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Synthetic Ditopic Receptors

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Abstract

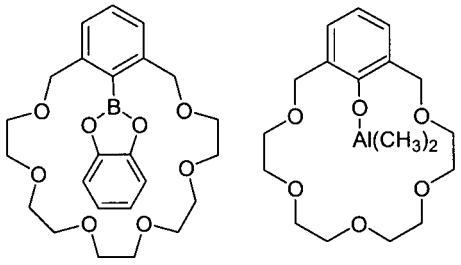
A small, but emerging field of topical interest in supramolecular chemistry is ion-pair recognition, in which a host simultaneously binds both cationic and anionic guests. Details of these receptors, which combine, for example, crown ethers and calixarenes for cation complexation, with Lewis acid centers, pyrroles, amides or urea groups for anion recognition, will be discussed. The predicate of this approach, successfully achieved in certain instances, is that the binding of one guest ion can induce electrostatic and conformational changes in the host, thereby enhancing the complexation of the counter ion.

Introduction

The field of supramolecular chemistry has advanced considerably in recent years and as such there is now a plethora of literature regarding the design, synthesis and study of receptors for cation binding [1]. Although the beginnings of anion recognition can be traced to the same period as that of their cation counterparts, the last twenty years have seen significant advances in the construction of supramolecular hosts for such guests [2]. By contrast, ditopic binding, the simultaneous complexation of cationic and anionic species to a multisite receptor, remains in its infancy [2, 3]. In theory, receptors designed for the latter purpose may exhibit cooperative or allosteric behavior, that is to say that the binding of one charged species may facilitate the co-ordination of the other ion, giving rise to association constants that are higher than if one species alone were bound. Investigation of such receptors is pertinent to the detection and extraction of toxic or detrimental ions from aqueous environments, and to the design of artificial carriers and channels for the symport (co-transport) of inorganic and organic salts across lipophilic membranes. This review will highlight progress made in the co-ordination of inorganic ion-pairs by ditopic receptors, but organic-salt recognition will also be discussed briefly.

Simultaneous complexation of inorganic ion-pairs

One early example of a ditopic receptor was provided by Reetz and coworkers who covalently linked a crown ether with a Lewis-acidic boron center to give **1** [4]. Receptor **1** was found to complex potassium and fluoride ions simultaneously. In the crystal structure, the K^+ ion is bound within the macrocyclic cavity, while the F^- ion binds to the Lewis acidic boron center. Evidence for the existence of the complex in solution was provided by ^{13}C and ^{11}B NMR spectroscopy. These researchers also showed that the 18-membered-phenolic crown ether analogue of **1** can be metalated with Me_3Al to give **2**, which was shown to form a ditopic complex with LiCl, both in solution and the solid-state [5].



1 **2**

Reinhoudt and co-workers have described the use of compound **3** as a ditopic receptor that simultaneously recognizes potassium and dihydrogen phosphate ions [6]. This host consists of a Lewis-acidic uranyl (UO_2^{2+}) center covalently bound to two benzo[15]crown-5 units [7]. Prior to this work, the Reinhoudt group had shown that uranyl-containing clefts could be used to bind $H_2PO_4^-$ and Cl^- ions [8], while others have demonstrated the use of amide subunits for anion recognition. Similarly, the ability of bis(benzo[15]crown-5) systems to form sandwich complexes with K^+, had been exploited by Lockhart and co-workers [9]. These latter researchers prepared a series of polyammonium-centred

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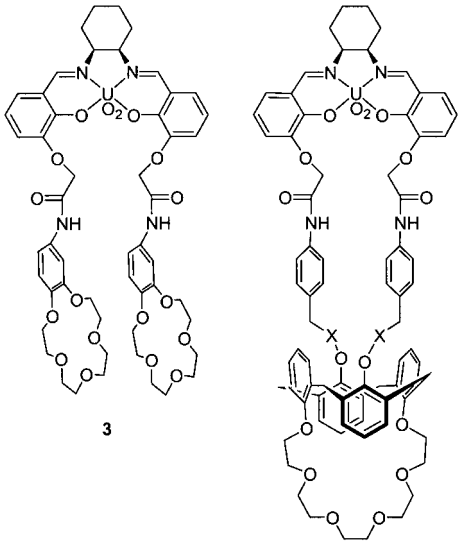
bis(crown)s, demonstrating that both potassium and chloride ions may be coordinated concurrently.



