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Review

Organometallic cavitands: Cation–π interactions and anion binding *via* π-metallation[☆]

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Abstract

While metal coordination through functional groups on cavitands has been known for many years, the interaction of a range of metals with the π-electrons of the arene rings has triggered great interest in the last 15 years. This article reviews the occurrence of this type of bonding and its effect on the shape and properties of calixarenes and related macrocycles. The review covers both cation–π interactions involving labile metals and the synthesis and inclusion chemistry of inert transitional metal organometallic cavitands.

Keywords: Cation–π; Calixarene; Organometallic; Anion binding; Host–guest; Alkali metal

1. Introduction

Metal-binding by cavitands containing aromatic π-surfaces and the resulting modifications in their properties is of enduring interest [1–13]. The calixarenes and their relatives, particularly the partially pre-organised cone isomer of calix[4]arenes have been studied for many years in this regard, Fig. 1 [14–17]. In the solid state the calixarenes exhibit an extensive inclusion chemistry with interesting gas and liquid sorption properties [18–22], although binding to neutral guests in solution by the unmodified hosts is weak. Related to the calixarenes is cyclotriveratrylene (CTV), a rigid, shallow bowl-shaped macrocycle with electron-rich aromatic rings that is also well known both as a host in its own right [23,24] and as a component in cavitands and cryptophanes [23,25,26]. In the solid state the compound stacks the base of each host in the cavity of an adjacent molecule. Neutral guests occupy channels created in the lattice void [27]. Classically there exist two principal CTV host phases (α and β) in which the guest is situated outside the cavitand bowl. The phase that occurs depends on the hydrogen bond donor ability of the guest [23]. The structure of a third type of CTV inclusion compound has also been established, which hosts solvent acetone molecules between two of the bowls [28]. More recent work has shown that larger guests such as carbaboranes and fullerenes give intra-cavity inclusion compounds [29,30]. CTV also has an extensive coordination chemistry *via* the ether oxygen atoms, resulting in extremely complex solid-state architectures, which have been recently reviewed [31].

The coordination of metal cations to macrocycles such as calixarenes and CTV can alter their shape and electronic properties, and thus change their ability to act as host for cationic, neutral or anionic guests [32]. Metallation of these compounds has been

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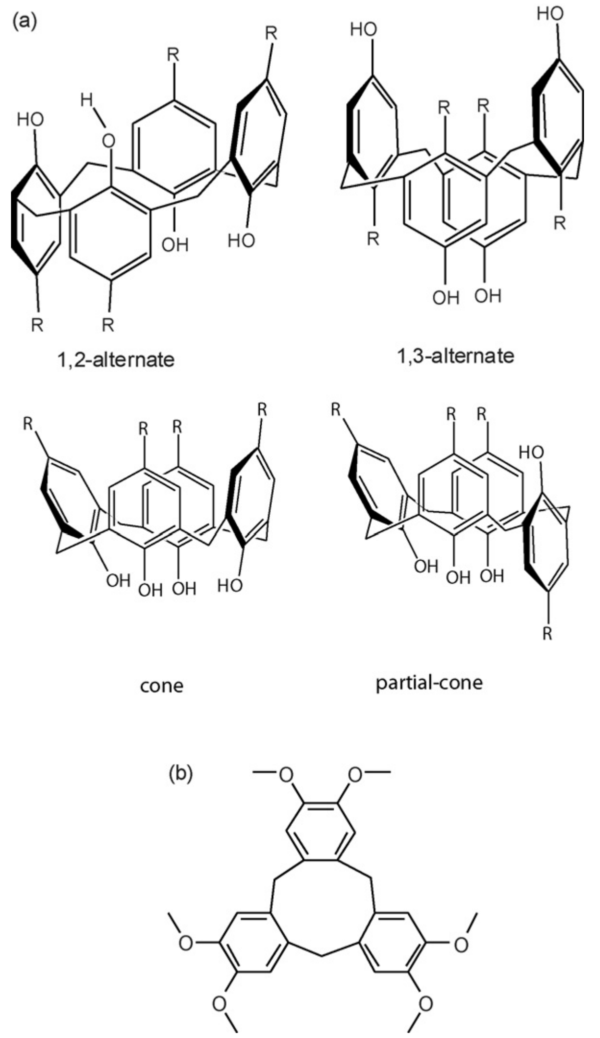

Fig. 1. (a) Structure and conformations of calix[4]arenes and (b) structure of cyclotriveratrylene (CTV).

performed mostly through the functionalisation of the oxygen atoms or the substituents of the calixarene upper (wide) rim. The first transition metal complexes of calixarenes exploited the binding properties of the phenolic oxygen atoms to form complexes of cobalt, iron and titanium [33]. The amido complexes of these metals were reacted with the calixarenes to simultaneously deprotonate the phenolic oxygen atoms and coordinate the metal. Each metal ion bridges between two calixarene molecules, however the oxygen-binding mode for each differs. Attachment of pendant arms functionalised with nitrogen, phosphorous, sulphur and oxygen donors has lead to the coordination of a range of metals. Many examples can be found in previous reviews of this work [34–36].

The interaction of ligand π-systems with transition metals has been known since Zeise's salt, $K[Pt(\eta^2\text{-}C_2H_4)Cl_3]\cdot H_2O$ was discovered in 1827 [37]. The bonding of metals with cyclic aromatic π-systems was first observed with the discovery [38] and structure determination [39] of the iron sandwich complex ferrocene in 1951 and 1956, respectively. Since this time, interactions between cations and π-systems has become an integral part of organometallic chemistry [40–42].

This article surveys the metal–π complexes of macrocycles such as the calixarenes and CTV, and the effect of binding metals to the π-system on the shape and properties of the macrocycles.

2. Alkali metal inclusion and Cs^+ selectivity

The affinity of varying sized calixarenes for alkali metals is well known, but the presence of metal–π interactions was not established until X-ray crystal structure determinations were performed on these systems [43]. Previously, it was thought that the phenolic oxygen atoms play the greatest role in the binding of the metal cations. However, Harrowfield et al. showed that the X-ray crystal structure of the mono-caesium derivative of *p-tert*-butylcalix[4]arene (**1**) involves a caesium cation included within the calixarene bowl, Fig. 2. The distance from the centroid of the aryl ring to the caesium ion is 3.57 Å, within the sum of Cs–C van der Waals radii, and far shorter than any oxygen–caesium distance.

Thus it was concluded that the major interaction was that of the cation–π interaction. ^1H and ^{133}Cs NMR spectroscopic studies in chloroform-*d* show that the caesium ion maintains its cavity-bound position in solution with the ligand in the cone conformation, in contrast to the fluxional free calixarene. Work on these inclusion compounds has been extended to bis(homooxa)-*p*-*t*Bu-calix[4]arene [7]. The calixarene binds the caesium ion in an analogous manner to **1** with additional interactions to the ether oxygen, the lower phenolic rim hydroxyl group of another calixarene molecule and three water molecules. The related hexahomooxacalix[3]arene as a lower-rim diethylamide derivative (**2a**) is able to complex two Na^+ ions as PF_6^- salts to give a complex displaying both lower rim oxygen coordination and a second combined oxygen and π-coordinated Na^+ ion within the calixarene bowl. The two Na^+ ions are bridged by a water molecule leading to the suggestion that the structure is a mimic of biological alkali metal cation transport, Fig. 3

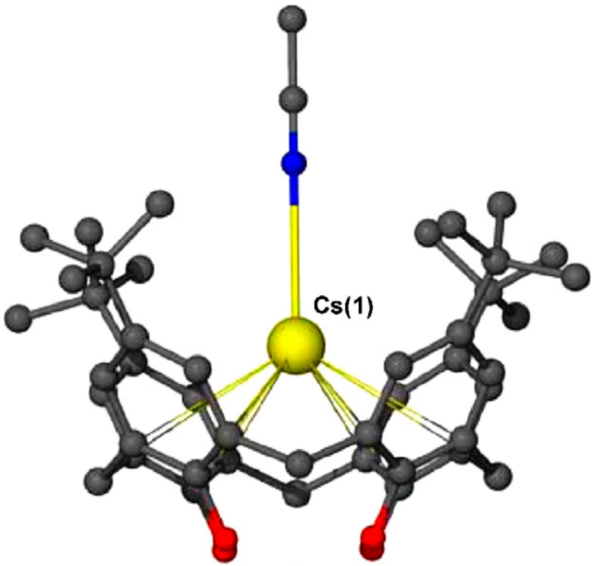

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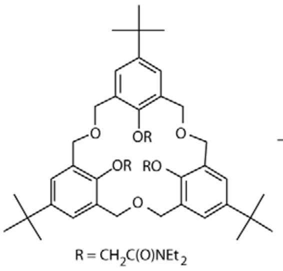
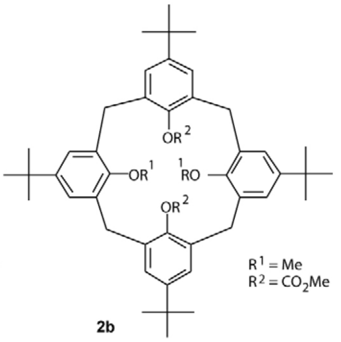
Fig. 2. Caesium bound in the cavity of calix[4]arene (**1**). The host adopts the cone conformation and a coordinating acetonitrile molecule caps the cavity [43].



