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Anion-Orchestrated Formation in the Crystalline State of [2]Pseudorotaxane Arrays

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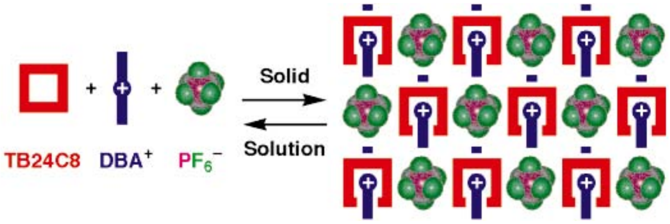
ABSTRACT



In contrast with dibenzo[24]crown-8 (DB24C8), when tetrabenzo[24]crown-8 (TB24C8) is mixed with dibenzylammonium hexafluorophosphate (DBA·PF_6) in noncompetitive solvents, the thermodynamically driven noncovalent synthesis of the threaded 1:1 complex—a [2]pseudorotaxane—does not occur. However, on crystallization from solution—in a process which is presumably kinetically controlled—TB24C8 molecules and DBA^+ cations form an array of [2]pseudorotaxanes stabilized by a plethora of [C–H···F] hydrogen bonds to highly ordered, interstitially located PF_6^- anions.

After many years, during which the focus of host−guest chemistry centered on the recognition and binding of cationic[1] substrates, the importance of taming and trapping their negatively charged counterparts (i.e., anions!) has only recently been realized.[2] The drive to design receptors capable of selective anion recognition is fueled largely by their environmental and biological significance.[3] This incentive has led to the syntheses of many ingeniously selective anion-recognizing receptors.[4] Consequently, a greater understanding of the supramolecular chemistry[5] of anions and the role they play in self-assembly[6] processes has emerged. This trend is demonstrated elegantly by the exploitation of anion binding

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(1) See Volume 1 of *Comprehensive Supramolecular Chemistry*; Atwood, J. L., Davies, J. E. D,; MacNicol, D. D., Vögtle, F., Eds.; Pergamon: Oxford, 1996; 11 Vols.

(2) Nowhere is this bias more apparent than when noting that Molecular Recognition: Receptors for Cationic Guests is the title of Volume 1 of *Comprehensive Supramolecular Chemistry* (ref 1) while the subject of anion binding/recognition appears only sparsely throughout the 11 volume series. For recent reviews of anion binding, see: (a) Schmidtchen, F. P.; Berger, M. *Chem. Rev.* **1997**, *97*, 1609−1646. (b) Beer, P. D.; Schmitt, P. *Curr. Opin. Chem. Biol.* **1997**, *1*, 475−482. (c) Antonisse, M. M. G.; Reinhoudt, D. N. *Chem. Commun.* **1998**, 443−448.

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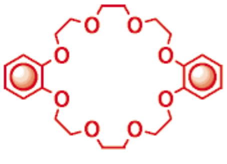
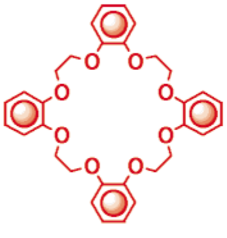
in the covalent synthesis of rotaxanes,[7] as well as in the noncovalent syntheses[8] of metal−ligand cages,[9] helicates,[10] and numerous other intricate supramolecular architectures.[11] We describe here the formation of a [2]pseudorotaxane array in the solid state—stabilized by a highly ordered matrix of PF_6^- anions responsible for numerous [C−H···F] interactions—despite the fact that no evidence for the formation of such a threaded complex could be detected during solution-state ^1H NMR spectroscopic studies.



DB24C8



TB24C8

DBA·PF$_6$

The discovery[12] that appropriately sized crown ethers—*e.g.*, dibenzo[24]crown-8 (DB24C8)—form 1:1 complexes with secondary dialkylammonium ions—*e.g.*, dibenzylammonium hexafluorophosphate (DBA·PF$_6$)—in which the threadlike cation pierces (Figure 1) the cavity of the ring, affording a [2]pseudorotaxane, has been exploited for the construction of novel interlocked molecules[13] and intertwined arrays.[14] This basic paradigm has recently been investigated in a series of experiments which reveal that substitution of either the thread[15] or the ring[16] can alter dramatically the affinity these components display for one another. Most notably, the solution-state binding of dialkylammonium salts by tetrabenzo[24]crown-8 (TB24C8) was shown[16] to be negligible, indicating that the equilibrium depicted in Figure 1 lies far over to the left-hand side, in favor of the free components.

