

Diaza-18-crown-6 Ethers Containing Partially-fluorinated Benzyl Sidearms: Effects of Covalently Bonded Fluorine on the Alkali Metal Complexation

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The stability constants for the diaza-18-crown-6 ethers **2-6** and alkali metal cations (Na^+ , K^+ , Rb^+ and Cs^+) were determined using potentiometry in 95% methanol. For each metal ion the stability constants of the partially-fluorinated ligands **3-6** were larger than that of the non-fluorinated ligand **2**, which might reflect an interaction between fluorine atoms and alkali metal cations. The stability constant of the ligand **4** was larger than that of the ligand **5** for each metal cation tested. This finding was also supported by the results of cation-induced chemical shifts in ^1H -, ^{19}F -NMR and extraction experiment. The potentiometry and NMR results as well as the X-ray crystal structures revealed that the position and number of fluorine atoms in the benzyl side arms was crucial for the enhanced interaction between a ligand and an alkali metal.

Key Words : Diaza-18-crown-6 ethers, Partially-fluorinated benzyl sidearms, Alkali metal cation complexation, Stability constant

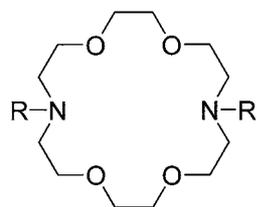
Introduction

Since Glusker's research¹ was reported in the early 1980s, coordination chemistry between covalently bonded fluorine atoms and metal cations has been attracting much attention. In the early stage, X-ray structures of complexes revealed the possible interaction between C-F and alkali/alkaline earth metal in a crystalline state. Such interaction in a solution has been studied from the late 1990s, however, the published results have been limited to a few.² The research results thus far have led us to believe that a covalently bonded fluorine atom behaves like an efficient δ donor for groups I and II hard metal ions.

Crown ethers and cryptand are also the well known ligands for various metal cations.³ Diaza-crown ethers have especially been focused on as useful ligands because of their versatility and applicability. The property of diaza-crown ether can be modified by altering its sidearms as well as macrocycle itself. The metal ion complexing ability of diaza-crowns can be significantly improved by functionalizing them with ligating sidearms.⁴ Attachment of appropriate sidearms enhances the complexing ability so that the double armed diaza-crowns may react as pseudo-cryptand. Izatt *et al.* recently prepared an 8-hydroxyquinoline containing diaza-18-crown-6 ligand, and they found that its sidearms form a pseudo-macro ring through π -stacking between the electron-rich chlorophenol and the electron-deficient pyridine moiety.⁵

Thus, we were also interested in finding out if diaza-crown ethers containing partially-fluorinated sidearms could have an extra interaction between the fluorine atoms and a metallic guest. In this study, the diaza-18-crown-6 ethers containing partially-fluorinated benzyl sidearms **3-6** were

synthesized, and their complexation with alkali metal cations were scrutinized. The unsymmetric ligand **3** containing electron-rich benzyl and electron-poor pentafluorobenzyl sidearms was prepared in the hope of forming an extra pseudo-ring through π -stacking. The symmetric ligands **4-6** with partially-fluorinated benzyl sidearms were also synthesized. The complex composition ratio between the synthesized ligands **2-6** and alkali metals (Na^+ , K^+ , Rb^+ and Cs^+) was examined by NMR titration and conductivity methods. The protonation and stability constants were determined by potentiometric titrations, and the metal complexing tendency of synthesized ligands was also evaluated using a solvent extraction method. X-ray crystal structures of the complexes **4-KSCN**, **5-KSCN** and **6-KSCN** have been analyzed, and the effect of fluorine atoms in the ligands **3-6** on the process of coordination with alkali metal cations is discussed.



- 1: R = R' = H
- 2: R = R' = benzyl
- 3: R = benzyl, R' = pentafluorobenzyl
- 4: R = R' = 2,6-difluorobenzyl
- 5: R = R' = 3,5-difluorobenzyl
- 6: R = R' = pentafluorobenzyl

Figure 1. Diaza-18-crown-6 crown ethers with various sidearms.

