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Isomeric 2,6-Pyridino-Cryptands Based on Dibenzo-24-crown-8

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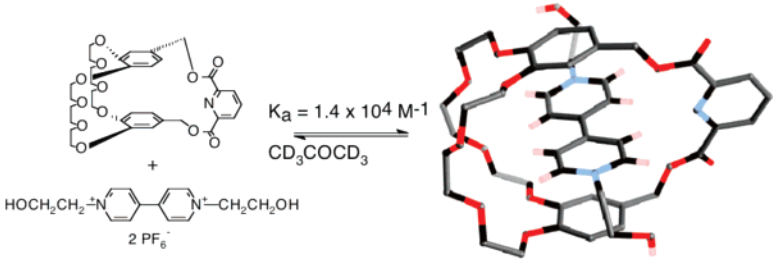

Cryptands **4** and **5** were synthesized from *cis*- and *trans*-bis(hydroxymethylbenzo)-24-crown-8 by reaction with pyridine-2,6-dicarboxylic acid chloride in 42 and 48% yields, respectively. The new cryptands form pseudorotaxanes with the paraquat derivative *N*,*N′*-bis(β-hydroxyethyl)-4,4′-bipyridinium bis(hexafluorophosphate) (“paraquat diol”, **6**): $K_a = 1.0 \times 10^4$ and 1.4×10^4 M^{-1}, respectively. The cryptands also form complexes with ammonium hexafluorophosphate. Formation of the paraquat/cryptand-based pseudorotaxanes can be switched off and on in a controllable manner on the basis of the cryptands’ abilities to complex KPF_6 strongly, providing a new mechanism for control of molecular shuttles. K^+ displaces paraquat diol from the cryptands, converting yellow-orange solutions to colorless; however, addition of 18-crown-6 binds the KPF_6 and allows the colored cryptand−paraquat complex to reform. Crystal structures are reported for both cryptands, both paraquat diol-based pseudorotaxanes, both NH_4PF_6 complexes, and both KPF_6 complexes.

Introduction

Host−guest chemistry is emerging as one of the key elements in nanoscience and technology[1] and thus the quest for improved systems that exhibit higher association constants and greater selectivity continues.[2] For example, one of our goals is self-assembly of supramolecular polymers with high degrees of polymerization (n);[3] this requires high association constants, K_a, since $n = (K_a[H]_0)^{1/2}$, in which $[H]_0$ is the initial concentration of host (and also guest) species.[3e,4] Crown ethers are a prototypical and seminal[5] class of hosts that have been widely employed for binding of cations[6] and formation of threaded structures, that is, pseudorotaxanes, rotaxanes, and catenanes;[7] however, the binding constants for the crown ether-based

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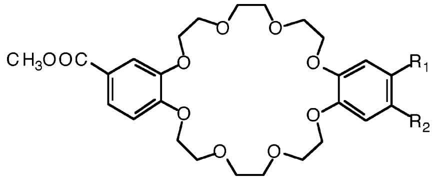
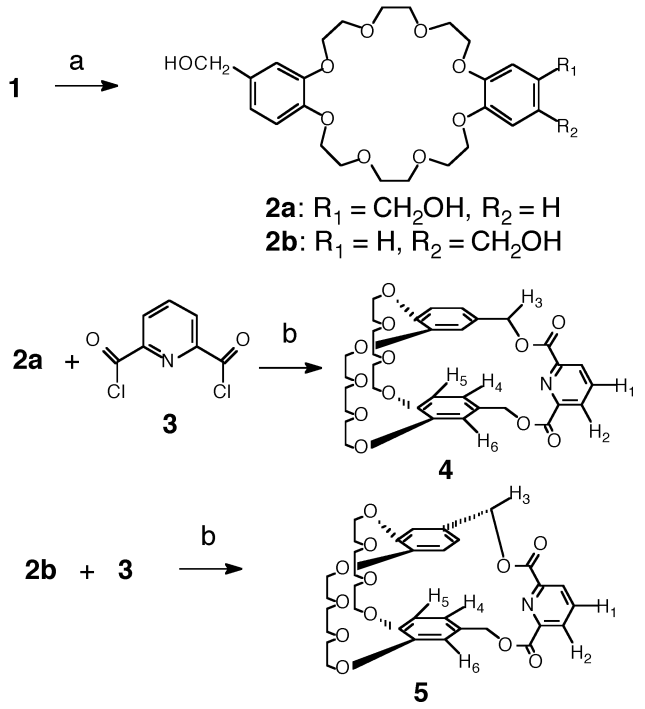
pseudorotaxanes are generally $<10^3$ M^{-1}, and this is too low to allow self-assembly of supramolecular polymers with 100 or more repeat units,[3e,4] considered a minimum value for useful covalent polymers. The formation of bicyclic hosts, cryptands,[8] is known to lead to higher binding constants and greater selectivity.[9] Indeed, we recently demonstrated this by the preparation and study of pseudocryptands[10] and cryptands[11] derived from bis(*m*-phenylene)-32-crown-10; in the latter, incorporation of a suitably positioned pyridine nitrogen in the cavity provided one of the highest binding constants reported for paraquat derivatives ($K_a = 5.0 \times 10^6$ M^{-1}). We also recently reported regiospecific syntheses of bis(carbomethoxybenzo)-24-crown-8 isomers **1a** and **1b**.[12] The belief that cryptands based on these systems would also lead to improved hosts led us to pursue the synthesis and study of such systems; some of the results of these studies are reported here, including a strategy for control of molecular shuttles derived from these paraquat/cryptand-based systems. Thus, our primary goal was to design and make improved hosts for paraquat-based pseudorotaxanes and rotaxanes.



1a: $R_1 = COOCH_3$, $R_2 = H$
1b: $R_1 = H$, $R_2 = COOCH_3$

SCHEME 1. Synthesis of *cis*- and *trans*-Cryptands from Dibenzo-24-crown-8 Diesters: (a) LAH/THF, 2a (90%), 2b (86%). (b) Pyridine/CH_2Cl_2, Pseudo-High Dilution, 2 Days, rt: 4 (42%), 5 (48%)



Results and Discussion

A. Syntheses of Dibenzo-24-crown-8-Based 2,6-Pyridino-Cryptands. The synthetic route to the cryptands is shown in Scheme 1. The diesters **1a** and **1b**[12] were reduced with LAH to the corresponding diols **2a** and **2b** in excellent yields. Using the pseudo-high dilution technique,[13] each diol was reacted with pyridine-2,6-dicarbonyl chloride (**3**); the resultant cryptands **4** and **5** were isolated in pure form in yields of 42 and 48%, respectively. They were both characterized by high-resolution mass spectrometry and the methods are described below.

Comparison of the ^1H NMR spectra of **4** and **5** (Figure 1) reveals the differences in symmetry between the two cryptands. The C_2 symmetry of the *cis*-cryptand **4** is clear from the facts that the benzylic methylene protons H_3 appear as a singlet and the proton signals of the two nonequivalent ethyleneoxy linkages are well resolved, in contrast to the facts that in C_s symmetric

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[8] A cryptand is defined (*IUPAC Compendium of Chemical Terminology*, 2nd ed.; 1997) as "a molecular entity comprising a cyclic or polycyclic assembly of binding sites that contains three or more binding sites held together by covalent bonds, and which defines a molecular cavity in such a way as to bind (and thus 'hide' in the cavity) another molecular entity, the guest (a cation, an anion or a neutral species), more strongly than do the separate parts of the assembly (at the same total concentration of binding sites). --- The term is usually restricted to bicyclic or oligocyclic molecular entities."

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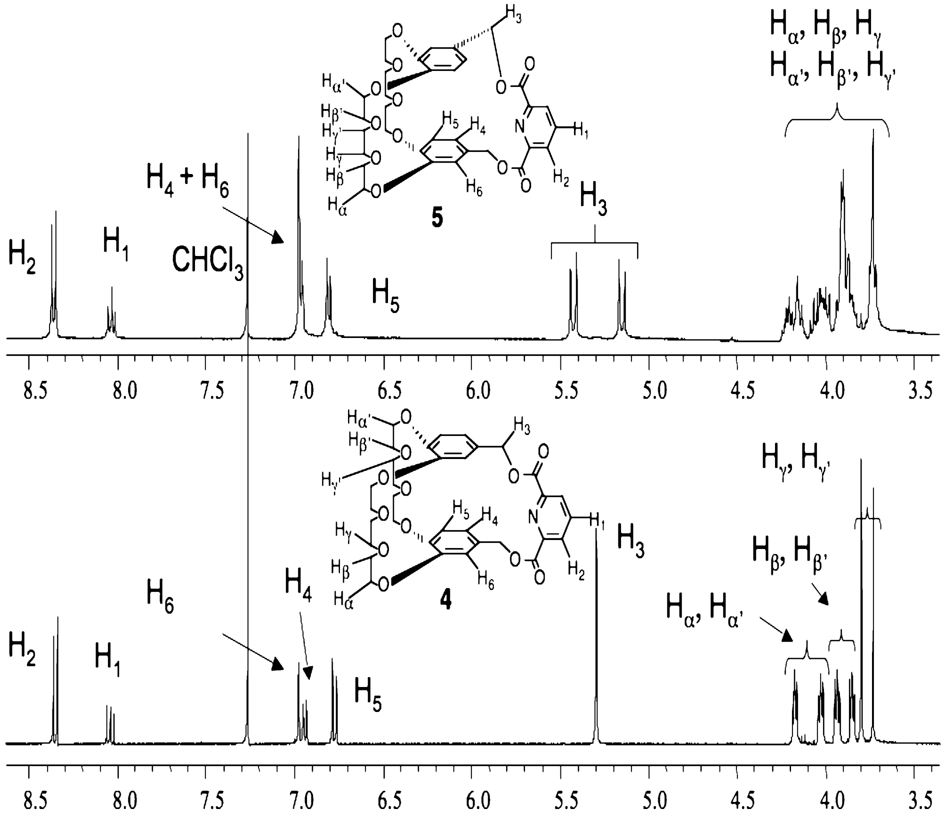


FIGURE 1. 400 MHz ^{1}H NMR spectra of cryptands **4** and **5** in $CDCl_3$.

