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Proton-Ionizable Crown Compounds. 11. Synthesis of Macrocyclic Ligands Containing Two Sulfonamide Groups and Chloro Substituents or Pyridine Subcyclic Units and a Preliminary Study of Cation Transport by Three of These Ligands

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Abstract. Five new macrocyclic ligands each containing two sulfonamide groups have been prepared. Three of these compounds contain one or two chloro substituents and the other two have one or two pyridine subcyclic units. A seventeen-membered ring ligand (**4**) was found to be an excellent transport agent for all alkali metal cations in a water–methylene chloride–water bulk liquid membrane system when the pH of the source phase was 13 or higher. The chlorine-substituted analog (**5**) was a poor transport agent for the alkali metal cations possibly because the chlorine atom blocked entry to the macrocycle cavity. An open-chain analog containing two sulfonamide groups was particularly effective in transporting cesium ions.

Key words: Macrocyclic compounds, proton-ionizable crown compounds, alkali metal cation transport.

1. Introduction

There is considerable interest in the design of proton-ionizable macrocyclic ligands for the selective separation of metal cations. Proton-ionizable ligands are unique in that an accompanying salt anion may not be needed when the metal cation is extracted into the organic phase. Most researchers have used crown compounds with pendant arms containing carboxyl or phenolic groups to extract metal cations from aqueous solutions into organic solvents [2–6]. Others have studied macrocyclic ligands containing phenolic groups wherein the hydroxy function is directed into the ring cavity [7, 8].

We have synthesized a number of macrocyclic ligands containing proton-ionizable groups which are part of the macroring cavity. Some of these ligands contain the 4-pyridone (compounds **1** and **2**, Figure 1) [9–11], 4-thiopyridone [11] and triazole (**3**) [12–14] subcyclic units. In addition, compounds containing two proton-ionizable sulfonamide groups (**4**, Figure 1) have been prepared and characterized [15, 16].

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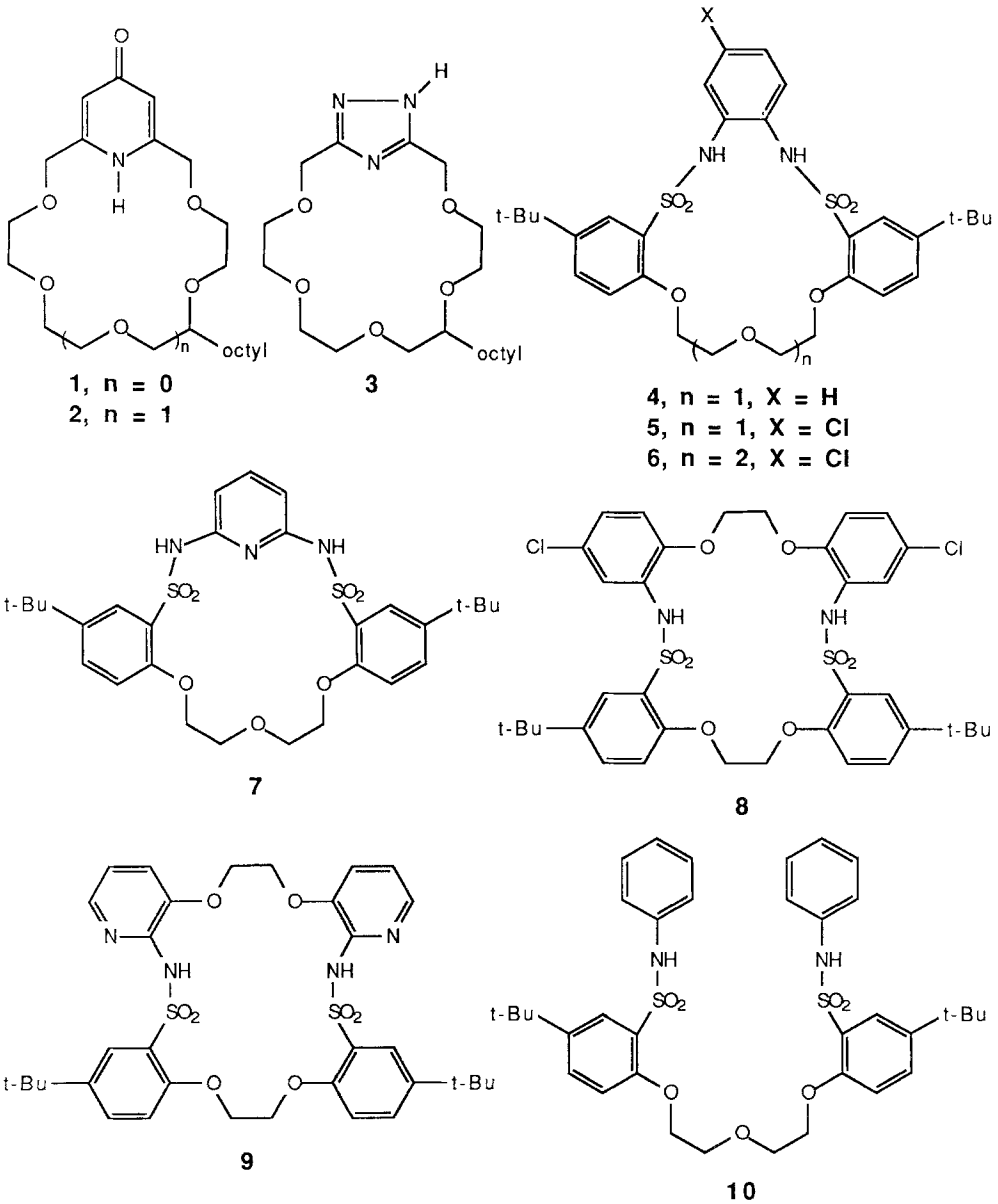


