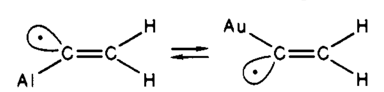
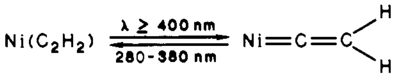
vinylidene indicate fluxional behavior as depicted in (2).[18] The


(2)

Au–C bond contains less ionic character than the Na–C bond, yet Au prefers a lone electron configuration. Nickel vinylidene has equivalent hydrogens, and atomic nickel tends to form double bonds. We thus tentatively propose a linear structure for nickel vinylidene as in sodium vinylidene but with a Ni–C double bond. Unfortunately, the nickel–carbon stretching frequency was not detected in the present study.

Concluding Remarks

1. The first identification of a transition-metal vinylidene by Fourier-transform infrared spectroscopy has been reported. Nickel is shown to form a π complex with acetylene which photoreversibly rearranges to nickel vinylidene:


$$Ni(C_2H_2) \underset{280-380\ nm}{\overset{\lambda \geq 400\ nm}{\rightleftharpoons}} Ni{=}C{=}CH_2$$

The implications of this acetylene/vinylidene interconversion are worth noting. Although an isolated acetylene/vinylidene reaction is endothermic, this same conversion becomes favorable in the presence of nickel, gold,[18] sodium,[19] and theoretically aluminum.[36] Other endothermic reactions such as methylcarbene/ethylene and methylnitrene/methylenimine rearrangements may become exothermic when complexed to a metal atom, cluster, or surface.[43,44] Metal systems that open new reaction channels and effectively convert endothermic reactions to exothermic processes are invaluable in catalysis and surface chemistry.

2. The complexes $Ni(C_2H_2)_2$, $Ni(C_2H_2)_3$, and $Ni_2(C_2H_2)$ have been isolated in argon matrices. The acetylene donates electrons through the C≡C π orbitals and is a π-acceptor through the C≡C π^* orbitals in these complexes, classical Dewar–Chatt–Duncanson bonding.

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Crystal and Molecular Structures of Double Macrocyclic Inclusion Complexes Composed of Cyclodextrins, Crown Ethers, and Cations

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Abstract: The crystal structures of γ-cyclodextrin·12-crown-4·LiSCN (3:3:1) inclusion complex ($C_{48}H_{80}O_{40}\cdot C_8H_{16}O_4\cdot {}^1/_3(LiSCN)\cdot 7.7H_2O$) (**1**) and γ-cyclodextrin·12-crown-4·KCl (3:3:1) inclusion complex ($C_{48}H_{80}O_{40}\cdot C_8H_{16}O_4\cdot {}^1/_3(KCl)\cdot 9H_2O$) (**2**) were determined by X-ray analyses. Crystals of **1** and **2** are isomorphous with space groups $P42_12$, $a = b = 23.75$ (2) Å, $c = 22.92$ (3) Å for **1** and $a = b = 23.842$ (2) Å, $c = 23.132$ (2) Å for **2**. Three γ-cyclodextrins are stacked along the fourfold rotation axis forming a channel type structure, and each of them includes a 12-crown-4 molecule with similar orientation. Three 12-crown-4 molecules have the same C_4 ring conformations, and two of them form a 2:1 sandwich structure complex of (12-crown-4)$_2$·cation, which is included in the hydrophobic channel formed by two γ-cyclodextrins, while the third one is free from a cation.

Cyclodextrins (CDs) are truncated cone-shaped cyclic oligosaccharides composed of six, seven, or eight α-1,4-linked D-glucoses. They have hydrophobic cavities and primary hydroxyl groups on the narrow sides of macrocycles (head) and secondary hydroxyl groups on the other sides (tail). As they are able to form stable inclusion complexes with various organic compounds as guest molecules, they have received much attention as relatively low molecular weight models for biological macromolecules.[1,2] Many structures of α-CD and β-CD complexes including hydrates were intensively investigated by the X-ray method. However, few X-ray studies on γ-CD complexes have been reported: two uncomplexed-hydrated γ-CDs[3,4] and the γ-CD·propan-1-ol complex.[5] In the γ-CD·propan-1-ol complex, the guest molecules, propan-1-ol, are not located in the cavities of γ-CDs, so structures of the inclusion complexes of γ-CDs, especially the locations of guest molecules, have not been elucidated yet.

On the basis of space-filling models, Vögtle and Müller indicated that small crown ether and cryptand just fit into the conical cavity of γ-CD, and mixing of aqueous solutions of γ-CD and 12-crown-4 leads to crystallization of a 1:1 inclusion complex. They also showed that a few cation complexes of crown ethers and cryptands, such as the 12-crown-4·LiSCN complex, can form inclusion complexes with γ-CDs.[6]

In order to elucidate the interaction between hydrophobic cavities of γ-CDs and crown ethers having an ability to form cation complexes, the X-ray crystallographic study of γ-CD·12-crown-4 inclusion complex **3** was undertaken by us.[7] According to this study, the γ-CDs include 12-crown-4 molecules by a 1:1 ratio, forming the novel double macrocyclic inclusion complexes, and these 12-crown-4 molecules have C_4 ring conformations, which

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is found in many 12-crown-4·cation complexes[8-11] e.g., 12-crown-4·LiSCN,[12] while the uncomplexed 12-crown-4 has the C_i ring conformation.[13] The 12-crown-4 molecules are square-shaped, with oxygen atoms located in side positions and directed toward the faces of the secondary hydroxyl groups of γ-CDs.

Here we report crystal structures of double macrocyclic inclusion complexes composed of γ-CD, 12-crown-4, and cations: γ-CD·12-crown-4·LiSCN (3:3:1) (**1**) and γ-CD·12-crown-4·KCl (3:3:1) (**2**), where the $(12\text{-crown-}4)_2$·cation sandwich structure complex is encapsulated by two γ-CDs in the tail-to-tail orientation. The complexes have some interesting points as follows. (1) Cations exist in the hydrophobic cavities of γ-CDs by the medium of 12-crown-4 molecules, and the complete capsulation of 12-crown-4·cation complexes by γ-CDs isolates cations from counteranions. (2) The 12-crown-4·cation complexes may change their geometrical structures through inclusion by the γ-CDs because van der Waals interaction between γ-CDs and 12-crown-4 molecules constrains the ring conformations of 12-crown-4 molecules. (3) They are the first inclusion complexes composed of CDs, crown ethers, and cations and the first example giving clear locations of guest molecules in γ-CDs.