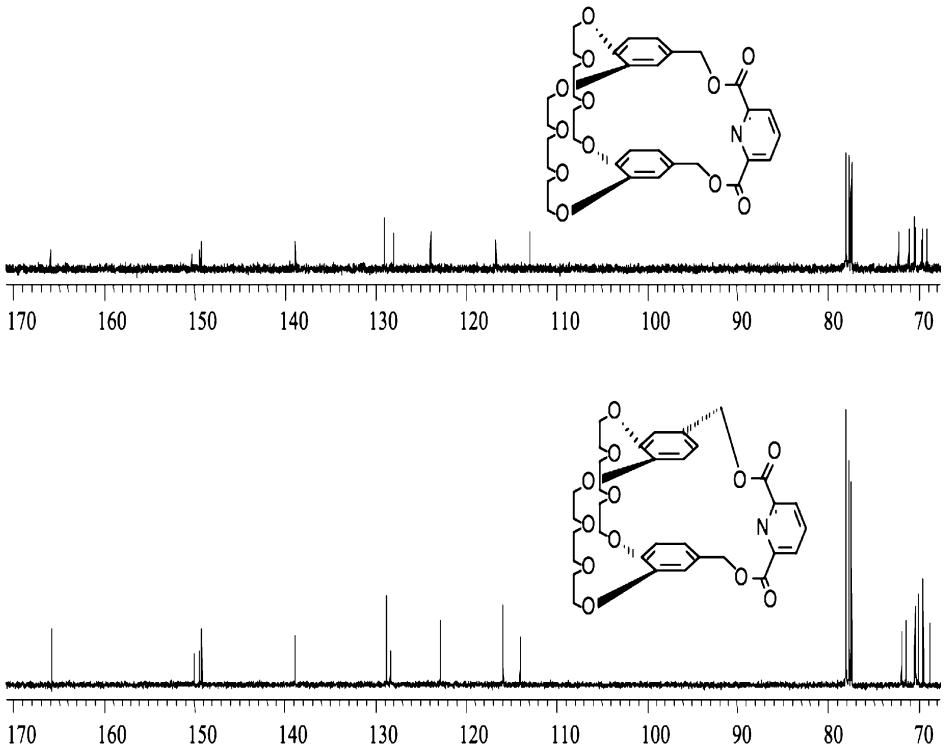


FIGURE 2. 100 MHz ^{13}C NMR spectra of cryptands **4** (top) and **5** (bottom) in $CDCl_3$.

trans-analogue **5** the benzylic methylene protons H_3 are diastereotopic and appear as an AB quartet and the end-to-end nonequivalent proton signals of the two identical ethyleneoxy linkages are not well resolved. The ^{13}C NMR spectra of the *cis*- and *trans*-cryptand isomers are also different (Figure 2), as expected because of the different symmetries.

Crystals of the *cis*- and *trans*-cryptand isomers suitable for X-ray diffraction were obtained by vapor diffusion of pentane

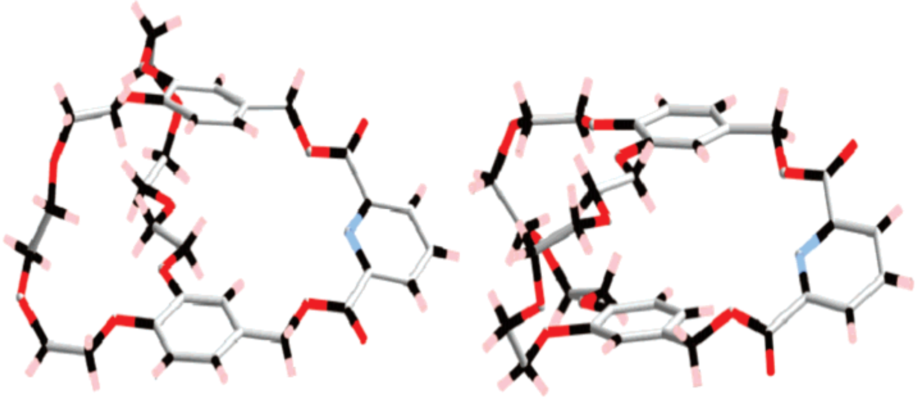


FIGURE 3. X-ray structures of dimorphs of *cis*-cryptand **4**: **I** (a, left) and **II** (b, right). In **I** the tetra(ethyleneoxy) chain shown in the back is disordered and the angle between the planes of the aromatic rings is 20.13°; the distance between the centroids of the aromatic rings is 6.190 Å. In **II** the ethyleneoxy linkers are ordered and the angle between the planes of the aromatic rings is 3.16°; the distance between the centroids of the aromatic rings is 5.098 Å.

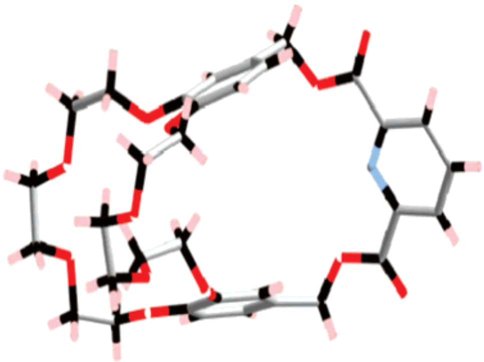
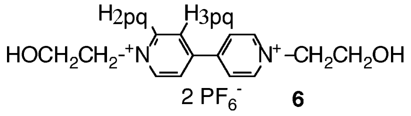


FIGURE 4. X-ray structure of *trans*-cryptand **5**. The tetra(ethyleneoxy) chain shown in the back is disordered and the angle between the planes of the aromatic rings is 22.95°; the distance between the centroids of the aromatic rings is 6.587 Å.

into acetone solutions at room temperature. The crystal structures reveal some structural differences in the molecules and also in the packing motifs. In the crystal structure of one of the dimorphs of the *cis*-isomer **4** (Figure 3a), one of the ethyleneoxy bridges is disordered (not shown) and considerably kinked. This renders the catechol rings nonparallel by ∼20° and makes the centroid−centroid distance between the aromatic rings 6.19 Å. In the second dimorph of **4** (Figure 3b), however, the ethyleneoxy linkers are ordered and the catechol rings are offset, but more nearly parallel: inclination angle ∼3°; the distance between aromatic ring centroids is 5.10 Å. Thus, there is approximately 1 Å difference in the spacing between the catechol rings in the dimorphic solid-state structures.

The crystal structure of the *trans*-isomer **5** (Figure 4) also reveals that one of the ethyleneoxy linkers is partially disordered (not shown) and collapsed, and the catechol rings are not parallel, angle 23°; the distance between the centroids of the catechol rings is 6.59 Å. The cavity of the *trans*-cryptand **5** is slightly more open than that of *cis*-isomer **4** in the solid state. In the crystal packing, the catechol rings of the *trans*-isomer π-stack; the *cis*-isomer, on the other hand, forms a more interdigitated arrangement in which the pyridine rings stack with the attached ester moieties (see Supporting Information (SI)).

B. Complexation of DB24C8-2,6-Pyridino-Cryptands. 1. *N,N′*-Bis(β-hydroxyethyl)-4,4′-bipyridinium Hexafluorophosphate (6).



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The studies of the complexation of the new cryptands with “paraquat diol” hexafluorophosphate (**6**) were carried out in deuterated acetone. In the case of the *cis*-cryptand **4**, complexation is a fast exchange process on the basis of the NMR time scale (Figure 5). In the presence of guest **6**, the largest chemical shifts are observed for the three protons on the benzo rings, H_4, H_5, and H_6, which move strongly upfield. Significant shifts are also observed for the ethyleneoxy protons, whose signals no longer show the resolution observed with **4** itself. The stoichiometry of the complexation was determined to be 1:1 using a mole ratio plot[14] (Figure 6).

The maximum chemical shifts, Δ_0, for H_4, H_5, and H_6 of **4** were determined by extrapolation of a plot of the observed chemical shifts, Δ, versus the inverse concentration of **6** (Figure 7). These values were 0.427, 0.480, and 0.698 ppm, respectively. Using these values, the percentage of host complexed in a given sample is $(\Delta/\Delta_0)(100\%)$.[14]

The *trans*-cryptand complex **5·6** was similarly demonstrated to have 1:1 stoichiometry and the Δ_0 value for H_6 was determined to be 0.943 ppm (see SI).

The NOESY spectra of cryptand isomers with paraquat diol are shown in Figure 8. Strong correlations between the pyridyl aromatic protons H_{2pq} and H_{3pq} of the guest and the γ-ethyleneoxy protons of the host were observed in both cases.

