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Construction of Pseudorotaxanes and Rotaxanes Based on Cucurbit[*n*]uril

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Abstract

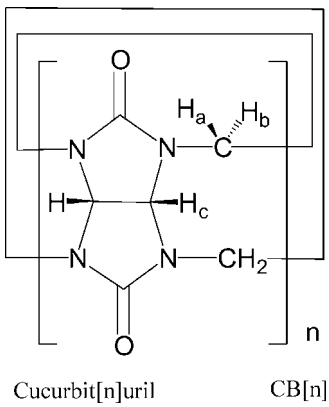
^{1}H-NMR spectroscopic analysis indicates that cucurbit[7]uril can form a stable inclusion complex with 1,6-hexanediamine, while cucurbit[5]uril cannot form pseudorotaxane with 1,6-hexanediamine under our experimental conditions. This was confirmed by the crystal structure of the complex. The cavity of cucurbit[8]uril seems to be large for binding 1,6-hexanediamine efficiently. And a simple, mild, high-yield (>80%) method has been described for the synthesis of rotaxanes through the self-assembly of pseudorotaxanes of cucurbit[*n*]uril ($n = 6$, 7)/1, 6-hexanediamine and sodium tetraphenylborate. The obtained rotaxanes are held intact solely by noncovalent interactions, and are characterized by elemental analysis, ^{1}H-NMR, ESI-MS and MALDI-TOF MS.

Introduction

Rotaxanes are a kind of interesting macromolecules that consist of dumbbell-like units (a rod and two bulky stoppers) threaded into wheel-like ones. The bulky stoppers prevent the cyclic entity from dethreading. They have been regarded as motifs for nano devices, such as motors, sensors, and switches amplifiers, based on their interlocked structures. Lots of natural and artificial macrocyclic compounds, such as cyclodextrin, crown ether, could act as the wheel [1].

Similar to cyclodextrin, cucurbit[6]uril (CB[6]) has a rigid structure with a hollow core, which is accessible from the exterior by two carbonyl-fringed portals [2]. Its rigid structure and capability of holding a guest molecule make CB [6] attractive as a candidate for a wheel in rotaxane and rotaxane-like molecule synthesis. Over the past decade, Kim *et al.* synthesized a wide variety of supramolecular species such as rotaxanes and pseudorotaxanes, 1D, 2D, 3D polyrotaxanes with transition metal ions, main-chain and side-chain (pseudo)polyrotaxanes, molecular necklaces, rotaxane dendrimers, and rotaxane-based molecular switches using CB[6] as a wheel [3]. Buschmann and coworkers also prepared (pseudo)polyrotaxanes of polyamides and CB[6] [4]. Steinke reported a novel way to produce rotaxanes and polyrotaxanes utilizing 1,3-dipolar cycloaddition between azide and alkyne inside the cavity of CB[6] [5]. CB[6]-based metallo-rotaxane has also been prepared [6].

Recently, several homologues of CB[6], which contain five, seven and eight glycoluril units respectively, have been reported [7]. Not long ago Buschmann *et al.* reported the synthesis of CB[5]-based rotaxane [8]. Nakamura *et al.* synthesized a novel unsymmetrically substituted CB[6], and converted it to a rotaxane incorporating bis(dinitrophenyl)- spermine [9]. However, the yield of cucurbit[*n*]uril-based rotaxanes is not very high. And up to now, none of these rotaxanes and rotaxane-like molecules has been synthesized using CB[7] as a wheel.



