

## Self-assembly of a [2]Pseudorotaxane Composed of Cucurbit[6]uril into Linear Pseudopolyrotaxanes by N–H···O, C–H···O and $\pi$ ··· $\pi$ Interactions

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### Abstract

The [2]pseudorotaxane of cucurbit[6]uril (Q6) with 1,6-bis(imidazol-1-yl)hexane dihydrobromide was synthesized and its crystal structure was described. The structure of [2]pseudorotaxane was mainly stabilized by host–guest C–H···O interactions. Self-assembly of the [2]pseudorotaxane produces infinite one-dimensional chains with intermolecular N–H···O, C–H···O, and  $\pi$ ··· $\pi$  interactions; thus, a linear non-covalent pseudopolyrotaxane is formed.

### Introduction

The pseudorotaxane and rotaxane have attracted more and more attention in recent years because of their interesting structures and properties, as well as potential applications for molecular devices [1]. Pseudorotaxane is a type of supramolecular assembly that consists of a cyclic molecule (the “wheel”), that is host and a threadlike molecule (the “axle”), that is guest [2]. There are a lot of works about rotaxanes, pseudorotaxanes and polyrotaxanes based on cucurbit[*n*]urils [3], which are cyclic methylene-linked glycoluril oligomers abbreviated as Q<sub>*n*</sub> (*n* = 5–10), and possess characteristic annular shape, with two carbonyl-fringed portals [4]. However, the linear pseudopolyrotaxanes based on cucurbiturils *via* weakly intermolecular hydrogen bonds and  $\pi$ ··· $\pi$  interactions are few, the known only one was reported by Kim *et al.* in 1996 [3k]. Most recently, Shen *et al.* have developed a new type bisimidazolyl groups [2] and [3]pseudorotaxane composed of  $\beta$ -cyclodextrin [5]. Herein, we report a detailed crystal structure study of a [2]pseudorotaxane prepared from 1,6-bis(imidazole-1-yl)hexane dihydrobromide(A) [6] with the cucurbit[6]uril (Scheme 1). The guest threads the host molecule forming the [2]pseudorotaxane [7], which self-assembly produces a linear pseudopolyrotaxane by intermolecular N–H···O, C–H···O [8], and  $\pi$ ··· $\pi$  [9] interactions.

### Results and discussion

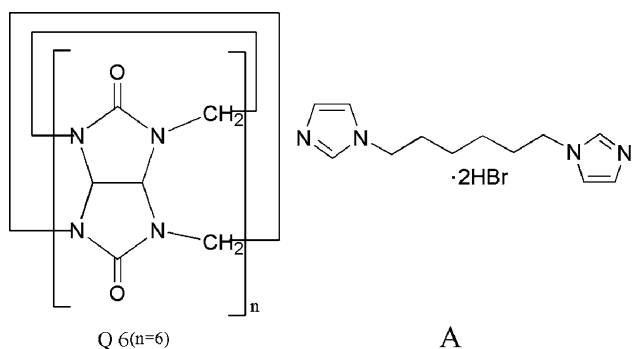
Single crystal X-ray analysis of the good quality crystals revealed a monoclinic crystal lattice with a  $P2_1/c$  space

group [10]. All atomic positions are well resolved in the crystal lattice. The crystal structure was shown in Figure 1. The guest molecule threaded the host molecule of CB[6] to form the [2]pseudorotaxane. The hexane chain moieties are located partly inside the cavity and the protonated imidazole rings resided outside the portal. The <sup>1</sup>H NMR spectrum characterized the structure of the 1:1 complex being proved only one set of signals (Figure 2). Atom C6 of the guest molecule disordered over two sites related to each other by an inversion center, with a ratio of 0.55(2):0.45(2) for the major and minor components, respectively. The two portal planes of O1/O2/O3 and O4/O5/O6 have an average distance of ~6.180 Å. The length (N1···N1A) of the guest molecule chain is ~8.186 Å. The N1 atom of the imidazole ring deviating from the plane of O4/O5/O6 is ~0.897 Å.

