

# Complexing Properties of 3',5'-Disubstituted-4'-Hydroxybenzyl Armed Monoaza-12-Crown-4 and Armed Monoaza-15-Crown-5 Ethers and Crystal Structures of the Alkali Metal Ion Complexes

Yoichi Habata\*[a], Sadatoshi Akabori [a], Xian Xin Zhang [b],  
Reed M. Izatt [b] and Jerald S. Bradshaw [b]

[a] Department of Chemistry, Faculty of Science, Toho University, Funabashi, Chiba 274-8510, Japan

[b] Department of Chemistry and Biochemistry, Brigham Young University, Provo, UT 84602, USA

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## Dedicated to Professor Jerald S. Bradshaw

A series of monoaza-15-crown-5 ethers (**2b-2h**) having 4'-hydroxy-3',5'-disubstituted benzyl groups have been prepared by the Mannich reaction of 2,6-disubstituted phenols with the corresponding *N*-methoxymethylmonoaza-crown ethers. Competitive transport through a chloroform membrane by 12-crown-4 derivatives (lithium, potassium and cesium) and 15-crown-5 derivatives (sodium, potassium and cesium) were measured under basic-source phase and acidic-receiving phase conditions. All ligands transported size-matched alkali-metal cations. Ligands **1h** and **2h** with two fluorine atoms in the side arm gave higher metal ion transport rates than those of dimethyl- (**1a** and **2a**), diisopropyl- (**1b** and **2b**), and butylmethyl- (**1d** and **2d**) derivatives. X-ray crystal structures of six alkali metal complexes with monoaza-12-crown-4-derivatives (**1b-LiSCN**, **1b-KSCN**, **1c-NaSCN**, **1d-LiSCN**, **1f-RbSCN** and **1h-LiSCN**) and three alkali metal complexes with 15-crown-5 derivatives (**2b-KSCN**, **2c-KSCN**, and **2e-KSCN**) along with crystal structures of some new ligands (**1b**, **1c**, **1d**, **1f**, and **2c**) are also reported. These X-ray analyses indicate that the crystal structures of the alkali metal ion complexes of these new armed-crown ethers changed depending on the substituents at the 3'- and 5'-positions of the appended hydroxybenzyl arms.

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Since the pioneering work by C. J. Pedersen [1], many crown ethers and analogues of crown ethers have been reported as ion specific ligands. To develop crown ethers having higher ion selectivities, new types of crown ethers containing functional side arms (the so called armed- or lariat crown ethers) have been prepared. These armed crown ethers can bind guest-cations selectively using both the crown ether ring and the additional binding sites of the side arms to give higher metal ion affinities and selectivities than crown ethers without the arms [2]. On the other hand, some research groups have reported that certain armed crown ethers form polymer-like complexes assemblies [3-7]. In those complexes, the side arms cause intermolecular interactions and the units are repeated. Often the ionic polymer matrix can incorporate other charged or neutral guests resulting in new properties for the crown ether system.

In order to develop new armed-crown ethers capable of forming polymer-like complexes with metal cations, we have reported the syntheses and reaction mechanisms to form new armed azacrown ethers by the Mannich reaction as well as the side reaction products and X-ray structures of their alkali metal complexes [8-14]. In those systems, small structural changes of the substituents next to the OH group of the hydroxybenzyl-side arm greatly influenced the structures of the complexes. In order to further investigate the steric and/or electronic effects of substituents next to the hydroxybenzyl OH group, a series

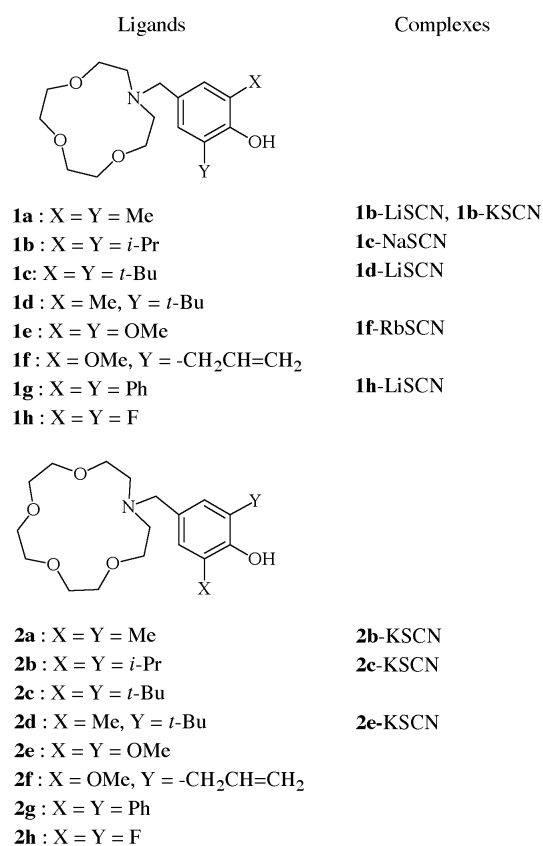


Figure 1

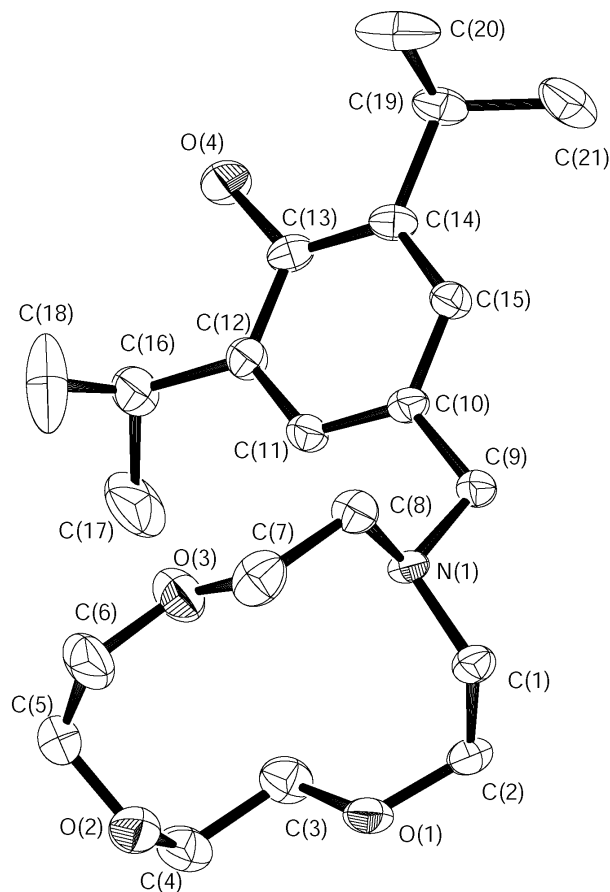


Figure 2. The ORTEP view of **1b** (hydrogen atoms omitted).

of monoazacrown ethers containing the hydroxybenzyl group with various substituents at the 3'- and 5'-positions were prepared. In this paper, we report the preparation of these armed-monoaza-15-crown-5 ethers (**2b–2h**), transport properties for alkali metal cations by monoaza-12-crown-4 derivatives (**1b–1h**) [9] and **2b–2h**, and nine X-ray crystal structures of alkali metal complexes with **1b**, **1c**, **1f**, **1h**, **2b**, **2c** and **2e**.

New armed monoaza-15-crown-5-ethers **2a–2h** (Figure 1) were prepared by Mannic aminomethylation as previously described for ligands **1a–1h** [9]. Structures of all new compounds were confirmed by  $^1\text{H}$  nmr, ei-ms and elemental analyses. Structures of some ligands, which were obtained as single crystals (**1b**, **1c**, **1d**, **1f**, and **2c**), were determined by X-ray crystallography (Table 1). Figure 2 shows the ORTEP view of ligand **1b**. One of the substituents at position 3' or 5' of the side arm is located on the top of the crown ether ring to provide for a more compact pack. A similar conformation of the side arm was observed in the structures of ligands **1c**, **1f**, **1h**, and **2c**.

