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Anion-Templated Rotaxane Formation

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Abstract: The development of an acyclic chloride anion template in which the chloride anion is coordinatively unsaturated and available for subsequent complexation to various hydrogen bond donating components is described. This template orients a neutral hydrogen bond donating ligand and a pyridinium cation orthogonally to one another. Incorporation of second-sphere interactions between the ligand and the pyridinium cation improved the efficacy of the chloride template. These results were exploited in the construction of a chloride anion-templated [2]rotaxane which, after anion template removal, was studied with regards to its anion recognition properties. Encirclement of the neutral macrocycle around the dumbbell-shaped pyridinium cation in the [2]rotaxane produced a dramatic increase in its selectivity for chloride anions as compared to the noninterlocked cation. This is interpreted as a function of the anion template used to create the [2]rotaxane superstructure.

Introduction

The synthesis of macrocyclic compounds and supramolecular arrays in recent years has been facilitated largely by the use of template methodology to their construction.[1] To date, most of these schemes depend on the use of neutral or cationic species to achieve the desired template effect, utilizing a variety of noncovalent forces such as metal−ligand coordination, hydrogen bonding, $\pi-\pi$ stacking, and solvophobic interactions.[1,2] The absence of anionic species as more general participants in this arena is often attributed to the relatively small ratio of charge to radius and sizable solvation energy as compared to cations.[3] However, there are a growing number of reports of anion templation accumulating in the literature, demonstrating the efficacy of such an approach. Examples include Hawthorne's mercuracarborands, Lehn's circular double helicates, Fujita's coordination nanotubes, Mingos and Vilar's amidinothiourea cages, Ward and McCleverty's tetrahedral Co^{2+} boxes, and Dunbar's tetranickel box, all of which depend on particular anionic species for their formation.[4]

It is within this context that there are very few instances of template synthesis employing anions in the construction of interpenetrated or mechanically bonded compounds (termed pseudorotaxanes, rotaxanes, catenanes, and knots). Stoddart et al. have published solid-state evidence for hexafluorophosphate anion templation in the formation of a [2]pseudorotaxane from dibenzylammonium threads and a polyether macrocycle.[5] In a similar system, Montalti and Prodi determined that threading of a dialkylammonium axle through a dibenzo-24-crown-8 wheel to form a [2]pseudorotaxane could be controlled by the interaction of the cation with chloride anions in solution.[6] The only examples of anion-templated formation of interlocked species are those developed by Vögtle et al., and studied by others, in which phenolates, thiophenolates, and sulfonamide anions are noncovalently bound to a cyclic tetralactam.[7,8] Subsequent covalent trapping of these intermediates by a

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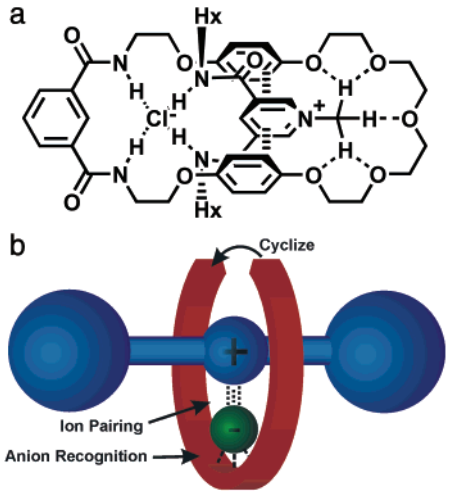

Figure 1. (a) An anion-templated [2]pseudorotaxane. (b) The "clipping" method for rotaxane formation based on an anion template.

sterically demanding electrophile generates rotaxane products with some of the highest yields reported for mechanically bonded systems. Vögtle's method depends on reaction of the anionic component during formation of the products, eliminating a possible contribution to their function. Hence, the anionic template does not "live on" within the resulting construction and, as such, is unavailable for manipulation of its co-conformational disposition. The conservation of the anion template within such a structure has the added potential of creating an anion recognition domain specific to the template used to construct it.

We have recently shown that chloride anions can be used to template the formation of [2]pseudorotaxanes selectively.[9] The basis of this approach involves a cationic thread designed to partially fill the coordination sphere of the strongly ion-paired chloride anion in a noncompetitive solvent. Thus, the anion remains coordinatively unsaturated, leaving an empty meridian for complexation by a neutral hydrogen bond donating ligand disposed orthogonally to the cation (Figure 1a). Selectivity observed in this system for chloride anions over other anionic species is a function of anion recognition by both the cation and the neutral ligand. This preference is further established through effective second-sphere coordination of the cationic thread by the remaining components of the macrocyclic framework, which act in concert with the anion recognition event. Participation of a less complementary anion in this design results in a disparity with the coordination environment created in the superstructure and an ensuing reduction in the ability of the cationic thread to reside within the cavity of the macrocycle.

Considering these results, our efforts have now turned to the question of whether this anion template approach can be applied to the more challenging task of constructing interlocked molecules and what possible properties these products might display. The obvious synthetic route to generate a rotaxane by "stoppering" the ends of a preformed pseudorotaxane[10] has

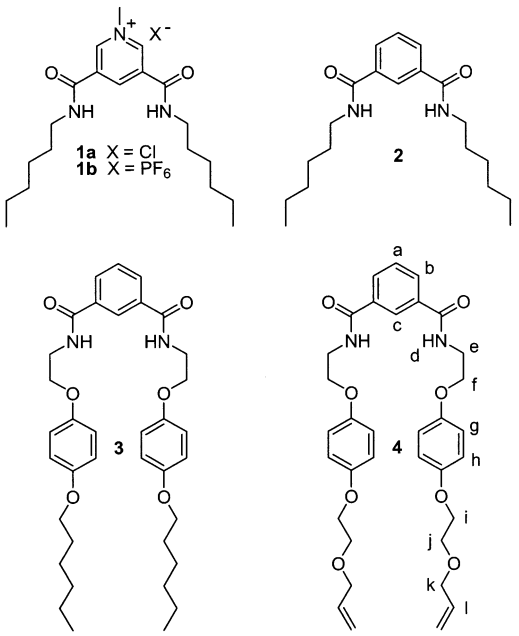

Figure 2. Structures of ion pairs **1** and hydrogen bond donating ligands **2**, **3**, and **4**.

proved to be problematic, prompting the exploration of other methods to generate the desired mechanical bond. This has resulted in the selection of a "clipping" methodology (Figure 1b), which has met with success in other systems.[11] Herein, we describe the development of an acyclic chloride anion template and its application in the synthesis of a [2]rotaxane which is evaluated in terms of its use as a chloride anion receptor.