Using nine different solutions with 20−80% complexation of the hosts, as required by the “Weber rule”,[14] values of the association constants $\{K_a = (\Delta/\Delta_0)/[1 - (\Delta/\Delta_0)]([\mathbf{6}]_o - (\Delta/\Delta_0)[\mathbf{4}\text{ or }\mathbf{5}]_o)\}$ calculated from the results for the H_6 signals

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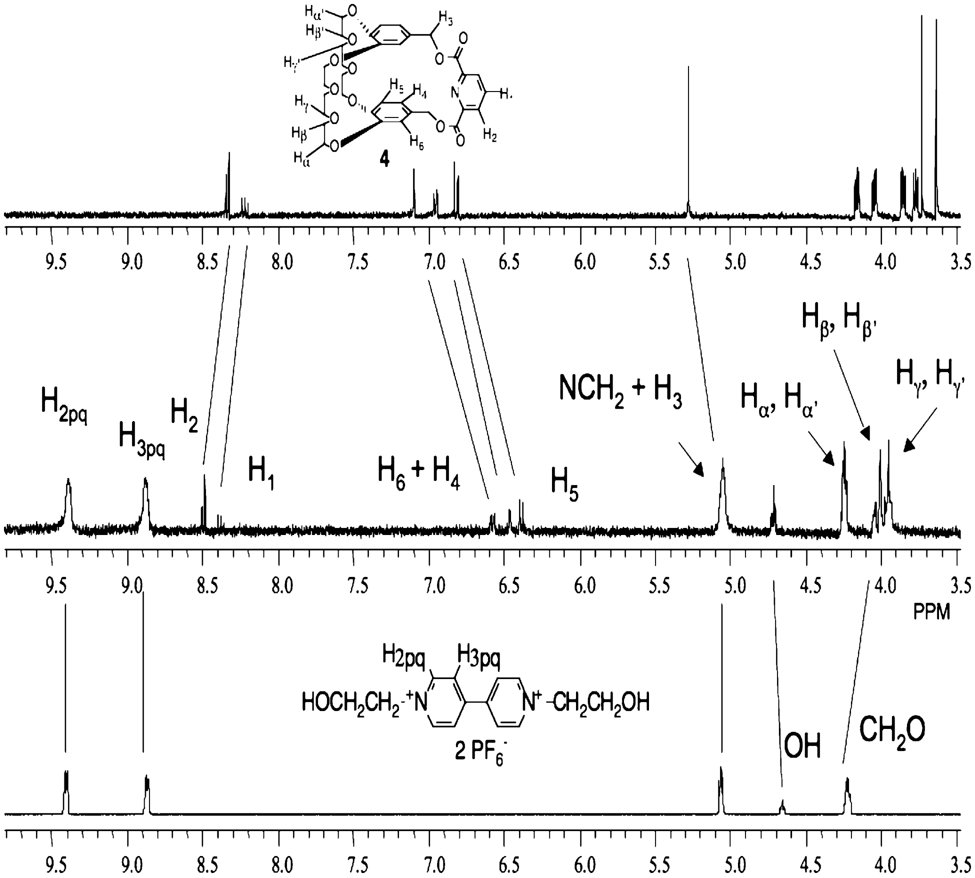

FIGURE 5. Partial 400 MHz ^{1}H NMR spectra of *cis*-cryptand (**4**) (top), *N,N′*-bis(β-hydroxyethyl)-4,4′-bipyridinium bis(hexafluorophosphate) (**6**) (bottom), and **4** (2.01 mM) with **6** (3.00 mM) (center) in CD_3COCD_3.

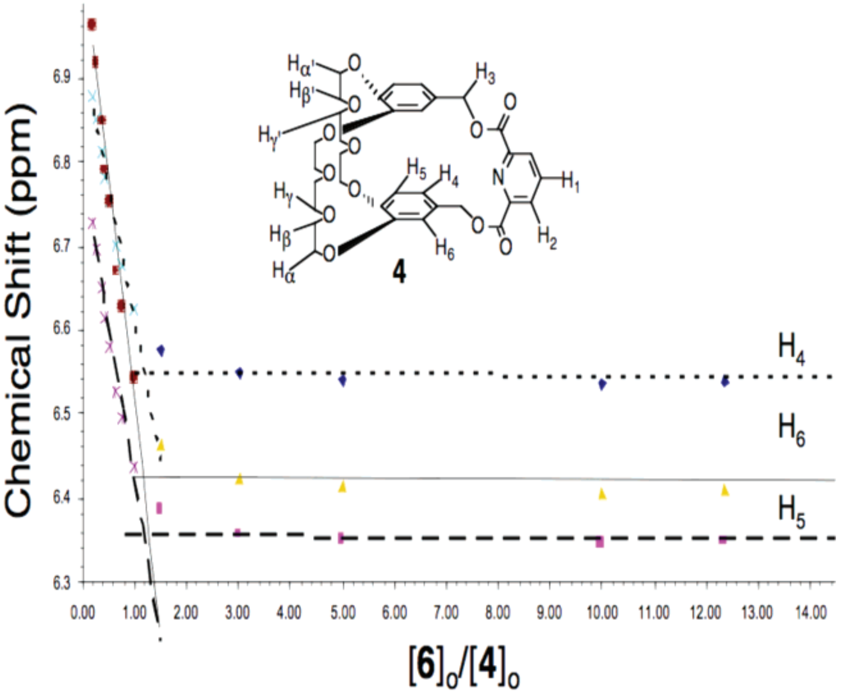

FIGURE 6. Mole ratio plot for determination of stoichiometry of complexation between *cis*-dibenzo-24-crown-8-based cryptand **4** and paraquat diol bis(hexafluorophosphate) (**6**) in CD_3COCD_3 using 400 MHz ^{1}H NMR data. $[\mathbf{4}]_o = 2.01$ mM.

were found not to vary with concentrations of the hosts and guest (see SI). This means that both complexes, **4·6** and **5·6**, are ion paired, as is guest salt **6**, and determination of K_a as outlined above is legitimate.[12,15] For the *cis*-cryptand complex

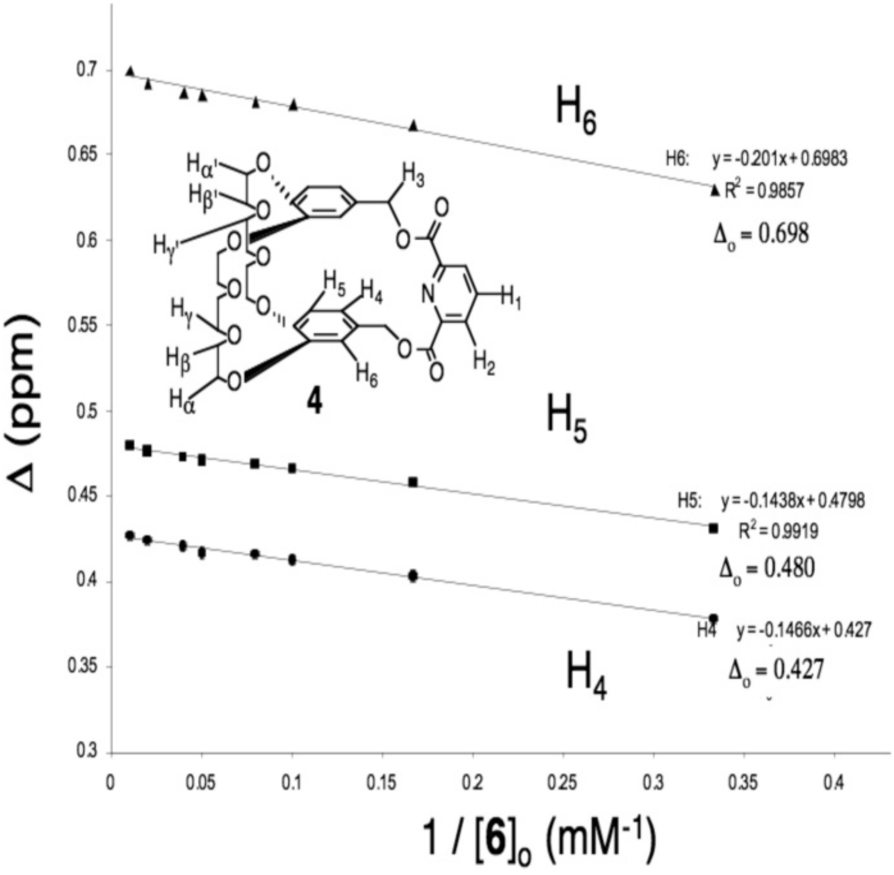

FIGURE 7. Determination of maximum chemical shifts (Δ_o) of host protons in the complex of *cis*-cryptand **4** and *N*,*N*′-bis(β-hydroxyethyl)-4,4′-bipyridinium bis(hexafluorophosphate) (**6**). $[\mathbf{4}]_o = 2.01$ mM.

4·6 $K_a = 1.0\ (\pm 0.1) \times 10^4\ \mathrm{M}^{-1}$ and for the *trans*-cryptand complex **5·6** $K_a = 1.4\ (\pm 0.1) \times 10^4\ \mathrm{M}^{-1}$.

The complex between *trans*-DB24C8 cryptand **5** and paraquat diol bis(hexafluorophosphate) (**6**) was detected by positive ion high-resolution fast atom bombardment (FAB) mass spectrometry after loss of a PF_6 counterion: *m*/*z* 1030.3335 (error 0.8 ppm). The corresponding *cis*-complex **4·6** yielded a peak at *m*/*z* 1030.3385 (error 5.7 ppm).

