

Synthesis, X-ray Structure and Binding Properties of Calix[6]arene-1,4-2,5-Biscrowns

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Received April 27, 2004

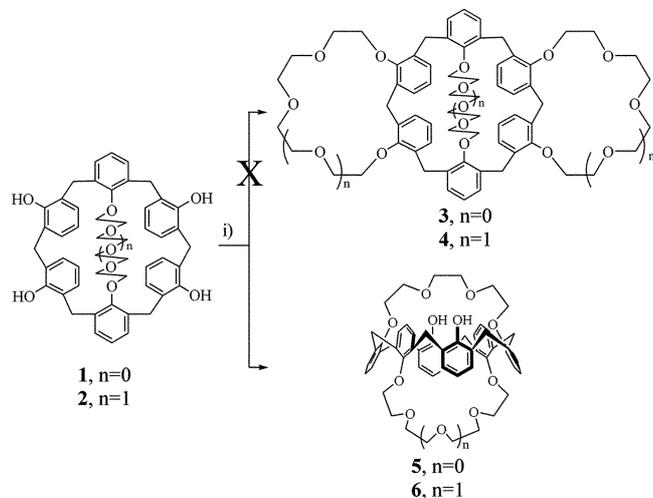
Key Words : Calix[6]biscrown, X-ray structure, Cesium selectivity

Calixcrowns¹ are a family of macropolycyclic molecules in which the subunits of calixarene and crown ethers are combined through the bridging of phenolic oxygen atoms of the calixarene by polyoxyethylene chains. The first member of this family was reported by Alfieri.² As calixcrowns possess well preorganized structures and more rigid binding sites in comparison with calixarenes and crown ethers, they exhibited superior recognition ability toward alkali metal cations. Much attention has been paid to more sophisticated molecules: calix-biscrowns. All possible types of calix[4]-arene biscrowns have been synthesized and their recognition properties toward alkali metal ions have been studied.³ However, only a few paper concerning the synthesis of calix[6]arene biscrowns has appeared to date.⁴ Even for calix[6]crown, only 1,4-*p-tert*-butylcalix[6]crown-5⁵ and 1,4-calix[6]crown-5 as well as 1,3-*p-tert*-butylcalix[6]crown-3⁶ have been synthesized.

Cesium-137 is a relatively abundant nuclear fission product and constitutes a major source of heat in nuclear wastes⁷ along with strontium-90. Much effort has been made to the development of improved processes⁸ for the removal of cesium-137 from nuclear wastes. For the purpose of developing cesium selective ion receptors, we prepared two

new calix[6]arene biscrowns: calix[6]arene-1,4-2,5-biscrown-4 (**5**) and calix[6]arene-1,4-crown-4-2,5-crown-5 (**6**) and investigated their X-ray structure and alkali metal ion binding properties.

By treating **1** and **2**^{5,6} with 2 equivalent of triethylene glycol ditosylate ((TsOCH₂CH₂OCH₂)₂), it was expected to produce the trisbridged calix[6]crowns **3** and **4** from the previous results in our lab.⁹ But, two bisbridged calix[6]-crowns **5** and **6**¹⁰ were obtained instead in 20% yield. It was believed that the long chain of poly ether unit did not allowed to react 2,3-position, rather to bridge 2,5-position of calixarene. Due to the complexity of ¹H NMR spectrum, the conformation of calix[6]arene biscrowns **5** and **6** could not be deduced. But the X-ray crystallography analysis provide



Scheme 1. Synthesis of calix[6]arene-1,4-2,5-biscrowns. i) (TsOCH₂CH₂OCH₂)₂/NaH, DMF

