The Self-assembly of Complexes with [2]Pseudorotaxane Superstructures

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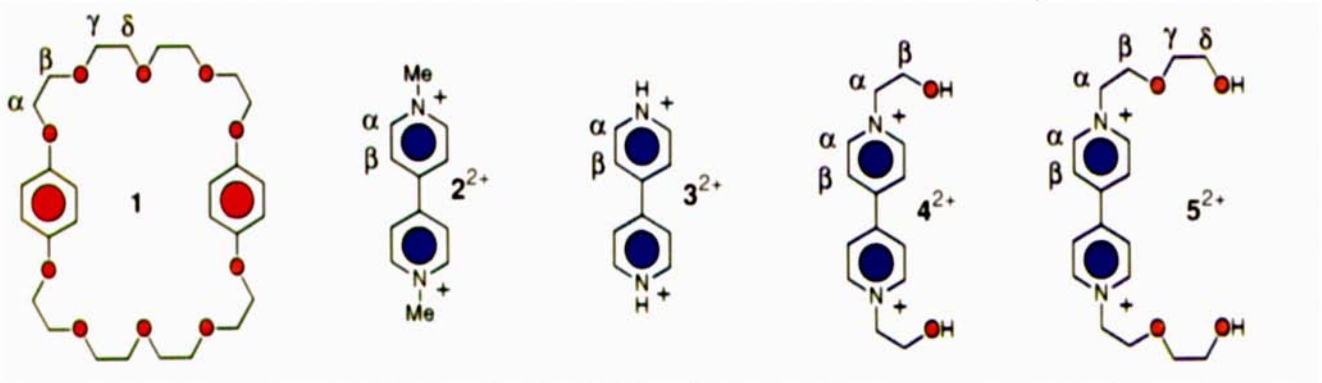
The application of X-ray crystallography, mass spectrometry, and NMR and UV–VIS spectroscopy has revealed that bis-*p*-phenylene-34-crown-10 **1** forms strong 1 : 1 complexes with the 4,4′-bipyridinium dication $\mathbf{3}^{2+}$ and two of its derivatives, namely, the dications $\mathbf{4}^{2+}$ and $\mathbf{5}^{2+}$ in which the substituents on the bipyridine nitrogen atoms are, respectively, 2-hydroxyethyl and 2-(2-hydroxyethoxy)ethyl groups.

Previously, we have shown[1–7] that the important bipyridinium herbicide Paraquat (PQT) forms a 1 : 1 complex with bis-*p*-phenylene-34-crown-10 (BPP34C10) **1**. The strong binding of the PQT^{2+} dication $\mathbf{2}^{2+}$ by **1** involves electrostatic and dispersive interactions, including charge transfer (CT), between the π-electron-deficient bipyridinium system in $\mathbf{2}^{2+}$ and the π-electron-rich hydroquinol rings in **1**. In addition, there is some further stabilisation of the 1 : 1 complex $[\mathbf{1}\cdot\mathbf{2}]^{2+}$ by [C–H···O] hydrogen bonding between the acidic hydrogen atoms (Me and α-bipy-CH) in $\mathbf{2}^{2+}$. Anticipating the synthesis of [2]rotaxanes[5–7] in which BPP34C10 **1** is the macrocyclic component, threaded by chains incorporating bipyridinium units, we have prepared‡ the bis(hexafluorophosphate) salts of the dications $\mathbf{3}^{2+}$, $\mathbf{4}^{2+}$ and $\mathbf{5}^{2+}$ where the Me groups in $\mathbf{2}^{2+}$ are replaced by H, CH_2CH_2OH, and $CH_2CH_2OCH_2CH_2OH$ substituents, respectively. Here, we report (*a*) the stability constants in acetone, (*b*) the ^1H NMR spectra in CD_3COCD_3, (*c*) the FABMS, and (*d*) the solid-state structures§ for the 1 : 1 complexes, $[\mathbf{1}\cdot\mathbf{3}][PF_6]_2$, $[\mathbf{1}\cdot\mathbf{4}][PF_6]_2$ and $[\mathbf{1}\cdot\mathbf{5}][PF_6]_2$.

