ChemComm
FEATURE ARTICLE

Anion selective recognition and optical/electrochemical sensing by novel transition-metal receptor systems

Paul D. Beer

Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford, UK OX1 3QR

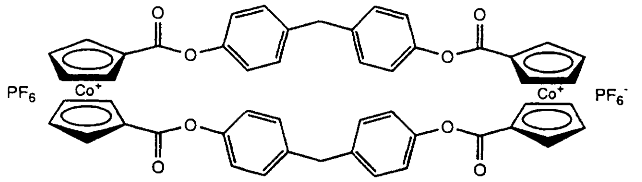
Appropriately designed charged or neutral redox- and/or photo-active transition-metal organometallic and coordination receptor systems can selectively recognise and sense anionic guest species by electrochemical and/or optical methodologies. The topological positioning of the transition-metal Lewis-acid centres and of the ubiquitous hydrogen-bonding functionalities, such as amide (CO–NH) groups, dictates the anion selectivity trend and sensing proficiency the particular receptor displays.

Introduction

The synthesis of positively charged or neutral electron-deficient abiotic receptor molecules designed to non-covalently bind anionic guest species is an area of ever increasing research activity.[1] Anions play numerous fundamental roles in biological and chemical processes,[2] for example, the majority of enzymes bind anions as either substrates or cofactors, and many anions act as nucleophiles, bases, redox agents and phase-transfer catalysts. In addition, the importance of being able to detect and/or extract certain environmental anionic pollutants[3] such as nitrate, phosphate and radioactive pertechnetate,[1] produced in the nuclear fuel cycle,[4] has only recently been recognised. It is surprising, then, that the construction of specific ligands that have the capability of *sensing* anions *via* optical[5] and/or electrochemical[6] methodologies in polar organic and aqueous media has not been fully exploited. For example, Vance and Czarnik[7] have described one of the very few anion fluorescent responsive types, based on acyclic anthracene appended polyammonium receptors. We have initiated a research programme aimed at the design and construction of innovative spectral and electrochemical sensory reagents for anions based on novel transition-metal organometallic and coordination receptor systems. This article reviews our current progress in this exciting multidisciplinary field of anion supramolecular chemistry.

Acyclic and Macrocyclic Cobaltocenium Receptor Systems

In 1989 we reported the synthesis of the first redox-responsive class of anion receptor based on the redox-active, pH independent positively charged cobaltocenium moiety.[8] The ester-linked cobaltocenium macrocyclic receptor **1** complexed and electrochemically detected the bromide guest anion. Unfortunately the general poor solubility of these types of macrocyclic ligands coupled with their arduous syntheses and lability to ester hydrolysis led us to a new synthetic strategy which utilised the ubiquitous amide linkage to construct novel acyclic anion receptors.



1

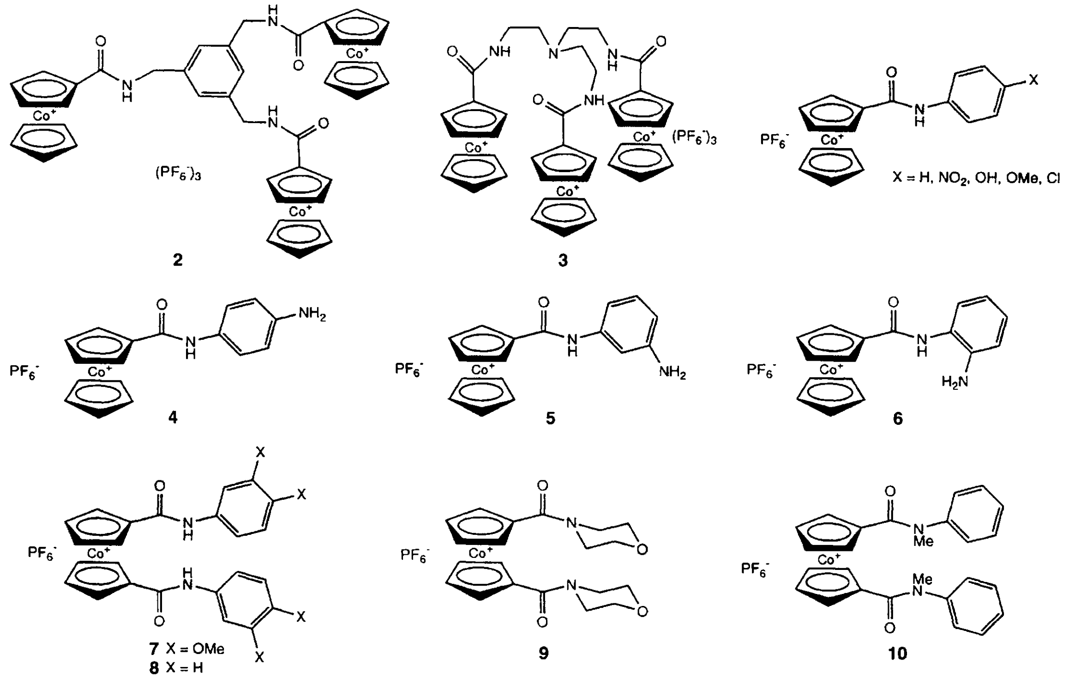


Fig. 1 Acyclic, mono-, bis- and tri-podal amide-linked cobaltocenium receptors

Simple mono- and 1,1′-bis-substituted cobaltocenium acid chloride or activated ester condensation reactions with alkyl and aryl amines produced a variety of new acyclic mono-, bis- and tri-podal amide-linked cobaltocenium receptors in very good yields[9,10] (Fig. 1).

The addition of tetrabutylammonium salts NBu_4X (X = Cl, Br, NO_3, HSO_4, H_2PO_4) to deuteriated acetonitrile or dimethyl sulfoxide ^1H NMR solutions of these receptors resulted in remarkable downfield shifts of the respective receptor's protons. Of particular note were the substantial downfield shifts of the amide protons, $\Delta\delta$ = 1.28 ppm for **2** and 1.52 ppm for **3** on addition of 1 equiv. of chloride. These results suggest a significant $-CO-NH\cdots X^-$ hydrogen-bonding interaction is contributing to the overall anion complexation process. The resulting titration curves suggested 1 : 1 receptor : anion stoichiometry in all cases. Stability constants were calculated from the titration curves and a selection of these are shown in Table 1. revealing Br^- hydrogen bonding to the amide proton and to aryl and It is noteworthy that with monosubstituted aryl cobaltocenium derivatives **4**–**6** the strength of chloride ion

Table 1 Stability constant data for cobaltocenium receptors with various anions

Receptor	Solvent	Anion	$K/dm^3\ mol^{-1}$ [a]
3	$(CD_3)_2SO$	Cl^-	100
3	$(CD_3)_2SO$	$H_2PO_4^-$	1200
4	CD_3CN	Cl^-	24
5	CD_3CN	Cl^-	770
6	CD_3CN	Cl^-	630
7	$(CD_3)_2SO$	Cl^-	30
7	$(CD_3)_2SO$	Br^-	25
8	$(CD_3)_2SO$	Cl^-	35
8	$(CD_3)_2SO$	$H_2PO_4^-$	320

[a] Errors estimated to be ≤10%.

