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Review

Influence of dimensionality and charge on anion binding in amide-based macrocyclic receptors

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Contents

Abstract

The influence of dimensionality and charge on anion binding and structure is explored for a selected series of amide-based macrocyclic receptors. Monocyclic, bicyclic and tricyclic hosts are described in terms of affinities towards simple oxo anions (including acetate) and halides. Binding propensities tend to vary, although some selectivity patterns emerge for similar ligand frameworks. Some anions also exert a template influence the cyclization reactions during the synthesis of host precursors. Structurally sandwich complexes are often formed in the monocycles, while bicycles tend to encapsulate their guests. Multiple anions plus water molecules are often found in the larger bicycles. Added charge via quaternization or protonation tends to enhance binding by one or two orders of magnitude while maintaining the same selectivity patterns.

Keywords: Anion; Receptor; Macrocycle; Dimensionality; Charge; Anion recognition

1. Introduction

The basic understanding of factors involved in the selective binding of anions has increased dramatically over the last two decades [1–9]. In polyaza macrocycles for example, dimensionality has been shown to play a significant role [10–12], with monocycles being less effective in binding singly charged anions as opposed to their bicyclic or tricyclic counterparts. Part of this difference comes from the capability of bicycles and tricycles to encapsulate anions. Likewise, in early seminal work on the influence of charge on anion binding, Schmidtchen explored the binding of quaternized tetraamine tricycles for binding and catalysis [13–17]. After the initial reports of polyammonium-based receptors researchers branched out to receptors containing different hydrogen bonding donor groups, such as ureas and thioureas [5–7], amides [18,19], thioamides [20–24], pyrroles [25,26], sulfonamides [27–31], and guanidiniums [32,33], including anion templated self-assembly of chiral bicyclic guanidiniums hosts [34]. There are also a number of cleverly crafted scaffolds that have been utilized for appending the donor groups just mentioned, such as calixarenes [35,36], cholopods [37], and metal

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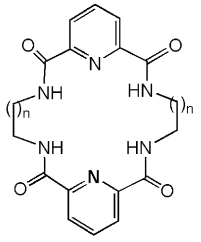
ion complexes [38,39]. Anion binding in amide-based receptors has been covered in a recent review [18], which included a comparison between acylic and macrocyclic hosts. This review will provide a slightly different slant by focusing on two key factors: dimensionality and charge, and their influence on anion binding including structural aspects, in simple amide-based *cyclic* receptor systems.

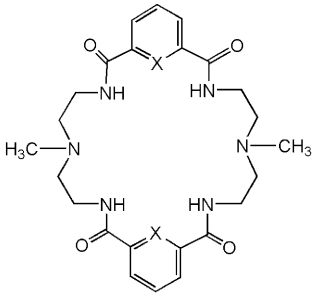
2. Dimensionality

2.1. Monocycles

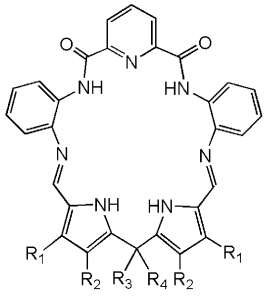
A series of polyamide frameworks, **1** through **5**, were chosen to explore monocyclic interactions with anions. The tetraamide receptor **1** is variable in size, with **1a**, **1b**, and **1c** containing 18, 20, and 24 atoms, respectively [40–42]. The mixed tetraamide/diamine **2** has a 24-membered ring and, with two tertiary amines, the potential for adding charge *via* quaternization [43,44]. Receptor **3**, with its 22-membered ring, is a hybrid diamide/dipyrromethane that provides a mixture of potential hydrogen bonding functional groups [45,46]. The triamide host **4**, with its 24-membered ring, provides additional rigidity via a biphenyl-based framework [47,48]. The host **5** also contains a 24-membered cavity and possesses three amide groups capable of hydrogen bonding with guest anions [49].



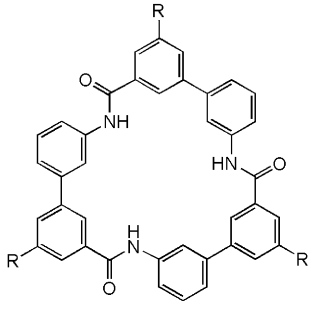
1a n=1
1b n=2
1c n=4



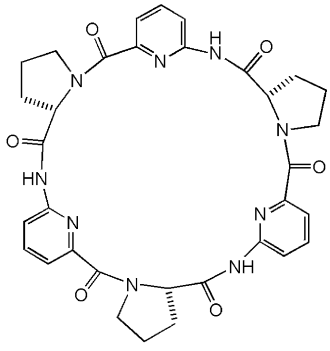
2a X=CH
2b X=N



3a R_1=R_2=H R_2=R_3=Me
3b R_1=Propyl, R_2=Me, R_3=H, R_4=Tolyl



4a R=CO_2Et
4b R=NHBoc



5

Binding in amide-based receptors is usually determined in non-aqueous solvents, and for these hosts, even monocycles can display significant binding for monoanions, especially $H_2PO_4^-$, as shown in Table 1 for DMSO. As a caveat, however, it should be noted that DMSO does not have the unique solvating influence on host and guest that water has, which makes designing receptors with high affinities for anions in aqueous conditions even more challenging. For guests **1**, **3**, and **5**, 'supersized' versions of **1** [50], **3** [51,52], and **5** [53] have been synthesized and will be described later.

Solvent plays a significant role in determining binding affinities, as seen in a comparison of the binding of **2a** and **4b** in DMSO-d_6 and $CDCl_3$ (Table 1). Affinities in DMSO are usually significantly diminished compared to those in $CHCl_3$. These observations can be attributed to a complex interplay among solvation and desolvation effects based on the protic/aprotic and polar/nonpolar nature of the solvent. Other energetic considerations operable in non-covalent interactions such as electrostatic, hydrophobic, hydrogen bonding, and stacking effects, among others, also factor into the solvent dependency of binding. As a general rule, however, anion affinities tend to increase in non-aqueous, aprotic, nonpolar solvents, which tend to have lower solvating capabilities [54].

A perusal of available crystallographic findings indicates striking structural similarities in the solid state for at least several of these receptors. For ligands **1a** [42], **2a** [43], and **5** [49], sandwich structures have been observed. In each of these three structures, an anion is wedged between two macrocycles (Fig. 1) and is held by hydrogen bonds with the macrocyclic amides.

In **1a**, an acetate is centered between the two tetraamide hosts. Each macrocycle forms four hydrogen bonds with one of the acetate oxygen atoms, resulting in a total of eight hydrogen bonds for just the two oxygen atoms [42] (Fig. 1A). The

Table 1
Association constants (K, M^{-1}) for **1–6** and **8**[a]

Receptor	Solvent	Cl^-	Br^-	I^-	$H_2PO_4^-$	HSO_4^-	NO_3^-	AcO^-
1a [42]	DMSO-d_6	65	<5	n.r.[b]	1680	<5	n.r.	2640
1b [41]	DMSO-d_6	1930	150	n.r.	7410	75	n.r.	3240
1c [41]	DMSO-d_6	18	<5	n.r.	450	<5	n.r.	310
2a [43,44]	DMSO-d_6	25	20	<10	830	790	<10	n.r.
	$CDCl_3$	500	n.r.	135	45700	31600	140	n.r.
2b [44]	DMS0O-d_6	490	510	<10	11000	110	<10	n.r.
3a[c] [45]	CH_3CN	2000	n.o.[d]	n.r.	342000 (26000)[e]	64000	n.o.	38000
3b[c] [46]	CH_3CN	n.o.	n.o.	n.r.	29000	108000	n.o.	12600
4b [47]	DMSO-d_6	<10	n.r.	<10	15000	1700	20	n.r.
	2% DMSO-d_6/$CDCl_3$	7600	n.r.	120000	n.r.	n.r.	n.r.	n.r.
5[f] [51]	50% D_2O/CD_3OD	n.r.	n.r.	30 (7670)[g]	n.o.	360 (8760)[g]	n.o.	n.o.
6a [51]	50% D_2O/CD_3OD	710	5300	8900	n.r.	350000	130	n.r.
6a[h] [52]	2:1 CH_3CN/H_2O	n.r.	n.r.	3300	n.r.	200000	n.r.	n.r.
6b[h] [52]	2:1 CH_3CN/H_2O	n.r.	n.r.	29000	n.r.	5400000	n.r.	n.r.
6c[h] [52]	2:1 CH_3CN/H_2O	n.r.	n.r.	56000	n.r.	6700000	n.r.	n.r.
8[c] [53]	CH_3CN	n.o.	n.o.	n.r.	191000 (60200)[e]	63500	n.o.	26000

[a] Calculated by NMR titrations using nBu$_4$N$^+$ as counterion if not otherwise indicated (errors in $K < 15\%$).
[b] n.r.: not reported.
[c] Binding calculated by UV/vis titrations.
[d] n.o.: no significant binding observed.
[e] 1:2 L:A complex ($LA + A \leftrightarrow LA_2$).
[f] NaX (X = anion) used for binding study (errors in $K < 40\%$).
[g] 2:1 L:A complex ($LA + L \leftrightarrow L_2A$).
[h] Calculated by isothermal titration microcalorimetry (ITC) using KX (X = anion) for binding study.