Fig. 1. Structures of macrocyclic compounds.

The new proton-ionizable crown compounds prepared in our laboratory are effective transport agents for the alkali metal cations in a water–methylene chloride–water bulk liquid membrane system [17]. For example, ligand **2** was found to be selective for the transport of potassium ions in this system [18, 19]. The transport of potassium was found to be dependent on the pH of the source phase with the best transport at pH values greater than 12. This pH value is slightly higher than the pK_a value (10.98) for the ionization of the proton from the non-octyl-substituted analog of **2** [10]. Ligand **1** has been found to be selective for the transport of lithium

cations in the liquid membrane system [20]. Again, the best transport occurred at high source phase pH values.

This paper reports the synthesis of new sulfonamide-containing macrocyclic compounds **5–9** and the open-chain analog **10**. A preliminary cation transport study using ligands **4**, **5** and **10** shows that these compounds are more effective than either **1** or **2** in transporting alkali metal ions in the bulk liquid membrane system. Compound **10** is particularly effective in transporting cesium ions in single cation experiments.

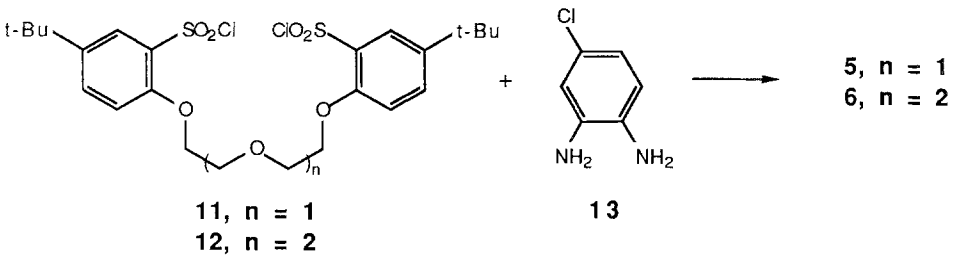
2. Experimental

Infrared (IR) spectra were obtained on a Beckman Acculab 2 spectrometer. The proton nuclear magnetic resonance (NMR) spectra were obtained on a JEOL FX-90Q spectrometer in $CDCl_3$. Molecular weights were obtained on a Hitachi-Perkin-Elmer Model 115 molecular weight apparatus. Field desorption (fd) mass spectra were obtained on a Varian MAT 711 system. Elemental analyses were performed by MHW Laboratories, Phoenix, Arizona. Melting points were taken on a Thomas-Hoover melting point apparatus and are uncorrected. Starting sulfonyl chlorides **11**, **12** and **15** (see Scheme 1) were prepared as reported [15, 16]. 4-Chloro-1,2-phenylenediamine (**13**) and 2,6-diaminopyridine (**14**) were used as purchased from Aldrich. Starting diamines **16** and **17** were prepared as outlined below.

