4)_2{\cdot}6H_2O$). The second step was the iron(II)-driven threading reaction. Two equivalents of the non-cyclic reagents **1** or **13** (Scheme 8) were added to the iron(II)-complexed ring **12**. The desired complexes [Fe(**12**)(**1**)$_2$]$^{2+}$ (**15**$^{2+}$) or [Fe(**12**)(**13**)$_2$]$^{2+}$ (**16**$^{2+}$) were obtained in high yield.

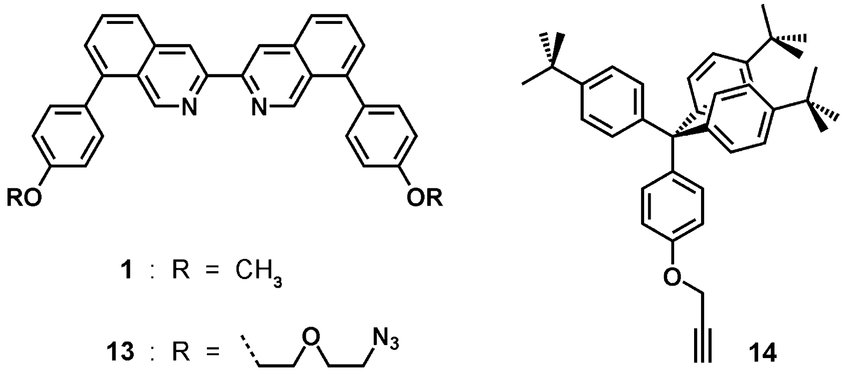
16[PF$_6$]$_2$, the precursor to the [3]rotaxane, was reacted with an excess of propargyl derivative **14** under conditions which are typical of copper(I)-catalyzed Huisgen 1,3-dipolar cycloaddition ("click" chemistry, developed by Sharpless, Medal and their coworkers) [34]: **16**$^{2+}$ and **14** were dissolved in CH_2Cl_2 and stirred with an aqueous solution of $CuSO_4$ using sodium ascorbate as reducing agent. The tetra-triazole derivative **17**$^{2+}$ was obtained as its PF_6^- salt after ion-exchange with KPF_6. The iron(II) complexes **15**[PF$_6$]$_2$, **16**[PF$_6$]$_2$ and **17**[PF$_6$]$_2$ were fully characterised by the classical analytical techniques.

Considerable difficulties were encountered when attempting to demetalate **17**$^{2+}$ in view of obtaining the corresponding metal-free [3]rotaxane. Demetalation could be carried out under very harsh conditions only (Na_3HEEDTA in DMSO at high temperature), leading to the unthreading products, the end-functionalised threads and the ring. Clearly, the very brutal conditions required for removing the iron(II) template were not compatible with the mechanical stability of the free rotaxane obtained by demetalation. This observation prompted us to look for an easier-to-remove metal. Cobalt(II) seemed to be very promising in this respect.

3.3. Cobalt(II)-driven double-threading reaction and [3]rotaxane synthesis

The cobalt(II)-induced threading reaction was performed analogously to that of the iron(II) complex. The synthesis of the model compound **18**$^{2+}$ was carried out by mixing macrocycle **12** (1 equiv.) and $Co(NO_3)_2{\cdot}6H_2O$ (1 equiv.) in CH_2Cl_2–CH_3CN solution. Without isolation of the intermediate macrocyclic complex, **1** (2 equiv.) was added to the reaction mixture. The paramagnetic complex **18**$^{2+}$ (**18**$^{2+}$ = [Co(**12**)(**1**)$_2$]$^{2+}$) was obtained and it was directly oxidised to **18**$^{3+}$. **18**$^{3+}$ was isolated as its PF_6^- salt (yield 89%) after chromatography and ion-exchange. Slow diffusion of diisopropyl ether into a solution of **18**(PF$_6$)$_3$ in acetone afforded crystals suitable for X-ray structure analysis. The molecular structure of **18**$^{3+}$ (Fig. 6) demonstrates the threaded nature of the compound. It reveals typical Co–N distances for cobalt(III) complexes with an average value equal to 1.934 Å. The structure is stabilised by π–π interactions in agreement with previous complexes containing three dpbiiq ligands [12].

