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Review

Metal-assembled anion receptors

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Contents

Abstract

This review describes the self-assembly of anion receptors from organic ligands and transition metal ions. These metal-assembled anion receptors can be synthesised from a number of different species; bidentate ligands with metals that prefer octahedral coordination geometries and monodentate ligands with metals that prefer square planar geometries are common. Anion binding transition metal helicates and systems where the coordination of metal ions results in the formation of an anion receptor by conformational locking are also reported. The effect of anion binding on the different properties of these complexes is discussed.

Keywords: Anion receptors; Octahedral metal; Ligands

1. Introduction

Over the past decade a vast number of different synthetic systems which are capable as acting as receptors to a range of different anions have been reported. These anion receptors vary considerably and can be organometallic, organic-metallocene, porphyrin or just solely organic frameworks. However, the use of transition metal ions to assemble anion receptors has received much less attention. This assembly of receptors is attractive because as long as suitable ligands are available, or capable of construction, self-assembly/coordination about a metal centre will result in the formation of a cavity capable of anion binding. Thus, the often simple act of coordination can result in the formation of highly organised and complex systems.

Although there are a number of different examples of metal-assembled anion receptors there are two main classes which have attracted the majority of attention. Firstly the formation of a C_3 or quasi-C_3 symmetric anion binding cavity, produced

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by coordination of an octahedral metal by bidentate ligands substituted with units capable of acting as hydrogen bond donors (commonly bipyridine or analogous ligands substituted with either protonated amines or amides). These cavities have been shown to bind a large range of different anions and can discriminate between ions on the basis of size, shape and charge.

The second type of metal-assembled anion receptors is based on complexes formed between mono-dentate ligands bearing attached anion-binding functionalities and a metal ion with a preference for square planar coordination geometry. As, generally, the ligand is derived from a 3-substituted pyridine, four distinct conformations of the receptor can be formed: firstly the cone where all four substituents point in the same direction, the partial cone where three of the substituents point in one direction and the fourth in another and the 1,2- and 1,3-alternate where *cis* or *trans* pairs of substituents are orientated in the same direction on each side of the metal square plane. Studies show that the actual conformations formed both in solution and the solid state are dependent upon what type of anion is bound. It is this last area, namely the ability of the anion to non-innocently interact with the host, which is increasingly attracting more attention, with examples of anions controlling both the isomers present within the host complex and the ligand recognition properties reported.

Examples reported in 2001 by Beer and Gale beautifully demonstrate that self-assembly of suitably substituted ligands with either Ru(II) or Pt(II) metal ions results in the formation of complexes that are excellent anion receptors. Thus, reaction of 2,2′-bipyridine ligand with amide substituents in the 5,5′-positions with $RuCl_3$ gives, after purification, ruthenium(II) tris(5,5′-diamide-2,2′-bipyridine) (**1**) [1]. The ligand coordinates the metal ion resulting in a distorted octahedral geometry, producing a C_3-symmetric cavity at each end of the molecule, which contain three amide functional groups each capable of forming hydrogen bonds to anions (Fig. 1). The selectivity of these assembled receptors to anions is dependant on both the solvent medium and the substituents present on the amide groups. Thus, the nitrate versus chloride selectivity can be modulated by changing the ratio of the CH_2Cl_2:MeOH solvent mixture or changing the lipophilicity of the amide substituents. Creating a similar type of receptor but with only one receptor cavity at one end of the complex is non-trivial, as reaction of "Ru(II)" with a mono-substituted ligand (e.g. 5-amide-2,2′-bipyridine) will result in both *mer*- and *fac*-isomers. The formation of the *mer*-isomer is favoured on both statistical and steric grounds and does not possess the required C_3-symmetric "amide cavity". This problem can be resolved by using a tripodal ligand system **2** which sufficiently reorganises the ligand such that only the *fac*-isomer is formed [2]. The tripodal organising group can be easily removed and subsequent reaction gives a *fac*-ruthenium(II) (5-amide-2,2′-bipyridine) complex (Fig. 2), which due to it's similarly to the ruthenium complex **1** should act as an efficient receptor to anions, although as yet no anion binding properties are reported.

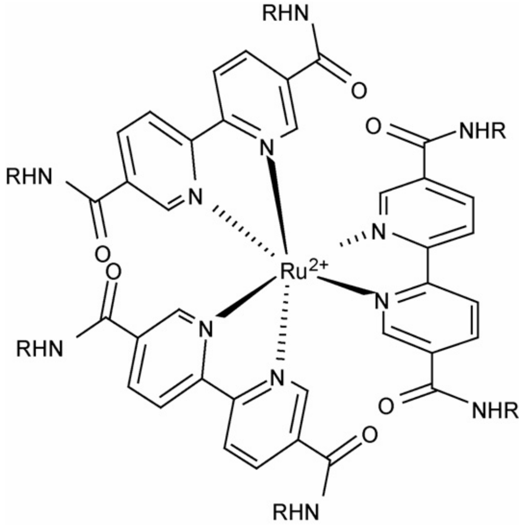


Fig. 1. $[Ru(\mathbf{1})_3]^{2+}$ anion receptor.

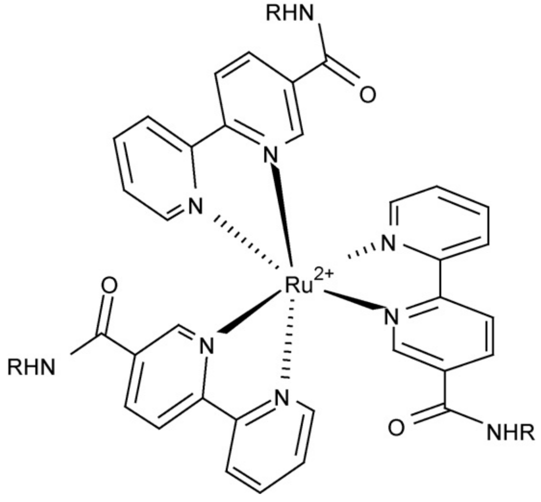
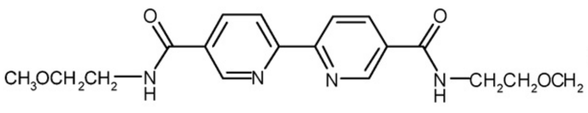


Fig. 2. The potential anion receptor *fac*-$[Ru(\mathbf{2})_3]^{2+}$.