Crystals of both complexes suitable for X-ray diffraction were obtained and examined. The crystal structures show that the pseudorotaxane complexes are stabilized by hydrogen bonding between host and guest and $\pi-\pi$ stacking between the pyridinium rings of the guest and the catechol rings of the cryptands. Complex **4·6** (Figure 9) is ion paired as shown by the short N^+-F distance (2.70 Å), in accord with its state in solution, and is consistent with previous systems;[15b] the fact that the guest salt and the complex are ion paired enables facile measurement of the association constant, as noted above. Two of the H_{3pq}-protons are hydrogen bonded to the pyridyl nitrogen atom (a and b), as observed in the analogous bis(*m*-phenylene)-32-crown-10-based cryptand.[11b] The other two H_{3pq}-protons are hydrogen bonded to an aliphatic ether oxygen atom (d and e) as are two of the H_{2pq}-protons (c and f). The H_{3pq}-protons H-bonded to the nitrogen of the host also are involved in bifurcated H-bonds with the ether oxygen atoms of the ester groups (CH−O 2.65 Å, 101° and 2.54 Å, 131°; 2.73 Å, 123° and 3.06 Å, 121°), indicative of some additional binding. The catechol rings of host **4** are nearly parallel to each other and to the aromatic rings of bipyridiumium guest **6** (within 10°); the interplanar distances between the catechol rings and the bipyridinium rings are nearly equal, 3.71 and 3.77 Å. Insertion of guest species **6** results in expansion of the cavity of host **4**, as can be seen by comparison to Figure 3; this occurs by extension of the ethyleneoxy moieties.

The crystal structure of the paraquat diol complex of the *trans*-isomer, **5·6**, is shown in Figure 10. The pseudorotaxane complex is ion paired as shown by the short N^+-F distance (2.98 Å), in accord with its NMR-deduced behavior in solution. There is hydrogen bonding between the anion and a H_{2pq} with an H−F distance of 2.12 Å and a P−F−H angle of 114.6°. The fact that the guest salt and the complex are both ion paired enables facile measurement of the association constant, as noted above. Overall, the structure is similar to that of the *cis*-analogue discussed above; the paraquat unit is threaded through the pyrido bridge so as to be π-stacked between the benzo rings of the host and to lie orthogonal to the pyridine ring. Two of the H_{3pq}-protons are hydrogen bonded to the pyridyl nitrogen atom (a and b), as observed in the analogous bis(*m*-phenylene)-32-crown-10-based cryptand.[11b] The other two H_{3pq}-protons are hydrogen bonded to aliphatic ether oxygen atoms (d and e) as are two of the H_{2pq}-protons (c and f). As in isomeric **4·6**, the H_{3pq}-protons H-bonded to the nitrogen of the host also are involved in bifurcated H-bonds with the ether oxygen atoms of the ester groups (CH−O 2.88 Å, 128° and 2.95 Å, 117°; 2.66 Å, 110° and 2.64 Å, 124°), indicative of some additional

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(15) (a) Jones, J. W.; Gibson, H. W. *J. Am. Chem. Soc.* **2003**, *125*, 7001−7004. (b) Huang, F.; Jones, J. W.; Gibson, H. W. *J. Am. Chem. Soc.* **2003**, *125*, 14458−14464.

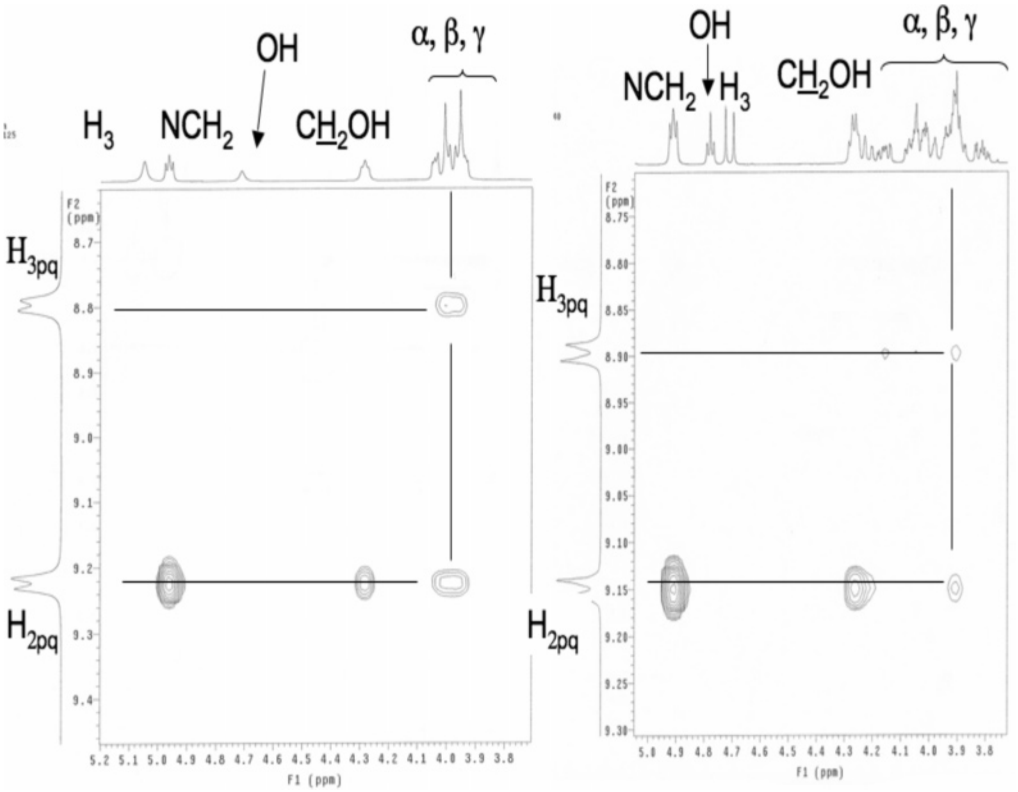

FIGURE 8. 400 MHz ^{1}H NMR NOESY spectra of solutions of paraquat diol salt (**6**) with *cis*-cryptand **4** (left) and *trans*-cryptand **5** (right) in CD_3COCD_3 (2.00 mM in each component) in CD_3COCD_3.

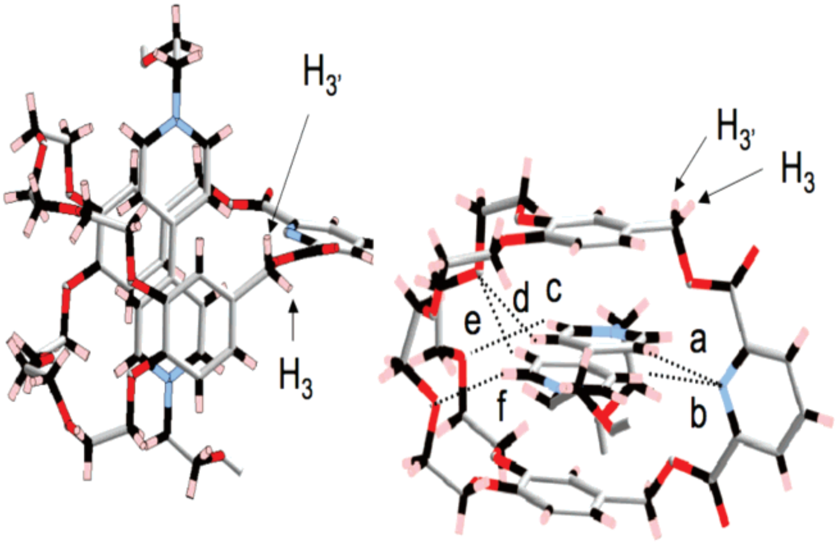

FIGURE 9. Single-crystal X-ray structure of complex **4·6**; the counterions have been omitted for clarity. CH−O(N) distances (Å) and angles (degrees) for H-bonds: (a) 2.40, 159.2; (b) 2.70, 175.9; (c) 2.84, 132.6; (d) 2.32, 130.6; (e) 3.22, 149.6; (f) 2.35, 133.9. Angle of inclination of the catechol rings: 9.89°, centroid−centroid separation: 6.980 Å; angle of inclination of "top" catechol ring and bipyridinium rings: 6.47°, centroid−centroid distance: 3.708 Å; angle of inclination of "bottom" catechol ring and bipyridinium rings: 3.46°, centroid−centroid distance: 3.769 Å. The CH_2OH moieties are disordered.

binding. The catechol rings of host **5** are ∼15° from parallel to each other but are more parallel to the aromatic rings of bipyridinium guest **6** (<10° deviation) and are closer together (6.88 Å) than in **4·6** (6.98 Å). The interplanar distances between the catechol rings and the bipyridinium rings are somewhat different, 3.62 and 3.31 Å, but are less than in **4·6** (3.71 and 3.77 Å). The closer spacing of the aromatic rings of the host and guest is most likely the source of the higher K_a value of **5·6** relative to **4·6**.

