

Chapter 7

First Pseudorotaxane-Like [3]Complexes Based on Cryptands and Paraquat: Self-Assembly and Crystal Structures

7.1. INTRODUCTION

The first cryptand was reported in 1968.^{1a} The original objective for designing cryptands was to strongly combine metal ions and small organic molecules by encapsulation.¹ Recently progress has been made in synthesis of cryptands that can complex large organic guests, such as paraquat derivatives and ammonium salts. We first reported very strong complexations between a cryptand and paraquat derivatives in 1999.² Three years later, we reported that the formation of supramolecular cryptands³ by chelation of a difunctional macrocycle can improve the complexations with paraquat derivatives⁴ and a diammonium salt.⁵ These cryptands have proven to be powerful hosts for organic guests as shown by their much higher association constants compared with analogous simple crown ethers.²⁻⁵ For all of studied complexation systems based on cryptands, 1:1 stoichiometry was found in solution, gaseous, and solid states based on NMR data, mass spectral characterization, and X-ray analysis. Here we report that complexes of 2:1 stoichiometry can also form as shown by the unique crystal structures of trimolecular pseudorotaxane-like^{2,6} complexes based on two different cryptands and paraquat **1**.

7.2. RESULTS AND DISCUSSIONS

A. Synthesis of a new cryptand, bis-(1,3,5-phenylene)tri(1,4,7,10-tetraoxatridecyl) (3a).

Bis-(1,3,5-phenylene)tri(1,4,7,10,13-pentaoxatridecyl) (**3b**), a reported cryptand, was synthesized in one step from bis(5-hydroxy-1,3-phenylene)-32-crown-10 (**2b**) and tetra(ethylene glycol) ditosylate in 38% yield using the pseudo-high dilution technique.² Bis-(1,3,5-phenylene)tri(1,4,7,10-tetraoxadecyl) (**3a**), a new smaller cryptand, was made from bis(5-hydroxy-1,3-phenylene)-26-crown-8 (**2a**) and tri(ethylene glycol) ditosylate in 25% yield by the same method (Scheme 1). The relatively lower yield of **3a** resulted from the more rigid starting material **2a** compared with **2b**.

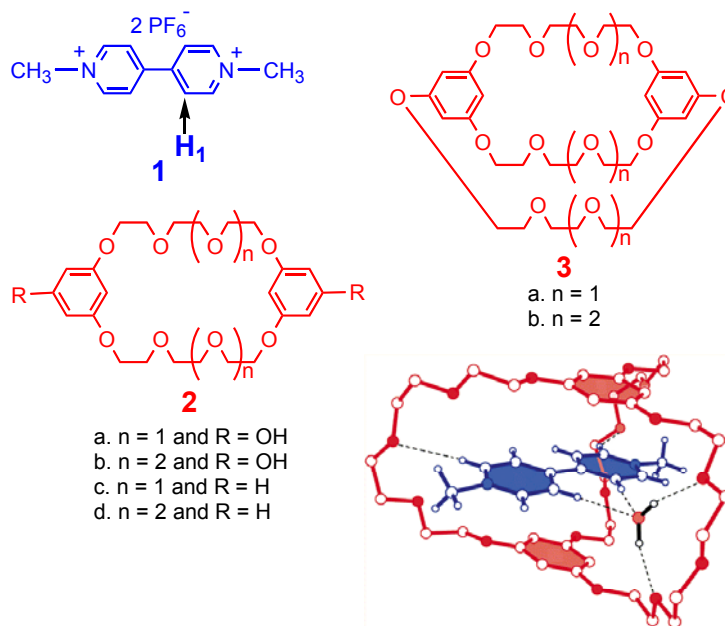


Figure 1. Compounds used in this study and the solid-state structure² of **3b•1**.