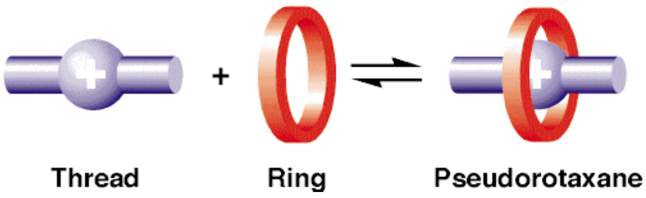


Figure 1. A schematic representation depicting the formation of a threaded 1:1 complex (a pseudorotaxane) formed between two complementary species whereupon the cavity of a suitably sized ring-shaped component is skewered by a linear thread-like one.

However, upon crystallization of an equimolar mixture of TB24C8 and DBA·PF$_6$ from a $CHCl_3$/MeCN/n-C_6H_{14} solution (7:3:3), X-ray quality single crystals of the [2]pseudorotaxane [TB24C8/DBA][PF$_6$] were isolated. No uncomplexed thread or ring components were present in this crystalline material. The X-ray analysis[17] of [TB24C8/DBA]-[PF$_6$] shows the crystals to contain four crystallographically independent 1:1 complexes in the asymmetric unit. Each of the complexes has (Figure 2) a very similar co-conformation,[18] the only significant difference being in the relative orientation of one of the benzyl groups with respect to the plane of the $C_{Ph}CH_2NH_2^+CH_2C_{Ph}$ backbone. The TB24C8 macrocycle adopts a shape with approximate tennis ball seam (D_{2d}) symmetry—a conformation similar to that observed[19] in TB24C8·2MeCN. The 1:1 complexes are all stabilized

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(17) *Crystal data for* [TB24C8/DBA][PF$_6$]:[$C_{46}H_{48}NO_8$][PF$_6$]·0.5 MeCN·0.125 CH_2Cl_2, $M = 919.0$, triclinic, space group $P\bar{1}$ (No. 2), $a = 14.182(1)$, $b = 23.357(2)$, and $c = 28.107(2)$ Å, $\alpha = 91.51(1)$, $\beta = 90.51(1)$, and $\gamma = 104.37(1)°$, $V = 9015(1)$ Å^3, $Z = 8$ (there are four crystallographically independent 1:1 complexes in the asymmetric unit), $\rho_c = 1.354$ g cm^{-3}, μ(Cu Kα) = 13.7 cm^{-1}, $F(000) = 3842$, $T = 183$ K.; clear platy prisms, 0.43 × 0.20 × 0.07 mm, Siemens P4 rotating anode diffractometer, graphite-monochromated Cu Kα radiation, ω-scans, 24143 independent reflections. The structure was solved by direct methods, and all the full occupancy non-hydrogen atoms were refined anisotropically. Disorder was found in the thread component of one of the four crystallographically independent pseudorotaxanes and in one of the included solvent MeCN molecules; in each case, two partial occupancy orientations were identified with only the non-hydrogen atoms of the major occupancy orientations being refined anisotropically (the rest being refined isotropically). Refinements were by blocked full matrix least-squares based on F^2 to give $R_1 = 0.089$, $wR_2 = 0.216$ for 12765 independent observed reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leq 115°$] and 2264 parameters. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 132801. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB12 1EZ, U.K. (fax: (+44)1223-336-033. e-mail: teched@ccdc.cam.ac.uk).

(18) Whereas the term "conformation" refers to the spatial arrangement of atoms in a single molecular species resulting from torsions about single or partial double bonds, the term "co-conformation" has been utilized to describe the relative three-dimensional dispositions of (a) the constituent parts (e.g., host and guest) in supramolecular systems and of (b) the components of interlocked molecular compounds, such as catenanes and rotaxanes. See: Fyfe, M. C. T.; Glink, P. T.; Menzer, S.; Stoddart, J. F.; White, A. J. P.; Williams, D. J. *Angew. Chem., Int. Ed. Engl*. **1997**, *36*, 2068−2070.

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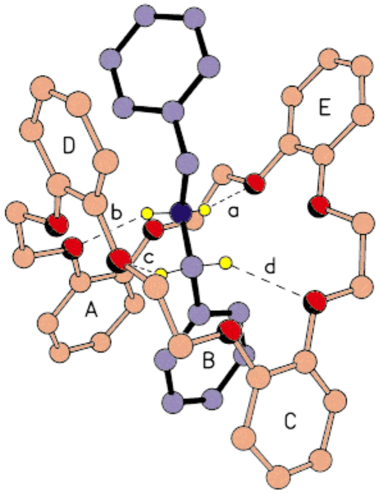

Figure 2. Ball-and-stick representation of one of the four crystallographically independent [2]pseudorotaxanes present in the crystals of [TB24C8/DBA][PF_6] showing the [N^+−H···O] and [C−H···O] hydrogen bonding. The hydrogen-bonding geometries and inter-ring separations are given in tables.

