

Cation-binding Properties of New Armed Macrocyclic Host Molecules and Their Applications to Phase-transfer Reactions and Cation Membrane Transport

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A new series of armed macrocyclic host molecules was prepared; the macrocycles were characterized by parent macrocyclic ligands and cation-ligating donor arms. Their cation-binding properties were significantly controlled by co-ordination characteristics of their parent macro-ring and donor side-arms, and chemical modifications of their basic structures provided interesting chemical functions. For example, a furan-bearing double armed crown ether showed high catalytic activity in some phase-transfer reactions; a multi-armed cyclam containing furan-oxygen atoms discriminated NH_4^+ ion from K^+ and other related cations effectively. Such chemical functions of these armed macrocycles were not attained with common crown ethers and cryptands. Hence, further variations of ligand structures may lead to a new series of host molecules showing unique and important chemical functions.

'Armed macrocycles' such as lariat ethers and functionalized cyclams have recently attracted much attention from chemists;^{1,2} these macrocycles are characterized by macrocyclic ligand skeletons and cation-ligating donor arm groups. In this class of compounds, the guest cation can be wrapped in such a way that additional donor groups on the flexible arms would provide further co-ordination to the guest cation trapped in the parent macro-ring.³ Their cation-binding structures are closely similar to those of bicyclic cryptand-type compounds, but high mobility of the ligating arms attached to the macro-ring may permit stable and dynamic complexations that are required for effective phase-transfer catalysts and cation-transport carriers.

In earlier publications, we described some armed macrocycles: double armed crown ethers⁴ and multi-armed cyclams.⁵ Interestingly, they showed highly characteristic cation-transport abilities which were largely dependent on their ligand structures; these abilities were not attained by common crown ethers and related macrocyclic ligands.

Here we report cation-binding properties of these armed macrocycles and their applications to phase-transfer reactions and cation membrane transport. Although lariat ethers and other armed macrocycles show excellent cation-binding properties, they have rarely been employed in membrane separation, chemical reactions, or related processes.⁶ We first demonstrated that these armed macrocycles exhibited specific cation-transport abilities and excellent catalytic activities. Since their cation-binding properties and subsequent functions were found to be varied by modification of the side-arm structure, alteration of the size of the parent macro-ring, and the use of macrocycles with different heteroatoms, the present study would provide further possibilities for designing new and highly functionalized host molecules.

Results and Discussion

Armed Macrocycles.—Two types of armed macrocycles were prepared for this study (Figure 1). Double armed crown ethers (3) and (4) were derived from 1,4,10,13-tetraoxa-7,16-diazacyclo-octadecane. Since the parent diaza-crown ring strongly binds K^+ , Ag^+ , and other alkali metal cations, their introduced furan or thiophene arm moieties are expected to act as additional ligating donors and completely wrap around the guest cations in a similar fashion to that of bicyclic cryptand compounds.

Multi-armed cyclam (7) has a characteristic ligand topology which is not attained with double armed crown ethers. Its

