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Interlacing Molecular Threads on Transition Metals: Catenands, Catenates, and Knots

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Introduction

People have long been fascinated by knots and interlocked rings. Interlaced and knotted threads have been used in art for centuries; one of the earliest and richest examples is the *Book of Kells*, a masterpiece of graphic art produced by 8th century Irish monks, which contains many beautiful representations of some very intractable knots.[1] A second intriguing example is the Borromean sign,[2] symbol of a powerful Italian family, which contains three interlocked rings so disposed that any one cut allows them all to be separated: no ring is interlocked to another without the help of the third component. More recently, the work of the Dutch artist Escher[3] contains examples of fantastic animals associated with impossible geometrical figures. Some of his work contains shapes, spaces, and interlaces closely related to modern molecular sciences, including attractive views of the trefoil knot.[3] Some views of knots and interlocked rings are shown in Figure 1.

Topology, in association with graph theory, is a branch of mathematics of renewed interest. In particular, low-dimensional topology is connected to other fields of scientific investigation, most notably chemistry and molecular biology. DNA is known to adopt complex topologies under the influence of certain enzymes. It was recognized over 20 years ago that the topology of circular duplex DNA can be deeply modified by "gyrase" enzymes;[4] this led to the discovery of DNA catenanes,[4] and in 1976, the first closed knotted form of DNA was reported.[5] Many of the pictures taken since then of various topological forms of DNA are of a rare beauty.[6,7]

Graph theory applied to chemistry has been called chemical topology. However, it is only very recently that a rigorous mathematical treatment has been applied to molecules. Walba's use of graph theory for describing molecular systems now provides a unified view,[8] and its theoretical basis should be sufficient for treating almost any synthetically accessible chemical species for decades. Before this rigorous treatment, many other scientists were interested in chemical topology, and the most outstanding contributions are worth mentioning.

Schill's book *Catenanes, Rotaxanes and Knots*,[9] written in 1971, is indispensable for the topologist. In addition to interesting theoretical considerations regarding interlocked rings and knots, it contains much information on the experimental approaches used by Lüttringhaus and, later, Schill and their co-workers to prepare such topologically novel systems. The possible existence of such compounds was envisaged as early as

Jean-Pierre Sauvage was born in Paris in 1944. He carried out graduate studies with Jean-Marie Lehn at the University of Strasbourg (Ph.D., 1971) and postdoctoral studies with M. L. H. Green at Oxford University. He is currently Research Director at the CNRS and at the University of Strasbourg, and his research interests include functionalized conducting polymer films, redox photocatalysis, intramolecular photoinduced electron transfer, models of natural photosynthesis, and chemical topology.

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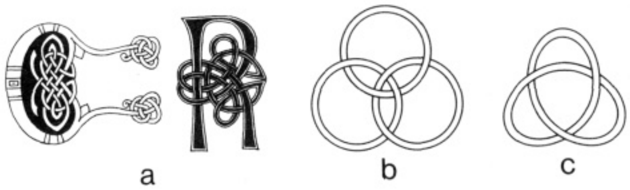

Figure 1. (a) A superb illumination due to Irish monks (Kelsch's book, 8th century). (b) The Borromean symbol. (c) A classical representation of the trefoil knot.

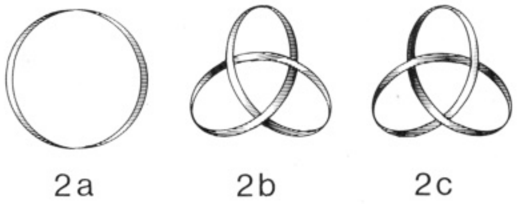

Figure 2. Three topological stereoisomers; isomers b and c are topological enantiomers.

the beginning of this century;[10] it is reported that Wilstätter postulated the formation of interlocked rings at a seminar in Zürich before 1912.

The first written theoretical discussion on the subject was a paper entitled "Chemical Topology", by Frisch and Wasserman.[11] It contains a very clear account of most of the ideas that constitute the background of chemical topology. For example, the idea of topological isomers is introduced by comparing a [2]-catenane (two interlocked rings) to the set of the two separate cyclic molecules. Another example is provided by considering a single closed curve, which can be a normal cycle (topologically trivial) or a knotted cycle, the simplest example being the trefoil knot. The three objects of Figure 2 are topological stereoisomers: although they consist of exactly the same atoms in the same sequence, and the same chemical bonds between them, they cannot be interconverted by any type of continuous deformation in three-dimensional space. In addition, the compounds of parts b and c of Figure 2 are topological enantiomers, since they are nonsuperimposable mirror images.

The expression "topologically nontrivial" can be defined more rigorously. The "molecular graph" of a system must be nonplanar for the molecule to be topologically nontrivial; that is, it will be impossible to draw the molecule on a sheet of paper—allowing any desired deformations of bond lengths and angles—without having crossing points. The catenanes are simple examples.[9-12] Apart from interlocked rings, only recently synthesized compounds have nonplanar molecular graphs. These include the Simmons–Paquette molecule based on propellane (1981),[13,14] its purely hydrocarbon analogue (1988),[15] and (a particularly notable accomplishment) the first molecular Möbius strip (1982).[16] The few nonknotted or catenane-like compounds whose molecular graphs have no planar representation are drawn in Figure 3.

