ELSEVIER

Coordination Chemistry Reviews
148 (1996) 97–113

COORDINATION
CHEMISTRY
REVIEWS

Alkylphosphoric acid armed crown ethers having a specific cation binding ability

Yoichi Habata, Sadatoshi Akabori

Department of Chemistry, Faculty of Science, Toho University, 2-2-1 Miyama, Funabashi, Chiba 274, Japan

Received 30 January 1995

Contents

Abstract

The syntheses, transport *via* a bulk liquid membrane, and cation binding properties of alkylphosphoric acid armed crown ethers are reported. The new armed crown ethers and monoaza crown ether containing 13–19-membered crown rings are synthesized by two methods: (a) the reaction of a hydroxymethyl-substituted crown ether with dichloroalkylphosphate followed by hydrolysis; (b) the one-pot reaction of a hydroxymethyl crown ether with an alkylphosphate in the presence of dicyclohexylcarbodiimide–pyridine. The transport experiments reveal that (i) the alkylphosphoric acid armed crown ethers exhibit specific transport abilities for alkali metal cations which fit the cavity size of their crown rings, (ii) the structure of the bridgehead carbon which bears the pendant arm (trimethylene unit and dimethylene unit) significantly influences the cation selectivity, and (iii) for the zwitterion-type phosphoric acid armed monoaza crown ether the cation selectivities can be controlled by altering the aqueous phase in the liquid membrane transport system. Computer and CPK modelling suggested that the phosphoric acid site is a cooperative coordination site. Spectroscopic data

SSDI 0010-8545(95)01191-9

(^{13}C nuclear magnetic resonance and IR) supported the proposed interaction of the cavity complexed crown ether with the side arm.

Keywords: Crown ether; Phosphoric acid; Alkali metal; Transport

---

1. Introduction

Since Pedersen's pioneering work in 1967 [1], the cation binding properties of macrocyclic compounds, such as the crown ether and related compounds, have received much attention. To develop specific cation-selective crown compounds, several groups have investigated named lariat ethers [2] or armed crown ethers [3], which have one or more side arms as an additional binding site. In particular, crown ethers possessing pendant ionizable groups such as phenolic OH [4], carboxylic [5] or arylphosphonyl [6] groups have recently attracted much attention. Here we mainly review the chemistry of the alkylphosphoric acid armed crown ethers.

2. Advantages of ionizable armed crown ethers

Liquid membrane transport is one of the noteworthy methods for cation separation [7]. Crown ethers having an ionizable group as a side arm, when compared with simple crown ethers, provide (i) rapid incorporation of cations from the basic aqueous phase into the organic phase and their rapid release to the acidic aqueous phase and (ii) enhancement of cation selectivity by formation of a three-dimensional cavity using the crown ring and the anion site of the pendant arm [8]. With these properties of the ionizable crown ether compound, an ion-selective active transport system can form as shown in Fig. 1. That is, the crown ether having an ionizable group can form complexes with cations using crown ether and ionizable sites at the interface between the basic aqueous phase and organic membrane, and then the cations of the complexes are released to the aqueous phase (acidic) by protonation of the ionizable site at the interface between the organic membrane and the acidic phase. Thus metal cations are actively transported from the basic to the acidic aqueous phases and protons are transported from the acidic to the basic aqueous phases in the transport system.

3. Molecular design of alkylphosphoric acid armed crown ethers

The first synthesis of crown ethers with phosphoric acid related functional groups was reported by Tazaki et al. in 1982 [6]. They synthesized monoaza and diaza crown ethers with a phosphonomethyl group. These armed aza crown ethers had unique selectivities for alkaline earth and several transition metals in aqueous solution. This indicated that the crown ethers bearing phosphorus acid related functional groups have a strong affinity toward metal cations. An application for liquid mem-

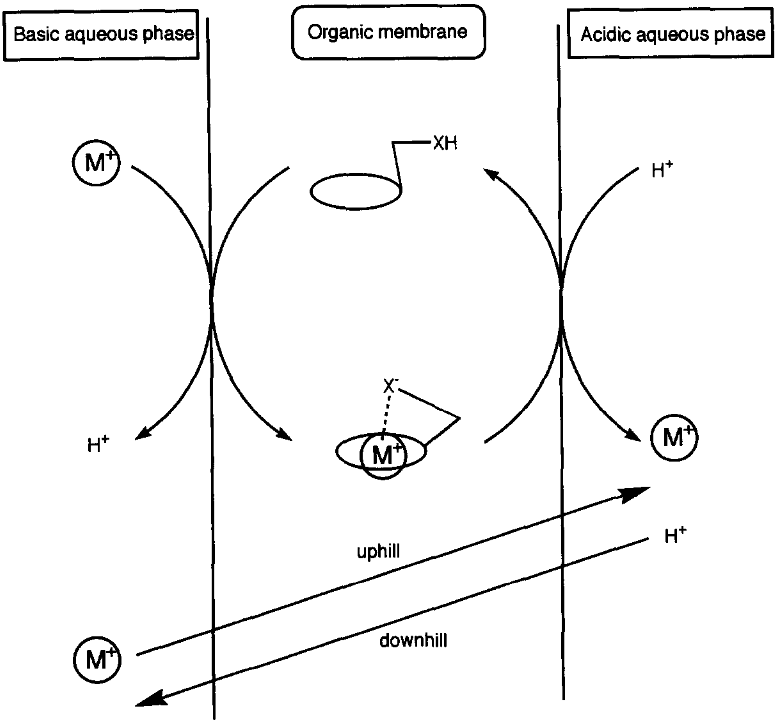
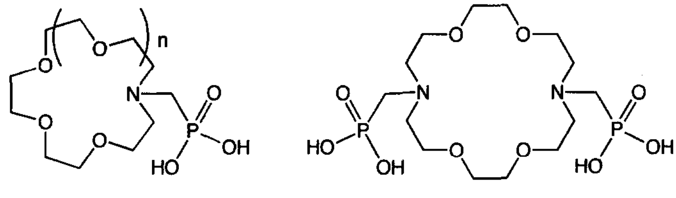


Fig. 1. Liquid membrane system for active transport: XH = an ionizable group.

