The self-assembly of a complex with a [3]pseudorotaxane superstructure

Peter R. Ashton,[a] Steven J. Langford,[a] Neil Spencer,[a] J. Fraser Stoddart,*[a] Andrew J. P. White[b] and David J. Williams[b]

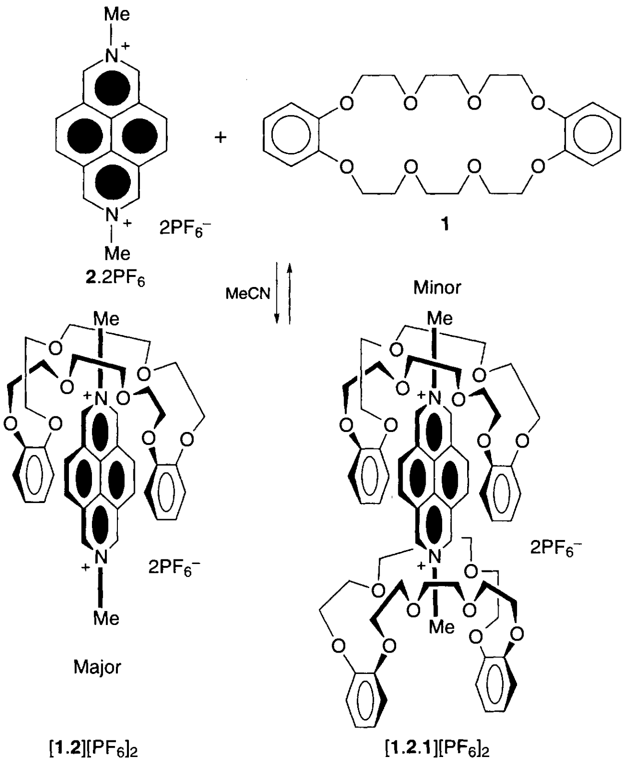
[a] *School of Chemistry, University of Birmingham, Edgbaston, Birmingham, UK B15 2TT*
[b] *Department of Chemistry, Imperial College, South Kensington, London, UK SW7 2AY*

Dibenzo-24-crown-8, which contains two π-electron rich catechol units, self-assembles with the π-electron deficient 2,7-dimethyldiazapyrenium dication in solution to form a mixture of 1:1 and 2:1 complexes that have the ability to undergo further self-organisation on crystallisation to form linear arrays of [3]pseudorotaxanes between which diisopropyl ether molecules are trapped.

In recent times, dibenzo-24-crown-8 (DB24C8)[1] **1** has found a niche in the supramolecular market as a result of its capacity not only to bind, but also to encircle secondary dialkylammonium cations. This act of supramolecular recognition signals the emergence of an important new family of threaded species that has already been expressed in the self-assembly[2] of numerous 1:1, 2:1, and 2:2 complexes of a pseudorotaxane type.[3] Our present interest[4] in using 2,7-disubstituted diazapyrenium dications (*e.g.* **2**·2PF$_6$) as a source of π-electron deficient building blocks in place of Paraquat bis(hexafluorophosphate) to fit in and around π-electron rich units, such as the hydroquinone rings in BPP34C10, led us to explore the nature and extent of the interactions between **2**·2PF$_6$ and DB24C8 **1**. Here, we report (*a*) the characterisation of the 2:1 complex [**1**·**2**·**1**][PF$_6$]$_2$ by X-ray crystallography† in the solid-state and (*b*) evidence for the existence of a 1:1, as well as a 2:1, complex in the solution state by LSIMS‡ and ^{1}H NMR spectroscopy.

When **1** is mixed progressively with more and more **2**·2PF$_6$§ in MeCN, a deep yellow coloured solution develops on account of the charge-transfer interactions between the π-electron rich and deficient entities in the two supramolecular components. The nature of the superstructure present in CD$_3$CN solution was investigated by ^{1}H NMR spectroscopy. At equimolar proportions of **1** and **2**·2PF$_6$, the large Δδ values for the ArH protons (Δδ = −0.94 ppm) in **1** and γ-CH protons (Δδ = −0.30 ppm) in **2**$^{2+}$ indicate that the DB24C8 and the 2,7-dimethyldiazapyrenium dication must lie in close proximity to each other–a geometry consistent with the presence of π–π stacking between these two components in the complex. A Job plot,[5] using protons from both **1** and **2**$^{2+}$ as ^{1}H NMR probes, and mixtures of 5 mmol dm^{-3} solutions of **1** and **2**·2PF$_6$, indicated that the dominant supramolecular species present in solution is a 1:1 complex, accompanied by a small amount of a much weaker 2:1 complex. A K_a value for the 1:1 complex of 840 ± 51 dm^3 mol^{-1} was determined by dilution methods¶ in MeCN using ^{1}H NMR probe protons in both components and recording their chemical shift changes (Δδ) for an equimolar mixture of **1** and **2**·2PF$_6$. Evidence for the presence, also in solution, of a 2:1 complex was obtained by LSIMS.‡ Very weak peaks, corresponding to the loss of one and two PF$_6^-$ counterions from the [3]pseudorotaxane [**1**·**2**·**1**][PF$_6$]$_2$, were present at *m/z* 1275 and 1130, respectively. Much more intense peaks, arising from the [2]pseudorotaxane–following the loss of one DB24C8 **1** component from the [3]pseudorotaxane–and corresponding to the loss of, once again, one and two PF$_6^-$ counterions, were observed at *m/z* 827 and 682, respectively.

