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Anion and ion-pair receptor chemistry: highlights from 2000 and 2001

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Contents

Abstract

This review article highlights advances made in abiotic anion coordination chemistry in 2000 and 2001. The structure of this review is that similar to the previous reviews in this series that covered 1997, 1998 and 1999 [P.A. Gale, Coord. Chem. Rev. 199 (2000) 181; P.A. Gale, Coord. Chem. Rev. 213 (2001) 79]. The review also includes examples of ion-pair receptors. 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 agent withdrawing electron density from the receptor; (iii) an organisational element in the receptor; (iv) a sensor; and (v) a co-bound guest in ion-pair receptor. Examples of the role of anions in directing the self-assembly of complex molecular architectures are presented in the final section.

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 [1–3]. The importance of anions in biological systems can scarcely be underestimated [4–7]. The aim of this review is to highlight advances made in the area of anion and ion-pair receptor chemistry in the years 2000 and 2001 and is the third in a series of reviews covering recent progress in these areas [1,2]. However, due to space considerations in this special issue of Coordination Chemistry Reviews, this review should not be regarded as being comprehensive.

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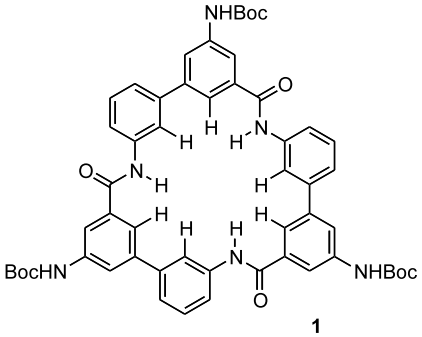
This review consists of three sections. The first covers organic ligands that employ hydrogen bonding and/or electrostatic interactions to form anion complexes. The second reviews the use of metal containing ligands as anion binding agents. The final section examines the role anions can play in directing self-assembly processes. Many of the receptors discussed could fit into a number of different sections of this review, as the use of a variety of different anion complexation moieties within a single receptor is now common. Therefore, the categories into which the receptors have been placed should be viewed as more fluid than rigid.



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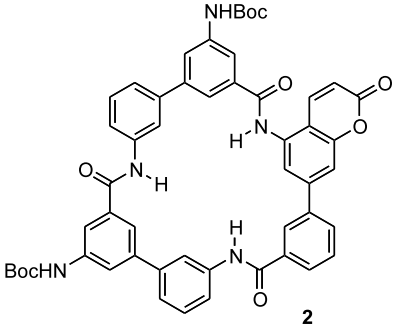

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2. Receptors employing hydrogen bonds and/or electrostatic interactions

2.1. Amide based receptors

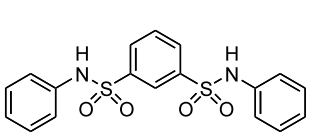
Amide NH groups have been employed to produce a wide range of receptors capable of coordinating anions [8]. A number of these systems contain metal anions and are therefore discussed later in this review. A general review of amides as anion receptors by Steve Loeb and Chantelle Bondy is included in this volume [9].

Choi and Hamilton have recently described the synthesis and anion binding properties of a new family of cyclic tri-amides such as receptor **1** [10]. NMR evidence suggests that this receptor binds iodide in a sandwich fashion at low I^- concentrations switching to a 1:1 binding mode at higher concentrations of the halide (as evidenced by an initial up-field of the NH resonances in the ^{1}H-NMR of **1** upon addition of I^- followed by a downfield shift after ca. 0.5 equivalents I^-). The receptor is selective for oxo-anions such as tosylate ($K = 2.1 \times 10^5$ M^{-1} in 2% DMSO-d_6/$CDCl_3$ at 296 K). Fluorescent sensors e.g. **2** based on the same macrocyclic skeleton have also been developed employing a 'dual channel' mechanism based upon proton transfer from the fluorophore in the excited state [11].

A variety of highly effective anion receptors containing 1,3-amide or sulfonamide substituted benzene rings, as first described by Crabtree and co-workers [12], have been synthesised during this period. Kavallieratos and Moyer have used the sulfonamide receptors **3**, **4** and **5** in combination with the calixcrown caesium receptor **6** to obtain improved extraction of caesium salts with the synergism following an anti-Hofmeister order [13]. Similar experiments show that the tris-amide **7** enhances the extraction of $CsNO_3$ by tetrabenzo-24-crown-8 with the amide acting as a nitrate receptor ($K_a = 250$ M^{-1} in 1,2-dichloroethane-d_4 at 18.1 °C) [14]. Tris(2-aminoethyl)amine triamide derivatives have also been used in these experiments [15].

Szumna and Jurczak have linked two pyridine clefts together to form an acetate selective macrocyclic receptor **8** (AcO^-: $K_a = 2640 \pm 270$ M^{-1}; $H_2PO_4^-$: $K_a = 1680 \pm 110$ M^{-1}; F^-: 830 ± 120 M^{-1} in DMSO-d_6 at 298K) [16]. Predominantly 1:1 receptor:anion complexes were formed in solution, however the crystal structure of the tetrabutylammonium acetate complex of **8** reveals the formation of a 2:1 receptor:anion complex in the solid state (Fig. 1).

Bowman-James and co-workers have used amine linkers to join two isophthalic acid derived amide clefts together producing receptor **9** [17]. This macrocycle forms remarkably strong complexes with phosphate and sulfate (added as dihydrogen phosphate and hydrogen sulfate, respectively). This is presumably due not only to complementarity between the receptor and oxo-anion but also to deprotonation of the anion by the amine groups present in the receptor so providing an electrostatic component to binding. Crystallisation of the receptor in the presence of tetrabutylammonium hydrogensulfate led to the isolation of crystals of a sandwich complex of sulfate with two tetrabutylammonium counter cations (Fig. 2).



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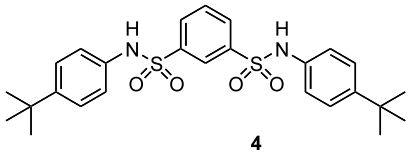

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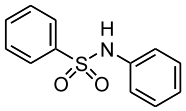

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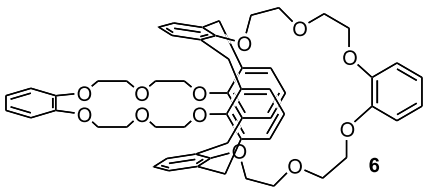

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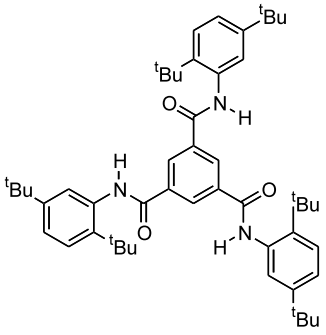

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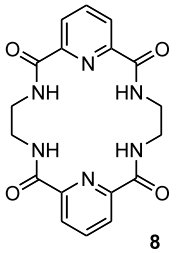

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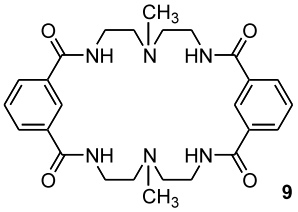

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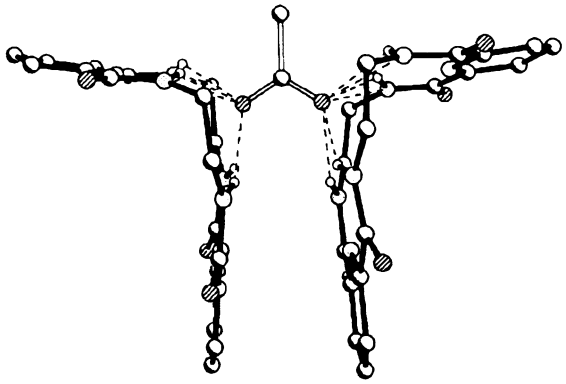
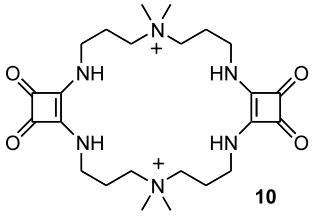


Fig. 1. X-ray crystal structure of **8**—AcO^- complex (counter cations omitted for clarity). (Reproduced with permission from Eur. J. Org. Chem. (2001) 4031, Copyright 2001, Wiley-VCH.)

Costa and co-workers have used receptor **10** in a fluorescent ensemble for monitoring sulfate concentrations in water [18]. The squaramide receptor **10** binds SO_4^{2-} with an association constant K_a of $(4.6 \pm 1.0) \times 10^6\ M^{-1}$ in methanol at 294 K. In addition this receptor quenches the fluorescence of fluorescein and so the **10**-fluorescein ensemble may be used as a displacement assay with sulfate competing for the squaramide binding site with the quenched bound fluorophore and so displacing it and restoring the macrocycle's fluorescence (Fig. 3).



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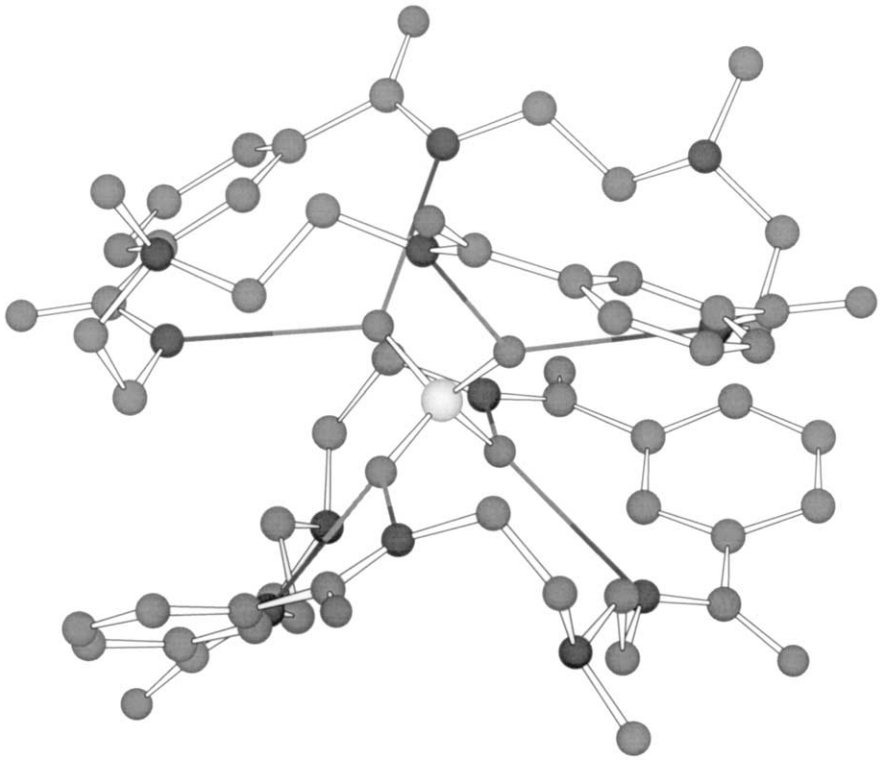


Fig. 2. X-ray crystal structure of the sulfate sandwich complex of compound **9** (counter cations omitted for clarity).

A variety of peptide based anion receptors have recently been reported. The cyclic hexapeptide **11** has been shown by Kubik et al. to complex a variety of anions in 80% D_2O/CD_3OD [19]. The crystal structure of the iodide complex of the L-proline and 6-aminopicolinic acid containing macrocycle reveals the halide guest bound in a sandwich fashion between two macrocycles by a total of six hydrogen bonds (Fig. 4). The same group have also investigated the anion receptor properties of cyclic peptides containing alternating natural amino acids and 3-aminobenzoic acids [20] whilst Spichiger and co-workers have identified linear polypeptides that interact with oxo-anions [21]. Kemp and co-workers have studied the stabilization effect of chaotropic anions on the helicity of short uncharged *N*-capped peptides [22].

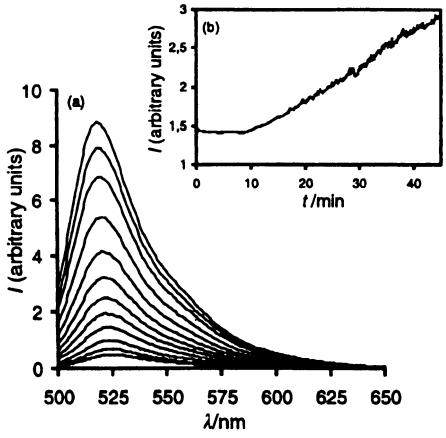
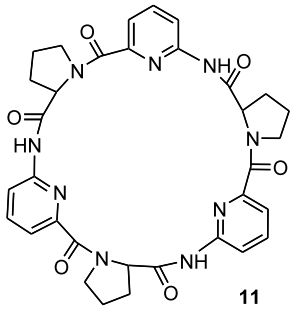


Fig. 3. (a) Fluorescence emission band ($\lambda_{exc.}$ 490 nm) of fluorescein = 1.4×10^{-5} M before (upper band) and after addition of **10**, [**10**] = 2.0×10^{-4} M (lowest band). Fluorogenic emission response with several concentrations of sulfate $[SO_4^{2-}] = 4.6$, 6.5, 8.4, 10.0, 11.7, 13.3, 14.8, 15.9×10^{-5} M. (b) In this experiment, after an approximate 10 min period, the sulfate concentration of a water solution was continuously increased from 0 to 200 ppm and mixed at 0.10 ml min^{-1} together with a stream of [**10**] = 2.6×10^{-4} M and fluorescein = 7.4×10^{-4} M in MeOH–H_2O (90:10 v/v) at a flow rate 0.90 ml min^{-1}. (Reproduced with permission from Chem. Commun. (2001) 1456, Copyright 2001, Royal Society of Chemistry.)



11

Ungaro and co-workers have attached *C*-linked peptide chains to the upper rim of calix[4]arene and shown these species act as receptors for oxo-anions and chloride [23]. A variety of receptors have been produced including calix[4]arene **12** that binds acetate in DMSO-d_6 with an association constant of 33 M^{-1} at 300 K.

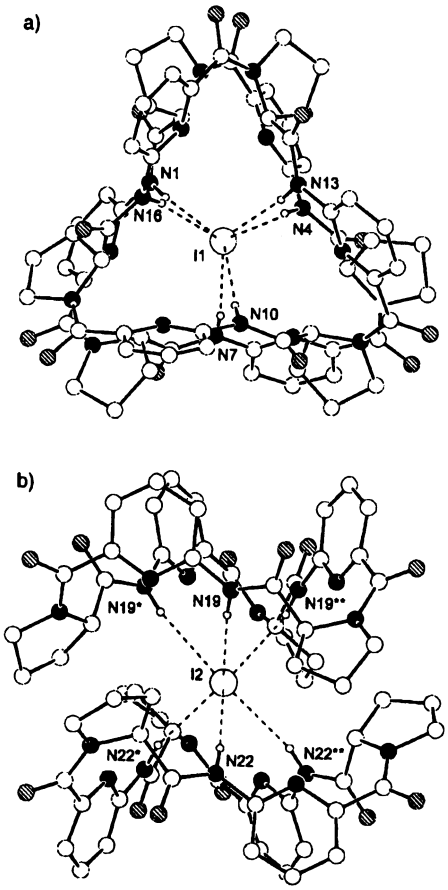
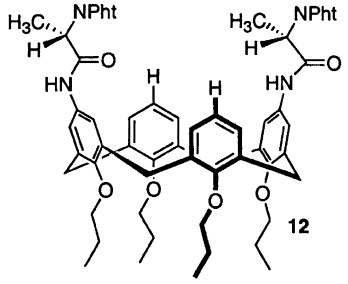


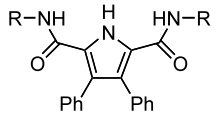
Fig. 4. Two views (a) top and (b) side of the iodide complex of receptor **11**. (Reproduced with permission from Angew. Chem. Int. Ed. Engl. 40 (2001) 2648, Copyright 2001, Wiley-VCH.)