The small chemical shift change (∼0.1 ppm) for one doublet of the AB quartet and the rather large shift (∼0.4 ppm) of the other doublet of the benzylic methylene protons H_3 of **5·6** relative to **5** are completely consistent with the X-ray structure; one set of methylene protons, designated H_3 (see SI Figure S5),

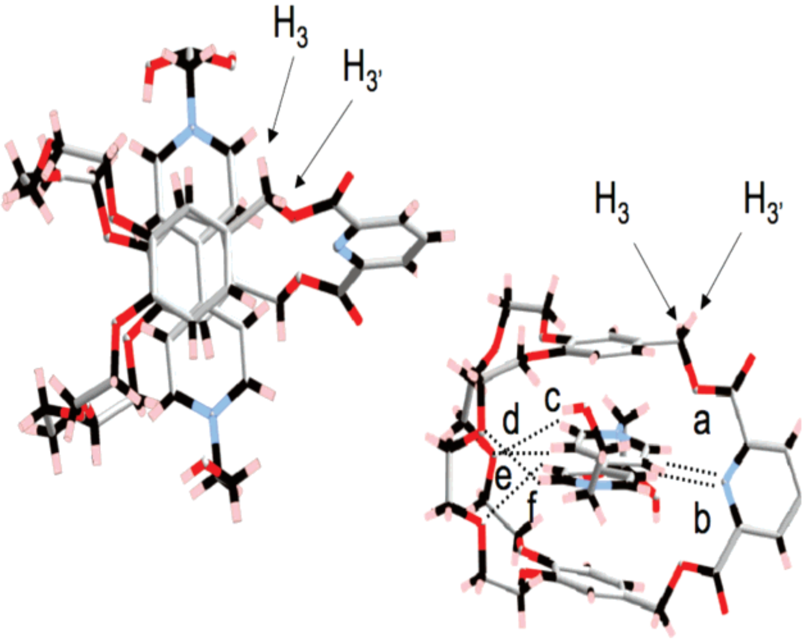

FIGURE 10. Single-crystal X-ray structure of complex **5·6**; the PF_6^- counterions and acetone solvate are omitted for clarity. CH−O(N) distances (Å) and angles (degrees) for H-bonds: (a) 2.47, 166.0; (b) 2.63, 174.5; (c) 2.53, 133.1; (d) 3.06, 111.0; (e) 2.80, 115.7; (f) 2.42, 138.2. Angle of inclination of the catechol rings: 14.57°, centroid−centroid distance: 6.879 Å; angle of inclination of "top" catechol ring and bipyridinium rings: 8.35°, centroid−centroid distance: 3.621 Å; angle of inclination of "bottom" catechol ring and bipyridinium ring: 6.31°, centroid−centroid distance: 3.308 Å. The CH_2OH moieties are disordered.

is nearly in the plane (dihedral angles 9.4°, 15.1°, Figure 10) of the benzo ring of the host, placing it in the shielding zone of the paraquat unit, while the other set of methylene protons, designated $H_{3'}$, is pointed away from the cavity (dihedral angles 44.7°, 50.5°, Figure 10).

2. Ammonium Hexafluorophosphate. Seprate solutions of *cis*- and *trans*-DB24C8 cryptands with ammonium hexafluorophosphate in acetone-d_6 were examined by ^1H NMR spectroscopy. The spectra (Figures 11 and 12) indicate that the complexations are rapid exchange processes. In **4**·NH_4PF_6 (Figure 11), protons H_4 and H_6 on the benzo rings of the host are shifted downfield (~0.1 ppm), the ethyleneoxy protons shift downfield (H_γ and $H_{\gamma'}$ by up to 0.2 ppm), but H_5, the pyridyl and the benzylic protons are not shifted significantly. In **5**·NH_4PF_6 (Figure 12), protons H_4 and H_5 on the benzo rings of the host are shifted downfield (~0.1 ppm), the ethyleneoxy protons shift downfield (H_α and $H_{\alpha'}$ by up to 0.3 ppm), but H_6, the pyridyl and the benzylic protons are shifted only slightly. As will be shown below, one complex is ion paired and the other is not; this means one system is dependent on two constants, an ion pair dissociation constant and a binding constant for the free cation,[12,15] while the other is not. Evaluation of the former system requires extensive data[12,15] and inasmuch as our primary focus is on paraquat pseudorotaxanes, no attempt was made to determine the association constants for these new complexes.

We were able to grow single crystals of both NH_4PF_6 complexes suitable for X-ray crystallography. The resultant structures are shown in Figure 13. The ammonium ion is bound in the crown ether portion of both hosts and does not interact with the benzyloxy or pyridyl moieties, consistent with the NMR observations.

In **4**·NH_4PF_6, there are four hydrogen bonds between the ammonium ion and ether oxygen atoms of the cryptand; the NH−O distances range from 2.00 to 2.15 Å with NH−O angles ranging from 152 to 159°, two of these to the phenolic oxygen atoms and two to the dialkyl ether oxygen atoms. There is no interaction of the ammonium ion with the aromatic rings; the binding to the ether oxygen atoms distorts the geometry such that the catechol rings lie at an angle of ~22° with respect to each other. The PF_6^- counterion is not close to the cation: N−P distance: 6.29 Å, H−F distances: >4.5 Å; thus, this complex is not ion paired in the solid state and most likely this is the case in solution as well; this is consistent with observations on other complexes of dibenzo-24-crown-8-based hosts.[12,15]

In **5**·NH_4PF_6, there are four hydrogen bonds between the ammonium ion and ether oxygen atoms of the cryptand; the NH−O distances again range from 2.00 to 2.15 Å with NH−O angles ranging from 150 to 166°; again, two of these involve the phenolic oxygen atoms and two involve the dialkyl ether oxygen atoms. As in the *cis*-analogue, this hydrogen bonding causes substantial distortion of the catechol moieties relative to the other structures; the interplanar angle is ~65°. However, in contrast to **4**·NH_4PF_6, in this case the PF_6^- counterion is close to the cation: N−P distance: 4.39 Å, H−F distances: 2.58, 2.64 Å; thus, **5**·NH_4PF_6 is ion paired in the solid state and most likely in solution as well.

3. Reversible Displacement of Paraquat Diol from Pseudorotaxane Complexes by KPF_6. Because dibenzo-24-crown-8 complexes potassium ion strongly ($K_a = 7.6 \times 10^3\ M^{-1}$, average from conductivity and solubility measurements in acetonitrile, 25 °C),[16] we used KPF_6 as an effective templating agent for formation of the diesters **1a** and **1b**.[12] Indeed, the complexes even survived column chromatography with ethyl acetate, and preliminary estimates indicated that K_a values for these new crown ethers were comparable to that of the parent dibenzo-

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[16] Takeda, Y. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 3600−3602. Takeda, Y.; Kudo, Y.; Fujiwara, S. *Bull. Chem. Soc. Jpn.*, **1985**, *58*, 1315−1316. Tawarah, K. M.; Mizyed, S. A. *J. Solution Chem.* **1989**, *18*, 387−401. Chantooni, M. K., Jr.; Roland, G.; Kolthoff, I. M. *J. Solution Chem.* **1988**, *17*, 175−189.

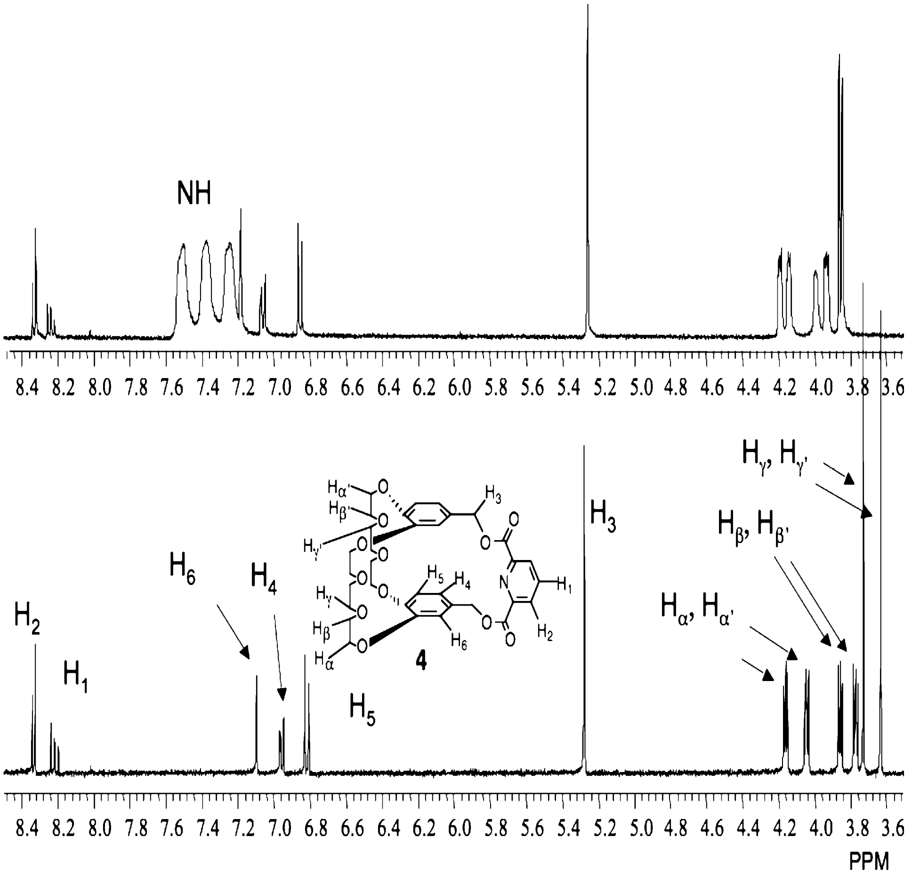

FIGURE 11. 400 MHz ^{1}H NMR spectra of solutions of *cis*-cryptand **4** (by itself, bottom, a) and with ammonium hexafluorophosphate (2.00 mM each, top, b) in CD_3COCD_3.

