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# Synthesis and X-Ray Structure of a Ditopic Ligand for Constructing Crown Ether-Based Metalloassemblies

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# Synthesis and X-Ray Structure of a Ditopic Ligand for Constructing Crown Ether-Based Metalloassemblies

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*A novel dialkylammonium salt, 1.$PF_6$, bearing a pyridyl group has been prepared and characterised by x-ray crystallography: triclinic space group P-1, a = 8.8141(1), b = 9.8902(2), c = 10.2611(1), Å and α = 82.008(1)°, β = 85.212(1)°, γ = 71.058(1)°, Z = 2, R = 0.0542 for 3902 independent reflections. The hydrogen-bonded tape generated within the crystal lattice is augmented by water molecules between the divided units in an N-H…O and O-H…$N_{py}$ manner. The nature of the [2]pseudorotaxane formed upon the addition of DB24C8 to 1.$PF_6$ ($K_a = 2293\ M^{-1}$) is characterised in the solid state (monoclinic space group P $2_1/c$, a = 14.3808(4), b = 15.0194(4), c = 18.2599(6), Å and β = 95.723(1)°, Z = 4, R = 0.0766 for 9313 independent reflections) by hydrogen bonds between $NH_2$ and $CH_2$ groups of the guest with polyether oxygens of the crown ether. These hydrogen bond distances vary with close contacts between 2.01 and 2.58 Å $^1$H NMR spectroscopy and mass spectrometry further support the presence of the [2]pseudorotaxane in solution.*

**Keywords:** $^1$H NMR spectroscopy; hydrogen bonding; pseudorotaxane; supramolecular chemistry; X-ray crystal structure

## INTRODUCTION

The success of the photosynthetic reaction centre [1] as an energy transduction device depends on the assembly being able to exert control over the separation and orientation of the various redox centres and the nature of the medium separating them. These design features expedite highly efficient electron transfer (ET) along a defined pathway. The same design principles must be adhered to in order to construct viable mimics (Fig. 1) that reflect either the complexity or

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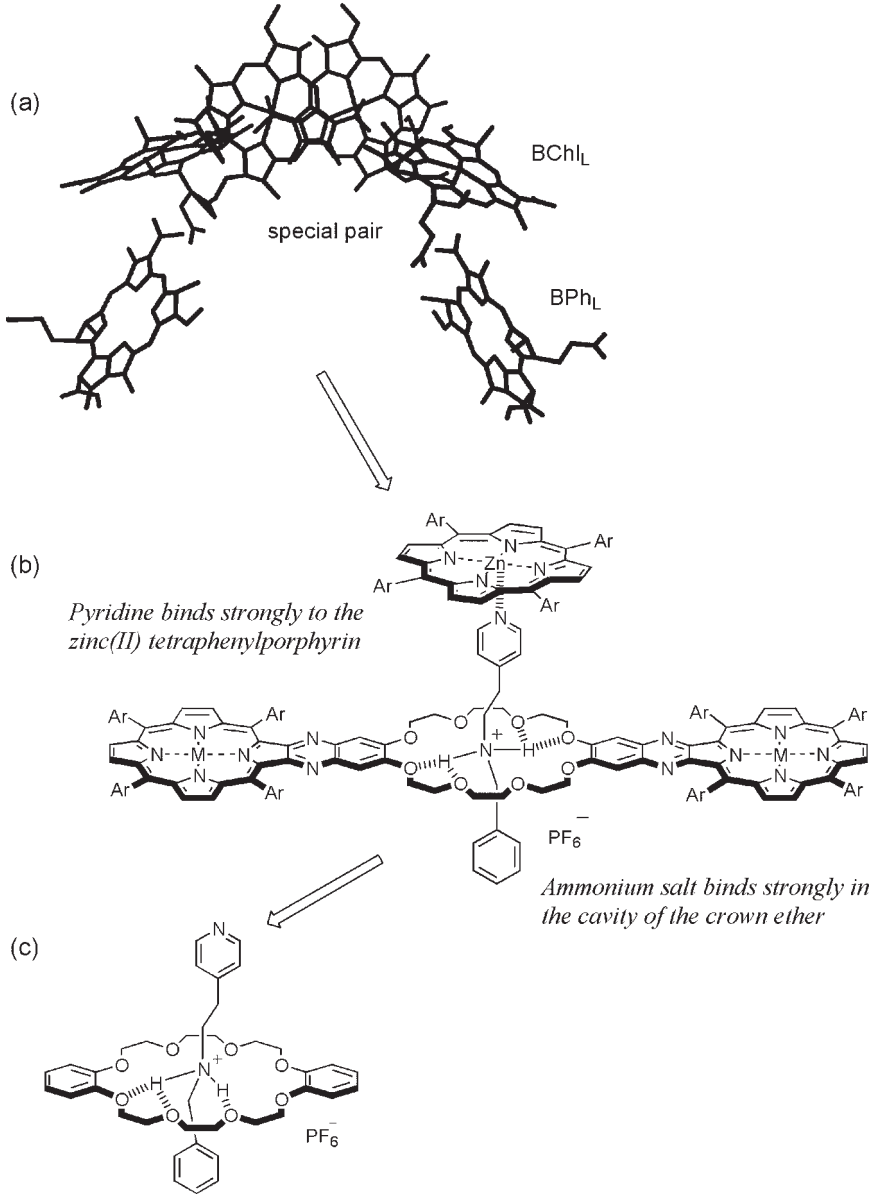