2a



2b

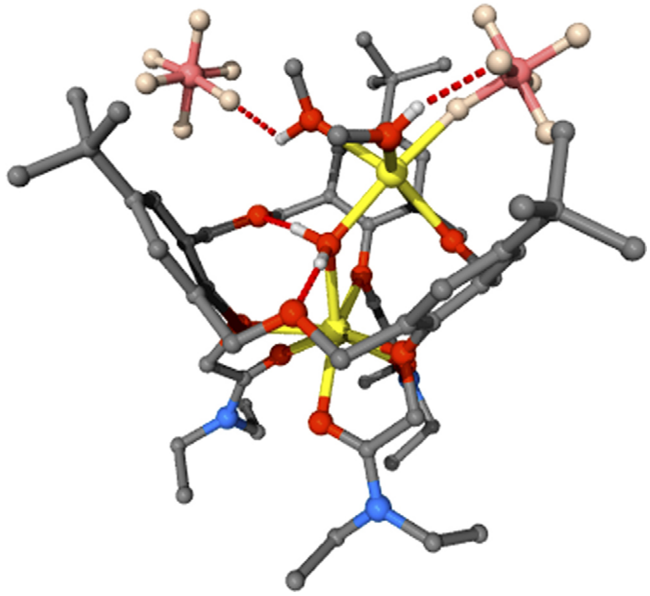


Fig. 3. X-ray structure of the disodium complex of **2a** showing the two different Na^+ environments and the intra-cavity bridging water molecule [44].

[44]. Simultaneous coordination of alkali metals by the aryl rings and a functionalised lower rim has also been observed in calix[4]arenes [45]. A dimethoxy, dimethylester functionalised *p-tert*-butylcalix[4]arene **2b** has been shown to bind potassium sodium and lithium ions through the dimethylester (R^2) groups. It has been shown by ^1H NMR spectroscopy that the Li^+ and Na^+ ions are bound by the cone conformation, whereas X-ray crystallographic studies of the potassium salt confirm that the 1,3-alternate conformation is present with the potassium ion held by both ester groups and between two distal aryl rings. The cation's closest contacts are to the carbonyl and phenolic oxygen atoms of the methylester groups, R_2, with K–O distances of 2.62–2.83 Å. However, the metal ion is also coordinated by the aromatic rings with K–C distances as short as 3.20 Å. The solid-state structure of the sodium analogue displays a partially flattened cone conformation of the calixarene with binding through the ester groups, R_2, and the oxygen atoms of the macrocyclic ring methoxy groups (R). The latter interaction replaces the cation–π interaction present in the K^+ example.

The strong preference for π-coordinated caesium is also evident in unsubstituted calix[4]arene [46]. In the caesium salt of the deprotonated calix[4]arene, **3**, the Cs^+ ion is included within the cavity partially by interactions with the π-system and partially by binding with the deprotonated phenolic oxygen atom to form one-dimensional calixarene–caesium chains (Fig. 4a). This binding is not shared equally by all four oxygen atoms so the calixarenes do not lie perpendicular to the Cs. . .Cs axis.

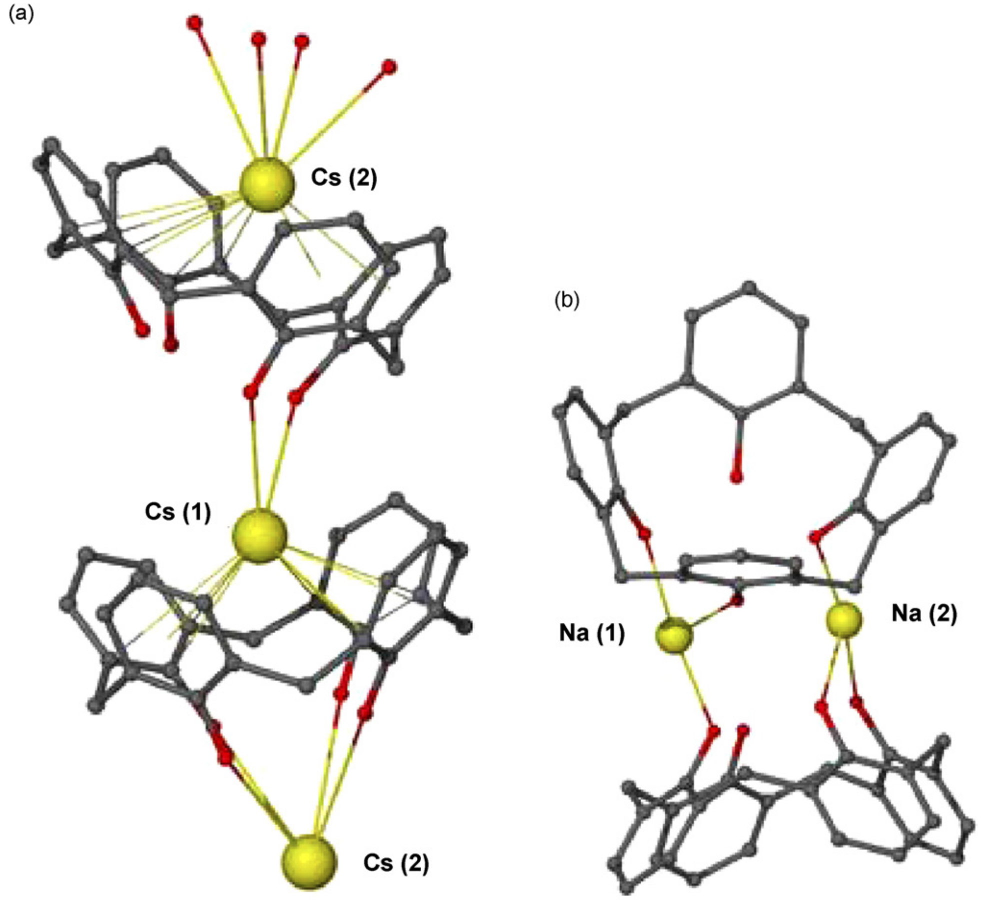
In the analogous sodium salt $\{Na_2(\text{calix[4]arene-H})_2[(CH_3)_2CO]_3\}\cdot 2Cl_3CH\cdot 2H_2O$ (**4**), the sodium ion is not held in the electron-rich cavity, but forms a dimeric structure bound by the lower rims of two calixarenes (Fig. 4b). The metal ions are bound in a bidentate fashion by one calixarene and in a monodentate mode by the other. The coordination sphere is completed by an acetone molecule capping each sodium cation and one acetone bridging the two sodium cations.

Similar polymeric chains to **3** are observed when coordinated uranyl oxo groups act as ligands to the alkali metal cations [47]. The products are obtained from reaction *p-t*Bu-tetrahomodioxacalix[4]arene (**5**) with both uranyl and alkali metal salts and the uranyl cations bind to the fully deprotonated lower rim. For the smaller, harder lithium and sodium cations, the axial oxygen atoms of the uranyl group coordinate only one cation each, resulting in monomeric $Li_2[UO_2(\mathbf{5})(H_2O)_5(CH_3OH)]$ and bridging dimeric $Na_2[UO_2(\mathbf{5})(H_2O)(CH_3OH)_6]_2$ structures. The terminal alkali metal cations are capped by solvent methanol and water molecules and there is no interaction with the aryl π-system. In contrast, the axial oxo groups of the coordinated uranyl group bind two cations each for the larger, softer potassium and caesium cations to give coordination polymers of $K_2[UO_2(\mathbf{5})(H_2O)_2(py)]$ (**6**) and $Cs_2[UO_2(\mathbf{5})(H_2O)_{0.5}(CH_3OH)_3]\cdot 0.5Cl_3CH$ (**7**), Fig. 5. For these cations, two metal atoms are coordinated within the calixarene cavity and some cation–π interaction is observed. In **6**, each cation is coordinated to a single arene ring with distances of K1. . .centroid 3.50 Å shortest K1. . .C contact 3.18 Å; K2. . .centroid 3.65 Å shortest K2. . .C contact 3.26 Å.

The coordination of the caesium ions in **7** is markedly different from the cation binding in **6**, with each cation coordinated to two aromatic rings each; Cs1. . .centroid 3.58 and 3.71 Å, shortest Cs1. . .C contact 3.60 and 3.61 Å; Cs2. . .centroid 3.79 and 3.73 Å, shortest Cs2. . .C contact 3.75 and 3.79 Å. The coordination of the caesium ion to both the arene rings of one calixarene and to the uranyl group of another, leads to the formation of coordination polymer chains. Limited ^1H NMR spectroscopic studies suggest that the cone conformation for all four alkali metal coordinated calixarenes is maintained in the solution state.

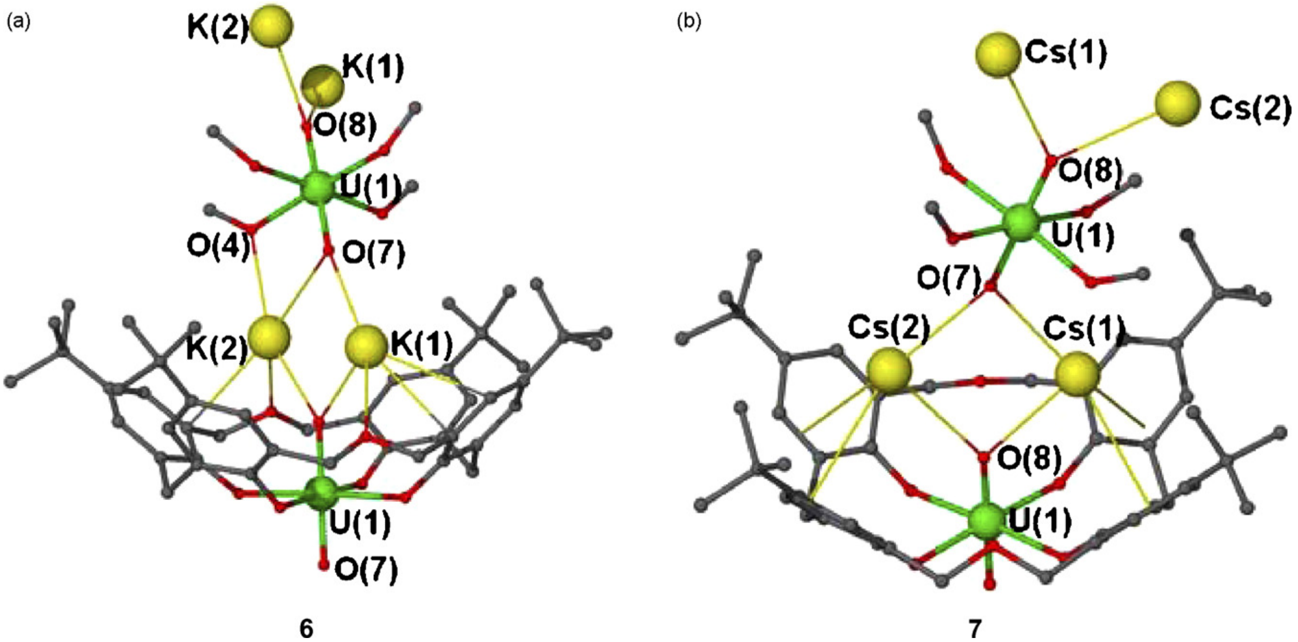
3. Engineering cation–π interactions

While the observation of the interaction of alkali metals with π-systems is often serendipitous, attempts have been made to specifically engineer three-dimensional cation binding by cation–π interactions in supramolecular systems through the use of lariat ethers [48] (Fig. 6). This work has been spurred on by the biological importance of the interaction between cations and π-systems, especially the issue of K^+ selectivity within membrane channels (albeit that such interactions are not observed in the structure of a natural K^+ channel [49]). Gokel and co-workers