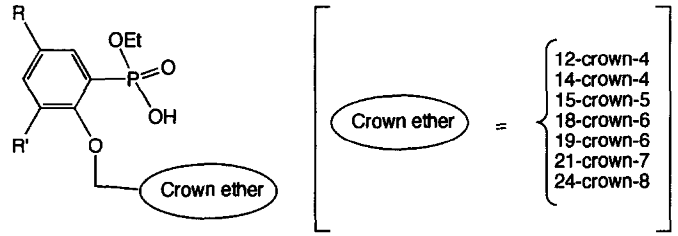
brane transport of an arylphosphonic acid armed crown ether toward alkali metal cations was carried out in 1987 by Bartsch's group [9], who synthesized a series of phosphonic acid monoethyl ester armed crown ethers (Fig. 2). Some groups have reported X-ray structural studies of ionizable armed crown ether complexes. Shoham et al. [10] and Sachleben et al. [11] reported the X-ray structures of an Li^+ ion complex of a dibenzo-14-crown-4 derivative with a carboxyl group and an Na^+ ion complex of a dibenzo-14-crown-4 derivative with an arylphosphonic acid functional group respectively (Fig. 3). They noted that the ionizable groups did not coordinate with the polyether ring complexed cations. Also, conformational requirements of this coordination force the carboxylate and phosphinate anions away from the metal site. These results have led us to design new armed crown ethers which have no coordination site except for the ionizable group in the side arm.

4. Synthesis

The new armed crown ethers were synthesized by two methods: (i) the reaction of dichloroalkylphosphate [12] with hydroxymethyl crown ethers followed by



Tazaki et al. (1982)



Bartsch et al. (1987)

Fig. 2. Some armed crown ethers with phosphonomethyl and phosphonyl functional groups.

hydrolysis and (ii) the reaction of monoalkylphosphate with hydroxymethyl crown ethers in the presence of dicyclohexylcarbodiimide (DCC) and pyridine [13,14].

Alkylphosphoric acid armed dibenzo-14-crown-4 (**2**) [15,16] and benzo-14-crown-4 (**4a**–**4c**) [16,17] were synthesized by the reaction of hydroxymethyl dibenzo-14-crown-4 (**1**) [16,18] and benzo-14-crown-4 (**3**) [19] respectively with dichloroalkylphosphate in benzene or THF followed by hydrolysis (Fig. 4).

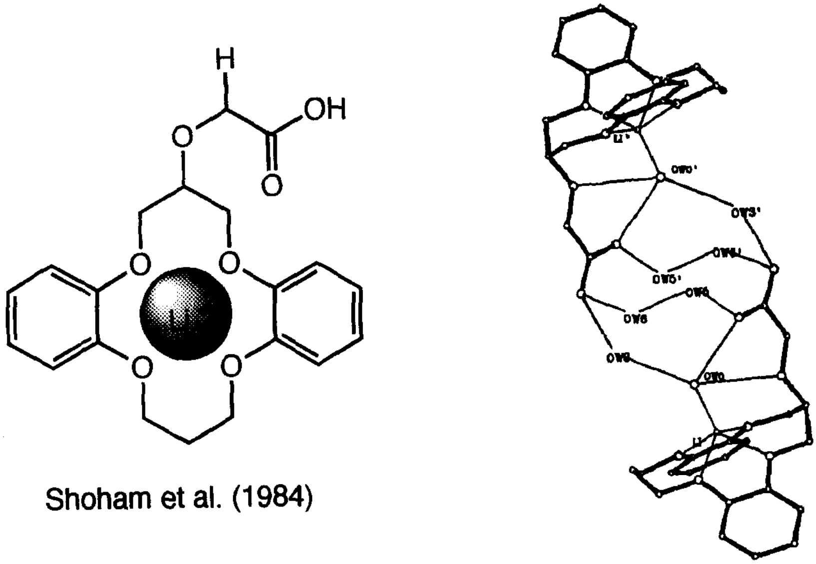
Aliphatic crown ethers with a dodecylphosphoric acid side arm (**6**, **8**, **10**, **12**, **14**, **16**) were prepared by a one-pot reaction of the appropriate hydroxymethyl 13-crown-4 (**5**) [20], 14-crown-4 (**7**) [20], 15-crown-5 (**9**) [21], 16-crown-5 (**11**) [22], 18-crown-6 (**13**) [23], and 19-crown-6 (**15**) [22] respectively with dodecylphosphate and DCC in pyridine at room temperature (Fig. 5) [24]. By this method, use of a dichloroalkylphosphate with a long alkyl chain is avoided. It was found to be difficult to purify such dichloroalkylphosphates by vacuum distillation.

The zwitterion-type alkylphosphoric acid armed aza crown ether **18** was also synthesized by the two methods mentioned above (Fig. 6) [25]. In the first method **17** was reacted with dichlorododecylphosphate in the presence of sodium hydride followed by hydrolysis and in the second method **17** was coupled with dodecylphosphate in the presence of DCC and pyridine.

5. Liquid membrane transport

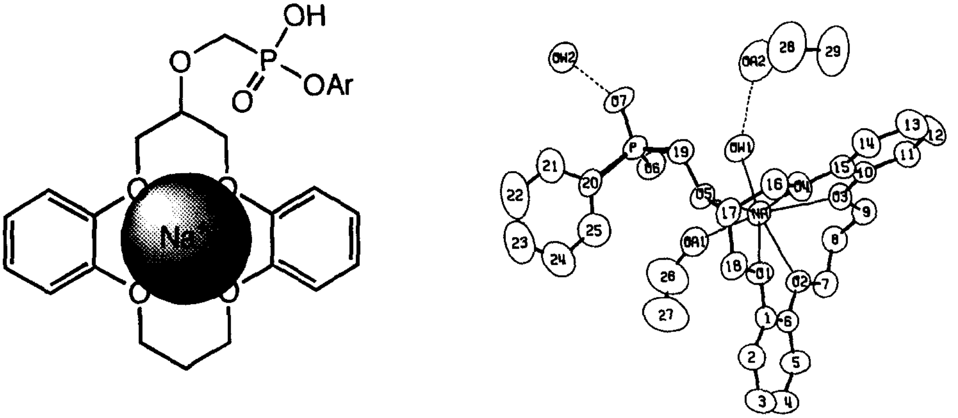
5.1. Transport apparatus

Several types of apparatus have been utilized for liquid membrane transport studies. Fig. 7 shows a typical U-tube type cell for the bulk liquid membrane trans-



