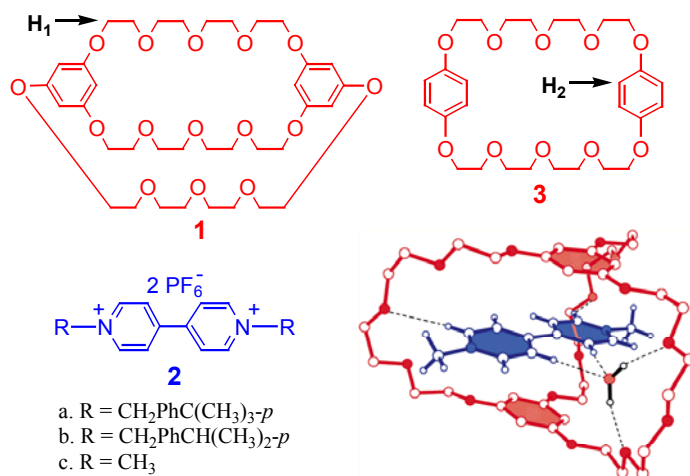


Chapter 6

A New Cryptand/Paraquat [2]Pseudorotaxane

6.1. INTRODUCTION

Host-guest chemistry is a topic of great current interest.¹ Paraquat and its derivatives (N,N'-dialkyl-4,4'-bipyridinium salts) are common guests in the field of pseudorotaxanes and rotaxanes.² They have been widely used to construct numerous host-guest complexes with bis(*p*-phenylene)-34-crown-10 (BPP34C10, **3**) derivatives and bis(*m*-phenylene)-32-crown-10 derivatives.² In order to improve complexation with paraquat derivatives, we introduced cryptands that have proved to be much better hosts than simple crown ethers.³ These reported complexes are only pseudorotaxane-like because paraquat is not long enough to extend outside of the cavities of cryptands.³ Here we report the first “true” cryptand/paraquat [2]pseudorotaxane in which the paraquat derivative guest is long enough to extend from the cavity of the host. This pseudorotaxane was compared with another new BPP34C10/paraquat [2]pseudorotaxane by proton NMR, mass spectrometry, and X-ray analysis.



6.2. RESULTS AND DISCUSSION

It is known that a *tert*-butyl end group is a big enough stopper for dibenzo-24-crown-8 derivatives.⁴ In order to make rotaxanes based on cryptand **1** and paraquat derivatives, we prepared two new paraquat derivative **2a** and **2b**. Acetone solutions of **1**^{3a} with **2a** and crown ether **3** with **2b** are yellow and orange, respectively, because of the charge transfer between the electron-rich aromatic rings of the hosts and the electron-poor pyridinium rings of the guests. A Job plot⁵ (Fig. 1) based on proton NMR data for H_1 of **1** demonstrated that its complex with **2a** was of 1:1 stoichiometry in solution. In the same way the complex between **3** and **2b** was proved to also have 1:1 stoichiometry in solution by using proton NMR data for H_2 . The apparent association constants ($K_{a,\text{exp}}$) of **1**•**2a** and **3**•**2b** calculated for 1:1 complexes were $1.4 (\pm 0.2) \times 10^4$ and $4.7 (\pm 0.5) \times 10^2 \text{ M}^{-1}$, respectively, at 1.00 mM initial concentrations of host and guest. # Electro spray ionization mass spectra confirmed the stoichiometry of **1**•**2a**: m/z 1322.20 (1%) [**1**•**2a** - $\text{PF}_6 + \text{H}]^+$, 1029.87 (75%) [**1**•**2a** - $2\text{PF}_6 - \text{CH}_2\text{C}_6\text{H}_4\text{C}(\text{CH}_3)_3]^+$, and 589.60 (3%) [**1**•**2** - $2\text{PF}_6 + 2\text{H}]^{2+}$. Here the base peak is 745.07 (100%) [**1** + $\text{H}_3\text{O}]^+$.