1,2-*Bis*(2-amino-4-chlorophenoxy)ethane (**16**) was prepared by the following sequence. A mixture of 18.5 g (0.05 mol) of ethylene glycol ditosylate, 19.1 g (0.11 mol) of 4-chloro-2-nitrophenol (Aldrich) and 16.6 g (0.12 mol) of anhydrous potassium carbonate was heated at 140 °C in 100 mL of stirring dimethylformamide for 20 h. The cooled reaction mixture was added to 800 mL of water and the resulting solid was filtered. The solid was recrystallized from toluene to give 11.7 g (63%) of 1,2-*bis*(4-chloro-2-nitrophenoxy)ethane, mp 149–149.5 °C; NMR (DMSO-d_6): δ 4.54 (*s*, 4H), 7.44 (*d*, 2H, $J = 8.5$ Hz), 7.72 (*dd*, 2H, $J = 8.5$ Hz and 2.6 Hz), 7.99 (*d*, 2H, $J = 2.6$ Hz). A 64% solution of hydrazine in water (6.7 mL) was slowly added (7–10 minutes) to a stirring mixture of 7.5 g (0.02 mol) of the dinitro compound, 0.07 g of ethanol moistened 10% palladium on carbon and 100 ml of 95% ethanol at 60 °C. An additional 0.07 g of the palladium catalyst was added and the resulting mixture was gently refluxed for 20 h. The mixture was filtered and then cooled to give colorless crystals. The solid was recrystallized twice from ethanol to give 1.6 g (26%) of **16**, mp 157.5–158 °C; IR (KBr): 3500, 3400 cm^{-1}; NMR (DMSO-d_6): δ 4.25 (*s*, 4H), 5.02 (*s*, 4H, signal disappeared in D_2O), 6.47 (*dd*, 2H, $J = 8.5$ Hz and 2.6 Hz), 6.63 (*d*, 2H, $J = 2.6$ Hz), 6.83 (*d*, 2H, $J = 8.5$ Hz). Compound **8**, a derivative of **16**, gave a satisfactory elemental analysis.

1,2-*Bis*(2-amino-3-pyridyloxy)ethane (**17**) was prepared as above for **16** from 15.4 g (0.11 mol) of 3-hydroxy-2-nitropyridine to give 6.4 g (42%) of 1,2-*bis*(2-nitro-3-pyridyloxy)ethane, mp 199–200.5 °C (toluene); NMR (DMSO-d_6): δ 4.61 (*s*, 4H), 7.65–8.17 (*m*, 6H); and after reducing, 3.6 g (73%) of **17**, mp 168.5–170 °C (ethanol/toluene); IR (KBr): 3460, 3290, 3155, and 1615 cm^{-1}; NMR (DMSO-d_6): δ 4.31 (*s*, 4H), 5.63 (*s*, 4H, signal disappeared in D_2O), 6.48 (*dd*, 2H, $J = 8.1$ Hz and 5.5 Hz), 7.07 (*dd*, 2H, $J = 8.1$ Hz and 1.5 Hz), 7.51 (*dd*, 2H, $J = 5.5$ Hz and 1.5 Hz). Compound **9**, a derivative of **17**, gave a satisfactory elemental analysis.

