

A Study of the Complexation of Bis(*m*-Phenylene) Crown Ethers and Secondary Ammonium Ions

William S. Bryant,[†] Ilia A. Guzei,[‡] Arnold L. Rheingold,[‡] Joseph S. Merola,[†] and Harry W. Gibson^{*,†}

Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061, and Department of Chemistry and Biochemistry, University of Delaware, Newark, Delaware 19716

Received November 26, 1997

Two macrocycles, bis(*m*-phenylene)-26-crown-8 (**1**) and bis(*m*-phenylene)-32-crown-10 (**2**), were combined with several linear components, dibenzyl- (**3**·PF₆), di-*n*-butyl- (**4**·PF₆), and diphenethyl- (**5**·PF₆) ammonium hexafluorophosphate salts. The smaller macrocycle **1** was shown *not* to complex effectively with any of the ammonium salts in solution by ¹H NMR, but 1:1 complexes were shown to exist in the “gas phase” as [1:3], [1:4], and [1:5] by high-resolution fast atom bombardment mass spectrometry (HRFABMS) and electrospray ionization mass spectrometry (ESIMS). The X-ray crystal structure of macrocycle **1** is reported. The larger macrocycle **2** *did* form 1:2 complexes with the ammonium salts in solution, which were observed as well in the solid and gas phases. X-ray crystal structures of the pseudorotaxanes [2:(3)₂]·2PF₆ and [2:(5)₂]·2PF₆ were determined and are discussed. The pseudorotaxanes are stabilized by hydrogen bonding between the ammonium hydrogens of the linear salt unit and the oxygens of the crown ether macrocycle. Secondary stabilization also occurs by edge-to-face π stacking.

Introduction

Scientists have tried to use the phenomenon of self-assembly by molecular recognition since the discovery that organic molecules can arrange themselves into complex arrangements to produce higher ordered molecular assemblies.¹ The use of the self-assembly concept can lead to the formation of rotaxanes and pseudorotaxanes, in which a linear unit is threaded through the cavity of a cyclic unit (Figure 1). Pseudorotaxanes differ from rotaxanes because they lack bulky end groups on the linear unit that prevent dethreading of the cyclic unit.²

Stoddart et al. recently reported on the self-assembly complexation of *o*- and *p*-phenylene crown ethers with secondary ammonium salts to form pseudorotaxanes.³ The complexes are a result primarily of hydrogen bonding between the ammonium protons and the ether oxygens of the crown ether. Further stabilization of the complexes is achieved through π-orbital interactions of the aromatic rings of both species.⁴ However, *m*-phenylene crown ethers were not discussed. Bis(*m*-phenylene) crown ethers are of special interest to us because we have

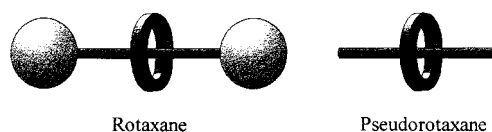


Figure 1. Representations of rotaxane and pseudorotaxane.

developed syntheses of a number of (5)-mono-⁵ and (5,5′)-difunctional⁶ derivatives of these crown ethers as precursors to self-assembled supermolecules⁷ and polymeric rotaxanes.^{2a,c} Because of their symmetric nature, these substituted bis(*m*-phenylene) crown ethers can be prepared as pure compounds without isomer separation and have simpler NMR spectra than those of their substituted bis(*o*-phenylene) and bis(*p*-phenylene) analogues. We have demonstrated the formation of a variety of polyro-

[†] Virginia Polytechnic Institute and State University.

[‡] University of Delaware.

(1) (a) Singer, S. J.; Nicholson, G. L. *Science* **1972**, *175*, 720. (b) Pedersen, C. J. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1021. (c) Lehn, J.-M. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 89. (d) Cram, D. J. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1009. (e) Lindsey, J. S. *New J. Chem.* **1991**, *15*, 153. (f) Philp, D.; Stoddart, J. F. *Synlett* **1991**, 445. (g) Lehn, J.-M. *Science* **1993**, *260*, 1762. (h) Lehn, J.-M. *Supramolecular Chemistry—Concepts and Perspectives*; VCH: Weinheim, Germany, 1995. (i) Philp, D.; Stoddart, J. F. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1155. (j) Feiters, M. C.; Fyfe, M. C. T.; Martinez-Diaz, M.-V.; Menzer, S.; Nolte, R. J. M.; Stoddart, J. F.; van Kan, P. J. M.; Williams, D. J. *J. Am. Chem. Soc.* **1997**, *119*, 8119.

(2) (a) Gong, C.; Gibson, H. W. *Curr. Opin. Solid State Mater. Sci.* **1998**, *2*, 647. (b) Fyfe, M. C. T.; Stoddart, J. F. *Acc. Chem. Res.* **1997**, *30*, 393. (c) Gibson, H. W. In *Large Ring Molecules*; Semlyen, J. A., Ed.; John Wiley and Sons: New York, 1996; Chapter 6, p 191. (d) Amabilino, D. B.; Stoddart, J. F. *Chem. Rev.* **1995**, *95*, 2725.