24-crown-8.[12] Seeking a simple method to modulate the interaction of paraquat guests with the new cryptands in pseudorotaxane-forming equilibria **4** + **6** = **4·6** and **5** + **6** = **5·6**, we investigated use of this salt. Equimolar solutions (1.00 mM) of *cis*- or *trans*-DB24C8 cryptands **4** or **5** with paraquat diol bis(hexafluorophosphate) (**6**) in acetone-d_6 are yellow or yellow-orange. When KPF_6 was titrated into the colored solutions, they gradually became colorless as the complexes between the cryptands and paraquat were dissociated by the competitive binding of the cryptands with the potassium cation. However, the process was reversed by titration with 18-crown-6; the colorless solution gradually reverted to yellow or yellow-orange. 18-Crown-6 does not complex the paraquat but forms a very strong complex with the potassium cation ($K_a = 1.3 \times 10^6$ M^{-1} in methanol at 25 °C),[17] freeing the cryptand, which then recomplexes paraquat (Figure 14). These visual observations are corroborated by ^{1}H NMR spectra (Figure 15 for **5·6**). This reversible complexation process provides a simple on−off switch for formation/dissociation of paraquat pseudorotaxanes; it could be configured to be a sensor for potassium (and other alkalai metal cations or ammonium ions), as recently reported using another host system.[18]

Single-crystal X-ray structures of the potassium complexes of both cryptands are shown in Figure 16. They are comparable to the structures of the ammonium complexes noted above (Figure 13) in that the guest cation resides in the crown ether portion of the host and does not interact with the pyridyl portion. In the *cis*-isomer **4**·K^+ PF_6^-, the complex is clearly ion paired; there are three short (2.7−3.0 Å) interaction distances of the K cation with the fluorine atoms of the counterion and six short-range (~2.8 Å) interactions of the K cation with the ether oxygen atoms of the cryptand. On the contrary, the *trans*-isomer **5**·K^+ PF_6^- is clearly not ion paired; the cation is 8-coordinate with the ether oxygen atoms (2.7−2.9 Å) and the K−F distances are all >4.3 Å. This is an interesting turnabout: as noted above, the *cis*-cryptand complex of the ammonium ion is not ion paired, but the *trans*-cryptand complex is ion paired, just the opposite of the situation here with the potassium ion complexes. This points out the importance of experimentally determining whether complexes derived from salts are indeed ion paired or not before attempting to estimate association constants, especially using NMR spectroscopy.[12,15]

In light of Figure 16, the displacement of the paraquat diol **6** by potassium ion can be understood: the K^+ cation strongly interacts with the ether oxygen atoms of the crown ether moiety, disrupting the PQ diol hydrogen bonding to two of the aliphatic ether oxygen atoms.

4. Complexation of Other Guests. We also examined the complexing abilities of the new cryptands with other guests. Interaction of the *cis*-cryptand **4** with benzylammonium tetrafluoroborate was demonstrated by ^{1}H NMR spectral evidence; except for the benzylic protons H_3 all the peaks of the host and guest shift upon complexation, some rather significantly, for example, the H_γ and $H_{\gamma'}$ signals (see SI). On the basis of the results for complexes of NH_4PF_6 and KPF_6 discussed above,

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[17] Frensdorff, H. K. *J. Am. Chem. Soc.* **1971**, *93*, 600−606.

[18] Yen, M.-L.; Li, W.-S.; Lai, C.-C.; Chao, I.; Chiu, S.-H. *Org. Lett.* **2006**, *8*, 3223−3226.

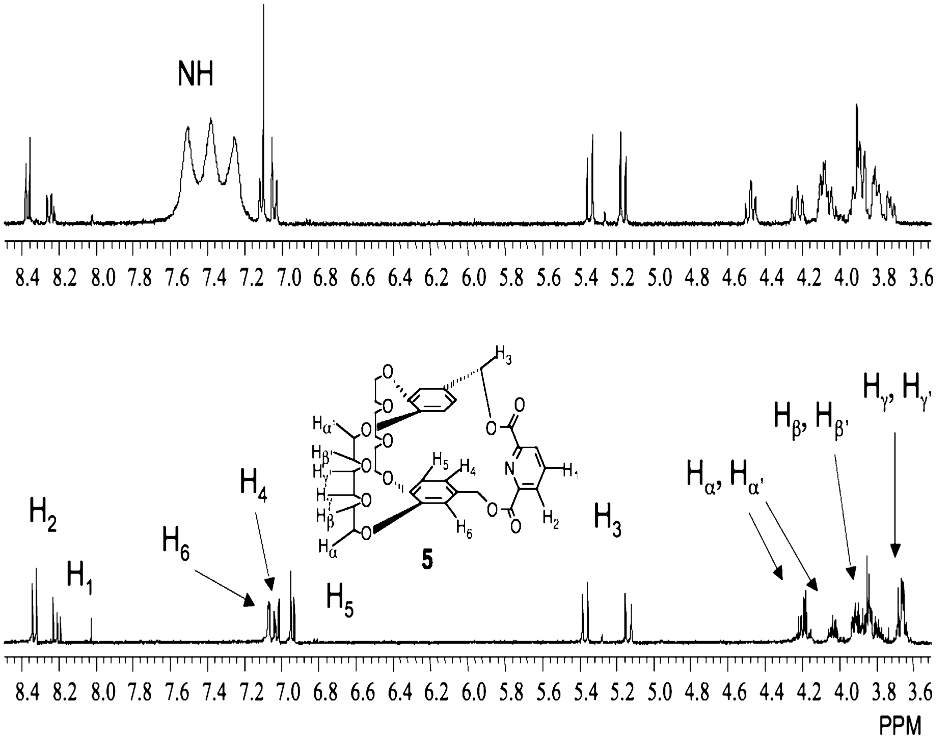

FIGURE 12. 400 MHz ^{1}H NMR spectra of solutions of *trans*-cryptand **5** (by itself, bottom, a) and with ammonium hexafluorophosphate (2.00 mM each, top, b) in CD_3COCD_3.

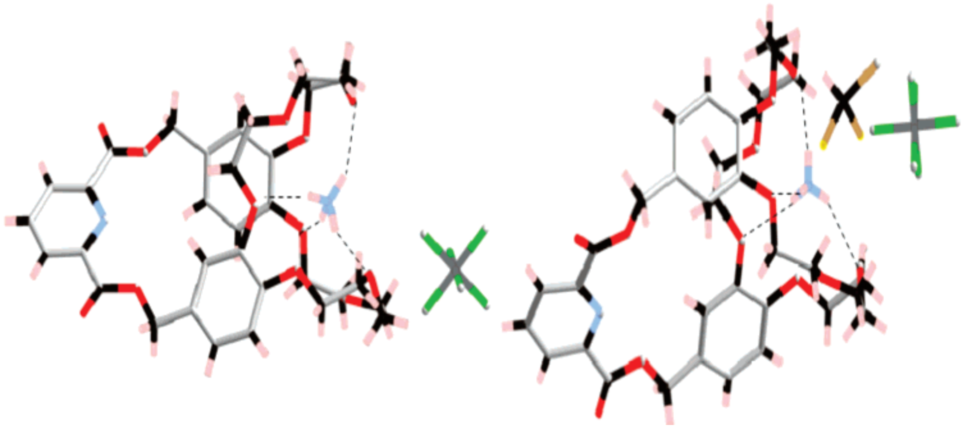

FIGURE 13. X-ray structures of the complexes of *cis*-cryptand **4** (left) and *trans*-cryptand **5** (right) with ammonium hexafluorophosphate. NH−O distances (Å) and angles (degrees) for H-bonds in **4**$\cdot NH_4PF_6$: 2.02, 152.4; 2.03, 159.1; 2.12, 153.2; 2.14, 158.0. NH−O distances (Å) and angles (degrees) for H-bonds in **5**$\cdot NH_4PF_6$: 2.07, 166.4; 2.09, 151.7; 2.15, 161.7; 2.15, 150.5. In **4**$\cdot NH_4PF_6$ closest N−P distance: 6.29 Å, closest N−F distance: 4.55 Å (not ion paired). In **5**$\cdot NH_4PF_6$ closest N−P distance: 4.39 Å, closest N−F distance: 3.00 Å, closest F−H distances: 2.58, 2.64 Å (ion paired). The solvent molecule in **5**$\cdot NH_4PF_6$ is $CHCl_3$; it is H-bonded to an oxygen atom of the host: CH−O 2.76 Å, 125°. Catechol ring centroid−centroid distances and angles: for **4** 5.498 Å, 21.96°; for **5** 7.227 Å, 64.56°.

this complex is probably also of the “perching-type”.[19] Here the conformation of the cryptand enforces the folding of the crown ether moiety, facilitating this type of host−guest interaction. We did not attempt to determine the association constant for this fast exchange system.

On the basis of the ^{1}H NMR spectral evidence, complexation of dibenzylammonium hexafluorophosphate with *cis*-cryptand **4** is rather weak; unlike the case with the crown ether diesters

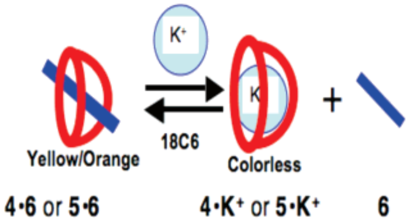

FIGURE 14. Reversible complexation of cryptands with *N*,*N*′-bis(*β*-hydroxyethyl)-4,4′-bipyridinium bis(hexafluorophosphate) (**6**) brought about by displacement with the cation from KPF_6 and the subsequent rebinding of **6** by the cryptands as K^+ is bound by added 18-crown-6.