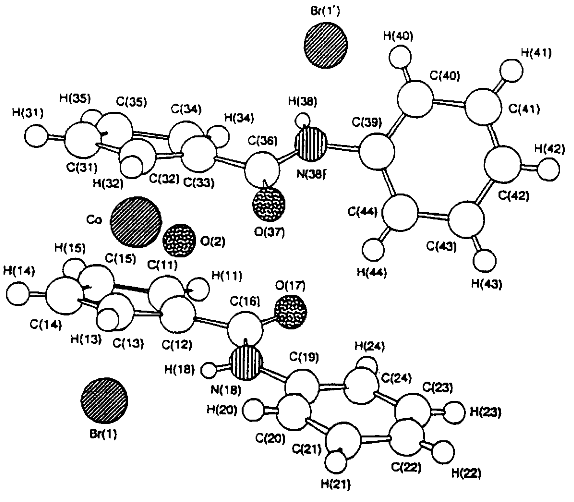


Fig. 2 Structure of the bromide complex of **8**

Table 2 Electrochemical data

Receptor	$E_{\frac{1}{2}}/V$ [a]	Anion	$\Delta E_{\frac{1}{2}}/mV$ [b]
3	-0.75 [c]	Cl^-	30
3	-0.75 [c]	$H_2PO_4^-$	200
4	-1.10	Cl^-	35
5	-1.08	Cl^-	30
6	-1.03	Cl^-	55
7	-0.80	Cl^-	90
7	-0.80	Br^-	40
7	-0.80	$H_2PO_4^-$	240
8	-0.83	Cl^-	85
8	-0.83	$H_2PO_4^-$	240

[a] Obtained in acetonitrile solution containing 0.2 mol dm^{-3} NBu_4BF_4 as supporting electrolyte. Solutions were *ca.* 1 × 10^{-3} mol dm^{-3} in receptor and potentials were obtained with reference to an Ag–Ag^+ electrode. [b] Cathodic shift in reduction potential produced by presence of anions (up to 10 equiv.) added as their tetrabutylammonium salts. [c] Three-electron reduction process as determined by coulometric experiments.

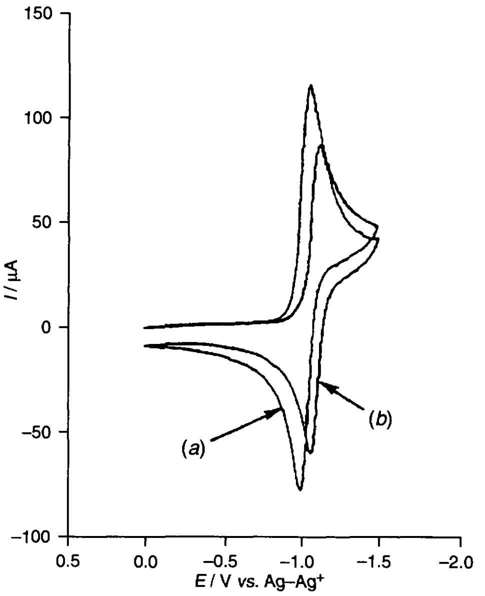


Fig. 3 Cyclic voltammograms in acetonitrile of **6** in the absence (*a*) and presence (*b*) of excess chloride ion

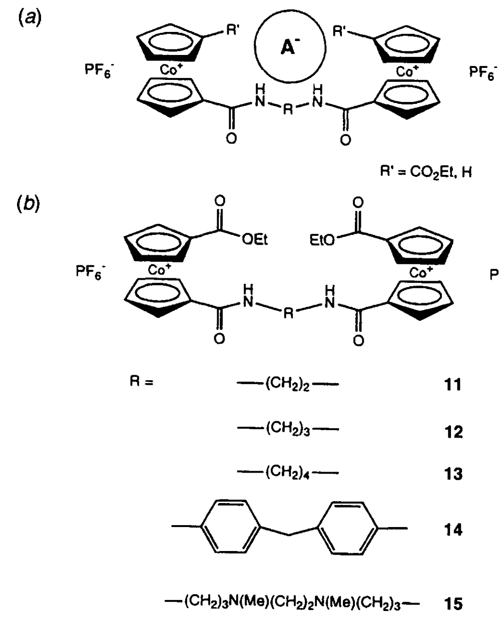


Fig. 4 (*a*) Schematic representation of anion recognition by a ditopic bis(cobaltocenium) receptor; (*b*) examples of ditopic receptors prepared

Table 3 Stability constant data for receptors **11**–**13** and halide anions in CD_3CN

	K/dm^3mol^{-1} [a]		
Receptor	Cl^-	Br^-	I^-
11	2500	330	450
12	1300	270	275
13	280	260	100

[a] Errors estimated to be ≤10%.

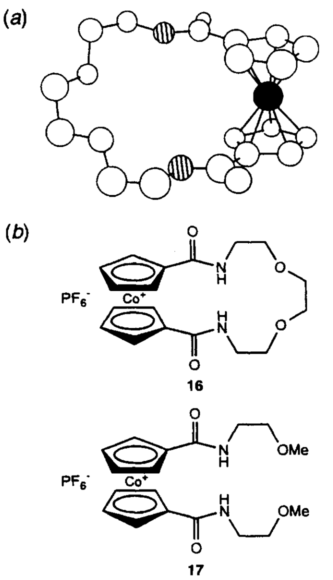


Fig. 5 (*a*) Structure of the macrocyclic amide-linked cobaltocenium receptor **16** and (*b*) acyclic receptor **17**

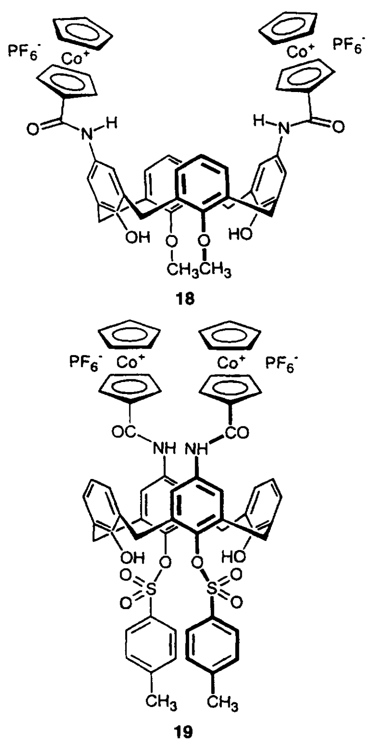


Fig. 6 Bis(cobaltocenium) calix[4]arene receptors **18** and **19**

Table 4 Stability constant data for bis- and tetra-cobaltocenium calix[4]arene receptors in $(CD_3)_2SO$