(3) (a) Ashton, P. R.; Campbell, P. J.; Chrystal, E. J. T.; Glink, P. T.; Menzer, S.; Philp, D.; Spencer, N.; Stoddart, J. F.; Tasker, P. T.; Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1865. (b) Ashton, P. R.; Campbell, P. J.; Chrystal, E. J. T.; Glink, P. T.; Menzer, S.; Philp, D.; Spencer, N.; Stoddart, J. F.; Tasker, P. T.; Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1869. (c) Ashton, P. R.; Glink, P. T.; Martinez-Diaz, M.-V.; Stoddart, J. F.; White, A. J. P.; Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1930. (d) Ashton, P. R.; Chrystal, E. J. T.; Glink, P. T.; Menzer, S.; Schiavo, C.; Spencer, N.; Stoddart, J. F.; Tasker, P. T.; White, A. J. P.; Williams, D. J. *Chem.—Eur. J.* **1996**, *2*, 709. (e) Ashton, P. R.; Glink, P. T.; Stoddart, J. F.; Tasker, P. T.; White, A. J. P.; Williams, D. J. *Chem.—Eur. J.* **1996**, *2*, 729.

(4) Raymo, F. M.; Houk, K. N.; Stoddart, J. F. Private communication.

(5) Nagvekar, D. S.; Yamaguchi, N.; Wang, F.; Bryant, W. S.; Gibson, H. W. *J. Org. Chem.* **1997**, *62*, 4798.

(6) (a) Delaviz, Y.; Gibson, H. W. *Org. Prep. Proced. Int.* **1991**, *23*, 382. (b) Gibson, H. W.; Delaviz, Y. *Polymer* **1994**, *34*, 1109. (c) Delaviz, Y.; Merola, J. S.; Berg, M. A. G.; Gibson, H. W. *J. Org. Chem.* **1995**, *60*, 516. (d) Nagvekar, D. S.; Gibson, H. W. *Org. Prep. Proced. Int.* **1997**, *29*, 237. (e) Nagvekar, D. S.; Gibson, H. W. *Can. J. Chem.* **1997**, *75*, 1375.

(7) Yamaguchi, N.; Nagvekar, D. S.; Gibson, H. W. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 2361. Yamaguchi, N.; Hamilton, L. M.; Gibson, H. W. *Angew. Chem., Int. Ed. Engl.* **1998**, in press. Yamaguchi, N.; Gibson, H. W. *Angew. Chem., Int. Ed. Engl.* **1998**, in press.

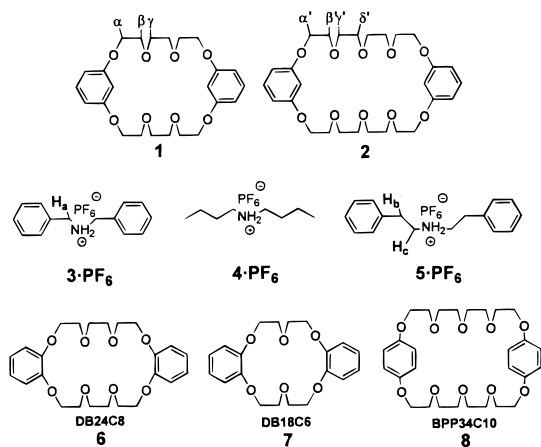


Figure 2. Bis(*m*-phenylene)-26-crown-8 (**1**), bis(*m*-phenylene)-32-crown-10 (**2**), dibenzyl- (**3**·PF₆), di-*n*-butyl- (**4**·PF₆), and diphenethyl- (**5**·PF₆) ammonium hexafluorophosphates, dibenzo-24-crown-8 (**6**), dibenzo-18-crown-6 (**7**), and bis(*p*-phenylene)-34-crown-10 (**8**).

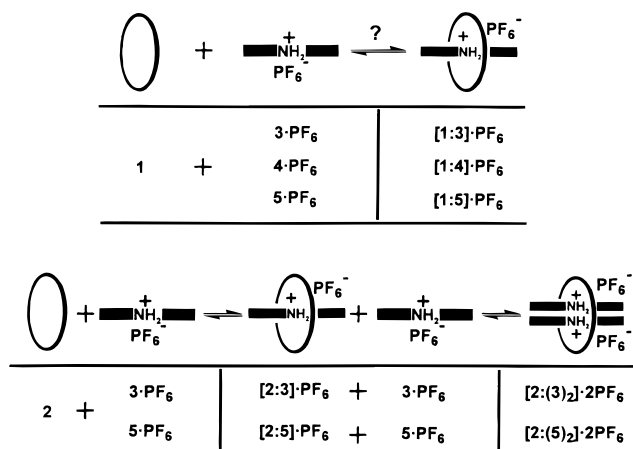


Figure 3. Possible pseudorotaxane products from mixtures of crown ethers and secondary ammonium salts.

taxanes from these macrocycles via hydrogen bonding.^{1a,8} Therefore, the complexations of the 26- and 32-membered bis(*m*-phenylene) crown ethers **1** and **2** with several secondary ammonium salts (**3**·PF₆, **4**·PF₆, and **5**·PF₆) were investigated (Figure 2). The possible pseudorotaxanes that can be assembled are shown in Figure 3.

