Specific Ag⁺ Ion Binding and Transport Properties of 'Tripod' Type Open-Chain Cryptands

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Tripod-type host molecules have shown new and characteristic cation binding and transport properties especially for Ag⁺ ion; they have a flexible open-chain skeleton as well as cryptand-like geometry. ¹H N.m.r. and binding studies have shown that the Ag⁺ ion is completely enveloped by the tripod molecule and, in consequence, barely exchanged with K⁺ and other alkali-metal cations. Such three-dimensional complexation, although similar to that of related double armed crown ethers and cryptands, because of its flexible nature, offers unique and specific transport of Ag⁺ ion.

A new series of host molecules having three-dimensional co-ordination chemistry have attracted much attention, because of their unique host–guest complexation properties and considerable chemical versatility.[1] Typically, lariat ethers[2] and double armed crown ethers,[3] which topologically lie at the borderline between crown ether and cryptand molecules, provided excellent cation transport abilities and high catalytic activities under phase-transfer reactions.

Tripods and other open-chain cryptands have also showed interesting cation binding properties,[4] which are characterized by three-dimensional ligand geometry and flexible molecular skeletons. In an earlier publication,[5] we showed that the tripod compound, 1,1′,1″-nitrilo-3,6-dioxaheptane†, transported Ag⁺ ion much more effectively than Pb²⁺, K⁺, and other metal cations. Since its cation transport properties were markedly different from those of the usual macrocyclic host molecules, this class of compounds was recognized as effective and specific carriers.

Here we report the cation binding and transport properties of the tripod host molecules (1) and (2), and compare them with those of the macrocyclic host molecules (3) and (4) (see Figure 1). ¹H N.m.r. spectroscopic and potentiometric studies showed that the tripod (1) formed a cryptand-like Ag⁺ ion complex with moderate stability and acted as an effective and specific carrier of Ag⁺ ion. Although tripods and related open-chain cryptands have the advantages of facile synthesis and versatility in molecular structure,[6] this is the first successful example of a tripod host molecule showing specific cation transport ability. Hence, the present study may provide fresh possibilities in designing new host molecules.

Results and Discussion

Structural Features and Tripods and Related Open-Chain Cryptands.—Cryptand compounds are well known to form three-dimensional complexes with alkali, alkaline earth, and heavy metal cations. Their rigid and bicyclic frameworks attain highly selective and strong cation bindings, but their complexation processes are kinetically very slow.[7] Since potential catalyst and ion transport carrier require selective and dynamic complexation, we examined tripod host molecules having high molecular mobilities. After ring opening of the bicyclic cryptand (4) two different types of polyether compounds (1)[8] (*via* ring-opening A) and (3)[9] (*via* ring-opening B) are formed (see Figure 1). Since the tripods (1) and (2) have flexible open-chain structures and cryptand-like co-ordination geometry, they are expected to envelop the guest cation completely and to release the cation rapidly. We compared their cation binding and transport properties with those of corresponding double armed crown ether (3) and parent cryptand (4). Although several kinds

of crystalline complexes of tripods with metal cations have been reported,[6] a tripod-mediated transport system has not yet been constructed.

¹H N.m.r. Studies.—The cation binding behaviour of the tripod (1) and related host molecules were investigated in [²H₄]methanol by means of ¹H n.m.r. spectroscopy. As typical examples, we described the experiments with Li⁺, Na⁺, and Ag⁺ cation–tripod (1) in Figure 2.

When 1.0 equivalent of the metal perchlorate salts was added to the tripod (1) solution, Ag⁺ ion induced larger ¹H n.m.r. spectral changes upon complexation than Li⁺ and Na⁺ ions (Figure 2). In particular, the singlet signal of the terminal OMe protons showed a marked shift to lower field compared with that for the free form; the signals for the OCH₂ protons showed a similar shift. Hence, the oxygen atoms of the terminal OCH₃ groups as well as other donor atoms seemed to participate in Ag⁺ cation binding. As reported for some tripod systems,[10] the guest Ag⁺ ion may be located in the centre of a three-dimensional cavity of the tripod (1) and co-ordinated to all the available donor atoms. Large spectral changes were also observed in the Ag⁺ ion–cryptand (4) system, and similar cation binding structures were suggested in both host systems.

