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[3] Crystal structure analysis of **2**: $H_{492}C_{24}Mo_{102}O_{534}$; $M = 19114.06$ g mol^{-1}, space group $C2/c$, $a = 44.586(1)$, $b = 26.365(1)$, $c = 44.565(1)$ Å, $\beta = 104.21(1)^\circ$, $V = 50782$ Å^3, $Z = 4$, $\rho = 2.500$ g cm^{-3}, $\mu = 2.550$ mm^{-1}, $F(000) = 36768$, crystal size $= 0.20 \times 0.08 \times 0.06$ mm^3. Crystals of **2** were removed from the mother liquor and immediately measured at 183(2) K on a Bruker axs SMART diffractometer (three-circle goniometer with a 1 K CCD detector, $Mo_{K\alpha}$ radiation, graphite monochromator; hemisphere of data collection at 0.3° wide ω scans over three runs of 606, 435, and 230 frames ($\phi = 0^\circ, 88^\circ, 180^\circ$) from a 5.00 cm-distant detector). A total of 148391 reflections ($1.54 < \Theta < 26.99^\circ$) were collected, of which 54698 unique reflections ($R(\text{int}) = 0.0811$) were used. An empirical absorption correction on the basis of symmetry-equivalent reflections was performed with the SADABS program. The structure was solved and refined with the SHELXS-97 and SHELXL-97 programs (G. M. Sheldrick, University of Göttingen, **1997**) to $R = 0.0713$ for 23929 reflections with $I > 2\sigma(I)$ and a max./min. residual electron density of $2.816/-3.078$ e Å^{-3}. Structure graphics were produced with the DIAMOND 2.1 program (K. Brandenburg, Crystal Impact GbR, **1999**). Due to disorder, not all positions of the water molecules inside the sphere and in the crystal lattice were localized. The same note applies to the acetate ligands. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-138289. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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A Molecular Knot with Twelve Amide Groups—One-Step Synthesis, Crystal Structure, Chirality[**]

Oliver Safarowsky, Martin Nieger, Roland Fröhlich, and Fritz Vögtle[*]

In memory of Eberhard Steckhan

Molecular knots are a little known class of substances.[1] Hitherto only some of the (historically first) phenanthroline type (Dietrich-Buchecker and Sauvage, 1989),[2] of the nucleic-acid type (Seeman, 1992),[3] and of the crown/quat type (Stoddart et al., 1997)[4] have been synthesized. We report here on probably the simplest synthesis of a new molecular trefoil knot in 20% yield, which proceeds under self-organization. Besides a 96-membered araliphatic skeleton this knot only includes twelve CONH groups.

In the course of the synthesis[5] of higher [*n*]catenanes[1]—with more than two interlacing wheels—we planned to prepare larger amounts of macrocycle **4**,[6] which should be favorable as a (ditopic) concave (host) template in the synthesis of [2]- and [3]catenanes.[7] For this purpose we treated the proven substrates 2,6-pyridinedicarboxylic acid dichloride **1** and diamine **2**[6] under dilution conditions (concentration 10^{-3} mM)[5] in dichloromethane together with the auxiliary base triethylamine. This reaction gave besides **3** (yield 15%) and **4** (yield 23%) a colorless product in 20% yield which had a molecular weight of m/z 2718.6 (MALDI-TOF-/FAB-MS), a melting point of >325 °C, and an R_f value