As shown in Figure 1b, the guest molecule is threaded through the center of the host CB[6] and bound by means of ten significant guest–host C–H···O hydrogen bonds between the guest [atoms C1, C3, C4, C5 acting donors] and host molecules [the carbonyl O3, O4 and O5 playing as acceptors] with H···O distance range at 2.36–2.54 Å. The detail hydrogen bonds information listed in Table 1.

Intermolecular interactions play an important role in the formation of stable and structurally well-defined supramolecular structures [11]. Especial host–guest interactions have received much attention recently [12]. In the crystal structure, there are three significant interactions formed between the [2]pseudorotaxane molecules: (i)  $\pi$ ··· $\pi$  stacking [9]. It is very noteworthy and significant that there is a face-to-face  $\pi$ ··· $\pi$  interactions (at:  $-x, 1-y, -z$ ) between the imidazole rings in one [2]pseudorotaxane and those in the next, the mean

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Scheme 1. The host CB[6] and the guest molecule A. A = 1,6-bis(imidazol-1-yl)hexane dihydrobromide.

imidazole/imidazole ring plane separation being 3.29 Å and the distance between the centroids of the facing imidazole rings being 3.976(2) Å. More significantly, the interaction assembled the [2]pseudorotaxane molecules into an extended chain-like structure along *c* axis; thus, a highly ordered linear pseudopolyrotaxane [13] is formed (Figure 3). (ii) The [2]pseudorotaxane molecules are also connected *via* intermolecular C–H···O and N–H···O hydrogen bonds between the guest molecule of one [2]pseudorotaxane and the host molecule (CB[6]) of the other [2]pseudorotaxane. Specifically, atom C2 of the imidazole ring was linked to the carbonyl O1 atom [H2A···O1 2.50 Å, C2···O1 3.380(4) Å, and ∠C2–H2A···O1 157°]; N2–H2···O2 hydrogen bonds with the N2 atoms of one guest molecule acting as a donor and the carbonyl O2 atoms from the other host molecule playing as acceptors were formed with H2···O2 1.98 Å, N2···O2 2.778(4) Å, and N2–H2···O2 151°. The two interactions steadied the formation of

the infinite linear pseudopolyrotaxane chain shown in Figure 3 (Table 2). The host CB[6] molecule inclines 75.94° to the guest  $\pi$ ··· $\pi$  array and the separation between neighboring CB[6] molecules is 12.578 Å. Though these three interactions link the [2]pseudorotaxane molecules into linear pseudopolyrotaxane formation, the self-assembly process can be driven by weak intermolecular  $\pi$ ··· $\pi$  interactions instead of hydrogen bonding when it was considered that the crystals were obtained from its aqueous solution where the possibility of the above-mentioned hydrogen bonds acting as drivers should be low.

## Conclusion

In summary, we synthesized a novel [2]pseudorotaxane by reacting cucurbit[6]uril and 1,6-bis(imidazol-1-yl)hexane dihydrobromide and investigated the solid state self-assembly of the [2]pseudorotaxane using single crystal X-ray analysis. The interpseudorotaxane C–H···O hydrogen bonds make the structure of the [2]pseudorotaxane to stabilize. The intermolecular N–H···O, C–H···O, and  $\pi$ ··· $\pi$  interactions assembled the host–guest molecule into a linear ordered superstructure of pseudopolyrotaxane. This observation is helpful to understanding the supramolecular chemistry of [2]pseudorotaxane containing cucurbit[6]uril and other CBs, and can provide useful guidance for developing the order structures or materials even nanotubes [14] in the fields of supramolecular chemistry, crystal engineering, and materials chemistry as described by Isaacs *et al.* in the latest one review [15]. Furthermore work is in progress along this line.

