

Lithium Ion-selective Alkylphosphoric Acid Armed Dibenzo- and Benzo-14-crown-4 Derivatives¹

Yoichi Habata,* Manami Ikeda and Sadatoshi Akabori*

Department of Chemistry, Faculty of Science, Toho University, Funabashi, Chiba 274, Japan

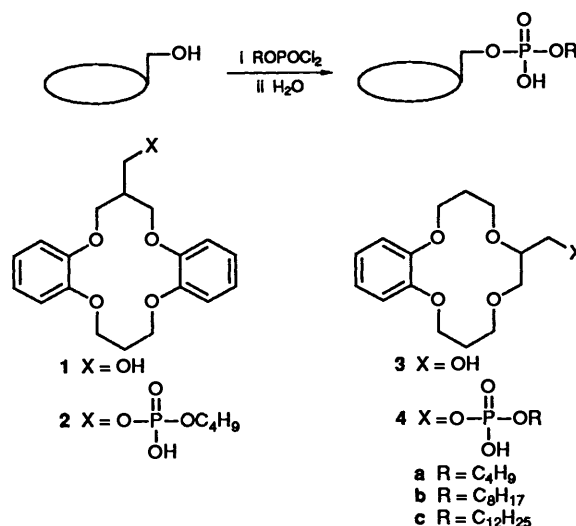
New dibenzo- **2** and benzo-14-crown-4 derivatives **4a–c** having an ionizable alkyl phosphoric acid moiety as an additional pendant arm binding site have been synthesized. Their complexing abilities have been measured by solvent extraction and transport experiments. It is shown that introduction of the pendant group into the dibenzo- and benzo-14-crown-4 derivatives significantly enhances their ability to extract and transport Li⁺ ion. IR spectroscopy, fast atom bombardment (FAB) mass spectrometry and ¹³C NMR spectroscopy were used to study the structure of the complex of **2** with Li⁺ ion. From these results, it was suggested that Li⁺ ion is strongly bound by both the crown oxygen and the phosphate anion of the side arm and is predominantly coordinated by the phosphate anion and the nearest oxygen atoms to the pendant site of the crown ring.

Increasing attention has been focused on the diverse uses of lithium not only in lithium batteries and for tritium production in atomic fusion but also in the field of medical science where during therapy for manic-depressive psychosis Li⁺ ion is monitored.

Many crown-4 derivatives have been reported as Li⁺ ion selective carriers.² Some research groups have developed Li⁺ ion selective carriers which have ionizable groups (e.g. phenolic OH, carboxylic or arylphosphonoyl groups), and mixed carrier systems comprising combinations of a crown ether with an alkanolic acid and dialkylphosphoric acid.³ Recently, Shoham *et al.* and Sachleben *et al.* reported⁴ the X-ray structures of a Li⁺ ion complex of the dibenzo-14-crown-4 derivative having a carboxy group and a Na⁺ ion complex of the dibenzo-14-crown-4 derivative having an arylphosphonic acid functional group. They reported that ionizable groups such as the carboxy and arylphosphonoyl could not coordinate to the cations which were incorporated by the crown ring, since the ether oxygen atoms bound to the crown ring carbon in the side arms coordinated to Li⁺ ion indirectly through a H₂O molecule and to Na⁺ ion directly. Also, conformational requirements of this coordination forces the carboxylate and phosphinate anions away from the metal site. These results have led us to synthesize new host compounds which have no coordination site except for the ionizable group in the side arm in order to develop more selective and efficient Li⁺ ion complexing agents. Here, we report the syntheses of the dibenzo- and benzo-14-crown-4 derivatives having a phosphoric acid functional group as an additional pendant binding site with high Li⁺ ion selective extraction and transport properties.