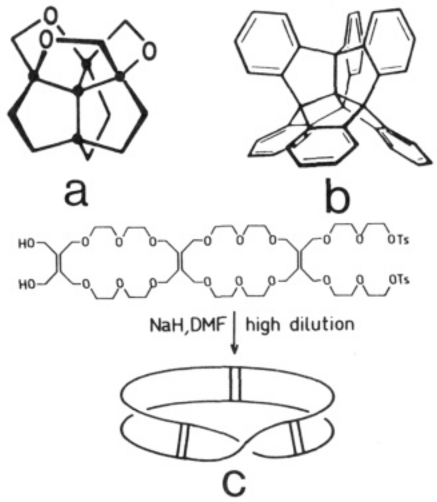

Figure 3. A few compounds with a nonplanar molecular graph. (a) Simmons–Paquette K_5 propellane.[13,14] (b) Kuck and Schuster K_5 hydrocarbon.[15] (c) Walba's synthesis of the first molecular Möbius strip ($K_{3,3}$).[16]

Two other important discussions of chemical topology are worth mentioning. The first is a very imaginative article by Van Gulick,[17] from the University of Oregon, which has unfortunately never been published; however, it still circulates among chemists and may still inspire much research. The second is a review by Sokolov[18] and is particularly relevant to this account since it suggests the remarkable idea of using a transition metal as a template to build a trefoil knot. Transition-metal ions are well-known for their templating properties,[19] and in particular the 3D template effect has been used in recent years to build interesting bicyclic systems.[20-24]

Synthesis of Catenates

We applied the 3D template synthesis around a transition-metal ion (copper(I)) to the synthesis of interlocked rings. The novelty of this approach with respect to previously used 3D template syntheses is that the chelating ligands collected by the metal, and organized in its coordination sphere, are not covalently linked *to each other* after the cyclization reaction. The strategy[25] is illustrated in Figure 4. In principle,

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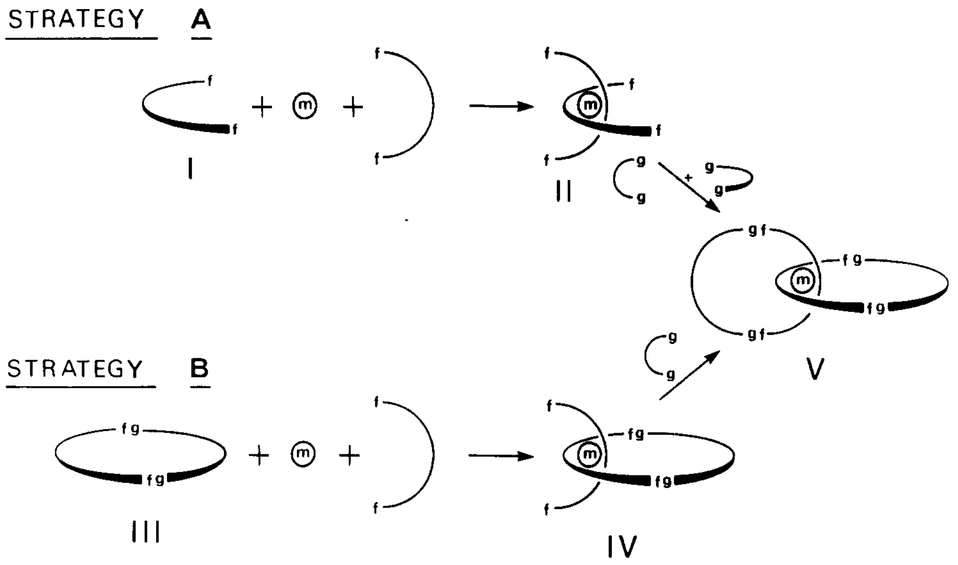

Figure 4. Synthesis of interlocked ring systems. The strategy is based on a 3D-template effect induced by a transition metal. The molecular fragment f–f interacts with a transition metal (circle). The f and g represent chemical functions able to react and form an f–g chemical bond.

strategy A is very simple. Both coordinating fragments I have to bind to the metal center M so as to be mutually perpendicular. By an appropriate choice of metal, chelates, linkers (g–g), and functional groups (f and g), the system (II) will react in the expected fashion: with formation of two interlocked rings (V) rather than by connecting the two f–f fragments of the complex. The only apparent weakness of strategy A is that a total of eight reaction points have to find one another in the double-cyclization reaction. The second strategy reduces this problem, since it involves only four reacting groups to be interconnected in a single cyclization (twice g–f) leading to V. The only requirement is that the starting macrocycle (III) has to be presynthesized before the template reaction is performed. This ring contains a coordinating fragment (f–f) and a noncoordinating linker (g–g), and it is also likely to be formed as an intermediate in strategy A. It is noteworthy that, provided the bis-chelate complex (IV) is stable enough, it must form *quantitatively* from a 1:1:1 mixture of the cycle (III), the metal ion, and the open-chain fragment (I). A statistical mixture of complexes, as would arise if two different open-chain ligands were reacted with a metal ion, cannot occur, because it is impossible for two of the cyclic ligands (III) to attach to the metal ion.

The choice of metal ion and chelate followed naturally from a collaboration with Professor D. R. McMillin, on the photochemical properties of hindered Cu(I) complexes with functionalized phenanthroline ligands bearing alkyl or aryl substituents α to the nitrogen atoms.[26] These complexes have a variety of interesting photochemical properties,[27-32] and as a spin-off we thought that entwined complexes like II of Figure 4 should be relatively easily converted into interlocked systems.

