

## Synthesis and Metal Ion Extraction of Calix[4]crown-6-azacrown-5

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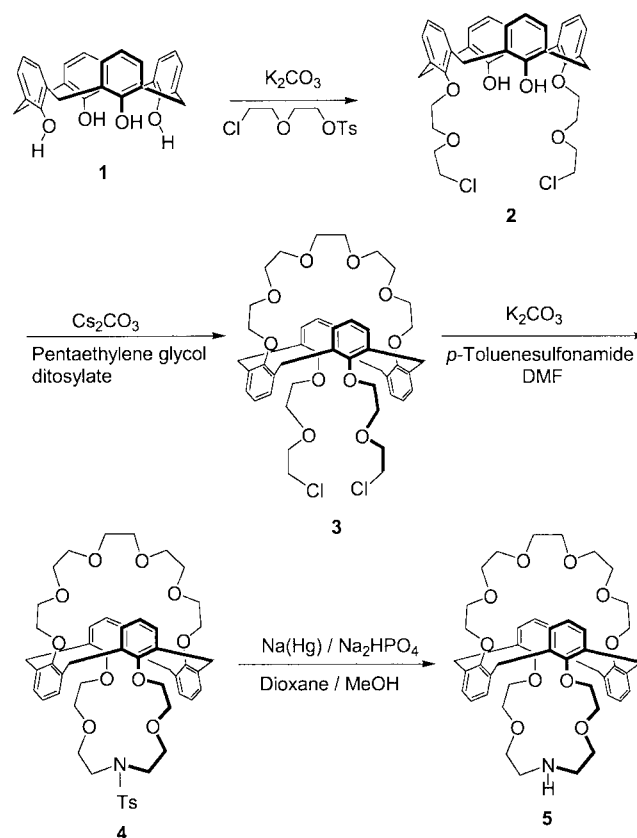
Azacrown ethers have been widely studied because cation-ligating side arms such as carboxylic acid,<sup>1-4</sup> chromogenic,<sup>1</sup> and fluorogenic groups<sup>5</sup> on the nitrogen atom can strongly and selectively interact with various charged and neutral guest molecules by three-dimensional encapsulation.<sup>6</sup> Calix[4]arenes have also been used as 3-D molecular building blocks for the synthesis of receptors with specific properties.<sup>7</sup> They can exist in four different conformations: cone, partial cone, 1,2-alternate, and 1,3-alternate.<sup>7</sup> Calix[4]arenes constrained to the 1,3-alternate conformation<sup>8</sup> and more particularly to 1,3-calix[4]-bis-crowns<sup>9-17</sup> and aza-crown systems<sup>18,19</sup> have received much attention because of their structural peculiarities. They present two binding sites located on both sides of the calixarene and are linked to each other by a  $\pi$ -basic aromatic tunnel.

Previously, we reported the synthesis of calix[4]azacrown ethers in which an oxygen atom is replaced by a nitrogen atom and their selective metal or ammonium ion complexation.<sup>18,19</sup> As part of our work on this calix[4]azacrowns we report herein the synthesis and solid-state structure of calix[4]crown-6-azacrown-5 (**4**) having two ligating sites (crown and azacrown) moiety on the calix[4]arene framework.

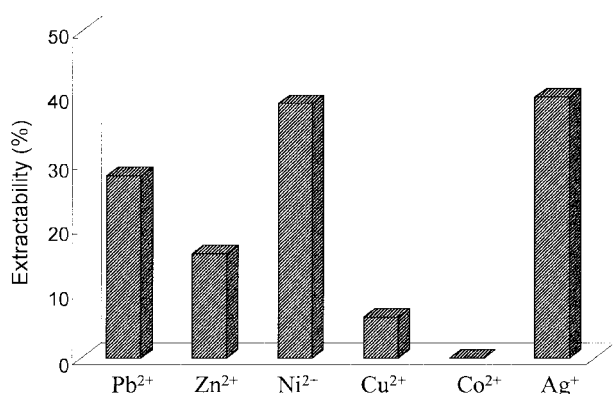
The synthetic scheme for preparing the target molecule **4** is shown in Scheme 1. Compound **2** was prepared from the reaction of calix[4]arene and tosylate of 2-chloroethoxyethanol in the presence of  $K_2CO_3$ . Compound **2** was deduced to be in cone conformation and selectively 1,3-dialkylated from the presence of two doublets at 3.40 and 4.45 ppm with  $J = 13.5$  Hz for the methylene protons of the ArCH<sub>2</sub>Ar of the calix and of only 2 triplets for the *para*-protons on the phenolic units. Glycolic-cyclization of the calix[4]arene **2** with penta(ethyleneglycol) *para*-ditosylate with 3 equivs of  $Cs_2CO_3$  as base was carried out in refluxing acetonitrile for 24 h to give **3** in the 1,3-alternate conformation with 73% yield. For **3**, we have changed the synthetic schemes. Cyclization of **1** with penta(ethyleneglycol) *para*-ditosylate prior to alkylation with tosylate of 2-chloroethoxyethanol gave a poor yield (less than 15%). With many trial reactions, we found the reverse scheme, as shown in Scheme 1, provided a better yield and could be optimized. This 1,3-alternate conformer of **3** was confirmed by <sup>1</sup>H (singlet peak of ArCH<sub>2</sub>Ar appeared at  $\delta$  3.74) and <sup>13</sup>C (ArCH<sub>2</sub>Ar at 38.7 ppm) NMR spectral assignments. Ring-closure of **3** was performed with

