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FEATURE ARTICLE

The genesis of a new range of interlocked molecules†

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Secondary dialkylammonium ions self-assemble with suitably sized macrocyclic polyethers, such as the well-known dibenzo-24-crown-8 and bis-*p*-phenylene-34-crown-10, into pseudorotaxane superstructures in (a) solution, (b) the solid state and (c) the 'gas phase'.

Preamble

Self-assembly,[1] as it is being applied now to wholly organic systems,[2] is proving to be an important technique for the construction[3] of large molecular assemblies and supramolecular arrays. The self-assembly paradigm relies upon the mutual recognition that exists between complementary molecules and ions through noncovalent bonding interactions. Adding to the repertoire of the known complementary molecules and ions affords the (supramolecular) chemist a greater choice in the number of different 'building blocks', or modules, with which to assemble increasingly more complex nanoscopic materials. Thus, the identification of new systems which self-assemble spontaneously into supramolecular arrays[4] of predetermined geometries is an important challenge[5] in contemporary chemistry. Ideally, these matching components should be simple in their constitutions, such that conventional chemical synthesis permits their incorporation into readily-attainable molecules which are then capable of assembling into supramolecular arrays and/or molecular assemblies.[6]

A useful method of studying noncovalent bonding interactions between matching components at a fundamental level and so explore their potential as building blocks in the self-assembly of supramolecular arrays is to utilise these weak interactions in the synthesis of interlocked molecules and entwined and entangled supermolecules.[7] A number of different types of interlocked molecules have been prepared based on the mutual recognition between matching components. These molecules include interlocked rings—the so-called catenanes—and rings trapped on the spindles of dumbbell-shaped components—the so-called rotaxanes (Fig. 1). Many examples of these architypical interlocked molecules have been reported over the last decade or so, particulary after the concept of self-assembly, as a useful synthetic paradigm for constructing chemical systems, became widely accepted. The most effective syntheses have relied upon template-directed procedures, most notably those utilising the association between (a) transition metal ions and cyclic ligands,[8] (b) amides and large ring lactams,[9] (c) cyclodextrins and included chains,[10] and (d) π-electron-deficient bipyridinium dications and π-electron-rich hydroquinone derivatives.[11] These matching components have not only been employed in the synthesis of catenanes and rotaxanes, but they have also led to the preparation of diverse supermolecules such as double helices,[12] grids,[13] knots[14] and mosaics.[15] Against this background, the question which we asked ourselves was this one—could a new, simple self-assembling system be uncovered—possessing a pseudorotaxane‡ architecture [Fig. 1(*c*)]—which would ultimately lead to the synthesis of a further range of interlocked molecular compounds with the structures of catenanes and rotaxanes?

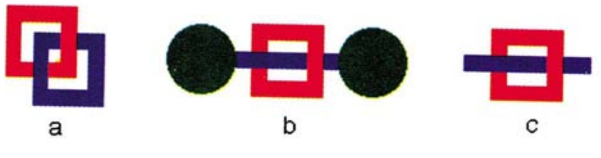


Fig. 1 Cartoon representations of (*a*) a [2]catenane, (*b*) a [2]rotaxane and (*c*) a [2]pseudorotaxane

The answer came from re-investigating one of the oldest[16] and most studied[17] supramolecular systems—the interaction between substituted ammonium ions and macrocyclic polyethers. These organic complexes are usually stabilised by the additive effects of multiple primary [N–H···O] hydrogen bonds and other ion–dipole interactions. Most of the complexes studied to date[18] have involved the interaction between primary alkylammonium ions (RNH_3^+) with macrocyclic polyethers which have been 18-crown-6 (**18C6**) and its derivatives since the configuration and conformation associated with the D_{3d} symmetric **18C6** structure are almost perfectly preorganised[19] for strong [N–H···O] hydrogen bonding interactions to occur with the RNH_3^+ ion. Additionally, the macrocycle is suitably proportioned to allow the NH_3^+ centre to be inserted quite deeply inside the cavity of the crown ether, thus maximising the ion–dipole interactions.[20]

Relatively little is known about the binding of secondary dialkylammonium ions with macrocyclic polyethers. A two-point [N–H···O] hydrogen-bonding motif is believed[21] to be discouraged by unfavourable steric interactions between **18C6** derivatives and the alkyl groups of the cation. As a result, secondary dialkylammonium ions have been shown to be suited to face-to-face association with crown ether derivatives *smaller* than **18C6**. In particular, 12-crown-4 derivatives have been found[22] to be effective receptors. By contrast, one might ask oneself—what would be the effect of enlarging the receptor to a ring size larger than **18C6**? Since RNH_3^+ ions prefer to bind **18C6** derivatives by penetrating deeply[20] into the cavity of the crown ether, then so too should $R_2NH_2^+$ ions (Fig. 2). The limitation for an $R_2NH_2^+$ ion to penetrate through the cavity of the ring is that the ring must be suitably sized such that one of the alkyl groups (R) at least can thread its way through the centre of the ring. The minimum number of atoms required in a ring to allow such a threading to occur is believed[23] to be about 24. However, research on the binding of NH_4^+ and RNH_3^+ ions with macrocyclic polyethers of this size has been limited,[24,25] and—prior to our investigations— few X-ray crystal structures of complexes involving crown ethers constituted by 24 ring atoms or more and $R–NH_3^+$ ions had been reported.[26,27] Nonetheless, one particular solid state superstructure is significant and was encouraging to us. Bradshaw and co-workers[27] had reported the superstructure formed between benzylammonium perchlorate and a furan dicarbonyl derivative of 24-crown-8 (**24C8**). In the 1 : 1 complex, the NH_3^+ centre of the benzylammonium cation nests within the polyether macrocycle such that two [N–H···O] hydrogen bonds are formed to the crown ether while the remaining NH_3^+ hydrogen atom is involved in a hydrogen bond with a ClO_4^- counterion located on the opposite face of the **24C8** derivative. Conceptually, we might consider replacing this hydrogen atom by an alkyl group and, in so doing, we would create a secondary dialkylammonium ion which is threaded through the centre of the **24C8** derivative with a pseudorotaxane-like geometry and stabilised by two-point [N–H···O] hydrogen bonds. Such a system would satisfy the goal we set ourselves at the outset of this research programme.

