

## ION-BINDING PROPERTIES OF N,N'-DISUBSTITUTED DIAZA-CROWN ETHERS

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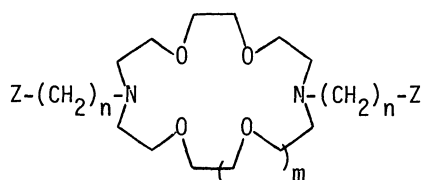
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Derivatives of diaza-18-crown-6 and diaza-15-crown-5 were synthesized and their complexation properties were examined by solvent extraction and liquid membrane transport of various cations. N,N'-Bis(aminoalkyl) derivatives were particular in exhibiting unusually high but non-selective ion-binding efficiency toward various cations.

Many investigations on the chemistry of crown ethers have been focused on the modification of chemical structures and the resulting ion-binding properties of those crown ligands.<sup>1)</sup> In the course of our study of macromolecular macrocyclic polyethers, we have had the need to synthesize a series of N,N'-disubstituted derivatives of diaza-crown ethers and to study their ion-binding properties. Some of those derivatives are known.<sup>2)</sup> However, a comparison of ion-binding properties of those derivatives of diaza-crown ethers which have different functional substituents is interesting, and we like to report the syntheses of those previously unreported derivatives and the preliminary results of our study of their ion-binding characteristics.

A series of N,N'-bis(aminoalkyl) derivatives of diaza-18-crown-6 and diaza-15-crown-5 were prepared by the reaction of (1a) and (5a) with respective N-(bromoalkyl)phthalimide followed by hydrazinolysis.<sup>3)</sup> The results are summarized in Table 1.<sup>4)</sup> Reactions of (1a) with bromopropane and with bromopropanol gave (1c) (low melting solid, 70% yield) and (4c) (oil, 54% yield), respectively. All the spectroscopic data of these compounds were in good agreement with the assumed structures.

With some of those derivatives, extraction experiments<sup>5)</sup> were carried out to investigate their ion-binding behavior and representative results are summarized in Table 2. As shown in Table 2,



- |     |                       |         |
|-----|-----------------------|---------|
| m=1 | (1) Z=H               |         |
|     | (2) Z=N-Phthalimido   | (a) n=0 |
|     | (3) Z=NH <sub>2</sub> | (b) n=2 |
|     | (4) Z=OH              | (c) n=3 |
|     |                       | (d) n=5 |
| m=0 | (5) Z=H               |         |
|     | (6) Z=N-Phthalimido   |         |
|     | (7) Z=NH <sub>2</sub> |         |

Table 1. Product Yields and NMR Data of Aminoalkyl Derivatives of Diaza-Crown Ethers

Crown compounds	Product yield(%) <sup>a</sup>	<sup>1</sup> H-NMR (ppm), CCl <sub>4</sub>	TLC(R <sub>f</sub> ) <sup>b</sup>
3b	52	1.43 (s, 4H, NH <sub>2</sub> )	0.58
3c	45	1.47 (m, 4H, CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub> ) 1.17 (s, 4H, NH <sub>2</sub> )	0.54
3d	41	1.36 (m, 12H, CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub> ) 0.91 (s, 4H, NH <sub>2</sub> )	0.48
7b	45	2.12 (s, 4H, NH <sub>2</sub> )	0.55
7c	46	1.50 (m, 4H, CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub> ) 1.95 (s, 4H, NH <sub>2</sub> )	0.48
7d	39	1.33 (m, 12H, CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub> ) 1.16 (s, 4H, NH <sub>2</sub> )	0.49

a. Based on (1a) or (5a).

b. All the compounds prepared are pure as shown by TLC. Alumina-precoated plastic sheets for TLC (Eastman) were used. Solvent: methanol/acetic acid/water, 10:1:1.

all the N,N'-disubstituted derivatives of (1a) exhibited enhanced extraction efficiencies compared with (1a) itself, although the selectivities were somewhat less pronounced.<sup>6)</sup> The most interesting to note is the extremely high but non-selective extraction efficiency of (3c). Low selectivity was observed even when lower concentration of (3c) was applied. This excessive extraction behavior of (3c) is not yet understandable to us. However, a plausible explanation may be that the amino groups in the flexible side arms participate by axial ligation in the formation of complexes, thereby enhancing the capability to form complexes. With the flexible complex-forming side arms the specificity towards metal ion of certain ionic size is least expected. The participation of side chain amino groups in complex formation is further supported by the very lower ion extraction efficiency exhibited by (1c), (2c) and (4c). It is interesting to observe that those substituted

Table 2. Extraction of Cation Picrates by Crown Ethers<sup>a</sup>

Cation	(% Cation extracted) <sup>b</sup>				
	(1a)	(1c)	(2c)	(3c)	(4c)
Li <sup>+</sup>	0	11.2	6.5	100	10.1
Na <sup>+</sup>	1.4	47.4	29.6	100	50.2
K <sup>+</sup>	4.2	67.7	72.0	100	67.8
NH <sub>4</sub> <sup>+</sup>	-	50.2	26.3	100	17.1

<sup>a</sup> H<sub>2</sub>O/CH<sub>2</sub>Cl<sub>2</sub> = 50/50 (v/v); [picric acid] = 7 × 10<sup>-5</sup> M; [hydroxide] = 0.01M  
[crown ether] = 35 × 10<sup>-5</sup> M, at 25°C.