1 equiv of *p*-toluenesulfonamide in the presence of  $K_2CO_3$  by heating at 70 °C in DMF for 24 h. The crude residue was chromatographed on silica gel to afford *N*-tosyl calix[4]crown-6-azacrown-5 (**4**) in 68% yield. The use of  $Cs_2CO_3$  as a base gave similar pattern in TLC but needed longer reaction time (72 hrs) than in the case of using  $K_2CO_3$ . The singlet peaks observed at  $\delta$  3.80 for ArCH<sub>2</sub>Ar in <sup>1</sup>H NMR and single peak appeared at 38.7 ppm for ArCH<sub>2</sub>Ar in <sup>13</sup>C NMR spectra indicate that **4** exists in the 1,3-alternate conformation. Detosylation of **4** by the use of Na(Hg)-amalgam in the presence of  $Na_2HPO_4$  in co-solvents of MeOH and dioxane gave the final product **5** with 60% yield.

The extractability of compound **5** to transition metal ions was determined from two-phase extraction experiment. Aza-



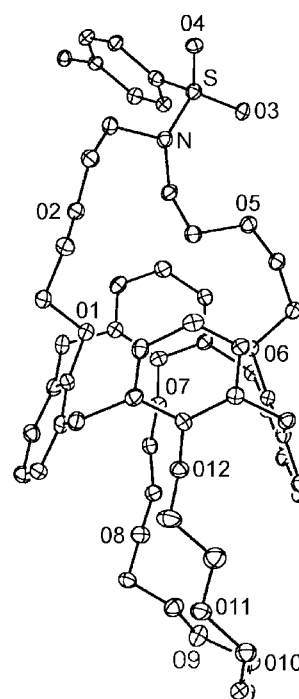
**Scheme 1.** Synthetic scheme for compound **4** and **5**.



**Figure 1.** Extractability of compound **5** for selected transition metal ions.

crown ether in which nitrogen atoms are substituted for oxygen atoms was known to show silver ion selectivity due to a good agreement of Ag-N preference based on HSAB theory. Silver ion was selectively extracted over Cu<sup>2+</sup> and Co<sup>2+</sup> from an aqueous source phase into a chloroform phase as shown in Figure 1. Moderate extractability for Pb<sup>2+</sup> and Ni<sup>2+</sup> is attributable to competitive coordination to the upper crown ring, which cannot be proven this time due to no success of crystal structure. This silver ion extractability could be applicable to selective separation of noble metal ions in waste stream.

Interestingly we could obtain the crystal structure of **4**. The asymmetric unit in the crystal structure comprises one molecule, represented in Figure 2. This structure confirms that the calixarene is fixed in the 1,3-*alternate* conformation by the two crown ether chains. The dihedral angles between the mean plane defined by the four methylenic carbon atoms (rms deviation 0.19 Å) and the four aromatic rings are 72.3(1), 45.7(1), 64.9(1) and 75.9(1)°, which indicates that the conformation is far less regular than usual in this family of compounds. Three rings assume positions close to those observed in most compounds previously described, but the fourth (the second in the list above) is closer to the mean plane defined by the methylene bridges. The influence of the solvent on the crown-6 conformation has been previously discussed and it has been shown that solvents able to form weak CH...O hydrogen bonds with the ether oxygen atoms (such as acetonitrile or nitromethane) result in crown conformations close to those obtained with complexed cations such as Cs<sup>+</sup> or K<sup>+</sup> (with, in particular, all the oxygen lone pairs directed towards the interior of the crown, the most frequent sequence of O-C-C-O *gauche* torsion angles being *g<sup>+</sup>g<sup>+</sup>g<sup>+</sup>g<sup>+</sup>*).<sup>10,20</sup> By contrast, in the absence of such solvent molecules, the crowns adopt more distorted conformations, which is also observed in the present case, with a torsion angles sequence *ag<sup>-</sup>g<sup>-</sup>g<sup>+</sup>a* (*a* = *anti*) and strong deviations of three C-O-C-C angles from the ideal *anti* geometry. This unusual crown conformation is likely associated with the peculiar position of one aromatic ring indicated above. The nitrogen-containing crown presents also an unusual conformation, with a sequence *g<sup>+</sup>g<sup>-</sup>g<sup>-</sup>g<sup>-</sup>* and strong deviations of three C-



