ELSEVIER

Coordination Chemistry Reviews
213 (2001) 79–128

COORDINATION CHEMISTRY REVIEWS

www.elsevier.com/locate/ccr

Anion receptor chemistry: highlights from 1999

Philip A. Gale *

Department of Chemistry, University of Southampton, Highfield, Southampton SO17 1BJ, UK

Received 14 January 2000; accepted 14 April 2000

Contents

Abstract

This review article highlights advances made in abiotic anion coordination chemistry in 1999. The structure of this review is similar to the previous review in this series that covered 1997 and 1998. The first section 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) an organisational element in anion receptor; and (iii) a sensor. Examples of the role of anions in directing the self-assembly of

* Tel.: +44-23-80593332; fax: +44-23-80596805.
E-mail address: philip.gale@soton.ac.uk (P.A. Gale).

0010-8545/01/$ - see front matter © 2001 Elsevier Science B.V. All rights reserved.
PII: S0010-8545(00)00364-7

complex molecular architectures are presented in the final section. © 2001 Elsevier Science B.V. All rights reserved.

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

1. Introduction

Interest in the coordination chemistry of anionic substrates continues to attract the attention of the supramolecular chemistry community [1,2]. The aim of this review is to present the advances made in this area of chemistry in the year 1999 and is the second in a series of reviews covering recent progress in anion binding [1].

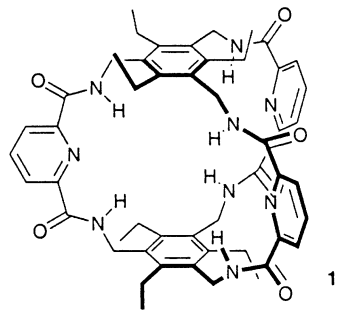
This review consists of three sections. The first discusses ligands that employ hydrogen bonding and/or electrostatic interactions to form anion complexes. The second reviews the use of metal containing ligands as anion binding agents. The final section covers ion-pair recognition and the role anions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

2. Anion receptors employing hydrogen bonds and/or electrostatic interactions

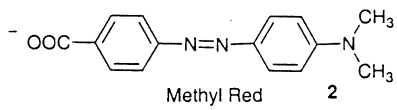
2.1. Amide based anion receptors

Amide NH groups have been employed to produce a wide range of receptors capable of coordinating anions. A number of these systems contain metal anions and are therefore discussed later in this review.

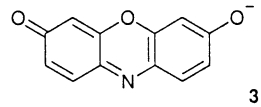
Anslyn and co-workers have extended their displacement assay paradigm [3,4] to include a molecular ensemble consisting of a previously reported nitrate selective trigonal amide box **1** [5] and a colorimetric dye such as resorufin (**3**) or Methyl Red (**2**). Changes in the absorbance of **2** and **3** upon addition of receptor **1** are shown in Fig. 1 [6]. The equilibrium between the complex **1**–**2** or **1**–**3** and its component parts is perturbed upon addition of nitrate anions resulting in large changes in absorbance. Consequently the complexes **1**–**2** and **1**–**3** act as optical sensing assays for nitrate. Receptor **1** has also been used to compare the effects of NH-π versus hydrogen bonding effects on carbon acid pK_a shifts [7].



1



Methyl Red **2**



3

resorufin

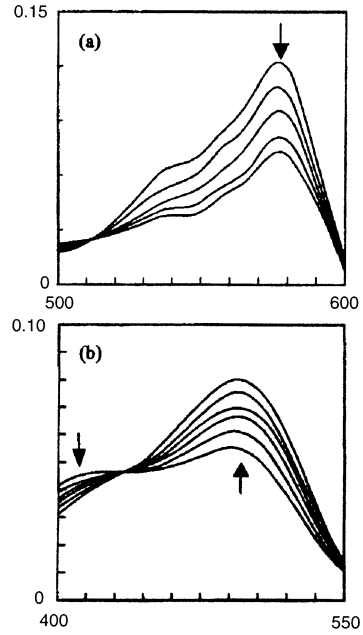
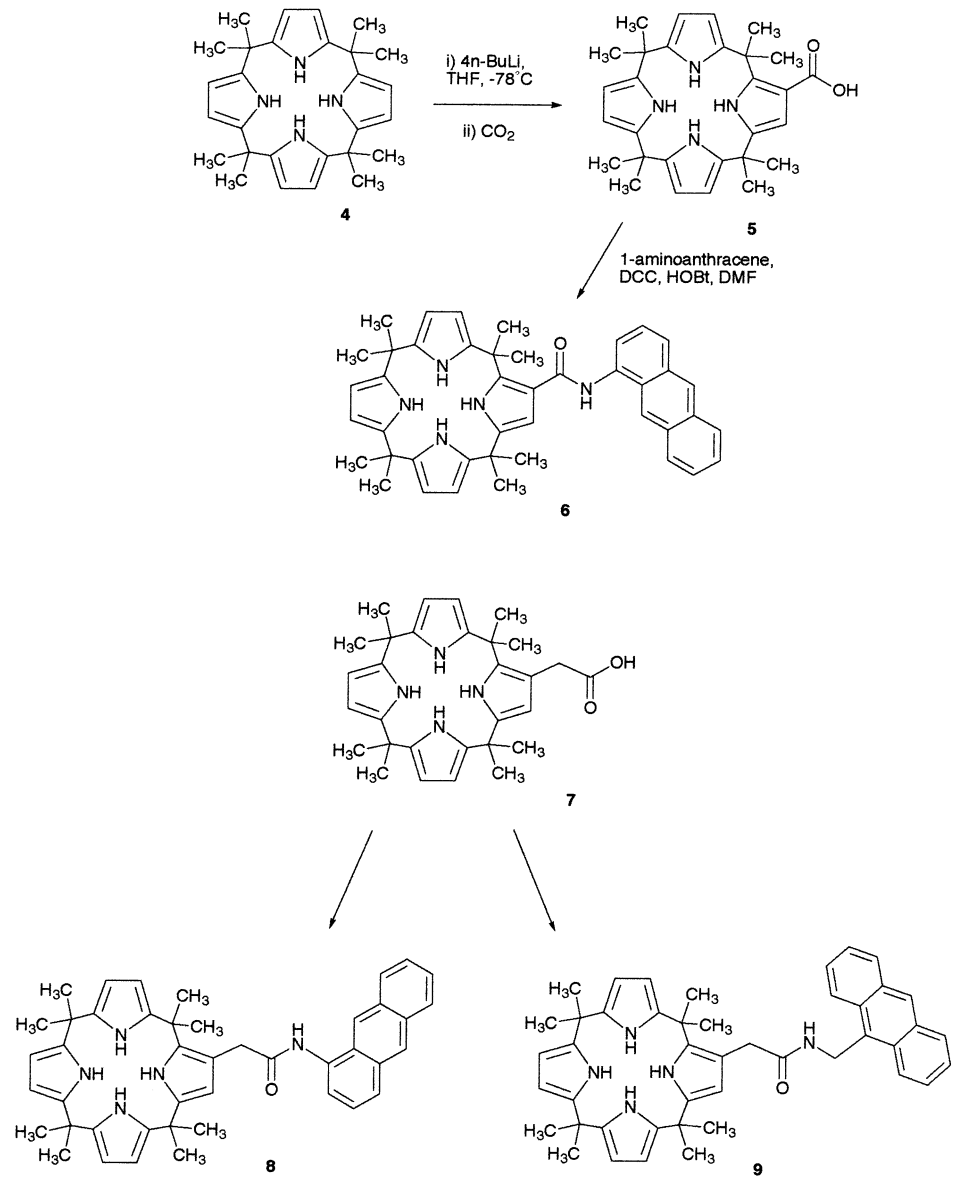


Fig. 1. UV–vis absorption spectra of: (a) Resorufin (**3**); and (b) Methyl Red (**2**) upon addition of receptor **1** in 1:1 MeOH–CH_2Cl_2 (v/v). [Indicator] = 2 μM, [**1**] = 0–20 mM. Reproduced with permission from *J. Chem. Soc. Perkin Trans.* 2 (1999) 1111, Copyright 1999, Royal Society of Chemistry.

Koca and co-workers have published computational studies on the stability of bis-aromatic amide complexes with bromide anions [8]. This work suggests that the stability of such complexes depends upon the length of the hydrogen bond formed to the anion along with induced non-planarity of the amide molecule which decreases possible unfavourable steric interactions.

2.2. Pyrrole based anion receptors

Sessler, Gale and Král have continued their studies of the anion binding abilities of calix[4]pyrrole macrocycles [9–15]. These tetrapyrrolic macrocycles bind anions by the formation of four pyrrole NH···anion hydrogen bonds. Sessler, Gale and co-workers synthesised a variety of calix[4]pyrrole anthracene conjugate compounds and demonstrated that these receptors can detect the presence of anions via significant perturbations in their fluorescence properties [16]. A new calix[4]pyrrole mono-acid derivative **5** was synthesised by treatment of *meso*-octamethyl-calix[4]pyrrole **4** with four equivalents of *n*-BuLi in THF at −78°C followed by addition of excess solid CO_2 (Scheme 1). This acid was then coupled to 1-aminoanthracene using DCC and HOBt in DMF to afford a calix[4]pyrrole–anthracene conjugate **6** (in 34% yield from the acid) that possesses a direct conjugated link



Scheme 1. Synthesis of fluorescent calix[4]pyrroles.

between the calix[4]pyrrole anion binding site and the anthracene fluorophore. Other calix[4]pyrrole–anthracene conjugates were synthesised by coupling the calix[4]pyrrole mono-acid **7** [11] with 1-aminoanthracene or 9-aminomethylanthracene using the BOP amide coupling agent to afford the conjugate compounds **8** and **9** in 63 and 51% yields, respectively. The matched set of compounds **6**, **8** and

9 therefore contain zero, one or two methylene groups between the calixpyrrole and anthracene fluorophore. Stability constants for anion binding were determined in acetonitrile-d_3 by ^{1}H-NMR titration techniques (Table 1). The fluorescence of receptors **6**, **8** and **9** was shown to be quenched significantly in the presence of certain anionic guests (most efficiently quenched by fluoride) and that of the three compounds, receptor **6** was most sensitive, having its fluorescence quenched most efficiently by the added anions. This may be due to the electron withdrawing effect of the directly linked amide group and also to the presence of the conjugated link between the anion binding site and fluorophore. The fluorescence spectrum of compound **6** upon addition of fluoride anions is shown in Fig. 2.

Gale, Twyman and co-workers have discovered a very simple colorimetric displacement assay for anions based on calix[4]pyrrole [17]. The 4-nitrophenolate anion **10** loses its intense yellow colour when bound to *meso*-octamethylcalix[4]pyrrole (**4**). This allows the calix[4]pyrrole–4-nitrophenolate complex **11** to be used as a colorimetric displacement assay (Scheme 2) in a similar manner to Anslyn's systems mentioned earlier. In this case anions, such as fluoride, displace the 4-nitrophenolate anion from the complex thus enhancing the absorbance of the 4-nitrophenolate anion. This was observed as a colourless to yellow colour change.

Král, Sessler, Gale and co-workers have produced ion selective electrodes (ISEs) containing calix[4]pyrrole moieties [18]. At lower pH values (e.g. 3.5 and 5.5), PVC derived ion selective electrodes containing **4** displayed strong anionic responses toward Br^-, Cl^- and $H_2PO_4^-$ and to a lesser extent F^-. However, at high pH 9.0 the calixpyrrole containing ISEs display non-Hofmeister selectivities ($Br^- < Cl^- < OH^- \approx F^- < HPO_4^{2-}$). At low pH the calixpyrrole macrocycles act as anion binding agents whereas at high pH the macrocycles are coordinating to

Table 1
Stability constants of compounds **6**, **8** and **9** with various anions in form of tetrabutylammonium salt determined by ^{1}H-NMR titration in acetonitrile-d_3 (errors < 15%).

Anion	Stability constant (log K) of compound **6** in CD_3CN	Stability constant (log K) of compound **8** in CD_3CN	Stability constant (log K) of compound **9** in CD_3CN
F^-	[a]	[a]	[a]
Cl^-	>4	>4	>4
Br^-	3.59	3.00	2.63
$H_2PO_4^-$	>4[b]	3.50	3.08
HSO_4^-	2.77	[c]	[c]

[a] NH resonance broadened precluding a determination of this value using NMR spectroscopic methods.
[b] Stability constant determined by following pyrrole CH resonance.
[c] Weak interaction $K < 20\ M^{-1}$.

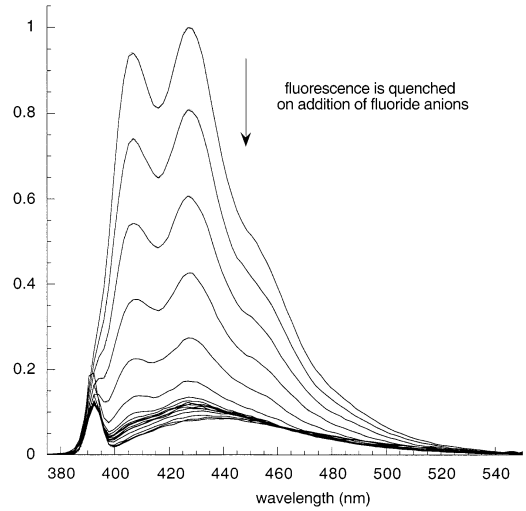
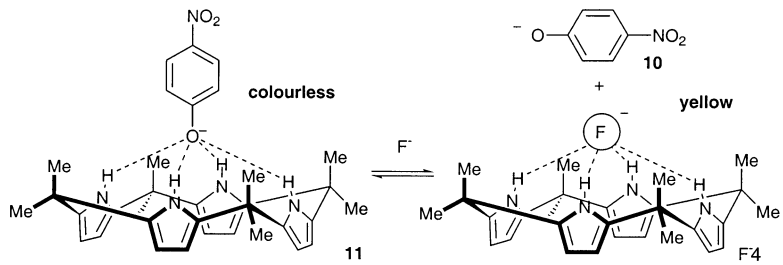


Fig. 2. Fluorescence spectrum of calixpyrrole **6** in CH_2Cl_2 (0.05 M) excited at 378 nm showing changes induced upon the addition of increasing quantities of tetrabutylammonium fluoride. Reproduced with permission from *Chem. Commun.* (1999) 1723, Copyright, 1999, Royal Society of Chemistry.

hydroxide anions. The behaviour of membranes containing dichlorocalix[2]-pyrrole[2]pyridine and tetrachlorocalix[4]pyridine were also reported.

Calix[4]pyrroles **12** formed from the condensation of 4-hydroxyphenylmethyl ketone (*p*-hydroxyacetophenone) have recently been reported (Fig. 3) [19,20]. The condensation of pyrrole with an unsymmetrically substituted ketone produces a calixpyrrole mixture consisting of a number of geometrical isomers. These isomers are referred to as αααα, αααβ, ααββ and αβαβ where the terms α and β indicate whether the bulkier substituent at the *meso*-position is oriented 'up' or 'down' relative to the plane of the macrocycle (Fig. 3).



Scheme 2. Colorimetric calix[4]pyrrole–nitrophenolate based displacement assay for anions.

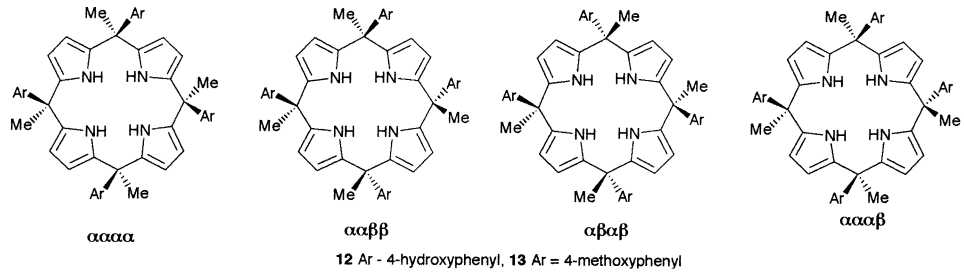


Fig. 3. Structures of calix[4]pyrroles (**12** Ar = 4-hydroxyphenyl; **13** Ar = 4-methoxyphenyl). Inequivalent CH positions are labelled with different letters (thus in αααα the CH protons are equivalent whilst in ααάβ there are four inequivalent sets of protons a, b, c and d.

Three of the isomers formed by the condensation of 4-hydroxyacetophenone and pyrrole (αααα, ααάβ and ααββ) have been isolated by column chromatography and their configuration confirmed by X-ray crystallography. The methoxy-derivatives **13** of these compounds were prepared by reaction of the pre-formed hydroxyphenyl calixpyrrole **12** with methyl iodide in acetonitrile in the presence of potassium carbonate. The stability constants of the various isomers of **12** and **13** with anions were determined by ^{1}H-NMR titration techniques. Although it was found that the stability constants of the isomers of **12** and **13** with anions were lower than compound **4** (Table 2), the identity of the particular isomer and the derivatisation of the hydroxy group was found to modulate the anion binding affinities of the receptor. The *meso*-substituents are therefore playing a role in the anion recognition process. The ease of functionalisation of these derivatives suggests that a wide variety of anion binding agents with tuneable selectivities will be accessible by simple derivatisation of the isomers of **12**. Floriani and co-workers subsequently reported the synthesis of similar compounds including 3-hydroxyphenyl derivatives [21].

Dehaen and co-workers have synthesised a variety of *N*-confused tetraspirocyclohexylcalix[4]pyrroles **15** and **16** by systematically altering the reaction conditions used for the pyrrole and cyclohexanone condensation reaction [22]. In all cases a significant quantity of the unconfused isomer **14** was also obtained.

