Synthesis of Crown Ethers Embodied Adamantane and Homoadamantane Skeletons (1)

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Abstract: Adamantano[2,4]-16-crown-5 and -19-crown-6 ethers **5**, **6**, and homoadamantano[4,5]-15-crown-5 and -18-crown-6 ethers **11**, **12** have been prepared and their some cation binding properties have been discussed based on the preliminary solvent extraction and PM3 calculation results.

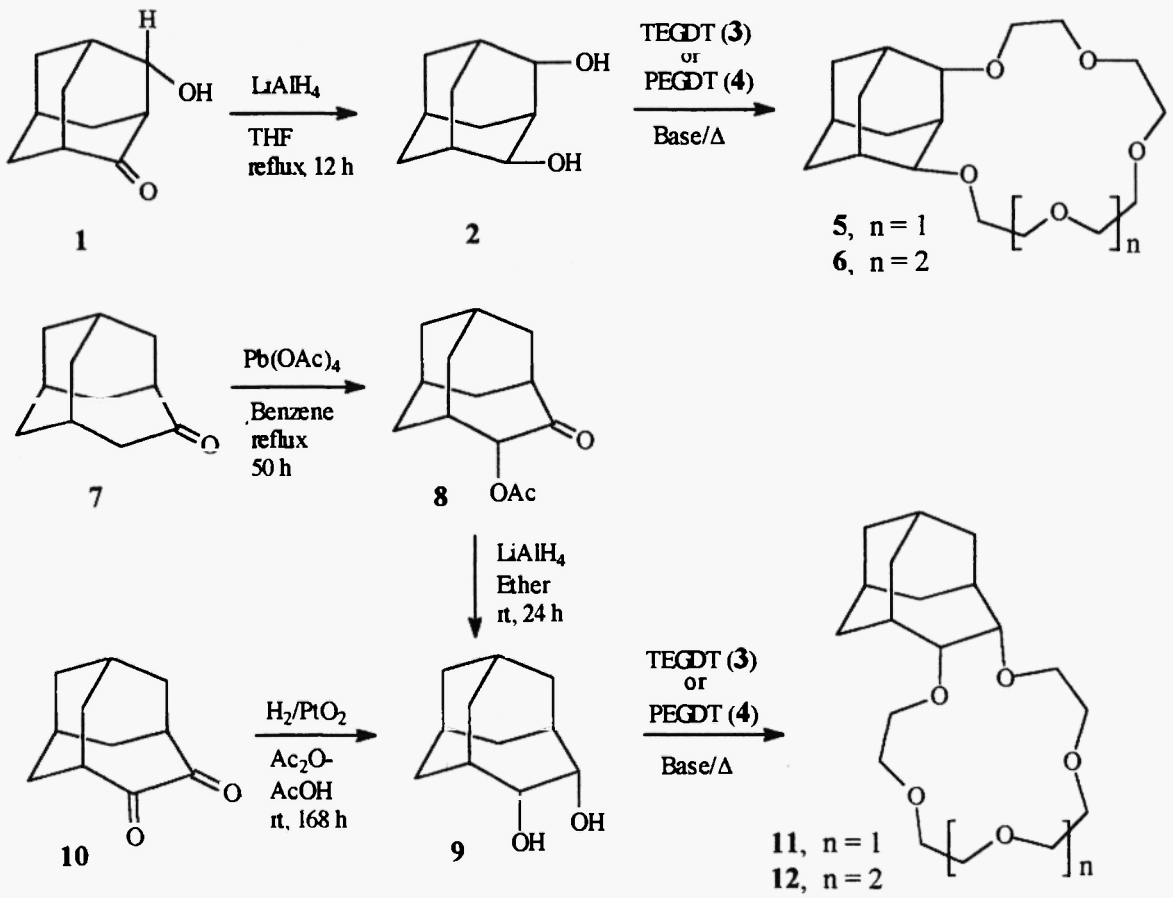
Introduction

The design of host compounds such as macrocyclic and macropolycyclic ligands by placing substituents in a way that they either directly or indirectly interact with the binding site of the host is one of the major area of host-guest chemistry (2). The addition of substituents may affect a receptor molecule in conformational mobility, possibly changing the effective size of the binding cavity, in number and topology of binding sites for lariat ethers (3), and in altering the electronic properties of the binding portion of the host (4). Crown ethers are well known to specifically form host-gest complexes with both alkali-, alkaline earth metal cations and ammonium cations (5). In such lipophilic complexes the reactivity of the counter anion increases because crown ether minimizing the interaction between cation and anion by complexing with cation, and the solutbility into the low-polar organic solvents increases. These unique properties have been applied fruitfully to organic synthesis using crown ethers as catalysts and modifiers (6,7). Hence the search for ligands which selectively interact

