New "Open-Chain Cryptands" with Specific Ion Transport Abilities

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Abstract: A new family of macrocyclic polyethers and polyamines having pendant "arms" available for cation binding were prepared and examined as synthetic ion carriers. They offered characteristic cation transport phenomena, based on their unique ligand topology. By appropriate choice of parent macrocyclic ligand and pendant donor group, specific transport of K⁺, Ba²⁺, Pb²⁺, and NH₄⁺ cations was realized.

1. Introduction

Several types of synthetic macrocyclic host molecules have been developed, which mimic the biological cation transport phenomena. In particular, cryptand molecules are well-recognized as specific carriers for alkali and alkaline earth cations. They offer highly stable and selective complexation as well as effective shielding of complexed guest cations. However, further dynamic complexing properties of the potential carriers (effective binding and rapid releasing) are required to realize efficient transport as observed in the naturally occurring ion carrier systems.

Here we present a new family of "open-chain cryptands" showing specific cation transport abilities, which are characterized by parent macrocyclic ligands (polyethers and polyamines) and ligating pendant donor arms. They are expected to wrap around the guest cations in such a way that pendant groups on their side arms would provide further coordination to the guest cations trapped into the parent macrocycles. Although their complex structures, based on three-dimensional ligand topology, are somewhat similar to those of cryptand systems, higher mobilities of the pendant arms attached to the macrocycles may permit the highly dynamic cation binding that is required for efficient cation transport.

We prepared two typical examples of "open-chain cryptands" — "double armed crown ethers" and "multi-armed cyclams" — and examined them in a bulk liquid membrane system. Some kinds of armed macrocycles have been reported, but we know only a few examples of effective
cation carriers. Hence, the present study can provide new possibilities in modelling biomembrane transport systems as well as in designing specific host molecules.

2. Experimental

2.1. Materials

"Double armed crown ethers" were prepared from corresponding diazacrown ethers (Kryptofix 21, 22, and 23, Merck Japan). Typically, Kryptofix 22 (1,7,10,16-tetraoxa-4,13-diazacycloclooctadecane) was condensed with 2-furoyl chloride, and the resultant diamide was reduced by diborane in THF. Recrystallization from CH₂Cl₂-hexane gave white crystals 4. Mp, 37-38°C. Elemental analysis: Calcd.; C 62.54, H 8.11, N 6.63. Found; C 62.76, H 7.91, N 6.86.¹H-NMR (CDCl₃, ppm from Me₂Si) 2.80 (8H) 3.67 (20H) 6.27 (4H) 7.40 (2H).

Crown ethers 2, 3, 5, and 6 were similarly obtained. The structures of the prepared "double armed crown ethers" are shown in Figure 1.

"Multi-armed cyclams" were also obtained from cyclam (Strem).³ Cyclam (1,4,8,11-tetraazacyclotetradecane) was condensed with 2-furoyl chloride, and the resultant tetraamide was reduced by diborane in THF. Recrystallization from ether-hexane gave colorless crystals 9. Mp, 83-84°C. Elemental analysis: Calcd.; C 69.20, H 7.74, N 10.76. Found; C 69.25, H 7.70, N 10.88.¹H-NMR (CDCl₃, ppm from Me₂Si) 1.67 (4H) 2.60 (16H) 3.67 (8H) 6.17 (4H) 6.40 (4H) 7.43 (4H).

Simple macrocyclic polyamine 8 and polyamide 10 were also employed for comparisons (see Figure 2).