Vapour diffusion of Pr$^i_2$O into a MeCN solution of a 1:1 mixture of **1** and **2**·2PF$_6$ afforded single crystals of a 2:1 complex that were suitable for X-ray crystallography.† X-Ray structural analysis shows (Fig. 1) the presence of a C_2 symmetric 2:1 complex in the solid state in which the 2,7-dimethyldiazapyrenium dication **2**$^{2+}$ (which has its N···N axis lying on the C_2 axis) is sandwiched between two DB24C8 **1** macrocycles. These two macrocycles are aligned, rotated by 52° to each other, with their concave faces co-directional along the C_2 axis. Both diazapyrenium methyl groups are positioned approximately centrally within each crown ether ring. There are four short [Me···O] contacts in the range 2.92–3.31 Å to polyether oxygen atoms in both crown ether rings, commensurate with the presence of [C–H···O] hydrogen bonding.|| There is also a proximal relationship (3.24 and 3.32 Å) between the diazapyrenium nitrogen atoms and the catechol oxygen atoms of the sandwiching DB24C8 **1** macrocycle. Accompanying this partial sandwiching of the diazapyrenium ring system between the catechol units of one of the DB24C8 **1** macrocycles are ring centroid [catechol···azapyrenyl] separations of 3.80 Å, indicating a degree of π–π stabilisation in this portion of the 2:1 complex. The distances between both sets of π-electron rich aromatic units are similar (7.48 and 7.59 Å), with the shorter of the two being that associated with the π–π stacking. The complexes are aligned along the crystallographic *b* direction and cavities are formed between the 'head' of one complex and



Scheme 1 Self-assembly of the [2]pseudorotaxane [**1**·**2**][PF$_6$]$_2$ and the [3]pseudorotaxane [**1**·**2**·**1**][PF$_6$]$_2$ in MeCN solution

the 'tail' of its lattice-translated counterpart within which the included Pr^i_2O molecules are trapped. The repeat separation between adjacent 2,7-dimethyldiazapyrenium units within these chains of complexes is 19.8 Å. The co-alignment of the central free pathways through the DB24C8 **1** macrocycles creates channels that extend through the crystal lattice (Fig. 2).

The fact that dibenzo-24-crown-8 **1** and the 2,7-dimethyldiazapyrenium dication $\mathbf{2}^{2+}$ self-assemble to form both 1 : 1 and 2 : 1 complexes, wherein the dication threads itself through the centre of the DB24C8 cavities, on account of [C–H···O] hydrogen bonding and π–π stacking interactions, opens up the prospect of constructing, by self-assembly,[2] yet another family of interlocked molecular compounds where the mechanical properties can be the subject of redox control.[6,7]

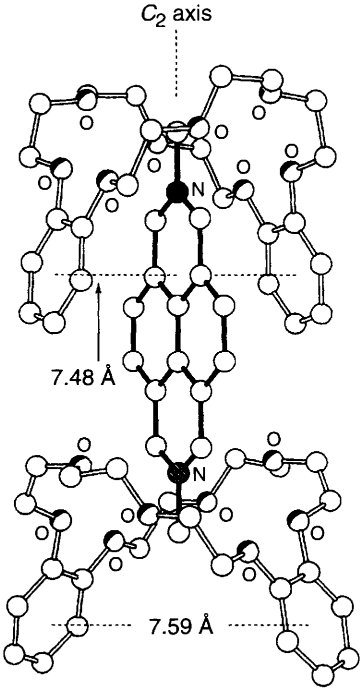


Fig. 1 A ball-and-stick representation of the [3]pseudorotaxane $[\mathbf{1}{\cdot}\mathbf{2}{\cdot}\mathbf{1}]^{2+}$ in the solid-state

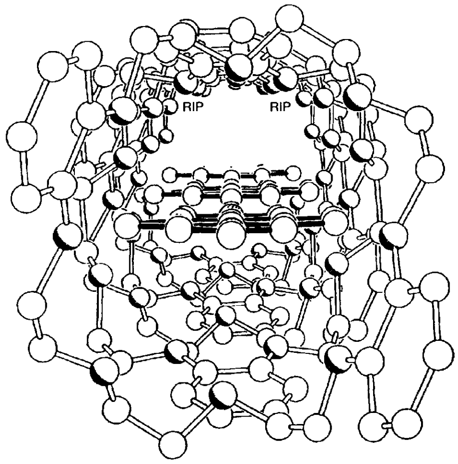


Fig. 2 A view down the *b* direction in the crystals of the [3]pseudorotaxane $[\mathbf{1}{\cdot}\mathbf{2}{\cdot}\mathbf{1}]^{2+}$ showing the DB24C8 channels and omitting the Pr^i_2O molecules for clarity

We wish to acknowledge financial support from the Ramsay Memorial Trust for providing S. J. L. with a postdoctoral fellowship and from the Engineering and Physical Sciences Research Council and the Wolfson Foundation.