Binding Studies.—By means of an electrochemical technique, we performed cation binding studies for the host molecules (1)—(4). The binding constants for Ag⁺ and Pb²⁺ ions were determined in water by using ion specific electrodes:[11] log K = 2.6 (Ag⁺) and 3.6 (Pb²⁺) for (1); 1.0 (Ag⁺) and 2.1 (Pb²⁺) for (2); 6.8 (Ag⁺) and >7.5 (Pb²⁺) for (3); >7.5 (Ag⁺) and >7.5 (Pb²⁺) for (4). Since the tripod (1) had greater log K values than the tripod (2), the nature of the groups constituting the donor arms clearly had a major effect on the cation binding abilities of the compounds. The double armed crown ether (3) and the bicyclic cryptand (4) were shown to bind Ag⁺ and Pb²⁺ ions much more strongly than the tripods (1) and (2), although they have a common ligand geometry. Vögtle *et al.* have investigated the complexation of the tripod (1) with alkali and alkaline earth cations,[8] other than Ag⁺ and Pb²⁺, and reported that its binding constants were lower than those of the double armed crown ether (3)[12] and the cryptand (4)[13] under comparable conditions.‡ Although we demonstrate below that the tripod (1)

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† 8-[2-(2-Methoxyethoxy)ethyl]-2,5,11,14-tetraoxa-8-azapentadecane.

