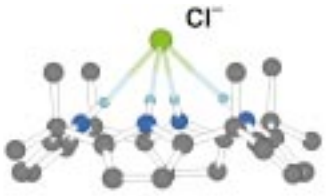
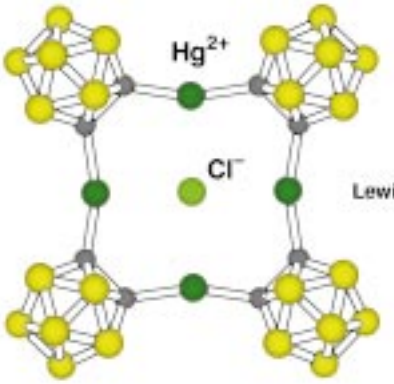
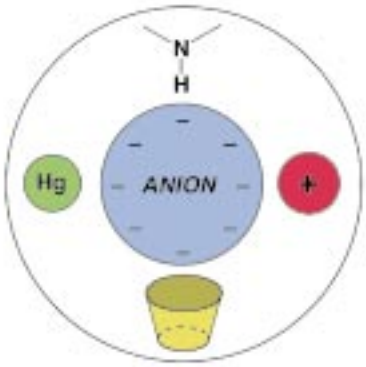
Binding



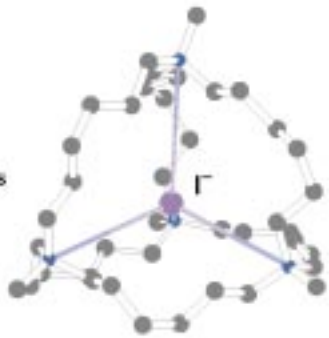
hydrogen bonds



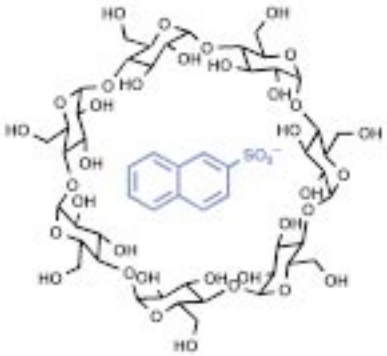
Lewis acids



electrostatics



hydrophobic effect



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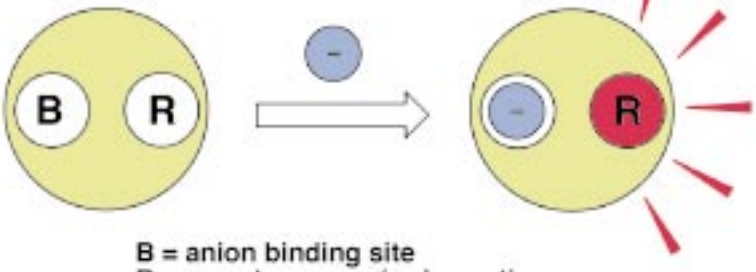
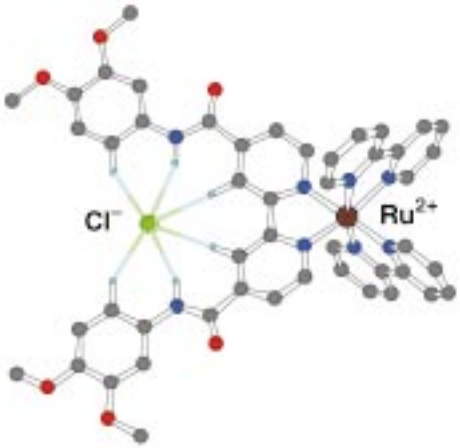
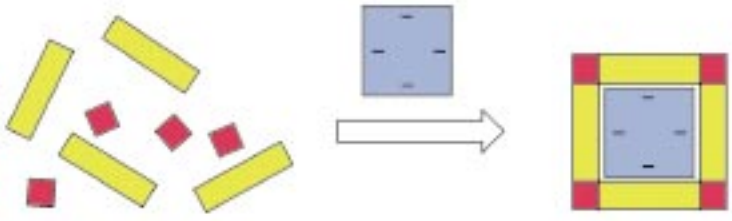
Sensing

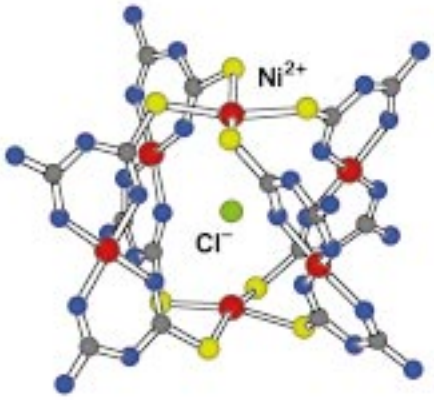


B = anion binding site
R = reporter group (redox active, fluorescent or colorimetric moiety)



Directed assembly





Anion Recognition and Sensing: The State of the Art and Future Perspectives

Paul D. Beer* and Philip A. Gale*

Anion recognition chemistry has grown from its beginnings in the late 1960s with positively charged ammonium cryptand receptors for halide binding to, at the end of the millennium, a plethora of charged and neutral, cyclic and acyclic, inorganic and organic supramolecular host systems for the selective complexation, detection, and separation of anionic guest species. Solvation effects and pH values have been shown to play crucial roles in the overall anion recognition process. More recent developments include exciting advances in anion-templated syntheses and directed self-assembly, ion-pair recognition, and the function of anions in supramolecular catalysis.

Keywords: anions · macrocycles · molecular recognition · self-assembly · sensors · supramolecular chemistry

1. Introduction

Anion recognition chemistry has its roots in work conducted in the late 1960s around the same time that Pedersen reported the synthesis and coordination chemistry of crown ethers and Lehn published the first accounts of cation coordination chemistry by cryptands. In the 1970s, the coordination chemistry of group 1 and 2 metal and ammonium cations attracted most interest and consequently cation recognition is now a well-developed and mature area of supramolecular chemistry. By contrast, the coordination chemistry of anions received little attention (with a few notable exceptions) and it has only been in the last twenty years that sustained effort has been applied to the problems inherent in binding anions.[1] There are a number of reasons for this sudden growth in this new area of coordination chemistry. Anions are ubiquitous throughout biological systems. They carry genetic information (DNA is a polyanion) and the majority of enzyme substrates and co-factors are anionic. A well known example is carboxypeptidase A,[2] an enzyme that coordinates to the C-terminal carboxylate group of polypeptides by the formation of an arginine – aspartate salt bridge, and catalyzes the hydrolysis of this residue. The salt-bridge binding motif is also observed in zinc finger/DNA complexes[3] and RNA stem loop – protein interactions.[4] Anions also play roles in the areas of medicine and catalysis, whilst pollutant anions have been linked to eutrophication of rivers (from the over use of phosphate-containing fertilizers)[5] and carcinogenesis (metabolites of nitrate).[6] The production of pertechnetate during the reprocessing of nuclear fuel (and its subsequent discharge into the seas and oceans) is also a matter of environmental concern.

The design of anion receptors is particularly challenging. There are a number of reasons for this. Anions are larger than isoelectronic cations (Table 1)[7] and therefore have a lower charge to radius ratio. This means that electrostatic binding interactions are less effective than they would be for the smaller cation. Additionally anions may be sensitive to pH values (becoming protonated at low pH and so losing their negative charge), thus receptors must function within the pH window of their target anion. Anionic species have a wide range of geometries (Figure 1) and therefore a higher degree of design may be required to make receptors complementary to their anionic guest.

Solvent effects also play a crucial role in controlling anion binding strength and selectivity. Electrostatic interactions

Table 1. A comparison of the radii r of isoelectronic cations and anions in octahedral environments.[7]

Cation	r [Å]	Anion	r [Å]
Na^+	1.16	F^-	1.19
K^+	1.52	Cl^-	1.67
Rb^+	1.66	Br^-	1.82
Cs^+	1.81	I^-	2.06

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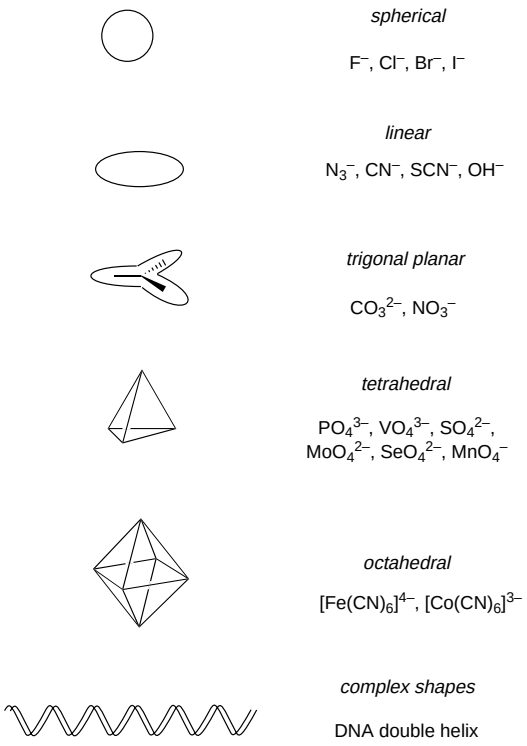
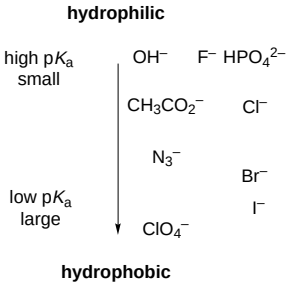


Figure 1. The structural variety of anions.

generally dominate in anion solvation, and hydroxylic solvents in particular can form strong hydrogen bonds with anions. A potential anion receptor must therefore effectively compete with the solvent environment in which the anion-recognition event takes place. For example, a neutral receptor that binds anions solely through ion–dipole interactions may only complex anions in aprotic organic solvents, whereas a charged receptor has the capacity to bind highly solvated (hydrated) anions in protic solvent media. It is no coincidence that biological anion receptor systems are optimized to operate in a very specific range of environments where the source of selectivity for the biological anion is the difference in free energy lost on dehydrating the anion and that gained by the interaction of the anion with the binding site.[8]

Hydrophobicity can also influence the selectivity of a receptor. The Hofmeister series[9] (Scheme 1), which was first established through studies on the effect of salts on the solubility of proteins, orders anions by their hydrophobicity (and therefore degree of aqueous solvation). Hydrophobic anions are generally bound more strongly in hydrophobic binding sites.



Scheme 1. Hydrophilic/hydrophobic series of anions.

This review article will highlight important developments in the recognition and sensing of anionic substrates and look at recent advances[10–13] that suggest that anion coordination chemistry will have a rich future in the 21st Century.

P. D. Beer

P. A. Gale

Paul D. Beer was born in Totnes, Devon (UK). In 1979 he obtained a first class honours degree in chemistry from King's College London, and remained there to undertake research in the field of organophosphorus chemistry under the supervision of Dr C. D. Hall. In 1982 he received a PhD, and a Royal Society postdoctoral fellowship enabled him to conduct research in supramolecular chemistry with Professor J.-M. Lehn at the Université Louis Pasteur, Strasbourg (France). After a demonstratorship at the University of Exeter in 1983, he took up a New Blood Lectureship at the University of Birmingham in 1984. In 1990 he moved to the University of Oxford, where he is also a tutorial fellow at Wadham College. He became a professor of chemistry in 1998. He was awarded the RSC Meldola medal in 1987, the UNESCO Javed Husain prize in 1993, and the RSC Corday-Morgan medal in 1994. His research interests cover many aspects of charged and neutral guest coordination chemistry, including the synthesis and coordination properties of redox- and photo-responsive receptors designed to selectively recognize and sense biological and environmentally important guest species.

Philip A. Gale was born in Liverpool (UK) in 1969. He graduated from Wadham College, Oxford with a BA (Hons.) in Chemistry in 1992 (and an MA in 1995). In 1992, he moved to Linacre College and carried out graduate work at the Inorganic Chemistry Laboratory. He graduated in 1995 (DPhil) for work carried out with Professor Paul D. Beer on the cation coordination chemistry of calix[4]diquinones and the functionalization of calix[5]arenes. He was awarded a Fulbright post-doctoral fellowship in 1995 and joined Professor Jonathan L. Sessler's research group at the University of Texas at Austin working on the synthesis, anion coordination properties, and applications of calix[4]pyrroles (meso-octaalkylporphyrinogens). In 1997, he took up a Royal Society University Research Fellowship at the Inorganic Chemistry Laboratory, Oxford. In 1999 he moved to his present position as Royal Society University Research Fellow and Lecturer at the University of Southampton. His research interests include many aspects of supramolecular chemistry including anion receptor chemistry.

2. Anion Recognition

The design of selective hosts for anions requires that the geometry and basicity of the anion and the nature of the solvent medium be taken into account. Complementarity between the receptor and anion is clearly crucial in determining selectivities. A useful way of categorizing anion receptors is to consider the types of noncovalent interaction used to complex the anionic guest. These include electrostatic interactions, hydrogen bonding, hydrophobicity, coordination to a metal ion, and combinations of these interactions working together. The work described in this section is not a comprehensive review of the literature. It is intended to be a series of paradigms that illustrate particular elements of anion recognition.

2.1. Electrostatic Interactions

In some very elegant early work, Schmidtchen produced the macrotricyclic quaternary ammonium hosts **1** and **2**[14, 15] and found that these receptors formed complexes with a variety of anionic guests in water.[16] The cavity in receptor **1** has an internal diameter of 4.6 Å and forms a strong complex with an iodide ion (diameter: 4.12 Å). The crystal structure of the iodide complex (Figure 2) reveals that the anion is encapsulated within the macrotricycle.[17] The larger receptor **2** is able to form complexes with anions such as *p*-nitrophenolate that are too large to form complexes with receptor **1**. Receptors **1** and **2** are positively charged and are therefore associated with counterions that may compete for the anion-binding site. To overcome this, Schmidtchen produced zwitterionic receptors such as **3** and **4** that are neutral.[18, 19] NMR experiments in water showed that receptor **4** forms stronger complexes with chloride, bromide, and iodide ions than receptor **1**.

Dipolar bonds can also be used for anion recognition.[20, 21] The phosphine oxide–disulfoxide macrocycle **5** contains three convergently arranged dipolar bonds that define an anion binding site below the macrocyclic ring. NMR studies in $CDCl_3/CD_3OD$ (98/2) reveal that weak complexes are obtained with chloride ($K = 65\ M^{-1}$) and other anions.

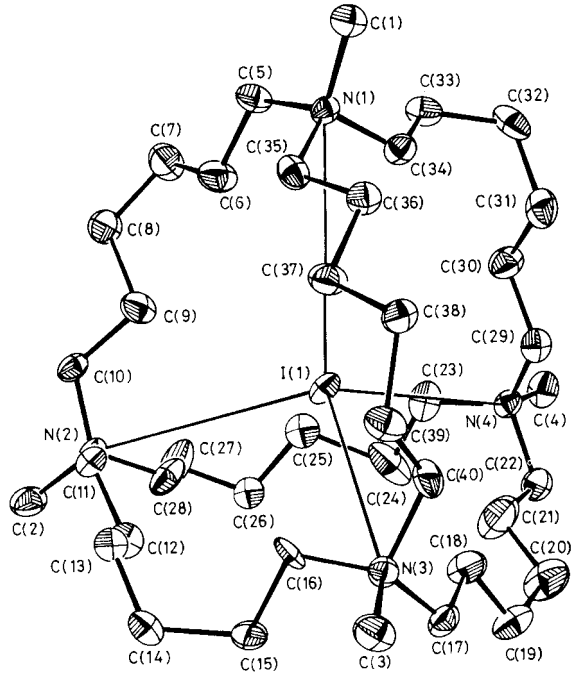
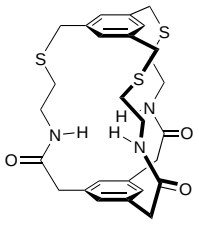


Figure 2. The X-ray crystal structure of the iodide complex of receptor **1** (hydrogen atoms are omitted). Reproduced with permission from ref. [17]. Copyright© The Royal Society of Chemistry 1984.

2.2. Hydrogen Bonds

Hydrogen bonds are directional, which allows for the possibility of designing receptors with specific shapes that are capable of differentiating between anionic guests with different geometries or hydrogen-bonding requirements in nonpolar solvents.

In 1986, Pascal prepared the first purely amide-based anion receptor.[22] Receptor **6** showed evidence of binding fluoride ions in $[D_6]$DMSO. In 1993 Reinhoudt and co-workers produced a series of acyclic tripodal receptors containing amide groups (**7**–**12**)[23] whilst Raposo et al. synthesized a preorganized amide-modified cyclohexyl ring **13**.[24] Receptors **7**–**13** are all C_3 symmetric and are consequently arranged to bind tetrahedral anions.



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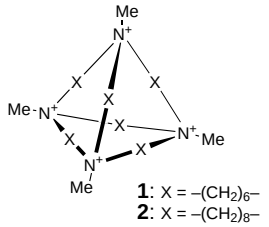
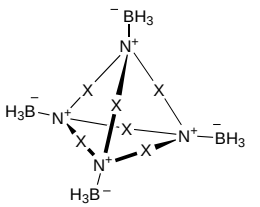
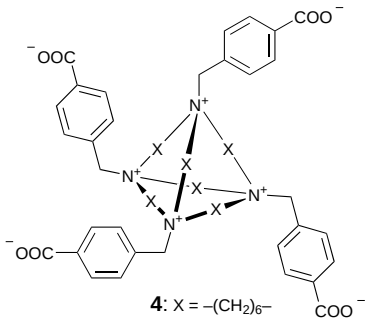


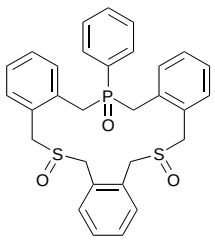
1: X = –$(CH_2)_6$–
2: X = –$(CH_2)_8$–



3: X = –$(CH_2)_6$–



4: X = –$(CH_2)_6$–



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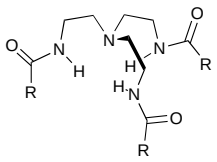
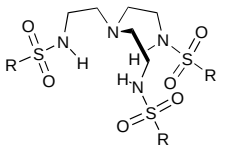
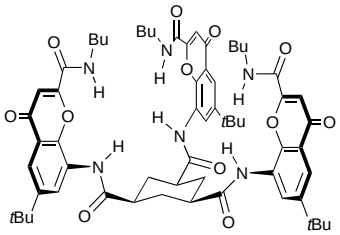


7: R = CH_2Cl
8: R = $(CH_2)_4CH_3$
9: R = C_6H_5
10: R = 4-$MeOC_6H_4$

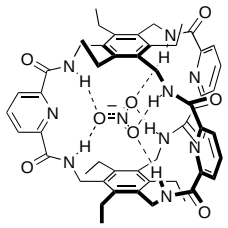


11: R = 4-MeC_6H_4
12: R = 2-Naphthyl



13

Anslyn and co-workers have recently reported the synthesis of a trigonal box by condensation of 1,3,5-tris(aminomethyl)-2,4,6-triethylbenzene with three equivalents of 2,6-pyridinedicarbonyl dichloride in dichloromethane in the presence of triethylamine.[25] The rigid cyclophane **14** was formed in 40 %



14 • NO_3^-

yield. Interestingly, because the amide NH groups in **14** are arranged in a trigonal prismatic array, they are able to coordinate to the π-electron system of planar anions such as carboxylates and nitrate. The crystal structure of the acetate complex of **14** is shown in Figure 3 and reveals that the acetate anion is bound within the cavity of the box. Anslyn et al. concluded that nitrate must also be bound within the cavity of the box because it is planar and bound very strongly (in CD_3CN/CD_2Cl_2 (3/1 (v/v)) solution it is bound only 2.6 times less strongly than acetate even though it is 10^6 times less basic). Therefore, receptor **14** represents a significant advance in the coordination of the normally weakly coordinating nitrate ion.

Urea and thiourea are particularly good hydrogen-bond donors and are excellent receptors for Y-shaped anions such as carboxylate through the formation of two hydrogen bonds. The very simple urea-based receptor **15** shows increasingly stable complexes with more highly charged and more basic bidentate anions (Table 2).[26]

Umezawa and co-workers have produced a series of ayclic thiourea cleft molecules including some highly preorganized systems containing a xanthene spacer.[27] Receptors **16** and **17** bind anions very strongly with stability constants up to

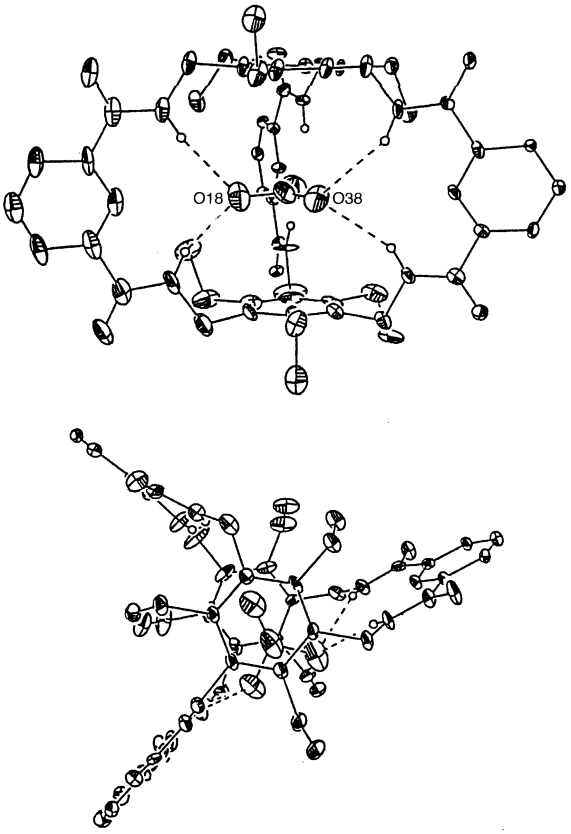
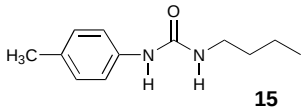


Figure 3. The X-ray crystal structure of the acetate complex of receptor **14** (hydrogen atoms are omitted). Reproduced with permission from ref. [25]. Copyright© WILEY-VCH 1997.



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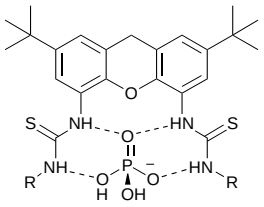
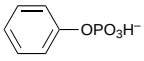
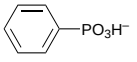
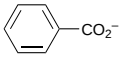
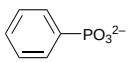
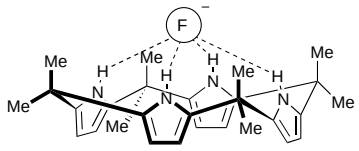


16: R = Bu
17: R = Ph

Table 2. The basicity and stability constants (in DMSO) of various bidentate anions with receptor **15**.