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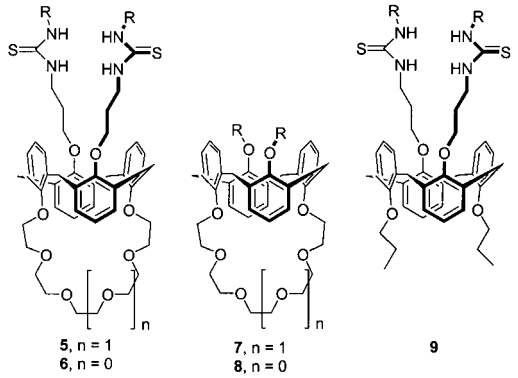
4, X = $(CH_2)_4$

Reinhoudt and co-workers replaced the benzo[15]crown-5 functionalities present in **3** with a rigid Cs^+ selective calix[4]arene crown-6 platform, giving compound **4** [10]. This bifunctional receptor was assessed for its ability to transport CsCl and $CsNO_3$ through a supported liquid membrane (SLM). Although Cl^- is much more hydrophilic than NO_3^-, a higher rate of flux was observed through the hydrophobic membrane for CsCl (1.20×10^{-7} mol m^{-2} s^{-1}) than for $CsNO_3$ (0.89×10^{-7} mol^{-2} s^{-1}) in the presence of **4**. However, not only was substrate selectivity demonstrated but more significantly this rate greatly exceeded that of CsCl transport observed when monofunctional analogues of compound **4**, were used. This was considered consistent with both binding sites being necessary to achieve efficient complexation and transport. Recently, a more detailed investigation into the facilitated transport of salts through SLMs revealed that the bis(thiouredio)-calix[4]-crown-6 **5** transports CsCl more efficiently than its mono-functional calix[4]-crown-6 analogue **7** [11]. However, with higher concentrations of CsCl in the source phase ([CsCl] > 0.3 M), a mixture of cation-binding **7** and anion-binding bis(thiouredio)calix[4]arene **9** receptors was found to give higher CsCl transport rates than the ditopic carrier **5**. Similar results were obtained for KCl transport with the calix[4]-crown-5 **6** being less effective than a mixture of its monofunctional analogues **8** and **9**. These findings were ascribed to a lower diffusion coefficient for the ditopic carriers than the monotopic systems.



5, n = 1
6, n = 0

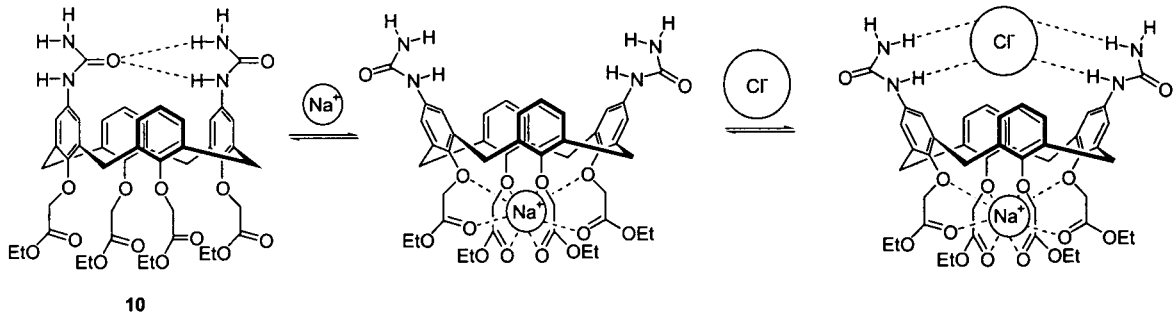
7, n = 1
8, n = 0

9

In another approach to the problem of ditopic receptor preparation, the Reinhoudt group generated a calix[4]arene scaffold with cation-binding ester groups on the lower rim and anion-binding urea groups on the upper rim [12]. In $CDCl_3$, the resulting receptor, calixarene **10**, adopts a pinched conformation due to intramolecular hydrogen bonding between the trans-like urea groups, thus preventing anion binding. However, when sodium ions are added, cation complexation at the lower rim alters the calix conformation, thereby breaking the hydrogen bonds between the urea groups. As a result, halide ions, such as Cl^- and Br^-, can be recognized at the upper rim, as evidenced by downfield shifts in the ^1H NMR signals of the urea hydrogens. This chemistry is summarized in Scheme 1.