with metal ions or have unique properties has been a field of active research (2-5). For example, the effects of methylene chain length and substitution effect in crown ethers have been studied extensively by Inoue and coworkers (4e,8). They found drastic enhancement in cation-binding ability by 14,16-bridging of 16-crown-5 ether (8b,9). From our interest in synthesis of adamantane derivatives and related compounds (10,11), we designed 15-crown-5 **5**, 16-crown-5 **6**, 18-crown-6 **11** and 19-crown-6 **12** ethers embodied adamantane and homoadamantane skeletons. This paper describes their synthesis and some preliminary results on their cation binding properties.

Results and Discussion

2ax,4ax-Adamantanediol **2** was readily obtained from 4-hydroxy-2-adamantanone **1** by $LiAlH_4$ reduction (12). This diol and tetraethylene glycol di-*p*-tosylate (13) (TEGDT) **3** (1.4 equiv.) in THF was heated in the presence of sodium hydride (2.50 equiv.). The product was purified on a PTLC to give 2ax,4ax-adamantano[2,4][14,16]-16-crown-5



Scheme 1

ether **5** in 33% yield as a viscous oil (Scheme 1). The structure was confirmed based on spectral and analytical data. MS (EI) had a molecular ion peak at m/z 326. ^{13}C-NMR spectrum had 11 lines in compatible with the *Cs* symmetry. Similarly the reaction of **2** with pentaethylene glycol di-*p*-tosylate (13) (PEGDT) **4** under the similar conditions afforded 2ax,4ax-adamantano[2,4][14,16]-19-crown-6 **(6)** in 37% yield as a viscous oil. The use of potssium hydride as the base did not improve the yield.

cis-4,5-Homoadamantanediol **9** was prepared from 4-homoadamantanone (14) **7** via the route as explained in Scheme 1. Acetoxylation of **7** with dried lead tetraacetate under reflux in benzene gave 5-acetoxy-4-homoadamantanone **8** in 63% yield (15). Lithium aluminum hydride reduction of **8** gave the diol **9** in 72% yield as a sublimable solid. The assigned *cis*-diol structure of **9** was evidenced by the spectral data. The MS(EI) had the molecualr ion peak at m/z 182. ^{13}C-NMR spectrum exhibited 7 lines indicating the *Cs* symmetry. This diol was also obtained by catalytic hydrogenation of 4,5-homoadamantanedione (16) **10** in a lower yield. The macrocyclization of **9** with TEGDT **3** was carried out similarly as above using sodium hydride as the base under heating to reflux for 24 h. The *cis*-homoadamantano[4,5-*b*]-15-crown-5 ether **11** was obatined as a viscous oil in 28% yield after PTLC. The reaction using 50% aq sodium hydroxide-THF and longer heating (31 h) conditions gave **11** in a better yield (39%). The assigned structure of **11** was supported by the spectral and analytical data. MS (EI) had a correct molecular ion peak at m/z 340. ^{13}C-NMR spectrum had 11 lines compatible with the *Cs* symmetry. The reaction of **9** with PEGDT **4** in the presence of sodium hydride under similar conditions (24 h refluxing) afforded *cis*-homoadamantano[4,5-*b*]-16-crown-6 ether **12** as a viscous oil in 24% yield, while the reaction using potassium hydride as the base gave **12** in 18% yield (Scheme 1). The assigned structure of **12** was supported by the spectral and analytical data. MS (EI) had a correct molecular ion peak at m/z 384. ^{13}C-NMR spectrum had 12 lines in compatible with the *Cs* symmetry.