Phenanthroline derivatives and copper(I) have been used in both routes of Figure 4. Since it was less risky, we started with strategy B, which led to an interlocked system in good yield.[25] Since then we have focused more on strategy A; the actual reaction carried out is shown in Figure 5.[33]

The diphenolic starting compound **1** is prepared from 1,10-phenanthroline in two steps (70% yield overall), and it is easily obtained on a multigram scale.[34,35] The precursor complex $\mathbf{2}^+$, containing two entwined ligands around a copper(I) center, is formed quantitatively from **1** (2 equiv) and $Cu(CH_3CN)_4(BF_4)$ and is used without any purification. Reaction of this with diiodopentaethyleneglycol (**3**) in DMF at 65 °C in the presence of Cs_2CO_3 under crude high-dilution conditions leads to the interlocked system $\mathbf{4}^+$ as a BF_4^- salt in 25–27% yield. Purification of the crude product is difficult, requiring extremelty careful chromatography. $\mathbf{4}^+{\cdot}BF_4^-$ is thus obtained on a real preparative scale (batches of 0.5–1 g) in four steps from the commercially available 1,10-phenanthroline in 20% yield overall. $\mathbf{4}^+$ was quantitatively demetalated to **5** with KCN, and X-ray crystallography of both compounds showed that a complete rearrangement occurs after demetalation.[36] From the compact and rigid topography of $\mathbf{4}^+$, with its two entwined ligands not only interacting with the copper(I) center but also undergoing several π–π interactions leading to close stacking, the disentangled and expanded structure of **5** was obtained. In the interlocked free ligand (two 30-membered rings), the chelating fragments are remote from one another, and the whole system is certainly highly flexible. $\mathbf{4}^+$ was

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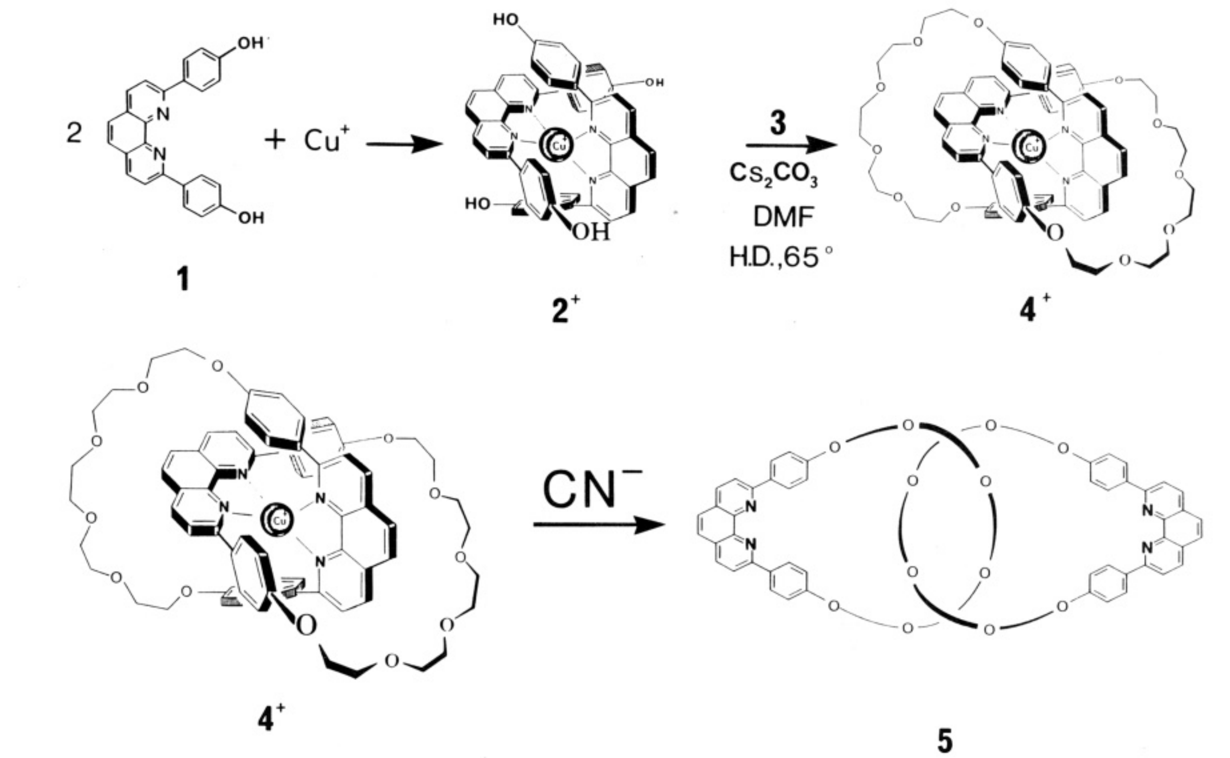

Figure 5. Preparation of the copper(I) catenate 4^+ and subsequent demetalation to the catenand **5**. **3** = $ICH_2(CH_2OCH_2)_4CH_2I$; H.D. = high dilution.