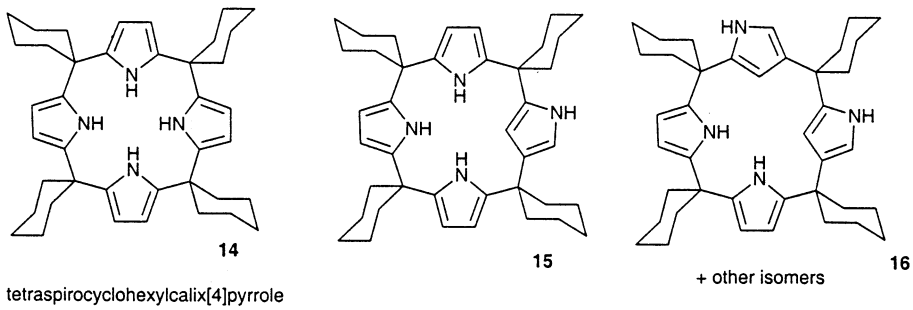


Table 2
Stability constants for compounds **4**, **12** and **13** (M^{-1}) with anionic substrates[a] in acetonitrile-d_3 (0.5% v/v D_2O) at 22°C

Compound	**4**	**12**			**13**		
Isomer		ααββ	αααβ	αααα	ααββ	αααβ	αααα
Fluoride	>10 000	>10 000	5000[c]	>10 000[b]	4600	1100[c]	>10 000
Chloride	>5000	1400[d]	260	320	<100	220	300
Phosphate	1300	520[d]	230	500	<100	<80	<100

[a] Acetonitrile-d_3 (0.5% v/v D_2O) solutions of receptors **12** and **13** (4.5 and 4.6 mM, respectively) were titrated by adding concentrated acetonitrile-d_3 (0.5% v/v D_2O) solutions of the anions in question (in the form of their tetrabutylammonium salts) that, to account for dilution effects, also contained receptors **12** and **13** at their initial concentrations. The data were fit according to the method of Wilcox using changes in both the NH and β-C*H* pyrrolic resonances unless otherwise indicated. Estimated errors were <15%. Binding stoichiometries, determined by Job plots, were 1:1 unless otherwise noted.

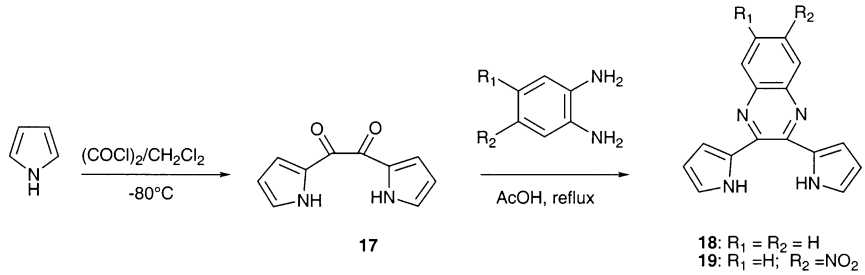
[b] At high [F^-]/[calixpyrrole] ratios, a second binding process, involving presumably interactions between the fluoride and the phenolic OH residues, is observed.

[c] Fit by following the change of two different β-pyrrole C*H* resonances.

[d] Fit by following the change of *meso*-aryl C*H* and β-pyrrole C*H* resonances.

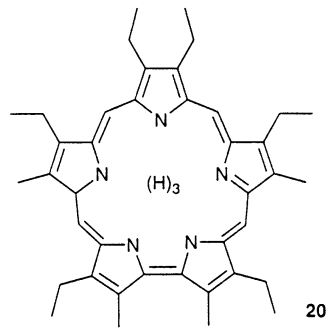
van Hoorn and Jorgensen have investigated the anion selectivities of calix[4]pyrroles using Monte Carlo simulations [23]. In agreement with experiment [9], they found that the 1,3-alternate isomer of calix[4]pyrrole was the most stable in the absence of anions whilst the cone conformer was the most stable conformation when the calix[4]pyrrole was bound to a halide anion. Free energy calculations on the binding of chloride, bromide and iodide in dichloromethane were found to be in excellent agreement with experiment, however the affinity of calix[4]pyrrole for fluoride anions was predicted to be higher than that which was observed (which was attributed to the presence of trace quantities of water in the NMR sample used to calculate the stability constant).

Sessler and co-workers have recently investigated 2,3-dipyrrol-2′-ylquinoxaline as a potential anion binding agent and sensor [24]. First synthesised in 1911 [25], the preparation of **18** was achieved by condensing oxalyl chloride with pyrrole at −80°C. Reflux of resulting 2,3-dipyrrol-2′-ylethanedione (**17**) with *ortho*-phenylenediamine in acetic acid affords 2,3-dipyrrol-2′-ylquinoxaline (**18**) in high yield (Scheme 3). Modification of this procedure with other 1,2-diaminobenzenes afforded a variety of 2,3-dipyrrol-2′-ylquinoxaline derivatives including 2,3-dipyrrol-2′-yl-6-nitroquinoxaline (**19**). UV–vis and fluorescence titration experiments were used to measure the anion affinity of **18** and **19**. The electronic influence of the functional groups present in the receptors play a crucial role in their recognition and sensing abilities. It was found that compound **19** has a higher affinity for fluoride in dichloromethane (1.2×10^5 M^{-1}), than compound **18** (2×10^4 M^{-1}). In fact, solutions of compound **19** undergo a dramatic yellow to purple colour change in the presence of fluoride. Both systems also display fluorescence emission spectra that are quenched in the presence of fluoride.



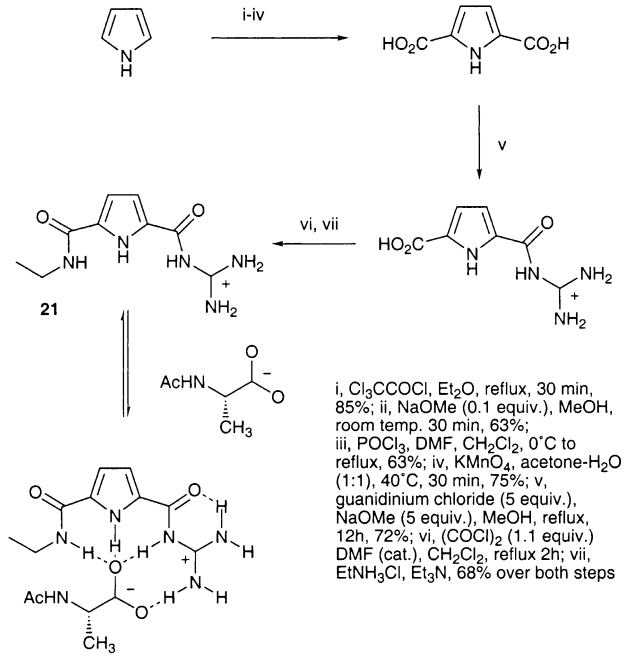
Scheme 3. Synthesis of colorimetric 23-dipyrrol-2′-ylquinoxaline anion sensors **18** and **19**.

Latos-Grazynski and Sessler have recently reported a detailed study of the NH-tautomerization of 2,7,18,23-tetramethyl-3,8,12,13,17,22-hexaethylsapphyrin (**20**) [26]. ^{1}H-NMR evidence showed that a planar 'pyrrole-in' macrocyclic geometry is favoured for **20** at all levels of protonation.



20

Schmuck has reported the synthesis of a pyrrole based receptor **21** for *N*-acetyl-α-amino acid carboxylates that functions in aqueous solution [27]. Compound **21** consists of a pyrrole ring substituted in the 2- and 5-positions by an amide group and a guanidinium moiety (Scheme 4). ^{1}H-NMR titration experiments in DMSO-d_6 revealed that 1:1 complexes are formed between **21** and *N*-acetyl-α-amino acid carboxylates. Binding was too strong to measure in DMSO alone hence solutions of the receptor were prepared in 40% H_2O–DMSO-d_6 and titrations carried out with and *N*-acetyl-α-amino acid carboxylates with a variety of different side chains. The results of these studies are shown in Table 3. Acetate is bound most strongly of all the carboxylates studied (presumably due to the absence of unfavourable steric interactions). The identity of the side chain present in the other carboxylates modulates the strength of the anion–receptor complex with π-stacking interactions between the acylguanidinium residue of the receptor and the aromatic ring of phenylalanine contributing to the stability of the **21**–Ac-L-Phe complex.



Scheme 4. Synthesis of pyrrole–guanidinium anion receptor **21**.

Table 3
Binding constants of **21** with various carboxylates[a]

Carboxylate	Solvent	K^b (M^{-1})	$-\Delta G$ (kJ mol^{-1})
Ac-L-Ala	DMSO-d_6	$>10^6$	
Ac-L-Ala	40% H_2O–DMSO-d_6	770	16.5
Ac-L-Phe	40% H_2O–DMSO-d_6	1700	18.4
Ac-L-Trp	40% H_2O–DMSO-d_6	810	16.6
Ac-L-Lys	40% H_2O–DMSO-d_6	360	14.6
Acetate	40% H_2O–DMSO-d_6	2790	19.7

[a] Measured by NMR titration, each one with ten measurements at 25°C; [carboxylate] = 1 mM in DMSO-d_6 or 40% H_2O–DMSO-d_6.
[b] Error limit in $K < \pm 5\%$.

2.3. Urea based anion receptors

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.

Stephan, Vögtle and co-workers have incorporated anion coordinating urea groups into the interior of lipophilic dendrimers **22**–**25** (Fig. 4) [28]. The dendrimers produced are soluble in organic solvents such as chloroform or

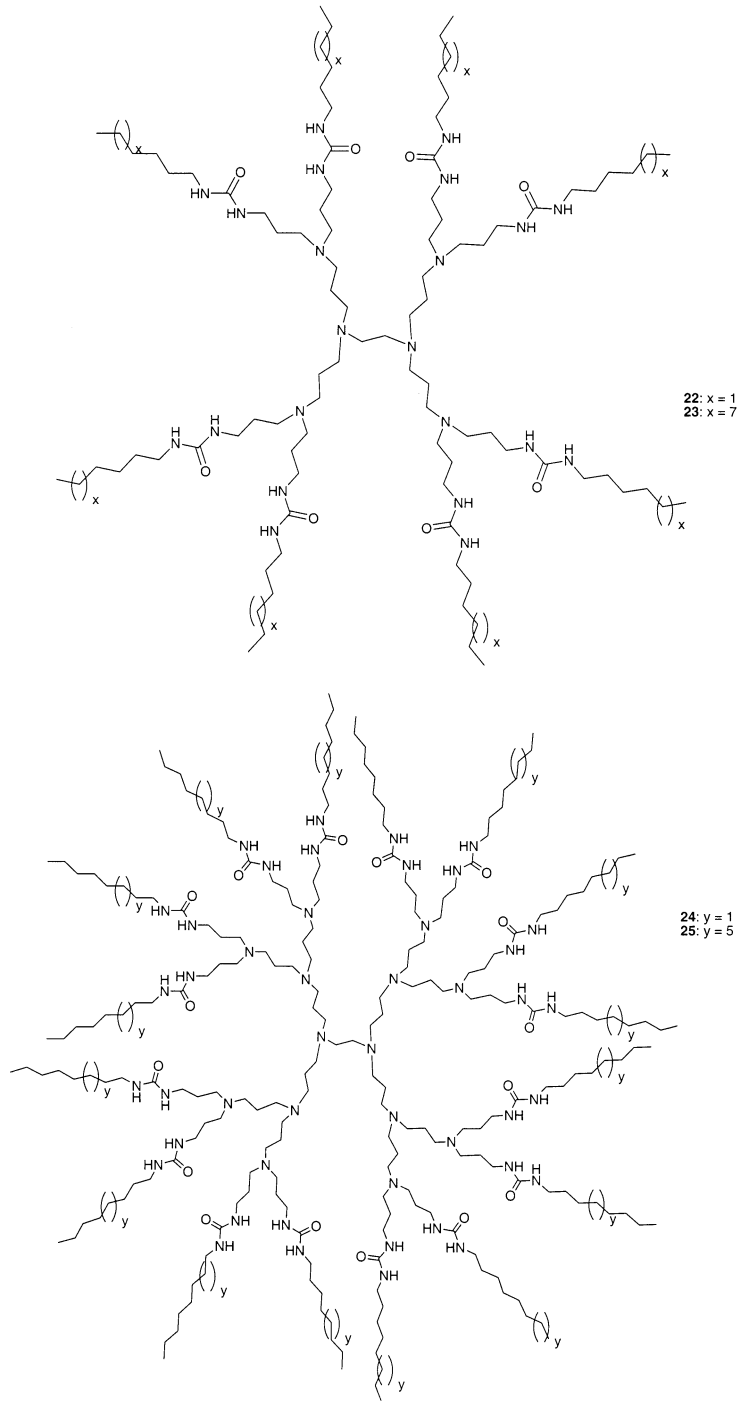


Fig. 4. Lipophilic dendrimers **22**–**25**.

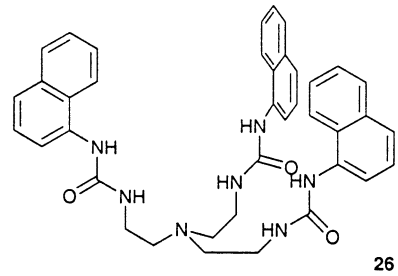
Table 4
Extractability of perrhenate, pertechnetate and nucleotides by dendrimers **22**–**25**

pH	Guest[a]	Percentage extraction			
		22	**23**	**24**	**25**
7.4	ReO_4^-	38.2	36.1	83.6	73.9
	TcO_4^-	48.5	45.9	90.3	82.9
	AMP	0.1	0.1	0.25	0.1
	ADP	0.1	0.1	1.0	0.6
	ATP	0.2	3.5	6.0	5.7
5.4	ReO_4^-	91.5	90.8	97.7	97.2
	TcO_4^-	95.7	95.3	98.8	98.6
	AMP	0.3	0.5	3.0	1.7
	ADP	3.8	9.9	73.5	61.7
	ATP	23.3	24.0	83.5	82.7

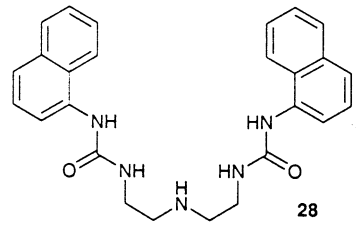
[a] $[KTcO_4] = [NH_4ReO_4] = [\text{nucleotide}] = 1 \times 10^{-4}$ mol dm^{-3}, pH 5.4 (MES–NaOH buffer), pH 7.4 (HEPES–NaOH buffer), [dendrimer] $= 1 \times 10^{-3}$ mol dm^{-3} in $CHCl_3$.

dichloromethane and are therefore suitable for performing liquid–liquid extraction of anions from aqueous solution. In fact the dendrimers were found to be capable of binding and transferring anions such as perrhenate, pertechnetate, AMP, ADP and ATP into an organic phase (Table 4) from aqueous solution. The stability of the pertechnetate complexes formed suggested that these systems may have potential applications as imaging agents.

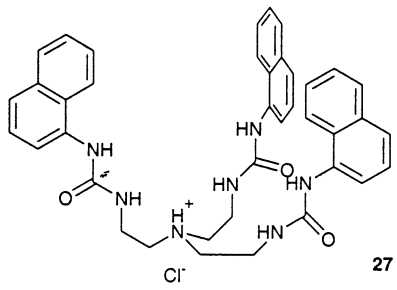
Wu and co-workers have synthesised tripodal hosts containing naphthylurea groups [29]. The anion coordination and fluorescence properties of **26** and **27** were compared with the model compounds **28** and **29**. They found that **26** is selective for $H_2PO_4^-$ in the presence of other putative anionic guest species.



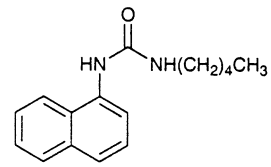
26



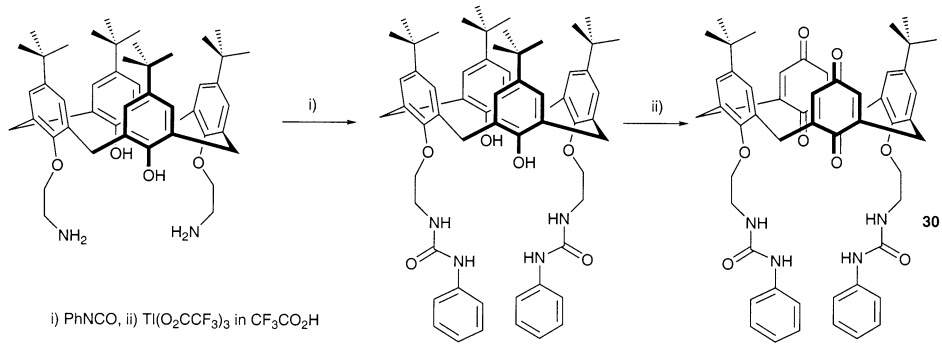
28



27



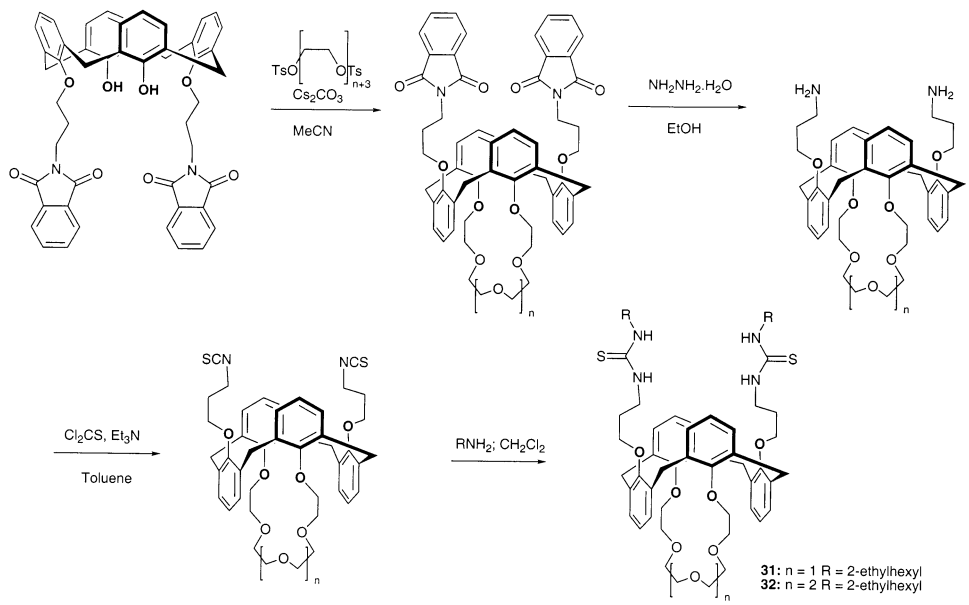
29



Scheme 5. Urea functionalised calix[4]diquinone synthesis.

Calix[4]diquinone with appended urea groups has been shown by Nam et al. to be selective for HSO_4^- over $H_2PO_4^-$, Cl^- and $CH_3CO_2^-$ [30]. The synthesis of receptor receptor **30** is shown in Scheme 5. Electrochemical experiments showed a corresponding cathodic shift of the quinone/semiquinone redox couple of 140 mV in the presence of HSO_4^- (smaller shifts occurred with other anions). Nam et al. have also studied the anion binding abilities of urea functionalised calix[4]arenes [31].

