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Amide based receptors for anions

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Abstract

This review article illustrates the contribution of amide based receptors to the development of anion complexing agents. Amides are incorporated into a wide variety of systems that can be divided into two broad categories; organic and inorganic. The first section is separated into cyclic and acyclic systems built on a solely organic framework. The second section is comprised of metal containing systems such as metallocenes, $[Ru(bipy)_3]^{2+}$ based complexes, porphyrins and other metallo-based receptors. Where appropriate, the results of solution binding studies and sensing outputs are summarized.

Keywords: Amide; Anion; Hydrogen-bond; Supramolecular chemistry

1. Introduction

An area of interest in supramolecular chemistry that continues to attract attention is the coordination of anions. The rapid growth in this area is due to the realization of the many roles that anions play in biology, medicine, catalysis and the environment [1,2]. It is interesting to note that anion binding by proteins is most often achieved by way of neutral amide functions employing the hydrogen-bond acceptor properties of the amido NH group [3]. The purpose of this review is to highlight the diversity of anion receptors that contain amide functional groups. This review is comprised of two sections. The first section is separated into cyclic and acyclic compounds built on a solely organic framework while the second section is comprised of metal containing systems.

2. Organic receptors

Amide receptors constructed on an organic scaffold most often utilize either solely hydrogen-bonding or a

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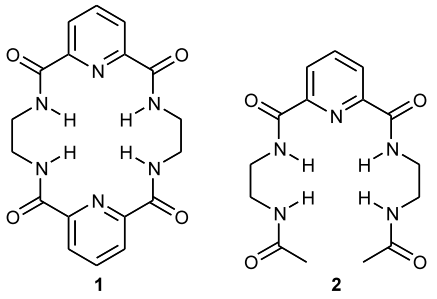


Fig. 1. A tetra-amide macrocyclic and open-chain analogue.

combination of hydrogen-bonding and electrostatic interactions. The amide binding units are most commonly preorganized to act cooperatively within some convergent molecular architecture. This can be achieved by lining the inside of a macrocycle or afixing the groups to an acyclic framework in a pendant fashion or as part of a cleft or some other rigid skeleton.

2.1. Macrocyclic amides

Szumna and Jurczak synthesized macrocycle **1** and the open-chain analog **2** (Fig. 1). The macrocycle allows for a relatively rigid molecule with all the N–H amide groups pointing into the cavity [4]. Due to the insolubility of **1** in common organic solvents, ^{1}H-NMR titrations were performed in DMSO-d_6. The resulting association constants showed this molecule had the largest affinity for OAc^- and $H_2PO_4^-$ (Table 1). Job plots were performed and a 1:1 host:guest ratio was found for all the anions including the bidentate OAc^-. The crystal structure of the OAc^- complex showed that only one oxygen from the anion interacts with all four N–H groups on the receptor. The second oxygen was found to either hydrogen-bond to another receptor or to a water molecule depending on the amount of water present in the solvent. In terms of the halides tested, the solution data showed the receptor to have a much higher association with F^- compared with Cl^-. When the crystal structures of these two complexes were examined, it was determined that the Cl^- was indeed too large to fit in the cavity. The smaller size of the fluoride ion allowed a much better fit into the cavity and the formation of shorter and stronger hydrogen-bonds.

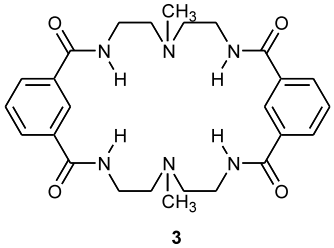


Fig. 2. A rigid macrocyclic with four convergent amide groups.

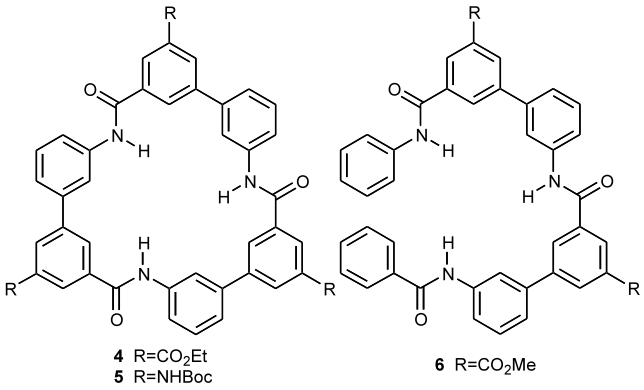


Fig. 3. C_3 symmetric receptors designed for tetrahedral anions.

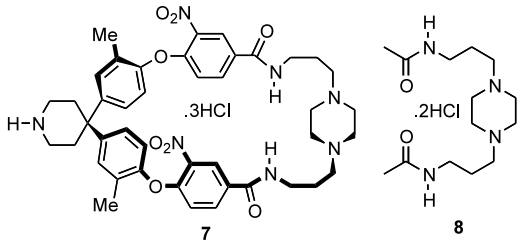


Fig. 4. Water soluble receptors capable of weakly binding organic anions.

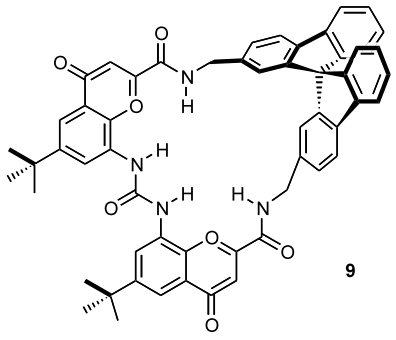


Fig. 5. A macrocyclic receptor with a chiral cavity.

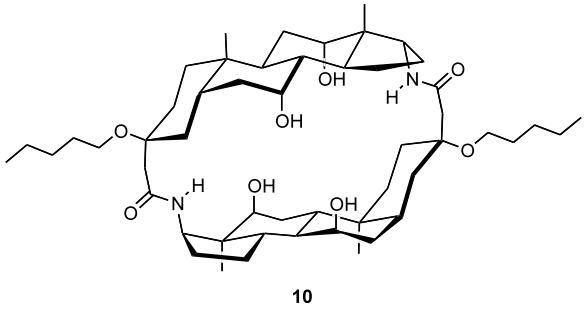


Fig. 6. A macro-dilactam receptor derived from cholic acid.

The synthesis of a rigid macrocycle that contains convergent groups for optimal binding of tetrahedral anions was accomplished by Bowman-James. The tetra-amide **3** (Fig. 2) also contains two tertiary amine groups that aid in binding [5]. Solution data showed this

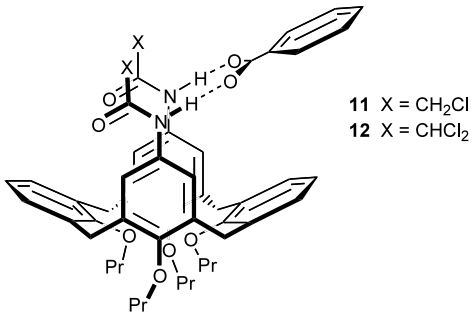


Fig. 7. A calix[4]arene receptor in the pinched-cone conformation.

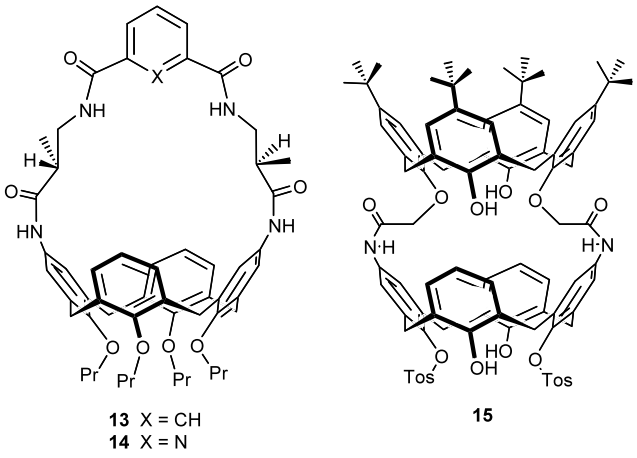


Fig. 8. Chiral calix[4]arenes (left) and a bis-calix[4]arene (right).

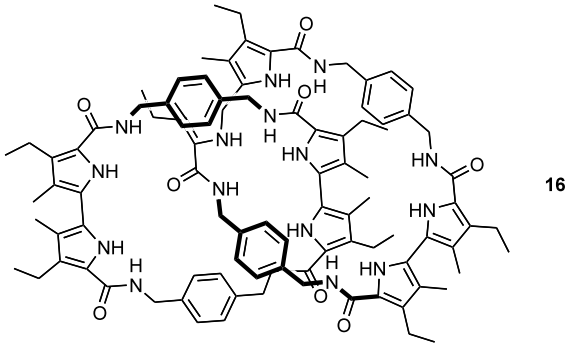


Fig. 9. A catenane receptor that uses interlocked rings for anion binding.

macrocycle bound $H_2PO_4^-$ and HSO_4^- preferentially, in $CDCl_3$, with association constants of $4.5 \times 10^4\ M^{-1}$ and $3.5 \times 10^4\ M^{-1}$, respectively. All ions tested exhibited a 1:1 binding ratio of receptor to anion. The crystal structure of the HSO_4^- complex showed a sandwich structure. The anion was deprotonated and each oxygen from the SO_4^{2-} ion was hydrogen-bonded to two different amides. It was thought that the presence of the basic amine aided in deprotonation of the acidic protons in both the HSO_4^- and $H_2PO_4^-$ cases which increased the negative charge of the anions and added to the increase in association between the dinegative anions and the protonated receptor.

Hamilton incorporated three amide groups into macrocycles **4** and **5** (Fig. 3) to produce C_3 symmetric

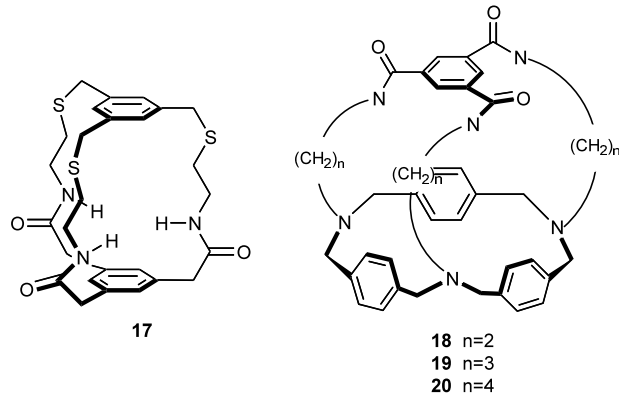


Fig. 10. C_3 symmetric macro-bicycles for binding trigonal anions.

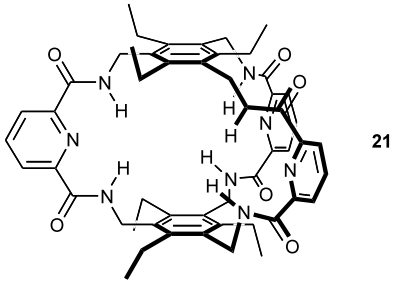


Fig. 11. A bicyclic receptor with C_3 symmetry for binding nitrate ions.

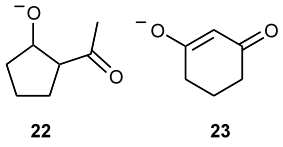


Fig. 12. Enolate substrates for **21**.

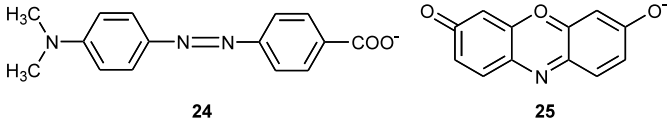


Fig. 13. Indicator substrates for **21**.

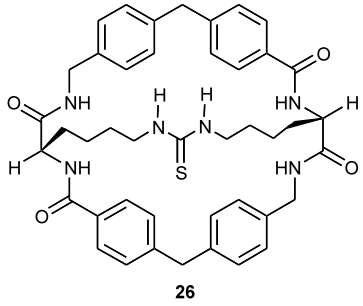


Fig. 14. A chiral receptor for the separation of D- and L-amino acids.

Hamilton incorporated three amide groups into macrocycles **4** and **5** (Fig. 3) to produce C_3 symmetric

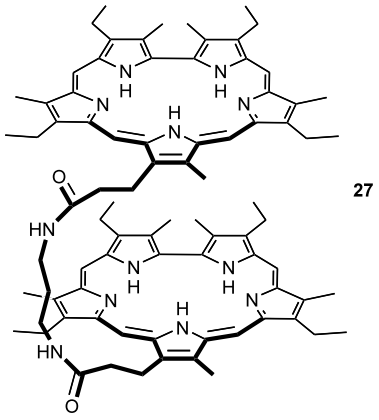


Fig. 15. A dimeric sapphryin receptor that binds dicarboxylates.

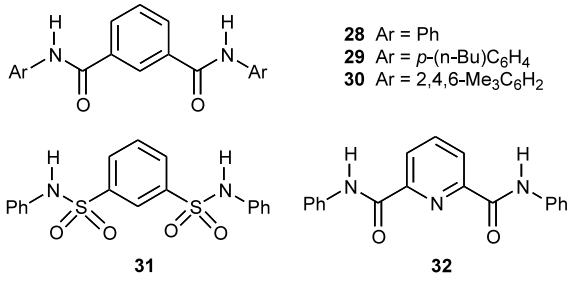


Fig. 16. Bis(amide) cleft receptors.