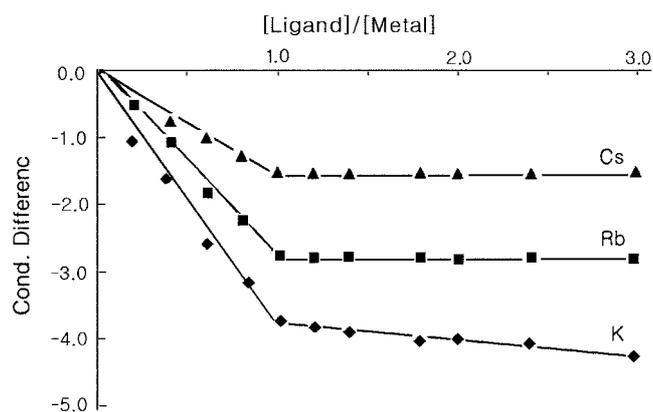


Figure 2. The equivalent conductance differences versus the ligand **2** to metal mole ratios in CH_3OH at 25°C .

Results and Discussion

The complex composition ratio between the ligand **2** and metal ions (K^+ , Rb^+ and Cs^+) was determined by checking the conductance of methanol solution in various ratios of $[\text{L}]/[\text{M}^+]$. The equivalent conductance differences between ligand/metal salt solutions and the pure metal salt solution were plotted against the ligand to metal ratios (Figure 2). The inflection points appeared at $[\text{L}]/[\text{M}^+]=1$, which proves that the ligand **2** forms a complex with metal cations by 1 : 1.

The partially-fluorinated ligands **3-6** were synthesized by the known procedure⁶ and examined by $^1\text{H-NMR}$ in various $[\text{K}^+]/[\text{L}]$ ratios. In Figure 3, typical $^1\text{H-NMR}$ spectra of the ligand **4** in various $[\text{K}^+]/[\text{L}]$ ratios are shown.

The cation-induced chemical shifts (CIS) of $^1\text{H-NMR}$ were evaluated and plotted against the $[\text{M}^+]/[\text{L}]$ ratios as shown in Figure 4. The CIS inflection points appeared when the metal to ligand mole ratio reached 1 : 1. This result indicates that the complexes form in the ratio 1 : 1 between the metal ions (K^+ and Cs^+) and the ligands **4-6**. The CIS of H_a , H_b and H_c

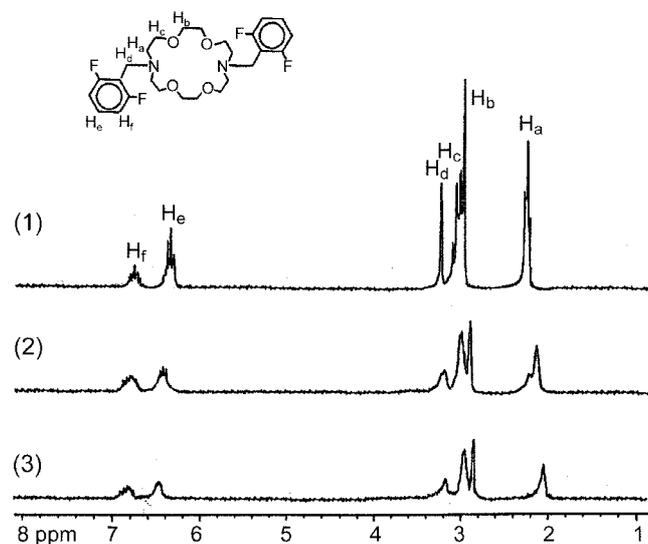


Figure 3. $^1\text{H-NMR}$ spectra of the ligand **4** in various $[\text{K}^+]/[\text{L}]$ ratios: (1) free ligand (2) 0.43 (3) 1.00.

