Pergamon

Tetrahedron 55 (1999) 6643–6656

TETRAHEDRON

Diamond Crowns : Design, Synthesis and X-ray Crystallographic Studies of a Novel Family of Adamantane-Containing Crown Ethers

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Received 21 December 1998; revised 16 March 1999; accepted 31 March 1999

Abstract: A novel family of crown ethers, containing adamantane units in the cyclic framework, has been designed and synthesized by a straightforward one-step procedure. The design strategy permits the incorporation of a variety of α–amino acids to provide adamantane-constrained chiral crown ethers for use as simple models in studying ion-transport and host-guest complexation. X-ray crystallographic studies on four members of this family have revealed interesting conformational features. Ion complexation studies of several members with alkali metal and ammonium ions are reported.

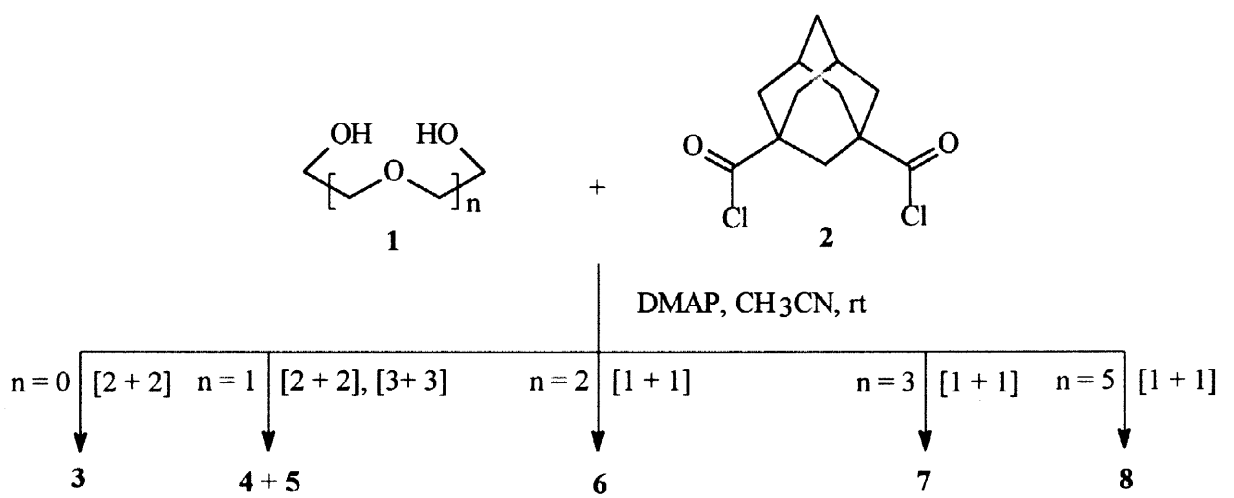
Since the discovery of crown ethers by Pedersen[1] in 1967, there has been a virtual explosion in the number of papers that have appeared in the literature[2,3] on the preparation of crown ethers incorporating aromatic, hetero-aromatic, non-aromatic, carbohydrate or steroid subunits in their cyclic framework. Pendant attachments (lariat crowns) have been made in order to increase their potential for forming three-dimensional complexes and as efficient ion-transporters in membranes. Cage-functionalized crown ethers have also been reported with cubane,[4] oxa-tetracyclodecane[5] and oxa-adamantyl moieties[6] as a part of the cyclic framework to provide

0040-4020/99/$ - see front matter
PII: S0040-4020(99)00311-7

relatively rigid crown ethers with modified ion-complexing properties and improved solubility in nonpolar solvents - a property particularly useful for studying molecular recognition and inclusion phenomena.

We report here the design, synthesis, and crystal structures of the first examples of a novel family of adamantane-containing crown ethers (named **Diamond Crowns**). The design strategy permits the incorporation of a variety of amino acids into the adamantano-crown backbone providing useful models for studying selective host-guest chemistry. An additional attractive feature in the design is the presence of built-in handles (as protected NH_2 and COOH groups) that can be ligated via peptide chemistry to a variety of ligand subunits providing attractive models for ion-complexation studies.

The single-step synthesis of simple adamantano-crowns envisaged here (Scheme 1) involves the condensation of 1,3-adamantanedicarbonyl dichloride (**2**) with the appropriate ethylene glycol (**1**) (Scheme 1).



Scheme 1

Interestingly, while simple ethylene glycol (**1**, n = 0) leads to an 18-membered [2+2] macrocycle (**3**) as the sole isolable product and diethylene glycol (**1**, n = 1) gives rise to a mixture of 24-membered (**4**) and 36-membered (**5**) **crowns** resulting from a [2+2] and [3 +3] cyclization reaction respectively, the higher oligomers of ethylene glycol (**1**; n = 2, 3 or 5) afforded exclusively the [1+1] macrocycles. For example, 15-membered (**6**), 18-membered (**7**) and 24-membered (**8**) mono-adamantano-crowns are the only products of the cyclization reaction