Footnotes

† *Crystal data* for $[\mathbf{1}{\cdot}\mathbf{2}{\cdot}\mathbf{1}][PF_6]_2{\cdot}Pr^i_2O$: $C_{64}H_{78}N_2O_{16}F_{12}P_2{\cdot}C_6H_{14}O$, M = 1523.4, orthorhombic, a = 18.165(4), b = 19.821(3), c = 20.835(4) Å, V = 7502(3) Å^3, space group *Pbcn*, Z = 4 (the complex has crystallographic C_2 symmetry), D_c = 1.35 g cm^{-3}, μ (Cu-Kα) = 13.7 cm^{-1}, $F(000)$ = 3200. 5238 Independent reflections ($2\theta \leqslant 116°$) were measured on a Siemens P4 diffractometer with Cu-Kα radiation (graphite monochromator) using ω scans; 2335 had $|F_o| > 4\sigma(|F_o|)$ and were considered to be observed. The structure was solved by direct methods and the non-hydrogen atoms were refined anisotropically by full-matrix least-squares (based on F^2) to give R_1 = 0.101 and wR_2 = 0.282. The high final value for R is a consequence of severe disorder in both the PF_6^- anions and the included Pr^i_2O solvent molecule. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/125.

‡ Liquid secondary ion mass spectometry (LSIMS) was carried out on a VG-Zab Spec mass spectrometer (accelerating voltage, 8 kV; resolution, 2000). A 2 : 1 molar ratio of **1** and $\mathbf{2}{\cdot}2PF_6$, in MeCN, was mixed in a small volume of 3-nitrobenzyl alcohol, which had previously been coated on to a stainless steel probe tip, Spectra were recorded in the positive ion mode at a scan speed of 5 s per decade.

§ 2,7-Dimethyldiazapyrenium hexafluorophosphate $\mathbf{2}{\cdot}2PF_6$ was prepared by methylation (MeI, Me_2SO, reflux) of 2,7-diazapyrene (see S. Hünig, J. Grosse, E. F. Lier, H. Quast, *Liebigs Ann. Chem.*, 1973, 339 for the preparation of 2,7-diazapyrene) followed by counterion exchange (NH_4PF_6, H_2O) [85%; mp > 300 °C; *m/z* (positive ion FABMS), 379 $[M - PF_6]^+$, 234 $[M - 2PF_6]^+$, 218 $[M - Me - 2PF_6]^+$; δ (CD_3CN, 300 MHz) 4.85 (6 H, s, NCH_2), 8.82 (4 H, s, γ-CH) and 9.81 (4 H, s, α-CH)].

¶ The data, expressed as changes in chemical shift (Δδ) *versus* the relative concentration of a 1 : 1 mixture of **1** and $\mathbf{2}{\cdot}2PF_6$ in MeCN, was treated on the non-linear curve fitting programUltrafit (BIOSOFT®, 49 Bateman Street, Cambridge, UK CB2 1LR) using an Apple MacIntosh Performa 475 computer.

|| We are unable to define the precise hydrogen bonding geometry since the methyl hydrogen atom positions could not be located. The shortest [α-CH···O] distances are 2.53 and 2.54 Å.

References

1 I. R. Hanson, D. L. Hughes and M. R. Truter, *J. Chem. Soc., Perkin Trans. 2*, 1976, 972.

2 G. M. Whitesides, E. E. Simanek, J. P. Mathias, C. T. Seto, D. N. Chin, M. Mammen and D. M. Gordon, *Acc. Chem. Res.*, 1995, **28**, 37.

3 P. R. Ashton, P. J. Campbell, E. J. T. Chrystal, P. T. Glink, S. Menzer, D. Philp, N. Spencer, J. F. Stoddart, P. A. Tasker and D. J. Williams, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1865; P. R. Ashton, E. J. T. Chrystal, P. T. Glink, S. Menzer, C. Schiavo, J. F. Stoddart, P. A. Tasker and D. J. Williams, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1869.

4 S. J. Langford and J. F. Stoddart, in *Magnetism: A Supramolecular Function*, NATO-ARW Series, ed. O. Kahn, in the press.

5 Z. D. Hill and P. MacCarthy, *J. Chem. Ed.*, 1986, **63**, 162 and references cited therein.

6 R. Ballardini, V. Balzani, A. Credi, M. T. Gandolfi, S. J. Langford, S. Menzer, L. Prodi, J. F. Stoddart, M. Venturi and D. J. Williams, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1054.

7 A. C. Benniston, A. Harriman and V. M. Lynch, *J. Am. Chem. Soc.*, 1995, **117**, 5275.

Received, 5th October 1995; Com. 5/06529A