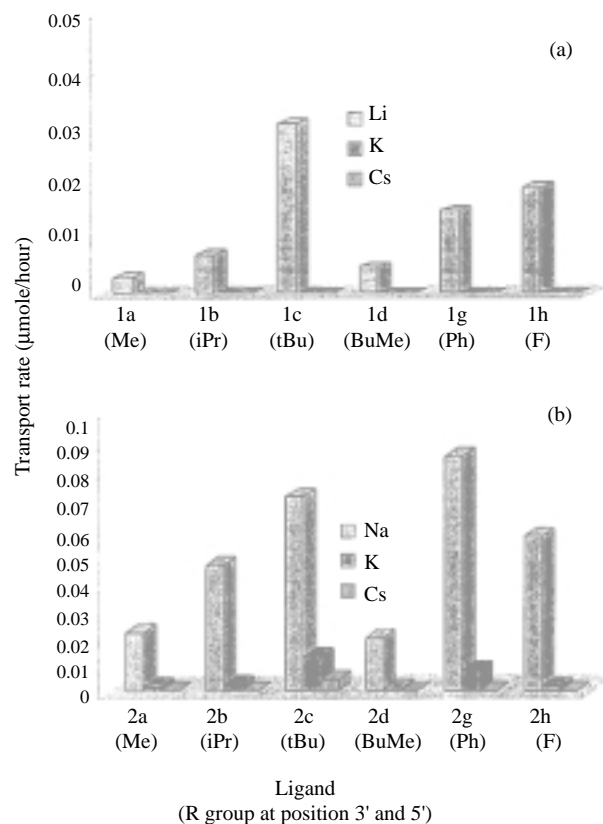


Figure 3. Competitive transport of alkali metal cations with **1a–1d**, **1g** and **1h** (a) and **2a–2d**, **2g** and **2h** (b).

Log  $K$ ,  $\Delta H$ , and  $\Delta S$  values for the interaction of some ligands (**2a**, **2b**, and **2h**) with sodium and potassium ions were measured by titration calorimetry in methanol. As shown in Table 2, ligands **2a** and **2b** form more stable complexes with potassium than with sodium while log  $K$  values for **2h** interactions with sodium and potassium ions are equal within experimental uncertainty. The cavity dimensions of monoaza-15-crown-5 are close to the ionic diameter of sodium. We have already reported that **2h** forms polymer-like complexes with sodium, potassium, and rubidium ions using the phenolic OH and fluorine atoms of the side arm in a mixture of acetonitrile- $d_3$  and deuterium oxide. Therefore, **2a** and **2b**, which have only phenolic OH group as a binding site in the side arm, would not form polymer-like complexes, but form 2:1 complexes (host/guest) under these conditions.

Competitive alkali metal ion transport by these ligands was studied using a double tube transport apparatus. Results of the transport experiments are summarized in Figure 3. Under basic-source phase/acidic-receiving phase conditions (using alkali-metal hydroxides), monoaza-12-crown-4 derivatives (**1a–1d**, **1g** and **1h**) and monoaza-15-crown-5 derivatives (**2a–2d**, **2g** and **2h**) exhibited lithium and sodium selective transport, respectively, among the metal ions studied. These transport experiments indicate that these ligands transport size-matched alkali-metal cations under

Table 1  
Crystal and Selected Experimental Data for **1b-1d**, **1f**, and **2c**[a]

	<b>1b</b>	<b>1c</b>	<b>1d</b>	<b>1f</b>	<b>2c</b>
Formula	C <sub>21</sub> H <sub>35</sub> NO <sub>4</sub>	C <sub>23</sub> H <sub>39</sub> NO <sub>4</sub>	C <sub>20</sub> H <sub>33</sub> NO <sub>4</sub>	C <sub>19</sub> H <sub>29</sub> NO <sub>5</sub>	C <sub>25</sub> H <sub>43</sub> NO <sub>5</sub>
<i>M</i>	365.51	393.57	351.49	351.44	437.62
Crystal system	triclinic	monoclinic	triclinic	monoclinic	triclinic
Space group	P-1	P2 <sub>1</sub> /a	P-1	P2 <sub>1</sub> /n	P-1
<i>a</i> /Å	9.222(4)	8.708(4)	9.097(7)	9.246(8)	10.195(2)
<i>b</i> /Å	16.259(5)	24.620(4)	16.389(8)	7.489(8)	14.325(2)
<i>c</i> /Å	7.258(2)	10.956(3)	7.091(5)	28.010(7)	8.814(2)
$\alpha$ /°	92.54(3)		93.70(5)		94.55(1)
$\beta$ /°	91.27(3)	92.433(3)	90.48(6)	97.91(4)	92.78(2)
$\gamma$ /°	78.76(3)		74.64(4)		98.50(1)
<i>U</i> /Å <sup>3</sup>	1066.2(7)	2346.7(10)	1017(1)	1921(2)	1266.7(4)
<i>Z</i>	2	4	2	4	2
Dc/g cm <sup>-3</sup>	1.138	1.114	1.147	1.215	1.147
<i>F</i> (000)	400.00	864.00	384.00	760.00	480.00
$\mu$ (Mo-K $\alpha$ )/cm <sup>-1</sup>	0.77	0.75	0.79	0.87	0.78
Crystal dimensions/mm	0.50x0.50x0.25	0.50x0.50x0.50	0.10x0.20x0.60	0.20x0.20x0.50	0.50x0.50x0.30
No. of reflections for unit cell determination (2 $\theta$ range)/°	25 (26.9-29.9)	20 (25.1-28.7)	25 (21.9-28.8)	25 (20.0-23.4)	25 (27.8-29.9)
Scan width/°	1.52+0.30tan $\theta$	0.73+0.30tan $\theta$	0.73+0.30 tan $\theta$	0.58+0.30tan $\theta$	1.63+0.30tan $\theta$
Limiting indices	-11 ≤ <i>h</i> ≤ 0 0 ≤ <i>k</i> ≤ 31 -14 ≤ <i>l</i> ≤ 14	-11 ≤ <i>h</i> ≤ 0 0 ≤ <i>k</i> ≤ 31 -14 ≤ <i>l</i> ≤ 14	-10 ≤ <i>h</i> ≤ 0 -19 ≤ <i>k</i> ≤ 18 -8 ≤ <i>l</i> ≤ 8	0 ≤ <i>h</i> ≤ 10 0 ≤ <i>l</i> ≤ -36	0 ≤ <i>h</i> ≤ 13 -18 ≤ <i>k</i> ≤ 18 -11 ≤ <i>l</i> ≤ 11
No. reflections measured	5207	5867	3835	4643	6218
unique ( <i>R</i> <sub>int</sub> )	4898 (0.033)	5521 (0.020)	3832 (0.016)	4357 (0.051)	5835 (0.047)
used[all data], <i>N</i> <sub>o</sub>	4892	5378	3832	4032	5834
<i>R</i>	0.135	0.118	0.096	0.139	0.134
<i>R</i> <sub>w</sub>	0.200	0.156	0.153	0.187	0.188
<i>R</i> <sub>1</sub> [ <i>I</i> > 2.0 $\sigma$ ( <i>I</i> )]	0.069	0.057	0.056	0.061	0.062
Goodness of fit	1.38	1.29	1.50	1.12	1.34
No. parameters, <i>N</i> <sub>p</sub>	235	253	226	226	280
Maximum shift/error in final cycle	0.001	0.001	0.001	0.001	0.001
Maximum, minimum peaks in final difference map/e Å <sup>-3</sup>	0.34, -0.25	0.41, -0.52	0.30, -0.36	0.57, -0.60	0.31, -0.32
2 $\theta$ <sub>max</sub>	55°	55°	50°	55°	55°

[a] Details in common:  $\omega$ -2 $\theta$  scan;  $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2}$ ,  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ , goodness of fit  $[\sum w(|F_o| - |F_c|)^2 / (N_o - N_p)]^{1/2}$ .

the conditions studied. The ligands having highly lipophilic substituents (*t*-Bu and Ph) at side arm positions 3' and 5' in monoaza-12-crown-4 and monoaza-15-crown-5 ethers gave higher transport rates. Interestingly, ligands **1h** and **2h** with two fluorine atoms in the side arm gave transport rates higher than that of dimethyl- (**1a** and **2a**), diisopropyl- (**1b** and **2b**), and butylmethyl- (**1d** and **2d**) derivatives. It is well

known that an introduction of lipophilic groups to the crown ethers increases metal ion transport rates [15]. Therefore, we presume that introduction of two fluorine atoms at positions 3' and 5' of the side arm enhances the lipophilicity of the whole molecule. Ligands with one or two methoxy groups in the side arm (**1e**, **1f**, **2e**, and **2f**) decomposed during the transport experiments.