When BPP34C10 **1** was mixed in turn with progressively more and more $\mathbf{3}\cdot 2PF_6$, $\mathbf{4}\cdot 2PF_6$ and $\mathbf{5}\cdot 2PF_6$ in acetone, deep orange coloured solutions resulted on account of the CT interactions. UV–VIS spectrophotometric titrations established that all the complexes formed have 1 : 1 stoichiometries and also afforded their associated stability constants (K_a). The K_a values and their derived free energies of complexation (ΔG°) are listed in Table 1. Whilst $\mathbf{3}\cdot 2PF_6$ forms a slightly weaker complex than $\mathbf{2}\cdot 2PF_6$ with BPP34C10 **1**, the strengths of $[\mathbf{1}\cdot\mathbf{4}][PF_6]_2$ and $[\mathbf{1}\cdot\mathbf{5}][PF_6]_2$ are very similar to that ($730\ dm^3\ mol^{-1}$) of $[\mathbf{1}\cdot\mathbf{2}][PF_6]_2$ in acetone.[7] Furthermore, there was evidence from FABMS (Table 2) for the existence of 1 : 1 complexes in all three cases. Clearly evident were peaks corresponding to the loss of one and two PF_6^- counterions, giving rise to signals with *m/z* values for $[M - PF_6]^+$ and $[M - 2PF_6]^+$ for all three complexes.

The solution-state structures of the 1 : 1 complexes were investigated by ^1H NMR spectroscopy in CD_3COCD_3 solutions. The results of these investigations are presented in



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‡ The bishydrochloride obtained (conc. HCl, EtOH) from 4,4′-bipyridine was converted (NH_4PF_6, H_2O) into $\mathbf{3}\cdot 2PF_6$ [89%; m.p. 198–200 °C; *m/z* (positive-ion FABMS), 303 for $[M - PF_6]^+$; δ (CD_3COCD_3, 250 MHz) 8.82–8.87 (4H, m, β-bipy-CH) and 9.42–9.46 (4H, m, α-bipy-CH). The dichloride salt obtained in 38% yield, on addition of EtOH, after heating an aqueous suspension of 4,4′-bipyridine under reflux for 6 h with 2-chloroethanol, was converted (NH_4PF_6, H_2O) into $\mathbf{4}\cdot 2PF_6$ [m.p. 215–220 °C; *m/z* (positive-ion FABMS), 391 for $[M - PF_6]^+$; δ (CD_3COCD_3, 250 MHz) 4.17–4.24 (4H, m, β-OCH_2), 4.68 (2H, t, *J* 5 Hz, OH), 5.05 (4H, t, *J* 5 Hz, α-NCH_2), 8.85 (4H, d, *J* 7 Hz, β-bipy-CH) and 9.39 (4H, d, *J* 7 Hz, α-bipy-CH). The dichloride salt, which was obtained after chromatography [Al_2O_3: $Pr^iOH–H_2O$ (4 : 1, v/v)] of the residue remaining after removal of the solvents following treatment of 4,4′-bipyridine in 2-methoxyethanol under reflux for 24 h with 2-(2-chloroethoxy)ethanol, was converted (NH_4PF_6, H_2O) into $\mathbf{5}\cdot 2PF_6$ [m.p. 240 °C (decomp); *m/z* (positive-ion FABMS), 479 for $[M - PF_6]^+$; δ (CD_3COCD_3, 250 MHz) 3.61 (8H, br.s, γ-OCH_2 and δ-OCH_2), 3.73 (2H, br.s, OH), 4.16 (4H, t, *J* 5 Hz, β-OCH_2), 5.13 (4H, t, *J* 5 Hz, α-NCH_2), 8.83 (4H, d, *J* 7 Hz, β-bipy-CH) and 9.43 (4H, d, *J* 7 Hz, α-bipy-CH).

