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Characterization of a slippage stopper for the 1,2-bis(pyridinium)ethane–[24]crown-8 ether [2]pseudorotaxane motif

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A B S T R A C T

Comparison of 1,2-bis(pyridinium)ethane axles containing *iso*-nicotinate esters (R=ethyl, *iso*-propyl, cyclohexyl, cycloheptyl) as the pyridinium unit shows that the cyclohexyl group provides a stopper size that allows slippage to be used as a method for pseudorotaxane/rotaxane formation employing dibenzo-24-crown-8 ether (**DB24C8**) as the wheel. Rates of complexation and decomplexation were measured in a number of solvent systems and the kinetic and thermodynamic parameters associated with the process reported.

1. Introduction

The synthesis of interlocked molecules is most commonly achieved by one of two basic methodologies (Fig. 1).[1] Both utilize supramolecular assistance to bring together complementary components, which are then covalently modified in an irreversible *clipping* or *stoppering* reaction that permanently interlocks the components. A less conventional procedure for preparing rotaxane-like molecules is *slippage* (Fig. 2).[2] In this strategy, the macrocyclic wheel and the pre-formed dumbbell are synthesized separately and then placed under 'appropriate conditions'[3] that allow the system to overcome the free energy of activation (ΔG_{ON}), and the macrocycle to pass over the stoppers of the dumbbell.

When designed properly, the non-covalent interactions present in the resulting pseudorotaxane will make it more stable than the precursor wheel and dumbbell by the free energy of complexation (ΔG^0). When the 'appropriate conditions' are removed, the free energy of activation for dissociation (ΔG_{OFF}) becomes insurmountable and the two components are trapped kinetically in an interlocked manner.

The concept of a pseudorotaxane can be quite vague and has been described by Stoddart using 'fuzzy' sets in which the set of pseudorotaxanes belongs to some extent to both the set of mechanically interlocked rotaxanes and the set of isolated chemical components.[2f] Stoddart has also described the transformation from a pseudorotaxane into a rotaxane as a progressive one, implying that some pseudorotaxanes possess more rotaxane-like character than others.[2f] This is a more realistic picture than one in which a distinct boundary is artificially created between the definitions of a rotaxane and pseudorotaxane.

For over ten years, we have been involved in the study of interpenetrated and interlocked molecules based on templating 1,2-bis(pyridinium)ethane axles and 24-membered crown ether wheels.[4] To date, we have utilized the threading followed by stoppering route to prepare a variety of rotaxanes.[4b] Herein, we explore the possibility of creating an appropriate 1,2-bis(pyridinium)ethane axle capable of undergoing slippage with dibenzo-24-crown-8 ether (**DB24C8**).

2. Results and discussion

In order to discover a slippage axle for the 1,2-bis(pyridinium)ethane–**DB24C8** rotaxane system, it was necessary to identify a stopper that could be easily varied in size while maintaining a strong association with the crown ether wheel. Previous studies in our laboratories showed that the presence of a strong electron withdrawing group such as an ester function substituted at the 4-position on the pyridinium ring yielded relatively high association constants.[4b] *iso*-Nicotinate esters were easily prepared from *iso*-

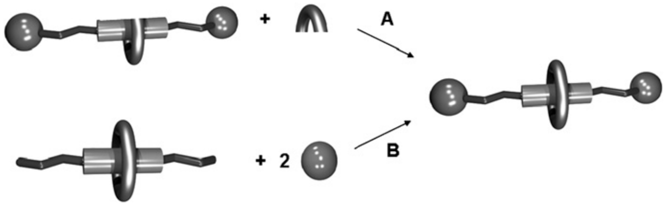

Figure 1. The 'threading' method (A) and the 'clipping' method (B) for the formation of rotaxanes.