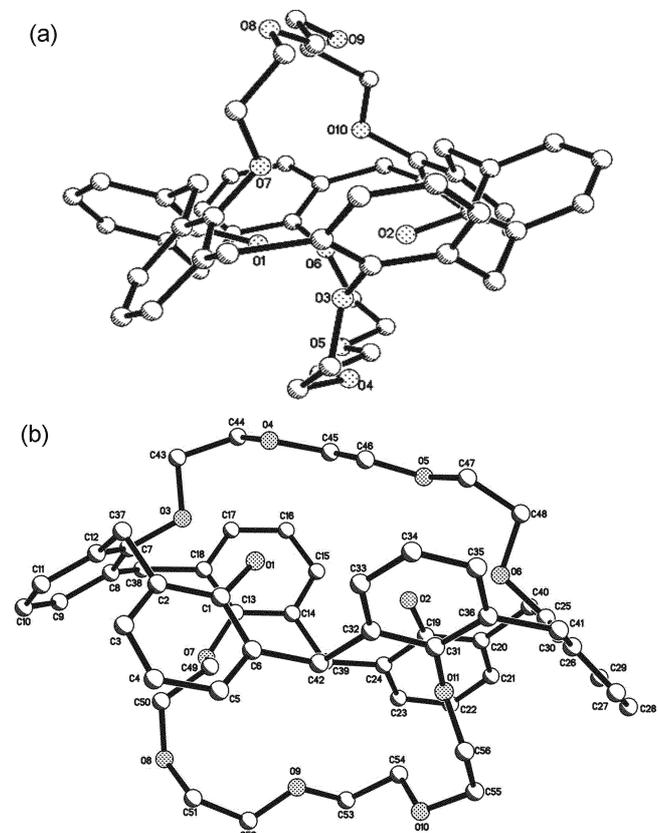


Figure 1. Crystal structure of (a) **5** and (b) **6**. Hydrogen atoms are omitted for clarity.

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Table 1. Crystal data and structure refinement for **5**

| | |
|-----------------------------------|---|
| Empirical formula | C _{54.33} H _{56.33} ClO ₁₀ (C ₅₄ H ₅₆ O ₁₀ ·1/3CHCl ₃) |
| Crystal system | Rhombohedral |
| Space group | R-3 |
| Unit cell dimensions | a = 25.0359(17) Å α = 116.1160(10)° b = 25.0359(17) Å β = 116.1160(10)° c = 25.0359(17) Å γ = 116.1160(10)° |
| Refinement method | Full-matrix least-squares on F ² |
| Goodness-of-fit on F ² | 1.748 |
| Final R indices [I > 2σ(I)] | R1 = 0.1574, wR2 = 0.3814 |
| R indices (all data) | R1 = 0.3526, wR2 = 0.4294 |
| Largest diff. peak and hole | 1.736 and -0.746 e.Å ⁻³ |

the alternate conformation.

Figure 1 showed a X-ray structure of alternate calix[6]-arene biscrown **5**. Two crown units stayed at the opposite side of calixarene circle. It is believed that this has been the first example of the X-ray structure of alternate conformer of calix[6]arene thus far. Table 1 showed the detail data for X-ray structure **5**. A similar X-ray structure of alternate calix[6]arene biscrown **6** was seen in Figure 1. Also two crown units stayed at the opposite side of calixarene circle. Table 2 showed the detail data for X-ray structure **6**.

The alkali metal binding properties were investigated from two phases extraction experiment where aqueous solutions of the picrate salts are shaken with methylene chloride solutions of ligands. The amount of metal ion was determined from picrate absorption in the UV spectrum. Table 3 showed the percent extraction of metal picrate salts by **5** and **6**. The ligand **5** extracted 93% of the cesium picrate from aqueous solution into the methylene chloride solution of the host, but also 87% of the rubidium, 61% of the potassium,

Table 2. Crystal data and structure refinement for **6**

| | |
|-----------------------------------|--|
| Empirical formula | C ₅₇ H ₆₄ O ₁₂ |
| Crystal system | Monoclinic |
| Space group | P2(1)/c |
| Unit cell dimensions | a = 12.3322(17) Å α = 90° b = 18.945(3) Å β = 97.668(3)° c = 21.445(3) Å γ = 90° |
| Refinement method | Full-matrix least-squares on F ² |
| Goodness-of-fit on F ² | 0.943 |
| Final R indices [I > 2σ(I)] | R1 = 0.0749, wR2 = 0.1878 |
| R indices (all data) | R1 = 0.1829, wR2 = 0.2441 |
| Largest diff. peak and hole | 0.496 and -0.277 e.Å ⁻³ |