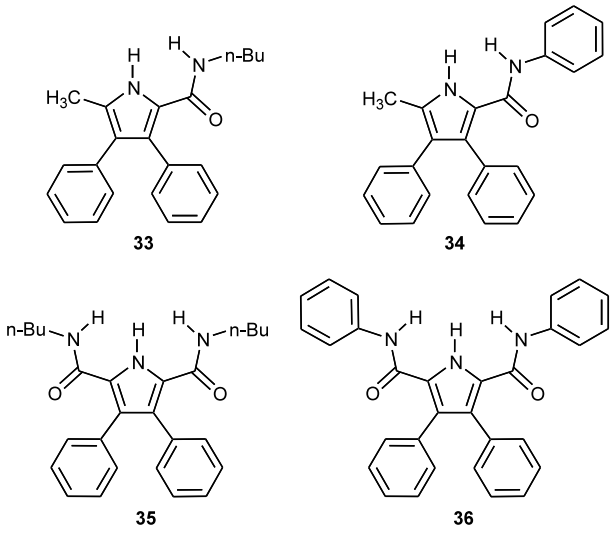


Fig. 17. Receptors containing both amide and pyrrole groups.

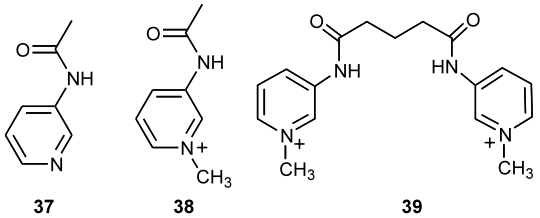


Fig. 18. Simple pyridinium based receptors.

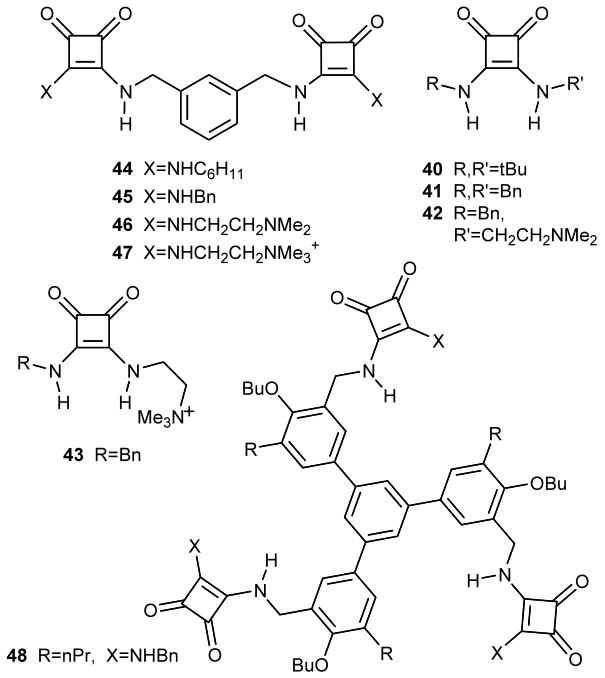


Fig. 19. Receptors containing squaramide groups.

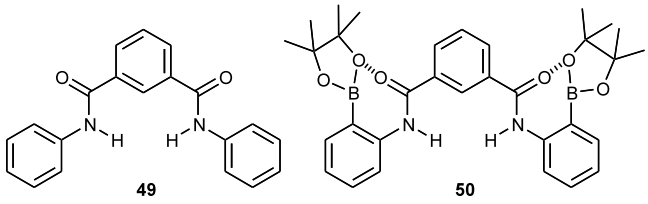


Fig. 20. Boron containing cleft receptors.

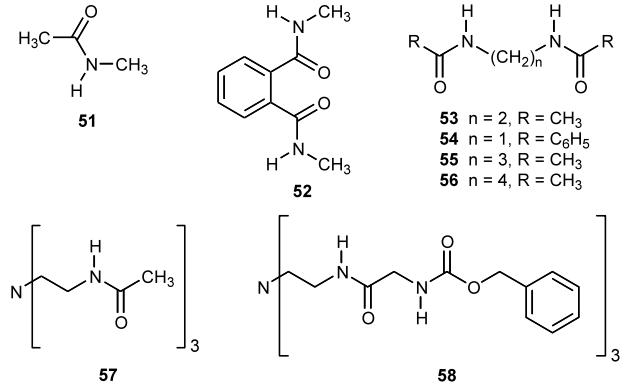


Fig. 21. Simple acyclic mono-, di-, and tri-amide receptors.

receptors designed to bind the triangular face of a tetrahedral anion [6]. Binding studies showed rather complex behavior. As the anion was added, there was an initial upfield shift of the amide protons. This occurred up to 0.5 equivalents of added anion, after which the protons shifted continuously downfield. This type of curve fit a 2:1 host:guest ratio for the initial formation and a 1:1 ratio after this point. The structure of the 2:1

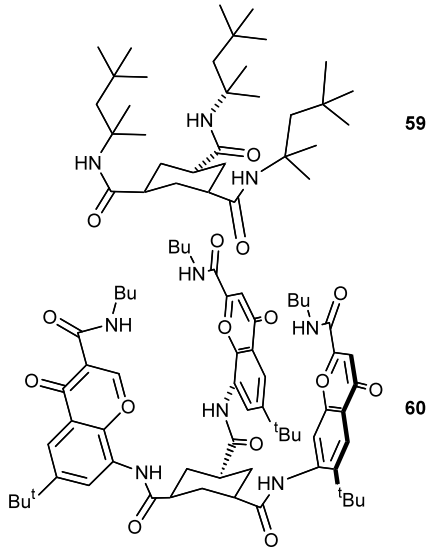


Fig. 22. An acyclic receptor that is selective for phosphate.

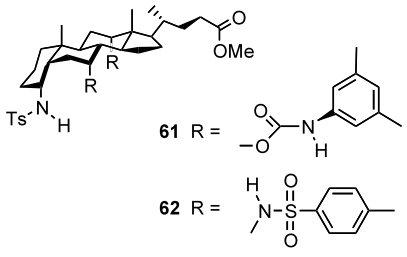


Fig. 23. Acyclic cholic acid based receptors.

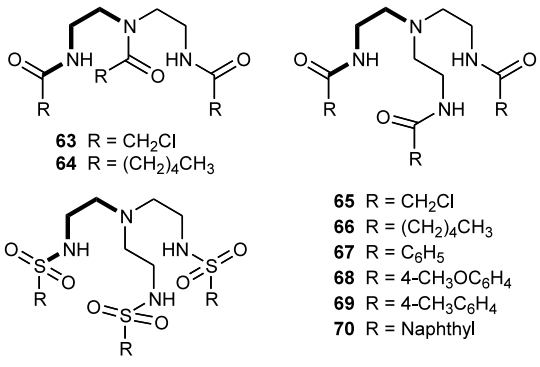


Fig. 24. Tripodal receptors to mimic the phosphate binding protein.

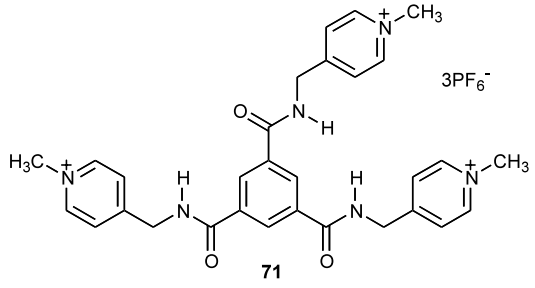


Fig. 25. An acyclic tripodal polypyridinium receptor.

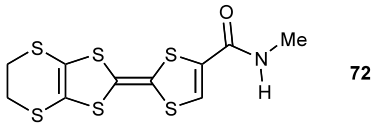
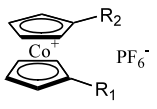
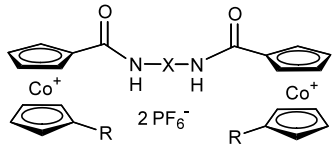


Fig. 26. An electrochemically active sensor based on TTF.

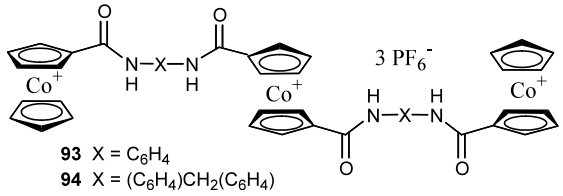


73 R_1 = $C(O)NHC_4H_9$, R_2 = H
74 R_1 = $C(O)NHCH_2(C_6H_5)$, R_2 = H
75 R_1 = R_2 = $C(O)NCH_3(C_6H_5)$
76 R_1 = R_2 = $C(O)N(CH_2CH_2OCH_2CH_2)$
77 R_1 = R_2 = $C(O)NH(p\text{-}C_5H_4N)$
78 R_1 = R_2 = $C(O)NH(m\text{-}C_5H_4N)$
79 R_1 = R_2 = $C(O)NH(p\text{-}C_5H_4N)CH_3(+)$
80 R_1 = $C(O)NH(p\text{-}C_5H_4N)$, R_2 = H
81 R_1 = $C(O)NH(p\text{-}C_5H_4N)CH_3(+)$, R_2 = H
82 R_1 = $C(O)NH(o\text{-}C_6H_4NH_2)$, R_2 = H
83 R_1 = $C(O)NH(m\text{-}C_6H_4NH_2)$, R_2 = H
84 R_1 = $C(O)NH(p\text{-}C_6H_4NH_2)$, R_2 = H
85 R_1 = R_2 = $C(O)NH((3,4\text{-}OMe)C_6H_3)$
86 R_1 = R_2 = $C(O)NH(C_6H_5)$
87 R_1 = R_2 = $C(O)NH((4\text{-}OH)C_6H_4)$
88 R_1 = R_2 = $C(O)NHCH_2CH_2OCH_2$-
89 R_1 = R_2 = $C(O)NHCH_2CH_2OMe$
90 R_1 = $C(O)NH(C_6H_4)CH_2(C_6H_4)NH_2$, R_2 = H
91 R_1 = $C(O)NH(C_5H_4N)NH_2$, R_2 = H

Fig. 27. Mononuclear cobaltocenium containing receptors.



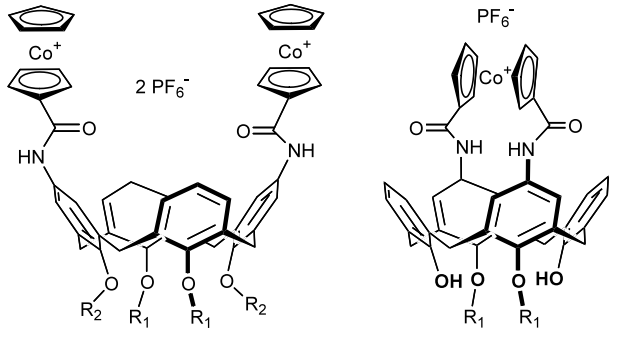
92 X = C_5H_3N, R = H
95 X = $(CH_2)_2$, R = CO_2Et
96 X = $(CH_2)_3$, R = CO_2Et
97 X = $(CH_2)_4$, R = CO_2Et
98 X = $C_6H_4CH_2C_6H_4$, R = CO_2Et
99 X = $C_6H_4OC_6H_4$, R = CO_2Et
100 X = $C_6H_4CH_2C_6H_4$, R = H
101 X = $(CH_2)_3NMe(CH_2)_2NMe$, R = H



93 X = C_6H_4
94 X = $(C_6H_4)CH_2(C_6H_4)$

Fig. 28. Receptors with multiple cobaltocenium groups.

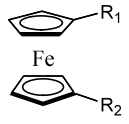
complex was described as a sandwiched structure with the anion in the center. The association constants for these two types of complexation were derived from the titration curve and are given in Table 2. The HSO_4^- and $H_2PO_4^-$ complexes were at slow equilibrium and, therefore, three sets of peaks were seen on the NMR timescale (receptor, 1:1 and 2:1 receptor:anion). When the anions are titrated in 100% DMSO-d_6 the 2:1 sandwich was not observed.



102 R_1 = Me, R_2 = H
103 R_1 = OTs, R_2 = H
104 R_1 = H, R_2 = OTs

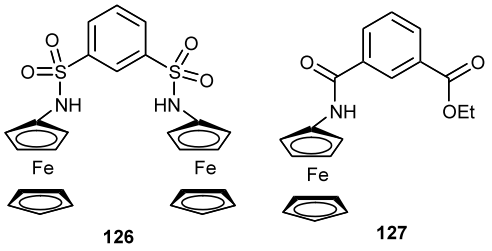
105 R_1 = OTs

Fig. 29. Calix[4]arenes receptors with upper-rim cobaltocenium groups.



