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Polymer-like complexes bridged by a fluorine substituent of the side arm in the 3′,5′-difluoro-4′-hydroxybenzyl-armed monoaza-15-crown-5 ether

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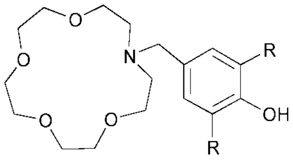
3′,5′-Difluoro-4′-hydroxybenzyl-armed monoaza-15-crown-5 ethers which form fluorine-bridged polymer-like complexes with MSCN in the solid state and in solution are reported.

Recently, we reported the molecular structure of alkali metal complexes with armed-monoazacrown ethers having 3′,5′-dialkyl-4′-hydroxybenzyl groups (alkyl = Me, *i*-Pr and *t*-Bu).[1] The molecular structure of the RbSCN complexes with these ligands was systematically changed depending upon the size of the R groups at positions 3′ and 5′ in the side arm (**1** (R = Me), a polymer-like $(1:1)_n$ complex; **2** (R = *i*-Pr), a mixture of 1:1 and polymer-like $(1:1)_n$ complexes; **3** (R = *t*-Bu), a dimeric 1:1 complex). To further investigate the electronic and steric effects of the substitutents next to the phenolic OH group in the side arm on the structure of the complexes, we have prepared a new armed-azacrown ether having fluorine atoms at positions 3′ and 5′ in the side arm (**4**). Computer modeling experiments suggest that the oxygen atom of the phenolic OH group cannot bind to metal cations incorporated into the crown part of the molecule so that the ligand can form polymer-like complexes with alkali metal cations.† It was also expected that the ligand would form polymer-like complexes using the electron donating properties of fluorine atoms next to the phenolic OH group.[2] Here we report the structures of polymer-like complexes of ligand **4** which are bridged by the fluorine atoms in the side arm.



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

New armed-azacrown ether, **4**,‡ was prepared by the Mannich reaction of *N*-methoxymethylmonoaza-15-crown-5 ether with 2,6-difluorophenol in benzene by the method previously reported.[3] Two alkali metal thiocyanate complexes, **4-KSCN** and **4-RbSCN**, were obtained (host–guest ratio = 1:1) as single crystals.§

The structures of **4-KSCN** and **4-RbSCN** complexes have been determined by X-ray analysis.¶ As shown in Fig. 1(*a*), the K^+ ion in **4-KSCN** is eight-coordinated by four ring O atoms, the ring N atom, and the O* atom of the phenolic OH group and an F* atom in the side arm of the nearest-neighbor molecule with the S atom of SCN^- as a counter ion. The complex is a polymer-like $(1:1)_n$ complex. The K(1)–O (ring), K(1)–O(5*), K(1)–N(1), K(1)–S(1) and K(1)–F(2*) bond lengths are in the range 2.757(2)–2.792(2), 3.028(2), 2.877(2), 3.253(1) and 2.783(2) Å, respectively. The K–O and K–N bond lengths are comparable with those of the potassium complex of the lariat monoaza-15-crown-5 ethers.[4] The K–F bond length is also comparable with those of complexes including CF–K^+ contacts.[5] Fig. 1(b) shows the ORTEP view of the **4-RbSCN** complex. The Rb^+ ion is also eight-coordinated by four ring O atoms, the ring N atom, the F atom in the side arm of the nearest-neighbor molecule with the two S atoms of SCN^- as counter ions. The complex is a polymer-like $(2:2)_n$ complex which is bridged by an F atom in the side arm. Interestingly, the O atom of the phenolic OH group in the side arm is not involved in the complex formation. The Rb(1)–O (ring), Rb(1)–N(1), Rb(1)–S(1), Rb(1)–S(1*) and Rb(1)–F(2*) bond lengths are in the range 2.860(7)–2.972(8), 3.087(7), 3.412(3), 3.475(3) and 3.001(6) Å, respectively. It is important to note that the F–Rb^+ bond length in **4-RbSCN** complex is classified as a short F–Rb^+ bond length which is a rare case.[5]