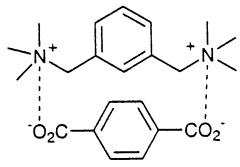
de Jong, Reinhoudt and co-workers have recently published a very detailed study of the transport of hydrophilic salts by mixtures of cation and anion receptors and by ditopic receptors [32]. The ditopic receptors **31** and **32** (Scheme 6) transported CsCl or KCl faster than other anion or cation receptors.



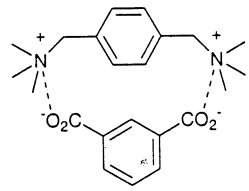
Scheme 6. Synthesis of ditopic calix[4]arene based ion pair receptors.

2.4. Polyammonium macrocycles and ammonium containing anion receptors

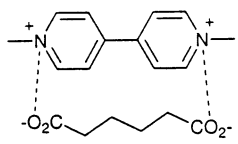
Some of the earliest examples of synthetic anion receptors were protonated or alkylated polyammonium macropolycycles. This topic continues to be an active area of research some 30 years later. Hossain and Schneider have measured the stability constants of the complexes formed between open-chain α,ω-dications (including bis-ammonium species) and α,ω-dianions by NMR titration techniques in water [33]. The structures of the complexes studied (**33**–**42**) are shown below. They found that although the number of flexible single bonds in the complexes range from six to 13, the strength of the complexes formed does not vary very much (ΔG values range from -12.6 to 16.3 kJ mol^{-1}). This leads the authors to conclude that importance of conformationally preorganised receptors for molecular recognition has been overestimated.



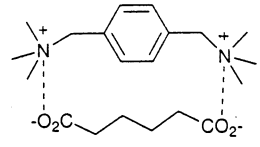
33



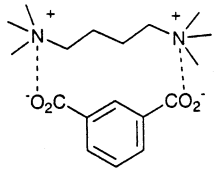
34



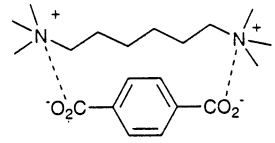
35



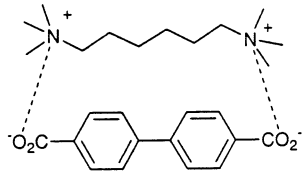
36



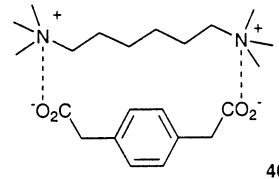
37



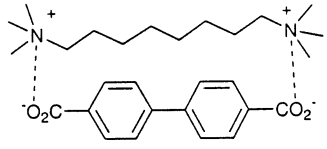
38



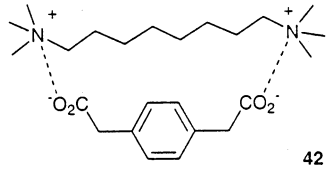
39



40

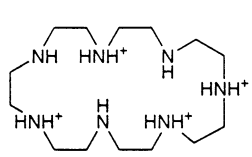


41

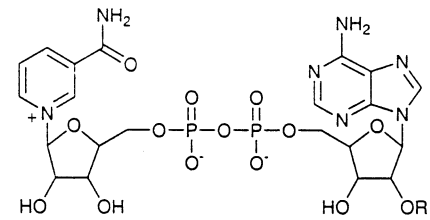


42

García-España, Celda, Bianchi and co-workers have continued their work on anion recognition by polyammonium macrocycles [34], and specifically the interaction of protonated 1,4,7,10,13,16,19-heptaazacyclohenicosane ([21]aneN$_7$) **43** with NAD$^+$ and NADP$^+$ in aqueous solution. This was studied using pH-metric titration, cyclic voltammetry and NMR. It was found that both NAD$^+$ and NADP$^+$ bind strongly to [21]aneN$_7$ (with varying degrees of protonation of the macrocycle). NADP$^+$ is selectively bound by the receptor over NAD$^+$ due to the extra phosphate moiety strongly interacting with two adjacent ammonium groups present in the receptor.

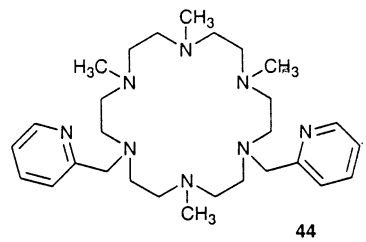


$H_4([21]aneN_7)^{4+}$ **43**



NAD$^+$ R = H
NADP$^+$ R = PO_3^{2-}

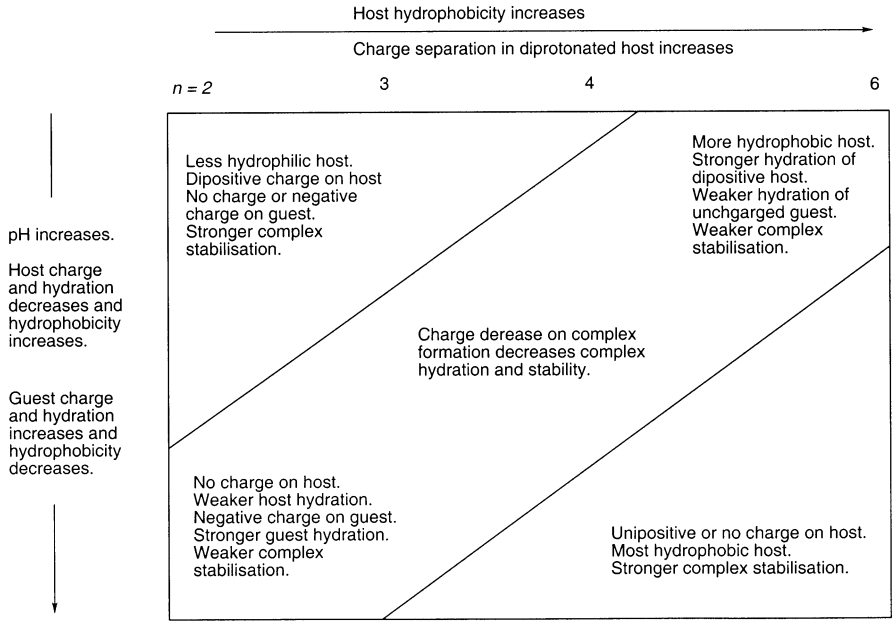
Benichi, Bianchi, Paoletti and co-workers have recently studied the cation and anion binding properties of receptor **44**, a hexaazamacrocycle containing two pyridine pendant arms showing that protonated forms of **44** are efficient receptors for ATP and ADP [35].



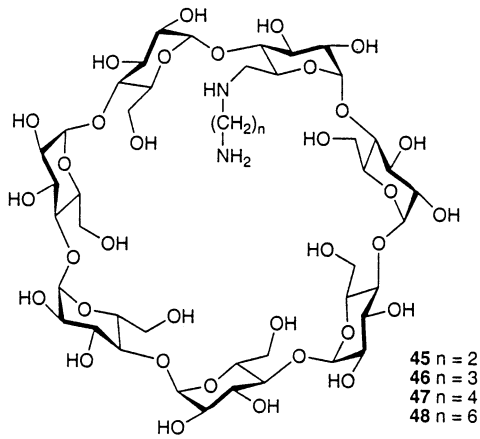
44

A very detailed account of the thermodynamics of phosphate and pyrophosphate anions by polyammonium receptors has also recently appeared [36] containing data on the interactions of phosphate and pyrophosphate with fourteen different receptors in aqueous solution.

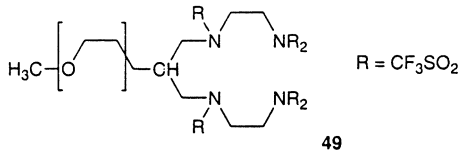
Lincoln and co-workers have studied the formation of complexes between 6^A-(ω-aminoalkylamino)-6^A-deoxy-β-cyclodextrins (**45**–**48**) and carboxylic acids/carboxylates in aqueous solution [37]. The charge and hydrophobicity of the receptor and guest were shown to be significant factors in controlling the stability of the complex. The weakest complex formed was that between **45**–H$^+$ and 4-methylbenzoate (140 ± 35 dm^3 mol^{-1}) and the strongest between **48** and (*S*)-2-phenylpropanoate (1760 ± 150 dm^3 mol^{-1}). A summary of the factors controlling complex stability is shown in Scheme 7.



Scheme 7. Factors affecting complex stability for **45**–**48**.

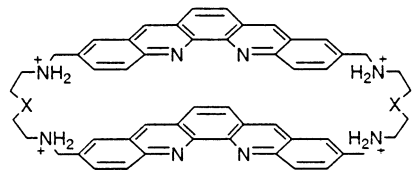


Lee et al. have synthesised a trifluoromethyl sulfonylated polyamine receptor **49** that complexes chloride anions in benzene [38]. The receptor was used to solubilise Neutral Red and Nile Blue chlorides in benzene.



49

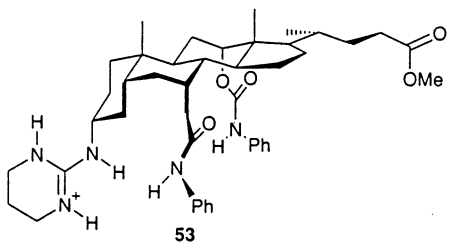
Cyclo-bis-intercaland receptors **50**–**52** have been reported by Tabet, Lehn and co-workers to coordinate anionic aromatic substrates such as nucleotides by a combination of π-stacking and electrostatic interactions [39]. Nucleoside monophosphates form 1:2 host–guest complexes with these receptors whilst nucleoside di- and triphosphates form 1:1 complexes with selectivity for guanosine derivatives. Compound **51** has also been shown act as a receptor for azobenzene dicarboxylates [40].



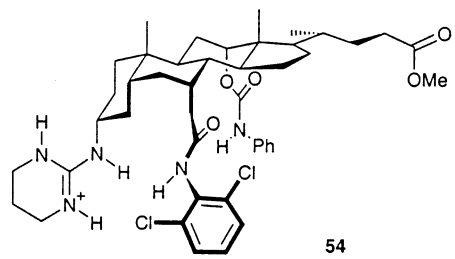
50 X = NH
51 X = O
52 X = CH_2-$N^+H(CH_3)$-CH_2

2.5. Guanidinium and amidinium

Davis and Lawless have synthesised two guanidinium functionalised steroids (**53** and **54**) and studied the extraction properties of these receptors with *N*-acetyl-α-amino acids [41]. **53**·Cl^- and **54**·Cl^- when dissolved in chloroform proved to be effective extraction agents for carboxylate anions from both neutral or alkaline solutions. *N*-acetyl-α-amino acids could also be extracted. However in these cases the extraction was enantiomer dependent (Table 5). Substrates with non-polar side chains were extracted with moderate to good efficiency, whilst the more polar *N*-Ac-asparagine was not extracted from aqueous solution. Molecular modelling of **54** and *N*-acetyl-L-valine suggests that the substrate carboxylate group accepts one hydrogen bond from the 7-carbamoyl group and two from the guanidinium moiety. Additionally, the acetyl oxygen atom is bound to the 12-carbamoyl NH group. This proposed structure is supported by NMR titration and NOE experiments.



53



54

By modifying gold surfaces with thiol-carboxylate compounds, Sellergren and co-workers have produced pH switchable self-assembled layers of bisbenzamidines

55 ($n = 2$, 5 or 8) [42,43]. They have recently shown that these monolayers can selectively adsorb oligonucleotides (Fig. 5) with binding being observed as an increase in the film thickness [44]. It was shown that when $n = 5$ the film preferen-

Table 5
Extractions by **53**·Cl^- and **54**·Cl^- of racemic *N*-acetyl-α-amino acids from aqueous buffer (pH 7.4) into $CHCl_3$[a]

Substrate	Receptor **53**		Receptor **54**	
	Extraction efficiency (mol%)[b]	Enantio-selectivity (L:D)[c]	Extraction efficiency (mol%)[b]	Enantio-selectivity (L:D)[c]
N-Ac-alanine	52	7:1	76	6:1
N-Ac-phenylalanine	87	7:1	93	9:1
N-Ac-tryptophan	83	7:1	92	6:1
N-Ac-valine	71	7:1	89	9:1
N-Ac-*tert*-leucine	[d]	[d]	82	5:2
N-Ac-methionine	[d]	[d]	93	9:1
N-Ac-proline	[d]	[d]	74	4:1
N-Ac-asparagine	0	–	0	–

[a] Solutions of receptor in $CHCl_3$ (6 mM, 1 ml), and substrate in phosphate buffer (7-8 mM, 5 ml) were stirred vigorously for 2 h. The organic phases were isolated, dried by passage through hydrophobic filter paper, then evaporated. The residues were dissolved in $CDCl_3$ (0.6 ml) and analysed by ^{1}H-NMR spectroscopy.
[b] Determined by ^{1}H-NMR integration of substrate α-CH and NH versus 7/12β-H of receptor.
[c] Determined by ^{1}H-NMR integration of α-CH and NH signals for enantiomers of substrates. Assignments confirmed through control experiments with enantiopure substrates.
[d] Not determined.

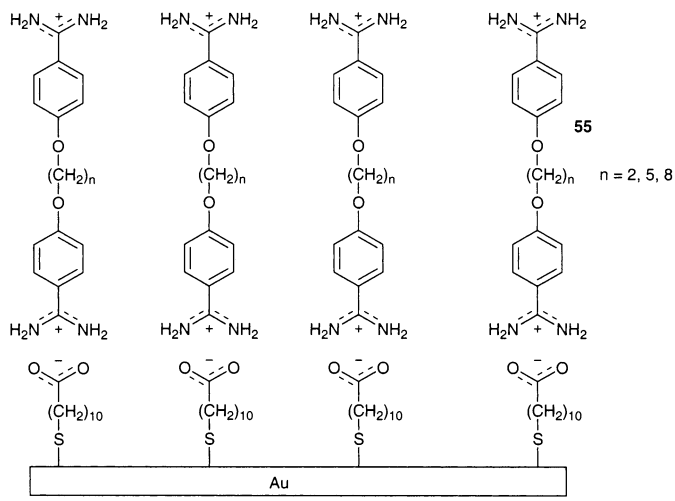


Fig. 5. 3′-dTTTTTTTTTT-5′ a self-assembled layer of bisbenzamidine bound to T10.

Table 6
Layer thicknesses upon consecutive addition of bisbenzamidines and a 10-mer DNA oligonucleotide to a self-assembled monolayer (SAM) of mercaptoundecanoic acid (MUA) on gold[a]

DNA	Layer thickness (Å)			
	$n = 5$		$n = 8$	
Oligo-nucleotide[b]	amidine[c]	DNA[d]	amidine[c]	DNA[d]
T10[e]	13 ± 1	14 ± 2	23 ± 1	33 ± 3
C10	12 ± 0	2 ± 1	24 ± 2	3 ± 3
G10	14 ± 1	11 ± 1	24 ± 3	2 ± 1
A10	14 ± 1	1 ± 1	25 ± 5	12 ± 1

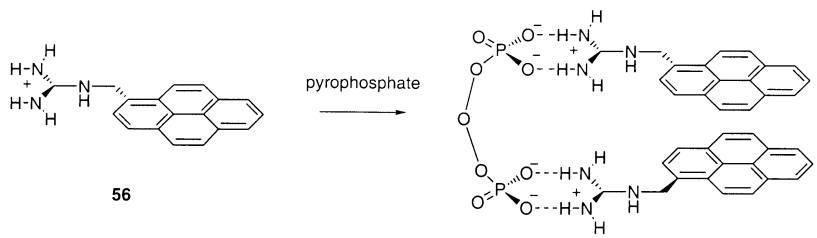
[a] The substrates were immersed in a quartz ellipsometric cuvette containing 5 ml sodium borate buffer (0.01 M, pH 8.7, prepared from boric acid) thermostatted to 25°C and equipped with a small magnetic stirrer and a pH electrode. Adsorption of compounds was then monitored in situ by null ellipsometry assuming a film refractive index of 1.45. The reported values were determined when the change in the polariser angle had levelled off. After one experiment the surfaces were restored by adjusting the pH to 2–3 with 0.1 M HCl followed by rinsing in water.

[b] 10mer DNA oligonucleotides of deoxythymidylic acid (T10), deoxycytidylic acid (C10), deoxyguanylic acid (G10) and deoxyadenylic acid (A10).

[c] Increase in layer thickness ca. 200 s after addition of bisamidine ($n = 5$) or bisamidine ($n = 8$) (100 μl of a 2.5 M stock solution).

[d] Increase in layer thickness 200–300 s after addition of the oligonucleotide (5 ml of a 0.5 mg ml^{-1} stock solution) to the solution described in note c. The spread of the thickness values from duplicate runs has been indicated.

[e] Using bisamidine ($n = 2$) the layer thickness was 11 ± 1 Å and of T10 was 5 ± 1 Å.

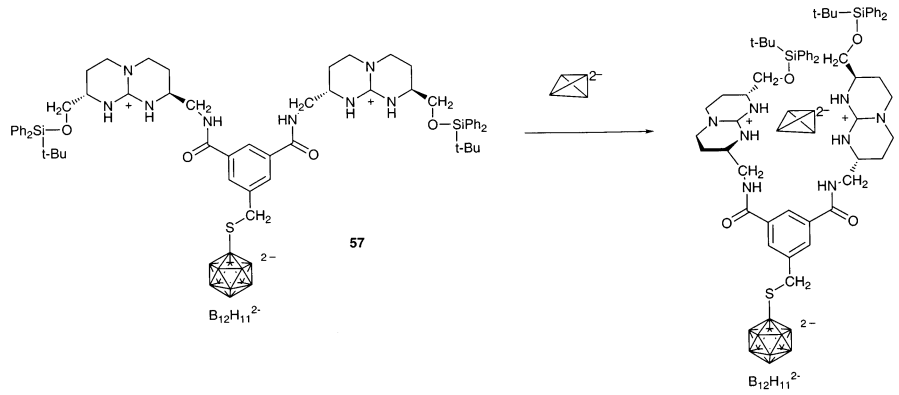


56

Scheme 8. Self-assembly of the 2:1 complex between pyrene functionalised monoguanidinium species **56** and pyrophosphate.

tially binds T10 and G10 whereas when $n = 8$ the film preferentially binds T10 and A10 (Table 6).

The pyrene functionalised monoguanidinium species **56** forms a 2:1 receptor–anion assembly with pyrophosphate (Scheme 8) that senses this anion via dramatic changes in the fluorescence of the pyrene moiety [45]. Other anions such as HPO_4^{2-}, $H_2PO_4^-$, $CH_3CO_2^-$, SCN^-, Cl^- or Br^-, do not trigger the formation of the self-assembled array and hence show much weaker perturbations in pyrene fluorescence.