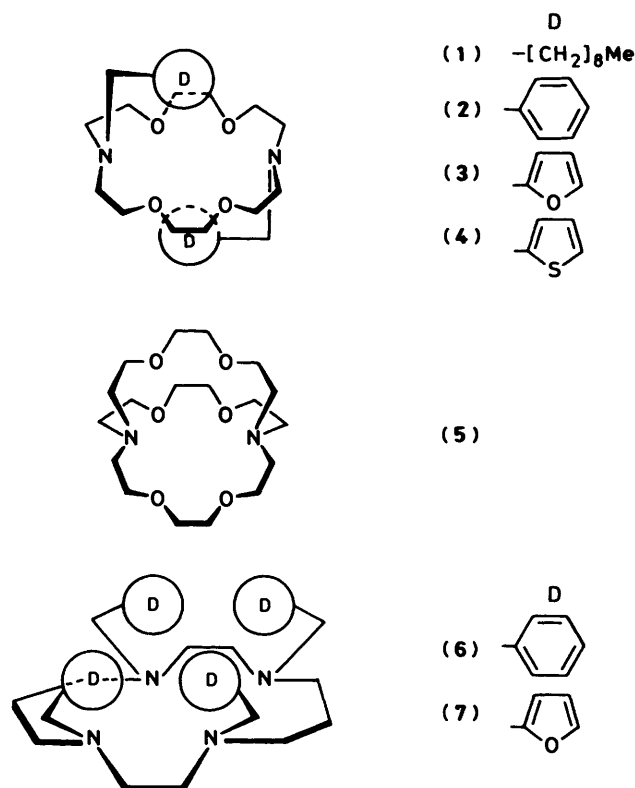


Figure 1. 'Armed macrocycles' examined in this work

macrocyclic polyamine skeleton and four flexible ligating arms can accommodate an uniquely ordered molecular cavity as observed with some polydand host molecules.⁷ As macrocyclic polyamine ligands form stable complexes with various ammonium cations and transition metal ions,⁸ the co-operative actions of the polyamine nitrogen and furan-oxygen atoms of the cyclam (7) would be effective for unique host-guest complexations.

Related diaza-crown ethers (1) and (2), cryptand (5), and a cyclam (6) were also investigated for comparison.

Cation-extraction Properties of Armed Crown Ethers and Multi-armed Cyclams.—In order to examine the cation-binding

Table 1. Extraction properties of 'armed macrocycles'

Salt	Extraction percentage (%) ^a					
	(2)	(3)	(4)	(5)	(6)	(7)
LiClO ₄	<1	0	0	<1	0	<1
NaClO ₄	1.7	2.4	<1	47.9	0	2.1
KClO ₄	3.4	5.2	3.2	83.8	0	0
AgClO ₄	85.7	87.4	37.8	36.8	83.9	<i>b</i>
NH ₄ ClO ₄	1.7	2.0	<1	78.0	3.2	5.0
CsClO ₄	0	0	0	0	<i>c</i>	<i>c</i>
Ba(ClO ₄) ₂	<1	<1	<1	<1	0	0
Pb(ClO ₄) ₂	11.8	25.0	16.4	2.4	2.1	<i>c</i>

^a Extraction percentages of ClO₄⁻ anion into CHCl₃ phase. See Experimental section. ^b Ag(0) was deposited on the test tube employed. ^c White precipitates appeared in these cases.

properties of armed macrocycles, we performed liquid-liquid extraction experiments by using a series of alkali and alkaline earth cations. Their extraction abilities were estimated on the basis of partition of the cation perchlorate between CHCl₃ and aqueous solution, and typical results are summarized in Table 1.

Introduction of cation-ligating arms to the diaza-crown ether systems significantly modified cation-extraction properties. For example, crown ether (3) bearing furan-oxygen atoms on its arms extracted K⁺, Ag⁺, and Pb²⁺ ions more effectively than did the corresponding simple crown ether (2), indicating that the furan-oxygen atoms of crown ether (3) were essentially involved in cation-binding and extraction processes. Its extraction efficiencies for Ag⁺ and Pb²⁺ ions were also higher than those of the bicyclic cryptand (5), while Na⁺, K⁺, and NH₄⁺ cations were much more efficiently extracted by cryptand (5). Although several complicating factors should strictly be considered,* the present results demonstrate that double armed crown ether (3) could form lipophilic complexes (with guest cations) of intermediate stability between those of crown ether (2) and those of cryptand (5). On the other hand, crown ether (4), bearing thiophene-sulphur atoms on its arms, showed a lower extraction efficiency for Ag⁺ ion than did the crown ether (2). Since the thenyl crown ether (4) extracted K⁺ and Pb²⁺ ions with comparable efficiency to that of the crown ether (2), the nature of the ligating donor arms markedly influenced the extraction efficiency and selectivity.

Table 1 indicates that crown ethers (2)–(4), having 18-membered diaza-crown ring systems, bound K⁺, Ag⁺, and Pb²⁺ ions more strongly than Na⁺, Ba²⁺, and Cs⁺ ions. As K⁺, Ag⁺, and Pb²⁺ ions fit the cavity of an 18-membered crown ring more tightly than do the other examined cations, the size of the parent crown ring must be an essential factor in determining the overall extraction profile. Therefore, appropriate choice of parent crown ring and ligating side-arm group should make it possible to design new armed crown ether derivatives for lanthanoid and other metal cations.⁹

The multi-armed cyclam (7), bearing furan-oxygen atoms as additional ligating arms, showed a unique extraction ability for NH₄⁺ ion. Nitrogen donor sites incorporated in the parent cyclam ring favoured complexation and extraction of 'soft' Ag⁺ and Pb²⁺ ions, but these metal ions were precipitated, and extracted to only a small extent, in the presence of cyclam (7). In

* Solubilities of the examined macrocycles are of particular importance. Among them, cryptand (5) was partly partitioned into the aqueous phase after extraction experiments. Protonation at the ring-nitrogen atoms of macrocycles (1)–(7) should also be considered at low pH conditions of the aqueous phase (pH < 5). The experimental pH conditions of the aqueous phases were almost 6–7.

