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Anion coordination and anion-directed assembly: highlights from 1997 and 1998

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Contents

Abstract

This review article highlights advances made in anion coordination chemistry in 1997 and 1998. The first section of the review examines anion receptors that do not contain metal ions. This is followed by a review of metal containing anion receptors in which the metal can function as (i) a coordination site for the anion; (ii) a non-coordinating reporter group that

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signals the presence of the anion by a perturbation of its physical properties; (iii) an element of a receptor designed to withdraw electron density from a π-electron system and so increase the affinity of a hydrophobic receptor for anions or (iv) part of a self-assembled array that is binding an anionic guest. The role of anions in directing the self-assembly of complex molecular architectures will also be examined.

Keywords: Anion binding; Supramolecular chemistry; Self-assembly; Sensors; Macrocycles

1. Introduction

Anion coordination has received little attention over the last 30 years when compared to that devoted to the coordination chemistry of cations. However, as the realisation of the important roles that anions play in biology [1,2], medicine [3], catalysis [4], and the environment [5–7] has grown, so interest in anion coordination has become more widespread. Several excellent review articles and a book on anion coordination have appeared, to which the reader is directed for a comprehensive view of this area of chemistry [8–12]. However, as interest has grown, so have the number of publications reported each year. There is therefore a need for an annual or biannual review of this topic, a need that this article is designed to meet for the years 1997 and 1998.

This review consists of three sections. The first discusses ligands that employ hydrogen bonding and/or electrostatic interactions to form anion complexes. The second reviews the use of metal containing ligands as anion binding agents. The final section examines the role anions can play in directing self-assembly processes.

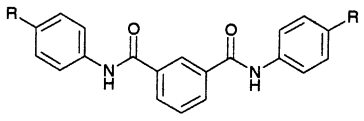
2. Metal free anion receptors

A number of research groups have synthesised receptors that utilise hydrogen bonds [13,14], electrostatic interactions [15] or both [16–18] to coordinate to anions. Nonetheless, there remains a critical need for additional anion binding agents that are selective in their substrate binding properties.

2.1. Amides

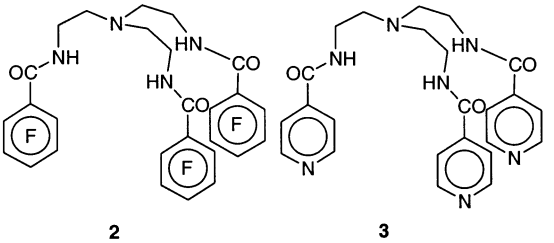
Amide NH groups have been employed to produce a wide range of receptors capable of coordinating anions [19,20]. A number of these systems contain metal anions and are therefore discussed later in this review. Crabtree and co-workers have recently shown that very simple amides such as the isophthalic acid derivatives, **1a** and **1b**, can bind anions [21]. Job plots show that in solution, receptor **1b** forms complexes with exclusively 1:1 host:anion stoichiometry. Stability constants were determined by ^{1}H-NMR and found to be 6.1×10^4 M^{-1} for chloride, 7.1×10^3 M^{-1} for bromide and 4.6×10^2 M^{-1} for iodide in dichloromethane-d_2. The crystal structure of the bromide complex of receptor **1** is shown in Fig. 1. The bromide anion is

coordinated to the amide NH group with H–Br = 2.39 and 2.68 Å. Additionally, there is a second bromide anion present in the crystal structure that is not coordinated to the receptor.



1a R = H
1b R = n-Bu

Tripodal tris-2-aminoethylamine (tren) based receptors containing amide bonds have been shown to be effective anion binding agents [19,22]. Stilbor has recently reported several tren-based receptors containing electron withdrawing fluorine substituents or electron poor pyridine rings that serve to activate the amide bond [23]. Tripodal receptors **2** and **3** were synthesised and their anion binding ability measured by ^{1}H-NMR titration techniques in a variety of different solvents. In all cases 1:1 receptor:anion complexes were observed. Receptor **2** was found to be selective for dihydrogen phosphate over other putative anionic guest species (Cl^-, Br^-, I^-, HSO_4^- and NO_3^-) in all the solvent systems studied. For example, in acetonitrile-d_3 solution a stability constant of 7550 ($\pm$ 310) M^{-1} was observed with $H_2PO_4^-$ compared to 1350 ($\pm$ 135) M^{-1} for Cl^-, the next most strongly bound anion. In contrast receptor **3** is selective for HSO_4^- over $H_2PO_4^-$. In chloroform-*d* solution receptor **3** binds HSO_4^- with a stability constant of 5120 ($\pm$ 740) M^{-1} whilst it binds $H_2PO_4^-$ anions with a stability constant of 154 ($\pm$ 16) M^{-1}.



2 **3**

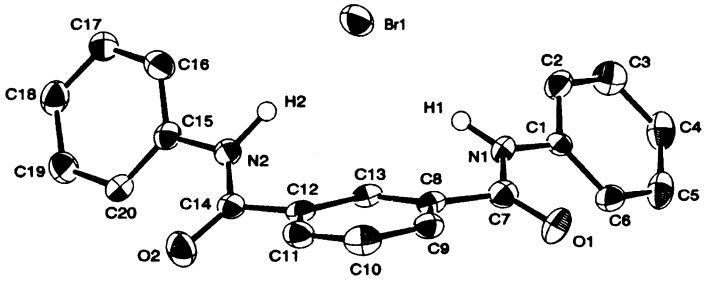
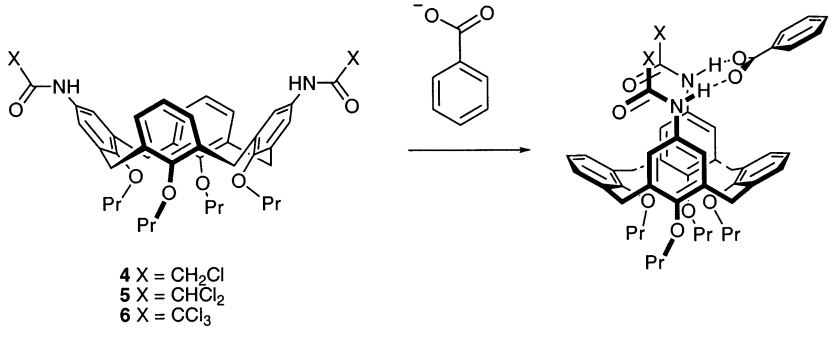


Fig. 1. The crystal structure of the bromide complex of compound **1a** (thermal ellipsoids are at the 50% probability level). (Reproduced with permission from J. Am. Chem. Soc. 119 (1997) 2325, Copyright 1997, The American Chemical Society.)

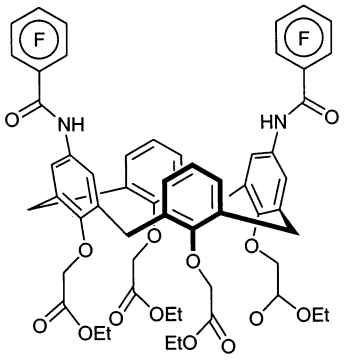
Calixarenes provide convenient scaffolds from which coordinating groups may be appended. Functionalised derivatives have been used as receptors for cations [24], anions [14] or neutral guests [25]. Cameron and Loeb have synthesised calix[4]arenes **4**, **5** and **6** containing amide groups with different numbers of electron withdrawing chloro-substituents at the 1 and 3 positions of the upper rim (Scheme 1) [26]. Receptor **5** proved to have the highest affinity for anionic guests. For example receptor **4** binds benzoate in chloroform-*d* with a stability constant of 107 M^{-1} whereas the receptor **5**-benzoate complex has a stability constant of 5160 M^{-1}. This increase in binding strength is attributed to the increased electron withdrawing effect of the $CHCl_2$ group in **5** compared to CH_2Cl in **4**. Compound **6** did not interact with anions. Model studies suggest that this is due to the steric bulk of the CCl_3 groups preventing the anion approaching the upper-rim anion-binding site. These receptors proved to be selective for Y shaped carboxylate over tetrahedral anions such as ReO_4^-. The strong binding of carboxylate anions is attributed to the calixarene adopting a 'pinched cone' conformation with the calixarene rings attached to the two amide groups becoming parallel, so allowing the amide groups to align in a complementary manner to the carboxylate guest (Scheme 1).



Scheme 1. The upper rim amide substituted calix[4]arenes **4**, **5** and **6** bind carboxylate anions selectively by the formation of a pinched cone conformation.

Stilbor has also employed calix[4]arenes as scaffolds from which to append activated amide groups [23]. Receptors **7** and **8** contain two amide groups at their upper rim. The affinity of these receptors for dicarboxylic acids was measured by ^{1}H-NMR techniques. The distance between the amide groups at the upper rim allows the receptors to discriminate between dicarboxylic acids on the basis of chain length. Adipate was bound selectively by **7** and **8** over other aliphatic diacids (agreeing with work published by Beer and co-workers on a similar system) [18] and terephthalate over other aromatic dicarboxylates.

In 1996 Davis and co-workers reported that a cholic acid based cryptand could coordinate halide anions via a three-dimensional array of hydrogen bonds [27]. More recently, this group have turned their attention to acyclic cholic acid hosts containing hydrogen bond donating carbamate or amide groups [28]. The cholic acid acts as a scaffold arranging the hydrogen bond donating groups in a suitable



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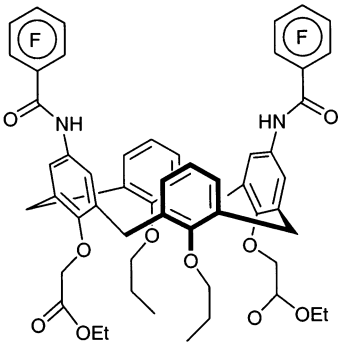

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orientation in space to bind an anion. The anion coordination ability of receptors **9** and **10** was studied by ^{1}H-NMR titration techniques and the results are shown in Table 1. Both receptors proved to be selective for smaller halide anions.

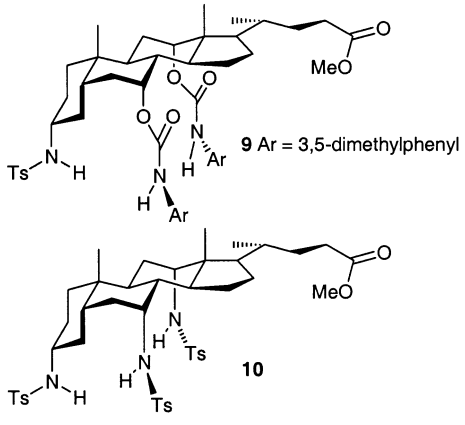
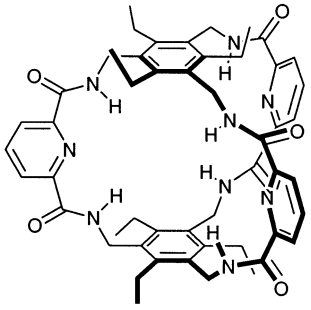


Table 1
Stability constants (M^{-1}) of **9** and **10** with tetrabutylammonium salts in $CDCl_3$[a]

Anion	Stability constant K (M^{-1})	
	Receptor **9**	Receptor **10**
F^-	15 400 ($\pm$ 1500)	[b]
Cl^-	7200 ($\pm$ 660)	92 000 ($\pm$ 28000)[c]
Br^-	7200 ($\pm$ 760)	9200 ($\pm$ 700)
I^-	930 ($\pm$ 70)	525 ($\pm$ 45)
TsO^-	865 ($\pm$ 120)	950 ($\pm$ 80)

[a] Bu_4N^+ salts were added to receptors in $CDCl_3$ that had been dried and de-acidified. Figures in parentheses represent standard deviations of the binding constant values calculated from each point on the curve. Dilution studies indicate that self-association of **9** and **10** was negligible at the concentrations used.
[b] Not determined.
[c] Value approaching the limiting stability constant accessible by NMR.



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Anslyn and co-workers have recently reported the synthesis of a trigonal box by condensation of 1,3,5-triaminomethyl-2,4,6-triethylbenzene with three equivalents of 2,6-pyridine dicarbonyl dichloride in dichloromethane in the presence of triethylamine. The rigid cyclophane **11** was formed in a 40% yield [29].

Table 2
Stability constants (M^{-1}) of anion complexes of compound **11** determined by ^{1}H-NMR titration techniques in acetonitrile-d_3-dichloromethane-d_2 3:1 (v/v) at 298 K together with pK_a values for the acids H^+[anion]$^-$

Anion	K (M^{-1})	pK_a of H^+[anion]$^-$
AcO^-	770 ± 120	4.6
NO_3^-	300 ± 30	−1.4
CN^-	115 ± 10	9.2
Cl^-	40 ± 8	−7
$H_2PO_4^-$	25 ± 5	2
Br^-	15 ± 8	−9
HSO_4^-	<5	−9

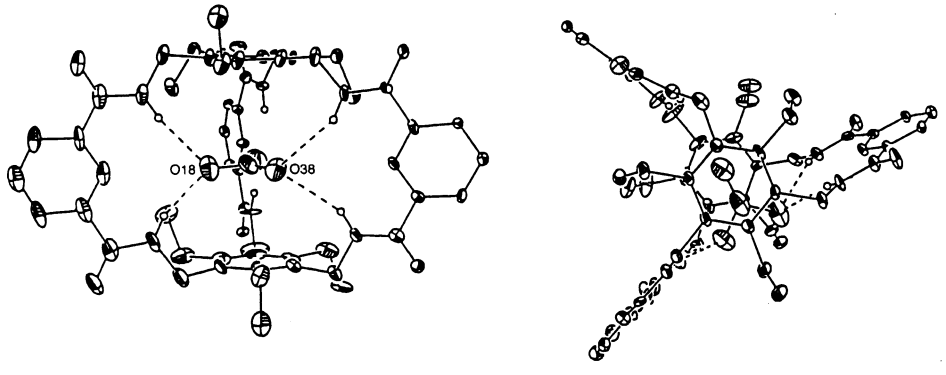
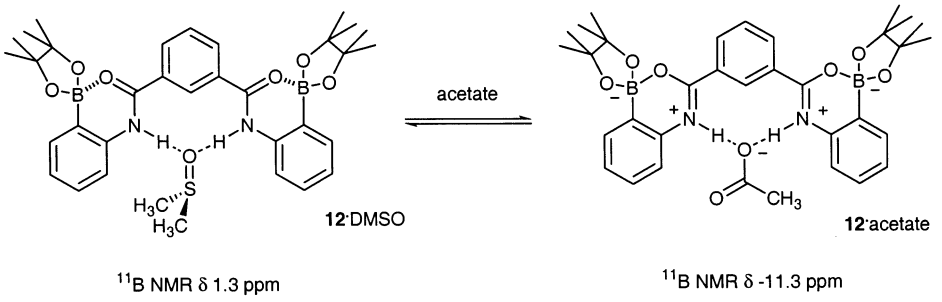


Fig. 2. The crystal structure of the acetate complex of **11**·2Bu$_4$NOAc (thermal ellipsoids are at the 20% probability level). (Reproduced with permission from Angew. Chem. Int. Ed. Engl. 36 (1997) 2340, Copyright 1997, Wiley-VCH.)

Interestingly, because the amide NH groups in compound **11** are arranged in a trigonal prismatic array, they coordinate to the π-electron system of planar anions such as carboxylates and nitrate. Stability constants for receptor **11** were determined by ^{1}H-NMR titration and are shown in Table 2.

The crystal structure of the acetate complex of **11** was elucidated and is shown in Fig. 2. The structure reveals that acetate is bound within the cavity of the box. The authors conclude that nitrate must also be bound within the cavity of the box because, like acetate, it is planar and bound very strongly (only 2.6 times less strongly than acetate even though it is 10^6 times less basic). Thus, receptor **11** represents a significant advance in the coordination of the environmentally sensitive and normally weakly coordinating nitrate anion.

Hughes and Smith have recently synthesised amide and urea based anion receptors containing Lewis acidic boron atoms. These receptors show enhanced anion coordination properties through a co-operative polarisation mechanism [30]. An amide based receptor **12** is shown in Scheme 2. Intramolecular coordination of the amide carbonyl oxygen to the boronate group enhances the anion binding affinity of this receptor by increasing the acidity of the NH proton. The acetate binding constant of **12** was determined by ^{1}H-NMR titration and found to be $2.1 \pm 0.2 \times 10^3$ M^{-1} in DMSO at 295 K.



Scheme 2. Enhanced anion coordination occurs within receptor **12** via intramolecular coordination of the amide carbonyl oxygen to the boronate group.

Kim and co-workers have investigated the interactions of cyclic tetra- **13** and hexa-peptides **14**, composed of glycine residues, with cations and anions using ab initio calculations [31]. The cyclic peptides were found to be amphi-ionophores binding either anions or cations. In the presence of a cation (Li^+, Na^+, Be^{2+}, Mg^{2+}) the peptide carbonyl groups orient towards the centre of the cycle forming a cation-binding site (Fig. 3). However, in the presence of anions (F^- and Cl^-) the peptide N–H groups were found to orient inwards so defining an anion-binding domain (Fig. 3).