Results and Discussion

Syntheses of Alkylphosphoric Acid Armed Crown Ethers.—Two types of crown ethers, dibenzo- **2** and benzo-14-crown-4 derivatives **4a–c**, have been prepared from the corresponding hydroxymethyl derivatives (Scheme 1). For example, **4a** was prepared by the reaction of equimolar amounts of **3** with butyl dichlorophosphate⁵ in refluxing THF followed by hydrolysis. After separation and purification by silica gel TLC and gel-permeation column chromatography, pure **4a** was obtained as a hygroscopic oil. The structures of **2** and **4a–c** were confirmed by ¹H NMR and mass spectroscopy and elemental analyses. From the elemental analyses, it was also confirmed that the **4a–c** contained 0.5 mol equiv. of water.



Scheme 1

Solvent Extraction toward Alkali Metal Cations with Alkylphosphoric Armed Crown Ethers.—The complexing abilities of compounds **1** and **2** were examined by solvent extraction experiments using various alkali-metal salts: the results of these experiments are summarized in Table 1 (Runs 1–8). Hydroxymethyldibenzo-14-crown-4, **1**, showed a low extractability under basic, neutral, and acidic aqueous conditions (Runs 1–4) despite different counter anions. Its selectivity is in the following order: Na⁺ > K⁺ > Li⁺, with Li⁺ ion only slightly extracted (0.1–0.3%). On the other hand, compound **2** having an alkylphosphoric acid functional group as a side arm extracted Li⁺, Na⁺, and K⁺ ions in 26.6, 4.9 and 2.9%, respectively, under basic conditions (Run 5), and Li⁺ ion selectivity was as follows: Li⁺/Na⁺ = 5.4, Li⁺/K⁺ = 9.1. Under neutral and acidic conditions (Runs 6–8), the Li⁺ ion extractability with compound **2** was reduced, and Li⁺ ion selectivities for Na⁺ and K⁺ ions were 1.4–2.5. From the results of the solvent extraction, it is suggested that the crown ether **2** has a relatively high complexing ability toward Li⁺ ion under basic conditions, and its complexing ability is remarkably reduced under neutral and acidic conditions. Also, Table 1 shows the extraction ratios between compounds **1** and **2** for each cation. It is noteworthy that the extractability toward Li⁺ ion by **2** was significantly

Table 1 Competitive extraction of various alkali-metal salts with **1**, **2**, **3** and **4a-c**

Run	Compd.	Conditions		Extractability (%) ^b			Selectivity		Extraction ratios		
		Counter anion ^a	[Crown]/mmol dm ⁻³	Li ⁺	Na ⁺	K ⁺	Li ⁺ /Na ⁺	Li ⁺ /K ⁺	Li ⁺	Na ⁺	K ⁺
1	1	OH	10	0.1	2.3	2.0	0.04	0.05	—	—	—
2	1	SCN	10	0.3	3.1	2.6	0.10	0.12	—	—	—
3	1	I	10	0.2	2.6	1.9	0.08	0.11	—	—	—
4	1	ClO ₄	10	0.2	2.4	2.1	0.08	0.01	—	—	—
[Compd. 2 /Compd. 1]											
5	2	OH	10	26.6	4.9	2.9	5.4	9.1	266.0	2.1	1.5
6	2	SCN	10	4.3	3.1	2.2	1.4	1.9	14.3	1.0	0.8
7	2	I	10	3.8	2.7	1.9	1.4	2.0	19.0	1.0	1.0
8	2	ClO ₄	10	4.1	2.2	1.6	1.9	2.5	20.5	0.9	0.8
[Compd. 4c /Compd. 3]											
9	3	OH	10	0.1	3.3	2.8	0.03	0.04	—	—	—
10	4c	OH	10	64.8	83.4	53.4	0.78	1.2	648.0	25.3	19.2
11	1	OH	1	<0.1	<0.1	<0.1	—	—	—	—	—
12	2	OH	1	0.5	<0.1	<0.1	—	—	—	—	—
13	3	OH	1	<0.1	<0.1	<0.1	—	—	—	—	—
14	4a	OH	1	0.5	<0.1	<0.1	—	—	—	—	—
15	4b	OH	1	6.6	2.3	1.8	2.9	3.7	—	—	—
16	4c	OH	1	40.7	12.1	7.7	3.4	5.3	—	—	—

^a pH of the aqueous solution (10 mmol dm⁻³) of hydroxide, thiocyanate, iodide, and perchlorate were 11.0, 5.1, 5.5 and 5.7, respectively.