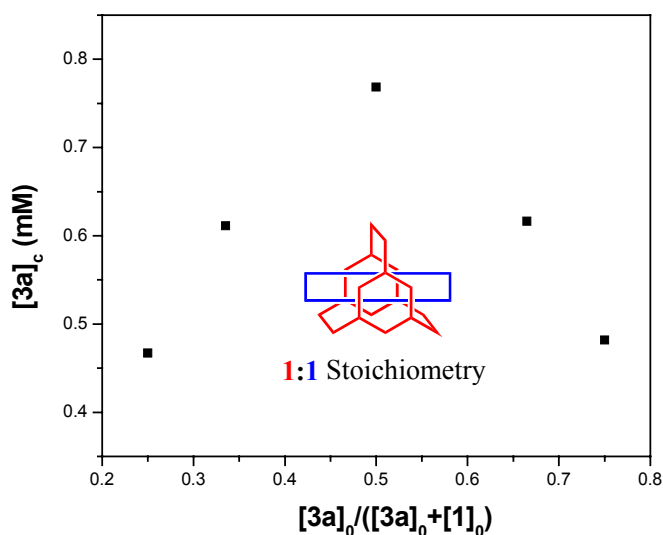


Figure 2. Job plot: the stoichiometry of the complex between **3a** and **1** in CD_3COCD_3 solution using data for the aromatic hydrogen atom of **3a**. $[3a]_c$ is the concentration of complexed **3a**. $[3a]_0 + [1]_0 = 2.00$ mM.

Four solutions containing **2c**, **2d**, **3a**, and **3b**, respectively, with equimolar **1** were characterized by proton NMR (Figure 3). As shown by these NMR spectra, the change of chemical shift of H_1 of paraquat **1** increased from **2c•1** to **2d•1** to **3a•1** to **3b•1**. Correspondingly, the apparent association constants (K_a)⁸ increased from $3.9 (\pm 0.3) \times 10^2 M^{-1}$ to $5.5 (\pm 0.5) \times 10^2 M^{-1}$ to $1.4 (\pm 0.6) \times 10^4 M^{-1}$ to $6.1 \times 10^4 M^{-1}$,² respectively at 1.00 mM initial concentration of host and guest. From **2c•1** to **3a•1**, K_a increased by about 36 times because of the formation of the cryptand structure. In the three ethyleneoxy bridges of the cryptand **3a** or **3b**, the aliphatic oxygen atoms are more basic than the phenolic oxygen atoms because of p - π conjugation in the latter; since there are more aliphatic oxygen atoms in **3b** than in **3a** it is understandable that from **3a•1** to **3b•1**, K_a increased about four times. A yellow color was observed in all four solutions due to the charge transfer interactions between the electron-rich aromatic rings of the host (**2c**, **2d**, **3a**, or **3b**) and the electron-poor guest **1**. However the color was the brightest in **3a•1** and **3b•1**. Therefore charge transfer interaction was strongest in **3a•1** and **3b•1**.