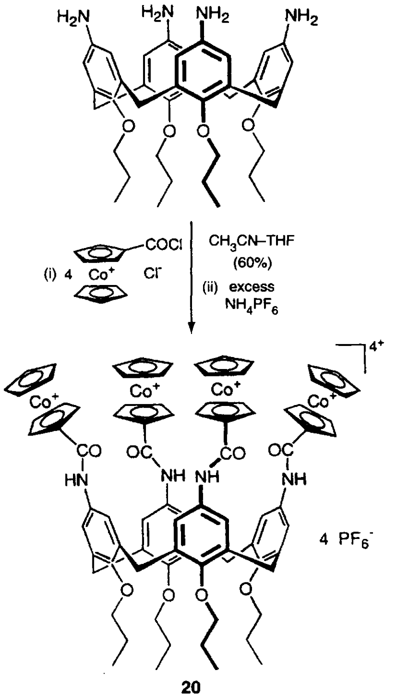
	K/dm^3 mol^{-1} [a]			
Receptor	Cl^-	Br^-	$H_2PO_4^-$	$^-O_2C(CH_2)_4CO_2^-$ [b]
18	5035	1680	2800	11510
19	10	—	3100	—
20	70	—	1200	—

[a] Errors estimated to be ≤10%. [b] Titration performed in $(CD_3)_2CO$.

binding is enhanced when additional favourable amine–halide hydrogen-bonding interactions are sterically accessible as is the case for **5** and **6** but not for **4**.[10] In addition, the 1,1′-bis-substituted aryl cobaltocenium analogues display an order of magnitude selectivity for the dihydrogenphosphate anion over halide anions. The importance of hydrogen bonding in anion recognition by the cobaltocenium class of receptor is further highlighted with receptors **9** and **10** containing the tertiary amide ($CONR_2$) linkage being unable to form solution halide anion complexes, as evidenced from ^1H NMR titration investigations. Hence it is the unique combination of the positively charged cobaltocenium moiety and the appending amide CO–NH unit which can form a favourable hydrogen bond with a coordinated anion guest, which are the essential components for successful anion complexation. This is again highlighted in the single-crystal structure of the bromide complex of **8** (Fig. 2) revealing Br^- hydrogen bonding to the amide proton and to aryl and cyclopentadienyl protons of the cobaltocenium receptor.[10]

Although polyammonium macrocycles have been shown from electrochemical measurements to stabilise hexacyanoferrate(II) and hexacyanocobalte(III) anions,[11] to our knowledge these cobaltocenium ligands represent the first redox-responsive class of anion receptor. Cyclic voltammetry was used to investigate the electrochemical anion recognition properties of these receptors and a selection of results are summarised in Table 2. Significant one-wave cathodic shifts of the cobaltocenium–cobaltocene redox couples of amide (CO–NH) containing receptors are observed with all anionic guest species (Fig. 3). The complexed anion effectively stabilises the positive charge of the cobaltocenium unit causing the redox couple to shift to a more negative potential. Very large cathodic perturbations are observed with the $H_2PO_4^-$ anion guest, an observation which complements the stability constant data (Table 1) in which the highest K values are obtained with this anion. The tertiary amide containing receptors displayed no electrochemical response to the addition of anions ruling out the possibility of the cathodic shift being caused by simple ion-pairing effects.

In an effort to impart selectivity and enhance complex stability for this class of anion receptor we have prepared novel ditopic bis(cobaltocenium) receptor molecules in which two



Scheme 1

positively charged metallocene centres, linked *via* various alkyl, aryl and calix[4]arene spacers, may cooperate in the molecular recognition of mono- or di-anionic guest substrates[12] (Fig. 4). Proton NMR halide anion coordination studies revealed the alkyl-linked derivatives **11**–**13** form 1 : 1 stoichiometric complexes in acetonitrile solution. Stability constant evaluations (Table 3) suggest that as the length of the alkyl chain increased the selectivity preference for chloride and the general stability of the halide complex decreased. This latter observation provides experimental evidence for the existence of an anionic chelate effect. Receptors **14** and **15** containing larger aryl and alkyl amino spacers form complexes of 2 : 1 halide anion : receptor stoichiometry. All the bis(cobaltocenium) systems were found to display electrochemical recognition of varied anion guests with $H_2PO_4^-$ again, as found with the monosubstituted cobaltocenium derivatives, producing the largest magnitude of cathodic shift (ΔE = 250 mV).

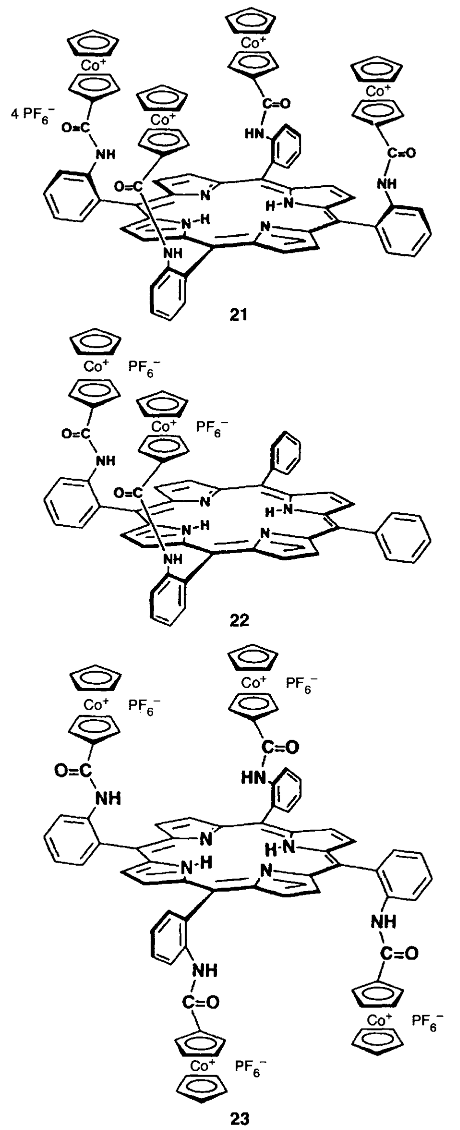


Fig. 7 Cobaltocenium porphyrin receptors **21**–**23**

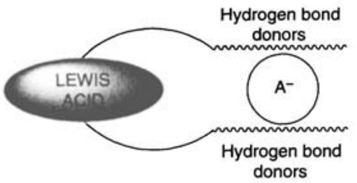


Fig. 8 Depicting the basic requirements for an anion receptor

The macrocyclic amide linked cobaltocenium receptor **16** has recently been prepared and its crystal structure elucidated[13] (Fig. 5). Chloride anion stability constant determinations with **16** and the related acyclic analogue **17** revealed the presence of an 'anion macrocyclic effect'. The stability constant value for the chloride complex of **16** in dimethyl sulfoxide (K = 250 dm^3 mol^{-1}) is at least an order of magnitude greater than the chloride complex of **17** (K = 20 dm^3 mol^{-1}).