2.2. Pyrrole based receptors

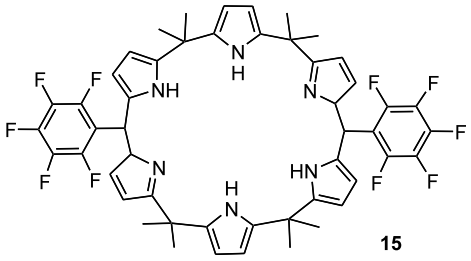
There have been a number of advances in the area of pyrrolic anion receptors in 2000 and 2001. A general review of pyrrolic anion receptors by Camiolo, Gale and Sessler is included in this volume. The anion complexation chemistry of the most simple pyrrole systems has recently begun to be explored. For example, the crystal structure of a pyrrole–chloride complex has recently been elucidated revealing the formation of pyrrole $NH\cdots Cl^-$ hydrogen bonds in the solid state [24].

2,5-Diamidopyrroles (**13** and **14**) have been shown by Gale et al. to be oxo-anion selective receptors in DMSO-d_6/0.5% water and acetonitrile solutions [25,26].

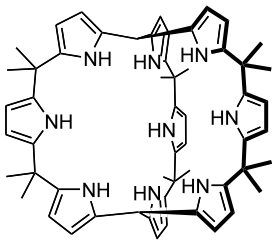


13 R = n-Bu
14 R = Ph

Many of the more recent developments in calixpyrrole chemistry [27] have previously been reviewed in this journal and therefore will not be covered here. The anion recognition chemistry of a related class of macrocycle, *the calixphyrins* [28] (porphyrin/calixpyrrole hybrids) has begun to be mapped out by Sessler and co-workers. These species contain at least one sp^3 hybridised *meso*-like bridging carbon in addition to sp^2 *meso*-carbons. Compound **15** was synthesised by reaction of pentafluorobenzaldehyde with a tripyrrane precursor (obtained from the TFA acid-catalysed condensation of pyrrole and acetone) [29]. No interaction was observed between the neutral form of the macrocycle and chloride, bromide, iodide, nitrate or hydrogensulfate anions. However, when either mono- or diprotonated, the receptor was found to interact with chloride, bromide, and iodide anions. Only the diprotonated receptor was found to form a simple 1:1 complex in solution. For example, an association constant of ca. $25\,000 \pm 900\ M^{-1}$ was estimated for the iodide complex of **15** in acetone solution although this value may be an underestimate due to the presence of competing hydrogen sulfate anions in solution.

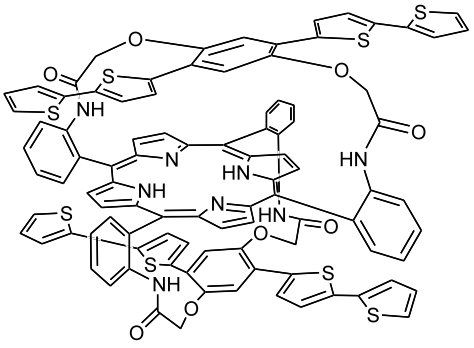


Extending pyrrolic anion receptors into the third dimension, Sessler and co-workers have reported the first example of cryptand-like calixpyrrole **16** [30]. ^{1}H-NMR titration experiments carried out in dichloromethane-d_2 and THF-d_8 reveal host–guest stoichiometries that depend directly upon the anion considered. For instance, fluoride was found to bind to six of the nine pyrrolic subunits, in a 1:1 fashion. However, chloride appears to interact with two molecules of **16** in solution (i.e. 2:1 host-to-anionic guest binding stoichiometry) being bound with an associated constant of $3.08 \times 10^6\ M^{-2}$ in dichloromethane-d_2 solution. Contrastingly, nitrate forms a 1:2 (host to guest) stoichiometry complex with association constants K_1 and K_2 of 1740 and 420 M^{-1}, respectively, in dichloromethane-d_2 solution.



16

Porphyrins continue to be used as scaffolds for anion complexation and recognition [31]. Swager and co-workers reported the synthesis of the 'doubly strapped' porphyrin **17** [32]. This receptor combines pyrroles and amides to bind two fluoride anions via a co-operative binding process in dichloromethane solution. Addition of larger anion such as chloride, bromide, iodide, acetate, cyanide, and dihydrogenphosphate, did not lead to perturbation of the UV spectrum, leading to the suggestion that they were not appreciably bound. The thiophene oligomers present in the receptor allow the molecule to be electropolymerised by potential cycling forming a conducting film. The redox-waves corresponding to the porphyrin in the film were found to shift to lower potentials upon addition of fluoride.



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Furuta et al. have used the derivative of a doubly *N*-confused porphyrin as an anion receptor [33]. Compound **19** was synthesised via the acid-catalysed condensation of an *N*-confused dipyrromethane **18** with pentafluorobenzaldehyde. Treatment of **19** with $SnCl_2$ for 8 h while heating in benzene at reflux was found to give rise to the fused system **20** in 6% yield (Scheme 1). This compound proved capable of binding anions with association constants comparable to those of typical, unsubstituted calix[4]pyrroles (e.g. $K_a \approx 10^4$ M^{-1} for fluoride anion in dichloromethane-d_2).

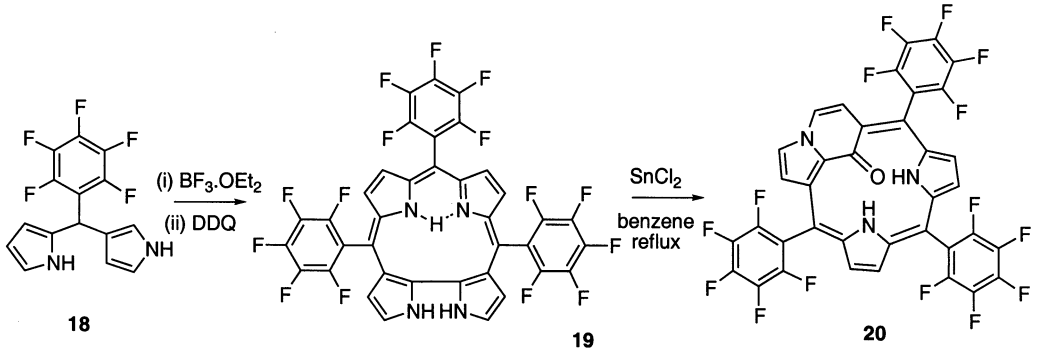
The anion complexation chemistry of core modified (O, S, Se) expanded porphyrins (sapphyrins, rubyrins and smaragdyrins) has been investigated by Chandrashekar and co-workers [34,35]. The magnitude of the anion association constants depending upon the number of NH groups present in the macrocycles.

2.3. Urea based receptors

A wide variety of urea containing anion receptors have been reported in 2000 and 2001. These include simple anion sensor systems containing a single urea group linked to a chromophore or fluorophore through urea containing clefts to more complex macrocyclic systems. Nitrobenzene appended thioureas $\mathbf{21}_n$ have been used by Hayashita et al. to achieve *hydrogen bond mediated* anion recognition within a vesicle in *aqueous* solution [36]. The anion complexation properties of the urea moiety was found to depend upon the position of the urea group within the vesicle as controlled by the length of the alkyl chain appended to the receptor.

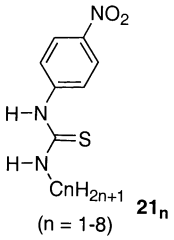
Gunnlaugsson has employed the anthracene–thiourea receptor **22** as a fluorescent photo-electron transfer chemosensor for anions. The fluorescence of **22** is quenched by AcO^-, F^- and $H_2PO_4^{2-}$ but not by Cl^- or Br^- in DMSO solution [37].

Wu has investigated a number of anthracene appended ureas (**23**–**25**) as fluorescent anion sensors [38]. The fluorescence of the bis-urea system **25** was found to quench upon addition of shorter chain α,ω-alkyl dicarboxylates in DMSO solution with NMR evidence showing the formation of a 1:1 receptor:dicarboxylate complex in solution, the magnitude of the association constant depending upon the length of the alkyl chain.



18 19 20

Scheme 1.



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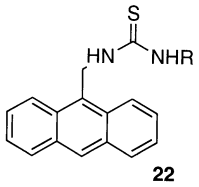

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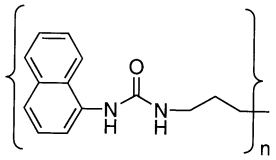
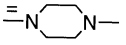
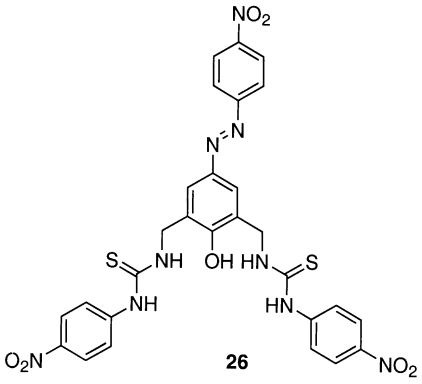


23 n = 1 R = Et
24 n = 1 R = $N(CH_3)_2$
25 n = 2 R =



By combining two different chromophores, namely azophenol and nitrophenyl, in a single receptor **26**, Hong and co-workers have produced a urea-based colorimetric sensor that can differentiate between anions of similar basicity ($H_2PO_4^-$ vs. AcO^-/F^-) [39]. The model compound **27** did not show colour differentiation between these anions.



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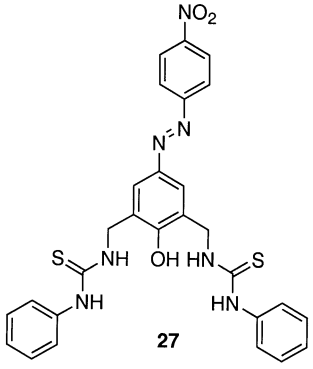

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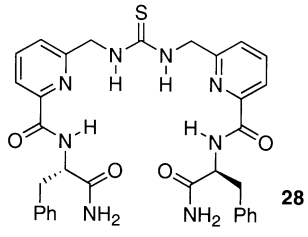
A study of the thermodynamic aspects of dicarboxylate complexation by bis-urea and bis-guanidinium receptors has recently been published by Hamilton and co-workers [40]. This suggests that in solvents such as DMSO, binding is predominantly enthalpically driven whilst in water/methanol mixtures the complexation process becomes endothermic and is entropically driven.

Kilburn and co-workers have combined a thiourea group with pyridine-amide moieties attached to chiral groups to produce a receptor (**28**) capable of enantioselective amino acid recognition [41]. The proposed binding mode of the receptor is shown in Fig. 5. Binding studies were conducted with compound **28** and a number of *N*-protected amino acid derivatives as their tetrabutylammonium salts by ^{1}H-NMR titration techniques in chloroform-*d*. For example, *N*-Ac–L-Gln–CO_2^- was bound with an association constant of 9000 M^{-1} whilst *N*-Ac–D-Gln–CO_2^- was bound with an association constant of 4520 M^{-1} confirming the ability of this receptor to differentiate between enantiomers. Mellet and co-workers have also used thiourea clefts for carboxylate and specifically biscarboxylate recognition [42].



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Using a similar binding motif, Caballero and co-workers have synthesised a number of receptors for α-heterocyclic and α-keto-acids [43]. These cleft species contain a hydrogen bond donor group designed to form a hydrogen bond to the heteroatom present in the heterocyclic guest. For example, receptor **30** binds furan-2-carboxylate 36 times more strongly than recep-

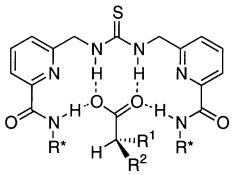


Fig. 5. Enantioselective recognition in Kilburn's urea based receptors.

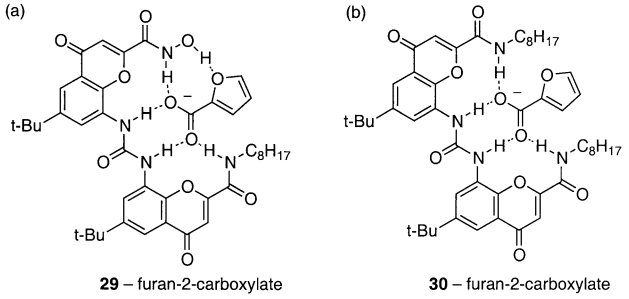


Fig. 6. Furan-2-carboxylate recognition by urea cleft species (a) **29** and (b) **30**.

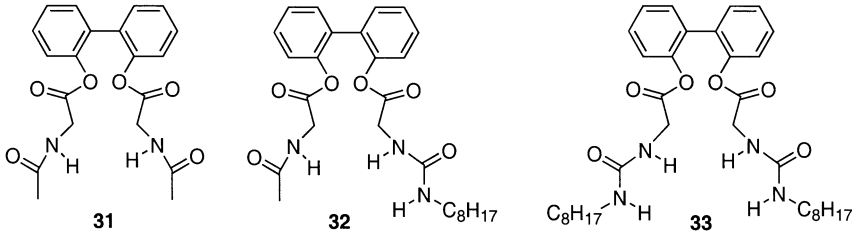
tor **29** in $CDCl_3/CD_3OD$ 99:1 v/v (Fig. 6). These workers have also synthesised similar macrocyclic receptors for chiral recognition of hydroxycarboxylates [44].

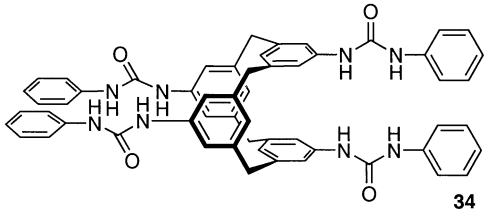
Albrecht et al. have made a series of cleft-like receptors **31**, **32** and **33** that contain two amides, one amide and one urea and two urea groups, respectively [45]. This enabled Albrecht to study the additive effect of extra hydrogen bonds on the stability of the nitrate complexes of these receptors since the receptors form two, three and four hydrogen bonds to this oxo-anion, respectively. These workers found that each additional hydrogen bond contributes between 2 and 3 kJ mol^{-1} to the stability of the complex in chloroform-*d*.

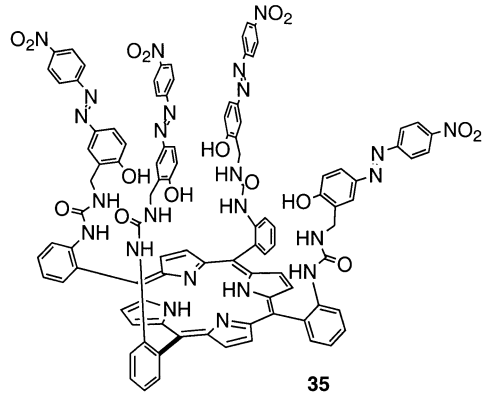
Moving on from clefts to macrocyclic receptors containing urea groups, there are two classes of receptor here, namely ureas appended to macrocycles and macrocycles composed of urea groups. In the former group, Lhoták and Stibor have recently reported the synthesis of a tetra-urea substituted calix[4]pyrrole in the 1,3-alternate conformation **34** [46]. Although receptor **34** contains two putative anion-binding sites, it was found that the receptor can only bind a single anion (presumably due to a conformational change in the calixarene upon binding the first anion altering the arrangement of the second binding site so rendering it unable to complex a second guest in addition to unfavourable electrostatic interactions).