A semiempirical quantum mechanical study on the relative stability of the crown ether and the corresponding ammonium complexes has been carried out in order to see the effect of adamantane and homoadamantane skeletons on the complexing property. The calculated heats of formation of the crowns **5**, **6**, **11-14**, **16**, **17**, and their complexes with ammonium ion using MNDO/PM3 (17) were used for reference. Isolated ammonium ion was chosen as the alternative cation because reliable parameters of common alkali

metals such as sodium and potassium are not available in the PM3 method. The results (Table 1) suggested the possibility of a few kcal/mol stabilization in each pair with the same size of the crown ring by adamantane and homoadamantane skeletons.

As a preliminary study on the complexing property of thus prepared crowns, the cation-binding abilities of the 15- (**5**) and 16-crown-5 (**11**), and 18- (**12**) and 19-crown-6 (**6**) derivatives as well as the corresponding parent 15-crown-5 (**13**) and 18-crown-6 (**14**) and dicyclohexano-18-crown-6 (**15**) were evaluated by the conventional solvent extraction experiments. Aqueous solutions of alkali metal picrates (1.00×10^{-4} M) were extracted with dichloromethane solutions of the respective crown ether (1.00×10^{-4} M) at 25 °C.

Table 1. Calculated H_f values of crown ethers and their ammonium complexes.[a]

crown ether	H_{f_2}[b]	H_{f_3}[c]	ΔH_f[d]
15-crown-5 (**13**)	-203.23	-74.60	-24.73
homoadamantano-15-crown-5 (**11**)	-207.07	-80.80	-27.09
16-crown-5 (**16**)	-206.40	-77.55	-24.51
adamantano-16-crown-5 (**5**)	-208.93	-91.18	-35.61
18-crown-6 (**14**)	-243.26	-123.82	-33.92
homoadamantano-18-crown-6 (**12**)	-243.06	-126.81	-37.11
19-crown-6 (**17**)	-242.69	-126.76	-37.43
adamantano-19-crown-6 (**6**)	-252.72	-141.32	-41.96

[a] Heat of formation of isolated ammonium ion H_{f_1} = 153.36 kcal/mol.
[b] Heat of formation of crown ethers in kcal/mol.
[c] Heat of formation of ammonium ion complexes in kcal/mol.
[d] Differences of heat of formation: $\Delta H_f = H_{f_3}-(H_{f_1} + H_{f_2})$ kcal/mol.

The results are summarized in Table 2, in which the reported values for related crowns including **16** and **17** under the similar conditions but using 30 and 50 times concentrated picrate solutions are also shown in parentheses. The extractabilities for adamantane- and homoadamantane-modified crowns were found to be only modest ones compared with unsubstituted ones although the obtained values for the known crowns were not in the same order as the reported ones. This may be due to the use of lower concentration of the

picrates. Sodium/potassium cation selectivity was rather lowered by introduction of adamantane- and homoadamantane skeletons. The rigid skeletons attached on the crown ethers seem to affect the confomational flexibilty required to form stable complexes. Complexing properties of **5**, **6**, **11** and **12** with other metal cations remain to be studied in future (18).

Table 2. Solvent extraction of aqueous metal picrates with crown ethers **5**, **6**, **11-15**.[a]

crown ether	Extractability, %[b]					
	Na^+			K^+		
15-crown-5 (**13**)	2.6	(13.2)[c]	(40.4)[d]	0.6	(14.3)[c]	(43.6)[d]
homoadamantano-15-crown-5 (**11**)	2.2			1.4		
16-crown-5 (**16**)		(13.5)[c]	(45.2)[d]		(3.0)[c]	(14.6)[d]
adamantano-16-crown-5 (**5**)	2.2			1.2		
18-crown-6 (**14**)	5.2	(6.3)[c]	(15.4)[d]	8.2	(69.0)[c]	(86.4)[d]
dicyclohexano-18-crown-6 (**15**)[e]	4.8			5.0		
homoadamantano-18-crown-6 (**12**)	3.4			4.4		
19-crown-6 (**17**)		(2.5)[c]				(22.4)[c]
adamantano-19-crown-6 (**6**)	2.3			4.1		

[a] Temperature 25.0 ± 0.1 °C; aqueous phase (10 mL): [picrate] = 1.00 x 10^{-4} M; organic phase: (CH_2Cl_2, 10 mL): [ligand] = 1.00 x 10^{-4} M (see Experimental Section).
[b] Defined as % picrate extracted into the CH_2Cl_2 phase.
[c] Reported values under the similar conditions but using 3.0 x 10^{-3} M picrate aqueous solution (see refs 8, 9).
[d] Reported values for the similar conditions but with 5 x 10^{-3} M picrate and 1 x 10^{-2} M crown solution (ref 8e).
[e] An isomer mixture of *cis-syn-cis* and *cis-anti-cis* isomers (Nisso Co.).