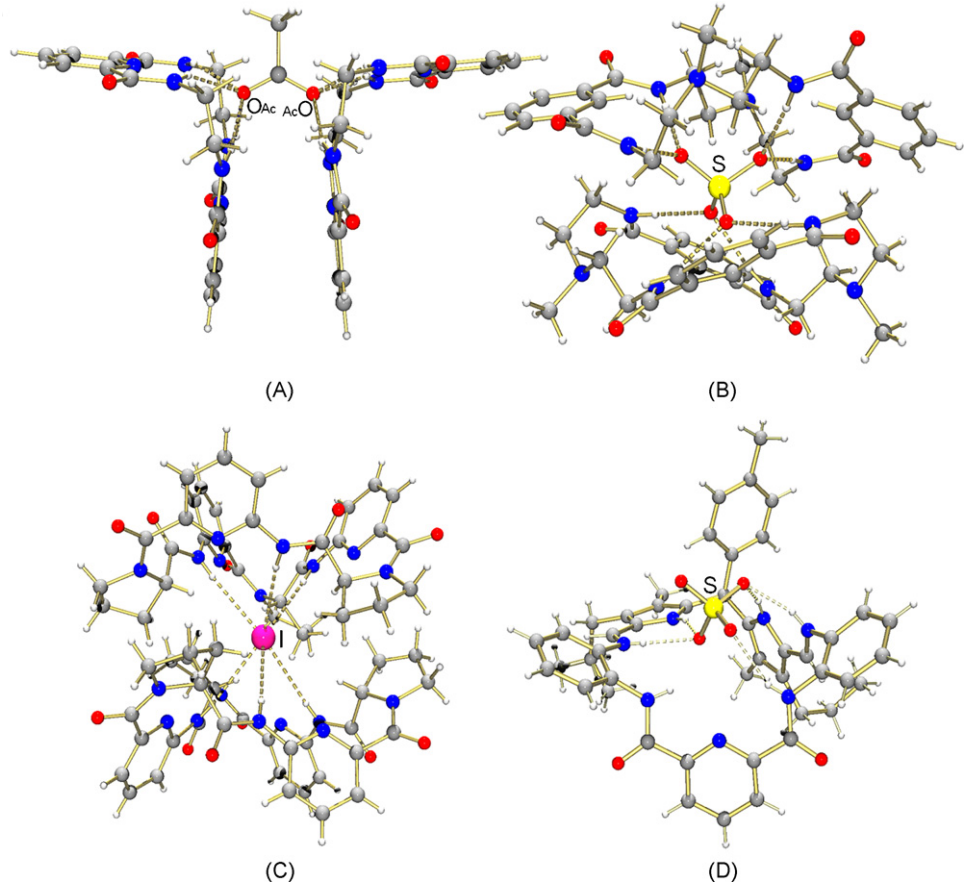
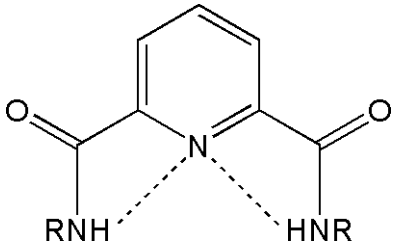


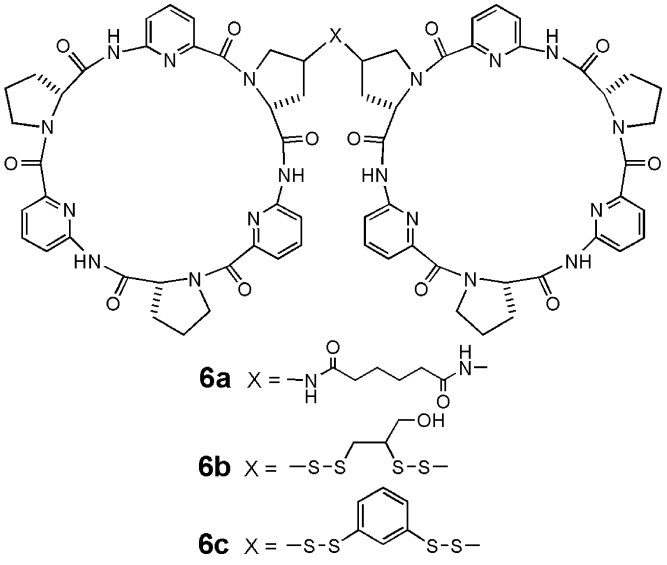
Fig. 1. Perspective views of the crystal structures of amide-based monocycles: (A) [(**1a**)$_2$(OAc)]$^-$ [42], (B) [(**2a**)$_2$(SO$_4$)]$^{2-}$ [43], (C) [(**5**)$_2$(I)]$^-$ [49], and (D) [(H$_2$**3b**)(SO$_4$)] [46]. The nBu$_4$N$^+$ counterions were omitted for clarity in (A), (B), and (C). For color version: C = gray, H = white, O = red, N = blue, S = yellow, I = purple, F = dark green, Cl = green. For b/w version: C = light gray, H = white, O = black, N = gray, S = I = F = Cl = dark gray. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

"upper" half of the macrocycle is bent away from the axial methyl group, while the lower half can be described as being in a pseudo-eclipsed conformation. The result is a somewhat skewed or tilted square prism coordination geometry. Binding studies performed by NMR titrations in DMSO-d_6 revealed that this smallest of the series, 18-membered macrocycle is a selective receptor for acetate over other anions including phosphate, $K(CH_3CO_2^-) = 2640\,M^{-1}$. In terms of the series, **1a–c**, however, binding studies revealed a significant dependence on cavity size, with a general trend of higher selectivity for both $H_2PO_4^-$ and acetate (Table 1) [40,41]. The largest affinity was observed for $H_2PO_4^-$ with the 20-membered **1b**, which was found to be the most effective anion receptor compared with the other two macrocycles. This higher affinity was attributed to both the flexibility of the propyl linkers along with the preorganization influence of the pyridine nitrogen atoms. That binding also persists in solution was indicated by the observation of H–F coupling between the amide hydrogen atoms and the bound fluoride, both in the ^1H and ^{19}F NMR spectra (doublet and quintet, respectively). ^{19}F NMR can be very informative in evaluating solution structure and chemistry in fluoride complexes with hosts, as expanded on in Section 2.2 on bicycles.

The 24-membered, mixed tetraamide/diamine host **2a** was also found to form a sandwich structure with sulfate, with the dinegative anion bound by eight hydrogen bonds [43]. In this case, however, each oxygen is held by just two hydrogen bonds (Fig. 1B), and the two macrocycles are rotated by 90° to accommodate the S_4 rotation axis of the anion while achieving the analogous binding pattern for both the top and bottom macrocycles. The result is a pseudo-square prismatic geometry. Host **2a** appears to be selective for oxo acids $H_2PO_4^-$ and HSO_4^- over oxo anions NO_3^- and ClO_4^- (the latter exhibiting virtually no binding, and not included in Table 1) [43,44]. This preference for oxo acids may be related to the presence of the tertiary amine, which could attract the oxo acid via a synergistic acid/base effect whereby the anion is deprotonated during complexation. The crystal structure, consisting of a dinegative sulfate with two tetra-*n*-butyl ammonium counterions, serves to support this postulate. Especially striking, however, is the higher affinity of **2b** for almost every anion compared to **2a**. This effect has been attributed by us [44] and others [40] to a preorganization influence of the pyridine nitrogen, which tends to promote orientation of the amide hydrogen atoms inward to participate in hydrogen bonding with the pyridine nitrogen:



In the third example of a sandwich complex, **5**, an iodide sits between the two ligands, and is coordinated with six of the amide hydrogen atoms in a trigonal primatic geometry [49]. The two cyclic peptides are essentially superimposed, one above the other, in an eclipsed conformation (Fig. 1C). Binding of both iodide and HSO_4^- is relatively high ($\log K \sim 3.9$) in a 1:1 solution of D_2O:CD_3OD when a 2:1 ligand:anion model is used. Kubik used this information to improve on his receptor by linking the two tripeptides with an adipinic spacer to form a covalent dimer, **6a** [51]. The covalently linked dimer showed enhanced binding over the monomer, with an exceptionally high affinity for sulfate, attributed to the cooperativity of the two cyclic peptides. While the binding of **6a** appeared to be predominantly the result of additive binding contributions of two molecules of **5**, it was noted that binding and cooperativity might be further enhanced by modifications of the spacer between the two macrocycles, for example by replacing the adipic spacer with dithiol-derived spacers. By using a dynamic combinatorial library (DCL) approach and reversible disulfide chemistry, Kubik and Otto were able to improve on the spacer, with new receptors **6b** and **c** (Table 1) [52].



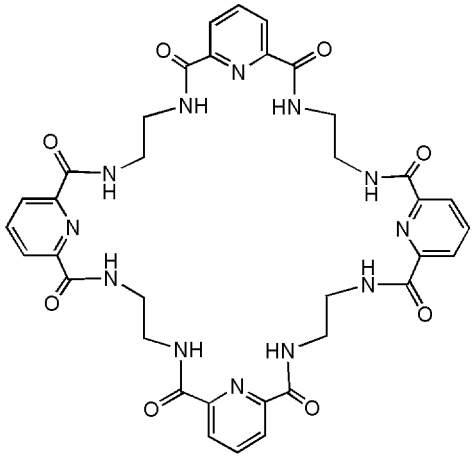
Although no crystal structures have been reported, Hamilton and coworkers have also seen evidence for 2:1 macrocycle:anion formation in NMR titration data for **4**. A 2:1 sandwich complex was also predicted for **4** with iodide using MM2 force field calculations [47]. This more rigid host also appears to be selective for oxo acids as seen for **2**, especially for $H_2PO_4^-$ in DMSO, where $\log K > 4$.

Sessler and coworkers reported a hybrid 2,6-diamidopyridine dipyrromethane macrocycle **3** which displays high selectivity for tetrahedral anions over other geometries. In the crystal structure of **3b** with sulfate, the two imine nitrogen atoms are protonated and hydrogen bonded with the dinegatively charged sulfate (Fig. 1D), which lies on top of the ligand. The sulfate is also hydrogen bonded to two pyrrole hydrogen atoms, an amide hydrogen, and a water molecule, resulting in a coordination number of six. Association constants determined by UV–vis titrations in CH_3CN indicated extremely high binding for the tetrahedral oxo acids $H_2PO_4^-$ and HSO_4^- (Table 1).

A design strategy to increase the selectivity of **3a** for sulfate over phosphate took advantage of the observation that a 2:1

$H_2PO_4^-$:receptor complex was observed as opposed to a 1:1 stoichiometry with sulfate. Modeling studies using DFT (PBE non-empirical functional, TZ2p basis set) calculations [45] indicated that **3b**, with sterically more demanding peripheral organic shrubbery, would be less susceptible to 2:1 anion:ligand complex formation, possibly reversing the selectivity. Results confirmed the prediction, with binding constants of 108,000 and 29,000 for HSO_4^- and $H_2PO_4^-$, respectively [46]. A more recent study of hybrid macrocycles combined diamidothiophene with dipyrromethane- and bipyrrole-derived groups, and explored the influence of ligand rigidity on anion binding [55]. The results indicated that the more flexible dipyrromethane derivative shows significantly higher binding for almost all anions compared to the more rigid bipyrrole-containing macrocycle.