**FIGURE 1** (a) A portion of the crystal structure of the photosynthetic reaction centre of *Rhodopseudomonas viridis* showing the spatial relationship between the special pair, bacteriochlorophyll and bacteriopheophytin, (b) A biomimetic model of the same region using non-covalent bonding to assemble the supramolecular scaffold, (c) The foundation of this biomimetic structure is the [2]pseudorotaxane formed between DB24C8 and a dialkylammonium salt.

mode of action of naturally occurring reaction centres [2]. In order for these goals to be realised, more has to be learnt about the interplay of molecular components bearing donor and acceptor groups and the appropriate design principles needed for the generation of such complex systems.

Figure 1 (a) A portion of the crystal structure of the photosynthetic reaction centre of *Rhodopseudomonas viridis* showing the spatial relationship between the special pair, bacteriochlorophyll and bacteriopheophytin, (b) A biomimetic model of the same region using non-covalent bonding to assemble the supramolecular scaffold, (c) The foundation of this biomimetic structure is the [2]pseudorotaxane formed between DB24C8 and a dialkylammonium salt.

We have been investigating the use of crown ethers as a possible organising precept [3], primarily through the antipodal functionalisation of these units with photo-active [4] and redox-active [5] chromophores. The elaboration of these simple systems into more complex photosynthetic mimics, such as that displayed in Figure 1, requires structural motifs that can elevate the structure from a pseudo two-dimensional molecule into a third dimension. In this regard, the affinity of crown ethers for dialkyl- and diaryl-ammonium salts [6–10], giving rise to [n]pseudorotaxane assemblies, offered a plausible approach.

In this paper, we add to the extensive work done by Stoddart, Busch and others [6,11–13] by describing the synthesis and solid-state characterisation of the ditopic ligand, $1.PF_6$, bearing both a pyridine and a dialkylammonium group, and extend the study into the investigation of its complex with DB24C8, both in solution and the solid-state.

## EXPERIMENTAL

Materials: benzylamine, 4-vinylpyridine and ammonium hexafluorophosphate were purchased from Aldrich and used without further purification. Glacial acetic acid, methanol, dichloromethane and diethyl ether were obtained from BDH Laboratory Supplies and used without further purification. Melting points were measured on a Stuart Scientific melting point apparatus, SMP3. Infrared spectra were recorded on a Bruker Equinox 55 Fourier transform infrared spectrophotometer, using an ATR microsampler (Specac Golden Gate ATR with single bounce diamond top-plate). $^{1}H$ and $^{13}C$ NMR spectra were recorded on Bruker DPX 300 MHz or DRX 400 MHz spectrometers. Low resolution electrospray ionisation (ESI) spectra were recorded on a Micromass Platform spectrometer (QMS-quadrupole mass electrospray). High resolution ESI spectra were recorded on a Bruker BioApex 47e Fourier Transform Mass Spectrometer fitted with an Analytica ESI

source. X-ray crystal diffraction patterns were determined using an Enraf Nonius FR590 KappaCCD Diffractometer with MoKα radiation at 123 K, and were solved and refined using SHELXS97 and SHELXL97, respectively [14, 15].

