Encapsulation of 4,4′-bipyridinium cations by two crown ether molecules: formation and structure of [3]pseudorotaxanes†

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Substituted 4,4′-bipyridinium cations (viologens) typically form 1 : 1 complexes with crown ethers. In this paper the formation of trimolecular [3]pseudorotaxanes whereby each viologen coordinates two dibenzo-24-crown-8, DB24C8, host units have been further studied. Because the viologen cations are tightly encapsulated into the cavity of two coordinated DB24C8 molecules the formation of these [3]pseudorotaxanes is very sensitive to the size of the substituents. Short-chain dialkyl- and diallylviologens furnish stable crystalline [3]pseudorotaxanes but closely related benzylviologens fail to form these complexes. While the apparent association constant for the 1 : 1 [2]pseudorotaxane in acetonitrile is significantly lower than that in acetone, a proton NMR study of dimethylviologen in the presence of various amounts of DB24C8 suggests that in acetonitrile solution the [3]pseudorotaxane stoichiometry is preserved. X-Ray crystal structure characterisation of [3]pseudorotaxanes revealed that the two N-alkylated pyridinium rings of the viologen adopt a twisted conformation and thread two crown ether molecules. The structure is possibly stabilised by hydrogen bonding and ion–dipole interactions.

Introduction

The progress in the field of artificial molecular machinery is maintained by our ability to build complex molecular systems using recognition and binding of the molecular components.[1] Both [*n*]rotaxanes and closely related [*n*]pseudorotaxanes comprising macrocyles and ammonium cations can be prepared since the affinity of the components is sufficient to drive a molecular self-assembly process.[2] Typically, the ether chains of a crown ether readily accommodate positively charged secondary, or tertiary, ammonium cations. For example, dibenzylammonium axles have been shown to bind dibenzo-24-crown-8, **2**, thus leading to [2]pseudorotaxanes. When several cationic centres are joined together each centre can bind one molecule of **2** in such a fashion that the overall cation : crown ratio is unity.[2c,3] Doubly positively charged 4,4′-bipyridinium dications (viologens, **3**) and structurally related 1,2-bis(pyridinium)ethane dications are also known to form 1 : 1 complexes with the crown ether **2** and its derivatives whereby the two ether chains of **2** bind to two positively charged pyridinium rings of **3** thus leading to an overall cation : crown ratio of 2.[4] Recent publications suggest, however, that viologens can potentially accommodate two macrocyclic moieties such as cyclodextrins[5a,b] and polycyclic cryptands forming [3]pseudorotaxane-like complexes[4e,6] or even a non-rotaxane 2 : 1 complex whereby the dication is tightly surrounded by two macrocylic molecules.[5c] These findings would further evoke a possibility of formation of [3]pseudorotaxanes, **1**, with a cation : crown ratio of **1** (Chart 1). This cation : crown ratio is also achieved when a crown ether coordinates bipyridinium monocations under high concentration conditions.[2f]

The affinity of crown ether hosts towards viologen guests depends on a number of parameters and can become a factor limiting their ability to form [3]pseudorotaxanes. In some cases the binding strength can be increased by the introduction of electrically charged groups in crown ethers.[2i] Although the formation of viologen-based [3]pseudorotaxanes in solution has previously been ruled out,[6e] it was interesting to look into possible multiple interactions between various doubly positively charged viologen cations, **3**, and electrically neutral crown ethers, such as **2**. It has previously been shown[4c] that 1 : 1 complexes between the crown ether **2** and certain viologens **3** (R = substituted benzyl) exist in solution and can be isolated as crystalline materials. Additionally, a recent detailed study by Stoddart, Kuzmic and co-workers demonstrated that in acetone[4e] dimethylviologen, **3a**, (R = Me) undergoes stepwise dissociation and forms host–guest complexes with **2** characterised by both 1 : 1 and 2 : 1 stoichiometries. This report prompts us to describe our own findings in this area.

