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Ring-contracted Crown Ethers: 14-Crown-5, 17-Crown-6, and Their Sila-analogues. Drastic Decrease in Cation-binding Ability

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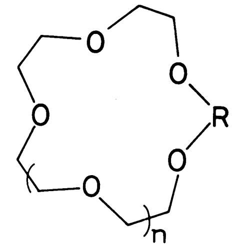
Synopsis. As compared with symmetrical 3*m*-crown-*m*, the ring-contracted(3*m*−1)-crown-*m* showed drastic decrease in cation-binding ability, which is attributable not to the diminished cavity size but to the disordered conformation induced by ring contraction.

The control of complexation phenomena has been the major subject of the crown ether chemistry. Recent investigations from this laboratory[1] have shown that the introduction of an extra methylene group into a symmetrical 3*m*-crown-*m* (*m*=4—6) affects remarkably its cation-binding ability toward alkali metal ions; *e.g.* 16-crown-5 derivatives possess much higher Na^+/K^+ selectivity than the parent 15-crown-5. Our subsequent interest in this field is directed toward ring-contracted (3*m*−1)-crown-*m* (*m*=5, 6). Pedersen first reported the effect of ring-contraction upon complex formation,[2] however, no clear-cut discussion was made. In the present study, we report the cation-binding ability of 14-crown-5 (**2**), 17-crown-6 (**5**), and their sila-analogues (**3**, **6**), and the results are discussed in view of the size-fit concept and conformational difference.

In order to evaluate the cation-binding ability, extrations of aqueous alkali metal picrates (Na^+, K^+, Rb^+, and Cs^+) were carried out at 25 °C with dichloromethane solutions of **2**, **3**, **5**, and **6**, and the results were compared with those for the parent 15-crown-5 (**1**) and 18-crown-6 (**4**) and also with those for acyclic analogues, tetraglyme (**8**) and pentaglyme (**9**).



1, $n=1$; $R=CH_2CH_2$
2, $n=1$; $R=CH_2$
3, $n=1$; $R=Si(CH_3)_2$
4, $n=2$; $R=CH_2CH_2$
5, $n=2$; $R=CH_2$
6, $n=2$; $R=Si(CH_3)_2$
7, $n=1$; $R=(CH_2)_4$

As can be seen from Table 1, the ring-contracted crown ethers **2**, **3**, **5**, and **6** showed extremely low extractabilities as is the case with the open-chain analogues **8** and **9** under the conditions employed,[3] where 15-crown-5 and 18-crown-6 gave moderate extractabilities. It should be noted that, in spite of the longer O-Si-O bond (3.3 Å) than the O-C-O bond (2.8 Å) of **2** and **5**, the sila-crown ethers **3** and **6** show practically the same extractabilities as the corresponding carbon analogues **2** and **5**. This result is very significant in ascertaining the origin of the extremely low extractability for the ring-contracted crown ethers, and may suggest that the reduced cavity size is not the most important factor which is responsible for the low extractability.

Table 1. Extraction of alkali metal picrates[a)]

Ligand	Extractability/%[b)]			
	Na^+	K^+	Rb^+	Cs^+
15-Crown-5 (**1**)	13.2	14.3	9.6	3.3
14-Crown-5 (**2**)	0.1	0.2	0.2	0.2
Sila-14-crown-5 (**3**)	0.1	0.4	0.5	0.5
Tetraglyme (**8**)	0.1	0.1	0.1	0.1
18-Crown-6 (**4**)	6.3	69.3	57.6	36.7
17-Crown-6 (**5**)	0.8	1.7	1.0	0.7
Sila-17-crown-6 (**6**)	0.3	1.8	1.1	0.7
17-Crown-5 (**7**)	1.8	1.9	0.9	0.7
Pentaglyme (**9**)	0.2	0.7	0.6	0.5

a) Temperature 25.0±0.1 °C; aqueous phase(10 mL): [picrate] $=3\times10^{-3}$ M; organic phase(CH_2Cl_2, 10 mL): [ligand] $=3\times10^{-3}$ M. b) % Picrate extracted into organic phase.

The drastic decrease in cation-binding ability of **2**, **3**, **5**, and **6** may rather be accounted for in terms of the disordered conformation of crown ether ring. Examinations with CPK molecular model revealed that one of the five or six donor oxygen atoms of **2**, **3**, **5**, and **6** can not be accomodated in the plane which is composed of the rest of the oxygen atoms, while the cavity sizes of the crown ethers do not differ significantly; *ca.* 1.7 Å for **1**-**3** and 2.5—2.6 Å for **4**-**6**.

17-Crown-5 (**7**) was synthesized in order to obtain additional support for the above explanation. It was synthesized in 16% yield by the reaction of 1,4-butanediol with tetraethylene glycol ditosylate in tetrahydrofuran in the presence of NaOH as a base.