Using the azide-bearing thread **13** instead of **1** in the same reaction sequence with macrocycle **12** (1 equiv.) and $Co(NO_3)_2{\cdot}6H_2O$ (1 equiv.) yields the cobalt(III) complex **19**$^{3+}$ (**19**$^{3+}$ = [Co(**12**)(**13**)$_2$]$^{3+}$). The subsequent stoppering reaction was performed in a similar way as for the corresponding iron(II)-complex (Scheme 9). The crude cobalt(III) complex **19**$^{3+}$ was dissolved in CH_2Cl_2 together with a large excess of the propargyl stopper precursor **14**. It was mixed with an aqueous solution of sodium ascorbate used in large excess. Aqueous KPF_6 and acetonitrile were added to the reaction mixture. Finally, an aqueous solution of $CuSO_4$ was added.



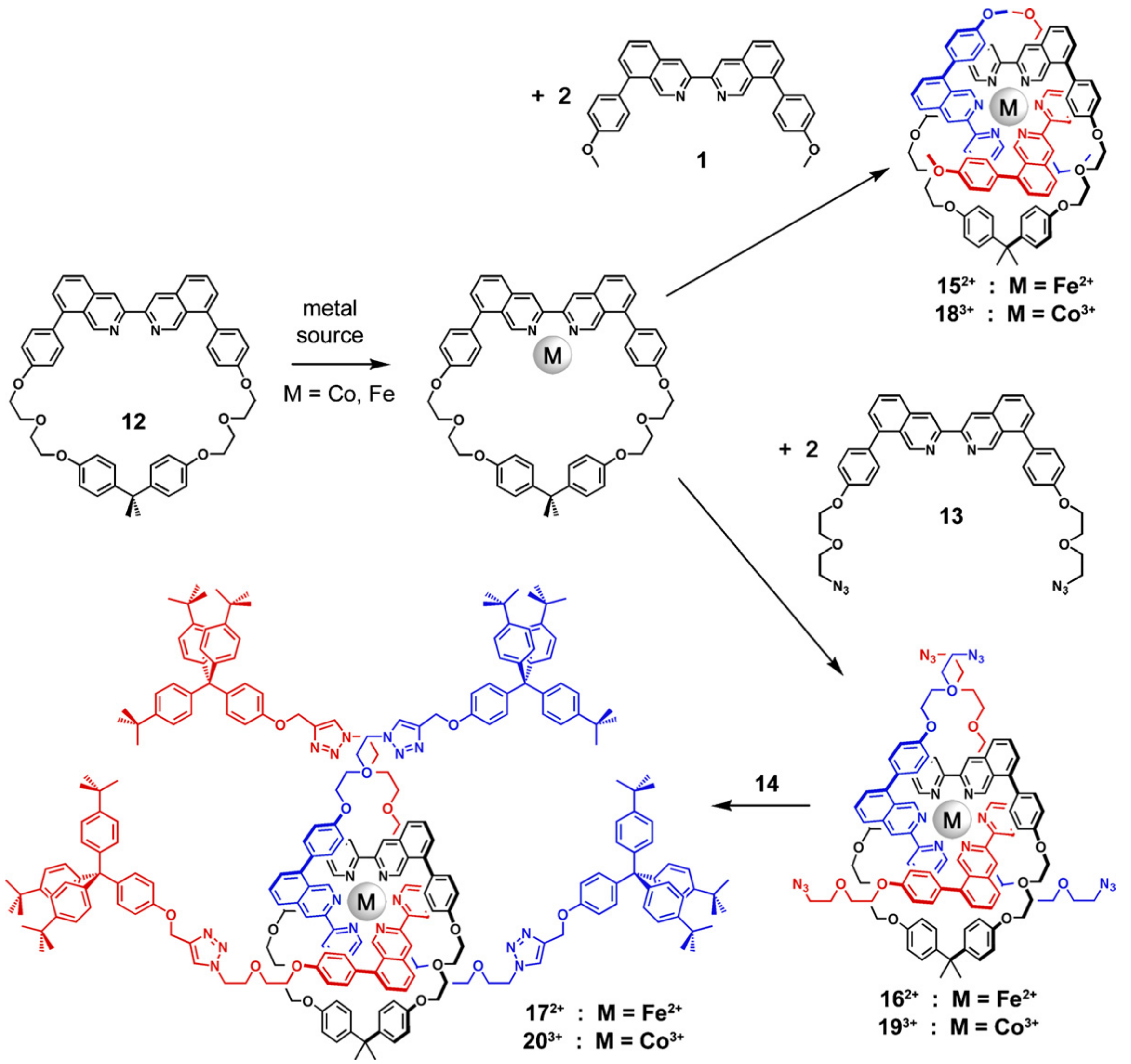
1 : R = CH_3

13 : R =

14

15^{2+} : [Fe(**12**)(**1**)$_2$]$^{2+}$ **16**$^{2+}$: [Fe(**12**)(**13**)$_2$]$^{2+}$

Scheme 8. The ligands used for the double-threading reaction (**1** and **13**) and the stoppering reagent **14**.



Scheme 9. Iron- and cobalt-driven double-threading of the model compound **1** or the azide-functionalised compound **13** through ring **12** and stoppering reaction. The corresponding [3]pseudorotaxanes **15**$[PF_6]_2$ and **16**$[PF_6]_2$ were obtained almost quantitatively. The stoppered-compound **17**$[PF_6]$ was also isolated in good yield after work-up and chromatographic purification.

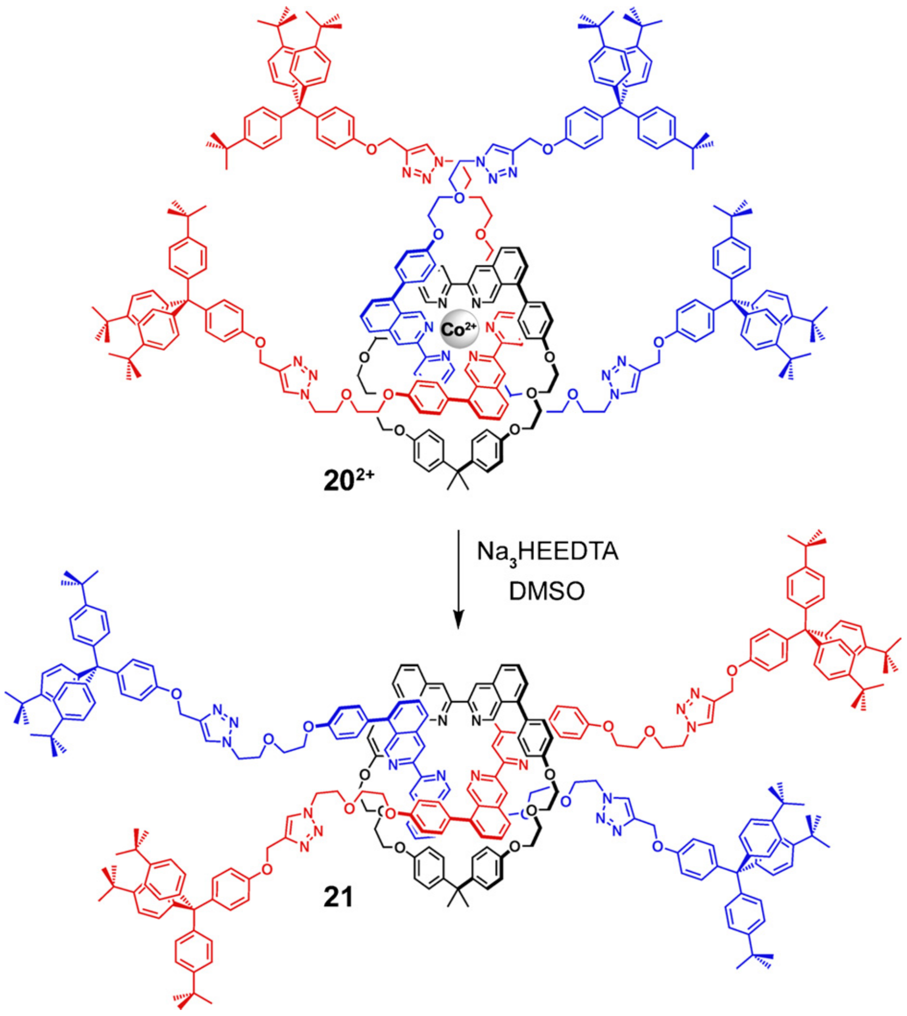
In the present case, the function of sodium ascorbate was also to reduce cobalt(III) to cobalt(II). The crude product was treated at ambient temperature with a large excess of Na_3HEEDTA in biphasic CH_2Cl_2–water medium. Fortunately, **20**$^{2+}$ was stable enough in dichloromethane to resist the complexation agent whereas non-stoppered complexes were decomposed completely. The desired [3]rotaxane cobalt(II) complex **20**$^{2+}$ was readily separated from the organic compounds by conventional column chromatography on silica. In order to characterise the doubly threaded species by ^{1}H NMR spectroscopy, paramagnetic **20**$^{2+}$ was oxidised and **20**$^{3+}$ (Scheme 9) was isolated as its PF_6^- salt in good yield (70% based on macrocycle **12**). The cobalt(III)-[3]rotaxane was characterised by ^{1}H NMR spectroscopy and by ES-MS. The molecular peak observed at 1457.35 (calc. 1457.42) corresponds to $[C_{289}H_{300}CoN_{18}O_{18}]^{3+}$ (**20**$^{3+}$).