We not only sought further direct structural evidence of [3]pseudorotaxane formation but we were also intrigued by the fact that, as had been earlier established by Gibson and co-workers, there were indications of **3a** coordinating two molecules of **2** in the solid state. Similar interactions have also been observed when two bicyclic cryptand species or, alternatively, a large cylindrical tricycle were involved in coordination with viologens.[6]

In this paper we present further NMR and UV/vis evidence suggesting that dialkylviologens, unlike benzylviologens, form 2 : 1 host : guest [3]pseudorotaxane complexes, **1**, in the presence of excess dibenzo-24-crown-8 in acetonitrile. Moreover, crystal structures of the new [3]pseudorotaxanes

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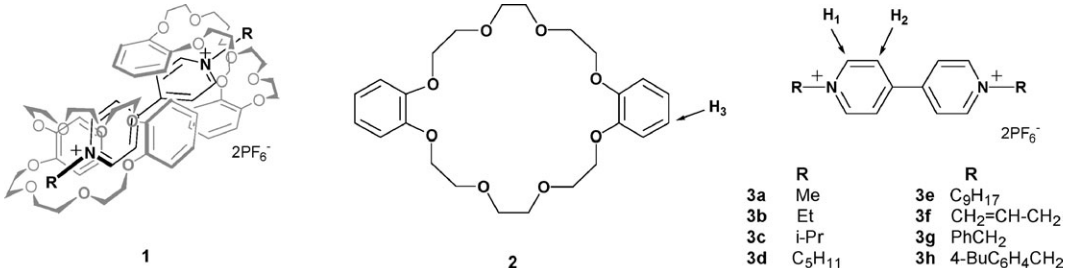


Chart 1 [3]Pseudorotaxanes, **1**, and their components: crown ether, **2**, and viologens, **3**.

clearly demonstrate that each positively charged pyridinium ring of viologen can fully accommodate a crown ether molecule. In particular, crystalline [3]pseudorotaxanes **1b** and **1e** contain two crown ether molecules which are structurally equivalent and, possibly, equally strongly attached. We note that these complexes are among the first known [3]pseudorotaxanes formed between viologens and monocyclic crown ethers.

Results and discussion

When hexafluorophosphate of the dimethylviologen guest, **3a**, and the crown ether host, **2**, were mixed in acetonitrile a bright yellow solution was formed indicating possible interaction of the π-electrons of the macrocylic component **2** with the LUMO of the viologen. The absorption spectra of **3a** in the presence of **2** were further studied to elucidate the stochiometry of the [*n*]pseudorotaxane complexes in solution. When the spectra of solutions containing 2.0 mM of **3a** and various amounts of **2** were recorded (Fig. 1a) it transpired that the mixtures containing up to one equivalent of the crown ether **2** absorbed at 393 nm but the solutions having more of **2** absorbed at 387 nm. Moreover, careful comparison of a calculated Job plot (solid line, Fig. 1b) with the experimental datapoints confirmed that the observed maximum at 0.5 was not symmetrical. The absorption of solutions containing excess **2** deviates from the calculated values. These findings might suggest that in acetonitrile the viologen **3a** possibly forms both [2]- and [3]pseudorotaxanes with the crown ether **2** and are in very good agreement with very recent results in acetone.[4e]

The equilibrium association constants, K_1, of the nominal [2]pseudorotaxanes **4** (Scheme 1) formed by the viologens **3** and the crown ether **2** were measured by using a Benesi–Hildebrand type dilution method.[2i,7] The measurements were carried out in the concentration range 1.67–5.0 mM. The equilibrium was monitored by UV-visible spectroscopy and the results are summarised in Table 1. In the case of **3a** the position of the absorption maximum, 393 nm, did not change with dilution indicating the presence of predominantly [2]pseudorotaxanes species. However, the colour changes were considerably less pronounced and the absorption peaks were not clearly observed for the viologens **3b–3h**. The data were treated assuming that the contribution of [3]pseudorotaxanes, **1**, under these conditions was negligible. This is quite a reasonable hypothesis taking into account the concentration range and relatively low expected values of *K*.[4c,2e,7b,8a]