Cucurbit[n]uril CB[n]

In this article, we give a survey of the interactions between CB[*n*] ($n = 5$, 6, 7, 8) and 1,6-hexanediamine dihydrochloride (**1**) by ^{1}H-NMR analysis. The results show that, in addition to CB[6], CB[7] can also form stable inclusion complexation with

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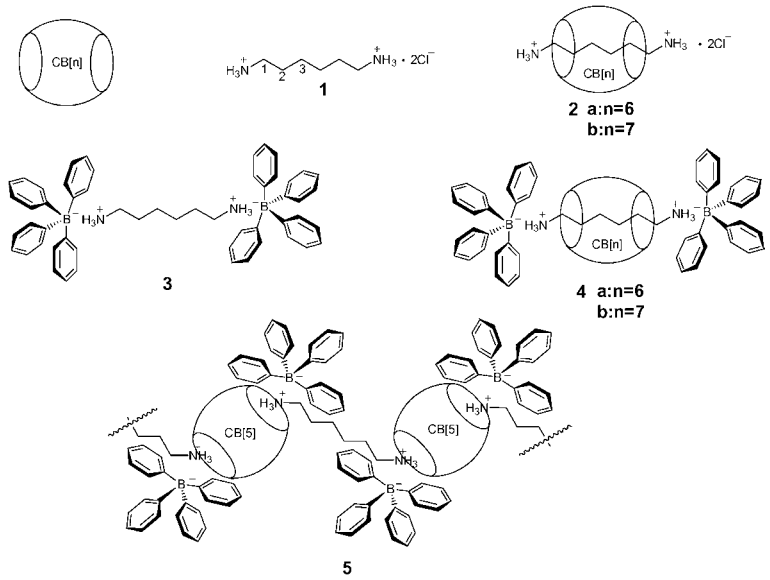

1,6-hexanedi- ammonium ions (1:1 mole ratio). While cucurbit[5]uril cannot form pseudorotaxane with **1** under our experimental conditions, this is confirmed by the crystal structure of CB[5] and **1**. Two rotaxanes have been synthesized based on CB[6] and CB[7]. And the rotaxane using CB[7] as a wheel is first prepared. The products are characterized using elemental analysis, ^{1}H-NMR, ESI-MS and MALDI-TOF MS.

Experimental

Elemental analyses were performed using a VarioEL III Elemental Analyzer. ^{1}H-NMR spectra were recorded on a Mercury VX-300 (Varian, 300 MHz) or an Inova-600 (Varian, 600 MHz) spectrometer. The solvents used were DCl/D_2O (20%), D_2O or DMSO-d_6 with TMS serving as internal standard. FAB-MS measurements were carried out on a Finnigan MAT 95 mass spectrometer. ESI-MS measurements were performed on Thermo Finnigan LCQ Deca XP at room temperature in HCOOH/H_2O or DMSO solution. MALDI-TOF MS measurements were performed on Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (REFLEX III, BRUKER).

Synthesis of CB[n] (n = 5, 6, 7, 8)

The synthesis and purification of CB[*n*] were completed by a modification of the literature [7b].

CB[5] ^{1}H-NMR (600 MHz, 20% DCl/D_2O) δ 4.445 (H_b, d, 10 H, $J = 15.6$ Hz), 5.549 (H_a, d, 10 H, $J = 15.6$ Hz), 5.608 (H_c, s, 10 H); ^{13}C-NMR 50.33 (CH_2), 68.94 (CH), 156.23 (CO). FAB-MS: m/z 831 $[M + H]^+$, 848 $[M + OH]^+$.

CB[6] ^{1}H-NMR (600 MHz, 20% DCl/D_2O) δ 4.327 (H_b, d, 12 H, $J = 15.6$ Hz), 5.546 (H_a, d, 12 H, $J = 15.6$ Hz), 5.564 (H_c, s, 12 H); ^{13}C-NMR 51.52 (CH_2), 70.48 (CH), 156.13 (CO). FAB-MS: m/z 997 $[M + H]^+$.

CB[7] ^{1}H-NMR (600 MHz, 20% DCl/D_2O) δ 4.272 (H_b, d, 14 H, $J = 15.6$ Hz), 5.567 (H_a, d, 14 H, $J = 15.6$ Hz), 5.553 (H_c, s, 14 H); ^{13}C-NMR 52.71 (CH_2), 71.04 (CH), 156.41 (CO). ESI(+)-MS: m/z 1163.5 $[M + H]^+$ 582.4 $[M + 2H]^{2+}$.