Shoham et al. (1984)

Reproduced with permission from American Chemical Society



Sachleben et al. (1988)

Reproduced with permission from American Chemical Society

Fig. 3. Crystal structures of Li^+ and Na^+ complexes of dibenzo-14-crown-4 derivatives having an ionizable side arm.

port. The aqueous and organic (membrane) phases were stirred at 135 rev min^{-1} and 540 rev min^{-1} respectively using constant-speed motors. The amounts of metal ions in the receiving phase were measured by atomic absorption spectrometry. The

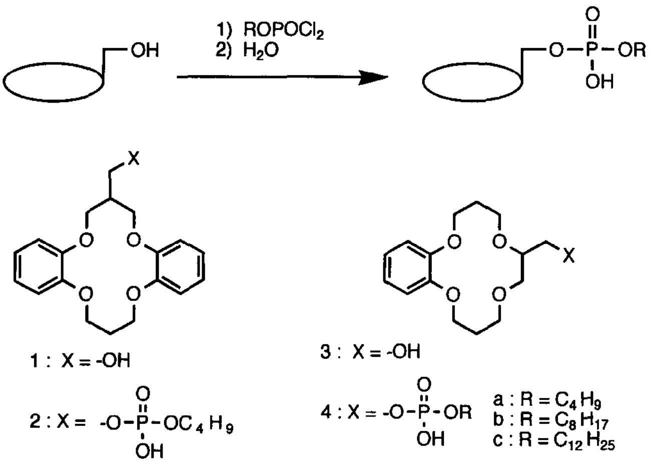


Fig. 4. Dibenzo- and benzo-14-crown-4 derivatives with an alkylphosphoric acid functional group. Adapted from The Royal Society of Chemistry.

initial transport rate was calculated from the increase in the cation concentration in the receiving phase after a period of 9 h. The transport rate reproducibility for alkali metal ions was found to be ±15% or better.

5.2. *Liquid membrane transport by alkylphosphoric acid armed crown ethers*

It is well known that the Li^+ ion is strongly hydrated by water and is only poorly extracted from an aqueous phase into an organic phase by neutral crown ether compounds [26]. The dibenzo- and benzo-14-crown-4 having ionizable phosphoric acid functional groups (**2** and **4a**–**4c**) can selectively transport Li^+ ion from a basic source phase to an acidic receiving phase via an organic membrane (Table 1). The selectivity for metal cations, in general, is inversely proportional to the transport rate in a transport system [27]. However, a series of benzo-14-crown-4 derivatives, **4a**–**4c**, also exhibited significant enhancement in the transport rate and maintained high Li^+ ion selectivity when compared with **2** and hydroxymethyl crown ethers (**1** and **3**).

In the alkylphosphoric acid armed aliphatic crown ethers, the structure around the bridgehead carbon bearing the pendant arm influences the selectivity of the alkali metal cation (Table 2). The hydroxymethyl aliphatic crown ethers (**5**, **7**, **9**, **11**, **13** and **15**) rarely exhibit a transport rate toward the tested cations (less than 0.01×10^{-6} mol h^{-1}) under these conditions because they have a hydrophilic character. In contrast, a drastic enhancement in the transport rate was observed by introduction of a dodecylphosphoric acid moiety into the crown ethers. Interestingly, there are significant differences in cation selectivity between **6** and **8**, and **10** and **12**, which had a pendant arm attached to the dimethylene and trimethylene units. Among the crown-4 derivatives, **8**, which had the pendant arm added to the 14-crown-4, displayed Li^+-selective transport, although **6** (13-crown-4 derivative) did not exhibit

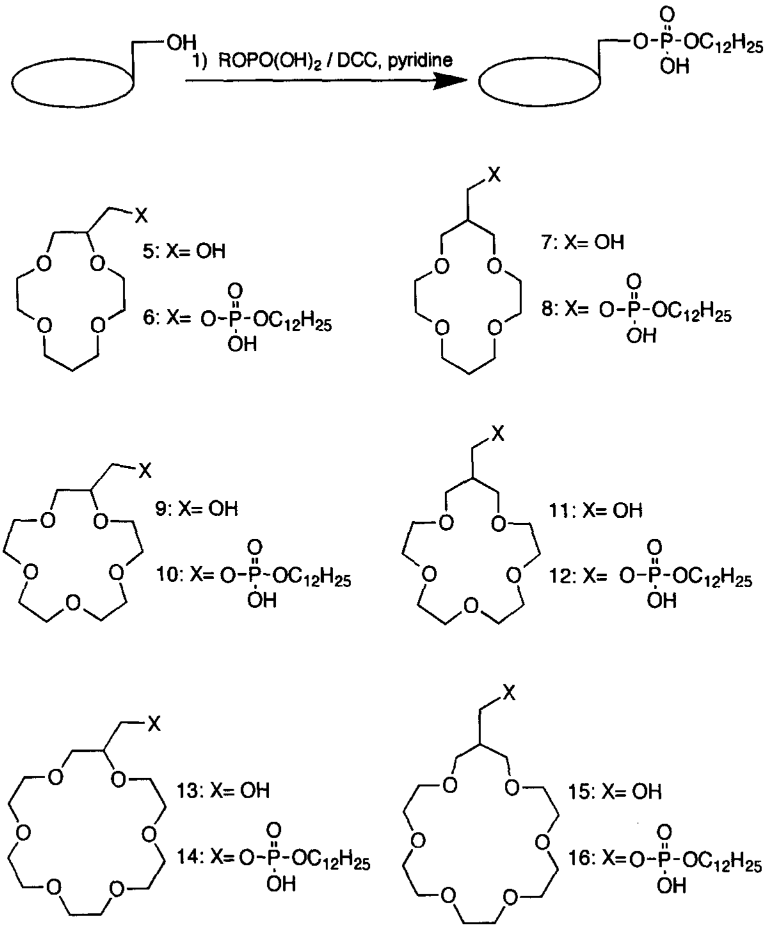
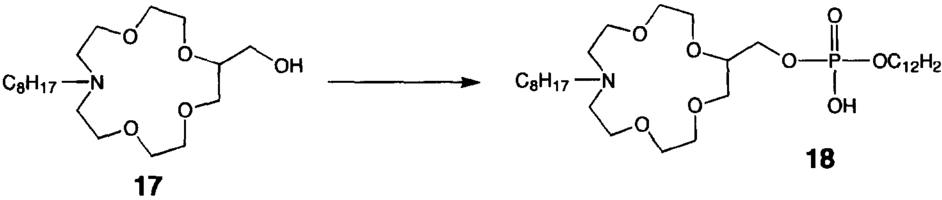


Fig. 5. 13-Crown-4–19-crown-6 derivatives with an alkylphosphoric acid functional side arm.



