the crude reaction mixtures indicated that <2% of crossover had occurred via boat-like transition states in these latter conversions, and no evidence could be found for the presence of enones **23** and **24**.

Finally, *at higher temperatures* (~*160 °C*) **8** *and* **9** *were directly converted to the ketal derivatives* **7a** *and* **7b**, *respectively, which upon mild acid hydrolysis afforded gnididione* (**1**) *and isognididione* (**2**) *in overall yields of 45% and 57%*.[20] The materials thus obtained were identical in all respects with authentic samples of **1** and **2**[1,18] and were isomerically pure to the limits of NMR and TLC detection. We believe this to be the first example of a sequential (oxy-Cope)–(Diels–Alder)–(retro-Diels–Alder) reaction, and we might only add that similar schemes can be envisioned for the synthesis of other guaiane and pseudoguaiane derivatives. This last possibility is currently under active tigation.

Supplementary Material Available: Physical and chemical properties of compounds **6–11** and **13–24** (5 pages). Ordering information is given on any current masthead page.

(18) We are grateful to Professor John Marx, of Texas Tech University, for providing us with an authentic sample of gnididione (**1**). Isognididione (**2**) was derived from **1** following the published procedure.[1]

(19) Beak, P.; Yamamoto, J.; Upton, C. J. *J. Org. Chem.* **1975**, *40*, 3052.

(20) The somewhat lower yield obtained for gnididione (**1**) appears to be associated with an inherent instability of ketal **7a**. For example, the overall yield for **1** was raised to 58% when hydrolysis of intermediate **6a** was carried out prior to the Diels–Alder reaction.

Templated Synthesis of Interlocked Macrocyclic Ligands: The Catenands

Christiane O. Dietrich-Buchecker and Jean-Pierre Sauvage*

*Laboratoire de Chimie Organo-Minérale
Institut de Chimie, 67000 Strasbourg, France*

Jean-Marc Kern

*Laboratoire d'Electrochimie Organique
Institut de Chimie, 67000 Strasbourg, France*

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The synthesis of molecules displaying novel topological properties has long been a challenge. In particular catenanes were discussed several decades ago,[1,2] but the development of synthetic procedures of practical significance is still very limited.

The directed synthesis of catenanes has been performed by Schill et al.;[1] statistical methods have also been used.[3-7] Another approach, taking advantage of the synthesis of a molecular Möbius strip, seems to be very promising.[8]

This report deals with an extremely short and convenient synthetic route to catenanes. The principle of the synthesis is based on a generalized template effect around a metal ion,[9] leading to a metallocatenane as intermediate. After demetalation, the new ligand obtained contains two interlocked macrocycles. We therefore propose the name catenand for this new class of coordinating molecules. We also report some of the exceptional properties of the cuprocatenane, which clearly demonstrate a strong catenand effect.

Recently, we described the synthesis of a cuprocatenane from a macrocyclic compound.[10] We have now developed a one-step synthesis of cuprocatenane **4**⁺ from **1**[10] and 1,14-diiodo-3,6,9,12-tetraoxatetradecane (**3**),[11] as shown in Figure 1. Cu-(CH₃CN)₄⁺·BF₄⁻ forms, with 2 equiv of the diphenol **1**, a very stable, deep red complex, **2**⁺. Reacting **2**⁺ and **3** in *N,N'*-dimethylformamide (DMF), under high dilution conditions, in the presence of Cs₂CO₃, affords **4**⁺ in 27% yield. The monocyclic compound **5**[12] is also obtained (20% isolated), as well as open-

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6

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(1) Schill, G. "Catenanes, Rotaxanes and Knots"; Academic Press: New York, 1971.

(2) Frisch, H. L.; Wasserman, E. *J. Am. Chem. Soc.* **1961**, *83*, 3789.

(3) Wasserman, E. *J. Am. Chem. Soc.* **1960**, *82*, 4433.

(4) Harrison, I. T.; Harrison, S. *J. Am. Chem. Soc.* **1967**, *89*, 5723.
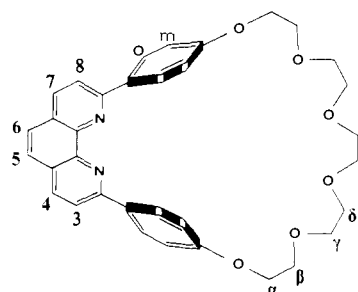
(5) Harrison, I. T. *J. Chem. Soc., Perkin Trans. 1* **1974**, 301.