Table 2. Catalytic activities of 'doubly armed crown ethers'

Reaction	Relative rate ^a		
	(2)	(3)	(5)
C ₈ H ₁₇ Br + LiI → C ₈ H ₁₇ I + LiBr	0.2	0.3	0.2
C ₈ H ₁₇ Br + NaI → C ₈ H ₁₇ I + NaBr	0.7	1.0	0.9
C ₈ H ₁₇ Br + KI → C ₈ H ₁₇ I + KBr	1	6.8 ^b	2.4
C ₈ H ₁₇ Br + CsI → C ₈ H ₁₇ I + CsBr	0.6	0.6	0.6
C ₈ H ₁₇ Br + KCN → C ₈ H ₁₇ CN + KBr	1	1.7 ^c	1.3
C ₈ H ₁₇ Br + KOAc → C ₈ H ₁₇ OAc + KBr	1	1.1 ^d	3.1
PhCH ₂ Br + KOAc → PhCH ₂ OAc + KBr	1	2.1 ^d	12.3

^a Reaction rates at initial stages, relative to those with crown ether (2) are indicated (see Experimental section). ^b Half-lives were obtained as 11.3 h (for *b*) and 13.5 h (for *c*). ^d These reactions occurred very slowly (half-life > 30 h).

marked contrast, NH₄⁺ ion was extracted by the multi-armed cyclam (7) more effectively than by the simple cyclam (6). Although its extraction efficiency was not so high, introduction of furan moieties into the cyclam ring clearly promoted extraction of NH₄⁺ ion. A CPK molecular model of cyclam (7)-NH₄⁺ cation complex strongly suggests that NH₄⁺ cation would be wrapped 'tetrahedrally', implying the presence of hydrogen bonds to the two diametrically opposed ring-nitrogen atoms as well as to two furan-oxygen atoms. A similar molecular cavity for tetrahedral guest-binding has been reported in the 1,4,7,10-tetrakis-(2-hydroxyethyl)1,4,7,10-tetraazacyclododecane system.¹⁰

Our armed macrocycles offered characteristic cation-extraction properties, based on variation of parent macrocyclic ligands and ligating donor side-arms. Such cation-extraction abilities should be effective in phase-transfer catalyses and cation-transport systems.

Catalytic Activity of Double Armed Crown Ethers in Phase-transfer Reactions.—Cryptands and other potential cation-ligating macrocycles are known to solubilize inorganic salts and to activate anions in non-polar solvents.¹¹ Their strong ligations impose complete shielding of guest cations and lead to activation of anions. Since the employed armed macrocycles were postulated to wrap around the guest cations *via* three-dimensional co-ordination, we examined the double armed crown ether (3) as an anion-activating catalyst in actual chemical reactions. As a preliminary research topic, typical phase-transfer reactions were carried out in benzene. The reactions were followed by monitoring the disappearance of substrates (alkyl bromide) and/or the appearance of products by means of g.l.c. (see Experimental section). The initial rates of double armed crown ether (3)-catalysed reactions are shown in Table 2 and compared with those of the simple crown ether (2) and those of cryptand (5). In the absence of these catalysts, no appreciable conversion was detected during experiment periods (< 14 h).

Double armed crown ether (3) showed excellent catalytic activity in some solid-liquid phase-transfer reactions (Table 2). Its catalytic activity varied considerably on altering the combination of nucleophile and substrate, but was generally higher than that observed with crown ether (2), and was sometimes comparable with that of cryptand (5). For example, octyl bromide was easily converted into octyl iodide at 34 °C in the presence of potassium iodide (2 equiv.) and a catalytic amount of crown ether (3) (0.05 equiv.). The half-life (11.3 h) of compound (3) was confirmed to be shorter than that of the corresponding cryptand (5) system (> 16 h). When lithium iodide, sodium iodide, and caesium iodide were employed as I⁻

ion source, reaction rates were slightly accelerated even on addition of the double armed crown ether (3). Under the employed phase-transfer reaction conditions, I^- ion was effectively transferred together with K^+ ion and well activated in the non-polar solvent (benzene). Since extraction experiments (Table 1) revealed that the crown ether (3) extracted $KClO_4$ more effectively than $LiClO_4$, $NaClO_4$, and $CsClO_4$, such catalytic behaviour was parallel to its extraction behaviour. These findings suggest that the double armed crown ether (3) formed as effective inclusion complex with K^+ cation so as to activate the counter-anion, in a similar manner to some cryptand compounds.