106 R_1 = C(O)NHBu , R_2 = H
107 R_1 = C(O)NH(C_5H_4N)NH_2, R_2 = H
108 R_1 = C(O)NHCH_2CO_2Me , R_2 = H
109 R_1 = C(O)NHCH_2CO_2Et , R_2 = H
110 R_1 = C(O)NHCH_2CO_2Bz , R_2 = H
111 R_1 = R_2 = C(O)NHCH_2-3-(2,2'-bipy)
112 R_1 = C(O)NHCH_2-3-(2,2'-bipy), R_2 = H
113 R_1 = R_2 = CO_2CH_2-3-(2,2'-bipy)
114 R_1 = CO_2CH_2-3-(2,2'-bipy), R_2 = H
115 R_1 = R_2 = CHO
116 R_1 = CHO, R_2 = H
117 R_1 = C(S)NHBu , R_2 = H
118 R_1 = C(O)NH$(CH_2)_2NHCO_2t$-Bu, R_2 = H
119 R_1 = C(O)NH$(CH_2)_2NH_2$, R_2 = H
120 R_1 = R_2 = C(O)NH$(CH_2)_2NHCO_2t$-Bu
121 R_1 = R_2 = C(O)NH$(CH_2)_2NH_2$
122 R_1 = R_2 = C(O)NH(C_5H_4N)NH_2
123 R_1 = C(O)NH(C_6H_4)OMe, R_2 = H
124 R_1 = R_2 = C(O)NH(C_6H_4)OMe
125 R_1 = R_2 = C(O)NH$(CH_2)_2$O-C_6H_4

Fig. 30. Neutral ferrocene-based receptors.



126 **127**

Fig. 31. Some neutral ferrocene-based receptors.

Mimicking biological receptors such as the natural antibiotic vancomycin was the focus of the Diedrich group [7]. Natural systems were of interest due to their ability to bind guests in aqueous solution. An efficient synthetic route was used to obtain receptor **7** (Fig. 4) and ^{1}H-NMR titrations were run in D_2O, buffered with 0.5 M KCl/DCl to a pD of 2. At low concentrations, the stability constants obtain for dansyl and benzenesulfonate ions were ca. 45 M^{-1}. Once higher concentrations of anions were obtained, the complex precipitated.

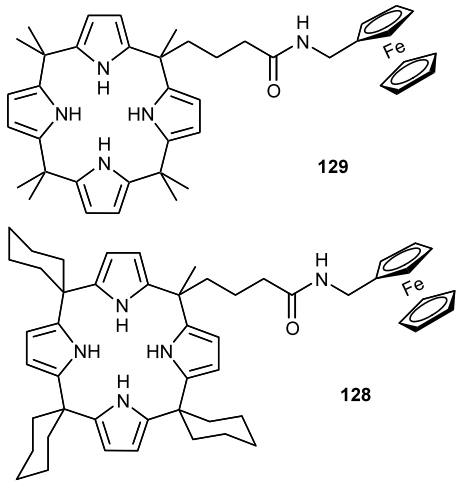


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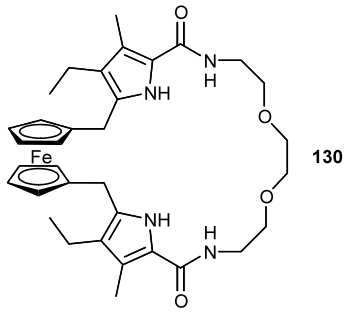
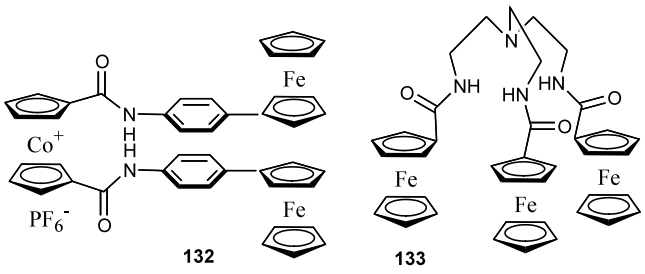
Fig. 32. Calix[4]pyrrole ferrocene-based receptors.



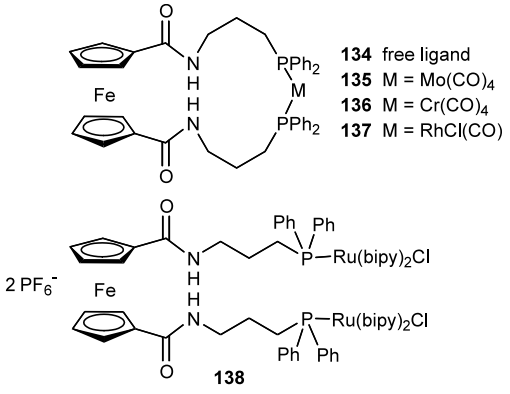
130

Fig. 33. A ferrocene containing pyrrole-based macrocycle.



132 **133**

Fig. 34. Combination ferrocene cobaltocenium receptors.



134 free ligand
135 M = $Mo(CO)_4$
136 M = $Cr(CO)_4$
137 M = RhCl(CO)

138

Fig. 35. Ferrocene receptors with ancillary binding sites.

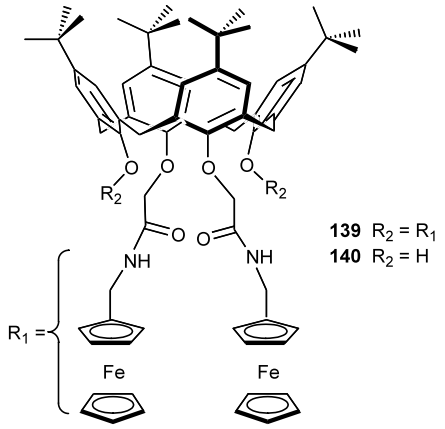


Fig. 36. Calix[4]arene receptors with cobaltocenium appendages.

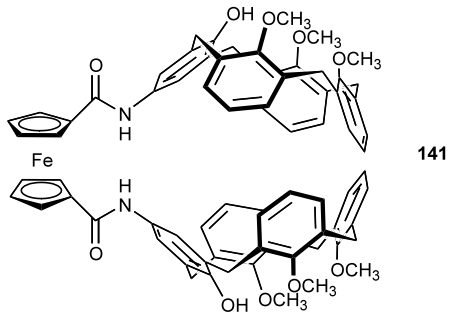


Fig. 37. A bis-calix[4]arene ferrocene receptor.

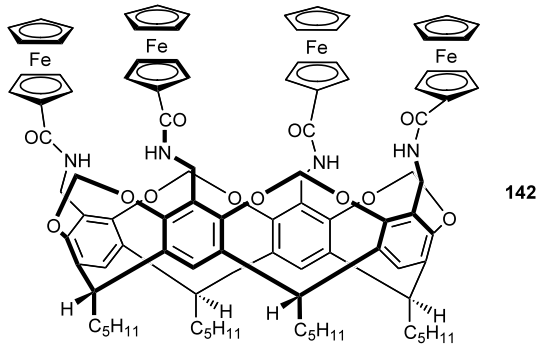


Fig. 38. A cavitand with ferrocene appendages.

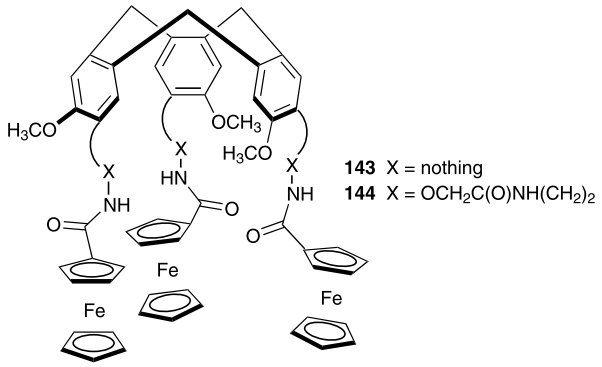


Fig. 39. CVT receptors appended with ferrocene units.

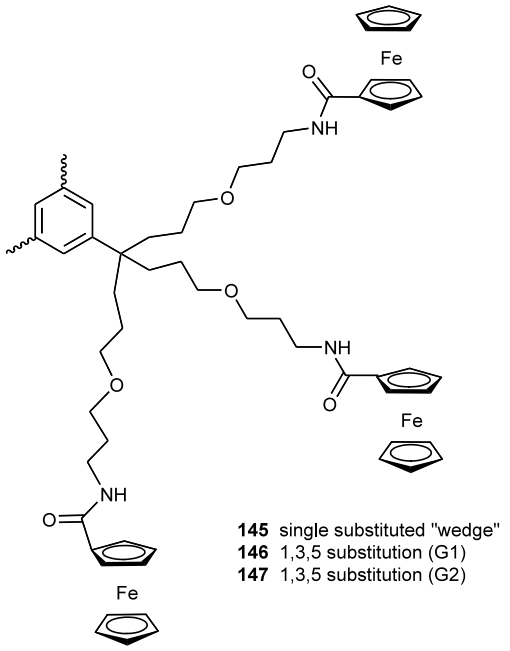


Fig. 40. Dendrimers adorned with ferrocene groups.

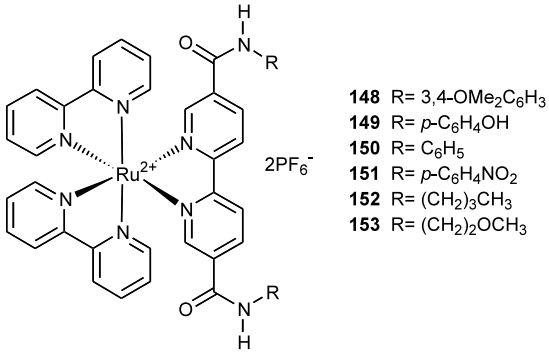


Fig. 41. $[Ru(bipy)_2(5,5'\text{-diamido-bipy})]^{2+}$ receptors.

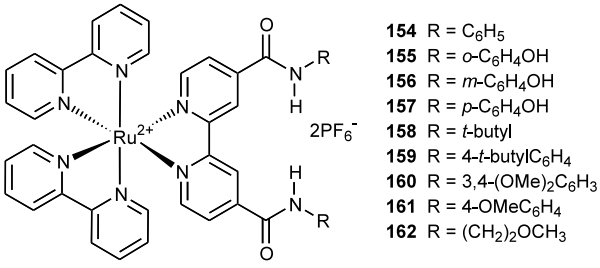
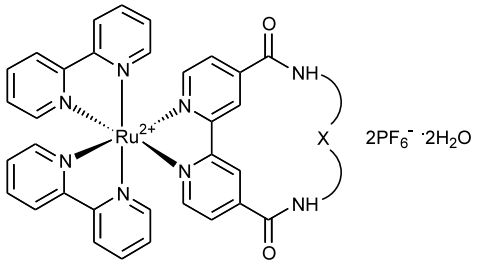


Fig. 42. $[Ru(bipy)_2(4,4'\text{-diamido-bipy})]^{2+}$ receptors.

Analysis of the solution data, before precipitation occurred, determined that a clatharate-type association occurred, in which the anion interacted with the receptor outside the cavity.

The recognition of chiral molecules is of great interest both industrially and technologically. Spirobifluorene is known for its capability to recognize chiral molecules. Morán showed that when combined with a bis-chrome-



163 X = $(CH_2)_2O(CH_2)_2O(CH_2)_2$
164 X = $CH_2C(Me)_2CH_2$
165 X = $(CH_2)_2NHC(O)(m\text{-}C_5H_5N)C(O)NH(CH_2)_2$
166 X = $(CH_2)_2NHC(O)(FeCp_2)C(O)NH(CH_2)_2$
167 X = $(CH_2)_2NHC(O)(CoCp_2)C(O)NH(CH_2)_2$
168 X = $(CH_2)_2NHC(O)(2,2'\text{-bipy})C(O)NH(CH_2)_2$

Fig. 43. Macrocyclic Ru-bipy receptors.

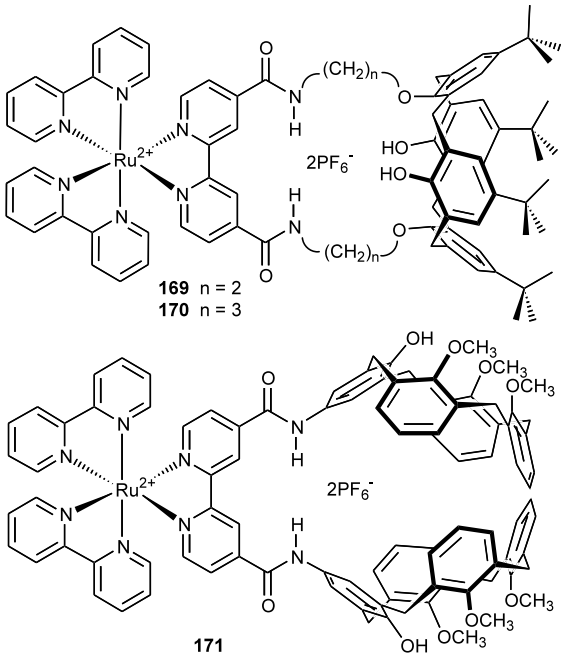


Fig. 44. Calix[4]arene Ru-bipy receptors.

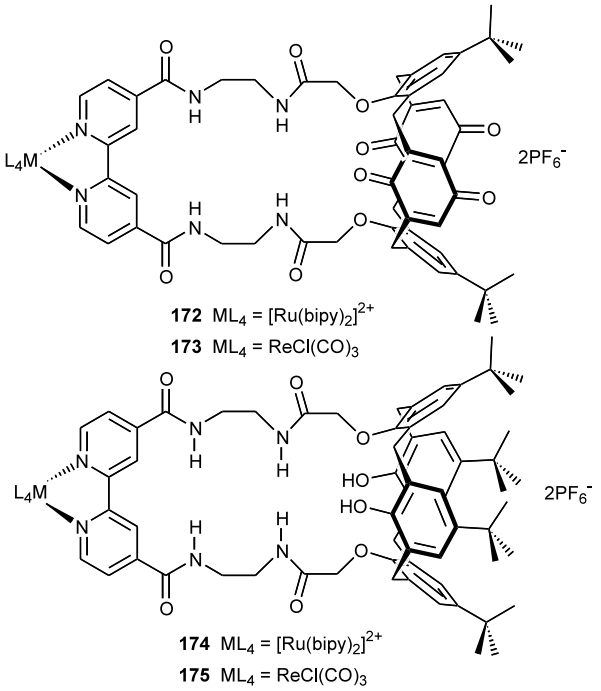


Fig. 45. Ru(II) and Re(I) calix[4]arene and calix[4]diquinone receptors.