Experimental

IR spectra were recorded on a JASCO FT/IR 5300 spectrometer, and UV/vis spectra on a Shimadzu UV-2200 spectrometer. ^1H (200 MHz) and ^{13}C (50 MHz) NMR spectra of $CDCl_3$ solution were obtained with a Varian Gemini 200 instrument. Chemical shifts are reported in parts per milion (ppm) relative to $(CH_3)_4Si$ as an internal standard and coupling constants in Hz. Mass spectra (EI) were recorded on ESCO EMD-05B or JEOL JMS-AX505H mass spectrometer at 70 eV. Microanalyses were performed with a Perkin-Elmer 2400B elemental analyzer. TLC analyses were conducted over Merck Kieselgel $60F_{254}$ or Merck Aluminium oxide F_{254} (type E) using the solvent system noted. Flash chromatography for separation of products was performed on a silica gel column (Fuji-Davison 300 mesh) or an alumina column (ICN Alumina N-Akt.1) eluted with the solvent noted. PM3 calculations were performed by Hypercube, Inc's HyperChem R4.0 on a DEC PC.

2ax,4ax-Adamantano[2,4][14,16]-16-crown-5 5:

To a stirred mixture of NaH (60% in mineral oil, 100 mg, 2.50 mmol) in THF (10 mL) was added a solution of 2ax,4ax-adamantanediol **2** (12) (73 mg, 0.43 mmol) and TEGDT (tetraethylene glycol di-*p*-tosylate **3** (13) (296 mg, 0.59 mmol) in THF (10 mL) under argon during 1 h and the mixture was heated to reflux for 24 h. To the cooled mixture was added MeOH (1 mL) in order to decompose the remaining NaH. After removal of the solvent under reduced pressure, the residue was extracted with CH_2Cl_2 (5 mL x 2) and the combined extracts were dried (Na_2SO_4). Removal of the solvent gave an oil which was purified on a PTLC (Merck Aluminium oxide $60F_{254}$, Type E) using hexane-AcOEt (1:3) to yield **5** as a colorless viscous oil (46 mg, 32.8%): R_f = 0.4 (AcOEt); IR (neat) ν (cm^{-1}) 2913, 2816, 1453, 1356, 1292, 1248, 1113; ^{1}H-NMR δ 1.2-2.5 (m, 12H), 3.4-3.8 (m, 18H); ^{13}C-NMR δ 25.92, 27.01, 31.48, 34.82, 35.90, 36.80, 68.06 (overlapped), 70.49, 70.97, 83.04; MS *m/z* (%) 326 (M^+, 1.4), 283 (4.2), 282 (3.4), 229 (3.5), 206 (8.4), 194 (14), 193 (11), 192 (20), 150 (30), 149 (32), 148 (20), 134 (41), 133 (34), 132 (100), 90 (99), 88 (68), 78 (98). Anal. Calcd for $C_{18}H_{30}O_5$ (326.42): C, 66.23; H, 9.26. Found: C, 66.43; H, 9.06.