Recently, we have reported[28,29] that this proposition does indeed hold true to form in the event. Macrocyclic polyethers, such as dibenzo-24-crown-8 (**DB24C8**) and bis-*p*-phenylene-34-crown-10 (**BPP34C10**), do form complexes with $R_2NH_2^+$ ions in such a manner that a pseudorotaxane-like geometry characterises them. In this review, we will present the evidence we have accrued to date which suggests that this simple self-assembling system operates to produce supramolecular arrays in the solid state, in solution, and in the 'gas phase'.

The new results and their significance

We have been very fortunate in this new line of research to have obtained a number of crystalline complexes which have proved to be suitable for X-ray crystallography. In essence, this project has been structurally driven. So far, each superstructure that has been unravelled has revealed the subtle differences which come about in the geometries of the complexes upon modification of the constitution of either the crown ether or the dialkylammonium ion components. Some remarkable superstructures have been uncovered. Here, we try to present in a progressive and logical manner the developments which have emerged from studying the stoichiometries and geometries of these complexes.

1 : 1 Complexes

Preliminary molecular modelling studies[28] on the superstructures resulting from secondary dialkylammonium ions threading through crown ether rings revealed that commercially-available **DB24C8** was suitably-sized and preorganised to achieve stabilising interactions with simple salts such as dibenzylammonium (**1**$^+$) and dibutylammonium (**2**$^+$) hexafluorophosphates. We have obtained[28] solid state structures for both of these 1 : 1 complexes. Co-crystallising **1**·PF_6 with **DB24C8** results in a crystal in which two independent complexes (**A** and **B**) exist in the unit cell (Fig. 3). Although these two complexes both have the geometry of pseudorotaxanes, they differ particularly in the oxygen atoms utilised in the hydrogen bonding interactions. In both complexes, stabilisation is brought about by two [N–H···O] and one [C–H···O] hydrogen bonds involving, as donors, both the hydrogen atoms of the NH_2^+ centre and one of the hydrogen atoms of an adjacent benzylic methylene group, and, as acceptors, three of the oxygen atoms on the **DB24C8** ring. In **A**, there is an additional stabilising π–π stacking interaction between one of the phenyl rings of **1**$^+$ and a catechol unit of the crown ether. The two independent complexes stack in the crystallographic *c* direction to form channels of crown ether rings through which are threaded the dibenzylammonium ions. The complexes alternate in this stack in the sequence **ABAB** to form a pseudopolyrotaxane[30] array (Fig. 4) in which adjacent ammonium centres are situated 9.3 and 9.7 Å apart from one another.

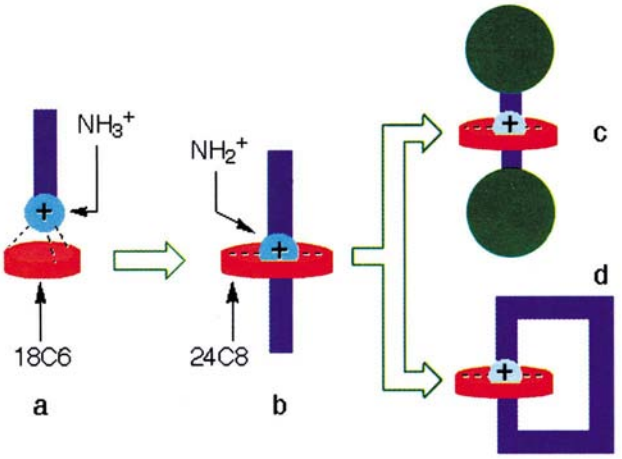
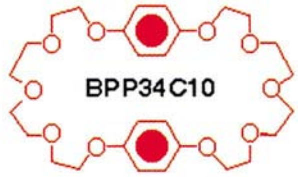
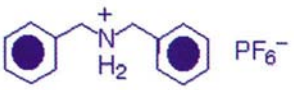
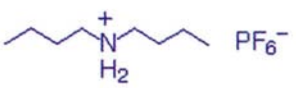


Fig. 2 A conceptual journey from (*a*) the face-to-face complexation exhibited by **18C6**-sized crown ethers (red) and primary alkylammonium cations (blue), *via* (*b*) a [2]pseudorotaxane geometry of complexation proposed for the complexation between **24C8**-sized crown ether rings and secondary dialkylammonium cations, to interlocked molecules such as (*c*) [2]rotaxanes and (*d*) [2]catenanes

