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Strong Embedding Effect of Decalin Walls on Cation Complexation in Crown Ethers

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Synopsis. Cylindrical crown ether, tridecalino-18-crown-6, shows strong embedding effect toward coordinated thallium ion.

Increasing attention has been paied to the host molecules such as cryptands,[1)] spherands,[2)] and cavitands,[2)] which have not only high complexing ability but also high complexing selectivity. In this context, we designed a new class of cylindrical crown ether with bicycloalkane walls.[3)] In this cylindrical system, it is expected that the coordinated metal ion may be embedded strongly by bicycloalkane moieties spread out above and below the crown ether ring. In this paper, we wish to report on strong embedding effect of three decalin moieties of tridecalino-18-crown-6[†] (**1**).

Results and Discussion

In the present cylindrical system, the embedding effect of bicycloalkane moieties constructing cylinder wall on complexation of cations can be estimated by the differences in magnitude between total stability of complexes and coordination ability of ethereal oxygen atoms. From the above concept, we selected thallium(I) and dimethylthallium(III) ions as stability and coordination probes, respectively, because it is well-known that the ionic radius of thallium(I) ion (1.40 Å)[4)] and that of dimethylthallium(III) ion (1.25 Å)[5)] are very close to that of potassium (1.33 Å)[4)] and that the larger spin–spin coupling constants between thallium nucleus and methyl protons reflect the stronger coordination ability of ligands surrounding cation.[6)]

First, spin–spin coupling constants between thallium nuclei and methyl protons of dimethylthallium (III) ion complexes were measured to estimate coordination ability of oxygens. As shown in Table 1, the cylindrical crown ethers, **1**, didecalino-18-crown-6 (**2**), and dibicyclooctano-18-crown-6[†] (**3**) had larger coupling constants than that of 18-crown-6 (**4**). These strong coordinations of cylindrical crown ether oxygens are ascribed to the location of oxygen atoms at the entropically favorable positions before and after complexation.

Next, complexation constants, K_c, were measured to determine total complex stabilities in chloroform according to Kimura's method.[7b,8)] As is indicated in Table 1, these crown ethers showed similar complexing behavior toward potassium and thallium(I) ions.[9)] Interestingly, tridecalino-18-crown-6 (**1**) having similar coordination ability to **2** gave ten-fold larger stability than that of **2** in chloroform. From these results, it may be concluded that total stability of complexes is mainly influenced by the bicycloalkane moieties of cylindrical system and, in addition, three decalin walls exhibit efficient embedding effect toward coordinated thallium ion.

Table 1. The values of coupling constants, $J(\mathrm{Tl{-}CH_3})$, of complexes and complexation constants, K_c

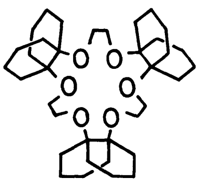
Crown ether	$J(\mathrm{Tl{-}CH_3})/\mathrm{Hz}$[a)]	log K_c	
	δ	K^+	Tl^+
None	400(1.23)		
1	435(1.24)[b)]	10.07	9.36
2	434(1.15)	9.36	8.26
3	440(0.93)	9.37	8.28
4	430(0.89)		
5[c)]	417(0.90)	7.46	6.22

a) In CD_3CN, 100 MHz spectra unless otherwise stated. b) In CD_3CN, 60 MHz spectrum. c) Dibenzo-18-crown-6.

Table 2. Extraction conditions

Crown ether	Metal ion	Concentration/mol dm^{-3}	
		(CE)°	M°
1	K^+, Tl^+	1×10^{-4}	$1-5\times10^{-4}$
2, 3	K^+	1×10^{-4}	$0.2-1\times10^{-4}$
2, 3	Tl^+	1×10^{-4}	$1-5\times10^{-4}$
5[a)]	K^+, Tl^+	1×10^{-4}	$1-5\times10^{-3}$

a) Dibenzo-18-crown-6.



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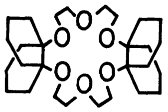

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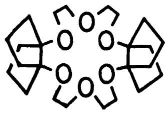

3

Experimental

^{1}H NMR specra were taken with JEOL JMN-PS-100 (100 MHz) and HITACHI R-600S (60 MHz) spectrometers in CD_3CN solutions with Me_4Si as an internal standard.

[†] Ortho fused cyclic compounds are tentatively named "decalino" and "bicyclooctano" for decahydronaphtho[4*a*,8*a*,] and octahydropentaleno[3*a*,6*a*], respectively.

Electronic spectra were measured on a HITACHI 356 spectrophotometer.

Tridecalino-18-crown-6 (1). **1** was prepared from 1,2:7,8-didecalino-3,6-dioxaoctane-1,8-diol and 4,5-decalino-3,6-dioxaoctane-1,8-diol ditosylate by the method similar to that described previously[3b)] and recrystallized from 1,2-dimethoxyethane (29%): mp 197—198 °C; IR (KBr) 1100, 1090 cm^{-1}, ^{1}H NMR (CDCl$_3$) δ=1.00—2.48 (m, 48H), 3.20—4.08 (m, 12H); ^{13}C NMR (CDCl$_3$, 60 °C) δ=21.7 (t, 6C), 23.0 (t, 6C), 30.8 (t, 6C), 61.7 (t, 6C), 78.0 (s, 6C); MS *m/z* 588 (M$^+$). Found: C, 73.30; H, 10.34%. Calcd for $C_{36}H_{52}O_6$: C, 73.43; H, 10.27%.