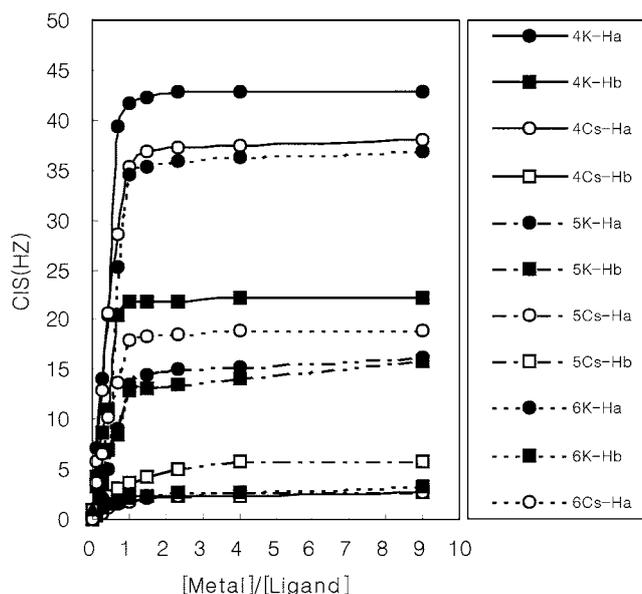


Figure 4. The cation-induced chemical shifts of the ligands **4-6** in various $[\text{M}^+]/[\text{L}]$ ratios.

in the process of complexation always revealed positive values. The H_a , H_b and H_c signals in a complex were shifted into up-field in contrast to those in a free ligand. The proton signals of ligands had a tendency to get broader when metal salts are added. These phenomena were ascribed to the result of anisotropic effects and also to the reduction of conformational flexibility by encapsulating a cation in the aza-crown ring.⁷ On the other hand, small down-field shifts of the aromatic protons H_e and H_f of **4** were noticed when metal cations (K^+ and Cs^+) were added to their solutions. This result can be explained in terms of the electron-donation interaction of aromatic rings and/or fluorine atoms with cations. It is also interesting to note that the CIS of H_a , H_b and H_c for the complex **4-K**⁺ were respectively larger than those of the complex **4-Cs**⁺. This fact suggests that the dative bond in the complex **4-K**⁺ might be stronger than that in the complex **4-Cs**⁺. Also, the ligand **4** revealed larger CIS values in $^1\text{H-NMR}$ titrations with alkali metal ions than the ligand **5**.

Table 1 lists the protonation constants for the synthesized ligands containing partially-fluorinated side arms evaluated using potentiometry. The log values of protonation constants for the ligand **2** were $\log K_{\text{H1}} = 8.81$, $\log K_{\text{H2}} = 7.55$. These values were smaller than those ($\log K_{\text{H1}} = 8.94^8$, $\log K_{\text{H2}} = 7.81^8$) of 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (**1**)

Table 1. Protonation constants for the ligands **2-6** in 95% methanol solution at 25°C and $\mu = 0.01 \text{ M } (\text{CH}_3)_4\text{NCl}$

Ligands	$\log K_{\text{H1}}$	$\log K_{\text{H2}}$
2	8.81	7.55
3	8.60	6.54
4	8.50	6.45
5	8.40	6.35
6	8.38	5.29

Table 2. The stability constants for the ligands 2-6 and alkali metal cations in 95% ethanol solution at 25 °C and $\pi=0.01$ M $(\text{CH}_3)_4\text{NCl}$

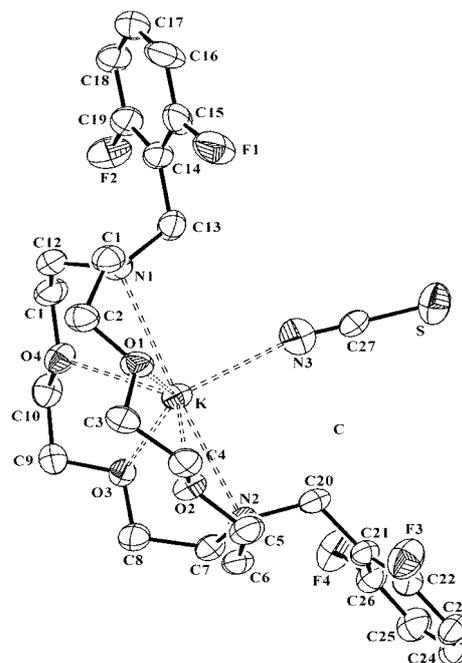
Ligands	Metal	Stability Constants (log K_{ML^+})			
		Na ⁺	K ⁺	Rb ⁺	Cs ⁺
2		2.52 (2.68 ⁸)	3.53 (3.38 ⁸)	2.80	2.23
3		—	3.64	3.04	2.44
4		2.73	3.94	3.17	2.92
5		2.57	3.55	2.97	2.49
6		2.60	3.79	2.93	2.61

