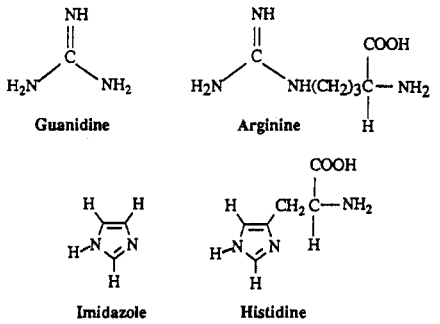
In the past decade, the role of complementary size, shape, and functionality in the molecular recognition of *neutral molecules* has been pointed out. Artificial receptor molecules have been designed with multiple recognition sites and a well-defined geometry, capable of strong and selective binding of the appropriate substrates by hydrogen bonding, ionic interaction, and/or hydrophobic interactions.[2-8] Rebek et al.[2] have used molecular clefts with acidic functions for the complexation of diamines, such as imidazole. Our group has shown that additional hydrogen-bond donors[9] or electrophilic metal centers,[10] incorporated in the cavities of macrocyclic polyethers, improve strongly the complexation of urea. This type of cocomplexation of a neutral guest by a host molecule either by hydrogen bonding or by coordination with a metal ion, is frequently observed in (metallo)enzymes.

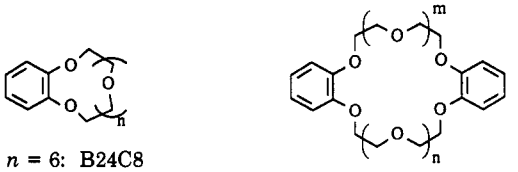
Imidazole and guanidine are two biologically important organic bases. These base residues are part of the essential amino acids histidine and arginine, and occur in many natural polypeptides.[11] Guanidine is one of the *strongest* organic bases (pK_a = 13.6),[12] and it will predominantly be present as the conjugated acid. On the other hand, imidazole is present as a free base in the pH range at which most enzymes function (pK_a = 6.99).[12] This may contribute to the unique properties of histidine residues in the active site of most enzymes where they can act either as proton donor or proton acceptor.



For the optimal complexation of polyfunctional cations such as uronium, and guanidinium salts, it has been shown that crown ethers with at least 27 ring atoms are needed for the formation of encapsulated complexes.[13-20] Otherwise, relatively weak perching complexes are formed.[21] Many X-ray structures of the encapsulated complexes have been reported.[16-20] The complexation of imidazole and/or imidazolium salts by macrocyclic ligands has hardly received substantial attention. Lehn et al.[15] have shown that a chiral 27-crown-9-hexacarboxylate forms a relatively stable complex with an imidazolium cation, even in aqueous solutions. They suggested that the imidazolium ion binds to the macrocyclic receptor by forming two NH···O hydrogen bonds with the oxygen atoms in the ring. Hitherto, this assumption has not been verified via an X-ray structure of a solid complex.

In this paper the complexation of imidazolium salts by a number of 24- to 33-membered macrocycles is described as an extension of the extraction and membrane transport experiments of guanidinium salts.[17,20] In addition, the competition between guanidinium and imidazolium ions in membrane transport has been studied.

Chart I. Structures of Carrier Ligands[a]



1, n = 6: B24C8
2, n = 7: B27C9
3, n = 8: B30C10
4, n = 9: B33C11

5, n = 1, m = 5: [3,7]DB30C10
6, n = 0, m = 6: [2,8]DB30C10
7, n = 2, m = 5: [4,7]DB33C11

[a] The following code was used in the abbreviated names: C = crown, B = benzo, D = di (or bis), [,] = code for the amount of hetero atoms between the functionalities.

Table I. Extraction Efficiency of Benzo and Dibenzo Crown Ethers for Imidazolium Perchlorate

crown ether	ring size	$[CE]_m^{o}$,[a] M	$[CE]_m^{t}$,[b] M	extraction efficiency[c]
1	24	0.20	0.19	<0.05
2	27	0.12	0.12	<0.05
3	30	0.20	0.18	0.62
4	33	0.18	0.18	0.65
5	30	0.15	0.15	0.56
6	30	0.11	0.11	0.21
7	33	0.20	0.20	<0.05

[a] The initial crown ether concentration in the organic phase. [b] The total crown ether concentration in the organic phase at equilibrium. [c] The ratio of the imidazolium perchlorate concentration and the total crown ether concentration in the organic phase at equilibrium; Standard deviation ±10%.