Polycobaltocenium Calix[4]arene Receptors

The calixarenes[14] are attractive host molecules on which to construct additional recognition sites for target guests. Although the calix[4]arene host structural framework has been modified at the lower rim for the recognition of metal cations,[15] the design and synthesis of calix[4]arene *anion* receptors is still relatively rare.[16] The bis-cobaltocenium calix[4]arene derivative[12,17] **18** (Fig. 6) was prepared and shown to form extremely stable 1 : 1 anion complexes in polar dimethyl sulfoxide

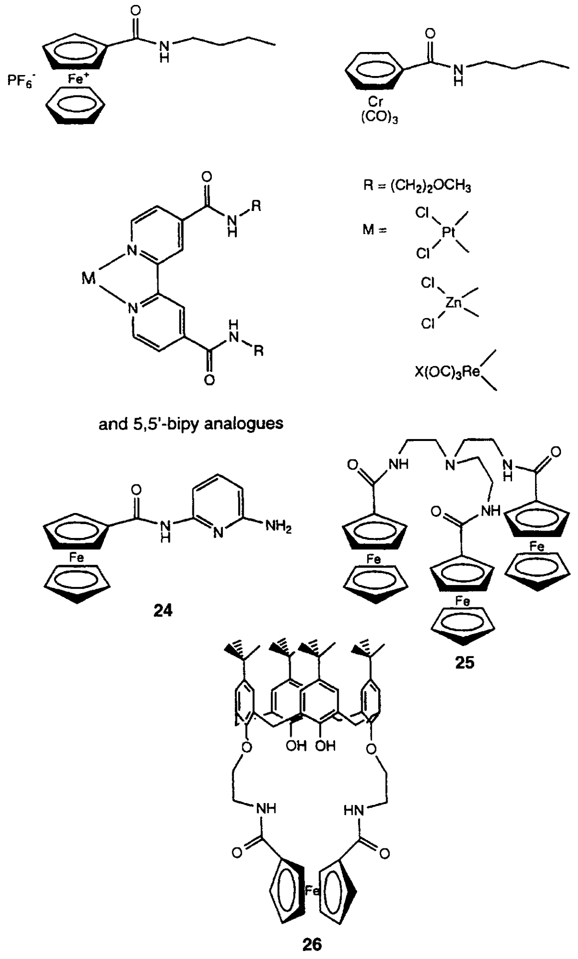


Fig. 9 New classes of charged and neutral anion receptors

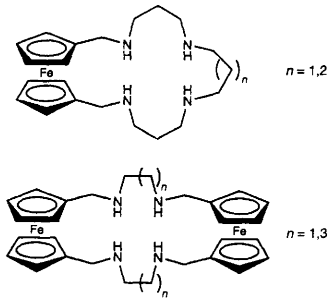


Fig. 10 Polyazaferrocene macrocycles

solutions and with the adipate anion in acetone (Table 4). Interestingly this receptor displays the uncommon anion selectivity preference of chloride over dihydrogen phosphate.[12]

Modifying the substituents on the calix[4]arene lower rim has a dramatic effect on the anion coordination properties of this type of receptor. For example, derivative **19** (Fig. 6) containing tosyl groups *para* to the upper-rim amide substituted cobaltocenium moieties exhibits the $H_2PO_4^- \gg Cl^-$ selectivity trend[18] (Table 4), the reverse of **18**. Presumably the bulky tosyl groups alter the topology of the upper-rim anion recognition site in favour of phosphate complexation.

Recently the novel tetrakis(cobaltocenium) calix[4]arene **20** has been synthesised[19] (Scheme 1). Table 4 shows this receptor exhibits a remarkable selectivity preference for $H_2PO_4^-$ over Cl^-. Electrochemical investigations disclose significant anion-induced cathodic shifts are observed with each calix[4]arene receptor, including **18** sensing adipate.

Halide and Nitrate Selective Cobaltocenium Porphyrin Receptors

A series of new cobaltocenium porphyrin receptors have been prepared and shown to spectrally and electrochemically sense anions[20,21] (Fig. 7). Notable anion selectivity differences are displayed by the various atropisomers which highlights the importance of the relative positions of the cobaltocenium amide moieties in the anion recognition process. For example, the *cis*-α,α,α,α-atropisomer **21** exhibits the selectivity trend $Cl^- > Br^- \gg NO_3^-$ in which all four cobaltocenium moieties cooperatively form a cavity complementary to the spherical halide anion guest.[20] In contrast the α,α,- **22** and α,α,ββ- **23** atropisomers display the rare selectivity sequence $NO_3^- > Br^- > Cl^-$ indicating a complementary trigonal host cavity exists for nitrate.[21]

New Classes of Anion Receptor containing Charged and Neutral Transition-metal Lewis-acidic Recognition Sites

Taking into account the crucial importance of hydrogen bonding to the anion recognition process[22] for cobaltocenium receptors we reasoned that in principle *any* Lewis-acidic centre in close proximity to one or more amide (CO–NH) groups may lead to the successful molecular recognition of an anionic guest species[23,24] (Fig. 8). The anion is complexed *via* the combination of favourable Lewis acid–anion electrostatic and amide (CO–NH)–anion hydrogen-bonding interactions. Substantial evidence in support of this simple concept came from the syntheses of a variety of new classes of anion receptor incorporating positively charged and neutral organometallic and coordination transition-metal Lewis-acidic binding sites in combination with amide groups (Fig. 9). Proton NMR anion titration experiments provided solution evidence of halide, HSO_4^- and $H_2PO_4^-$ anion complexation. With the neutral acyclic **24**, tripodal **25** and calix[4]arene **26** ferrocene receptors significant anion guest induced cathodic perturbations of the respective ferrocenyl oxidation wave were observed.[24] Of interest to the future design of amperometric chemical sensors were the novel results of electrochemical competition experiments, in agreement with stability constant determinations, which demonstrated **24–26** were capable of detecting the $H_2PO_4^-$ anion in the presence of tenfold excess amounts of HSO_4^- and Cl^- ions.[24]

We have recently prepared a series of water-soluble polyaza ferrocene macrocyclic ligands[25] (Fig. 10) which are able to electrochemically recognise phosphate anions (HPO_4^{2-}, ATP) in an aqueous environment at pH values of 6–7.