Development of an Acyclic Anion Template

Three ligands were initially synthesized and assessed for their ability to coordinate the chloride anion in the ion pair **1a** (Figure 2). Crabtree has shown that simple isophthalamide ligands are good receptors for chloride anions in noncompetitive solvents.[12] The syntheses of **1**, **2**, and **5** have been described elsewhere.[9] Compounds **3** and **4** were synthesized from **5** by S_N2 addition to 2 equiv of either 1-bromohexane or the tosylate of ethyleneglycol monoallyl ether, respectively, in a mixture of DMF and K_2CO_3 (Scheme 1).

Ligand **2** incorporates a chloride-specific anion-binding cleft formed by the amide protons and the isophthalamide ring proton at the 2-position. Likewise, the cation $\mathbf{1}^+$ contains the same functionality in addition to the tight ion-pairing provided by the positively charged pyridinium ring, serving to locate the anion within its hydrogen bonding cleft in nonpolar solvents. The strength and nature of the ligation of **1a** by anion receptor **2** were established by titration of the ligand with the ion pair in

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Scheme 1. Synthesis of **3** and **4**

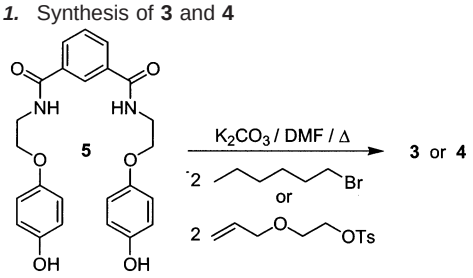

Table 1. Association Constants, Free Energies of Complexation, and Selected ^{1}H NMR Shifts of **2**, **3**, and **4** with **1a** in CD_2Cl_2-d_2 at 298 K

			chemical shift ($\Delta\delta$ in ppm)[a]		
complex	K_a (M^{-1})	$-\Delta G$ (kJ mol^{-1})	c	d	g and h
1a·2	25	7.98	0.02	0.14	
1a·3	50	9.69	0.08	0.23	−0.03
1a·4	260	13.8	0.31	0.70	−0.19

[a] Shifts determined from a 1:1 mixture of the two components at 5×10^{-3} M.

methylene chloride and by analyzing the resulting shifts in the ^{1}H NMR spectra. As can be seen in Table 1, the shifts of both the amide and the aryl protons in the ligand are small, and the calculated association constant (25 M^{-1}, $-\Delta G = 7.98$ kJ mol^{-1}) is low. This is interpreted as a consequence of strong polarization of the chloride anion within the cleft of the cation, making it a poor hydrogen bond acceptor and resulting in a weak interaction with hydrogen bond donating ligand **2**. A similar titration of **2** with **1b** displayed no observable change in the system, confirming the assumption that the association is a result of chloride anion recognition.

Ligands **3** and **4** were designed to investigate whether second-sphere coordination of the chloride anion could improve the anion template interaction. Ligand **3** contains electron-rich hydroquinone rings in its pendant arms, which were expected to reach around the chloride anion and engage the electron-poor pyridinium ring in a classic donor−acceptor π-stacking interaction.[13] This modification yields a modest increase in the free energy of association over that of **2** ($K_a = 50$ M^{-1}, $-\Delta G = 9.69$ kJ mol^{-1}) when titrated with **1a**. The magnitudes of the shifts of the amide and isophthalamide ring protons also increase by a significant margin in both cases, indicating a greater ability of the ligand to participate in hydrogen bonding with the anion. The presence of π-stacking between the ligand and the cation is revealed by small upfield shifts of the hydroquinone protons during the titration. This is further demonstrated by the observation of a charge-transfer absorption at approximately 380 nm upon the admixture of the two colorless components, conferring a pale yellow color to the solution (Figure 3).

Ligand **4** includes both hydroquinone rings in its structure as well as the addition of terminal ether linkages designed to augment the second-sphere coordination of the chloride anion by providing C−H···O hydrogen bonds to the N^+−Me group and α-protons of the pyridinium ring in **1a**. The success of this strategy is borne out by the resulting increase in the free energy of association ($K_a = 260$ M^{-1}, $-\Delta G = 13.8$ kJ mol^{-1}) over the other two ligands. This enhancement is again exhibited in

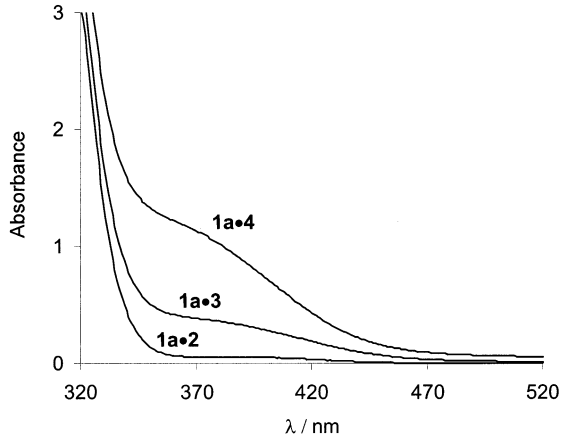

Figure 3. UV−vis spectra of 1:1 mixtures of **1a** with **2**, **3**, and **4** in methylene chloride at 5×10^{-3} M.

the observation of the amide and isophthalamide ring protons of **4**, which now experience marked downfield shifts during the titration with **1a**, denoting an even greater engagement of the anion within its hydrogen bond donating cleft. Larger shifts of the hydroquinone ring protons upfield in the ^{1}H NMR spectra, induced by π-stacking with the pyridinium ring of **4**, are observed, leading to the conclusion that the influence of the terminal ether oxygen atoms serves to orient the rings in this manner to a greater extent. This inference is supported by the UV−vis spectrum of the 1:1 complex of **1a** and **4**, which displays a more intense charge-transfer absorption than that of **1a** with **3** (Figure 3).

