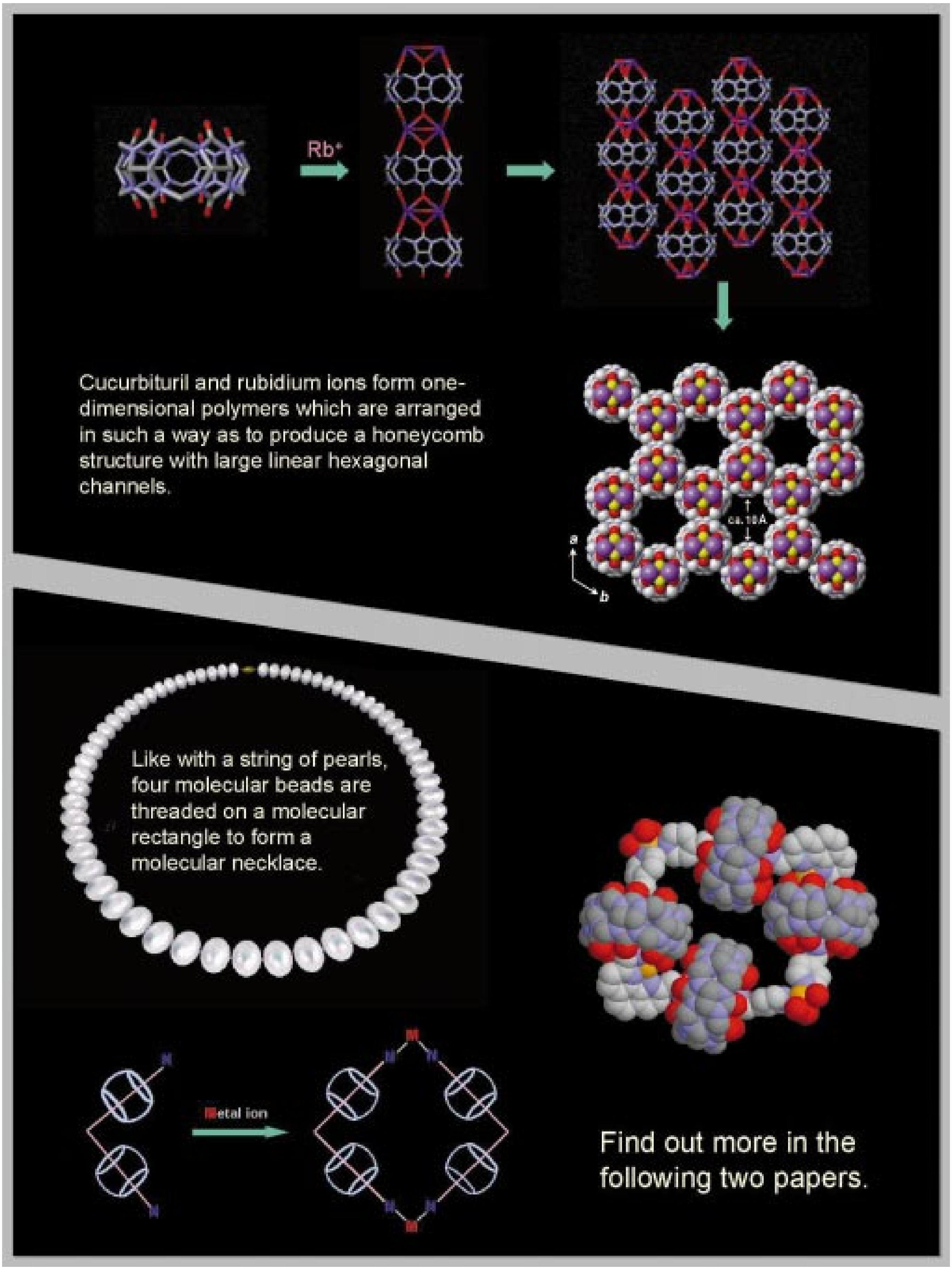


Cucurbituril and rubidium ions form one-dimensional polymers which are arranged in such a way as to produce a honeycomb structure with large linear hexagonal channels.

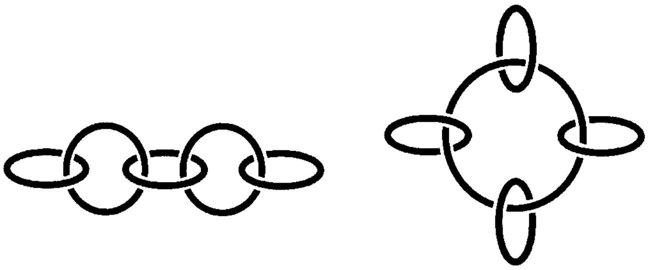
Like with a string of pearls, four molecular beads are threaded on a molecular rectangle to form a molecular necklace.