Results and Discussion

I. Complexation of 26-Membered Macrocycle 1 with Ammonium Salts. Stoddart et al. have demonstrated by ¹H NMR and high-resolution fast atom bom-

bardment mass spectrometry (HRFABMS) that dibenzo-24-crown-8 (DB24C8, **6**) can complex with dibenzylammonium ions (**3**·PF₆) and di-*n*-butylammonium ions (**4**·PF₆) in 1:1 stoichiometries.³ The complexes were shown to exist in pseudorotaxane forms in the solid state. However, we observe that when the 26-membered meta analogue **1** is placed in solution (CD₃CN, CDCl₃, or acetone-*d*₆) with **3**·PF₆, **4**·PF₆, or **5**·PF₆, there is no change in the chemical shifts of the proton signals,⁹ even though the cavity size of the molecule is large enough to allow threading to take place.¹⁰ Another indication of the lack of complexation was the observation that **3**·PF₆, **4**·PF₆, and **5**·PF₆ do not dissolve in the presence of **1** in chloroform. Stoddart et al. have demonstrated that these chloroform-insoluble salts become soluble by complexation in the presence of DB24C8.³ As noted by Pedersen¹¹ and Izatt et al.¹² with dibenzo-18-crown-6 (DB18C6, **7**), an unfavorable crown ether conformation may be the reason no detectable complexation of **1** takes place in solution.

However, 1:1 complexes, perhaps [2]pseudorotaxanes, of **1** with **3**·PF₆, **4**·PF₆, and **5**·PF₆ were determined to exist by HRFABMS and electrospray ionization mass spectrometry (ESIMS). Solids obtained by evaporation of equimolar solutions of the components gave peaks at *m/z* 646.5, 578.5, and 674.6, respectively, corresponding to the 1:1 complex cations [1:3], [1:4], and [1:5] (Figures 4–6) for ESIMS. A comparison of the peak intensities of the ammonium salt and the complex in each spectrum gives a relative indication of the strength of the complexation. In Figures 4 and 5, the peaks for the complexes are 2 times as intense as the peaks for the salts; this indicates that fairly stable complexes exist. However, in Figure 6 the peak for the salt is about 6 times as intense as the peak for the complex. This indicates that the complex 1:5 is not as strong as 1:3 or 1:4. Attempts to grow crystals of these complexes suitable for X-ray crystallography have so far been futile.

Crystal Structure of 1. A crystal suitable for X-ray crystallographic analysis was obtained by slow evaporation of an acetone solution containing both **1** and **5**·PF₆. The crystals formed were of **1** alone (Figure 7). The structure of the macrocycle differs from that of previously reported phenylene-based macrocycles.^{13–15} Instead of the “all-gauche” conformation of the polyether bridges adopted by other macrocycles, there exist two trans bonds (C5–C6 and C17–C18). The cavity of the macrocycle is collapsed, and the overall shape of the macrocycle is reminiscent of DB24C8.¹² However, the phenyl rings in **1** are almost opposite each other along the short axis (centroid–centroid distance 7.12 Å) rather than along the long axis. They also exist in an edge-to-edge conformation rather than the more open face-to-face orientation.

(8) (a) Gibson, H. W.; Liu, S.; Gong, C.; Joseph, E. *Macromolecules* **1997**, *30*, 3711. (b) Gong, C.; Gibson, H. W. *J. Am. Chem. Soc.* **1997**, *119*, 5862. (c) Gong, C.; Gibson, H. W. *Macromol. Chem. Phys.* **1997**, *198*, 2321. (d) Gong, C.; Ji, Q.; Glass, T. E.; Gibson, H. *Macromolecules* **1997**, *30*, 4807. (e) Gong, C.; Gibson, H. W. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2331. (f) Gong, C.; Gibson, H. W. *J. Am. Chem. Soc.* **1997**, *119*, 8585. (g) Gibson, H. W.; Nagvekar, D. S.; Powell, J.; Gong, C.; Bryant, W. S. *Tetrahedron* **1997**, *59*, 15197. (h) Gong, C.; Gibson, H. W. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2331. (i) Gong, C.; Gibson, H. W. *Macromolecules* **1997**, *30*, 8524. (j) Gong, C.; Gibson, H. W. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 310. (k) Gong, C.; Gibson, H. W. *Macromolecules* **1998**, *31*, 308. (l) Gong, C.; Subramanian, C.; Ji, Q.; Gibson, H. W. *Macromolecules* **1998**, *31*, 1814. (m) Gibson, H. W.; Gong, C.; Liu, S.; Nagvekar, D. *Macromol. Symp.* **1998**, *128*, 89. (n) Gong, C.; Balandra, P. B.; Gibson, H. W. *Macromolecules* **1998**, *31*, 5278. (o) Gong, C.; Gibson, H. W. *Macromol. Chem. Phys.* **1998**, *199*, in press.

(9) ¹H NMR and LRFABMS spectra have been submitted as Supporting Information.

(10) The minimum number of cyclic C, N, or O atoms required for the threading of a polymethylene chain is 22. See: Harrison, I. T. *J. Chem. Soc., Chem. Commun.* **1972**, 231.

(11) Pedersen, C. J. *J. Am. Chem. Soc.* **1967**, *89*, 7017.

(12) Izatt, R. M.; Lamb, J. D.; Izatt, N. E.; Rossiter, B. E., Jr.; Christensen, J. L.; Haymore, B. L. *J. Am. Chem. Soc.* **1979**, *101*, 6273.

(13) Hanson, I. R.; Hughes, D. L.; Truter, M. R. *J. Chem. Soc., Perkin Trans. 2* **1976**, 972.

(14) Allwood, B. L.; Shahriari-Zavareh, H.; Stoddart, J. F.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1987**, 1058.

(15) (a) Allwood, B. L.; Spencer, N.; Shahriari-Zavareh, H.; Stoddart, J. F.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1987**, 1061. (b) Slawin, A. M. Z.; Spencer, N.; Stoddart, J. F.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1987**, 1070.

