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TRIAZAMACROCYCLE HAVING PYRIDINE-PENDANT ARMS AS A NEW Na^+ ION-SELECTIVE IONOPHORE

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A new type of azamacrocycles having pyridine-pendant arms mediated highly selective and efficient transport of Na^+ ion via three-dimensional complexation, which was not attained by common azamacrocycle, crown, and hemispherand compounds.

In view of new synthetic strategy in host-guest chemistry, macrocyclic ligands having cation-ligating arms represent a new class of host molecules, so-called "armed macrocycles".[1] Typically, double-armed crown ethers form encapsulated complexes with several metal cations and provide characteristic chemical functions.[2,3] Since high mobility of ligating pendant arms promises kinetically labile complexation, these armed macrocycles are recently recognized as the most suitable candidates for synthetic ionophores of metal cations.

Here we present a new series of "pyridine-armed azamacrocycles" exhibiting specific binding and transport abilities for "hard" metal cations. Although several armed azamacrocycles show interesting ligand potentials for "soft" transition metal cations,[4,5] we first demonstrated that some pyridine-armed azamacrocycles specifically transported Na^+ ion via three dimensional complexation.[6] Since they showed transport selectivity and efficiency for Na^+ ion superior to crown- and hemispherand-type compounds, the present result offers new possibilities in designing of specific host molecules based on polyamine macrocycles.

We prepared a series of pyridine-armed azamacrocycles **1**, **4**, and **5** having 9-, 14-, and 15-membered rings from corresponding macrocyclic polyamines and chloromethylpyridine,[7] and compared their cation-binding and transport functions with those of related azamacrocycles **2** and **3** and Na^+ ion-selective ionophores **6**[3] and **7**[8] (Figure 1). The transport of various metal cations across a CH_2Cl_2 liquid membrane was studied by using a U-tube glass cell (2.0cm, i.d.) as described before,[1] and the transported amounts of guest metal cations and co-transported ClO_4^- anion were determined by means of atomic absorption and ion-selective electrode techniques. The obtained initial transport rates are summarized in Table 1.