Results

The crown ether carriers used in the extraction and transport experiments are depicted in Chart I.

Liquid–Liquid Phase Transfer of Imidazolium Perchlorate. The complex formation of benzo (1–4) and

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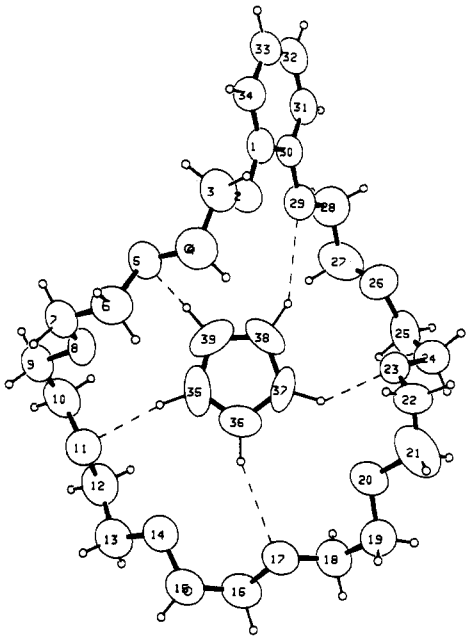

Figure 1. ORTEP[22] view, showing 50% probability thermal ellipsoids for non-H atoms, of the structure of benzo-30-crown-10-imidazolium perchlorate, with atom numbering. Hydrogen bonds are indicated by dashed lines. The perchlorate anion is not shown.

dibenzo crown ethers (**5–7**) with imidazolium salts was studied by means of two-phase liquid–liquid extraction experiments. The amount of salt that is transferred to the organic phase was determined by ^{1}H NMR spectroscopy, after separation of the two liquid phases. The solubility of the crown ethers in water was verified, with use of 1,2,4,5-tetramethylbenzene as an internal standard in the organic phase, by comparing the ratio of crown ether to 1,2,4,5-tetramethylbenzene in the chloroform solution before and after equilibration. Further details of the extraction experiments are described in the Experimental Section. The amount of imidazolium perchlorate transferred to the organic phase is expressed as the extraction efficiency, which represents the ratio between the complexed imidazolium perchlorate and the total crown ether concentration in the organic phase at equilibrium. The results of the extraction experiments with the crown ethers **1–7** are summarized in Table I. Firstly, the results indicate that for complexation of imidazolium a ring size of at least 30 ring atoms is needed; smaller rings do not extract any imidazolium salts. Secondly, the incorporation of a *second* aromatic ring reduces the extraction efficiency and renders the extraction more dependent on variation of the conformation of the crown ether ring (**5–7**).

In the case of benzo-30-crown-10, a crystalline compound was obtained from the $CDCl_3$ layer upon addition of a small amount of diethyl ether. This was a 1:1 complex of benzo-30-crown-10 with imidazolium perchlorate as proven by single-crystal X-ray analysis (see Figure 1) and ^{1}H NMR spectroscopy. In this complex the imidazolium cation[23] is encapsulated in the macrocyclic cavity, with short nonbonding distances between NH and CH groups of the cation and ether oxygens of benzo-30-crown-10 (see Table II). These short contacts can be described as weak nonlinear hydrogen bonds.[24] In the ORTEP view only the most linear hydrogen bond for every donating group is depicted;

Table II. Short Nonbonded Distances and Angles in the Structure of Benzo-30-crown-10–Imidazolium Perchlorate[a]

donor atom D	acceptor atom A	distance D···A, Å	distance H···A, Å	angle D–H···A, deg
N35	O8	3.01	2.40	121
N35	O11	3.14	2.22	161
C36	O14	3.27	2.56	131
C36	O17	3.35	2.46	156
N37	O20	3.04	2.32	131
N37	O23A[b]	2.76	2.00	134
N37	O23B[b]	2.97	2.10	149
C38	O26	3.53	2.83	130
C38	O29	3.55	2.70	149
C39	O5	3.18	2.51	127
C39	O8	3.15	2.71	108