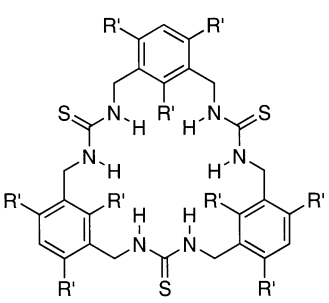
Hong and co-workers have used a porphyrin scaffold as the basis for a colorimetric anion sensor [47]. Four chromophoric units were appended to the *meso*-phenyl groups of the αααα-isomer to afford receptor **35** which exhibits a dramatic yellow to blue colour change in the presence of fluoride.

The tris-thiourea macrocycles **36** and **37** have been synthesised Lee and Hong and shown to be selective for dihydrogenphosphate (800 M^{-1}) in the case of **36** and acetate (5300 M^{-1}) in the case of **37** in DMSO-d_6 solution binding the anions with a 1:1 receptor:anion stoichiometry [48].

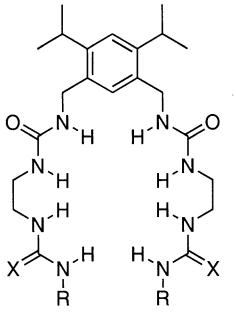




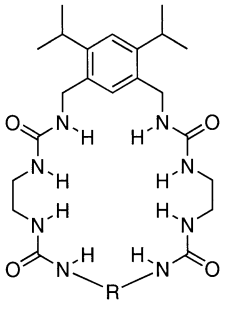




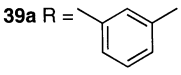
36 R' = H
37 R' = Et



38a X=O, R = C_3H_7
38b X=O, R = Ph
38c X=O, R = SO_2Ph
38d X=S, R = Ph



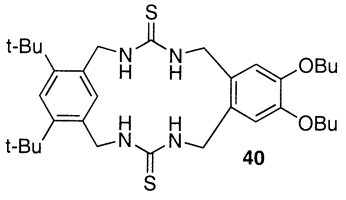
39a R =



39b = CH_2CH_2

Reinhoudt and co-workers have synthesised clefts **38a**–**d** and macrocycles **39a** and **b** [49]. The cleft-like receptors (**38**) bind dihydrogenphosphate in a 1:2 receptor:anion stoichiometry (e.g. receptor **38b** binds $H_2PO_4^-$ with $\beta_2 = 5 \times 10^7\ M^{-2}$ in DMSO-d_6) whilst the analogous macrocyclic systems bind this oxo-anion in a 1:1 receptor anion stoichiometry e.g. receptor **39a** binds $H_2PO_4^-$ with an association constant $K = 2.5 \times 10^3\ M^{-1}$ in DMSO-d_6 and Cl^- with an association constant of 500 M^{-1} under the same conditions. The more flexible and smaller receptor **39b** binds chloride with an association constant of less than 50 M^{-1} giving in this case a selectivity for $H_2PO_4^-$ of ≥ 100.

Tobe and co-workers have continued their work on thiourea anion receptors and have synthesised a variety of cyclic thiourea macrocycles **40**–**44** and a cleft-like receptor **45** [50]. The association constants of these receptors with a variety of anions in DMSO solution are presented in Table 1. Compound **42** did not interact with any of the anions studied. The remaining receptors



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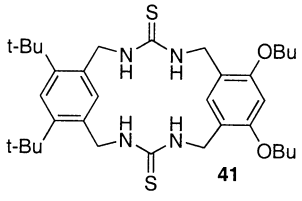

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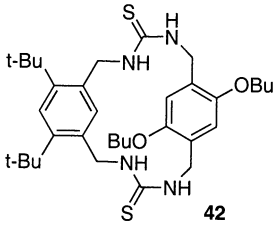

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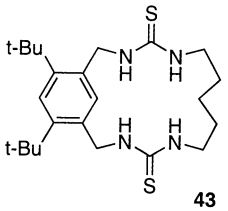

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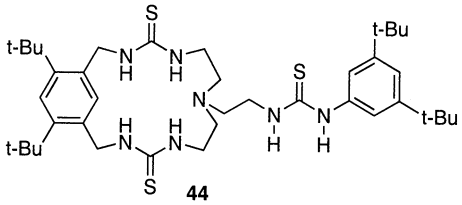

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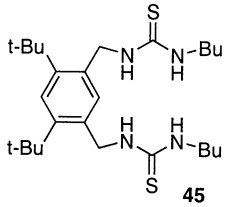

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Table 1
Association constants of receptors **40**, **41** and **43**–**45** with guest anions [a]

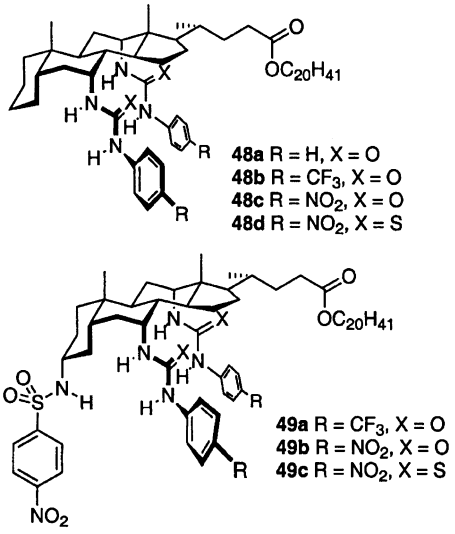
Anion [b]	Receptor				
	40	**41**	**43**	**44**	**45**
$H_2PO_4^-$	12 000	2500	4800	[c]	520
AcO^-	2200	390	560	8300	110
Cl^-	120	14	54	1500	7
HSO_4^-	19	2	4	120	1
Br^-	12	<1	3	40	<1

[a] Measured in DMSO-d_6 at 60 °C by the ^{1}H-NMR titration method.
[b] Anions were used as their tetrabutylammonium salts.
[c] The association constant was too large to measure accurately.

were found to be selective for $H_2PO_4^-$ with the lariat system **44** having the highest affinity for anions.

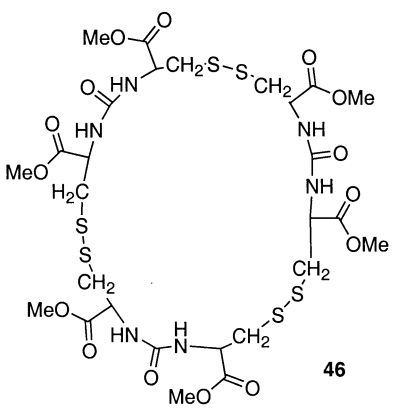
By condensing L-cystine dimethyl ester with triphosgene under high dilution conditions Ranganathan and Lakshmi have isolated two cyclic ureas **46** and **47** [51]. Receptor **46** was found to bind chloride with an association constant of 2.05×10^3 M^{-1} in $CDCl_3$ and bromide with an association constant of 2.01×10^2 M^{-1}. The larger macrocycle **47** was found to bind squarate with an association constant of 3.21×10^3 M^{-1}.

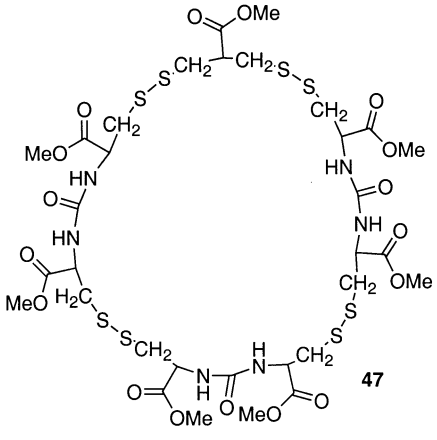
Over recent years, Davis and co-workers have produced a variety of anion receptors based upon cholic acid (see article in this volume). Very recently, new urea derivatized receptors termed 'cholapods' have been synthesised that form remarkably strong complexes with bromide and chloride anions in water saturated chloroform solution [52]. Receptors **48a**–**d** contain two urea/thiourea groups with electron withdrawing substituents (CF_3/NO_2) linked to the chloic acid skeleton whilst **49a**–**c** contain an additional sulfonamide group. The attachment of the hydrogen bonding groups to the steroid skeleton largely prevents the formation of intramolecular hydrogen bonding, whilst the electron-withdrawing units increase the acidity of the urea moieties thus increasing their affinity for anions. This is reflected in the very high association constants with chloride ($K_a = 1.03 \times 10^{11}$ M^{-1} with receptor **49c** in wet chloroform). These molecules are predicted to show excellent phase transfer properties as well as displaying biological activity possibly as membrane transport agents for chloride.



2.4. Polyammonium macrocycles and ammonium containing anion receptors

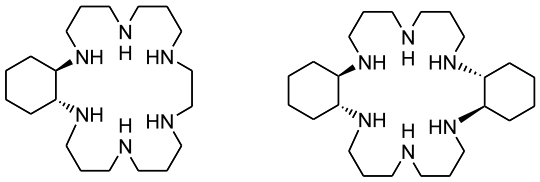
This issue of Coordination Chemistry Reviews commemorates Simmons and Park's paper in the Journal of the American Chemical Society reporting the first





example of a synthetic anion receptor that consisted of a cryptand-like macrobicycle containing two protonated ammonium groups [53]. Some 35 years on, the field of anion recognition by ammonium and polyammonium receptors is still very active [54]. A general review of this area by Bowman-James and co-workers is included in this issue. Great strides forward in the understanding of the thermodynamics of anion complexation by polyammonium macrocycles have been made in this area recently. A general review of the thermodynamics of anion complexation by Schmidtchen also appears in this issue. The reader is also directed to an excellent account of this area by Bianchi and García-España which appeared in 1997 [55]. In 2000 and 2001, work has continued in this area, not only using polyammonium macrocycles as complexation agents (for inorganic anions such as phosphates [56–58] and sulfate [59,60] and also nucleotides [57,58,61]) but also as catalysts for reactions including the hydrolysis of ATP [62].

Gotor and co-workers have examined the anion complexation properties of two chiral hexaazamacrocycles **50** and **51** [63]. These receptors were synthesised using a chemoenzymatic approach [64]. Protonation constants for the macrocycles were determined and association constants for the macrocycles with a variety of chiral anions measured by potentiometric titration with K values being determined for complexes containing 3, 4, 5 and 6 protons in 0.1 M Me_4Cl aqueous solutions at 298 K. Hexaprotonated receptor **50** was found to preferentially bind D-tartarate ($\log K = 4.10$) over its enantiomer ($\log K = 3.49$) whilst hexaprotonated receptor **51** preferentially binds *N*-Ac–D-aspartate ($\log K = 5.34$) over *N*-Ac–L-aspartate ($\log K = 4.57$).



50 **51**

A number of groups have continued their studies of polyammonium cryptand systems. Nelson, McKee and co-workers have continued to study the anion complexation properties of cryptand receptors **52** and **53**. For example, hexaprotonated receptor **52** has been recently shown to be selective for di-negative tetrahedral oxo-anions (CrO_4^{2-}, SeO_4^{2-} and SSO_3^{2-}) over mono-negative analogues (ClO_4^-) in both solution and the solid state [65]. The crystal structure of the chromate complex is shown in Fig. 7. In the absence of dinegative anions the receptors function as hosts for perchlorate and nitrate (Fig. 8) [66].

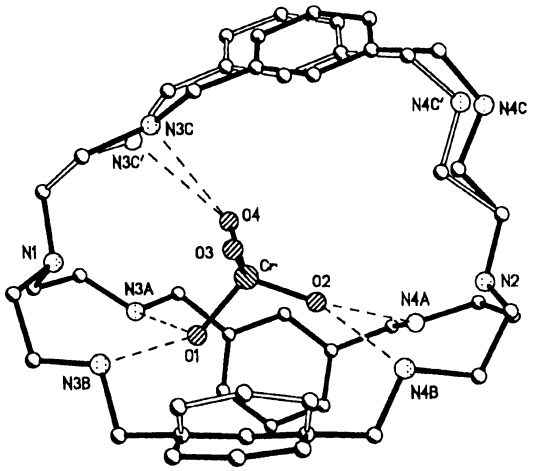


Fig. 7. The X-ray crystal strcture of hexaprotonated **52** binding CrO_4^{2-} (disorder in the cryptand is shown). (Reproduced with permission from J. Chem. Soc. Dalton Trans. (2001) 1395, Copyright 2001, Royal Society of Chemistry.)

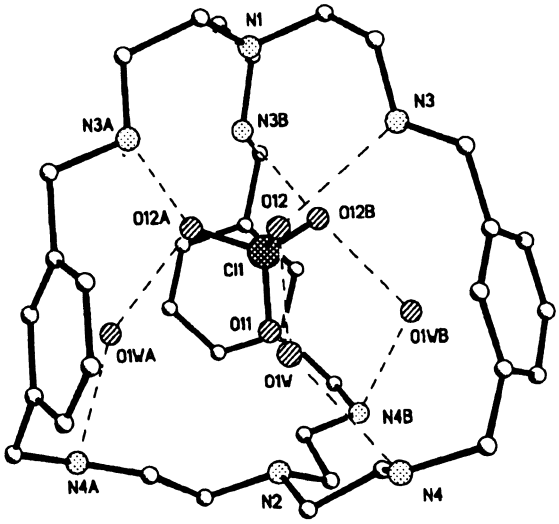
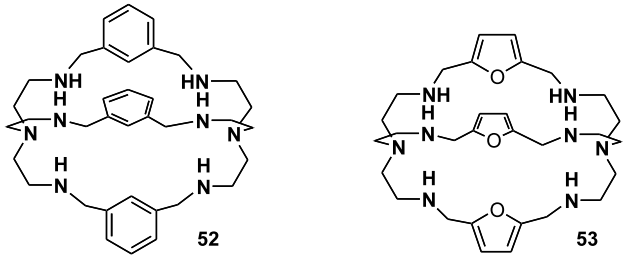


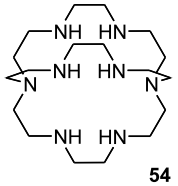
Fig. 8. The perchlorate complex of **52** showing interactions with bound waters. (Reproduced with permission from J. Chem. Soc. Dalton Trans. (2000) 2856, Copyright 2000, Royal Society of Chemistry.)



52 **53**

Bowman-James and co-workers have studied the fluoride anion-binding ability of receptor **52**. ^{19}F-NMR solution studies were performed and crystallographic studies of the complex revealed that **52** can simultaneously encapsulate a fluoride and a water molecule [67]. The same group have studied the com-

plexation properties of the 'tiny' octaazacryptand **54** [68]. Between pH 2.5 and 5.5, the receptor was found to have a strong affinity for fluoride and little affinity for other anions, however below pH 2.5 the receptor was found to complex chloride. Crystallographic evidence indicates the formation of six ammonium-chloride hydrogen bonds with N–Cl distances ranging from 2.99(1) to 3.18(1) Å in the solid state. Wipff and co-workers have carried out molecular dynamics simulations on the same system revealing different solution complex structures for the fluoride complex from that found in the solid state [69].



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By tricapping the lower-rim of a tribenaldehyde functionalised calix[4]arenes with tren, followed by sodium borohydride reduction, Tuntulani et al. have synthesised receptors **55** and **56** containing both a phenolic oxygen metal binding site and an apparently tetra-protonated anion-binding pocket [70]. The association constants of **55** and **56** with bromide and iodide in the presence of various cations in a variety of solvents are shown in Table 2. In the absence of a metal ion, both receptors bind iodide more strongly. However, addition of a metal ion to receptor **56** reduced the affinity of the receptor for both bromide and iodide possibly due to the alkali metal not being effectively bound by the calixarene and hence competing with the calixarene for the anion. In the presence of potassium cations, receptor **55** increases its affinity for bromide suggesting that the ion-pair is bound within the receptor.