Macrocycles with larger expanded cavities can result from higher order condensations as byproducts during either 1:1 or 2:2 condensations of macrocyclic precursors. For example, the supersized octaamidopyridine macrocycle, **7**, was isolated from the cyclization of dimethyl pyridine-2,6-dicarboxylate and ethylenediamine as a 4:4 minor product, while **1a** was the major product [50]. The crystal structure of the chloride complex of this gigantic neutral macrocycle revealed a flat cavity that is big enough to hold two chlorides bridged by two water molecules. The two chlorides were separated by 4.88 Å and coordinated via four hydrogen bonds each to amide hydrogen atoms and water molecules [50].



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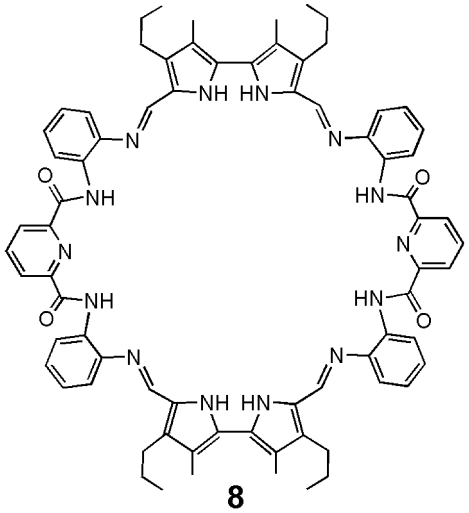
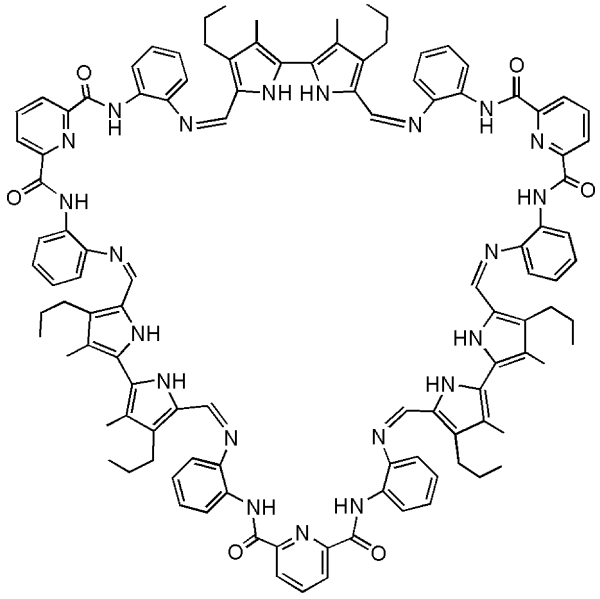
Sessler and coworkers have also isolated and characterized expanded, supersized macrocycles **8** and **9**, resulting from [2 + 2] and [3 + 3] condensations, respectively, of 2,6-diamidopyridine and bipyrrole. Like **3**, **8** is also selective toward tetrahedral oxo acids (Table 1). The acids used in the condensation reactions of these larger ring systems were found to play critical roles not only in promoting the cyclization, but also in influencing product distribution. For example, in the presence of sulfuric acid **8** was isolated with only minor byproduct formation [53], while acetic, trifluoroacetic, and phosphoric acids led to **8** with significant contamination from oligopolymers. These findings were attributed to an anion template effect promoted in this case by sulfate. The larger 3:3 condensate **9** resulted from allowing **8** to sit for 5 days in acetonitrile solution in the presence of $H_2PO_4^-$ and HSO_4^- [53]. Quantitative yield of **9** was observed in the presence of $H_2PO_4^-$. The authors suggest that **9** is the thermodynamic product of the condensation, while **8** is the kinetic product formed during the initial reaction. These subtle variations in products as a function of reaction conditions illustrate the intricate chemical balance operating in these condensations.



8

In solution



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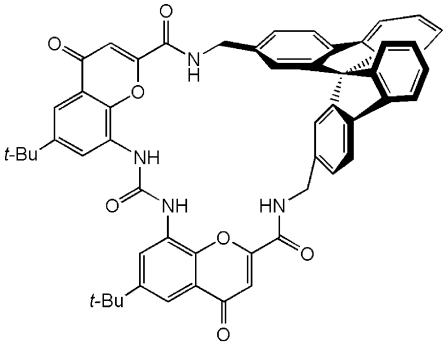
Several additional amide-containing macrocycles are of note, although in general these receptors have not been explored as extensively for the gamut of small molecules, e.g., halides and oxo anions. These hosts include a chiral receptor, **10**, reported by Morán [56], a macrocyclic dilactam, **11**, derived from the steroid cholic acid reported by Davis [57], and a colorimetric biphenyl-containing sensor for fluoride, **12**, reported by Costero and coworkers [58].



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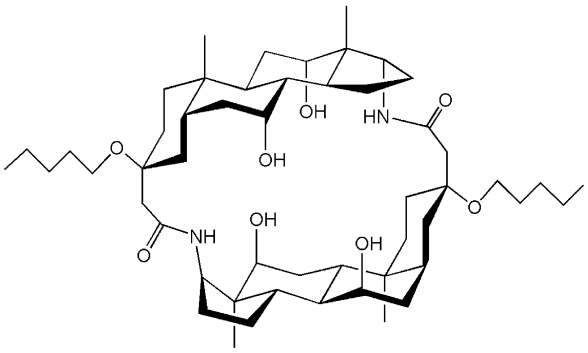
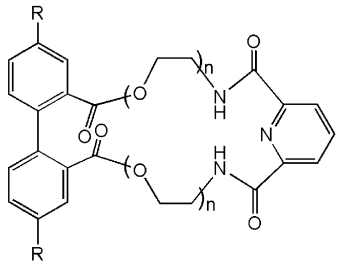


11



12a R= NO_2 n=1
12b R= NO_2 n=2

An area that has not been explored extensively within the anion binding realm is chiral recognition, although a review of the field recently appeared [59]. Ligand **10** results from using spirobifluorene and bis-chromenylurea as building blocks to yield a macrocycle capable of chiral recognition for organic guests [56]. The resulting ligand was found to bind mandelate ion with *K*s of 2.8×10^4 M^{-1} for (*R*)- and 1.7×10^3 M^{-1} for (*S*)-mandelate. The twofold difference in selectivity was enough to resolve a racemic mixture.

The rigid macrodilactam **11** has a relatively small cavity with six hydrogen bond donors, including four hydroxyl groups and two amides [57]. This receptor is one of a few that has been designed with potential OH in addition to NH groups for the hydrogen bond donors. Host **11** was found to bind fluoride with $K = 3220$ in $CDCl_3$, while affinity for the larger halides decreased with increasing size.

Costero and coworkers originally synthesized **12**, containing biphenyl and pyridine moieties, for transition metal binding [60]. More recently, however, they found these ligands to be colorimetric sensors specific for fluoride [58]. Anion binding studies for **12** in CH_3CN revealed a striking color change from colorless to orange in the presence of fluoride due to the formation of a charge-transfer complex. This color change occurs only in the presence of fluoride, and not for other halides, $H_2PO_4^-$, or HSO_4^-. When the nitro group is substituted by a dimethylamino group, no color change is observed. In the presence of excess fluoride, NMR indicates deprotonation of the amide hydrogen and the formation of bifluoride in solution.

2.2. Bicycles

Amide-based cryptands are relative newcomers to anion coordination chemistry, although Raymond in seminal work utilized 3,6-catechol-diamide frameworks as models for siderophores [61]. The appeal of bicycles is that they can

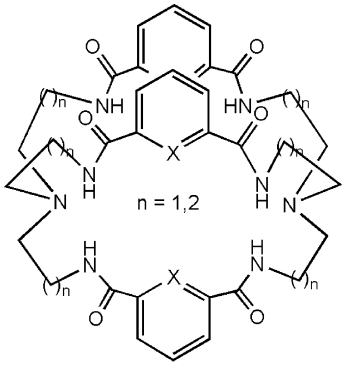
Table 2
Association constants (*K*, M^{-1}) for **13**, **16**, and **18**[a]

Receptor	F^-	Cl^-	Br^-	$H_2PO_4^-$	HSO_4^-	NO_3^-	CH_3COO^-	FHF^-
13a [63]	33000	820	<5	–[b]	–[b]	<5	n.r.[c]	n.r.
13b [62]	$>10^5$	3000	40	2000	68	85	2400	n.r.
13c [65]	$>10^5$	180	7	170	2700	<5	130	n.r.
16[d] [68]	n.r.	40	15	25	<5	300	770	n.r.
18 [82]	–[b]	42	15	740	49	<5	100	5500

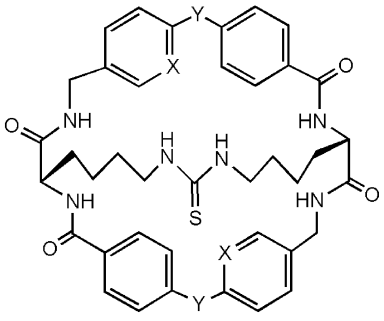
[a] Calculated by NMR titrations using nBu_4N^+ as counterion in DMSO-d_6 if not specifically indicated (errors in $K < 15\%$).
[b] Calculation not possible due to peak broadening.
[c] n.r.: not reported.
[d] In 25% CD_2Cl_2/CD_3CN.

provide a more rigid framework for encapsulating and holding anions within their cavities, as observed for polyprotonated azacryptands [10–12]. However, in terms of amides, the supply of bicycles is as yet limited. As anticipated, however, in the crystal structures obtained to date, these bicyclic cryptands tend to incorporate either a single anion, or, in the case of some of the larger cavities, multiple guests, including water. The anion binding capabilities of two simple amide-containing bicycles, **13** and **14**, the former with tren as bridgehead for the three arms (**13**) are described below.