[a] Estimated standard deviations less than 0.01 Å and 1° (no contribution from calculated H atom positions). [b] Majority (A) and minority (B) position of disordered atom O23.

there are no hydrogen bonds between the imidazolium cation and perchlorate anion. Solid complexes of imidazolium perchlorate with the other investigated macrocycles could not be isolated. Extraction experiments have also been carried out with excess of a mixture of both guanidinium and imidazolium perchlorate (ratio 1:1) in the aqueous phase, and the crown ethers **3** and **7**, respectively, in the organic phase. In the ^{1}H NMR spectra only guanidinium protons were observed, indicating a selective complexation of guanidinium cations.

Bulk Liquid Membrane Transport. The transport experiments have been carried out in a rectangular U-tube of well-defined shape and dimensions at a constant temperature of 25.0 ± 0.5 °C. A detailed description of the measurement set up and the dimensions has been published previously.[20] Further experimental conditions are included in the Experimental Section. After completion of the transport experiments, the receiving phase was analyzed for imidazolium salt. In the case of the selectivity studies the receiving phase was analyzed for both imidazolium and guanidinium salts by a potentiometric titration.

A comparison of the transport of imidazolium salts with the results of guanidinium thiocyanate transport[20] requires that the same anion is used, in order to eliminate the anion effect.[25] However, imidazolium thiocyanate is not commercially available, and preparation from imidazolium chloride by anion exchange resulted in an impure product. Therefore, imidazolium mesylate was prepared from imidazole and methanesulfonic acid. The transport of imidazolium mesylate with crown ether **3** as a carrier was investigated, but no transport was observed. Thiocyanate anions were introduced in the source phase by the addition of 1 equiv of lithium thiocyanate. For each of the crown ethers the flux of lithium thiocyanate has been determined in an independent experiment with only lithium thiocyanate present in the source phase, and the flux never exceeded 1×10^{-9} mol cm^{-2} h^{-1}. In the transport of imidazolium thiocyanate three equilibria of complexation at the interface between source and membrane phase can be distinguished (eq 2–4),[26] depending on the pH of the source phase (eq 1).[26] During these experiments the pH of the

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(26) ImH^+ = imidazolium cation; Im = imidazole; A^- = anion; CE = crown ether; m = membrane phase; w = aqueous phase. Equation 1 has a pK_a value equal to 6.99.

$$(ImH^+)_w \overset{K_a}{\rightleftharpoons} (Im)_w + (H^+)_w \quad (1)$$

$$(ImH^+)_w + (A^-)_w + (CE)_m \overset{K_{ex}(1)}{\rightleftharpoons} (ImH^+\cdot CE\cdot A^-)_m \quad (2)$$

$$(Im)_w + (CE)_m \overset{K_{ex}(2)}{\rightleftharpoons} (Im\cdot CE)_m \quad (3)$$

$$(H^+)_w + (A^-)_w + (CE)_m \overset{K_{ex}(3)}{\rightleftharpoons} (H^+\cdot CE\cdot A^-)_m \quad (4)$$

source phase is maintained at 5.1, which means that the imidazolium concentration is about 80 times larger than the imidazole concentration. The extraction equilibrium constant $K_{ex}(1)$ will be larger than $K_{ex}(2)$ because the complexes formed with charged molecules are more stable than complexes of hosts with neutral molecules.[27] Consequently, the concentration of $(ImH^+\cdot CE\cdot A^-)_m$ will be much larger than the concentration of $(Im\cdot CE)_m$. The effect of proton transport (eq 4) on the overall flux is dependent on the ratio between $[K_{ex}(3)][H^+]_w$ and $[K_{ex}(1)][ImH^+]_w$. At a pH of 5.1 the $[H^+]_w$ is much smaller than $[ImH^+]_w$ and $K_{ex}(3)$ will be much smaller than $K_{ex}(1)$ because no measurable $[H_3O^+]$ could be detected after completion of the transport experiments. Therefore eq 4 is of minor importance, and this means that the complex concentration in the membrane phase is mainly determined by eq 2. On the basis of these arguments we can conclude that in our experiments the transport mechanism and corresponding equations are comparable with the crown ether mediated transport of guanidinium thiocyanate.[20]