3 **4**

Fig. 4. Structures of (a) the caesium salt of calix[4]arene where Cs^+ inclusion into the cavity and coordination of phenolic oxygen atoms gives a coordination polymer in **3** [46] and (b) the sodium salt of the calix[4]arene yields a discrete sodium bridged dimer in **4** [47].



6 **7**

Fig. 5. X-ray structures of coordination polymers formed in the alkali metal salts of calix[4]arene, **6** and **7**. For (a) the potassium salt **6**, each cation is coordinated to one aryl ring within the cavity and for (b) the caesium salt **7**, the cation is coordinated to two aryl rings [47].

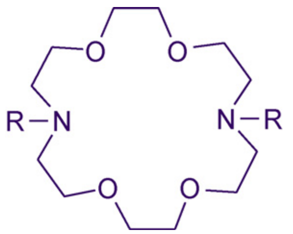
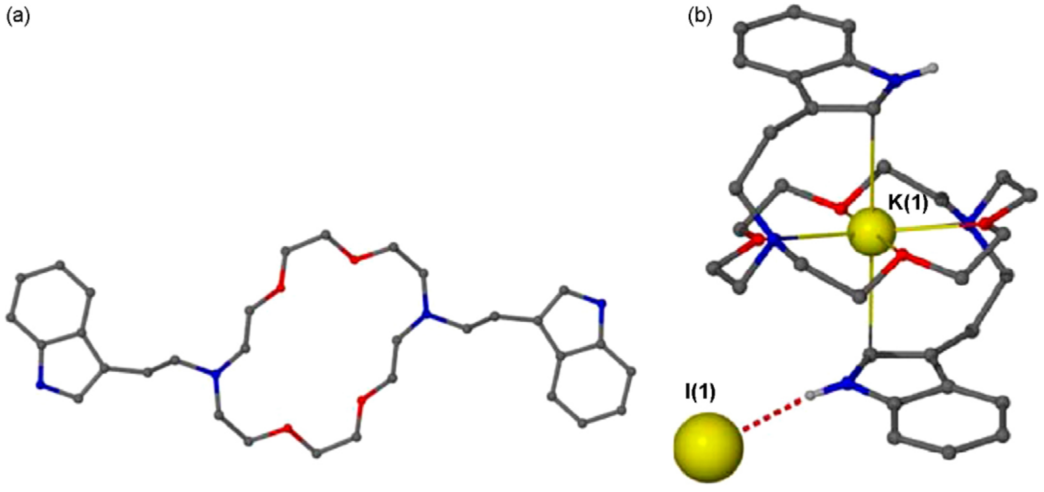


Fig. 6. Structure of lariat ethers **8**–**14**. **8**: R = H; **9**: R = $CH_2CH_2CH_3$; **10**: R = $CH_2CH{=}CH_2$; **11**: R = CH_2CCH; **12**: R = CH_2Ph; **13**: R = CH_2CH_2Ph; **14**: R = $CH_2CH_2C_6H_4OH$; **15**: R = CH_2CH_2-indolyl; **16**: R = $CH_2CH_2C_6F_5$ [50,51].

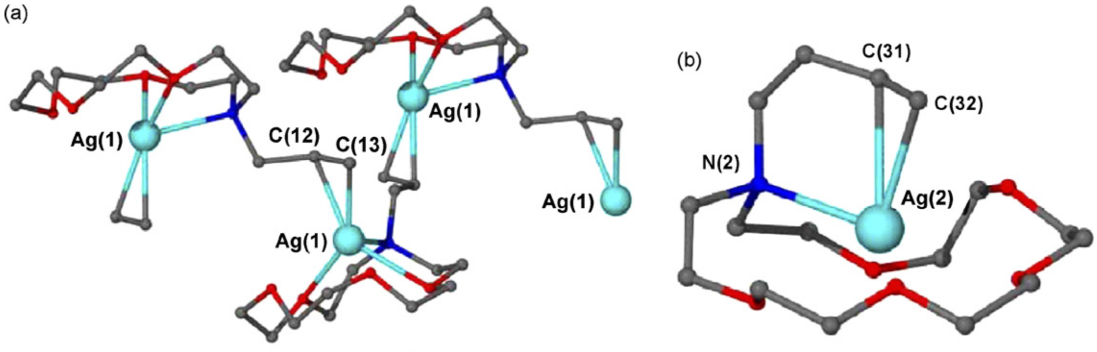
have synthesised lariat ethers with pendant arms containing alkene, alkyne and arene groups (**10**–**12**) to study the interaction of the side arms with the metal cation. Binding of Na^+ and K^+ by the macrocycle is observed but solid-state structures of **10** and **11** show that there is no interaction between the side arms and the metal cation [50,51].

Hence Gokel and co-workers have synthesised lariat ethers with longer side arms containing aromatic groups that emulate the amino acids phenylalanine, tyrosine, and tryptophan (**13**, **14**, and **15**, respectively) [52–54]. Solid-state structures for **15** and its KI complex were obtained by X-ray crystallography. The uncomplexed macrocycle has both side arms pointing away from the macrocycle ring. In contrast, on metal complexation both side arms arrange themselves to interact directly with the metal cation, one above and below the macrocycle ring, as seen in Fig. 7. In **15**·KI the pyrrole ring is positioned closest to the metal cation with the shortest contact being 3.3 Å. The iodide counter ion is hydrogen bonded to the NH group of one of the pyrrole rings. Structures were also obtained of **13** and **14** as their KI complexes. These systems undergo the same conformational change upon K^+ complexation to give a cation–π interaction. For **14** the iodide is again hydrogen bonded to the macrocyclic ring *via* the phenolic hydroxyl group, however no hydrogen bonding interaction is observed for the KI complex of **13**. To investigate whether these structures were formed from attractive cation–π interactions or were the result of crystal packing induced short contacts, complexation of KI with the fluorophenyl derivative, **16**, was investigated. If packing forces are dominant then the electron-poor fluorinated analogue, which is similar in size and shape to the phenyl derivative, should show similar packing. The solid-state structure of the complex however shows the K^+ cation bound in the macroring with both side arms directed away from



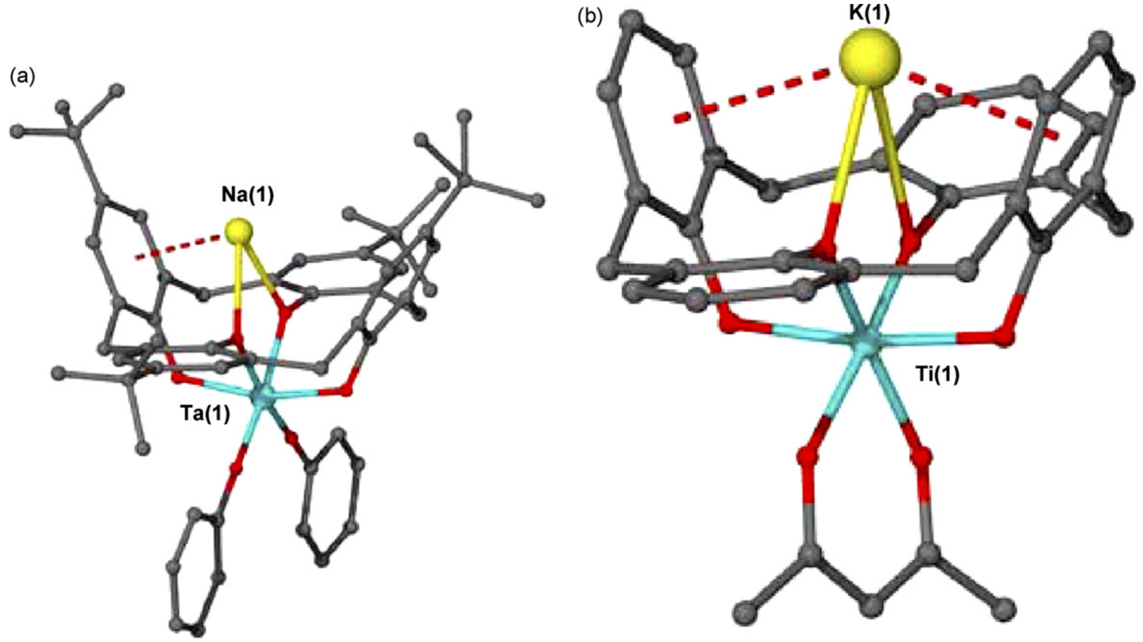
15 **15•KI**

Fig. 7. (a) Free ligand **15** with pendant arms positioned away from macrocycle, and (b) **15** coordinated to K^+ with interaction to the cation from above and below the macrocycle from pendant arms [52–54].