2.2. Pyrroles

Over recent years, Jonathan Sessler's group at the University of Texas at Austin have pioneered the use of pyrrole containing macrocycles as anion binding agents

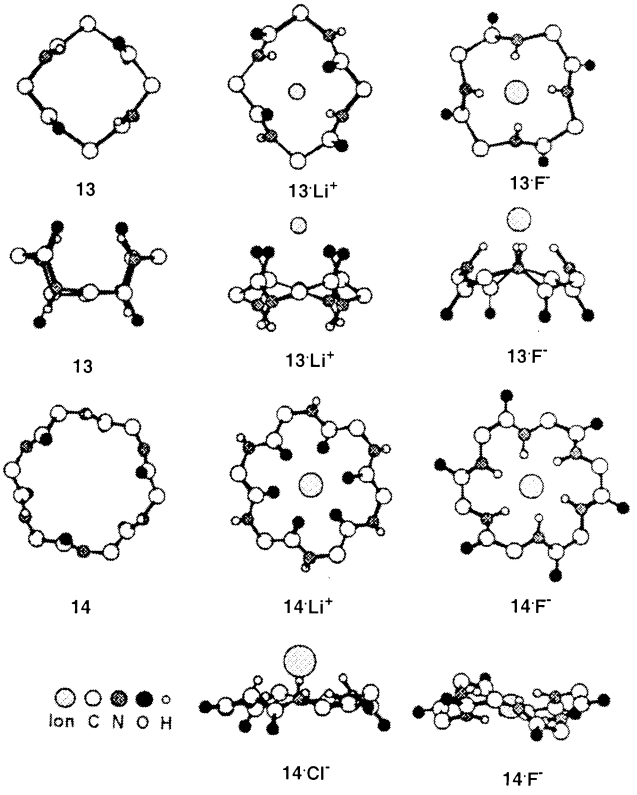
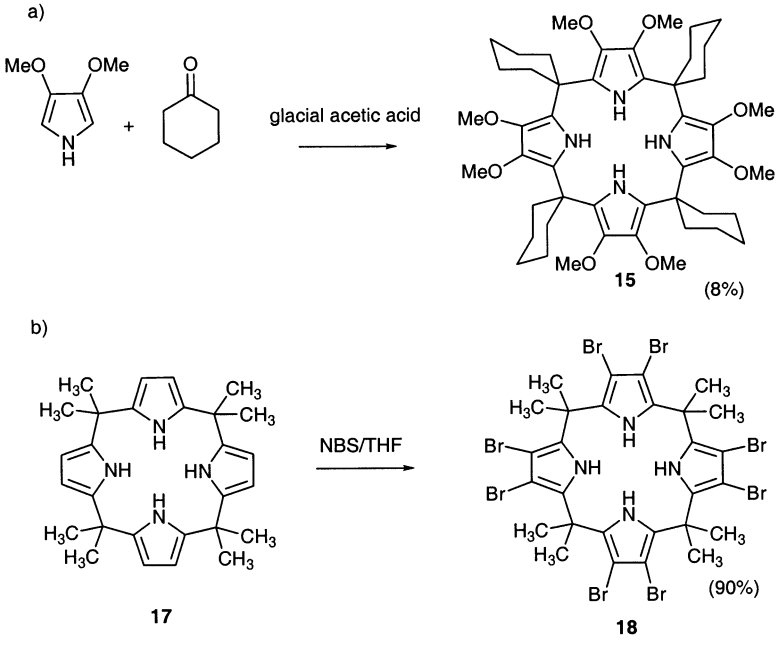
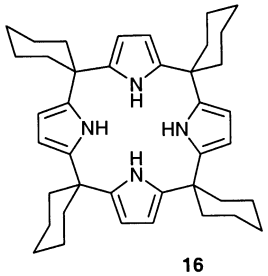


Fig. 3. Selected structures of cyclic tetra- (**13**) and hexa- (**14**) peptides and their ion complexes. (Reproduced with permission from J. Chem. Phys. B 102 (1998) 461, Copyright 1998, American Chemical Society.)

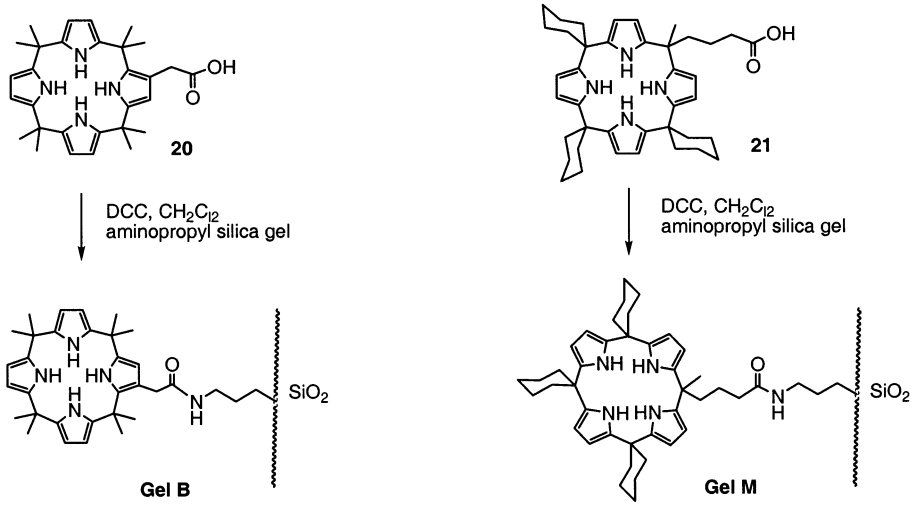
[17,32,33]. In 1996, Sessler and co-workers reported that calixpyrroles (*meso*-octaalkylporphyrinogens), macrocycles first synthesised by Baeyer over 100 years ago [34], can coordinate to certain anions via NH-anion hydrogen bonds [35]. Indeed the macrocycles proved to be selective for fluoride anions over other potential anionic guests. Recently, synthetic routes have been discovered that allow synthetic modification of the periphery or *C*-rim of the calixpyrrole [36]. Receptor **15** was synthesised by condensation of 3,4-dimethoxypyrrole with cyclohexanone (Scheme 3(a)). The electron donating OMe groups at the *C*-rim of the calix[4]pyrrole reduce the acidity of the pyrrole NH protons so reducing the affinity of receptor **15** for anions (compared to the 'β-free' analogue **16**). Receptor **18** was synthesised by reaction of *meso*-octamethylcalix[4]pyrrole **17** with *N*-bromosuccinimide in THF (Scheme 3(b)). The electron withdrawing bromo- groups serve to increase the acidity of the pyrrole NH protons and therefore increase the anion binding affinity of compound **18** with respect to the parent calixpyrrole **17**.



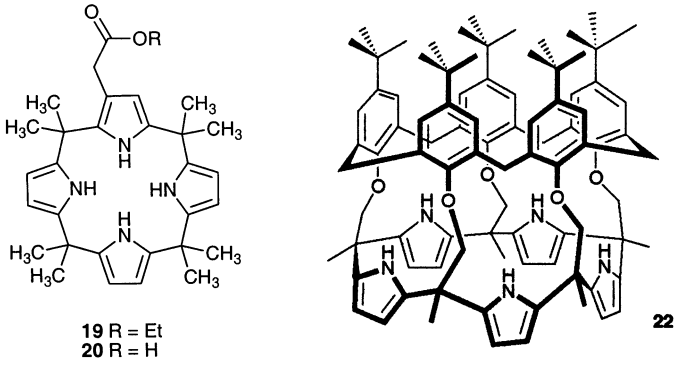
Scheme 3. The synthesis of β-subsitituted calix[4]pyrroles **15** and **18** via (a) synthesis using a 3,4-dimethoxysubstituted pyrrole and (b) bromination of the *C*-rim of the calixpyrrole using NBS in THF.



The same research group have produced modified solid supports containing calix[4]pyrroles that are capable of separating mixtures of anions [37]. Ester groups could be introduced onto the *C*-rim of compound **17** by deprotonation with *n*-BuLi and subsequent reaction with ethylbromoacetate affording compound **19** in a 26% yield. Subsequent saponification yielded the β-monoacid **20**. Compound **20** and a *meso*-mono-acid calix[4]pyrrole **21** [38] were attached to aminopropyl silica gel using an amide coupling reagent (Scheme 4) to produce two new column materials: gel **B** (from the β-mono-acid) and gel **M** (from the *meso*-mono acid) for use in HPLC. Both columns were successful in separating mixtures of AMP, ADP and ATP (Fig. 4), oligonucleotides, phenyl anions and Cbz-protected amino acids [37].

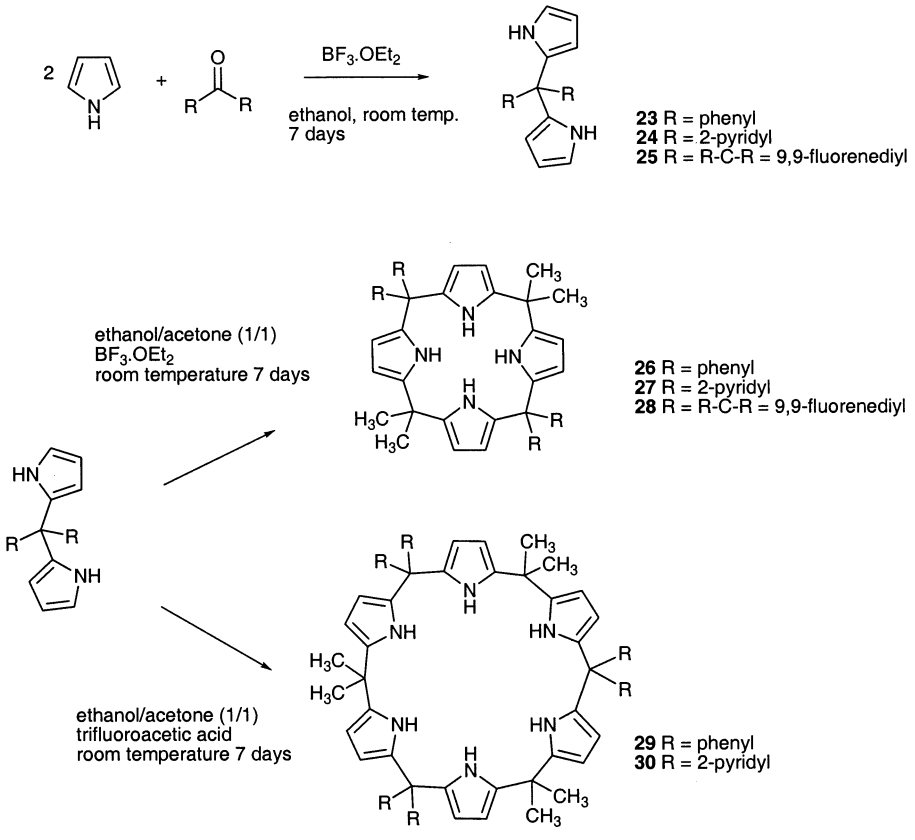


Scheme 4. Synthesis of calixpyrrole modified silica gels.



The first examples of expanded calix[*n*]pyrroles ($n > 4$) have been reported in the last 2 years. The first, a calix[5]arene-calix[5]pyrrole pseudo-dimer **22**, was produced in 1997. This material was synthesised by condensation of *p-tert*-butylcalix[5]arene penta-methyl ketone with pyrrole catalysed by $BF_3{\cdot}OEt_2$. The anion coordination properties of this material have not been reported in great detail, although this cylindrical receptor has been shown to interact with chloride anions [39].

Very recently, the synthesis of a calix[6]pyrrole was achieved [40]. Eichen and co-workers condensed pyrrole with sterically bulky diketones including benzophenone, di-(2-pyridyl)ketone and 9-fluorenone to produce di-(2-pyrrolyl)methanes (**23**, **24** and **25** Scheme 5). These products failed to react further with the corresponding ketone to produce calix[4]pyrrole but could be condensed with acetone in the presence of $BF_3{\cdot}OEt_2$to produce calix[4]pyrroles with different substituents in the *meso*- positions (**26**, **27** and **28**). However, in the presence of trifluoroacetic acid the



Scheme 5. The synthesis of calix[6]pyrroles.

reaction proceeds along a different course and the calix[6]pyrroles **29** and **30** can be isolated in 25 and 2%, respective yields. The anion coordination abilities of **29** and **30** have yet to be reported, but it is likely that these species may show contrasting selectivities to their tetrameric analogues, in particular displaying selectivity for larger anionic species.

Early work by Sessler explored the anion binding ability of expanded porphyrins such as sapphyrin (a pentapyrrolic expanded porphyrin first synthesised by Woodward and co-workers [41]) [17]. A sapphyrin modified silica gel has recently been produced (Fig. 5) that is capable of separating mixtures of anions [42]. It was found that this material gave a qualitative anion binding order of arsenate > phosphate > chloride > sulfate > nitrate = bromide > iodide > acetate. However, these supports could not separate mixtures of functionally analogous but structurally different anions (e.g. aromatic carboxylates).

Latos-Grazynski and co-workers have recently published a detailed study of the effects of protonation and anion binding on the conformation of 5,10,15,20-te-

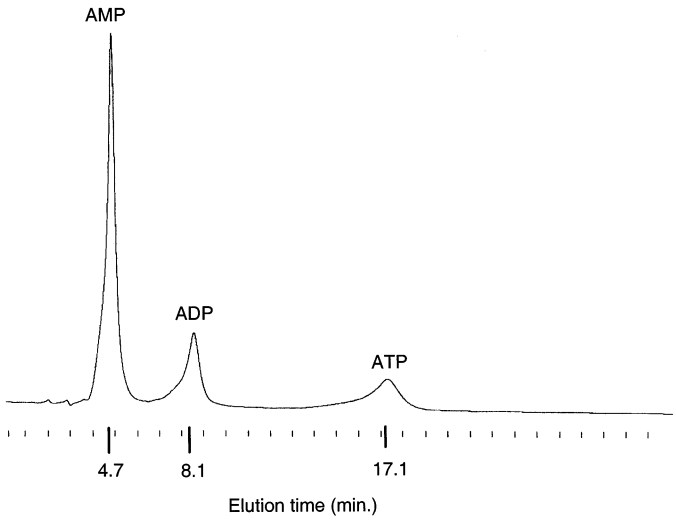
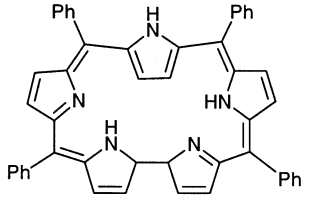


Fig. 4. HPLC separation of AMP, ADP and ATP on calixpyrrole modified silica gel **M**. Flow rate 0.3 ml min^{-1}, mobile phase 200 mM sodium phosphate (isochratic), pH 7.0, column temperature 25°C, UV detection at 262 nm. (Reproduced with permission from Chem. Eur. J. 4 (1998) 1095, Copyright 1998, Wiley-VCH).

traphenylsapphyrin **31** that contains an inverted pyrrole ring in its unbound and unprotonated state [43].



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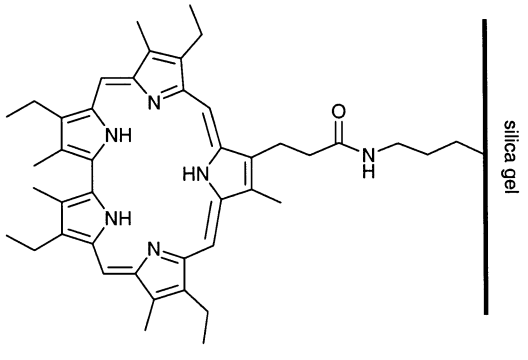


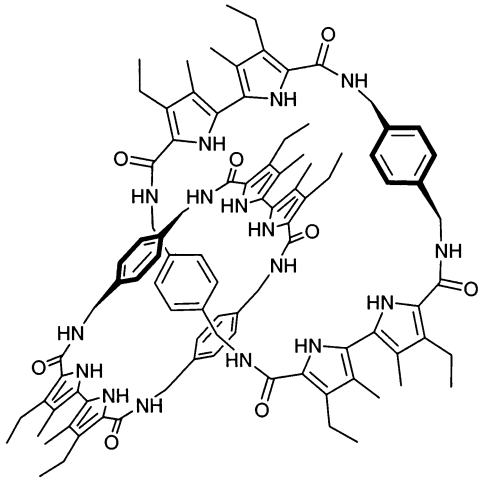
Fig. 5. Sapphyrin modified silica gel.

Table 3
Stability constants (M^{-1})[a] from ^{1}H-NMR titration experiments for compound **32** and anions in 1,1,2,2-tetrachloroethane-d_2

Anion[a]	K_a (M^{-1}) of **32**
F^-	1.48×10^5
Cl^-	3.55×10^6
Br^-	[b]
$H_2PO_4^-$	$>1 \times 10^7$
AcO^-	9.63×10^5

[a] Tetrabutylammonium salts.
[b] Very small perturbations in the ^{1}H resonances precluded an accurate analysis of the stability complex of this complex.

Very recently, Sessler and Vögtle have reported the synthesis of a bipyrrole-based [2]catenane that forms extremely stable complexes with anions [44]. Compound **32** was synthesised in both a single step (2% yield) and by a stepwise synthetic procedure (4% yield). Anion coordination studies were conducted using ^{1}H-NMR titration techniques in 1,1,2,2-tetrachloroethane-d_2 (Table 3). The catenane was found to bind anions with very high stability constants (up to 10^7 M^{-1} with $H_2PO_4^-$). This is attributed to the formation of a tetrahedral cavity between the rings that provides an ideal coordination geometry for anion coordination (Fig. 6).



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2.3. Ureas

Urea and thiourea are particularly good hydrogen bond donors and are excellent receptors for anions such as carboxylate via the formation of two hydrogen bonds (Fig. 7) [13,45,46].

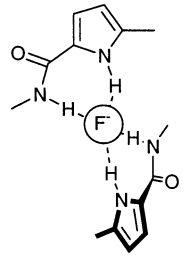


Fig. 6. A tetrahedral arrangement of hydrogen bonds in the catenane **32** leads to remarkably stable anion complexes.

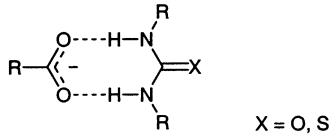
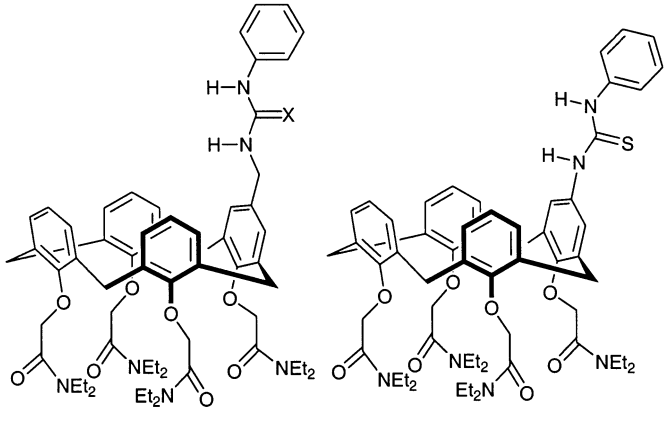


Fig. 7. The ideal two-point interaction between (thio)urea and carboxylate anions.