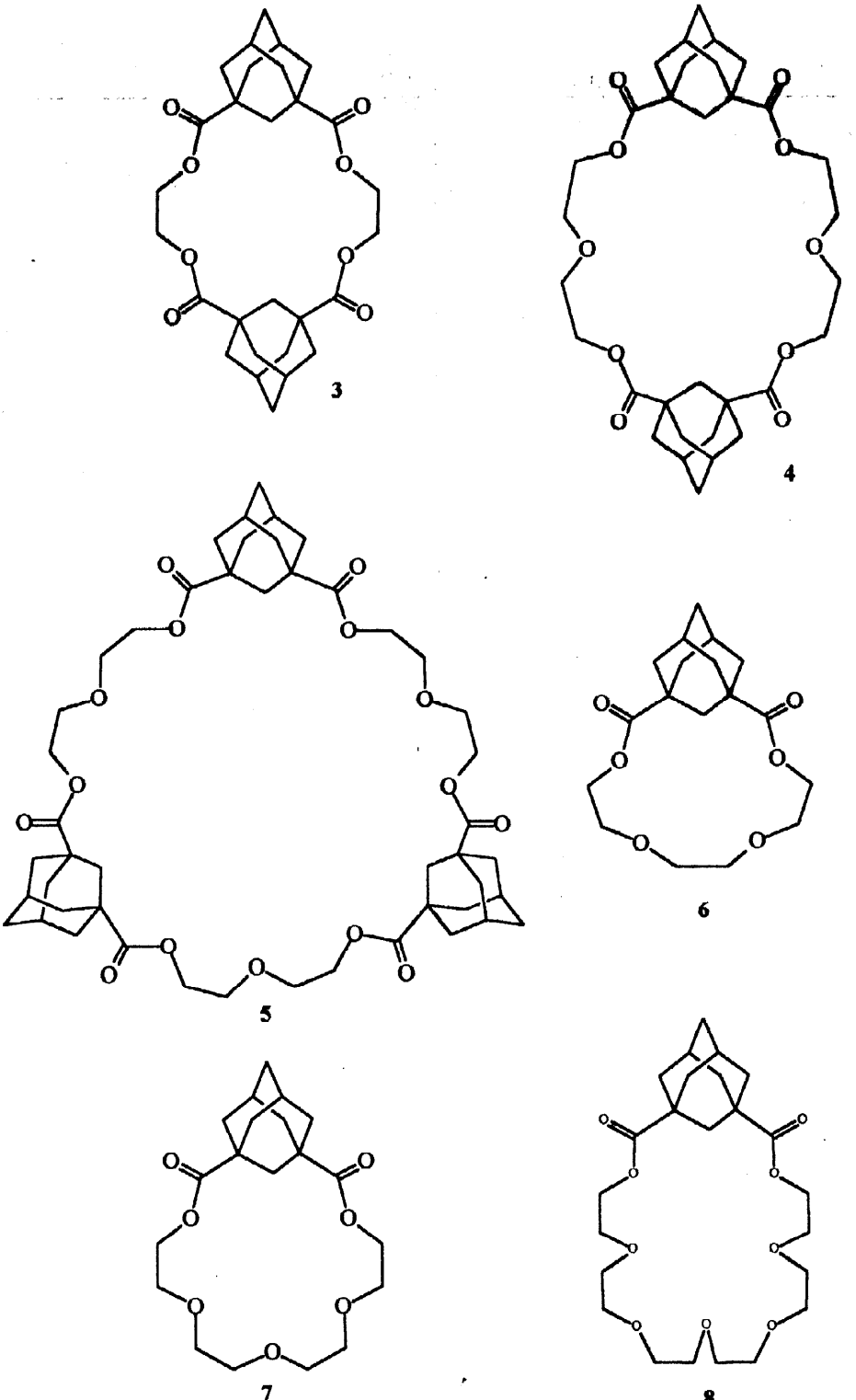


Figure 1

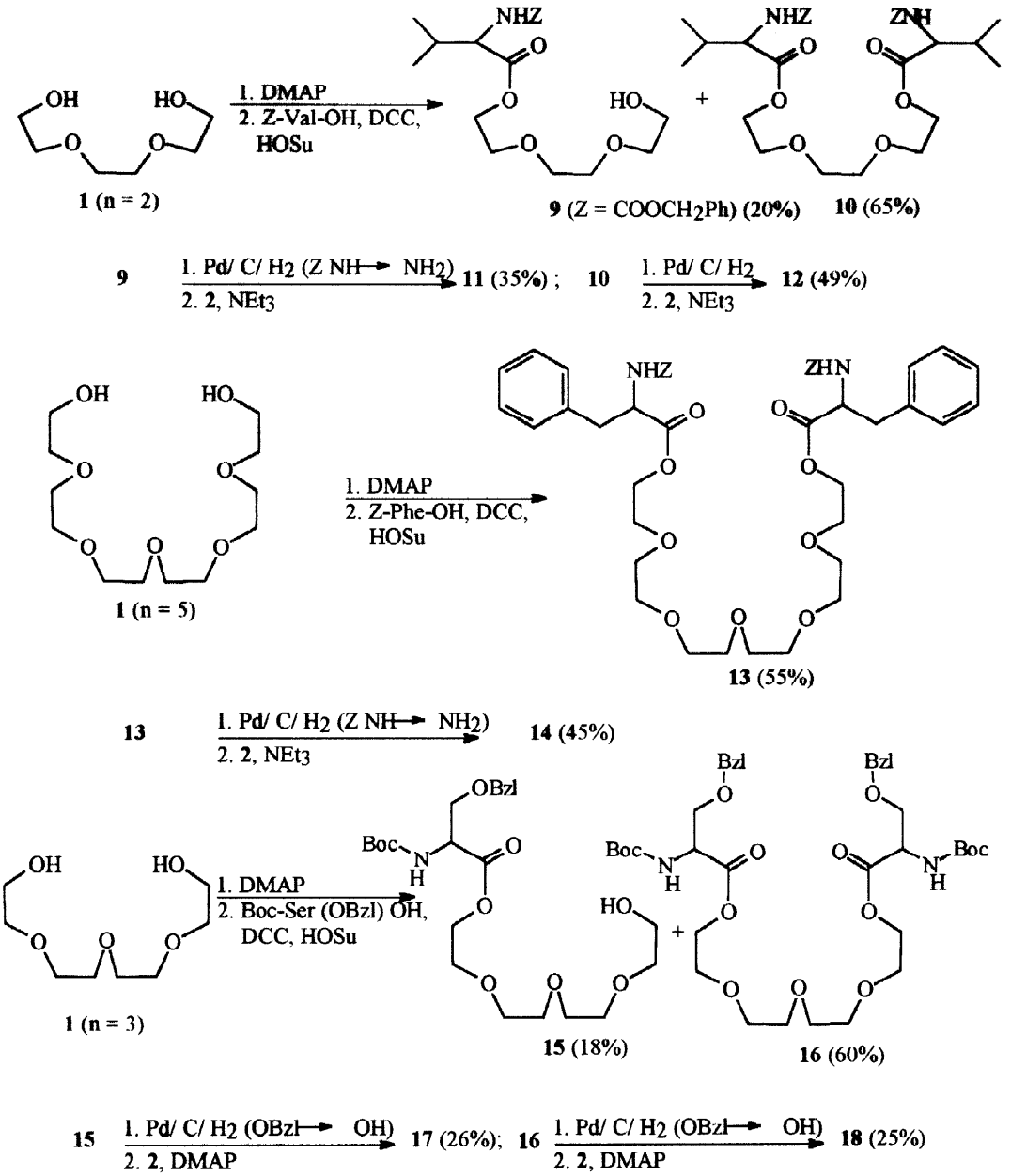
(Figure 1). Macrocycles **3**, **4** and **5** represent examples of polynuclear 18-crown-4, 24-crown-6 and 36-crown-9 ligands, respectively, while **6**, **7** and **8** are simple examples of mononuclear 1,3-bridged adamantanodiester crown-4, crown-5 and crown-7 ligands in 15, 18 and 24-membered rings, respectively (Figure 1)