Dibicyclooctano-18-crown-6 (3). **3** was prepared from *cis*-bicyclo[3.3.0]octane-1,5-diol as described previously[3a)] and recrystallized from ether: mp 73—75 °C; IR (KBr) 1150, 1120, 1090 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.12—2.20 (m, 24H), 3.65 (br s, 16H); ^{13}C NMR (CDCl$_3$) δ=21.8 (t, 4C), 36.9 (t, 8C), 64.1 (t, 4C), 71.1 (t, 4C), 91.7 (s, 4C); MS *m/z* 424 (M$^+$). Found: C, 67.67; H, 9.56%. Calcd for $C_{24}H_{40}O_6$: C, 67.89; H, 9.50%.

Preparation of Crown Ether Complexes with Dimethylthallium(III) Perchlorates. Complexes were prepared by the method similar to that described previously[5)] in an appropriate solvent (2-propanol, acetone, or acetonitrile-*d*$_3$) and purified by recrystallization from acetone/peteroleum ether or dichloromethane/hexane.

Metal Picrates. Potassium and thallium picrates were prepared according to the described methods.[7)]

Extraction. The extraction procedures were similar to those described by Kimura.[7b,8)] Equal volumes (10 ml) of chloroform solution of crown ether and aqueous metal picrate solution were placed in a stoppered flask and shaken for 40 min at 25±0.1 °C. After the phase separated, aliquots varying from 0.50 to 8.00 ml of organic phase (depending on its color intensity) were very carefully removed from organic phase and evaporated to dryness. Aliquots varying from 4.00 to 20.00 ml of acetonitrile were added to the residue. Then concentration of the metal complex with crown ethers were determined spectrophotometrically. In the case of thallium picrate, a mixture of equal volumes of chloroform and acetonitrile was employed as a solvent for spectrophotometry, because a considerable amount of uncomplexed crown ether which was insoluble in acetonitrile existed. The molar absorptivities of picrates were 1.50×10^4 mol dm^{-3} cm^{-1} for potassium and thallium(I) picrates at 374 nm.

Calculations. The extraction equilibrium constant, K_e, for 1:1 crown ether/metal ion complexes is defined by

$$\mathrm{M^+_{aq} + Pic^-_{aq} + CE_{org}} \rightleftharpoons \mathrm{M(CE)Pic_{org}}$$

$$K_e = \frac{[\mathrm{M(CE)Pic}]_{\mathrm{org}}}{[\mathrm{M^+}]_{\mathrm{aq}}[\mathrm{Pic^-}]_{\mathrm{aq}}[\mathrm{CE}]_{\mathrm{org}}} \tag{1}$$

where M$^+$, Pic$^-$, and CE are metal ion, picrate anion, and crown ether, respectively. The existence of uncomplexed crown ether and complexed crown ether in aqueous solution is negligible, because these cylindrical crown ethers have very lipophilic bicycloalkane moieties. Therefore, the following assumption can be made:

$$\mathrm{D} = [\mathrm{M(CE)A}]_{\mathrm{org}}/[\mathrm{M^+}]_{\mathrm{aq}} \tag{2}$$

$$[\mathrm{M^+}]_{\mathrm{aq}} = [\mathrm{Pic^-}]_{\mathrm{aq}} = \mathrm{M^\circ} - \mathrm{A} \tag{3}$$

$$[\mathrm{CE}]_{\mathrm{org}} = (\mathrm{CE})^\circ - \mathrm{A}, \tag{4}$$

where M° and (CE)° denote the initial alkali metal ion and initial crown ether concentration, respectively, and A the concentration of picrate transferred to the chloroform solution. Then Eq. 1 is rewritten as follows:

$$D = K_e(\mathrm{M^\circ - A})[(\mathrm{CE})^\circ - \mathrm{A}]. \tag{5}$$

The K_e values were calculated directly by Eq. 5 and checked by the slope of the plots, log *D vs.* log (M° − A)[(CE)° − A], being unity.

The distribution and complexing constants, K_d and K_c, respectively, are defined by

$$\mathrm{M^+_{aq} + Pic^-_{aq}} \rightleftharpoons \mathrm{MPic_{org}}$$

$$K_d = \frac{[\mathrm{MPic}]_{\mathrm{org}}}{[\mathrm{M^+}]_{\mathrm{aq}}[\mathrm{Pic^-}]_{\mathrm{aq}}} \tag{6}$$

$$\mathrm{MPic_{org} + CE_{org}} \rightleftharpoons \mathrm{M(CE)Pic_{org}}$$

$$K_c = \frac{[\mathrm{M(CE)Pic}]_{\mathrm{org}}}{[\mathrm{MPic}]_{\mathrm{org}}[\mathrm{CE}]_{\mathrm{org}}} \tag{7}$$

$$K_c = K_e/K_d. \tag{8}$$

The K_c values are estimated form Eq. 8. The reported K_d values (K$^+$ 2.67×10^{-3} and Tl$^+$ 4.68×10^{-2}) were quoted for K_c calcuration.[7b,8)]

Extraction conditions were listed in Table 2.

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9) The similar tendency was observed for silver ion.