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PYRIDINO-ARMED DIAZA-CROWN ETHERS FOR SPECIFIC TRANSPORT OF "TRANSITION METAL CATIONS"

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A new series of double armed diaza-crown ethers, bearing pyridino- and quinolino-arm groups, were first shown to effectively bind and transport some "transition metal cations" via three-dimensional complexations, which were not attained by common crown ethers.

Double armed crown ethers and related macrocycles are designed to mimic naturally occurring ionophores, which are characterized by parent macrocyclic ligand and flexible donor-arm groups.[1] They form three-dimensional complexes with alkali, alkaline earth,[2] heavy,[3] and inorganic ammonium cations,[4] and mediate effective transport of them. Recently various types of armed crown ethers such as lariat ethers have also been prepared,[5] but we know only a few examples of crown ether derivatives showing excellent transport abilities for "transition metal cations".[6]

Here we report a new series of double armed diaza-crown ethers which efficiently mediated transport of Cu^{2+}, Co^{2+}, and Zn^{2+} ions. Incorporation of pyridino-functionalized arms into the 15-, 18-, and 21-membered diaza-crown rings offered largely different cation-binding and transport properties from those of common crown ether derivatives. We successfully demonstrated that the molecular combinations of diaza-crown ring and pyridino-arm groups provided three-dimensional and dynamic complexations with transition metal cations as required for efficient membrane transport. Therefore, the present results may open new possibilities in designing crown-type ionophores for transition metal and related guest cations.

We prepared a series of pyridino-armed diaza-crown ethers having 15-, 18-, and 21-membered rings from corresponding diaza-crown ethers and chloromethylpyridines, and compared their transport properties with those of other pyridine-containing macrocycles (Figure 1). The transport of transition metal cations across a CH_2Cl_2 membrane was studied by using a U-tube glass cell (2.0 cm,i.d.) as described before,[2] and the transported amounts of guest cations and co-transported anion (ClO_4^-) were determined by means of ion-selective electrode and atomic absorption techniques.

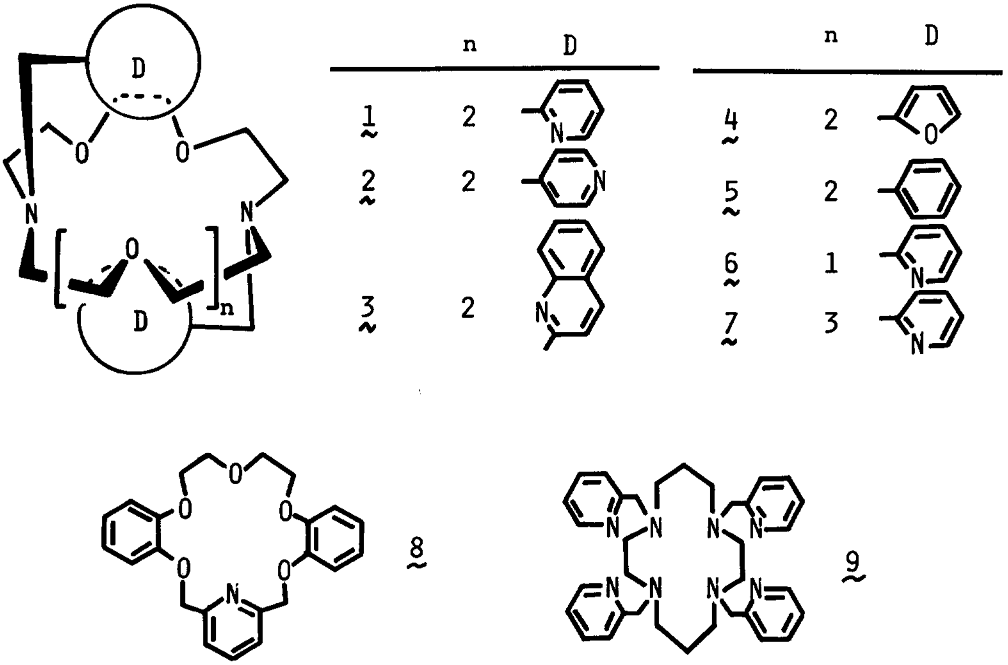

Figure 1. Pyridino-Armed Diaza-Crown Ethers and Related Macrocycles

The double-armed diaza-crown ethers 1 and 3, bearing pyridine and quinoline rings as secondary donor groups, effectively transported Cu^{2+} and Zn^{2+} ions as well as Ba^{2+} and Pb^{2+} ions, while furfuryl- and benzyl-armed diaza-crown ethers 4 and 5 hardly mediated transport of any transition metal cations (Table 1). Since crown ring is known to favor hard alkaline metal cations, the pyridino-nitrogen atoms on both arms clearly enhanced binding and transport abilities for soft transition metal cations. In a marked contrast, the other type of pyridino-armed diaza-crown ether 2 showed much lower transport abilities. Probably, its pyridino-nitrogen atoms may be too remote to interact with a guest cation trapped into the parent diaza-crown ring. The pyridine-containing macrocycles 8 and 9 were also examined as ionophores, but their transport rates for transition metal cations were largely small. Therefore, cooperative actions of pyridino-arms and parent crown ring are believed to play an important role in the transport process of transition metal cations.