Guest	pK_b	K [M^{-1}]
	13	30
	12	140
	10	150
	7	2500

195000 M^{-1} for receptor **17** and $H_2PO_4^-$ ions in [D_6]DMSO. This is a consequence primarily of the high degree of preorganization present in these receptors. The selectivity for $H_2PO_4^-$ ions can be attributed to the complementary hydrogen-bonding array present in these clefts that can form four hydrogen bonds to each $H_2PO_4^-$ ion. Pyrrole NH groups may also form hydrogen bonds to anions. In 1996, Sessler and co-workers reported that calix[4]pyrroles (*meso*-octaalkylporphyrinogens), macrocycles first synthesized in the nineteenth century by Baeyer,[28] also coordinate to anions.[29] *meso*-Octamethylcalix[4]pyrrole **18** was shown to form complexes with fluoride, chloride, and dihydrogen phosphate with stability constants of 17200, 350, and 100 M^{-1} respectively in CD_2Cl_2. The conformation of the macrocycle in the solid state



18 • F^-

changes dramatically upon anion complexation. The free calixpyrrole adopts a 1,3-*alternate* conformation wherein adjacent rings are oriented in opposite directions. However the crystal structure of the chloride complex of **18** reveals that the macrocycle adopts a *cone* conformation with the four pyrrole NH groups forming hydrogen bonds to the bound chloride ion (Figure 4).

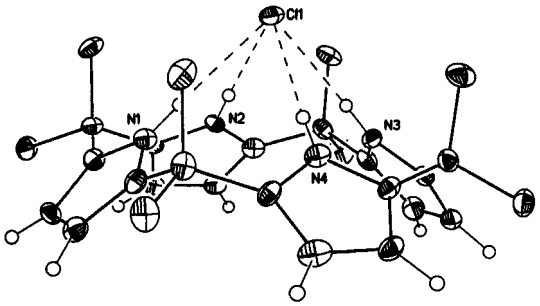


Figure 4. The X-ray crystal structure of the chloride complex of receptor **18**. Reproduced with permission from ref. [29]. Copyright© American Chemical Society 1996.

The ease of preparing calixpyrroles in high yield makes them amenable to industrial applications. Indeed, Sessler and co-workers have already produced calixpyrrole-modified solid supports (such as Gel M; Figure 5) for the separation of anions by high-performance liquid chromatography (HPLC).[30] The separation of oligonucleotides between twelve and eighteen bases in length by Gel M is shown in Figure 5.[31] Other uses for these macrocycles include their incorporation in ion-selective electrodes,[32] in electrochemically active discrete molecular hosts[33] designed to sense anionic guests, and in optical sensors for anions.[34]

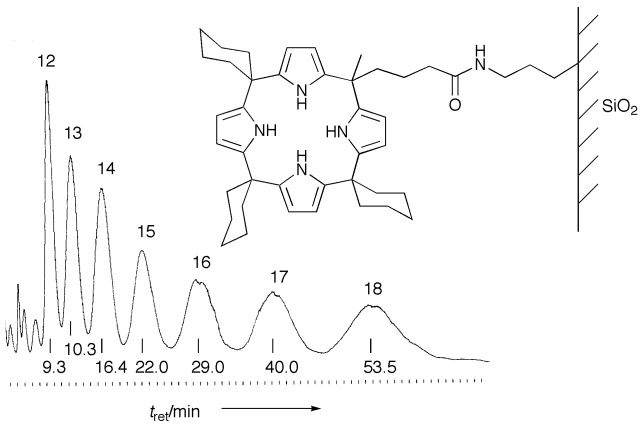
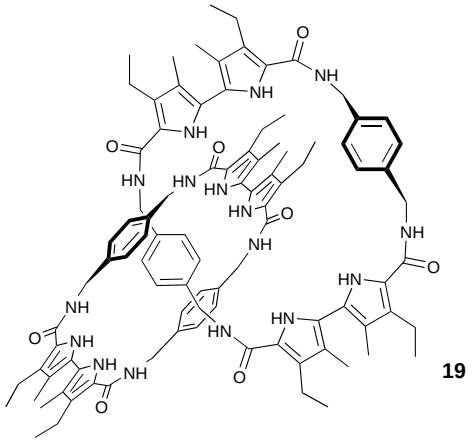


Figure 5. Separation of $dT_{12}-dT_{18}$ on calixpyrrole-modified silica gel. Flow rate 0.4 mL min^{-1}, mobile phase MeCN/[aq NaCl (250 mM)/aq Na_3PO_4 (50 mM)] 1/1 (v/v; isochratic), pH 7.0, column temperature 25 °C, UV detection at 265 nm. t_{ret} = retention time. Reproduced with permission from ref. [31]. Copyright© The Royal Society of Chemistry 1998.

Sessler, Vögtle and co-workers have reported the synthesis of a bipyrrole-based [2]catenane **19** that forms extremely stable complexes with anions. NMR titration techniques



19

revealed that the catenane binds anions with very high stability constants (up to 10^7 M^{-1} with $H_2PO_4^-$ in [D_2]1,1,2,2-tetrachloroethane).[35] This high stability is attributed to the formation of a tetrahedral cavity between the rings which provides an ideal coordination geometry for tetrahedral anion coordination (Figure 6).

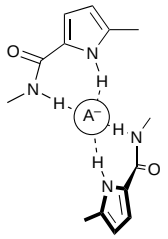
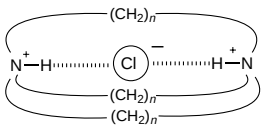


Figure 6. Catenane **19** provides an array of tetrahedral donor hydrogen bonds.

2.3. Electrostatic Interactions and Hydrogen Bonds

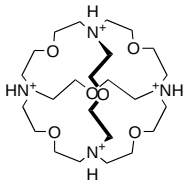
Hydrogen bonds and electrostatic interactions can be used together to produce very effective receptors for anions. In fact, the earliest example of a macrocyclic synthetic anion receptor, reported in 1968, bound anions by a combination of these interactions. Park and



20: $n = 9$
21: $n = 10$

Simmons produced several macrobicyclic ammonium cages, for example, **20** and **21**, which coordinate to halide ions through electrostatic interactions and hydrogen bonds.[36] NMR and crystallographic analysis showed that the halide ions are bound within the cage between the two protonated nitrogen atoms.

Eight years after this work, Graf and Lehn described the binding of halide ions by compound **22**. Receptor **22** is a tetraprotonated macrotricyclic *size*-selective ligand,[37] which binds chloride ions with a stability constant ($\lg K$) of more than 4 in aqueous solution.[38] The larger iodide ion is too big to fit into the cavity and is therefore bound only weakly. On the other hand, receptor **23**, an ellipsoidal hexaprotonated macrobicyclic ligand, was reported by Lehn et al. to be selective for linear anions such as azide N_3^- ($\lg K = 4.3$ in aqueous solution) that are complementary to the *shape* of the cavity.[39, 40]



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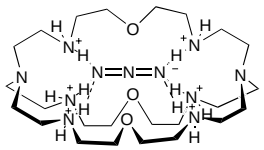
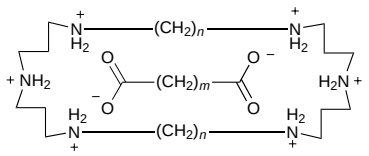


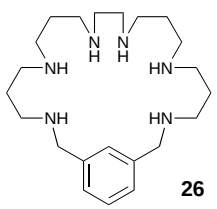
23 • N_3^-

In the 1980s, Hosseini and Lehn reported that protonated ammonium macrocycles **24** and **25** could discriminate between dicarboxylate ions on the basis of size.[41, 42] Receptor **24** binds shorter chain carboxylates ($m = 2$, 3) more strongly, whilst **25** preferentially binds those with longer alkyl chains ($m = 5$, 6).



24: $n = 7$
25: $n = 10$
$m = 2,3,5,6$

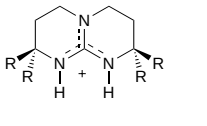
The protonated version of the hexaazametacyclophane **26** has been shown to bind AMP, ADP, and ATP in aqueous solution.[43] The anionic phosphate groups of the nucleotides coordinate to the macrocycle through a combination of electrostatic and hydrogen-bonding interactions, whilst NMR studies have indicated that the nucleoside base π stacks with the benzene ring present in the macrocycle.



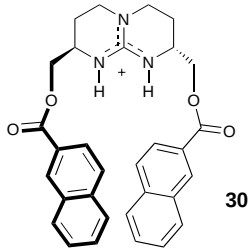
26

As has already been mentioned in the introduction, care must be taken with protonated polyammonium receptors so that the environment is sufficiently acidic for them to remain protonated whilst not too acidic to protonate any putative anionic guest. Guanidine is readily protonated to form the guanidinium ion, which is stabilized by resonance and charge delocalization. With a pK_a of 13.6, the guanidinium cation is approximately three orders of magnitude more stable than a protonated secondary amine ($pK_a \approx 10.5$). Guanidinium therefore remains protonated up to high pH values, and is ideal for extending the pH range over which anion receptors operate.

Schmidtchen and co-workers incorporated the guanidinium group into a bicyclic ring to form **27**–**29**. These receptors possess hydrogen-bonding arrays similar to those present in ureas. This has led to extensive use of guanidinium-based receptors for binding complementary carboxylate or phosphate guests. For example, receptor **27** forms a very stable complex ($K = 1.4 \times 10^5\,M^{-1}$) with *p*-nitrobenzoate in chloroform.[44] The chiral receptor **30**, synthesized by de Mendoza, Lehn, and co-workers, shows a preference for extracting *tert*-butoxycarbonyl (Boc)-protected L-tryptophane into chloroform from a racemic mixture in water.[45] In this case, the guanidinium–carboxylate interaction is further enhanced by π–π stacking.

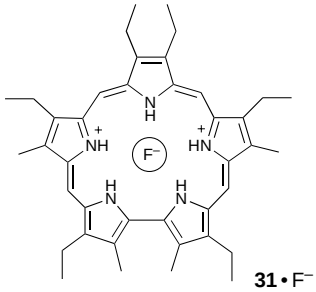


27: R =
28: R = OH
29: R = H



30

Pyrrolic NH groups can be combined with electrostatic interactions to produce receptors that have an extremely high affinity for anions. Early work by Sessler et al. demonstrated that sapphyrins (pentapyrrolic expanded porphyrins first synthesized by Woodward and co-workers[46]) are capable of coordinating to anions. The core of the sapphyrin macrocycle **31** may be doubly protonated to form a receptor with a positive charge and an array of five NH hydrogen-bonding groups. Solution-phase experiments indicated that fluoride



31 • F^-

ions bind over 10^3 times more strongly to diprotonated sapphyrin than either bromide or chloride ions.[47, 48] X-ray crystallographic analysis revealed that the fluoride ion is held in the plane of the sapphyrin ring by five N–H···F^- hydrogen bonds (Figure 7).[49]

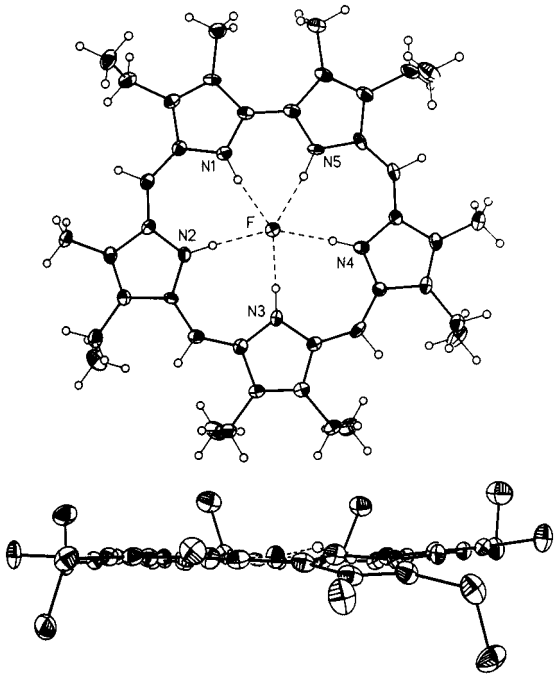
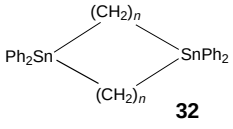


Figure 7. The crystal structure of the fluoride complex of diprotonated sapphyrin **31**. Reproduced with permission from ref. [49]. Copyright© American Chemical Society 1992.

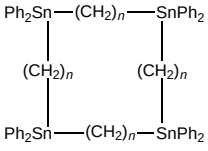
2.4. Metal or Lewis Acid Coordination

Electron-deficient Lewis-acidic centers are able to bind to anions by an orbital overlap that causes a bonding interaction. This has led to the production of many new chelating and macrocyclic hosts for anions containing atoms such as boron, mercury, silicon, germanium, and tin.

In 1984, Azuma and Newcomb reported the synthesis of a series of tin-based macrocycles **32** and **33**.[50] Coordination studies with **32** showed that this family of macrocycles would form 1:1 and 1:2 host:anion complexes with chloride ions in

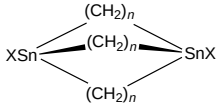


32



33

n = 4, 5, 6, 8, 10, 12



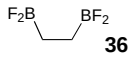
n = 6, 8, 10, 12

34: X = Ph
35: X = Cl

acetonitrile solution,[51] with stability constants ranging from 400 to 850 M^{-1}.

Newcomb et al. have also synthesized a series of cryptand-like tin-containing macrobicycles **34** and **35**.[52] Anion binding by these cage systems was found to be kinetically slower than that observed in the case of the macrocyclic receptors **32** and **33** with exclusively 1:1 complexes being observed.[53] ^{119}Sn NMR studies showed that fluoride ions were bound five orders of magnitude more strongly than chloride ions in chloroform.[54] Crystallographic studies later revealed that both ions were bound within the cavity. The fluoride ion was coordinated to both tin atoms ($r_{Sn\text{-}F} = 2.12/2.28$ Å) whereas chloride was located much closer to one tin atom than the other.[55]

One of the earliest examples of synthetic anion coordination was reported in 1967 by Shriver and Biallas.[56] The chelating boron-based receptor **36** was found to form stronger complexes with methoxide ions than monodentate boron trifluoride. Katz has also produced chelating boron-based receptors for anions.[57, 58] The anion-coordinating ability of receptor **37** (with hydride, fluoride, and hydroxide) was compared with that of the mondentate analogue **38**. It was found that **37** could extract hydride or fluoride ions that were bound to compound **38**. The crystal structures of the hydride and chloride complexes of **37** show the anions are bound between the boron atoms.[59]



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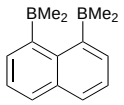

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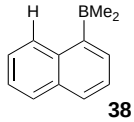
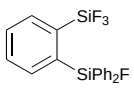
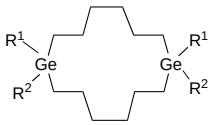


38

A variety of silicon- and germanium-based receptors including **39**–**41** have been synthesized. Compound **39** has been shown to coordinate to fluoride ions with a stability constant of $\lg K > 9$ in [D_6]acetone.[60] Germanium-based macrocycles, for example, **40** and **41** have also been prepared.[61, 62] Receptor **40** transports chloride ions more efficiently than bromide ions across organic phases.[63]

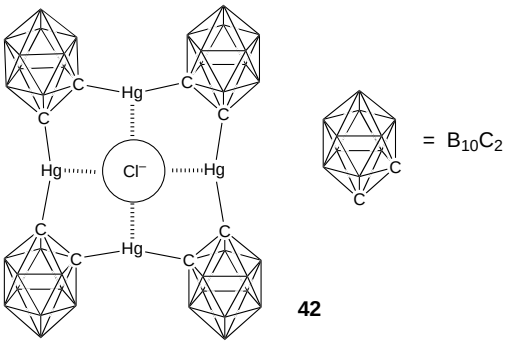


39



40: $R^1 = R^2 = Me$
41: $R^1 = Cl$, $R^2 = Me$

Mercury has been used as a Lewis-acidic center in a number of anion receptors.[64, 65] Some of the most elegant examples of this type of receptor are the mercuracarboranes produced by Hawthorne and co-workers.[66] These receptors consist of carborane cages linked through their carbon atoms by mercury atoms. One example containing four carborane units is receptor **42**. The X-ray crystal structure of this material



42

shows that a chloride ion is bound in the plane of the macrocycle equidistant (2.94 Å) from the four mercury atoms (Figure 8a). Hawthorne and co-workers have proposed that chloride ions present during the synthesis of this material act

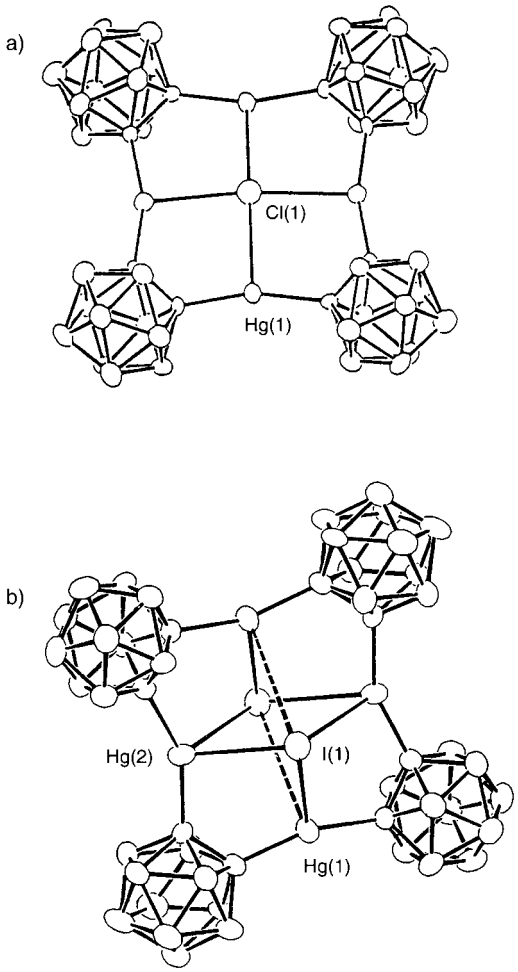
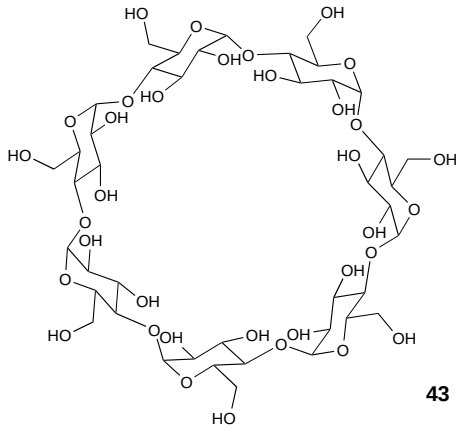


Figure 8. The X-ray crystal structures of the chloride (a) and the iodide (b) complexes of receptor **42**. a) Reproduced with permission from ref. [66]. Copyright© VCH 1991. b) Reproduced with permission from ref. [67]. Copyright© American Chemical Society 1992.

as templates around which the receptor forms. Indeed when chloride was excluded from the synthesis the yield of the product decreased. Iodide ions are too large to fit into the cavity of this receptor and instead perch over the cavity (Figure 8b).[67] Further examples of anion-templated processes are discussed in Section 4.2.

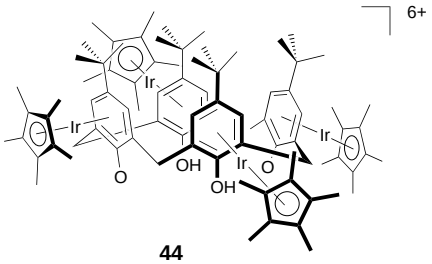
2.5. The Hydrophobic Effect

Inoue and co-workers have studied the inclusion of a series of naphthalenesulfonates by β-cyclodextrin **43** in water.[68] The binding interaction in these complexes is primarily a result of the hydrophobic effect, with the naphthalene residue displacing water molecules from the internal cavity of the cyclodextrin. The anionic sulfonate group remains outside the cavity in contact with the solvent, thereby controlling the orientation of the naphthalene group within the cavity.



43

Atwood, Steed, and co-workers have coordinated transition metals to the outside of calixarenes in order to reduce the electron density present in the "cup", thus making the cavity more amenable to hydrophobic anionic guests.[13, 69, 70] The crystal structures of anions bound in the calixarene cavity of a number of receptors were elucidated, including the HSO_4^- complex of **44** (Figure 9). Stability constants as high as 550 M^{-1} were observed for chloride complexation in aqueous solution.[71]



44

3. Anion Sensors

With the aim of advancing chemical sensor technology, considerable recent attention has focused on the design of receptors that have the ability to selectively bind and sense the anion recognition event through a macroscopic electrochemical or optical response.[11, 72, 73]

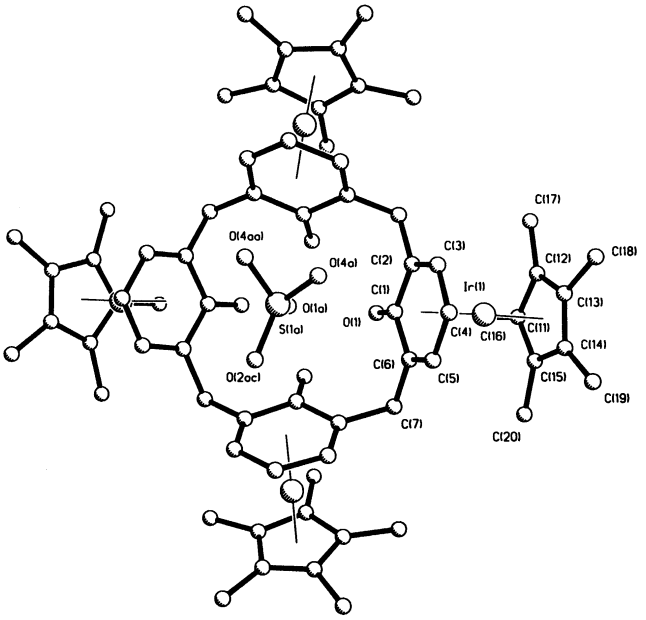
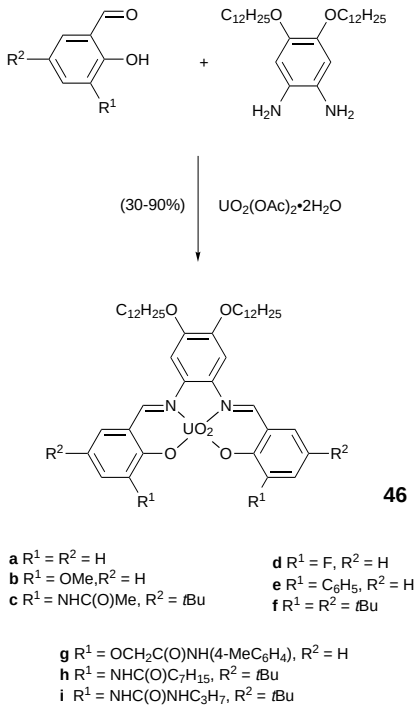


Figure 9. The X-ray crystal structure of the HSO_4^- complex of receptor **44** (hydrogen atoms are omitted). Reproduced with permission from ref. [71]. Copyright© American Chemical Society 1997.