Table 2
Association constants of receptors **55** (in DMSO-d_6) and **56** (in a mixture of $CDCl_3$ and CD_3OD) towards Br^- and I^- in the presence of various counter cations [a]

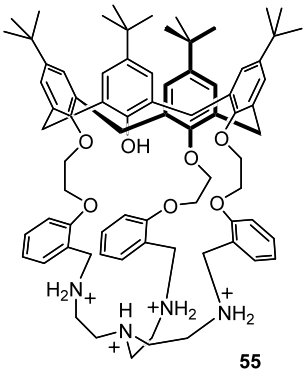
Metal	Anion	K (M^{-1})	
		55	**56**
None [b]	Br^-	84.2	76.5
Na^+	Br^-	58.6	53.0
K^+	Br^-	120.1	34.9
None [b]	I^-	108.9	137.9
Na^+	I^-	77.2	57.3
K^+	I^-	103.3	66.3

[a] All experiments were carried out at 298 K, errors estimated to be less than 15%.
[b] Using Bu_4N^+ as countercation.

2.5. Guanidinium, amidinium and thiouronium based receptors

Guanidinium, amidinium and thiouronium receptor groups like ammonium, combine hydrogen and electrostatics to bind anions. Their complementarity to oxo-anions such as carboxylates and phosphates has meant that many (but not all) of the receptors synthesised containing these groups have been designed to complex biologically interesting species such as the phosphate groups of nucleotides and oligonucleotides and the carboxylate termini of peptide chains. In an interesting recent paper, Hamilton and co-workers have studied the binding, of nitronate anions by a variety of urea and guanidinium functionalised receptors and the effect of receptors on the kinetics and regiochemistry of nitronate alkylation [71].

By attaching a thiouronium group to an anthracene fluorophore, Kubo et al. have synthesised an acetate selective fluorescent receptor **57** [72]. The fluorescence of



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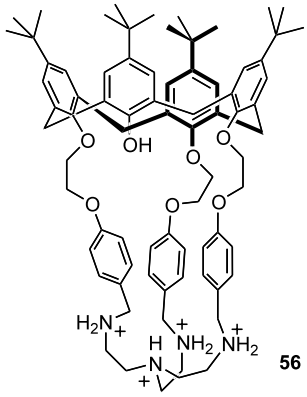

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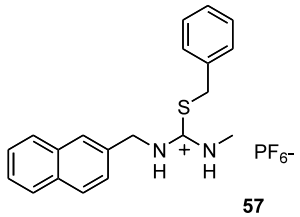
57 is enhanced upon addition of oxo-anions. Acetate is particularly strongly bound ($K_a > 10^6$ M^{-1}) followed by $(BuO)_2P(O)O-$ ($K_a = 5.6 \times 10^4$ M^{-1}) in acetonitrile at 25 °C. The fluorescence response to chloride was too low to determine an association constant.



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Gale and co-workers have shown that receptors **58** and **59** bind a variety of bis-carboxylates in DMSO-d_6 solution. NMR titration evidence suggests he formation of lower-rim bridged complexes during the addition of tetrabutylammonium bis-carboxylate salts to the receptors. The crystal structure of the malonate complex of receptor **59** was elucidated revealing three different binding modes for malonate in the solid state—bridging, end-on (normal) and side on (Fig. 9) [73]. The serendipitous isolation of a difluorophosphinate salt of **58** revealed that this anion can accept hydrogen bonds from amidinium through both fluorine and oxygen [74].

Diederich and co-workers have reported a cleft-like bis-amidinium receptor **60** based upon a 1,1′-binaphthalene scaffold [75]. This receptor also binds bis-carboxylates, forming a complex with glutarate with $K_a = 8.2 \times 10^3$ M^{-1} in methanol. Isothermal calorimetry

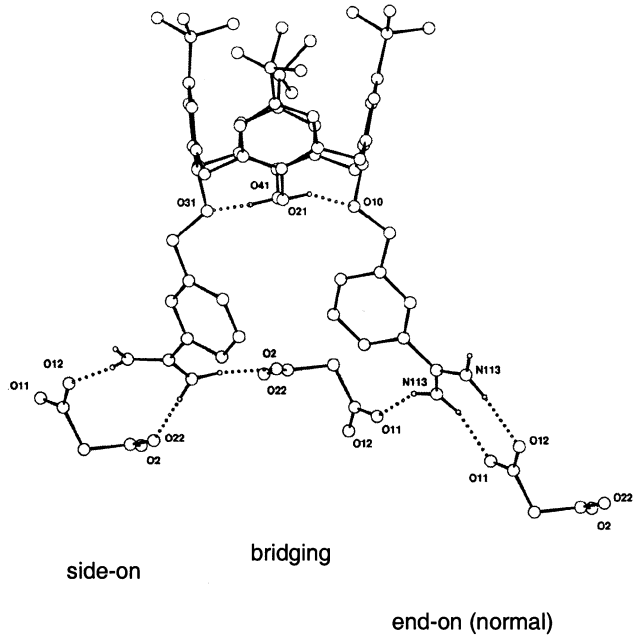
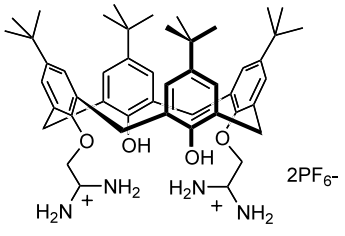


Fig. 9. Malonate complex of **59** showing three carboxylate binding modes.

Schmuck has continued his studies on the anion-complexation and self-assembly properties of guandinium functionalised pyrroles [77]. This work has included a study of the self-assembly of 2-(guanidiniocarbonyl)-pyrrole-4-carboxylate **62** in DMSO solution [78]. As was the case with Diederich's



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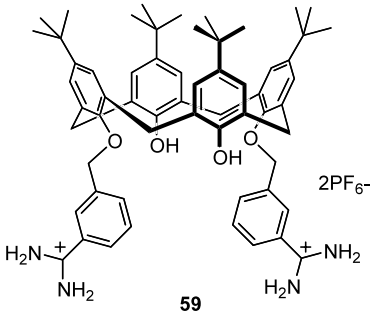
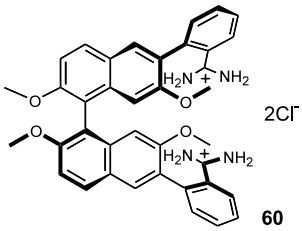


59

and van't Hoff analysis revealed that the complexation is strongly entropy driven (presumably due to solvation effects) with an unfavourable enthalpic change upon guest binding. The same group have studied the binding of carboxylates to the tetra-amidinium functionalised calix[4]resorcinarene **61** [76]. Isophthalates were found to bind to the amidinium functionalised upper rim in (in a 1:2 receptor:guest stoichiometry) whilst in water one of the guests was found to bind in the cavity of the calix. amidinium–carboxylate complexation process [75], the formation of guanidinium–carboxylate salt bridges in solution to form non-covalently linked oligomers of **62** was found to be an entropy driven process. The dimerisation of compound **63** (chloride or hexafluorophosphate salt) has also been studied in DMSO solution [79]. The molecule forms discrete dimers via the formation of amidinium–ester hydrogen bonds together with a contribution from a pyrrole–pyrrole π-stacking inter-



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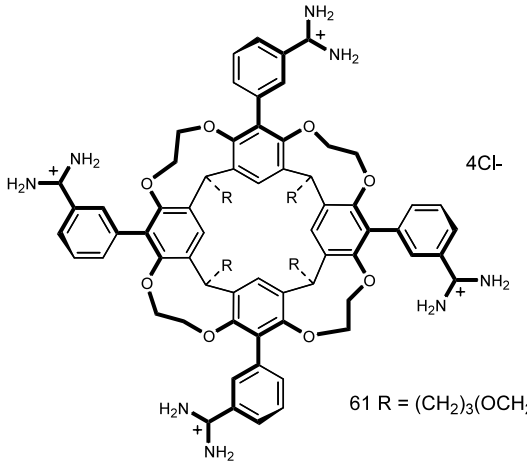


action (Fig. 10a). The addition of picrate anions breaks up the dimer and the receptor forms a picrate complex (Fig. 10b). Meanwhile, Schmuck has shown that the chiral receptor **64** is capable of discriminating between enantiomeric carboxylates in 40% water/DMSO-d_6 solution (e.g. Ac–L-AlaO$^-$: $K_a = 1610\ M^{-1}$; Ac–D-AlaO$^-$: $K_a = 930\ M^{-1}$) [80].

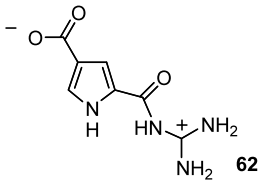
phosphate buffer solution into chloroform was measured. Good enantioselectivites were observed with for example receptor **66** showing an enantioselectivity of 10:1 (L:D) when extracting *N*-Ac–DL-alanine.

Anslyn's group have continued to develop new anion receptors containing guandinium groups [82]. Anslyn has recently reviewed the concept of 'generalised' or 'differential' sensing wherein a number of different sensors are used in an array that produces a particular pattern of response upon exposure to mixtures of analytes. An analogy is drawn between this approach and the senses of smell and taste in mammals. The reader is directed to this excellent account of a new approach to molecular recognition [83].

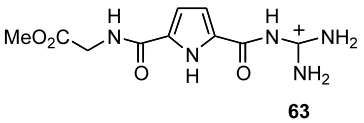
2.6. Other non-metallated anion receptors

Sessler and Miyaji have investigated a number of chromophoric aromatic compounds containing hydrogen bond donors as potential colourimteric anion sensors [84]. A variety of commercially available compounds were tested in DMSO or dichloromethane solution. The candidate sensors use a variety of hydrogen bond donor groups including amines, amides, urea and alcohols. The results are summarised in Fig. 11—a checked box indicating that a 'naked-eye' detectable colour change is observed upon addition of 100 equivalents of the anionic analyte.

Martínez-Máñez and co-workers have used a novel approach to ATP sensing [85]. The 1,3,5-triarylpent-2-en-1,5-dione **72** undergoes an acid catalysed cyclisation



62



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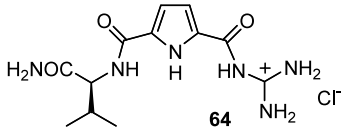


64

We have already seen the high anion affinities that receptors based upon steroid scaffolds are able to achieve. Davis has also produced guanidinium functionalised cholic acid derivatives (cholapods) (e.g. receptors **65**–**71**) that also contain anion-binding carbamate groups [81]. The ability of these cationic species to extract chiral carboxylate anions from an aqueous

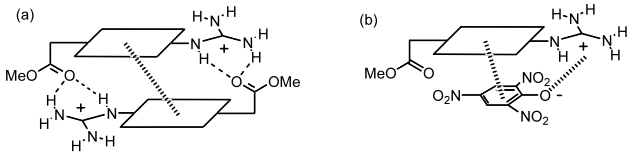
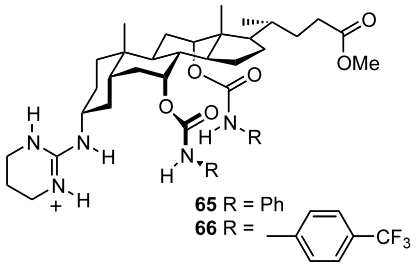
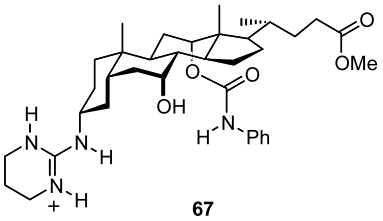
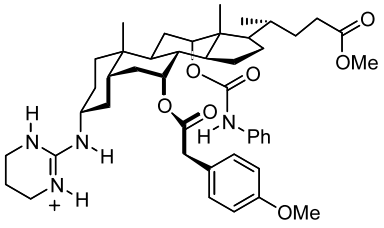
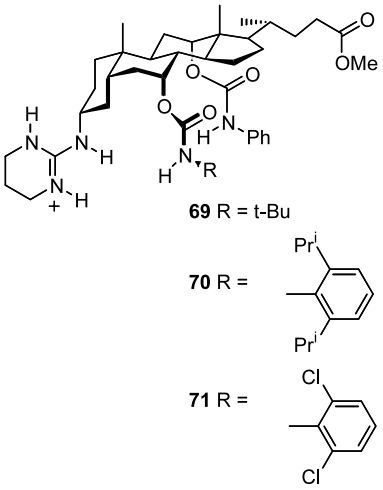


Fig. 10. Dimerisation of Schmuck's system is disrupted by picrate.









to form a pyrylium cation **73** (Scheme 2). This cyclisation is accompanied by a dramatic yellow to magenta colour change. Martínez-Máñez and co-workers discovered that at pH 6 in dioxane/water (70/30 v/v) **72** forms a yellow solution with bromide, chloride, phosphate, GMP or ADP. Upon addition of sulfate the solution turns paled red, however upon addition of ATP the solution turns bright magenta. The authors attribute the remarkable selectivity to coordination between **72** and ATP causing the pK_a of the amine group present in **72** to increase, therefore favouring cyclisation at higher pH values.

Cyclodextrins (CDs) continue to be used as receptors for anions [86–87]. Kano and co-workers have shown that carboxylate anions form complexes with CDs and linear polydextrins in DMSO-d_6 by hydrogen bond formation to the vicinal hydroxy groups (of CDs) (Fig. 12) [88] binds *para*-methylbenzoate (added as the sodium salt) with an association constant of 792 ± 45 M^{-1} at 298.15 K in DMSO-d_6. The addition of a small amount of water was found to disrupt the hydrogen bonding interaction.

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 2000 and 2001. The metal ions in these receptors play a number of different roles which may be classified as follows:

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 organisation element in an anion receptor.
v) a co-bound guest in an ion-pair receptor.

