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 **5**$\cdot 14\,NO_3^-$: $[Ni(H_2O)_4\{(C_{34}H_{45}N_8)Ni(H_2O)_3\cdot(C_{36}H_{36}N_{24}O_{12})_2\}_2](NO_3)_{14}\cdot 82\,H_2O$, $M_r = 7642.70$, 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 (**4**$\cdot 14\,NO_3$) and CCDC-102727 (**5**$\cdot 14\,NO_3$). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, 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 **3**$\cdot 4\,NO_3^-$, as judged by ^1H NMR spectroscopy, yields a mixture from which we have been so far unable to isolate pure compounds (en = ethylenediamine).

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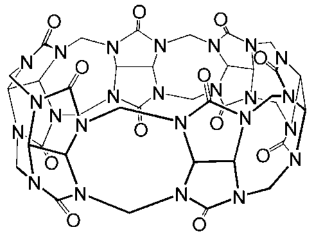
Shape-Induced, Hexagonal, Open Frameworks: Rubidium Ion Complexed Cucurbituril[**]

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.

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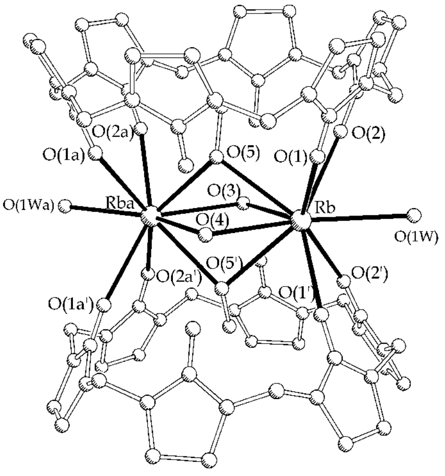


Figure 1. Coordination geometry around the rubidium ions in **1**. The rubidium ions, bridging hydroxide ions, and bound water molecules are disordered over three sites due to the crystallographically imposed threefold symmetry. Only one orientation is depicted. Selected bond lengths [Å]: Rb–O(1) and Rb–O(1′) 2.952(5), Rb–O(2) and Rb–O(2′) 2.938(5), Rb–O(3) 2.93(2), Rb–O(4) 2.94(1), Rb–O(5) and Rb–O(5′) 2.96(1), Rb–O(1W) 3.17(1).

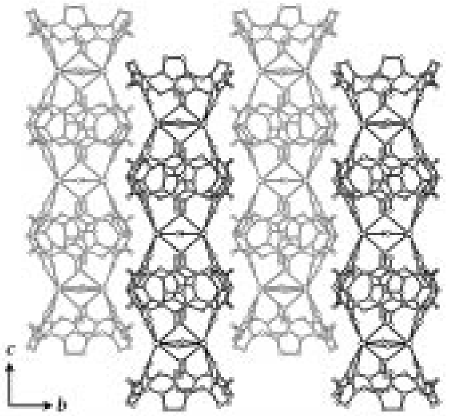


Figure 2. Section of the one-dimensional coordination polymer comprising cucurbituril molecules and $Rb_2(\mu\text{-}OH)_2(OH_2)_2$ units, and their packing in **1** (view of the *bc* plane). The neighboring chains are offset by one-half of the repeating unit along the *c* axis, and by one-half of the cucurbituril unit along the *a* axis. The $Rb_2(\mu\text{-}OH)_2(OH_2)_2$ unit is disordered over three sites due to the crystallographically imposed threefold symmetry passing through the center of the coordination polymer along the *c* axis. Only one orientation is depicted. The weakly coordinating water molecules are also omitted for clarity.