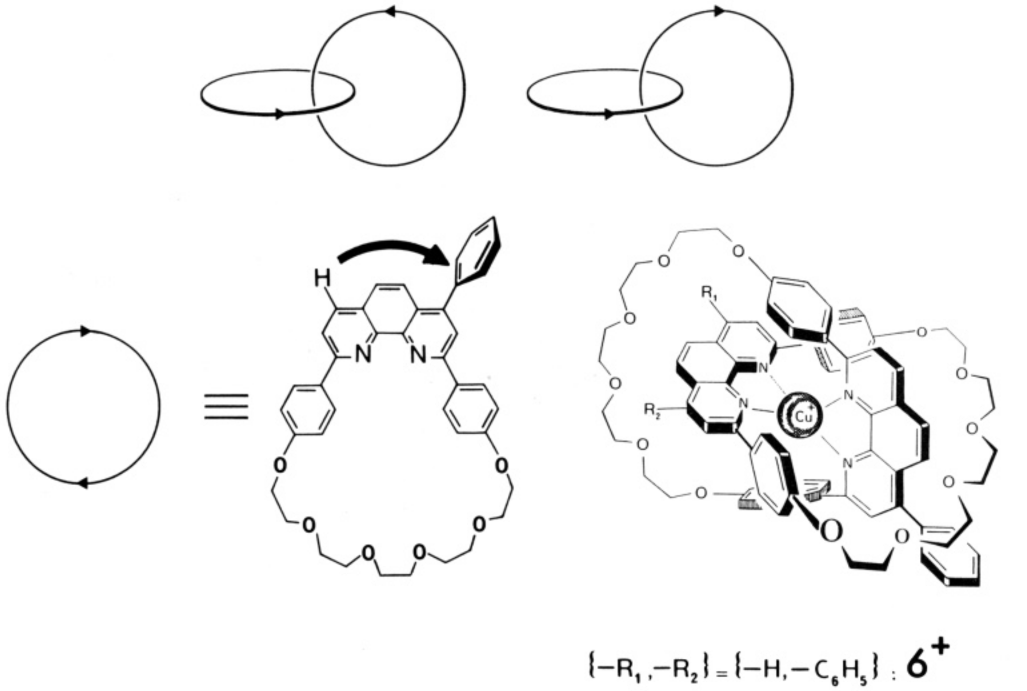

Figure 6. Topologically chiral molecules: oriented interlocked rings.

named a catenate, and the free ligand **5** a catenand; they are the prototypes of a novel family of molecular systems consisting of coordinating interlocked rings.

The catenand **5** can be quantitatively recomplexed with a large variety of cationic species: H^+,[37] Li^+, and transition metals such as Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^+, Zn^{2+}, Ag^+, and Cd^{2+}.[38] In every case the entwined topography of the catenate was reformed. Detailed studies of catenand **5** and its numerous catenates have been performed: spectroscopic,[38] electrochemical,[33,38,39] kinetic,[40] thermodynamic,[41] and molal volume[42] properties have been investigated.

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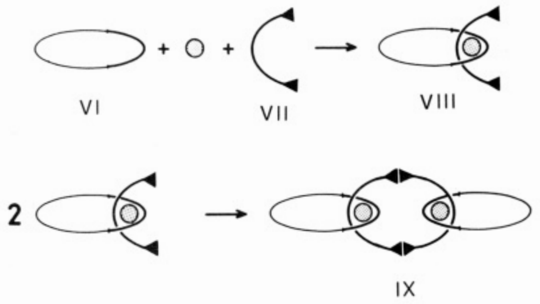

Figure 7. Synthesis of dimetallic [3]-catenates: strategy based on the 3D-template effect of a transition metal (circle) followed by a cyclodimerization reaction. The triangles represent chemical functions able to react with one another to form a chemical link under appropriate conditions.

Stereochemistry and chirality are invariably associated. We have thus been interested in *topologically chiral* catenates and catenands. Classical chirality refers to mirror image chemical objects that cannot be interconverted by chemically allowed operations such as rotation about a bond. In chemical topology, all of the seemingly forbidden operations of chemistry are allowed *except* the cleavage of a bond. Only a chemical species whose molecular graph has no planar representation may be topologically chiral; otherwise the plane of the graph (i.e., the sheet of paper on which it is drawn) would be a plane of symmetry.

The prototypical example of a topologically chiral system is that of *oriented* interlocked rings, as shown in Figure 6. The chiral catenate $\mathbf{6}^+$ was prepared by the same strategy as for $\mathbf{4}^+$.[43,44] It was shown to be chiral by NMR studies using a chiral reagent,[43] and analytical resolution of the enantiomers was subsequently achieved by chromatography on a chiral support.[44] The pure enantiomers of $\mathbf{6}^+$ may have unusual optical properties and may also participate in enantioselective electron transfer[45] and enantiospecific interaction with DNA.[46]

After a [2]-catenate, the next logical step is to prepare multiring interlocked systems coordinated to several metal centers. Not only may these systems provide simple ways for building di- or polynuclear species with a strictly controlled arrangement of photo- and electroactive centers suitable for long-range electron transfer studies, but they will also have considerable topological and aesthetic appeal.