with no arms, which was attributed to the steric hindrance by sidearms.

The stability constants for the ligands 2-6 and alkali metals were also measured by potentiometry and listed in Table 2. The stability constants of all the ligands were in the order of $\text{K}^+ > \text{Rb}^+ > \text{Cs}^+ > \text{Na}^+$. The size similarity between the cavity of diazacrown (1.34-1.43 Å) and potassium ion (1.38 Å) might explain the largest stability constant with K^+ . The stability constants for the partially-fluorinated ligands 3-6 and metal ions were larger than those for the non-fluorinated ligand 2, which demonstrates an extra interaction between fluorine atoms and metal cation. Interestingly, the stability constants for the ligands 4-6 and any metal cations tested were in the order of $4 > 6 > 5 > 2$. It is reasonable to assume that the *ortho*-positioned fluorine atoms in the ligand 4 make a stronger coordination with the metal ion captured in a macrocycle than the *meta*-positioned fluorine atoms in the ligand 5. This is also supported by the fact that the ligand 4 revealed a larger absolute CIS value in ^{19}F -NMR titrations with Cs^+ than the ligand 5. (-264 vs -36 in the metal to ligand mole ratio of 1.00) It is also reasonable to postulate that the *ortho*-positioned fluorine atoms in the ligand 6 make a weaker coordination with a metal ion than those in the ligand 4 because of the presence of neighboring electronegative fluorine atoms in 6. However, no decisive evidence could be found for the formation of extra pseudo macro-ring

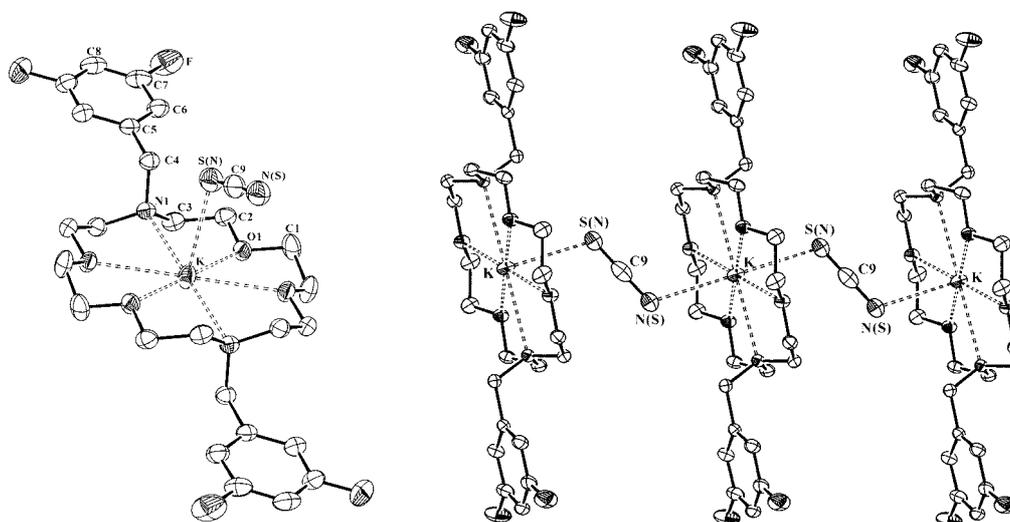
Table 3. Extraction percentages of alkali metal cations by the ligands 4-6

Ligands	Metal		
	K ⁺	Rb ⁺	Cs ⁺
2	19.7	8.0	5.7
4	35.2	16.9	6.6
5	8.3	2.2	2.1
6	23.1	8.9	6.6

**Figure 5.** An ORTEP drawing of the complex 4-KSCN.

through π -stacking of sidearms of the ligand 3.