Method 1: 1) $C_{12}H_{25}OP(O)Cl_2$ / NaH in THF, 2) H_2O

Method 2: $C_{12}H_{25}OP(O)(OH)_2$ / DCC - pyridine in $CHCl_3$

Fig. 6. Monoaza-15-crown-5 with an alkylphosphoric acid functional group. Adapted from Hetero Corporation.

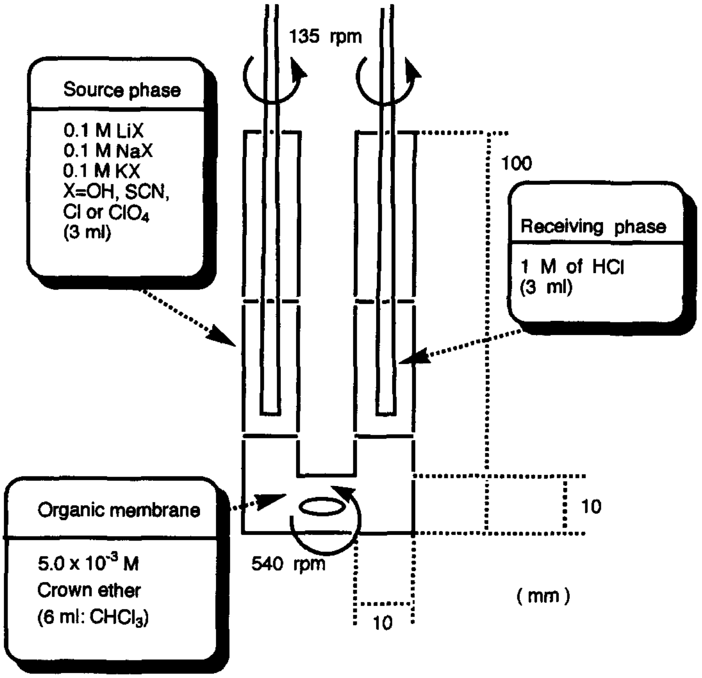


Fig. 7. U-tube cell for transport experiments.
Adapted from Elsevier Science Publishers.

Table 1
Competitive facilitated transport with **1**–**4c**

Compound	Transport rate ($\times 100$ μmol h^{-1})			Selectivity			Ratios of transport rate		
	Li^+	Na^+	K^+	$Li^+:Na^+$	$Li^+:K^+$	$Na^+:K^+$	Li^+	Na^+	K^+
1	2.0	1.5	0.4	1.3	5.0	3.8	**2**:1		
2	281.5	19.5	3.8	14.4	74.0	5.1	140.7	13.0	9.5
3	28.2	14.1	11.7	1.9	2.4	1.2	**4a**–**4c**:**3**		
4a	129.0	26.7	24.1	4.8	5.4	1.1	4.6	1.9	2.1
4b	941.4	163.9	128.1	5.7	7.3	1.3	33.4	11.6	10.9
4c	1342.1	235.7	165.3	5.7	8.1	1.4	47.5	16.7	14.1

Adapted from The Royal Society of Chemistry.

selectivity toward Li^+. Species **12** (16-crown-5 derivative) also selectively transports Na^+, although **10** (15-crown-5 derivative) had some selectivity toward K^+. From an examination of a CPK molecular model and computer modelling, the differences in cavity size between **6** and **8**, **10** and **12**, and **14** and **16** were estimated to be 0.1 Å [28]. Bartsch and coworkers reported that lipophilic carboxylic acid armed

Table 2
Competitive transport of alkali metal cations with **5–16**

Carrier	Transport rate ($\times 10^6$ mol h^{-1})			Carrier	Transport rate ($\times 10^6$ mol h^{-1})			Selectivity of **6, 8, 10, 12, 14** and **16**	
	Li^+	Na^+	K^+		Li^+	Na^+	K^+		
								$Li^+:Na^+$	$Li^+:K^+$
5	<0.01	<0.01	<0.01	**6**	0.79	1.18	0.78	0.7	1.0
7	<0.01	<0.01	<0.01	**8**	0.81	0.14	0.02	5.8	40.5
								$Na^+:Li^+$	$Na^+:K^+$
9	<0.01	<0.01	<0.01	**10**	0.33	0.47	0.52	1.4	0.9
11	<0.01	<0.01	<0.01	**12**	0.35	1.44	0.51	4.1	2.8
								$K^+:Li^+$	$K^+:Na^+$
13	<0.01	<0.01	0.01	**14**	0.04	0.17	1.15	18.8	6.8
15	<0.01	<0.01	<0.01	**16**	0.31	0.19	1.21	3.9	6.4

Adapted from American Chemical Society.

13-crown-4 and 15-crown-5 derivatives (Fig. 8) efficiently extracted size-matched alkali metal cations [29]. Therefore, the selectivity changes in these new crown ethers having the same oxygen atoms may be attributed to the introduction of the dodecylphosphoric acid moiety to the crown ring.