Experimental Section

Preparation of Crystalline Complexes. **γ-CD·12-crown-4·LiSCN (3:3:1) (1)**: The crystal of 12-crown-4·LiSCN complex was prepared by dissolving equimolar quantities of dry LiSCN and 12-crown-4 in aqueous methanol, evaporating the solution, and drying the solid at 100 °C.[14] The very thin plate crystals were obtained. Mixing of 12-crown-4·LiSCN complex and a concentrated, aqueous solution of γ-CD in a 1:1 molar ratio at 50 °C gave a cloudy solution. Hot water was added to the mixture at 50 °C with stirring until a clear solution was obtained. By slow evaporation of this solution at 50 °C suitable crystals for X-ray data collection were obtained.

γ-CD·12-crown-4·KCl (3:3:1) (2): Equimolar quantities of dry KCl, 12-crown-4, and γ-CD were dissolved in hot, aqueous solution. Beautiful crystals of γ-CD·12-crown-4·KCl were obtained by the same procedure as used for **1**.

X-ray Structure Determination. The crystals for data collection, rectangular blocks of 0.4 × 0.4 × 0.5 mm for **1** and 0.3 × 0.3 × 0.3 mm for **2**, were sealed in glass capillaries with a drop of mother liquor to avoid crystal degradation. Diffraction intensities were measured on Rigaku automatic diffractometers, using Mo Kα radiation ($\lambda = 0.7107$ Å) for **1** and Cu Kα radiation ($\lambda = 1.542$ Å) for **2**. Lattice constants were determined by least-squares methods with 20 reflections for both crystals ($18° < 2\theta < 20°$ for **1**, $44° < 2\theta < 45°$ for **2**. 3487 independent reflections (1908 with $I > 3\sigma(I)$) for **1** and 5082 independent reflections (1505 with $I > 3\sigma(I)$) for **2** were collected up to 40° in 2θ (Mo Kα) and 120° in 2θ (Cu Kα), using the ω-scan mode and the $\omega/2\theta$-scan mode at room temperature, respectively. No correction was made for an absorption effect. Crystal data are as follows. **1**: $C_{48}H_{80}O_{40}\cdot C_8H_{16}O_4\cdot {}^1/_3(\text{LiSCN})\cdot 7.7H_2O$, tetragonal, space group $P42_12$, $a = b = 23.75$ (2) Å, $c = 22.92$ (3) Å, $Z = 6$. **2**: $C_{48}H_{80}O_{40}\cdot C_8H_{16}O_4\cdot {}^1/_3(\text{KCl})\cdot 9H_2O$, tetragonal, space group $P42_12$, $a = b = 23.842$ (2) Å, $c = 23.132$ (2) Å, $Z = 6$.

These two complexes are isomorphous with the γ-CD·12-crown-4 inclusion complex **3** which we reported previously.[7] The phase problems for **1** and **2** were solved by using atomic coordinates of γ-CDs of **3**; guest molecules and water molecules were located by difference Fourier syntheses. One of the primary oxygen atoms O(6)1 is disordered at two positions (O(6)A1 and O(6)B1), and the site occupancies of O(6)A1 and O(6)B1 were determined to be 0.32 and 0.68 for **1** and 0.46 and 0.54 for **2**, respectively, by the constrained refinement of these factors. Carbon and nitrogen atoms of SCN⁻ could not be located in an electron density map because they were highly disordered. The structures were refined to $R = 0.16$ for **1** and $R = 0.15$ for **2** by full-matrix least-squares methods,[15] using isotropic temperature factors for all atoms. These R values are pretty high because of insufficient data at high angles in 2θ. The quantity minimized was $\sum\omega(|F_o| - |F_c|)^2$ with $\omega = 1.0/(\sigma^2(F_o) + 0.015F_o^2)$. Final atomic coordinates and temperature factors are given in Table I.

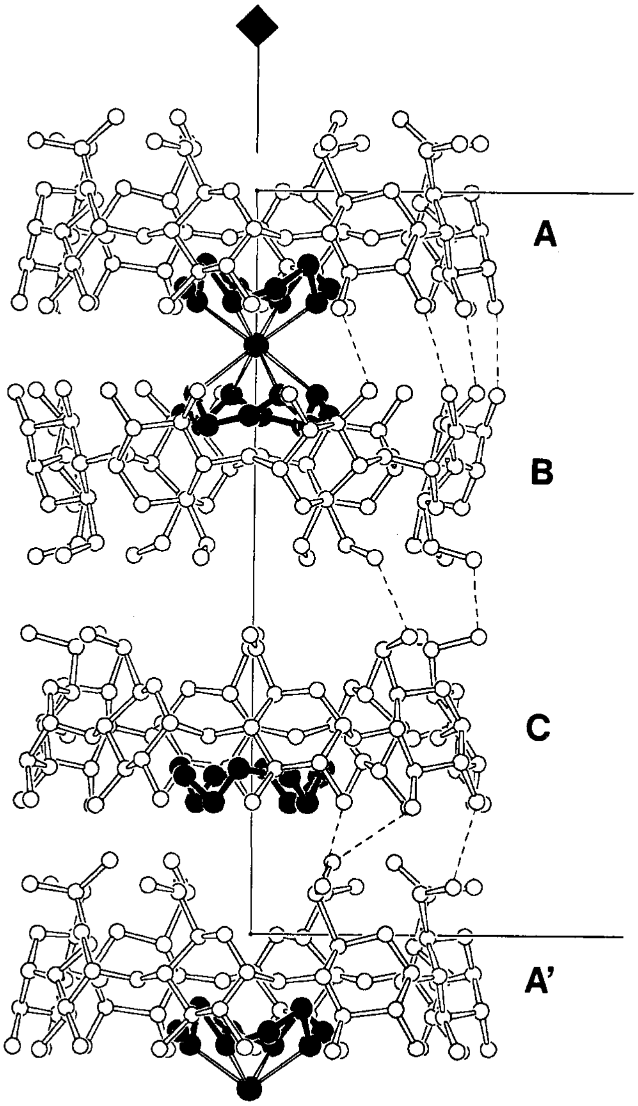

Figure 1. The channel-type structure of γ-CD·12-crown-4·LiSCN (3:3:1) inclusion complex. Li^+ and 12-crown-4 molecules are shown by full circles. Only symmetry independent intermolecular hydrogen bonds are indicated by dotted lines, and water molecules and SCN⁻ are not drawn for clarity.