(6) Agam, G.; Graiver, D.; Zilkha, A. *J. Am. Chem. Soc.* **1976**, *98*, 5214.
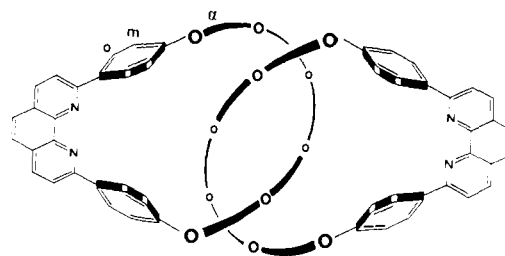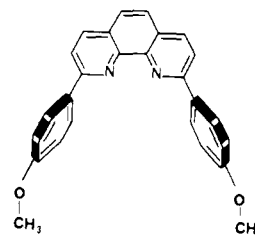
(7) Schill, G.; Schweickert, N.; Fritz, H.; Vetter, W. *Angew. Chem.* **1983**, *95*, 909.

(8) Walba, D. M.; Richards, R. M.; Haltiwanger, R. C. *J. Am. Chem. Soc.* **1982**, *104*, 3219. See also: *Chem. Eng. News* **1982**, July 12, 21. Walba, D. M. In "Chemical Applications of Topology and Graph Theory"; King, R. B., Ed.; Elsevier: New York, 1983.

(9) Another example of three-dimensional template effect is furnished by the synthesis of cobalt(III) sepulchrate: Creaser, I. I.; Geue, R. J.; Harrowfield, J. McB; Hertl, A. J.; Sargeson, A. M.; Snow, M. R.; Springborg, J. *J. Am. Chem. Soc.* **1982**, *104*, 6016 and references cited.

(10) Dietrich-Buchecker, C. O.; Sauvage, J. P.; Kintzinger, J. P. *Tetrahedron Lett.* **1983**, *46*, 5095.

(11) **3** was obtained by NaI treatment of the ditosylate of pentaethylene glycol; the latter was purified according to: Fenton, D. E.; Parkin, D.; Newton, R. F. *J. Chem. Soc., Perkin Trans. 1*, **1981**, 449.
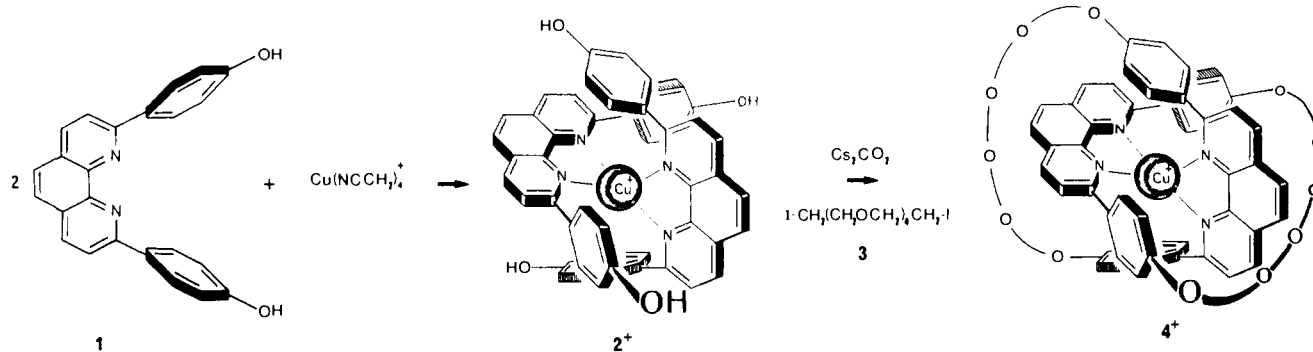
Figure 1.

chained compounds of high molecular weight ($M_r > 1500$). Decomplexation of the metallocatenane 4^+ is quantitatively carried out by treatment with tetramethylammonium cyanide[13] in acetonitrile–water. The catenand 6 thus obtained was characterized by ^{1}H NMR, as shown in Figure 2.