| | |
|---|---|
| **1**.$PF_6$ | CCDC 213720 |
| DB24C8.**1**$PF_6$ | CCDC213362 |



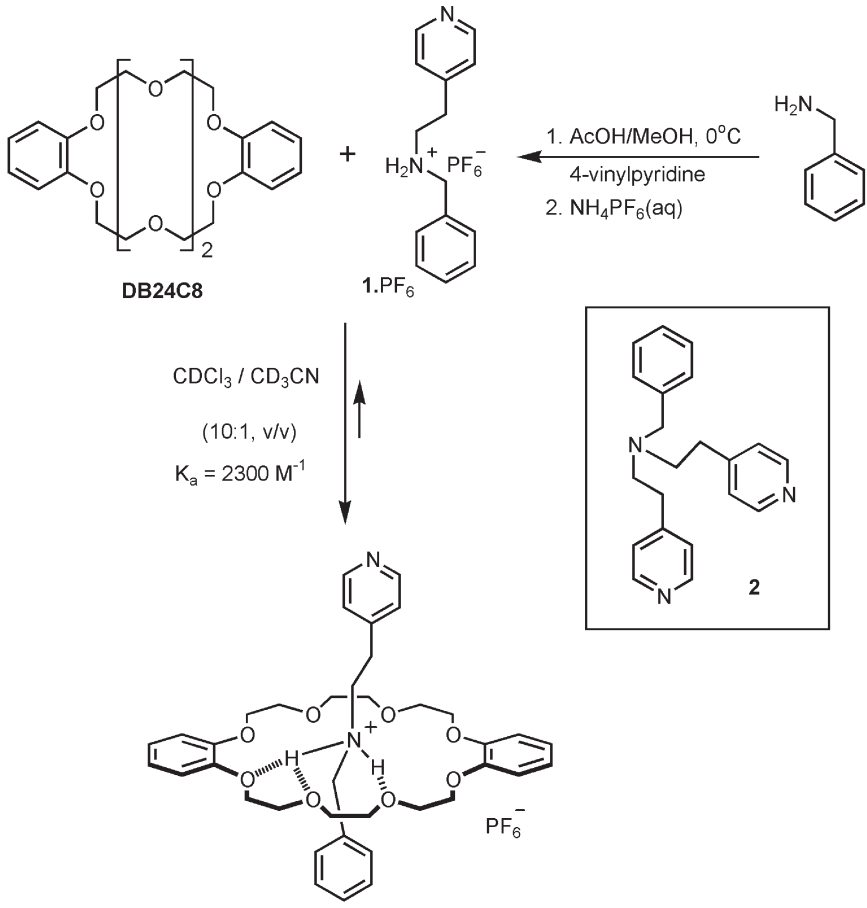
### *N*-benzyl-(2-(pyridin-4-yl)ethyl)ammonium hexafluorophosphate, 1.$PF_6$