Of course, a receptor may fall into more than one of these categories. It should therefore be noted that these

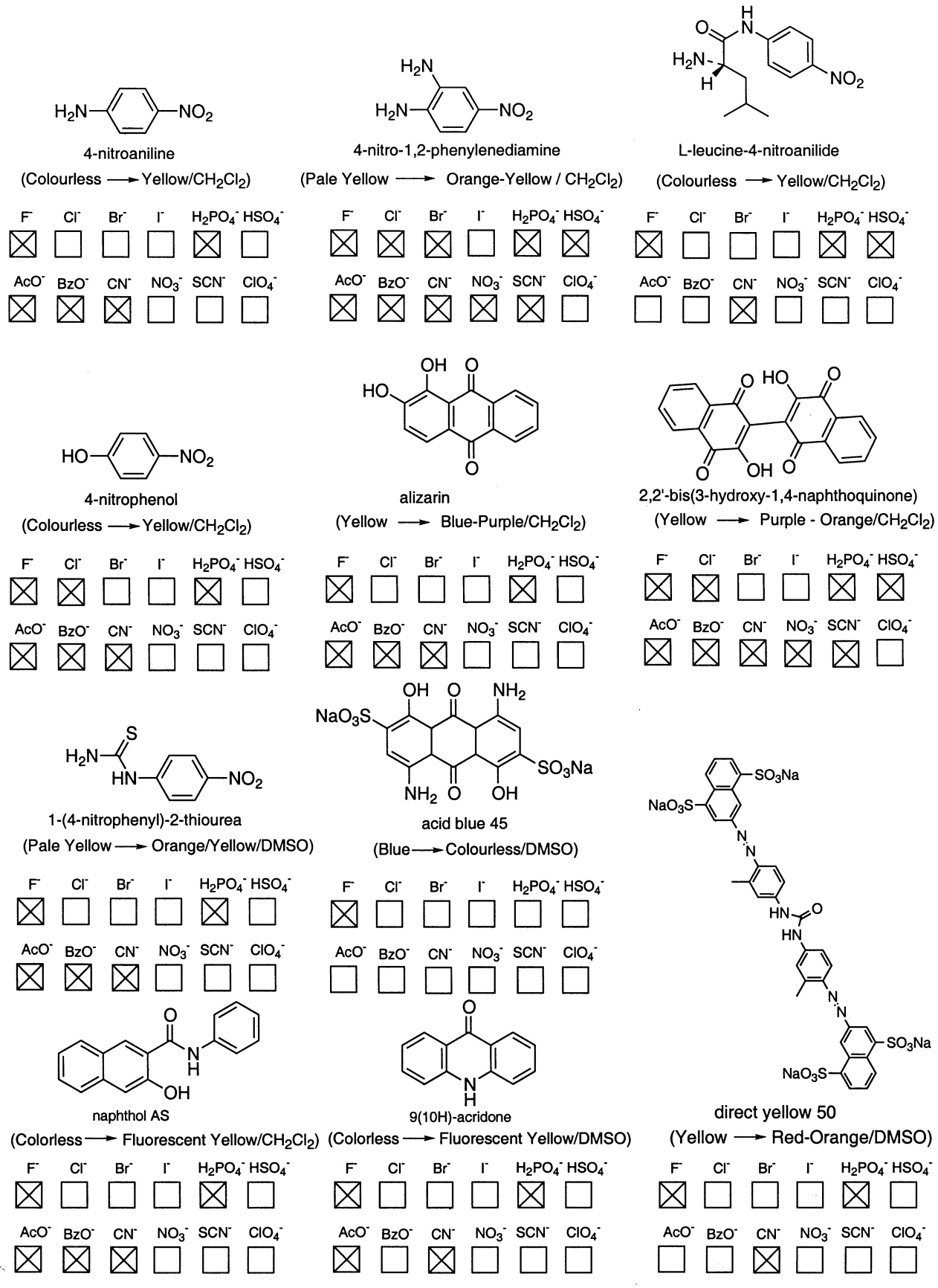


Fig. 11. Off the shelf colorimetric anion sensors.

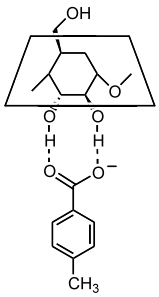
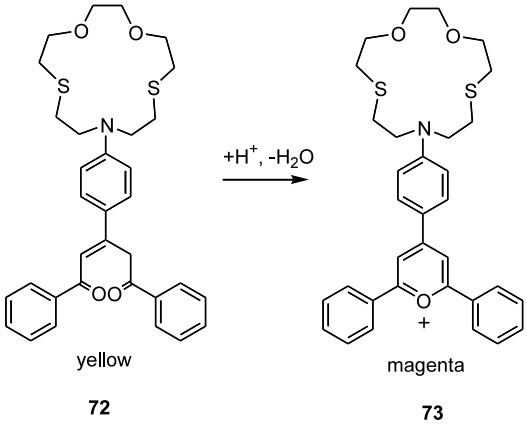


Fig. 12. Carboxylate binding to a cyclodextrin.



Scheme 2.

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

Fabbrizzi and co-workers have obtained the crystal structure of a di-copper complex of **53** [89]. The crystal structure of the di-copper cryptand reveals a bromide anion bound between the two copper ions in a 'cascade-complex' fashion (Fig. 13). Association constants were

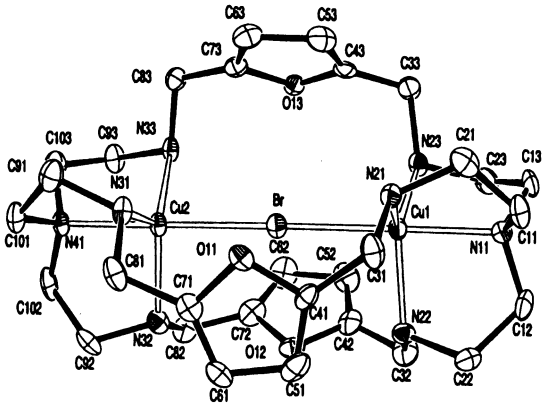
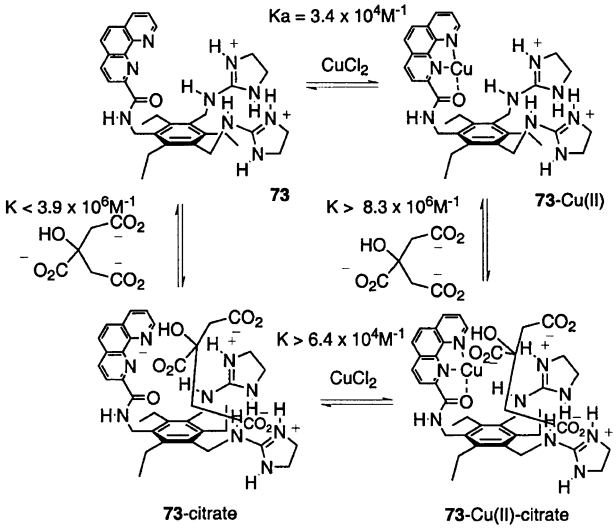


Fig. 13. X-ray crystal structure of the cascade complex [**53**-Cu(II)2Br]$^{3+}$. (Reproduced with permission from Angew. Chem. Int. Ed. Engl. 39 (2000) 2917, Copyright 2000, Wiley-VCH.)

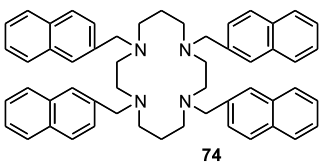


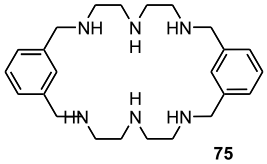
Scheme 3.

determined by UV–vis titration techniques in buffered (pH 5.2) aqueous solution. The di-copper complex was found to be selective for chloride anions (log $K = 3.98$). The same workers have utilised di-copper cryptand complexes as displacement assays using a bound coumarine 343 guest in a carbonate sensing system that operates in aqueous solution [90].

Anslyn and co-workers have continued their studies of receptors based upon the 2,4,6-triethyl-1,3,5-trisubstituted benzene skeleton [91] Compound **73** can bind citrate or copper(II) ions. The presence of one guest enhances the binding of the other (see Scheme 3) and in addition the copper(II) ion quenches the fluorescence of the 1,10-phenanthroline group. Addition of citrate decreases this effect so increasing the fluorescence of the ensemble, allowing the complex to be used as a sensor for citrate in micromolar concentrations.

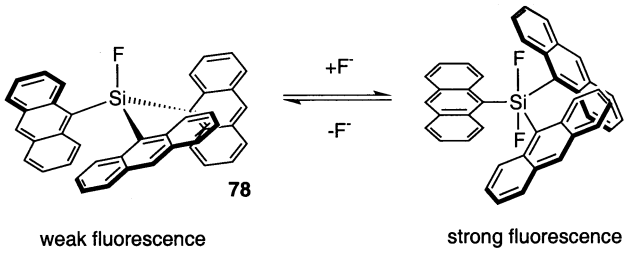
Metal complexes of aza-macrocycles have been used as anion receptors by a number of groups. Martínez-Máñez and co-workers have also used metals in fluorescent anion receptor systems. The fluorescence of the copper(II) complex of **74** was found to be selectively enhanced by sulfate anions in THF:water mixtures [92] whilst Pauwels et al. have studied the anion complexation properties of zinc complexes of **75** [93].


74

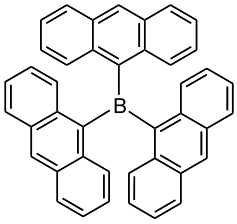

75

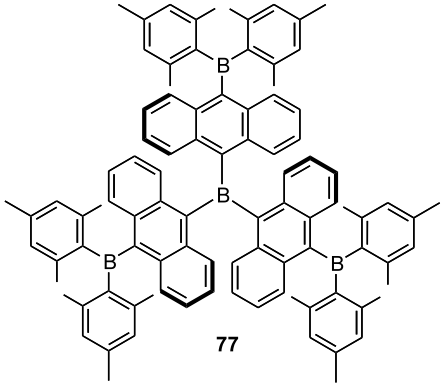
By inserting Lewis acidic boron [94] or silicon atoms [95] in extended π-conjugated systems, Yamaguchi, Akiyama amd Tamao have produced new colorimetric sensors for fluoride anions. In the presence of fluoride,

triarylboranes such as **76** are converted to borates. This conversion disrupts the π-electron delocalisation in the receptor (Scheme 4) causing a colour change (from orange to colourless in the case of **76**). In the case of receptor **77**, the UV–vis spectra revealed the formation of three fluoride complexes corresponding to fluorides binding to the three outer boron atoms. In the silicon based receptors produced by the same group, the addition of fluoride to trianthrylfluorosilanes e.g **78** (Scheme 5) causes a change in the through space interactions between the anthracene moieties so causing a change in the receptor's fluorescence.



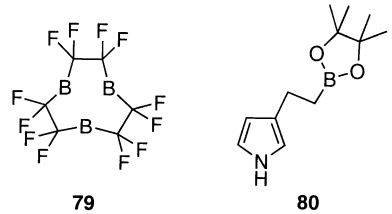
Scheme 5.

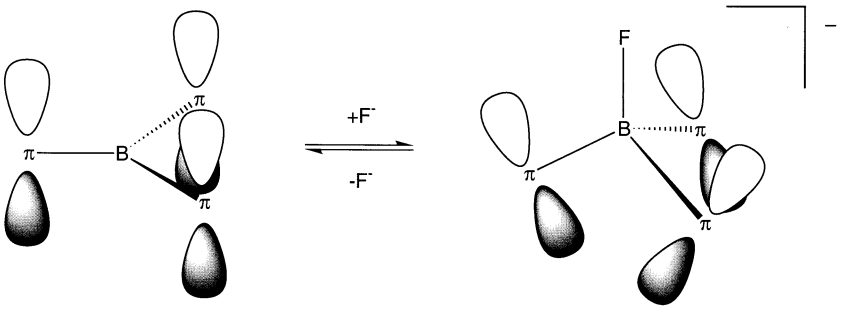




Aldridge and co-workers have conducted DFT studies on a variety of boron containing species. Their results suggest that compound **79** binds CH_3^- very strongly [96]. Fabre and co-workers have continued their studies of Lewis acid containing electropolymerised films extending their work from polypyrrole to polythiophene and polyaniline systems. Cyclic voltammetry revealed a negative shift in the oxidation waves of polypyrrole films grown from monomer **80** in the presence of fluoride anions [97]. Anion-selective electrodes containing mercury containing receptors based upon *N*-benzyloxyamide derivatives have been shown by Suzuki and co-workers to display anti-Hofmeister selectivity [98].

By hydrolysing $[CH_2\{SnPh_2CH_2Si(O^iPr)Me_2\}_2]$ under acid conditions and subsequent treatment with

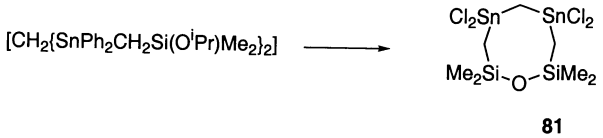




Scheme 4. Schematic representation of the switching of π-conjugation in the LUMO of boron-based π-electron systems: π stands for π-conjugated moieties.

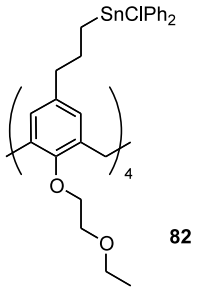
mercuric chloride, Jurkschat and co-workers have isolated a new di-tin di-silicon macrocycle **81** (Scheme 6) [99]. The crystal structure of this material is shown in Fig. 14a. The macrocycles form dimers in the solid state linked via a weak Cl–Sn interaction (3.684(1) Å). The chloride complexation properties of the receptor were followed using a $^{119}Sn\{^{1}H\}$ titration in dichloromethane indicating the formation of a 1:1 complex in solution. The crystal structure of the chloride complex confirmed this stoichiometry and is shown in Fig. 14b (Sn(1)–Cl(5) 2.891(1), Sn(2)–Cl(5) 2.781(1) Å).

Blanda and Herren have synthesised a calix[4]arene **82** carrying four alkyl-$SnClPh_2$ groups attached to the upper rim [100]. The receptor binds 4 equivalents of chloride (i.e. each Sn binding site operates independently).



81

Scheme 6. Synthesis of the eight-membered ring **81**: (i) 0.5 M H_2SO_4, Et_2O ($-2^{i}PrOH$); (ii) $4HgCl_2$, acetone ($-4PhHgCl$).



82

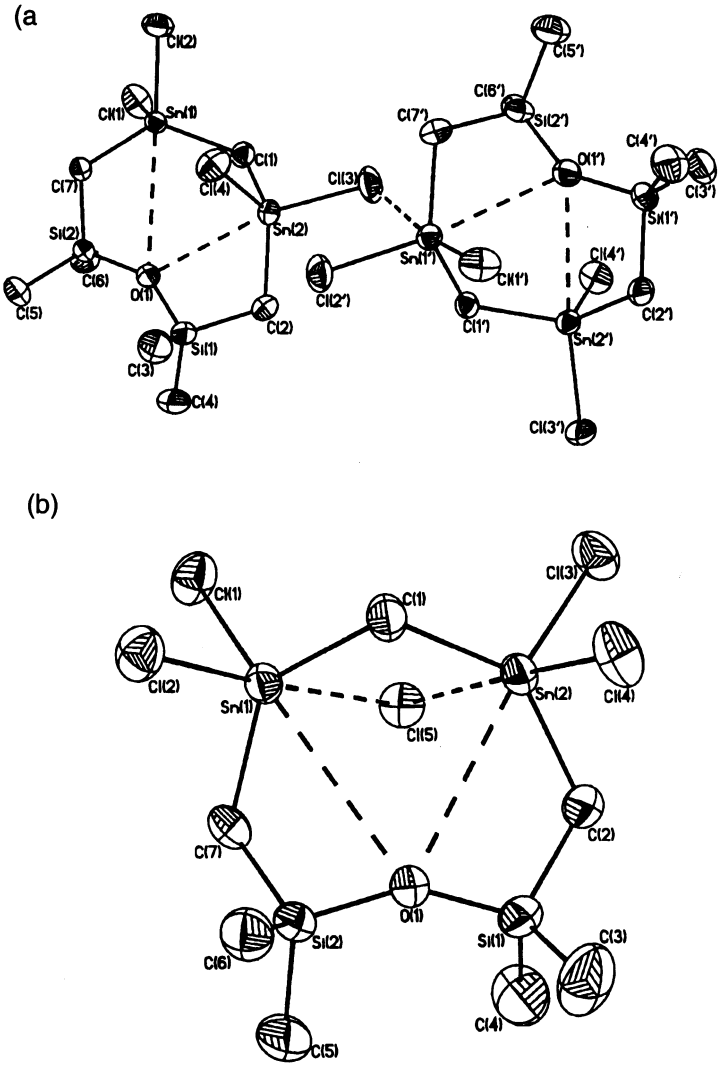


Fig. 14. (a) The X-ray crystal structure of **81** showing dimerisation via a Cl···Sn interaction. (b) The chloride complex of **81**. (Reproduced with permission from Chem. Eur. J. 7 (2001) 347, Copyright 2001, Wiley-VCH.)