<sup>b</sup> Based on total amount of picrate salt.

Table 3. Initial Transport Rates and Carrier Saturation of Alkali Metal Ion Transport by Derivatives of Diaza-Crown Ethers<sup>a</sup>

Carrier	Initial transport rate ( $\mu$ mole/hr)			Carrier saturation(%)		
	Na <sup>+</sup>	K <sup>+</sup>	Cs <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Cs <sup>+</sup>
1a	48.8	63.6	50.0	8	17	16
1c	56.0	92.0	47.6	21	33	14
2c	22.4	72.0	18.8	9	30	5
3c	4.0	9.8	9.1	67	69	66
4c	26.0	35.6	17.4	7	10	7
5a	13.6	11.2	9.6	3	2	2
6c	61.6	15.0	4.3	21	13	2
7b	6.6	8.8	8.4	44	49	43
7c	5.3	10.4	7.3	55	62	51
7d	4.1	9.0	9.3	62	64	56

<sup>a</sup> See reference (8) for the experimental set-up and procedure.

crown ethers with poor extraction efficiency show rather improved selectivities in complexing with metal ions of different ionic sizes. The increasing tendency of N-alkylated (1c), (2c) and (4c) to form complexes with various cations in comparison with (1a) may be attributed to the increased donor character of ring nitrogens by the presence of third alkyl groups.<sup>7)</sup>

The complexation behavior of those crown ethers was further investigated by metal ion transport experiment employing a water/chloroform/water liquid membrane system. Metal picrates were transported at 25°C from an "in" to an "out" aqueous phase in a U-shape glass tube with proper stirring. Initial transport rates and carrier saturation values<sup>9)</sup> were measured and the representative results are summarized in Table 3.

As seen in Table 3 notable substituent effects on the rate and carrier saturation were observed. Among the [2,2] diaza-crown ether ligands studied (2c) appears to be the most selective with highly effective rate, while the (3c) with strongly complexing terminal amino groups is the least effective. The derivatives of [2,1] diaza-crown ether of smaller cavity size also exhibited the same trend; thus (6c) being the most effective carrier. This observation confirms the view that the good ion-transport carriers are those ligands that form rather moderately stable complexes than very stable complexes.<sup>9)</sup>

Another notable feature of the data in Table 3 is that the lengths of side arm alkyl groups unexpectedly have little influence upon the initial transport rates and saturation values. (c.f. the values of (7b), (7c) and (7d)). This result is rather surprising to us, because it was expected that if any axial ligation is involved, the length of side arms may play an important role in forming favorable conformation for stable complexes.

The present results are very suggestive information to us in designing the structures of macromolecular crown ethers and in studying their metal complexing properties. The full accounts of our study of diaza-crown ethers and their macromolecular derivatives will be published elsewhere.

References and Notes

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- 2) C.K. Chang, *J. Am. Chem. Soc.*, **99**, 1819 (1977); M. Takagi, M. Tazaki, and K. Ueno, *Chem. Lett.*, **1978**, 1179; S.J. Leigh and I.O. Sutherland, *J. Chem. Soc. Perkin, I*, 1089 (1979).
- 3) J.C. Sheehan and W.A. Bolhofer, *J. Am. Chem. Soc.*, **72**, 2786 (1950).
- 4) These liquid compounds do not give any molecular-ion peak ( $M^+$ ) in their electron-impact mass spectra. The chemical-impact mass spectra of the compounds (1c), (3c), (4c) and (7c) show  $(M+1)^+$ -peaks.
- 5) S. Kopolow, T.E. Hogen Esch, and J. Smid, *Macromolecules*, **6**, 133 (1973); J.K. Frensdorff, *J. Am. Chem. Soc.*, **93**, 4684 (1971).
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- 8) Two water phases (IN; metal picrate, 0.01 M, 50 ml, OUT; iminodiethanol/HCl buffer at pH 10, 50 ml) were bridged by 40 ml of chloroform membrane in which the carrier was dissolved ( $7.5 \times 10^{-4}$  M). All layers were stirred at 250 rpm and maintained at  $25.0 \pm 0.5^\circ\text{C}$ . Moles of cation transported into the receiving phase were plotted against time for each carrier-containing system to obtain the transport rates. The carrier saturations were calculated from the ratio of the concentration of picrate ion in chloroform membrane phase at the end of experiments (about 6h after) and initial carrier concentration.
- 9) M. Kirch and J.M. Lehn, *Angew. Chem., Int. Ed. Engl.*, **14**, 555 (1975).

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