Fluorescence Emission Spectral and Electrochemical Sensing of Anions by Acyclic, Macrocyclic and Calix[4]arene Ruthenium(II) Bipyridyl Receptor Molecules

We have recently incorporated the Lewis-acidic redox- and photo-active ruthenium(II) bipyridyl moiety, in combination with amide (CO–NH) groups, into acyclic, macrocyclic and lower-rim calix[4]arene structural frameworks to produce a new class of anion receptor with the dual capability of sensing anionic guest species *via* electrochemical and optical methodologies[26,27] (Fig. 11). Single-crystal X-ray structures of **27**·Cl^- (Fig. 12) and **31**·$H_2PO_4^-$ (Fig. 13) display again the importance of hydrogen bonding to the overall anion complexation process. In the former complex (Fig. 12) six hydrogen bonds (two amide and four C–H groups) stabilise the Cl^- anion and three hydrogen bonds (two amide and one calix[4]arene hydroxy) effect $H_2PO_4^-$ complexation with **31** (Fig. 13). Stability constant determinations in dimethyl sulfoxide demonstrated these receptors form strong, and in the case of the macrocyclic **30** and calix[4]arene containing receptor **31**, highly selective complexes with $H_2PO_4^-$ (Table 5). Substantial anion-induced cathodic perturbations of the respective ligand-centred amide substituted bipyridyl reduction redox couple were detected in electrochemical anion recognition experiments (Table 6) with **31**, in agreement with stability-constant values, able to sense $H_2PO_4^-$ in the presence of tenfold excess amounts of HSO_4^- and Cl^-.

Fluorescence emission spectroscopic measurements were also undertaken to probe anion binding.[27,28] All receptors

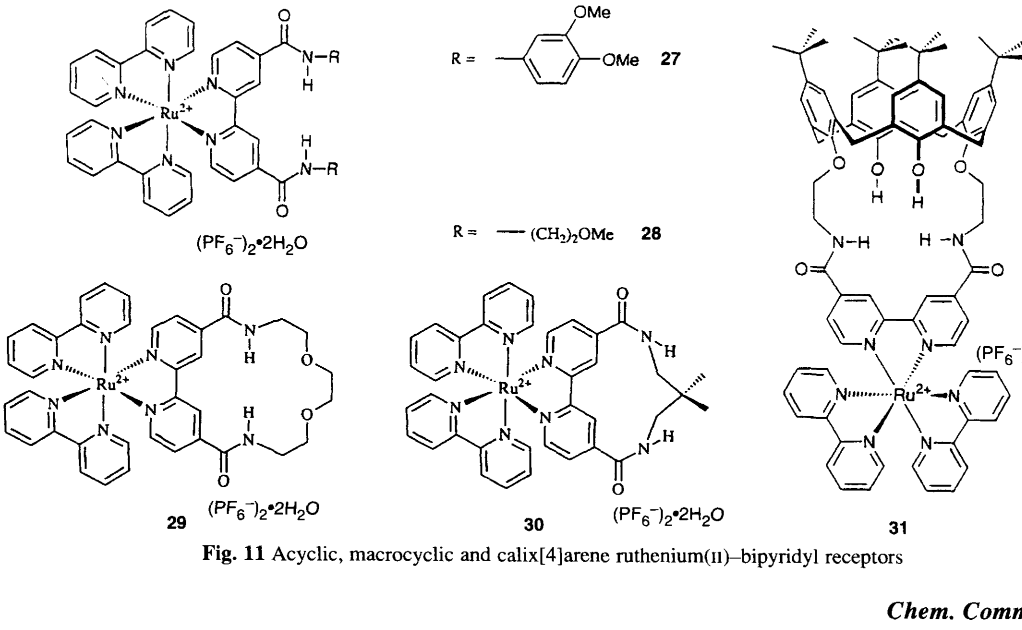


Fig. 11 Acyclic, macrocyclic and calix[4]arene ruthenium(II)–bipyridyl receptors

exhibited significant blue shifts in the respective MLCT λ_{max} emission band on addition of Cl^- and $H_2PO_4^-$, not observed with $[Ru(bpy)_3]^{2+}$, with **31** displaying the largest perturbation of 16 nm (Fig. 14). These shifts were accompanied by large increases in emission intensity (higher quantum yields) (Fig. 14) which may be a consequence of the bound anion rigidifying the receptor, inhibiting vibrational and rotational relaxation modes of non-radiative decay.

Upper-rim substituted calix[4]arenes functionalised with two and four ruthenium(II) bipyridyl amide groups have also been very recently prepared by our group[26,29] (Fig. 15) and shown to selectively sense *via* fluorescence emission and electrochemical investigations the $H_2PO_4^-$ anion.

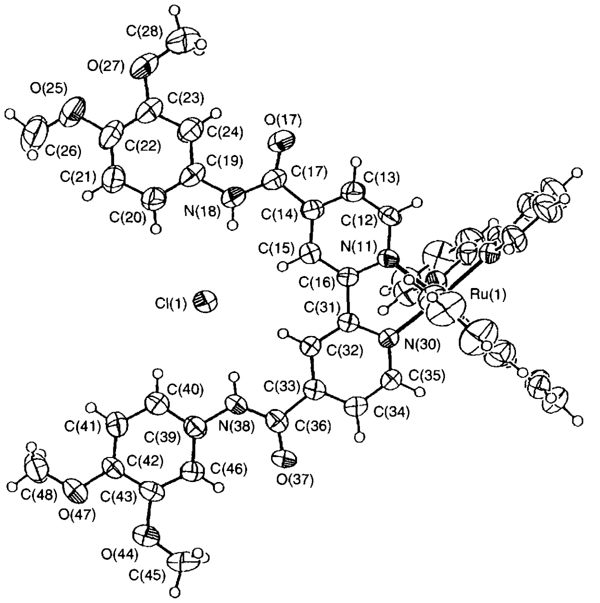


Fig. 12 Structural view of the chloride complex of **27**, with thermal ellipsoids at 50% probability

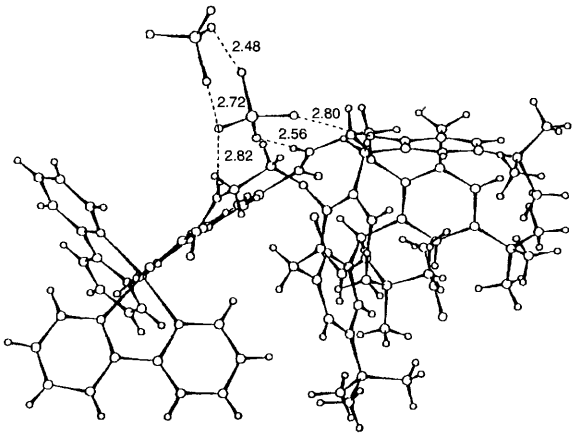


Fig. 13 Structure of the dihydrogen phosphate complex of **31**; in the solid state the anion hydrogen bonds to another anion molecule

Table 5 Stability constant data for acyclic, macrocyclic and calix[4]arene ruthenium(II) bipyridyl receptors in $(CD_3)_2SO$

	$K/dm^3\ mol^{-1}$ [a]	
Receptor	Cl^-	$H_2PO_4^-$
27	500	8000
28	480	7700
29	90	5600
30	420	8000
31	1600	28000

[a] Errors estimated to be ≤5%.