The use of heteroditopic ruthenium(II)- and rhenium(I)-bipyridyl-bis(benzocrown) receptors **11** and **12**, introduced by Beer, exemplifies how K^+ binding can not only give an allosteric effect but also induce a switch in anion selectivity [13]. In the absence of K^+, both ligands exhibit a selectivity preference for $H_2PO_4^-$ over Cl^- with a 1 : 1 stoichiometry (for **12**, $K_{H_2PO_4}$ = 205 M^{-1} *vs.* K_{Cl} = 55 M^{-1} in DMSO-d_6). However, after the formation of the intramolecular K^+-biscrown sandwich complex, both receptors exhibit a reverse selectivity. A concurrent decrease in association constant for $H_2PO_4^-$ and increase in those for Cl^- is also observed (for **12**, in the presence of K^+, $K_{H_2PO_4}$ = 35 M^{-1} *vs.* K_{Cl} = 300 M^{-1} in DMSO-d_6).

Positive binding cooperativity was further demonstrated by Beer in the case of the bis(calix[4]arene) rhenium(I)-bipyridyl receptors **13** and **14** [14]. In the presence of two equivalents of alkali metal salt (Li^+, Na^+, K^+), the affinity for iodide was seen to increase significantly. The enhanced affinity was attributed to lower rim complexation of the metal cations by the ester groups, a process thought to introduce rigidity into the calixarene scaffold, thereby preorganizing the central cavity for iodide binding. The largest cooperative anion binding effect was seen for the tetraester **14** with Na^+ (K_I in the presence Na^+ = 320 M^{-1} *vs.* K_I= 40 M^{-1} in its absence; CD_3CN).



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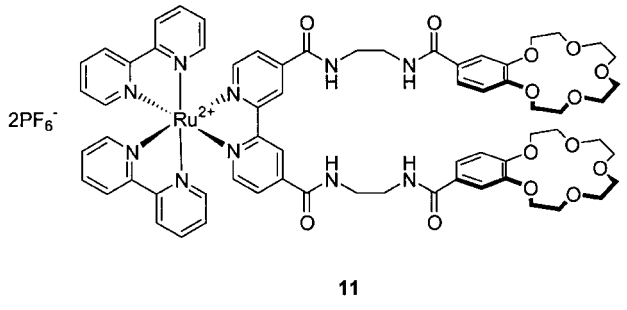
Scheme 1. Proposed sequential binding of Na^+ and Cl^- by receptor **10**.



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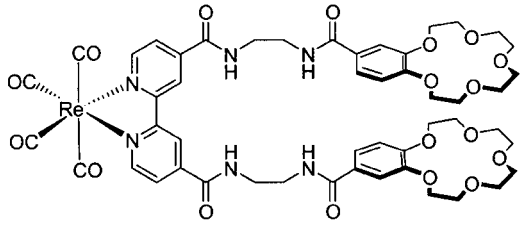

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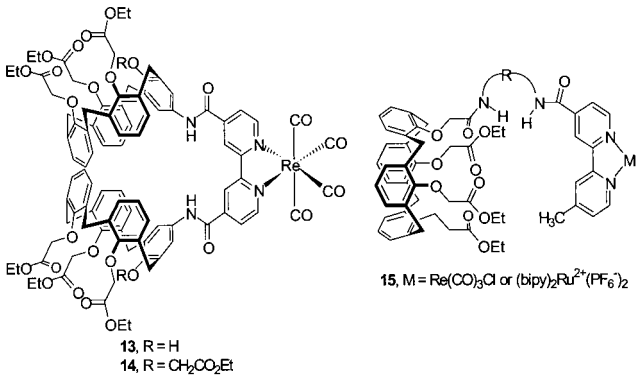
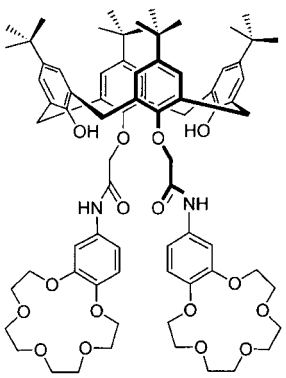


13, R = H
14, R = CH_2CO_2Et

15, M = $Re(CO)_3Cl$ or $(bipy)_2Ru^{2+}(PF_6^-)_2$

More recently, the Beer group has reported a series of calix[4]arene esters linked to a single ruthenium(II)- or rhenium(I)-bipyridyl metal site (e.g., **15**) [15]. In separate ^1H NMR titration experiments, results consistent with the formation of 1 : 1 complexes are reported for the binding of Br^- and I^- anions, and Li^+ and Na^+ cations. In the presence of one equivalent of the alkali metal cations, all the ligands studied show significant increases in the association constants for both Br^- and I^-. The enhanced affinities for these anions in the presence of the co-bound cation is believed to arise from mutual cation-anion attraction, preorganizational effects and increased strength in hydrogen bonding to the bound anion owing to cation complexation disrupting an intramolecular hydrogen bond between the amide NH proton and a calixarene ester moiety.