Extraction⁶ of metal picrates by the ligands 2 and 4-6 was performed, and the results are summarized in Table 3. The selectivity is in the order of $\text{K}^+ > \text{Rb}^+ > \text{Cs}^+$ for all the ligands tested, and this order is exactly the same as that in the

**Figure 6.** ORTEP drawings of the complex 5-KSCN and its polymeric structure.

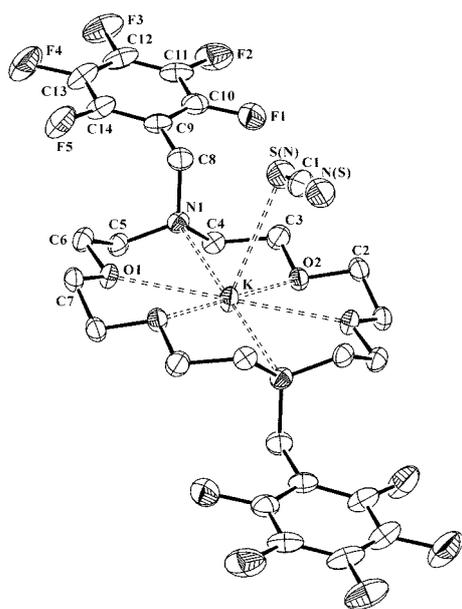


Figure 7. An ORTEP drawing of the complex **6-KSCN**.

stability constants. The extraction efficiency of ligands is in the order of **4** > **6** > **2** > **5**. The order of extraction efficiency is also similar to that of stability constants except the order of **2** and **5**.

The X-ray crystal structures of the complexes **4-KSCN** (Fig. 5), **5-KSCN** (Fig. 6) and **6-KSCN** (Fig. 7) were analyzed. For the structural analysis of **5-KSCN** and **6-KSCN**, the X-ray data were refined in consideration of the coordination disorder such as K-S-C-N-K' and K-N-C-S-K'. The X-ray data collection and structure solution parameters

are listed in Table 4, together with standard discrepancy indices, *R* and *wR*. As shown in Figure 5, two sidearms in **4-KSCN** were placed in a syn-fashion in a crystalline state. On the other hand, the X-ray structures of **5-KSCN** and **6-KSCN** indicated that two sidearms were positioned in an anti-fashion, and that the repeating units appeared as a linear polymer, as shown in Figures 6 and 7.

Thus, it is believed that the syn structure of **4-KSCN** could provide another reason for the large stability constants of the ligand **4** with metal ions in a liquid solution.

Conclusions

Conductimetry and ¹H-NMR titration experiments demonstrated that the ligands and alkali metals form a supramolecular complex in the ratio 1 : 1. The stability constants for the ligands **2-6** and alkali metal cations (Na⁺, K⁺, Rb⁺ and Cs⁺) were determined using potentiometry in 95% methanol. The stability constants were in the order of K⁺ > Rb⁺ > Cs⁺ > Na⁺ for all the ligands. The size compatibility between ligand cavity and metal cations could explain the order of stability. The stability constants for the partially-fluorinated ligands **3-6** and each metal ion are larger than that for the non-fluorinated ligand **2**, which might reflect the plausible interaction between fluorine atoms and alkali metal cation. It is interesting to note that the stability constants for the ligand **4** and alkali metal cations are larger than those for the ligand **5**. This fact is also supported by the results of characteristic cation-induced chemical shifts in ¹H-, ¹⁹F-NMR and extraction experiment. The crystal structures revealed another clue for the understanding of stability difference between **4** and **5**. The X-ray crystal structures of the complexes

