

# C–F···Rb<sup>+</sup> interaction in a fluorinated cage compound complex

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**Abstract**—A rubidium complex of a cage compound which is composed of fluorobenzene, ethylenedioxy, and bridgehead nitrogen donor units was prepared. The C–F···Rb<sup>+</sup> interaction was clarified and evaluated for the first time by crystallographic analysis. The contribution degree of the three kinds of donor atoms for the cation binding was estimated by Brown's bond valence equation. © 2006 Elsevier Ltd. All rights reserved.

In the previous reports, we described cation affinity of the fluorobenzene unit. The essential driving force of the interaction is cation–dipole interaction and all alkali metal cations are encapsulated by the fluorinated cage compounds. The structural information is very important for such study, and thus, those of K<sup>+</sup>, Cs<sup>+</sup>, Tl<sup>+</sup>, and La<sup>3+</sup> complexes of **1** were clarified and estimated by Brown's bond valence theory.<sup>1</sup>

However, in the series of this study, the Rb<sup>+</sup> ion was not specially noted. This tendency is the same as in the case of crown ethers and cryptands. In a simple search using SciFinder™ by the 'M & crown ether; M = lithium, sodium, potassium, rubidium, and cesium' as keywords, we found 108 examples for lithium, 215 for sodium, 292 for potassium, 43 for rubidium, and 82 for cesium on August 7, 2006. A review of CF···M<sup>+</sup> also described that the reports of CF···Rb<sup>+</sup> short contact are very rare, and only four examples were shown in it.<sup>2</sup> The two of the four reports did not refer to the CF···Rb<sup>+</sup> short contacts and short comments were given in the other two reports (2b and 2c). Hence, a study of CF···Rb<sup>+</sup> in our ligand system stimulates us and becomes important because it offers detailed data about CF···Rb<sup>+</sup> interaction (Fig. 1). Therefore, this is the first report evaluating the CF···Rb<sup>+</sup> interaction by the structural analysis. The methodologies of this study have been already established by previous researches,<sup>1</sup> that is, <sup>19</sup>F-, <sup>13</sup>C NMR, X-ray crystallographic analysis, and its estimation using Brown's bond valence theory.

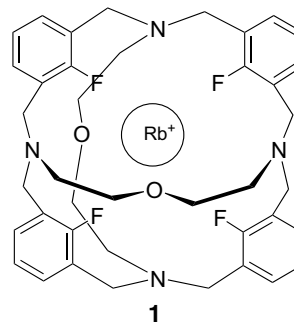


Figure 1. Structure of Rb<sup>+</sup> ⊂ **1**.

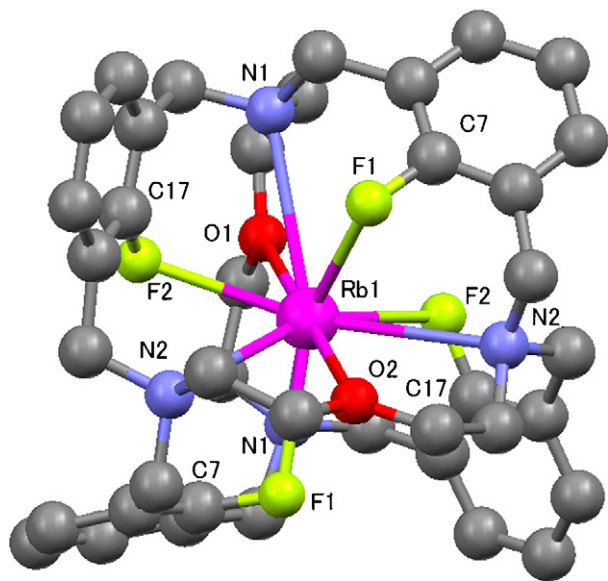
As reported previously, the <sup>19</sup>F NMR signal appeared at –120.9 ppm and this is 4.2 ppm higher than that of metal-free **1** (–116.7 ppm), which is also common to other metal complexes.<sup>1,2</sup> In the <sup>13</sup>C NMR, the <sup>19</sup>F–<sup>13</sup>C coupling constant (244.0 Hz) is reduced to about 12.6 Hz and it is comparable to other alkali metal complexes. These two spectroscopic features are representative evidences of the C–F···M<sup>+</sup> interaction as reported previously.<sup>1,2</sup> The linear relationships between  $\delta F$  versus ionic radii and  $J_{C-F}$  versus  $\log K_s$  (stability constants of M<sup>+</sup> ⊂ **1**) have already been shown in a previous report.<sup>1c</sup>

In the <sup>19</sup>F NMR, almost all of the metal complexes (Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, and La<sup>3+</sup>) showed a sharp singlet. In some cases, the metal complexes of **1** and its analog showed <sup>19</sup>F···M<sup>+</sup> couplings (M = Cs and Tl). We were thus interested in whether the Rb<sup>+</sup> ⊂ **1** shows <sup>19</sup>F···<sup>85,87</sup>Rb ( $I = 5/2$  for <sup>85</sup>Rb, and  $I = 3/2$  for <sup>87</sup>Rb) coupling. However, in this case, the coupling was not observed in <sup>19</sup>F NMR at room temperature or at low temperatures

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**Figure 2.** Structure of  $\text{Rb}^+ \cdot 1\text{-Pic}^-$  resulted from crystallographic analysis (picrate anion is omitted for clarity).