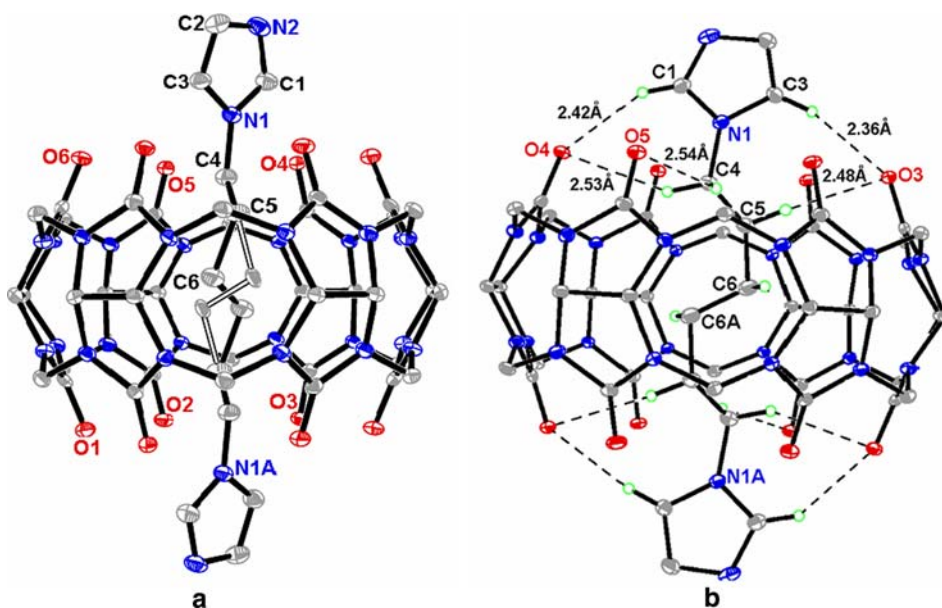


Figure 1. The crystal structure of [2]pseudorotaxane. (a) Side view the structure, all H atoms, Br<sup>−</sup> anions, and solvent (H<sub>2</sub>O) are omitted for clarity. (b) the host–guest interactions were showed. Only atoms involving hydrogen bonds were labeled. The minor disorder of C6 was omitted. [C1–H1···O4 (2.42 Å, 140°); C3–H3···O3 (2.36 Å, 150°) at  $-x, 1-y, 1-z$ ; C4–H4A···O4 (2.53 Å, 145°); C4–H4B···O5 (2.54 Å, 122°); C5–H5A···O3 (2.48 Å, 168°) at  $-x, 1-y, 1-z$ ].

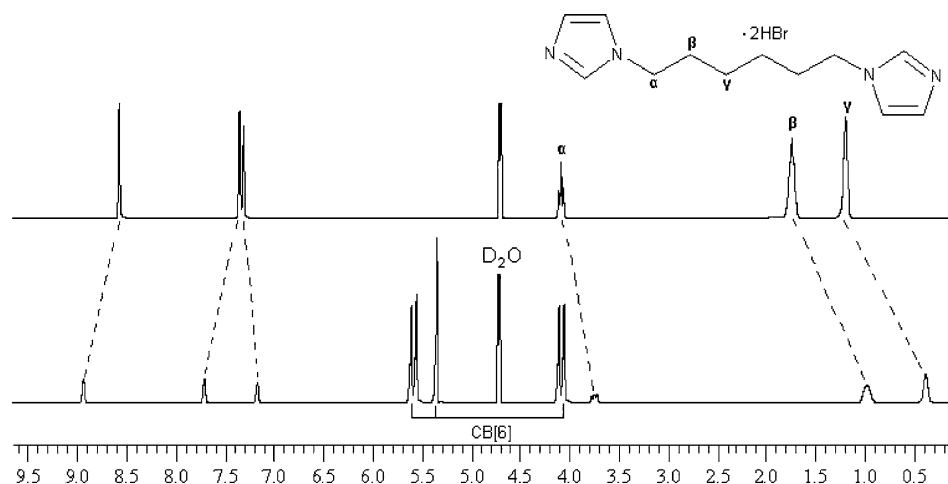


Figure 2.  $^1\text{H}$  NMR (300 MHz, 25  $^\circ\text{C}$ ) spectra in  $\text{D}_2\text{O}$ . Top: the guest molecule A; Bottom: the [2]pseudorotaxane. The signals for the methylene groups located inside CB[6] are shifted to higher field due to the shielding effected of CB. ( $\alpha\text{-CH}_2$ : 4.05 to 3.73;  $\beta\text{-CH}_2$ : 1.71 to 0.96;  $\gamma\text{-CH}_2$ : 1.16 to 0.37).