17 **18**

Fig. 8. (a) coordination polymer formed by the silver(I) complex of *N*-allylaza-15-crown-5 (**17**) compared to (b) the discrete 'scorpionate' structure of the silver(I) complex of (*N*-3-butenylaza-18-crown-6 (**18**) [55].



18

19

Fig. 9. (a) Molecular structure Ta–calix[4]arene complex with a sodium ion bound in the cavity by one aryl ring, and (b) molecular structure of Ti–calix[4]arene with a potassium ion bound within the cavity by two aryl rings [59].

it. The iodide counter ion is in direct contact with the cation and forms an infinite chain of $K^+ \ldots I^-$ stacks.

Similar lariat ether structures with allyl side arms complex silver cations with differing $Ag^+ \ldots \pi$ interaction depending on the length of the side arm [55]. The structure of silver-coordinated *N*-allylaza-15-crown-5 (**17**) was obtained (Fig. 8a). The soft Ag^+ sits within the crown macrocycle with the closest ring contact being with the nitrogen atom. With the short propenyl side arm, there is a cation–π interaction from the terminal allyl group with a silver ion bound by another lariat ether. The side arm from this second ether lariat is coordinated to another silver ion bound by a further lariat ether molecule to give a coordination polymer. The Ag. . .π interaction is shown in the short contacts to the allylic group Ag(1). . .C(12) 2.36 Å and Ag(1). . .C(13) 2.42 Å.

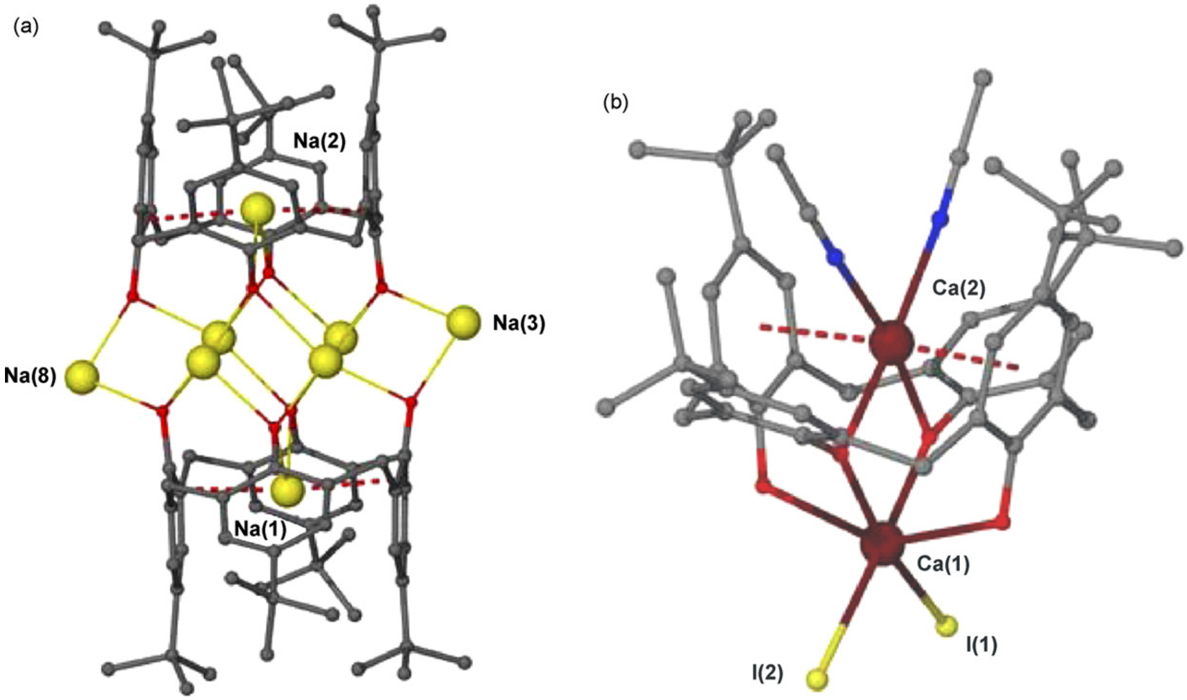
The structure of the silver(I) complex of *N*-3-butenylaza-18-crown-6 (**18**) was also obtained and shows a different silver coordination mode to **17**, Fig. 8b). As observed in complexes **10–15**, extending the side arm length by a single CH_2 group provides enough 'reach' for the alkene to coordinate the silver bound within its own crown ether. Again the nitrogen provides the closest contact of the ring donors with distances Ag(2)–N(2) 2.49 Å and there is also an interaction with the π-electrons of the allylic group. This is illustrated by the short Ag–C contacts with distances of Ag(2)–C(32) 2.58 Å and Ag(2)–C(31) 2.61 Å. These longer-arm lariat ethers also bind potassium cations in the solid state [48,55–58] albeit with much longer K. . .C distances but there is less evidence for K^+–π interactions in solution, unlike the Ag^+ analogues.

4. Inclusion involving transition metals

The Cs–π interaction is prevalent in calix[4]arenes, while interaction of smaller alkali metal ions with the cavity π-system is less common. By coordinating transition metals to the oxygen atoms of the lower phenolic rings and treating these compounds with an excess of the alkali metal cations, potassium and even sodium cations have been included in the cavity, bound by the π-rings. The first such example [59] utilised reaction of $MC1_5$ (M = Ta, Nb) with *p*-*t*Bu-calix[4]arene to form a dimeric calixarene structure with bridging metal. This was then subjected to an excess of alkali metal phenolate to yield lithium, sodium and potassium cations (M*) bound within the cone conformation cavity [*p*-*t*Bu-calix($O_4M(OPh)_2$)(M*($THF)_2$)]. Many of the compounds obtained are isostructural, emphasising the ability of the transition metal to shape the calixarene conformation for the smaller alkali metals.

For the sodium adduct **18** (Fig. 9a), the metal is held asymmetrically within the cavity by one of the aromatic rings in an η^6 fashion with Na. . .centroid 2.47 Å, shortest Na. . .C contact 3.01 Å. There is additional coordination from the two phenolic oxygen atoms of the uncoordinated aromatic rings. This gives a distorted cone conformation of *pseudo*-C_{2v} symmetry where the two coordinating aromatic rings are positioned nearly vertically and the oxygen coordination pushes the other two rings to a more horizontal position.

A similar hetero bimetallic system investigated the influence of alkali metal on the coordination of calix[4]arenes with titanium(IV) [60,61]. By deprotonating the lower phenolic rim with potassium metal and introducing 1 equiv. of $[Ti(acac)_2(OPr^i)_2]$, a monomeric complex, **19**, is formed (Fig. 9b). The titanium cation occupies the lower phenolic rim of the calixarene, while the potassium ion is held within the cavity. The K^+ ion is held by two distal aromatic rings with crystallographic two-fold symmetry. The K^+. . .centroid distances are 3.02 and 3.08 Å showing the similar interaction between each ring in contrast to **18**. As



20 **21**

Fig. 10. Crystal strictures of (a) polymetallated Na–calix[4]arene structure **20**, showing bridging Na_6O_8 clusters and cavity-bound Na^+ ions, and (b) Ca–calix[4]arene complex **21** with a Ca^{2+} ion held within the cavity by two distal aryl rings [62,63].

expected the analogous caesium salts also include the caesium ion within the cavity.

The coordination of the lower rim phenolic oxygen atoms with small alkali metals themselves has been effective in introducing small alkali metals into the calix[4]arene cavity [62,63]. Monomeric calixarenes M_4(*p*-*t*Bu-calix[4]arene-4H)·2THF (M = Li, Na, K), that coordinate four alkali metal cations on the lower rim can change their coordination mode upon recrystallisation.

The rearrangement produces dimeric structures in which six metal atoms form bridging M_6O_8 (M = Na, K) clusters, with each cluster capped by solvent molecules. This leaves one remaining metal cation per calixarene which occupies the cavities, held by two distal aromatic rings in the cone conformation. The structure of the sodium adduct, **20**, is shown in Fig. 10a. The cations situated within the cavity are bound by M. . .π interactions, with comparable C. . .aromatic distances. Short Na–C distances are also exhibited with shortest NalA. . .C contacts 2.87 and 2.83 Å; shortest NalB. . .C contacts 2.87 and 2.81 Å.

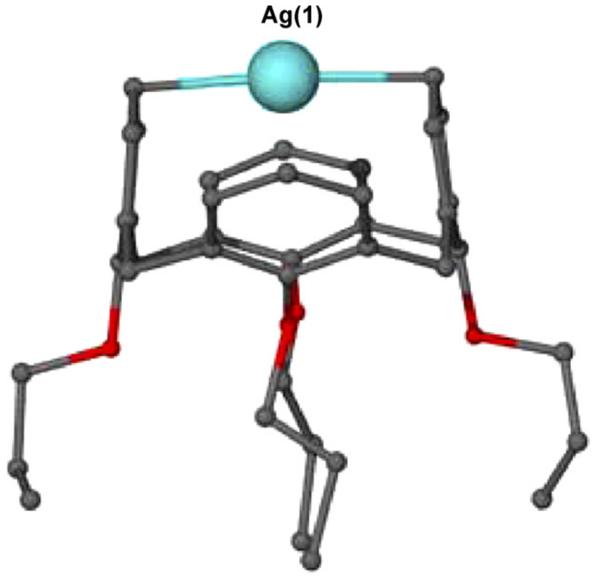
Included in this study was the reaction of a lower rim di-*O*-pentyl derivative of *p*-*t*Bu-calix[4]arene with calcium to yield the monomeric structure stabilised with TMEDA with one calcium cation held at the lower rim. However, the reaction of this calcium complex with an excess of $CaI_2(thf)_4$ yields the complex $Ca_2(MeCN)_2I_2$(dipentyl-*p*-*t*Bu-calix[4]arene) (**21**) with one phenolic oxygen coordinated calcium ion and a cavity-bound calcium ion, Fig. 10b. Again an η^6 interaction with the calixarene aromatic rings holding the cation within the cavity is present. The coordination sphere of the intra-cavity metal ion is capped with two acetonitrile solvent molecules. The binding mode of the calixarene is similar to the potassium and titanium coordinated calixarene, **19**, and shares similar metal to centroid distances of Ca(2). . .centroid 2.86 and 2.94 Å.