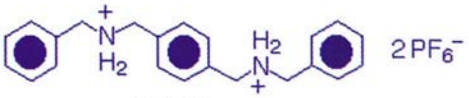




1·PF_6



2·PF_6



3·$2PF_6$

The solid state structure of the complex formed between **2**·PF_6 and **DB24C8** reveals that it is also a pseudorotaxane with 1 : 1 stoichiometry.[28] In this case (Fig. 5), however, only one complex is observed in the unit cell of the crystal, although it exhibits some disorder in the butyl chains of **2**$^+$ and in a portion of one of the polyether loops of **DB24C8**. This complex has an [N–H···O] hydrogen bonding geometry similar to that observed in the **B** variation of the [**DB24C8**·**1**]$^+$ complex. Once again, a [C–H···O] hydrogen bonding interaction is observed between one of the hydrogen atoms located on a carbon atom immediately adjacent to the NH_2^+ centre and one of the oxygen atoms in **DB24C8**. It is well documented[31] that these CH_2N^+ hydrogen atoms bear a considerable amount of the formal positive charge associated with the NH_2^+ centre, and consequently [C–H···O] hydrogen bonds involving these methylene groups provide significant stabilisation to the complex. There are no dominant intercomplex stabilising interactions in the crystals of the [**DB24C8**·**2**]$^+$ complex.

What evidence do we have that these 1 : 1 complexes exist in solution as well as in the solid state? The most direct evidence comes from the observations that both **1**·PF_6 and **2**·PF_6 dissolve in chlorinated solvents such as $CDCl_3$, CD_2Cl_2 and $CDCl_2CDCl_2$ in the presence of one or more molar equivalents of **DB24C8**. Yet, both salts are practically insoluble in these same solvents in the absence of the macrocyclic polyether. The gross geometries of the complexes follow from ^1H NMR spectra obtained in a number of different solvents. For example, the ^1H NMR spectrum of an equimolar mixture of **1**·PF_6 and **DB24C8** in CD_3CN displays (Fig. 6) an interesting phenomenon: sharp signals are present for three different species which can be identified as (i) uncomplexed **1**·PF_6, (ii) uncomplexed **DB24C8** and (iii) the 1 : 1 complex formed between these two species. The signals for the uncomplexed species resonate at the same δ values as they do in the ^{1}H NMR spectra of the individual components, and the stoichiometry of the complex is readily determined as 1 : 1 by integration of relevant probe protons on both the host and guest species. Clearly, a situation of slow kinetics of complexation and decomplexation characterises this system on the ^{1}H NMR timescale at both 300 and 400 MHz. On the other hand, the ^{1}H NMR spectrum of an equimolar mixture of **2**·PF$_6$ and **DB24C8** in a range of different solvents displays only one set of signals for each of the two components—*i.e.* fast kinetic exchange occurs on the ^{1}H NMR timescale between the complexed and uncomplexed species at room temperature. Taken together, these two observations are consistent with the geometries of both the [**DB24C8·1**][PF$_6$] and [**DB24C8·2**][PF$_6$] complexes being those of pseudorotaxanes in solution. Inspection of Corey–Pauling–Koltun (CPK) space-filling molecular models suggests that a phenyl ring has some difficulty in threading through the cavity of **DB24C8** and so the rates of complexation and decomplexation of the **1**$^+$ cation through the centre of this macrocyclic polyether are, understandably, slow.

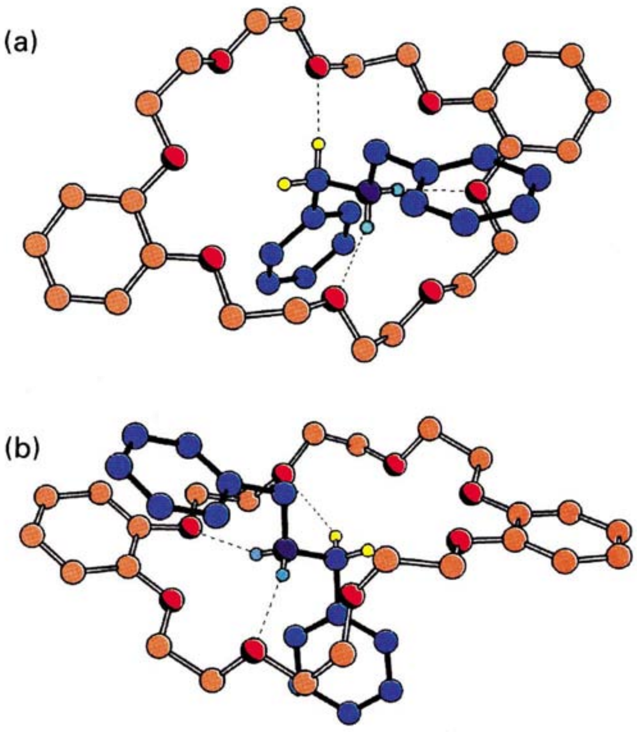


Fig. 3 The two independent 1 : 1 complexes (*a*) **A** and (*b*) **B** observed in the unit cell upon crystallisation of **1**·PF$_6$ and **DB24C8**. Stabilising hydrogen bonding interactions are shown as dashed lines.