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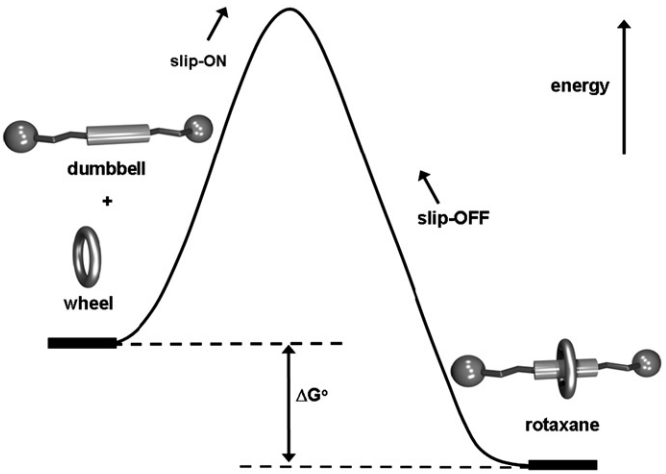
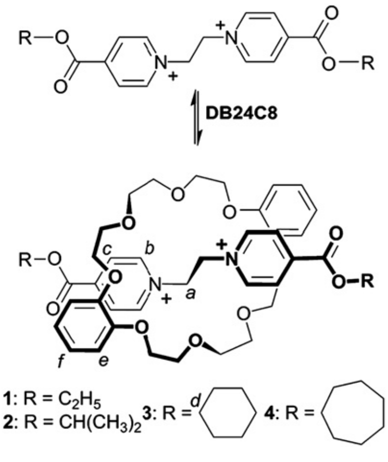


Figure 2. An energy profile for the formation of a [2]rotaxane by slippage from individual dumbbell and wheel components.

nicotinoyl chloride and the appropriate alcohol. Double alkylation with 1,2-dibromoethane and anion exchange to the tetrafluoroborate salt gave a series of symmetrical 1,2-bis(pyridinium)ethane axles[4b] with R=ethyl, *iso*-propyl, cyclohexyl, and cycloheptyl. The interaction of these axles with **DB24C8** could potentially result in the formation of [2]pseudorotaxanes as outlined in Scheme 1.

Initially, CD_3CN solutions containing equimolar amounts of each axle ($\mathbf{1}^{2+}$, $\mathbf{2}^{2+}$, $\mathbf{3}^{2+}$, and $\mathbf{4}^{2+}$) and **DB24C8** at a concentration of 1.0×10^{-2} M were prepared and the ^{1}H NMR spectra recorded immediately at 25 °C to determine whether [2]pseudorotaxane formation had occurred. For axles $\mathbf{1}^{2+}$ and $\mathbf{2}^{2+}$ containing the smaller ethyl and *iso*-propyl groups, there was evidence of [2]pseudorotaxane formation but for the axles $\mathbf{3}^{2+}$ and $\mathbf{4}^{2+}$ with larger cyclohexyl and cycloheptyl groups only the two original axle and wheel components were detected. The spectrum of each sample was then recorded again after a further 24 h. The samples containing axles $\mathbf{1}^{2+}$, $\mathbf{2}^{2+}$, and $\mathbf{4}^{2+}$ showed no change but the NMR spectrum for the mixture of $\mathbf{3}^{2+}$ and **DB24C8** now exhibited peaks due to complexation that were not present in the original mixture. Our conclusions were (i) the ethyl and *iso*-propyl groups were too small to prevent or even slow down threading, (ii) the larger cycloheptyl group was an efficient stopper, which prevented threading, and (iii) the cyclohexyl group was very slowly threading and had the potential to act as a slippage stopper. Further monitoring of the sample confirmed the very gradual formation of [2]pseudorotaxane $[\mathbf{3}\subset\mathbf{DB24C8}]^{2+}$ from $\mathbf{3}^{2+}$ and **DB24C8** via slippage at 25 °C and 1.0×10^{-2} M; Figure 3 shows NMR spectra taken at regular time intervals.



Scheme 1. Formation of [2]pseudorotaxanes from 1,2-bis(pyridinium)ethane axles with ester groups at the 4-position of the pyridine ring and **DB24C8**. The numbering for NMR spectral assignments in Figure 3 is given for R=cyclohexyl.