Atomic Absorption Analysis for Identification of Cations of 1. It is likely that Li^+ is replaced in part by Na^+, because the isotropic temperature factor of Li^+ (4 (3) Å²) is small compared to those of the oxygen atoms coordinating to Li^+. The presence of Na^+ in **1** was checked by atomic absorption analysis. The precipitated crystals in the batch which gave crystals used in diffraction experiment were separated off by filtration, washed by water, and kept in a desiccator for 1 day. The precipitate (40 mg) was heated for 90 min with 4 mL of HNO_3 (61%) in a kjeldahl flask. The resultant residue was dissolved into 5 mL of water. The mole fractions of Na^+ in this solution were determined to be 0.019 by the atomic absorption analysis. It is concluded that only 1.9% of Li^+ is replaced by Na^+ and the structure of **1** can be regarded as the Li^+ complex.

Results and Discussion

1. The Crystal Structure of the γ-CD·12-crown-4·LiSCN Inclusion Complex 1. Three γ-CD molecules are stacked along the c axis forming the channel-type structure, and 12-crown-4 molecules are included in 1:1 stoichiometry in γ-CD at the secondary sides of the hosts, as shown in Figure 1.[16] Host and guest

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Table I. Fractional Coordinates and Temperature Factors with Estimated Standard Deviations for **1** and **2**