‡ Reported binding constants are as follows: tripod (1) (in MeOH–H₂O, 45:6); log K = 2.0 for Li⁺, 2.2 for Na⁺, 2.2 for K⁺, 2.1 for Sr²⁺, and 2.7 for Ba²⁺. Double armed crown ether (3) (in MeOH); log K = 4.75 for Na⁺, 5.46 for K⁺, and 4.48 for Ca²⁺ (in H₂O); log K = 7.25 for Ag⁺ and 8.39 for Pb²⁺. Cryptand (4) (in MeOH–H₂O, 95:5); log K = 7.21 for Na⁺, 9.75 for K⁺, 8.40 for Cs⁺, 7.60 for Ca²⁺, and 12.00 for Ba²⁺ (in H₂O); log K = 9.6 for Ag⁺ and 12.0 for Pb²⁺.
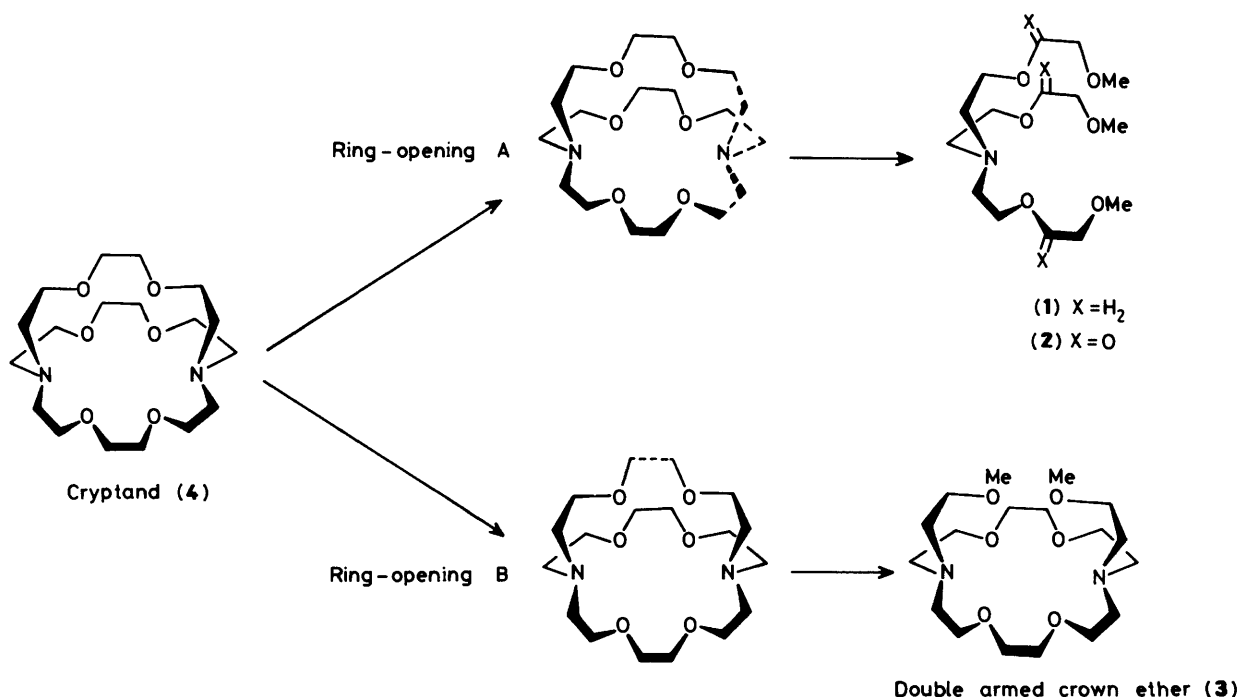
Figure 1. Molecular structures of the tripods and related host compounds
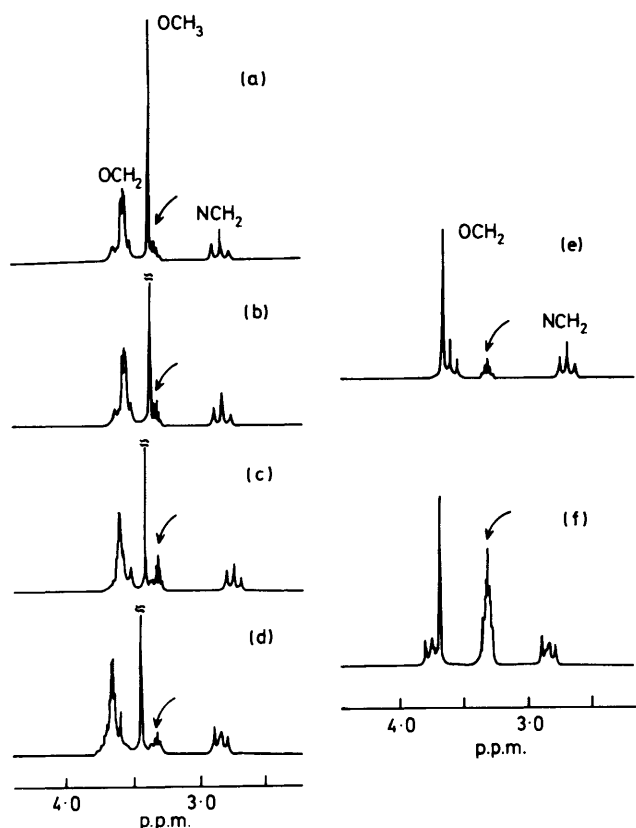

Figure 2. ¹H N.m.r. Spectral changes of the tripod (1) and the cryptand (4) by addition of the metal perchlorates; (a) tripod (1) (no metal salt); (b) tripod (1) + LiClO₄ ($\triangle\delta_{OCH_3}$ 0.1 Hz, $\triangle\delta_{OCH_2}$ 0.2 Hz, $\triangle\delta_{NCH_2}$ 0.2 Hz); (c) tripod (1) + NaClO₄ ($\triangle\delta_{OCH_3}$ 5.1 Hz, $\triangle\delta_{OCH_2}$ 6.4 Hz, $\triangle\delta_{NCH_2}$ −6.7 Hz); (d) tripod (1) + AgClO₄ ($\triangle\delta_{OCH_3}$ 7.7 Hz, $\triangle\delta_{OCH_2}$ 9.4 Hz, $\triangle\delta_{NCH_2}$ 1.9, 2.8 Hz); (e) cryptand (4) (no metal salt); (f) cryptand (4) + AgClO₄ (concentration, see Experimental section).

