

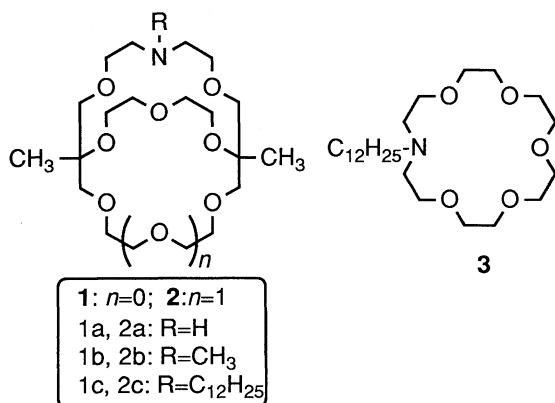
## Synthesis, Structure, and Complexation Properties of Monoazacryptands

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New types of monoazacryptands were prepared and their complexation properties towards alkali metal cations were examined using the solvent extraction method, UV spectroscopy, X-ray crystal analysis, and liquid membrane transport. A lipophilic macrobicyclic polyether consisting of two 18-crown-6 rings and one 20-crown-6 ring was found to be a highly selective potassium ion carrier through a bulk liquid membrane by pH control.

Liquid membrane transport is one of the more effective separation methods for useful substances. A variety of macrocyclic polyethers and analogous open chain compounds have been developed as the ion carriers in such transport system.<sup>1</sup> The cation selectivity is mainly dominated by the recognition of the ionophore's cavity size. In order to attain a higher selectivity, macrobicyclic polyethers having a three-dimensional coordination sphere should be desirable, however, cryptands are not suitable as ion carriers because of the extremely high stability constants of their complexes.<sup>2</sup> On the other hand, we previously found that lipophilic monoazacrown ethers selectively transport alkali metal cations by pH control in the uphill transport system.<sup>3</sup> Therefore, monoazacryptands are expected to work as selective carriers for alkali metal cations with the assistance of a proton gradient. From this standpoint, we will describe the synthesis of new types of monoazacryptands and their complexation properties towards alkali metal cations.



Compounds **1a** and **2a** were prepared by the reaction of *cis*-2,9-bis(bromomethyl)-2,9-dimethyl-15-crown-5<sup>4</sup> and *cis*-2,12-bis(bromomethyl)-2,12-dimethyl-18-crown-6 with diethanolamine, respectively, under basic conditions.<sup>5</sup> These types of N-unsubstituted compounds are potentially useful as key intermediates for functionalized monoazacryptands. Compounds **1b** and **2b** were obtained by the reductive methylation of **1a** and **2a**, respectively, using formalin and formic acid. Compounds **1c** and **2c** were also prepared by the reaction of **1a** and **2a**,

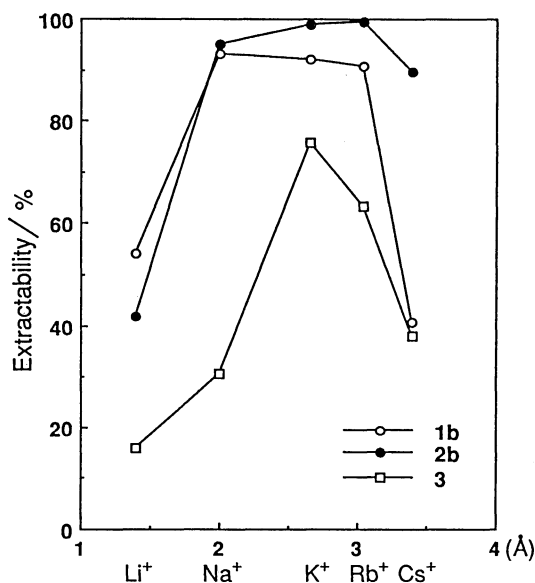


Figure 1. Extractability of compounds **1b**, **2b** and **3** for alkali metal picrates