Single crystals of **2a** and **1**•**2a** for X-ray analysis were grown from acetone solutions, while these of **3**•**2b** were grown from an acetone/dichloromethane solution. § In the solid state the dihedral angle between the pyridinium rings of **2a** is 41° (Fig. 2). However, for parent paraquat **2c** the corresponding value is 0° .⁹ Just like **1**•**2c**,^{3a} **1**•**2a** is stabilized by hydrogen bonding and face-to-face π -stacking interactions in the solid state

(Fig. 3). Furthermore a water molecule acts as a hydrogen bridge between the β -protons of the guest and the ether oxygen atoms of **1** in both **1•2a** and **1•2c**. However there are some obvious differences. In **1•2c**, methyl protons of **1** are not involved in any hydrogen bonding, but in **1•2a** two methylene hydrogens are involved in hydrogen bonds (**B** and **D**) to host **1**. Therefore, totally **1•2a** is stabilized by 10 hydrogen bonds. Complexation influences the conformation of the guest **2a**. In order to optimize face-to-face π -stacking interactions, the dihedral angle between the pyridinium rings of **2a** decreases from 41° to 7.6° after complexation with **1**. The successful preparation of **1•2a** demonstrated that the *tert*-butyl group is not big enough to be a stopper for rotaxanes based on **1**.

BPP34C10 derivatives are the most common hosts for paraquat derivatives.² Complex **3•2b** (Fig. 4) is stabilized by face-to-face π -stacking interactions, but by only four hydrogen bonds, much less than the ten hydrogen bonds in **1•2a**. This is consistent with the 30-fold lower $K_{a,exp}$ value of **3•2b**, compared with **1•2a**. The dihedral angle between the pyridinium rings in **3•2b** is $26.29(8)^\circ$, while in **3•2c** the corresponding value is 0° .¹⁰

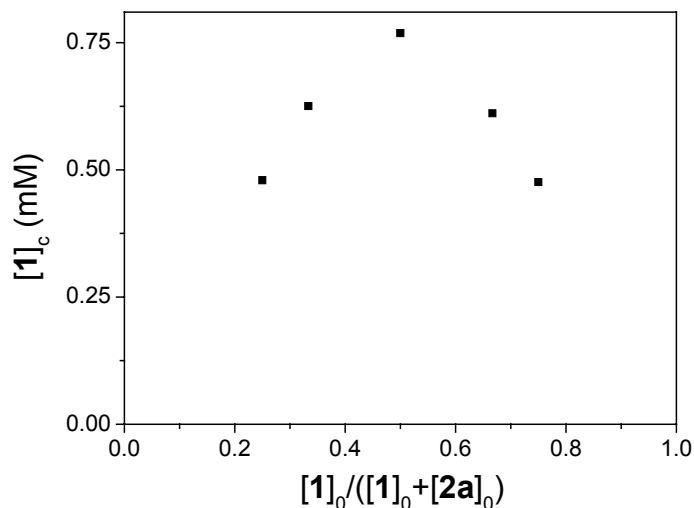


Figure 1. Job plot showing the 1:1 stoichiometry of the complex between **1** and **2a** in CD_3COCD_3 solution using data for H_1 of **1**. $[1]_c$ is the concentration of complexed **1**. $[1]_0 + [2a]_0 = 2.00$ mM.

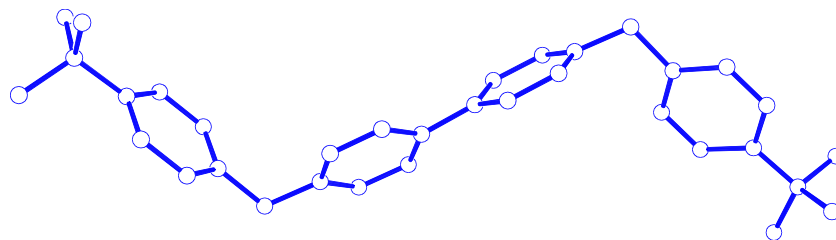


Figure 2. X-ray structure of **2a**, as determined by X-ray crystallography. Solvent molecules, two PF_6^- ions, and hydrogens have been omitted for clarity. The centroid-centroid distance (\AA) and dihedral angle (deg) between the pyridinium rings: 4.26 and 41.