Arrows mean signals of deuteriated methanol.

binds Ag⁺ and Pb²⁺ ions much more strongly than K⁺ and other guest cations (see Table 1), similar sequences of binding constants of these host molecules for Ag⁺ and Pb²⁺ ions were observed: (1) < (3) < (4).

The binding of Ag⁺ ion in competition with other guest cations was also studied in aqueous solution. Thus the amount of Ag⁺ ion complexed with each host molecule was measured before and after adding a competitive guest cation such as Na⁺, K⁺, NH₄⁺, Ba²⁺, or Pb²⁺, and an 'Ag⁺ ion-binding index' was calculated for each host molecule (see Table 1). The complexes formed by the tripod (1), the crown ether (3), and the cryptand (4) with Ag⁺ ion were far more stable than those formed with Na⁺, K⁺, NH₄⁺, and Ba²⁺ ions, the former giving little release of ligand even in the presence of equimolar concentrations of alkali or alkaline earth cations. Among the competitive guest cations so examined, only Pb²⁺ ion was easily exchanged with Ag⁺ ion bound to the host molecules, the former ion binding more strongly than the latter, with the double armed crown ether (3) and the cryptand (4) bound Pb²⁺. These results agree with earlier published work which showed that the complexes formed by many crown ethers with Pb²⁺ ion are more stable than those with Ag⁺ ion.[14]

Cation Transport Properties of Tripods and Related Host Molecules.—The cation transport properties of tripod and related host molecules (1)—(4) were studied in a CHCl₃ liquid membrane system. As shown in Figure 3, the host molecule, dissolved in the membrane, facilitates the transport of a guest cation and anion from the source aqueous phase (Aq. I) through the membrane to the receiving aqueous phase (Aq. II) by complexing and solubilizing the guest cation. Since the overall transport rate is determined both by the cation extraction rate at the Aq. I/membrane interface and by the cation releasing rate at the membrane/Aq. II interface, a tight but dynamic cation binder could act as an efficient carrier. The transported amounts of cations and anions were determined individually by using ion specific electrodes (see Experimental section). The initial transport rates of the guest salts, calculated from anion concentrations, are summarized in Table 2.

Table 1. Ag$^+$ Ion-binding index

		Ag$^+$ Ion-binding index (%)[a]				
Host	Competitive cation	Na$^+$	K$^+$	NH$_4$$^+$	Ba^{2+}	Pb^{2+}
(1)		100	100	100	100	62
(3)		100	100	100	100	29
(4)		100	100	100	98	12

[a] [Ag$^+$ ion-binding index] = [Ag$^+$ ion complexed in the presence of competitive guest cation]/[Ag$^+$ ion complexed in the absence of competitive guest cation] × 100. Conditions: AgClO$_4$, 1.0×10^{-3}M. Competitive guest cation perchlorate, 1.0×10^{-3}M. Host, 8.0×10^{-4}M in water at ca. 17 °C.

Table 2. Transport properties of tripods and other host molecules[a]

	Transport rate × 10^6 (mol/h)[b]			
Guest cation	(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
Ca^{2+}	0	0	0.3	0.8
Ba^{2+}	0	0	10.9[c]	7.3
Pb^{2+}	1.8[c]	0	1.7	1.6[c]

[a] Transport conditions: see Experimental section. [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 these host molecules were partially soluble in the aqueous phases used, the guest cations could not be determined by the electrode method.

