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COMPLEXING ABILITY OF N-OLIGOETHYLENE GLYCOL MONOAZA CROWN ETHERS WITH SODIUM AND POTASSIUM CATIONS

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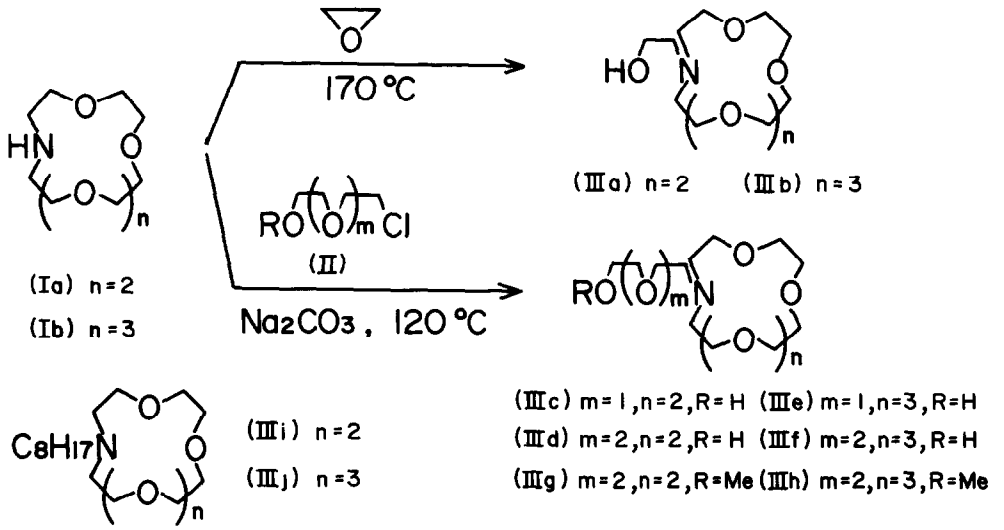
Summary: N-Oligoethylene glycol monoaza crown ethers were prepared, and the notable effect of oxyethylene oxygen atoms of the side chain on complexing ability with sodium and potassium cations was confirmed.

Since we found a facile synthesis of N-unsubstituted monoaza crown ethers Ia,b,[1] the syntheses and properties of their derivatives have been under investigation. Recently, Gokel et al. prepared the crown ethers with the side chain including oxygen atoms, and determined the extraction abilities with sodium and potassium cations[2] and the stability constants with sodium cation.[3] They reported that the side chain contributed to the complexation with cations evaluated from extraction of picrates in the CH_2Cl_2-H_2O system, but in 90% aq. MeOH the binding properties of the 15-crown-5 derivatives with sodium cation were diminished by the effect of heavily hydrogen bonded side chain.

N-Oligoethylene glycol monoaza crown ethers (IIIa-h) were prepared from Ia,b and their stability constants with sodium and potassium cations in pure MeOH were measured. Thus, compounds having one oxyethylene unit in the side chain (IIIa,b) were prepared by the reaction of Ia,b with ethylene oxide at 170°C.[4] Other compounds (IIIc-h) were prepared by the reaction of Ia,b with oligoethylene glycol monochlorides (II) at 120°C in the presence of Na_2CO_3.



The products were isolated by the Kugel-Rohr distillation, and their purities were confirmed by GLC, MASS, IR, NMR spectra, and elemental analyses.

Table. Stability Constants for N-Oligoethylene Glycol Monoaza Crown Ethers

Compound	log K'		Compound	log K'	
	Na^+	K^+		Na^+	K^+
(IIIa)	3.92	3.67	(IIIb)	4.75	5.49
(IIIc)	4.68	4.42	(IIIe)	4.34	5.88
(IIId)	4.34	4.77	(IIIf)	4.26	5.69
(IIIg)	4.32	4.85	(IIIh)	4.28	5.96
(IIIi)	2.91	3.05	(IIIj)	3.51	4.65
(Ia)	2.06	2.72	(Ib)	2.77	4.18(3.90)[5]

Stability constants were measured on mixtures of 0.45-3.20 mM in ligand and 0.37-0.50 mM in NaCl or KCl in MeOH at 25°C with a Beckman 4500 digital pH meter and Toko ion-selective electrodes (Type Na^+ 1100, K^+ 1200).

The stability constants (log K') for these compounds (Ia,b,IIIa-h) with sodium and potassium cations in pure MeOH at 25°C were measured according to the Frensdorff's method[5] and are listed in the table, together with those for N-octyl monoaza crown ethers (IIIi,j) of which synthesis we have reported previously.[6]

It was observed that the stability constants were enhanced by the introduction of olygoethylene side chain on the nitrogen atom of monoaza crown ether. Thus, the complexing abilities for N-oligoethylene glycol monoaza crown ethers with both sodium and potassium cations are superior to those for N-octyl monoaza crown ethers as well as N-unsubstituted monoaza crown ethers. From these results, it is clear that oxyethylene oxygen atoms in the side chain make a remarkable contribution to the complexation with metal cations.

In a series of the monoaza 18-crown-6 derivatives, IIIb having one oxyethylene unit in the side chain and IIIe having two oxyethylene units exhibit the maximum complexing abilities toward smaller sodium cation and larger potassium cation, respectively. Introduction of additional oxyethylene units to the side chain of these derivatives rather reduces the complexing abilities with each cation. This finding may be explained by considering that the effect of steric hindrance by the too long side chain surpasses the contribution of oxygen atoms in the side chain to the complexation, as observed in the crown ethers having an alkyl chain.[7]

In a series of the monoaza 15-crown-5 derivatives, one-unit-larger oxyethylene chains are necessary for the maximum complexing abilities toward both sodium and potassium cations in comparison with the monoaza 18-crown-6 derivatives. Thus, IIIc having two oxyethylene units in the side chain and IIIg having three oxyethylene units were the most effective ligands toward sodium and potassium cation, respectively.

From the facts described above, it may be reasonable to conclude that the complexing abilities for a series of N-oligoethylene glycol monoaza crown ethers become optimum in case the cation size fits the three dimensional cavity composed of the monoaza crown ring and the side oligoethylene glycol chain, and

that oxyethylene oxygen atoms act effectively on complexation.

Compounds having a methoxy group in the terminal of the side chain (IIIg,h) indicated the similar or better complexing abilities compared to the corresponding compounds having a hydroxyl group (IIId,f), due to the inductive effect of methyl group. The stability constant for IIIh with potassium cation exceled that for (N-methoxyethoxyethyl-N'-methyl)diaza 18-crown-6 (log K'=4.80 in 95% aq. MeOH) reported by Lehn et al.,[8] even though the effect of the polarity of the solution is considered, and was comparable to that for 18-crown-6. Furthermore, IIIb showed the highest complexing ability with sodium cation among the reported crown compounds so far.

The three dimensional coordination with a spherical metal cation gives rise to the more stable complexation as observed in cryptates compared to the two dimensional coordination. As the agent for extraction or transportation of metal cations, however, the N-oligoethylene glycol monoaza crown ethers may function more effectively than cryptands, because of their more flexible structures than cryptands.

References and Notes[9]

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