The values of transport of imidazolium thiocyanate as given in Table III are the average of at least two independent experiments with a maximum standard deviation of ±10%. In analogy with the extraction experiments, leakage of the carrier from the membrane is negligible. When no carrier is present in the membrane phase, the amount of imidazolium thiocyanate transported through the membrane during 24 h was below the detection limit ($<2 \times 10^{-9}$ mol cm^{-2} h^{-1}). Crown ether **3** shows the highest flux of imidazolium thiocyanate, but the flux is significantly lower than in the guanidinium thiocyanate transport (Table III).[28] When the rates of transport of imidazolium thiocyanate are compared with the extraction efficiencies of the corresponding crown ethers given in Table I, the same tendency is observed. The highest extraction efficiencies correspond to the highest fluxes in the case of the carriers **3–5**. Because of the lower limit of detection of imidazolium ($<5 \times 10^{-6}$ M) a quantitative analysis of the receiving phase for the carriers **2**, **6**, and **7** was not possible.

The selectivity of the crown ethers was investigated in competition experiments with both guanidinium and imidazolium cations present in the source phase. These experiments are only interesting for the crown ethers **3–5** because these carriers are able to transport both cations, as was shown in independent experiments. The amounts of imidazolium transported to the receiving phase are nearly the same as in the single transport experiments, but in addition guanidinium thiocyanate is transported. At the source phase interface there will be a competition between the crown ether molecules and both the guanidinium and imidazolium salts. When the concentrations

Table III. Flux of Imidazolium and Guanidinium Thiocyanate in Single Transport and in Competition Experiments

	single transport		competition[c]	
crown ether	$10^8 J$-(ImHSCN),[a] mol cm^{-2} h^{-1}	$10^8 J$-(GuHSCN),[b] mol cm^{-2} h^{-1}	$10^8 J$-(ImHSCN), mol cm^{-2} h^{-1}	$10^8 J$-(GuHSCN), mol cm^{-2} h^{-1}
–	*d*	*d*	*d*	*d*
2	*d*	15.2	*d*	19.4
3	3.0	16.9	2.9	22.2
4	0.8	9.0	1.1	13.1
5	1.0	9.2	1.0	10.6
6	*d*	11.6	*d*	14.8
7	*d*	6.9	*d*	6.9

[a] Source phase, 0.5 M imidazolium mesylate and 0.5 M lithium thiocyanate (pH = 5.1); membrane phase, 10^{-3} M carrier; receiving phase, distilled deionized water; T = 298 K; standard deviation ±10%. [b] Extrapolated from the experiment with 1.0 M guanidinium thiocyanate in the source phase with eq 5; standard deviation ±10%. [c] Source phase, 0.5 M imidazolium mesylate and 0.5 M guanidinium thiocyanate; membrane phase, 10^{-3} M carrier; receiving phase, distilled deionized water; T = 298 K; standard deviation ±10%. [d] J(ImHSCN) ≅ J(GuHSCN) $< 2 \times 10^{-9}$ mol cm^{-2} h^{-1}.

Table IV. Selectivity Coefficients for the Crown Ethers in Relation to Guanidinium and Imidazolium Salts

	$10^2 K_{ex}$,[a] M^{-2}		selectivity
crown ether	imidazolium	guanidinium	coefficient[b]
2	<1.2	120	>100
3	22	130	6
4	5.0	62	12
5	6.2	67	11
6	<1.2	84	>70
7	<1.2	46	>38

[a] Calculated with eq 5 from the measured flux. [b] The ratio between the extraction equilibrium constant of guanidinium and imidazolium; standard deviation at most ±20%.