Table 2  
Log *K*,  $\Delta H$ (kJ · mol<sup>-1</sup>) Values for the 1:1 Interaction of **2a**, **2b** and **2h** With Sodium and Potassium Cations in Methanol Solution at 25°

Ligand	Cation	log <i>K</i>	$\Delta H$	T $\Delta S$	[Lit.]
<b>2a</b>	Na <sup>+</sup>	3.22 ± 0.02	-18.7 ± 0.3	-0.3	
	K <sup>+</sup>	3.55 ± 0.05	-19.7 ± 0.6	0.6	
<b>2b</b>	Na <sup>+</sup>	3.02 ± 0.02	-17.3 ± 0.4	-0.1	
	K <sup>+</sup>	3.21 ± 0.06	-17.8 ± 0.5	0.5	
<b>2h</b>	Na <sup>+</sup>	2.96 ± 0.03	-16.5 ± 0.2	0.4	[13]
	K <sup>+</sup>	2.95 ± 0.05	-23.1 ± 0.7	-6.3	[13]

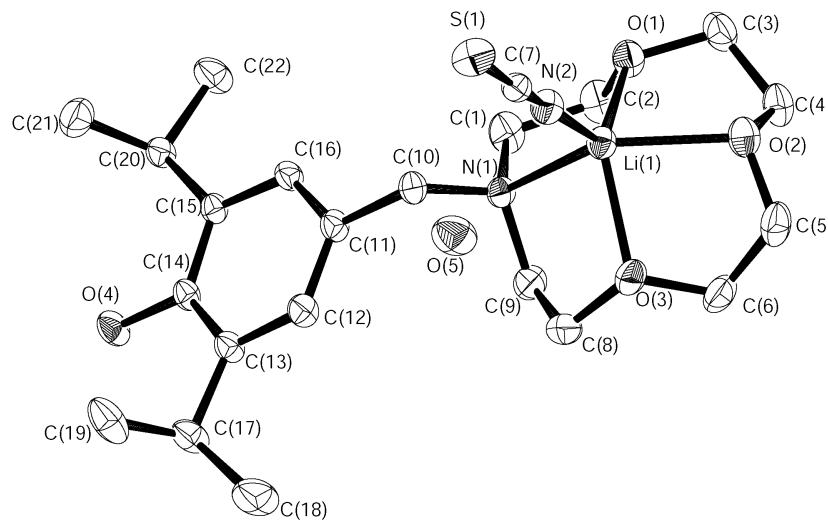


Figure 4(a)

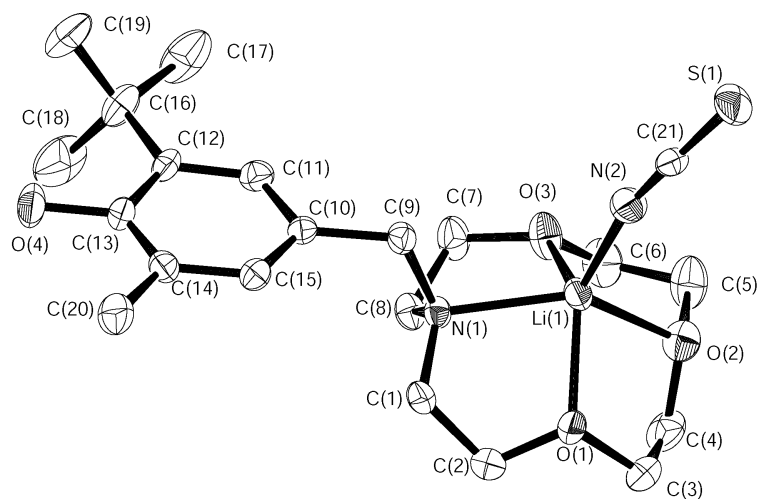


Figure 4(b)

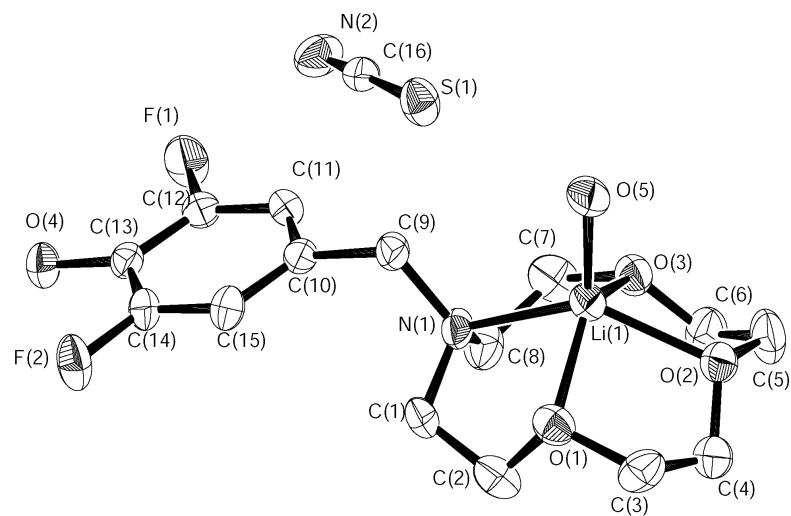
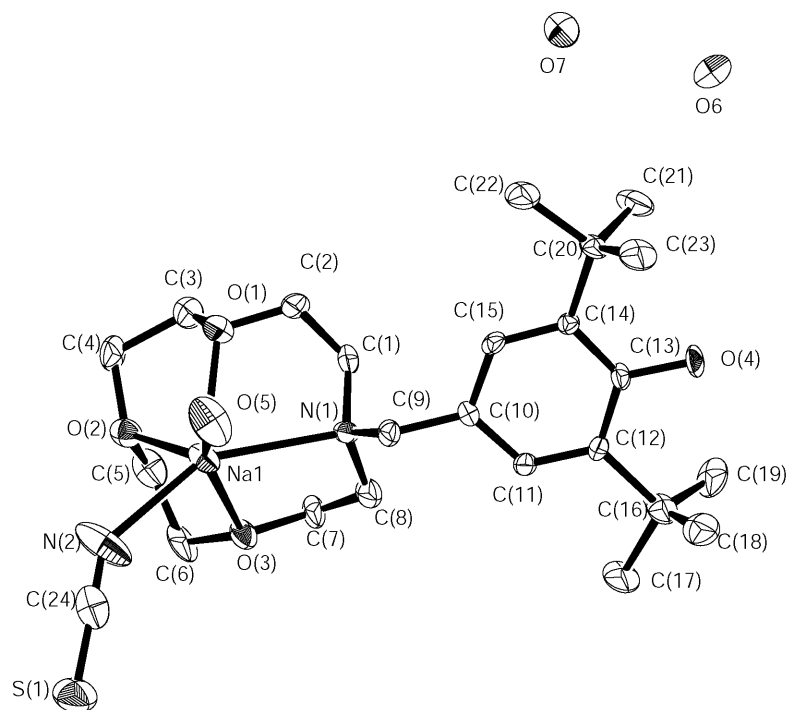
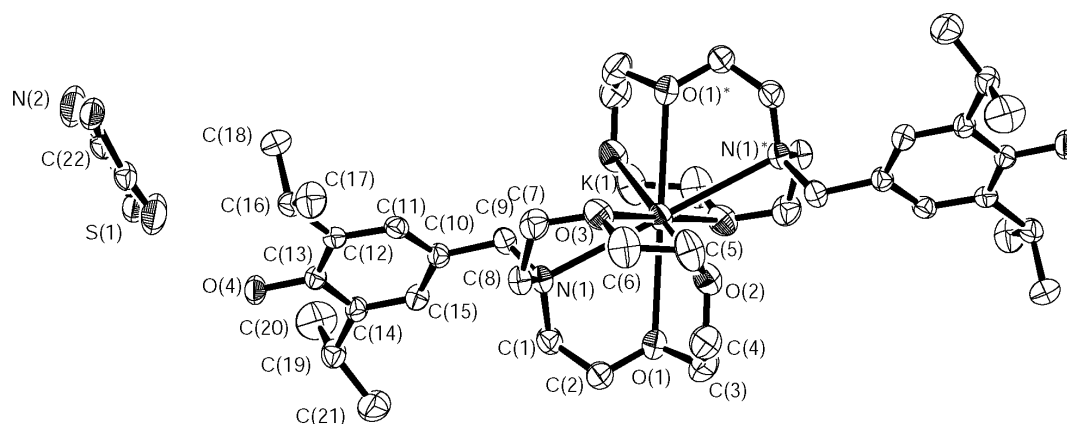