Figure 3. Liquid membrane system for cation transport: H = host molecule; M$^+$ = guest metal cation; X$^-$: co-transported anion (ClO$_4$$^-$).

Figure 4. Relationship between transport rate and binding constant for Ag$^+$ ion.

The tripod (1) showed effective and specific cation transport properties for Ag$^+$ ion, which were markedly different from those of the tripod (2) and the related macrocycles (3) and (4). The tripod (1), bearing three polyether linkages, effectively transported Ag$^+$ and Pb^{2+} ions, while being ineffective with K$^+$, NH$_4$$^+$, Cs$^+$, and other guest cations. Although its transport properties were closely similar to those observed in above-mentioned binding experiments (see Table 1), the transport rate of Pb^{2+} ion was unexpectedly lower than that of the Ag$^+$ ion. Probably, the dipositive Pb^{2+} ion was tightly complexed but too hydrophilic to be effectively solubilized into the membrane by the tripod (1). The tripod (2), bearing three ester groups, was also employed but hardly mediated transport of any guest cations. Both cation binding and transport abilities were influenced by the nature of the tripod donor group. Thus when the macrocycles (3) and (4) were employed as carriers, Na$^+$ and Ba^{2+} ions were more effectively transported than Ag$^+$, K$^+$, and Pb^{2+} ions, and transport rates of Ag$^+$ and Pb^{2+} ions were modestly suppressed. This was because the ions were more strongly bound than with the tripod (1), to give more stable complexes and, consequentially, slower rates of transport.

Figure 4 shows the relationship between the binding constants obtained in water and the transport rates measured with the host molecules (1)—(4) for Ag$^+$ ion. This plot has a distinct maximum and suggests that the guest cation, complexed moderately with host molecule, was effectively transported. Lamb,[15] Behr,[16] and other investigators[17] have studied similar carrier-mediated transport systems, and concluded that effective transport occurred if the binding constant of the carrier with guest cation was in the range 10^{4-6} l mol^{-1} in MeOH. Since binding constants are generally lower in water than in meth-

anol, the tripod (1) is believed to show a suitable binding constant for Ag$^+$ ion as an effective carrier.
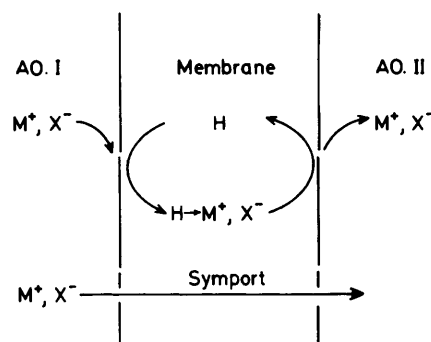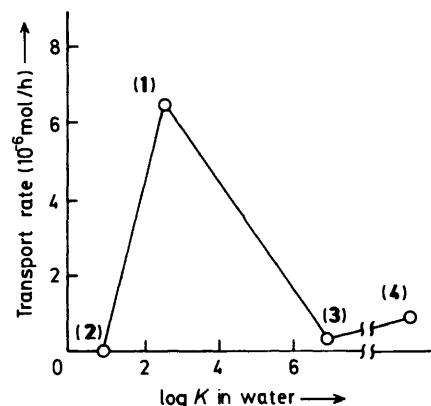
Experimental

Materials—The tripod (1) and the cryptand (4) were purchased from Fluka and Merck, respectively and employed as received.

The tripod (2), 1,1',1''-nitrilo-3,6-dioxaheptan-4-one*, was prepared from 2,2',2''-nitrilotriethanol and methoxyacetyl chloride, and purified by column chromatography on alumina with CHCl$_3$ as eluant (80%, yellowish oil): δ_H (90 MHz; CDCl$_3$; standard Me$_4$Si) 2.87 (6 H, t, 3 × NCH$_2$), 3.45 (9 H, s, 3 × OCH$_3$), 4.04 (6 H, s, 3 × COCH$_2$), and 4.21 (6 H, t, 3 × OCH$_2$); $\nu_{max.}$(neat) 1 740(ester) and 1 190 and 1 130(ether) (Found: M^+, m/z 365.168. C$_{15}$H$_{27}$NO$_9$ requires M, 365.168).

