Cooperative Host/Guest Interactions via Counterion Assisted Chelation: Pseudorotaxanes from Supramolecular Cryptands

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Supplemental Material (1 page)

General Experimental Procedures. Compounds **1**-2PF_6, **2**, **3**, **5**-2PF_6, and **7** were prepared as described in the literature (see text for references). Compounds **4**-X and **6**-TFA were purchased commercially and used without further purification.

For every complexation study, precisely weighed amounts of each component were added to a 5.00 mL volumetric flask (±0.02 mL) equipped with a ground glass stopper to make a moderately concentrated (32.0 mM) master solution, which was then sequentially diluted as needed in transferring exactly half of the higher concentration solution to a clean volumetric flask by means of to-deliver volumetric pipettes (±0.006 mL) and diluting to the 5.00 mL mark. The fresh solutions were then passed through a filter before 0.500 mL of each solution component (both host and guest) at a specified concentration was then transferred to a 5 mm NMR tube and ^{1}H NMR data collected on a temperature controlled Varian Unity 400 MHz spectrometer.

Association constants were estimated according to Eq. 1, where Δ represents the difference in δ values (ppm) for any given proton between the shift which was observed experimentally upon mixing **2** or **7** (hereafter referred to as **host**) and **1**-2PF_6 or **5**-2PF_6 (hereafter referred to as **guest**) versus the chemical shift of the same given proton of **host** in the absence of **guest**, and where Δ_0 represents the difference in δ values between the chemical shift of the same given proton of **host** in the absence of **guest** versus the chemical shift of fully complexed **host**, which may only be realized by overloading **host** with **guest**. $[\mathbf{Host}]_{uc}$ and $[\mathbf{Guest}]_{uc}$ represent concentrations of uncomplexed host and guest, respectively. For present purposes, we observed the chemical shift of H_b to derive Δ while taking Δ_0 directly from prior studies as described in the text.

$$\text{apparent } K_a = \frac{[\mathbf{host/guest}]}{[\mathbf{host}]_{uc}[\mathbf{guest}]_{uc}} = \frac{[\mathbf{host}]_0 \frac{\Delta}{\Delta_0}}{\left([\mathbf{host}]_0 - [\mathbf{host}]_0 \frac{\Delta}{\Delta_0}\right)\left([\mathbf{guest}]_0 - [\mathbf{host}]_0 \frac{\Delta}{\Delta_0}\right)} \quad (1)$$

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