2ax,4ax-Adamantano[2,4][14,16]-19-crown-6 6:

Method A. To a stirred mixture of NaH (60% in mineral oil, 100 mg, 2.50 mmol) in THF (10 mL) was added a solution of 2ax,4ax-adamantanediol **2** (12) (90 mg, 0.54 mmol) and PEGDT (pentaethylene glycol di-*p*-tosylate **4** (13) (350 mg, 0.70 mmol) in THF (10 mL) under argon during 1 h and the mixture was heated to reflux for 24 h. To the cooled mixture was added MeOH (1 mL) in order to decompose the remaining NaH. After removal of the solvent under reduced pressure, the residue was extracted with CH_2Cl_2 (5 mL x 2) and the combined extracts were dried (Na_2SO_4). Removal of the solvent gave an oil which was purified on a PTLC (Merck Aluminium oxide $60F_{254}$, Type E) using hexane-AcOEt (1:3) to yield **6** as a colorless viscous oil (73 mg, 36.5 %): R_f = 0.4 (AcOEt); IR (neat) ν (cm^{-1}) 2913, 1453, 1352, 1246, 1113; ^{1}H-NMR δ 1.2-2.5 (m, 12H), 3.4-3.8 (m, 22H); ^{13}C-NMR δ 26.03, 27.03, 31.71, 34.58, 35.81, 36.81, 68.22, 70.89, 70.98, 71.15, 71.37, 83.10; MS *m/z* (%) 370 (M^+, 1.4), 327 (2.0), 326 (2.5), 283 (2.5), 239 (3.7), 237 (3.6), 221 (4.2), 206 (9.2), 197 (2.1), 195 (19), 176 (13), 150 (17), 149 (29), 148 (25), 134 (54), 133 (60), 132 (100), 104 (39), 102 (71). Anal. Calcd for $C_{20}H_{34}O_6$ (370.47): C, 64.84; H, 9.25. Found: C, 64.64; H, 9.45.

Method B. Potassium hydride (30% in mineral oil, 340 mg, 2.54 mmol) in a flask under argon was washed with anhydrous pentane (5 mL x 2), the pentane being removed by a syringe, and THF (10 mL) was added. To this mixture was added a solution of the diol **2** (88 mg, 0.52 mmol) and PEGDT **4** (350 mg, 0.64 mmol) in THF (10 mL) with a stirring at room temperature during 1 h, and the mixture was heated under reflux for 17 h. To the cooled mixture was added slowly EtOH (1.5 mL) to decompose the remaining potassium hydride. Removal of the solvent under reduced pressure gave a residue which was extracted with CH_2Cl_2 (5 mL x 2). The combined extracts were dried (Na_2SO_4) and evaporated to give an oil which was purified on a PTLC (Merck Aluminium oxide $60F_{254}$, Type E) using hexane-AcOEt-MeOH (60:45:1) to yield **6** as a colorless viscous oil (57 mg, 29.4 %).

5-Acetoxy-4-homoadamantanone 8:

Commercially available lead tetraacetate (Wako, 90% purity, 20.2 g, 41.0 mmol) was taken in a flask and dried under reduced pressure. 4-Homoadamantanone 7(14) (6.82 g, 41.0 mmol) and anhydrous benzene (10 mL) was added to the dried lead tetraacetate, and the mixture was heated to reflux for 89 h under argon atmosphere. The coold mixture was diluted with benzene (80 mL) and water (80 mL). The organic layer was separated and dried (Na_2SO_4). Removal of the solvent under reduced pressure gave an oily residue which was purified on a silica gel column eluting with hexane-AcOEt (5:1) to give acetoxyhomoadamantanone **8** as a colorless solid (5.77 g, 63.3%): R_f = 0.15 (hexane-AcOEt 5:1); m.p. 56.5-59.0 °C; IR (neat) ν (cm^{-1}) 2950, 2880, 1760, 1720, 1460, 1389, 1245, 1040; ^{1}H-NMR δ 1.6-1.8 (m, 4H), 1.8-2.1 (m, 9H), 2.17 (s, 3H), 2.18 (m, 1H), 5.41 (s, 1H); MS *m/z* (%) 222 (M^+, 12), 180 (56), 151 (23), 125 (26), 124 (100), 123 (35), 119 (93). Anal. Calcd for $C_{13}H_{18}O_3$ (222.27): C, 70.24; H, 8.16. Found: C, 70.20; H, 8.21.

