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[8] The yield of **8** increased as the boiling temperature of the solvent was raised on going from benzene to toluene to xylene. In addition, when one of the ethylene bridges in **7** was replaced by a less sterically demanding *o*-phenylene bridge, the cyclization occurred readily at room temperature in 53% yield: Y. Miyahara, K. Handou, T. Inazu, unpublished results.

[9] X-ray structure analysis of $H^+@\mathbf{1}\cdot Br^-$: Measurements were carried out on a colorless prism ($0.3\times0.3\times0.2\ mm^3$) in a sealed capillary at $-120\,^{\circ}C$; Rigaku RAXIS II instrument with an imaging plate area detector, graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.7107$ Å) up to $2\theta = 54.9^{\circ}$. Of 5363 total reflections collected, 3733 were observed [$I > 3.0\sigma(I)$]; Lorentz polarization corrections were made. Crystal data: $C_{12}H_{24}N_4\cdot Br\cdot 2\,CHCl_3$, $M_r = 543.01$, orthorhombic, space group *Pbca* (no. 61), $a = 21.078(3)$, $b = 17.378(3)$, $c = 12.560(3)$ Å, $V = 4600(2)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.57\ g\,cm^{-3}$, $\mu(Mo_{K\alpha}) = 24.95\ cm^{-1}$. The structure was solved by direct methods (SHELXS86). All the hydrogen atoms (except the encrypted proton) were found, but refined as fixed at idealized positions. The final residuals $R = 0.051$ and $Rw = 0.025$ were obtained after refinement against $|F|$; min./max. residual electron density $-1.25/1.08\ e\,Å^{-3}$. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-103234. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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A Potassium Complex of a Fluorine-Containing Macrocyclic Cage Compound: Interactions between Fluorine Atoms and Metal Ions**

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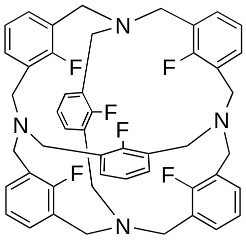
Takahiko Inazu

Interactions between covalently bonded fluorine atoms (C–F) and metal cations have been observed in the solid state and discussed based on crystallographic data.[1] Theoretical studies also predict such interactions in solution.[2] On the other hand, few reports are available of experimental elucidation of these interactions.[3] The first attempt to obtain experimental evidence was made in 1984 by Cram and co-workers.[4] However, the fluorinated spherands did not show any complexation phenomena toward alkali metal cations.

Most recently, Plenio et al. synthesized several types of macrocyclic compounds which contain oxygen and fluorine as the donor atoms.[5] Based on ^{13}C and ^{19}F NMR spectral data, X-ray crystallographic analyses, and determinations of stability constants, they concluded that the fluorine atom plays an important role in the complexation of alkali and alkaline earth metal cations. These results are probably the first experimental proof of $C{-}F\cdots M^+$ interactions. However, the molecules contain the ethyleneoxa moiety, and there is no doubt that the oxygen atoms significantly contribute to the trapping of metal cations. Therefore, it is a drawback that the effect of oxygen has to be subtracted from the total cation affinities, and careful handling of each datum is required to discuss the $C{-}F\cdots M^+$ interactions.

Is it possible to observe the interactions with the fluorine atom as the sole donor? To give an unequivocal answer to this question, we began to design a host molecule in which only the fluorine atom acts as a donor. Previously, we reported the simple synthesis of the cage compound **2** and its analogues.[6] The pyridine analogue of **2** is an ideal host molecule for spherical cations because it has a preorganized structure and an "enforced" cavity. Actually, the pyridine analogue showed strong binding phenomena toward alkali metal cations, ammonium ions, and protons. We applied these structures to capture metal cations by fluorine; replacing pyridine or benzene units by fluorobenzene promises a preorganized cavity in which six C–F donor units are pointing toward the cavity (**1**). We now report the synthesis of the host molecule **1** and its ability to complex cations as well as the structure elucidation of the potassium complex of **1**.



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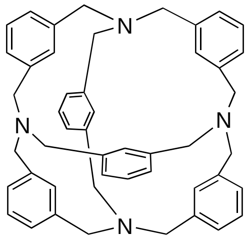
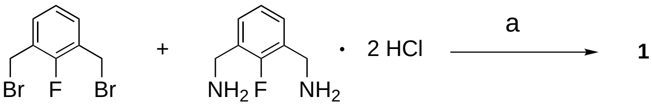


2

Compound **1** was synthesized in a manner similar to that for **2**.[6f] The reaction of 2-fluoro-1,3-bis(bromomethyl)benzene and 2-fluoro-1,3-bis(aminomethyl)benzene dihydrochloride under phase-transfer conditions (CH_2Cl_2/Bu_4NBr/aq. KOH) afforded **1** in 2.3% yield (Scheme 1). To estimate the complexation ability of **1**, extraction experiments with metal



Scheme 1. Synthesis of cage compound **1**. a) CH_2Cl_2/aq. KOH, Bu_4NBr.

