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Polymer-like Structures of LiSCN, NaSCN, KSCN, RbSCN, and CsSCN Complexes with an Armed Monoaza-15-crown-5 Ether Bearing a 3′,5′-Difluoro-4′-hydroxybenzyl Group

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Structures of LiSCN, NaSCN, KSCN, RbSCN, and CsSCN complexes with 3′,5′-difluoro-4′-hydroxybenzyl-armed monoaza-15-crown-5 ether (**5**) were investigated. The Li^+ and Na^+ complexes are $(1:1)_n$ polymer-like complexes bridged by hydrogen bonding. On the other hand, the K^+, Rb^+, and Cs^+ complexes are polymer-like complexes bridged by the fluorine atoms of the side arms. The titration calorimetry and ^{19}F NMR titration experiments suggest that one or both fluorine atoms along with the oxygen atom of the phenolic OH group coordinate to the alkali metal ions incorporated in the crown part of a second armed ligand to give polymer-like complexes in solution. The FAB-MS data indicated that larger alkali metal ions form more stable polymer-like complexes.

Introduction

Armed macrocycles bearing one or more pendant binding sites have been used not only as new ligands with specific binding properties but also as building blocks to construct supramolecular structures.[2] During our research efforts on the development of new armed-azacrown ethers, armed-azathiacrown ethers, and armed-cyclens, we found that substituents on aromatic side arms affect structures of metal complexes.[3a−3n] For example, the structures of the RbSCN complexes with armed-monoaza-15-crown-5 ethers bearing 3′,5′-dialkyl-4′-hydroxybenzyl groups (alkyl = Me, *i*-Pr, and *t*-Bu) systematically changed depending upon the size of the R groups at positions 3′ and 5′ in the side arm; ligands **1** (R = Me), **2** (R = *i*-Pr), and **3** (R = *t*-Bu) form a polymer-like $(1:1)_n$ complex, a mixture of 1:1 and polymer-like $(1:1)_n$ complexes, and a dimeric 1:1 complex, respectively.[3c] On the other hand, the structure of the KSCN complex with **1** was a polymer-like $(1:1)_n$ complex,[3a] while **2** and **3** form

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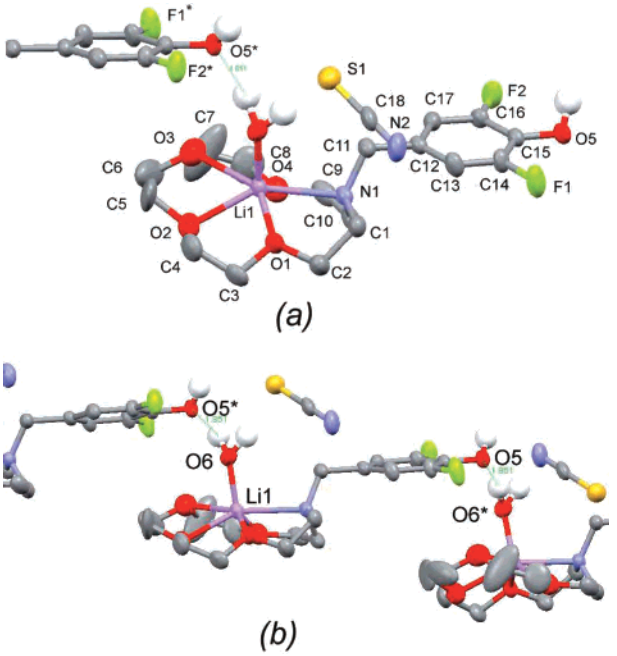
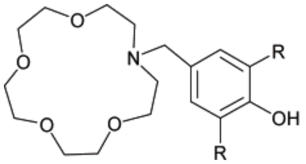


Figure 1. Ellipsoid display (a) and a partial magnified view of a packing diagram (b) of **5**-LiSCN showing thermal ellipsoids at 30% probability. Hydrogen atoms except phenolic OH groups and water molecules are omitted.

dimeric 1:1 complexes.[3h] In addition, the KSCN complex with **4** having two dimethoxy groups at positions 3′ and 5′ of the aromatic side arm formed a [4.4]cyclophane-like complex.[3h]

To further investigate the electric and steric effects of the substitutents next to the phenolic OH groups in the side arms, we prepared a new armed-monoaza-15-crown-5 ether having fluorine atoms at positions 3′ and 5′ in the aromatic side arm (**5**). Computer modeling experiments suggest that the



1: R = Me
2: R = *i*-Pr
3: R = *t*-Bu
4: R = OMe
5: R = F

oxygen atom of the phenolic OH group and the F atoms of **5** cannot bind to the metal cation incorporated into the crown part of the molecule so that **5** should form polymer-like complexes with alkali metal cations.[4] It is also expected that **5** would form polymer-like complexes using the electron-donating properties of fluorine atoms next to the phenolic OH group.[5] Here we report the molecular structures of LiSCN, NaSCN, KSCN, RbSCN, and CsSCN complexes with **5** in the solid state and in solution.