Transport Properties of Double Armed Crown Ethers.—Cation-transport properties of armed macrocycles (1)–(7) were studied in a $CHCl_3$ or CH_2Cl_2 liquid-membrane system. Membrane transport is composed of a series of complicated elementary processes, but some of them are similar to those of cation-extraction and phase-transfer processes: the macrocycle solubilizes the guest cation salt into the non-polar membrane and facilitates transport from the source aqueous phase (Aq. I) through the membrane to the receiving aqueous phase (Aq. II) (Figure 2).^{1,2} The measured values of initial transport rates are summarized in Table 3.

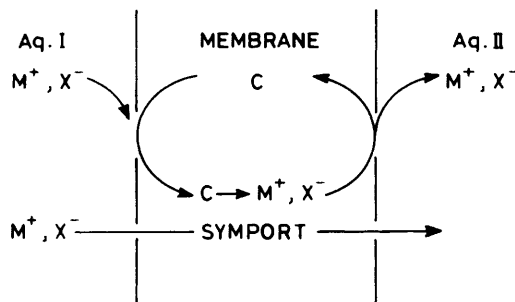


Figure 2. Liquid membrane systems for transport of cation perchlorates. C: Macrocylic carrier; M^+ : Guest cation; X^- : Perchlorate anion

Double armed crown ethers (3) and (4) showed characteristic transport properties which were, by and large, different from those of the simple crown ethers (1) and (2) and the cryptand (5) (Table 3). Among the examined alkali and alkaline earth cations, crown ether (3), bearing furan-oxygen atoms on its side-arms, mediated transport of K^+ , Ba^{2+} , NH_4^+ , and Pb^{2+} ions very effectively. Since its transport efficiencies were much higher than those of crown ethers (1) and (2), introduction of ligating donor arms significantly enhanced cation-transport abilities as well as cation-extraction abilities. When crown ether (4), bearing thiophene-sulphur atoms, was employed as a carrier, its transport efficiencies were generally lower than those of the furan-bearing crown ether (3), but transport of Pb^{2+} ion was highly facilitated with (4). These transport properties of double armed crown ethers were apparently determined by the size of the parent diaza-crown ring, but the nature of the ligating donor-arm groups also affected the transport characteristics.

Figure 3 shows the relationships between cation-extraction abilities and cation-transport abilities of diaza-crown ether derivatives (2)–(5). Each plot shows a distinct maximum, suggesting that the guest cation, complexed moderately with macrocycle, was effectively transported. Although direct comparisons are difficult, similar conclusions have been reported in simple crown ether and cryptand systems.^{1,3} Since cation-binding efficiencies and selectivities of the armed crown ethers were determined by co-ordination characteristics of their ligand

Table 3. Transport properties of 'double armed crown ethers'

Salt	10^6 Transport rate ^a (mol/h)				
	(1)	(2)	(3)	(4)	(5)
$LiClO_4$	<0.3	<0.3	<0.3	<0.3	0.84
$NaClO_4$	<0.3	<0.3	0.78	<0.3	6.54
$KClO_4$	2.16	0.97	7.52	2.59	1.21
$AgClO_4$	0.68	1.82	1.68	<i>b</i>	2.02
NH_4ClO_4	2.93	1.23	4.93	1.67	2.04
$CsClO_4$	<0.3	0.33	0.92	0.56	1.42
$Ca(ClO_4)_2^c$	<0.3	<0.3	<0.3	<0.3	0.75
$Sr(ClO_4)_2^c$	0.37	0.30	1.37	0.32	2.85
$Ba(ClO_4)_2^c$	3.76	0.53	12.50	1.86	7.33
$Pb(ClO_4)_2^c$	2.32	9.09	8.17	16.00	1.63

^a Initial transport rates of ClO_4^- anion across a $CHCl_3$ liquid membrane are indicated (see Experimental section). ^b Ag^+ was deposited on the wall of the transport cell. ^c These divalent cations were confirmed to be transported with half the efficiency of the indicated rates.