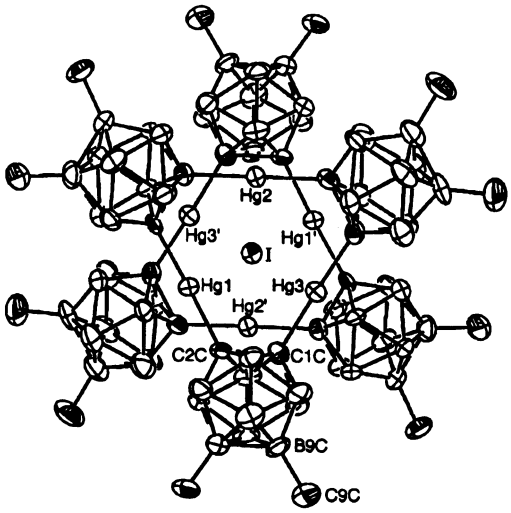


Fig. 15. The X-ray crystal structure of the iodide sandwich complex $(\mathbf{83})_2I^-$. (Reproduced with permission from Angew. Chem. Int. Ed. Engl. 39 (2000) 776, Copyright 2000, Wiley-VCH.)

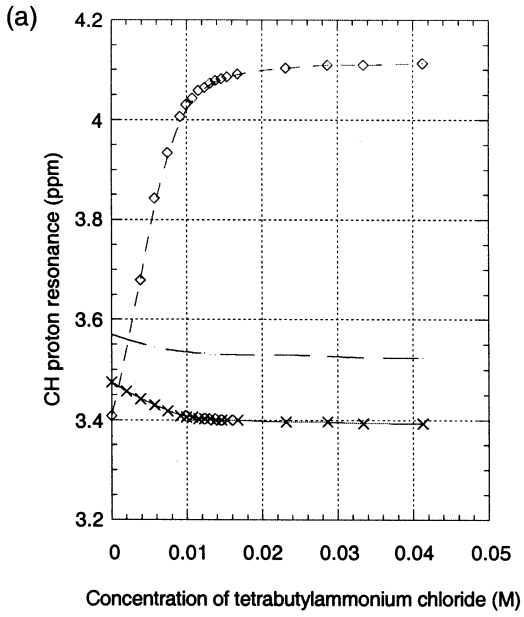
Continuing their work on the anion receptor properties of mercuracarborands, Hawthorne and co-workers have recently reported the synthesis of a sandwich complex consisting of two trimeric *B*-hexamethyl-9-mercuracarborand-3 [9,12-$(CH_3)_2$–$C_2B_{10}H_8Hg]_3$ receptors (**83**) and an iodide anion [101]. The complex was formed by reaction of the receptor with LiI. The crystal structure of the complex shown in Fig. 15 reveals that the iodide anion is bound to six mercury atoms with Hg···I distances between 3.2492(5) and 3.2728(5) Å.

The transport of salts from aqueous to organic solutions by uranyl salophene receptors has been studied n detail by de Jong and co-workers [102].

3.2. Metals and Lewis acids in anion sensors

Ferrocene-appended aza-macrocycles [103–105] and amides [106,107] have been synthesised and studied by a number of research groups. These systems are the subject of a review by Beer et al. in this issue of Coordination Chemistry reviews and will not be covered in detail here.

The ferrocene appended calixpyrrole **84** has been synthesised by Gale et al. by co-condensing cyclohexanone, pyrrole and acetylferrocene [108]. NMR evidence (in acetonitrile-d_3/DMSO-d_6 9:1 v/v) suggests that there may be an interaction between a cyclopentadienyl hydrogen atom and the bound anion in solution (Fig. 16). Cathodic shifts of the ferrocene/ferrocenium redox couple were observed upon addition of a variety of anions with the largest shift ($\Delta E = 100$ mV (approximately) being observed upon addition of dihydrogenphosphate).



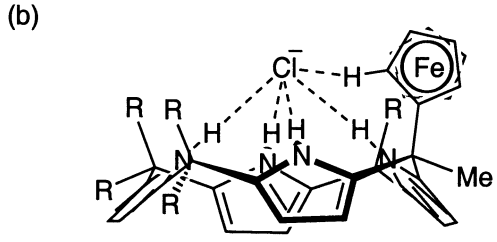
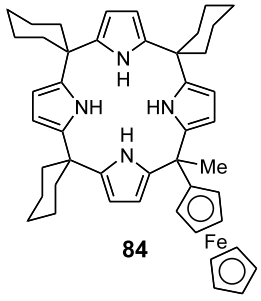
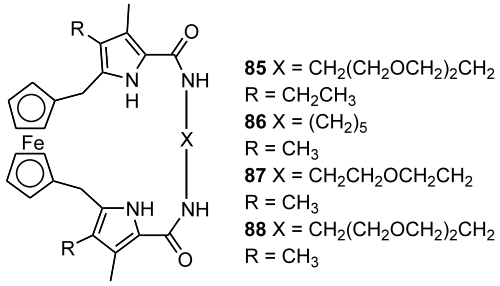


Fig. 16. (a) Proton NMR titration profile for addition of chloride to **84** in CD_3CN:DMSO-d_6 9:1 (v/v) solution; and (b) proposed CH-anion interaction in complex.



84

Sessler et al. have also reported the synthesis of a series of macrocyclic pyrrole-containing *ansa*-ferrocenes **85**–**88** [109]. By increasing the number of oxygen atoms in the linker, Sessler increased the affinity of this class of receptor for dihydrogen phosphate (Table 3) although the increase in association constant is only partially reflected in the shift of the ferrocene/ferrocenium redox couple.



85 X = $CH_2(CH_2OCH_2)_2CH_2$
R = CH_2CH_3
86 X = $(CH_2)_5$
R = CH_3
87 X = $CH_2CH_2OCH_2CH_2$
R = CH_3
88 X = $CH_2(CH_2OCH_2)_2CH_2$
R = CH_3

Table 3
Association constants and electrochemical data for $H_2PO_4^-$ complexes formed with receptors **86**, **87** and **88**

Receptor	Oxygens in linker	K_a [a] (M^{-1})	$E_{1/2}$ [b] (mV)	ΔE_c [c] (mV)
86	0	4050±300	432±5	128
87	1	13 200±1500	428±5	140
88	2	81 400±9700	432±4	140

[a] Association constants for anion binding recorded in 2% dimethylsulfoxide-d_6–dichloromethane-d_2 determined by ^{1}H-NMR titration techniques.

[b] Determined in dichloromethane containing 0.1 M n-Bu_4NPF_6 as the supporting electrolyte. Solutions of **86**–**88** were 0.001 M and the potentials were determined with reference to Ag/AgCl.

[c] Cathodic shift observed after the addition of 5 molar equivalents of n-$Bu_4NH_2PO_4$.

Sun and Lees have synthesised a Crabtree-type [12] amide cleft containing luminescent rhenium centres for use as an anion sensor [110]. The synthesis of receptor **89** is shown in Scheme 7. The luminescence of **89** is quenched by a variety of anions (the change upon addition of fluoride is shown in Fig. 17). The highest affinity was observed for CN^- followed by $F^- > I^- > Cl^- = Br^- = OAc^- \gg H_2PO_4^- > NO_3^- > ClO_4^-$.

Jurkschat et al. have incorporated ferrocene groups into silicon and tin containing macrocycles forming new electrochemical anion sensors e.g. **90** [111]. This receptor displays anion dependent cathodic shifts (Cl^- $\Delta E = 130$ mV; F^- $\Delta E = 210$ mV; $H_2PO_4^-$ $\Delta E = 480$ mV) in CH_2Cl_2 in the presence of anions.

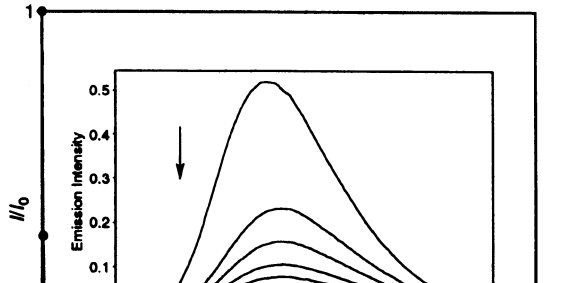
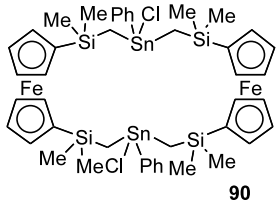


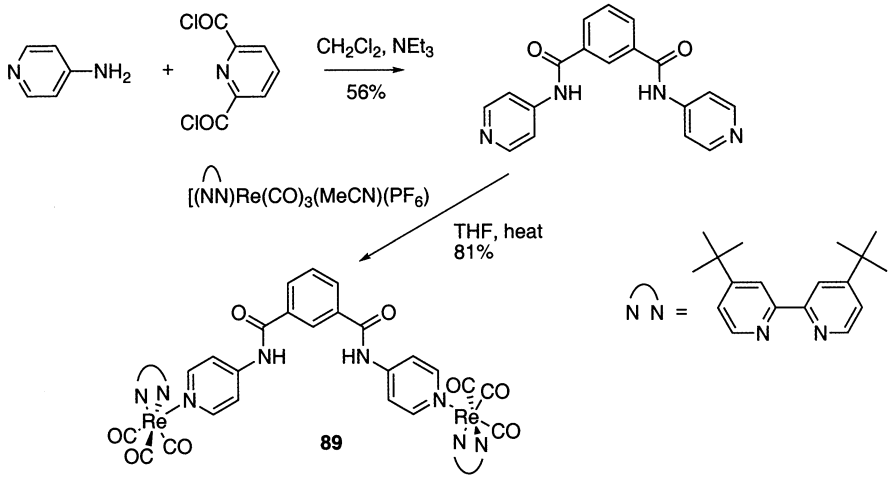
Fig. 17. Titration curve of the addition of F^- anions (as tetrabutylammonium salt). The inset shows the change of the emission intensity of **89** in CH_2Cl_2 solution upon addition of F^- anions. Excitation wavelength is 360 nm. (Reproduced with permission from Chem. Commun. (2000) 1687, Copyright 2000, Royal Society of Chemistry.)



90

3.3. Metals as electron-withdrawing agents in anion receptors

Atwood and co-workers pioneered the use of metals as electron withdrawing agents in metallated calixarene

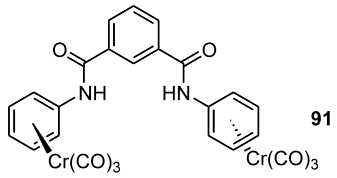


89

Scheme 7.

and resorcinarene anion receptors. This area of research is the topic of a separate review in this issue of Coordination Chemistry Reviews.

Gale and co-workers have attached $Cr(CO)_3$ groups to a Crabtree-type amide cleft [12] to produce a highly selective receptor for chloride [112]. Receptor **91** was synthesised by condensing 1,3-isophthaloyl chloride with (η^6-aniline)$Cr(CO)_3$ and isolated in 74% yield. Association constants were determined by ^{1}H-NMR titration techniques in acetonitrile revealing selectivity for chloride ($K_a > 10^4$ M^{-1}).



91

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

There have been a number of advances in this area over the last 2 years. Two detailed studies following up on previously communicated work stand out in this area, namely Dalcanale and co-workers work on cavitand-based coordination cages encapsulating anions [113] and Lippert's studies on anion-encapsulating bipyrazine based platinum and palladium molecular triangles [114].

Square planar platinum complexes have been used by Bondy et al. as scaffolding upon which to construct an anion receptors [115]. Receptor **92** was synthesised from nicotinamide and $PtCl_2(EtCN)_2$ followed by metathesis with $AgPF_6$. The receptor provides both hydrogen bond donating groups and an electrostatic contribution to binding from the metal centre. Interestingly, this receptor binds planar anions such as nitrate or acetate in a 2:1 anion:receptor stoichiometry, whilst tetrahedral or pseudo-tetrahedral anions bind 1:1. The crystal structure of the perrhenate complex of **92** is shown in Fig. 18. The anion is bound by two amide NH–O hydrogen bonds and two pyridine CH–O interactions.

Ruthenium(II) tris(5.5′-diamide-2,2′-bipyridine) complexes have been shown by Beer and co-workers to provide two convergent anion binding sites [116]. The synthesis of receptors **93**–**96** is shown in Scheme 8. The six amide moieties form two binding sites as shown in the X-ray crystal structure of receptor **93** and chloride (Fig. 19). Association constants determined by UV–vis titration techniques reveals that $\log \beta_1$ and $\log \beta_2$ for chloride binding by **93** in 9:1 CH_2Cl_2/MeOH are 7.47 and 12.9, respectively. Uppadine et al. have also investigated chiral rhenium and ruthenium receptors for enantioselective recognition of anionic guests [117].

The dithiocarbamate copper macrocycles **97**–**103** have been investigated by Beer and co-workers as potential electrochemical anion sensors [118]. The electrochemical properties of compounds **98**, **100** and **103** were monitored in CH_2Cl_2/CH_3CN 1:1 solution with tetrabutylammonium tetrafluoroborate as supporting electrolyte upon addition of chloride, bromide, nitrate, perrhenate and dihydrogenphosphate anions. Of the macrocycles and anions studied, only compound **100** showed a significant cathodic shift of its dtc-copper(II)–(III) redox couple upon addition of perrhenate or dihydrogen phosphate anions (both anions causing a shift of 85 mV).

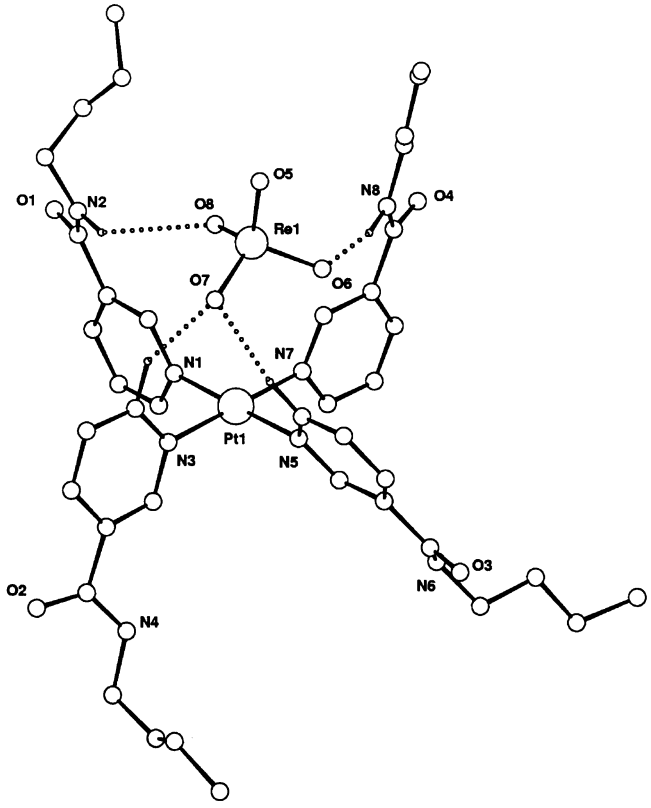
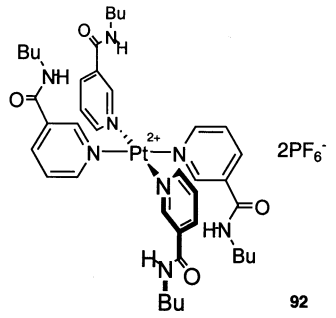
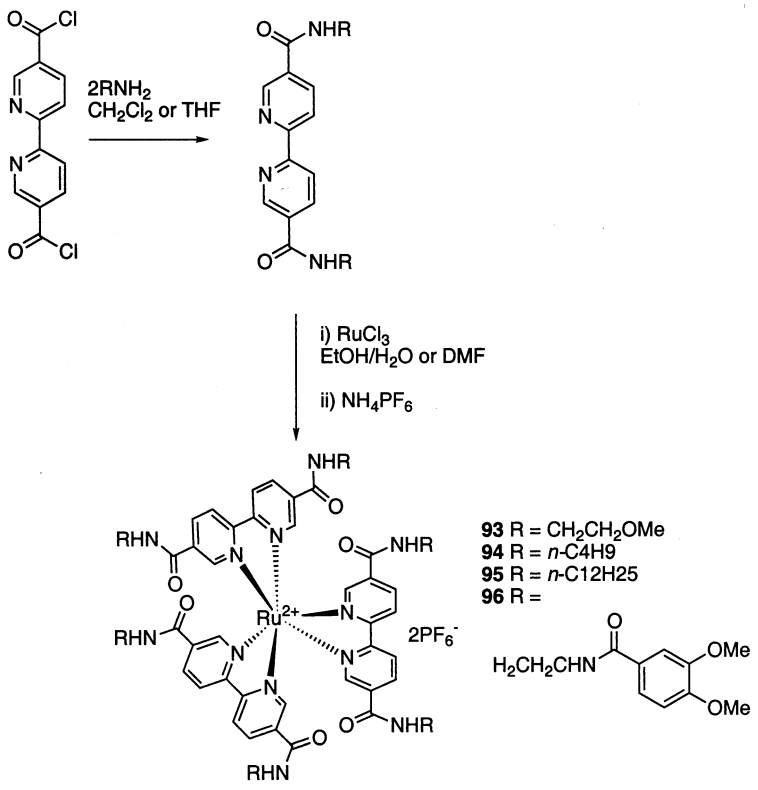


Fig. 18. The X-ray crystal structure of the perrhenate complex of **92** showing the anion bound by two NH–O and two CH–O hydrogen bonds.