As in the case of ligand **2**, titration of **3** or **4** with hexafluorophosphate derivative **1b** gave no detectable change in the system. Thus, the template hinges around the chloride anion recognition event, the efficacy of which can then be enhanced by the inclusion of ancillary groups to provide favorable second-sphere coordination of the cation.

Anion-Templated Rotaxane Formation

As mentioned previously, a logical extension of the successful anion coordination of the ion pair **1a** by ligand **4** is the formation of a rotaxane utilizing this anion template via a clipping procedure. Toward this end, the stoppered thread-shaped compound **8** was synthesized as depicted in Scheme 2. Coupling of the triphenylmethylaniline[15] **6** to 3,5-pyridinedichlorocarbonyl produced dumbbell-shaped pyridine compound **7**, which was then quaternized with methyl iodide to give the corresponding pyridinium thread as the iodide salt **8b**. Anion exchange of **8b** with NH_4Cl or $AgPF_6$ formed the desired **8a** and **8c**, respectively.

The generation of a [2]rotaxane from complex **4·8a** was effected by the use of Grubbs' ring-closing metathesis (RCM) on the allylic end groups of the ligand (Scheme 3).[14] Orientation of the arms of **4** around dumbbell-shaped **8a**, in a manner similar to that described with **1a**, now serves not only to support the chloride anion template but to facilitate the ring closure reaction about the ion pair, resulting in a mechanical bond to produce the [2]rotaxane **9a** in 47% yield. Although the macrocyclization reaction has the possibility of producing both cis and trans

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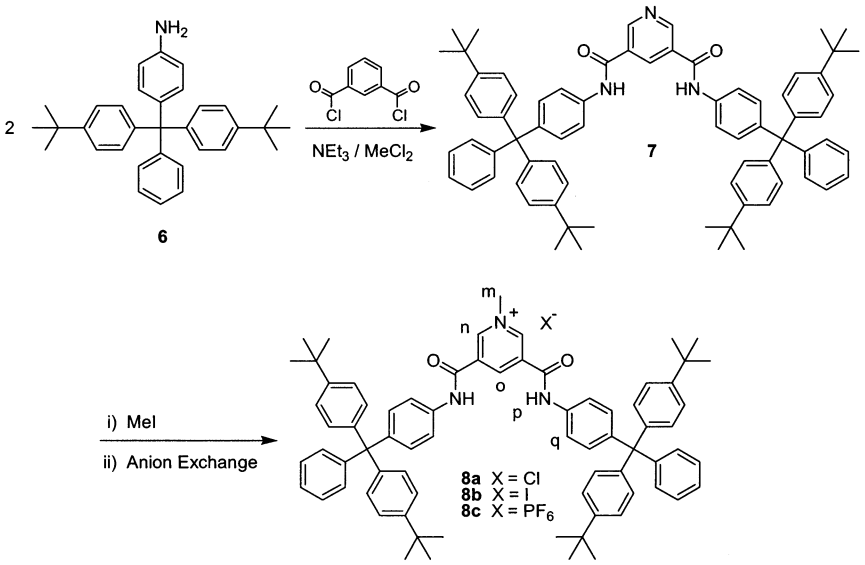
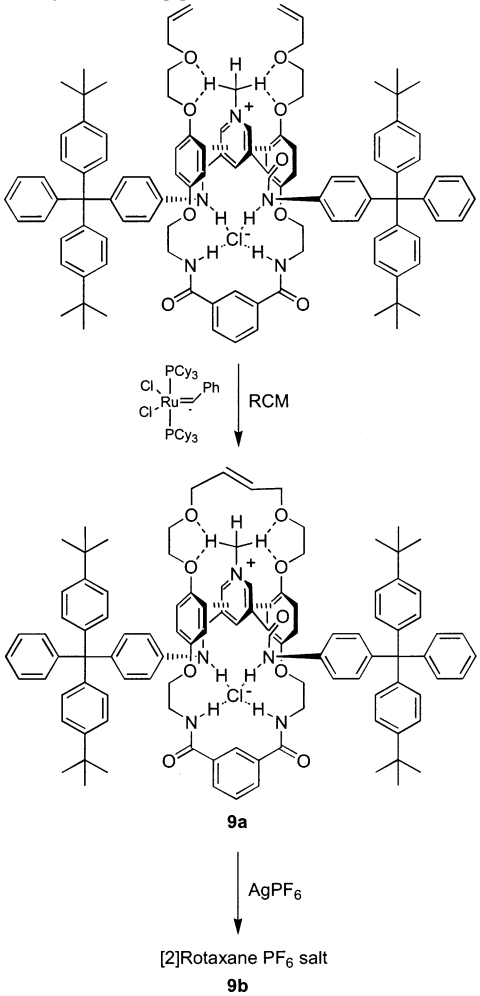
Scheme 2. Synthesis of Ion Pairs **8a**−**c**



Scheme 3. Synthesis of [2]Rotaxanes **9a** and **9b**



isomers at the double bond of the product, only the trans isomer was observed. This is presumably a function of the metathesis reaction, which equilibrates to a thermodynamic mixture, the trans isomer being the more stable derivative.