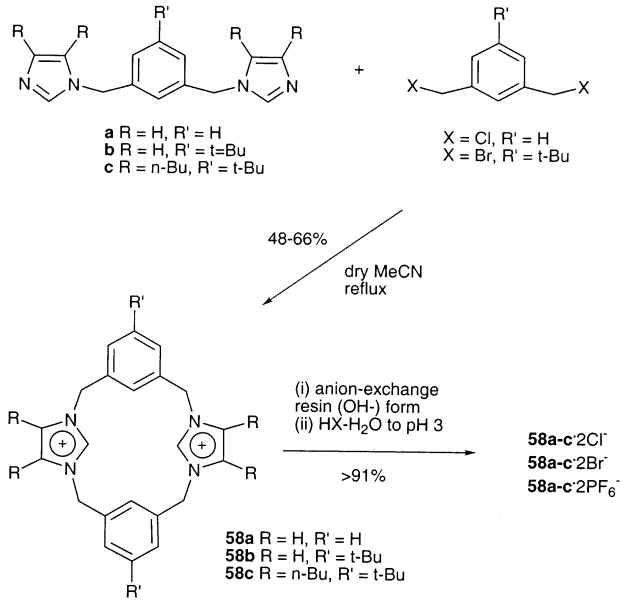
Scheme 9. Receptor **57** forming a complex with a tetrahedral anion.

The zwitterionic guanidinum receptor **57** (Scheme 9) has been shown to act as an extremely efficient receptor for anions ($K = 3.1 \times 10^4$ M^{-1} for squarate in DMSO). In an extremely elegant paper [46], Berger and Schmidtchen have used titration calorimetry to show the major role that entropy plays in complex formation overriding positive binding enthalpies. Thus complexation in this case is predominantly entropy driven.

2.6. Other non-metallated anion receptors

Alcalde and co-workers have shown that imidazoliophane macrocycles act as anion receptors via the formation of unusual CH···anion hydrogen bonds [47]. Receptor **58** was synthesised by a '3 + 1' convergent synthesis shown in Scheme 10 and the chloride, bromide and hexafluorophosphate salts then prepared using an anion exchange resin. The X-ray crystal structure of **58a**·$2Cl^-$·$2H_2O$ revealed hydrogen bonding between a chloride anion and the macrocycle *m*-xylyl hydrogen and the acidic hydrogen on the imidazolium ring (Fig. 6). The chloride anion is also hydrogen bonded to a water molecule. Solution studies showed significant downfield shifts of the imidazolium ring protons upon addition of anions with the following anions giving progressively smaller shifts in DMSO-d_6: dihydrogenphosphate > fluoride > acetate > cyanide > chloride.

Sato and co-workers have synthesised a tripodal receptor **59** containing three imidazolium groups that coordinate anions via a combination of hydrogen bonding and electrostatic interactions (Scheme 11) [48]. Model compounds **60** and **61** were also synthesised and the stability constants of all three receptors measured with halide anions in acetonitrile-d_3. The results are shown in Table 7. The tripodal receptor **59** is more preorganised for anion coordination than **60** or **61** giving rise to larger stability constants. These results concur with those of Anslyn and co-workers who have produced a number of similar preorganised tripodal anion receptors containing different anion coordinating moieties [3,49,50].



Scheme 10. Synthesis of receptor **58**.

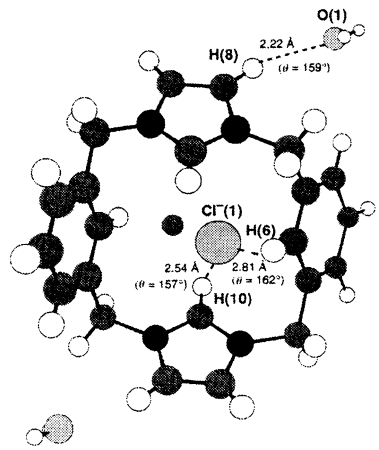
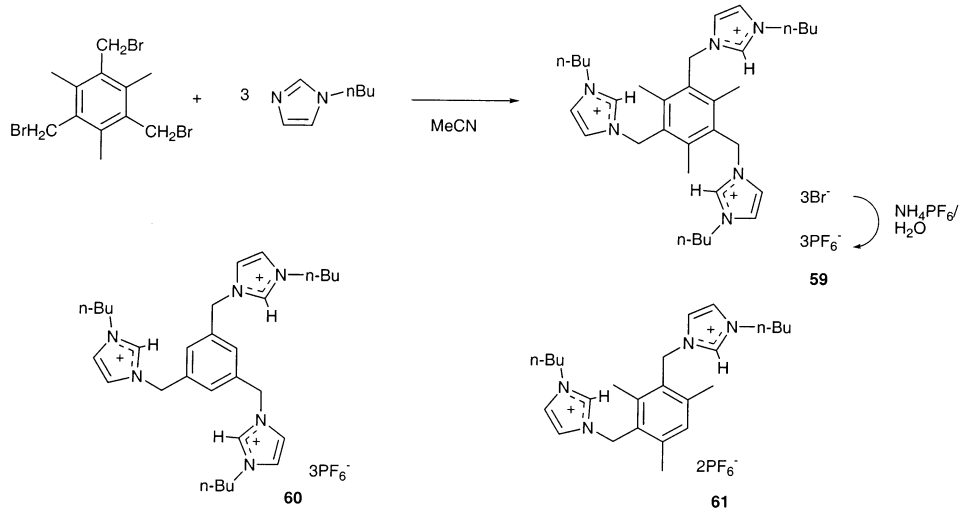


Fig. 6. Molecular structure of **58a**·2Cl·2H_2O. Reproduced with permission from *Chem. Commun.* (1999) 295, Copyright 1999, Royal Society of Chemistry.

An interesting account of chiral anion recognition by cyclodextrins has been published by Kano and co-workers [51]. They found that native β-cyclodextrin **62** binds the two enantiomeric forms of the tetrahelicene **64** with significantly different stability constants (18700 ± 1700 dm^3mol^{-1} for the *M* enantiomer and 2200 ± 100 dm^3mol^{-1} for the *P* enantiomer). γ-Cyclodextrin **63** forms weaker complexes with



Scheme 11. Synthesis of receptor **59** and structures of **60** and **61**.

64. However enantioselectivity is also observed for the larger host. This effect is caused by the deeper penetration of the *P* form of the helicene into the cyclodextrin cavity. This leads to a favourable entropic component to the binding (*P* enantiomer will desolvate to a greater degree than the *M* enatiomer) but an unfavourable enthalpic component. The enatioselectivity is dominated by the enthalpic differences between the complexation of the two enantiomers.

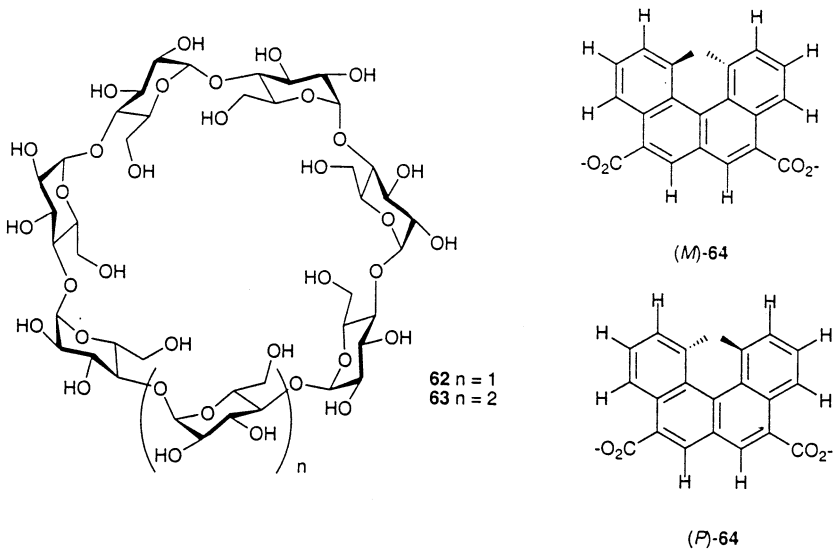


Table 7
Association constants for receptors **59**–**61** with halide anions in acetonitrile-d_3 at 298 K (errors $\pm$ 10%)

Receptor	Anion	K (M^{-1})
59	Cl^-	75 000
59	Br^-	46 000
59	I^-	7200
60	Cl^-	1500
61	Cl^-	1300

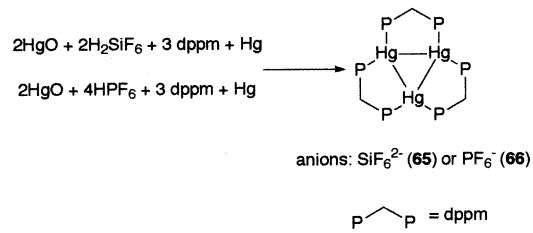
3. Metals and Lewis acids

The previous section of this review covered metal-free anion receptors. We will now go on to look at metal or Lewis acid containing anion receptors that have appeared in the literature in 1999. The metal ions in these receptors play a number of different roles which may be classified as follows:
1. metals or Lewis acids as binding sites in anion receptors;
2. metals or Lewis acids as organisational elements in anion receptors;
3. metals or Lewis acids in anion sensors.

Of course, a receptor may fall into more than one of these categories. It should therefore be noted that these categories are not hard and fast and are only in place as an aid to the reader.

3.1. Metals or Lewis acids as binding sites in anion receptors

Peringer and co-workers have prepared the subvalent mercury clusters Hg_3(μ-dppm)$_3(SiF_6)_2$ (**65**) and Hg_3(μ-dppm)$_3(PF_6)_4$ (**66**) (Scheme 12) and shown that the mercury containing cations coordinate counter anions [52]. They determined the crystal structures of these salts in addition to the structures of Hg_3(μ-dppm)$_3(O_3SCF_3)_4$, Hg_3(μ-dppm)$_3(O_3SCF_3)_4$·MeOH, Hg_3(μ-dppm)$_3(O_3SCH_3)_4$ and Hg_3(μ-dppm)$_3(O_3SCH_3)_4$·$4H_2O$ and found in all cases two anions inside the cavities formed by the twelve phenyl groups (Fig. 7). Solution NMR studies of the salts in dichloromethane-d_2 showed a shift of the ^{31}P resonance with different counter anions (Table 8).



Scheme 12. Synthesis of complexes **65** and **66**.

Following on from their earlier work [53], Mulvey and co-workers have synthesised a heterobimetallic amide-supported macrocycle **67** containing a positively charged $(N_4K_2Mg_2)^{2+}$ octagonal ring system that encapsulates a dianionic O_2^{2-} core [54]. The peroxo-centred macrocycle was synthesised according to Scheme 13 in 23% yield. The crystal structure of **67** is shown in Fig. 8 and reveals the oxygen

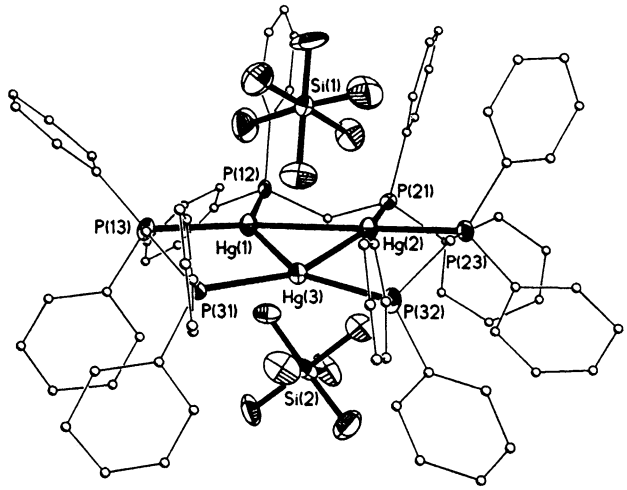
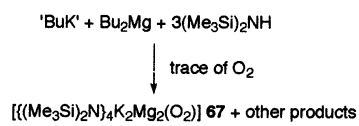


Fig. 7. An ORTEP representation of **65**. Reproduced with permission from *J. Chem. Soc. Dalton Trans.* (1999) 2526, Copyright 1999. Royal Society of Chemistry.

Table 8
^{31}P-NMR chemical shifts of the cluster $[Hg_3(\mu\text{-dppm})_3]^{4+}$ with different oxo- and fluoro-anions (solvent dichloromethane-d_2)

Anion	δ ^{31}P
SO_4^{2-}	44.7
$CH_3SO_3^-$	49.4
SiF_6^{2-}	49.9
$CF_3SO_3^-$	54.7
PF_6^-	60.5



Scheme 13. Synthesis of **67**.

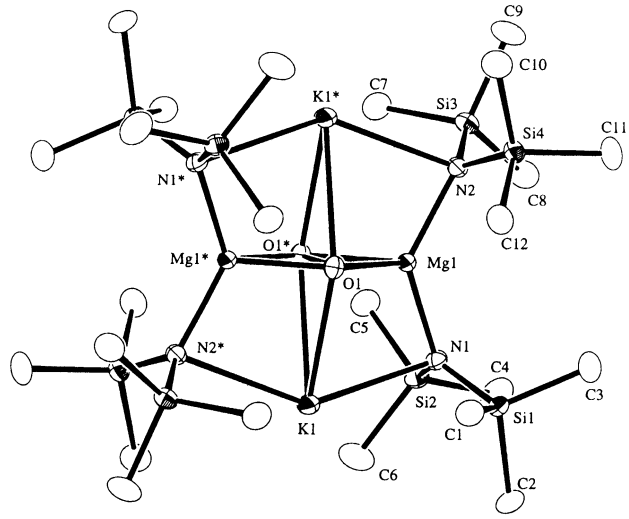


Fig. 8. Double asymmetric unit of **67**. Hydrogen atoms have been omitted for clarity. Reproduced with permission from *Chem. Commun.* (1999) 353, Copyright 1999, Royal Society of Chemistry.

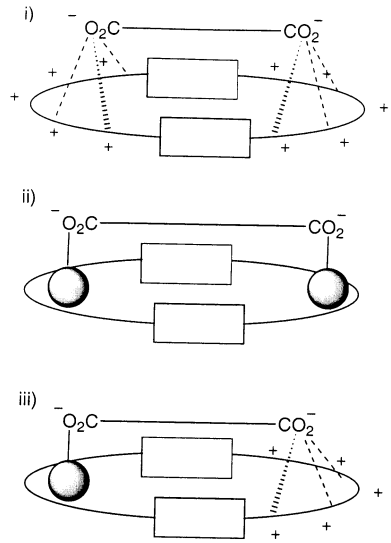


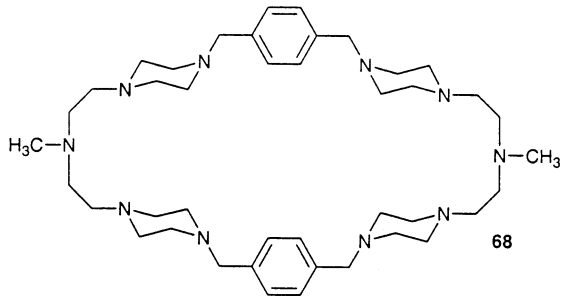
Fig. 9. Supramolecular and coordinative binding modes of dicarboxylate anions by the ditopic cyclophane ligand and its 1:1 and 1:2 complexes with Cu(II).

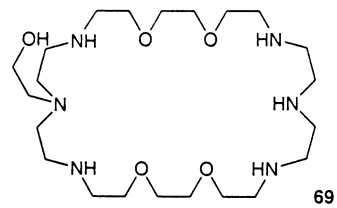
anion bound to the macrocycle metal atoms with oxygen atom-metal distances between 2.010(1) and 2.903(1) Å.

Bencini, Bianchi, Garcia-España and co-workers have synthesised a ditopic cyclophane ligand **68** composed of two pentamine moieties each one containing two piperazine rings [55]. This receptor contains two binding sites, each composed of

five nitrogen atoms, which may be protonated or coordinate to a metal ion. In the absence of metal ions the protonated forms of **68** binds pimelate anions in addition to hydrogen pimelate and pimelic acid with varying stability constants across the pH range. In the presence of copper(II) both 1:1 and 2:1 metal–receptor complexes are formed. The proposed coordination modes of dicarboxylate anions by **68** and its metal complexes are shown in Fig. 9. The crystal structure of the pimelate–dicopper complex of **68** was elucidated (Fig. 10) and revealed that the dicarboxylate is indeed coordinated to both copper centres. It was found that above pH 8, the guest anion is released upon formation of a dihydroxylated dicopper complex.

The same research group have also studied the hydrolysis of carboxy- and diphosphate esters by the dizinc complex of receptor **69** [56].





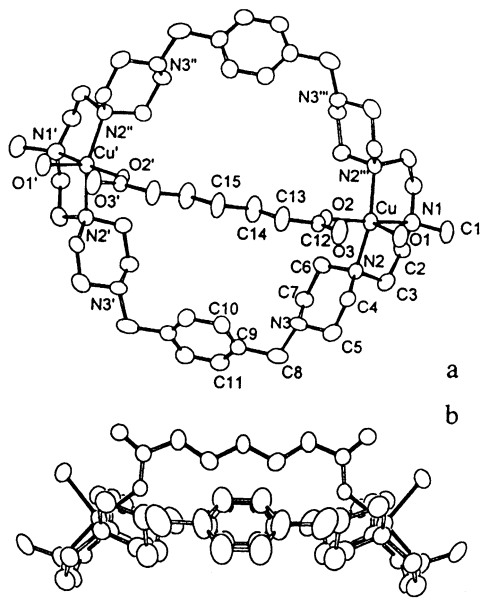


Fig. 10. ORTEP representation of $\{[Cu_2\mathbf{68}(H_2O)_2]$–pimelate$\}^{2+}$ complex (thermal ellipsoids are at the 30% probability level. Reproduced with permission from *Inorg. Chem.* 38 (1999) 620, Copyright 1999, American Chemical Society.

Herman and co-workers have prepared the dicopper complex of receptor **70** and shown that it acts as a host for alanine, valine, leucine, norleucine, norvaline and serine anions (the alanine complex is shown in Fig. 11) [57]. Complexation was investigated using potentiometric pH-metry, spectrophotometric titrations and by IR spectroscopy. The stability constants of the complexes are shown in Table 9.