Results and Discussion

3′,5′-Difluoro-4′-hydroxybenzyl-armed monoaza-15-crown-5 ether (**5**) was prepared as previously reported.[1,3j] To prepare single crystals for X-ray analyses of alkali metal thiocyanate

Table 1. Mulliken Charges, Electrostatic Charges, and Natural Charges of 2,6-Dimethyl- and 2,5-Difluorophenols (electrons)

	2,6-dimethylphenol	2,6-difluorophenol
Mulliken charge	−0.647	−0.630
electrostatic charge	−0.501	−0.473
natural charge	−0.697	−0.675

Table 2. Selected Bond Distances (Å)

	5-LiSCN	**5**-NaSCN	**5**-KSCN	**5**-RbSCN	**5**-CsSCN
M^+−ring O(1)	2.109(6)	2.37(2)	2.7774(17)	2.975(9)	3.107(9)
M^+−ring O(2)	2.267(6)	2.503(11)	2.7854(19)	2.898(7)	3.040(7)
M^+−ring O(3)	2.449(6)	2.44(2)	2.7565(19)	2.863(7)	3.038(7)
M^+−ring O(4)	2.124(6)	2.347(13)	2.7916(17)	2.941(7)	3.150(8)
M^+−ring N(1)	2.398(5)	2.61(2)	2.877(2)	3.081(7)	3.214(7)
M^+−H_2*O*(6)	1.921(5)				
M^+−SC*N*(2)		2.392(9)			
M^+−Ph*O*(5*)H			3.028(2)	4.343(9)	4.135(9)
M^+−Ph *F*(1*)			2.7831(16)	3.003(5)	3.202(5)
M^+−*S*(1)CN			3.25269(9)	3.411(3)	3.582(3)
M^+−*S*(1*)CN				3.476(3)	3.641(3)
M^+−*C*(14*)					3.653(9)

complexes, **5** in acetonitrile was treated with alkali metal thiocyanates in methanol. Crystals of the corresponding alkali metal thiocyanate complexes were obtained quantitatively on evaporation of the solvent.

The structures of the alkali metal complexes, **5**-LiSCN, **5**-NaSCN, **5**-KSCN, **5**-RbSCN, and **5**-CsSCN, have been determined by X-ray analysis.

Parts a and b of Figure 1 show the ORTEP diagram and a partial magnified view of a packing diagram of **5**-LiSCN, respectively. Selected bond distances are summarized in Table 2.

The Li^+ ion of **5**-LiSCN is six-coordinated by the four ring O atoms, the ring N atom, and the O atom of the water molecule. The Li1−O(ring), Li1−N1, and Li1−O6(water) bond distances are in the range 2.109(6)−2.449(6), 2.398(5), and 1.921(5) Å, respectively. The Li1−O(ring) bond distances are comparable with those of Li^+ complexes with 15-crown-5 ethers.[6] The SCN anion is not coordinated because the Li^+ ion is completely incorporated in the cavity of the crown ring and the O6 atom of the water molecule binds to the Li^+ ion. As shown in Figure 1b, the complex forms a polymer by hydrogen bonding between the phenolic OH groups and the water molecules bound to the lithium ion. The O5*−O6 distance is 2.889 Å. It is well known that O−O bond distances of hydrogen bonding are in the range 2.7−3.2 Å.[7] Therefore, **5**-LiSCN is a $(1:1)_n$ polymer-like complex, which can be denoted as $[Li(\mathbf{5})(H_2O)]_n(SCN)_n$, bridged by hydrogen bonding between the phenolic OH

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(4) SPARTAN *Pro* (Version 1.03, Wavefunction Inc, 1999) was used as the computer-modeling software. Minimization was carried out using the ab initio 3-21(G*) basis set.

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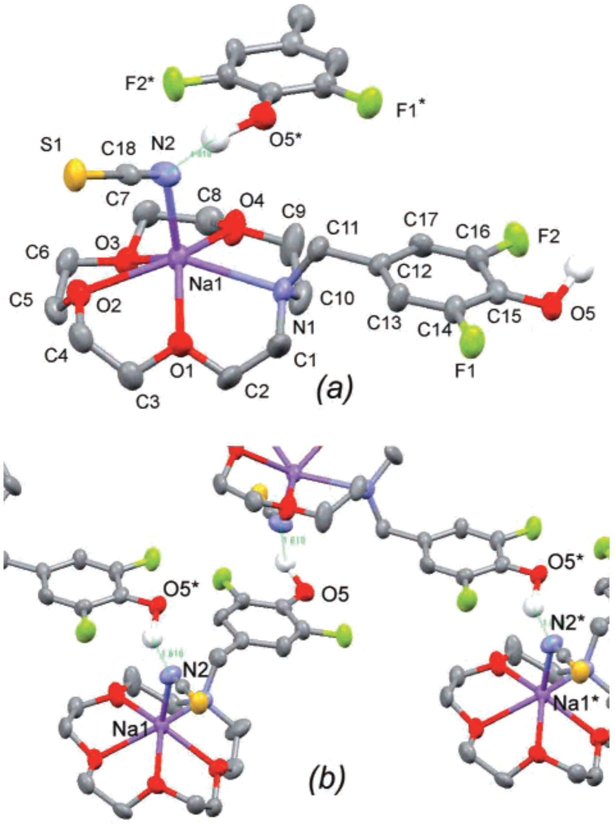

Figure 2. Ellipsoid display (a) and a partial magnified view of a packing diagram (b) of **5**-NaSCN showing thermal ellipsoids at 30% probability. Hydrogen atoms except the phenolic OH groups and water molecules are omitted.