The analogous reaction of **8c** with ligand **4** failed to produce any detectable mechanically bonded products. This is predictable considering the complete lack of affinity of **4** for the similar ion pair **1b** and further demonstrates the chloride anion template upon which the synthetic scheme depends.[16]

Analysis of the ^{1}H NMR spectrum of **9a** in comparison with **4** and **8a** reveals the interlocked nature of the components (Figure 4). Large downfield shifts of the amide and their mutually *ortho*-isophthalamide ring protons in the macrocycle ($\Delta\delta = 2.24$ and 0.70 ppm, respectively) indicate the complexation of the anion within this hydrogen bond donating cleft. This is mirrored by a concomitant shift upfield of the amide and *para*-pyridinium ring protons in the dumbbell-shaped axle ($\Delta\delta = -0.61$ and -0.99 ppm, respectively), a consequence of polarization of the chloride anion away from the cationic cleft by the neutral wheel. Inclusion of the pyridinium ring within the macrocyclic cavity generates π-stacking-induced upfield shifts of the protons at the *ortho* position ($\Delta\delta = -0.22$ ppm) and those attached to the hydroquinone rings which split into separate signals ($\Delta\delta = -0.42$ and -0.64 ppm) due to the asymmetric environment presented by the interlocked cation. The presence of the pyridinium ring within the cavity is also supported by C−H···O hydrogen bonding between the polyether chain of the macrocycle and the N^+−Me group of the cation, these protons shifting downfield ($\Delta\delta = 0.58$ ppm) as a result of the interaction.

Single crystals of **9a** suitable for X-ray diffraction analysis were grown by the slow diffusion of diisopropyl ether into a chloroform solution of the [2]rotaxane. The structural analysis reveals the expected interlocked product in which the macrocycle encircles the ion pair (Figure 5a). The chloride anion fits well into the cleft of the pyridinium ring, forming hydrogen bonds with five hydrogen atoms directed toward it with X−H···Cl distances of C(55A) 3.633, N(53A) 3.337, C(1A) 3.335, N(13A) 3.403, and C(19A) 3.821 Å and X−H···Cl angles of 147, 168, 155, 167, and 145°, respectively (Figure 5b). These five atoms form a pentagonal girdle for the chloride anion, and least squares planes calculations show that C(55A), N(53A), C(1A), N(13A), and C(19A) are coplanar to within 0.03 Å, the anion being 0.48 Å from the plane described by them. The angles of intersection between the central pyridinium and the

(16) Analogous reactions of **8b** or the bromide pyridinium stoppered thread with **4** also failed to produce any evidence for rotaxane formation.

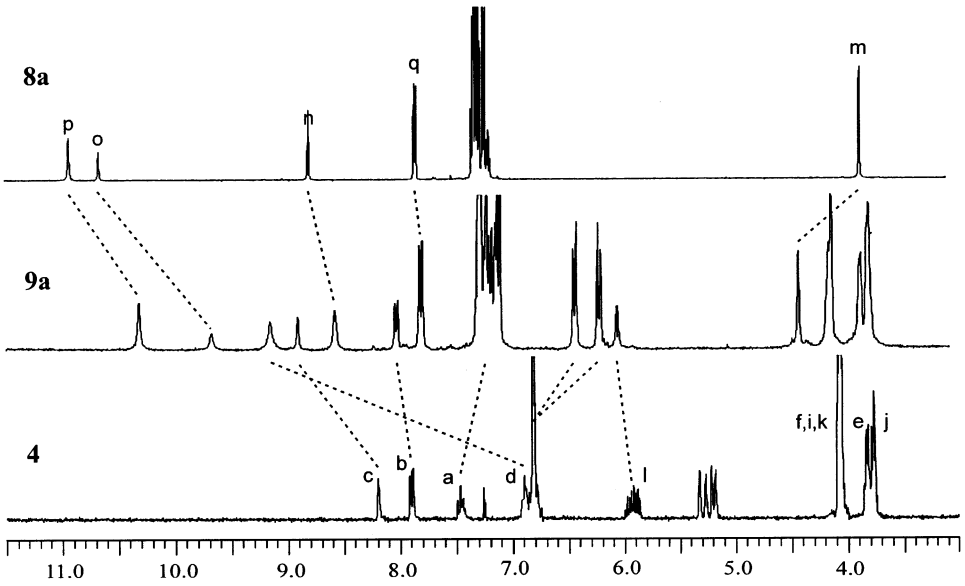


Figure 4. ^{1}H NMR spectra of **4**, **8a**, and **9a** in $CDCl_3$ at 298 K.

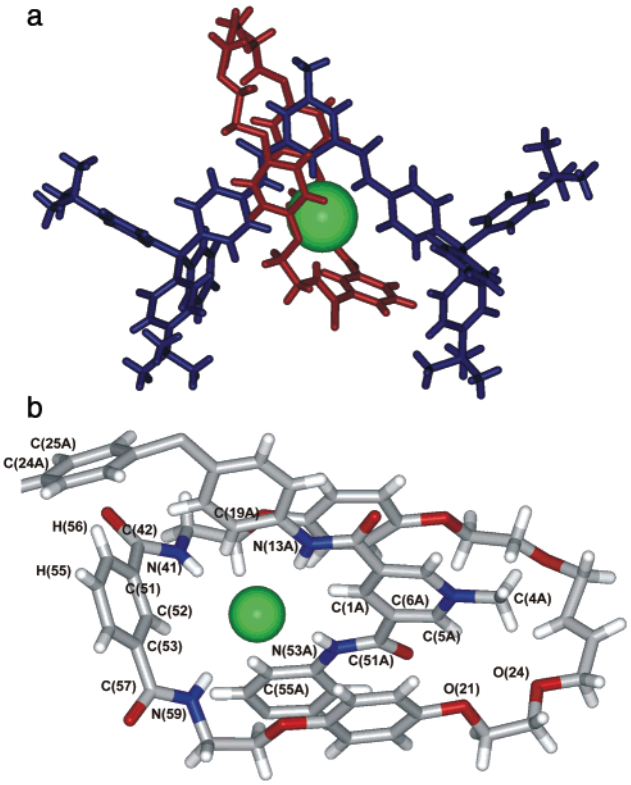


Figure 5. (a) Stick representation of the solid-state structure of [2]rotaxane **9a** illustrating the interlocked nature of the components (red, macrocycle; blue, pyridinium cation; green, chloride anion as CPK sphere). Solvent molecules have been removed, and only one occupancy of the *tert*-butyl groups is shown for clarity. (b) Stick representation of the solid-state structure of [2]rotaxane **9a** with atom numbering scheme (chloride anion as green sphere). Solvent molecules have been removed, and only one *tert*-butyl phenyl group of the (*tert*-butylphenyl)$_2$(phenyl)methyl stoppers is shown for clarity.

two adjacent phenyl rings of the cation are 18.8 and 11.7°, respectively.