of the salts in the membrane phase are similar, the difference in transport of guanidinium and imidazolium salts is attributed to the difference in complexation constant. On the basis of the complexation equilibrium it is obvious that the complex concentration of imidazolium salts has to decrease in the presence of guanidinium salts, because the crown ether concentration available for complexation is reduced. However, the difference in the flux of imidazolium salts between the single and competition experiment is of the order of accuracy of the experiments. The same explanation is valid for the transport of guanidinium salts in the attendance of imidazolium salts. It should be noted that the values of the flux for a single experiment are calculated with eq 5[20,28] by extrapolation of the initial

$$J = \frac{D_m}{l}[\text{complex}]_m = \frac{D_m[CE]_m^\circ}{l}\left\{\frac{K_{ex}\{[\text{salt}]_w^\circ\}^2}{1 + K_{ex}\{[\text{salt}]_w^\circ\}^2}\right\} \quad (5)$$

salt concentration in the source phase from 1.0 to 0.5 M. Since an enlargement of the flux in a competition experiment is not likely (only when due to a common-ion effect), the calculated values are probably too low. An explanation is presumably a saturation of the organic phase with salt at high salt concentrations in the aqueous phase (1.0 M). In that case the experimentally determined partition coefficient does not have the real value.

The selectivity of the crown ethers with regard to the guanidinium and imidazolium salts appears from the difference between the fluxes of these salts in competition experiments. The selectivity of a ligand is in no case directly related to the relative fluxes, J(guanidinium)/J-

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(28) In eq 5 D_m = diffusion coefficient of the complex in the membrane phase (cm^2 s^{-1}); l = thickness of the unstirred Nernst layer (cm); []° = initial concentration. D_m/l is equal to $(1.9 \pm 0.1) \times 10^{-4}$ cm s^{-1} and K_{ex} is equal to the product of the partition coefficient of the salt and the association constant of the complex in the membrane phase.[9]

(imidazolium), measured in *single* experiments.[29] The *thermodynamic extraction selectivity*, K_{ex}(guanidinium)/K_{ex}(imidazolium), of a ligand is a better reflection of the competition experiment. The values of K_{ex} can be calculated from the measured fluxes and eq 5.[28]

In the case of carriers **2**, **6**, and **7** only a lower limit of the extraction equilibrium constant can be calculated from the lower limit of the flux of imidazolium thiocyanate. The calculated values of K_{ex} are collected in Table IV. The selectivity coefficients of **2**, **6**, and **7** are larger than 100, 70, and 38, respectively. Crown ethers **3**, **4**, and **5** have selectivity coefficients equal to 6, 12, and 11, respectively.

Discussion

Structure of the Benzo-30-crown-10–Imidazolium Complex. The benzo- and dibenzo crown ethers with 27- to 33-membered rings display a different behavior in relation to the complexation of guanidinium or imidazolium cations. Benzo-27-crown-9 extracts guanidinium efficiently and forms a 1:1 encapsulated complex, while imidazolium is not complexed by this crown ether (extraction efficiency <0.05). According to CPK models the 27-membered ring is too small to encapsulate the imidazolium cation. When the crown ether ring is enlarged with one ethylene oxide moiety, an encapsulated imidazolium complex is possible. However, in the absolute sense the extraction efficiency determined experimentally was not as high as for the extraction of guanidinium perchlorate with crown ether **2**.[17]