		(1)					(2)		
ATOM	X	Y	Z	8	ATOM	X	Y	Z	8
C(1) 1	0.672(2)	0.244(2)	0.946(2)	4.(1)	C(1) 1	0.671(3)	0.241(3)	0.954(3)	5.(2)
C(2) 1	0.705(1)	0.228(1)	0.899(1)	1.7(7)	C(2) 1	0.708(2)	0.227(2)	0.900(2)	3.(1)
C(3) 1	0.710(2)	0.165(2)	0.890(2)	1.8(8)	C(3) 1	0.711(2)	0.163(2)	0.895(3)	3.(1)
C(4) 1	0.732(2)	0.136(2)	0.948(2)	1.8(8)	C(4) 1	0.733(2)	0.141(2)	0.944(3)	4.(1)
C(5) 1	0.689(2)	0.149(2)	0.994(2)	3.(1)	C(5) 1	0.688(2)	0.151(2)	0.996(3)	3.(1)
C(6) 1	0.707(2)	0.123(2)	1.056(2)	4.(1)	C(6) 1	0.711(3)	0.127(3)	1.051(3)	7.(2)
O(2) 1	0.680(1)	0.252(1)	0.850(1)	2.3(6)	O(2) 1	0.683(2)	0.249(2)	0.851(2)	5.(1)
O(3) 1	0.752(1)	0.154(1)	0.843(1)	1.7(5)	O(3) 1	0.750(2)	0.154(1)	0.845(2)	3.6(9)
O(4) 1	0.734(1)	0.077(1)	0.938(1)	1.7(5)	O(4) 1	0.735(2)	0.079(1)	0.937(2)	3.3(9)
O(5) 1	0.687(1)	0.211(1)	1.001(1)	2.3(5)	O(5) 1	0.688(1)	0.210(1)	1.001(2)	3.5(8)
O(6)A1	0.668(4)	0.141(4)	1.099(4)	5.(2)	O(6)A1	0.666(4)	0.136(4)	1.097(4)	7.(3)
O(6)B1	0.770(2)	0.142(2)	1.065(2)	3.(1)	O(6)81	0.769(3)	0.139(3)	1.064(3)	3.(2)
C(1) 2	0.451(2)	0.284(2)	0.950(2)	1.8(8)	C(1) 2	0.445(2)	0.288(3)	0.950(3)	5.(2)
C(2) 2	0.484(2)	0.306(2)	0.898(2)	2.4(9)	C(2) 2	0.485(3)	0.301(3)	0.900(3)	6.(2)
C(3) 2	0.534(2)	0.263(2)	0.890(2)	3.(1)	C(3) 2	0.535(2)	0.260(2)	0.891(2)	3.(1)
C(4) 2	0.569(2)	0.258(2)	0.943(2)	4.(1)	C(4) 2	0.571(3)	0.262(3)	0.951(3)	5.(2)
C(5) 2	0.528(2)	0.243(2)	0.996(2)	2.7(9)	C(5) 2	0.529(2)	0.240(2)	0.996(3)	4.(1)
C(6) 2	0.557(2)	0.243(2)	1.056(2)	4.(1)	C(6) 2	0.559(3)	0.236(3)	1.055(3)	6.(2)
O(2) 2	0.451(1)	0.305(1)	0.846(1)	2.9(6)	O(2) 2	0.448(2)	0.305(2)	0.844(2)	5.(1)
O(3) 2	0.569(1)	0.287(1)	0.845(1)	3.2(6)	O(3) 2	0.571(2)	0.285(2)	0.847(2)	5.(1)
O(4) 2	0.612(1)	0.221(1)	0.937(1)	1.6(5)	O(4) 2	0.612(1)	0.221(1)	0.942(2)	3.2(9)
O(5) 2	0.482(1)	0.280(1)	1.000(1)	2.6(6)	O(5) 2	0.482(2)	0.281(2)	1.000(2)	4.8(9)
O(6) 2	0.590(2)	0.286(2)	1.068(2)	9.(1)	O(6) 2	0.591(3)	0.287(3)	1.065(3)	11.(2)
C(1) 3	0.640(2)	0.260(2)	0.623(2)	2.4(8)	C(1) 3	0.644(3)	0.259(3)	0.629(3)	5.(1)
C(2) 3	0.610(2)	0.287(2)	0.673(2)	2.9(9)	C(2) 3	0.613(2)	0.284(2)	0.678(3)	3.(1)
C(3) 3	0.554(1)	0.267(1)	0.687(1)	1.1(7)	C(3) 3	0.554(2)	0.262(2)	0.689(2)	3.(1)
C(4) 3	0.517(2)	0.273(2)	0.633(2)	2.9(9)	C(4) 3	0.522(2)	0.269(2)	0.630(2)	3.(1)
C(5) 3	0.547(1)	0.237(1)	0.581(2)	1.3(8)	C(5) 3	0.551(2)	0.232(2)	0.585(2)	2.(1)
C(6) 3	0.516(2)	0.242(2)	0.524(2)	4.(1)	C(6) 3	0.524(3)	0.232(3)	0.523(3)	6.(2)
O(2) 3	0.646(1)	0.284(1)	0.727(1)	2.1(6)	O(2) 3	0.646(2)	0.277(2)	0.730(2)	6.(1)
O(3) 3	0.525(1)	0.297(1)	0.732(1)	3.4(6)	O(3) 3	0.525(2)	0.293(2)	0.731(2)	5.(1)
O(4) 3	0.4633(9)	0.246(1)	0.642(1)	1.6(5)	O(4) 3	0.462(1)	0.246(1)	0.641(1)	2.5(8)
O(5) 3	0.605(1)	0.259(1)	0.576(1)	1.8(5)	O(5) 3	0.606(2)	0.261(2)	0.579(2)	4.(1)
O(6) 3	0.514(1)	0.296(1)	0.505(1)	3.7(6)	O(6) 3	0.521(2)	0.291(2)	0.508(2)	10.(1)
C(1) 4	0.780(2)	0.082(2)	0.623(2)	2.9(9)	C(1) 4	0.777(3)	0.087(3)	0.622(3)	6.(2)
C(2) 4	0.780(2)	0.124(2)	0.676(2)	2.0(8)	C(2) 4	0.781(3)	0.130(3)	0.680(3)	6.(2)
C(3) 4	0.717(2)	0.148(2)	0.686(2)	1.9(8)	C(3) 4	0.716(3)	0.148(3)	0.687(3)	4.(1)
C(4) 4	0.701(2)	0.177(2)	0.626(2)	4.(1)	C(4) 4	0.706(2)	0.176(2)	0.628(2)	3.(1)
C(5) 4	0.696(2)	0.131(2)	0.583(2)	2.0(8)	C(5) 4	0.703(2)	0.137(2)	0.583(3)	3.(1)
C(6) 4	0.681(2)	0.152(2)	0.525(2)	3.1(9)	C(6) 4	0.685(3)	0.156(3)	0.519(3)	6.(2)
O(2) 4	0.803(1)	0.096(1)	0.727(1)	3.7(7)	O(2) 4	0.799(2)	0.095(2)	0.727(2)	5.(1)
O(3) 4	0.722(1)	0.191(1)	0.730(1)	1.9(5)	O(3) 4	0.720(2)	0.189(2)	0.732(2)	4.2(9)
O(4) 4	0.6467(8)	0.1960(9)	0.6426(9)	1.7(5)	O(4) 4	0.648(1)	0.196(1)	0.642(2)	3.3(9)
O(5) 4	0.754(1)	0.107(1)	0.576(1)	2.2(5)	O(5) 4	0.756(2)	0.110(2)	0.578(2)	3.2(9)
O(6) 4	0.717(1)	0.199(1)	0.507(1)	4.9(7)	O(6) 4	0.720(2)	0.197(2)	0.508(2)	8.(1)
C(1) 5	0.737(2)	0.163(2)	0.286(2)	1.9(8)	C(1) 5	0.742(3)	0.162(3)	0.283(3)	4.(2)
C(2) 5	0.774(2)	0.140(2)	0.236(2)	1.8(8)	C(2) 5	0.775(3)	0.136(3)	0.235(3)	5.(2)
C(3) 5	0.753(2)	0.078(2)	0.223(2)	2.4(9)	C(3) 5	0.753(3)	0.078(3)	0.222(3)	4.(1)
C(4) 5	0.762(1)	0.047(1)	0.279(1)	1.8(7)	C(4) 5	0.765(3)	0.046(3)	0.276(3)	5.(2)
C(5) 5	0.730(2)	0.070(2)	0.326(2)	3.(1)	C(5) 5	0.729(3)	0.070(3)	0.326(3)	6.(2)
C(6) 5	0.731(3)	0.049(3)	0.393(3)	7.(2)	C(6) 5	0.726(3)	0.042(3)	0.387(3)	7.(2)
O(2) 5	0.763(1)	0.172(1)	0.181(1)	2.7(6)	O(2) 5	0.765(2)	0.168(2)	0.181(2)	4.(1)
O(3) 5	0.797(1)	0.058(1)	0.180(1)	3.6(7)	O(3) 5	0.792(2)	0.053(2)	0.178(2)	7.(1)
O(4) 5	0.749(1)	-0.010(1)	0.270(1)	2.6(5)	O(4) 5	0.748(2)	-0.016(1)	0.269(1)	3.6(8)
O(5) 5	0.747(1)	0.132(1)	0.332(1)	2.6(6)	O(5) 5	0.747(2)	0.128(2)	0.328(2)	6.(1)
O(6) 5	0.793(1)	0.050(1)	0.406(2)	5.4(8)	O(6) 5	0.788(3)	0.047(2)	0.398(3)	10.(2)
C(1) 6	0.556(2)	0.288(2)	0.287(2)	2.0(8)	C(1) 6	0.562(2)	0.288(2)	0.285(3)	3.(1)
C(2) 6	0.596(2)	0.297(2)	0.239(2)	2.5(9)	C(2) 6	0.594(3)	0.292(2)	0.231(3)	4.(1)
C(3) 6	0.623(2)	0.237(2)	0.226(2)	3.1(9)	C(3) 6	0.632(3)	0.233(3)	0.215(3)	6.(2)
C(4) 6	0.656(2)	0.223(2)	0.278(2)	1.7(8)	C(4) 6	0.661(2)	0.217(2)	0.282(3)	4.(1)
C(5) 6	0.608(2)	0.212(2)	0.330(2)	2.1(8)	C(5) 6	0.613(2)	0.213(3)	0.323(3)	4.(1)
C(6) 6	0.634(2)	0.200(2)	0.387(2)	3.(1)	C(6) 6	0.641(2)	0.195(2)	0.384(2)	4.(1)
O(2) 6	0.563(1)	0.312(1)	0.184(1)	3.0(6)	O(2) 6	0.567(2)	0.307(2)	0.181(2)	5.(1)
O(3) 6	0.663(1)	0.244(1)	0.174(1)	2.2(6)	O(3) 6	0.666(2)	0.240(2)	0.171(2)	4.(1)
O(4) 6	0.681(1)	0.165(1)	0.268(1)	2.2(5)	O(4) 6	0.687(2)	0.165(2)	0.265(2)	5.(1)
O(5) 6	0.581(1)	0.267(1)	0.336(1)	2.9(6)	O(5) 6	0.586(2)	0.266(2)	0.334(2)	4.0(9)
O(6) 6	0.673(1)	0.242(1)	0.404(1)	3.1(6)	O(6) 6	0.680(2)	0.235(2)	0.403(2)	5.(1)
O(1) A	0.508(2)	0.083(2)	0.846(2)	9.(1)	O(1) A	0.527(4)	0.086(3)	0.875(3)	15.(3)
C(1) A	0.557(3)	0.083(3)	0.885(3)	9.(2)	C(1) A	0.562(5)	0.085(5)	0.923(5)	15.(4)
C(2) A	0.589(3)	0.043(3)	0.867(3)	9.(2)	C(2) A	0.592(5)	0.029(6)	0.895(5)	13.(4)
O(1) 8	0.577(2)	0.046(3)	0.724(2)	10.(2)	O(1) 8	0.583(3)	0.051(3)	0.715(3)	12.(2)
C(1) 8	0.550(4)	0.084(4)	0.671(4)	12.(3)	C(1) 8	0.556(6)	0.082(6)	0.685(5)	13.(4)
C(2) 8	0.489(4)	0.104(4)	0.691(3)	12.(2)	C(2) 8	0.498(4)	0.095(6)	0.670(4)	15.(3)
O(1) C	0.532(5)	0.081(4)	0.201(3)	18.(4)	O(1) C	0.528(4)	0.086(4)	0.188(4)	17.(3)
C(1) C	0.579(4)	0.051(4)	0.231(4)	15.(3)	C(1) C	0.582(4)	0.064(4)	0.202(3)	8.(2)
C(2) C	0.590(4)	-0.006(5)	0.258(4)	14.(3)	C(2) C	0.589(6)	-0.001(8)	0.232(6)	21.(5)
LI(1)	0.50000	0.00000	0.784(5)	4.(3)	K(1)	0.50000	0.00000	0.796(2)	14.(2)
S(1)	0.105(3)	0.161(4)	0.555(4)	7.(2)	CL(1)	0.114(5)	0.171(5)	0.544(5)	7.(3)
OW1	0.809(3)	0.156(3)	0.461(3)	17.(2)	OW1	0.586(4)	0.408(4)	0.851(4)	19.(3)
OW2	0.414(2)	0.417(2)	0.169(2)	12.(1)	OW2	0.921(3)	0.081(3)	0.170(3)	14.(2)
OW3	0.077(3)	0.085(3)	0.182(3)	17.(2)	OW3	0.540(3)	0.422(3)	0.709(3)	16.(3)
OW4	0.562(2)	0.419(2)	0.383(2)	13.(2)	OW4	0.566(2)	0.411(3)	0.592(2)	11.(2)
OW5	0.540(4)	0.405(4)	0.057(3)	22.(3)	OW5	0.798(4)	0.156(4)	0.472(5)	25.(4)
OW6	0.117(3)	0.172(3)	0.543(3)	12.(2)	OW6	0.586(3)	0.028(3)	0.054(3)	15.(2)
					OW7	0.126(9)	0.178(9)	0.53(1)	24.(9)