A zwitterion-type carboxylic acid armed monoaza crown ether (Fig. 9, **20**) was reported by Shinkai *et al.* in 1983 [30]. They reported that **20** and the Ca^{2+} complex of **20** can be used for the transport of alkali metal and alkaline earth metal cations and several amino acids respectively. We designed a new zwitterion-type armed crown ether (**18**) in order to develop a "selectively controllable host compound", which can control the cation selectivities through the pH of the aqueous phase. Competitive transport experiments for alkali metal cations with a zwitterion-type crown ether **18** were also performed (Table 3). When the source phase was about pH 5.6, compounds **18**, **19** and **10** effectively transported sodium ions. On the contrary, when the source phase was about pH 11, compound **18** exhibited unique

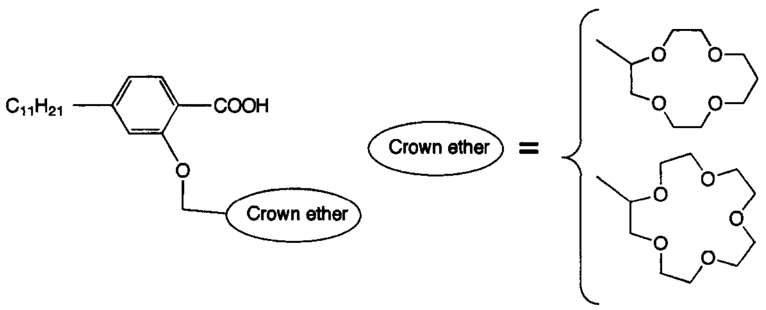
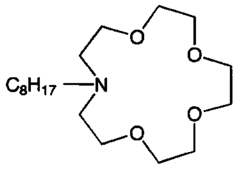
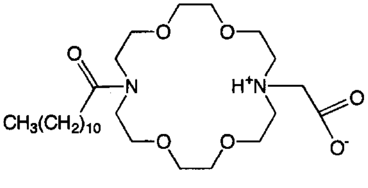


Fig. 8. Carboxylic acid armed 13-crown-4 and 15-crown-5 ethers.



19



20

Fig. 9. *N*-octylmonoaza-15-crown-5 (**19**). Zwitterion-type diazacrown ether (**20**) reported by Shinkai et al. [30].

Table 3
Competitive transport of **18**, **19** and **10** for alkali metal cations

Run	Compound	Counter-anion	pH of source phase	Transport rate ($\times 10^6$ mol h^{-1})			Selectivity		
				Li^+	Na^+	K^+	$Li^+:Na^+$	$Li^+:K^+$	$Na^+:K^+$
1	**18**	SCN^-	5.6	<0.01	0.16	0.04	—	—	4.0
2	**19**	SCN^-	5.6	<0.01	0.04	0.02	—	—	2.0
3	**10**	SCN^-	5.6	<0.01	0.13	0.03	—	—	4.0
4	**18**	OH^-	11.0	<0.14	0.09	0.08	1.6	1.7	1.1
5	**19**	OH^-	11.0	<0.01	<0.01	<0.01	—	—	—
6	**10**	OH^-	11.0	0.33	0.47	0.52	0.7	0.6	0.9

Adapted from the Hetero Corporation.

selectivity for lithium ion despite possessing a cavity which fits the diameter of the sodium ion. The azacrown ether **19** did not transport any cations, and the transport rate of potassium ions with **10** was comparable with that of sodium ions.

6. Cation binding properties

6.1. Binding properties of benzo- and dibenzo-14-crown-4 derivatives

Concerning the significant enhancement of the extractability and the transport rate toward Li^+ ions by **2** and **4a**–**4c** compared with **1** and **3**, the CPK molecular model and computer modelling (Fig. 10) showed that **2** and **4a**–**4c** formed a three-dimensional cavity which fits a Li^+ ion using the phosphate anion and the nearest oxygen atoms of the pendant site of the crown ring.

IR (Table 4), fast atom bombardment (FAB) mass (Fig. 11) and ^{13}C nuclear magnetic resonance (NMR) (Fig. 12) spectral studies were carried out in order to assess the hypotheses developed from the modelling experiment. As shown in Table 4, there are remarkable differences in phosphate site absorption between **2** and its Li^+ complex. Some groups reported that FAB mass spectrometry can be used to assess the binding ability between the crown ether and cation [31–35]. Fig. 11 shows the FAB mass spectrum using *m*-nitrobenzyl alcohol (NBA) as the matrix. Not only is

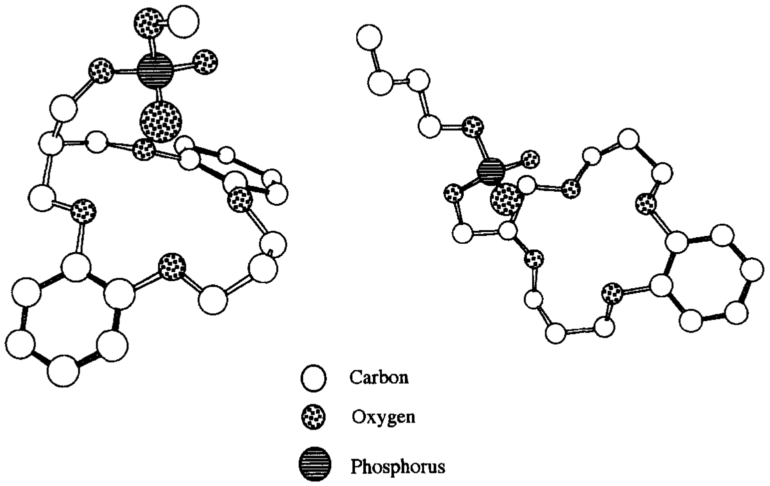


Fig. 10. Postulated conformations of **2** and **4a**.

Table 4
IR spectral data[a] of **2** and its Li^+ ion complex

Compound	$\nu(PO-H)$ (cm^{-1})	$\nu(PO-C)$ (cm^{-1})	$\nu(P=O)$ (cm^{-1})
2	2330	1000	1240
Li^+ complex	—	980	1240, 1100

Adapted from The Royal Society of Chemistry.
[a] KBr disk.

the ion peak due to the 1:1 complex $[\mathbf{2}^- + Li^+ + H^+]^+$ and an associated ion peak $[2(\mathbf{2}^- + Li^+) + H^+]^+$ observed but also unique one crown-two cation ion $[\mathbf{2}^- + 2Li^+]^+$ and two crown-three cation ion $[2(\mathbf{2}^- + Li^+) + Li^+]^+$ peaks in the Li^+ complex of **2**. These IR and FAB mass spectra suggest that the Li^+ ion in the complex is strongly bound by the ether oxygen of the crown ring and the phosphate anion. Also, as shown in Fig. 12, ^{13}C NMR spectral data indicated that the pendant phosphate anion and the nearest oxygen atom (*f* in Fig. 12) of the pendant site of the crown ring provide the major coordination for the Li^+ ion. These spectral studies support the modelling analysis.