In the ^{1}H NMR spectra, the polynuclear crowns **3**, **4** and **5** exhibited consistently two resonances at δ 3.50 - 3.65 and δ 4.15 - 4.20, each integrating for equal numbers of ethylenoxy protons, thus, indicating the presence of a centre of symmetry in these molecules. The mononuclear adamantano-crowns **6**, **7** and **8** on the other hand showed an unequal distribution of ethylenoxy protons with CH_2 resonances (4 protons) proximal to ester bonds appearing consistently at lower field (~ 4.20 δ). The adamantane-proton resonances appeared as a multiplet at ~ δ 1.45-2.20 in all the macrocycles.

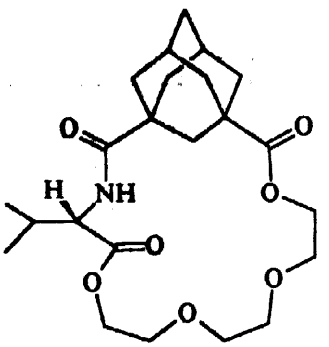
For the preparation of amino acid-containing adamantano-crowns (Figure 2), ethylene glycol (**1**) was first converted into $N^{\alpha}Z$ or N^{α}Boc-protected bis amino acid ester derivatives (**10**, **13**, **16**, Scheme 2) by treatment with N-protected ($N^{\alpha}Z$ Val / Phe) or N, O protected [N^{α}Boc-Ser (-CH_2OBzl) OH] amino acid in the presence of DMAP under DCC / N-OH succinimide coupling conditions (Scheme 2). Small amounts (~20 %) of monoacylated products (**9**, **15**) were also isolated in the coupling reaction. In the second step, the mono or bis-acylated product was N or O-deprotected (Pd/ C/ H_2) and directly treated with **2** and DMAP under high dilution conditions to give the crown depsipeptides (25-50 % yield) listed in Figure 2.

As observed in the monoadamantano-crowns, the ethylenoxy protons in amino acid-containing crowns appear as two sets of resonances with ester-linked protons (four in number) appearing at relatively lower field. No other significant features were noticed in the ^{1}H NMR (ROESY) spectra of the adamantano-crowns.

Suitable crystals for X-ray studies could be obtained for bisadamantano-crowns **3** and **4** and monoadamantano-crowns **6** and **7**. The crystal structures of diadamantano-crowns **3** (Figure 3a) and **4** (Figure 3b) showed the presence of a centre of symmetry in the molecules. The 1, 3-adamantane carbonyls in crystal **3** are both directed outward while in crystal **4** the carbonyls are oriented in an anti (one inside and the other outside the cavity) fashion. The cavity sizes in **3**


1. DMAP
2. Z-Val-OH, DCC, HOSu
1 (n = 2)
9 (Z = COOCH2Ph) (20%)
10 (65%)
9 1. Pd/ C/ H2 (Z NH→ NH2) 2. 2, NEt3 11 (35%) ; 10 1. Pd/ C/ H2 2. 2, NEt3 12 (49%)
1. DMAP
2. Z-Phe-OH, DCC, HOSu
1 (n = 5)
13 (55%)
13 1. Pd/ C/ H2 (Z NH→ NH2) 2. 2, NEt3 14 (45%)
1. DMAP
2. Boc-Ser (OBzl) OH, DCC, HOSu
1 (n = 3)
15 (18%)
16 (60%)
15 1. Pd/ C/ H2 (OBzl→ OH) 2. 2, DMAP 17 (26%); 16 1. Pd/ C/ H2 (OBzl→ OH) 2. 2, DMAP 18 (25%)