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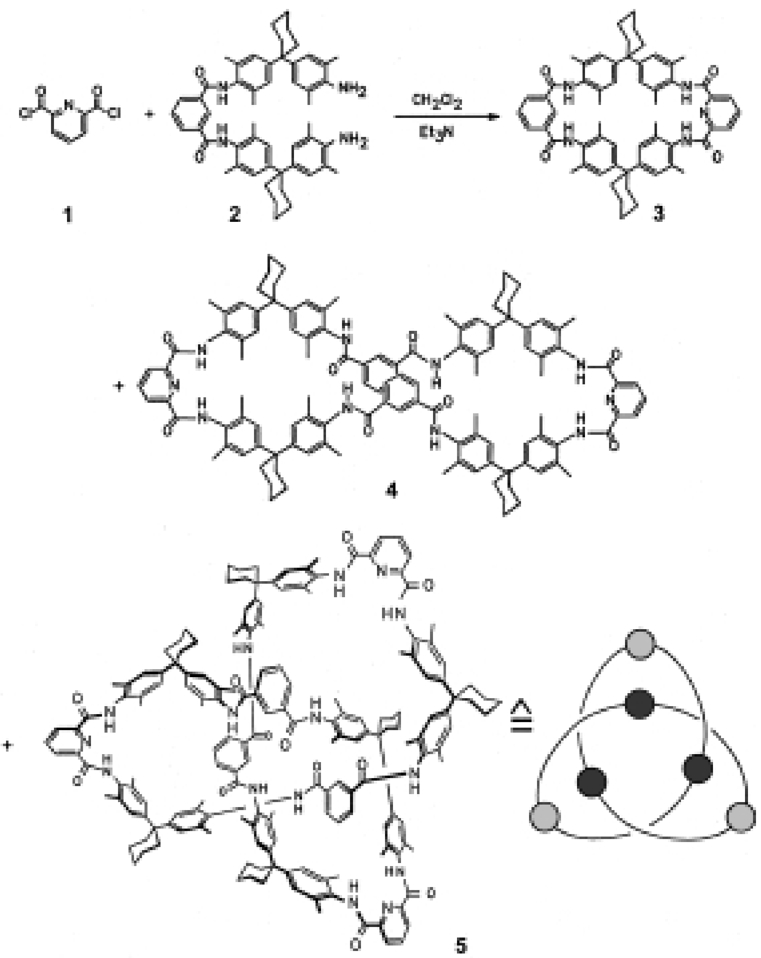
[**] Extracts were presented during a talk at the Universität Düsseldorf on January 11, 2000. We thank Dr. Christian Seel and Dr. Rudolf Hartmann for suggestions and measurements.



of 0.075 (TLC on HPTLC plates, eluent dichloromethane/methanol 35:1). The latter product of this reaction thus corresponds to that from a 3:3 macrocyclization. The formation of the catenane of the same weight consisting of the two cycles **3** and **4** can be excluded, as the corresponding fragment peaks at m/z 906.2 and m/z 1812.4 are absent.

Encouraged by our recent successful crystallization of amide catenanes and rotaxanes,[8] we also tried in this case to examine the hydrogen-bonding pattern (in the crystal) which is important for the template interaction and a prerequisite for high-yield syntheses of new mechanically linked assemblies.[9] The X-ray crystal structure analysis[10] of the crystals obtained by slow crystallization from trichloromethane/methanol over several weeks did not, however, lead to the non-knotted macrocycle, but surprisingly to the molecular knot **5** (Figure 1). The knot connectivity as well as entrapped peripheral solvent molecules (CH_3OH, H_2O, $CHCl_3$) can be discerned—similar to peptides. Only four of the twelve NH hydrogen atoms in the knot molecule participate in intramolecular hydrogen bonds. The hydrogen-bonding pattern resembles that recently found in a [2]rotaxane.[8b]

Despite the regluar alternating sequence of its building blocks (P1-I1-P2-I2-P3-I3; P: pyridine dicarbamide, I: isophthaloyl diamide, linked by diphenylmethane units), the crystal of the trefoil clover knot has no C_3 symmetry. This is due to four hydrogen bonds between the building blocks and to the conformation of one of the three isophthaloyl amides (I1). In this moiety both carbonyl groups point towards the inside, whereas in the other five isophthaloyl units the diamide groups are all directed towards the outside. The carbonyl oxygen atom of I2 (I2-CO$_b$), second in terms of the sequence, forms a bifurcated hydrogen bond to both amide protons of P1 (303 and 335 pm, respectively). Hence, this leaf of the knot is narrowed, whereas in the two other loops each cavity is occupied by a methanol molecule, which is also fixed by a bifurcated hydrogen bond between its oxygen atom and the amide protons of P2 and P3, respectively. Both of the "inverted" carbonyl groups of I1 form hydrogen bonds to the amide protons of the two other isophthaloyl moieties (I1-CO$_a\cdots$I2-NH$_b$, I1-CO$_b\cdots$I3-NH$_b$), causing a stronger deformation. Additionally, the typical bifurcated hydrogen bonds between NH hydrogen atoms and the pyridine nitrogen atoms are formed for all pyridine dicarbamide groups. Furthermore, a third methanol molecule is