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picrates (metal = Li^+, Na^+, K^+, Rb^+, Cs^+, Ag^+, NH_4^+; picrate = Pic^- = 2,4,6-$(NO_2)_3C_6H_2O^-$) were carried out. Figure 1 shows the distribution ratios of the picrates between the aqueous phase and the $CHCl_3$ phase. Compound **1** shows K^+ selectivity among alkali metal ions, and the affinities for Ag^+ and NH_4^+ are strong. The cation affinity of **1** is size-sensitive, and this property implies the preorganized cavity of **1**. Analysis of the extraction data showed formation of a 1:1 complex for K^+, Ag^+, and NH_4^+. Stability constants lg K_s were estimated to be 5.58, 4.57, and 4.37 for K^+, Ag^+, and NH_4^+, respectively. As previously reported, **2**, which is free of fluorine atoms, does not show cation affinity.[6] Compound **2** was used as a reference compound in these experiments, and it was confirmed that **2** did not extract metal picrates at all.

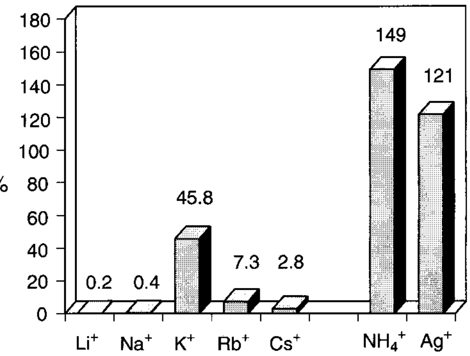

Figure 1. Distribution ratios D[%] of metal picrates. $D[\%] = [Pic^-]_{org}/([Pic^-]_i - [Pic^-]_{org}) \times 100$; $[Pic^-]_i$ is the initial concentration of picrate in the aqueous phase, and $[Pic^-]_{org}$ is the observed concentration of picrate in the organic phase. Ligand **1**: 1.0×10^{-3} M in chloroform; the metal picrates are formed from 0.10 M metal chloride or nitrate (Ag^+) and 1.01×10^{-3} M lithium picrate.

A solution of $K^+ \subset \mathbf{1}$ was prepared by addition of potassium picrate to **1** in $CHCl_3/CH_3CN$ (1/1). Elemental analysis of crystals obtained from the solution gave a satisfactory result and showed the composition to be $K^+ \subset \mathbf{1} \cdot C_6H_2N_3O_7 \cdot 2H_2O$. The K^+ complex formation was also confirmed by the ^1H, ^{13}C, and ^{19}F NMR spectra. The ^1H NMR spectra of the complex in $CDCl_3$ showed a significant low-field shift ($\delta = 0.16$) of the methylene proton signals compared to those for metal-free **1**. The ^{19}F NMR spectra displayed a characteristic high-field shift of the ^{19}F signal (free ligand: $\delta = -110.50$, $K^+ \subset \mathbf{1}$: $\delta = -126.26$). The features of the ^{13}C NMR spectra are the signal of the C–F carbon atom, which was slightly shifted high field ($\delta = 1.1$), and the $^1J_{C-F}$ coupling, which is remarkably reduced upon complexation (free ligand: $J = 260.5$, $K^+ \subset \mathbf{1}$: $J = 247.8$ Hz). These typical phenomena coincided with those reported by Plenio et al.[5]

To clarify the coordination structure of $K^+ \subset \mathbf{1}$, we carried out an X-ray crystallographic analysis (Figure 2). The single crystal suitable for the analysis was obtained by slow evaporation of the solution of the complex in $CHCl_3$. The six fluorine atoms are coordinated to K^+ in a distorted octahedral fashion. The four equatorial fluorine atoms F2, F4, F5, and F6 as well as K^+ are almost coplanar, and are capped by the two axial fluorine atoms F1 and F3. The distances between K^+ and the fluorine atoms are in the range of 2.56–2.92 Å. To the best of our knowledge, the value of 2.56 Å is among the shortest reported.[3] It is noteworthy that a shorter K···F distance tends to make the bond angle C–F···K closer to linear. The N···K^+ distances (3.28–3.74 Å) are much longer than the F···K^+ distances, and formation of the chelate –N···K^+···F– is not observed. Bridgehead nitrogen atoms do not participate in the K^+ coordination, and this feature is supported by the fact that the fluorine-free compound **2** does not show any ability to complex cations.