Find out more in the following two papers.

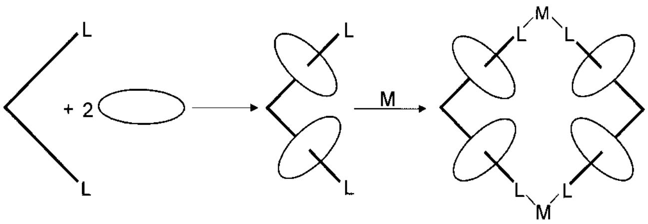
Synthesis of a Five-Membered Molecular Necklace: A 2+2 Approach[**]

Soo-Gyun Roh, Ki-Min Park, Gil-Jae Park,
Shigeru Sakamoto, Kentaro Yamaguchi,
and Kimoon Kim[*]

We have been interested in highly efficient syntheses of interlocked structures[1] such as rotaxanes, polyrotaxanes, and molecular necklaces.[2] Molecular necklaces (MN) are supramolecular species in which a number of small rings are threaded onto a large ring. They are topological isomers of linear oligocatenanes, where rings are mechanically interlocked in a linear fashion (Scheme 1).[3] Formation of a mixture of molecular necklaces [n]MN ($n = 4-7$), some of which were isolated and characterized by electrospray (ESI) mass spectrometry, was first reported by Sauvage et al.[4] Recently, we reported a one-pot, nearly quantitative self-assembly of a minimal molecular necklace [4]MN[5] in which three molecular "beads" are threaded onto a molecular triangle.[2d] This supramolecular compound is formed from nine species: three molecular beads, three "strings", and three "angle connectors". In principle, the same approach can be used for the synthesis of a molecular necklace [5]MN containing four molecular beads threaded onto a molecular square.[6] However, this method often produces a mixture of [4]MN and [5]MN.[7] Therefore, we now take another approach to [5]MN, which we call a "2+2" approach. Using a preorganized, L-shaped molecule, we first synthesize a pseudorotaxane containing two molecular beads and then allow a metal ion (or a metal complex with *cis* vacant coordination sites) to react with the pseudorotaxane to form a [5]MN (Scheme 2). Here we report the synthesis and X-ray crystal structure of a [5]MN prepared by this approach.



Scheme 1. Schematic representation of a linear [5]catenane (olympiadane; left) and a molecular necklace [5]MN (right).



Scheme 2. Schematic representation of the 2+2 approach for the synthesis of molecular necklaces [5]MN. The two ends L of the bent building blocks are ligands atoms (such as pyridine nitrogen atoms) that coordinate to a metal center. The ellipsoids symbolize molecular beads, for example cucurbituril (**1**).

The [5]MN $\mathbf{4}\cdot 14\,NO_3^-$ is constructed by threading two equivalents of cucurbituril (**1**)[8] with the L-shaped phenanthroline derivative **2** and then allowing the resulting pseudorotaxane $\mathbf{3}\cdot 4\,NO_3^-$ to react with $Cu(NO_3)_2$ (Scheme 3). The X-ray crystal structure[9] of $\mathbf{4}\cdot 14\,NO_3^-$ reveals that four molecular beads are threaded onto a molecular square in which two copper ions (Cu(1) and Cu(3)) occupy two opposite corners (Figure 1). Each of these copper ions is coordinated by two pyridyl units of $\mathbf{3}^{4+}$ and three water molecules in a distorted square pyramidal geometry with the pyridyl units at two adjacent basal positions. Two additional copper ions (Cu(2) and Cu(4)) are bound inside the phenanthroline units making up corners of the square. Each of these copper ions is coordinated by two phenanthroline nitrogen atoms, a secondary amine nitrogen atom, and two oxygen atoms of cucurbituril in a distorted square pyramidal geometry with an oxygen atom (O(201) for Cu(2) and O(401) for Cu(4)) at the apical position. Coordination of the amine nitrogen atoms N(225) and N(425) to the copper ions (Cu(2) and Cu(4), respectively) makes two sides of the molecular square considerably shorter than the other two; therefore, the necklace framework is better described as a rectangle with dimensions of about 19.3 × 17.0 Å.[10] The cucurbituril beads threaded on the longer side of the molecular rectangle are held in place by hydrogen bonds between their carbonyl oxygen atoms and the protonated amine groups of **2**. The beads on the shorter side are held in place by such hydrogen-bonding interactions at one end and by coordination to the metal center at the other end (Figure 1). A space-filling representation of the structure of $\mathbf{4}^{14+}$ is displayed in Figure 2. The space inside the molecular necklace is filled with nitrate ions and water molecules.