The site occupancy of L1(1) is 0.25, S(1) 0.25, and OW6 0.75.

The site occupancy of K(1) is 0.25, CL(1) 0.25, and OW7 0.75.

molecules are centered on the four-fold crystallographic rotation axis so that three-quarters of the γ-CD molecules are in the asymmetric unit. The γ-CD A (the γ-CD molecule in the complex A) and the γ-CD B, B and C, and C and A′ are in the tail-to-tail, the head-to-head, and the tail-to-head orientation, respectively. Therefore, γ-CDs A and C point in the same direction, while B points in the opposite direction. Hydrogen bonds are formed between O(2,3) (secondary hydroxyl groups (see Figure 3)) of

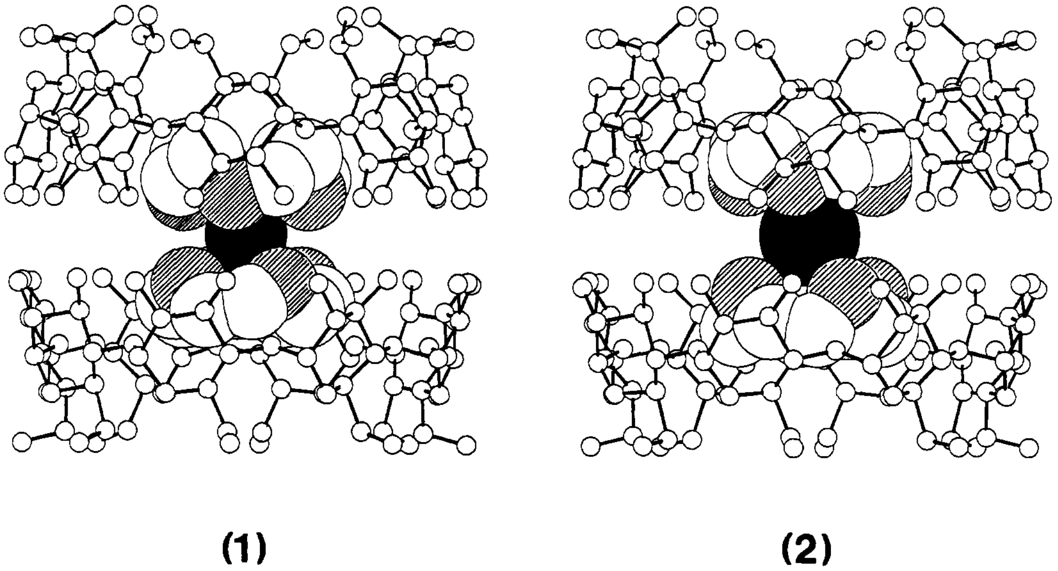

Figure 2. The structures of γ-CD·12-crown-4·Li$^+$ (left) and γ-CD·12-crown-4·K$^+$ (right) (2:2:1) inclusion complexes. Cations and 12-crown-4 molecules are plotted in the space filling mode, indicated by full and hatched circles, respectively.