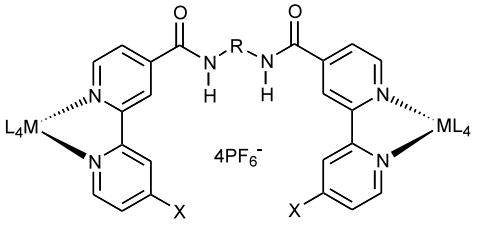


Fig. 46. Dinuclear receptors with Ru(II), Os(II) and Re(I).

nyl urea unit, which has a large affinity for carboxylates, the resulting receptor **9** (Fig. 5) had the ability to resolve racemic mixtures of mandalate ion [8]. The enantiomerically pure receptor was titrated in DMSO-d_6 with a racemic mixture of mandelate ions and the association constants obtained were 2.8×10^4 M^{-1} for (*R*)-mandelate and 1.7×10^4 M^{-1} for (*S*)-mandelate. This resulted in a 16:1 ratio of isomers with the source of chiral recognition determined to be steric. The (*R*) enantiomer had higher selectivity due to the α-hydrogen of the anion being small enough to fit close to the upper aromatic group of the spirobifluorene group. When the (*S*) enantiomer was inside the cavity, the OH group was positioned in the congested area of the spirobifluorene and a reduction in the stability of this complex was observed.

Davis developed a steroid-based cryptand **10** (Fig. 6) that recognized halide anions [9]. The system was comprised of a macrodilactam derived from the steroid cholic acid. The macrocycle formed a small, rigid cavity with four hydroxyl groups and two amide N–H groups directed inside the cavity. Modeling showed the cavity was a good size for F^- and may also fit Cl^- and Br^-. ^{1}H-NMR titrations in $CDCl_3$ showed a downfield shift for the N–H proton and 1:1 binding constants; 3220 ± 350 M^{-1} for F^-, 990 ± 80 M^{-1} for Cl^- and 250 ± 20

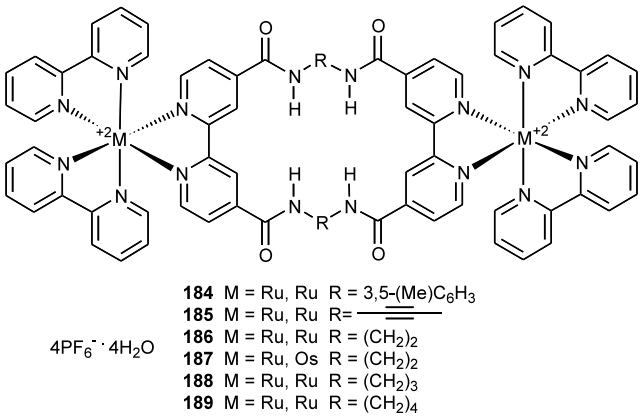


Fig. 47. Macrocyclic dinuclear receptors with Ru(II) and Os(II).

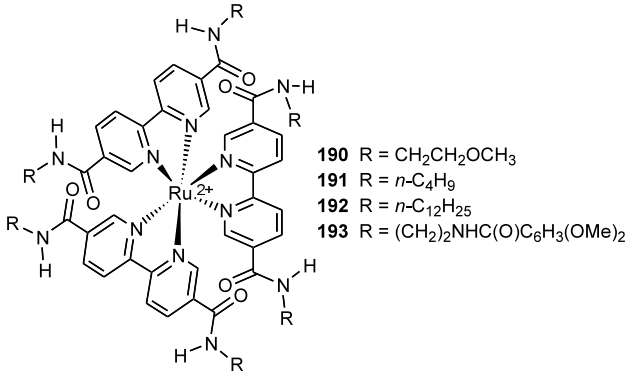


Fig. 48. Tris(5,5′-diamide-2,2′-bipyridyl) Ru(II) complexes.

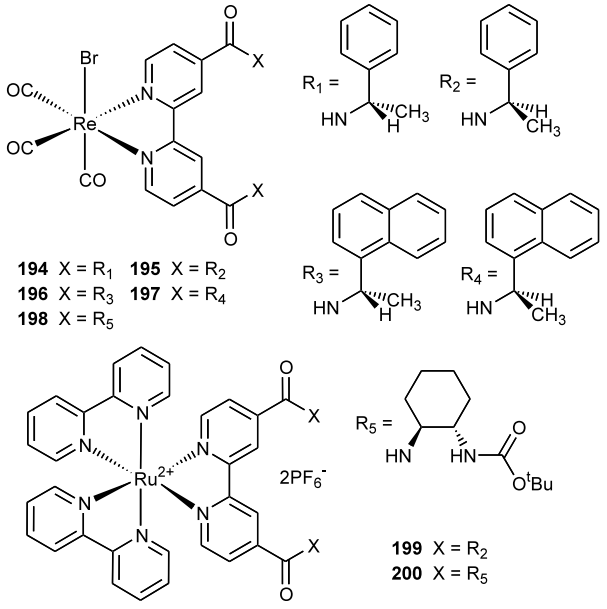


Fig. 49. Chiral versions of the Ru(II) and Re(I) receptors.

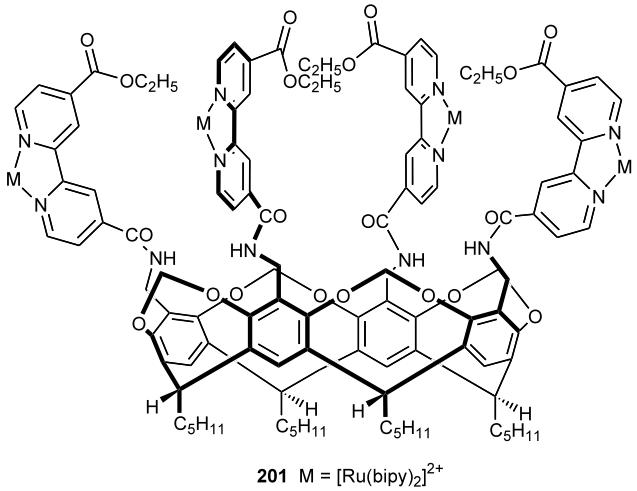


Fig. 50. A Ru(II) bipyridyl resorcinarene cavitand.

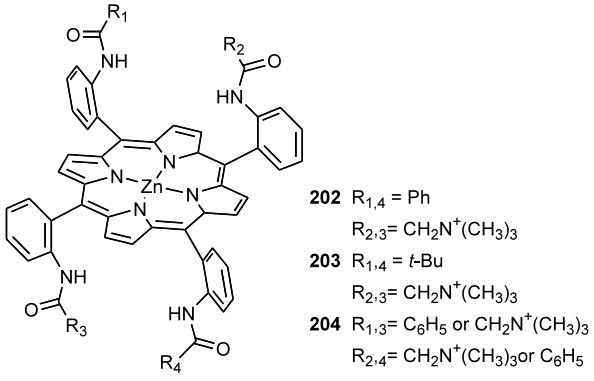


Fig. 51. Zn-porphyrin carboxylate receptors.

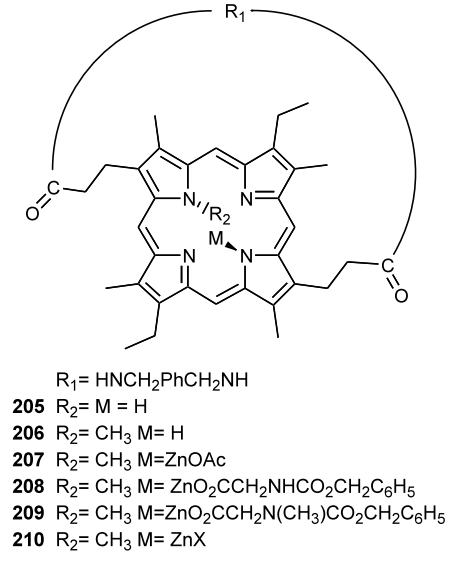


Fig. 52. Asymmetric Zn-porphyrins with an amide strap.

M^{-1} for Br^-. When compared with the acyclic version the preorganized macrocycle proved to be a much better host.

Receptors that bind tetrahedral-shaped anions have been studied extensively while less attention has been focused on other shaped anions such as acetate and

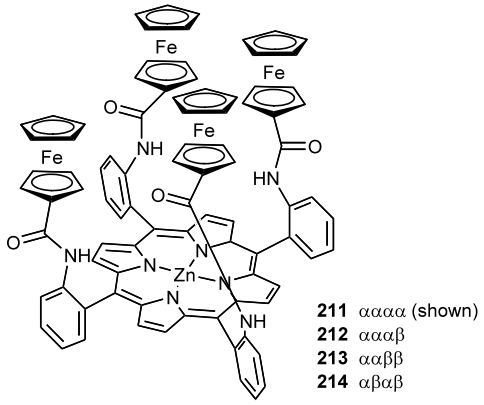


Fig. 53. Zn-porphyrins appended with ferrocene units.

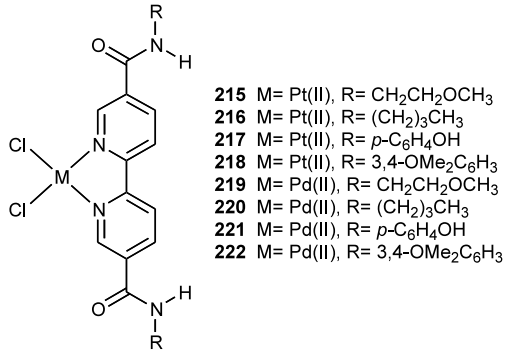


Fig. 54. $PtCl_2$ and $PdCl_2$ complexes of 5,5′-bisamido-2,2′-bipyridine.

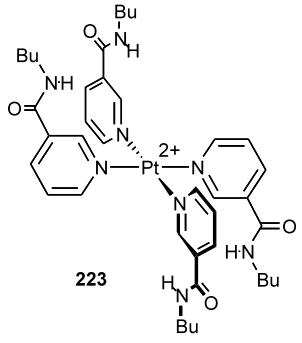


Fig. 55. Pt(II)–nicotinamide complexes analogous to calix[4]arene.

benzoate which are 'Y-shaped'. Loeb synthesized a calix[4]arene **11** (Fig. 7) that contained amide functional groups on the upper rim in the one and three positions [10]. The association constants obtained showed a large preference for the 'Y-shaped' carboxylate anions compared to the tetrahedral anions; ReO_4^-, $H_2PO_4^-$ and HSO_4^- (Table 3). It was proposed that binding of the carboxylates caused a pinched cone conformation, which allowed for two linear hydrogen-bonds to be formed between receptor and anion. When X was changed to improve the acidity of the N–H group, **12**, a much higher association constant of 5160 M^{-1} was determined for benzoate. When receptor **12** was tested

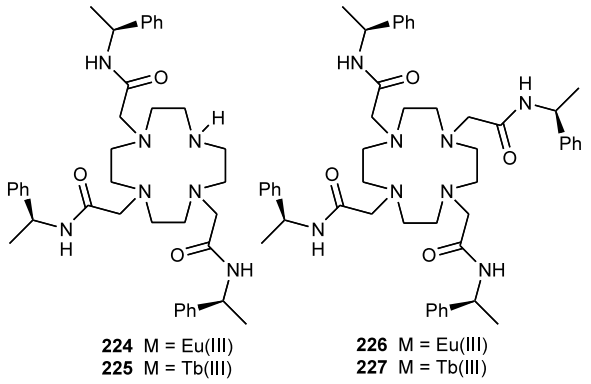


Fig. 56. Ligands used to bind Eu(III) and Tb(III) ions to form receptors.

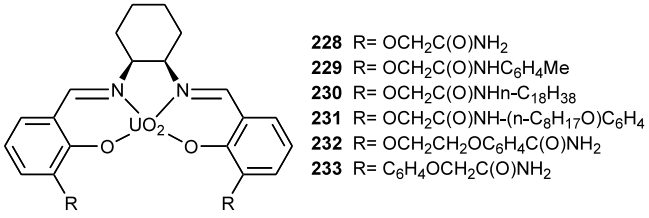


Fig. 57. UO_2 salen complexes with amide groups.

Table 1
Association constants (M^{-1}) for **1** and **2** (DMSO-d_6) [a]

Anion	1	2
Cl^-	65	12
$H_2PO_4^-$	1680	
F^-	830	11
OAc^-	2640	45
p-$NO_2C_6H_4O^-$	67	

[a] Errors < 15%.