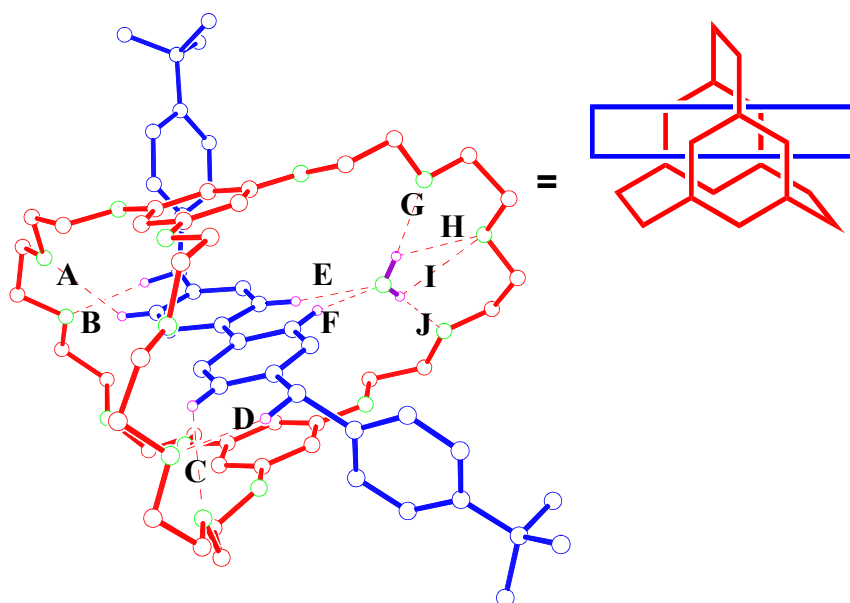


Figure 3. X-ray structure of **1•2a**. Oxygens are green, hydrogens are magenta, **1** is red, **2a** is blue, and water is purple. Solvent molecules, two PF_6^- ions, and hydrogens except the ones involved in hydrogen bonding have been omitted for clarity. Hydrogen-bond parameters: C(O) \cdots O distances (\AA), H \cdots O distances (\AA), C(O)-H \cdots O angles (deg) **A**, 3.20, 2.49, 132; **B**, 3.27, 2.30, 169; **C**, 3.45, 2.55, 117; **D**, 3.32, 2.36, 164; **E**, 3.21, 2.26, 174; **F**, 3.20, 2.27, 168; **G**, 2.89, 2.10, 172; **H**, 3.05, 2.64, 115, **I**, 3.05, 2.69, 110; **J**, 2.87, 2.09, 176. Face-to-face π -stacking parameters: centroid-centroid distances (\AA) 3.76, 3.89, 4.23, 4.09; ring plane/ring plane inclinations (deg): 6.7, 7.1, 4.2, 7.6. The centroid-centroid distance (\AA) and dihedral angle (deg) between the pyridinium rings of **2a**: 4.29 and 7.6.

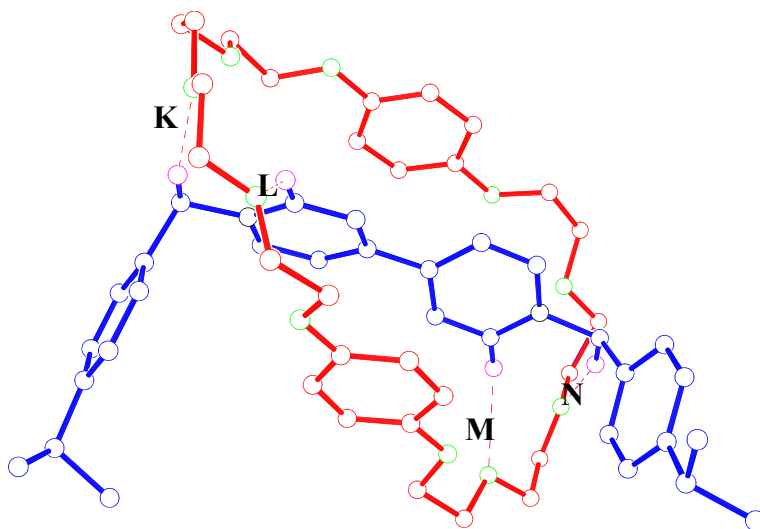


Figure 4. X-ray structure of **3•2b**. Oxygens are green, hydrogens are magenta, **3** is red, and **2b** is blue. Solvent molecules, two PF₆⁻ ions, and hydrogens except the ones involved in hydrogen bonding have been omitted for clarity. Hydrogen-bond parameters: C···O distances (Å), H···O distances (Å), C-H···O angles (deg) **K**, 3.387(5), 2.42, 165; **L**, 3.378(5), 2.57, 143; **M**, 3.368(5), 2.53, 147; **N**, 3.398(5), 2.44, 163. Face-to-face π -stacking parameters: centroid-centroid distances (Å) 4.35, 3.94, 4.32, 4.06; ring plane/ring plane inclinations (deg): 14, 12, 13, 15. The centroid-centroid distance (Å) and dihedral angle (deg) between the pyridinium rings of **2b**: 4.28 and 26.29(8).