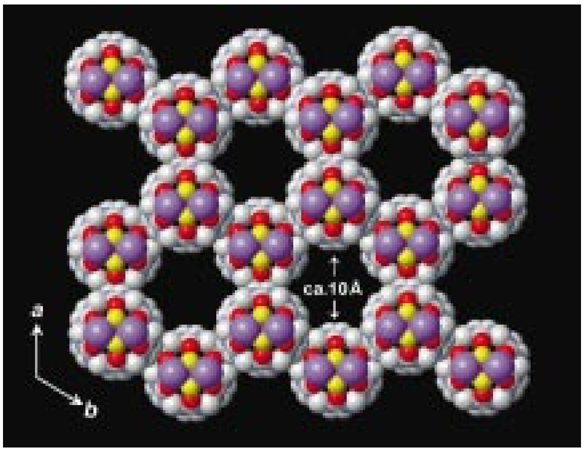
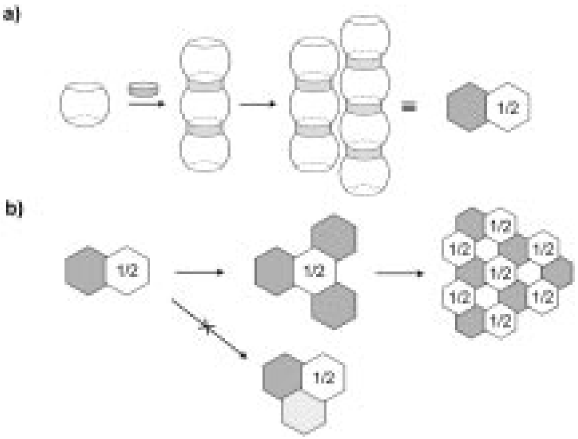


Figure 3. X-ray crystal structure of **1** viewed down the *c* axis showing large hexagonal channels with a mean diameter of about 10 Å. The $Rb_2(\mu\text{-}OH)_2$ unit is disordered over three sites; only one orientation is depicted. Water molecules in the channels are omitted for clarity. The Rb atoms are purple, the O atoms of the bridging hydroxide ions yellow, the O atoms of cucurbituril red, the N atoms blue, and the C atoms gray.

The most interesting feature of the crystal structure is that the coordination polymer chains in **1** are arranged in such a way as to produce a honeycomb structure with linear, hexagonal channels extended along the *c* axis (Figure 3). The coordination polymer chains are surrounded by three neighboring chains. The chain at the center is offset by one-half of the repeating unit along the *c* axis so that the "bumps" of the chain fit into "hollows" of the neighboring chains (Figure 2). This structure appears to be stabilized by efficient van der Waals interactions between the coordination polymer chains arising from their self-complementary curvature. The void volume of the channels, whose mean diameter is about 10 Å, is estimated to be around 23% of the total volume.[12] The channels are filled with water molecules (34 water molecules per unit cell) that form a complicated hydrogen-bonding network among themselves as well as with the water molecules coordinated to the metal centers (O(1W)). Once removed from the mother liquor, however, the crystals quickly lose solvent and crystallinity.[13] Diffusion of THF or ethylenediamine into an aqueous solution of cucurbituril/Rb_2SO_4 also produces a rubidium ion complexed cucurbituril with the same honeycomb structure, except that a THF or ethylenediamine molecule is encapsulated in the cavity of cucurbituril.[14] No organic molecules are found in the channels as in **1**.

Although such large hexagonal channel structures have precedence,[5, 6a] the way that the present structure is built up is unique (Scheme 2). Here, cucurbituril, a barrel-shaped molecule with D_{6h} symmetry, is used as a bulky, linear, bifunctional building block. The "barrels" are stacked up with metal ion "cement" to form a rigid column with alternating bumps and hollows (Scheme 2a). In the crystal, the next column is offset by one-half of the repeating unit along the column direction to maximize the interactions between the



Scheme 2. Simplified representation of how the structure of **1** is built up in the crystal.

two columns with a self-complementary curvature by fitting the bumps of one column into hollows of the other. However, placing a third column at the indentation between the two touching columns to achieve a closed-packing structure is not allowed, because the third column cannot be offset by one-half of a unit with respect to both the first and the second columns. Instead, the offset relationship of one-half of a unit between the neighboring columns and the threefold cross-sectional symmetry of the column result in a preferred Y-shaped arrangement of columns, which eventually turns into the hexagonal open-framework structure (Scheme 1 b).[15] This structure not only demonstrates that the shape and symmetry of a building block can induce a specific crystal structure, but also provides a new strategy to open frameworks with linear hexagonal channels. This novel structure and building principle may provide further insight into designing new porous materials as well as other supramolecular architectures.