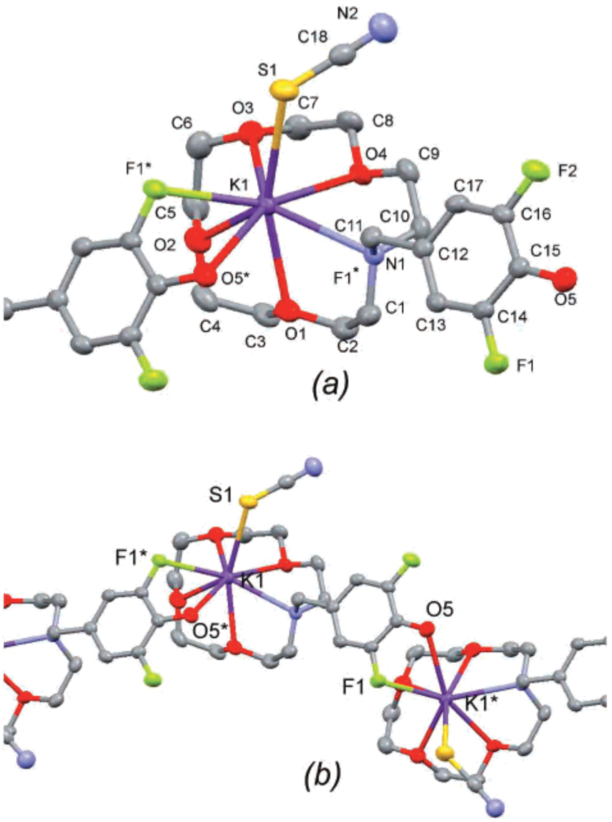

Figure 3. Ellipsoid display (a) and partial enlargement diagram (b) of **5**-KSCN showing thermal ellipsoids at 30% probability. Hydrogen atoms are omitted.

group and the water molecule. The **5**-LiSCN complex is the first instance for monoaza-15-crown-5/lithium complex in which the lithium ion incorporated in the crown ether ring.[8]

In the **5**-NaSCN complex (Figure 2a), the Na^+ ion is also six-coordinated by the four ring O atoms, the ring N atom, and the N atom of the thiocyanate anion. The Na1−O(ring), Na1−N1, and Na1−N2(SCN) distances are in the range 2.37(2)−2.503(11), 2.61(2), and 2.392(9) Å, respectively. The bond distances between the sodium ion and the donor atoms are comparable with those of the NaSCN complex with **1** having 3′,5′-dimethylbenzyl groups as a side arm.[3a] Interestingly, the sodium complex with **5** bearing a difluorobenzyl group is a $(1{:}1)_n$ polymer-like complex, which can be denoted as $[Na(\mathbf{5})SCN]_n$, bridged by hydrogen bonding between the phenolic OH group and the N2 atom of the SCN ion, although **1**-NaSCN formed a polymer-like $(1{:}1)_n$ complex which the O atom of the phenolic OH group in the side arm binds to the sodium ion incorporated in the cavity of the nearest-neighbor molecule.

The difference in the structures between the **1**-NaSCN and **5**-NaSCN complexes might be explained by atomic charges on the phenolic O atoms of the side arms. Table 1 shows Mulliken, electrostatic, and natural charges of 2,6-dimethylphenol and 2,6-difluorophenol by the B3LYP/6-31G* calculations.[9] As shown in Table 1, the calculated negative atomic charges on the O atom of 2,6-dimethylphenol are greater than those of 2,6-difluorophenol. Thus, the O atom of 2,6-dimethylphenol has more electrons than that of 2,6-difluorophenol. The calculation data suggest that the O atom of 2,6-dimethylphenol moiety of **1** would bind sodium ions more strongly than that of the 2,6-difluorophenol moiety of **5**.

In contrast, the K^+ ion in **5**-KSCN is eight-coordinated by the four ring O atoms, the ring N atom, the O5* atom of the phenolic OH group, and an F1* atom in the side arm of the nearest-neighbor molecule with the S atom of SCN^- as a counterion (Figure 3a). The complex is a polymer-like $(1{:}1)_n$ complex (Figure 3b), which can be denoted as $[K(\mathbf{5})\text{-}SCN]_n$. The K1−O (ring), K1−O5*, K1−N1, K1−S1, and K1−F1* bond lengths are in the range 2.7565(19)−2.7916(17), 3.028(2), 2.877(2), 3.25269(9), and 2.7831(16) Å, respectively. The K−O and K−N bond lengths are comparable with those of the potassium complex of the **1**-KSCN complex.[3a] The K−F bond length is also comparable with those of complexes including $CF{-}K^+$ contacts.[10]

As shown in the ORTEP diagrams (Figures 4 and 5), the Rb^+ and Cs^+ ions are eight-coordinated by the four ring O atoms, the ring N atom, the F atom in the side arm of the nearest-neighbor molecule, and with the two S atoms of SCN as counterions. The complexes are polymer-like $(2{:}2)_n$ complexes which are bridged by the F atom in the side arm, and are isomorphous. Interestingly, the O atoms of the

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(8) We carried out the document retrieval using ConQuest ver. 1.9 at the Cambridge Crystallographic Data Centre, 2007.

