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Cyclotriveratrylene Crown Ethers: Metal Ion Extraction and Transport Abilities through Organic Membrane

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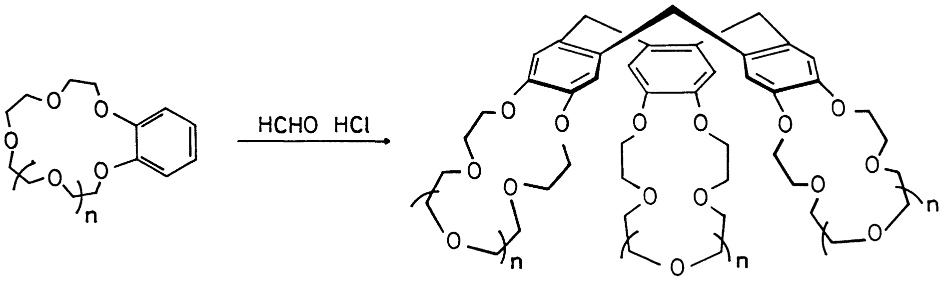
Synopsis. Extraction abilities of cyclotriveratrylene crown ethers (**2**) toward alkali, alkaline earth, and other metal ions were examined. Transport of metal ions by **2** through a liquid membrane was also examined.

Many research groups are recently modifying crown ethers in order to develop a new kind of functionality in the host-guest chemistry.[1] Cyclotriveratrylene attracts considerable attention for the following reasons: i) it exists in a "crown (or cone)" conformation with a high energy barrier for interconversion;[2,3] ii) it forms stoichiometric inclusion compounds with small neutral molecules.[4] Although syntheses of the cyclotriveratrylene crown ethers such as **2b** and **2c** and the isolation of their 1 : 3 complexes with sodium and potassium thiocyanates have already been reported by Frensch and Vögtle,[5] the complexing ability of **2** for metal ions has not been studied in detail. In this paper we report the extraction and transport of metal ions by **2**.

Cyclotriveratrylene crown ethers **2a**, **2b**, and **2c** were prepared by the method of Frensch and Vögtle with minor modification.[5] Thus, compound **2a** was obtained in a 4.8% yield by the reaction of benzo-12-crown-4 (**1a**) with formaldehyde in the presence of hydrochloric acid.

The extraction abilities of the crown ethers **1a**—**c** and **2a**—**c** toward alkali, alkaline earth, and other metal ions were determined by the method described in our previous paper.[6] However, the measurement of extraction and transport abilities was carried out using a three-fold concentration of **1a**—**c** compared with that of **2a**—**c** in order to clarify the selectivities of **2a**—**c** and the corresponding monomers **1a**—**c**. The results are summarized in Table 1. The extraction ability of cyclotriveratrylene crown ether **2a** toward alkali, alkaline earth metals, and other bivalent metal ions is low or zero. Similar results were obtained with the corresponding monomer **1a**. In addition, it was found that **2c** showed a relatively high extraction ability toward alkali metal (excluding lithium) ion, alkaline earth metal ions, silver(I) ion, and thallium(I) ion, while it showed little or no extraction ability toward Li^+, Mg^{2+}, Ca^{2+}, Co^{2+}, Ni^{2+}, and Cu^{2+}. Furthermore, **2c** showed only slightly higher extraction abilities toward Na^+, Rb^+, Cs^+, Sr^{2+}, Ba^{2+}, and Ag^+ than those of the corresponding monomer **1c**. Similar results were obtained in the case of **2b** (except for Sr^{2+} and Ba^{2+}), although the extraction ability of **2b** is relatively low compared with that of **2c**. Consequently, the extraction abilities of cyclotriveratrylene crown ethers **2a**, **2b**, and **2c** are very similar to those of the corresponding monomers **1a**, **1b**, and **1c**, although the complexing manner of the cyclotriveratrylene



1a: n=0
1b: n=1
1c: n=2

2a: n=0
2b: n=1
2c: n=2

Table 1. Extraction of Metal Picrates from the Aqueous to the Organic Phase (%)