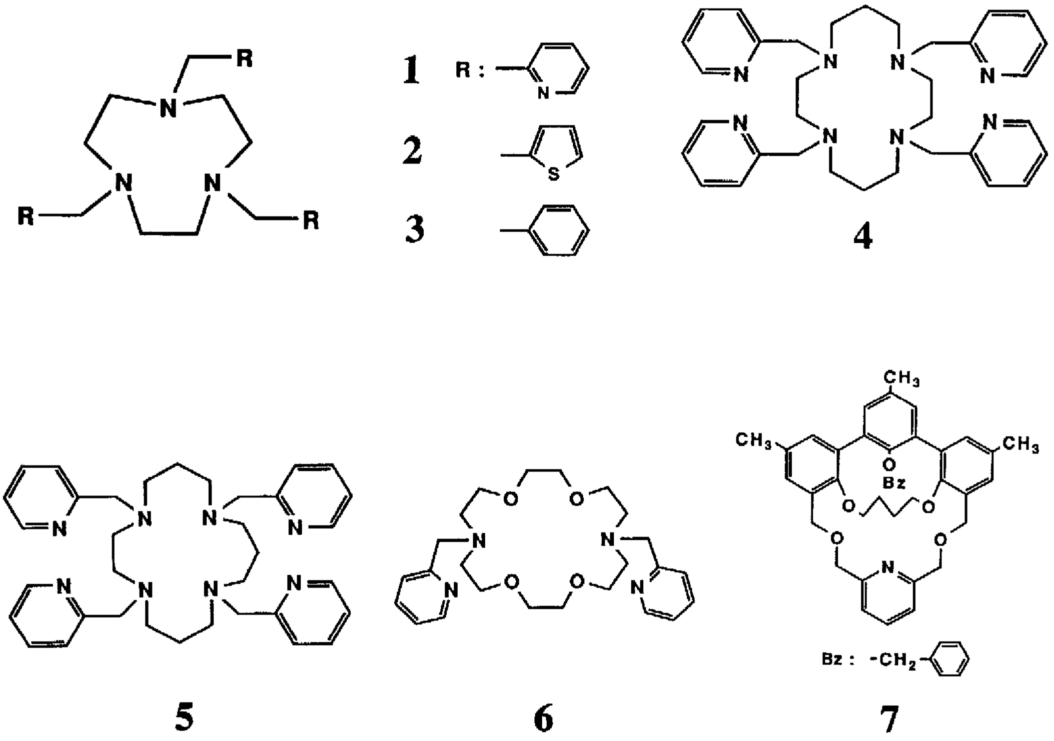


Figure 1. Examined Armed Azamacrocycles and Related Ionophores

Pyridine-armed triazamacrocycle **1** selectively and efficiently transported hard Na^+ ion, while related triazamacrocycles having thiophene- and benzene-pendant arms **2** and **3** could not act as effective carriers for any examined cations (Table 1). Since pyridine-armed azamacrocycles **4** and **5** showed lower transport abilities, combination of triazamacrocyclic ring and pyridine-pendant arm clearly offered excellent transport abilities for hard alkali metal cation. Interestingly, its transport selectivity and efficiency were higher than those of crown- and hemispherand-type ionophores **6** and **7**. Thus this class of armed azamacrocycles was confirmed as new and effective ionophores for hard alkali metal cations.

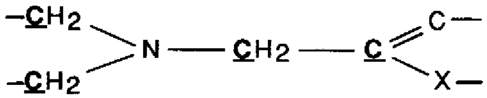
Table 1. Transport Properties of Pyridine-Armed Azamacrocycles and Related Ionophores

Ionophore	Transport Rate x 10^6 (mol/h)									
	Li^+	Na^+	K^+	Cs^+	Mg^{2+}	Ca^{2+}	Ba^{2+}	Cu^{2+}	Ni^{2+}	Zn^{2+}
1	*	6.4	*	*	*	0.7	1.0	3.9	*	*
2	*	*	*	*	*	*	*	*	*	*
3	*	*	*	*	*	*	*	*	*	*
4	0.4	2.2	*	*	*	*	*	0.4^a	0.3	*
5	0.4	*	*	*	*	*	*	*	*	*
6	5.0	10.5	7.9	7.3	*	11.5	3.4	2.2	*	4.1
7	*	2.2	0.4	*	*	*	*	-	-	-

*: below limit of detection ($<$ 0.3), -: not done, a: precipitate appeared in this case.

Cation binding properties of azamacrocycles **1**, **2**, and **5** were investigated in DMF/D_2O solution (4/1, v/v) by means of ^{13}C-NMR spectroscopy (Table 2). The addition of an equimolar $NaClO_4$ salt to the pyridine-armed triazamacrocycle **1** solution offered remarkable spectral changes upon complexation,[9] while $KClO_4$ salt

Table 2. Guest-Induced Changes in ^{13}C-NMR Chemical Shifts of Azamacrocycles **1**, **2**, and **5**

Azamacrocycle	Guest Cation	Guest-Induced Shift Value (ppm)^a		
				
1	Na^+	-1.6	-0.2	-0.7
	K^+	-0.2	-0.1	-0.1
2	Na^+	-0.2	-0.1	-0.2
	K^+	-0.1	0	0
5	Na^+	-0.1	-0.1	-0.2^b
	K^+	-0.1	-0.1	-0.1^b

Azamacrocycle, 0.050 mmol; Guest perchlorate, 0.050 mmol / $DMF-D_2O$ (4:1), 0.5 ml. a: - means up-field shift; b: calculated from averaged shifts of two carbon signals.

induced only slight changes. Since the signals for carbons on pendant pyridine-ring and parent polyamine-ring significantly shifted, the guest Na^+ ion may be located on polyamine-ring and effectively coordinated by pyridine- and macroring-nitrogen atoms. Although pyridine- and polyamine-nitrogen atoms are not so strong donor atoms toward hard Na^+ ion, a unique three dimensional arrangement of nitrogen donor atoms in the triazamacrocycle **1** system may provide such a selective and encapsulated Na^+ complex. Thiophene-armed triazamacrocycle **2** and pyridine-armed tetraazamacrocycle **5** were also examined, but their spectral changes were almost negligible in the presence of Na^+ and K^+ ions. Hence, cooperative binding of pendant donor-arm and parent azamacrocycle was not realized in these systems.

The present study provides the first example of armed azamacrocycles exhibiting excellent binding and transport abilities for hard alkali metal cations. Since their guest-selectivities could be significantly adjusted by appropriate choice of parent polyamine-ring and pendant-arm group, further variations may offer specific host molecules for a new series of guest cations.

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9. ^{13}C-NMR titration curves showed clear saturation behaviors, indicating that azamacrocycle **1** formed a labile and 1 : 1 complex with Na^+ ion.

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