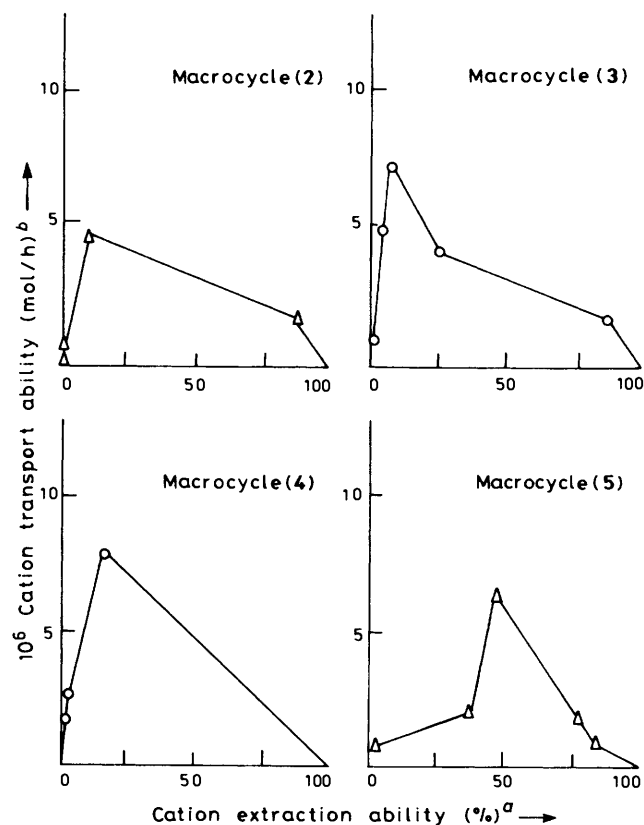


Figure 3. Relationships between cation-extraction ability and cation-transport ability of macrocycle. (a) see Table 1; (b) see Table 3

components, they may be easily modified to form complexes, with a desired guest cation, of moderate stability which are suitable for rapid extraction and smooth release of the cation.

Transport Properties of Armed Cyclams (6) and (7).—Armed macrocycles derived from an aza-macrocycle (cyclam) were also applied to our investigation of cation membrane transport. The characteristics of heteroatom macrocycles led to new and specific transport phenomena. Typical results are shown in Table 4.

Table 4. Transport properties of 'armed macrocycles'

Salt	10 ⁶ Transport rate ^a (mol/h)			
	(6)		(7)	
LiClO ₄	<0.3	(<0.3)	<0.3	(<0.3)
NaClO ₄	<0.3	(<0.3)	<0.3	(<0.3)
KClO ₄	<0.3	(<0.3)	<0.3	(<0.3)
AgClO ₄	<0.3	(0.35)	<0.3	(<0.3)
NH ₄ ClO ₄	<0.3	(1.29)	1.15	(3.35)
CsClO ₄	<0.3	(<0.3)	<0.3	(<0.3)
Ba(ClO ₄) ₂	<0.3	(<0.3)	<0.3	(<0.3)
Pb(ClO ₄) ₂	<0.3	(<0.3)	<0.3	(<0.3)

^a Initial transport rates of ClO₄⁻ anion across a CHCl₃ liquid membrane are indicated. The values shown in parentheses are those across a CH₂Cl₂ liquid membrane.

An armed aza-macrocycle, the multi-armed cyclam (7), specifically discriminated NH₄⁺ ion from K⁺ and related cations in transport processes. It mediated selective transport of NH₄⁺ ion, while H⁺, K⁺, and other examined cations were hardly transported (Table 4). Since the simple cyclam (6) exhibited a low transport rate of NH₄⁺ ion, the co-operative action of furan-arms and parent cyclam skeleton must be essential for promoting the NH₄⁺ ion transport process. Such a selective transport of NH₄⁺ ion was not realized by the double armed crown ether (3) having similar furan moieties, and this type of aza-macrocycle can be considered as a unique receptor molecule capable of specific guest-binding. Other types of heteromacrocycles show interesting cation-binding properties, and further extensions of this study may lead to new and excellent host molecules.¹⁴

Conclusions

Armed macrocycles are a new class of host molecules which are characterized by cation-ligating donor arms and parent macrocyclic ligand skeletons. Their unique ligand structures allowed (i) formation of stable and lipophilic complexes with several guest cations *via* three-dimensional co-ordinations and (ii) versatile cation-binding selectivities depending on combinations of cation donor sites.