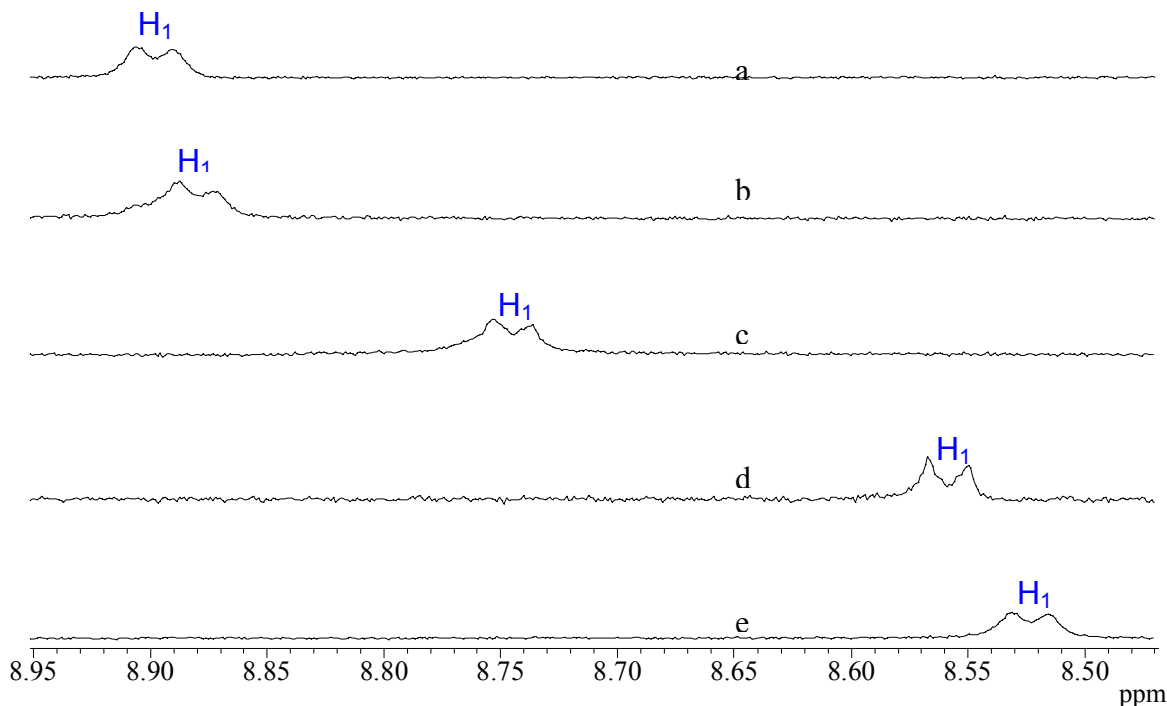


Figure 3. Partial ^1H NMR spectra (400 MHz, CD_3COCD_3 , 298K) of (a) 1.00 mM **1**, (b) 1.00 mM **2c** and 1.00 mM **1**, (c) 1.00 mM **2d** and 1.00 mM **1**, (d) 1.00 mM **3a** and 1.00 mM **1**, (e) 1.00 mM **3b** and 1.00 mM **1**.

Low-resolution fast-atom bombardment mass spectroscopy (LRFAB-MS, matrix: GLY/PEG) was carried out on the crystals of **3a•1**. A peak was observed that gave direct evidence for the formation of the 1:1 complex **3a•1**: m/z 925.35 (**3a** + **1** - PF_6).¹⁰ No peaks related to other stoichiometries were found.

C. Solid state structure of a new 2:1 inclusion complex of large cryptand **3b** with paraquat (**1**).

Previously we reported 1:1 stoichiometry for the complexation between **3b** and **1** in solution, gaseous, and solid states based on proton NMR data, mass spectral characterization, and X-ray analysis (Figure 1).² Here we report the crystal structure¹¹ (Figure 4a and 4b, Tables 1 and 2) of a 2:1 complex based on **3b** and **1**. These 2:1 complex crystals were grown from an acetone solution. Just like the 1:1 complex **3b•1**,

the 2:1 complex **3b•1•3b** is stabilized by hydrogen bonding and face-to-face π -stacking interactions in the solid state and methyl protons of **1** are not involved in any hydrogen bonding. However, there are differences. A unique feature of the 2:1 crystal structure is that each paraquat unit is shared by one half of two cryptand moieties, whereas in all other reported systems, including **3b•1**, each cavity is fully occupied by one paraquat unit.^{2,14} The centroid-centroid distance between the phenylene rings of the **3b** host molecules on the same side of the complex is 8.97 Å. There are six water and three acetone molecules per unit cell, while there are only one water and one acetone molecule per unit cell for the 1:1 complex **3b•1**. In the 1:1 complex **3b•1** the only water molecule is acting as a hydrogen bonding bridge between the β -protons of **1** and the ether oxygen atoms of **3b**, but in the 2:1 complex two water molecules act as hydrogen bonding bridges between the α -protons of **1** and the ether oxygen atoms of the two molecules of **3b**. In **3b•1•3b** each of the four β -protons of **1** forms a bifurcated hydrogen bond with two ethyleneoxy oxygen atoms of each of the **3b** molecules directly without water bridges. The changes of the stoichiometry of the complex and interactions between host and guest moieties have important influences on the conformation of the guest, **1**. From **3b•1** to **3b•1•3b**, the dihedral angle between the two pyridinium rings of **1** changes from 5.8° to and 0°, while in the crystal structure of **1** itself, the corresponding value is 0°.¹⁵ In **3b•1•3b**, the guest **1** does not extend from the cavity of the two **3b** molecules, so strictly speaking it is not a pseudorotaxane (Figures 4a and 4e).

D. Solid state structure of a new 2:1 inclusion complex of small cryptand 3a with paraquat (1).

In contrast to the 1:1 stoichiometry observed in solution and gaseous states, single crystals of the complex between the smaller cryptand **3a** and **1** were of 2:1 stoichiometry as shown by its crystal structure (Figures 4c and 4d, Tables 2 and 3).¹⁶ The 2:1 complex **3a•1•3a** has stabilization forces (hydrogen bonding and face-to-face π -stacking interactions) similar to the homologous 2:1 complex **3b•1•3b** from the large cryptand. However, there are some differences resulting from the change in the cavity size of the