Definitive evidence arises from the comparison of extractabilities of 17-crown-5 and 17-crown-6. In spite of the reduced number of donor oxygen atoms from six to five, 17-crown-5 still gave comparable extractabilities for all cations. This clearly indicates that one of the formal donor oxygen atoms of 17-crown-6 and probably of 14-crown-5 and their sila-analogues **3** and **6** no longer acts as an effective donor atom due to the conformational disorder of the ring-contracted crown ethers.

Experimental

General. Infrared spectra were obtained on a JASCO A-100 grating spectrophotometer. Mass spectra were measured at 20 eV using Hitachi RM-50GC instrument. ^1H and

^{13}C NMR spectra were obtained in chloroform-*d* solution containing 1% tetramethylsilane as an internal standard, using JEOL PMX-60 and FX-60 spectrometers. UV-VIS spectra were recorded on a Shimiadzu UV-300 spectrophotometer.

Synthesis. 14-Crown-5(**2**) and 17-crown-6 (**5**) were synthesized according to the procedure described in the literature.4)

1,4,7,10,13-Pentaoxacycloheptadecane (17-Crown-5, 7). 1,4-Butanediol (5.4 g, 0.06 mol) in tetrahydrofuran(THF) (100 mL) was added to a stirred suspension of sodium hydroxide (6.0 g, 0.15 mol) in THF (300 mL) at 66 °C, and the stirring was continued for 1 h at 66 °C. To the mixture was added tetraethylene glycol ditosylate5) (25.1 g, 0.05 mol) in THF (150 mL) dropwise over 2 h and stirring was continued for 24 h at 66 °C under a nitrogen atmosphere. The solvent was evaporated and the residue was extracted with chloroform. The chloroform extract was dried over magnesium sulfate and the solvent was evaporated. Distillation of the product under a reduced pressure gave 2.0 g (16%) of **7**: bp 105—107 °C/0.13 Torr(1 Torr=133.322 Pa); MS, *m/z* 248 (M^+); ^{1}H NMR δ=3.63—3.83 (20H, m) and 1.60—1.80 (4H, m); ^{13}C NMR δ=71.8(t), 71.1(t), and 27.5(t, $OCH_2\underline{C}H_2\underline{C}H_2CH_2O$); IR(neat) 2850, 1450, 1350, 1290, 1250, and 1100 cm^{-1}. The ^{1}H NMR spectrum was in agreement with published data.6)

2,5,8,11,14,17-Hexaoxaoctadecane (Pentaglyme, 9) was prepared from ethylene glycol monomethyl ether (5.3 g, 0.07 mol) and triethylene glycol ditosylate5) (13.8 g, 0.03 mol) in the presence of sodium hydroxide in THF according to the procedure described above. Distillation of the product gave 3.7 g (46%) of **9**: bp 100—108 °C/0.27 Torr; MS, *m/z* 266 (M^+); ^{1}H NMR δ=3.55—3.78 (20H, m) and 3.38 (6H, s); ^{13}C NMR δ=73.0 (t), 71.6 (t), and 59.3 (q, CH_3O); IR (neat) 2800, 1450, 1350, 1290, 1240, and 1110 cm^{-1}; Found: C, 54.19; H, 10.11; Calcd for $C_{12}H_{26}O_6$: C, 54.12; H, 9.84.

Extraction. Sodium, potassium, rubidium, and cesium picrates were prepared according to Wong's method.7,8) Commercially available 15-crown-5 (Nisso Co.), 18-crown-6 (Nisso Co.), tetraglyme (Nakarai Chemical Co.), and sila crown ethers **3** and **6** (Petrarch Systems Inc.) were used without further purification. The extraction procedures were similar to those reported by Kimura *et al.*9) Equal volumes (10 mL) of a dichloromethane solution of a ligand (3×10^{-3} M) and of an aqueous alkali metal picrate (3×10^{-3} M) were introduced into an Erlenmeyer flask, which was then stoppered and shaken for 10 min at 25.0±0.1 °C using a TAIYO M100L incubator. The mixture was then allowed to stand for at least 2 h at that temperature in order to complete the phase separation. After the phase separation 2 mL of the dichloromethane phase was withdrawn, to which 2 mL of acetonitrile was added. After further dilution, if necessary, with a 1:1 mixture of dichloromethane and acetonitrile, the picrate concentration in the organic phase was determined from its absorption at 375 nm. The molar extinction coefficients at 375 nm for sodium, potassium, rubidium, and cesium picrates are 18600, 19000, 18800, and 18500 M^{-1} cm^{-1}, respectively.

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8) Caution should be taken in working with the picrate salts since they are heat- and shock-sensitive when dry, as is the picric acid itself.

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