CB[8] ^{1}H-NMR (600 MHz, 20% DCl/D_2O) δ 4.235 (H_b, d, 16 H, $J = 15.6$ Hz), 5.582 (H_a, d, 16 H, $J = 15.6$ Hz), 5.544 (H_c, s, 16 H); ^{13}C-NMR 53.82 (CH_2), 71.84 (CH), 156.96 (CO). ESI(+)-MS: m/z 665.4 $[M + 2H]^{2+}$.

*Synthesis of the inclusion complexes **2a** and **2b***

A mixture of 0.15 mmol CB[6]·8H_2O or CB[7]·10H_2O and 0.16 mmol **1** in 50 mL 3 M HCl was stirred, until a clear solution was obtained. Addition of methanol to the solution produced an inclusion complex as a white precipitate. The product was filtered and washed with methanol, and then dried under vacuum.

2a: ^{1}H-NMR (300 MHz, 20% DCl/D_2O): δ 0.31–0.44 (m, 4 H, **1**-CH_2), 0.44–0.58 (m, 4 H, **1**-CH_2), 2.76–2.85 (m, 4 H, **1**-CH_2), 4.34 (H_b, d, 12 H, $J = 15.5$ Hz), 5.55 (H_a, d, 12 H, $J = 15.5$ Hz), 5.56 (H_c, s, 12 H). FAB-MS: m/z 1113 $[CB[6] + H_2N(CH_2)_6NH_2 + H]^+$.

2b: ^{1}H-NMR (300 MHz, 20% DCl/D_2O): δ 0.36–0.50 (m, 4 H, **1**-CH_2), 0.60–0.74 (m, 4 H, **1**-CH_2), 2.31–2.46 (m, 4 H, **1**-CH_2), 4.26 (H_b, d, 14 H, $J = 15.5$ Hz), 5.54 (H_a, d, 14 H, $J = 15.5$ Hz), 5.53 (H_c, s, 14 H). FAB-MS: m/z 1279 $[CB[7] + H_2N(CH_2)_6NH_2 + H]^+$.

*Synthesis of the exclusion complex **2c***

A mixture of 400 mg CB[5]·10H_2O (0.40 mmol) and 90 mg **1** (0.48 mmol) in 8 mL water was stirred, and soon

a clear solution was obtained. Crystals were obtained by slow evaporation of the solvent during a period of two weeks.

^{1}H-NMR (300 MHz, 20% DCl/D_2O): δ 1.28–1.39 (m, 4 H, **1**-CH_2), 1.52–1.68 (m, 4 H, **1**-CH_2), 2.88–2.98 (m, 4 H, **1**-CH_2), 4.39 (H_b, d, 10 H, $J = 15.5$ Hz), 5.48 (H_a, d, 10 H, $J = 15.5$ Hz), 5.54 (H_c, s, 10 H).; (300 MHz, D_2O): δ 1.36–1.44 (m, 4 H, **1**-CH_2), 1.61–1.78 (m, 4 H, **1**-CH_2), 2.97 (t, 4 H, **1**-CH_2), 4.22 (H_b, d, 10 H, $J = 15.5$ Hz), 5.53 (H_a, d, 10 H, $J = 15.5$ Hz), 5.41 (H_c, s, 10 H). FAB-MS: m/z 947 $[CB[5] + H_2N(CH_2)_6NH_2 + H]^+$, 831 $[CB[5] + H]^+$.

*Synthesis of the rotaxanes **4a**, **4b** and complex **5***

A mixture of 0.12 mmol CB[n] ($n = 5$, 6, or 7) and 0.11 mmol **1** in 50 mL 3 M HCl was stirred, until a clear solution was obtained. An aqueous solution (20 mL) of sodium tetraphenylborate (0.30 mmol) was introduced in a dropwise fashion, the resulting white precipitate was filtered and washed with 30 mL 3 M HCl. It was added in 20 mL ethanol, and stirred for 10 min. Then the product was filtered and washed with 15 mL acetone, dried under vacuum.