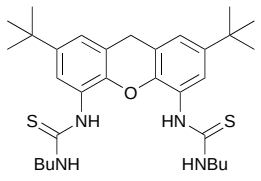
a $R^1 = R^2 = H$
b $R^1 = OMe, R^2 = H$
c $R^1 = NHC(O)Me, R^2 = tBu$
d $R^1 = F, R^2 = H$
e $R^1 = C_6H_5, R^2 = H$
f $R^1 = R^2 = tBu$
g $R^1 = OCH_2C(O)NH(4\text{-}MeC_6H_4), R^2 = H$
h $R^1 = NHC(O)C_7H_{15}, R^2 = tBu$
i $R^1 = NHC(O)NHC_3H_7, R^2 = tBu$

Scheme 2. Synthesis of uranylsalophane complexes **46.**

3.1. Electrochemical Recognition of Anions

Electrochemical molecular recognition is an expanding research area at the interface of electrochemistry and supramolecular chemistry.[74, 75] Three strategies have been applied to the electrochemical detection of the formation of receptor–anion complexes: 1) extraction of a charged guest into a membrane by a nonelectroactive host and detection of the resulting membrane potential (ion-selective electrodes (ISEs), chemically modified field-effect transistors (CHEMFETs), potentiometric sensors), 2) detection of a current/potential perturbation of the properties of a redox-active host on complex formation (voltammetric/amperometric sensors), and 3) production of a chemically modified electrode (CME) consisting of a redox-active matrix and an anion-selective binding site.

Many of the neutral lipophilic urea- and thiourea-containing receptors discussed earlier have been successfully incorporated into ion-selective electrodes (ISEs) which are capable of selective anion detection. For example, Umezawa and co-workers have recently produced chloride-selective membranes based on bis-urea systems such as **45**.[76]



45

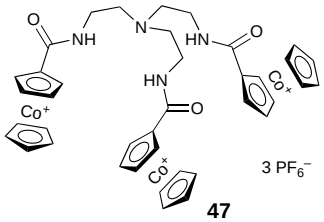
Reinhoudt and co-workers have incorporated an array of lipophilic uranylsalophane derivatives such as **46a–i** (Scheme 2) into chemically modified field-effect transistor (CHEMFET) membranes and shown that these devices are capable of selectively detecting a range of anions (for example, fluoride may be detected in the presence of a 150-fold excess of SCN^-), and is dependent upon the lipophilic and hydrogen-bond donor/acceptor substituents near the uranyl binding site of the receptor.[77–79]

Recently Král et al. have incorporated calixpyrrole macrocycles (for example, **18**) into ISEs and shown that the membrane is capable of acting as an anion sensor at low pH values.[32]

A variety of organic, organometallic, and inorganic redox-active centers have been incorporated into various host frameworks and been shown to electrochemically detect charged and neutral guests.[80, 81]

The first redox-active class of anion receptor based on the cobaltocenium moiety was reported by Beer and Keefe in 1989.[82] Since then, a plethora of acyclic, macrocyclic, and calixarene receptors containing cobaltocenium have been prepared (for example, **47–52**[83–87]). Cyclic voltammetric experiments demonstrated that all these receptors could electrochemically sense anions. The addition of anions to solutions of the receptors in acetonitrile resulted in significant cathodic shifts of the reversible Cp_2Co^+/Cp_2Co redox couple. The complexed anionic guest effectively stabilizes the positively charged cobalt center making it more difficult to reduce. For example, complexation of chloride ions by receptors **47** and **48** induced cathodic shifts of 30 mV and 85 mV, respectively, whereas larger magnitudes of 200 mV and 240 mV were observed for the complexation of dihydrogen phosphate. The electrochemical results correlate well with stability constants determined by ^1H NMR spectroscopy, with the highest K values obtained with the $H_2PO_4^-$ ion.

The anion-coordination properties of the cobaltocenium-bridged calix[4]arene receptors are dependent upon the degree of preorganization of the upper rim.[88–90] Stability constant values for the isomeric receptors **50** and **51** suggests that exchanging the positions of the tosyl substituent on the



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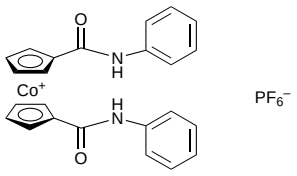

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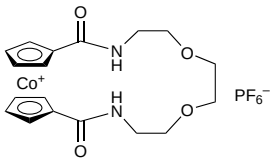

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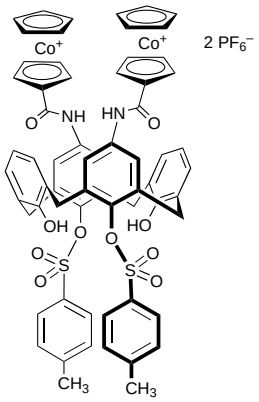
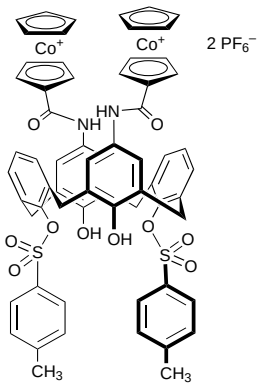


50



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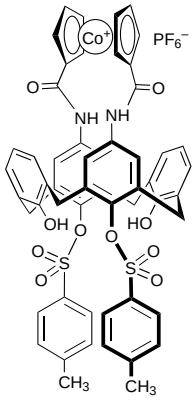


52

lower rim of the calix[4]arene has a dramatic influence on the anion coordination properties of the upper rim. For example, **50** binds acetate much better than $H_2PO_4^-$, whereas the selectivity preference is reversed with isomeric **51**. The cobaltocenium-bridged calix[4]arene **52** forms thermodynamically stronger anion complexes with carboxylate and $H_2PO_4^-$ ions than either **50** or **51**, and with a notable selectivity for acetate. As evidenced from the crystal structure of the chloride complex of **52** (Figure 10), this selectivity preference may be rationalized by the hydrogen bond donor cavity from the upper rim bidentate amide group being of complementary topology for complexing bidentate anions such as carboxylates.

Electrochemical investigations demonstrated that each of these receptors could sense a variety of anions, with substantial cathodic perturbations of the respective Cp_2Co^+/Cp_2Co redox couple by up to $\Delta E = 120$ mV for **50** and 155 mV for **52** with acetate being observed. Cathodic shifts of both the Cp_2Co^+/Cp_2Co and porphyrin oxidation redox couples were noted by voltammetric methods on complexation of receptor **53** with anions.[91]

The redox-active ferrocene moiety has also been exploited in the electrochemical sensing of anions, both in organic and aqueous media.[80, 81] Ferrocene units appended with secondary amides have also been used for anion recognition.[92, 93] Being neutral these receptors have no inherent electrostatic attraction for anions, which makes the stability constants, as determined by NMR spectroscopy, smaller than those of the analogous cobaltocenium systems. Electrostatic interaction can, however, be switched on by oxidation of the ferrocene group to the ferrocenium ion, and consequently these molecules exhibit interesting electrochemical anion-recognition effects. For example, **54**–**57** were capable of detecting $H_2PO_4^-$ ions in acetonitrile as shown by large cathodic shifts of up to 240 mV in the presence of a tenfold excess of HSO_4^- and Cl^- ions. In contrast receptor **58** binds HSO_4^- ions selectively in the presence of $H_2PO_4^-$ ions. The basic amine functionality of **58** is protonated by the acidic hydrogen

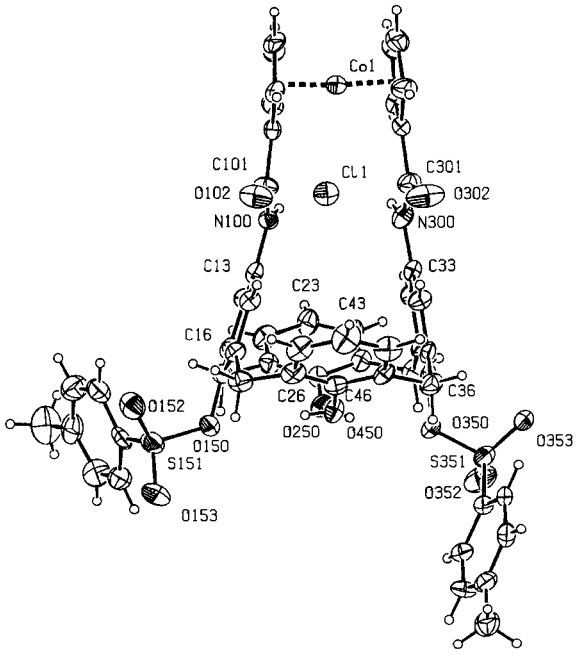
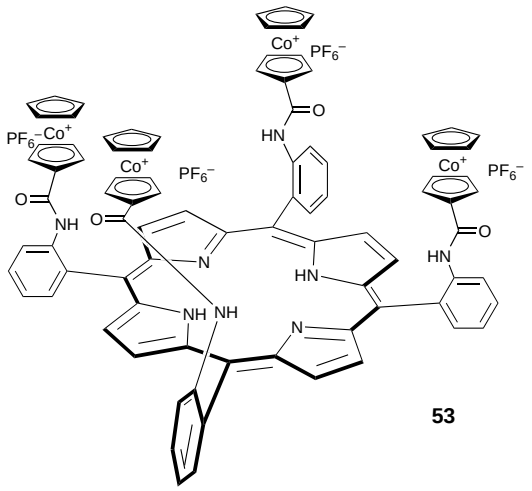
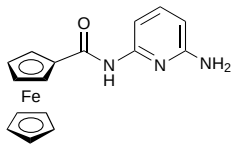


Figure 10. The X-ray crystal structure of the chloride complex of receptor **52**. Reproduced with permission from ref. [90]. Copyright© American Chemical Society 1999.



53

sulfate ion and the positively charged receptor strongly binds the produced SO_4^{2-}, as noted by a marked electrochemical reductive-stripping response.



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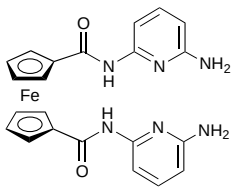

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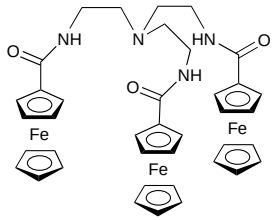

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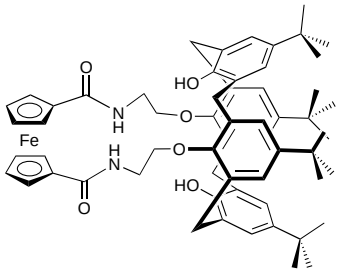

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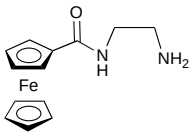
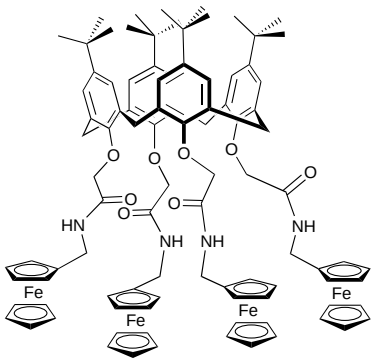


58

Astruc and co-workers have produced dendrimers **59**–**61** containing 3, 9, and 18 ferrocene units,[94] respectively and found evidence for a dendritic effect in the anion-recognition process. The largest induced cathodic shift was observed on addition of $H_2PO_4^-$ ions. Interestingly as the size of the dendrimer increases so does the perturbation caused by a particular anion. Recently the same research group reported that a cationic metallodendrimer with 24 [CpFe(η^6-*N*-alkylaniline)]$^+$ termini is capable of recognizing chloride and bromide ions.[95] Lower rim polyferrocene-substituted calixarenes **62**–**64** have recently been shown to bind and electrochemically sense anions, with maximum cathodic perturbations of 160 mV being observed for $H_2PO_4^-$.[96]



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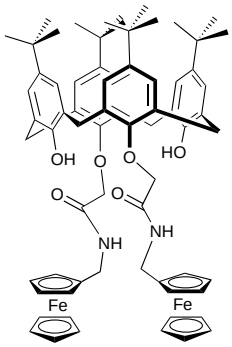

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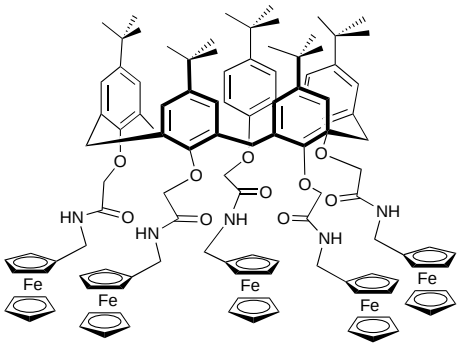
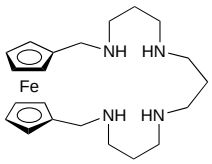


64

Beer et al. have synthesized a series of acyclic and macrocyclic ferroceneamine ligands (for example, **65** and **66**) that can selectively bind and electrochemically detect phosphate and sulfate (in various states of protonation) as well as nucleotide ions in water.[97–99] For example, **65** senses phosphate ions at pH 7 as shown by a cathodic shift of 50 mV, whereas sulfate does not induce a redox response. In contrast **66** electrochemically discriminates for sulfate over phosphate at pH 4 in aqueous THF with a cathodic shift of 54 mV. Calibration curves of the change in the half-wave potential ΔE versus the [A$^-$]/[L] ratio at a certain pH value showed that



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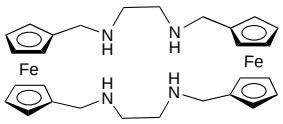

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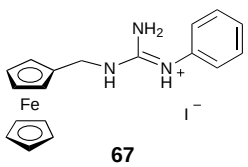

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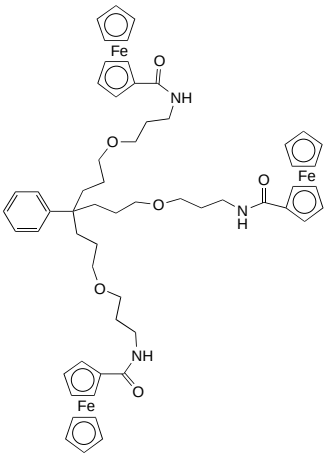

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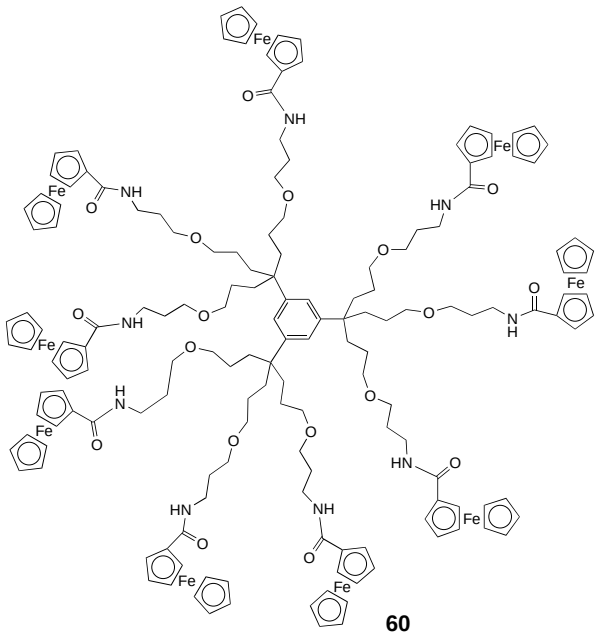

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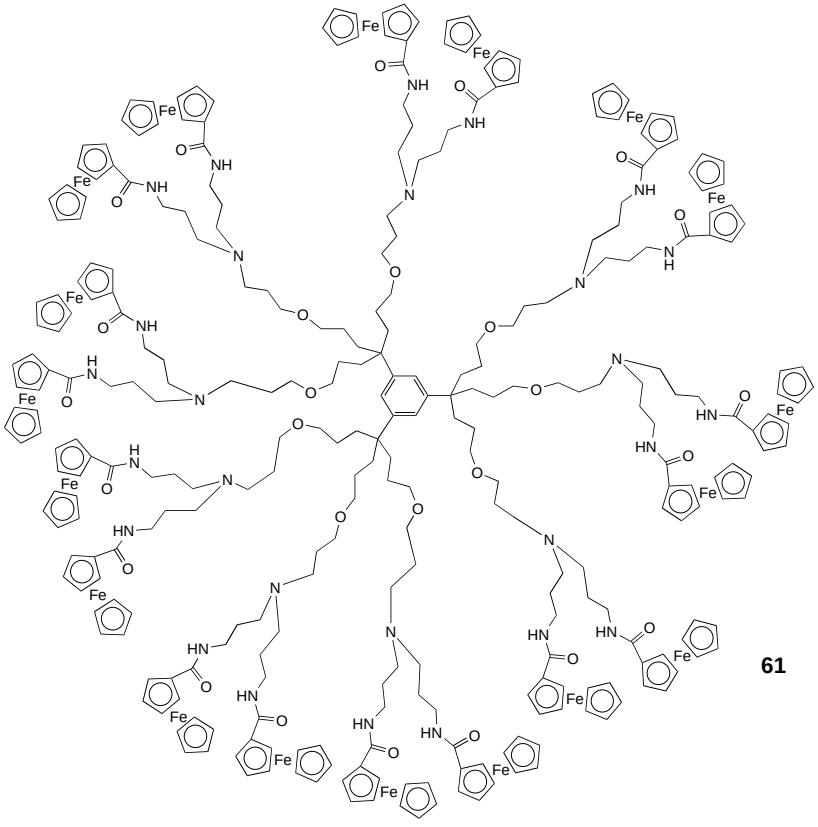
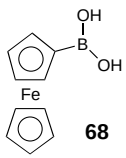


61

it was possible to quantitatively determine phosphate and sulfate concentrations in the presence of competing anions with **65** and **66**. This result demonstrates their potential use as prototype anion sensors.[99] The ferrocene-appended guanidinium receptor **67** senses pyrophosphate in methanol/water mixtures and exhibits cathodic shifts of 70 mV.[100]

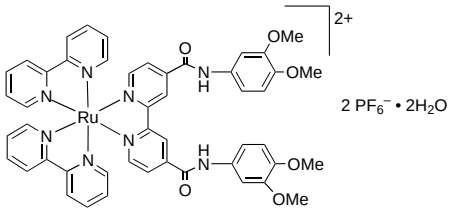
Shinkai and co-workers have reported that ferroceneboronic acid **68** is capable of acting as an electrochemical sensor.[101] This simple molecule has excellent selectivity for fluoride ions in the presence of other halides and ions such as SCN^-, SO_4^{2-}, and $H_2PO_4^-$. They found a K_{ox} value of $1000\,M^{-1}$ in MeOH/H_2O (1/9) for fluoride compared to values of less than $2\,M^{-1}$ for chloride and bromide. The interaction between the boronic acid group and the fluoride ion is attributed to the hardness of



68

the boron atom, which strongly interacts with fluoride (a hard base). On oxidation, the ferrocene group becomes more electron-withdrawing, so decreasing the electron density of the boron atom and increasing the strength of the fluoride complex.

An alternative approach to electrochemical anion detection is to produce an electropolymerizable monomer containing an anion binding site and polymerize it onto the surface of an electrode to produce an anion-selective chemically modified electrode (CME). Fabre and co-workers have recently produced boronate-functionalized polypyrrole membranes (poly-**69**; Scheme 3) that are selective for fluoride over other putative anionic guests.[102]



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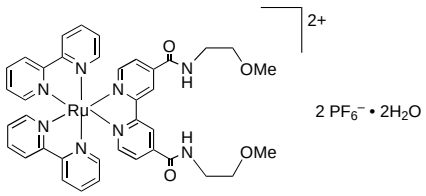

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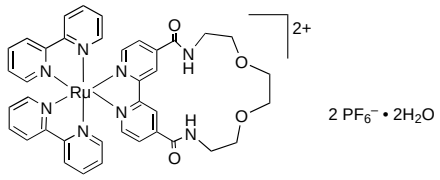

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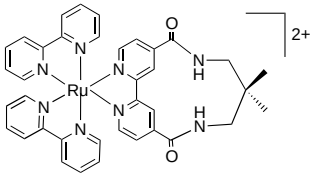

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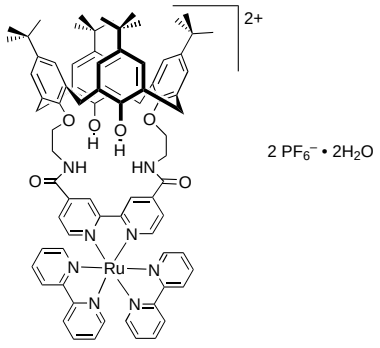

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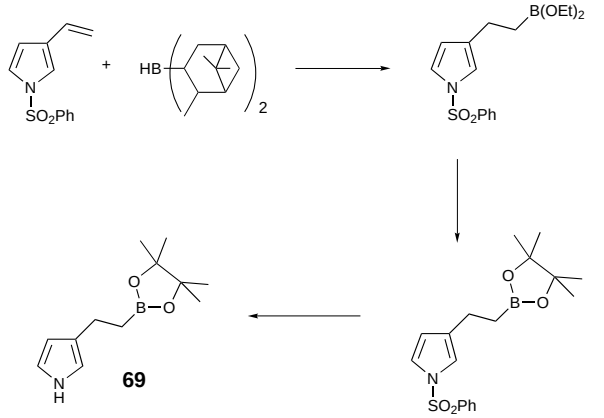


69

Scheme 3. Synthesis of **69**.