( $\sim -90^\circ\text{C}$ ), and a sharp  $^{19}\text{F}$  signal was maintained even at  $-90^\circ\text{C}$ . At low temperatures, conformation of the cage structure of **1** is frozen and positions of the F atoms are fixed.

Since spectral features are common to other metal complexes, structural data were estimated based on the crystallographic analysis (Fig. 2). As shown in Table 1, the results of the crystallographic analysis of  $\text{Rb}^+ \cdot 1\text{-Pic}^-$

**Table 1.** Results of crystallographic analysis of  $\text{Rb}^+ \cdot 1\text{-Pic}^-$

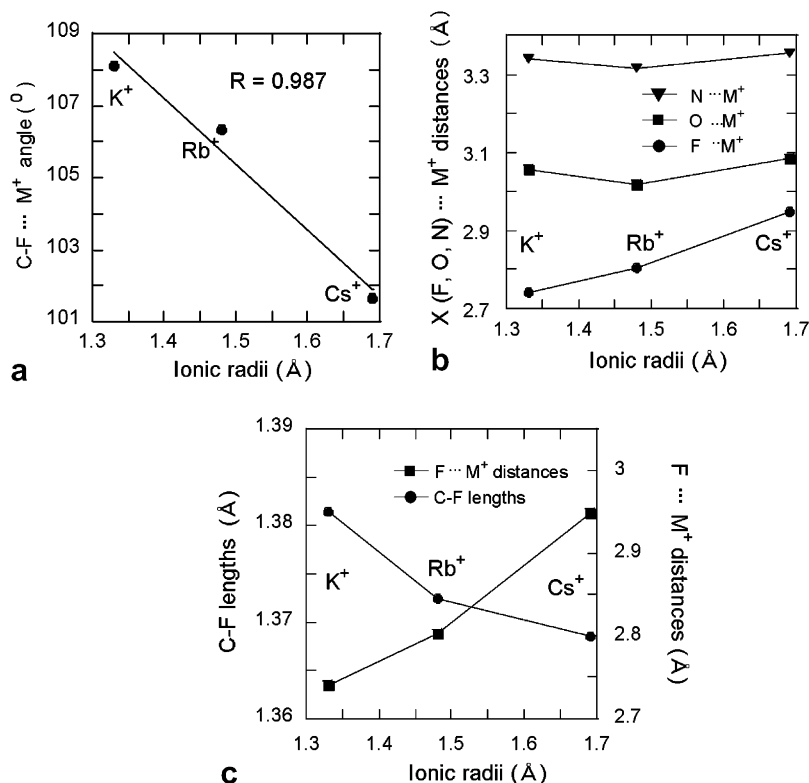
| Bond lengths (Å) | Interatomic distances (Å) | Bond angles (°)       |
|------------------|---------------------------|-----------------------|
| C7–F1 1.375(4)   | F1···Rb 2.803(2)          | C7–F1···Rb 106.02(2)  |
| C17–F2 1.370(3)  | F2···Rb 2.804(2)          | C14–F2···Rb 106.67(2) |
|                  | O1···Rb 2.976(3)          | O1–Rb···O2 180.0      |
|                  | O2···Rb 3.061(3)          |                       |
|                  | N1···Rb 3.300(3)          | F1–Rb···F1* 131.61(8) |
|                  | N2···Rb 3.329(2)          | F2–Rb···F2* 132.45(7) |

$r_{\text{C-F}}$ (average) of metal-free is 1.356 Å.

showed that C–F bond lengths, C7–F1 = 1.375(4) and C17–F2 = 1.370(3) Å, are longer than those of metal-free **1** (1.356 Å, in average).<sup>3</sup> The F···Rb<sup>+</sup> distance is 2.803 Å, and much shorter than the sum of van der Waals radius (1.47 Å) of the F atom and ionic radius of Rb<sup>+</sup> (1.66 Å). Thus, it is clear that CF and Rb<sup>+</sup> interaction is an attractive one.

As described above, four articles reported CF–Rb<sup>+</sup> short contacts, but these values are inconsistent (2.80–3.538 Å)<sup>2</sup> and could not be considered to correlate to our case.

As shown in Figure 3, the relationship between the structure of the complexes and the ionic radii of the cations were revealed. The CF···M<sup>+</sup> (M = K, Rb, and Cs) angles and cation sizes have a good linear relationship (Fig. 3a). As the cation size becomes smaller, CF···M<sup>+</sup> angles become larger. Thus, K<sup>+</sup> ion fits to the ligand cavity size, but larger ion, Rb<sup>+</sup> and Cs<sup>+</sup> changes the



**Figure 3.** Relationship between ionic radii of the cations (Å) and (a) C–F···M<sup>+</sup> angles (°), (b) X (X = F, O, and N)···M<sup>+</sup> distances (Å), and (c) C–F lengths of the complexes and their F···M<sup>+</sup> distances.