***cis*-4,5-Homoadamantanediol 9:**

Method A. To a stirred and ice-cooled mixture of $LiAlH_4$ (395 mg, 10.4 mmol) in ether (10 mL) was added 5-acetoxy-4-homoadamantanone **8** (1.00 g, 4.50 mmol) under nitrogen atomosphere. After the stirring was continued for 24 h at room temperature, the mixture was treated with a few pieces of ice and was diluted with water (2 mL). The precipitates were filtered and washed with CH_2Cl_2 (5 mL). The combined washings and filtrate were dried (Na_2SO_4). Removal of the solvent under reduced pressure gave a colorless solid which was purified by a flash chromatography over silica gel (hexane-EtOAc 4:1) to give the diol **9** as a colorless solid (0.59 g, 72.0%): R_f = 0.40 (hexane-AcOEt 4:1); m.p. 233-236 °C (sealed tube); IR (neat) ν (cm^{-1}) 3340, 2920, 2850, 1065; ^{1}H-NMR δ 1.3-1.6 (m, 6H), 1.80-2.05 (m, 6H), 2.10-2.22 (m, 2H), 2.70 (br s, 2H), 4.03 (t, J = 2.0 Hz, 2H); ^{13}C-NMR δ 26.51, 27.11, 30.08, 34.45, 36.70, 37.62, 74.95; MS *m/z* (%) 182 (M^+, 31), 164 (46), 151 (11), 125 (32), 93 (52), 91 (51), 81 (47), 80 (50), 79 (100), 67 (64), 55 (67). Anal. Calcd for $C_{11}H_{18}O_2$ (182.25): C, 72.49; H, 9.96. Found: C, 72.34; H, 9.95.

Method B. 4,5-Homoadamantanedione **10** (16) (180 mg, 1.0 mmol) was hydrogenated in glacial acetic acid (5.0 mL) and acetic anhydride (3 mL) in the presence of PtO_2 (40 mg) under hydrogen at room temperature for 168 h. After concentration of the mixture under reduced pressure, the mixture was diluted with CH_2Cl_2 (15 mL) and the catalyst was removed by filtration and washed with CH_2Cl_2 (2 mL). The combined filtrate and washings were washed with 5% sodium hydrogen carbonate (5 mL x 2) and dried (Na_2SO_4). Removal of the solvent under reduced pressure gave a solid residue which was chromatographed on a silica gel (hexane-AcOEt 1:1) to afford the diol **9** as a colorless solid (81 mg, 30.1%).

***cis*-Homoadamantano[4,5-*b*]-15-crown-5 ether 11:**

Method A. To a stirred mixture of NaH (60% in mineral oil, 100 mg,) in THF (10 mL) was added a solution of the diol **9** (87 mg, 0.48 mmol) and TEGDT **3** (13) (296 mg, 0.59 mmol) in THF (10 mL) under argon during 1 h and the mixture was heated to reflux for 24 h. To the cooled mixture was added MeOH (1 mL) in order to decompose the remaining NaH. After removal of the solvent under reduced

pressure, the residue was extracted with CH_2Cl_2 (5 mL x 2) and the combined extracts were dried (Na_2SO_4). Removal of the solvent gave an oil which was purified on a PTLC (Merck Aluminium oxide $60F_{254}$, Type E) using hexane-AcOEt (1:3) to yield **11** as a colorless viscous oil (46 mg, 27.8%): R_f = 0.4 (AcOEt); IR (neat) ν (cm^{-1}) 2897, 1446, 1352, 1294, 1117; ^{1}H-NMR δ 1.1-2.3 (m, 14H), 3.4-3.8 (m, 18H); ^{13}C-NMR δ 27.09, 27.15, 30.46, 34.32, 34.94, 37.04, 69.48, 70.75, 71.05, 84.02, 84.09; MS *m/z* (%) 340 (M^+, 2.7), 296 (3.8), 252 (6.2), 224 (5.4), 207 (15), 206 (18), 164 (36), 163 (57), 147 (50), 146 (100), 135 (45), 132 (88), 118 (69), 104 (61). Anal. Calcd for $C_{19}H_{32}O_5$(340.46): C, 67.03; H, 9.47. Found: C, 66.94; H, 9.38.