Scheme 2



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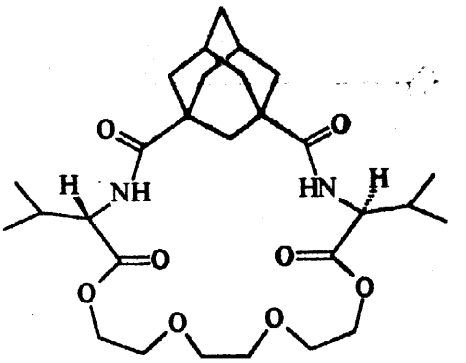

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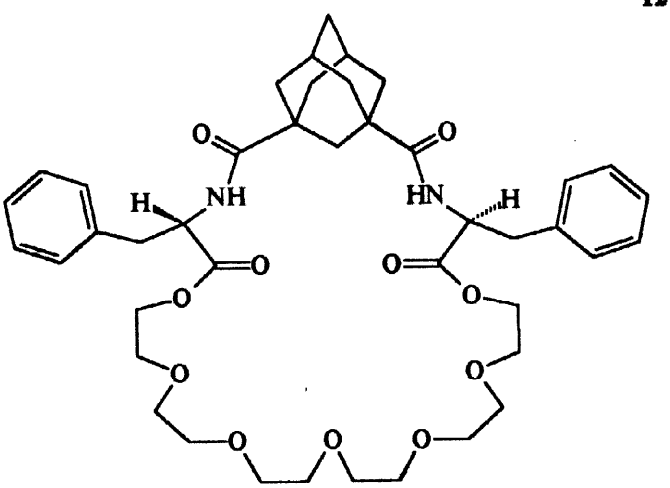

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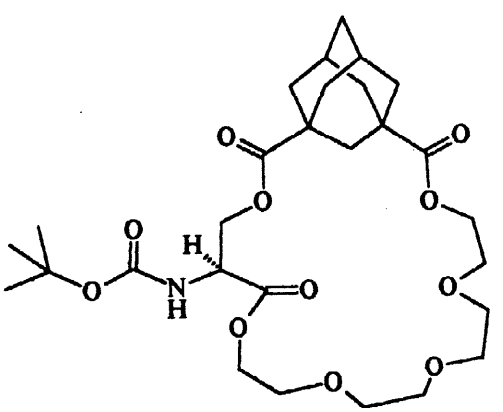

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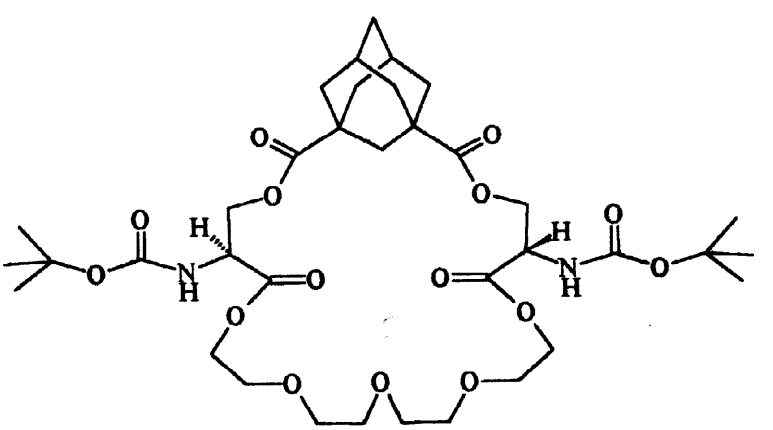

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Figure 2

and **4** are 5.23 x 5.89 Å (C_9-C_{9A} , O_{15}-O_{15A}) and 7.16 x 4.15 Å (O_{12}-O_{12A}, O_{12}-O_{18}) respectively (Figure 3a-b).

The monoadamantano-crown **6** has an approximate two-fold rotation axis while molecule **7** with an additional -CH_2CH_2O- moiety displays no internal symmetry. In both **6** and **7** (Figures 4a and 4b) the admantane-1,3-carbonyl groups are directed outward from the cavity (in **6** the cavity size is 4.75 x 4.88 Å ; O_{15}-O_{21}, O_{12}-O_{18}) and in **7** it is 6.13 x 5.41 Å (O_{12}-O_{21}, O_{15}-O_{24}). In both **4** and **7**, the additional -CH_2CH_2O- groups, as compared to **3** and **6**, are essentially exocyclic to the crown rings.

The alkali-metal ion complexation capability of non-peptidic adamantano-crowns (**3-7**) was tested both by FAB MS and picrate extraction methods. In FAB MS, metal ion doping experiments with **3-7** indicated a strong tendency for the uptake of alkali metal ions. The order in crowns for uptake of alkali metal ion (M^+) ion was found to be **8** > **7** > **4** > **3** > **6** and signal intensity for **8**+M^+, **7**+M^+, **4**+M^+, **3**+M^+ and **6**+M^+ appeared in the order of Li > Rb > Cs > K > Na; Rb > Li > Cs > K > Na; Rb > Li > Cs > K > Na; Rb > Li > Cs > K > Na and Rb > Li > K > Cs > Na, respectively . The preference in the uptake of alkali metal ions by crowns **3-8** in the FAB MS indicate hole size as the main controlling factor. The FAB MS results are in agreement with the crystal structure data. Interestingly, NH_4^+ ion doping experiments in the FAB MS showed maximum uptake by the macrocycle **8**. This result was also supported by the observed shift (~ 0.1 ppm) of the guest n-butyl protons in ^{1}H NMR experiments with **8** and n-butyl ammonium picrate in CD_3OD + $CDCl_3$ (1:9) solvent mixture.