Table II. Geometrical Data

complex	H-bond distance (Å) 1	H-bond distance (Å) 2	distance (Å) 1	distance (Å) 2	tilt angle (deg) 1	tilt angle (deg) 2
A G1	2.76	2.80	4.48	4.49	9.6	11.1
G2	2.79	2.76	4.50	4.55	12.0	13.8
B G3	2.86	2.76	4.51	4.59	16.1	13.7
G4	2.87	2.87	4.56	4.44	20.8	19.7
C G5	2.92	2.93	4.45	4.55	17.7	16.2
G6	2.89	2.79	4.53	4.52	16.1	17.9

[a] The H-bond distance is defined as the O(3)*n*–O(2)*n*+1 distance. [b] The distance is defined as the O(4)*n*–O(4)*n*+1 distance. [c] The tilt angle is defined as the angle made by O(4) atoms plane and the plane formed by the O(4)*n*+1,C(1)*n*,C(4)*n*,O(4)*n* of each glucose residue.

the γ-CD A and O(2,3) of the γ-CD B, O(6) (primary hydroxyl groups) of B and O(6) of C, O(2,3) of C and O(6) of A′, giving a column of γ-CDs connected by these intermolecular hydrogen bonds; the hydrogen bond distance of O(2)1–O(2)3 is 3.03, O(3)1–O(3)4 is 2.86, O(2)2–O(2)4 is 2.97, O(3)2–O(3)3 is 2.79, O(6)3–O(6)5 is 2.82, O(6)4–O(6)6 is 2.77, O(2)5–O(6)B1 is 2.75, O(2)6–O(6)2 is 2.80, and O(3)6–O(6)A1 is 2.99 Å. In this channel, there are two possible positions at which cations coordinate to 12-crown-4 molecules; one is between the complexes A and B where a cation coordinates to two 12-crown-4 molecules and another is between the complexes C and A′ where a cation coordinates to only the 12-crown-4 molecule of the complex C. However, in fact, only the first position is occupied by a Li$^+$. The Li$^+$ coordinates to eight oxygen atoms of two 12-crown-4 molecules of the complexes A and B to form a 1:2 sandwich complex, while in the complex C there is a free 12-crown-4 molecule. This (12-crown-4)$_2$·Li$^+$ complex is included in the hydrophobic region formed by γ-CDs A and B in the tail-to-tail orientation, so Li$^+$, 12-crown-4, and γ-CD molecules form the inclusion complex by a 1:2:2 ratio, as is shown in Figure 2.[17] The counteranion is not in the hydrophobic channel but in the space between the columns of γ-CDs. The shortest distance between a Li$^+$ and a SCN$^-$ is 11.8 Å, showing very weak electrostatic interaction between a cation and a counteranion.

The conformation of the complex A is shown in Figure 3, and the geometrical data of γ-CDs are given in Table II. In the macrocyclic structures of the three γ-CDs, all glucose residues display $^4C_1$ chair conformations. The secondary hydroxyl groups between neighboring glucose residues form intramolecular hydrogen bonds, which may maintain the round shape of the γ-CD ring; O(2)*n*–O(3)*n*+1 hydrogen bond distances are in the range 2.76–2.92 Å. The eight glycosidic O(4) oxygen atoms are coplanar within 0.01, 0.01, and 0.02 Å for γ-CDs A, B, and C, and the average contact distances of O(4)*n*–O(4)*n*+1 in each complex are 4.49, 4.53, and 4.49 Å, which agree with the corresponding average value of 4.50 Å in **3**. The glucose residues are inclined to the fourfold rotation axis so as to make the primary hydroxyl group side narrow and the secondary hydroxyl group side wide. The tilt angles of glucose residues are defined as the angles made by the O(4) atoms plane and the plane formed by O(4)*n*+1,C(1)*n*,C(4)*n*,O(4)*n* of each glucose.[18] The average tilt angles are 10.7, 18.4, and 16.9° for A, B, and C, respectively. In the previous X-ray study of the γ-CD·12-crown-4 inclusion complex **3** in which all γ-CDs include free 12-crown-4 molecules, the differences of tilt angles among three γ-CDs (12.2, 17.5, and 16.1° for A, B,

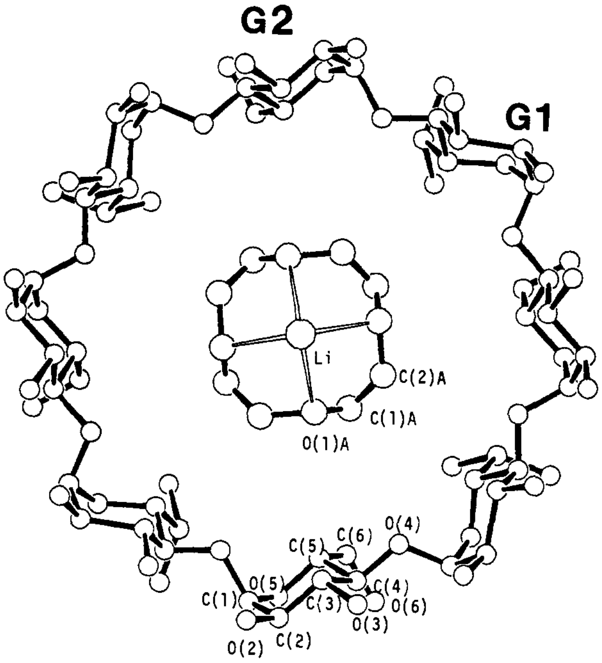

Figure 3. The structure of complex A of **1** with C_4 symmetry.