Glacial acetic acid (1.11 g, 19 mmol) was added drop-wise to an ice-cold solution of benzylamine (1.96 g, 18 mmol) in methanol (10 mL). The solution was warmed to room temperature and 4-vinylpyridine (1.95 g, 19 mmol) added. The resultant mixture was refluxed (12 h), cooled to room temperature, and the solvent removed under reduced pressure. The residue was poured onto ice, and the mixture made strongly basic with 4 M NaOH. The basic mixture was extracted with $Et_2O$ ($3 \times 30$ mL), dried over anhydrous $Na_2SO_4$, and the solvent removed under reduced pressure giving a yellow oil (3.67 g). This oil was redissolved in $Et_2O$ (10 mL), and a saturated aqueous solution of $NH_4PF_6$ was added. After standing overnight, the precipitate was collected, washed with a mixture of $CH_2Cl_2/Et_2O$ (1:1, $3 \times 50$ mL), water ($1 \times 50$ mL), then air-dried. The product, **1**.$PF_6$, was obtained as a cream-coloured solid (2.70 g, 41 %). Melting point: 185°C with decomposition. $\upsilon_{max}$ (neat): 3223 m, 2558 w, 2324 w, 1612 m, 1424 m, 1405 m, 1225 w, 1070 w, 1023 w, 1006 w, 966 w, 818 s, 747 m, 697 $cm^{-1}$ m. $^1$H NMR (300 MHz, $CD_3CN$): δ 2.91, 2 H, m, $N^+$-$CH_2$; 3.32, 2 H, m, py-$CH_2$; 4.19, 2 H, s, $CH_2$; 7.25, 2 H, m, py-H; 7.46, 5 H, m, ArH; 8.50, 2 H, m, py-H. $^{13}$C NMR (75 MHz, $CD_3CN$): δ 32.0, 48.8, 52.8, 125.3, 130.2, 130.8, 121.1, 131.5, 146.5, 151.0. HR ESI-MS (+ve) $m/z$: found 213.1385 $[M]^+$, calculated $C_{14}H_{17}N_2^+ = 213.1392$.

## RESULTS AND DISCUSSION

### Synthesis

The synthesis of **1**.$PF_6$, as outlined in Scheme 1 follows a variation of the method described by Reich and Levine [16]. Crucial to the use of **1**.$PF_6$ as a ditopic ligand is the generation of the ammonium salt over the pyridinium salt, which would hinder complexation studies with, for example, Zn(II) tetraphenylporphyrin (Fig. 1b). This is achieved by taking advantage of the difference in $pK_a$ between the amine and




**SCHEME 1**

pyridine nitrogens. The use of methanol as a solvent also precludes the formation of the dipyridylated product **2**, which otherwise formed in high (>50%) yield [17].

Crystals suitable for X-ray crystallography were grown by slow evaporation of **1** from a 1:1:1 mixture (v/v) of $Et_2O/CH_2Cl_2/NH_4PF_6$(aq.). The crystal structure is dominated (Fig. 2a,b) by hydrogen bonded tapes consisting of molecules of **1** linked from the ammonium hydrogens of one molecule to the pyridine nitrogen of a second molecule by N–H...O and O–H...$N_{py}$ interactions of the linking water molecules [H(1B)...O(1) = 1.78Å, H(1A)...N(2)#2 = 1.88 Å]. The tapes, in turn, are separated from each other by $PF_6^-$ counterions (Fig. 2c).