One of the first examples of inclusion of transition metals into the calixarene cavity was with silver(I) [4]. The Ag^+ complex [Ag(tetra-*O*-propylcalix[4]arene)](CF_3SO_3) (**22**) exhibits inclusion of the Ag^+ ion within the calixarene cavity in the solid state, Fig. 11. For the cone calixarene conformation the cation sits within the cavity-bound by two distal phenyl rings. These distal rings are strained from the conventional four-fold symmetric bowl shape to effectively bind the metal ion. The silver(I) centre is held at the top of the cavity with the shortest contact involving the carbon atoms *para* to the O–Pr substituent: Ag^+. . .C_{para} distances are 2.39 and 2.40 Å, Fig. 11.

From variable temperature NMR spectroscopy, there is evidence for solution interconversion of C_{2v} states, and thus evidence for alternate Ag. . .π bond formation and scission. Comparative studies show that the uncomplexed calixarene also experiences this interconversion, and from the coalescence temperature it is found that the silver coordination considerably retards this process. The partial cone conformation was also studied, and exhibits a similar binding mode for the silver ion.

5. Direct π-metallation and guest inclusion

Direct metallation of the exterior of a macrocycle provides a vacant cavity with altered electrostatic properties. The first direct metallation of calixarenes was performed by Shinkai and co-workers in 1993, who prepared mono- and bis(tricarbonylchromium) complexes of cone-tetra-*O*-propyl

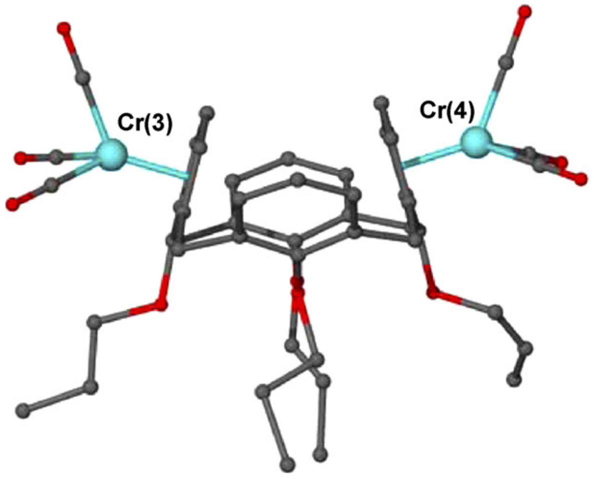


22

Fig. 11. Molecular structure of **22** showing Ag$^+$ ion held at the apex of the calix[4]arene cavity by two distal aryl rings resulting in distortion of the cone conformation [4].

calix[4]arene. The X-ray molecular structure of the dichromium complex **23** is shown in Fig. 12 [5,64]. In both the mono and bimetallic complexes of the cone calixarene, a "bis-roof' conformation is adopted, conformationally similar to **22**. In contrast to **22**, the metal is coordinated on the exterior of the distal phenyl rings. The flattening of the other rings is attributed to steric crowding of the lower rim. When this steric crowding is removed in the 1,3-alternate isomer, there is only a small change in the structure from the uncomplexed calixarene.

Chromium coordination has also been observed for a species of triarenes, 10-methyltribenzotriquinacene (**24**) closely related to CTV, Fig. 13a, where six complexes of mono-, bis- and tris(tricarbonylchromium) coordinated species $[\{Cr(CO)_3\}_n(\mathbf{24})]$ ($n = 1$–3) have been isolated [65]. Both complexation at the concave (*syn*) inner face and convex



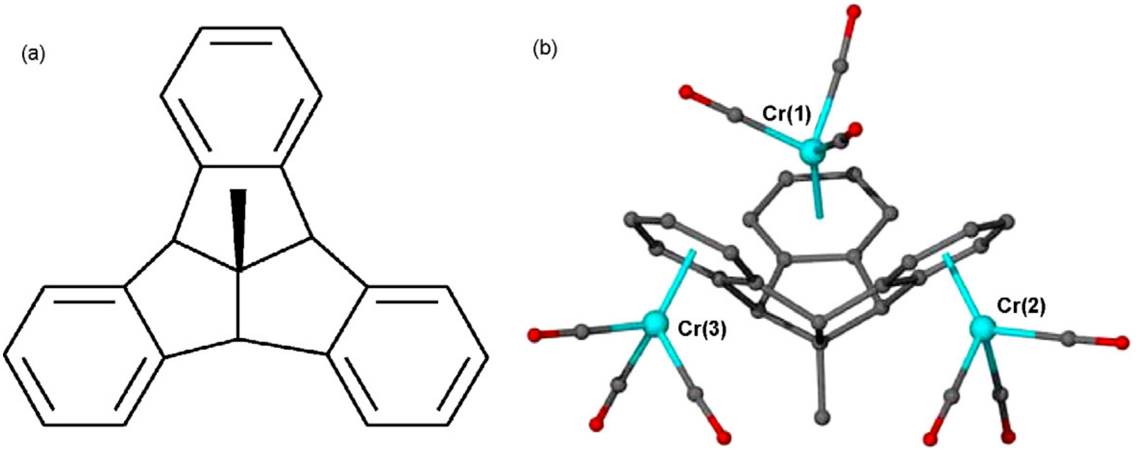
23

Fig. 12. Molecular structure of the chromium(0) calix[4]arene complex, **23**, showing a "bis-roof" conformation [64,65].

(*anti*) outer face of the bowl molecule is observed, with the six complexes being the *anti*- and *syn*-monometallic complexes, *anti,syn*- *anti,anti*-bimetallic, and *anti,anti,syn*- and *anti,anti,anti*-trimetallic.

From ^{1}H NMR spectroscopic and X-ray crystallographic studies it is apparent that the *syn* conformations are less stable, not only due to steric crowding of the appended metal carbonyl fragments but also electronic interaction of the carbonyl groups with coordinated and uncoordinated aryl rings. In the bi-metallated *anti,syn* conformation there appears to be a repulsive interaction between the carbonyl and the π-electron cloud of the uncoordinated aryl ring. In contrast, on coordination with the third aryl ring an energetically favoured interaction between this third ring and the carbonyl group is observed, Fig. 13b.

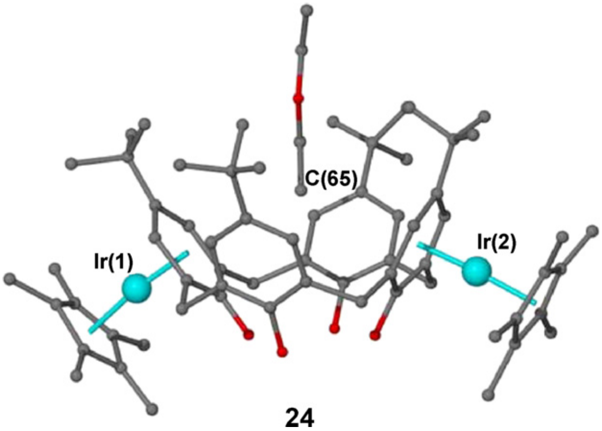
Coordination of manganese(I) to methyltribenzotriquinacene gives a monometallic cationic species $[Mn(CO)_3(\mathbf{24})](BF_4)$ [66]. An X-ray crystal structure of the complex shows three molecules in the asymmetric unit, all of which have manganese



24

anti,anti,syn-**24•[Cr(Co)$_3$]$_3$**

Fig. 13. (a) Structure of 10-methyltribenzotriquinacene (**24**) and (b) molecular structure of its trichromium complex in the *anti*,*anti*,*syn* conformation [66].



24

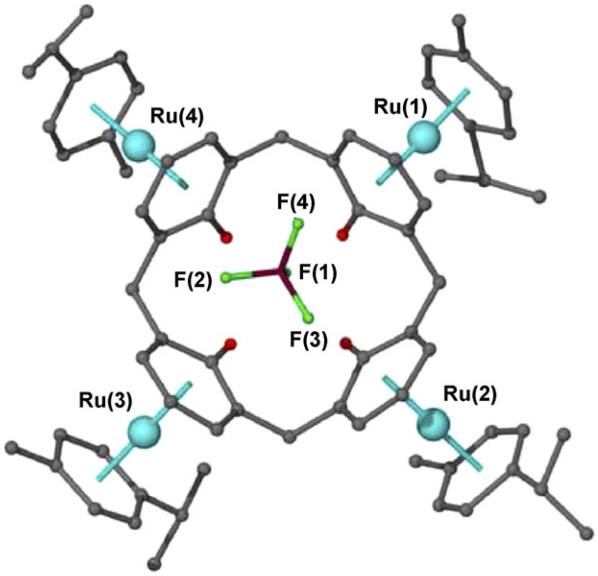
Fig. 14. Molecular structure of di-iridium calix[4]arene complex **25**, showing inclusion of a diethyl ether solvent molecule [11].

coordinated to the convex face. The tetrafluoroborate counterion does not display any cavity inclusion, but fills lattice voids. The primary effect of the coordination is to activate the metallated ring towards nucleophilic attack. Addition of both hydride from BH_4^- and pinacolonate ($CH_2C(O)CMe_3^-$) nucleophiles has been observed, resulting in a distribution of attack of 5:1 at the *ortho* position for the smaller hydride and a 1:1 *ortho:meta* isomer ratio for the larger pinacolonate nucleophile. Nucleophilic addition to aromatic rings could be facilitated by this methodology through means of demetallation, removal of an endo hydride with acid and re-aromatisation methods [67].