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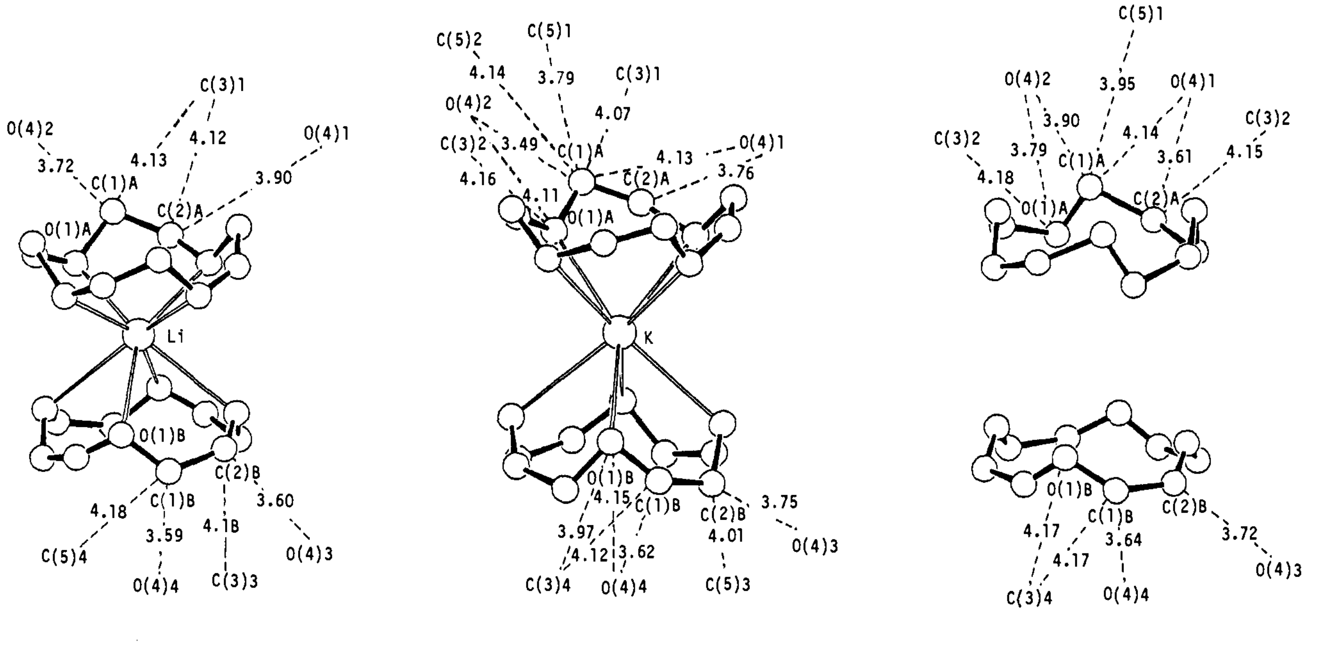

(1) **(2)** **(3)**

Figure 4. The structures of (12-crown-4)$_2$·cation complexes and the corresponding 12-crown-4 molecules of **3**. Intermolecular contacts with γ-CDs (less than 4.2 Å) are shown by dotted lines.

and C) are closely related to the locations of guest molecules (12-crown-4) in the hydrophobic cavities of γ-CDs. The 12-crown-4 molecule most deeply enters the cavity of the γ-CD A, where the γ-CD has the smallest tilt angle and an almost cylindrical structure because the intermolecular hydrogen bonds between the γ-CDs A and C make the ring of the γ-CD A wider at the primary side; on the other hand, in the complex B and C, the guest molecules are shallowly included because of the more inclined cone-structure of the γ-CD macrocycles. However, in **1**, the existence of Li$^+$ modifies this tendency of tilt angles and the locations of guest molecules, as described later.

The structure of the (12-crown-4)$_2$·Li$^+$ complex in the hydrophobic cavities of γ-CD molecules is quite interesting. The Li$^+$ has the rare coordination number of 8, and this complex has a configuration with approximate D_4 symmetry. The Li$^+$–O bond distances at the sites of the complexes A and B are 2.45 (8) and 2.54 (8) Å, respectively. In terms of esd's, these bond distances are almost the same. The average value (2.51 Å) of these bond distances is longer than that of the 12-crown-4·LiSCN 1:1 complex where Li$^+$ has a coordination number of 5; the Li$^+$–O average bond distance is 2.08 Å.[12] The coordination number 8 was found in [Li(12-crown-4)$_2$][AsPh$_2$]·THF and [Li(12-crown-4)$_2$][PPh$_2$][19] where the Li–O average bond distance is 2.35 Å which is also shorter than that of **1**.

The conformation of the (12-crown-4)$_2$·Li$^+$ complex and the main short contacts between the γ-CD molecules and the (12-crown-4)$_2$·Li$^+$ complex are shown in Figure 4. There are fewer short contacts than in **3** because the electrostatic interaction between Li$^+$ and the oxygen atoms of 12-crown-4 molecules draws the two 12-crown-4 molecules closer to each other while the two enclosing γ-CDs are prevented from approaching each other by the intermolecular hydrogen bonds between secondary hydroxyl groups. The interplanar distances between the four O(1)A atoms plane (four oxygen atoms of the 12-crown-4 molecule of complex A) and the eight O(4) atoms plane of γ-CD A, and the four O(1)B atoms plane and the eight O(4) atoms plane of γ-CD B are 2.09 and 1.86 Å, respectively, which are larger in comparison with 1.25 and 1.64 Å in **3**, showing that the 12-crown-4 molecules of the complexes A and B in **1** are less deeply included in the γ-CD cavities than those of **3**. The 12-crown-4 molecules are located on the positions where the electrostatic interaction between Li$^+$ and 12-crown-4 molecules and van der Waals interaction between 12-crown-4 molecules and γ-CD molecules are balanced. This explains the long distances of Li$^+$–O in **1**.

Because of unusually long distances of Li$^+$–O, this inclusion complex might be geometrically unfavorable in comparison with the inclusion complexes of other cations, especially larger ones. It would be expected that in the inclusion complex with K$^+$ cation, 12-crown-4 molecules are included in the γ-CD cavities more deeply than in the inclusion complex with Li$^+$ to give larger van der Waals stabilization between 12-crown-4 molecules and γ-CD molecules. The cavity diameter of the 12-crown-4 molecule (1.2 Å) is too small to fit K$^+$ with a cation diameter of 2.66 Å,[20] and the affinity of K$^+$ for 12-crown-4 is less than that of Li$^+$. But in the presence of γ-CD, the interaction among γ-CDs, 12-crown-4 molecules, and cations might effect the different affinity of 12-crown-4 molecules to cations.

