

1,2-Bis(4,4'-dipyridinium)ethane: a versatile dication for the formation of [2]rotaxanes with dibenzo-24-crown-8 ether

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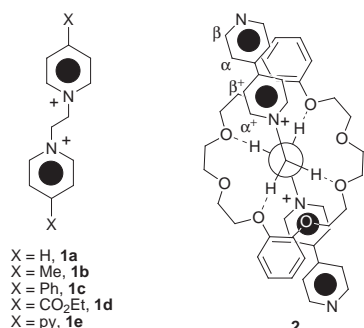
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The 1,2-bis(4,4'-dipyridinium)ethane dication threads through dibenzo-24-crown ether (DB24C8) to form a [2]pseudorotaxane which is easily stoppered to form [2]rotaxanes either by alkylation or coordination of a transition metal complex.

To date, most [2]rotaxanes involving crown ethers have been templated by either the stacking interactions between π -electron rich and π -electron poor aromatic rings¹ or hydrogen bonding between secondary dialkylammonium ions and crown ether oxygen atoms.² We have recently demonstrated that various 1,2-bis(pyridinium)ethane dications **1a–d** will thread through the 24-membered crown ethers 24C8, B24C8 and DB24C8 to form [2]pseudorotaxanes in which the major templating forces are $N^+\cdots O$ and $C-H\cdots O$ interactions.³ By adding various substituents (X) to the 4-position of the pyridinium ring, it was possible to prepare a series of interlocked molecules containing DB24C8 with K_a values ranging from 105 dm³ mol⁻¹ for **1a** to 1200 dm³ mol⁻¹ for **1d** in MeCN solution.

We have now turned our attention to converting these [2]pseudorotaxanes into permanently interlocked [2]rotaxanes. Our strategy was to prepare an appropriate 1,2-bis(pyridinium)ethane dication which could form a stable [2]pseudorotaxane and be easily stoppered to form a [2]rotaxane. In a straightforward variation of our previous work, these criteria were met by using 4,4'-bipyridinium units; X = 4-pyridine, **1e**.⁴ The 1:1 interaction of **1e** with DB24C8 resulted in formation of the [2]pseudorotaxane **2** (Scheme 1) as identified by ¹H NMR spectroscopy, ESI-MS and an association constant of 920 dm³ mol⁻¹ measured at 298 K in MeCN. Spectroscopic data are consistent with binding *via* $N^+\cdots O$ interactions, $C-H\cdots O$ hydrogen bonds and π -stacking analogous to that found in solution for **1a–d** and in the solid state, by X-ray crystallography, for **1d** (X = CO₂Et).³

Two routes were used to convert the [2]pseudorotaxane **2** to a permanently interlocked [2]rotaxane. First, **2** was alkylated at the terminal, pyridine nitrogen atoms with bulky *tert*-butylbenzyl groups by vigorously stirring a two-phase MeNO₂-saturated NaBF₄(aq) solution containing 1 equiv. of **1e**, 6 equiv.

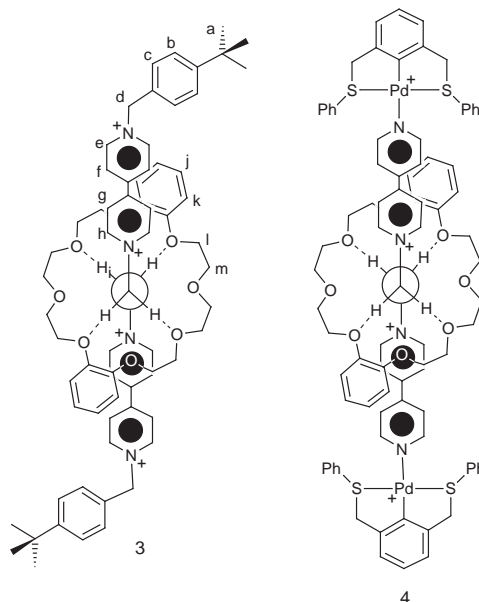


Scheme 1 Formation of [2]pseudorotaxane **2** from the 1,2-bis(4,4'-dipyridinium)ethane dication **1e** and DB24C8. **2** is viewed along the $+NCH_2CH_2N^+$ vector in a Newman type projection emphasizing four of the stabilizing $C-H\cdots O$ interactions.