Initial attempts to prepare a [3]-catenane (three rings interlocked) gave very poor yields,[47] although an X-ray structure of a 30-54-30 catenate (each number representing the number of atoms in the ring) was obtained.[48] The more efficient procedure finally adopted is schematically represented in Figure 7. Using the 3D template effect of a transition metal, and starting from a prebuilt macrocycle VI containing a coordinating fragment, the first step is formation of the tripartite precursor VIII from equivalent amounts of M, VI, and the open-chain fragment VII. As with strategy B of Figure 4, there is no problem with statistical mixtures of complexes: VIII must form quantitatively, provided that the bis-chelate complexes of M are sufficiently strong to discourage chelating fragments from remaining uncoordinated. By an appropriate choice of reacting functions (the dark triangles of Figure 7) and metric parameters (ring size, length of VII, etc.), it should be possible to prevent VIII from undergoing an intermolecular cyclization. If VII is sufficiently short to prevent intramolecular cyclization, the cyclodimer species IX should form. Some higher cyclooligomers may also be obtained, leading to even more topologically complex interlocked systems.

The approach used, again based on copper(I) complexes with two phenanthroline-type chelates, is depicted in Figure 8.[49] The oxidative acetylenic coupling (Glaser reaction)[50] was surprisingly efficient. In its previous applications to the synthesis of macrocycles,[51,52] fine control of the experimental conditions was necessary to give reasonable yields, and the same was observed in our case. From virtually 0% yield in the first attempts, the 30-44-30 compound $\mathbf{10}^{2+}$ was finally obtained in 58% yield by careful control of solvent (DMF), temperature (ambient), amounts of copper(I) and copper(II) salts (large), presence of O_2 (compulsory), and concentration. It is noteworthy that the cyclodimerization leading to $\mathbf{10}^{2+}$ does not require high-dilution conditions at all. Typical concentrations are in the range 5–10 mM **7** and **8**, so that 1 g of $\mathbf{10}^{2+}\cdot 2BF_4$ can be prepared in 250 mL of solvent. Surprisingly, a 20% yield of the cyclotrimer was also obtained. This compound is a trinuclear copper(I) complex, consisting of a central 66-membered cycle interlocked to three 30-membered rings. The total yield of identifiable cyclic products from the oxidative coupling reaction of $\mathbf{9}^+$ was 78%!

The [3]-catenate $\mathbf{10}^{2+}$ has been studied in detail by ^1H NMR spectroscopy (chemical shift studies and NOE experiments to determine the conformation and morphology of the system in solution) as well as by X-ray crystallography.[53] The agreement between the two methods is excellent. As shown in Figure 8, the molecular shape of $\mathbf{10}^{2+}$ is compacted and globular due to strong π-type stacking interactions between the two copper(I) complex subunits, involving the 1,10-phenanthroline nuclei and phenyl rings. This results in a distance of only 8.1 Å between the copper(I) centers, whereas in an expanded arrangement this distance would have been over 12 Å. This situation is favorable to intramolecular communication between two metal centers occupying the copper(I) sites.

With the aim of inducing electron transfer from one site (MLCT excited state of one copper(I) subcomplex) to the other, the synthesis of heterobimetallic catenates has been undertaken. Cu(I)/Ag(I) and Cu(I)/Co(II)

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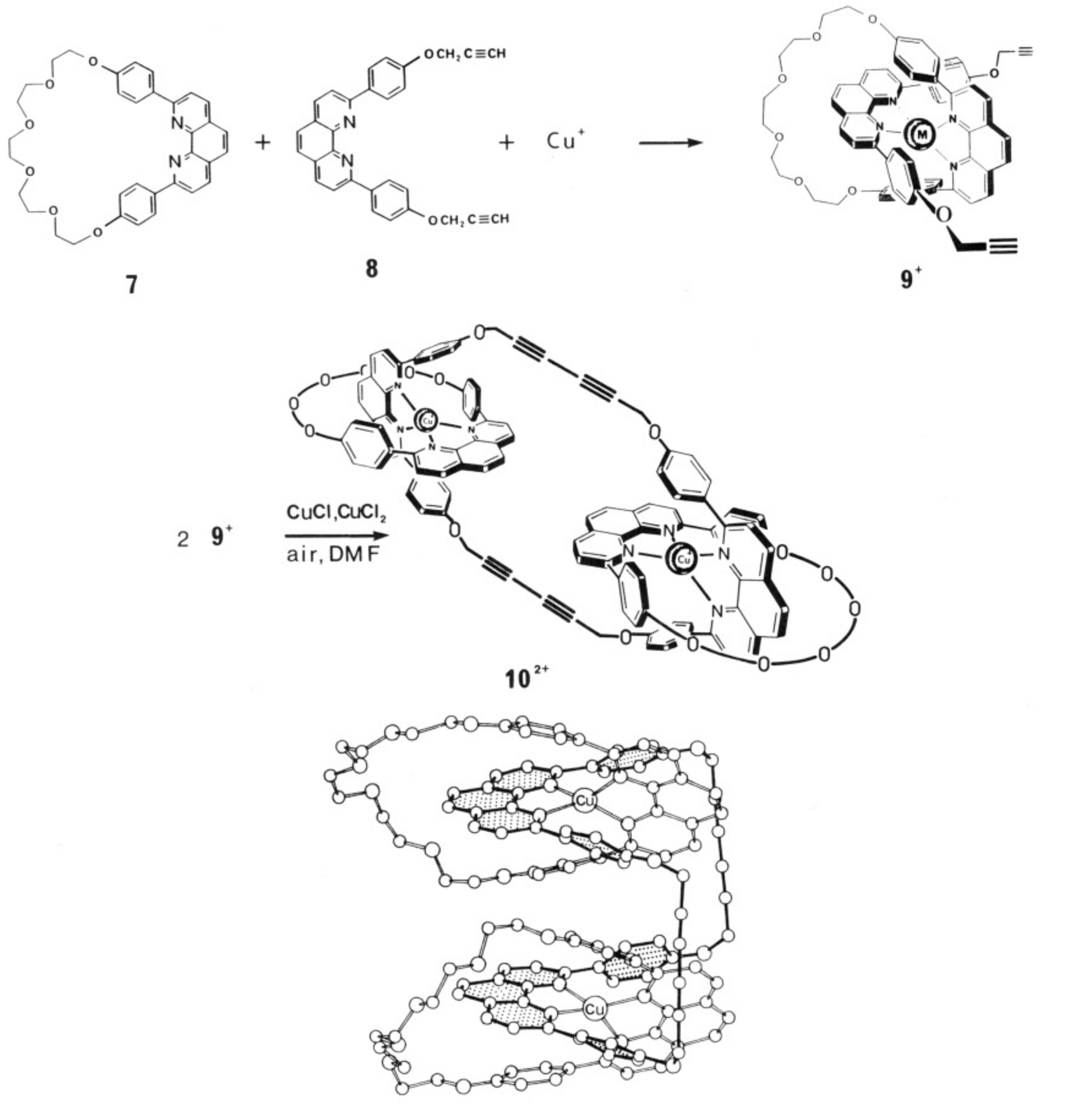