Fabbrizzi and co-workers have followed on from their earlier work [58] and published a detailed account of redox driven anion translocation between transition metal centres in complex **71** (Scheme 14) [59]. Complex **71** consists of a four-coordinate nickel(II) cyclam-like macrocycle attached to a tripodal tren group coordi-

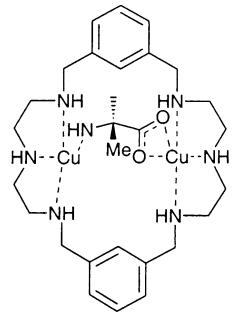
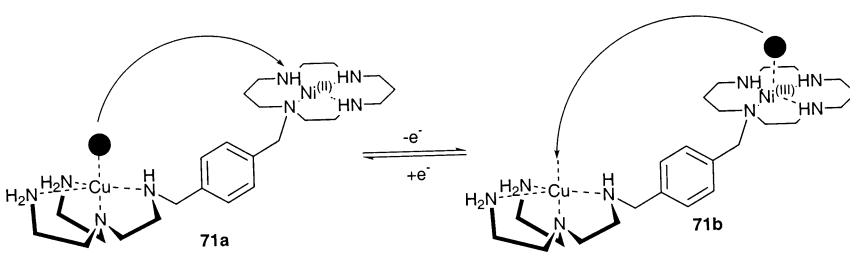


Fig. 11. The alanine complex of **70**–Cu_2.

Table 9
Stability constants for the ternary complexes formed in the Cu(II):**70**:guest system ($I = 0.10$ mol dm^{-3} $NaClO_4$; 25°C)

Equilibrium[a,b]	log K					
	Alanine	Leucine	Norleucine	Norvaline	Serine	Valine
$Cu\mathbf{70}H_2 + G \leftrightarrow Cu\mathbf{70}GH_2$	4.03	4.03	4.13	4.13	4.13	4.13
$Cu_2\mathbf{70} + G \leftrightarrow Cu_2\mathbf{70}G$	6.83	6.83	7.16	6.92	6.56	6.92
$Cu_2\mathbf{70}(OH) + G \leftrightarrow Cu_2\mathbf{70}G(OH)$	4.32	4.92	5.85	5.65	4.85	–

[a] Charges omitted for clarity.
[b] No differences were obtained between the D- and L-isomers.



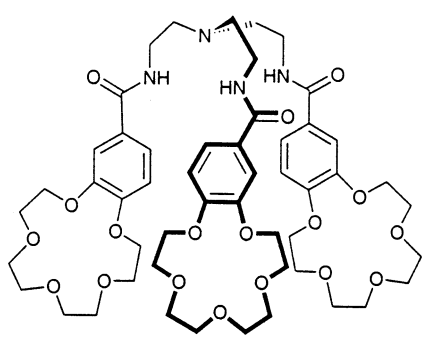
Scheme 14. Redox-driven anion translocation in complex **71**.

nated to a single copper(II) metal ion. Inorganic anions can displace water molecules bound to the copper(II) centre forming complex **71a** (Scheme 14). The nickel centre may then be oxidised electrochemically to Ni(III) — an oxidation state that requires a further ligand in the axial position. Oxidation therefore causes reversible translocation of copper bound anions (such as chloride) to the Ni(III) ion. The process is reversible, with reduction of **71b** causing a translocation of the nickel bound anion back to the copper centre.

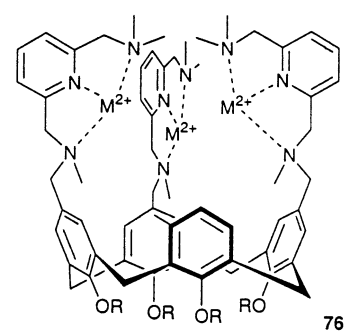
Astruc and co-workers have continued their work [60] on anion binding iron containing dendrimers [61]. The multiply positively charged dendrimer **72** was synthesised by a divergent synthetic procedure in 61% yield. The anion recognition properties of **72** (24Fe–Ar) were measured by ^{1}H-NMR titration techniques in DMSO-d_6 and compared with those of the model compounds **73** (1Fe–Ar) and **74** (3Fe–Ar) (Fig. 12). In all these cases the anion is presumably bound via a combination of electrostatic and hydrogen bonding interactions. The stability constants revealed that the dendrimer is selective for chloride and bromide (Table 10). This is attributed to the formation of peripheral cavities formed between the dendrimer branches.

Beer and co-workers have reported that the tren-based receptor **75**, that contains an amidic anion-binding cavity linked to three cation binding benzo-15-crown-5 groups, efficiently extracts sodium pertechnetate from simulated aqueous nuclear waste streams [62]. In the absence of co-bound cations, the anion binding affinity of the receptor was considerably reduced (Table 11). In this case the pertechnetate anions are presumably bound by a mixture of hydrogen bonding and electrostatic interactions.

Calix[4]arene based tris-zinc complexes have been shown by Engbersen, Reinhoudt and co-workers to cleave RNA dinucelotides (3′,5′-NpN) by the cooperative action of the zinc centres [63]. Receptor **76** (M = Zn) cleaves GpG 8.5 times faster than UpU and 160 times faster than ApA. A proposed mechanism for this selectivity is presented in this paper together with catalysis data for mixed metal systems and analogues with only two metal binding sites.



75



76

M = Cu, Zn

R = CH_2CH_2OEt

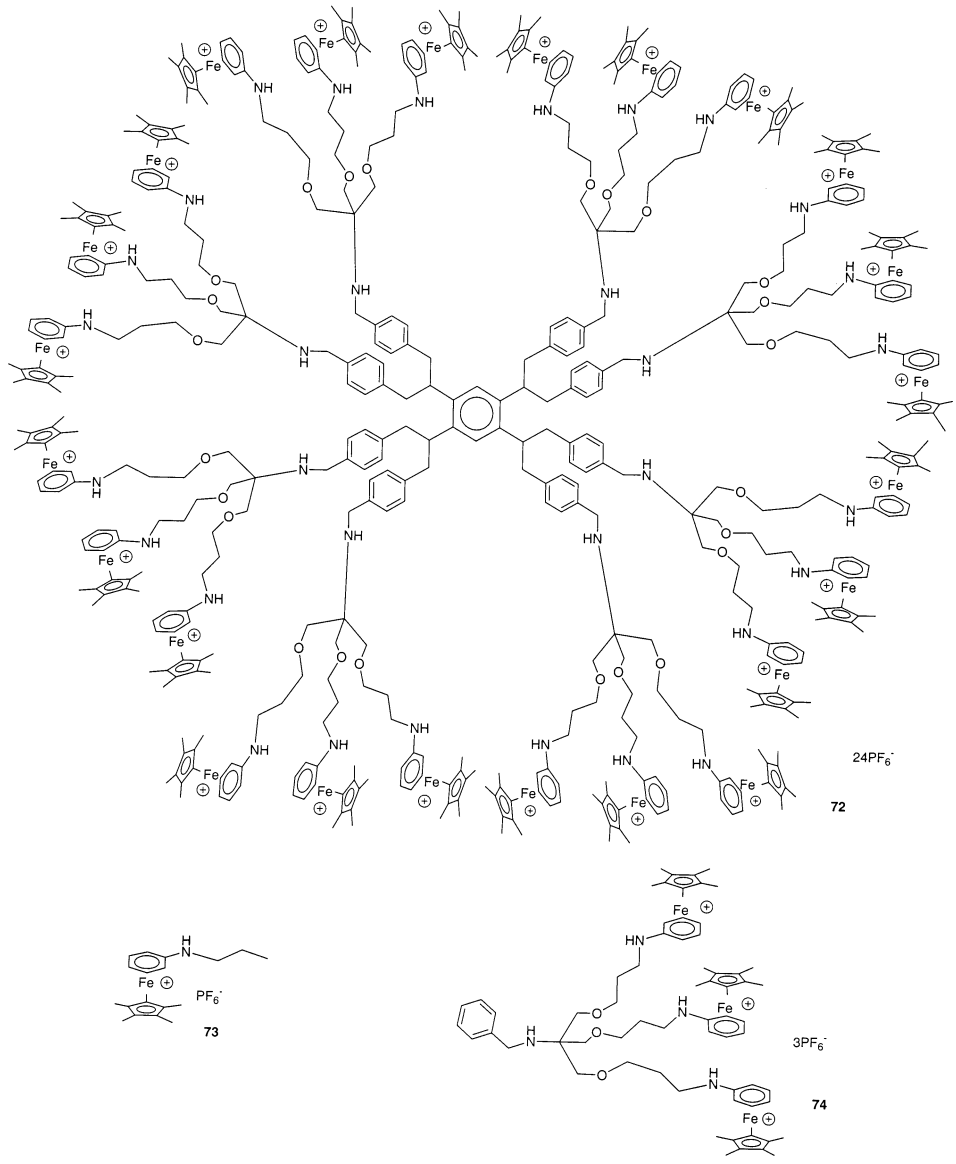


Fig. 12. Dendrimer **72** and model compounds **73** and **74**.

Table 10
Apparent association constants K_{app} (M^{-1}) determined from the variation of the NH signal in DMSO-d_6 at 20°C

	73 (1Fe–Ar)	**74** (3Fe–Ar)	**72** (24Fe–Ar)
Cl^-	10	118	1221
Br^-	2	129	431
HSO_4^-	14	461	6

Table 11
Stability constants for anion binding by **75** in the presence and absence of sodium picrate in chloroform-*d*

Guest	K (M^{-1})
Cl^-	60[a1]
$Cl^-(+Na^+)$[b1]	520[c1]
I^-	30[a1]
$I^-(+Na^+)$[b1]	390[c1]
ReO_4^-	40[a1]
$ReO_4^-(+Na^+)$[b1]	840[c1]

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

3.2. Metals or Lewis acids as organisational elements in anion receptors

Palladium and platinum metal ions have been used by Lippert and co-workers to construct a highly charged (+ 12) anion receptor [64]. Receptor **77** (Fig. 13(a)) was synthesised by addition of (en)Pd(II) to Lippert's previously synthesised molecular triangle [65]. The crystal structure of $\mathbf{77}^{12+}$ reveals that the platinum atoms form an equilateral triangle with side lengths of 7.88(1) Å. The top and side views of the cation are shown in Fig. 13(b and c), respectively and shows that the Pd(en) groups define calixarene like cavities on both the top and bottom faces of the receptor. The X-ray crystal structure also reveals a nitrate ion bound at the bottom of the cavity with its oxygen atoms pointing directly at the platinum metal centres (Fig. 13(d)) (Pt–O 3.49(1), 3.26(1), 3.39(1) Å). A hexafluorophosphate anion is bound above the nitrate ion with three of its fluorine atoms directed at the platinum metals (Fig.

Table 12
Association constants for receptor **77** (nitrate salt) with a variety of anions in water at 20°C pD = 2.9[a1]

Anions	$K \pm 3\sigma$ (M^{-1})
PF_6^-	10.6 ± 3.9
ClO_4^-	9.6 ± 4.5
BF_4^-	4.1 ± 1.1
SO_4^{2-}	255.8 ± 57.3
TSP	0.0

[a] TSP = sodium-3-(trimethylsilyl)propancesulfonate.

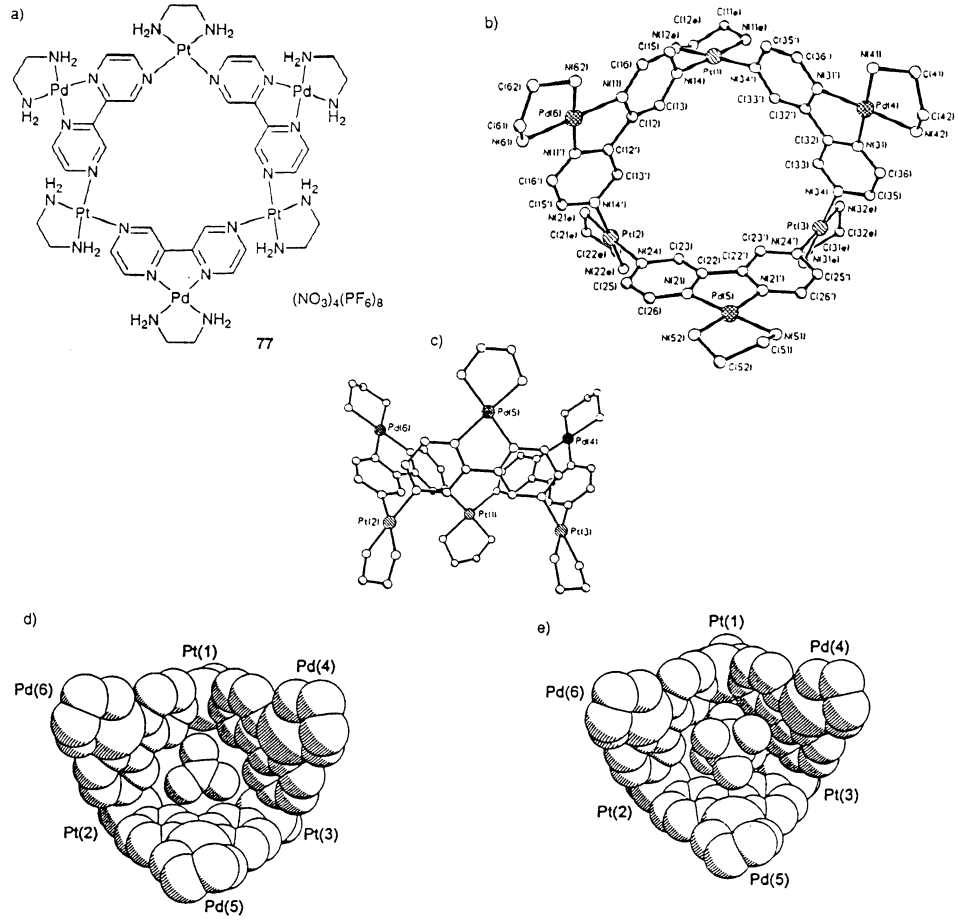


Fig. 13. Structure of **77** (a) top and side views (b) and (c) of the crystal structure of **77**. Space filling model (d) of the cation **77** with an NO_3^- ion at the bottom of the calixarene like cavity, and spacefilling model (e) of the encapsulation of the PF_6^- ion in **77** (NO_3^- omitted for clarity). Reproduced with permission from *Angew. Chem. Int. Ed.* 38 (1999) 168, Copyright 1999, Wiley–VCH.

13(e)). ^{1}H-NMR titration studies of the pure hexanuclear nitrate salt of **77** in water revealed the selectivity of the receptor for doubly charged SO_4^{2-} over monoanionic guests (Table 12).

Arion and co-workers have synthesised a series of nickel(II) and cobalt(III) complexes of *S*-substituted isothiosemicarbazides (**78**–**85**) [66]. They have shown

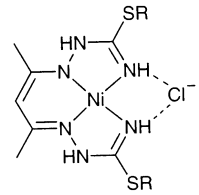
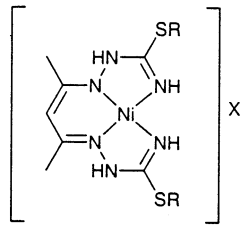
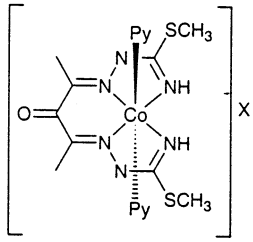


Fig. 14. Anion binding mode of *S*-substituted isothiosemicarbazide metal complexes.

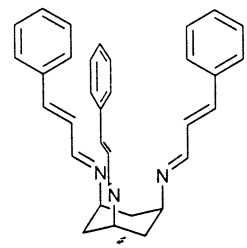
that nickel based complexes **82**–**84** act as receptors for chloride in DMSO-d_6 solution with stability constants in the range 60–100 M^{-1} (Fig. 14). The cobalt based receptor **85** forms a more stable chloride complex ($K = 220\ M^{-1}$) and forms an acetate complex with $K = 4420\ M^{-1}$.





78 R = CH_3 X = I
79 R = $C_{12}H_{25}$ X = I
80 R = $CH_2CH_2C_6H_5$ X = I
82 R = CH_3 X = PF_6
83 R = $C_{12}H_{25}$ X = PF_6
84 R = $CH_2CH_2C_6H_5$ X= PF_6

81 X = I
85 X = PF_6



86

Boxwell and Walton have elucidated the crystal structures of [Co(II)(**86**)-$(NO_3)(HOCH_3)_n$]BPh_4 with $n = 4$ or 5 in order to study modes of anion binding to the metal centre as a model for bicarbonate binding in the active site of carbonic anhydrase [67]. Condensation of 4-*tert*-butylcinnamaldehyde with *cis*-1,3,5-triaminocyclohexane afforded *cis*,*cis*-1,3,5-tri[(4-*tert*-butylphenyl)propenylideneamino]cyclohexane (**86**) in 58% yield. Slow evaporation of a solution of **86** in ca. 10:90 CH_2Cl_2–CH_3OH (v/v) in the presence of $Co(NO_3)_2 \cdot 6H_2O$ gave crystals of [Co(**86**)$(HOCH_3)_3$]$(NO_3)(HOCH_3)_2(BPh_4)$ (**87**) in 65% yield. By changing the solvent conditions to ca. 30:70 CH_2Cl_2–CH_3OH (v/v) crystals of [Co(**86**)(NO_3)-$(HOCH_3)$] $(HOCH_3)_3(CH_2Cl_2)_2(BPh_4)$ (**88**) were obtained in 74% yield. In complex **87**, the nitrate ion is hydrogen bonded to two methanol molecules that are in-turn coordinated to the cobalt centre (Fig. 15(a)). However in complex **88**, the nitrate ion is directly coordinated to the cobalt metal centre together with one methanol molecule (Fig. 15(b)). The authors suggest that these complexes shed light on the mechanism of the transfer of bicarbonate in and out of the active site of carbonic anhydrase, i.e. bicarbonate binding through a hydrophobic active site may be achieved without complete desolvation of the anion.

White, Tasker and co-workers have produced a receptor that contains a dianionic binding site for transition metal cations and a dicationic binding site for anions (Fig. 16) [68]. Receptor **89** (Scheme 15) contains a salen-based binding site 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. The presence of the transition metal forces the receptor into a conformation such that the protonated morpholine groups come into close proximity, defining an anion-

binding site. Metal binding therefore enhances the anion binding affinity of the receptor. Extraction experiments at pH 3.8 demonstrated that **89** is capable of extracting $CuSO_4$ into chloroform with a near 100% loading of receptor.

