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"ARMED THIA-CROWN ETHER": A SPECIFIC CARRIER FOR SOFT METAL CATION

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Macrocyclic polythiaether having two ligating "arms" for soft metal cations showed new and specific transport ability for Ag^+ ion, based on cooperative actions of parent thia-crown ring and side arms.

Armed crown ethers such as lariat ethers [1] and double armed crowns [2),3] are a new class of cation-host molecules, which are characterized by parent macrocyclic ring and ligating arms. Since their cation-binding properties are essentially determined by coordination characters of macroring and donor arms, wide variations of their basic structures may lead to the design of new and specific host molecules for a given guest cation. [4]

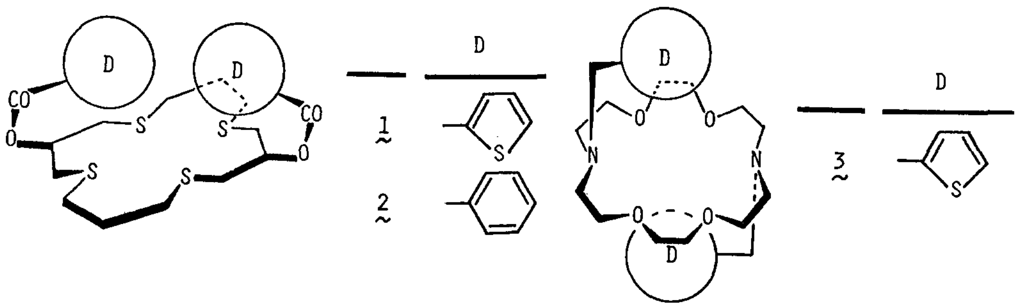

Figure. Employed "Armed Crown Ether"-Type Cation-Carriers

Here we present a new "armed thia-crown ether" having specific transport ability for Ag^+ ion. Our employed thia-crown 1, [5] composed of parent thia-crown ring and cation-ligating arms, was expected to form stable and specific complexes with "soft" guest cations, in which thiophene-sulfur atoms on its arms would provide further coordinations to the guest cation trapped into the thia-crown ring. We examined cation-transport properties of three typical crown ethers by using a chloroform liquid membrane systems: [6] thiophene-armed thia-crown 1; simple thia-crown 2; thiophene-armed aza-crown 3(Figure). Although some armed oxa- and aza-crown ethers are known as effective cation carriers, probably, this is the first example of "armed thia-crown ether" with specific transport properties for soft metal cation.

Armed thia-crown 1 specifically transported Ag^+ ion, while K^+, Pb^{2+}, Hg^{2+}, and other cations were hardly transported under the employed conditions(Table). Since armed aza-crown 3 bearing thiophene arms[3] showed high transport rates for various cations, thia-crown ring of the crown 1 was confirmed to play important roles in the selective binding and transport of soft Ag^+ cation. A simple thia-crown 2 exhibited a parallel transport trend to the armed thia-crown 1, but its transport rate of Ag^+ ion was relatively lower. Hence, cooperative actions of parent thia-crown ring and thiophene-arms effectively promoted transport process.

Other soft metal cations such as Cu^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, and Cd^{2+} ions were also examined as guest cations. Since the present armed thia-crown 1 showed low transport rates for these cations($<0.2\times10^{-6}$ mol/h), further modifications of ring-size, donor-group, and ligating arm of the armed macrocycle should be required. A variety of armed macrocycles are now going to be prepared in our laboratory.

Table. Cation-Transport Properties of "Armed Crowns"

Guest Cation	(diameter, Å)	Transport Rate $\times10^6$ (mol/h)		
		1	2	3
Li^+	(1.20)	0.2	0.1	0.2
Na^+	(1.90)	0.2	0.1	0.2
Ag^+	(2.52)	3.6	1.0	*
K^+	(2.66)	0.3	0.1	2.6
NH_4^+	(2.84)	0.1	0.2	1.8
Cs^+	(3.34)	0.2	0.2	0.9
Hg^{2+}	(2.20)	0.1	0.1	0.8
Pb^{2+}	(2.40)	0.1	0.1	16.0
Ba^{2+}	(2.70)	0.2	0.1	1.9

Transport conditions: Aq. I; Guest cation perchlorate, 0.5 mmol/H_2O, 5 ml. Membrane; Carrier, 0.0372 mmol/$CHCl_3$, 5 ml. Aq.II; H_2O, 5 ml. Transport experiments were performed in a U-shape glass cell(i.d., 1.7 cm). The valeus shown above were calculated from the initial rates of appearance of guest cations and perchlorate anion into the Aq.II, which were determined by means of ion-selective electrodes (see Ref. 3). *Ag(0) was deposited.

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5) 3,11-Dithenoyloxy-1,5,9,13-tetrathiacyclohexadecane 1 and 3,11-dibenzoyloxy-1,5,9,13-tetrathiacyclohexadecane 2 were derived from 1,5,9,13-tetrathia-cyclohexadecane-3,11-diol(a mixture of cis and trans isomers, Aldrich). They showed satisfactory spectral and elemental analysis data.
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