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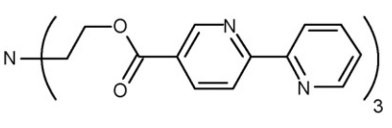

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In the example reported by Gale the anion receptor is formed by reaction of nicotinamide with $PtCl_2(NCEt)_2$ resulting in the formation of a square planar $[PtL_4]^{2+}$ complex **3** [3]. In the solid state the structure adopts a 1,2-alternate conformation with *cis* pairs of amide substituents pointing above and below the plane of the platinum metal ion (Fig. 3). Association constants show

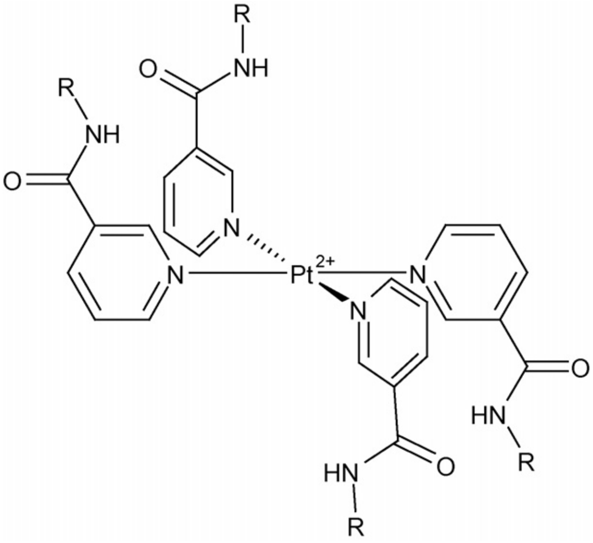


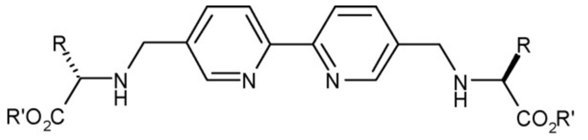
Fig. 3. $[PtL_4]^{2+}$ complex showing a 1,2-alternate conformation.

that this self-assembled receptor is an effective host for a variety of anions, with the tetrahedral or pseudo tetrahedral anions bound in a 1:1 receptor:anion ratio, where as planar bidentate anions are bound in a 1:2 receptor:anion ratio highlighting how the shape of a receptor can influence its ability to bind ions. Interestingly the binding of acetate ions to this complex in a mixture of CD_3CN and DMSO (1:9) displays a positive allosteric effect where K_2 is more than twice that of K_1. Presumably in solution the complex can adopt a variety of different conformations rather than just the 1,2-alternate observed in the solid state. However, upon binding of the first acetate ion the remaining unbound amides will adopt the 1,2-alternate conformation creating a binding unit which is an ideal match for acetate ions.

2. Anion receptors from octahedral metals

2.1. 5,5′-Disubstituted-2,2-bipyridine-based systems

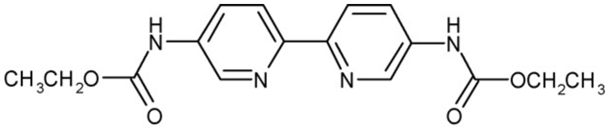
There are a number of examples of other anion receptors formed by reaction of suitably functionalised bidentate ligands with metal ions that adopt octahedral coordination geometry. The formation of tris-coordinated mononuclear complexes results in the self-assembly of an anion-binding pocket. For example, the L-valine or L-alanine 5,5′-disubstituted-2,2-bipyridine ligands **4a** and **4b** reacts with Fe(II), Co(II) and Co(III) in dilute HCl forming the Δ-M(L)$_3$ complex diastereospecifically [4]. The formation of such a complex results in the self-assembly of an anion binding cavity as each substituent is present in a C_3-symmetric arrangement at both ends of the molecule. The X-ray crystal structure of the iron(II) complex of **4a** reveals that the amine groups are protonated and form hydrogen bonds to chloride ions bound within each cavity. No anion binding was detected in water for both the iron(II) and cobalt complexes of **4a** but constants of 60 and 24 M^{-1} are observed in methanol for the binding of chloride ions to the iron(II) and cobalt(II) complexes, respectively. In both cases the complexes form diastereoselectively, regardless of whether chloride ions are present, as long as the amines are protonated. ^1H NMR and CD studies show that at high pH this selectivity is not observed with d.e.'s of 33 and 64% for Fe^{2+} and Co^{2+}, respectively. Complexes of the alanine-substituted ligands $[Fe(\mathbf{4b})]^{2+}$ and $[Co(\mathbf{4b})]^{2+}$ showed that even at low pH, and hence where the amide substituents are protonated, a mixture of diastereomers is formed. This decrease in selectivity is presumably as a consequence of the less sterically demanding methyl substituents [5].



4a R = $CH(CH_3)_2$, R' = H
4b R = CH_3, R' = H
5 R = $CH(CH_3)_2$, R' = CH_3

This ability to form complexes diastereoselectively when protonated and bind chloride anions has some interesting consequences when studying ligand recognition properties. Thus, reaction of Co^{2+} with the amide substituted ligand **5** and 2,2′-bipridine (in the ratio 2:3:3) results in the formation of eight different species; both Λ and Δ–diastereomers of the homoleptic species $[Co(\mathbf{5})_3]^{2+}$ and $[Co(bipy)_3]^{2+}$ as well as both diastereomers of the heteroleptic species $[Co(\mathbf{5})_2(bipy)]^{2+}$ and $[Co(\mathbf{5})(bipy)_2]^{2+}$. Protonation of the amide substituents results in a decrease in the dynamic combinatorial library as this leads to the formation of only the Δ isomer in any of the ligand **5**-containing complexes ($[Co(\mathbf{5}H_2)_3]^{8+}$, $[Co(\mathbf{5}H_2)_2(bipy)]^{6+}$ and $[Co(\mathbf{5}H_2)(bipy)_2]^{4+}$). Addition of chloride ions to these protonated complexes sees a further decrease in the number of species resulting in sole formation of the homoleptic species $[Cl_2{\subset}\Delta{-}Co(\mathbf{5}H_2)_3]^{6+}$ and Λ and Δ– $[Co(bipy)_3]^{2+}$. Thus, reaction of the neutral ligands with Co^{2+} results in the formation of eight different species but upon addition of HCl results in only three species [6].