6.2. *Binding properties of aliphatic crown ether derivatives*

Concerning differences in cation selectivity between **6** and **8**, and **10** and **12**, the CPK molecular model and computer modelling (Fig. 13) also showed that **8** and **12** formed three-dimensional cavities which fit Li^+ and Na^+ respectively using the phosphate anion of the side arm and the oxygen atom of the crown ring. However, **6** and **10** could not favourably form cavities to bind these ions. ^{13}C NMR spectral

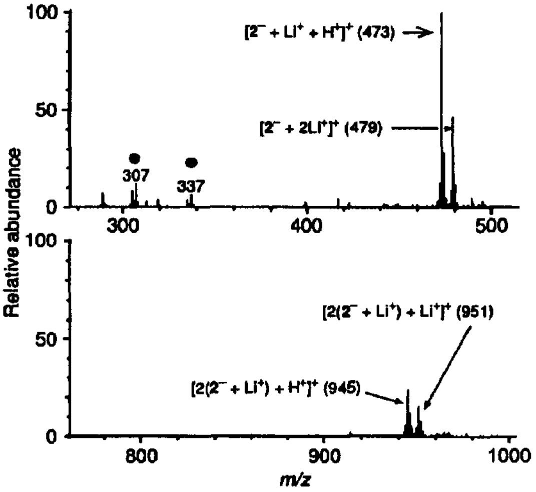


Fig. 11. FAB mass spectrum of the Li^+ ion complex of 2: ●, peaks originating from the NBA matrix system. Reproduced with permission from The Royal Society of Chemistry.

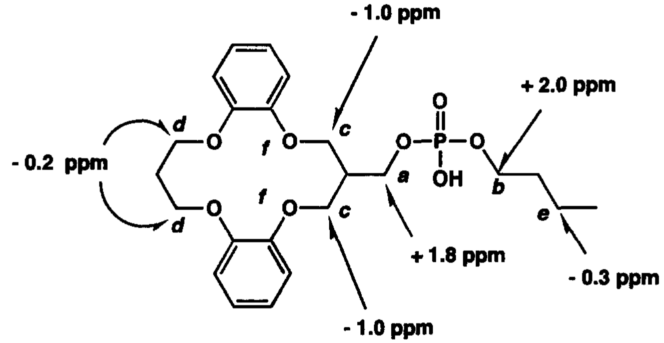
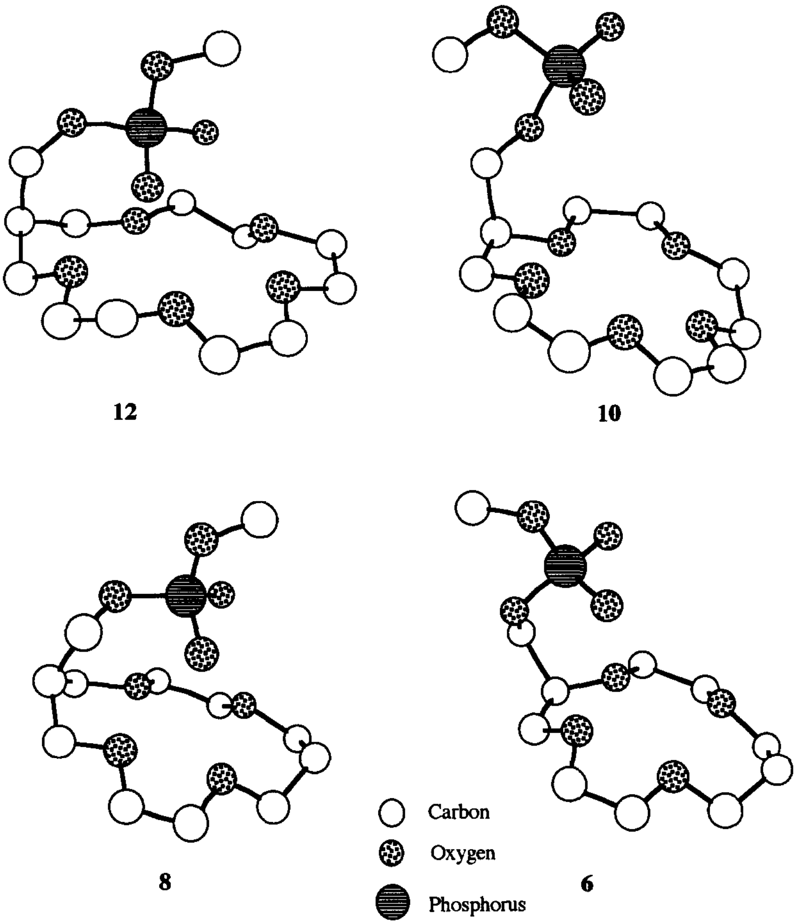


Fig. 12. ^{13}C NMR shift changes between 2 and the Li^+ ion complex of 2. Reproduced with permission from The Royal Society of Chemistry.

studies were also carried out in order to obtain more detailed structural information on the alkali metal complexes of **6**, **8**, **10**, **12**, **14** and **16** (Table 5). Significant chemical shift changes upfield of the methylene carbon atoms ($C^{a'}$) in the trimethylene unit of **8** and **12** were observed for the addition of size-matched alkali metal hydroxides (**8**+LiOH, +2.3 ppm; **12**+NaOH, +1.7 ppm), although small shift changes were observed when larger metal cations were added. As described in Section 6.1, the upfield shifts of the $C^{a'}$ carbon atoms suggested that the nearest oxygen atoms of the pendant site in the crown ring provide the major coordination site for the cations. On the contrary, the signals of the bridgehead methine (C^b) and the adjacent methylene (C^a) carbon atoms in the dimethylene unit of **6** and **10** shifted only +0.3 to −0.3 ppm in all cases. Fig. 14 illustrates the ^{13}C NMR titration profile of **8** on



12 10

8 6

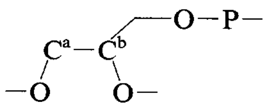
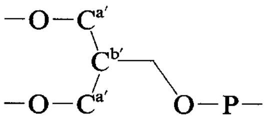
Fig. 13. Postulated conformations of **6**, **8**, **10** and **12**. Reproduced with permission from The American Chemical Society.

addition of NaOH and LiOH (**8**–Na^+–Li^+ system). Although no spectral change was observed on the addition of 1 equivalent and 2 equivalents of NaOH, significant chemical shift changes upfield of the $C^{a'}$ carbon atoms and downfield of the dimethylene carbon (OCH_2CH_2O) atoms were observed following the addition of 1 equivalent of LiOH in the presence of 2 equivalents of NaOH. These titration experiments suggested that three-dimensional cavities may be formed to facilitate the addition of size-matched cations in **8** and **10** which have the trimethylene unit. These results also support the CPK molecular model and computer modelling analysis.