The alkali metal picrate extraction[7] profile for crowns **4**, **6** and **7** was examined by comparing absorption intensities of a blank (chloroform extraction of an aqueous solution of the alkali metal picrate alone) and the sample consisting of a chloroform solution of the crown host and alkali metal picrate. The extraction data showed the metal ion uptake in the order $Cs^+ > K^+ > NH_4^+ > Na^+ > Li^+$ for **4**, $K^+ > Li^+ > Cs^+ > NH_4^+ > Na^+$ for **6** and $Cs^+ > K^+ > NH_4^+ > Na^+ > Li^+$ for **7**. Thus, in the picrate extraction method, while the percentage extraction of alkali metal ion varies in **4-7**, maximum affinity (~ 23 %) for K^+ ion[8] was shown by all the three crowns.

In summary the present work provides a straightforward entry into a novel class of adamantane-constrained crown ethers. The simple mono or multinuclear adamantano-crowns

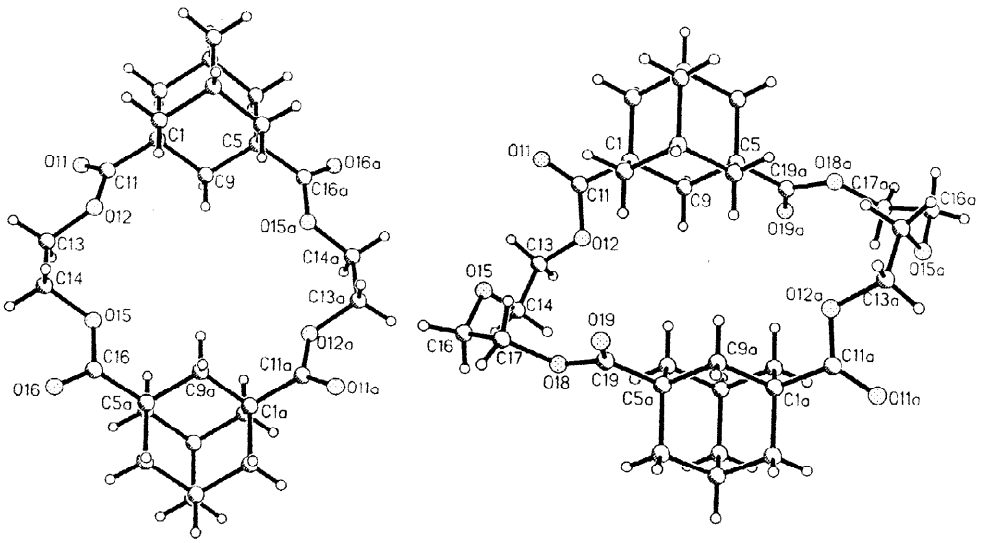

Figure 3

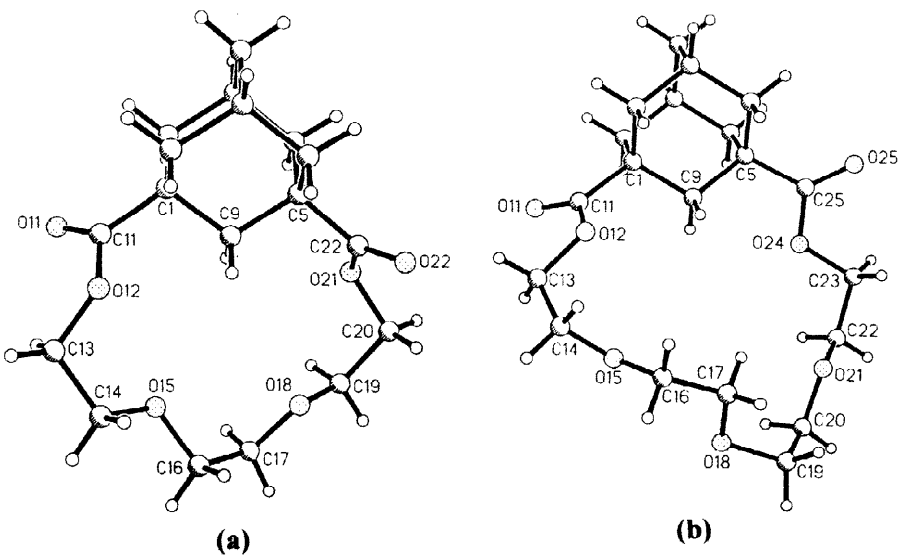

Figure 4

(3-8) have been demonstrated to complex a large variety of alkali metal ions. The flexibility in synthetic strategy with proper choice of ring-inserts is likely to provide these crown ethers with promise to act as selective hosts in molecular recognition and transport phenomena.

EXPERIMENTAL SECTION

All amino acids used were of L-configuration. Melting points were recorded on a Fisher-Johns melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 882 IR spectrometer as neat liquids or as KBr pellets, and prominent peaks are expressed in cm^{-1}. ^{1}H NMR spectra were recorded on Perkin Elmer-200 and Brucker WM-300 instruments and chemical shifts are reported in δ (ppm) with TMS at 0.00 as an internal reference. FAB MS were obtained on a JEOL SX-120 / DA-6000 instrument using *m*-nitrobenzyl alcohol as the matrix. Reactions were monitored wherever possible by TLC. Silica gel G (Merck) was used for TLC and column chromatography was done on silica gel (100-200 mesh) columns, which were generally made from a slurry in hexane or a mixture of hexane and ethyl acetate. Products were eluted with either a mixture of ethyl acetate / hexane or chloroform / methanol. The polyethylene glycols were purchased from Aldrich Co. and directly used for the reaction.