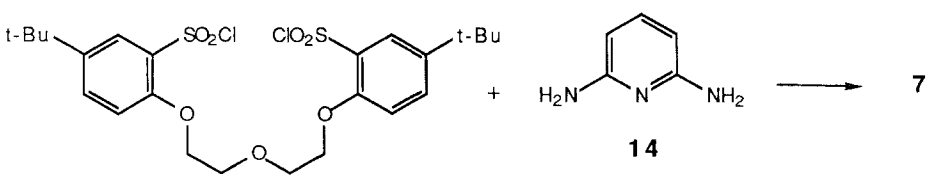
A. Ligands 5 and 6



11, n = 1
12, n = 2

13

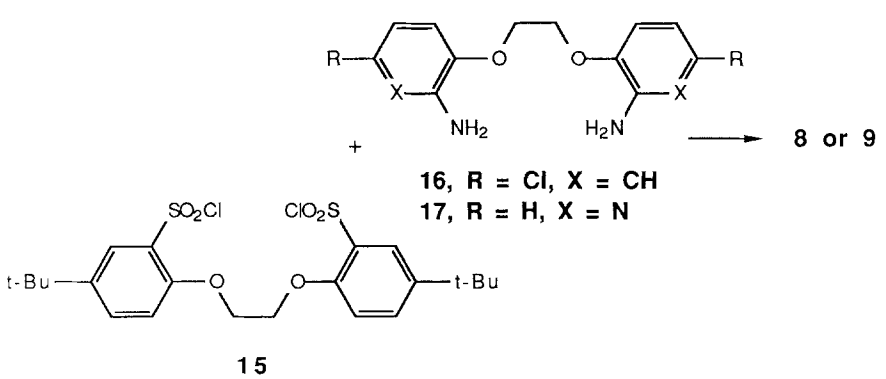
B. Ligand 7



12

14

C. Ligands 8 and 9



16, R = Cl, X = CH
17, R = H, X = N

15

Scheme 1. Preparation of macrocyclic ligands.

2.1. PREPARATION OF **5** (SCHEME 1.A.)

4′,5‴-Di-*t*-butyl-5″-chloro-8,9,12,13,16,17-tribenzo-11,14-diaza-1,4,7-trioxa-10,15-dithiacycloheptadecane-10,10,15,15-tetraoxide (**5**) was prepared by the following sequence (Scheme 1.A.). Solutions of 5.8 g (10.25 mmol) of **11** in 30 mL of methylene chloride and 1.46 g (10.25 mmol) of **13** in 30 mL of methylene chloride were added simultaneously over a one hour period to a mixture of 50 mL of methylene chloride and 5 mL of pyridine at 0 °C. The resulting mixture was stirred at 0 °C for 1 h and then slowly heated to reflux temperature and stirred for an additional 30 minutes. The mixture was cooled and extracted twice with 2 M aqueous hydrochloric acid and once with water. The organic phase was evaporated and the product was chrom-

atographed on silica gel using methylene chloride and then chloroform as eluants. The fractions containing a substance with a silica gel TLC $R_f = 0.59$ (chloroform/acetone, 2/1) were combined and evaporated to give a thick oil. The product crystallized in ethyl ether, methanol or 2-propanol to give 0.65 g (10%) of **5**, mp 232–234 °C; IR (Nujol): 3320 cm^{-1}; NMR: δ 1.25 (*s*, 18H), 4.15 (*m*, 4H), 4.4 (*m*, 4H), 6.75–7.95 (*m*, 9H), 7.85 and 8.05 (*s*, 2H, signals disappeared in D_2O). Anal. Calcd for $C_{30}H_{37}N_2S_2O_7Cl$: C, 56.55; H, 5.85; S, 10.06; M^+, 637.22. Found: C, 56.70; H, 6.00; S, 10.12; M^+, 636.

2.2. PREPARATION OF **6** (SCHEME 1.A.)

4′,5‴-Di-*t*-butyl-5″-chloro-11,12,15,16,19,20-tribenzo-14,17-diaza-1,4,7,10-tetraoxa-13,18-dithiacycloeicosane-13,13,18,18-tetraoxide (**6**) was prepared from **12** and **13** as above for **5** to give 1.37 g (19.5%) of **6**, mp 305–306 °C (acetone); IR (Nujol): 3320, 3150 cm^{-1}; NMR (DMSO-d_6): δ 1.24 (*s*, 18H), 3.66 (*s*, 4H), 3.92 (*m*, 4H), 4.4 (*m*, 4H), 6.9–7.9 (*m*, 9H), 8.42 (*s*, 2H, signal disappeared in D_2O). Anal. Calcd for $C_{32}H_{41}N_2S_2O_8Cl$: C, 56.42; H, 6.06; S, 9.41; M^+, 681.27. Found: C, 56.32; H, 5.90; S, 9.23; M^+, 681.