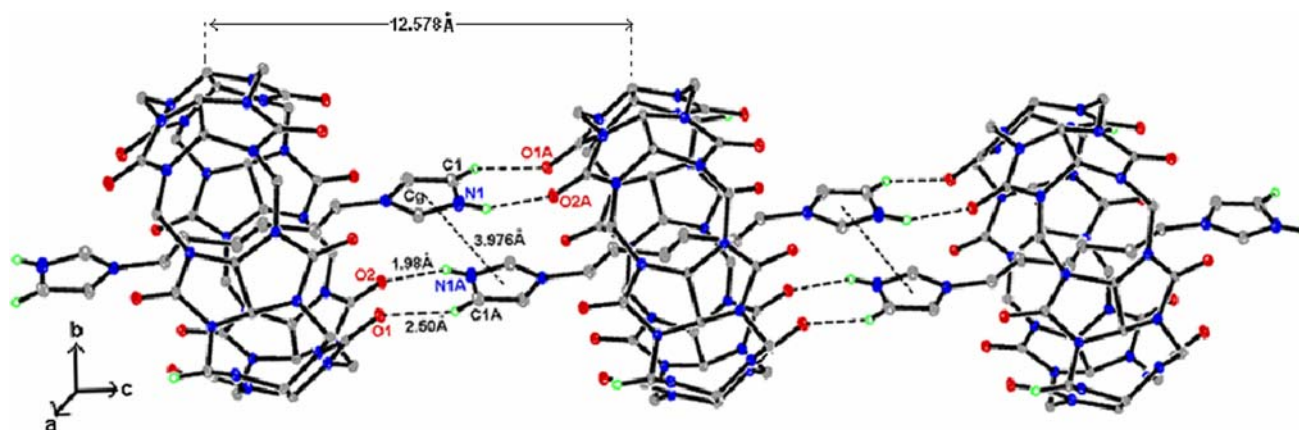


Figure 3. The linear superstructure formation of the pseudopolyrotaxane is linked by  $\text{C-H}\cdots\text{O}$ ,  $\text{N-H}\cdots\text{O}$  and  $\pi\cdots\pi$  ( $\text{Cg}$  for imidazole ring;  $-x, 1-y, -z$ ).

Table 1. Geometrical parameters (interatomic distances in  $\text{\AA}$  and bond angles in  $^\circ$ ) for host-guest hydrogen bonds in the molecular structure of [2] pseudorotaxane<sup>a</sup>

D-H $\cdots$ A	D-H	H $\cdots$ A	D $\cdots$ A	$\angle(\text{D-H}\cdots\text{A})$
C1-H1 $\cdots$ O4	0.94	2.42	3.194(4)	140
C3-H3 $\cdots$ O3 <sup>i</sup>	0.94	2.36	3.208(5)	150
C4-H4A $\cdots$ O4	0.98	2.53	3.380(5)	145
C4-H4B $\cdots$ O5	0.98	2.54	3.163(5)	122
C5-H5A $\cdots$ O3 <sup>i</sup>	0.98	2.48	3.445(5)	168

<sup>a</sup>Symmetry operators is (i)  $-x, 1-y, 1-z$ .

Table 2. Significant intermolecular interactions (interatomic distances in  $\text{\AA}$  and bond angles in  $^\circ$ )<sup>a</sup>

D-H $\cdots$ A	D-H	H $\cdots$ A	D $\cdots$ A	$\angle(\text{D-H}\cdots\text{A})$
N2-H2 $\cdots$ O2 <sup>viii</sup>	0.87	1.98	2.778(4)	151
C2-H2A $\cdots$ O1 <sup>viii</sup>	0.94	2.50	3.380(4)	157
$\pi\cdots\pi$	—	—	3.976(2)	—

<sup>a</sup> $\pi\cdots\pi$  actions for imidazole ring( $\text{Cg}_7$ ) at  $-x, 1-y, -z$ . [Symmetry operators is (viii)  $x, y, -1+z$ ].