^b Reproducibility was confirmed as $\pm 10\%$ or better.

enhanced by *ca.* 270 times relative to **1** under basic conditions but enhanced only *ca.* 20 times under neutral and acidic conditions. The extractability toward Na⁺ and K⁺ ions, however, was only slightly enhanced (0.8–2.1 times).

The results of the competitive extraction of alkali-metal cations with **3** and **4a-c** are also summarized in Table 1 (Runs 9–16). First, we performed the extraction experiments with a concentration of 10 mmol dm⁻³ of the crown ethers (Runs 9 and 10). Table 1 indicates that the benzo-14-crown-4 having a dodecylphosphate **4c** (Run 10) extracted Na⁺ ion selectively,* whilst **2** (Run 5) extracted Li⁺ ion selectively. However, the extraction ratio of **4c** (Run 10) over **3** (Run 9) was enhanced *ca.* 650 times by the introduction of the phosphoric acid functional group into the benzo-14-crown-4 compared with that of the corresponding hydroxymethyl derivative **3**. Bartsch *et al.* reported⁷ that the dibenzo-14-crown-4 derivative of the lipophilic carboxylic acid shows Na⁺ ion selectively (Li⁺/Na⁺ = 0.6) under conditions of competitive extraction, while the corresponding benzo-14-crown-4 derivative showed Li⁺ ion selectivity (Li⁺/Na⁺ = 4.7). In contrast, Li⁺ ion selectivity over Na⁺ ion by the dibenzo-14-crown-4 derivative **2** (Run 5, Li⁺/Na⁺ = 5.4) was superior to that of the benzo-14-crown-4 derivative **4c** (Run 10, Li⁺/Na⁺ = 0.78), although the transport rate of **2** toward alkali-metal cations was slower than those of **4b** and **4c**.

With a concentration of 1 mmol dm⁻³ of the crown ethers (Runs 11–16), both **4b** and **4c** selectively extracted Li⁺ ion (extractability medium to high for Runs 15 and 16). The extractabilities were enhanced with increased length of the alkyl group at the phosphoric acid site. The hydroxymethyl derivatives **1** and **3** failed to extract any cations (Runs 11 and 13), whilst compounds **2** and **4a** having the butylphosphate extracted Li⁺ ion only slightly (Runs 12 and 14).† It is suggested, therefore, that the introduction of the alkylphosphoric functional group into the benzo-14-crown-4 molecule enhances its ability to extract Li⁺ ion selectively. From these results, we thus expected that the alkylphosphoric acid armed dibenzo- or

benzo-14-crown-4 derivatives might give accelerated Li⁺ ion transport between the basic source phase and the acidic receiving phase.

Competitive Transport Across a Liquid Membrane by Alkylphosphoric Acid Armed Crown Ethers.—With the new functionalized crown ethers, competitive transport experiments were performed in a U tube using chloroform as a liquid membrane. The results are summarized in Table 2, along with those for the hydroxymethyl-14-crown-4 derivatives, **1** and **3**. The results clearly suggested that the ionizable phosphoric acid functional group facilitates not only Li⁺ ion selective complexation during the extraction process from the basic source phase to the organic membrane phase but also the release of Li⁺ ion in the back-extraction process from the organic membrane phase into the acidic receiving phase. In general, the selectivity for metal cations is inversely proportional to the transport rate in a transport system.⁶ However, a series of benzo-14-crown-4 derivatives, **4a-c**, showed an extreme enhancement of the transport rate which maintained high Li⁺ ion selectivity when compared with **1**, **2** and **3**. Concerning this significant enhancement of the extractability and the transport rate toward Li⁺ ion by **2** and **4a-c** compared with **1** and **3**, the CPK molecular model showed that **2** and **4a-c** formed a three-dimensional cavity into which a Li⁺ ion fits using the phosphate anion and the nearest oxygen atoms (f in Fig. 2) of the pendant site of the crown ring; the pendant arms of **2** and **4a-c** are, however, too short to form a cooperative coordination site for Na⁺ and K⁺ ions. Therefore, the introduction of the phosphoric acid functional group into the dibenzo- and benzo-14-crown-4 derivatives gave rise to highly selective Li⁺ ion transport, and the long alkyl group of the phosphate increased the transport rate compared with the corresponding compound having a short alkyl group.