It was possible to accelerate the formation of [2]pseudorotaxane $[\mathbf{3}\subset\mathbf{DB24C8}]^{2+}$ by heating an CH_3CN solution at reflux and in the presence of 5 equiv of **DB24C8** near quantitative conversion was achieved after 7 days. Removal of the solvent and washing the residue with $CDCl_3$ to remove uncomplexed **DB24C8** allowed for facile isolation of the product.[5] Recrystallization from $MeNO_2$ yielded X-ray quality crystals of $[\mathbf{3}\subset\mathbf{DB24C8}][BF_4]_2$. Figure 4 shows the structure of the [2]pseudorotaxane, which is very similar to that previously reported for $[\mathbf{1}\subset\mathbf{DB24C8}]^{2+}$.[4a] The much larger cyclohexyl groups of $[\mathbf{3}\subset\mathbf{DB24C8}]^{2+}$ do not appear to perturb the non-covalent interactions between axle and wheel as the ester R-groups are fairly distant from the core of the molecule.

Further solution studies were undertaken on $[\mathbf{3}\subset\mathbf{DB24C8}]^{2+}$ to characterize the kinetics and thermodynamics of the slippage process. Unfortunately, these experiments were restricted to a relatively narrow range of solvents as more polar solvents competed with the non-covalent interactions responsible for [2]pseudorotaxane formation and less polar solvents caused solubility problems. Figure 5 shows the results of monitoring the rate of formation (slippage) of $[\mathbf{3}\subset\mathbf{DB24C8}]^{2+}$ in CD_3CN as well as 1:1 and 1:2 mixtures of CD_3CN and $CDCl_3$. Figure 6 shows similar plots for decomposition (extrusion) of $[\mathbf{3}\subset\mathbf{DB24C8}]^{2+}$ into $[\mathbf{3}]^{2+}$ and

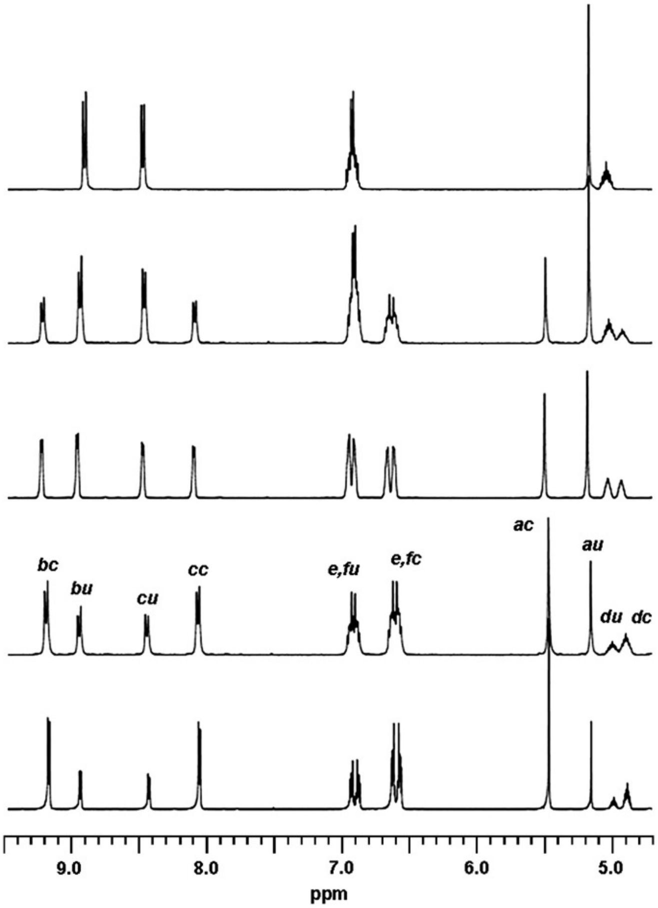


Figure 3. Partial ^{1}H NMR spectra (500 MHz, CD_3CN, 1.0×10^{-3} M, 25 °C) showing formation of the [2]pseudorotaxane $[\mathbf{3}\subset\mathbf{DB24C8}]^{2+}$ from $\mathbf{3}^{2+}$ and **DB24C8** by slippage. From top to bottom: time=0, 9, 14, 30, 55 days. Labeling scheme is shown in Scheme 1; designations c=complexed and u=uncomplexed.

