

Review

Calixarenes as platforms for the construction of multimetallic complexes

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Received 15 April 2004; accepted 30 July 2004

Available online 15 September 2004

Abstract

This review article covers the use of calix[*n*]arenes ($n = 4-6$) in building up multi-metal species based on group 1 or 2 ions and early transition metal ions, through synergistic metal–O and metal· · π interactions, depending on the conformation of the calixarenes and the nature of the group 1 or 2 ions. Recent advances on metal alkyl/cyclopentadienyl complexes are also discussed, along with future prospects on the use of calixarenes in general in building up multi-metal complexes in a controlled way.

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Keywords: Calixarenes; Heterometallic complexes; Transition metal; Group 1 and 2; Metal· · π

1. Introduction

The assembly of highly organised multimetallic architectures features in catalysis, magnetism, new materials, medicine, molecular electronic devices and associated nano-technologies. Developing methods for tailoring properties and tuning the stoichiometries of metals in multimetallic complexes is a considerable challenge, and for this purpose various synthetic methodologies have been established. The initial limited scope of unidentate ligands in mediating the formation of mixed-metal species through bridging led to the use of multidentate ligands including bi/tri-dentate functionalised moieties [1–4]. Another approach, which is receiving increasing attention, is the use macrocyclic ligands. Here the organic backbone of the macrocycle provides a platform for the assembly of several metal centres in relatively close proximity. Moreover, the preparation

of targeted multimetallic species may be greatly facilitated using macrocyclic ligands that are heterotopic in having two distinct types of coordination sites to bind different types of metal ions.

Although macrocyclic ligands capable of binding different metals have been prepared [5,6], their syntheses are generally complicated and low yielding, and accordingly can be inherently expensive. For major applications it is essential that the macrocyclic ligands are readily available, cheap and easy to prepare. Calix[*n*]arenes are potential candidates. They are macrocyclic ligands consisting of phenolic units linked by methylene bridges at their *ortho*-positions [7], and the hydroxy functionalities are poised to coordinate several metals simultaneously. In addition, the calixarenes can be organised through their conformational flexibility with shape-specific π -rich cavities capable of metal· · π -arene interactions as well as the metal to oxygen centre interplay. In this article, we focus on multi-organo-metallic calixarene complexes formed purely through O-phenolate complexation, and also those formed through a combination of O-phenolate and metal· · π -arene interaction, with a view of illustrating

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how these macrocycles can be used strategically to prepare multimetallic complexes with control over the metal stoichiometries. This is paramount in preparing complexes of even higher complexity. The discussion focuses on the parent calixarenes and *p*-alkyl substituted analogues. Metal complexes of highly specialised and functionalised calixarenes including *p*-sulfonated and O-derivatives have been extensively studied and are more akin to classical coordination chemistry, and are covered elsewhere [7,8].

2. Calix[4]arenes

Calix[4]arenes are the lowest oligomers in the series and are readily available, and numerous metal complexes have been prepared and structurally authenticated. It is also the species for which $M \cdots \pi$ complexation is both most predictable and most commonly observed, which is related to its small ring size with well-defined cavities for metal ion inclusion. In the unsubstituted form, calix[4]arenes display four distinct structural conformations at room temperature, these are identified as cone, partial cone, 1,2-alternate and 1,3-alternate [7], Fig. 1. Normally the cone conformation is favoured since it allows maximum intramolecular hydrogen bonding between phenol groups.

In the cone conformation the metal ions can bind to the phenolic (or phenolate) oxygen centres either by residing inside or outside of the calixarene cavity, *endo* and *exo*, respectively, Fig. 2. In the *endo* case a metal

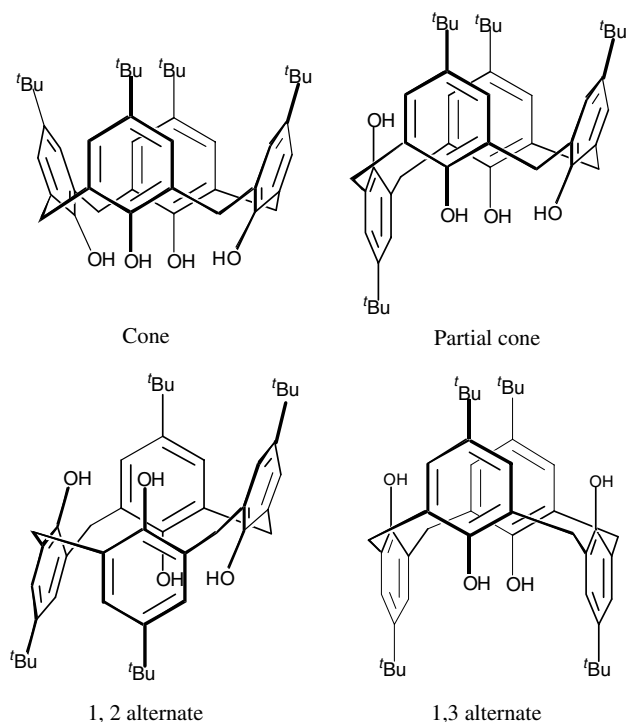


Fig. 1. Conformations of calix[4]arene.

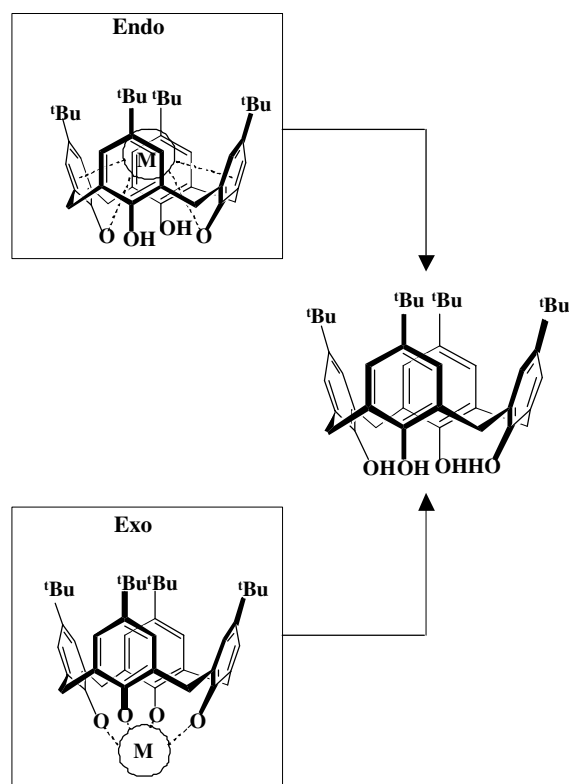


Fig. 2. *Endo* versus *exo* cavity binding in calix[4]arenes.

ion may interact with the π -faces of the aromatic groups whilst simultaneously interacting with the calix[4]arene phenol oxygens, whereas in the *exo* case a metal ion can interact with up to four phenol oxygens. The difference in strength and nature of these binding sites allows