Further evidence that the pseudorotaxane geometry is preferred by this complex in solution was provided by an ^{1}H NMR spectroscopic NOE enhancement experiment in CDCl$_3$ in which the signals corresponding to [**DB24C8·1**][PF$_6$] were irradiated independently and the effects upon the other protons in the spectrum was observed. It was noted[28] that irradiation of either the protons on the methylene or *ortho*-positions of the benzyl groups of **1**$^+$ affected most strongly the α-, β- and γ-OCH$_2$ proton signals arising from the **DB24C8** ring and *vice versa*. These observations are consistent with the complex having a gross geometry similar to that already characterised in the solid state.

The observation of signals for both complexed and uncomplexed **1**$^+$ as well as free **DB24C8** in ^{1}H NMR specta in a number of different solvents provides the basis for convenient single point analyses of the association constants (K_a) in these solvents at a range of concentrations. In poorly coordinating solvents, such as CDCl$_3$, the K_a value is large (*ca.* 27 000 l mol^{-1}), in solvents of intermediate polarity , such as CD$_3$CN and CD$_3$COCD$_3$, the K_a's are much lower (*ca.* 300–400 l mol^{-1}), and in strongly coordinating solvents, such as CD$_3$SOCD$_3$, no complexation is observed at all. The K_a value for the association of the [**DB24C8·2**][PF$_6$] complex in CD$_3$CN lies in the range 50–70 l mol^{-1}, as determined by both dilution and titration experiments,[32] based on ^{1}H NMR spectroscopy. This K_a value is signficantly lower than that obtained for the [**DB24C8·1**][PF$_6$] complex in CD$_3$CN and may reflect the stronger binding of **1**$^+$ to the crown ether as a result of (i) the restricted flexibility of this ion, (ii) stronger [C–H···O] hydrogen bonding, involving the benzylic methylene protons, and (iii) the potential for π–π stabilising interactions on account of the phenyl groups present in **1**$^+$.

Using the FAB technique, both the [**DB24C8·1**]$^+$ and [**DB24C8·2**]$^+$ cationic complexes are observed[28] as the peaks of highest mass in their respective mass spectra. In fact, the [**DB24C8·1**]$^+$ ion is the base peak in its mass spectrum, suggesting that the complex formed is strong and has a slow rate of dissociation during its flight through the spectrometer. By

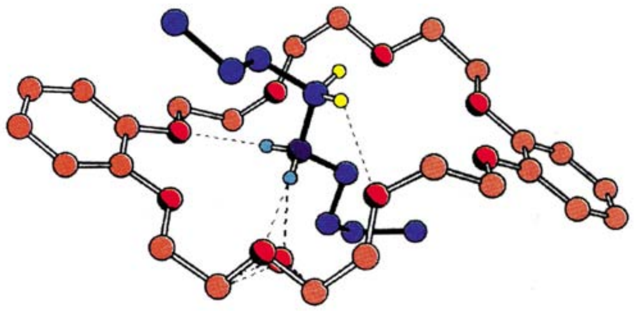


Fig. 5 The solid state superstructure of the 1 : 1 complex formed between **DB24C8** and **2**·PF$_6$

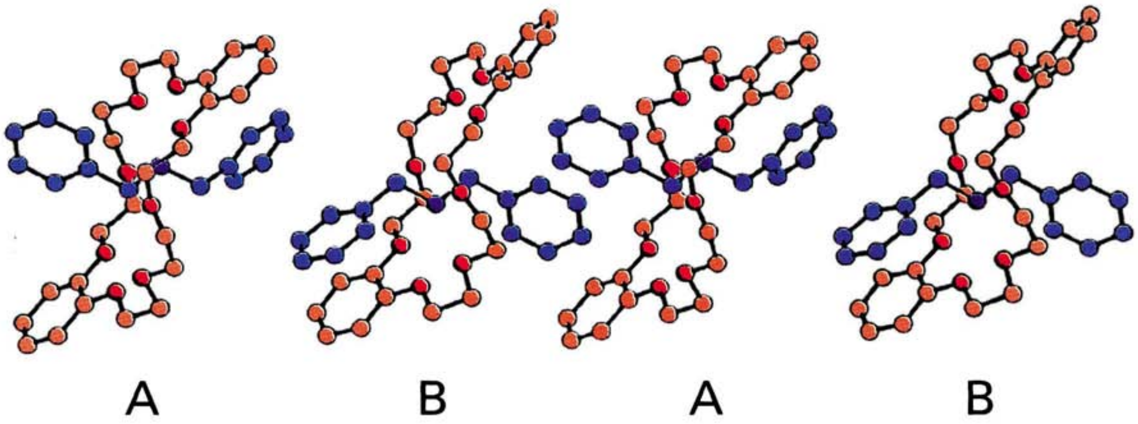


Fig. 4 Packing within the lattice of the [**DB24C8·1**]$^+$ complex. The two independent 1 : 1 complexes align to form a pseudopolyrotaxane-like array.

contrast, the peak for the [**DB24C8·2**]$^+$ ion in its mass spectrum has an intensity which is approximately 20% that of the base peak, which indeed corresponds to the 2$^+$ cation itself.