(9) Spartan 04, Wavefunction, Inc. Irvine, CA.

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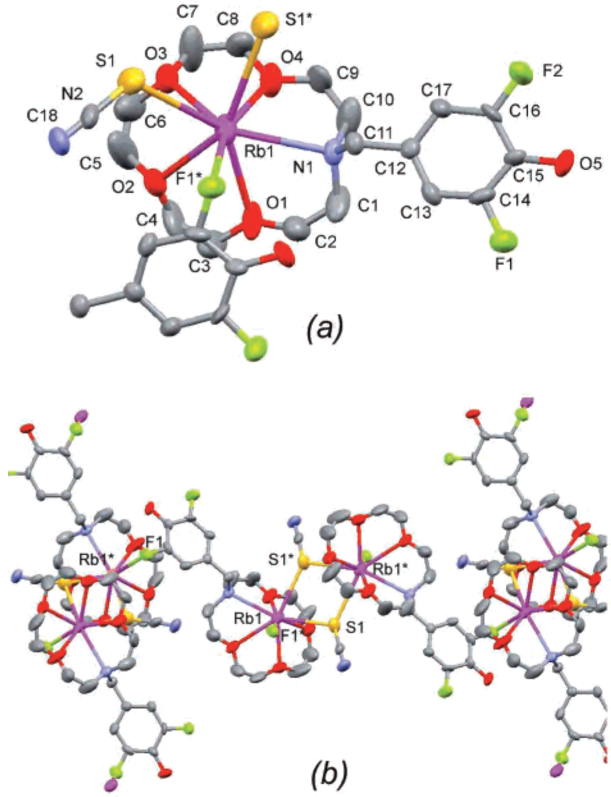

Figure 4. Ellipsoid display (a) and partial packing diagram (b) of **5**-RbSCN showing thermal ellipsoids at 30% probability. Hydrogen atoms are omitted.

phenolic OH groups in the side arms are not involved in the complex formation.

The Rb1−O (ring), Rb1−N1, Rb1−S1, Rb1−S1*, and Rb1−F1* bond distances are in the range 2.863(7)−2.975(9), 3.081(7), 3.411(3), 3.476(3), and 3.003(5) Å, respectively. It is important to note that the F−Rb$^+$ bond distance in **5**-RbSCN is classified as a short F−Rb$^+$ bond length which is a rare case.[10]

In **5**-CsSCN (Figure 5), the Cs1−O (ring), Cs1−N1, Cs1−S1, Cs1−S1*, and Cs1−F1* bond distances are in the range 3.038(7)−3.150(8), 3.214(7), 3.582(3), 3.641(3), and 3.202(5) Å, respectively. A cation−π contact is observed between the Cs1 and the C14* (aromatic ring carbon) of the nearest-neighbor molecule, and the distance is 3.623(9) Å. Werner et al.[11] reported that π-electron−Cs contacts between Cs ions and edge of mesityl groups were observed in cesium−triorganofluorometarate complexes, and the mean distances are in the range 3.367−3.761 Å. We believe that the Cs1 interacts with the C14 in the **5**-CsSCN complex. The Rb$^+$ and Cs$^+$ complexes with ligand **5** are denoted as $\{[\mathrm{Rb}(\mathbf{5})\mathrm{SCN}]_2\}_n$ and $\{[\mathrm{Cs}(\mathbf{5})\mathrm{SCN}]_2\}_n$, respectively.

To the best of our knowledge, this is the first instance for X-ray structures of five alkali metal complexes with a monoaza-15-crown-5 ether derivative.[12] A schematic drawing of the structures of these alkali metal complexes is shown in Figure 6.

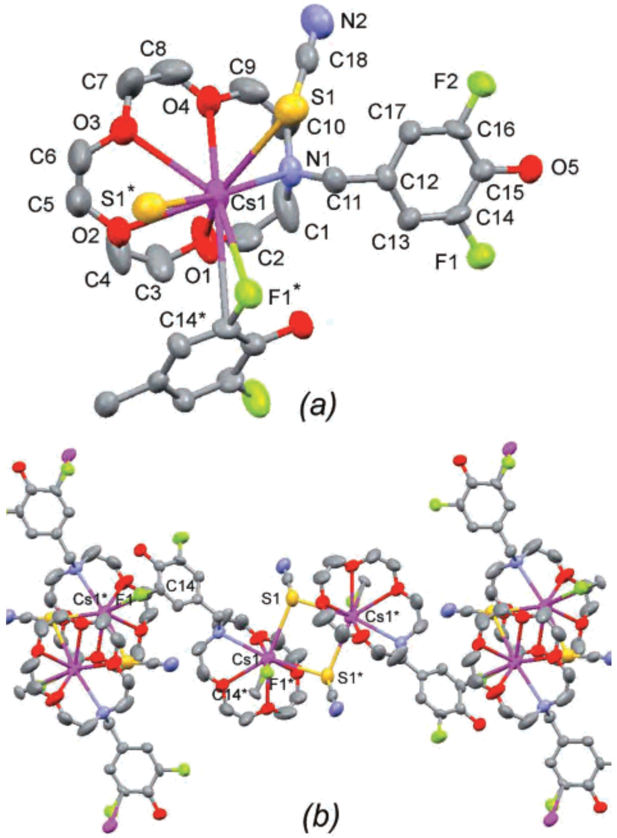

Figure 5. Ellipsoid display (a) and partial packing diagram (b) of **5**-CsSCN showing thermal ellipsoids at 30% probability. Hydrogen atoms are omitted.