3.2. Optical Sensing of Anions: Luminescent Sensors

The high sensitivity of fluorescent techniques for sensing target guest species has stimulated an enormous amount of interest in the covalent attachment of organic and inorganic luminophores in proximity to charged guest-recognition sites.[103] Examples of luminescent anion-responsive systems have combined the anthracene fluorophore with polyammonium,[104] guanidinium,[105] zinc(II) amine,[106] and very recently calixpyrrole[34] anion recognition sites. Cyclen-appended phenanthridinium europium and terbium complexes have been shown to sense halide and hydroxide ions in water.[107, 108]

Tris(2,2′-bipyridyl)ruthenium(II) ($[Ru(bpy)_3]^{2+}$) has been one of the most extensively investigated complexes as a result of its chemical stability, redox properties, excited-state reactivity, and luminescent emission.[109, 110] Beer and co-workers have incorporated this moiety into acyclic, macrocyclic, and calix[4]arene structural frameworks to produce a new class of anion receptor capable of optical and electrochemical sensing; examples are **70**–**74**.[72, 111, 112] Single-crystal X-ray structures of the chloride complex of **70** (Figure 11) and the $H_2PO_4^-$ complex of **73** highlight the importance of hydrogen bonding to the anion-complexation process. The determination of stability constants in DMSO demonstrated that the acyclic receptors form strong complexes with Cl^- and

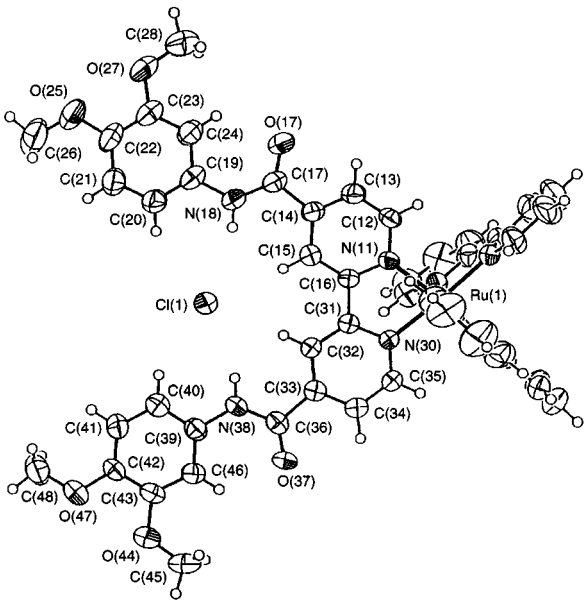
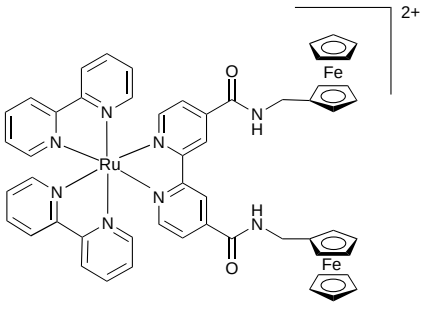


Figure 11. The X-ray crystal structure of the chloride complex of receptor **70**. Reproduced with permission from ref. [111]. Copyright© American Chemical Society 1996.

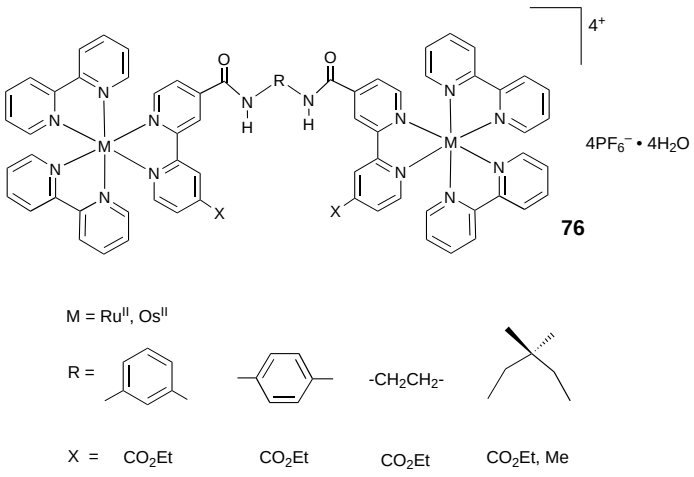
$H_2PO_4^-$ ions. The macrocyclic and calix[4]arene receptors **72**–**74** form highly selective and thermodynamically stable complexes with $H_2PO_4^-$ ions. Electrochemical anion-recognition experiments showed substantial anion-induced cathodic perturbation of the redox couple associated with the ligand-centered amide-substituted 2,2′-bipyridine reduction. These perturbations were in agreement with stability constant values, with **73** electrochemically sensing $H_2PO_4^-$ ions in the presence of a tenfold excess of HSO_4^- and Cl^- ions. Luminescence emission measurements were also undertaken to probe the anion-binding process. All receptors exhibited significant blue shifts in the metal-ligand-charge-transfer (MLCT) emission band λ_{max} on addition of Cl^- and $H_2PO_4^-$ ions, with **73** displaying the largest perturbation (16 nm). These shifts are not observed with unfunctionalized $[Ru(bpy)_3]^{2+}$ and were accompanied by large increases in emission intensity (higher quantum yields). It was proposed that this could be a consequence of the bound anion rigidifying the receptor and inhibiting vibrational and rotational relaxation modes of nonradiative decay.

An acyclic $[Ru(bpy)_3]^{2+}$-ferrocene receptor **75** in which the emission of the ruthenium center in the free receptor is quenched by the ferrocene units has also been prepared by Beer et al.[113] Interestingly the addition of $H_2PO_4^-$ ions switches on the emission with a 20-fold increase. This effect was not observed with Cl^- or HSO_4^- ions. A competition experiment conducted in the presence of five equivalents of both Cl^- and HSO_4^- ions reproduced the emission increase on addition of $H_2PO_4^-$, thus confirming the property of **75** as a $H_2PO_4^-$-selective luminescent anion sensor.



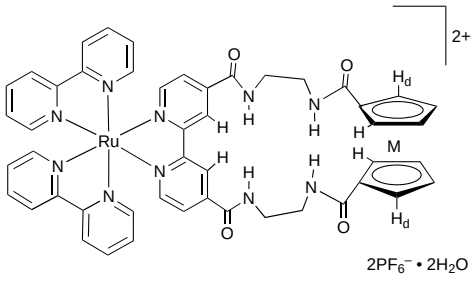
75

Other mixed-metal receptors have included the cleft-type, in which the d^6 metals Ru^{II}, Os^{II}, and Re^{I} with various different bridging groups **76** were employed.[114] These, like the previous examples, display selectivity for dihydrogen phosphate over chloride. The strength of binding can be tuned by the choice of the spacer/bridging moiety to quite a dramatic effect. For example, the complex with the *meta*-phenylene-bridged ligand gives a stability constant with dihydrogen phosphate of $55\,M^{-1}$ in $[D_6]$DMSO, while that with the *para* analogue is $4320\,M^{-1}$. Other spacers were utilized, such as ethyl and 2,2′-dimethylpropyl. The corresponding Os^{II} receptors displayed larger anion stability constants indicating the efficient Lewis-acidic character of the $[Os(bpy)_3]^{2+}$ moiety.

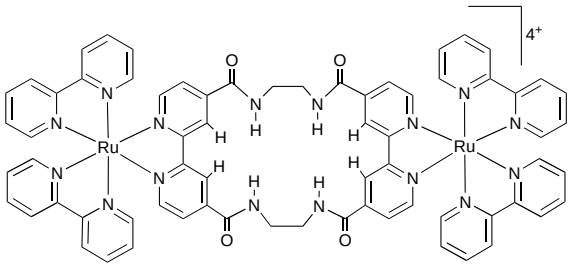


76

It is noteworthy that few of the receptors discussed so far exhibit specific binding and sensing of the chloride ion. Beer et al. recently prepared the macrocyclic receptors **77**–**79** which form extremely stable 1:1 complexes on binding chloride ions in $[D_6]$DMSO, with stability constants of up to $4 \times 10^{-4}\,M^{-1}$.[115] ^1H and ^{31}P NMR experiments on **79** showed



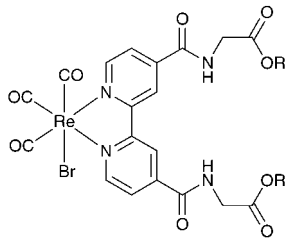
77: M = Fe
78: M = Co^+



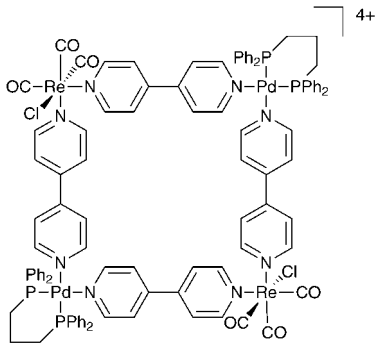
79

no evidence for the binding of $H_2PO_4^-$ ions. This remarkable selectivity may be attributed to the inherently rigid structure of the macrocycle, since acyclic analogues bind $H_2PO_4^-$ more strongly than Cl^-. The larger size and tetrahedral shape of $H_2PO_4^-$ make this ion noncomplementary for the receptor's cavity. Luminescence studies indicated a blue-shift of the MLCT emission band with significant intensity enhancement in response to chloride ions, but no response to $H_2PO_4^-$ ions. Interestingly increasing the size of the macrocyclic cavity by two or four methylene units dramatically reverses the trend in anion selectivity.

The neutral isoelectronic rhenium(I) – bipyridylamide receptors **80** and **81** have been prepared and shown to selectively bind and optically sense acetate ions in DMSO by MLCT enhancement.[116] The mixed Re^{I}-Pd^{II} metal macrocycle **82** binds a perchlorate ion, which also results in significant MLCT enhancement in acetone.[117]

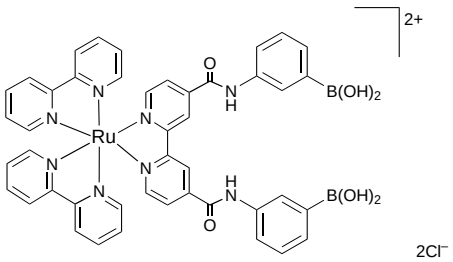


80: R = Me
81: R = CH_2Ph



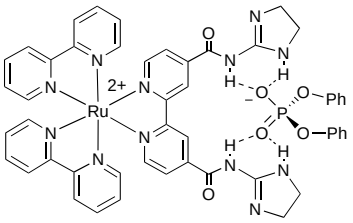
82

Deetz and Smith have synthesized an analogous compound containing saccharide-binding boronic acid groups (**83**) and shown that this material will sense the presence of phosphorylated sugars in aqueous solution through perturbations in the luminescent properties of the complex.[118] The phosphate group of the sugar is presumably bound to the amide NH protons present in the cleft whilst the boronic acid groups coordinate to the sugar. Rhenium analogues of this material had previously been used to bind simple sugars.[119]

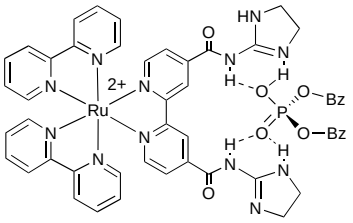


83

Watanabe et al. have produced imidazole-functionalized ruthenium – bipyridyl complexes such as **84** which recognize anionic and neutral phosphodiesters with luminescent signal enhancement observed for anionic phosphodiesters in acetone.[120] The corresponding 1:1 complexes are proposed to form between **84** and tetraethylammonium diphenyl phosphate (TDPP) or dibenzylphosphate (DBHP; Bz = benzyl).

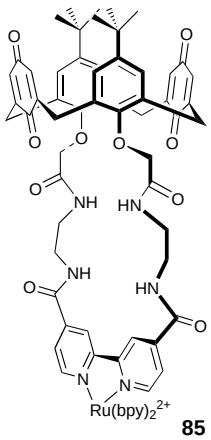


84 • DPP



84 • DBHP

Ruthenium(II)– and rhenium(I) – bipyridylcalix[4]diquinone receptors **85** and **86** selectively bind and sense acetate ions through remarkable retrieval effects of the luminescent emission intensity.[121] The addition of acetate ions to solutions of **85** in acetonitrile caused a 500 % increase in the intensity of the emission, which suggests that anion binding inhibits the intramolecular oxidative electron transfer quenching mechanism between the ruthenium(II) – bipyridyl and calix[4]diquinone centers.



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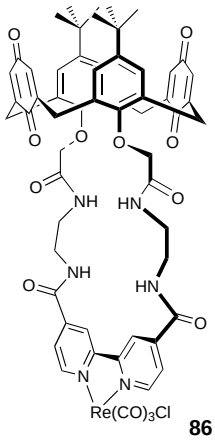
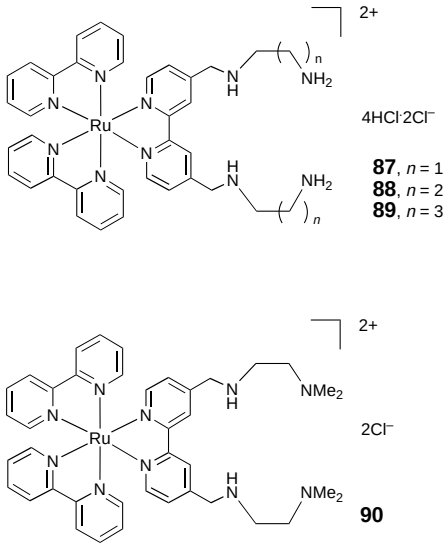


86

Water-soluble ruthenium(II) – bipyridyl – polyamine receptors such as **87** – **90** have very recently been prepared and shown to bind and detect phosphate ions in aqueous media by MLCT luminescent emission quenching.[122]

Anslyn and co-workers have published several papers on the recognition of tricarboxylate and triphosphate polyanions by trisguanidinium receptor species such as **91** (Scheme 4).[123] This molecule contains three guanidinium groups and is therefore complementary to guests containing three carboxylate groups. The stability constant determinations revealed that guests containing three anionic moieties, such as citrate, are bound more strongly than those with fewer anionic groups



(for example, acetate). The crystal structure of the tricarballate complex (tricarballate = 1,2,3-propanetricarboxylate) of **91** is shown in Figure 12. This receptor has been used by Anslyn and co-workers to produce a displacement-assay-type chemosensor for citrate in beverages.[123] 5-Carboxyfluorescein (**92**) is a commercially available fluorescent probe containing two carboxylate groups. Its fluorescence is particularly sensitive to changes in pH values. The two carboxylate groups present in **92** coordinate to **91**. The pK_a of the phenol moiety of **92** is lowered in the complex because of the positively charged microenvironment. A citrate ion displaces the carboxyfluorescein from the complex and results in a shift in the pK_a of the phenolate group such that **92** is in a higher state of protonation when uncomplexed (Scheme 4).[124] The fluorescence and absorbance of **92** decrease with increasing protonation. These changes could be calibrated against standard solutions of citrate to produce a quantitative sensor.

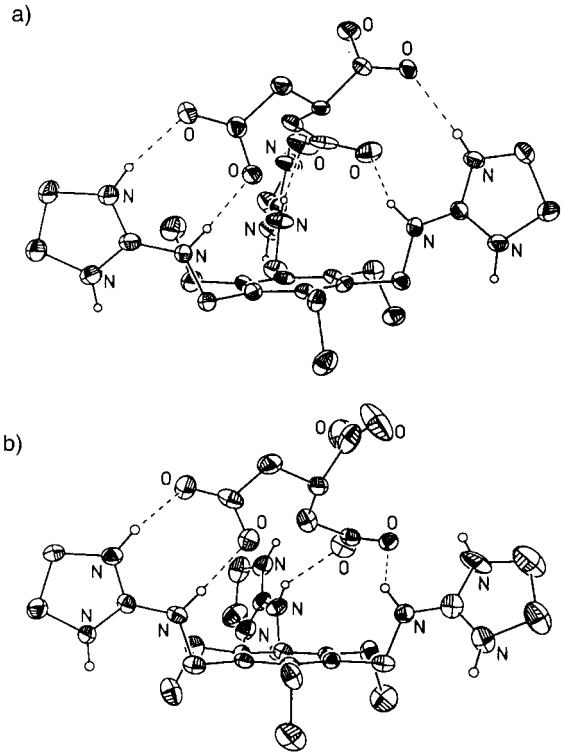
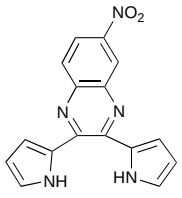


Figure 12. The X-ray crystal structure of the tricarballate complex of receptor **91** (C-bound hydrogen atoms are omitted). The unit cell contains two different host–guest complexes (a and b). Reproduced with permission from ref. [123]. Copyright© WILEY-VCH 1997.

3.3. Optical Sensing of Anions: Colorimetric Sensors

Colorimetric sensors do not require the use of a potentiostat or spectrometer to detect redox or optical perturbations (color changes are detectable by eye!) and therefore have advantages over other molecular sensors.

Sessler and co-workers reported that 2,3-dipyrrol-2′-ylquinoxalines such as **93** provide a simple, hitherto unexplored class of anion receptors that allow for the detection of fluoride ions in dichloromethane and DMSO under both visual (that is, naked eye) and fluorescence emission conditions.[125] In fact, **93** undergoes a clear yellow to purple color change on addition of fluoride ions that is not observed on addition of other anions. The observed color changes also take place in DMSO but are reversed upon addition of water. This is presumably because water competes with the pyrrolic NH hydrogen bond donating sites for fluoride ions. Compound **93** shows a remarkable selectivity for the fluoride ion (K_a(F)/K_a(Cl) > 1800; K_a(F)/K_a($H_2PO_4^-$) > 1400).



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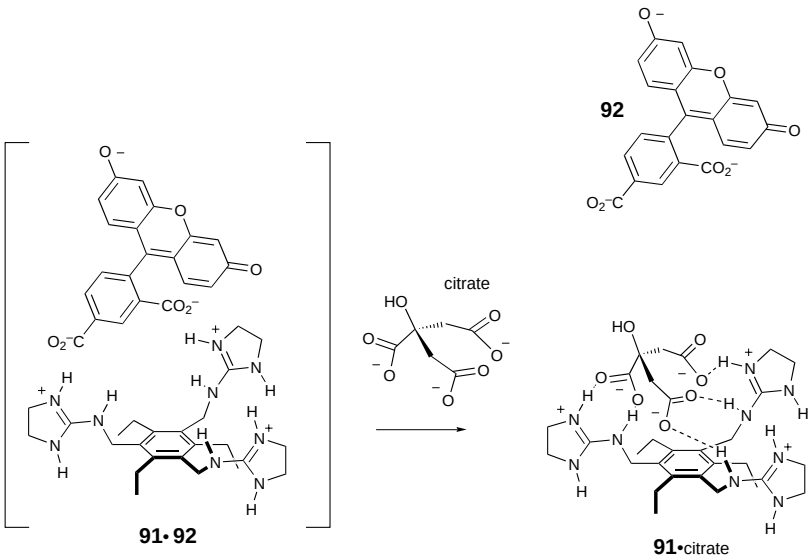
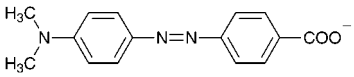
Anslyn and co-workers have extended their displacement-assay approach to include a molecular ensemble con-



Scheme 4. Recognition of citrate ions by the trisguanidinium receptor **91**. An initially bound molecule of **92** is displaced by a citrate ion.

sisting of the nitrate-selective trigonal amide box[25] **14** and a variety of colorimetric dyes such as Resorufin (**94**) or Methyl Red (**95**).[126] The resulting molecular ensembles show large changes in their absorbance upon addition of nitrate ions.



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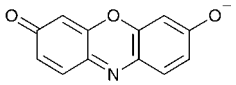

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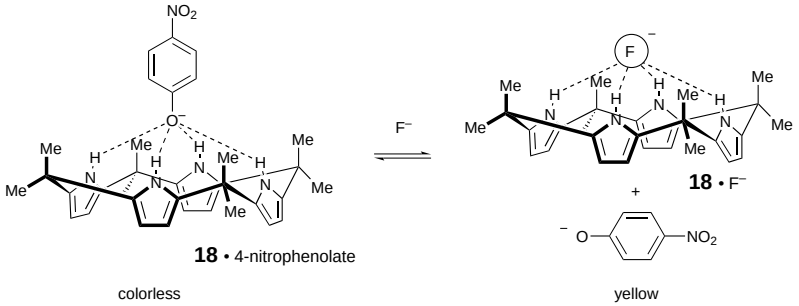
The generality of the approach of Anslyn and co-workers has been confirmed by Gale et al.[127] The intense yellow color of the 4-nitrophenolate ion in dichloromethane or acetonitrile has been shown to dissipate upon addition of calix[4]pyrrole as a consequence of the formation of a calix[4]pyrrole – 4-nitrophenolate complex. The addition of anions causes the regeneration of the bright yellow color as the added anion displaces the phenolate ion from the calix[4]pyrrole (Scheme 5). The intensity of the color is dependent upon the affinity of the calixpyrrole for the added anion and the anion concentration.



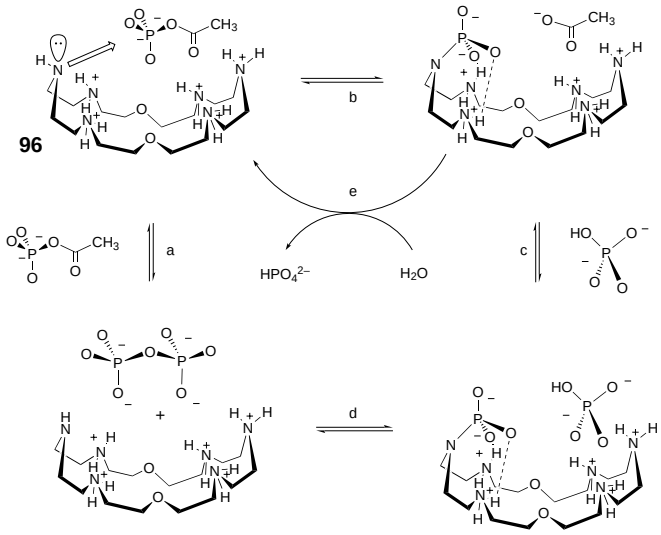
Scheme 5. F^--dependent equilibrium between **18** · 4-nitrophenolate and **18** · F^-.

4. Into the New Millennium: Templation, Anion-Directed Self-Assembly, Catalysis, and Ion-Pair Recognition

The previous sections have illustrated through the discussion of a range of artificial receptors the recognition and sensing of anionic guest species in organic and aqueous solvent media. The field of anion coordination chemistry is catching up with cation coordination chemistry and has recently turned its attention towards supramolecular catalysis, anion-template effects, and directed self-assembly. In addition, at the interface of anion and cation coordination chemistry, new heteroditopic multisite ligands for the simultaneous complexation of anionic and cationic guest species (ion-pair recognition) have been reported.