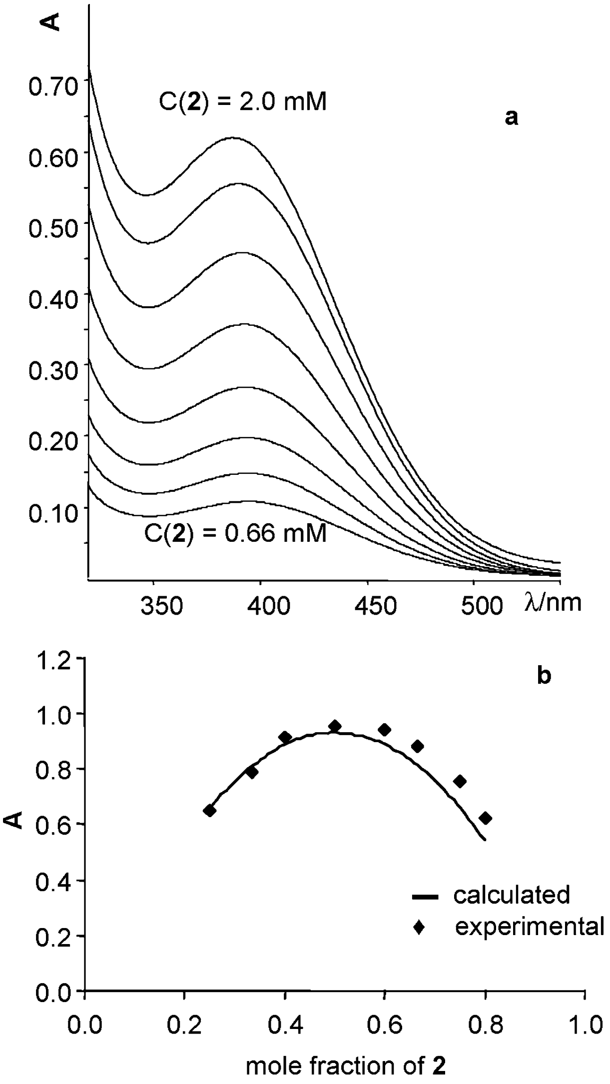
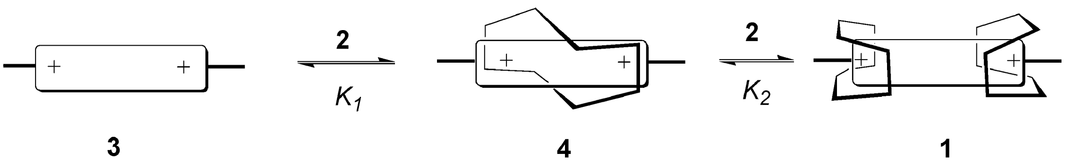


Fig. 1 (a) Absorption spectra of viologen **3a** (acetonitrile, 298 K, C = 2.0 mM) in the presence of **2** (C = 0.66–8.0 mM); (b) calculated Job plot for total C = 10.0 mM and the experimental data points, ◆, showing a positive divergence at and above 0.5.

The results can be compared to the previously published data on the complexation of viologens **3a** and **3g** with the crown ether **2**.[2,4c,6e] We found that the equilibrium constant for **3a** in acetonitrile, K_1 = 350 M^{-1} is significantly lower than that in acetone, K_1 = 1600 M^{-1}. The latter value is in reasonable agreement with the recent findings in acetone.[4e] We believe that the dilution method is more accurate than the single-point NMR technique for the reasons discussed later in the text. It is, however, noted that association constant



Scheme 1 Cartoon representation of stepwise formation of [2]- and [3]pseudorotaxanes incorporating viologens **3** and the crown ether **2**.

Table 1 Association equilibrium constants,[a] K_1, and proton NMR CIS values, δ(H_2)

Viologen	Complex	R	K_1, M^{-1}	δ(H_2), ppm[b]
3a	**4a**	Me	350 ± 50[cd]	−0.98
3b	**4b**	Et	90 ± 20	−0.11
3c	**4c**	*i*-Pr	40 ± 10	0.01
3d	**4d**	*n*-C_5H_{11}	120 ± 20	−0.06
3e	**4e**	*n*-C_9H_{19}	250 ± 50	−0.03
3f	**4f**	$CH_2{=}CH{-}CH_2$	100 ± 20	−0.04
3g	**4g**	Bn	60 ± 10[e]	0.01
3h	**4h**	*n*-$BuC_6H_4CH_2$	160 ± 30	−0.03

[a] Dilution method, acetonitrile, 298 K, C(**3**) = C(**2**) = 1.67–5.00 mM. [b] δ = δ(pseudorotaxane) − δ(free viologen), acetonitrile, 298 K, C(**3**) = 20 mM, C(**2**) = 40 mM. [c] K_1 = 312 M^{-1}, acetone, 295 K, C(**3**) = C(**2**) = 2.00 mM, single-point NMR method.[6e] [d] K_1 = 1600 ± 200 M^{-1}, acetone, 295 K, dilution method. [e] K_1 = 82 ± 16 M^{-1}.[4b]

K_1 = 60 ± 10 M^{-1} for the dibenzylviologen, **3g**, is in good agreement with the previously reported value for **3g** at 298 K, K = 82 ± 16 M^{-1} as determined by isothermal titration calorimetry (ITC) measurements.[4c] No apparent association could be demonstrated by NMR at ambient temperature due to very poor binding of dibenzylviologens and **2** in acetonitrile.