Compd	Li^+	Na^+	K^+	Rb^+	Cs^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Ag^+	Tl^+
2a[a]	0	9	10	11	12	4	0	0	2	0	1	0	12	27
1a[b]	0	8	14	15	17	4	0	0	3	0	1	0	9	31
2b[a]	6	48	87	81	37	2	2	2	4	3	3	1	72	95
1b[b]	3	44	81	60	23	1	1	1	2	2	2	1	57	85
2c[a]	6	53	99	96	98	5	7	55	36	5	10	3	94	100
1c[b]	3	35	98	90	88	1	3	43	25	3	7	2	88	99

a) Solvent: Water and dichloromethane (equal volumes). Picric acid=7.0×10^{-5} M. Metal nitrate=0.1 M. Crown ether=7.0×10^{-4} M. b) Crown ether=2.1×10^{-3} M.

crown ether **2** with metal ions cannot be determined from the present results.

Alkali metal cation transport mediated by **1** and **2** through an organic liquid membrane was investigated using a double cylindrical glass cell in which the inner and outer aqueous phases were bridged by a dichloromethane solution containing crown ether **1** or **2**. Practically no ion transport occurred in the absence of the crown ether. The results and the selectivity of Rb^+ over other alkali metal cations are summarized in Tables 2 and 3, respectively. The rate of ion transport is dependent on the ring size of the cyclotriveratrylene crown ethers and the kind of metal ions. Crown ethers **2a** and **2c** showed a similar tendency of ion transport abilities toward alkali metal cations with the corresponding monomers **1a** and **1c**, although **1a** and **1c** generally showed slightly higher ion transport abilities compared with **2a** and **2c**, respectively. However, **2b** showed much higher ion transport abilities toward alkali metal cations compared with those of the corresponding monomer **1b**. Interestingly, **2b** transported Rb^+ more efficiently than **1b**, while the transport abilities of **2b** and **1b** toward Li^+, Na^+, K^+, and Cs^+ were nearly the same. These observations suggest that the Rb^+ ion is incorporated into the cavity surrounded by the three benzocrown ether moieties of **2b**, thereby forming a 1 : 1 complex. Furthermore, **2b** showed higher transport abilities toward K^+ and Cs^+ ions compared with the corresponding monomer **1b**, although complexing manner cannot be detailed at present. As shown in Table 3, the difference in the selectivity of Rb^+ over other alkali metal cations between **1** and **2** may be insignificant and the preference of Rb^+ over Na^+ in the transport was in the range from 0.3 to 6.9 except for **2c**. However, it is noticeable that the selectivity (Rb^+/Na^+) of **2c** in the transport was 43.8. This value is very large compared with that (5.5) of the corresponding monomer **1c**, or those of the other crown ethers **1a**, **1b**, **2a**, and **2b**. It is well known that in ion-transport from an IN aq phase to an OUT aq phase across a liquid membrane, there exist two possible rate-determing steps: ion-extraction from the IN aq phase to the membrane phase and ion-releasing from the membrane phase to the OUT aq phase. Therefore, the high selectivity of **2c** for Rb^+/Na^+ may be mainly due to the slow ion-releasing step of Na^+, because the extraction abilities (48 and 53%) of **2b** and **2c** for Na^+ are nearly the same, while the transport abilities (2.18 and 0.66) of **2b** and **2c** for Na^+ are very different.

Table 2. Amounts of Alkali Metal Ions Transported through Liquid Membranes (μmol)a)

Carrier	Li^+	Na^+	K^+	Rb^+	Cs^+
2a b)	0.00	0.38	0.08	0.12	0.17
1a c)	0.00	0.45	0.33	0.13	0.37
2b b)	0.76	2.18	8.82	15.06	2.27
1b c)	0.70	3.61	5.97	3.40	0.91
2c b)	0.30	0.66	6.44	28.90	7.70
1c c)	0.28	7.31	27.19	39.89	13.43

a) In 24 h. b) 0.33 mM. c) 1.0 mM.