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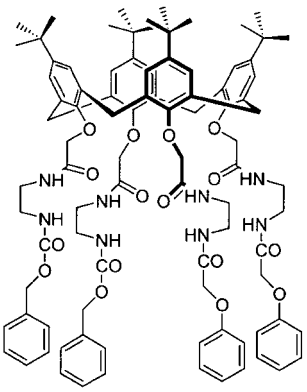

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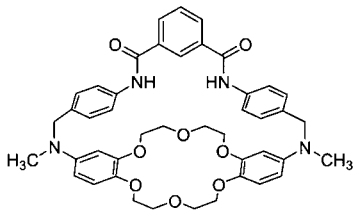
One further example of a calix[4]arene based ditopic receptor has been reported by the Beer group. Receptor **16**, consists of two benzo[15]crown-5 groups attached to a calixarene through amide linkers [16]. Compound **16** alone showed very little affinity for anions. In the presence of K^+ or NH_4^+ ions, however, a sandwich complex is formed between the two benzocrown units, which in turn brings the amide groups into closer mutual proximity. These conformational changes, coupled with the increased electrostatic attraction provided by the co-bound cation, led to a particularly strong binding of dihydrogen phosphate. Receptor **17**, similar in design, was found to complex Na^+ and various anions in a positive cooperative manner [17]. The enhancements for Br^-, Cl^--, and HSO_4^- were found to be ca. 5.5-, 8-, and 14-fold, respectively.



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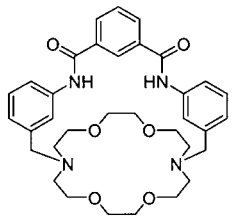


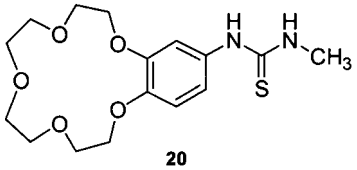
19

Smith and co-workers combined dibenzo-18-crown-6 and 1,3-phenyldicarboxamide subunits to form the preorganized macrobicyclic receptor **18** [18]. Compound **18** is capable of coordinating alkali metal and chloride ions sim-

ultaneously. Binding cooperativity in host **18** was demonstrated by a series of complexation experiments carried out in DMSO-d_6/CD_3CN (3 : 1). These studies revealed that in the presence of 1 molar equivalent of Na^+ or K^+ (added as their tetraphenylborate salts), chloride affinities are enhanced (for Na^+, K_{Cl} = 410 M^{-1}; for K^+, K_{Cl} = 470 M^{-1}) relative to what is seen in the absence of cation (K_{Cl} = 50 M^{-1}). The crystal structure of the NaCl complex shows that in the solid-state compound **18** binds NaCl as a solvent-separated ion pair. As expected, the Na^+ ion is bound within the dibenzocrown unit, with an axial water molecule completing the coordination sphere, whilst the Cl^- anion is hydrogen-bonded to the two NH residues. The central cavity is occupied by either a $CHCl_3$ molecule or two molecules of water, with the ion-ion separation being 7.31 Å.

Subsequently, receptor **19**, an analogue of **18** was synthesized. It was designed with a view to shortening the potential distance between the cobound cations and anions [19]. Results of ^1H NMR titration experiments (DMSO-d_6) provided support for the contention that the chloride anion affinities normally displayed by **19** (K_{Cl} = 35 M^{-1}) are significantly increased in the presence of K^+ (K_{Cl} = 460 M^{-1}) but not Na^+ (K_{Cl} = 50 M^{-1}). Single crystal X-ray diffraction structures were obtained for the NaCl and KCl complexes of **19**. In order to accommodate the Na^+ ion, the diazacrown unit in NaCl·**19** adopts a structure wherein the effective cavity size is reduced relative to the KCl complex (average K—O distance is 2.77 Å *vs.* 2.45 Å for Na—O). Additionally, in NaCl·**19**, the average Cl—O distance is 4.20 Å, significantly shorter than that observed in KCl·**19** (average Cl—O distance is 4.7 Å). The implication is that once a K^+ cation is bound, receptor **19** is better able to form a favorable contact ion-pair with Cl^- than is true in the case of NaCl·**19**.