host. Because of the smaller size of the cavity of **3a**, the guest **1** protrudes out from the cavity to form a pseudorotaxane-like [3]complex^{2,6} (Figures 4c and 4f). Also because of the smaller ring size, no bridging water molecules are found in **3a•1•3a**. Therefore, there are no bridging O-H...O hydrogen bonds in **3a•1•3a**. Every pyridinium proton of **1** is involved in direct hydrogen bonding to ethyleneoxy oxygen atoms of host **3a** molecules. In **3b•1•3b** four β -protons of **1** share two oxygen atoms in hydrogen bonding while in **3a•1•3a** four β -protons of **1** form hydrogen bonds with four different oxygen atoms of the smaller host. The centroid-centroid distance between adjacent phenylene rings of the two cryptand molecules decreases from 8.97 Å to 6.89 Å from **3b•1•3b** to **3a•1•3a**. The two cryptand molecules of **3a•1•3a** are connected by two hydrogen bonds with a C...O distance of 3.31 Å, an H...O distance of 2.37 Å, and a C-H...O angle of 158° (**L** in Figures 4c and 4d). These interactions between complexed hosts stabilize the trimolecular complex in a manner not common in multimolecular complexes.^{15,20}

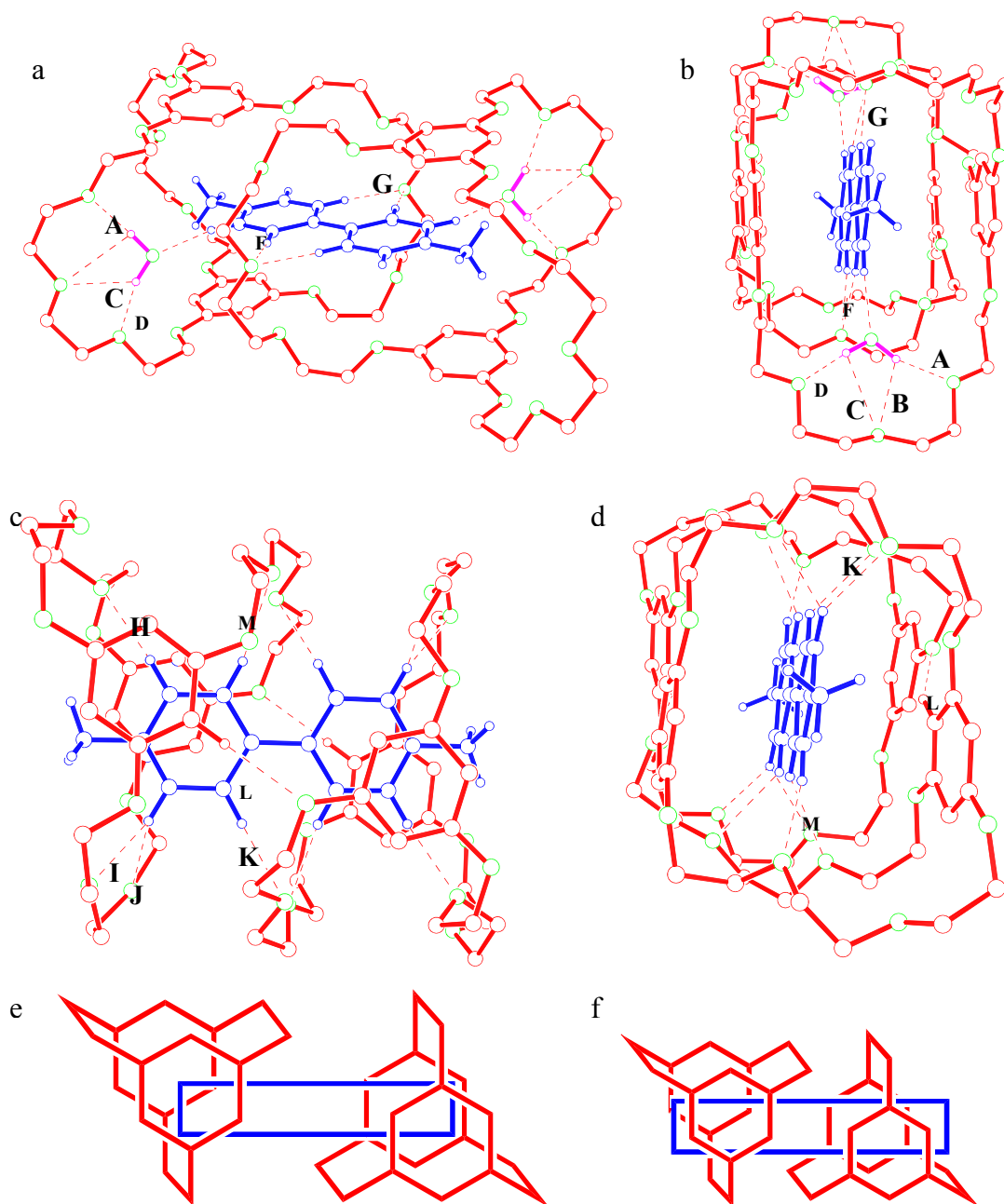


Figure 4. Solid state structures of **3b•1•3b** (a and b) and **3a•1•3a** (c and d) and cartoon representations of **3b•1•3b** (e) and **3a•1•3a** (f). Hosts (**3a** or **3b**) are red, the guest (**1**) is blue, and water molecules are magenta. (a) and (b) Four water molecules, two acetone molecules, two PF_6^- ions, and hydrogens except the ones in paraquat and water molecules have been omitted for clarity. Hydrogen-bond and face-to face π -stacking parameters are listed in Tables 1 and 2. (c) and (d) One disordered acetone molecule, two PF_6^- ions, and

hydrogens except the ones in paraquat have been omitted for clarity. Hydrogen-bond and face-to face π -stacking parameters are listed in Tables 3 and 2. (e) and (f) Hosts (**3a** or **3b**) are red, and the guest (**1**) is blue.

Table 1. Hydrogen-Bond Parameters for **3b•1•3b**.

Parameters	A	B	C	D	E	F	G
C \cdots O or O \cdots O distances (Å)	2.86	3.06	3.06	2.82	3.11	3.34	3.26
H \cdots O distances (Å)	1.87	2.70	2.50	1.88	2.18	2.39	2.32
C-H \cdots O or O-H \cdots O angles (deg)	174	102	117	163	166	174	172

Table 2. Selected Distances and Angles for **3b•1•3b** and **3a•1•3a**.

Parameters	3b•1•3b	3a•1•3a
face-to-face π -stacking centroid-centroid distances (Å)	4.25, 4.32	3.97, 3.51