4.1. Catalysis

Hosseini and Lehn are pioneers in the area of supramolecular catalysis of anionic substrates. The results of their extensive work have recently been condensed into a book chapter to which the interested reader is directed for further information.[128] One example, a proposed catalytic cycle for acetyl phosphate hydrolysis and pyrophosphate synthesis by macrocycle **96** at pH 7, is shown in Scheme 6. The mechanism

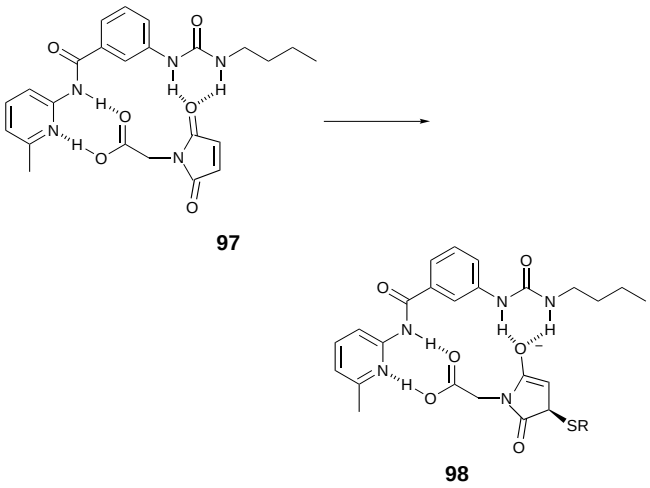


Scheme 6. Proposed catalytic cycle for acetyl phosphate hydrolysis and pyrophosphate synthesis in the presence of macrocycle **96**.

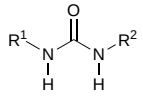
of this reaction is extremely pH sensitive with the percentage of pyrophosphate formed being a maximum at pH 7. This result arises because the mechanism of the transformation relies on the macrocycle being in the correct protonation state.

Hamilton and co-workers have used an anion-binding strategy to stabilize an oxyanion transition state and so accelerate the 1,4-addition of a thiol to a maleimide (Scheme 7).[129] The build up of negative charge on the carbonyl oxygen atom in the enol transition state of this reaction is stabilized by hydrogen bonding from a urea group. The hydrogen bonds to the enol oxygen atom in complex **98** are stronger than those to the carbonyl oxygen atom in the starting material (**97**). Therefore the transition state is stabilized relative to the starting material and catalysis occurs.

Reinhoudt and co-workers have recently demonstrated that addition of anion-binding urea-based receptors to palladium(II)-catalyzed hydrocarbonylation reactions of cyclopentene can significantly increase hydroacylation relative to hydroformylation.[130] The N,N′-disubstituted urea derivatives **99** – **103** significantly influence the performance of the [PdX_2(dppp)] catalyst (dppp = 1,3-bis(phenylphosphanyl)-propane) in hydrocarbonylation reactions by coordinating to the counterions (X = OTs, TFA, OAc), which leads to a decrease in their metal-binding strength. More weakly coordinating anions X enhance the electrophilicity of the Pd^{II}



Scheme 7. Anion binding results in an accelerated 1,4-adition of thiols to a maleimide.



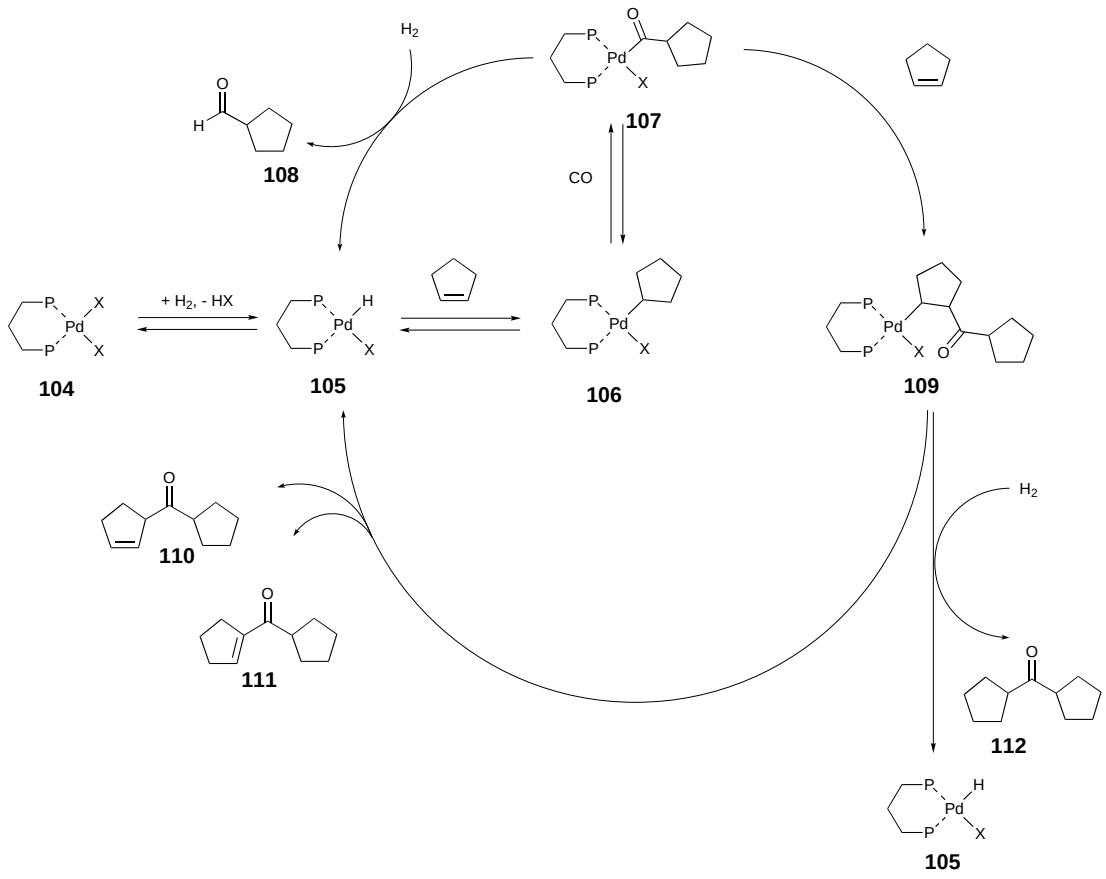
99: $R^1 = R^2 =$ Ph
100: $R^1 = p\text{-}F_3CC_6H_4$, $R^2 =$ Ph
101: $R^1 = R^2 = p\text{-}F_3CC_6H_4$
102: $R^1 = n$Bu, $R^2 =$ Ph
103: $R^1 = R^2 = n$Bu

metal ion and are more easily displaced from the complex, thus facilitating the formation of **107** (increased turnover) and **109** (increased selectivity for ketones; Scheme 8). The largest effect was observed on addition of compound **101**.

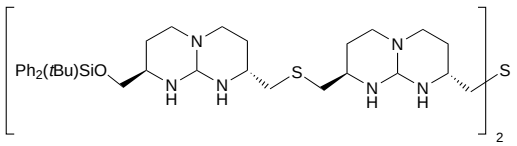
4.2. Anion Templation and Directed Self-Assembly

Examples of metal ions and other cationic species that act as templates for the formation of cyclic molecules or other molecular systems are widespread in the literature.[131] Examples of anions performing the same function were, until a few years ago, difficult to find. However, this situation has now changed, and reports of the templating influence of anions are now becoming widespread. We have already discussed how anion templation assisted in the synthesis of Hawthorne's mercuracarborand receptor **42**. Other early examples of anion templation (or anion-directed self-assembly) include an interesting templation effect by nitrate in the synthesis of expanded porphyrins by Sessler et al.,[132] the organization of organophosphate–oxovanadium clusters around chloride ions,[133] and the construction of polyoxovanadate cages by Müller et al.[134, 135] Recently, Müller et al. have employed $H_2PO_2^-$ ligands in the formation of nanosized rings of formula $Na_{21}[Mo^{VI}_{126}Mo^{V}_{28}O_{462}H_{14}(H_2O)_{54}(H_2PO_2)_7]\cdot x\,H_2O$ ($x \approx 300$).[136]

de Mendoza and co-workers have synthesized a tetraguanidinium strand (**113**) that self-assembles around sulfate ions to form a double helix.[137] Evidence for the anion-directed helical structure was provided by ROESY NMR spectroscopy. The complexation behavior of this and other tetraguanidinium reagents with α-helical peptides containing negatively charged aspartate residues has been reported by Hamilton, de Mendoza, and co-workers.[138]



Scheme 8. Mechanism for the Pd^{II}-catalyzed hydrocarbonylation of cyclopentene.



113

Lehn and co-workers have discovered a striking example of anion-directed assembly (Scheme 9).[139, 140] The pentametallic circular helicate **115** only forms in the presence of chloride ions. It may be produced by mixing the tris(bipyridine) ligand **114** with an equimolar amount of $FeCl_2$ in ethylene glycol at 170 °C. The chloride ion bound in the center of the helicate is locked in place and cannot be exchanged for other anions such as hexafluorophosphate or trifluoroacetate (triflate). If other iron(II) salts such as tetrafluoroborate or sulfate are used instead of chloride a hexameric complex **116** is obtained (Scheme 9). The chloride ion is therefore playing a role in the assembly of this beautiful complex (Figure 13).

Fujita et al. have used a variety of carboxylate guest ions to template the formation of metal complexes[141] and have recently succeeded in constructing coordination nanotubes. (**118**–**120**; Scheme 10).[142] For example, pentakis(3,5-pyridine) **117** quantitatively forms a coordination nanotube **118** with $[Pd(en)(NO_3)_2]$ (en = ethylenediamine) in the presence of a linear template such as 4,4′-biphenylenedicarboxylate.

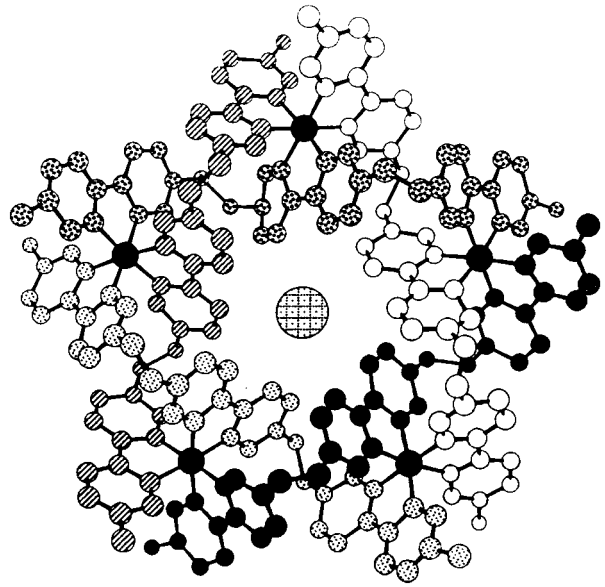
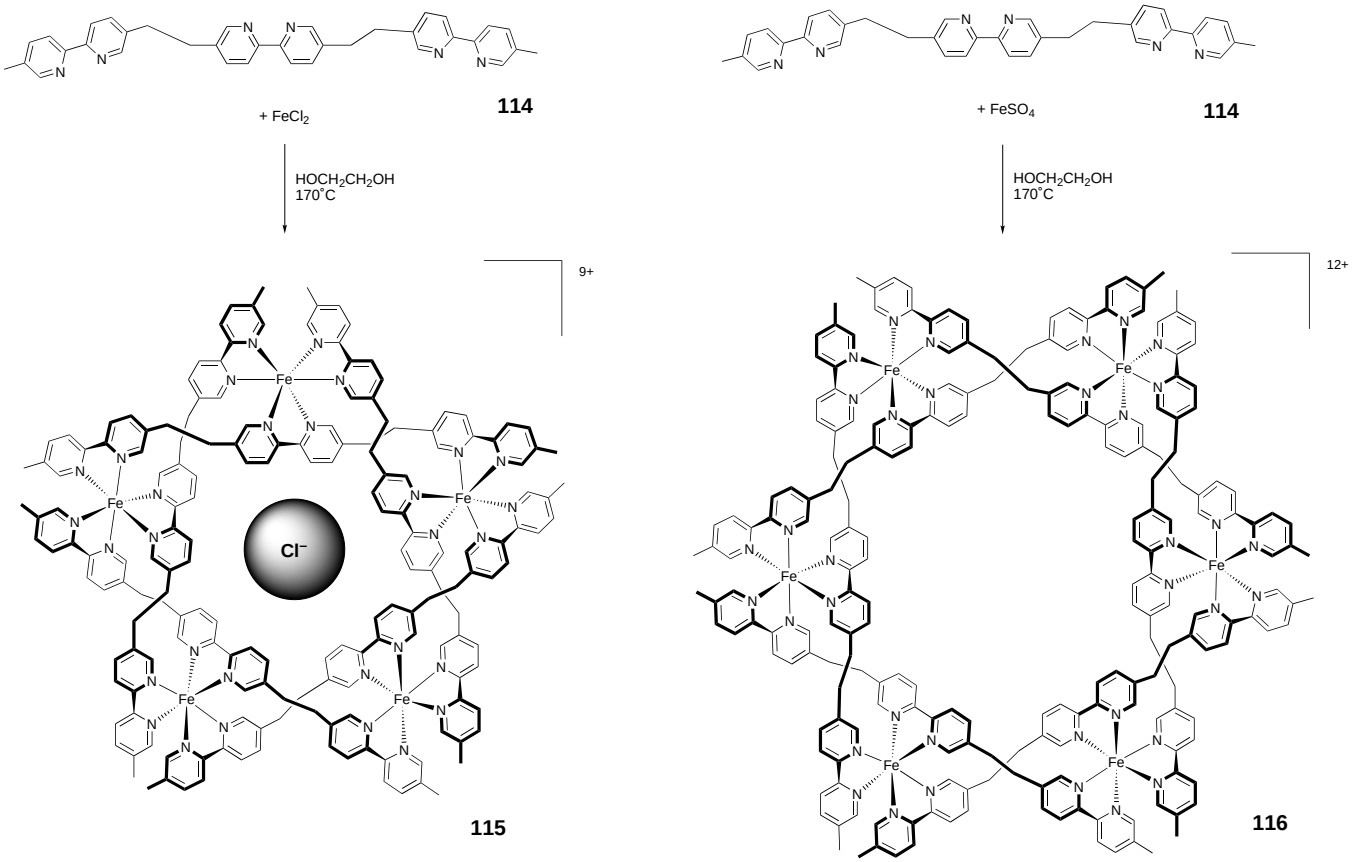
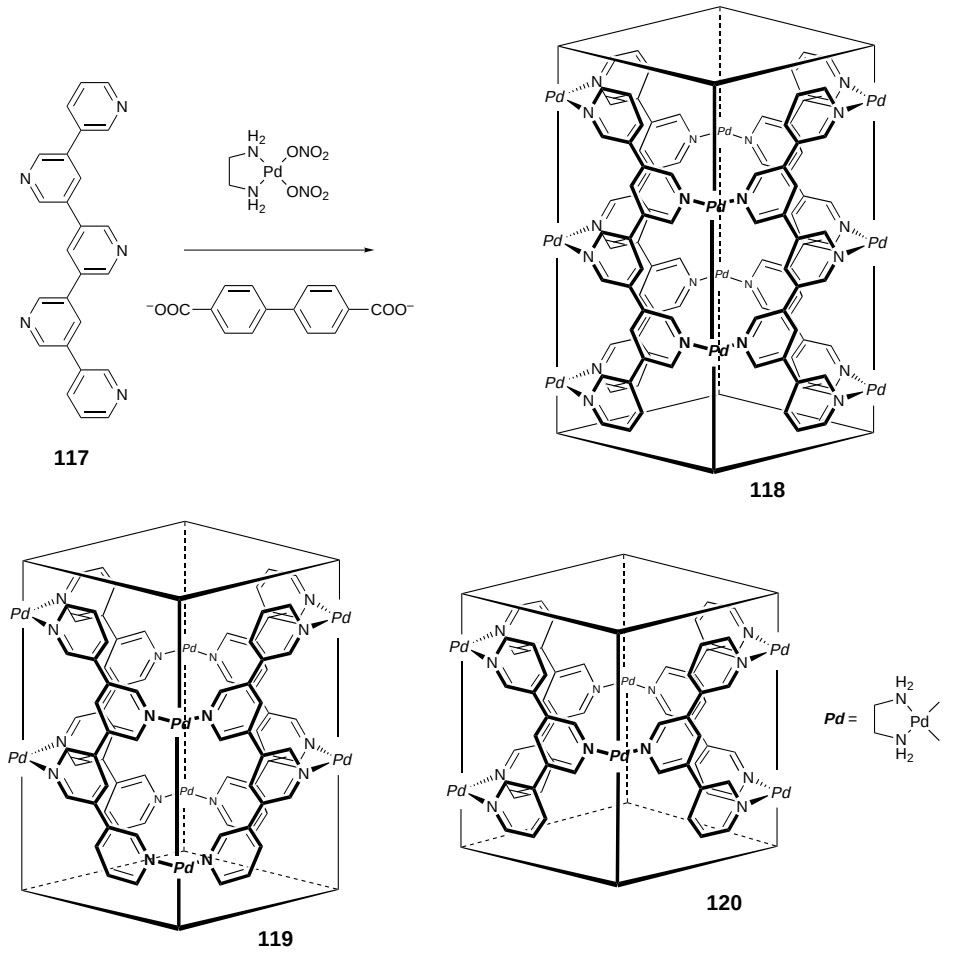


Figure 13. The X-ray crystal structure of the circular double helicate **115** (hydrogen atoms are omitted). The templating chloride ion can be clearly seen at the center of this beautiful complex. Reproduced with permission from ref. [139]. Copyright© VCH 1996.

Neutral linear templates such as biphenyl and *p*-terphenyl were also effective as templates, however, the nanotube did not form in the absence of any template. The crystal structure



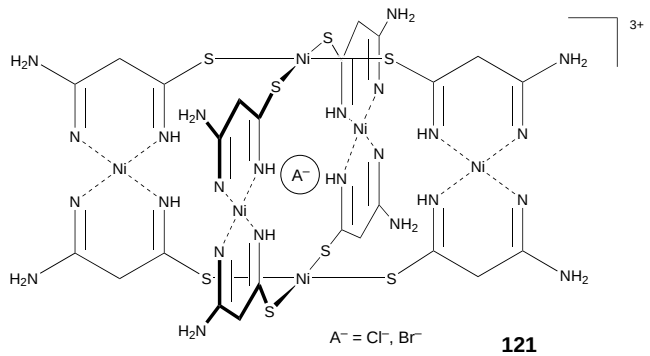
Scheme 9. Synthesis of helicates **115** and **116**.



Scheme 10. Synthesis of the coordination nanotubes **118**–**120**.

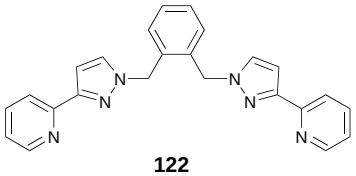
of [**120**(4,4′-biphenylenedicarboxylate)$_2$(NO_3^-)$_{10}$] has been elucidated and reveals that the anionic template is bound within the tube by π–π and CH–π interactions.

Another example of anion-directed assembly was reported by Mingos and co-workers.[143] Reaction of $NiCl_2$ with amidinothiourea (atu) in methanol produces a cage complex **121**. The complex consists of eight amidinothiourea units that



coordinate six nickel ions through both nitrogen and sulfur donor atoms. A chloride ion is bound in the center of the cage by eight N–H···Cl hydrogen bonds (Figure 14). A cage complex can also be formed by replacing $NiCl_2$ with $NiBr_2$, however syntheses using nickel acetate, nitrate, or perchlorate salts produce simple monomeric $[Ni(atu)_2]^{2+}$ complexes. If chloride ions are subsequently added to these complexes (as KCl) the cage complex spontaneously forms around the halide ion.

McCleverty, Ward, and co-workers have shown that BF_4^- ions template the formation of tetrahedral complexes consisting of four cobalt(II) ions and six ligands **122**.[144] The templation



process appears to be driven primarily by electrostatic interactions as the fluorine atoms are not directed towards the cobalt centers at the corners of the tetrahedron (Figure 15) but rather towards the center of the triangular faces of the tetrahedron. This is presumably a consequence of the

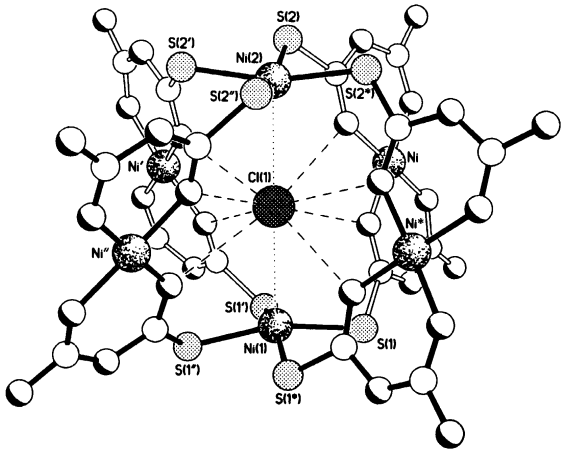


Figure 14. The X-ray crystal structure of cage complex **121** (hydrogen atoms are omitted). Reproduced with permission from ref. [143]. Copyright© WILEY-VCH 1998.

anion adopting an orientation that best fits the internal shape of the cavity. The tetrahedral complex could not be isolated without an encapsulated anion, and anion exchange between the cavity and bulk solvent was slow (at least on the NMR timescale). These facts suggest that the anion is essential in the assembly process of this complex.

Chloride ions have been used by Zheng and co-workers to direct the assembly of europium(III)–tyrosine cluster com-

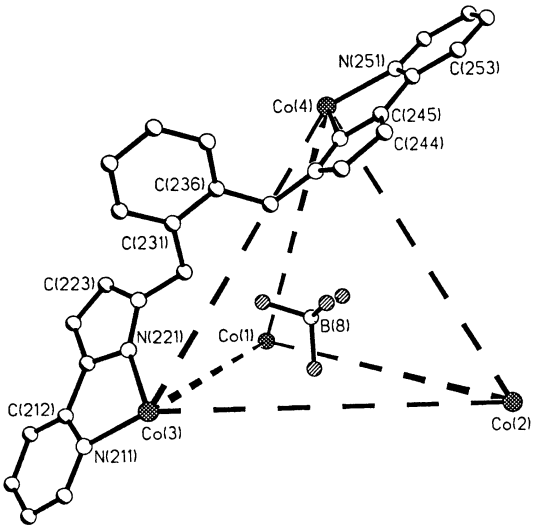


Figure 15. A partial representation of the crystal structure of the BF_4^--templated cage complex **122** (hydrogen atoms are omitted). Reproduced with permission from ref. [144]. Copyright© WILEY-VCH 1998.

pounds[145] such as $[Eu_{15}(Cl)(\mu_3\text{-tyr})10(\mu_3\text{-OH})_{20}(\mu_2\text{-}H_2O)_5(OH)_{12}(H_2O)_8][ClO_4]_2 \cdot 56\,H_2O$ (**123**; Figure 16). The metal ions are assembled into three layers with each containing five metal ions. The cage is templated around a chloride ion at the center of the cluster that is coordinated to five europium atoms with an average Eu ··· Cl distance of 3.31 Å.