Table 2
Association constants (M^{-1}) for **4**, **5** and **6** [a,f]

Anion	4 [b]	5 [b]	5 [c]	6
I^-	1.3×10^5 (11.1×10^4)	1.2×10^5 (9.0×10^3)	< 10	120 [b]
Cl^-	8.8×10^3 (1.7×10^3)	7.6×10^3 (1.9×10^3)	< 10	
NO_3^-	4.6×10^5 (2.1×10^3)		20	620 [b]
$pOTs^-$	2.6×10^5	2.1×10^5	780	
HSO_4^-	Slow equilibrium [d]		1.7×10^3	
$H_2PO_4^-$	Slow equilibrium [d]		1.5×10^4 [e]	500 [c]

[a] K_a of 2:1 complex in parentheses.
[b] 2% DMSO-d_6/$CDCl_3$.
[c] DMSO-d_6.
[d] Slow equilibrium among free macrocycle; 1:1 complex and 2:1 complex at room temperature (r.t.). K_a not calculated.
[e] Slow equilibrium at r.t.
[f] Errors < 20%.

Table 3
Association constants (M^{-1}) for **11** (CD_3CN)

Anion	$H_2PO_4^-$	HSO_4^-	ReO_4^-	OAc^-	$C_6H_5CO_2^-$
K_a	22	27	< 10	88	107

with other carboxylates a higher affinity for benzoate was still observed (Table 4).

Ungaro designed calix[4]arene based receptors **13** and **14** (Fig. 8) containing two alanine units used to form a strap. These preorganized chiral receptors bound carboxylate anions very tightly with association constants ranging from 4900 to 44 000 M^{-1}, in acetone-d_6. Although no chiral recognition was observed, there was selectivity towards benzoate due to its ability to π-stack with the aromatic rings of the strap and/or calixarene unit. These receptors showed much higher affinity towards the carboxylate anions compared with the more flexible unstrapped versions [11].

Calixarenes can also be tuned to preferentially bind halides [12]. Beer developed a calixarene **15** that bound F^- with an association constant of 1330 M^{-1} compared with 172 M^{-1} for Cl. Since, this bis-calix[4]arene is comprised of the lower rim of one calixarene covalently linked to the upper rim of another calixarene by two amide groups, the cavity was too small for Cl^-, HSO_4^- and $H_2PO_4^-$ but was a very good match for F^-.

Sessler and Vögtle showed that catenanes could provide a new and exciting type of anion receptor. The synthesis of the bipyrrole based amido-[2]catenane **16** (Fig. 9) was accomplished by both a one pot method and in a stepwise fashion [13]. The pyrrole and amide groups provided the interactions needed for aiding in the templating of the catenane. These two groups also provided the binding pocket for anion coordination. This receptor was found to bind F^- in 1,1,2,2-tetrachloroethane-d_2, with an association constant of 1.48×10^5 M^{-1}, Cl^- with 3.55×10^6 M^{-1} and OAc^- with 9.63×10^5 M^{-1}.

In 1986, Pascal, Spergel and van Engen developed a bicyclic receptor **17** (Fig. 10). This easily synthesized receptor consisted of three amide N–H groups pointing into a central cavity. From the X-ray crystal structure, the dimensions of the cavity seemed to be favorable for small anions such as fluoride. ^{1}H-NMR titrations in DMSO-d_6 revealed only a small affinity for fluoride [14].

Table 4
Association constants (M^{-1}) for **12** (CD_3CN)

X^-	Benzoate [a]	Nicotinate [a]	Acetate [a]	Oxalate [a]	Isophthalate [b]	Terephthalate [b]	Fumarate [b]
K_a	5160	821	609	707	$> 10^6$	$> 10^6$	$> 10^6$

[a] Stoichiometry is 1:1.
[b] Stoichiometry is 1:2 and values are $\beta(K_1K_2)$.

Table 5
Association constants (M^{-1}) for **21** (1:3 CD_2Cl_2/CD_3CN)

Anion	**21**
OAc^-	770 ± 120
NO_3^-	300 ± 30
CN^-	115 ± 10
Cl^-	40 ± 8
$H_2PO_4^-$	22 ± 5
Br^-	15 ± 8
HSO_4^-	< 5

Table 6
Association constants (M^{-1}) for **29**–**32** (CD_2Cl_2) [a]

Anion	**29**	**30**	**31**	**32**
F^-	3.0×10^4	7.5×10^3	$K_1 = 5.5 \times 10^4$ [b] $K_2 = 1.0 \times 10^3$	2.4×10^4
Cl^-	6.1×10^4	5.3×10^3	2.0×10^4	1.5×10^3 [b]
Br^-	7.1×10^3	1.4×10^3	4.6×10^3	57
I^-	460	220	1.2×10^3	< 20
OAc^-	1.98×10^4	2.8×10^3	$K_1 = 2.1 \times 10^4$ [b] $K_2 = 300$	525

[a] Errors ≤ 15%.
[b] Errors ≤ 30%.

Table 7
Association constants (M^{-1}) for **33**–**36** [a]

Anion	**33** [b]	**35** [b]	**36** [c]
F^-	134	85	74
Cl^-	28	138	11
Br^-	< 10	< 10	< 10
$H_2PO_4^-$	89	357	1450
$C_6H_5CO_2^-$	202	2500	560

[a] Errors < 15%.
[b] CD_3CN.
[c] DMSO-d_6/D_2O 0.5%.

The 3-fold symmetry of Lehn's bicyclic macrocycles had the ideal conformation for binding trigonal anions such as nitrate [15]. When receptor **18** was fully protonated it showed a preference for nitrate in ^{1}H-NMR studies. On the other hand, receptor **19** and **20** did not form stable protonated species when the anions where added to solution and no associations were measured.

Anslyn also synthesized and studied a bicyclic receptor **21** (Fig. 11), with 3-fold symmetry. This receptor was designed to interact with the anion's π system and the available six hydrogen-bonding amides. Initial studies were performed with NO_3^- and OAc^-. Findings showed OAc^- with a K_a of 770 ± 120 M^{-1} and NO_3^- with a value of 300 ± 30 M^{-1} to be more strongly bound compared with CN^-, Cl^-, $H_2PO_4^-$ and Br^- (Table 5) [16].

Upon further study, Ansyln found that the N–H hydrogen-bonding with the π-system of enolates altered the pK_a of carbon acids more than hydrogen-bonding with the lone pair. Receptor **21** was capable of the formation of four hydrogen-bonds to the π-system of the enolates while the aromatic caps, which are 7.0 Å apart, were capable of π-stacking with the guest. ^{1}H-NMR titration experiments in 95%CD_3CN/CD_2Cl_2 showed **22** to have the highest affinity with 3060 ± 180 M^{-1} and **23** to have the lowest affinity with 95 ± 10 M^{-1} (Fig. 12) [17].

Finally, Anslyn showed that optical sensing can be accomplished by the presence of indicators that are not covalently attached to the receptor. Receptor **21** plus methyl Red, **24**, or Resorufin, **25** (Fig. 13), gave UV–vis spectra with isobestic points at 440 and 513 nm and association constants of 1200 and 600 M^{-1}, respectively, in 50%MeOH/CH_2Cl_2. UV–vis competition assays showed that as the presence of nitrate ion was increased the amounts of bound **25** decreased. This occurred until the nitrate ion concentration was 40 nM and the competition of the receptor to the indicator was completely eliminated. This competitive inhibition by the anions towards the complexation of **25** and the indicator was used to measure the association constants of NO_3^-, ClO_4^- and Br^-. Results showed NO_3^- was competitive towards both indicators and, therefore, the best fit for this receptor [18].

Pernia synthesized macrocycle **26** (Fig. 14) that was originally designed for encapsulating *N*-acetyl amino acid carboxylates [19]. After several solution binding studies, it was determined that the receptor did not completely surround any of the amino acids as hoped. It was, however, found, after extensive 2D NMR studies, that receptor **26** could distinguish between D- and L-amino acid substrates. L-amino acid substrates were able to bind inside the cavity through hydrogen-bonds while the D-amino acid substrate remained bound predominantly on the outside of the cavity.

Sessler designed a covalently linked sapphyrin dimer **27** (Fig. 15) to selectively bind dicarboxylates. The covalent linker was comprised of a diaminopropane unit. Preliminary tests were carried out by running FAB mass spectrometric analysis with several dicarboxylates. These results showed the interaction with the anions was strong enough to withstand these conditions. ^{1}H-NMR titrations in CD_3OD showed **27** to have high affinity and selectivity for several dicarboxylate anions. Nitroterephthalate had the highest affinity (9100 M^{-1}) while oxalate had the lowest (260 M^{-1}). This system showed selectivity for linear or aromatic anions over bent or aliphatic anions [20].

2.2. Acyclic receptors

Simple acyclic, non-preorganized diamide receptors **28**–**32** (Fig. 16) were designed by Crabtree. These receptors showed strong and selective anion binding due in part to their flexibility. This flexibility allowed for adjustments in the size of the cavity as well as for the formation of almost linear hydrogen-bonds [21]. The acidity of the N–H bond also played a role in the association values (Table 6). Receptor **28**, which had the least acidic N–H, showed a marked decrease in association constants for the same anions compared with **29**. The crystal structure of the Br^- complex was obtained in a *syn–syn* conformation allowing both amide N–H groups to point inward and form H-bonds with the anion [22].

Gale designed several pyrrole based amide and diamide compounds (Fig. 17) [23]. The X-ray structures of these compounds showed extensive hydrogen-bonding between the pyrrolic N–H and the oxygen of the amide resulting in the formation of dimers. Receptor **36** also crystallized in a semi-cleft conformation, which demonstrated a possible binding mode for the anions. ^{1}H-NMR titrations were performed in CD_3CN for receptors **33** and **35**; receptor **34** had precipitation problems that inhibited acquiring results and receptor **36** was titrated in DMSO-d_6/0.5%D_2O. Receptor **33** and **35** had the highest association with benzoate and receptor **36** preferred the $H_2PO_4^-$ ion (Table 7). The association constant for **35**-benzoate was ten times that of **33**-benzoate, which was subsequently shown by X-ray crystallography to be due to the formation of a cleft conformation [24,25].

The incorporation of CH···O and NH···O hydrogen-bonds into anion receptors was the goal of Jeong. This was accomplished by using pyridinium salts along with amide functional groups to prepare **37**–**39** (Fig. 18). Initially, **37** was tested with benzoate and a rather small association constant (16 M^{-1}) was obtained in DMSO-d_6. When the quaternary salt **38** was tested, the acidity of the CH and NH protons increased and so did the association constants, ($\sim 10^2$ M^{-1}). Finally the addition of two amide groups to the bispyridinium receptor **39** yielded high affinity (3000 M^{-1}) to the anion adipate in 90%DMSO-d_6/D_2O [26].

The recognition of specific anions in solvents such as H_2O and DMSO in order to mimic natural environments was the goal of many research groups [27]. Prohen investigated the synthesis and characterization of squaramido-based receptors designed for recognition

Table 8
Association constants (M^{-1}) for **40**–**48** [g]

	Acetate	Glutarate	Trimesoate	*cis*-Cyclohexene-tricarboxylate
40	217 [a]			
41	1980 [a]			
41	48 [b]			
42	1120 [a]			
43	14 200 [a,h]			
43	311 [b]			
43	965 [c,h]			
43	396 [d,h]			
45		1400 [d]		
45		150 [e,h]		
47		560 [f]		
48			3900 [b]	
48				7700 [b,h]

[a] DMSO-d_6.
[b] 10%D_2O/DMSO-d_6.
[c] 50%CD_3OD/$CDCl_3$.
[d] 10%D_2O/CD_3CN.
[e] 15%D_2O/DMSO-d_6.
[f] 30%D_2O/CD_3CN.
[g] Errors $\leq$ 15%.
[h] Errors $<$ 30%.

Table 9
Association constants (M^{-1}) for **51**–**58** ($CDCl_3$) [a]

Anion	**51**	**52**	**53**	**54**	**55**	**56**	**57**	**58**
$H_2PO_4^-$	26							
$C_6H_5CO_2^-$	14	54	328	53	78	48	195	213
Cl^-	10	21	108	<10	37	29	307	395
Br^-	8	16	18	<5	21	28	125	30
I^-	5	9	39	<5	27	26	52	17

[a] Errors $<$ 10%.

Table 10
Association constants (M^{-1}) for **77**–**81** (DMSO-d_6) [a]

Receptor	Cl^-	Br^-
77	50	63
78	10 000 [b]	
79	20	32
80	126	63
81	200	

[a] Errors $<$ 20%.
[b] CD_3CN.

of carboxylates in highly competitive solvents (Fig. 19). These receptors were tailored for the binding of certain mono, di and tricarboxylates. Receptors **40**–**43** all showed a 1:1 binding ratio for acetate with **43** having an 8–10-fold increase in association constant compared with the other receptors. Receptors **44**–**47** were tested with glutarate ion in wet solvents and the association constants obtained are summarized in Table 8. Finally,

Table 11
Association constants (M^{-1}) for **82**–**86** [a]

Receptor	Cl^-	Br^-	$H_2PO_4^-$
82 [b]	24		
83 [b]	770		
84 [b]	630		
85 [c]	30	25	
86 [c]	35	25	320

[a] Errors $\leq$ 10%.
[b] CD_3CN.
[c] DMSO-d_6.

Table 12
Association constants (M^{-1}) for **90**–**92** (DMSO-d_6) [a]

Receptor	Cl^-	$H_2PO_4^-$
90	750 [b]	
91	60 [b]	250
92	30	Precipitation

[a] Errors $\leq$ 10%.
[b] CD_3CN.

the trimesoate ion and the *cis*-cyclohexentricarboxylate ion were titrated with receptor **48** in 10%D_2O/DMSO-d_6 and the association constants obtained were 3.9×10^3 and 7.7×10^3 M^{-1}, respectively.

