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"TRIPODE"-TYPE IONOPHORE FOR SPECIFIC TRANSPORT OF Ag^+ ION

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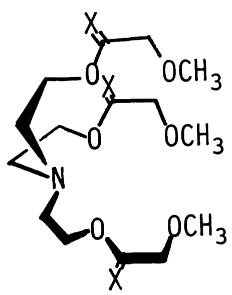
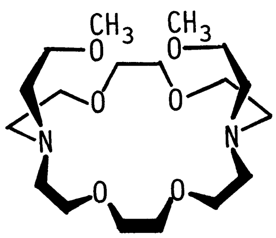
"Tripode"-type ionophore, tris(dioxa-3,6-heptyl)amine, showed specific transport properties especially for Ag^+ ion, which were largely different from those observed with common double armed crown ether and bicyclic cryptand ionophores.

A new series of host molecules having three-dimensional coordination chemistry have attracted much attention, because of their unique host-guest complexations and interesting chemical functions. Typically, lariat ethers and double armed crown ethers, which topologically lie at the borderline between crown ether and cryptand, provided excellent cation transport abilities and high catalytic activities in phase transfer reactions.[1,2]

Here we demonstrate that open-chain cryptand 1, tris(dioxa-3,6-heptyl)amine, mediated specific transport of Ag^+ ion. Tripode-type ionophore 1 formed three-dimensional complexes with guest cations as observed with double armed crown ether 3 and bicyclic cryptand 4, but flexible open-chain skeleton attained new and characteristic transport functions. Although several tripodes and related open-chain cryptands have been presented,[3] probably, this is the first successful example of tripode-type ionophore showing excellent transport abilities. We examined cation transport properties of three different types of ionophores by using a chloroform liquid membrane system:[2] tripodes 1[4] and 2; double armed crown ether 3;[4] bicyclic cryptand 4. The transported amounts of guest salts were determined by ion-selective electrode technique[2] and typical transport results are summarized in Table 1.



1 ($X=H_2$) 2 ($X=O$)



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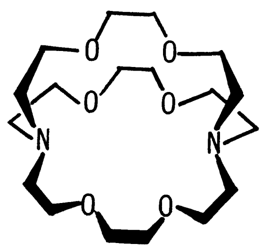

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Tripode **1** transported Ag^+ ion much more effectively than Pb^{2+}, K^+, NH_4^+, and other examined cations under the employed conditions (Table 1). Such a specific transport of Ag^+ ion was not attained by using double armed crown ether **3** and cryptand **4**. Although ionophores **3** and **4** showed high Ag^+ ion binding constants,[5] tripode **1** could form Ag^+ ion complex of suitable stability for efficient ion transport. Ester-armed tripode **2** was also examined, but hardly mediated transport of guest cations. Ether oxygen atoms of the arms were confirmed to play important roles in the present transport process. Therefore, appropriate combinations of donor arm groups and open-chain skeletons may provide further possibilities in designing new and specific open-chain host molecules.

Table 1. Transport Properties of Tripodes and Other Ionophores[a]

Guest cation	Transport rate $\times 10^6$/mol·h^{-1}			
	1	**2**	**3**	**4**
Li^+	0	0	0.2	0.8
Na^+	0	0	4.8	6.5
Ag^+	6.5	0	0.8	2.0
K^+	0.2	0	9.8	1.2
NH_4^+	0.4	0	6.1	2.0
Cs^+	0	0	0.9	1.4
Ba^{2+}	0	0	10.9[c]	7.3
Pb^{2+}	1.8[c]	0	1.7	1.6[c]

a) Transport experiments were performed in a U-shaped glass cell(i.d., 1.7 cm): Aq.I; Guest perchlorate, 0.50 mmol/H_2O, 5 ml. Membrane; Ionophore, 0.0372 mmol/$CHCl_3$, 12 ml. Aq.II; H_2O, 5 ml. Reproducibility; $< \pm 15\%$.

b) Initial transport rates of ClO_4^- anion were shown, and divalent cations were found to be transported with half efficiency of the indicated values.

c) Since ionophores were partially soluble in the aqueous phases used, these guest cations could not be determined by the electrode method.

References

1) L.Echegoyen, D.A.Gustowski, V.J.Gatto, and G.W.Gokel, J.Chem.Soc.,Chem. Commun., 1986, 220. And references cited.

2) H.Tsukube, J.Chem.Soc.,Chem.Commun., 1984, 315.

3) E.Weber and F.Vögtle, "Topics in Current Chemistry," Springer-Verlag, Berlin (1981), Vol. 98, p. 11.

4) Their syntheses have been reported. Tripode **1**: U.Heimann, M.Herzhoff, and F.Vögtle, Chem.Ber., 112, 1392 (1979). Double armed crown ether **3**: S.Kulstad and L.A.Malmsten, Acta Chem. Scand., 1979, 469.

5) An ion specific electrode (DKK, TYPE 7080) was used to obtain Ag^+ ion binding constants in H_2O at ca. 17 °C: LogK= 2.6 for **1**; 1.0 for **2**; 4.3 for **3**; >7.5 for **4**.

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