Interestingly, the equilibrium constants K_1 for dimethylviologen, **3a**, and dinonylviologen, **3e**, are relatively high when compared to the rest of the series, in particular with diisopropylviologen, **3c**, or dibenzylviologen, **3g**. Apparently, the affinity of the crown ether **2** to viologens is controlled by a complex interplay of several factors such as steric size of the substituents and polarity of the medium.

Having obtained initial UV-visible spectroscopic evidences of the formation of [3]pseudorotaxane complex **1a** in acetonitrile in a concentration range of 1.67–5.0 mM we studied this equilibrium by proton NMR spectroscopy. NMR experiments were run with solutions having a concentration of **1a** up to 20 mM. Moreover, since the solubility of the crown ether **2** in acetonitrile at 298 K is close to 0.3 M it was interesting to follow the equilibrium at very high host : guest ratios. It is evident that in solution containing the viologen **3a** and crown ether **2** the very significant upfield chemically induced shifts (CIS) indicate the presence of [*n*]pseudorotaxane complexes (Fig. 2a). However, when a proton NMR study was attempted with viologens **3b–g**, no further reliable information on the relationship between the viologen binding sites and the macrocycle during the complexation at room temperature was obtained due to low CIS (Table 1). It can be seen from Table 1, however, that the values of CIS poorly correlate with the association constants K_1. Consequently, the formation of [*n*]pseudorotaxanes, **1** and **4**, can not be ruled out for **3b–g**.

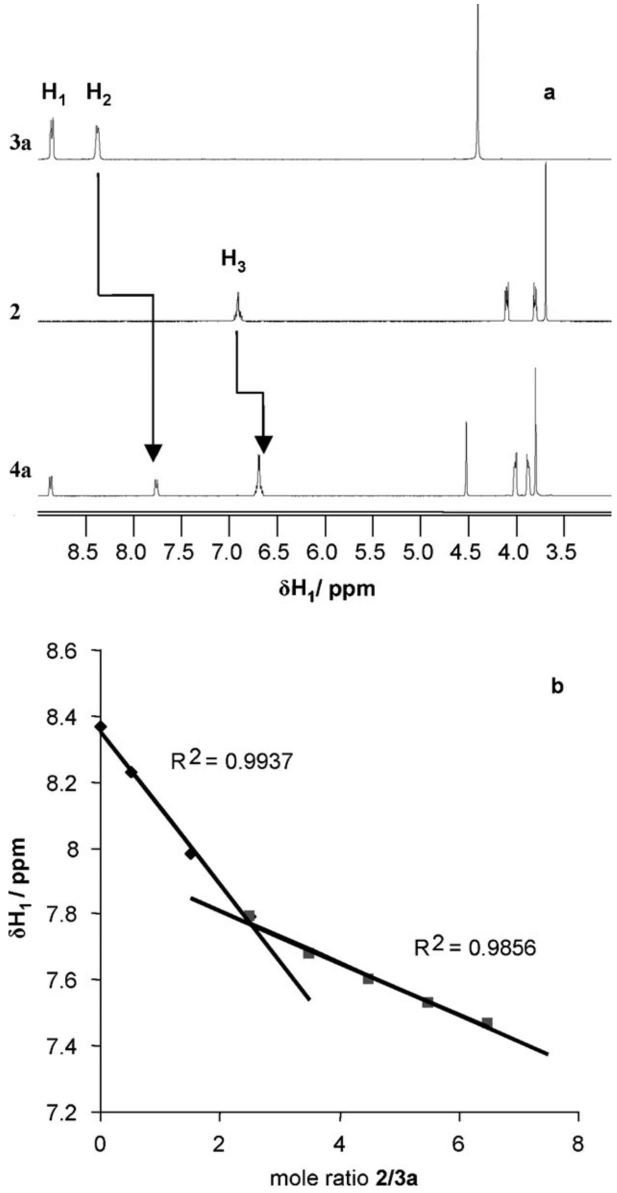


Fig. 2 (a) Partial NMR spectra of viologen **3a**, crown **2** and their 1 : 1 complex **4a**, C(**3a**) = 20 mM; (b) a mole ratio plot for **3a** and **2** in acetonitrile, C(**3a**) = 2 mM.