Janiak and co-workers have shown that 2,2′-bipyridine ligands containing carbamate substituents have also been shown to bind anions. Reaction of Fe^{2+} with the suitably substituted ligand **6** forms the complex $[Fe(\mathbf{6})_3]^{2+}$ which contains a C_3-symmetric cavity at each end of the molecule, which contains three carbamate functional groups each capable of forming hydrogen bonds to larger anions. Single crystal X-ray studies of the sulfate, nitrate and perchlorate derivatives show that the N–H functionality of the carbamate substituent is involved in binding anions. In the case of the sulfate complex this anion is encapsulated within only one of the cavities through three H bonds between its oxygen atoms and the three N–H groups contained within the cavity. In contrast in the presence of perchlorate the cationic host encapsulated two perchlorates, one in each cavity, although only one H-bond between the carbamate and the oxygen atom of the perchlorate is observed. In the case of the nitrate derivative again both cavities encapsulate anions and only one H-bond between the carbamate and the oxygen atom of the anion is observed. Detailed examination of the solid state structure indicates that the sulfate is bound more strongly that the other two anions as not only are three N–H anion interactions observed, compared with only one for both nitrate and perchlorate, but the sulfate has shorter N–H···O bond distances and is sited deeper within the receptor cleft [7].



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2.2. Pyrazole-based systems

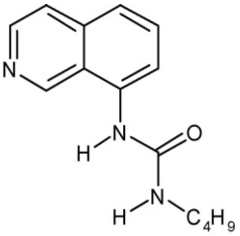
An unprecedented formation of a C_3-symmetric anion receptor cavity from a monodentate ligand has been reported. Reaction of 3,5-dimethylpyrazole and [Re(OTf)(CO)$_5$] gives *fac*-[Re(CO)$_3$(Me$_2$pz)]$^+$ (Me$_2$pz = 3,5-dimethylpyrazole) which has three pyrazole ligands capable of hydrogen bonding to anions in a *facial* arrangement around the rhenium metal centre. ^{1}H NMR titration studies show that chloride ions bind the complex in a 1:1 ratio (6385 and 4692 M^{-1} in MeCN for the Me$_2$pz and 3(5)-*tert*-butylpyrazole complexes, respectively) [8].

3. Anion receptors from square planar metal ions

3.1. 3-Substituted pyridine-based systems

Loeb and Gale have shown that reaction of a urea substituted isoquinoline ligand **7** with Pt^{2+} results in the formation of an anion receptor. The resulting complex [Pt(**7**)$_4$]$^{2+}$ contains a square planar platinum centre coordinated by four isoquinoline ligands. Single crystal diffraction studies of the chloride adduct show that the receptor adopts a 1,2-alternate conformation in which two pairs of adjacent urea groups form hydrogen bonds to separate chloride anions resulting in a 1:2 receptor:anion ratio. Each chloride anion forms close interactions with four N–H donors, two from each urea functionality. This is supplemented by a C–H···Cl$^-$ hydrogen bond between the ligand framework and the anion. Interestingly in the presence of sulfate a 1:1 receptor:anion ratio results. In the solid state the complex adopts a cone conformation with all four ligands orientated in the same direction with all four urea functional groups forming NH···O interactions with three of the sulfate oxygen atoms.

These anion dependant binding modes have a dramatic effect on the stability constants between the complex [Pt(**7**)$_4$]$^{2+}$ and various anions. Thus, with the halides, which bind in a 1:2 receptor:anion ratio formed by either a 1,2- or 1,3-alternate arrangement, constants of 11693, 1364 and 1431 M^{-1} are observed for Cl$^-$, Br$^-$ and I$^-$, respectively, in DMSO solution. However, for H$_2$PO$_4^-$ and SO$_4^{2-}$, which form a 1:1 receptor:anion adduct, constants >10^5 M^{-1} are observed [9].



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A similar platinum-containing system has been derived from 3-(pyrrol-2-yl)pyridine (**8**) ([Pt(**8**)$_4$]$^{2+}$). The complex was shown in the solid state to bind to two BF$_4^-$ anions by adopting a 1,2-alternate conformation. The complex was also shown to strongly bind anions in DMSO solution. However, although it might be expected that ions bind via the NH of the pyrrole unit (Fig. 4a), ^{1}H NMR studies showed large downfield shifts of the pyrrole CH proton indicating that at least in solution the binding of anions is through the CH rather than the NH unit (Fig. 4b). The only exception is the basic carboxylate ions which bind to the complex via the NH donors. Interestingly the mode in which the complex binds anions can be reversed, thus in DMSO the complex binds the methanesulfonate anion via both CH donors on both the pyridine and pyrrole ring (Fig. 4b). If nitromethane is used as the solvent the complex changes its binding mode and binds the anion via CH donors on the pyridine ring and the NH donor unit on the pyrrole ring. It seems likely that binding mode b will be stabilised by hydrogen bonding from the DMSO solvent, which is a good hydrogen bond acceptor, to the NH donor unit [10].

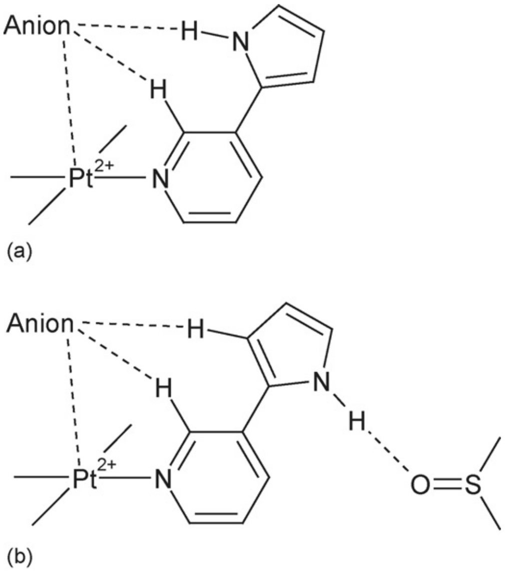
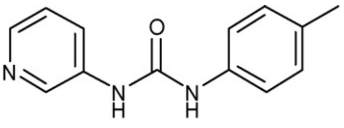


Fig. 4. (a) N–H anion binding mode of ([Pt(**8**)$_4$]$^{2+}$). (b) C–H anion binding mode of ([Pt(**8**)$_4$]$^{2+}$).