By contrast, complexation of the anion by the isophthalamide macrocycle is far more distorted. The chloride anion is close to three hydrogen atoms directed toward the cavity. Distances are N(59) 3.394, C(52) 3.369, and N(41) 3.458 Å. However, in this case, the C−H···Cl and N−H···Cl angles are 167, 112, and 170°, respectively, indicating that only the two nitrogen atoms form strong hydrogen bonds. The orientation of the phenyl ring around C(52) is particularly interesting as it is tilted out of the plane such that N(59)−C(57)−C(53)−C(52) and N(41)−C(42)−C(51)−C(52) torsion angles are 30.3 and −38.0°, respectively. Thus, the chloride anion can be considered as having seven hydrogen bonds, with those of the pyridinium cation forming a pentagonal plane, with the two contributed by the isophthalamide macrocycle being located in approximately axis positions.

The macrocycle surrounds the cation such that the two hydroquinone rings are approximately parallel and sandwich the central pyridinium ring. Least squares plane calculations show that the two phenyl rings in the macrocycle are 6.95 Å apart and are parallel to within 9.4°. These two rings therefore allow enough room for π-stacking with the enclosed cation. However, these two rings do not overlap the pyridinium ring completely but rather two atoms in one amide linkage and two carbon atoms in the pyridinium ring. Thus, atoms N(53A), C(51A), C(6A), and C(1A) form the sandwich, and their plane intersects those of the two hydroquinone rings at angles of 11.5 and 3.5°, respectively. Distances between these four atoms and the overlapping atoms in the hydroquinone rings range from 3.37 to 3.80 Å. The positioning of the pyridinium ring is not symmetric with respect to the macrocycle and veers to one side such that C(5A) is 3.07 Å from O(21) and the N^+−Me group C(4A) is 3.50 Å from O(24). Presumably the reason for this asymmetry is the formation of a hydrogen bond between the methyl group C(4A) and the ether oxygen O(24). The H···O distance is 2.61 Å, and the C−H···O angle is 154°. This hydrogen atom is also directed at the alkenyl double bond of the macrocycle, but the distances from these carbon atoms of 3.57 and 3.66 Å are too long to indicate any C−H···π interaction.

The positioning of the isophthalamide ring is asymmetric with respect to the cation, being tilted toward an aromatic *tert*-butyl phenyl group in one of the stoppers. Indeed, it would appear that the reasons for this asymmetry are C−H···π interactions

Table 2. Association Constants (M^{-1}) Determined by Titration of **8c** and **9b** with TBA Salts of Three Anions in 1:1 $CDCl_3$:CD_3OD at 298 K

	receptor			
anion	**8c**		**9b**	
Cl^-	K_{11}	125	K_{11}	1130
$H_2PO_4^-$	K_{11}	260	K_{11}	300
AcO^-	K_{11}	22 000	K_{11}	100
	K_{12}	140	K_{12}	40

between two of the hydrogen atoms on the phenyl ring of the isophthalamide ring (viz. H(55) and H(56)) and two of the carbon atoms of the *tert*-butyl phenyl stopper (C24A and C25A) with C−H···C distances of 3.36, 3.45, 3.04, and 3.82 Å.

Anion Recognition

One of the central motives for the development of the anion-templated [2]rotaxane described was the possibility of employing it as a chloride-specific anion receptor once the templating anion had been removed. Toward this end, the chloride anion in **9a** was replaced with the noncompetitive PF_6 anion by treatment with $AgPF_6$ in methylene chloride to yield [2]rotaxane **9b**. Comparison of the $CDCl_3$ ^1H NMR spectra of the two rotaxanes indicates that replacement of the chloride anion with hexafluorophosphate does little to displace the cationic dumbbell $\mathbf{8}^+$ from the cavity of the macrocycle in this solvent. This conclusion is supported by the small differences between the π-stacking-induced shifts of the hydroquinone protons ($\Delta\delta = 0.06-0.08$ ppm) in the macrocyclic components of both species with the pyridinium cation.

To determine the effect that rotaxane formation has upon anion recognition, both free dumbbell-shaped **8c** and [2]rotaxane **9b** were titrated with three different anions in a 1:1 mixture of $CDCl_3$:CD_3OD (Table 2), monitoring the resulting shift of the proton at the *para*-position of the pyridinium ring using ^1H NMR. This solvent mixture was chosen due to problems with the solubility of either the starting compounds or the complexed products during titration in other competitive solvents such as DMSO-d_6 or pure CD_3OD. As can be seen from the table, the free axle **8c** shows a much greater preference for binding acetate anions over dihydrogen phosphate and chloride, as well as 1:1 and 1:2 (receptor:anion) binding stoichiometry. Titrations of **8c** with chloride and dihydrogen phosphate anions both display 1:1 stoichiometry, but the association constants are moderate with the least preference for chloride, even though the hydrogen bond donating cleft of the cation is of the correct size and shape for this particular anion. These results may be interpreted as a function of the basicity of the oxoanions being the contributing factor in their greater affinity for this receptor.

Titrations of [2]rotaxane **9b** with the same anions display the opposite selectivity pattern in comparison with **8c**. As a result of encirclement of the pyridinium cation by the macrocyclic ligand, the rotaxane now binds chloride anions more strongly than acetate and dihydrogen phosphate. Acetate is still bound with 1:1 and 1:2 stoichiometries, but the magnitudes of the interactions are reduced greatly in relation to **8c**. The extent of anion recognition with dihydrogen phosphate remains essentially unchanged ($K_a = 300\ M^{-1}$) by the transition to interlocked **9b**. These differences in anion selectivity can be ascribed to the creation of a unique hydrogen bond donating pocket formed by the diamide clefts of the cation and macrocycle in the [2]rotaxane superstructure, which is of complementary topology for the chloride anion. Larger anions such as dihydrogen phosphate and acetate must either penetrate this pocket, which should be sterically demanding and displace the pyridinium cation from the macrocyclic cavity, or bind to the periphery of the rotaxane, a configuration which must involve less than the full complement of possible hydrogen bond donors that the [2]rotaxane can present to a chloride anion.[17]

Conclusions

The results presented here have demonstrated the rational development of a chloride anion template involved in the orthogonal coordination of a neutral hydrogen bond donating ligand and a pyridinium cation. Efficacy of the template was improved by the incremental incorporation of π-stacking and hydrogen bond second-sphere interactions between the cationic and neutral components, which in concert aid the complexation of the chloride anion template. This anionic template was then applied to the formation of a [2]rotaxane by a clipping procedure using ring-closing metathesis. Comparison of the anion recognition properties of the dumbbell-shaped pyridinium cation and the [2]rotaxane derived from it has illustrated that incorporation of a macrocyclic hydrogen bond donating ligand about the central axle can dramatically effect its selectivity for a particular anion. The rotaxane product exhibits a dramatic increase in its selectivity for chloride as compared to the noninterlocked cation.