Ungaro and co-workers have synthesised a series of calix[4]arene based ditopic receptors containing an anion binding urea or thiourea group at the upper rim in addition to cation binding amide groups at the lower rim (**33a,b** and **34**) [47]. Quantitative binding studies in DMSO-d_6 with compound **34** showed that sodium complexation at the lower rim increases the efficiency but decreases the selectivity of anion binding at the top of the calixarene. Compound **33a** has a methylene group between the thiourea and calixarene and, in contradistinction to **34**, the addition of sodium ions had little effect on the anion coordination ability of the receptor (Table 4).



33a X = S
33b X = O

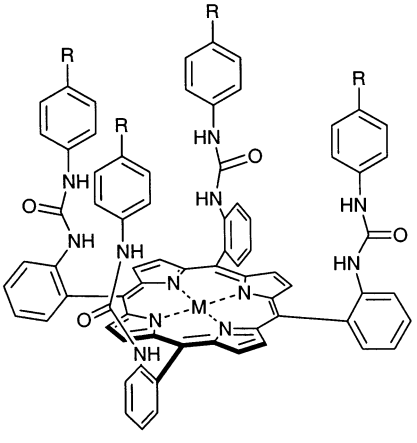
34

Table 4
Stability constants (M^{-1})[a] from ^{1}H-NMR titration experiments for compounds **33a**, and **34** and anions in DMSO-d_6 at 300 K

Anion[b]	pK_a[c]	Host			
		33a	**33a**–Na^+	**34**	**34**–Na^+
Br^-	–	<5	[d]	<5	[d]
Cl^-	–	160	[d]	10	[d]
Benzoate	10.90	175	190	250	1100
Formate	10.26	[d]	[d]	230	[e]
Acetate	12.60	470	330	940	1200
Propionate	[f]	280	215	250	1000
n-Butyrate	12.8	220	100	[d]	[d]
Isobutyrate	[f]	400	200	260	800

[a] Averaged over at least three experiments.
[b] As tetrabutylammonium salt.
[c] Of corresponding carboxylic acids in DMSO.
[d] Not determined.
[e] A substantial broadening of the NH resonances was observed.
[f] Data not available.

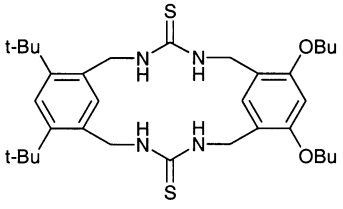
Amide substituted (*cis*)-5,10,15,20-tetrakis[2-(amido)phenyl]porphyrins have been shown to be effective and selective anion receptors [48]. Jagessar and Burns extended this work to a series of (*cis*)-5,10,15,20-tetrakis[2-(arylurea)phenyl]-porphyrins containing different substituents (**35**–**37**) [49,50]. The metallated derivatives of these materials (**38**–**40**) have also been prepared. Compounds **35**, **36** and **37** proved to be selective for chloride over nitrate and dihydrogen phosphate anions in DMSO-d_6 solution, forming complexes with a 1:1 stoichiometry.



35 M = 2H R = H
36 M = 2H R = Cl
37 M = 2H R = F

38 M = Zn R = H
39 M = Zn R = Cl
40 M = Zn R = F

A series of metacyclophane-based cyclic thiourea anion receptors have been synthesised by Tobe and co-workers. Receptors **41**, **42** and **43** were designed to be rigid hosts whereas receptor **44** contains a more flexible linking group. The acyclic analogue **45** previously studied by Umezawa and co-workers [46] was used as a reference. ^{1}H-NMR titration studies showed that receptors **41**, **42**, **44** and **45** selectively bind $H_2PO_4^-$ over other anionic guest species (see Table 5). As expected, the cyclic receptors (excepting compound **43**) showed higher stability constants with anions than compound **45**. However, receptor **43** did not show any affinity for anions. An X-ray crystal structure of this material showed that the thiourea groups adopt a *cis–trans* conformation that is not suitable for anion coordination.



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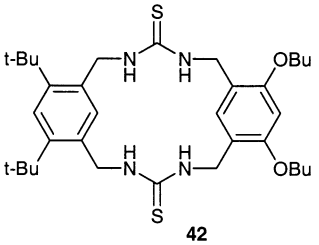

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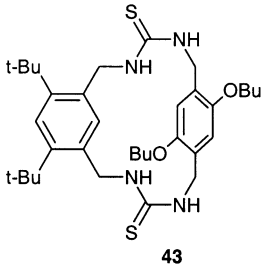

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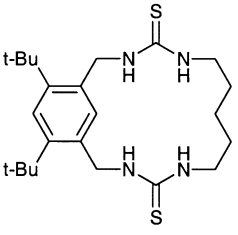

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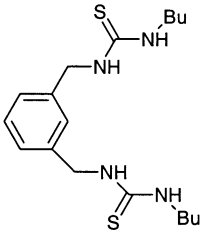


45

Umezawa and co-workers have continued their studies of ayclic thiourea cleft molecules [51]. The synthesis of some highly preorganised systems containing a xanthene spacer has been described. Receptors **48** and **49** bind anions very strongly

Table 5
Stability constants (M^{-1})[a] from ^{1}H-NMR titration experiments in DMSO-d_6 at 333 K

Anion[a]	Host			
	41	**42**	**44**	**45**
$H_2PO_4^-$	12 000	2500	4800	520
CH_3COO^-	2200	390	560	110
Cl^-	120	14	54	7
HSO_4^-	19	2	4	1
Br^-	12	<1	3	<1

[a] Added as tetrabutylammonium salts.

indeed with stability constants up to 195 000 M^{-1} for receptor **49** and $H_2PO_4^-$ anions in DMSO-d_6 (see Table 6). This is primarily due to the high degree of preorganisation present in these receptors. The selectivity for $H_2PO_4^-$ can be attributed to the complementary hydrogen-bonding array present in these clefts that can form four hydrogen bonds to each $H_2PO_4^-$ anion (Fig. 8). The more flexible receptors **45**, **46** and **47** show the same selectivity trend as **48** and **49** but with considerably smaller stability constants due to their lower degree of preorganisation. Replacement of the butyl groups in compounds **45** and **48** with phenyl groups (compounds **46** and **49**) increases the affinity of these receptors for anions. This is attributed to the electron withdrawing effect of the aromatic rings increasing the acidity of the urea NH protons. Compound **47** contains naphthyl groups attached to the urea moieties. These bulky rings make it impossible for the receptor to bind $H_2PO_4^-$ and maintain co-planarity. This decreases the conjugation between the urea and the naphthyl rings so lowering the anion binding affinity of the receptor.

The same research group have incorporated receptor **48** into a PVC membrane on the surface of an electrode forming a chloride selective polymeric membrane electrode [52].

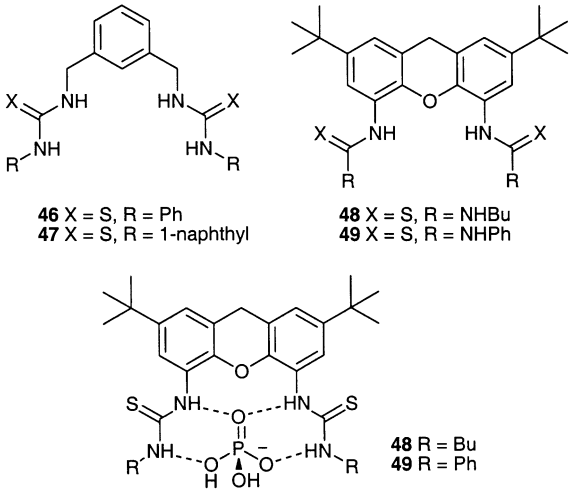


Fig. 8. Receptors **48** and **49** can coordinate dihydrogen phosphate anions via four hydrogen bonds.

Table 6
Stability constants (M^{-1})[a] from ^{1}H-NMR titration experiments in DMSO-d_6

Anion[a]	Host				
	45	**46**	**47**	**48**	**49**
$H_2PO_4^-$	820	4600	1000	55 000	195 000
CH_3COO^-	470	2300	350	38 000	[b]
Cl^-	9	10	5	840	1000

[a] Added as tetrabutylammonium salts.
[b] Not determined.

Hamilton and co-workers have used interactions between carboxylate anions and urea groups to control solid-state packing of phenylurea derivatives [53]. The angle between the carboxylate and urea groups in **50** and **51** (Fig. 9) was shown to control the type of solid-state packing observed in the crystalline state. Compound **51** (with a 60° angle between groups) crystallised in a more compact ribbon-like motif than compound **50** (with a 120° angle).

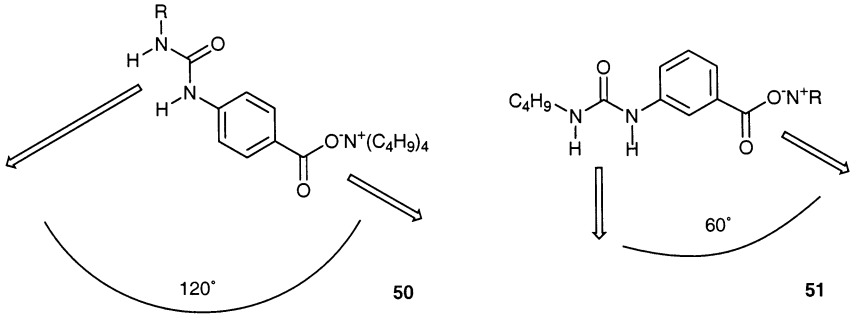
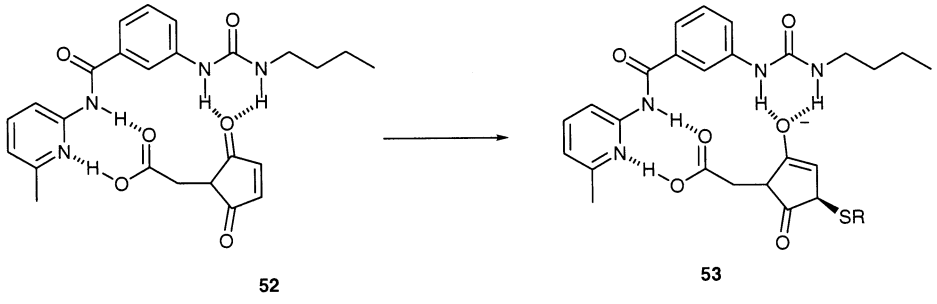


Fig. 9. The binding sites in compounds **50** and **51** are disposed at 120 and 60°, respectively.

Hamilton has used an anion-binding strategy to stabilise an oxyanion transition state and so accelerate the 1,4-addition reaction of a thiol to a maleimide (Scheme 6) [54]. The build up of negative charge on the carbonyl oxygen in the enol transition state of this reaction is stabilised by hydrogen bonding from a urea group. The hydrogen bonds to the enol oxygen in complex **53** are stronger than those to the starting material's carbonyl oxygen (in complex **52**). Therefore, the transition state is stabilised relative to the starting material and catalysis occurs.

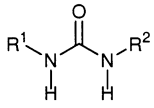


Scheme 6. Acceleration of a 1,4-addition reaction by stabilization of an enol intermediate.

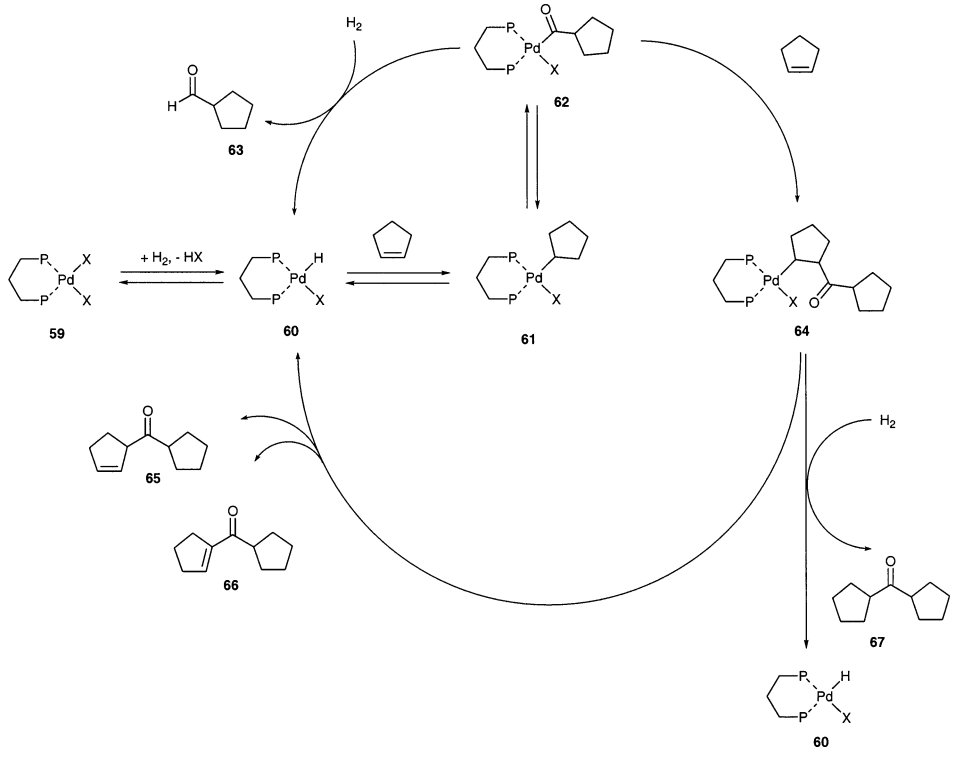
Reinhoudt has recently demonstrated that addition of anion binding urea-based receptors to palladium(II) catalysed hydrocarbonylation reactions of cyclopentene can significantly increase hydroacylation relative to hydroformylation [4]. The *N,N'*-disubstituted urea derivatives **54**–**58** significantly influence the performance of (dppp)PdX_2 catalyst (dppp = 1,3-bis(phenylphosphino)propane) in hydrocarbonyla-

tion reactions by coordinating to the counterions (X = OTs, TFA, OAc) leading to a decrease in their metal-binding strength.

More weakly coordinating anions X enhance the electrophilicity of the Pd(II) metal ion and are more easily displaced from the complex facilitating the formation of **62** (increased turnover) and **64** (increased selectivity for ketones) (Scheme 7). The largest effect was observed on addition of compound **56**.



54 $R^1 = R^2 = Ph$
55 $R^1 = p\text{-}F_3CC_6H_4$, $R^2 = Ph$
56 $R^1 = R^2 = p\text{-}F_3CC_6H_4$
57 R^1 = n-Bu, $R^2 = Ph$
58 $R^1 = R^2$ = n-Bu



Scheme 7. Catalytic cycle for the Pd(II) catalyzed hydrocarbonylation of cyclopentene.

2.4. Ammonium macrocycles

Some of the earliest examples of synthetic anion receptors were protonated or alkylated polyammonium macropolycycles. This area of research continues to bear fruit [55–57] some 30 years after Simmons and Park reported the first evidence of anion binding by such a receptor [58]. This is the topic of another article [59] to which the interested reader is directed for the latest developments in this field.

2.5. Guanidinium and amidinium

The positively charged guanidinium moiety can, like ureas or thioureas, form two hydrogen bonds to anions such as carboxylate and phosphate. The combination of hydrogen bonding and electrostatic interactions leads to the formation of strong complexes (Fig. 10(a)), even in very competitive hydrogen bond accepting and donating solvents such as water. In fact, nature uses guanidinium moieties to coordinate to anionic groups. The HIV-1 Tat protein employs a guanidinium group to coordinate to two phosphate groups that are close together in space (via a bridging motif known as an 'arginine fork') [60] so recognising bulges and loops in RNA (Fig. 10(b)).

Anslyn and co-workers have published several papers on the recognition of tri-carboxylate and tri-phosphate polyanions by tris-guanidinium receptor species. Receptor **68** was synthesised by a multi-step synthetic procedure (Scheme 8) [61]. This molecule contains three guanidinium groups and is therefore complementary to guests containing three carboxylate groups. The stability constants of a number of carboxylate containing guests are shown in Table 7. This data reveals that guests containing three anionic moieties, such as citrate, are bound more strongly than those with fewer anionic groups (e.g. acetate). The crystal structure of the tricarballate complex of **68** is shown in Fig. 11.

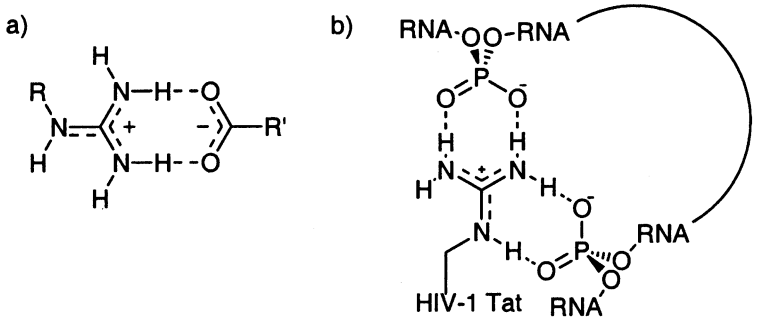
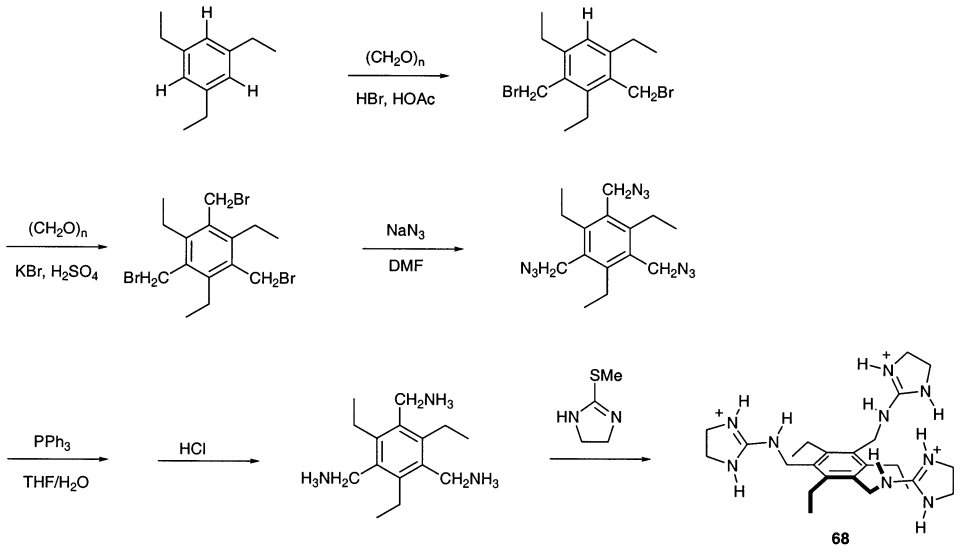


Fig. 10. (a) The guanidinium-carboxylate salt bridge and (b) the 'arginine-fork' binding motif.