§ *Crystal data* for $\mathbf{1}\cdot\mathbf{3}\cdot 2PF_6$: $C_{38}H_{50}F_{12}N_2O_{10}P_2$, $M = 984.8$, triclinic, space group $P\bar{1}$, $a = 9.123(2)$, $b = 10.439(3)$, $c = 12.209(3)$ Å, $\alpha = 91.56(2)$, $\beta = 106.00(2)$, $\gamma = 98.47(2)^\circ$, $U = 1103$ Å^3, $Z = 1$ (the complex is disposed about a centre of symmetry), $D_c = 1.48\ g\ cm^{-3}$, $\mu = 19\ cm^{-1}$.

Crystal data for $\mathbf{1}\cdot\mathbf{4}\cdot 2PF_6\cdot Me_2CO$: $C_{45}H_{64}F_{12}N_2O_{13}P_2$, $M = 1130.9$, monoclinic, space group $I2/c$ (body-centred cell chosen because *C*-face-centred cell had $\beta = 139^\circ$), $a = 18.723(4)$, $b = 11.827(2)$, $c = 24.880(7)$ Å, $\beta = 101.61(2)^\circ$, $U = 5397$ Å^3, $Z = 4$ (the complex is disposed about a centre of symmetry and the Me_2CO molecule about a two-fold axis), $D_c = 1.39\ g\ cm^{-3}$, $\mu = 16\ cm^{-1}$.

Crystal data for $\mathbf{1}\cdot\mathbf{5}\cdot 2PF_6$: $C_{46}H_{66}F_{12}N_2O_{14}P_2$, $M = 1161.0$, triclinic, space group $P\bar{1}$, $a = 10.677(2)$, $b = 10.973(2)$, $c = 12.489(2)$ Å, $\alpha = 97.95(1)$, $\beta = 95.30(1)$, $\gamma = 104.99(1)^\circ$, $U = 1387$ Å^3, $Z = 1$ (the molecule is disposed about a centre of symmetry), $D_c = 1.39\ g\ cm^{-3}$, $\mu = 16\ cm^{-1}$.

Data for all three structures were measured on a Nicolet R3m diffractometer with graphite monochromated Cu-Kα radiation using ω-scans. The structures were solved by direct methods and refined anisotropically to give (*a*) for $\mathbf{1}\cdot\mathbf{3}\cdot 2PF_6$, $R = 0.055$, $R_w = 0.070$, for 2588 independent observed reflections $[|F_o| > 3\sigma(|F_o|), 2 \leqslant 110^\circ]$, (*b*) for $\mathbf{1}\cdot\mathbf{4}\cdot 2PF_6\cdot Me_2CO$, $R = 0.077$, $R_w = 0.097$ for 2435 independent observed reflections $[|F_o| > 3\sigma(|F_o|), 2\theta \leqslant 100^\circ]$, and (*c*) for $\mathbf{1}\cdot\mathbf{5}\cdot 2PF_6$, $R = 0.094$, $R_w = 0.116$ for 2487 independent observed reflections $[|F_o| > 3\sigma(|F_o|), 2\theta \leqslant 100^\circ]$.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