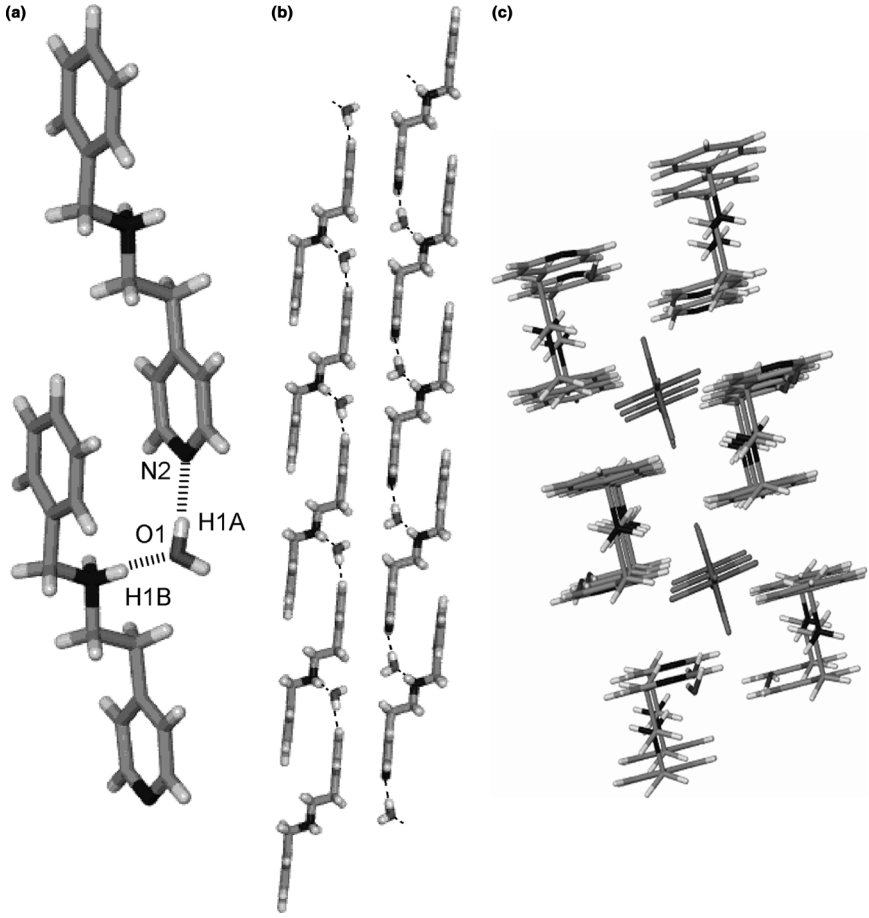



**FIGURE 2** (a) Crystal structure of **1**.$PF_6$, H(1B)...O(1) = 1.78, H(1A)...N(2)#2 = 1.88, Å (b) the tape-like arrangement of the crystal array, and (c) separation of the tapes by $PF_6^-$ counterions.

Figure 2. (a) Crystal structure of 1.$PF_6$, H(1B)...O(1) = 1.78, H(1A)...N(2)#2 = 1.88, Å (b) the tape-like arrangement of the crystal array, and (c) separation of the tapes by $PF_6^-$ counterions.

## Solution Studies – [2]pseudorotaxane

$^1$H NMR spectroscopy and mass spectrometry have been used successfully in the past to validate the existence of pseudorotaxanes generated between ammonium salts and crown ethers [6,9,12,13,18,19].

The $^1$H NMR spectrum obtained upon mixing equimolar amounts of 1.$PF_6$ and DB24C8 in 10:1 $CDCl_3/CD_3CN$ (Fig. 3) indicates the presence of signals attributable to both complexed and uncomplexed species. Since signals attributed to **1**.$PF_6$ and DB24C8 resonate at the same δ values as in the $^1$H NMR spectra of the individual components (Fig. 3), the stoichiometry of the complex can be readily determined as 1:1 by integration of relevant probe protons on both the thread and wheel components. The ability to observe signals for both complexed and uncomplexed species at 400 MHz and 300 K can be ascribed to a situation of slow kinetics between complexation and decomplexation of the [2]pseudorotaxane. This situation also conveniently permits determination of an association constant ($K_a = 2293\ M^{-1}$) by single