The X-ray structure of the complex of benzo-30-crown-10 and imidazolium perchlorate provides information about the conformation of the complex. The shape of the thermal ellipsoids of the imidazolium atoms suggests that the cation undergoes considerable rotational motion in the cavity, probably accompanied by a variation in the geometry of the hydrogen bonding. This may be due to the absence of a good complementarity between host and guest in their relative hydrogen bond acceptor and donor positions. Moreover, the cavity of the 30-membered macrocyclic ring is somewhat too large for the imidazolium cation as can be concluded from the irregular and partly disordered conformation of the macrocycle and from some rather long donor–acceptor distances. This structure confirms the assumption of Lehn et al.[15] that the imidazolium ion binds to the macrocyclic receptor molecule by forming two strong NH···O hydrogen bonds (Figure 1: distance H···O, 2.22 and 2.00 Å) with two oxygen atoms separated by three ethylene oxide fragments. However, there are also three weak CH···O hydrogen bonds (distance H···O, 2.46, 2.70, and 2.51 Å) and two N···O electrostatic interactions. In the case of the complexation of guanidinium with both the 27-membered[16-19] and 30-membered[17,20] crown ether there are six strong NH···O hydrogen bonds and three considerable electrostatic N···O interactions with the crown ether oxygens that are not involved in hydrogen bonding. Therefore, the guanidinium cations are expected to be more strongly coordinated to the host than the imidazolium cations. The incorporation of a second catecholic moiety in **3** and **4** has the same effect on the extraction efficiency of imidazolium perchlorate as was noticed for the extraction of guanidinium perchlorate.[17] The difference in extraction efficiencies is attributed to a combination of ring size, extension of the less basic catechol oxygen atoms, and enhancement of the rigidity of the crown ether. It is known that small variations in the structure of the host molecule can have substantial effects on the hydrogen bonding between guanidinium and **5** or **6**.[20] In analogy with these results, **5** and **6** show different extraction efficiencies with imidazolium perchlorate and consequently different complexation constants. From CPK models it can be concluded that **6** is more rigid than **5**, and that for complexation of an imidazolium cation by **6** at least two catecholic oxygens are needed. In the case of **5** only one catecholic oxygen will take part in hydrogen bonding. The catecholic oxygens have a lower basicity than the aliphatic ether oxygens, and therefore, the hydrogen bonds will have a smaller contribution to the free energy of complexation. Because of this and with the difference in rigidity, **5** will be a better host for imidazolium than **6**. A larger reduction of the extraction efficiency is observed for the 33-membered crown ethers **4** and **7**. Although the catecholic oxygens are not needed in the hydrogen bonding, the rigidity of **7** will be too large for adopting the optimal conformation needed for complexation.

Complexation Constants. The large difference in the fluxes of imidazolium and guanidinium salts through the liquid membrane can be attributed to the difference in extraction equilibrium constant K_{ex}. This is the product of the partition coefficient of the salt and the complexation constant. The complexation constant for imidazolium can be calculated from K_{ex} when the partition coefficient of the imidazolium salt is known, assuming complexation in the membrane phase. However, the amounts of imidazolium thiocyanate in the organic phase are too low for accurate analysis.[30] Since both guanidinium and imidazolium are monovalent polyfunctional organic cations, and since there is a common anion, the partition coefficients of the salts can be expected to be roughly the same. Therefore the complexation constants are the deciding factor in determining selectivity. A qualitative analysis of the value of the complexation constant is possible from the X-ray studies. Only on the basis of the number of strong NH···O bridges it is likely that K_m(imidazolium) is smaller than K_m(guanidinium). In the literature only the complexation constants of the complexes of both guanidinium and imidazolium salts with 27-crown-9-hexacarboxylate have been reported (in water: 9000 vs 350 M^{-1}, respectively).[15] These data are in line with the statement of a lower complexation constant of the imidazolium complex compared with the guanidinium complex.

Selectivity Coefficient. The selectivity coefficient of compound **2** is high compared with the other values due to the ring size, which discriminates imidazolium cations very well, while it possesses a good fitting cavity for guanidinium complexation. The compounds **6** and **7** also have good selectivity coefficients, but the absolute amount of transported guanidinium will be lower. Preferential transport of imidazolium in the presence of guanidinium under similar conditions probably will never take place as long as the complexation occurs by encapsulation together with hydrogen bonding.

Conclusions

The results described in this paper reveal that for encapsulation of imidazolium salts macrocyclic crown ethers are necessary with at least 30 ring atoms. The first solid complex of an imidazolium salt, encapsulated in a cavity of a crown ether, is isolated. The X-ray structure shows that two NH···O hydrogen bonds and three CH···O hy-

(29) Behr, J.-P.; Kirch, M.; Lehn, J.-M. *J. Am. Chem. Soc.* **1985**, *107*, 241.