The two diphenylphenanthroline fragments fit in together in the complex 4^+; consequently, due to the ring current effect of the phenanthroline nucleus, H_o, H_m, and $CH_{2\alpha}$ resonance signals appear at high field:[10] 7.375, 6.024, and 3.62 ppm, respectively (spectrum a). After decomplexation, the two phenanthroline subunits separate and the chemical shifts for H_o, H_m, and $CH_{2\alpha}$ take normal values: 8.440, 7.233, and 4.372 ppm, respectively (spectrum b). In fact, the spectrum of the catenand 6 is very similar to that of the monomeric macrocycle 5 (spectrum c).

The mass spectroscopy study of 6 provided the definitive proof of its catenane structure. The molecular peak of 6 is observed at M 1132. As soon as the cleavage of one of the interlocked macrocycles has taken place, a mechanical link between the two subunits no longer exists. Thus, the linear part is threaded out from the intact ring, and both species undergo further fragmentations. Consequently, no ion is detected between 566 and 1132. Such characteristic mass spectra of catenanes have previously been obtained.[14]

To check the coordinating properties of the catenand 6 we prepared metallocatenanes by mixing the latter with the appropriate metal salt. ^{1}H NMR spectroscopy showed that the two diphenylphenanthroline subunits refit together while encaging the complexed cation: Li$^+$, Cu$^+$, Ag$^+$, etc.

The particular topography of the ligand is expected to highly favor a tetrahedral geometry around the metal center. In addition, due to the interlocking of the two coordinating macrocyclic subunits, highly stable complexes are expected; this is indeed the case for the copper complex 4^+, which could not be electrochemically demetalated (mercury cathode at -1.8 V vs. SCE in DMF) whereas its open equivalent, $Cu(7)_2^+$, is readily decomplexed electroreductively (mercury cathode at -1.7 V vs. SCE in DMF).

In fact, cyclic voltammetry shows the couple $4^+/4$ to be highly reversible in DMF, even at a very slow scan rate, as shown in Figure 3. Thus, dark blue solutions of the formally copper(0) complex 4 can be electrogenerated at -1.67 V vs. SCE in DMF. This complex shows a strong ESR signal at $g = 2.000 \pm 0.002$ at room temperature (line width $\Delta H = 39$ G). This behavior is somewhat similar to that of $Ru(bpy)_3^+$.[15]
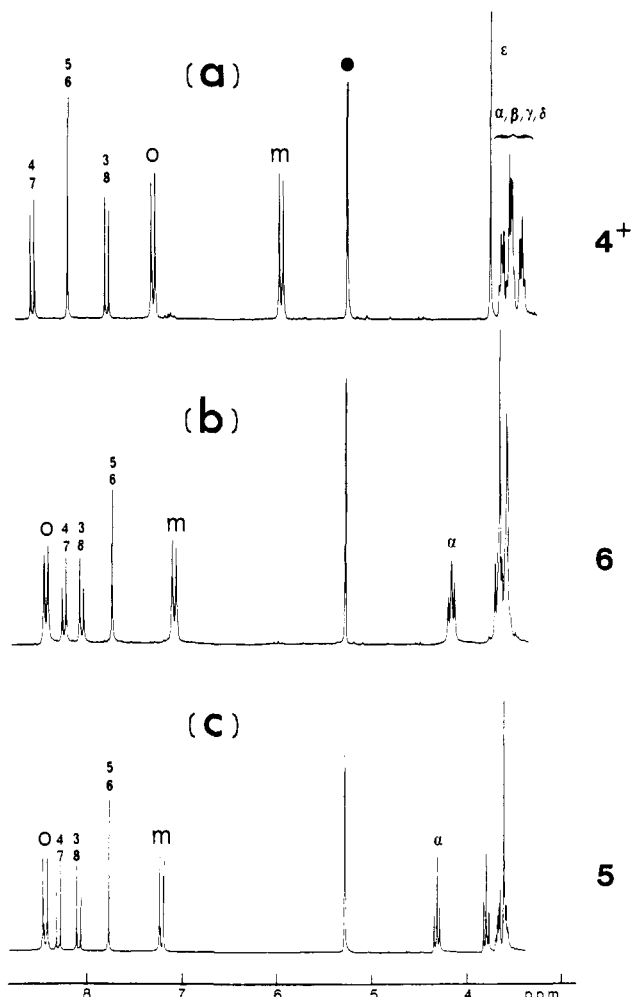
(12) Dietrich-Buchecker C. O.; Sauvage, J. P. *Tetrahedron Lett.* **1983**, *46*, 5091.