Reaction of Co^{2+} with the urea-containing ligand **9** results in the formation of $[Co(\mathbf{9})_4(H_2O)_2]^{2+}$, with each of the pyridyl ligands coordinating the cobalt centre in the equatorial regions with the two axial positions occupied by water molecules. This complex, in an analogous fashion to the Pd^{2+} examples, can adopt a series of different conformations. However, in the presence of nitrate the structure adopts a 1,2-alternate conformation with each ligand interacting with a different nitrate anion. The copper analogue $[Cu(\mathbf{9})_4(H_2O)_2]^{2+}$, where the four ligands again occupy the equatorial positions, also adopts a 1,2-alternate conformation but in contrast to the cobalt species the nitrate anions are bound by cavities formed by two pairs of ligands in each complex [11].



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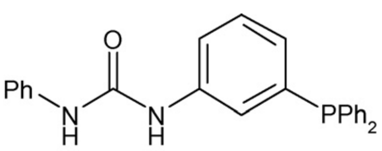
3.2. Phosphine systems

The ligand **10** reacts with "$PdCl_2$" to form initially the *cis*-$[PdCl_2(\mathbf{10})_2]$ complex, with a 1:3 mixture of the *cis*/*trans* isomers observed with prolonged reaction times. The solid state structure of this complex grown from DMSO solution shows that *trans*-$[PdCl_2(\mathbf{10})_2]$:2DMSO adduct results with each of the urea units hydrogen bonding to a molecule of DMSO. Reaction of this species with chloride ions results in the 1:1 species *trans*-$[PdCl_2(\mathbf{10})_2Cl]^-$ which in the solid state shows that the chloride ion is hydrogen bonded to all four urea hydrogen atoms. Investigation of the effect of anions on the catalytic properties of a complex derived from **10** and Pd(0) dibenzylideneacetone was carried out. However, the addition of anions had no observable effect on the catalytic activity and no asymmetric induction was observed when the chiral lactate anion was employed [12].



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3.3. Thiolate systems

The formation of an anion receptor results from the complexation of $[Pd(dppe)]^{2+}$ and the urea-containing ligand $HSCH_2CH_2NHC(=O)NHPh$ (**11**) giving the dinuclear complex $[Pd(dppe)\{\mu\text{-}SCH_2CH_2NHC(=O)NHPh\}]_2]^{2+}$. The single crystal X-ray structure of the triflate salt shows that one anion is encapsulated by the ureas from the two thiolate arms (Fig. 5a).

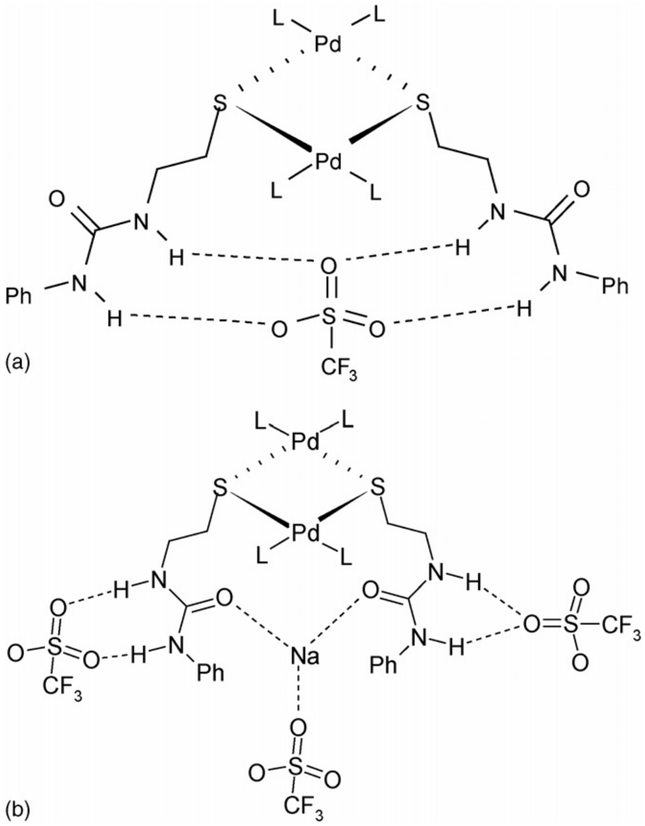


Fig. 5. (a) The 1:1 host guest species with $[Pd_2(\mathbf{11})_2]^{2+}$ and triflate anions. (b) The 1:3 host guest species formed with $[Pd_2(\mathbf{11})_2]^{2+}$ and triflate anions.

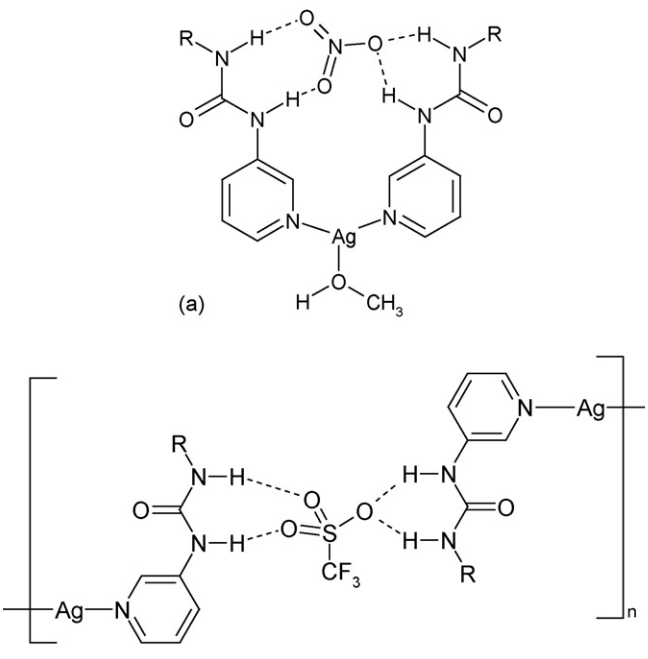


Fig. 6. (a) Assembly of the 1:1 host guest species with Ag^+ and **12**. (b) Assembly of the polymeric host guest species with Ag^+ and **12**.