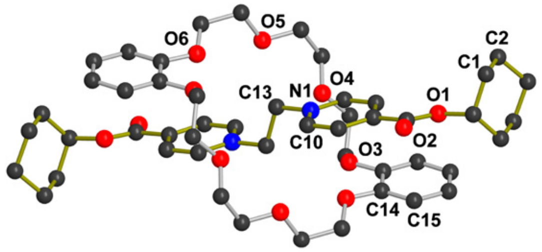


Figure 4. A ball-and-stick representation[6] of the X-ray structure of [2]pseudorotaxane [**3**⊂**DB24C8**]$^{2+}$; hydrogen atoms and BF_4^- anions are omitted for clarity. Axle=gold bonds; wheel=silver bonds; C=black; O=red; N=blue.

DB24C8 in the same solvents. Table 1 summarizes the relevant kinetic and thermodynamic parameters derived from these experiments. As the slippage process combines two molecular components together into one interlocked molecule, the rate of slippage (k_{ON}) is second order. The corresponding rates of extrusions (k_{OFF}) are, however, first order as would be expected. The availability of both k_{ON} and k_{OFF} from experiment allows calculation of the association constant K_a as the ratio k_{ON}/k_{OFF}. The rates k_{ON} and k_{OFF} can be converted to the free energies of activation for the slippage ($\Delta G^{\neq}{}_{ON}$) and extrusion ($\Delta G^{\neq}{}_{OFF}$) processes and the free energy of association (ΔG^0) was derived from the association constant K_a; these values are also included in Table 1.

The very slow formation of [**3**⊂**DB24C8**]$^{2+}$ at 25 °C allows the conclusion that the new axle **3**$^{2+}$ containing two cyclohexyl groups does indeed allow for synthesis by slippage. Once formed, the pseudorotaxane has a half-life of 287 days in CH_3CN solution. As with other slippage systems, the interpretation of whether [**3**⊂**DB24C8**]$^{2+}$ is a [2]pseudorotaxane or [2]rotaxane is a matter of experimental conditions and remains fuzzy.[2f] There is, however, no question that this pseudorotaxane can be easily prepared by slippage and then manipulated in solution for short periods of time without concern of decomposition by extrusion. The association constant (K_a) for the [2]pseudorotaxane [**3**⊂**DB24C8**]$^{2+}$ in CD_3CN (2.58×10^3 M^{-1}) is of the same magnitude but slightly larger than that reported for [**1**⊂**DB24C8**]$^{2+}$ (1.94×10^3 M^{-1}) measured by the conventional single-point method from a single NMR spectrum undergoing slow exchange at 25 °C.[4b]

As a further demonstration of the stability of [**3**⊂**DB24C8**]$^{2+}$ the extrusion process was monitored in DMSO-d_6 solution. Figure 7 shows the results of monitoring a 1.0×10^{-2} M solution at 25 °C using ^1H NMR spectroscopy. Figure 8 shows a plot of ln[axle] versus time and the derived values for k_{OFF} and $\Delta G^{\neq}{}_{OFF}$ are reported in Table 1. These are the harshest conditions possible for this supramolecular system as the polarity of DMSO-d_6 is such that the non-covalent interactions between axle and wheel are essentially eliminated. Axle **1**$^{2+}$ with a smaller ethyl group showed no evidence of [2]pseudorotaxane formation in DMSO-d_6 solution but a substantial barrier to extrusion remains for [**3**⊂**DB24C8**]$^{2+}$; the half-life of the [2]pseudorotaxane is 165 min.

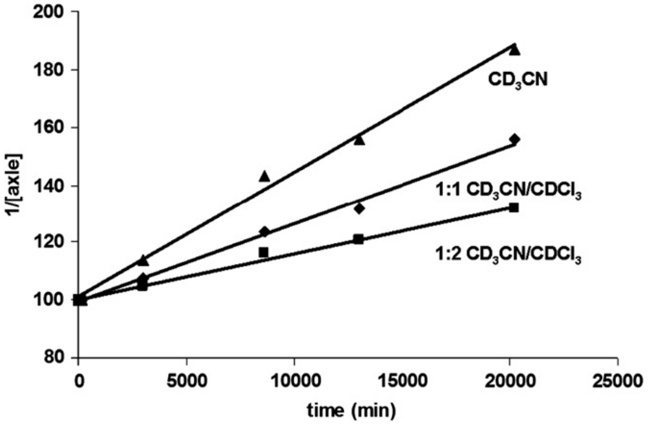


Figure 5. Plots of 1/[axle] versus time demonstrating the second-order rate of formation of [2]pseudorotaxane [**3**⊂**DB24C8**]$^{2+}$ from **3**$^{2+}$ and **DB24C8** in various solvent mixtures at 25 °C.