(13) In the early stages of our work, we encountered difficulties with NaCN or KCN, due to complexation of the cation by the catenand. This problem was solved by using a tetralkylammonium cyanide. 4^+ is treated by $N(CH_3)_4^+\cdot CN^-$ in $CH_3CN–H_2O$ (1:4) at room temperature. After workup, a white solid is obtained. An analytical sample was prepared by recrystallization in $CH_2Cl_2–C_6H_6$. mp 183–184 °C. Anal. Calcd for $C_{68}H_{68}O_{12}N_4$ (Found): C, 72.1 (72.1); H, 6.0 (6.1); N, 4.9 (4.7).

(14) Vetter, W.; Logemann, E.; Schill, G. *Org. Mass. Spectrom.* **1977**, *12*, 351 and references cited.

Figure 2. 200-MHz ^{1}H NMR spectra of 4^+, 5, and 6 in CD_2Cl_2: (●) solvent.

We have developed a fast[16] and efficient synthetic method for preparing metallocatenanes from 1,10-phenanthroline (three steps; 19% overall yield). Demetalation affords the first member of a new class of ligands, the catenands, whose coordinating properties are presently under study. The special combination of topology *and* topography of the catenands has already allowed the solution

(15) Motten, A. G.; Hanck, K.; De Armond, K. *Chem. Phys. Lett.* **1981**, *79*, 541 and referenced cited.

(16) The metathesis of cyclic olefins has also been envisaged as a short route to catenanes; indeed, hydrocarbon catenanes have been detected by mass spectrometry among the products obtained by cyclododecene metathesis. See: Wolovsky, R. *J. Am. Chem. Soc.* **1970**, *92*, 2132. Ben-Efraim, D. A.; Batich, C.; Wasserman, E. *Ibid.* **1970**, *92*, 2133.
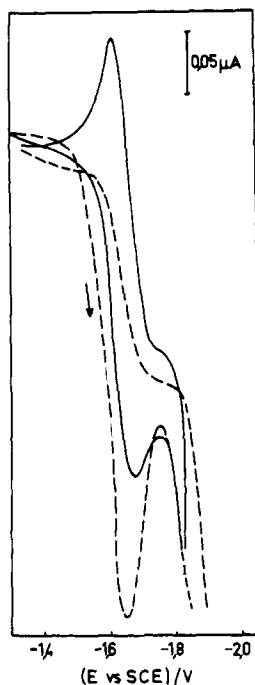
Figure 3. Cyclic voltammograms of **4⁺** (—) and Cu(7)₂⁺ (------) in DMF; 0.1 M N(C₄H₉)₄⁺·ClO₄⁻; room temperature; mercury cathode; scan rate = 10 mV/s.

preparation of a formally copper(0) complex of exceptional stability.

Formation of Ferryltetraphenylporphyrin by Laser Irradiation

Krzysztof Bajdor and Kazuo Nakamoto*

*Todd Wehr Chemistry Building, Marquette University
Milwaukee, Wisconsin 53233*

The crucial step in the reaction cycle of cytochrome P-450 is the formation of the ferryl group via the cleavage of dioxygen bonded to iron protoporphyrin. The main purpose of this communication is to report the first observation of the resonance Raman (RR) spectra of ferryltetraphenylporphyrin, OFe(TPP), which was formed unexpectedly during our measurement of the RR spectra of Fe(TPP)O₂ in pure O₂ matrices at ∼15 K.

A stable, "base-bound" complex, Fe(TPP)(pip)₂ (pip = piperidine), was placed in a miniature oven under the cold tip of our matrix isolation Raman apparatus.[2] The oven was heated at ∼180 °C under vacuum until the vacuum gauge indicated complete dissociation of the base from the complex. The "base-free" Fe(TPP) thus obtained was vaporized by heating the oven at ∼225 °C by laser beam and cocondensed with pure oxygen on the inclined surface of the cold tip which was cooled to ∼15 K by a CTI Model 21 closed-cycle helium refrigerator. As our previous matrix-isolation IR studies[3] indicate, such cocondensation reactions produce five-coordinate, "base-free" Fe(TPP)O₂. Resonance Raman spectra of the cocondensation

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(1) For example, see: Alexander, L. S.; Goff, H. M. *J. Chem. Educ.* **1982**, *59*, 179.