More detailed proton NMR characterisation of the individual **2** and **3a** and their mixtures in acetonitrile revealed that, as expected, the complexes and the individual components undergo fast exchange on the NMR timescale. Initial studies were done with 2.0 mM solutions of **3a** which was similar to the UV-visible spectroscopy concentration range, 1.67–5.00 mM. The mole ratio plot shown in Fig. 2b demonstrates that in acetonitrile, like in acetone,[4e] the stoichiometry of the complex is 2 : 1 as one would expect for a [3]pseudorotaxane. This finding is in good agreement with the observations made by UV-visible spectroscopy. On the basis of the NMR data the average extent of complexation, p, and observed association constants, $K_1 = p/[(1 - p)(C(\mathbf{2}) - C(\mathbf{3a})p)]$, were calculated for $C(\mathbf{3a}) = 2.0$ mM. The association constant value, $K_1 = 132 \pm 10\ \mathrm{M}^{-1}$ determined in acetonitrile by NMR spectroscopy is significantly lower than that determined by UV-visible spectroscopy, $K_1 = 350\ \mathrm{M}^{-1}$. This persistent discrepancy between the dilution method at constant host : guest ratio 1 : 1 and the single-point NMR can be attributed, in our view, to an underestimation of the degree of complexation, p, when using extrapolated chemical shift values for fully complexed species.[8b] Moreover, a Scatchard plot made for the **2–3a** system is not linear which indicates that there is a second complexation stage involving, presumably, [3]pseudorotaxane, **1**.[6,9] Further NMR studies were done with solutions having concentration of the host **3a** 20.0 mM and up to 260 mM of the crown ether **2**. In this concentration range the calculated K_1 is only $50 \pm 5\ \mathrm{M}^{-1}$, and a mole ratio plot clearly demonstrates that a 2 : 1 host : guest stoichiometry is present. Significant concentration dependence of the observed association constant, K_1, also indicates the presence of 2 : 1 complexes in solution.[4e]

When acetonitrile solution of a 2 : 1 mixture of colourless **2** and **3a** was evaporated bright yellow crystals were formed. However when evaporation of the crown ether **2** and viologens **3b–g** mixtures were carried out the formation of yellow crystalline materials was observed only for straight-chain dialkylviologens **3b–3d**, and diallylviologen **3f** while in other cases the precipitation of individual components, **2** and **3**, or formation of a glassy solid was observed. The resulting crystals, the [3]pseudorotaxane complexes, **1**, were analysed and studied by X-ray diffractometry. An X-ray diffraction study of the diisopropyl derivative, **1c**, revealed that the isopropyl groups exhibit substantial disorder so that precise determination of the molecular parameters is not possible. The metrical parameters of the remaining [3]pseudorotaxanes **1a**, **1b**, **1d**, **1f** are summarized in Table 2.

The structures of the [3]pseudorotaxanes **1a**, **1b**, **1d** and **1f** appear as Fig. 3. In **1b** and **1f** the viologen dication is situated on a twofold axis and accommodates two symmetry-equivalent crown ether molecules. Unlike in the [2]pseudorotaxanes formed by viologens with other crown ethers[2] and the complexes of dimethylviologen with cryptands,[6] the viologen moiety in **1b** is not flat so that the pyridinium rings adopt a dihedral angle of about 56 degrees. Since the pyridinium ring centroids and the catechol centroids are separated by at least 3.9 Å it is unlikely that any significant π–π-stacking interaction can be expected to contribute to the formation of this complex. Instead, some interaction can be observed of the α-pyridinium hydrogens H_1 of the guest ($D_{(H\cdots O)} = 2.24$ Å) and CH_2 of the guest ($D_{(H\cdots O)} = 2.56$–2.97 Å) with the ether oxygen atoms of the host. Additionally, the structure is possibly stabilised by ion–dipole interaction between the viologen cation and the highly polar ether chains.

The molecular structures of [3]pseudorotaxanes **1a**, **1d** and **1f** replicate the main features of **1b** (Table 2). The viologen moiety in **1** is not flat so that the pyridine rings adopt a dihedral angle of 44–55 degrees. The catechol-pyridinium centroid separation is often in excess of 4 Å and the catechol-catechol interplanar angles are at least 40 degrees. As in **1b** interactions between the α-pyridinium hydrogen atoms and oxygen atoms from the surrounding ether are found (see Table 2). It can clearly be seen that the spatial arrangement of the molecular components in all four [3]pseudorotaxanes, **1**, leads to a high degree of steric crowdedness which is possibly the reason why these high-coordinated molecular complexes are not stable if a bulky substituent is attached to the viologen moiety. It is unlikely, therefore, that an additional bulky group can be further accommodated without considerable distortion of the geometry. Accordingly all attempts to crystallise possible [3]pseudorotaxanes formed by N-benzyl and N-aromatic viologens failed. Even the presence of a long-chain alkyl substituent at the viologen, *e.g.* *n*-nonyl in **3e**, is sufficient to prevent the formation of a [3]pseudorotaxane.