Scheme 8. The synthesis of the citrate receptor **68**.

This receptor has been used by Metzger and Anslyn to produce a chemosensor for citrate in beverages [62]. 5-Carboxyfluorescein (**69**) is a commercially available fluorescent probe containing two carboxylate groups. Its fluorescence is particularly sensitive to changes in pH. The two carboxylate groups present in **69** coordinate to **68** forming a complex. The pK_a of the phenol moiety of **69** is lowered in the complex due to the positively charged microenvironment. Citrate displaces the carboxyfluores

Table 7
Stability constants (M^{-1})[a] from ^{1}H-NMR titration experiments for receptor **68** with various carboxylates in D_2O[c]

Host	Guest	Stability constant (M^{-1})
68[a]	Citrate	6.9×10^3
68[b]	Tricarballate	7.3×10^3
68[b]	Succinate	2.1×10^2
68[b]	Glutarate	2.2×10^2
68[b]	Acetate	<10
68[b]	ATP^{4-}	1.2×10^3
68[b]	3′-Up	2.1×10^2
68[b]	Cyclo-2,3-Up	2.4×10^3

[a] Guest signals (1.1 mM) were followed.
[b] Signals of receptor were followed (1.8–3.0 mM).
[c] Error $\pm 15\%$.

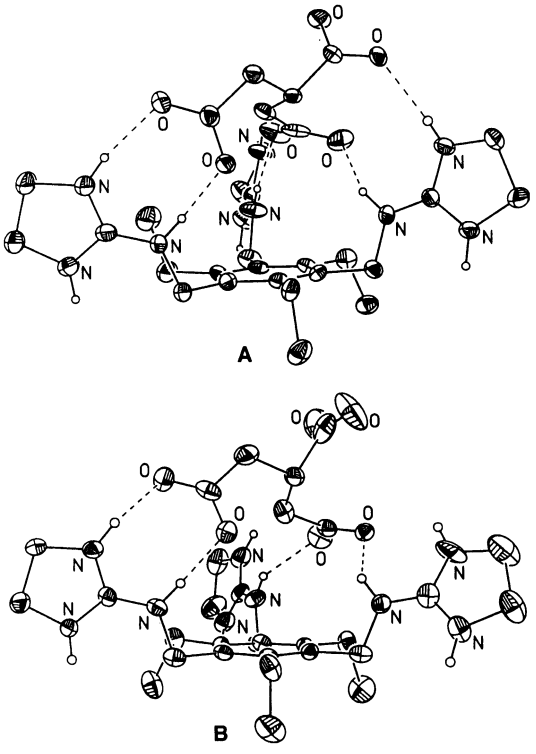
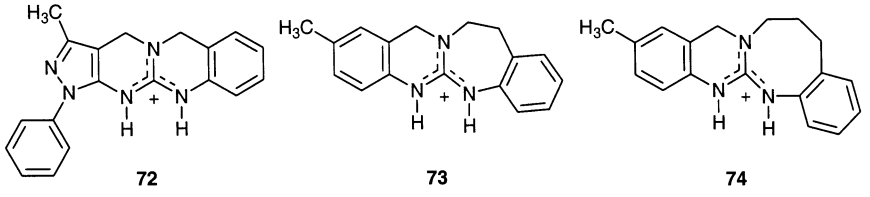


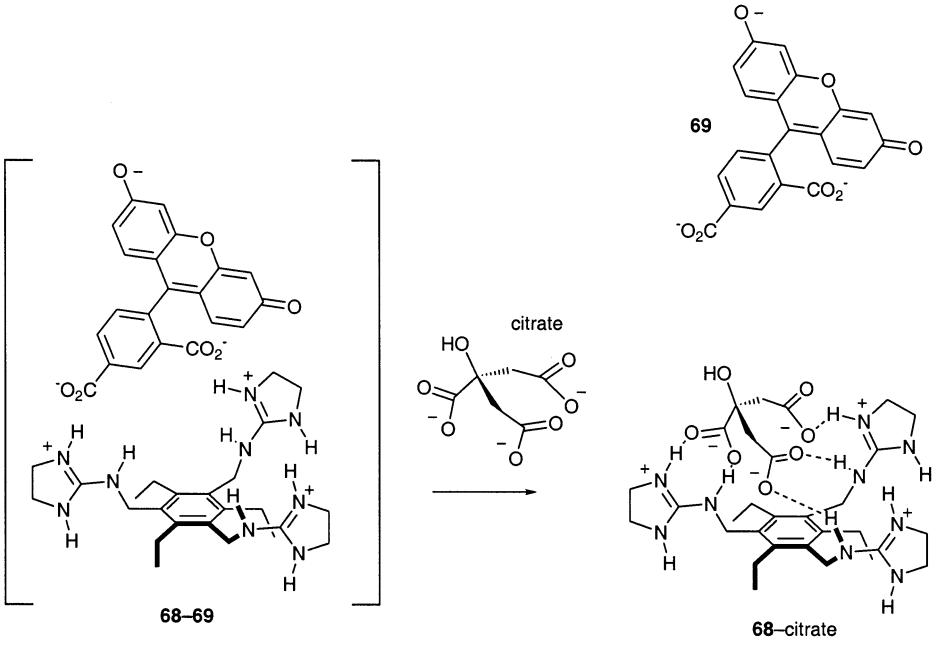
Fig. 11. The crystal structure of the tricarballate complex of **68**. One unit cell contains two different complexes A and B. (Reproduced with permission from Angew. Chem. Int. Ed. Engl. 36 (1997) 862, Copyright 1997, Wiley-VCH.)

cein from the complex so shifting the pK_a of the phenol anion such that **69** is in higher state of protonation when uncomplexed (Scheme 9). The fluorescence and absorbance of **69** decrease with increasing protonation. These changes could be calibrated against standard solutions of citrate to produce a quantitative sensor. This research group applied a similar strategy to produce chemosensor ensembles **70** and **71** for quantitative inositol-triphosphate detection (Scheme 10) [63].

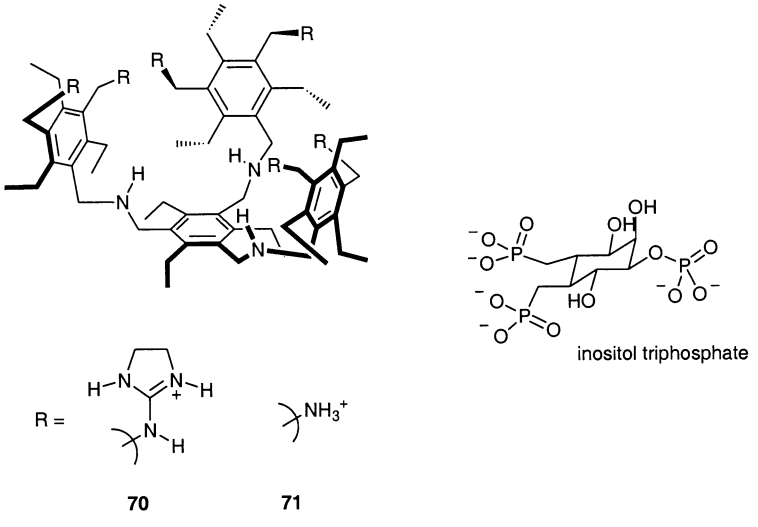
Bachas and co-workers have incorporated guanidinium containing receptors **72**–**74** into PVC membranes in order to produce ion-selective electrodes (ISEs). They found that ISEs fabricated from receptor **73** demonstrated a selective response to salicylate. ^{1}H-NMR titrations confirmed that this receptor forms a strong 1:1 complex with salicylate in DMSO-d_6.



72 **73** **74**



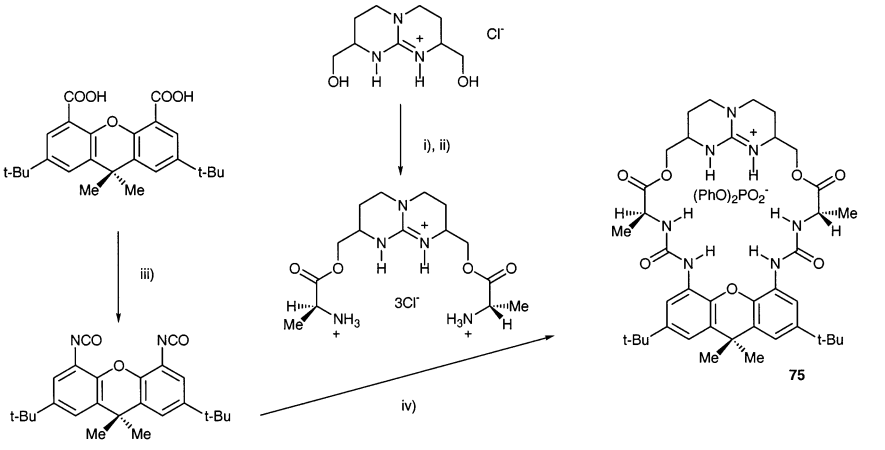
Scheme 9. The 5-carboxyfluorescein-**68** ensemble can be used to quantitatively sense citrate concentrations in beverages (see text).



Scheme 10. Inositol triphosphate and receptors **70** and **71**.

de Mendoza and co-workers have recently synthesised a pre-organised macrocycle **75** that contains a bicyclic guanidinium subunit and two urea groups [64]. The synthesis of this macrocycle, that possesses six hydrogen bond donor NH groups,

is shown in Scheme 11. NMR experiments were performed to determine the stability constants of **75** with a variety of anionic guests. Compound **75** was isolated as the diphenylphosphate salt and anion exchanged to the chloride salt. The stability constant of diphenylphosphate was determined relative to chloride and found to be 10^3 M^{-1}.



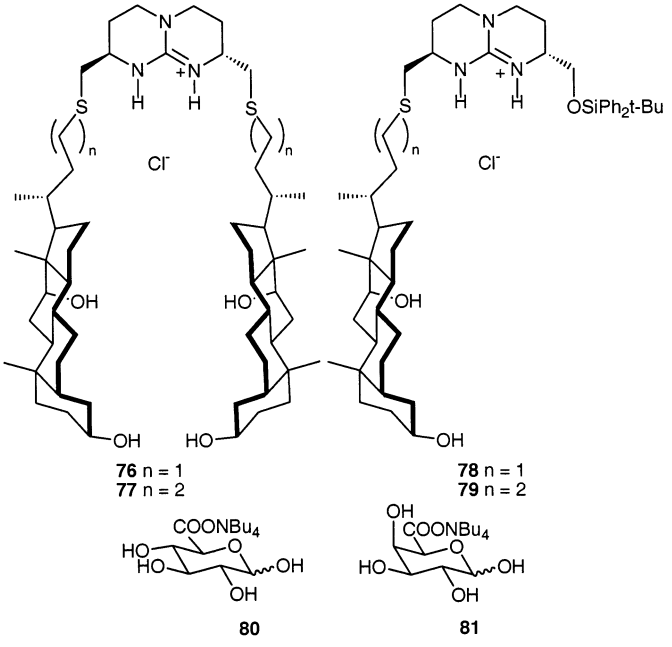
i) BOC-L-Ala, CDI, DMF, 25°C, 88%; ii) 3N HCl (EtOAc), 25°C, 100%; iii) DPPA, Et_3N, toluene, 70°C, then iv) CH_2Cl_2, Et_3N, 40°C, 40% overall yield

Scheme 11. Synthesis of the macrocyclic receptor **75**.

The same research group have synthesised several bicyclic guanidinium based receptors containing deoxychloic acid substituents that are designed for the complexation of uronic acid salts [65]. The receptors **76**–**79** coordinate to the carboxylate group present in the uronic acid salts **80** and **81** via the guanidinium group, so promoting contacts between the hydroxyl groups on the glycopyranosyl guest and the hydroxy groups of the deoxycholic acid moieties in the host. It was found that the receptors with shorter chains ($n = 1$) linking the guanidinium and deoxycholic acid derivatives had considerably higher stability constants with both salts than the more flexible $n = 2$ derivatives (Table 8).

Table 8
Stability constants (M^{-1}) from ^{1}H-NMR titration experiments for receptors **76–79** with various uronic acid salts $CD_3CN/CDCl_3$ (92:8) at 298 K

Host	Guest	Stability constant K (M^{-1})
76	**80**	7000
76	**81**	5800
77	**80**	2800
77	**81**	3200
78	**80**	5900
78	**81**	5500
79	**80**	3300
79	**81**	3500



Weber and co-workers have studied the electrochemical molecular recognition of dicarboxylate anions by xylenyl bis-iminoimidazolinium receptors [66]. The receptor **82** proved to be moderately selective for glutarate over other longer chain di-carboxylate anions (Fig. 12).

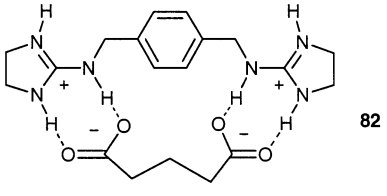


Fig. 12. Compound **82** can electrochemically recognise dicarboxylate anions.

Amidinium groups have been attached to the lower rim of calix[4]arenes in order to produce templates which coordinate carboxylate anions. Gale has reported the synthesis of two calix[4]arenes **83** and **84** and shown by UV–vis spectroscopy that anions such as carboxybenzo-[15]crown-5 assemble at the lower rim producing non-covalently linked arrays containing two binding sites (cation binding crown ethers or anion binding calixpyrroles) in close proximity (Fig. 13) [67].

2.6. Pyridinium

Pyridinium groups are positively charged and contain CH hydrogen atoms that may form hydrogen bonds to anions. Jeong and Cho have used C–H···O hydrogen

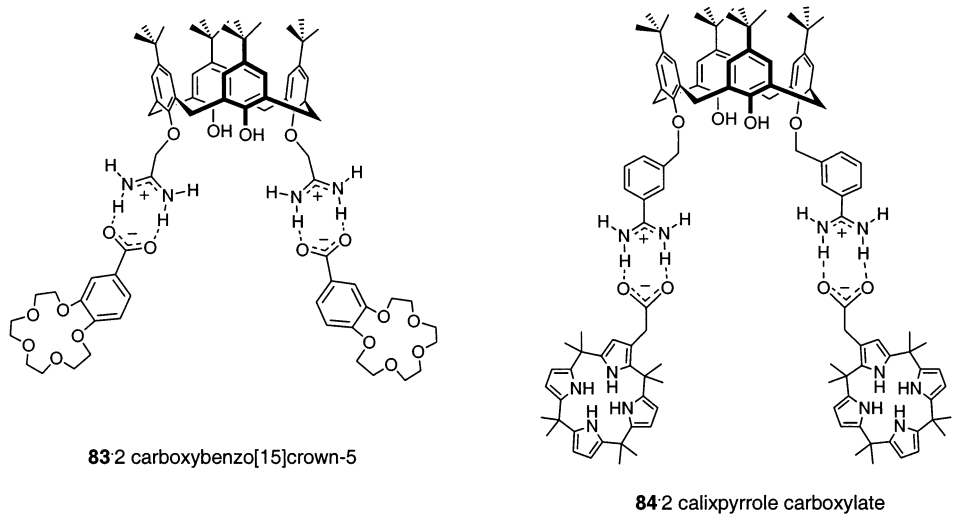
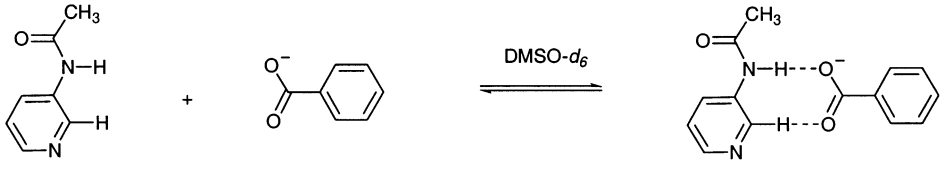


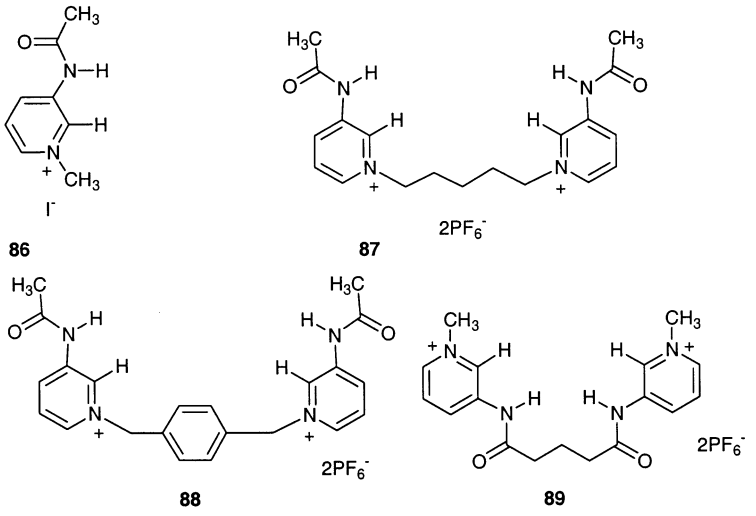
Fig. 13. The bis-amidinium calixarenes **83** and **84** form salt bridges with added carboxylate anions forming self-assembled molecular ensembles.

bonds from pyridinium units in conjunction with amide NH groups to coordinate to carboxylate anions [68]. Initially, the complexation behaviour of 3-(acetylamino)pyridine (**85**) and tetrabutylammonium benzoate (Scheme 12) was studied using ^{1}H-NMR titration techniques in DMSO-d_6. It was found that **85** forms a complex with benzoate with a relatively modest stability constant of 16 ± 1 M^{-1} at 298 K. The hydrogen bond donating ability of the receptor was increased by quaternisation of the pyridine nitrogen atom by reaction with methyl iodide (forming the pyridinium iodide salt **86**). The stability constant with benzoate was re-measured and now found to be 300 M^{-1}. Several bis-pyridinium receptors were synthesised (**87**–**89**) and their complexation behaviour with a dicarboxylate anion (adipate) studied in 10% D_2O/DMSO-d_6. In the case of **89** and adipate the complex was found to have a stability constant of 3090 M^{-1}.