Table 3. Log *K*, Δ*H* (kJ/mol), and *T*Δ*S* (kJ/mol) Values for the 1:1 Interaction of Ligand **5** with Metal Ions in Methanol Solution at 25 °C

alkali metal ion	log *K*	Δ*H*	*T*Δ*S*
Na$^+$	2.96 + 0.03	−16.5 ± 0.2	0.4
K$^+$	2.95 + 0.05	−23.1 ± 0.7	−6.3
Rb$^+$	2.79 + 0.06	−17.5 ± 0.4	−1.6
Cs$^+$	2.74 + 0.05	−8.2 ± 0.4	7.4

To investigate the complexation ability of **5** in solution, stability constants, *K*, and thermodynamic values (Δ*H* and *T*Δ*S*) were measured by titration calorimetry in methanol solution (Table 3). Interestingly, the log *K* values for Na$^+$ (2.96), K$^+$ (2.95), Rb$^+$ (2.79), and Cs$^+$ (2.74) were almost equal. Davidson et al. reported that log *K* values for the interactions of *N*-butyl-monoaza-15-crown-5 with Na$^+$ and K$^+$ ions are 3.22 and 2.99, respectively.[13] These log *K* values suggest that ligand **5** coordinates to the alkali metal cations not only by the crown ether moiety but also by the binding sites of the side arm because the log *K* value for Na$^+$ which fits to the cavity size of monoaza-15-crown-5 ether is not remarkably higher than that for the other alkali metal cations.[14] The Δ*H* and *T*Δ*S* values indicate the effects of the side arms. The Δ*H* and *T*Δ*S* values for the interactions of K$^+$−Cs$^+$ ions with ligand **5** were decreased and increased,

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(11) Werner, B.; Kräuter, T.; Neumüller, B. *Organometallics* **1996**, *15*, 3746.

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Table 4. MSCN-Induced Changes in ^{19}F NMR Chemical Shifts of 2,6-Difluorophenol and Ligand **5**[a]

	2,6-difluorophenol	**5**
chemical shift[b]	−135.92	−135.90
+1.0 NaSCN	+0.12	+0.72
+1.0 KSCN	+0.19	+0.83
+1.0 RbSCN	+0.14	+0.78

[a] Positive numbers show downfield shifts. [b] α,α,α-Trifluorotoluene (−63.72 ppm) was used as an internal standard.

respectively, with the cavity size. The less positive $T\Delta S$ for the Na^+ ion means that less conformation changes of the crown ring is required to accommodate the Na^+ ion.[13] The less negative and positive $T\Delta S$ values were observed in the Rb^+ and Cs^+ systems that the F atoms of the side arms interact with the metal cations incorporated in the nearest-neighbor molecules (Figures 4 and 5). Inoue et al. reported that the slope (α) of the enthalpy−entropy compensation (plot of $T\Delta S$ versus ΔH) indicates conformational changes of host compounds on complex formation.[15] The α value was calculated as 0.923 ($r^2 = 0.994$) from the plot of $T\Delta S$ versus ΔH. This α value is close to the average (0.89) of typical armed-crown ethers. The α value indicates that significant conformational changes would occur when the ligand forms complexes. Therefore, the log K values and the α value support the supposition that ligand **5** forms complexes with alkali metal cations by both the crown moiety and the side arm in solution.

Plenio and Diodone reported that the ^{19}F NMR chemical shift changes when fluorine atoms coordinate to metal cations in fluorine-containing azacrown ethers and cryptands.[5] The ^{19}F NMR titration experiments were carried out in a CD_3CN solution (Table 4) to determine F atom participation from the side arm. We used NaSCN, KSCN, and RbSCN salts for the ^{19}F NMR titration experiments. When 1.0 equiv of NaSCN, KSCN, and RbSCN were added to a CD_3CN solution of ligand **5**, the chemical shifts of the fluorine atoms next to the phenolic OH group shifted to lower field by about 0.7−0.8 ppm. These values are much greater than the 0.1−0.2 ppm shifts observed with the addition of 1.0 equiv of MSCN to a CD_3CN solution of 2,6-difluorophenol. These chemical shift changes strongly suggest that one or both fluorine atoms along with the oxygen atom of the phenolic OH group coordinate to the alkali metal cations incorporated in the crown part of a second armed-ligand to give polymer-like complexes in solution.