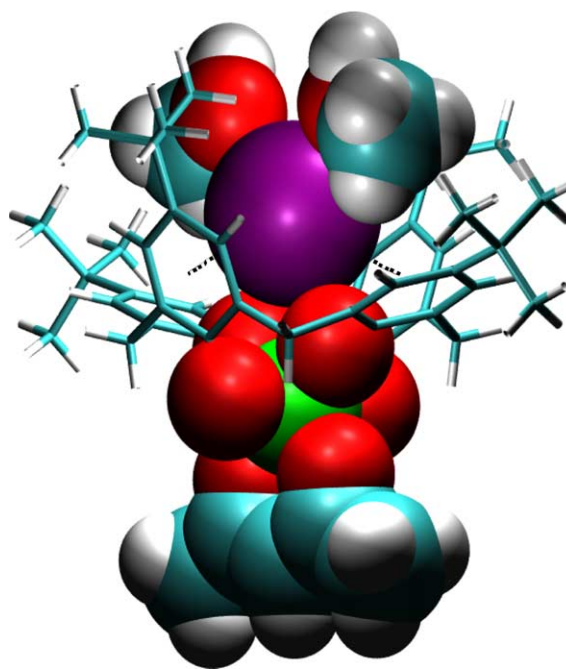
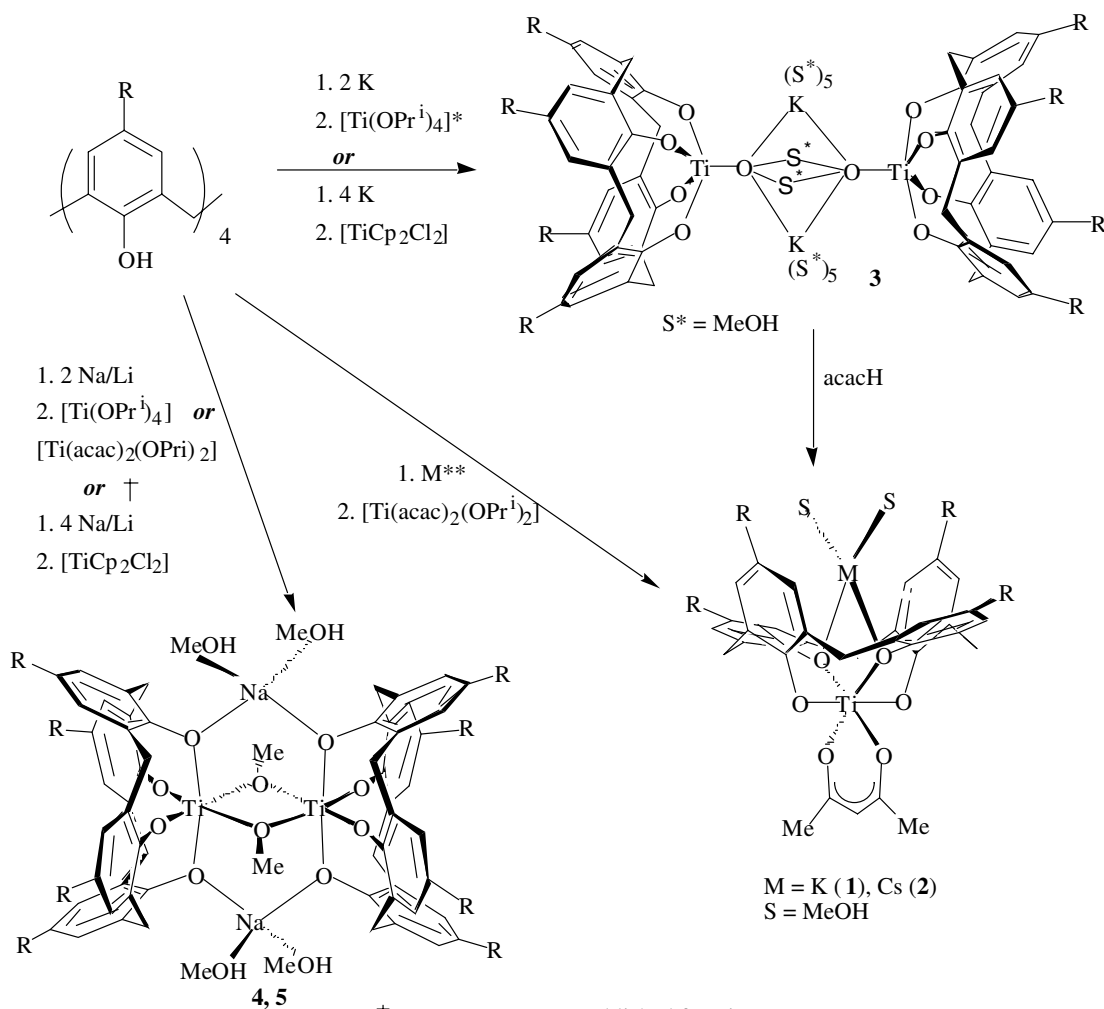


Fig. 3. Molecular projection of Cs-Ti calix[4]arene complex' dotted lines represent Cs... π interactions [9].

access to heterobimetallic complexes. An interesting feature of *endoxo* complexes is that synergistic binding relationships often exist, whereby the coordination geometry of the *exo*-binding metal shapes the calix[4]arene cavity to promote *endo* metal coordination, by facilitating greater $M \cdots \pi$ interactions. Notably, few cations are large enough to participate in multiple cation $\cdots \pi \cdots$ arene interactions within the aromatic cavity of the cone shaped calixarene, which is a feature that makes *endo* coordination unfavourable, particularly when alternative coordination maybe available through solvent and/or O-phenolate interaction. Thus in order to form particular multimetallic complexes exploiting the *exo/endo* coordination capacity of calix[4]arenes, several variables need to be considered/controlled. These include: *exo* metal coordination geometry and calixarene shape, size/charge of *endo* cations, and the choice of solvent.

A detailed study on the effect of these variables on mixed alkali-metal–titanium calixarene complexes has recently appeared [9]. Mono-calixarene K/Cs–Ti complexes, **1** and **2**, Fig. 3, are accessible by the addition of one equivalent of potassium metal or sodium metal followed by cesium chloride, as a metathesis reaction, to calix[4]arene in methanol followed by the addition of $[\text{Ti}(\text{acac})_2(\text{OPr}^i)_2]$. The cesium sits snugly in the calixarene cavity forming metal $\cdots \pi$ interactions to opposite rings with coordinated solvent molecules directed towards the other pair of aromatic rings which are splayed out. The Cs \cdots Centroid distances at 3.353 Å, are similar to those in the mono-metallic calix[4]arene cesium complex where the same cation sits symmetrical with respect to all aromatic rings [10].

A dimeric *exo*-K-*exo*-Ti(IV)-calix[4]arene complex forms in the absence of acetylacetonate, **3**, Scheme 1.