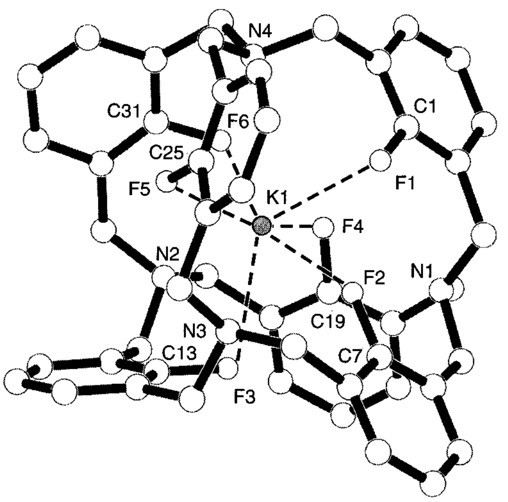

Figure 2. Crystal structure of $K^+ \subset \mathbf{1}$ (H atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: K1–F1 2.920(3), K1–F2 2.563(3), K1–F3 2.786(3), K1–F4 2.704(3), K1–F5 2.727(3), K1–F6 2.722(3), K1–N1 3.739(4), K1–N2 3.276(4), K1–N3 3.629(4), K1–N4 3.295(4); C1-F1-K1 95.1(2), C7-F2-K1 148.2(3), C13-F3-K1 105.4(2), C19-F4-K1 116.2(2), C25-F5-K1 109.9(2), C31-F6-K1 98.4(2).

In conclusion, the C–F···M^+ interaction was proven very simply with $K^+ \subset \mathbf{1}$, and it was elucidated that the fluorine atom undoubtedly acts as a donor atom toward cations. A new donor (C–F) can now be added to the field of host–guest chemistry, and it can be widely used as a receptor unit for the design of host molecules.

Experimental Section

1: A mixture of 2-fluoro-1,3-bis(aminomethyl)benzene hydrochloride (4.70 g, 20.7 mmol), CH_2Cl_2 (350 mL), Bu_4NBr (0.37 g, 1.15mmol), and 4 N aq. KOH (30 mL) was heated under reflux with vigorous stirring. A solution of 2-fluoro-1,3-bis(bromomethyl)benzene (6.78 g, 24.0 mmol) in CH_2Cl_2 (150 mL) was added to the mixture over a period of 3.5 h, and additional heating was continued overnight. The organic layer was separated and dried over $MgSO_4$. After evaporation of the solvent, the resultant material was purified by column chromatography on alumina with benzene as an eluent. The white powder obtained was recrystallized from CH_2Cl_2/benzene to afford colorless prisms (111 mg, 2.3 %). M.p. 337.1–337.5 °C (decomp. in a sealed, Ar-filled tube); ^1H NMR (400.1 MHz, $CDCl_3$, TMS): $\delta = 7.14$ (brs, 12 H, ArH), 6.95, 6.93, 6.90 (t, ^3J(H,H) = 7 Hz, 6 H, ArH), 3.49 (s, 24 H, CH_2); ^{13}C NMR (100.6 MHz, $CDCl_3$, TMS): δ = 162.30, 159.71 (d, ^1J(C,F) = 260.5 Hz), 130.75 (s), 126.09, 125.94 (d, ^2J(C,F) = 14.5 Hz), 121.38 (s), 52.34 (s); ^{19}F NMR (564.7 MHz, $CDCl_3$, $CFCl_3$): $\delta = -110.50$; MS (FAB): m/z (%): 789 (16) [M^++1]; elemental analysis of a sample recrystallized from CH_2Cl_2/hexane: calcd for $C_{48}H_{42}N_4F_6 \cdot CH_2Cl_2$: C 67.35, H 5.08, N 6.41; found: C 67.60, H 5.18, N 6.41; the quantity of the solvent included in the analytical sample was confirmed by means of the ^1H NMR spectrum.

$K^+ \subset \mathbf{1} \cdot Pic^-$: M.p. > 271.2 °C (decomp. in a sealed, N_2-filled tube); ^1H NMR (400.1 MHz, $CDCl_3$, TMS): $\delta = 7.24$, 7.22 (d, ^3J(H,H) = 8 Hz, 12 H, ArH), 7.09, 7.07, 7.05 (t, ^3J(H,H) = 8 Hz, 6 H, ArH), 3.65 (s, 24 H, CH_2); ^{13}C NMR

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(100.6 MHz, $CDCl_3$, TMS): $\delta = 161.16$, 158.70 (d, $^1J(C,F) = 247.8$ Hz), 131.89 (s), 126.56 (s), 124.31 (s), 55.89 (s); ^{19}F NMR (564.7 MHz, $CDCl_3$, $CFCl_3$): $\delta = -126.26$; MS (FAB): m/z (%): 827 (100) [M+K$^+$]; elemental analysis of a sample recrystallized from $CHCl_3$: calcd for $C_{48}H_{42}N_4F_6 \cdot C_6H_2N_3O_7K \cdot 2H_2O$: C 59.39, H 4.43, N 8.98; found: C 59.47, H 4.30, N 8.93.