Nishizawa *et al.* have demonstrated cooperative binding for a series of anions in the presence of Na^+, utilizing the thiourea-functionalized benzo-15-crown-5 (**20**) [20]. In the presence of 2 equivalents of $Na(BPH_4)$ (conditions under which Na^+ is over 95% bound) receptor **20** in CD_3CN exhibits an approximate ten-fold increase in anion binding affinity for NO_3^- (K_{NO_3} = 6.0M^{-1} *vs.* K_{NO_3} (Na) = 66 M^{-1}) and Br^- (K_{Br} = 25 M^{-1} *vs.* K_{Br}(Na) = 260 M^{-1}), and a five-fold increase for I^- (K_I = 4.3 M^{-1} *vs.* K_I(Na) = 20 M^{-1}).



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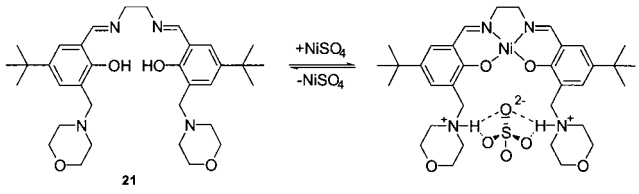
With regard to the application of novel ligands in the area of separation technology, White, Tasker and co-workers prepared receptor **21** which combines both cationic and anionic binding sites (Scheme 2) [21]. Complexation of a transition metal cation, such as Cu(II) or Ni(II) to the salen-based cation-recognition pocket results not only in the phenolic protons being transferred to the nitrogen atoms of the morpholine moieties, but also brings the two groups into proximity for cooperative anion binding. This finding was underscored by an X-ray diffraction analysis of **21**·$NiSO_4$, which revealed the sulfate dianion being bound to the quarternized amines *via* two separate bifurcated hydrogen bonds. Electrostatic interactions with the salen-bound Ni^{2+} cation also contribute to binding. The authors demonstrated that receptor **21** could be used to extract $CuSO_4$ into chloroform from an aqueous solution of $CuSO_4$ at pH 3.8.



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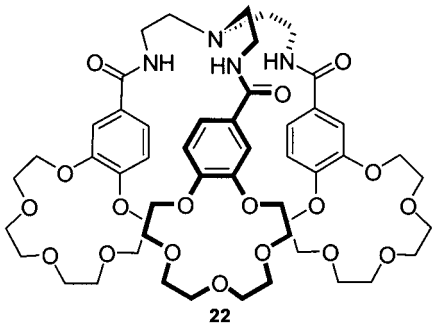
Scheme 2. Complexation of Ni^{2+} and SO_4^{2-} by receptor **21**.

Table 1. Binding constants for **22** in the presence and absence of sodium picrate in $CDCl_3$. From Ref. [22].

Anion	K/M^{-1}
Cl^-	60[a]
Cl^- (+ Na^+)[b]	520[c]
I^-	30[a]
I^-(+ Na^+)[b]	390[c]
ReO_4^-	40[a]
ReO_4^-(+ Na^+)[b]	840[c]

[a]At 298 K, errors estimated to be ≤10%.
[b]Titration carried out in the presence of 1 equiv. of sodium picrate.
[c]At 298 K, errors estimated to be ≤15%.

Beer and co-workers have prepared compound **22**, a tripodal tris(amido benzo[15]crown-5] [22]. In the presence of 1 equivalent of sodium picrate, **22** acts as a ditopic receptor, showing enhanced anion binding for Cl^-, I^- and ReO_4^- ions (Table 1). Compound **22** was shown to extract sodium pertechnetate ($NaTcO_4$) efficiently under conditions designed to simulate aqueous waste streams containing this radioactive waste material.