*Structural Study of Li⁺ Ion complex of **2** by IR, FAB Mass and ¹³C NMR Spectroscopy.*—The Li⁺ ion complex of **2**, which was isolated by mixing equimolar amounts of **2** in methanol and LiOH in water, was confirmed by elemental analysis as the 1:1 complex of **2** with Li⁺ ion containing 1 mol of H₂O.

IR spectral data for **2** and its Li⁺ ion complex are shown in Table 3. There are remarkable differences for the

* An emulsion formed in the organic phase.

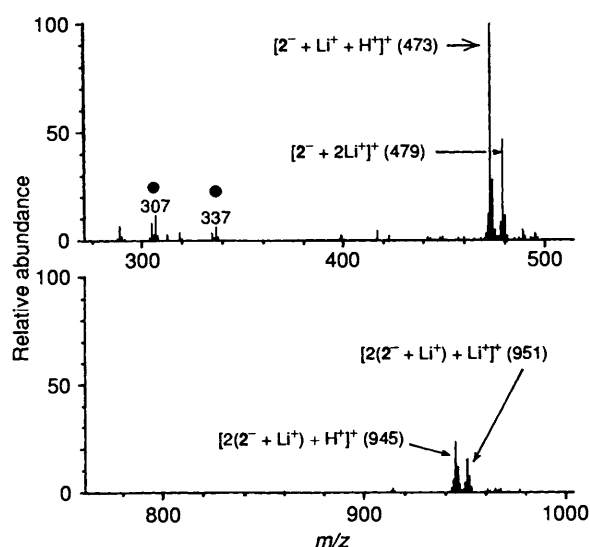
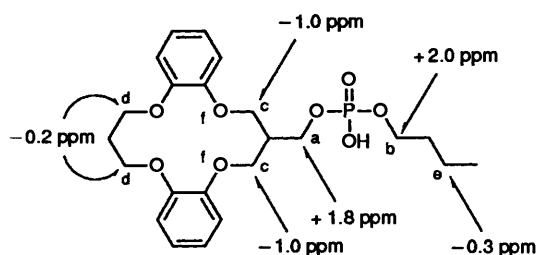
† Compounds **4b** and **4c** having long alkyl groups were slightly distributed to aqueous phase (<3%), although **4a** having a butyl group was distributed to aqueous phase *ca.* 70% under the conditions.

Table 2 Competitive facilitated transport with **1**, **2**, **3** and **4a-c**

Compd.	Transport rate ^a × 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	[Compd. 2 /Compd. 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	[Compd. 4a-c /Compd. 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

^a Reproducibility was confirmed as ±10% or better.**Table 3** IR spectral data (ν/cm⁻¹)^a of **2** and its Li⁺ ion complex

	ν(PO-H)	ν(P-OC)	ν(P=O)
2	2330	1000	1240
Li ⁺ complex	—	980	1240, 1100

^a KBr disc.**Fig. 1** FAB mass spectrum of the Li⁺ ion complex of **2**; ●, peaks originated from the NBA matrix system**Fig. 2** ¹³C NMR shift changes between **2** and the Li⁺ ion complex of **2**

phosphate site absorptions between **2** and its complex. In the Li⁺ ion complex, the PO-H stretching band at 2330 cm⁻¹ disappeared, and the P-OC stretching band in the 1000 cm⁻¹ region of **2** was shifted to a lower frequency by ca. 20 cm⁻¹. In addition, the new P=O stretching band which arises from a (RO)₂PO₂⁻ type compound⁸ appeared at 1100 cm⁻¹. From these results, it is suggested that the phosphate anion of **2** is bound directly to the Li⁺ ion in the complex.