2.3. PREPARATION OF **7** (SCHEME 1.B.)

4′,5″-Di-*t*-butyl-4,5,13,14-dibenzo-2,16,21-triaza-6,9,12-trioxa-3,15-dithiabicyclo[15.3.1]henicosa-17,19,21(1)-triene-3,3,15,15-tetraoxide (**7**) was prepared from **12** and **14** as above for **5** to give 70 mg (1%) of 7, mp 131–133 °C; IR (Nujol): 3200 cm^{-1}; NMR: δ 1.25 (*s*, 18H), 3.7–4.5 (*m*, 8H), 6.7–7.95 (*m*, 9H), 8.0 (*s*, 2H, signal disappeared in D_2O). Anal. Calcd for $C_{29}H_{37}N_3S_2O_7$: C, 57.69; H, 6.18; S, 10.62; M^+, 603.76. Found: C, 57.44; H, 6.45; S, 10.43; M^+, 603.

2.4. PREPARATION OF **8** (SCHEME 1.C.)

4′,5⁗-Di-*t*-butyl-5‴,4‴-dichloro-5,6,9,10,15,16,19,20-tetrabenzo-8,17-diaza-1,4,11,14-tetraoxa-7,18-dithiacycloeicosane-7,7,18,18-tetraoxide (**8**) was prepared using the reported procedure [16]. Two solutions of 1.31 g (2.5 mmol) of **15** and 1.57 g (5 mmol) of **16**, each in 200 mL of methylene chloride were dropped simultaneously into 200 mL of vigorously stirring methylene chloride over a period of 3 hours. After stirring the reaction mixture under reflux for 9 days, the solvent was replaced by 400 mL of tetrahydrofuran and the solution was further refluxed for 6 days. The precipitates were filtered and the filtrate was evaporated to give a solid product. The product was chromatographed on silica gel using methylene chloride as eluant to give 0.48 g (25%) of **8**, mp 290–293 °C (ethanol/dioxane); IR (KBr): 3330, 3290 cm^{-1}; NMR: δ 1.28 (*s*, 18H), 3.98 (*s*, 4H), 4.52 (*s*, 4H), 6.68 (*d*, 2H), 6.96 (*m*, 4H), 7.52 (*m*, 4H), 7.72 (*s*, 2H, signal disappeared in D_2O), 7.88 (*d*, 2H). Anal. Calcd for $C_{36}H_{40}N_2S_2O_8Cl_2$: C, 56.61; H, 5.28; S, 8.40; mol. wt., 763.76. Found: C, 56.41; H, 5.31; S, 8.56; mol. wt., 809 ± 40.

2.5. PREPARATION OF **9** (SCHEME I.C.)

4′,5⁗-Di-*t*-butyl-5,6,9,10,15,16,19,20-tetrabenzo-6″,3‴,8,17-tetraaza-1,4,11,14-tetra-

oxa-7,18-dithiacycloeicosane-7,7,18,18-tetraoxide (**9**) was prepared as above for **8** from 1.05 g (2 mmol) of **15** and 0.49 g (2 mmol) of **17**, each in 150 mL of pyridine. The reaction mixture was stirred under reflux for 2 days. The solvent was evaporated and the residue was dissolved in 20 mL of methylene chloride and the undissolved precipitates were filtered. The filtrate was chromatographed on silica gel using methylene chloride/acetone (49 : 1 and then 5 : 1) to give 0.08 g (6%) of **9**, mp 253–256 °C (dioxane); IR (KBr): 3400, 3230, 1620 cm^{-1}; NMR: δ 1.31 (*s*, 18H), 4.39 (*s*, 8H), 6.83 (*m*, 4H), 7.13 (*d*, 2H), 7.45 (*dd*, 2H), 7.74 (*d*, 2H), 7.89 (broad, 2H, signal disappeared in D_2O), 8.13 (*d*, 2H). Anal. Calcd for $C_{34}H_{40}N_4S_2O_8$: C, 58.60; H, 5.79; mol. wt., 696.84. Found: C, 58.38; H, 6.02; mol. wt. 624 ± 25.