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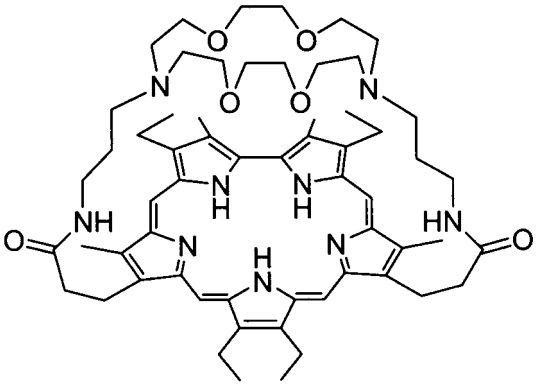
Our own efforts towards ion-pair recognition had their origins with the synthesis of crowned sapphyrin **24**, whose HCl salt was shown to complex simultaneously ammonium

Table 2. Binding constants for **24** and **25** in CD_2Cl_2.

Anion/cation pair	Binding constant for **24**[a]/M^{-1}	Binding constant for **25**[a]/M^{-1}
NBu_4Cl	$>1.0 \times 10^{4}$[b]	9.0×10^{2}
NBu_4Br	5.8×10^{2}	3.0×10^{1}

[a]At 298 °C, errors to be ≤10%.
[b]The calculated binding constant was 1.4×10^4 M^{-1}.

and fluoride ions, in the crown and sapphyrin units, respectively [23]. More recently, we have used a similar approach to form a calix[4]pyrrole-crown ditopic receptor **25** [24]. This product, containing a calixpyrrole anion recognition center, was prepared in 44% yield by coupling a β-"hooked" calix[4]pyrrole **24** [25] with 4-aminobenzo-15-crown-5 using BOP and triethyl amine in DMF. An "appropriate" control system 26 was synthesized by the same means using 3,4-dimethoxyaniline as the amine. This compound was obtained in 65% yield.



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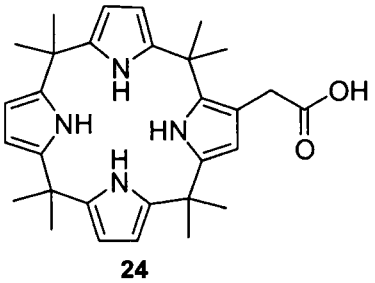
Preliminary ^{1}H NMR spectroscopic studies, carried out in CD_2Cl_2, revealed that system **25** binds both Cl^- and Br^- (as their tetra *n*-butyl ammonium salts) roughly 15 times more effectively than **26** (Table 2).



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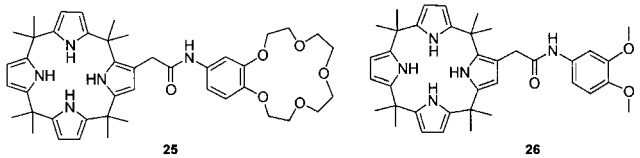
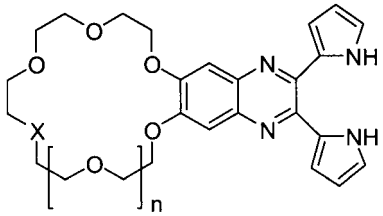


25 **26**

Recently, dipyrrolylquinoxalines have emerged as a new class of neutral anion receptors [26]. In view of this, we felt that covalent conjugates, wherein a dipyrrolylquinoxaline moiety is linked to a cation-selective crown ether, would result in receptors capable of effecting complementary anion and cation complexation. In accord with such thinking, dipyrrolylquinoxalines **27–30** were prepared by reaction of the appropriate 1,2-diamino-benzocrown and dipyrrolylethanedione. Crystals of **27**, suitable for X-ray diffraction analysis, were obtained by slowly evaporating a MeOH solution of the free ligand. The results of this analysis show that **27** exists as a dimeric pair in the solid-state. The planes of the fused aromatic rings are nearly parallel (3.36 Å apart) and appear to be π-stacked. The NH of one pyrrole is within hydrogen bonding distance of two oxygen atoms present on an adjacent crown ether giving a total of four hydrogen bonds. The actual NH$\cdots$O bond distances are long, as would befit the bifurcated nature of the interaction (average N-O distance is 3.26 Å). Preliminary ^{1}H NMR spectroscopic titrations, carried out in CD_3CN, have provided qualitative support for the proposal that sodium and fluoride ions can be bound by **27**. Unfortunately, ion pairing between 'free' NaF is a dominant feature under the conditions of the experiment (i.e., in CD_3CN) and this has so far limited quantitative analyses. Further studies of these new dipyrrolylquinoxalines are currently ongoing.