92



Scheme 8.

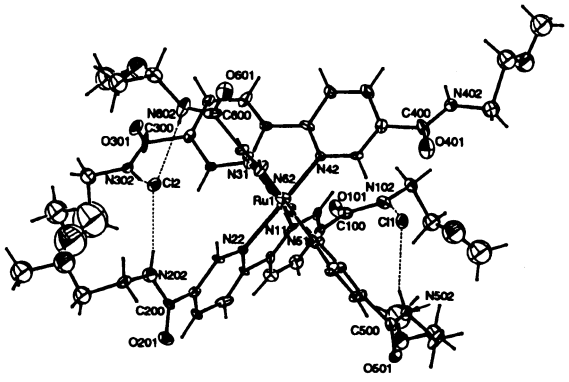


Fig. 19. The X-ray crystal structure of the bis-chloride complex of **93**. (Reproduced with permission from Chem. Commun. (2001) 291, Copyright 2001, Royal Society of Chemistry.)

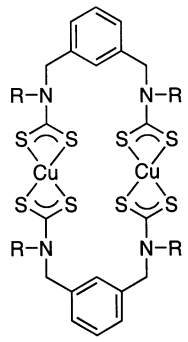
Espinet and co-workers have reported an interesting anion template reaction. Reaction of the Pd precursors **104** or **105** with halides QX (Q = PPh_4 or bis(diphenylphosphane)-iminium (PPN), X = Cl, Br, I) in dichloromethane forms a pyramidal tetrapalladium complex **106** with a halide at the apex (Scheme 9) [119]. The crystal structure of one complex $(PPN)(Pd_4Fmes)_4Cl_5$ is shown in Fig. 20.

Kim and co-workers have reported the first example of an anion encapsulated with a metal-directed 'tennis-ball' type complex **107** [120]. *trans*-(±)-1,2-Diaminocyclohexane platinum bis(ethylthio)methylenepropanedioate (Scheme 10) binds to copper(II) and in the presence of tetrafluoroborate assembles around the anion forming an interlocked tennis-ball structure in methanol.

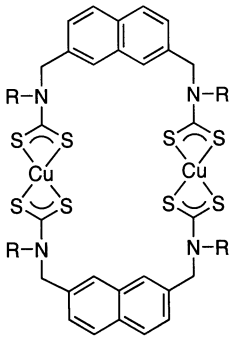
3.5. Metals as a co-bound guest in an ion-pair receptor

Moving into the realm of ion-pair complexation, Smith and co-workers have shown that alkali metal cations can successfully compete with neutral anion receptors for guest anions [121]. For example, an NMR titration showing dihydrogen phosphate complexation by **108** in CD_3CN is shown in Fig. 21 in the absence and presence of potassium tetraphenylborate. The potassium ions sequester the initial additions of dihydrogen phosphate until the cations and anions are at the same concentration. Only then do the added anions interact with the host receptor. Smith found that the ion-sequestering ability of the Group 1 metal cations was is the order $Cs^+ < K^+ < Na^+$ matching their ion-pairing ability. In analogous receptors containing crown ether groups, the anion binding ability of the receptor was either enhanced or suppressed depending upon the nature of the receptor and the ion-pairing ability of the cationic guest.

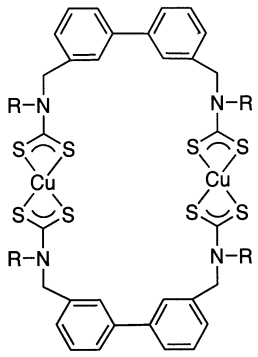
In order to complex an ion-pair successfully, Smith and co-workers have synthesised a variety of compounds including the strapped crown ether diamide



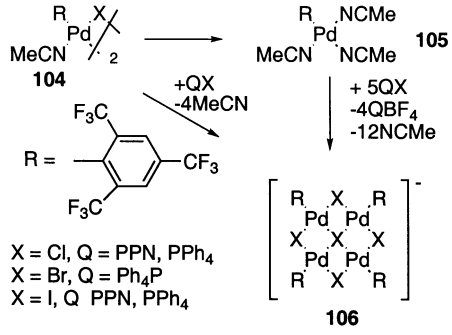
97 R = n-Pr
98 R = n-Bu
99 R = n-Hexyl



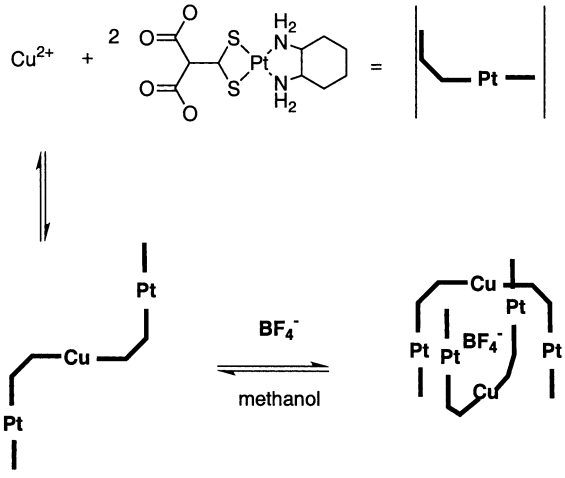
100 R = n-Pr
101 R = n-Hexyl



102 R = n-Pr
103 R = n-Bu



Scheme 9.



Scheme 10.

cleft receptors **109a** that is capable of binding *a solvent separated* ion-pair (Na^+ $CHCl_3$ Cl^-) [122] and **109b** that is capable of recognizing KCl *contact* ion-pairs [123]. The association constant of receptor **109** with chloride is enhanced from 35 M^{-1} in DMSO-d_6 at 295

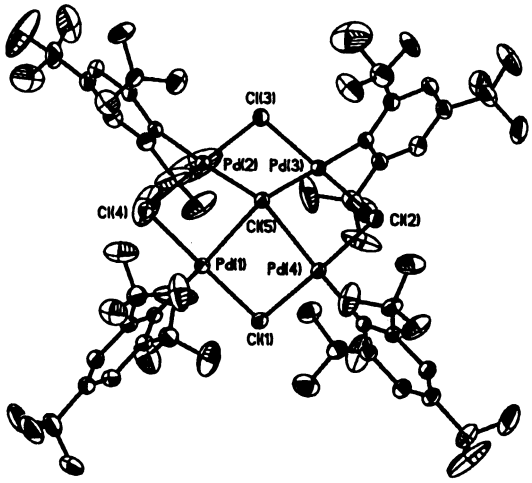


Fig. 20. X-ray crystal structure of the chloride tipped complex **106**. (Reproduced with permission from Angew. Chem. Int. Ed. Engl. 40 (2001) 2521, Copyright 2001, Wiley-VCH.)

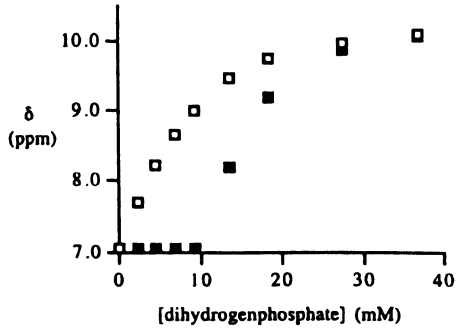


Fig. 21. Chemical shift for aryl-NH in **108** (initially 10 mM) in CD_3CN and 295 K upon addition of tetrabutylammonium dihydrogen phosphate: presence (solid square), and absence (outline sqaure) of potassium tetraphenylborate (initially 10 mM). The signal for the alkyl-NH in **108** shows the same behaviour. (Reproduced with permission from Org. Lett. 2 (2000) 3099, Copyright 2000, American Chemical Society.)

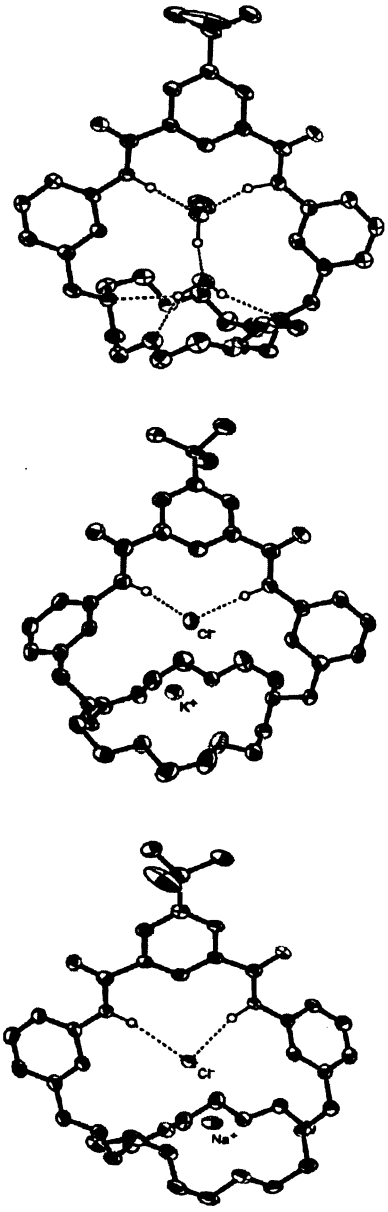
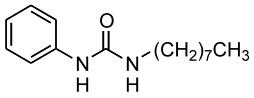


Fig. 22. X-ray crystal structures of **109** with water and methanol (top), **109** complex of KCl (middle) and the complex of **109** with NaCl (bottom). (Reproduced with permission from J. Am. Chem. Soc. 123 (2001) 5847, Copyright 2001, American Chemical Society.)

K to 460 M^{-1} in the presence 1 equivalent of potassium tetraphenylborate. Addition of sodium to the receptor only increases its affinity for chloride to a K_a of 50 M^{-1} under the same conditions. X-ray crystal structures of the NaCl and KCl complexes reveal that the sodium cation is bound more closely to the crown ether than the potassium cation so increasing ion-dipole repulsions between the chloride anions and the crown ether oxygens (Fig. 22).

By attaching two thiourea groups to dibenzo-diaza-30-crown-10, Kubo and co-workers have synthesised an



108

ion-pair receptor **110** [124]. The addition of potassium ions causes the crown ether to wrap around the metal so bringing the thiourea groups into close proximity forming a binding site for anions such as $(PhO)_2P(O)O^-$ (Fig. 23). In fact the affinity of the receptor for $(PhO)_2P(O)O^-$ increases by a factor of 19 in the presence of potassium cations in acetonitrile-d_3 at 297 K (K increases from 490 to 9200 M^{-1}).

Beer and co-workers have reported a number of calixarene-based ion-pair receptors and sensors [125,126]. For example, receptors **111** and **112** bind alkali metal cations at the lower rims of the two calix[4]arene units and an anion in the amide cleft of the ferrocene or bipyridyl unit. The co-bound metal enhances the anion affinity of the receptor with for example the affinity of **112** for iodide increasing from 40 to 305 M^{-1} upon addition of lithium cations in CD_3CN. The ferrocene/ferrocenium redox couple of **111** is perturbed upon addition of anions in acetonitile solution with the maximum cathodic shift being obtained in the presence of acetate (155 mV).

Pochini and co-workers have found a positive allosteric effect during ion-pair binding by extended cavity calix[4]arenes in the cone conformation [127]. In complex **113**, the sulfonate anion hydrogen bonds to the phenolic supper rim of the calixarene, preorganising the binding cavity for tetramethylammonium cation complexation.

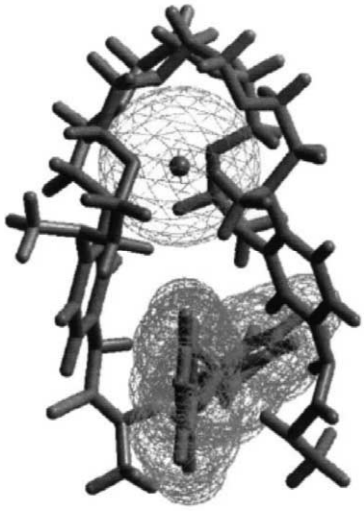
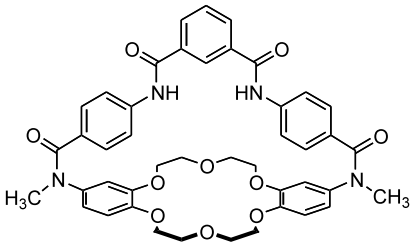
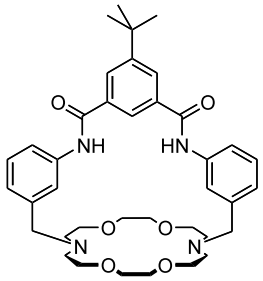


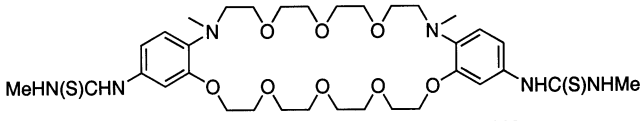
Fig. 23. Energy minimized complex of **110** with $K^+(PhO)_2P(O)O^-$. (Reproduced with permission from Tetrahedron Lett. 41 (2000) 5219, Copyright 2000, Elsevier.)