of *tert*-butylbenzyl chloride and 3 equiv. of DB24C8. The [2]rotaxane **3** was isolated in 46% yield by extraction of the product into CH₂Cl₂ (Scheme 2). Significant *downfield* shifts (ppm) for α^+ (0.34) and $+NCH_2$ (0.33) protons were indicative of $C-H\cdots O$ hydrogen bonding to crown ether O-atoms and *upfield* shifts were observed for the α (0.03), β (0.28), β^+ (0.27) and crown aromatic protons (0.26, 0.50) indicating π -stacking between the catechol and bipyridinium aromatic rings. An X-ray crystal structure determination[†] of **3** verified the nature of the interaction and an ORTEP diagram is shown in Fig. 2.

The [2]rotaxane, **3** exhibits $N^+\cdots O$ interactions ranging from 3.41 to 4.50 Å and eight $C-H\cdots O$ hydrogen bonds with $C\cdots O$ distances in the range 3.18–3.69 Å. The orange colour of the solid material is consistent with charge transfer interactions between the normally colourless crown ether and dipyridinium fragments. The S-shaped conformation of the dibenzo-24-crown ether molecule allows this π -stacking phenomenon to occur through both *intramolecular* and *intermolecular* interactions as shown in Fig. 2.

In a metal–ligand, self-assembly reaction, the [2]pseudorotaxane **2** was used as a ligand and stoppered with organopalladium fragments to form the metallo-[2]rotaxane **4**. This was done by simply mixing 1 equiv. of **1e**, with 2 equiv. of [Pd{C₆H₃(PhSCH₂)₂}(MeCN)]BF₄ and 3 equiv. of DB24C8 in MeCN solution. The ¹H NMR spectrum of this solution showed that the [2]rotaxane **4** was formed in quantitative yield. As for **3**, significant *downfield* shifts for α^+ (0.41) and NCH_2 (0.38) protons were observed indicative of $C-H\cdots O$ hydrogen bonding to crown ether O-atoms, while *upfield* shifts were observed for the α (0.24), β (0.32), β^+ (0.38) and crown aromatic protons (0.31, 0.58) indicating π -stacking between the two sets of



Scheme 2 [2]Rotaxanes can be formed from **2** by adding 'stopper' groups.

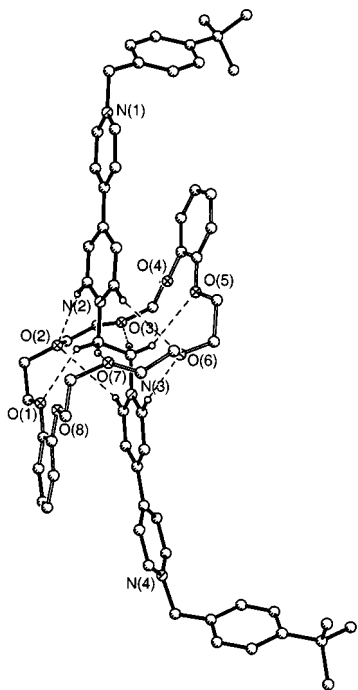


Fig. 1 An ORTEP diagram of the [2]rotaxane **3** showing the basic numbering scheme. N(2)⁺...O distances; O(1) 4.52, O(2) 3.79, O(3) 3.93, O(4) 3.41, O(5) 3.55, O(6) 4.06, O(7) 3.80, O(8) 4.50 Å. N(3)⁺...O distances; O(1) 3.43, O(2) 3.97, O(3) 4.05, O(4) 4.68, O(5) 4.64, O(6) 3.74, O(7) 4.22, O(8) 3.65 Å. C–H...O bonds: C(19)...O(2) 3.33, C(20)...O(6) 3.62, C(24)...O(2) 3.69, C(28)...O(6) 3.18, C(22)...O(1) 3.29, C(22)...O(7) 3.27, C(23)...O(3) 3.24, C(23)...O(5) 3.54 Å.

aromatic rings. An X-ray crystal structure determination of **4** verified the nature of the interaction and an ORTEP diagram is shown in Fig. 3.