Table 3. Selectivity of Liquid Membrane Transport

Carrier	Rb^+/Na^+	Rb^+/K^+	Rb^+/Cs^+
2a	0.3	1.5	0.7
1a	0.8	1.2	1.1
2b	6.9	1.7	6.6
1b	0.9	0.6	3.7
2c	43.8	4.5	3.8
1c	5.5	1.5	3.0

Experimental

All melting points are uncorrected. ^1H NMR spectra were measured on a Hitachi R-1100 spectrometer (60 MHz) with TMS as the internal standard. Mass spectra were taken on a Hitachi M-80 spectrometer.

Materials. Benzo-12-crown-4 (**1a**), benzo-15-crown-5 (**1b**), and benzo-18-crown-6 (**1c**) were prepared according to a method reported in the literature.7) Other reagents employed were either commercially available or synthesized by the usual methods. The solvents were purified by distillation.

6,9,12,15,23,26,29,32,40,43,46,49-Dodecaoxaheptacyclo[$O^{3,18}.O^{5,16}.O^{20,35}.O^{22,33}.O^{37,1}.O^{39,50}$]heptaconta-3,5(16),17,20,22(33),34,37,39(50),51-nonaene (2a). To a mixture of concentrated hydrochloric acid (135 ml) and 37% formalin (10 ml, 0.13 mol), benzo-12-crown-4 (**1a**) (4.03 g, 18 mmol) was added under stirring at 0 °C. After being stirred for 7 h at 30 °C, the viscous solution was poured onto water. The mixture was then extracted with chloroform and the extracts were washed with water until they became neutral. The combined extract was dried over $MgSO_4$ and concentrated under reduced pressure. Chromatography on silica gel using ethyl acetate as the eluent gave a colorless solid. Recrystallization of the solid from chloroform-hexane gave **2a** (0.2g, 4.8%) as a colorless powder, mp 253-256 °C. ^1H NMR ($CDCl_3$) δ=6.99(s, 6H), 4.75 (d, J=14.0 Hz, 3H), 4.40—3.72 (m, 36H), 3.54 (d, J=14.0 Hz, 3H). MS m/z 708 (M^+). Found: C, 62.09, H, 6.52%. Calcd for $C_{39}H_{48}O_{12}$·1/2$CHCl_3$: C, 61.74, H, 6.36%.

Compounds **2b** and **2c** were also obtained by a method similar to that previously described.5)

2b: Yield 3.6%, mp 204.5—206.0 °C (lit,5) 203.5—205.5 °C).

2c: Yield 12%, mp 166.0—167.0 °C (lit,5) 169—172 °C).

Solvent Extraction. Equal volumes (5 ml) of dichloromethane containing 7×10^{-4} M of **2** and/or 2.1×10^{-3} M of **1** and an aqueous solution containing 0.1 M of metal nitrate and 7.0×10^{-5} M of picric acid were mixed and agitated (1 M=1 mol dm^{-3}). The solution was then separated by centrifugation. The upper solution was withdrawn and its absorbance was measured at 380 nm. A similar extraction and measurement were performed with pure dichloromethane and an aqueous solution containing 0.1 M metal nitrate and 7.0×10^{-5} M picric acid. Extraction abilities were calculated by the following equation: extraction ability=$(A_0-A)/A_0\times100$. A_0 is the absorbance in the absence of a crown ether and A is the absorbance in its presence.

Cation Transport through Liquid Membranes. Cation transport experiments were conducted using a double cylindrical glass cell (cylinder diameter: inner, 7 mm; outer, 16 mm) in which the inner cylinder had small channels connecting the inner and outer areas at its bottom. A dichloromethane solution (5 ml) containing 0.33 mM of crown ether **2** or 1 mM of crown ether **1** was placed at the bottom. Atop the dichloromethane solution inside the inner cylinder was placed 1.5 ml of water. Simultaneously, atop the outer ring of the dichloromethane solution was placed an aqueous solution (3 ml) containg metal thiocyanate (1 M). The organic phase was gently stirred at ca. 130 rpm and 24 °C using a stirrer. At specified time intervals, the concentrations of metal ion in the receiving phase were determined by atomic absorption spectroscopy.

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