In these initial investigations, we believe that we have uncovered a fundamentally new and general mode of binding of secondary dialkylammonium ions by macrocyclic polyethers. Next, we were interested in studying the effects of changing the ring size of the crown ether component or the number of NH_2^+ centres in the thread-like component upon the stoichiometries, geometries and strengths of complexation.

A 1 : 2 complex

BPP34C10 is a macrocyclic polyether which was first synthesised by Cram[25] in order to determine its binding affinity towards primary alkylammonium cations. The association constants were found to be quite low—at least, relative to those for smaller crown ethers, such as **18C6** derivatives—presumably because the relatively poor preorganisation of **BPP34C10** necessitates that only two point [N–H···O] hydrogen bonding can occur with RNH_3^+ cations. Since we had utilised this macrocyclic polyether to good effect in the self-assembly of a range of catenanes,[11] rotaxanes[33] and pseudorotaxanes[34] based on its highly efficient binding with bipyridinium dications, we were intrigued to explore its potential for binding secondary dialkylammonium ions. We were surprised by the results we obtained with this crown ether.

A complex between **BPP34C10** and **1**·PF_6 was obtained—from an equimolar mixture of the two species in an acetone–pentane solution—in a crystalline form suitable for X-ray structure analysis. The solid state structure revealed[29] that not only is it a complex with pseudorotaxane-like geometry formed (Fig. 7) but it is also one in which two dibenzylammonium cations **1**$^+$ are threaded simultaneously through the same **BPP34C10** ring. This 1 : 2 complex [**BPP34C10·1**$_2$]$^{2+}$ is a rare example of a double-stranded pseudorotaxane, the likes of which has been observed previously, for example, for inclusion complexes of γ-cyclodextrin derivatives[35] and cyclobis(paraquat-4,4′-biphenylene).[36] The centrosymmetric complex is stabilised by a two-point [N–H···O] hydrogen bonding interaction at each NH_2^+ centre and aromatic–aromatic edge-to-face interactions between one of the phenyl rings in each of the dications and one of the hydroquinone rings of the crown ether. Unlike the solid state structures (Figs. 3 and 5) of the 1 : 1 complexes, no [C–H···O] hydrogen bonding is present in the superstructure of the 1 : 2 complex. Once again, the **BPP34C10** rings are aligned in the crystallographic *c* direction to form channels through which are threaded pairs of **1**$^+$ cations, resulting in a pseudopolyrotaxane-like stacking motif (Fig. 8).

Next, the question arises—is this 1 : 2 complex stable in solution? We believe so. Our evidence is based, once again, on the ability of the macrocyclic polyether to facilitate the dissolution of **1**·PF_6 in non-coordinating solvents, such as $CDCl_3$ and CD_2Cl_2. Thus, when a solution of **BPP34C10** in CD_2Cl_2 is treated with an excess of **1**·PF_6 and the mixture is filtered, the ^{1}H NMR spectrum of the complex indicates[29] that 2 equiv. of the salt are taken up into solution relative to the concentration of **BPP34C10**. The stoichiometry is determined readily from integration of signals for relevant probe protons present in both the host and guest species. The δ values of the resonances for the protons of the crown ether's OCH_2 groups are shifted significantly (Δδ values between −0.03 and −0.43 ppm) from the positions of these resonances in the absence of the salt. The ^{1}H NMR spectrum shows a time-averaged set of signals for the host and guest components—a situation which is to be expected on account of the substantial cavity present in the **BPP34C10** macrocycle allowing fast association and dissociation of the components on the ^{1}H NMR timescale at 400 MHz at room temperature.

FAB Mass spectrometry indicates[29] that a complex of 1 : 2 (host : guest) stoichiometry exists in the 'gas phase'. This peak is, however, present in an abundance of less than 1% relative to the base peak in the spectrum, which corresponds to the protonated, but uncomplexed, **BPP34C10**.

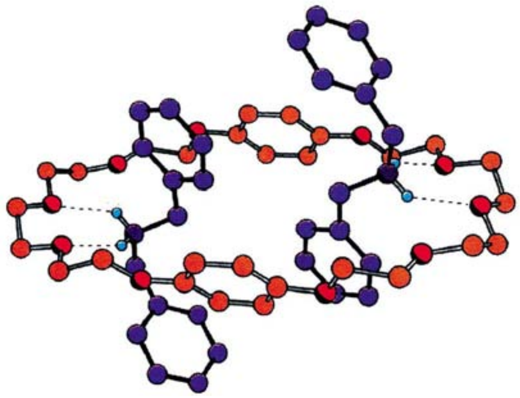


Fig. 7 The solid state superstructure of the double-threaded 1 : 2 complex [**BPP34C10·1**$_2$]$^{2+}$