Smith studied the binding of carboxylates with a receptor that contained a Lewis acidic boronate group [28]. When receptor **50** was titrated in DMSO-d_6 with acetate the binding constant was 2.1×10^3 M^{-1}, which was ten times that of receptor **49** that does not contain the Lewis acid center (Fig. 20). NOE experiments showed receptor **50** to be in a cleft arrangement with the ^{11}B-NMR showing an upfield shift upon the addition of acetate ion. This lead to the conclusion that the binding of acetate to the N–H of the amide caused a cooperative polarization and resulted in the strengthening of the carbonyl–boron bond.

Simple mono, di and triamide receptors **51**–**58** (Fig. 21) were synthesized, by Schneider. The mono-amide receptor (**51**) was titrated in $CDCl_3$ and the association constants were found to be highest for the $H_2PO_4^-$ ion followed by benzoate and finally the halides [29]. Receptors **52**–**56** all showed higher affinities for anions compared with receptor **51**, which was to be expected due to the presence of the second amide group. The preorganization of the amides in receptor **52** allowed for higher affinities toward the anions compared with receptors **53**–**55**. However, the addition of a third amide group to the receptors did not have as much of a marked increase in the association constants as compared with addition of the second amide (Table 9).

A cyclohexane unit was used by Morán as the main building block for an acyclic receptor that preferred phosphates. The favorable triangular shape formed by

Table 13
Association constants (M^{-1}) for **95**–**102** (CD_3CN) [a]

Receptor	Cl^-	Br^-	I^-	$H_2PO_4^-$	HSO_4^-	Adipate[c]
95	2500	330	450			
96	1300	270	275			
97	280	260	100			
98	$K_1 = 1260$, $K_2 = 250$	$K_1 = 1000$, $K_2 = 65$				
99	$K_1 = 1260$, $K_2 = 400$	$K_1 = 800$, $K_2 = 130$				
100	$K_1 = 2500$, $K_2 = 130$	$K_1 = 950$, $K_2 = 50$				
101 [b]	$K_1 = 3160$, $K_2 = 90$	$K_1 = 3160$, $K_2 = 50$				
102 [b]	5035	1680		2800	$K_1 = 990$, $K_2 = 495$	11 510

[a] Errors ≤ 10%.
[b] DMSO-d_6.
[c] Acetone-d_6.

Table 14
Association constants (M^{-1}) for **106**, **117**–**120** ($CDCl_3$) [a]

Receptor	Cl^-	Br^-	$H_2PO_4^-$	HSO_4^-	I^-	NO_3^-
106	4.7		5.0			
117	21		6.0			
118			5.0 [e]	8.5 [e]		
119	17[b]		120/130 [b]	> 10 000/7500 [b]		15
120	22.5/29.5 [c]/5.0 [d]	24			23	

[a] Errors ≤ 10%.
[b] MeCN-d_3.
[c] 50%CD_3CN/50%$CDCl_3$.
[d] DMSO-d_6.
[e] Errors ≤ 33%.

three amide substituents was the ideal geometry to attract the tetrahedral shaped phosphate (Fig. 22). The association constant obtained from the addition of phenyl phosphate was 1.0×10^2 M^{-1} for receptor **59** in DMSO-d_6. Receptor **60** allowed six amides to be available for hydrogen-bonding to phenylphosphonate (1.5×10^4 M^{-1}) and phosphate ($> 10^5$ M^{-1}) in DMSO-d_6 [30].

Davis designed an acyclic system where cholic acid was used as the scaffolding unit. Receptor **61** showed more flexibility in the rotation of the carbomoyl sulfonamide bond to the scaffolding and modeling of receptor **62** showed that the sulfonamides in the 7α and 12α positions were locked in place with the N–H groups pointing into the cavity (Fig. 23). Both these receptors showed preference for halides with the association constant values for **62** slightly larger due to the preorganization of the molecule [31,32].

In 1993, Reinhoudt designed tripodal receptors that mimicked the structure of a phosphate binding protein. Receptors **63**–**70** (Fig. 24) were synthesized in relatively high yields (70–90%) and were titrated in $CDCl_3$ [33]. ^{1}H-NMR studies revealed that the receptors had higher specificity for $H_2PO_4^-$ compared with HSO_4^- and Cl^-. Receptor **70** had the highest binding constant of 14 200 M^{-1} for $H_2PO_4^-$ due to the preorganization of the sulfonamide groups and the π-stacking interactions of the naphthalenes.

Table 15
Association constants (M^{-1}), $E_{1/2}$ and ΔE (mV) for **128**–**129** [a]

	128 ($E_{1/2\ \text{no anion}} = 511$)			**129** ($E_{1/2\ \text{no anion}} = 503$)		
	Cl^-	F^-	$H_2PO_4^-$	Cl^-	F^-	$H_2PO_4^-$
Binding	202	–	40	444	1496	40
$E_{1/2}$	718	525	502	481	566	534
ΔE	207	14	−9	−22	63	31

[a] Errors < 20%.

Table 16
Association constants (M^{-1}), $E_{1/2}$ and ΔE (mV) for **130**–**131** [a]

Anion	**130** ($E_{1/2\ \text{no anion}} = 396$)			**131** ($E_{1/2\ \text{no anion}} = 424$)		
	Binding	$E_{1/2}$	ΔE	Binding	$E_{1/2}$	ΔE
F^-	$> 10^5$	316	80	$> 10^5$	368	56
Cl^-	9031	372	24	1260	388	36
Br^-	857	388	8	66	404	20
HSO_4^-	889	380	16	258	392	32
$H_2PO_4^-$	11 305	260	136	4181	280	144

[a] Errors < 15%.

Acyclic quaternary polybipyrimidinium receptors containing 4,4′ and 5,5′ disubstituted *N*-*N*′-dimethyl-

Table 17
Association constants (M^{-1}) for **134**–**138** (CD_2Cl_2) [a]

Receptor	Cl^-	Br^-	I^-	$H_2PO_4^-$
134	10			10
135	70	50	10	20
136	70	60	15	20
137	20	–	–	–
138	240	320	250	Precipitation

[a] Errors $\leq 20\%$.

Table 18
Association constants (M^{-1}) for **141** in various solvents [a]

Anion	CD_2Cl_2	CD_3CN	DMSO-d_6
Cl^-	40	70	5200
$C_6H_4CO_2^-$	117	360	940
OAc^-	26	120	6000

[a] Errors $< 10\%$.

Table 19
Association constants (M^{-1}) for **123**–**125**, **143**–**144** (CD_2Cl_2) [a]

Receptor	F^-	$H_2PO_4^-$	ATP^{2-}	HSO_4^-
123	20	40		
124	230	65		
125	110	25		10
143	–	–		
144	69	89	63	

[a] CD_3CN

Table 20
Association constants (M^{-1}) for **154**–**159** (DMSO-d_6) [a]

Receptor	Cl^-	Br^-	I^-
154	Z	20	10
155	20	–	< 5
156	140	30	15
157	150	35	20
158	80	20	< 5
158	6700 [b]	–	120 [b]
159	205	95	25

[a] Errors $\leq 5\%$.
[b] CD_3CN.

2,2′bipyridinium segments have been studied by Beer and compared with a polypyridinium based triamide receptor **71** (Fig. 25) [34]. ^{1}H-NMR solution data showed that the presence of the amide groups in this type of receptor doubled the binding constant for Cl^-; 110 M^{-1} in DMSO-d_6. These findings demonstrated the significance of the amide N–H hydrogen-bonding in the receptor–anion interaction.

Using electrocrystallization along with solution studies, Batail investigated the ability of 3-methylamino-3′,4′-ethylenedithio-tetrathiofulvalene (**72**) (Fig. 26)to bind Cl^- in DMSO-d_6 [35]. The results showed a weak association of 10 M^{-1} where the N–H from the amide along with the C–H from the *ortho* position on the adjacent ring formed hydrogen-bond tweezers. The complexation induced chemical shift was followed in both these two protons during the titration. An X-ray crystal structure determination verified this interaction.

3. Inorganic receptors

The incorporation of metal ions into anion receptors can be achieved in a variety of ways. Most often this is done by including a metal chelating unit or by utilizing an organometallic building component in the original skeletal structure. The most common reason for introducing a metal center is to provide a physical property that can be monitored as a reporting or sensing output. This turns a receptor into a receptor by providing a method to 'read-out' the degree of anion binding to a receptor. Electrochemcial and optical (color or fluorescence) outputs are the most common.

3.1. Metallocene receptors

Beer investigated receptors combining amide donors and charged cobaltocenium units (Fig. 27). When cobaltocenium itself was titrated there were no changes observed to chemical shifts but when the simple receptors **73** and **74** were titrated shifts in the proton peaks were evident. Replacement of the amide protons with non-hydrogen-bonding groups in **75** and **76** no chemical shift changes were observed once again. The electrochemical results concurred with the NMR results, as significant cathodic perturbations were observed upon addition of anion only when the amide hydrogens were present [36,37].

The use of cobaltocenium amide substituted receptors was further explored by comparing pyridyl and pyridinium substituents in **77**–**81**. ^{1}H-NMR titration in DMSO-d_6 showed mono or bisamide substituted complexes had *ca*. the same affinity for all the halide anions tested (Table 10). The incorporation of a quaternized pyridinium salts, however, did show a 10-fold increase in association. The addition of Cl^-, HSO_4^- or $H_2PO_4^-$ anions to the receptor showed considerable cathodic perturbations in MeCN [38].

Cobaltocenium with amide-linked aminophenyl groups, **82**–**84**, provided other possible hydrogen-bonding groups. These receptors were synthesized with amine groups in the *ortho*, *meta* and *para* positions. ^{1}H-NMR titration experiments in CD_3CN revealed the affinity for chloride was greatly increased with the amine in the *ortho* and *meta* positions. This was due to the proximity of the amine hydrogens to the anion. Receptors **85** and

Table 21
Association constants (M^{-1}) for **160**–**164**, **169**–**171** (DMSO-d_6)

Receptor	Cl^-	$H_2PO_4^-$	OAc^-	$PhCOO_2^-$	$PhCH_2CO_2^-$	Br^-
160 [a]	5.0×10^2	8.0×10^3				
161 [a]	4.8×10^2	7.7×10^3				
162 [a]	1.8×10^2	1.6×10^3				
163 [a]	4.2×10^2	5.6×10^3				
164 [a]	0.9×10^2	8.0×10^3				
169 [a]	1.6×10^2	2.8×10^4				3.6×10^2
170 [a]	4.1×10^2	5.2×10^3				0.8×10^2
171 [b]	145	630	160	750	650	

[a] Errors ≤ 5%.
[b] Errors ≤ 15%.

Table 22
Association constants (M^{-1}) for **172**–**175** (DMSO-d_6) [a]

Receptor	Cl^-	OAc^-	$H_2PO_4^-$
172	1050	9990	215
173	255	1790	160
174	840	4060	240
175	435	760	185

[a] Errors < 10%.

Table 23
Association constants (M^{-1}) for **176**–**183** (DMSO-d_6) [a]

Receptor	Cl^-	Br^-	$H_2PO_4^-$
176	25	45	55
177	55	40	4320
178	70	60	10
179	245	170	19 700
180	310	220	15 480
181	825		> 30 000
182	440		22 150
183	120		1820

[a] Errors < 10%.

Table 24
Association constants (M^{-1}) for **184**–**189** (DMSO-d_6) [a]

Receptor	Cl^-	OAc^-	$H_2PO_4^-$
184	4.0×10^4	3.6×10^3	
185	4.9×10^4	1.3×10^2	0.4×10^2
186	3.0×10^3	2.2×10^6	$> 10^5$
187	3.0×10^2	6.9×10^2	$> 10^5$
188	0.6×10^2	3.7×10^2	$> 10^5$
189	3.7×10^2	7.3×10^2	$> 10^5$

[a] Errors ≤ 10%.

86 were titrated with Cl^-, Br^- and $H_2PO_4^-$ in DMSO-d_6. A significant affinity for $H_2PO_4^-$ was observed with receptor **86** but no selectivity was seen for chloride or bromide from either receptor (Table 11). The cyclic voltammetry experiments were in agreement with these results where all receptors showed cathodic shifts when Cl^- was present with receptor **85** and **86** having the largest shifts when $H_2PO_4^-$ was added [39].

Table 25
Association constants (M^{-1}) for **202**–**204** (aqueous) [a,b]

Carboxylate anion	**202**	**203**	**204**
Butylamine [c]	27	6	28
Gly	87	57	89
DL-Phe	360	270	350
DL-Trp	1000	830	1100
L-Trp	1000	810	1100
DL-Asp [d]	310	300	340
Gly-DL-Trp	500	230	560
Gly-L-Trp	480	240	460

[a] Errors < 10%.
[b] $NaHCO_3$–Na_2CO_3 buffer solution (pH 10.4, $I = 0.02$).
[c] 0.01 M K_2CO_3 (pH 11.5, $I = 0.03$).
[d] Errors < 23%.

The anion coordination chemistry of chloride and bromide were compared using acyclic and macrocyclic cobaltocenium receptors. The acyclic receptors **87** and **89** did not exhibit strong binding towards Cl^- or Br^-, however, the macrocyclic version, **88**, displayed stability constants of a magnitude higher (200 M^{-1}). All the receptors showed electrochemical recognition for both chloride and bromide [40].