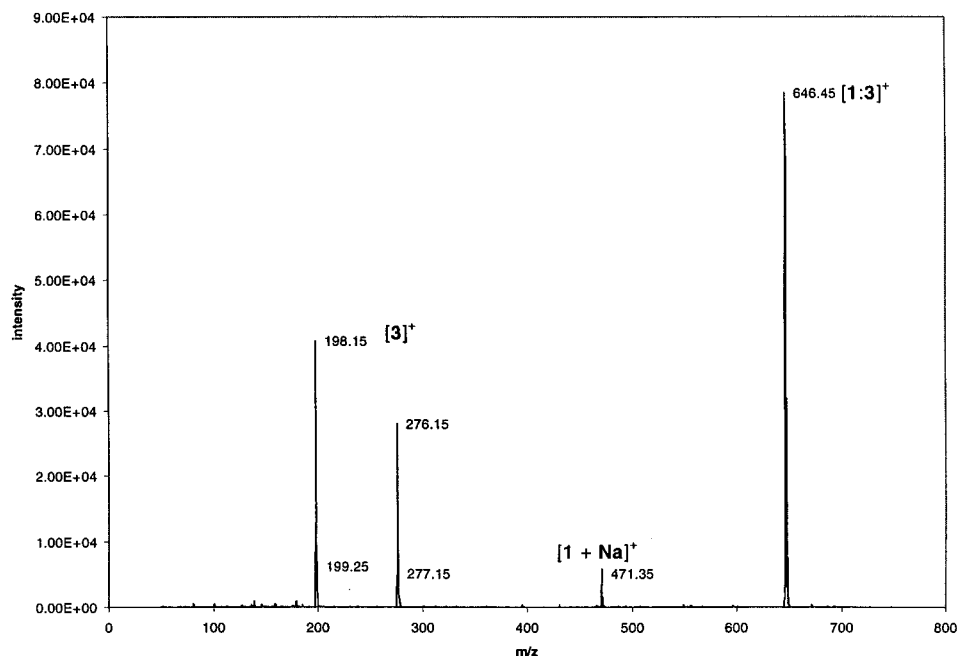


Figure 4. ESIMS for a 1:1 mixture of **1** and **3**·PF₆.

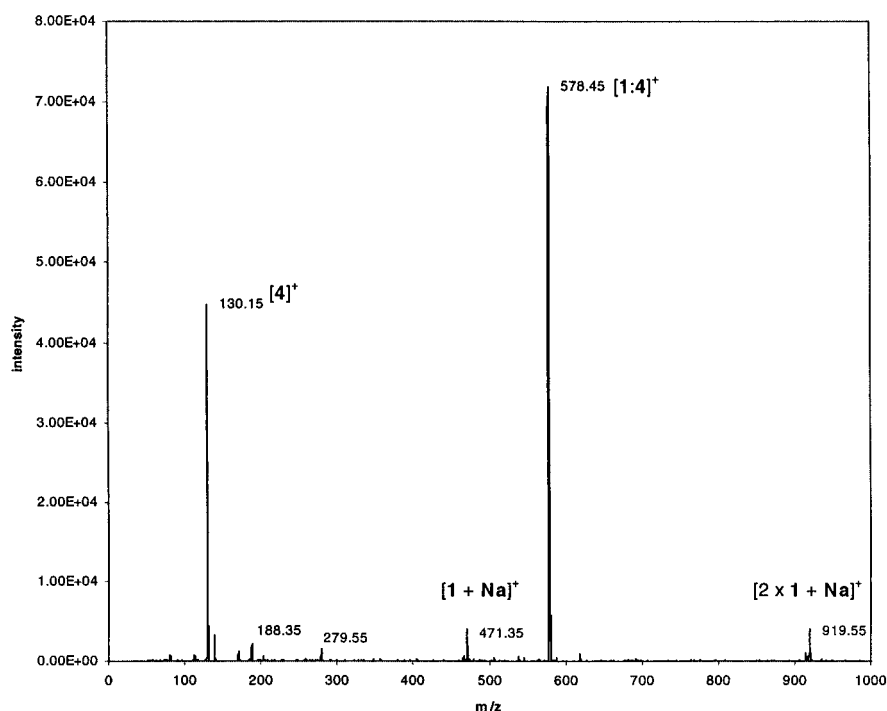


Figure 5. ESIMS for a 1:1 mixture of **1** and **4**·PF₆.

II. Complexation of 32-Membered Macrocycle **2 with Ammonium Salts.** Encouraged by the result that bis(*p*-phenylene)-34-crown-10 (BPP34C10, **8**) forms a [3]-pseudorotaxane with **3**·PF₆,³ we investigated the complexation between **2** and **3**·PF₆. Because the threading and dethreading processes are fast on the NMR time scale, one observes a time-averaged coalesced signal for the “complexed” and “uncomplexed” forms.⁹ The overall association constant, as measured by ¹H NMR (CD₃CN), was $\sim 5 \pm 2 \text{ M}^{-2}$.¹⁶ The FABMS results corroborate the formation of a 1:2 complex by the presence of a peak at *m/z* 1077.6, corresponding to the [3]pseudorotaxane [2:(**3**)₂]·PF₆. The ratio of peak intensities for **2** alone

relative to that for [2:(**3**)₂]·PF₆ was $\sim 400:1$. Also observed was a peak at *m/z* 734.2, which is the [2]pseudorotaxane [2:3]. The peak intensity for [2:3] was approximately 90% as large as that of **2** alone.⁹

X-ray crystallography confirmed the [3]pseudorotaxane structure for [2:(**3**)₂]·2PF₆ (Figure 8). The complex resides on an inversion center, with two N–H–O hy-

(16) The overall association constant was determined by a titration method where [3·PF₆] \gg [2]. For the method, see: Dobson, B.; Foster, R.; Bright, A. A. S.; Foreman, M. I.; Gorton, J. *J. Chem. Soc. B* **1971**, 1286. The association constant for the 2:1 complex between **3**·PF₆ and bis(*p*-phenylene)-34-crown-10 was estimated to be higher ($\sim 10^3$ – 10^4 M^{-1} [sic]).