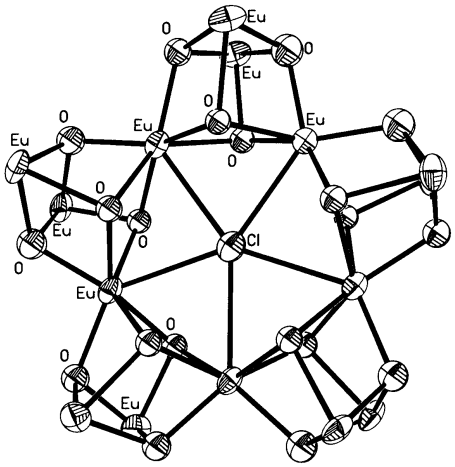


Figure 16. A plane through the X-ray crystal structure of **123** (only the Eu and O atoms are shown) showing the templating chloride ion. Reproduced with permission from ref. [145]. Copyright© 1999, WILEY-VCH.

Chen and co-workers have formed cyclic hexanuclear complexes containing quadruply bonded Mo_2 units around carbonate ions.[146] The cyclic complex *trans*-$[\{Mo_2(O_2CCF_3)_2(\mu\text{-dppa})\}_3(\mu_6\text{-}CO_3)(\mu_3\text{-}Cl)_3]F$ (**124**; Figure 17) was prepared by reaction of *trans*-$[Mo_2(O_2CCF_3)_2(MeCN)_6][BF_4]_2$ and K_2CO_3 with *N*,*N*′-bis(diphenylphosphanyl)amine (dppa) in dichloromethane. The chloride ions present in **124** presumably originate from the solvent. The analogous reaction carried out in acetonitrile followed by the addition of ZnX_2 (X = Br or I) afforded the analogous bromide or iodide complexes (**125** or **126**).

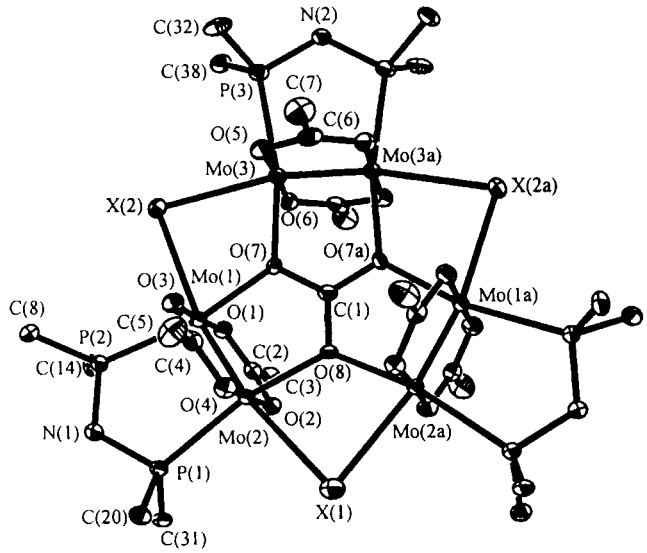
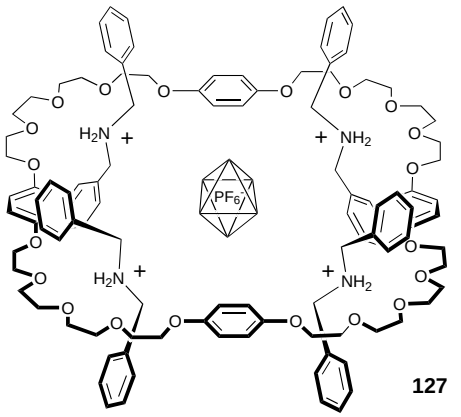


Figure 17. The crystal structure of complexes **124**–**126** (X = Cl, Br, and I, respectively; the CF_3 groups are not shown and only the *ipso* atom of the phenyl groups are shown). Reproduced with permission from ref. [146]. Copyright© The Royal Society of Chemistry 1999.

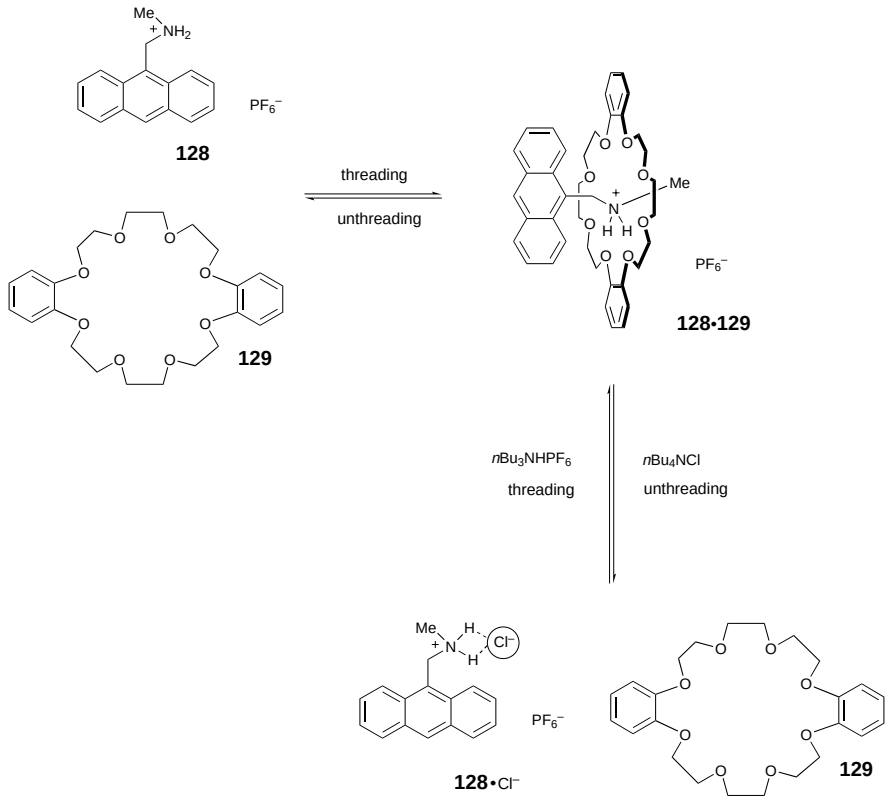
Stoddart and co-workers have also employed anions in self-assembly processes.[147] The pseudorotaxane **127** is formed from tetrakis-*p*-phenylene[68]crown-20 and four dibenzylammonium ions. The crystal structure of this assembly shows an



127

ordered PF_6^- ion bound in the center of the rotaxane. Unbound hexafluorophosphate ions are disordered in the crystal structure, that is, the octahedrally disposed fluorine atoms are not constrained to point in particular directions. However, in this case the ordering of the anion suggests the formation of C–H ··· F hydrogen bonds with the rest of the assembly, which locks the anion into a single orientation. The presence of the anion is therefore likely to reduce any electrostatic repulsion between the dibenzylammonium cations in the pseudorotaxane, thus assisting the assembly process.

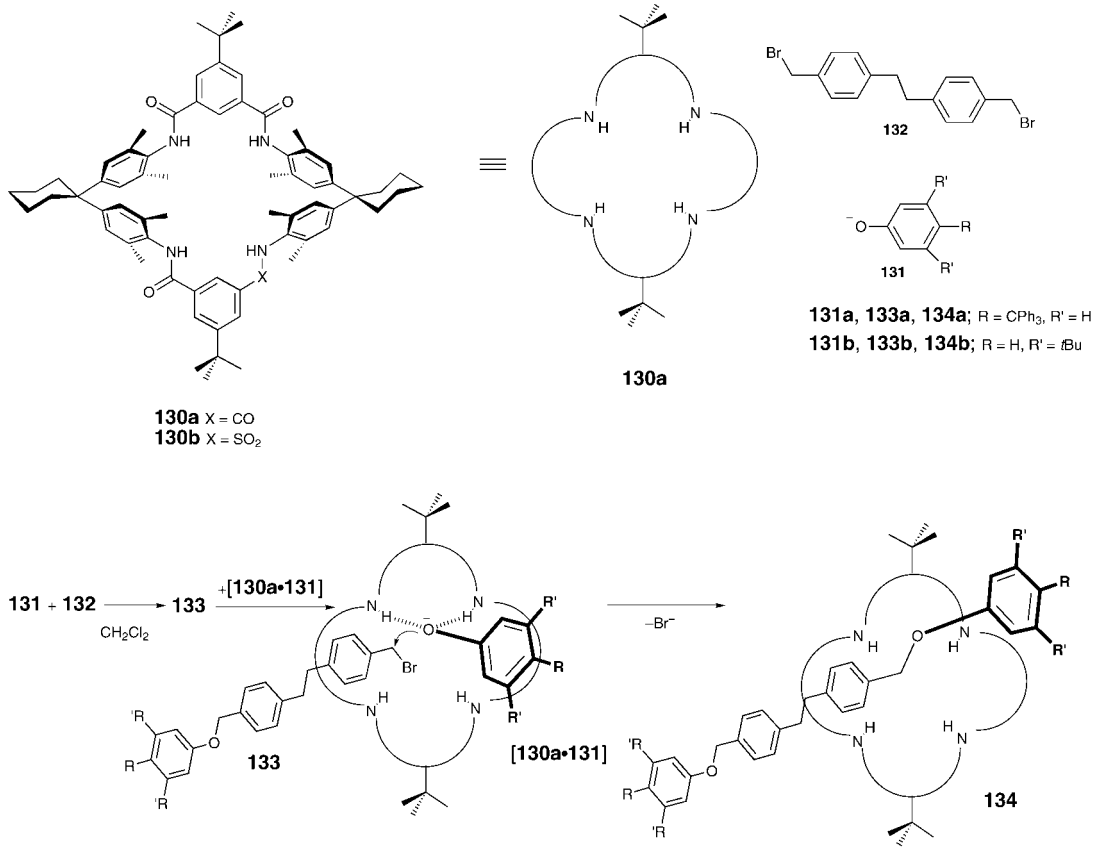
Montalti and Prodi have shown that chloride ions can control the threading and unthreading of a pseudorotaxane formed between (9-anthrylmethyl)methylammonium hexafluorophosphate **128** and dibenzo-[24]crown-8 (**129**; Scheme 11).[148] Chloride ions form a strong ion pair with



Scheme 11. Threading and dethreading processes with **128** and **129**.

the ammonium group of **128** which prevents the threading process and effectively breaks up the pseudorotaxane ensembles present in solution. Subsequent addition of Bu_3NH^+ ions (which can compete for the chloride ions bound in the ion pairs) drives the equilibrium back in favor of the pseudorotaxane.

Vögtle and co-workers have employed anion coordination in a high-yielding rotaxane synthesis. They discovered that phenolates, thiophenolates, and sulfonamide ions are strongly bound in the tetralactam macrocycles. The bound organic anion was found to be capable of reacting as a nucleophile and therefore could be utilized in rotaxane synthesis. For example, the complex **130a · 131** (Scheme 12) reacts with molecule **133** to form rotaxane **134** in 95% yield (probably one of the highest yields ever reported for this kind of synthesis).[149, 150]



Scheme 12. Efficient formation of a rotaxane by precoordination of nucleophilic anions.

A synthetic solid-state anion channel has recently been produced by Lippert and co-workers.[151] Lippert found that reaction of $[Pt(en)(H_2O)_2]^{2+}$ and 2,2-bipyrazine (bpz) produces the triangular complex $[\{Pt(en)(2,2'\text{-bpz-}N^4,N^{4'})\}_3]^{6+}$. Subsequent reaction with additional $[Pd(en)]^{2+}$ gives a hexametallic triangular complex $[\{(en)Pd\}_{2.5}(2,2'\text{-bpz})_3\{(NH_3)_2Pt\}_3][ClO_4)_6][NO_3]_5 \cdot 5H_2O$ (**135**; Figure 18) with one of the corner Pd atoms having 50% occupancy. A single perchlorate ion is bound at the center of the triangle. The triangles are held together by bridging nitrate ions and water molecules to form channels (Figure 18c, the perchlorate ions are omitted for clarity). Therefore this structure not only contains anions but is also held together by anions. A side view is shown in Figure 18d.

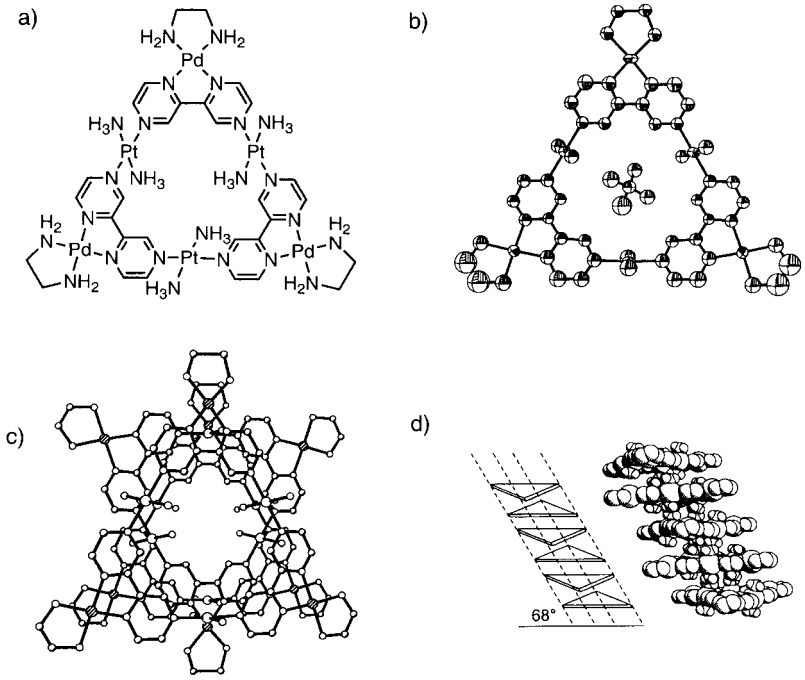
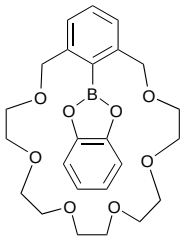


Figure 18. The cationic molecular triangle of complex **135**. a) Structure. b) X-ray crystal structure with encapsulated perchlorate ion (hydrogen atoms are omitted). c) Packing diagram showing the anion channel (perchlorate ions are omitted for clarity). d) Side view of the channel. b)–d) Reproduced with permission from ref. [151]. Copyright© The Royal Society of Chemistry 1999.

4.3. Ion-Pair Recognition

Ion-pair recognition, the simultaneous complexation of cationic and anionic guest species by multisite receptors, is a new, emerging, and topical field of coordination chemistry. These heteroditopic ligands can be designed to exhibit novel co-operative and allosteric behavior, whereby the binding of one charged guest can influence, through electrostatic and conformational effects, the subsequent coordination of the pairing ion. Such systems have potential as new selective extraction and transportation reagents for ion-pair species of environmental importance and for zwitterion recognition.

For example, compound **136** is capable of coordinating to potassium and fluoride ions simultaneously. Reetz et al. showed that the potassium ion is bound by the crown ether moiety present in this receptor whilst the fluoride ion is held by a combination of orbital overlap with the Lewis-acidic boron atom and electrostatic interactions with the potassium ion.[152, 153] The crystal structure of the potassium fluoride complex is shown in Figure 19.



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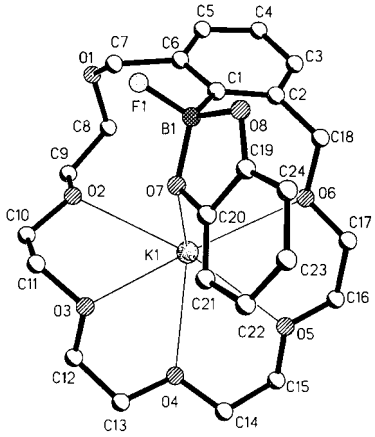
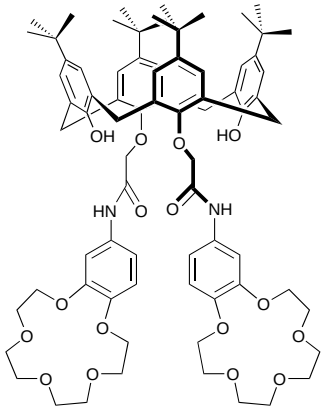


Figure 19. The X-ray crystal structure of the potassium fluoride complex of receptor **136** (hydrogen atoms are omitted). Reproduced with permission from ref. [152]. Copyright© VCH 1991.

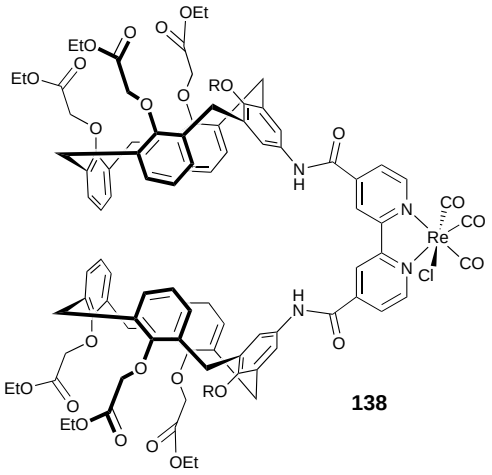
A series of calixarene-based ditopic receptors have been synthesized by Beer and co-workers. For example, receptor **137** consists of two benzo[15]crown-5 moieties attached to the lower rim of calix[4]arene through an amide linker. In the absence of an alkali metal cation, receptor **137** showed very little interaction with anions in CD_3CN. Upon addition of potassium ions, a sandwich complex is formed between the two benzocrown ether units. This results in the amide groups being held close together, and along with the electrostatic attraction of the alkali metal cation, preorganizes **137** to bind anions. Dihy-



137

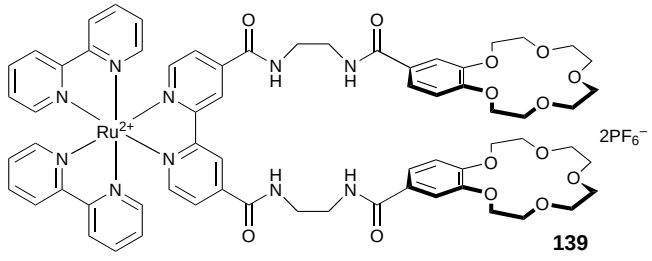
drogen phosphate was found to be particularly strongly bound ($\lg K > 4$) in CD_3CN.[154]

The bis(calixarene)rhenium(I) receptor **138** has been shown to simultaneously bind alkali metal cations and iodide ions with positive co-operativity. The enhanced affinity of the bis(calixarene) lower rim ester metal complexes of **138** for iodide ions is believed to result from electrostatics and a rigidifying effect of the ester-bound metal cation on the calixarene frameworks, which results in a central cavity that is preorganized for iodide binding.[155]



138

Beer and Dent have also recently reported the synthesis of new heteroditopic ruthenium(II)– and rhenium(I)–bipyridyl–bisbenzocrown ether receptors which, as evidenced from stability constant evaluations, complex KCl ion pairs in a co-operative fashion.[156] It is noteworthy that the anion selectivity properties of the bisbenzo[15]crown-5 receptors **139** and **140** are dramatically switched on binding K^+ ions. In the absence of K^+ the receptors are selective for $H_2PO_4^-$ over Cl^-, whereas following the formation of the intramolecular K^+–biscrown sandwich complex the reverse selectivity (Cl^- over $H_2PO_4^-$) is exhibited. The K^+-induced co-operativity of Cl^- binding may be a consequence of favorable electrostatic attraction and conformational effects wherein the sandwich complex results in a pseudomacrocyclic preorganized structure suitable for Cl^- binding (Figure 20).



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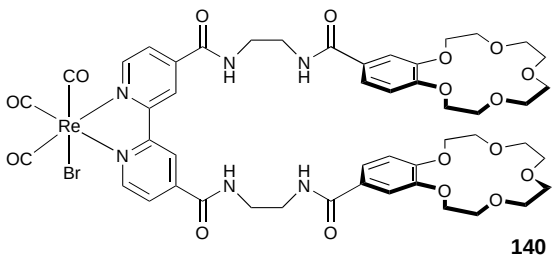

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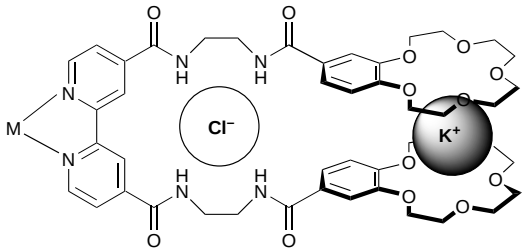
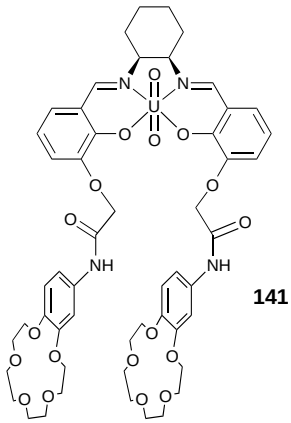


Figure 20. A pseudo-macrocyclic cavity is formed upon addition of potassium ions to **139** or **140** that switches on binding chloride ions.

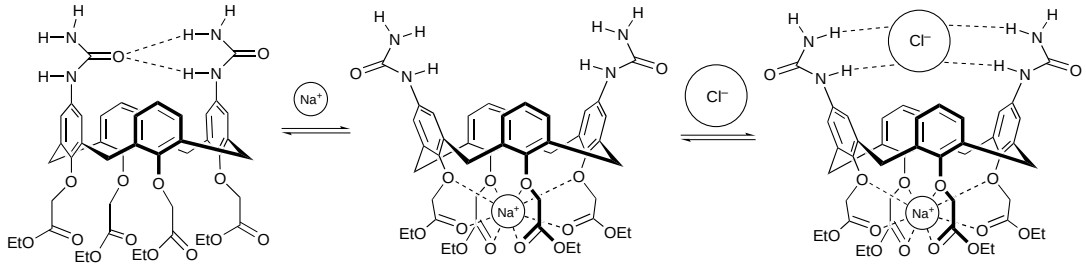
Using a similar strategy, Reinhoudt and co-workers constructed a receptor containing anion-binding Lewis-acidic UO_2^+ and amide moieties together with cation-binding crown ether groups.[157] A variety of complexation experiments revealed that receptor **141** is capable of binding potassium and dihydrogen phosphate ions simultaneously.