6.3. Binding properties of the monoaza-15-crown-5 derivative

Since **18** gave LiOH- and NaSCN-selective transport under basic and neutral source phase conditions respectively, the cation binding behaviour of **18** for LiOH

Table 5
Alkali metal cation induced changes in ^{13}C nuclear magnetic resonance chemical shifts of **6**, **8**, **10**, **12**, **14** and **16**[a,b]

Compound					Other ring carbon atoms
	C^a	C^b	$C^{a'}$	$C^{b'}$	
6+LiOH	−0.2	+0.3			−0.2
6+NaOH	−0.2	+0.1			−0.2
8+LiOH			+2.3	−0.2	+2.0[c], −0.3
8+NaOH			<±0.1	−0.1	−0.1
10+NaOH	−0.2	−0.3			−0.2 to −0.3
10+KOH	−0.2	−0.3			−0.2 to −0.3
12+NaOH			+1.7	−0.1	−0.1 to −0.3
12+KOH			+0.3	<±0.1	−0.1 to −0.3
14+NaOH	<±0.1	<±0.1			<±0.1
14+KOH	−0.1	<±0.1			+0.3 to −0.5
16+NaOH			<±0.1	<±0.1	<±0.1
16+KOH			+0.5	<±0.1	+0.5 to −0.1

[a] Conditions: [crown] = 0.05 mmol, [alkali metal hydroxide] = 0.05 mmol in CD_3CN–D_2O (1:1), 0.65 ml.

[b] Positive is downfield shift.

[c] The methylene carbon atoms attached to oxygen in the other trimethylene unit.

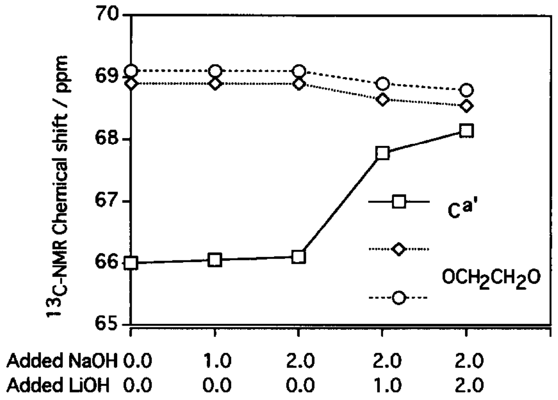


Fig. 14. Titration profile of **8** on addition of NaOH and LiOH. Reproduced with permission from The American Chemical Society.

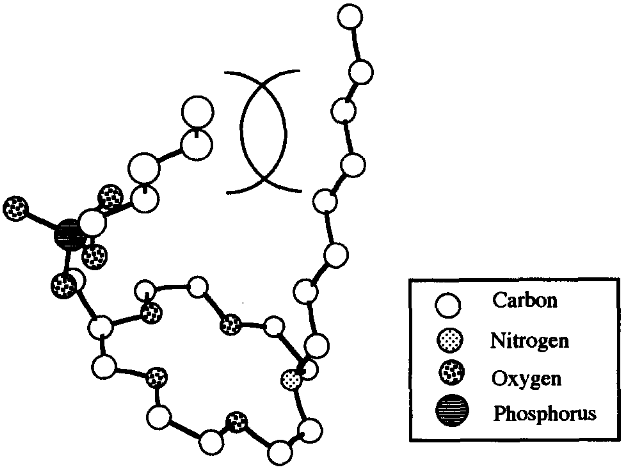


Fig. 16. Postulated conformation of a partial structure of **18**. Reproduced with permission from The Hetero Corporation.

Therefore, the dodecylphosphoric acid armed *N*-octylmonoaza-15-crown-5 is a "selectively controllable host compound", which can control cation selectivity through the pH of the aqueous phase.

Acknowledgment

This research was partially supported by the Hoso Bunka Kikin Foundation of Japan.

References

[1] C.J. Pedersen, J. Am. Chem. Soc., 89 (1967) 7017.
[2] G.W. Gokel, D.M. Dishong and C.J. Diamond, J. Chem. Soc., Chem. Commun., (1980) 1053.
[3] H. Tsukube, J. Chem. Soc., Chem. Commun., (1984) 315.
[4] H. Sakamoto, K. Kimura and T. Shono, Anal. Chem., 59 (1987) 1513.
[5] W. Wierenga, B.R. Evans and J.A. Wolterson, J. Am. Chem. Soc., 101 (1979) 1334. R.A. Bartsch, G.S. Heo, S.I. Kang, Y. Liu and J. Strzelbicki, J. Org. Chem., 47 (1982) 457.
[6] M. Tazaki, K. Nita, M. Takagi and K. Ueno, Chem. Lett., (1982) 571.
[7] T. Akari and H. Tsukube (Eds.), Liquid Membranes: Chemical Applications, CRC Press, Boca Raton, FL, 1990, Chaps. 3 and 4.
[8] G.W. Gokel, J.E. Trafton, A.E. Kaifer, L. Echegoyen and S. Shinkai, in Y. Inoue and G.W. Gokel (eds.), Cation Binding by Macrocycles, Dekker, New York, 1990, Chaps. 6, 8 and 9.
[9] W. Walkowiak, P.B. Czech, J.P. Shukla and R.A. Bartsch, J. Membrane Sci., (1987) 59.
[10] G. Shoham, D.W. Christianson, R.A. Bartsch, G.S. Heo, U. Olsher and W.N. Lipscomb, J. Am. Chem. Soc., 106 (1984) 1280.
[11] R.A. Sachleben, J.H. Burns and G.M. Brown, Inorg. Chem., 27 (1988) 1787.
[12] T. Mizuma, Y. Minaki and S. Toyoshima, Yukagaku Zassi, 81 (1961) 51.