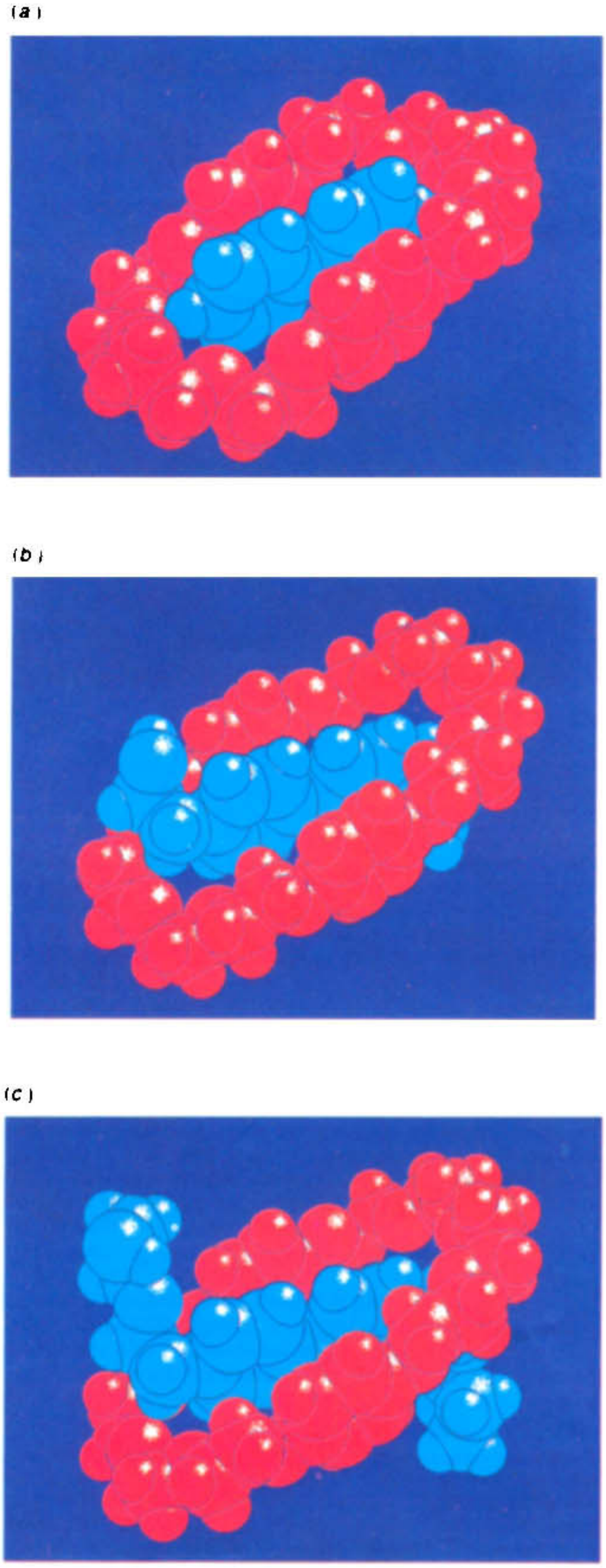

Fig. 1 Space-filling representations of (*a*) [**1·3**]$^{2+}$, (*b*) [**1·4**]$^{2+}$ and (*c*) [**1·5**]$^{2+}$ in their solid states. The BPP34C10 **1** macrocycles are shaded red and the dications **3**$^{2+}$, **4**$^{2+}$ and **5**$^{2+}$ are light blue.

Table 1 The stability constants (K_a/dm^3 mol^{-1}) and the derived free energies of complexation ($\Delta G°$/kcal mol^{-1}; 1 cal = 4.184 J) for the 1 : 1 complex formed between BPP34C10 **1** and **2**·2PF$_6$, **3**·2PF$_6$, **4**·2PF$_6$ and **5**·2PF$_6$ in Me$_2$CO at 27 °C

Complex	λ_{max}[a]/nm	K_a	$\Delta G°$
[**1·2**][PF$_6$]$_2$[b]	436	730	3.95
[**1·3**][PF$_6$]$_2$	434	390	3.56
[**1·4**][PF$_6$]$_2$	437	700	3.93
[**1·5**][PF$_6$]$_2$	438	810	3.99

[a] The wavelengths at which the spectrophotometric titrations were performed. [b] Ref. 7.

Table 2 FABMS[a] of [**1·3**][PF$_6$]$_2$, [**1·4**][PF$_6$]$_2$ and [**1·5**][PF$_6$]$_2$

Complex	M[b]	[M – PF$_6$]$^+$	[M – 2PF$_6$]$^+$
[**1·3**][PF$_6$]$_2$	984	839	694
[**1·4**][PF$_6$]$_2$	1072	927	782
[**1·5**][PF$_6$]$_2$	1160	1015	870

[a] FABMS was carried out on a Kratos MS80RF mass spectrometer (accelerating voltage, 3 kV; resolution, 1500) coupled to a DS90 data system. The atom gun was an adapted saddle field source (Ion Tech Ltd.) operated at *ca.* 7 keV with a tube current of *ca.* 2 mA. Xenon was used to provide a primary beam of atoms and samples of **3**·2PF$_6$, **4**·2PF$_6$ and **5**·2PF$_6$ and their 1 : 1 complexes with BPP34C10 **1** were dissolved 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 30 s per decade. [b] This value is the calculated mass of the complex with all counterions. These peaks are not observed.