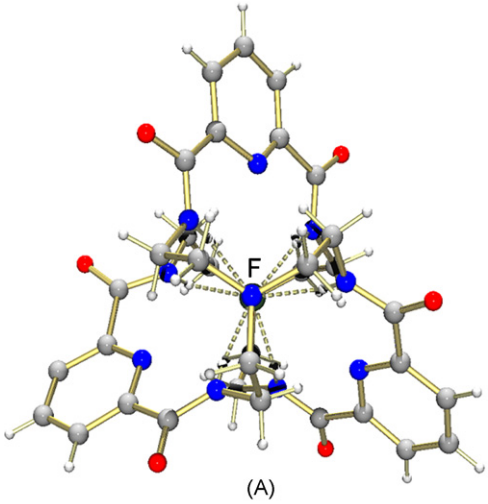
The bicycles **13** were synthesized to add a "second dimension" to the class of mixed amide/amine monocycles **2** [62–65]. As seen in Table 2, the results of binding studies of all three derivatives of **13** indicate exceptionally high affinity for fluoride. The crystal structures of both **13a** and **b** with fluoride indicate multiple hydrogen bond interactions possibly accounting for the high observed affinities. In both structures the fluoride is centered, with six hydrogen bonds to the amide hydrogen atoms of **13b** (Fig. 2A), and nine to both amide and phenyl CHs in



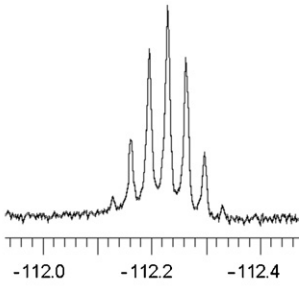
13a X= CH n=1
13b X= N n=1
13c X= N n=2



14a X= CH Y= CH_2
14b X= N Y= O



(A)



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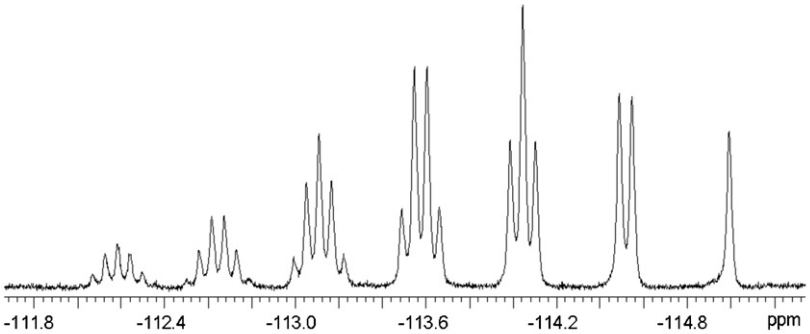


(C)

Fig. 2. Solid state and solution structures of [(**13b**)(F)]$^-$ [62,63]: (A) crystallographic perspective view; (B) ^{19}F NMR spectrum of encapsulated fluoride in a 1:2 [**13b**]:[F^-] solution in DMSO-d_6; (C) ^{19}F spectrum of (B) after 10 days.

13a [62,63]. The geometry is almost midway between trigonal prismatic and octahedral, with a trigonal twist angle of 37°.

A key question that always surfaces in host guest inclusion chemistry, however, is whether encapsulation persists in solution. ^{19}F NMR studies indicate that this is indeed the case for **13a** and **b**. For **13b**, the ^{19}F NMR spectrum in DMSO-d_6 consists of a septet, indicative of coupling of an internally held fluoride with the six amide hydrogen atoms (Fig. 2B) [62]. For **13a**, an unresolved multiplet higher than seven is observed, as anticipated for the additional CH···F$^-$ interactions [63]. For both **13a** and **b**, other multiplets appear in the ^{19}F NMR spectra over time, as a result of deuterium exchange between the amide hydrogen atoms and DMSO-d_6 [63] as shown for **13b** (Fig. 2C).

Binding studies exploring size influences for the amidocryptands **13** for a gamut of anions indicated diminished binding in general for the larger **13c**, with the exception of HSO_4^- [65] (Table 2). Perhaps the propylene spacers provide too much flexibility to afford tight binding for most small anions. Crystallographic findings indicate a more relaxed "fit" for **13c** as seen in a comparison of the structure of the sulfate complex with **13b** [64] (Fig. 3). In **13b**, the sulfate is tightly held inside the cavity via eight hydrogen bonds, six to amide hydrogen atoms and two to protonated bridgehead amines in a bicapped trigonal prismatic structure (Fig. 3A and B) [64]. In the encapsulated sulfate structure with **13c**, however, there are only four hydrogen bonds from the sulfate to the cryptand, two to amide hydrogen atoms and two to the protonated bridgehead amines (Fig. 3C and D) [65]. Three other hydrogen bonds are formed with adjacent water molecules, which are also partially in the cavity, resulting in seven coordinate binding. In both structures, **13b** and **c** with sulfate, however, the bridgehead amines are protonated, providing charge complementarity for the dianion.

In the chloride structure with **13c**, the cryptand also engulfs several guests with two chlorides bridged by a single water molecule (Fig. 4A and B). Again the bridgehead amines are protonated, yielding a neutral complex without the necessity for an external countercation. The latter structure is reminiscent of a similar binding pattern observed for the fluoride complex with an azacryptand reported by us [66,67], and strikingly like that seen by Anslyn for the biaryl capped cryptand described below [68].

A bicyclic receptor **14**, consisting of a monocycle with four amide functionalities and an aliphatic bridge containing thiourea was reported by Kilburn and coworkers [69–71], and showed

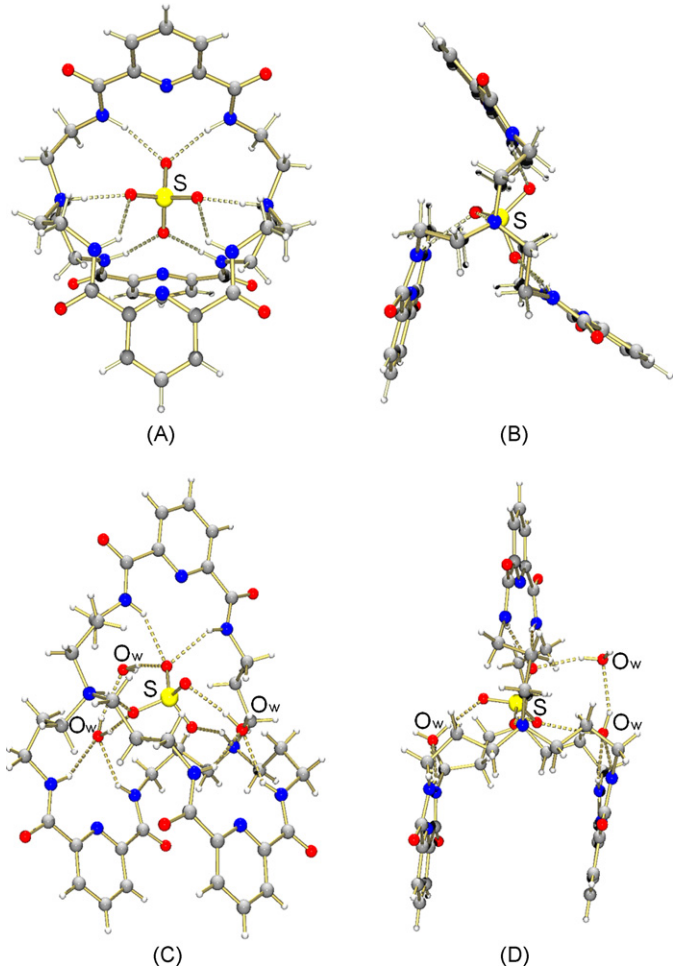


Fig. 3. Perspective views of [(H$_2$**13b**)(SO$_4$)] (A and B) [64] and [(H$_2$**13c**)(SO$_4$)]·3H$_2$O (C and D) [65].

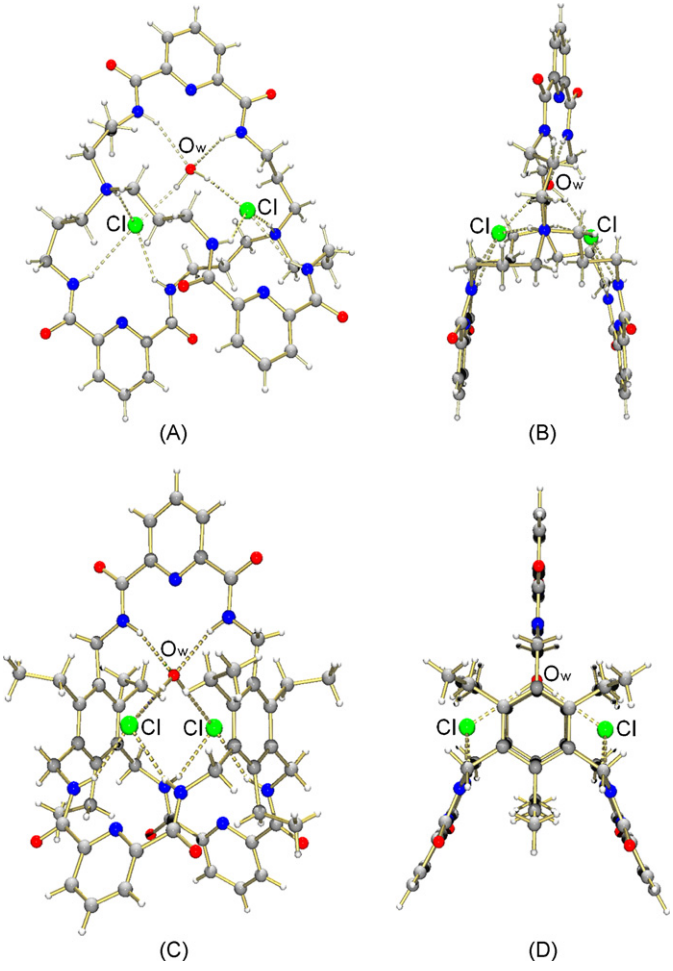
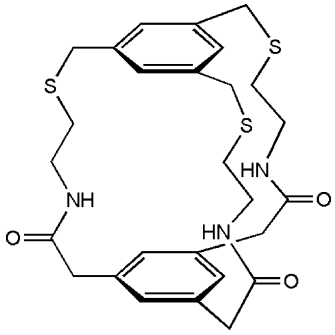


Fig. 4. Perspective views of [(H$_2$**13c**)(Cl)$_2$(H$_2$O)] (A and B) [65] and [(**16**)(Cl)$_2$(H$_2$O)]$^{2-}$ (C and D) [68]. The nBu$_4$N$^+$ counterions were omitted for clarity in (C) and (D).

significant affinities for simple acylated amino acids. Especially high affinity was observed between **14a** and N^{α}-Ac-L-lysine ($K = 130{,}000\ M^{-1}$), which was attributed to hydrogen bonding interactions between the free amine of the lysine and **14a** [69]. However, for other amino acid derivatives with long side chains such as alanine, phenylalanine, glutamine, asparagine, etc., affinity decreased, presumably due to steric hindrance. Extended 2D NMR studies indicated that L-amino acid substrates (*N*-Ac-L-phenylalanine and *N*-Ac-L-alanine) bind inside the cavity while D-amino acids bind externally [69,70]. The pyridine analog **14b**, which adds additional hydrogen bonding sites for guests, showed high affinity for *N*-Ac-L-asparagine carboxylate, in CH_2Cl_2 ($K = 55{,}000\ M^{-1}$) [71].