These cation-binding properties of armed macrocycles offered excellent catalytic activities for phase-transfer reactions and characteristic membrane transport abilities, which were not attained with simple crown ethers and related macrocycles. Since their cation-binding properties and subsequent chemical functions were significantly controlled by appropriate choice of ligating donor arms and parent macro-ring, the present type of armed macrocycles may provide new possibilities in the design of novel macrocyclic host molecules with unique and useful chemical functions.

Experimental

M.p.s were measured on a Yanaco MP-3 micro-melting point apparatus and are uncorrected. ¹H N.m.r. spectra were measured on a JEOL-PMX60 spectrometer for CDCl₃ solutions with SiMe₄ as internal reference, and i.r. spectra were obtained for Nujol mulls on a Hitachi 260-30 spectrophotometer. Microanalyses were performed by MES Testing and Research Centre Co. Ltd, Tamano, Okayama.

Materials.—Crown ether (1) and cryptand (5) were purchased from Merck Japan and employed as received. Other reagents such as metal perchlorates and solvents were also commercially available and used without further purifications.

Synthesis.—7,16-Dibenzyl-1,4,10,13-tetraoxa-7,16-diaza-cyclo-octadecane (2). A CHCl₃ solution (15 ml) of benzyl chloride (3.48 g) was added dropwise to an aqueous solution (15 ml) of Kryptofix 22 (Merck Japan; 3.00 g) and NaOH (2.00 g). After the mixture had been vigorously stirred at room temperature overnight, the organic phase was washed successively with aqueous HCl and water, and dried over Na₂SO₄. The solvent was removed and recrystallization from ether gave white crystals of the title product (2) (60%), m.p. 82 °C, with physical properties identical with those reported previously.¹⁵

7,16-Difurfuryl-1,4,10,13-tetraoxa-7,16-diaza-cyclo-octadecane (3).* To a stirred tetrahydrofuran (THF) solution (30 ml) of Kryptofix 22 (1.20 g) and pyridine (0.80 ml) was added dropwise furoyl chloride (1.44 g). After the mixture had been refluxed for 8 h, the solvent was evaporated off. A CHCl₃ solution (200 ml) of the residue was washed successively with aqueous HCl and water (100 ml each), and dried over Na₂SO₄. The white solid amide was purified by chromatography on alumina (CHCl₃) and dried *in vacuo*.

The obtained amide was reduced by diborane under dry nitrogen as follows. The amide (1.70 g) was suspended in a 1M solution of diborane in THF (40 ml). The reaction mixture was refluxed for 8 h. After the usual work-up, pure *title compound* (3) was obtained by recrystallization from ether-hexane (50%), m.p. 37–38 °C; δ_H 2.80 (8 H, CH₂N), 3.63 (16 H, CH₂O), 3.73 (4 H, CH₂furyl), 6.27 (4 H, furan), and 7.40 (2 H, furan); ν_{max} 3 090, 1 500, 1 450, 1 140, 1 105, and 770 cm⁻¹ (Found: C, 62.8; H, 7.9; N, 6.9. C₂₂H₃₄N₂O₆ requires C, 62.5; H, 8.1; N, 6.6%).

7,16-Dithienyl-1,4,10,13-tetraoxa-7,16-diaza-cyclo-octadecane (4). The synthesis of crown ether (4) was analogous to that of compound (3). Chromatography (alumina; CHCl₃) followed by recrystallization (ether-hexane) afforded the *title compound* (4) as a white crystalline solid (60%), m.p. 60–61 °C; δ_H 2.87 (8 H, CH₂N), 3.63 (16 H, CH₂O), 3.97 (4 H, CH₂thienyl), and 6.97–7.27 (6 H, thiophene); ν_{max} 3 090, 1 530, 1 160–1 050, and 750 cm⁻¹ (Found: C, 58.0; H, 7.55; N, 6.3; S, 13.8. C₂₂H₃₄N₂O₄S₂ requires C, 58.1; H, 7.5; N, 6.2; S, 14.1%).