Table 3 in the form of chemical shift changes ($\Delta\delta$) that compare δ values for probe protons in both host and guests in complexed and uncomplexed forms. Inspection of the $\Delta\delta$ values shows qualitatively that the 1 : 1 complex [**1·3**]$^{2+}$ is quite different supramolecularly from the 1 : 1 complexes [**1·2**]$^{2+}$, [**1·4**]$^{2+}$ and [**1·5**]$^{2+}$. Since [**1·2**]$^{2+}$ is pseudorotaxane-like in character, we conclude that [**1·4**]$^{2+}$ and [**1·5**]$^{2+}$ adopt very similar superstructures in solution. However, in the case of [**1·3**]$^{2+}$, it is not unreasonable to suggest that the N$^+$···N$^+$ vector of the dication **3**$^{2+}$ lies within the mean plane of the macrocycle **1**. In this particular supramolecular arrangement [N$^+$–H···O] hydrogen bonding can be achieved: it also affords deeper inclusion of the bipyridinium unit within the cavity of **1** and hence maximises overlap between the π-systems of the host and guest. This deeper inclusion of the guest within the host cavity would also account for the much greater shielding effect experienced in the 1 : 1 complex by the α-bipy-CH and β-bipy-CH protons in the dication **3**$^{2+}$ as well as the vastly different chemical shift pattern observed for the resonances of the BPP34C10 protons. These conclusions regarding the geometries of the solution-state superstructures are supported by the solid-state geometries found for these 1 : 1 complexes (*vide infra*).

Vapour diffusion of diisopropyl ether into acetone solutions of [**1·3**][PF$_6$]$_2$, [**1·4**][PF$_6$]$_2$ and [**1·5**][PF$_6$]$_2$ afforded single crystals of their 1 : 1 complexes that were suitable for X-ray crystallography. In all three cases, the dications **3**$^{2+}$, **4**$^{2+}$ and **5**$^{2+}$ are threaded in a centrosymmetric fashion (Figs. 1 and 2) through the middle of the BPP34C10 **1** macrocycle. In both [**1·4**][PF$_6$]$_2$ and [**1·5**][PF$_6$]$_2$, the macrocycles adopt essentially identical conformations with the aromatic OCH$_2$ groups oriented *syn* with respect to each other. The tilts of the N$^+$···N$^+$ vectors of the bipyridinium units relative to the O···O vectors of the hydroquinol rings are *ca.* 26°. This is in marked contrast to the supramolecular structure observed for [**1·3**][PF$_6$]$_2$ where (*a*) the aromatic OCH$_2$ groups display an *anti* geometry with a consequent distortion of the conforma-

Table 3 ^{1}H NMR chemical shift changes[a] ($\Delta\delta$) for the complexes $[\mathbf{1}\cdot\mathbf{3}][\mathrm{PF}_6]_2$, $[\mathbf{1}\cdot\mathbf{4}][\mathrm{PF}_6]_2$ and $[\mathbf{1}\cdot\mathbf{5}][\mathrm{PF}_6]_2$

	Bipy-CH		N^+-substituent CH_2				BPP34C10 **1** protons				
Complex	α	β	α	β	γ	δ	ArH	α	β	γ	δ
$[\mathbf{1}\cdot\mathbf{3}][\mathrm{PF}_6]_2$	−0.34	−0.73	—	—	—	—	−0.39	+0.06	+0.03	+0.10	+0.10
$[\mathbf{1}\cdot\mathbf{4}][\mathrm{PF}_6]_2$	−0.15	−0.32	+0.03	+0.05	—	—	−0.31	−0.19	−0.01	+0.10	+0.10
$[\mathbf{1}\cdot\mathbf{5}][\mathrm{PF}_6]_2$	−0.19	−0.40	0.00	+0.06	+0.14	+0.14	−0.33	−0.18	−0.03	+0.14	+0.14

[a] ^{1}H NMR spectra were recorded at 250 MHz in $\mathrm{CD_3COCD_3}$ using a Bruker AM250 spectrometer. $\Delta\delta = \delta(\text{complex}) - \delta(\text{free})$.