(Tables 1 and 2) by a combination of [N^+−H···O] (*a* and *b*) and [C−H···O] (*c* and *d*) hydrogen-bonding interactions (Figure 2) and $\pi-\pi$ stacking between the phenyl ring B of the DBA^+ cation and the catechol rings A and C of the crown ether. The most novel feature of the solid-state superstructure is the arrangement of the sets of four 1:1 complexes and their associated highly ordered PF_6^- anions (Figure 3). This unusual lack of disorder in these anions indicates that they are playing a key role in the kinetic assembly of the superstructure in the solid state. The [TB24C8/DBA]$^+$ complexes are arranged in layers with the PF_6^- anions embedded into the clefts formed by groups of four 1:1 complexes (Figure 3b). Each PF_6^- anion has (Table 3) not less than five [F···H] contacts (of 2.6 Å or less) involving no fewer than four of the F atoms to H bond donors in either (i) the catechol rings or (ii) the OCH_2OCH_2O linkages in TB24C8 or (iii) the phenyl rings of the DBA^+ cation. There is no instance where there is not at least one cation/anion [C−H···F] interaction for each PF_6^- anion. Adjacent C_2-symmetrically related layers are almost in register, thereby completely encapsulating all of the anions.

Table 1. [N^+−H···O] and [C−H···O] Hydrogen-Bonding Parameters *a*−*d* (Figure 2) for the Four Independent [TB24C8/DBA][PF_6] Supermolecules (**1**−**4**) That Exist in the Solid State

	supermolecule			
interaction	**1**	**2**	**3**	**4**
a				
[N^+···O] (Å)	2.91	2.96	2.98	2.92
[H···O] (Å)	2.03	2.08	2.11	2.03
[N^+−H···O] (deg)	158	167	159	169
b				
[N^+···O] (Å)	3.05	3.04	2.99	3.00
[H···O] (Å)	2.20	2.16	2.13	2.13
[N^+−H···O] (deg)	165	164	164	164
c				
[C···O] (Å)	3.34	3.29		3.27
[H···O] (Å)	2.51	2.33		2.31
[C−H···O] (deg)	144	175		178
d				
[C···O] (Å)	3.16	3.14	3.12	3.19
[H···O] (Å)	2.32	2.33	2.18	2.43
[C−H···O] (deg)	146	141	160	136

Table 2. Centroid−Centroid Separations (Å) for Pairs of Aromatic Rings (Figure 2) in the Four Independent [TB24C8/DBA][PF_6] Supermolecules (**1**−**4**) That Exist in the Solid State

	supermolecule			
interaction	**1**	**2**	**3**	**4**
[cat.···cat.][a]				
[A···C]	7.67	7.93	7.90	7.66
[D···E]	7.96	8.64	7.86	8.09
[cat.···Ph][b]				
[A···B]	3.86	3.71	3.86	3.55
[B···C]	3.96	4.23	4.22	4.12

[a] The catechol rings of the TB24C8 macrocycle are assigned the descriptor cat. [b] The phenyl rings of the DBA^+ cation are assigned the descriptor Ph.

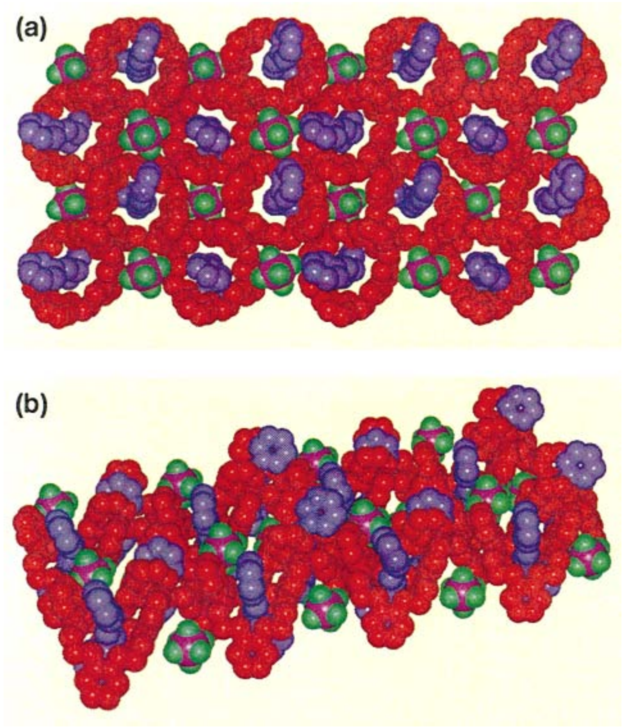

Figure 3. Space-filling representations (hydrogen atoms omitted for clarity) showing (a) the regular array of the 1:1 complexes (TB24C8 in red and the DBA^+ cation in blue) and their associated PF_6^- anions (P in purple and F in green) and (b) the embedding of the anions into the egg-box-like clefts formed by the array of [2]-pseudorotaxanes.