141

By taking the ditopic receptor strategy a step further the same workers have produced a switchable anion receptor. Receptor **142** consists of a calix[4]arene with cation-binding ester groups at the lower rim and anion-binding urea groups at the upper rim (Scheme 13).[158] The two urea groups are hydrogen-bonded together in chloroform, and so are not available for hydrogen bonding to any putative anionic guest species. However when sodium ions are added, they bind to the ester groups of the calixarene, which causes the lower rim to contract. This rearrangement forces the urea groups at the upper rim apart breaking the hydrogen bonds between the urea groups, thus making them available for anionic guests.

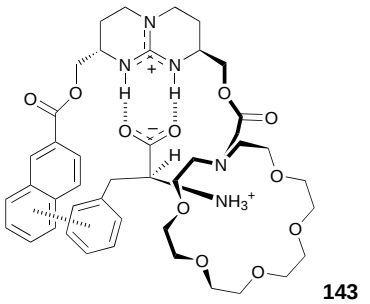
Receptor **143**, synthesized by de Mendoza, Lehn, and co-workers, provides an elegant example of zwitterion recognition.[45] The receptor extracts amino acids from aqueous solution into dichloromethane. This occurs selectively, with a strong preference for amino acids with aromatic side chains, such as phenylalanine and tryptophan. A three-point binding mode has been proposed, with the carboxylate ion bound by the guanidinium unit, the protonated amine by the aza-crown, and $\pi-\pi$ interactions between the phenyl side chain of the amino acid and the receptor's naphthalene unit enhancing the strength and selectivity of complex formation. Additionally,



142

Scheme 13. The Na^+ dependence of chloride binding by **142**.

receptor **143** is optically active, and is selective for L- over D-amino acids. In fact, no extraction of D-amino acids is observed.



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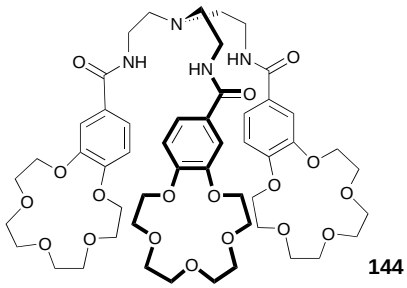


144

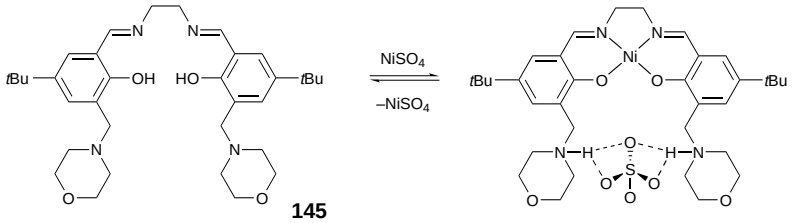
The use of ditopic ion-pair receptors as sequestration agents for environmentally deleterious pollutants has recently begun to be explored. Radioactive pertechnetate anions are generated during the nuclear fuel reprocessing process and are currently discharged into the sea. Beer and co-workers have reported that the tren-based receptor **144** (tren = tris(2-aminoethyl)amine), which contains an amidic anion-binding cavity linked to three cation-binding benzo[15]crown-5 groups, has been shown to efficiently extract sodium pertechnetate from simulated aqueous nuclear waste streams.[159] In the absence of a co-bound cation, the anion binding affinity of the receptor was considerably reduced.

White et al. have produced a receptor that contains a dianionic binding site for transition metal cations and a dicationic binding site for anions.[160] Receptor **145** (Scheme 14) contains a salen-based binding site (salen = *N*,*N*′-bis(salicylidene)ethylenediamine dianion) capable of coordinating to transition metal cations such as Cu^{II} or Ni^{II}. Upon complexation, the phenolic protons transfer to the morpholine nitrogen atoms. Additionally the presence of the transition metal forces the receptor into a conformation such that the protonated morpholine groups are in proximity, and define an anion-binding site. Metal binding therefore enhances the anion-binding affinity of the receptor. Extraction experiments at pH 3.8 demonstrated that **145** is capable of extracting $CuSO_4$ into chloroform with a near 100 % loading of receptor.

5. Conclusion

As this brief review has illustrated with a discussion of a range of artificial anion receptor systems which function through a variety of molecular interactions, the relatively new field of anion coordination chemistry has become an established area in supramolecular chemistry. Additionally, many of the well-known concepts of cation coordination chemistry such as the chelate, macrocyclic, and template effects have transferred across to the sister field of anion coordination.

Generally, it is possible to rationalize thermodynamic stability and selectivity trends exhibited by abiotic anion receptors on the basis of complementary receptor–anion size and shape, binding site topology, and anion basicity. Calorimetric studies are essential in order to elucidate the specific contributions such as electrostatics, hydrogen bonding, hydrophobicity, and the crucial role the solvent has on the anion-recognition process. To date there is unfortunately a paucity of enthalpic and entropic data available.[161, 162] As a consequence there is little doubt that this is an area of anion coordination chemistry that will have to be addressed in order for the field to develop further. However, based on our current understanding, it is possible to make simple predictions. Consideration of the nature of the solvent medium in

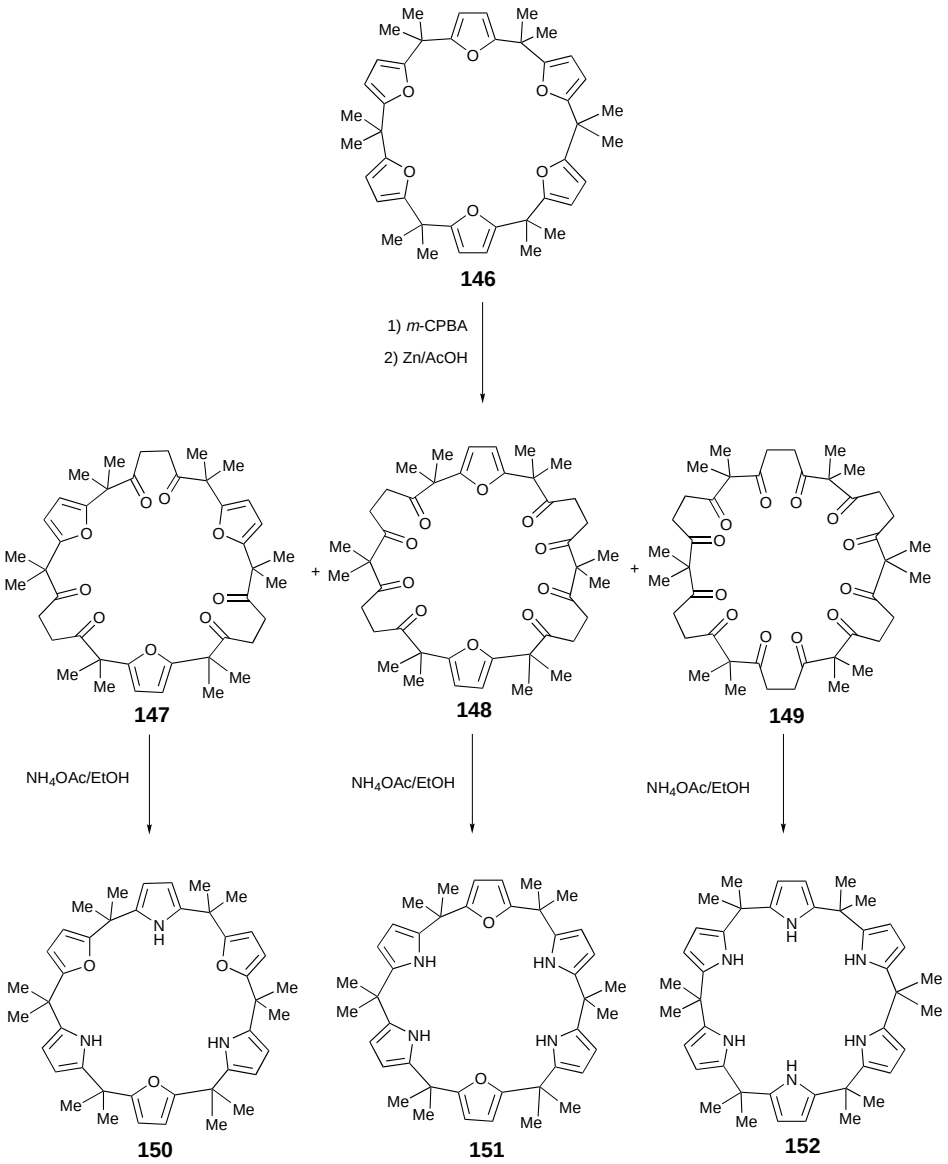


145

Scheme 14. The Ni^{2+} dependence of sulfate binding by **145**.

which the anion recognition event takes place is of paramount importance. For example, in aqueous solvents receptors that bind anions solely by hydrogen bonding will not function efficiently, and positively charged receptors or ones that employ a combination of hydrogen bonds and electrostatic interactions are required to overcome competing solvation effects. Correlations between the anion stability/selectivity properties of neutral ferrocenoyl receptors and the solvent Gutmann acceptor number have been noted.[163] The nature of the target anion must be taken into account: Multidentate guanidinium receptors, for example, are more effective for coordinating oxoanions such as phosphate or carboxylate wherein convergent preorganized hydrogen bond donor groups complement the hydrogen bond acceptor sites of the guest anion.

Ultimately, we hope to fully understand how nature selectively binds, functionalizes, and transports negatively charged species and so reach a stage where a specific receptor can be readily chosen when a target anion is to be bound in a particular environment. At the start of the new Millennium, it is predicted that the anion coordination chemist will meet this challenge and so provide answers to the many exciting environmental, biological, and medicinal challenges.



Scheme 15. Synthesis of the expanded calix[*n*]arene macrocycles **150**–**152**. *m*-CPBA = *meta*-chloroperbenzoic acid.

Addendum

Since the submission of this manuscript there have been considerable advances in the synthesis of expanded or "higher-order" calix[*n*]pyrrole macrocycles ($n > 4$).[164, 165] Very recently, Kohnke and co-workers found that *meso*-dodecamethylcalix[6]pyrrole **152**, *meso*-dodecamethylcalix[3]furan[3]pyrrole **150**, and *meso*-dodecamethylcalix[2]furan[4]pyrrole **151** may be prepared from *meso*-dodecamethylcalix[6]furan **146** (Scheme 15).[166] Reaction of the calix[6]furan **146** with *meta*-chloroperbenzoic acid (*m*-CPBA) followed by zinc/AcOH opens either some or all of the furan rings to afford a mixture of macrocycles **147**–**149** containing α,δ-diketone functionalities. These groups can be converted into pyrrole by treatment with ammonium acetate (Scheme 15).

Although the anion–calix[6]pyrrole stability constants for calix[6]pyrrole **152** have not been reported, transport studies have been carried out in order to compare the abilities of *meso*-octamethylcalix[4]pyrrole and *meso*-dodecamethylcalix[6]pyrrole **152** to transport halide ions from an aqueous (D_2O) to an organic (CD_2Cl_2) phase.[167] These studies show that **152** extracts chloride ions from D_2O to CD_2Cl_2 most efficiently. The crystal structures of both the chloride and bromide complexes of *meso*-dodecamethylcalix[6]pyrrole **152** were obtained and revealed that the anions are coordinated at the center of the macrocycle through six N–H···Cl/Br hydrogen bonds. The crystal structure of the chloride complex is shown in Figure 21.

Sessler et al. have discovered a direct synthetic route to expanded calixpyrroles. Reaction of acetone with 3,4-difluoropyrrole, rather than pyrrole, gives amongst it products significant quantities of calix[5]pyrrole **154** and calix[8]pyrrole **155** (Scheme 16, Figure 22).[168] The use of the less

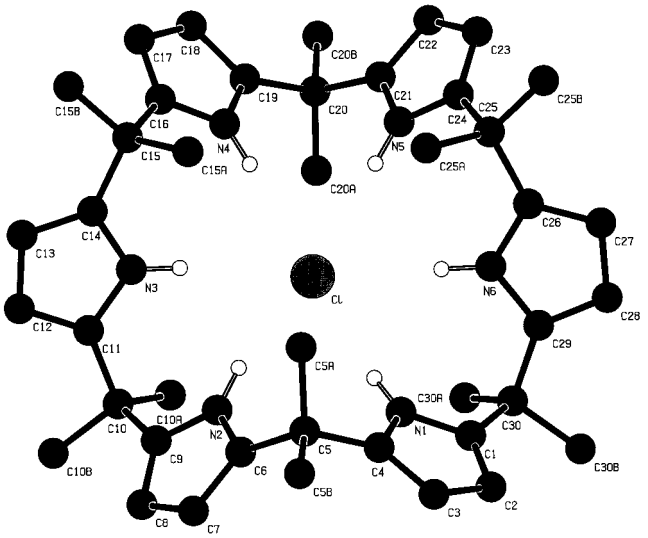
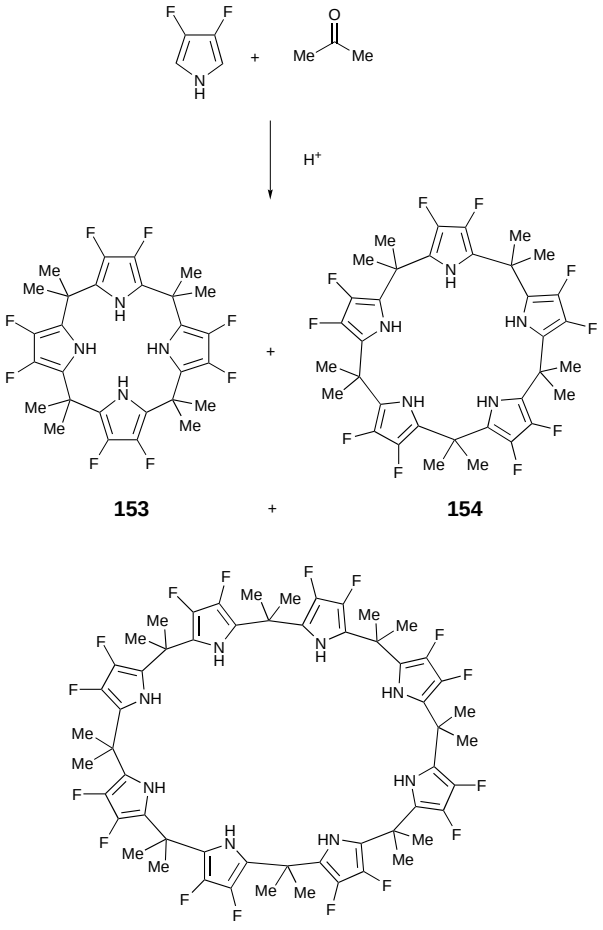


Figure 21. The X-ray crystal structure of the chloride complex of *meso*-dodecamethylcalix[6]pyrrole **152** (hydrogen atoms are omitted). Reproduced with permission from ref. [166].



Scheme 16. Synthesis of fluorocalixpyrroles **153**–**155**.

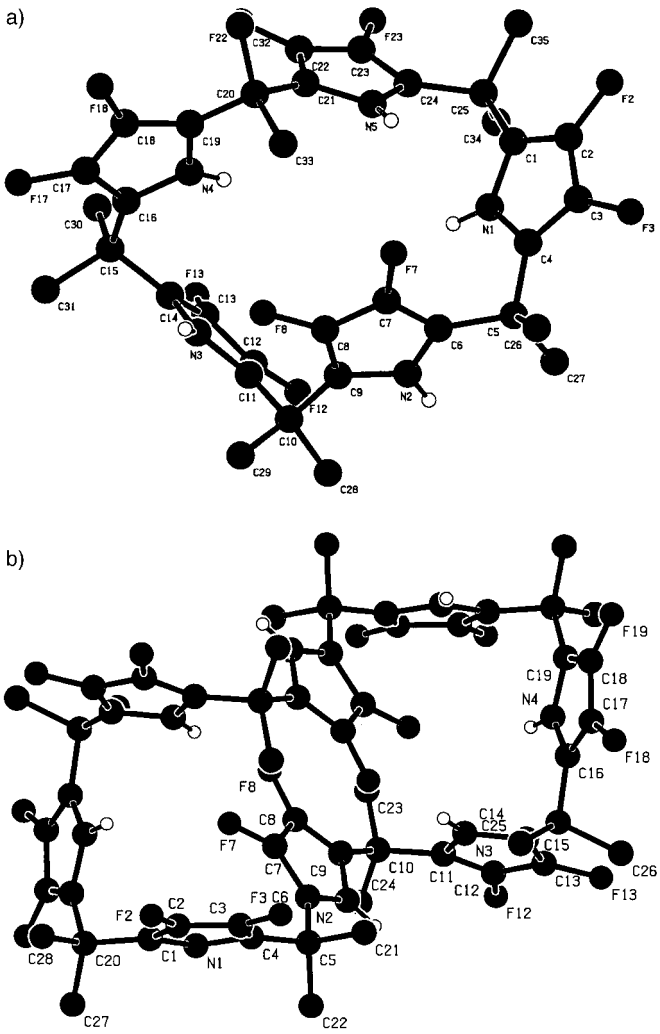


Figure 22. The X-ray crystal structures of decafluorocalix[5]pyrrole **154** and dodecafluorocalix[8]pyrrole **155** (hydrogen atoms are omitted). Reproduced with permission from ref. [168].

reactive 3,4-difluoropyrrole in the condensation allows the macrocylization reaction to proceed under kinetic, rather than thermodynamic, control at room temperature. In preliminary work, Sessler et al. have found that decafluorocalix[5]pyrrole **154** exhibits a higher affinity for chloride ions ($K = 41\,000\,\text{M}^{-1}$) than the corresponding octafluorocalix[4]pyrrole analogue **153** ($K = 11\,000\,\text{M}^{-1}$) as determined by ^{1}H and ^{19}F NMR titration experiments in [D_3]acetonitrile (0.5 % D_2O).

Significant progress has also been made recently in the detection of oxyanions by lanthanide-containing receptors.[169] Parker has shown that reversible anion binding to alkylphenanthridinium chromophore appended heptadentate cyclentriamide or polycarboxylate Eu^{III}- or Tb^{III}-containing receptors such as **156** in aqueous solution is signalled by changes in the ^{1}H NMR spectrum, emission intensity, and circular polarization following excitation with the more highly charged anions (citrate, malonate) forming the strongest complexes.[170]

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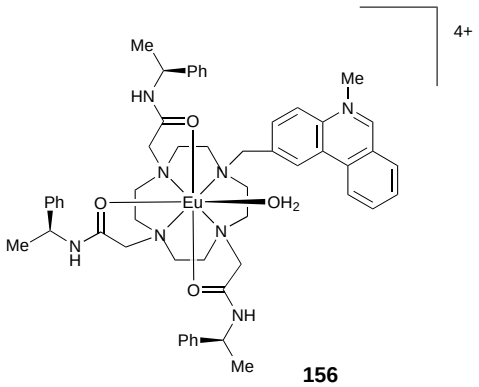