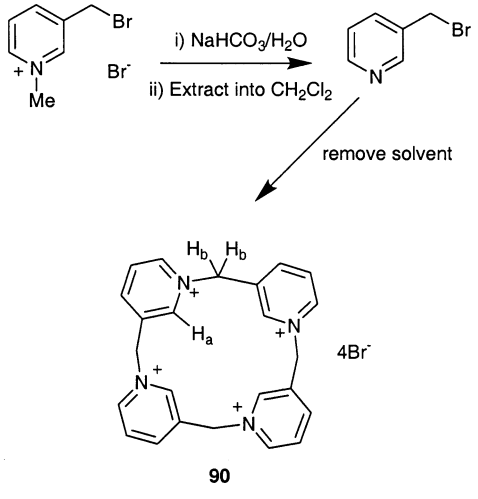


85

Scheme 12. Receptor **85** coordinates to carboxylate anions via both amidic and pyridinic hydrogen atoms.



Shinoda and co-workers have synthesised a tetrapyridinium macrocycle (**90**) by self-condensation of 3-bromomethylpyridine (Scheme 13). The crystal structure of **90**·2H_2O revealed that the bromide counter anions form hydrogen bonds to the pyridinium macrocycles with H–Br distances between 2.65 and 2.79 Å (Fig. 14). The binding constants of this macrocycle with a number of tricarboxylate anions were elucidated by ^{1}H-NMR titration techniques in D_2O and found to be in the range $4.1 < \log K < 5.1$.



Scheme 13. The synthesis of receptor **90**.

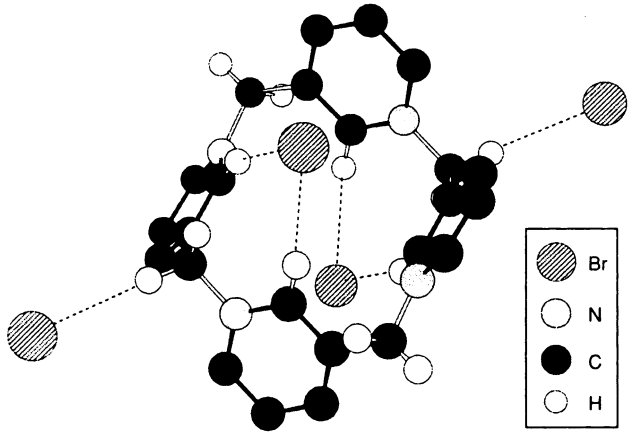
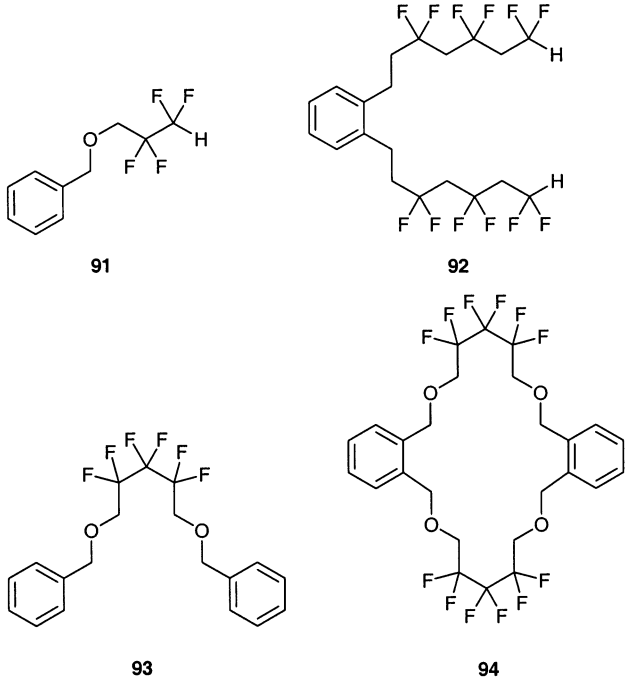


Fig. 14. Crystal structure of **90**·2H_2O. (Reproduced with permission from Chem. Commun. (1998) 181, Copyright 1998, The Royal Society of Chemistry.)

2.7. Other non-metallated anion receptors

Fluorinated polyether compounds have been used by Suzuki and co-workers as components of ion-selective electrodes designed to sense anions in solution [69]. Compounds **91**–**94** contain acidic hydrogen atoms capable of forming hydrogen bonds with anionic guest species. The macrocyclic receptor **94** showed a large



response to perchlorate anions when incorporated into a PVC film and a response trend with other anions roughly following the Hofmeister series.

Douglas and Young have adapted the protein coat of a virus to act as a host for anionic polyoxometalate species [70]. The coat of cowpea chlorotic mottle virus consists of 180 identical protein subunits. Under the right conditions, it will spontaneously self-assemble from the constituent protein subunits to form a capsule with an internal diameter of 150 Å. At pH > 6.5, the viral coat swells opening up 60 separate pores, each with a diameter of approximately 20 Å (Fig. 15(b)). This allows the exchange of material between the capsule interior and the bulk medium. At pH values lower than 6.5, the virus contracts, closing the pores and trapping any material that is inside (Fig. 15(a)).

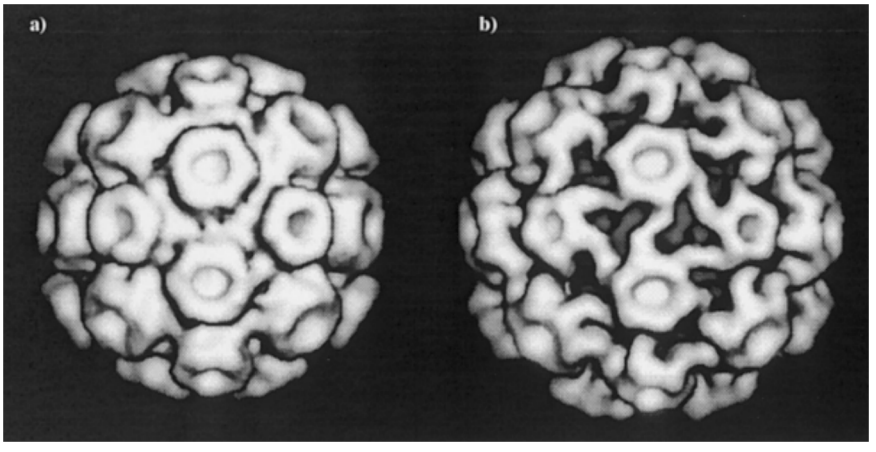


Fig. 15. Cryo electron microscopy and image reconstruction of the cowpea chlorotic mottle virus (CCMV). In (a) an unswollen condition is induced by low pH. In (b) a swollen condition is induced by high pH. Swelling results in the opening of 60 portals in the virus coat. (Reproduced with permission from Nature 393 (1998) 152. Copyright 1998, Macmillan Magazines Ltd.)

Douglas and Young incubated empty virons at pH > 6.5 with WO_4^{2-} ions. These ions oligomerise under acidic conditions to form paratungstate ($H_2W_{12}O_{42}^{10-}$) polyanionic clusters. When the pH was lowered, the protein coats contracted resulting in the spatially selective entrapment of paratungstate clusters within the viruses.

Transmission electron microscopy was used to image the mineralised virus particles (Fig. 16(A)). These images indicate that the paratungstate anions crystallised within the cavity as their diameter of 150 Å matches the internal cavity size of the virus. A negative stain of the mineralised virus particles reveals the intact viral coats surrounding the polyanionic paratungstate core (Fig. 16(B)).

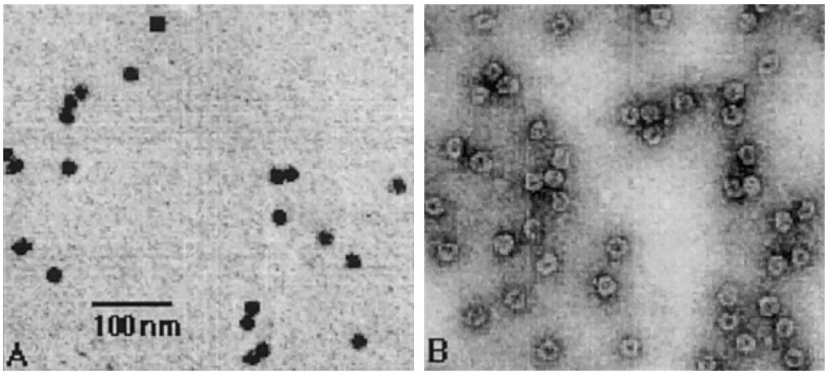


Fig. 16. Transmission electron microscopy images of paratungstate-mineralized virus particles. In (A) the electron dense paratungstate cores may be observed. In (B) a negatively stained sample reveals the intact virus protein coats surrounding each core. (Reproduced with permission from Nature 393 (1998) 152. Copyright 1998, Macmillan Magazines Ltd.)

3. Anion receptors containing metals

The previous section of this review covered metal-free anion receptors. We will now go on to look at metal containing anion receptors that have appeared in the literature in 1997 and 1998. The metal ions in these receptors play a number of different roles:

(i) a coordination site for the anion;

(ii) a non-coordinating reporter group that signals the presence of the anion by a perturbation of its physical properties (i.e. by changes in redox or spectroscopic properties);

(iii) an element in the receptor designed to withdraw electron density from a π electron system and so increase the affinity of a hydrophobic receptor for anions;

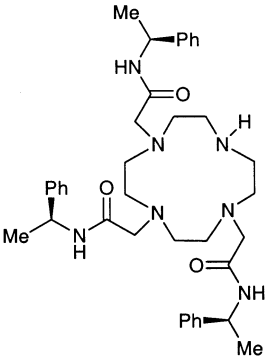
(iv) an element of a self-assembled array that binds an anionic guest (whether by an interaction with the metal or another part of the array).

Each of these roles will be considered in turn.

3.1. Anions coordinated to metals

Parker and co-workers have recently reported that the complexes of ligand **95**, $(Eu–\mathbf{95})^{3+}$ and $(Tb–\mathbf{95})^{3+}$, can be used as sensors for anions in aqueous environments [71]. In water, both complexes contain two coordinated water molecules. These molecules quench luminescence properties of the lanthanide ions. In the presence of certain anions they may be displaced from the metal coordination sphere so increasing the luminescence of the metal. Chloride, bromide, iodide and nitrate did not displace the bound water molecules but fluoride, acetate and sulfate displaced up to one water leading to enhanced luminescence lifetimes. Hydrogen carbonate displaced both water molecules by binding in a bidentate fashion so

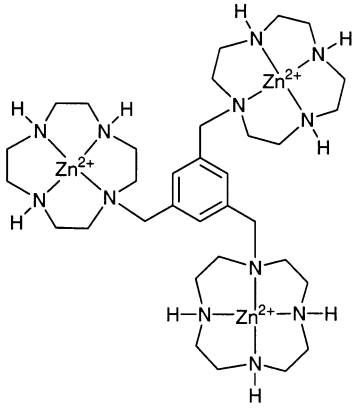
filling two coordination sites. This produced a large change in the luminescent lifetime of the complex.



95

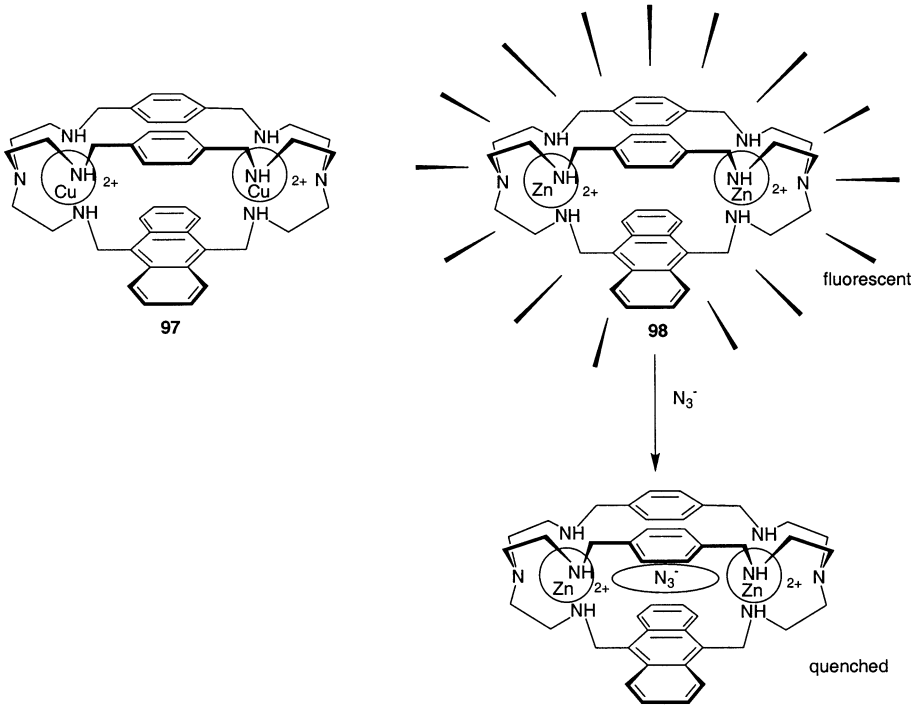
Lanthanide(III) tris(β-diketonate) complexes have been used by Tsukube and co-workers to coordinate to the carboxylate moieties of unprotected amino acids and transport them through liquid membrane systems [72,73].

Kimura and co-workers have used a new tris-(Zn(II)–1,4,7,10-tetraazacyclodecane) zinc complex as a receptor for phosphate dianions in aqueous solution [74]. A potentiometric pH titration of **96**–$3H_2O$ showed that the deprotonation constants of the coordinated water molecules are 6.1, 7.3 and 8.6 at 25°C with $I = 0.1$ ($NaNO_3$). This data together with ^{1}H-NMR studies suggest that there are strong intramolecular hydrogen bonds between the zinc bound water molecules (that are disrupted at pH > 9). In a very detailed and elegant study, Kimura elucidated the conformational and hydrogen bonding changes that occur upon complexation and protonation. Stability constants (log K) were found to be 5.8 with 4-nitrophenylphosphate, 6.6 with phenylphosphate, 7.0 with α-D-glucose-1-phosphate and 7.9 with phenyl phosphonate (in aqueous solution).



96

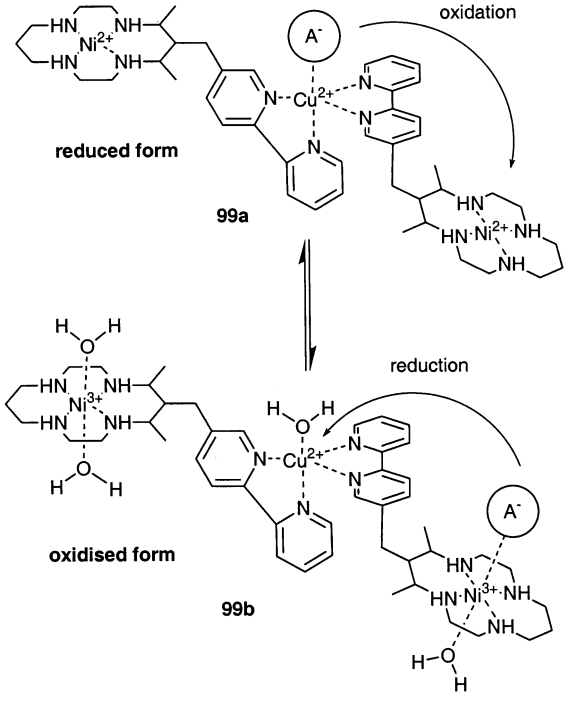
Fabbrizzi and co-workers have synthesised an anthracene bis-tren cage system containing two Cu^{2+} (**97**) or Zn^{2+} (**98**) metal ions as potential fluorescent sensors for anions in aqueous solution (Scheme 10) [75]. The dicopper complex **97** forms a cascade complex with ambidentate anions (N_3^-, NCO^-) bound between the two metal ions. However, the fluorescence of this complex is quenched by the copper ions via an electron or energy transfer reaction. Complex **98** proved to be a better candidate as a fluorescent sensor. The fluorescence of this complex is not quenched by the zinc ions but rather by ambidentate anions such as N_3^- that bind between the two zinc centres. It is speculated that quenching is caused by electron transfer from the electron-rich azide anion to the anthracene moiety (Scheme 14).



Scheme 14. Receptors **97** and **98**. The fluorescence of **98** is quenched in the presence of ambidentate anions (e.g. N_3^-).

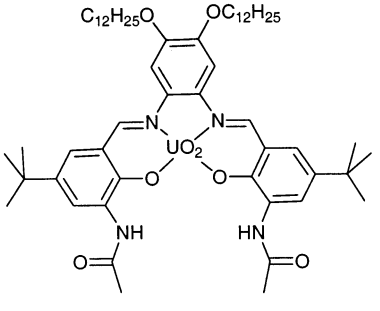
In a separate publication, Fabbrizzi has reported the synthesis a multicomponent coordination assembly **99** that can be electrochemically switched between two different forms [76]. Complex **99** consists of two four-coordinate nickel(II) cyclam-like macrocycles each attached to a separate bipyridine fragment that are coordinated to a single copper(II) metal ion. Inorganic anions (N_3^-, NCO^-, NCS^-) can displace the water molecule bound to the copper(II) centre forming complex **99a** (Scheme 15). The nickel centres are then oxidised electrochemically to Ni(III)—an oxidation state that requires a further ligand in the axial position. Differential pulse voltammetry experiments showed that the anion coordinated to the copper(II)

centre jumps across and coordinates to the Ni(III) forming **99b** (Scheme 15). Fabbrizzi is therefore able to exert precise electrochemical control over the position of the anion in this complex.