The molecular necklace $\mathbf{4}\cdot 14\,NO_3^-$ is soluble in water (and also in acetonitrile when the counterions are exchanged with PF_6^-). Owing to the paramagnetic metal centers, the NMR spectrum of $\mathbf{4}\cdot 14\,NO_3$ is not informative. Nevertheless, the ESI mass spectrum of $\mathbf{4}\cdot 14\,PF_6^-$ is consistent with the

---

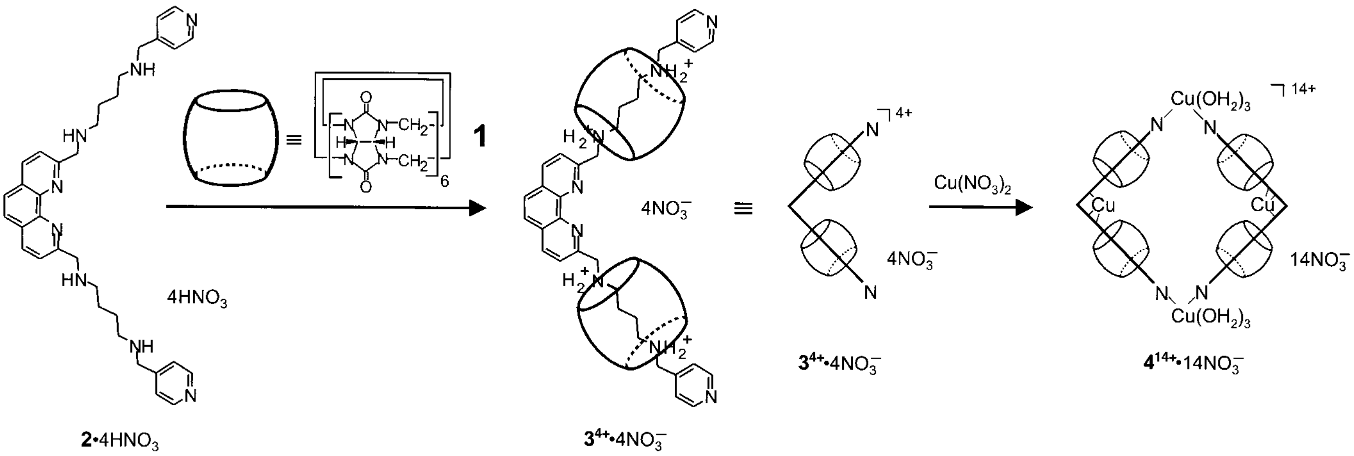
[*] Prof. K. Kim, Dr. S.-G. Roh, Dr. K.-M. Park, G.-J. Park
National Creative Research Initiative Center
for Smart Supramolecules
and
Department of Chemistry
Pohang University of Science and Technology
San 31 Hyojadong, Pohang 790-784 (South Korea)
Fax: (+82) 562-279-8129
E-mail: kkim@postech.ac.kr

Shigeru Sakamoto, Prof. Kentaro Yamaguchi
Chemical Analysis Center, Chiba University
Yayoicho, Inage-ku, Chiba 2638522 (Japan)

[**] This work was supported by the Creative Research Initiative Program of the Korean Ministry of Science and Technology. We thank Professor Jong Hoon Hahn and Ms. Young Ah Kim for low-resolution electrospray ionization mass spectrometry, Mr. Eunsung Lee for technical assistance, and Professor G. V. Smith for helpful comments on the manuscript.

Supporting information for this article is available on the WWW under http://www.wiley-vch.de/home/angewandte/ or from the author.

1433-7851/99/3805-0638 $ 17.50+.50/0



Scheme 3. Synthesis of the molecular necklace $\mathbf{4}^{14+}$ by the 2+2 approach through incorporation of Cu^{2+} ions.