Figure 8. Preparation of the dicopper(I) [3]-catenate $\mathbf{10}^{2+}$ (58% yield from **7** and **8**); X-ray structure of $\mathbf{10}^{2+}$.

[3]-catenates have already been obtained,[54] and electrochemical studies indicate that there is a ground-state electrostatic interaction between the subunits. Photophysical studies are underway.

Regarding multicatenands, it should be stressed that the making of interlocked ring polymers similar to real molecular chains or collars has been dreamt of by polymer chemists for a long time. Although it is too early to know whether such interlocked polycyclic materials will display magic mechanical or rheological properties, their synthesis represents an extremely challenging problem to tackle. Indeed, interpenetrating network polymers and cyclic polymers trapped into network structures display nontrivial topological properties.[55] These materials are of growing practical importance. An extension of the cyclodimerization approach (Figure 7) can easily be imagined, leading to

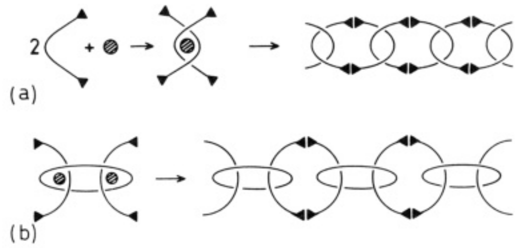

Figure 9. Possible strategies for making interlocked ring polymers.

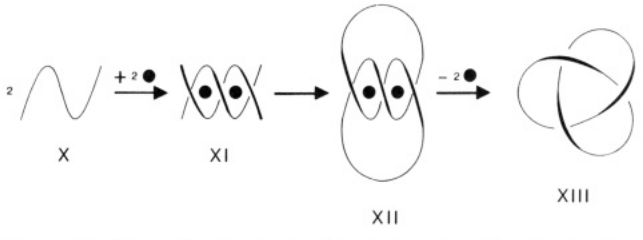

Figure 10. Toward molecular knots: strategy based on the double 3D-template effect of two transition metals able to twine two molecular threads.

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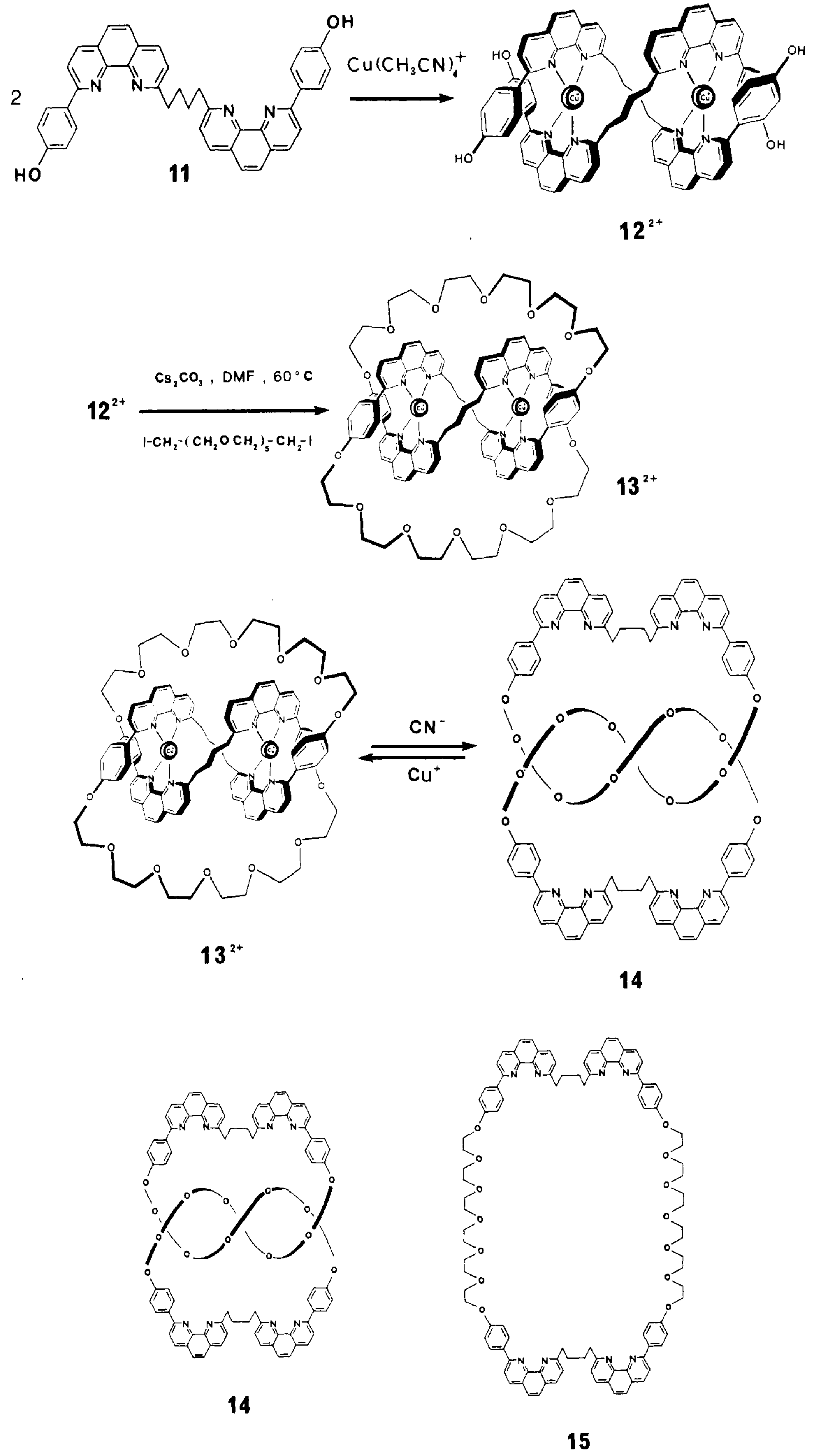