† No structure was established for Li

* $[\text{Ti}(\text{OPr}^i)_4]$ premixed with one equivalent of TMEDA

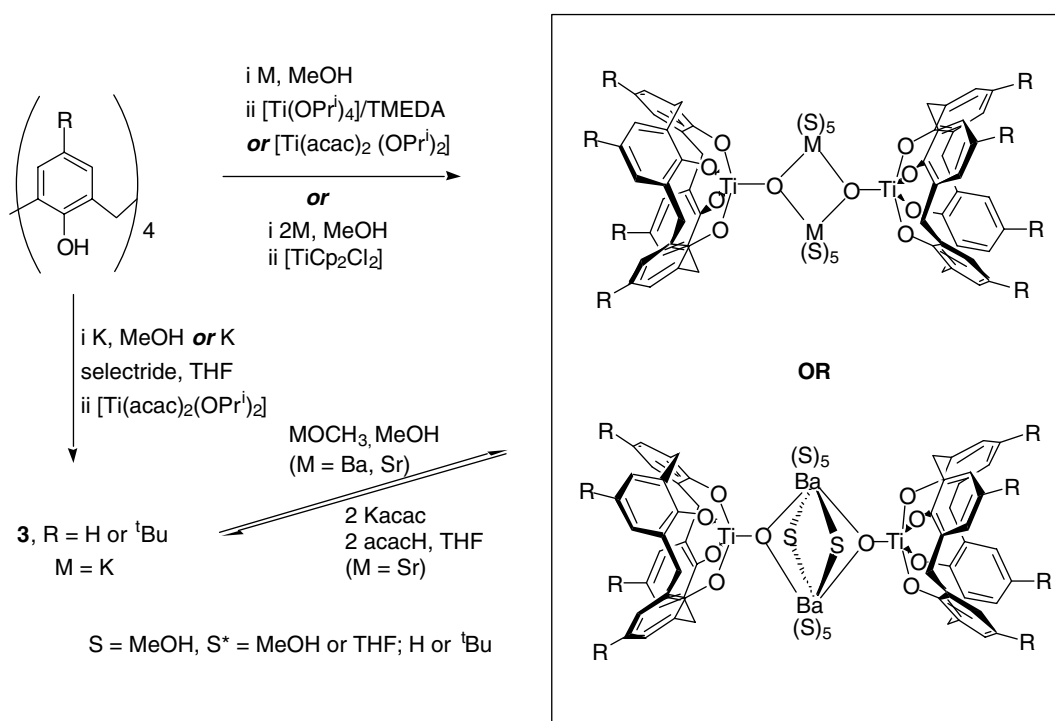
** For **2**, 1 equivalent of CsCl was added to the solution formed on reaction of 1 equivalent of sodium with calix[4]arene in methanol

Scheme 1.

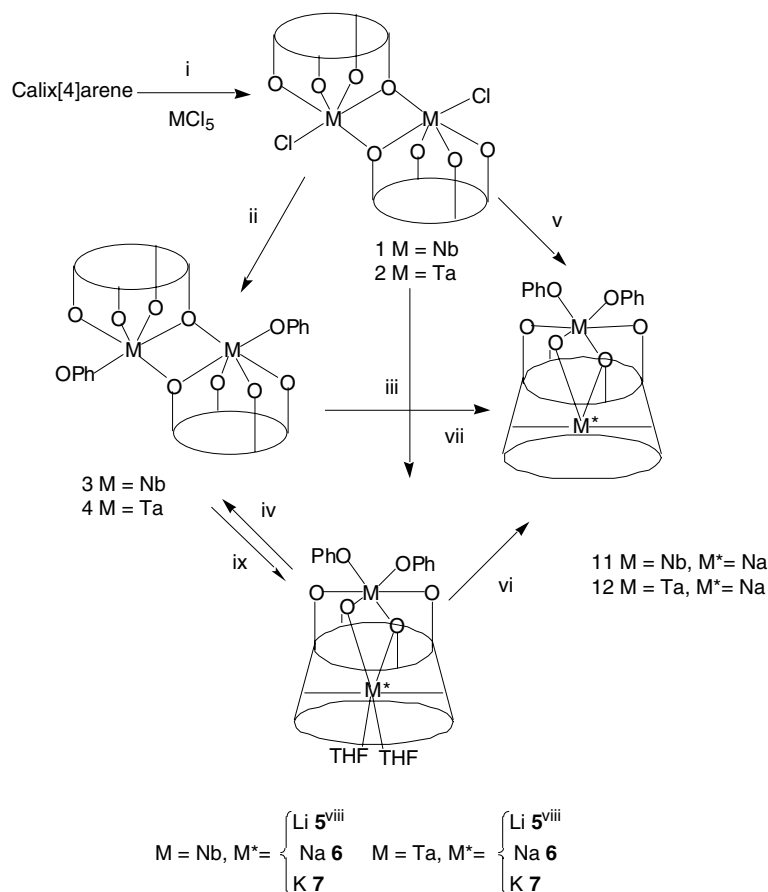
When sodium or lithium metal are used in place of the heavier group 1 metals, under the same conditions, no calixarene complexes could be isolated. However, increasing the ratio of sodium or lithium to the calix[4]arene affords dimeric *exo* Li/Na–Ti structures, **4** and **5**. For complexes **1** and **2**, the distortion resulting from the octahedral coordination of titanium(IV) brings two opposing phenyl groups of calix[4]arene into close proximity. This distortion favours binding of potassium/cesium ions within the calix[4]arene cavity through metal··· π interactions (in concert with the metal-oxygen interplay) even in the presence of potentially competing methanol (or THF) coordination/solvation of the group 1 ions. In contrast, for complex **3** square pyramidal binding of titanium results in a more symmetrical cone conformation of the calixarene, which presumably has opposite phenyl rings too remote from each other for any cooperative *endo* potassium metal··· π and O-centre complexation. This highlights the importance of *exo*-metal coordination geometry in shaping the calix[4]arene cavity for binding other metal ions. Similar chemistry has been mapped out for the reaction of calix[4]arenes with calcium, strontium or barium metal, Scheme 2 [11], replacing the use of potassium metal in Scheme 1. The new dimeric strontium and barium complexes can be interconverted to the same *exo*-K-*exo*-Ti(IV)-calix[4]arene complex, **3**, merely by changing the solvent, with the appropriate cation present in solution.

The inability to obtain analogous sodium and lithium complexes above, under the same conditions, suggests that the bonding of the smaller alkali metals by the calix[4]arene cavity is not competitive with *exo* complexation in methanol, even with the favourable energetics associated with chelation of titanium(IV) and the accompanying pinching distortions of the calix[4]arene cavity. Essentially for Li^+ and Na^+ the desolvation penalty upon entering the calix[4]arene cavity cannot be compensated by π ···arene interactions. Support for this view is evident in a Na–Ti dimeric structure consisting of tetrahedral sodium and octahedral oxo-bridged titanium centres linking calix[4]arene units, with additional sodium atoms occupying *endo*-positions, as expected on electrostatic and entropic grounds, but do not participate in cation··· π interactions [12].