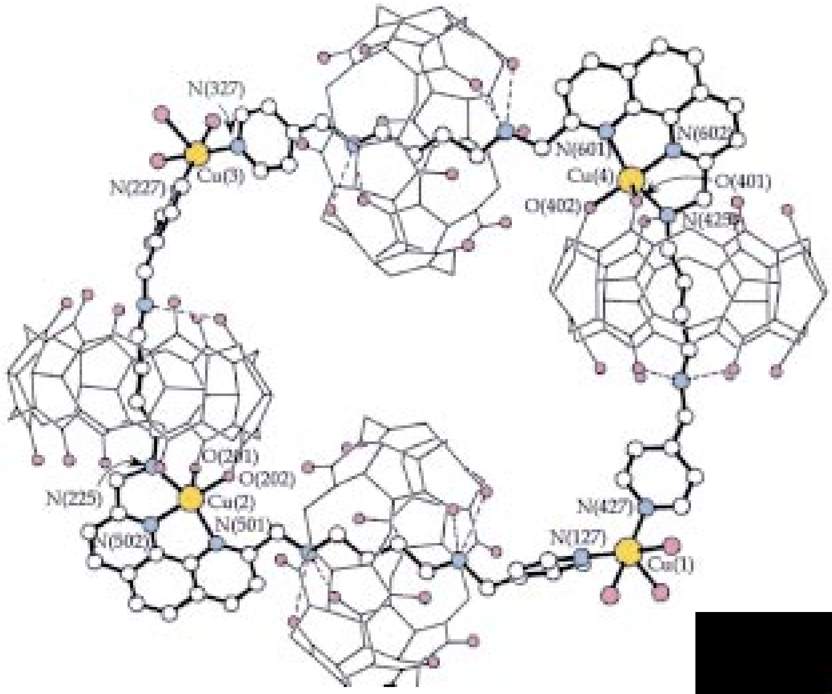


Figure 1. Structure of $\mathbf{4}^{14+}$ in $\mathbf{4}\cdot 14NO_3^-$. Nitrate ions and water molecules in the lattice are omitted for clarity. Hydrogen-bonding interactions are indicated by dashed lines. Selected bond lengths [Å] and angles [°]: Cu(1)–N(127) 2.014(5), Cu(1)–N(427) 2.029(6), N(127)-Cu(1)-N(427) 93.2(2); Cu(3)–N(227) 2.020(6), Cu(1)–N(327) 2.010(5), N(227)-Cu(3)-N(327) 91.2(2); Cu(2)–N(501) 2.146(5), Cu(2)–N(502) 1.911(5), Cu(2)–N(225) 2.058(5), Cu(2)–O(201) 2.275(5), Cu(2)–O(202) 1.953(4); Cu(4)–N(601) 2.141(5), Cu(4)–N(602) 1.903(5), Cu(4)–N(425) 2.063(5), Cu(4)–O(401) 2.258(5), Cu(4)–O(402) 1.952(4).

necklace structure (see Experimental Section), which suggests that this structure of $\mathbf{4}^{14+}$ is maintained in solution.

Nitrate salts of other transition metal ions such as Ni^{2+}, Zn^{2+}, Cd^{2+}, and Ag^+ do not yield molecular necklaces when they are allowed to react with the preorganized pseudorotaxane $\mathbf{3}\cdot 4NO_3$. For instance, slow diffusion of an aqueous solution of $Ni(NO_3)_2$ into a solution of $\mathbf{3}\cdot 4NO_3$ results in the [5]rotaxane (or [5]pseudorotaxane) $\mathbf{5}\cdot 14NO_3$ (Scheme 4). The X-ray crystal structure of $\mathbf{5}\cdot 14NO_3$ shows that a $[Ni(OH_2)_4]^{2+}$ unit links two $\mathbf{3}^{4+}$ ions through the coordination of their pyridyl groups (one pyridyl group from each) at the axial positions of the Ni ion with an octahedral geometry (see the supporting information).[9] The *trans* coordination of the two pyridyl groups to the metal center results in the [5]pseudorotaxane with a sigmoidal shape. Details of this and other supramolecular structures derived from $\mathbf{3}\cdot 4NO_3$ and the transition metal ions (and other metal complexes)[11] will be reported elsewhere.

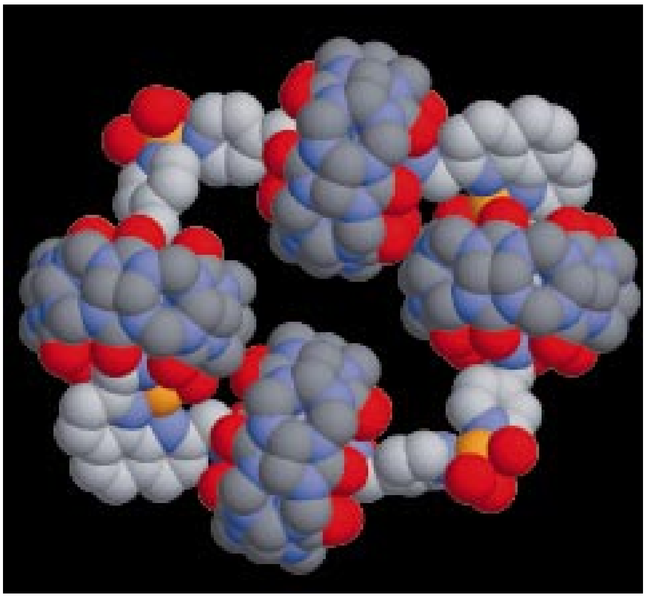
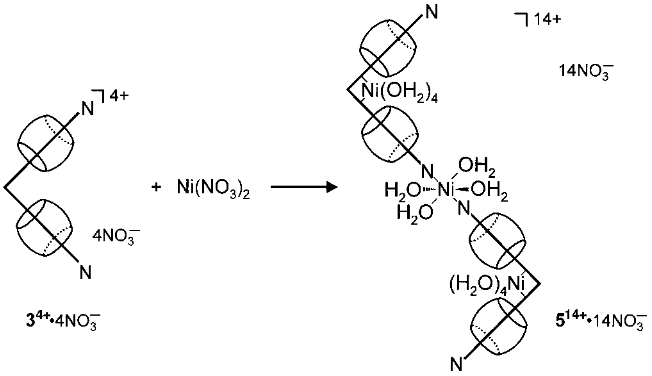