**Figure 2.** X-ray crystal structure of **4**. Hydrogen atoms omitted for clarity. Displacement ellipsoids drawn at the 20% probability level.

O-C-C angles from the ideal *anti* geometry. These conformations result in some oxygen atoms lone pairs to be directed away from the crown center, and in this sense the molecule cannot be said to be perfectly preorganized for cation complexation.

## Experimental Section

Unless specified otherwise, reagent-grade reactants and solvents were obtained from chemical suppliers and used as received. Dry solvents were prepared as follows: acetonitrile was freshly distilled from calcium hydride; DMF was dried over 4 Å molecular sieves. Starting material **1** were prepared as described in the literature.<sup>7</sup> NMR spectra for synthesized compounds were obtained by the use of Bruker DMX600 in Korea Basic Science Institute, Daejeon.

**25,27-Bis(5-chloro-3-oxapenthyloxy) calix[4]arene (2).** Calix[4]arene **1** (10.02 g, 23.6 mmol), tosylate of 2-(2-chloroethoxy)ethanol (13.87 g, 49.5 mmol), K<sub>2</sub>CO<sub>3</sub> (3.31 g, 23.6 mmol) and acetonitrile (200 mL) were refluxed for 24 h under N<sub>2</sub>. The crude residue was solubilized in CH<sub>2</sub>Cl<sub>2</sub> and acidified (10% aqueous HCl). The organic layer was dried (MgSO<sub>4</sub>). Recrystallization from Et<sub>2</sub>O gave **2** in 90% yield as a solid, mp 174-175 °C. IR (KBr pellet, cm<sup>-1</sup>): 3390.3, 2924.37, 2871.71, 1593.05, 1465.02, 1336.04, 1252.71, 1201.59, 1136.26, 1088.91, 921.51, 814.13, 760.91, 608.71. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.34 (s, 2H, -OH), 7.08 (d, *J* = 7.5 Hz, 4H, ArH<sub>m</sub>-calix), 6.90 (d, *J* = 7.5 Hz, 4H, ArH<sub>m</sub>-calix), 6.77 (t, *J* = 7.5 Hz, 2H, ArH<sub>p</sub>-calix), 6.70 (t, 2H, *J* = 7.5 Hz, ArH<sub>p</sub>-calix), 4.45 (d, *J* = 13.5 Hz, 4H, ArCH<sub>2</sub>Ar), 4.21-4.19 (m, 4H, ArOCH<sub>2</sub>CH<sub>2</sub>), 4.06-4.04 (m, 4H, OCH<sub>2</sub>CH<sub>2</sub>Cl),

3.99 (t,  $J = 6.5$  Hz, 4H, ArOCH<sub>2</sub>CH<sub>2</sub>), 3.75 (t,  $J = 6.5$  Hz, 4H, OCH<sub>2</sub>CH<sub>2</sub>Cl), 3.40 (d,  $J = 13.5$  Hz, 4H, ArCH<sub>2</sub>Ar). <sup>13</sup>C NMR (CDCl<sub>3</sub>): 153.87, 152.43, 133.98, 129.68, 129.21, 128.75, 126.12, 119.67, 76.10, 72.38, 70.72, 43.47, 31.85 ppm. FAB-MS  $m/z$  ( $M^+$ ) calcd. 634.9, found 635.2. Anal. Calcd for C<sub>36</sub>H<sub>38</sub>Cl<sub>2</sub>O<sub>6</sub>: C, 68.03; H, 5.98. Found: C, 68.00; H, 5.95.