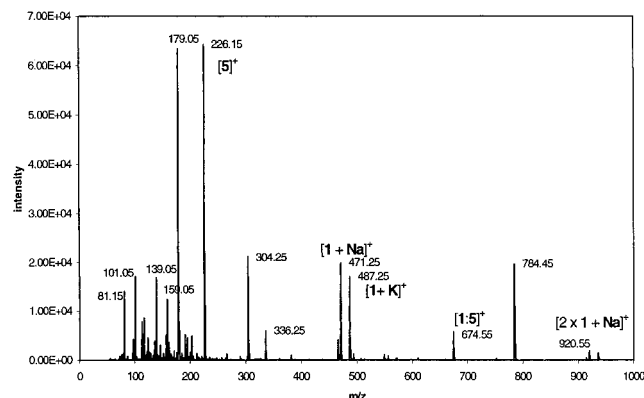


Figure 6. ESIMS for a 1:1 mixture of **1** and **5**·PF₆.

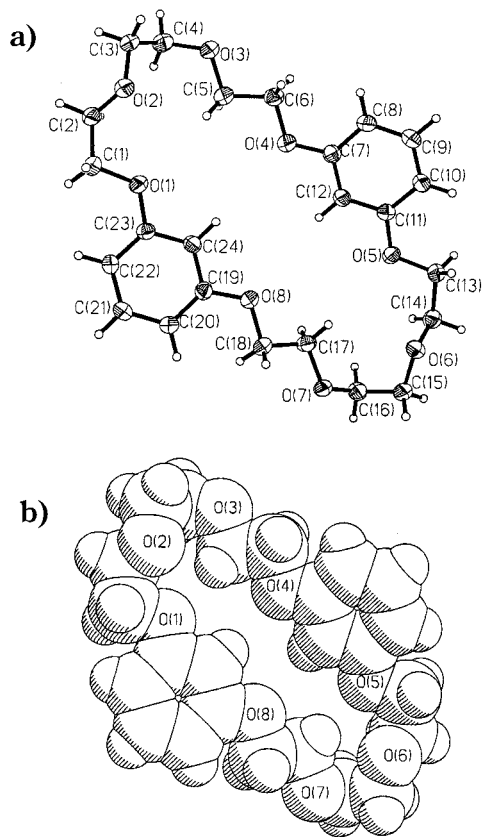


Figure 7. X-ray structure of 26-membered macrocycle **1** (a) ORTEP drawing and (b) space-filling representation.

drogen bonds per ammonium salt stabilizing the interaction. The hydrogen bonds involve alternate 1,3-ether oxygens [O(2), O(3); O(2a), O(3a)] on the same ethyleneoxy bridge. Further stabilization occurs from two aromatic–aromatic edge-to-face interactions¹⁷ between one of the ortho aromatic hydrogen atoms of each ammonium ion and a resorcinol ring. There appear to be no strong stabilizing interactions between the complexes in the crystal lattice.

Stoddart et al. have demonstrated that face-to-face π stacking further stabilizes the complexation of some of the crown ether/ammonium salt pseudorotaxanes.³ It

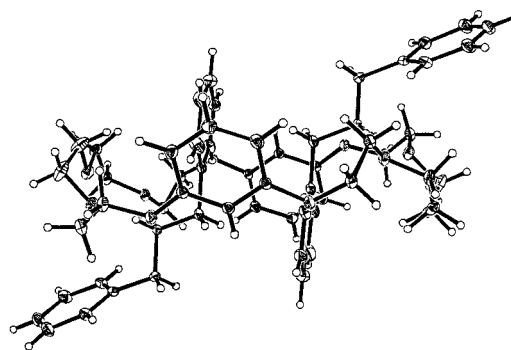


Figure 8. Side-on and top views of the X-ray structure of the pseudorotaxane **[2:(3)₂]·2PF₆** (PF₆ anions have been omitted for clarity). The hydrogen bonds have the following distances and angles: [N–O] 3.02 Å, 2.88 Å; [H–O] 2.12 Å, 1.98 Å; [N–H–O] 176°, 170°. The aromatic–aromatic edge-to-face interactions have the following parameters: centroid–centroid distance, 5.50 Å; C–H–centroid angle, 140°; H–centroid distance, 3.48 Å.

must be noted, however, that the interaction is a secondary stabilization interaction and that hydrogen bonding is the much stronger, primary stabilizing variable in these systems. Using CPK models, it was found that the addition of two extra methylene units to the ammonium salt **3**·PF₆ to give **5**·PF₆ might make it possible to increase the face-to-face π stacking affinity and thus increase the contribution of the secondary stabilizing interaction.