Extraction conditions: dichloromethane (10 mL) / water (10 mL); [MOH] =  $5.0 \times 10^{-2}$  M; [extractant] = [picric acid] =  $5 \times 10^{-4}$  M; 25 °C; 9 h.

respectively, with dodecyl bromide in the presence of sodium carbonate. All structures were ascertained by <sup>1</sup>H NMR and IR spectroscopy, mass spectrometry and elemental analysis.<sup>6</sup>

Extraction profiles conducted under the conditions using equimolar amounts of the ionophore and alkali metal picrate<sup>7</sup> are shown in Figure 1. As expected, both **1b** and **2b** showed much higher extractabilities towards all alkali metal cations than did N-dodecylmonoaza-18-crown-6 (**3**). Since the extractabilities towards Na<sup>+</sup>, K<sup>+</sup> and Rb<sup>+</sup> almost reached their maxima, the cation selectivity was hardly observed.

In order to clarify the cation selectivity of these types of compounds, competitive transport experiments were carried out in a U-type cell at 25 °C according to the literature.<sup>3</sup> The detailed transport conditions and the results in the presence of Li<sup>+</sup>, Na<sup>+</sup> and K<sup>+</sup> are summarized in Table 1. Ionophores **1c** and **2c** selectively transported Na<sup>+</sup> and K<sup>+</sup>, respectively, using pH control. Lehn *et al.* reported that a lipophilic cryptand [2.2.2] was not suitable as the ion carrier because of its excessively strong binding ability.<sup>2,8</sup> In this transport system using pH control, however, lipophilic monoazacryptands succeeded in transporting alkali metal cations. This finding clearly shows that the protonation to the nitrogen atom of the macrocycle assisted the release of the cation captured at the acidic interface and the deprotonation of the monoazacryptand salt was successfully done at the basic interface. A remarkably high K<sup>+</sup>/Na<sup>+</sup> selectivity (over 400 times) was realized by **2c**, where chloride ion was used

**Table 1.** Competitive passive transport data<sup>a</sup> toward Li<sup>+</sup>, Na<sup>+</sup> and K<sup>+</sup>

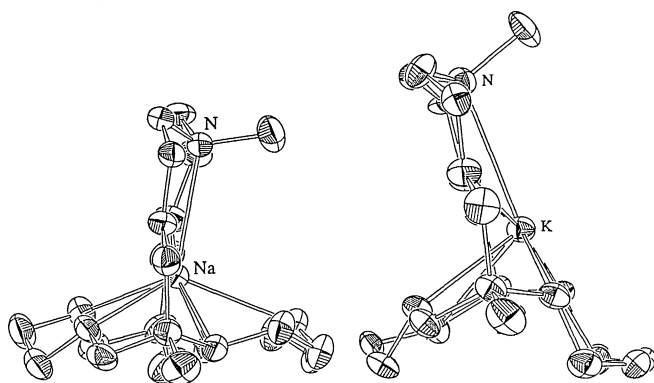
Compd. No.	transport velocity <sup>b</sup>			selectivity	
	Li <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Na <sup>+</sup> /K <sup>+</sup>	K <sup>+</sup> /Na <sup>+</sup>
<b>1c</b>	<0.002	7.0	1.0	7.0	-
<b>2c</b>	nd	0.019	7.8	-	410
<b>3</b>	nd	0.006	0.029	-	4.8

<sup>a</sup> Transport conditions: aqueous phase 1 (10 mL), [LiCl] = [NaCl] = [KCl] = [Me<sub>4</sub>NOH] = 0.1 M; organic phase (CH<sub>2</sub>Cl<sub>2</sub>, 20 mL), [ionophore] = 2.5 × 10<sup>-3</sup> M; aqueous phase 2 (10 mL), [HCl] = 0.1 M, 25 °C. <sup>b</sup> × 10<sup>6</sup> mol/h

as the counter anion. This selectivity should be ascribed to the fitness between the sizes of the cryptand cavity and the potassium cation.<sup>5</sup> Under the same transport conditions, compound **3**, which was an efficient K<sup>+</sup> carrier in the presence of a lipophilic picrate anion,<sup>3</sup> scarcely transported metal cations. This finding also demonstrates a high complexing ability of **2c** towards potassium ion.