The [2]rotaxane, **4** shows a series of N⁺...O interactions ranging from 3.51 to 4.90 Å and eight C–H...O hydrogen bonds with C...O distances in the range 3.18–3.62 Å. The SPh rings of the metal fragment do not interact with the rest of the molecule. The organopalladium fragment is large enough to prevent unthreading and acts as a stopper in the designed manner.

The ability of the 1,2-bis(4,4'-dipyridinium) dication to form [2]rotaxanes using simple synthetic methodologies demonstrates that this component has the potential to be an important building block for the construction of more complex mechanically linked systems such as [2+n]rotaxanes, molecular necklaces⁵ [n]MN and [n]catenanes.

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Fig. 2 A space-filling model showing the packing of two adjacent molecules of **3** in the unit cell.

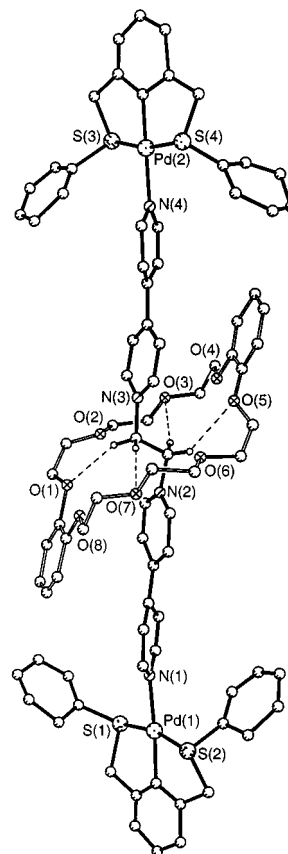


Fig. 3 An ORTEP diagram of the metal-capped [2]rotaxane **4** showing the basic numbering scheme. N(2)⁺...O distances; O(1) 3.51, O(2) 3.78, O(3) 4.51, O(4) 4.85, O(5) 4.64, O(6) 3.80, O(7) 3.92, O(8) 3.55 Å. N(3)⁺...O distances; O(1) 4.47, O(2) 3.68, O(3) 3.87, O(4) 3.54, O(5) 3.58, O(6) 3.86, O(7) 4.48, O(8) 4.90 Å. C–H...O bonds: C(28)...O(2) 3.31, C(29)...O(6) 3.28, C(33)...O(2) 3.18, C(37)...O(6) 3.42, C(31)...O(3) 3.62, C(31)...O(5) 3.44, C(32)...O(1) 3.44, C(32)...O(7) 3.51 Å.

Notes and references

† *Crystal data*: for **3**: C₆₈H₈₂B₄F₁₆N₄O₈, *M* = 1430.62, triclinic, space group *P* $\bar{1}$, *a* = 13.9669(3), *b* = 17.0627(3), *c* = 17.0640(3) Å, α = 86.686(1), β = 80.281(1), γ = 75.390(1)°, *U* = 3878.1(1) Å³, *T* = 293(2) K, *Z* = 2, μ = 0.104 mm⁻¹, 9521 independent reflections (*R*_{int} = 0.0293), *R*1 = 0.1297, *wR*2 = 0.3690 (*I* > 2σ), *R*1 = 0.1847, *wR*2 = 0.4310 (all data), Goodness-of-fit (*F*²) = 0.908.

For **4**: C₈₆H₈₆B₄F₁₆N₄O₈Pd₂S₄, *M* = 1991.87, monoclinic, space group *Pc*, *a* = 17.8929(3), *b* = 14.3181(2), *c* = 19.4361(3) Å, β = 116.800(1)°, *U* = 4444.5(1) Å³, *T* = 298(2) K, *Z* = 2, μ = 0.589 mm⁻¹, 11604 independent reflections (*R*_{int} = 0.0500), *R*1 = 0.0569, *wR*2 = 0.1198 (*I* > 2σ), *R*1 = 0.0977, *wR*2 = 0.1431 (all data), Goodness-of-fit (*F*²) = 0.974. Data were collected on a Siemens SMART CCD instrument and solutions performed using the SHELXTL 5.03 Program Library for Structure and Solution and Molecular Graphics, Siemens Analytical Instrument Division, Madison, WI, USA, 1995. CCDC 182/1085. See <http://www.rsc.org/suppdata/cc/1998/2757/> for crystallographic files in .cif format.

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