Guest inclusion into π-metallated complexes of this type was first observed in calix[4]arenes directly metallated with pentamethylcyclopentadienyl (Cp*) complexes of rhodium and iridium. Using methods previously devised for small molecule analogues [68,69], chloride bridged half-sandwich complexes were reacted with *p*-*t*Bu-calix[4]arene [11]. With excess of the metal starting complex, the bimetallic species were formed preferentially, and the metal centres occupy opposite faces on the cone conformer. The coordination of the metal complexes leads to a great increase in acidity of the phenolic hydroxyl groups, so that double deprotonation of these groups is observed on treatment with potassium carbonate or upon recrystallisation from DMF. The crystal structure of the single deprotonated iridium bimetallic species $[\{Ir(\eta^5\text{-}Cp^*)\}_2(\eta^6\text{:}\eta^6\text{-}p\text{-}t\text{Bu-calix[4]arene-H})](BF_4)_3\cdot Et_2O\cdot MeNO_2$ (**25**) includes molecules of both solvents of crystallisation: nitromethane and diethyl ether, with the latter occupying the calixarene cavity, Fig. 14.

One of the polar diethyl ether molecules has been included into the cavity of the calixarene, with the terminal methyl group of the solvent molecule in close contact with the aromatic rings; C(65)...centroid distances of 3.53, 3.62, 3.69, and 3.83 Å. From calculated hydrogen atom positions there is a weak C–H...π interaction [70] with the uncoordinated rings, and avoidance of the partially positively charged coordinated rings.

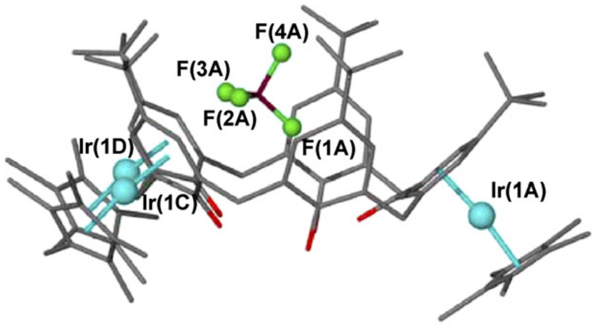
In contrast to the *t*-butyl derivative, reaction of unsubstituted calix[4]arene with both Cp*Ir(III) and (*p*-cymene)Ru(II) precursors results in metallation of all four phenolic rings in the presence of non-coordinating anions to give the water-soluble tetrametallated ruthenium complex $[\{Ru(\eta^6\text{-}p\text{-}MeC_6H_4CHMe_2)\}_4(\eta^6\text{:}\eta^6\text{:}\eta^6\text{:}\eta^6\text{-}C_{28}H_{22}O_4)]^{6+}$ (**26a**) and $[\{Ir(\eta^5\text{-}Cp^*)\}_4(\eta^6\text{:}\eta^6\text{:}\eta^6\text{:}\eta^6\text{:-}C_{28}H_{22}O_4)]^{6+}$ (**26b**) which incorporate a partially positively charged hydrophobic cavity, Fig. 15 [71]. The cationic hosts have an overall charge of 6+ because of the loss of two calixarene phenolic protons to give a dianionic calixarene ligand in the presence of four dipositive metal fragments. The symmetrical substitution and cone conformation of the calixarene was deduced from ^{1}H NMR spectroscopy and confirmed by X-ray crystallography in the case of the BF_4^- and I^- salts of **26a** and the SO_4^{2-}/HSO_4^- salt of **26b**. In each case the cavity is occupied by anions instead of solvent molecules (*cf*. compound **25**). For example in the case of the BF_4^- salt of **26a** three of the fluorine atoms lie just above the upper rim of the macrocyclic aromatic rings, the fourth points directly into the host cavity.



26·BF$_4$

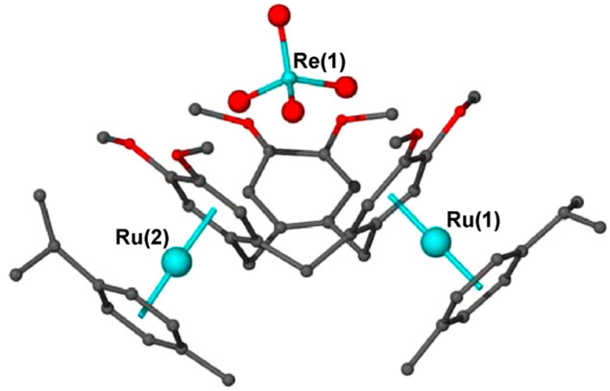
Fig. 15. Crystal structure of tetraruthenium calix[4]arene complex **26**, showing inclusion of a tetrafluoroborate anion within the cavity. F1 penetrates the ring most deeply [72].

Distances of this fourth fluorine atom (F1) to the centroids of the rings are 3.10, 3.15, 3.41, and 3.46 Å. The deep penetration of this atom into the cavity is shown by the very short distance to the lower rim carbon of the aromatic ring of 2.85 Å. The iodide salt arises from anion metathesis with $(NBu_4)I$ with an iodide anion included into the cavity. This unusual anion hosting is only made possible by the electron-withdrawing effect of the exterior metallation [8]. The anion binding of compounds of type **26** was investigated by ^{1}H NMR spectroscopic titrations. The titrations were performed in the highly competitive solvent water due to the environmental sensing interest in aqueous anion hosts. The triflate salt of **26a** was titrated against a range of sodium salts. For halides a shift in the signal for the methylene protons is observed with binding constants K_1 of 551 M^{-1}, 133 M^{-1}, and 51 M^{-1} for Cl^-, Br^- and I^-, respectively. The general trend shows some selectivity for the smaller anion despite chloride possessing a higher free energy of hydration than either bromide or iodide. No binding is observed for SO_4^{2-} or $H_2PO_4^-$ anions due to the high free energy of hydration of these anions.



28

Fig. 16. Crystal structure of tri-iridium calix[5]arene complex **28**, showing inclusion of a tetrafluoroborate anion within the cavity [9].

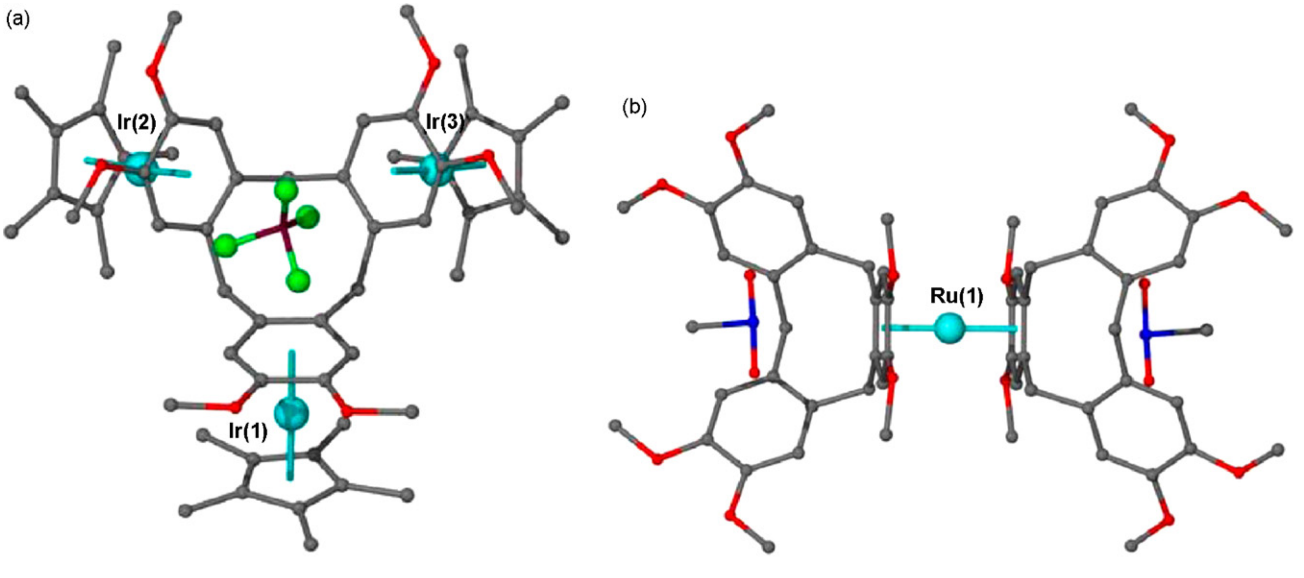


29b·ReO_4^-

Fig. 17. Crystal structure of diruthenium CTV complex **29b**, showing the position of a ReO_4^- anion within the bowl cavity [12].

The metallation of *p*-*t*Bu-calix[5]arene in the presence of excess Cp*Ir(III) precursor results in the coordination of three iridium fragments and gives the loss of one phenolic proton to give the tri-iridium host $[\{Ir(\eta^5\text{-}Cp^*)\}_3(\eta^6{:}\eta^6{:}\eta^6\text{-}C_{55}H_{69}O_5)][BF_4]_5$ (**28**) in high yield [9]. The X-ray crystal structure of **28**, Fig. 16, shows a 1,2,4-substitution pattern of the five phenolic rings and inclusion of a tetrafluoroborate anion within the wide cavity near the two adjacent Ir(III) centres. There is deep penetration of F1A into the cavity and distances to the closest aryl ring centroids are 3.66 and 3.88 Å. This result, in contrast to the structure of **24** (Fig. 14) implies that two adjacent metallated rings are needed to induce intra-cavity anion inclusion. The close anion. . .C_{arene} contacts suggest significant anion–π interactions in these systems, an interaction that is increasingly recognized [72–76].