Notwithstanding these arguments, mixed transition-alkali metal calix[4]arene complexes have been prepared with sodium and lithium ions *endo* to the calix[4]arene [13]. Their syntheses involve first coordinating the transition metal and then using an alkali metal metathesis reaction in THF to bind the alkali metal, Scheme 3. Under these circumstances, no competing coordination is available to the alkali metal. For a series of structural authenticated tantalum(V) complexes, where the transition metal is octahedral, the K^+ , Na^+ and Li^+ ions reside in the *endo*-positions with metal··· π interactions [13]. These vary from exclusively bis- η^6 -coordination for potassium to a single η^6 -coordination for sodium and single η^3 -co-



Scheme 2.



Scheme 3. Reagents and conditions: (i) toluene, reflux; (ii) 1 equiv. NaOPh, THF, room temp.; (iii) excess of M^*OPh , THF; (iv) 1 equiv. of **1** in THF or 1 equiv. of **2** in C_6H_6 ; (vii) excess NaOPh, C_6H_6 ; (viii) a single THF is bonded to Li^+ ; (ix) NaOPh, THF, room temperature [12].

ordination for lithium. The ‘misfit’ for symmetrical bis- η^6 -arene interaction for the smaller cations is consistent with discussions above, as is octahedral coordination of tantalum(V) involving binding *exo* to all four calix[4]arene O-centres bringing opposing phenyl groups closer together, and almost parallel. This is where the group 1 metal $\cdot\cdot\pi$ interactions occur. Results for the tantalum(V) studies highlight the comparatively weak binding of Li^+ and Na^+ ions within the cavity of the calix[4]arene, and explains why the titanium(IV) chemistry outlined above [9] does not extend to the use of sodium and lithium. Other examples of mixed transition-alkali metal calix[4]arene complexes prepared under similar circumstances include those of tungsten with potassium [14], Fig. 4(a), molybdenum with potassium, Fig. 4(b) [15], and chromium with lithium, Fig. 4(c) [15].

Hetero-metallic *endo/exo* calix[4]arene complexes are not limited to alkali-transition metal combinations. It extends to homometallic and heteropolymetallic alkali and alkaline earth metal species. Overall, the alkali and alkaline earth metal cations can be considered as featureless spheres, differentiated by size and charge density, such that their bonding exhibits none of the directional properties of transition elements. Accord-

ingly, their complexation with calixarene differs greatly from that of transition metals. In particular, there is a greater tendency for alkali and alkaline earth metals to complex within the calixarene cavity where the metal ion can bind through phenolic/phenolate complexation and multiple cation $\cdot\cdot\pi$ interactions. Thus, the choice of *endo* or *exo* coordination depends on the relative affinities of the metal towards interaction with the phenolic/phenolate oxygens on the so called lower rim of the calixarene versus cation $\cdot\cdot\pi$ interactions with the arene rings within the cavity. This also depends on the relative hard vs soft character of the metal ions. Hard cations prefer the oxygen donor ligands through *exo* coordination, whereas soft cations should favour some metal $\cdot\cdot\pi$ arene interaction through *endo* coordination. This aside, solvation affects and crystal packing forces are also important in determining the stability of the resulting complex. For the softer alkali metals such as cesium, which has a significant affinity for π -electrons [14], *endo* complexation occurs for both *p*-^tBu-calix[4]arene [10] and calix[4]arene [16]. Notably the *endo* Cs^+ cation in calix[4]arene complexes, Fig. 5 [16], also coordinates *exo* to a second calix[4]arene, whereas for the *p*-^tBu-calix[4]arene complex [10], the bulk of the

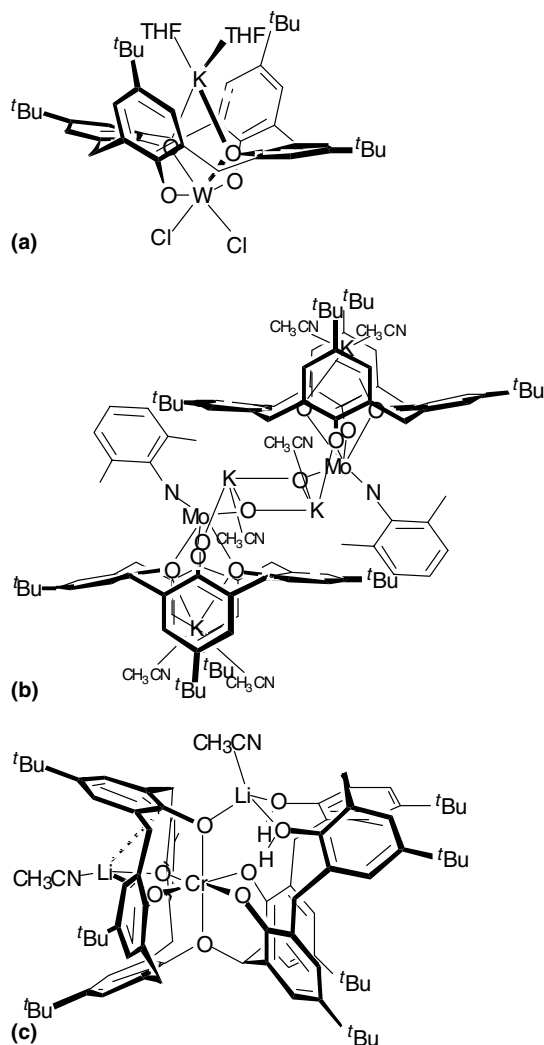
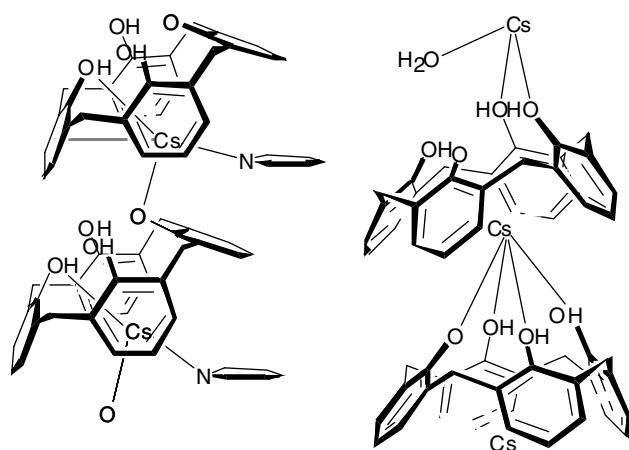
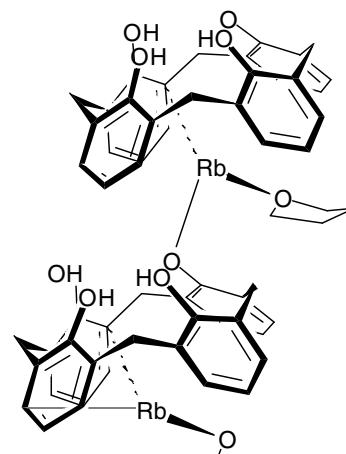


Fig. 4. Group 6 alkali metal calix[4]arene complexes [14,15].

Fig. 5. Calix[4]arene Cs⁺ complexes [16].