Remarkable Chloride Selective Macrocyclic Ruthenium(II)– Bipyridyl–Metallocene Receptors

The majority of the various anion receptors already discussed in this article exhibit pronounced selectivity for the dihydrogen phosphate anion in preference to halide anions. Indeed it is

Table 6 Cathodic perturbations of the first ligand-centred amide-substituted bipyridyl reduction couple observed on addition of various anions[a]

Receptor	$\Delta E(H_2PO_4^-)$ /mV	$\Delta E(HSO_4^-)$ /mV	$\Delta E(Cl^-)$ /mV	$\Delta E(Br^-)$ /mV
27	[b]	[b]	40	30
29	175	—	70	10
30	150	20	65	—
31	175	15	70	60

[a] Obtained in acetonitrile solution containing 0.1 mol dm^{-3} NBu_4PF_6 as supporting electrolyte. Cathodic shifts of reduction potential produced by presence of anions (up to 10 equiv.) added as their tetrabutylammonium salts. [b] Precipitation of complex prevented a ΔE value from being determined.

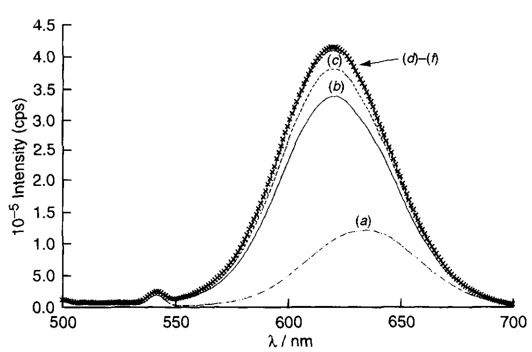


Fig. 14 The effect of addition of stoichiometric amounts of $H_2PO_4^-$ on the fluorescence emission spectrum of **31** in dimethyl sulfoxide; 0 (*a*), 3 (*b*), 6 (*c*), 9 (*d*), 12 (*e*) or 15 equiv. (*f*) of $H_2PO_4^-$

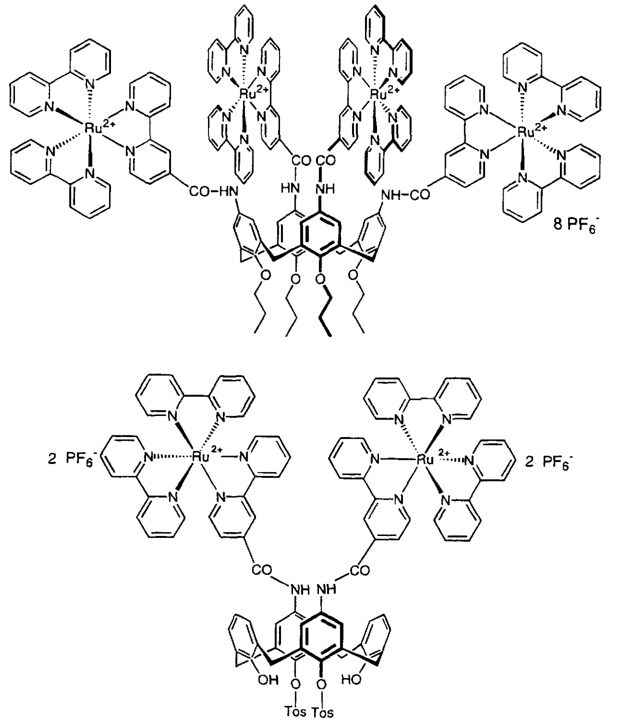
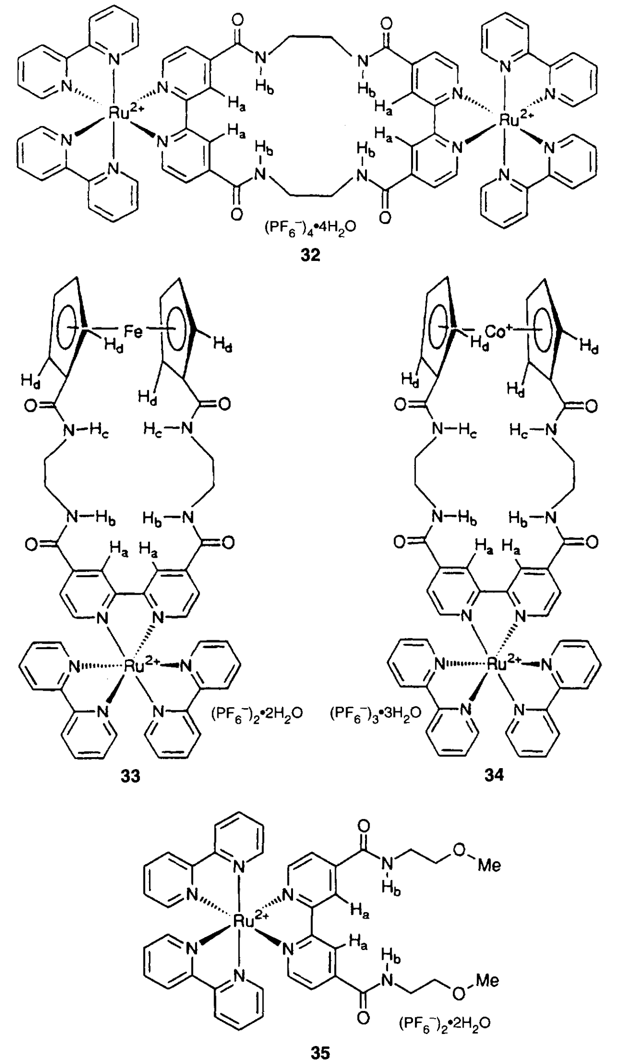


Fig. 15 Upper-rim bis- and tetra-ruthenium(II) bipyridyl calix[4]arenes

noteworthy that this selectivity trend is also displayed by uranyl amide based receptors.[30] The chloride anion is crucial for a large number of biological processes.[31] For example, the relatively common hereditary disease cystic fibrosis is known to result from a genetically caused misregulation of chloride anion channels.[32] Thus there is a real need for selective detection as established methods for chloride determination based on titrimetric analysis lack selectivity and are not suitable for biological applications.[33]