2. The Crystal Structure of the γ-CD·12-crown-4·KCl Inclusion Complex 2. The crystal structure of **2** is isomorphous with that of **1**. The relative orientation and geometrical data of three γ-CD molecules almost agree with those of **1**, as is listed in Table II. Two γ-CDs A and B in tail-to-tail orientation include the (12-crown-4)$_2$·K$^+$ sandwich structure complex where the K$^+$ also coordinates to eight oxygen atoms of two 12-crown-4 molecules, as shown in Figure 2, and the γ-CD C only includes a free 12-crown-4 molecule, as in **1**.

The conformation of the (12-crown-4)$_2$·K$^+$ complex and its main short contacts with the γ-CDs are shown in Figure 4. As expected from the larger cation diameter of K$^+$, 12-crown-4 molecules of the complexes A and B are more deeply included in the cavities of the γ-CD molecules and there exist more short contacts between 12-crown-4 molecules and γ-CDs than in **1**. The interplaner distances between the four O(1) atoms planes of 12-crown-4 molecules and the eight O(4) atoms planes of the γ-CD molecules

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are 1.50 and 1.69 Å at the sites of the complexes A and B, respectively. Although these values are intermediate between those of **1** and **3**, they are closer to those of **3**, indicating that the van der Waals interaction between 12-crown-4 molecules and γ-CDs of **2** is comparable to that of **3**.

The bond distances of K$^+$–O are 2.80 (8) and 2.99 (9) Å at the sites of the complexes A and B, respectively. The average value of these bond distances is almost normal compared with the K$^+$–O distances of 2.77–2.83 Å in the (18-crown-6)·KSCN complexes.[21]

The (12-crown-4)$_2$·cation complex in **2** has an approximate S_8 symmetry, while that in **1** has an approximate D_4 symmetry. In **2**, the chirality of the 12-crown-4 ring in the complex A is opposite to that in the complex B in spite of the same chirality of the two γ-CDs. Since the γ-CD A is in a near cylindrical form and γ-CD B has a more cone-like structure in both **1** and **2**, van der Waals interactions between the 12-crown-4 molecules and the γ-CDs in the complexes A and B differ. In **2**, where the 12-crown-4 molecule of the complex B is deeply included in the cavity of the γ-CD B because of the large diameter of K$^+$, the closer contacts between the 12-crown-4 molecule and the γ-CD B may be the reason why the chirality of the 12-crown-4 molecules of the complex B is inverted with respect to that in **1**.

Conclusion

It is confirmed by this X-ray study that cations can exist in hydrophobic environment by forming the inclusion complexes between the crown ethers·cation complexes and γ-CDs.

The interactions between 12-crown-4 molecules and γ-CDs affect the cation–oxygen distances of the 12-crown-4·cation complexes and the chirality of 12-crown-4 molecules. Thus, each 12-crown-4 molecule suffers from particular constraints depending on the geometry of γ-CD which includes it. This is reflected in the location and the orientation of the guest molecule in the cavity and also influences the structures of 12-crown-4·cation complexes.

These inclusion complexes might be able to exhibit ion selectivity because of the complicated interaction among cations, crown ethers, and CDs. Since in **1** unusually long distances of Li$^+$–O and few short contacts between 12-crown-4 and γ-CD molecules are found, while in **2** normal K$^+$–O distances and many short contacts to γ-CDs are found, we assume that the former would be less stable than the latter. The present X-ray results suggest that the cation diameter of K$^+$ is just small enough that complexes with 12-crown-4 fit into the cavities of γ-CD.

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Supplementary Material Available: Tables of complete bond distances and bond angles for **1** and **2** (8 pages); listing of observed and calculated structure factor amplitudes (4 pages). Ordering information is given on any current masthead page.

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Elimination Reactions of Alkanesulfinyl Derivatives: Mechanism and Reactivity in Base-Induced Sulfine Formation from Methyl Diarylmethanesulfinates

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Abstract: Upon treatment in methanol at room temperature with methoxide ion methyl diarylmethanesulfinates, ArAr'CHS(O)OCH$_3$ (**1**), and methyl 9-fluorenesulfinate (**2**) undergo elimination readily to afford the corresponding sulfines (**3** and **4**) in quantitative yield. Studies in CD$_3$O$^-$/CD$_3$OD show that, surprisingly, elimination of **1** to give **3** is significantly faster than nucleophilic substitution by methoxide ion at the sulfinyl group (exchange of CH$_3$O by CD$_3$O). Even more unexpected, the kinetic isotope effect for elimination of **2-9-*d*** (k_H/k_D = 6.1) and the absence of detectable H/D exchange of the methine proton of **1** in CD$_3$OD prior to sulfine formation establish that, even though the leaving group is MeO$^-$, the elimination takes place by either an irreversible ElcB or an E2 mechanism, rather than the reversible ElcB mechanism found (ref 4 and 7) for the analogous sulfene-forming elimination of arylmethanesulfonate esters with oxyanion leaving groups of comparable pK_a. Reaction of amines with **2** in methanol also gives sulfine **4**, and the amine-induced elimination, which has a large Brønsted β, also proceeds by either an (ElcB)$_{irrev}$ or an ElcB-like E2 mechanism. Why sulfine-forming eliminations of **1** and **2** favor an (ElcB)$_{irrev}$ or E2 mechanism whereas sulfene-forming eliminations of arylmethanesulfonates with even better leaving groups proceed by an (E1cB)$_{rev}$ mechanism is considered and a possible explanation presented.

Base-induced eliminations of sulfinyl compounds leading to the formation of sulfines (B$^-$ + >CHS(O)Y → BH + >C=S=O + Y$^-$) have been known since 1964.[2,3] For analogous *sulfene*-forming eliminations of alkanesulfonyl derivatives (B$^-$ + >CHS(O)$_2$Y → BH + >C=SO$_2$ + Y$^-$), considerable information is available,[4-8] regarding the effect of various parameters (nature of B$^-$, Y, and structure of the alkanesulfonyl group) on rate of elimination, competition between elimination and substitution at

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