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"MULTI-ARMED CYCLAM" FOR SPECIFIC TRANSPORT OF NH_4^+ CATION

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New macrocyclic polyamine bearing furan oxygen atoms on its side arms offered characteristic cation transport phenomena. It specifically transported NH_4^+ cation, based on its unique ligand topology, while K^+ and other cations were hardly transported.

Crown ethers, cryptands, and related macrocycles are known to transport some cations like as bio-ionophores.[1] Here we present a new "armed macrocycle" showing unique NH_4^+ cation transport ability which has not been observed with common crown ethers and cryptands. The employed "multi-armed cyclam", 1,4,8,11-tetrafurfuryl-1,4,8,11-tetraazacyclotetradecane (1), is characterized by parent macrocyclic polyamine (cyclam) skeleton and ligating pendant arms (Fig. 1). This is expected to wrap around the guest cation in such a way that pendant arms would provide further coordination to the guest cation trapped in the cyclam ring. Such a coordination geometry is closely similar to those of cryptand compounds, but high mobility of the ligating pendant arms may permit the highly dynamic ion binding that is required for efficient ion carrier. Although a variety of armed cyclams have been reported,[2] only a limited number of examples are known to mediate effective ion transport.[3]

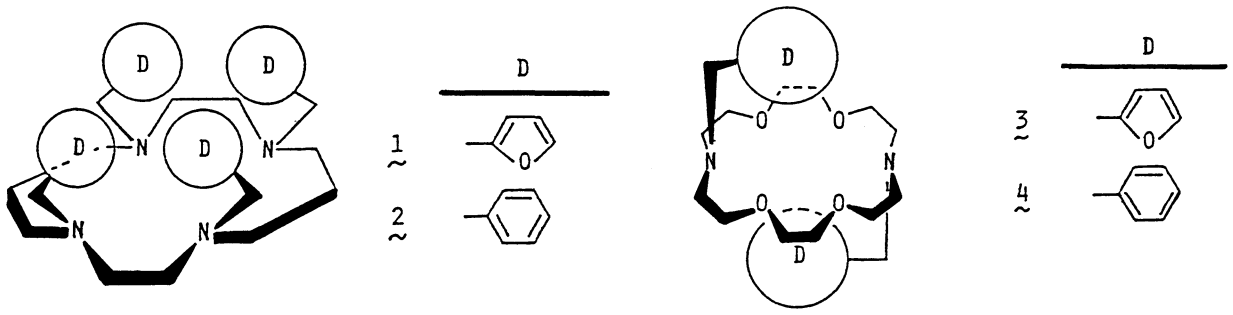

Fig. 1. "Multi-Armed Cyclams" and "Double Armed Crown Ethers."

"Multi-armed cyclam" 1,[4] bearing furan oxygen atoms on its arms, mediated specific transport of NH_4^+ cation across a bulk liquid membrane, while H^+, K^+, and other metal cations were hardly transported under the employed conditions (Table 1). Since simple cyclam, 1,4,8,11-tetrabenzyl-1,4,8,11-tetraazacyclotetradecane (2), exhibited a low transport rate of NH_4^+ cation, the furan oxygen atoms attached to the cyclam ring may play an important role in complexation and transportation of NH_4^+ cation. Furan-bearing crown, 4,13-difurfuryl-1,7,10,16-tetraoxa-4,13-diazacyclooctadecane (3),[5] could not discriminate NH_4^+ cation from K^+ cation,

and showed high transport efficiencies for both cations. Although the details of transport mechanism are not clear, NH_4^+ cation may be distinguished from K^+ cation not by "ion size" (NH_4^+: 2.89 Å; K^+: 2.66 Å) but by "charge distribution" (NH_4^+: tetrahedral; K^+: spherical). CPK molecular model of cyclam 1 • NH_4^+ cation complex suggests that NH_4^+ cation can be wrapt, "tetrahedrally", donating two hydrogen bonds to two diametric ring nitrogen atoms as well as two furan oxygen atoms.[6]

Further modifications of macrocyclic ring and pendant donor groups of the armed macrocycles are currently in progress. This work was supported by the Grant-In-Aid for the Special Project Research on the Properties of Molecular Assembries (No. 59212026) from the Ministry of Education, Science, and Culture, Japan.

Table 1. Transport Properties of "Multi-Armed Cyclam" and Related Carriers

Carrier	Transport rate / 10^{-6} mol·h^{-1}				
	Li^+	Na^+	K^+	NH_4^+	Cs^+
1	< 0.02	< 0.02	< 0.02	1.15	< 0.02
1[a)]	< 0.02	< 0.02	< 0.02	3.55	< 0.02
2	< 0.02	< 0.02	< 0.02	0.24	< 0.02
3	0.08	0.72	7.40	4.93	0.71
4	0.12	0.17	0.85	1.23	0.12

Transport experiments were performed in a U-tube glass cell as described.[7] Aq. I; Guest perchlorate, 0.50 mmol/ H_2O, 5 ml (pH=5.00-6.00). Membrane; Carrier, 0.0372 mmol/$CHCl_3$, 12 ml. Aq. II; H_2O, 5 ml.

The concentrations of guest salts in two aqueous phases were determined by means of ion selective eletrodes (Orion 95-12 for NH_4^+, 93-19 for K^+, and 93-81 for ClO_4^-). a) CH_2Cl_2 was employed as membrane phase.

References

1) Recent review: J. M. Lehn, "Physical Chemistry of Transmembrane Ion Motion," ed by G. Spach, Elsevier Sci. Pub., Amsterdam (1983), p.181.

2) Th. A. Kaden, "Topics in Current Chemistry," ed by F. L. Boschke, Springer-Verlag, Berlin, Heidelberg (1984), Vol.121, p.158.

3) H. Tsukube, J. Chem. Soc., Chem. Commun., 1983, 970.

4) 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 a colorless crystals 1 (mp 83.0-84.5 °C). ^{1}H-NMR ($CDCl_3$, δ) 1.67(4H) 2.60(16H) 3.67(8H) 6.17(4H) 6.40(4H) 7.43(4H). Found; C 69.25, H 7.70, N 10.88%. Calcd for $C_{30}H_{40}N_4O_4$; C 69.20, H 7.74, N 10.76%. Cyclam 2: see Ref. 3; Crowns 3 and 4: also see Ref. 5.

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

6) 1,4,7,10-Tetrahydroxyethyl-1,4,7,10-tetraazacyclododecane is known to accomodate tetrahedral cavity for guest species: S. Buøen, J. Dale, P. Groth, and J. Kran, J. Chem. Soc., Chem. Commun., 1982, 1172.

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