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[10] Cucurbituril decahydrate (0.390 g) was added to a saturated solution of Rb_2SO_4 (10 mL). After the mixture was stirred for 1 h, the undissolved cucurbituril was filtered. Methanol vapor was allowed to diffuse into the filtrate at room temperature for a week before the crystalline product **1** was collected, washed with water, and dried in the air. Elemental analysis was performed on the air-dried sample. Elemental analysis (%) calcd for $[(C_{36}H_{36}N_{24}O_{12})Rb_2(OH)_2(CH_3OH)_2] \cdot 3H_2O$: C 34.58, H 3.97, N 25.47; found: C 34.36, H 4.28, N 25.71.

[11] Crystal data of **1**: $[(C_{36}H_{36}N_{24}O_{12})Rb_2(OH)_2(H_2O)_2 \cdot (CH_3OH)_2] \cdot 17H_2O$, $M_r = 1608.23$, hexagonal, space group $P6_3/mmc$, $a = 19.628(6)$, $c = 10.544(3)$ Å, $V = 3518(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.518$ g cm^{-3}, $T = 188$ K, Siemens SMART CCD diffractometer, $Mo_{K\alpha}$ ($\lambda = 0.71073$ Å), $\mu = 14.95$ cm^{-1}. The structure was solved by Patterson methods (SHELXS-86). All non-hydrogen atoms were refined anisotropically (SHELXL-93). Final full-matrix least-squares refinement on F^2 with all 1049 reflections and 117 variables converged to $R1 = 0.092$ ($I > 2\sigma(I)$), $wR2 = 0.30$ (all data), and GOF = 1.12. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-103350. 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).

[12] The void volume of the channels was estimated by the method described in reference [3b].

[13] Upon loss of the solvate molecules (water) the open-framework structure collapses to become a denser amorphous material.

[14] Diffusion of THF into the solution of cucurbituril/Rb_2SO_4 produces needle-shaped crystals first, which have the same honeycomb structure as **1**. However, the crystals change their morphology slowly to block-shaped crystals which have different cell parameters: monoclinic, space group $C2/m$, $a = 22.8361(4)$, $b = 10.4759(2)$, $c = 19.8560(4)$ Å, $\beta = 113.483(1)$, $V = 4356.7(1)$ Å^3. X-ray structural analysis on this crystal is in progress.

[15] In another way to look at the structure one may consider cucurbituril as a "pseudosphere". The pseudospheres are forced to line up vertically upon formation of the coordination polymer with the rubidium ions. This vertical lineup prevents the classical hexagonal or cubic closed packing, but leads to the "hexagonal open packing" observed here.

Statistical Investigation into the Structural Complementarity of Natural Products and Synthetic Compounds

Thomas Henkel,* Roger M. Brunne, Hartwig Müller, and Felix Reichel

Natural products represent a rich source of biologically active compounds. They have played a considerable part in the exploration and development of new drugs and crop protection products, which can be informally derived from the retrospective analysis of important commercial products.[1, 2] This historical point of view does not give any information in regard to the question as to how far the structural properties of natural products differ from the easily accessible synthetic substances. With the entrance of high-throughput-screening (HTS) as well as combinatorial chemistry in the lead-finding process this question however becomes of central importance in defining the future role of natural products in this research area. There is a need to evaluate whether natural products

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