Table 4. Crystallographic data for **4-KSCN**, **5-KSCN** and **6-KSCN**

	4-KSCN	5-KSCN	6-KSCN
Formula	C ₂₇ H ₃₄ F ₄ KN ₃ O ₄ S	C ₂₇ H ₃₄ F ₄ KN ₃ O ₄ S	C ₂₇ H ₂₈ F ₁₀ KN ₃ O ₄ S
F.W.	611.73	611.73	719.68
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Space group	P na21	C mca	P na21
<i>a</i> , Å	14.219(3)	14.332(3)	28.103(3)
<i>b</i> , Å	14.921(3)	8.208(2)	14.287(2)
<i>c</i> , Å	14.344(3)	25.905(5)	7.636(2)
β , deg.	90	90	90
Z	4	4	4
V, Å ³	3043.2(11)	3047.5(11)	3065.9(10)
ρ_{calc} , Mg/m ³	1.335	1.333	1.559
θ range, deg.	1.97-27.47	1.57-27.45	1.45-24.98
Measured reflections	3629	1822	2689
No. of parameters	361	103	211
<i>I</i> > 2 σ	2005	1266	1534
G. O. F	1.170	1.098	1.085
μ , mm ⁻¹	0.303	0.303	0.341
<i>R</i> _{<i>I</i>} (<i>I</i> > 2 σ (<i>I</i>))	0.0704	0.0479	0.0585
<i>R</i> _w (<i>I</i> > 2 σ (<i>I</i>))	0.1126	0.0955	0.1714
$\Delta\rho_{\text{max}}$ and $\Delta\rho_{\text{min}}$, eÅ ⁻³	0.26, -0.371	0.212, -0.210	0.260, -0.372

between the ligands **5** and **6**, and KSCN revealed that both benzylic sidearms are placed in an anti-fashion. On the other hand, the crystal structure of the complex between the ligand **4** and KSCN showed that two sidearms are in syn each other. All the experimental results told us that the covalently bonded fluorine atoms in the ligand **3-6** affects the strength of coordination between the ligands and alkali metals. Also the position of fluorine atoms in sidearms was crucial for the enhanced interaction between a ligand and an alkali metal.

Experimental Section

Reagents and instruments. Starting materials (benzyl bromide, pentafluorobenzyl bromide, 2,6-difluorobenzyl bromide and 3,5-difluorobenzyl bromide) were purchased from Aldrich and used without further purification. TLC plates (silica gel 60 F₂₅₄, 20 cm × 20 cm) and silica gel (230-400 mesh) were purchased from Merck. Solvents (methanol, ethyl acetate and hexanes) for column chromatography were purified by simple distillation prior to use. For the analysis of synthetic products, NMR spectra were recorded in CDCl₃ solution with TMS as the internal standard for ¹H-NMR (300 MHz) or with CFCl₃ for ¹⁹F-NMR (282.4 MHz). Mass spectra were obtained using a KRATOS Profile HV-3 or Shimadzu GC MS-QP 5050 spectrometer. The melting points were determined with a MEL-TEMP[®] 1201D capillary melting point apparatus, and they were uncorrected. Metrohm 736 GP Titration System with glass electrode (Ag/AgCl, standard electrode; Metrom EA 427) was used for a potentiometric titration. Reagents (HCl; 0.1 N, (CH₃)₄NOH; 1.0 M, (CH₃)₄NCl, metal chlorides, metal hydroxides and picric acid) for potentiometry and extraction experiments were also purchased from Aldrich and used without further purification. Conductance measurement was performed in water bath at 25 ± 0.1 °C by using a TOA CM 60S. X-ray structures were analyzed by STOE-STADI4 or NONIUS-CAD4 diffractometer. UV-spectra were recorded at 25 °C with a Varian CARY 100 CONE.

Synthesis. The diaza-18-crown-6 ethers **3-6** containing partially-fluorinated sidearms were synthesized with 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (**1**) and various benzyl bromides according to the known procedure⁶.