4a: Yield: 177 mg (87%). Anal. calcd for $C_{90}H_{94}B_2N_{26}O_{12}\cdot 9H_2O$: N, 19.01; C, 56.43; H, 5.89; found N, 18.89; C, 56.41; H, 5.66. ^{1}H-NMR (300 MHz, DMSO-d_6): δ 0.31–0.50 (m, 8 H, **1**-CH_2), 2.83–2.92 (m, 4 H, **1**-CH_2), 4.36 (H_b, d, 12 H, $J = 15.0$ Hz), 5.46 (H_c, s, 12 H), 5.57 (H_a, d, 12 H, $J = 15.0$ Hz), 6.74–7.28 (m, 40H, Ph). ESI(+)-MS: m/z 1433.5 $[M + H - BPh_4]^+$; ESI(−)-MS: m/z 319.4 $[BPh_4 - H]^-$.

4b: Yield: 191 mg (84%). Anal. calcd for $C_{96}H_{100}B_2N_{30}O_{14}\cdot 12H_2O$: N, 19.67; C, 53.99; H, 5.85; found N, 19.25; C, 53.70; H, 5.80. ^{1}H-NMR (300 MHz, DMSO-d_6): δ 0.54–0.62 (m, 4 H, **1**-CH_2), 0.66–0.82 (m, 4 H, **1**-CH_2), 2.28–2.40 (m, 4 H, **1**-CH_2), 4.24 (H_b, d, 14 H, $J = 15.0$ Hz), 5.42 (H_c, s, 14 H), δ 5.58 (H_a, d, 14 H, $J = 15.0$ Hz), 6.74–7.28 (m, 40H, Ph). ESI(+)-MS: m/z 1599.6 $[M + H - BPh_4]^+$; ESI(−)-MS: m/z 319.2 $[BPh_4 - H]^-$.

5: Yield: 158 mg (88%), Anal. calcd for $C_{90}H_{94}B_2N_{26}O_{12}\cdot 3H_2O$: N, 18.77; C, 61.47; H, 5.77; found N, 18.47; C, 61.13; H, 5.53. ^{1}H-NMR (300 MHz, DMSO-d_6): δ 1.46–1.59 (m, 4 H, **1**-CH_2), 1.71–1.89 (m, 4 H, **1**-CH_2), 2.97–3.16 (m, 4 H, **1**-CH_2), 4.47 (H_b, d, 10 H, $J = 15.0$ Hz), 5.43 (H_c, s, 10 H), δ 5.46 (H_a, d, 10 H, $J = 15.0$ Hz), 6.74–7.28 (m, 40H, Ph). ESI(+)-MS: m/z 947.5 $[CB[5] + H_2N(CH_2)_6NH_2 + H]^+$, 849.3 $[CB[5] + OH]^+$, 831.6 $[CB[5] + H]^+$.

X-ray crystallography

We tried to prepare crystals of CB[5] and CB[7] with **1**. Fortunately, we obtained crystals of the exclusion complex (**2c**) of CB[5] with **1** by slow evaporation of the solvent. But attempts to form crystals of the inclusion complex of CB[7] with **1** failed.

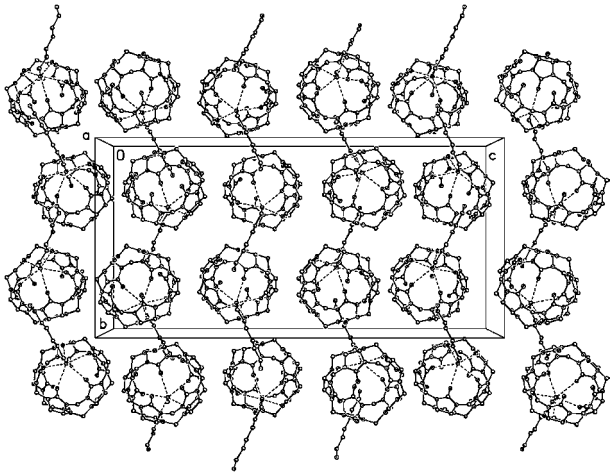

Figure 1. Crystal structure of the exclusion complex **2c**. All H_2O molecules and H atoms are omitted for clarity.