Figure 4(c)

The ORTEP views of **1b-LiSCN** (a), **1d-LiSCN** (b) and **1h-LiSCN** (c) (hydrogen atoms omitted).

Figure 5. The ORTEP view of **1c-NaSCN** (hydrogen atoms omitted).Figure 6. The ORTEP view of **1b-KSCN** (hydrogen atoms omitted).

The molecular structures of **1b-LiSCN**, **1b-KSCN**, **1c-NaSCN**, **1d-LiSCN**, **1f-RbSCN**, **1h-LiSCN**, **2b-KSCN**, **2c-KSCN**, and **2e-KSCN** have been determined by X-ray crystal analyses (Table 3). Figure 4 shows the ORTEP views of the lithium thiocyanate complexes with **1b**, **1d**, and **1h**. Selected bond lengths are summarized in Table 4. In these lithium complexes with monoaza-12-crown-4 derivatives having alkyl groups at side arm positions 3' and 5' (**1b** and **1d**), lithium ions (Li(1)) are five-coordinated by the ring nitrogen atom (N(1)), the three ring oxygen atoms

(O(1)-O(3)) and the nitrogen atom (N(2)) of the counter thiocyanate anion. In all cases, phenolic hydroxyl groups of the side arms do not coordinate to the lithium ions. When fluorine atoms are introduced at side arm positions 3' and 5' (**1h**), the oxygen atom (O(5)) of a water molecule coordinates to the lithium ion instead of to the nitrogen atom of the thiocyanate anion. Complexes **1b-LiSCN** and **1d-LiSCN** are the first instances for monoaza-12-crown-4/lithium complex systems in which a thiocyanate anion coordinates directly to the lithium ion incorporated in the crown ether ring [16]. All

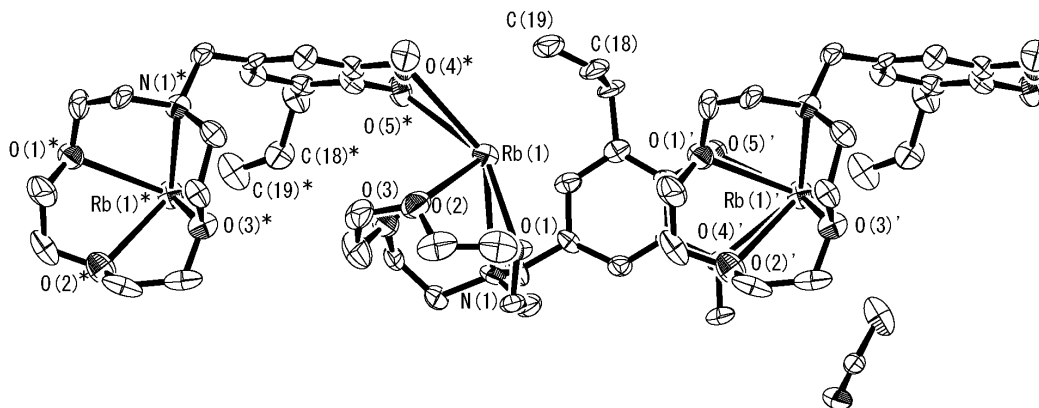


Figure 7(a)

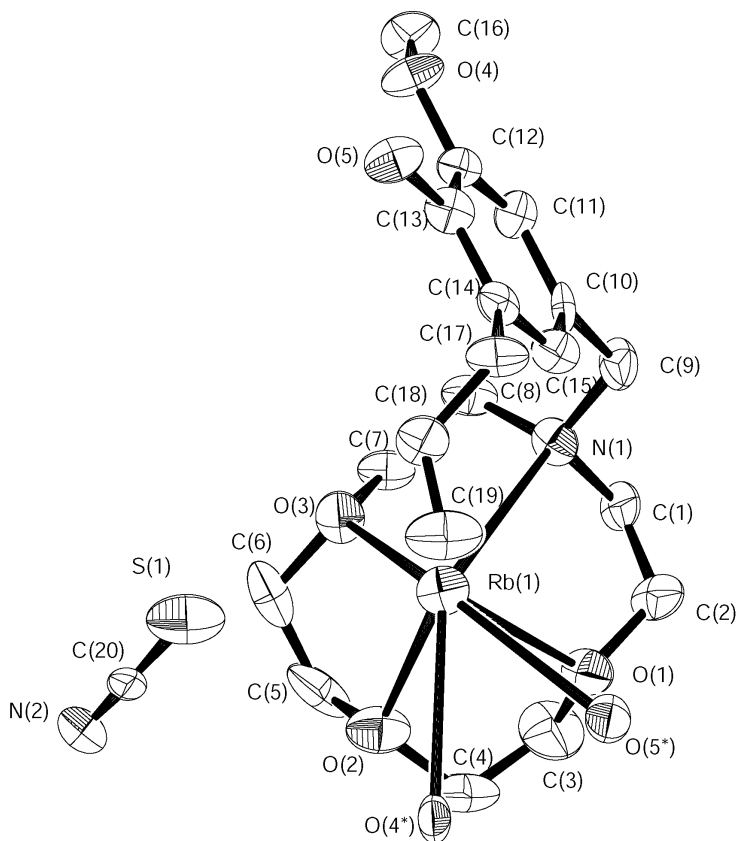


Figure 7(b)

The ORTEP views of **1f-RbSCN**, side view (a) and top view (b) (hydrogen atoms omitted).

distances between lithium ion and hetero atoms are comparable with those of complexes **1a-LiSCN** and **1a-LiBr** previously reported [8].

Ligand **1c** forms a 1:1 complex with sodium thiocyanate (Figure 5). The sodium ion (Na(1)) is six coordinated by the ring nitrogen atom (N(1)), the three ring oxygen atoms

Table 3  
Crystal and Selected Experimental Data for 1b-LiSCN, 1b-KSCN, 1c-NaSCN, 1d-LiSCN, 1f-RbSCN, 1h-LiSCN, 2b-KSCN, 2c-KSCN and 2e-KSCN[a]