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- The guest molecule: Yield 85%. <sup>1</sup>H NMR (300 MHz, 25 °C, D<sub>2</sub>O): δ 8.53 (s, 2H), 7.31 (d, 4H), 4.05 (t, 4H, α-CH<sub>2</sub>), 1.71 (m, 4H, β-CH<sub>2</sub>), 1.16 (m, 4H, γ-CH<sub>2</sub>); <sup>13</sup>C NMR (300 MHz, D<sub>2</sub>O): δ 136.60, 124.04, 121.96, 51.55, 31.40, 27.21; Elemental analysis (calcd. %): C, 37.89; N, 14.73; H, 5.26. Found: C, 37.66; N, 14.64; H, 5.23.
- General procedure for preparation of the [2] pseudorotaxane: A solution of 1, 6-bis(imidazol-1-yl)hexane dihydrobromide (0.1 mmol) in H<sub>2</sub>O (20 ml) was added CB[6] (0.1 mmol) in small portions and the mixture was stirred for 24 h at 80 °C. The solution was concentrated to 5 ml by evaporation. Addition of THF (30 ml) to the solution produced a white precipitate, which was filtered and dried in vacuum condition, affording the rotaxane complex. Yield 76%. <sup>1</sup>H NMR (300 MHz, 25 °C, D<sub>2</sub>O): δ 8.93 (s, 2H), 7.70 (s, 2H), 7.16 (s, 2H), 5.59 (d, 12H), 5.33 (s, 12H), 4.10 (d, 12H), 3.73 (t, 4H), 0.962 (m, 4H), 0.366 (m, 4H); <sup>13</sup>C NMR (300 MHz, D<sub>2</sub>O): δ 158.2, 137.6, 125.7, 119.2, 72.6, 53.7, 50.9, 29.7, 25.2; Elemental analysis (calcd. %) for [C<sub>6</sub>H<sub>6</sub>N<sub>4</sub>O<sub>2</sub>]<sub>6</sub> · C<sub>12</sub>H<sub>18</sub>N<sub>4</sub> · 2HBr · 8H<sub>2</sub>O: C, 37.89; N, 25.78; H, 4.73. Found: C, 37.48; N, 25.42; H, 4.61.
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- The crystals suitable for single-crystal X-ray diffraction were grown from its water solution evaporating at room temperature for over a week. Crystallographic data were collected using a Bruker SMART 2000 CCD diffractometer with MoKα (λ = 0.71073 Å). Intensities were integrated using the SAINT program and corrected for absorption and other effects using the SADABS program. Structures were solved and refined using the SHELXS-97 and SHELXL-97 programs. All hydrogens were located in a difference Fourier map and their geometry idealized, and refined by using a riding model with O-H = 0.85 Å (s.u. = 0.02) and Uiso(H) = 1.2 Ueq(O). The positions of hydrogen atoms, bonded to carbon atoms, were idealized with their thermal parameters of 1.2 times those of attached atoms. Crystal data for C<sub>36</sub>H<sub>36</sub>N<sub>24</sub>O<sub>12</sub> · C<sub>12</sub>H<sub>20</sub>N<sub>4</sub> · 8 · H<sub>2</sub>O · 2Br: crystal size 0.2 × 0.2 × 0.2, monoclinic, space group P21/c (No.14). a = 12.445(3) Å, b = 20.081(4) Å, c = 12.578(3) Å, β = 113.088°, V = 2891.6(10) Å<sup>3</sup>, Z = 2, T = 203 K, θ<sub>max</sub> = 25.01°, 11578 reflections measured, 5029 unique (R<sub>int</sub> = 0.0412). Final residual for 476 parameters and 5029 reflections with I > 2σ(I): R<sub>1</sub> = 0.0440, wR<sub>2</sub> = 0.0901 and GOF = 0.872. CCDC 265575 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/cif, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223/336-033; e-mail: data\_request@ccdc.cam.ac.uk.
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