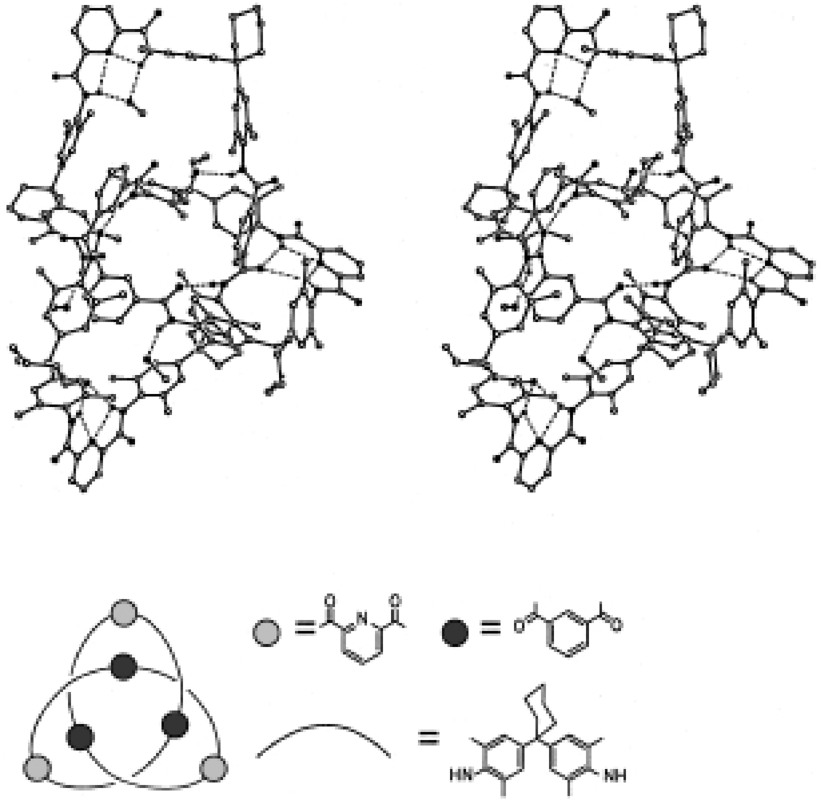


Figure 1. X-ray crystal structure analysis of **5** (stereoview). Apart from the amide protons, hydrogen atoms are omitted, hydrogen bonds are shown by dashed lines. Solvent molecules: methanol.

bound to I2-NH$_a$ through hydrogen bonds. The carbonyl groups not involved in the intramolecular hydrogen-bonding pattern form hydrogen bonds with solvent molecules, leading to an intermolecular cross-linkage of the individual knots.[10]

The ^{1}H NMR spectra of **5** show more signals than the spectra of comparable catenanes and macrocycles.[5, 7, 12]

The preferred formation of knot **5** over formation of a topologically isomeric catenane or the non-knotted topologically isomeric macrocycle (with 12 CONH groups each) is attributed to hydrogen bonds between amide groups, as in comparable template syntheses of catenanes and rotaxanes.[12, 13] Instead of the usual macrocyclic tetralactam host (of type **3**) the middle loop of the knot could, however, act as a noncyclic concave template for a CONH guest group.[14]

Molecular trefoil knots, for which we propose the name "knotanes", are topologically chiral, and in some cases Sauvage succeeded in the resolution of racemates.[2] The centrosymmetric unit cell of **5** proves that both enantiomers exist. Orientating attempts to separate the enantiomers of the new knot **5** by means of HPLC using cellulose carbamate column material (retention times $R_t = 8$ and 9 min, eluent: *n*-hexane/ethanol 85/15), which we successfully performed for catenanes, rotaxanes, and pretzelanes with similar structure elements,[15] revealed that more effort is required for a quantitative separation, as for Sauvage's knots.[2]

Sauvage's hope in 1999 that[2] "hopefully, chemical knots will expand to other fields than transition metal chemistry in the future" has come true surprisingly soon. The results obtained should be interesting not only for higher mechanically linked assemblies but also for combinations with knots of the phenanthroline and other types[16, 17]—a treasury for topological stereochemistry and topological chirality.

Received: January 17, 2000, [Z 14541]

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[14] The X-ray crystal structure analysis shows clearly that the loop is helically wound, but that it only reveals a low pitch and is additionally held together by hydrogen bonds at the crossing points. Thus, this concave template resembles the macrocycles of type **3** used hitherto.

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[17] J.-P. Sauvage, A. von Zelewsky, J. Becher, A. M. Brouwer, F. Vögtle, co-operation planned in the European CERC 3 program.

Highly Regioselective Oxygenation of C–H Bonds: Diamidomanganese Constructs with Attached Substrates as Catalyst Models**

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The functionalization of the hydrocarbon framework of an organic compound is an exciting challenge of wide-reaching consequences.[1] The regioselective functionalization of C–H bonds of complex organic compounds is of significant synthetic potential.[2] The catalytic or reagent-driven transfer of an oxygen,[3] carbon,[4] or boron atom[5] into C–H bonds

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[**] Financial support has been provided by Columbia University and the Camille and Henry Dreyfus Foundation. P.M.W. acknowledges the REU-NSF program for summer support. We also thank Dr. J. B. Schwarz (manuscript preparation) and Dr. Y. Itagaki (mass spectrometry).

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