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[1] *Supramolecular Chemistry of Anions* (Eds.: A. Bianchi, K. Bowman-James, E. Garcia-España), WILEY-VCH, New York, **1997**.
[2] D. W. Christianson, W. N. Lipscomb, *Acc. Chem. Res.* **1989**, *22*, 62.
[3] J. M. Berg, *Acc. Chem. Res.* **1995**, *28*, 14.
[4] J. D. Puglisi, L. Chen, A. D. Frankel, J. R. Williamson, *Proc. Nat. Acad. Sci. USA* **1993**, *90*, 3680.
[5] B. Moss, *Chem. Ind.* **1996**, 407.
[6] C. Glidewell, *Chem. Br.* **1990**, *26*, 137.
[7] R. D. Shannon, *Acta Crystallogr. Sect. A* **1976**, *32*, 751.
[8] S. Mangani, M. Ferraroni in *Supramolecular Chemistry of Anions* (Eds.: A. Bianchi, K. Bowman-James, E. Garcia-España), WILEY-VCH, New York, **1997**, p. 63.
[9] F. Hofmeister, *Arch. Exp. Pathol. Pharmakol.* **1888**, *24*, 247.
[10] a) P. A. Gale, *Coord. Chem. Rev.* **2000**, *199*, 181. b) P. A. Gale, *Phil. Trans. R. Soc. Lond. A.* **2000**, *358*, 431.
[11] M. M. G. Antonisse, D. N. Reinhoudt, *Chem. Commun.* **1998**, 443.
[12] M. Berger, F. P. Schmidtchen, *Chem. Rev.* **1997**, *97*, 1609.
[13] J. L. Atwood, K. T. Holman, J. W. Steed, *Chem. Commun.* **1996**, 1401.
[14] F. P. Schmidtchen, *Angew. Chem.* **1977**, *89*, 751; *Angew. Chem. Int. Ed. Engl.* **1977**, *16*, 720.
[15] F. P. Schmidtchen, *Chem. Ber.* **1980**, *113*, 864.
[16] F. P. Schmidtchen, *Chem. Ber.* **1981**, *114*, 597.
[17] F. P. Schmidtchen, G. Muller, *J. Chem. Soc. Chem. Commun.* **1984**, 1115.
[18] K. Worm, F. P. Schmidtchen, A. Schier, A. Schäfer, M. Hesse, *Angew. Chem.* **1994**, *106*, 360; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 327.
[19] K. Worm, F. P. Schmidtchen, *Angew. Chem.* **1995**, *107*, 71; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 65.
[20] P. B. Savage, S. K. Holmgren, S. H. Gellman, *J. Am. Chem. Soc.* **1994**, *116*, 4069.
[21] P. B. Savage, S. K. Holmgren, S. H. Gellman, *J. Am. Chem. Soc.* **1993**, *115*, 7900.
[22] R. A. Pascal, J. Spergel, D. V. Engbersen, *Tetrahedron Lett.* **1986**, *27*, 4099.
[23] S. Valiyaveettil, J. F. J. Engbersen, W. Verboom, D. N. Reinhoudt, *Angew. Chem.* **1993**, *105*, 942; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 900.
[24] C. Raposo, N. Perez, M. Almaraz, M. L. Mussons, M. C. Caballero, J. R. Moran, *Tetrahedron Lett.* **1995**, *36*, 3255.
[25] A. P. Bisson, V. M. Lynch, M. K. C. Monahan, E. V. Anslyn, *Angew. Chem.* **1997**, *109*, 2435; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2340.
[26] T. R. Kelley, M. H. Kim, *J. Am. Chem. Soc.* **1994**, *116*, 7072.
[27] P. Bülmann, S. Nishizawa, K. P. Xiao, Y. Umezawa, *Tetrahedron* **1997**, *53*, 1647.
[28] A. Baeyer, *Ber. Dtsch. Chem. Ges.* **1886**, *19*, 2184.
[29] P. A. Gale, J. L. Sessler, V. Král, V. Lynch, *J. Am. Chem. Soc.* **1996**, *118*, 5140.
[30] J. L. Sessler, P. A. Gale, J. W. Genge, *Chem. Eur. J.* **1998**, *4*, 1095.
[31] P. A. Gale, J. L. Sessler, V. Král, *Chem. Commun.* **1998**, 1.
[32] V. Král, J. L. Sessler, T. V. Shishkanova, P. A. Gale, R. Volf, *J. Am. Chem. Soc.* **1999**, *121*, 8771.
[33] J. L. Sessler, A. Gebauer, P. A. Gale, *Gazz. Chim. Ital.* **1997**, *127*, 723.
[34] H. Miyaji, P. Anzenbacher, Jr, J. L. Sessler, E. R. Bleasdale, P. A. Gale, *Chem. Commun.* **1999**, 1723.
[35] A. Andrievsky, F. Ahuis, J. L. Sessler, F. Vögtle, D. Gudat, M. Moini, *J. Am. Chem. Soc.* **1998**, *120*, 9712.
[36] C. H. Park, H. E. Simmons, *J. Am. Chem. Soc.* **1968**, *90*, 2431.
[37] E. Graf, J.-M. Lehn, *J. Am. Chem. Soc.* **1976**, *98*, 6403.
[38] B. Metz, J. M. Rosalky, R. Weiss, *J. Chem. Soc. Chem. Commun.* **1976**, 533.
[39] J.-M. Lehn, E. Sonveaux, A. K. Willard, *J. Am. Chem. Soc.* **1978**, *100*, 4914.
[40] B. Dietrich, J. Guilhem, J.-M. Lehn, C. Pascard, E. Sonveaux, *Helv. Chim. Acta* **1984**, *67*, 91.
[41] M. W. Hosseini, J.-M. Lehn, *J. Am. Chem. Soc.* **1982**, *104*, 3525.
[42] M. W. Hosseini, J.-M. Lehn, *Helv. Chim. Acta* **1986**, *69*, 587.
[43] J. A. Aguilar, E. García-España, J. A. Guerrero, S. V. Luis, J. M. Linares, J. F. Miravet, J. A. Ramírez, C. Soriano, *J. Chem. Soc. Chem. Commun.* **1995**, 2237.
[44] G. Müller, J. Riede, F. P. Schmidtchen, *Angew. Chem.* **1988**, *100*, 1574; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1516.
[45] A. Echavarren, A. Galan, J. de Mendoza, A. Salmeron, J.-M. Lehn, *J. Am. Chem. Soc.* **1989**, *111*, 4994.
[46] V. J. Bauer, D. L. J. Clive, D. Dolphin, J. B. Paine III, F. L. Harris, M. M. King, J. Loder, S.-W. C. Wang, R. B. Woodward, *J. Am. Chem. Soc.* **1983**, *105*, 6429.
[47] J. L. Sessler, M. J. Cyr, V. Lynch, E. McGhee, J. A. Ibers, *J. Am. Chem. Soc.* **1990**, *112*, 2810.
[48] J. L. Sessler, M. Cyr, H. Furuta, V. Král, T. Mody, T. Morishima, M. Shionoya, S. J. Weghorn, *Pure Appl. Chem.* **1993**, *65*, 393.
[49] M. Shionoya, H. Furuta, V. Lynch, A. Harriman, J. L. Sessler, *J. Am. Chem. Soc.* **1992**, *114*, 5714.
[50] Y. Azuma, M. Newcomb, *Organometallics* **1984**, *3*, 9.
[51] M. Newcomb, A. M. Madonik, M. T. Blanda, J. K. Judice, *Organometallics* **1987**, *6*, 145.
[52] M. Newcomb, M. T. Blanda, Y. Azuma, T. J. Delord, *J. Chem. Soc. Chem. Commun.* **1984**, 1159.
[53] M. Newcomb, J. H. Horner, M. T. Blanda, *J. Am. Chem. Soc.* **1987**, *109*, 7878.
[54] M. Newcomb, M. T. Blanda, *Tetrahedron Lett.* **1988**, *29*, 4261.
[55] M. Newcomb, J. H. Horner, M. T. Blanda, P. J. Squattrito, *J. Am. Chem. Soc.* **1989**, *111*, 6294.
[56] D. F. Shriver, M. J. Biallas, *J. Am. Chem. Soc.* **1967**, *89*, 1078.
[57] H. E. Katz, *J. Am. Chem. Soc.* **1985**, *107*, 1420.
[58] H. E. Katz, *J. Org. Chem.* **1985**, *50*, 5027.
[59] H. E. Katz, *Organometallics* **1987**, *6*, 1134.
[60] K. Tamao, T. Hayashi, Y. Ito, *J. Organomet. Chem.* **1996**, *506*, 85.
[61] K. Ogawa, S. Aoyaki, Y. Takeuchi, *J. Chem. Soc. Perkin Trans. 2* **1993**, 2389.
[62] S. Aoyagi, K. Tanaka, I. Zicmane, Y. Takeuchi, *J. Chem. Soc. Perkin Trans. 2* **1992**, 2217.
[63] S. Aoyagi, K. Tanaka, Y. Takeuchi, *J. Chem. Soc. Perkin Trans. 2* **1994**, 1549.
[64] J. D. Wuest, B. Zacharie, *Organometallics* **1985**, *4*, 410.
[65] V. B. Shur, I. A. Tikhonova, A. I. Yanovsky, Y. T. Struchkov, P. V. Petrovskii, S. Y. Panov, G. G. Furin, M. E. Vol'pin, *J. Organomet. Chem.* **1991**, *418*, C29.
[66] X. Yang, C. B. Knobler, M. F. Hawthorne, *Angew. Chem.* **1991**, *103*, 1519; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1507.
[67] X. Yang, C. B. Knobler, M. F. Hawthorne, *J. Am. Chem. Soc.* **1992**, *114*, 380.
[68] Y. Inoue, T. Hakushi, Y. Liu, L.-H. Tong, B.-J. Shen, D.-S. Jin, *J. Am. Chem. Soc.* **1993**, *115*, 475.

[69] J. W. Steed, R. K. Juneja, J. L. Atwood, *Angew. Chem.* **1994**, *106*, 2571; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2456.
[70] J. W. Steed, C. P. Johnson, R. K. Juneja, J. L. Atwood, R. S. Burkhalter, *Supramol. Chem.* **1996**, *6*, 235.
[71] M. Staffilani, K. S. B. Hancock, J. W. Steed, K. T. Holman, J. L. Atwood, R. K. Juneja, R. S. Burkhalter, *J. Am. Chem. Soc.* **1997**, *119*, 6324.
[72] P. D. Beer, *Acc. Chem. Res.* **1998**, *31*, 71.
[73] P. D. Beer, *Chem. Commun.* **1996**, 689.
[74] P. D. Beer, P. A. Gale, G. Z. Chen, *J. Chem. Soc. Dalton Trans.* **1999**, 1897.
[75] P. L. Boulas, M. Goméz-Kaifer, L. Echegoyen, *Angew. Chem.* **1998**, *110*, 226; *Angew. Chem. Int. Ed.* **1998**, *37*, 216.
[76] K. P. Xiao, P. Bühlmann, S. Nishizawa, S. Amemiya, Y. Umezawa, *Anal. Chem.* **1997**, *69*, 1038.
[77] M. M. G. Antonisse, B. H. M. Snellink-Ruël, A. C. Ion, J. F. J. Engbersen, D. N. Reinhoudt, *J. Chem. Soc. Perkin Trans 2* **1999**, 1211.
[78] M. M. G. Antonisse, B. H. M. Snellink-Ruël, J. F. J. Engbersen, D. N. Reinhoudt, *J. Chem. Soc. Perkin Trans 2* **1998**, 773.
[79] M. M. G. Antonisse, B. H. M. Snellink-Ruël, J. F. J. Engbersen, D. N. Reinhoudt, *Sens. Actuators B* **1998**, *47*, 9.
[80] P. D. Beer, P. A. Gale, G. Z. Chen, *Adv. Phys. Org. Chem.* **1998**, *31*, 1.
[81] P. D. Beer, P. A. Gale, G. Z. Chen, *Coord. Chem. Rev.* **1999**, *185–186*, 3.
[82] P. D. Beer, A. D. Keefe, *J. Organomet. Chem.* **1989**, *375*, C40.
[83] P. D. Beer, D. Hesek, J. Hodacova, S. E. Stokes, *J. Chem. Soc. Chem. Commun.* **1992**, 270.
[84] P. D. Beer, C. Hazlewood, D. Hesek, J. Hodacova, S. E. Stokes, *J. Chem. Soc. Dalton Trans.* **1993**, 1327.
[85] P. D. Beer, M. G. B. Drew, A. R. Graydon, D. K. Smith, *J. Chem. Soc. Dalton Trans.* **1995**, 403.
[86] P. D. Beer, D. Hesek, J. E. Kingston, D. K. Smith, S. E. Stokes, M. G. B. Drew, *Organometallics* **1995**, 3288.
[87] P. D. Beer, M. G. B. Drew, J. Hodacova, S. E. Stokes, *J. Chem. Soc. Dalton Trans.* **1995**, 3447.
[88] P. D. Beer, M. G. B. Drew, D. Hesek, M. Shade, F. Szemes, *Chem. Commun.* **1996**, 2161.
[89] P. D. Beer, M. G. B. Drew, D. Hesek, K. C. Nam, *Chem. Commun.* **1997**, 107.
[90] P. D. Beer, M. G. B. Drew, D. Hesek, K. C. Nam, *Organometallics* **1999**, *18*, 3933.
[91] P. D. Beer, M. G. B. Drew, D. Hesek, R. Jagessar, *J. Chem. Soc. Chem. Commun.* **1995**, 1187.
[92] P. D. Beer, Z. Chen, A. J. Goulden, A. R. Graydon, S. E. Stokes, T. Wear, *J. Chem. Soc. Chem. Commun.* **1993**, 1834.
[93] P. D. Beer, A. R. Graydon, A. O. M. Johnson, D. K. Smith, *Inorg. Chem.* **1997**, *36*, 2112.
[94] C. Valério, J.-L. Fillaut, J. Ruiz, J. Guittard, J.-C. Blais, D. Astruc, *J. Am. Chem. Soc.* **1997**, *119*, 2588.
[95] C. Valério, E. Alonso, J. Ruiz, J. C. Blais, D. Astruc, *Angew. Chem.* **1999**, *111*, 1855; *Angew. Chem. Int. Ed.* **1999**, *38*, 1747.
[96] P. A. Gale, Z. Chen, M. G. B. Drew, J. A. Heath, P. D. Beer, *Polyhedron* **1998**, *17*, 405.
[97] P. D. Beer, Z. Chen, M. G. B. Drew, J. Kingston, M. I. Ogden, P. Spencer, *J. Chem. Soc. Chem. Commun.* **1993**, 1046.
[98] P. D. Beer, Z. Chen, M. G. B. Drew, A. O. M. Johnson, D. K. Smith, P. Spencer, *Inorg. Chim. Acta* **1996**, *246*, 143.
[99] P. D. Beer, J. Cadman, J. M. Lloris, R. Martínéz-Máñez, M. E. Padilla-Tosta, T. Pardo, D. K. Smith, J. Soto, *J. Chem. Soc. Dalton Trans.* **1999**, 127.
[100] P. D. Beer, M. G. B. Drew, D. K. Smith, *J. Organomet. Chem.* **1997**, *543*, 259.
[101] C. Dusemund, K. R. A. S. Sandanayake, S. Shinkai, *J. Chem. Soc. Chem. Commun.* **1995**, 333.
[102] M. Nicolas, B. Fabre, J. Simonet, *Chem. Commun.* **1999**, 1881.
[103] A. P. de Silva, H. Q. N. Gunaratne, T. Gunnlaugsson, A. J. M. Huxley, C. P. McCoy, J. T. Rademacher, T. E. Rice, *Chem. Rev.* **1997**, *97*, 1515.
[104] A. W. Czarnik, *Acc. Chem. Res.* **1994**, *27*, 302.
[105] A. P. de Silva, H. Q. N. Guarantee, C. McVeigh, M. G. E. Maguire, P. R. S. Maxwell, E. O'Hanlon, *Chem. Commun.* **1996**, 2191.
[106] L. Fabbrizzi, G. Francese, M. Licchelli, A. Perotti, A. Taglietti, *Chem. Commun.* **1997**, 581.
[107] D. Parker, K. Senanayake, J. A. G. Williams, *J. Chem. Soc. Perkin 2* **1998**, 2129.
[108] D. Parker, K. Senanayake, J. A. G. Williams, *Chem. Commun.* **1997**, 1777.
[109] V. Balzani, F. Barigeletti, L. D. Cola, *Top. Curr. Chem.* **1990**, *158*, 31.
[110] A. Juris, V. Balzani, F. Barigeletti, S. Campagna, P. Belser, A. von Zelewsky, *Coord. Chem. Rev.* **1988**, *84*, 85.
[111] F. Szemes, D. Hesek, Z. Chen, S. W. Dent, M. G. B. Drew, A. J. Goulden, A. R. Graydon, A. Grieve, R. J. Mortimer, T. Wear, J. S. Weightman, P. D. Beer, *Inorg. Chem.* **1996**, *35*, 5868.
[112] P. D. Beer, S. W. Dent, T. Wear, *J. Chem. Soc. Dalton Trans.* **1996**, 2341.
[113] P. D. Beer, A. R. Graydon, L. R. Sutton, *Polyhedron* **1996**, *15*, 2457.
[114] P. D. Beer, S. W. Dent, G. S. Hobbs, T. J. Wear, *Chem. Commun.* **1997**, 99.
[115] P. D. Beer, F. Szemes, V. Balzani, C. M. Salà, M. G. B. Drew, S. W. Dent, M. Maestri, *J. Am. Chem. Soc.* **1997**, *119*, 11864.
[116] P. D. Beer, R. Wilson, unpublished results.
[117] R. V. Slone, D. I. Yoon, R. M. Calhoun, J. T. Hupp, *J. Am. Chem. Soc.* **1995**, *117*, 11813.
[118] M. J. Deetz, B. D. Smith, *Tetrahedron Lett.* **1998**, *39*, 6841.
[119] V. W.-W. Yam, A. S.-F. Kai, *Chem. Commun.* **1998**, 109.
[120] S. Watanabe, O. Onogawa, Y. Komatsu, K. Yoshida, *J. Am. Chem. Soc.* **1998**, *120*, 229.
[121] P. D. Beer, V. Timoshenko, M. Maestri, P. Passaniti, V. Balzani, *Chem. Commun.* **1999**, 1755.
[122] P. D. Beer, J. Cadman, *New J. Chem.* **1999**, *23*, 347.
[123] A. Metzger, V. M. Lynch, E. V. Anslyn, *Angew. Chem.* **1997**, *109*, 911; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 862.
[124] A. Metzger, E. V. Anslyn, *Angew. Chem.* **1998**, *110*, 682; *Angew. Chem. Int. Ed. Engl.* **1998**, *37*, 649.
[125] C. B. Black, B. Andrioletti, A. C. Try, C. Ruiperez, J. L. Sessler, *J. Am. Chem. Soc.* **1999**, *121*, 10438.
[126] K. Niikura, A. P. Bisson, E. V. Anslyn, *J. Chem. Soc. Perkin 2* **1999**, 1111.
[127] P. A. Gale, L. J. Twyman, C. I. Handlin, J. L. Sessler, *Chem. Commun.* **1999**, 1851.
[128] M. W. Hosseini in *Supramolecular Chemistry of Anions* (Eds.: A. Bianchi, K. Bowman-James, E. García-España), WILEY-VCH, New York, **1997**.
[129] E. K. Fan, C. Vicent, A. D. Hamilton, *New J. Chem.* **1997**, *21*, 81.
[130] J. Scheele, P. Timmerman, D. N. Reinhoudt, *Chem. Commun.* **1998**, 2613.
[131] L. F. Lindoy, *The Chemistry of Macrocyclic Ligand Complexes*, Cambridge University Press, Cambridge, **1989**.
[132] J. L. Sessler, T. D. Mody, V. Lynch, *Inorg. Chem.* **1992**, *31*, 529.
[133] J. Salta, Q. Chen, Y. Chang, J. Zubieta, *Angew. Chem.* **1994**, *106*, 781; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 757.
[134] A. Müller, K. Hovemeier, R. Rohlfing, *Angew. Chem.* **1992**, *104*, 1214; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1192.
[135] A. Müller, R. Rohlfing, E. Krickemeyer, H. Bogge, *Angew. Chem.* **1993**, *105*, 916; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 909.
[136] A. Müller, S. K. Das, H. Bögge, C. Beugholt, M. Schmidtmann, *Chem. Commun.* **1999**, 1035.
[137] J. Sánchez-Quesada, C. Seel, P. Prados, J. de Mendoza, *J. Am. Chem. Soc.* **1996**, *118*, 277.
[138] M. W. Peczuh, A. D. Hamilton, J. Sánchez-Quesada, J. de Mendoza, T. Haack, E. Giralt, *J. Am. Chem. Soc.* **1997**, *119*, 9327.
[139] B. Hasenknopf, J.-M. Lehn, B. O. Kneisel, G. Baum, D. Fenske, *Angew. Chem.* **1996**, *108*, 1987; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1838.
[140] B. Hasenknopf, J.-M. Lehn, N. Boumediene, A. Dupont-Gervais, A. Van Dorsselaer, B. Kneisel, D. Fenske, *J. Am. Chem. Soc.* **1997**, *119*, 10956.
[141] M. Fujita, S. Nagao, K. Ogura, *J. Am. Chem. Soc.* **1995**, *117*, 1649.
[142] M. Aoyagi, K. Biradha, M. Fujita, *J. Am. Chem. Soc.* **1999**, *121*, 7457.
[143] R. Vilar, D. M. P. Mingos, A. J. P. White, D. J. Williams, *Angew. Chem.* **1998**, *110*, 1323; *Angew. Chem. Int. Ed.* **1998**, *37*, 1258.
[144] J. S. Flemming, K. L. V. Mann, C.-A. Carraz, E. Psillakis, J. C. Jeffery, J. A. McCleverty, M. D. Ward, *Angew. Chem.* **1998**, *110*, 1315; *Angew. Chem. Int. Ed.* **1998**, *37*, 1279.
[145] R. Wang, Z. Zheng, T. Jion, R. J. Staples, *Angew. Chem.* **1999**, *111*, 1929; *Angew. Chem. Int. Ed.* **1999**, *38*, 1813.

[146] M.-C. Suen, G.-W. Tseng, J. D. Chen, T.-C. Keng, J.-C. Wang, *Chem. Commun.* **1999**, 1185.
[147] M. C. T. Fyfe, P. T. Glink, S. Menzer, J. F. Stoddart, A. J. P. White, D. J. Williams, *Angew. Chem.* **1997**, *109*, 2158; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2068.
[148] M. Montalti, L. Prodi, *Chem. Commun.* **1998**, 1461.
[149] G. M. Hübner, J. Gläser, C. Seel, F. Vögtle, *Angew. Chem.* **1999**, *111*, 395; *Angew. Chem. Int. Ed.* **1999**, *38*, 383.
[150] C. Reuter, W. Wienard, G. M. Hübner, C. Seel, F. Vögtle, *Chem. Eur. J.* **1999**, *5*, 2692.
[151] R.-D. Schenbeck, E. Freisinger, B. Lippert, *Chem. Commun.* **1999**, 675.
[152] M. T. Reetz, C. M. Niemeyer, K. Harms, *Angew. Chem.* **1991**, *103*, 1515; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1472.
[153] M. T. Reetz, C. M. Niemeyer, K. Harms, *Angew. Chem.* **1991**, *103*, 1517; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1474.
[154] P. D. Beer, Z. Chen, P. A. Gale, J. A. Heath, R. J. Knubley, M. I. Ogden, *J. Incl. Phenom.* **1994**, *19*, 343.
[155] P. D. Beer, J. B. Cooper, *Chem. Commun.* **1999**, 129.
[156] P. D. Beer, S. W. Dent, *Chem. Commun.* **1998**, 825.
[157] D. M. Rudkevich, Z. Brzozka, M. Palys, H. C. Viser, W. Verboom, D. N. Reinhoudt, *Angew. Chem.* **1994**, *106*, 480; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 467.
[158] J. Scheerder, J. P. M. van Duynhoven, J. F. J. Engbersen, D. N. Reinhoudt, *Angew. Chem.* **1996**, *108*, 1172; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1090.
[159] P. D. Beer, P. K. Hopkins, J. D. McKinney, *Chem. Commun.* **1999**, 1273.
[160] D. J. White, N. Laing, H. Miller, S. Parsons, S. Coles, P. A. Tasker, *Chem. Commun.* **1999**, 2077.
[161] A. Bianchi, E. García-España in *Supramolecular Chemistry of Anions* (Eds.: A. Bianchi, K. Bowman-James, E. Garcia-España), WILEY-VCH, New York, **1997**, p. 217.
[162] M. Berger, F. P. Schmidtchen, *Angew. Chem.* **1998**, *110*, 2840; *Angew. Chem. Int. Ed.* **1998**, *37*, 2694.
[163] P. D. Beer, M. Shade, *Chem. Commun.* **1997**, 2377.
[164] P. A. Gale, J. L. Sessler, V. Lynch, P. I. Sansom, *Tetrahedron Lett.* **1996**, *37*, 7881.
[165] B. Turner, M. Botoshansky, Y. Eichen, *Angew. Chem.* **1998**, *110*, 2633; *Angew. Chem. Int. Ed.* **1998**, *37*, 2475.
[166] G. Cafeo, F. H. Kohnke, G. L. L. Torre, A. J. P. White, D. J. Williams, *Angew. Chem.* **2000**, *112*, 1556; *Angew. Chem. Int. Ed.* **2000**, *39*, 1496.
[167] G. Cafeo, F. H. Kohnke, G. L. L. Torre, A. J. P. White, D. J. Williams, *Chem. Commun.* **2000**, 1207.
[168] J. L. Sessler, P. Anzenbacher, Jr, J. A. Shriver, K. Jursíková, V. M. Lynch, M. Marquez, *J. Am. Chem. Soc.* **2000**, *122*, 12061.
[169] D. Parker, *Coord. Chem. Rev.* **2000**, *205*, 109.
[170] J. I. Bruce, R. S. Dickens, L. J. Govenlock, T. Gunnlaugsson, S. Lopinski, M. P. Lowe, D. Parker, R. D. Peacock, J. J. B. Perry, S. Aime, M. Botta, *J. Am. Chem. Soc.* **2000**, *122*, 9674.