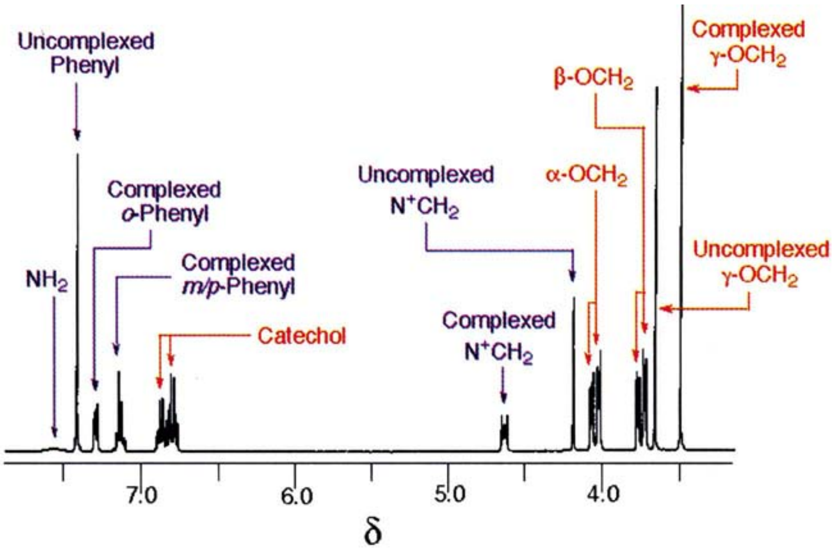


Fig. 6 Partial ^{1}H NMR spectrum recorded at 25 °C at 400 MHz of a 1 : 1 mixture of **1**·PF_6 and **DB24C8**. Three distinct sets of signals are observed—those attributable to the [**DB24C8·1**][PF_6] complex, as well as uncomplexed **1**·PF_6 and **DB24C8**.

The observation of a 1 : 2 complex between **BPP34C10** and **1**·PF_6 prompted us to investigate the complexation of the bis(dialkylammonium) salt **3**·$2PF_6$ with this same macrocyclic polyether. We wondered—would both NH_2^+ centres of 3^{2+} be incorporated within one single **BPP34C10** ring, or would each dication be threaded through two independent rings?

A 2 : 2 complex

Equimolar amounts of **BPP34C10** and **3**·$2PF_6$ in an acetone–pentane solution resulted in single crystals suitable for X-ray crystallography. The solid state structure revealed[29] the presence of an astonishing 2 : 2 complex $[(\mathbf{BPP34C10})_2\cdot\mathbf{3}_2]^{4+}$ in which two 3^{2+} dications are threaded simultaneously through the cavities of two **BPP34C10** macrocycles positioned immediately adjacent to one another (Fig. 9). This asymmetric complex—a doubly encircled, double-stranded pseudorotaxane—is stabilised by a series of ten [N–H···O] and four [C–H···O] hydrogen bonding interactions between the hydrogen atoms of both the NH_2^+ centres and their adjacent benzylic methylene groups, and oxygen atoms of the crown ether macrocycle. Although there are no dominant intercomplex interactions, the 2 : 2 complex forms stacks in the crystallographic *b* direction in which pairs of **BPP34C10** tori align themselves to form extended tube-like arrays through which are threaded the pairs of 3^{2+} dicationic units (Fig. 10).

We have no evidence to support the existence of the 2 : 2 $[(\mathbf{BPP34C10})_2\cdot\mathbf{3}_2][PF_6]_4$ complex in either the solution state or the 'gas phase'. In solution, as evidenced by ^1H NMR spectroscopy, substantial changes are observed[29] in the chemical shifts of the resonances associated with protons of both the host and guest components where their stoichiometry is 1 : 1. Similarly, FAB mass spectrometry indicates no peak is present for a 2 : 2 complex: rather, a peak corresponding to a 1 : 1 complex is observed in the spectrum.

A 2 : 1 complex

The salt **3**·$2PF_6$ was expected to form a stable 2 : 1 (host : guest) complex with **DB24C8**. Indeed, cocrystallisation of **DB24C8** with **3**·$2PF_6$ resulted in a complex of 2 : 1 stoichiometry. X-Ray structural analysis revealed[29] a centrosymmetric complex in which two **DB24C8** rings are threaded on to the same 3^{2+} dicationic thread (Fig. 11). The $[(\mathbf{DB24C8})_2\cdot\mathbf{3}]^{2+}$ complex is stabilised by a series of six [N–H···O] and two [C–H···O] hydrogen bonding interactions. Additionally, the three components are held together by an almost parallel π–π stacking interaction between the central *p*-xylyl unit of the thread-like 3^{2+} dication and one of the catechol rings from each of the two complexed **DB24C8** rings. Between 2 : 1 complexes, there are no dominant noncovalent bonding interactions.

The salt **3**·$2PF_6$ cannot be dissolved in a $CDCl_3$ solution containing two or more equivalents of **DB24C8**, presumably as a result of the difficulty of solvating two NH_2^+ centres simultaneously in the solid state. However, a solution of the salt in a small volume of CD_3CN can be diluted with a solution of **DB24C8** in $CDCl_3$, such that no precipitation occurs from what is essentially a $CDCl_3$ solution. In solution, the 1 : 1 and 2 : 1 complexes between **DB24C8** with **3**·$2PF_6$ can be detected as discrete species on account of the slow rates of complexation and decomplexation between the two components on the ^1H NMR timescale at both 300 and 400 MHz. In fact, in CD_3CN solution, four discrete species are present—uncomplexed salt **3**·$2PF_6$ and uncomplexed **DB24C8**, together with a 1 : 1 complex and a 2 : 1 complex between the two species—which results in an extremely complicated ^1H NMR spectrum. In order to determine which signals in the spectrum correspond to the 2 : 1 complex, a $CDCl_3$–CD_3CN solution containing **3**·$2PF_6$ in the presence of a large excess of **DB24C8** was prepared. In this case, only two major species are present in solution—the 2 : 1 complex and excess of the uncomplexed **DB24C8**. The stoichiometry of this complex is established by the relative integration of the resonances of pertinent probe protons in both the host and guest species.