6.3. CONCLUSIONS

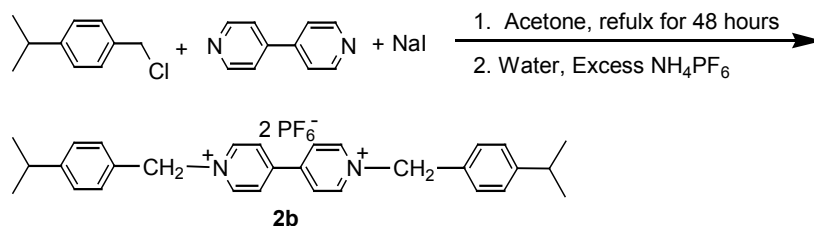
In summary, we prepared the first cryptand/paraquat [2]pseudorotaxane. We demonstrated that the *tert*-butyl group is not big enough to be a stopper for rotaxanes based on **1**. Currently we are preparing some cryptand-based rotaxanes.

6.4. ACKNOWLEDGEMENTS

This work was supported by the National Science Foundation (NSF) via DMR0097126 (HWG). We thank the NSF (Grant CHE-0131128) for funding of the purchase of the Oxford Diffraction Xcalibur2 single crystal diffractometer.

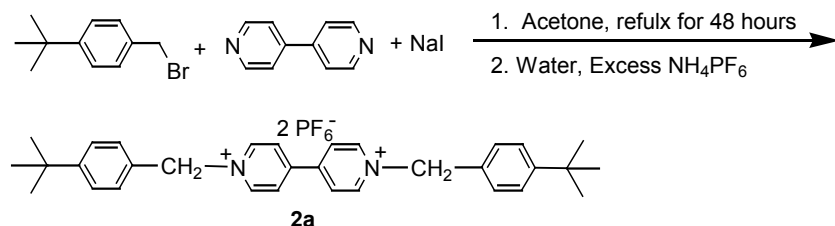
6.5. SUPPORTING INFORMATION

Synthesis of **2b**



A mixture of 0.62 g (4.0 mmol) 4,4'-bipyridine, 2.52 g (15.0 mmol) 4-isopropylbenzyl chloride, 3.00 g (20.0 mmol) sodium iodide, and 20 mL acetone was heated at reflux for 48 hours, cooled and filtered. The solid was washed with chloroform and dissolved in a minimum amount of deionized water. Excess ammonium hexafluorophosphate was added until no further precipitation could be observed. The precipitate was collected, dried and dissolved in a minimum amount of acetone. Excess deionized water was added. The precipitate was collected and dried. This process was repeated three times to afford pure product, **2b** (2.28 g, 80%), mp 277.1-277.8. ^1H NMR (400 MHz, acetone- d_6 , 22 °C) δ (ppm): 9.57 (4H, d, $J = 6.8$ Hz), 8.88 (4H, d, $J = 6.8$ Hz), 7.63 (4H, d, $J = 8.4$ Hz), 7.43 (4H, d, $J = 8.4$ Hz), 6.17 (4H, s), 2.98 (2H, sept, $J = 6.9$ Hz), and 1.26 (12H, d, $J = 6.9$ Hz). Anal. calcd for $\text{C}_{30}\text{H}_{34}\text{N}_2\text{P}_2\text{F}_{12}$: C, 50.57; H, 4.81; N, 3.93. Found: C, 50.07; H, 4.55; N, 3.87.

Synthesis of **2a**



2a was prepared analogously to **2b** from 0.31 g (2.0 mmol) 4,4'-bipyridine, 2.28 g (10.0 mmol) 4-(tert-butyl)benzyl bromide, 3.00 g (20.0 mmol) sodium iodide, and 20 mL acetone. **2a** (1.56 g, 85%), mp 313.4-314.6. ¹H NMR (400 MHz, acetone-d₆, 22 °C) δ(ppm): 9.58 (4H, d, *J* = 6.8 Hz), 8.88 (4H, d, *J* = 6.8 Hz), 7.64 (4H, d, *J* = 8.4 Hz), 7.59 (4H, d, *J* = 8.4 Hz), 6.17 (4H, s), and 1.34 (18H, s). Anal. calcd for C₃₂H₃₈N₂P₂F₁₂: C, 51.90; H, 5.17; N, 3.78. Found: C, 52.01, 52.12; H, 5.22, 5.13; N, 3.85, 3.72.

REFERENCES AND NOTES

¹H NMR characterizations were done on solutions with constant [**1**] and varied [**2a**]. Based on these NMR data, Δ₀, the difference in δ values for H₁ of **1** in the uncomplexed and fully complexed species, was calculated by using the Benesi-Hildebrand method.⁶ Then *K*_{a,exp} was calculated from $K_{a,exp} = (\Delta/\Delta_0)/\{1-(\Delta/\Delta_0)\} \{[2a]_0 - (\Delta/\Delta_0)[1]_0\}$. Errors are based on a 5% variation in Δ/Δ₀ values. *K*_{a,exp} for **3•2b** was obtained analogously using proton NMR data for H₂ of **3**. *K*_{a,exp} values for some pseudorotaxane systems are concentration dependent,⁷ so it is necessary to specify initial concentrations.