The formation of the [3]pseudorotaxane **[2:(5)₂]·2PF₆** caused a small change in the chemical shifts for the time-averaged proton signals of both species.⁹ FABMS detected only a 1:1 complex, as evidenced by a peak at m/z 762.2, which may correspond to the pseudorotaxane complex **[2:5]**. The peak intensity for **[2:5]** was approximately 55% as large as that of **2** alone.⁹ Both of these observations suggest a lower association constant for this system than that for the complex between **2** and **3**·PF₆. The lower association constant is probably due to the decreased acidity of the benzylic methylene groups and the ammonium center. Because there is no longer an sp² carbon beta to the ammonium center, the through-bond effects that increase the acidity of the ammonium center in **3**·PF₆ are not as profound in **5**·PF₆.

X-ray crystallography did confirm the structure of the [3]pseudorotaxane **[2:(5)₂]·2PF₆** (Figure 9). The complex is stabilized by two N–H–O hydrogen bonds per am-

(17) (a) Jorgensen, W. L.; Severance, D. L. *J. Am. Chem. Soc.* **1990**, *112*, 4768. (b) Grossel, M. C.; Cheetham, A. K.; Hope, D. A.; Weston, S. C. *J. Org. Chem.* **1993**, *58*, 6651. (c) Paliwal, S.; Geib, G.; Wilcox, C. S. *J. Am. Chem. Soc.* **1994**, *116*, 4497.

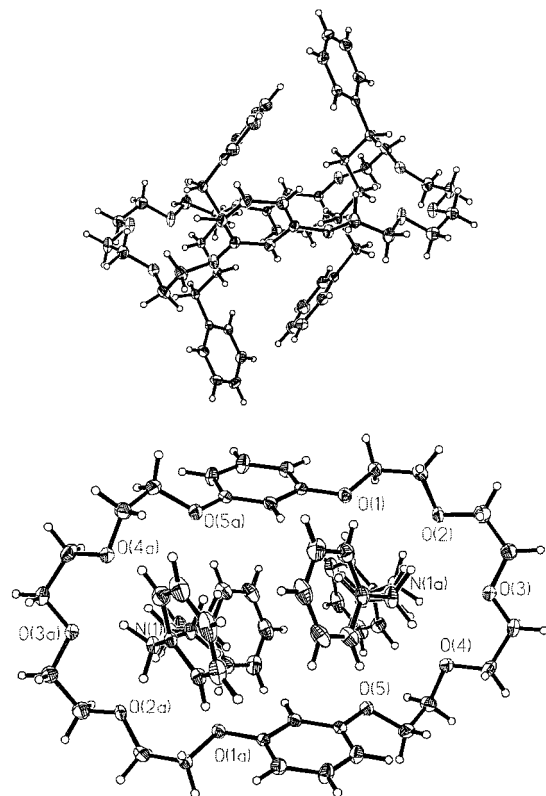


Figure 9. Side-on and top views of the X-ray structure of the pseudorotaxane $[2:(5)_2] \cdot 2PF_6$ (PF_6 anions have been omitted for clarity). The hydrogen bonds have the following distances and angles: [N–O] 2.85 Å, 2.84 Å; [H–O] 1.96 Å, 1.93 Å; [N–H···O] 165°, 175°. The aromatic–aromatic edge-to-face interactions have the following parameters: centroid–centroid distance, 4.83 Å; C–H···centroid angle, 142°; H–centroid distance, 2.80 Å.

monium salt involving alternate 1,3-ether oxygens [O(2), O(3); O(2a), O(3a)] on the same ethyleneoxy bridge. There is also further stabilization by two aromatic–aromatic edge-to-face interactions. However in this case, the interactions occur between the aromatic rings of the two ammonium ions and not the benzyl groups with the resorcinol rings of the macrocycle. Thus, the anticipated π stacking of $5 \cdot PF_6$ with 2 was not observed. There appear to be no strong stabilizing interactions between the complexes in the crystal lattice.

The ability of 2 to adapt its conformation to include different ammonium ions is evident by comparing the crystal parameters of the pure macrocycle¹³ to those of the macrocycle in $[2:(3)_2] \cdot 2PF_6$ and $[2:(5)_2] \cdot 2PF_6$ (Table 1). The all-gauche conformation of the ethyleneoxy bridges is maintained in both complexes. Although there appears to be little change in the distances between the NH_2 centers, the dimensions of the macrocyclic cavity change substantially. The macrocycle in $[2:(3)_2] \cdot 2PF_6$ expands in both dimensions relative to 2 alone, whereas in $[2:(5)_2] \cdot 2PF_6$ it expands along one axis but shrinks along the other. Also, the centroid–centroid distances of the aromatic rings of the macrocycle increase in $[2:(3)_2] \cdot 2PF_6$ but decrease in $[2:(5)_2] \cdot 2PF_6$ relative to pure 2 .

Conclusion

The threading of secondary ammonium ions through the cavity of the 32-membered bis(*m*-phenylene) crown

ether to form pseudorotaxanes has been demonstrated here. The 32-membered crown ether 2 forms complexes in solution as determined by NMR ($K_a \approx 5 M^{-2}$ in acetone- d_6 at 22 °C). The complexes are stable enough to be detected in the gas phase by MS and were obtained in single crystal form. However, it appears that the 26-membered macrocycle 1 does not efficiently form complexes in solution, but such structures were observed by MS.