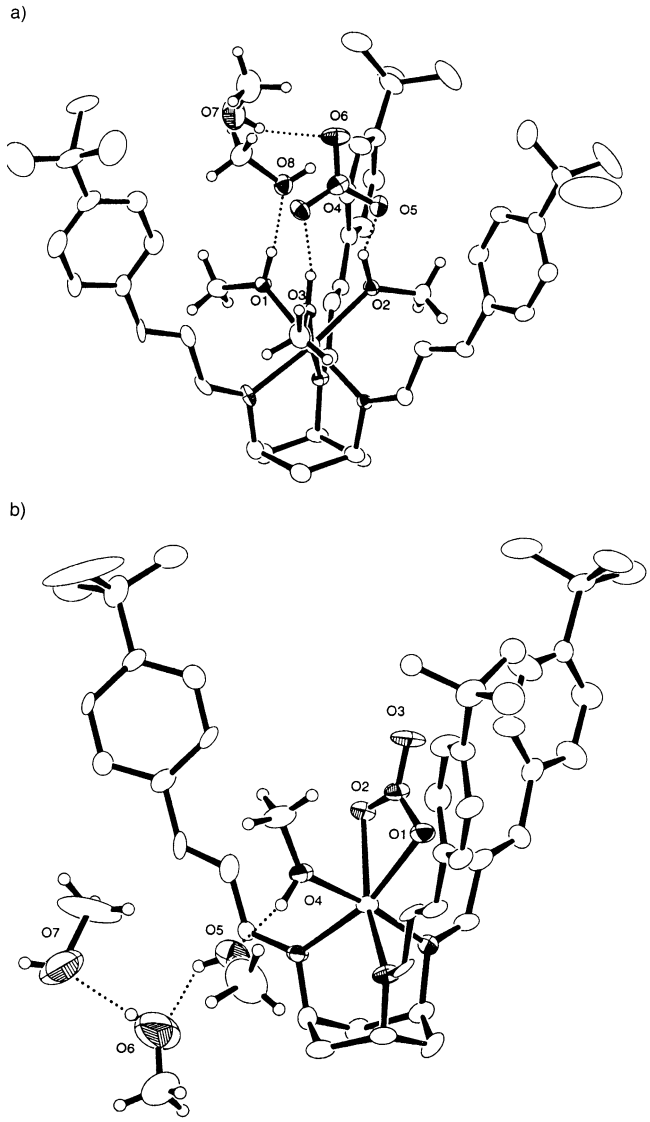


Fig. 15. ORTEP representations of the structures of: (a) **87**; and (b) **88**. Reproduced with permission from *Chem. Commun.* (1999) 1647. Copyright 1999, Royal Society of Chemistry.

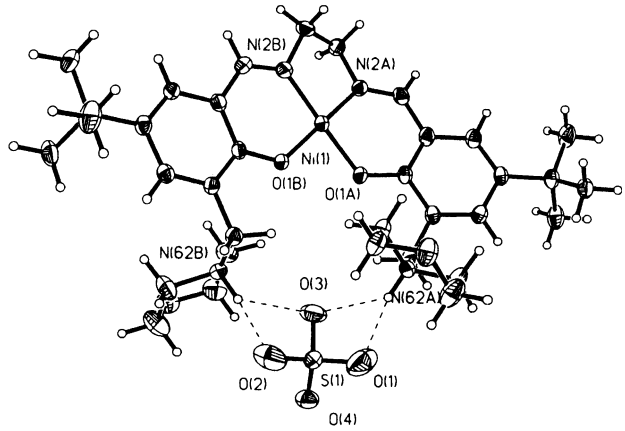
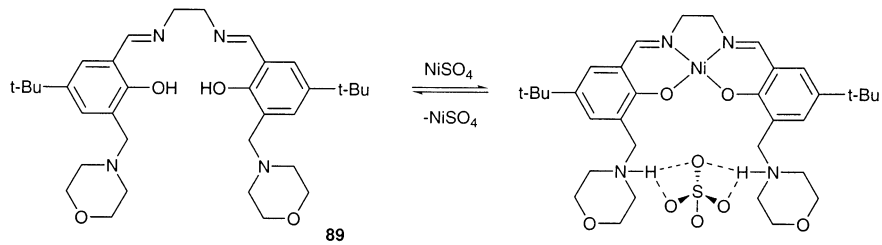


Fig. 16. Molecular structure of Ni**89**SO_4. Reproduced with permission from *Chem. Commun.* (1999) 2077. Copyright 1999, Royal Society of Chemistry.

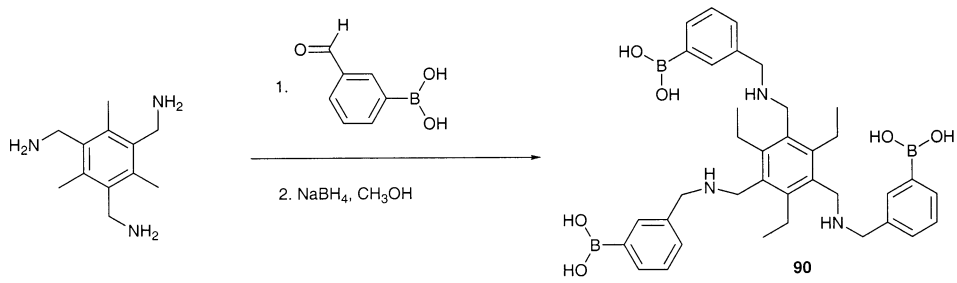


Scheme 15. $NiSO_4$ complexation by receptor **89**.

3.3. Metals and Lewis acids in anion sensors

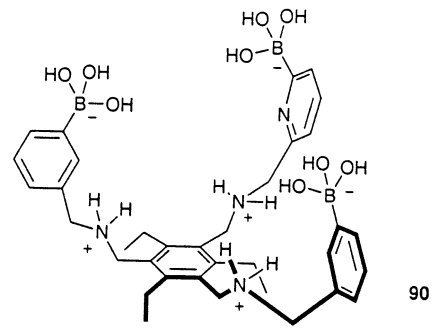
Anslyn and co-workers have developed a tris-boronic acid receptor that can function as a displacement assay (with carboxyfluorescein) for determining glucose-6-phosphate concentrations [50]. Receptor **90** was synthesised by reaction of 1,3,5-tris-aminomethyl-2,4,6-triethylbenzene with 3-formylbenzeneboronic acid under reducing conditions (Scheme 16). The receptor is designed to form reversible covalent bonds with the hydroxyls of the glucose-6-phosphate via the boronic acid moieties and also coordinate to the phosphate groups via the secondary amine groups. This allowed the receptor to discriminate between glucose-6-phosphate and glucose or phosphate buffers.

Beer and co-workers have synthesised the ruthenium(II) and rhenium(I) bipyridyl calix[4]diquinone receptors **91** and **92** and shown that these molecules selectively

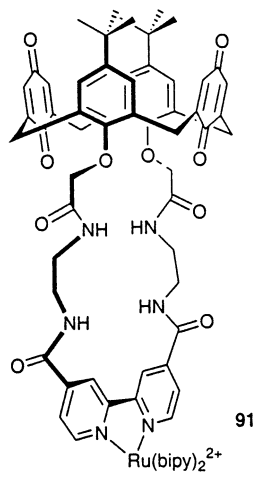


Scheme 16. Synthesis of receptor **90**.

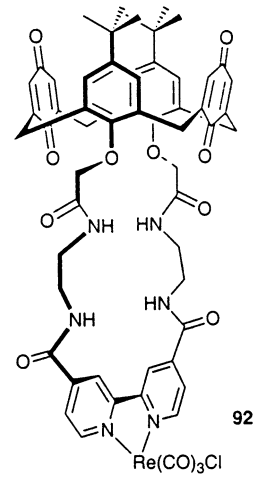
bind and sense acetate anions via a remarkable luminescent emission intensity retrieval effect [69]. Acetate addition to receptor **91** in acetonitrile caused a 500% emission intensity increase. This suggests that anion binding inhibits intramolecular oxidative electron transfer between the ruthenium(II) bipyridyl and calix[4]diquinone centres that would otherwise quench the emission.



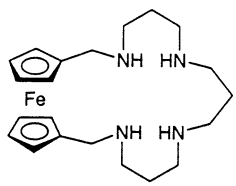
Beer and co-workers have synthesised a series of acyclic and macrocyclic ferrocene amine ligands, e.g. **93** and **94** that can selectively bind and electrochemically detect phosphate and sulfate anions in water [70]. For example at pH7 compound **93** senses phosphate via a cathodic shift of 50 mV whereas sulfate does not induce a redox response. In contrast **94** in aqueous THF solutions electrochemically discriminate for sulfate over phosphate at pH4 with a cathodic shift of 54 mV. Calibration curves of the change in the half-wave potential ΔE versus $[A^-]/[L]$ ratio at a certain pH value enabled **93** and **94** to quantitatively determine phosphate and sulfate concentrations in the presence of competing anions.



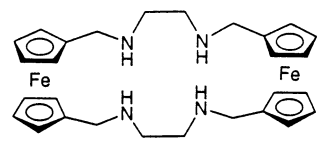
91



92



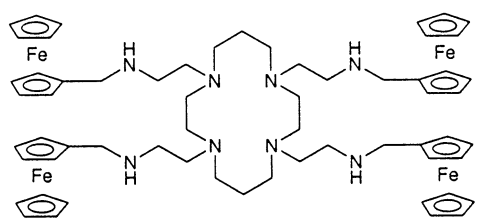
93



94

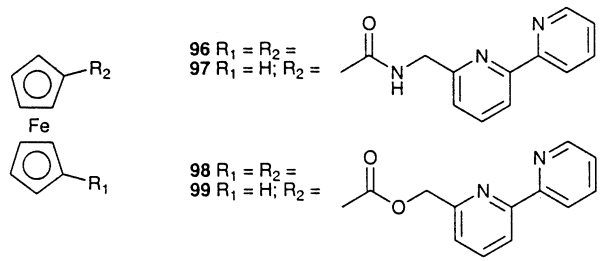
Martínez-Máñez, Garcia-España, Luis, Sinn and co-workers have recently reported a detailed electrochemical study of the anion recognition properties (sulfate, phosphate and ATP) of 1,4,8,11-tetrakis(4-ferrocenyl-3-azabutyl)-1,4,8,11-tetraazacyclotetradecane (**95**) [71].

The electrochemical responses of a series of ferrocenyl receptors containing 2,2′-bipyridyl arms **96**–**99** have recently been reported by Moutet and co-workers [72].

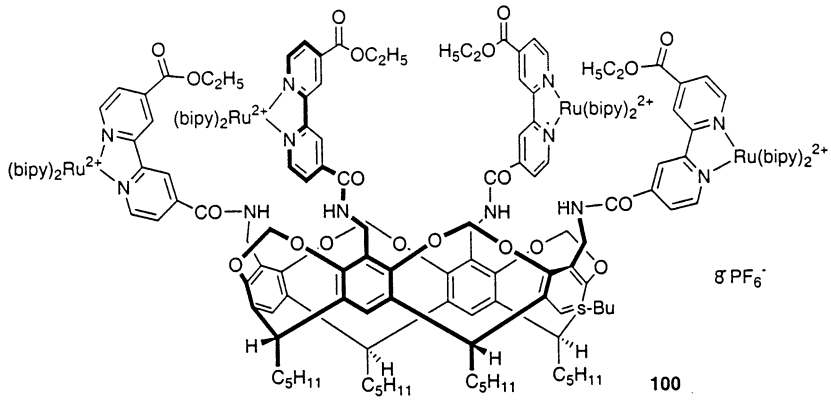


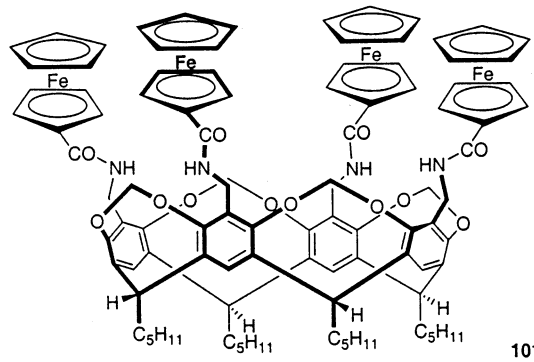
95

Ruthenium(II) bipyridyl amide **100** and ferrocene amide cavitand **101** receptors have been prepared by Beer and co-workers by condensation of either 4-chlorocarbonyl-4′-ethoxycarbonyl-2,2′-bipyridine or chlorocarbonylferrocene with tetra-(aminomethyl)cavitand (and in the former case subsequent reflux with $[RuCl_2(bipy)_2]\cdot 2H_2O$) [73]. Receptor **100** has been shown by UV absorbance and fluorescence emission experiments to selectively bind carboxylates over chloride anions.



Water soluble ruthenium(II) bipyridyl polyaza receptors, e.g. **102**–**105** have been prepared and shown to bind and detect phosphate anions in aqueous media via MLCT luminescent emission quenching [74].





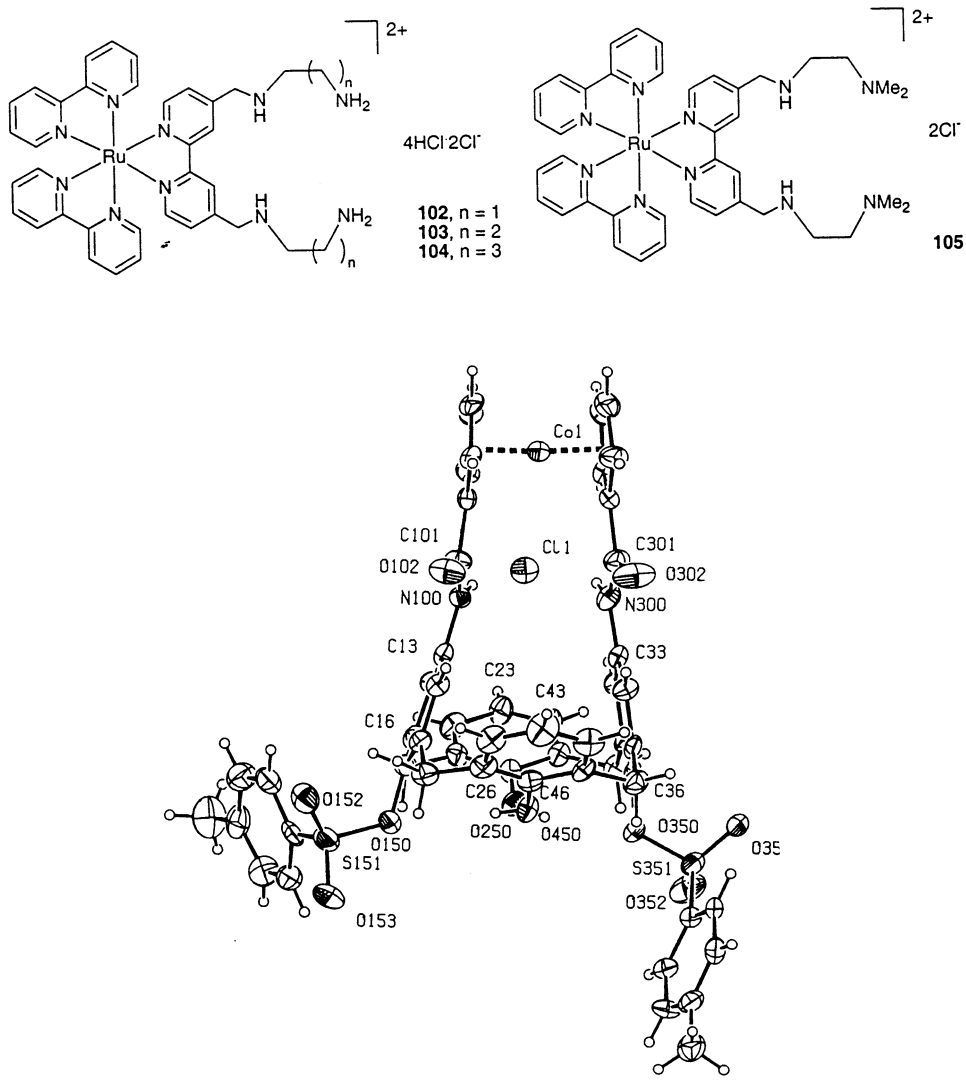


Fig. 17. The crystal structure of the **108**–chloride complex. Reproduced with permission from *Organometallics* 18 (1999) 3933. Copyright 1999, American Chemical Society.

The anion coordination properties of the cobaltocenium–calix[4]arene receptors are dependent upon the degree of preorganisation of the upper-rim anion recognition site [75]. Stability constant values for the isomeric receptors **106** and **107** suggest that exchanging the positions of the tosyl substituent on the calix[4]arene

lower rim has a dramatic influence on the anion coordination properties of the upper rim. For example **106** displays the selectivity trend $MeCO_2^- \gg H_2PO_4^-$ whereas with isomeric **107** the selectivity preference is reversed. Cobaltocenium bridged calix[4]arene **108** forms thermodynamically stronger anion complexes with carboxylate and $H_2PO_4^-$ anions than either **106** or **107** (with selectivity for acetate). The crystal structure of the **108**–chloride complex (Fig. 17), suggests that this selectivity preference may be rationalised by the upper-rim bidentate amide hydrogen bond donor cavity being of complementary topology to bidentate anions such as the carboxylates.

The electrochemical properties of **106**–**108** were investigated [75] using cyclic voltammetry in acetonitrile. Substantial one-wave cathodic shifts of the respective cobaltocenium/cobaltocene redox couple of up to 155 mV for **108** in the presence of acetate were observed.

Ferrocene amide compounds **109**–**112** that contain phosphine groups coordinated to a variety of transition metals have been synthesised (Scheme 17) and shown to sense a variety of anions via perturbations in the electrochemical responses of both the ferrocene and transition metal redox centre in each receptor [76].

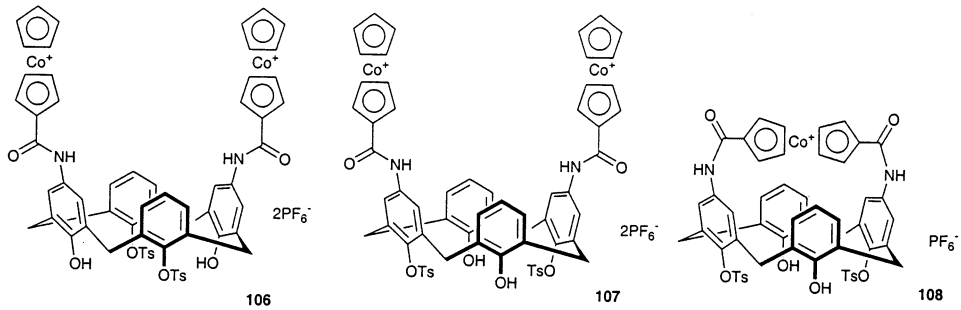
Reinhoudt and co-workers have incorporated an array of lipophilic uranyl salophane derivatives such as **113a**–**i** (Scheme 18) into chemically modified field effect transistor (CHEMFET) membranes [77]. These devices are capable of selectively detecting a range of anions (e.g. fluoride may be detected in the presence of a 150-fold excess of SCN^-) dependent upon the lipophilic and hydrogen bond donor–acceptor substituents near the uranyl binding site of the receptor.