and NaSCN was investigated using IR and ^{13}C NMR spectroscopy. Although the IR spectra (Table 6) revealed remarkable differences in the phosphate site absorption between **18** and its Li^+ ion complex as with the Li^+ complex of **2**, there were only slight changes in the phosphate site absorption between **18** and its NaSCN complex. In the ^{13}C NMR, the ring carbon atoms attached to the oxygen and nitrogen atoms shifted +1.4 to +0.2 ppm and −0.9 ppm respectively with the addition of NaSCN, indicating that the Na^+ ion was bound by the crown ring. In contrast, there was no shift change at the ring carbon atoms attached to the oxygen on the addition of LiOH, although there was a slight shift in the ring NCH_2 carbon atoms of about +0.6 ppm. From these spectral data, we proposed that **18** binds a cation in two different fashions (Fig. 15, types A and B) under acidic and basic conditions respectively. Thus, **18** does not incorporate cations using the three-dimensional cavity using the crown ring and the phosphoric acid site, but the crown site and the phosphoric acid site act independently on the cations; only the crown site of **18** significantly coordinates to cations under neutral source phase conditions (type A), and the phosphate anion is mainly employed under basic conditions (type B). As described in Section 6.1, the phosphoric acid armed crown ether **10** can not favourably form a three-dimensional cavity capable of fitting sodium ions using the phosphate anion of the side arm and oxygen atoms of the crown ring. An examination of the CPK molecular model and computer modelling (Fig. 16) suggested that the phosphate anion of the pendant arm of **18** could not bear the crown ring owing to a steric repulsion between the dodecyl and octyl groups. Several research groups reported [9,36,37] that acidic extracting reagents such as dialkylphosphate and phosphonic acid selectively transported lithium ion in the liquid membrane.

Table 6
IR spectra of **18** and its LiOH and NaSCN complexes

Additive salt	ν(PO—H) (cm^{-1})	ν(P—OC) (cm^{-1})	ν(P=O) (cm^{-1})
None	2625, 2330	970	1250
LiOH complex	—	980	1240, 1105
NaSCN complex	2625, 2330	970	1240

Adapted from The Hetero Corporation.

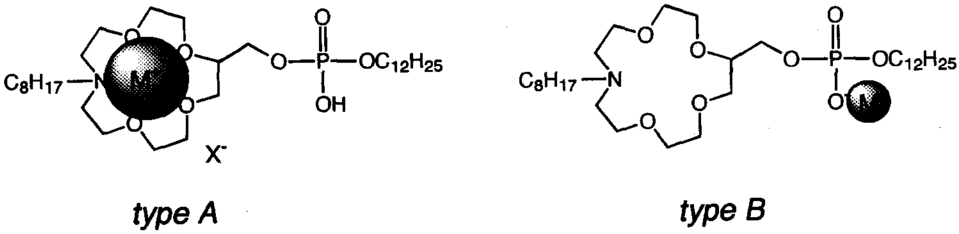


Fig. 15. Cation binding by **18** under neutral source phase (type A) and basic source phase (type B) conditions. Reproduced with permission from The Hetero Corporation.

[13] M. Smith, J.G. Moffatt and H.G. Khorana, J. Am. Chem. Soc., 80 (1958) 6204.
[14] P.T. Gilham and H.G. Khorana, J. Am. Chem. Soc., 80 (1958) 6212.
[15] Y. Habata, M. Ikeda and S. Akabori, Tetrahedron Lett., 33 (1992) 3157.
[16] Y. Habata, M. Ikeda and S. Akabori, J. Chem. Soc., Perkin Trans. 1, (1992) 2651.
[17] Y. Habata and S. Akabori, Tetrahedron Lett., 33 (1992) 5818.
[18] U. Olsher, F. Frolow, G. Shoham, E. Luboch, Z. Yu and R.A. Bartsch, J. Incl. Phenom., 9 (1990) 125.
[19] B.P. Czech, A. Czech, B. Son, H.K. Lee and R.A. Bartsch, J. Heterocycl. Chem., 23 (1986) 465.
[20] B.P. Czech, D.A. Babb, B. Son and R.A. Bartsch, J. Org. Chem., 49 (1984) 4805.
[21] B.P. Czech, Tetrahedron Lett., 21 (1980) 4197.
[22] M. Tomoi, O. Abe, M. Ikeda, K. Kihara and H. Kakiuchi, Tetrahedron Lett., (1978) 3031.
[23] E. Weber, Liebigs Ann. Chem., (1983) 770.
[24] Y. Habata, H. Ugajin and S. Akabori, J. Org. Chem., 59 (1994) 676.
[25] Y. Habata and S. Akabori, J. Heterocycl. Chem., 31 (1994) 1605.
[26] Y. Takeda, Bull. Chem. Soc. Jpn., 53 (1980) 2393.
[27] For example, R.M. Izatt, G.C. Lindh, P. Huszthy, G.A. Clark, R.L. Bruening, J.S. Bradshaw and J.J. Christensen, J. Incl. Phenom., 7 (1989) 501.
[28] M. Ouchi, Y. Inoue, T. Kanzaki and T. Hakushi, J. Org. Chem., 49 (1984) 1408.
[29] W. Walkoxiak, S.I. Kang, L.E. Stewart, G. Ndip and R.A. Bartsch, Anal. Chem., 62 (1990) 2022.
[30] S. Shinkai, H. Kanda, Y. Araragi and O. Manabe, Bull. Chem. Soc. Jpn., 56 (1983) 559.
[31] R.A. Johnstone and M.E. Rose, J. Chem. Soc., Chem. Commun., (1983) 26.
[32] R.A. Johnstone, I.A.S. Lewis and M.E. Rose, Tetrahedron, 39 (1983) 1597.
[33] D. Parker, J. Chem. Soc., Chem. Commun., (1985) 1129.
[34] K. Laali and R.P. Lattimer, J. Org. Chem., 54 (1989) 496.
[35] K. Yamada, S. Matsutani, A. Uchiyama and T. Takahashi, J. Incl. Phenom., 11 (1991) 49.
[36] T. Takahasi, Y. Habata and Y. Iri, J. Incl. Phenom., 11 (1991) 379.
[37] Y. Habata, K. Uchida, Y. Sato and S. Akabori, J. Membrane Sci., 85 (1993) 175.