^tBu groups sterically inhibits interaction with a second calixarene. For Rb⁺ *endo/exo* coordination is observed for calix[4]arene, Fig. 6 [17], but only *exo* coordination

Fig. 6. A calix[4]arene Rb⁺ complex [17].

is observed for *p*-^tBu-calix[4]arene [17]. For group 1 cations smaller than Rb⁺ only *exo* coordination is observed for partially metallated complexes, whereas the fully metallated alkali metal calix[4]arenes exhibit a mixture of *endo* and *exo* complexation of Li⁺, Na⁺ and K⁺ ions [18,19]. An example of a fully metallated K complex is shown in Fig. 7 where each calixarene has a metal in the cavity with K⋯π interactions to two opposite aromatic rings [20]. A related dibenzo-18-crown-6 derivate has each 'K(THF)₃' replaced by 'K(dibenzo-18-crown-6)(THF)', with these alkali metal centres attached only to one phenolate O-centre [21]. A similar sodium analogue has each 'K(THF)₃' replaced by 'Na(18-crown-6)(THF)' [21].

The alkaline earth complexation chemistry of calix[4]arene has comparatively few examples, featuring *endo/exo* complexation. A di-calcium complex provides

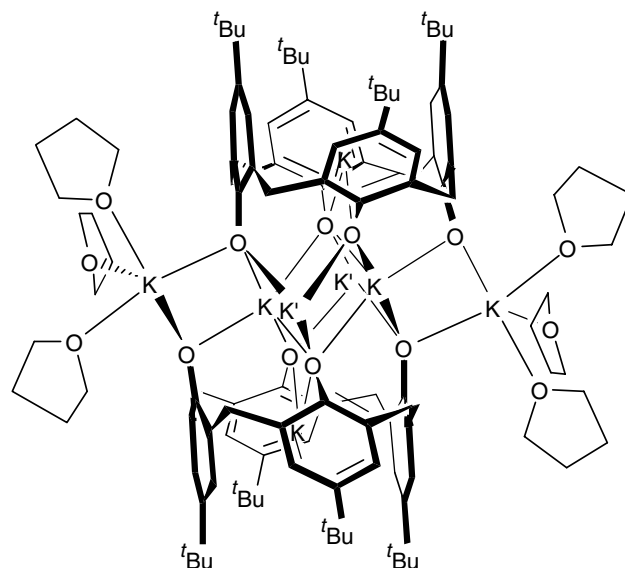


Fig. 7. A octapotassium-bis-calix[4]arene complex [20].

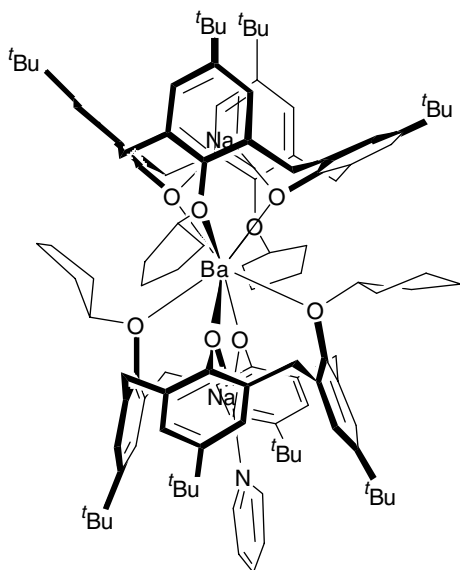
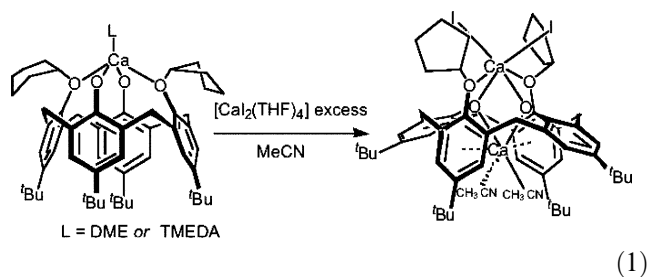


Fig. 8. A mixed barium/sodium calix[4]arene complex [20].

a unique example of the metal bound within the calix[4]arene cavity, prepared by addition of excess $\text{CaI}_2(\text{THF})_4$ to the preformed mono-calcium complex of the 1,3-dicyclopentyl ether of calix[4]arene in acetonitrile, Eq. (1). The hexa-coordinate *exo* bound metal centre may serve to shape the calix[4]arene cavity for *endo* inclusion of the second calcium cation, and the associated metal $\cdots\pi$ interactions. Reaction of the sodium salt of the calixarene in Eq. (1) with $\text{BaI}_2(\text{THF})_4$ (2:1 ratio) affords a heterometallic complex based on a central barium core bridging two calix[4]arenes, with sodium cations bound within the calixarene cavities, and also involved in metal $\cdots\pi$ interactions, Fig. 8 [20].



3. Calix[6]arenes

Whereas the relatively rigid calix[4]arene forms complexes predominately in the cone conformation, the larger calix[6]arene is more flexible, offering a greater variety of conformations and coordination interactions, and cavities with different shapes and sizes, with the potential to include larger guest molecules. From a coordination chemistry perspective, calix[6]arene macrocy-

cles have great potential in the design of new complexes containing several metal centres. Nevertheless, there is a dearth of structural information on how this calixarene binds to metal centres coupled with limited synthetic methodologies to prepare the metal complexes [22–27].

The conformational flexibility and higher degree of functionality of calix[6]arenes facilitates the binding of metal centres and the possibility of formation of metal $\cdots\pi$ -arene interactions, particularly where the metal is drawn over the face of the arene rings through constraints imposed by classical metal–phenolate-coordination elsewhere within the macrocycle. Relative to calix[4]arenes, it is better equipped to accommodate cations with high coordination numbers, such as the heavier alkaline earth metals, although, this comes at the expense of the increased conformational flexibility of the calix[6]arene. Controlling this is a difficulty, as is controlling the number of metal ions complexed to a larger number of *exo* binding sites.

A strategy in forming hetero-metallic complexes is the use of one metal to pre-organise the calix[6]arene structure to facilitate binding of the second type of metal centre. This can involve O-phenolate complexation of one metal to create aromatic pockets for π -arene coordination of the other or *visa versa*. For example, in a mixed cesium–uranium complex, the cesium cation appears to hold the ligand in a pinched cone conformation, by binding to two protonated calix[6]arene oxygen atoms and to the inner faces of two 1,3-disposed phenolic rings [28], Fig. 9. In contrast, for mixed 2:1 Ba-(Ti/Zr(IV)) calix[6]arene complexes, Fig. 10, the coordination of either titanium or zirconium appears to stabilise the *endo*-complexation of barium by fixing the calix[6]arene in the 1,3 alternate conformation [29,30]. While attempts to make mono-barium calix[6]arene complexes have been unsuccessful, an interesting complementarity of coordination modes is displayed in the multi-metallic barium calix[6]arene complex, Fig. 11, where the *endo* complexation of barium by calix[6]arene is also stabilised by additional *exo* coordination

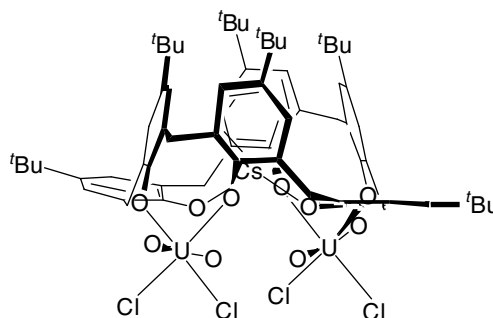


Fig. 9. Mixed cesium/uranium calix[6]arene complex [28].