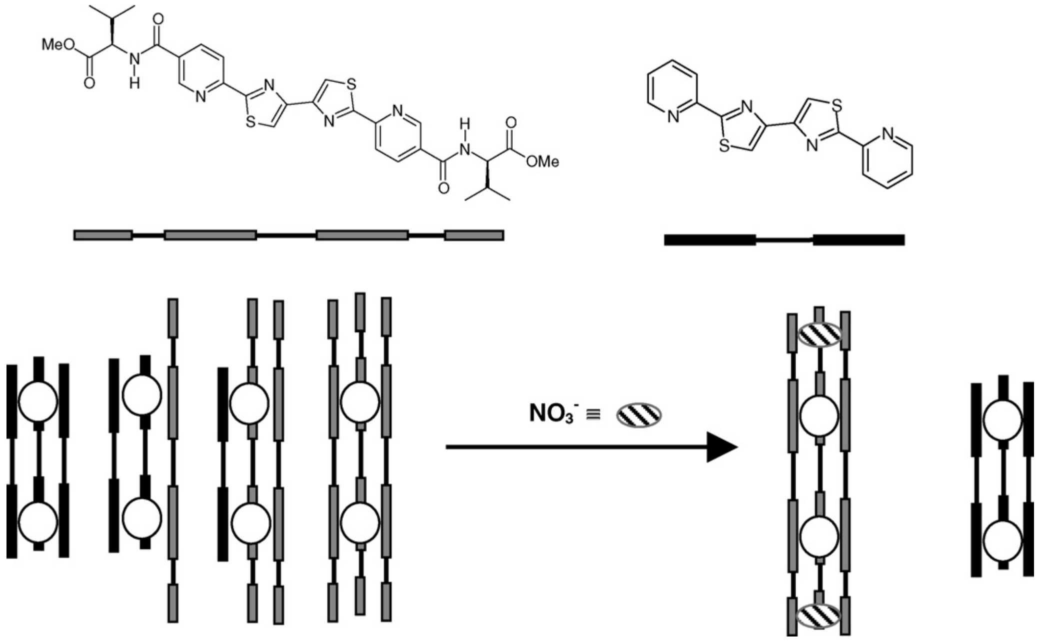


Fig. 7. Diagrammatic representation of the control of ligand recognition by nitrate anions.

Interestingly the addition of sodium ions to the complex results in a quite different receptor where the complex forms a 1:3 receptor anion species. Without sodium ions the complex forms a cavity where the two urea H-bond donors bind the anion (Fig. 5a). However, addition of sodium ions results in the inversion of the urea arms due to coordination of the cation by the urea oxygen atoms (supplemented by some Na· · ·π interactions), producing a divergent species (Fig. 5b). Each urea now binds one triflate anion, with the third triflate coordinated to the sodium ion. In DMSO solution only a 1:1 receptor anion species was observed [13].

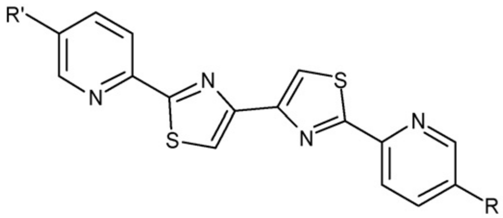
4. Anion receptors from trigonal planar/linear metal ions

Rather than resulting in the formation of discrete binding units, the anion binding cavities formed by reaction of the urea substituted ligand **12** and Ag^+ are controlled by the type of anion present. For example, reaction of **12** with $AgNO_3$ gives a discrete 1:1 host guest assembly where both ureas from the complex hydrogen bond the nitrate anion (Fig. 6a). With triflate and sulfate polymeric structures result, with each anion surrounded by an array of two or four urea groups (for triflate and sulphate, respectively) all of which come from ligands attached to different metals (Fig. 6b) [14].

5. Anion receptors from helicate systems

5.1. Pyridyl-thiazole ligands

Although most metal-assembled anion receptors are based on mononuclear systems there are a few examples where transition metal helicate systems are employed. For example, the pyridyl-thiazole containing ligand **13** forms dinuclear triple helicates with metals, as is common with this type of species, that prefer octahedral coordination geometry. Thus, reaction of **13** with $Co(ClO_4)_2$ results in the helicate species $[Co_2(\mathbf{13})_3]^{4+}$. The solid state structure shows that the two Co^{2+} ions are coordinated by three bridging ligands in a triple helical arrangement. Due to incorporation of amide substituents the self-assembly of the helicate species results in a C_3-symmetric cavity containing the amide hydrogen bond donors in a similar fashion to mono-nuclear bipyridine complexes reported by Beer and co-workers [1], Janiak and co-workers [7] and Williams and co-workers [4–6]. Interestingly in the solid state perchlorate anions are encapsulated within both of the self-assembled cavities via two hydrogen bonding interactions between the oxygen atoms of the perchlorate and –NH donors of the amides.