32 **33** **34** **35**

Fig. 16 Macrocyclic bis[ruthenium(II)–bipyridyl] **32** and ruthenium(II)–bipyridyl–metallocene receptors **33** and **34**

Table 7 Stability constant data for receptors **32–35** and chloride anion in $(CD_3)_2SO$

Receptor	Proton of receptor monitored[b]	$K/dm^3\ mol^{-1}$ [a]
32	H_a	4.05×10^4
	H_b	3.95×10^4
33	H_a	9.00×10^3
	H_b	9.95×10^3
	H_c	1.00×10^4
	H_d	9.88×10^3
34	H_a	1.86×10^4
	H_d	1.23×10^4
35	H_a	2.07×10^2
	H_b	1.52×10^2
35 + $H_2PO_4^-$	H_a	1.57×10^3
	H_b	1.57×10^3

[a] Errors estimated to be ≤10%. [b] EQNMR analysis of titration curve of particular receptor proton.

We have prepared the novel macrocyclic bis[ruthenium(II) bipyridyl] and ruthenium(II)–bipyridyl–metallocene receptors **32–34** (Fig. 16) and ^1H NMR titration studies suggested each receptor formed an extremely stable 1 : 1 stoichiometric complex with chloride in $(CD_3)_2SO$ solutions.[34] In fact the magnitudes of the stability constants (Table 7) are amongst the largest known for any anion–abiotic amide receptor complex and are *ca.* two orders of magnitude greater than the stability constant obtained for the acyclic receptor **35** (Table 7). Analogous ^1H and ^{31}P NMR titration experiments with $H_2PO_4^-$ gave *no* evidence of binding this anion by these macrocyclic receptors in $(CD_3)_2SO$ solution. This contrasts with acyclic receptor **35** which forms a stronger complex with $H_2PO_4^-$ than Cl^- (Table 7). This remarkable Cl^- over $H_2PO_4^-$ selectivity preference exhibited by the macrocyclic systems may be attributed to their inherently rigid structures. Molecular modelling calculations (MM2) and C.P.K. models suggest the minimised structure of **32** has all the amide and 3,3′-bipyridyl protons lying in a coplanar arrangement which creates a host cavity of similar dimensions to the chloride anion (r = 1.81 Å) capable of forming eight hydrogen bonds with this spherical anionic guest species. The larger size and tetrahedral shape of $H_2PO_4^-$ is non-complementary to the macrocyclic receptor's host cavity and consequently complex formation with this anion is not favoured.

Fluorescence emission spectroscopic measurements corroborated the NMR findings. Although excess amounts of $H_2PO_4^-$ had no effects on the emission spectra of the macrocyclic receptors the addition of chloride produced substantial blue shifts ($\Delta\lambda_{max}$ = 6 nm) with significant intensity increases (Fig. 17) demonstrating **32–34** are first-generation prototype chloride selective sensory reagents.

Conclusions

We have seen in this article a variety of transition-metal organometallic and coordination receptor systems which are capable of recognising and sensing anionic guest species both by electrochemical and spectroscopic means. The respective topological positioning of redox-/photo-active transition-metal Lewis-acidic centres and hydrogen-bonding functionalities such as amide (CO–NH) groups in particular, dictates not only the receptor–anion complex thermodynamic stability and sensing proficiency, but also crucially the distinct anion

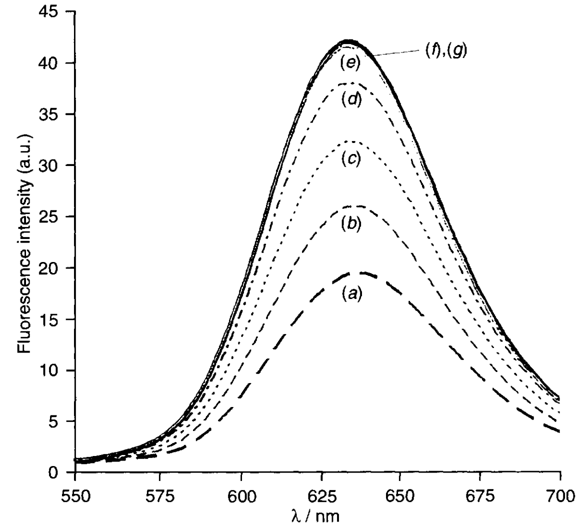


Fig. 17 Fluorescence emission spectra of **34** in acetonitrile with addition of chloride; 0 (*a*), 0.2 (*b*), 0.4 (*c*), 0.6 (*d*), 0.8 (*e*), 1.0 (*f*) and 1.2 equiv. (*g*) of Cl^-

selectivity trend the receptor displays. For example, this is highlighted by receptors **19**, **23** and **32** exhibiting respective selectivities towards $H_2PO_4^-$, NO_3^- and Cl^-. Having established the basic requisite types of building blocks needed for the potential sensing of anions it remains the imagination of the coordination chemist to further design and synthesise more specific and complementary shaped receptors for target anionic substrates of particular environmental and medical concern. The fabrication of these types of systems into membranes, electronically conducting polymeric supports and optical fibres will no doubt produce novel prototype molecular sensory devices of the future.

Acknowledgements

I thank my postgraduate and postdoctoral coworkers for their undaunting motivation and determination to succeed in this multidisciplinary research field; their names appear in the references. Special thanks go to Dr Michael G. B. Drew for his many structure determinations and molecular modelling expertise. I gratefully acknowledge the financial support of EPSRC, The Royal Society, Kodak Limited, MediSense and Serpentix.

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

References

1 F. P. Schmidtchen, *Nachr. Chem. Tech. Lab.*, 1988, **36**, 8; H. E. Katz, in *Inclusion Compounds*, ed. J. L. Atwood, J. E. D. Davies, and D. D. MacNicol, Oxford University Press, New York, 1991, vol. 4, p. 391; B. Dietrich, *Pure Appl. Chem.*, 1993, **65**, 1457; M. F. Hawthorne, X. Yang and C. Knubler, *Angew. Chem., Int. Ed Engl.*, 1991, **30**, 1507; J. L. Sessler and A. K. Burrell, *Top. Curr. Chem.*, 1992, **161**, 177; D. N. Reinhoudt, D. M. Rudkevich, W. R. P. V. Stauthamer, W. Verboom, J. F. J. Engersen and S. J. Harkenna, *J. Am. Chem. Soc.*, 1994, **116**, 4341; K. T. Holman, M. M. Halihan, J. W. Steed, S. S. Jurisson and J. L. Atwood, *J. Am. Chem. Soc.*, 1995, **117**, 7848; W. Xu, J. J. Vittal and R. J. Puddephatt, *J. Am. Chem. Soc.*, 1995, **117**, 8362.