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[19] De Boer, J. A. A.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **1985**, *107*, 5347−51. Cram, D. J. *Science* **1988**, *240*, 760−767. Ozbey, S.; Kaynak, F. B.; Togrul, M.; Demirel, N.; Hosgoren, H. *Z. Kristallogr.* **2003**, *218*, 381−384.

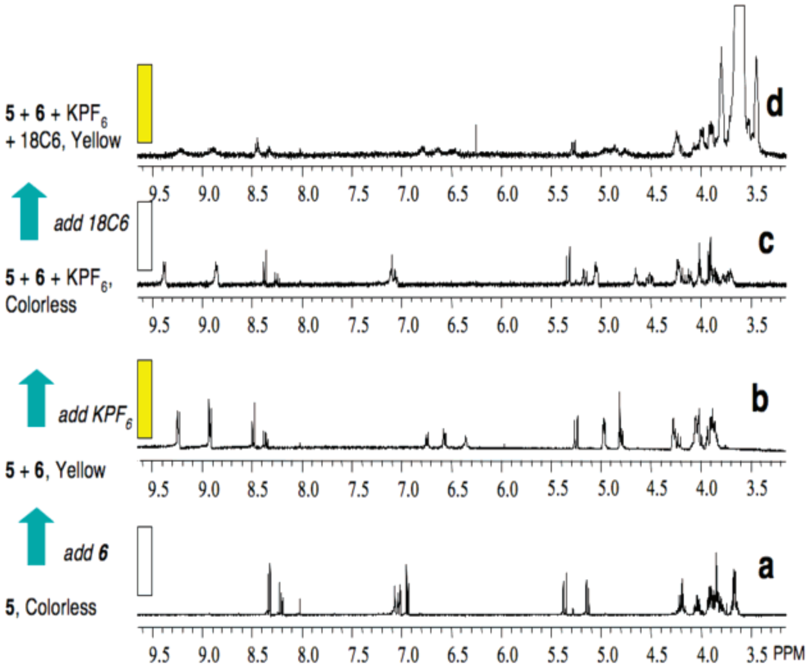

FIGURE 15. 400 MHz ^{1}H NMR spectra of a solution of *trans*-cryptand **5** (a), **5** and *N*,*N*′-bis(*β*-hydroxyethyl)-4,4′-bipyridinium bis-(hexafluorophosphate) (**6**) in CD_3COCD_3 (1.0 mM each) before (b) and after (c) addition of KPF_6, and then (d) 18-crown-6.

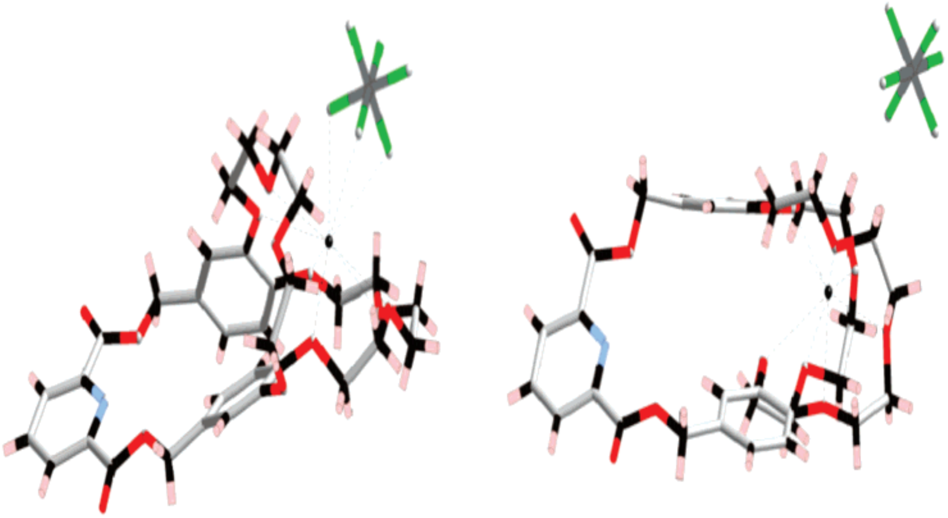

FIGURE 16. X-ray structures of the complexes of *cis*-cryptand **4** (left) and *trans*-cryptand **5** (right) with potassium hexafluorophosphate. Distances (Å) for K−O in **4**$\cdot KPF_6$: 2.84, 2.83, 2.83, 2.78, 2.77, and 2.76. Distances (Å) for K−O in **5**$\cdot KPF_6$: 2.93, 2.80, 2.78, 2.78, 2.75, 2.73, 2.71, and 2.69. In **4**$\cdot KPF_6$ K−P distance: 3.50 Å, K−F distances: 2.74, 2.86, and 2.95 (ion paired). In **5**$\cdot NH_4PF_6$ K−P distance: 5.67 Å, K−F distances: 4.38, 5.27, and 5.35 (not ion paired). Catechol ring centroid−centroid distances and angles: for **4** 5.702 Å, 57.29°; for **5** 6.961 Å, 23.87°.

1a and **1b** (K_a = 190 and 312 M^{-1} for binding the free dibenzylammonium cation, respectively, in 2:3 CD_3CN:$CDCl_3$ at 23 °C),[12] signal doubling (slow exchange) was not observed and chemical shift changes were rather modest (see SI), suggesting a weak interaction. We therefore conclude that, relative to the flexible crown ethers and in constrast to the situation with the primary ammonium salt discussed above, the folded and more rigid structure of **4** is detrimental for complexation of the dibenzylammonium cation that is primarily based on hydrogen bonding of the N−H protons to ether oxygen atoms. Nonetheless, the 1:1 complex was detected by high-resolution mass spectrometry [*m*/*z* 837.3600 (NBA/PEG); calculated for $C_{47}H_{53}N_2O_{12}$ $(M-PF_6)^+$: *m*/*z* 837.3599].

Solutions of the *cis*- and *trans*-cryptands **4** and **5** individually with *p*-nitrophenol in acetone-d_6 were examined by NMR. The spectra (see SI) indicate no complexation in either case.

Conclusions

Two new dibenzo-24-crown-8-based cryptands **4** and **5** were prepared from isomeric diester derivatives of dibenzo-24-crown-8 (**1**) after conversion to the diols **2** by reactions of the latter with pyridine-2,6-dicarbonyl chloride. The new cryptands are effective hosts for paraquat (viologen) compounds, ammonium and potassium ions. The significant binding constants for paraquat diol **6** (K_a = 1.0 × 10^4 and 1.4 × 10^4 M^{-1}) are lower than the analogous bis(*m*-phenylene)-32-crown-10 cryptand analogue (5.0 × 10^6 M^{-1}),[11b] but the ease of synthesis of the precursors (particularly the *cis*-diester **1a**, which is formed in 100% yield in the cyclization reaction)[12] of the present compounds affords a significant advantage in terms of availability relative to the tedious, lower yield route to the analogous bis(*m*-phenylene)-32-crown-10 diol precursor.[20] Therefore, these new cryptands are viewed as very good candidate components for construction of supramolecular polymers with high degrees of polymerization (n); compared to systems based on analogous crown ethers, n values 10 times higher should be achievable since $n = (K_a[H]_0)^{1/2}$. The ability of K^+ to displace paraquats from pseudorotaxanes derived from these cryptands provides a new switching mode for molecular shuttles comprised of appropriately constructed rotaxane analogues.

Experimental

***cis*-Bis(hydroxymethylbenzo)-24-crown-8 (2a).** To a suspension of LAH (0.67 g, 18 mmol) was added dropwise a solution of ester **1a**[12] (5.00 g, 8.86 mmol) in 250 mL of THF at 0 °C. The reaction mixture was stirred at room temperature (rt) 12 h and excess LAH was quenched with ethyl acetate. The solid was removed by filtration. The filtrate was concentrated to give a colorless solid, which was dissolved in chloroform and was washed with water and saturated NaCl solution. After drying over anhydrous Na_2SO_4 and concentration to remove solvent, a colorless solid, 4.06 g (90%), was obtained and recrystallized from hexane-ethyl acetate, mp 98.3−99.0 °C. ^1H NMR ($CDCl_3$) δ: 3.82 (s, 8H), 3.91 (m, 8H), 4.17 (m, 8H), 4.48 (s, 4H), 6.78 (d, $J = 5$ Hz, 2H), 6.89−6.95 (m, 4H). ^{13}C NMR ($CDCl_3$) δ: 65.2, 69.4, 69.5, 71.3, 113.0, 113.9, 120.0, 134.2, 148.5, 149.2 (11 peaks, theoretical: 13 peaks). LR FAB MS (NBA/PEG): m/z 509.5 [55%, $(M + H)^+$], 491.5 [100%, $(M - OH)^+$], 460.4 [39%, $(M - CH_2OH{-}OH)^+$], HR FAB MS: calcd. for $C_{26}H_{36}O_{10}$ $[M]^+$: m/z 508.2308; found (NBA/PEG): m/z 508.2301 (error 1.5 ppm).