Table 3. Hydrogen Bond Lengths (Å) for the Interactions between the F Atoms of the PF_6^- Anions and H Atoms Situated on Either the DBA^+ Cation or TB24C8 Macrocycle (Figure 2) in the Four Independent [TB24C8/DBA][PF_6] Supermolecules (**1**−**4**) That Exist in the Solid State

	supermolecule			
interaction	**1**	**2**	**3**	**4**
[F···H(*m*-Ph)]	2.60	2.45	2.47	2.55
[F···H(*p*-Ph]	2.55	2.60	2.55	
	2.55			
[F···H(*o*-cat.)]	2.56	2.34	2.52	2.43
[F···H(polyether)]	2.55	2.45	2.47	2.35
	2.59	2.54	2.55	2.57
	2.49		2.57	2.59
			2.55	2.58

Liquid secondary ion mass spectrometric (LSI-MS) investigations into this system also provide an insight into the different behavior exhibited in the solution and solid states. The crystalline material (from which the crystal subjected to X-ray crystallography was taken) was analyzed by LSI-MS, revealing the base peak in the spectrum to be at m/z = 742.4, corresponding to the 1:1 complex formed between TB24C8 and DBA^+. The peak arising from the free DBA^+ cation has an intensity of only 23% of the base peak. In contrast, when a $(CD_3)_2CO$ solution containing equimolar quantities of TB24C8 and $DBA{\cdot}PF_6$ was analyzed, the base peak in the spectrum occurred at an m/z value of 198.2, corresponding to DBA^+, and the peak arising from a 1:1 association of TB24C8 with DBA^+ is only half as intense. These mass spectrometric observations[20] are in agreement with the data obtained from previous ^1H NMR spectroscopic investigations,[16] which suggest that the 1:1 complex, although present exclusively in the solid state, cannot be detected in solution. Additionally, subsequent dissolution of these crystals in a mixture of $CDCl_3/CD_3CN$ (2:1), followed by ^1H NMR spectroscopic analysis, gave rise to a spectrum in which only resonances for the free components could be observed, i.e., the [2]pseudorotaxane present in the solid state falls apart in solution.

Although the self-assembly[6] of TB24C8 with DBA^+ cations in solution to form a [2]pseudorotaxane is not a thermodynamically favored process, the act of crystallization—an inherently kinetic event—in the presence of PF_6^- anions drives the equilibrium shown in the graphical abstract to the right-hand side. Previously, with this class of crown ether/dialkylammonium ion recognition motif, we have observed[21] the PF_6^- anion-assisted formation of discrete supermolecules—*i.e.*, 1:1, 1:2, 1:3, 1:4, 2:2, 2:4, etc., complexes with pseudorotaxane geometries—in which the PF_6^- anions stabilize the supermolecules by means of a multitude of complementary [C−H···F] hydrogen-bonding interactions,[22] particularly in the crystalline state.[23] Here—*the anion-orchestrated formation of a continuous supramolecular array, containing a cationic [2]pseudorotaxane which does not form at all as a discrete supermolecule in solution, has been demonstrated only to occur in the solid state upon crystallization*.

Acknowledgment. We thank UCLA and EPSRC in the U.K. for generous financial support.

Supporting Information Available: Crystal data for [TB24C8/DBA][PF_6]. This material is available free of charge via the Internet at http://pubs.acs.org.

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[20] In our experience, if the [2]pseudorotaxane is a major solution-state component in such an equilibrium process, this observation is usually reflected in the LSI-MS with the base peak of the spectrum arising from the 1:1 complex and the free components giving rise to much less intense peaks. Conversely, if threading in solution is negligible, a peak arising from the 1:1 association of the two components is often observed in the mass spectrum. However, this signal may arise as a consequence of face-to-face complexation rather than of a threaded geometry and its intensity is usually less than that observed for the signals arising from the free components. See: Ashton, P. R.; Baxter, I.; Fyfe, M. C. T.; Raymo, F. M.; Spencer, N.; Stoddart, J. F.; White, A. J. P.; Williams, D. J. *J. Am. Chem. Soc*. **1998**, *120*, 2297−2307.

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[22] For recent insight into the role of PF_6^- anions in [C−H···F] hydrogen bonding and its importance in the solid state, see: Grepioni, F.; Cojazzi, G.; Draper, S. M.; Scully, N.; Braga, D. *Organometallics* **1998**, *17*, 296−307.

[23] Crystallization has also been used to advantage in a high-yielding preparation of a [3]rotaxane following a reversible oxidative coupling of the thiol groups of two [2]pseudorotaxane supermolecules by a so-called molecular riveting action. See: Kolchinski, A. G.; Alcock, N. W.; Roesner, R. A.; Busch, D. H. *Chem. Commun*. **1998**, 1437−1438.