Three other bicyclic receptors, **15**–**17** contain cyclophane caps instead of bridgehead amines. The first and earliest entrée to these cyclophane-capped bicycles, **15**, contains a relatively small internal cavity thought to be ideal for small anions. Only weak binding was observed even for fluoride, however [72].



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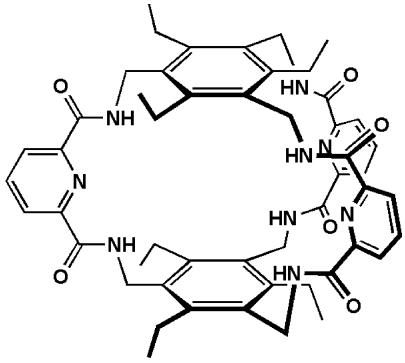

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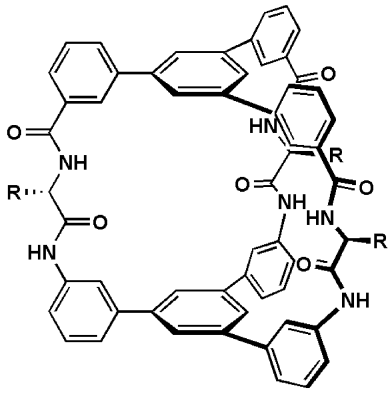


17a R = CH_2CHMe_2
17b R = CH_2Ph

Host **16** was also found to bind both acetate and nitrate with high affinities [68] (Table 2). In the acetate crystal structure the anion is inside the bicyclic cavity, with each of its oxygen atoms hydrogen bonded to two amide hydrogen atoms from the acyl pyridines (Fig. 5A and B). NMR studies indicated a similar encapsulation for nitrate; however, crystallographic confirmation was not obtained.

Host **16** was also used to explore the influence of NH-π versus NH-lone pair hydrogen bonding on carbon acidity in enolates, with results indicating that receptors targeting the π system were more effective in stabilizing the enolate form over the conjugate base [73]. Ligand **16** also forms complexes with anionic dyes, with significant changes in the UV–vis spectra upon complexation with other anions such as nitrate, bromide, and perchlorate. This colorimetric assay provides a useful, readily accessible method for determining binding affinities [74].

The more rigid expanded bicycle, **16**, synthesized by Anslyn and coworkers contains pyridine spacers and additional hydrogen bonding sites spanning the phenyl caps [68]. The capping phenyl groups are separated by 7.0 Å and the cavity "size" is 78.3 $Å^3$. The crystal structure of the chloride complex indicated a tritopic cascade-like structure (Fig. 4C and D) strikingly similar to that seen with **13c** and chloride (Fig. 4A and B). The Cl···Cl separation is 4.95 Å (∠ClOCl = 101°) in **13c** and 5.42 Å (∠ClOCl = 113°) in **16**, the larger separation and angles being reflective of the expanded cavity size provided by the "bridgehead" phenyl groups of **16** as opposed to the tertiary amines of **13** (Fig. 4D and B, respectively). The fact that anion complexes with very similar coordination geometries can be isolated in two structurally different receptors lends support to the hypothesis that these coordination geometries are not just happenstance, but are the result of true binding preferences of these anions adjusted to the ligand environment.

Receptor **17** reported by Diederich and coworkers, and also based on a phenyl-capped framework, contains two 1,3,5-triarylbenzene units linked by three amino acid chains. The

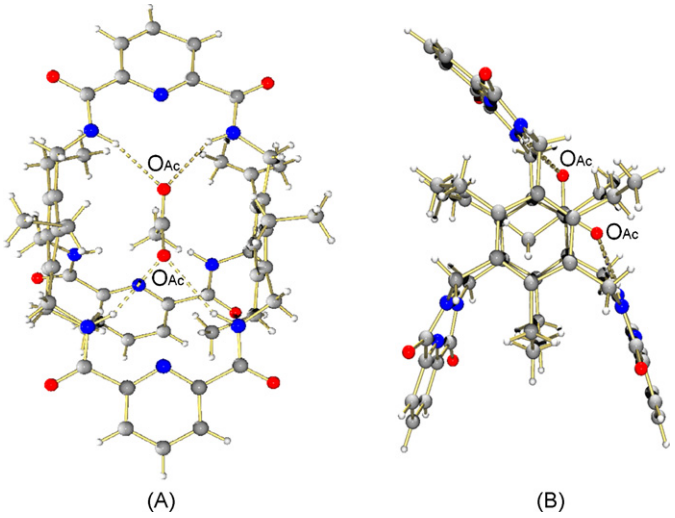


Fig. 5. Perspective views of [(**16**)(OAc)]$^-$ [68]. The nBu$_4$N$^+$ counterion was omitted for clarity.

result is a chiral cage [75], designed to bind amino acid derivatives selectively. ^{1}H NMR titrations in $CDCl_3$ indicated strong binding for an N-protected amino acid, *N*-*Z*-L-Asp, with $-\Delta G = 3.5$ kcal/mol. While the amino acids are presumed to be in their neutral (not anionic) form due to the aprotic solvent, this study nonetheless illustrates the influence of using natural (i.e., amino acid-based) fragments within the design of enantioselective receptors. The differentiating ability of **17a** for *N*-*Z*-L-Glu over *N*-*Z*-D-Glu was found to be $\Delta(\Delta G) = 1.0$ kcal/mol in $CDCl_2CDCl_2$.

2.3. Tricycles

Tricycles allow for even larger cavities, which by design can possibly encapsulate more complex or larger anionic guests. While there are several examples of amide-based synthetic tricycles [76–81], **18** is the primary receptor that has been explored for anion binding. The tricyclic host was prepared by coupling two macromonocycles via ethylene linkers, the monocycles being based on the framework of **2b** minus the *N*-methyl groups. The resulting tricycle was found to be an excellent and selective receptor for the triatomic bifluoride ion [82]. The isolation and structural characterization of an encapsulated bifluoride ends a quest for such a species that has spanned over two decades, ever since the structural characterization of an encapsulated azide in an azacryptand by Lehn and coworkers [83]. While **18** is not an azacryptand, the fact that the crystals were isolated from a solution of a fluoride salt is yet another indication that at least in the solid state **18** is highly selective for bifluoride. In the crystal structure, the bifluoride ion spans the two capping macrocycles with an F–H–F distance of 2.475(4) Å, with two hydrogen bonds from each macrocycle to the terminal fluorides, holding the bifluoride in place (Fig. 6). A circular hydrogen bonding network holds each of the macrocycles in a fixed conformation (Fig. 6A). ^{1}H NMR titration studies of **18** also indicated high selectivity for bifluoride ion, with an association constant of

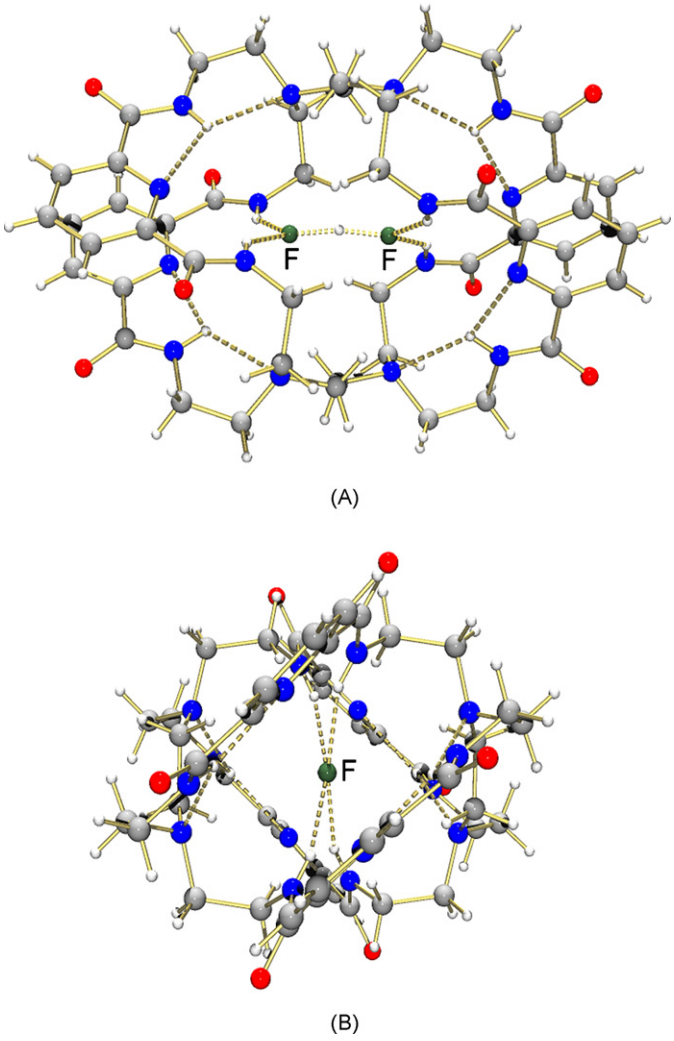
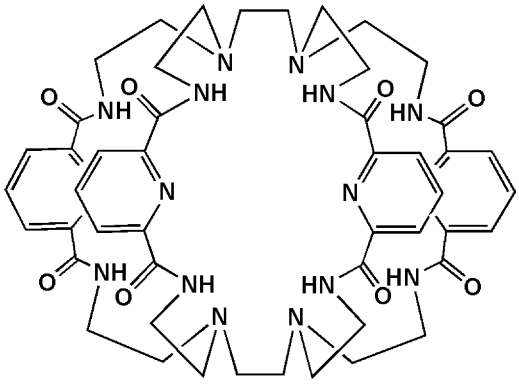


Fig. 6. Perspective views of [(**18**)(FHF)]$^-$ [82]: (A) showing the circular hydrogen bonding network within the macrocycles and (B) down the FHF$^-$ axis. The nBu$_4$N$^+$ counterion was omitted for clarity.