***trans*-Bis(hydroxymethylbenzo)-24-crown-8 (2b).** To a suspension of LAH (1.50 g, 3.97 mmol) in dry THF (100 mL) was added dropwise a solution of ester **1b**[12] (0.96 g, 1.7 mmol) in anhydrous THF (100 mL) at 0 °C. The reaction mixture was stirred at rt 18 h and excess LAH was quenched with ethyl acetate. The solid was removed by filtration. The filtrate was concentrated to give a colorless solid, which was dissolved in chloroform and was washed with water and saturated NaCl solution. After drying over anhydrous Na_2SO_4 and concentration to remove solvent, a colorless solid was obtained and recrystallized from hexane-ethyl acetate, 0.65 g (86%), mp 121.1−122.0 °C. ^1H NMR ($CDCl_3$) δ: 3.82 (s, 8H), 3.91 (m, 8H), 4.15 (m, 8H), 4.59 (s, 4H), 6.80−6.92 (m, 6H). ^{13}C NMR (ref $CDCl_3$, 77.7 ppm): δ 65.9, 70.0, 70.2, 70.6, 70.6, 72.0, 113.7, 114.6, 120.6, 134.9, 149.1, 149.7 ppm (12 peaks; theoretical: 13). HR FAB MS: calcd for $C_{26}H_{36}O_{10}$ $[M]^+$: m/z 508.2308; found (NBA/PEG): m/z 508.2299 (error: 1.9 ppm).

***cis*-DB24C8-Based 2,6-Pyridino-Cryptand 4.** To a solution of pyridine (0.1 mL, 1 mmol) in CH_2Cl_2 (1.5 L), was added *cis*-DB24C8 diol **2a** (0.30014 g, 0.590 mmol) in CH_2Cl_2 (20 mL) and pyridine-2,6-dicarbonyl chloride (0.12039 g, 0.590 mmol) in CH_2Cl_2 (20 mL) simultaneously with two separate syringes via a syringe pump at 0.75 mL/h. After addition, the reaction mixture was stirred at rt 2 days. The solvent was evaporated. The residue was subjected to silica gel column chromatography. The cryptand was isolated as a colorless solid with ethyl acetate as eluent, 160 mg (42%), mp 162.0−162.5 °C. ^1H NMR ($CDCl_3$, TMS reference): δ 3.72 (s, 4H), 3.80 (s, 4H), 3.85 (m, 4H), 3.93 (m, 4H), 4.02 (m, 4H), 4.18 (m, 4H), 5.30 (s, 2H), 6.78 (d, $J = 8.7$, 2H), 6.93 (dd, $J = 2.1$, $J = 8.7$, 2H), 6.98 (d, $J = 2.1$, 2H), 8.03 (t, $J = 7.8$, 1H), 8.36 (d, $J = 7.8$, 2H) ppm. ^{13}C NMR (ref $CDCl_3$, 77.7 ppm): δ 69.2, 69.7, 69.9, 70.5, 70.6, 71.2, 72.2, 113.00, 116.8, 124.0, 127.9, 129.0, 138.9, 149.2, 149.4, 150.4, 166.0 ppm (17 peaks observed; theoretical: 17). LR FAB MS (NBA/PEG): $[M + H + K]^+$ 679.41. HR FAB MS (NBA/PEG): calcd for $C_{33}H_{38}NO_{12}$ $[M + H]^+$: 640.2394; found: 640.2381 (error 2.0 ppm).

***trans*-DB24C8-Based 2,6-Pyridino-Cryptand 5.** To a solution of pyridine (0.1 mL, 1 mmol) in CH_2Cl_2 (3.0 L) was added *trans*-DB24C8 diol **2b** (0.30058 g, 0.591 mmol) in CH_2Cl_2 (80 mL) and pyridine-2,6-dicarbonyl chloride (0.12042 g, 0.590 mmol) in CH_2Cl_2 (80 mL) simultaneously with two separate syringes via syringe pump at 3 mL/h. After addition, the reaction mixture was stirred at rt 3 days. The solvent was evaporated. The residue was subjected to silica gel column chromatography. The cryptand was obtained as colorless solid with ethyl acetate as eluent, 180 mg (48%), mp 163.2−165.8 °C. ^1H NMR ($CDCl_3$, TMS reference): δ 3.93−3.71 (m, 16 H), 4.08−3.98 (m, 4H), 4.24−4.11 (m, 4H), 5.15 (d, $J = 11.9$, 2H), 5.42 (d, $J = 11.9$, 2H), 6.80 (d, $J = 8.7$, 2H), 6.96 (dd, $J = 2.1$, $J = 8.7$, 2H), 6.97 (d, $J = 2.1$, 2H), 8.03 (t, $J = 7.8$, 1H), 8.36 (d, $J = 7.8$, 2H) ppm. ^{13}C NMR (ref $CDCl_3$, 77.7 ppm): δ 69.1, 69.5, 69.7, 70.3, 70.4, 71.1, 72.21 113.0, 116.7, 123.9, 127.9, 129.0, 138.8, 149.2, 149.4, 150.3, 165.9 ppm (17 peaks observed; theoretical: 17). HR FAB MS (NBA/PEG): calcd for $C_{33}H_{38}NO_{12}$ $[M + H]^+$: m/z 640.2394; found: m/z 640.2361 (error 5.2 ppm); calcd for $C_{33}H_{37}NO_{12}$ $[M]^+$: m/z 639.2316, found: m/z 639.2324 (error 1.3 ppm).

Complexation Studies. Solutions were prepared by precisely weighing a minimum of 1.0×10^{-2} g of each host and guest component by means of an analytical balance which read to 1.0×10^{-4} g (five significant figures) into a 5.00 (±0.02) or 10.00 (±0.02) mL volumetric flask equipped with a ground glass stopper to make a moderately concentrated (nominally 16.0 mM) master solution. This solution was then sequentially diluted (no more than four sequential dilutions per master solution) by transferring specific volumes of the higher concentration solution to a clean volumetric flask via a to-deliver volumetric pipet (±0.006 mL) and diluting to the mark. The fresh solutions were filtered through a cotton-filled disposable pipet before 0.500 (±0.006 mL) mL of each solution component (both host and guest) at a specified concentration was transferred via a to-deliver pipet to a 5.0 mm NMR tube. NMR spectroscopic data were collected on a temperature-controlled 400 MHz spectrometer within 1 h of mixing the host and guest solutions. The results in the area of 20∼80% complexation of both components were used to calculate the association constants (see SI). The ± values quoted are standard deviations. The major source of absolute error in calculated K values is error in the absolute concentration on the basis of errors in weighing and volumes: ∼±2% relative.

The complex between *trans*-DB24C8 cryptand **5** and paraquat diol bis(hexafluorophosphate) (**6**)[21] was detected by mass spectrometry after loss of a PF_6 counterion [LR FAB (NBA): 1174.80 (M^+); HR FAB^+, MS calcd for $[M - PF_6]^+$ $C_{47}H_{55}N_3O_{14}PF_6$: m/z 1030.3326, found (NBA/PEG/NaCl): m/z 1030.3335 (error 0.8 ppm)]. Likewise, the complex between *cis*-DB24C8 cryptand **4** and paraquat diol bis(hexafluorophosphate) (**6**)[21] was detected by high-resolution FAB^+ mass spectrometry after loss of a PF_6 counterion: m/z 1030.3385 (error: 5.7 ppm).

Crystal Structure Determinations. Colorless crystals of **4** ($0.12 \times 0.10 \times 0.015$ mm^3) and **5** ($0.45 \times 0.40 \times 0.25$ mm^3) were formed in acetone or chloroform by vapor diffusion of pentane at rt. Crystals of **4·6** (orange triangular plate, $0.045 \times 0.129 \times 0.129$ mm^3), **5·6** (orange plate, $0.04 \times 0.18 \times 0.32$ mm^3), **4**·NH_4PF_6 (colorless plate, $0.051 \times 0.234 \times 0.235$ mm^3), **5**·NH_4PF_6 (colorless prism, $0.460 \times 0.196 \times 0.132$ mm^3), and **5**·KPF_6 (colorless plate, $0.044 \times 0.14 \times 0.14$ mm^3) were grown from acetone solutions by vapor diffusion of pentane at rt. **4**·KPF_6 crystals (colorless plate, $0.05 \times 0.10 \times 0.17$ mm^3) were grown from chloroform by vapor diffusion of pentane at rt. The data collection routine, unit cell refinement, and

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data processing were carried out with the program CrysAlis[22] or SMART.[23] The structures were solved by direct methods and were refined using SHELXTL NT.[24] The program packages SHELXTL NT[24] and PLATON[25] were used to generate crystallographic tables.

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Supporting Information Available: General experimental details, ^{1}H NMR spectra of **5** with **6** in acetone-d_6, **4** with benzylammonium tetrafluoroborate in $CDCl_3$, **4** with dibenzylammonium hexafluorophosphate in 2:3 v:v CD_3CN:$CDCl_3$, **4** with *p*-nitrophenol in acetone-d_6, and **5** with *p*-nitrophenol in acetone-d_6; mole ratio plot for **5** with **6** in acetone-d_6; determination of Δ_0 for proton H_6 of **5** in complexation with **6** in acetone-d_6; results from complexation of cryptands **4** and **5** with **6** in acetone-d_6 as determined by ^{1}H NMR chemical shift measurements; association constants for complexes **4·6** and **5·6** in acetone-d_6; packing diagrams for **4**, **5**, **4·6**, and **5·6** in the solid state; crystallographic (cif) files for **4**, **5**, **4·6**, **5·6**, **4**·NH_4PF_6, **5**·NH_4PF_6, **4**·KPF_6, **5**·KPF_6. This material is available free of charge via the Internet at http://pubs.acs.org.

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[23] *SMART*, Bruker Analytical X-Ray Systems, Inc.: Madison, WI, 2001.

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[25] Spek, A. L. *J. Appl. Cryst.* **2003**, *36*, 7−13.