Figure 2. Space-filling representation of the molecular necklace $\mathbf{4}^{14+}$ in $\mathbf{4}\cdot 14NO_3^-$. Nitrate ions and water molecules in the lattice are omitted for clarity; carbon (molecular rectangle): gray; carbon (cucurbituril bead): dark gray; nitrogen: blue; oxygen: red; copper: yellow.



Scheme 4. Formation of rotaxane $\mathbf{5}^{14+}$ through incorporation of Ni^{2+} ions.

In summary, we present an efficient synthesis of a molecular necklace [5]MN using a preorganized L-shaped pseudorotaxane and a metal ion. Here, as well as in our earlier work,[2] we demonstrate that such topologically intriguing supramolecular species can be readily assembled from carefully designed organic building blocks and properly chosen metal ions or complexes.

Experimental Section

2: A solution of *N*-(4-pyridylmethyl)-1,4-diaminobutane trihydrobromide (4.50 g, 10.7 mmol) and triethylamine (9 mL) in methanol (60 mL) was added dropwise under argon to a solution containing 1,10-phenanthroline-2,9-dialdehyde[12] (1.26 g, 5.34 mmol) and anhydrous magnesium chloride (1.01 g, 10.68 mmol) in dry methanol (80 mL), and then stirred for 18 h. At 0 °C sodium borohydride (0.722 g, 19.1 mmol) was added to the solution in small portions (caution: evolution of gas). After 15 h of stirring, water (150 mL) was added, and the mixture was concentrated to 150 mL. After extraction with CH_2Cl_2 (3 × 100 mL), the combined organic phase was dried over magnesium sulfate and the solvent evaporated. The light red oil was then dissolved in ethanol, and conc. HCl was added slowly to yield **2** · 4HCl (yield: 0.80 g, 21 %). M.p. 170 °C (decomp.); ^1H NMR (300 MHz, D_2O): $\delta = 1.92$ (8H, brs), 3.33 (8H, m), 4.62 (4H, s), 4.73 (4H, s), 7.93 (4H, d, $J = 8.14$ Hz), 8.06 (2H, d, $J = 6.70$ Hz), 8.16 (2H, s), 8.64 (2H, d, $J = 8.26$ Hz), 8.78 (4H, d, $J = 6.76$ Hz). The mass spectra were obtained with the free amine **2**, which was generated by treating **2** · 4HCl with NaOH. FAB-MS: m/z: 563.2 $[M+H^+]$. The nitrate salt **2** · $4HNO_3$ was prepared by dissolution of the chloride salt in water and treatment of the solution with 40 % NaOH to adjust the pH to about pH 12 followed by extraction with CH_2Cl_2, concentration, and addition of ethanol and conc. HNO_3. The NMR spectrum of the nitrate salt is essentially the same as that of the chloride salt. Both salts are very hygroscopic and unstable; therefore, the nitrate salt was used immediately in the synthesis of **3** · $4NO_3^-$, which is stable.

3 · $4NO_3^-$: At room temperature a slightly excess amount of **1** · $10H_2O$ (1.79 g, 1.52 mmol) was suspended in a solution of **2** · $4HNO_3$ (0.59 g; 0.73 mmol) in H_2O (50 mL). After the mixture was stirred for about 16 h, undissolved **1** was filtered off. The filtrate was concentrated, and the product isolated by addition of ethanol. The nearly colorless solid was collected and dried to afford **3** · $4NO_3^-$ (yield: 1.90 g, 87 %). The ^1H NMR spectrum indicates that $\mathbf{3}^{4+}$ contains two molecules of cucurbituril. ^1H NMR (300 MHz, D_2O): $\delta = 0.71$ (8H, brs), 2.49 (4H, brs), 2.80 (4H, brs), 4.40 (24H, d, $J = 15.70$ Hz), 4.62 (4H, s), 4.91 (4H, s), 5.66–5.77 (48H, m), 8.11 (2H, s), 8.15 (4H, d, $J = 8.91$ Hz), 8.63 (2H, d, $J = 8.43$ Hz), 8.72 (2H, d, $J = 8.37$ Hz), 8.79 (2H, m); ESI-MS: m/z: 1425.2 $[\mathbf{3} \cdot 2PF_6]^{2+}$, 901.7 $[\mathbf{3} \cdot PF_6]^{3+}$, 640.7 $[\mathbf{3}]^{4+}$ (the counterions were exchanged with PF_6^- for mass spectrometry); elemental analysis calcd for $C_{106}N_{56}O_{24}H_{118} \cdot 4NO_3 \cdot 10H_2O$: C 42.60, H 4.65, N 28.12; found: C 42.24, H 4.56, N 28.50.