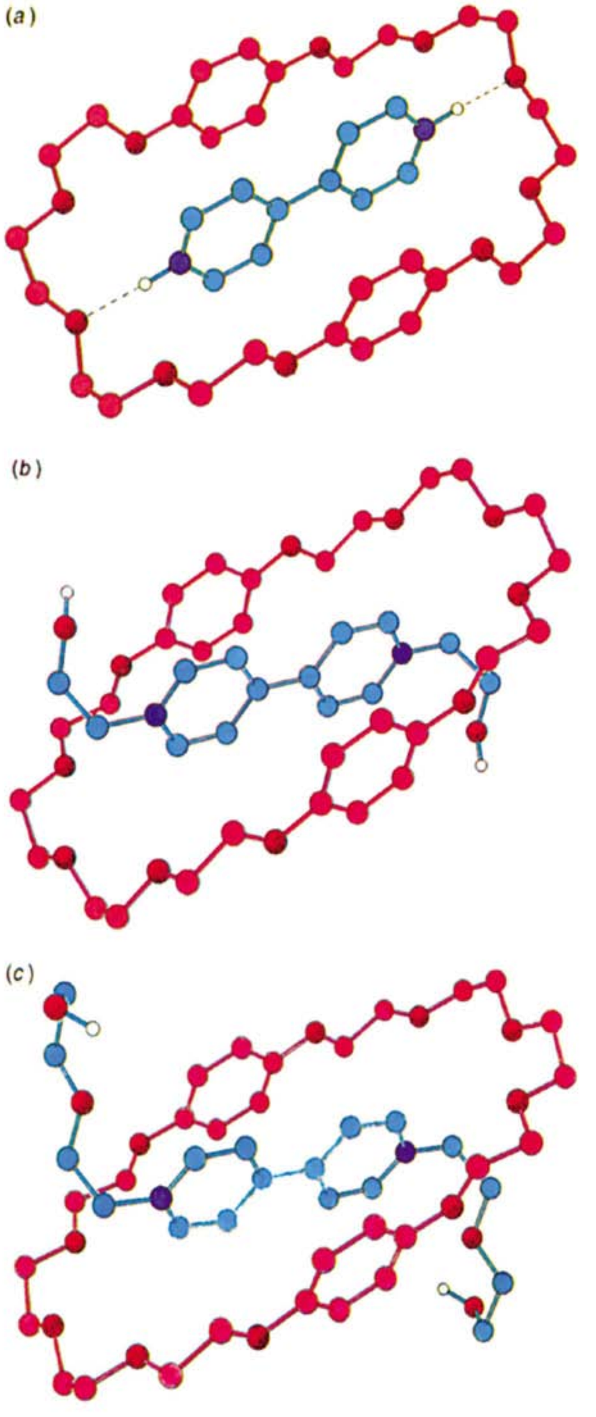

Fig. 2 Ball and stick representations of (*a*) $[\mathbf{1}\cdot\mathbf{3}]^{2+}$, (*b*) $[\mathbf{1}\cdot\mathbf{4}]^{2+}$ and (*c*) $[\mathbf{1}\cdot\mathbf{5}]^{2+}$ in their solid states. The BPP34C10 **1** macrocycles are shaded red with the O atoms hatched dark red and the dications $\mathbf{3}^{2+}$, $\mathbf{4}^{2+}$ and $\mathbf{5}^{2+}$ are shaded blue with N atoms dark blue, O atoms hatched dark red, and NH and OH hydrogen atoms open circles.