Because of its small cavity size, 1 can only form 1:1 complexes with ammonium salt moieties, thus simplifying analyses of possible systems that incorporate its structure. However because the complexation does *not* occur to an appropriate extent in solution, the 26-membered macrocycle is not a suitable choice for use in supramolecular assembly with secondary ammonium ion species but does offer opportunities for selective supramolecular self-assembly.

The formation of a variety of novel supramolecular structures, including main-chain and side-chain polyrotaxanes,^{1a,c,8} based on the above-mentioned ammonium salt moieties and bis(*m*-phenylene)-32-crown-10 units does appear possible and is currently under study in our laboratories.

Experimental Section

General Methods. Reagent grade reactants and solvents were used as received unless otherwise specified. Bis(*m*-phenylene)-26-crown-8 (1),¹⁸ bis(*m*-phenylene)-32-crown-10 (2),¹⁹ dibenzylammonium hexafluorophosphate ($3 \cdot PF_6$),^{3a} and di-*n*-butylammonium hexafluorophosphate ($4 \cdot PF_6$)^{3a} were prepared by literature methods. 1H NMR spectra were recorded at ambient temperature on a 400-MHz spectrometer.

Diphenethylammonium Hexafluorophosphate ($5 \cdot PF_6$). A solution of $C_6H_5CH_2CHO$ (5.38 g, 44.8 mmol), $C_6H_5CH_2CH_2NH_2$ (5.45 g, 45.0 mmol), and ~75 mL of toluene was heated at reflux with a Dean–Stark trap for 2 h and then cooled to room temperature. The solvent was removed by rotoevaporation to give a yellow oil. The oil was dissolved in CH_3OH (100 mL), and $NaBH_4$ (1.7 g, 44.8 mmol) was added over 1 h. The resulting suspension was heated at reflux for 15 min. Deionized (DI) H_2O (100 mL) was then added. The solvent was removed by rotoevaporation, and another 100 mL of DI H_2O was added at ~0 °C. A tacky, yellow oil was observed, and the H_2O was decanted. CH_3OH (25 mL) was added to the oil followed by 2 M HCl (250 mL) at ~0 °C. The resulting solution was stirred for 2 h. A yellow oil was observed in the bottom of the flask. The CH_3OH/H_2O layer was decanted. The solvents were removed by rotoevaporation to give a yellow solid. Mp: 264.8–266.2 °C (lit.²⁰ 265–266 °C). 1H NMR (400 MHz, $DMSO-d_6$, ambient T): δ 7.26 (m, 10H), 2.94 (m, 8H). ^{13}C NMR (100 MHz, $DMSO-d_6$, ambient T): δ 137.6, 128.7, 126.8, 40.0, 33.0. The chloride salt was stirred in hot H_2O , and solid NH_4PF_6 was added until precipitation ceased. The white precipitate was filtered and then dried in a desiccator. Yield: 12.08 g (72.3%). Mp: 155 °C (sublimes). 1H NMR (400 MHz, CD_3CN , ambient T): δ 7.31 (m, 10H), 3.23 (t, $J = 8.4$ Hz, 8H), 2.94 (t, $J = 8.4$ Hz, 8H). ^{13}C NMR (100 MHz, $DMSO-d_6$, ambient T): δ 136.9, 128.6, 126.8, 47.7, 31.5.

Mass Spectroscopic Analysis of Complexes. Equimolar solutions of both components were made in acetone, and the solvent was allowed to evaporate slowly. HRFABMS: m/z 646.3384 (dev. 0.6), 578.3715 (dev. 3.8), 674.3614 (dev. –11.7), 1077.4785 (dev. –4.1), and 762.4224 (dev. 0.8) for $[1:3]^+$, $[1:4]^+$, $[1:5]^+$, $\{[2:(3)_2] \cdot PF_6\}^+$, and $[2:5]^+$, respectively. The matrix was

(18) Lindsten, G.; Wennerstroem, O.; Isaksson, R. *J. Org. Chem.* **1987**, *52*, 547.

(19) Delaviz, Y.; Gibson, H. W. *Polym. Commun.* **1991**, *32*, 103.

(20) Yates, P.; Giles, R. G. F.; Farnum, D. G. *Can. J. Chem.* **1969**, *47*, 3997.

Table 1. Comparison of Crystal Parameters (in angstroms)

compound or complex	2	[2:(3) ₂]:2PF ₆	[2:(5) ₂]:2PF ₆
cavity size	7.8 × 4.9	8.2 × 6.7	8.6 × 4.1
centroid–centroid distance of aromatic rings in macrocycle	8.8	10.3	8.3
mean plane separation between aromatic rings of macrocycle	7.0	8.2	5.6
distance between the two NH ₂ centers	N/A	7.2	7.0