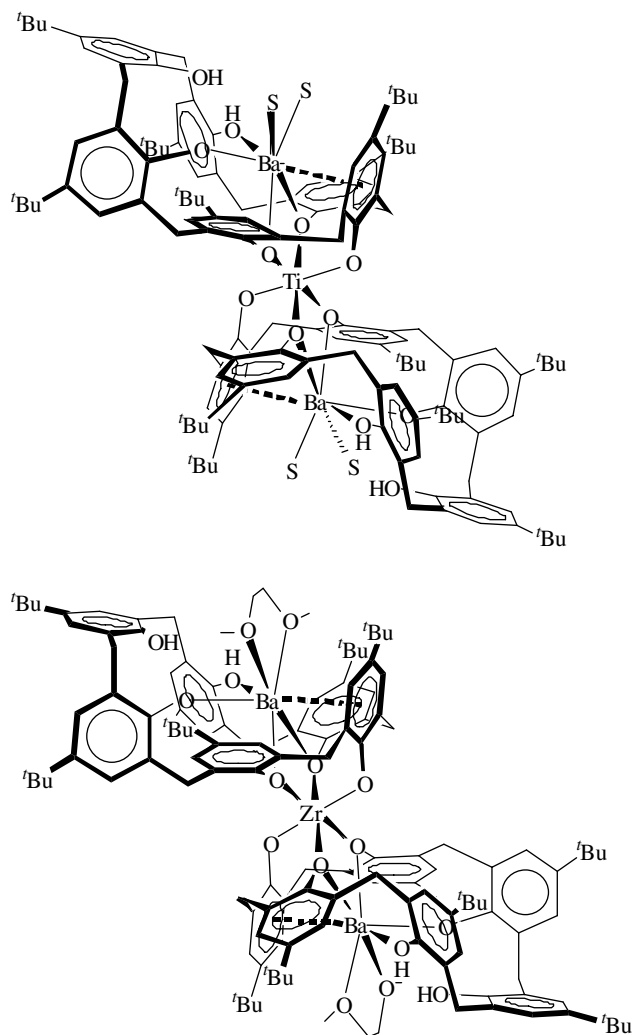


Fig. 10. Mixed barium/group 4 complexes of calix[6]arene [29,30].

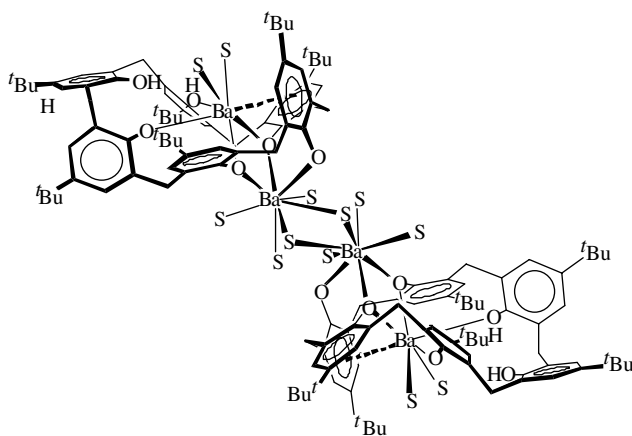


Fig. 11. Tetranuclear barium complex of calix[6]arene [30].

of barium to calix[6]arene [30]. Multimetallic complexes of potassium, cesium and a mixed potassium–rubidium complex also manifest multiple cation $\cdots\pi$ interactions for these systems, Fig. 12 [17].

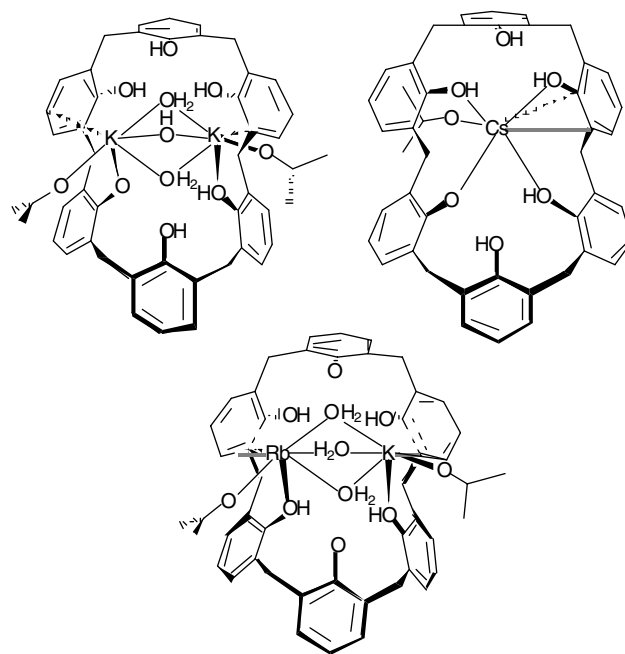


Fig. 12. Group 1 complexes of calix[6]arene [17].

4. Calix[5]arenes

Like calix[4]arenes, calix[5]arenes are usually predisposed to the cone conformation both in solution and in the solid state, through the formation of strong intramolecular hydrogen bonded torus. However unlike the synthesis of calix[4]arenes, the synthesis of calix[5]arenes low yielding and difficult to prepare [7], which may account for the paucity of structurally characterised complexes [31–33].

An unsymmetrical mixed potassium–titanium calix[5]arene dimer represents the only calix[5]arene complex exhibiting both O-phenolate and metal $\cdots\pi$ interactions [34], Fig. 13(a,b). The complex has a diverse array of metal–ligand connectivities and nicely demonstrates that while the calix[5]arene provides a larger cavity than calix[4]arene and is much less flexible than calix[6]arene, its five O-phenolate donors are spaced too widely for simultaneous coordination to a relatively small titanium(IV) centre. Overall, the disposition of the O-centres in the symmetrical cone conformation or unsymmetrical conformations lack simple complementarity with common binding geometries for small transition metal ions. This is reflected in the structure in Fig. 13(b) where each calix[5]arene has only some of its O-phenolate donors attached to titanium(IV) centres. The two potassium ions are in different environments, one with metal $\cdots\pi$ interactions. Moreover, the structure highlights the difficulty in predicting structural outcomes of complexes based on this macrocycle. Accordingly, it is doubtful that this calixarene will be a useful