N-Benzyl-N'-pentafluorobenzyl-1,4,10,13-tetraoxa-7,16-diazacyclo octadecane (3). Yellow liquid; yield 42%; ¹H-NMR (CDCl₃, 300 MHz): δ 2.81 (t, *J* = 4.7 Hz, 8H), 3.61 (s, 8H), 3.64 (t, *J* = 4.6 Hz, 8H), 3.68 (s, 2H), 3.87 (s, 2H), 7.30 (m, 5H); ¹⁹F-NMR (CDCl₃, 282 MHz): δ -142.0 (m, 2F), -155.7 (t, *J* = 22.6 Hz, 1F), -162.7 (m, 2F); MS (*m/z*): 532 (M⁺), 351 (M⁺-C₇H₅F₅).

N,N'-Bis(2',6'-difluorobenzyl)-1,4,10,13-tetraoxa-7,16-diazacyclo octadecane (4). White solid; mp 76-78 °C; yield 51%; ¹H-NMR (CDCl₃, 300 MHz): δ 2.81 (t, *J* = 5.5 Hz, 8H), 3.62 (s, 8H), 3.64 (t, *J* = 5.6 Hz, 8H), 3.81 (s, 4H), 6.86 (t, *J* = 7.8 Hz, 2H), 7.26 (m, 4H); ¹⁹F-NMR (CDCl₃, 282 MHz): δ -113.8(s); MS (*m/z*): 515 (M⁺), 387 (M⁺-C₇H₅F₂).

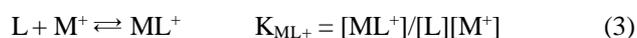
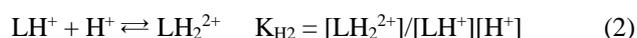
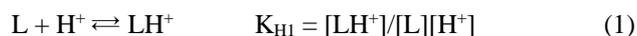
N,N'-Bis(3',5'-difluorobenzyl)-1,4,10,13-tetraoxa-7,16-diazacyclo octadecane (5). White solid; mp 58 °C; yield

71%; ¹H-NMR (CDCl₃, 300 MHz): δ 2.81 (t, *J* = 5.7 Hz, 8H), 3.61 (s, 8H), 3.62 (t, *J* = 5.8 Hz, 8H), 3.67 (s, 4H), 6.64 (t, *J* = 8.7 Hz, 2H), 6.93 (d, *J* = 7.8 Hz, 4H); ¹⁹F-NMR (CDCl₃, 282 MHz): δ -111.2 (s); MS (*m/z*): 515 (M⁺), 387 (M⁺-C₇H₅F₂).

Determination of complex composition ratio by conductimetry and NMR titration methods. The complex composition ratio between the ligand **2** and metal salts (KCl, RbCl and CsCl) were determined by conductimetry.⁹ Specific conductance (*κ*) of methanol solutions was checked in the ligand to metal mole ratios of 0.0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.4, 2.0, 2.4 and 3.0. The equivalent conductance (*Λ*) was calculated by: $\Lambda = 1000 \kappa/C$, where *C* is a molar concentration of metals.

NMR titration¹⁰ method was also applied for the determination of the complex composition ratio between the ligands **4-6** and metal salts (KCl and CsCl). The chemical shifts in a mixed solvent of CD₃OH and CDCl₃ (4 : 1, v/v) were checked in the metal to ligand mole ratios of 0.00, 0.11, 0.25, 0.43, 0.67, 1.00, 1.50, 2.33, 4.00 and 9.00. The CIS (Cation-Induced Shift) of NMR is defined as $A \times [\delta_{\text{free ligand}}(\text{ppm}) - \delta_{\text{complex}}(\text{ppm})]$ Hz. (*A* = 300 for ¹H-NMR, 282 for ¹⁹F-NMR)