4 · $14NO_3^-$: A 3.1×10^{-3} M stock solution of pseudorotaxane **3** · $4NO_3$ (0.196 g; 0. 0656 mmol) in H_2O (21 mL) was prepared and divided into seven portions. Each portion was layered over a 0.3 M solution of $Cu(NO_3)_2$ in H_2O (3 mL) in a diffusion tube to produce in a week sky blue, plate-shaped crystals of **4** · $14NO_3$ suitable for an X-ray crystal structure analysis (yield: 32 mg, 13 %). Elemental analysis calcd for $Cu_4(C_{212}N_{112}O_{48}H_{234})(H_2O)_6(NO_3)_{14} \cdot 64H_2O$: C 33.94, H 5.02, N 23.52; found: C 34.10, H 5.22, N 23.60. The high-resolution ESI mass spectrometry data were obtained with the sample whose counterions had been exchanged with PF_6^- ions. ESI-MS: positive ion: m/z: 3025.8 (calcd: 3026.2) $[(\mathbf{4} - 8H^+)^{6+} \cdot 4PF_6^-]^{2+}$ or $[Cu_4(C_{212}N_{112}O_{54}H_{238})(PF_6)_4]^{2+}$; negative ion: m/z: 3461.9 (calcd: 3462.1) $[(\mathbf{4} - 6H^+)^{8+} \cdot 10PF_6^-]^{2-}$, 3388.8 (calcd: 3389.1) $[(\mathbf{4} - 7H^+)^{7+} \cdot 9PF_6^-]^{2-}$. The observed isotopic patterns of the ion clusters match the calculated patterns well.

Received: August 25, 1998 [Z12337IE]
German version: *Angew. Chem.* **1999**, *111*, 672–675

Keywords: catenanes · copper · N ligands · rotaxanes · supramolecular chemistry

---

[1] Reviews: a) J.-P. Sauvage, *Acc. Chem. Res.* **1990**, *23*, 319; b) D. B. Amabilino, J. F. Stoddart, *Chem. Rev.* **1995**, *95*, 2725; c) D. Philp, J. F. Stoddart, *Angew. Chem.* **1996**, *108*, 1242; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1154; d) H. Gibson, M. C. Bheda, P. T. Engen, *Prog. Polym. Sci.* **1994**, *19*, 843; e) R. Jäger, F. Vögtle, *Angew. Chem.* **1997**, *109*, 966; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 930.

[2] a) Y.-M. Jeon, D. Whang, J. Kim, K. Kim, *Chem. Lett.*, **1996**, 503; b) D. Whang, Y.-M. Jeon, J. Heo, K. Kim, *J. Am. Chem. Soc.* **1996**, *118*, 11333; c) D. Whang, K. Kim, *J. Am. Chem. Soc.* **1997**, *119*, 451; d) D. Whang, K.-M. Park, J. Heo, P. Ashton, K. Kim, *J. Am. Chem. Soc.* **1998**, *120*, 4899.

[3] Molecular necklaces constitute a subset of catenanes. For a given number of rings, a molecular necklace is uniquely defined. A molecular necklace consisting of a total of n rings ($n-1$ small rings threaded onto one larger ring) is denoted as [*n*]MN, which is a topological stereoisomer of [*n*]catenane. For example, the molecular necklace [5]MN described here and olympiadane synthesized by Stoddart and coworkers (D. B. Amabilino, P. R. Ashton, A. S. Reder, N. Spencer, J. F. Stoddart, *Angew. Chem.* **1994**, *106*, 450; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 433) are topological stereoisomers. The minimal molecular necklace is [4]MN; the smaller molecular necklaces [2]MN and [3]MN are equivalent to [2]catenane and [3]catenane, respectively.

