'Double Armed' Crown Ethers with Specific Cation Transport Ability

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Macrocyclic polyethers having two 'arms' available for cation binding provide new and characteristic transport abilities, based on their unique ligand topology, which were not attained in the usual crown ether and cryptand systems.

Several types of synthetic carriers have been developed,[1] which mimic the biological transport processes. In particular, cryptand molecules[2] are recognized as specific carriers for alkali and alkaline earth cations. They offer highly stable and selective complexations as well as effective shielding of the complexed cations, as in the natural ionophores. However, more dynamic complexing properties of these potential carriers are required to realize the effective transport as observed in the biological systems.[3]

Here we present a new class of synthetic carrier molecules, which are characterized by the parent crown ether ring and functionalized 'arms' (Figure 1). They are expected to wrap around the guest cation in such a way that secondary donor groups on both arms would provide axial co-ordination to the guest cation trapped in the parent crown ether ring. Their complex structures are closely similar to those of cryptand compounds, but higher mobility of the two 'arms' attached to the crown ether ring may permit the highly dynamic complexation and decomplexation that are required for efficient transport. We prepared three kinds of 'double armed' crown ethers, (**2**)—(**4**), as new cation carriers,[4] from 1,10-diaza-4,7,13,16-tetraoxa-18-crown-6.† The conventional diaza-crown ether (**1**) and cryptand[2.2.2] (**5**) were also examined. The transport experiments were performed in a U-type glass cell[5] under the conditions shown in Table 1, and the transported amounts of the guest salts were determined by means of the ion selective electrode technique.

The 'double armed' crown ether (**3**), bearing furan rings as secondary oxygen donor groups, transported K^+ ion much more effectively than simple diaza-crown ethers (**1**) and (**2**). Its oxygen donor groups on both 'arms' clearly enhanced complexing and transporting abilities for the K^+ ion. Cryptand (**5**), which forms a highly stable but static complex with the K^+ ion,[3] showed lower transport efficiency than the carrier (**3**). Although the present carrier (**3**) has a cryptand-like topology, its cation binding behaviour would be dynamic as observed with 'single armed' crown ethers ('lariat ethers').[6] Carrier (**3**) also exhibited higher transport abilities for the Ba^{2+} ion, while simple crown ethers (**1**) and (**2**) modestly transported alkaline earth cations. This result strongly suggests that the three dimensional topology of the carrier (**3**) would allow the complete inclusion and effective shielding of the hydrophilic alkaline earth cations as in the cryptand complexes.

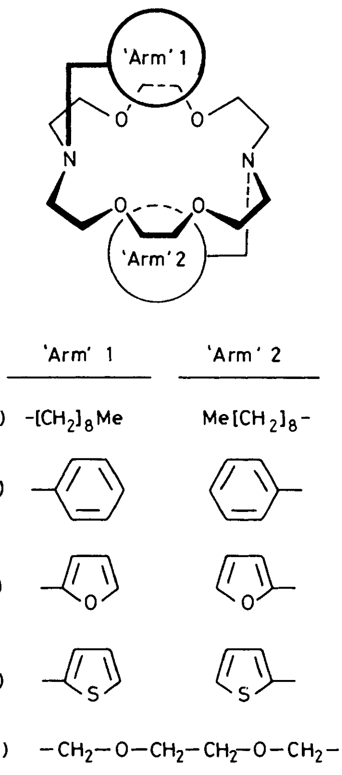

Figure 1

The thiophene ring-bearing crown ether (**4**) showed excel-

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† The diaza-crown ether was condensed with an acid chloride (benzoyl chloride, 2-furoyl chloride, or 2-thienoyl chloride), and the resultant corresponding diamide was reduced by diborane in tetrahydrofuran. Compounds (**2**)—(**4**) were characterised by spectroscopic and analytical data. (**2**) m.p. 82—83 °C; (**3**) m.p. 37—38 °C; (**4**) m.p. 60—61 °C.

Table 1. Carrier-mediated cation transport by 'double armed' crown ethers.[a]

	Transport rate of ClO_4^- anion[b] × 10^6/mol h^{-1}								
	Li^+	Na^+	Ag^+	K^+	Cs^+	Ca^{2+}	Sr^{2+}	Pb^{2+}	Ba^{2+}
(1)	0.22	0.24	0.68	2.16	0.29	0.23	0.37	2.32	3.76
(2)	0.20	0.23	1.82	0.97	0.33	0.27	0.25	9.09	0.53
(3)	0.16	0.78	1.68	7.52	0.92	0.16	1.37	8.17	12.50
(4)	0.23	0.23	[c]	2.59	0.56	0.26	0.32	16.00	1.86
(5)	0.84	6.54	2.02	1.21	1.42	0.75	2.85	1.63	7.33

[a] Transport conditions: Aq.I; metal perchlorate (0.50 mmol)–H_2O (5 ml). Membrane; carrier (0.0372 mmol)–$CHCl_3$ (12 ml). Aq.II; H_2O (5 ml). pH Values of Aq.I were *ca.* 6, except for Pb^{2+} systems (pH *ca.* 3). [b] In all experiments, concentrations of cotransported ClO_4^- in the Aq.II were determined by means of an ion selective electrode (Orion Model 93-81). K^+, Ba^{2+}, and Pb^{2+} were also monitored (Orion Model 92-32 for Ba^{2+}, Orion Model 94-82 for Pb^{2+}, valinomycin-containing electrode prepared by Dr. T. Katsu of Okayama University for K^+). [c] Considerable amounts of Ag(0) were deposited on the cell wall.

lent transport ability for the Pb^{2+} ion. The replacement of oxygen atoms in the carrier (**3**) by sulphur atoms in the carrier (**4**) decreased transport efficiencies for K^+ and Ba^{2+} ions, but provided fast transport of Pb^{2+} ion. Since we confirmed that Cu^{2+} and other transition metal ions were hardly transported by the carrier (**4**), the present transport process was significantly controlled by two factors, *i.e.*, the cavity size of the parent crown ether ring and the nature of the secondary donor group on the two arms. Further modifications of these factors could offer new possibilities in designing a specific carrier for transition metal and lanthanoid cations as well as other alkali and alkaline earth cations.

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