Alkali metal picrates were freshly prepared[9] and dried before use. In a typical extraction procedure, a solution of metal picrate (2.72 mM, 0.25 mL in H_2O) was admixed with a $CHCl_3$ solution of the host (13.6 mM) and the two-phase system vortexed for ~ 5 min. The layers were separated by centrifugation and the extent of metal ion extraction by the host was determined by comparing the absorption intensities of the blank (aqueous layer of a chloroform solution of the metal picrate alone) and the experimental sample (aqueous layer) containing the metal picrate with the host. The absorption intensities of the alkali metal picrate solution were measured at 356 nm by using UV-Visible spectrophotometer HP model 8L1524. The percentage of cation extraction was calculated using the formula [A_{356} (without host) -A_{356} (with host) / A_{356} (without host)]x 100. Duplicate runs were made in each case.

General Procedure for the Preparation of Adamantano-Crowns 3-8 Listed in Figure 1

A solution of 1,3-adamantanedicarbonyl dichloride[10] (**2**, 1 mmol) in dry CH_2Cl_2 (50 mL) was added dropwise over a period of 0.5 h to a well-stirred and ice-cooled solution of polyethylene glycol (**1**, 1 mmol) in dry CH_3CN (200 mL) containing N,N'-dimethyl -4-aminopyridine (DMAP, 2 mmol) and the mixture stirred at room temperature for 12 h. Solvents were evaporated *in vacuo*, the residue was triturated with benzene (100 mL) and the benzene extract was evaporated *in vacuo*. The residue was chromatographed on a small column of silica gel using a mixture of benzene and hexane as eluent to afford the adamantano-crowns.

3 :Yield 20 %; colourless needles; mp. 254-255°C; IR (KBr) 2947, 2904, 2866, 1729, 1458, 1412, 1371, 1285, 1256, 1222, 1103, 1070 cm^{-1} ; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.60-2.25 (m, 28H), 4.27 (s, 8H); FAB MS (m / z) (%) 501 (75) $(MH)^+$; HRMS : MH^+, found 501.2479. $C_{28}H_{36}O_8$ requires 501.2488.

4 :Yield 15%; colourless needles; mp. 174-175°C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.45-2.22 (m, 28H), 3.65 (t, J = 5.0 Hz, 8H), 4.20 (t, J = 5.0 Hz, 8H); FAB MS (m /z) (%) 589 (100) $(MH)^+$; HRMS : MH+, found 589.3042. $C_{32}H_{44}O_{10}$ requires 589.3012.

5 :Yield 24%; syrup; IR (neat) 2885, 2829, 1716, 1448, 1232, 1133, 1094 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.55-2.20 (m, 42H), 3.63 (m, 12H); 4.15 (m, 12H); FAB MS (m / z) (%) 883 $(MH)^+$; HRMS : MH+, found 883.4496. $C_{48}H_{66}O_{15}$ requires 883.4479.

6 :Yield 40%; colurless needles; mp. 102-104°C; IR (KBr) 2953, 2916, 2875, 1733, 1461, 1384, 1355, 1287, 1248, 1204, 1113 cm^{-1} ; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.54-2.20 (m, 14H), 3.51 (m, 8H), 4.23 (t, J = 5.0 Hz, 4H); FAB MS (m / z) (%) 339 (96) $(MH)^+$; HRMS : MH+, found 339.1800. $C_{18}H_{26}O_6$ requires 339.1807.

7 :Yield 18%; colourless needles; mp. 73-75°C; IR (KBr) 2949, 2861, 1729, 1617, 1457, 1354, 1281, 1251, 1205, 1104 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.60-2.22 (m, 14H), 3.65 (m, 12H), 4.20 (t, J = 5.0 Hz, 4H); FAB MS (m / z) (%) 383 (100) $(MH)^+$; HRMS : MH^+, found 383.2062. $C_{20}H_{30}O_7$ requires 383.2069

8 :Yield 38%; syrup; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.50-2.20 (m, 14H), 3.68 (m, 20H), 4.23 (m, 4H); FAB MS (m / z) (%) 471 (100) $(MH)^+$; HRMS : MH^+; found 471.2608. $C_{24}H_{38}O_9$ requires 471.2594

Synthesis of amino acid-containing adamantano-crowns 11, 12, 14, 17 and 18 listed in Figure 2

General Procedure :

(a) Preparation of precursor 1, ω-mono and bis α-amino acylated polyethylene glycols listed in Scheme 2:

To a well-stirred and ice-cooled mixture of N^{α} Z or N^{α} Boc-amino acid (2 mmol), DCC (2 mmol), and N-hydroxy succinimide (HOSu, 2 mmol) in dry CH_2Cl_2 (20 mL) was added, a solution of polyethylene glycol (1, 1 mmol) in CH_2Cl_2 (20 mL) containing DMAP (2 mmol). After 24 h of stirring at room temperature, the reaction mixture was filtered. The residue was washed with CH_2Cl_2 (3 x 10 mL) and the combined filtrates were washed sequentially with 20 mL each of ice-cold 2N H_2SO_4, H_2O and 5% aqueous $NaHCO_3$. The organic layer was dried over anhydrous $MgSO_4$, evaporated *in vacuo* and the residue was chromatographed on a column of silica gel using either a mixture of EtOAc / hexane or $CHCl_3$ / MeOH as eluents to afford the partial and fully α-amino acylated glycols.