109a

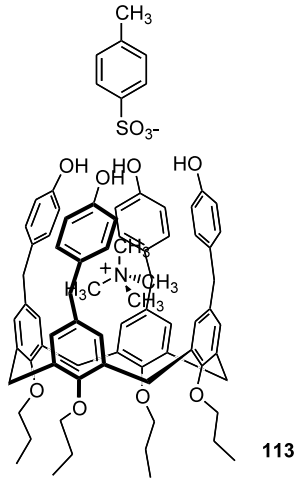


109b



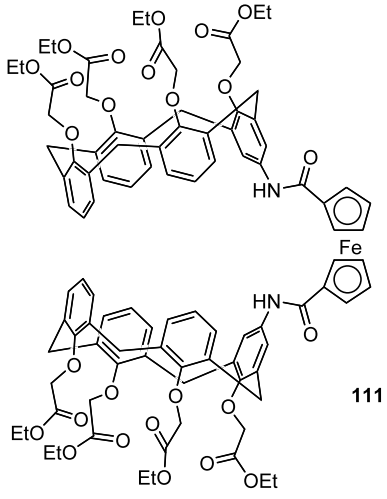
110

Tasker and co-workers have continued their studies of ditopic receptors for transition metal salts [128]. These workers have synthesised a series of receptors **114**–**117**. Transition metal (nickel(II) or copper(II)) binding causes proton transfer from the salen unit to the morpholine amine groups so creating a binding site for an oxo-anion. In the solid state, the nickel sulfate complex of **115** dimerises via the two anion bridging between two nickel complexes of **115** (Fig. 24).

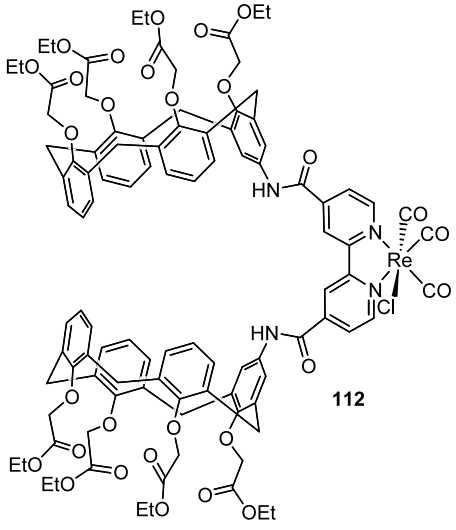


113

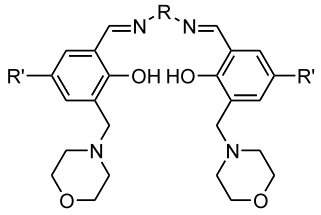
By linking azathioether macrocycles to urea groups, Schröder and co-workers have synthesised receptors for



111



112



	R	R'
114	-$(CH_2)_2$-	t-Bu
115	±trans 	t-Bu
116	o-C_6H_4	C_9H_{19}
117	-$(CH_2)_2$-	Me

transition metal salts (compounds **118a** and **118b**) [129]. A number of crystal structure determinations of transition metal complexes of these receptors were conducted

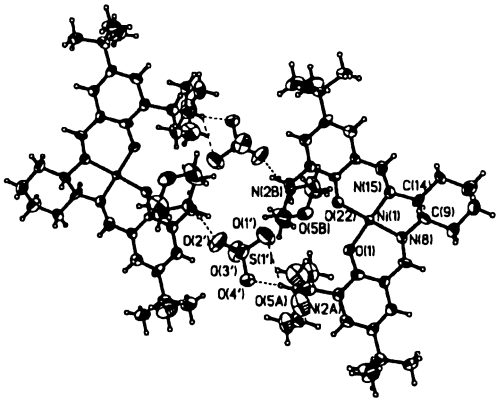


Fig. 24. Crystal structure of the nickel sulfate complex of **115**. The receptors dimerise via sulfate bridges. (Reproduced with permission from J. Chem. Soc. Dalton Trans. (2000) 3773, Copyright 2000, Royal Society of Chemistry.)

including the complex CuCl(**118b**)$CuCl_4$ showing a single hydrogen bond from the receptor to a bridging anion (Fig. 25).

Finally, Davis and co-workers have employed ion-pair binding to assemble G-quartets e.g. $(\mathbf{119})_4$ into

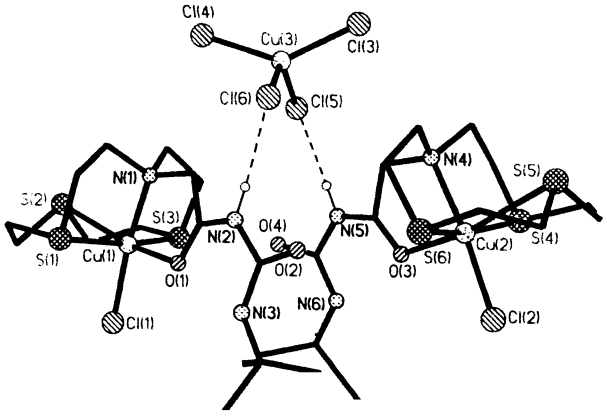


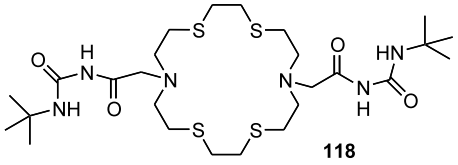
Fig. 25. Crystal structure of $[CuCl(\mathbf{118b})]_2CuCl_4$. (Reproduced with permission from Chem. Commun. (2001) 2678, Copyright 2001, Royal Society of Chemistry.)

stacked hexadecamer structures $(\mathbf{119})_{16}$ in CD_2Cl_2 solution (Scheme 11) [130].

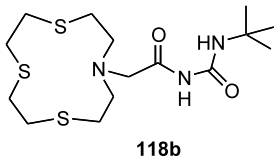
4. Anion directed assembly

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 (as we have already seen in the case of Kim's tennis-ball assembling around a BF_4^- anion) [120] are now becoming widespread.

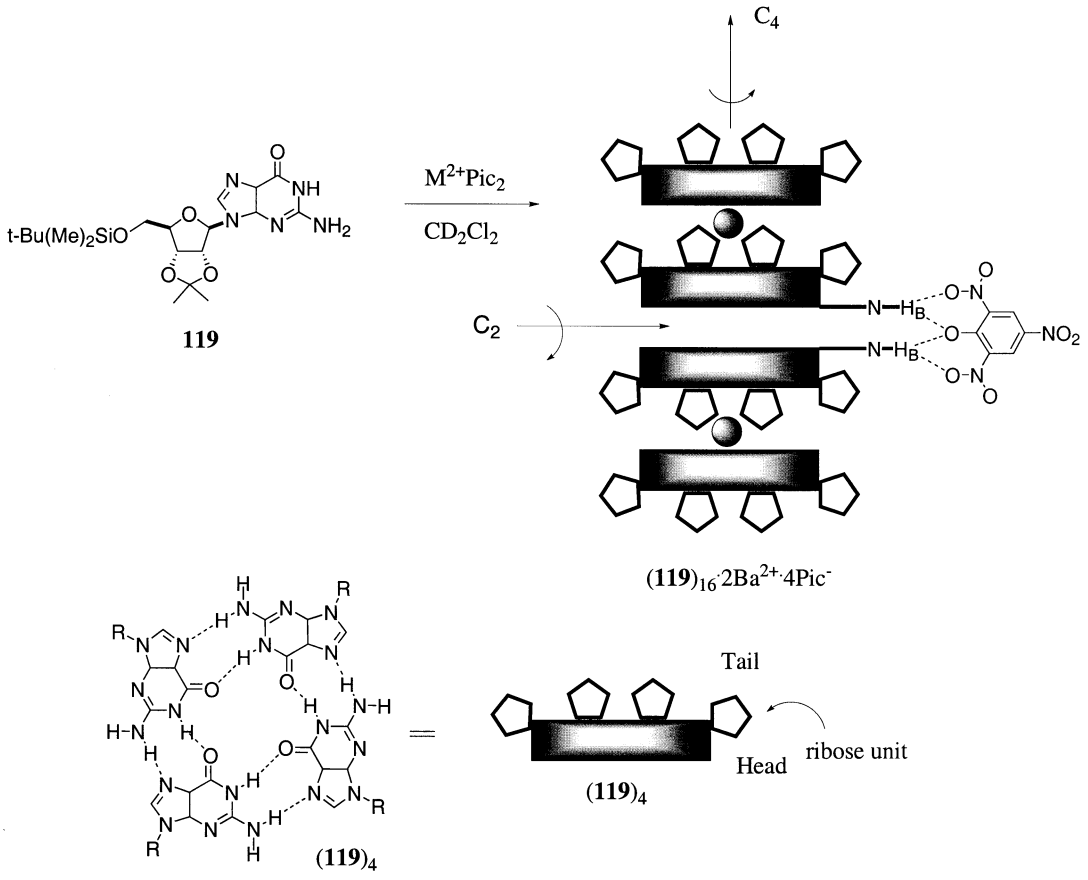
Vilar and Mingos have recently reported the anion-directed assembly of silver-alkynyl cage compounds [131]. When $AgBF_4$ in THF was mixed with a solution of tBuCCH and triethylamine in THF, a white precipitate $(Ag(CCtBu))_n$ was formed. This material was found to be insoluble in a variety of solvents apart from chloroform in which it dissolved readily. Addition of diethyl ether gave a white precipitate that was soluble in acetone, ethanol and THF suggesting that the white precipitate had been chemically modified by chloroform. Crystals of the new material **120** were obtained from an



118



118b



Scheme 11.

ethanolic solution of the compound, revealing that the new material was a silver-alkynyl cage assembled around a chloride anion. The crystal structure of this material is shown in Fig. 26. This cage could also be synthesised directly from $AgBF_4$, *t*BuCCH and triethylamine with a stoichiometric quantity of Me_4NCl present. This could be repeated with Bu_4NBr to produce a bromide centred cage **121**. Vilar has also published a full account of the anion-directed assembly of Ni/Pd amidinothiourea complexes that have been previously communicated [132].

Kruger and co-workers have reported the anion directed assembly of a dinuclear double helicate [133]. The crystal structure of the hydrochloride salt of **122** was obtained, revealing the formation of a double helicate formed via pyridinium N–H–Cl^- hydrogen bond formation (Fig. 27).

An anion-directed pseudo-rotaxane has been reported by Wisner et al. [134]. Mixing the zwitterion **123** with macrocycle **124** results in the formation of a pseudo rotaxane **125** in acetone-d_6 with an association constant of 2400 M^{-1} (Scheme 12). The pseudo-rotaxane is stabilised by chloride–HN hydrogen bonds, π–π stacking interactions and CH–O hydrogen bonds. The crystal structure of this complex is shown in Fig. 28. Analogues of **123** containing other counter anions such as bromide, iodide or hexafluorophosphate assemble with **124** with

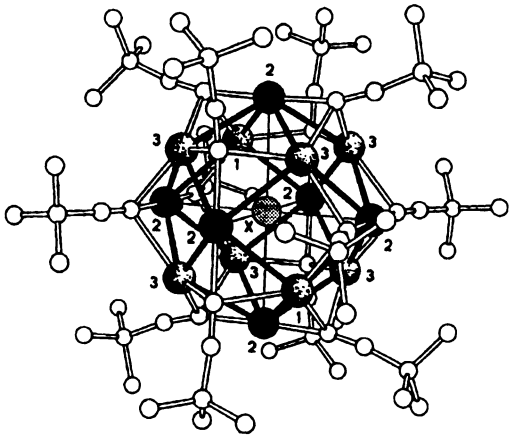


Fig. 26. The silver cage complexes **120** (X = Cl) and **121** (X = Br). (Reproduced with permission from Angew. Chem. Int. Ed. Engl. 40 (2001) 3464, Copyright 2001, Wiley-VCH.)

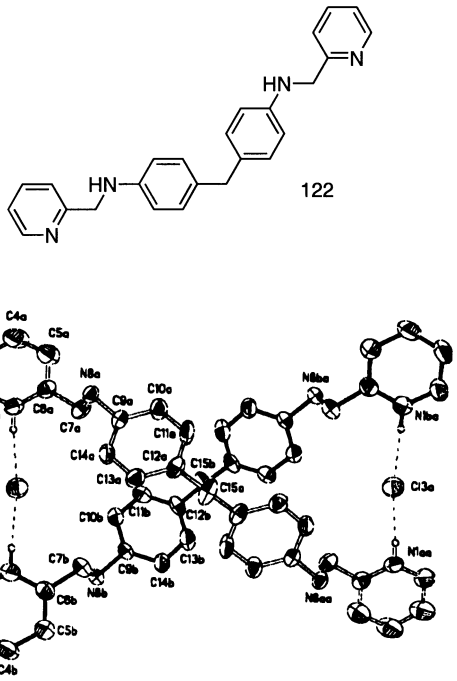


Fig. 27. X-ray crystal structure of the chloride bridged double helicate $((H_4(\mathbf{122})Cl)_2 \cdot 6Cl \cdot H_2O$. (Reproduced with permission from Chem. Commun. (2001) 2192, Copyright 2001, Royal Society of Chemistry.)

lower association constants than the chloride complex (700, 65 and 35 M^{-1} respectively).

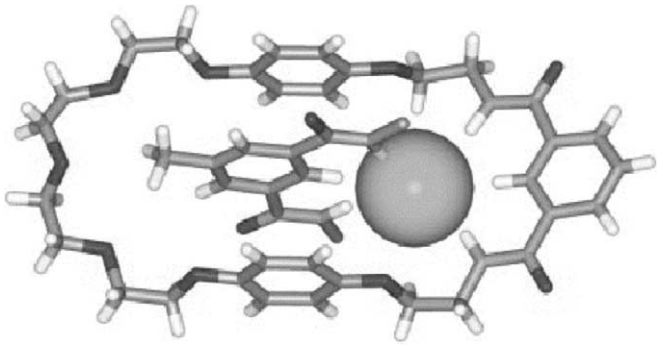


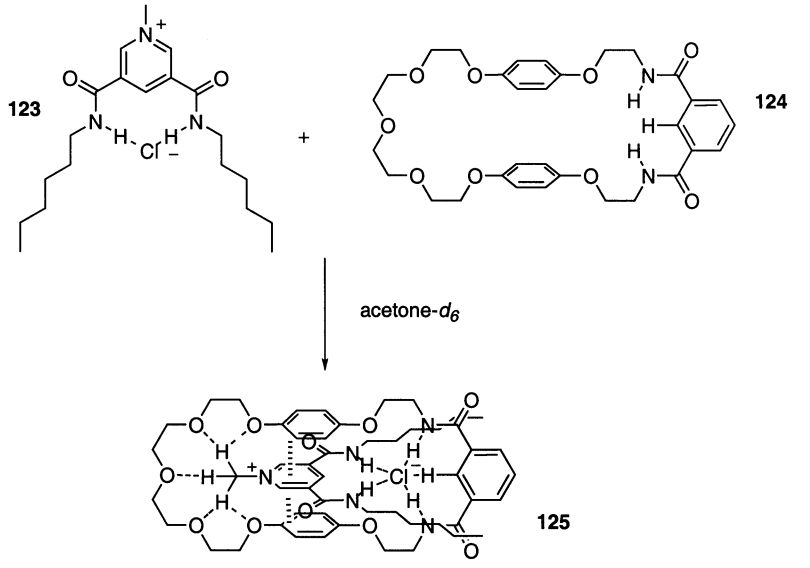
Fig. 28. Stick representation of the pseudorotaxane **125**. (Reproduced with permission from Angew. Chem. Int. Ed. 40 (2001) 3606, Copyright 2001, Wiley-VCH.)

5. Conclusions

Year upon year, the effort devoted to the production of new anion receptors by the supramolecular chemistry community increases. Over 2000 and 2001 we have seen great strides forward in the chiral recognition of amino-acids by urea based receptors and in the development of anion directed self-assembly. From its beginnings in the late 60s to the state of the art developments reviewed here, anion receptor chemistry has made great advances over the last third century. The area continues as a vigorous area of research and is yet to be fully explored.

Acknowledgements

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



Scheme 12.

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