**Table 2.** Brown's bond valence,  $s$ , of the complexes

| $s$                    | $K^+ \subset 1$ | $Rb^+ \subset 1$ | $Cs^+ \subset 1$ |
|------------------------|-----------------|------------------|------------------|
| $\sum s(F \cdots M^+)$ | 0.620           | 0.636            | 0.689            |
| $\sum s(O \cdots M^+)$ | 0.178           | 0.261            | 0.329            |
| $\sum s(N \cdots M^+)$ | 0.212           | 0.347            | 0.395            |
| $V = \sum \sum s_X$    | 1.01            | 1.244            | 1.413            |

position of C–F unit. This result coincided with the affinity of the cations.<sup>1e</sup> Although O, N $\cdots$ M<sup>+</sup> distances are almost constant, F $\cdots$ M<sup>+</sup> distances increased in proportion to cation ionic radii (Fig. 3b). Contrary to this, C–F lengths become longer as F $\cdots$ M<sup>+</sup> distances become short (Fig. 3c). Therefore, it is considered that F $\cdots$ M<sup>+</sup> attractive force effectively lengthens the C–F bond.

By using Brown's bond valence equation,<sup>4</sup> we can estimate the bonding contribution of each donor atom to the Rb<sup>+</sup> cation and compare the bond valences among the three complexes. Table 2 summarizes the results. The bonding contribution of each one donor atom ( $\sum s(X \cdots Rb^+)/n$ , X = F, O, and N) increased in the order of N $\cdots$ Rb<sup>+</sup> (0.087)  $\ll$  O $\cdots$ Rb<sup>+</sup> (0.131) < F $\cdots$ Rb<sup>+</sup> (0.159). Total bond valence,  $V = \sum \sum s_X$ , of K<sup>+</sup>  $\subset$  1, Rb<sup>+</sup>  $\subset$  1, and Cs<sup>+</sup>  $\subset$  1 and the ionic radii of the cations are in a good linear relationship ( $R = 0.992$ ). The  $V$  values of Rb<sup>+</sup>  $\subset$  1 and Cs<sup>+</sup>  $\subset$  1 are larger than 1.0 and this was explained by the relationship between the rigidity of the ligand structure and metal ion size.<sup>1e,5</sup>

In conclusion, a very rare C–F $\cdots$ Rb<sup>+</sup> interaction was observed and its structural features were revealed by crystallographic analysis. By comparing the previously reported K<sup>+</sup> and Cs<sup>+</sup> complex structures, the relationship among cation sizes and ligand structures (C–F bond lengths, C–F $\cdots$ M<sup>+</sup> angles and X $\cdots$ M<sup>+</sup> distances) was clarified. The C–F bond elongation and short contact between the F and Rb<sup>+</sup> atoms are representative evidence of the interaction, and the bond valence equation showed superiority of the C–F donor nature over O and N atoms.

## References and notes

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- Crystallographic data of compound Rb<sup>+</sup>  $\subset$  1·Pic<sup>-</sup>*: C<sub>46</sub>H<sub>46</sub>F<sub>4</sub>N<sub>7</sub>O<sub>9</sub>Rb,  $M_r = 1002.4 \text{ g mol}^{-1}$ , yellow granules (grown from CH<sub>2</sub>Cl<sub>2</sub>–CH<sub>3</sub>CN), size 0.54 × 0.44 × 0.42 mm, monoclinic, space group C2/c (#15),  $a = 20.9389(4) \text{ \AA}$ ,  $b = 19.9019(3) \text{ \AA}$ ,  $c = 12.7228(3) \text{ \AA}$ ,  $\alpha = 90^\circ$ ,  $\beta = 124.3618(4)^\circ$ ,  $\gamma = 90^\circ$ ,  $V = 4376.7(2) \text{ \AA}^3$ ,  $Z = 4$ ,  $\rho_{\text{calcd.}} = 1.521 \text{ g cm}^{-3}$ ,  $\mu(\text{MoK}\alpha) = 12.15 \text{ cm}^{-1}$ ,  $F(000) = 2064$ ,  $T = 113(2) \text{ K}$  using the  $\omega$ - $2\theta$  scan technique to a maximum  $2\theta$  value of 55°. A total of 4995 reflections were collected. The final cycle of the full-matrix least-squares refinement was based on 3980 observed reflections ( $I > 2\sigma(I)$ ) and 145 variable parameters and converged with unweighted and weighted agreement factors of  $R = 0.0579$ ,  $R_w = 0.1744$ , and  $\text{GOF} = 1.352$ . The maximum and minimum peaks on the final difference Fourier map corresponded to 0.847 and  $-1.037 \text{ e}^-/\text{\AA}^3$ , respectively. Crystallographic data (excluding structure factor) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication No. CCDC 617154. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: +44 1223 33603; e-mail: deposit@ccdc.cam.ac.uk).
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