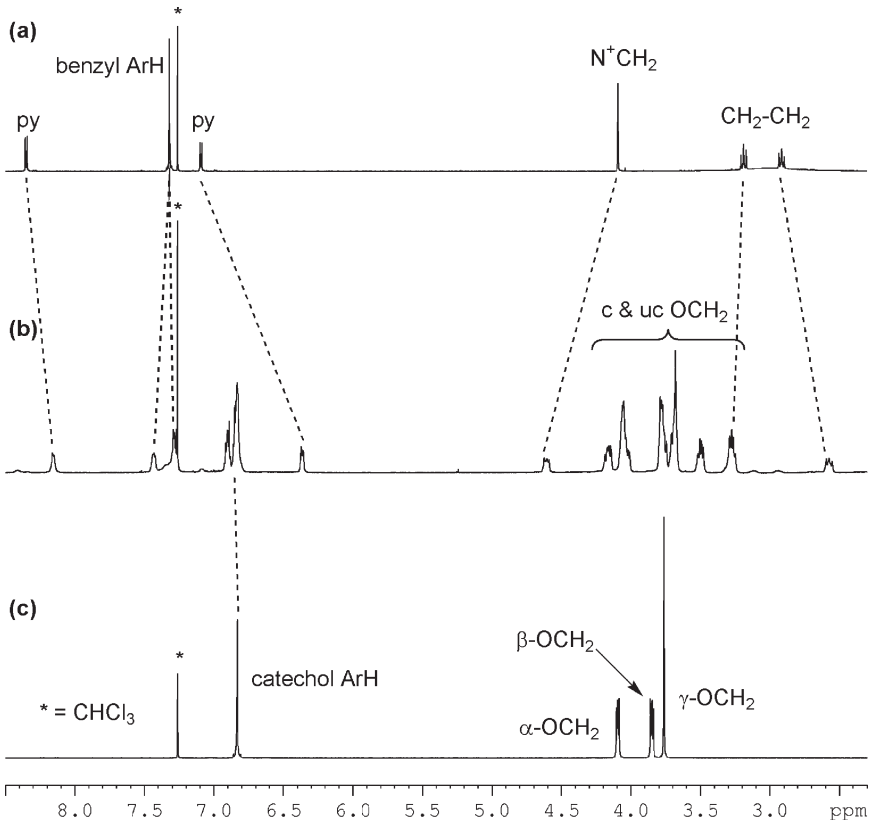



**FIGURE 3** 400 MHz $^1$H NMR spectra of (a) **1**.$PF_6$, (b) **1**.$PF_6$ and DB24C8, and (c) DB24C8, in 10:1 $CDCl_3$/ $CD_3CN$. Insolubility of **1**.$PF_6$ in $CDCl_3$ precluded the use of neat solvent.

point analysis [20]. As a result of the use of mixed solvents, the value of the association constant is lower than that expected in $CDCl_3$, consistent with the results obtained by Stoddart [8] in a number of organic solvents.

Figure 3. 400 MHz $^1$H NMR spectra of (a) 1.$PF_6$, (b) 1.$PF_6$ and DB24C8, and (c) DB24C8, in 10:1 $CDCl_3$/ $CD_3CN$. Insolubility of 1.$PF_6$ in $CDCl_3$ precluded the use of neat solvent.

Characteristic within the $^1$H NMR spectrum of the complex is the appearance of a line-broadened triplet at $\delta$ 4.60, attributable to the $N^+CH_2$-Ph protons of **1**. These protons experience a downfield shift upon complexation, due to the deshielding effects of hydrogen bonding with crown ether oxygens. Inclusion of **1**.$PF_6$ into the 24C8 cavity influences the chemical shift of the guest protons in different ways. Upon complexation, most protons of the guest are shifted upfield in relation to their proximity to the catechol rings of the crown ether, while phenyl protons remain largely unaffected, consistent with the crystal structure for the complex (Fig. 4).

Mass spectral analysis provides further evidence to support the formation of the complex in solution. Clearly evident are peaks corresponding to the 1:1 complex $[DB24C8 + \mathbf{1}]^+$ ($m/z$ 661). Also evident are strong peaks at $m/z$ 213 and 471, corresponding to $\mathbf{1}^+$ and $[DB24C8 + Na]^+$.