2.6. PREPARATION OF 10

N,N'-Diphenyl-*bis*-sulfonamide **10** was prepared by mixing a two-fold excess of aniline with **12** in methylene chloride. The product was recrystallized from acetic acid to give a 25% yield of solid **10**, mp 173–175 °C; IR (Nujol): 3230 cm^{-1}; NMR (DMSO-d_6): δ 1.20 (*s*, 18H), 3.93 (*m*, 4H), 4.23 (*m*, 4H), 6.9–8.33 (*m*, 16H), 9.7 (*s*, 2H, signal disappeared in D_2O). Anal. Calcd for $C_{36}H_{44}N_2S_2O_7$: C, 63.51, H, 6.51; S, 9.42. Found: C, 63.30; H, 6.48; S, 9.49.

2.7. CATION TRANSPORT STUDIES OF 4, 5, AND 10

Membrane transport experiments were carried out using bulk liquid membranes described previously [17, 19, 20]. The metal compounds were obtained in the highest grade available from the indicated suppliers and were used without further purification: cation hydroxides of Li^+ and K^+ (Spectrum), Rb^+ and Cs^+ (Aldrich), and Na^+ (Anachema – carbonate free, Harleco – carbonate free); cation nitrates of Li^+ (Baker), Na^+ (Baker, Mallinckrodt), K^+ (Fisher, Baker), and Rb^+ and Cs^+ (Aldrich). Reagent grade HNO_3 (Fisher, Mallinckrodt, Ashland) and spectroquality methylene chloride (CH_2Cl_2) (EM) were used. The metal solutions were prepared using distilled deionized water.

Source phases of different pH were prepared from appropriate amounts of MNO_3 and MOH. After 24 hours, the receiving phase was sampled and analyzed for cation concentration using a Perkin Elmer model 603 atomic absorption spectrophotometer. The pH values of the source phase solutions were measured using a Sargent Welch miniature combination pH electrode and found to correspond closely to the calculated values. The pH values of 1.0 M M^+ solutions listed in the Tables (see below) are the calculated values based upon the initial MOH concentration.

For those systems where appreciable cation transport occurred, the organic phase became cloudy approximately one-half hour after stirring began. The cloudiness was much more intense for systems in which the receiving phase pH was 1.5 than for those containing water except in the case of Li^+ where the reverse was true. This correlation between cloudiness and cation flux was not investigated further, but it may be a result of water being extracted with the cation into the membrane phase.

Each experiment was repeated at least 3 times, and the results are reported as the average of the three determinations. The standard deviations from the mean among the values in each experiment is less than 15 % except where the flux was below 100 and in a few other cases which are marked in the Tables. Experiments performed

in which no carrier was present in the membrane showed cation fluxes to be less than 0.3 (mol s^{-1} m^{-2}) $\times 10^8$.

3. Results and Discussions

The new macrocyclic compounds were prepared by the reactions of the appropriate *bis*-sulfonyl chlorides and diamines as shown in Scheme 1 and given in the Experimental Section above. The proposed structures are consistent with data obtained from their NMR and IR spectra and molecular weights or fd mass spectra. The NMR

Table I. Single M^+ fluxes[a] in a bulk H_2O–CH_2Cl_2–H_2O liquid membrane[b] system using **4** as carrier

M^+	Receiving Phase pH	Source Phase pH				
		11	12	13	13.5	14
Li^+	7			110	290*	3480
	1.5			30	180	1020
Na^+	7	6	9	34	1860	2060
	1.5	14	17	40	2530	5750
K^+	7	1	2	17	1490*	4190
	1.5	3	5	28	1070*	5440
Rb^+	7	1	2	25	980	370
	1.5	1	3	38	3400	940
Cs^+	7	2	3	97	4690*	8980*
	1.5	4	4	98	6800*	4090*

[a] J_M = (mol s^{-1} m^{-2}) $\times 10^8$; flux values were ±15% except for fluxes below 100 and those with an * where the values were ± greater than 15%.
[b] Phase compositions: Source: 1.0 M in each metal cation using appropriate amounts of MNO_3 and MOH to achieve the initial source phase pH. Membrane: 0.001M **4** in CH_2Cl_2. Receiving: initial pH 7 (H_2O) or 1.5 (HNO_3), as indicated.