3.4. *Demetalation of the cobalt(II)-complexed [3]rotaxane and study of the unthreading reaction*

Treatment of **20**$^{2+}$ with a large excess of Na_3HEEDTA in a DMSO solution (at ambient temperature) led to a quantitative yield of the metal-free [3]rotaxane **21** (see Scheme 10).

From previous experiments with the analogous iron(II) complex **17**$^{2+}$, it was expected that **21** is a metastable species and indeed the ^{1}H NMR spectrum of a freshly prepared sample (in CD_2Cl_2) evolves with time and also exhibits signals of the macrocycle **12** and the stopper-bearing thread as represented in a schematic fashion in Fig. 7.

A kinetic study showed that the metal-free rotaxane **21** is reasonably stable at low temperature but, at room temperature, relatively fast unthreading was observed. The half-lives for the [3]rotaxane ($t_{1/2} = \ln 2/k$; k: rate constant for the dissociation reaction of Fig. 7) is around 200 h at 298 K whereas it is approximately 50 h at 333 K. Although direct comparison to other systems [35] is impossible, it must be noted that the enthalpic contribution ($\Delta H^\ddagger$) to the unthreading barrier is rather low whereas the entropic component (k_∞ and $\Delta S^\ddagger$) is remarkably high: $\Delta H^\ddagger = 33 \pm 3\,\mathrm{kJ\,mol^{-1}}$ and $\Delta S^\ddagger = -182 \pm 55\,\mathrm{J\,K^{-1}\,mol^{-1}}$, from which $\Delta G^\ddagger$ (298 K) = $87 \pm 9\,\mathrm{kJ\,mol^{-1}}$ was deduced. The high activation entropy indicates that the unthreading reaction has a highly ordered transition state, i.e., it is strongly dependent on the relative orientation of the ring and the two strings. For example, unthreading may be favourable if the bulky stopper of one string is placed near the axle of the other, as suggested by the drawing of Fig. 7.



Scheme 10. Synthesis of the metal-free [3]rotaxane **21**.

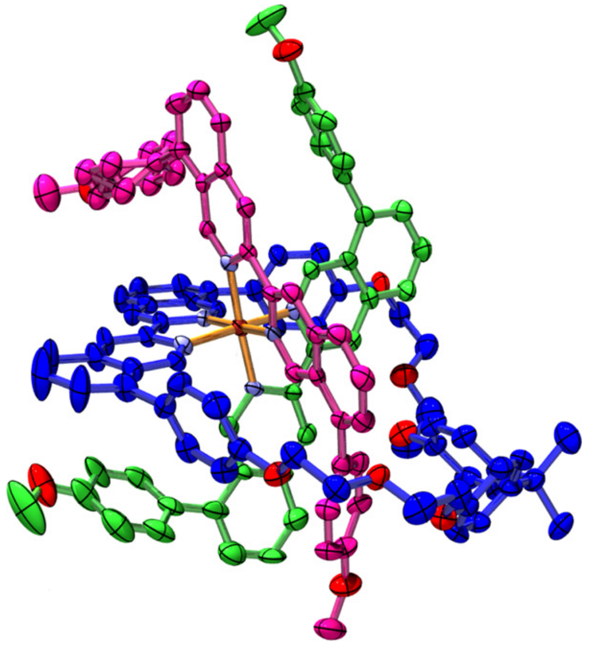


Fig. 6. X-ray crystal structures of the $\mathbf{18}^{3+}$ cation. The ORTEP-plot shows thermal ellipsoids at 50% probability. The acetone solvent molecules and PF_6^- anions included in the structure are omitted for clarity; the carbon atoms of the three ligands are shown with different colours.