Formula	1b-LiSCN	1b-KSCN	1c-NaSCN	1d-LiSCN	1f-RbSCN	1h-LiSCN	2b-KSCN	2c-KSCN	2e-KSCN
<i>M</i>	C <sub>22</sub> H <sub>37</sub> N <sub>2</sub> O <sub>5</sub> SLi 448.55	C <sub>43</sub> H <sub>70</sub> N <sub>3</sub> O <sub>8</sub> KS 828.20	C <sub>24</sub> H <sub>42</sub> N <sub>2</sub> O <sub>5.5</sub> Na 501.66	C <sub>21</sub> H <sub>33</sub> N <sub>2</sub> O <sub>4</sub> SLi 416.50	C <sub>20</sub> H <sub>28</sub> N <sub>2</sub> O <sub>5</sub> SRb 493.98	C <sub>66</sub> H <sub>23</sub> N <sub>2</sub> O <sub>5</sub> SLiF <sub>2</sub> 400.37	C <sub>24</sub> H <sub>39</sub> N <sub>2</sub> O <sub>5</sub> SK 506.74	C <sub>26</sub> H <sub>43</sub> N <sub>2</sub> O <sub>8.5</sub> SK 534.79	C <sub>20</sub> H <sub>31</sub> N <sub>2</sub> O <sub>7</sub> SK 482.63
Crystal system	triclinic	triclinic	monoclinic	orthorhombic	monoclinic	triclinic	monoclinic	triclinic	orthorhombic
Space group	P-1	P-1	P2 <sub>1</sub> /c	Pna2 <sub>1</sub>	Cc	P-1	P2 <sub>1</sub> /n	P-1	Pbca
<i>a</i> /Å	11.599(2)	11.418(4)	16.259(3)	13.691(6)	14.411(2)	10.637(2)	9.724(4)	12.446(2)	17.087(2)
<i>b</i> /Å	12.309(3)	13.482(5)	10.000(5)	11.961(6)	11.042(2)	11.190(3)	16.625(5)	13.221(2)	17.849(3)
<i>c</i> /Å	9.871(2)	8.509(3)	18.368(4)	14.264(9)	15.428(1)	9.291(2)	17.778(3)	9.894(2)	16.048(3)
$\alpha$ /°	110.17(1)	101.02(3)	103.11(2)			107.20(2)			
$\beta$ /°	101.73(1)	93.82(3)				109.99(2)			
$\gamma$ /°	99.03(2)	112.05(2)				74.51(2)			
<i>U</i> /Å <sup>3</sup>	1255.0(4)	4331(8)	2908(1)	2335(3)	2332.4(5)	975.7(4)	2858(1)	1507.8(5)	4894(1)
<i>Z</i>	2	2	4	4	4	2	4	2	8
Dc/g cm <sup>-3</sup>	1.187	1.168	1.145	1.184	1.407	1.363	1.178	1.178	1.310
<i>F</i> (000)	484.00	448.00	1084.00	896.00	1020.00	420.00	1088.00	576.00	2048.00
$\mu$ (Mo-K $\alpha$ )/cm <sup>-1</sup>	1.61	2.07	1.61	1.65	22.39	2.12	2.92	2.80	3.43
Crystal dimensions/mm	0.40x0.50 x0.50	0.50x0.30 x0.13	0.50x0.50 x0.13	0.25x0.20 x0.25	0.10x0.15 x0.25	0.35x0.20 x0.50	0.70x0.50 x0.10	0.50x0.50 x0.60	0.80x0.50 x0.80
No. of reflections for unit cell determination	25 (29.6-30.0)	25 (20.3-28.7)	20 (20.2-24.6)	25 (20.1-24.7)	25 (20.2-23.9)	25 (23.8-27.6)	25 (20.6-23.7)	25 (29.5-30.0)	25 (27.0-29.2)
(2 $\theta$ range)/° Scan width/°	1.73+0.30tan $\theta$	0.58+0.30tan $\theta$	1.47+0.30 tan $\theta$	1.31+0.30tan $\theta$	0.89+0.30tan $\theta$	0.58+0.30 tan $\theta$	0.58+0.30tan $\theta$	1.63+0.30tan $\theta$	1.63+0.30 tan $\theta$
Limiting indices	0 ≤ <i>h</i> ≤ 15 -15 ≤ <i>k</i> ≤ 15 -12 ≤ <i>l</i> ≤ 12	-11 ≤ <i>h</i> ≤ 0 0 ≤ <i>k</i> ≤ 31 -14 ≤ <i>l</i> ≤ 14	-20 ≤ <i>h</i> ≤ 19 0 ≤ <i>k</i> ≤ 11 -21 ≤ <i>l</i> ≤ 0	0 ≤ <i>h</i> ≤ 16 0 ≤ <i>k</i> ≤ 14 0 ≤ <i>l</i> ≤ 16	-16 ≤ <i>h</i> ≤ 15 0 ≤ <i>k</i> ≤ 13 -18 ≤ <i>l</i> ≤ 0	-12 ≤ <i>h</i> ≤ 13 -13 ≤ <i>k</i> ≤ 14 -12 ≤ <i>l</i> ≤ 0	0 ≤ <i>h</i> ≤ 10 0 ≤ <i>k</i> ≤ 19 -21 ≤ <i>l</i> ≤ 21	-16 ≤ <i>h</i> ≤ 16 -15 ≤ <i>k</i> ≤ 17 -12 ≤ <i>l</i> ≤ 0	0 ≤ <i>h</i> ≤ 22 0 ≤ <i>k</i> ≤ 23 -20 ≤ <i>l</i> ≤ 0
No. reflections measured	6034	5628	6077	2360	2137	4748	4475	7316	6198
unique (R <sub>int</sub> )	5750 (0.010)	5624 (0.028)	5547 (0.092)	2140	1952 (0.072)	4474 (0.020)	4152 (0.056)	6914 (0.030)	
used[all data], <i>N</i> <sub>o</sub>	5750	5614	5490	2140	1952	4473	3977	6914	
<i>R</i>	0.077	0.100	0.275	0.082	0.160	0.089	0.115	0.104	0.107
<i>R</i> <sub>w</sub>	0.154	0.185	0.347	0.117	0.179	0.196	0.169	0.155	0.172
<i>R</i> 1 [ <i>I</i> > 2.0 $\sigma$ ( <i>I</i> )]	0.050	0.060	0.116	0.042	0.059	0.066	0.059	0.057	0.055
Goodness of fit	1.44	1.23	1.45	1.14	1.17	1.61	1.09	1.32	1.34
No. parameters, <i>N</i> <sub>p</sub>	280	268	316	262	262	244	298	316	280
Maximum shift/error in final cycle	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
Maximum, minimum peaks in final difference map/e Å <sup>-3</sup> 2 $\theta$ <sub>max</sub>	0.43, -0.40	0.58, -0.48	0.97, -0.86	0.44, -0.52	1.03, -1.79	0.61, -0.46	0.65, -0.55	0.67, -0.52	0.57, -0.70
	55°	55°	55°	55°	50°	55°	50°	55°	55°

[a] Details in common:  $\omega$ -2 $\theta$  scan;  $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2}$ ,  $R_1 = \sum(|F_o| - |F_c|) / \sum |F_o|$ , goodness of fit  $[\sum w(|F_o| - |F_c|)^2 / (N_o - N_p)]^{1/2}$ .

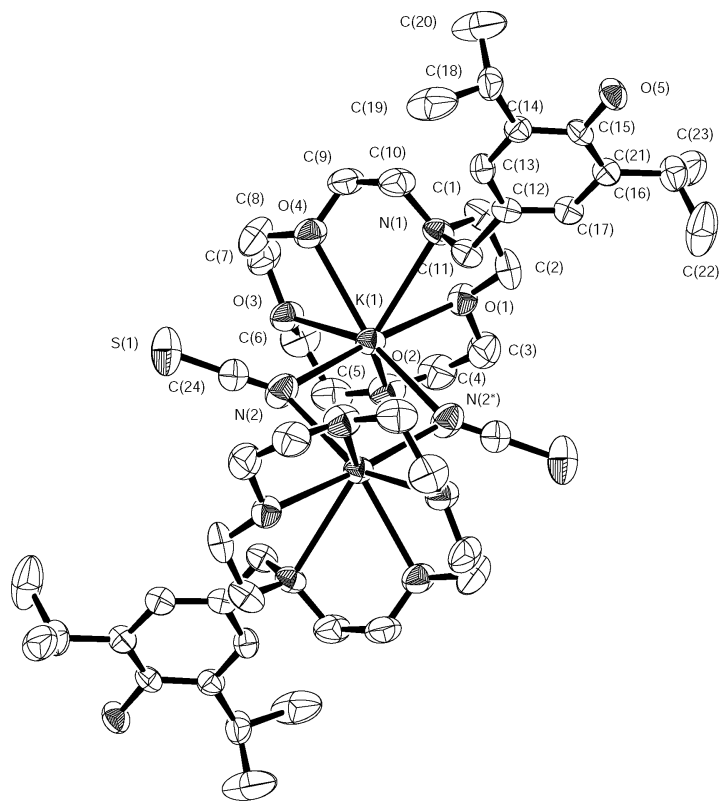


Figure 8(a)