FAB Mass spectrometry results in a peak corresponding to the 2 : 1 complex $[(\mathbf{DB24C8})_2\cdot\mathbf{3}-H]^+$. It is the peak of highest mass with an intensity of *ca.* 10% of that of the base peak which corresponds to the 1 : 1 complex between **DB24C8** and 3^{2+}. Such an intense signal for a 2 : 1 complex suggests that this ternary complex is quite stable; also, the 2 : 1 complex experiences slow rates of dissociation of its components during its flight through the spectrometer.

Reflections

We hope that we have demonstrated the generality of the concept that complexation of secondary dialkylammonium ions—which have very simple constitutions—with some very

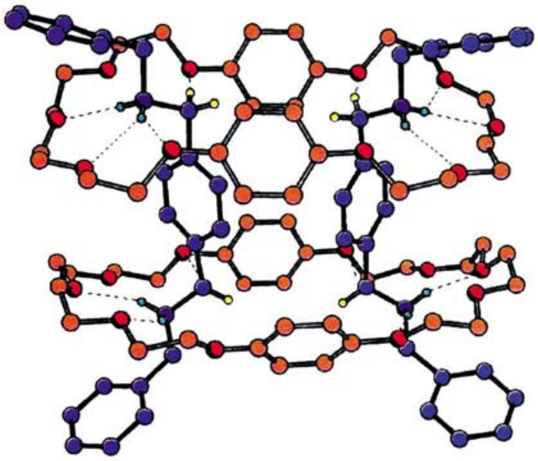


Fig. 9 The solid state superstructure of the double-threaded and doubly-encircled 2 : 2 complex $[(\mathbf{BPP34C10})_2\cdot\mathbf{3}_2]^{4+}$

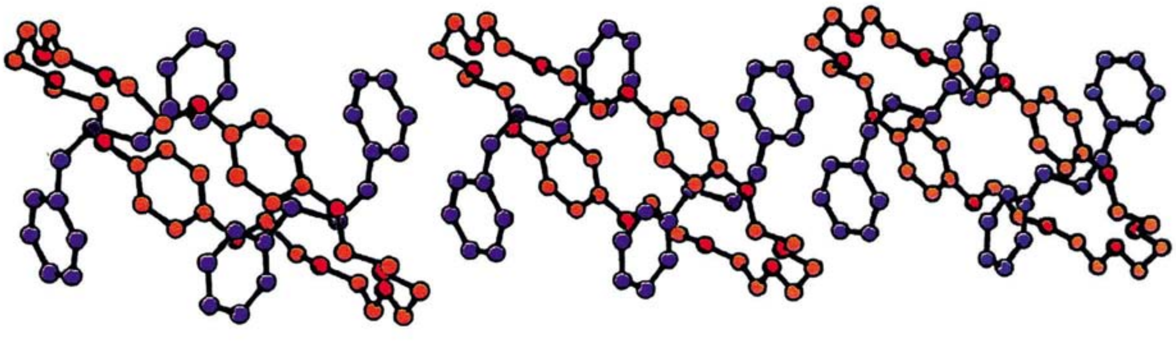


Fig. 8 Portion of the lattice of the $[\mathbf{BPP34C10}\cdot\mathbf{1}_2]^{2+}$ complex displaying an extended pseudopolyrotaxane-like array

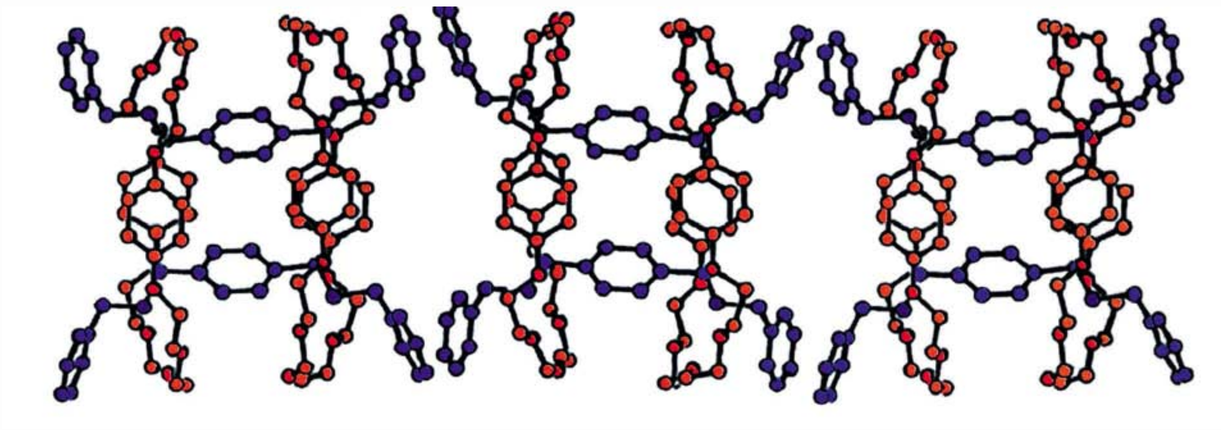


Fig. 10 The pseudopolyrotaxane-like array observed in the lattice of the solid state structure of $[(\mathbf{BPP34C10})_2 \cdot \mathbf{3}_2]^{4+}$