To investigate the complexation ability of ligand **4** in solution, stability constants K and thermodynamic values (ΔH and $T\Delta S$) were measured by titration calorimetry in MeOH solution (Table 1).‖ Interestingly, the log K values for Na^+ (log K = 2.96), K^+ (log K = 2.95), Rb^+ (log K = 2.79) and Cs^+ (log K = 2.74) were almost equal. The log K values suggest that ligand **4** coordinates to the alkali metal cations not only by the crown ether moiety but also by the binding sites of the side-arm,

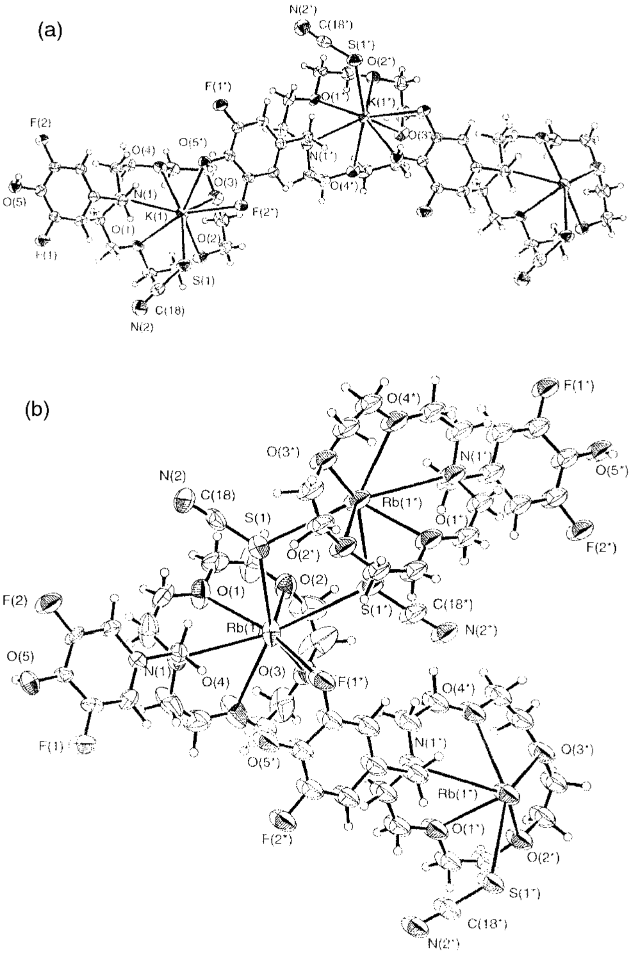


Fig. 1 The ORTEP diagrams of (a) **4-KSCN** and (b) **4-RbSCN**. Thermal ellipsoids are drawn at the 30% probability level.

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Table 1 Log K, ΔH(kJ mol^{-1}), and $T\Delta S$(kJ mol^{-1}) values for the 1:1 interaction of ligand **4** with metal cations in methanol solution at 25 °C

Cation	log K	ΔH	$T\Delta S$
Na^+	2.96 ±0.03	−16.5 ±0.2	−1.4
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

because the log K value for Na^+ which fits to the hole size of the monoaza-15-crown-5 ether is not remarkable higher than that for the other alkali metal cations.[6] Inoue and Gokel 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.[7] The α value was calculated as 0.923 ($r^2 = 0.994$) from the plot of $T\Delta S$ versus ΔH, which is close to the average (0.89) of typical armed-crown ethers, and 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 **4** forms complexes with alkali metal cations by both the crown moiety and the side arm.

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.[2] The ^{19}F NMR titration experiments were carried out in a CD_3CN solution (Table 2) to determine F atom participation from the side-arm. When 1.0 equiv. of NaSCN, KSCN and RbSCN were added to a CD_3CN solution of ligand **4**, the chemical shifts of the fluorine atoms next to the phenolic OH group shifted to a 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.