We anticipate that the principles exploited here can be developed further to include different anionic, cationic, and neutral components, resulting in new interlocked receptors selective for the anion template employed. Research is currently proceeding in our laboratories toward this end in addition to elaboration and refinement of the system presented here to further improve selectivity of the [2]rotaxane for the templating chloride anion.

Experimental Section

General Methods. Chemicals were purchased from Aldrich and used as received. All reactions were carried out under an atmosphere of dry N_2 unless otherwise stated. All solvents were dried and distilled before use according to standard laboratory procedures. Bis(4-*tert*-butylphenyl)phenyl-methanol[15] and 2-allyloxyethanol-*p*-toluenesulfonate[18] were prepared according to literature methods. Chromatography was performed on 240−400 mesh silica gel-60. ^1H and ^{13}C NMR spectra were recorded on Varian 300 MHz Mercury VX Works and 500 MHz Unity Plus spectrometers. UV−vis spectra were recorded at a concentration of 5×10^{-3} M on a Perkin-Elmer Lambda 6 UV−vis spectrometer.

(3). Compound **5** (0.300 g, 0.687 mmol) and 1-bromohexane (0.308 g, 1.72 mmol) were dissolved in a mixture of dimethylformamide (30 mL) and K_2CO_3 (0.200 g, 1.44 mmol) and were heated to 60 °C for 16 h. The mixture was cooled to room temperature and filtered to remove insolubles. The solvent was then removed by rotoevaporation, and the remaining light brown oil was chromatographed (silica gel, 95:5 $CHCl_3$:MeOH) to give the product as a white solid (0.154 g, 37%). ^1H NMR ($CDCl_3$, 300 MHz, TMS, 298 K): δ (ppm) 8.20 (s, 1H), 7.93 (d, $J =$ 7.6 Hz, 2H), 7.51 (t, $J = 7.6$ Hz, 1H), 6.83 (m, 8H), 6.75 (b, 2H), 4.11 (m, 4H), 3.90 (m, 8H), 1.77 (m, 4H), 1.46 (m, 4H), 1.36 (m, 8H), 0.92 (m, 6H). ^{13}C NMR: δ (ppm) 166.7, 153.8, 152.4, 134.8, 130.2, 129.2, 125.6, 115.7, 115.6, 69.0, 67.7, 40.3, 32.2, 29.9, 26.3, 23.2, 14.7. Elem.

(17) Analogous ^1H NMR titration experiments of **9b** with bromide and iodide showed the rotaxane does not bind either halide.
(18) Maynard, H. D.; Grubbs, R. H. *Macromolecules* **1999**, *32*, 6917.

Anal. Calcd for $C_{36}H_{48}N_2O_6$: C, 71.50; H, 8.00; N, 4.63. Found: C, 71.30; H, 7.72; N, 4.52.

(4). Compound **5** (0.300 g, 0.687 mmol) and 2-allyloxyethanol-*p*-toluenesulfonate (0.440 g, 1.72 mmol) were dissolved in a mixture of dimethylformamide (30 mL) and K_2CO_3 (0.200 g, 1.44 mmol) and were heated to 60 °C for 16 h. The mixture was cooled to room temperature and filtered to remove insolubles. The solvent was then removed by rotoevaporation, and the remaining light brown oil was chromatographed (silica gel, 95:5 $CHCl_3$:MeOH) to give the product as a white solid (0.174 g, 42%). ^{1}H NMR ($CDCl_3$, 300 MHz, TMS, 298 K): δ (ppm) 8.20 (s, 1H), 7.91 (d, J = 8.4 Hz, 2H), 7.47 (t, J = 8.4 Hz, 1H), 6.90 (b, 2H), 6.82 (m, 8H), 5.92 (m, 1H), 5.29 (d, J = 16.4 Hz, 1H), 5.20 (d, J = 10.6 Hz, 1H), 4.07 (m, 12H), 3.83 (m, 4H), 3.77 (t, J = 5.4 Hz, 4H). ^{13}C NMR: δ (ppm) 166.4, 153.0, 152.3, 134.4, 134.2, 129.8, 128.7, 125.2, 117.2, 115.5, 115.2, 72.3, 68.6, 68.0, 67.2, 39.9. Elem. Anal. Calcd for $C_{34}H_{40}N_2O_8$: C, 67.53; H, 6.67; N, 4.63. Found: C, 67.19; H, 6.88; N, 4.58.

4-[Bis(4-*t*-butylphenyl)phenylmethyl]aniline (6). Bis(4-*tert*-butylphenyl)phenyl-methanol (6 g, 16.1 mmol) was dissolved in acetyl chloride (30 mL) and refluxed for 12 h. The resulting solution was cooled to room temperature, and the solvent was removed under vacuum to leave a yellow solid. The solid was dissolved in aniline (30 mL) and heated to 100 °C for 48 h, during which time it changed from deep red to dark purple. The solution was again cooled to room temperature and added slowly to a rapidly stirred solution of concentrated HCl (16 mL) in water (300 mL) to form a purple solid. The solid was filtered off, dissolved in $MeCl_2$ (200 mL), and passed through a plug of silica (50 g). The silica was further eluted with $MeCl_2$ (200 mL), and the solvent was evaporated to leave the crude orange/brown product. Recrystallization from toluene/hexane gave the product as a white crystalline solid (5.19 g, 72%). ^{1}H NMR ($CDCl_3$, 300 MHz, TMS, 298 K): δ (ppm) 7.22 (m, 9H), 7.10 (d, J = 8.5 Hz, 4H), 6.97 (d, J = 9.0 Hz, 2H), 6.57 (d, J = 9.0 Hz, 2H), 3.60 (b, 2H), 1.27 (s, 18H). ^{13}C NMR: δ (ppm) 148.3, 147.7, 144.3, 144.0, 137.5, 132.2, 131.3, 130.9, 127.3, 125.7, 124.3, 114.3, 63.8, 34.8, 31.9. Elem. Anal. Calcd for $C_{33}H_{37}N$: C, 88.54; H, 8.33; N, 3.13. Found: C, 88.43; H, 8.38; N, 3.19.