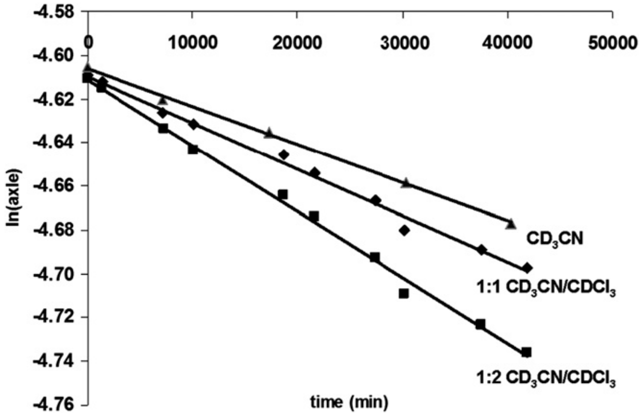


Figure 6. A plot of ln(concentration) versus time for the first-order decomposition of [2]pseudorotaxane [**3**⊂**DB24C8**]$^{2+}$ into axle **3**$^{2+}$ and **DB24C8** in various solvent mixtures at 25 °C.

3. Conclusions

The discovery that a cyclohexyl group is sufficient to generate a slippage stopper for the 1,2-bis(pyridinium)ethane–**DB24C8** rotaxane system is a significant step in the development of the chemistry of this templating motif. However, the fact that a cyclohexyl group was the correct size and shape required for slow threading through **DB24C8** is not surprising, since Stoddart showed that a cyclohexyl group was a suitable slippage stopper for dialkylammonium threads when **DB24C8** was used as the wheel.[2f] It appears that the barrier to slippage and extrusion is higher for the 1,2-bis(pyridinium)ethane axles. This is probably due to the extra rigidity provided by fusing the cyclohexyl ester function directly to the pyridinium ring. Future applications of the slippage process to more complicated systems involving interlocked molecules based on the 1,2-bis(pyridinium)ethane–**DB24C8** templating motif will be reported in due course.

4. Experimental

4.1. General

All chemicals including **DB24C8** were purchased from Aldrich Chemicals and used without further purification. The solvents were dried and distilled prior to use. ^1H NMR spectra were recorded on Bruker Avance 500 locked to the deuterated solvent operating at 500 MHz. Mass spectra were performed on a Micromass LCT electrospray ionization ToF spectrometer. *iso*-Nicotinate esters were prepared from the acid chloride and corresponding alcohol by a standard procedure[7] in essentially quantitative yields. A general procedure for the syntheses of 1,2-bis(pyridinium)ethane axles as the tetrafluoroborate salt is given in Ref. 4b.

4.2. Preparation of [3⊂DB24C8][BF$_4$]$_2$

[**3**][BF_4]$_2$ (0.2 g, 0.33 mmol) and excess **DB24C8** (0.654 g, 1.46 mmol) were refluxed in CH_3CN (20 mL) for 7 days. The solvent

Table 1
Kinetic and thermodynamic data for preparation[a] of [2]pseudorotaxane [**3**⊂**DB24C8**]$^{2+}$ from **3**$^{2+}$ and **DB24C8** by slippage at 25 °C and 1.0×10^{-2} M