(30) Direct analysis of imidazolium thiocyanate in chloroform is not possible with the titration technique. Evaporation of the chloroform yielded besides imidazolium thiocyanate also traces of an acidic pollution originated from chloroform. The acidic compound disturbs the titration of imidazolium.

drogen bonds are created during complexation. The complexation constant of the imidazolium complex is expected to be lower than the complexation constant of the guanidinium complex for similar crown ethers on the basis of the solid-state data of the complexes as well as the fluxes measured in a competition experiment. The facilitated transport rate of imidazolium thiocyanate through a bulk liquid membrane is the highest with benzo-30-crown-10, but the absolute rate is lower than for the transport of guanidinium thiocyanate. Benzo-27-crown-9 is extremely suited for selective transport of guanidinium in the presence of imidazolium.

Experimental Section

Melting points were determined with a Reichert melting point apparatus and are uncorrected. The ^1H NMR spectra were recorded with a Bruker WP-80, in $CDCl_3$ with Me_4Si as an internal standard. Mass spectra were obtained with a Varian Mat 311A.

Materials. Benzo-24-crown-8 (**1**),[31] benzo-27-crown-9 (**2**),[31] benzo-30-crown-10 (**3**),[31] benzo-33-crown-11 (**4**),[31] [3,7]dibenzo-30-crown-10 (**5**),[17] [2,8]dibenzo-30-crown-10 (**6**),[20] and [4,7]dibenzo-33-crown-11 (**7**)[17] were prepared according to literature procedures.

Imidazolium mesylate was prepared from imidazole (Janssen Chimica) and methanesulfonic acid (Janssen Chimica). Imidazole (0.44 mol) was dissolved in 100 mL of water, and 1 equiv of methanesulfonic acid was added dropwise under stirring. The solution was extracted with chloroform, and the phases were separated. The water was evaporated in vacuo. The solid was treated twice with ethanol and dried under vacuum after filtration: yield 80%; ^1H NMR (D_2O) δ 8.7 (s, 1 H, CH=N), 7.5 (br s, 2 H, HC=CH), 2.8 (s, 3 H, CH_3). Anal. Calcd for $C_4H_8N_2SO_3$: C, 29.29; H, 4.91; N, 17.06; S, 19.53. Found: C, 29.38; H, 5.04; N, 17.07; S, 19.67. A purity (≥99.4 ± 0.1%), was determined by a potentiometric titration (vide infra).

Guanidinium thiocyanate was obtained from Fluka and used without further purification. Lithium thiocyanate (ICN Biomedicals) was used without purification and contained 31.2 ± 0.8% crystal water. Dimethylformamide (Aldrich) of HPLC quality was distilled over calcium hydride before use. Acetonitrile (Merck) was of DNA synthesis quality. Tetrabutylammonium hydroxide (Merck, 0.1 M in methanol) was diluted until 0.01 M with a mixture of 2-propanol (Merck, p.a. grade) and methanol (Merck, p.a. grade) in the ratio 3/1 (v/v).

Extraction Experiments. A $CDCl_3$ solution (1 mL) containing 0.2 mmol of crown ether and 0.2 mmol of 1,2,4,5-tetramethylbenzene was agitated for 17 h with 1 mL of an aqueous solution, containing 0.5 mmol of imidazolium mesylate and 0.5 mmol of perchloric acid (11.6 M). Subsequently, the $CDCl_3$ layer was separated off and dried over molecular sieves (4 Å). The amount of crown ether transferred to the aqueous phase during equilibration was determined by comparing the ratios of crown ether and 1,2,4,5-tetramethylbenzene of the chloroform solution before and after equilibration. The ratio of crown ether to imidazolium perchlorate in the chloroform phase was calculated from the intensities in the ^1H NMR spectra.

Benzo-30-crown-10–Imidazolium Perchlorate (1:1). The complex was isolated from the organic layer, obtained from an extraction experiment, by the addition of diethyl ether to the chloroform layer. The crystals formed were filtered off: mp 128–131 °C; ^1H NMR δ 9.2 (s, 1 H, CH=N), 8.0 (d, J = 1.2 Hz, 2 H, HC=CH), 6.9 (s, 4 H, Ar H), 4.3–3.7 (m, 36 H, OCH_2). No satisfying elemental analysis could be obtained.