The complexation behavior of **5** was measured by FAB-MS. Figure 7 shows a FAB mass spectrum of **5**-LiSCN. In this spectrum, a fragment ion peak arising from $[\mathbf{5} + Li]^+$ was observed at 368 as a base peak. Higher fragment ion peaks, $[\mathbf{5} + 2Li - H]^+$, $[\mathbf{5} + 2Li + LiSCN - H]^+$, $[2(\mathbf{5} + Li) + Li - 2H]^+$, and $[2(\mathbf{5} + Li) + LiSCN + Li - 2H]^+$ were observed at 374 (15.0%), 439 (2.0%), 741 (1.2%), and 806 (0.9%), respectively. The FAB-MS of all complexes are summarized in the Supporting Information. The fragment ion peaks of the alkali metal thiocyanate complexes along with normalized intensities (A−E) are summarized in Table 5. In all complexes, fragment ion peaks, $[\mathbf{5} + M]^+$, $[\mathbf{5} + 2M - H]^+$, $[\mathbf{5} + 2M + MSCN - H]^+$, $[2(\mathbf{5} + M) + M - 2H]^+$, and $[2(\mathbf{5}^- + M) + MSCN + M - 2H]^+$ were assigned nicely. Interestingly, the ratios between sum of the intensities of the fragment ion peaks and the intensities of the base peaks, (B + C + D + E)/(A), increase according to the size of alkali metal ions: **5**-LiSCN (0.19) < **5**-NaSCN (0.27) < **5**-KSCN (0.36) < **5**-RbSCN (0.58) < **5**-CsSCN (0.99). The FAB-MS data suggests that larger alkali metal ions tend to form more stable polymer-like complexes.

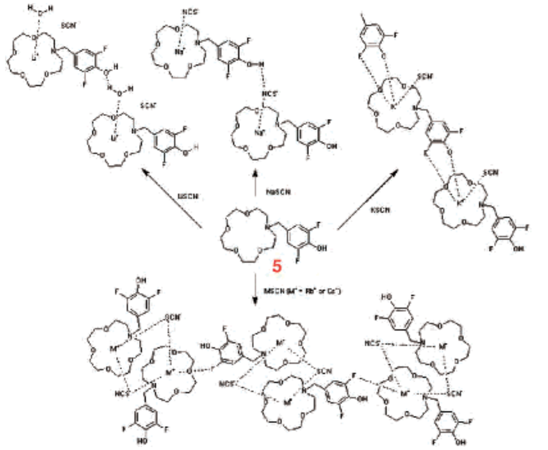

Figure 6. Schematic drawing of the structures of alkali metal thiacyanate complexes with **5**.

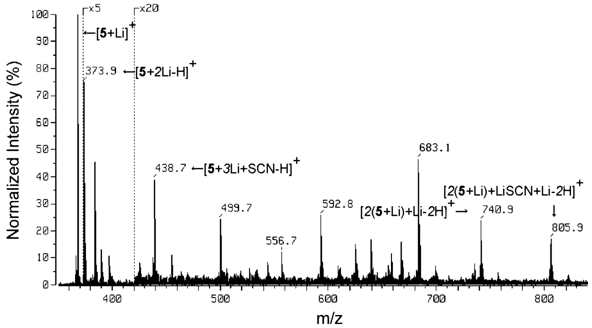

Figure 7. FAB-MS of **5**-LiSCN (matrix: *m*-nitrobenzylalcohol).

Cold ESI-MS is a powerful tool in the determination of structures of unstable complexes.[3k,3n,16] Figure 8 shows observed ion peaks and theoretical ion distributions for $[\mathbf{5} + M + CH_3OH]^+$ and $[\mathbf{5} + 2M + 2CH_3OH - H]^+$ of the alkali metal complexes with **5** (0.25 mmol/L in methanol; nitrogen as a nebulizer gas; nebulizer gas temperature = 20 °C). The fragment ion peaks with one methanol molecule, $[\mathbf{5} + M + CH_3OH]^+$, of **5**-LiSCN, **5**-NaSCN, **5**-KSCN, **5**-RbSCN, **5**-CsSCN were observed at 400, 416, 432, 478, and 526, respectively. In contrast, the fragment ion peaks with two methanol molecules, $[\mathbf{5} + 2M + 2CH_3OH - H]^+$, were observed at 439 in the lithium complex. The results of the cold ESI-MS clearly suggest that **5**-LiSCN binds solvents such as methanol or water molecules tightly more than the other alkali metal complexes. Therefore, **5**-LiSCN would