13 R = R' = *S*-$CONHCH(CH(CH_3)_2)CO_2Me$
14 R = R' = H
15 R = H R' = *S*-$CONHCH(CH(CH_3)_2)CO_2Me$

Reaction of this species with NO_3^- anions results in displacement of the perchlorates. In the nitrate analogue all three oxygen atoms form hydrogen bonds to all three –NH donors of the amides. Furthermore, the anion hydrogen bond lengths are shorter for the nitrate derivative and it is sited deeper within the receptor cleft (av. $\text{Co}\cdots N\text{O}_3$ 4.42Å, $\text{Co}\cdots Cl\text{O}_4$ 5.00 Å) indicating that the binding of the nitrate anion is stronger than that of the perchlorate. This stronger binding has interesting consequences in ligand recognition studies. Reaction of $Co(ClO_4)_2$ with the unsubstituted ligand **14** and **13** (in a 1.5:1.5:2 molar ratio) results in the formation of both homoleptic and heteroleptic species $[Co_2(\mathbf{13})_3]^{2+}$, $[Co_2(\mathbf{14})_3]^{2+}$, $[Co_2(\mathbf{13})_2(\mathbf{14})]^{2+}$ and $[Co_2(\mathbf{13})(\mathbf{14})_2]^{2+}$ in the ratio 1:1:3:3. The lack of any ligand–ligand recognition and thus the formation of a statistical mixture of species is not surprising as both ligands contain the same basic coordination domains. However, upon addition of nitrate anions, only the homoleptic species are formed $[Co_2(\mathbf{12})_3]^{2+}$ and $[Co_2(\mathbf{13})_3]^{2+}$ (Fig. 7). As a consequence of addition of nitrate anions, which have been shown to bind to the amide receptor cavity more strongly than perchlorate anions, the formation of the anion receptor complex is now thermodynamically favoured [15].

A similar type of effect is observed with the pyridyl-thiazole ligand **15**. Reaction of this ligand with $Co(ClO_4)_2$ gives rise to the dinuclear double helicate $[Co_2(\mathbf{12})_3]^{2+}$. Due to the unsymmetrical nature of the ligand produces both head-to-head-to-head (HHH) and head-to-head-to-tail (HHT) isomers in a ratio 1:3 HHH:HHT. Presumably the predominance of the HHT isomer reflects the fact that unfavourable steric interactions between the amide substituents are minimised in this isomer. Upon addition of nitrate anions to this helicate species 95% conversion to the HHH isomer is observed. Thus, in the presence of perchlorate both the C_1- and C_3-symmetric isomers result. However, in the presence of nitrate, which interacts with the amide cavity more strongly the major product is the C_3-symmetric HHH isomer (Fig. 8) [16].

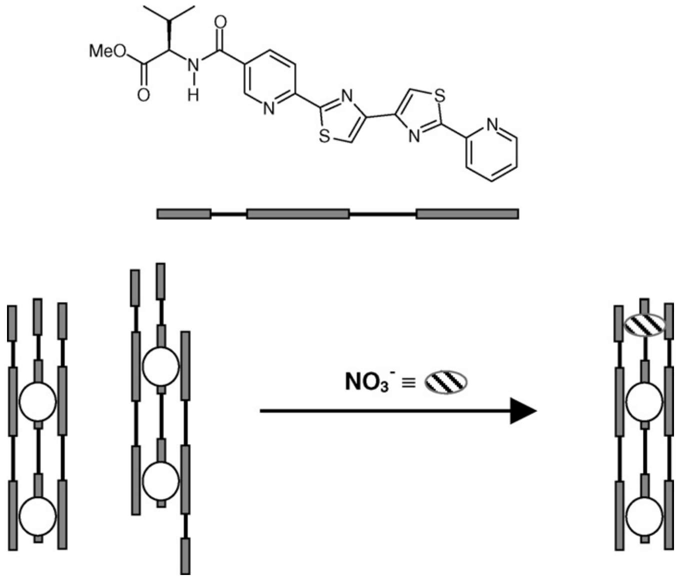
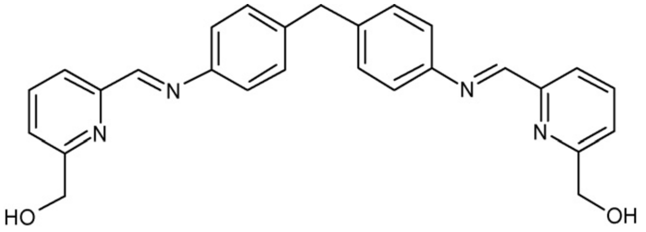


Fig. 8. Diagrammatic representation of the control of HHH/HHT isomers by nitrate anions.

5.2. Schiff base ligands

Reaction of the ligand **16** with Cu^+ generates a dinuclear double helicate $[Cu_2(\mathbf{16})_2]^{2+}$. Each of the helicate units has two hydroxyl units at each end of the assembly which act as alternating donors and acceptors in the presence of the PF_6^- anion, resulting in an infinite chain (Fig. 9a). Addition of chloride ions also results in a infinite chain but each helicate species is separated by chloride ions which are bound by hydroxyl hydrogen bond donors (Fig. 9b) [17].



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5.3. 2,2-Bipyridine ligands

A recent example of an anion binding helicate has been reported by Kruger, where reaction of the amide-containing bis-bipyridine ligand **17** with Fe(II) results in the formation of a

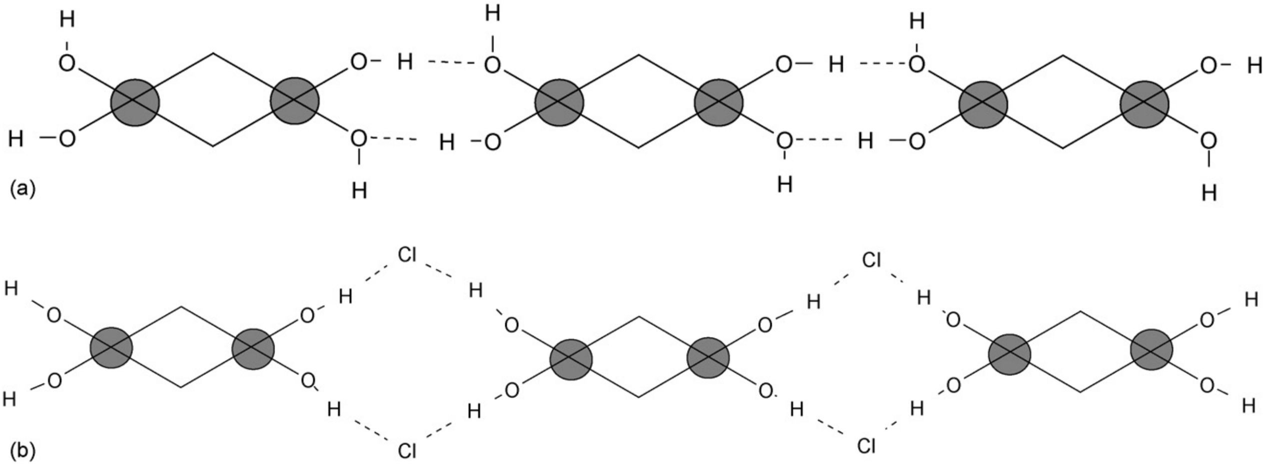
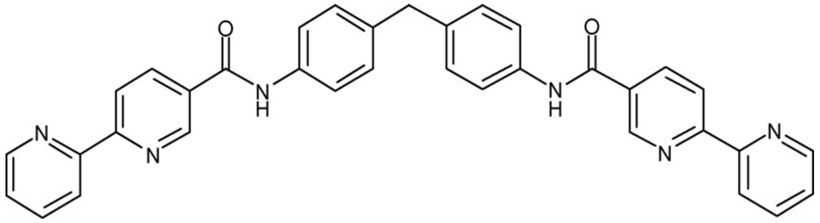