face-to-face π -stacking ring plane/ring plane inclinations (deg)	8.3, 5.7	4.4, 10.3
centroid-centroid distance (Å) between two phenylene rings of the cryptand	6.95	6.81
dihedral angle (deg) between two phenylene rings of the cryptand	7.8	7.0
centroid-centroid distance (Å) between two pyridinium rings of 1	4.29	4.30
dihedral angle (deg) between two pyridinium rings of 1	0	0
centroid-centroid distance (Å) between two phenylene rings of two cryptand molecules on the same side	8.97	6.89

Table 3. Hydrogen-Bond Parameters for **3a•1•3a**.

Parameters	H	I	J	K	L	M
C \cdots O distances (Å)	3.25	3.40	3.07	3.48	3.31	3.35
H \cdots O distances (Å)	2.26	2.50	2.27	2.63	2.37	2.47
C-H \cdots O angles (deg)	169	150	136	142	158	147

7.3. CONCLUSIONS

It has again been demonstrated that the formation of the cryptand structure is an efficient method to improve complexations with paraquat derivatives.² Two unique 2:1 complexes were found. **3a•1•3a** is unique not only because the guest is encapsulated in the cavities of two cryptand molecules but also because it is stabilized by the interactions between the two host molecules. **3b•1•3b** represents the first case in cryptand-based complexes that different stoichiometries result from the same host-guest pair.

7.4. ACKNOWLEDGEMENTS

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7.5. EXPERIMENTAL SECTION

General Procedures. Dimethylformamide (DMF) was distilled under reduced pressure. Other chemicals were reagent grade and used as received. All solvents were HPLC or GC grade. The NMR spectra were recorded on a Varian Unity or Inova Instrument. Low-resolution electron impact mass spectroscopy (LREIMS) was carried out on VG-Quohro4000 (direct probe inlet) Triple Quodrupole Mass Spectrometer. High-resolution fast-atom bombardment mass spectroscopy (HRFABMS) was carried out on HX110 Dual Focusing Mass Spectrometer using xenon gas for ionization. Melting points were taken in capillary tubes and were uncorrected. Elemental analyses were performed by Atlantic Microlabs of Norcross, GA. X-ray diffraction of **3b•1•3b** was carried out at 120K on an Enraf-Nonius CAD4 diffractometer equipped with MoK α radiation ($\lambda = 0.71073 \text{ \AA}$) and a graphite monochromator. X-diffraction of **3a•1•3a** was carried out on

an Oxford Diffraction XCalibur2™ diffractometer equipped with the Enhance X-ray Source™ (MoK α radiation; $\lambda = 0.71073 \text{ \AA}$) and a Sapphire 2™ CCD detector.