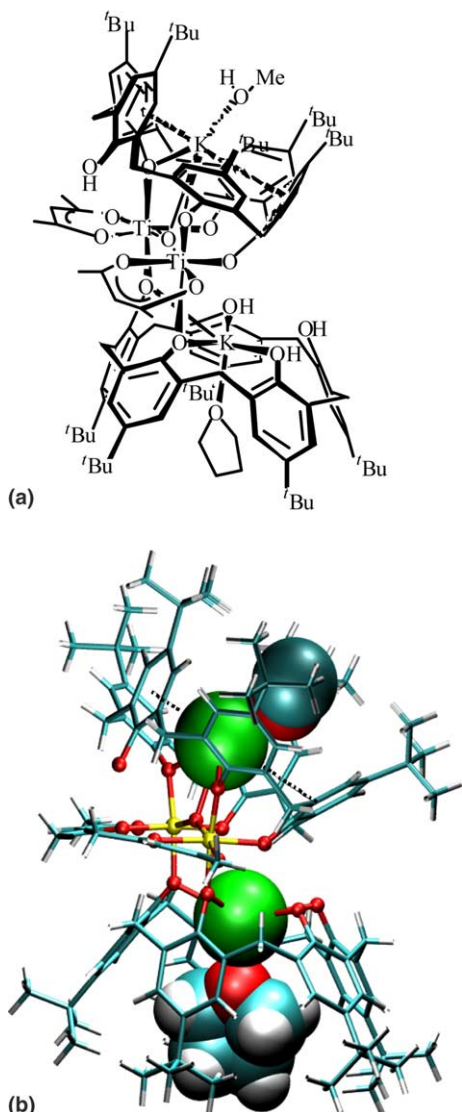


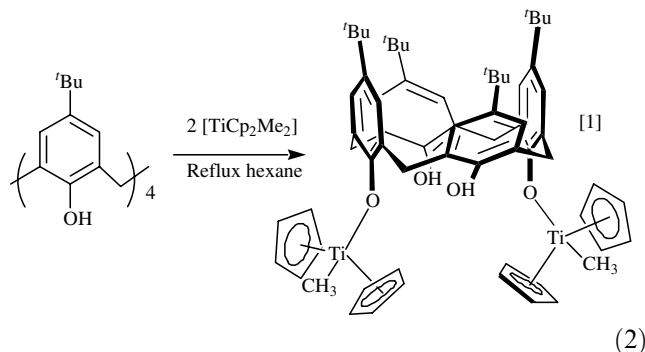
Fig. 13. (a) A mixed potassium–titanium(IV) complex based on two calix[5]arenes [34] and (b) molecular projection of a mixed potassium–titanium(IV) complex based on two calix[5]arenes; $K \cdots \pi$ interaction are shown as broken lines [34].

platform for building up novel metal complexes in a controlled way, at least for smaller ions.

5. Organometallic complexes constructed from O-phenolate coordination

As constrained multidentate hydroxy functionalised ligands, calixarenes have a unique capacity to coordinate several metals centres via O-phenolate complexation. For example, in the partially flattened cone arrangement, identified in aluminium [34], gallium [35] and zinc [36] complexes, Fig. 14, calix[4]arene is able to accommodate from two to four metal atoms simultaneously.

The reaction of two equivalents $TiCp_2Me_2$ with calix[4]arene in refluxing hexane, Eq. (2), affords a unique complex comprising of calix[4]arene bearing two $TiCp_2Me$ groups in the 1,3 arrangement [37]. Essentially the molecule is functionalised as a strong Lewis base (alkyl groups) and a weak Lewis acid (phenol groups), with scope for cleavage of one or more of the cyclopentadienyl moieties. These offer potential for using the complex to build up other structures of higher complexity.



Another feature of this chemistry is the role of steric hindrance, presumably in accounting for the high regioselective 1,3-disposition of the titanium centres relative to the calixarene. However the role of sterically demanding ancillary ligands in the *p*-positions of the calixarene can also be used to fine tune complex structures in other ways. In the case of titanium, the reaction of underivatized calix[4]arene, $[L(OH)_4]$, with titanium(IV) precursors such as $TiCl_4$ [38] or $Ti(NMe_2)_4$ [39] leads to the formation of dimeric titanium-bridged complexes. The tendency of such titanium precursors to form metallo-bridged dimers is undoubtedly due to the facile elimination of all four ligands from the titanium precursor by the acidic protons of the calix[4]arenes. The presence of the bulky and non-labile cyclopentadienyl ligand circumvents the formation of metallo-bridged species through steric buttressing effects. More support for this notion is evidenced in the formation of a novel monocalixarene/tetra-nuclear complex $[{}^tBu-L(O)_4Ti_4O_4Cp_4]$, Fig. 15. Interestingly, although there are numerous structurally characterised examples of two or more calix[4]arenes binding several transition metal ions simultaneously, this is a remarkable complex in having four transition metal atoms attached to one calix[4]arene, in a way which effectively locks the calixarene in a cone conformation [40].

For unsubstituted calix[6]arene high degrees of metalation have been observed; the reaction of trimethylaluminium with the calixarene in toluene results in a pentaaluminium complex [41], Fig. 16, the calix[6]arene effectively behaving as a hexa-anion. Tetrahedral

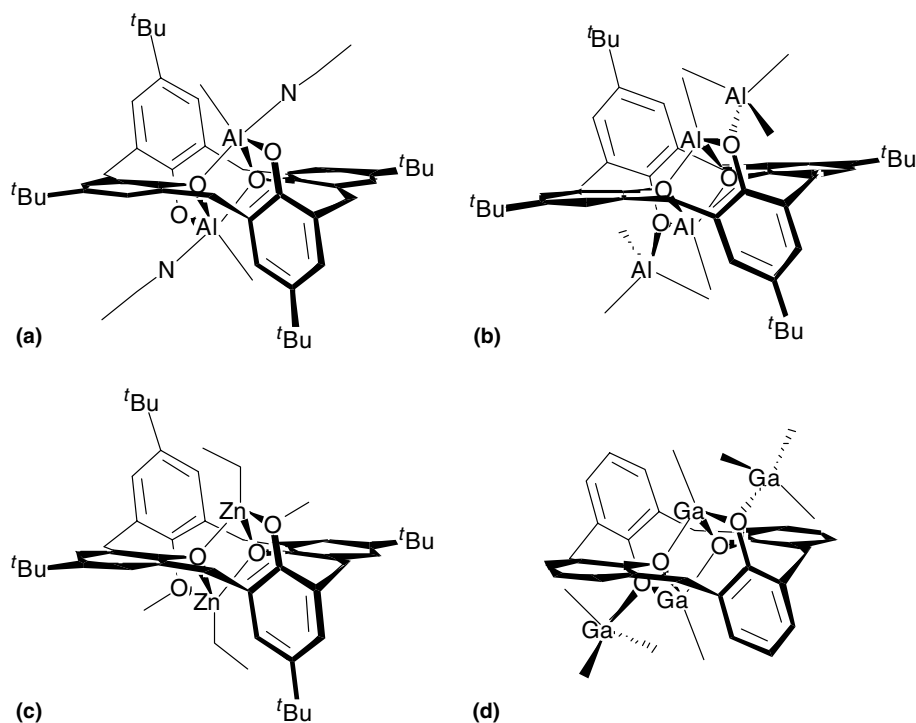


Fig. 14. Various organometallic complexes based on calix[4]arene [34,35].