The hosting of anions is also observed in the metallated derivatives of CTV. Mono-, di- and trimetallic derivatives have been prepared but it is only the di- and trimetallic derivatives of Ru(II) and Ir(III) that contain adjacent metallated rings and hence function as anion hosts. For example, coordination to ruthenium(II) moieties in an analogous fashion to the calixarene **26** leads to the cationic host $[\{Ru(\eta^6\text{-}p\text{-}MeC_6H_4CHMe_2)\}_2(\eta^6{:}\eta^6\text{-}CTV)]^{4+}$ (**29b**) [12]. Binding studies were performed on the triflate salt $[\{Ru(p\text{-}MeC_6H_4CHMe_2)\}_2(\eta^6{:}\eta^6\text{-}CTV)][CF_3SO_3]_4$ to determine the degree of ReO_4^- and TcO_4^- complexation by radiochemical tracer methods. The extraction of these anions from an aqueous saline phase into the nitromethane organic phase is observed with efficiency, with 71% $^{188}ReO_4$ and 84% $^{99m}TcO_4$ extracted into the organic phase by the host. This compares favourably with the 7% $^{188}ReO_4$ and 6% $^{99m}TcO_4$ that transfers across the phase in the control experiment. Competition studies with other anions show that there is selectivity of these hosts towards the large tetrahedral oxo-anions of ReO_4^- and TcO_4^- over smaller perchlorate, nitrate and chloride anions and the highly hydrated sulphate. Only ClO_4^- significantly competes. The X-ray crystal



31 **32**

Fig. 18. Crystal structure of (a) tri-iridium CTV complex **31**, showing the inclusion of a tetrafluoroborate anion the bowl cavity, and (b) ruthenium twin-bowl structure of **32**, with cavity inclusion of nitromethane solvent [10].

structure of **29**·ReO_4^- shows that the rigid macrocyclic host has a complimentary structure for the large tetrahedral anion guest, Fig. 17.

Comparing the Re-centroid distances of 3.96 and 4.06 Å for the metallated rings and 4.51 Å for the unmetallated ring clearly shows the preference of the anion towards the metallated sites. This work was extended to a series of ruthenium and iridium cationic hosts involving mono-, bi- and tri-metallated CTV hosts $[\{M(L)\}_n(CTV)]^{2n+}$ (M = Ru, L = *p*-$MeC_6H_4CHMe_2$, $n = 1$, **29a**; 2, **29b**; 3, **29c**; M = Ir, L = C_5Me_5, $n = 1$, **30a**; 2, **30b**; 3, **30c**), which all show intra-cavity guest inclusion, in contrast to classical CTV inclusion compounds [10]. In the case of the monometallic complexes **29a** and **30a** the disruption of the columnar CTV packing mode [27] creates a cavity for neutral guest inclusion such as nitromethane. For structures with two or three metal centres inclusion of an anionic guest is observed in every instance, and a preference for pertechnetate and perrhenate is observed. The X-ray crystal structure of the trimetallic iridium complex containing the **30c** cation $[\{Ir(\eta^5\text{-}Cp^*)\}_3(\eta^6{:}\eta^6{:}\eta^6\text{-}CTV)][BF_4]_6$ (**31**) shows that the complex hosts one tetrafluoroborate counter ion within its cavity, Fig. 18. The anion is situated off-centre near a pair of metallated rings suggesting it is too small for the host. The closest fluorine to CTV carbon contact is relatively short at 2.82 Å as the anion has two fluorine atoms penetrating the ring in contrast to the tetraruthenium(II) calix[4]arene derivative, **26**.

The electrochemistry of the Ru(II) series **29a–c** is particularly interesting since the rigid CTV macrocycle holds the metal centres in close proximity resulting in the observation of two and three separate reduction waves for the triflate salts of **29b** and **29c**, respectively. Addition of iodide and HSO_4^- anions results in merging of these waves [10,77].

In an attempt to metallate both interior and exterior of the CTV, a twin-bowl structure $[Ru[(\eta^6\text{-}CTV)_2]][BF_4]_2{\cdot}2NO_2Me$ (**32**) was prepared where a ruthenium ion bridges two exterior faces of the bowl, Fig. 18. One metal centre between two CTV molecules is sufficient to disrupt the columnar packing and allow each cavity to host a disordered nitromethane solvent molecule with the closest host–guest contact around 3.2 Å.

In an attempt to lower the overall positive charge of the complexes norbornadiene rhodium(I) CTV complexes have been prepared. The X-ray crystal structure of a co-crystal of the mono- and bi-metallic species $[Rh(\eta^4\text{-}nbd)(\eta^6\text{-}CTV)](BF_4)$ and $[\{Rh(\eta^4\text{-}nbd)\}_2(\eta^6\text{-}CTV)](BF_4)_2$ (**33**) has been determined [78]. In contrast to bimetallic complex **29b**, no BF_4^- anion inclusion is observed in either complex. Instead, the cavity of the bimetallic complex contains the norbornadiene ligand of an adjacent complex, forming an inclusion polymer linked by CH...π interactions [71]. Anion metathesis with 10 mol equiv. of $(NBu_4)I$ lead to no change in the ^1H NMR spectrum of **33**, suggesting that the absence of cavity-bound anion shown in the solid state is also true in solution. It is thought back bonding from the electron-rich Rh(I) and thus the increased electron-rich nature of the cavity may prevent anion binding.

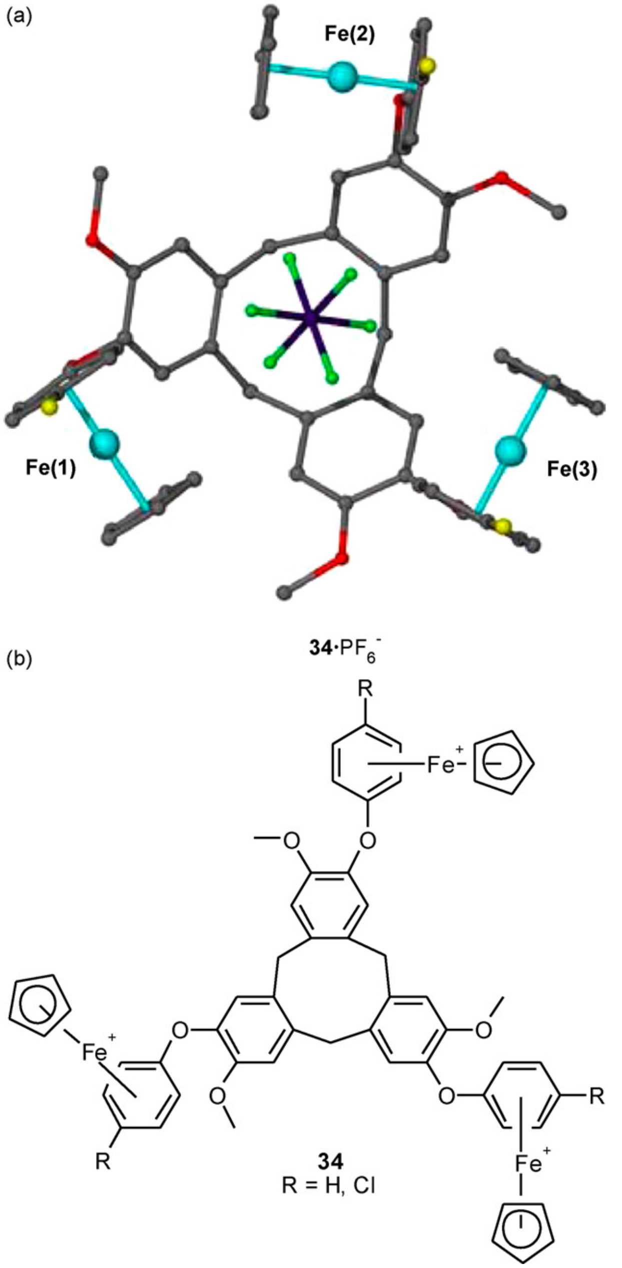
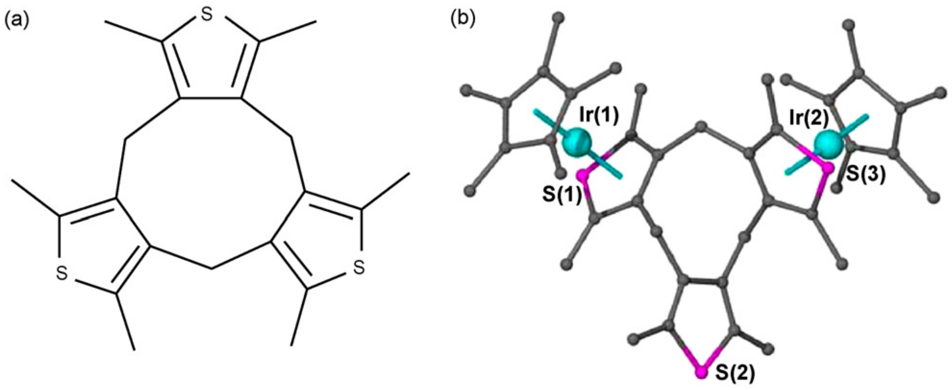


Fig. 19. Crystal structure of $[CpFe(arene)]^+$ appended CTV derivative **34** showing the inclusion of a hexafluorophosphate anion [13].

A $[CpFe(arene)]^+$ derived CTV has been synthesised by reacting *rac*-cyclotriguaiacylene (CTG) with $[CpFe(chloroarene)]^+$ to give complex **34** which proved to be effective as a deep cavity anion host, Fig. 19 [13,79]. Changes in the ^1H NMR spectrum are observed on titration with bromide and chloride. Precipitation of the host halide complexes occurred after addition of 1 equiv. of halide preventing determination of association constants. However, the protons orientated towards the centre of the cavity are shifted the most, with a near linear dependence on anion concentration suggesting strong binding within the cavity. An X-ray crystal structure of **34** with a molecule of PF_6^- included in the cavity is shown in Fig. 19.