(7). 4-[Bis(4-*tert*-butylphenyl)phenylmethyl]aniline (1.00 g, 2.23 mmol) and triethylamine (0.34 g, 3.4 mmol) were dissolved in $MeCl_2$ (40 mL), and 3,5-pyridinedichlorocarbonyl (0.228 g, 1.12 mmol) was added as a solid to the reaction mixture. The resulting solution was stirred for 4 h, after which time the solvent was removed by rotary evaporation to leave a yellow solid. The residue was refluxed in ethanol (50 mL) for 1 h and, after cooling to room temperature, filtered off to give the pure product as a white solid (0.977 g, 85%). ^{1}H NMR (DMSO-d_6, 300 MHz, TMS, 298 K): δ (ppm) 10.59 (b, 2H), 9.19 (s, 2H), 8.70 (s, 1H), 7.66 (d, J = 9.0 Hz, 4H), 7.14 (m, 30H), 1.27 (s, 32H). Elem. Anal. Calcd for $C_{73}H_{75}N_3O_2$: C, 85.42; H, 7.37; N, 4.09. Found: C, 85.05; H, 7.39; N, 4.20.

(8b). Compound **7** (1.00 g, 0.974 mmol) was suspended in a solution of acetone (50 mL) and methyl iodide (10 mL) and refluxed for 72 h. The resulting mixture was cooled to room temperature, and the yellow solid was filtered off to give pure product (0.983 g, 86%). ^{1}H NMR (DMSO-d_6, 300 MHz, TMS, 298 K): δ (ppm) 10.90 (b, 2H), 9.61 (s, 2H), 9.45 (s, 1H), 7.67 (d, J = 9.0 Hz, 4H), 7.14 (m, 30H), 4.48 (s, 3H), 1.26 (s, 32H). ^{13}C NMR: δ (ppm) 160.4, 148.5, 147.3, 144.0, 143.8, 136.3, 134.1, 131.6, 130.9, 130.6, 128.3, 125.2, 120.2, 80.0, 35.1, 32.1. Elem. Anal. Calcd for $C_{74}H_{78}IN_3O_2$: C, 76.07; H, 6.73; N, 3.60. Found: C, 75.07; H, 6.77; N, 3.82.

(8a). Compound **8b** (0.150 g, 0.128 mmol) was suspended in chloroform (100 mL) and washed with 1 M aqueous NH_4Cl (8 × 100 mL) and water (2 × 100 mL). The organic layer was dried with $MgSO_4$, filtered, and rotoevaporated to give the pure product as a yellow solid (0.130 g, 94%). ^{1}H NMR ($CDCl_3$, 300 MHz, TMS, 298 K): δ (ppm) 10.92 (b, 2H), 10.65 (s, 1H), 8.77 (s, 2H), 7.80 (d, J = 9.0 Hz, 4H), 7.19 (m, 30H), 3.79 (s, 3H), 1.26 (s, 32H). ^{13}C NMR: δ (ppm) 148.5, 147.1, 144.8, 143.8, 135.3, 134.6, 131.8, 131.2, 130.7, 127.6, 125.9, 124.5, 119.8, 77.6, 64.3, 34.8, 31.9. Elem. Anal. Calcd for $C_{74}H_{78}ClN_3O_2$: C, 82.53; H, 7.30; N, 3.90. Found: C, 82.22; H, 7.70; N, 4.00.

(8c). Compound **8b** (0.150 g, 0.128 mmol) and $AgPF_6$ (0.048 g, 0.19 mmol) were suspended in $MeCl_2$ (30 mL) and stirred in the absence of light for 16 h. The resulting mixture was filtered through a pad of Celite, and the solvent was evaporated to give the pure product as a yellow solid (0.146 g, 96%). ^{1}H NMR ($CDCl_3$, 300 MHz, TMS, 298 K): δ (ppm) 10.02 (b, 2H), 9.36 (s, 1H), 8.76 (s, 2H), 7.49 (d, J = 9.0 Hz, 4H), 7.19 (m, 30H), 3.76 (s, 3H), 1.26 (s, 32H). ^{13}C NMR: δ (ppm) 147.8, 146.4, 145.2, 144.1, 143.1, 135.2, 134.5, 131.2, 130.5, 130.1, 127.0, 125.3, 124.0, 119.4, 77.2, 63.9, 34.6, 31.7. Elem. Anal. Calcd for $C_{74}H_{78}F_6N_3O_2P$: C, 74.92; H, 6.63; N, 3.54. Found: C, 74.48; H, 6.68; N, 3.84.