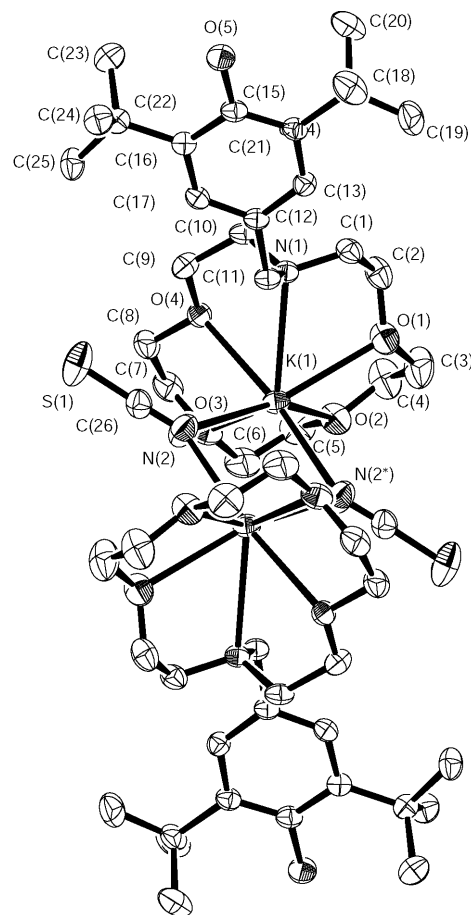


Figure 8(b)

The ORTEP views of **2b-KSCN** (a) and **2c-KSCN** (b) (hydrogen atoms omitted).

Table 4  
Selected Bond Lengths (Å)

	<b>1b-LiSCN</b>	<b>1d-LiSCN</b>	<b>1h-LiSCN</b>	<b>1c-NaSCN</b>	<b>1b-KSCN</b>	<b>1f-RbSCN</b>
M <sup>+</sup> - ring O	2.076(4)	2.086(10)	2.053(6)	2.444(6)	2.823(2)	3.01(1)
2.149(4)	2.109(10)	2.094(6)	2.455(7)	2.761(2)	3.04(2)	
	2.116(4)	2.10(1)	2.101(7)	2.446(6)	2.857(2)	2.85(1)
M <sup>+</sup> - ring N	2.199(4)	2.158(4)	2.189(6)	2.651(7)	2.976(2)	3.25(1)
M <sup>+</sup> - SCN	1.976(4)	1.97(1)	--	2.461(10)	--	--
M <sup>+</sup> - H <sub>2</sub> O	--	--	1.889(6)	2.311(8)	--	--
M <sup>+</sup> - PhOH	--	--	--	--	--	3.02(1)
M <sup>+</sup> - PhOMe	--	--	--	--	--	3.20(1)
	<b>2b-KSCN</b>	<b>2c-KSCN</b>	<b>2e-KSCN</b>			
M <sup>+</sup> - ring O	2.846(4)	2.789(3)	2.827(1)			
	2.771(5)	2.828(2)	2.789(3)			
	2.806(4)	2.792(2)	2.841(3)			
	2.758(4)	2.798(2)	2.751(3)			
M <sup>+</sup> - ring N	2.948(4)	2.972(2)	2.998(3)			
M <sup>+</sup> - SCN	2.845(6)	2.850(3)	2.958(4)			
M <sup>+</sup> - SCN*	2.839(6)	2.805(3)	--			
M <sup>+</sup> - PhOH	--	--	3.02(1)			
M <sup>+</sup> - PhOMe	--	--	3.20(1)			



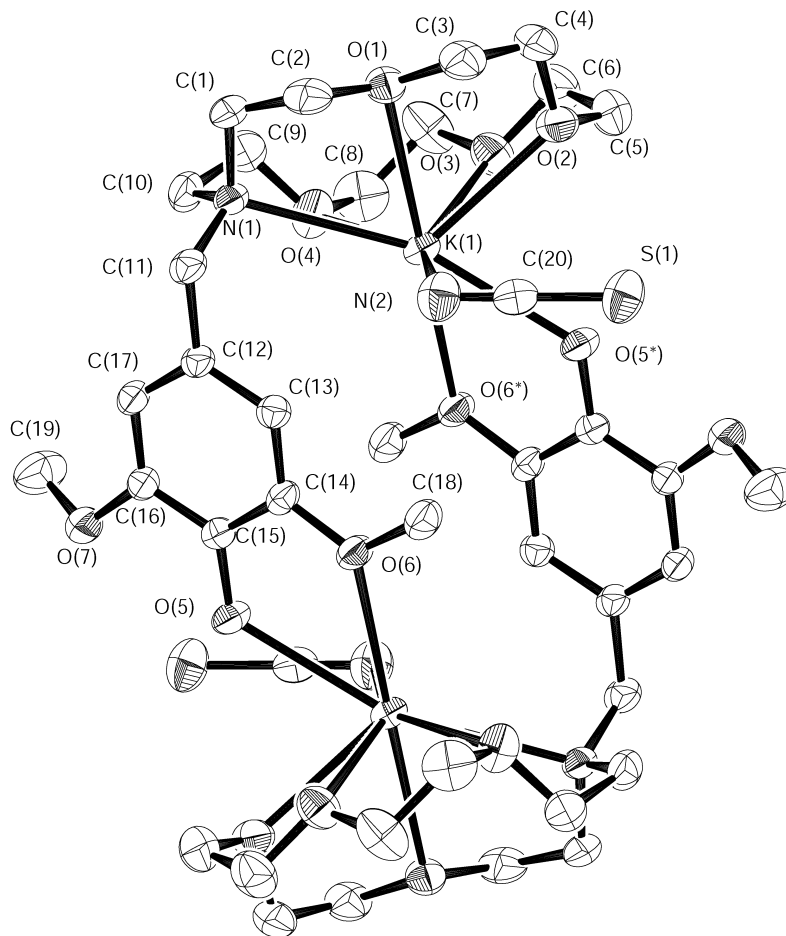


Figure 9. The ORTEP view of **2e-KSCN** (hydrogen atoms omitted).

(O(1)-O(3)), the nitrogen atom of the counter thiocyanate anion (N(2)), and an oxygen atom of water (O(5)). Large thermal ellipsoids for O(5) and the N(2) were observed as shown in Figure 5. Usually, 12-crown-4/sodium complex systems form 2:1 (host/guest) complexes [16]. Because the structure of part in this complex is unstable, the *R* factors would not fall to less than 10 %.

Because ligand **2b**, a monoaza-15-crown-5 containing diisopropyl groups in the side arm, forms a mixture of 1:1 and polymer-like complexes in a unit cell [14], we expected that ligand **1b** would form an unusual complex. However, **1b** forms a 2:1 (host/guest) complex with potassium thiocyanate (Figure 6). The potassium ion (K(1)) is eight coordinated by two ring nitrogen atoms (N(1) and N(1\*)), six oxygen atoms (O(1), O(1\*), O(2), O(2), O(3), and O(3\*)). The phenolic hydroxyl groups do not participate in the coordination.

On the other hand, ligand **1f**, having an eugenol unit as the side arm, forms a polymer-like (1:1)<sub>n</sub> complex with rubidium thiocyanate (Figures 7a and 7b). The rubidium ion (Rb(1)) is seven coordinated by the ring nitrogen atom

(N(1)), three ring oxygen atoms (O(1)-O(3)), two oxygen atoms (O(4\*) and O(5\*)) of the phenolic hydroxyl and methoxy groups, respectively, in the nearest-neighbor molecules. As shown in Figure 7b, a vinyl group of the side arm covers the open space around the rubidium ion (the Rb(1)-C(19) distance is 3.37 Å). Hoffmann *et al* reported that toluene forms 1:1 complex with rubidium ion in the presence of *N,N,N',N'',N'''*-pentamethyldiethylenetriamine, and the bond lengths between rubidium and aromatic carbons are in the range 3.14-3.57 Å [17]. Thus, we believe that the rubidium ion (Rb(1)) interacts with the vinyl

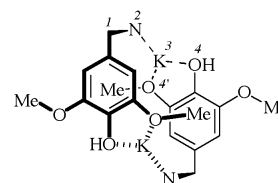


Figure 10. Schematic drawing of the [4.4]cyclophane skeleton in **2e-KSCN** complex.

carbon (C(19)). We have reported that **1a-RbSCN** complex forms a polymer-like  $(2:2)_n$  complex and the rubidium ion is seven coordinated as the first 1:1 stoichiometric complex between rubidium and 12-membered crown ether [8]. The rubidium complex with **1f** is also the first instance of the six-coordinated rubidium complex with the 12-, 15-, and 18-membered crown ethers [16].