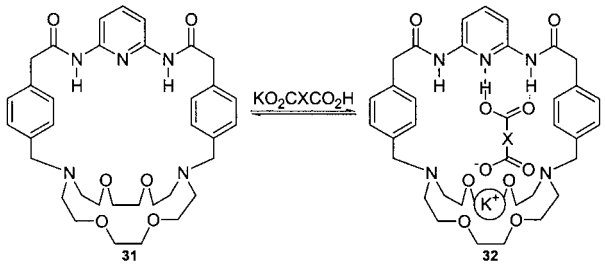


27, X = O, n = 0
28, X = O, n = 1
29, X = NH, n = 0
30, X = NH, n = 1

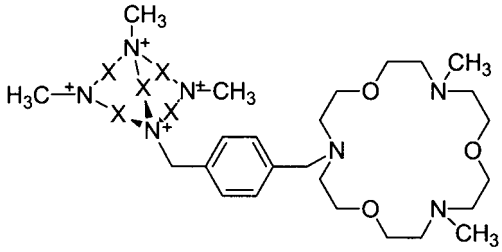
Simultaneous complexation of organic ion-pairs

Another important aspect of ditopic binding is the recognition of organic ion-pairs. Much of the impetus for this line of investigation comes for the realization that at physiological pH amino acids exist as zwitterions. Consequently, a brief discussion of receptors that recognize organic salts is warranted. Kilburn and co-workers prepared receptor **31**, structurally related to **19**, which was shown by a series of solid-liquid and liquid-liquid extraction experiments to take up variable amounts of the mono-potassium salts of various dicarboxylic acids from water into $CDCl_3$ [27]. The proposed mode of binding is depicted as structure **32** in Scheme 3.

Schmidtchen covalently linked triaza-18-crown-6 with a positively-charged polyammonium macrocycle to give the ditopic receptor **33**, a species that was found to bind efficiently zwitterionic compounds such as γ-amino butyric acid [28].



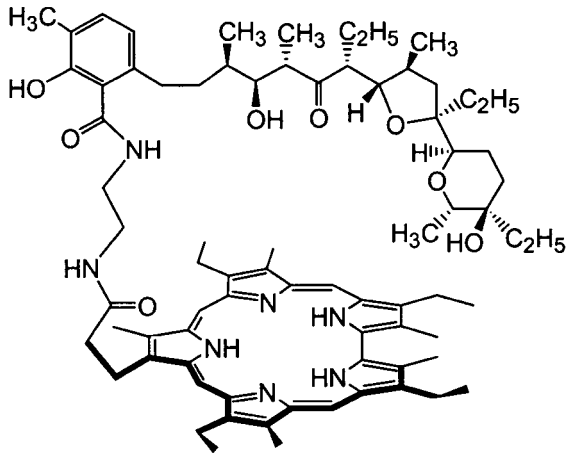
Scheme 3. View of the proposed binding interactions involved in the binding of dicarboxylic acid mono-potassium salts.



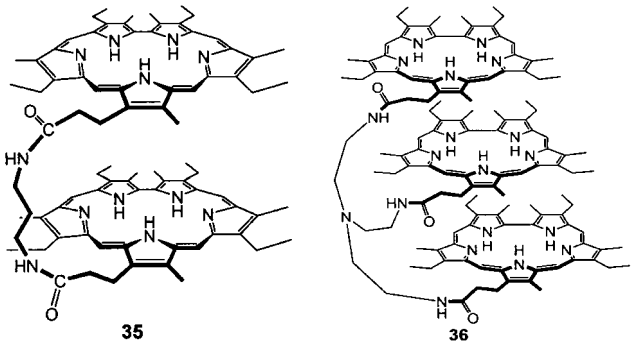
33, X = $(CH_2)_6$

Our own group has also reported several ditopic receptors for organic salts. In one study, performed after an initial analysis revealed that monomeric sapphyrins perform poorly as organic transport agents, we showed that a sapphyrin-lasalocid conjugate **34** was able not only to transport aromatic α-amino acids, but do so in a selective manner [29]. This structure showed two different types of selectivity with respect to structure. A first type of selectivity involved the type of aromatic α-amino acid used, with very different transport rates being observed for L-phenylalanine, L-tryptophan, and L-tyrosine (k_t(10^{-5} mol cm^{-2} h^{-1}): L-Phe = 20.0, L-Trp = 5.0, L-Tyr = 0.02). A second type of selectivity involved the stereochemistry of the amino acid, e.g., (k_t(10^{-5} mol cm^{-2} h^{-1}): L-Phe = 20.0, *vs.* D-Phe = 12.7). Calculated binding constants provided support for the conclusion that L-Phe was indeed bound more strongly than L-Trp or L-Tyr. By contrast, equilibrium analyses revealed that L-Phe and D-Phe were bound with roughly the same affinity. It was thus suggested that off rates play a critical role in modulating the transport rates and cannot necessarily be correlated with the binding constant.