Figure 11. Synthesis of the molecular knots 13^{2+} and 14 (3% yield from 11). 14 and 15 are topological stereoisomers (Figure 2), both being 86-membered rings.

interlocked polymers, as schematically represented in Figure 9.

Synthesis of the Trefoil Knot

Despite many early difficulties, recent results from our group[56] open the door to the preparation of knots constructed around transition-metal ion templates. As noted earlier, the synthesis of chemical knots is a particularly appealing task linked to the graphic arts,[1-3] mathematics, and molecular biology.[4-7] Our strategy is shown in Figure 10. The strategy rests on the formation of a helicoidal intermediate (XI) from two bis-chelating threads (X) and two metal ions. The first difficulty will be a possible lack of selectivity in the reaction leading to XI. Although the choice of chelating moiety in X was dictated by our experience with 1,10-phenanthroline based systems, the choice of linker between the two chelating subunits was much less obvious. Several geometrical factors had to be considered: (1) The linkage must be short and rigid enough to prevent X from forming a mononuclear complex by the folding up of the bis-chelate metal thread onto one metal center. (2) However, the pitch of the double helix (XI) will be much more favorable to the cyclization leading to XII if the linker is sufficiently long. (3) The linker must be as thin as possible, to avoid steric compression in XII. (4) Formation of cyclic or linear oligomer complexes of X and the metal has to be inhibited. In addition, the linker must be sufficiently chemically robust to withstand the synthesis of X and cyclization to XII. Several bi- or polynuclear complexes with a double-helical arrangement of ligands have been reported.[57-61]

Although far from being ideal, the $-(CH_2)_4-$ linker between two substituted 1,10-phenanthroline subunits provided a molecular thread which formed a suitable double-helical complex with copper(I). The synthetic pathway is shown in Figure 11.

The thread **11** was obtained in three steps from 1,10-phenanthroline in 65% yield. It can be readily prepared on a gram scale. After addition of a stoichiometric amount of $Cu(CH_3CN)_4^+ \cdot BF_4^-$, a small proportion of the double-helicoidal complex $\mathbf{12}^{2+}$ was formed. Detailed ^1H NMR studies carried out on the O-methylated analogue of **11** indicated that a 1:1 mixture of Cu(I) and the ligand contains about 15% of the desired dicopper(I) double helix. This may explain the low yield (3%) of $\mathbf{13}^{2+}$ in the cyclization reaction (1:1 mixture of **11** and $Cu(CH_3CN)_4^+ \cdot BF_4^-$ in DMF at 60 °C, with excess Cs_2CO_3). Purification required difficult chromatographic separation, since various other cyclic products were also isolated and characterized from this reaction.[62]

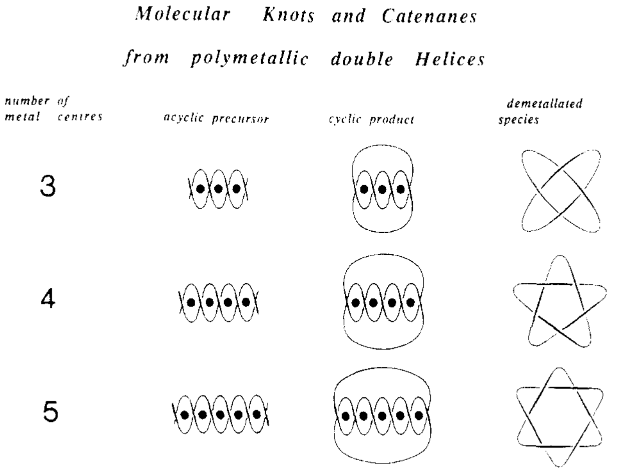

Figure 12. A possible strategy for synthesizing multiply interlocked rings or knotted single curves from polymetallic double helices.