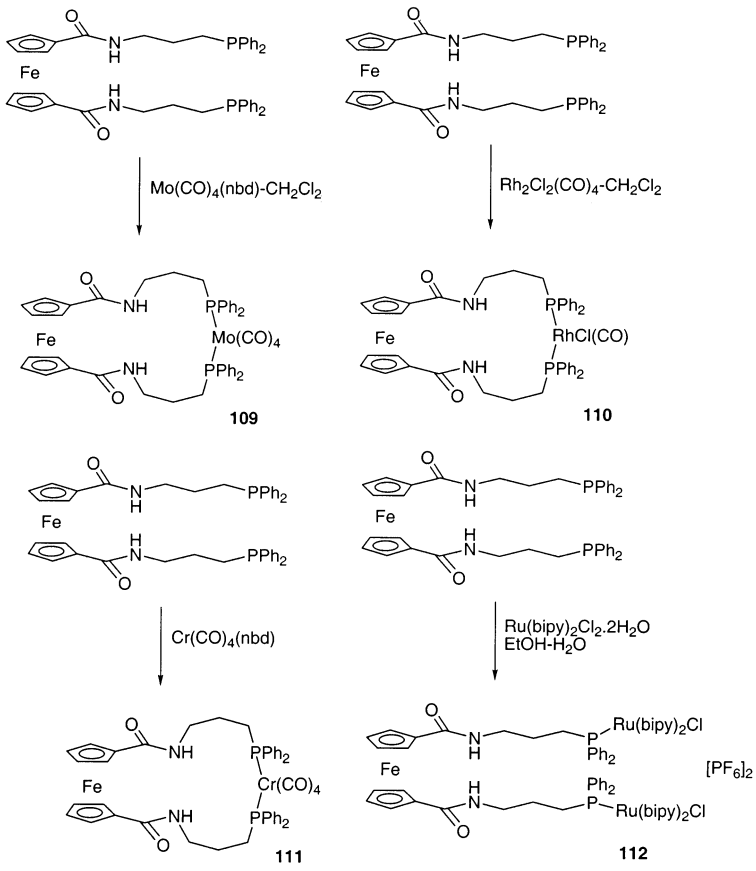
Fabre and co-workers have recently electrochemically produced boronate functionalised polypyrrole membranes on electrode surfaces (poly-**114** see Scheme 19) that are selective for fluoride over other putative anionic guests (Fig. 18) [78], whilst Král and co-workers have produced a variety of electrodes coated with electropolymerised aminophenylporphyrin **115** in both the free base and metallated forms and studied their interactions with anions [79].

4. Anion directed assembly

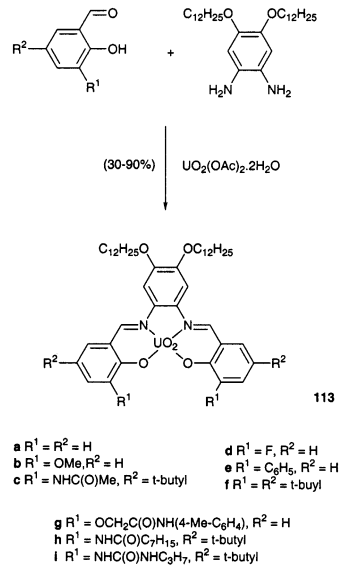
Examples of anions directing the formation of molecular architectures were, until a few years ago, difficult to find. However, this situation has now changed, and reports of the templating influence of anions are now becoming widespread [1].

Chloride anions have been used by Zheng and co-workers to direct the assembly of europium(III)–tyrosine clusters. One such complex, $[Eu_{15}(Cl)(\mu_3\text{-}OH)_{20}(\mu_2\text{-}H_2O)_5(OH)_{12}(H_2O)_8][ClO_4]_2{\cdot}56H_2O$ (**116**) is shown in Fig. 19 [80]. The complex contains 15 europium(III) metal ions and 10 tyrosine residues in addition to

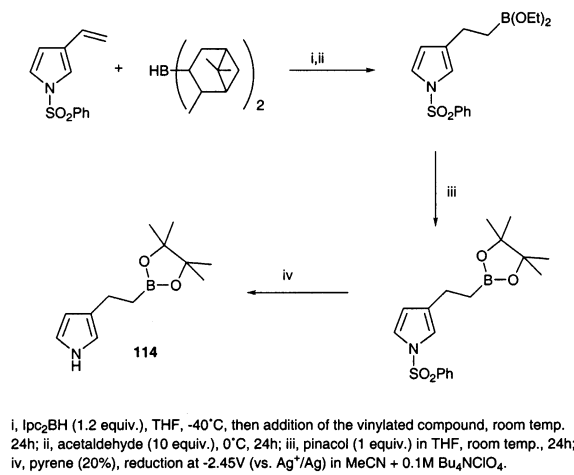


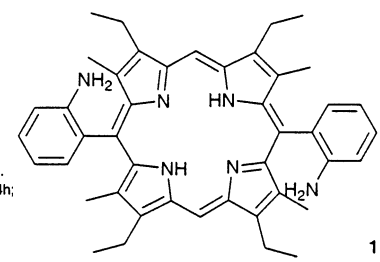


Scheme 17. Synthesis of **109–112.**



Scheme 18. Synthesis of receptor **113**.





Scheme 19. Synthesis of receptor **114**.

hydroxo and aquo ligands. The europium ions form three layers each containing five metals. The cage is templated around a chloride anion at the centre of the cluster that is coordinated to five europium atoms with an average Eu–Cl distance of 3.314 Å.

Cyclic hexanuclear complexes containing quadruply bonded Mo_2 units around carbonate anions have been reported by Chen and co-workers [81]. Complex **117** (Fig. 20) 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(diphenylphosphino)amine (dppa) in dichloromethane. The chloride atoms present in **117** originate from the dichloromethane solvent. The analogous reaction carried out in acetonitrile followed by the addition of ZnX_2 (X = Br or I) afforded the bromide or iodide complexes, respectively.

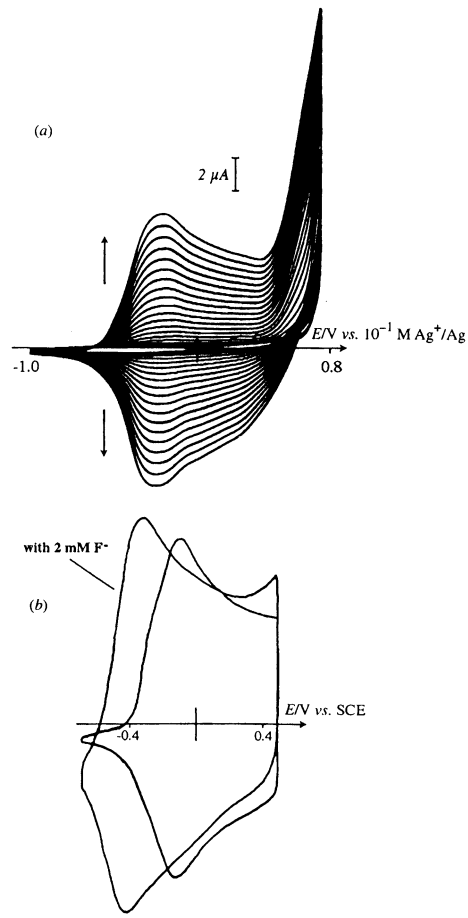


Fig. 18. (a) Successive cyclic voltammograms of **114** (10^{-2} M) in CHCN + 10^{-1} M Bu_4NPF_6 (final electropolymerization charge: 70 mC cm^{-2}). (b) Electrochemical response of corresponding poly(**114**) in 1:1 H_2O–CH_3CN (v/v) + 5×10^{-1} M $LiClO_4$ in the absence and presence of 2 mM KF. Potential scan rate: 100 mV s^{-1}. Reproduced with permission from Chem. Commun. (1999) 1881. Copyright 1999, Royal Society of Chemistry.

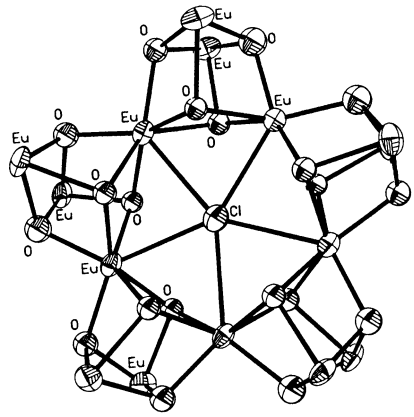


Fig. 19. A plane through the X-ray crystal structure of **116** showing the templating chloride anion. Reproduced with permission from *Angew. Chem. Int. Ed. Engl.* 38 (1999) 1813, Copyright 1999, Wiley–VCH.

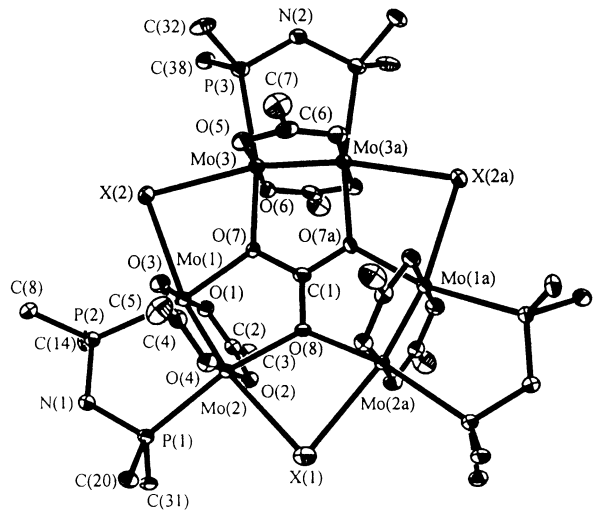


Fig. 20. A representative ORTEP drawing for complexes **117** (X = Cl). Reproduced with permission from *Chem. Commun.* (1999) 1185, Copyright 1999, Royal Society of Chemistry.

Following on from their earlier work [82], Mingos and co-workers have synthesised a nickel–palladium amidothiourea cage **118** (Fig. 21) using chloride or bromide anions as templates. The crystal structure of the chloride templated cage is shown in Fig. 21 [83].

Anion templated assembly of 3,6-bis(2-pyridyl)-1,2,4,5-tetrazine (bptz) nickel complexes **119** has been reported by Dunbar and co-workers [84]. Reaction of $[Ni(CH_3CN)_6][BF_4]_2$ with bptz in a 1:1 molar ratio affords a dark green solid, which was recrystallised by diffusion of toluene into an acetonitrile solution of the

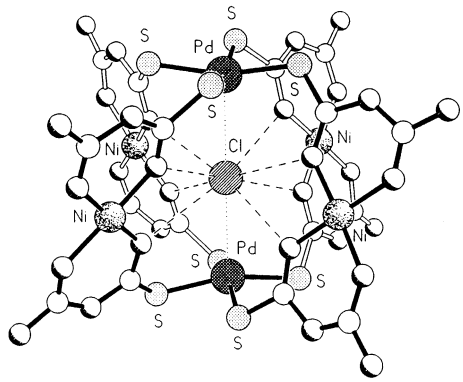


Fig. 21. The molecular structure of the mixed metal cage cation $\mathbf{118}^{3+}$ showing the encapsulation of a chloride anion. Reproduced with permission from *Chem. Commun.* (1999) 2229. Copyright 1999, Royal Society of Chemistry.

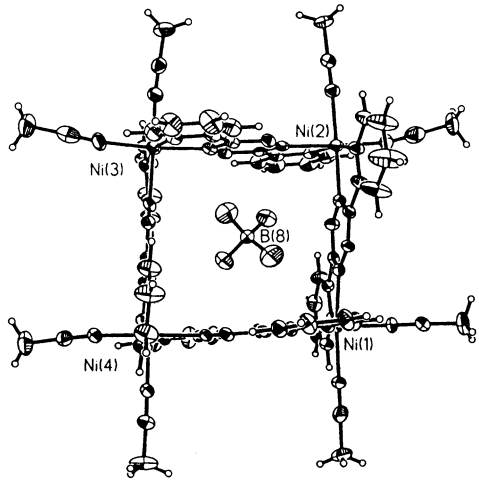
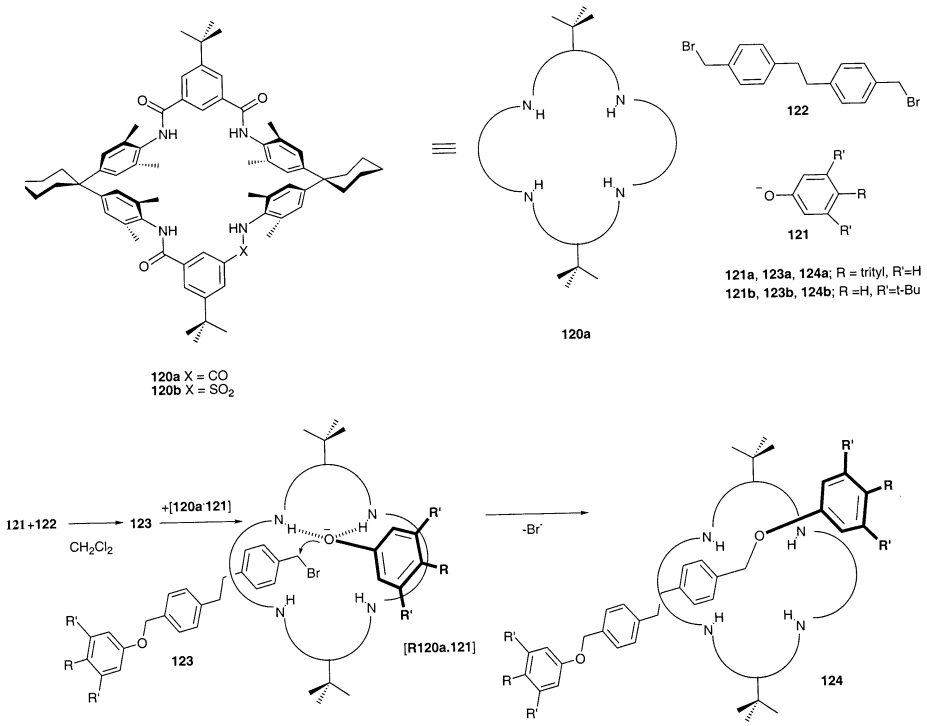


Fig. 22. An ORTEP drawing of the molecular structure of the $[Ni_4(bptz)_4(CH_3CN)_8]^{8+}$ ion with encapsulated BF_4^-. Thermal ellipsoids are drawn at the 50% probability level. Reproduced with permission from *Angew. Chem. Int. Ed. Engl.* 38 (1999) 3477, Copyright 1999, Wiley–VCH.



Scheme 20. Vögtle's anion templated assembly of rotaxane **124**.

complex. The nickel square structure is shown in Fig. 22. The squares do not form if the bis-hexafluorophosphate salt of nickel(II) hexaacetonitrile is used. This suggests that the squares assemble around the BF_4^- anions.

Vögtle and co-workers have employed anion coordination in a high yielding rotaxane synthesis. They discovered that phenolates, thiophenolates and sulfonamide anions when bound to tetralactam macrocycles are capable of reacting as a nucleophile and therefore may be used in rotaxane synthesis. Complex **120a·121** (Scheme 20) reacts with molecule **123** to form rotaxane **124** in an excellent 95% yield [85,86].

A synthetic solid state anion channel has recently been produced by Lippert and co-workers. Reaction of $[(en)Pt\{H_2O)_2]^{2+}$ and 2,2-bipyrazine produces the triangular complex $[\{(en)Pt(2,2'\text{-bpz-}N^4,N^{4\prime})\}_3]^{6+}$ [87]. Subsequent reaction with additional (en)Pd(II) gives a hexametallic triangular complex $[\{(en)Pd_{2.5}(2,2'\text{-bpz})_3\text{-}\{(NH_3)_2Pt\}_3](ClO_4)_6(NO_3)_5\cdot 5H_2O$ (**125**) (Fig. 23) with one of the corner Pd atoms having 50% occupancy. A single perchlorate anion is bound at the centre of the

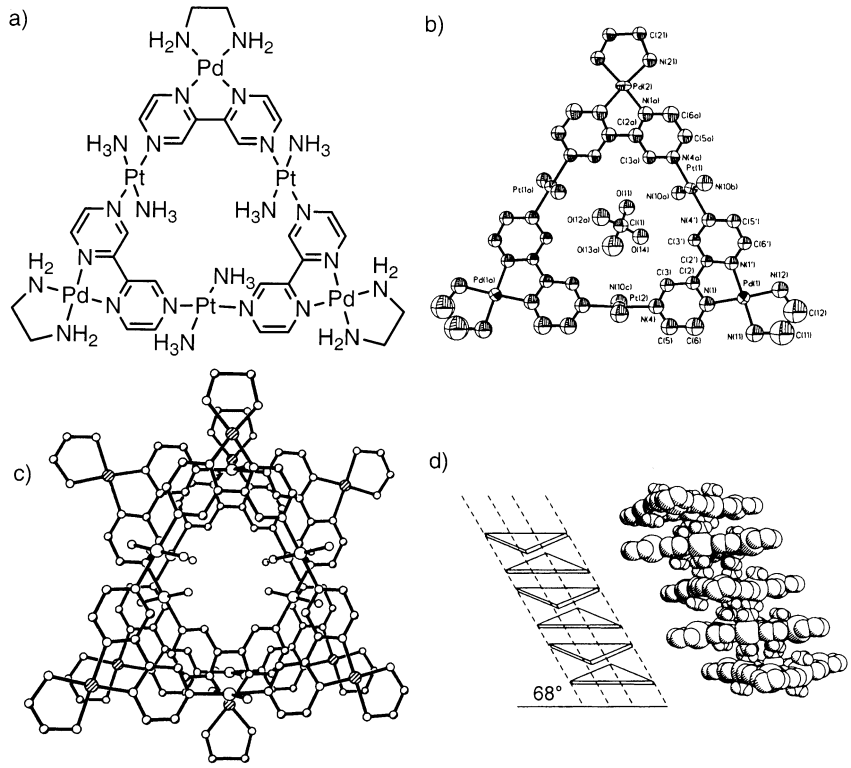


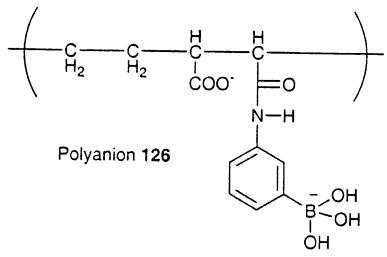
Fig. 23. The structure of: (a) the molecular triangle **125**; (b) the X-ray metal structure of **125** with encapsulated perchlorate anion; (c) a packing diagram showing the anion channel (perchlorate anions omitted for clarity); and (d) a side view of the channel. Parts (b, c and d) reproduced with permission from *Chem. Commun.* (1999) 6175. Copyright 1999, The Royal Society of Chemistry.