The crystal structure (Figure 1) of **2c** was determinated using a Siemens SMART CCD diffractometer with Mo-Kα radiation ($\lambda = 0.71073$ Å) at 293(2) K in the range of $2.42° < \theta < 25.04°$. The structure was solved by direct method (SHELXL-97) and refined against F^2 in anisotropic approximation (SHELXL-97). Crystal data: $C_{30}H_{30}N_{20}O_{10} + ClH_3NC_6H_{12}NH_3Cl + 11.75\ H_2O$, $M = 1231.55$, orthorhombic, space group *Pccn*, $a = 11.8994(2)$ Å, $b = 21.14410(10)$ Å, $c = 43.2075(8)$ Å, $U = 10871.1(3)$ Å^3, $Z = 8$, $\rho_{cal} = 1.505$ Mg/m^3, $\mu = 0.217$ mm^{-1}, 25341 reflections collected, 9372 unique ($R_{int} = 0.0558$) which were used in all calculations. $R_1 = 0.1567$ $[I > 2\sigma(I)]$, $wR_2 = 0.4390$ $[I > 2\sigma(I)]$; $R_1 = 0.1961$ (all data), $wR_2 = 0.4761$ (all data).

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Results and discussion

^{1}H-NMR spectroscopic studies of interactions between CB[n] ($n = 5$, 6, 7, 8) and 1,6-hexanediamine dihydrochloride

It is already known that the interior of CB[6] comprises a proton-shielding region relative to the acidic aqueous medium, so substrates bound within CB[6] typically exhibit ^{1}H-NMR signals 1 ppm in the direction of higher field relative to the corresponding resonances of the same species free in solution. When any exchange between bound and free guests is fast on the NMR time scale, an averaged NMR spectrum should be observed. Using NMR experiments, Mock found CB[6] to form inclusion complexes with different aliphatic and aromatic amine compounds [10].

We investigated the interactions between CB[n] ($n = 5$, 6, 7, 8) and **1** in acidic aqueous solution using NMR technique. The ^{1}H-NMR analysis (Figure 2c) shows that when an excess of **1** is present, both sets of NMR signals of bound and free