Monoaza-15-crown-5 derivatives having isopropyl and *tert*-butyl groups at positions 3' and 5' of the side arm hydroxybenzyl groups (**2b** and **2c**) form dimeric 1:1 complexes with potassium ions (Figures 8a and 8b). The potassium ions (K(1)) in these complexes are seven coordinated by the ring nitrogen atom (N(1)), four ring oxygen atoms (O(1)-O(4)), and two nitrogen atoms (N(2) and N(2\*)) of thiocyanate anions. The thiocyanate anions bridge between two incorporated potassium ions. Monoaza-15-crown-5 having methyl groups at positions 3' and 5' of the side arm forms a polymer-like  $(1:1)_n$  complex with potassium ions [8].

A [4.4]cyclophane-like complex was obtained in a potassium thiocyanate complex with ligand **2e** (Figure 9). The potassium ions (K(1)) are seven coordinated by the ring nitrogen atom (N(1)), four ring oxygen atoms (O(1)-O(4)), and two oxygen atoms (O(5\*) and O(6\*)) of the phenolic hydroxyl and methoxy groups in the side arm of a neighboring ligand. Thiocyanate anions do not participate in the coordination. Two benzene rings are bridged by four atoms (-C(11)-N(1)-K(1)-O(5\* or 6\*)-) and the partial structure of the complex is in the form of [4.4]cyclophane-like structure (Figure 10). Two benzene rings are parallel and the distance between them is about 3.7 Å (The O(6\*)-C(14) and C(15\*)-O(5) distances are 3.72 and 3.69 Å, respectively).

In conclusion, we reported complexing properties of a series monoaza-12-crown-4 and monoaza-15-crown-5 ethers containing 4'-hydroxy-3',5'-disubstituted benzyl groups in a side arm. Also, X-ray crystal structures of some alkali metal complexes with these ligands were reported. These results indicated that the substituents next to the phenolic hydroxyl group of the side arm remarkably affect the transport properties and the structures of the complexes.

## EXPERIMENTAL

General Procedure for 2,6-Disubstituted Phenols with *N*-Methoxymethylazacrown Ethers.

A mixture of *N*-methoxymethylmonoazacrown ether (1.0 mmoles) and 2,6-disubstituted phenol (1.0 mmoles) in absolute benzene (20 ml) was refluxed under a nitrogen atmosphere for 24 hours. The reaction mixture was cooled and then concentrated under reduced pressure. The residual oil was separated and purified by silica-gel and then gel-permeation column chromatography to give the following products.

*N*-(4'-Hydroxy-3',5'-diisopropylbenzyl)-1,4,7,10-tetraoxa-13-azacyclopentadecane (**2b**).

This compound was isolated in a 74 % yield as a pale yellow oil;  $^1\text{H}$  nmr:  $\delta$  7.00 (s, 2H), 4.71 (s, 1H), 3.76-3.61 (m, 18H), 3.21-3.07 (m, 2H), 2.78 (t, 4H,  $J = 6.1$  Hz), 1.25 (d, 12H,  $J = 6.8$  Hz); ms: ei (m/z) 410 ( $M^+ + 1$ , 100 %).

*Anal.* Calcd. for  $\text{C}_{23}\text{H}_{39}\text{NO}_5$ : C, 67.45; H, 9.60; N, 3.42. Found: C, 67.40; H, 9.90; N, 3.24.

*N*-(4'-Hydroxy-3',5'-di-*tert*-butylbenzyl)-1,4,7,10-tetraoxa-13-azacyclopentadecane (**2c**).

This compound was isolated in a 59 % yield as pale yellow white crystals; mp 73-78° (recrystallized from hexane);  $^1\text{H}$  nmr:  $\delta$  7.10 (s, 2H), 5.10 (s, 1H), 3.68-3.60 (m, 18H), 2.79 (t, 4H,  $J = 6.1$  Hz), 1.43 (s, 18H); ms: ei (m/z) 438 ( $M^+ + 1$ , 100 %).

*Anal.* Calcd. for  $\text{C}_{25}\text{H}_{43}\text{NO}_5 \cdot 0.5\text{H}_2\text{O}$ : C, 67.92; H, 9.92; N, 3.17. Found: C, 67.89; H, 10.17; N, 3.10.

*N*-(4'-Hydroxy-3'-*tert*-butyl-5'-methylbenzyl)-1,4,7,10-tetraoxa-13-azacyclopentadecane (**2d**).

This compound was isolated in a 68 % yield as a pale yellow crystals; mp 88-90° (recrystallized from hexane);  $^1\text{H}$  nmr:  $\delta$  7.05 (s, 1H), 6.97 (s, 1H), 4.69 (s, 1H), 3.68-3.57 (m, 18H), 2.70 (t, 4H,  $J = 6.0$  Hz), 2.23 (s, 3H), 1.40 (s, 9H); ms: ei (m/z) 396 ( $M^+ + 1$ , 100 %).

*Anal.* Calcd. for  $\text{C}_{23}\text{H}_{39}\text{NO}_5$ : C, 66.81; H, 9.43; N, 3.54. Found: C, 66.60; H, 9.81; N, 3.54.

*N*-(4'-Hydroxy-3',5'-dimethoxybenzyl)-1,4,7,10-tetraoxa-13-azacyclopentadecane (**2e**).

This compound was isolated in a 68 % yield as a pale yellow oil;  $^1\text{H}$  nmr:  $\delta$  6.59 (s, 2H), 3.87 (s, 6H), 3.67-3.61 (m, 19H), 2.80 (t, 4H,  $J = 6.0$  Hz); ms: ei (m/z) 386 ( $M^+ + 1$ , 100 %).

*Anal.* Calcd. for  $\text{C}_{19}\text{H}_{31}\text{NO}_7 \cdot 0.25\text{H}_2\text{O}$ : C, 58.52; H, 8.14; 3.59. Found: C, 58.42; H, 8.18; N, 3.28.

*N*-(4'-Hydroxy-3'-allyl-5'-methoxybenzyl)-1,4,7,10-tetraoxa-13-azacyclopentadecane (**2f**).

This compound was isolated in a 21 % yield as a pale yellow oil;  $^1\text{H}$  nmr:  $\delta$  6.79 (s, 1H), 6.66 (s, 1H), 6.17-5.95 (m, 1H), 5.62 (s, 1H), 5.09-5.03 (m, 2H), 3.88 (s, 3H), 3.68-3.58 (m, 18H), 3.38 (d, 2H,  $J = 6.3$  Hz), 2.78 (t, 4H,  $J = 6.0$  Hz); ms: ei (m/z) 396 ( $M^+ + 1$ , 14 %), 177 ( $[\text{HOC}_6\text{H}_2(\text{OCH}_3)(\text{CH}_2\text{-CH=CH}_2\text{-CH}_2\text{)]}^+$ , 100 %).

*Anal.* Calcd. for  $\text{C}_{21}\text{H}_{33}\text{NO}_6 \cdot 0.25\text{H}_2\text{O}$ : C, 63.06; H, 8.44; N, 3.50. Found: C, 63.24; H, 8.70; N, 3.51.

*N*-(4'-Hydroxy-3',5'-diphenylbenzyl)-1,4,7,10-tetraoxa-13-azacyclopentadecane (**2g**).