Some groups reported⁹ that FAB mass spectrometry can be

used to assess the binding ability between the crown ether and cation. Thus, we examined by FAB mass spectrometry the Li⁺ ion complex with **2**. The FAB mass spectrum using *m*-nitrobenzyl alcohol (NBA) as the matrix is shown in Fig. 1. The ion peak due to the 1:1 complex, [2⁻ + Li⁺ + H⁺]⁺, at *m/z* 473 as the base peak and an associated ion peak, [2(2⁻ + Li⁺) + H⁺]⁺, at *m/z* 945 (25%) were observed. A unique one crown-two cation ion peak, [2⁻ + 2Li⁺]⁺, and a two crown-three cation ion peak, [2(2⁻ + Li⁺) + Li⁺]⁺, where Li⁺ ions may be bound by both the crown and phosphate anion site independently, were also detected at *m/z* 479 (46%) and 951 (15%), respectively. However, the metal-free ion peak (*m/z* 466) was not observed. There has been no report on these binuclear ion peaks due to the one crown-two cation and two crown-three cation complex ion peaks in the cases of FAB mass spectra for the complexes of neutral crown ethers with alkali-metal cations, although one crown-one cation and two crown-two cation ion peaks derived from the 1:1 complex, and two crown-one cation ion peak due to the 2:1 complex have been reported.^{9a} From these observations, it is suggested that Li⁺ ion in the complex was strongly bound by the ether oxygen of the crown ring and the phosphate anion. This is the first instance of FAB mass spectrometry of a complex for an ionizable crown ether.

In order to obtain more detailed structural information of the complex, ¹³C NMR spectra was measured in CD₃OD solution (50 °C). As shown in Fig. 2, a significant shift in the signals for carbons a, b (-CH₂-O-P-O-CH₂-) and carbon c (-CH₂O-) was observed, while the signals for carbon d of the crown ring and carbon e of the butyl group shifted only -0.2 and -0.3 ppm, respectively. The spectral shifts suggested that the phosphate anion as a pendant group and the nearest oxygen atoms (f in Fig. 2) of the pendant site of the crown ring provide the major coordination for the Li⁺ ion. These facts support the CPK molecular model examination, and showed that the structure in the neighbourhood of the bridgehead carbon bearing the pendant arm plays an important role in Li⁺ ion selectivity. Therefore, the difference in Li⁺ ion selectivity between dibenzo- and benzo-14-crown-4 derivatives in this series may be attributed to the difference in the structure's neighbourhood in the bridgehead carbon bearing the pendant arm, such as the trimethylene unit and dimethylene unit.

Experimental

M.p.s were recorded using a Ishii melting point apparatus and are uncorrected. The mass spectra were taken on a Hitachi M80 mass spectrometer. The ¹H and ¹³C NMR spectra were obtained on Hitachi R-1100 and JEOL 400GX spectrometers with TMS as the internal standard. The IR spectra were recorded with a JASCO IR 810 spectrophotometer. The FAB mass spectrum was measured on a JEOL JMS-HX100 mass spectrometer using *m*-nitrobenzyl alcohol as the matrix. The concentrations of the alkali-metal cations were determined with

a Perkin-Elmer 5100 atomic absorption spectrometer. The UV-VIS spectra was measured using a Hitachi 330 spectrophotometer.

Materials.—Alkyl dichlorophosphates,⁵ 3-chloro-2-chloromethylprop-1-ene,¹⁰ 1,3-bis(2-hydroxyphenoxy)propane¹¹ and hydroxymethylbenzo-14-crown-4¹² were prepared according to the procedure described in the literature.