5-Benzoyloxyresorcinol (5). Phloroglucinol dihydrate, 32.00 g, (197 mmol) was placed in a 100 mL round bottom flask equipped with a Dean Stark trap and dehydrated using 75 mL toluene. After removal of the water and evaporation of the solvent dry phloroglucinol (4) was dissolved in 200 mL DMF and added via a 250 mL addition funnel to a suspension containing 12.27 g K₂CO₃ (88.8 mmol) in 200 mL DMF. The mixture was stirred with a mechanical stirrer for 10 min. 15.19 g benzyl bromide (88.8 mmol) was diluted with 200 mL DMF and added dropwise over 3 h to the reaction mixture. After complete addition the reaction mixture was stirred for 1 h. The mixture was then filtered and the solvent was removed by rotaevaporation to afford a brown oil, which was adsorbed on silical gel and purified by flash column chromatography (CH₂Cl₂; CH₂Cl₂:Et₂O, 85:15) to provide 7.04 g (37%) **5**, an oil. ¹H NMR (400 MHz, CDCl₃, 25 °C) δ 7.94 (s, 2H), 7.32 (m, 5H), 6.08 (d, $J = 2.0$ Hz, 2H), 6.05 (t, $J = 2.0$ Hz, 1H), 4.92 (s, 2H); ¹³C NMR (100 MHz, CDCl₃, 25 °C) δ 160.7, 157.9, 136.9, 128.4, 127.8, 127.5, 96.1, 94.8, 69.8.

3,5-Bis(8-chloro-3,6-dioxaundecyloxy)benzyloxybenzene (6). 10.3 g (47.6 mmol) **5** and 89.10 g (476 mmol) tri(ethylene glycol) dichloride were dissolved in a suspension of 29.7 g (215 mmol) potassium carbonate in acetonitrile (~ 25 mL) at 70 °C. The mixture was stirred with a mechanical stirrer for 140 h, cooled to RT and filtered. The solvent was removed from the filtrate by rotaevaporation. The resulting brown oil was dissolved in chloroform and washed with water (2 \times 200 mL). The organic layer was evaporated to give a brown oil. The excess dichloride was removed by vacuum distillation (61 °C @ 0.25 mmHg). The distillate was subjected to liquid-liquid extraction using petroleum ether for 16 days, resulting in the isolation of 12.7 g of **6**. The crude material was subjected to flash column chromatography (ethyl ether) and 2.23 g (62 %) **6** was obtained. ¹H NMR (400 MHz, CDCl₃, 25 °C) δ 7.35 (m, 5H), 6.18 (d, $J = 2.0$ Hz, 2H), 6.13 (t, $J = 2.0$ Hz, 1H), 4.99 (s, 2H), 4.07 (m, 4H), 3.83 (m, 4H), 3.68 (m, 16H); ¹³C NMR (100 MHz) δ 160.5, 136.7, 128.5, 127.9, 127.5, 94.5, 94.4, 71.3, 70.7, 70.6, 70.0, 69.6, 67.4, 42.7.

Bis(5-benzyloxy-1,3-phenylene)-26-crown-8 (7) and Bis(5-hydroxy-1,3-phenylene)-26-crown-8 (2a). In a 3 L, 3-neck Morton flask, equipped with a mechanical stirrer, reflux condenser, nitrogen inlet, rubber septum, and thermometer, 2.5 L acetonitrile was heated to 70 °C under nitrogen. Potassium carbonate 48.07 g (347.4 mmol) was added, followed by a 100 mL acetonitrile solution of 11.66 g (23.16 mmol) **6** and 5.01 g (23.16 mmol) **5** at a rate of 0.75 mL/h. The final mixture was stirred for 10 d, cooled to RT and filtered through Celite[®]. After removal of the solvent by rotoevaporation the resulting oil, **7**, (17.55 g) was dissolved in a 50:50 mixture of chloroform:methanol in a hydrogenation flask. To the flask was added palladium on carbon (500 mg, 5 wt % Pd/wet, Englehard) and the flask was pressurized to 60 psi and shaken for 24 h. The mixture was then filtered through Celite[®]. The solvent was removed from the filtrate by rotoevaporation to give a brown oil. Trituration with acetonitrile gave a brownish precipitate, which was filtered and washed with acetonitrile to afford 833 mg (8 %) **2a**, mp 192.2 – 193.1 °C. ¹H NMR (400 MHz, CDCl₃, 25 °C) δ 9.43 (s, 2H), 5.93 (d, *J* = 2.0 Hz, 4H), 5.91 (t, *J* = 2.0 Hz, 2H), 3.96 (m, 8H), 3.69 (m, 8H), 3.58 (m, 8H); ¹³C NMR (100 MHz) δ 160.1, 159.0, 94.0, 92.7, 69.9, 68.7, 66.8. Anal. calcd for C₂₄H₃₂O₁₀: C, 59.99; H, 6.71. Found: C, 59.85; H, 6.89. LREIMS *m/z* 480 [M]⁺; HRFABMS (matrix, NBA/PEG) *m/z* calcd for [M + H]⁺ C₂₄H₃₃O₁₀, 481.20737, found 481.20691, error 1.0 ppm.