In the structure of new [3]pseudorotaxanes, **1**, the viologen dication is effectively encapsulated into a case formed by two folded crown ether host molecules facing each other in such a fashion that their aromatic catechol moieties are moved into the folds provided by ether chains. This situation of complete encapsulation is illustrated even more clearly in the space-filling representation (Fig. 3, bottom panels) of the X-ray crystal structure of **1b** and **1d**. It is obvious that the presence of the two host molecules causes a steric hindrance of the molecular framework such that the catechol aromatic moieties of **2** deviate through about 20° away from the planes of pyridinium rings adopting an interplanar angle of about 39–41 degrees. This hindrance is also evident when considering that the ether chains of **2** are folded around nitrogen atoms of the host **3** leaving very little room for the N-alkyl substituents. In **1d** these two alkyls are not equivalent and they clearly protrude outside of the crown ether cavities adopting slightly different conformations. These steric constraints and related energy costs are the most likely reasons why the formation of [3]pseudorotaxanes incorporating benzylviologens is not observed.[4]

Table 2 Interplanar angles, and non-covalent interaction distances for [3]pseudorotaxanes, **1**

Parameter	1a	1b	1d	1f
Bipyridinium interplanar angle (°)	55.1	56.5	49.5	44.0
Catechol interpanal angle (°)	44.8	41.5	38.7	40.0
Catechol-pyridinuim centroid distance (Å)	3.76; 4.32	3.89; 4.42	4.23; 4.33	4.23; 4.29
Shortest hydrogen-bond distance, CH···O (Å)	2.13	2.24	2.14	2.27
Hydrogen-bond angle C–H···O (°)	161	167	166	154