The X-ray crystal structures of complexes **1b** with NaI and KI are shown in Figure 2.<sup>9</sup> Both cations were captured in the three dimensional cavity of the macrobicyclic ligand. All hetero atoms (seven oxygen and one nitrogen) were nicely coordinated to the metal cation. Although Na<sup>+</sup> exists in the center of the cavity, K<sup>+</sup> is biased to the center of monoaza-18-crown-6 ring. Thus, Na<sup>+</sup> is deeply encapsulated in the cavity of **1b** in comparison with K<sup>+</sup>, which may result in giving the higher extractability towards Na<sup>+</sup>. This difference partly explains the Na<sup>+</sup> selectivity of **1c** observed in the transport experiment.

Other evidence for the three-dimensional coordination was given by the UV spectroscopy study. The position in the UV spectrum of the picrate anion is a measure of the ion pair type.<sup>10</sup> When **1b** complexed with sodium picrate in THF, a peak at 380 nm was observed. Since this absorption was assigned to the loose ion pair, the cation should be encapsulated in the three-dimensional cavity.

**Figure 2.** ORTEP drawings of **1b**·NaI and **1b**·KI.

In conclusion, a new series of C,C-bridged monoazacryptands were developed and their complexation properties were disclosed. Especially, unsubstituted derivatives **1a** and **2a** are potentially useful for further functionalized materials. Further modification of the ligand structures to improve the complexing ability is now in progress.

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## References and Notes

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- 6 Satisfactory spectral and microanalytical data were obtained for new compounds. Representative data are as follows. Compound **1a**: a slightly yellow liquid, <sup>1</sup>H NMR(CDCl<sub>3</sub>) δ 1.11 (s, 6H), 2.70 (s, 1H), 2.75-2.91 (m, 4H), 3.49-3.86 (m, 24H). Anal. Found: C, 57.10; H, 9.38; N, 3.44%. Calcd for C<sub>18</sub>H<sub>35</sub>O<sub>7</sub>N: C, 57.27; H, 9.35; N, 3.71%. Compound **2a**: a slightly yellow liquid, <sup>1</sup>H NMR(CDCl<sub>3</sub>) δ 1.11 (s, 6H), 2.83 (s, 1H), 2.83 (t, 4H), 4.49-3.86 (m, 28H). Anal. Found: C, 54.53; H, 9.12; N, 3.19%. Calcd for C<sub>20</sub>H<sub>39</sub>O<sub>8</sub>N·H<sub>2</sub>O: C, 54.65; H, 9.40; N, 3.19%.
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- 9 Crystal data for **1b** NaI: C<sub>19</sub>H<sub>37</sub>NO<sub>7</sub>NaI, M=541.40, space group C2/c, a=21.626(7)Å, b=10.399(6)Å, c=22.896(5)Å, β=101.45(2)°, V=5046(3)Å<sup>3</sup>, Z=8, Dc=1.425g/cm<sup>3</sup>. Intensity data were collected by the ω-2θ scan mode with 2θ up to 55.0° on a Rigaku AFC5R automated four-cycle diffractometer using graphite monochromated Mo-Kα radiation. The structure was solved by direct methods (SHELXS86) and refined by the full-matrix least-squares method to give R=0.045 and Rw=0.042 for 4516[|Fo|>3σ|Fo|] reflections. Crystal data for **1b** KI: C<sub>19</sub>H<sub>37</sub>NO<sub>7</sub>KI, M=557.51, space group P2<sub>1</sub>/c, a=10.430(4)Å, b=16.715(3)Å, c=15.144(9)Å, β=91.49(5)°, V=2639(1)Å<sup>3</sup>, Z=4, Dc=1.403g/cm<sup>3</sup>, R=0.089 and Rw=0.117 for 3900[|Fo|>3σ|Fo|] reflections.
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