Bis-(1,3,5-phenylene)tri(1,4,7,10-tetraoxadecyl) (3a). A solution of 700 mg (1.46 mmol) of **2a** and 668 mg (1.46 mmol) of tri(ethylene glycol) ditosylate in 40 mL DMF was added at 0.75 mL/h into a suspension containing 2.07 g K₂CO₃ (15.0 mmol) and TBAI (5 mg) in 400 mL DMF at 110 °C. After complete addition, the reaction mixture was stirred at 110 °C for 4 days. The cooled mixture was roto-evaporated under reduced pressure to remove DMF, treated with chloroform, and filtered. Removal of chloroform afforded a crude product, which was purified by flash column chromatography, eluting with ethyl ether gradually increasing to ethyl acetate to give 334 mg of unreacted tri(ethylene glycol) ditosylate and 108 mg of **3a** [25% based on reacted tri(ethylene glycol) ditosylate]: mp 81.2-81.9 °C. ¹H NMR (400 MHz, acetone-d₆, 25 °C) δ 5.94 (s, 6H), 3.94 (t, *J* = 5.4 Hz, 12H), 3.76 (t, *J* = 5.4 Hz, 12H), 3.65 (s, 12H).

LREIMS m/z 595 $[M + H]^+$, 594 $[M]^+$; HRFABMS (matrix, NBA/PEG) m/z calcd for $[M + H]^+$ $C_{30}H_{43}O_{12}$, 595.27545, found 595.27753, error 3.5 ppm.

Keywords: cryptand, crown ether, complex, paraquat, stoichiometry

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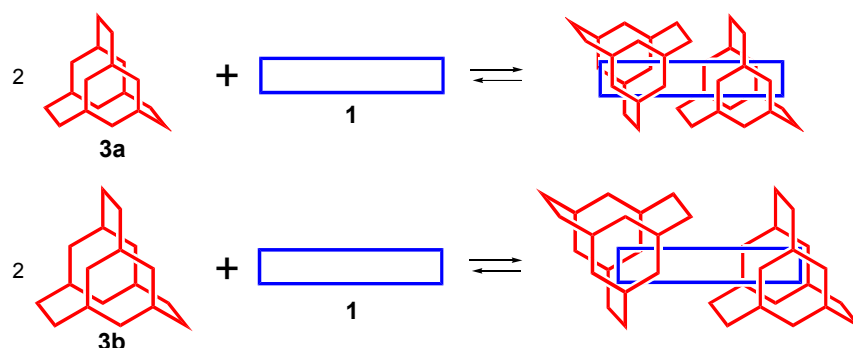
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8. ¹H NMR characterizations were done on solutions with constant initial host (**2c**, **2d**, or **3a**) concentration, [host]₀, and varied initial guest (**1**) concentration, [guest]₀. Based on these NMR data, Δ_0 , the difference in δ values for a proton of the host in the uncomplexed and fully complexed species, was calculated by using the Benesi-Hildebrand method.⁹ The complexed host and guest concentrations are

represented by $[\text{host}]_c$ or $[\text{guest}]_c$, while $[\text{host}]_{uc}$ and $[\text{guest}]_{uc}$ represent the uncomplexed host and guest concentrations. Then $[\text{host}]_c = [\text{guest}]_c = (\Delta/\Delta_0)[\text{host}]_0$, $[\text{host}]_{uc} = (1 - \Delta/\Delta_0)[\text{host}]_0$, $[\text{guest}]_{uc} = [\text{guest}]_0 - [\text{guest}]_c$, $K_a = [\text{host}]_c / \{[\text{host}]_{uc} [\text{guest}]_{uc}\}$. K_a for **2c•1**, **2d•1**, and **3a•1** were calculated at 1.00 mM initial concentration of host and guest. Errors were calculated by assuming $\pm 5\%$ error in Δ/Δ_0 . We found that apparent association constants K_a for these systems are concentration dependent so it is necessary to specify initial concentrations.