The penetration of this anion is demonstrated by the position of the phosphorous atom 0.6 Å below the plane created by the iron(II) centres. Relatively close contacts of 5.16, 5.14, and



35 **36**

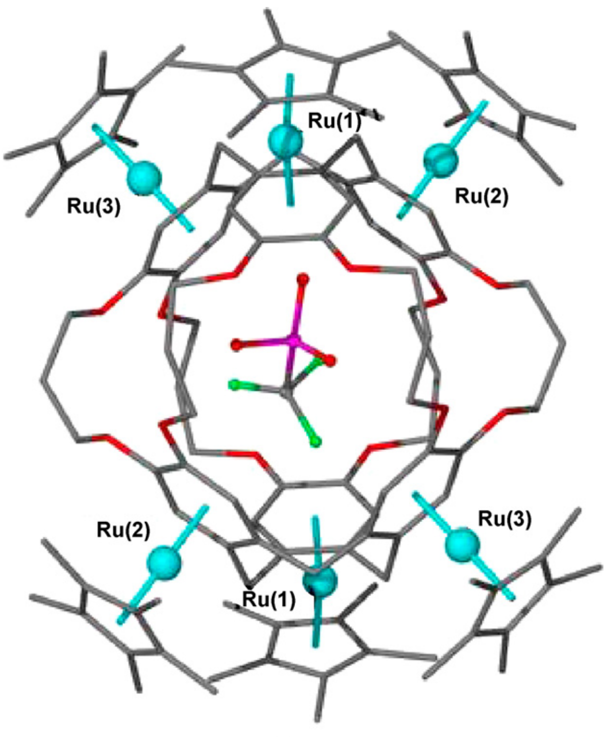
Fig. 20. X-ray molecular structure of di-iridium complex of **35** showing saddle conformation (**36**) [81].

5.08 Å between the phosphorus atom and each of the iron(II) ions demonstrates the charge pairing. Two-phase aqueous-nitro methane extractions were used to test the anion selectivity and removal efficiency of these hosts. Deep cavity host **34** effectively removes pertechnetate from water in a single extraction over competing anions of $SO_4{}^{2-}$, $C1O_4{}^{-}$, $HPO_4{}^{2-}$ and $NO_3{}^{-}$. The optimal pH to extract the radioactive anion is at pH 7. Therefore the selectivity of these hosts for large tetrahedral oxoanions, in particular pertechnetate, observed for the directly metallated CTV hosts is preserved and the efficiency of anion extraction is increased in this second generation host.

The anion binding ability of a bimetallic Cp*Ir(III) complex of cyclotris(dimethylthiophenylene) (**35**) has been examined. Macrocycle **35** possesses the same core nine-membered ring structure as CTV but adopts a 'saddle' conformation as a result of steric interactions between the methyl groups [80]. It was found by X-ray crystallography that the monometallic arene ruthenium(II) complex $[Ru(p\text{-}MeC_6H_4CHMe_2)(\eta^5\text{-}C_{21}H_{24}S_3)](CF_3SO_3)_2$, and the bimetallic Cp* iridium(III) complex $[\{Ir(C_5Me_5)\}_2(\eta^5{:}\eta^5\text{-}C_{21}H_{24}S_3)](CF_3SO_3)_4$ (**36**) both also adopt this saddle conformation, Fig. 20. Because the saddle conformation lacks a significant cavity no neutral or anion host inclusion is observed in contrast to the CTV analogues, however a molecule of disordered DMF is observed in a void space.

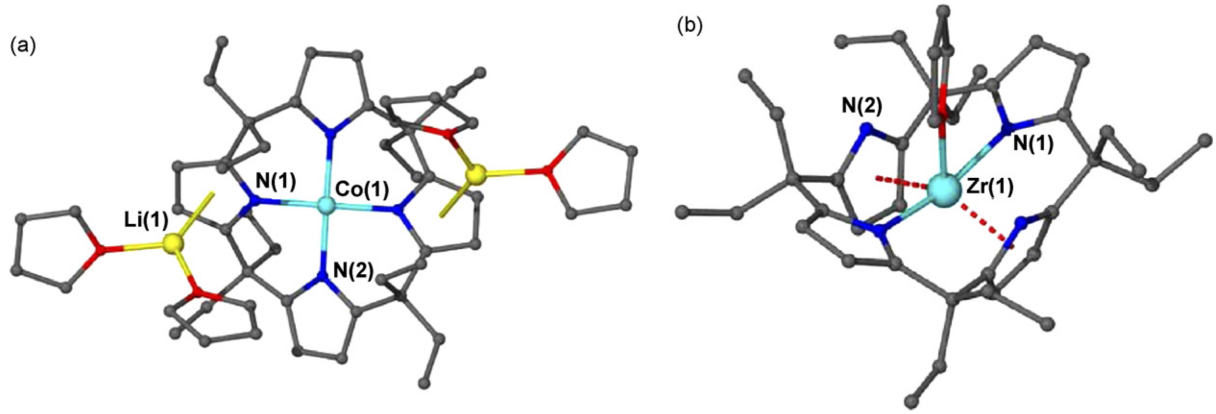
The anion binding of **36**, was compared to the bimetallic ruthenium CTV species, **29**, by ^{1}H NMR spectroscopic titration studies in a range of solvents. Host **29b** shows significant affinity for halides in particular chloride ions with a binding constant $K_1 = 1.25(7) \times 10^3\ M^{-1}$ and a $\Delta\delta$ of 1.40 ppm. In contrast, **36** showed little or no differential binding of anions even after addition of 1000 equiv. of anion. Therefore the conformation of these metallated macrocycles is fundamental to their ability to host neutral and anionic guest molecules.

The chemistry used in the synthesis of **34** can be used to cap molecules of this type with a second CTV type unit to give extended analogues of cryptophanes [81]. Demetallation then gives the free cryptophane. Very recently the anion binding abilities of metallated cryptophanes have been studied [82]. Cryptophanes have the ability to completely enclose small guest species resulting in constrictive bonding [83]. Cryptophane-E reacts with areneophilic Cp*ruthenium(II) fragments to produce the permetallated cryptophanes $[(Cp^*Ru)_6((\pm)\text{-cryptophane-E})]X_6$ ($X = CF_3SO_3{}^-$, $SbF_6{}^-$) (**37**). The X-ray crystal structures of both salts demonstrate encapsulation of $CF_3SO_3{}^-$ and $SbF_6{}^-$, respectively, Fig. 21. The complementarity of this organometallic cage structure for large anions is shown by the close anion–arene contact. For $[\mathbf{37}\cdot SbF_6]^{5+}$ the "axial" fluorine atoms display close contacts with all six aryl rings with closest distances F...C = 2.97 Å and F...centroid 3.08 Å. ^{1}H NMR spectroscopy reveals a simple spectrum highlighting the three-fold symmetry of the host. Competition for the cavity is observed between triflate and competing $PF_6{}^-$ or $SbF_6{}^-$ anions, however equilibrium is only achieved after weeks. There is also a



$\mathbf{37{\cdot}CF_3SO_3}$

Fig. 21. Crystal structure of $[(Cp^*Ru)_6((\pm)\text{-cryptophane-E})][X]_6$ **37**, showing inclusion of a triflate anion within the cage structure [83].



38 **39**

Fig. 22. Comparison of (a) the cobalt porphyrinogen complex **38** with coordination to the metal cation by four nitrogen atoms within the macrocycle, and (b) the zirconium porphyrinogen complex **39** with coordination to the metal cation from two nitrogen atoms within the macrocycle and through two pyrrole rings *via* an η^5-interaction [85,86].

very interesting solvent dependence such that in nitromethane solution the triflate cryptate is the only species present with distinct ^{19}F NMR signals observed for bound and free anion. In CD_2C1_2, however, over a period of *ca*. 3 weeks the signals for the anion inclusion compound are joined by signals assigned to a solvent-occupied cryptophane. Isolation of this mixture and re-dissolution in nitromethane results in slow conversion back to the anion cryptate and allows the determination of the "constrictive binding" energy $\Delta G^{\ddagger} = 18.0\,\mathrm{kcal\,mol^{-1}}$ considerably larger than the value of $13.3\,\mathrm{kcal\,mol^{-1}}$ determined for $CDC1_3$ binding by cryptophane-E in dichloroethane [82].

Finally extensive work by Floriani has concerned the interaction of metal cations with pyrrole-derived ligands. As with calixarenes, the flexibility of calixpyrrole or porphyrinogen-type macrocycles results in many binding modes to metals. An example is the contrast between the complexation of an electron-rich metal such as iron(II), cobalt(II) or nickel(II), versus an electron-poor metal cation such as zirconium(IV) by *meso*-octalkylporphyrinogen.

The Co(II) ion in (**38**) binds to all four nitrogen atoms, Fig. 22a [84]. There is also coordination of lithium cations to the π-electrons of two of the pyrrole rings. Complexation for electron-poor metal cations such as zirconium(IV) (**39**), however, is observed through two distal nitrogen atoms and through two pyrrole rings *via* η^5-interactions, Fig. 22b [85]. This contrast has led to a great deal of work on metal interactions with this type of macrocycle [86,87].

6. Conclusions

The π-electron density of arenes and related heterocycles is capable of bonding strongly to metals in competition with more conventional heteroatom donor ligand groups. Interaction range from electrostatic cation–π binding [2] for relatively hard or closed shell metal ions through to covalent synergic bonding for electron-rich transition metals with a partially filled d-shell. Metal coordination to π-electrons results in significant changes in the properties of macrocyclic hosts and can have synthetic utility. While outside the scope of the present review we also note that calixarene-type macrocycle can also host interesting non-metal cations such as NMe_4^+ and NO^+ *via* interactions with the aromatic rings [88,89].

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