Crystallographic data for $K^+ \subset \mathbf{1} \cdot Pic^- \cdot 2H_2O$ ($C_{54}H_{48}N_7O_9F_6K$): $M_r = 1092.10$, $T = 23\,°C$, $Mo_{K\alpha}$ (Rigaku RAXIS-IV imaging plate area detector, $\lambda = 0.71070$ Å), crystal dimensions $0.40 \times 0.30 \times 0.50\ mm^3$ (yellow prism); triclinic, space group $P\bar{1}$ (no. 2), $a = 13.980(4)$, $b = 18.336(8)$, $c = 11.198(5)$ Å, $\alpha = 98.38(1)$, $\beta = 110.54(3)$, $\gamma = 102.04(2)°$, $Z = 2$, $\mu_{Mo} = 1.87\ cm^{-1}$, $V = 2552.6(8)$ Å^3, $\rho_{calcd} = 1.391\ g\,cm^{-3}$, $2\theta_{max} = 55°$, $F(000) = 1106$. Indexing was performed from three oscillations which were exposed for four minutes. A total of 31 oscillation images (5.00°) were collected, each being exposed for ten minutes. Of the 8043 reflections collected, 6178 were unique and 8000 were independent with $I > 3\sigma(I)$. The structure was solved by direct methods and refined on SAPI 91. Data were corrected for Lorentz and polarization effects. The data/parameter ratio was 6.86; $R = 0.071$, $Rw = 0.065$, GOF = 1.55, max./min. residual density $+0.95/-0.58\ e\,Å^{-3}$. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-103215. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Novel Aluminum-Containing Ring Systems: An Octanuclear Structural Analogue of a Calix[4]pyrrole**

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The study of the coordination chemistry of Group 13 alkyl derivatives to give complexes of differing nuclearities is being actively pursued, prompted by the relevance of such species to alkylaluminoxanes, $(RAlO)_n$,[1] and as single-source precursors to semiconducting and electronic materials, for example GaN.[2] In recent studies, a number of unusual aluminum-containing ring and cage structures have been described. For example, difunctional molecules such as 1,2-diaminobenzene ($1,2\text{-}(NH_2)_2C_6H_4$), salicylic acid ($1\text{-}(CO_2H)\text{-}2\text{-}(OH)C_6H_4$), and 1,2-diphosphanylbenzenes ($1,2\text{-}(PR_2)_2C_6H_4$; R = H, Me) have been shown to react with Me_3M (M = Al, Ga) to give ring and cage structures for both aluminum and gallium;[3] other ring and cage structures have been accessed from reactions involving the use of primary or secondary amines[4] and phenylhydrazine.[5]

In separate studies, gallium-mediated coupling reactions involving acetonitrile have recently been described. For example, the trimethylgallium-induced trimerization of acetonitrile, in the presence of a catalytic amount of caesium salt, was supported by the isolation and crystal structure determination of the heterocycle $[Me_2Ga\{HNC(Me)\}_2C(CN)]$;[6] further reaction with Me_3Ga/MeCN gave $[(Me_2Ga)_4(MeGa)_2\{HNC(Me)C(CN)CH(NCMe)_2\}_2]$. Here we describe two remarkable reactions of Me_3Al with 1,1-disubstituted hydrazines to give novel macrocyclic ring structures arising by reaction of Me_3Al with the hydrazine followed by insertion of acetonitrile into the so-generated Al–N bonds.

Addition of two molar equivalents of Me_3Al to 1,1-dimethylhydrazine (Me_2NNH_2) in toluene results in rapid evolution of methane and formation of a colorless solution. After removal of the solvent, the residue was dissolved in acetonitrile, warmed at 80 °C for 10 min, and then cooled to −20 °C to give large colorless prisms of complex **1**. The crystal structure[7] of **1** (Figure 1 a) shows the molecule to be made up of four five-membered AlN_3C rings linked by Me_2Al bridges, and it may be viewed as a structural analogue of the calix[4]pyrroles.[8] The molecule has non-crystallographic S_4 symmetry, adopting a 1,3-*alternate* conformation (Figure 1 b) very similar to the aforementioned calix[4]pyrroles. The four bridging aluminum atoms of the 16-membered ring are coplanar to within 0.19 Å, with the four near-planar AlN_3C rings inclined by 59–67° to this plane. The geometries at the bridging aluminum centers are only slightly

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