(9a). Compounds **4** (0.125 g, 0.207 mmol) and **8a** (0.125 g, 0.116 mmol) were dissolved in dichloromethane and stirred for 5 min. Grubbs' catalyst was added (20 mol %), and the solution was stirred for a further 16 h. The solvent was evaporated, and the red-brown solid was chromatographed (silica gel, 93:7 $CHCl_3$:MeOH), collecting the first yellow band eluted. The fractions were evaporated and crystallized by slow diffusion of diisopropyl ether into chloroform to yield the final product as a bright yellow crystalline solid (0.091 g, 47%). ^{1}H NMR ($CDCl_3$, 300 MHz, TMS, 298 K): δ (ppm) 10.31 (b, 2H), 9.66 (b, 1H), 9.14 (b, 2H), 8.89 (b, 1H), 8.55 (b, 2H), 8.00 (d, J = 7.5 Hz, 2H), 7.78 (d, J = 9.0 Hz, 4H), 7.16 (m, 31H), 6.40 (d, J = 8.7 Hz, 4H), 6.18 (d, J = 8.7 Hz, 4H), 6.02 (b, 2H), 4.37 (b, 3H), 4.08 (b, 8H), 3.82 (b, 4H), 3.75 (b, 8H), 1.33 (s, 36H). ^{13}C NMR: δ (ppm) 167.1, 158.2, 153.5, 151.9, 148.6, 147.1, 145.4, 144.7, 143.6, 135.0, 134.1, 133.6, 131.9, 131.7, 131.2, 130.8, 130.2, 128.9, 127.6, 126.0, 124.5, 120.3, 77.6, 71.4, 69.8, 68.4, 66.2, 64.3, 41.1, 34.9, 31.9. Elem. Anal. Calcd for $C_{106}H_{114}ClN_5O_{10}$: C, 77.00; H, 6.95; N, 4.24. Found: C, 76.48; H, 6.72; N, 4.01.

(9b). Compound **9a** (0.050 g, 0.030 mmol) was dissolved in methylene chloride (10 mL), and $AgPF_6$ (0.012 g, 0.045 mmol) was added to the solution, which was then stirred in the absence of light for 16 h. The resulting mixture was filtered through Celite, which was washed with two further aliquots of methylene chloride (2 × 5 mL). The solvent was evaporated to yield the pure product as a yellow green solid (0.048 g, 90%). ^{1}H NMR ($CDCl_3$, 300 MHz, TMS, 298 K): δ (ppm) 10.14 (b, 2H), 9.06 (b, 1H), 8.91 (b, 2H), 8.62 (b, 1H), 8.17 (d, J = 7.5 Hz, 2H), 7.96 (b, 2H), 7.67 (d, J = 9.0 Hz, 4H), 7.53 (t, J = 9.0 Hz, 1H), 7.25 (m, 22H), 7.13 (d, J = 7.5 Hz, 8H), 6.48 (d, J = 8.7 Hz, 4H), 6.24 (d, J = 8.7 Hz, 4H), 5.85 (b, 2H), 4.12 (b, 3H), 4.01 (b, 4H), 3.96 (b, 4H), 3.81 (b, 8H), 3.75 (b, 4H), 1.33 (s, 36H). ^{13}C NMR: δ (ppm) 166.2, 157.6, 152.3, 151.5, 148.0, 146.4, 144.4, 144.1, 142.9, 134.2, 133.8, 133.3, 131.4, 131.0, 130.6, 130.2, 129.6, 128.6, 127.0, 125.5, 123.9, 119.7, 115.4, 114.8, 114.3, 77.2, 72.4, 70.9, 69.2, 67.6, 63.9, 40.1, 34.6, 31.7. Elem. Anal. Calcd for $C_{106}H_{114}F_6N_5O_{10}P$: C, 72.21; H, 6.52; N, 3.97. Found: C, 71.45; H, 6.34; N, 3.98.

^{1}H NMR Titrations. Titrations were performed with a starting concentration of **2**, **3**, **4**, **8c**, and **9b** at 5 × 10^{-3} M and the addition of the appropriate aliquots of titrant with a microsyringe. Data from all titrations were analyzed using the program EQNMR[19] to obtain association constants. Data were obtained during titrations of **2**, **3**, and **4** by observing the shifts in the proton resonances of the amide groups and the 2-position of the isophthalamide ring upon addition of **1a**, which gave the same values of association constants within error. Data were obtained during titrations of **8c** and **9b** by observing shifts in the resonance of the proton at the *para*-position of the pyridinium ring upon addition of TBA salts of the three anions. All titrations fit 1:1 or 1:2 binding models as appropriate. The stoichiometry of complexation was verified by Job plot analysis where necessary. Job plot analysis of the titration of **9b** with dihydrogen phosphate indicated that the

(19) Hynes, M. J. *J. Chem. Soc., Dalton Trans.* **1993**, 311.

stoichiometry of complexation was 1:1. However, the data were only fit satisfactorily with the inclusion of a weak 2:1 (anion:receptor) contribution ($K_{21} = 50\ M^{-1}$). Estimated errors are ≤10% for K_a values greater than 100 M^{-1} and ≤20% for K_a values less than 100 M^{-1}.

X-ray Crystallography. Crystal data for **9a**·1.5C_2H_5OH·1.5CH_3OH·0.5H_2O: $C_{112}H_{131.5}ClN_5O_{12.5}$, $M = 1783.17$, triclinic, space-group *P*-1, $a = 14.731(23)$, $b = 18.514(27)$, $c = 21.150(27)$, $\alpha = 100.25(1)$, $\beta = 106.68(1)$, $\gamma = 101.87(1)°$, $U = 5257$ Å^3, $Z = 2$, $\rho_{calc} = 1.127$ g cm^{-3}. Intensity data were collected with Mo Kα radiation using the Marresearch Image Plate System. The crystal was positioned at 70 mm from the Image Plate. One hundred frames were measured at 2° intervals with a counting time of 4 min to give 19 156 independent reflections. Data analysis was carried out with the XDS program.[20] The structure was solved using direct methods with the Shelx86 program.[21] Several of the *tert*-butyl groups were disordered, and two sets of positions for the three methyl groups were refined with occupancies *x* and 1 − *x*. The asymmetric unit also contained several solvent molecules, three ethanol and three methanol molecules, and one water molecule, all refined with 50% occupancy. Apart from the disordered atoms and the solvent molecules, all non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atom to which they were attached. The structure was refined on F^2 using Shelxl.[22] The final *R* values were R1 0.113 and wR2 0.286 for 4797 data with $I > 2\sigma(I)$. Details of the structure have been deposited at the CCDC Reference No. 187740. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Supporting Information Available: Tables giving the crystal data and structure refinement information, bond lengths and bond angles, atomic and hydrogen coordinates, and isotropic and anisotropic displacement coordinates for **9a** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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