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10. High resolution fast-atom bombardment mass spectrometry (matrix, GLY/PEG) gave m/z 925.34760 (deviation 0.1 ppm).
11. Crystals of **3b•1•3b** were grown by slow evaporation of an acetone (undried) solution; care was taken to keep the crystals wet, because they were destroyed when dried. Data were collected to $\theta = 29^\circ$. The structure was solved by direct methods using SIR¹² and refined by full-matrix least squares, using the Enraf-Nonius MolEN programs¹³ Nonhydrogen atoms were treated anisotropically except those of the disordered solvent molecule. Hydrogen atoms were placed in calculated positions, except those on the water molecules and the paraquat methyl groups, which were placed from difference maps. Acetone H atoms and those of water molecule O3w were not located. Crystal data: prism, orange, $0.85 \times 0.68 \times 0.22$ mm, $(\text{C}_{36}\text{H}_{54}\text{O}_{15})_2:\text{C}_{12}\text{H}_{14}\text{N}_2(\text{PF}_6)_2:(\text{H}_2\text{O})_6:(\text{C}_3\text{H}_6\text{O})_3$, FW 2212.2, triclinic, space group $P-1$, $a = 13.298(2)$, $b = 13.641(1)$, $c = 15.622(1)$ Å; $\alpha = 94.485(7)$, $\beta = 101.04(1)$, $\gamma = 99.14(1)^\circ$; $V = 2728(1)$ Å³, $Z = 1$, $D_c = 1.346$ g cm⁻³, $T = 120\text{K}$, $\mu = 1.4$ cm⁻¹. Convergence was achieved with $R = 0.077$, $R_w = 0.086$ and maximum residual density 0.77 e•Å⁻³ for 6871 data having $I > 3\sigma(I)$.
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16. Crystals of **3a**:**1**:**3a** were grown by vapor diffusion of pentane into an acetone solution of 1.00 mM **3a** and 5.00 mM **1**. The data collection routine, unit cell refinement, data processing, the face-indexed numerical absorption correction were carried out with the program CrysAlis.¹⁷ Data were collected from $\theta = 2.828^\circ$ to $\theta = 29.386^\circ$. Crystal data: prism, yellow, $0.50 \times 0.18 \times 0.10$ mm, $C_{72}H_{98}O_{24}N_2P_2F_{12}:(C_3H_6O)$, *FW* 1723.57, Triclinic, space group *P*-1, $a = 10.831(2)$, $b = 13.165(2)$, $c = 14.474(3)$ Å; $\alpha = 93.030(14)^\circ$, $\beta = 93.740(15)^\circ$, $\gamma = 105.361(15)^\circ$; $V = 1980.6(6)$ Å³, $Z = 1$, $D_c = 1.445$ g cm⁻³, $T = 100$ K, $\mu = 1.62$ cm⁻¹, 40888 measured reflections, 10001 independent reflections, 533 parameters, $F(000) = 906$, $R1 = 0.1014$, $wR2 = 0.1159$ (all data), $R1 = 0.0470$, $wR2 = 0.0766$ [$I > 2\sigma(I)$], maximum residual density 0.78 e•Å⁻³, and goodness-of-fit (F^2) = 0.9627. The structure was solved by SIR92¹⁸ and refined by Crystals.¹⁹ Nonhydrogen atoms were treated anisotropically and hydrogen atoms were placed in calculated positions. 4019 reflections were used in refinements by full-matrix least-squares on F^2 .
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TOC Graphic:

Abstract: A new cryptand, bis-(1,3,5-phenylene)tri(1,4,7,10-tetraoxadecyl) (**3a**), has been synthesized in good yield from bis(5-hydroxy-1,3-phenylene)-26-crown-8 (**2a**) and tri(ethylene glycol) ditosylate using pseudo-high dilution conditions. **3a** forms a strong 1:1 complex with paraquat (**1**) in acetone solution with a high apparent association constant, $1.4 \times 10^4 \text{ M}^{-1}$. 1:1 stoichiometry was also observed by mass spectrometry in the gaseous state. However in the solid state as determined by X-ray crystallography, the two complexes of **3a** and the previously reported homologous cryptand, bis-(1,3,5-phenylene)tri(1,4,7,10,13-pentaoxatridecyl) (**3b**), with paraquat (**1**) have 2:1 stoichiometry. A unique feature of these trimolecular pseudorotaxane-like complexes is that the guest occupies parts of the cavities of two cryptand molecules. For the first time it was found that in cryptand-based complexes, different stoichiometries are possible for the same host-guest pair.