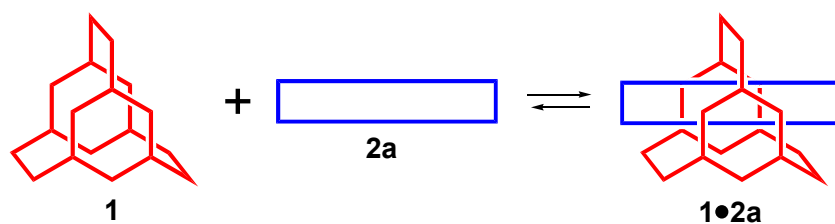
§ Crystal data of **2a**: prism, colorless, C₃₃H₄₄F₁₂N₂O₁P₂, FW 798.67, Triclinic, space group *P*-1, *a* = 11.538(2), *b* = 16.039(3), *c* = 22.108(5) Å, α = 96.830(17)°, β = 91.636(17)°, γ = 110.181(19)°, *V* = 3802.2(14) Å³, *Z* = 4, *D*_c = 1.395 g cm⁻³, *T* = 100 K, μ = 2.04 cm⁻¹, 41202 measured reflections, 19478 independent reflections, 946 parameters, *F*(000) = 1656, *R*1 = 0.0723, *wR*2 = 0.1045 [*I* > σ(*I*)], and goodness-of-fit (*F*²) = 0.8138, CCDC 215764. Crystal data of **1•2a**: prism, orange, C_{80.17}H_{118.35}F₁₂N₂O_{20.58}P₂, FW

1729.45, Triclinic, space group $P-1$, $a = 12.3458(10)$, $b = 16.5867(18)$, $c = 22.003(2)$ Å, $\alpha = 82.423(8)^\circ$, $\beta = 84.072(7)^\circ$, $\gamma = 81.507(8)^\circ$, $V = 4401.2(7)$ Å³, $Z = 2$, $D_c = 1.305$ g cm⁻³, $T = 100$ K, $\mu = 1.43$ cm⁻¹, 28096 measured reflections, 11552 independent reflections, 1055 parameters, $F(000) = 1832$, $R1 = 0.0667$, $wR2 = 0.1841$ [$I > 2\sigma(I)$], and goodness-of-fit (F^2) = 1.090, CCDC 215765. Crystal data of **3•2b**: plate, orange, C₆₃H₈₄ClF₁₂N₂O_{11.50}P₂, FW 1378.71, Monoclinic, space group $P2(1)/n$, $a = 14.6515(17)$, $b = 26.939(3)$, $c = 17.1601(19)$ Å, $\beta = 96.043(2)^\circ$, $V = 6735.3(13)$ Å³, $Z = 4$, $D_c = 1.360$ g cm⁻³, $T = 100$ K, $\mu = 1.96$ cm⁻¹, 40086 measured reflections, 15255 independent reflections, 791 parameters, $F(000) = 2892$, $R1 = 0.1064$, $wR2 = 0.2435$ [$I > 2\sigma(I)$], and goodness-of-fit (F^2) = 1.502, CCDC 215763. The structures were solved by direct methods using SIR^{8a} (**2a**) and SHELXTL^{8b} (**1•2a** and **3•2b**) and refined by full-matrix least squares using the Crystals^{8c} (**2a**) and SHELXTL^{8b} (**1•2a** and **3•2b**). Acetone and dichloromethane solvent molecules in **3•2b** are highly disordered around centers of symmetry and were treated by SQUEEZE.^{8d} Correction of the X-ray data by SQUEEZE (179 electron/cell) was close to the required value (152 electron/cell). See <http://www.rsc.org/suppdata/cc/...> for CIF files of these crystal structures.

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TOC Graphic:



Abstract: A new cryptand/paraquat [2]pseudorotaxane (**1•2a**) and a crown ether analog were synthesized and characterized by proton NMR, mass spectrometry, and single crystal X-ray analyses. The enhanced association constant for the cryptand complex ($K_a = 1.4 \times 10^4 \text{ M}^{-1}$) reflects a total of 10 H-bonding interactions vs. only 4 H-bonding interactions for the crown complex ($K_a = 4.7 \times 10^2 \text{ M}^{-1}$).