Table 2. Crystal Data and Data Collection Parameters

data	1	[2:(3) ₂]:2PF ₆	[2:(5) ₂]:2PF ₆
formula	C ₂₄ H ₃₂ O ₈	C ₅₆ H ₇₂ F ₁₂ N ₂ O ₁₀ P ₂	C ₆₀ H ₈₀ F ₁₂ N ₂ O ₁₀ P ₂
formula weight (g/mol)	448.51	1223.10	1279.20
lattice type	monoclinic	triclinic	monoclinic
space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 1	<i>P</i> 2 ₁ / <i>n</i>
<i>T</i> (K)	298(2)	222(2)	243(2)
<i>a</i> (Å)	11.382(3)	11.0034(2)	12.250(2)
<i>b</i> (Å)	16.111(2)	11.88170(10)	11.294(4)
<i>c</i> (Å)	12.8971(11)	13.1435(2)	23.473(3)
α (deg)		102.9690(1)	
β (deg)	102.479(11)	113.7160(10)	98.522(5)
γ (deg)		96.0480(10)	
<i>V</i> (Å ³)	2309.2(7)	1495.81(4)	3211.8(12)
<i>Z</i>	4	1	2
<i>D</i> _c (g cm ⁻³)	1.290	1.358	1.323
<i>F</i> (000)	960	1280	1344
μ (mm ⁻¹)	0.096	0.167	0.158
Θ range (deg)	2.05–22.50	3.5–56.2	4.0–45.0
no. of unique reflections			
measured	2913	6409	4182
observed		5515	2264
no. of variables	290	370	388
<i>R</i> (%)	4.26	5.57	6.67
<i>R</i> _w (%)	9.25	22.35	15.89

3-NBA. For ESIMS, the samples were diluted to an unknown concentration in acetone/methanol (20/80%), and the fragmentor was run at a low fragmentor potential of 27 V: *m/z* 646.5, 578.5, and 647.6 for [1:3]⁺, [1:4]⁺, and [1:5]⁺, respectively.

Determination of Association Constant for [2:(3)₂]:2PF₆. Solutions were made in CD₃CN; the concentration of 3·PF₆ was varied from 0.05 to 0.60 M while the concentration of **2** was held constant at 5.0 × 10⁻³ M. The overall association constant, *K* = *K*₁*K*₂, was determined by observing the change in the chemical shift for the δ' proton of **2** and solving the following equation⁶ for both *K*₁ and *K*₂:

$$\Delta/[3\cdot\text{PF}_6]_0 = -\Delta K_1(1 + [3\cdot\text{PF}_6]_0 K_2) + K_1\{\Delta_0(1) + \Delta_0(2)[3\cdot\text{PF}_6]_0 K_2\} \quad (1)$$

where Δ₀(1) = chemical shift of the measured nucleus in the complex [2:3]·PF₆ relative to the chemical shift of the same nucleus in pure **2** (δ₂ - δ_{[2:3]·PF₆}); Δ₀(2) = corresponding value for the [2:(3)₂]:2PF₆ complex (δ₂ - δ_{[2:(3)₂]:2PF₆}); Δ = line position of the measured nucleus of **2** in the equilibrium mixture relative to the line position of the same nucleus in a solution of **2** alone (δ₂ - δ_{obs}); and [3·PF₆]₀ = total stoichiometric amount of 3·PF₆ in the solution.

Crystallographic Structural Determination. Crystals suitable for X-ray crystallography were grown for **1** by slow evaporation of an acetone solution and for [2:(3)₂]:2PF₆ and [2:(5)₂]:2PF₆ by vapor diffusion of *n*-pentane into an equimolar acetone solution of both components. Crystal, data collection, and refinement parameters are given in Table 2.

All software and sources of the scattering factors are contained in the *SHELXTL* (version 5.03) program library (G. Sheldrick, Siemens XRD, Madison, WI). All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were treated as idealized contributions.

For 1: X-ray crystallographic data were obtained using a Siemens R3m/v single-crystal diffractometer. Structures were solved with *SHELXTL* software.

For [2:(3)₂]:2PF₆ and [2:(5)₂]:2PF₆: X-ray crystallographic data were obtained using a Siemens CCD-detector-equipped P4 diffractometer (a four-circle SMART system). Structures were solved with *SHELXTL* software. The systematic absences in the diffraction data were consistent for the reported space group for [2:(5)₂]:2PF₆ and space groups *P*1 and *P*1 for [2:(3)₂]:2PF₆. Even though the E statistics for the latter strongly suggested the noncentrosymmetric space group *P*1₂, both possibilities were explored, but only space group *P*1 yielded chemically reasonable and computationally stable results and refinement. The structures were solved using direct methods, completed by subsequent difference Fourier synthesis, and refined by full-matrix least-squares procedures. In both structures, the crown ethers reside on inversion centers. In the case of [2:(5)₂]:2PF₆, two carbon atoms [C(9) and C(10)] are disordered between two positions in a 2:1 ratio and were refined isotropically.

Acknowledgment. This research was funded by the National Science Foundation (U.S.A.) (Grant CHE-9521738). Mass spectrometry was provided by the Washington University Mass Spectrometry Resource, an NIH Research Resource (Grant P41RRR0954).

Supporting Information Available: Stacked ¹H NMR plots for **1**, **1** + 3·PF₆, 3·PF₆, **2**, **2** + 3·PF₆, 3·PF₆, and **2**, **2** + 5·PF₆, 5·PF₆; LRFABMS for **2** + 3·PF₆ and **2** + 5·PF₆; crystal data and structure refinements for **1**, [2:(3)₂]:2PF₆, and [2:(5)₂]:2PF₆; bond lengths and angles for **1**, [2:(3)₂]:2PF₆, and [2:(5)₂]:2PF₆; atomic coordinates for **1**, [2:(3)₂]:2PF₆, and [2:(5)₂]:2PF₆; anisotropic displacement coefficients for **1**, [2:(3)₂]:2PF₆, and [2:(5)₂]:2PF₆; H-atom coordinates for [2:(3)₂]:2PF₆ and [2:(5)₂]:2PF₆ (22 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of this journal, and can be ordered from the ACS; see any current masthead page for ordering information.