5500 M^{-1} in DMSO. As can be seen from Table 2, the affinity of **18** for other simple anions is minimal, although by virtue of the two macrocyclic binding sites, it may be a potential receptor for ditopic anions such as dicarboxylates.



18

3. Charge

3.1. Introduction

Much of the preceding discussion was devoid of an important factor in anion binding, i.e., the need for a counter ion. Charge compensation can be accomplished by incorporation within the receptor or as a separate entity. The bond energy of an ionic bond, in the absence of any other forces, is proportion to $1/r$, the distance between the positive and negative ion. The potential energy of a dipole–dipole interaction is proportional to $1/r^3$, and hydrogen bonding has been suggested to be extension of this type of interaction [84]. Suffice it to say, therefore, in terms of actual magnitude, a +/− electrostatic attraction outweighs the strength of a single hydrogen bond. The leverage of the hydrogen bond is in the flexibility of placement, i.e., topological complementarity that can influence selectivity. Nonetheless, receptors possessing positively charged sites, such as ammonium [8,9] and guanidinium [32–34] salts often display stronger affinities for anions compared with neutral receptors, even in strongly hydrogen bonding media such as water.

3.2. Monocycles

There are some examples for enhanced anion binding in mixed amide/amine hosts when the amine functionality is protonated, such as in the monocycle **19** reported by Diederich [85]. For example, **19** was found to bind dansyl and benzensulfonate ions with stability constants of ~45 M^{-1} for 1:1 complexes in buffered D_2O at pD 2 at low concentrations. Unfortunately precipitation prevented studies at higher concentrations [85]. The crystal structure of the Cl^- complex of **19** indicated that the chloride ions are positioned close to the protonated ammonium centers between the molecules (similar to **20a**), resulting in a chain-like infinite H-bonding network (Fig. 7A).

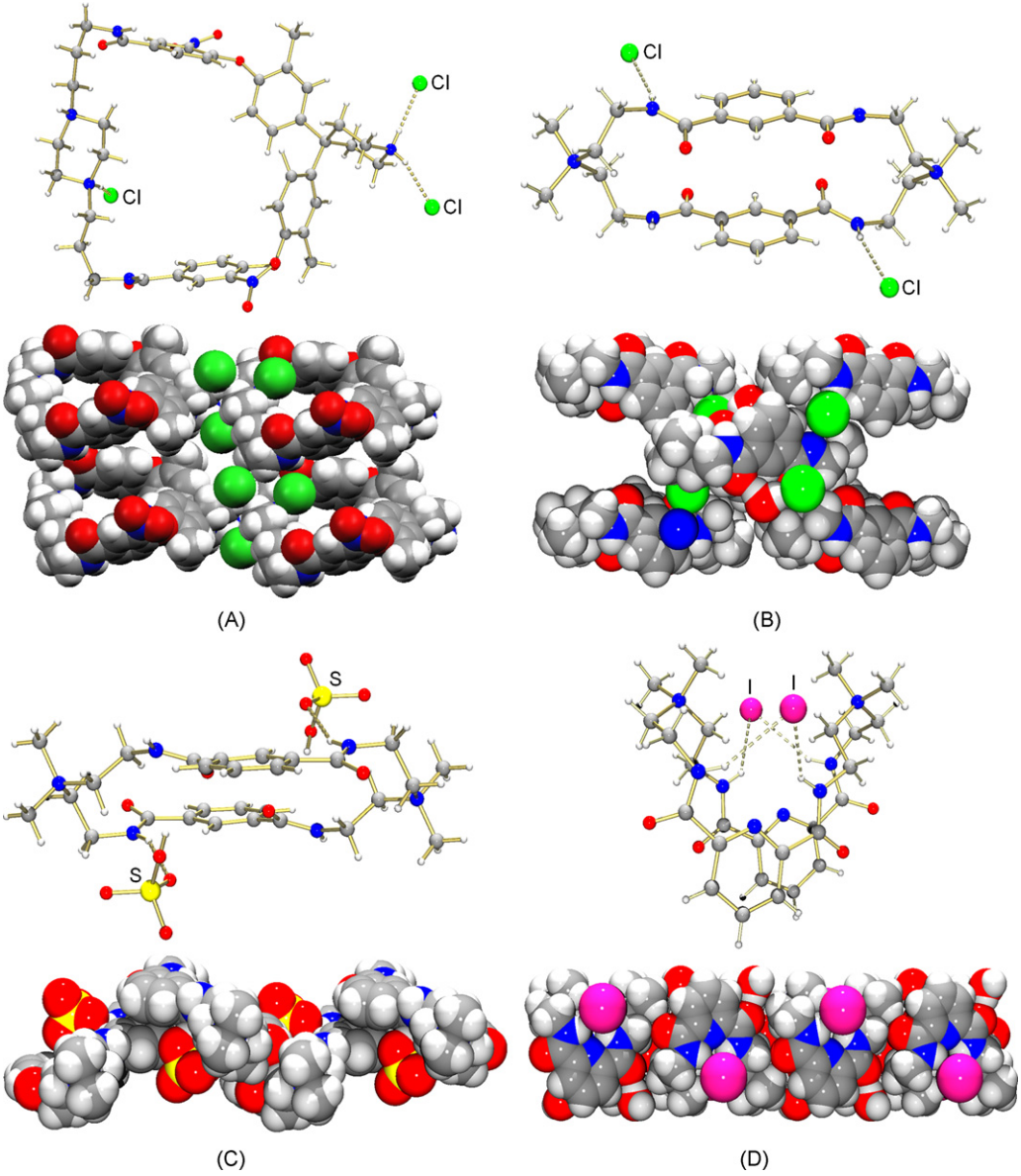
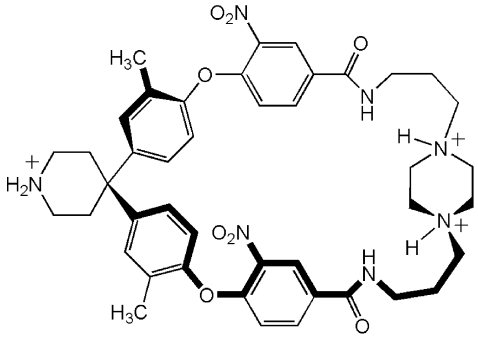


Fig. 7. Perspective views (above) and packing (below) of (A) [(H_3**19**)$(Cl)_3$] [85], (B) [(**20a**)$(Cl)_2$] [44], (C) [(**20a**)$(HSO_4)_2$], and (D) [(**20b**)$(I)_2$] [44].

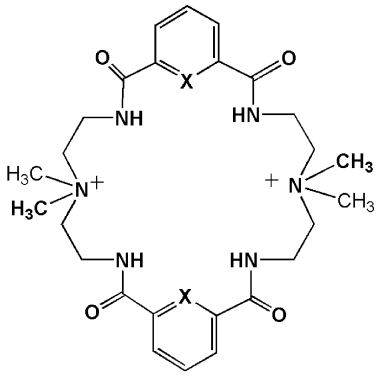
Table 3
Association constants (K, M^{-1}) for **20** and **21** in DMSO-d_6[a]

Receptor	F^-	Cl^-	Br^-	I^-	$H_2PO_4^-$	HSO_4^-	NO_3^-	ClO_4^-
20a [44]	480	1700	140	100	11500	–[b]	45	40
20b [44]	110	56000	24000	160	209000	7900	210	250
21 [65]	–[b]	3100	1300	n.o.[c]	12000	340	92	n.o.

[a] Calculated by NMR titrations using nBu$_4$N$^+$ as counterion (errors in $K < 15\%$).
[b] Calculation not possible due to peak broadening.
[c] n.o.: no significant binding observed.



H_3**19**$^{3+}$

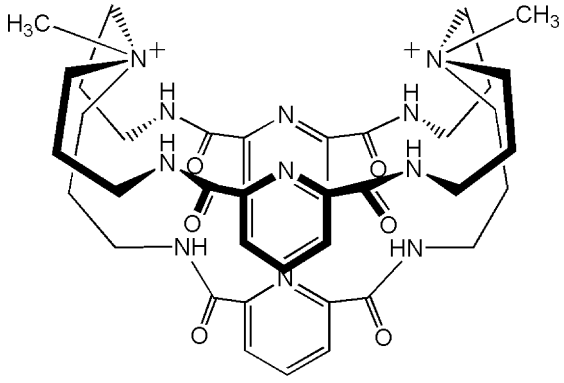


20a X = CH
20b X = N

In the mixed amide/amine monocycle **2**, quaternization of the amines yields the dipositively charged host, **20** [44]. Initial binding studies using iodide as counterion indicated little or no enhanced binding of anions compared to the monocycles. However, by using a bulkier more "innocent" counteranion, [Ph_4B^-], binding was observed for all anions, and was, as anticipated, significantly higher compared to the neutral corollary host, **2**, (Tables 1 and 3), for both the pyridine and *m*-xylyl spacers. For each anion binding was enhanced by one or two orders of magnitude, but the relative selectivity was unchanged. Once again, the pyridine macrocycle showed increased affinity over the *m*-xylyl analog, indicative of the preorganization effect discussed earlier. This effect is seen more clearly in a comparison of three crystal structures, the *m*-xylyl-containing **20a** with chloride and bisulfate and the pyridine-containing **20b** structure with iodide [44]. In the quaternized *m*-xylyl-containing macrocycles, charge repulsion apparently results in the formation of an elliptical conformation, with the two quaternized amines at the far ends of the elongated macrocycles. The anions are located outside of the cavity, and the result is layered (chloride) or helical (bisulfate) packing structures (Fig. 7B and C). In the bisulfate structure an additional proton links two of the macrocyclic carbonyls, thus requiring an additional bisulfate anion, which also lies outside the cavity. However, in the quaternized pyridine analog, **20b**, the macrocycle folds and the amide hydrogen atoms point in the direction of the pyridine nitrogen. The result is chelate-like binding of iodide, although the anion is still outside of the cavity. The iodide complex packs in a columnar-like structure (Fig. 7D).

3.3. Bicycles

Building upon the monocyclic quaternized host **20**, a quaternized cryptand, **21**, was synthesized and characterized [65]. Note that the framework of **21** contains propyl spacers derived from the precursor amine, tris(3-aminopropyl)amine (trpn). Attempts to isolate the quaternized version of **13b** with ethyl spacers were unsuccessful, possibly because of the smaller, more congested cavity. Binding studies indicated increased anion affinities over the neutral host **13c**, but a lessened affinity than the quaternized monocycle **20**. The crystal structures of **21** with both chloride and oxalate indicated a bowl-like shape for the host, with the anions sitting on top of the receptor (Fig. 8). Hydrogen bonding interactions with numerous water molecules within and surrounding the receptor appear to play an important role in shaping the structure.