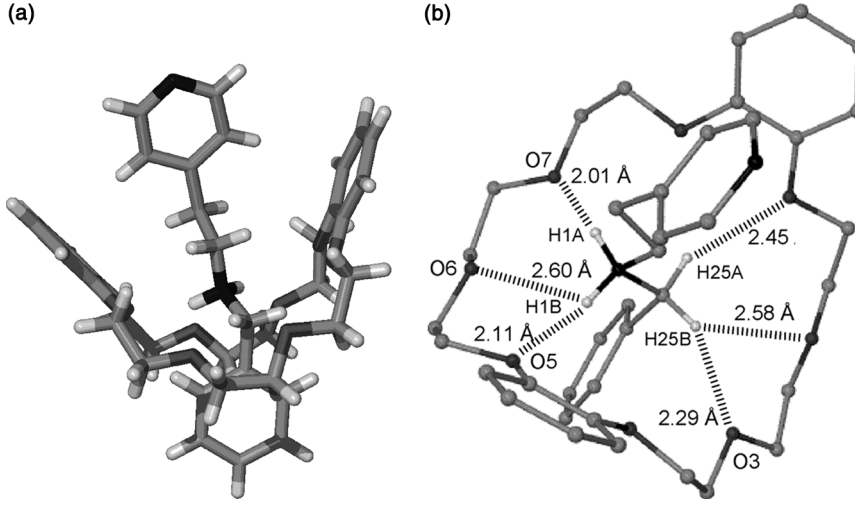



**FIGURE 4** (a) a view of the $\psi$-shaped complex showing the cupped nature of the DB24C8 macrocycle, and (b) hydrogen bonds within the complex.

## Solid State Studies–[2]pseudorotaxane

Crystals suitable for X-ray diffraction measurements were obtained by slow evaporation of a 1:1 mixture of **1**.$PF_6$ and DB24C8 in 10:1 $CDCl_3/CD_3CN$. The X-ray crystal structure clearly shows that **1**.$PF_6$ is threaded through the centre of the crown ether cavity, forming the [2]pseudorotaxane. The crown ether exists in a cupped (dihedral angle between catechol planes = 64°; closest contact of catechol rings = 7.4 Å) rather than flat conformation, the effect of which is to stabilise the complex through a CH...$\pi$ interaction (H(38)...Ar = 2.8 Å), brought about by the orthogonal arrangement of the catechol rings to the pyridine of **1**.$PF_6$. This psi-like complex ($\psi$) differs from that observed for the complex DB24C8.$NH_4PF_6$ [21], in which the crown ether completely encapsulates the ammonium cation. The encapsulation is due to participation of all four hydrogen atoms of the ammonium cation in hydrogen bonding interactions with the 24C8 oxygens, causing the crown ether to fold and twist to allow for maximal interaction. In contrast to $NH_4PF_6$, the ligand **1**.$PF_6$ only offers two ammonium hydrogens for participation in hydrogen bonding interactions with DB24C8 [H(1B)...O(7) = 2.01 Å; H(1A)...O(5) = 2.11 Å; H(1A)...O(6) = 2.60 Å]. However, as can be seen from the crystal structure (Fig. 4), the ligand is further oriented such that its $N^+CH_2$-Ph hydrogens are also able to participate in weaker hydrogen bonding with the crown ether oxygens [H(25B)...O(1) = 2.45 Å; H(25A)...O(3) = 2.29 Å; H(25A)...O(2) = 2.58 Å], contributing significantly to the stability of the [2]pseudorotaxane.

Figure 4. (a) a view of the $\psi$-shaped complex showing the cupped nature of the DB24C8 macrocycle, and (b) hydrogen bonds within the complex.

## CONCLUSIONS

We have found that the ditopic ligand **1**.$PF_6$ is able to form a [2]pseudorotaxane in both solution and solid state. This ligand is placed orthogonally with respect to the encircling host, DB24C8, differing from previously studied dialkylammonium guests [8,22], and is stabilised by six hydrogen bonds of variable strengths. Additionally, the conformation of the DB24C8 macrocycle about the thread does not obstruct the pyridine arm of **1**.$PF_6$, which can potentially axially ligate to redox-active metalloporphyrins [23]. Indeed, preliminary $^1H$ NMR and mass spectroscopic results from complexations between crown ether, **1**.$PF_6$ and the metalloporphyrins, Zn(II)tetraphenylporphyrin and Ru(II)(CO)tetraphenylporphyrin, have indicated that the three-component

complex is able to form in solution. Therefore, we anticipate that steric properties of the porphyrin end groups may circumvent folding of the crown ether for the pseudorotaxane formed between **1**.$PF_6$ and bis-porphyrin-24-*crown*-8 (Figure 1b).

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