Scheme 15. The position of the anion in receptor **99** can be electrochemically switched between copper and nickel centres.

The incorporation of anion binding agents into chemically modified field effect transistors (CHEMFETs) for use as anion sensors is an area of analytical chemistry pioneered by David N. Reinhoudt. Recently, Reinhoudt and co-workers have incorporated a uranylsalophene bis-amide receptor (**100**) [77] into a CHEMFET and produced a fluoride selective anion sensing device [78]. Compound **100** contains a Lewis acidic uranium atom and amide NH groups that can form hydrogen bonds stabilising the anion complex. Dihydrogen phosphate selective systems have also been produced by the same workers [79].

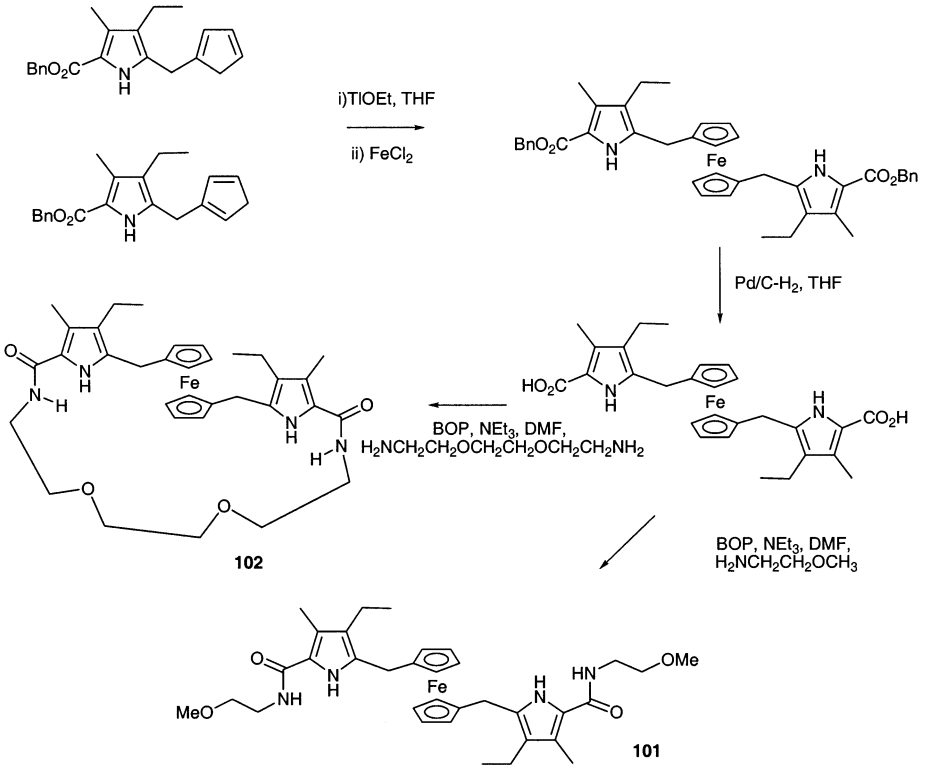


100

3.2. Non-coordinating metals as sensors

The incorporation of metal ions into anion receptors to act as non-coordinating reporter groups for the electrochemical or optical sensing of anions is an area of anion coordination that has attracted much attention recently [9]. Some work in this area on the inclusion of ferrocene [80–83], cobaltocenium [84], and ruthenium bipyridyls [85,86] in such receptors and their subsequent use as electrochemical sensors for anions has been covered in a recent review article in this journal to which the interested reader is directed for further information [87].

Sessler and co-workers have combined ferrocene and pyrrole moieties in a new series of anion receptors [88]. Compounds **101** and **102** were synthesised according to the synthetic route shown in Scheme 16.



Scheme 16. Synthesis of receptors **101** and **102**.

These receptors contain both pyrrolic and amidic NH groups and are therefore very good candidates to be effective anion coordination agents. Stability constants with anionic guests were determined by ^{1}H-NMR titration techniques in acetonitrile-d_3 and are shown in Table 9. Not surprisingly, the macrocyclic receptor **102**

Table 9
Stability constants (M^{-1})[a] from ^{1}H-NMR titration experiments and electrochemical data for compounds **101** and **102**

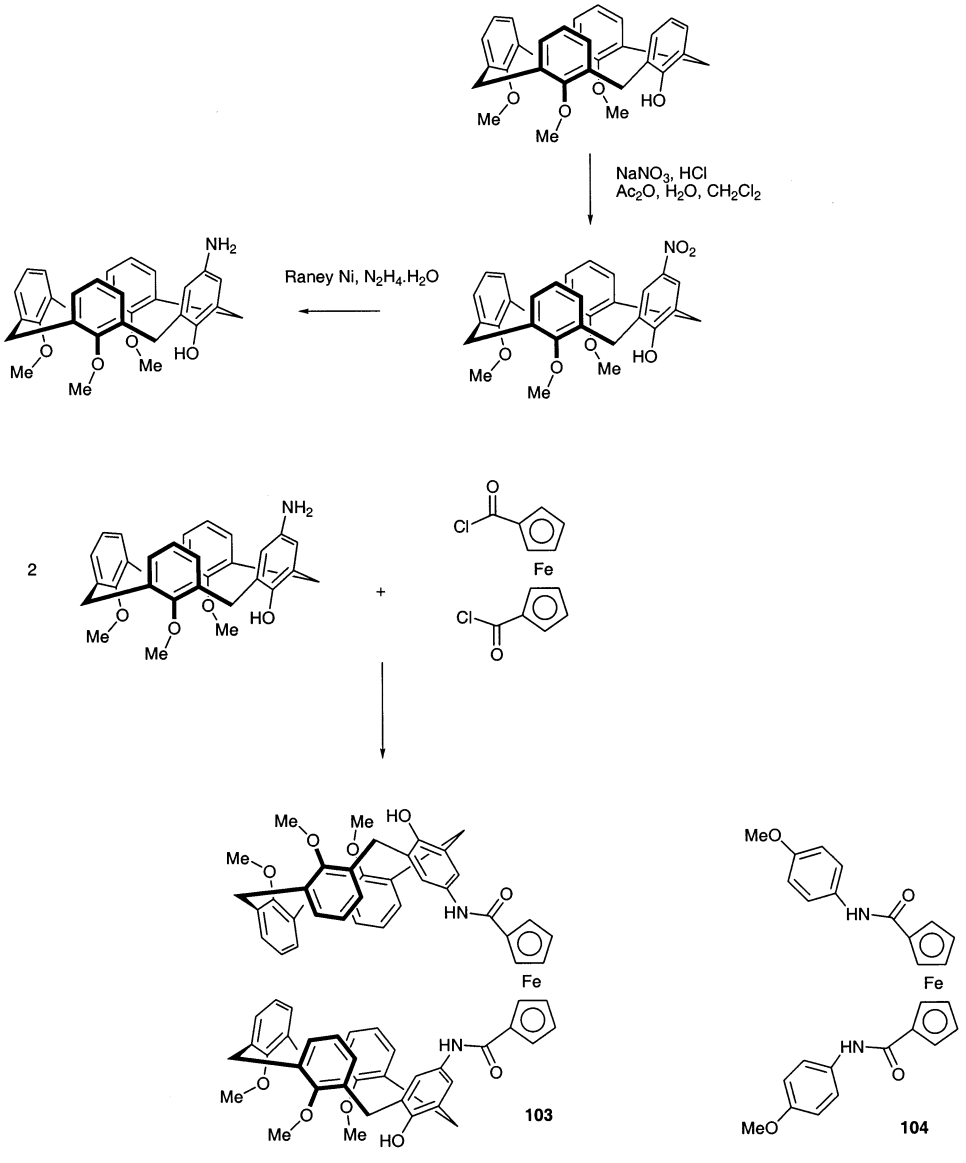
Anion	Receptor **101**			Receptor **102**		
	K_a[b] ($dm^3\ mol^{-1}$)	$E_{1/2}$[c] (mV)	ΔE[d] (mV)	K_a[b] ($dm^3\ mol^{-1}$)	$E_{1/2}$[c] (mV)	ΔE[d] (mV)
None	n/a	424	n/a	n/a	396	n/a
F^-	$>10^5$	386	56	$>10^5$	316	80
Cl^-	1260	388	36	9031	372	24
Br^-	66	404	20	857	388	8
HSO_4^-	258	392	32	889	380	16
$H_2PO_4^-$	4181	280	144	11305	260	136

[a] *n*-Tetrabutlyammonium salts.
[b] Stability constants for anion binding; recorded in acetonitrile-d_3; errors $<15\%$; determined from $\Delta\delta$/ppm NH(amide).
[c] Determined in acetonitrile containing 0.1 M *n*-Bu_4NPF_6 as the supporting electrolyte. Solutions were 5×10^{-4} M and potentials were determined with reference to Ag | AgCl, 10 Hz frequency in square wave voltammetry.
[d] Cathodic shift observed after addition of 5 molar equivalent of added anion.

shows a higher affinity for anions than the acyclic analogue **101** with both receptors being selective for fluoride over other putative anionic guest species. Two fluoride anions bind to each receptor in solution whereas the other anions tested bind solely in a 1:1 stoichiometry. Addition of dihydrogen phosphate to receptor **102** caused the largest shift in the ferrocene/ferrocenium couple of all the receptor–anion complexes under study (a cathodic shift of 144 mV was observed). The self-assembly properties of these types of pyrrolic ferrocene systems have also been studied [89].

Beer and Shade have recently reported the synthesis of a ferrocene-1,1′-bis calix[4]arene anion receptor **103** that shows interesting solvent dependent anion selectivity (Scheme 17) [90]. The anion coordination properties of **103** and the model compound **104** were studied in a variety of solvents using ^{1}H-NMR titration techniques. The results are presented in Table 10. Beer found that there is no clear relationship between the complex stability and the bulk solvent properties (relative permittivity and dipole moment). However, there is a relationship between the stability constant and the Gutmann acceptor number (AN) of the solvent (a measure of the solvent's hydrogen bond donor ability). As AN increases the stability constants of the anion complexes decrease. Interestingly, Beer found that the anion selectivity of the receptors changed as the AN decreases. **103** shows the solvent dependent trends $(CD_2Cl_2)PhCO_2^- > Cl^- > MeCO_2^-$; $(CD_3CN)PhCO_2^- > MeCO_2^- > Cl^-$; $[(CD_3)_2CO]MeCO_2^- > Cl^- > PhCO_2^-$ whilst **104** shows $(CD_2Cl_2)PhCO_2^- = MeCO_2^- > Cl^-$; $[(CD_3)_2CO]MeCO_2^- > PhCO_2^- > Cl^-$. The anion coordination properties of analogous rhenium [91] and ruthenium bipyridyl [92] bis-calixarene receptors have also been reported.

Beer and co-workers have synthesised a number of anion receptor species containing coordinatively saturated Lewis acidic centres. The complexes of the cleft ligands **105**, **106**,**107** and **108a** and **108b** were prepared with a variety of metals (Scheme 18 and Table 11) and their anion coordination properties studied by ^{1}H-NMR titration techniques [93]. In these systems the anionic guest binds between the two metallic centres held there by a combination of electrostatic interactions

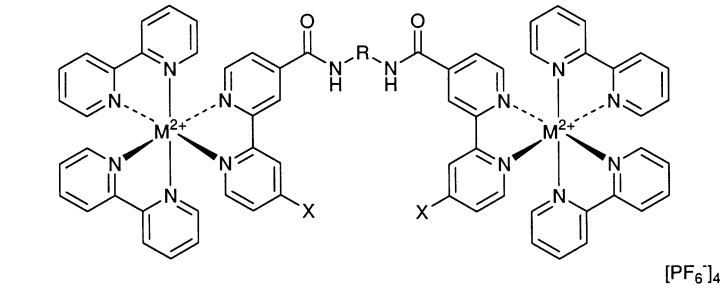


Scheme 17. Synthesis of receptors **103** and **104**.

Table 10
Solvent effects on the stability constant values of the anion complexes of **103** and **104**[a]

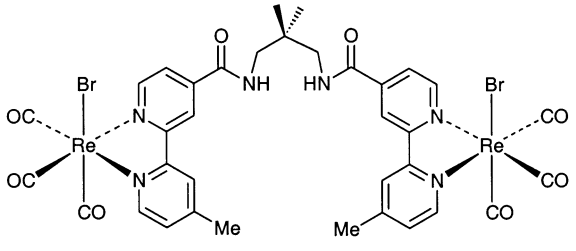
Receptor	Solvent	ε	μ	K[b] M^{-1} anion			
				AN	Cl^-	$PhCO_2^-$	$MeCO_2^-$
103	CD_2Cl_2	8.9	1.5	20.4	40	117	26
103	CD_3CN	36.0	3.96	18.9	70	360	120
103	$(CD_3)_2CO$	20.7	2.86	12.5	5200	940	6000
104	CD_2Cl_2	8.9	1.5	20.4	175	215	210
104	$(CD_3)_2CO$	20.7	2.86	12.5	400	1500	3000

[a] Receptor **104** insoluble in CD_3CN.
[b] Estimated errors < 10%; ε, relative permittivity; μ, dipole moment; AN, acceptor number of solvent.



R =

105 X = CO_2Et **106** X = CO_2Et **107** X = CO_2Et **108a** X = CO_2Et **108b** X = Me

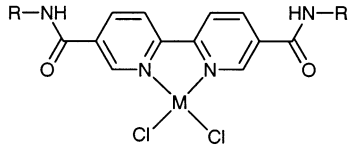


Re-**108b**-Re

Scheme 18. Receptors **105**–**108**.

and hydrogen bonds from the amide moieties. Systems containing neutral Re bind anions more weakly than the positively charged Ru and Os analogues, due to the lack of an electrostatic component in the binding interaction (Table 11). Receptors containing Os were found to bind anions more strongly than those containing Ru. This was attributed to the greater Lewis acidity of the Os centres. This metal Lewis acidity presumably increases the acidity of the amide NH protons so enhancing the strength of the anion–receptor complexes.

5,5′-Bis-amide substituted platinum- and palladium-bipyidyl receptors **109** and **110** have also been synthesised by Beer and co-workers and shown to coordinate to chloride anions with moderate stability constants ranging from 32 to 36 M^{-1} [94].



109 R = methoxyethyl M = Pt or Pd
110 R = 4-hydroxyphenyl M = Pt or Pd

Beer has produced a number of metal-containing cleft systems that are capable of coordinating to an anion and a cation simultaneously. Compounds **111** and **113** contain an anion binding cleft linked to cation binding crown ether groups [95]. The anion binding abilities of these receptors were measured in the absence and presence of potassium cations in DMSO and compared to results obtained for the model compounds **112** and **114** which do not contain any cation binding moieties. The affinity of compounds **111** and **113** for chloride increased in the presence of potassium cations due to the electrostatic interaction between the crown ether bound potassium and the amide bound anion (Table 12). The anion affinity of the model compounds **112** and **114** did not significantly change in the presence of potassium cations. Interestingly, the affinity of receptors **111** and **113** for $H_2PO_4^-$

Table 11
Stability constant data for the dinuclear cleft anion receptors **105**–**108** in DMSO

Receptor	K (Cl^-)[a,b] (M^{-1})	K (Br^-)[a,b] (M^{-1})	K ($H_2PO_4^-$)[a,b] (M^{-1})
Ru–**105**–Ru	25	45	55
Ru–**106**–Ru	55	40	4320
Ru–**107**–Ru	70	60	10
Ru–**108a**–Ru	245	170	19 700
Re–**108b**–Re	120	[c]	1820
Ru–**108b**–Ru	310	220	15 480
Ru–**108b**–Os	440	[c]	22 150
Os–**108b**–Os	825	[c]	>30 000

[a] Average for amide and bpy protons.
[b] Errors estimated to be <10%.
[c] Not determined.

anions drops in the presence of potassium. This is presumably due to the formation of an intramolecular sandwich complex between the two [15]-crown-5 moieties and the potassium cation that restricts the size of the amidic cavity so enforcing a strict size selectivity on the receptor (Fig. 17). Chloride can fit into the restricted cavity whereas $H_2PO_4^-$ is too large to coordinate efficiently. Therefore, in the presence of potassium compounds **111** and **113** selectively coordinate Cl^- whilst in the absence of potassium they are selective for $H_2PO_4^-$ (Table 12).