Table II. Single M^+ fluxes[a] in a bulk H_2O–CH_2Cl_2–H_2O liquid membrane[b] system using **5** as carrier

M^+	Receiving Phase pH	Source Phase pH				
		11	12	13	13.5	14
Li^+	7	0	0	37	57	30
	1.5	0	0	65	26	13
Na^+	7	3	13	18	20	34
	1.5	7	13	25	30	27
K^+	7	0	1	23	14	7
	1.5	1	2	22	8	8
Rb^+	7	0	2	190	24	11
	1.5	0	2	34	22	7
Cs^+	7	0	37	860	190	38
	1.5	0	29	400	290	300

[a] J_M = (mol s^{-1} m^{-2}) $\times 10^8$; flux values were ±15% except for fluxes below 100.
[b] Phase compositions: Source: 1.0 M in each metal cation using appropriate amounts of MNO_3 and MOH to achieve the initial source phase pH. Membrane: 0.001M **5** in CH_2Cl_2. Receiving: initial pH 7 (H_2O) or 1.5 (HNO_3), as indicated.

Table III. Single M^+ fluxes[a] in a bulk H_2O–CH_2Cl_2–H_2O liquid membrane[b] system using **10** as carrier

M^+	Receiving Phase pH	Source Phase pH				
		11	12	13	13.5	14
Li^+	7	0	0	0	4	8
	1.5	0	0	2	8	19
Na^+	7	0	1	14	500*	1200
	1.5	2	3	16	580	1630*
K^+	7	0	0	7	440*	1790*
	1.5	0	1	6	460	4320*
Rb^+	7	0	0	4	50	240
	1.5	0	1	8	480*	6190
Cs^+	7	1	2	10	450	[c]
	1.5	4	4	22	1010*	[c]

[a] $J_M = (\text{mol s}^{-1}\ \text{m}^{-2}) \times 10^8$; flux values were ±15% except for fluxes below 100 and those marked with an * where the flux values were ±25%.

[b] Phase compositions: Source: 1.0 M in each metal cation using appropriate amounts of MNO_3 and MOH to achieve the initial source phase pH. Membrane: 0.001M **10** in CH_2Cl_2. Receiving: initial pH 7 (H_2O) or 1.5 (HNO_3), as indicated.

[c] Complete transport of Cs^+ was observed in 24 hours.

spectra for **5** and **8** are similar to those of the non-chloro-substituted analogs. The structures of the unsubstituted analogs were determined by X-ray crystal-structure analyses [15, 16]. The open-chain *bis*- amide **10** was prepared by reacting the *bis*-sulfonyl chloride with two equivalents of aniline.

Ligands **4**, **5** and **10** were tested as carriers for cations in a water–methylene chloride–water bulk liquid membrane system using transport cells patterned after the Shulman Bridge and which have been described [17, 19, 20]. Flux values for the transport of the alkali metal cations by these ligands are given in Tables I–III, respectively. In each case, little or no transport occurred at source phase pH values below 13. The pK_{a_1} value for these compounds should be about 9 [21]. The pK_{a_2} value should be about 12, so that ionization of both protons seems to be a requirement for transport.