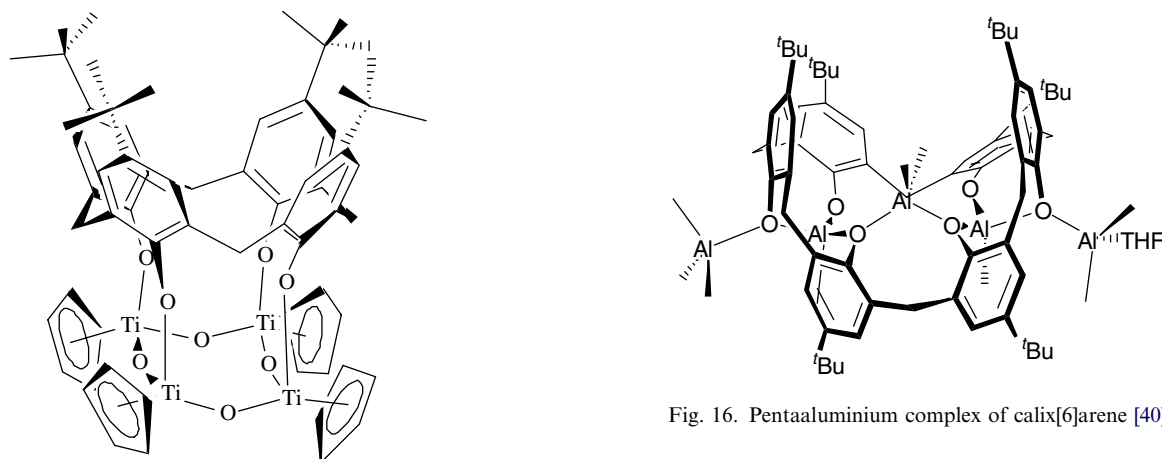


Fig. 15. Tetranuclear titanium(IV) oxo-bridged cavitanid [39].

aluminium(III) centres are coordinatively satisfied by different levels of methyl and phenolate moieties. Controlled sequential multi-metallation of calix[6]arene is possible by selective preparation of mono-titanium(IV) and di-titanium(IV) complexes, Scheme 4 [26]. Metallation of the three phenolic groups in the mono-titanium complex offers scope for incorporating other metals.

6. Future prospects

Calixarenes are versatile macrocycles for building up hetero-multi-metallated species based on two different

metals, taking advantage of metal–O and metal– π interactions, depending on how the conformation of the calixarenes in forming complexes with one metal type effects the proximity of oxygen centres (phenolic/phenolate moieties) and arene rings for binding of metal centres of the same or different type. Hetero-multi-metallated organometallic species are also possible by direct reaction of reactive organometallic reagents with the calixarenes.

The key to building up new structures based on different metal types is to control the conformation of the calixarene; any conformational change can manifest itself in accommodating one metal type over another, depending on metal coordination and stereochemical requirements. This may be possible for calix[8]arene,

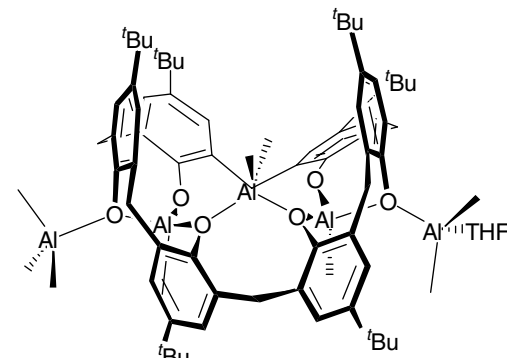
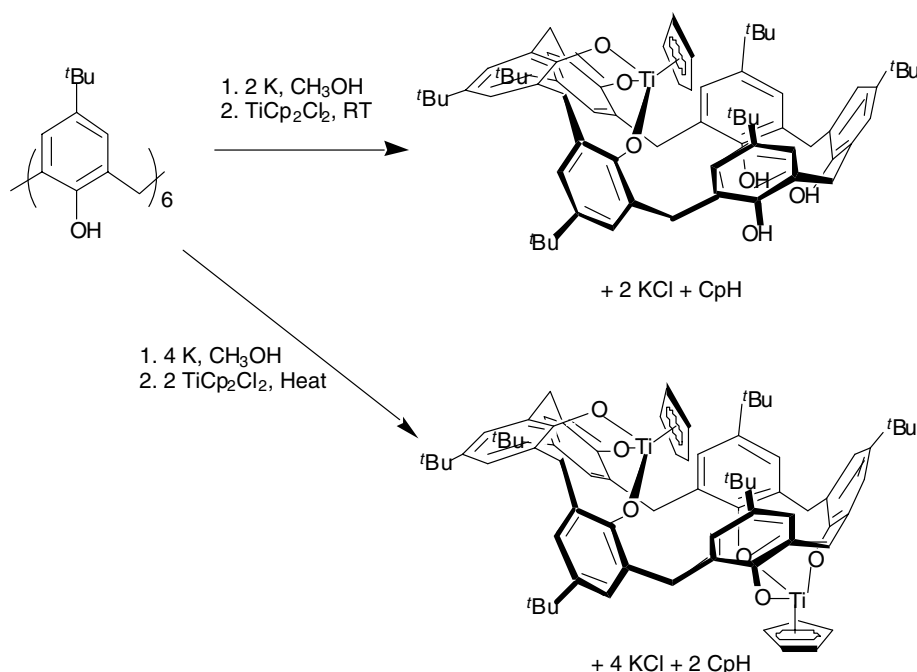


Fig. 16. Pentaaluminium complex of calix[6]arene [40].



Scheme 4.

and even larger calixarenes, for which multi-metal ion chemistry is yet to be developed. The same also applies to the *p*-substituted analogues. The number of combinations and permutations here are much higher and controlling how complexes of these calixarenes assemble will be a formidable challenge. This will require developing new synthetic strategies, possibly as a starting point adapting the recent advances for the calix[5]-arene and calix[6]arene complexes discussed herein.

The multi-metallated species have potential as precursors in delivering mixtures of metal ions in predetermined stoichiometries for bulk material. This has been demonstrated in principle with the dimeric alkaline earth/titanium(IV) complexes in [Scheme 2](#), where preliminary results indicate that the compounds sublime under high vacuum and that annealing of this sublimate gives a crystalline perovskite phase [11]. There is scope for building up specific size/function nano-particles based on discrete complexes, or using such complexes to build up larger nano-meter size arrays. The number of combinations of metals for binary, ternary and higher systems is large, compounded by the different ring size macrocycles, and the different types of alkyl and aryl substituents possible in the *p*-positions of the calixarenes. Combinatorial chemistry can facilitate taking this chemistry and ensuing applications to greater heights.

Acknowledgement

We thank the ARC for support of this work.

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