

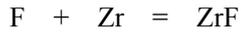
Experimental Section

All chemicals were of reagent grade quality obtained from commercial sources and used without further purification. The elemental analyses of C, H and N were performed on a Perkin-Elmer 240C elemental analyzer at the Analysis Center of Nanjing University. Electrospray mass spectra were carried out on a LCQ system (Finnigan MAT, USA) using methanol as mobile phase. 500 MHz ^1H NMR spectroscopic measurements were performed on a Bruker AM-500 NMR spectrometer, using TMs (SiMe_4) as an internal reference at 25 °C. The intensities of complexes **3** and **4** were collected on a Siemens SMART-CCD diffractometer with graphite-monochromatic Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) using SMART and SAINT program. The structure was solved by direct methods and refined on F^2 with the full-matrix least-squares methods using SHELXTL version 5.1. The perchlorate and the tetrafluoroborate anions were refined disordered. Anisotropic thermal parameters were refined for non-hydrogen atoms. Hydrogen atoms of the host were located geometrically and refined in a riding model.

Preparation of compound **2**: In a stirring 5 mL dry xylene solution containing 0.18 g 1,4,7,10,13,16,21,24-octaazabicyclo[8,8,8] hexacosane at 120°C, 0.24 g triethyl orthoformate in 3 mL dry xylene were added dropwise. After refluxing for 3 hrs, 0.15 g NH_4BF_4 was added. The reaction was carried out at 120°C for another 3 hrs, and then heated to 137°C, kept for 1 hr. White powder of crude product was obtained by cooling the solution to room temperature. Colorless crystalline solid **2** was obtained by recrystallization the original powder with water and dried under vacuum, yield 0.40 g, Anal. calcd. $(\text{C}_{21}\text{H}_{39}\text{N}_8)(\text{NH}_4)(\text{BF}_4)_4 \cdot \text{H}_2\text{O}$: C, 32.02, H, 5.72, N, 16.15; Found: C, 32.20, H, 5.46, N, 15.64. For compound **2** with the perchlorate anion: A solution of compound **2** in water was eluted through an anionic exchange column in the base form. The elutant was neutralized with a concentrated aqueous solution of HClO_4 . The result solution was condensed by evaporator and placed over P_2O_5 . Colorless crystal was obtained in high yield (near 100%) after several days. Anal. calcd. $(\text{C}_{21}\text{H}_{39}\text{N}_8)(\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$: C, 35.02, H, 5.70, N, 15.57; Found: C, 34.98, H, 5.74, N, 15.40.

For the interior compound $\text{F}^- \cdot 2 \cdot \text{H}_2$: crystals of $\text{F}^- \cdot 2 \cdot \text{H}_2$ suitable for X-ray structure analysis were formed by evaporating compound **2** in 0.1 M HClO_4 and 0.1M NaBF_4 solution. Anal. calcd. $(\text{C}_{21}\text{H}_{39}\text{N}_8\text{F})(\text{BF}_4)_2(\text{ClO}_4)_2 (\text{H}_2\text{O})_{0.5}$: C, 31.42, H, 5.00, N, 14.00; Found: C, 31.32, H, 5.18, N, 13.64.

For a high affinity host, the concentration of the fluoride anion [F⁻] is quite small; since the [Zr⁴⁺] is constant (0.5M) which is larger than [F⁻], only the comproportion of the ZrF is considered. In this case, the competition reactions quoted are as bellow:



$$[AF] / ([A] [F]) = K_s$$

$$[ZrF] / ([F] [Zr]) = \beta$$

$$[F] = [ZrF] / (\beta * [Zr]) = 2 [ZrF] / \beta$$

$$K_s = [AF] * \beta / ([A] * 2[ZrF])$$

$$2K_s/\beta = [AF] / ([A] [ZrF])$$

Where [A] is the concentration of the free crypt, [AF] is the concentration of the interior compound, [ZrF] is the concentration of the competition product.

Assume the beginning concentration of [A] is c_0 , [AF] = xc_0 , then [A] = $(1-x)c_0$.

Assume the chemical shift before added the fluoride anion is δ_0 , and the δ_L is the chemical shift of the pure interior compound. And δ is the chemical shift at the time the concentration of the added fluoride anion of ac_0 ,

Assume [AF] = xc_0 , then [A] = $(1-x)c_0$ then:

$$x = (\delta_L - \delta) / (\delta_L - \delta_0)$$

$$1 - x = (\delta - \delta_0) / (\delta_L - \delta_0)$$

$$[ZrF] = c_0 (a - x) = c_0 [a - (\delta_L - \delta) / (\delta_L - \delta_0)]$$

$$2K_s c_0/\beta = [AF] / ([A] [ZrF]) = (\delta_L - \delta) / \{(\delta - \delta_0) * c_0 [a - (\delta_L - \delta) / (\delta_L - \delta_0)]\}$$

$$2K_s c_0/\beta [a - (\delta_L - \delta) / (\delta_L - \delta_0)] = (\delta_L - \delta) / (\delta - \delta_0)$$

$$2K_s c_0/\beta [a / (\delta_L - \delta) - 1 / (\delta_L - \delta_0)] = 1 / (\delta - \delta_0)$$

$$a / (\delta_L - \delta) - 1 / (\delta_L - \delta_0) = (\beta/2K_s c_0) / (\delta - \delta_0)$$

Draw the plot $[a / (\delta_L - \delta)]$ vs $[1 / (\delta - \delta_0)]$, the K_s value could be obtained ($\log\beta = 8.8$ for our calculation).

Table 1. Interaction energy and electron density topological properties for the complex **3**.

	Interactions	$10^2\rho(r)$	$10^2\nabla^2\rho(r)$
CP(3,-1)	H(1A)-F(1)	4.468	15.518
	H(4A)-F(1)	4.404	15.285
	F(1)-C(3)	1.800	6.198
	F(1)-C(10)	1.821	6.260
	F(1)-C(17)	1.934	6.770
	F(1)-C(17)-N(7)-C(16)-C(15)-N(1)-H(1A)	0.549	2.589
CP(3,1)	F(1)-C(17)-N(8)-C(20)-C(21)-N(4)-H(4A)	0.566	2.700
	F(1)-C(3)-N(2)-C(2)-C(1)-N(1)-H(1A)	0.597	2.738
	F(1)-C(3)-N(3)-C(6)-C(7)-N(4)-H(4A)	0.594	2.834
	F(1)-C(10)-N(5)-C(9)-C(8)-N(1)-H(1A)	0.578	2.721
	F(1)-C(10)-N(6)-C(13)-C(14)-N(4)-H(4A)	0.627	2.867
ΔE (Kcal/Mol)		-505.83	