(2) Scheuermann, W.; Nakamoto, K. *Appl. Spectrosc.* **1978**, *32*, 251, 302.

(3) Nakamoto, K.; Watanabe, T.; Ama, T.; Urban, M. W. *J. Am. Chem. Soc.* **1982**, *104*, 3744. Watanabe, T.; Ama, T.; Nakamoto, K. *J. Phys. Chem.* **1984**, *88*, 440.
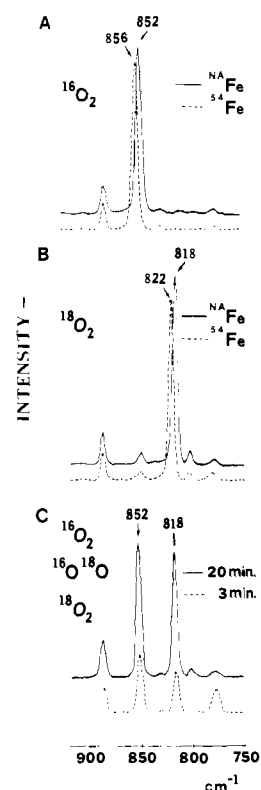
Figure 1. Resonance Raman spectra of Fe(TPP) cocondensed with dioxygen at ∼15 K (406.7-nm excitation, 1–2 mW). (A) ᴺᴬFe(TPP) with ¹⁶O₂ (solid line) and ⁵⁴Fe(TPP) with ¹⁶O₂ (broken line). (B) ᴺᴬFe(TPP) with ¹⁸O₂ (solid line) and ⁵⁴Fe(TPP) with ¹⁸O₂ (broken line). (c) ᴺᴬFe(TPP) with isotopically mixed dioxygen (¹⁶O₂/¹⁶O¹⁸O/¹⁸O₂ = 1/2/1). The solid and broken lines indicate that spectra after 20 and 3 min of laser irradiation, respectively.
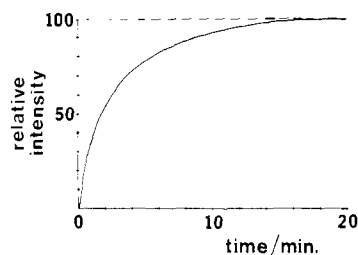
Figure 2. A plot of relative intensity of the 852-cm⁻¹ band of ¹⁶OᴺᴬFe(TPP) vs. time of laser irradiation.

products were measured using a Spex Model 1401 double monochromator in conjunction with a Spectra-Physics Model 164-01 Kr ion laser. Throughout this investigation, the samples were excited with 1–2 mW of the 406.7-nm radiation (Soret excitation).

The solid line of Figure 1A shows the RR spectrum of ᴺᴬFe(TPP)(ᴺᴬFe: Fe in natural abundance, 92% pure ⁵⁶Fe) cocondensed with ¹⁶O₂. It shows a strong signal at 852 cm⁻¹ in addition to the normal Fe(TPP) bands. The intensity of this band is time dependent, reaching the maximum after about 20 min. This intensity remains constant as long as the matrix temperature is kept at ∼15 K. The intensities of all other bands remain almost unchanged during this period. A plot of the relative intensity of the 852-cm⁻¹ band vs. the time of laser irradiation is shown in Figure 2. It is clear that the above photolysis follows the first-order kinetics.

The 852-cm⁻¹ band was shifted to 818 cm⁻¹ in an ¹⁸O₂ matrix (Figure 1, trace B). Similar experiments with an isotopically scrambled oxygen (¹⁶O₂/¹⁶O¹⁸O/¹⁸O₂ = 1/2/1) produced two bands at 852 and 818 cm⁻¹ as shown in trace C. (The broken line in trace C indicates the spectrum obtained after 3 min of laser irradiation). These results indicate quite clearly that the 852- and 818-cm⁻¹ bands are due to the ν(¹⁶O–Fe) and ν(¹⁸O–Fe),