Table 2 MSCN Induced changes in ^{19}F NMR chemical shifts of 2,6-difluorophenol and **4**^{a}

	2,6-Difluorophenol	4
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} 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^{-1} in CD_3CN; RbSCN: 0.001 mmol μL^{-1} in CD_3CN–D_2O (95:5)) to 2,6-difluorophenol or ligand **4** (0.01 mmol, 0.65 mL in CD_3CN). Positive numbers show down field shifts. ^{b} α,α,α-Trifluorotoluene (δ −63.72) was used as an internal standard.

In conclusion, we have demonstrated that the fluorine atoms in the side arm of ligand **4** coordinate to alkali metal cations incorporated in a second ligand in the solid state and in solution. This first example for a fluorine-bridged polymer-like complex has potential for the design of new supramolecular systems. Further studies of the new armed-azacrown ethers are in progress.

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Notes and references

† 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*).[8]

‡ A mixture of *N*-methoxymethylmonoaza-15-crown-5 ether (1.0 mmol) and 2,6-difluorophenol (1.0 mmol) in absolute benzene (20 ml) was refluxed under a nitrogen atmosphere for 24 h. 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 ligand **4**: ^{1}H NMR ($CDCl_3$): δ 6.81 (d, 2H, J_{HF} = 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 $C_{17}H_{25}F_2NO_5{\cdot}0.75H_2O$: C, 54.46; H, 7.12; N, 3.74%. Found: C, 54.62; H, 7.48; N, 3.87%.

§ Ligand **4** (0.01 mmol) in MeCN (1 mL) was reacted with the alkali metal thiocyanate (0.01 mmol) MeOH (1 mL). After the solvent had evaporated, the crystals were recrystallized from MeCN. The crystals were dried with an Abderhalden's dryer (50 °C, 0.5 Torr). The elemental analyses of these complexes are as follows: **4**-KSCN: Anal. calcd. for $C_{17}H_{25}F_2NO_5$-KSCN: C, 47.15; H, 5.49; N, 6.11%. Found: C, 47.35; H, 5.50; N, 6.42%. **4**-RbSCN: Anal. calcd. for $C_{17}H_{25}F_2NO_5{\cdot}$RbSCN: C, 42.82; H, 4.99; N, 5.55%. Found: C, 42.72; H, 5.05; N, 5.53%.

¶ *Crystal data* for $C_{18}H_{25}N_2O_5SF_2K$, **4**-KSCN: M = 458.56, monoclinic, a = 8.564(2), b = 16.354(2)°, c = 15.510(2) Å, β = 93.81(2)°, U = 2167.6(7) Å^3, T = 295 K, space group $P2_1/n$ (no. 14), Z = 4, μ(Mo-Kα) = 3.89 cm^{-1}, 5331 reflections measured, 5152 unique (R_{int} = 0.042) which were used in all calculations. R_1 = 0.048 [$I > 2\sigma(I)$], R = 0.114 and Rw = 0.136 [all data]. Crystal data for $C_{18}H_{25}N_2O_5SF_2Rb$, **4**-RbSCN: M = 504.93, monoclinic, a = 8.875(3), b = 18.627(4), c = 13.359(3) Å, β = 93.72(2)°, U = 2203.8(10) Å^3, T = 295 K, space group $P2_1/n$ (no. 14), Z = 4, μ(Mo-Kα) = 23.84 cm^{-1}, 4294 reflections measured, 4024 unique (R_{int} = 0.062) which were used in all calculations. R_1 = 0.060 [$I > 2\sigma(I)$], R = 0.180 and Rw = 0.156 [all data]. CCDC 182/1699. See http//www.rsc.org/suppdata/cc/b0/b003451g/ for crystallographic files in .cif format. X-Ray data are available as supplementary data from BLDSC (SUPPL. NO. 57710, pp. 27) or the RSC Library. See Instructions for Authors available *via* the RSC web page (http://www.rsc.org/authors).

‖ Log K, ΔH, and $T\Delta S$ values were determined as described[9] 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 M) 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 two-fold excess of the metal cations.

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