Different substituents on the cobaltocenium-amide receptors lead to significant selectivity for Cl^- and $H_2PO_4^-$. Receptor **90** was highly selective for Cl^- but showed no chemical shifts in the proton NMR titrations for $H_2PO_4^-$. On the other hand, receptors **91** and **92** showed significant affinity towards $H_2PO_4^-$ and very little affinity for Cl^- (Table 12). This was due to the presence of the nitrogen lone pair on the pyridine ring that formed hydrogen-bonds with the $H_2PO_4^-$ but repulsed the Cl^-. Receptors **93** and **94** (Fig. 28), which have the same binding units as receptor **90** exhibited no affinity for $H_2PO_4^-$ but did associate well with Cl^-. Cyclic voltammetry was not performed with $H_2PO_4^-$ due to precipitation problems, however, upon the addition of Cl^- **90** showed considerable cathodic shifts [41].

Table 26
Association constants (M^{-1}) for **228**–**233** (99%CH_3CN/DMSO)

Receptor	$H_2PO_4^-$	Cl^-	HSO_4^-	SCN^-	NO_2^-
228	1.9×10^4	4.0×10^3	[c]	[c]	8.9×10^2
229	$> 10^5$	1.7×10^3	1.4×10^2	7.1×10^1	4.5×10^2
230 [b]	8.0×10^3	< 5			< 5
231	$> 10^5$	2.9×10^3			4.7×10^3
232 [a]	6.5×10^4	$< 3 \times 10^2$			4.5×10^2
233	1.6×10^3	$< 3 \times 10^2$			$< 3 \times 10^2$

[a] Value determined from pure CH_3CN.
[b] Values determined by ^{1}H-NMR in 90%$CDCl_3$/DMSO-d_6.
[c] Values not obtained due to insolubility.

Biscobaltocenium-amide substituted receptors were synthesized and studied. The selectivity for halides was tested by varying the size of the spacers between the cobaltocenium units. An ethyl linkage provided the optimum space for a chloride ion. As the linkers progressed from ethyl to butyl (**95**–**97**) the affinity for chloride decreased. Receptor **98**–**101** showed 1:2 host:anion stoichiometries with relatively high affinity for chloride. The presence of the ester did not aid in the stability or selectivity for these anions. The calix[4]arene receptor (**102**) showed high affinity and electrochemical response for the dianion adipate in a 1:1 stoichiometry (Table 13) [42].

Anion recognition studies on calix[4]arenes with upper-rim amido-cobaltocenium substituents were performed using spectroscopic and electrochemical techniques (Fig. 29). Isomers **103** and **104** showed dramatically different selectivity and stability properties. Overall **104** had high association constants and preferred OAc^- compared with **103** which had much lower affinities and preferred $H_2PO_4^-$. The preference for **104** was due to the position of the tosyl group, which held the cobaltocenium substituents in close proximity [43]. Receptor **105** had very large association constants especially for acetate. The bridging cobaltocenium unit brought the two amide groups into close proximity and formed an optimal geometry for the carboxylates to bind. The electrochemical response of these systems showed the stabilization of the cobaltocenium unit upon the addition of anion [44].

Neutral ferrocene molecules can also be incorporated into anion receptors (Fig. 30). An amide substituted ferrocene receptor, **106**, was titrated with Cl^-, HSO_4^- and $H_2PO_4^-$ in $CDCl_3$. This receptor did not show high affinity or selectivity to any of these anions (20–45 M^{-1}). Receptor **107**, which contained an additional pyridine and amino group had the ability to form two more hydrogen-bonding interactions. This receptor showed no affinity for Cl^-, low affinity for $H_2PO_4^-$ (50 ± 5 M^{-1}) and strong affinity for HSO_4^- (370 ± 37 M^{-1}). Ion pairing effects were seen in the cyclic voltammetry experiments for both receptors. The anion interacted with the neutral molecule through the amide N–H and after the ferrocene was oxidized the anion also formed electrostatic interactions with the ferrocenium. In the charged state both receptors preferred $H_2PO_4^- > HSO_4^- > Cl^-$ [45].

Simple ferrocenyl glycine esters **108**–**110** were investigated by Gallagher. These receptors were tested electrochemically and the most significant perturbation occurred in the presence of $H_2PO_4^-$. Hydrogen sulfate, chloride and tetrafluoroborate also caused cathodic shifts in the redox couple [46].

Moutet varied the substituent on the ferrocene moiety from amide to carboxyester to aldehyde, **111**–**116**, which lead to a demonstration of the importance of hydrogen-bonding. ^{1}H-NMR spectroscopy revealed association between **111** and $H_2PO_4^-$ occurred in a multidentate fashion with the amide and bipyridyl units. This interaction was also sensed electrochemically. The association of F^-, HSO_4^- and Cl^- with the receptors occurred mostly through ion-pairing after the oxidation of the ferrocene unit. The absence of the hydrogen-bonding units in the carboxyester and aldehyde receptor lead to much weaker perturbations in the NMR titrations and cyclic voltammetry experiments [47].

Beer also used ferrocene complexes containing both amide and amine groups to prepare HSO_4^- specific receptors. First a comparison of **106** and **117** showed that the thioamide was more sensitive to the anions tested compared with the carboxyamide due to the increased acidity of the proton (Table 14). When **119** was titrated in $CDCl_3$ the proton from the amide was shifted further downfield compared with the amine protons for $H_2PO_4^-$, Cl^- and NO_3^- but the opposite was observed for HSO_4^-. Since HSO_4^- is more acidic than $H_2PO_4^-$ two binding modes for HSO_4^- were occurring. The first involved simple hydrogen-bonds with both the amide and the amine. The second mode occurred though electrostatics where the amine acted as a proton acceptor for HSO_4^- and became positively charged. **122** also contained both an amide and an amine group and showed the same type of perturbation patterns as **119** towards $H_2PO_4^-$ and HSO_4^- but

precipitation occurred during the titrations. **106** and **117** both showed an EC mechanism when the electrochemical properties were tested. This occurred due to the anion first associating to the receptor though hydrogen-bonds then when the ferrocene was oxidized electrostatic interactions were formed. **120** had a significant cathodic perturbation when the halides were added and **122** showed a large cathodic shift for $H_2PO_4^-$ and a large increase in UV–vis intensity [48].

A comparison of receptors **126** and **127** (Fig. 31), by Crabtree, demonstrated the advantages of having two converging amide units as opposed to a single unit in the binding of chloride. The proton NMR titrations produced data for the determination of the association constants. Receptor **126** had an association constant of 9500 M^{-1} and **127** had an association constant of 30 M^{-1} for Cl^- in CD_2Cl_2. The cyclic voltammogram for **126** showed perturbations in the presence of Cl^- while **127** had negligible shifts [49].

Receptors **128** and **129** (Fig. 32) were synthesized by Sessler and tested for anion recognition and electrochemical sensing. These calix[4]pyrroles demonstrated anion coordination to $H_2PO_4^-$, F^- and Cl^-. Both the pyrrole N–H and C–H chemical shifts were monitored. The electrochemical recognition to these anions was somewhat surprising and not easily interpreted. The addition of F^- and Cl^- to receptor **128** lead to a cathodic shift while $H_2PO_4^-$ shifted the peak anodically. Receptor **129** had cathodic shifts for F^- and $H_2PO_4^-$ and anodic shifts for Cl^- (Table 15) [50].

Ferrocene along with pyrroles and amides was incorporated together to form an anion receptor, **130** (Fig. 33), that was highly selective for Cl^- and $H_2PO_4^-$. These ferrocene based receptors formed a *trans*-type arrangement with the substituents forming a cavity where the anions could coordinate to the molecule. Job plots revealed the smaller fluoride anion bound in a 1:2 fashion while the rest of the anions bound in 1:1 stoichiometries. The association constants for the cyclic **130** compared with the acyclic version **131** (not shown) of this receptor were much larger due to the preorganization of the cyclic complex (Table 16). Cathodic shifts for these receptors were also seen when the anions were added to the MeCN solution with $H_2PO_4^-$ showing the largest shift [51].

The ferrocene and cobaltocenium containing receptor **132** (Fig. 34) formed a 1:1 stoichiometry with $H_2PO_4^-$, HSO_4^- and Cl^- in CD_3CN solution. Upon the addition of $H_2PO_4^-$ to the electrochemical cell, the cyclic voltammogram revealed significant cathodic shifts for the cobaltocenium and both ferrocenes. Receptor **133** also exhibited a 1:1 stoichiometry in CD_3CN/DMSO-d_6 solution with $H_2PO_4^-$, HSO_4^- and Cl^-. Electrochemical cyclic voltammograms of **133** showed preference for $H_2PO_4^-$ even in the presence of a 10-fold excess of HSO_4^- or Cl^- [52].

Receptors **134**–**138** (Fig. 35) were designed to probe the importance of electrostatic interactions as well as hydrogen-bonding in the binding of anions by ferrocene containing receptors. Receptor **134** was used as a model to determine the importance of the Lewis acid centers and electrostatic interactions. The largest increase in association compared with **134** was observed for **138**, which contained positively charged ruthenium(II) centers. The association constants for **135** and **136** were also much larger than **134** due to the presence of a neutral Lewis acid center. The size of the cavity also played a role in the selectivity. Receptors **135** and **136** had binding constants that decreased as the size of the anion increased due to the small size of the receptor's cavity (Table 17). These receptors all showed large cathodic shifts upon the addition of anion [53].

Calix[4]arene receptors containing two or four ferrocene units were synthesized (Fig. 36) and their anion coordination was tested by ^{1}H-NMR titrations in CD_2Cl_2. Receptor **139** formed a 1:1 calixarene:anion stoichiometry and an association constant of 55 M^{-1} for chloride. However, **140** did not associate to any anions tested. The affinity of **139** for chloride may have been due to a more favorable cavity size. The electrochemical properties of **139** showed cathodic shifts when $H_2PO_4^-$, HSO_4^- or Cl^- was present [54].

The neutral bis-calix[4]arene ferrocene receptor **141** (Fig. 37) exhibited drastic changes in binding constant depending on the solvents used (Table 18). The association constant obtained for Cl^- in CD_2Cl_2 was 100-fold less than that in DMSO-d_6. An even larger difference was seen for OAc^-. The binding of these anions to the receptor always effected the same protons in every solvent, therefore, the same binding mode was occurring in each solvent. The chemical shifts verified the anions were binding to the amide protons and the upper-rims of the calixarenes [55].

The ferrocene appended cavitand **142** (Fig. 38) was titrated with Cl^- in CD_2Cl_2. The association constant obtained was 66 M^{-1} with a 1:1 stoichiometry. The binding occurred though a cooperative interaction between the four ferrocenyl amide units [56].

Reynes synthesized and investigated several novel amido-ferrocene receptors (Fig. 39). These molecules varied in the amount of preorganization, the number of ferrocene units and the number of amide substituents. The incorporation of neutral ferrocene units allowed for proton NMR titrations to measure the effect of the hydrogen-bonding amides and cyclic voltammetry to observe the effect of electrostatic interactions when ferrocene was oxidized. The association constants for **143** were negligible for all anions due to the size and rigidity of the receptor. Receptors **123** and **144** bound the $H_2PO_4^-$ anion through hydrogen-bonds with the amide groups as demonstrated by significant downfield shifts of the NH protons. Receptors **123**–**125** bound F^-

by hydrogen-bonding to the Cp units, which showed large shifts in these protons compared with the amide hydrogens (Table 19). All receptors showed perturbation in the voltammograms upon addition of anion [57].

Several different dendrimeric receptors **145**–**147** (Fig. 40) have been synthesized by Astruc. These receptors contained three, nine and 18 ferrocene centers, respectively, and displayed dendritic effects upon addition of anions to the system. The cyclic voltammograms revealed that as the number of ferrocene units increased so too did the amount of cathodic shift. The largest shifts were observed for the $H_2PO_4^-$ anion [58].

3.2. $[Ru(bipy_3)]^{2+}$ related receptors

Derivatives of the well known and well studied tris(2,2′-bipyridine)ruthenium(II) cation have been explored extensively by Beer due to their ability to recognize and sense anions in a variety of manners. These complexes can be tested and characterized by optical and NMR spectroscopy and electrochemistry. Receptors **148**–**153** (Fig. 41) all possessing a 2,2′-bipyridyl ligand, substituted with amido groups at the 5 and 5′-positions, were titrated with both Cl^- and Br^- in DMSO-d_6. The association constants obtained revealed none of the receptors showed a large affinity for Cl^- (all values $\sim 45\ M^{-1}$) and receptor **148** was the only receptor to complex Br^- ($40\ M^{-1}$). Therefore, differentiating the substituents on the amide group did not aid in the selectivity towards a specific anion in these systems. Cyclic and square wave voltammetry along with fluorescence emission have both demonstrated chloride recognition through considerable cathodic perturbation and quenching of the MLCT emission band [59,60].

Beer also synthesized $[Ru(bipy)_2L][PF_6]_2$ where L is 2,2′-bipy with amido substituents in the 4 and 4′-positions (**154**–**159**) (Fig. 42). Proton NMR titrations in DMSO-d_6 revealed that all the receptors preferred $Cl^- > Br^- > I^-$ (Table 20) The presence of the phenolic OH in the *meta* and *para* position showed a marked increase in the association constant due to the increase in the number of hydrogen-bond donors [60,61]. Steric problems were evident in a decrease in association constant for the *ortho*-substituted phenol. Receptor **158** preferred Cl^- over the larger I^- in both CD_3CN and DMSO-d_6 due to the proximity of the *tert*-butyl group to the amide binding site. The spectroscopic and electrochemical studies showed both electrostatic and hydrogen-bonding interactions played a role in the association of the halides to the receptors.