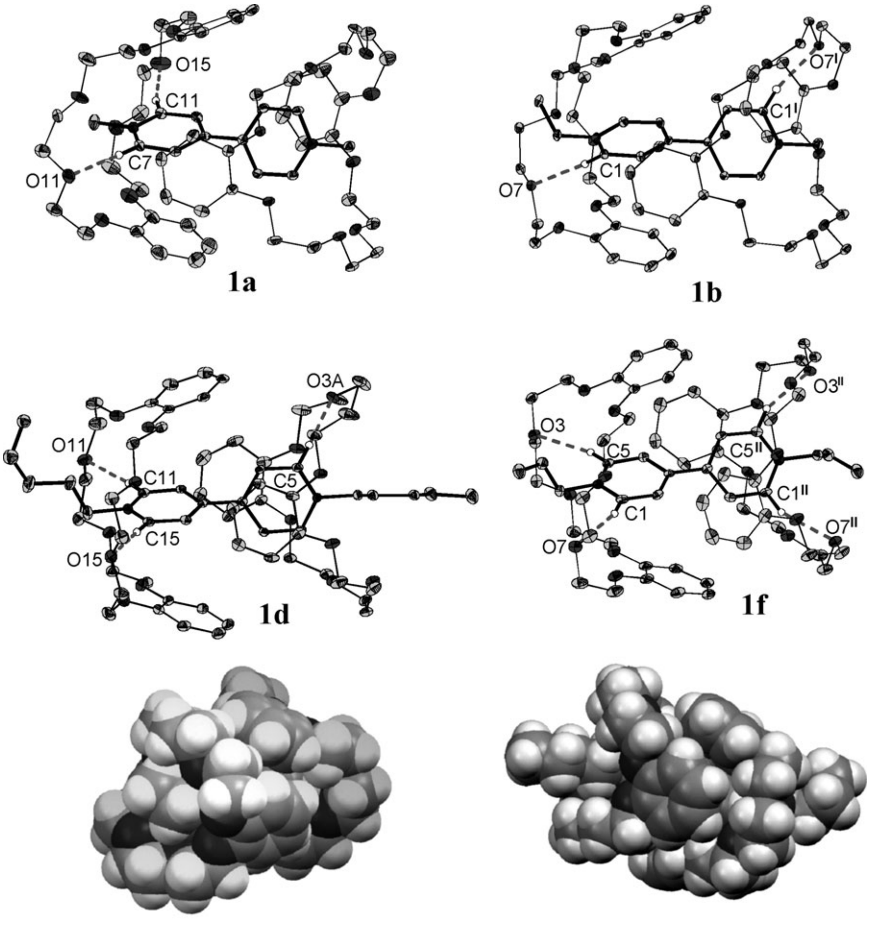


Fig. 3 Top: molecular structures of the [3]pseudorotaxanes (anions and solvent molecules have been omitted for clarity; shown are possible hydrogen-bonding close contacts): in [3]pseudorotaxanes **1a**, **1d** the two crown ether molecules are non-equivalent; the crown ether molecules are symmetry-equivalent in **1b** and **1f** (symmetry operations:$^{\text{I}}$ $2 - x, y, \frac{1}{2} - z$; $^{\text{II}}$: $-x, y, \frac{1}{2} - z$); Bottom: *mercury* space-filling representation shows that in **1b** the viologen core is fully encapsulated by the crown ether molecules; in **1d** the alkyl chains protrude outside.

Conclusions

New [3]pseudorotaxanes (**1a** to **1d** and **1f**) formed by dialkylviologens and a single-macrocycle crown ether, dibenzo-24-crown-8, have been prepared and characterised by X-ray crystallography. While trimolecular complexes of the dimethylviologen guest, **3a**, with macrocyclic hosts have previously been described we here report additional spectroscopic evidences of their existence in acetonitrile solution in full agreement with a very recent study of this system in acetone.[4e] For the rest of viologens, **3b** to **3h**, due to relatively insignificant changes in NMR and UV spectra of [*n*]pseudorotaxanes it was not possible to ascertain whether [3]pseudorotaxane coordination was present in solution.

In the solid state the structure of [3]pseudorotaxanes is stabilised by hydrogen bonding and probably to a lesser extent, by π–π-interactions. The encapsulation of the dialkylviologen moiety by two crown ether molecules leads to highly overcrowded complexes and their formation is not observed with viologen bearing aromatic, benzylic or long-chain substituents. It is more likely, however, that this coordination mode will become more feasible should any additional strong interactions, *e.g.* electrostatic forces, between viologen and crown ether moieties be introduced. It will also be challenging to prepare structurally analogous [3]rotaxanes by permanently locking the crown ether fragments in their positions.

Experimental section

Melting points were estimated using a Gallenkamp melting point device and were not corrected. Reagents and solvents were purchased from commercial suppliers and used as received. NMR spectra were recorded using Varian Inova spectrometers in acetonitrile at 298 K.

Association constants K_a were measured by using a dilution method monitored by UV-visible spectroscopy as recently described elsewhere.[2i,7]

Crystal data were collected using a Bruker SMART APEX CCD area detector diffractometer. A full sphere of the reciprocal space was scanned by phi-omega scans. Pseudo-empirical absorption correction based on redundant reflections was performed by the program SADABS.[10a] The structure was solved by direct methods using SHELXS-97 and refined by full matrix least-squares on F^2 for all data using SHELXL-97.[10b,c]

Hydrogen atoms were added at calculated positions and refined using a riding model. Their isotropic temperature factors were fixed to 1.2 times (1.5 times for methyl groups) the equivalent isotropic displacement parameters of the carbon atom the H-atom is attached to. Hydrogen atoms of water molecules could not be located. Anisotropic temperature factors were used for all non-disordered non-hydrogen atoms. In **1f** the Platon SQUEEZE[10d] procedure was used to treat regions with disordered solvents which could not be modeled in terms of atomic sites. Crystallographic data for this paper can be found in the ESI,† CCDC 721642 (**1b**), 721643 (**1f**), 721644 (**1a**) and 721645 (**1d**).

Viologen salts3a–h were prepared from the corresponding viologen halides by metathesis with KP_6 in aqueous solution.[2i, 9]

[3]Pseudorotaxane1a: **3a** (0.024 g, 0.05 mmol) and **2** (0.045 g, 0.1 mmol) were dissolved in acetonitrile (2 cm^3) and the solution was slowly concentrated in air to give **1a** as a yellow solid: mp 176 °C (dec); δ_H (CD_3CN, 300 MHz) 8.87 (d, 4H, J = 7.0 Hz), 7.40 (d, 4H, J = 7.0 Hz), 6.76 (m, 16H), 4.57 (s, 6H), 4.04 (m, 16H), 3.87 (m, 16H), 3.76 (s, 16H); found: C, 51.80; H, 5.62; N, 2.00. Calc. for $(C_{60}H_{78}F_{12}N_2O_{16}P_2)\cdot 0.6H_2O$: C, 51.70; H, 5.86; N, 2.04. **Crystal data**. $C_{60}H_{79.2}N_2O_{16.6}F_{12}P_2$, M = 1382.44 monoclinic, a = 16.3602(17) Å, b = 13.2368(14) Å, c = 29.792(3) Å, $\alpha = \gamma = 90°$, β = 90.006(2)°, U = 6451.6(12) $Å^3$, T = 100 K, space group $P2_1/c$, Z = 4, independent reflections 11061, R_{int} = 0.0390, R indices (all data) R_1 = 0.0728, wR_2 = 0.1844.