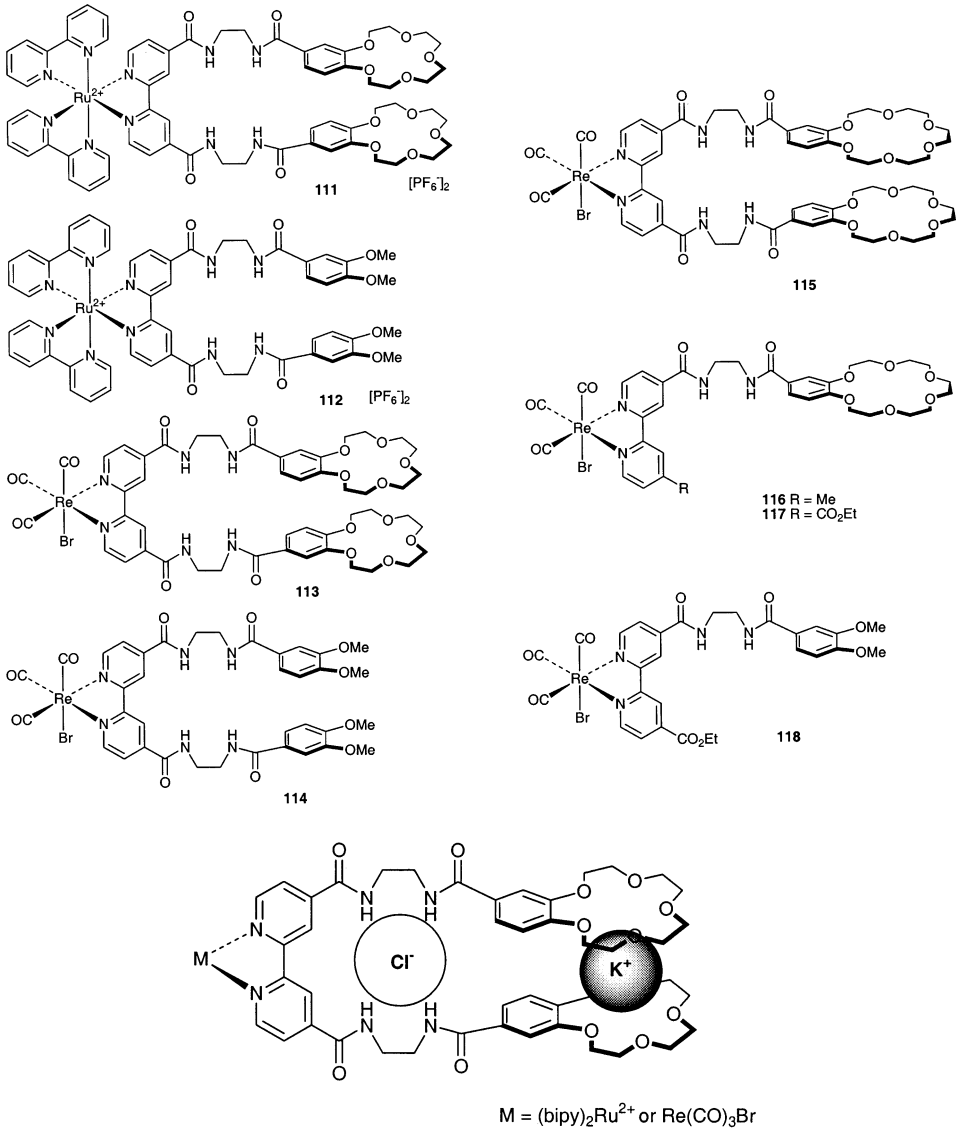


Fig. 17. Potassium cation binding by receptors **111** and **113** causes the formation of an intramolecular sandwich complex that restricts the size of the anion binding amidic cavity switching anion selectivity from dihydrogen phosphate to chloride.

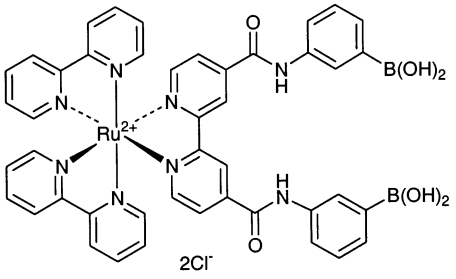
Table 12
Stability constants for Cl^- and $H_2PO_4^-$ binding in the presence and absence of K^+ in DMSO by receptors **111–114**

Receptor	K (Cl^-)[a] (M^{-1})	K ($H_2PO_4^-$)[a] (M^{-1})
111	190	900
111+2 equiv. KPF_6	660	60
112	195	[b]
112+2 equiv. KPF_6	165	[b]
113	55	205
113+2 equiv. KPF_6	300	35
114	46	[b]
114+2 equiv. KPF_6	55	[b]

[a] Errors estimated to be <10%.
[b] Precipitation problems prevented complete titration curves from being obtained with **112** and **114**.

The binding properties of a series of rhenium substituted analogues containing benzo-[18]crown-6 moieties have also been studied (compounds **115**, **116** and **117** along with model compound **118**) in which the potassium cation complexation again enhances the anion coordination ability of the crown ether containing ligands [96]. The crystal structure of [**116**–$KCl]_2 \cdot 2H_2O$ is shown in Fig. 18.

Deetz and Smith have synthesised an analogous compound containing boronic acid saccharide binding groups (**119**) and shown that this material will sense the presence of phosphorylated sugars in aqueous solution via perturbations in the luminescent properties of the complex [97]. 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 [98].



119

3.3. Metals coordinated to π systems of hydrophobic anion receptors

Atwood and Steed have pioneered the use of calixarenes containing transition metals coordinated to the outside of the calixarene cone as anion binding agents

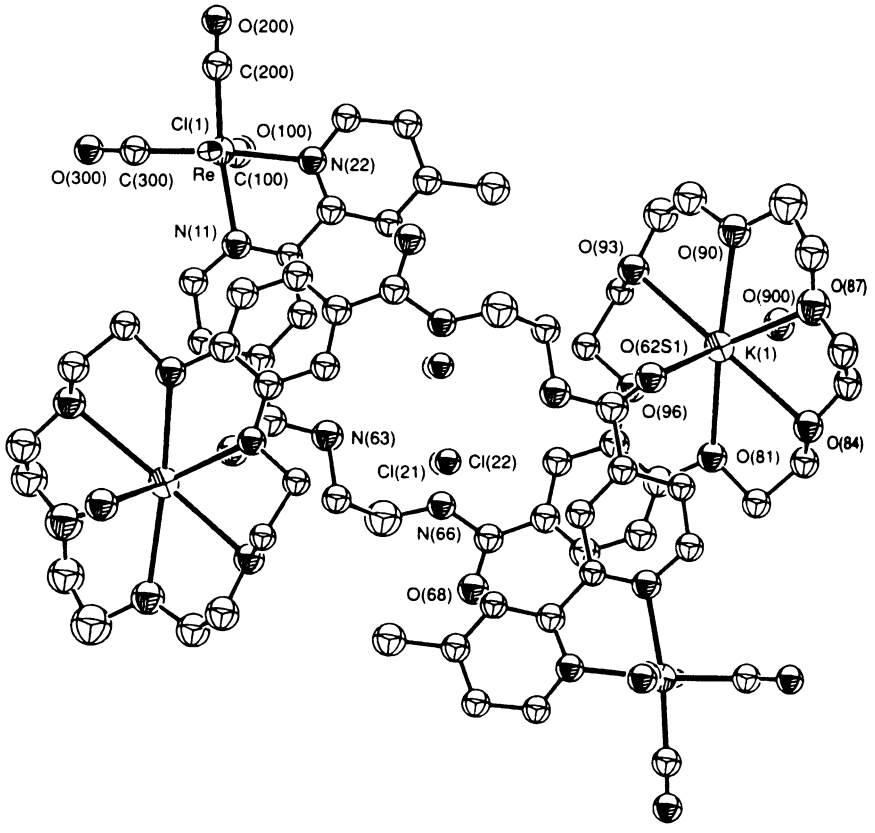
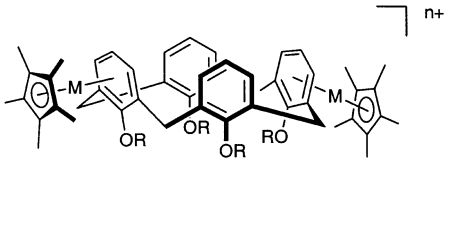
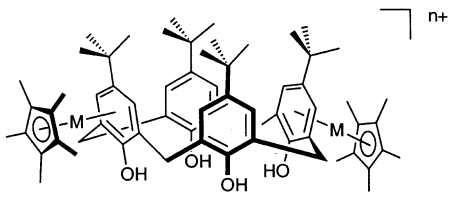


Fig. 18. The centrosymmetric dimer (**116**–$KCl)_2 \cdot 2H_2O$ with ellipsoids shown at the 20% probability level together with the atomic numbering scheme. (Reproduced with permission from Chem. Commun. (1998) 231, Copyright 1998, The Royal Society of Chemistry.)

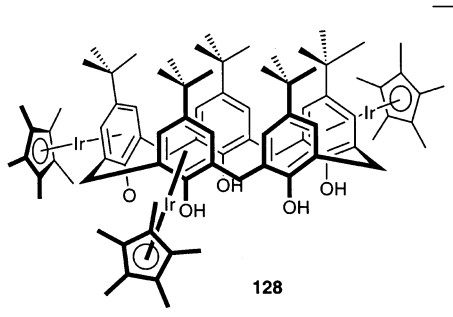
[99–101]. In 1997 these workers published a full account of their work in this area [102]. A number of calixarene metal complexes have been prepared including compounds **120**–**129**. Crystal structures of anions bound in the calixarene cavity of some of these receptors were elucidated including the HSO_4^- complex of **129** (Fig. 19). Anion binding constants as high as 550 M^{-1} were observed for chloride complexation in aqueous solution.



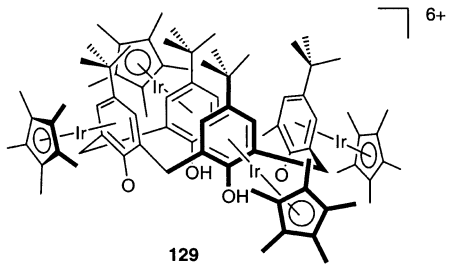
120 n = 4, 4R = H, M = Rh
121 n = 3, 3R = H, M = Rh
122 n = 2, 3R = H, M = Ir
123 n = 4, R = n-Pr, M = Ir



124 n = 4, M = Rh
125 n = 4, M = Ir
126 n = 3, M = Rh
127 n = 3, M = Ir



128

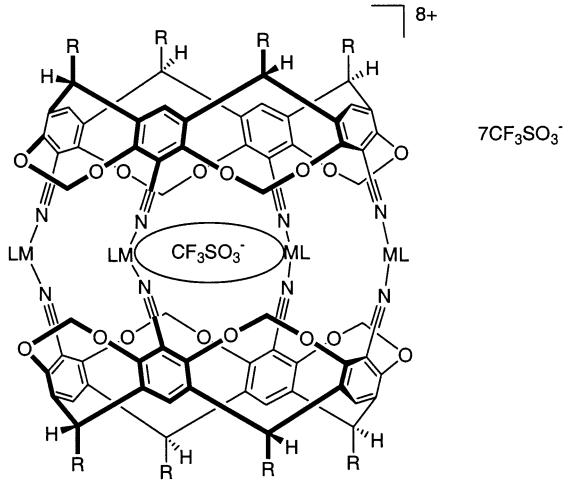


129

3.4. Anions bound to metal-directed self-assembled arrays

Anions can be bound in self-assembled arrays either by being trapped in a cavitand like structure or by coordinating directly to metal ions or to other elements present in the array. The use of anions to direct the formation of self-assembled arrays is discussed in the next section.

Jacopozzi and Dalcanale recently reported the metal directed assembly of a series of cavitand based cage molecules [103]. Organopalladium and organoplatinum cage molecules **130**–**132** were synthesised by reaction of a tetranitrile substituted cavitand with either $Pt(dppp)_2(OSO_2CF_3)_2$ or $Pd(dppp)_2(OSO_2CF_3)_2$. The cages formed immediately as the only product, each imprisoning a $CF_3SO_3^-$ anion within the self-assembled cavity.



130 R = $C_{11}H_{23}$, M = Pd, L = 1,3-bis(diphenylphosphino)propane
131 R = $C_{11}H_{23}$, M = Pt, L = 1,3-bis(diphenylphosphino)propane
132 R = C_6H_{13}, M = Pd, L = 1,3-bis(diphenylphosphino)propane

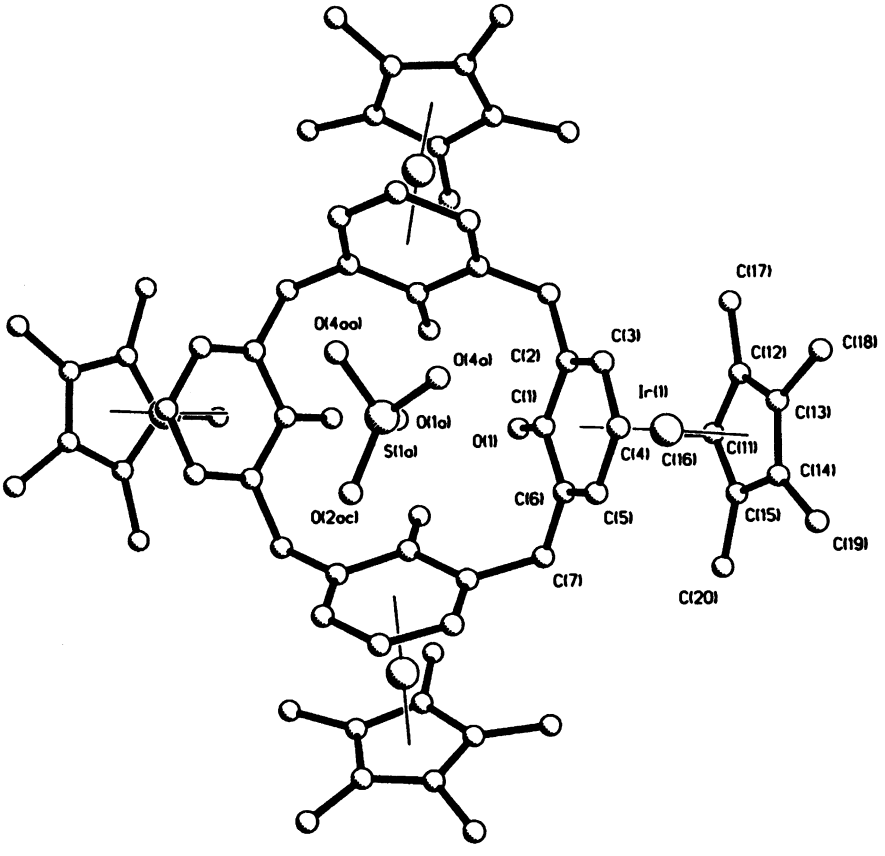
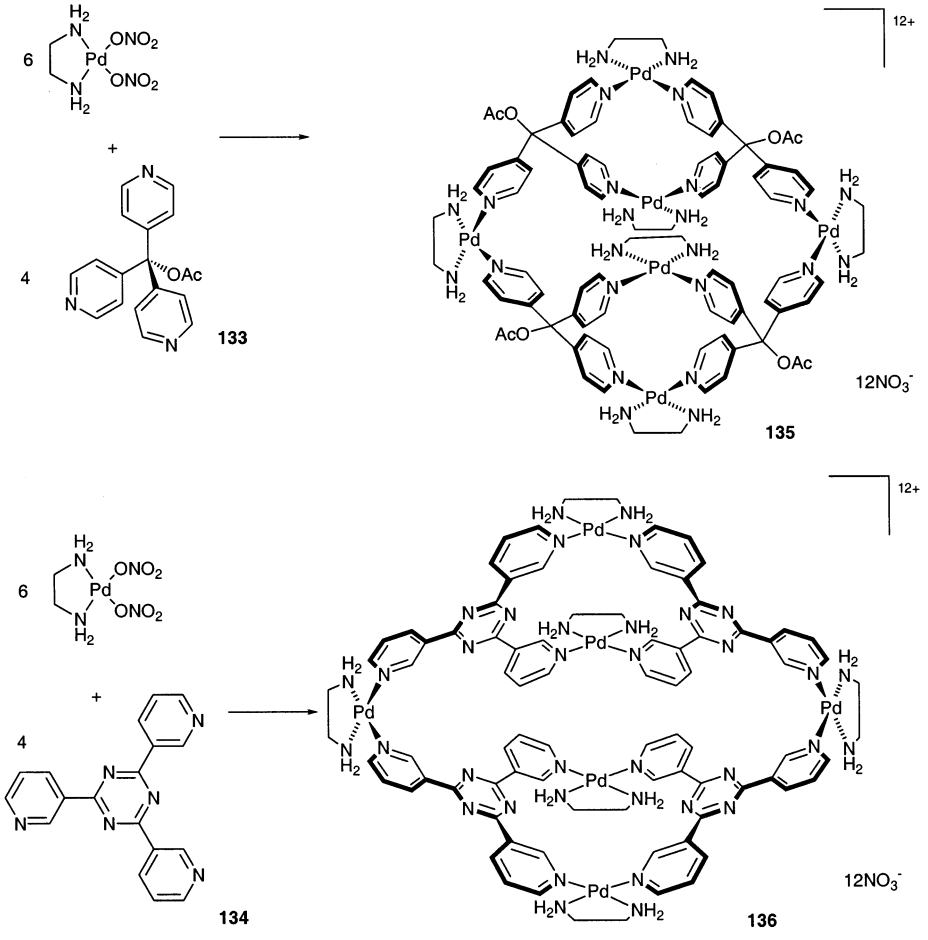


Fig. 19. The crystal structure of the hydrogen sulfate complex of **129**. The anion is bound within the hydrophobic cavity of the metallated calixarene. (Reproduced with permission from J. Am. Chem. Soc. 119 (1997) 6331, Copyright 1997, The American Chemical Society.)

Makoto Fujita and his co-workers have produced a wide variety of self-assembled molecular architectures by combining pyridine based ligands with Pd(II) and Pt(II) metal ions [104–106]. Recently, these researchers have assembled nanometer-sized macrotricyclic networks in which four ligand molecules are held together by six metal ions [107]. The pyridine containing ligands **133** and **134** are combined with $Pd(NO_3)_2(H_2NCH_2CH_2NH_2)$] in a 6:4 ratio resulting in the assembly of cages **135** and **136** (Scheme 19).

Both complexes **135** and **136** bind dicarboxylate anions. 1,4-Phenylenediacetate and terephthalate were bound in the cavity of both **135** and **136**. For **135** this is presumably due to a two-point electrostatic interaction between the metal ions and the carboxylate groups as a simple mono-carboxylate (*p*-methoxyphenylacetate) interacted only very weakly with this receptor. However, this anion was bound strongly to **136** suggesting that the aromatic rings in **136** are also contributing to aromatic anion binding.