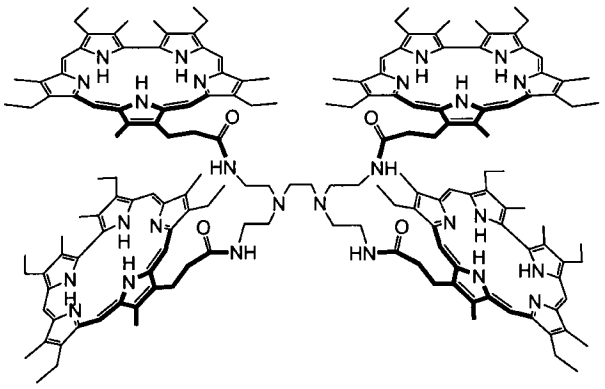
Protonated sapphyrin, as anion binding subunits, have also been used to prepare receptors for polyanions. This led to the synthesis of, for example, the sapphyrin dimer **35** [30], as well as its trimeric **36** and tetrameric **37** cogeners [31]. The protonated form of dimer **35** was found to bind dicarboxylate anions in methanolic solvent. Binding constants ranged from 260 M^{-1} for oxalate dianion up to nearly 10^4 M^{-1} for nitroterephthalate. Systems **36** and **37**, on the other hand, were found to be effective receptors for ADP and ATP. For ADP, binding constants in water-methanol (1 : 1) ranged from 2.2×10^3 M^{-1} for **36** to 4.0×10^3 M^{-1} for **37**, whereas for ATP the binding affinities were 5.0×10^3 M^{-1} for **36** and 6.8×10^3 M^{-1} for **37**.



34



35 **36**



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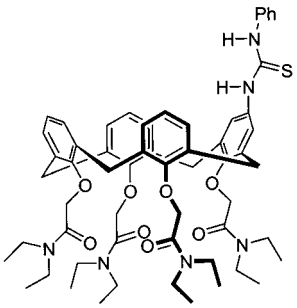
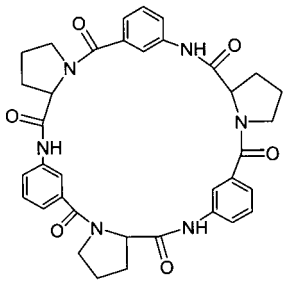
The calix[4]arene system **38**, prepared recently by Ungaro and co-workers, represents a different approach to carboxylate recognition. In this case, binding of Na^+ by four amide groups on the lower rim of the calix is found to increase the binding of carboxylate anions, such as benzoate, propionate and isobutyrate [32]. The explanation put forward by the authors for this effect is that sodium complexation rigidifies the calixarene apolar cavity and induces a small electron-withdrawing effect on the upper-rim thiourea group. This, in turn, enhances the hydrogen-bond donating ability of the thiourea NH groups, thereby increasing carboxylate anion recognition.

An alternative approach to the design of receptors for ion-pair recognition employs cyclic peptides. Kubik and Goddard demonstrated that the cyclic peptide **39** binds vari-

ous ammonium iodide salts with positive cooperativity [33]. The peptide is found to adopt a conformation analogous to the cone conformation of calixarenes. It is also found to bind cations by cation-π interactions, while complexing the iodide ion *via* peptidic NH hydrogen bonds.



38



39

Conclusions

This review has highlighted the incipient, but emerging field of ditopic receptor-based ion-pair recognition. In general, ditopic receptors combine functionalities such as cation-binding crown ethers and calixarenes, and anion-binding Lewis-acidic metal centers, pyrroles, amido, and urea groups that have been shown to complex well individual classes of ions (anions or cations) with a high degree of selectivity and affinity. Such a high degree of independent recognition is of interest in light of the fact that 'free' ion-pairing forces in solution are often dominant in the highly coordinating solvents needed to overcome inherent problems of salt insolubility. This need to start with effective individual subunits and to overcome ion-pairing forces and other ion-assembly processes that occur in solution, has limited the number of functioning systems reported to date. On the other hand, the challenges and importance of ion pair recognition is such that it can be predicted safely that a range of new, and improved, systems will be forthcoming in the next few years.

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