[3]Pseudorotaxane1b: **3b** (0.025 g, 0.05 mmol) and **2** (0.045 g, 0.1 mmol) were treated as above to give **1b** as a yellow solid: mp 128 °C (dec); δ_H (CD_3CN, 300 MHz) 8.91 (d, 4H, J = 7.0 Hz), 8.27 (d, 4H, J = 7.0 Hz), 6.87 (m, 8H), 4.67 (q, 4H, J = 7.5 Hz), 4.07 (m, 16H), 3.80 (m, 16H), 3.70 (s, 16H), 1.64 (t, 6H, J = 7.5 Hz); found: C, 52.74; H, 5.85; N, 1.93. Calc. for $(C_{62}H_{82}F_{12}N_2O_{16}P_2)\cdot 0.58H_2O$: C, 52.74; H, 5.94; N, 1.98. **Crystal data**. $C_{62}H_{83.16}F_{12}N_2O_{16.58}$, M = 1411.92, orthorhombic, a = 13.7147(17) Å, b = 29.563(4) Å, c = 16.500(2) Å, U = 6689.8(14) $Å^3$, T = 100 K, space group $Pbcn$, Z = 4, independent reflections 8182, R_{int} = 0.0245, R indices (all data) R_1 = 0.0733, wR_2 = 0.2004

[3]Pseudorotaxane1d: **3d** (0.029 g, 0.05 mmol) and **2** (0.045 g, 0.1 mmol) were treated as above to give **1d** as a yellow solid: mp 82–83 °C (dec); δ_H (CD_3CN, 300 MHz) 8.95 (d, 4H, J = 6.0 Hz), 8.32 (br, 4H), 6.90 (m, 8H), 4.62 (t, 4H, J = 7.5 Hz), 4.10 (m, 16H), 3.82 (m, 16H), 3.70 (s, 16H), 2.04 (m, 4H), 1.40 (m, 8H), 0.95 (t, 6H, J = 7 Hz); found: C, 53.93; H, 6.40; N, 1.87. Calc. for $(C_{68}H_{94}F_{12}N_2O_{16}P_2)\cdot 2H_2O$: C, 53.68; H, 6.49; N, 1.84. **Crystal data**. $C_{68}H_{98}F_{12}N_2O_{18}P_2$, M = 1521.42, monoclinic, a = 16.5359(10) Å, b = 14.4572(9) Å, c = 31.097(2) Å, $\alpha = \gamma = 90°$, β = 93.492(1)°, U = 7420.4(8) $Å^3$, T = 100 K, space group $P2_1/c$, Z = 4, independent reflections 6741, R_{int} = 0.0391, R indices (all data) R_1 = 0.0663, wR_2 = 0.1287.

[3]Pseudorotaxane1f: **3f** (0.026 g, 0.05 mmol) and **2** (0.045 g, 0.1 mmol) were treated as above to give **1f** as a yellow solid: mp 134 °C (dec); δ_H (CD_3CN, 300 MHz) 8.92 (d, 4H, J = 7.0 Hz), 8.35 (d, 4H, J = 7.0 Hz), 6.91 (m, 8H), 6.2 (m, 2H), 5.6 (m, 2H), 5.29 (d, 4H, J = 7 Hz), 4.10 (m, 16H), 3.83 (m, 16H), 3.72 (s, 16H); found: C, 55.0; H, 6.10; N, 1.91. Calc. for $(C_{64}H_{82}F_{12}N_2O_{16}P_2)\cdot 2(CH_3)_2CO\cdot 1/4H_2O\cdot 1/4CH_3CN$: C, 54.41; H, 6.17; N, 2.03. **Crystal data**. $C_{70.5}H_{95.25}N_{2.25}O_{18.25}F_{12}P_2$, M = 1556.18, monoclinic, a = 14.1988(10) Å, b = 32.459(2) Å, c = 16.0338(11) Å, U = 7329.6(9) $Å^3$, T = 100 K, space group $C2/c$, Z = 4, $\alpha = \gamma = 90°$, β = 97.301(1)°, independent reflections 4530, R_{int} = 0.0342, R indices (all data) R_1 = 0.0665, wR_2 = 0.1373.

Notes and references

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