X-ray Crystallography. X-ray diffraction measurements were performed at 167 K on an Enraf-Nonius CAD4 diffractometer, with graphite monochromated Mo Kα radiation. Lattice parameters were determined by least-squares methods from 20 centered reflections. Crystal data: $C_{27}H_{45}ClN_2O_{14}$, fw = 657.12, monoclinic, spacegroup $P2_1/n$, a = 9.574 (2) Å, b = 12.734 (3) Å, c = 27.357 (6) Å, β = 92.16 (1)°, V = 3333 (2) Å^3, Z = 4, D_c = 1.31 g cm^3, $F(000)$ = 1400, μ = 1.8 cm^{-1}. A total of 5839 intensities was measured in the $\omega/2\theta$ scan mode ($3 < \theta < 22.5°$) and corrected for the decay of three control reflections, measured every hour, and for Lorentz polarization, but not for absorption.

The structure was solved by direct methods.[32] A total of 2570 reflections with $F_o^2 > \sigma(F_o^2)$ were considered observed and included in the refinement (on F) by full-matrix least-squares calculations; weights were calculated as $w = 4F_o^2/\sigma^2(F_o^2)$, $\sigma^2(F_o^2) = \sigma^2(I) + (pF_o^2)^2$, $\sigma(I)$ is based on counting statistics, and p is an instability factor (value 0.05) obtained from plots of F_o vs weighted error. All H atoms were put in calculated positions and treated as riding on their parent atom. Further details concerning the treatment of the H atoms are in the supplementary material. The structure was found to be disordered; for the fragment C22–C25 two partially occupied positions were found and refined to occupancies of 56 and 44%, respectively. A total of 434 parameters were refined; overall scale factor, positional and anisotropic thermal parameters for non-H atoms, occupancy factor for the disordered fragment. Refinement converged to final agreement values of R = 9.8% and R_w = 6.9%, with shift/error ratios larger than unity only in the disordered region. A final difference Fourier map showed no significant features. All calculations were done with SDP.[33]

Potentiometric Titration. The imidazolium and guanidinium concentrations in the receiving phase were determined by a potentiometric acid/base titration with tetrabutylammonium hydroxide (0.01 M) as a titrant. First, the water was evaporated, and the residue was dissolved in 5 mL of dimethylformamide (solvent for imidazolium thiocyanate) with an ultrasonic bath at 50 °C. Subsequently, 35 mL of acetonitrile was added to dissolve guanidinium thiocyanate, and the solution was titrated with a solution of tetrabutylammonium hydroxide in a mixture of 2-propanol and methanol (3/1 (v/v)). In the titrations, carried out at room temperature with an automatic titrator (Metrohm titroprocessor E 636; electrode, glass/calomel Metrohm 6.0203.100), three inflection points were found. The first equivalence point corresponds to imidazolium, the second to guanidinium and the blank (small traces of acid in dimethylformamide and acetonitrile), and the last equivalence point is attributed to the deprotonated ion of imidazole. The guanidinium salt concentration was corrected for the blank.

Membrane Transport Experiment.[20] The membrane phase, chloroform containing 1.0 mM of carrier, was stirred magnetically at 200 rpm. The source phase consisted of a 0.5 M of an aqueous solution of lithium thiocyanate, imidazolium mesylate, and lithium thiocyanate or imidazolium mesylate and guanidinium thiocyanate, respectively. The receiving phase of distilled deionized water was analyzed for the amount of imidazolium and/or guanidinium at the end of 24 h by means of a potentiometric titration.

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Registry No. **1**, 72216-45-6; **2**, 63144-76-3; **3**, 77963-50-9; **4**, 104946-62-5; **5**, 104946-52-3; **6**, 104946-54-5; **7**, 87586-46-7; imidazolium perchlorate, 61335-48-6; guanidinium thiocyanate, 593-84-0; benzo-30-crown-10–imidazolium perchlorate, 118725-01-2; imidazolium thiocyanate, 118725-02-3; imidazolium mesylate, 82220-44-8.

Supplementary Material Available: Lists of positional parameters for all atoms, anisotropic thermal parameters for heavy atoms, isotropic thermal parameters for hydrogen atoms, and lists of bond lengths and bond angles for the benzo-30-crown-10–imidazolium perchlorate (1:1) complex, as determined by X-ray diffraction (8 pages). Ordering information is given on any current masthead page.

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