Method B. To a stirred mixture of solid NaOH (45 mg) and 50% aqueous NaOH (100 mg) in THF (30 mL) was added a solution of the diol **9** (90 mg, 0.49 mmol) and TEGDT **3** (280 mg, 0.55 mmol) in THF (10 mL) under argon at room temperature, and the mixture was heated under reflux for 31 h. The cooled mixture was diluted with water (30 mL) and extracted with CH_2Cl_2 (10 mL x 3). The combined extracts were dried (Na_2SO_4) and evaporated to give an oily residue which was purified on a PTLC (Merck Aluminium oxide $60F_{254}$, Type E) using hexane-AcOEt (1:1) to yield **11** as a colorless viscous oil (65 mg, 39.0%).

cis-Homoadamantano[4,5-*b*]-18-crown-6 12:

Method A. To a stirred mixture of NaH (60% in minearal oil, 110 mg,) in THF (10 mL) was added a solution of the diol **9** (80 mg, 0.44 mmol) and PEGDT (pentaethylene glycol di-*p*-tosylate) **4** (13) (300 mg, 0.55 mmol) in THF (10 mL) under argon during 1 h and the mixture was heated to reflux for 24 h. To the cooled mixture was added MeOH (1 mL) in order to decompose the remaining NaH. After removal of the solvent under reduced pressure, the residue was extracted with CH_2Cl_2 (5 mL x 2) and the combined extracts were dried (Na_2SO_4). Removal of the solvent gave an oil which was purified on a PTLC (Merck Aluminium oxide $60F_{254}$, Type E) using hexane-AcOEt-MeOH (60:45:1) to yield **12** as a colorless viscous oil (40 mg, 23.6%): R_f = 0.4 (AcOEt); IR (neat) ν (cm^{-1}) 2897, 1447, 1352, 1294, 1117; ^{1}H-NMR δ 1.2-2.3 (m, 14H), 3.4-3.8 (m, 22H); ^{13}C-NMR δ 27.10, 27.15, 30.95, 34.52, 34.94, 37.07, 69.31, 70.73, 70.80, 70.95, 71.12, 83.84; MS *m/z* (%) 384 (M^+, 3.6), 207 (28), 176 (23), 164 (50), 148 (65), 147 (100), 135 (44), 133 (98), 119 (67), 105 (72); HRMS calcd for $C_{21}H_{36}O_6$(M^+) 384.2513, found 384.2512. Anal. Calcd for $C_{21}H_{36}O_6$(384.50): C, 65.59; H, 9.44. Found: C, 65.37; H, 9.70.

Method B. Potassium hydride (30% in mineral oil, 340 mg, 2.54 mmol) in a flask under argon was washed with anhydrous pentane (5 mL x 2), the pentane being removed by a syringe, and THF (10 mL) was added. To this mixture was added a solution of the diol **9** (90 mg, 0.49 mmol) and PEGDT **4** (340 mg, 0.62 mmol) in THF (10 mL) with a stirring at room temperature during 0.5 h, and the mixture was heated under reflux for 24 h. To the cooled mixture was added slowly EtOH (0.5 mL) to decompose the remaining potassium hydride. Removal of the solvent under reduced pressure gave a residue which was extracted with CH_2Cl_2 (5 mL x 2). The combined extracts were dried (Na_2SO_4) and evaporated to give an oil which was purified on a PTLC (Merck Aluminium oxide $60F_{254}$, Type E) using hexane-AcOEt-MeOH (60:45:1) to yield **12** as a colorless viscous oil (33 mg, 17.5%).

Solvent extraction:

The solvents CH_2Cl_2 and H_2O were saturated each other prior to use. Equal volumes (6.0 mL) of a CH_2Cl_2 solution of respective crown ether (1.00×10^{-4} M) and of an aqueous soltuion of each metal picrate (1.00×10^{-4} M) were introduced into a stoppered sealed tube. The mixture was stirred with a magnetic stirrer for 2 h at 25.0 ± 0.1 °C. The equilibrium mixture was then allowed to stand for 2 h at the same temperature to complete phase separation. Each 4.0 mL of the aqueous phase was taken by pipette and the concentration of metal picrates was determined by the absorption at 354 nm using ε values 13,650 for sodium picrate and 14,800 for potassium picrate, respectively. The percent extractabilities were calculated based on the remaining amount of metal picrate in aqueous phase determined as above. An average value of each two or three runs was employed: error < 1.0 (Table 2).

Relative stability of the ammonium complexes was estimated based on the calculated heats of formation by PM3 method (Table 1).

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