2 J. J. R. Frausto da Silva and R. J. P. Williams, *Struct. Bonding (Berlin)*, 1976, **29**, 67.

3 C. F. Mason, *Biology of Freshwater Pollution*, 2nd edn, Longman, Harlow, 1991.

4 E. Holm, *Radiochim. Acta*, 1993, **63**, 57.

5 A. W. Czarnick, *Acc. Chem. Res.*, 1994, **27**, 302.

6 P. D. Beer, *Adv. Mater.*, 1994, **6**, 607.

7 D. H. Vance and A. W. Czarnik, *J. Am. Chem. Soc.*, 1994, **116**, 9397.

8 P. D. Beer and A. D. Keefe, *J. Organomet. Chem.*, 1989, **375**, C40.

9 P. D. Beer, D. Hesek, J. Hodacova and S. E. Stokes, *J. Chem. Soc., Chem. Commun.*, 1992, 270; P. D. Beer, C. Hazlewood, D. Hesek, J. Hodacova and S. E. Stokes, *J. Chem. Soc., Dalton Trans.*, 1993, 1327.

10 P. D. Beer, M. G. B. Drew, A. R. Graydon, D. K. Smith and S. E. Stokes, *J. Chem. Soc., Dalton Trans.*, 1995, 403.

11 F. Peter, M. Gross, M. W. Hosseini, J.-M. Lehn and R. B. Sessions, *J. Chem. Soc., Chem. Commun.*, 1981, 1067; A. Bencini, A. Bianchi, E. Garcia-Espana, M. Guisti, S. Mangani, M. Micheloni, P. Orioli and P. Paoletti, *Inorg. Chem.*, 1987, **26**, 3902.

12 P. D. Beer, D. Hesek, J. E. Kingston, D. K. Smith, S. E. Stokes and M. G. B. Drew, *Organometallics*, 1995, 3288.

13 P. D. Beer, M. G. B. Drew and S. E. Stokes, *J. Chem. Soc., Dalton Trans.*, 1995, 3447.

14 C. D. Gutsche, *Calixarenes*, ed. J. F. Stoddart. Monographs in Supramolecular Chemistry, The Royal Society of Chemistry, Cambridge and London, 1989, vol. 1.

15 R. Ungaro and A. Pochini, *Calixarenes, a Versatile Class of Macrocyclic Compounds*, ed. J. Vicens and V. Böhmer. Kluwer, Dordrecht, 1990, p. 133; F. Arnaud-Neu, G. Barrett, S. J. Hams, M. Owens, M. A. McKervey, M. J. Schwing-Weill and P. Schwinte, *Inorg. Chem.*, 1993, **32**, 2644 and references therein.

16 Y. Morzheim, D. M. Rudkevich, W. Verboom and D. N. Reinhoudt, *J. Org. Chem.*, 1993, **58**, 7602; D. M. Rudkevich, W. Verboom and D. N. Reinhoudt, *J. Org. Chem.*, 1994, **59**, 3683; J. W. Steed, R. K. Junega and J. L. Atwood, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 2456.

17 P. D. Beer, M. G. B. Drew, C. Hazlewood, D. Hesek, J. Hodacova and S. E. Stokes, *J. Chem. Soc., Chem. Commun.*, 1993, 229.

18 P. D. Beer and D. Hesek, unpublished work.

19 P. D. Beer, D. Hesek and R. J. Mortimer, unpublished work.

20 P. D. Beer, M. G. B. Drew, D. Hesek and R. Jagessar, *J. Chem. Soc., Chem. Commun.*, 1995, 1187.

21 P. D. Beer, D. Hesek and R. Jagessar, unpublished work.

22 For examples of organic based ligands that complex anions exclusively through hydrogen bonding, see R. A. Pascal, J. Spergal and D. van Engen, *Tetrahedron Lett.*, 1986, **27**, 4099; S. Voliyavaeettil, J. F. J. Engersen, W. Verboom and D. N. Reinhoudt, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 900; C. Raposo, M. Crego, M. L. Mussons, M. C. Caballero and J. R. Morán, *J. Am. Chem. Soc.*, 1993, **155**, 369; S. Nishizawa, P. Bühlmann, M. Iwao and Y. Umbezawa, *Tetrahedron Lett.*, 1995, **36**, 6483.

23 P. D. Beer, C. A. P. Dickson, N. C. Fletcher, A. J. Goulden, A. Grieve, J. Hodacova and T. Wear, *J. Chem. Soc., Chem. Commun.*, 1993, 828.

24 P. D. Beer, Z. Chen, A. J. Goulden, A. R. Graydon, S. E. Stokes and T. Wear, *J. Chem. Soc., Chem. Commun.*, 1993, 1834.

25 P. D. Beer, Z. Chen, M. G. B. Drew, J. Kingston, M. I. Ogden and P. Spencer, *J. Chem. Soc., Chem. Commun.*, 1993, 1045; P. D. Beer, Z. Chen, M. G. B. Drew, A. O. M. Johnson, D. K. Smith and P. Spencer, *Inorg. Chim. Acta*, 1996, in the press.

26 P. D. Beer, Z. Chen, A. J. Goulden, A. Grieve, D. Hesek, F. Szemes and T. Wear. *J. Chem. Soc., Chem. Commun.*, 1994, 1269.

27 F. Szemes, D. Hesek, Z. Chen, S. W. Dent, M. G. B. Drew, A. J. Goulden, A. R. Graydon, A. Grieve, R. J. Mortimer, T. Wear, J. S. Weightman and P. D. Beer, *J. Am. Chem. Soc.*, submitted.

28 P. D. Beer, R. J. Mortimer, N. R. Stradiotto, F. Szemes and J. S. Weightman, *Anal. Commun.*, 1995, **32**, 419.

29 P. D. Beer, D. Hesek and R. J. Mortimer, unpublished work.

30 D. M. Rudkevich, W. P. R. V. Stauthamer, Z. Brzoka, M. J. Palys, W. Verboom, J. F. J. Engbersen, G. J. van Hummel, S. M. Franken, S. Harkenna and D. N. Reinhoudt, *J. Am. Chem. Soc.*, 1994, **116**, 4341.

31 K. L. Kirk, *Biochemistry of the Elemental Halides*, Plenum, New York, 1991.

32 W. Kaim and B. Schwederski, *Bioinorganic Chemistry: Inorganic Elements in the Chemistry of Life*, Wiley, New York, 1991, p. 283.

33 *Official and Standardized Methods of Analysis*, ed. C. A. Watson. The Royal Society of Chemistry, Cambridge, 3rd edn., 1994.

34 P. D. Beer and F. Szemes, *J. Chem. Soc., Chem. Commun.*, 1995, 2245.

Received, 27th October 1995; 5/07102J