Solvent system	k_{ON}[b] ($M^{-1}\,s^{-1}$)	$\Delta G^{\neq}_{ON}$[c] (kJ mol^{-1})	k_{OFF}[d] (s^{-1})	$\Delta G^{\neq}_{OFF}$[c] (kJ mol^{-1})	K_a[e] (M^{-1})	ΔG^{0}[f] (kJ mol^{-1})
CD_3CN	4.33×10^{-3}	86.5	1.68×10^{-6}	106.0	2.58×10^{3}	19.5
$CD_3CN/CDCl_3$ (1:1)	2.81×10^{-3}	87.6	2.10×10^{-6}	105.4	1.34×10^{3}	17.8
$CD_3CN/CDCl_3$ (1:2)	1.59×10^{-3}	89.0	3.02×10^{-6}	104.5	5.26×10^{2}	15.5
DMSO-d_6	[g]	—	4.19×10^{-3}	86.6	—	—

[a] The reactions were followed using ^{1}H NMR spectroscopy by monitoring the changes in the relative intensities of the signals associated with the central $^+NCH_2$ group, which resonates as a sharp singlet.

[b] Second-order rate constants (k_{ON}) for the slippage process were obtained from the slope of the plot of 1/[axle] versus time as shown in Figure 5.

[c] The free energies of activation for the slippage ($\Delta G^{\neq}_{ON}$) and extrusion ($\Delta G^{\neq}_{OFF}$) processes were calculated using the relationships $\Delta G^{\neq}_{ON}=-RT\ln((k_{ON})h/kT)$ and $\Delta G^{\neq}_{OFF}=-RT\ln((k_{OFF})h/kT)$, respectively; R, h, and k correspond to the gas constant, the Planck constant, and the Boltzmann constant, respectively.

[d] First-order rate constants for the extrusion process ($\Delta G^{\neq}_{OFF}$) were calculated from the plots of ln[axle] versus time as shown in Figures 6 and 8.

[e] The K_a values were calculated from the relationship $K_a=k_{ON}/k_{OFF}$.

[f] The free energies of association (ΔG^0) were calculated using the relationship $\Delta G^0=-RT\ln K_a$.

[g] The rate for the slippage process could not be measured because the association constant is almost negligible at 25 °C.

was removed by slow evaporation. The residue was dissolved in a minimal amount of acetonitrile and then precipitated with diethyl ether. The yellow solid was collected by filtration and then rinsed with chloroform to remove any excess **DB24C8**. Yield 0.328 g (95%). ^{1}H NMR (CD_3CN, 500 MHz) δ 9.24 (d, 4H, J=6.7 Hz), 8.14 (d, 4H, J=6.7 Hz), 6.66–6.76 (m, 8H), 5.59 (s, 4H), 5.04 (m, 2H), 3.97–4.02 (m, 24H), 1.49–1.99 (m, 20H). $^{13}C\{^1H\}$ NMR (CD_3CN, 75.4 MHz) 161.4, 148.0, 147.5, 145.6, 127.5, 122.1, 113.3, 76.6, 71.3, 71.0, 68.4, 59.4, 31.7, 25.9, 23.8. IR (KBr) ν (C═O) 1729 cm^{-1}. HR-ESI-MS: m/z [**3**⊂**DB24C8**·BF_4]$^+$ calcd: 973.4654, found: 973.4655.

4.3. X-ray crystal structure determination

The crystal was mounted on a short glass fiber attached to a tapered copper pin. A full hemisphere of data were collected with 30 s frames on a Bruker APEX diffractometer fitted with a CCD based detector using Mo Kα radiation (0.71073 Å). Decay (<1%) was monitored by 50 standard data frames measured at the beginning and end of data collection. Diffraction data and unit-cell parameters were consistent with the assigned space group. Lorentzian polarization corrections and empirical absorption corrections, based on redundant data at varying effective azimuthal angles, were applied to the data set. The structure was solved by direct methods,

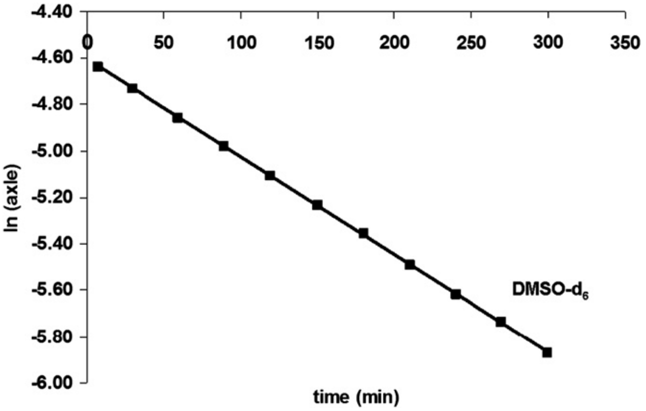


Figure 8. A plot of ln(concentration) versus time for the first-order decomposition of [2]pseudorotaxane [**3**⊂**DB24C8**]$^{2+}$ into axle **3**$^{2+}$ and **DB24C8** in DMSO at 25 °C.