The pyridino-armed diaza-crown ethers having other membered rings 6 and 7 showed excellent transport abilities for transition metal cations, which are almost similar to those observed with 18-membered crown ether 1. Since Cu^{2+}, Zn^{2+}, and other transition metal cations have much smaller ion diameters than cavity sizes of crown rings, so-called "ion-cavity concept" is questioned in these armed crown ether-transition metal complexes. Other factors should control the cation-binding and transport phenomena.

Table 1. Transport Properties of Pyridino-Armed Diaza-Crown Ethers and Related Macrocycles[a)]

Crown	Transport Rate $\times 10^6$ (mol/h)							
	Mg^{2+}	Ca^{2+}	Ba^{2+}	Pb^{2+}	Cu^{2+}	Ni^{2+}	Co^{2+}	Zn^{2+}
1	<0.1	11.5	3.4	1.6	$2.2^{b)}$	0.3	$0.8^{b)}$	4.1
2	<0.1	<0.1	0.2	0.4	0.1	0.1	0.3	<0.1
3	<0.1	0.1	10.2	1.0	2.9	0.1	0.2	0.5
4	<0.1	0.1	17.6	3.6	$<0.1^{b)}$	$0.2^{b)}$	0.2	$0.1^{b)}$
5	<0.1	<0.1	2.4	2.9	$<0.1^{b)}$	0.2	0.1	$0.2^{b)}$
6	0.2	6.4	$4.0^{b)}$	1.6	2.3	0.7	2.0	2.6
7	0.1	$0.4^{b)}$	7.8	1.0	2.6	0.6	0.7	4.0
8	<0.1	<0.1	<0.1	0.1	0.1	<0.1	<0.1	<0.1
9	0.1	0.1	0.1	0.2	$0.4^{b)}$	0.3	$0.5^{b)}$	$0.2^{b)}$

a) Transport conditions: Aq. I; Guest perchlorate, 0.50 mmol/H_2O, 5.0 ml. Membrane, Crown, 0.0372 mmol/ CH_2Cl_2, 12 ml. Aq.II; H_2O, 5 ml. Initial transport rates of guest cations were described.

b) In these cases, some precipitates appeared.

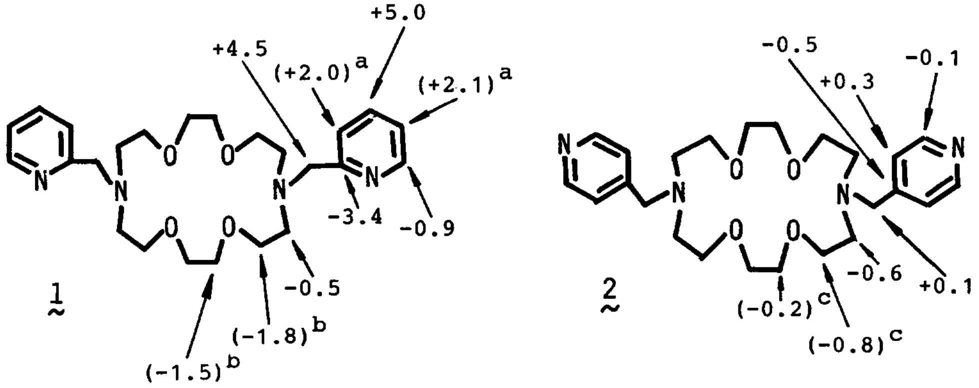

Figure 2. Zn^{2+} Ion-Induced Changes in C-13 N.m.r. Chemical Shifts of Pyridino-Armed Diaza-Crown Ethers 1 and 2 (ppm)

Crown, 0.050 mmol; $Zn(ClO_4)_2$, 0.050 mmol; in DMF-D_2O (4:1), 1.0 ml.
a,b,c: These signals could not be unequivocally assigned.

The cation-binding behaviors of the pyridino-armed diaza-crown ethers 1 and 2 were investigated by C-13 n.m.r. spectroscopy (Figure 2). When an equimolar $Zn(ClO_4)_2$ salt was added to the crown ether 1 solution, remarkable spectral changes were induced upon complexation.[8] Since the signals for the carbons on pyridino-arms and diaza-crown ring largely shifted, the Zn^{2+} ion may be located in the center of a three-dimensional cavity of the crown ether 1, and coordinated to all the available donor atoms. On the other hand, the C-13 n.m.r. spectrum of the pyridino-armed diaza-crown ether 2 was slightly changed by addition of Zn^{2+} ion, indicating that intramolecular cooperative binding of pyridino-nitrogen atoms and diaza-crown ring was not realized in the crown 2 system. These observations strongly suggest that the three dimensional topology of the pyridino-armed diaza-crown ether 1 would allow the complete inclusion and the effective transport of transition metal cations. Since introduction of pyridino-nitrogen donor arms effectively modified cation-binding and transport properties of diaza-crown ethers, further combinations of arm-donor groups and parent crown ring may offer specific ionophores for a new series of guest cations.

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7) Reported ion diameters of the examined metal cations (Å) are as follows: Mg^{2+}(1.30); Ca^{2+}(1.98); Ba^{2+}(2.70); Pb^{2+}(2.40); Cu^{2+}(1.44); Ni^{2+}(1.38); Co^{2+}(1.48); and Zn^{2+}(1.48).
8) C-13 N.m.r. spectral changes supported 1 : 1 complexation between crown ether 1 and Zn^{2+} ion.

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