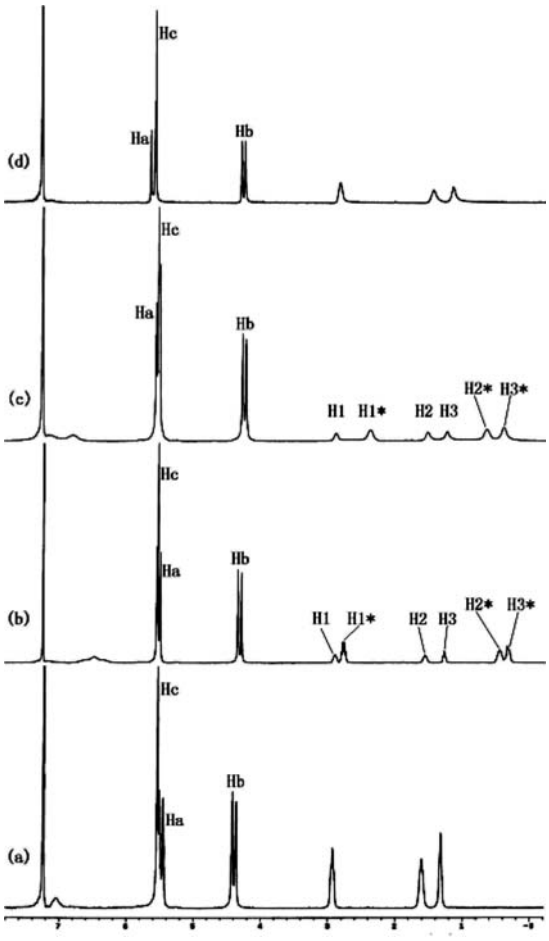

Figure 2. The ^{1}H-NMR spectrum of (a) CB[5]:**2** = 1:1.5. (b) CB[6]:**2** = 1:1.5. (c) CB[7]:**2** = 1:1.5. (d) CB[8]:**2** = 1:1.5 in 20% DCl/D_2O. Peaks marked with asterisks (∗) represent **1** encapsulated in the cavity of CB[*n*].

1,6-hexanediammonium ions are seen; this indicates the formation of an inclusion complex between CB[7] and **1**. The complexation is stoichiometric (1:1, by NMR integration), and apparently any exchange between external and internal environments is slow. At the same time we observe that the signal of H1 of **1** shifts significantly upfield (0.50 ppm), compared with CB[6] (0.12 ppm, Figure 2b). This is because the proton-shielding region of CB[7] is larger than that of CB[6].

In the acidic aqueous solution of CB[5] and excess of **1**, the ^{1}H-NMR signals (Figure 2a) do not show the characteristic upfield chemical shifts. Only an averaged NMR peak shifting slightly downfield is observed throughout. We think that the postulated external binding mode could explain this phenomenon. The proposed lack of inclusion of **1** in CB[5] was further supported by the crystal structure of **2c** (Figure 1).

The ^{1}H-NMR spectrum of CB[8] and **1** (Figure 2d) reveals that the signals of protons of **1** shift slightly upfield and become wider, indicating that for **1** the exchange between the interior of CB[8] and the uncomplexed state is fast. We conclude that the cavity of CB[8] seems to be large for binding **1** efficiently, 1,6-hexanediammonium ions can enter into or leave the cavity of CB[8] freely.

Construction of rotaxanes

In 1990, Lawrence and co-workers described the synthesis of template-driven self-assembly of rotaxanes, in which tetraphenylborate anions acted as stoppers [11].

Similarly, adding an aqueous solution of sodium tetraphenylborate to the mixture solution of CB[*n*] and **1**, we obtained two rotaxanes (**4a**, **4b**) and an adduct (**5**) as white precipitates. They are all solvable in DMSO (pure CB[*n*] and **2a**, **2b**, **2c** are all insolvable in DMSO). The structures of these complexes are assigned by using ^{1}H-NMR, ESI-MS and MALDI-TOF MS analysis.

All ^{1}H-NMR spectra of these complexes integrate to 1:1:2 CB[*n*]:**1**:$(C_6H_5)_4B$. Figure 3c indicates that the signals of H1 of **4a** shift downfield about 0.13 ppm instead of in DMSO, compared with that of **1** in the presence of CB[6] (upfield 0.12 ppm, Figure 2b). The ^{1}H-NMR spectrum of rotaxane 4**b** (Figure 3d) also indicates encapsulation of 1,6-hexanediammonium ions within