The crown ether (3) 4,7,13,16-tetraoxa-1,10-diazabicyclo[8.8.8]hexacosane† was also synthesized according to a literature method[9] (60%, yellowish oil): δ_H (90 MHz, CDCl$_3$, Me$_4$Si) 2.74 and 2.84 (12 H, t + t, 6 × NCH$_2$), 3.32 (6 H, s, 2 × OCH$_3$), 3.45 (4 H, t, 2 × OCH$_2$), and 3.60 (16 H, t + s, 8 × OCH$_2$); $\nu_{max.}$(neat) 1 110 and 950(ether); m/z 378(M^+).

^{1}H *N.m.r. Studies.*—^{1}H N.m.r. studies were carried out in [^{2}H$_4$]methanol at a frequency of 90 MHz with a JEOL 90A spectrometer. The tripod (1) was in a concentration of ca.

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* 8-[2-(2-Methoxyacetoxy)ethyl]-2,5,11,14-tetraoxa-8-azapentadecane-4,12-dione.

† N,N'-Bis(3-oxabutyl)-1,4,10,13-tetraoxa-7,16-diazacyclo-octadecane.

5.0 × 10^{-2} M. A solution of the Ag$^+$ ion–cryptand (**4**) at a similar concentration gave a white precipitate; this was filtered off and a spectrum of the filtrate is shown in Figure 2f.

Binding Studies.—Binding constants of the host molecules (**1**)—(**4**) for Ag$^+$ and Pb^{2+} ions were determined potentiometrically by a modification of the Frensdorff method.[11] The e.m.f. was measured with a Denki Kagaku Keiki Model IOC-10 digital ion-meter that has a sensitivity of 0.1 mV. Ion specific electrodes (Denki Kagaku Keiki, Model 7080 and 7180) were used to ascertain binding constants for Ag$^+$ and Pb^{2+} ions. The reference electrode was Ag/AgCl (Orion, Model 90–01). The binding constants were determined in water at *ca.* 17 °C.

The activities of Ag$^+$ and Pb^{2+} ions were measured in a solution of guest cation perchlorates both in the absence and presence of each host molecule: guest cation perchlorate, 1.0 × 10^{-3} M; host, 3.0 × 10^{-3} M. The e.m.f.s of the salt and the salt–host solutions were measured alternately, and each run consisted of at least three-measurements of each solution. The e.m.f. values of each solution were averaged and these averaged values were used to calculate the binding constants.

The binding index for Ag$^+$ ion was also determined by using an ion selective electrode technique. The calibration was made in the presence of each competitive guest cation, and the complexed amounts of Ag$^+$ ion were calculated under the conditions stated in Table 1.

Transport Experiments.—Transport experiments were performed at room temperature in a U-tube glass cell (2.0 cm, i.d.). The host molecule, dissolved in CHCl$_3$ (0.0372 mmol/12 ml), was placed in the base of the U-tube, and two aqueous phases (Aq. I: MClO$_4$, 0.5 mmol/water, 5 ml; Aq. II: water, 5 ml) were placed in the arms of the U-tube, floating on the CHCl$_3$ membrane phase. The membrane phase was constantly stirred with a magnetic stirrer. The transport rates were calculated from the initial rates of appearance of guest cations and co-

transported ClO$_4^-$ anion into Aq. II phase, which were determined by means of ion specific electrode techniques (Orion Model 93—81 for ClO$_4^-$, 93—19 for K$^+$, 97—11 for Na$^+$, 95—10 for NH$_4^+$, 92—32 for Ba^{2+}). Reproducibilities were confirmed as 15% or better.

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