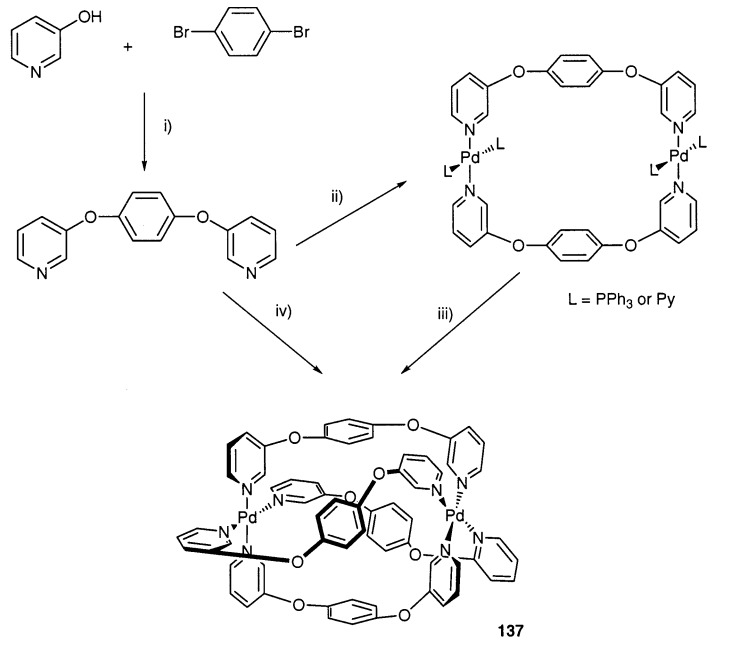


Scheme 19. Metal directed assembly nanometer size molecular-boxes capable of coordinating anions.

McMorran and Steel have recently reported the formation of a quadruple helicate **137** that binds a hexafluorophosphate anion [108]. The synthesis of the helicate is shown in Scheme 20. The complex encapsulates a PF_6^- anion making weak contacts with the two metal atoms [Pd1–F11 = 2.789(5); Pd2–F15 = 2.911(5) Å]. These interactions are represented by the dashed lines in Fig. 20. ^{1}H-NMR spectra in DMSO-d_6 suggest the anion remains inside the helicate in solution.

4. Anion directed self-assembly

The role of anions in promoting the formation of self-assembled arrays has only recently been exploited and by extending the remit of this review article back to



i) K_2CO_3, $Cu^{(0)}$, dimethylacetamide, heat; ii)L = PPh_3: [$PdCl_2(PPh_3)_2$], AgOTf, CH_2Cl_2, L = Py: [$PdI_2(Py)_2$, AgOTf, acetone, NH_4PF_6; iii) $MeCN/Et_2O$; iv) 0.5 equiv [$PdI_2(Py)_2$], AgOTf, MeCN, NH_4PF_6, OTf = Trifluoromethanesulfonate (triflate).

Scheme 20. Assembly of a quadruple helicate **137**.

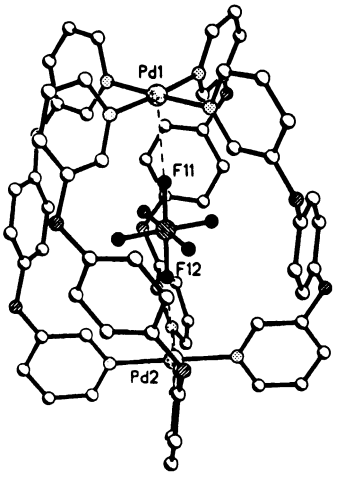


Fig. 20. A hexafluorophosphate anion bound within a quadruple helicate. (Reproduced with permission from Angew. Chem. Int. Ed. Engl. 37 (1998) 3295, Copyright 1998, Wiley-VCH.)

1996 it is possible to provide a fairly comprehensive review of this area. Early examples include copper(II)-arginine complexes [109] and cyclic bis-amidinium species [110] that form self-assembled structures with aromatic dicarboxylates and self-assembling diamidopyridinium phosphates [111]. Sessler and co-workers have shown that compound **21**, a calixpyrrole *meso*-mono-acid, self assembles forming dimeric cyclic structure in the solid state. Similar behaviour was observed for sapphyrin carboxylates in both the solid state and in solution [38].

Lehn and co-workers have discovered a striking example of anion directed assembly (Scheme 21) [112,113]. The pentametallic circular helicate **139** forms when the tris-bipyridine ligand **138** is mixed with an equimolar amount of $FeCl_2$ in ethylene glycol at 170°C. The chloride anion bound in the centre of the helicate cannot be exchanged for other anions such as PF_6^- or $CF_3SO_3^-$. If another iron salt is used in the reaction, such as $Fe(BF_4)_2$ or $FeSO_4$, the pentametallic structure does not form and instead a hexameric complex **140** is obtained (Scheme 21). The chloride anion is therefore playing a role in the assembly of this beautiful complex (Fig. 21).

An example of anion directed assembly of a nickel cage complex has been reported by Mingos and co-workers [114]. Reaction of $NiCl_2$ with amidinothiourea in methanol yields crystals of the cage complex **141** shown in Fig. 22(a). The cage $[Ni_6(atu)_8Cl]Cl_3$ consists of eight amidinothiourea units that coordinate six nickel ions through both nitrogen and sulfur donor atoms. A chloride anion is bound in the centre of the cage by eight NH–Cl hydrogen bonds (the crystal structure is

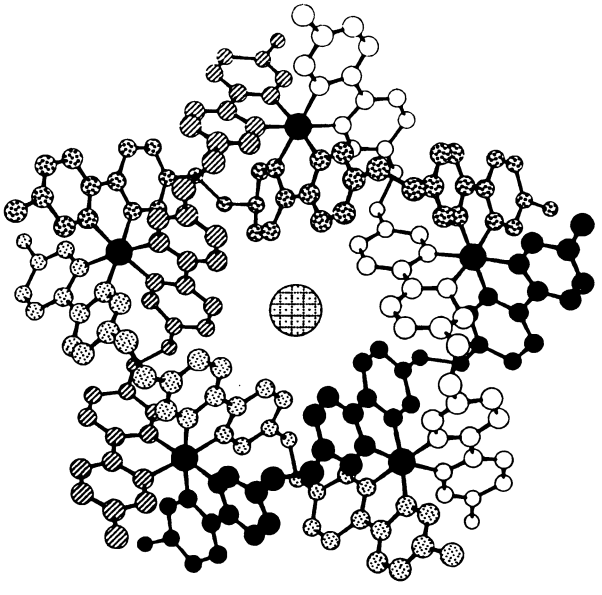
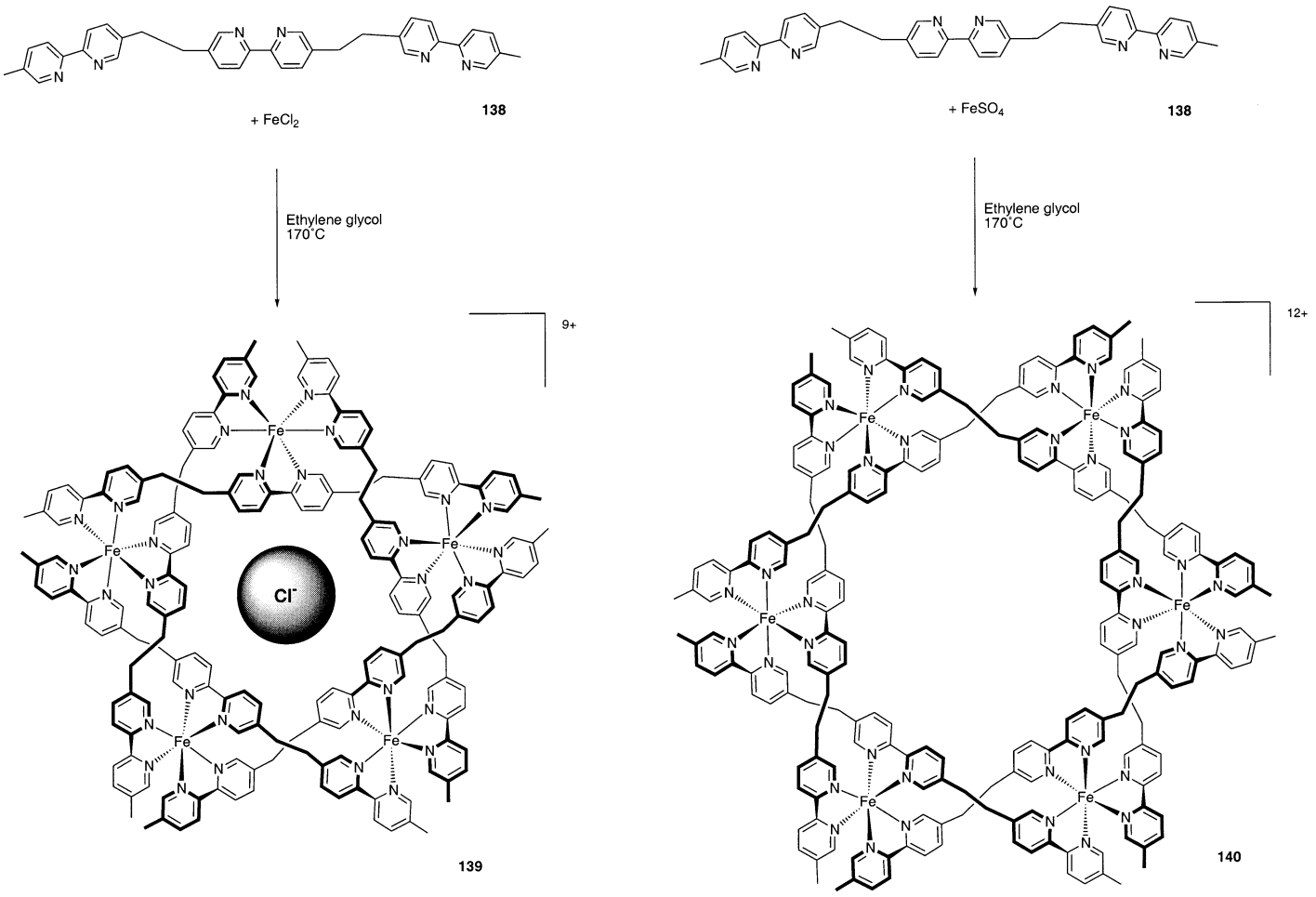


Fig. 21. Ball and stick representation of the crystal structure of the circular double helicate **139** showing a chloride anion bound in the centre of the assembly. (Reproduced with permission from Angew. Chem. Int. Ed. Engl. 35 (1996) 1838, Copyright 1998, Wiley-VCH.)



Scheme 21. The anion directed synthesis of **139** and the synthesis of **140**.

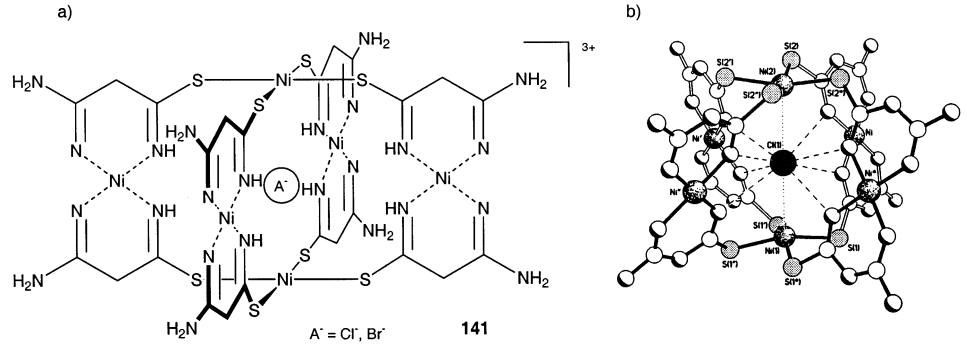


Fig. 22. The structure and crystal structure of the anion directed cage $[Ni_6(atu)_8Cl]Cl_3$ **141**. (Reproduced with permission from Angew. Chem. Int. Ed. Engl. 37 (1998) 1258, Copyright 1998, Wiley-VCH.)

shown in Fig. 22(b)). An analogous cage complex can also be formed using $NiBr_2$, but when nitrate, acetate or perchlorate salts are used, the simple monomer $[Ni(atu)_2]^{2+}$ complexes are formed. If chloride anions are subsequently added to these complexes (as KCl) the cage complex spontaneously forms around the halide.

Stoddart and co-workers have also employed anions in self-assembly processes [115]. Fig. 23 shows a pseudorotaxane **142** formed from tetrakis-*p*-phenylene[68]crown-20 (TPP68C20) and four dibenzylammonium ions. The crystal structure of this assembly shows an ordered PF_6^- anion bound in the centre of the rotaxane. Normally, PF_6^- anions are disordered in crystal structures, that is the octahedrally disposed fluorine atoms are not constrained to point in particular directions. In this case, however, the ordering of the anion suggests that it is forming C–H···F hydrogen bonds with the rest of the assembly, so locking it into

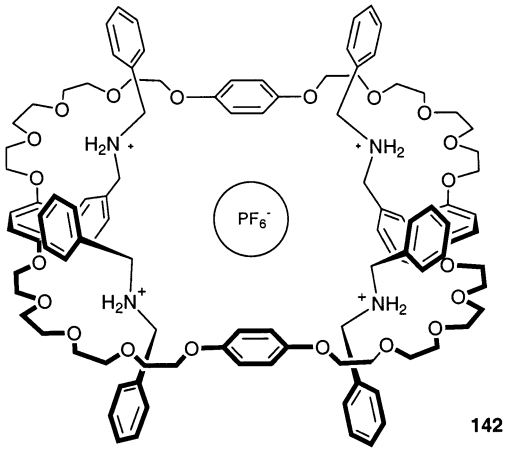
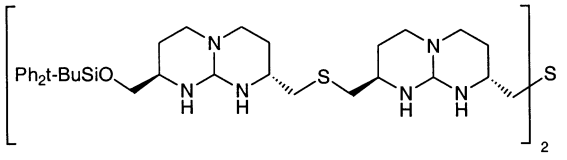


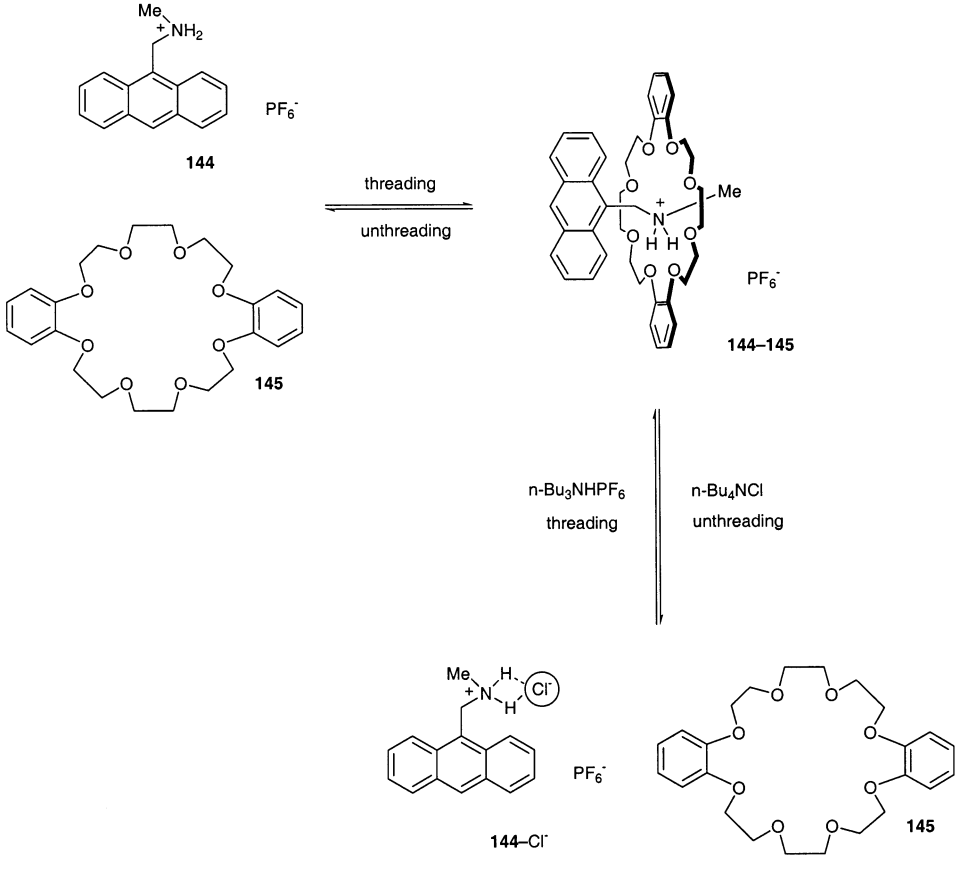
Fig. 23. Stoddart's polyrotaxane **142** formed via anion assisted assembly.

a single orientation. The presence of the anion is likely to reduce any electrostatic repulsion between the dibenzylammonium cations in the pseudorotaxane, thus, assisting the assembly process.

de Mendoza and co-workers have synthesised a tetraguanidinium strand (**143**) that self-assembles around sulfate anions to form a double helix [116]. Evidence for the anion directed helical structure was provided by ROESY NMR spectroscopy. The complexation behaviour of this and other tetraguanidinium reagents with α-helical peptides containing negatively charged aspartate residues has recently been reported by Hamilton and de Mendoza [117].



143



Scheme 22. Anion controlled unthreading of a pseudo-rotaxane **144**–**145**.

Montalti and Prodi have recently shown that chloride anions can exert control over the threading and unthreading of the pseudo-rotaxane formed between (9-anthrylmethyl)methylammonium hexafluorophosphate **144** and dibenzo-[24]crown-8 **145** (Scheme 15) [118]. Chloride anions form a strong ion pair with the ammonium group of **144** preventing the threading process and effectively breaking up the pseudo-rotaxane ensembles present in solution. Subsequent addition of Bu_3NH^+ cations (that can compete for the chloride anions bound in the ion pairs) drives the equilibrium back in favour of the pseudo-rotaxane. These changes can be followed by monitoring the fluorescence of the components in solution (Scheme 22).

5. Summary and conclusions

This article has highlighted advances in anion coordination chemistry made in 1997 and 1998. Excellent progress has been made in the area of self-assembly around anionic templates. The use of anion binding receptors in ion selective electrodes and in media for use in the HPLC separation of anions are exciting 'real-world' uses of anion coordination. The role of anion coordination in catalysis has yet to be fully exploited and will provide a challenging field of study for the coordination chemist.

Acknowledgements

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Note added in proof

The author would also like to direct the reader to the work of McCleverty, Ward and co-workers who have used anions to template the formation of pyrazolyl–pyridine cage complexes with Co(II) ions [119].

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