**25,27-Bis(5-chloro-3-oxapenthyloxy) calix[4]arene crown-6 (3).** Compound **2** (10.0 g, 16.5 mmol), penta(ethylene-glycol) *para*-ditosylate (9.92 g, 18.15 mmol), Cs<sub>2</sub>CO<sub>3</sub> (16.15 g, 49.5 mmol) and acetonitrile (200 mL) were refluxed for 24 hrs under N<sub>2</sub>. The crude mixture was solubilized in CH<sub>2</sub>Cl<sub>2</sub> and acidified (10% aqueous HCl). The organic layer was dried (MgSO<sub>4</sub>). Column chromatography on silica gel with 1 : 2 EtOAc : hexane as eluent gave 9.6 g of **3** with 73% yield as an oil. IR (KBr window, neat, cm<sup>-1</sup>): 2923.21, 2872.88, 1735.01, 1456.54, 1356.19, 1299.43, 1249.12, 1201.52, 1150.29, 1046.95, 930.45, 828.58, 769.41, 733.60, 662.77. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.08-7.05 (m, 8H, ArH<sub>m</sub>-calix), 6.85-6.78 (m, 4H, ArH<sub>p</sub>-calix), 3.74 (s, 8H, ArCH<sub>2</sub>Ar), 3.68 (s, 4H, -CH<sub>2</sub>-), 3.64 (s, 4H, -CH<sub>2</sub>-), 3.56 (s, 16 H, -CH<sub>2</sub>-), 3.49 (s, 4H, -CH<sub>2</sub>-), 3.38-3.35 (t, 4H, -CH<sub>2</sub>-), 3.28-3.26 (t, 4H, -CH<sub>2</sub>-), <sup>13</sup>C NMR (CDCl<sub>3</sub>): 157.33, 156.89, 134.50, 131.26, 123.17, 122.93, 71.92, 71.86, 71.68, 71.28, 70.64, 70.49, 69.93, 69.29, 54.46, 43.77, 38.28. Anal. Calcd for C<sub>46</sub>H<sub>56</sub>Cl<sub>2</sub>O<sub>10</sub>: C, 54.89; H, 6.68. Found: C, 54.78; H, 6.59.

**N-Tosyl calix[4]crown-6-azacrown-5 (4).** *p*-Toluenesulfonamide (1.64 g, 9.56 mmol), K<sub>2</sub>CO<sub>3</sub> (2.6 g, 26.07 mmol) and DMF (100 mL) were heated to 70 °C for 30 min. Then compound **3** (7.30 g, 8.69 mmol) dissolved in DMF (20 mL) was added dropwise for 3 h. After refluxing for 24 h, the crude mixture was solubilized in CH<sub>2</sub>Cl<sub>2</sub> and then treated with 10% aqueous NaHCO<sub>3</sub> solution. The organic layer was dried (MgSO<sub>4</sub>). Column chromatography on silica gel with 1 : 2 EtOAc : hexane as eluent gave **4** as an oil. IR (KBr, cm<sup>-1</sup>): 2923.29, 1455.62, 1341.92, 1249.02, 1201.55, 1156.23, 1101.82, 1093.58, 1052.89, 925.34, 821.74, 769.80, 732.94, 652.29, 551.51. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.72 (d,  $J = 8.1$  Hz, 2H, ArH-tosyl), 7.31 (d,  $J = 8.1$  Hz, 2H, ArH-tosyl), 7.10 (d,  $J = 7.5$  Hz, 4H, ArH<sub>m</sub>-calix), 7.05 (d,  $J = 7.5$  Hz, 4H, ArH<sub>m</sub>-calix), 6.89 (t,  $J = 8.7$  Hz, 2H, ArH<sub>p</sub>-calix), 6.82 (t,  $J = 8.7$  Hz, 2H, ArH<sub>p</sub>-calix), 3.80 (s, 8H, ArCH<sub>2</sub>Ar), 3.63 (s, 4H, OCH<sub>2</sub>CH<sub>2</sub>O), 3.57 (s, 4H, OCH<sub>2</sub>CH<sub>2</sub>NH), 3.49-3.46 (m, 8H, ArOCH<sub>2</sub>CH<sub>2</sub>O), 3.34-3.28 (m, 8H, ArOCH<sub>2</sub>CH<sub>2</sub>O), 3.16-3.07 (m, 12H, OCH<sub>2</sub>CH<sub>2</sub>O), 2.46 (s, 3H, ArCH<sub>3</sub>-tosyl). <sup>13</sup>C NMR (CDCl<sub>3</sub>): 171.71, 157.55, 143.88, 137.45, 134.46, 130.45, 128.86, 123.24, 71.70, 71.50, 71.14, 70.49, 70.10, 61.02, 49.13, 38.74, 22.21, 21.71 ppm. Anal. Calcd for C<sub>53</sub>H<sub>63</sub>NO<sub>12</sub>S: C, 67.80; H, 6.82. Found: C, 67.82; H, 6.79.