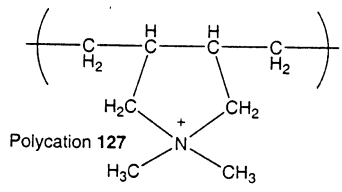
triangle. The complexes are held together via bridging nitrate anions and water molecules to form channels (this is shown in Fig. 23(c) with the perchlorate anions omitted for clarity and a side view is shown in Fig. 23(d)).

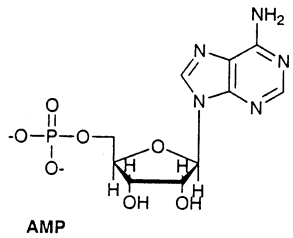
Shinkai and co-workers have used 'molecular imprinting' techniques in polyion complexes to create cavities selective for AMP [88]. Polyanions functionalised with boronic acid groups **126** (capable of interacting with the *cis*-diol of AMP) were mixed with a polycation **127** (forming a 1:1 polycation–polyanion complex) and AMP. After removal of the AMP template, a cleft remains in the polymer that possesses a high affinity for AMP (Scheme 21).

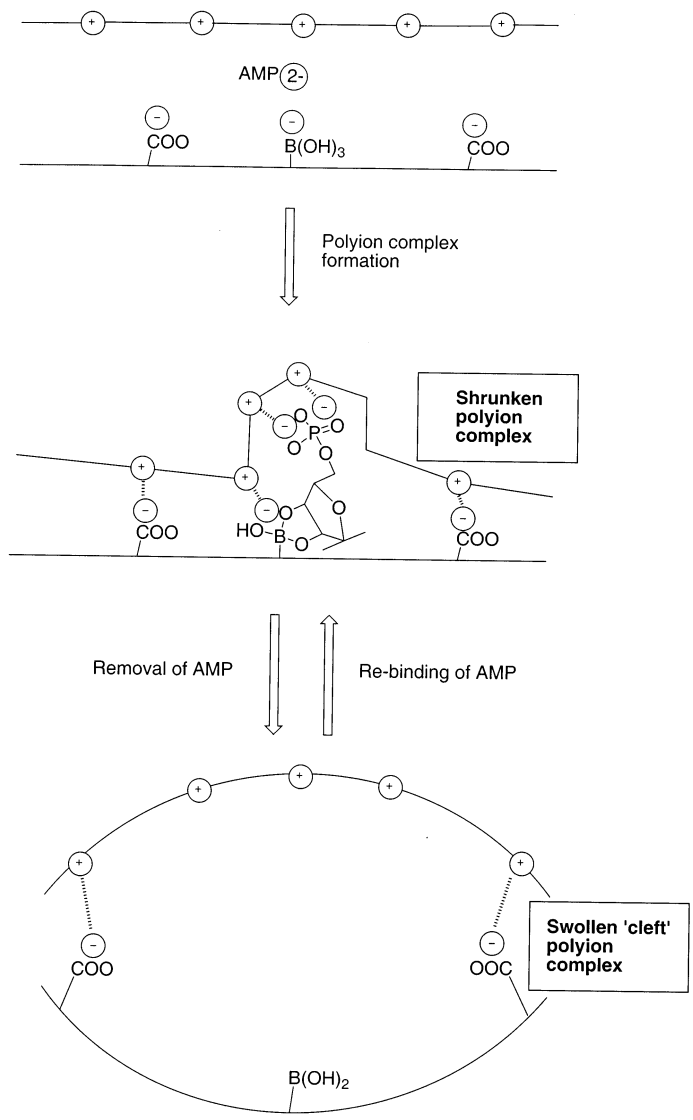
5. Conclusions

Interest in anion coordination continues to grow with many examples of anion directed assembly, sensors and receptors for anions or cation-anion pairs being reported in the last year. As we enter the new Millennium, there is no reason to suppose that interest in this area of chemistry will wane, indeed the use of anion coordination in the production of catalytic supramolecular systems involving anion coordination is an area that is ready to be more fully explored.









Scheme 21. Molecular imprinting produces a polymer containing AMP recognition sites.

Acknowledgements

I would like to thank the Royal Society for a University Research Fellowship.

References

[1] P.A. Gale, Coord. Chem. Rev. 199 (2000) 181.
[2] V. Král, O. Rusin, T. Shishkanova, R. Volf, P. Matejka, K. Volka, Chem. Listy 93 (1999) 546.
[3] A. Metzger, E.V. Anslyn, Angew. Chem. Int. Ed. 37 (1998) 649.

[4] K. Niikura, A. Metzger, E.V. Anslyn, J. Am. Chem. Soc. 120 (1998) 8533.
[5] A.P. Bisson, V.M. Lynch, M.K.C. Monahan, E.V. Anslyn, Angew. Chem. Int. Ed. 36 (1997) 2340.
[6] K. Niikura, A.P. Bisson, E.V. Anslyn, J. Chem. Soc. Perkin 2 (1999) 1111.
[7] T.S. Snowden, A.P. Bisson, E.V. Anslyn, J. Am. Chem. Soc. 121 (1999) 6324.
[8] M. Cajan, I. Stibor, J. Koca, J. Phys. Chem. A 103 (1999) 3778.
[9] P.A. Gale, J.L. Sessler, V. Král, V. Lynch, J. Am. Chem. Soc. 118 (1996) 5140.
[10] P.A. Gale, J.L. Sessler, V. Lynch, P.I. Sansom, Tetrahedron Lett. 37 (1996) 7881.
[11] P.A. Gale, J.L. Sessler, W.E. Allen, N.A. Tvermoes, V. Lynch, Chem. Commun. (1997) 665.
[12] P.A. Gale, J.W. Genge, V. Kral, M.A. McKervey, J.L. Sessler, A. Walker, Tetrahedron Lett. 38 (1997) 8443.
[13] P.A. Gale, J.L. Sessler, V. Král, Chem. Commun. (1998) 1.
[14] J.L. Sessler, A. Andrievsky, P.A. Gale, V. Lynch, Angew. Chem. Int. Ed. 35 (1996) 2782.
[15] J.L. Sessler, P.A. Gale, J.W. Genge, Chem. Eur. J. 4 (1998) 1095.
[16] H. Miyaji, P. Anzenbacher Jr., J.L. Sessler, E.R. Bleasdale, P.A. Gale, Chem. Commun. (1999) 1723.
[17] P.A. Gale, L.J. Twyman, C.I. Handlin, J.L. Sessler, Chem. Commun. (1999) 1851.
[18] V. Král, J.L. Sessler, T.V. Shishkanova, P.A. Gale, R. Volf, J. Am. Chem. Soc. 121 (1999) 8771.
[19] J.L. Sessler, P. Anzenbacher, Jr., K. Jursíková, H. Miyaji, J.W. Genge, N.A. Tvermoes, W.E. Allen, J.A. Shriver, P.A. Gale, V. Král, Pure Appl. Chem. 70 (1998) 2401.
[20] P. Anzenbacher, Jr., K. Jursíková, V.M. Lynch, P.A. Gale, J.L. Sessler, J. Am. Chem. Soc. 121 (1999) 11020.
[21] L. Bonomo, E. Solari, G. Toraman, R. Scopelliti, M. Latronico, C. Floriani, Chem. Commun. (1999) 2413.
[22] S. Depraetere, M. Smet, W. Dehaen, Angew. Chem. Int. Ed. 38 (1999) 3359.
[23] W.P. van Hoorn, W.L. Jorgensen, J. Org. Chem. 64 (1999) 7439.
[24] C.B. Black, B. Andrioletti, A.C. Try, C. Ruiperez, J.L. Sessler, J. Am. Chem. Soc. 121 (1999) 10438.
[25] B. Oddo, Gazz. Chim. Ital. 41 (1911) 248.
[26] K. Rachlewicz, L. Latos-Grazynski, A. Gebauer, A. Vivian, J.L. Sessler, J. Chem. Soc. Perkin Trans. 2 (1999) 2189.
[27] C. Schmuck, Chem. Commun. (1999) 843.
[28] H. Stephan, H. Spies, B. Johannsen, L. Klein, F. Vögtle, Chem. Commun. (1999) 1875.
[29] H. Xie, S. Yi, X. Yang, S. Wu, New J. Chem. 23 (1999) 1105.
[30] K.C. Nam, S.O. Kang, H.S. Jeong, S. Jeon, Tetrahedron Lett. 40 (1999) 7343.
[31] K.C. Nam, S.O. Kang, S.W. Ko, Bull. Korean Chem. Soc. 20 (1999) 953.
[32] L.A.J. Chrisstoffels, F. de Jong, D.N. Reinhoudt, S. Sivelli, L. Gazzola, A. Casnati, R. Ungaro, J. Am. Chem. Soc. 121 (1999) 10142.
[33] M.A.S. Hossain, H.J. Schneider, Chem. Eur. J. 5 (1999) 1284.
[34] A. Doménech, E. García-España, J.A. Ramírez, B. Celda, M.C. Martínez, D. Monleón, R. Tejero, A. Bencini, A. Bianchi, J. Chem. Soc. Perkin 2 (1999) 23.
[35] C. Bazzicalupi, A. Bencini, A. Bianchi, V. Fedi, V. Fusi, C. Giorgi, P. Paoletti, L. Tei, B. Valtancoli, J. Chem. Soc. Dalton. Trans. (1999) 1101.
[36] C. Bazzicalupi, A. Bencini, A. Bianchi, M. Cecchi, B. Escuder, V. Fusi, E. Garcia-España, C. Giorgi, S.V. Luis, G. Maccagni, V. Marcelino, P. Paoletti, B. Valtancoli, J. Am. Chem. Soc. 121 (1999) 6807.
[37] S.D. Kean, B.L. May, P. Clements, S.F. Lincoln, C.J. Easton, J. Chem. Soc. Perkin Trans. 2 (1999) 1257, ibid (1999) 2231.
[38] H.S. Lee, X.Q. Yang, J. McBreen, D. Vyprachticky, Y. Okamoto, Can. J. Chem. 77 (1999) 738.
[39] O. Baudoin, F. Gonnet, M.-P. Teulade-Fichou, J.-P. Vigneron, J.-C. Tabet, J.-M. Lehn, Chem. Eur. J. 5 (1999) 2762.
[40] P. Cudic, J.-P. Vigneron, J.-M. Lehn, M. Cesario, T. Prangé, Eur. J. Org. Chem. (1999) 2479.
[41] A.P. Davis, L.J. Lawless, Chem. Commun. (1999) 9.
[42] B. Sellergren, A. Swietlow, T. Arnebrandt, K. Unger, Anal. Chem. 68 (1996) 402.
[43] F. Auer, D.W. Schubert, M. Stamm, T. Arnebrandt, A. Swietlow, M. Zizlsperger, B. Sellergren, Chem. Eur. J. 5 (1999) 1150.
[44] B. Sellergren, F. Auer, T. Arnebrant, Chem. Commun. (1999) 2001.
[45] S. Nishizawa, Y. Kato, N. Teramae, J. Am. Chem. Soc. 121 (1999) 9463.
[46] M. Berger, F.P. Schmidtchen, J. Am. Chem. Soc. 121 (1999) 9986.

[47] E. Alcalde, C. Alvarez-Rua, S. Garcia-Granda, E. Garcia-Rodriguez, N. Mesquida, L. Perez-Garcia, Chem. Commun. (1999) 295.
[48] K. Sato, S. Arai, T. Yamagishi, Tetrahedron Lett. 40 (1999) 5219.
[49] A. Metzger, V.M. Lynch, E.V. Anslyn, Angew. Chem. Int. Ed. 36 (1997) 862.
[50] L.A. Cabell, M.-K. Monahan, E.V. Anslyn, Tetrahedron Lett. 40 (1999) 7753.
[51] K. Kano, H. Kamo, S. Negi, T. Kitae, R. Takaoka, M. Yamaguchi, H. Okubo, M. Hirama, J. Chem. Soc. Perkin 2 (1999) 15.
[52] A. Knoepfler-Mühlecker, B. Scheffter, H. Kopacka, K. Wurst, P. Peringer, J. Chem. Soc. Dalton Trans. (1999) 2525.
[53] A.R. Kennedy, R.E. Mulvey, R.B. Rowlings, Angew. Chem. Int. Ed. Engl. 37 (1998) 3180.
[54] A.R. Kennedy, R.E. Mulvey, C.L. Raston, B.A. Roberts, R.B. Rowlings, Chem. Commun. (1999) 353.
[55] C. Bazzicalupi, A. Bencini, A. Bianchi, V. Fusi, E. García-España, C. Giorgi, J.M. Llinares, J.A. Ramirez, B. Valtancoli, Inorg. Chem. 38 (1999) 620.
[56] C. Bazzicalupi, A. Bencini, E. Berni, A. Bianchi, V. Fedi, V. Fusi, C. Giorgi, P. Paoletti, B. Valtancoli, Inorg. Chem. 38 (1999) 4115.
[57] T.F. Pauwels, W. Lippens, P.W. Smet, G.G. Herman, A.M. Goeminne, Polyhedron 18 (1999) 1029.
[58] G. DeSantis, L. Fabbrizzi, D. Iacopino, P. Pallavicini, A. Perotti, A. Poggi, Inorg. Chem. 36 (1997) 827.
[59] L. Fabbrizzi, F. Gatti, P. Pallavicini, E. Zambarbieri, Chem. Eur. J. 5 (1999) 682.
[60] C. Valério, J.-L. Fillaut, J. Ruiz, J. Guittard, J.-C. Blais, D. Astruc, J. Am. Chem. Soc. 119 (1997) 2588.
[61] C. Valerio, E. Alonso, J. Ruiz, J.C. Blais, D. Astruc, Angew. Chem. Int. Ed. 38 (1999) 1747.
[62] P.D. Beer, P.K. Hopkins, J.D. McKinney, Chem. Commun. (1999) 1253.
[63] P. Molenveld, J.F.J. Engbersen, D.N. Reinhoudt, Angew. Chem. Int. Ed. 38 (1999) 3189.
[64] R.D. Schnebeck, E. Freisinger, B. Lippert, Angew. Chem. Int. Ed. 38 (1999) 168.
[65] R.-D. Schnebeck, L. Randaccio, E. Zangrando, B. Lippert, Angew. Chem. Int. Ed. Engl. 37 (1998) 119.
[66] V.B. Arion, P.D. Beer, M.G.B. Drew, P. Hopkins, Polyhedron 18 (1999) 451.
[67] C.J. Boxwell, P.H. Walton, Chem. Commun. (1999) 1647.
[68] D.J. White, N. Laing, H. Miller, S. Parsons, S. Coles, P.A. Tasker, Chem. Commun. (1999) 2077.
[69] P.D. Beer, V. Timoshenko, M. Maestri, P. Passaniti, V. Balzani, Chem. Commun. (1999) 1755.
[70] P.D. Beer, J. Cadman, J.M. Lloris, R. Martínez-Máñez, M.E. Padilla, T. Pardo, D.K. Smith, J. Soto, J. Chem. Soc. Dalton Trans. (1999) 127.
[71] J.M. Lloris, R. Martínez-Máñez, M.E. Padilla-Tosta, T. Pardo, J. Soto, E. García-España, J.A. Ramírez, M.I. Burguete, S.V. Luis, E. Sinn, J. Chem. Soc. Dalton Trans. (1999) 1779.
[72] M. Buda, A. Ion, J.C. Moutet, E. Saint-Aman, R. Ziessel, J. Electroanal. Chem. 469 (1999) 132.
[73] I. Dumazet, P.D. Beer, Tetrahedron Lett. 40 (1999) 785.
[74] P.D. Beer, J. Cadman, New J. Chem. 23 (1999) 347.
[75] P.D. Beer, D. Hesek, K.C. Nam, M.G.B. Drew, Organometallics 18 (1999) 3933.
[76] J.E. Kingston, L. Ashford, P.D. Beer, M.G.B. Drew, J. Chem. Soc. Dalton Trans. (1999) 251.
[77] M.M.G. Antonisse, B.H.M. Snellink-Ruel, A.C. Ion, J.F.J. Engbersen, D.N. Reinhoudt, J. Chem. Soc. Perkin Trans. 2 (1999) 1211.
[78] M. Nicolas, B. Fabre, J. Simonet, Chem. Commun. (1999) 1881.
[79] R. Volf, T.V. Shishkanova, P. Matejka, M. Hamplova, V. Král, Anal. Chim. Acta 381 (1999) 197.
[80] R. Wang, Z. Zheng, T. Jin, R.J. Staples, Angew. Chem. Int. Ed. 38 (1999) 1813.
[81] M.-C. Suen, G.-W. Tseng, J.D. Chen, T.-C. Keng, J.-C. Wang, Chem. Commun. (1999) 1185.
[82] R. Vilar, D.M.P. Mingos, A.J.P. White, D.J. Williams, Angew. Chem. Int. Ed. 37 (1998) 1258.
[83] R. Vilar, D.M.P. Mingos, A.J.P. White, D.J. Williams, Chem. Commun. (1999) 229.
[84] C.S. Campos-Fernández, R. Clérac, K.R. Dunbar, Angew. Chem. Int. Ed. 38 (1999) 3477.
[85] G.M. Hübner, J. Glaser, C. Seel, F. Vogtle, Angew. Chem. Int. Ed. 38 (1999) 383.
[86] C. Reuter, W. Wienand, G.M. Hübner, C. Seel, F. Vögtle, Chem. Eur. J. 5 (1999) 2692.
[87] R.-D. Schenbeck, E. Freisinger, B. Lippert, Chem. Commun. (1999) 675.
[88] Y. Kanekiyo, Y. Ono, K. Inoue, M. Sano, S. Shinkai, J. Chem. Soc. Perkin Trans. 2 (1999) 557.