Table 3. Percentage extraction (%) of alkali picrates from water into CH₂Cl₂ at 25 °C^a

| Ligands | % Extraction | | | | | | |
|----------|-----------------|-----------------|----------------|-----------------|-----------------|------------------------------|--|
| | Li ⁺ | Na ⁺ | K ⁺ | Rb ⁺ | Cs ⁺ | NH ₄ ⁺ | Me ₂ NH ₂ ⁺ |
| 5 | 6 | 37 | 61 | 87 | 93 | 5 | 2 |
| 6 | 0 | 13 | 28 | 78 | 89 | 3 | 2 |

^a1 × 10⁻³ M receptor solution in CH₂Cl₂ was shaken (15 hrs) with 1 × 10⁻⁴ M picrate salt solution in H₂O.

37% of the sodium and 6% lithium was extracted. Extraction percentage of cesium salt slightly decreased to 89% for **6**, potassium and sodium extraction was reduced remarkably as compared to ligand **5**, indicating that the large crown unit could inhibit the effective binding for small metal ions. ISE experiments are in progress using PVC membrane electrodes.

Acknowledgment. This research was supported by Grant (No. KRF-2002-042-C00044) of Cooperative Research Project from Korea Research Foundation.

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- Some representative spectroscopic data for calix[6]arene-37,40-38,41-bis-crown-4 (**5**) and calix[6]arene-37,40-crown-4-38,41-crown-5 (**6**) are as follows. **5**: mp > 220 °C dec.; ¹H NMR (CDCl₃) δ 7.38 (s, 2H, OH), 7.30 (d of d, 2H, ArH, J = 7.38 Hz), 7.11 (d, 4H, ArH, J = 7.41 Hz), 7.08-6.93 (m, 10H, ArH), 6.79 (t, 4H, ArH, J = 7.47 Hz), 5.52 (s, 2H, -OCH₂CH₂O-), 4.46-4.38 (d of d, 4H, ArCH₂Ar, J = 15.3 Hz), 4.11 (s, 2H, ArCH₂Ar), 3.74-3.69 (m, 2H, -OCH₂CH₂O-), 3.64-3.56 (m, 8H, -OCH₂CH₂O-), 3.41-3.20 (m, 14H, -OCH₂CH₂O- and ArCH₂Ar), 2.65 (m, 2H, -OCH₂CH₂O-), 2.40 (m, 2H, -OCH₂CH₂O-). ¹³C NMR (CDCl₃) δ 154.46, 153.32, 135.16, 133.49, 129.81, 128.69, 127.97, 126.90, 124.21 and 119.25 (Ar), 72.74, 70.62 and 70.27 (-OCH₂-), 36.10 and 31.32 (ArCH₂Ar). **6**: mp > 202 °C dec.; ¹H NMR (CDCl₃) δ 7.55 (s, 2H, OH), 7.30 (d of d, 2H, ArH, J = 7.44 Hz), 7.23 (d of d, 2H, ArH, J = 9.18 Hz), 7.11-6.98 (m, 6H, ArH), 6.94 (d of d, 2H, ArH, J = 8.88 Hz), 6.87 (t, 2H, ArH, J = 7.5 Hz), 6.75 (t, 2H, ArH, J = 7.44 Hz), 6.52 (d, 2H, ArH, J = 6.72 Hz), 4.49 (d, 2H, ArCH₂Ar, J = 16.9 Hz), 4.19-4.08 (m, 6H, ArCH₂Ar and -OCH₂CH₂O-), 3.84 (t, 2H, -OCH₂CH₂O-), 3.71-3.57 (m, 9H, -OCH₂CH₂O-), 3.49 (d, 1H, -OCH₂CH₂O-, J = 5.55 Hz), 3.41-3.05 (m, 14H, -OCH₂CH₂O- and ArCH₂Ar), 2.89 (m, 2H, -OCH₂CH₂O-), 2.47 (m, 2H, -OCH₂CH₂O-), 2.15 (m, 2H, -OCH₂CH₂O-). ¹³C NMR (CDCl₃) δ 156.42, 152.92, 134.65, 133.96, 133.62, 130.23, 129.74, 126.60, 124.00, 123.86, 123.47 and 99.82 (Ar), 72.72, 70.85, 70.06 and 57.67 (-OCH₂-), 31.77 and 31.55 (ArCH₂Ar).