Ligand **4** showed effective and generally similar transport of all alkali metal cations at source phase pH values of 13.5 and 14 (Table I). The flux values of 5750 for Na^+, 5440 for K^+ and 8980 (mol sec^{-1} $\text{m}^{-2}) \times 10^8$ for Cs^+ are 3 to 4 fold higher than the flux values of 1600 plus for K^+ and Rb^+ observed for compound **2** [19]. Generally, the best transport by ligand **4** was observed for the systems containing acid in the receiving phase (Table I). The transport of Li^+ at all source phase pH values, K^+ at a source phase pH value of 13.5 and Cs^+ at a source phase pH value of 14 was higher into a neutral receiving phase (Table I). The better transport of lithium ions by a factor of 4 into a neutral source phase is probably a result of the formation of an LiOH complex which would help remove Li^+ from the ligand at the receiving phase–CH_2Cl_2 interface. Similar behavior was found for the Li^+–**1** system [20]. Potassium, on the other hand, was transported best by **2** into an acidic receiving phase [18, 19]. The reason for the increased transport of K^+ and Cs^+ by **4** into neutral receiving phases is not yet understood.

Table IV. Competitive M^+ fluxes[a] in a bulk H_2O–CH_2Cl_2–H_2O liquid membrane[b] system using **10** as carrier

$\frac{M_1^+}{M_2^+}$	Receiving Phase pH		$\frac{M_1^+}{M_2^+}$	Receiving Phase pH		$\frac{M_1^+}{M_2^+}$	Receiving Phase pH	
	7	1.5		7	1.5		7	1.5
$\frac{Li^+}{Na^+}$	$\frac{120}{680}$	$\frac{225*}{840}$	$\frac{Na^+}{K^+}$	$\frac{1420*}{1280*}$	$\frac{2830}{1890*}$	$\frac{K^+}{Rb^+}$	$\frac{1150*}{1170*}$	$\frac{5020}{6030}$
$\frac{Li^+}{K^+}$	$\frac{192}{749}$	$\frac{170}{600}$	$\frac{Na^+}{Rb^+}$	$\frac{1780}{1970*}$	$\frac{4780}{5300*}$	$\frac{K^+}{Cs^+}$	$\frac{1390}{1030}$	$\frac{5230}{3300}$
$\frac{Li^+}{Rb^+}$	$\frac{130*}{580*}$	$\frac{150}{640}$	$\frac{Na^+}{Cs^+}$	$\frac{1660*}{5700*}$	$\frac{4690*}{22890}$	$\frac{Rb^+}{Cs^+}$	$\frac{890}{490}$	$\frac{5670}{1680}$
$\frac{Li^+}{Cs^+}$	$\frac{280}{2540}$	$\frac{360}{3350}$						

[a] $J_M = (\text{mol s}^{-1}\ \text{m}^{-2}) \times 10^8$; flux values were ±20% except for flux values marked with an * which were ±30%.

[b] Phase compositions: Source: initial pH 14, 0.5 M in each metal hydroxide. membrane: 0.001 M **10** in CH_2Cl_2. Receiving: initial pH 7 (H_2O or 1.5 (HNO_3), as indicated.

While ligand **4** proved to be an excellent transport agent for the alkali metal cations, **5** is a poor transport agent for these cations (Table II). Compounds **4** and **5** differ only in that **5** has a chlorine moiety attached to the benzene ring situated between the two amide nitrogens. The crystal structure of **4** showed that the molecule is in the form of a shallow cup and that the benzene ring is part of the lip of the cup [15]. A relatively large chlorine substituent on the benzene ring could block the cavity so that the normal complexation does not take place.

The open-chain ligand **10** proved to be an excellent transport agent for Cs^+ ions (Table III). Essentially all of the Cs^+ cations were transported in 24 hours at a source phase pH value of 14. Large flux values for K^+ and Rb^+ where the receiving phase was acidic were also observed. Compound **10** probably is able to wrap around these cations effectively to form a methylene chloride-soluble complex. The extremely low transport of Li^+ ions by **10** suggests that the ionised ligand has a cavity and that the cavity is larger than that found in compounds **4** and **5**.

A study of competitive transport of pairs of alkali metal cations by **10** proved to be interesting. The results in Table IV show that all alkali metal cations larger than Li^+ were selectively transported over Li^+. Cesium ions were selected over Na^+ but there was little selectivity in any of the other cases. A more complete cation transport study of these interesting new ligands will be reported when the work is finished.

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