9 :Yield 20%; syrup; IR (KBr) 3393 (br), 2974, 2889, 1734 (br), 1634, 1576, 1534, 1501, 1459 cm^{-1} ; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.90 (d, J = 6.7 Hz, 3H), 1.00 (d, J = 7.0 Hz, 3H), 2.19 (m, 1H), 3.64 (m, 10H), 4.32 (m, 3H), 5.11 (s, 2H), 5.58 (d, J = 9.2 Hz, 1H), 7.36 (s, 5H); FAB MS (m / z) (%) 384 (58) $(MH)^+$; HRMS : MH^+, found 384.2033. $C_{19}H_{29}NO_7$ requires 384.2022.

10 :Yield 65%; syrup; IR (KBr) 3383 (br), 2972, 2887, 1735 (br), 1528, 1472, 1456, 1398, 1345, 1314 cm^{-1} ; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.89 (d, J = 6.7 Hz, 6H), 0.97 (d, J = 6.6 Hz, 6H), 2.18 (m, 2H), 3.64 (m, 8H), 4.31 (m, 6H), 5.11 (s, 4H), 5.35 (d, J = 8.1 Hz, 2H), 7.35 (s, 10H); FAB MS (m / z) (%) 617 (52) $(MH)^+$; HRMS : MH^+, found 617.3080. $C_{32}H_{44}N_2O_{10}$ requires 617.3074.

13 :Yield 55%; syrup; $[\alpha]_D^{28}$ +21.72 (c 4.14, $CHCl_3$); IR (KBr) 3401, 3042, 2911, 2884, 1734, 1652, 1627, 1522, 1507, 1449, 1402, 1345, 1262 cm^{-1} ; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.12 (m, 4H), 3.61 (m, 20H), 4.26 (m, 4H), 4.67 (m, 2H), 5.09 (s, 4H), 5.35 (d, J = 7.8 Hz, 2H), 7.12 (m, 4H), 7.24 (m, 6H), 7.33 (s, 10H); FAB MS (m/z) (%) 977 (100) $(M+Cs^+)$; HRMS : MH+, found 845.3871. $C_{46}H_{56}N_2O_{13}$ requires 845.3860.

15 :Yield 18%; syrup; IR (KBr) 3429 (br), 2940, 2896, 1723 (br), 1647, 1633, 1577, 1522, 1500, 1458 cm^{-1} ; ^{1} H NMR (300 MHz, $CDCl_3$) δ 1.44 (s, 9H), 3.65 (m, 16H), 3.88 (m, 1H), 4.30 (m, 2H), 4.49 (m, 2H), 5.50 (brd, 1H), 7.30 (m, 5H); HRMS : MH^+, found 472.2563. $C_{23}H_{37}NO_9$ requires 472.2546.

16 :Yield 60%; syrup; IR (KBr) 3440 (br), 2985, 2940, 2879, 1757, 1722, 1633, 1579, 1503, 1458, 1370, 1350, 1291, 1252, 1169, 1115 cm^{-1} ; ^{1} H NMR (300 MHz, $CDCl_3$) δ 1.44 (s, 18H), 3.57-3.87 (m, 16H), 4.28 (brs, 4H), 4.48 (m, 6H), 5.43 (brd, 2H), 7.28 (brs, 10H); FAB MS (m / z) (%) 755 (20) $(M+Li^+)$, 649 (31) $(M\text{-}Boc+H)^+$, 549 (14) $(M\text{-}2 \times Boc+H)^+$.

(b) Condensation of N or O-deprotected mono or bis-glycol esters with 1,3-adamantanedicarbonyl dichloride (2).

A solution of 1,3-adamantanedicarbonyl dichloride (1 mmol) in dry CH_2Cl_2 (50 mL) was added dropwise to a well-stirred and ice-cooled solution of 1 mmol of N or O-deprotected (Pd/C, 5%, H_2) precursors (**9**, **10**, **13**, **15** or **16** listed in scheme 2) in dry ethyl acetate (~100 mL) containing DMAP (2 mmol) in the case of O-deprotected and triethylamine (2 mmol) in N-deprotected compounds. The reaction mixture was stirred at room temperature for 12 h and solvents evaporated *in vacuo*. The residue was redissolved in chloroform (~100 mL) and chloroform solution washed, sequentially, with ice-cold 1 N H_2SO_4, H_2O and 5% aqueous $NaHCO_3$ (20 mL each), dried (anhydrous $MgSO_4$), evaporated *in vacuo* and the residue chromatographed on a small column of silica gel using $CHCl_3$ / MeOH or hexane / ethyl acetate as eluents to afford the amino acid-containing adamantano-crowns listed in Figure 2.

11 :Yield 35%; syrup; IR (KBr) 3397 (br), 2940, 2917, 2865, 1733, 1670, 1657, 1524, 1501, 1462 cm^{-1} ; ^{1} H NMR (200 MHz, $CDCl_3$) δ 0.92 (m, 6H), 1.60-2.28 (m, 15H), 3.67 (m, 8H), 4.24 (m, 4H), 4.58 (m, 1H), 6.26 (d, J = 8.0 Hz, 1H); FAB MS (m / z) (%) 438 (100) $(MH)^+$; HRMS : MH+, found 438.2509. $C_{23}H_{35}NO_7$ requires 438.2491.