In summary, using an octahedrally coordinated metal centre such as cobalt(II) or iron(II), in conjunction with chelates of the 8,8′-diphenyl-3,3′-biisoquinoline (dpbiiq) family, the preparation of doubly threaded species could be carried out in good yield. A particularly attractive X-ray structure was obtained for a [3]pseudorotaxane, which consists of a dpbiiq-incorporating 41-membered ring, a central cobalt(III) ion and two 8,8′-di(*p*-anisyl)-3,3′-biisoquinoline fragments. Cobalt is ideally adapted to the preparation of dpbiiq complexes such as rotaxane-like compounds since cobalt(II) is labile enough to allow for efficient preparation of the doubly threaded species and, after oxidation, the corresponding cobalt(III) species is kinetically very stable, which facilitates handling of the complexes. Using dpbiiq threads bearing terminal azide functions, a real rotaxane could be prepared from the cobalt(III) precursor. In a first step, a cobalt(II) complex was

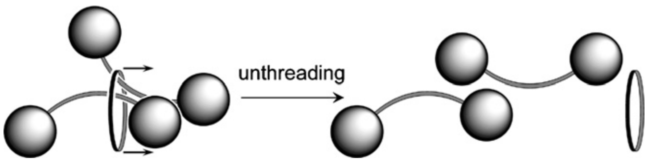


Fig. 7. Schematic representation of the unthreading process from the metal-free [3]rotaxane **21**; the drawing suggests that the two threaded fragments cannot unthread simultaneously and that the stoppers have to be disposed in a relatively precise arrangement for the dissociation reaction to take place.

generated. The highly stable reoxidised cobalt(III) species was fully characterised, in particular by ^{1}H NMR and ES-MS. The divalent complex was easily demetalated to afford a free [3]rotaxane in good yield. This rotaxane disassembled spontaneously by unthreading of the two-string-like fragments from the ring in a slow but quantitative process (half-life of the free [3]rotaxane ~200 h at 298 K).

4. Conclusion

The present review article summarises the work done recently in our group on 3,3′-biisoquinoline ligands and their complexes. More than twenty-five years ago, copper(I) and 2,9-diphenyl-1,10-phenanthroline led to the preparation of [2]catenanes by taking advantage of the sterically hindering character of the crescent-shaped ligand and its propensity to generate two-component entanglements once complexed to a tetrahedral metal. A logical extension was to use another type of crescent-shaped ligands, namely disubstituted 3,3′-biisoquinoline ligands, for generating three-component entanglements (Fig. 1) and, after covalently interlinking the entangled ligands in the proper way, synthesizing a threefold symmetry [3]catenane. The preparation of such a topology has not been achieved as yet but, alternatively, other projects were undertaken with the same series of compounds in relation to rotaxanes and molecular machines. The non-sterically hindering nature of the ligands has been exploited to make and study fast-moving two-station molecular shuttles. Remarkably, the system can be set in motion several orders of magnitude faster than the analogous dpp-based molecular machines. This observation will now be used for constructing another generation of molecular shuttles in which the end-stations will be separated by a longer distance or which will include an intermediate station between the two terminal ones. These more sophisticated shuttles, after suitable modifications, should enable the transport of matter on a long distance, either within the same phase or across a membrane. The second line of research derived from the original [3]catenane project led to the efficient synthesis of unusual [3]pseudorotaxanes and [3]rotaxanes using either Fe(II) or Co(II/III) as gathering and threading metal centre. These new species contain two molecular filaments threaded through the same ring, a very uncommon feature in the field of catenanes and rotaxanes. By modifying the chemical structure of the threads, it is easy to imagine the preparation of multistable molecular machines, in particular by introducing additional complexing groups in the axes.

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