Fig. 9. (a) Diagrammatic representation of hydrogen bonded helicate chain in $[Cu_2(\mathbf{16})_2]^{2+}$. (b) Diagrammatic representation of the binding of chloride anions by $[Cu_2(\mathbf{16})_2]^{2+}$.



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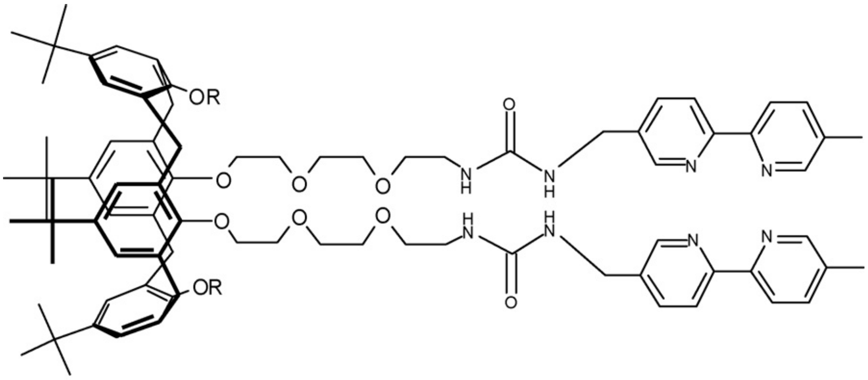


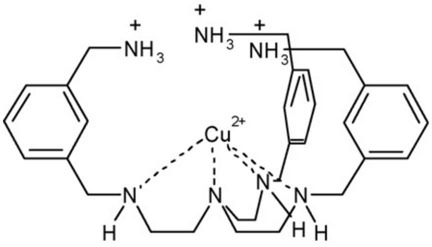
18

dinuclear triple helicate $[Fe_2(\mathbf{17})_3]^{4+}$. This complex contains two quasi-C_3-symmetric amide cavities between the two metal centres bridged by a diphenyl methane unit. In DMSO solution ^1H NMR studies show that the complex binds anions weakly. However, addition of chloride anions shows significant changes in the spectra indicating that the complex is specific to this anion. The formation of a 1:2 host:guest complex and the observed NH shift in the ^1H NMR indicated that both quasi-C_3-symmetric amide cavities bind anions. Interestingly the complex contains both *rac*- and *meso*-isomers but upon addition of chloride ions only the *rac*-isomer results [18].

6. Other systems

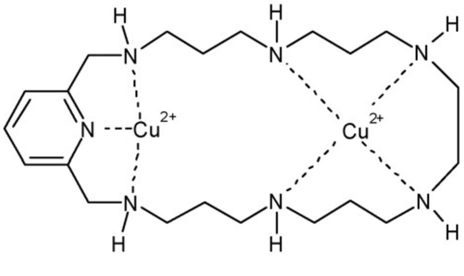
As well as assembling anions receptors metal ions can also lock existing receptors into a certain conformation, so that an anion binding cavity is produced, and/or be involved in the coordination of the anion itself. The ligand **18** contains two arms with N-donor, O-donor and urea functionalities, linked by a calixarene. Binding of nitrate anions is maximised when the bipyridine units are coordinated by Ag^+ and the polyethylene glycol units are coordinated to sodium ions (for addition of NO_3^- in $CDCl_3/CD_3CN$ (9:1) solution, $\log K_a$ **18** = 1.88; **18**·Ag^+ = 3.31; **18**·Na^+ = 3.82; **18**·Ag^+Na^+ = 5.07 M^{-1}). A similar series of results were also observed for $CF_3SO_3^-$ and BF_4^-. The observed increase in association constants is thought to arise from two factors; firstly, upon addition of the Ag^+ ions the coordination of the bipyridine ligands reduces the conformational mobility of the urea units (effectively making an anion binding cavity) and secondly, addition of both Ag^+ and Na^+ increases the favourable electrostatic interactions [19].

Reaction of the ligand **19** with Cu^{2+} ions not only reduces conformational mobility such that an anion binding cavity is formed, but the metal ion can also bind to the anion. The shape of the resultant cavity makes the receptor highly size discriminatory and is correspondingly selective to dianionic tetrahedral anions [20].



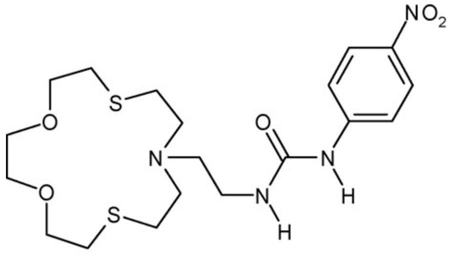
19

Reaction of the azacrown **20** with Cu^{2+} gives the dinuclear species $[Cu_2(\mathbf{20})]^{4+}$ with the metals coordinated to each end of the ligand. The distance between these two cationic ions allows discrimination between L-glutamate and L-aspartate anions, with the longer L-glutamate anions a better size match allowing it to bridge the two cations [21].