1,4,8,11-Tetrabenzyl-1,4,8,11-tetra-azacyclotetradecane (6). Cyclam (6) was obtained in a similar manner to crown ether (2). White crystals of the *product* (70%), m.p. 154–155 °C, were purified by recrystallization from CH₂Cl₂-methanol, δ_H 1.63–1.93 (4 H, CH₂CH₂CH₂), 2.40–2.73 (16 H, CH₂N), 3.47 (8 H, CH₂Ph), and 7.27 (20 H, Ph); ν_{max} 1 602 cm⁻¹ (Found: C, 81.1; H, 8.4; N, 10.1. C₃₈H₄₈N₄ requires C, 81.4; H, 8.6; N, 10.0%).

1,4,8,11-Tetra-furfuryl-1,4,8,11-tetra-azacyclotetradecane (7). The *title product* was obtained in a similar manner to crown ether (3), in the form of white crystals (30%), m.p. 84–85 °C; δ_H 1.67 (4 H, CH₂CH₂CH₂), 2.60 (16 H, CH₂N), 3.67 (8 H, CH₂furyl), 6.17 (4 H, furan), 6.40 (4 H, furan), and 7.43 (4 H, furan); ν_{max} 3 130, 3 110, 1 505, 1 470, and 735 cm⁻¹ (Found: C, 69.25; H, 7.7; N, 10.9. C₃₀H₄₀N₄O₄ requires C, 69.2; H, 7.7; N, 10.8%).

Extraction Experiment.—Extraction experiments were conducted by adding a CHCl₃ solution of macrocycle (0.02 mmol/2 ml) to an aqueous solution of metal perchlorate (0.02 mmol/2 ml). After the mixture had been stirred for 3 h, the aqueous phase was separated. The concentrations of ClO₄⁻ anion in the aqueous phase were determined by an ion-selective electrode (Orion Model 93-81) for all runs. The concentrations of several cations were similarly determined (Orion Model 93-19 for K⁺, 97-11 for Na⁺, 95-10 for NH₄⁺, 92-32 for Ba²⁺, 94-82 for Pb²⁺, and DKK Model 7080 for Ag⁺ ions). They agreed with those obtained for ClO₄⁻ anion [except for some

* Another synthetic method for crown ether (3) has recently been reported: V. J. Gatto and G. W. Gokel, *J. Am. Chem. Soc.*, 1984, **106**, 8240.

extractions with cryptand (5)]. Since cryptand (5) is partially soluble in the aqueous phase used, Ag^+ , Pb^{2+} , and other cations could not be determined by the ion-selective electrode method in this case. Hence, the extraction efficiencies of cryptand (5) (Table 1) were calculated from the concentrations of ClO_4^- anion alone. Table 1 summarizes the average values of three independent experiments.

Phase-transfer Reaction Conditions.—Inorganic salt (2 mmol) was added at ambient temperature to a solution of substrate (alkyl bromide, 1 mmol) and diphenyl ether (internal standard for g.l.c. analysis) in benzene (5 ml; water content <0.1%). After sonication (Bransonic 2) for 10–15 min, a macrocyclic catalyst (0.05 mmol) was added to the solution. Then the stirred mixture was immersed in a thermostatted water-bath ($34 \pm 0.5^\circ\text{C}$). The reaction rates were determined by g.l.c. (FID; 1 m \times 3 mm in 15% silicone DC-550 on 60–80 mesh Uniport B; oven temperature 150–160 $^\circ\text{C}$). When crown ether (2) and cryptand (5) were employed as catalysts, the decreases in [substrate] and increase in [product] obeyed pseudo-first-order kinetics as described previously.¹¹ However, double armed crown ether (3)-catalysed reactions could not be analysed easily. Hence, the observed rates at the initial stages of reaction (<5 h) were compared for these catalyst systems. The values indicated in Table 2 were the averages of three independent runs.

Transport Experiments.—Transport experiments were carried out at room temperature in a U-tube glass cell (2.0 cm, i.d.) as reported previously.¹² A solution of a macrocycle in CHCl_3 or CH_2Cl_2 (0.0372 mmol/12 ml) was placed in the base of the U-tube, and two aqueous phases (Aq. I: MClO_4 , 0.5 mmol/5 ml; Aq. II: distilled water, 5 ml) were placed in the arms of the U-tube, floating on the membrane phase. The membrane phase was constantly stirred with a magnetic stirrer. The transport rates were calculated from the initial rates of appearance of guest cations and co-transported ClO_4^- anion into the Aq. II phase, which were determined by means of ion-selective electrode techniques as mentioned above. Reproducibilities were confirmed as $\pm 15\%$ or better.

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