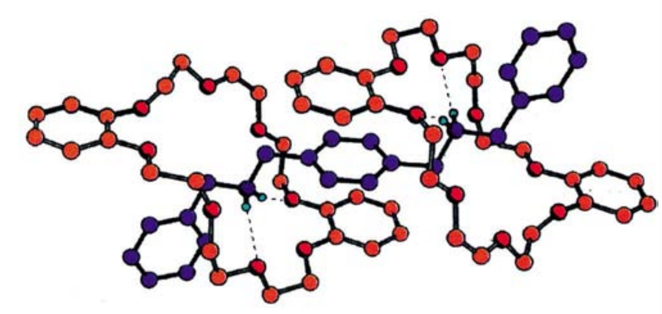


Fig. 11 The solid state superstructure of the doubly-encircled 2 : 1 complex $[(\mathbf{DB24C8})_2 \cdot \mathbf{3}]^{2+}$

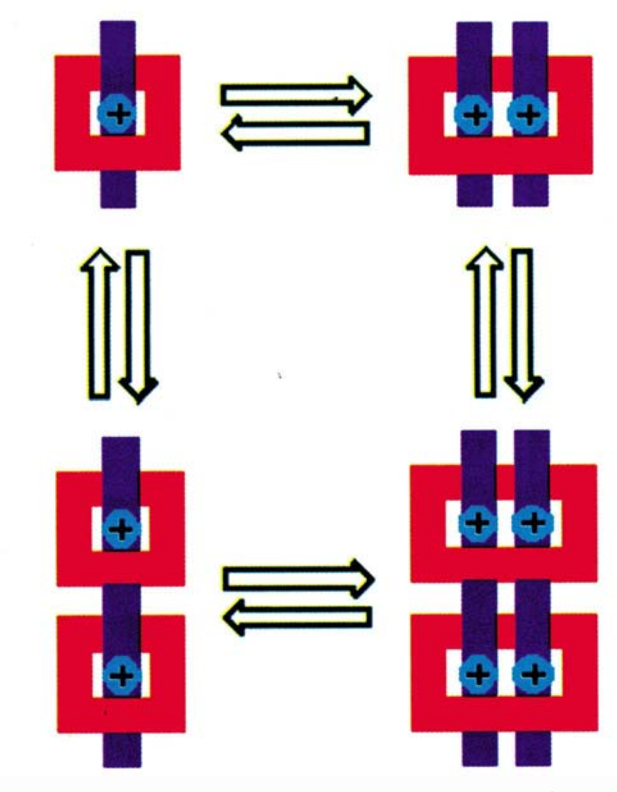


Fig. 12 Cartoon representations of the four different types of complexes with pseudorotaxane-like geometries that have been described in this article. Crown ether rings are depicted in red whilst cationic thread-like units are coloured blue. By increasing or reducing either the size of the crown ether rings or the number of cationic centres in the thread-like components, we are able to proceed full-circle around this path.

well-established macrocyclic polyethers results in the self-assembly of intricate superstructures with pseudorotaxane-like geometries. In the five complexes described in this article, we have demonstrated that changes in the constitution of either the crown ether or the dialkylammonium ions components can result in significant changes (i) in the stoichiometries of the complexes, (ii) in their relative geometries, and (iii) in the stabilising intracomplex and intercomplex interactions that are utilised in the solid state. A variety (Fig. 12) of complexes have been prepared in which we have shown that, by changing the size of the macrocycle or the number of NH_2^+ centres in the thread-like component, we can go full circle from 1 : 1 to 1 : 2, to 2 : 2, to 2 : 1 and then back to 1 : 1 complexes. We are engaged actively[37] in the extension of this research to take on board yet larger macrocycles and oligomeric and polymeric thread-like components. By mixing modules—incorporating NH_2^+ centres into molecules which contain other molecular recognition sites—we are also trying[38] to prepare novel self-assembling systems which are capable of exhibiting selective binding localised with respect to their particular subunits. In addition, we are exploring[39] the possibility of utilising this remarkably simple self-assembling system in the template-directed synthesis of mechanically-interlocked molecules, such as rotaxanes[40] and catenanes.

The ease with which the components for this particular self-assembling system can be prepared augers well for their inclusion and use as important new modules in the modular chemist's 'toolkit'.

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Footnotes

† A multimedia version of this feature article will be temporarily available from the CLIC page http://chemistry.rsc.org/rsc/clic.htm

‡ *Pseudorotaxanes* have been defined as inclusion complexes in which a thread-like molecule is encircled by one or more ring-like molecules in such a way that the two ends of the thread are projected well away from the centre of the ring. In a *rotaxane* (Latin: *rota*, wheel; *axis*, axle), the two ends of the thread are terminated by bulky groups which do not allow the passage of the ring(s) over them and thus the two (or more) components are mutually interlocked. The prefix *pseudo* denotes that in a pseudorotaxane the two or more molecules are not interlocked: instead, they are free to dissociate because the ends of the thread-like molecule are small enough to allow passage of the ring-like molecule(s) over them. See, for example, P. R. Ashton, D. Philp, N. Spencer and J. F. Stoddart, *J. Chem. Soc., Chem. Commun.*, 1991, 1677.

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