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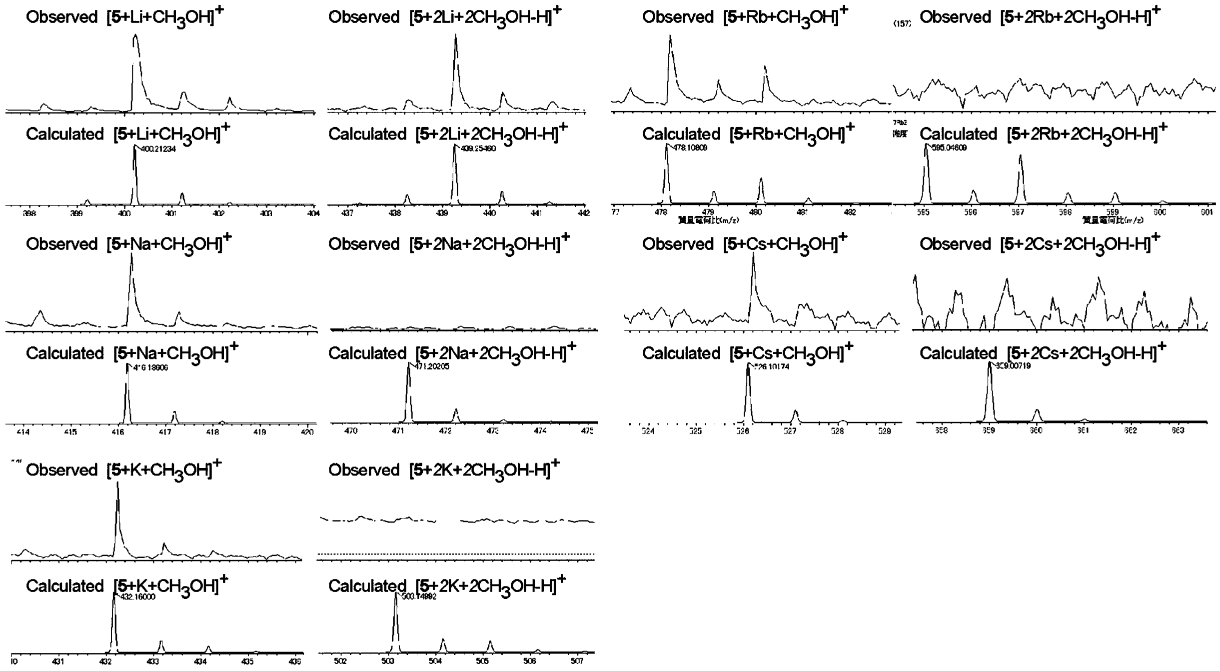

Figure 8. Observed ion peaks and theoretical ion distributions of **5**-LiSCN, **5**-NaSCN, **5**-KSCN, **5**-RbSCN, and **5**-CsSCN.

Table 5. Fragment Ion Peaks and Intensities of **5**-MSCN Complexes (Normalized Intensities 10%))

complex	$[\mathbf{5} + M]^+$ (A)	$[\mathbf{5} + 2M - H]^+$ (B)	$[\mathbf{5} + 2M + MSCN - H]^+$ (C)	$[2(\mathbf{5}^- + M) + M - 2H]^+$ (D)	$[2(\mathbf{5}^- + M) + MSCN + M - 2H]^+$ (E)	ratio[a]
5-LiSCN	367 (10.8%)	373 (2.9%)	438 (0.5%)	740 (0.4%)	805	
	368 (100%)	374 (15.0%)	439 (2.0%)	741 (1.2%)	806 (0.9%)	0.19
5-NaSCN	384 (100%)	406 (20.4%)	486 (4.2%)	789 (1.0%)	870 (1.2%)	0.27
5-KSCN	400 (100%)	438 (28.4%)	534 (6.1%)	837 (1.4%)	935 (0.3%)	0.36
	402 (10.3%)	440 (5.0%)	536 (1.7%)	839 (0.4%)	937 (0.1%)	
5-RbSCN	446 (100%)	529 (41.7%)	672 (6.0%)	975 (0.5%)	1119 (0.2%)	0.48
	448 (40.2%)	531 (32.9%)	674 (7.5%)	977 (0.6%)	1121 (0.2%)	
5-CsSCN	493 (100%)	626 (85.7%)	816 (11.5%)	1119 (1.4%)	1309 (0.8%)	0.99

[a] Ratio = (B + C + D + E)/A. Measured by the FAB method using *m*-nitrobenzylalcohol as a matrix. The intensity of each peak was normalized on the basis of that of $[\mathbf{5} + M]^+$. Natural abundances of $^6Li/^7Li$, $^{39}K/^{41}K$, and $^{85}Rb/^{87}Rb$ are 7.42:92.58, 93.08:6.91, and 72.15:27.85, respectively.

form a polymer-like $(1:1)_n$ complex bridged by hydrogen bonding between the phenolic OH group and the water molecule.

In conclusion, we have demonstrated that the fluorine atom in the side arm of **5** coordinates to alkali metal ions incorporated in a second ligand in the solid state and in solution. The first example for a fluorine-bridged polymer-like complex has potential for the design of new supramolecular systems.

Experimental Section

Ligand **5** (0.01 mmol) in acetonitrile (1 mL) was reacted with each of the alkali metal thiocyanates (0.01 mmol) in methanol (1 mL). Crystals of the corresponding alkali metal thiocyanate complex were obtained quantitatively on evaporation of the solvent. The crystals were dried with an Abderhalden's dryer (50 °C, 0.5 Torr) before X-ray analyses. **5**-LiSCN: Anal. Calcd for $C_{17}H_{25}NF_2O_5$-$LiSCN\cdot 1.75H_2O$: C, 47.21; H, 6.27; N, 6.12. Found: C, 47.15; H, 6.03; N, 6.49. **5**-NaSCN: Anal. Calcd for $C_{17}H_{27}NF_2O_6NaSCN\cdot 0.5H_2O$: C, 47.89; H, 5.80; N, 6.21. Found: C, 47.55; H, 5.59; N, 6.46. **5**-KSCN: Anal. Calcd for $C_{17}H_{25}NF_2O_5KSCN$: C, 47.15; H, 5.49; N, 6.11. Found: C, 47.35; H, 5.50; N, 6.42. **5**-RbSCN: Anal. Calcd for $C_{17}H_{25}NF_2O_5RbSCN$: C, 42.82; H, 4.99; N, 5.55. Found: C, 42.72; H, 5.05; N, 5.53. **5**-CsSCN: Anal. Calcd for $C_{17}H_{25}NF_2O_5CsSCN\cdot H_2O$: C, 37.90; H, 4.77; N, 4.91. Found: C, 37.90; H, 4.45; N, 5.27.