Determination of protonation constants and stability constants. Potentiometric titrations were carried out with a Metrohm 736 GP titration system fitted with a glass electrode and Ag/AgCl reference electrode system. The pH electrode was calibrated with standard pH 4.00, pH 7.00 and pH 10.0 buffers before each titration. NaCl, KCl, RbCl, and CsCl were purchased in 99.999% purity and used without further purification. The stock solution was prepared from HPLC grade methanol and triply-distilled water. A typical solution for potentiometric equilibrium studies consisted of the following reagents: 1.0 × 10⁻⁴ M ligand, 1.0 × 10⁻⁴ M metal ion, 2.4 × 10⁻⁴ M HCl and 1.0 × 10⁻² M (CH₃)₄NCl of the background electrolyte in 95% methanol solution. Every titration was performed under a CO₂-free nitrogen atmosphere, and the cell was thermostated to 25.0 ± 0.1 °C. For the protonation constants determination, a standard HCl solution was added to protonate all the basic sites of the ligand and the solution was then titrated with a standardized Me₄NOH solution. For the stability constants measurement, metal salt was added to the protonated ligand solution, and the pH profile of an acidified ligand-metal ion (1 : 1 molar ratio) solution was determined by slow addition (0.025 mL at a time) of Me₄NOH solution. The protonation equilibrium constants and stability constants obtained were defined as follows:



Protonation-deprotonation processes of the tested ligands were expressed by equations (1) and (2). Equation (3) describes a complex formation in a neutral medium, where [L] and [M⁺] represent the equilibrium concentrations of free

ligand and metal cation, respectively. Calculations for stability constants were performed with the BEST program developed by A. E. Martell.¹¹

Metal picrates extraction with organic solvent.⁶ An aqueous metal picrate solution (1.00 mL, 5.0×10^{-3} M) and a ligand solution in chloroform (1.00 mL, 5.0×10^{-3} M) were placed into a capped, metal free, plastic centrifuge tube. The resulting solution in the tube was shaken on a vortex mixer for 10 min for a thorough mixing, then centrifuged for 5 min for a complete phase separation. A part (20 μ L) of the aqueous phase was removed with a micro syringe and transferred to a volumetric flask (10 mL). The flask was filled to the mark with spectrophotometric grade acetonitrile and the absorbance of the acetonitrile solution at 375 nm was measured with a UV spectrophotometer. The percent extraction was calculated by the following equation: % Extraction = $100(\text{Abs}_{\text{before}} - \text{Abs}_{\text{after}})/\text{Abs}_{\text{before}}$, where $\text{Abs}_{\text{before}}$ is the absorbance of the diluted metal picrate solution before extraction and $\text{Abs}_{\text{after}}$ is the absorbance of the corresponding metal picrate solution after extraction.

Crystal structure determination of the complexes 4-KSCN, 5-KSCN and 6-KSCN. The ethanol solution (1:1 mole ratio) of a ligand and KSCN was heated at reflux for 30 min. X-ray quality crystals of the complexes **4**-, **5**- and **6**-KSCN were respectively obtained by slow diffusion of ethyl acetate into a saturated ethanol solution. Data were collected on a STOE STADI4 four-circle diffractometer using graphite monochromatized Mo-K α radiation by ω -2 θ scan.¹² Unit cell parameters were determined by least-squares fit of 41 (**4-KSCN**) and 30 (**5-KSCN**), and 30 (**6-KSCN**) reflections having θ values in the ranges of 9.6-10.5 (**4-KSCN**), 9.8-10.5 (**5-KSCN**) and 9.7-10.5 (**6-KSCN**) respectively. Intensities of three check reflections were measured after every 1 hr during the data collection to monitor the crystal stability for both complexes and there was no significant change in the intensities of the check reflections. Absorption correction for all compounds was not applied. The structures were solved by direct method¹³ and refined on F^2 by full-matrix least-squares procedures.¹⁴ All non-hydrogen atoms were refined using anisotropic thermal parameters. Hydrogen atoms were included in the structure factor calculation at idealized positions by using a riding model, but not refined.

Supporting information available. Crystallographic data for the structure reported here have been deposited with the Cambridge Crystallographic Data Center (Deposition No. CCDC-248923 (**4-KSCN**), 248924 (**5-KSCN**) and 248925 (**6-KSCN**)). The data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the

CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

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