[4] a) F. Bitsch, G. Hegy, C. Dietrich-Buchecker, E. Leize, J.-P. Sauvage, A. V. Dorsselaer, *J. Am. Chem. Soc.* **1991**, *113*, 4023; b) F. Bitsch, C. O. Dietrich-Buchecker, A.-K. Khemiss, J.-P. Sauvage, A. V. Dorsselaer, *New J. Chem.* **1994**, *18*, 801.

[5] Very recently, Stoddart and co-workers also isolated and characterized a [4]MN in the synthesis of oligocatenanes: D. B. Amabilino, P. R. Ashton, V. Balzani, S. E. Boyd, A. Credi, J. Y. Lee, S. Menzer, J. F. Stoddart, M. Venturi, D. J. Williams, *J. Am. Chem. Soc.* **1998**, *120*, 4295.

[6] Reviews on molecular squares: a) M. Fujita, K. Ogura, *Bull. Chem. Soc. Jpn* **1996**, *69*, 1471; b) P. J. Stang, B. Olenyuk, *Acc. Chem. Res.* **1997**, *30*, 502.

[7] J. Heo, K.-M. Park, K. Kim, unpublished results.

[8] Reviews: a) W. L. Mock in *Comprehensive Supramolecular Chemistry, Vol. 2* (Ed.: F. Vögtle) Pergamon, Oxford, **1996**, p. 477; b) W. L. Mock, *Top. Curr. Chem.* **1995**, *175*, 1; c) P. Cintas, *J. Incl. Phenom. Molec. Reco. Chem.* **1994**, *17*, 205.

[9] Crystal data of **4** · $14NO_3^-$: $[Cu(H_2O)_3\{(C_{34}H_{45}N_8)Cu\} \cdot (C_{36}H_{36}N_{24}O_{12})_2]_2(NO_3)_{14} \cdot 76H_2O$, $M_r = 7718.72$, triclinic, $P\bar{1}$, $a = 23.284(1)$, $b = 25.189(1)$, $c = 29.835(1)$ Å, $\alpha = 100.7458(6)$, $\beta = 107.8604(7)$, $\gamma = 93.5909(4)^\circ$, $V = 16228(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.580$ g cm^{-3}, $T = 188$ K, Siemens SMART CCD diffractometer, $Mo_{K\alpha}$ ($\lambda = 0.71073$), $\mu = 3.88$ cm^{-1}. The structure was solved by Patterson methods. All the alkylamine nitrogen atoms, except the ones (N(225) and N(425)) that are coordinated to the copper ions bound to the phenanthroline units, are protonated, as judged by the difference electron density map and our earlier observations.[2] The overall charge of the necklace species was therefore assigned to be +14. Of the 14 counterions, 12 nitrate ions behave well during the refinement. One nitrate ion has large thermal parameters, and its structure

deviates considerably from an ideal geometry. One nitrate ion was not found. All non-hydrogen atoms were refined anisotropically. Final block-diagonal matrix least-squares refinement on F^2 with all 46961 reflections and 4611 variables converged to $R1$ $(I > 2\sigma(I)) = 0.086$, $wR2$ (all data) $= 0.271$, and GOF $= 1.07$. Crystal data of $\mathbf{5}\cdot 14NO_3^-$: $[Ni(H_2O)_4\{(C_{34}H_{45}N_8)Ni(H_2O)_3\cdot(C_{36}H_{36}N_{24}O_{12})_2\}_2](NO_3)_{14}\cdot 82H_2O$, $M_r = 7642.70$, triclinic, $P\bar{1}$, $a = 16.1173(2)$, $b = 21.0397(3)$, $c = 24.2956(2)$ Å, $\alpha = 96.3974(10)$, $\beta = 103.6400(4)$, $\gamma = 94.2966(8)^\circ$, $V = 7912.7(2)$ Å^3, $Z = 1$, $\rho_{calcd} = 1.604$ g cm^{-3}, $T = 188$ K, Siemens SMART CCD diffractometer, $Mo_{K\alpha}$ ($\lambda = 0.71073$), $\mu = 3.09$ cm^{-1}. Full-matrix least-squares refinement on F^2 with all 23393 reflections and 2311 variables converged to $R1$ $(I > 2\sigma(I)) = 0.144$, $wR2$ (all data) $= 0.389$ and GOF $= 1.10$. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-102726 ($\mathbf{4}\cdot 14NO_3$) and CCDC-102727 ($\mathbf{5}\cdot 14NO_3$). 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).

[10] The numbers correspond to the distances from the central ring of the phenanthroline to the copper corners.

[11] Reaction of the metal complexes $[Pt(en)(NO_3)_2]$ and $[Pd(en)(NO_3)_2]$ with $\mathbf{3}\cdot 4NO_3^-$, as judged by ^1H NMR spectroscopy, yields a mixture from which we have been so far unable to isolate pure compounds (en = ethylenediamine).