**Calix[4]crown-6-azacrown-5 (5).** To a solution of dioxane (100 mL) and methanol (20 mL) were carefully added **4** (5.4 g, 5.78 mmol), NaHPO<sub>4</sub> (1.81 g, 12.7 mmol) and 6% Na(Hg) (19.3 g, 0.335 mol). The mixture refluxed for 2 days at 80 °C under N<sub>2</sub>. The crude mixture was dissolved in CH<sub>2</sub>Cl<sub>2</sub> and treated with saturated NaHCO<sub>3</sub> aqueous solution. The organic layer was dried (MgSO<sub>4</sub>). Recrystallization from hexane gave 2.72 g of **5** as a solid in 60% yield.

mp 168-170 °C. <sup>1</sup>H-NMR (CDCl<sub>3</sub>):  $\delta$  9.55 (broad s, 1H, NH), 7.19 (d,  $J = 7.5$  Hz, 4H, ArH<sub>m</sub>-calix), 7.00 (s, 4 H, ArH<sub>m</sub>-calix), 6.94 (t,  $J = 7.5$  Hz, 4H, ArH<sub>p</sub>-calix), 3.90-3.88 (m, 12H, OCH<sub>2</sub>CH<sub>2</sub>O), 3.79 (s, 8H, Ar-CH<sub>2</sub>-Ar), 3.65-3.61 (m, 12H, OCH<sub>2</sub>CH<sub>2</sub>NH, OCH<sub>2</sub>CH<sub>2</sub>O), 3.56 (t,  $J = 6.5$  Hz, 4H, ArOCH<sub>2</sub>CH<sub>2</sub>O-crown-5), 3.28 (t,  $J = 6.5$  Hz, 4H, ArOCH<sub>2</sub>CH<sub>2</sub>O-crown-5), 2.98 (s, 4H, OCH<sub>2</sub>CH<sub>2</sub>NH). Anal. Calcd for C<sub>46</sub>H<sub>57</sub>NO<sub>10</sub>: C, 70.49; H, 7.27. Found: C, 70.47; H, 7.24.

**Crystal structure determination.** Compound **4** was crystallized from the slow evaporation of a solution of MeOH and dichloromethane. Crystal data for **4**, C<sub>53</sub>H<sub>63</sub>NO<sub>12</sub>S:  $M = 938.10$ , triclinic, space group *P*-1,  $a = 10.538(2)$ ,  $b = 10.946(2)$ ,  $c = 21.437(3)$  Å,  $\alpha = 91.696(3)$ ,  $\beta = 90.812(3)$ ,  $\gamma = 108.573(3)^\circ$ ,  $V = 2342.2(8)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 1.330$  g cm<sup>-3</sup>,  $\mu = 0.136$  mm<sup>-1</sup>,  $F(000) = 1000$ ,  $T = 100$  K. The data were collected on a Nonius Kappa-CCD area detector diffractometer<sup>21</sup> using graphite-monochromated Mo-K $\alpha$  radiation (0.71073 Å). The crystal was introduced in a Lindemann glass capillary with a protecting "Paratone" oil (Exxon Chemical Ltd.) coating. The data were processed with DENZO-SMN.<sup>22</sup> The structure was solved by direct methods with SHELXS-97<sup>23</sup> and subsequent Fourier-difference synthesis and refined by full-matrix least-squares on  $F^2$  with SHELXL-97.<sup>24</sup> Absorption effects were corrected empirically with the program MULABS from PLATON.<sup>25</sup> Hydrogen atoms were introduced at calculated positions as riding atoms with a displacement parameter equal to 1.2 (CH, CH<sub>2</sub>) or 1.5 (CH<sub>3</sub>) times that of the parent atom. All non-hydrogen atoms were refined anisotropically, leading to a final *R*1 factor of 0.075 for 7842 unique reflections and 605 parameters ( $wR2$  0.147). The molecular plot was drawn with SHELXTL.<sup>26</sup> All calculations were performed on a Silicon Graphics R5000 workstation.

**Two phase extraction.** A heterogeneous mixture of **5** (3.0 mL, 0.1 mM) in chloroform and metal nitrate (3 mL, 0.2 mM) in deionized water was shaken for 30 min then centrifuged at 25 °C. Concentration of the metal nitrate extracted from the organic layer was analyzed with an Atomic Absorption Spectrometer (Thermo Jarell Ash, SH-4000). The extractability obtained from three independent experiment was calculated by extracted metal nitrate concentration/initial ligand concentration X 100.

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