3-Methylenedibenzo-14-crown-4.—Under a nitrogen atmosphere, NaOH (6.58 g, 165 mmol) in water (25 cm³) was added dropwise to 1,3-bis(2-hydroxyphenoxy)propane (20.38 g, 78 mmol) in butan-1-ol (700 cm³). The reaction mixture was stirred at 100 °C for 1 h and then 3-chloro-2-chloromethylprop-1-ene (9.74 g, 86 mmol) was added to it. Stirring was then continued at 100 °C for 12 h after which the reaction mixture was cooled and the solid material present was filtered off. The solid was washed with CHCl₃. The filtrate was concentrated under reduced pressure and the residue was combined with the CHCl₃ solution. The CHCl₃ solution was washed with water, dried (MgSO₄) and then evaporated under reduced pressure. The residual solid was extracted with hot heptane and then the extract was cooled to room temperature. The resulting solid was recrystallized from heptane to give 3-methylenedibenzo-14-crown-4 (71%) as a white powder, m.p. 91.5–92.0 °C; *m/z* (20 eV) 312 (M⁺) (Found: C, 73.0; H, 6.5. Calc. for C₁₉H₂₀O₄: C, 73.6; H, 6.45; δ_{H} (60 MHz; CDCl₃; Me₄Si): 6.92 (s, 8 H), 5.38 (s, 2 H), 4.73 (s, 4 H), 4.25 (t, *J* 6.0, 4 H) and 2.26 (m, 2 H).

3-Hydroxymethyldibenzo-14-crown-4 1.—A published procedure for the syntheses of the 3-hydroxymethyl-crown ethers was adapted.¹³ Under a nitrogen atmosphere, the (CH₃)₂S·BH₃ complex (16 cm³; BH₃ concentration, 10.0–10.2 mol dm⁻³; Aldrich) was added dropwise to a solution of 3-methylenedibenzo-14-crown-4 (17.42 g, 55.8 mmol) in freshly distilled THF (80 cm³) at 0 °C. Stirring was continued for 2 h at 0 °C followed by 2 h at room temperature. Water (10 cm³) was then carefully added to the reaction mixture to give an exothermic reaction. When this was complete, 3 mol dm⁻³ NaOH (160 cm³) and 30% H₂O₂ (11 cm³) were added successively at 20–30 °C. The mixture was stirred at 50 °C for 2 h and then cooled. The organic layer was separated and the water layer was saturated with NaCl and extracted with CHCl₃. The organic layer and CHCl₃ layer were combined, dried (MgSO₄) and then evaporated under reduced pressure. The residual solid was recrystallized from benzene to give **1** as a white powder (54%), m.p. 161.0–161.5 °C; *m/z* (20 eV) 330 (M⁺) (Found: C, 69.0; H, 6.7. Calc. for C₁₉H₂₂O₅: C, 69.07; H, 6.71%; δ_{H} (60 MHz; CDCl₃; Me₄Si) 7.00 (s, 8 H), 4.50–3.85 (m, 10 H), 3.71 (br s, 1 H) and 2.75–1.96 (m, 3 H).

General Procedure for the Reaction of Hydroxymethyl-crown Ethers with Alkyl Dichlorophosphate.—A mixture of hydroxymethyl-crown ether (4.2 mmol) and alkyl dichlorophosphate (4.5 mmol) in freshly distilled THF or benzene (30 cm³) was stirred for 24 h at room temperature. The solvent was removed under reduced pressure and water (30 cm³) was added to the residue. The mixture was stirred for 5 h at 100 °C and then cooled and extracted with CHCl₃ (20 cm³ × 3). The combined organic extracts were washed with water, dried (Na₂SO₄) and then evaporated under reduced pressure. Separation and purification by silica gel TLC (Wako-gel B-5F, CHCl₃–EtOAc–MeOH 10:10:1 as eluent) and gel-permeation column chromatography (Sephadex LH-20, EtOH as eluent) gave pure **2**, **4a**, **4b** and **4c**. Selected data for the new crown compounds are summarized below.

2: Yield 31%, m.p. 129.5–130.5 °C; *m/z* (20 eV) 466 (M⁺)

(Found: C, 59.2; H, 6.6. Calc. for C₂₃H₃₁O₈P: C, 59.22; H, 6.70%; δ_{H} (400 MHz; CD₃OD) 6.98 (m, 2 H), 6.91 (m, 2 H), 4.32–4.19 (m, 10 H), 4.02 (q, *J* 7.0, 2 H), 2.62 (m, 1 H), 2.23 (m, 2 H), 1.66 (quintet, *J* 7.3, 2 H), 1.42 (sextet, *J* 7.3, 2 H) and 0.93 (t, *J* 7.3, 3 H).