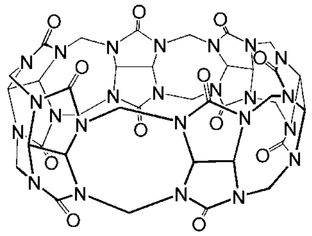
[12] a) U. Lüning, M. Müller, *Liebig Ann. Chem.* **1989**, 367; b) C. J. Chandler, L. W. Deady; J. A. Reiss, *J. Heterocycl. Chem.* **1981**, *18*, 599.

Shape-Induced, Hexagonal, Open Frameworks: Rubidium Ion Complexed Cucurbituril[**]

Jungseok Heo, Soo-Young Kim, Dongmok Whang, and Kimoon Kim*

Metal-organic solids containing large pores or channels with controlled sizes, shapes, and chemical environments have drawn much attention in recent years because they may have applications in separation, catalysis, and optoelectronics. The "modular" approach has been successfully employed in the construction of metal-organic open-framework materials; various organic building blocks and metal ions have been used to assemble a variety of porous three-dimensional networks.[1–6] Although these efforts have contributed greatly to our understanding of how to build such solid-state structures, we still need to explore new building blocks and building principles before we are truly able to design and build specifically engineered solid-state architectures. We present herein a crystal structure that demonstrates a novel way to construct metal-organic open-framework materials with large hexagonal channels using the modular approach.

Cucurbituril[7, 8] is a macrocyclic cavitand with D_{6h} symmetry, having a hollow core with a diameter of about 5.5 Å and two identical portals surrounded by carbonyl groups (Scheme 1). We recently reported novel molecular container assemblies comprising cucurbituril and alkali metal ions, which are capable of the reversible encapsulation and release of guest molecules in solution.[9] In an effort to understand the host–guest interactions in the molecular container assemblies, we studied their structures in the solid state by X-ray crystallography. In contrast to the case with other alkali metal ions, rubidium and cucurbituril form a one-dimensional coordination polymer in the solid state in which cucurbituril molecules stack atop one another through coordination of their carbonyl groups to the rubidium ions in between. More interestingly, the coordination polymer chains are arranged in such a way as to produce a honeycomb structure with large linear hexagonal channels parallel to the polymer chains.



Scheme 1. Cucurbituril.

Vapor diffusion of methanol into an aqueous solution containing cucurbituril and Rb_2SO_4 yields the needle-shaped crystalline product **1**.[10] The X-ray structure of **1** reveals a one-dimensional coordination polymer of alternating cucurbituril molecules and $Rb_2(\mu\text{-}OH)_2(OH_2)_2$ units that extends along the *c* axis (Figures 1 and 2).[11] A threefold axis parallel to the *c* axis passes through the center of the coordination polymer. The $Rb_2(\mu\text{-}OH)_2(OH_2)_2$ unit lies on a mirror plane perpendicular to the threefold axis. The two Rb ions are separated by 4.395(5) Å and are related to each other by a twofold symmetry axis passing through the oxygen atoms of the bridging OH groups. Each rubidium ion is coordinated by four portal oxygen atoms of two cucurbituril molecules (two oxygen atoms from each cucurbituril molecule: Rb–O(1) and Rb–O(1′) 2.952(5), Rb–O(2) and Rb–O(2′) 2.938(5) Å), two bridging hydroxide ions (Rb–O(3) 2.93(2), Rb–O(4) 2.94(1) Å), two methanol molecules encapsulated in the cucurbituril molecules (Rb–O(5) and Rb–O(5′) 2.96(1) Å), and a weakly coordinating water molecule (Rb–O(1W) 3.17(1) Å; Figure 1). The coordination geometry of the rubidium ion is best described as a capped square antiprism. The $Rb_2(OH)_2$ plane is parallel to the plane formed by six oxygen atoms of cucurbituril and separated from it by a mean distance of 2.190(4) Å. The $Rb_2(\mu\text{-}OH)_2(\mu\text{-}CH_3OH)_2(OH_2)_2$ unit is disordered over three sites due to the crystallographically imposed threefold symmetry.

---

[*] Prof. K. Kim, J. Heo, S.-Y. Kim, Dr. D. Whang
National Creative Research Initiative Center for
Smart Supramolecules
and
Department of Chemistry
Pohang University of Science and Technology
San 31 Hyojadong, Pohang 790-784 (South Korea)
Fax: (82) 562-279-8129
E-mail: kkim@postech.ac.kr

[**] This work was supported by the Creative Research Initiative Program of the Korean Ministry of Science and Technology. We thank Professors M. J. Zaworotko and G. V. Smith for helpful comments on the manuscript.