Demetalation of $\mathbf{13}^{2+}$ was carried out as usual with KCN, leading quantitatively to the free knotted ligand **14**. The interconversion between $\mathbf{13}^{2+}$ and **14** could be performed several times without noticeable change: it involves a large molecular reorganization since the topography of the dicopper(I) complex $\mathbf{13}^{2+}$ is very different from that of **14** according to ^1H NMR studies. The structure of **14** (an 86-membered ring) was confirmed in two ways: (1) We also isolated 0.4% of **15**, the unraveled topological stereoisomer of **14**, and both compounds behave similarly in FAB mass spectroscopy[62] (calculated molecular weight 1610, found 1609.9) as expected for compounds having exactly the same sequence of atoms and valence bonds. (2) ^1H NMR studies showed the trefoil knot **14** to be chiral, whereas the topological stereoisomer **15** showed no sign of chirality.

The dicopper(I) complex $\mathbf{13}^{2+}$ is a crystalline solid whose X-ray structure is currently under investigation.[63] At the present stage, we have only 50 mg of the free ligand **14**, which should exhibit fascinating dynamic and conformational properties. We are confident that it will be possible to improve the yields of knotted systems dramatically by slight structural modifications and that we shall one day be able to visualize these molecules with crystallographic methods.

Finally, we note that the concept of using polynuclear double helices as precursors to more complex interlocked and knotted systems can be generalized. The principle is explained schematically in Figure 12, but at the moment this is just an intellectual game. As a general rule, if the number of metal centers is even, the number of crossing points in the molecular graph after cyclization is odd, and a single closed knotted curve is formed (trefoil, pentafoil, heptafoil, etc. from two, four, six, etc. metal centers, respectively). If the double helix is built around an odd number of templating metals, there will be an even number of crossing points, which

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(64) **Note Added in Proof**: (a) After this paper was written, the remarkable template synthesis of a [2]-catenane by Stoddart and coworkers was published. It is based on donor–acceptor stacks preorganized before the last cyclization step: Ashton, P. R.; Goodnow, T. T.; Kaifer, A. E.; Reddington, M. V.; Slawin, A. M. Z.; Spencer, N.; Stoddart, J. F.; Vicent, C.; Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1396–1399. (b) The X-ray structure of the dicopper trefoil knot $\mathbf{13}^{2+}$ has been solved: Dietrich-Buchecker, C. O.; Guilhem, J.; Pascard, C.; Sauvage, J.-P. *Angew. Chem.*, in press.

will result in multiply interlocked [2]-catenanes (two singly, doubly, triply, etc. interlocked rings from one, three, five, etc. metals, respectively).

I express my gratitude to the talented researchers who have made this topological adventure possible. This work would never have reached its present stage without the outstanding contribution of C. Dietrich-Buchecker. The synthetic work of P. Marnot, R. Ruppert, J. Weiss, A. Khemiss, D. Mitchell, J.-C. Chambron, and C. Hemmert is also acknowledged. I also thank the many researchers whose collaboration turned out to be particularly fruitful: J.-P. Kintzinger, A. Edel, P. Maltese (NMR), P. Federlin, J.-M. Kern (photochemistry and electrochemistry), C. Pascard, M. Cesario, J. Guilhem (crystallography), A.-M. Albrecht-Gary, Z. Saad (kinetics), F. Arnaud, E. Marques, M.-J. Schwing-Weill (thermodynamics), J.-P. Morel, N. Morel-Desrosiers (molal volumes), R. Huber, F. Bitsch, G. Teller, A. Van Dorsaeler (mass spectroscopy), and D. R. McMillin, whose collaboration was the real starter of this research. I am grateful to M. Ward for critical reading of the manuscript. Finally, the constant financial support of the CNRS is also gratefully acknowledged.

Photodissociation of Intraadsorbate Bonds at Adsorbate–Metal Interfaces

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While photochemistry of gases and liquids is a mature research field[1,2] and photochemistry on semiconductors is relatively well-studied,[3] photochemistry at metal surfaces is a newly emerging area.[4-14] This Account describes the status of our current research on the surface science of photochemistry at *adsorbate–metal* interfaces; it forms part of an expanding, worldwide effort to understand, for metals,[4-14] semiconductors,[3] and insulators,[15] the role of the surface on the mechanistic and dynamical aspects of photon-driven surface processes. Our work, summarized in Table I, has focused on *intraadsorbate* bond-breaking processes. Particular examples, illustrating important points, are discussed below.

When a molecule is near a metal surface, its chemical and optical properties are altered, and the metal substrate itself can play a direct photochemical role by absorbing light and serving as a source of energy for activating the adsorbate. It can also quench excited adsorbates. Thus, we expect gas- and liquid-phase photo processes to change qualitatively and quantitatively at surfaces. For example, it is well-known that fluorescence, a nanosecond phenomenon, is very strongly quenched near metal surfaces,[16-18] an effect attributed to nonradiative energy transfer.[17,19] For adsorbed molecules, electronic quenching can proceed through charge transfer,[19,20] which occurs on a time scale from a few femtoseconds (fs = 10^{-15} s) for resonant electron tunneling[20,21] to $\sim 10^2$ fs for Auger neutraliza-

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