21

3.4. Tricycles

Tricyclic amide-based neutral receptors are rare, and the charged tricycles are apparently even more so. A tricyclic

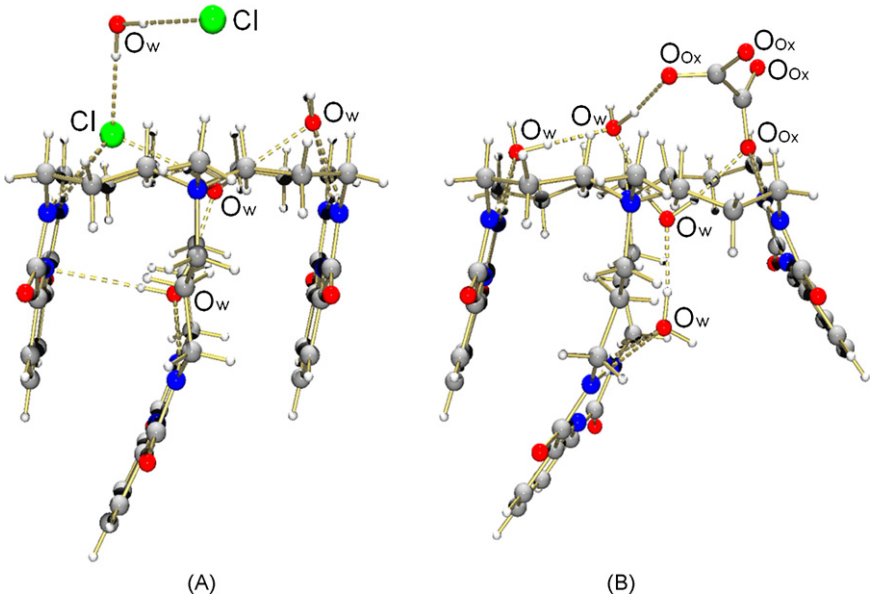
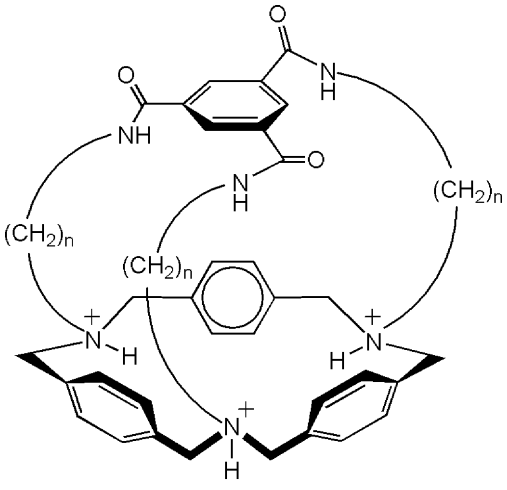


Fig. 8. Perspective views of (A) [(**21**)$(Cl)_2$]·$4H_2O$ [65] and (B) [(**21**)(C_2O_4)]·$4H_2O$ [65].

receptor, **22**, possessing three amide and three amine functionalities forms a cylindrical shape when a triamine-containing cyclophane with three appended aliphatic amine chains is coupled with 1,3,5-benzenetricarboxylic acid chloride [86]. The cavity size of tricycle was varied from one to three methylene units, with the lowest yields for the smallest, **22a**, due to steric hindrance. When fully protonated the tricycle has six potential binding sites for anions. Studies of H_3**22c**$^{3+}$ using NMR techniques indicated a stable complex for the trigonal planar nitrate ion, which is not surprising in view of the trigonal symmetry of the host.



H_3**22a**$^{3+}$ n=1
H_3**22b**$^{3+}$ n=2
H_3**22c**$^{3+}$ n=3

4. Conclusions

Both dimensionality and charge influence binding in amide-based receptors. Size is also important, with larger more flexible hosts being less effective in tightly capturing an anionic target. The logical progression in dimensionality from monocyclic to bicyclic to tricyclic in the three macrocycles based on similar frameworks, **2b**, **13b**, and **18**, provides insight to some of the issues of dimensionality. For example, a distinct shift in anion preference is observed by comparing the monocycle, **2b**, to the bicycle, **13b**. The former host exhibits selectivity for oxo acids while the latter preferentially binds halides, especially fluoride (Fig. 9A). The very large and flexible tricyclic **18** shows lessened affinity in general for the 'routine' anions, but a distinct selectivity for bifluoride and potential for binding other ditopic species such as dicarboxylates. A similar trend is seen with respect to decreased binding with increase in size and flexibility in comparing the smaller amido cryptand **13b** to the expanded **13c** (Table 2 and Fig. 9B). In the larger macrobicycle, **13c**, lessened binding is observed for all anions with the exception of a distinct selectivity for bisulfate. In terms of charge, affinity of the quaternized versions of **2b** and **13c**, **20b** and **21**, respectively, appear to increase relatively proportionately over the neutral hosts, with the exception of bisulfate with **21**, which actually shows lessened binding than the expanded bicycle **13c** (Fig. 9B).

In terms of structure, the monocycles tend to form either sandwich complexes or complexes in which the anion is poised above the macrocyclic cavity. Bicycles definitely show a preference for forming inclusion complexes, with multiple hydrogen bonds to the sequestered guest. In fact, both fluoride structures with **13a** and **b** indicate numerous hydrogen bonds, nine and six, respectively, holding fluoride firmly in the cavity even in solution, which may be a major influence on the high binding observed for fluoride with these hosts. The large and flexible nature of the tricycle, **18**, makes it ultimately suitable for larger guests as well as for bifluoride. Furthermore, the structures in charged ligands appear to be more "salt-like" in terms of anion positioning. What notably stands out for crystal structures of anion complexes, however, is that there are definite trends in binding preferences and coordination, for example in the sandwich struc-

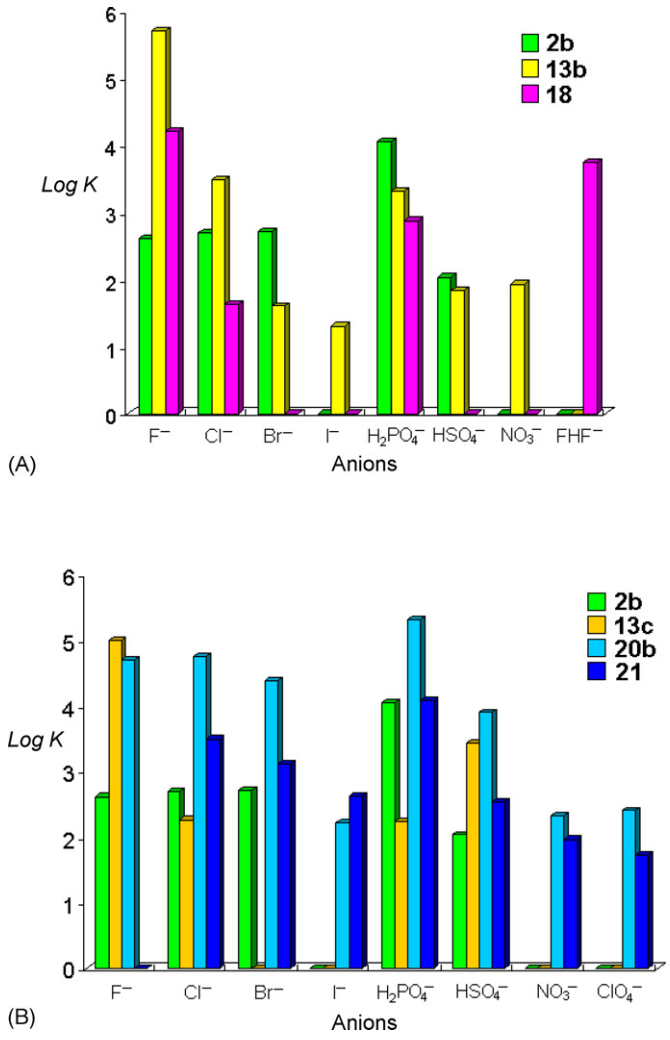


Fig. 9. Comparison of anion binding (A) for neutral **2b**, **13b**, and **18** and (B) for neutral **2b** and **13c**, and quaternized **20b** and **21**.

tures formed with several of the monocycles and anions, and in the similarity of the two chloride structures seen for **13c** and **16**. As the factors behind these structural preferences as linked to binding patterns are beginning to be understood, anion chemists will be able to more ably design highly selective receptors for the future.