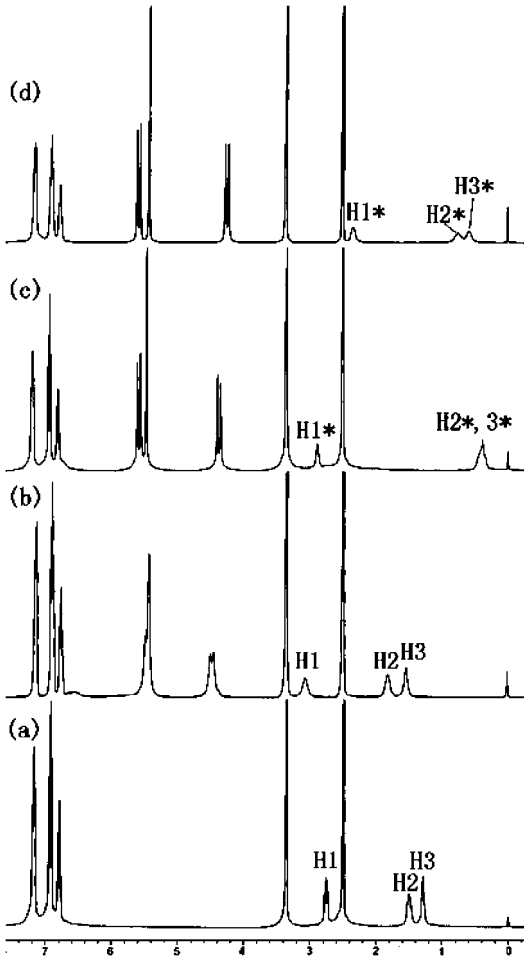

Figure 3. The ^{1}H-NMR spectrum of (a) dumbbell molecule **3**. (b) The complex **5**. (c) CB[6]-based rotaxane **4a**. (d) CB[7]-based rotaxane **4b** (DMSO-d_6). Peaks marked with asterisks (∗) represent **1** encapsulated in the cavity of CB[*n*].

the cavity of CB[7]. The formation of rotaxanes (**4a**, **4b**) is also confirmed by the ESI-MS experimentation. The positive ion spectrum of **4b** shows that $m/z = 1599.6$ is the rotaxane without one stopper, and $m/z = 319.2$ is $[BPh_4 - H]^-$ negative ion. The same as **4b**, the positive ion spectrum of **4a** exists as a peak of the rotaxane without one stopper ($m/z = 1433.5$). The results of MALDI-TOF MS are the same as ESI-MS experimentation.

As for the compound **5**, its structure is presumed based on the following considerations: (1) Free CB[5] is insoluble in DMSO; (2) ^{1}H-NMR of the complex is consistent with a compound that contains the number of components in the proper ratios [CB[5]:**1**: $(C_6H_5)_4B = 1:1:2$]; (3) The ^{1}H-NMR spectra of **5** (Figure 3b) show that the signals of all protons of 1,6-hexanediammonium ion shift downfield since they are in the deshielding region of CB[5]; (4) Similar CB[6](or CB[7])-rotaxane peaks do not appear in the positive ion spectrum of **5**; (5) According to the crystal structure of **2c**, one portal of CB[5] binds one end of 1,6-hexanediammonium ion, another portal binds one end of another 1,6-hexanediammonium ion to form 1:1 exclusion complex.

These complexes could be crystallized by slow infusion of water into their DMSO solutions. But none of the crystals is suitable to X-ray structural analysis. Redissolution of the isolated needle-like crystals reproduced the original NMR spectra in an identical stoichiometric ratio.

Conclusion

The results show that in addition to CB[6], CB[7] can also form a stable inclusion complex with 1,6-hexanediammonium ion. This gives a hint that CB[7] could include longer alkyl-ammonium ions, such as 1,7-heptanediammonium ions, spermine ions, due to its large cavity. This would be interesting for constructing a wide variety of supramolecular assemblies using CB[7] as a wheel. But the cavity of CB[5] is too small to accommodate 1,6-hexanediammonium ions in acidic or neutral solution (298 K). Buschmann *et al*. also found that CB[5] derivatives (decamethylcucurbit[5]uril) cannot form an inclusion complex with 1,6-hexanediamine, but they thought aliphatic amines could be complexed within the cavity of CB[5] [12]. And they reported the synthesis of CB[5]-spermine-[2]rotaxane [8]. Our results are not in accordance with the conclusion reported by them.

We have constructed a rotaxane using CB[7] as a wheel in aqueous media, at room temperature, and in high yield via noncovalent interactions. This suggests that a variety of highly organized supramolecular entities can be efficiently prepared from appropriately designed subunits via noncovalent forces [11].

Acknowledgements

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