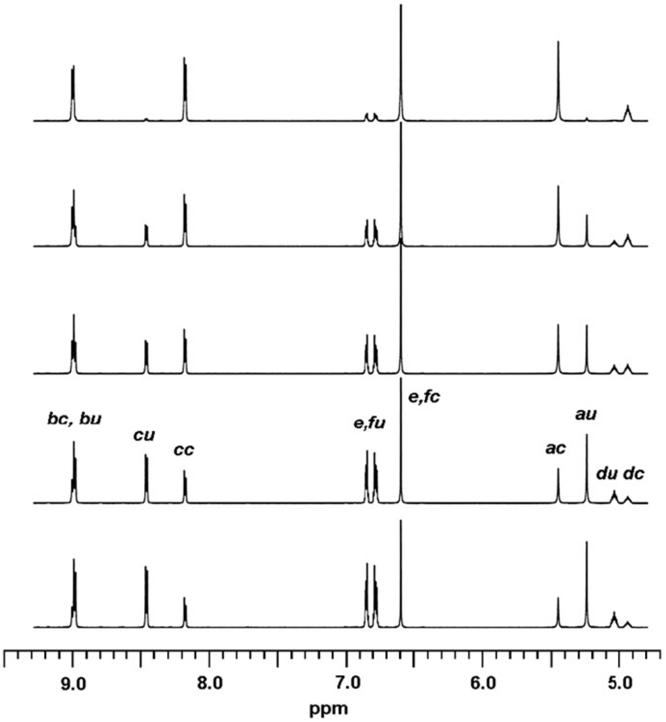


Figure 7. Partial ^{1}H NMR spectra (500 MHz, DMSO-d_6, 1.0×10^{-3} M, 25 °C) showing decomposition of the [2]pseudorotaxane [**3**⊂**DB24C8**]$^{2+}$ into **3**$^{2+}$ and **DB24C8**. From top to bottom: time=7, 90, 150, 240, 300 min. Labeling scheme is shown in Scheme 1; designations c=complexed and u=uncomplexed.

Table 2
X-ray crystal data, solution, and refinement parameters

Compound	[**3**⊂**DB24C8**][BF_4]$_2$·2($MeNO_2$)
Formula	$C_{52}H_{72}B_2F_8N_4O_{12}$
Formula weight	11,182.76
Crystal system	Monoclinic
Space group	$P2_1/c$ (14)
T (K)	173(2)
a (Å)	14.272(3)
b (Å)	16.144(3)
c (Å)	12.297(2)
α (°)	
β (°)	94.467(3)
γ (°)	
V (Å^3)	2824.9(10)
Z	2
ρ (g cm^{-3})	1.390
μ (mm^{-1})	0.118
Reflections used	4967
Variables	370
R_1 [$I>2\sigma(I)$][a]	0.0833
R_1 (all data)	0.2102
R_2w [$I>2\sigma(I)$][b]	0.1301
R_2w (all data)	0.2450
GoF on F^2	1.022

[a] $R_1=\Sigma||F_o|-|F_c||/\Sigma|F_o|$.

[b] $R_2w=[\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$, where $w=q[\sigma^2(F_o^2)+(aP)^2+bP]^{-1}$.

completed by subsequent Fourier syntheses and refined with full-matrix least-squares methods against $|F^2|$ data. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were treated as idealized contributions. Scattering factors and anomalous dispersion coefficients are contained in the SHELXTL 5.03 program library.[8] Crystal data collection, solution, and structure refinement parameters are listed in Table 2. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 680883. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 (0) 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgements

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