Acknowledgements

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References

[1] A. Bianchi, K. Bowman-James, E. García-España (Eds.), Supramolecular Chemistry of Anions, Wiley–VCH, New York, 1997.
[2] P.D. Beer, P.A. Gale, Angew. Chem. Int. Ed. 40 (2001) 486.
[3] F.P. Schmidtchen, M. Berger, Chem. Rev. 97 (1997) 1600.
[4] V. Amendola, L. Fabbrizzi, C. Mangano, P. Pallavicini, A. Poggi, A. Taglietti, Coord. Chem. Rev. 219–221 (2001) 821.
[5] S. Kubik, C. Reyheller, S. Stüwe, J. Inclusion Phenom. Macrocyclic Chem. 52 (2005) 137.
[6] P.A. Gale, Coord. Chem. Rev. 240 (2003) 191.
[7] R.J. Fitzmaurice, G.M. Kyne, D. Douheret, J.D. Kilburn, J. Chem. Soc., Perkin Trans. 1 (2002) 841.
[8] J.M. Llinares, D. Powell, K. Bowman-James, Coord. Chem. Rev. 240 (2003) 57.
[9] V. McKee, J. Nelson, R.M. Town, Chem. Soc. Rev. 32 (2003) 309.
[10] B. Dietrich, M.W. Hosseini, J.M. Lehn, R.B. Sessions, J. Am. Chem. Soc. 103 (1981) 1282.
[11] T. Clifford, A. Danby, J.M. Llinares, S. Mason, N.W. Alcock, D. Powell, J.A. Aguilar, E. García-España, K. Bowman-James, Inorg. Chem. 40 (2001) 4710.
[12] J.A. Aguilar, T. Clifford, A. Danby, J.M. Llinares, S. Mason, E. García-España, K. Bowman-James, Supramol. Chem. 13 (2001) 405.
[13] F.P. Schmidtchen, Angew. Chem. Int. Ed. 16 (1977) 720.
[14] F.P. Schmidtchen, G. Müller, J. Chem. Soc., Chem. Commun. (1984) 1115.
[15] F.P. Schmidtchen, Top. Curr. Chem. 132 (1986) 101.
[16] K. Worm, F.P. Schmidtchen, A. Schier, A. Schäfer, M. Hesse, Angew. Chem. Int. Ed. 33 (1994) 327.
[17] K. Worm, F.P. Schmidtchen, Angew. Chem. Int. Ed. 34 (1995) 65.
[18] C.R. Bondy, S.J. Loeb, Coord. Chem. Rev. 240 (2003) 77.
[19] K. Choi, A.D. Hamilton, Coord. Chem. Rev. 240 (2003) 101.
[20] M.A. Hossain, S.O. Kang, J.M. Llinares, D. Powell, K. Bowman-James, Inorg. Chem. 42 (2003) 5043.
[21] Y. Inoue, T. Kanbara, T. Yamamoto, Tetrahedron Lett. 44 (2003) 5167.
[22] Y. Inoue, T. Kanbara, T. Yamamoto, Tetrahedron Lett. 45 (2004) 4603.
[23] S.J. Coles, P.A. Gale, M.B. Hursthouse, M.E. Light, C.N. Warriner, Supramol. Chem. 16 (2004) 469.
[24] T. Zieliński, J. Jurczak, Tetrahedron 61 (2005) 4081.
[25] J.L. Sessler, S. Camiolo, P.A. Gale, Coord. Chem. Rev. 240 (2003) 17.
[26] P.A. Gale, Chem. Commun. (2005) 3761.
[27] S. Valiyaveettil, J.F.J. Engbersen, W. Verboom, D.N. Reinhoudt, Angew. Chem. Int. Ed. 32 (1993) 900.
[28] K. Kavallieratos, C.M. Bertao, R.H. Crabtree, J. Org. Chem. 64 (1999) 1675.
[29] K. Kavallieratos, S. Hwang, R.H. Crabtree, Inorg. Chem. 38 (1999) 5184.
[30] P. Anzenbacher Jr., K. Jursikova, J.L. Sessler, J. Am. Chem. Soc. 122 (2000) 9350.
[31] J.M. Boon, T.N. Lambert, B.D. Smith, A.M. Beatty, V. Ugrinova, S.N. Brown, J. Org. Chem. 67 (2002) 2168.
[32] M.D. Best, S.L. Tobey, E.V. Anslyn, Coord. Chem. Rev. 240 (2003) 3.
[33] R.J.T. Houk, S.L. Tobey, E.V. Anslyn, Top. Curr. Chem. 255 (2005) 199.
[34] J. Sánchez-Quesada, C. Seel, P. Prados, J. de Mendoza, I. Dalcol, E. Giralt, J. Am. Chem. Soc. 118 (1996) 277.
[35] P. Lhotak, Top. Curr. Chem. 255 (2005) 65.
[36] S.E. Matthews, P.D. Beer, Supramol. Chem. 17 (2005) 411.
[37] A.P. Davis, J.-B. Joos, Coord. Chem. Rev. 240 (2003) 143.
[38] P.D. Beer, E.J. Hayes, Coord. Chem. Rev. 240 (2003) 167.
[39] P.D. Beer, S.R. Bayly, Top. Curr. Chem. 255 (2005) 125.
[40] J. Chmielewski, J. Jurczak, Chem. Eur. J. 11 (2005) 6080.
[41] M. Chmielewski, J. Jurczak, Tetrahedron Lett. 45 (2004) 6007.
[42] A. Szumna, J. Jurczak, Eur. J. Org. Chem. (2001) 4031.
[43] M.A. Hossain, J.M. Llinares, D. Powell, K. Bowman-James, Inorg. Chem. 40 (2001) 2936.
[44] M.A. Hossain, S.O. Kang, D. Powell, K. Bowman-James, Inorg. Chem. 42 (2003) 1397.
[45] J.L. Sessler, E. Katayev, G.D. Pantos, Y.A. Ustynyuk, Chem. Commun. (2004) 1276.
[46] J.L. Sessler, E. Katayev, G.D. Pantos, P. Scherbakov, M.D. Reshetova, V.N. Khrustalev, V.M. Lynch, Y.A. Ustynyuk, J. Am. Chem. Soc. 127 (2005) 11442.
[47] K. Choi, A.D. Hamilton, J. Am. Chem. Soc. 123 (2001) 2456.
[48] K. Choi, A.D. Hamilton, J. Am. Chem. Soc. 125 (2003) 10241.
[49] S. Kubik, R. Goddard, R. Kirchner, D. Nolting, J. Seidel, Angew. Chem. Int. Ed. 40 (2001) 2648.

[50] A. Szumna, J. Jurczak, Helv. Chim. Acta 84 (2001) 3760.
[51] S. Kubik, R. Kirchner, D. Nolting, J. Seidel, J. Am. Chem. Soc. 124 (2002) 12752.
[52] S. Otto, S. Kubik, J. Am. Chem. Soc. 125 (2003) 7804.
[53] E.A. Katayev, G.D. Pantos, M.D. Reshetova, V.N. Khrustalev, V.M. Lynch, Y.A. Ustynyuk, J.L. Sessler, Angew. Chem. Int. Ed. 44 (2005) 7386.
[54] A. Bianchi, E. García-España, in: A. Bianchi, K. Bowman-James, E. García-España (Eds.), Supramolecular Chemistry of Anions, Wiley–VCH, New York, 1997, p. 217.
[55] J.L. Sessler, V. Roznyatovskiy, G.D. Pantos, N.E. Borisova, M.D. Reshetova, V.M. Lynch, V.N. Khrustalev, Y.A. Ustynyuk, Org. Lett. 7 (2005) 5277.
[56] A. Tejeda, A.I. Oliva, L. Simón, M. Grande, M.C. Caballero, J.R. Morán, Tetrahedron Lett. 41 (2000) 4563.
[57] A.P. Davis, J.F. Gilmer, J.J. Perry, Angew. Chem. Int. Ed. 35 (1996) 1312.
[58] A.M. Costero, M.J. Bañuls, M.J. Aurell, M.D. Ward, S. Argent, Tetrahedron 60 (2004) 9471.
[59] I. Stibor, P. Zlatušková, Top. Curr. Chem. 255 (2005) 31.
[60] A.M. Costero, M.J. Aurell, M.J. Bañuls, L.E. Ochando, F.J. Tamarit, A. Domenech, J. Inclusion Phenom. Macrocyclic Chem. 45 (2003) 241.
[61] T.B. Karpishin, T.D.P. Stack, K.N. Raymond, J. Am. Chem. Soc. 115 (1993) 182.
[62] S.O. Kang, J.M. Llinares, D. Powell, D. VanderVelde, K. Bowman-James, J. Am. Chem. Soc. 125 (2003) 10152.
[63] S.O. Kang, D. VanderVelde, D. Powell, K. Bowman-James, J. Am. Chem. Soc. 126 (2004) 12272.
[64] S.O. Kang, M.A. Hossain, D. Powell, K. Bowman-James, Chem. Commun. (2005) 328.
[65] S.O. Kang, D. Powell, K. Bowman-James, J. Am. Chem. Soc. 127 (2005) 13478.
[66] M.A. Hossain, J.M. Llinares, S. Mason, P. Morehouse, D. Powell, K. Bowman-James, Angew. Chem. Int. Ed. 41 (2002) 2335.
[67] M.A. Hossain, P. Morehouse, D. Powell, K. Bowman-James, Inorg. Chem. 44 (2005) 2143.
[68] A.P. Bisson, V.M. Lynch, M.-K.C. Monahan, E.V. Anslyn, Angew. Chem. Int. Ed. 36 (1997) 2340.
[69] G.J. Pernía, J.D. Kilburn, M. Rowley, Chem. Commun. (1995) 305.
[70] G.J. Pernía, J.D. Kilburn, J.W. Essex, R.J. Mortishire-Smith, M. Rowley, J. Am. Chem. Soc. 118 (1996) 10220.
[71] V. Jullian, E. Shepherd, T. Gelbrich, M.B. Hursthouse, J.D. Kilburn, Tetrahedron Lett. 41 (2000) 3963.
[72] R.A. Pascal, J. Spergel, D.V. Engen, Tetrahedron Lett. 27 (1986) 4099.
[73] K. Niikura, A.P. Bisson, E.V. Anslyn, J. Chem. Soc., Perkin Trans. 2 (1999) 1111.
[74] T.S. Snowden, A.P. Bisson, E.V. Anslyn, J. Am. Chem. Soc. 121 (1999) 6324.
[75] R.J. Pieters, F. Diederich, Chem. Commun. (1996) 2255.
[76] P. Lipkowski, D.T. Gryko, J. Jurczak, J. Lipkowski, Tetrahedron Lett. 39 (1998) 3833.
[77] G. Das, P. Tripathi, A. Tripathi, P.K. Bharadwaj, Tetrahedron 56 (2000) 1501.
[78] A.P. Davis, R.S. Wareham, Angew. Chem. Int. Ed. 37 (1998) 2270.
[79] A.P. Davis, R.S. Wareham, Angew. Chem. Int. Ed. 38 (1999) 2978.
[80] G. Lecollinet, A.P. Dominey, T. Velasco, A.P. Davis, Angew. Chem. Int. Ed. 41 (2002) 4093.
[81] E. Klein, M.P. Crump, A.P. Davis, Angew. Chem. Int. Ed. 44 (2005) 298.
[82] S.O. Kang, D. Powell, V.W. Day, K. Bowman-James, Angew. Chem. Int. Ed. 45 (2006) 1921.
[83] J.-M. Lehn, E. Sonveaux, A.K. Willard, J. Am. Chem. Soc. 100 (1978) 4914.
[84] J.E. Huheey, E.A. Keiter, R.L. Keiter, Inorganic Chemistry, Principles and Reactivity, 4th ed., HarperCollins College, New York, NY, 1993, p. 290.
[85] B. Hinzen, P. Seiler, F. Diederich, Helv. Chim. Acta 79 (1996) 942.
[86] T. Fujita, J.-M. Lehn, Tetrahedron Lett. 29 (1988) 1709.