12 :Yield 49%; syrup; IR (KBr) 3420 (br), 2971, 2937, 2869, 1744, 1671, 1647, 1563, 1532 cm^{-1} ; ^{1} H NMR (200 MHz, $CDCl_3$) δ 0.92 (m, 12H), 1.64-2.31 (m, 16H), 3.65 (m, 8H), 4.11-4.47 (m, 4H), 4.61 (m, 2H), 6.31 (d, J = 8.0 Hz, 2H); FAB MS (m /z) (%) 537 (100) $(MH)^+$; HRMS : MH^+, found 537.3203. $C_{22}H_{44}N_2O_8$ requires 537.3175.

14 :Yield 45%; semisolid; $[\alpha]_D^{28}$ +7.81 (c 0.95, $CHCl_3$); IR (KBr) 3444 (br), 2916, 2865, 1737, 1662, 1651, 1534 (br), 1478, 1458 cm^{-1} ; ^{1} H NMR (300 MHz, $CDCl_3$) δ 1.57-2.20 (m, 14H), 3.11 (m, 2H), 3.17 (m, 2H), 3.62 (m, 20H), 4.20 (m, 2H), 4.34 (m, 2H), 4.87 (m, 2H), 6.33 (d, J = 7.6 Hz, 2H), 7.14 (m, 4H), 7.27 (m, 6H); FAB MS (m / z) (%) 765 (100) $(MH)^+$; HRMS : MH^+, found 765.3994. $C_{42}H_{56}N_2O_{11}$ 765.3962

17 :Yield 26 %; syrup; IR (KBr) 3446 (br), 2939, 2868, 1734, 1542, 1513, 1458, 1372, 1279, 1252, 1213, 1170, 1097 cm^{-1} ; ^{1} H NMR (300 MHz, $CDCl_3$) δ 1.44 (s, 9H), 1.54-2.22 (m, 14H), 3.66 (m, 12H), 4.27 (m, 4H), 4.40 (m, 1H), 4.55 (m, 2H), 5.73 (brd, 1H); FAB MS (m / z) (%) 570 (10) $(MH)^+$, 470 (100) $(M\text{-}Boc+H)^+$.

18 :Yield 25%; thick syrup; IR (KBr) 3356 (br), 2932, 2863, 1733, 1718, 1641, 1576, 1555, 1523, 1501, 1466, 1372 cm^{-1} ; ^{1} H NMR (300 MHz, $CDCl_3$) δ 1.46 (s, 18H), 1.67-2.06 (m, 14H), 3.64 (m, 12H), 4.59 (m, 8H), 4.61 (m, 2H), 5.45 (br, 2H); FAB MS(m/z)(%):779(100) $(M+Na^+)$

X-ray diffraction analysis. The crystallographic parameters for the crystals are :

(3) $C_{28}H_{36}O_8$, sp. gr. $P2_1/n$ with a = 9.420(1) Å, b = 6.449(1) Å, c = 20.567(2) Å, β = 93.08(1)^0, V = 1247.67(18) Å, Z = 2, d_{calc} = 1.332 g/cm^3. Colorless laths with dimensions 1.0x0.27x0.07 mm., Cu rad. (λ = 1.54178 Å), R = 5.35 %. (**4**) $C_{32}H_{44}O_{10}$, sp. gr. $P2_1/n$, a = 11.231(1) Å, b = 6.887(1) Å, c = 19.346(1) Å, β = 98.65(1)^0, V = 1479.35(22) Å^3, Z = 2, d_{calc} = 1.322 g/cm^3. Heavy prisms with dimensions 0.50x0.45x0.35 mm., Cu rad. R = 5.72%. (**6**) $C_{18}H_{26}O_6$, sp. gr. $P2_1/c$ with a = 10.078(3) Å, b = 9.431(3) Å, c = 18.313(4), β = 94.057(9)^0, V = 1736.3(10) Å^3, Z = 4, d_{calc} = 1.295 g/cm^3. Irregular pitted plate with dimensions 1.1x0.70x0.25 mm., Mo rad. (λ = 0.71073 Å), R = 4.55 %. (**7**) $C_{20}H_{30}O_7$, sp. gr. $P2_1/c$ with a = 10.803(1) Å, b = 19.118(2) Å, c = 10.741(1) Å, β = 118.74(0) Å, V = 1945.08 Å^3, Z = 4, d_{calc} = 1.309 g/cm^3. Irregular shape, rough surface with dimensions 0.60x0.40x0.27 mm., Mo rad., R = 8.27 %.

X-ray data were collected on an automated diffractometer in the θ / 2θ mode, constant scan speed of 10 deg./sec., 1^0 scan width with 2θmax = 115^0 when CuKα radiation (λ = 1.54178 Å). Three check reflections were monitored after every 97 measurements. The structure determinations were straightforward within direct methods as programmed in SHELXTL, Version 4.2 (Siemens Analytical X-Ray Instr. Co., Madison, WI, U.S.A). Full-matrix anisotropic

least squares were performed with the hydrogen atoms placed in ideal positions and allowed to ride with the C or N atoms to which each was bonded. Lists of structure factors are deposited at the Cambridge Crystallographic Data Centre.

ACKNOWLEDGEMENT: We are most grateful to Professor S. Ranganathan and Professor D. Balasubramanian for helpful discussions. Financial assistance from DST, New Delhi, and from the office of Naval Research and the National Institutes of Health, (U.S.A) Grant GM-30902 is acknowledged. DR thanks Jawaharlal Nehru Centre for Advanced Scientific Research for an honorary Faculty position.

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8. The percentage value of ~ 23 % for K^+ ion metal uptake by crowns **4-7** lies between the values shown by 15-crown-5 (~14 %), benzo-15-crown-5 (~19 %) and 18-crown-6 (~68 %) (Reference 6).
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