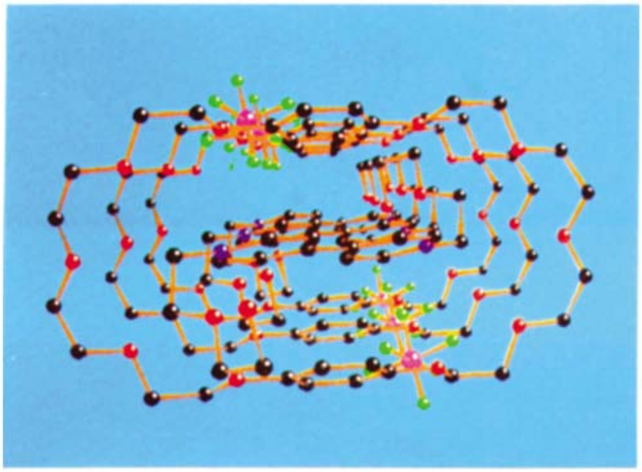

Fig. 3 A view looking down part of one of the infinite channels of BPP34C10 **1** with $\mathbf{5}^{2+}$ dications threaded down through its centre. The $\mathrm{PF_6}^-$ counterions lie within the periphery of the channel. C Atoms are black, O atoms are red, N atoms are blue, P atoms are violet, and F atoms are green.

tions of the polyether chains and (*b*) the $\mathrm{N}^+\cdots\mathrm{N}^+$ vector of the bipyridinium unit aligns itself almost parallel with respect to the O···O vectors of the hydroquinol rings. This arrangement allows the formation of two strong and nearly linear $[\mathrm{N}^+\text{–}\mathrm{H}\cdots\mathrm{O}]$ hydrogen bonds (2.83 Å) to the central oxygen atoms of each polyether linkage. The bipyridinium dication $\mathbf{3}^{2+}$ is thus almost totally encapsulated [Fig. 1(*a*)] within the BPP34C10 **1** receptor site. This host–guest relationship contrasts with the pseudorotaxane-like character of $[\mathbf{1}\cdot\mathbf{4}][\mathrm{PF}_6]_2$ [Fig. 1(*b*)] and $[\mathbf{1}\cdot\mathbf{5}][\mathrm{PF}_6]_2$ [Fig. 1(*c*)]. In all three 1 : 1 complexes, the separations between the mean planes of the π-electron-rich hydroquinol rings and the π-electron-deficient bipyridinium units are *ca.* 3.5 Å. Both $[\mathbf{1}\cdot\mathbf{3}][\mathrm{PF}_6]_2$ and $[\mathbf{1}\cdot\mathbf{5}][\mathrm{PF}_6]_2$ form continuous stacked arrangements of the BPP34C10 **1** macrocycles, creating infinitely long channels (Fig. 3) in the crystallographic *b* directions, though, in $[\mathbf{1}\cdot\mathbf{3}][\mathrm{PF}_6]_2$, the counterions block the free passage through the stack.

The fact that $\mathbf{4}^{2+}$ and $\mathbf{5}^{2+}$ form stable 1 : 1 complexes in which the dications are threaded through the centre of the macrocyclic cavity of **1** in a pseudorotaxane-like manner in both solution and solid states anticipates[8] the next development—*i.e.* the synthesis of rotaxanes¶ and molecular shuttles[9]

¶ After our research in this area had been completed, it came to our attention that the complex $[\mathbf{1}\cdot\mathbf{4}][\mathrm{PF}_6]_2$ has also been isolated and characterised using X-ray crystallography by H. W. Gibson *et al.* at the Virginia Polytechnic Institute and State University. This group have also described the synthesis of a family of viologen-containing polyurethane rotaxanes from bis(*p*-isocyanatophenyl)methane, *N*,*N*′-bis(2-hydroxyethyl)-4-4′bipyridinium bis(hexafluorophosphate) $\mathbf{4}\cdot 2\mathrm{PF}_6$, and bis-*p*-phenylene-34-crown-10 **1**, as well as some polyrotaxane model studies. See Y. X. Shen, P. T. Engen, H. W. Gibson and J. S. Merola, *Abstracts 201 Am. Chem. Soc. National Meeting, Atlanta*, 14–19 April 1991, ORGN 325: H. W. Gibson, P. T. Engen, Y. X. Shen, J. Sze, C. Lim, M. Bheda and C. Wu, *Am. Chem. Soc. Div. Polym. Chem. Polym. Preprints*, 1991, **32(1)**, 423; *Makromol. Chem.*, in the press.

based on dumbell components incorporating bipyridinium units and the macrocyclic component, BPP34C10 **1**—in our synthetic strategy involving self-assembly processes.[10]

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