4a: Yield 10%, colourless oil; *m/z* (20 eV) 418 (M⁺) (Found: C, 54.0; H, 7.5. Calc. for C₁₉H₃₁O₈P·1/2H₂O: C, 53.96; H, 7.51%; δ_{H} (60 MHz; CDCl₃) 6.94 (s, 4 H), 4.56–3.25 (m, 15 H), 2.00 (quint, *J* 5.4, 4 H), 1.73–1.10 (m, 4 H) and 0.93 (t, *J* 5.0, 3 H).

4b: Yield 10%, colourless oil; *m/z* (20 eV) 474 (M⁺) (Found: C, 57.1; H, 8.3. Calc. for C₂₃H₃₉O₈P·1/2H₂O: C, 57.21; H, 8.14%; δ_{H} (60 MHz; CDCl₃) 7.02 (s, 4 H), 4.56–3.25 (m, 15 H), 2.05 (quint, *J* 5.4, 4 H), 1.75–1.06 (m, 12 H) and 0.90 (t, *J* 5.0, 3 H).

4c: Yield 15%, colourless oil; *m/z* (20 eV) 530 (M⁺) (Found: C, 60.1; H, 9.0. Calc. for C₂₇H₄₇O₈P·1/2H₂O: C, 60.25; H, 9.15%; δ_{H} (60 MHz; CDCl₃) 7.03 (s, 4 H), 4.52–3.25 (m, 15 H), 2.03 (quint, *J* 5.4, 4 H), 1.70–1.10 (m, 20 H) and 0.90 (t, *J* 5.0, 3 H).

Preparation of Li⁺ Complex of 2.—A mixture of the chloroform solution of **2** (10 mmol dm⁻³; 20 cm³) and an aqueous solution of LiOH (200 mmol dm⁻³; 20 cm³) was stirred at room temperature for 12 h. The chloroform layer was separated, dried (Na₂SO₄) and evaporated under reduced pressure. Recrystallization of the resulting solid from acetonitrile–benzene gave a Li⁺ ion complex as a white powder (16%), m.p. 166.0–167.0 °C (Found: C, 55.9; H, 6.7. Calc. for C₂₃H₃₀O₈PLi·H₂O: C, 56.33; H, 6.58%).

Extraction Experiments.—The extraction experiments were performed at 25 ± 2 °C. Initial conditions of the competitive extraction were in as follows: [aqueous phase] = aqueous solution (2 cm³) containing 1 mmol dm⁻³ of LiOH, NaOH and KOH; [organic phase] = 1 mmol dm⁻³ of **2** or **4a–c** in CHCl₃ (2 cm³). After extraction, the organic phase was back extracted with 1 mol dm⁻³ HCl and then the amounts of metal ions were determined by atomic absorption spectrometry.

Transport Experiments.—The transport experiments were carried out using a U-tube (surface area = 3.5 cm²) at 25 ± 2 °C. Initial conditions of the competitive transport were as follows: [source phase] = aqueous solution (3 cm³) containing 0.1 mol dm⁻³ of LiOH, NaOH and KOH; [membrane phase] = 5 mmol dm⁻³ of crown ether in CHCl₃ (6 cm³); [receiving phase] = 1 mol dm⁻³ of HCl (3 cm³). The concentration of the receiving phase was determined by atomic absorption spectrometry. The transport rates were calculated from the amounts of alkali-metal cations in the receiving phase. The aqueous and organic phases were stirred at 135 and 540 rpm, respectively, by synchronous motors in order to avoid a stirring error.

Distribution Experiments.—The distribution of **4a–c** between CHCl₃ and water were measured under the following conditions: [aqueous phase] = aqueous solution (4 cm³) containing 0.1 mol dm⁻³ of LiOH, NaOH and KOH, [organic phase] = 5 mmol dm⁻³ of **4a–c** in CHCl₃ (2 cm³). The mixture of the aqueous and organic solutions was shaken for 30 min and centrifuged. The concentration of these crown compounds in the organic and aqueous layers were measured using a UV-VIS spectrophotometer.

Acknowledgements

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