This compound was isolated in a 59 % yield as a pale yellow oil;  $^1\text{H}$  nmr:  $\delta$  7.58-7.35 (m, 10H), 7.24 (s, 2H), 3.69-3.60 (m, 18H), 2.83 (t, 4H,  $J = 6.1$  Hz); ma; ei (m/z): 478 ( $M^+ + 1$ , 52 %), 259 ( $[\text{HOC}_6\text{H}_2(\text{C}_6\text{H}_5)_2\text{CH}_2\text{]}^+$ , 100 %), 220 ( $[\text{monoaza-15-crown-5} + \text{H}]^+$ , 100 %).

*Anal.* Calcd. for  $\text{C}_{29}\text{H}_{35}\text{NO}_5 \cdot 0.25\text{H}_2\text{O}$ : C, 72.25; H, 7.42; N, 2.91. Found: C, 72.04; H, 7.66; N, 2.76.

*N*-(4'-Hydroxy-3',5'-difluorobenzyl)-1,4,7,10-tetraoxa-13-azacyclopentadecane (**2h**).

This compound was isolated in a 72 % yield as a pale yellow oil;  $^1\text{H}$  nmr:  $\delta$  6.81 (d, 2H,  $J = 8.0$  Hz), 3.73-3.37 (m, 19H), 2.77 (t, 4H,  $J = 5.4$  Hz); ms: ei ( $m/z$ ) 362 ( $M^+ + 1$ , 100 %).

*Anal.* Calcd. for  $\text{C}_{17}\text{H}_{25}\text{F}_2\text{NO}_5 \cdot 0.75\text{H}_2\text{O}$ : C, 54.46; H, 7.12; N, 3.74. Found: C, 54.62; H, 7.48; N, 3.87.

Preparation of Alkali Metal Thiocyanate Complexes with Armed-azacrown Ethers, **1** and **2**.

Ligand **1** or **2** (0.01 mmole) in acetonitrile (1 ml) was reacted with alkali-metal thiocyanate (0.01 mmole) in methanol (1 ml). After the solvent had evaporated, the crystals were recrystallized from acetonitrile. The crystals were dried with an Abderhalden's dryer (50°, 0.5 Torr). The elemental analyses of these complexes are as follows.

#### 1b-LiSCN Complex.

*Anal.* Calcd. for  $\text{C}_{21}\text{H}_{35}\text{NO}_4 \cdot \text{LiSCN} \cdot \text{H}_2\text{O}$ : C, 58.91; H, 8.31; N, 6.25. Found: C, 58.71; H, 8.38; N, 6.25.

#### 1b-KSCN Complex.

*Anal.* Calcd. for  $(\text{C}_{21}\text{H}_{35}\text{NO}_4)_2 \cdot \text{KSCN} \cdot 1.6\text{H}_2\text{O}$ : C, 60.26; H, 8.61; N, 4.90. Found: C, 59.89; H, 8.15; N, 5.53.

#### 1c-NaSCN Complex.

*Anal.* Calcd. for  $\text{C}_{23}\text{H}_{39}\text{NO}_4 \cdot \text{NaSCN} \cdot 1.5\text{H}_2\text{O}$ : C, 57.58; H, 8.25; N, 5.60. Found: C, 57.46; H, 8.33; N, 5.44.

#### 1d-LiSCN Complex.

*Anal.* Calcd. for  $\text{C}_{20}\text{H}_{33}\text{NO}_4 \cdot \text{LiSCN} \cdot 1.2\text{H}_2\text{O}$ : C, 57.57; H, 8.14; N, 6.39. Found: C, 57.35; H, 7.71; N, 6.23.

#### 1f-RbSCN Complex.

*Anal.* Calcd. for  $\text{C}_{20}\text{H}_{29}\text{N}_2\text{O}_5 \cdot \text{LiSCN}$ : C, 48.53; H, 5.91; N, 5.66. Found: C, 48.43; H, 6.08; N, 5.64.

#### 1h-LiSCN Complex.

*Anal.* Calcd. for  $\text{C}_{15}\text{H}_{21}\text{NF}_2\text{O}_4 \cdot \text{LiSCN} \cdot \text{H}_2\text{O}$ : C, 48.00; H, 5.79; N, 7.00. Found: C, 47.82; H, 5.51; N, 7.49.

#### 2b-KSCN Complex.

*Anal.* Calcd. for  $\text{C}_{23}\text{H}_{39}\text{NO}_5 \cdot \text{KSCN}$ : C, 56.89; H, 7.76; N, 5.53. Found: C, 56.71; H, 7.66; N, 5.15.

#### 2c-KSCN Complex.

*Anal.* Calcd. for  $\text{C}_{25}\text{H}_{43}\text{NO}_5 \cdot \text{KSCN}$ : C, 58.39; H, 8.10; N, 5.24. Found: C, 58.16; H, 8.15; N, 5.43.

#### 2e-KSCN Complex.

*Anal.* Calcd. for  $\text{C}_{19}\text{H}_{31}\text{NO}_7 \cdot \text{KSCN} \cdot 0.5\text{H}_2\text{O}$ : C, 48.86; H, 6.56; N, 5.70. Found: C, 48.83; H, 6.46; N, 5.65.

#### Determination of Thermodynamic Values.

Log  $K$ ,  $\Delta H$ , and  $\Delta S$  values were determined as described [18] in methanol at  $25.0 \pm 0.1^\circ$  by titration calorimetry using a Tronac Model 450 calorimeter equipped with a 20-ml reaction vessel. The metal cation solutions (0.08-0.12 mole/l) were titrated into the armed-azacrown ether solutions ( $1.3 \times 10^{-3} - 2.6 \times 10^{-3}$  mole/l) and the titrations were carried out to a two-fold excess of the metal cations.

#### Metal Ion Transport Experiments.

The transport experiments were carried out using a double tube apparatus (diameter of the inner and outer tubes are 10 mm and 20 mm, respectively) at  $25 \pm 2^\circ$ . Initial conditions of the competitive transport were as follows: [basic source phase] = aqueous solution containing a mixture of 0.1 mole/l of sodium hydroxide, potassium hydroxide and cesium hydroxide (4 ml); [membrane phase] = 2 mmoles/l of crown ether in chloroform (4 ml); [acidic receiving phase] = 0.1 mole/l of hydrochloric acid (1 ml). The concentration of the receiving phase was determined by ion chromatography. The transport rate was calculated from the amounts of alkali-metal cations in the receiving phase. The aqueous and organic phases were stirred by a stirring bar (10 mm) at 500 rpm by a synchronous motor in order to avoid a stirring error. The amounts of metal ions in the receiving phases were measured by ion chromatography. The initial transport rate was calculated from the increase of the cation concentration in the receiving phase after a period of 6 hours.

#### Crystallography.

The crystallographic and experimental data are listed in Tables 1 and 3. Each of the single crystals was mounted in a glass capillary. All measurements were made at 298 K on a Rigaku AFC5S four-circle diffractometer with graphite-monochromated Mo  $K\alpha$  radiation (0.71069 Å) and a 12kW rotating-anode generator. Cell contacts and an orientation matrix for data collection were obtained from a least-squares refinement. The data were collected using the  $\omega$ - $2\theta$  scan technique to an above maximum  $2\theta$  value of  $50.0^\circ$  or  $55.0^\circ$ . All intensities were corrected for Lorentz and polarization effects. The structure was solved by direct methods (SIR 92) [19]. The non-hydrogen atoms were refined anisotropically. The coordinates of all hydrogen atoms except the hydrogen atoms of the phenolic OH group were calculated at ideal positions and were refined (Tables 1 and 3). Neutral atom scattering factors were taken from Cromer and Weber [20]. Anomalous dispersion effects were included in Fc [21]; the values for  $\Delta f'$  and  $\Delta f''$  were those of Creagh and McAuley [22]. The values for the mass attenuation coefficients are those of Creagh and Hubbel [23]. All calculations were made using the Texsan™ crystallographic software package of Molecular Structure Corporation [24].

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#### Supplementary Material.

Atomic coordinates, displacement parameters, bond lengths and angles have been deposited at the Cambridge Crystallographic Centre.

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