X-ray Structure Determination. The crystals of alkali metal thiocyanate complexes with **5** were mounted on the tip of a glass fiber. All measurements of **5**-MSCN (M = Li, Na, K, Rb, and Cs) were made at 298 K on a Rigaku AFC5S four-circle diffractometer with graphite-monochromated Mo Kα radiation (0.71069 Å) and a 12 kW 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 2θ value of 50° or 55.0°. All intensities were corrected for Lorentz and polarization effects. The structure was solved by direct methods (SIR 92).[17] The non-hydrogen atoms were refined anisotropically. The coordinates of all hydrogen atoms were calculated at ideal positions and were refined. Neutral atom scattering factors were those of Cromer and Weber.[18] Anomalous dispersion effects were included in Fc;[19] the values for $\Delta f'$ and

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Table 6. Crystal and Selected Experimental Data for **5**-MSCN Complexes

	5-LiSCN	**5**-NaSCN	**5**-KSCN	**5**-RbSCN	**5**-CsSCN
formula	$C_{18}H_{27}N_2O_6F_2SLi$	$C_{18}H_{25}N_2O_5F_2SNa$	$C_{18}H_{25}N_2O_6F_2SK$	$C_{18}H_{25}N_2O_5F_2SRb$	$C_{18}H_{25}N_2O_5F_2SCs$
M	444.42	442.45	458.56	504.93	552.37
T/K	296	296	296	296	296
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$ (No. 14)	$P2_1$(No. 4)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)
a/Å	8.587(5)	7.900(3)	8.564(2)	8.875(3)	8.95(1)
b/Å	15.613(7)	13.041(4)	16.354(2)	18.627(4)	18.30(2)
c/Å	16.838(4)	10.909(4)	15.510(2)	13.359(3)	13.95(1)
β/°	99.42(3)	107.07(3)	93.81(2)	93.72(2)	94.51
U/Å^3	2226(1)	1074.3(6)	2167.6(7)	2203.8(1)	2278(3)
Z	4	2	4	4	4
D_{calcd}/g cm^{-3}	1.325	1.368	1.351	1.522	1.610
μ(Mo Kα)/cm^{-1}	1.97	2.19	3.89	23.84	17.63
reflns corrected	5644	2589	5331	4294	5037
unique reflns (R_{int})	5107 (0.030)	2406 (0.061)	5152 (0.042)	4024 (0.062)	4551 (0.044)
used [all data], N_o	5099	2402	4966	3881	4542
R_F	0.107	0.140	0.114	0.181	0.122
R_w [all data]	0.175	0.165	0.136	0.175	0.166
R^a [$I > 2.0\sigma(I)$]	0.061	0.058	0.048	0.060	0.058
no. of params, N_p	271	263	262	262	262
GOF	1.22	1.02	1.31	1.03	1.13
T_{min}, T_{max}	0.53, −0.53	0.80, −0.67	0.26, −0.36	1.61, −0.79	1.16, −1.26

^{a} $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o{}^2]^{1/2}$, $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

$\Delta f''$ were those of Creagh and McAuley.[20] The values for the mass attenuation coefficients are those of Creagh and Hubbell.[21] All calculations were made using the Texsan crystallographic software package of Molecular Structure Coropration.[22] The crystallographic refinement parameters of the alkali metal thiocyanate complexes with **5** are summarized in Table 6.

Measurements of log *K*, Δ*H*, and *T*Δ*S* Values. Log K, ΔH, and $T\Delta S$ values were determined as described[23] in MeOH at 25.0 ± 0.1 °C by titration calorimetry using a Tronac Model 450 calorimeter equipped with a 20 mL reaction vessel. The metal cation solutions (0.08−0.12 mol/L) were titrated into the armed-azacrown ether solutions (1.3×10^{-3}−2.6×10^{-3} M), and the titrations were carried out to a 2-fold excess of the metal cations.

^{1}H NMR Titration Experiments. Titration experiments were carried out at 298 K by addition of 0.5, 0.75, 1.0, 1.5, and 2.0 equiv of MSCN (NaSCN and KSCN: 0.001 mmol/μL in CD_3CN; RbSCN: 0.001 mmol/μL in CD_3CN/D_2O (95:5)) to 2,6-difluorophenol or ligand **5** (0.01 mmol/ 0.65 mL in CD_3CN).

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Supporting Information Available: X-ray data (CIF format) of **5**-LiSCN, **5**-NaSCN, **5**-KSCN, **5**-RbSCN, and **5**-CsSCN, FAB-MS, and cold ESI-MS data. This material is available free of charge via the Internet at http://pubs.acs.org.

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