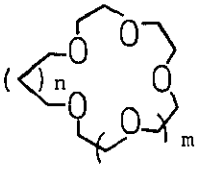
# CROWN ETHERS OF LOW SYMMETRY. 14- TO 17-CROWN-5 AND 17- TO 22-CROWN-6

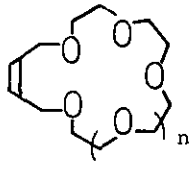
Mikio Ouchi, Yoshihisa Inoue, and Tadao Hakushi
Department of Applied Chemistry, Himeji Institute of Technology,
2167 Shosha, Himeji, Hyogo 671-22, Japan

Controlling complexation phenomena has been the major subject of crown ether chemistry. Although a wide variety of highly functionalized crown ethers of lower symmetry have been synthesized, their cation binding abilities have not been correlated with the change of molecular symmetry.

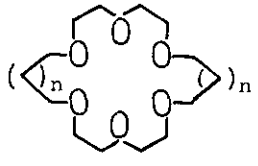
We now report the synthesis of a series of less symmetrical crown ethers with or without C-C multiple bonds **1-3**, and discuss their cation-binding abilities evaluated by picrate extraction experiments. As can be seen from Table, the cation extractabilities of the crown ethers **1-3** are generally lower than common symmetrical crown ethers **4**, for which less-symmetrical arrangement of the donor oxygen atoms must be responsible. It should be noted that 16-crown-5 **1c** shows the highest relative selectivity for $Na^+$, although the cation selectivities are accounted for in terms of the size-fit concept. In the presentation, the symmetry-extractability relationship will be discussed in detail.



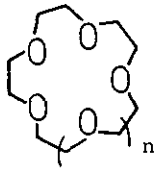
**1a**:m=1,n=1
**1b**:m=1,n=2
**1c**:m=2,n=1
**1d**:m=2,n=2
**1e**:m=2,n=4



**3a**:n=1
**3b**:n=2



**2a**:n=1
**2b**:n=2



**4a**:n=1
**4b**:n=2

Table. Extraction of alkali metal picrates

| Crown ether | Extractability(%) $Na^+$ | $K^+$ | $Rb^+$ | $Cs^+$ |
|---|---|---|---|---|
| 15-Crown-5 **4a** | 13.2 | 14.3 | 9.6 | 3.3 |
| 16-Crown-5 **1a** | 13.5 | 3.0 | 2.1 | 0.9 |
| 17-Crown-5 **1b** | 1.8 | 1.9 | 0.9 | 0.7 |
| $\Delta^{15}$-17-Crown-5 **3a** | 0.9 | 1.3 | 1.0 | 1.0 |
| 18-Crown-6 **4b** | 6.3 | 69.0 | 57.6 | 36.7 |
| 19-Crown-6 **1c** | 2.5 | 22.4 | 17.0 | 7.4 |
| 20-Crown-6 **1d** | 1.1 | 14.1 | 19.7 | 18.1 |
| 22-Crown-6 **1e** | 0.5 | 1.2 | 1.7 | 2.5 |
| $\Delta^{18}$-20-Crown-6 **3b** | 0.6 | 3.8 | 6.8 | 8.1 |
| 20-Crown-6 **2a** | 2.1 | 2.6 | 1.8 | 0.9 |
| 22-Crown-6 **2b** | 0.5 | 0.6 | 1.0 | 1.8 |

Temperature 25.0 + 0.1°C; aqueous phase: [picrate]=3 x $10^{-3}$M; organic phase($CH_2Cl_2$): [crown ether]=3 x $10^{-3}$M.