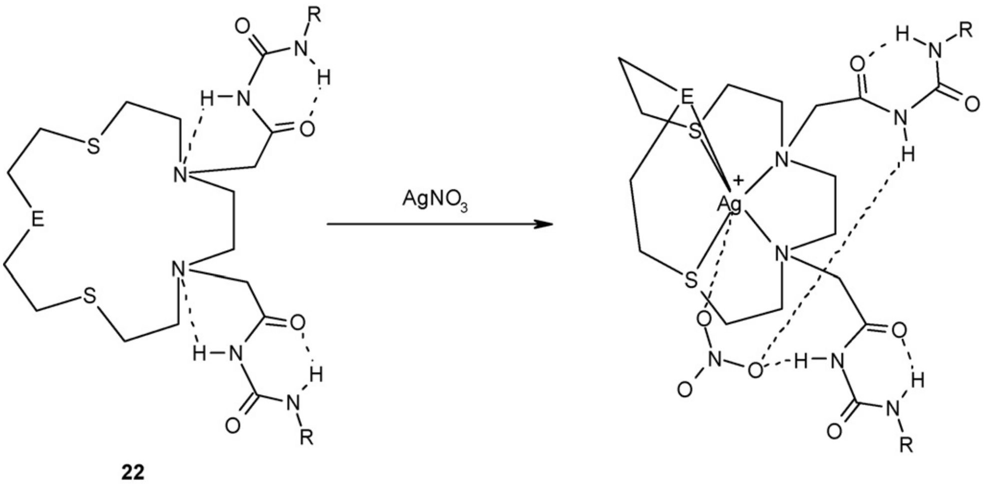
20

Another example of metal enhanced anion binding is seen in the ligand **21** where coordination of the NS_2O_2 crown with Ag^+ induces a 10^3–10^6-fold enhancement of the anion association constant in MeCN. This change in binding constant is attributed to interaction of the O atoms of the urea functional group with the metal centre (Fig. 10). Interestingly the authors speculate that in the presence of nitrite the urea–silver interactions do not occur and the anion is simultaneously bound by both Ag^+ and urea units (Fig. 10b) [22].

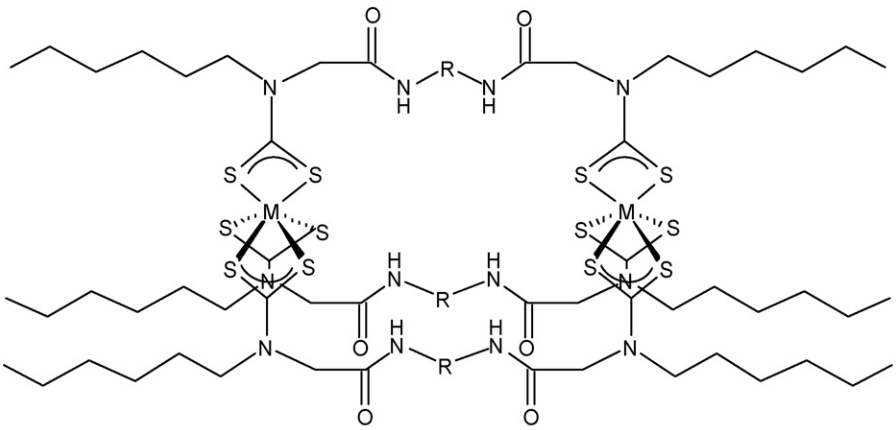


21

The amide functional groups in the aza-thioether ligand **22** undergo substantial intermolecular hydrogen bonding and correspondingly no binding of anions to the free ligand is observed. However, the hydrogen bonds to the macrocyclic nitrogen atoms are broken upon coordination of $AgNO_3$, which effectively generates two amides from the urea moieties, which are now capable as acting as hydrogen bond donors. Resultantly the ligand is "switched" and now can act as an anion receptor. Solid state studies show that in derivatives of **22** hydrogen bonding to nitrate anions, from the urea nitrogen atoms is observed [23]. The self-assembly of a cavity capable of binding anions has been shown to occur by reaction of the dithiocarbamate ligand **23** with an octahedral metal salt, resulting in the assembly of a dinuclear species $[M_2(\mathbf{23})_3]^{4+}$. As a result of this assembly a cryptand unit is formed which contains six amide hydrogen bond donor groups. Only preliminary data was given but electrochemical studies suggest that binding to nitrate and chloride anions occurs [24].



22 **22**·AgNO$_3$



23

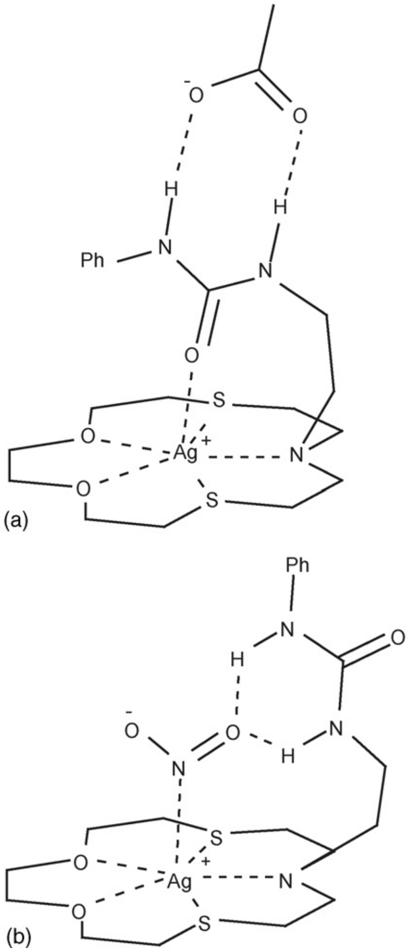


Fig. 10. (a) Binding of acetate anions by activation of the urea group through coordination to silver metal ions. (b) Simultaneous binding of nitrite by both urea and silver ions.

7. Conclusion

This review has described a variety of metal-assembled species which can act as anion receptors and although the number of examples is small compared to other anion binding species this area is increasingly gaining interest.

Using metals as a scaffold to build anion receptors can be extremely advantageous, as the resultant anion binding complexes have been shown to selectively bind anions depending upon the size, shape and charge of the anionic species. Interestingly, in a few cases the ability of these complexes to bind anions affects other properties such as the geometric isomers present and ligand recognition properties. It would seem highly likely that the use of metal ions to assemble anion receptors will increase and there is no doubt that the examples reported in this review will serve as a spring board for further study.

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