The association constant obtained for receptors **160**–**164** with Cl^- and $H_2PO_4^-$ revealed that all the receptors preferred $H_2PO_4^-$ over Cl^-. This was most dramatically demonstrated by receptor **164**, which showed a 100-fold increase in association for $H_2PO_4^-$. The X-ray structure obtained for **160** plus Cl^- contained six hydrogen-bonds to the chloride anion demonstrating the importance of hydrogen-bonding in anion recognition. Optical studies showed a large increase in emission intensity for receptors **165**–**168** (Fig. 43) when chloride was added to the MeCN solution [62,63].

The calix[4]arene containing receptors **169** and **170** (Fig. 44) were titrated with Cl^-, Br^- and $H_2PO_4^-$ in DMSO-d_6. The stability constants obtained showed a trend for both receptor **169** and **170** where $H_2PO_4^- > Cl^- > Br^-$, however, receptor **169** had higher values overall due to a smaller, more compact cavity (Table 21). The high preference for $H_2PO_4^-$ was also observed using electrochemistry when a 10-fold excess of Cl^- or HSO_4^- was added to a MeCN solution of receptor **169**. The observed shift that occurred in the reduction couple towards the cathode was by the same amount as when the $H_2PO_4^-$ was the only anion present. Fluorescence emission studies also revealed significant perturbation for **169** when $H_2PO_4^-$ was added to the system [63,64]. The bis(calix[4]arene) receptor (**171**) showed binding of the anions took place in the cavity at the upper-rim of the calixarenes. This was demonstrated by a significant shift in the proton NMR of the amide N–H, the protons *ortho* to the amide and the proton in the 3-position on the bipyridine [65].

Novel ruthenium(II) and rhenium(I) calix[4]arene and calix[4]diquinone receptors (**172**–**175**) (Fig. 45) where titrated in DMSO-d_6 with OAc^-, $H_2PO_4^-$ and Cl^-. The results showed OAc^- was favored for all the receptors and the values were larger than the acyclic version. The calix[4]diquinone containing receptors had higher affinities for OAc^- compared with the calix[4]arene analogues and also exhibited optical sensing for OAc^- and Cl^-. A drastic increase in the intensity of 500% was observed when acetate was added to **172** (Table 22) [66].

Beer also prepared dinuclear receptors **176**–**183** (Fig. 46). These receptors formed cleft-shapes where the Ru(II), Re(I) and Os(II) Lewis acid centers provided an increase in affinity towards the anions. The resulting receptors showed high selectivity towards $H_2PO_4^-$ compared with the halides. By altering the bridging groups the association constants varied greatly from **176** ($55\ M^{-1}$) to **177** ($4320\ M^{-1}$) for $H_2PO_4^-$ in DMSO-d_6. The selectivity for $H_2PO_4^-$ over Cl^- was greatly demonstrated in receptors **179**–**183** where a 10-fold increase in association constants was observed (Table 23) [67].

Macrocyclic dinuclear ruthenium(II) and osmium(II) receptors **184**–**189** (Fig. 47) were also synthesized. The optical, electrochemical and spectroscopic properties where examined when anions such as Cl^-, OAc^- and $H_2PO_4^-$ were added to these systems. The shapes and sizes of the cavity determined the selectivity of the receptor, which was demonstrated by the ^{1}H-NMR titrations. Receptor **184** had an association constant of

40 000 M^{-1} for Cl^- while the affinity for $H_2PO_4^-$ was immeasurable in DMSO-d_6 (Table 24) [62,68].

Using tris(5,5′-diamido-2,2′-bipyridyl) complexes of ruthenium(II), Beer demonstrated the effects of the amide substituents and solvent systems on the selectivity of the receptor. The anions tested where Cl^-, NO_3^- and OAc^- in solvents mixtures of dichloromethane and methanol. They found all the association constants decreased as the amount of methanol was increased. Receptors **190** and **191** (Fig. 48) showed the highest affinity for Cl^- in all solvents due to a favorable shape for chloride. Receptors **192** and **193** preferred Cl^- in the 9:1 and 7:3 CH_2Cl_2:MeOH solvent mixtures and NO_3^- in the 1:1 CH_2Cl_2:MeOH mixtures. This due to NO_3^- having a lower desolvation energy compared with Cl^- [69].

Receptors for chiral anions have not been widely synthesized or studied in the past. Beer developed new receptors **194**–**200** containing rhenium(I) and ruthenium(II) cores to recognize chiral anions. The rhenium(I) receptors **194**–**198** recognized chirality through the chiral amide substituents, which allowed the hydrogen-bonding sites on the bipyridyl and amide to be maintained. The second type of receptor **163** obtained its chirality from the helical ruthenium(II) center. Finally the third type of receptors **199**–**200** (Fig. 49) contained the same ruthenium(II) core with chiral substituents on the amide. Proton NMR titrations of these compounds revealed binding for carboxylate anions with no preference for a specific enantiomer [70].

The ruthenium(II) bipyridyl resorcinarene cavitand **201** (Fig. 50) was used in anion coordination studies. ^{1}H-NMR titrations in MeCN-d_3 with Cl^-, OAc^- and $C_6H_4CO_2^-$ resulted in chemical shifts of the amide and bipyridyl protons in the 3-position. UV–vis titrations were also performed in order to obtain stability constants. The carboxylate anions had higher affinity for the cavitand (19 953 M^{-1}) compared with chloride (2512 M^{-1}). Increase in emission intensities were also seen when excess amount of anion was added to the solution [56].

3.3. Porphyrin metalloreceptors

Zinc porphyrins have been known to act as receptors for both amino acids and peptides but few have been soluble in water. Imai synthesized and characterized zinc porphyrin receptors **202**–**204** (Fig. 51) that associated with amino carboxylates through coordinative, Coulombic and hydrophobic interactions [71]. The porphyrin contained a water molecule coordinated to the zinc and when the anions were added the water was replaced by the coordination of the anion through the nitrogen of the amino group. UV–vis titrations were carried out in $NaHCO_3$–Na_2CO_3 buffered solutions to pH 10.4 for the amino carboxylates while K_2CO_3 was used for butylamine at pH 11.5 (Table 25). The results showed that butylamine, which does not contain a negative charge had a consistently smaller association constant compared with the amino carboxylates. This proved there were stronger Coulombic interactions due to the presence of the carboxylate groups towards the $-[N(CH_3)_3]^+$. Hydrophobic interactions were observed between both the porphyrin ring and the phenyl side chains and the hydrophobic side chains of the anions. Since Phe and Trp contain hydrophobic side chains, in contrast to Gly and Asp, the association constants obtained were larger for these two amino carboxylates. Receptor **204** did not show any chiral recognition.

Inoue also used zinc porphyrins **205**–**210** (Fig. 52) to bind amino acid carboxylates. In this case, the chiral porphyrin contained an achiral rigid *p*-xylene strap bound to the porphyrin by two amide linkages [72]. The unstrapped face contained a N-substitutent (R_2) which blocked any interactions at that face. The resulting enantiomeric zinc porphyrin complexes were separated by chiral HPLC. The somewhat less restricted strapped face lined with electrostatic, hydrogen-bonding and van der Waals interactions allowed for highly enantioselective binding of the carboxylates anions. Single extraction experiments using N-protected amino acids and a racemic mixture of receptor **207** showed the greatest enantioselectivity for the carboxylate anions of 3,5-dinitrobenzyl and acetyl amino acids. This high selectivity was attributed to the hydrogen-bonding interactions between the anion and the receptor's strapped face.

The creation of a new type of anion binding cavity was achieved by Beer. This cavity consisted of a porphyrin with four amido-metallocene appendages. ^{1}H-NMR titrations of receptors **211**–**214** (Fig. 53) in CD_2Cl_2 showed affinity for Cl^-, Br^-, NO_3^- and HSO_4^- while their metal-free analogues did not show any significant chemical shifts [73]. However, the metal-free cobaltocenium analogue did show association to Cl^-, Br^- and NO_3^- in CD_3CN [74]. Therefore, a combination of both electrostatic interactions with the metallocene or metallated porphyrin and the amide hydrogen-bonds contributed to the binding of the anions. The atropisomer receptors **211**–**214** also demonstrated some selectivity. Receptor **212** showed selectivity for NO_3^- over Cl^- and HSO_4^- while the halides were preferred by the other isomers. Electrochemical results obtained from a CH_2Cl_2/MeCN solvent mixture revealed considerable cathodic shifts for the porphyrin oxidation and only slight shifts for the ferrocene couple when anions were added to the system.

3.4. Other metalloreceptors

The synthesis and study of neutral $PtCl_2$ and $PdCl_2$ complexes of 5,5′-bisamido-2,2′-bipyridine as receptors

were carried out by Beer. ^{1}H-NMR titrations were performed in DMSO-d_6 using chloride with receptors **215**–**222** (Fig. 54). The significant downfield shift of the amide N–H proton upon the addition of Cl^- suggested the importance of a NH···Cl hydrogen-bonding interaction in the receptors. Although there were precipitation problems with receptors **216**, **217**, **220** and **221** association constants were obtained for **215**, **218**, **219** and **222**. All the values obtained ranged from 32 to 36 M^{-1} and showed 1:1 stoichiometries. Therefore, the strength of the Cl^- interaction was independent of the nature of the d^8 metal or the alkyl or aryl amide side chains used [75].

Platinum(II) was also used as the central building block to organize four amide hydrogen-bond donors units for anion binding analogous to a calix[4]arene. Loeb explored the use of *n*-butyl-nicotinamide ligands complexed to square planar Pt(II) metal center forming a 2+ cationic species (Fig. 55) [76]. The receptor was synthesized as the PF_6^- salt due to the limited interaction of this anion to the receptor. This was shown in the X-ray structure of **223** · $2CH_2Cl_2$ where there were only electrostatic interactions between the PF_6^- anions and the platinum, the hydrogen-bonding took place between the amide C=O and the methylene hydrogens of the CH_2Cl_2 solvent. This structure also showed that a 2:1 anion:host ratio was possible. The ^{1}H-NMR titrations demonstrated receptor **223** was an effective host for several different oxo-anions. There was an increase in selectivity for the planar bidentate anions such as NO_3^- and OAc^-. This was attributed to the shape specific match between the two *cis*-amido groups and the bidentate anions. More weakly bound ReO_4^-, $CF_3SO_3^-$ and HSO_4^- all showed 1:1 receptor:anion binding ratios.

The selectivity of reversible anion binding was studied by Parker using chiral Eu(III) and Tb(III) receptors **224**–**227** (Fig. 56). This was carried out in aqueous media and characterized by ^{1}H-NMR spectroscopy and the changes in intensity and form of circularly polarized luminescence peaks. The complexes consisted of a heptadentate triamide ligand with up to two bound water molecules. The results showed citrate and malonate had the highest association for the receptors while lactate and hydrogen carbonate caused a displacement of both the water molecules bound to the metal center due to the formation of a chelated ternary complex [77]. Fluoride, acetate and sulfate displaced up to one water molecule while chloride, bromide, iodide and nitrate did not displace any [78]. The presence of these two water molecules quenched the luminescent properties of the Eu(III) and Tb(III) ions.

The incorporation of Lewis acid binding sites plus a secondary binding site allowed increased specificity and affinity of the receptor for the anions. In this case, uranyl groups were incorporated into a salophene ligand containing two amide substituents (Fig. 57). These receptors had association constants for $H_2PO_4^-$ and Cl^- an order of magnitude higher than the amide free receptors in 99%MeCN/DMSO solution (Table 26) [79–81]. Reinhoudt is also the pioneer of chemically modified field effect transistors (CHEMFETs). The neutral anion binding receptors have been incorporated into CHEMFETs. In these systems, the uranyl-salophene bis-amide selectively bound fluoride anions. This interaction was stabilized through interactions with the Lewis acidic uranium center and the hydrogen-bond donating amide groups via N–H···anion [82–84]. The receptors containing urea substituents have also shown selectivity for fluoride in the presence of 150-fold excess of SCN^- [85].

4. Summary and conclusions

The amide functional group is easily accessible synthetically and is often used to link structural components. This allows for a great deal of variety in receptor architecture as seen in this review. The hydrogen-bonding of an –C(O)NH– group to a substrate anion is easily recognized by significant downfield shifts of the NH proton in ^{1}H-NMR spectroscopy experiments. The degree of hydrogen-bonding and NH shift are both solvent and concentration dependent allowing the measurement of association constants. The introduction of an electrostatic component to the receptor–anion interaction can significantly improve binding strengths. The use of complexed metal ions (ferrocene, cobaltocenium, $[Ru(bipy)_3]^{2+}$, Zn(porphyrin) etc.) not only contributes to this electrostatic influence but also provides a reporter group that can signal the anion coordination event by an electrochemical or optical mechanism output that is proportional to the degree of interaction.

The amide functional group should continue to be important in anion receptors because of its ease of synthesis and biological precedence. Future advances should focus on binding in competitive solvents, such as water, as well as the efficiency of the reporter group; in particular sensing by facile methods at low concentrations.

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